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| United States Patent | 12384747 |
| Kind Code | B2 |
| Date of Patent | August 12, 2025 |
| Inventor(s) | Ow; Hooisweng et al. |


## Tracers for petroleum reservoirs


### Abstract

The disclosure features methods of analyzing a fluid extracted from a reservoir, the methods including introducing a first composition featuring a first complexing agent into a reservoir at a first location, extracting a fluid from the reservoir at a second location different from the first location, combining the fluid with a second composition featuring a concentration of a lanthanide ion to form a third composition featuring a concentration of a complex formed by the first complexing agent and the lanthanide ion, exposing a quantity of the complex to electromagnetic radiation for a first time period ending at a time t.sub.0, detecting fluorescence emission from the quantity of the complex for a second time period starting at a time t.sub.1>t.sub.0, where t.sub.1−t.sub.0 is greater than 2 microseconds, and determining information about a fluid flow path between the first location and the second location.



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**Appl. No.:** **18/671211**

**Filed:** **May 22, 2024**

### Prior Publication Data

| Document Identifier | Publication Date |
|---|---|
| US 20240308962 A1 | Sep. 19, 2024 |

### Related U.S. Application Data

division parent-doc US 18162495 20230131 US 12077504 child-doc US 18671211
division parent-doc US 17551598 20211215 ABANDONED child-doc US 18162495

division parent-doc US 16252228 20190118 US 11230919 20220125 child-doc US 17551598
us-provisional-application US 62758046 20181109
us-provisional-application US 62619000 20180118

## Publication Classification

**Int. Cl.:** **C07D213/55** (20060101); **C07D213/79** (20060101); **C07D213/89** (20060101); **C07D401/04** (20060101); **C07D471/04** (20060101); **C09K8/03** (20060101); **C09K11/07** (20060101); **E21B43/16** (20060101); **E21B47/11** (20120101); **E21B49/08** (20060101); **G01N21/64** (20060101)

**U.S. Cl.:**

CPC **C07D213/55** (20130101); **C07D213/79** (20130101); **C07D213/89** (20130101); **C07D401/04** (20130101); **C07D471/04** (20130101); **C09K8/03** (20130101); **C09K11/07** (20130101); **E21B43/16** (20130101); **E21B47/11** (20200501); **E21B49/08** (20130101); **G01N21/6408** (20130101); **G01N21/643** (20130101); C09K2211/1018 (20130101); C09K2211/182 (20130101); E21B49/0875 (20200501); G01N2021/641 (20130101); G01N2021/6441 (20130101); G01N2201/129 (20130101)

## Field of Classification Search

**CPC:** C07D (213/55); C07D (213/79); C07D (213/89); C07D (401/04); C07D (471/04); C09K (8/03); C09K (11/07); C09K (2211/1018); C09K (2211/182); E21B (43/16); E21B (47/11); E21B (49/08); E21B (49/0875); G01N (21/6408); G01N (21/643); G01N (2021/641); G01N (2021/6441); G01N (2201/129)

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## Background/Summary

CROSS-REFERENCE TO RELATED APPLICATIONS (1) This application is a divisional of and claims the benefit of priority to U.S. patent application Ser. No. 18/162,495, filed on Jan. 31, 2023, which is a divisional of U.S. patent application Ser. No. 17/551,598, filed on Dec. 15, 2021, which is a divisional of U.S. patent application Ser. No. 16/252,228, filed on Jan. 18, 2019, now issued as U.S. Pat. No. 11,230,919 on Jan. 25, 2022, which claims priority to U.S. Provisional Application No. 62/619,000, filed on Jan. 18, 2018, and to U.S. Provisional Application No. 62/758,046, filed on Nov. 9, 2018, the entire contents of each of which are incorporated herein by reference.

TECHNICAL FIELD

(1) This disclosure relates to the analysis of petroleum reservoirs using tracers, and methods of making tracers.

BACKGROUND

(2) A petroleum reservoir is an underground pool of hydrocarbon compounds contained in porous or fractured rock formations. The petroleum in the reservoir is accessed through one or more borings in the earth that penetrate the material above the reservoir and enable transport of the petroleum to the surface. Water flooding is used, for example, to increase the pressure within the reservoir, thereby increasing oil production rates; and to displace hydrocarbons with the reservoir. Water is ideal for flooding reservoirs due to its ready availability and immiscibility with hydrocarbons. Determining the presence of fluid flow paths between oil wells, and the flow capacity between them, allows for a more detailed description of reservoir heterogeneity and facilitates water flood rate management.

SUMMARY

(3) Cross-well tracers, also referred to as inter-well tracers, can be used to obtain information about reservoir fluid flow patterns by injecting the tracer at an injection location, and subsequently retrieving and analyzing a quantity of the injected tracer at a producing location downstream from the injection location. The ease-of-use and overall utility of a cross-well tracer depends on a number of attributes, including (1) lesser retention in rock and earth that the tracer is exposed to when traversing a fluid flow path in a reservoir, (2) thermal stability and inertness to the various compounds and materials the tracer encounters in the reservoir, (3) minimal purification, workup, and derivatization after extraction from the reservoir, (4) detectability at lesser concentrations after extraction from the reservoir, (5) a measurable and sensitive response independent of minor variations in the structure of the tracer, and (6) detectability of the response over competing measurement signals attributable to natural constituents in fluid extracted from a reservoir, such as polyaromatic hydrocarbons and salts (that is, background noise).

(4) This disclosure features complexing agents for use as cross-well tracers. The complexing agents exhibit weak retention in rock, are thermally and chemically stable, and are typically used without purification after extraction. Instead of undergoing chemical derivatization after extraction, the complexing agents can conveniently be exposed to compositions including one or more lanthanide ions to form complexes.

(5) The complexes formed, when exposed to excitation light, emit a fluorescence signal that is temporally delayed relative to fluorescence signals from other components of the extracted reservoir fluid. As a result, time-gated detection methods can be used to eliminate the fluorescence signals from the other components, allowing essentially background-free measurement of the complexes. Detection of tracer concentrations of parts-per-quadrillion (ppq) or even less, on a mass/mass (m/m) basis, can be achieved. For example, tracer concentrations of 100 ppq m/m or less (such as 50 ppq m/m or less, 25 ppq m/m or less, 20 ppq m/m or less, 15 ppq m/m or less, 10 ppq m/m, 5 ppq m/m, 2 ppq m/m, 1 ppq m/m) can be achieved. Within extracted fluid, tracer

concentrations of 10 picomolar (pM) or less (such as 1 pM or less, 500 femtomolar (fM) or less, 200 fM or less, 100 fM or less, 50 fM or less, 25 fM or less, 15 fM or less, 10 fM or less, 5 fM or less, 1 fM or less, 500 attomolar (aM) or less, 200 aM or less, 100 aM or less, 50 aM or less) can be quantitatively detected.

(6) Complexing agents can also be derivatized to generate libraries of structurally unique identifiers which can be independently injected at multiple injection locations and extracted at a producing location, thus allowing the evaluation and comparison of fluid flow paths that span from each of the injection location to the producing location. Thus, the disclosed complexing agents can be used to reduce the time and costs associated with mapping the connectivity and heterogeneity of petroleum reservoirs and the management of water flooding-based petroleum extraction.

(7) In a first aspect, this disclosure features methods for analyzing a fluid extracted from a reservoir. The methods can include the steps of introducing a first composition that includes a first complexing agent into a reservoir at a first location, extracting a fluid from the reservoir at a second location different from the first location, where the extracted fluid includes a concentration of the first complexing agent, combining the fluid with a second composition that includes a concentration of a lanthanide ion to form a third composition having a concentration of a complex formed by the first complexing agent and the lanthanide ion, exposing a quantity of the complex to electromagnetic radiation for a first time period ending at a time t.sub.0, detecting fluorescence emission from the quantity of the complex for a second time period starting at a time t.sub.1>t.sub.0, where t.sub.1−t.sub.0 is greater than 2 microseconds, and determining information about a fluid flow path between the first location and the second location within the reservoir based on the detected fluorescence emission.

(8) Examples of the methods can include any one or more of the following features.

(9) The complex can include water. The complex can have a 1:1:2 molar ratio of lanthanide ion to first complexing agent to water. Alternatively, the complex can have a 1:2:0 molar ratio of lanthanide ion to first complexing agent to water. As another alternative, the complex can have a 1:2:1 molar ratio of lanthanide ion to first complexing agent to water. As a further alternative, the complex can have a 1:3:0 molar ratio of lanthanide ion to first complexing agent to water.

(10) The lanthanide ion can be a member of the group that includes samarium, europium, terbium, and dysprosium.

(11) The methods can include, prior to extracting the fluid from the reservoir, introducing a fourth composition with a second complexing agent into the reservoir at a third location, where the third location is different from the first location and the second location, and where the extracted fluid includes a concentration of the second complexing agent. The amount of the first complexing agent introduced into the reservoir can be the same as the amount of the second complexing agent introduced into the reservoir.

(12) The methods can include, prior to extracting the fluid from the reservoir, introducing a fourth composition with a second complexing agent into the reservoir at a third location, where the third location is different from the first location and the second location, and introducing a fifth composition with a third complexing agent into the reservoir at a fourth location, where the fourth location is different from the first location, the second location, and the third location, and where the extracted fluid includes a concentration of the second complexing agent and a concentration of the third complexing agent. The amounts of the first, second, and third complexing agents introduced into the reservoir can be the same.

(13) The methods can include, prior to combining the fluid with the second composition, separating the first complexing agent from the second complexing agent in the fluid, and separating the third complexing agent from the first and second complexing agents if the fluid includes the third complexing agent. The steps of separating the first and third complexing agents can include performing a chromatographic separation.

(14) A wavelength of the electromagnetic radiation can be in an ultraviolet spectral region. The

time interval t.sub.1−t.sub.0 can be greater than 5 microseconds (for example, greater than 25 microseconds).
(15) The information about the fluid flow path can include any one or more of a concentration of the first complexing agent, a concentration of the second complexing agent, and a concentration of the third complexing agent.
(16) The first complexing agent can be a tridentate ligand. The first complexing agent can be a compound having a general structure given by Formula (I), or an anion or salt of the structure given by Formula (I):
(17) ##STR00001##
(18) In Formula (I), X can be present or absent, and when present, can be a member of the group that includes: C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each of C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene can be optionally interrupted by one O, S, or NH.
(19) In Formula (I), R can be a member of the group that includes (i) hydrogen, (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy, optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (v) —COH, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including from 5-10 ring atoms, where 1-4 ring atoms are each independent members of the group that includes N, NH, O, and S, and where the heteroaryl can be optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl, including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes N, NH and O, and where the heterocyclyl can be optionally substituted with 1-4 independent units of R.sup.b, (xvii) C.sub.1-4 thioalkoxy, (xviii) —N.sub.3, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, (xxi) —SO.sub.1-2(R.sup.a), and (xxii) —O.sub.nP(O).sub.nY.sub.2, where each occurrence of n can independently be 0 or 1, and where each occurrence Y can independently be one of —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl.
(20) Each occurrence of R.sup.a in Formula (I) can independently be one of (i) H, (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms can each be independently members of the group that includes NH, O, and S, and where the heterocyclyl can optionally be substituted with from 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl can be optionally substituted with from 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms can each be independent members of the group that includes N, NH, O, and S, and where the heteroaryl can optionally be substituted with from 1-3 independent units of R.sup.b.
(21) Each occurrence of R.sup.b in Formula (I) can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are each independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where 1-4 of the ring atoms can each be independent members of the group that includes N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)

(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″).
(22) Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring that includes from 3-8 ring atoms, and the ring can include: (a) from 1-7 ring carbon atoms; and (b) 0-3 ring heteroatoms, in addition to the atom attached to R′ and R″, which are each independent members of the group that includes N, NH, O, and S.
(23) In Formula (I), X can be C.sub.1-10 alkylene. R can be selected from the group that includes (ii) —OR.sup.a, where the R.sup.a of —OR.sup.a is not (i) H or (ii) C.sub.1-8 alkyl substituted with —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl, (vi) —CO.sub.2R.sup.a, where the R.sup.a of —CO.sub.2R.sup.a is not H, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with from 1-3 independent units of R.sup.b, (xiv) -heteroaryl including from 5-10 ring atoms, where 1-4 ring atoms are independent members of the group that includes N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with from 1-4 independent units of R.sup.b, (xvi) -heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes N, NH and O, and where the heterocyclyl is optionally substituted with from 1-4 independent units of R.sup.b, (xx) —C(O)R.sup.a, and (xxi) —SO.sub.1-2(R.sup.a). Each occurrence of R.sup.a can be an independent members of the group that includes (i) H, (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including from 5-10 ring atoms, where 1-4 of the ring atoms can be independent members of the group that includes N, NH, O, and S, and where the heteroaryl can be optionally substituted with 1-3 independent units of R.sup.b. Each occurrence of R.sup.b can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms can be independent members of the group that includes NH, O, and S, and where the heterocyclyl can be optionally substituted with 1-4 independent units of C.sub.1-4 alkyl; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms can be independent members of the group that includes N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″). Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring that includes 3-8 ring atoms, where the ring includes (a) 1-7 ring carbon atoms, and (b) 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independent members of the group that includes N, NH, O, and S.
(24) In Formula (I), X can be —CH.sub.2—. In Formula (I), R can be (ii) —OR.sup.a, where the R.sup.a of —OR.sup.a is not (i) H or (ii) C.sub.1-8 alkyl substituted with —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl.

(25) In Formula (I), R can be a member of the group that includes (ix) —NR.sup.aR.sup.a, where one R.sup.a is H, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, where at least one R.sup.a is H, (xi) —NR.sup.aC(O)OR.sup.a, where the R.sup.a bonded to N is H, and (xii) —NR.sup.aC(O)R.sup.a.
(26) In Formula (I), R can be a member of the group that includes (vi) —CO.sub.2R.sup.a, where the R.sup.a of —CO.sub.2R.sup.a is not H, and (xx) —C(O)R.sup.a.
(27) The first complexing agent can be tetradentate.
(28) The first complexing agent can be a compound having a general structure given by Formula (II), or an anion or salt of a compound having the general structure of Formula (II):
(29) ##STR00002##
(30) In Formula (II), each of X.sup.1 and X.sup.2 can be independently present or absent, and when one or both are present, each can be an independent member of the group that includes C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH.
(31) In Formula (II), each R.sup.1 and R.sup.2 is an independent member of the group that includes (i) hydrogen, (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (v) —COH, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including 5-10 ring atoms, where 1-4 ring atoms are each independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms can each be independent members of the group that includes N, NH and O, where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (xvii) C.sub.1-4 thioalkoxy, (xviii) —N.sub.3, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, (xxi) —SO.sub.1-2(R.sup.a), and (xxii) —O.sub.nP(O),Y.sub.2, where each n is independently 0 or 1, and each Y is an independent member of the group that includes —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl.
(32) Each occurrence of R.sup.a can be an independent member of the group that includes (i) H, (ii) C.sub.1-8 alkyl optionally substituted with 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes N, NH, O, and S, and the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b.
(33) Each occurrence of R.sup.b can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes of N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″).

