JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Post-assembly Modification of Kinetically Metastable $Fe^{II}_2L_3$ Triple Helicates

Derrick A. Roberts, Ana M. Castilla, Tanya K. Ronson, and Jonathan R. Nitschke*

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

Supporting Information

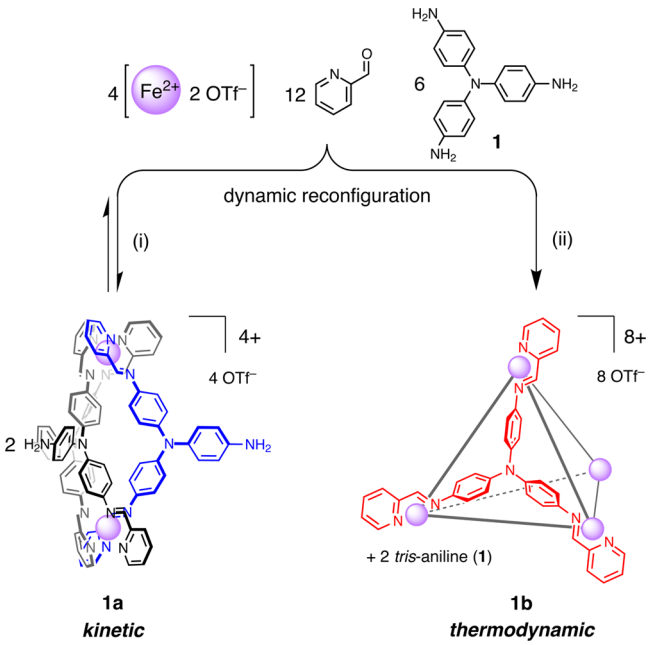
ABSTRACT: We report the covalent post-assembly modification of kinetically metastable amine-bearing $Fe^{II}_2L_3$ triple helicates via acylation and azidation. Covalent modification of the metastable helicates prevented their reorganization to the thermodynamically favored $Fe^{II}_4L_4$ tetrahedral cages, thus trapping the system at the non-equilibrium helicate structure. This functionalization strategy also conveniently provides access to a higher-order tris(porphyrinatoruthenium)−helicate complex that would be difficult to prepare by *de novo* ligand synthesis.

The self-assembly of a stable supramolecular complex is a multistep process involving the formation and reconfiguration of transitory intermediates, which are coupled together by a series of elementary equilibria.[1] Occasionally, one of these intermediates is sufficiently long-lived that it can be isolated before it reconfigures to a more stable product. Although rarely identified, these kinetically metastable intermediates constitute an interesting subclass of labile supramolecular structures that can provide insights into the mechanisms of self-assembly.[2] For instance, we have recently reported self-assembled metal−organic polyhedra that arise from the thermodynamically driven reconfiguration of low-nuclearity metastable intermediates.[3] In these systems, a kinetic intermediate (a helicate[3a,b] or tetrahedron[3c,d]) forms rapidly and persists for up to several days before the system spontaneously equilibrates to afford the more complex thermodynamic product (a tetrahedron,[3b] pentagonal prism,[3d] cuboid,[3c] or icosahedron[3a]). Meijer et al. have also observed that metastable kinetic intermediates are important off-pathway species in chain-growth supramolecular polymerization,[4] which recently led to a report of living supramolecular polymerization by Sugiyasu et al.[5] Kinetically metastable species also feature in biological self-assembly, such as during the initial stages of protein folding.[6] Biological systems are able to trap these metastable polypeptides through covalent post-assembly modification reactions, providing a route to active proteins that contain out-of-equilibrium motifs.[7]

Post-assembly modification of discrete supramolecular complexes has received increasing attention in recent years, complementing the prominent role that postsynthetic modification plays in polymer chemistry[8] and metal−organic frameworks.[9] Modification reactions have been used to "lock down" supramolecular complexes by replacing dynamic interactions with covalent bonds,[10] to close mechanical bonds around metal coordination sites,[11] to access unique architectures through subcomponent substitution,[12] and to alter parts of assembled structures without resorting to multistep *de novo* ligand synthesis.[13]

