CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200903553

Anion-Assisted Complexation of Paraquat by Cryptands Based on Bis(*m*-phenylene)-[32]crown-10

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Abstract: The complexation of tightly ion-paired divalent salts such as paraquat dichloride by cryptands based on crown ethers can be improved by the introduction of ion-pair recognition as a means of also binding the counteranions. A series of diamide-based cryptands derived from bis(*m*-phenylene)-[32]crown-10 and designed to complex the bipyridinium dication with anion assistance was synthesized. The ion-pair recognition process was fully characterized by ^{1}H NMR spectroscopy, UV/Vis spectroscopy, electrospray ionization mass spectrometry and single crystal X-ray analysis. ^{1}H NMR spectroscopy demonstrated that these new heteroditopic cryptand hosts can complex both the positive and negative components of the paraquat dichloride salt. UV/Vis spectroscopy showed that the addition of chloride anion into equimolar solutions of cryptands **3c** or **3g** with paraquat bis(hexafluorophosphate) salt (**2a**) improves the binding of the cryptands to the paraquat guest. Electrospray ionization mass spectrometry and single-crystal X-ray analysis confirmed the 1:1 stoichiometries and ion-pair recognition of these cryptand/paraquat complexes. It was found that the cryptand **3g**, with 13 atoms and an isophthalamide moiety in the third chain, exhibited the best binding affinity for tightly ion-paired paraquat dichloride (**2b**), due to the combination of its spatial compatibility and additional anion-binding site.

Keywords: anions · cryptands · host–guest systems · ion-pair recognition · paraquat

Introduction

Threaded structures have attracted much attention not only because of their topological importance but also as a result of their many potential applications.[1] Bistable [2]rotaxane molecules, for example, can serve as data storage elements.[2a] In some bioactive peptides, knotted arrangements in which the C termini thread through N-terminal macrolactam rings can even be found.[2b] The efficiencies of preparations of these threaded structures are strongly dependent on the strength of host–guest complexation between the components, based on weak noncovalent forces such as hydrogen bonding, π–π stacking and electrostatic interactions. As a result of the incorporation of additional binding sites and preorganization of complexation conformations, cryptands based on crown ethers have proved to be powerful hosts for metal ions, nonmetallic ions and some organic salts.[3] The strong interactions between cryptands and guests have been exploited in the efficient preparation of threaded structures such as rotaxanes and catenanes.[4] The high affinities of the cryptand hosts are partly attributed to their spatial compatibility, which plays a key role in the design of these receptors.

Most cation binding studies have used salts with noncompeting counterions, especially hexfluorophosphate anions, for their good solubility and relatively weak ion-pairing in organic solvents. However, the luxury of the noncompeting counterion is not always available and the organic salts usually exist in many real-life situations or are commercially available as tight ion-pairs. Actually, the important roles of anions cannot be neglected either in biological processes or in some artificial systems. Anions have been used elegantly in the control of pseudorotaxane formation,[5a] operation of molecular machines[5b] and morphological evolution of crystals.[5c]

An alternative paradigm for salt complexation is ion-pair recognition, in which cations and anions are simultaneously bound by heteroditopic receptors. This has proved to be an effective method to promote the binding abilities of receptors for salt guests.[6,7,8] Various ion-pair recognition hosts

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200903553.

have been synthesized to date, and they exhibit excellent affinities for inorganic salts.[7] Ion-pair recognition of organic salts, however, especially those existing as tight ion-pairs, has been investigated only to a very limited extent.[8]

Paraquat (*N*,*N*′-dimethyl-4,4′-bipyridinium) dichloride is an effective but highly toxic herbicide widely used in agriculture and horticulture.[9] It and its derivatives have been widely used in the fabrication of numerous supramolecular systems, due to their easy availability and interesting physicochemical properties.[10] Improvement of the binding of paraquat and its derivatives is not only important for environmental monitoring and human health[9] but also critical for the fabrication of large supramolecular systems.[11] The crown-ether-based cryptand **1** (Figure 1) has proved to be a powerful host for the paraquat salt **2a**.[3a] According to the

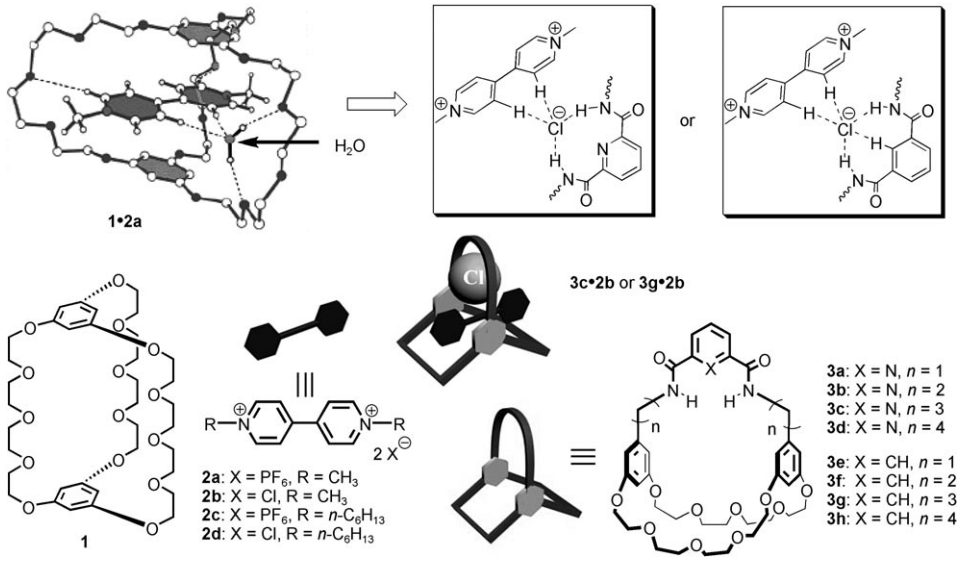


Figure 1. Compounds used in this study, together with the X-ray crystal structure of the **1**·**2a**·H_2O complex.

X-ray structure of the complex **1**·**2a**, the bipyridinium dicationic part threads into the cavity of the crown-ether-based cryptand **1** with the assistance from two hydrogen bonds formed between the two acidic β-pyridinium hydrogen atoms and the oxygen atom of a water molecule that bridges to the ether oxygen atoms of the third ethylenoxy chain. This unique structure inspired us to develop ion-pair recognition for paraquat derivatives. Because the van der Waals radius (1.75 Å) of the chlorine atom is close to that (1.52 Å) of the oxygen atom,[12] we envisioned that the replacement of the water molecule in the crystal structure of complex **1**·**2a** with a chloride anion should result in a similar complex structure if an additional anion binding moiety—such as isophthalamide or 2,6-pyridinedicarboxamide unit—were introduced in the third chain of the cryptand host. On the basis of these considerations we designed and synthesized a series of new cryptands **3** (Scheme 1) possessing third chains of different lengths and containing anion-binding moieties. It was believed that ion-pair recognition of paraquat dichloride (**2b**), which is commercially available, should be controlled not only by the cryptand cavity size but also by the anion-binding moiety (Figure 1). Cryptands **3c** and **3g** each contains 13 atoms in their third chain backbones, so they are considered to have the best structural similarity with **1**. Other cryptands were also synthesized to probe the effects of cryptand cavity size and anion-binding moiety on their complexation to paraquat derivatives. ^{1}H NMR spectroscopy, electrospray ionization mass spectrometry, UV/Vis spectroscopy and single-crystal X-ray analysis were employed to characterize the binding of paraquat by these heteroditopic cryptands.

