Vapor-Induced Luminescence Switching in Crystals of the *Syn* Isomer of a Dinuclear (Bipyridine)platinum(II) Complex Bridged with Pyridine-2-Thiolate Ions[**]

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Assembled metal complexes of platinum(II) and gold(I) ions often exhibit a characteristic color and intense luminescence based on electronic metal–metal interactions. Such complexes have recently attracted particular interest as sensor materials.[1] Herein, we report a new dinuclear platinum(II) complex, *syn*-$[Pt_2(bpy)_2(pyt)_2][PF_6]_2$ (bpy = 2,2′-bipyridine, pyt = pyridine-2-thiolate ion), which exhibits a remarkable change in its luminescence in the presence of organic vapors such as acetonitrile or ethanol.

Dark-red polyhedral crystals of *syn*-$[Pt_2(bpy)_2(pyt)_2][PF_6]_2\cdot CH_3CN$ were isolated from an acetonitrile/ethanol solution as the minor component of two geometrical isomers containing the $[Pt_2(bpy)_2(pyt)_2]^{2+}$ ion. The *syn* isomer has a head-to-head configuration of two bridging pyridine-2-thiolate ions (Figure 1), with the platinum ions adopting different coordination environments: Pt1 is bonded to four nitrogen atoms, whereas Pt2 has N_2S_2 coordination. This arrangement is in contrast to the *anti* isomer, which has a head-to-tail configuration (Figure 2), and is obtained as orange needlelike crystals. The Pt⋯Pt separations for the *syn*- and *anti* isomers are 2.923(1) and 2.997(1) Å, respectively. These separations are amongst the shortest Pt⋯Pt interactions observed in divalent platinum complexes.[2] Similar dinuclear complexes have been reported by Che an co-workers.[3]

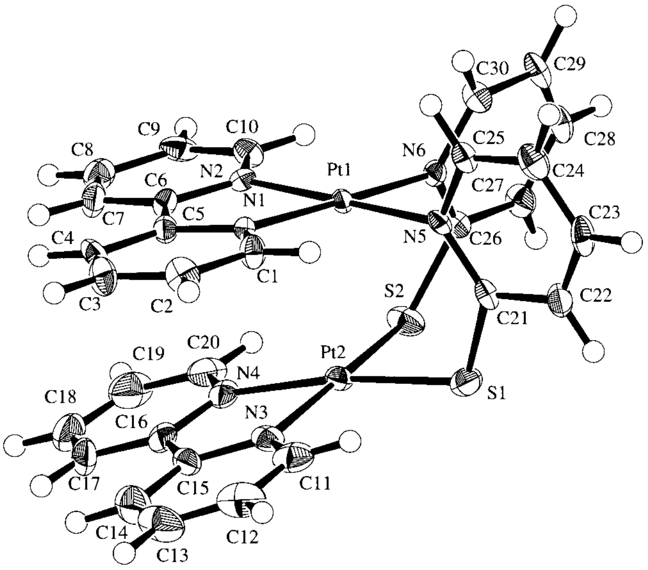

Figure 1. Single-crystal X-ray structure of the *syn* isomer.

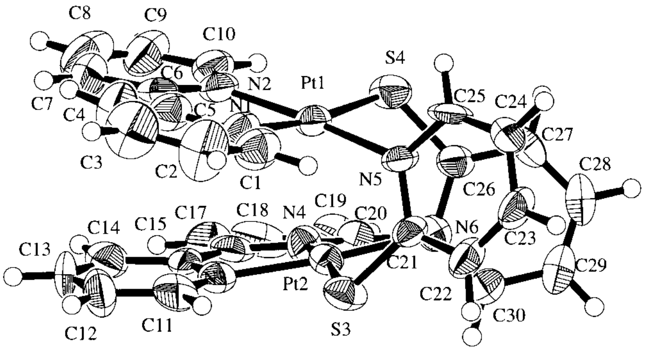

Figure 2. Single-crystal X-ray structure of the *anti* isomer.

