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Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-06-2018-005159.R2
Article Type:	Communication

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Journal Name

COMMUNICATION

A Four-State Fluorescent Molecular Switch

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Four distinct fluorescent states are achieved in a single WLA (Weak-Link Approach) construct bearing pyrene and tetraphenylethene moieties. The fluorescence of the compound in both the solution and solid phase can be manipulated through reversible coordination chemistry at the Pt^{II} center.

Stimuli-responsive molecules and materials with tunable photoluminescence properties integrate target recognition and signal transduction processes, and thus, can be useful for the development of sensing and imaging techniques.¹⁻⁶ Moreover, the incorporation of multiple responsive and signalling motifs into one structure enables the detection of different stimuli within one system, thereby expanding their potential utility. However, the design of multi-stimuli-responsive photoluminescent systems remains challenging due to interference that can take place between the different fluorescence pathways that are affected by chemical and physical stimuli.⁷⁻⁹ To address this challenge, we introduce a new strategy based on a molecular system where a structural change or phase transition, triggered by different stimuli, can be used to independently and deliberately switch between different fluorescent states. Moreover, in certain cases one can use mixtures of different stimuli to modulate fluorescence states.

Among the ways to construct stimuli-responsive systems, the WLA provides a coordination chemistry-based strategy for the assembly of supramolecular constructs that can be toggled between different coordination states via ligand displacements

at the transition-metal center using allosteric effectors (such as small molecules or ions).¹⁰⁻¹¹ Through synthetic incorporation of multiple photoluminescent motifs into the ligands, the changes in coordination modes of the WLA complexes result in different fluorescence outputs, such as emission intensity, fluorescence lifetimes, and emission spectral features.¹² Based upon these changes in fluorescent properties, WLA assemblies have been exploited as fluorescent probes,¹² photoredox switches,¹³ and light-harvesting arrays.¹⁴⁻¹⁵ We hypothesized that by incorporating a pair of fluorescent motifs with different emission mechanisms into the WLA assembly, changes in the coordination or phase state of the WLA complex triggered by different chemical stimuli could tune the fluorescent profile of these two fluorophores orthogonally, leading to multiple fluorescence outputs.

Herein, we report the first example of heteroligated Pt^{II} WLA complexes with hemilabile ligands bearing both a conventional (pyrene) and an unconventional fluorophore (tetraphenylethene, TPE).¹⁶⁻¹⁸ As shown in Fig. 1, in solution, the displacement of the Pt-S bond with the an anionic effector, such as Cl⁻ ion, in the pyrene-functionalized phosphino-thioether (P,S) ligand converts the closed complex to the semi-open state, resulting in a “turn-on” fluorescence response of the pyrene due to the distance-dependent heavy atom effect (HAE).^{12, 19-20} When the solvent polarity is reduced, for instance by the addition of hexane, these complexes precipitate due to reduced solubility, and the pyrene fluorescence is quenched,²¹ while the emission of the TPE moiety²²⁻²⁴ is turned on due to restriction of intramolecular rotation (RIR) in the solid phase.²⁵⁻²⁶ In addition, the geometric differences between the semi-open (**1**) and the closed (**2**) states also lead to different spectral features in the solid state. In this vein, a four-state fluorescent switch can be realized through the design and synthesis of a single supramolecular construct with orthogonally tuned fluorophores.

Our design of the (P,S) hemilabile ligands was motivated by the hypothesis that a heteroligated WLA complex can be assembled into a semi-open state from a Pt^{II} metal precursor

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Electronic Supplementary Information (ESI) available: synthesis, HR-MS, NMR spectra, computational results, and optical data. See DOI: 10.1039/x0xx00000x

