Inorg. Chem. **2005**, *44*, 4029–4036

Inorganic Chemistry
Article

Reversible Luminescence Switching in a Ruthenium(II) Bis(2,2′:6′,2′′-terpyridine)-Benzoquinone Dyad

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Received January 14, 2005

An electroactive luminescent switch has been synthesized that comprises a hydroquinone-functionalized 2,2′:6′,2′′-terpyridine ligand coordinated to a ruthenium(II) (4′-phenylethynyl-2,2′:6′,2′′-terpyridine) fragment. The assembly is sufficiently rigid that the hydroquinone–chromophore distance is fixed. Excitation of the complex via the characteristic metal-to-ligand charge-transfer (MLCT) absorption band produces an excited triplet state in which the promoted electron is localized on the terpyridine ligand bearing the acetylenic group. The triplet lifetime in butyronitrile solution at room temperature is 46 ± 3 ns but increases markedly at lower temperature. Oxidation of the hydroquinone to the corresponding benzoquinone switches on an electron-transfer process whereby the MLCT triplet donates an electron to the quinone. This reaction reduces the triplet lifetime to 190 ± 12 ps and essentially extinguishes emission. The rate of electron transfer depends on temperature in line with classical Marcus theory, allowing calculation of the electronic coupling matrix element and the reorganization energy as being 22 cm^{-1} and 0.84 eV, respectively. The switching behavior can be monitored using luminescence spectroelectrochemistry. The on/off level is set by temperature and increases as the temperature is lowered.

Introduction

The rational design of means by which to regulate the photonic output from molecular-scale systems is an area of great topical interest, with switching methods such as redox alteration,[1] pH gradient,[2] cation capture,[3] anion recognition,[4] and variable-frequency excitation[5] under active consideration as the input stimulus. To operate at maximum efficacy, it is recognized that these systems must display a clear on/off signal and possess two states that are chemically robust. A popular approach is to make use of a luminescent center that, after introduction of an efficient quenching pathway by the switching operation, results in total extinction of the emission or vice versa.[6] Some pertinent organic luminophores include pyrene,[7] anthracene,[8] and naphthalene.[9] Metal-based octahedral ruthenium(II) complexes of polypyridyl ligands such as 2,2′-bipyridine (bipy) have also been used extensively,[10] primarily because a single ligand can be functionalized with a receptor[11] or redox site[12] that resides close to the lumino-

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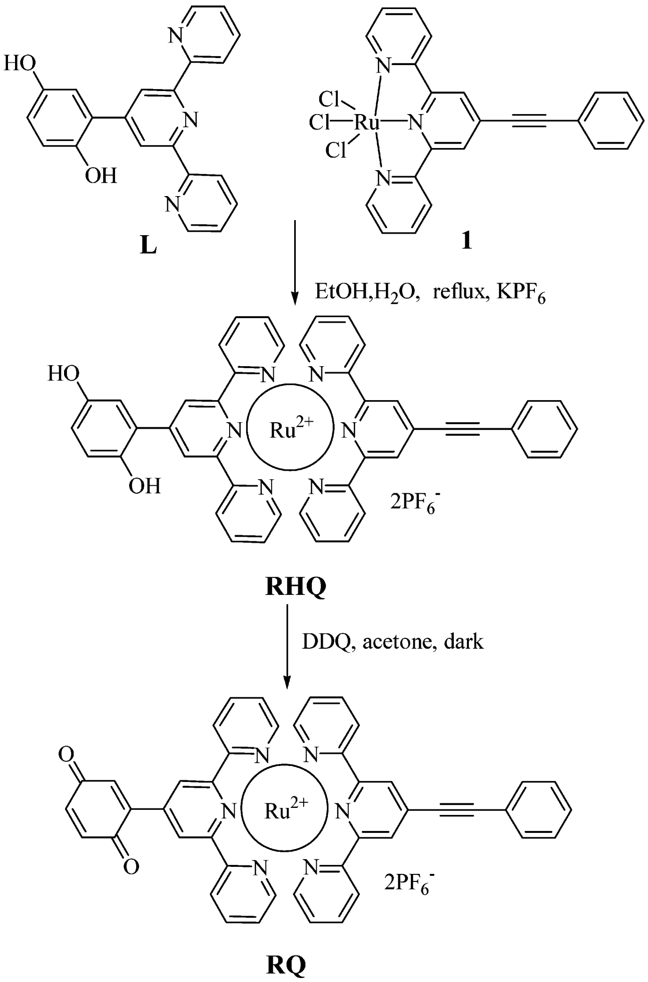
10.1021/ic050059c CCC: $30.25

phore. For example, Lehn and co-workers[13] described a luminescent switch based on a benzoquinone unit attached via a flexible hydrocarbon chain to a Ru-bipy core. Luminescence from the Ru-bipy site was quenched by light-induced electron transfer to the benzoquinone, but upon selective electrochemical reduction of the benzoquinone, this quenching pathway is eliminated. More recently, systems have been described that make use of a Ru-bipy/benzoquinone/Co-bipy triad core.[14] One drawback of these systems involves the use of flexible linkages to couple the quencher to the luminophore. Such tethers do not facilitate collection of mechanistic information about the electron-transfer process and, more importantly, introduce unnecessary conformational heterogeneity when used in viscous media. Replacing bipy with 2,2′:6′,2”-terpyridine (terpy) is an obvious way to eliminate the introduction of enantiomers, and strategies are now readily available that allow the use of rigid or geometrically constrained linkers.[15] Consequently, we have sought to design a new prototypic electroactive luminescent switch based on Ru-terpy and exhibiting a restricted geometry.

