Anion-Controlled Ion-Pair Recognition of Paraquat by a Bis(*m*-phenylene)-32-crown-10 Derivative Heteroditopic Host

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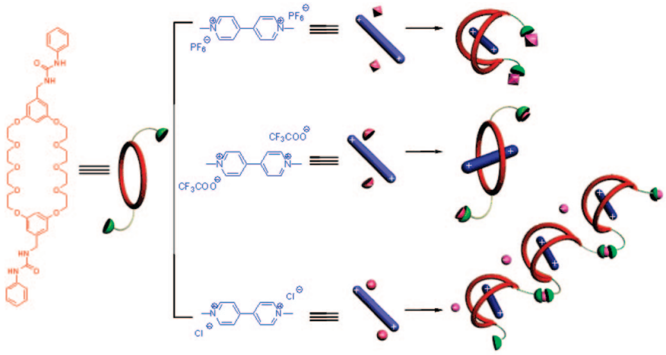

It has been demonstrated that the complexation of the divalent salts of paraquat can be greatly improved (a K_a increase up to 219 times was observed) by the introduction of ion-pair recognition through use of urea moieties on the crown ether. This improvement is controlled by not only the solvent polarity but also the nature of the anion. Furthermore, it was found that the binding motif for paraquat guest incorporation into the heteroditopic host is anion-controlled in the solid state. The host−guest complex is a pseudorotaxane in the solid state when the two counterions of paraquat are trifluoroacetate anions while it is a taco complex when the two counterions are hexafluorophosphate or chloride anions.

Introduction

Anions control many important biological processes in nature.[1] For example, anions control the information processing in retina[1a] and arginine metabolism in chicken kidney and liver.[1b] The cation (such as sodium and calcium cations) conductance in human red blood cells is chloride anion-controlled induced by oxidation.[1g] In artificial systems, people have elegantly used anions to control the formation of pseudorotaxanes,[2a] fabrication of supramolecular capsules,[2b] operation of molecular machines,[2c] and morphological evolution of crystals.[2d] The control of how the guest is incorporated into the host and the relative positional changes that take place within the complexes is critical for the preparation of molecular machines and storage materials.[3,4]

Ion-pair recognition has attracted much attention in recent years for its great potential for biological, analytical, and environmental applications.[5] By the combination of anion and cation receptors, the heteroditopic hosts used in ion-pair recognition often exhibit cooperative and allosteric effects, whereby the association of one ion alters the binding affinity of the counterion through electrostatic and conformational effects. Since Reetz et al. reported one of the first successful

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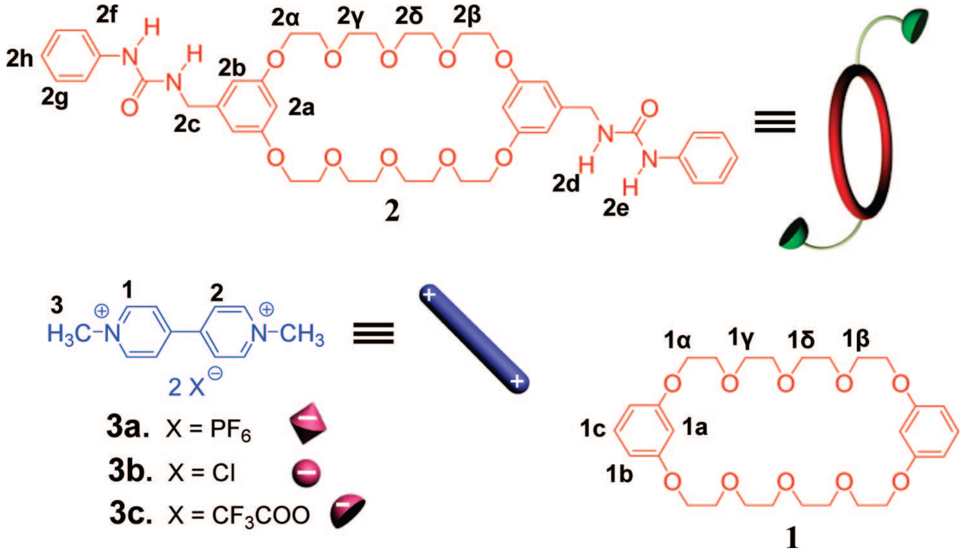

FIGURE 1. Compounds used in this study.

examples of heteroditopic receptors for associated ion-pairs in 1991,[5c] much work has been done in this field.[5] With the assistance of the ion-pair recognition process, the binding affinity of the host can be enhanced and even the binding selectivity of the host can be reversed.[5f,n] The heteroditopic host can be developed to act as an efficient extraction and carrier transporting reagent for environmentally deleterious pollutants.[5d,e] The ion-pair recognition can also play an important role in controlling the geometry of self-assembly. For instance, by the complementary of nitrate, a discrete host−guest assembly can be formed in a Ag^+−ligand system.[5l] Also the assembly of a 22-component complex can be mediated by the cooperation of ligands, cations, and anions.[5g] By the introduction of ion-pair recognition, it has been demonstrated that the strong binding of biologically important reagents can be achieved even in water.[5h−k] Though the application of ion-pair recognition to improve the complexation of monovalent organic or inorganic salts has been widely studied up to now, to the best of our knowledge, much less has been explored on the ion-pair recognition of divalent organic salts.

