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Synthesis of new viologen macrocycles with intramolecular charge transfer

Elena Pía, Rosa Toba, Marcos Chas, Carlos Peinador* and José Mª Quintela*

Departamento de Química Fundamental, Facultad de Ciencias, Universidade da Coruña, Campus A Zapateira s/n, 15071 A Coruña, Spain

Abstract—The syntheses of three new macrocycles composed of an acceptor (viologen) and a donor (dioxoaryl) are reported. These compounds exhibit intramolecular charge transfer and their X-ray analyses revealed that the aromatic systems are situated in parallel planes with a mean interplanar distance of 3.32 Å.
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4,4′-Bipyridinium dication salts (usually called viologens) are a well-known electron-deficient components in many supramolecular structures. Their electrochemical behavior, synthetic availability, and electronic properties make them ideal components for the synthesis of many supramolecular assemblies.[1] Viologen acceptor character has been widely used in many charge-transfer (CT) complexes, particularly with polycyclic arenes[2] including rotaxanes and catenanes.[3] It is well known that the CT complex between a π electron-donor and viologen as acceptor requires that the donor and the acceptor units pack closely in a suitable geometry. The optimal interplanar distance between donor and acceptor parts is about 3.4 Å.[4] The CT complex formation is associated with the appearance of a characteristic broad band in the UV–vis spectrum.[5]

Intramolecular charge-transfer (ICT) compounds are composed of donor and acceptor parts linked by a σ or π bond bridge. Topics of interest for ICT compounds include molecular electronic devices,[6] organic metals,[7] chromophores for dyes[8] and nonlinear optics,[9] excited-state energy transfer processes (including synthetic light-harvesting systems).[10] Surprisingly, ICT compounds incorporating viologen units have remained relatively rare.[11]

In this letter, we report the synthesis of new cyclophanes with intramolecular charge-transfer composed of an acceptor (viologen) connected to a donor (dioxoaryl) by a polyether chain.

Scheme 1 outlines the synthesis of macrocycles **3a–c·2PF$_6$**. Reaction of diols **1a–c**[12] with mesyl chloride afforded derivatives **2a–c** in high yields. Nucleophilic displacement of mesyl groups with 4,4′-bipyridine in high dilution conditions gave macrocycles **3a–c·2PF$_6$** in moderate yields after counter anion exchange. Compound **3a·2PF$_6$** was obtained as a light yellow powder, **3b·2PF$_6$** as an orange solid, and macrocycle **3c·2PF$_6$** as a dark violet powder. All these compounds were well characterized by ^{1}H NMR, ^{13}C NMR, MS, UV–vis, and elemental analyses.[13]
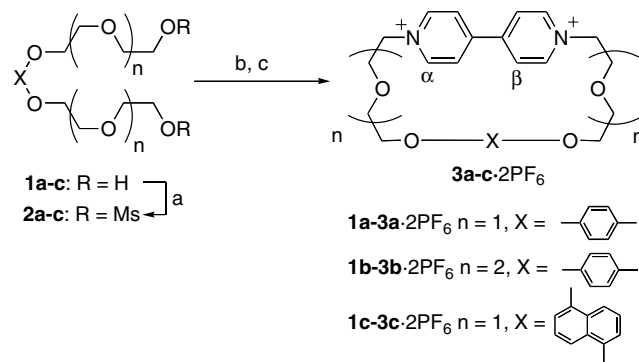
Scheme 1. Reagents and conditions: (a) CH$_3$SO$_2$Cl, NEt$_3$, CH$_2$Cl$_2$, rt, 3 h; (b) 4,4′-bipyridine, KI, CH$_3$CN, 70 °C, 4 d; (c) NH$_4$PF$_6$, H$_2$O.

* Corresponding authors. Tel.: +34 981 167000; fax: +34 981 167065; e-mail addresses: capeveqo@udc.es; jqqoqf@udc.es
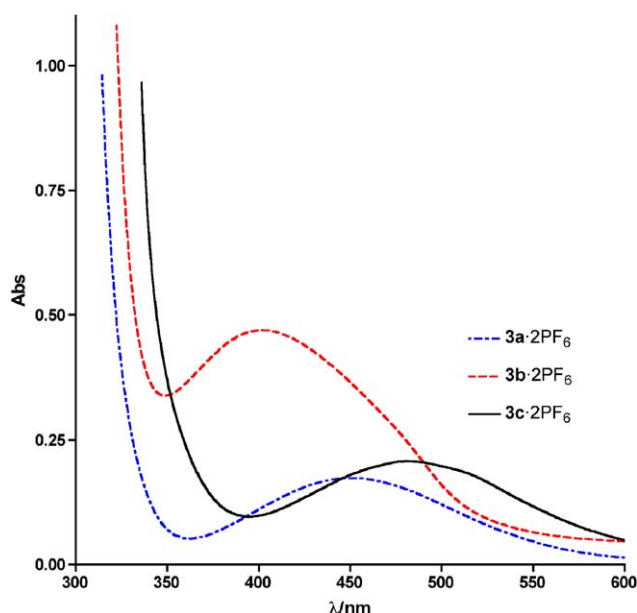
Figure 1. Absorption spectra of **3a–c**·2PF$_6$ measured in acetonitrile solutions at room temperature.