(34) Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring including 3-8 ring atoms, where the ring includes (a) 1-7 ring carbon atoms, and (b) 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″) which are each independent members of the group that includes N, NH, O, and S.
(35) In Formula (II), each of X.sup.1 and X.sup.2 can be independently present or absent, and when one or both are present, each can be an independent member of the group that includes C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH. Each of R.sup.1 and R.sup.2 can be an independent member of the group that includes (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes N, NH and O, and where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, and (xxi) —SO.sub.1-2(R.sup.a). Each occurrence of R.sup.a can be an independent member of the group that includes (i) H, (ii) C.sub.1-8 alkyl optionally substituted with 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms can be independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b. Each occurrence of R.sup.b can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 ring atoms are independent members of the group that includes N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″). Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring including 3-8 ring atoms, where the ring includes (a) 1-7 ring carbon atoms, and (b) 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independent members of the group that includes N, NH, O, and S.
(36) In Formula (II), X.sup.1 and X.sup.2 can both be absent.
(37) In Formula (II), R.sup.1 and R.sup.2 can each be independent members of the group that

includes (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, and (xii) —NR.sup.aC(O)R.sup.a. Alternatively, in Formula (II), R.sup.1 and R.sup.2 can each be independent members of the group that includes (ix) —NHR.sup.a, (x) —NHC(O)NHR.sup.a, (xi) —NHC(O)OR.sup.a, and (xii) —NHC(O)R.sup.a. As another alternative, in Formula (II), R.sup.1 and R.sup.2 can each be (ix) —NHR.sup.a.

(38) In Formula (II), R.sup.a can be (ii) C.sub.1-8 alkyl substituted with 1-3 independent units of R.sup.b, where at least one of the R.sup.b is (xv) —OH. Alternatively, in Formula (II), R.sup.1 and R.sup.2 can each be (x) —NHC(O)NHR.sup.a. As another alternative, in Formula (II), R.sup.1 and R.sup.2 can each be (xi) —NHC(O)OR.sup.a. As a further alternative, in Formula (II), R.sup.1 and R.sup.2 can each be (xii) —NHC(O)R.sup.a.

(39) In Formula (II), each of R.sup.1 and R.sup.2 can be the same, or alternatively, each of R.sup.1 and R.sup.2 can be different.

(40) The first complexing agent can be a compound having a general structure given by Formula (III), or an anion or salt of a compound having the general structure of Formula (III):

(41) ##STR00003##

(42) In Formula (III), each of X.sup.1 and X.sup.2 can be independently present or absent, and when one or both are present, each can be an independent member of the group that includes C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH.

(43) In Formula (II), each R.sup.1 and R.sup.2 is an independent member of the group that includes (i) hydrogen, (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (v) —COH, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including 5-10 ring atoms, where 1-4 ring atoms are each independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms can each be independent members of the group that includes N, NH and O, where the heterocyclyl is optionally substituted with 1-4 independent units of RD, (xvii) C.sub.1-4 thioalkoxy, (xviii) —N.sub.3, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, (xxi) —SO.sub.1-2(R.sup.a), (xxii) —O.sub.nP(O).sub.nY.sub.2, where each n is independently 0 or 1, and (xxiii) halo (e.g., —F, —Cl, —Br, or —I), and each Y is an independent member of the group that includes —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl.

(44) Each occurrence of R.sup.a can be an independent member of the group that includes (i) H, (ii) C.sub.1-8 alkyl optionally substituted with 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes N, NH, O, and S, and the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b.

(45) Each occurrence of R.sup.b can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3

alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes of N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″).

(46) Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring including 3-8 ring atoms, where the ring includes (a) 1-7 ring carbon atoms, and (b) 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″) which are each independent members of the group that includes N, NH, O, and S.

(47) In Formula (III), each of X.sup.1 and X.sup.2 can be independently present or absent, and when one or both are present, each can be an independent member of the group that includes C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH. Each of R.sup.1 and R.sup.2 can be an independent member of the group that includes (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes N, NH and O, and where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, and (xxi) —SO.sub.1-2(R.sup.a). Each occurrence of R.sup.a can be an independent member of the group that includes (i) H, (ii) C.sub.1-8 alkyl optionally substituted with 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms can be independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b. Each occurrence of R.sup.b can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 ring atoms are independent members of the group that includes N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and

(xxiii) —C(═O)N(R′)(R″). Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring including 3-8 ring atoms, where the ring includes (a) 1-7 ring carbon atoms, and (b) 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independent members of the group that includes N, NH, O, and S.
(48) In Formula (III), X.sup.1 and X.sup.2 can both be absent.
(49) In Formula (III), R.sup.1 and R.sup.2 can each be independent members of the group that includes (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, and (xii) —NR.sup.aC(O)R.sup.a. Alternatively, in Formula (III), R.sup.1 and R.sup.2 can each be independent members of the group that includes (ix) —NHR.sup.a, (x) —NHC(O)NHR.sup.a, (xi) —NHC(O)OR.sup.a, and (xii) —NHC(O)R.sup.a. As another alternative, in Formula (III), R.sup.1 and R.sup.2 can each be (ix) —NHR.sup.a.
(50) In Formula (III), R.sup.a can be (ii) C.sub.1-8 alkyl substituted with 1-3 independent units of R.sup.b, where at least one of the R.sup.b is (xv) —OH. Alternatively, in Formula (III), R.sup.1 and R.sup.2 can each be (x) —NHC(O)NHR.sup.a. As another alternative, in Formula (III), R.sup.1 and R.sup.2 can each be (xi) —NHC(O)OR.sup.a. As a further alternative, in Formula (III), R.sup.1 and R.sup.2 can each be (xii) —NHC(O)R.sup.a.
(51) In Formula (III), each of R.sup.1 and R.sup.2 can be the same, or alternatively, each of R.sup.1 and R.sup.2 can be different.
(52) Embodiments of the methods can also include any of the other features discussed, including features associated with different embodiments, in any combination unless expressly stated otherwise.
(53) In another aspect, this disclosure features methods of forming a complex that includes a complexing agent and a lanthanide ion, the methods including introducing the complexing agent into a subterranean reservoir at a first location, allowing the complexing agent to propagate through at least a portion of the reservoir to a second location different from the first location, extracting the complexing agent from the reservoir at the second location, and combining the extracted complexing agent with a solution that includes the lanthanide ion to form the complex, where the complexing agent has a general structure given by Formula (I), or an anion or salt of the structure given by Formula (I):
(54) ##STR00004##
(55) In Formula (I), X can be present or absent, and when present, can be a member of the group that includes: C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each of C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene can be optionally interrupted by one O, S, or NH. R can be a member of the group that includes (i) hydrogen, (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy, optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (v) —COH, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including from 5-10 ring atoms, where 1-4 ring atoms are each independent members of the group that includes N, NH, O, and S, and where the heteroaryl can be optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl, including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes N, NH and O, and where the heterocyclyl can be optionally substituted with 1-4 independent units of R.sup.b, (xvii) C.sub.1-4 thioalkoxy, (xviii) —N.sub.3, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, (xxi) —SO.sub.1-2(R.sup.a), and (xxii) —O.sub.nP(O).sub.nY.sub.2, where each occurrence of n can independently be 0 or 1, and where each occurrence Y can independently be one of —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl.

Each occurrence of R.sup.a in Formula (I) can independently be one of (i) H, (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms can each be independently members of the group that includes NH, O, and S, and where the heterocyclyl can optionally be substituted with from 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl can be optionally substituted with from 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms can each be independent members of the group that includes N, NH, O, and S, and where the heteroaryl can optionally be substituted with from 1-3 independent units of R.sup.b. Each occurrence of R.sup.b in Formula (I) can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are each independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where 1-4 of the ring atoms can each be independent members of the group that includes N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″). Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring that includes from 3-8 ring atoms, and the ring can include: (a) from 1-7 ring carbon atoms; and (b) 0-3 ring heteroatoms, in addition to the atom attached to R′ and R″, which are each independent members of the group that includes N, NH, O, and S.

(56) Embodiments of the methods can include any one or more of the following features.

(57) X, R, each occurrence of R.sup.a, each occurrence of R.sup.b, each occurrence of R′ and R″, and combinations of these structural units, can have any of the features discussed in connection with Formula (I) for these structural units.

(58) The complex can include water. The complex can include a molar ratio of lanthanide ion to complexing agent to water of 1:1:2, or 1:2:1, or 1:3:0. The lanthanide ion can be selected from the group that includes samarium, europium, terbium, and dysprosium.

(59) Embodiments of the methods can also include any of the other features discussed, including features associated with different embodiments, in any combination unless expressly stated otherwise.

(60) In a further aspect, this disclosure features methods of forming a complex that includes a complexing agent and a lanthanide ion, the methods including introducing the complexing agent into a subterranean reservoir at a first location, allowing the complexing agent to propagate through at least a portion of the reservoir to a second location different from the first location, extracting the complexing agent at a second location, and combining the extracted complexing agent with a solution that includes the lanthanide ion to form the complex, where the complexing agent has a general structure given by Formula (II), or an anion or salt of the structure given by Formula (II):

(61) ##STR00005##

(62) In Formula (II), each of X.sup.1 and X.sup.2 can be independently present or absent, and when one or both are present, each can be an independent member of the group that includes C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH.

Each R.sup.1 and R.sup.2 is an independent member of the group that includes (i) hydrogen, (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (v) —COH, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including 5-10 ring atoms, where 1-4 ring atoms are each independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms can each be independent members of the group that includes N, NH and O, where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (xvii) C.sub.1-4 thioalkoxy, (xviii) —N.sub.3, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, (xxi) —SO.sub.1-2(R.sup.a), and (xxii) —O.sub.nP(O),Y.sub.2, where each n is independently 0 or 1, and each Y is an independent member of the group that includes —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl. Each occurrence of R.sup.a can be an independent member of the group that includes (i) H, (ii) C.sub.1-8 alkyl optionally substituted with 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes N, NH, O, and S, and the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b. Each occurrence of R.sup.b can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes of N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″). Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring including 3-8 ring atoms, where the ring includes (a) 1-7 ring carbon atoms, and (b) 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″) which are each independent members of the group that includes N, NH, O, and S.

(63) Embodiments of the methods can include any one or more of the following features.

(64) X.sup.1, X.sup.2, R.sup.1, R.sup.2, each occurrence of R.sup.a, each occurrence of R.sup.b, each occurrence of R′ and R″, and combinations of these structural units, can have any of the features discussed in connection with Formula (II) for these structural units.

(65) The complex can include water. A molar ratio of lanthanide ion to complexing agent to water can be 1:1:2 or 1:2:0. The lanthanide ion can be selected from the group that includes samarium, europium, terbium, and dysprosium.

(66) Embodiments of the methods can also include any of the other features discussed, including

features associated with different embodiments, in any combination unless expressly stated otherwise.

(67) In another aspect, this disclosure features methods of forming a complex that includes a complexing agent and a lanthanide ion, the methods including introducing the complexing agent into a subterranean reservoir at a first location, allowing the complexing agent to propagate through at least a portion of the reservoir to a second location different from the first location, extracting the complexing agent at a second location, and combining the extracted complexing agent with a solution that includes the lanthanide ion to form the complex, where the complexing agent has a general structure given by Formula (III), or an anion or salt of the structure given by Formula (III):

(68) ##STR00006##

(69) In Formula (III), each of X.sup.1 and X.sup.2 can be independently present or absent, and when one or both are present, each can be an independent member of the group that includes C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH. Each R.sup.1 and R.sup.2 is an independent member of the group that includes (i) hydrogen, (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (v) —COH, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including 5-10 ring atoms, where 1-4 ring atoms are each independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 Cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms can each be independent members of the group that includes N, NH and O, where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (xvii) C.sub.1-4 thioalkoxy, (xviii) —N.sub.3, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, (xxi) —SO.sub.1-2(R.sup.a), (xxii) —O.sub.nP(O).sub.nY.sub.2, where each n is independently 0 or 1, and (xxiii) halo (e.g., —F, —Cl, —Br, or —I), and each Y is an independent member of the group that includes —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl. Each occurrence of R.sup.a can be an independent member of the group that includes (i) H, (ii) C.sub.1-8 alkyl optionally substituted with 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes N, NH, O, and S, and the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b. Each occurrence of R.sup.b can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes of N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii)

—C(═O)OH, and (xxiii) —C(═O)N(R′)(R″). Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring including 3-8 ring atoms, where the ring includes (a) 1-7 ring carbon atoms, and (b) 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″) which are each independent members of the group that includes N, NH, O, and S.
(70) Embodiments of the methods can include any one or more of the following features.
(71) X.sup.1, X.sup.2, R.sup.1, R.sup.2, each occurrence of R.sup.a, each occurrence of R.sup.b, each occurrence of R′ and R″, and combinations of these structural units, can have any of the features discussed in connection with Formula (III) for these structural units.
(72) The complex can include water. A molar ratio of lanthanide ion to complexing agent to water can be 1:1:2 or 1:2:0. The lanthanide ion can be selected from the group that includes samarium, europium, terbium, and dysprosium.
(73) Embodiments of the methods can also include any of the other features discussed, including features associated with different embodiments, in any combination unless expressly stated otherwise.
(74) In a further aspect, this disclosure features complexing agents having a general structure given by Formula (I), and anions and salts of the general structure of Formula (I):
(75) ##STR00007##
(76) In Formula (I), X can be present or absent, and when present, can be a member of the group that includes: C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each of C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene can be optionally interrupted by one O, S, or NH. R can be a member of the group that includes (i) hydrogen, (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy, optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (v) —COH, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including from 5-10 ring atoms, where 1-4 ring atoms are each independent members of the group that includes N, NH, O, and S, and where the heteroaryl can be optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl, including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes N, NH and O, and where the heterocyclyl can be optionally substituted with 1-4 independent units of R.sup.b, (xvii) C.sub.1-4 thioalkoxy, (xviii) —N.sub.3, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, (xxi) —SO.sub.1-2(R.sup.a), and (xxii) —O.sub.nP(O),Y.sub.2, where each occurrence of n can independently be 0 or 1, and where each occurrence Y can independently be one of —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl. Each occurrence of R.sup.a in Formula (I) can independently be one of (i) H, (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms can each be independently members of the group that includes NH, O, and S, and where the heterocyclyl can optionally be substituted with from 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene) —(C.sub.6-10 aryl), where the aryl can be optionally substituted with from 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms can each be independent members of the group that includes N, NH, O, and S, and where the heteroaryl can optionally be substituted with from 1-3 independent units of R.sup.b. Each occurrence of R.sup.b in Formula (I) can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii)

C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are each independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where 1-4 of the ring atoms can each be independent members of the group that includes N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″). Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring that includes from 3-8 ring atoms, and the ring can include: (a) from 1-7 ring carbon atoms; and (b) 0-3 ring heteroatoms, in addition to the atom attached to R′ and R″, which are each independent members of the group that includes N, NH, O, and S.

(77) Embodiments of the complexing agents can include any one or more of the following features.

(78) X, R, each occurrence of R.sup.a, each occurrence of R.sup.b, each occurrence of R′ and R″, and combinations of these structural units, can have any of the features discussed in connection with Formula (I) for these structural units.

(79) Embodiments of the complexing agents can also include any of the other features discussed, including features associated with different embodiments, in any combination unless expressly stated otherwise.

(80) In another aspect, this disclosure features complexing agents having a general structure given by Formula (II), and anions and salts of the general structure of Formula (II):

(81) ##STR00008##

(82) In Formula (II), each of X.sup.1 and X.sup.2 can be independently present or absent, and when one or both are present, each can be an independent member of the group that includes C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH. Each R.sup.1 and R.sup.2 is an independent member of the group that includes (i) hydrogen, (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (v) —COH, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including 5-10 ring atoms, where 1-4 ring atoms are each independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms can each be independent members of the group that includes N, NH and O, where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (xvii) C.sub.1-4 thioalkoxy, (xviii) —N.sub.3, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, (xxi) —SO.sub.1-2(R.sup.a), and (xxii) —O.sub.nP(O).sub.nY.sub.2, where each n is independently 0 or 1, and each Y is an independent member of the group that includes —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl. Each occurrence of R.sup.a can be an independent member of the group that includes (i) H, (ii) C.sub.1-8 alkyl optionally substituted with 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl

is optionally substituted with 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes N, NH, O, and S, and the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b. Each occurrence of R.sup.b can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes of N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″). Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring including 3-8 ring atoms, where the ring includes (a) 1-7 ring carbon atoms, and (b) 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″) which are each independent members of the group that includes N, NH, O, and S.

