Synthesis of Bis(*m*-phenylene)-32-crown-10-Based Discrete Rhomboids Driven by Metal-Coordination and Complexation with Paraquat

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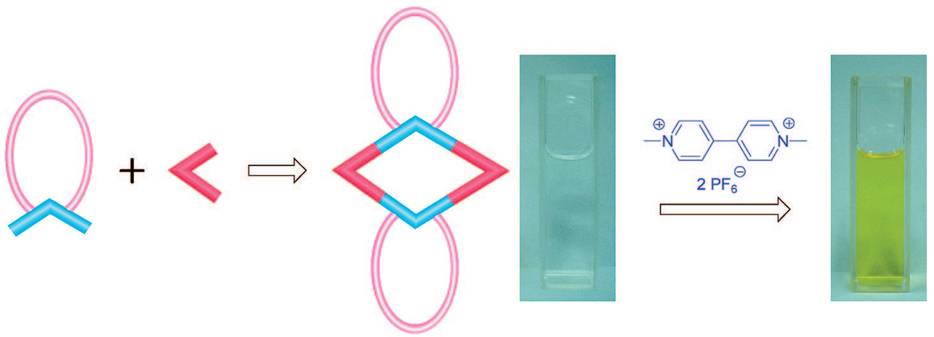

Two bis(*m*-phenylene)-32-crown-10 derivatives containing two pyridyl or carboxyl groups were made. They were used to prepare three bis(*m*-phenylene)-32-crown-10-based discrete rhomboids by coordination-driven self-assembly with high yields. The formation of these crown ether-based rhomboids was confirmed by NMR, UV−vis, CSI-TOF-MS, and elemental analysis. The complexation of these crown ether-based assemblies with paraquat (*N*,*N*′-dimethyl-4,4′-bipyridinium) was studied. The complexation of neutral bis(crown ether) rhomboid **1** with paraquat was found to be statistical with a 1:2 stoichiometry. The average apparent association constant K_{av} of the complexation of rhomboid **1** with paraquat was found to be about $8.8(\pm 0.8) \times 10^3$ M^{-1} in acetone, about 17 times higher than the reported association constant value for the complexation of the corresponding simple bis(*m*-phenylene)-32-crown-10 with paraquat. This is possibly because the carboxylate groups provide additional noncovalent interactions between the host and guest. No obvious complexation was observed between the cationic rhomboids and paraquat when studied by NMR, UV−vis, and CSI-TOF-MS analysis. This could be attributed to the combination of the charge repulsion between cationic pyridinium rings and cationic platinum atoms and the weak $\pi-\pi$ stacking and charge transfer interactions between the phenyl rings and the pyridinium rings caused by the electron-withdrawing effect of the cationic platinum atoms.

Introduction

Supramolecular self-assemblies have attracted great interest due to their potential applications in sensing devices,[1] catalysis,[2] and host−guest materials.[3] Coordination-driven transition-metal-mediated self-assembly has been proven to be a highly efficient strategy for the construction of discrete two-dimensional (2-D) and three-dimensional (3-D) architectures with predetermined shapes, sizes, andgeometries.[4] These metal−organic assemblies,

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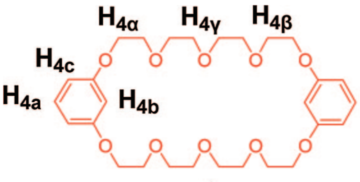
possessing unique magnetic, photophysical, and/or redox properties which are not accessible from purely organic systems, have shown promise as a new class of functional receptor meolecules.[1c,5] By incorporating functionalities, such as porphyrin,[6] carborane,[7] calixarene,[8] cavitand,[9] ferrocene,[10] and crown ether,[5d,e,11] into the final discrete assemblies, artificial functional nanoscale devices with precisely controlled shapes, sizes, and geometries can be constructed.[12]

Crown ethers have attracted much attention for their interesting binding properties with metal and organic cations.[13] They have been widely used in the preparation of chemosensors, molecular machines, and supramolecular polymers.[14] Previous work has illustrated that crown ethers can also be used as flexible building blocks to construct discrete complexes.[11] More recently, Stang et al. reported several discrete cavity-cored self-assemblies containing multiple pendant dibenzo-24-crown-8 (DB24C8) derivatives.[5d,e] These DB24C8-containing hosts have a similar ability to bind dibenzylammonium guest(s) as does DB24C8 in nonpolar solvents, such as dichloromethane.[5d,e]



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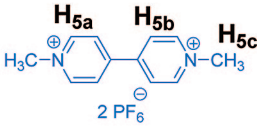

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The significant recognition motif based on bis(*m*-phenylene)-3-crown-10 (BMP32C10) (**4**) and paraquat (*N*,*N*′-dimethyl-4,4′-bipyridinium) (**5**) derivatives has been employed to prepare numerous host−guest complexes[15a−f] and a fluorescence chromophore.[15g] We envisioned that the combination of the BMP32C10-based bispyridyl or dicarboxyl donor units and appropriately designed Pt(II) acceptors can afford novel functionalized molecular devices with precisely controlled shapes, sizes, and geometries via the coordination-driven self-assembly process. The resulting multicrown ether-based self-assemblies, varying in location and total number of incorporated crown ether moieties, may exhibit different affinities for guest(s) compared with that of the single bis(*m*-phenylene)-32-crown-10 host. For example, it is possible to use metal-coordination to control the binding of the BMP32C10 units to paraquat if the bispyridyl or dicarboxyl donor units are conjugated or very close to the crown ether moieties. Herein, we report the synthesis of three BMP32C10-based discrete supramolecular rhomboids[16] by metal-coordination-driven self-assembly of the 60° Pt(II)-based building blocks and functionalized dicarboxyl or bispyridyl bridging ligands, and the study of the complexation of these multicrown ether-based self-assemblies with paraquat.

