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Cation Chelating [2]Catenanes and Cyclophanes based on 2,2'-Bipyridine.

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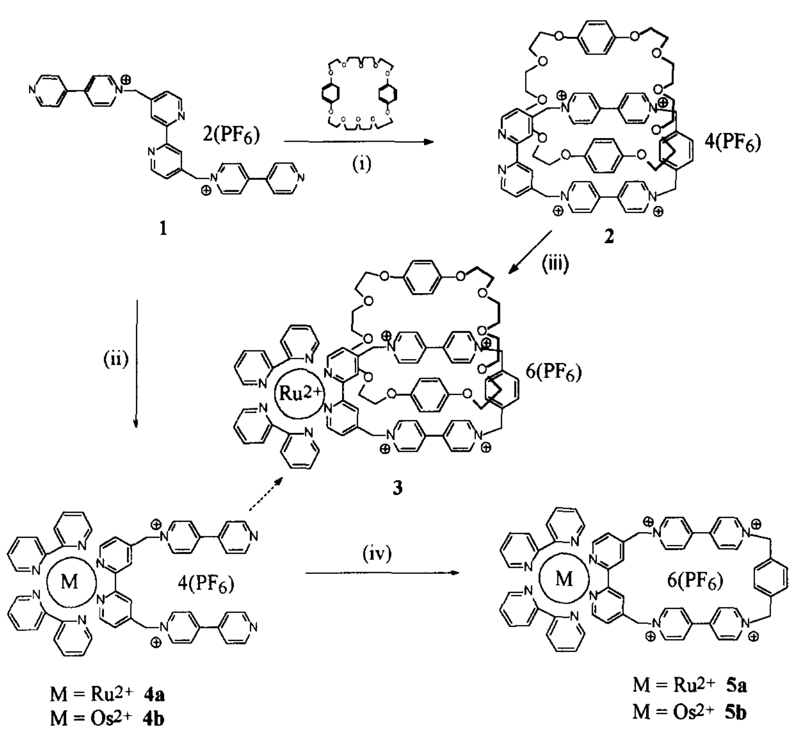
Abstract: Several tetracationic N,N'-bipyridinium-based [2]catenanes and cyclophanes have been synthesised containing, as part of the overall structure, the cation chelating 2,2'-bipyridyl (bipy) subunit. The metal binding unit is used to generate photoactive ruthenium(II) and osmium(II) assemblies, and a potential site for further metal cluster formation.

Construction of molecular architectures in which an individual component is triggered by external stimulus to bring about large-scale conformational changes, or initiate a vectorial electron cascade reaction, is a rapidly expanding field of supramolecular science.[1-3] Particular attention has focused on the [2]rotaxane and counterpart [2]catenane supramolecular species,[4] incorporating such diverse units as porphyrins,[5,6] anthracenes[7] and azobenzene[8] moieties, that are able to be activated by light illumination or redox changes. More recently, however, there has been an increased interest in the preparation of hybrid molecular species incorporating both metal binding and donor-acceptor moieties as prototypes for *ionactive* molecular switches.[9] This amalgamation of discordant functional groups is appealing as selective activation in one segment of a molecule controls its overall mechanical performance. To this end, we considered whether this hybrid approach to molecular engineering could be used to manipulate photophysical or electronic traits of an assembly, and in particular to specifically control a photoinduced electron transfer pathway.

Herein, we accordingly report the synthesis of 2,2'-bipyridyl-based cyclophanes in which the chelator unit is built-in so as to explicitly bind exogenous metal ions such as ruthenium(II) and osmium(II), or produce metallic clusters. In general, the light focusing antenna are further covalently coupled to two rigidly-held chemically identical electron acceptors, whose redox potential can be altered by the introduction or removal of donor-acceptor interactions.



