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Temperature-Responsive Fluorescent Organoplatinum(II) Metallacycles

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Abstract

The synthesis, characterization, and temperature-responsive properties of two fluorescent organoplatinum(II) metal-lacycles are reported. Metallacycles **M1** and **M2** were prepared via the coordination-driven self-assembly of a 120° triarylamine ligand **L1** and a 120° diplatinum(II) acceptor **Pt-1** or 180° diplatinum(II) acceptor **Pt-2**, respectively. **M1** and **M2** are hexagonal metallacycles, comprising of three or six freely rotating anthracene pendants on their periphery, respectively. In response to the temperature variation between –20 and 60 °C, the ligand displays irregular emission changes, whereas both metallacycles show reversible absorption and emission spectral changes in THF. The changes in their green emission intensity also exhibit a linear correlation to the temperature variation, with an average sensitivity of –0.67% and –0.77% per °C for **M1** and **M2**, respectively. Furthermore, in coordinating solvents, such as DMF and CH₃CN, **M1** and **M2** show different behaviors: in the lower temperature range, i.e. below 30 °C, their spectral changes are similar to what was observed in THF, however, at a higher temperature the metal-lacycles were destroyed by the solvents and displayed ratiometric fluorescent responses including a cyan emission of the ligand **L1**.

Graphical Abstract

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⊥ Author Contributions

These authors contributed equally to this work.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Additional experimental data and characterization spectra, including Figures S1 – S28.

Notes

The authors declare no competing financial interest.

INTRODUCTION

Temperature-responsive fluorescence phenomenon has a wide array of applications. To date, organic dyes,^{1–4} polymers,^{5–7} biomaterials,^{8–9} nanomaterials,^{10,11} coordination metal complexes^{10–12} and polymers¹³ have been developed for temperature sensing^{14–17} and bioapplications.^{15–20} In general, two types of fluorescent changes are observed in response to temperature. In most cases, the emission intensity of the material increases or decreases as the temperature varies. This response is simple and straightforward and the material functions as a thermometer by monitoring the emission intensity changes. In contrast, a ratiometric fluorescent response is based on the change of the emission intensity ratio at two different wavelengths, which improves the measuring accuracy and precision via a self-calibration.^{18–19} Current efforts have been focused on the design and synthesis of new materials with improved accuracy and reproducibility by diminishing the background interference or invoking a ratiometric response.¹³

Coordination-driven self-assembly is a well-established methodology for fabricating well-defined supramolecular coordination complexes (SCCs) by the spontaneous formation of multiple metal-ligand bonds among carefully selected Lewis-acid metallic acceptors and Lewis-base organic donors.^{20–29}

Due to their diverse shape and size, SCCs have been used in a wide range of applications including host-guest chemistry,^{25,30–39} catalysis,^{40–44} biological and chemical sensing.^{45–52} Recent studies show that the incorporation of photo-active motifs into 2D or 3D SCCs leads to new fluorescent materials with intriguing photophysical properties.^{35,39,53–57} We envisioned that the relatively rigid geometry of SCCs would be beneficial for developing sensitive and reproducible temperature-responsive materials that can diminish the background interference. Although, some temperature-responsive metal complexes have been reported,^{12,15} thermal responsive fluorescent SCCs remain a largely unexplored area.

In this work, we present the synthesis and temperature-responsive emissions of two hexagonal metallacycles **M1** and **M2** assembled from a 120° organic donor **L1** and 120° (**Pt-1**) or 180° (**Pt-2**) diplatinum(II) acceptor, respectively (Figure 1). Ligand **L1** is a triarylamine derivative containing one anthracene and two pyridine moieties. The presence of the anthracene unit makes **L1** highly emissive via an internal charge transfer (ICT) excitation. The attachment of two pyridine units further allows **L1** to function as a 120° organic donor for the coordination assembly with **Pt-1** or **Pt-2**. **M1** and **M2** were designed and synthesized to examine the effect of size and different number of rotating anthracene pendants on the emission properties and responsive behavior of these SCCs.

RESULTS AND DISCUSSION

Synthesis and Characterization.