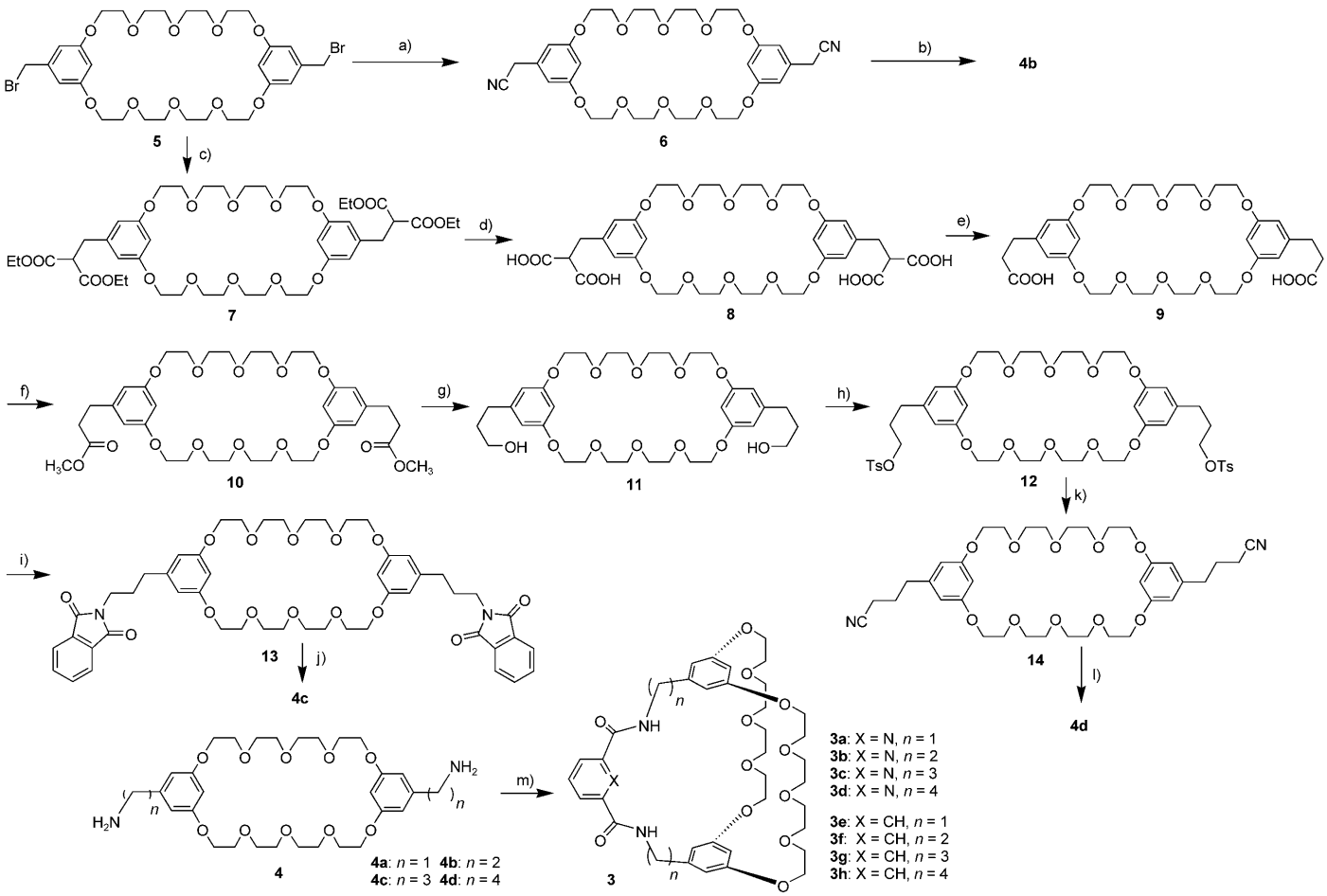
Results and Discussion

Design and synthesis of cryptands 3, based on bis(*m*-phenylene)-[32]crown-10: It has been reported that the binding affinities of cryptands based on bis(*m*-phenylene)-[32]crown-10 for paraquat can be dramatically enhanced by optimizing the length of the third chain.[11c] From the X-ray crystal structure of the complex of **1**·**2a** (Figure 1) and the size similarity between the chloride atom and the oxygen atom, we envisioned that the best number of atoms in the backbone of the third chain of the heteroditopic cryptand host should be 13. In order to probe the influence of the length of the third chain, cryptands with different lengths—containing nine, 11, 13 or 15 atoms in their third chains—were designed and synthesized in order to examine their geometries and intrinsic hydrogen bonding abilities.

The key starting material **5**[11c] and the diamino intermediate **4a**[10k] were synthesized by literature procedures. As outlined in Scheme 1, treatment of **5** with sodium cyanide and subsequent reduction afforded the diamino intermediate **4b** in good yield.

The intermediate **7** was obtained by treatment of **5** with diethyl malonate in tetrahydrofuran. Hydrolysis of **7** with subsequent decarboxylation and methylation afforded **10**. The intermediate **12** was produced by the reduction of **10** and then toluenesulfonylation.

The diamino intermediate **4c** was synthesized by a method reported for **4a**.[10k] Treatment of **12** with excess potassium phthalimide afforded **13**, and hydrazinolysis of **13** in methanol afforded the diamino intermediate **4c** in good yield.



Scheme 1. Synthesis of cryptand hosts **3**, based on bis(*m*-phenylene)-[32]crown-10: a) NaCN, THF/H_2O, reflux, 85%; b) borane methylsulfide, THF, reflux, 84%; c) $CH_2(COOEt)_2$, NaH, THF, 98%; d) i) NaOH (2M), EtOH, reflux; ii) HCl, H_2O, 99% (two steps); e) 140°C, N_2, 75%; f) H_2SO_4, CH_3OH, 89%; g) $LiAlH_4$, THF, 92%; h) TsCl, Et_3N, CH_2Cl_2, 73%; i) potassium phthalimide, DMF, 90°C, 93%; j) i) hydrazine monohydrate, CH_3OH, reflux; ii) HCl, H_2O, iii) NaOH, H_2O, 90% (three steps); k) NaCN, DMF, 80°C, 92%; l) borane methylsulfide, THF, reflux, 88%; m) isophthaloyl dichloride or 2,6-dipyridinecarbonyl dichloride, Et_3N, CH_2Cl_2, 6–54%.

The diamino intermediate **4d** was obtained by the same method as used for **4b**. Treatment of **12** with sodium cyanide followed by reduction afforded the diamino intermediate **4d** in good yield.

The cryptands **3** were finally obtained in reasonable yields by cyclization of the precursors **4** with isophthaloyl dichloride or 2,6-dipyridinecarbonyl dichloride, as appropriate, in CH_2Cl_2. Even cryptands with larger cavities can be obtained by these carbon-chain-extending reactions and ring-closure methods.

Complexation of the new cryptands 3 with paraquat: Equimolar (0.500 mM) acetonitrile solutions of **2a** and each of the eight new cryptands **3** are yellow, due to charge transfer between the electron-rich aromatic rings of the cryptand host and the electron-poor pyridinium rings of the guest **2a**. The same yellow colour in equimolar (0.500 mM) $CHCl_3$/CH_3OH (1:1) solutions of **3** with **2b** provided evidence that the charge transfer interaction also occurred when the PF_6 anions were replaced by the chloride anions. Job plots[13] (Figure 2) based on UV/Vis spectroscopy absorbance data in $CHCl_3$/CH_3OH (1:1) demonstrated that the complexes of **3** with **2b** were of 1:1 stoichiometry in solution. Most of the positive electrospray ionization mass spectra (see the Supporting Information) of equimolar mixtures of **3** and **2b** gave mass fragments corresponding to $[\mathbf{3}\cdot\mathbf{2b}-2\,Cl]^{2+}$ and $[\mathbf{3}\cdot\mathbf{2b}-Cl]^{+}$, confirming the 1:1 stoichiometries of these cryptand/paraquat complexes.

The association constant (K_a) values (Table 1) for complexes **3·2b** were determined by probing the charge-transfer bands of the complexes by UV/Vis spectroscopy with employment of a titration method (Figures S69–S80 in the Supporting Information). In the pyridine series, complex **3c·2b** complex gives the highest K_a value, corresponding to a complexation free energy of 5.0 kcal mol^{-1}, when compard to **3a·2b**, **3b·2b** and **3d·2b**. Also in the benzene series, complex **3g·2b** ($n=3$) gives the highest K_a value, corresponding to a complexation free energy of 5.8 kcal mol^{-1}, when compared to **3e·2b**, **3f·2b** and **3h·2b**. These differences in K_a values indicated that the cryptands **3c** and **3g** offered the

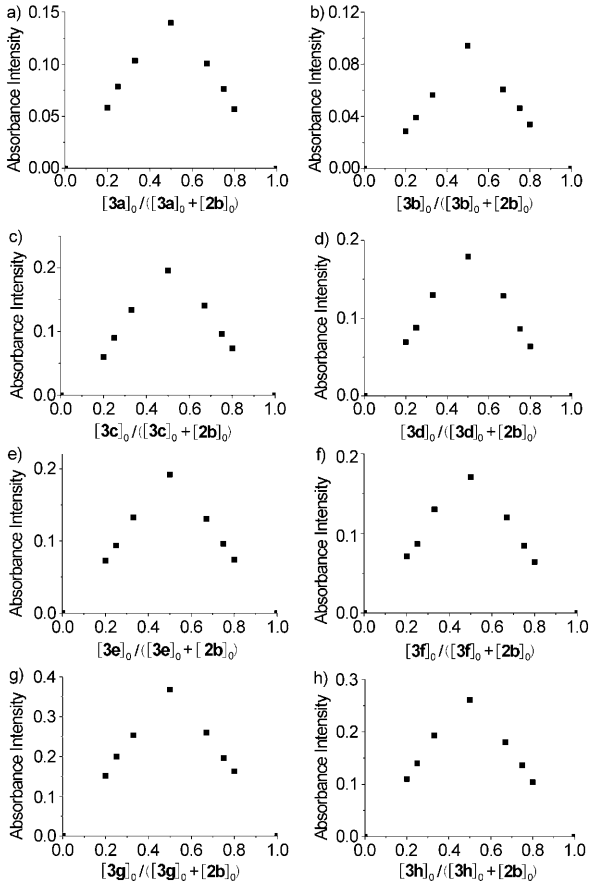


Figure 2. Job plots showing the 1:1 stoichiometries of the complexes formed between hosts **3** and **2b** in $CHCl_3/CH_3OH$ (1:1). The absorbance intensities at $\lambda = 388$ nm (the host–guest charge-transfer band) were plotted against the mole fractions of the hosts. $[\mathbf{3}]^0$ and $[\mathbf{2b}]_0$ are initial concentrations of **3** and **2b**, respectively. a) $[\mathbf{3a}]^0+[\mathbf{2b}]_0 = 2.00$ mM; b) $[\mathbf{3b}]^0+[\mathbf{2b}]_0 = 2.00$ mM; c) $[\mathbf{3c}]^0+[\mathbf{2b}]_0 = 1.00$ mM; d) $[\mathbf{3d}]^0+[\mathbf{2b}]_0 = 1.00$ mM; e) $[\mathbf{3e}]^0+[\mathbf{2b}]_0 = 1.00$ mM; f) $[\mathbf{3f}]^0+[\mathbf{2b}]_0 = 1.00$ mM; g) $[\mathbf{3g}]^0+[\mathbf{2b}]_0 = 1.00$ mM; h) $[\mathbf{3h}]^0+[\mathbf{2b}]_0 = 1.00$ mM.

