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# Synthesis of a New Bimetallic Re(I)–NCS–Pt(II) Complex as Chemodosimetric Ensemble for the Selective Detection of Mercapto-Containing Pesticides

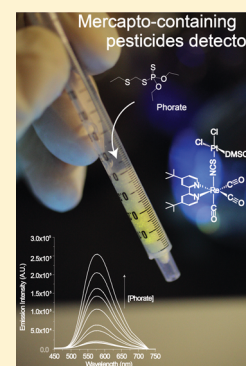
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## S Supporting Information

**ABSTRACT:** Detection of mercapto-containing pesticides plays a crucial role in food and water safety. A new Re(I)–NCS–Pt(II) complex, [Re(4,4'-di-*tert*-butyl-2,2'-bipyridine)(CO)<sub>3</sub>(NCS)]–[Pt(DMSO)(Cl)<sub>2</sub>] (**1**), was synthesized and characterized. The synthetic procedure, characterization results, and photophysical data for **1** are reported in this paper. Solvated complex **1** demonstrated luminescent chemodosimetric selectivity for phorate, demeton, and aldicarb (three common mercapto-containing pesticides) with method detection limits (MDLs) of 1.00, 2.87, and 2.08 ppm, respectively. The binding constants (log *K*) of **1** toward them were in the 3.24–3.44 range. The analyte selectivity of the complex was found to be dependent on the bridging linkage (C≡N and N=C=S) between the Re(I) and Pt(II) centers. The solid-supported dosimetric device **1** was fabricated by blending complex **1** with Al<sub>2</sub>O<sub>3</sub> and poly(vinyl chloride) (PVC) powder. The MDLs of the device toward the mercapto-containing pesticides were 0.48–0.60 ppm. The device was applicable to pesticides in real water bodies such as taps, rivers, lakes, and underground water bodies with excellent recoveries and relative standard deviations of 76.2–108.0% and 2.9–6.7%, respectively. Its spectrofluorimetric changes could be analyzed by naked eye within 20 min with a linear luminometric response toward increases in the phorate concentration (0–8.0 ppm) with *R* = 0.999.



The extensive use and improper disposal of pesticides by agricultural industries have led to significant water pollution problems worldwide. Pesticides are popular substances used in agriculture because they are highly effective for the eradication of insects.<sup>1</sup> However, their residues that remain on agricultural products and in the groundwater are known to be hazardous to human health and result in problems such as eye irritation, abdominal pain, seizures, and respiratory failure.<sup>2</sup> For example, medical and biological research have demonstrated that organophosphate pesticides inhibit the activity of the acetylcholinesterase enzyme, which consequently leads to the toxic accumulation of neurotransmitter acetylcholine.<sup>2e–j</sup> Over the past decade, there have been many devastating reports and incidents that involve the contamination of the food supply chain. Not only have these issues eroded the confidence of consumers, but they have also led to serious financial, political, and health implications. In view of the above facts, 19 types of pesticides, including three aliphatic mercapto-containing pesticides (phorate, demeton, and aldicarb), have been strictly regulated by many countries in order to limit their use and prevent them from exceeding their maximum residue levels.<sup>3</sup> There is urgent demand for their control and monitoring, and thus, the development of simple and rapid detection methods with high selectivity and sensitivity for such pesticides in food and the environment is necessary. Current technology for detecting pesticides mainly relies on analytical instruments, molecular imprinting polymers, mass-spectrometric methods,

electrochemical detection, and enzyme immunoassays.<sup>4</sup> However, these means usually involve complicated procedures and lack specificity, and the related equipment is costly. Chemosensing methods for pesticide detection have also been developed,<sup>5</sup> but they are seldom specifically for organosulfur pesticides.

Development of chemodosimeters for environmentally and biologically important analytes is an emerging field. Chemodosimeters are molecular probes and used for the imaging of analytes to yield measurable signals that are irreversible.<sup>6</sup> They have properties and functions that are very suitable for food monitoring purposes. Since the signals that indicate contamination cannot be altered and erased (irreversible responses), warnings can be provided at any stage of food processing at which contamination has occurred. Therefore, a selective, low-cost, and easy to use chemodosimeter for pesticide detection is highly desirable in many applications.

Of particular interest is the use of bimetallic donor–acceptor ensembles (BmDAEs)<sup>7</sup> as chemodosimeters, since their intrinsic properties (such as optical wavelength and luminescent chemodosimetric properties) are easy to tune through the sensible combination of metal complexes, organic ligands, and

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bridging molecules. We have reported a series of cyano-bridged BmDAEs,  $M_A-C\equiv N-M_B$  [ $M_A = Fe(II)$ ,  $Ru(II)$ ,  $Os(II)$ , and  $Re(I)$ , and  $M_B = Fe(III)$ ,  $Ni(II)$ ,  $Cu(II)$ ,  $Pt(II)$ , and  $Ln(III)$ ], as chemodosimeters for biological and environmental analytes such as amino acids,<sup>8a</sup> peptides,<sup>8a</sup> cyanides,<sup>8b</sup> biogenic amines,<sup>8d</sup> biogenic sulfides,<sup>8c</sup> oxalic acid,<sup>8f</sup> and other common anions.<sup>8c</sup> However, application of these BmDAE systems as chemodosimeters for mercapto-containing pesticides has not been examined thus far. We have attempted to explore the possibility of tuning the selectivity of BmDAEs by varying the combinations of metallic components in the complex design. Our focus in this study is to illustrate that the selectivity of BmDAEs can be regulated by using suitable bridging ligands such as  $C\equiv N$  and  $N=C=S$ .

