

Molecular Architecture via Coordination: Marriage of Crown Ethers and Calixarenes with Molecular Squares, Unique Tetranuclear Metallamacrocycles from Metallacrown Ether and Metallacalixarene Complexes via Self-Assembly

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Abstract: Reaction of metallacrown and metallacalixarene platinum bistriflates with bipyridine as well as other bidentate connector ligands results in the formation of tetranuclear macrocycles via self-assembly that combine crown ether and calixarene chemistry with molecular squares. Multinuclear NMR spectroscopy and electrospray mass spectrometry are employed to characterize these unique supramolecular species. The calixarene metallamacrocycles are used in simple transport experiments to carry sulfonate salts from one aqueous phase into another through chloroform.

Introduction

Crown ethers^{1,2} and calixarenes,³ along with other classical macrocycles such as cyclophanes,⁴ cyclodextrins,⁵ cavitands, cryptands, and clathrates are the progenitors of current supramolecular chemistry.^{6–15} They played pivotal roles in the development of host–guest chemistry and inclusion

phenomenon^{16–19} and continue to be of active research interest.^{6–19} An interesting subclass of crown ethers and calixarenes are metallacrowns²⁰ and metallacalixarenes²¹ that, analogous to crown ethers and calixarenes, are capable of binding hard metal cations and small molecules, respectively.^{22,23}

Recently, molecular squares^{24–34} have emerged as the latest members of the family of supramolecular species. Molecular

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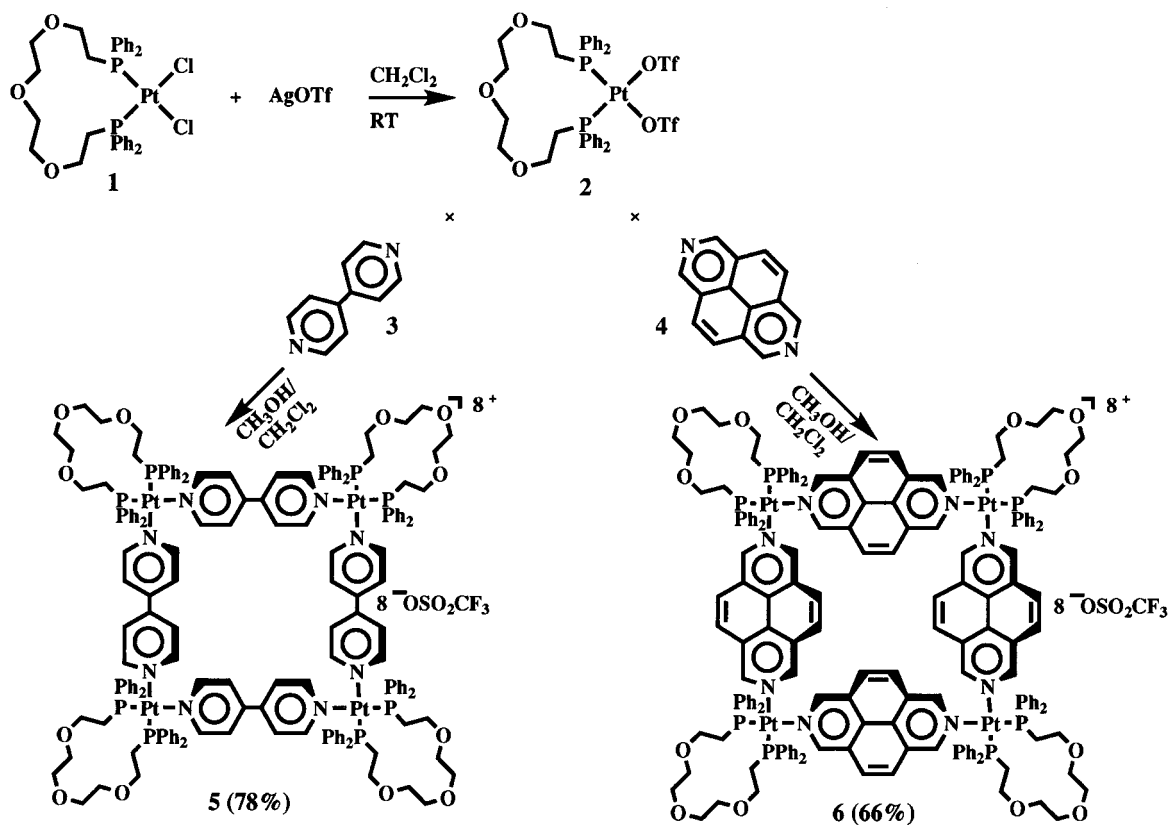
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Scheme 1. Self-Assembly of Macrocyclic Metallacrown Ether Molecular Squares

squares are examples of discrete cyclic assemblies where 90° angles establish a well-defined geometry and shape. This feature, combined with the conformational rigidity and multiple positive charges at the corners of these unique molecular squares make them attractive hosts for electron rich guests.^{29,35} Hence, crown ethers, host par excellence for hard metal cations and calixarenes premier hosts for neutral guests, nicely complement molecular squares that may serve as hosts for electron rich and perhaps anionic species. Therefore, we reasoned that it would be interesting to combine these different types of macrocycles into single, unique, molecular assemblies. Herein we report the preparation in high isolated yields, via self-assembly, as well as the characterization of the first examples of metallacrown ether and metallacalixarene based cationic, tetranuclear, macrocyclic molecular squares and some preliminary chemistry.