Covalent post-assembly modification of kinetically metastable intermediates poses a challenge, as these complexes are not only potentially unstable toward modification reactions but will also spontaneously equilibrate to the thermodynamic product over time. A successful modification reaction must therefore compete with dynamic reconfiguration without causing decomposition. If successful, covalent modification can be used to trap a kinetically metastable intermediate, thus offering a powerful means of controlling product distributions in supramolecular synthesis, independent of the natural thermodynamic preferences of the equilibrating system.

Scheme 1. Subcomponent Self-Assembly of C_3-Symmetric Tris(4-aminophenyl)amine with 2-Formylpyridine and Iron(II) Triflate[a]



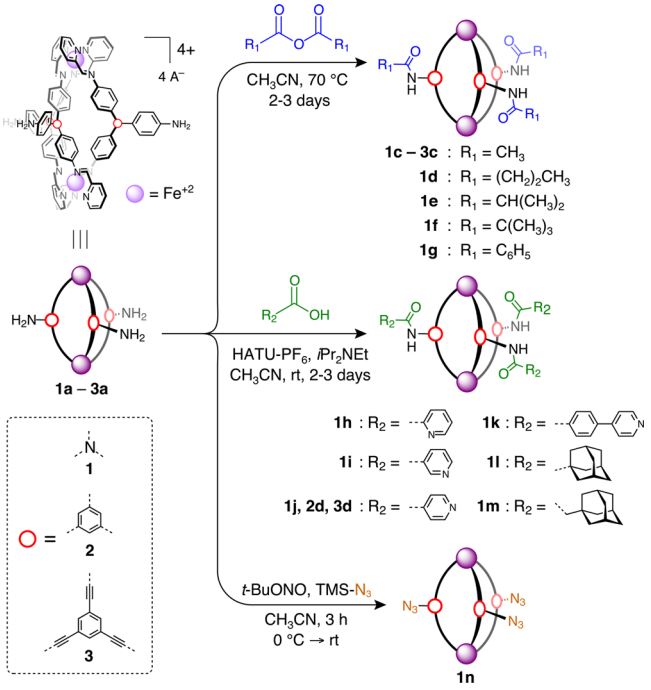
[a]Tris-aniline $Fe^{II}_2L_3$ helicate (**1a**) forms initially as the kinetic product. Upon extended heating, the system equilibrates to the thermodynamically favored $Fe^{II}_4L_4$ tetrahedron (**1b**). (i) 50 °C, 2 h, CH_3CN; (ii) 70 °C, c.a. 6 days, CH_3CN.

Received: April 30, 2014
Published: May 23, 2014

   dx.doi.org/10.1021/ja5042397 | J. Am. Chem. Soc. 2014, 136, 8201−8204

Herein we report covalent post-assembly modifications on a class of kinetically metastable $Fe^{II}_2L_3$ triple helicates, prepared by subcomponent self-assembly[14] from Fe^{II} salts, 2-formylpyridine, and three-fold-symmetric tris-anilines exemplified by compound **1** (Scheme 1). Helicate **1a** is kinetically metastable and will reorganize completely to the thermodynamically favored $Fe^{II}_4L_4$ face-capped tetrahedron (**1b**) after heating at 70 °C for c.a. 6 days.[3b] This phenomenon is general: when tris-aniline **1**, **2**, or **3** (Scheme 2) was combined with 2-formylpyridine and a suitable iron(II) salt in the correct stoichiometry to form a tetrahedron (**1b**–**3b**), the helicate (**1a**–**3a**) was initially formed as the kinetic product in each case.[3b] Reaction of the exposed aniline residues of these helicates with various electrophiles intercepted the equilibration process, thereby trapping the system away from equilibrium while endowing the helicate with additional functionality (Scheme 2).