The immobilization of chemodosimeters into solid-supported materials is important for their perusal in applicable systems.<sup>9</sup> However, the ability to sensitively and quickly detect analytes by using solid-supported chemodosimetric material is fundamentally challenging. There are few studies in the literature that have used bimetallic complexes<sup>10</sup> as solid-supported chemodosimeter.<sup>8d</sup> In this work, we explore the feasibility of (1) using a BmDAE as a chemodosimeter to detect aliphatic mercapto-containing pesticides, (2) using the bridging ligand between  $M_A$  and  $M_B$  to fine-tune the sensitivity and selectivity of the dosimetric responses, and (3) immobilizing the BmDAE into an easy to use solid-supported chemodosimetric device. Realized through a molecular design, a  $Re(I)$ -based indicator was linked to a  $Pt(II)$ -based metallic receptor via an isocyano linkage to form a bimetallic based chemodosimetric system. After the pesticides that contain mercapto are introduced into the system, the mercapto functionality coordinates with the  $Pt(II)$  receptor, then displaces the  $Re(I)$  indicator, and thus an optical signal is produced. The chemodosimetric device produces luminescent signals that are specific to pesticides with aliphatic mercapto down to the part-per-million levels [method detection levels (MDLs): 0.48 ppm for phorate and 0.60 ppm for demeton].

## EXPERIMENTAL SECTION

**Materials and General Procedures.** 4,4'-Di-*tert*-butyl-2,2'-bipyridine (*t*Bu-bpy),  $K_2(PtCl_4)$ ,  $Re(CO)_5Br$ , KCN, and KSCN were purchased from Aldrich. Complexes *fac*-[ $Re(Lig)(CO)_3Cl$ ],<sup>11</sup>  $Re(Lig)(CO)_3CN$ ,<sup>12</sup>  $Re(Lig)(CO)_3NCS$ ,<sup>13</sup> and  $Pt(DMSO)_2Cl_2$ <sup>14</sup> were prepared in accordance with the reported methods. All of the organic solvents used were analytical grade.

**Synthesis and Characterization.**  $Re(tBu-bpy)(CO)_3(NCS)$ : An ethanol/water (4:1 v/v) solution (100 mL) that contained *fac*-[ $Re(tBu-bpy)(CO)_3Cl$ ] (0.2870 g, 0.500 mmol) and KSCN (2.40 g, 0.025 mol) was refluxed under an  $N_2$  atmosphere for 24 h. During the course of reaction, the solution became clear and bright yellow with orange emission. The solution was then evaporated until dried in vacuo, and the resultant yellow crude product was extracted three times by using water and diethyl ether. The complex product was obtained as an air-stable pale yellow solid (yield = 88%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 8.88 (d,  $J = 6.0$  Hz, 2H), 8.04 (s, 2H), 7.48 (dd,  $J = 1.0, 6.0$  Hz, 2H), 1.42 (s, 18H). <sup>13</sup>C NMR (150 MHz): 30.27, 35.73, 119.71, 124.80, 133.58 (NCS), 152.89, 155.68, 164.38, 191.81, 195.35. IR (KBr):  $\nu_{C=N} = 2088$   $cm^{-1}$ ;  $\nu_{C=O} = 2022$  and  $1894$   $cm^{-1}$ . ESI-MS (+ve mode):  $m/z$  597.8 {[ $Re(tBu-bpy)(CO)_3(NCS)]\cdot H}^+$ . Anal. Calcd for

$C_{22}H_{24}N_3O_3ReS$ : C, 44.28; H, 4.05; N, 7.04. Found: C, 44.19; H, 4.08; N, 7.05.