Table 1. K_a values for complexes **3·2b** in $CHCl_3/CH_3OH$ (1:1) at 25 °C.

	3a·2b	**3b·2b**	**3c·2b**	**3d·2b**	**3e·2b**	**3f·2b**	**3g·2b**	**3h·2b**
$10^{-3}\times K_a$ [M^{-1}]	0.90 (±0.10)	0.32 (±0.01)	4.8 (±0.2)	2.7 (±0.5)	3.3 (±0.4)	2.2 (±0.5)	17 (±2)	5.6 (±0.2)
$-\Delta G_{298\,K}$ [kcal mol^{-1}]	4.0	3.4	5.0	4.7	4.8	4.6	5.8	5.1

best spatial fit for the 4,4′-bipyridinium dication with chloride anions. The K_a value for the **3g·2b** complex is about 2.5 times higher than that for the **3c·2b** complex. This can be attributed to the additional anion-binding site supplied by the acidic third-chain phenyl hydrogen atom in **3g**.[14]

The determination of the K_a values of the complexes of cryptands **3** with **2a** in $CHCl_3/CH_3OH$ (1:1) failed because of the poor solubility of **2a** in this solvent system. In order to estimate the anion effect in the promotion of the binding affinity, the K_a values (Table 2) for complexes **3c·2c**, **3g·2c**, **3c·2d** and **3g·2d** were determined in this solvent system.

Table 2. K_a values for complexes **3c·2c**, **3g·2c**, **3c·2d** and **3g·2d** in $CHCl_3/CH_3OH$ (1:1) at 25 °C.

	3c·2c	**3c·2d**	**3g·2c**	**3g·2d**
$10^{-3}\times K_a$ [M^{-1}]	0.78 (±0.05)	2.4 (±0.1)	0.63 (±0.04)	3.4 (±0.2)
$-\Delta G_{298\,K}$ [kcal mol^{-1}]	3.9	4.6	3.8	4.8

The K_a values for the **3c·2d** and **3g·2d** complexes were about 2.1 and 4.4 times greater, respectively, than the K_a values for the **3c·2c** and **3g·2c** complexes. These increases in the K_a value indicated that the addition of Cl^- could enhance the binding affinities of cryptands **3** for 4,4′-bipyridinium dication. The higher K_a value for complex **3g·2d** than for **3c·2d** confirmed that the isophthalamides were better anion receptors than 2,6-pyridinecarcarboxamides.[14] It is worth noting that the K_a value for the **3c·2c** complex is slightly higher than that for **3g·2c**. This can be attributed to the preference for the *syn-syn* conformation of the two amide NH groups on the 2,6-pyridinecarboxamide fragment of **3c** when no Cl^- is present.[14c] Without the anion assistance, **3c** can exhibit better binding affinity for the 4,4′-bipyridinium dication than **3g**.

Here the cryptands **3** gave lower binding affinities than **1** for the incorporation of anions.[3a] However, this incorporation makes it possible to recognize paraquat dichloride as a tight ion pair and to fabricate anion-driven molecular machines or other self-assembly systems based on the new molecular recognition motif of **3** for paraquat.

Anion-assisted complexation of paraquat by cryptand 3c: The pale yellow colour of an equimolar (0.500 mM) acetonitrile solution of cryptand **3** with paraquat **2a** indicated weak interaction between the host and guest. Upon gradual addition of tetrabutylammonium chloride (TBACl), however, the intensity of the charge-transfer band (388 nm) increased without any new band being observed (Figure 3). This intensity reached its maximum after addition of 2.0 equiv of Cl^-. These results indicated that the addition of Cl^- enhanced the complexation between the cryptand host **3c** and the paraquat guest. The positive electrospray ionization mass spectrum (Figure S61 in the Supporting Information) of an equimolar mixture of **3c** and **2b** in CH_3CN/CH_3OH (9:1, v/v) gave mass fragments corresponding to $[\mathbf{3c}\cdot\mathbf{2b}-2\,Cl]^{2+}$ at m/z 483.7 (100%) and $[\mathbf{3c}\cdot\mathbf{2b}-Cl]^+$ at m/z 1002.4 (31%), confirming the 1:1 stoichiometry and ion-pair complexation.

The anion-assisted complexation was also detected by a proton NMR titration study (Figure 4). Relatively small upfield shifts after complexation were observed for the aromatic protons (H_e and H_f) of host **3c** and the pyridinium protons (H_α and H_β) of **2a** (spectra a, b and g in Figure 4),

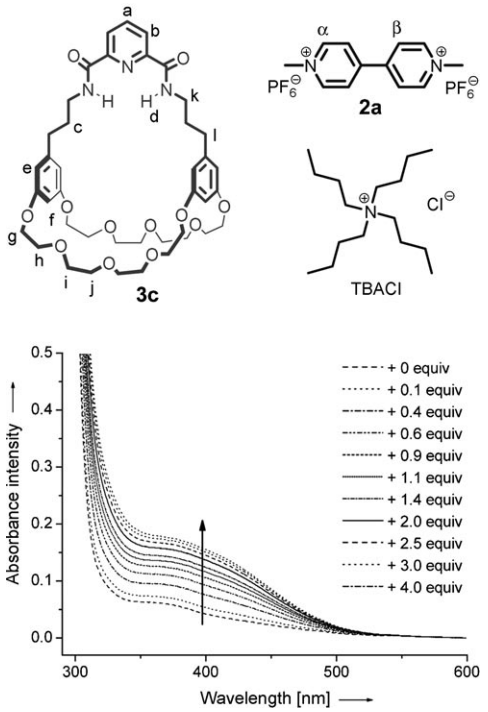


Figure 3. Absorbance spectral changes of an equimolar solution (2.00 mL) of **3c** (0.500 mM) and **2a** (0.500 mM) upon addition of TBACl (from 0 to 2.00 mM).

indicating relatively weak host–guest binding relative to reported complexation between cryptands and paraquat **2a**.[11c] The significant downfield shift of the amide protons (H_d) of cryptand **3c** indicated the dramatic change in the chemical environment in the cryptand cavity after the complexation. Upon the addition of Cl^-, the chemical shift of the amide protons H_d moved even further downfield, due to the hydrogen bond formation between the chloride anion and amide protons. The signals of protons H_e, H_f and H_g moved even further upfield, indicating enhanced host–guest binding, consistently with the above UV/Vis titration study. The pyridinium protons H_β moved downfield upon addition of Cl^- whereas no clear change was observed for the pyridinium protons H_α. This difference can be attributed to the hydrogen bonding between protons H_β and the chloride anion, as would be expected.

Crystals of the **3c**$_2$·**2a**$_2$·**2b** complex suitable for single-crystal X-ray analysis were obtained by vapour diffusion of isopropyl ether into a 1:1:1 solution of **3c**, **2a** and TBACl in acetonitrile/methanol (20:1, v/v) at room temperature. The X-ray crystal structure of the **3c**$_2$·**2a**$_2$·**2b** complex (Figure 5) confirmed the ion-pair recognition process. A chloride atom was found to fill into the "pocket" in the inclusion complex structure formed on threading of the bipyridinium dication guest into the cavity of the cryptand host, in accordance with our design. The chloride atom forms three hydrogen bonds with the two amide hydrogens H_d and one pyridinium hydrogen H_β (Figure 5a and 5b).[15] These three hydrogen bonds adopt a "cone" conformation, indicating that the chloride anion is somewhat too large to fit completely into the cryptand host cavity to form the "tetrahedral" conformation we expected. As in the X-ray crystal structure of the **1**·**2a** complex (Figure 1), water bridges can also be found in this structure (Figure 5b). Here, however, the two water bridges are between two chloride anions to connect two cryptand/paraquat complexes (Figure 5b) whereas in the X-ray crystal structure of **1**·**2a** a water bridge exists between the cryptand host and paraquat guest, providing additional noncovalent interactions between the cryptand host and paraquat guest (Figure 1). The two chloride anions form four hydrogen bonds (**d** and **e** in Figure 5b) with the four hydrogen atoms of two water molecules. Two cryptand/paraquat complexes are linked in the packing structure by the combination of the resulting "rhombus" and "cone" conformations. What is more interesting is that two cryptand/paraquat complexes are also noncovalently connected together by a paraquat molecule through face-to-face π-stackings between the pyridine ring of the **3c** molecule in one cryptand/paraquat complex and a pyridinium ring of a paraquat molecule and between the other pyridinium ring of the paraquat mol-