The organic ligand **L1** was synthesized by a Pd-catalyzed Suzuki-Miyaura cross-coupling reaction between 4-bromo-*N,N*-bis(*p*-(pyrid-4-yl)phenyl)aniline⁵⁸ and 9-anthracenylboronic acid. The hexagonal metallacycles **M1** and **M2** were readily prepared by stirring an equimolar mixture of **L1** and **Pt-1** or **Pt-2** in a mixed solvent of CH₂Cl₂/CH₃OH (2/1, v/v) for 10 h.²³ The formation of discrete metallacyclic assemblies were confirmed by ¹H NMR, ³¹P{¹H} NMR and electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) data. As shown in Figure 2a, the metallacycles **M1** and **M2** show very similar ¹H NMR spectral changes compared to the free ligand **L1**. The H_β protons of the pyridyl groups exhibit a large downfield shift after the formation of the metal-ligand coordination bonds ($\delta = -0.45$ ppm for both **M1** and **M2**), while the H_α protons display minor changes. The assignments of these protons are further supported by ¹H-¹H COSY NMR analysis (see Figures S1–S3). The ³¹P{¹H} NMR spectra of **M1** and **M2** both display a sharp singlet with concomitant ¹⁹⁵Pt satellites ($\delta = 16.60$ ppm for **M1** and 16.84 ppm for **M2**, respectively, Figure 2b), indicative of a single phosphorous environment for forming discrete and highly symmetric metallacyclic assemblies. These peaks are around 6 ppm upfield shifted relative to those of the relevant starting material **Pt-1** and **Pt-2**. This change and the decreased coupling of the flanking ¹⁹⁵Pt satellites in **M1** and **M2**, compared to those of **Pt-1** and **Pt-2**, respectively, reflect the electron back-donation from the platinum centers ($J = -45.2$ Hz for **M1** and -26.2 Hz for **M2**). The stoichiometry of the formation of discrete metallacycles was further confirmed by the ESI-TOF-MS analysis, which showed peaks at *m/z* at 967.31 and 865.68 Da for the [**M1** - 5OTf]⁵⁺ and [**M2** - 11OTf]¹¹⁺ species, respectively (Figure S4). This supports the stoichiometry of **M1** and **M2** as shown in Figure 1.

To gain insight into the structural characteristics of the obtained metallacycles, PM6 semi-empirical calculations were performed with the PEt₃ ligands on platinum being modeled as PH₃ ligands (Figure 3). These results suggest that **M1** and **M2** are roughly planar hexagonal structures with three or six appended anthracene moieties. The simulated cavity size of **M1** and **M2** is about 3.2 and 6.6 nm, respectively.

Photophysical Properties and Computational Results.

The photophysical properties of **L1**, **M1**, and **M2** were investigated in different solvents (Figure 4 and Table 1). Ligand **L1** shows an absorption band at 370 nm in THF. In contrast,

the absorptions of **M1** and **M2** are bathochromically shifted about 50 nm and showed a significantly enhanced molar absorption coefficients due to the inclusion of multiple ligands in one metallacyclic structure.⁵⁹ The absorption band at 335 nm for **M2** is likely derived from the **Pt-2** moieties (Figure S5). The effects of solvent polarity on the absorption spectra of these three compounds are insignificant (Figures S6–S8). However, the emission band of **L1** is distinctly shifted to the lower-energy region in solvents with increasing polarity. For instance, **L1** displays an emission maximum ($\lambda_{\text{em,ma}}$) at 436 nm in toluene and it shifts to around 500 nm in CH₃CN and DMF. The emissions of **M1** and **M2** are also bathochromically shifted in polar solvents (Figure 4c and 4d). However, the degree of shift is much smaller with respect to that of **L1**, indicating that the formation of metal-ligand coordination bonds likely mitigates the effects to a large extent. These results also suggest that the emissions of these compounds are associated with the ICT excited states.^{60–61} The emission quantum yield (Φ) of **L1** is over 25% in all solvents examined (Table 1), while those of **M1** and **M2** are in the range of 2.9%–12.9%. The decreased Φ of the metallacycles is attributed to a heavy atom effect which was also observed in similar SCC systems.⁵⁴ The emission lifetime of **L1**, **M1**, and **M2** are all around a few ns with two exponential components in THF ($\tau_1 = 2.4$ ns, $\tau_2 = 7.5$ ns for **L1**; $\tau_1 = 2.9$ ns, $\tau_2 = 1.0$ ns for **M1**; $\tau_1 = 2.3$ ns, $\tau_2 = 7.5$ ns for **M2**; Figure S9). The presence of two exponential components may be caused by the coexistence of different CT excited states from different conformations.^{4,62}

