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]$_2$·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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Sebastiano Campagna, and Krishnan Rajeshwar

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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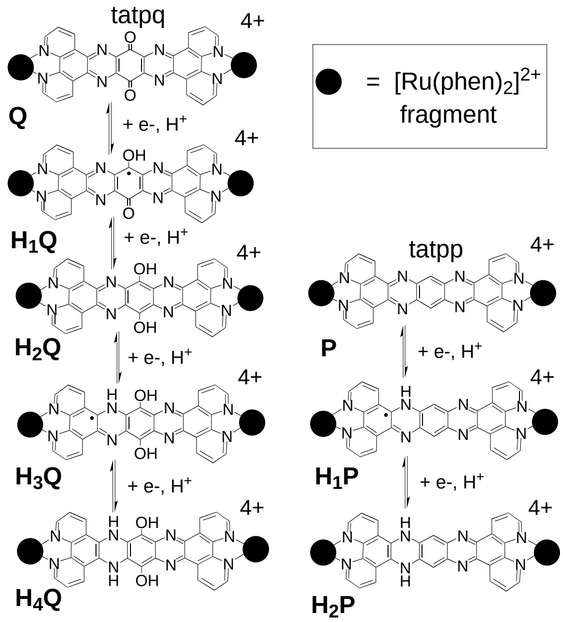

Scheme 1. Structures and redox reactions for **Q** and **P**? phen = 1,10-phenanthroline.

Q (16 µM) and 0.35 M triethylamine (TEA) in acetonitrile is irradiated with visible light[8] and monitored periodically (Figure 1 A,B). We first observe appearance of a peak at 630 nm (Figure 1 A), assigned to a two-electron reduction of **Q**→**H$_2$Q**. Subsequently, this peak diminishes with concomitant growth of the peak at 1070 nm (Figure 1 B (blue to red)), assigned as the **H$_2$Q**→**H$_3$Q** transformation. Finally, the peak at 1070 nm diminishes with the gradual appearance of the final three peaks at 650, 725, and 790 nm assigned to the **H$_3$Q**→**H$_4$Q** reduction (also shown in Figure 1 B (red to green)). These assignments are made with a combination of data from cyclic voltammetry (CV), spectroelectrochemistry (SEC), as described below, and by comparison with a related two-electron photocatalyst, [(phen)$_2$Ru-tatpp-Ru-(phen)$_2$][PF$_6$]$_4$ (**P**; Scheme 1).

The cyclic voltammetric scan of **Q** (MeCN/1 % acetic acid) shows two reversible one-electron reductions at 0.01 V and −0.18 V versus Ag/Ag$^+$ quasi-reference. Controlled potential spectral scans in a spectroelectrochemical thin-layer cell[9] at 0.0, −0.4, and −0.8 V resulted in the absorption spectra shown in Figure 1 C. The peak at 630 nm is associated with a two-electron reduction and is consistent with formation of the hydroquinone species (**H$_2$Q**). Unfortunately, the redox behavior of this complex at more negative potentials is obscured by H$_2$ evolution and other interfering processes at the electrode surface. We note, however, that a similar spectral change (appearance of a peak at 630 nm) upon photoirradiation of the hydrocarbon 5,7,12,14-tetraazapentacene-6,13-quinone (which is closely related to tatpq in terms of the structure) was also assigned to a doubly reduced product of which the hydroquinone was one possible tautomer.[10] The assignment of **H$_2$Q** as the hydroquinone follows from the discussion below.