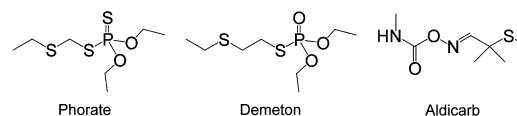
[ $Re(tBu-bpy)(CO)_3(NCS)$ ]-[ $Pt(DMSO)_2Cl_2$ ] (1): Complex 1 was synthesized by adding  $Pt(DMSO)_2Cl_2$  (0.0708 g, 0.167 mmol) and  $Re(tBu-bpy)(CO)_3(NCS)$  (0.1000 g, 0.167 mmol) in a 1:1 mixture of MeOH/ $CHCl_3$  (70 mL) under ambient condition with stirring for a period of 20 h. The reaction mixture was then evaporated until dried in vacuo, and the crude product was washed three times with MeOH. The complex was isolated with a reasonable yield (88%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 8.85 (d,  $J = 6.0$  Hz, 2H), 8.15 (s, 2H), 7.57 (dd,  $J = 1.0, 6.0$  Hz, 2H), 3.36 (s, 6H), 1.49 (s, 18H). <sup>13</sup>C NMR (150 MHz): 29.71, 35.64, 45.08, 120.54, 121.29 (NCS), 125.19, 153.04, 156.06, 164.94, 191.45, 194.43. IR (KBr):  $\nu_{C=N} = 2161$   $cm^{-1}$ ;  $\nu_{C=O} = 2030$  and  $1916$   $cm^{-1}$ . ESI-MS (+ve mode):  $m/z$  979.9 {[ $Re(tBu-bpy)(CO)_3(NCS)$ ]-[ $Pt(DMSO)_2Cl_2$ ] $\cdot K$ }<sup>+</sup>. TLC: silica gel and ethyl acetate/hexane (2:1),  $R_f = 0.65$ . Anal. Calcd for  $C_{24}H_{30}Cl_2N_3O_4PtReS_2$ : C, 30.64; H, 3.21; N, 4.47. Found: C, 30.55; H, 3.27; N, 4.42.

**UV-Vis Spectroscopic and Spectrofluorimetric Titrations.** The measurements were taken after equilibrium was established. The 1:1 receptor-substrate interaction was analyzed in accordance with a Benesi-Hildebrand equation.<sup>15</sup> All of the solvents that were used in the experiments were analytical grade.

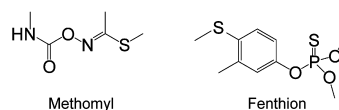
### Selectivity of Complex 1 toward Various Analytes.

Various types of pesticides, including phorate, demeton, aldicarb, methomyl, fenthion, malathion, methyl parathion, cygon, monitor, phosdrin, dichlorvos (DDVP), and naled (0 to  $3.00 \times 10^{-4}$  M), were mixed with solutions of complex 1 ( $1.00 \times 10^{-4}$  M). The titrations were then performed by using  $CHCl_3$  at room temperature. The responses were plotted as a function of the mole ratio of the analytes.

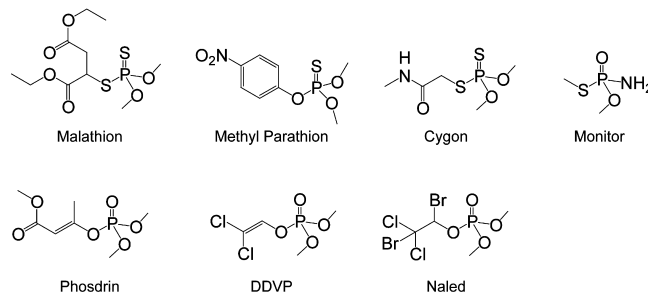
#### Aliphatic mercapto-containing pesticides



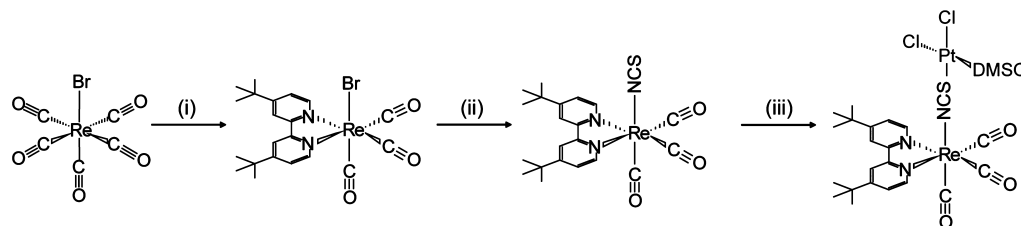
#### Aromatic or conjugated mercapto-containing pesticides



#### Common pesticides without mercapto functionality



**Solid-Supported Chemodosimeter 1.** Solid-supported complex 1 was fabricated by suspending complex 1 (0.0042 g) and  $Al_2O_3$  (50–200  $\mu m$ , 0.2115 g) in 4.00 mL of  $CHCl_3$ . After the  $CHCl_3$  suspension was evaporated at room temperature, a powder was obtained. This powder (0.2000 g) was then diluted with  $Al_2O_3$  (0.8600 g, 50–200  $\mu m$ ), and the diluted powder

Scheme 1. Synthesis of  $[\text{Re}(\text{Lig})(\text{CO})_3(\text{NCS})]-[\text{Pt}(\text{DMSO})(\text{Cl})_2]$  (**1**)<sup>a</sup>

<sup>a</sup>Reaction conditions: (i) reflux with *t*Bu-bpy in toluene; (ii) reflux with one equiv of KSCN in aqueous ethanol; (iii) stirring with one equiv of  $[\text{Pt}(\text{DMSO})_2\text{Cl}_2]$  in a MeOH/ $\text{CHCl}_3$  mixture (1:1) at ambient condition.

