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A 24-Crown-8 Bearing Naphthalene and Naphthoquinone Chromophores

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The novel bichromophoric crown ether N24C8NQ 3 has been synthesised in good yield by the conjugate addition of a polyether diol 1 to 2,3-dichloronaphthoquinone in the presence of base. Crown ether 3 was further reacted with malononitrile in the presence of $TiCl_4$ to prepare the tetracyano-1,4-napthoquinodimethane derivative 4. Electrochemical and photophysical studies on 3 and 4 have been undertaken. The addition of alkali metal cations to the crown ether 3 causes significant changes in the first and second reduction potentials of the naphthoquinone (NQ) chromophore. In the case of the first process, a correlation exists between the reversible potential and cation "fit". Crown ethers 3 and 4 exhibit red-shifted absorption bands attributed to intramolecular charge transfer interactions between the chromophores. Fluorescence from the naphthalene chromophore in 3 and 4 is quenched substantially (>80%) as compared to the model 5. The weak nature of the complex between 3 and the guest dibenzylammonium hexafluorophosphate ($K_a < 50\,M^{-1}$) was compared to another electron deficient crown, tetranitrodibenzo-24-crown-8, the results of which suggest that the oxygens within the crown ether macrocycle, bearing electron withdrawing chromophores, play an important role in stabilising such pseudorotaxane complexes.

Keywords: Crown ether; Electrochemistry; Naphthoquinone; Electrochemistry; Alkali metal; Ion complexation; Fluorescence

INTRODUCTION

One of the major aspects in designing artificial photosynthetic devices is the selection of an organising principle that will control the interactions among the chromophoric units [1–3]. These interactions play a significant role in dictating the rates and efficiency of electron (ET) and energy (EnT) transfer that in turn are determined by the spatial separations and the intervening medium. From our perspective, the electrostatic interactions that give rise to metal ion-crown [4,5] and dialkylammonium-crown [6,7] complexes are thought to be useful in providing electronic and structural roles for the facilitation of electron and energy transfer processes from one antipodal position to the other across the crown (Fig. 1) [8–12]. Using this approach, factors such as the bridge conformation, the redox properties of the chromophores, the orientation of the chromophores, and the superexchange properties of the bridge, could be varied in a *readily controlled* and *systematic way* through the appropriate choice of metal cations or ammonium salts. We have already reported on the bichromophoric system N18C6NQ [13], bearing a naphthalene (N) donor and naphthoquinone (NQ) acceptor, and demonstrated that the addition of alkali metal cations to N18C6NQ modulates the first and second reduction potentials of the naphthoquinone chromophore. Furthermore, steady-state fluorescence spectra of N18C6NQ were quenched substantially (>90%) as compared with model systems, indicative of ET between the chromophores [13]. This success has recently led us to prepare a porphyrin-18C6-C60 system that demonstrates accelerated rates of ET in the presence of Na^+ exclusively [14]. In this paper, we report the synthesis and characterisation of N24C8NQ derivatives **3** and **4** (Scheme 1) and further evaluate these systems as suitable models with which to investigate ET and EnT processes using cation binding, electrochemistry and photophysical studies.

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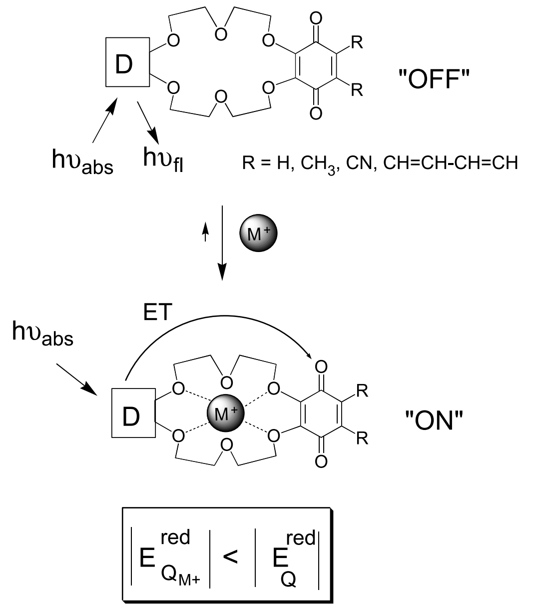


FIGURE 1 The general structure of crown ether-based multichromophoric systems bearing a quinone (Q) acceptor. Addition of a cationic species (M^+) capable of binding within the cavity of the crown causes changes in the redox properties of the chromophores switching "ON" ET processes from donor (D) to acceptor (Q). Examples of a complexed cation (M^+) are an alkali metal, a primary alkylammonium or a secondary ammonium ion.