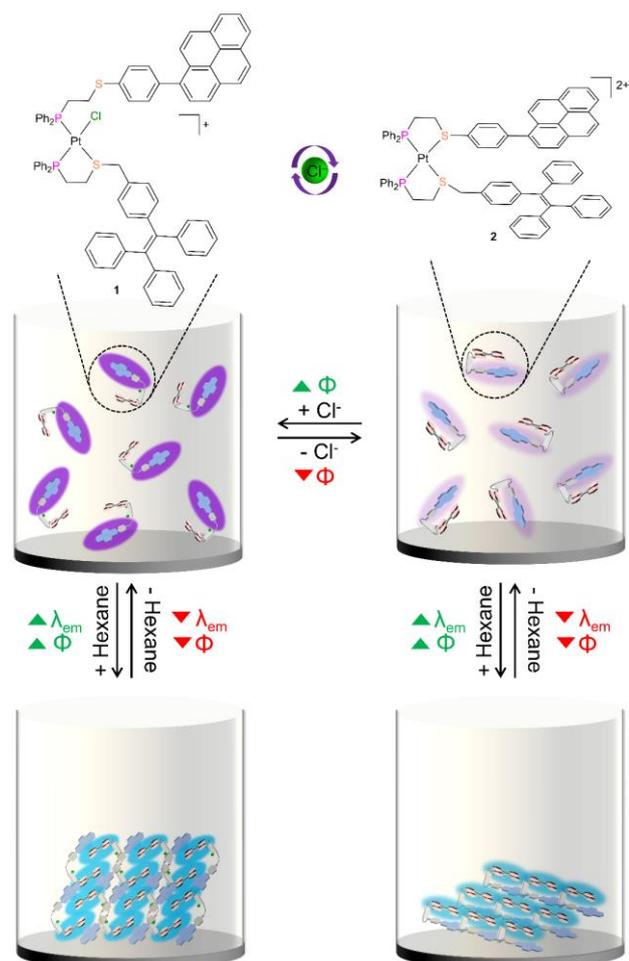


Fig. 1. Modulation of fluorescent properties via coordination-chemistry based system. Four distinct fluorescence states can be achieved with this WLA system via the change of coordination states of the complexes (left column: semi-open vs. right column: closed) and change between solution (top row) and solid states (bottom row). λ_{em} : wavelength of maximum fluorescence emission. Φ : quantum yield of fluorescence emission. Arrows indicate an increase or decrease in λ_{em} and Φ upon changing state. Counterions have been omitted for clarity.

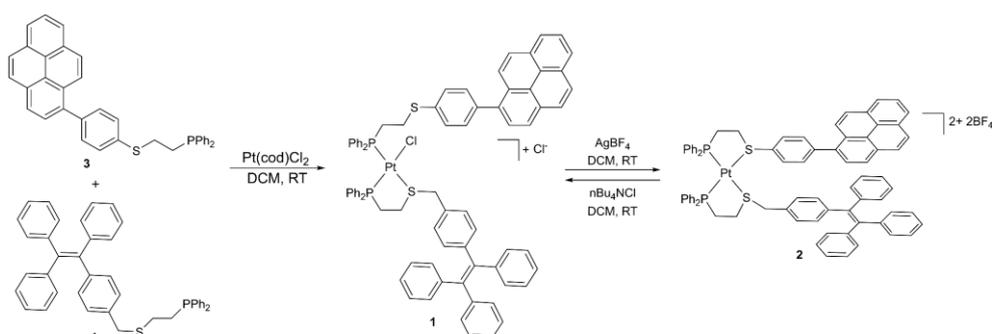
and two (P,S) ligands with different S atom electron donating abilities.²⁷ Based on this hypothesis, we designed, synthesized, and characterized the hemilabile ligand **3** with an electron-withdrawing phenylene spacer between the pyrene and sulphur atom, and ligand **4**, which possesses an electron-donating methylene spacer between the TPE and sulfur atom (see Scheme S1, ESI). These two ligands were characterized by ¹H

and ³¹P NMR spectroscopy as well as high-resolution mass spectrometry (HR-MS) (See ESI).