The electron-accepting power of the viologen moiety in combination with the electron donor aromatic groups gives rise to intramolecular charge-transfer absorptions. The longest-wavelength absorption maximum of the macrocycles **3a–c**·2PF$_6$ appears at $\lambda = 450$, 403, and 481 nm, respectively (Fig. 1). The hypsochromic shift observed between **3a** and **3b** is probably due to the fact that in the charge-transfer state of the cyclophanes both the bipyridinium and the hydroquinone rings should bear positive charges, resulting in a repulsion of the donor and acceptor, which becomes more pronounced, the shorter the polyether chains. Linear correlations (see Supplementary data) between absorption and concentration are observed, indicating the absence of intermolecular interactions.

On irradiation of the bipyridinium protons of macrocycle **3a**·2PF$_6$, in addition to enhancement of the neighboring protons, transannular NOEs arising from the dioxoaryl protons were also observed. The intensities of the transannular NOEs were about 15% of those of the normal NOEs of the neighboring bipyridinium protons. The enhancements of the dioxoaryl hydrogen signals were generally more pronounced on irradiation of the inner bipyridinium hydrogen atoms β than on irradiation of the outer bipyridinium hydrogen atoms α. Macrocycle **3c**·2PF$_6$ also shows transannular NOEs but there are not significant differences between α and β protons. These NOEs evidently demonstrate approaches of the donor and acceptor units in the cyclophanes **3b,c**·2PF$_6$ for at least several hundreds of milliseconds.

The molecular structures of **3a–c**·2PF$_6$ were determined by single-crystal X-ray analysis (Fig. 2).[14] Single crystals were obtained by diffusion of isopropyl ether into a solution of **3a–c**·2PF$_6$ in acetonitrile. The X-ray analysis of cyclophanes with the short polyether chain ($n = 1$) **3a,c**·2PF$_6$ revealed the expected structure in which the
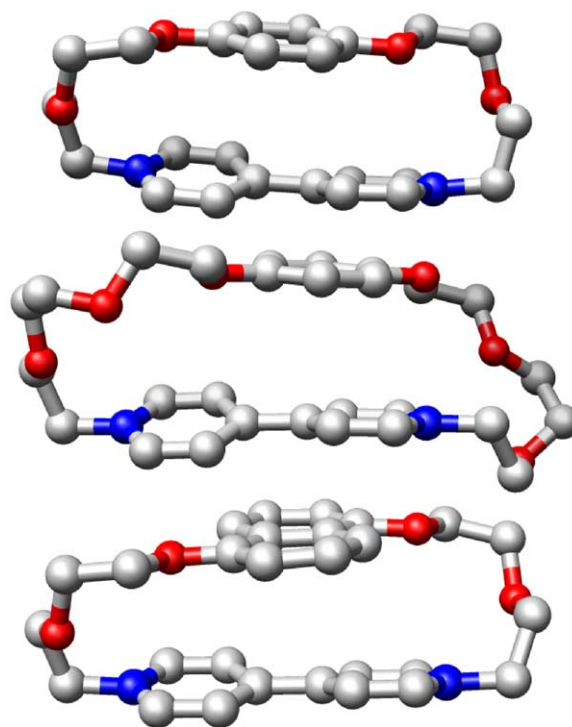

Figure 2. Crystal structures of **3a**·2PF$_6$ (top), **3b**·2PF$_6$ (middle), **3c**·2PF$_6$ (bottom). Solvent molecules and PF$_6$ anions are omitted for clarity.

aromatic systems are situated in parallel planes with a mean interplanar distance of 3.34 and 3.32 Å, respectively (Table 1). The plane described by the hydroquinol residues extends to include not only the phenoxymethylene units as expected but also the next carbon atom in each direction along the polyether chains. The bipyridinium units are distorted from the normal planar geometry, involving both twisting ($\theta = 20°$ and 18°) and bowing ($\tau = 17°$ and 18°) of their aromatic rings. Compounds **3a,c**·2PF$_6$ present a C_2 axis passing through the centroids of the bipyridinium and dioxoaryl ring systems because the aromatic donor component is centered with respect to the central C–C bond within the bipyridinium.