Results and Discussion

Reaction of the known²² platinum-metallacrown ether complex **1** with a slight excess of $\text{AgOSO}_2\text{CF}_3$ in CH_2Cl_2 afforded the required square planar metallacrown ether Pt bistriflate **2**. Interestingly, the $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2**, in contrast to the spectra of previous square planar Pt and Pd triflate complexes,²⁹

showed a broad singlet (line width at half height = 169 Hz) at room temperature, which turned into the usual sharp singlet (line width at half height = 19 Hz) only at 95°C . We attribute this behavior to the likely intramolecular complexation of the crown ether oxygens of **2** to the Pt metal center. Interaction of **2** with either bipyridine, (**3**) or diazapyrene (**4**), respectively, afforded the desired macrocyclic products **5** and **6** via self-assembly in $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ in good isolated yields (Scheme 1).

Likewise, reaction of the known²¹ calix[4]arene–platinum(II) chloride complex **7** with a 10% molar excess of AgOTf in CH_2Cl_2 afforded the desired bistriflate complex **8**. Interaction of **8** with bipyridine **3** in CH_2Cl_2 at room temperature resulted in the self-assembly of the desired calixarene molecular square **9** in essentially quantitative yield (Scheme 2). Similarly, interaction of **8** with the known²⁸ bisheteroaryliodonium salt **10** resulted in the novel hybrid calixarene–iodonium–Pt molecular square **11** in good isolated yield (Scheme 3).

These unique hybrid macrocyclic crown ether and calixarene molecular squares are stable colorless microcrystalline solids and are characterized by elemental analyses as well as infrared and multinuclear NMR methods and, for complexes **5** and **9**, an electrospray mass spectrum. In accord with the symmetry requirements of these macrocyclic molecular squares, the $^{31}\text{P}\{^1\text{H}\}$ spectra display a single sharp singlet, with appropriate Pt-satellites, for the eight equivalent chelating phosphorus groups. The presence of the triflate counterions is indicated by the ^{19}F singlet between -76 and -77.8 ppm as well as by the infrared absorptions around 1250, 1100, and 1030 cm^{-1} characteristic of ionic triflates.³⁶ The ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra, although complex, are not only diagnostic of the proposed structures of **5**, **6** and **9**, **11** but are consistent with the respective spectral data of the constituent metallacrown ether²² and calixarene²¹ complexes and the molecular square²⁹ components,

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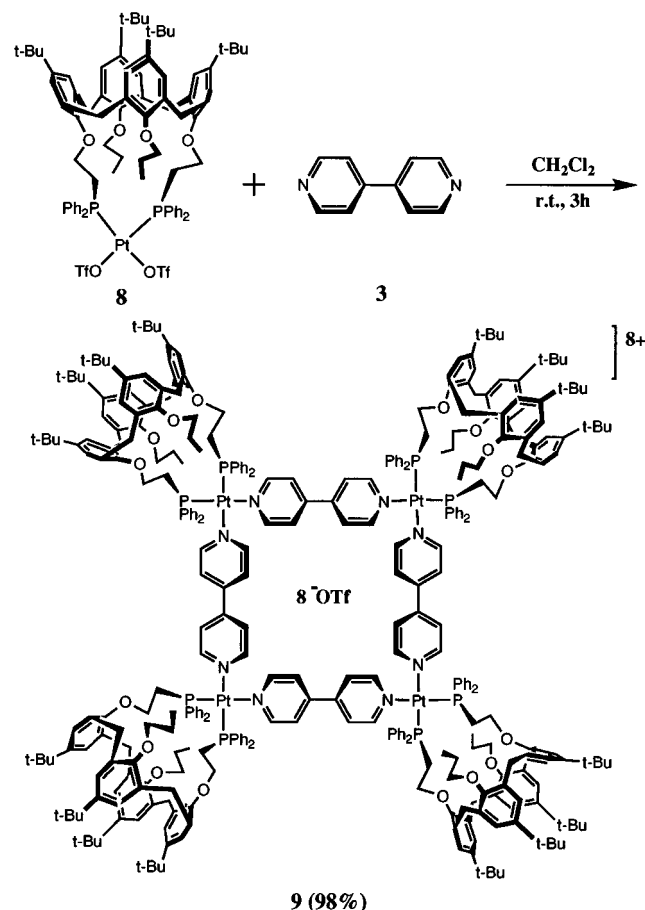
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Scheme 2. Self-Assembly of Macrocyclic Metallacalix[4]arene Molecular Square **9**