Crystals of the *anti* isomer exhibit very intense orange luminescence (λ_{max} = 603 nm), even at room temperature (Figure 3a). On the basis of the spectral profile and the emission lifetime (τ = 240 ns), the luminescene can be assigned as emission from the triplet metal–metal-to-ligand charge-transfer state, which has been observed in diimineplatinum(II) complexes with short Pt⋯Pt separations.[4] The emission state is thought to also include a contribution from the sulfur orbitals of the pyridine-2-thiolate ligands.[3a,5]

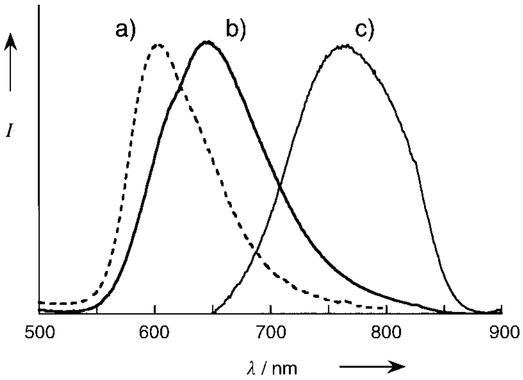

Figure 3. Luminescence spectra at room temperature for a) the *anti* isomer, b) the light-red (desolvated) form of the *syn* isomer, and c) the dark-red (solvated) form of the *syn* isomer.

Crystals of the *syn* isomer are initially dark-red in appearance, but appear to become lighter in color upon standing in air for several hours at room temperatue (Figure 4). Luminescence spectroscopy of these materials shows the generation of a concomitant emission (Figure 3b and c). It is noteworthy that the luminescent light-red form reverts back to the nonemissive darker immediately upon exposure to acetonitrile or ethanol vapor, formwhich could be monitored

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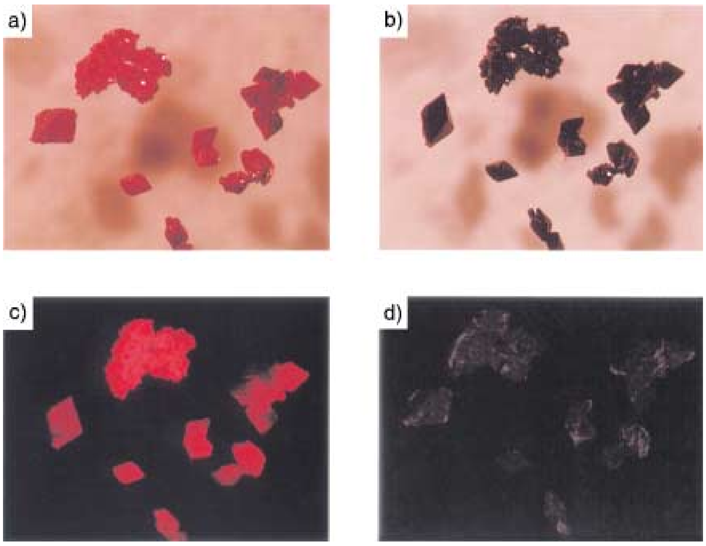

Figure 4. Photographic images of crystals of the *syn* isomer, illustrating vapochromic effects: a) the light-red (desolvated) form in air and b) the dark-red form after exposure of (a) to acetonitrile vapor. Luminescence images of c) the light-red and d) dark-red forms.

spectroscopically: the IR spectrum of the dark-red form possesses a band corresponding to acetonitrile at 2248 cm^{-1} which disappears after standing in air. In addition, ^1H NMR spectroscopy gives evidence that acetonitrile (or ethanol) is inherent to the complex after exposure to the vapor (see Supporting Information). Thus, crystals of the *syn* isomer exhibit vapor-induced luminescence switching. Such vapochromic behavior is characteristic of the *syn* isomer in the presence of particular organic vapors such as nitriles and alcohols. However, the sensitivity is reduced with increasing size and bulkiness of vapor molecules. For example, the *syn* isomer is less sensitive to isopropanol than ethanol, but exhibits no sensitivity at all to *tert*-butanol despite their similar vapor pressures (see Supporting Information). In addition, the *syn* isomer is also very sensitive to dichloromethane, while no changes are observed on exposure to either chloroform or carbon tetrachloride. Thus the observed vapochromism of this system is also unique from the viewpoint of sensitivity.