Results and Discussion

A. Synthesis of Crown Ether-Based 120° Donor Precursors 9 and 11. The key starting material **7** was prepared according to the literature.[17] The intermediate BMP32C10-based macrocyclic 120° donor precursors, **8** and **10**, were obtained in

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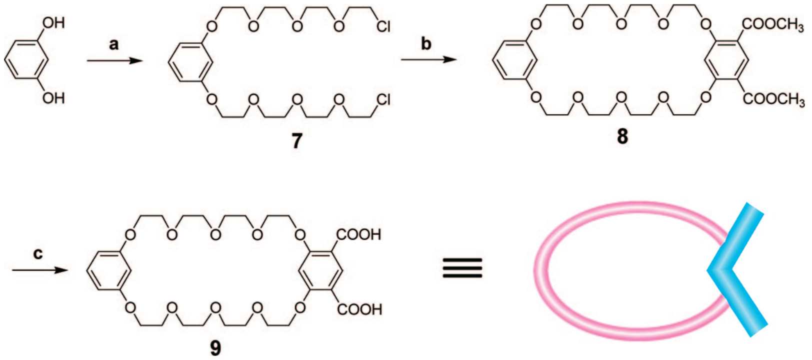
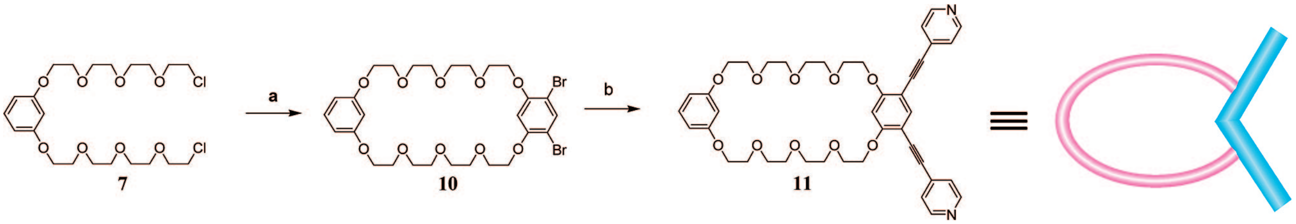
SCHEME 1. Synthesis of Crown Ether-Based 120° Donor Precursor 9[a]



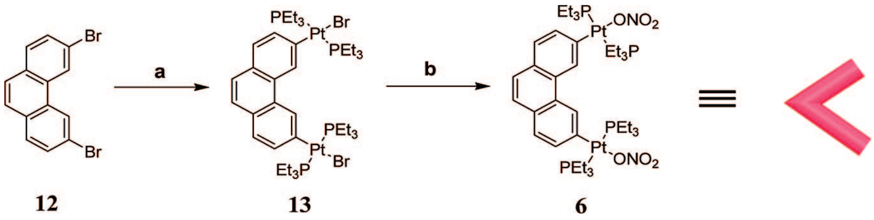
[a] Reagents and conditions: (a) (i) NaH, DMF, 50 °C, (ii) tetra(ethylene glycol) dichloride, N_2, K_2CO_3, DMF, 110 °C, 24 h, 65% (two steps); (b) dimethyl 4,6-dihydroxyisophthalate, K_2CO_3, TBAB, NaI, N_2, DMF, 110 °C, 5 days, 35%; (c) (i) NaOH, EtOH, 12 h, (ii) HCl, H_2O, 95% (two steps).

SCHEME 2. Synthesis of Crown Ether-Based 120° Donor Precursor 11[a]



[a] Reagents and conditions: (a) 4,6-dibromoresorcinol, K_2CO_3, TBAB, NaI, N_2, DMF, 110 °C, 5 days, 45%; (b) 4-ethynylpyridine hydrochloride, $Pd(Ph_3P)_2Cl_2$, CuI, *i*-Pr_2NH, reflux, 24 h, 83%.

SCHEME 3. Synthesis of Pt(II)-Containing 60° Corner[a]



[a] Reagents and conditions: (a) $Pt(PEt_3)_4$, N_2, toluene, 40 °C, 24 h, 50%; (b) $AgNO_3$, CH_2Cl_2, 90%.

reasonable yields by a pseudohigh dilution method for preparing **4** reported by Gibson et al.[17] As outlined in Scheme 1, cyclization of **7** with dimethyl 4,6-dihydroxyisophthalate in the presence of TBAB and NaI afforded the dicarbomethoxy intermediate **8** in 35% isolated yield followed by the hydrolysis of **8** with NaOH in EtOH and recrystallization from acetone to give the pure BMP32C10-based macrocyclic 120° donor precursor **9** almost quantitatively (95%). The dibromo intermediate **10** was prepared by cyclization of **7** with 4,6-dibromoresorcinol by the same method in 45% isolated yield. The bispyridyl 120° donor precursor **11** was finally obtained from **10** and 4-ethynylpyridine via the Sonogashira coupling reaction in 83% isolated yield (Scheme 2).

B. Synthesis of Pt(II)-Containing 60° Corner 6. The Pt(II)-containing 60° corner was prepared from 2,9-dibromophenanthrene (**12**) in two steps according to the literature.[16a] The intermediate **13** was obtained by a double oxidative addition of tetrakis(triethylphosphine)platinum(0). Exchanging the bromine atoms to more liable nitrates by reaction with $AgNO_3$ afforded the pure Pt(II)-containing 60° corner **6** (Scheme 3).

C. Self-Assembly and Spectral Studies of BMP32C10-Based Supramolecular Rhomboids 1, 2, and 3. The neutral supramolecular rhomboid **1** was assembled according to a method reported by Stang et al.[16a] The 120° dicarboxy building block **9** was dissolved in an aqueous $NaHCO_3$ solution to afford the disodium salt. Adding this disodium salt solution to an acetone solution containing 1.0 equiv of the 60° corner **6** resulted in a near-colorless solution. The rhomboid **1** could be precipitated as a white solid in 95% isolated yield by slow evaporation of acetone upon stirring in the open air or adding water.

The cationic rhomboid **2** was assembled in CH_2Cl_2 from the Pt(II)-containing 60° corner **6** and the 120° bispyridyl building block **11**.[10b] By stirring at room temperature for 12 h, a homogeneous yellow solution was formed. The nitrate salt **2** can be precipitated by adding pentane to the resulting yellow solution. It also can be purified by a vapor diffusion method often employed to obtain single crystals. Since **2** has a poor solubility in acetone, which is a good solvent for complexation study, the nitrate salt was exchanged with KPF_6 in deionized water to afford the hexafluorophosphate salt **3**.