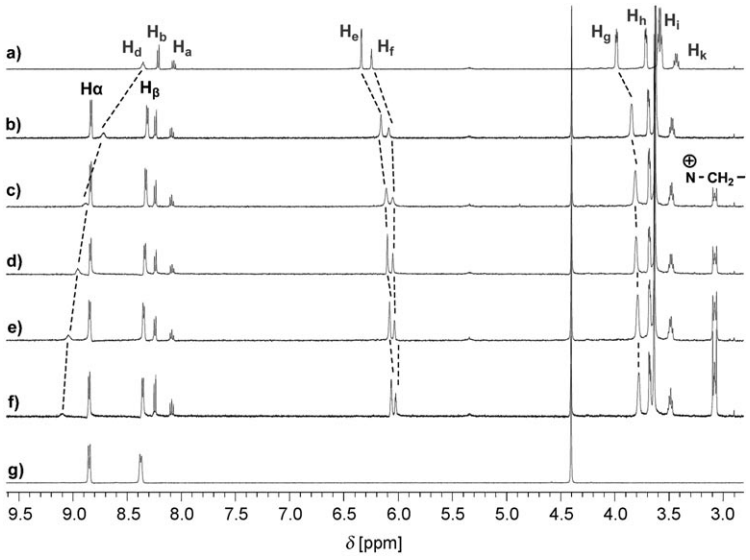


Figure 4. Partial ^{1}H NMR spectra (500 MHz, CD_3CN, 20 °C) of: a) **3c** (0.500 mM), b) an equimolar mixture of **3c** (0.500 mM) and **2a** (0.500 mM), c) (b)+TBACl (0.180 mM), d) (b)+TBACl (0.220 mM), e) (b)+TBACl (0.500 mM), f) (b)+TBACl (1.00 mM), and g) **2a** (1.00 mM).

ecule and the pyridine ring of the **3c** molecule in another cryptand/paraquat complex (Figure 5c). This unique connection may provide extra stability for the crystal structure. These results, combined with the above NMR study, confirmed the improved complexation of paraquat assisted by anion binding.

Anion-assisted complexation of paraquat by cryptand 3g: An equimolar (0.500 mM) acetonitrile solution of cryptand **3g** with paraquat **2a** also gives a weak yellow colour due to charge transfer between the host and guest. Upon gradual addition of Cl^-, however, the intensity of the charge transfer band (388 nm) again increased without any new band being observed (Figure 6). After addition of 2.0 equiv of Cl^-, the solution reached its maximum absorption. The resulting light yellow colour of the solution, which resulted from enhanced charge transfer, indicated that the addition of Cl^- also enhanced the complexation between the cryptand **3g** and the bipyridinium dication. The positive electrospray ionization mass spectrum (Figure S63 in the Supporting Material) of an equimolar mixture of **3g** and **2b** in CH_3CN/CH_3OH (9:1, v/v) gave mass fragments corresponding to $[\mathbf{3g}\cdot\mathbf{2b}-2\,Cl]^{2+}$ at *m*/*z* 483.6 (100%) and $[\mathbf{3g}\cdot\mathbf{2b}-Cl]^{+}$ at *m*/*z* 1001.1 (26%), confirming the 1:1 stoichiometry and ion-pair complexation.

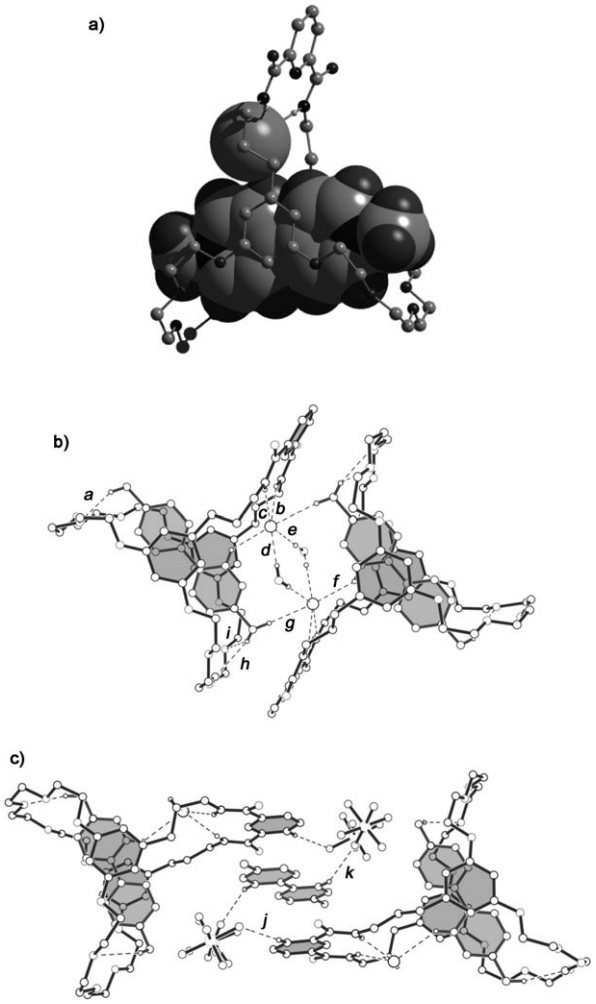


Figure 5. Views of the X-ray crystal structure of the $\mathbf{3c}_2\cdot\mathbf{2a}_2\cdot\mathbf{2b}$ complex. a) **3c** is shown as a ball and stick model and chloride and bipyridinium dication are shown as space-filling models. b) and c) Ball and stick representation of the packing of two adjacent cryptand/paraquat complexes in the unit cell in different directions. Noninteracting hydrogen atoms have been omitted for clarity. Hydrogen bond parameters: H···O(F, Cl) distance [Å], C(N)-H···O(F, Cl) angle [°], C(N)···O(F, Cl) distance [Å]. ***a***) 2.75, 143, 3.57, ***b***) 2.56, 154, 3.35, ***c***) 2.50, 151, 3.27, ***d***) 2.38, 178, 3.23, ***e***) 2.33, 178, 3.18, ***f***) 2.69, 142, 3.47, ***g***) 2.91, 132, 3.63, ***h***) 2.54, 129, 3.23, ***i***) 2.49, 136, 3.35, ***j***) 2.70, 151, 3.91, and ***k***) 2.49, 149, 3.91. Face-to-face π-stacking parameters: centroid–centroid distances [Å]: 4.60, 3.8, 4.49, 3.69; ring plane/ring plane inclinations [°]: 5.0, 6.0, 1.82, 1.19.

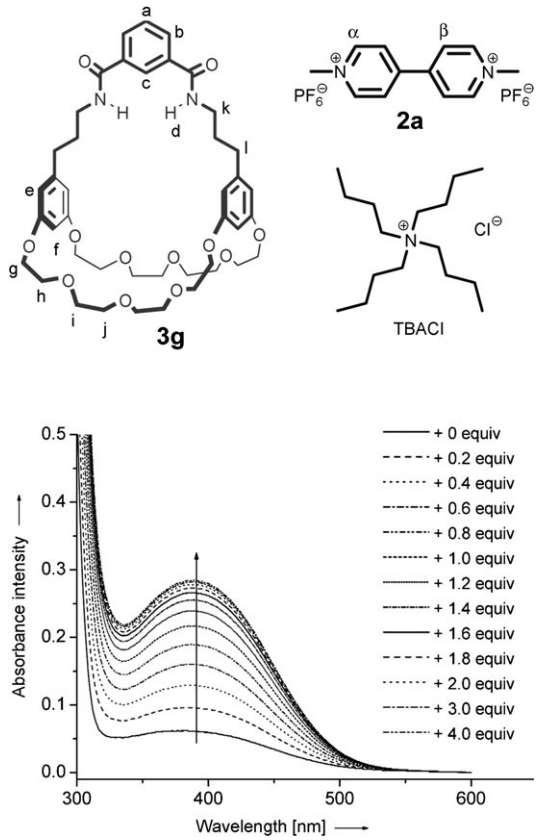


Figure 6. Absorbance spectral changes of an equimolar solution (2.00 mL) of **3g** (0.500 mM) and **2a** (0.500 mM) upon addition of TBACl (from 0 to 2.00 mM).

The anion-assisted complexation of **3g** with bipyridinium dication was also detected by a proton NMR titration study (Figure 7). Relatively small upfield shifts after complexation were observed for the aromatic protons (H_e and H_f), the ethylenoxy protons H_g of host **3g** and the pyridinium protons (H_α and H_β) of **2a** (spectra a, b and f in Figure 7), indicating relatively weak host–guest binding relative to previously reported complexation between cryptands and paraquat **2a**.[11c] Upon addition of Cl^-, the chemical shifts of pro-

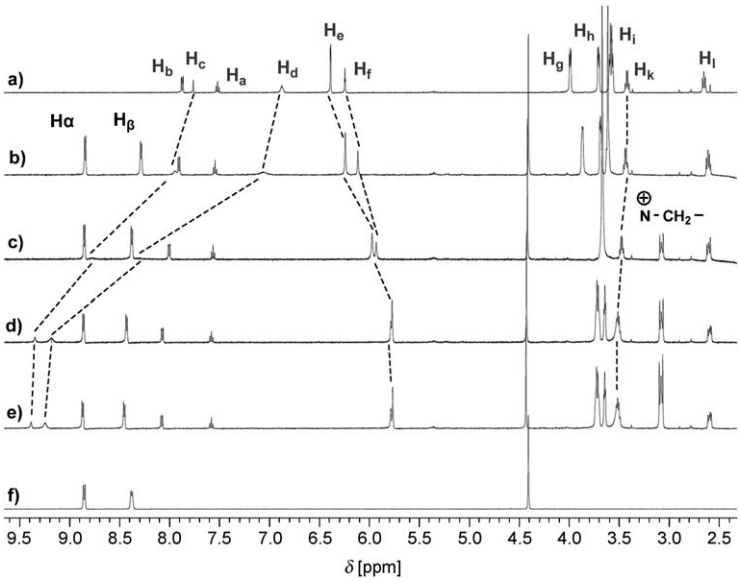


Figure 7. Partial ^{1}H NMR spectra (500 MHz, CD_3CN, 20 °C) of: a) **3g** (0.500 mM), b) an equimolar mixture of **3g** (0.500 mM) and **2a** (0.500 mM), c) (b)+TBACl (0.200 mM), d) (b)+TBACl (0.500 mM), e) (b)+TBACl (1.00 mM), and f) **2a** (0.500 mM).

tons H_d and H_c were shifted even further downfield due to the hydrogen bond formation between these protons and Cl^-. The two peaks corresponding to protons H_e and H_f became a single broadened peak and moved even further upfield. These chemical shift changes indicate enhanced charge transfer, which is consistent with the above UV/Vis titration study. The pyridinium protons H_β were shifted downfield upon addition of Cl^-, whereas no clear chemical shift change was observed for protons H_α. This can be attributed to the hydrogen bonding between hydrogens H_β and the chloride anion, as would be expected.