Paraquat (*N*,*N*′-dimethyl-4,4′-bipyridinium) is an effective but highly toxic herbicide widely used in agriculture and horticulture.[6] It and its derivatives have been widely used in the fabrication of numerous supramolecular systems with crown ethers including bis(*m*-phenylene)-32-crown-10 (BMP32C10, **1**) due to their easy availability and interesting physicochemical properties.[3e,4,7] The improvement of the binding of paraquat and its derivatives is not only important for environmental monitoring and human health,[3e,6] but it is also critical for the fabrication of large supramolecular systems.[8] Herein, we report the synthesis of a heteroditopic BMP32C10 derivative receptor **2** (Figure 1), which was designed to have a BMP32C10 moiety for binding the dicationic bipyridinium part of paraquat **3** and two urea groups for binding the two anions of paraquat **3**,[1f,7,9] and its complexation with paraquat **3** with different anions with the objective of improving the binding of paraquat.

Results and Discussion

A. Synthesis of Heteroditopic Bis(*m*-phenylene)-32-crown-10 Derivative Host 2. The key starting material **4**[10] and bis(*m*-

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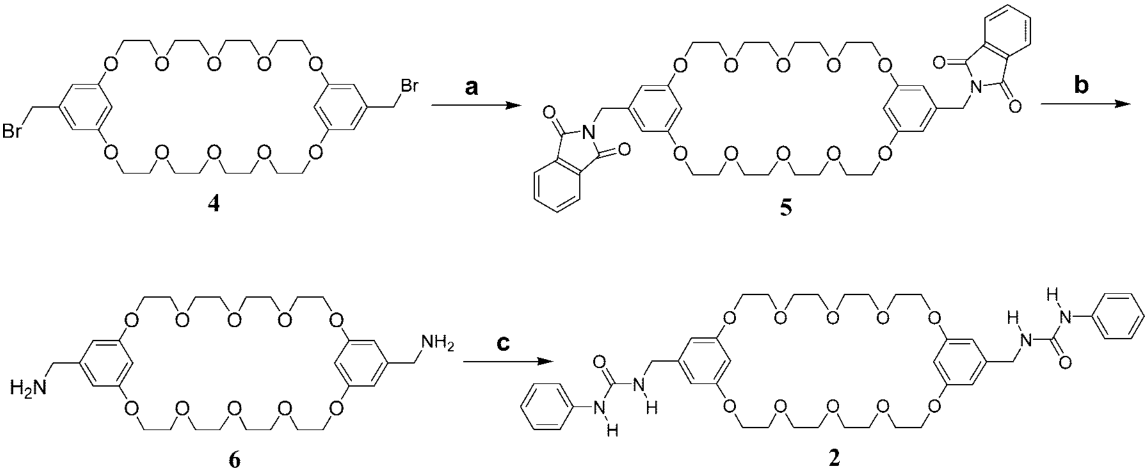
SCHEME 1. Synthesis of Heteroditopic Bis(*m*-phenylene)-32-crown-10 Derivative Host 2 [a]



[a] Reagents and conditions: (a) potassium phthalimide, DMF, 90 °C, 91%; (b) (i) hydrazine monohydrate, CH_3OH, reflux, (ii) NaOH, H_2O, 89% (two steps); (c) phenylisocyanate, $CHCl_3$, N_2, 95%.

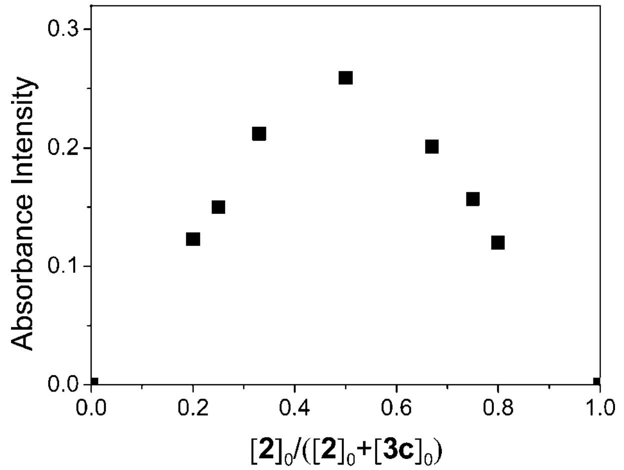


FIGURE 2. Job plot showing the 1:1 stoichiometry of the complex between **2** and **3c** in CH_3CN:CH_3OH (9:1, v:v) by plotting the absorbance intensity at $\lambda = 376$ nm (the host−guest charge transfer band) against the mole fraction of the host. $[\mathbf{2}]_0$ and $[\mathbf{3c}]_0$ are initial concentrations of **2** and **3c**. $[\mathbf{2}]_0 + [\mathbf{3c}]_0 = 1.00$ mM.

phenylene)-32-crown-10 (BMP32C10, **1**)[11] were synthesized according to literature procedures. The diamino intermediate **6** was synthesized according to a similar method for monofunctionalization of a phenyl crown ether reported by Gibson et al.[12] As illustrated in Scheme 1, the reaction of **4** with excess potassium phthalimide afforded **5**. The diamino intermediate **6** was obtained from the hydrazinolysis of **5** in methanol in good yield. The bis(*m*-phenylene)-32-crown-10 derivative heteroditopic host **2** was obtained in 95% yield by the reaction of **6** with phenylisocyanate in $CHCl_3$.