The luminescence spectra of the two *syn*-isomeric forms indicate that the light-red form (that is, without solvent) has an intense luminescence at a slightly longer wavelength than that of the *anti*-isomer ($\lambda_{max} = 644$ nm, $\tau = 170$ ns), while the dark-red form emits light at a wavelength almost beyond the visible region ($\lambda_{max} = 766$ nm).

To clarify the origin of such a remarkable vapor-induced change in luminescence, we investigated the crystal structure of the dark-red, acetonitrile-solvated form in detail. The molecules are arranged co-planar to the N_2S_2 coordination plane, thus forming a tetranuclear motif within the crystal structure (Figure 5 (top)). The Pt2···Pt2* separation is 3.384(1) Å, which is short enough to suggest that intermolecular (metal–metal) electronic interactions could occur between stacked complexes. In fact, the Pt···Pt separation for the emissive red form of [$PtCl_2$(bpy)] is reported to be 3.449(1) Å at room temperature.[6] A channel can be observed within the crystal structure, as indicated by the asterisk in Figure 5 (bottom). The structure should contain one acetonitrile molecule per complex within this channel, as suggested by NMR spectroscopy and the crystal density. In fact, the Fourier map of the X-ray analysis indicated several peaks of electron density in the channel. However, the atomic coordinates for the acetonitrile molecule could not be determined with certainty, even at −150 °C, because of the level of disorder. Nevertheless, this indicates that there are no distinct interactions between the main body of the complex and the

