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Thermochromic Absorption and Photoluminescence in [Pt(ppy)(μ -Ph₂pz)]₂

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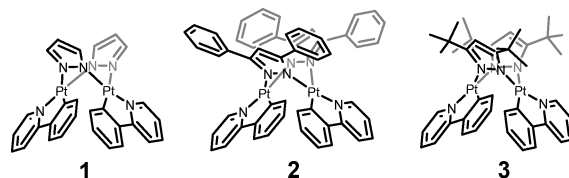
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The temperature effects on the spectral properties and photophysics of a new d⁸–d⁸ dinuclear Pt^{II} chromophore, [Pt(ppy)(μ -Ph₂pz)]₂ (ppy is 2-phenylpyridine and Ph₂pz is 3,5-diphenylpyrazolate), have been investigated. The thermochromic shifts are tentatively ascribed to intramolecular σ interactions between the two pseudocofacial d_{z²} orbitals. Substantial emission profile changes occur in the solid state, solution, and doped polymer films.

Dinuclear transition-metal complexes have captured the imagination of researchers in a variety of applications including photocatalysis, solution and solid-state luminescence, and photoinduced energy and electron transfer.^{1–3} In addition to these desirable characteristics, Pt^{II} chromophores possess the ability to tune their photophysical characteristics with a judicious choice of ancillary and charge-transfer (CT) ligands.⁴ Recently, it was demonstrated that systematic manipulations in the structure of bridging ligands

controlled intramolecular Pt–Pt distances in select dinuclear structures, ultimately tuning the photophysics in a predictive manner.^{5–7} We note that temperature-dependent luminescence and photophysics have recently been observed for pyrazolato-bridged trinuclear complexes of the coinage metals.⁸

In this contribution, we investigate the temperature effects on the spectral properties and photophysics in [Pt(ppy)(μ -Ph₂pz)]₂ (**2**; ppy is 2-phenylpyridine and Ph₂pz is 3,5-diphenylpyrazolate). The thermochromic responses are tentatively ascribed to intramolecular σ interactions occurring between the two pseudocofacial d_{z²} orbitals. We also demonstrate significant emission profile changes in the solid state, solution, and chromophore-doped polymer films of **2**. Presented below are the structures of three dinuclear Pt^{II} complexes (**1–3**) investigated for their thermochromic response (see the Supporting Information for full synthetic details). These molecules feature two square-planar Pt^{II} centers with 2-phenylpyridine as the CT ligand bridged by symmetrically substituted 3,5-R₂-pyrazolates, where R = H (**1**), Ph (**2**), or *t*-Bu (**3**). These substitutions were selected to coarsely control the Pt–Pt distance.^{5–7} Compound **1** is expected to have the largest Pt–Pt separation and exhibit mononuclear-like photophysics. In contrast, **3** should provide the shortest Pt–Pt distance and, thus, dinuclear-based photophysics. Accordingly, model chromophores **1** and **3** exhibit well-defined absorption/emission properties, enabling comparative temperature-dependent studies in concert with the title compound.



The molecules were isolated in good yield as microcrystalline solids or powders ranging in color from bright yellow (**1**)

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to orange (**2**) to red (**3**) at room temperature (RT). However, the solids with the most steric bulk (**2** and **3**) exhibit drastic instantaneous reversible color changes when cooled to 77 K. Provided in Figure 1 are representative digital color photographs of powdered samples of **2** and **3**. At RT, the solids appear orange or red; upon exposure to liquid nitrogen, the absorption immediately blue-shifts, producing yellow coloration. This is in direct opposition to earlier examples of solid-state thermochromism arising from intermolecular Pt^{II}–Pt^{II} interactions in the “red form” of both Pt(bpy)Cl₂ and Pt(bpy)(CN)₂, where cooling to 10 K produced a systematic contraction along the intermolecular *z* axis, red-shifting the absorbance and emission spectra.^{9,10} To delineate between an intra- versus intermolecular mechanism, the absorption spectra of dilute toluene solutions of **2** and **3** ($\sim 7 \times 10^{-5}$ M) were collected between 273 and 373 K (Figure S1 in the Supporting Information), where a red shift is clearly observed when the samples are heated. This provides evidence that the thermochromism we observe in the solids and solutions most likely arises from intramolecular interactions in both **2** and **3**. We believe that the net σ overlap of the two d_{z²} orbitals decreases as the temperature is lowered. However, more quantitative studies on the molecular structure (X-ray) of the solids remain a point of interest for future investigations.