RESULTS AND DISCUSSION

The synthesis of crown ethers **3** and **4** is outlined in Scheme 1. The diol **1** was prepared from commercially available 2,3-dihydroxynaphthalene by literature methods [13].[†] Reaction of **1** with 2,3-dichloro-1,4-naphthoquinone (Et_3N, toluene, Δ) *via* a 1,4-addition of the alcohol to the quinone [15], gave **2** in 62% yield after column chromatography. Mass spectrometry was consistent with the formation of the product, in particular showing the isotopic pattern expected for the presence of a chlorine atom within the molecular structure. Efficient cyclisation of **2** to give the crown ether N24C8NQ **3** was achieved under dry, strongly basic conditions (^{t}BuOK, THF, $N_2\Delta$) in 53% yield as an orange semi-solid after purification on silica. We believe that the potassium *t*-butoxide used in the macrocyclisation reaction not only serves to act as a strong, non-nucleophilic base, but the potassium ion plays an important role by acting as a templating cation. The need for a stronger base than triethylamine to facilitate the macrocylisation is likely a result of the conjugative effects of the introduced alkoxy group on C3. Attempts at a one-pot synthesis using **1** and 2,3-dichloro-1,4-naphthoquinone in the presence of *t*-BuOK were extremely low yielding. Both NMR and ESIMS supported the structure for **3**. In particular the symmetry generated upon the transition from **2** to **3** is evident by NMR spectrometry, while a peak in the mass spectrum at m/z 601.3 is consistent with $[M + Na]^+$. The crown **3** was converted to tetracyano-1,4-napthoquinodimethane **4** under Lehnert conditions, giving a green solid in 30% yield after chromatography [16].[‡] Again the results of NMR and mass spectroscopy (m/z $697.1 = [M + Na]^+$) were supportive of product formation. In particular, the ^{13}C NMR spectrum revealed signals at δ 83.22 and 83.33 corresponding to the two sets of inequivalent nitrile groups on **4**.