(0.0719 g) was further mixed with poly(vinyl chloride) (PVC) powder (0.0719 g, 0.212–0.424 mm), which produced solid-supported chemodosimeter **1**. The chemodosimetric material was isolated as an air-stable yellow powder. Emission  $\lambda_{\text{max}}$ : 540 nm. Excitation  $\lambda_{\text{max}}$ : 389 nm. IR (KBr):  $\nu_{\text{C}=\text{N}}$  = 2145  $\text{cm}^{-1}$ ;  $\nu_{\text{C}=\text{O}}$  = 2025 and 1921  $\text{cm}^{-1}$ . Chemodosimetric material **1** (0.144 g) was packed into a syringe (4.65 mm diameter) that was prepacked with PVC powder (0.042 g, 0.212–0.424 mm) as a base. Additional PVC powder (0.112 g) was packed on top of chemodosimetric material **1** as a cover. All materials in the syringe were then pretreated by flowing 0.5 mL of deionized (DI) water from the top of the syringe. Emission intensity of the entire setup was recorded for baseline correction. A 10 mL water sample spiked with different concentrations of phorate was flowed into the syringe. The filtrate was collected and reapplied into the syringe with a flow rate of 1.0 mL/min. The spectrofluorimetric changes of solid-supported chemodosimeter **1** were analyzed.

## RESULTS AND DISCUSSION

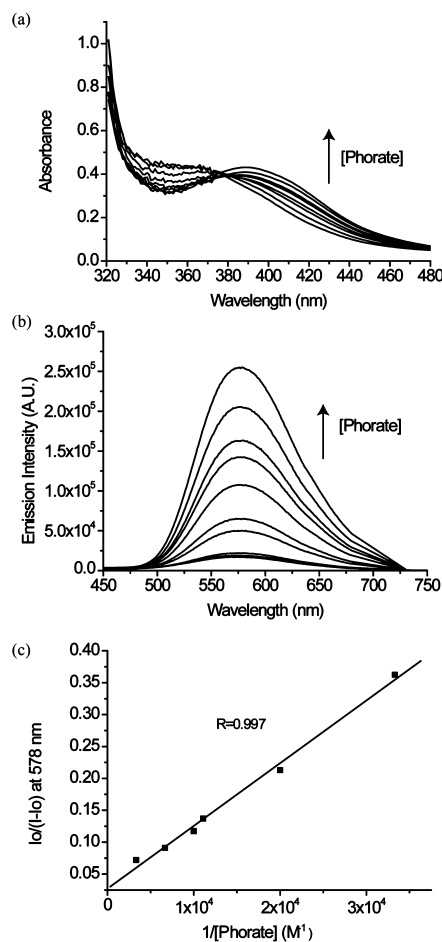
### Synthesis and Characterization of Complex **1**.

Complex **1**, which is a neutral Re(I)–Pt(II) bimetallic supramolecule, was synthesized by simply stirring  $\text{Pt}^{\text{II}}(\text{DMSO})_2\text{Cl}_2$  with  $\text{Re}^{\text{I}}(t\text{Bu-bpy})(\text{CO})_3(\text{NCS})$  in 1:1 mol ratio in an MeOH/ $\text{CHCl}_3$  mixture (1:1) at ambient condition (Scheme 1). Complex **1** was an air-stable compound which is very soluble in acetonitrile, chloroform, and dichloromethane, but insoluble in aqueous medium. The Re–NCS–Pt coordination of complex **1** was demonstrated by its electrospray mass spectrometry peaks:  $\{[\text{Re}(t\text{Bu-bpy})(\text{CO})_3(\text{NCS})]-[\text{Pt}(\text{DMSO})\text{Cl}_2]\cdot\text{K}\}^+$  at 979.9  $m/z$  (Supporting Information Figure 3). The formation of an isocyano-bridged bimetallic complex was also confirmed through the use of an infrared (IR) spectroscopic analysis; the  $\nu_{\text{N}=\text{C}=\text{S}}$  peak of  $\text{Re}(t\text{Bu-bpy})(\text{CO})_3(\text{NCS})$  at 2161  $\text{cm}^{-1}$  shifted to 2088  $\text{cm}^{-1}$  for complex **1** (Supporting Information Table 1). The new bimetallic complex was also characterized by using  $^1\text{H}$  NMR spectroscopy (Supporting Information Figure 7) and provided satisfactory elemental analysis results.