The absorption and emission spectra of all three chromophores in 2-methyltetrahydrofuran (MTHF) are provided in Figure 2. In agreement with previous results, the lowest-energy CT absorption maximum systematically shifts to lower energy from 366 nm (**1**) to 406 nm (**2**) to 497 nm (**3**) as the steric bulk on the bridging pyrazolate increases. This is attributed to increasing intramolecular Pt–Pt interactions (decreasing Pt–Pt distances), culminating with the most red-absorbing (**3**). Consequently, the Franck–Condon state is assigned as mononuclear CT for **1**, while **2** and **3** are assigned as dinuclear metal–metal-to-ligand CT (MMLCT). The RT emission also systematically changes in shape and position across the series. The “mononuclear” model, **1**, produces high-energy structured photoluminescence with a maximum at 488 nm ($\Phi_{\text{em}} = 0.07$; $\tau = 750$ ns), consistent with a ³LC/MLCT excited state.⁵ While two geometrical isomers of **1** are observable by ¹H NMR (see the Supporting Information), both *cis* and *trans* isomers exhibit identical photophysical behavior, consistent with a mononuclear-like excited state. Here, *cis* and *trans* define the relative positions of the nitrogen atoms in the two ppy ligands. The emission from **2** is broad and unstructured centered at ~ 625 nm ($\Phi_{\text{em}} = 0.15$; $\tau = 2.0$ μ s), most consistent with MMLCT (³ $\pi^* \rightarrow \sigma^*$) parentage. The MMLCT emission from **3** is also broad and featureless and is the most red-shifted, $\lambda_{\text{max}} = 650$ nm ($\Phi_{\text{em}} = 0.03$; $\tau = 950$ ns). The RT photoluminescence assignments in **1** and **3** appear to be preserved at 77 K. However, **2** generates a more complex emission profile at 77 K (Figure 2). Hence, we further investigated the emission temperature dependence of **2** in MTHF.

These data are presented in Figure 3. When the solution is heated through the glass transition temperature ($T_g \sim 91$ K)¹¹ (panel A), the emission profile simply red-shifts and loses the

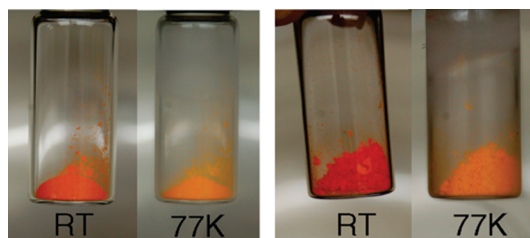


Figure 1. Digital images illustrating the reversible thermochromic color changes of **2** (left) and **3** (right) as solid powders.

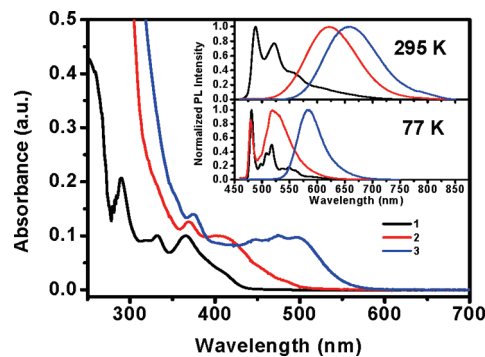


Figure 2. Steady-state absorption and emission (inset) spectra of dilute MTHF solutions containing dinuclear Pt^{II} complexes. Emission spectra were acquired on argon-degassed solutions at concentrations of $\sim 10^{-5}$ M.

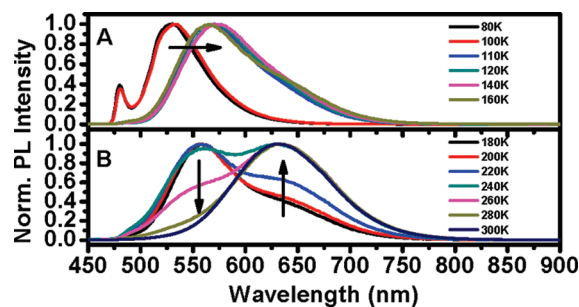


Figure 3. Photoluminescence temperature dependence of **2** in MTHF (10^{-5} M; $\lambda_{\text{ex}} = 410$ nm). Panel A depicts changes in the emission profile around the glass transition of the solvent ($T_g = 91$ K). Panel B depicts emission profile changes at temperatures above the glass transition temperature.

high-energy vibrational structure. However, upon heating from 180 to 300 K (panel B), the emission maximum at ~ 550 nm concomitantly decreases with the appearance of a new emission maximum at ~ 625 nm. Finally, only one photoluminescence band near 625 nm is observed at 300 K, in agreement with the RT data in Figure 2. From the temperature-dependent data, the molecule apparently displays mononuclear (³LC at 480 nm and ³MLCT at 525 nm) emission in the temperature range of 77–140 K.^{12,13} The ³MLCT emission at 80 K (525 nm) shifts to ~ 550 nm above 100 K. Above 160 K, the ground state appears to traverse an activated barrier crossing, revealing dinuclear (MMLCT) emission. In essence, the ground-state geometry undergoes a reorganization that somehow enforces more significant Pt–Pt σ overlap with potentially shorter Pt–Pt distances at higher

