Pergamon

SCIENCE @ DIRECT®

Tetrahedron Letters 44 (2003) 3947–3949

TETRAHEDRON
LETTERS

Controlling the torsion angle via adventitious cation binding

Andrew C. Benniston,* Peiyi Li and Craig Sams

Molecular Photonics Laboratory, School of Natural Sciences (Chemistry), University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK

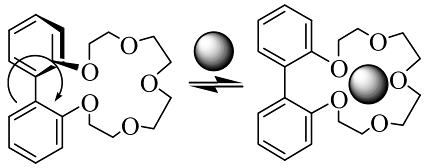
Received 12 February 2003; revised 12 March 2003; accepted 21 March 2003

Abstract—We report herein the synthesis of a linear binuclear ruthenium(II) complex, and the corresponding free ligand, for which the organic connector is a geometrically-constrained crown ether that binds added cations. © 2003 Elsevier Science Ltd. All rights reserved.

A growing problem in the field of molecular-scale electronics concerns how to control and vary the angle between adjacent subunits so as to optimise electronic connectivity along the molecular axis. In an effort to address this issue, we note that certain crown ethers bind added cations in such a way that their average conformation changes according to the nature of the cation.[1] In particular, the level of structural control imposed on the crown ether is effected by the size, shape, charge and polarizability of the guest cation.[2] This is particularly evident in the modification in the shape and rigidity of simple crown ethers upon binding alkali and alkali earth metal cations of differing ionic radii.[3] Numerous intricate superstructures have been synthesised over the past decade that incorporate crown ethers intended to provide a means by which to modify the overall physical and chemical properties upon cation binding.[4] Specific examples include molecular-scale fluorescent reporters for metal ions,[5] anion sensors,[6] switches,[7] and molecular wires.[8]

There have been few attempts, however, to use the crown ether as a modulator by including it as a ratchet by which to tighten the angle between adjacent phenylene units. Thus, we have focussed attention on the biphenylene-based crown ether, **DP17-C-5**, which has the polycycle linked through the 2,2′-positions of a biphenylene group. This compound has the necessary functionality to bind added cations within its central cavity (Fig. 1). This cavity is relatively small but, because of the biphenylene unit, is highly flexible by way of rotation of one of the phenylene rings. Furthermore, the biphenylene unit is easily functionalised with, for example, photoactive transition metal complexes attached at one or both of the 4,4′-positions. The strategy selected for functionalisation of the crown ether 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.[9] It is well known that the extent of electron delocalisation 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.[10] It is our conjecture that the extent of electron delocalisation will be controlled, at least to some degree, by the torsion angle between the central phenylene rings. The novel crown ether strap introduced here is intended to provide the necessary variation in torsion angle.

In this communication, we describe the synthesis of the functionalised ligand $\mathbf{L_1}$ and the corresponding ruthenium(II) bis(2,2′:6′,2″-terpyridine) complex. To better illustrate the feasibility of our approach we include the results of computer molecular modelling studies carried



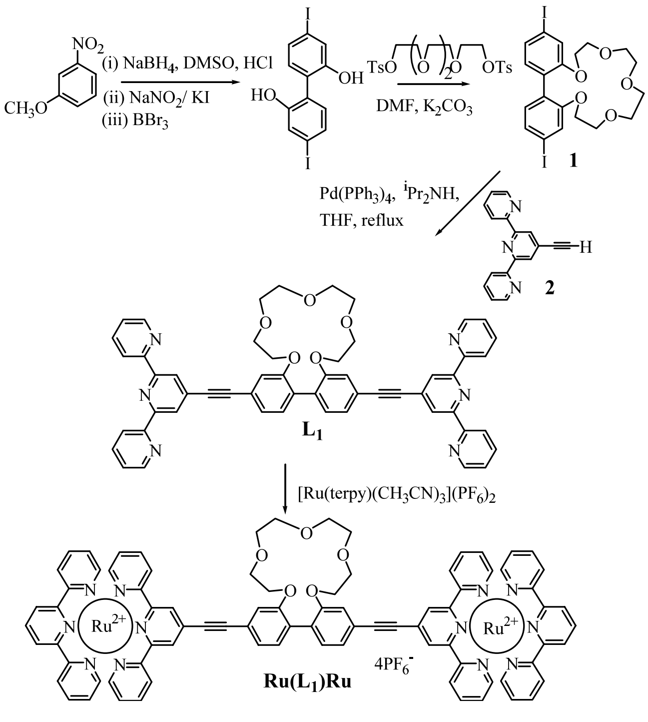
DP17-C-5

Figure 1.