In earlier work, Colbran and co-workers[16] described preparation of the ligand **L** (Scheme 1) along with its benzoquinone analogue. Homoleptic and heteroleptic complexes were prepared from various first-row transition metals and from ruthenium(II). However, no detailed photophysical studies were described for $[Ru(\mathbf{L})_2]^{2+}$ or the corresponding benzoquinone derivative. In fact, it is highly unlikely that these materials will function as viable luminescent switches because the emission lifetime of most Ru-terpy complexes is extremely short. The parent complex, $[Ru(terpy)_2]^{2+}$, for example, is essentially nonluminescent in solution at room temperature.[17] This means that the on/off levels for switches based on modules such as $[Ru(\mathbf{L})_2]^{2+}$ are likely to be too small for exploitation. This particular problem can be overcome by proper functionalization of the coordination sphere around the cation. A simple strategy is to replace one of the **L** ligands with 4′-phenylethynyl-2,2′:6′,2′′-terpyridine (phterpy) as this approach ensures that visible light illumination causes charge transfer from the metal center to the acetylene-bearing terpy ligand.[18] As a result, the triplet lifetime should be increased significantly.[19] The prolonged triplet lifetime should favor emission from the hydroquinone form. Positioning the quinone close (i.e., ca. 7.7 Å) to the metal center is likely to guarantee that the excited triplet state is effectively quenched by way of fast electron donation to the quinone.[12,20] We now test these ideas and report on the photophysical properties of the putative terpy-based luminescent switch.

Scheme 1. Methods Used in the Preparation of the Molecular Switching Unit **RQ**



Results and Discussion

The synthesis of **RQ**, as outlined in Scheme 1, was carried out by coupling **L** to the known metallo-synthon **1** so as to generate the hydroquinone derivative **RHQ**. This complex was purified by column chromatography on Sephadex LH20, eluting with methanol, before being converted to the

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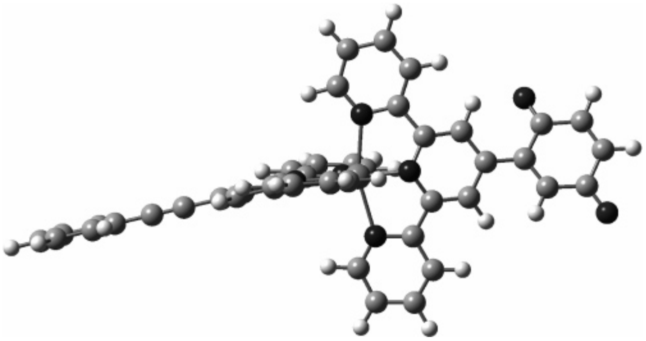

Figure 1. Ball-and-stick representation of the energy-minimized structure of **RQ**.

hexafluorophosphate salt. Oxidation of the hydroquinone fragment to the corresponding benzoquinone was achieved using DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in acetone and keeping the reaction mixture in the dark. Despite careful chromatography and shielding of the column from stray light, the sample of **RQ** thus obtained was always contaminated (<5%) with **RHQ**. Samples used for subsequent photophysical studies were freshly prepared and purified by thin layer chromatography (TLC) immediately before the experiment. All solutions were handled in the dark and were prepared in freshly distilled solvent.

The energy-minimized structure of **RQ** is depicted in Figure 1 and confirms the expected pseudo-octahedral geometry about the metal core. The benzoquinone unit lies coplanar with the appended terpy ligand, although there is free rotation around the connecting C−C bond, as evidenced by molecular dynamics simulations. There appears to be no steric hindrance between hydrogen atoms on terpy and quinone fragments. Likewise, the phenylene ring is free to rotate about the acetylene linker but prefers to remain coplanar with the terpy ligand. The closest distance between the distal phterpy ligand and the benzoquinone is ca. 7.7 Å. The computational studies also showed that the LUMO is centered on the quinone moiety in **RQ** but on the coordinated phterpy ligand in **RHQ**. The HOMO in both complexes is localized on the cation.

