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Encapsulation of Aromatic Molecules in Hexanuclear Arene Ruthenium Cages: A Strategy to Build Up Organometallic Carceplex Prisms with a Dangling Arm Standing Out

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Self-assembly of 2,4,6-tris(pyridin-4-yl)-1,3,5-triazine (tpt) subunits with *p*-cymene (*p*-Pr^{i}C$_6$H$_4$Me) or hexamethylbenzene (C$_6$Me$_6$) ruthenium building blocks and 2,5-dihydroxy-1,4-benzoquinonato (dhbq) or 2,5-dihchloro-3,6-dihydroxy-1,4-benzoquinonato (dchq) bridges affords the triangular prismatic organometallic cations [Ru$_6$(*p*-Pr^{i}C$_6$H$_4$Me)$_6$(tpt)$_2$(dhbq)$_3$]$^{6+}$ ([**1**]$^{6+}$), [Ru$_6$(*p*-Pr^{i}C$_6$H$_4$Me)$_6$(tpt)$_2$(dchq)$_3$]$^{6+}$ ([**2**]$^{6+}$), [Ru$_6$(C$_6$Me$_6$)$_6$(tpt)$_2$(dhbq)$_3$]$^{6+}$ ([**3**]$^{6+}$), and [Ru$_6$(C$_6$Me$_6$)$_6$(tpt)$_2$(dchq)$_3$]$^{6+}$ ([**4**]$^{6+}$). These hexanuclear cationic cages are isolated in good yield as their triflate salts. The assembly of **1**−**4** can also be achieved in the presence of large aromatic molecules such as pyrene, fluoranthene, benzo[*e*]pyrene, triphenylene, or coronene to give the corresponding inclusion systems [aromatic⊂**1**]$^{6+}$, [aromatic⊂**2**]$^{6+}$, [aromatic⊂**3**]$^{6+}$, and [aromatic⊂**4**]$^{6+}$. The closed proximity of the encapsulated molecule with the different components of the cage and the carceplex nature of these systems are confirmed by one-dimensional ROESY ^{1}H NMR experiments, mass spectrometry, and the single-crystal structure analysis of [pyrene⊂**1**][O$_3$SCF$_3$]$_6$ and [benzo[*e*]pyrene⊂**1**][O$_3$SCF$_3$]$_6$. Pyrene can be encapsulated even if it contains a functionalized aliphatic substituent; in this case the aromatic moiety is included in the cage, while the functionalized side arm stands out. Thus, methyl 4-(pyren-1-yl)butanoate (pyrene-R) is encapsulated in **1** to give the carceplex [pyrene-R⊂**1**]$^{6+}$, in which the methyl butyrate arm dangles outside the cage while the pyrene moiety is firmly trapped by the metallo-prismatic cation, as demonstrated by ^{1}H NMR experiments and ESI-MS.

Introduction

Self-assembly is a process leading to the formation of discrete nanometer-sized objects or well-defined aggregates in which the overall structure is controlled by the symmetry of the different building blocks.[1] In the case of metallo-supramolecular assemblies, the coordination mode of the metal center as well as the symmetry of the ligands needs to be controlled in order to allow the formation of the desired aggregates.[2] The square-planar geometries of platinum(II) and palladium(II) have been extensively exploited to generate supramolecular assemblies.[3] However, a variety of other metals with octahedral geometries have also been used for the self-assembly of supramolecular complexes.[4] Encapsulation of guest molecules in this type of metallo-supramolecular assemblies is of great interest and the subject of many studies.[5] These molecular capsules have many potential applications, ranging from drug delivery systems to molecular reaction chambers for catalysis and stabilization of reactive intermediates.[6]

Recently, we synthesized a cationic triangular metallo-prism, [Ru$_6$(*p*-Pr^{i}C$_6$H$_4$Me)$_6$(tpt)$_2$(dhbq)$_3$]$^{6+}$ ([**1**]$^{6+}$), which allowed the encapsulation of square-planar complexes M(acac)$_2$ [M = Pd, Pt; acac = acetylacetato][7] and triphenylene derivatives.[8] The cytotoxic activities of the "complex-in-a-complex" derivatives [(acac)$_2$M⊂**1**]$^{6+}$ were evaluated in comparison with free M(acac)$_2$ and showed that, like a "Trojan horse", once inside a cell, leaching of the guest from the cage accelerates and increases the cytotoxic effect.[7] Permanent encapsulation of a large aromatic guest such as hexahydroxytriphenylene [C$_{18}$H$_6$(OH)$_6$] and hexamethoxytriphenylene [C$_{18}$H$_6$(OMe)$_6$] was

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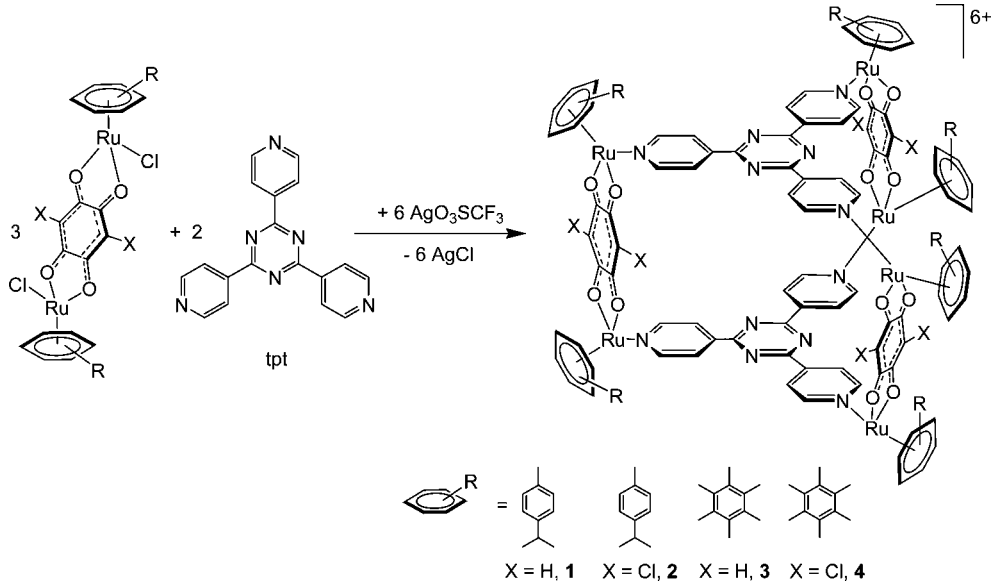
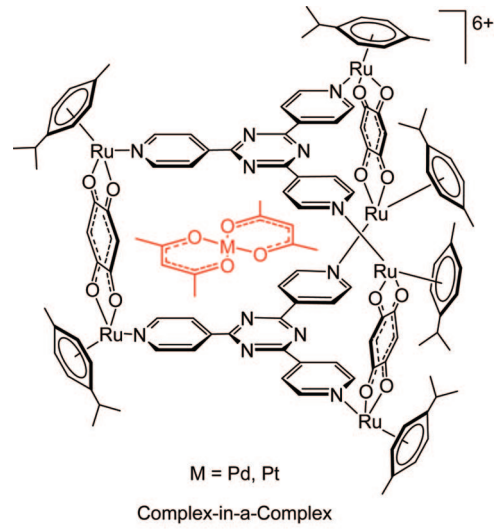
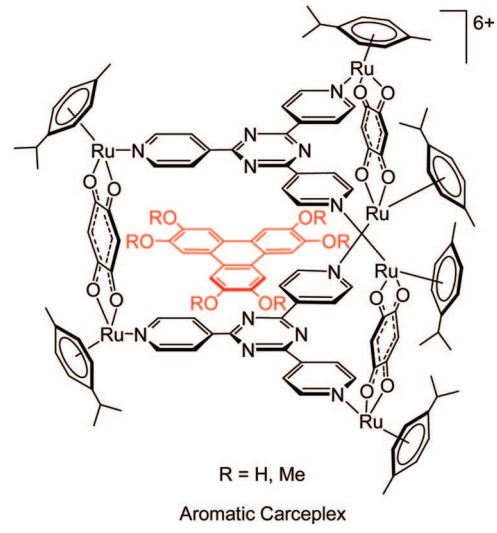
Scheme 1. Synthesis of the Empty Metallo-Prisms



observed as well, with the cationic cage $[\mathbf{1}]^{6+}$ giving rise to carceplex systems such as $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$ and $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$.[8]

Herein we report the synthesis and characterization of the cationic triangular metallo-prisms $[Ru_6(p\text{-}Pr^iC_6H_4Me)_6(tpt)_2(dchq)_3]^{6+}$ ($[\mathbf{2}]^{6+}$), $[Ru_6(C_6Me_6)_6(tpt)_2(dhbq)_3]^{6+}$ ($[\mathbf{3}]^{6+}$), and $[Ru_6(C_6Me_6)_6(tpt)_2(dchq)_3]^{6+}$ ($[\mathbf{4}]^{6+}$), analogues of $[Ru_6(p\text{-}Pr^iC_6H_4Me)_6(tpt)_2(dhbq)_3]^{6+}$ ($[\mathbf{1}]^{6+}$), incorporating *p*-cymene or hexamethylbenzene ruthenium building blocks, bridged by 2,5-dihydroxy-1,4-benzoquinonato (dhbq) or 2,5-dihchloro-3,6-dihydroxy-1,4-benzoquinonato (dchq) ligands, and connected