The related tatpp complex (**P**)[7] offers valuable insight into the photochemistry of **Q**. Irradiation of **P** under similar conditions[11] as for **Q** results in the appearance of two photoproducts, observed sequentially. First, a band at 970 nm grows in (Figure 2 A) and finally this decreases and three new peaks at 725, 660, and 590 nm concomitantly appear (Figure 2 B). The cyclic voltammetric scan of **P** (MeCN) shows two reversible one-electron reductions at −0.18 V and −0.56 V versus Ag/Ag$^+$. Spectroelectrochemistry at set potentials of 0, −0.4, and −0.9 V (Figure 2 C,D) clearly shows that the spectral changes in Figure 2 A and 2 B are associated with two one-electron reductions of **P**.[12] As shown in Scheme 1, these reductions are assigned to the formation of a hydropyrazine–benzene–pyrazine radical (**H$_1$P**) and the dihydropyrazine–benzene–pyrazine (**H$_2$P**), respectively. The ^{1}H NMR and absorption spectra of the related hydrocarbon dihydro-5,7,12,14-tetraazapentacene (**1**), which exists as the benzoid tautomer, support this structure for **H$_2$P** but we cannot rule out the quinoid tautomer.[12] Importantly, the visible spectrum of **1** shows a characteristic three-peak spectral signature (at 490, 510, and 560 in dimethylacetamide (DMA)) which is remarkably similar to the spectra observed for the final (most reduced) forms of **Q** and **P**.

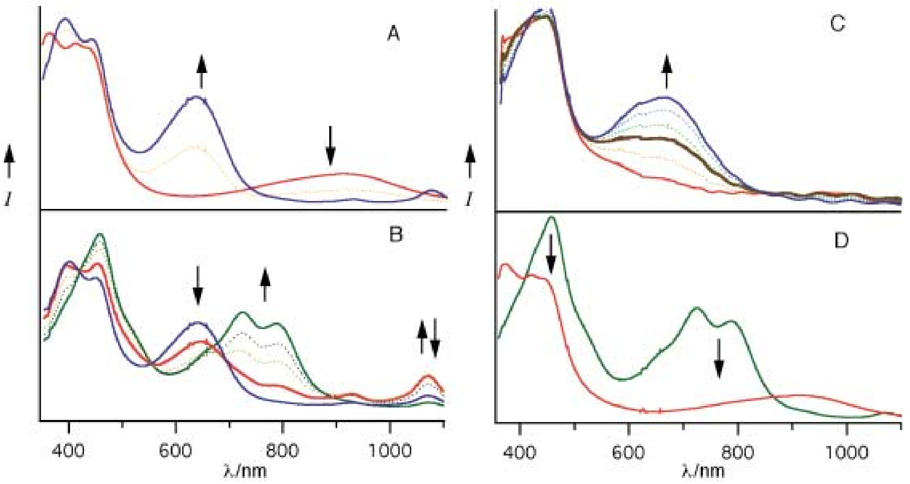

Figure 1. Evolution of the visible spectrum of **Q** (16 µM) observed during photoirradiation[8]: A) 0 to 3 min; note: the broad band at 920 nm for **Q** is presumably is a charge-transfer band between TEA and **Q** as it is not observed in the absence of TEA, B) 3 to 12 min. Conditions: MeCN, 0.25 M TEA, 23 °C. C) The spectral changes observed during controlled potential electrolysis (SEC) of **Q** (0.2 mM): 0.0 to −0.4 V (red to brown), −0.4 to −0.8 V (brown to blue). Conditions: MeCN, 2.5 % HOAc/5 % TEA, 0.1 TBAPF$_6$, 23 °C. D) Regeneration of **Q** from **H$_4$Q** by exposure to air. TBA = tetrabutylammonium.

Remarkably, the entire process is reversible upon exposure of **H$_4$Q** to air as shown in Figure 1 D and, upon degassing with N$_2$, the entire photocatalytic cycle can be repeated. Complex **H$_2$P** is similarly re-oxidized to **P** by air, however, some irreversible oxidization is observed.