The electrochemistry of **RHQ** and **RQ** was examined by cyclic voltammetry in dried, deoxygenated acetonitrile solution at room temperature. Half-wave potentials ($E_{1/2}$), where appropriate, were determined as the averages of the anodic and cathodic peaks [$E_{1/2} = (E_{pa} + E_{pc})/2$]. Upon oxidative scanning, the voltammogram for **RHQ** displayed a one-electron irreversible wave at +0.98 V and a quasireversible wave with $E_{1/2} = 1.35$ V ($\Delta E = 80$ mV) vs Ag/AgCl. Comparison with related Ru-terpy complexes[21] indicates that the more anodic wave corresponds to the one-electron oxidation of the ruthenium(II) center. The first wave, therefore, can be attributed to the irreversible oxidation of the hydroquinone moiety. This wave is not seen in the electrochemistry of related complexes lacking the hydroquinone group. Also, it is known that oxidation of hydroquinones is electrochemically irreversible because of fast disproportionation and proton loss.[22] Two quasireversible, one-electron waves are seen on reductive scans that correspond to $E_{1/2}$ of −1.07 V ($\Delta E = 60$ mV) and −1.48 V ($\Delta E = 130$ mV) vs Ag/AgCl. It is realized that substitution into the 4′ position of terpy with an electron-withdrawing acetylene group raises the reduction potential.[23] Hence, the first cathodic wave is assigned to reduction of the 4′ethynyl-2,2′:6′,2″-terpyridine, whereas the second wave is attributed to reduction of the hydroquinone functionalized ligand.

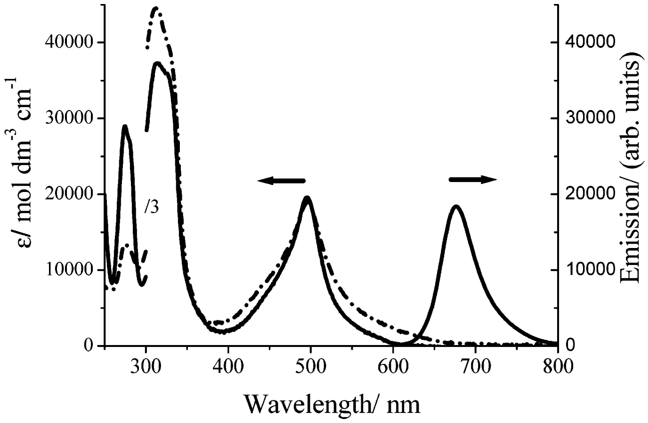

Figure 2. Absorption and emission spectra for **RHQ** (—) and absorption spectrum for **RQ** (− • − • −) in butyronitrile. Absorption spectra were recorded at room temperature, whereas the emission spectrum was run at 200 K.

Oxidative cyclic voltammograms recorded for **RQ** revealed a quasireversible, one-electron wave with $E_{1/2} = 1.35$ V ($\Delta E = 80$ mV) vs Ag/AgCl. The similarity of this value to that found for **RHQ** implies little electronic communication between the cation and the appended quinone. Reductive cyclic voltammograms showed quasireversible waves with $E_{1/2} = -1.15$ ($\Delta E = 70$ mV) and −1.59 V ($\Delta E = 90$ mV) vs Ag/AgCl. Presumably, the ethynylated ligand is easier to reduce than the quinone-functionalized terpy ligand. Each process occurs at a slightly more negative potential than found for **RHQ**. This situation probably arises because of an electrostatic effect associated with prior reduction of the quinone moiety. Indeed, the quinone group undergoes one-electron reduction steps with $E_{1/2}$ of −0.15 V ($\Delta E = 150$ mV) and −0.67 V vs Ag/AgCl. Both steps are poorly reversible. The first process can be assigned to formation of the quinone π-radical anion. This reduction is somewhat easier than for simple benzo-1,4-quinones in aprotic solvent, probably because of electronic charge provided by the cation. The quinone π-radical anion appears to be relatively stable against disproportionation under these conditions. The second reduction corresponds to formation of the quinone π-dianion. This latter step becomes irreversible if trace amounts of water are present.

Absorption and emission spectra recorded for **RHQ** and **RQ** are shown in Figure 2. Both complexes display the

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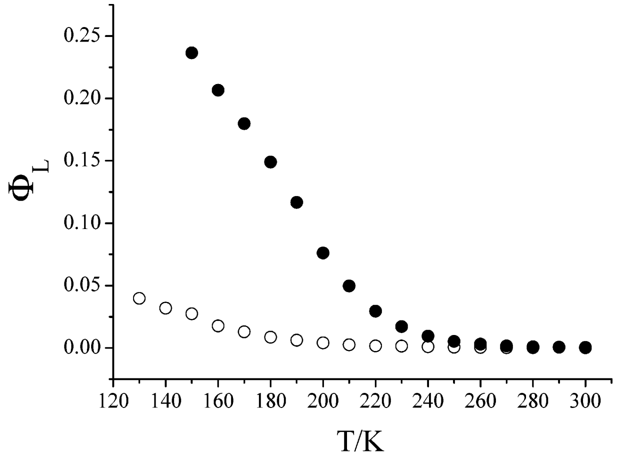

Figure 3. Variation with temperature of the quantum yield of luminescence for **RHQ** (●) and **RQ** (○) in N_2-purged butyronitrile.

archetypal metal-to-ligand charge-transfer (MLCT) absorption bands in the low-energy visible spectral region; both absorption maxima appear at 496 nm. Because of the less negative reduction potential of the phterpy ligand, as evidenced by electrochemical measurements, the excited states of both complexes can be formulated as [Ru(III)(terpy)(phterpy$^-$)]$^{2+}$. The high-energy parts of the absorption spectra are dominated by relatively intense $\pi-\pi^*$ transitions ascribable to the various terpy ligands and their appendages. In particular, the ethynylated ligand absorbs in the near UV around 300−360 nm, and the other terpy ligand shows prominent absorption around 280 nm. Transitions associated with the quinone moiety are hidden beneath the more intense bands due to the terpy ligands. At low energy, the spectra contain contributions from the spin-forbidden MLCT transitions.