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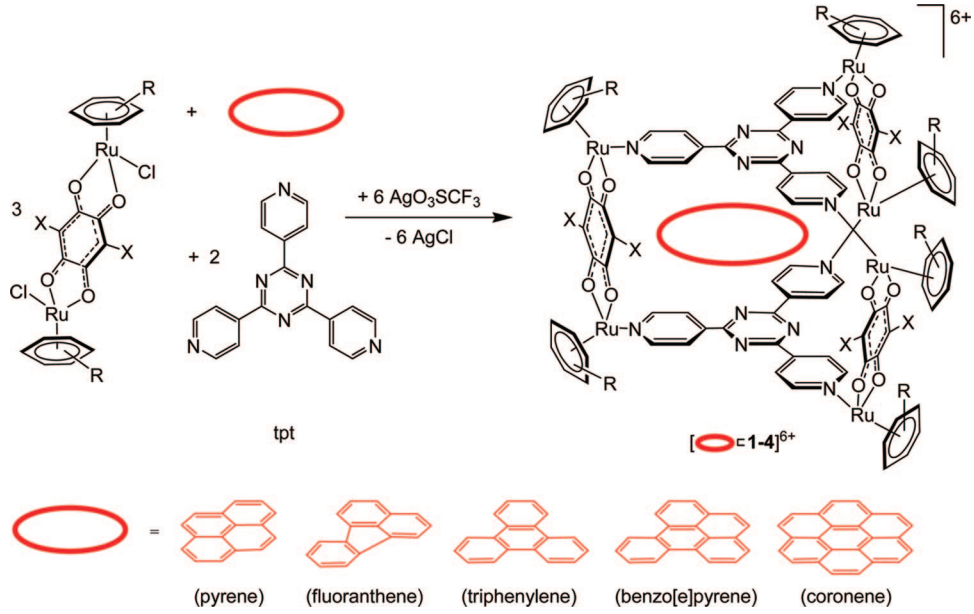
Scheme 2. Synthesis of the Filled Metallo-Prisms



by two 2,4,6-tris(pyridin-4-yl)-1,3,5-triazine (tpt) subunits. These systems allow the permanent inclusion of large aromatic molecules such as pyrene, fluoranthene, benzo[*e*]pyrene, triphenylene, and coronene or the inclusion of functionalized aromatic molecules in which the aromatic part is encapsulated while the functional group is hanging out of the cage. The single-crystal structure analyses of [pyrene⊂**1**][O_3SCF_3]$_6$ and [benzo[e]pyrene⊂**1**][O_3SCF_3]$_6$ are also presented.

Results and Discussion

The hexametallic cations **1**−**4** are prepared following a two-step strategy, in which the dinuclear 2,5-dihydroxy-1,4-benzoquinonato (dhbq) complexes [Ru_2(*p*-$Pr^iC_6H_4Me$)$_2$(dhbq)Cl_2][7] and [$Ru_2(C_6Me_6)_2$(dhbq)Cl_2] or the dinuclear 2,5-dihchloro-3,6-dihydroxy-1,4-benzoquinonato (dchq) complexes [Ru_2(*p*-$Pr^iC_6H_4Me$)$_2$(dchq)Cl_2] and [$Ru_2(C_6Me_6)_2$(dchq)Cl_2] are used as a bimetallic connector (see Scheme 1). The coordinatively unsaturated intermediate formed upon addition of AgO_3SCF_3 to the "molecular clip" presumably allows the Ru_2(arene)$_2$-$(C_6X_2O_4)^{2+}$ moieties (X = H, Cl) to adopt a *syn* geometry upon coordination to the tpt molecular paneling unit. The four complexes are isolated and characterized in good yield as their triflate salts, [Ru_6(*p*-$Pr^iC_6H_4Me$)$_6$(tpt)$_2$(dhbq)$_3$][O_3SCF_3]$_6$ ([**1**][O_3SCF_3]$_6$), [Ru_6(*p*-$Pr^iC_6H_4Me$)$_6$(tpt)$_2$(dchq)$_3$][O_3SCF_3]$_6$ ([**2**][O_3SCF_3]$_6$), [$Ru_6(C_6Me_6)_6$(tpt)$_2$(dhbq)$_3$][O_3SCF_3]$_6$ ([**3**][O_3SCF_3]$_6$), and [$Ru_6(C_6Me_6)_6$(tpt)$_2$(dchq)$_3$][O_3SCF_3]$_6$ ([**4**][O_3SCF_3]$_6$), respectively. The carceplex properties (potential of forming permanent inclusion complexes) of these four hexacationic metallo-prismatic cages have been evaluated with a whole range of aromatic molecules.

The assembly of cages **1**−**4** can be achieved in the presence of large aromatic molecules without affecting the overall yield (see Scheme 2). Indeed, if 1 equiv of pyrene, fluoranthene, benzo[*e*]pyrene, triphenylene, or coronene is initially added to the reaction mixture, the hexacationic carceplex systems [pyrene⊂**1**]$^{6+}$, [fluoranthene⊂**1**]$^{6+}$, [triphenylene⊂**1**]$^{6+}$, [benzo[e]pyrene⊂**1**]$^{6+}$, [coronene⊂**1**]$^{6+}$, [fluoranthene⊂**2**]$^{6+}$, [triphenylene⊂**2**]$^{6+}$, [fluoranthene⊂**3**]$^{6+}$, [triphenylene⊂**3**]$^{6+}$, [fluoranthene⊂**4**]$^{6+}$, and [triphenylene⊂**4**]$^{6+}$ are obtained.

The preference of cage [**1**]$^{6+}$ for different aromatic molecules has also been studied. If a 1:1:1 mixture of coronene, triphenylene, and pyrene is initially added, before the formation of cage [**1**]$^{6+}$, only coronene is found encapsulated by the cage, [coronene⊂**1**][O_3SCF_3]$_6$ being exclusively isolated after workup. Similarly, just triphenylene is encapsulated if a 1:1 mixture of triphenylene and pyrene is used. Therefore, it is clear that cage [**1**]$^{6+}$ prefers aromatic molecules in the order coronene > triphenylene > pyrene. The formation of these inclusion systems can easily be monitored by ^{1}H NMR spectroscopy. As expected, the ^{1}H NMR spectrum of [**1**]$^{6+}$ shows a well-organized structure with a quite simple set of signals. However, unlike the empty cage [**1**]$^{6+}$, where the H_α and H_β of the pyridyl groups are found at expected positions (8.77 and 8.71 ppm in acetone-d_6) as compared to the uncoordinated tpt unit, upon encapsulation of an aromatic molecule, the H_α and H_β signals are strongly shifted upfield (see Figure 1). Moreover, the protons (H_q) of the hydroxybenzoquinonato bridging ligands are shifted downfield, while the signals of the aromatic protons (H_{ar}) of the *p*-cymene ligand remain almost unchanged upon insertion of an aromatic molecule. Similarly, the protons of the methyl and isopropyl groups of the *p*-cymene ligand are not chemically affected by the presence of the large aromatic guest within the cavity of [**1**]$^{6+}$.

For comparison, triphenylene as well as fluoranthene were encapsulated in the different cages **1**−**4**. The carceplex properties of the four cages are all the same, and the encapsulation of triphenylene by **1**−**4** is clearly demonstrated by ^{1}H NMR spectroscopy (see Figure 2). The two signals associated with the protons of the encapsulated triphenylene molecule (H_g and $H_{g'}$) are well separated and shifted upfield due to the special environment provided by the hydrophobic cavity of the cages. Indeed, H_g is shifted by 1.2 ppm, while $H_{g'}$ is shifted by as much as 3.6 ppm, suggesting a strong interaction between triphenylene and the components of the cage, especially the tpt units. Similarly, the protons (H_g) of encapsulated fluoranthene molecules in cages **1**−**4** are strongly shifted upfield as compared to free fluoranthene (see Figure 3).

Interestingly, in the [pyrene⊂**1**]$^{6+}$, [fluoranthene⊂**1**]$^{6+}$, and [benzo[*e*]pyrene⊂**1**]$^{6+}$ systems, in which the cage symmetry (D_{3h}) does not match the encapsulated molecule symmetry (D_{2h}), only the minimal numbers of signals are observed for [**1**]$^{6+}$, even at low temperature (−50 °C). This suggests that in solution

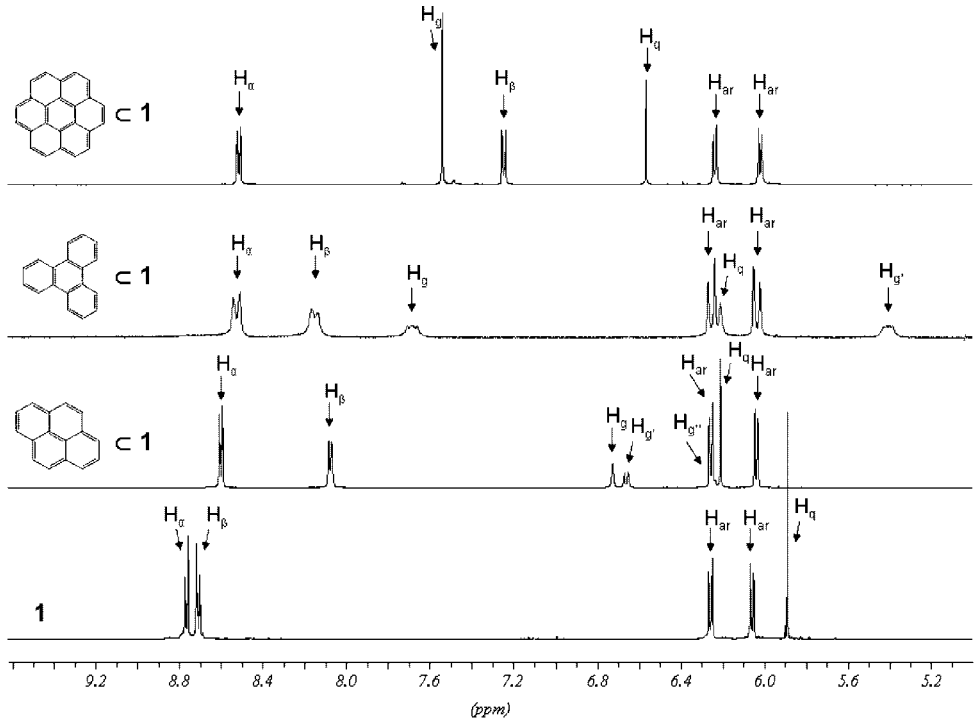


Figure 1. Aromatic region of the ^{1}H NMR spectra (400 MHz, acetone-d_6) of $[\mathbf{1}]^{6+}$ and of [pyrene⊂$\mathbf{1}$]$^{6+}$, [triphenylene⊂$\mathbf{1}$]$^{6+}$, and [coronene⊂$\mathbf{1}$]$^{6+}$.