(83) Embodiments of the complexing agents can include any one or more of the following features.

(84) X.sup.1, X.sup.2, R.sup.1, R.sup.2, each occurrence of R.sup.a, each occurrence of R.sup.b, each occurrence of R′ and R″, and combinations of these structural units, can have any of the features discussed in connection with Formula (II) for these structural units.

(85) Embodiments of the complexing agents can also include any of the other features discussed, including features associated with different embodiments, in any combination unless expressly stated otherwise.

(86) In a further aspect, this disclosure features complexing agents having a general structure given by Formula (III), and anions and salts of the general structure of Formula (III):

(87) ##STR00009##

(88) In Formula (III), each of X.sup.1 and X.sup.2 can be independently present or absent, and when one or both are present, each can be an independent member of the group that includes C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH. Each R.sup.1 and R.sup.2 is an independent member of the group that includes (i) hydrogen, (ii) —OR.sup.a, (iii) C.sub.1-4 alkoxy optionally substituted with 1-3 independent units of R.sup.b, (iv) C.sub.1-4 haloalkoxy, (v) —COH, (vi) —CO.sub.2R.sup.a, (vii) —CONR.sup.aR.sup.a, (viii) cyano, (ix) —NR.sup.aR.sup.a, (x) —NR.sup.aC(O)NR.sup.aR.sup.a, (xi) —NR.sup.aC(O)OR.sup.a, (xii) —NR.sup.aC(O)R.sup.a, (xiii) -aryl that is optionally substituted with 1-3 independent units of R.sup.b, (xiv) -heteroaryl including 5-10 ring atoms, where 1-4 ring atoms are each independent members of the group that includes N, NH, O, and S, and where the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b, (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with 1-4 independent units of R.sup.b, (xvi) -heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms can each be independent members of the group that includes N, NH and O, where the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (xvii) C.sub.1-4 thioalkoxy, (xviii) —N.sub.3, (xix) —CO.sub.2H, (xx) —C(O)R.sup.a, (xxi) —SO.sub.1-2(R.sup.a), (xxii) —O.sub.nP(O).sub.nY.sub.2, where each n is independently 0 or 1, and (xxiii) halo (e.g., —F, —Cl, —Br, or —I), and each Y is an independent member of the group that includes —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6

alkyl. Each occurrence of R.sup.a can be an independent member of the group that includes (i) H, (ii) C.sub.1-8 alkyl optionally substituted with 1-3 independent units of R.sup.b, (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with 1-4 independent units of R.sup.b, (iv) —(C.sub.0-6 alkylene)-heterocyclyl including 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and the heterocyclyl is optionally substituted with 1-4 independent units of R.sup.b, (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with 1-5 independent units of R.sup.b, or (vi) —(C.sub.0-6 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes N, NH, O, and S, and the heteroaryl is optionally substituted with 1-3 independent units of R.sup.b. Each occurrence of R.sup.b can be an independent member of the group that includes (i) halo, (ii) cyano, (iii) C.sub.1-6 alkyl, (iv) C.sub.2-6 alkenyl, (v) C.sub.2-6 alkynyl, (vi) C.sub.1-4 haloalkyl, (vii) C.sub.1-4 alkoxy, (viii) C.sub.1-4 haloalkoxy, (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where 1-3 of the ring atoms are independent members of the group that includes NH, O, and S, and where the heterocyclyl is optionally substituted with 1-4 independent units of C.sub.1-4 alkyl, (xi) —(C.sub.0-3 alkylene)-phenyl, (xii) —(C.sub.0-3 alkylene)-heteroaryl including 5-10 ring atoms, where 1-4 of the ring atoms are independent members of the group that includes of N, NH, O, and S, (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl), (xiv) —NR′R″, (xv) —OH, (xvi) —S(O).sub.1-2(NR′R″), (xvii) —C.sub.1-4 thioalkoxy, (xviii) —NO.sub.2, (xix) —N(R′)(C(═O)C.sub.1-3 alkyl), (xx) —C(═O)(C.sub.1-4 alkyl), (xxi) —C(═O)O(C.sub.1-4 alkyl), (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″). Each occurrence of R′ and R″ can be an independent member of the group that includes H and C.sub.1-4 alkyl, or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached can form a ring including 3-8 ring atoms, where the ring includes (a) 1-7 ring carbon atoms, and (b) 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″) which are each independent members of the group that includes N, NH, O, and S.

(89) Embodiments of the complexing agents can include any one or more of the following features.

(90) X.sup.1, X.sup.2, R.sup.1, R.sup.2, each occurrence of R.sup.a, each occurrence of R.sup.b, each occurrence of R′ and R″, and combinations of these structural units, can have any of the features discussed in connection with Formula (III) for these structural units.

(91) Embodiments of the complexing agents can also include any of the other features discussed, including features associated with different embodiments, in any combination unless expressly stated otherwise.

Definitions

(92) As used throughout, the terms “about” and “approximately” are used interchangeably, and when used to refer to modify a numerical value, encompass a range of uncertainty of the numerical value of from ½ of the numerical value to twice the numerical value.

(93) As used throughout, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise.

(94) As used throughout, the term “distinguishing moiety” refers to a moiety bonded to the fluorescent (for example, aromatic) portion of a complexing agent that distinguishes the complexing agent on the basis of chemical structure from other complexing agents with different moieties bound to their respective fluorescent portions.

(95) As used throughout, the terms “tracer”, “cross-well tracer”, and “inter-well tracer” each refer to a compound or agent (for example, a complexing agent) that is typically injected into one location of a reservoir, and then extracted from another location (that is, as part of a sample of fluid extracted from the reservoir). The presence or absence of the tracer, for example, can provide information about the connectivity between the injection and extraction locations, and the concentration of the tracer can provide information about flow capacity between the two locations.

(96) As used throughout, the term “hydrocarbon” refers to a fluid that includes 1% or more by volume of one or more organic compounds from natural sources. For example, the one or more organic compounds can include naturally occurring compounds extracted or otherwise liberated from a subterranean reservoir. The fluid can also include other compounds such as, but not limited to, water.
(97) The details of one or more embodiments are set forth in the accompanying drawings and the description. Other features will also be apparent from the description, drawings, and claims.

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## Description

DESCRIPTION OF DRAWINGS
(1) FIG. **1** is a schematic plot of time-resolved luminescence emission of components of a fluid extracted from a petroleum reservoir.
(2) FIG. **2**A is a luminescence spectrum of a complexed lanthanide ion and a bare lanthanide ion.
(3) FIG. **2**B is a schematic diagram showing absorption of incident light and luminescence emission from a complexed lanthanide ion.
(4) FIG. **3** is a schematic diagram showing examples of two complexing agent structures.
(5) FIG. **4** is a schematic diagram showing a process for the use of a complexing agent as a cross-well tracer, and subsequent complex formation.
(6) FIG. **5** is a schematic diagram showing a process for recovery, purification, and analysis of three different complexing agents.
(7) FIG. **6** is a plot showing luminescence emission as a function of wavelength for a complexing agent heated for different times.
(8) FIG. **7**A is a plot showing luminescence emission as a function of wavelength for complexed and un-complexed europium.
(9) FIG. **7**B is a plot showing luminescence emission as a function of wavelength for complexed europium, water extracted from a reservoir, and un-complexed europium.
(10) FIG. **8** is a plot of normalized concentration of a complexing agent against pore volumes for a complexing agent and a sodium bromide (NaBr) tracer.
(11) FIG. **9** is a plot of normalized concentration of a complexing agent vs. pore volumes for a complexing agent and a fluorinated benzoic acid (FBA) tracer.
(12) FIG. **10** is a flowchart showing example steps for a method of analyzing a fluid that includes a complexing agent extracted from a reservoir.
(13) FIG. **11** is a flowchart showing example steps for a method of analyzing a fluid that includes three complexing agents extracted from a reservoir.
(14) FIG. **12** is a schematic diagram showing a process for the use of several complexing agents as cross-well tracers.
(15) FIG. **13**A is a high-pressure liquid chromatography (HPLC) trace of response factor against retention time for four dipicolinic acid (DPA) analogs.
(16) FIG. **13**B is a plot of fluorescence intensity against wavelength for three DPA analogs.
(17) FIG. **14**A is a plot of fluorescence intensity against wavelength for a DPA analog complexed with terbium ions in an acetate buffer.
(18) FIG. **14**B is a plot of fluorescence intensity against wavelength for a DPA analog complexed with terbium ions in produced water from an extraction site.
(19) FIG. **15**A is a plot showing recovered normalized concentration as a function of pore volume for a molecular tracer and KCl reference tracer in a limestone core.
(20) FIG. **15**B is a plot showing cumulative recovery as a function of pore volume for a molecular tracer and KCl reference tracer in a limestone core.
(21) FIG. **16** is a schematic diagram showing injector and producer wells in an oilfield.

(22) FIG. **17** is a recovery curve for a molecular tracer in produced water.
(23) FIGS. **18**A-**18**C are plots showing reference reservoir models.
(24) FIGS. **18**D-**18**F are plots showing history-matched oilfield production rates for the reservoir models of FIGS. **18**A-**18**C.
(25) FIGS. **18**G-**18**I are plots showing net present value for reservoirs managed with and without molecular tracer information for the reservoir models of FIGS. **18**A-**18**C.
(26) FIG. **19** is a set of plots showing liquid chromatograms for nine different molecular tracers.
(27) Like reference symbols in the various drawings indicate like elements.

DETAILED DESCRIPTION

(28) Using cross-well tracers to map the connectivity and heterogeneity of hydrocarbon reservoirs enables the identification of wells that are contributing to hydrocarbon production and fluid tracing, allowing informed adjustment of well rates to achieve a more balanced water flood. Further, for mature fields under peripheral water flooding programs that could benefit from infill drilling, implementation of a full-field cross-well tracer program that elucidates the existence of faults and greater permeability zones can greatly reduce the uncertainties for waterflood management and justify the expensive drilling/workover programs for the field.
(29) A commonly used category of tracer is fluorinated benzoic acids (FBA's). FBA's have exhibited weak interactions with reservoir matrices and can be detected using ultra-sensitive gas chromatography mass spectrometry (GC/MS). When using GC/MS to detect FBA tracers under favorable conditions (that is, under correct ionization mode), the FBA's can be detected between 10-100 parts per trillion (ppt), depending on the fluorinated benzoic acid used and the unique response of the other components that naturally occur in produced fluids. In general, separate calibrations are used for each different analyte that undergoes mass spectral analysis.
(30) Recent simulations have suggested that data obtained from long-term deployment of inter-well tracers may improve both history matching and production optimization in realistic reservoir models. To facilitate the collection and quantification of injected tracers in large fields, the present disclosure features families of inter-well tracers that can be detected rapidly (e.g., in real time or near-real time), that can be sampled automatically with reduced work-up relative to conventional tracers, that can be transported comparatively long distances between injection and production sites, and that exhibit reduced retention in the reservoir matrix relative to conventional tracers.
(31) After injection at a particular location in a reservoir, the molecular tracers (also referred to as complexing agents) described are able to traverse a pathway from the injection location to a designated producing well for extraction. The tracers are designed to have relatively high solubility in fluids that naturally occur and circulate in reservoirs (for example, water or hydrocarbon compounds), and a relatively weak affinity for the various bedrock and earth formations that the tracers are exposed to while moving through the reservoir.
(32) These features contribute to the tracers disclosed herein having a relatively high reservoir mobility. For certain tracers, having a relatively high mobility manifests as having a relatively low retention in reservoir rocks. For example, in some embodiments, the tracers disclosed herein have a retention in reservoir rocks of less than 50 micrograms per gram (Tg/g) of reservoir rocks (such as less than 40 Tg/g, less than 30 Tg/g, less than 20 Tg/g, less than 15 Tg/g, less than 10 Tg/g, less than 5 Tg/g, less than 2 Tg/g, less than 1 Tg/g).
(33) Without wishing to be bound by theory, it is believed that the various structural features of the tracers may be responsible for the relatively high reservoir fluid solubility and relatively low earth retention characteristics of the tracers. This may be due, for example, to the combination of polar functional groups and lipophilic aromatic groups present in some embodiments of the tracers. The relatively high mobility of the tracers will later be demonstrated and discussed in the context of mobility experiments that simulate the conditions that the tracers encounter in reservoirs.
(34) The tracers, after recovery from a producing well, are optically detectable in the produced fluid at parts per quadrillion concentrations or less after a facile and selective complex formation

step with trivalent lanthanide elements, and with minimal background signal due to other contaminants. Not wishing to be bound by theory, it is believed that when used as inter-well tracers, the disclosed complexing agents encounter reservoir fluids with excess naturally-occurring divalent and trivalent ions. Such divalent and trivalent ions may bind with lanthanide ions competitively, generating complexes that may also fluoresce, thus contributing to the fluorescence background. The fluorescence background may also contain, for example, contributions due to polyaromatic hydrocarbons (PAH's).

(35) FIG. **1** is a schematic plot of time-resolved fluorescence and luminescence emission of components of a fluid extracted from a petroleum reservoir, after exposure to trivalent lanthanide elements. After flash excitation **100**, which ends at a time t.sub.0, the lanthanide complexes formed between the tracers and lanthanide elements have a long excited state lifetime **104**, luminescing on a time scale of milliseconds (ms) to microseconds (μs). In some embodiments, the complex's luminescence occurs for a time period greater than 5 microseconds (for example, greater than 8 μs, greater than 10 μs, greater than 15 μs, greater than 20 μs, greater than 25 μs, greater than 30 μs, greater than 35 μs, greater than 40 μs, greater than 50 μs, greater than 100 μs, greater than 200 Ts, greater than 300 Ts, greater than 500 Ts, greater than 700 Ts, greater than 1 millisecond (ms), greater than 2 ms, greater than 5 ms, greater than 10 ms) after excitation is complete.

(36) Without wishing to be bound by theory, the long excited state lifetime occurs due to parity-forbidden transitions between lanthanide ion excited and ground states, which occur significantly more slowly than parity-allowed state-to-state transitions during excitation and further, significantly more slowly than background fluorescence arising from parity allowed excited-to-ground state transitions among other components of the reservoir fluid. When a lanthanide ion is in close proximity to a sensitizing chromophore that either has a strong dipole moment or is anionic such that is can associate ionically with the lanthanide ion, significant enhancement of the lanthanide ion luminescence occurs because the sensitization process circumvents the LaPorte selection rules that normally forbid f-f transitions.

(37) This difference in time scales separates the luminescence signal of the lanthanide complex from the background fluorescent signals **102**, which are emitted from the other components (which, in some embodiments, are contaminants) found in the extracted fluid, and become undetectable at a time t.sub.1. In turn, the difference in excited state lifetimes and concomitant difference in the temporal evolution of emission from the lanthanide complexes and background components allows gating of the optical detector such that the detector can be used to measure luminescence from the complex alone, after fluorescence from background components in the extracted fluid has decayed.