B. Complexation of Heteroditopic Bis(*m*-phenylene)-32-crown-10 Derivative Host 2 with Paraquat 3. A Job plot[13] (Figure 2) based on UV−vis spectroscopy absorbance data in CH_3CN:CH_3OH (9:1, v:v) demonstrated that the complex of **2** with **3c** was of 1:1 stoichiometry in solution. The complexes of **2** with **3a** and **2** with **3b** also have a 1:1 stoichiometry in solution (see the Supporting Information), the same as those of **1** with **3**.[7] Positive electrospray ionization mass spectra in CH_3CN (see the Supporting Information) of equimolar mixtures of **2** and **3a**, **2** and **3b**, and **2** and **3c** gave strong mass fragments of $[\mathbf{2}\cdot\mathbf{3}-2X]^{2+}$: *m/z* 509.3 (100%) for $[\mathbf{2}\cdot\mathbf{3a}-2PF_6]^{2+}$, 509.3 (100%) for $[\mathbf{2}\cdot\mathbf{3b}-2Cl]^{2+}$, and 509.2 (100%) for $[\mathbf{2}\cdot\mathbf{3c}-2CF_3COO]^{2+}$, respectively. Also a common mass fragment corresponding to $[\mathbf{2}\cdot\mathbf{3}-X]^{+}$ was found: *m/z* 1163.4 (35%) for $[\mathbf{2}\cdot\mathbf{3a}-PF_6]^{+}$, 1053.5 (25%) for $[\mathbf{2}\cdot\mathbf{3b}-Cl]^{+}$, and 1131.5 (27%) for $[\mathbf{2}\cdot\mathbf{3c}-CF_3COO]^{+}$. These results confirmed the 1:1 complexation stoichiometry between **2** and **3**.

The proton NMR spectra of equimolar (2.00 mM) acetonitrile solutions of **2** and **3** (Figures 3−5) showed the complexation is a fast exchange system as the reported complexation between **1** and **3**.[7] The complexation was stronger than that of **1** with **3** on the basis of the significant upfield shifts of the bipyridinium protons (H_1 and H_2) and methyl protons (H_3) of **3** and the aromatic protons (H_{2a} and H_{2b}) and α-ethyleneoxy protons ($H_{2\alpha}$) of **2**. The phenyl protons (H_{2f}, H_{2g}, and H_{2h}) and the urea protons (H_{2d} and H_{2e}) of **2** moved downfield after complexation. The changes of the chemical shifts of H_{2d} and H_{2e} after the complexation between **2** and **3a** (0.01 and 0.02 ppm) are significantly smaller than those after the complexation between **2** and **3b** (1.29 and 1.64 ppm) and those after the complexation between **2** and **3c** (1.57 and 1.63 ppm), which is attributed to the very weak binding affinity of the urea portion to the large, diffusely charged hexafluorophosphate anion compared with the case of the chloride or trifluoroacetate anion.[9] More interestingly, the three peaks corresponding to ethyleneoxy protons ($H_{2\alpha}$, $H_{2\beta}$, $H_{2\gamma}$, and $H_{2\delta}$) of **2** merged together to become one broad peak upon complexation of **2** with **3a** or **3b** (spectra a and b in Figure 3 and spectra a and b in Figure 4), while clearly three separate peaks were observed for these ethyleneoxy protons after the complexation of **2** with **3c** (spectra a and b in Figure 5). These differences indicated that the complexation of **2** with **3c** in solution might have a different host−guest complexation geometry from the complexation of **2** with **3a** or **3b**, resulting from the differences in the counteranions of the paraquat salt guests **3**.

C. Association Constant Comparison between the Complexation of 2 with 3 and That of 1 with 3. The yellow color, which resulted from charge transfer between electron-

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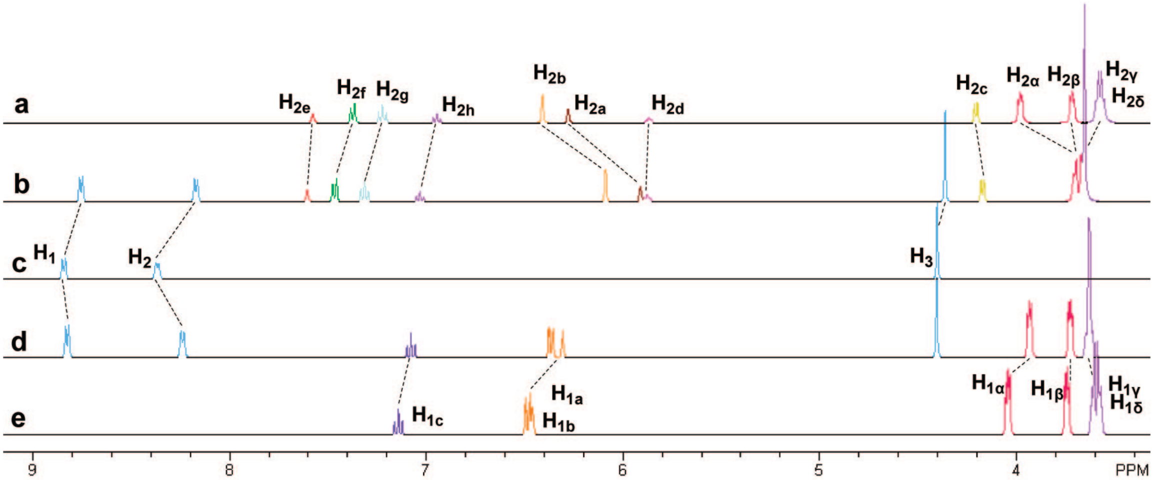

FIGURE 3. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 22 °C) of 2.00 mM **2** (a), 2.00 mM **2** and **3a** (b), 2.00 mM **3a** (c), 2.00 mM **1** and **3a** (d), and 2.00 mM **1** (e).