Illumination of **RHQ** in N_2-purged butyronitrile at room temperature gives rise to a weak emission profile centered at 675 nm. The excitation spectrum is in good agreement with the absorption spectrum recorded over the entire spectral range. Under these conditions, the emission lifetime (τ_{LUM}) is 46 ± 3 ns and remains closely comparable to that reported earlier for the metal complex lacking the hydroquinone group ($\tau_{LUM} = 40$ ns).[24] The same triplet lifetime was observed by transient absorption spectroscopy. The quantum yield for luminescence (Φ_L) is only 0.0004 ± 0.0001 at room temperature. These various observations are entirely consistent with the luminescent state being the lowest-energy MLCT triplet associated with the Ru-terpy complex. No emission could be observed for **RQ** under these conditions.

The emission yield for **RHQ** in deoxygenated butyronitrile increases steeply with decreasing temperature (Figure 3), although there is no change in spectral profile. Separate studies showed that the emission decay kinetics remain strictly monoexponential but that the lifetime increases progressively with decreasing temperature. The temperature dependence noted for the triplet lifetime could be explained in terms of eq 1, taking due account of prior investigations with related systems.[25] Here, k_0 refers to the rate constant for activationless decay of the lowest-energy MLCT triplet as seen at low temperature. This latter triplet is coupled to a second triplet state lying at slightly higher energy. The relevant energy gap is designated as E_A, and the rate constant for decay of this upper triplet is termed k_1. It is generally assumed that the upper triplet is also of MLCT type but includes more singlet character.[26] Both triplets are coupled to a high-lying excited state that is most likely a metal-centered (MC) triplet.[24] The MC state is reached by passing over a substantial barrier, termed E_B. The sum of the rate constants for accessing the MC state from the two triplet states is referred to as k_2. Statistical analysis of the kinetic data allows calculation of E_A and E_B as being 835 and 2630 cm^{-1}, respectively. The derived activated rate constants k_1 and k_2 are 1.1×10^7 and 6.7×10^{12} s^{-1}, respectively. Finally, the best fit to the experimental data gives a k_0 value of 2.9×10^4 s^{-1}. These values remain in good agreement with estimates obtained for related complexes[24,25] and indicate that the triplet manifold of **RHQ** is set by the MLCT triplet state localized on the phterpy ligand.

$$k_D = \frac{k_0 + k_1 \exp(-E_A/k_BT) + k_2 \exp(-E_B/k_BT)}{1 + \exp(-E_A/k_BT)} \qquad (1)$$

$$\Delta G^o = -nF(E_{oo} - E_{ox} + E_{red} + E_s) \qquad (2)$$

Spectral analysis[27] of the emission band recorded for **RHQ** in butyronitrile solution indicates that the triplet energy (E_T) is 15560 cm^{-1} and the total reorganization energy accompanying decay of the lowest-energy MLCT triplet is 685 cm^{-1}. This analysis indicates that a medium-frequency vibrational mode of 1370 cm^{-1} is also coupled to deactivation of the MLCT triplet. Taking the measured triplet energy in conjunction with the half-wave potentials recorded for **RHQ**, we can estimate the thermodynamic driving force for light-induced electron transfer within this dyad on the basis of eq 2.[28] Here, E_s refers to the change in electrostatic free energy upon forming the radical pair in a bath of butyronitrile molecules. This term is difficult to calculate precisely because of uncertainties about the distance over which the dipole is separated[29] but lies within the range between −0.18 and −0.12 eV. As such, the overall change in Gibbs free energy associated with light-induced oxidation of the hydroquinone fragment by the MLCT triplet state is ca. +0.50 eV. Clearly, this process is unlikely to compete with nonradiative decay of the excited state. In contrast, the same calculation made for **RQ** indicates that the overall change in Gibbs free energy associated with light-induced reduction of the quinone fragment by the MLCT triplet state is ca. −0.31 eV. This might explain the absence of emission from **RQ** at room temperature.