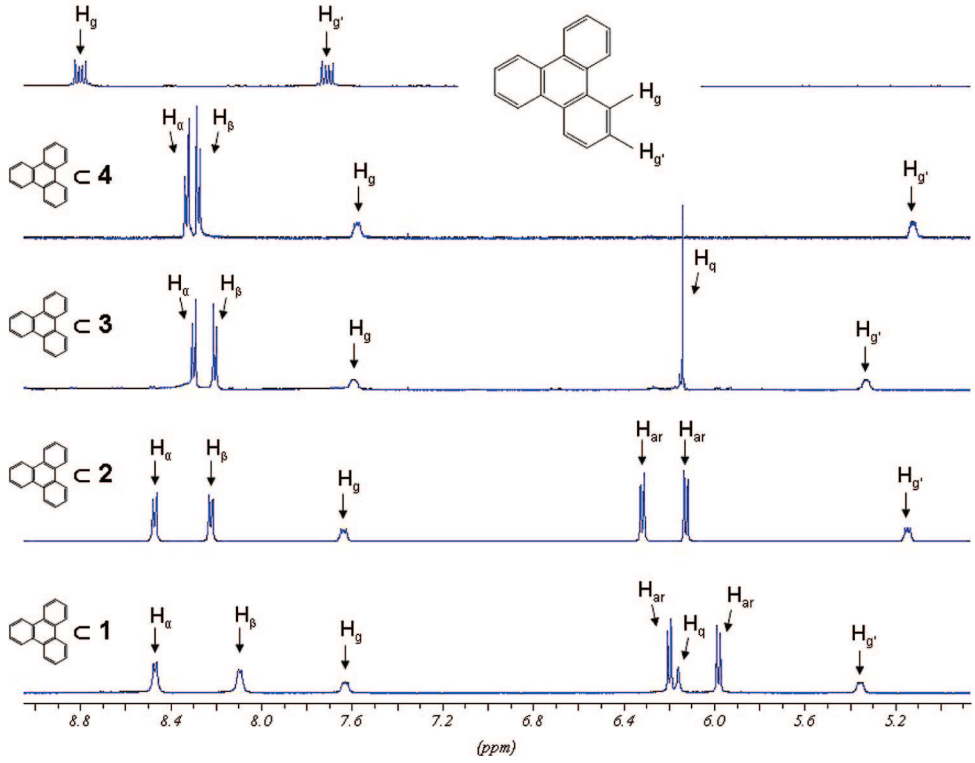


Figure 2. Aromatic region of the ^{1}H NMR spectra (400 MHz, acetone-d_6) of [triphenylene⊂$\mathbf{1}$]$^{6+}$, [triphenylene⊂$\mathbf{2}$]$^{6+}$, [triphenylene⊂$\mathbf{3}$]$^{6+}$, [triphenylene⊂$\mathbf{4}$]$^{6+}$, and free triphenylene.

an unrestricted rotation of the large aromatic molecule within the hydrophobic cavity of $[\mathbf{1}]^{6+}$ takes place.

One-dimensional ROESY ^{1}H NMR experiments confirm the spatial proximity of the different components of the empty cages **1**−**4**. Indeed, in $[\mathbf{1}]^{6+}$, a strong interaction between the proton (H_q) of the dihydroxybenzoquinone and the H_α of the tpt units is observed. Moreover, but only for the filled cage [triphenylene⊂$\mathbf{1}$]$^{6+}$, intense cross-peaks are observed between the protons of the encapsulated molecule (H_g and $H_{g'}$) and the protons of the different connecting components of the cage molecule (H_q, H_α, and H_β) (see Figure 4). This strong interaction between the encapsulated molecule and the cationic cage $[\mathbf{1}]^{6+}$ suggests an eclipsed conformation of the tpt−triphenylene−tpt π-stacking arrangement. This is in agreement with the confor-

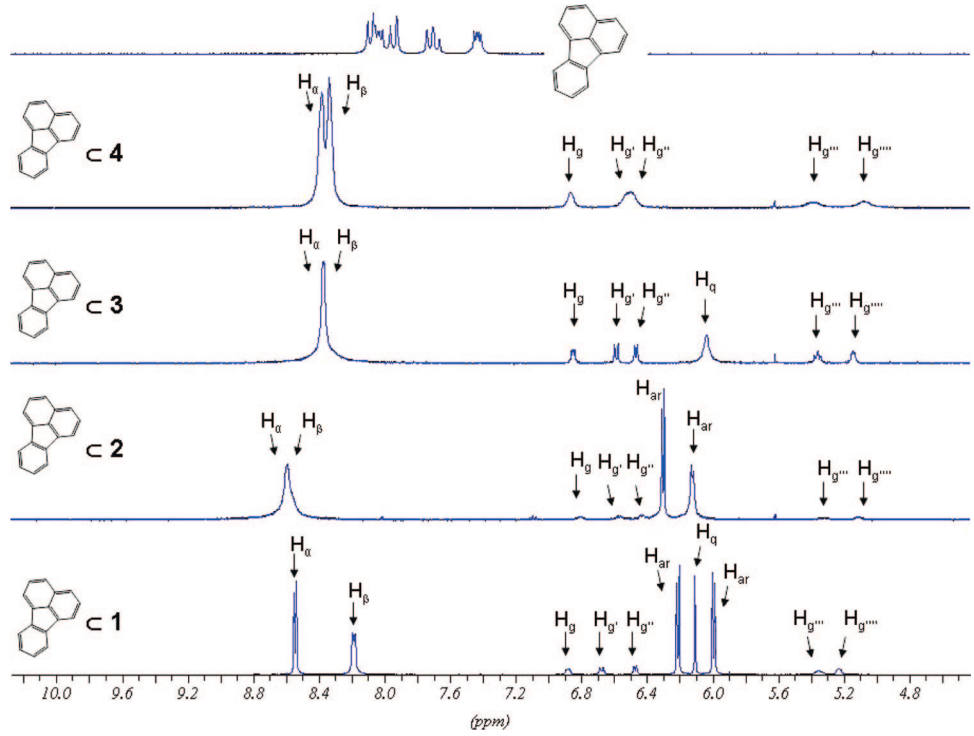


Figure 3. Aromatic region of the ^{1}H NMR spectra (400 MHz, acetone-d_6) of [fluoranthene⊂**1**]$^{6+}$, [fluoranthene⊂**2**]$^{6+}$, [fluoranthene⊂**3**]$^{6+}$, [fluoranthene⊂**4**]$^{6+}$, and free fluoranthene.

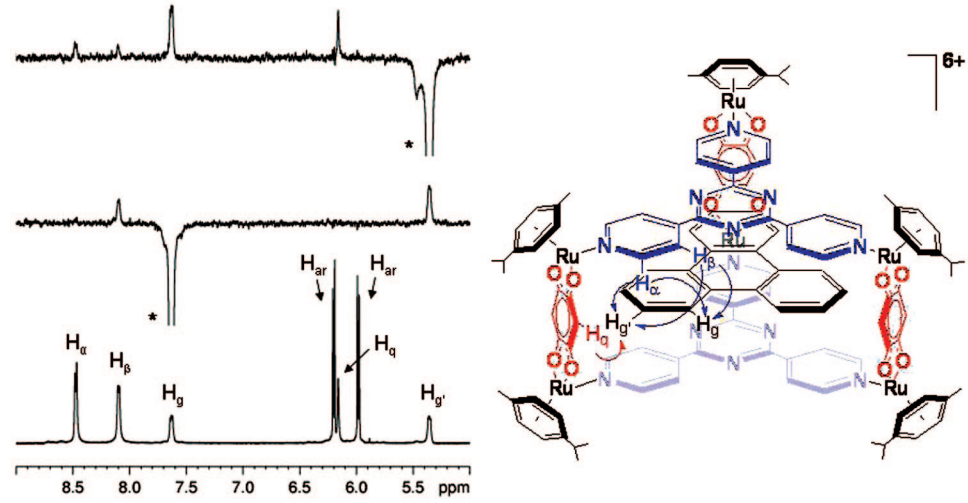


Figure 4. 1-D ROESY spectrum (400 MHz, acetone-d_6) and schematic representation of the corresponding cross-peaks observed in the system [triphenylene⊂**1**]$^{6+}$.

mation observed in [$C_{18}H_6(OMe)_6$⊂**1**]$^{6+}$[8] and in the prismatic cage [$Pt_6(NH_2CH_2CH_2NH_2)_6(tpt)_2(C_4H_4N_2)_3$]$^{12+}$ encapsulating also a hexamethoxytriphenylene molecule.[9] However, the other systems show no cross-peaks between the protons of the aromatic molecule and the protons of the components of [**1**]$^{6+}$, as expected for rotationally unrestricted encapsulated molecules.