(38) In addition to reducing or eliminating confounding effects of background fluorescence, the relatively greater sensitivity that can be achieved when measuring the disclosed tracers is in part due to the relatively strong luminescence emission of the complexes. FIG. **2**A is a luminescence spectrum of a complexed lanthanide ion and a bare lanthanide ion. The bare lanthanide ion has a peak **200** that is of lesser intensity than the intensity of the complexed lanthanide ion peak **202**. FIG. **2**B is a schematic diagram showing absorption of incident light and luminescence emission from a complexed lanthanide ion. The greater quantum yield of luminescence from the lanthanide complex is due to the antenna-like function of the fluorophoric complexing agent **210**, which absorbs incident light **212**. The ligand then transfers this excitation by process **214** to the lanthanide ion **216**, which then emits fluorescence **218**. In effect, the ligand functions as an energy harvester to, for example, overcome the lesser magnitude molar absorptivities of lanthanide ions and bypass the selection rules associated with transitions to the luminescent lanthanide excited state, thus increasing the quantum yield of the luminescence process.

(39) As a result, luminescence can be enhanced by, for example, three orders of magnitude relative to a bare lanthanide ion. The luminescence intensities of lanthanide ions can be enhanced to this degree by exposing the ions to a molar excess of tracer (also referred to as complexing agent) relative to the ion. It is believed that this results in the exclusion of water molecules from the

formed complex, thus maximizing the number of complexing ligands included in the complex.
(40) Another feature of the disclosed tracers is the ability to derivatize the tracers with functional groups (also referred to as “distinguishing moieties”) to generate analogs. Each of several of these analogs can be injected at a different injection location in a reservoir. After extracting a fluid from a producing well, the various analogs can be separated by virtue of their different chemical identities. The resulting purified tracers form complexes with lanthanide ions and are detected via luminescence emission. Since the light-capturing portion of each tracer is the same, each complex will luminesce with similar intensity, and over a similar temporal window. This allows for information to be gathered on multiple flow paths extending between different injection sites and a common recovery site.

Analyzing a Fluid Extracted from a Reservoir

(41) FIG. **10** is a flowchart showing a series of example steps for a method of analyzing a fluid extracted from a reservoir. In step **1002**, a first composition including a first complexing agent is introduced into a reservoir at a first location. In some embodiments, the first location is an injection well.
(42) In step **1004**, a fluid is extracted from the reservoir at a second location different from the first location, the fluid including a concentration of the first complexing agent that is present in the fluid following injection at the first location in step **1002**. The fluid may also include materials and compounds typically found in the earth's crust, for example: water, heavy metals (for example, iron, manganese, chromium, vanadium, or zirconium), salts (for example, potassium salts, calcium salts, magnesium salts, or sodium salts (for example, sodium chloride)), naturally occurring radioactive material (for example, uranium, thorium, radium, or radon), zinc, lead, sulfur, barium, or any combination of the previously listed components. In some embodiments, the fluid includes hydrocarbons (for example, hydrocarbons derived from various forms of petroleum including, but not limited to, paraffinic petroleum, paraffinic-naphthenic petroleum, naphthenic petroleum, paraffinic-naphthenic-aromatic petroleum, and aromatic petroleum) and polyaromatic hydrocarbons. In some embodiments, a separation of the complexing agent from one or more of the other components in the fluid is performed, for example to reduce or eliminate spectral contributions from the other components (that is, “background noise”) during measurement, a discussion of which is forthcoming.
(43) In step **1006**, the extracted fluid (or a separated/purified portion of the fluid) is combined with a second composition including a concentration of a lanthanide ion to form a third composition that includes a concentration of a complex formed by the first complexing agent and the lanthanide ion. As previously discussed, a separation of the complex that is formed from one or more of the other components in the third composition can optionally be performed at this stage to purify the complex prior to subsequent detection.
(44) In step **1008**, a quantity of the third composition (or a purified solution derived from the third composition) is exposed to electromagnetic radiation to detect (and, in some embodiments, quantitatively measure) the complex. In some embodiments, the wavelength of the exciting electromagnetic radiation is in the ultraviolet region of the spectrum.
(45) In general, exposure to the illumination radiation occurs for a first time period ending at a time t.sub.0. As explained previously, background components in the third composition undergo fluorescence from time t.sub.0 (which is defined as the time point at which the excitation process has ended) until a later time t.sub.1 (which is defined as the time point at which fluorescence from the background components has decayed to an intensity level that is no longer detectable).
(46) In step **1010**, luminescence emission is detected from the irradiated complex, beginning at time t.sub.1>t.sub.0. In general, the interval t.sub.1−t.sub.0 is selected to ensure that the measured luminescence emission from the irradiated complex is not contaminated with significant contributions from background components (that is, other components present in the third composition). In some embodiments, for example, the interval t.sub.1−t.sub.0 is greater than 2

microseconds (for example, greater than 5 microseconds, greater than 8 μs, greater than 10 μs, greater than 15 μs, greater than 20 μs, greater than 25 μs, greater than 30 μs, greater than 35 μs, greater than 40 μs, greater than 50 μs, or greater than 100 μs).

(47) In step **1012**, information is determined about fluid flow between the first location (the injection site) and the second location (the extraction site) within the reservoir based on the detected luminescence emission. The information can indicate, for example, whether a particular injection bore and extraction bore are interconnected through the reservoir, and, if connected, can also indicate how fluid flows through the reservoir.

(48) For example, if a tracer is introduced into a reservoir and subsequent sample extraction from a producing bore shows the presence of the tracer, a connection exists between the point of injection and the point of extraction.

(49) Correlations between the presence of the tracer in the extracted fluid and the elapsed time between injection and detection of the tracer can also provide information about fluid flow through the reservoir. As an example, the elapsed time between injection and the appearance of the tracer in the extracted fluid (for example, in a measurement process where fluid is extracted periodically and analyzed) can provide information about the fluid flow capacity of the reservoir, the interconnected-ness of flow pathways, and residual oil saturation, which is difficult to acquire directly by other means.

(50) In some embodiments, the information includes the concentration of the first complexing agent. Due to the enhancement of luminescence of the complexes and reduction or elimination of background fluorescence, as discussed previously, a minimum concentration of the first complexing agent in the third composition (formed in step **1006**) that can be detected is between about 1 part per million and about 1 part per sextillion (for example, about 1 part per million and about 299 parts per billion, about 300 parts per billion (ppb) and about 1.1 parts per billion (ppb), about 1 part per billion (ppb) and about 499 parts per quadrillion (ppq), about 500 parts per quadrillion and about 1.1 parts per quadrillion, about 1 part per quadrillion (ppb) and about 499 parts per quintillion (ppq), about 500 parts per quintillion and about 1.1 parts per quintillion, about 1.1 part per quintillion and about 499 parts per sextillion, about 500 parts per sextillion and about 1 part per sextillion).

(51) FIG. **4** is a schematic diagram showing an example of a process for the use of a complexing agent as a cross-well tracer. The complexing agent **400** is introduced into the reservoir **404** through an injection bore at a first location **401**, and propagates through at least a portion of the reservoir **402**. A fluid sample is collected from a producing bore at a second location **406** different from the first location **401**. The fluid sample, which includes the complexing agent, is mixed with a solution **408** containing a specific concentration of one or more lanthanide ions (which, when bare or uncomplexed, have low fluorescence intensities), resulting in the formation of one or more types of complexes **410**.

(52) In general, it is possible to use more than one (for example, 2, 3, 4, 5, from 6 to 10, from 11 to 20, from 21 to 50, or from 51 to 100) complexing agents in the disclosed methods, for example to determine information about flow paths between multiple injection locations and an extraction location of a reservoir.

(53) FIG. **11** is a flowchart showing a series of example steps of a procedure for analyzing a fluid extracted from a reservoir. In the procedure shown in FIG. **11**, multiple complexing agents, each including a different distinguishing moiety, are introduced into the reservoir at different injection sites. Deployment of multiple complexing agents, each injected at a different location into a reservoir, allows determination of information about flow paths (such as flow rates) between each injection site and the extraction site. In general, unless expressly stated otherwise, the features and aspects of the method of FIG. **11** are similar to those already discussed in connection with FIG. **10**.

(54) In FIG. **11**, a first composition that includes a first complexing agent is introduced into a reservoir at a first location in step **1102**. Similarly, in steps **1104** and **1106**, fourth and fifth

compositions (which include a second complexing agent and a third complexing agent, respectively, with the designations of these being consistent with the designations previously discussed in connection with FIG. **10**) are introduced into the reservoir at third and fourth locations, respectively. The fourth composition includes a second complexing agent, and the fifth composition includes a third complexing agent. Each of the first, third, and fourth locations are different.

(55) Although not shown in FIG. **11**, the procedure can also include introducing additional compositions into the reservoir at additional locations. In general, any number of compositions can be introduced. For example, the number of compositions that are introduced can be three or more (e.g., five or more, ten or more, 15 or more, 2 or more, 3 or more, 4 or more, 5 or more, 7 or more, 10 or more, 15 or more, 20 or more, or even more).

(56) Typically, at each location, the complexing agent introduced differs from the complexing agents introduced at the other locations so that information specific to the flow path between that location and the extraction location can be determined. Each of the complexing agents that are introduced can correspond to one of the complexing agents discussed in a subsequent section.

(57) Further, in some embodiments, step **1106** is omitted and the resulting method includes the introduction of only the first and second complexing agents, with subsequent steps excluding the processing and presence of the third complexing agent.

(58) In step **1108**, a fluid is extracted from the reservoir at a second location that differs from each of the locations where the various compositions were introduced into the reservoir. The extracted fluid generally includes a quantity (that is, a concentration) of each of the first, second, and third complexing agents. Optionally, a separation procedure can be performed on the extracted fluid to isolate portions of the first, second, and third complexing agents from one another to facilitate analysis of the complexing agents.

(59) Suitable separation procedures for isolating the different complexing agents include, but are not limited to, chromatographic separation techniques such as liquid chromatography and gas chromatography. In general, these techniques can isolate a relative large number of different complexing agents from an initial mixture. For example, FIG. **19** shows liquid chromatographic traces for nine different complexing agents, each of which elutes from the chromatography column at a different retention time (and is therefore separated from the other complexing agents).

(60) In step **1110**, the extracted fluid (or the complexing agents isolated from the extracted fluid) is (are) combined with a second composition that includes a concentration of one or more types of lanthanide ions to form a third composition. In general, complexes are formed between each of the complexing agents present in the extracted fluid and the one or more types of lanthanide ions. Following formation of the different types of complexes (for example, complexes involving lanthanide ions and each of the first, second, and third complexing agents), a separation procedure is typically performed to isolate quantities of the various types of complexes. Each type of complex formed acts, in effect, as a “reporter” for fluid flow information within the reservoir between the injection site of the corresponding complexing agent and the extraction site. A variety of different separation procedures can be used in step **1110**, including (but not limited to) chromatographic methods (for example, liquid chromatography), extraction, and fractionation.

(61) In step **1112**, each of the isolated quantities of the various complexes are exposed to electromagnetic radiation for a time period ending at time t.sub.0 to induce luminescence emission from each of the complexes. The luminescence emission is detected in step **1114** starting at time t.sub.1>t.sub.0, following the end of the illumination. As discussed previously, the interval t.sub.1−t.sub.0 is selected so that at time t.sub.1, fluorescence emission from background components has decayed to a nearly (or completely) undetectable level, such that measurement of luminescence emission from each of the complexes occurs without confounding spectral contributions from background components. As in the methods of FIG. **10**, in some embodiments, the interval t.sub.1−t.sub.0 can be greater than 2 microseconds.

(62) In step **1116**, information is determined about fluid flow paths between the various injection sites of the complexing agents (the first, third, and fourth locations) and the extraction site (the second location) from the measured luminescence of each of the complexes formed from complexing agents recovered at the extraction site. As discussed previously in connection with FIG. **10**, this information can include concentrations of each of the complexes (or complexing agents) recovered at the extraction site, flow rates between the various injection sites and the extraction site, and other information about the reservoir structure.
(63) FIG. **12** is a schematic diagram showing an example of a process for the use of several complexing agents as cross-well tracers as discussed previously in connection with FIG. **11**. In FIG. **12**, a first complexing agent is introduced into a reservoir **1200** at a location **1202**, a second complexing agent is introduced into the reservoir at location **1204**, and a third complexing agent is introduced into the reservoir at location **1206**. Reservoir fluid is extracted at location **1208**, the fluid generally including concentrations of the first, second, and third complexing agents, which have propagated from their respective injection locations through the reservoir to location **1208**. The extracted reservoir fluid is then analyzed as discussed previously.
(64) To purify the extracted reservoir fluid from location **1208**, the example process shown in FIG. **5** can be used, as the process is generally applicable to the purification and analysis of any number of complexing agents. When the extracted fluid includes concentrations of the first complexing agent **500**, the second complexing agent **502**, and the third complexing agent **504**, the process of FIG. **5** is used to isolate quantities of each of the complexing agents. Various separation procedures can be used to isolate the complexing agents. For example, in some embodiments, liquid chromatographic methods (such as ultra-high performance liquid chromatography, high-performance liquid chromatography) can be performed using one or more chromatography columns **506** to separate the complexing agents. In certain embodiments, other methods can be used in addition to, or as an alternative to, chromatographic separations. Examples of such methods include solid phase extraction, liquid-liquid extraction and fractionation.
(65) Each complexing agent, now substantially isolated from the other complexing agents, is then combined with a composition that includes lanthanide ions to form complexes, and fluorescence/luminescence spectroscopy methods are used to detect and, in some embodiments, determine quantitative information about the complexes.
Complexing Agents
(66) A variety of different complexing agents can be used as molecular tracers to determine information associated with petroleum reservoirs according to the methods that have been discussed. In this section of the disclosure, various example complexing agents are described. It should be understood that any of the complexing agents discussed in this section can be used alone or in combination with any of the methods discussed in the previous sections of this disclosure to determine information about subsurface reservoirs and fluid flow through the reservoirs. In particular, any of the first, second, and third complexing agents referenced previously can be selected from among the various compounds corresponding to Formula (I), Formula (II), Formula (III), or any combination of these, as will be explained in detail.
(67) FIG. **3** is a schematic diagram showing examples of two complexing agent structures. The structures of the complexing agents are designed to have three features, shown for two different structures: (1) lanthanide binding group(s) **300** that are capable of chelating lanthanide ions with large equilibrium constants, (2) a light-absorbing region **302** with large extinction coefficient capable of absorbing excitation light efficiently, and (3) derivatizable molecular “handles” **304** that allow for installation of different moieties to generate analogs that can each be deployed at a unique location in a reservoir. The complexing agents are monodentate, bidentate, tridentate, or tetradentate ligands that bind to lanthanides through, for example, basic ring member nitrogens, carboxylate groups, or both.
(68) In some embodiments, the complexing agent is a compound of Formula (I), or an anion or salt

thereof:
(69) ##STR00010##
where: X is present or absent, and when present, is selected from the group consisting of: C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH; R is selected from the group consisting of: (i) hydrogen; (ii) —OR.sup.a; (iii) C.sub.1-4 alkoxy optionally substituted with from 1-3 R.sup.b; (iv) C.sub.1-4 haloalkoxy; (v) —COH; (vi) —CO.sub.2R.sup.a; (vii) —CONR.sup.aR.sup.a; (viii) cyano; (ix) —NR.sup.aR.sup.a; (x) —NR.sup.aC(O)NR.sup.aR.sup.a; (xi) —NR.sup.aC(O)OR.sup.a; (xii) —NR.sup.aC(O)R.sup.a; (xiii) -aryl that is optionally substituted with from 1-3 R.sup.b; (xiv) -heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 R.sup.b; (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with from 1-4 R.sup.b, (xvi) heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of N, NH and O, where the heterocyclyl is optionally substituted with from 1-4 R.sup.b, (xvii) C.sub.1-4 thioalkoxy; (xviii) —N.sub.3; (xix) —CO.sub.2H; (xx) —C(O)R.sup.a; (xxi) —SO.sub.1-2(R.sup.a); and (xxii) —O.sub.nP(O).sub.nY.sub.2, where n is independently 0 or 1, and where Y is independently selected from —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl; each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b; (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independently selected R.sup.b; (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected R.sup.b; (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with from 1-5 independently selected R.sup.b; or (vi) —(C.sub.0-6 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 independently selected R.sup.b; each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (iv) C.sub.2-6 alkenyl; (v) C.sub.2-6 alkynyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (viii) C.sub.1-4 haloalkoxy; (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl); and (xiv) —NR′R″; (xv) —OH; (xvi) —S(O).sub.1-2(NR′R″); (xvii) —C.sub.1-4 thioalkoxy; (xviii) —NO.sub.2; (xix) —N(R′)(C(═O)C.sub.1-3 alkyl); (xx) —C(═O)(C.sub.1-4 alkyl); (xxi) —C(═O)O(C.sub.1-4 alkyl); (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″); each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl; or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached forms a ring including from 3-8 ring atoms, where the ring includes: (a) from 1-7 ring carbon atoms; and (b) from 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independently selected from the group consisting of N, NH, O, and S. In some embodiments, X is C.sub.1-10 alkylene; R is selected from the group consisting of: (ii) —OR.sup.a; where the R.sup.a of —OR.sup.a is not (i) H or (ii) C.sub.1-8 alkyl substituted with —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl; (vi) —CO.sub.2R.sup.a, where the R.sup.a of —CO.sub.2R.sup.a is not H; (viii) cyano; (ix) —NR.sup.aR.sup.a; (x) —