The heteroligated semi-open complex **1** was prepared via sequential addition of ligands **3** and **4** to a dichloromethane (DCM) solution of dichloro(1,4-cyclooctadiene)platinum(II) [Pt(cod)Cl₂] at room temperature (Scheme 1). The formation of semi-open complex **1** was confirmed by HR-MS and two diagnostic sets of ³¹P{¹H} NMR resonances arising from the P-bound ligand **3** (δ 8.6 ppm, $J_{P-P} = 14$ Hz, $J_{P-Pt} = 3171$ Hz) and chelated ligand **4** (δ 42.6 ppm, $J_{P-P} = 14$ Hz, $J_{P-Pt} = 3500$ Hz).²⁸ The semi-open complex **1** was quantitatively converted into the closed form **2** via the extraction of Cl⁻ with silver tetrafluoroborate (AgBF₄), as evidenced by the diagnostic ³¹P{¹H} NMR resonances of the two non-equivalent chelated phosphine ligands (δ 44.6 ppm, $J_{P-P} = 12$ Hz, $J_{P-Pt} = 3129$ Hz; δ 46.3 ppm, $J_{P-P} = 12$ Hz, $J_{P-Pt} = 3105$ Hz).²⁸ The closed complex **2** can be converted back to the semi-open form **1** by the addition of tetrabutylammonium chloride (TBACl), illustrating the reversibility of the system.

We next investigated the optical properties of complexes **1** and **2** in both the solution and solid states, using the homoligated complexes bearing only pyrene or TPE moieties for comparison purposes (see Table S1, ESI). In DCM, both complexes exhibit maximum absorption at 344 nm. Fluorescence measurements determined that the semi-open complex **1** exhibited a much higher quantum yield (10.5%) than the closed complex **2** (0.9%), while the center of the emission peak remains almost unchanged (407 nm for **1** vs. 404 nm for **2**, see ESI). We hypothesize that the significant reduction in quantum yield in the closed complex is due to the HAE.^{12, 19-20} As reported in previous fluorescent WLA systems, the distance between the heavy Pt^{II} center and pyrene moiety is shorter in the closed state than in the semi-open state, which facilitates spin-orbital coupling and quenches the fluorescence.^{12, 19-20} To verify this hypothesis, we calculated the distances between the Pt^{II} center and pyrene moiety in the energy-optimized structures of **1** and **2** using density functional theory (DFT). We found that the Pt-pyrene distance in **2** was 2.5 Å shorter compared to **1**, supporting the distance-dependent HAE as the main cause for the decrease of the quantum yield in solution (see Fig. S1, ESI).

The fluorescence properties of **1** and **2** in the solid phase were explored. UV irradiation of solids **1** and **2** resulted in stronger fluorescence emission than **1** and **2** in solution with maxima at 475 and 470 nm, respectively. These values are



Scheme 1. Synthesis of the heteroligated Pt^{II}-WLA complexes from the hemilabile (P,S) ligands with pyrene and TPE moieties.

comparable to the reported values for TPE in the literature and the homoligated complex bearing only TPE fluorophores (see Table S1, ESI).^{17, 29-30} Notably, a lower quantum yield was observed for solid-state **2** (10.0%) than solid-state **1** (29.8%). The difference in solid-state fluorescence efficiency is attributed to the different packing and out-of-plane distortion of the TPE moiety in the open and the closed complexes. In particular, the shorter inter-ligand distance between pyrene and TPE ligands in the closed complex results in inefficient packing and a distorted geometry for TPE, which is known to influence its emission efficiency.^{24, 30}

The fluorescence properties of these complexes in both the solution and solid states can be described based upon four distinct emission behaviours (fluorescence maxima and quantum yields). These properties can be observed by studying the *in-situ* fluorescence changes when **2** is converted into **1** in solution, and when **1** and **2** are precipitated from solution. Indeed, when a sub-stoichiometric amount of TBACl is added to