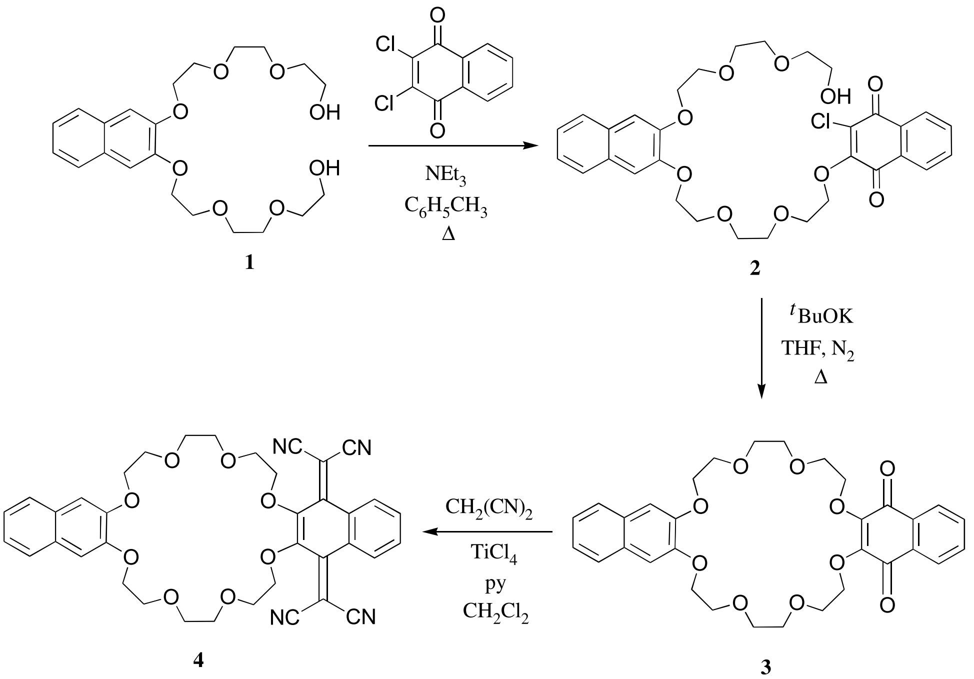
Electrochemistry

The cyclic voltammametric response of **3** dissolved in MeCN containing 0.1 M TBAP as supporting electrolyte, at various scan rates, is shown in Fig. 2. In the absence of metal cations, there are two well defined redox processes situated at -0.98 V and -1.39 V vs ferrocene (Fc/Fc^+). These values are similar to those reported for unsubstituted naphthoquinone compounds in aprotic media [17], and the waves can be readily ascribed to the formation of the semiquinone radical anion ($N24C8[NQ]^{\cdot-}$) and the quinone dianion species ($N24C8[NQ]^{2-}$). In both cases the peaks show a typical semi-infinite diffusional response expected for a stationary disc electrode. The peak heights scale linearly with the square root of the scan rate and the slopes of such plots yield a value for the diffusion coefficient of $7 \times 10^{-6}\,cm^2\,s^{-1}$. The separation between the anodic and cathodic branches of the voltammogram (ΔE_p) is slightly larger for the first reduction process than for the second (136 mV and 120 mV respectively at $0.05\,V\,s^{-1}$) indicating that, although both processes are electrochemically reversible, heterogeneous electron transfer is slightly more facile for the second reduction.

When a 25 μm platinum microelectrode is used for the analysis, to remove any ohmic effects, ΔE_p values of 142 mV and 112 mV are observed (at $4\,V\,s^{-1}$) for the first and second reductions, respectively. These values and other data collected at a range of scan rates allow us to estimate values of $0.015\,cm\,s^{-1}$ and $0.025\,cm\,s^{-1}$ for the heterogeneous electron transfer rate constants (k) in each case. Virtually identical behaviour to that described above was observed when 0.1 M $TBAPF_6$ was used as the supporting electrolyte, and the voltammetric behaviour was qualitatively the same but with a slight (10–15 mV) negative shift in potentials when CH_2Cl_2 was used as the solvent.

[†] Diol **1** was formed in 80% yield. ^1H NMR (400 MHz, $CDCl_3$) 7.63, 2H, m; 7.30, 2H, m; 7.12, 2H, s; 4.25, 4H, m; 3.93, 4H, m; 3.76, 4H, m; 3.68, 8H, m; 3.58, 4H, m; 3.10, 2H, br s. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.87; 129.26; 126.24; 124.20; 108.40; 72.63; 70.85; 70.30; 69.45; 68.29; 61.59. ESIMS: m/z 425.4 $[M + H]^+$, 447.3 $[M + Na]^+$.

[‡] The reaction yield of crown **4** is higher than the 30% isolated yield quoted. Care must be taken as this crown degrades on purification by chromatography on silica.



SCHEME 1 Synthesis of the two naphthoquinone 24C8 analogues **3** and **4**.

In order to investigate the effects of metal ion complexation on reduction potentials of the NQ in **3**, voltammetric experiments were performed in the presence of K$^+$, Na$^+$ and Li$^+$ ions. In the presence of these metal ions, the cyclic voltammetric response is substantially different to that observed in TBAClO$_4$. Here, the response is characterised by a single quasi-reversible couple situated at a potential positive of -0.98 V. This couple did not become more reversible at faster scan rates. The apparent disappearance of the second reduction process may be due to particularly strong interactions between NQ^{2-} and the metal ions, resulting in the formal potential being shifted to a value more positive than the first reduction process. However, due to the chemical and electrochemical irreversibility associated with the wave in the presence of metal ions, this could not be definitively confirmed. The observed shift in potential for the first reduction process depends markedly on the identity of the metal ion present.