Scheme 1 Reagents and Conditions. (i) α,α'-dibromo-*p*-xylene, ambient temperature, 7 days, SiO_2 column chromatography, $MeOH/NH_4Cl(aq)/MeNO_2$ (14:5:1), 20% yield, (ii) Ethylene glycol/10% H_2O, *cis*-/Ru(bipy)$_2$Cl$_2$], 4-6 hrs, SiO_2 chromatography, 62% yield, or *cis*-[Os(bipy)Cl$_2$], 160 °C, SiO_2 chromatography, 27% yield. (iii) *cis*-[Ru(bipy)$_2$Cl$_2$], $MeOH/H_2O$ (1:1), sephadex® chromatography, 68% yield, (iv) α,α'-dibromo-*p*-xylene, CH_3CN, reflux, 7-9 days, column chromatography: (5a) sephadex®, CH_3CN, 70% yield, (5b) Al_2O_3 $MeOH/NH_4Cl(aq)/MeNO_2$ (7:2:1), and sephadex®, CH_3CN, 60% yield.

The general procedure used in the synthesis of the outlined metallo-architectures is depicted in Scheme 1. Reaction of 4,4'-*bis*(bromomethyl)-2,2'-bipyridine[10] with 2.2 equivalents of 4,4'-bipyridine affords, after recrystallisation from acetone/water, derivative **1** in a reasonable yield of 43%.[11] Although the synthetic procedure for formation of viologen containing [2]catenanes is now well established[12] its applicability to reaction mixtures in which an unfavourable starting material conformation has to be overcome (as shown) has not been tested. Despite the ground-state *transoid* bipyridyl conformation in 1, cyclisation to the [2]catenane 2 is possible, albeit in rather low yield.[13] Subsequent reaction of 2 with an equimolar amount of *cis*-[Ru(bipy)$_2$Cl$_2$][14] in refluxing aqueous methanol, followed by careful column chromatography, generates the photoactive [2]catenane 3.[15] Although successful in preparing 2, our attempts to prepare an uncatenated version by replacing **34C10**[16] with a single π-stacking hydroquinol-based thread resulted in rather limited success, as a great deal of starting material 1 and oligomeric products dominated the reaction mixtures.[17] Purification of these mixtures by column chromatography with varying solvents met with rather limited success. We attribute this restricted cyclisation to the template being unable to create adequate associative interactions (*e.g.* donor-acceptor, hydrogen bonding) to form sufficient amounts of precursor for ring closure (Figure 1). At this stage, however, we cannot rule out the possibility that a better electron-donating thread, increased pressures, or a different synthetic strategy would produce improved yields. As the major goal was to produce metal-based systems it was considered a better option to prearrange 1 to the desired conformer before cyclisation by attaching $[M(bipy)_2]^{2+}$ units, where M = Os^{2+} or Ru^{2+}. Refluxing aqueous ethylene glycol solutions of 1 with equimolar amounts of *cis*-$[M(bipy)_2Cl_2]$[14], M= Ru^{2+}, Os^{2+}, followed by thorough silica gel column chromatography produced 4a and 4b in respectable yields.[18] Using high-dilution conditions to avoid polymerisation, α,α'-dibromo-*p*-xylene was added slowly to a heated solution of 4a or 4b in acetonitrile and left refluxing for an average of 6-9 days. Extensive chromatographic purification of the crude reaction mixtures yielded the metallo-cyclophanes 5a and 5b in unoptimised yields of 70% and 60%, respectively.[19] As a completion to the synthetic applicability of precoordination, it also seems possible to produce analogues of 3 directly from 4a using the previously described self-assembly method.[20]

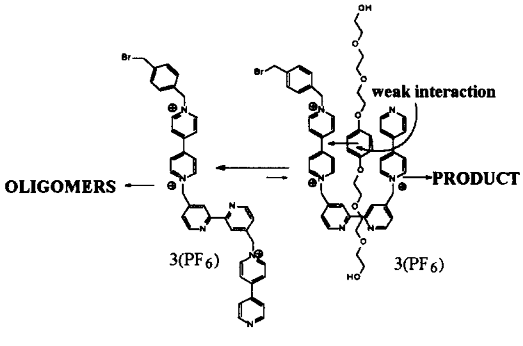


Figure 1

The potential use of cyclophanes 2, 3, 5a and 5b and precursors as nanoscale devices is limited only by the imagination. Although future applications are intriguing, more importantly they represent a class of compounds specifically designed and constructed in which their electronic properties are readily perturbed by external factors (*e.g.* protonation of the bipy unit in 4). Perhaps more significantly, the presence of the "free" bipy ligand in 2 is consummate for construction of larger metallic clusters containing spatially well-resolved redox- and photo-active donor-acceptor [2]catenanes.