DFT calculations (B3LYP/LANL2DZ/6–31G*) suggest that the LUMO of **L1** is localized on the anthracene unit, while the HOMO is delocalized over the anthracene-triphenylamine segment (Figure 5). To gain insight into the electronic properties of **M1** and **M2**, DFT calculations were performed on a model compound **Pt-3**, which holds **L1** and two [(PMe₃)₂Pt(C≡CPh)] moieties via coordination bonds (Figure 5). The metallacycles **M1** and **M2** are expected to have similar electronic properties as **Pt-3**. The results suggest that the electronic properties of **L1** changed after coordination to the platinum centers. In **Pt-3**, the LUMO is associated with the phenylpyridine segments, while the HOMO is localized on the anthracene unit. These changes are likely because the coordination bonds that comprise the phenylpyridine and triphenylamine segments are electron-deficient compared to **L1**.⁶³ TDDFT results on the ground state of **L1** and **Pt-3** indicate that the HOMO → LUMO transition is mainly responsible for the lowest excitation (Table S1 and Figures S10 and S11). In addition, TDDFT results of the singlet excited state of **L1** and **Pt-3** suggest that their emissions are associated with the triphenylamine to anthracene charge transfer and the anthracene to diphenylpyridine charge transfer, respectively (Table S2 and Figures S12 and S13).

Temperature-Responsive Properties.

A number of organic dyes with ICT character have successfully been reported as fluorescent thermometers.^{4,16,64} However, the use of fluorescent SCCs in temperature sensing has not been exploited to date. The unique metallacyclic structures of **M1** and **M2** prompted us to examine their thermo-responsiveness, because temperature may have a strong effect on the degree of concerted rotation of these appended anthracene groups and thus on the emission properties of the complexes. As shown in Figure 6, upon increasing temperature from –20 to 60 °C, the absorptions at 400 nm of **M1** and **M2** in THF significantly decreased, while those

between 300 and 350 nm remain essentially unchanged. Accordingly, the emission intensity of **M1** and **M2** at 520 nm significantly decreased. In particular, the emission intensity of **M2** dropped by 60% over this temperature range. The heating-cooling cycling experiments indicated that these spectral change processes good reversibility (Figure 6c and S14). The temperature-dependent emission response of **M1** and **M2** can be fitted with a linear decay (Figure 6f), with a average sensitivity S_A of -0.66% and -0.76% per $^{\circ}\text{C}$ for **M1** and **M2** respectively² (where $S_A = I/(I_{\text{ref}} \times T)$). Upon increasing temperature, the rotations of the appended anthracene groups are expected to speed up, which will disrupt the anthracene-associated charge transfer absorptions and emissions and thereby decrease the absorbance and emissions of **M1** and **M2**. This is further supported by the fact that **M2** with six anthracene groups is slightly more temperature sensitive relative to **M1**, having only three anthracene groups.

In contrast, the emission spectrum and intensity of the ligand **L1** shows rather irregular changes in response to temperature variations from -20 to 60 $^{\circ}\text{C}$ in THF (Figure S15). Unlike the metallacycles **M1** and **M2**, all structural units of **L1** can rotate freely. This may account for the irregular emission changes of **L1** in response to temperature, thus suggesting the advantages of metallacycles in thermo-responsiveness.

When the temperature response of **M1** was investigated in DMF, a two-step spectral change was observed. In the temperature range between -20 and 30 $^{\circ}\text{C}$, **M1** behaves in a similar manner to what was described for THF (Figures 7 and S16). When temperature was further increased up to 70 $^{\circ}\text{C}$, the absorption between 400 and 450 nm significantly decreased and new absorption bands between 300 and 370 nm appeared. At the same time, the emission maximum gradually shifted from 530 to 490 nm. This change can be seen by the emission color change from green to cyan. The emission change cannot be reversed by decreasing the temperature of the DMF solution. However, upon removal of the solvent, the emission of **M1** can be essentially recovered (Figure S17). As is shown in Figure 7c, the ratio between the emission intensity at 460 and 530 nm (I_{460}/I_{530}) remains almost constant below 30°C . However, when the temperature was further elevated (particularly above 40 $^{\circ}\text{C}$), the I_{460}/I_{530} ratio increased sharply, and indicated that the temperature has surpassed a specific limit (in this case 40 $^{\circ}\text{C}$), suggesting the potential application of the two-step emission response as ratiometric sensing of temperature. Similar temperature-responsive two-step emission spectral changes were observed for **M2** in DMF and **M1** in CH_3CN , indicating the generality of this method (Figures S18 and S19). The ^1H NMR spectrum of **M1** at 60 $^{\circ}\text{C}$ in CD_3CN exhibits distinct changes relative to it at 25 $^{\circ}\text{C}$, where the H_{β} signal of **M1** decreases and shows the ^1H NMR characteristics of **L1** (Figures S20), suggesting a small amount of decomposing of **M1**. These results indicate that the metallacycle may decompose at elevated temperature by the coordinating solvents. A similar self-destructive mechanism has previously been reported for amino acid sensing using fluorescent platinum(II) cages.⁴⁵