Fig. 3 shows the square wave voltammetric responses for **3** dissolved in MeCN in the presence of 0.1 M concentrations of KClO$_4$, NaClO$_4$, LiClO$_4$, and TBAClO$_4$. This figure shows the positive shift in reduction potential for the NQ moiety, relative to the control solution, in the presence of each alkali metal ion and also illustrates the apparent disappearance of the second reduction process when these ions are present. The order of the potential shifts was Li$^+$(252 mV) $>$ Na$^+$(164 mV) $>$ K$^+$(77 mV) (Table I), which mirrors the order of the crystallographic ionic

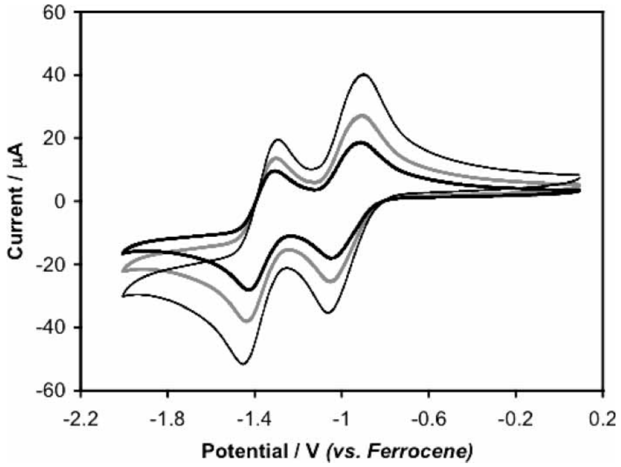


FIGURE 2 Cyclic voltammetry of 6.5 mM **3** dissolved in MeCN in the presence of 0.1 M TBAP using a 1.5 mm diameter glassy carbon electrode at scan rates of 0.05, 0.1 and 0.2 V s^{-1}.

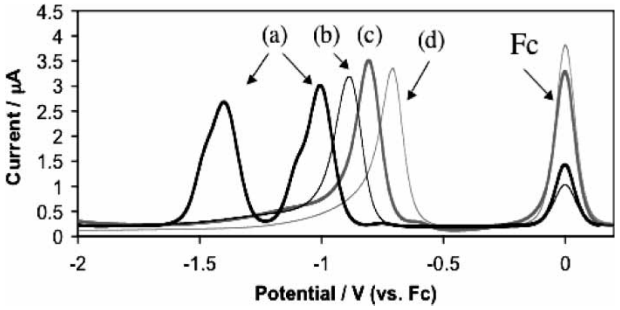


FIGURE 3 Square wave voltammetric responses for **3** dissolved in MeCN in the presence of 0.1 M concentrations of (a) TBAP, (b) KClO$_4$ (c) NaClO$_4$, and (d) LiClO$_4$. The overlayed peaks at 0 V are a result of the ferrocene internal standard. The concentration of **3** is approximately 2 mM in each case.

TABLE I Formal potentials for the reduction of **3** and **4** in MeCN in the presence of various supporting electrolytes

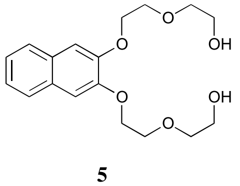
Compound	Electrolyte (0.1 M)	$E°_1/V^a$	$E°_2/V$
3	$TBAPF_6$	− 0.994	− 1.382
	$TBAClO_4$	− 0.981	− 1.394
	$KClO_4$	-0.904^b	–
	$NaClO_4$	-0.817^b	–
	$LiClO_4$	-0.729^b	–
4	$TBAPF_6$	-0.415^b	-0.977^c

[a] Formal potentials were calculated as the average of the reduction and oxidation peak potentials of the cyclic voltammograms. All potentials are quoted relative to the Fc/Fc^+ couple. [b] Quasi reversible. [c] Irreversible.

diameters of the metal cations (Li^+ being the smallest). Since quinones are known to interact sufficiently strongly with metal cations to form contact ion-pairs, the observed trend is consistent with electrostatic terms being dominant in determining the value of the formal potential (E°) for this process [18]. However, it should be noted that the magnitudes of the potential shifts are significantly larger than would be expected if ion pairing were the only factor involved [19]. Since the magnitude of the ion-pairing interaction would be expected to be stronger for the dianion (NQ^{2-}) than the radical anion ($NQ^{\cdot -}$), our earlier assumption of a large positive shift in the formal potential for the second reduction is still supported. As expected, the first and second reduction potentials for the crown ether **4** are substantially lower than for **3** (Table I). However, crown **4** behaves quite differently leading to a quasi-reversible first reduction and a totally irreversible second reduction peak, in line with the general instability found with this compound.†