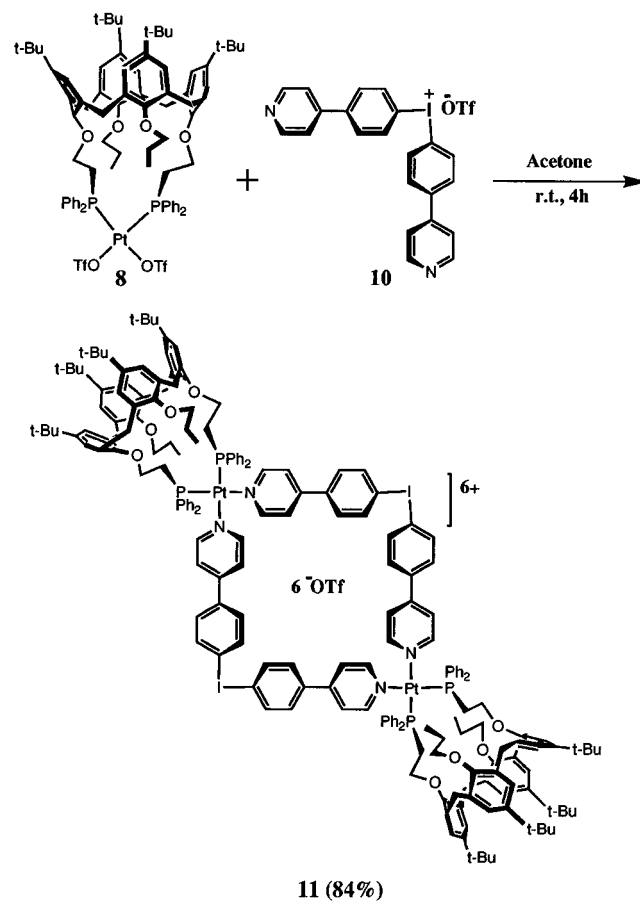
whose individual structures have been confirmed by single-crystal X-ray determinations.

More specifically, the protons α to N in **5** resonate at 8.9 ppm and the comparable proton resonance for the dppp-chelated Pt-molecular square²⁹ is at 9.0 ppm. For **6**, the protons α to N are at 9.9 ppm and the comparable protons for the Et_3P -Pt-diazapyrene square are at 10 ppm. Each of these hydrogen signals is shifted downfield relative to free bipyridyl (bipy **3**) and diazapyrene (**4**), as expected upon chelation. Likewise, the C_α for **5** in the ^{13}C NMR spectra are at 152.6 and at 151.8 ppm for the related dppp-Pt-bipy square,²⁹ whereas for **6**, C_α is at 146.4 ppm and in the related Et_3P -Pt-diazapyrene square C_α is at 147.0 ppm. Similarly, the CH_2 signals α to the chelating P in **5** and **6** are consistent with those in the metallacrown ether, as are the proton signals of the remaining methylene units.

A similar situation exists for molecular squares **9** and **11** and the constituent components calix[4]arene and "parent" molecular squares, as can be seen by close examination of the respective experimental data.

A noteworthy feature of complexes **5**, **6**, and **9**, **11** is the relatively high number of water molecules occluded in the solid state. Moreover, the water from either **5** or **6** was not removed even upon heating at 100 °C under vacuum for a week. We hypothesize that the water is likely to be interacting with the cationic Pt via the oxygen lone pairs and simultaneously hydrogen bonded to the crown ether oxygens as illustrated in Figure 1. A similar explanation has been suggested³⁷ to account for the high water content of the Pt-group metallacrown ethers.

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Scheme 3. Self-Assembly of Hybrid Calix[4]arene-Platinum-Iodinium Molecular Square **11**

The tetrameric nature of the macrocycle, in addition to the presence of water for **9**, was unambiguously determined by ESI-FTICR mass spectrometry.³⁸ Figure 2 shows the isotopically resolved ESI-FTICR mass spectrum of complex **9**. The isotopically resolved signals centered at m/z 2260 and 2266 correspond to the $[\text{M} - 3\text{OTf}]^{3+}$ and $[\text{M} - 3\text{OTf} + \text{H}_2\text{O}]^{3+}$ species, respectively, which clearly indicate a tetrameric complex. The inset in Figure 2 shows an expansion plot of the 3+ charge-state of the complex **9** and comparison with the theoretical isotopic distribution of the predicted elemental composition of the 3+ molecular ion (i.e., loss of three triflate counteranions) $[\text{C}_{357}\text{H}_{408}\text{F}_{15}\text{N}_8\text{O}_{31}\text{P}_8\text{Pt}_4\text{S}_5]$. These data provide: (a) an experimental MW of 6780.612 for **9**, which agrees well with the theoretical MW of 6780.555; (b) evidence for the presence of at least one noncovalent H_2O adduct in **9** (theoretical MW 6798.566, experimental MW 6798.619); and (c) a near perfect match of the experimental and theoretical isotopic envelopes for macrocycle **9**, supporting the tetrameric nature of complex **9**, and along with the multinuclear spectral data, its structure.³⁹ Similarly, the 2+ charge-state was observed for complex **5** and resulted in an experimental MW of 4421.695, which compares well with the theoretical MW of 4421.732.

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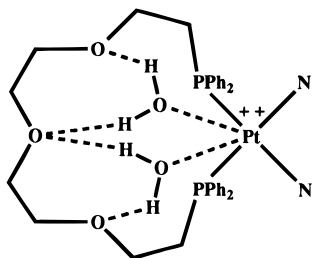


Figure 1. Possible water coordination by cationic squares **5** and **6** in the crown ether portion of the assembly.