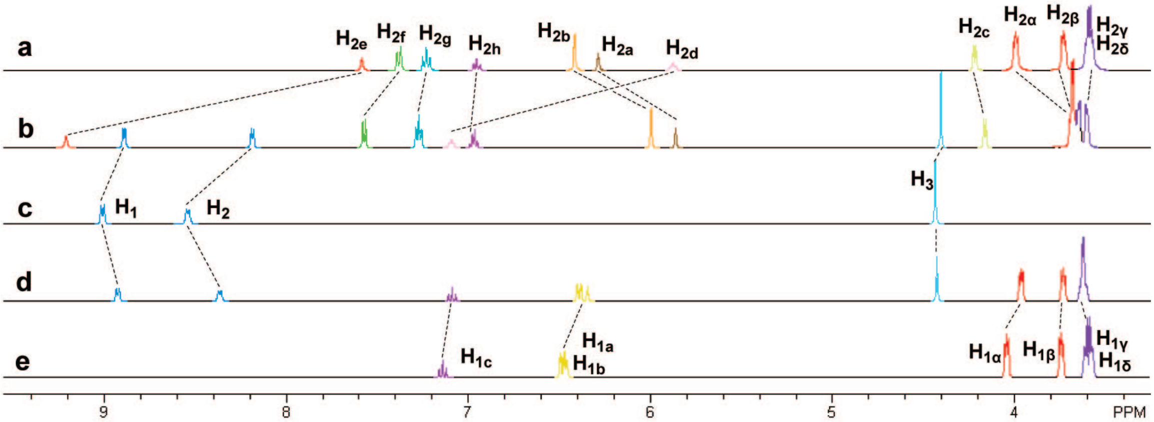

FIGURE 4. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 22 °C) of 2.00 mM **2** (a), 2.00 mM **2** and **3b** (b), 2.00 mM **3b** (c), 2.00 mM **1** and **3b** (d), and 2.00 mM **1** (e).

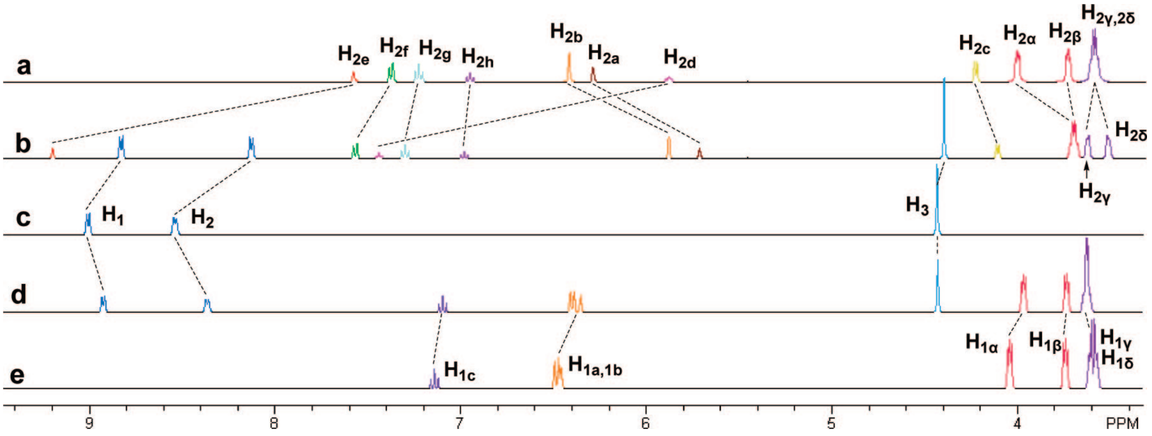

FIGURE 5. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 22 °C) of 2.00 mM **2** (a), 2.00 mM **2** and **3c** (b), 2.00 mM **3c** (c), 2.00 mM **1** and **3c** (d), and 2.00 mM **1** (e).

rich aromatic rings of the host and electron-poor pyridinium rings of the guest, of equimolar (2.00 mM) CH_3CN:CH_3OH (9:1, v:v) solutions of **2** and **3** was deeper than that of the corresponding solutions of **1** and **3**. This gave direct evidence that the binding of the anions with the urea groups can enhance the binding of the crown ether cavity to the dicationic bipyridinium part through ion-pair recognition. The association constant (K_a) values of complexes **1·3** and **2·3**, as shown in Table 1, were determined by probing the charge-transfer band of the complexes by UV−vis spectroscopy and employing a titration method (Figure 6 as well as Figures S15−S36 in the Supporting Information). All complexes **2·3** exhibited K_a increases compared with the corresponding complexes **1·3** induced by the ion-pair recognition. However, there are two things worth noting. First, when the solvent polarity was reduced, the K_a increase rose. For example, the K_a increase from