Absorption and Emission Studies

The absorption spectrum of N24C8NQ **3** and an equimolar mixture of the naphthalene and naphthoquinone model species **5** and **6** in MeCN are shown in Fig. 4a. The absorption spectra were matched at the naphthalene absorption band at 322 nm to facilitate comparison. The dyad spectrum is broadened and exhibits red-shifted bands not present in the equimolar mixture of **5** and **6**.‡



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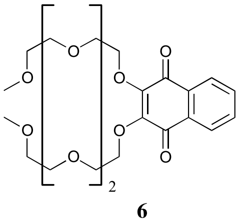

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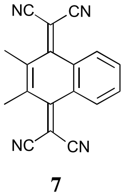

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The absorption spectrum of **4** (Fig. 4b) similarly features red-shifted bands in MeCN, at 570 nm and 850 nm, which are not present in the absorption spectra

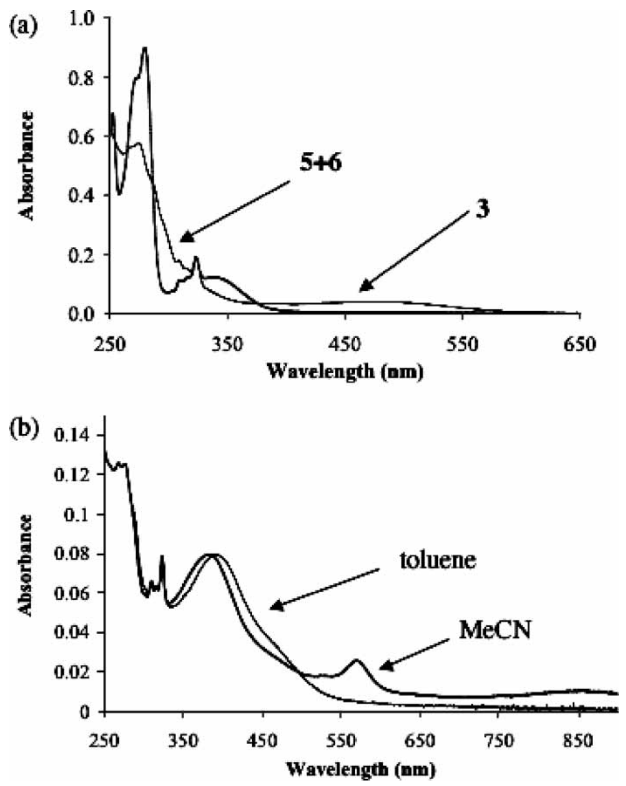


FIGURE 4 (a) Absorption spectra of the dyad **3** and an equimolar mixture of **5** and **6** in MeCN. (b) Absorption spectra of the dyad **4** in MeCN and toluene. Absorbances for (a) and (b) were matched at 322 nm.

of the relevant model systems **5** and **7**. Formation of an intramolecular complex between the chromophores of the dyads **3** and **4** requires folding of the flexible 24C8 to bring the two chromophores in close contact. For both dyads the new absorption bands were more prominent and red-shifted in more polar solvents, and were strongly reduced in the non-polar solvent toluene (Fig. 4b) indicating that the interactions between chromophores in the dyads have some charge-transfer character. Chemical reduction of **7** with $NaBH_4$ in MeCN reproduced the red-shifted bands observed at 570 nm and 850 nm in **4**, further indicating that a charge-transfer complex is formed between the chromophores of the dyad in the ground state.

The absorption spectra of the dyads **3** and **4** and model systems **5**–**7** were unchanged upon addition of a large excess of $TBAClO_4$ in MeCN. However, small changes in the absorption spectrum of the dyads were detected upon addition of the metal perchlorates. Generally, a small increase in the red-shifted charge-transfer absorption bands was observed, together with a small blue shift in the naphthalene absorption bands (1 nm for $KClO_4$, 3 nm for $NaClO_4$ and 2 nm for $LiClO_4$). Similar blue shifts were observed upon addition of the metal perchlorates to **5**. The changes in the absorption spectra of the dyads upon metal perchlorate addition are attributed to the weak inclusion of the metal ions into the crown ether bridging the chromophores of