Molecular orbital calculations[7] for tatpq show two orbitals, the LUMO

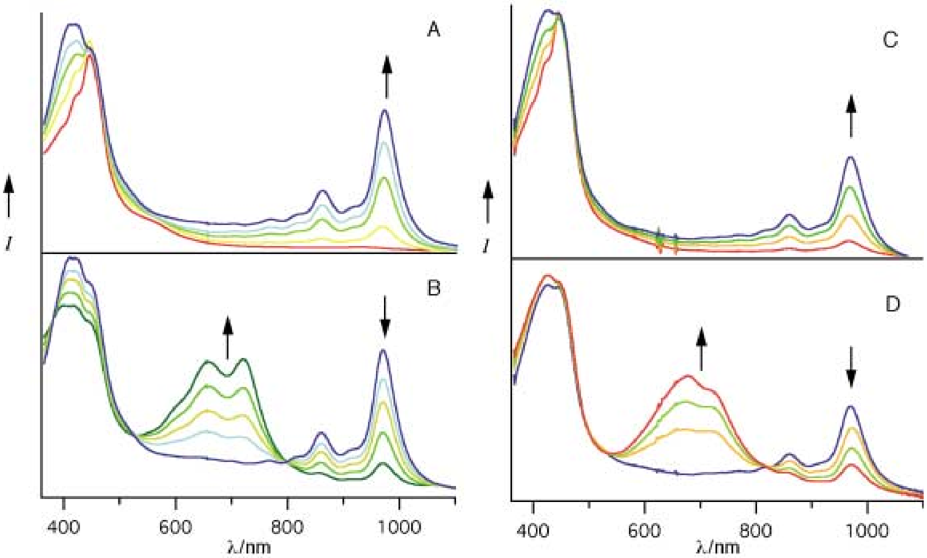

Figure 2. Evolution of the visible spectrum of **P** (50 μM) observed during photoirradiation[8]: A) 0 to 2 min, B) 2 to 10 min. Conditions: MeCN, 0.25 M TEA, 23 °C. Spectral changes observed during controlled potential electrolysis (SEC) of **P** (0.5 mM): C) 0.0 to −0.4 V, D) −0.4 to −0.9 V Conditions: MeCN, 0.1 $TBAPF_6$, 23 °C.

(quinone-like) and the LUMO + 1 (centered on the pz-bz-pz unit), below the phenanthroline-like LUMO + 2 which is initially populated by a metal-to-ligand charge-transfer (MLCT) transition. Similar calculations on tatpp show one orbital, the pz-bz-pz like LUMO, below the phenanthroline-like LUMO + 1. This MO picture, along with the CV and SEC data, collectively yields a simple picture of the photoreduction processes involved in **Q** and **P**. Thus, **P** undergoes two sequential one-electron reductions (by electron transfer from the initially populated MLCT states), to fill the pz-bz-pz LUMO and is readily identified by the characteristic visible spectrum of the benzoid form of the dihydrotetraazapentacene unit.[13] On the other hand, **Q**, with an additional lower-lying orbital, accepts two electrons to first fill the quinone-based LUMO and subsequently accepts two more electrons in the pz-bz-pz LUMO + 1. For both **Q** and **P**, TEA serves as a sacrificial reductant and proton donor by restoring the Ru^{II} chromophore(s) after each electron-transfer event.[14] The various absorption peaks observed between 500 and 1100 nm are ligand-centered transitions associated with the multiple oxidation states of the bridge.

Interestingly, each photoinduced electron-transfer process is coupled with protonation of the reduced site, a feature which has been proposed to be essential in most natural light-activated energy-storing processes.[15] Currently, the exact protonation states of the central bridging ligands are speculative but we believe they are essential to avoid excessive build-up of negative charge on the ligand. The presence of two Ru^{2+} ions in **P** and **Q** may be necessary to stabilize the charge-separated state (Ru^{III}–$BL^{\bullet-}$–Ru^{II}) and is being investigated further. Indeed, the influence of internal electric fields on the stabilization of electron-transfer products has already been reported.[16]

To the best of our knowledge, **Q** is the first synthetic species capable of a storing more than two electrons in its structure, and the localization of these electrons in two "overlapping" MOs on the tatpq ligand suggests that they may be delivered to substrates in a concerted fashion, mimicking one essential property of natural photosynthetic systems.

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[12] Our assignment is in agreement with the very recently reported spectroelectrochemistry of a dinuclear Ru^{II} compound containing a bridging ligand which is related to that which is present in **P** (see: M. Staffilani, P. Belser, L. De Cola, F. Hartl, *Eur. J. Inorg. Chem.* **2002**, 335).

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