TABLE 1. Association Constants (K_a/M^{-1}) for the 1:1 Complexes between Hosts 1 and 2 and Guests 3 in Different Solvents at 25 °C

host	solvent (v:v)	**3a** (X = PF_6)	**3b** (X = Cl)	**3c** (X = CF_3COO)
1	CH_3CN:CH_3OH (9:1)	$1.9(\pm0.2) \times 10^2$	$1.2(\pm0.1) \times 10^2$	$0.9(\pm0.2) \times 10^2$
	CH_3CN	$3.2(\pm0.3) \times 10^2$	[a]	$1.3(\pm0.1) \times 10^2$
	CH_3CN:$CHCl_3$ (1:1)	$8.6(\pm0.9) \times 10^2$	[a]	$4.2(\pm0.3) \times 10^2$
	CH_3CN:$CHCl_3$ (1:2)	$1.3(\pm0.2) \times 10^3$	[a]	$7.8(\pm1.3) \times 10^2$
	CH_3CN:$CHCl_3$ (1:3)	$1.9(\pm0.7) \times 10^3$	[a]	$1.0(\pm0.2) \times 10^3$
2	CH_3CN:CH_3OH (9:1)	$5.5(\pm0.5) \times 10^2$	$5.6(\pm0.5) \times 10^2$	$4.7(\pm0.3) \times 10^2$
	CH_3CN	$1.4(\pm0.1) \times 10^3$	[a]	$1.2(\pm0.1) \times 10^3$
	CH_3CN:$CHCl_3$ (1:1)	$3.7(\pm0.3) \times 10^3$	[a]	$2.5(\pm0.3) \times 10^4$
	CH_3CN:$CHCl_3$ (1:2)	$7.1(\pm2.6) \times 10^3$	[a]	$1.0(\pm0.1) \times 10^5$
	CH_3CN:$CHCl_3$ (1:3)	$1.3(\pm0.3) \times 10^4$	[a]	$2.2(\pm0.1) \times 10^5$

[a] Could not be determined due to the poor solubility of the salt in these solvents.

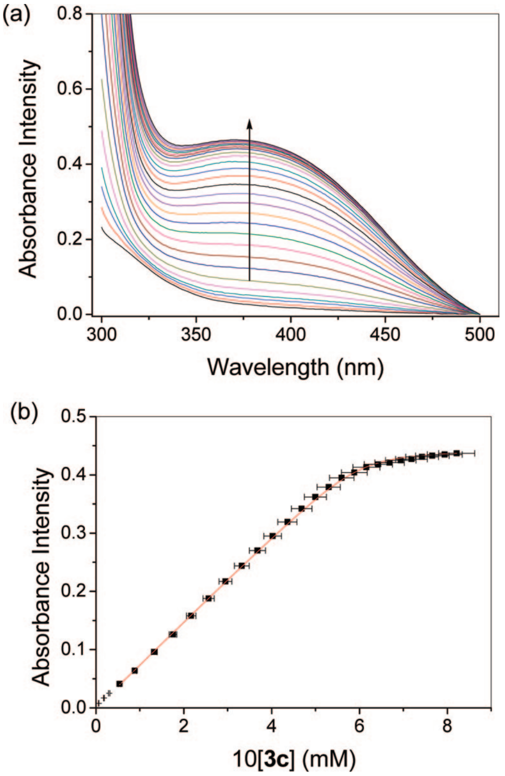

FIGURE 6. Determination of K_a of **2·3c** in CH_3CN:$CHCl_3$ (1:3, v:v). (a) The absorbance spectral changes of **2** (0.600 mM, 2.00 mL) upon addition of **3c** (2.00 mM) and (b) the absorbance intensity changes at $\lambda = 376$ nm upon addition of **3c** (from 0 to 0.82 mM). The red solid line was obtained from the nonlinear curve-fitting.

1·3c to **2·3c** was 4.2 times in 9:1 acetonitrile:methanol, 8.2 times in acetonitrile, 59 times in 1:1 acetonitrile:chloroform, 127 times in 1:2 acetonitrile:chloroform, and 219 times in 1:3 acetonitrile:chloroform, respectively. Second, when the counterions are different, the K_a increases are different. In 9:1 acetonitrile:methanol, the K_a increase is 1.9, 3.7, and 4.2 times respectively from **1·3a** to **2·3a**, from **1·3b** to **2·3b**, and from **1·3c** to **2·3c**. In 1:1 acetonitrile:chloroform, the K_a increase is 3.3 and 59 times, respectively, from **1·3a** to **2·3a** and from **1·3c** to **2·3c**. In an even lower polarity solvent system, 1:3 acetonitrile:chloroform, the difference of the K_a increase is even more apparent. The K_a value increased 5.8 and 219 times, respectively, from **1·3a** to **2·3a** and from **1·3c** to **2·3c**. The K_a increase difference for the paraquat guest salts reflects the different binding strengths of the urea groups with the different counteranions.[9] This result is in accordance with the above-mentioned changes of ^{1}H NMR chemical shifts of the urea protons after complexation with different paraquat salts (Figures 3−5). The high K_a value $2.2(\pm0.1) \times 10^5$ M^{-1}, for **2·3c** in 1:3 acetonitrile:chloroform can be attributed to both the enhanced binding affinity of the crown ether portion for the bipyridinium cation via ion-pair recognition and the enhanced hydrogen bonding strength in this lower polarity solvent system. Therefore, the binding improvement induced by ion-pair recognition is not only solvent polarity controlled but also anion controlled.