NR.sup.aC(O)NR.sup.aR.sup.a; (xi) —NR.sup.aC(O)OR.sup.a; (xii) —NR.sup.aC(O)R.sup.a; (xiii) -aryl that is optionally substituted with from 1-3 R.sup.b; (xiv) -heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 R.sup.b; (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with from 1-4 R.sup.b, (xvi) -heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of N, NH and O, where the heterocyclyl is optionally substituted with from 1-4 R.sup.b, (xx) —C(O)R.sup.a; and (xxi) —SO.sub.1-2(R.sup.a); each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b; (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independently selected R.sup.b; (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected R.sup.b; (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with from 1-5 independently selected R.sup.b; or (vi) —(C.sub.0-6 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 independently selected R.sup.b; each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (iv) C.sub.2-6 alkenyl; (v) C.sub.2-6 alkynyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (viii) C.sub.1-4 haloalkoxy; (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl); and (xiv) —NR′R″; (xv) —OH; (xvi) —S(O).sub.1-2(NR′R″); (xvii) —C.sub.1-4 thioalkoxy; (xviii) —NO.sub.2; (xix) —N(R′)(C(═O)C.sub.1-3 alkyl); (xx) —C(═O)(C.sub.1-4 alkyl); (xxi) —C(═O)O(C.sub.1-4 alkyl); (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″); each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl; or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached forms a ring including from 3-8 ring atoms, where the ring includes: (a) from 1-7 ring carbon atoms; and (b) from 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independently selected from the group consisting of N, NH, O, and S. In some embodiments, X is —CH.sub.2—. In some embodiments, X.sup.1 and X.sup.2 are both absent. In some embodiments, R is (ii) —OR.sup.a, and where the R.sup.a of —OR.sup.a is not (i) H or (ii) C.sub.1-8 alkyl substituted with —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl. In some embodiments, R is selected from the group consisting of: (ix) —NR.sup.aR.sup.a, where 1 R.sup.a is H; (x) —NR.sup.aC(O)NR.sup.aR.sup.a, where at least 1 R.sup.a is H; (xi) —NR.sup.aC(O)OR.sup.a, where the R.sup.a bonded to N is H; and (xii) —NR.sup.aC(O)R.sup.a. In some embodiments, R is selected from the group consisting of: (vi) —CO.sub.2R.sup.a, where the R.sup.a of —CO.sub.2R.sup.a is not H; and (xx) —C(O)R.sup.a. In any of the previous embodiments, each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b. In any of the previous embodiments, each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiv) —NR′R″; (xv) —OH. In any of the

previous embodiments, each occurrence of R.sup.b is independently selected from the group consisting of: (iii) C.sub.1-6 alkyl; (vii) C.sub.1-4 alkoxy; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xv) —OH. In any of the previous embodiments, each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl. In some embodiments, the complexing agent is a compound of Formula (II), or an anion or salt thereof:

(70) ##STR00011##

where: each of X.sup.1 and X.sup.2 is independently present or absent, and when one or both are present, each is independently selected from the group consisting of: C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH; each of R.sup.1 and R.sup.2 is independently selected from the group consisting of: (i) hydrogen; (ii) —OR.sup.a; (iii) C.sub.1-4 alkoxy optionally substituted with from 1-3 RD; (iv) C.sub.1-4 haloalkoxy; (v) —COH; (vi) —CO.sub.2R.sup.a; (vii) —CONR.sup.aR.sup.a; (viii) cyano; (ix) —NR.sup.aR.sup.a; (x) —NR.sup.aC(O)NR.sup.aR.sup.a; (xi) —NR.sup.aC(O)OR.sup.a; (xii) —NR.sup.aC(O)R.sup.a; (xiii) -aryl that is optionally substituted with from 1-3 R.sup.b; (xiv) -heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 R.sup.b; (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with from 1-4 R.sup.b, (xvi) -heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of N, NH and O, where the heterocyclyl is optionally substituted with from 1-4 R.sup.b, (xvii) C.sub.1-4 thioalkoxy; (xviii) —N.sub.3; (xix) —CO.sub.2H; (xx) —C(O)R.sup.a; (xxi) —SO.sub.1-2(R.sup.a); and (xxii) —O.sub.nP(O).sub.nY.sub.2, where n is independently 0 or 1, and where Y is independently selected from —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl; each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b; (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independently selected R.sup.b; (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected R.sup.b; (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with from 1-5 independently selected R.sup.b; or (vi) —(C.sub.0-6 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 independently selected R.sup.b; each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (iv) C.sub.2-6 alkenyl; (v) C.sub.2-6 alkynyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (viii) C.sub.1-4 haloalkoxy; (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl); and (xiv) —NR′R″; (xv) —OH; (xvi) —S(O).sub.1-2(NR′R″); (xvii) —C.sub.1-4 thioalkoxy; (xviii) —NO.sub.2; (xix) —N(R′)(C(═O)C.sub.1-3 alkyl); (xx) —C(═O)(C.sub.1-4 alkyl); (xxi) —C(═O)O(C.sub.1-4 alkyl); (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″); each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl; or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each

is attached forms a ring including from 3-8 ring atoms, where the ring includes: (a) from 1-7 ring carbon atoms; and (b) from 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independently selected from the group consisting of N, NH, O, and S. In some embodiments, each of X.sup.1 and X.sup.2 is independently present or absent, and when one or both are present, each is independently selected from the group consisting of: C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH; each of R.sup.1 and R.sup.2 is independently selected from the group consisting of: (ii) —OR.sup.a; (iii) C.sub.1-4 alkoxy optionally substituted with from 1-3 R.sup.b; (iv) C.sub.1-4 haloalkoxy; (vi) —CO.sub.2R.sup.a; (vii) —CONR.sup.aR.sup.a; (viii) cyano; (ix) —NR.sup.aR.sup.a; (x) —NR.sup.aC(O)NR.sup.aR.sup.a; (xi) —NR.sup.aC(O)OR.sup.a; (xii) —NR.sup.aC(O)R.sup.a; (xiii) -aryl that is optionally substituted with from 1-3 R.sup.b; (xiv) -heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 R.sup.b; (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with from 1-4 R.sup.b, (xvi) -heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of N, NH and O, where the heterocyclyl is optionally substituted with from 1-4 R.sup.b, (xix) —CO.sub.2H; (xx) —C(O)R.sup.a; and (xxi) —SO.sub.1-2(R.sup.a); each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b; (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independently selected R.sup.b; (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected R.sup.b; (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with from 1-5 independently selected R.sup.b; or (vi) —(C.sub.0-6 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 independently selected R.sup.b; each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (iv) C.sub.2-6 alkenyl; (v) C.sub.2-6 alkynyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (viii) C.sub.1-4 haloalkoxy; (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl); and (xiv) —NR′R″; (xv) —OH; (xvi) —S(O).sub.1-2(NR′R″); (xvii) —C.sub.1-4 thioalkoxy; (xviii) —NO.sub.2; (xix) —N(R′)(C(═O)C.sub.1-3 alkyl); (xx) —C(═O)(C.sub.1-4 alkyl); (xxi) —C(═O)O(C.sub.1-4 alkyl); (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″); each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl; or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached forms a ring including from 3-8 ring atoms, where the ring includes: (a) from 1-7 ring carbon atoms; and (b) from 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independently selected from the group consisting of N, NH, O, and S. In some embodiments, X.sup.1 and X.sup.2 are both —CH.sub.2—. In some embodiments, X.sup.1 and X.sup.2 are both absent. In some embodiments, R.sup.1 and R.sup.2 are independently selected from: (ix) —NR.sup.aR.sup.a; (x) —NR.sup.aC(O)NR.sup.aR.sup.a; (xi) —NR.sup.aC(O)OR.sup.a; and (xii) —NR.sup.aC(O)R.sup.a. In some embodiments, R.sup.1 and

R.sup.2 are independently selected from: (ix) —NHR.sup.a; (x) —NHC(O)NHR.sup.a; (xi) —NHC(O)OR.sup.a; and (xii) —NHC(O)R.sup.a. In some embodiments, R.sup.1 and R.sup.2 are each (ix) —NHR.sup.a (for example, —NH.sub.2). In certain of these embodiments, R.sup.a is selected from (ii) C.sub.1-8 alkyl substituted with from 1-3 independently selected R.sup.b, where at least one of the R.sup.b is (xv) —OH. In some embodiments, R.sup.1 and R.sup.2 are each (x) —NHC(O)NHR.sup.a. In some embodiments, R.sup.1 and R.sup.2 are each (xi) —NHC(O)OR.sup.a. In some embodiments, R.sup.1 and R.sup.2 are each (xii) —NHC(O)R.sup.a. In some embodiments, each of R.sup.1 and R.sup.2 is the same. In some embodiments, each of R.sup.1 and R.sup.2 is different. In any of the previous embodiments, each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b. In any of the previous embodiments, each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiv) —NR′R″; (xv) —OH. In any of the previous embodiments, each occurrence of R.sup.b is independently selected from the group consisting of: (iii) C.sub.1-6 alkyl; (vii) C.sub.1-4 alkoxy; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xv) —OH. In any of the previous embodiments, each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl. In some embodiments, the complexing agent is a compound of Formula (III), or an anion or salt thereof: (71) ##STR00012##

where: each of X.sup.1 and X.sup.2 is independently present or absent, and when one or both are present, each is independently selected from the group consisting of: C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH; each of R.sup.1 and R.sup.2 is independently selected from the group consisting of: (i) hydrogen; (ii) —OR.sup.a; (iii) C.sub.1-4 alkoxy optionally substituted with from 1-3 R.sup.b; (iv) C.sub.1-4 haloalkoxy; (v) —COH; (vi) —CO.sub.2R.sup.a; (vii) —CONR.sup.aR.sup.a; (viii) cyano; (ix) —NR.sup.aR.sup.a; (x) —NR.sup.aC(O)NR.sup.aR.sup.a; (xi) —NR.sup.aC(O)OR.sup.a; (xii) —NR.sup.aC(O)R.sup.a; (xiii) -aryl that is optionally substituted with from 1-3 R.sup.b; (xiv) -heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 R.sup.b; (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with from 1-4 R.sup.b, (xvi) -heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of N, NH and O, where the heterocyclyl is optionally substituted with from 1-4 R.sup.b, (xvii) C.sub.1-4 thioalkoxy; (xviii) —N.sub.3; (xix) —CO.sub.2H; (xx) —C(O)R.sup.a; (xxi) —SO.sub.1-2(R.sup.a); (xxii) —O.sub.nP(O).sub.nY.sub.2, where n is independently 0 or 1, and where Y is independently selected from —OR.sup.a, NR.sup.aR.sup.a, and C.sub.1-6 alkyl; and (xxiii) halo (e.g., —F, —Cl, —Br, —I); each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b; (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independently selected R.sup.b; (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected R.sup.b; (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with from 1-5 independently selected R.sup.b; or (vi) —(C.sub.0-6 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each

independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 independently selected R.sup.b; each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (iv) C.sub.2-6 alkenyl; (v) C.sub.2-6 alkynyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (viii) C.sub.1-4 haloalkoxy; (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl); and (xiv) —NR′R″; (xv) —OH; (xvi) —S(O).sub.1-2(NR′R″); (xvii) —C.sub.1-4 thioalkoxy; (xviii) —NO.sub.2; (xix) —N(R′)(C(═O)C.sub.1-3 alkyl); (xx) —C(═O)(C.sub.1-4 alkyl); (xxi) —C(═O)O(C.sub.1-4 alkyl); (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″); each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl; or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached forms a ring including from 3-8 ring atoms, where the ring includes: (a) from 1-7 ring carbon atoms; and (b) from 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independently selected from the group consisting of N, NH, O, and S. In some embodiments, each of X.sup.1 and X.sup.2 is independently present or absent, and when one or both are present, each is independently selected from the group consisting of: C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, where each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH; each of R.sup.1 and R.sup.2 is independently selected from the group consisting of: (ii) —OR.sup.a; (iii) C.sub.1-4 alkoxy optionally substituted with from 1-3 R.sup.b; (iv) C.sub.1-4 haloalkoxy; (vi) —CO.sub.2R.sup.a; (vii) —CONR.sup.aR.sup.a; (viii) cyano; (ix) —NR.sup.aR.sup.a; (x) —NR.sup.aC(O)NR.sup.aR.sup.a; (xi) —NR.sup.aC(O)OR.sup.a; (xii) —NR.sup.aC(O)R.sup.a; (xiii) -aryl that is optionally substituted with from 1-3 R.sup.b; (xiv) -heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 R.sup.b; (xv) —C.sub.3-10 cycloalkyl that is optionally substituted with from 1-4 R.sup.b, (xvi) -heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of N, NH and O, where the heterocyclyl is optionally substituted with from 1-4 R.sup.b, (xix) —CO.sub.2H; (xx) —C(O)R.sup.a; (xxi) —SO.sub.1-2(R.sup.a); and (xxii) halo (e.g., —F, —Cl, —Br, —I); each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b; (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, where the cycloalkyl is optionally substituted with from 1-4 independently selected R.sup.b; (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected R.sup.b: (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), where the aryl is optionally substituted with from 1-5 independently selected R.sup.b; or (vi) —(C.sub.0-6 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, where the heteroaryl is optionally substituted with from 1-3 independently selected R.sup.b; each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (iv) C.sub.2-6 alkenyl; (v) C.sub.2-6 alkynyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (viii) C.sub.1-4 haloalkoxy; (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, where from 1-3 ring atoms are each