**UV–Vis and Luminescence Properties of **1**.** The electronic absorption and spectrofluorimetric properties of the  $\text{Re}(t\text{Bu-bpy})(\text{CO})_3(\text{NCS})$  chromophore before and after coordination with the  $\text{Pt}(\text{DMSO})\text{Cl}_2$  are shown in Supporting Information Table 2. The UV–vis absorption maximum of  $\text{Re}(t\text{Bu-bpy})(\text{CO})_3(\text{NCS})$ , which is identified as the  $[\text{d}\pi(\text{Re}) \rightarrow \pi^*(t\text{Bu-bpy})]$  metal-to-ligand charge-transfer (MLCT) transition,<sup>16</sup> is 389 nm in  $\text{CHCl}_3$ . However, the MLCT transition of **1** shifts to a higher energy (356 nm) after the coordination of the Pt(II) complex. By comparing to the emission of  $\text{Re}(t\text{Bu-bpy})(\text{CO})_3(\text{NCS})$ , complex **1** shows a

relatively weak yellow emission. The emission maximum of the  $^3\text{MLCT}$  of  $\text{Re}(t\text{Bu-bpy})(\text{CO})_3(\text{NCS})$  is 578 nm. Upon coordination with the Pt(II) acceptor, the  $^3\text{MLCT}$  emission blue-shifts to 572 nm and is significantly quenched.<sup>17</sup>

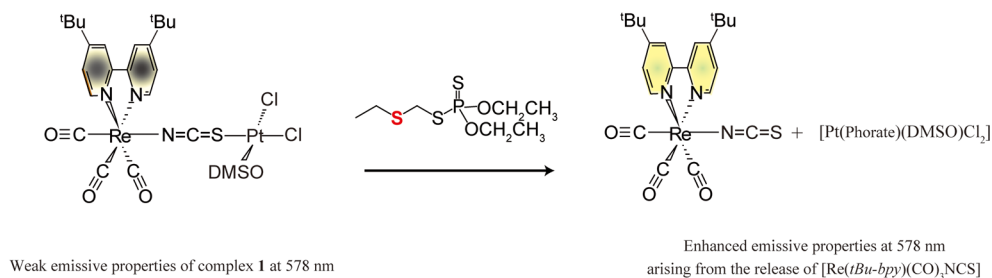
**Chemodosimetric Response of Complex **1** toward Pesticides with Aliphatic Mercapto.** The electronic absorptions of **1** in the  $\text{CHCl}_3$  were indicative of perturbation induced by the presence of the mercapto-containing pesticides, such as phorate. Parts a and b of Figure 1 show the UV–vis spectroscopic and spectrofluorimetric titrations of complex **1**



**Figure 1.** (a) UV–vis spectroscopic titrations and (b) spectrofluorimetric titrations of complex **1** ( $1 \times 10^{-4}$  M) with phorate ( $0-3 \times 10^{-4}$  M) ( $\lambda_{\text{ex}}$  = 389 nm). (c) Plotting of  $I_0/(I_0 - I)$  vs  $1/[\text{phorate}]$ : Slope and  $y$ -intercept of the best-fit line are 0.0272 and  $9.83 \times 10^{-6}$  M, respectively;  $\log K = 3.44 \pm 0.03$  at 578 nm. All the experiments were carried out in  $\text{CHCl}_3$ .



## Scheme 2. Proposed Chemodosimetric Mechanism of Complex 1 with Phorate

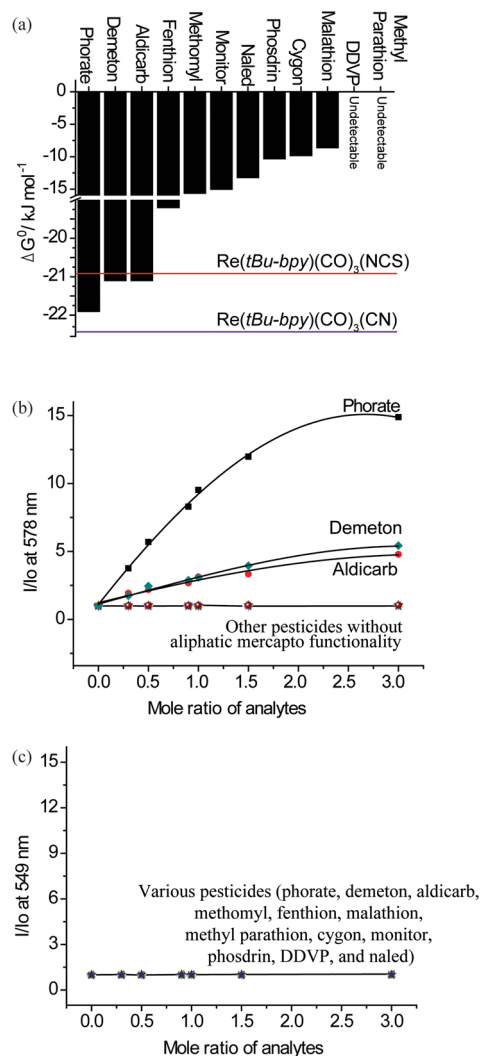
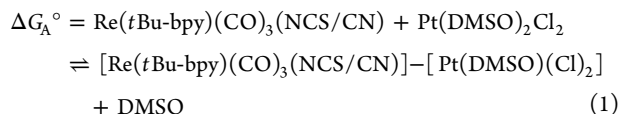


with phorate, respectively. When phorate was added to complex 1, its MLCT transition shifted from 370 to 390 nm (Figure 1a) while the  $^3\text{MLCT}$  transition remained at 578 nm but was significantly increased in intensity (Figure 1b). When the titration curves were fitted with the 1:1 Benesi–Hildebrand equation (Figure 1c),  $\log K$ , the formation constant, of complex 1 toward phorate was calculated as  $3.43 \pm 0.03$ . Therefore, the Pt(II) receptor in complex 1 is suggested to be able to bind one molecule of phorate (Scheme 2).