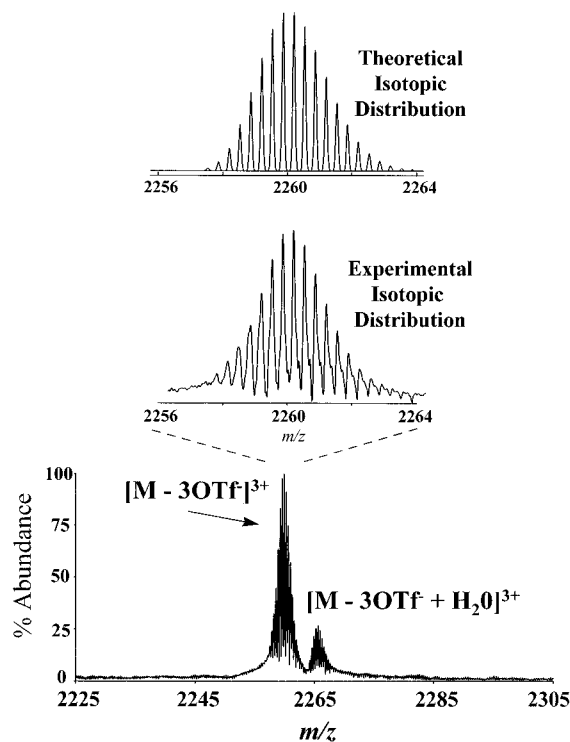


Figure 2. ESI-FTICR of metallamacrocycle **9** (top), theoretical (middle), experimental isotopic distribution for the $[M - 3OTf]^{3+}$ charge-state (bottom).

Transport of Organic Sulfonate Anions via Molecular Square **9.** Having established the structure of these novel supramolecular assemblies, which combine the classical covalent crown ethers and calixarenes with the coordinated molecular squares, we set out to investigate, in a preliminary manner, their chemistry. One of the more interesting and potentially useful properties of supramolecular species is molecular recognition and complexation.^{6–10} One way of assessing molecular recognition and complexation of organic substrates is their transport across a concentration gradient, in a U-type cell (Figure 3), by macrocyclic hosts.⁴⁰ We measured the transport of the sodium salt of arenesulfonic acids from one aqueous phase into a second aqueous phase through a chloroform phase in the presence and absence of host **9** in the chloroform phase. Periodic NMR (¹H) sampling of the second D₂O phase (right-hand arm in Figure

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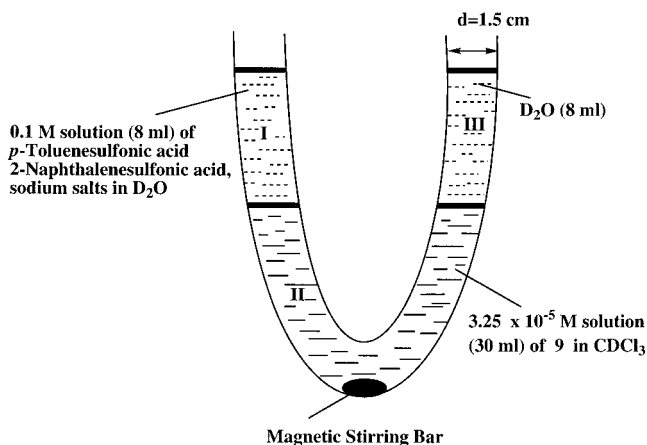
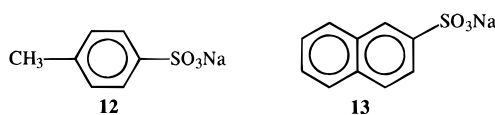


Figure 3. U-Tube transport setup.

3) established that both sodium tosylate **12** and **13** were readily transported by the metallamacrocycle **9** across the chloroform phase.



No transport occurred in the absence of host **9** in the chloroform phase. When an equal molar mixture of **12** and **13** was employed, NMR sampling indicated that in the initial phases (first 10–20%) of transport sodium tosylate was preferentially carried across the chloroform phase by host **9** over the sodium salt of 2-naphthalenesulfonic acid with a selectivity of 1.5–2.0. This selectivity for the smaller of the two sodium arenesulfonates by host **9**, although admittedly small, is nevertheless interesting. At present we have insufficient data and insight to rationalize this preference. Moreover, such “passive transport” along a concentration gradient⁴⁰ is complicated by the fact that after about 10–15% of the amount of initially present substrate (in the left-hand aqueous phase in Figure 3) is carried into the receiving phase by the host, back transport becomes significant. Back transport limits both the selectivity and the efficiency of material separations in such simple passive transport systems. Nevertheless, these experiments can provide useful insights into the molecular recognition and complexation properties of supramolecular macrocyclic hosts. In the present instance, the fact that these novel macrocycles act as anion hosts is particularly noteworthy as much less is known about anion complexation⁴⁶ than cation and neutral substrate interactions by molecular hosts.⁴⁷ Finally, very preliminary experiments indicate that host **9** is able to transport aromatic amino acids as well.

Conclusions

The preparation, via self-assembly, of a set of novel supramolecular species that combine the classical covalent crown ether and calixarene macrocycles with the coordinated molecular squares is reported. Multinuclear NMR along with elemental analyses and ESI-FTICR mass spectrometry are used to fully characterize these supramolecular assemblies. The excellent agreement between the experimental and theoretical molecular

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weights along with the match of isotopic envelopes for macrocycles **5** and **9** unambiguously establish the tetrameric nature of these complexes. Simple, "passive transport" experiments demonstrate that macrocycle **9** is capable of transporting sodium tosylate **12** as well as **13** from one aqueous phase into another through chloroform. A small selectivity of 1.5–2.0 is observed for the preferential transport of **12** over **13**.