D. Solid State Structures of Complexes 2·3a, 2·3b, and 2·3c. Suitable crystals of **2·3a**, **2·3b**, and **2·3c** for single-crystal X-ray analysis were all obtained by a vapor diffusion method. The X-ray crystal structures (Figure 7) of complexes **2·3a**, **2·3b**, and **2·3c** confirmed the ion-pair recognition between **2** and **3** since the BMP32C10 moiety of **2** binds the dicationic bipyridinium part of **3** and the two urea groups of **2** bind the two anions of **3** as we designed. All three 1:1 complexes **2·3a**, **2·3b**, and **2·3c** are stabilized by hydrogen bonding (Tables 2−4) between α-pyridinium hydrogens of **2** and oxygens of **3** and face-to-face π-stacking interactions (Table 5) between the two electron-rich phenylene rings of **2** and the two electron-poor pyridinium rings of **3** in the solid state. None of the methyl and β-pyridinium hydrogens are involved in hydrogen bonding between the host and guest. This is the same for a previously reported complex based on a bis(*m*-phenylene)-32-crown-10 derivative and **3a**.[11] What is interesting is that the oxygen atoms of the two carbonyl groups of **2** form C−H···O hydrogen bonds (**d**, **i**, **q**, **v**, and **a1** in Figure 7) with α-pyridinium hydrogens of **3** in these three crystal structures, which also stabilizes these three complexes in the solid state.

Both **2·3a** and **2·3b** are taco complexes, in which the bipyridinium part of **3** is sandwiched between two phenylene rings of **2**, in the solid state (parts a and b of Figure 7). However, a significant difference between the crystal structure of **2·3a** and that of **2·3b** is that **2·3b** forms a poly(taco complex)[14] packing structure (part b of Figure 7) because one chloride anion coordinates to two urea groups with a distorted tetrahedral geometry.[9] The poly(taco complex) packing structure formed by strong N−H···Cl hydrogen bonding contributed to the stability of the crystals of **2·3b**, which were stable in open air for several months. What is surprising and more interesting is that **2·3c** is a pseudorotaxane, in which the dicationic bipyridinium part of **3** threads through the cavity of **2**, instead of a taco complex in the solid state (part c of Figure 7). This is unique since **2·3a**, **2·3b**, and all previously reported host−guest complexes based on BMP32C10 and paraquat derivatives are

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(14) Huang, F.; Fronczek, F. R.; Gibson, H. W. *Chem. Commun.* **2003**, 1480–1481.

(15) Here a hydrogen bond is thought to exist when the H···O (F, Cl) distance is less than the sum, 2.72 (2.67, 2.95) Å, of van der Waals radii (Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451) of the hydrogen atom and the acceptor O (F, Cl) atom, and the C−H···O (F, Cl) angle is greater than 90°.[3e]

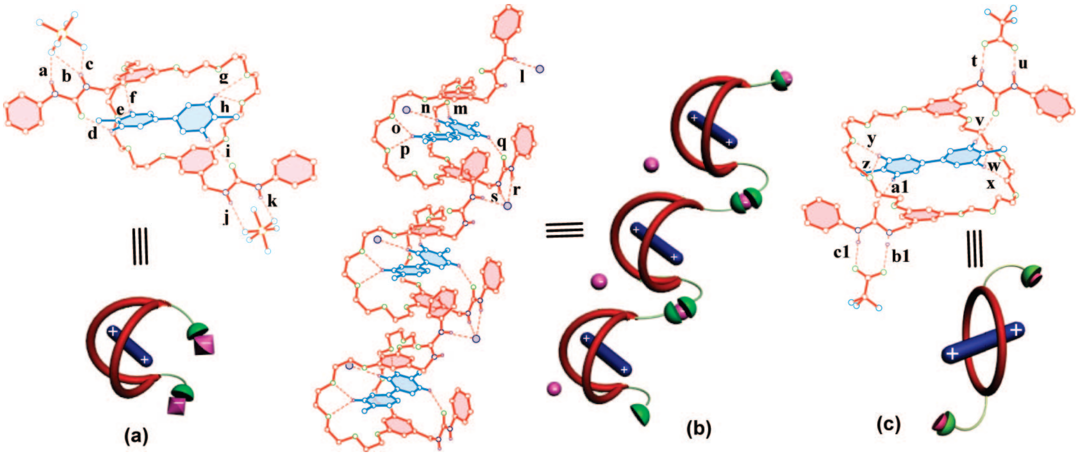

FIGURE 7. Ball-stick views and cartoon representations of the X-ray structures of **2**·**3a** (a), **2**·**3b** (b), and **2**·**3c** (c). Color key: **2** is red, **3** is blue, hydrogens are purple, oxygens are green, nitrogens are dark blue, phosphorus are yellow, fluorins are light blue, and chlorides are black. Solvent molecules and hydrogens except the ones involved in hydrogen bonding between **2** and **3** were omitted for clarity.