The ^{31}P NMR spectrum of **1** (Figure 1b) indicates the formation of a single, highly symmetric structure by the sharp singlet at 17.78 ppm with concomitant ^{195}Pt satellites. It shifted approximately 2.38 ppm upfield relative to its position in precursor **6**, which is similar to that of the rhomboid prepared from isophthalate and **6**.[16b] The small change in the position of the phosphorus signal could be attributed to the similar Pt−O coordinate bond (Pt−OOC− vs. Pt−ONO_2) in the starting Pt(II)-containing 60° corner. The chemical environments of the phosphorus atoms in the cavity are only slightly changed even

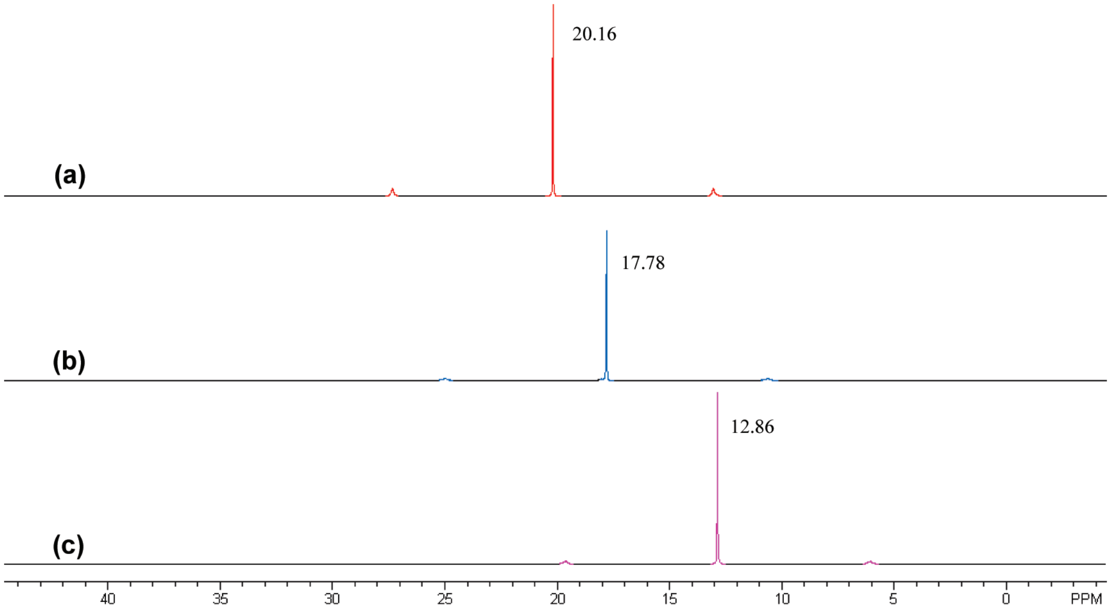
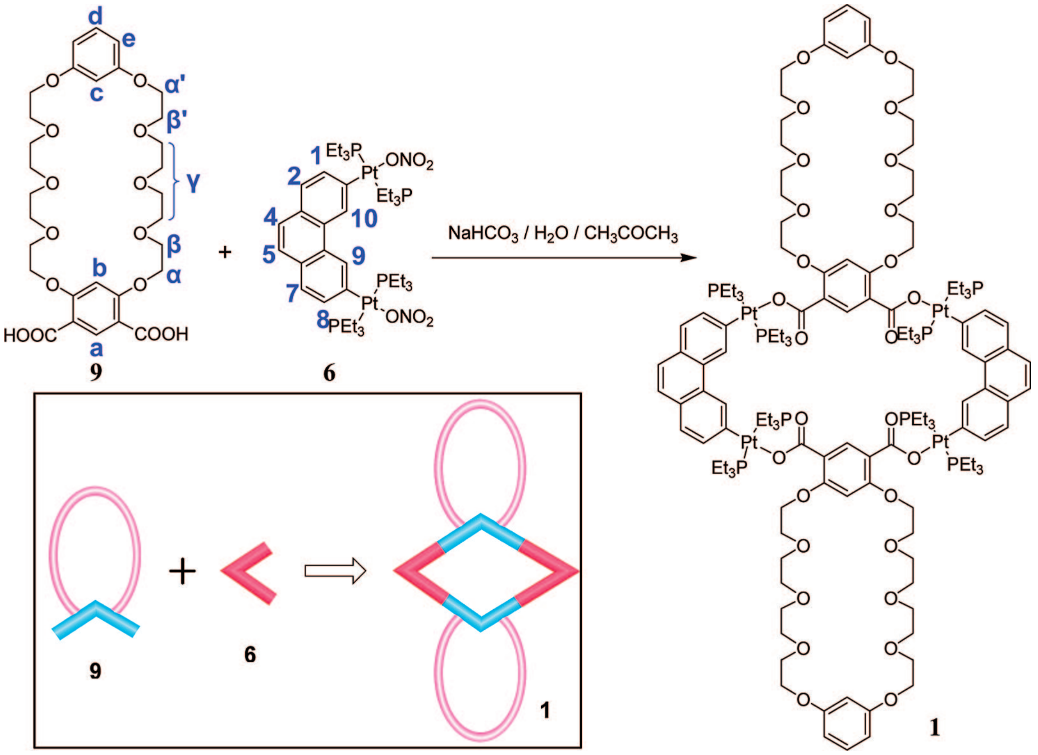


FIGURE 1. Partial ^{31}P NMR spectra (202.3 MHz, $CDCl_3$, 22 °C) of 4.00 mM **6** (a), 2.00 mM **1** (b), and 2.00 mM **2** (c).

SCHEME 4. Synthesis of BMP32C10-Based Neutral Supramolecular Rhomboid 1



when the electron-rich crown ethers are incorporated. The ^{31}P NMR spectrum of **2** (Figure 1c) also gave a sharp singlet but more upfield chemical shift at 12.86 ppm with accompanying ^{195}Pt satellites. The relatively bigger upfield shift is possibly due to the fact that the pyridine nitrogen atom in rhomboid **2** is a better electron donor than the carboxylate oxygen atom in rhomboid **1**. This spectral evidence suggests both **1** and **2** are single macrocyclic species. Furthermore, the ^{1}H NMR spectra (spectrum b in Figure 2 and spectrum b in Figure 3) of **1** and **2** also confirmed the highly symmetric structure and display significant spectroscopic differences from the precursor building blocks. The small downfield shifts of H_1, H_4, H_5, and H_8 and the slight upfield shifts of H_2, H_7, H_9, and H_{10} after **6** was incorporated into the rhomboid **1** could be also attributed to the similar Pt−O coordinate bond (Pt−OOC− vs. Pt−ONO_2) in the starting Pt(II)-containing 60° corner. The proton H_a on the isophthalate moiety exhibited a relatively large upfield shift, about 0.75 ppm, after the Pt−O coordinate bond was formed. The metal-coordination could also affect the ethyleneoxy protons on the crown ether deeply by changing the electron density of the crown ether. The overlapped signal position for $H_{\alpha'}$ and H_β was obviously split into two separated peaks. All the protons on the phenanthrene exhibited downfield shifts when the Pt−N coordination was formed in the rhomboid **2** (Figure 3). Also