The stability of cage [**1**]$^{6+}$ is remarkable, and the encapsulation of the large aromatic molecule is definitive, even under mass spectrometry conditions. The ESI-MS spectra of [triphenylene⊂**1**]$^{6+}$, [benzo[*e*]pyrene⊂**1**]$^{6+}$, and [coronene⊂**1**]$^{6+}$ show peaks corresponding to [aromatic⊂**1** + $(O_3SCF_3)_4$]$^{2+}$ at *m*/*z* 1637.6, 1649.6, and 1673.6, respectively. These peaks have been assigned unambiguously on the basis of their characteristic Ru_6 isotope pattern. Furthermore, in the ESI-MS spectra of [pyrene⊂**1**]$^{6+}$, [triphenylene⊂**1**]$^{6+}$, [benzo[*e*]pyrene⊂**1**]$^{6+}$, and [coronene⊂**1**]$^{6+}$, major peaks corresponding to [**1** + $(O_3SCF_3)_4$]$^{2+}$ at *m*/*z* 1523.6, [{Ru_4(*p*-Pr^i$C_6H_4Me)_4$-(tpt)$_2$($C_6H_2O_4$)$_2$} + $(O_3SCF_3)_2$]$^{2+}$ at *m*/*z* 1070.1, and [**1** + $(O_3SCF_3)_3$]$^{3+}$ at *m*/*z* 966.1 are observed as well.

Single crystals of [pyrene⊂**1**][O_3SCF_3]$_6$ and [benzo[*e*]-pyrene⊂**1**][O_3SCF_3]$_6$ suitable for X-ray structure analysis were obtained by the slow diffusion of benzene in an acetone solution of the salts. The two molecular structures show parallel

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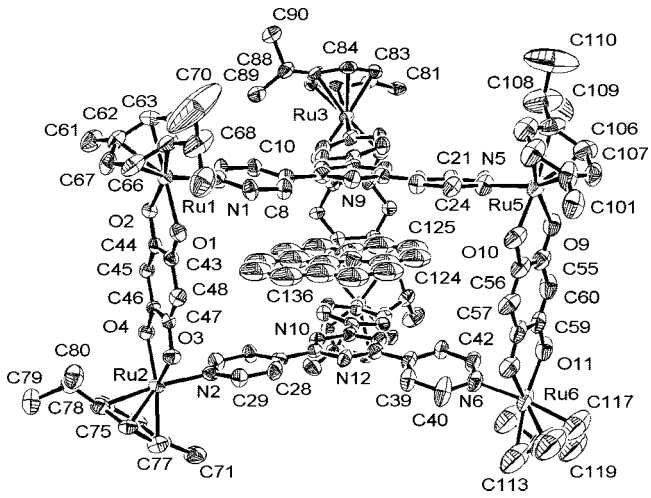

Figure 5. ORTEP drawing of the cation [pyrene⊂**1**]$^{6+}$, at the 35% probability level, with hydrogen atoms and O_3SCF_3 anions omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2) 7.930(1), Ru(3)−Ru(4) 7.928(2), Ru(5)−Ru(6) 7.927(2), Ru(1)−N(1) 2.102(10), Ru(2)−N(2) 2.124(11), Ru(3)−N(3) 2.121(10), Ru(4)−N(4) 2.130(11), Ru(5)−N(5) 2.124(10), Ru(6)−N(6) 2.106(11); O(1)−Ru(1)−O(2) 77.3(3), O(3)−Ru(2)−O(4) 77.5(3), O(5)−Ru(3)−O(6) 77.3(3), O(7)−Ru(4)−O(8) 77.5(3), O(9)−Ru(5)−O(10) 76.1(4), O(11)−Ru(6)−O(12) 77.5(5).

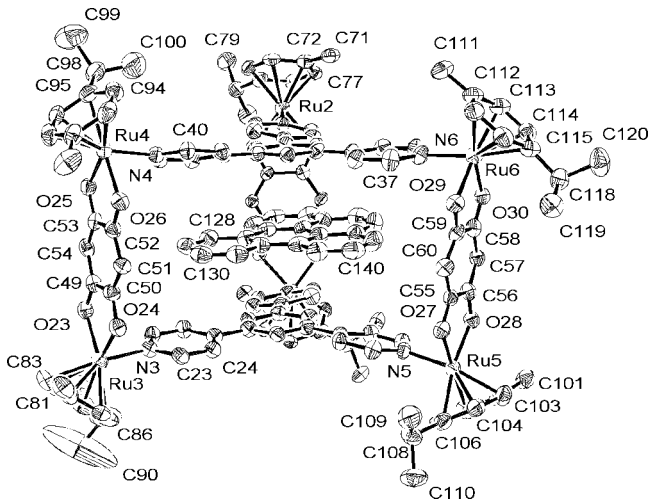

Figure 6. ORTEP drawing of the cation [benzo[*e*]pyrene⊂**1**]$^{6+}$, at the 35% probability level, with hydrogen atoms and O_3SCF_3 anions omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2) 7.938(1), Ru(3)−Ru(4) 7.938(1), Ru(5)−Ru(6) 7.934(1), Ru(1)−N(1) 2.103(7), Ru(2)−N(2) 2.108(7), Ru(3)−N(3) 2.097(7), Ru(4)−N(4) 2.114(7), Ru(5)−N(5) 2.101(7), Ru(6)−N(6) 2.108(8); O(19)−Ru(1)−O(20) 77.8(2), O(21)−Ru(2)−O(22) 76.7(2), O(23)−Ru(3)−O(24) 77.4(2), O(25)−Ru(4)−O(26) 77.5(2), O(27)−Ru(5)−O(28) 76.8(2), O(29)−Ru(6)−O(30) 77.4(2).

π-stacking interactions between the aromatic rings of the tpt subunits and the large aromatic molecule (see Figures 5 and 6).

The single-crystal X-ray structure analyses of [pyrene⊂**1**]-$[O_3SCF_3]_6$and [benzo[e]pyrene⊂**1**]$[O_3SCF_3]_6$ reveal an average Ru−Ru separation of 7.93 Å for the 2,5-dihydroxy-1,4-benzoquinonato-bridged units and an average Ru−Ru separation of 13.2 Å in the plane of the tpt units: The volume of these hexanuclear metallo-prisms is on the order of 700 Å^3.

It is clear from the van der Waals representations of the carceplex systems [pyrene⊂**1**]$^{6+}$ and [benzo[e]pyrene⊂**1**]$^{6+}$ that

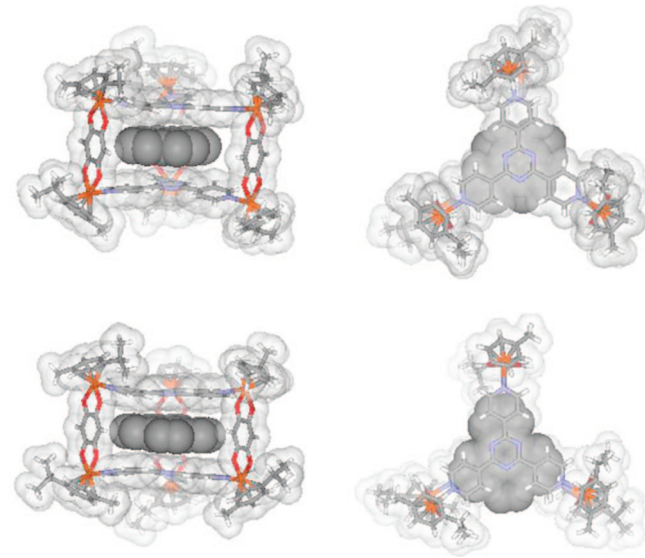

Figure 7. Top and side view representations of [pyrene⊂**1**]$^{6+}$ (top) and [benzo[*e*]pyrene⊂**1**]$^{6+}$ (bottom). Anions and hydrogen atoms of the aromatic molecules are omitted for clarity.

the pyrene and benzo[*e*]pyrene are permanently encapsulated in [**1**]$^{6+}$ (see Figure 7). The interplanar separation observed between the aromatic moieties (∼3.42 Å) is shorter than the theoretical value calculated for this stacking mode,[10] but comparable to the 3.46 Å separation observed between the triazine rings of two independent tpt units in the crystal packing of $[Ir_3(C_5Me_5)_3(tpt)\{S_2C_2(B_{10}H_{10})\}_3]$.[11] The pyrene and benzo[*e*]pyrene molecules are slightly disordered within the cavity of [**1**]$^{6+}$, thus supporting the observation that these aromatic molecules are rotationally unrestricted in solution. In the crystal packing of [pyrene⊂**1**]$[O_3SCF_3]_6$ and [benzo[*e*]pyrene⊂**1**]-$[O_3SCF_3]_6$, no π-stacking interacting systems are observed between independent molecules. The empty spaces left between the cationic hexanuclear cations are filled with CF_3SO_3 anions.

In order to examine the stability of cage [**1**]$^{6+}$ in solution, we recorded the ^{1}H NMR spectra in various deuterated solvents (D_2O, CD_2Cl_2, CD_3CN, $(CD_3)_2CO$, $(CD_3)_2SO$) with different coordinating ability. At room temperature and even elevated temperature, ^{1}H NMR experiments for [**1**]$^{6+}$ in D_2O, CD_2Cl_2, CD_3CN, and $(CD_3)_2CO$ showed no signal changes, indicating the destruction of the cage or the presence of free tpt units. However, in deuterated DMSO, cage [**1**]$^{6+}$ shows additional signals attributed to species generated by coordination of $(CD_3)_2SO$ ligands in line with decomplexation of the different building blocks.

The cage [**1**]$^{6+}$ can encapsulate functionalized aromatic molecule as well. Indeed, if 1 equiv of methyl 4-(pyren-1-yl)butanoate (pyrene-R) is initially added to the reaction mixture, the hexacationic carceplex systems [pyrene-R⊂**1**]$^{6+}$ is obtained (see Scheme 3). The methyl butanoate dangling arm points away from the cage, while the pyrenyl moiety is clearly encapsulated in the cavity, as confirmed by ^{1}H NMR spectroscopy.