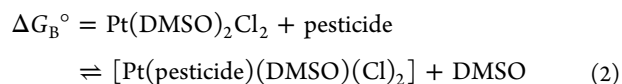
Figure 2b summarizes the spectrofluorimetric titrations of complex 1 ( $1.00 \times 10^{-4}$  M) with three different classes of common pesticides, including (i) aliphatic mercapto-containing pesticides (phorate, demeton, and aldicarb), (ii) aromatic/conjugated mercapto-containing pesticides (methomyl and fenthion), and (iii) other pesticides (malathion, methyl parathion, cygon, monitor, phosdrin, DDVP, and naled). Among the pesticides, only those with an aliphatic mercapto functionality, RSR (R = alkyl), induced a spectrofluorimetric response. Other common moieties, including aromatic/conjugated mercapto functionalities and thiophosphates (P=S and P–S), did not produce any spectrofluorimetric changes that could be observed. We also found that the chemodosimetric responses of complex 1 toward dimethyl sulfide ( $\text{CH}_3\text{SCH}_3$ ) were similar to those of the aliphatic mercapto-containing pesticides (Supporting Information Figure 11). Thus, complex 1 only responds to aliphatic mercapto functionality (RSR, where R = alkyl group). Through the spectrofluorimetric methods, the method detection limits (MDLs) of 1 toward phorate, demeton, and aldicarb were found to be 1.00, 2.87, and 2.08 ppm, respectively, via the Hubaux and Vos method.<sup>18</sup>

The similarity of the excitation and emission spectroscopic properties between the complex 1–phorate mixture and those of  $\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{NCS})$  suggests that the isothiocyanide of the binuclear complex is cleaved after phorate binds to the Pt(II) center. This possibility is further verified through the subsequent observation of  $\{\text{H}[\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{NCS})]\}^+$  ( $m/z$  597.8  $[\text{M} + \text{H}]^+$ ).

**Analyte Selectivity.** The thermodynamic of a BmDAE is a crucial consideration in its selectivity in indicator displacement assays. In this context, the competitive displacement of the Re(I) indicator through the use of pesticides with aliphatic mercapto in the presence of BmDAE systems take place resultant of the two following equilibria:



**Figure 2.** Chemodosimetric responses of complexes 1 and 2 toward pesticides. (a) The binding strengths ( $\Delta G^\circ$ ) of Pt(II)(DMSO) $_2$ Cl $_2$ –analyte adducts were shown in the bar chart, whereas  $\Delta G^\circ$  of complexes 1 and 2 is shown as the horizontal lines. (b and c) The results of the spectrofluorimetric titration ( $I/I_0$ ) of complexes 1 and 2 ( $1.00 \times 10^{-4}$  M), respectively, with pesticides (phorate, demeton, aldicarb, methomyl, fenthion, malathion, methyl parathion, cygon, monitor, phosdrin, DDVP, and naled) as a function of their increasing concentration.

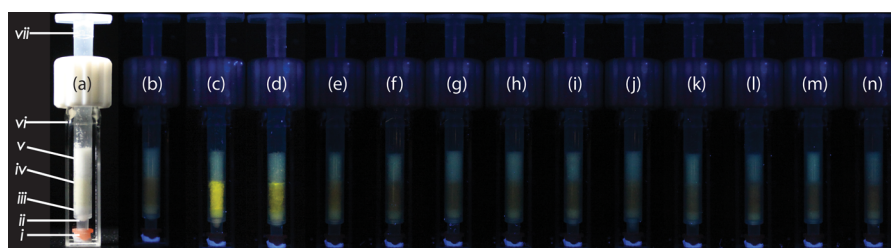


where  $\Delta G_A^\circ$  and  $\Delta G_B^\circ$  are the Gibbs free energy changes of the reactions of equilibria 1 and 2, respectively. To determine

