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Towards molecular T-junction relays

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Abstract—The synthesis of a ditopic 2,2′:6′,2″-terpyridine ligand and bis-ruthenium(II) complex is described which incorporates in its molecular backbone a light-activated spiropyran moiety.

Effective methods of controlling rate and directionality of electron migration along molecular-scale wires will need to be addressed if the technology these systems promise is to be realized.[1] It is recognized that efficient and fast electron migration could be maintained in an organic wire if there is proficient orbital overlap between connecting subunits.[2] Mastering this challenge will hopefully see the emergence in the near future of molecular-scale assemblies capable of manipulating information over distances of 100–200 Å.[3] Real wires, however, contain junctions along their path which when selectively activated alter the direction of electron flow. To perform such a task at the molecular level requires the design and synthesis of sophisticated assemblies. So far we have observed the emergence of 'molecular switches' capable of performing on/off tasks,[4] but the added sophistication of coupling this to electron directionality is yet to be fully realized. Hence, we have taken on the challenge of creating molecular-scale assemblies capable of directing electron migration along disparate pathways. To ensure fast gating a photon initiated process has been deemed crucial if we are to achieve this goal. The basic design idea is conceptually illustrated in Figure 1, and the term T-junction relay is coined to describe the mode of action. Electron flow via D to A_1 is the dominant photoinitiated process which is switched off upon activation of the T-junction arm via a second photon controlled event. Charge migration then proceeds via the alternative pathway of D to A_2. In designing such a T-junction assembly we have identified linear ditopic 2,2′:6′,2″-terpyridine complexes[5] as critical, which incorporate in the bridge a light-activated spiropyran moiety. Spiropyrans have found wide applications in switching devices since they readily undergo ring opening into their coloured merocyanine-based form which display disparate photophysical properties.[6,7]

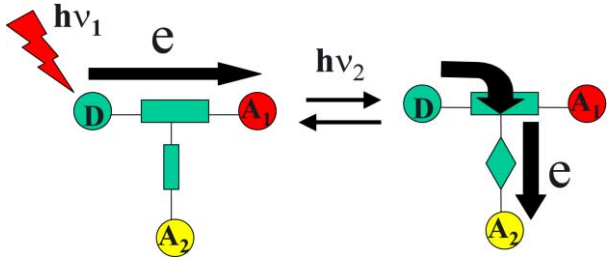

Figure 1. Pictorial representation of a T-junction relay.

The strategy selected for functionalization of the spiropyran is outlined in Scheme 1 for the particular case of equipping the system with terminal ruthenium(II) bis(2,2′:6′,2″-terpyridine) complexes. It should be noted that prior work has shown that such metal complexes are photoactive only if substituted with an electron-withdrawing group like an alkyne.[8] It is known that the extent of electron delocalization along the molecular axis at the triplet level in such photoactive dyads is controlled by the degree of π-electron conjugation over the bridging polytopic ligand. It is our conjecture that the extent of electron delocalization and direction will be controlled, at least to some degree, by the open or closed state of the spiropyran group.

The ditopic ligand $\mathbf{L}_1$ was prepared in six steps starting from the readily prepared 2,5-dibromobenzene-1,4-diol **1**.[9] Although it has been reported that **1** is selectively converted to the mono-aldehdye[10] using Duff's reac-

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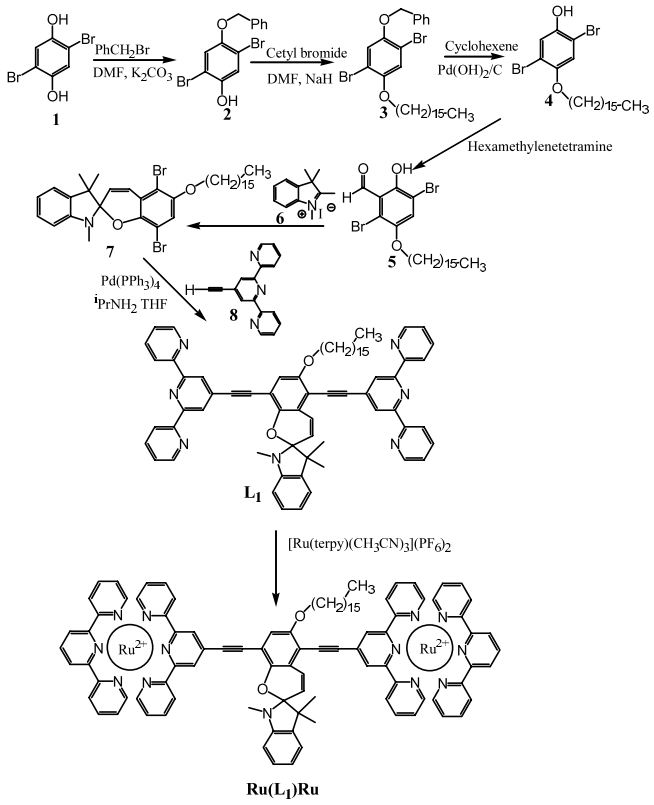