TABLE 2. Hydrogen-Bond Parameters for 2·3a[15]

parameters	a	b	c	d	e	f	g	h	i	j	k
C(N)···O(F) distances (Å)	3.19	3.22	3.00	3.16	3.30	3.19	3.39	3.31	3.20	3.21	3.09
H···O(F) distances (Å)	2.37	2.43	2.25	2.42	2.45	2.46	2.57	2.69	2.40	2.35	2.25
C(N)−H···O(F) angles (deg)	159	154	143	136	152	135	148	125	144	171	166

TABLE 3. Hydrogen-Bond Parameters for 2·3b[15]

parameters	l	m	n	o	p	q	r	s
C(N)···O(Cl) distances (Å)	3.29	3.37	3.63	3.17	3.33	3.11	3.31	3.50
H···O(Cl) distances (Å)	2.50	2.51	2.71	2.44	2.53	2.49	2.48	2.71
C(N)−H···O(Cl) angles (deg)	163	145	170	136	145	124	165	153

TABLE 4. Hydrogen-Bond Parameters for 2·3c[15]

parameters	t	u	v	w	x	y	z	a1	b1	c1
C(N)···O distances (Å)	2.91	2.84	3.16	3.00	3.19	3.19	3.00	3.16	2.91	2.84
H···O distances (Å)	2.08	2.00	2.39	2.39	2.31	2.31	2.39	2.39	2.08	2.00
C(N)−H···O angles (deg)	162	157	140	122	159	159	122	140	162	157

TABLE 5. Selected Distances and Angles for 2·3a, 2·3b and 2·3c

parameters	2·3a	2·3b	2·3c
face-to-face π-stacking centroid-centroid distances (Å)	3.53, 3.59	3.56, 3.69	3.66, 3.66
face-to-face π-stacking ring plane/ring plane inclinations (deg)	7.5, 3.7	5.6, 3.1	7.0, 7.0
centroid−centroid distance (Å) between two phenylene rings of **2**	7.59	7.45	7.61
dihedral angle (deg) between two phenylene rings of **2**	20	18	0
centroid−centroid distance (Å) between two pyridinium rings of **3**	4.28	4.29	4.27
dihedral angle (deg) between two pyridinium rings of **3**	28	22	0

taco complexes in the solid state.[7f−h,11,14] Possibly due to the difference in the host−guest complexation geometry of **2**·**3c** compared with **2**·**3a** and **2**·**3b**, both the dihedral angle between the two phenylene rings of **2** and the dihedral angle between the two pyridinium rings of **3** are 0°, very different from the corresponding values (20° and 28° or 18° and 22°) for these two angles in the case of **2**·**3a** or **2**·**3b** (Table 5). Therefore, the complexation motif for incorporation of paraquat guest **3** into heteroditopic host **2** is anion controlled in the solid state.

Conclusions

The complexation of divalent salts such as paraquat by crown ethers can be greatly improved (a K_a increase up to 219 times was observed here) by the introduction of ion-pair recognition as a means of also binding the counterions. The improvement is controlled by not only the solvent polarity but also the nature of the anion. This enables us to control the host−guest binding strength by simply changing anions. Furthermore, it was found that the complexation motif relating to the geometry of inclusion of paraquat guest **3** in the cavity of heteroditopic host **2** is anion controlled in the solid state. This is a new way to control the host−guest complexation geometry and should be useful in the future fabrication of molecular machines and storage materials.

Experimental Section

***N,N′*-Dimethyl-4,4′-bipyridinium trifluoroacetate (3c).** A mixture of 4,4′-bipyridine (1.60 g, 10.0 mmol) and methyl iodide (1.70 g, 12.0 mmol) was refluxed in CH_3CN for 12 h and a red solid was precipitated. The red solid was filtered and washed with CH_3CN and dried. The dried *N,N′*-dimethyl-4,4′-bipyridinium iodide (220 mg, 0.500 mmol) was dissolved in deionized water (2.00 mL) and an aqueous solution (2.00 mL) containing silver trifluoroacetate (440 mg, 1.00 mmol) was slowly added with vigorously stirring. The resulting mixture was centrifugated and the supernatant liquid was isolated. After the solvent was evaporated under reduced pressure, a white solid was obtained. This crude product was redissolved into CH_3CN and precipitated by adding isopropyl ether, affording the pure trifluoroacetate salt **3c** (165 mg, 80%). Mp 185−190 °C dec. ^1H NMR (400 MHz, CD_3CN, 22 °C) δ 9.01 (d, $J = 6.4$ Hz, 4H), 8.54 (d, $J = 6.4$ Hz, 4H), 4.43 (s, 6H). Anal. Calcd for $C_{16}H_{14}N_2O_4F_6$: C, 46.61; H, 3.42; N, 6.79. Found: C, 46.50; H, 3.40; N, 6.82.