**Table 1.** Log  $K$  and  $\Delta G^\circ$  for Complexations of Various Pesticides,  $\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{NCS})$ , and  $\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{CN})$  with  $\text{Pt}(\text{DMSO})_2\text{Cl}_2$ 

	acceptor	donor	log $K^a$	$\Delta G^\circ/\text{kJ mol}^{-1}$
1	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	$\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{CN})$	3.93	−22.4
2	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	phorate	3.84	−21.9
3	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	demeton	3.70	−21.1
4	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	aldicarb	3.69	−21.1
5	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	$\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{NCS})$	3.67	−20.9
6	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	fenthion	3.36	−19.2
7	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	methomyl	2.73	−15.6
8	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	monitor	2.63	−15.0
9	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	naled	2.32	−13.2
10	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	phosdrin	1.81	−10.3
11	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	cygon	1.72	−9.8
12	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	malathion	1.50	−8.6
13	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	DDVP	<i>b</i>	<i>b</i>
14	$\text{Pt}(\text{DMSO})_2\text{Cl}_2$	methyl parathion	<i>b</i>	<i>b</i>

<sup>a</sup>Binding strengths were measured by using UV spectroscopic titration and determined with the Benesi–Hildebrand 1:1 equation. All of the titrations conducted in  $\text{MeOH}/\text{CHCl}_3$  (1:1) at 298 K. <sup>b</sup>Too small to be determined.



**Figure 3.** Photographs of luminometric responses of solid-supported chemodosimeter **1** with various pesticides (8.0 ppm) at 298 K in aqueous DI water. Photo taken under normal illumination of (a) **1** only, (i) plastic base, (ii) cotton, (iii) PVC powder, (iv) solid-supported chemodosimeter **1**, (v) PVC powder, (vi) quartz cuvette, and (vii) plastic syringe. Photos taken under illumination at  $\lambda_{\text{ex}} = 365 \text{ nm}$  of (b) **1** only, (c) **1** + phorate, (d) **1** + demeton, (e–n) **1** + aldicarb, methomyl, fenthion, malathion, methyl parathion, cygon, monitor, phosdrin, DDVP, and naled, respectively.

how the  $\text{Re}(\text{I})\text{--NCS}\text{--Pt}(\text{II})$  stability and  $\text{Pt}(\text{II})\text{--pesticides}$  adducts affect the selectivity of complex **1** (i) a new  $\text{Re}(\text{I})\text{--Pt}(\text{II})$  bimetallic complex with cyanide bridge,  $[\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{CN})]\text{--}[\text{Pt}(\text{DMSO})(\text{Cl})_2]$  (**2**), was synthesized and (ii) the behaviors of both complexes **1** and **2** with different  $\Delta G_A^\circ$  and  $\Delta G_B^\circ$  were compared in detail. A comparison of the energy of formation ( $\Delta G^\circ$ ) of the adducts between  $\text{Pt}(\text{DMSO})_2\text{Cl}_2$  and the pesticides,  $\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{NCS})$ , and  $\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{CN})$  is provided in Table 1 and Figure 2a. The  $\Delta G^\circ$  values of complexes **1** and **2** are  $-20.9$  and  $-22.4 \text{ kJ mol}^{-1}$ , respectively, which indicate that the ensemble between Re and Pt with an CN bridge is stronger than that with an NCS bridge (Supporting Information Figures 9 and 10).

It has been suggested that displacement of the indicator can only successfully take place when  $\Delta G^\circ$  of the indicator–receptor is greater than that of the resultant receptor–analyte (i.e.,  $\Delta G_A^\circ > \Delta G_B^\circ$ , when more stable receptor–analyte can be formed).<sup>19</sup> The chemodosimetric responses of the “stronger” complex, that is, complex **2**, toward the pesticides are shown in Figure 2c. As its  $\Delta G_A^\circ$  is smaller than those of all the  $\text{Pt}(\text{II})\text{--pesticides}$ , complex **2** was not responsive to any of the pesticides. Figure 2b shows the luminescent responses of the “appropriate  $\text{Re}(\text{I})\text{--Pt}(\text{II})$  combination”, i.e., complex **1**, toward the pesticides. As  $\Delta G^\circ$  of complex **1** is lower than that of all of the  $\text{Pt}(\text{II})\text{--pesticides}$  adducts with the exception of the adducts between  $\text{Pt}(\text{II})$  and the aliphatic mercapto-containing pesticides, complex **1** only responded to phorate,

demeton, and aldicarb. The results obtained from these  $\text{Re}(\text{I})\text{--Pt}(\text{II})$  bimetallic complexes suggest that analyte selectivity can be tuned with the use of different donor and acceptor linkages, which contribute to the previous practice of using different combinations of metallic acceptor–metallic donor and metal–ligand.<sup>8a,e</sup>