Scheme 1. Synthetic methods used in the preparation of $\mathbf{L}_1$ and Ru($\mathbf{L}_1$)Ru.

tion, in our hands the yields were extremely low. Since we required for solubility reasons a lipophilic alkyl group attached to $\mathbf{L}_1$, it was decided to carry this out before introducing the aldehyde functional group. Hence, compound **1** was firstly monoprotected using benzyl bromide to afford **2** in a modest, yet unoptimised, 59% yield. Reaction of **2** with NaH in DMF and cetyl bromide produced **3** in 80% yield. Deprotection of the benzyl ether was carried out by the H-atom transfer method using cyclohexene/$Pd(OH)_2$ to afford **4** in almost quantitative yield. Reaction of **4** using standard Duff chemical conditions proceeded smoothly (60% yield), and introduced the carbonyl functional group into the aromatic ring with the required regioselectivity. Spiropyran **7** was prepared by reaction of **5** with **6** in good yield (60%) despite the existence of the bulky groups. Coupling of **7** to 4′-ethenyl- [2,2′:6′,2″]-terpyridine **8**[11] was carried out using Sonogashira cross-coupling conditions[12] to yield after careful column chromatography (silica gel, petrol ether:ethyl acetate (17:3)) ditopic ligand $\mathbf{L}_1$ in 13% yield.[13] It was noticed that the reaction did not go to completion and that starting materials were recovered from the reaction mixture. We can only surmise that the catalyst gets poisoned during the coupling reaction, and so this reaction will require further study. Reaction of $\mathbf{L}_1$ with $[Ru(terpy)(CH_3CN)_3](PF_6)_2$[14] produced the complex Ru($\mathbf{L}_1$)Ru which was purified by column chromatography (basic alumina: CH_3CN/0.1M KNO_3(19:1)).[15]

Irradiation of an acetonitrile N_2–purged solution of $\mathbf{L}_1$ at room temperature with UV-visible light ($\lambda > 350$ nm) resulted in the appearance of a blue solution that rapidly converted back to its original yellow colour. The colour changes are fully consistent with ring opening to generate the merocyanine form, and thermal reformation of the spiropyran. Unfortunately, the rapid colour change prohibited collection of the room temperature UV-visible spectrum of the open form. However, at lower temperatures the colouration of the solution lasted much longer. Illustrated in Figure 2 is the UV-visible spectrum of $\mathbf{L}_1$ recorded at 288 K in acetonitrile before and after irradiation.[16] At this temperature the ring closure reaction is slow enough to permit collection of the merocyanine form spectrum. Reformation of the spiropyran closed form was monitored by decay of the signal at $\lambda = 665$ nm over time, and least-squares fitted to a single exponential decay to afford a rate constant k of 9×10^{-3} s^{-1}. Rate constants were also collected over a modest temperature range (263–293 K) to afford an activation energy $E_a = 91$ kJ mol^{-1} and a pre-exponential factor $A = 3.2\times10^{14}$. These results are particularly encouraging since the switching action of the ligand is fast and reversible.

Detailed molecular orbital calculations were performed on $\mathbf{L}_1$ in the open and closed forms to ascertain the relative energies and sites of the HOMO and LUMO orbitals.[17] The molecular orbital diagrams illustrated in Figure 3 clearly show that there is significant perturbation of the molecular orbitals. In the closed form (Fig. 3**A**) the HOMO/LUMO orbitals clearly reside on the linear portion of the bridge unit and span across the two 2,2′:6′,2″-terpyridyl ligands. In contrast the HOMO/LUMO orbitals of the open form (Fig. 3**B**) are more localized on the merocyanine portion of the ligand. Thus, we can speculate that for the complex Ru($\mathbf{L}_1$)Ru the MLCT state, which is known to involve the LUMO of the ligand, will span across both terminals in the closed form, but delocalise onto the T-junction relay in the open form. Current detailed photophysical studies are underway on complex Ru($\mathbf{L}_1$)Ru in the two different states to ascertain if this is the case, and will be reported elsewhere at a later date.