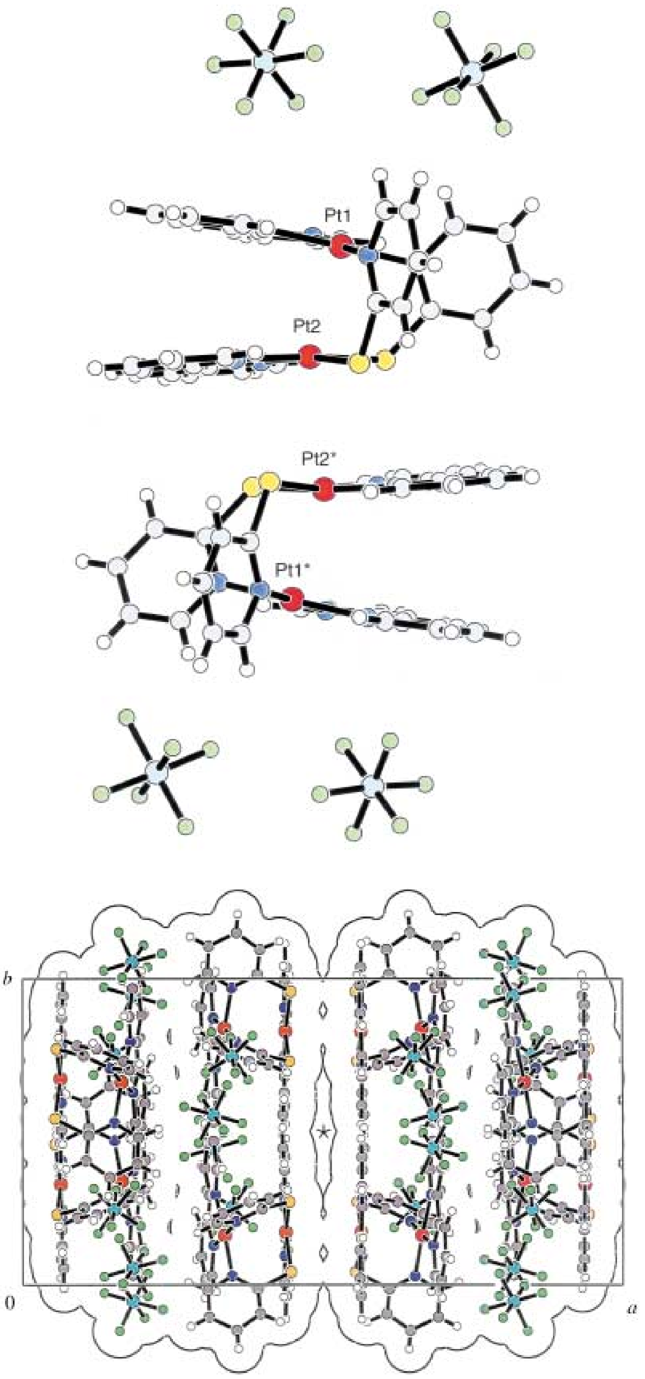

Figure 5. Top: X-ray structural diagram indicating the tetranuclear motif found in the *syn* isomer; bottom: X-ray packing diagram of the *syn* isomer at room temperature with van der Waals outline.

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acetonitrile solvate molecule, and also suggests that there is a pathway that allows the organic vapor to easily penetrate the crystal through the channel. Thus, vapochromism may occur as a result of changes in Pt···Pt interactions as the channel fills with organic vapor molecules. The fact that the *anti* isomer possesses no channels within its crystal structure, and does not exhibit vapochromism, lends support to this conclusion.

Experimental Section

[$PtCl_2$(bpy)] was prepared according to the literature method.[7] Pyridine-2-thiol was purchased from Aldrich. A suspension of [$PtCl_2$(bpy)] (421 mg, 1 mmol) and pyridine-2-thiol (114 mg, 1 mmol) in water (40 mL) was heated at 70 °C for 24 h. After filtration, an excess of NH_4PF_6 was added to the dark-brown solution to yield an orange-red precipitate. Yield 98 %. The ratio of *syn* to *anti* isomers in the precipitate was approximately 1:3, based on ^{1}H NMR spectral data. Recrystallization from CH_3CN/EtOH gave orange needlelike crystals of the *anti* isomer. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 7.26$ (t, 1 H), 7.42 (dd, 1 H), 7.57 (t, 1 H), 7.68 (t, 1 H), 7.99 (d, 1 H), 7.83 (d, 1 H), 8.21 (d, 2 H), 8.26 (t, 1 H), 8.33 (d, 1 H), 8.78 (d, 1 H), 9.02 ppm (d, 1 H). Elemental analysis calcd for $Pt_2C_{30}H_{24}N_6S_2P_2F_{12}$: C 29.71, H 1.99, N 6.93; found: C 29.69, H 1.87, N 6.96.

Dark-red (solvated) polyhedral crystals of the *syn* isomer were obtained from the filtrate by slow evaporation. ^{1}H NMR (300 MHz, [D$_6$]DMSO, dark-red form): $\delta = 2.06$ (CH_3CN, s, 1.5 H), 7.26 (t, 1 H), 7.30 (t, 1 H), 7.64 (m, 2 H), 7.83 (t, 1 H), 7.88 (d, 1 H), 8.22 (t, 1 H), 8.25 (d, 1 H), 8.35 (d, 1 H), 8.40 (t, 1 H), 8.75 (d, 1 H), 8.84 ppm (d, 1 H). For the light-red form, the spectrum is identical except that the resonance at 2.06 ppm is absent, which indicates that no CH_3CN was present. Elemental analysis (for the unsolvated light-red form) calcd for $Pt_2C_{30}H_{24}N_6S_2P_2F_{12}$: C 29.71, H 1.99, N 6.93; found: C 29.58, H 2.22, N 7.13.