Scheme 2. Covalent Functionalization of Helicates 1a–3a by Acid Anhydride Acylation, Active Ester Acylation, and Azidation[a]



[a]A^- = OTf^- or PF_6^- for **1**, and NTf_2^- or PF_6^- for **2** and **3**.

We first investigated *N*-acylation due to the scope of conditions under which it can be performed and the variety of functional groups that can be introduced through amide bond formation. Initial attempts to acetylate helicate **1a** using acetyl chloride were complicated by triflate–chloride metathesis, causing a reddish-brown solid to precipitate from acetonitrile (see SI, Section S6). Acetylation was therefore performed under milder conditions using acetic anhydride: the reaction of **1a** with 3.3 equiv of acetic anhydride in CD_3CN proceeded at 70 °C, cleanly affording the tris-acetylated helicate (**1c**) as the sole reaction product within 32 h (Figure 1). The ^{1}H DOSY NMR spectrum showed that the new $-CH_3$ resonance at 2.02 ppm diffused with the aromatic helicate resonances (Figure 1a). The helicate decomposed only slightly during acetylation, as indicated by the observation of 2-formylpyridine in the ^{1}H NMR spectrum. The pure tris-acetylated helicate (**1c**) was

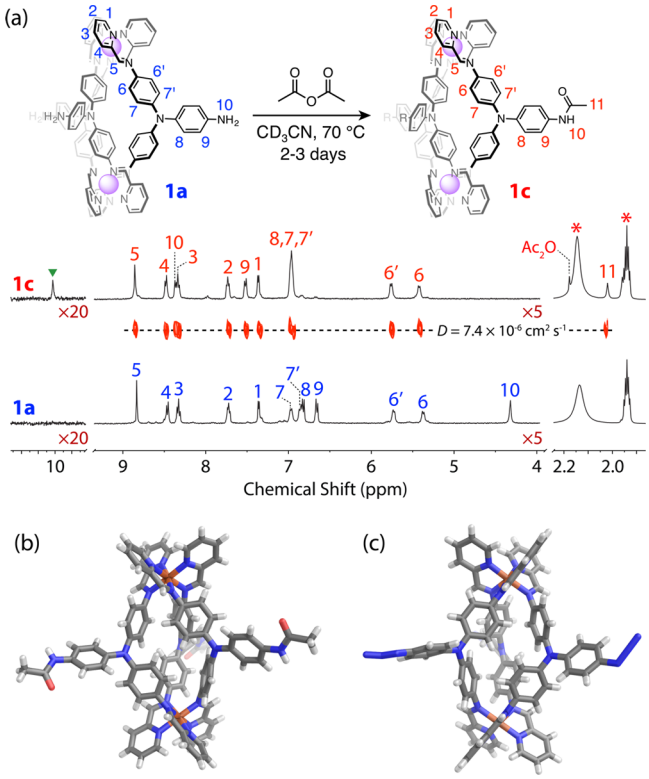


Figure 1. (a) ^{1}H NMR spectra (400 MHz, 298 K, CD_3CN) of helicates **1a** and **1c**. The appearance of a new acetyl $-CH_3$ singlet at $\delta = 2.02$ ppm and the high symmetry of the final NMR spectrum allow us to infer efficient conversion to the acetylated helicate. Only very slight decomposition of **1a** was observed, as indicated by the aldehyde signal at 10 ppm. Intensities have been scaled for clarity. Asterisks denote residual solvent peaks. (b) Cationic portion of the X-ray crystal structure of acetylated helicate **1a**. (c) Cationic portion of the X-ray crystal structure of azido helicate **1n**. Disorder is omitted in both structures for clarity.

isolated following dropwise addition of the reaction mixture into diethyl ether. The ^{1}H NMR spectrum showed that the procedure selectively afforded the tris-acetylated helicate with no evidence of products having lower degrees of acylation. ESI-MS and single crystal X-ray diffraction (Figure 1b) analyses confirmed the structure of **1c** as a pseudo-D_3 symmetric triple helicate.[15] The structurally related metastable $Fe^{II}_2L_3$ triple helicates **2a** and **3a** also reacted efficiently with acetic anhydride, selectively affording the analogous tris-acetylated helicates (see SI, Section S10).