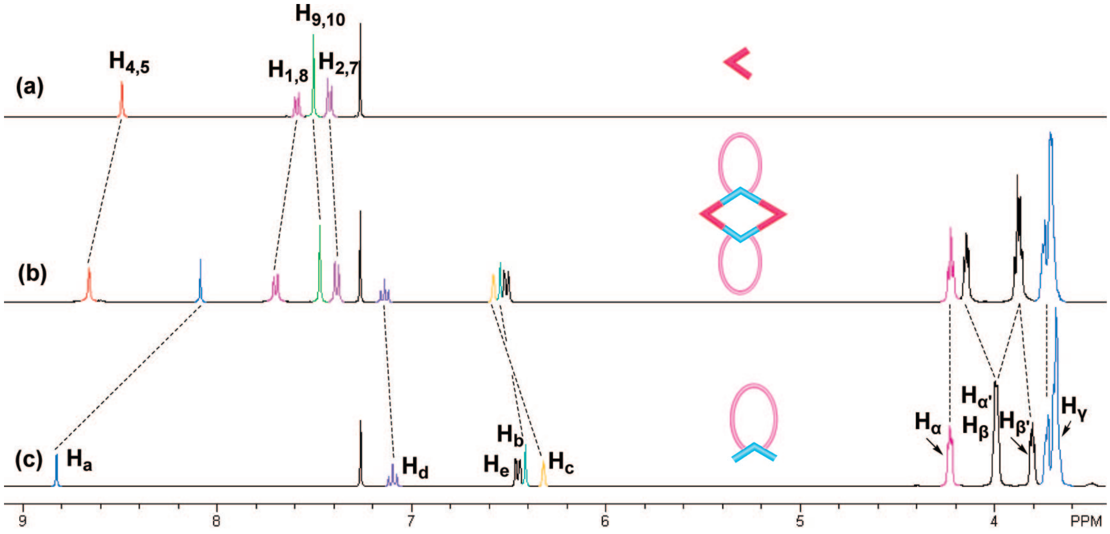


FIGURE 2. Partial ^{1}H NMR spectra (400 MHz, 22 °C) of 4.00 mM **6** (a), 2.00 mM **1** (b), and 4.00 mM **9** (c) in $CDCl_3$.

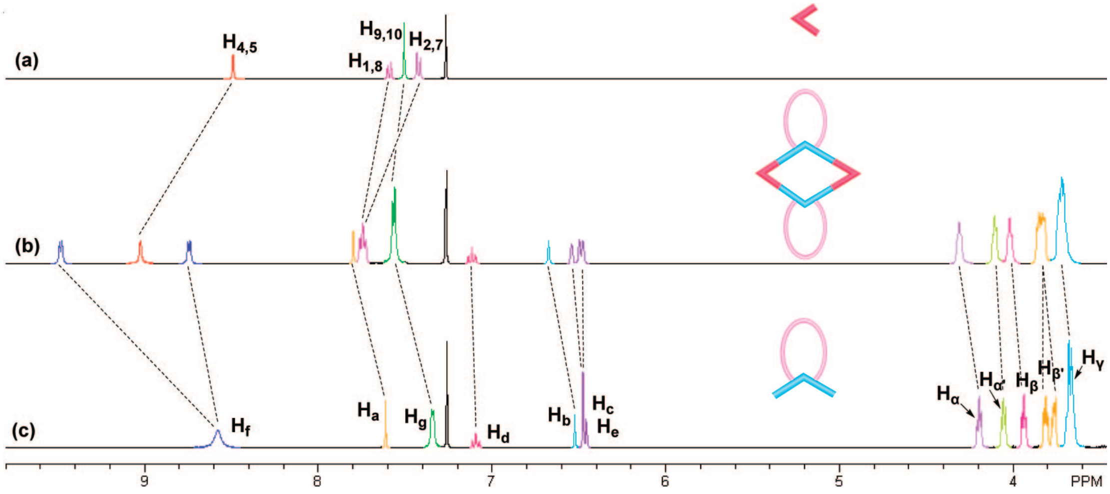


FIGURE 3. Partial ^{1}H NMR spectra (400 MHz, 22 °C) of 4.00 mM **6** (a), 2.00 mM **2** (b), and 4.00 mM **11** (c) in $CDCl_3$.

the Pt−N coordination had the same influence on all of the protons on the crown ether-based bispyridyl ligand which all moved downfield. The singlet peak of the α-pyridine protons H_f was split into two doublets, indicating the different environments for the inner and outer pyridine protons caused by the confined rotation of the Pt−N bond (spectra b and c in Figure 3). This is a characteristic feature of the ^{1}H NMR spectrum of such a discrete rhomboid.[16d]

The UV−vis spectra show there is no band shift, but an increase in intensity was observed for self-assembly **1** after the crown ether was incorporated (Figure S38, see the Supporting Information). In the fluorescence spectra, the strong emission intensity of bispyridyl ligand **11** at 389 nm, excited at 353 nm, was quenched after the Pt−N coordination was formed and shifted to a weak emission band at 422 nm (Figure S40, see the Supporting Information). All of this spectroscopic evidence confirmed that the dicarboxy **9** was incorporated into the self-assembly **1** and the bispyridine **11** was incorporated into the self-assembly **2** (Schemes 4 and 5).