Crystals of the **3g·2b** complex suitable for single crystal X-ray analysis were obtained by vapour diffusion of isopropyl ether into a 1:1 solution of **3g** and **2b** in acetonitrile/methanol (30:1, v/v) at room temperature. The X-ray crystal structure (Figure 8) of the **3g·2b** complex confirmed the ion-pair recognition. A chloride anion fills the "pocket" in the inclusion complex structure formed on threading of the pyridinium dication into the cavity of the cryptand **3g**, as we designed. Unlike in the crystal structure of the **3c**$_2$·**2a**$_2$·**2b** complex, the Cl^- forms four hydrogen bonds with the two amide protons, one pyridinium proton (H_β) and one phenyl proton (H_c). The four hydrogen bonds also adopt a "cone" conformation, again indicating that the chloride is somewhat too large to form the "tetrahedral" conformation, similarly to what we had observed in the crystal structure of the **3c**$_2$·**2a**$_2$·**2b** complex. One of the pyridinium protons H_β forms a hydrogen bond with the oxygen atom of a carbamide of the adjacent **3g**. This results in a polymer-like packing structure (Figure 8c). The higher K_a value for complex **3g·2b** than for complex **3c·2b** can be explained by the additional H-bonding between the chloride anion and the phenyl proton H_c (Figure 8b). The cryptand **3g** was therefore demonstrated to be an effective host for **2b** through ion-pair recognition.

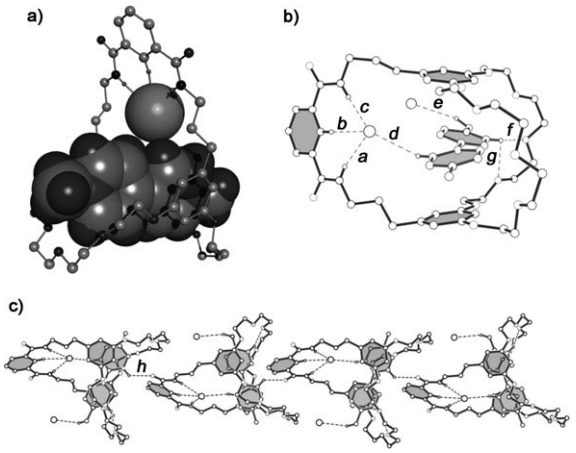


Figure 8. Views of the X-ray crystal structure of the **3g·2b** complex. a) **3g** is shown as a ball and stick model and chloride and bipyridinium dication are shown as space-filling models. b) Ball and stick representation of the **3g·2b** complex. c) Ball and stick representation of the packing structure of the **3g·2b** complex. Noninteracting hydrogen atoms have been omitted for clarity. Hydrogen bond parameters: H···O(F, Cl) distance [Å], C(N)-H···O(Cl) angle [°], C(N)···O(Cl) distance [Å]. ***a***) 2.58, 166, 3.42, ***b***) 2.57, 169, 3.49, ***c***) 2.51, 161, 3.34, ***d***) 2.80, 141, 3.58, ***e***) 2.83, 160, 3.74, ***f***) 2.34, 156, 3.21, ***g***) 2.56, 103, 2.92, and ***h***) 2.40, 129, 3.07. Face-to-face π-stacking parameters: centroid-centroid distances [Å]: 3.68, 4.80, 4.65, 3.84; ring plane/ring plane inclinations [°]: 7.7, 22.3, 9.07, 13.9.

Solid-state structure of the 3a·2a complex: The relatively low K_a values of the complexes **3a·2b** and **3e·2b** are considered to result from the smaller cavities of these two cryptands, which cannot bind cations and anions simultaneously. The failure to observe any mass fragments corresponding to ion-pair-binding complexes in the MS analysis may also be a consequence of this spatial problem. Although attempts to prepare single crystals from solutions either of **3a** and **2b** or of **3e** and **2b** with different host/guest molar ratios and organic solvents failed, crystals of the **3a·2a** complex suitable for single-crystal X-ray analysis were obtained by vapour diffusion of pentane into an equimolar solution of **3a** and **2a** in acetone. The X-ray crystal structure of the **3a·2a** complex is shown in Figure 9. The phenylene rings of the [32]crown-10 part are face-to-face π-stacked with only one pyridinium ring of the guest, whereas in most of the previously reported 1:1 cryptand/paraquat complexes the phenylene rings are face-to-face π-stacked with both pyridinium rings of the paraquat guest.[3a,4,11b,c,16] This big difference in the solid-state structure means that the cavity of the cryptand **3a** is too small to bind Cl^- and bipyridinium dication simultaneously. One fluorine atom of the PF_6 anion is hydrogen-bonded (**a**, **b** and **c** in Figure 9a) to the two amide hydrogen atoms of the cryptand **3a** host and one β-pyridinium hydrogen (H_β) of the paraquat guest and another fluorine atom is hydrogen-bonded (**d** in Figure 9a) to an α-pyridinium hydrogen (H_α) of the paraquat guest. This structural fea-

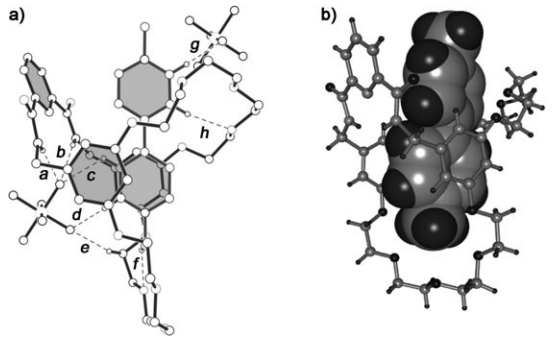


Figure 9. Views of the X-ray crystal structure of the **3a**·**2a** complex. a) Ball and stick representation of the **3a**·**2a** complex. b) **3a** is shown as a ball and stick model, and the bipyridinium cation is shown as a space-filling model. Noninteracting hydrogen atoms have been omitted for clarity. Hydrogen bond parameters: H···O(F, Cl) distance [Å], C(N)–H···O(Cl) angle [°], C(N)···O(Cl) distance [Å]. ***a***) 2.30, 156, 3.11, ***b***) 2.29, 146, 3.05, ***c***) 2.57, 123, 3.18, ***d***) 2.39, 163, 3.30, ***e***) 2.43, 159, 3.35, ***f***) 2.48, 141, 3.28, ***g***) 2.31, 162, 3.21, and ***h***) 2.34, 166, 3.25. Face-to-face π-stacking parameters: centroid–centroid distances [Å] 3.60, 5.25, 3.65, 5.57; ring-plane/ring-plane inclinations [°]: 4.5, 29.5, 0.64, 27.4.

ture indicates that the complexation of paraquat with crypt- and **3a** can also be assisted by anion-binding.

Conclusion

The complexation of divalent salts such as paraquat by cryptands can be improved through the introduction of ion-pair recognition as a means of also binding the counterions. We have designed and synthesized a series of diamide-based cryptands based on bis(*m*-phenylene)-[32]crown-10. The anion-assisted complexation of bipyridinium dications with these new cryptands was confirmed by a combination of ^{1}H NMR characterization, UV/Vis spectroscopy, electrospray ionization mass spectrometry and single-crystal X-ray analysis. It was found that the cryptand **3g**, with its third chain incorporating 13 backbone atoms and an isophthalamide moiety, exhibited the best binding affinity for the tightly ion-paired paraquat dichloride salt (**2a**) through ion-pair recognition. The relatively smaller cavities in the cryptands **3a** and **3e** may make it possible for them to bind bipyridinium dication more efficiently through employment of anions smaller than chloride, such as fluoride. These studies demonstrated that the efficient complexation of tight ion-pairs, such as paraquat dichloride (**2b**), in organic solvents can be achieved through the introduction of heteroditopic cryptand hosts, such as **3**. This anion-assisted recognition motif can be used not only in the efficient preparation of threaded structures, but can also be applied to the development of anion-driven switchable molecular devices. Currently we are focusing on these projects.