Acetylation of helicate **1a** prevented structural reorganization to the $Fe^{II}_4L_4$ tetrahedron (Scheme 1), thus trapping the metastable helicate away from thermodynamic equilibrium. The thermodynamically favored tetrahedron, whose aniline residues are not available for reaction with electrophiles, was not susceptible to these modes of post-assembly modification once formed, indicating that **1b** lies in a deep potential energy well relative to **1a**.

A range of alkyl and aryl carboxylic acid anhydrides also effectively acylated **1a**, cleanly producing trifunctionalized helicates with good to excellent conversion after heating at 70 °C for up to 5 days (Scheme 2; SI, Table S1). Additionally, we employed 1-hydroxy-7-azabenzotriazole active esters,[16] prepared by treating the desired carboxylic acid with the peptide coupling reagent HATU-PF_6,[17] as a more general route for *N*-acylation. Active ester functionalization of the helicates proceeded efficiently at room temperature, selectively affording the target

dx.doi.org/10.1021/ja5042397 | J. Am. Chem. Soc. 2014, 136, 8201–8204

triacylated helicates in good yields. The structure of each helicate derivative was confirmed by two-dimensional NMR techniques and ESI-MS (see SI, Sections S4–S10). Single crystal X-ray diffraction analysis was also performed for those helicates that gave crystals of sufficient quality (see SI, Section S14 for details). It is crucial that covalent modification of the helicate core be highly efficient, since the tetracationic charge of **1a**–**3a** and their derivatives makes purification of partially functionalized mixtures very challenging by fractional crystallization and chromatography. Active ester-mediated coupling thus provides a robust, convenient, and versatile route for introducing a wide range of functional groups to an amine-bearing scaffold in the context of post-assembly modification of supramolecular complexes.

While *N*-acylation proceeded efficiently in most cases, particularly slow reactions, e.g., those involving sterically hindered substrates, competed with helicate-to-tetrahedron interconversion to afford mixtures of the functionalized helicate and tetrahedron **1b**. For example, the reactions of **1a** with pivalic anhydride (3.5 equiv) did not proceed to completion even after heating at 90 °C for 11 days. An improved result was obtained by repeating the reaction in the presence of catalytic 4-(dimethylamino)pyridine (DMAP),[18] which gave predominantly trifunctionalized **1f**, along with ∼13 mol % mono- and diacylation products and ∼6 mol % tetrahedron **1b**, as estimated from the ^{1}H NMR spectrum of the reaction mixture. Similarly, the active ester coupling of adamantane-1-carboxylic acid to **1a** required heating to 70 °C. In contrast to the anhydride coupling, the ^{1}H NMR spectrum of the product mixture contained trifunctionalized **1l** as the only helicate product with no evidence of partially acylated products and ∼10 mol % tetrahedron **1b** (SI, Figure S12). This observation suggests that monofunctionalization of **1a** "locks down" the helicate structure so that the subsequent functionalization events can occur.

Although acylation is a versatile route for grafting various functional groups onto the helicate core, we also sought additional reactions complementary to amide formation. The azide group is useful to install as it can undergo diverse transformations.[19] While azide-bearing supramolecular complexes have been reported previously,[13f,20] there are, to the best of our knowledge, no reports of introducing an azide group to a preassembled complex through post-synthetic modification. We found that the exposed aniline residues of **1a** could be transformed into azides via diazotization.[21] Treating **1a** with *t*-BuONO and TMS-N_3 at 0 °C in one pot afforded only the tris-azide appended helicate (**1n**) in good purity. Slight broadening of the ^{1}H NMR spectrum of **1n** compared to **1a** suggested that the helicate decomposed slightly during the reaction, consistent with oxidation by *t*-BuONO. Indeed, **1a** was observed to decompose upon reaction with *t*-BuONO alone, possibly due to the instability of the intermediate diazonium salt (SI, Figure S17). Installation of the azide groups was confirmed by ESI-MS, FTIR, and X-ray crystallography (Figure 1c; SI, Section S9).