CONCLUSION

Two hexagonal platinum(II) metallacycles **M1** and **M2** with three and six appended anthracene groups respectively, were designed and synthesized by the supramolecular coordination of a 120° organic donor **L1** with a 120° or 180° diplatinum(II) acceptor,

respectively. Complexes **M1** and **M2** are emissive in common organic solvents. In THF, **M1** and **M2** exhibited reversible absorption and emission spectral changes in response to temperature variation between -20 and 60 °C. The larger metallacycle **M2** displayed a slightly higher sensitivity than **M1**, while the precursor ligand **L1** only showed irregular fluorescent changes in the same temperature range. On the other hand, two-step spectral changes were observed for **M1** and **M2** in solvents such as DMF and CH_3CN . In the lower temperature range, emission spectral changes followed the trend as observed in THF. At elevated temperature, these complexes displayed ratiometric emission spectral changes via a self-destruction mechanism. This work demonstrates that fluorescent metallacycles possess interesting and promising temperature-responsive properties and it opens up a new arena for the development of stimuli-responsive materials.

EXPERIMENTAL SECTION

Materials and Methods.

All reagents were commercially available and used as supplied without further purification. 4-bromo-*N,N*-bis(*p*-(pyrid-4-yl)phenyl)aniline⁵⁸ and diplatinum acceptor **Pt-1** and **Pt-2** were prepared according to the reported procedures.²⁹ ^1H NMR and ^{13}C NMR spectra were recorded in the designated solvents on a Varian Inova 500 or 400 MHz spectrometer. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Unity 300 MHz spectrometer, using an external unlocked sample of 85% H_3PO_4 ($\delta = 0$) as reference. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. Absorption and fluorescence spectra were recorded on a Hitachi U-4100 and Hitachi F-7000 Spectrophotometer, equipped with 1 cm quartz cuvette from Starna Cells, Inc. The temperature-dependent fluorescent experiments were conducted on a Hitachi F-3000 fluorescence spectrophotometer. The luminescence lifetime was obtained on Quantaurus-Tau Fluorescence lifetime spectrometer C11367 from Hamamatsu Photonics.

Synthesis of 4-bromo-*N,N*-bis(*p*-(pyrid-4-yl)phenyl)aniline.

A suspension of tri(*p*-bromophenyl)amine (2.41 g, 5.0 mmol), pyrid-4-yl boronic acid (0.93 g, 7.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (115.6 mg, 0.10 mmol) and K_2CO_3 (1.66 g, 12.0 mmol) in a mixture of 50 mL of 1,4-dioxane and 25 mL of H_2O was refluxed at 100 °C for 24 h under N_2 atmosphere. After cooling to room temperature, the reaction mixture was extracted with copious CH_2Cl_2 (3×50 mL). The combined organic layers were concentrated and subjected to flash column chromatography on silica gel (eluent: ethyl acetate/methanol, 100/4, v/v) to afford 900 mg of 4-bromo-*N,N*-bis(*p*-(pyrid-4-yl)phenyl)aniline as a pale yellow solid in 38% yield. ^1H NMR (400 MHz, CDCl_3): δ 8.64 (d, $J = 5.5$ Hz, 4H), 7.56 (d, $J = 8.7$ Hz, 4H), 7.47 (d, $J = 8.0$ Hz, 4H), 7.42 (d, $J = 8.9$ Hz, 2H), 7.19 (d, $J = 8.6$ Hz, 4H), 7.05 (d, $J = 8.8$ Hz, 2H). ESI-TOF-HRMS calcd for $[\text{M} + \text{H}]^+$ $\text{C}_{28}\text{H}_{20}\text{BrN}_3$ (m/z): 478.0919. Found: 478.0919.

Synthesis of ligand **L1**.