independently selected from the group consisting of NH, O, and S, where the heterocyclyl is optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl); and (xiv) —NR′R″; (xv) —OH; (xvi) —S(O).sub.1-2(NR′R″); (xvii) —C.sub.1-4 thioalkoxy; (xviii) —NO.sub.2; (xix) —N(R′)(C(═O)C.sub.1-3 alkyl); (xx) —C(═O)(C.sub.1-4 alkyl); (xxi) —C(═O)O(C.sub.1-4 alkyl); (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″); each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl; or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached forms a ring including from 3-8 ring atoms, where the ring includes: (a) from 1-7 ring carbon atoms; and (b) from 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independently selected from the group consisting of N, NH, O, and S. In some embodiments, X.sup.1 and X.sup.2 are both —CH.sub.2—. In some embodiments, X.sup.1 and X.sup.2 are both absent. In some embodiments, R.sup.1 and R.sup.2 are independently selected from: (ix) —NR.sup.aR.sup.a; (x) —NR.sup.aC(O)NR.sup.aR.sup.a; (xi) —NR.sup.aC(O)OR.sup.a; and (xii) —NR.sup.aC(O)R.sup.a. In some embodiments, R.sup.1 and R.sup.2 are independently selected from: (ix) —NHR.sup.a; (x) —NHC(O)NHR.sup.a; (xi) —NHC(O)OR.sup.a; (xii) —NHC(O)R.sup.a; and (xiii) halo (—F, —Cl, —Br, —I). In some embodiments, R.sup.1 and R.sup.2 are each (ix) —NHR.sup.a (for example, —NH.sub.2). In certain of these embodiments, R.sup.a is selected from (ii) C.sub.1-8 alkyl substituted with from 1-3 independently selected R.sup.b, where at least one of the R.sup.b is (xv) —OH. In some embodiments, R.sup.1 and R.sup.2 are each (x) —NHC(O)NHR.sup.a. In some embodiments, R.sup.1 and R.sup.2 are each (xi) —NHC(O)OR.sup.a. In some embodiments, R.sup.1 and R.sup.2 are each (xii) —NHC(O)R.sup.a. In some embodiments, R.sup.1 and R.sup.2 are each —Cl. In some embodiments, each of R.sup.1 and R.sup.2 is the same. In some embodiments, each of R.sup.1 and R.sup.2 is different. In any of the previous embodiments, each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b. In any of the previous embodiments, each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiv) —NR′R″; (xv) —OH. In any of the previous embodiments, each occurrence of R.sup.b is independently selected from the group consisting of: (iii) C.sub.1-6 alkyl; (vii) C.sub.1-4 alkoxy; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, where from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xv) —OH. In any of the previous embodiments, each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl. In some embodiments, the complex includes water. In some embodiments, the complex includes two or more different complexing agents. Combinations of different complexing agents can be selected from among any of the agents disclosed previously. In general, depending upon the one or more complexing agents used to form the complex and the lanthanide ion complexed, the resulting complex can have a variety of different geometries about the lanthanide ion. Examples of such geometries include, but are not limited to: trigonal bipyramidal; square pyramidal; octahedral; trigonal prismatic; pentagonal bipyramidal; face capped octahedral; trigonal prismatic, square face monocapped; cubic; square antiprismatic; dodecahedral; trigonal hexagonal bypyramidal; octahedral, trans-bicapped; trigonal prismatic, triangular face bicapped; trigonal prismatic, square face bicapped; and tricapped trigonal prismatic. In general, any of the lanthanide elements can be used to form luminescent complexes for tracer detection. In some embodiments, the lanthanide ion in each complex can be selected from the group consisting of lanthanum, cerium, praseodymium,

neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. For example, the lanthanide ion is selected from the group consisting of samarium, europium, terbium, and dysprosium. In some embodiments, the complex of Formula (I) includes a 1:1:2 molar ratio of lanthanide ion to complexing agent to water. In some embodiments, the complex of Formula (I) includes a 1:2:0 molar ratio of lanthanide ion to complexing agent to water. In some embodiments, the complex of Formula (II) includes a 1:1:2 molar ratio of lanthanide ion to complexing agent to water. In some embodiments, the complex of Formula (II) includes a 1:2:1 molar ratio of lanthanide ion to complexing agent to water. In some embodiments, the complex of Formula (II) includes a 1:3:0 molar ratio of lanthanide ion to complexing agent to water.

Analysis and Enhancement of Reservoir Production

(72) The information obtained using the methods described above can be used to analyze and improve reservoir production. Specifically, information obtained from cross-well tracers that incorporate the foregoing complexing agents can be used to adjust a variety of control parameters such as water injection rates and fluid extraction rates, to manage reservoir production. The use of tracer information can increase constraints on history matching processes that are used for reservoir analysis, and can provide a more cost-effective and non-instrusive method for monitoring and managing reservoirs than conventional methods such as pressure interference studies, loggings, additional well drillings, and tomography.

(73) For example, inter-well tracer information can be integrated into algorithms such as an ensemble smoother with multiple data assimilation (ES-MDA-Tracer), which can improve history matching using using integrated production and tracer information, thereby generating accurate reservoir geological models with improved prediction accuracy. Such models can then be used to improve or optimize reservoir production.

(74) Examples of methods of using tracer-derived information for analysis and improvement of reservoir production are described, for example, in U.S. patent application Ser. No. 15/786,372 entitled “Enhancing Reservoir Production Optimization Through Integrating Inter-Well Tracers”, filed on Oct. 17, 2017, the entire contents of which are incorporated herein by reference.

EXAMPLES

(75) This section provides a number of specific examples to further illustrate the previous disclosure. These examples are not intended to limit the scope of the disclosure in any manner.

Example 1—Synthesis of Complexing Agents

(76) Compounds of Formula (I)

(77) A variety of complexing agents of Formula (I), each having distinguishing moieties, were prepared through the derivatization of dimethyl 4-(hydroxymethyl)pyridine-2,6-dicarboxylate and dimethyl 4-chloropyridine-2,6-dicarboxylate as depicted in forthcoming Scheme 2. First, a versatile hydroxymethylated scaffold was prepared through hydroxymethylation of dimethyl pyridine-2,6-dicarboxylate (part “a”). Next, various transformations (for example, tosylation, iodination, part “b”) were carried out to generate a variety of complexing agents. Part “c” depicts the functionalization of a separate DPA derivative, dimethyl 4-chloropyridine-2,6-dicarboxylate, with imidazole-based moieties. Part “d” illustrates the functionalization of dimethyl 4-carboxypyridine-2,6-dicarboxylate, a synthetic precursor achieved from the oxidation of dimethyl 4-(hydroxymethyl)pyridine-2,6-dicarboxylate (shown in part “b”). Zwitterionic derivatives of DPA may also be synthesized from its imidazole-conjugated variants, as shown in part “e”.

(78) ##STR00013##

(79) ##STR00014## ##STR00015##

Synthesis of Dimethyl 2,6-Pyridine Dicarboxylate (DMDPA)

(80) A solution of dipicolinic acid (4.00 grams (g), 24 millimoles (mmol)) in methanol (50 milliliters (ml)) and concentrated sulfuric acid (10 ml) was heated for 18 hours (h). Water (30 ml) was added and the aqueous solution was neutralized with sodium carbonate. The solution was

acidified with concentrated HCl and extracted with chloroform (4×25 ml). The combined extracts were dried, filtered and concentrated to leave a white solid. Crystallization from chloroform gave dimethyl dipicolinate as a white powder (2.87 g, 96%). Proton nuclear magnetic resonance spectral peaks (.sup.1H NMR) (500 Megahertz (MHz), CDCl.sub.3) δ=8.33 (doublet (d), 2H), 8.03 (triplet (t), 1H), 4.03 (singlet (s), 6H).
(81) Synthesis of Dimethyl 4-hydroxymethylpyridine-2,6-dicarboxylate
(82) Solutions of Fe(ClO4)2.Math.6H2O (4.64 g, 12.8 mmol) in H2O (4.7 mL) and H2O2 (30% weight/weight (w/w) aqueous solution, 8 mL, 77.6 mmol) were added dropwise at 0° C. over 30 minutes (min) to a mixture of DPA dimethyl ester (2.5 g, 12.8 mmol) 7, MeOH (7.5 mL) and HClO4 (70% w/w aqueous solution, 5.6 mL, 9.32 g, 64.9 mmol). The reaction mixture was allowed to warm up slowly to room temperature and it was stirred at this temperature for 3 h. The volatile components were evaporated under reduced pressure, and the pH of the residue was adjusted to 9 with saturated Na2CO3 solution. The aqueous solution was extracted with EtOAc (3×30 mL) and the combined organic phase was dried over MgSO4, filtered and the solvent was removed. The residue was recrystallized from toluene to give the titled compound (1.87 g, 65%) as white crystals. Melting point (mp): 158-159° C. (toluene) (literature mp (lit. mp): 154-158° C.), Rf=0.11 (SiO2 thin-layer chromatography (TLC); EtOAc-toluene 1:1). .sup.1H NMR (500 MHz, CDCl.sub.3) δ=8.32 (s, 2H), 4.91 (d, 2H), 4.03 (s, 6H), 2.06 (t, 1H).
(83) Synthesis of Dimethyl 4-carboxypyridine-2,6-dicarboxylate
(84) To a solution of dimethyl 4-(hydroxymethyl)pyridine-2,6-dicarboxylate (2 g, 8.8 mmol) in 50 ml acetone was added solid KMnO4 (4.21 g, 26.6 mmol), with stirring. The reaction mixture was allowed to stir for 3 hours at room temperature, then quenched with aqueous NaHSO3 within an ice bath. The resulting solution was then filtered over celite and the collected precipitate was washed with water. Concentration of the collected filtrate (to remove acetone) was followed by acidification of the remaining aqueous phase to pH 2 using 1 molar (M) HCl, which was then subjected to extraction with ethyl acetate. The combined organic phase was dried with MgSO4, filtered, and concentrated to afford the product as a white powder (50%). .sup.1H NMR (500 MHZ, DMSO-d.sub.6) δ=14.29 (broad (br), 1H), 8.55 (s, 2H), 3.95 (s, 6H).
(85) Synthesis of Dimethyl 4-tosyloxymethylpyridine-2,6-dicarboxylate
(86) To a cooled solution of dimethyl 4-hydroxymethylpyridine-2,6-dicarboxylate (2.15 g, 9.56 mmol) in dichloromethane (20 ml) was added dropwise a solution of tosyl chloride (2.37 g, 12.4 mmol), after which the resulting solution was stirred for 20 min at 0° C. Triethylamine (6 ml) was then added dropwise in three portions at 20 min intervals. After the addition was complete, the solution was allowed to stir at 0° C. for an additional 15 min, followed by 15 min at room temperature. The resulting solution was diluted with EtOAc (40 ml), washed with water (2×20 ml) and 3M HCl (2×20 ml). The organic phase was then dried over MgSO4, filtered, and the solvent removed in vacuo to yield a brown powder, which was washed with diethyl ether (3×10 ml) to give the product as a tan powder (2.52 g, 70%). .sup.1H NMR (500 MHz, CDCl.sub.3) δ=8.17 (s, 2H), 7.82 (d, 26H), 7.35 (d, 2H), 5.18 (s, 2H), 4.02 (s, 6H), 2.45 (s, 3H).
(87) Synthesis of Diethyl 4-chloromethylpyridine-2,6-dicarboxylate
(88) To a solution of dimethyl 4-hydroxymethylpyridine-2,6-dicarboxylate (3.0 g, 13.3 mmol) in anhydrous CHCl3 was added SOCl2 (2.4 g, 20 mmol) dropwise under argon atmosphere at −5° C. with continuous stirring for 40 min. Excess solvent was removed in vacuo and the crude product was recrystallized from EtOH (50 ml) to give the product as a yellow solid after drying in vacuum (2.8 g, 86%). .sup.1H NMR (500 MHZ, CDCl.sub.3) δ=8.30 (s, 2H), 4.67 (s, 2H), 4.50 (q, 4H), 1.47 (t, 6H).
(89) Synthesis of Dimethyl 4-iodomethylpyridine-2,6-dicarboxylate
(90) To a solution of NaI (4.50 g, 30 mmol) in acetone (250 ml) was added dimethyl 4-tosyloxylmethylpyridine-2-6-dicarboxylate (7.58 g, 20 mmol). The reaction mixture was then heated at reflux for 2.5 h, after which the cooled solution was diluted with EtOAc (550 ml), and the

organic phase was washed with water (3×150 ml), 3% HCl (3×120 ml), and 5% w/w Na2SO3 (2×50 ml). The organic phase was dried over Na2SO4 in darkness and concentrated in vacuo to give the product (5.23 g, 78%). .sup.1H NMR (500 MHz, CDCl.sub.3) δ=8.27 (s, 2H), 4.44 (s, 2H), 4.03 (s, 6H).

(91) Synthesis of 4-(1H-imidazol-1-yl)pyridine-2,6-dicarboxylic Acids

(92) Mixtures of dimethyl 4-chloropyridine-2,6-dicarboxylate (1 equivalent (eq.)) and imidazole/4-methylimidazole/4-ethylimidazole (5 (eq.)) were heated to 130° C. for 3.5 h in the absence of solvent. Upon cooling the dark reaction mixture was diluted with water and acidified to pH 3-4 using 1M HCl, precipitating the product as a brown powder (70-80%). 4-(1H-imidazol-1-yl)pyridine-2,6-dicarboxylic acid: .sup.1H NMR (500 MHZ, DMSO-d.sub.6) δ=13.63 (br, 2H), 8.76 (s, 1H), 8.5 (s, 2H), 8.19 (s, 1H), 7.19 (s, 1H). 4-(4-methyl-1H-imidazol-1-yl)pyridine-2,6-dicarboxylic acid: .sup.1H NMR (500 MHZ, DMSO-d.sub.6) δ=13.56 (br, 2H), 8.63 (s, 1H), 8.41 (s, 2H), 7.86 (s, 1H), 2.17 (s, 3H). 4-(4-ethyl-1H-imidazol-1-yl)pyridine-2,6-dicarboxylic acid: .sup.1H NMR (500 MHZ, DMSO-d.sub.6) δ=13.59 (br, 2H), 8.65 (s, 1H), 8.44 (s, 2H), 7.89 (s, 1H), 2.53 (quadruplet (q), 2H), 1.21 (t, 3H).

Sulfonation of 4-(1H-imidazol-1-yl)pyridine-2,6-dicarboxylic Acids

(93) The pyridine dicarboxylic acids were first esterified to their methyl esters according to the procedure outlined below. A mixture of the resultant product (1 eq.) and 1,3-propanesultone (3 eq.) was then heated at 130° C. for 2 h. Upon cooling, the crude reaction was washed with MeOH and the resulting precipitate was filtered to give the desired product as a brown powder. Subsequent acid catalyzed hydrolysis was carried out as follows: compounds (dimethyl ester form) were suspended in 2 M HCl and heated at 80° C. for 2.5 h. Upon cooling, the desired product formed as a precipitate. The mixture was then filtered and washed with acetone to afford the product as a tan to brown powder. 1-[2,6-bis(methoxycarbonyl) —4-pyridyl]-3-(3-sulfopropyl)-4-methyl-1H-imidazolium: .sup.1H NMR (500 MHZ, D.sub.2O) δ=9.59 (s, 1H), 8.57 (s, 2H), 7.89 (s, 1H), 4.38 (t, 2H), 3.98 (s, 6H), 2.96 (t, 2H), 2.39 (s, 3H), 2.31 (sext, 2H). 1-[2,6-bis(methoxycarbonyl)-4-pyridyl]-3-(3-sulfopropyl) —1H-imidazolium: .sup.1H NMR (500 MHZ, D.sub.2O) δ=9.69 (s, 1H), 8.62 (s, 2H), 8.13 (s, 1H), 7.81 (s, 1H), 4.48 (t, 2H), 3.99 (s, 6H), 2.93 (t, 2H), 2.36 (sext, 2H).