Helicates **1a**–**3a** were resistant to post-assembly modification using ethyl isocyanate, affording complex mixtures of partially functionalized products even in the presence of dibutyltin dilaurate as a catalyst at 50 °C (SI, Section S11). This result contrasts with previous work, in which post-assembly modification of metallosupramolecular complexes through reaction with isocyanates was reported.[13b,g] We infer this difference in reactivity to be due to the comparatively poor nucleophilicity of the aniline residues of helicates **1a**–**3a**. Hence, their highly efficient reaction with the electrophiles reported herein suggests that other amine-bearing complexes may also be transformed into their acyl- and azide-bearing congeners, complementing other post-assembly modification strategies.

Post-assembly modification of metastable supramolecular structures offers a modular route for building more complex architectures from a preformed supramolecular core. To demonstrate this idea, helicate **1k**, prepared from helicate **1a** and 4-(4-pyridinyl)benzoic acid, was shown to react with the carbonylruthenium(II) chelate of 5,10,15,20-tetraphenylporphine, Ru(TPP)(CO), to give a 3:1 coordination complex. ^{1}H DOSY NMR spectroscopy revealed the porphyrin–helicate complex to diffuse as a single species on the NMR time scale, consistent with the high association constants typically reported for porphyrinatoruthenium(II)–pyridine coordination complexes (Figure 2).[22] Proton resonances assigned to the helicate

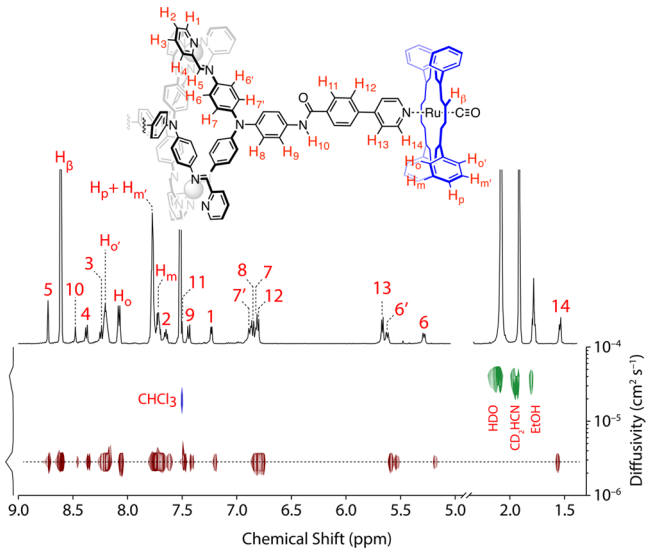


Figure 2. ^{1}H NMR and DOSY spectra (500 MHz, $CD_3CN/CDCl_3$ = 1:1 v/v, 298 K) of the 3:1 (**1k**)$[Ru(TPP)(CO)]_3$ complex. Full assignment of the spectrum and slow exchange dynamics of the complex are consistent with the proposed three-fold-symmetric architecture.

core indicate that the complex has a pseudo-C_3 symmetry axis along the central Fe–Fe vector, which is consistent with the 3:1 stoichiometry of the complex.

Following porphyrin binding, the proton resonances of H_{13} and H_{14} were observed at $\Delta\delta$ = −5.57 ppm and −8.71 ppm, respectively, from their chemical shifts in free **1k** (Figure 2). We attribute these shifts to the proximity of the protons to the aromatic ring current shielding zone of the Ru(TPP)(CO) moiety. NOE correlations between H_{14} of the helicate and both H_β and H_o of the porphyrin directly confirm the Ru-pyridine connectivity of the complex (SI, Figure S22). Interestingly, the shorter-armed isonicotinyl helicate (**1j**) did not form a stable 3:1 complex with Ru(CO)(TPP), but its spectra were instead consistent with a distribution of products in which incomplete porphyrinatoruthenium(II)–pyridine coordination was present (SI, Figure S13).