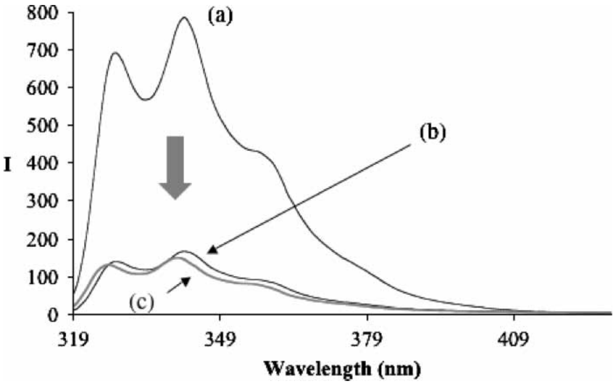


FIGURE 5 Fluorescence spectra of (a) an equimolar mixture of model systems **5** and **6**, (b) the dyad **3** in MeCN, (c) the dyad **3** in the presence of 0.1M $NaClO_4$. All solutions were optically matched at the excitation wavelength (309 nm).

the dyads. No further changes to the absorption spectra of the dyads were noted at metal perchlorate concentrations greater than 0.1 M.

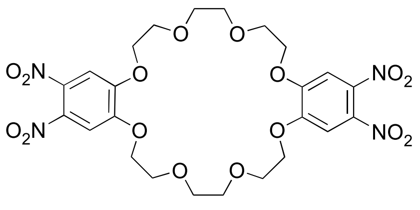
Excitation of **3** at the naphthalene absorption band (309 nm) in MeCN resulted in characteristic naphthalene emission from the dyad, however the fluorescence was strongly quenched (80%) when compared with an optically matched, equimolar mixture of the respective model systems **5** and **6** (Fig. 5). Efficient quenching of naphthalene emission (>80%) was also observed for **4**. The addition of excess $TBAClO_4$ did not affect the fluorescence of the dyads **4** and **5** however the addition of metal perchlorates ($LiClO_4$, $NaClO_4$, $KClO_4$) led to a blue shift in the dyad fluorescence spectra of a similar magnitude to that observed in the absorption spectroscopy studies. However, the quenching efficiency in the dyads was modulated only slightly by metal ion complexation (Fig. 5), with a small (ca.10%) reduction observed for each metal salt.

The incorporation of the metal ions in the crown ether can be expected to have a number of consequences. While the metal ion can be expected to decrease the flexibility of the bridge and affect molecular conformation, calculations on related crown ether systems have shown that the ion insertion can also influence the molecular orbital distribution of the chromophores and thus the electronic coupling between donor and acceptor [14]. The overall impact of these factors on absorption and fluorescence properties can be expected to be complex and highly dependent on the ions and chromophores involved.

Complexation Studies

Addition of an equimolar amount of dibenzylammonium hexafluorophosphate to **3** in $CDCl_3$ led to the formation of a very weak complex (Scheme 2) with an estimated association constant (K_a) of $< 50\,M^{-1}$.

The surprising low value prompted us to investigate **8** [12], a 24C8 derivative bearing electron deficient chromophores. In this case, the ^1H NMR spectrum of an equimolar mixture of dibenzylammonium hexafluorophosphate and **8** revealed signals for both the uncomplexed components and complexed species, exhibiting slow kinetics on the NMR timescale. Calculation of the association constant in $CDCl_3/CD_3CN$ (10:1) solution gave a value of $49 \pm 5\,M^{-1}$. Despite the use of CD_3CN which is competitive for hydrogen bonding, the values presented here are much lower than the association constants calculated for similar complexations employing DB24C8 as reported by Stoddart [20]. It's apparent that the phenolic oxygens within the crown ether (bearing electron withdrawing chromophores) play important roles in stabilising the complex. Removal of electron density by inductive effects limits their ability to interact with the dialkylammonium guest.