Experimental Section

All commercial-grade chemicals were used without further purification. Solvents were either employed as purchased or dried as described in the literature. ^{1}H NMR spectra were collected with a Bruker Avance DMX 500 spectrometer or a Varian Unity INOVA-400 spectrometer with TMS as internal standard. ^{13}C NMR spectra were recorded with a Bruker Avance DMX 500 spectrometer at 125 MHz or a Varian Unity INOVA-400 spectrometer at 100 MHz. Mass spectra were obtained with a Bruker Esquire 3000 plus mass spectrometer (Bruker–Franzen Analytik GmbH Bremen, Germany) with an ESI interface and ion trap analyzer. HRMS were obtained with a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billelica, MA, USA). C, H and N were analyzed with a Carlo Erba 1110 elemental analyzer. The starting materials **4a**[10k] and **5**[11c] were synthesized by literature procedures. The paraquat salt **2b** was purchased from Aldrich. The other salts **2a**,[3a] **2c**[17] and **2d**[18] were synthesized by literature procedures.

General method for the syntheses of the cryptands 3a–3h: A solution of isophthaloyl dichloride or 2,6-pyridinedicarboxyl dichloride (0.400 mmol) in CH_2Cl_2 (15.0 mL) was added by syringe pump at a speed of 1.00 mL h^{-1} under N_2 to a stirred solution of **4** (0.400 mmol) and Et_3N (4.00 mmol) in CH_2Cl_2 (300 mL). After addition, the mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated to about 100 mL and washed with HCl solution (0.1 M). The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The desired product **3** was obtained by flash column chromatography (SiO_2, dichloromethane/acetone 3:1).

Bis(1,3,5-phenylene)di(1′,4′,7′,10′,13′-pentaoxatridecyl)-[2″,6″-di(methyleneacarboxamido)pyridine] (3a): Yield: 11%; m.p. 160–162°C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ=8.46 (d, J=8.0 Hz, 2H), 8.12 (t, J=8.0 Hz, 1H), 7.93 (br, 2H), 6.44 (d, J=2.0 Hz, 4H), 6.38 (s, 2H), 4.61 (d, J=6.0 Hz, 2H), 3.99 (t, J=4.0 Hz, 8H), 3.78 (t, J=4.0 Hz, 8H), 3.66–3.62 ppm (m, 16H); MS (ESI+): m/z (%): 748.5 (100) $[M+Na]^+$; HRMS (ESI): m/z: calcd for $C_{37}H_{47}N_3O_{12}Na$: 748.3057 $[M+Na]^+$; found: 748.3009 (error 6.5 ppm).

Bis(1,3,5-phenylene)di(1′,4′,7′,10′,13′-pentaoxatridecyl)-[2″,6″-di(ethylenecarboxamido)pyridine] (3b): Yield: 30%; m.p. 144–145°C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ=8.33 (d, J=8.0 Hz, 2H), 8.04 (t, J=8.0 Hz, 1H), 7.53 (t, J=6.0 Hz, 2H), 6.49 (d, J=1.6 Hz, 4H), 6.36 (s, 2H), 4.05 (t, J=4.4 Hz, 8H), 3.85 (t, J=4.4 Hz, 8H), 3.70–3.76 (m, 20H), 2.77 ppm (t, J=7.2 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 22°C): δ=162.9, 160.2, 148.5, 140.9, 139.1, 124.7, 107.9, 99.3, 70.9, 70.9, 69.6, 67.6, 39.6, 35.9 ppm; MS (ESI+): m/z (%): 776.5 (100) $[M+Na]^+$, 771.6 (19) $[M+NH_4]^+$; HRMS (ESI): m/z: calcd for $C_{39}H_{52}O_{12}N_3$ 754.3546 $[M+H]^+$; found: 754.3542 (error 0.5 ppm).

Bis(1,3,5-phenylene)di(1′,4′,7′,10′,13′-pentaoxatridecyl)-[2″,6″-di(propylenecarboxamido)pyridine] (3c): Yield: 20%; m.p. 152–154°C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ=8.34 (d, J=7.6 Hz, 2H), 8.02 (t, J=7.6 Hz, 1H), 7.66 (br, 2H), 6.29 (m, 6H), 3.98 (m, 8H), 3.80 (m, 8H), 3.68 (m, 16H), 3.46 (m, 4H), 2.62 (t, J=7.2 Hz, 4H), 1.94 ppm (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$, 22°C): δ=163.6, 159.9, 148.8, 143.6, 138.9, 124.9, 107.3, 98.8, 70.8, 70.8, 69.7, 67.4, 39.0, 33.5, 30.8 ppm; MS (ESI+): m/z (%): 782.9 (100) $[M+H]^+$; HRMS (ESI): m/z: calcd for $C_{41}H_{56}N_3O_{12}$: 782.3859 $[M+H]^+$; found: 782.3830 (error 3.7 ppm).

Bis(1,3,5-phenylene)di(1′,4′,7′,10′,13′-pentaoxatridecyl)-[2″,6″-di(butanecarboxamido)pyridine] (3d): Yield: 24%; m.p. 147–148°C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ=8.27 (d, J=7.6 Hz, 2H), 7.98 (t, J=7.6 Hz, 1H), 7.47 (br, 2H), 6.34 (m, 4H), 6.22 (s, 2H), 4.01 (t, J=3.6 Hz, 8H), 3.80 (t, J=3.6 Hz, 8H), 3.66–3.69 (m, 16H), 3.43 (m, 4H), 2.56 (t, J=5.6 Hz, 4H), 1.65–1.68 (4H, m), 1.53–1.56 ppm (4H, m); MS (ESI+): m/z (%): 810.5 (100) $[M+H]^+$; HRMS (ESI): m/z: calcd for $C_{43}H_{60}N_3O_{12}$: 810.4177 $[M+H]^+$; found: 810.4148 (error 3.6 ppm).

Bis(1,3,5-phenylene)di(1′,4′,7′,10′,13′-pentaoxatridecyl)-(*N*″,*N*″-dimethyleneisophthalamide) (3e): Yield: 6%; m.p. 157–158°C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ=8.17 (d, J=8.0 Hz, 2H), 7.79 (s, 1H), 7.61 (t, J=8.0 Hz, 1H), 6.44 (m, 8H), 4.47 (s, 4H), 4.01 (m, 8H), 3.79 (m, 8H), 3.57–3.67 ppm (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): δ=166.3,

160.1, 139.8, 134.2, 131.6, 129.5, 122.9, 107.6, 100.6, 70.7, 69.6, 67.5, 44.9 ppm; MS (ESI+): *m/z* (%): 747.4 (100) $[M+Na]^+$, 742.4 (91) $[M+NH_4]^+$, 725.4 (23) $[M+H]^+$. MS (ESI−): *m/z* (%): 759.4 (100) $[M+Cl]^-$; HRMS (ESI): *m/z*: calcd for $C_{38}H_{48}O_{12}N_2Na$: 747.3099 $[M+Na]^+$; found: 747.3065 (error 4.5 ppm).

Bis(1,3,5-phenylene)di(1′,4′,7′,10′,13′-pentaoxatridecyl)-(*N*″,*N*″-diethyleneisophthalamide) (3f): Yield: 13%; m.p. 136–138°C; ^{1}H NMR (500 MHz, $CDCl_3$, RT): $\delta=7.94$ (d, $J=7.5$ Hz, 2H), 7.50 (m, 4H), 6.38 (d, $J=2.0$ Hz, 4H), 6.32 (t, $J=2.0$ Hz, 2H), 6.19 (br, 2H), 4.02 (t, $J=4.5$ Hz, 8H), 3.79 (t, $J=4.5$ Hz, 8H), 3.66–3.73 (m, 20H), 2.88 ppm (t, $J=6.0$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta=167.4$, 160.0, 141.2, 134.8, 130.7, 129.3, 124.1, 107.9, 99.7, 70.7, 70.6, 69.6, 67.5, 40.7, 35.2 ppm. MS (ESI): *m/z* (%): 791.4 (13) $[M+K]^+$, 775.5 (100) $[M+Na]^+$, 753.5 (31) $[M+H]^+$; HRMS (ESI): *m/z*: calcd for $C_{40}H_{52}N_2O_{12}Na$: 775.3412 $[M+Na]^+$; found: 775.3444 (error 4.1 ppm).

Bis(1,3,5-phenylene)di(1′,4′,7′,10′,13′-pentaoxatridecyl)-(*N*″,*N*″-dipropyleneisophthalamide) (3g): Yield: 33%; m.p. 140–142°C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta=7.76$ (d, $J=7.6$ Hz, 2H), 7.43 (t, $J=7.6$ Hz, 1H), 7.32 (s, 1H), 6.40 (d, $J=2.0$ Hz, 4H), 6.23 (t, $J=2.0$ Hz, 2H), 6.09 (br, 2H), 3.98 (m, 8H), 3.78 (m, 8H), 3.65–3.69 (m, 16H), 3.50 (q, $J=6.4$ Hz, 4H), 2.68 (t, $J=6.8$ Hz, 4H), 2.00 ppm (m, 4H); MS (ESI+): *m/z* (%): 798.6 (100) $[M+NH_4]^+$, 819.4 (23) $[M+K]^+$, 803.5 (93) $[M+Na]^+$, 781.5 (11) $[M+H]^+$. MS (ESI−): *m/z* (%): 815.7 (67) $[M+Cl]^-$, 779.6 (100) $[M-H]^-$; HRMS (ESI): *m/z*: calcd for $C_{42}H_{56}N_2O_{12}Na$: 803.3731 $[M+Na]^+$; found: 803.3646 (error 9 ppm).

