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Synthesis of a multitopic pyrene–thiophene–anthracene-2,2′:6′,2″-terpyridine array

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Abstract—A one-pot synthesis of a multitopic ligand is described, along with its complexes with zinc(II) and ruthenium(II) cations.

Multitopic ligands containing two or more functional units have been widely developed in the supramolecular photochemistry field for promoting and controlling electron migration at the molecular-scale dimension.[1] Much attention has been focused on mixed-metal complexes containing ruthenium(II) and osmium(II) polypyridyl centres linked via a bridging unit that aids in the electronic coupling, and hence passage of electrons between the metal centres.[2] Candidates for the bridge portion have been varied and include alkenes,[3] alkynes[4] and various aromatic moieties.[5] There has recently been a keen interest in the use of thiophene-based residues for the bridge.[6] In particular, Ziessel and co-workers have focused on bis(ethynylene)-thiophene linkers[7] to promote electronic communication between remote sites. Our attention has concentrated on a related pyrene–ethynylene–thiophene assembly L (Fig. 1) that displays intense charge-transfer (CT) emission, which is associated with a photoexcited pyr$^+$-thio$^-$ state.[8] For this particular ligand, cation binding (e.g., Zn^{2+}) at the 2,2′:6′,2″-terpyridine (terpy) site leads to dramatic luminescence quenching, and formation of an extended dipole from the pyrene to the terpy site. In this specific case the acetylene unit X is a simple conduit for promoting electron migration. In contrast, exchange of X for an alternative electron acceptor gives the opportunity for controlling the extent of electron delocalization along the ligand backbone. Here we describe the use of anthracene as the linker unit X, and the change in luminescence upon zinc cation binding. The complexation of the 'Ruterpy' unit to L_1 further increases the complexity of the array since an alternative photoactive electron donor is introduced.

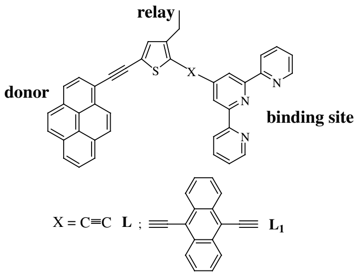

Figure 1. Examples of multitopic ligands incorporating the pyrene–ethynylene–thiophene unit.

The synthesis of L_1 and the corresponding zinc(II) and ruthenium(II) complexes is outlined in Scheme 1. The pyrene–thiophene starting materials **1**[8] and 4′-ethynyl-[2,2′:6′,2″]terpyridine **3**[9] were prepared by literature methods. It has been reported that **2** can be selectively mono-functionalized with **3** to generate a synthon, which contains a single bromide reactive site.[10] In our hands, however, the yield of this product was poor, and a workable quantity of material was difficult to obtain. In fact the major product isolated was the bis(2,2′:6′,2″-terpyridyl-ethynylene)-anthracenyl ligand. This observation led us to believe that incorporation of one terpy unit onto **2** activated the other bromide position. Hence, a 'one-pot' reaction was attempted in which a mixture of **1** and **3** was added slowly to a solution of **2** under

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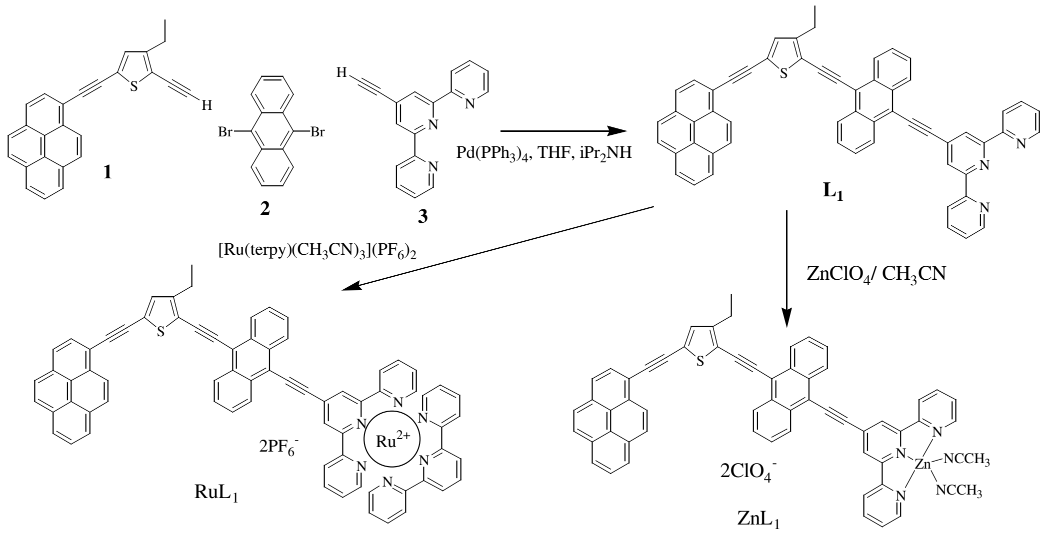

Scheme 1. Synthetic procedures used in the preparation of RuL_1 and ZnL_1.