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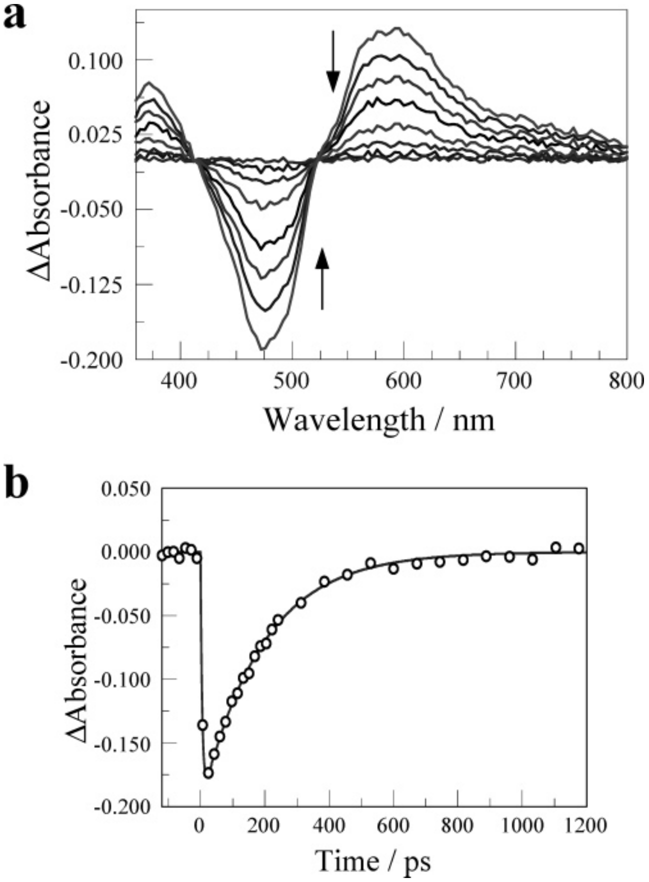

Figure 4. (a) Differential transient absorption profiles recorded for **RQ** at various time delays after 532-nm laser excitation in N_2-purged butyronitrile with a 20-ps laser pulse. (b) Least-squares single-exponential decay kinetics fit to the transient bleach signals.

Illumination of **RHQ** in N_2-purged butyronitrile solution at 22 °C with a 10-ns laser pulse delivered at 532 nm afforded a differential transient absorption spectral profile containing a distinct bleach in the 490-nm region and a broad absorption band centered around 600 nm. Decay of this transient signal follows first-order kinetics at all monitoring wavelengths and corresponds to an averaged lifetime of 46 ± 5 ns. The signal is quenched by the presence of molecular oxygen or benzo-1,4-quinone. It is assigned to the lowest-energy MLCT triplet. Nanosecond laser flash photolysis experiments performed on **RQ** under identical conditions showed only very weak transient records that could be assigned to small amounts of **RHQ** impurity.

Excitation of **RQ** in N_2-purged butyronitrile solution at 22 °C with a 20-ps laser pulse delivered at 532 nm afforded the transient absorption profiles illustrated in Figure 4. The overall appearance of the transient records is remarkably similar to that obtained for **RHQ** using nanosecond flash photolysis. Again, the signal decayed cleanly via first-order kinetics to restore the prepulse baseline, provided fresh samples were used. The average lifetime measured for the MLCT triplet state associated with **RQ** is 190 ± 10 ps. This is considerably shorter than that measured for **RHQ** under similar conditions. Taking account of the electrochemical studies and the fact that benzo-1,4-quinone quenches the triplet state of **RQ**, it seems likely that quenching in **RQ** is due to intramolecular electron transfer from the triplet state to the appended quinone. The rate constant for this step (k_{CS}) can be estimated from eq 3 as being 5.4×10^9 s^{-1} at room temperature. It should be noted that the transient records provided no indication for the intermediate formation of charge-separated products.[30]

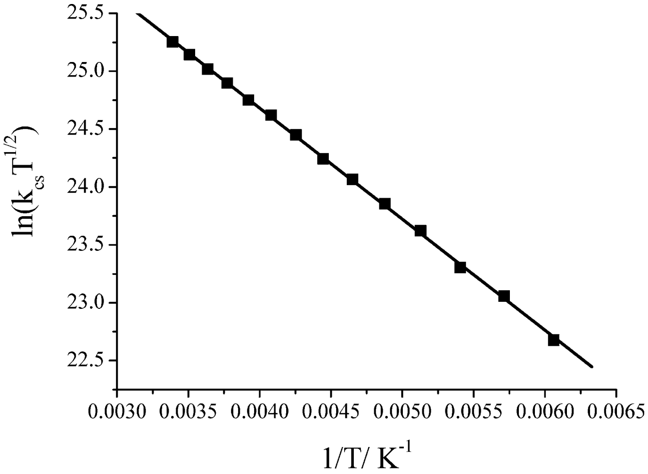

Figure 5. Dependence of the rate of charge separation (k_{CS}) with temperature (T). The solid line represents the optimum least-squares fit to the data points.