A suspension of 4-bromo-*N,N*-bis(*p*-(pyrid-4-yl)phenyl)aniline (239.2 mg, 0.50 mmol), 9-anthracenylboronic acid (222.1 mg, 1.0 mmol), $\text{Pd}(\text{PPh}_3)_4$ (57.8 mg, 0.05 mmol) and K_2CO_3

(207.4 mg, 1.5 mmol) in a mixture of 20 mL 1,4-dioxane and 10 mL of H₂O was refluxed at 100 °C for 24 h under N₂ atmosphere. After cooling to room temperature, the reaction mixture was extracted with copious CH₂Cl₂ (3 × 50 mL). The combined organic layers were concentrated and subjected to flash column chromatography on silica gel (eluent: ethyl acetate/methanol, 100/4, v/v) to afford 120 mg of **L1** as a yellow solid in 42% yield. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.62 (*J* = 6.6 Hz, 4H), 8.53 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 9.8, 2H), 7.68 (d, *J* = 8.6 Hz, 4H), 7.54 (d, *J* = 6.2 Hz, 4H), 7.48 (t, *J* = 8.2 Hz, 2H), 7.45 – 7.39 (m, 10H). ¹³C NMR (125 MHz, CD₂Cl₂): δ 150.55, 148.57, 147.52, 146.48, 136.75, 134.44, 132.70, 132.59, 131.71, 130.56, 128.64, 128.20, 126.92, 126.82, 125.69, 125.44, 125.15, 124.54, 121.14. ESI-TOF-HRMS calcd for [M + H]⁺ C₄₂H₂₉N₃ (*m/z*): 576.2440. Found: 576.2437.

Synthesis of M1.

To a mixture of 4 mL of CH₂Cl₂ and 2 mL of CH₃OH were added ligand **L1** (5.76 mg, 10.0 μmol) and **Pt-1** (12.8 mg, 10.0 μmol). After stirring at room temperature for 10 h, the system was concentrated by flushing with N₂ gas, followed by the addition of 7 mL of diethyl ether. The resulting precipitate was collected by centrifugation to give 14 mg of **M1** in 90% yield. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.62 (*J* = 5.6 Hz, 12H), 8.55 (s, 3H), 8.09 (d, *J* = 8.5 Hz, 6H), 7.97 (d, *J* = 5.8, 12H), 7.89 (d, *J* = 8.9 Hz, 12H), 7.80 (d, *J* = 8.8 Hz, 6H), 7.18 – 7.53 (m, overlapped, 48H), 1.83–1.86 (m, overlapped, 72H), 1.17–1.24 (m, overlapped, 108H). ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂): δ 16.60 (s, ¹⁹⁵Pt satellites, ¹*J*_{Pt-P} = 2333.6 Hz). ESI-TOF-MS calcd for [M – 5OTf]⁵⁺ (*m/z*): 967.33. Found: 967.31.

Synthesis of M2.

According to the same procedure for the synthesis of **M1**, **M2** was prepared from ligand **L1** (5.76 mg, 10 μmol) and **Pt-2** (12.85 mg, 10 μmol) in 91% yield as a yellow solid (16 mg of **M2** was isolated). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.60 (*J* = 5.6 Hz, 24H), 8.57 (s, 6H), 8.11 (d, *J* = 8.5 Hz, 12H), 7.98 (d, *J* = 6.1 Hz, 24H), 7.91 (d, *J* = 8.5 Hz, 24H), 7.81 (d, *J* = 9.7 Hz, 12H), 7.45 – 7.55 (m, overlapped, 72H), 7.26 (s, 24H), 1.85–1.88 (m, overlapped, 144H), 1.15–1.25 (m, overlapped, 216H). ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂, 298 K): δ 16.84 (s, ¹⁹⁵Pt satellites, ¹*J*_{Pt-P} = 2323.8 Hz). ESI-TOF-MS calcd for [M – 11OTf]¹¹⁺ (*m/z*): 865.66. Found: 865.68.

Calculation Methods.

DFT calculations were carried out using the B3LYP exchange correlation function and implemented in the *Gaussian* 09 package. The electronic structures were optimized using a general basis set with the Los Alamos effective core potential LANL2DZ basis set for Pt and 6–31G* for other atoms.⁶⁵ No symmetry constraints were used in the optimization (nosymm keyword was used). All orbitals have been computed at an isovalue of 0.02 e/bohr³. TDDFT calculations were performed on the DFT-optimized structures on the same level of theory.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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REFERENCES