As shown in Figure 8, the protons of the pyrenyl moiety are strongly shifted upfield, while the protons of the dangling ester groups remain almost unchanged upon encapsulation. The CH_2 directly attached to the pyrenyl group is shifted upfield by 0.85

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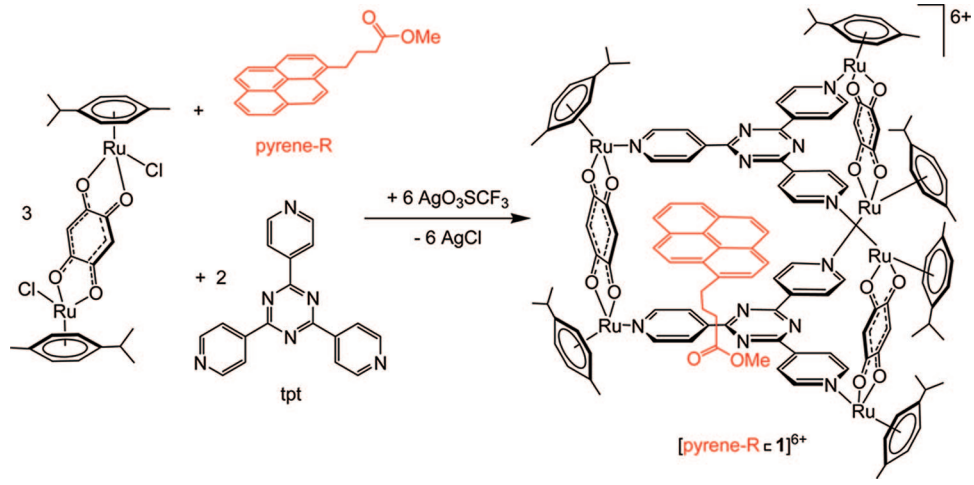
Scheme 3. Synthesis of the Filled Metallo-Prism [pyrene-R⊂1]$^{6+}$



ppm, while its neighboring CH_2 group is shifted by 0.48 ppm. The remaining CH_2 and CH_3 groups show almost no chemical shift due to the proximity of the cage. At room temperature, only the minimal numbers of signals are observed for $[\mathbf{1}]^{6+}$ despite the presence of the standing out dangling arm. However, at low temperature (−50 °C), eight badly resolved signals are observed for the pyridyl protons of the unsymmetrical tpt units, which is in accordance with the symmetry of the encapsulated functionalized pyrenyl derivative.

The encapsulation of pyrene-R in $[\mathbf{1}]^{6+}$ is further confirmed by mass spectrometry. The ESI-MS spectrum of [pyrene-R⊂**1**]$^{6+}$ shows peaks corresponding to [pyrene-R⊂**1** + $(O_3SCF_3)_3]^{3+}$ at *m*/*z* 1067.1 and [pyrene-R⊂**1** + $(O_3SCF_3)_4]^{2+}$ at *m*/*z* 1674.7 (see Figure 9).

In conclusion, we have opened a simple and straightforward access to the preparation of arene ruthenium metallo-prismatic cages able to encapsulate aromatic and functionalized aromatic molecules. They show carceplex properties and therefore can potentially find applications in molecular recognition, in catalysis, or as drug delivery containers.

Experimental Section

General Remarks. All organic solvents were degassed and saturated with nitrogen prior to use. $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(\mu\text{-}Cl)_2Cl_2]$,[12] $[Ru_2(C_6Me_6)_2(\mu\text{-}Cl)_2Cl_2]$,[13] 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt),[14] and methyl 4-(pyren-1-yl)butanoate (pyrene-R)[15] were prepared according to published methods. All other reagents were commercially available and used as received. The ^1H, $^{13}C\{^1H\}$, and ROESY NMR spectra were recorded on a Bruker AMX 400 spectrometer using the residual protonated solvent as internal standard. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer FTIR 1720 X spectrometer. Microanalyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland). The 1-D ROESY (400 MHz, acetone-d_6) spectra were recorded using a 150 ms mixing time with irradiation of the H_g resonances. Electrospray ionization mass spectrometry conditions for all complexes except [pyrene-R⊂**1**][O_3SCF_3]$_6$: Bruker instrument APEX II 9.4-tesra FT-ICR-MS equipped with an Apollo II electrospray ion source, sample conditions 10−50 μmol/L in MeOH at 30 °C, end plate voltage 3500 V, and capillary voltage 4000 V. Electrospray ionization mass spectrometry conditions for [pyrene-R⊂**1**][O_3SCF_3]$_6$: JMS-T100 (JEOL) instrument, sample conditions 10−50 μmol/L in MeOH at 30 °C, needle voltage 2500 V, orifice voltage 45 V, and ring lens voltage 16 V.

Synthesis of $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dhbq)Cl_2]$. A mixture of $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(\mu\text{-}Cl)_2Cl_2]$ (184 mg, 0.3 mmol) and 2,5-dihydroxy-1,4-benzoquinone (42 mg, 0.3 mmol) was suspended in MeOH (30 mL) and stirred for 2 h at room temperature. The blood-red precipitate was filtered, washed with diethyl ether, and dried *in vacuo*. Yield: 165 mg (81%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.82 (s, 2H, H_q), 5.66 (d, 4H, $^3J_{H-H}$ = 6.12 Hz, H_{ar}), 5.41 (d, 4H, H_{ar}), 2.97 (sept, 2H, $^3J_{H-H}$ = 6.72 Hz, CH), 2.32 (s, 6H, CH_3), 1.35 (d, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 184.45, 139.12, 119.46, 102.29, 97.03, 81.55, 79.60, 31.70, 22.87, 19.09. IR (cm^{-1}): 1528(s), 1377(s), 1257(s). Anal. Calcd for $C_{26}H_{30}Cl_2O_4Ru_2$: C, 45.90; H, 4.45. Found: C, 45.72; H, 4.60.

Synthesis of $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dchq)Cl_2]$. This compound is prepared by the same procedure as described above for $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dhbq)Cl_2]$ using $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(\mu\text{-}Cl)_2Cl_2]$ (306 mg, 0.5 mmol) and chloranilic acid (105 mg, 0.5 mmol). Yield: 275 mg (74%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.74 (d, 4H, $^3J_{H-H}$ = 6.20 Hz, H_{ar}), 5.48 (d, 4H, H_{ar}), 2.98 (sept, 2H, $^3J_{H-H}$ = 7.00 Hz, CH), 2.34 (s, 6H, CH_3), 1.36 (d, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 184.72, 137.45, 118.41, 102.36, 98.62, 82.07, 76.44, 31.72, 21.53, 18.59. IR (cm^{-1}): 1639(s), 1496(s), 1370(s). Anal. Calcd for $C_{26}H_{28}O_4Cl_4Ru_2$: C, 41.70; H, 3.77. Found: C, 41.61; H, 3.82.

Synthesis of $[Ru_2(C_6Me_6)_2(dhbq)Cl_2]$. This compound is prepared by the same procedure as described above for $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dhbq)Cl_2]$ using $[(C_6Me_6)Ru(\mu\text{-}Cl)_2Cl_2]$ (200 mg, 0.3 mmol) and 2,5-dihydroxy-1,4-benzoquinone (42 mg, 0.3 mmol). Yield: 170 mg (77%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.90 (s, 2H, H_q), 2.17 (s, 36H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 182.96, 114.62, 105.88, 90.55, 16.24. IR (cm^{-1}): 1638(s), 1617(s), 1551(s), 1532(m), 1374(m), 1255(s), 620(s). Anal. Calcd for $C_{30}H_{38}O_4Cl_2Ru_2$: C, 48.98; H, 5.20. Found: C, 48.77; H, 5.94.

Synthesis of $[Ru_2(C_6Me_6)_2(dchq)Cl_2]$. This compound is prepared by the same procedure as described above for $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dhbq)Cl_2]$ using $[Ru(C_6Me_6)_2(\mu\text{-}Cl)_2Cl_2]$ (200 mg, 0.3 mmol) and chloranilic acid (63 mg, 0.3 mmol). Yield: 185 mg (77%). ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 2.02 (s, 36H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 184.53, 126.27, 107.36, 92.64, 15.18. IR (cm^{-1}): 1638(s), 1617(s), 1499(m), 1363(m), 1111(m), 620(s). Anal. Calcd for $C_{30}H_{36}O_4Cl_4Ru_2$: C, 44.79; H, 4.51. Found: C, 44.89; H, 4.73.