$$k_{CS} = \left(\frac{1}{\tau_{RQ}} - \frac{1}{\tau_{RHQ}}\right) \qquad (3)$$

The triplet lifetime recorded for **RQ** in butyronitrile was also found to increase with decreasing temperature. In fluid solution, it was observed that the rate constant for light-induced electron transfer decreased smoothly with decreasing temperature, as might be expected for an activated process. The overall behavior was consistent with classical Marcus theory[31] and, on the basis of Figure 5, allowed calculation of the change in free energy of activation ($\Delta G^{\#}$) as being 0.083 eV. This latter value, when used with the thermodynamic driving force of $\Delta G° = -0.31$ eV, indicates that the total reorganization energy (λ) accompanying electron transfer is 0.84 eV. As such, light-induced electron transfer will fall within the Marcus normal region, but subsequent charge recombination ($\Delta G° = -1.50$ eV) will be inverted. This suggests that charge recombination will be at least as fast as charge separation and might explain why the transient absorption spectral records do not show evidence for the electron-transfer products. Using eq 4 and the intercept of Figure 5, the electronic coupling matrix element (V_{DA}) has a value of 22 ± 2 cm^{-1}. The size of the coupling element is consistent with values found by Mataga et al. for a series of porphyrin−linker−benzoquinone derivatives ($V_{DA} \approx 21-57$ cm^{-1}).[32]

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$$k = \frac{2\pi}{\hbar} \frac{{V_{\mathrm{DA}}}^2}{(4\pi k_{\mathrm{B}} T\lambda)^{1/2}} \exp\left[\frac{-(\Delta G^{\mathrm{o}} + \lambda)^2}{4\lambda k_{\mathrm{B}}\mathrm{T}}\right] \qquad (4)$$

A further factor that might count against the formation of long-lived charge-separated products concerns the nature of the two electron-transfer steps. Thus, production of the MLCT triplet state involves initial charge injection into the acetylene-substituted terpy ligand. This has the effect of directing charge away from the quinone moiety. Electron transfer from the triplet state to the quinone is a relatively long-range process as the electron has to cross the ancillary terpy ligand. Charge recombination, on the other hand, simply requires the electron to move from the π^* orbital on the quinone to the cation (Figure 6). Although spin-forbidden, the presence of the metal ion is likely to promote the charge-recombination step by way of spin−orbit coupling.[33]

At room temperature, the appended quinone in **RQ** quenches the excited triplet state to an extent of ca. 99.6% and essentially extinguishes luminescence. Reversible switching between the quinone/hydroquinone states was made possible by way of luminescence spectroelectrochemistry. This technique[34,35] is not as well developed as other forms of spectroelectrochemistry[36−38] but works well in the present case. Thus, the emission yield for **RHQ** in acetonitrile was monitored as a function of percent oxidation using a setup adapted from that described by Kirchoff.[34] In a typical experiment, the oxidation potential was stepped to +1.0 V vs Ag/AgCl and held at that value for a fixed time. The luminescence recorded from the solution gradually decreased with time as **RHQ** was converted to **RQ**. Similarly, stepping the potential to −0.9 V for fixed time periods reconverted **RQ** to **RHQ** and recovered the luminescence profile (Supporting Information). Although the system displays genuine switching ability at room temperature, it is limited by the poor on/off response. The latter is due to the restricted emission yield from **RHQ**.

It is noted that the two steps that set the on/off level, namely, nonradiative decay of the triplet state in **RHQ** and light-induced electron transfer in **RQ**, are activated processes. The fact that the two activation energies differ markedly provides an opportunity to improve the on/off signal by changing the temperature. Indeed, lowering the temperature causes a significant increase in emission from **RHQ** but a much more modest increase in luminescence from **RQ** in deoxygenated butyronitrile. Temperature has no obvious effect on the electrochemistry, provided the solvent remains fluid. Figure 7 shows the effect of temperature on the on/off ratio; the latter being the ratio of emission yields found upon electrochemical switching between **RHQ** and **RQ**. It is seen that optimal conditions require a temperature of around −100 °C. Here, the on/off ratio is ca. 6300 compared to a room-temperature ratio of ca. 25. At −100 °C, the emission lifetime of **RHQ** is increased to 25 μs, and the luminescence quantum yield is 0.225. The temperature is easily controlled by the rate at which liquid N_2 is evaporated around the spectroelectrochemical cell.

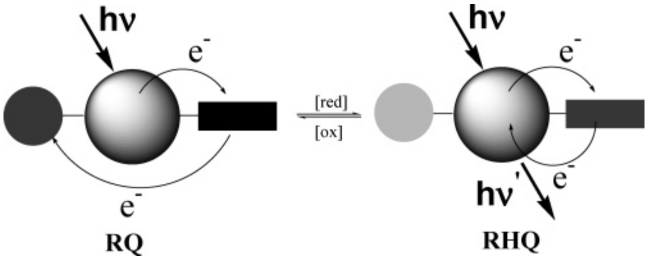

Figure 6. Pictorial representation of directional opto-redox switching in a chromophore−quencher molecular diad.