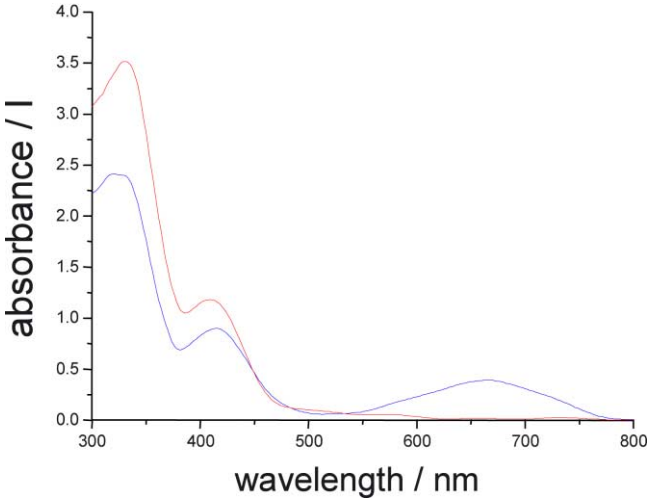

Figure 2. UV-visible spectrum of $\mathbf{L}_1$ (conc. = 0.097 mmol) in acetonitrile before (red) and after (blue) irradiation.

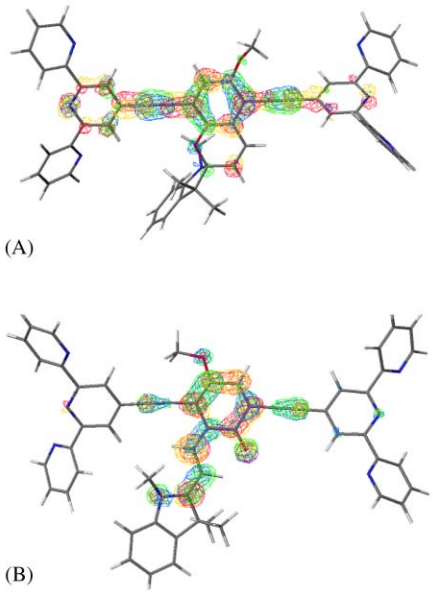

Figure 3. Representation of the HOMO/LUMO molecular orbitals of a methyl chain modified version of $\mathbf{L}_1$ in the closed form (**A**) and open form (**B**).