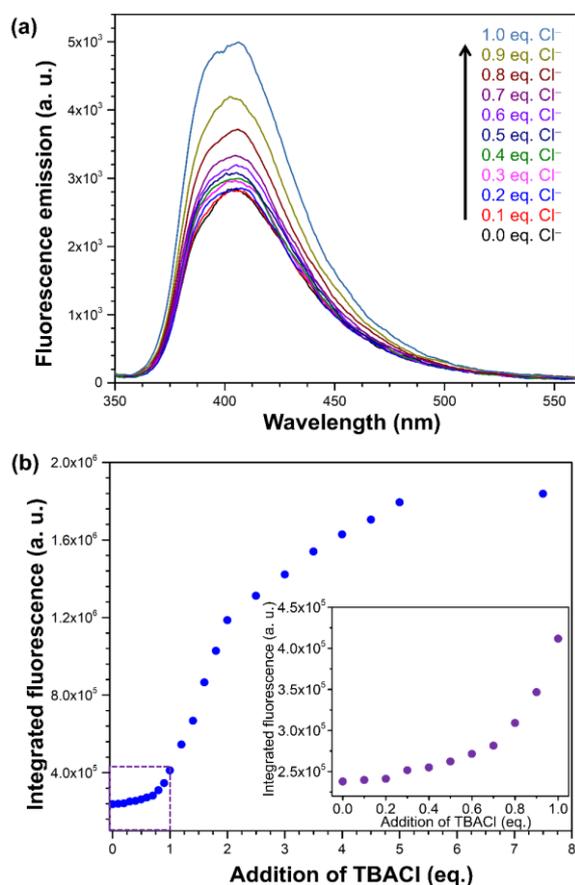


Fig. 2. Addition of TBACl to a DCM solution of **2** (3.8 μM) results in increased fluorescence emission. Excitation wavelength: 344 nm. (a) Stacked fluorescence spectra of the solution upon addition of Cl⁻ up to 1.0 eq. (b) Plot of integrated fluorescence vs. the addition of TBACl (eq.) to 7.5 eq. Inset: plot of integrated fluorescence vs. the addition of TBACl (eq.) to 1.0 eq.

a DCM solution of **2**, the pyrene emission intensity increases as the closed complex **2** is gradually converted into the semi-open complex **1**, consistent with the higher solution quantum yield for **1** compared to **2**. The fluorescence emission profile reached a plateau at around 7.5 eq. of TBACl, a consequence of complete outer-sphere counterion exchange (Fig. 2).

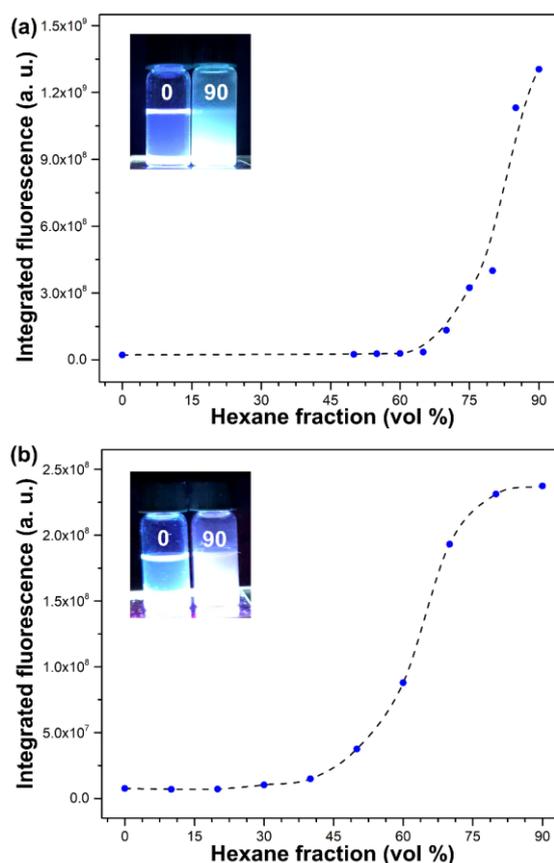


Fig. 3. Plot of Integrated fluorescence of the solutions or suspensions of complexes (a) **1** (0.4 mM) and (b) **2** (0.5 mM) in DCM/hexane mixtures vs. hexane fraction (vol %). Inset: photographs of solutions of complexes (a) **1** and (b) **2** in pure DCM and in a DCM/hexane (90 vol % hexane) mixture taken under UV illumination.