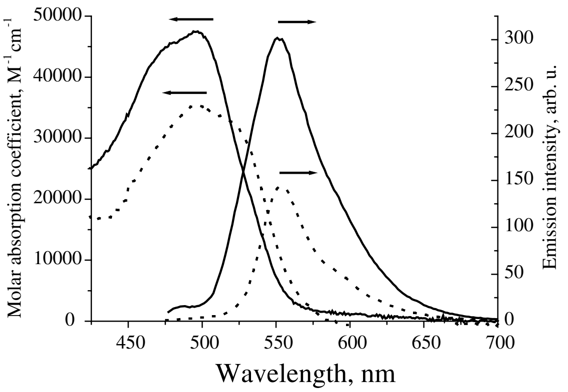

Figure 2. Absorption and emission spectra of L_1 (solid line) and ZnL_1 (dotted line).

standard Sonogashira cross-coupling conditions.[11] Although the outcome of such a reaction could have been a mixture of inseparable cross-coupled products, the ligand L_1 was isolated, albeit in low yield (10%), by very careful column chromatography [silica gel/petrol/ethyl acetate, gradient elution].[12] Reaction of L_1 with $[Ru(terpy)(CH_3CN)_3](PF_6)_2$[13] or $Zn(ClO_4)_2$ afforded the mono-nuclear complexes RuL_1[14] and ZnL_1,[15] respectively. The authenticity of L_1 and its complexes was clearly established by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

The electrochemical behaviour of L_1 in acetonitrile (0.2 M TBATFB background electrolyte) was dominated by poorly reversible redox processes. The oxidative scan cyclic voltammogram displayed a peak at 1.30 V versus Ag/AgCl, which can be assigned to removal of an electron from the pyrene unit. Oxidation of the thiophene group could not be discerned from the solvent cut-off peak. Upon reductive scanning, a quasi-reversible wave was observed at $E_1 = -0.90$ V versus Ag/AgCl and corresponds to reduction of the anthracene unit. The irreversible redox electrochemistry of the thiophene group was observed at a more cathodic potential (E_2) of −1.40 V versus Ag/AgCl. The reductive electrochemistry of the terpy segment of L_1 could not be differentiated from the solvent cut-off peak. Thus, in contrast to L the CT state can be considered to be pyr^+-thio-$anth^-$-terpy in which the thiophene moiety is a conduit for promoting electron migration.

The free ligand L_1 shows moderately strong absorption across the 300–550 nm region, with a broad peak centred at 490 nm (Fig. 2). The compound fluoresces in acetonitrile solution, with the peak maximum lying at ca. 540 nm (Fig. 2). The fluorescence quantum yield (Φ_F) is 0.35 in acetonitrile while the emission lifetime (τ_F) is 1.9 ns. The peak of the fluorescence profile is somewhat sensitive towards the solvent polarity and the observed Stokes shift corresponds to a difference in dipole moment between ground and excited singlet states of 18.9 D.[16] The corresponding triplet excited state can be detected by laser flash photolysis following excitation at 355 nm. The transient differential absorption spectrum shows bleaching of the absorption peak around 490 nm and strong absorption at longer wavelength. The triplet state decays via first-order kinetics with a lifetime of 18 μs in deoxygenated DMSO. Interestingly, the triplet lifetime is hardly affected by the solvent polarity, being 25 μs in deoxygenated cyclohexane. No phosphorescence could be detected in a low-temperature glass, even in the presence of excess iodoethane.

In the presence of a slight excess of zinc perchlorate, the absorption spectrum underwent a small red shift and slight loss of intensity (Fig. 2). There was a corresponding decrease in the fluorescence yield ($\Phi_F = 0.16$) and the appearance of a slight shoulder on the red end of the spectral profile. It was not possible to detect phosphorescence from the 1:1 complex at 77 K but the intermediate population of the triplet state was con-