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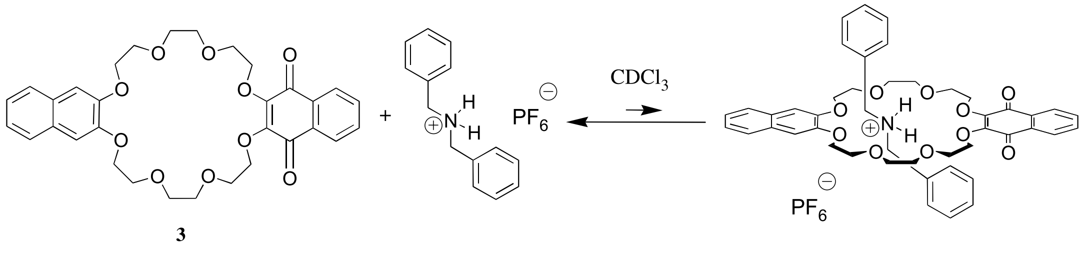
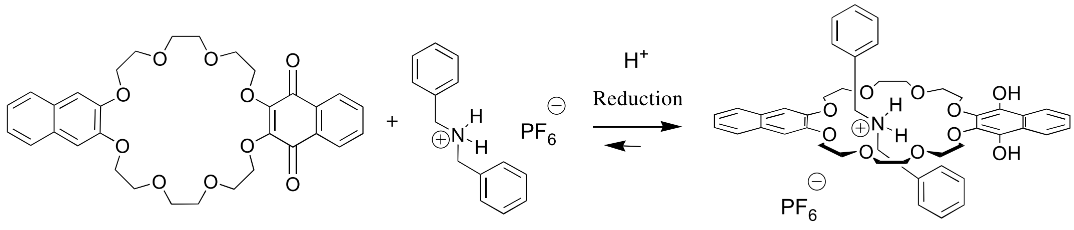
CONCLUSION

We have demonstrated that large crown ethers bearing quinones with the potential to bind organic cations can be synthesised in good yield in two steps from literature precursors and that these crowns can be further functionalised to modulate the redox properties of the crown ether. An electrochemical investigation on **3** and **4** illustrated that metal



SCHEME 2 Weak [2]pseudorotaxane complexes form between **3** and dibenzylammonium hexafluorophosphate in $CDCl_3$.



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SCHEME 3 Reduction of the quinone in the presence of dibenzylammonium hexafluorophosphate should induce [2]pseudorotaxane formation.

perchlorates can modify the reduction potentials of the naphthoquinone moiety, thereby demonstrating that modulation of the energetics and dynamics of electron transfer by metal cation inclusion and/or ion pairing is possible. Photophysical studies indicate an intramolecular charge transfer interaction between chromophores in **3** and **4** in the ground state, suggesting a folded structure for the dyads in solution. The close proximity of chromophores induces efficient fluorescence quenching in **3** and **4** when compared with an equimolar mix of the models **5** with either **6** or **7** and metal ion complexation has little effect on the quenching efficiency. Despite the low association constant for **3** with dibenzylammonium hexaflourophosphate, which is consistent with other electron deficient systems, the well-behaved electrochemical nature of **3** offers the potential for redox-induced pseudorotaxane formation (Scheme 3). This work is in progress.

EXPERIMENTAL

Analytical reagent grade MeCN and DCM (Aldrich) were stored over molecular sieves prior to use and the electrolytes, $TBAClO_4$ (tetrabutylammonium perchlorate) and $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) (GFS) were recrystallised twice from $EtOH/H_2O$. Other electrolytes, $KClO_4$, $NaClO_4$ and $LiClO_4$ (Aldrich) were of analytical grade and were dried under vacuum prior to use. All solutions were thoroughly deoxygenated using nitrogen prior to undertaking electrochemical experiments. All measurements were carried out at ambient temperature (20 ± 2°C). Voltammetric measurements were carried out with a μ-Autolab II potentiostat (ECO-Chemie, Utrecht, Netherlands). A conventional three-electrode assembly was used: the working electrode consisted of a 3 mm diameter (CH instruments) or 1.5 mm diameter (Cypress Systems) glassy carbon disk shrouded in Teflon or a 25 μm diameter Pt microelectrode sealed in glass, while a 1 cm^2 Pt gauze was used as the auxiliary electrode. The reference electrode consisted of a silver wire separated from the test solution by a fritted Teflon tube filled with the same solvent and electrolyte which was used in the test solution. Potentials throughout are quoted relative to the formal potential (E^0) of the Fc/Fc^+ couple which was measured *in situ* in each solution. Steady state absorption spectroscopy measurements were conducted on a Varian Cary 50 Bio UV–Visible spectrophotometer. Steady state fluorescence spectroscopy measurements were performed using a Varian Cary Eclipse fluorescence spectrophotometer. Solutions for photochemical analysis were prepared in spectroscopy grade solvents.