Experimental Section

^1H , ^{13}C , ^{19}F , and ^{31}P NMR spectra were recorded on a Varian XL-300 spectrometer at 300, 75, 282, and 121 MHz, respectively. ^1H chemical shifts are reported relative to the residual nondeuterated solvent of acetone at δ 2.05 or methylene dichloride at δ 5.32. The ^{13}C chemical shifts are referenced relative to CD_3COCD_3 at δ 29.0 or CD_2Cl_2 at δ 52.0. The ^{19}F NMR spectra are referenced to CFCl_3 (sealed capillary) at δ 0.00, and the ^{31}P chemical shifts are referenced to 85% H_3PO_4 (sealed capillary) at δ 0.00 in the appropriate solvent. Melting points were obtained with a Mel-Temp capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

All reactions were performed in oven-dried glassware under an inert atmosphere of dry N_2 , and solvents used during the workup were reagent or HPLC grade except hexanes which was distilled from CaH_2 and was stored over molecular sieves (3 Å). Dry CH_2Cl_2 and DMF used for reactions were distilled from CaH_2 , and were stored over molecular sieves (3 Å) if not used immediately after distillation. Acetone used for the preparation of square was HPLC grade and stored over molecular sieves (3 Å). *p*-Toluenesulfonic acid and 2-naphthalenesulfonic acid, sodium salts, were commercially available compounds (Aldrich) and were recrystallized from $\text{CH}_3\text{OH}/\text{H}_2\text{O}$. 2,7-Diazapyrene was prepared by modified literature procedure.²⁹

Preparation of [Pt(PPh₂(CH₂CH₂O)₃CH₂CH₂PPh₂)(OTf)₂] **2.** To a solution in a Schlenk flask containing 111 mg (0.14 mmol) of $\text{Pt}(\text{PPh}_2(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{PPh}_2)(\text{Cl})_2$ ²² in 60 mL of CH_2Cl_2 was added 108 mg (0.42 mmol) of AgOTf . The reaction mixture was stirred at 25 °C for 48 h with the exclusion of light. To the heterogeneous mixture was added 30 mL of CH_3OH , which was then filtered through a coarse-porosity glass frit containing Celite. The clear filtrate was concentrated to 10 mL under reduced pressure, followed by the addition of diethyl ether to precipitate the metal triflate complex. Collection under an atmosphere of nitrogen and drying under vacuum in a drying tube gave a tan-colored powder, 112 mg (78%) of **2**: mp 50–55 °C (dec.); IR (CCl_4) 3099, 3038, 1252, 1225, 1160, 1104 cm^{-1} ; ^1H NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ 7.52–7.44 (bm, PPh_2), 7.43–7.33 (bm, PPh_2), 4.25 (bs, CH_2), 3.98 (t, CH_2), 3.91 (bm, CH_2), 2.8 (bm, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ 133.7 (d, C_o , $J_{\text{CP}} = 11$ Hz), 133.5 (d, C_p , $J_{\text{CP}} = 2.5$ Hz), 129.7 (d, C_m , $J_{\text{CP}} = 12$ Hz), 122.2 (d, C_{ipso} , $J_{\text{CP}} = 70$ Hz), 121.0 (q, C_{OTf} , $J_{\text{CF}} = 319$ Hz), 73.6 (s, C_3 or C_4), 68.4 (s, C_3 or C_4), 32.2 (C_1 or C_2 , $J_{\text{CP}} = 37$ Hz), 27.8 (d, C_1 or C_2 , $J_{\text{CP}} = 46$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ 14.0 (vb), $J_{\text{PP}} = 4000$ Hz; ^{19}F NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ -76 (s, 2 CF_3SO_3). Anal. Calcd for $\text{C}_{34}\text{H}_{36}\text{Pt}_2\text{S}_2\text{O}_5\text{F}_6 \cdot 4\text{H}_2\text{O}$: C, 37.27; H, 4.05; S, 5.85. Found: C, 37.28; H, 3.69; S, 5.93.

Preparation of [Pt(PPh₂(CH₂CH₂O)₃CH₂CH₂PPh₂)(4,4'-bipyridyl)(OTf)₂] **5.** To a 50 mL Schlenk flask, equipped with a stir bar, containing 81 mg (0.078 mmol) of **2** in 30 mL of CH_2Cl_2 and CH_3OH (1:1 mixture) was added 19 mg (0.12 mmol) of 4,4'-bipyridine. The resulting homogenous reaction mixture was allowed to stir at 25 °C for 2 h. The reaction mixture was filtered through a coarse-porosity glass frit lined with a Whatman 934-AH glass microfibre to afford a clear, colorless solution. The filtrate was reduced in volume by 75% by rotary evaporation, followed by addition of diethyl ether to afford a tan-colored solid, 72 mg (78%) of **72**: mp 210–222 °C (dec.); IR (CCl_4) 3131, 3069, 1255, 1221, 1104, 1106 cm^{-1} ; ^1H NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ 8.91 (d, H_{α} , $J_{\text{HH}} = 7$ Hz), 7.75 (d, H_{β} , $J_{\text{HH}} = 6.5$ Hz), 7.69–7.63 (m, H_o), 7.52–7.47 (m, H_p), 7.35–7.30 (m, H_m), 4.20–4.05 (bm, CH_2), 4.07–3.95 (bm, 2 CH_2), 2.50 (bs, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ 152.6 (C_{α}), 145.5 (C_{γ}), 134.1 (C_o), 133.4 (C_p), 130.2 (C_m), 126.4 (C_{ipso}), 125.3 (C_{β}), 121.5 (q, C_{OTf} , $J_{\text{CF}} = 320$ Hz), 71.0 (C_3), 70.6 (C_4), 67.3 (C_2); $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ -1.24 (s), $J_{\text{PP}} = 3310$ Hz; ^{19}F NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ -76 (s, 8 CF_3SO_3). Anal.