Esterification of 4-(1H-imidazol-1-yl)pyridine-2,6-dicarboxylic Acids

(94) The dicarboxylic acid (1 eq.) was charged with methanol (50 ml) and concentrated sulfuric acid (3 eq.) and subsequently refluxed for 16 h. The methanol was then concentrated in vacuo and the residue was triturated with saturated NaHCO.sub.3, then water. The combined organic layers were dried over Na.sub.2SO.sub.4 and then the solvent was removed under reduced pressure to afford the desired ester as a tan solid.

(95) General Procedure for the Hydrolysis of Dipicolinic Acids

(96) The following procedure was used to hydrolyze most 4-substituted dimethyl 2,6-pyridine dicarboxylate derivatives in addition to dimethyl 4-carboxypyridine-2,6-dicarboxylate. To a stirred solution of dimethyl ester in MeOH (10 ml) was added an equal volume of NaOH (20% weight/volume (w/v)). The reaction mixture was stirred overnight at room temperature and concentrated in vacuo. The residue was dissolved in the minimum required amount of water and acidified with conc. HCl. If a precipitate was obtained at this stage, the solution was cooled on ice and the precipitate was isolated by filtration and dried in vacuo to afford the desired carboxylic acid. If no precipitation occurred at this stage, the aqueous phases were repeatedly extracted with EtOAc, the organic layers were combined, dried (Na2SO4) and concentrated in vacuo to afford the desired carboxylic acid.

(97) Compounds of Formula (II)

(98) A variety of complexing agents of Formula (II), each having a unique distinguishing moiety, were prepared through the derivatization of bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) as shown in Scheme 3a. Chlorination of bathocuproine followed by subsequent oxidation yields 4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxylic acid (DPPDA), an intermediate

product which undergoes treatment with HClSO.sub.3 to ultimately give 4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxylic acid disulfonate (BCPDCA). As shown in Scheme 3b, DPPDA may also undergo nitration to afford 4,7-bis(nitrophenyl)-1,10-phenanthroline-2,9-dicarboxylic acid, which may undergo further reduction to yield 4,7-bis(aminophenyl)-1,10-phenanthroline-2,9-dicarboxylic acid.

(99) ##STR00016## ##STR00017##

Synthesis of 2,9-bis(trichloromethyl)-4,7-diphenyl-1,10-phenanthroline

(100) A mixture composed of bathocuproine (1.5 g, 4.13 mmol), N-chlorosuccinimide (3.375 g, 25.1 mmol), benzoyl peroxide (4.1 mg) and 36 ml chloroform was stirred and refluxed for 6 hrs in an oil bath at 90° C. The mixture was refrigerated overnight to allow precipitation of succinimide crystals, which were removed by vacuum filtration. The filtrate was then washed/extracted with 100 ml (2×50 ml) of saturated potassium carbonate solution (112 g/100 ml) and the organic layer was then dried over anhydrous MgSO4. Removal of solvent yielded the pale yellow solid product. Yield=81-93%. .sup.1H NMR (500 MHz, CDCl.sub.3) δ=8.27 (s, 2H), 8.0 (s, 2H), 7.57 (m, 10H).

(101) Synthesis of 4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxylic Acid (DPPDA)

(102) A 25 mL microwave vial was charged with 2,9-bis(trichloromethyl)-4,7-diphenyl-1,10-phenanthroline (1.612 g, 2.848 mmol) and 4 mL of concentrated H2SO4. The solution was stirred in a 90° C. oil bath for 2 h. After cooling to room temperature, 11 ml of deionized (DI) water was added dropwise to the continuously stirred reaction mixture. The resulting suspension was heated for an additional hour at 90° C. Upon cooling to room temperature, the solution was quenched into a 40 mL mixture of crushed ice and water. The resulting precipitate was collected via vacuum filtration. Yield=95% (hydrated). .sup.1H NMR (500 MHZ, DMSO-d.sub.6) δ=13.7 (br, 2H), 8.29 (s, 2H), 8.04 (s, 2H), 7.65 (m, 10H).

(103) Synthesis of 4,7-bis(chlorosulfonylphenyl)-1,10-phenanthroline-2,9-dicarboxylic Acid

(104) To a 25 mL microwave vial was added 5 mL of 97% ClSO3H. The solution was cooled by placing in an ice bath. Cautiously, small aliquots of 4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxylic acid was added to the stirred mixture until a total of 1 g was added. The mixture was then heated to 80° C. for 4 h. Upon cooling to room temperature, the solution was quenched into 100 mL of ice water in a drop wise fashion (Caution—this process is extremely exothermic). The resulting light yellow/beige powder was collected via vacuum filtration and lyophilized. Yield=79%. .sup.1H NMR (500 MHZ, DMSO-d.sub.6) δ=8.29 (s, 2H), 8.05 (s, 2H), 7.58-7.9 (multiplet (m), 8H), 5.7 (br, 2H).

(105) Synthesis of 4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxylic Acid Disulfonate (BCPDCA)

(106) Hydrolysis of 4,7-bis(chlorosulfonylphenyl)-1,10-phenanthroline-2,9-dicarboxylic acid was carried out using dilute NaOH (aqueous (aq)) pH 10 solutions. The chlorosulfonyl compound was suspended in pH 10 solution and mechanically stirred at room temperature until fully dissolved. The pH of the resulting solution was adjusted using dilute HCl solution until a final value of pH 6 was obtained.

(107) Synthesis of 4,7-bis(nitrophenyl)-1,10-phenanthroline-2,9-dicarboxylic Acid

(108) To 3 ml of cold 90% HNO3 was added DPPDA (0.42 g, 1 mmol) in small portions, after which the mixture was stirred for 4.5 h in an ice bath. The reaction mixture was then poured over 100 ml crushed ice, yielding a yellow solid, and subsequently filtered and lyophilized to give the final product (96%). .sup.1H NMR (500 MHZ, DMSO-dF.sub.6) δ=13.8 (br, 2H), 8.54-7.56 (m, 12H).

(109) Compounds of Formula (III)

(110) A variant of complexing agents of Formula (III), each having distinguishing moieties, was prepared through the derivatization of 1,10-phenanthroline-2,9-dicarboxylic acid as depicted in forthcoming Scheme 4. First, precursor a was synthesized; subsequent reactions using a as a precursor yielded compound b, identified as 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline.

Compound b then underwent further transformations to yield 4,7-dichloro-1,10-phenanthroline-2,9-dicarboxylic acid.
(111) Synthesis of 5,5′-((1,2-phenylenebis(azanediyl))bis(ethan-1-yl-1-ylidene))bis(2,2-dimethyl-1,3-dioxane-4,6-dione) (a)
(112) Trimethyl orthoformate (500 mL, 3.83 mol) and Meldrum's acid (20.0 g, 139 mmol) was brought to a gentle reflux for 15 min. The resulting yellow solution was cooled (80° C.) and o-phenylenediamine (6.90 g, 63.1 mmol) was added portionwise (exothermic reaction). The resulting mixture was refluxed for 2 h, and left under stirring at rt for 16 h, where a white precipitate formed. The precipitate was filtered off, washed with diethyl ether (4×100 mL) and dried to afford the product as a flaky white solid.
(113) Synthesis of 2,9-dimethyl-1,10-phenanthroline-4,7(1H,10H)-dione
(114) To diphenyl ether (500 mL) at 240° C. was added a (17.5 g, 38.7 mmol) in small portions, resulting in vigorous gas evolution. The resulting orange solution was brought to reflux for 30 min, and was then allowed to cool to 70° C., where a dark-brown solid precipitated. The formed precipitate was washed with acetone (2×90 mL), hexane (2×90 mL) and Et2O (2×90 mL) and dried to afford a fine dark-brown powder.
(115) Synthesis of 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline (b)
(116) To phosphoryl chloride (220 mL) under nitrogen was added 2,9-dimethyl-1,10-phenanthroline-4,7(1H, 10H)-dione (8.50 g, 35.4 mmol) and the resulting solution was stirred at 90° C. for 3.5 h. The hot solution was slowly added to a well-stirred mixture of ice (700 g) in water (300 mL). After stirring for 15 min, chloroform (200 mL) was added and the resulting two-layer system was carefully brought to pH 13-14 by adding NaOH solution (42.5%, ca. 450 mL). The organic layer was separated and the aqueous layer was extracted four times with 200 mL of chloroform. The combined organic layers were washed with NaOH solution (42.5%, 200 mL) and dried over MgSO.sub.4. Evaporation of the brown colored solvent afforded b as light tan crystals.
(117) Synthesis of 4,7-dichloro-2,9-bis(trichloromethyl)-1,10-phenanthroline
(118) A stirred solution of b (9.00 g, 32.5 mmol), N-chlorosuccinimide (31.2 g, 234 mmol) and a catalytic amount of benzoyl peroxide (20 mg) in chloroform (700 mL) was refluxed overnight. The reaction mixture was washed with saturated aqueous K.sub.2CO.sub.3 (2×200 mL), dried over MgSO.sub.4 and concentrated to afford a solid, which was purified by flash-chromatography (2% EtOAc in petroleum ether) to give the product as white crystals.
(119) Synthesis of 4,7-dichloro-1,10-phenanthroline-2,9-dicarboxylic Acid
(120) A stirred mixture of 4,7-dichloro-2,9-bis(trichloromethyl)-1,10-phenanthroline (13.00 g, 26.9 mmol) in concentrated H.sub.2SO.sub.4 (16 mL) was heated to 95° C. for 2 h. After cooling, H.sub.2O (50 mL) was slowly added with rapid stirring. The resulting mixture was heated to reflux for 1 h. The mixture was cooled and the formed precipitate was washed with H.sub.2O (5×40 mL) and Et.sub.2O (2×30 mL) and dried to afford the product as a light tan solid.
(121) ##STR00018##
Example 2—Thermal Stability Test
(122) One advantageous feature of molecular tracers for reservoir characterization is relatively uniform physical and chemical properties across a broad range of (1) salinity (for example, from about 60,000 ppm to about 250,000 ppm total dissolved salts) and (2) temperature (for example, from about 60° C. to about 105° C.), over relatively long periods of time, for example, while the tracer traverses a path from the injection well to the producing well. To evaluate properties of the disclosed tracers, the BCPDCA ligand was subjected to thermal stability tests in synthetic seawater at reservoir-like temperature. The composition of the synthetic seawater used is shown in Table 1.
(123) 200 ppb of BCPDCA, complexed with europium (III) using a 10.sup.−5M solution of europium ions, was maintained at 103° C. in synthetic seawater over 11 days to determine whether its fluorescence intensity had changed. FIG. **6** is a plot showing fluorescence emission as a function of wavelength for BCPDCA heated for different times. Data shown in the six plots in FIG. **6** were

measured on six different days over a 12-day interval. The near superposition of the plots indicated that the complex was thermally stable.

(124) TABLE-US-00001 TABLE 1 Composition of Synthetic Seawater Weight Percentage in Salt Synthetic Seawater NaCl 3.949 CaCl.sub.2•2H.sub.2O 0.2297 MgCl.sub.2•6H.sub.2O 1.6998 BaCl.sub.2 0.00 Na.sub.2SO.sub.4 0.611 NaHCO.sub.3 0.0159 Na.sub.2CO.sub.3 0.00

Example 3—Photophysical Characterization of BCPDCA

(125) Photophysical characterizations of the complexes including lanthanide ions and complexing agents were performed under experimental conditions that favored the formation of a 1:1 complex between a ligand and a lanthanide ion by including an excess of the lanthanides in solution. FIG. **7**A is a plot showing luminescence emission as a function of wavelength for complexed and un-complexed europium ions. In deionized water, the limits of detection were determined to be in the 100's of parts-per-quadrillion (ppq) for complexes that formed between BCPDCA and europium (III) ions in solution, shown by plot **702**. For reference, the un-complexed europium background plot **700** is also shown.

(126) Next, formation of the complex in produced water (which is oil contaminant-containing water) from a hydrocarbon reservoir, in which there existed excess calcium ions in solution, was performed. FIG. **7**B is a plot showing luminescence emission as a function of wavelength for complexed europium, water extracted from a reservoir, and un-complexed europium. It was observed that the PAH's in produced water sensitized the lanthanide ions measurably, as shown by plot **704**. In spite of this, it was possible to detect the presence of the complex to 10's of parts-per-trillion as shown by plot **706**, without any chromatographic separation, pre-concentration, or purification. For reference, the un-complexed europium background is plot **708**. Based on these results, it is expected that purification of the produced water by, for example, ultra-high performance liquid chromatography, would enable a detection limit close to that observed in the deionized water experiment.

(127) As shown in FIGS. **14**A and **14**B, similar results were obtained in analogous experiments for complexing agents of Formula (I) when complexed with excess terbium ions at 10.sup.−6 M concentration to form primarily complexes having a 1:1 ratio of complexing agent to lanthanide ion. It was possible to detect concentrations of hundreds of parts-per-trillion (weight/weight) in acetate buffer, and concentrations smaller than 20 parts-per-billion (weight/weight) in produced water.

Example 4—Photophysical Characterization of BCPDCA

(128) To determine the retention of BCPDCA materials in reservoir rocks under simulated reservoir conditions, mobility experiments were performed with parameters and results tabulated in Table 2, and described in forthcoming detail.

(129) TABLE-US-00002 TABLE 2 Summary of Conditions for Mobility Experiments Core Identification: Indiana Limestone, 70 milliDarcy (mD) as marked from Kocurek Industries Core Permeability (brine): 312 mD Core Pore Volume: 9.06 mL Core Diameter: 1.49 inches Core Length: 2.00 inches Confinement Pressure (P.sub.conf): 4,400 pounds per square inch (psi) Pore Pressure (P.sub.pore): 3,200 psi Saturation Fluid: degassed filtered (0.45 μm) synthetic seawater (57,670 milligrams per liter (mg/L) total dissolved solids (TDS)) Permeability Test Fluid: degassed filtered (0.45 μm) synthetic seawater (57,670 mg/L TDS) Temperature (T): 90° C. Injection Rate (Q): 0.5 mL/min Concentration of Solution 200 ppm BCPDCA tracer in synthetic seawater (C.sub.solution): Solution Preparation: no pre-filtration, no pre-heating Injection Pore Volume (PV.sub.inject): 3.48 Flushing Solution: degassed filtered (0.45 μm) synthetic seawater (57,670 mg/L TDS) Flush Pore Volume (PV.sub.flush): 5 Sampling Frequency: 5+ vials per pore volume (PV) injected Effluent Analysis: Ultraviolet-visible absorbance (UV-VIS) at 290 nanometers (nm) Irreversible Tracer Retention: 6 μg/g ± 10%

Coreflood Device and Conditions

(130) A CoreTest Systems Inc. BPS-805Z Permeability System was used as a coreflood device. For

the carbonates studied, values of confinement pressure P.sub.conf=4,400 psi, pore pressure P.sub.pore=3,200 psi, and temperature T=90° C. were used to replicate conditions in parts of the Ghawar reservoir in Saudi Arabia.

(131) Saturation and Injection Brines

(132) To reduce variables from transient salinity, the salinity of both the saturation fluid and injection fluid were matched for each respective experiment (for synthetic seawater, the core was saturated and flooded in seawater and the subsequent tracer ligand injection and flushes were all performed with seawater). The seawater used was intended to mimic the ionic composition of the injected fluid used throughout Saudi Arabia during water-flooding operations.