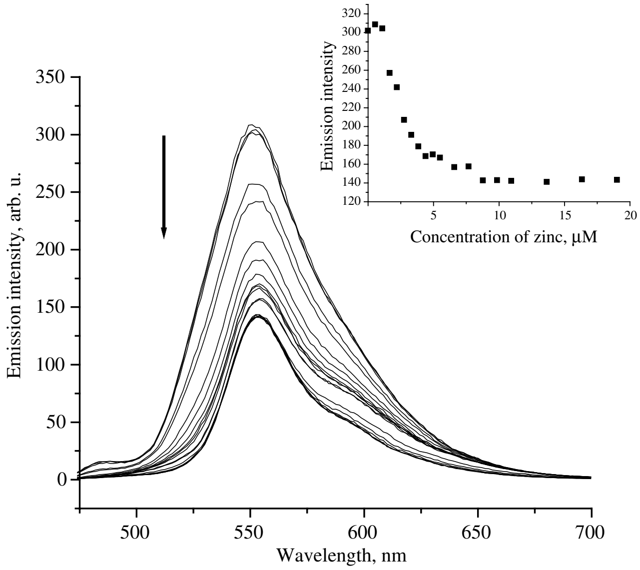

Figure 3. Changes in the fluorescence profile of L_1 (concn = 2.8×10^{-6} M) upon addition of aliquots of $Zn(ClO_4)_2$. Insert shows this change graphically.

firmed by laser flash photolysis. Here, the triplet lifetime was found to be 95 μs in deoxygenated DMSO. Progressive addition of zinc perchlorate to a solution of L_1 in acetone caused partial extinction of the fluorescence (Fig. 3). The fluorescence yield reached a plateau value (~50% of the original intensity) at higher concentrations of cation, presumably corresponding to the emission yield of the 1:1 complex. Fitting the titration data to a successive complexation model gave overall stability constants for $\log\beta_1$ and $\log\beta_2$, respectively, of 4.7 and 10.1. As such, there seems to be no real sign of positive cooperativity for forming the 1:2 complex.

$$\beta_1 = \frac{\left[(\mathrm{ZnL}_1)^{2+}\right]}{[\mathrm{Zn}^{2+}][L_1]}$$

$$\beta_2 = \frac{\left[(\mathrm{Zn}(L_1)_2)^{2+}\right]}{[\mathrm{Zn}^{2+}][L_1]^2}$$

It should be noted that zinc(II) binding to L_1 does not lead to complete electron delocalization onto the terpy ligand; this is in contrast to what is observed with L. Hence, quenching of the fluorescence from L_1 is likely a result of enhanced triplet formation, by way of heavy-atom perturbation of the anthracenyl unit by the adjacent zinc(II) cation.

Ligand L_1 also coordinates ruthenium(II) cations in the form of the bis(2,2′:6′,2″-terpyridine) complex. The absorption spectrum recorded for this complex is similar to that found for L_1 but contains a pronounced shoulder around 500 nm that can be attributed to the metal-to-ligand, charge-transfer band localized on the metal complex. Interestingly, this molecule appears not to emit in deoxygenated acetonitrile at ambient temperature. This suggests that the triplet state localized on the ligand lies at lower energy than the MLCT triplet state associated with the terminal metal complex.

Acknowledgements

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12. Analytical data L_1 ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.53$ (t, 3H, $J = 7.6$ Hz, CH_3), 3.11 (q, 2H, $J = 7.6$ Hz, CH_2), 7.42 (s, 1H, CH_{thio}), 7.47 (m, 2H, CH_{terpy}), 7.78 (m, 4H, CH_{anth}), 7.98 (td, 2H, $J = 7.8$ Hz, $J' = 1.8$ Hz, 2H, CH_{terpy}), 8.09–8.32 (m, 8H, CH_{pyrene}), 8.68 (d, 1H, $J = 9.2$ Hz, CH_{pyrene}), 8.71 (m, 2H, CH_{anth}), 8.75 (d, 2H, $J = 7.9$ Hz, CH_{terpy}), 8.85 (m, 6H, $4\times CH_{terpy}$, $2\times CH_{anth}$). ^{13}C NMR (125.65 MHz, $CDCl_3$) = 14.79, 23.46, 88.36, 90.73, 94.00, 94.05, 95.50, 100.38, 117.07, 117.37, 119.26, 119.81, 121.43, 122.64, 124.12, 124.26, 124.43, 124.56, 125.36, 125.72, 125.79, 126.30, 127.04, 127.09, 127.22, 127.33, 128.38, 128.45, 128.55, 129.42, 131.04, 131.23, 131.50, 131.67, 131.82, 131.95, 132.05, 132.13, 132.43, 132.70, 133.40, 137.01, 149.18, 155.67. HR-MS (EI) calcd for $C_{57}H_{33}N_3S$: 791.2395, found 791.2388.
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(d, 2H, $J = 8.6\,\text{Hz}$, CH_{anth}), 8.95 (d, 2H, $J = 8.6\,\text{Hz}$, CH_{terpy}), 9.08 (s, 2H, CH_{terpy}). ESI-MS values for $C_{72}H_{44}N_6SRuP_2F_{12}$; m/z 1271.4 for M−[PF$_6$], $m/z =$ 563.4 for M−2[PF$_6$].

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