Calcd for $\text{C}_{176}\text{H}_{176}\text{Pt}_4\text{P}_8\text{S}_8\text{N}_8\text{O}_{36}\text{F}_{24} \cdot 12\text{H}_2\text{O}$: C, 42.83; H, 4.08; N, 2.27; S, 5.20. Found: C, 42.51; H, 3.77; N, 2.39; S, 5.40.

Preparation of [Pt(PPh₂(CH₂CH₂O)₃CH₂CH₂PPh₂)(2,9-diazapyrene)(OTf)₂] **6.** In analogy with the preparation of **5**, 26 mg (0.025 mmol) of **2** was reacted with 6 mg (0.028 mmol) of 2,9-diazapyrene²⁹ in 40 mL of CH_2Cl_2 and CH_3OH (1:1 mixture) for 3 h at 25 °C. A similar workup resulted in the formation of a light yellow solid, 20 mg (66%) of **6**: mp 215–218 °C (dec.); IR (CCl_4) 3095, 3037, 1258, 1155, 1104, 1029 cm^{-1} ; ^1H NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ 9.9 (d, H_{α} , $J_{\text{HP}} = 2.3$ Hz), 8.1 (s, H_{β}), 7.77–7.73 (bm, H_o), 7.28–7.24 (bm, H_m , p), 4.4–4.29 (bm, CH_2), 4.03–4.01 (bm, 2 CH_2), 2.81 (bs, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ 146.4 (C_{α}), 133.7 (C_o), 133.0 (C_p), 129.8 (C_m), 128.6 (C_{γ}), 128.2 (C_{ipso} , diazapyrene), 125.5 (C_{ipso} , Ph), 124.2 (C_{β}), 121.4 (q, C_{OTf} , $J_{\text{CF}} = 319$ Hz), 70.3 (C_3 or C_4), 70.0 (C_3 or C_4), 66.8 (C_2); $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ -0.98, $J_{\text{PP}} = 2900$ Hz; ^{19}F NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$) δ -76 (s, 8 CF_3SO_3). Anal. Calcd for $\text{C}_{192}\text{H}_{176}\text{Pt}_4\text{P}_8\text{S}_8\text{N}_8\text{O}_{36}\text{F}_{24}$: C, 46.95; H, 3.61; N, 2.28; S, 5.22. Found: C, 43.92; H, 3.64; N, 1.89; S, 4.51.

Synthesis of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis((diphenylphosphino)ethoxy)-26,28-dipropoxycalix[4]arene-Platinum Bistriflate **8.** To a solution of calix[4]arene-platinum chloride²¹ (1.581 g, 1.11 mmol) in 20 mL CH_2Cl_2 , AgOTf (0.600 g, 2.34 mmol) was added at room temperature, and the reaction mixture was stirred overnight. The insoluble material (AgCl) was removed by filtration and washed with CH_2Cl_2 ; during the filtration, additional insoluble material precipitated and was filtered. This filtration procedure was repeated 2–3 times until a clear filtrate resulted. The solvent from the combined filtrates was evaporated by blowing N_2 to a small quantity, which was triturated with dry hexanes, and the precipitate thus formed was collected by filtration and dried under vacuum to afford 1.51 g of the desired product **8** as an off-white solid (yield 82%): mp 215–219 °C (dec., shrunk at 196 °C); ^1H NMR (CD_2Cl_2) δ 7.70 (m, 8 H, $\text{H}_{o-\text{PPh}}$), 7.61 (m, 4 H, $\text{H}_{p-\text{PPh}}$), 7.50 (m, 8 H, $\text{H}_{m-\text{PPh}}$), 7.13 and 6.42 (2s, 4 H each, H_{ArO}), 4.16 and 3.20 (AB quartet, $J = 12.7$ Hz, 4 H each, ArCH_2Ar); 4.13 (m, overlap, $\text{ArOCH}_2\text{CH}_2\text{PPh}_2$), 3.91 (t, overlap, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$), 3.86 (m, overlap, $\text{ArOCH}_2\text{CH}_2\text{PPh}_2$), 1.77 (m, 4 H, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$), 1.30 and 0.80 (2s, 18 H each, *tert*-butyl), 1.00 (t, 6 H, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (CD_2Cl_2) δ 154.3 and 152.1 (2s, $\text{C}_{\text{Ar}25-28}$), 147.1 and 145.2 (2s, $\text{C}_{\text{Ar}11,23,5,17}$), 135.9 and 132.1 (2s, $\text{C}_{\text{Ar}1,9,13,21,3,7,15,19}$), 133.4 (s, $C_{p-\text{PPh}}$), 133.1 (t, $C_{o-\text{PPh}}$), 130.0 (t, $C_{m-\text{PPh}}$), 126.3 and 125.2 (2s, $\text{C}_{\text{Ar}10,12,22,24,6,16,18}$), 124.3 (m, $C_{\text{ipso}-\text{PPh}}$), 120.4 (q, $J = 317.0$ Hz, CF_3), 78.2 (s, $\text{ArOCH}_2\text{CH}_2\text{PPh}_2$), 69.3 (s, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$), 34.6 and 34.1 (2s, $\text{C}(\text{CH}_3)_3$); 31.9 and 31.4 (2s, $\text{C}(\text{CH}_3)_3$); 31.8 (s, ArCH_2Ar), 28.2 (m, $\text{ArOCH}_2\text{CH}_2\text{PPh}_2$), 23.3 (s, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$), 10.3 (s, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$); ^{31}P NMR (CD_2Cl_2) δ -4.4 (s, $J_{\text{PP}} = 3917$ Hz); ^{19}F NMR δ -79.1 (s). Anal. Calcd for $\text{C}_{80}\text{H}_{94}\text{F}_6\text{O}_{10}\text{P}_2\text{PtS}_2 \cdot 2\text{H}_2\text{O}$: C, 56.97; H, 5.86; S, 3.80. Found: C, 56.66; H, 5.81; S, 3.78.