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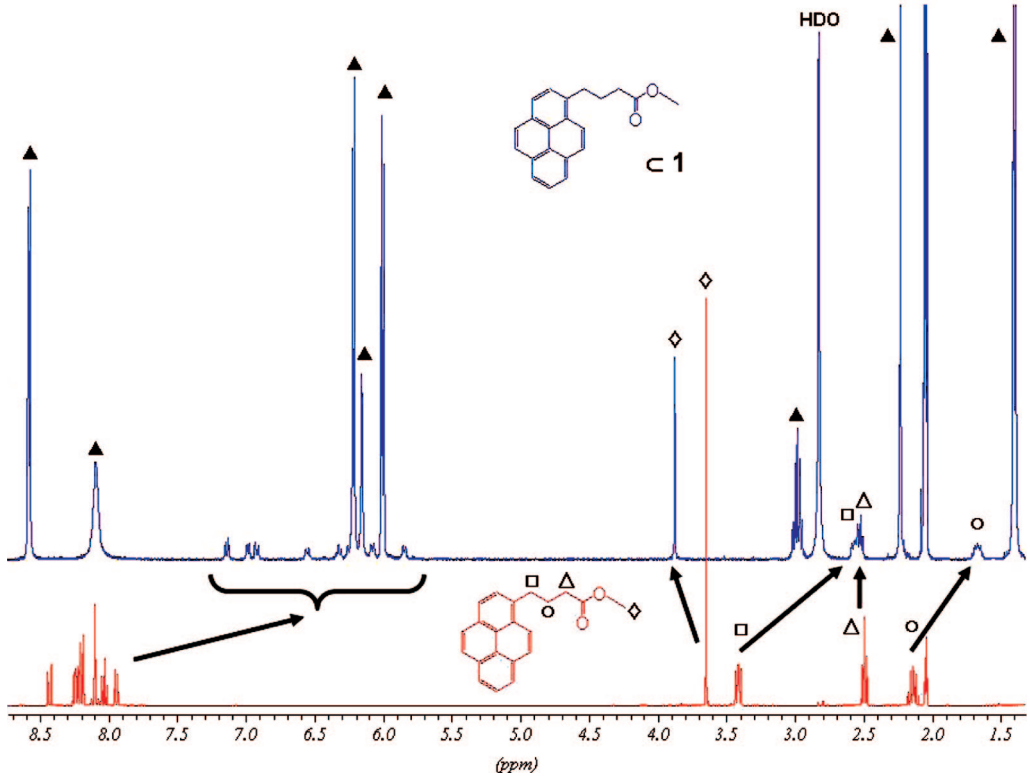

Figure 8. ^{1}H NMR spectra (400 MHz, acetone-d_6) of [pyrene-R⊂**1**]$^{6+}$ and free pyrene-R (▲ = protons of cage [**1**]$^{6+}$).

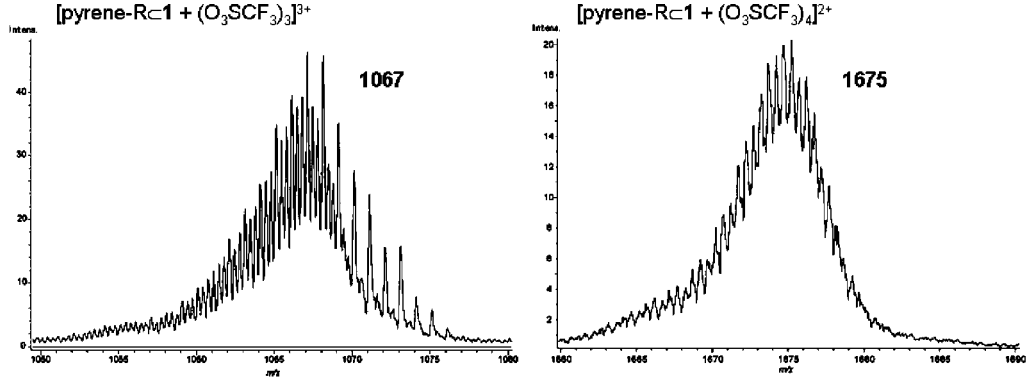

Figure 9. Selected peaks from the ESI-MS spectrum of [pyrene-R⊂**1**][O_3SCF_3]$_6$.

Synthesis of [Ru$_6$(*p*-Pr^{i}C$_6$H$_4$Me)$_6$(tpt)$_2$(dhbq)$_3$][O_3SCF_3]$_6$ ([1][O_3SCF_3]$_6$). A mixture of [Ru$_2$(*p*-Pr^{i}C$_6$H$_4$Me)$_2$(dhbq)Cl$_2$] (60 mg, 0.09 mmol) and AgO_3SCF_3 (46 mg, 0.18 mmol) in MeOH (20 mL) was stirred at room temperature for 2 h, then filtered. To the red filtrate was added tpt (18.4 mg, 0.06 mmol). The mixture was stirred at RT for 48 h, and the solvent removed under vacuum. The dark residue was taken up in CH_2Cl_2 (20 mL), and after filtration, the solution was concentrated (3 mL) and diethyl ether was added to precipitate a red solid. Yield: 75 mg (75%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.75 (dd, 12H, $^3J_{H-H}$ = 5.36 Hz, $^4J_{H-H}$ = 1.56 Hz, H$_\alpha$), 8.68 (dd, 12H, H$_\beta$), 6.24 (d, 12H, $^3J_{H-H}$ = 6.32 Hz, H$_{ar}$), 6.03 (d, 12H, H$_{ar}$), 5.87 (s, 6H, H$_q$), 3.00 (sept, 6H, $^3J_{H-H}$ = 6.92 Hz, CH), 2.28 (s, 18H, CH_3), 1.41 (d, 36H, CH_3). ^{13}C {^{1}H} NMR (100 MHz, acetone-d_6): δ (ppm) 170.04, 154.86, 144.66, 125.15, 123.26, 120.24, 104.42, 102.16, 99.53, 84.19, 82.72, 31.57, 21.98, 17.63. IR (cm^{-1}): 1635(s), 1524(s), 1377(m), 1259(s), 1161(m), 1031(m), 639(s). Anal. Calcd for $C_{120}H_{114}N_{12}O_{30}F_{18}S_6Ru_6$: C, 43.09; H, 3.44; N, 5.02. Found: C, 42.96; H, 3.33; N, 4.86.

Synthesis of [Ru$_6$(*p*-Pr^{i}C$_6$H$_4$Me)$_6$(tpt)$_2$(dchq)$_3$][O_3SCF_3]$_6$ ([2][O_3SCF_3]$_6$). This cage is prepared in the same procedure as described above for [**1**][O_3SCF_3]$_6$ using [Ru$_2$(*p*-Pr^{i}C$_6$H$_4$Me)$_2$(dchq)Cl$_2$] (60 mg, 0.08 mmol), AgO_3SCF_3 (42 mg, 0.164 mmol), and tpt (17 mg, 0.053 mmol). Yield: 65 mg (68%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.72 (dd, 12H, $^3J_{H-H}$ = 5.28 Hz, $^4J_{H-H}$ = 1.56 Hz, H$_\alpha$), 8.62 (dd, 12H, H$_\beta$), 6.29 (d, 12H, $^3J_{H-H}$ = 6.44 Hz, H$_{ar}$), 6.12 (d, 12H, H$_{ar}$), 3.04 (sept, 6H, $^3J_{H-H}$ = 6.84 Hz, CH), 2.36 (s, 18H, CH_3), 1.46 (d, 36H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ (ppm) 178.93, 170.48, 155.06, 145.60, 125.78, 120.56, 107.16, 104.97, 99.88, 84.76, 83.87, 32.22, 22.45, 18.18. IR (cm^{-1}): 1744(s), 1408(s), 1218(s), 1092(s), 1032(s), 904(s), 797(s). Anal. Calcd for $C_{120}H_{108}N_{12}Cl_6O_{30}F_{18}S_6Ru_6$: C, 40.60; H, 3.01; N, 4.73. Found: C, 40.36; H, 3.17; N, 4.52.

Synthesis of [Ru$_6$(C$_6$Me$_6$)$_6$(tpt)$_2$(dhbq)$_3$][O_3SCF_3]$_6$ ([3][O_3SCF_3]$_6$). This cage is prepared in the same procedure as described above for [**1**][O_3SCF_3]$_6$ using [Ru$_2$(C$_6$Me$_6$)$_2$(dhbq)Cl$_2$] (60 mg, 0.081 mmol), AgO_3SCF_3 (43 mg, 0.167 mmol), and tpt (17 mg, 0.054 mmol). Yield: 45 mg (47%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.85 (dd, 12H, $^3J_{H-H}$ = 5.12 Hz, $^4J_{H-H}$ = 1.48 Hz, H$_\alpha$), 8.46 (dd, 12H, H$_\beta$), 5.84 (s, 6H), 2.17 (s, 108H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ (ppm) 183.69, 169.42, 153.69, 144.09, 125.23, 105.31, 101.90, 93.66, 14.65. IR (cm^{-1}): 1748(s),

1388(s), 1221(s), 1092(s), 781(s). Anal. Calcd for $C_{132}H_{138}N_{12}O_{30}F_{18}S_6Ru_6$: C, 45.12; H, 3.96; N, 4.78. Found: C, 45.54; H, 3.76; N, 4.59.

Synthesis of $[Ru_6(C_6Me_6)_6(tpt)_2(dchq)_3][O_3SCF_3]_6$ ([4][O_3SCF_3]$_6$). This cage is prepared in the same procedure as described above for [**1**][O_3SCF_3]$_6$ using $[Ru_2(C_6Me_6)_2(dchq)Cl_2]$ (70 mg, 0.087 mmol), AgO_3SCF_3 (46 mg, 0.178 mmol), and tpt (18 mg, 0.058 mmol). Yield: 85 mg (79%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.89 (dd, 12H, $^3J_{H-H}$ = 6.60 Hz, $^4J_{H-H}$ = 1.44 Hz, H_α), 8.44 (dd, 12H, H_β), 2.20 (s, 108H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ (ppm) 177.41, 169.49, 153.58, 144.40, 125.53, 108.84, 106.14, 94.01, 14.80. IR (cm^{-1}): 1742(s), 1374(s), 1206(s), 1092(s), 849(s). Anal. Calcd for $C_{132}H_{132}N_{12}O_{30}F_{18}S_6Cl_6Ru_6$: C, 42.62; H, 3.58; N, 4.52. Found: C, 42.81; H, 3.25; N, 4.78.