We then examined the fluorescence emission of complexes **1** and **2** during the solvent-induced precipitation process. As shown in Fig. 3, for both complexes, the emission is enhanced when hexane is added to DCM solutions of **1** and **2**, respectively. Since both complexes are insoluble in hexane, they form precipitates at high hexane content, thereby turning on the fluorescence of the TPE moiety and quenching the fluorescence of the pyrene moiety. Furthermore, a dramatic increase in fluorescence intensity for **1** was observed at 80 vol% of hexane, whereas this increase occurred at ~ 65 vol% of hexane for **2** (see Fig. S2, ESI). We attribute the difference to the decreased solubility when the complex was switched from a +1 to +2 state. The structure-property relationship diagram of the molecular switch is shown in Fig. 4. The change of fluorescence properties is correlated with the change of the structure of the complex between two states: 1) the quantum yield in solution is related to the Pt^{II}-pyrene distance; 2) the quantum yield in the solid state is related to the inter-ligand distance; 3) the peak shift during solution-to-solid transition is related to the relative contribution from TPE and pyrene emission.

In summary, we have reported a multi-stimuli-responsive WLA system with four distinct fluorescent outputs. Different chemical stimuli (Cl⁻ or hexane) independently trigger a structure change or phase transition for this WLA assembly, which results in a modulation of the fluorescent profiles of the pyrene and TPE motifs. This present work expands the scope of

fluorescent WLA systems and provides a novel coordination chemistry-based approach for the design of multi-stimuli-responsive photoluminescent systems. These constructs will be useful for the development of novel sensing and imaging techniques.

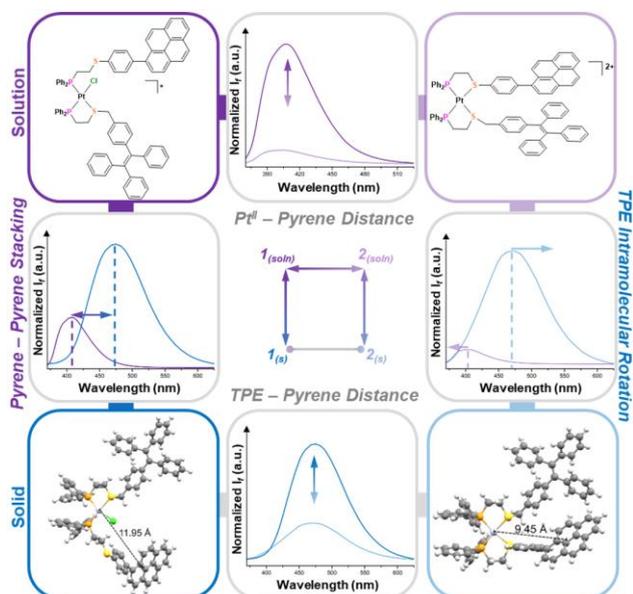


Fig. 4. The four-state photoluminescent molecular switch using WLA coordination complexes. Switching between the solution [$1_{(soln)}$ and $2_{(soln)}$] and solid state [$1_{(s)}$ and $2_{(s)}$] results in peak shifting and a change in quantum yield, while switching between the semi-open [$1_{(soln)}$] and the closed [$2_{(soln)}$] coordination states causes changes in fluorescent quantum yield. Counterions have been omitted for clarity. I_f = fluorescence intensity. Soln = solution. S = solid.

This material is based on work supported by the following awards: National Science Foundation grant CHE-1709888, Sherman Fairchild Foundation, U.S. Army grant W911NF-15-1-0151, Air Force Research Laboratory award FA8650-15-2-5518, and National Cancer Institute of the National Institutes of Health award U54CA199091 (C.A.M.), and Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, DOE under grant no. DE-FG02-99ER14999 (M.R.W.). The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health, the Air Force Research Laboratory, or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon.

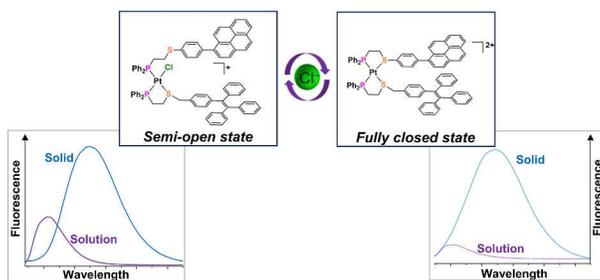
Conflicts of interest

There are no conflicts to declare.

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A four-state fluorescent switch is realized in a single supramolecular construct *via* tuning the emission of two types of fluorophores.