2:1 (0.5 g, 1.17 mmol) was combined with 2,3-dichloro-1,4-naphthoquinone (0.87 g, 3.84 mmol) in toluene (10 mL) and heated to 90°C under N_2, resulting in a light rose coloured solution. Upon adding TEA (0.5 g, 5.0 mmol) the colour changed to dark red and the solution was heated at reflux for 2 days. Purification by column chromatography (silica) eluting successively with $CHCl_3$ then $EtOAc:CHCl_3:MeOH$ (4.5:4.5:1) afforded **2** (0.45 g, 62%) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) 8.03, 2H, m; 7.65, 4H, m; 7.29, 2H, m; 7.09, 2H, s; 4.72, 4H, m; 4.26, 2H, m; 4.17, 2H, m; 3.94, 2H, m; 3.82, 2H, m; 3.76, 2H, m; 3.68, 10H, m; 3.60, 2H, m. ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.60; 178.61; 157.03; 148.77; 134.12; 133.77; 131.03; 130.84; 129.29; 129.25; 128.84; 126.76; 126.70; 126.29; 126.26; 124.24; 108.41; 73.28; 72.51; 71.19; 70.89; 70.85; 70.32; 69.52; 69.40; 68.21; 61.67. ESIMS $C_{32}H_{35}O_{10}Cl_1$ *m/z*: 637.2, $[M + Na]^+$.

3:2 (113 mg, 184.0 μmol) was dissolved in THF (30 mL) and heated at reflux with KO^tBu (23 mg, 205.0 μmol) for 2 days under an Ar atmosphere producing a red coloured solution. The THF was removed by rotary evaporation and the residue dissolved in $CHCl_3$. The organic layer was washed with water and the aqueous layer was treated with HCl (10%) and extracted with $CHCl_3$. The combined organic layers were dried (Na_2SO_4) and the volume of solution concentrated to 5 mL. Filtration through a plug of silica eluting with acetone:DCM (1:1) yielded a red-orange semi-solid. (56.3 mg, 53%) ^1H NMR (400 MHz, $CDCl_3$) 7.99, 2H, m; 7.63, 4H, m; 7.28, 2H, m; 7.09, 2H, s; 4.54, 4H, m; 4.24, 4H, m; 3.96, 4H, m; 3.84, 8H, m; 3.74, 4H, m. ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.87; 149.01; 147.27; 133.47; 130.83; 129.25; 126.21; 126.01; 124.11; 108.13; 72.95; 71.16; 70.82; 70.37; 69.64; 68.96. ESIMS $C_{32}H_{34}O_{10}$ *m/z*: 601.3, $[M + Na]^+$. HRMS: $C_{32}H_{34}O_{10}Na$ requires $m/z = 601.2049$, found $m/z = 601.2045$.

4:3 (86.5 mg, 149.6 μmol) was dissolved in DCM (20 mL) and treated with $TiCl_4$ (2.5 mL, 1 M in DCM) at 0°C forming a dark blue coloured solution. Malononitrile (148 mg, 2.24 mmol) was then added producing a brown precipitate followed by the drop-wise addition of pyridine (177 mg, 2.24 mmol) over 20 minutes. After removal of the ice bath the reaction was refluxed for 5 minutes and the DCM removed by rotary evaporation. The residue was stirred vigorously with HCl (40 mL, 15%) for 30 minutes before extracting with $CHCl_3$ and drying (Na_2SO_4). Purification by column chromatography (silica) eluting with $CHCl_3$:MeOH (98:2) yielded **7** as a green solid (30 mg, 30%) ^{1}H NMR (200 MHz, $CDCl_3$) 8.32, 2H, m; 7.65, 4H, m; 7.32, 2H, m; 7.09, 2H, s; 4.52, 4H, m; 4.21, 4H, m; 3.92, 8H, m; 3.74, 8H, m. ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.20; 149.03; 132.33; 129.37; 127.91; 127.77; 126.34; 124.41; 108.47; 83.22; 82.33; 71.12; 70.92; 69.73; 69.35; 68.89. ESIMS $C_{38}H_{34}N_4O_8$ m/z: 697.1, $[M + Na]^+$.

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