Synthesis of [aromatic⊂1][O_3SCF_3]$_6$. A mixture of $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dhbq)Cl_2]$ (70 mg, 0.1 mmol) and AgO_3SCF_3 (54 mg, 0.2 mmol) in MeOH (20 mL) was stirred at room temperature for 2 h, then filtered. To the red filtrate were added tpt (21 mg, 0.07 mmol) and the aromatic molecule (pyrene 7.6 mg, 0.038 mmol; fluoranthene 7 mg, 0.035 mmol; triphenylene 9.0 mg, 0.037 mmol; benzo[*e*]pyrene 9.5 mg, 0.038 mmol; coronene 12 mg, 0.036 mmol). The mixture was stirred at room temperature for 24 h, and the solvent removed *in vacuo*. The dark residue was taken up in CH_2Cl_2 (20 mL), and after filtration, the solution was concentrated (3 mL) and diethyl ether was added to precipitate a red solid.

[pyrene⊂**1**][O_3SCF_3]$_6$: yield 85 mg (82%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.56 (dd, 12H, $^3J_{H-H}$ = 5.04 Hz, $^4J_{H-H}$ = 1.36 Hz, H_α), 8.04 (dd, 12H H_β), 6.68 (s, 4H, H_g), 6.62 (d, 4H, $^3J_{H-H}$ = 7.44 Hz, H_g), 6.22 (d, 12H, $^3J_{H-H}$ = 6.24 Hz, H_{ar}), 6.20 (d, 2H, H_g), 6.17 (s, 6H, H_q), 6.00 (d, 12H, H_{ar}), 2.99 (sept, 6H, $^3J_{H-H}$ = 7.00 Hz, CH), 2.22 (s, 18H, CH_3), 1.39 (d, 36H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ (ppm) 185.06, 168.55, 144.28, 130.30, 127.87, 126.45, 125.10, 123.42, 104.91, 102.82, 100.16, 84.78, 83.10, 32.07, 22.49, 18.09. IR (cm^{-1}): 1638(s), 1617(s), 1524(s), 1377(m), 1259(s), 1159(m), 1030(m), 636(s). Anal. Calcd for $C_{136}H_{124}N_{12}O_{30}F_{18}S_6Ru_6$: C, 45.63; H, 3.49; N, 4.69. Found: C, 45.93; H, 3.77; N, 4.53.

[fluoranthene⊂**1**][O_3SCF_3]$_6$: yield 85 mg (81%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.54 (dd, 12H, $^3J_{H-H}$ = 5.12 Hz, $^4J_{H-H}$ = 1.48 Hz, H_α), 8.18 (dd, 12H H_β), 6.88 (br, 2H, H_g), 6.67 (d, 2H, $^3J_{H-H}$ = 7.80 Hz, H_g), 6.47 (d, 2H, $^3J_{H-H}$ = 6.60 Hz, H_g), 6.21 (d, 12H, $^3J_{H-H}$ = 6.36 Hz, H_{ar}), 6.11 (s, 6H, H_q), 5.99 (d, 12H, H_{ar}), 5.35 (br, 2H, H_g), 5.23 (br, 2H, H_g), 2.98 (sept, 6H, $^3J_{H-H}$ = 7.08 Hz, CH), 2.22 (s, 18H, CH_3), 1.39 (d, 36H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ (ppm) 184.12, 168.18, 153.75, 143.49, 134.71, 128.30, 126.69, 124.49, 121.49, 120.10, 117.03, 113.18, 104.03, 101.86, 99.27, 83.88, 82.19, 31.18, 21.59, 17.20. IR (cm^{-1}): 1716(s), 1524(m), 1435(m), 1363(s), 1221(s), 1092(m), 1032(m), 850(s). Anal. Calcd for $C_{136}H_{124}N_{12}O_{30}F_{18}S_6Ru_6$: C, 46.05; H, 3.52; N, 4.74. Found: C, 46.21; H, 3.85; N, 4.63.

[triphenylene⊂**1**][O_3SCF_3]$_6$: yield 95 mg (72%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.47 (d, 12H, $^3J_{H-H}$ = 6.08 Hz, H_α), 8.10 (d, 12H, H_β), 7.62 (dd, 6H, $^3J_{H-H}$ = 2.72 Hz, H_g), 6.20 (d, 12H, $^3J_{H-H}$ = 6.24 Hz, H_{ar}), 6.16 (s, 6H, H_q), 5.98 (d, 12H, H_{ar}), 5.35 (dd, 6H, H_g), 2.96 (sept, 6H, $^3J_{H-H}$ = 6.80 Hz, CH), 2.21 (s, 18H, CH_3), 1.38 (d, 36H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ (ppm) 184.64, 168.23, 153.87, 143.49, 128.61, 127.03, 124.98, 123.42, 104.48, 102.37, 99.72, 84.35, 82.65, 31.64, 22.05, 17.66. IR (cm^{-1}): 1638(s), 1617(s), 1524(s), 1377(s), 1259(s), 1162(m), 1031(s), 638(s). Anal. Calcd for $C_{138}H_{126}N_{12}O_{30}F_{18}S_6Ru_6$: C, 45.97; H, 3.52; N, 4.66. Found: C, 45.81; H, 3.88; N, 4.45.

[benzo[*e*]pyrene⊂**1**][O_3SCF_3]$_6$: yield 90 mg (68%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.48 (d, 12H, $^3J_{H-H}$ = 5.20 Hz, H_α), 7.90 (d, 2H, $^3J_{H-H}$ = 8.00 Hz, H_g), 7.88 (d, 12H, H_β), 7.82 (dd, 4H, $^3J_{H-H}$ = 5.96 Hz, H_g), 7.39 (s, 2H, H_g), 6.27 (s, 6H, H_q), 6.20 (d, 12H, $^3J_{H-H}$ = 6.24 Hz, H_{ar}), 5.99 (d, 12H, H_{ar}), 5.75 (dd, 2H, $^3J_{H-H}$ = 7.48 Hz, H_g), 5.50 (dd, 2H, H_g), 2.97 (sept, 6H, $^3J_{H-H}$ = 6.92 Hz, CH), 2.21 (s, 18H, CH_3), 1.40 (d, 36H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ (ppm) 184.25, 167.44, 153.44, 142.68, 128.24, 126.32, 124.19, 122.35, 120.43, 119.73, 118.27, 113.36, 106.71, 104.05, 102.01, 99.22, 83.86, 82.25, 31.18, 21.60, 17.21. IR (cm^{-1}): 1634(s), 1619(s), 1524(s), 1375(s), 1225(m), 1160(m), 1031(s), 638(s). Anal. Calcd for $C_{140}H_{126}N_{12}O_{30}F_{18}S_6Ru_6$: C, 46.74; H, 3.53; N, 4.67. Found: C, 46.72; H, 3.80; N, 4.42.

[coronene⊂**1**][O_3SCF_3]$_6$: yield 95 mg (70%). ^{1}H NMR (200 MHz, acetone-d_6): δ (ppm) 8.48 (dd, 12H, $^3J_{H-H}$ = 5.50 Hz, $^4J_{H-H}$ = 1.48 Hz, H_α), 7.50 (s, 12H, H_g), 7.20 (dd, 12H, H_β), 6.53 (s, 6H, H_q), 6.19 (d, 12H, $^3J_{H-H}$ = 6.60 Hz, H_{ar}), 5.97 (d, 12H, H_{ar}), 3.03 (sept, 6H, $^3J_{H-H}$ = 6.96 Hz, CH), 2.21 (s, 18H, CH_3), 1.40 (d, 36H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ (ppm) 184.49, 166.25, 153.50, 141.80, 127.63, 126.03, 123.54, 120.78, 104.12, 102.27, 99.14, 83.77, 82.40, 31.17, 21.61, 17.21. IR (cm^{-1}): 1638(s), 1617(s), 1522(s), 1377(s), 1259(s), 1225(m), 1161(s), 1030(s), 638(s). Anal. Calcd for $C_{144}H_{126}N_{12}O_{30}F_{18}S_6Ru_6$: C, 51.03; H, 3.74; N, 4.96. Found: C, 51.09; H, 3.83; N, 4.29.

Synthesis of [aromatic⊂2][O_3SCF_3]$_6$. These carceplex systems are prepared in the same procedure as described above for [aromatic⊂**1**][O_3SCF_3]$_6$ using $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dchq)Cl_2]$ (70 mg, 0.09 mmol), AgO_3SCF_3 (49 mg, 0.19 mmol), tpt (20 mg, 0.06 mmol), and the aromatic molecule (fluoranthene 7 mg, 0.03 mmol; triphenylene 8 mg, 0.03 mmol).

[fluoranthene⊂**2**][O_3SCF_3]$_6$: yield 87 mg (75%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.59 (m, 24H, H_α, H_β), 6.81 (m, 2H, H_g), 6.57 (m, 2H, H_g), 6.43 (m, 2H, H_g), 6.30 (d, 8H, $^3J_{H-H}$ = 6.33 Hz, H_{ar}), 6.12 (d, 12H, $^3J_{H-H}$ = 5.49 Hz, H_{ar}), 5.32 (m, 2H, H_g), 5.12 (m, 2H, H_g), 3.05 (sept, 6H, $^3J_{H-H}$ = 6.94 Hz, CH), 2.35 (s, 18H, CH_3), 1.46 (d, 36H, $^3J_{H-H}$ = 6.92 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ (ppm) 177.86, 153.94, 144.26, 135.79, 129.82, 127.48, 127.15, 125.85, 123.95, 122.51, 120.91, 120.75, 120.72, 106.52, 104.40, 99.28, 84.05, 83.08, 31.45, 21.67, 17.41. IR (cm^{-1}): 1618(w), 1574(w), 1500(vs), 1373(s), 1313(w), 1258(s), 1224(m), 1159(m), 1057(w), 1030(s), 867(w), 810(w), 638(s). Anal. Calcd for $C_{140}H_{126}N_{12}O_{30}F_{18}S_6Ru_6$: C, 43.51; H, 3.17; N, 4.48. Found: C, 36.46; H, 3.25; N, 4.49.