#### Detection of Pesticides by the Solid-Supported Chemodosimetric Materials **1** in Aqueous Samples.

Chemodosimetric solid-supported material **1** was fabricated by blending a chloroform solution of complex **1** with  $\text{Al}_2\text{O}_3$  (50–200  $\mu\text{m}$ ) and PVC powder (0.212–0.424 mm). The chemodosimetric material was packed into a syringe with extra PVC powder as the base and cover. Without performing pretreatment processes, a water sample with a known concentration of phorate was flowed across the dosimetric material. The spectrofluorimetric changes of solid-supported chemodosimeter **1** could be analyzed within 20 min. Figure 3 is a photo of the luminometric responses of complex **1** to the pesticides in aqueous samples. Only phorate and demeton induced naked-eye responses from solid-state chemodosimeter **1**. When the concentration of phorate was increased, a linear response ( $R = 0.999$ ) was found from the solid-state chemodosimeter. In the best-fitted curve,  $I/I_0$  versus [phorate], the slope and  $y$ -intercept are 6.40 and 5.35, respectively (Supporting Information Figure 14). Supporting Information Figure 15 shows the spectrofluorimetric response of the chemodosimeter toward demeton. Interestingly, the MDLs<sup>18</sup> of the solid-supported chemodosimetric material toward

phorate and demeton were 0.48 and 0.60 ppm, which indicates higher sensitivity than that of complex **1** itself. The lack of aldicarb detection by chemodosimetric materials **1** may be due to the dissociation of the molecule via the cleavage of its oxime group in the presence of  $\text{Al}_2\text{O}_3$ .

The selectivity of the solid-state chemodosimeter **1** was further tested by detecting phorate in the presence of different pesticides. Supporting Information Figure 16 shows that the spectrofluorimetric responses of the chemodosimeter toward a mixture of phorate (4 ppm) and the common pesticides (methomyl, fenthion, malathion, methyl parathion, cygon, monitor, phosdrin, DDVP, and naled; each at 40 ppm) were similar to those toward phorate alone (4 ppm). However, there was no change in its chemodosimetric responses when spiking with a mixture of the pesticides (Supporting Information Figure 16, sets 3 and 4). These results indicate that there is no interference of the pesticides on the luminescent response of the solid-state chemodosimeter **1** toward phorate. Supporting Information Figure 17 shows the selectivity of the chemodosimeter toward demeton.

For final verification of the solid-supported chemodosimeter, the material was used to detect phorate in drinking water sources. The samples were collected from water sources in Hong Kong, China. The samples were passed through membrane filters that were  $0.45\ \mu\text{m}$  in pore size (Pall Corporation) to remove any insoluble substances prior to examination. In the studies of the spectrofluorimetric phorate detection in real samples using this material, samples from various sources (river, tap, lake, and underground) were spiked with 0.50 ppm of phorate and analyzed by solid-supported chemodosimeter **1** at room temperature with a developed calibration curve (Supporting Information Figure 14b). The analytical results show that the solid-supported chemodosimeter can measure the concentrations of phorate in drinking water samples with a reasonable recovery and relative standard deviation (RSD, %) of 76.2–108.0% and 2.9–6.7%, respectively (Table 2). These results demonstrate the suitability

**Table 2. Results of Phorate Detection in Different Water Samples with Solid-Supported Chemodosimeter **1****

phorate detection in various water bodies				
water samples	phorate added (ppm)	phorate found (ppm)	recovery (%)	RSD (%)
tap water	0.5	$0.44 \pm 0.02$	87.8	5.6
lake	0.5	$0.49 \pm 0.01$	98.2	2.9
river	0.5	$0.38 \pm 0.01$	76.2	3.6
underground	0.5	$0.54 \pm 0.04$	108.0	6.7

and practicality of the solid-supported chemodosimeter for the detection of pesticides with aliphatic mercapto functionalities in fresh water samples without affecting by other environmentally relevant competitive parameters.

## CONCLUSION

A new bimetallic complex,  $[\text{Re}(\text{tBu-bpy})(\text{CO})_3(\text{NCS})]-[\text{Pt}(\text{DMSO})(\text{Cl})_2]$  (**1**), has been synthesized and fully characterized in this study. The related photophysical data have also been recorded. Complex **1** appears to be the first chemodosimeter for pesticides with aliphatic mercapto functionality and has a detection limit that can detect mercapto as low as 1 ppm. The bridging linkage ( $\text{C}\equiv\text{N}$  and  $\text{N}=\text{C}=\text{S}$ ) between the two metal centers in this bimetallic chemodosimetric approach

seems to be a versatile way to control analyte selectivity. A dosimetric device was fabricated by blending complex **1** with  $\text{Al}_2\text{O}_3$  and PVC powder. The device could generate a naked-eye luminometric response that is selective for phorate and demeton. Its spectrofluorimetric changes could be analyzed within 20 min with a linear luminometric response toward increases in the phorate concentration (0–8.0 ppm) with  $R = 0.999$ . The device was applicable in analyzing real drinking water with a reasonable recovery and RSD of 76.2–108.0% and 2.9–6.7%, respectively. The MDLs toward phorate and demeton were 0.48 and 0.60 ppm, respectively.

## ASSOCIATED CONTENT

### Supporting Information

The synthetic procedures, the spectroscopic/spectrofluorimetric analyses of complexes **1** and **2**, and all of the UV–vis spectroscopic and spectrofluorimetric titrations. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b00684.

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### Notes

The authors declare no competing financial interest.

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