---

* Corresponding author. Tel.: +44 (0)191 222 5706; fax: +44 (0)191 222 6929; e-mail: a.c.benniston@ncl.ac.uk

doi:10.1016/S0040-4039(03)00753-6



Scheme 1. Synthetic procedure used in the preparation of $\mathbf{L_1}$ and $[Ru(\mathbf{L_1})Ru](PF_6)_4$.

out for the molecular fragment comprising the central crown ether and added cations. Results for the extent of electron delocalisation at different stages of excitation will be reported elsewhere.

The synthetic protocol used for preparation of $\mathbf{L_1}$ is illustrated in Scheme 1, starting from the readily available 3-nitroanisole. Using a slight adaptation of the literature procedures[11,12] this starting material can be converted in three steps to 4,4′-diiodo-2,2′-biphenol, with an overall yield of 16%. Following the reported procedure for cyclisation of related structures,[13] the crown ether macrocycle **1**[14] was prepared in a respectable 35% yield. Derivative **1** was subsequently coupled to 4′-ethenyl-[2,2′:6′,2″]terpyridine **2**[15] using standard Sonogashira conditions[16] and purified by column chromatography (basic alumina: EtOAc/petrol) to afford the ditopic ligand $\mathbf{L_1}$ in an unoptimized yield of 43%.[17] The corresponding binuclear complex $Ru(\mathbf{L_1})Ru$ was afforded by refluxing $\mathbf{L_1}$ with $[Ru(terpy)(CH_3CN)_3](PF_6)_2$[18] in a $CHCl_3/MeOH/CH_3COCH_3$ mixture. The crude reaction product was purified by extensive column chromatography [basic alumina, $Et_2O/CH_3CN/H_2O$] and anion exchange with KPF_6. The purity of the resultant complex was deemed to be satisfactory on the basis of standard analytical techniques.[19]

The key feature of this system is the ability to vary and control the torsion angle between the central phenylene rings by including cations into the crown ether void. As such, a set of detailed molecular dynamics simulations was carried out on $\mathbf{L_1}$ both in the absence and presence of added cations (H^+, Li^+, Na^+, K^+, Rb^+, NH_4^+).[20] Snap-shots of some of the resultant structures are shown in Figure 2 whilst the corresponding biphenylene torsion angles and the Pauling radius of the cation are collected in Table 1. The size of the macrocyclic polyether ring is consummate for the binding of small cations and, as a consequence, H^+, Li^+ and Na^+ cations are seen to sit comfortably within the guest cavity. It should be noted that the proton migrates between identical sites within the polycycle, binding to three adjacent O atoms at any given time, such that this structure is highly dynamic. For the larger cations (K^+, Rb^+, NH_4^+), the pocket provided by the polyether is too small to permit complete ion encapsulation, and the cations necessarily reside outside the macrocycle core.

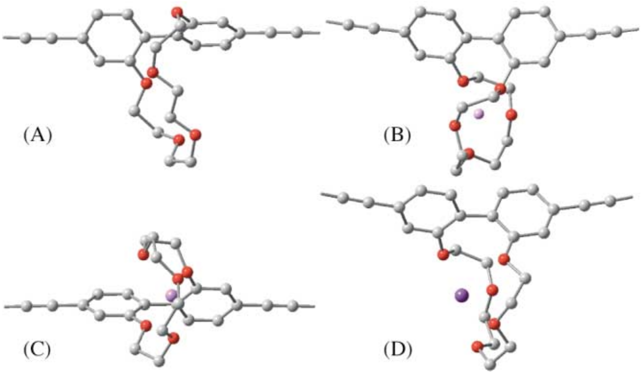


Figure 2. Computer generated ball and stick representations of the biphenylene portion of $\mathbf{L_1}$ (A) and in the presence of Li^+ (B), Na^+ (C) and Rb^+ (D) cations. The calculations were carried out in vacuo.

Table 1.