Crystal data for *syn*-[$Pt_2(bpy)_2(pyt)_2$][PF_6]$_2\cdot CH_3CN$. $Pt_2C_{32}H_{27}N_7S_2P_2F_{12}$, $M_r = 1253.84$, orthorhombic, space group *Pbcn* (no. 60), $a = 26.475(7)$, $b = 13.863(4)$, $c = 20.454(5)$ Å, $V = 7507(3)$ Å^3, $Z = 8$, $T = -150\,°C$, $\rho_{calcd} = 2.22\ g\,cm^{-1}$, $\mu(Mo_{K\alpha}) = 77.14\ cm^{-1}$. The final R indices: $R(F) = 0.056$ based on 8266 reflections ($I > 2\sigma(I)$), $wR(F^2) = 0.130$ based on 8573 observed reflections (all data) and 487 parameters, GOF = 1.27. Lattice constants and density of the same crystal at 25 °C: $a = 27.270(5)$, $b = 13.930(2)$, $c = 20.660(3)$ Å, $V = 7848(2)$ Å^3, $\rho_{calcd} = 2.12\ g\,cm^{-1}$, $\rho_{measured} = 2.13\ g\,cm^{-1}$. Crystal data for *anti*-[$Pt_2(bpy)_2(pyt)_2$][PF_6]$_2$. $Pt_2C_{30}H_{24}N_6S_2P_2F_{12}$, $M_r = 1212.79$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.738(7)$, $b = 20.11(1)$, $c = 7.405(4)$ Å, $\alpha = 99.26(1)$, $\beta = 100.34(2)$, $\gamma = 95.50(2)°$, $V = 1826(1)$ Å^3, $Z = 2$, $T = 25\,°C$, $\rho_{calcd} = 2.21\ g\,cm^{-1}$, $\rho_{measured} = 2.22\ g\,cm^{-1}$, $\mu(MoK\alpha) = 7.916\ mm^{-1}$. The final R indices: $R(F) = 0.077$ based on 5183 reflections ($I > 2\sigma(I)$), $wR(F^2) = 0.163$ based on 7912 observed reflections (all data) and 487 parameters, GOF = 1.12. CCDC-181956 and -181957 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Ruthenium Photocatalysts Capable of Reversibly Storing up to Four Electrons in a Single Acceptor Ligand: A Step Closer to Artificial Photosynthesis**

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Dedicated to the memory of Hongwei Ye

Artificial photosynthesis occupies a central focus of chemical research. Natural systems provide useful guidelines for the design of efficient artificial photosynthetic systems that function at the molecular level: complimentary functionally organized components are needed, such as 1) antennas, 2) reaction centers, and 3) light-driven multielectron catalysts.[1] While research on synthetic analogues of components 1) and 2) is relatively well-developed,[2,3] efficient photoactivated synthetic multiredox catalysts are very rare.[4] Here we report the first example, to the best of our knowledge, of an artificial system which, upon visible irradiation, is capable of reversibly storing up to four electrons in a molecularly localized fashion.

Ru^{II} polypyridyl complexes have long been studied because of their favorable stability and photophysical properties, however the vast majority of these species are only capable of catalyzing one-electron processes.[5] In the ruthenium polypyridine family, only [{(bpy)$_2$Ru(2,3-bis(pyridyl)-benzoquinoxaline)}$_2$IrCl$_2$]$^{4+}$ forms a stable doubly reduced product upon irradiation,[6] and the two electrons are stored on different acceptor ligands. Herein, we describe a photoactive ruthenium(II) dimer, [(phen)$_2$Ru-tatpq-Ru(phen)$_2$]$^{4+}$ (**Q**),[7] which reversibly stores up to four electrons in the central bridging ligand (Scheme 1).

The photoreduction process is relatively rapid and easily monitored by absorption spectroscopy. A degassed solution of

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