Further evidence for the formation of the desired self-assembly was obtained by cold spray ionization mass spectrometry (CSI-MS).[18] For the self-assembly **1**, peaks were observed corresponding to $[\mathbf{M} + H]^+$ (*m/z* 3323.00) and $[\mathbf{M} + Na]^+$ (*m/z* 3344.96). These were all isotopically resolved and are in excellent agreement with their theoretical distributions (Figure S26a, see the Supporting Information). As for the self-assembly **2**, peaks were found attributable to the consecutive loss of counterions in excellent agreement with their theoretical distributions: $[\mathbf{M} - 2NO_3]^{2+}$ (*m/z* 1839.68), $[\mathbf{M} - 3NO_3]^{3+}$ (*m/z* 1205.72), $[\mathbf{M} - 4NO_3]^{4+}$ (*m/z* 888.86) (Figure S26b, see the Supporting Information). The isotopically resolved peaks at *m/z* 1922.77, 1233.45, and 888.81 agree very well with the theoretical distribution of the species, $[\mathbf{M} - 2PF_6]^{2+}$, $[\mathbf{M} - 3PF_6]^{3+}$, and $[\mathbf{M} - 4PF_6]^{4+}$, corresponding to consecutive loss of counterions of self-assembly **3** (Figure S27, see the Supporting Information). Also a peak at *m/z* 1294.77 was found and attributed to the $[\mathbf{M} - 2PF_6 + K]^{3+}$ species.

D. The Study of the Complexation of Rhomboid 1 with Paraquat 5. The X-ray structural analysis of the complex

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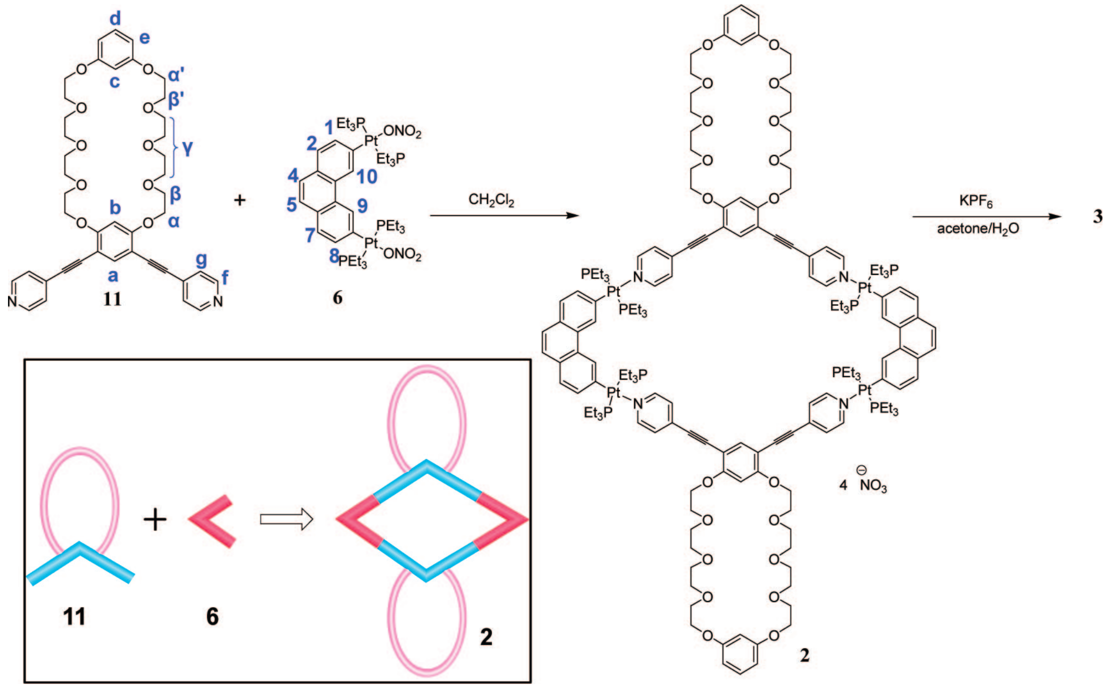
[17] Gibson, H. W.; Nagvekar, D. S.; Yamaguchi, N.; Wang, F.; Bryant, W. S. *J. Org. Chem.* **1997**, *62*, 4798–4803.

[18] CSI-TOF-MS is a sort of electrospray ionization (ESI) MS operated under low temperature: (a) Sakamoto, S.; Fujita, M.; Kim, K.; Yamaguchi, K. *Tetrahedron* **2000**, *56*, 955–964. (b) Yamanoi, Y.; Sakamoto, Y.; Kusukawa, T.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 980–981. (c) Sakamoto, S.; Yoshizawa, M.; Kusukawa, T.; Fujita, M.; Yamaguchi, K. *Org. Lett.* **2001**, *3*, 1601–1604. (d) Yamaguchi, K. *J. Mass Spectrom.* **2003**, *38*, 473–490.

SCHEME 5. Synthesis of BMP32C10-Based Cationic Supramolecular Rhomboid 2 and 3



between **1** and **5** was unsuccessful due to the instability of the orange crystals obtained by vapor diffusion of pentane into a mixed solution of **1** (2.00 mM) and **5** (4.00 mM) in acetone.[19] The complexation of **1** with paraquat **5** was characterized by UV−vis, proton NMR, ^{31}P NMR, and CSI-TOF-MS. When a 2.00 mM acetone solution of **1** and a 4.00 mM solution of **5** were mixed, a yellow color resulted. The absorption spectrum of the mixture shows a new band (Figure 4) that can be attributed to the charge transfer between electron-rich aromatic rings of the host and electron-poor pyridinium rings of the guest. A Job plot[20] (Figure 5) based on UV−vis absorbance data of the charge transfer band (λ = 403 nm) demonstrated that the complex was of 1:2 stoichiometry in solution. The ^{1}H NMR spectrum of a mixed solution of **1** (2.00 mM) and **5** (4.00 mM) in acetone-d_6 showed the complexation is a fast exchange system (Figure 6), the same as the reported complexation between **4** and **5**. The upfield shifts of H_1, H_4, H_5, and H_8 and the downfield shifts of H_2, H_7, H_9, and H_{10} after complexation (spectra a, b, and c in Figure 6) were opposite to the chemical shift changes of these protons when **6** and **9** were assemblied into the rhomboid **1** (Figure 2) and gave evidence about the change of the electron density of the phenanthrene moieties after complexation. The significant chemical shift change of protons H_a, H_b, H_c, H_d, and H_e on **1** (spectra a, b, and c in Figure 6) indicated the π−π stacking between the phenyl rings of **1** and the pyridinium rings of **5**. The signals of H_α, H_β, $H_{\alpha'}$, and $H_{\beta'}$ of **1** moved upfield, while those of H_γ moved downfield after complexation between **1** and **5** (spectra a, b, and c in Figure 6). These are similar to what happened on the corresponding protons on **4** after complexation between **4** and **5** (spectra c, d, and e in Figure 6), indicating that the host−guest interaction between the crown ether moieties of **1** and paraquat guest **5** is similar to that between the corresponding simple crown ether **4** and paraquat guest **5**. The ^{31}P{^{1}H} NMR spectra of a mixed solution of **1** (2.00 mM) and **5** (4.00 mM) in acetone-d_6 (Figure S33, see the Supporting Information) exhibited a slight change ($\Delta\delta$ = 0.4 ppm) indicating that the binding of the bipyridium cation can change the chemical environment of the phosphorus atoms.