Cation	Dihedral angle[a] (°)	Variation in dihedral angle[b] (°)	Pauling cation radius (Å)[c]
None	142.59	76.7–159	–
H^+	59.86	22.9–98.0	–
Li^+	50.89	25.5–95.1	0.60
Na^+	61.95	30.8–104	0.95
K^+	79.71	34.3–156	1.33
Rb^+	83.29	49.5–146	1.48
NH_4^+	81.32	39.7–142	1.48

[a] Dihedral angle taken from the energy-minimized structure.

[b] Taken from molecular dynamics simulations, details of which are described in the text.

[c] Taken from Ref. 25.

We note throughout the series Na^+ to NH_4^+ there is a good correlation between the calculated biphenylene torsion angles and the Pauling cation radii. Specifically, the two phenylene rings become more orthogonal with increasing cation radius. Similar control of molecular structure upon cation binding has been reported for somewhat related biphenylene, bipyridyl and thiophene-based crown ether assemblies.[21–24]

It is important to note, however, that there is considerable flexibility within these structures. This is apparent from molecular dynamics simulations that report on the total variation in the torsion angle during the lifetime of the cation complex (Table 1). Even so, the energy-minimised structures provide clear indications that the dihedral angle about the central biphenylene unit can be controlled over a wide variation by this strategy. It now remains to establish whether-or-not cation complexation can alter the degree of electron delocalisation along the molecular axis.

Acknowledgements

This work was supported by the Engineering and Physical Sciences Research Council (GR/23305/01). We thank the EPSRC Mass Spectrometry Facility at Swansea and Professor A. Harriman for many helpful discussions.