- (1). Homma M; Takei Y; Murata A; Inoue T; Takeoka S *Chem. Commun* 2015, 51, 6194–6197.
- (2). Pais VF; Lassaletta JM; Fernández R; El - Sheshtawy HS; Ros A; Pischel U *Chem. Eur. J* 2014, 20, 7638–7645. [PubMed: 24861774]
- (3). Liu X; Li S; Feng J; Li Y; Yang G *Chem. Commun* 2014, 50, 2778–2780.
- (4). Li K; Liu Y; Li Y; Feng Q; Hou H; Tang BZ *Chem. Sci* 2017, 8, 7258–7267. [PubMed: 29081958]
- (5). Okabe K; Inada N; Gota C; Harada Y; Funatsu T; Uchiyama S *Nat. Commun* 2012, 3, 705. [PubMed: 22426226]
- (6). Chen Z; Zhang KY; Tong X; Liu Y; Hu C; Liu S; Yu Q; Zhao Q; Huang W *Adv. Funct. Mater* 2016, 26, 4386–4396.
- (7). Gota C; Okabe K; Funatsu T; Harada Y; Uchiyama SJ *Am. Chem. Soc* 2009, 131, 2766–2767.
- (8). Ebrahimi S; Akhlaghi Y; Kompany-Zareh M; Rinnan Å *ACS Nano*. 2014, 8, 10372–10382. [PubMed: 25265370]
- (9). Wong FH; Banks DS; Abu-Arish A; Fradin CJ *Am. Chem. Soc* 2007, 129, 10302–10303.
- (10). Yam VW-W; Au VK-M; Leung SY-L *Chem. Rev* 2015, 115, 7589–7728. [PubMed: 26158432]
- (11). Chakraborty S; Hong W; Endres KJ; Xie T-Z; Wojtas L; Moorefield CN; Wesdemiotis C; Newkome GR J. *Am. Chem. Soc* 2017, 139, 3012–3020. [PubMed: 28165736]
- (12). Chan AK-W; Ng M; Wong Y-C; Chan M-Y; Wong W-T; Yam VW-W J. *Am. Chem. Soc* 2017, 139, 10750–10761. [PubMed: 28759219]
- (13). Rao X; Song T; Gao J; Cui Y; Yang Y; Wu C; Chen B; Qian GJ *Am. Chem. Soc* 2013, 135, 15559–15564.
- (14). Liebsch G; Klimant I; Wofbeis OS *Adv. Mater* 1999, 11, 1296–1299.
- (15). Wang X.-d; Wofbeis OS; Meier RJ *Chem. Soc. Rev* 2013, 42, 7834–7869. [PubMed: 23793774]
- (16). Feng J; Tian K; Hu D; Wang S; Li S; Zeng Y; Li Y; Yang G *Angew. Chem. Int. Ed* 2011, 50, 8072–8076.
- (17). Plakhotnik T; Doherty MW; Cole JH; Chapman R; Manson NB *Nano Lett.* 2014, 14, 4989–4996. [PubMed: 25102035]
- (18). Takei Y; Arai S; Murata A; Takabayashi M; Oyama K; Ishiwata S. i.; Takeoka S; Suzuki M *ACS Nano*. 2013, 8, 198–206. [PubMed: 24354266]
- (19). Brites CDS; Lima PP; Silva NJO; Millan A; Amaral VS; Palacio F; Carlos LD *Nanoscale* 2012, 4, 4799–4829. [PubMed: 22763389]
- (20). Avestro AJ; Belowich ME; Stoddart JF *Chem. Soc. Rev* 2012, 41, 5881–5895. [PubMed: 22773163]
- (21). Fujita M; Tominaga M; Hori A; Therrien B *Acc. Chem. Res* 2005, 38, 369–378. [PubMed: 15835883]
- (22). Sun Q-F; Sato S; Fujita M *Nat. Chem* 2012, 4, 330. [PubMed: 22437720]
- (23). Lescop C *Acc. Chem. Res* 2017, 50, 885–894. [PubMed: 28263559]
- (24). Huang SL; Hor TSA; Jin GX *Coord. Chem. Rev* 2017, 333, 1–26.
- (25). Xu L; Wang YX; Chen LJ; Yang HB *Chem. Soc. Rev* 2015, 44, 2148–2167. [PubMed: 25723131]
- (26). Li H; Yao ZJ; Liu D; Jin GX *Coord. Chem. Rev* 2015, 293, 139–157.
- (27). Chen L; Chen QH; Wu MY; Jiang FL; Hong MC *Acc. Chem. Res* 2015, 48, 201–210. [PubMed: 25517043]