The cyclophanes **3a,c**·2PF$_6$ pack in the crystal to form π-stacked structures, the dioxoaryl ring system of one

Table 1. Distances (Å) and angles (°) characterizing the geometries of macrocycles **3a–c**·2PF$_6$

Compound	d^b	ϕ^c	θ^d	τ^e
3a·2PF$_6$	3.34	20	2.5	17
3b·2PF$_6$[a]	3.32	23	4.2	0
3c·2PF$_6$	3.32	18	1.2	18

[a] For **3b** the angle θ was defined as the angle between the hydroquinone and the pyridine planes, and d is the mean interplanar distance between dioxoaryl and pyridinium units.
[b] Mean interplanar distance between dioxoaryl and bipyridinium units.
[c] The torsional angle about the central C–C bond within the bipyridinium.
[d] The angle between mean dioxoaryl and bipyridinium planes.
[e] The bowing of the bipyridine residues is expressed by the angle τ, subtended by the two N$^+$–CH$_2$ bonds emanating from the bipyridinium rings.
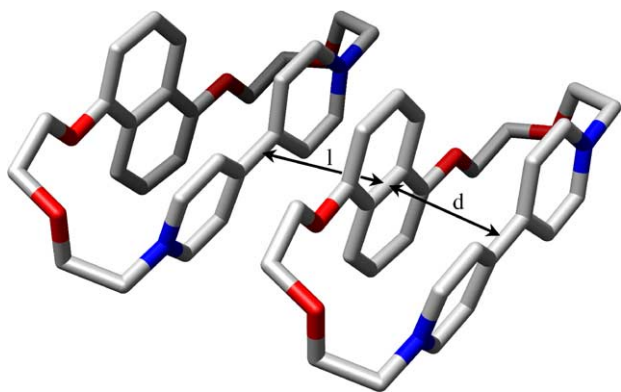
Figure 3. A perspective view of the two independent molecules found in the crystal structure of **3c**·2PF$_6$ showing mean interplanar distances $d = 3.32$ Å and $l = 3.26$ Å.

molecule being aligned parallel with the bipyridinium units of the next (Fig. 3). The mean interplanar separation of the extended π-systems is $l = 3.33$ Å for **3a**·2PF$_6$ and 3.26 Å for **3c**·2PF$_6$.

The solid-state geometry (Fig. 2) of the macrocycle **3b**·2PF$_6$ departs from the C_2 symmetric arrangement observed for the other two macrocycles. In this case, the dioxoaryl ring system is displaced with respect to the molecular C_2 axis, such that it is positioned preferentially over one of the pyridinium rings of the bipyridinium unit. The mean interplanar separation between the hydroquinone ring and this pyridinium ring is 3.32 Å. In contrast to **3a,c**·2PF$_6$, there is no bowing of the bipyridine residue, probably due to the longer polyether chains that connect both aromatic systems. Moreover, there are no additional π-stacking interactions that extend beyond the molecule.

In summary, we synthesized new viologen cyclophanes composed by an acceptor part (bipyridinium) and a donor (dioxoaryl) part. The appearance of a characteristic broad band in the UV–vis spectra confirms a charge-transfer interaction. The crystal structures of the three compounds revealed the intramolecular proximity of the bipyridinium and dioxoaryl moieties; furthermore, in **3a** and **3c** this proximity is also intermolecular with mean interplanar distances of 3.33 and 3.26 Å, respectively.

Acknowledgements

Supplementary data

UV–vis dilution experiments in acetonitrile solutions for **3a,c**·2PF$_6$ can be found as supplementary data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.01.073.

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13. General procedure for **3a–c**. To a solution of 4,4′-bipyridine (0.219 g, 1.40 mmol) in CH$_3$CN (200 ml) a solution of **2a–c** (1.54 mmol) in CH$_3$CN (10 ml) and a catalytic amount of KI were added. The reaction was stirred at 70 °C for 72 h. After cooling, the solvent was evaporated in vacuo and the residue was triturated with ether (250 ml). The solid was purified by flash chromatography (acetone/1.5 M NH$_4$Cl/MeOH 5:4:1). The product-containing fractions were combined, and the solvents were removed in vacuo. The residue was dissolved in water (20 ml), and a saturated solution of NH$_4$PF$_6$ was added. The precipitate was filtered and washed with water to yield