In conclusion, we present an initial report of covalent post-assembly modification of a kinetically metastable supramolecular intermediate. Covalent modification prevented metastable helicates **1a**–**3a** from reorganizing to the thermodynamically favored $Fe^{II}_4L_4$ tetrahedral cages, thus trapping the system out of equilibrium. Additionally, we have demonstrated that tandem combinations of covalent and noncovalent post-assembly modification offer powerful means of altering a preformed

dx.doi.org/10.1021/ja5042397 | *J. Am. Chem. Soc.* 2014, 136, 8201–8204

supramolecular core without having to employ *de novo* ligand synthesis. These techniques contribute to the growing supramolecular "toolbox", which continues to offer ever more powerful means of building complex matter beyond the molecule.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis details and characterization data. Crystallographic data are deposited with the CCDC (numbers 997230−997233). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

jrn34@cam.ac.uk

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Diamond Light Source (UK) for synchrotron beamtime on I19 (MT8464) and the EPSRC National Crystallography Service for X-ray data collection. This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC). D.A.R. acknowledges the Gates Cambridge Trust for Ph.D. (Gates Cambridge Scholarship) and conference funding.

■ REFERENCES

(1) (a) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975. (b) Caulder, D. L.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185. (c) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369. (d) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (e) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810. (f) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37. (g) Gianneschi, N. C.; Masar, M. S.; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825. (h) Smulders, M. M. J.; Riddell, I. A.; Browne, C.; Nitschke, J. R. *Chem. Soc. Rev.* **2013**, *42*, 1728. (i) Lehn, J.-M. *Angew. Chem., Int. Ed.* **1990**, *29*, 1304. (j) Davis, A. V.; Yeh, R. M.; Raymond, K. N. *P. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4793.

(2) Cangelosi, V. M.; Carter, T. G.; Zakharov, L. N.; Johnson, D. W. *Chem. Commun.* **2009**, 5606.

(3) (a) Bilbeisi, R. A.; Ronson, T. K.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2013**, *52*, 9027. (b) Bilbeisi, R. A.; Clegg, J. K.; Elgrishi, N.; de Hatten, X.; Devillard, M.; Breiner, B.; Mal, P.; Nitschke, J. R. *J. Am. Chem. Soc.* **2011**, *134*, 5110. (c) Riddell, I. A.; Hristova, Y. R.; Clegg, J. K.; Wood, C. S.; Breiner, B.; Nitschke, J. R. *J. Am. Chem. Soc.* **2013**, *135*, 2723. (d) Riddell, I. A.; Smulders, M. M. J.; Clegg, J. K.; Hristova, Y. R.; Breiner, B.; Thoburn, J. D.; Nitschke, J. R. *Nat. Chem.* **2012**, *4*, 751.

(4) Korevaar, P. A.; George, S. J.; Markvoort, A. J.; Smulders, M. M. J.; Hilbers, P. A. J.; Schenning, A. P. H. J.; De Greef, T. F. A.; Meijer, E. W. *Nature* **2012**, *481*, 492.

(5) Ogi, S.; Sugiyasu, K.; Manna, S.; Samitsu, S.; Takeuchi, M. *Nat. Chem.* **2014**, *6*, 188.

(6) Berg, J. M., Tymoczko, J. L., Stryer, L., Stryer, L. B. *Biochemistry*, 7th ed.; W.H. Freeman & Co.: New York, 2012.

(7) Walsh, C. T. *Posttranslational Modification of Proteins: Expanding Nature's Inventory*; Roberts & Co.: Englewood, CO, 2005.