Bis(5-phthalimidomethyl-*m*-phenylene)-32-crown-10 (5). Compound **5** was synthesized according to a similar method for monofunctionalization of phenyl crown ethers.[12] A solution of **4**[10] (3.61 g, 5.00 mmol), potassium phthalimide (2.00 g, 10.8 mmol), and DMF (50.0 mL) was held at 90 °C for 24 h and then cooled to room temperature. The solvent was evaporated under reduced pressure. The residue was dissolved in 200 mL of CH_2Cl_2 and washed with 100 mL of water twice. The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacum to afford the crude product, which was isolated by flash column chromatography with the CH_2Cl_2/CH_3OH (v:v = 20:1) as the eluent to afford **5** as a white solid (3.90 g, 91%). Mp 144−145 °C. ^1H NMR (400 MHz, $CDCl_3$, 22 °C) δ 7.81 (m, 4H), 7.68 (m, 4H), 6.52 (d, $J = 2.4$ Hz, 4H), 6.33 (t, $J = 2.4$ Hz, 2H), 4.71 (s, 4H), 4.00 (t, $J = 4.4$ Hz, 8H), 3.78 (t, $J = 4.4$ Hz, 8H), 3.64−3.68 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C) δ 168.0, 160.0, 138.3, 133.9, 132.0, 123.3, 107.2, 100.7, 70.8, 70.8, 69.5, 67.5, 41.5. Low-resolution ESI-MS *m/z* 872.7 (100%) $[\mathbf{5} + NH_4]^+$ and 877.7 (45%) $[\mathbf{5} + Na]^+$. Anal. Calcd for $C_{46}H_{50}N_2O_{14}$: C, 64.63; H, 5.90; N, 3.28. Found: C, 64.45; H, 5.93; N, 3.27.

Bis(5-aminomethyl-*m*-phenylene)-32-crown-10 (6). Compound **6** was synthesized according to a similar method for monofunctionalization of phenyl crown ethers.[12] A solution of **5** (2.60 g, 3.00 mmol), hydrazine monohydrate (0.500 mL, 8.50 mmol), and methanol (10.0 mL) was refluxed for 12 h, cooled, and concentrated by rotary evaporation. The mixture was filtered and the solid was washed with 5 mL of methanol twice. The combined filtrate was neutralized to pH >12 with 2.00 M NaOH and extracted with $CHCl_3$. The combined extracts were dried over anhydrous Na_2SO_4 and evaporated in vacuo to afford **6** (1.60 g, 89%) as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$, 22 °C) δ 6.42 (d, $J = 2.4$ Hz, 4H), 6.31 (t, $J = 2.4$ Hz, 2H), 4.02 (t, $J = 4.8$ Hz, 8H), 3.79 (t, $J = 4.8$ Hz, 8H), 3.71 (s, 4H), 3.62−3.69 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C) δ 159.7, 145.1, 105.6, 99.6, 70.5, 69.4, 67.2, 46.1. Low-resolution ESI-MS: *m/z* 595.3 (100%) $[\mathbf{6} + H]^+$. HR ESI-MS *m/z* calcd for $[M + H]^+$ $C_{30}H_{47}N_2O_{10}$ 595.3225, found 595.3222, error 0.5 ppm.

Bis[5-(phenylureidomethylene)-*m*-phenylene]-32-crown-10 (2). A solution of 590 mg (1.00 mmol) of **6** and 240 mg (2.00 mmol) of phenylisocyanate in 30.0 mL of $CHCl_3$ was stirred at room temperature for 12 h under N_2 atmosphere. The reaction mixture was added with 10 mL of 1.00 M HCl aqueous solution and the organic layer was then washed with 10 mL of brine twice. After drying over Na_2SO_4, the solvent was removed by a rotary evaporator to afford the crude product, which was recrystallized from acetone to give **2** as a white solid (790 mg, 95%). Mp 202−203 °C. ^1H NMR (400 MHz, CD_3CN, 22 °C) δ (ppm) 7.58 (s, 2H), 7.38 (d, $J = 8.0$ Hz, 4H), 7.23 (t, $J = 8.0$ Hz, 4H), 6.95 (t, $J = 7.2$ Hz, 2H), 6.41 (d, $J = 1.6$ Hz, 4H), 6.28 (s, 2H), 5.87 (t, $J = 5.2$ Hz, 2H), 4.21 (d, $J = 5.6$ Hz, 4H), 3.98 (t, $J = 4.8$ Hz, 8H), 3.72 (t, $J = 4.8$ Hz, 8H), 3.56−3.60 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C) δ 207.1, 159.8, 156.3, 153.7, 141.2, 139.4, 138.9, 128.8, 122.8, 122.4, 119.5, 119.2, 106.1, 100.4, 70.5, 70.4, 69.8, 67.3, 43.9. Low-resolution ESI-MS *m/z* 833.5 (71%) $[\mathbf{2} + H]^+$ and 855.4 (100%) $[\mathbf{2} + Na]^+$. Anal. Calcd for $C_{46}H_{50}N_2O_{14}$: C, 63.45; H, 6.78; N, 6.73. Found: C, 63.46; H, 6.74; N, 6.73.

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Note Added after ASAP Publication. The expression $[\mathbf{2}\cdot\mathbf{3}{-}X]^+$ was incorrectly printed as $[\mathbf{2}\cdot\mathbf{3}{-}X]^{2+}$ in section B in the version published ASAP January 6, 2009; the corrected version was published ASAP January 8, 2009.

Supporting Information Available: Determination of association constants, ^1H and ^{13}C NMR spectra, electrospray ionization mass spectra, X-ray crystallographic files (CIF) for **2·3a**, **2·3b**, and **2·3c**, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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