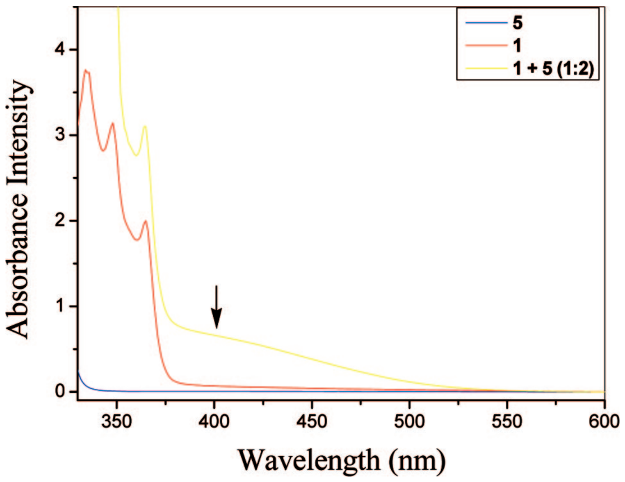


FIGURE 4. UV−vis spectra of 2.00 mM **1** (red), 2.00 mM **1** and 4.00 mM **5** (yellow), and 4.00 mM **5** (blue) in acetone.

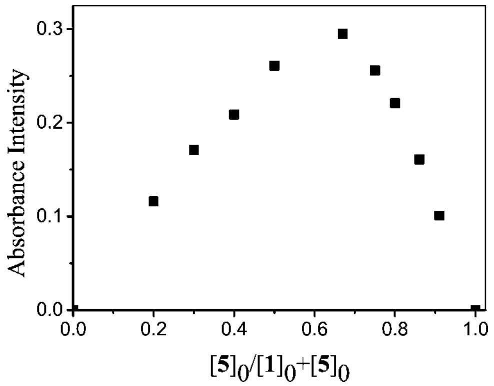


FIGURE 5. Job plot showing the 1:2 stoichiometry of the complex between **1** and **5**. $[\mathbf{1}]_0 + [\mathbf{5}]_0$ = 6.00 mM. $[\mathbf{1}]_0$ and $[\mathbf{5}]_0$ are the initial concentrations of **1** and **5**.

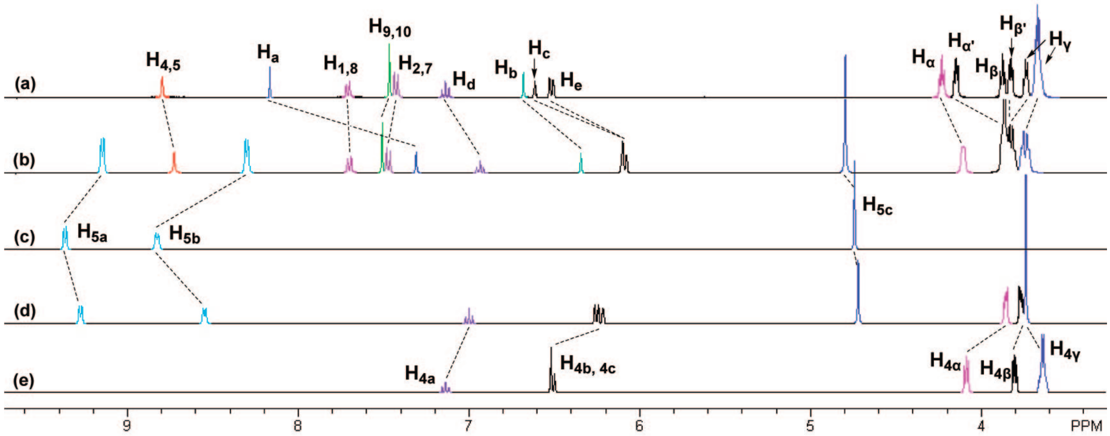


FIGURE 6. Partial 400 MHz ^{1}H NMR spectra of 2.00 mM **1** (a), 2.00 mM **1** and 4.00 mM **5** (b), 4.00 mM **5** (c), 4.00 mM **4** and 4.00 mM **5** (d), and 4.00 mM **4** (e) in acetone-d_6.

The CSI-MS spectra (Figure S36, see the Supporting Information) of the mixture of **1** and **5** in acetone further confirmed the 1:2 stoichiometry by the fragments: $[\mathbf{1} + \mathbf{5} + \mathbf{5} - 3\mathrm{PF}_6]^{3+}$ (m/z 1279.68) and $[\mathbf{1} + \mathbf{5} + \mathbf{5} - 4\mathrm{PF}_6]^{4+}$ (m/z 923.73).