References

1. Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351.
2. Steed, J. W. *Coord. Chem. Rev.* **2001**, *215*, 171.
3. Christensen, J. J.; Hill, J. O.; Izatt, R. M. *Science* **1971**, *174*, 459.
4. Tanaka, M.; Nakamura, M.; Salhin, M. A. A.; Ikeda, T.; Kamada, K.; Ando, H.; Shibutani, Y.; Kimura, K. *J. Org. Chem.* **2001**, *66*, 1533.
5. Sasaki, S.; Hashizume, A.; Citterio, D.; Fujii, E.; Suzuki, K. *Tetrahedron Lett.* **2002**, *43*, 7243.
6. Beer, P. D.; Dent, S. W. *Chem. Commun.* **1998**, 825.
7. McSkimming, G.; Tucker, J. H. R.; Bouas-Laurent, H.; Desvergne, J. P.; Coles, S. J.; Hursthouse, M. B.; Light, M. E. *Chem. Eur. J.* **2002**, *8*, 3331.
8. Ballardini, R.; Balzani, V.; Clemente-Leon, M.; Credi, A.; Gandolfi, M. T.; Ishow, E.; Perkins, J.; Stoddart, J. F.; Wenger, S. *J. Am. Chem. Soc.* **2002**, *124*, 12786.
9. Harriman, A.; Ziessel, R. *Coord. Chem. Rev.* **1998**, *171*, 331.
10. Harriman, A.; Hissler, M.; Ziessel, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4203.
11. Feiring, A. E.; Auman, B. C.; Wonchoba, E. R. *Macromolecules* **1993**, *26*, 2779.
12. Goodson, F. E.; Wallow, T. I.; Novak, B. M. *Macromolecules* **1998**, *31*, 2047.
13. Simpson, J. E.; Daub, G. H.; Hayes, F. N. *J. Org. Chem.* **1973**, *38*, 1771.
14. Analytical data (**1**): ^{1}H NMR ($CDCl_3$) $\delta = 3.54$–3.71 (m, 4H, CH_2CH_2), 3.73–3.83 (m, 4H, CH_2CH_2), 3.95–4.01 (m, 4H, CH_2CH_2), 4.13–4.21 (m, 4H, CH_2CH_2), 6.85 (d, 2H, $J = 7.8$ Hz, Ar-H$_6$), 7.29 (d, 2H, $J = 1.5$ Hz, Ar-H$_3$), 7.33 (dd, 2H, $J = 7.8$ Hz, $J' = 1.5$ Hz, Ar-H$_5$). MS(EI) $m/z = 596$ (M$^+$).
15. (a) Potts, K. T.; Konwar, D. *J. Org. Chem.* **1991**, *56*, 4815; (b) Constable, E. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1405; (c) Grosshenny, V.; Romero, F. M.; Ziessel, R. *J. Org. Chem.* **1997**, *62*, 1491.
16. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.
17. Analytical data (**L$_1$**): ^{1}H NMR ($CDCl_3$) $\delta = 3.60$–3.74 (m, 4H, CH_2CH_2), 3.83–3.87 (m, 4H, CH_2CH_2), 4.05–4.16 (m, 4H, CH_2CH_2), 4.26–4.33 (m, 4H, CH_2CH_2), 7.21–7.25 (m, 6H, Ar-H$_{3,5\ \mathrm{and}\ 6}$), 7.38 (ddd, 4H, $J = 7.5$ Hz, $J' = 4.8$ Hz, $J'' = 1.2$ Hz, terp-H$_{5,5''}$), 7.90 (td, 4H, $J = 7.7$ Hz, $J' = 1.8$ Hz, terp-H$_{4,4''}$), 8.62 (s, 4H, terp-H$_{3'}$), 8.65 (m, 4H, terp-H$_{3,3''}$), 8.75 (m, 4H, terp-H$_{6,6''}$). ^{13}C NMR ($CDCl_3$) $\delta = 68.4$, 69.9, 71.3, 71.4, 87.7 ($C{\equiv}C$), 94.3 ($C{\equiv}C$), 115.5, 121.5, 122.9, 123.1, 124.3, 124.6, 129.5, 131.5, 133.7, 137.2, 149.5, 155.8, 156.0, 156.6. MS(EI) $m/z = 854$ (M$^+$). Elemental analysis calcd (found) for $C_{54}H_{42}N_6O_5$ C, 75.86 (75.99); H, 4.95 (4.95); N, 9.83 (9.80).
18. Suen, H. F.; Wilson, S. W.; Pomerantz, M.; Walsh, J. L. *Inorg. Chem.* **1989**, *28*, 786.
19. Analytical data [Ru(**L$_1$**)Ru](PF$_6$)$_4$ ^{1}H NMR ($CDCl_3$) $\delta =$ 3.58–3.66 (m, 4H, CH_2CH_2), 3.81–3.85 (m, 4H, CH_2CH_2), 4.15–4.19 (m, 4H, CH_2CH_2), 4.36–4.41 (m, 4H, CH_2CH_2), 7.15–7.21 (m, 8H, terp-H$_{4,4''}$), 7.35–7.40 (m, 10H, Ar-H$_6$, terp-H$_{3,3''}$), 7.46 (dd, 2H, $J = 7.6$ Hz, $J' = 1.5$ Hz, Ar-H$_5$), 7.49 (d, 2H, $J = 1.5$ Hz, Ar-H$_3$), 7.91–7.97 (m, 8H, terp-H$_{5,5''}$), 8.43 (t, 2H, $J = 8.2$ Hz, terp-H$_{4'}$), 8.46–8.53 (m, 8H, terp-H$_{6,6''}$), 8.76 (d, 4H, $J = 8.2$ Hz, terp-H$_{3'}$), 8.89 (s, 4H, terp-H$_{3'}$). MALDI-MS (dithranol matrix) $m/z = 1523.5$ (M−4PF$_6$)$^+$, 1189.4 (M−Ru(terpy)4PF$_6$)$^+$, 762.2 (M−4PF$_6$)$^{2+}$. Elemental analysis calcd (found) for $C_{84}H_{64}N_{12}O_5Ru_2P_4F_{24}{\cdot}2H_2O$ C, 47.16 (47.03); H, 3.20 (2.81); N, 7.86 (7.81).
20. Molecular dynamics and geometry optimisation calculations were carried out using the Discover 3 module available in Insight II running on a Silicon Graphics O2 workstation. For all calculations, partial charges were assigned using the ESFF force field parameter. In a typical simulation optimised geometries were obtained using the Newton method, and subsequent molecular dynamics calculations were performed over a period of 200 ps with a step function of 1 fs. All molecular structures and subsequent calculations were performed in the gas phase.
21. (a) McFarland, S. A.; Finney, N. S. *Chem. Commun.* **2003**, 388; (b) McFarland, S. A.; Finney, N. S. *J. Am. Chem. Soc.* **2002**, *124*, 1178.
22. Lindsten, G.; Wennerström, O.; Isaksson, R. *J. Org. Chem.* **1987**, *52*, 547.
23. McFarland, S. A.; Finney, N. S. *J. Am. Chem. Soc.* **2001**, *123*, 1260.
24. Marselle, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214.
25. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry—A Comprehensive Edition*; 4th ed.; 1980; p. 14.