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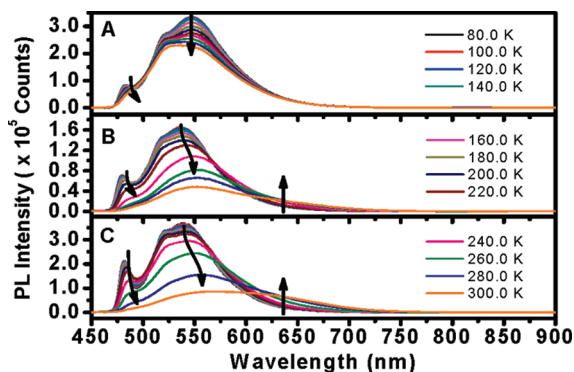


Figure 4. Photoluminescence temperature dependence of **2** in PMMA (A), Tecoflex EG-80A (B), and Carbothane (C). The spectra displayed are at 80–300 K in 20 K increments; $\lambda_{\text{ex}} = 410$ nm.

temperature. Variable-temperature excitation scans reveal temperature-dependent spectral changes that must be attributed to modification in the ground-state structure (Figure S2 in the Supporting Information). Approximating 160 K as the critical temperature provides a gross estimation of the activation energy, 0.014 eV (113 cm^{-1} , $0.32 \text{ kcal mol}^{-1}$). Notably, dilute MTHF solutions of **3** simply display a smooth transition in the emission maximum and a broadening in the profile as the temperature increases from 80 to 300 K (Figure S3 in the Supporting Information). This behavior is not limited to dilute solutions because we also observe similar behavior in microcrystalline films of **2** deposited on glass slides (Figure S4 in the Supporting Information). However, our model compounds **1** and **3** only exhibit a narrowing of the respective $^3\text{LC/MLCT}$ and $^3\text{MMLCT}$ emission in solid thin films (Figure S5 in the Supporting Information). It therefore appears that the ground-state structural reorganization is exclusive to **2**.

We have also investigated the emission temperature dependence of **2** in several host polymer films. Presented in Figure 4 is the emission temperature dependence of **2** in three different polymer matrices of varying rigidity. While poly(methyl methacrylate) (PMMA) is a rigid glass at RT ($T_g = 378 \text{ K}$),¹⁴ the rubbery Tecoflex EG-80A and Carbothane provide a less rigid environment ($T_g < \text{RT}$) and present the opportunity to probe both temperature and rigidity effects simultaneously. In PMMA (panel A), the emission profile at 77 K resembles that observed in MTHF at 77 K. The most significant changes in the emission profile arise simply from a loss in the vibronic structure upon heating to RT. We conclude that only mononuclear photoluminescence is observed for a PMMA film of **2** throughout the temperature range of 77–300 K. Only upon heating of the PMMA film to

temperatures exceeding the glass transition does the emission shift to much longer wavelengths similar to those seen in MTHF at 295 K (Figure S6 in the Supporting Information). Hence, the rigid nature of the polymer prevents the chromophore from undergoing important structural reorganizational changes at higher temperatures. The incorporation of **2** into softer polymer matrices such as Tecoflex EG-80A and Carbothane (panels B and C, respectively) yields distinctively different spectroscopic behavior than that of rigid PMMA. During heating from 80 to 240 K in Tecoflex EG-80A, the emission intensity decreases with a red shift in the emission maximum to 550 nm. Upon further heating, photoluminescence decreases in intensity while a shoulder at ~ 625 nm emerges. Carbothane provides similar transitions in the emission profile (panel C). However, the shoulder at ~ 625 nm is now much more pronounced at 300 K. Control experiments of **1** in Tecoflex EG-80A do not exhibit similar spectral shifts (Figure S7 in the Supporting Information), further suggesting that geometric reorganization is necessary to produce MMLCT photoluminescence in the softer polymer matrices.

In conclusion, we have reported the temperature effects on the absorption/emission properties of three dinuclear Pt^{II} chromophores. The ability to design a molecule whose spectroscopic properties can be carefully controlled simply through variation in the temperature has been achieved. The title compound demonstrates a thermochromic shift in the solid state and solution, likely to arise through intramolecular σ interactions between the two pseudocfacial $d^8 \text{Pt}^{\text{II}}$ centers. It is rather interesting to note that this *intramolecular* thermochromism produces color changes in opposition to the corresponding *intermolecular* processes occurring between Pt^{II} complexes in the solid state. Compound **2** was shown to traverse an activated barrier at temperatures above 160 K, demonstrated by dramatic changes in the emission profile. This phenomenon is observable in a variety of media and is consistent with intimate intramolecular σ interactions occurring between the two metal centers in the ground state.

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Supporting Information Available: Synthetic and experimental details as well as additional spectroscopic measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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