The yellow color of the acetone-d_6 solution of **1** (2.00 mM) and **5** (4.00 mM) was deeper than that of the equimolar acetone-d_6 solution of **4** and **5** at 4.00 mM, indicating the stronger $\pi-\pi$ stacking and charge transfer interactions between the host and guest for **1** and **5** than for **4** and **5**. The average association constant (K_{av}) of $\mathbf{1}\cdot\mathbf{5}_2$ was determined by probing the charge transfer band of the complex by UV−vis spectroscopy and employing a titration method.[21] Progressive addition of an acetone solution with high guest **5** concentration and low host **1** concentration to an acetone solution with the same host **5** concentration results in an increase of the intensity of the charge transfer band of the complex. Treatment of the collected absorbance data at $\lambda = 403$ nm by a Scatchard plot[22] afforded the corresponding K_{av} value. The linear nature of this plot demonstrated that the complexation between host **1** and guest **5** is statistical (Figure S42b, see the Supporting Information). From the slope and the intercept of the Scatchard plot, the K_{av} value was determined to be $8.8(\pm0.8) \times 10^3$ M^{-1} for $\mathbf{1}\cdot\mathbf{5}_2$. As a 1:2 stoichiometry, statistical complexation system, the K_1, $[\mathbf{1}\cdot\mathbf{5}]/\{[\mathbf{1}][\mathbf{5}]\}$, and K_2, $[\mathbf{1}\cdot\mathbf{5}_2]/\{[\mathbf{1}\cdot\mathbf{5}][\mathbf{5}]\}$, were calculated to be $1.4(\pm0.1) \times 10^4$ and $3.5(\pm0.3) \times 10^3$ M^{-1}, respectively (see the Supporting Information). The value of K_{av} for $\mathbf{1}\cdot\mathbf{5}_2$ is about 17 times higher than the reported association constant value, 487 M^{-1}, for the complexation beween **4** and **5**.[15g] This result shows that the affinity of the BMP32C10 portion for paraquat was enhanced after the crown ether moiety was incorporated into the neutral self-assembly **1**. This is possibly because the carboxylate groups provide additional noncovalent interactions between the host and guest. The sensitivity of the neutral rhomboid **1** to paraquat makes it a possible chemosensor for paraquat.[15g]

E. The Study of the Complexation of Rhomboids 2 and 3 with Paraquat 5. The UV−vis spectra and the ^{1}H NMR spectra of a mixed solution of **3** (2.00 mM) and **5** (4.00 mM) in acetone-d_6 gave no evidence for the complexation between **3** and **5**. The UV−vis spectra displayed little change after the cationic self-assembly **3** was mixed with **5** (Figure S39, see the Supporting Information). All the protons on **3** in the ^{1}H NMR spectrum of the mixed solution of **3** (2.00 mM) and **5** (4.00 mM) in acetone-d_6 were observed to have almost the same chemical shift as the ^{1}H NMR spectrum of **3** (spectra a and b in Figure S31, see the Supporting Information). The negligible change of the chemical shift of the proton H_{5b} on **5** (spectra b and c in Figure S31, see the Supporting Information) may be attributed to the side-on interactions between the electron-rich phenyl rings of **3** and electron-poor pyridinium rings of **5**.[15f] The ^{31}P{^{1}H} NMR spectrum of a mixed solution of **3** (2.00 mM) and **5** (4.00 mM) in acetone-d_6 does not show any detectable change compared with that of **3** (Figure S34, see the Supporting Information), also indicating no complexation between **3** and **5**. Though a 1:1 complex with a very weak intensity could be found in the CSI-MS spectra of a mixture of **2** and **5** (Figure S37, see the Supporting Information), no complexation could be found in that of a mixture of **3** and **5**. The poor affinity of rhomboid **2** or **3** for paraquat may result from two things. First, the repulsion between the cationic **2** or **3** and the cationic bipyridinium cation can severely weaken the complexation between the crown ether portion and the bipyridinium cation. Second, since the pyridine units are conjugated with the phenylene rings of the BMP32C10 moieties in rhomboid **2** or **3**, the electron-withdrawing cationic platinum can reduce the electron density of the phenyl rings of the crown ether moieties and then weaken the $\pi-\pi$ stacking and charge transfer interactions between them and the pyridinium rings. Though no complexation was observed between rhomboid **2** or **3** and the bipyridinium cation, the cationic assembly may be a suitable host for metal, neutral, or anionic guests.[23]

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(19) The orange crystals obtained by the vapor diffusion method are readily to lose the lattice solvents under ambient condition even at low temperature. Therefore, the X-ray structural analysis of the complex $\mathbf{1}\cdot\mathbf{5}_2$ was unsuccessful.

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(22) Marshall, A. G. *Biophysical Chemistry*; J. Wiley and Sons: New York, 1978; pp 70−77. Freifelder, D. M. *Physical Biochemistry*; W. H. Freeman and Co.: New York, 1982; pp 659−660. Connors, K. A. *Binding Constants*; J. Wiley and Sons: New York, 1987; pp 78−86.

(23) (a) Whiteford, J. A.; Lu, C. V.; Stang, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 2524–2533. (b) Lee, S. B.; Hwang, S. G.; Chung, D. S.; Yun, H.; Hong, J.-I. *Tetrahedron Lett.* **1998**, *39*, 873–876. (c) Müller, C.; Whiteford, J. A.; Stang, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 9827–9837. (d) Whiteford, J. A.; Stang, P. J. *Inorg. Chem.* **1998**, *37*, 5595–5601.

Conclusion

In summary, two donor units incorporated with BMP32C10 were designed and synthesized. By employing these new units, three bis(*m*-phenylene)-32-crown-10-based discrete rhomboids were synthesized via coordination-driven self-assembly and characterized by NMR, UV−vis, and CSI-TOF-MS. The complexation of these assemblies with paraquat was studied. The neutral bis(crown ether) rhomboid **1** exhibited an enhanced affinity for paraquat compared with simple bis(*m*-phenylene)-32-crown-10 while no complexation was observed between the cationic rhomboid **2** or **3** and paraquat **5**. Therefore, it was demonstrated that metal-coordination could be used to control the binding of the BMP32C10 units to paraquat because the bispyridyl or dicarboxyl donor units are conjugated or very close to the crown ether moieties in the three rhomboids reported here. Moreover, the convenient preparation and simple isolation and purification of these rhomboids make it possible to prepare functionalized self-assemblies on large scales as molecular devices and our current efforts are focusing on developing chemical sensors and large molecular machines based on these self-assemblies.