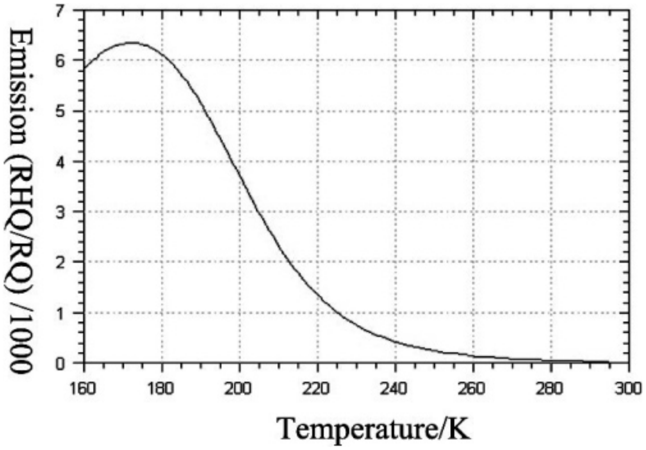

Figure 7. Effect of temperature on the ratio of emission from **RHQ** and **RQ** in N_2-purged butyronitrile.

Conclusion

It has been demonstrated that light-induced electron transfer from the lowest-energy MLCT triplet state of an ethynylated Ru-terpy derivative to a nearby quinone is reasonably efficient and the corresponding hydroquinone is not a quencher. This realization provides the basis for the design of an electroluminescence switch. However, it was necessary to operate the switch at low temperature in order to achieve an acceptable on/off ratio. This is because of the poor luminescence properties of **RHQ**. Having demonstrated the basic principles, there is considerable scope for improving the optical properties of this switch. The most obvious strategy is to replace the terminal phenylene unit on phterpy with pyrene, as this approach is known to greatly prolong

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the emission lifetime.[39] An alternative design would seek to replace the Ru^{II} center with Os^{II} as the latter is more luminescent.[40] It is recognized that the photophysical properties of Os-terpy are less sensitive to changes in temperature and the absorption spectral profile is more attractive than that of Ru-terpy. Attempts are now underway to amalgamate these design features into new optical switches that operate in the solid state at room temperature.

Experimental Section

Raw materials were purchased from Aldrich Chemical Co. and used as received. Solvents were dried by standard literature methods before being distilled and stored under nitrogen over 4 Å molecular sieves.[41] ^1H and ^{13}C NMR spectra were recorded with a JEOL Lambda 500 spectrometer. Routine mass spectra and elemental analyses were obtained using in-house facilities. The starting materials 4′-(2,5-dihydroxyphenyl-2,2′:6′,2″-terpyridine[16] and [$RuCl_3$-(4′-phenylethynyl-(2,2′:6′,2″-terpyridine)][24] were prepared and purified by literature methods.

Cyclic voltammetry was performed using a fully automated HCH Instruments electrochemical analyzer and a three-electrode setup consisting of a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. All experiments were performed in dry CH_3CN containing tetra-*N*-butylammonium tetrafluoroborate (0.2 mol dm^{-3}) as a background electrolyte. Solutions were deoxygenated by purging with dried N_2. Luminescence spectroelectrochemical measurements were carried out in a purpose-built cell adapted from the design described by Kirchoff.[34] The cell was machined from a Teflon block to hold a 1-cm^2 quartz cuvette fitted with a macroreticular carbon electrode (80 pores per inch). Two cylindrical holes of 2-mm diameter were drilled through the electrode in order to provide for excitation and emission ports. The carbon electrode was maintained in contact with a Pt wire counter electrode and a Ag wire reference by way of an upper chamber filled with electrolyte solution. The wire electrodes were maintained in close proximity to the carbon electrode. The solution was thoroughly purged with N_2 prior to electrolysis (Supporting Information).

Absorption spectra were recorded with a Hitachi U3310 spectrophotometer, and fully corrected luminescence spectra were recorded with a Yvon-Jobin Fluorolog tau-3 spectrophotometer. All luminescence measurements were made using optically dilute solutions and were corrected for spectral imperfections of the instrument by reference to a standard lamp. Emission quantum yields were measured relative to ruthenium(II) tris(2,2′-bipyridine).[42] Temperature dependence studies were made with sealed sample cells housed in an Oxford Instruments Optistat DN cryostat. Nanosecond laser flash photolysis studies were conducted at the FRRF housed in the Daresbury Laboratory (Cheshire, United Kingdom). Excitation was achieved with a frequency-doubled, Q-switched Nd:YAG laser (fwhm = 10 ns, $\lambda = 532$ nm). The monitoring beam was provided with a pulsed, high-intensity Xe arc lamp. Picosecond laser flash photolysis studies were performed with a mode-locked frequency doubled Nd:YAG laser (fwhm = 20 ps). The monitoring pulse was a white-light continuum, delayed with respect to the excitation pulse by a computer-controlled optical delay line. The monitoring pulse was dispersed with a Princeton Instruments spectrograph and detected with a dual-diode array spectrometer. Approximately 150 individual laser shots were averaged at each delay line. Solutions for photophysical studies were deoxygenated by purging with N_2 and were thermostated at the desired temperature.

Computational studies were made with the Insight II package run on a silicon graphics workstation. Several geometry optimizations were performed using the semiempirical AM1 method, starting from different initial geometries. All calculations were run in vacuo and in the absence of the counterions.