(133) Tracer Injection and Analysis

(134) The experiments were conducted at displacement velocities of 0.5 mL/min in Indiana Limestone. The brine flushing phase was conducted at the same displacement velocities as the tracer injections to avoid mobilization resulting from advection gradients. A tandem injection scheme was used. For the DPA and FBA comparison experiment, first FBA (˜3 PV) was injected, followed by a flush of 5 pore volume of seawater before the DPA tracers are injected as a slug (˜3 PV). A similar injection scheme was adopted for the BCPDCA & NaBr coreflood experiment.

(135) For determining the tracer concentration, an Agilent spectrophotometer was used to measure the UV-VIS absorbance at a wavelength of 270 nm for DPA, and 290 nm for BCPDCA. For the ideal non-reactive ionic tracer NaBr, a bromine ion selective electrode was used to measure the eluents. A new 5-point calibration curve was made for each experiment measured. By comparing the effluent sample absorbance to the known values of the standards, a normalized concentration was derived for each fraction collected, annotated as C/C.sub.0 (fraction of effluent sample concentration divided by input concentration; a value of 1.0 indicates the effluent solution is equal to the injected concentration). The fraction collector vials were weighed before and after sample collection to determine a collected mass from each vial. The known mass along with the known densities of the injection fluids allowed for volume calculations and validation of the injection rates.

(136) Coreflood Tests using BCPDCA

(137) BCPDCA in synthetic seawater was injected into a core at 200 mg/L at 90° C. Another test using an ionic tracer known to not attach to the rock matrix (0.1M NaBr in this case) in the same core was performed as well. FIG. **8** is a plot of normalized concentration of BCPDCA vs. pore volumes for a complexing agent and an NaBr tracer. The effluent curve **800** of the BCPDCA tracer was very similar to that of the 0.1M NaBr non-reactive ionic tracer curve plot **802**, indicating that the core allowed passage of the complexing agent. The vertical solid and dotted lines indicate when a flush was initiated in the BCPDCA and NaBr experiments, respectively. The relatively steep slope of the plots as they approach C/C.sup.0=1.0 indicates there is very little retention, thus showing that BCPDCA performed suitably as an inter-well tracer.

(138) A similar test was conducted using DPA, and a fluorinated benzoic acid (FBA) as the inert reference. FIG. **9** is a plot of normalized concentration of DPA vs. pore volumes for DPA and a fluorinated benzoic acid (FBA) tracer. Overall, the effluent curve **900** of the DPA tracer tracked very closely with that of the FBA curve **902**. The steep increase before 1 pore volume indicated little to no retention of the tracers. These results suggest that DPA, too, exhibits suitable characteristics as an inter-well tracer for a carbonate reservoir.

Example 5—DPA Barcodes Separation by HPLC and Photophysical Comparison

(139) Derivatives substituted with imidazolyl, 4-methylimidazolyl, and 4-ethylimidazolyl substituents at the 4-position of DPA were synthesized as shown in Scheme 2c. A mixture of DPA and three DPA derivatives substituted with imidazol-1-yl (DPA-im), 4-methylimidazol-1-yl (DPA-Mim) and 4-ethylimidazol-1-yl (DPA-Eim) groups at concentrations of 10 ppm each in water was chromatographically separated by UHPLC. FIG. **13**A is an HPLC trace of response factor vs. retention time for DPA and each of the three DPA derivatives. The order of elution was (1) DPA,

represented by peak **1306**, (2) 4-ethylimidazol-1-yl DPA, represented by peak **1304**, (3) 4-methylimidazol-1-yl DPA, represented by peak **1302**, and (4) imidazol-1-yl DPA, represented by peak **1300**,

(140) Fluorescence intensities of DPA, imidazol-1-yl DPA, and 4-methylimidazol-1-yl DPA at the same molar concentrations were measured after complexation with terbium ions. FIG. **13**B is a plot of fluorescence intensity vs. wavelength for the 3 analogs. Plot **1350** shows the curve for DPA, plot **1352** shows the curve for 4-methylimidazol-1-yl DPA, and plot **1354** shows the curve for imidazol-1-yl DPA. These results indicated that the light harvesting capability of the derivatives remained unchanged after the chemical modification, as evidenced by the similar fluorescence intensities.

Example 6—Tracer Mobility Characterization

(141) To assess the mobility of the molecular tracers through carbonate rocks under simulated reservoir conditions, coreflood experiments were performed. A one-foot long limestone core (permeability ˜200 mDarcy, other properties shown in Table 3) was flooded with synthetic seawater, then flooded with Arabic medium crude (API ˜30°) and aged for three weeks at 100° C. At the end of aging, the core was oil flooded again and initial oil saturation, S.sub.oi, was calculated by mass balance. Then, the core was waterflooded with seawater to obtain residual oil saturation, S.sub.orw, by mass balance. For the tracer flood, both the ideal ionic tracer, potassium chloride (KCl), and one of the molecular tracers described above were injected at the same pulse width of 0.5 pore volume (PV). The concentration of KCl was 1000 ppm in seawater, whereas the molecular tracer concentration was 100 ppm. Injection was followed by several PV chase of synthetic seawater. The concentration of potassium ions in the effluent was determined using ion chromatography while the concentration of the molecular tracer was measured by UV-Vis spectrophotometry.

(142) TABLE-US-00003 TABLE 3 Limestone Core Properties for Coreflood Measurements Rock Type Indiana limestone Diameter 3.81 cm Length 30.96 cm Mass 776.3 g Bulk Volume 352.97 cm.sup.3 Porosity 0.179% Area 11.40 cm.sup.2 Pore Volume 63.1 cm.sup.3

(143) Coreflood experimental conditions are summarized in Table 4.

(144) TABLE-US-00004 TABLE 4 Coreflood Experimental Conditions Flood Brine Oil Brine Tracer Fluid Synthetic Arab medium Synthetic 1000 ppm KCl, seawater crude seawater 100 ppm molecular tracer in seawater Flow Rate 5 5 1 0.09 (mL/min) Frontal 116 116 23 2 Velocity (ft/day)

(145) FIG. **15**A is a plot showing normalized recovered concentrations (breakthrough curves) of the KCl and molecular tracers as a function of eluted pore volumes. Since the experiment was performed with both tracers injected in the same pulse width, many potential sources of experimental error were eliminated. The slight tailing associated with the distal portion of the curve for the molecular tracer was attributed to diffusion or retention. Since the small ions of the KCl tracer should be at least as diffusive as the larger tracer molecules, it is likely that greater reversible retention of the tracer (small molecules) compared to the K+ ions occurred, similar to what has been observed in other studies.

(146) FIG. **15**B shows mass recovery plots for both tracers. The plots suggest that there was negligible irreversible retention of the molecular tracer, indicating good transport through the rock matrices at simulated reservoir temperature and pressure.

Example 7—Detectability Characterization

(147) To assess the detectability of the molecular tracers in the field, a study was performed using a specific well pair. FIG. **16** is a schematic diagram showing well sites in a specific field. For this study, well pair I3-P3 was chosen (a separation of 475 m). For this well pair, connectivity has been thoroughly characterized in previous water tracer studies and nanoagent tracer field tests.

(148) A total of 5 kg of the first molecular tracer was first dissolved in approximately 200 L of deionized water. At the well site, a pre-flush of 4 barrels of treated seawater was administered at a rate of 0.35 bbl/min. Then, the molecular tracer was injected at I3 at a rate of 0.40 bbl/min. After the injection, a post flush with 10 barrels of treated seawater was injected at 0.5 bbl/min. Seawater

injection at 3000 psi at a rate of approximately 8000 bbl/day resumed immediately post flush.
(149) Produced water samples from producer well P3 were collected twice weekly. A cursory clean-up procedure involving solid phase extraction and fraction collection on a high performance liquid chromatograph was performed before the addition of lanthanide ions for the fluorescence measurements. With these additional steps, the cycle time for sample work up was still comparatively shorter than tracer detection methodologies for FBAs using quadrupole GC/MS.
(150) The recovery curve of the first molecular tracer is shown in FIG. **17**. The data point on Day 0 refers to the background noise floor level to be expected for the analysis method for this particular tracer. Consistent above-background signal from the tracer could be detected after Day 50 and the signal trended upward unambiguously. However, due to long periods of well shut down for planned maintenance, no samples were collected between 100 days and 130 days after injection, as indicated on the plot. Other significant well shut down periods are also indicated. When the sample collection resumed, the upward trend of detectable tracer concentration continued, signifying breakthrough of the first molecular tracer.

Example 8—Tracer Information for Reservoir Management

(151) Reservoir modeling methodologies have shown that active rate management is an effective way to augment productivity, particularly in mature fields. Although the value of tracer data in elucidating reservoir heterogeneity and reducing uncertainties is undeniable, its utility in fortifying the fidelity of reservoir history matching and enhancing production optimization algorithms does not appear to have been studied systematically.
(152) Using reservoir history matching and production optimization algorithms, it was recently demonstrated that tracer data can improve field production net present values (NPVs) by +0.3% to +9.4% for non-homogeneously flooded reservoirs. The present example shows results of further feasibility studies for scaled-up reservoir models.
(153) Permeability fields of the scaled-up reference reservoir models with five-spot waterflood patterns are shown in FIGS. **18**A-**18**C. Each of the models was constructed on a 50×50×1 grid block system with block sizes of Δx=Δy=250 6 ft and Δz=80 ft. Values of constant porosity φ=0.2 and initial water saturation S.sub.w=0.1 were used. Initial water injection rates were q.sub.0=20,000 ft.sup.3/day on the 4 injectors for the interval from 0 to 5,000 days. In addition, 4 unique molecular tracers were also injected in each injector and collected from the producer well for history matching.
(154) FIGS. **18**D-**18**F are plots showing history matching results from the ensemble smoother with multiple data assimilation with molecular tracer data (ES-MDA-Tracer) algorithm. As shown in the figures, very good history matching was achieved for the first two models (FIGS. **18**D and **18**E) with early water and tracer breakthroughs. In contrast, for the third model (FIG. **18**F), late water breakthrough resulted in less optimal history matching.
(155) FIGS. **18**G-**18**I are plots showing field production net present value (NPV) for the period from 5,000 to 10,000 days with waterflood optimization using reservoir models history matched with and without molecular tracer data. For models exhibiting good history matching (FIGS. **18**D and **18**E), increases of +5.6% and +2.1% NPV were observed with molecular tracer data (+$11.1 M and +$9.2 M/1 well/13 yrs), as shown in FIGS. **18**G and **18**H. For the less optimal model (FIG. **18**F), a minor −0.2% NPV loss was observed with tracer data (−$1.0 M/1 well/13 yrs), as shown in FIG. **18**I. Based on this data, the financial incentives are high if data from the molecular tracers are used to guide management of the reservoir models.

Other Embodiments

(156) A number of embodiments have been described. Nevertheless, it will be understood that various modifications may be made without departing from the scope of the disclosure. Accordingly, other embodiments are within the scope of the following claims.

## Claims

1. A complexing agent of Formula (I), or an anion or salt thereof: ##STR00019## wherein: X is present or absent, and when present, is selected from the group consisting of: C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene, wherein each C.sub.1-10 alkylene, C.sub.2-10 alkenylene, and C.sub.2-10 alkynylene is optionally interrupted by one O, S, or NH; R is —CONR.sup.aR.sup.a; each occurrence of R.sup.a is independently selected from the group consisting of: (i) H; (ii) C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b; (iii) —(C.sub.0-6 alkylene)-C.sub.3-10 cycloalkyl, wherein the cycloalkyl is optionally substituted with from 1-4 independently selected R.sup.b; (iv) —(C.sub.0-6 alkylene)-heterocyclyl including from 3-10 ring atoms, wherein from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, wherein the heterocyclyl is optionally substituted with from 1-4 independently selected R.sup.b; (v) —(C.sub.0-6 alkylene)-(C.sub.6-10 aryl), wherein the aryl is optionally substituted with from 1-5 independently selected R.sup.b; or (vi) —(C.sub.0-6 alkylene)-heteroaryl including from 5-10 ring atoms, wherein from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S, wherein the heteroaryl is optionally substituted with from 1-3 independently selected R.sup.b; each occurrence of R.sup.b is independently selected from the group consisting of: (i) halo; (ii) cyano; (iii) C.sub.1-6 alkyl; (iv) C.sub.2-6 alkenyl; (v) C.sub.2-6 alkynyl; (vi) C.sub.1-4 haloalkyl; (vii) C.sub.1-4 alkoxy; (viii) C.sub.1-4 haloalkoxy; (ix) —(C.sub.0-3 alkylene)-C.sub.3-6 cycloalkyl optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (x) —(C.sub.0-3 alkylene)-heterocyclyl including from 3-10 ring atoms, wherein from 1-3 ring atoms are each independently selected from the group consisting of NH, O, and S, wherein the heterocyclyl is optionally substituted with from 1-4 independently selected C.sub.1-4 alkyl; (xi) —(C.sub.0-3 alkylene)-phenyl; (xii) —(C.sub.0-3 alkylene)-heteroaryl including from 5-10 ring atoms, wherein from 1-4 ring atoms are each independently selected from the group consisting of N, NH, O, and S; (xiii) —S(O).sub.1-2(C.sub.1-4 alkyl); and (xiv) —NR′R″; (xv) —OH; (xvi) —S(O).sub.1-2(NR′R″); (xvii) —C.sub.1-4 thioalkoxy; (xviii) —NO.sub.2; (xix) —N(R′)(C(═O)C.sub.1-3 alkyl); (xx) —C(═O)(C.sub.1-4 alkyl); (xxi) —C(═O)O(C.sub.1-4 alkyl); (xxii) —C(═O)OH, and (xxiii) —C(═O)N(R′)(R″); and each occurrence of R′ and R″ is independently selected from the group consisting of: H and C.sub.1-4 alkyl; or, if R′ and R″ are bonded to the same atom, R′ and R″ together with the atom to which each is attached forms a ring including from 3-8 ring atoms, wherein the ring includes: (a) from 1-7 ring carbon atoms; and (b) from 0-3 ring heteroatoms (in addition to the atom attached to R′ and R″), which are each independently selected from the group consisting of N, NH, O, and S.
2. The complexing agent of claim 1, wherein X is absent.
3. The complexing agent of claim 1, wherein X is C.sub.1-10 alkylene.
4. The complexing agent of claim 1, wherein R.sup.a is H.
5. The complexing agent of claim 1, wherein R.sup.a is C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b.
6. The complexing agent of claim 1, wherein: R is —CONHR.sup.a; and R.sup.a is C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b.
7. The complexing agent of claim 6, wherein each occurrence of R.sup.b is independently selected from the group consisting of C.sub.1-6 alkyl and —C(═O)O(C.sub.1-4 alkyl).
8. The complexing agent of claim 6, wherein each occurrence of R.sup.b is C.sub.1-6 alkyl.
9. The complexing agent of claim 6, wherein each occurrence of R.sup.b is —C(═O)O(C.sub.1-4 alkyl).
10. The complexing agent of claim 1, wherein: R is —CONHR.sup.a; R.sup.a is C.sub.1-8 alkyl optionally substituted with from 1-3 independently selected R.sup.b; and each occurrence of RD is independently selected from the group consisting of C.sub.1-6 alkyl and —C(═O)O(C.sub.1-4

alkyl).

11. The complexing agent of claim 1, wherein the complexing agent is ##STR00020##

12. A complex, comprising the complexing agent of claim 1 and a lanthanide ion, wherein the complexing agent chelates the lanthanide ion.