Acknowledgements

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13. Analytical data $\mathbf{L}_1$: ^{1}H NMR (500 MHz, $CDCl_3$) $\delta=0.79$ (m, 3H, CH_3), 0.97–1.37 (m, 26H, $C_{13}H_{26}$), 1.51 (s, 6H, $2\times CH_{3gem}$), 1.88 (m, 2H, CH_{2alkyl}), 2.72 (s, 3H, N-CH_3), 3.99 (t, 2H, $J=6.4$ Hz, CH_{2alkyl}), 5.89 (d, 1H, $J=10.35$ Hz, CH_{db}), 6.50 (d, 1H, $J=8.0$ Hz, CH_{ph},), 6.60 (t, 1H, $J=7.5$ Hz, CH_{ph}), 6.80 (s, 1H, CH_{ph}), 6.97 (t, 1H, $J=7.6$ Hz, CH_{ph}), 7.04 (d, 1H, $J=7.3$ Hz, CH_{ph},), 7.31 (m, 4H, 4 x CH_{terpy}), 7.40 (d, 1H, $J=10.40$ Hz, CH_{ph}), 7.81 (m, 4H, $4\times CH_{terpy}$), 8.04 (s, 2H, $2\times CH_{terpy}$), 8.46 (d, 2H, $J=8.0$ Hz, $2\times CH_{terpy}$), 8.56 (s, 2H, $2\times CH_{terpy}$), 8.58 (d, 2H, $J=8.4$ Hz, $2\times CH_{terpy}$), 8.68 (d, 2H, $J=4.3$ Hz, $2\times CH_{terpy}$), 8.70 (d, 2H, $J=4.4$ Hz, $2\times CH_{terpy}$). ^{13}C NMR (125.65 MHz, $CDCl_3$) $\delta=14.11$, 20.44, 22.68, 25.14, 26.20, 29.27, 29.35, 29.48, 29.67 (8C), 31.92 (2C), 51.82 (2C), 69.76 (2C), 87.67, 89.07, 93.37, 97.42, 105.14, 107.04, 110.47, 115.57, 119.30, 121.27 (2C), 121.31 (2C), 122.45, 122.77 (4C), 123.84 (2C), 124.01 (2C), 127.37, 133.31, 133.43, 136.75 (2C), 136.89 (2C), 148.17, 149.10 (2C), 149.20 (2C), 149.73, 153.40, 155.52, 155.61, 155.74, 155.93. (Note: 7 quaternary carbons are coincidental with other aromatic resonances). HR-MS calculated for $C_{69}H_{69}N_7O_2$: 1027.5513. Found: 1027.5450.
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15. Analytical data Ru($\mathbf{L}_1$)Ru: ^{1}H NMR (500 MHz, CD_3CN): $\delta=0.54$ (t, 3H, $J=7.2$ Hz, CH_{3alkyl}), 0.64–0.88 (m, 26H, $CH_{13}H_{26}$), 0.89 (s, 3H, CH_{3gem}), 1.02 (s, 3H, CH_{3gem}), 1.10 (m, 2H, CH_{2alkyl}), 3.03 (s, 3H, N-CH_3), 3.81 (t, 2H, $J=6.1$ Hz, CH_{2alkyl}), 5.80 (d, 1H, $J=10.4$ Hz, CH_{db}), 6.30 (d, 1H, $J=7.6$ Hz, CH_{ph}), 6.53 (td, 1H, $J=7.2$ Hz, $J'=0.9$ Hz, CH_{ph}), 6.74 (td, 1H, $J=6.5$ Hz, $J'=1.3$ Hz, CH_{ph}), 6.85 (m, 8H, $6\times CH_{terpy}$, $2\times CH_{ph}$), 7.04 (d, 2H, $J=4.8$ Hz, $2\times CH_{terpy}$), 7.07 (d, 2H, $J=5.2$Hz, $2\times CH_{terpy}$), 7.31 (s, 2H, $2\times CH_{terpy}$), 7.35 (m, 5H, 4 x CH_{terpy}, CH_{db}), 7.40 (d, 2H, $J=4.0$ Hz, $2\times CH_{terpy}$), 7.41 (d, 2H, $J=3.7$ Hz, $2\times CH_{terpy}$), 7.43 (d, 2H, $J=3.6$ Hz, $2\times CH_{terpy}$), 7.61 (m, 8H, 8 x CH_{terpy}), 8.11 (t, 2H, $J=8.2$ Hz, $2\times CH_{terpy}$), 8.17 (d, 2H, $J=7.7$ Hz, $2\times CH_{terpy}$), 8.21 (d, 2H, $J=7.9$ Hz, $2\times CH_{terpy}$), 8.26 (d, 2H, $J=8.3$ Hz, $2\times CH_{terpy}$), 8.44 (d, 2H, $J=8.2$ Hz, $2\times CH_{terpy}$), 8.52 (s, 2H, $2\times CH_{terpy}$). ESI-MS results showed multiple fragment ions from breakdown of the cetyl chain. Calcd. for $C_{99}H_{90}N_{13}O_2Ru_2P_4F_{24}$ $m/z=339.17$ find 339.2 for $[M-4PF_6-H^+]^{5+}$.
16. In a typical experiment the sample in a sealed cuvette was cooled to the required temperature using a fully automated Oxford Instruments Optistat cryostat. The sample was then irradiated in the sample chamber via a fibre optic cable using light ($\lambda>350$ nm) from a Dolan–Jenner Fibre Lite PL-800 white light generator.
17. Molecular orbital calculations were performed using the commercial package Gaussian 98 at the ZINDO level. (a) Thompson, M. A.; Zerner, M. C. *J. Am. Chem. Soc*. **1991**, *113*, 8210; (b) Zerner, M. C. In *Reviews of Computational Chemistry*; Lipkowitz, K. B.; Boyd, D. B. Eds; VCH Publishing, New York, 1991, vol. 2, 313; (c) Zerner, M. C.; Correa de Mello, P.; Hehenberger, M. *Int. J. Quant. Chem*. **1982**, *21*, 251; (d) Hanson, L. K.; Fajer, J.; Thompson, M. A.; Zerner, M. C. *J. Am. Chem. Soc*. **1987**, *109*, 4728.