Preparation of Molecular Square **9.** 4,4'-Bipyridine (0.0300 g, 0.192 mmol) was allowed to react with calix[4]arene-Pt(OTf)₂ (**8**) (0.348 g, 0.211 mmol) in CH_2Cl_2 (20 mL) at room temperature for 3 h. The colorless solution was evaporated with N_2 to one third of its volume and then was layered with distilled hexanes (~30 mL) for several days. The cotton-like crystalline material was collected by filtration, washed well with hexanes, and dried under vacuum to give the desired product (**9**) (0.342 g, 98%) as a white solid: mp 306–308 °C (dec., shrunk at 296 °C); ^1H NMR (CD_2Cl_2) δ 8.66 (d, $J = 4.73$ Hz, 16 H, $\text{H}_{\alpha-\text{Py}}$), 7.81 (m, 32 H; $\text{H}_{o-\text{PPh}}$), 7.54 (m, 48 H, $\text{H}_{m,p-\text{PPh}}$), 7.27 (d, $J = 6.65$ Hz, 16 H, $\text{H}_{\beta-\text{Py}}$), 7.12 and 6.39 (2s, 16 H each, H_{ArO}), 4.50 and 4.25 (2bs, overlap, $\text{ArOCH}_2\text{CH}_2\text{PPh}_2$), 4.14 and 3.15 (AB quartet, $J = 12.8$ Hz, 16 H each, ArCH_2Ar), 3.76 (t, 16 H, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$), 1.97 (s, H_2O), 1.48 (m, 16 H, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$), 1.30 and 0.79 (2s, 72 H each, *tert*-butyl), 0.87 (t, 24 H; $\text{ArOCH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (CD_2Cl_2) δ 154.2 and 151.1 (2s, $\text{C}_{\text{Ar}25,27-28}$), 151.6 (s, $C_{\alpha-\text{Py}}$), 146.6 and 144.6 (2s, $\text{C}_{\text{Ar}11,23,5,17}$); 143.1 (s, $C_{\gamma-\text{Py}}$), 135.8 and 131.9 (2s, $\text{C}_{\text{Ar}1,9,13,21,3,7,15,19}$), 133.3 (m, $C_{o-\text{PPh}}$), 133.1 (bs, $C_{p-\text{PPh}}$), 130.2 (m, $C_{m-\text{PPh}}$), 125.9 and 124.7 (2s, $\text{C}_{\text{Ar}10,12,22,24,6,16,18}$), 124.2 (m, $C_{\text{ipso}-\text{PPh}}$); 123.8 (s, $C_{\beta-\text{Py}}$), 121.0 (q, $J = 320.1$ Hz, CF_3), 77.5 (s, $\text{ArOCH}_2\text{CH}_2\text{PPh}_2$), 69.5 (s, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$), 34.3 and 33.7 (2s, $\text{C}(\text{CH}_3)_3$), 31.8 (obscured by $\text{C}(\text{CH}_3)_3$; ArCH_2Ar), 31.6 and 31.0 (2s, $\text{C}(\text{CH}_3)_3$), 29.1 (m, $\text{ArOCH}_2\text{CH}_2\text{PPh}_2$), 22.4 (s, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$), 9.8 (s, $\text{ArOCH}_2\text{CH}_2\text{CH}_3$); ^{31}P NMR (CD_2Cl_2) δ -6.9 (s, $J_{\text{PP}} = 3231$ Hz); ^{19}F NMR (CD_2Cl_2) δ -78.7 (s). Anal. Calcd for $\text{C}_{360}\text{H}_{408}\text{F}_{24}\text{N}_8\text{O}_{40}$

$\text{P}_8\text{Pt}_4\text{S}_8 \cdot 8\text{H}_2\text{O} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 58.40; H, 5.78; N, 1.51; S, 3.46. Found: C, 58.03; H, 5.46; N, 1.42; S, 3.60.