(8) (a) Barker, I. A.; Hall, D. J.; Hansell, C. F.; Du Prez, F. E.; O'Reilly, R. K.; Dove, A. P. *Macromol. Rapid Commun.* **2011**, *32*, 1362. (b) Konkolewicz, D.; Gray-Weale, A.; Perrier, S. *J. Am. Chem. Soc.* **2009**, *131*, 18075. (c) Sun, M. H.; Bo, Z. S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 111. (d) Gody, G.; Rossner, C.; Moraes, J.; Vana, P.; Maschmeyer, T.; Perrier, S. *J. Am. Chem. Soc.* **2012**, *134*, 12596.

(9) (a) Garibay, S. J.; Wang, Z.; Tanabe, K. K.; Cohen, S. M. *Inorg. Chem.* **2009**, *48*, 7341. (b) Golas, P. L.; Matyjaszewski, K. *Chem. Soc. Rev.* **2010**, *39*, 1338. (c) Tanabe, K. K.; Cohen, S. M. *Chem. Soc. Rev.* **2011**, *40*, 498.

(10) (a) Mosquera, J.; Zarra, S.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2014**, *53*, 1556. (b) Kaucher, M. S.; Harrell, W. A.; Davis, J. T. *J. Am. Chem. Soc.* **2005**, *128*, 38. (c) Ayme, J.-F.; Beves, J. E.; Campbell, C. J.; Leigh, D. A. *Chem. Soc. Rev.* **2013**, *42*, 1700.

(11) (a) Fuller, A.-M.; Leigh, D. A.; Lusby, P. J.; Oswald, I. D. H.; Parsons, S.; Walker, D. B. *Angew. Chem., Int. Ed.* **2004**, *43*, 3914. (b) Leigh, D. A.; Lusby, P. J.; McBurney, R. T.; Morelli, A.; Slawin, A. M. Z.; Thomson, A. R.; Walker, D. B. *J. Am. Chem. Soc.* **2009**, *131*, 3762. (c) Barran, P. E.; Cole, H. L.; Goldup, S. M.; Leigh, D. A.; McGonigal, P. R.; Symes, M. D.; Wu, J.; Zengerle, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 12280. (d) Fuller, A.-M. L.; Leigh, D. A.; Lusby, P. J.; Slawin, A. M. Z.; Walker, D. B. *J. Am. Chem. Soc.* **2005**, *127*, 12612.

(12) (a) Cangelosi, V. M.; Zakharov, L. N.; Johnson, D. W. *Angew. Chem., Int. Ed.* **2010**, *49*, 1248. (b) Carnes, M. E.; Collins, M. S.; Johnson, D. W. *Chem. Soc. Rev.* **2014**, *43*, 1825. (c) Cangelosi, V. M.; Carter, T. G.; Crossland, J. L.; Zakharov, L. N.; Johnson, D. W. *Inorg. Chem.* **2010**, *49*, 9985. (d) Zheng, Y.-R.; Lan, W.-J.; Wang, M.; Cook, T. R.; Stang, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 17045.

(13) (a) Chakrabarty, R.; Stang, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 14738. (b) Wang, M.; Lan, W.-J.; Zheng, Y.-R.; Cook, T. R.; White, H. S.; Stang, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 10752. (c) Kong, G.-Q.; Ou, S.; Zou, C.; Wu, C.-D. *J. Am. Chem. Soc.* **2012**, *134*, 19851. (d) Han, Y.-F.; Jin, G.-X.; Hahn, F. E. *J. Am. Chem. Soc.* **2013**, *135*, 9263. (e) Frank, M.; Hey, J.; Balcioglu, I.; Chen, Y.-S.; Stalke, D.; Suenobu, T.; Fukuzumi, S.; Frauendorf, H.; Clever, G. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 10102. (f) Han, S.; Ma, Z.; Hopson, R.; Wei, Y.; Budil, D.; Gulla, S.; Moulton, B. *Inorg. Chem. Commun.* **2012**, *15*, 78. (g) Young, M. C.; Johnson, A. M.; Hooley, R. J. *Chem. Commun.* **2014**, *50*, 1378. (h) Schneider, M. W.; Oppel, I. M.; Griffin, A.; Mastalerz, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 3611. (i) Zhao, D.; Tan, S.; Yuan, D.; Lu, W.; Rezenom, Y. H.; Jiang, H.; Wang, L.-Q.; Zhou, H.-C. *Adv. Mater.* **2011**, *23*, 90.