Bis(1,3,5-phenylene)di(1′,4′,7′,10′,13′-pentaoxatridecyl)-(*N*″,*N*″-dibutaneisophthalamide) (3h): Yield: 54%; m.p. 135–137°C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta=7.94$ (m, 2H), 7.87 (s, 1H), 7.49 (t, $J=6.0$ Hz, 1H), 6.29 (m, 8H), 4.01 (t, $J=4.0$ Hz, 8H), 3.81 (t, $J=4.0$ Hz, 8H), 3.42–3.46 (m, 16H), 3.44 (q, $J=5.6$ Hz, 4H), 2.56 (t, $J=5.6$ Hz, 4H), 1.54–1.70 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta=166.8$, 159.7, 144.0, 134.6, 130.4, 129.1, 124.3, 107.4, 98.8, 70.7, 69.7, 67.4, 39.9, 35.3, 28.5, 27.8 ppm; MS (ESI+): *m/z* (%): 831.5 (100) $[M+Na]^+$; HRMS (ESI): *m/z*: calcd for $C_{44}H_{60}N_2O_{12}Na$: 831.4038 $[M+Na]^+$; found: 831.4041 (error 1.0 ppm).

Bis[5-(2′-aminoethylene)-*m*-phenylene]-[32]crown-10 (4b): A solution of **6** (85.0 mg, 0.138 mmol) in THF (20.00 mL) was cooled to 0°C and borane methylsulfide (0.400 mL, 3.92 mmol) was added by syringe. After addition, the reaction mixture was heated at reflux for 5 h and then allowed to cool to room temperature. Methanol (2.00 mL) was added, the mixture was stirred for an hour, and concentrated HCl (5.00 mL) was then added. The resulting mixture was heated at reflux for two hours and then neutralized to pH >12. The solvent was evaporated under reduced pressure and the residue was partitioned between CH_2Cl_2 (50.0 mL) and water (20.0 mL). The organic layer was dried over Na_2SO_4 and concentrated to afford a light yellow oil. Yield: 75.0 mg (84%); ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta=6.35$ (s, 6H), 4.06 (m, 8H), 3.83 (m, 8H), 3.69 (m, 16H), 3.63 (t, $J=6.8$ Hz, 4H), 2.91 (t, $J=6.0$ Hz, 4H), 2.64 ppm (t, $J=6.4$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 22°C): $\delta=160.2$, 108.1, 107.8, 99.4, 77.1, 70.0, 69.1, 45.2, 29.6 ppm. MS (ESI): *m/z* (%): 623.5 (100) $[M+H]^+$; HRMS (ESI): *m/z*: calcd for $C_{32}H_{51}N_2O_{10}$: 623.3538 $[M+H]^+$; found: 623.3543 (error 0.9 ppm).

Bis[5-(3′-aminopropyl)-*m*-phenylene]-[32]crown-10 (4c): A solution of **13** (91.1 mg, 0.100 mmol), hydrazine monohydrate (2.00 mL, 34.0 mmol) and methanol (15.0 mL) was heated at reflux for 17 h. The mixture was allowed to cool to room temperature and concentrated by rotary evaporation. Concentrated HCl (5.00 mL) was added. The resulting mixture was heated at reflux for 2 h. After it had cooled to room temperature, a solid precipitated and was filtered off. The filtrate was neutralized to pH >12 with NaOH (2N) and extracted with $CHCl_3$ (50.0 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford a light yellow oil. Yield: 58.8 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta=6.32$–6.34 (m, 6H), 4.05 (t, $J=4.8$ Hz, 8H), 3.83 (t, $J=4.8$ Hz, 8H), 3.70 (m, 16H), 2.69 (t, $J=7.2$ Hz, 4H), 2.55 (t, $J=8.0$ Hz, 4H), 1.72 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta=159.8$, 144.3, 107.3, 99.7, 70.8, 69.6, 67.3, 41.7, 35.0, 33.4 ppm; MS (ESI): *m/z* (%): 651.6 (100%) $[M+H]^+$; HRMS (ESI): *m/z*: calcd for $C_{34}H_{55}O_{10}N_2$: 651.3857 $[M+H]^+$; found: 651.3873 (error 2.5 ppm).

Bis[5-(4′-aminobutyl)-*m*-phenylene]-[32]crown-10 (4d): A solution of **14** (200.0 mg, 0.300 mmol) in THF (20.0 mL) was cooled to 0°C and borane methylsulfide (0.400 mL, 3.92 mmol) was added by syringe. After addition, the reaction mixture was heated at reflux for 12 h and then allowed to cool to room temperature. The excess borane methylsulfide was destroyed by addition of methanol, the mixture was stirred for an hour, and concentrated HCl (5.00 mL) was then added. The resulting mixture was heated at reflux for an hour and then neutralized to pH >12. The solvent was evaporated under reduced pressure and the residue was partitioned between CH_2Cl_2 (50.0 mL) and water (20.0 mL). The organic layer was dried over Na_2SO_4 and concentrated to afford a colourless oil. Yield: 180 mg (88%); ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta=6.31$ (m, 6H), 4.05 (m, $J=4.8$ Hz, 8H), 3.82 (m, $J=4.8$ Hz, 8H), 3.67–3.71 (m, 16H), 2.67 (t, $J=7.2$ Hz, 4H), 2.51 (t, $J=7.2$ Hz, 4H), 1.42–1.61 ppm (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$, 22°C): $\delta=160.0$, 145.0, 119.8, 107.7, 98.9, 71.0, 69.9, 67.6, 42.3, 36.2, 33.7, 28.7 ppm; MS (ESI): *m/z* (%): 679.7 (100) $[M+H]^+$; HRMS (ESI): *m/z*: calcd for $C_{36}H_{59}O_{10}N_2$: 679.4170 $[M+H]^+$; found: 679.4146 (error 3.5 ppm).

Bis[5-(cyanomethyl)-*m*-phenylene]-[32]crown-10 (6): A mixture of **5** (100 mg, 0.140 mmol), NaCN (30.0 mg, 0.610 mmol) and THF/H_2O (10:1, 20.0 mL) was heated at reflux for 25 h. The mixture was cooled and the solvent was removed on a rotary evaporator. The residue was dissolved in $CHCl_3$ (10.0 mL) and washed with water (10.0 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was separated by flash column chromatography with $CHCl_3$/CH_3OH (30:1) as the eluent to afford **6** as a white solid (73.6 mg, 85%). M.p. 192–193°C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta=6.47$ (s, 4H), 6.23 (s, 2H), 4.07 (t, $J=4.8$ Hz, 8H), 3.85 (t, $J=4.8$ Hz, 8H), 3.69–3.73 (m, 16H), 3.65 ppm (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 22°C): $\delta=160.6$, 132.1, 118.0, 107.1, 101.2, 71.1, 69.8, 67.9, 23.9. MS (ESI): *m/z* (%): 654.6 (19) $[M+K]^+$, 637.5 (100) $[M+Na]^+$, 632.6 (51) $[M+NH_4]^+$; elemental analysis (%) calcd for $C_{32}H_{42}O_{10}N_2$: C 62.53, H 6.89, N 4.56; found: C 62.93, H 6.80, N 4.38.

Bis[5-(2′,2′-dicarbethoxyethyl)-*m*-phenylene]-[32]crown-10 (7): NaH (60% in mineral oil, 100 mg, 2.50 mmol) and **5** (300 mg, 0.415 mmol) were added sequentially to a mixture of diethyl malonate (400 mg, 2.50 mmol) and THF (10.0 mL). The resulting mixture was stirred at room temperature for 24 h, and the solvent was removed in vacuum, followed by addition of CH_2Cl_2 (10.0 mL). The mixture was isolated by flash column chromatography with ethyl acetate/petroleum ether (2:1) as the first eluent and CH_2Cl_2/MeOH (50:1) as the second eluent. The desired product was obtained from the second fraction as a colourless oil (360 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, RT): $\delta=6.30$ (s, 6H), 4.00–4.13 (m, 8H), 3.99 (t, $J=4.8$ Hz, 8H), 3.76 (t, $J=4.8$ Hz, 8H), 3.63–3.67 (m, 16H), 3.55 (t, $J=8.0$ Hz, 2H), 3.06 (d, $J=8.0$ Hz, 4H), 1.16 ppm (t, $J=6.4$ Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta=169.8$, 160.1, 140.2, 106.2, 101.3, 71.5, 69.9, 68.1, 53.7, 51.9, 35.2 ppm; MS (ESI): *m/z* (%): 903.6 (100%) $[M+Na]^+$, 881.6 (34%) $[M+H]^+$; HRMS (ESI): *m/z*: calcd for $C_{44}H_{65}O_{18}$: 881.4171 $[M+H]^+$; found: 881.4150 (error 2.4 ppm).

Bis[5-(2′,2′-dicarboxyethyl)-*m*-phenylene]-[32]crown-10 (8): NaOH (2.0M, 3.0 mL) was added to a solution of **7** (360 mg, 0.409 mmol) in EtOH (5.0 mL). The mixture was heated at reflux for 10 h. The starting material disappeared as monitored by TLC. The ethanol was removed by evaporation, and the remaining aqueous portion was washed with chloroform. The washed aqueous portion was acidified to pH 2 with cold HCl. The precipitated olivine solid was washed twice with water and dried at 60°C for 10 h (310 mg, 99%). M.p. 240–243°C; ^{1}H NMR (400 MHz, $[D_6]$DMSO, RT): $\delta=6.35$ (s, 6H), 4.00 (t, $J=4.4$ Hz, 8H), 3.69 (t, $J=4.4$ Hz, 8H), 3.53–3.57 (m, 16H), 3.33 (br, 2H,), 2.92 ppm (d, $J=7.6$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta=170.8$, 160.0, 141.2, 107.9, 99.3, 70.6, 69.4, 67.6, 53.7, 34.9 ppm; MS (ESI): *m/z* (%): 767.5 (100) $[M-H]^-$; elemental analysis (%) calcd for $C_{36}H_{48}O_{18}$: C 56.24, H 6.29; found: C 55.92, H 6.30.