Preparation of Hybrid Molecular Square 11. In a 50 mL round bottom flask, bis[4-(4'-pyridyl)phenyl]iodonium triflate²⁸ (35.4 mg, 0.0606 mmol) was suspended in 20 mL of acetone, and then calix[4]-arene-Pt(OTf)₂ (**8**) (0.103 g, 0.0607 mmol) was added all at once. A pale yellow solution resulted within a few minutes. After 4 h of stirring at room temperature, the solvent was evaporated with N₂. The residue was taken up in CH₂Cl₂ (~10 mL), and then triturated with Et₂O. The white precipitate thus formed was collected by filtration, washed with Et₂O, and dried under vacuum to give 0.103 g of **11** as a white solid. From the filtrate, a second crop of **11** (0.014 g) was obtained to give a total yield of 84%: mp 246 °C (dec., darkened at 238 °C); ¹H NMR (acetone-*d*₆) δ 8.97 (d, *J* = 4.88 Hz, 8 H, H_{α-Py}), 8.39 (d, *J* = 8.82 Hz, 8 H, H_{α-IPh}), 7.96 (m, 16 H, H_{o-PhP}); 7.76 (d, *J* = 8.82 Hz, 8 H, H_{β-IPh}), 7.58 (m, overlap, H_{m,p-PhP}), 7.52 (d, *J* = 6.52 Hz, overlap, H_{β-Py}), 7.23 and 6.51 (2s, 8 H each, H_{ArO}), 4.42–4.41 (2bs, overlap, ArOCH₂CH₂PPh₂), 4.28 and 3.22 (AB quartet, *J* = 12.81 Hz, 8 H each, ArCH₂Ar), 3.93 (t, 8 H, ArOCH₂CH₂CH₃), 2.88 (bs, H₂O) 1.62 (m, 8 H, ArOCH₂CH₂CH₃), 1.32 and 0.83 (2s, 36 H each, *tert*-butyl), 0.89 (t, 12 H, ArOCH₂CH₂CH₃), ¹³C NMR (acetone-*d*₆) δ 155.0 and 152.0 (2s, C_{Ar25,27-28}), 152.1 (s, C_{α-Py}), 150.2 (s, C_{γ-Py}), 146.9 and 145.0 (2s, C_{Ar11,23,5,17}), 139.6 (s, C_{γ-IPh}), 137.4 (s, C_{α-IPh}), 136.4 and 132.8 (2s, C_{Ar1,9,13,21,3,7,15,19}), 134.1 (t, C_{o-PhP}), 133.5 (s, C_{p-PhP}), 131.7 (s, C_{β-Ph}), 130.8 (t, C_{m-PhP}); 126.7 and 125.5 (2s, C_{Ar10,12,22,24,4,6,16,18}), 125.7 (s, C_{β-Py}), 125.5 (m, C_{ipso-PhP}), 122.2 (q, *J* = 321.2 Hz; CF₃), 117.5 (s, Cl), 78.3 (s, ArOCH₂CH₂PPh₂), 70.5 (s, ArOCH₂CH₂CH₃), 34.8 and 34.3 (2s, C(CH₃)₃), 32.2 (s, ArCH₂Ar), 32.0 and 31.6 (2s, C(CH₃)₃), 29.7 (m, ArOCH₂CH₂PPh₂), 23.1 (s, ArOCH₂CH₂CH₃), 10.3 (s, ArOCH₂CH₂CH₃); ³¹P NMR (acetone-*d*₆) δ -8.3 (s, *J*_{PtP} = 3180 Hz); ¹⁹F NMR (acetone-*d*₆) δ -77.9 (s). Anal. Calcd for C₂₀₆H₂₂₀F₁₈N₄I₂O₂₆P₄Pt₂S₆·4H₂O·0.3CH₂Cl₂: C, 53.60; H, 4.98; I, 7.14; N, 1.21; S, 4.16. Found: C, 53.97; H, 4.88; I, 7.14; N, 1.11; S, 4.43.

Mass Spectrometry. The electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, which is based on an Oxford 7 T superconducting magnet, used for the present study has been described in detail elsewhere.⁴¹ The macrocycle (*ca.* 1 mg/mL in CH₂Cl₂) was electrosprayed at a flow rate of 0.3 μL/min. A source potential of *ca.* 2.5 kV was applied to produce a stable positive-ion current. The resistively heated desolvation capillary temperature was reduced to 35 °C, and the capillary-skimmer potential was reduced

to 20 V; both parameters were decreased to avoid thermal or collisional dissociation, respectively, and correspond to very gentle source conditions. To enhance the signal-to-noise and dynamic range, broad band quadrupolar excitation was employed for ion accumulation during the ion injection event.^{42,43} Specifically, to enhance the 3+ charge-state of complex **9**, a tailored noise wave form was applied from *m/z* = 2200 to 2300 at 2 V peak-to-peak. Similarly, to enhance the 2+ charge-state of complex **5**, a single ion accumulation wave form was applied at *m/z* = 2210 at 0.8 V peak-to-peak. The theoretical molecular weights and isotopic patterns were calculated using GOOGLY software⁴⁴ which utilizes an algorithm previously reported.⁴⁵

Transport Experiments. Two simple U-tubes, as illustrated in Figure 3, were set up at room temperature side-by-side, with the second one serving as a control, for each set of experiments. Into tube 1 was placed 30 mL of a 3.25 × 10⁻⁵ M solution of macrocycle **9** in CDCl₃ along with a small magnetic stirring bar. The left arm was carefully layered with 8 mL of a 0.1 M solution (nearly saturated) of sodium tosylate **12** in D₂O. The right arm was layered with 8 mL of pure D₂O. U-Tube 2 was identical except that the bottom layer consisted of pure CDCl₃ (no host). After stirring was commenced, the right arm was periodically sampled by ¹H NMR. After approximately 24 h, the substrate was detected by NMR in tube 1, and equilibrium was reached after 10–14 days. No substrate (substance **12** or **13**) was detected in the control tube even after 14 days. A similar experiment with substrate **13** gave the same results. An experiment where both substrates **12** and **13** were present in equal molar concentrations (Figure 3) established that sodium tosylate **12** was favored in the transport by a factor of 1.5–2.0 in the initial samplings as determined by integration of the respective proton signals in the ¹H NMR. A simultaneous control experiment once again established that no arenesulfonate anions passed through the chloroform phase in the absence of macrocycle **9**.

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