Experimental Section

4,6-Dicarboxyl-*m*-phenylene-*m′*-phenylene-32-crown-10-Based Rhomboid (1). The dicarboxy precursor **9** was neutralized with an equivalent amount of $NaHCO_3$ at ambient temperature, assisted by ultrasonication, to produce the disodium salt. To a 4.00 mL acetone solution of **6** (11.6 mg, 0.010 mmol) was added an aqueous solution (4.00 mL) of disodium salt of **9** (0.010 mmol) dropwise with continuous stirring (5 min). After the resulting mixture was stirred for another 12 h at room temperature in the open air, a white solid precipitated. Deionized water was added until no further precipitation was observed. The white precipitate was centrifuged and washed three times with water and dried in vacuo. Yield 32.0 mg (95%); ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) δ (ppm) 8.67 (s, 4H), 8.08 (s, 2H), 7.70 (d, 4H, $J = 8.0$ Hz), 7.47 (s, 4H), 7.38 (d, 4H, $J = 8.0$ Hz), 7.14 (t, 2H, $J = 8.0$ Hz), 6.49−6.58 (s, 8H), 4.22 (t, 8H, $J = 4.8$ Hz), 4.14 (t, 8H, $J = 4.8$ Hz), 3.88 (m, 16H), 3.66−3.76 (m, 32H), 1.56 (m, 48H), 1.15 (m, 72H); ^{13}C NMR (125 MHz, $CDCl_3$, 22 °C) δ (ppm) 171.5, 160.2, 158.7, 136.9, 134.0, 131.6, 130.2, 130.0, 129.7, 128.1, 126.5, 124.5, 122.4, 107.5, 102.1, 101.1, 71.1, 71.1, 70.0, 69.9, 68.7, 67.9, 13.6, 8.0; ^{31}P {^{1}H} NMR (202.3 MHz, $CDCl_3$, 22 °C) δ (ppm) 17.8 (s, $J_{Pt-P} = 2908$ Hz); CSI-TOF-MS *m*/*z* 3323.00 [**M** + H]$^+$ and 3344.96 [**M** + Na]$^+$. Anal. Calcd for $C_{136}H_{212}O_{28}P_8Pt_4$: C, 49.15; H, 6.43. Found: C, 49.01; H, 6.40.

4,6-Bis(4-pyridylethynyl)-*m*-phenylene-*m′*-phenylene-32-crown-10-Based Rhomboid (2). **11** (7.38 mg, 0.010 mmol) was dissolved in CH_2Cl_2 (1.00 mL) and added to a solution of **6** (9.26 mg, 0.010 mmol) in CH_2Cl_2 (1.00 mL) dropwise. The mixture was stirred in the dark at room temperature for 24 h, resulting in a yellow solution. By adding pentane, the nitrate salt **2** was precipitated as a pale yellow solid. The solid was washed by toluene then pentane and dried in vacuo. Yellow crystals were obtained by the diffusion of acetone into a CH_2Cl_2 solution. Yield 14.0 mg (91%); ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) δ (ppm) 9.48 (d, 4H, $J = 6.0$ Hz), 9.02 (s, 4H), 8.74 (d, 4H, $J = 6.0$ Hz), 7.80 (s, 2H), 7.73−7.76 (m, 8H), 7.56 (m, 12H), 7.11 (t, 2H, $J = 8.0$ Hz), 6.67 (s, 2H), 6.54 (s, 2H), 6.48 (m, 4H), 4.30 (t, 8H, $J = 4.4$ Hz), 4.10 (t, 8H, $J = 4.4$ Hz), 4.01 (t, 8H, $J = 4.4$ Hz), 3.82−3.86 (m, 16H), 3.70−3.81 (m, 24H), 1.37 (m, 48H), 1.11 (m, 72H); ^{31}P {^{1}H} NMR (202.3 MHz, $CDCl_3$, 22 °C) δ (ppm) 12.9 (s, $J_{Pt-P} = 2746$ Hz); CSI-TOF-MS *m*/*z* 1839.68 [**M** − $2NO_3$]$^{2+}$, 1205.72 [**M** − $3NO_3$]$^{3+}$, and 888.86 [**M** − $4NO_3$]$^{4+}$. Anal. Calcd for $C_{160}H_{228}N_8O_{32}P_8Pt_4$: C, 50.07; H, 5.75; N, 3.07. Found: C, 49.92; H, 5.79; N, 3.09.

4,6-Bis(4-pyridylethynyl)-*m*-phenylene-*m′*-phenylene-32-crown-10-Based Rhomboid (3). A solution of **2** (190 mg, 0.0500 mmol) in deionized water (1.00 mL) was stirred at room temperature. A saturated KPF_6 aqueous solution (5.00 mL) was added dropwise and a pale nearly white solid precipitated. The solid was centrifuged and washed with deionized water (3 × 1.0 mL) and dried in vacuo. Yield 20.0 mg (99%); ^{1}H NMR (500 MHz, CD_3COCD_3, 22 °C) δ (ppm) 9.09 (d, 4H, $J = 5.0$ Hz), 9.03 (d, 4H, $J = 5.0$ Hz), 8.74 (s, 4H), 7.91 (d, 4H, $J = 5.5$ Hz), 7.87 (s, 2H), 7.85 (d, 4H, $J = 5.5$ Hz), 7.77 (d, 4H, $J = 7.5$ Hz), 7.69 (d, 4H, $J = 7.5$ Hz), 7.66 (s, 4H), 7.13 (t, 2H, $J = 8.5$ Hz), 7.00 (s, 2H), 6.48 (m, 6H), 4.43 (t, 8H, $J = 4.5$), 4.08 (t, 8H, $J = 4.5$), 4.00 (t, 8H, $J = 4.5$), 3.80 (m, 16H), 3.63−3.70 (m, 24H), 1.52 (m, 48H), 1.24 (m, 72H); ^{13}C NMR (125 MHz, CD_3COCD_3, 22 °C) δ (ppm) 164.0, 160.4, 152.4, 136.5, 135.0, 129.9, 129.3, 128.9, 128.3, 126.6, 125.4, 124.4, 107.0, 103.6, 101.6, 98.2, 95.1, 89.3, 70.9, 70.7, 70.6, 69.6, 69.4, 67.7, 13.5, 7.2; ^{31}P {^{1}H} NMR (202.3 MHz, CD_3COCD_3, 22 °C) δ (ppm) 14.8 (s, $J_{Pt-P} = 2682$ Hz); CSI-TOF-MS *m*/*z* 1922.77 [**M** − $2PF_6$]$^{2+}$, *m*/*z* 1294.77 [**M** − $2PF_6$ + K]$^{3+}$, *m*/*z* 1233.45 [**M** − $3PF_6$]$^{3+}$, and *m*/*z* 888.81 [**M** − $4PF_6$]$^{4+}$.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, mass, and UV−vis spectra of compounds and ^{1}H NMR and CSI-TOF-MS spectra of equimolar acetone solutions of **1** and **5**, and **2** and **5**; determination of association constants of complex $\mathbf{1 \cdot 5_2}$ and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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