Bis[5-(3′-carboxyethyl)-*m*-phenylene]-[32]crown-10 (9): Compound **8** (110 mg, 0.143 mmol) was heated at 140°C under N_2 for 2 h and the resulting oil was dissolved with $CHCl_3$ (10.0 mL) and isolated by flash column chromatography with $CHCl_3$/CH_3COOH (100:1) as the eluent to afford the pure product as a white solid (73.0 mg, 75%). M.p. 190–

191 °C; ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 148.7, 147.6, 121.3, 119.8, 113.9, 113.1, 71.0, 69.8, 69.3, 69.1 ppm. MS (ESI): *m*/*z* (%): 679.4 (100%) $[M-H]^-$; HRMS (ESI): *m*/*z*: calcd for $C_{34}H_{48}O_{14}Na$: 703.2942 $[M+Na]^+$; found: 703.2904 (error 5.4 ppm).

Bis[5-(3′-carbomethoxyethyl)-*m*-phenylene]-[32]crown-10 (10): A mixture of **9** (100 mg, 0.147 mmol), sulfuric acid (1.00 mL) and methanol (20.0 mL) was heated at reflux for 12 h. The solution was cooled and diluted with water (20.0 mL). The methanol in the solution was removed with a rotary evaporator. The residue was extracted with $CHCl_3$ (20.0 mL × 2). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was separated by flash column chromatography with ethyl acetate as the eluent to afford **10** as a white solid (92.0 mg, 89%). M.p. 145–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 6.28–6.37 (m 6H), 4.04 (t, *J* = 4.4 Hz, 8H), 3.82 (t, *J* = 4.4 Hz, 8H), 3.66–3.70 (m, 22H), 2.84 (t, *J* = 6.8 Hz, 4H), 2.58 ppm (t, *J* = 6.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 173.3, 160.0, 142.7, 107.3, 99.3, 70.9, 69.7, 67.5, 51.7 35.5, 31.1 ppm; MS (ESI): *m*/*z* (%): 731.6 (100%) $[M+Na]^+$; elemental analysis (%) calcd for $C_{36}H_{52}O_{14}$: C 61.00, H 7.39; found: C 61.20, H 7.43.

Bis[5-(3′-hydroxypropyl)-*m*-phenylene]-[32]crown-10 (11): A mixture of **10** (92.0 mg, 0.131 mmol), $LiAlH_4$ (100 mg, 2.63 mmol) and THF (20.0 mL) was stirred at room temperature for 4 h. The reaction was quenched with water and the reaction mixture was filtered. The solvent in the solution was removed with a rotary evaporator. The residue was extracted with $CHCl_3$ (20.0 mL × 2). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was separated by flash column chromatography with $CHCl_3$/CH_3OH (10:1) as the eluent to afford **11** as a white solid (79.0 mg, 92%). M.p. 122–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 6.32–6.36 (m, 6H), 4.06 (t, *J* = 4.8 Hz, 8H), 3.84 (t, *J* = 4.8 Hz, 8H), 3.69–3.73 (m, 16H), 3.64 (t, *J* = 6.4 Hz, 4H), 2.61 (t, *J* = 7.4 Hz, 4H), 1.85 (t, *J* = 7.0 Hz, 4H), 1.68 ppm (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 160.1, 144.3, 107.7, 99.1, 71.0, 69.9, 67.7, 62.3, 34.1, 32.5 ppm; MS (ESI): *m*/*z* (%): 653.5 (25) $[M+H]^+$, 675.5 (100) $[M+Na]^+$; HRMS (ESI): *m*/*z*: calcd for $C_{34}H_{52}O_{12}Na$: 675.3351 $[M+Na]^+$; found: 675.3327 (error 3.6 ppm).

Bis[5-(3′-(tosyloxyl)propyl)-*m*-phenylene]-[32]crown-10 (12): A mixture of **11** (65.2 mg, 0.100 mmol), TsCl (100 mg, 0.530 mmol) and Et_3N (0.100 mL) in THF (10.0 mL) was stirred at room temperature for 12 h. The solvent was evaporated and the residue was washed first with HCl (0.100 M, 50.0 mL) and then with brine (50.0 mL). The organic layer was dried over Na_2SO_4 and concentrated to afford a yellow oil. The crude product was passed through a short pad of SiO_2 eluted with CH_2Cl_2/MeOH (60:1) to give the title compound as a colourless oil (70.0 mg, 73.0%). ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 7.78 (d, *J* = 8.0 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 6.32 (s, 2H), 6.27 (m, 4H), 4.00–4.05 (H, 12 m), 3.82–3.84 (m, 8H), 3.70–3.84 (m, 16H), 2.56 (t, *J* = 7.2 Hz, 4H), 2.46 (s, 6H), 1.88–1.95 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 160.2, 145.0, 142.9, 133.2, 130.1, 128.1, 107.6, 99.4, 71.1, 69.9, 67.6, 31.9, 30.5, 21.9 ppm; MS (ESI−): *m*/*z* (%): 995.4 (100) $[M+Cl]^-$; HRMS (ESI): *m*/*z*: calcd for $C_{48}H_{65}O_{16}S_2$: 961.3709 $[M+H]^+$; found: 961.3692 (error 1.8 ppm).

Bis[5-(3′-phthalimidopropyl)-*m*-phenylene]-[32]crown-10 (13): A solution of **12** (0.960 g, 1.00 mmol), potassium phthalimide (1.00 g, 5.40 mmol) and DMF (25.0 mL) was heated at 90 °C for 16 h. After the mixture had cooled to room temperature, water (100 mL) was added and the mixture was then extracted with $CHCl_3$. The extract was washed with NaOH (0.100 M) and concentrated to give a crude oil. Recrystallization from CH_3CN/iPr_2O afforded pure **13** as a white solid (847 mg, 93.0%). M.p. 203–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 7.82–7.79 (m, 4H), 7.68–7.71 (m, 4H), 6.31 (s, 4H), 6.15 (s, 2H), 4.02 (t, *J* = 4.4 Hz, 8H), 3.82 (t, *J* = 4.4 Hz, 8H), 3.70–3.74 (m, 20H), 2.59 (t, *J* = 7.6 Hz, 4H), 2.00 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 168.6, 167.1, 160.0, 143.3, 134.6, 134.0, 132.2, 131.9, 124.0, 123.4, 107.3, 99.2, 71.1, 69.9, 67.6, 40.6, 38.0, 33.7, 29.4 ppm; MS (ESI): *m*/*z* (%): 933.6 (100) $[M+Na]^+$; elemental analysis (%) calcd for $C_{50}H_{58}N_2O_{14}$: C 65.92, H 6.42, N 3.08; found: C 65.78, H 6.40, N 3.08.

Bis[5-(3′-cyanopropyl)-*m*-phenylene]-[32]crown-10 (14): A mixture of **12** (135 mg, 0.140 mmol) and NaCN (30.0 mg, 0.610 mmol) in DMF (2.00 mL) was heated at 80 °C for 12 h. The product had the same R_f value as the starting material **12** when monitored by TLC (SiO_2, ethyl acetate). After the reaction mixture had cooled to room temperature, CH_2Cl_2 (30.0 mL) and water (100 mL) were added. The organic phase was washed with water (50.0 mL × 2), dried over anhydrous Na_2SO_4 and concentrated. The residue was isolated by flash column chromatography (SiO_2, petroleum ether/ethyl acetate 1:2, v/v) as a white solid (86.0 mg, 92%). M.p. 150–152 °C; ^{1}H NMR (500 MHz, $CDCl_3$, RT): δ = 6.34 (m, 6H), 6.32 (t, *J* = 2.0 Hz, 2H), 4.06 (t, *J* = 4.5 Hz, 8H), 3.84 (t, *J* = 4.5 Hz, 8H), 3.68–3.72 (m, 16H), 2.67 (t, *J* = 7.0 Hz, 4H), 2.29 (t, *J* = 7.0 Hz, 4H), 1.93 ppm (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 22 °C): δ = 160.3, 142.1, 119.8, 107.7, 99.6, 71.1, 69.9, 67.7, 34.7, 26.8, 16.5 ppm; MS (ESI): *m*/*z* (%): 693.4 (100) $[M+Na]^+$, 671.5 (21) $[M+H]^+$; HRMS (ESI): *m*/*z*: calcd for $C_{36}H_{50}N_2O_{10}Na$: 693.3363 $[M+Na]^+$; found: 693.3359 (error 0.6 ppm).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20774086 and 20834004), the National Basic Research Program (2009CB930104), the Chinese Universities Scientific Fund (2009QNA3008), and the Project-sponsored by SRF for ROCS, SEM (J20080410). We thank Prof. Wanzhi Chen, Dr. Jie Han, and Mr. Jiyong Liu for their kind assistance with X-ray crystallography.

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Received: December 27, 2009
Revised: February 12, 2010
Published online: April 13, 2010