3a–c·2PF$_6$. Compound **3a**: yield: 32%. ^{1}H NMR (300 MHz, CD$_3$CN): $\delta = 3.60$ (m, 4H), 3.79 (m, 4H), 4.10 (m, 4H), 4.74 (m, 4H), 6.39 (s, 4H), 8.15 (d, $J = 6.9$ Hz, 4H), 8.85 (d, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (CD$_3$CN): $\delta = 63.1$, 68.4, 69.8, 70.6, 115.4, 126.7, 146.7, 148.9, 152.8 ppm. MS (FAB): $m/z = 553$ (M−PF$_6^-$)$^+$, 408 (M−2PF$_6$)$^+$, 204 (M−2PF$_6^-$)$^{2+}$. Anal. Calcd for C$_{24}$H$_{28}$F$_{12}$N$_2$O$_4$P$_2$ (698.13): C, 41.27; H, 4.04; N, 4.01. Found C, 41.33; H, 4.26; N, 3.92. Compound **3b**: yield: 22%. ^{1}H NMR (300 MHz, CD$_3$CN): $\delta = 3.6$–3.9 (m, 10H), 4.01 (m, 5H), 4.11 (m, 5H), 4.80 (m, 4H), 6.79 (s, 4H), 7.79 (d, $J = 6.9$ Hz, 4H), 8.95 (d, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (CD$_3$CN): $\delta = 62.1$, 68.9, 69.1, 70.2, 70.4, 70.8, 116.3, 127.1, 147.2, 150.6, 153.9 ppm. MS (FAB): $m/z = 787$ (MH)$^+$, 641 (M−PF$_6^-$)$^+$, 496 (M−2PF$_6^-$)$^+$, 248 (M−2PF$_6^-$)$^{2+}$. C$_{28}$H$_{36}$N$_2$O$_6$P$_2$F$_{12}$ (786.52); calcd: C, 42.76; H, 4.61; N, 3.56; enc: C, 42.53; H, 4.34; N, 3.80. Compound **3c**: yield: 30%. ^{1}H NMR (300 MHz, CD$_3$CN): $\delta = 4.01$ (s, 8H), 4.18 (m, 4H), 4.73 (m, 4H), 6.69 (d, $J = 7.5$ Hz, 2H), 7.29 (m, 4H), 7.55 (d, $J = 6.9$ Hz, 4H), 8.74 (d, $J = 6.9$ Hz, 4H) ppm. ^{13}C NMR (CD$_3$CN): $\delta = 62.8$, 68.3, 69.7, 70.3, 105.7, 114.9, 125.9, 126.5, 146.4, 148.3, 154.3 ppm. MS (ES): $m/z = 603$ (M−PF$_6^-$)$^+$, 458 (M−2PF$_6^-$)$^+$. C$_{28}$H$_{30}$F$_{12}$N$_2$O$_4$P$_2$ (748.48); calcd: C, 44.93; H, 4.04; N, 3.74; enc: C, 45.06; H, 4.12; N, 4.01.

14. X-ray data for compounds **3a–c** were collected at 293(2) K on a Bruker Smart-CCD1000 diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELX-97) and refined by full-matrix least-squares on F^2. Compound **3a**: C$_{24}$H$_{28}$F$_{12}$N$_2$O$_4$P$_2$, MW = 698.13, crystal size: $0.30 \times 0.29 \times 0.28$ mm^3, crystal system: monoclinic, space group: $P2_1/c$, cell parameters: $a = 15.206(5)$ Å, $b = 15.435(5)$ Å, $c = 13.436(5)$ Å, $V = 3150.4(19)$ Å^3, $Z = 4$, Dc = 1.559 mg/m^3, $F_{000} = 1512$, R and $wR2$ are 0.0559 [$I > 2\sigma(I)$] and 0.1515 (all data). Compound **3b**: C$_{28}$H$_{36}$F$_{12}$N$_3$O$_4$P$_2$, MW = 786.53, crystal size: $0.37 \times 0.36 \times 0.09$ mm^3, crystal system: triclinic, space group: $P1$, cell parameters: $a = 11.100(5)$ Å, $b = 11.830(5)$ Å, $c = 13.894(5)$ Å, $V = 1650.5(12)$ Å^3, $Z = 2$, Dc = 1.583 mg/m^3, R and $wR2$ are 0.0437 [$I > 2\sigma(I)$] and 0.1089 (all data). Compound **3c**: C$_{28}$H$_{36}$N$_2$O$_6$P$_2$F$_{12}$, MW = 786.19, crystal size: $0.47 \times 0.41 \times 0.20$ mm^3, crystal system: orthorhombic, space group: $Pna2_1$, cell parameters: $a = 27.557(5)$ Å, $b = 6.731(5)$ Å, $c = 15.909(5)$ Å, $V = 2951(2)$ Å^3, $Z = 4$, Dc = 1.685 mg/m^3, $F_{000} = 1528$, R and $wR2$ are 0.0376 [$I > 2\sigma(I)$] and 0.0966 (all data). Crystallographic data (excluding structure factors) for **3a–c** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers **3a**: CCDC 291340, **3b**: CCDC 291341, **3c**: CCDC 291342. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 (0) 1223 33603 or e-mail: deposit@ccdc.cam.ac.uk).