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

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The temperature effects on the spectral properties and photophysics of a new d8–d6 dinuclear PtII 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 dπ 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, PtII 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 for pyrazolato-bridged trinuclear complexes of the coinage metals5–7 controlled intramolecular Pt–Pt distances in select dinuclear structures, ultimately tuning the photophysics in a predictable 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 dπ 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 PtII complexes (1–3) investigated for their thermochromic response (see the Supporting Information for full synthetic details). These molecules feature two square-planar PtII 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–Pt 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. To delineate between an intra- versus intermolecular mechanism, the absorption spectra of dilute toluene solutions of 2 and 3 (7 × 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 overlap of the two dπₗ 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-methylytetrahydrofuran (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–Condor 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 (Φₐm = 0.07; τ = 750 ns), consistent with a 3LC/MLCT excited state. 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 pyppy ligands. The emission from 2 is broad and unstructured centered at ~625 nm (Φₐm = 0.15; τ = 2.0 μs), most consistent with MMLCT (3σₗ → σ*) parentage. The MMLCT emission from 3 is also broad and featureless and is the most red-shifted, λₘₐₓ = 650 nm (Φₐm = 0.03; τ = 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 (Tg ~ 91 K) (panel A), the profile simply red-shifts and loses the 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. The 3MLCT emission at 80 K (252 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 overlap with potentially shorter Pt–Pt distances at higher

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 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 the Supporting Information. However, our model compound matrices of varying rigidity. While poly-(methyl methacrylate) (PMMA) is a rigid glass at RT ($T_g = 378$ K), the rubbery Tecoflex EG-80A and Carbothane provide a less rigid environment ($T_g < RT$) 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 reorganization 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 distinctly 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 $\sim 625$ nm emerges. Carbothane provides similar transitions in the emission profile (panel C). However, the shoulder at $\sim 625$ 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$^{{\text{II}}}$ 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 $\sigma$ interactions between the two pseudocofacial $d^8$ 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$^{{\text{II}}}$ 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 $\sigma$ 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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*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; $\lambda_{ex} = 410$ nm.

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