(14) (a) Ronson, T. K.; Zarra, S.; Black, S. P.; Nitschke, J. R. *Chem. Commun.* **2013**, *49*, 2476. (b) Zhou, X.-P.; Wu, Y.; Li, D. *J. Am. Chem. Soc.* **2013**, *135*, 16062. (c) Wu, Y.; Zhou, X.-P.; Yang, J.-R.; Li, D. *Chem. Commun.* **2013**, *49*, 3413. (d) Zhou, X.-P.; Liu, J.; Zhan, S.-Z.; Yang, J.-R.; Li, D.; Ng, K.-M.; Sun, R. W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2012**, *134*, 8042. (e) Dömer, J.; Slootweg, J. C.; Hupka, F.; Lammertsma, K.; Hahn, F. E. *Angew. Chem., Int. Ed.* **2010**, *49*, 6430. (f) Bunzen, H.; Nonappa; Kalenius, E.; Hietala, S.; Kolehmainen, E. *Chem.—Eur. J.* **2013**, *19*, 12978. (g) Sham, K.-C.; Yiu, S.-M.; Kwong, H.-L. *Inorg. Chem.* **2013**, *52*, 5648−5650. (h) Yi, S.; Brega, V.; Captain, B.; Kaifer, A. E. *Chem. Commun.* **2012**, *48*, 10295. (i) Campbell, V. E.; Guillot, R.; Riviere, E.; Brun, P.-T.; Wernsdorfer, W.; Mallah, T. *Inorg. Chem.* **2013**, *52*, 5194.

(15) Coles, S. J.; Gale, P. A. *Chem. Sci.* **2012**, *3*, 683.

(16) (a) Valeur, E.; Bradley, M. *Chem. Soc. Rev.* **2009**, *38*, 606. (b) Carpino, L. A.; Imazumi, H.; El-Faham, A.; Ferrer, F. J.; Zhang, C.; Lee, Y.; Foxman, B. M.; Henklein, P.; Hanay, C.; Mügge, C.; Wenschuh, H.; Klose, J.; Beyermann, M.; Bienert, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 441.

(17) Carpino, L. A. *J. Am. Chem. Soc.* **1993**, *115*, 4397.

(18) Ragnarsson, U.; Grehn, L. *Acc. Chem. Res.* **1998**, *31*, 494.

(19) (a) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188. (b) Heinrich, T.; Traulsen, C. H. H.; Darlatt, E.; Richter, S.; Poppenberg, J.; Traulsen, N. L.; Linder, I.; Lippitz, A.; Dietrich, P. M.; Dib, B.; Unger, W.; Schalley, C. A. *RSC Adv.* **2014**, *4*, 17694. (c) Lewis, J.; Elliott, A. B. S.; McAdam, C. J.; Gordon, K. C.; Crowley, J. D. *Chem. Sci.* **2014**, *5*, 1833. (d) Lewis, J. E. M.; John McAdam, C.; Gardiner, M. G.; Crowley, J. D. *Chem. Commun.* **2013**, *49*, 3398.

(20) Ma, Z.; Han, S.; Hopson, R.; Wei, Y.; Moulton, B. *Inorg. Chim. Acta* **2012**, *388*, 135.

(21) Barral, K.; Moorhouse, A. D.; Moses, J. E. *Org. Lett.* **2007**, *9*, 1809.

(22) (a) Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141. (b) Mak, C. C.; Bampos, N.; Sanders, J. K. M. *Chem. Commun.* **1999**, 1085.