Preparation of RHQ. A solution of 4′-(2,5-dihydroxyphenyl)-2,2′:6′,2’’terpyridine (**L**) (0.24 g, 0.70 mmol), [Ru(4′-phenylethynyl-2,2′:6′,2’’terpyridine)]Cl_3 (0.38 g, 0.70 mmol), distilled water (12 mL), and triethylamine (12 drops) in methanol (230 mL) was refluxed for 24 h under a dry N_2 atmosphere. The solution was allowed to cool to room temperature before removal of the solvent under reduced pressure. The crude product was dissolved in a minimum of methanol and purified using gel permeation chromatography (Sephadex LH20) with methanol as the eluant. Fractions containing the bright red complex were combined and the volume reduced to 10 mL under reduced pressure. An aqueous 0.1 mol dm^{-3} KPF_6 solution was added slowly to precipitate the desired product. The resultant solid was filtered and washed with distilled water (2 × 20 mL) and diethyl ether (3 × 20 mL). It was air-dried for 10 min and vacuum-dried to produce a dark red compound (0.53 g, 71%). An analytically pure sample for photophysical studies was obtained by dissolving some of the sample in acetonitrile and then performing preparative TLC using alumina plates and an acetonitrile/diethyl ether (3:17) mixture. m.p. >250 °C. ^1H NMR (CD_3CN): δ 8.94 (s, 2H), 8.80 (s, 2H), 8.47−8.43 (apparent t, 4H, $J = 7$ Hz), 7.90−7.81 (m, 4H), 7.75−7.65 (br s, 2H), 7.55−7.45 (m, 3H), 7.38−7.30 (dd, 4H, $J = 5$ Hz and $J' = 11$ Hz), 7.25−7.20 (br s, 1H), 7.16−7.05 (m, 4H), 7.00−6.97 (d, 1H, $J = 9$ Hz), 6.90−6.87 (dd, 1H, $J = 8$ Hz and 2 Hz). ^{13}C NMR (CD_3CN): δ 157.7, 157.2, 154.9, 153.9, 151.9, 151.8, 150.3, 147.9, 146.5, 137.6, 137.5, 131.2, 129.3, 128.2, 127.2, 126.8, 124.6, 124.0, 123.7, 123.1, 120.7, 117.4, 116.8, 116.7, 116.1, 95.8, 85.7, 76.9. Electrospray-MS: *m*/*z* calcd for $[M - PF_6]^+ = 921.1$, found 921.1; *m*/*z* calcd for $[M - 2PF_6]^{2+} = 388.1$, found 388.1. IR (KBr): 3535, 2957, 2216, 1607, 1420, 837 cm^{-1}. Elemental analysis calcd (found) for $C_{44}H_{30}N_6F_{12}O_2P_2Ru{\cdot}Et_2O$: C, 50.58 (50.49); H, 3.54 (3.49); N, 7.37 (7.40).

Preparation of RQ. The following synthetic method was carried out with minimum exposure to light. A solution containing **RHQ** (0.10 g, 0.09 mmol) and DDQ (0.05 g, 0.22 mmol) in acetone (10 mL) was stirred under a N_2 atmosphere for 4 h. Diethyl ether (25 mL) was added, and the precipitate was filtered and washed with diethyl ether (2 × 25 mL). The product was then vacuum-dried to produce a dark red compound (0.07 g, 70%). An analytically pure sample for photophysical studies was obtained by dissolving the solid in acetonitrile and then performing preparative TLC using alumina plates and developing with an acetonitrile/dichloromethane (3:17) mixture. m.p. >250 °C. ^1H NMR $\{9CD_3)_2CO]$: δ 9.28 (s, 2H), 9.25 (s, 2H), 8.97−8.92 (apparent t, 4H, $J = 7$ Hz), 8.16−8.11 (apparent t, 4H, $J = 8$ Hz), 7.88−7.86 (d, 2H, $J = 5$ Hz), 7.81−7.79 (d + s, 4H), 7.62 (br s, 4H), 7.41−7.37 (m, 4H), 7.26−7.23 (d, 1H, $J = 10$ Hz), 7.16−7.12 (dd, 1H, $J = 1$ Hz and $J' = 10$ Hz). ^{13}C NMR $[(CD_3)_2CO]$: δ 188.3, 186.8, 159.4, 159.1, 156.7, 156.6, 154.1, 154.0, 143.6, 142.0, 139.8, 138.6, 138.3, 136.6, 133.3, 132.0, 131.5, 130.3, 129.3, 129.2, 128.9, 126.8, 126.2, 126.1,

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125.3, 122.8, 98.1, 87.8. IR (KBr): 3079, 2214, 1658, 1604, 1422, 1409, 1286, 1224, 1034, 785 cm^{-1}.

Acknowledgment. This work was supported by the EPSRC (GR/R92615/01) and by the University of Newcastle. We thank the EPSRC-supported Mass Spectrometry Service at Swansea (U.K.) for recording the electrospray mass spectra. The nanosecond laser flash photolysis studies were carried out at the FRRF housed at the Daresbury Laboratory.

Supporting Information Available: PDF file containing extra figures and ^{1}H NMR spectrum of **RHQ**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050059C