- (28). Saha ML; Yan X; Stang PJ *Acc. Chem. Res* 2016, 49, 2527–2539. [PubMed: 27736060]
- (29). Cook TR; Stang PJ *Chem. Rev* 2015, 115, 7001–7045. [PubMed: 25813093]
- (30). Winter A; Hoeppener S; Newkome GR; Schubert US *Adv. Mater* 2011, 23, 3484–3498. [PubMed: 21751263]
- (31). Wang QQ; Gonell S; Leenders S; Durr M; Ivanovic-Burmazovic I; Reek JNH *Nat. Chem* 2016, 8, 225–230. [PubMed: 26892553]
- (32). Therrien B; Suss-Fink G; Govindaswamy P; Renfrew AK; Dyson PJ *Angew. Chem. Int. Ed* 2008, 47, 3773–3776.
- (33). Zhou Z; Yan X; Saha ML; Zhang M; Wang M; Li X; Stang PJ *J. Am. Chem. Soc* 2016, 138, 13131–13134.
- (34). Zhukhovitskiy AV; Zhong MZ; Keeler EG; Michaelis VK; Sun JEP; Hore MJA; Pochan DJ; Griffin RG; Willard AP; Johnson JA *Nat. Chem* 2016, 8, 33–41. [PubMed: 26673262]
- (35). Howlader P; Das P; Zangrando E; Mukherjee PS *J. Am. Chem. Soc* 2016, 138, 1668–1676. [PubMed: 26771202]
- (36). Browne C; Ramsay WJ; Ronson TK; Medley-Hallam J; Nitschke JR *Angew. Chem. Int. Ed* 2015, 54, 11122–11127.
- (37). Zhang MM; Yin SC; Zhang J; Zhou ZX; Saha ML; Lu CJ; Stang PJ *Proc. Natl. Acad. Sci. USA* 2017, 114, 3044–3049. [PubMed: 28265080]
- (38). Chakraborty S; Newkome GR *Chem. Soc. Rev* 2018,
- (39). Zhou Z; Yan X; Cook TR; Saha ML; Stang PJ *J. Am. Chem. Soc* 2016, 138, 806–809. [PubMed: 26761393]
- (40). Toste FD; Sigman MS; Miller SJ *Acc. Chem. Res* 2017, 50, 609–615. [PubMed: 28945415]
- (41). Qiao YP; Zhang L; Li J; Lin W; Wang ZQ *Angew. Chem. Int. Ed* 2016, 55, 12778–12782.
- (42). Mondal P; Sarkar S; Rath SP *Chem. Eur. J* 2017, 23, 7093–7103. [PubMed: 28317181]
- (43). Kaphan DM; Levin MD; Bergman RG; Raymond KN; Toste FD *Science* 2015, 350, 1235–1238. [PubMed: 26785485]
- (44). Neelakandan PP; Jimenez A; Thoburn JD; Nitschke JR *Angew. Chem. Int. Ed* 2015, 54, 14378–14382.
- (45). Yeung MC-L; Yam VW-W *Chem. Soc. Rev* 2015, 44, 4192–4202. [PubMed: 25588608]
- (46). Eryazici I; Moorefield CN; Newkome GR *Chem. Rev* 2008, 108, 1834–1895. [PubMed: 18543874]
- (47). Zhang MM; Saha ML; Wang M; Zhou ZX; Song B; Lu CJ; Yan XZ; Li XP; Huang FH; Yin SC; Stang PJ *J. Am. Chem. Soc* 2017, 139, 5067–5074.
- (48). Li XZ; Wu JG; Chen LY; Zhong XM; He C; Zhang R; Duan CY *Chem. Commun* 2016, 52, 9628–9631.
- (49). Liu CL; Zhang RL; Lin CS; Zhou LP; Cai LX; Kong JT; Yang SQ; Han KL; Sun QF *J. Am. Chem. Soc* 2017, 139, 12474–12479. [PubMed: 28837322]
- (50). Vardhan H; Yusubov M; Verpoort F *Coord. Chem. Rev* 2016, 306, 171–194.
- (51). Ahmad N; Younus HA; Chughtai AH; Verpoort F *Chem. Soc. Rev* 2015, 44, 9–25. [PubMed: 25319756]
- (52). Wang J; He C; Wu PY; Wang J; Duan CY *J. Am. Chem. Soc* 2011, 133, 12402–12405. [PubMed: 21749065]
- (53). Ni XL; Chen SY; Yang YP; Tao ZJ *Am. Chem. Soc* 2016, 138, 6177–6183.
- (54). Zhang QW; Li DF; Li X; White PB; Mecinovic J; Ma X; Agren H; Nolte RJM; Tian HJ *Am. Chem. Soc* 2016, 138, 13541–13550.
- (55). Zhu MR; Yang CL *Chem. Soc. Rev* 2013, 42, 4963–4976. [PubMed: 23436004]
- (56). Yan XZ; Cook TR; Wang P; Huang FH; Stang PJ *Nat. Chem* 2015, 7, 342–348. [PubMed: 25803473]
- (57). Tian Y; Yan X; Saha ML; Niu Z; Stang PJ *J. Am. Chem. Soc* 2016, 138, 12033–12036. [PubMed: 27608138]
- (58). Zhang MD; Shi ZQ; Chen MD; Zheng HG *Dalton Trans.* 2015, 44, 5818–5825. [PubMed: 25715030]