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10. Prepared according to the literature method with one minor modification that the solvent mixture was CCl_4/CH_2Cl_2(9:1). see: Gould, S.; Strouse, G. F.; Meyer, T. J.; Sullivan, P. B.; *Inorg. Chem.* **1991**, 30, 2942-2949.
11. Analytical data **1** ^{1}H NMR (d$_6$-acetone) 360MHz: 6.23 (s, 4H); 7.61-7.65 (d,d, 2H, J= 2Hz, J= 5Hz); 7.98-8.01 (d, 4H, J=6.2Hz); 8.46-8.47 (d, 2H, J=1Hz); 8.66-8.69 (d, 4H, J= 7Hz); 8.72-8.74 (d,d, 2H, J= 5Hz, J'= 0.7Hz; 8.79-8.82 (d, 4H, J= 6.2Hz); 9.37-9.40 (d, 4H, J=7Hz) FAB-MS (NBA matrix) m/z = 639 (M-PF$_6$)$^+$; 493 (M-2PF$_6$)$^+$.
12. Stoddart, J. F.; Philp, D. *Synlett*, **1991**, 7, 445-458 and references therein.
13. Analytical data **2** ^{1}H NMR (d$_6$-acetone) 360MHz, 298K: 3.46 (m, 8H); 3.61 (m, H); 3.89-3.93 (m,16H); 6.08 (s, 4H); 6.15 (s, 4H); 7.94 (m, 2H); 8.00 (s, 4H); 8.10-8.14 (2xd, 8H, J= 8Hz); 8.18 (m, 2H); 8.90-8.92 (d, 2H, J= 5Hz); 9.27-9.29 (d, 4H, J= 5.2Hz); 9.32-9.34 (d, 4H, J= 7Hz). Note: Owing to relatively fast interchange of the bound/unbound hydroquinol groups of the interlocked crown ether moiety eight protons are missing. The appropriate signals are severely broadened into the baseline but upon cooling of the sample can be located. FAB-MS (NBA matrix) m/z = 1569 (M-PF$_6$)$^+$; 1425 (M-2PF$_6$)$^+$; 1280 (M-3PF$_6$)$^+$; 1135 (M-4PF$_6$)$^+$.
14. *cis*-[M(bipy)$_2$Cl$_2$], where M= Os^{2+} and Ru^{2+}, prepared according to: Kendrick, M. S.; Dawson, J. H. *Inorg. Chimica. Acta.* **1985**, 97, L41.
15. Analytical data **3** ^{1}H NMR (d$_6$-acetone) 360MHz, 298K: 3.45-3.48 (m, 4H); 3.61-3.63 (m, 8H); 3.69-3.72 (m, 8H); 3.79-3.85 (m, 12H); 3.93-4.10 (m, 4H); 6.10 (s, 4H); 6.23 (s, 4H); 6.26 (s, 4H); 7.57-7.73 (q, 4H, J=7.5Hz); 7.92-7.94 (d, 2H, J= 5.6Hz); 7.98 (s, 4H); 8.00-8.02 (d, 2H, J= 5.3Hz); 8.02-8.22 (m, 10H); 8.23-8.31 (g, 4H, J= 7.8Hz); 8.34-8.36 (d, 2H, J= 5.7Hz); 8.82-8.87 (m, 6H); 9.34-9.36 (d, 4H, J= 5Hz). Electrospray-MS (CH$_3$CN,H$_2$O,HCOOH (0.1%)) m/z = 661 (M-3PF$_6$)$^{3+}$; 460 (M-4PF$_6$)$^{4+}$; 339 (M-5PF$_6$)$^{5+}$.
16. The acronym **34C10** corresponds to 1,4,7,10,13,20,23,26,29,32-decaoxa[13.13]paracyclophane.
17. A FAB mass spectrum of the crude reaction mixture shows clusters of peaks at m/z = 1032 (M-PF$_6$)$^+$; 888 (M-2PF$_6$)$^+$; 743 (M-3PF$_6$)$^+$ consistent with the "free" cyclophane ligand. Other peaks in the mass spectral records are also compatible with products in which one and two α,α'-dibromo-*p*-xylenes had reacted and formed oligomers.
18. Analytical Data **4a** ^{1}H NMR (d$_6$-acetone) 360MHz 298K: 6.28 (s, 4H); 7.55 (m,4H); 7.65 (d, 2H, J= 5.7Hz); 7.96-8.01 (m, 8H); 8.11-8.22 (m, 6H); 8.62 (d, 4H, J= 6.4Hz); 8.75-8.91 (m, 6H); 9.05 (m, 4H); 9.28 (d, 4H, J= 6.3Hz). FAB-MS (NBA + CH$_3$CN matrix): 1343 (M-PF$_6$)$^+$; 1197 (M-2PF$_6$)$^+$; 1052 (M-3PF$_6$)$^+$. Elemental analysis: calc. $C_{56}H_{52}N_{10}P_4F_{24}Ru_1$ C: 43.02%, H: 3.35%, N: 8.96% found C: 42.91%, H: 3.21%, N: 9.05%. UV-Visible (acetone): λ_{max} (nm) 355; 395; 455.