- (59). Yan X; Wang M; Cook TR; Zhang M; Saha ML; Zhou Z; Li X; Huang F; Stang PJ J. Am. Chem. Soc 2016, 138, 4580–4588. [PubMed: 26982213]
- (60). Liu X; Li SY; Feng J; Li Y; Yang GQ Chem. Commun 2014, 50, 2778–2780.
- (61). Rao M,R; Liao C-W; Su W-L; Sun S-SJ Mater. Chem. C 2013, 1, 5491–5501.
- (62). Fang Q; Li J; Li S; Duan R; Wang S; Yi Y; Guo X; Qian Y; Huang W; Yang G Chem. Commun 2017, 53, 5702–5705.
- (63). Chen J-S; Zhao G-J; Cook TR; Han K-L; Stang PJ J. Am. Chem. Soc 2013, 135, 6694–6702. [PubMed: 23560763]
- (64). Wang X Chem. Soc. Rev 2013, 42, 7834. [PubMed: 23793774]
- (65). Hay PJ; Wadt WR J. Chem. Phys 1985, 82, 299–310.

Figure 1.
Synthetic routes to metallacycles **M1** and **M2**.

Figure 2.

(a) ^1H NMR (500 MHz, CD_2Cl_2 , 298 K) and (b) $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2 , 298 K) spectra of compounds studied in this work.

Figure 3. PM6-simulated geometrical structures of (a) PH₃-M1 and (b) PH₃-M2.

Figure 4.

(a) Absorption spectra of **L1**, **M1** and **M2** in THF. (b,c,d) Normalized emission spectra of (b) **L1**, (c) **M1**, and (d) **M2** in different solvents. ($\lambda_{\text{ex}} = 370 \text{ nm}$, $c = 2.0 \times 10^{-5} \text{ M}$ for **L1**; $\lambda_{\text{ex}} = 400 \text{ nm}$, $c = 2.0 \times 10^{-6} \text{ M}$ for **M1** and **M2**).

Figure 5.
Isodensity plots of the LUMO and HOMO of **L1** and the model diplatinum complex **Pt-3**.

Figure 6.

Temperature-responsive absorption and emission properties of **M1** and **M2** in THF recorded between -20 and 60 °C ($\lambda_{\text{ex}} = 400 \text{ nm}$; $c = 2.0 \mu\text{M}$; 10 °C temperature intervals). (a,d) Absorption spectral response of (a) **M1** and (d) **M2**. (b,e) Emission spectral response of (b) **M1** and (e) **M2**. The inset shows the image of the solution under UV illumination (365 nm) at -20 and 60 °C, respectively. (c) The cyclic switching of fluorescence intensity upon heating and cooling for **M1**. The cycling switching of **M2** is shown in Figure S12. (f) The temperature dependence of the normalized emission intensity at 520 nm. $R^2 = 0.98$ for the linear fitting of both series of data.

Figure 7.

Temperature-responsive absorption and emission properties of **M1** in DMF recorded between -20 and 70 °C ($\lambda_{\text{ex}} = 400$ nm; $c = 2.0$ μM ; 10 °C temperature intervals). (a) absorption spectral changes. (b) Emission spectral changes. The inset shows the image of the solution under UV illumination (365 nm) at -20 and 70 °C, respectively. (c) Temperature dependence of the emission intensity at 530 nm (I_{530}) and 460 nm (I_{460}) and the ratio between I_{460} and I_{530} .

Table 1.Photophysical data in different solvents.^a

Comp.	Toluene		THF		Ethyl acetate		CH ₃ CN		DMF	
	λ_{em}/nm	$\Phi\%$	λ_{em}/nm	$\Phi\%$	λ_{em}/nm	$\Phi\%$	λ_{em}/nm	$\Phi\%$	λ_{em}/nm	$\Phi\%$
L1	436	39.0	458	34.5	454	36.5	501	26.4	498	33.1
M1	503	12.9	526	10.1	512	9.1	529	7.5	531	7.4
M2	505	2.9	520	8.4	511	4.9	527	6.9	529	6.8

^aEmission quantum yield was estimated by referencing to that of quinine sulfate in 0.1 M H₂SO₄ ($\Phi = 56\%$).