    Analytical Data **4b** ^{1}H NMR (d$_6$-acetone) 360MHz, 298K: 6.31 (s, 4H); 7.47 (m, 6H0; 7.84-7.99 (m, 10H); 8.25 (d, 4H, J= 6.4Hz); 8.65 (d, 4H, J= 6.9Hz); 8.73-8.74 (m, 6H); 9.04 (m, 4H); 9.30 (d, 4H); J= 8.9Hz). Electrospray-MS (CH$_3$CN/H$_2$O (2:1) + HCOOH (0.1%)): m/z = 1433 (M-PF$_6$)$^+$; 1287 (M-2PF$_6$)$^+$; 1141 (M-3PF$_6$)$^+$. UV-Visible (acetone) λ_{max} (nm): 255; 290; 370; 425; 495.
19. Analytical Data **5a** ^{1}H NMR (d$_6$-acetone) 360MHz, 298K: 6.15 (s, 4H); 6.25 (s, 4H); 7.79-7.55 (m, 12H); 7.90 (s, 4H); 7.91-8.11 (m, 4H); 8.23 (m, 4H); 5.51 (d, 4H, J= 6.2 Hz); 8.70-8.85 (m, 6H); 9.33-9.55 (m, 8H). FAB-MS (NBA + CH$_3$CN matrix): m/z = 1737 (M-PF$_6$)$^+$; 1591 (M-2PF$_6$)$^+$; 1446 (M-3PF$_6$)$^+$. UV-Visible (CH$_3$CN) λ_{max} (nm): 250; 295; 420; 480.

    Analytical Data **5b** ^{1}H NMR (d$_6$-acetone) 360MHz 298K: 6.12 (s, 4H); 6.15 (s, 4H); 7.45 (m, 6H); 7.74-7.86 (m, 6H); 7.91 (s, 4H); 7.92 -8.10 (m, 4H); 8.51 (d, 4H, J=7.9Hz); 8.60 (d, J= 7.2Hz); 8.75 (m, 6H); 9.29 (d, 4H, J= 6.8Hz); 9.47 (d, 4H, J= 7.6Hz) Electrospray-MS (MeCN): m/z = 840 (M-2PF$_6$)$^{2+}$; 512 (M-3PF$_6$)$^{3+}$; 348 (M-4PF$_6$)$^{4+}$. UV-Visible (CH$_3$CN) λ_{max} (nm): 255; 295; 370; 430; 490.
20. Using the asymmetric crown **46C14** this general method of ring closure has been used to generate metallated catenanes, the results of which are to be published later.

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