[triphenylene⊂**2**][O_3SCF_3]$_6$: yield 80 mg (68%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.47 (d, 12H, $^3J_{H-H}$ = 6.60 Hz, H_α), 8.22 (d, 12H, H_β), 7.63 (dd, 6H, $^3J_{H-H}$ = 6.08 Hz, 3.16 Hz, H_g), 6.31 (d, 12H, $^3J_{H-H}$ = 6.36 Hz, H_{ar}), 6.12 (d, 12H, H_{ar}), 5.14 (dd, 6H, H_g), 3.03 (sept, 6H, $^3J_{H-H}$ = 7.12 Hz, CH), 2.32 (s, 18H, CH_3), 1.46 (d, 36H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ (ppm) 177.65, 167.90, 153.31, 143.35, 128.39, 125.96, 125.04, 123.34, 120.45, 106.68, 104.44, 99.42, 84.14, 83.04, 31.46, 21.55, 17.29. IR (cm^{-1}): 1723(s), 1504(s), 1414(s), 1227(s), 1152(m), 1032(m), 1092(s), 901(s), 829(s). Anal. Calcd for $C_{138}H_{120}N_{12}O_{30}F_{18}S_6Cl_6Ru_6$: C, 43.85; H, 3.20; N, 4.45. Found: C, 43.45; H, 3.61; N, 4.25.

Synthesis of [aromatic⊂3][O_3SCF_3]$_6$. These carceplex systems are prepared in the same procedure as described above for [aromatic⊂**1**][O_3SCF_3]$_6$ using $[Ru_2(C_6Me_6)_2(dhbq)Cl_2]$ (60 mg, 0.08 mmol), AgO_3SCF_3 (43 mg, 0.016 mmol), tpt (17 mg, 0.05 mmol), and the aromatic molecule (fluoranthene 6 mg, 0.03 mmol; triphenylene 6 mg, 0.03 mmol).

[fluoranthene⊂**3**][O_3SCF_3]$_6$: yield 55 mg (51%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.37 (m, 24H, H_α, H_β), 6.85 (dd, 2H, $^3J_{H-H}$ = 3.15, 5.39 Hz, H_g), 6.58 (d, 2H, $^3J_{H-H}$ = 8.10 Hz, H_g), 6.47 (d, 2H, $^3J_{H-H}$ = 6.60 Hz, H_g), 6.04 (s, 6H, H_q), 5.36 (dd, 2H, $^3J_{H-H}$ = 7.51 Hz, H_g), 5.14 (m, 2H, H_g), 2.16 (s, 108H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ (ppm) 184.26, 153.71, 144.06, 138.34, 135.30, 134.51, 127.26, 127.18, 125.62, 123.83, 122.14, 120.67, 120.62,102.55, 94.26, 15.24. IR (cm^{-1}): 1628(w), 1518(vs), 1374(s), 1257(s), 1157(w), 1031(m), 811(w), 638(m). Anal. Calcd for $C_{148}H_{148}Cl_6N_{12}O_{30}F_{18}S_6Ru_6 \cdot 4\ H_2O$: C, 44.44; H, 3.93; N, 4.20. Found: C, 44.47; H, 4.41; N, 4.32.

Table 1. Crystallographic and Selected Experimental Data for [pyrene⊂1][O$_3$SCF$_3$]$_6$ and [benzo[*e*]pyrene⊂1][O$_3$SCF$_3$]$_6$

	[pyrene⊂**1**][O$_3$SCF$_3$]$_6$	[benzo[*e*]pyrene⊂**1**][O$_3$SCF$_3$]$_6$
chemical formula	$C_{136}H_{124}F_{18}N_{12}O_{30}Ru_6S_6$	$C_{140}H_{126}F_{18}N_{12}O_{30}Ru_6S_6$
fw	3547.25	3597.31
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
cryst color and shape	red block	red block
cryst size (mm)	0.17 × 0.14 × 0.13	0.18 × 0.15 × 0.14
a (Å)	18.782(1)	19.109(1)
b (Å)	19.3610(9)	18.771(1)
c (Å)	26.714(1)	26.8471(16)
α (deg)	74.084(4)	85.978(5)
β (deg)	85.777(4)	73.075(4)
γ (deg)	62.672(3)	63.455(4)
V (Å^3)	8283.6(7)	8221.6(8)
Z	2	2
T (K)	173(2)	173(2)
D_c (g·cm^{-3})	1.422	1.453
μ (mm^{-1})	0.696	0.702
scan range (deg)	2.44 < 2θ < 51.42	2.44 < 2θ < 51.44
no. of unique reflns	31 211	30 936
no. of reflns used [$I > 2\sigma(I)$]	17 640	15 477
R_{int}	0.0744	0.0706
final *R* indices [$I > 2\sigma(I)$][a]	0.1279, wR_2 0.3357	0.0844, wR_2 0.2237
R indices (all data)	0.1747, wR_2 0.3672	0.1384, wR_2 0.2455
goodness-of-fit	1.203	0.917
max., min. $\Delta\rho$/e (Å^{-3})	4.873, −4.426	2.728, −1.853

[a] Structures were refined on F_o^2: $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

[triphenylene⊂**3**][O$_3$SCF$_3$]$_6$: yield 50 mg (49%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.30 (dd, 12H, $^3J_{H-H}$ = 5.08 Hz, H$_\alpha$), 8.20 (dd, 12H, H$_\beta$), 7.59 (dd, 6H, $^3J_{H-H}$ = 4.68 Hz, H$_g$), 6.14 (s, 6H, H$_q$), 5.32 (dd, 6H, H$_g$), 2.15 (s, 108H, CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ (ppm) 184.61, 169.23, 153.54, 144.52, 128.41, 126.35, 125.85, 123.22, 108.62, 103.46, 94.56, 15.54. IR (cm^{-1}): 1759(s), 1523(m), 1448(s), 1224(s), 1032(m), 904(s). Anal. Calcd for $C_{150}H_{150}N_{12}O_{30}F_{18}S_6Ru_6$: C, 48.15; H, 4.05; N, 4.49. Found: C, 48.36; H, 4.06; N, 4.09.

Synthesis of [aromatic⊂4][O$_3$SCF$_3$]$_6$. These carceplex systems are prepared in the same procedure as described above for [aromatic⊂**1**][O$_3$SCF$_3$]$_6$ using [Ru$_2$(C$_6$Me$_6$)$_2$(dchq)Cl$_2$] (60 mg, 0.07 mmol), Ag(O$_3$SCF$_3$) (39 mg, 0.015 mmol), tpt (16 mg, 0.05 mmol), and aromatic molecules (fluoranthene 6 mg, 0.03 mmol; triphenylene 6 mg, 0.03 mmol).

[fluoranthene⊂**4**][O$_3$SCF$_3$]$_6$: yield 77 mg (77%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.36 (m, 24H, H$_\alpha$, H$_\beta$), 6.86 (m, 2H, H$_g$), 6.50 (m, 4H, H$_g$), 5.38 (m, 2H, H$_g$), 5.08 (m, 2H, H$_g$), 2.20 (s, 108H, CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ (ppm) 178.10, 169.02, 153.82, 144.58, 127.34, 127.15, 126.37, 124.18, 122.71, 121.05, 120.97, 107.33, 95.12, 15.77. IR (cm^{-1}): 1623(br), 1574(w), 1500(vs), 1372(s), 1263(s), 1152(m), 1031(s), 866(w), 811(w), 637(m). Anal. Calcd for $C_{148}H_{142}Cl_6N_{12}O_{30}F_{18}S_6Ru_6$: C, 45.32; H, 3.65; N, 4.29. Found: C, 37.93; H, 3.45; N, 3.64.

[triphenylene⊂**4**][O$_3$SCF$_3$]$_6$: yield 55 mg (56%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.33 (dd, 12H, $^3J_{H-H}$ = 5.00 Hz, H$_\alpha$), 8.27 (dd, 12H, H$_\beta$), 7.58 (dd, 6H, $^3J_{H-H}$ = 6.12 Hz, H$_g$), 5.12 (dd, 6H, H$_g$), 2.19 (s, 108H, CH$_3$). ^{13}C {^{1}H} NMR (100 MHz, acetone-d_6): δ (ppm) 177.13, 167.59, 163.71, 152.41, 143.16, 126.01, 125.51, 123.15, 110.85, 106.40, 94.13, 14.77. IR (cm^{-1}): 1709(s), 1411(m), 1217(s), 1093(s), 1032(m), 906(s), 787(s). Anal. Calcd for $C_{150}H_{144}N_{12}O_{30}F_{18}S_6Cl_6Ru_6$: C, 45.63; H, 3.68; N, 4.26. Found: C, 45.32; H, 3.76; N, 4.21.

Synthesis of [pyrene-R⊂1][O$_3$SCF$_3$]$_6$. A mixture of [Ru$_2$(*p*-Pr^{i}C$_6$H$_4$Me)$_2$(dhbq)Cl$_2$] (50 mg, 0.074 mmol) and AgO$_3$SCF$_3$ (40 mg, 0.155 mmol) in MeOH (25 mL) was stirred at room temperature for 2 h, then filtered. To the red filtrate were added tpt (15.4 mg, 0.05 mmol) and methyl 4-(pyren-1-yl)butanoate (pyrene-R) (10 mg, 0.033 mmol). The mixture was stirred at 45 °C for 24 h, and the solvent removed *in vacuo*. The dark residue was taken up in CH_2Cl_2 (20 mL), and after filtration, the solution was concentrated (3 mL) and diethyl ether was added to precipitate a red solid. Yield: 64 mg (72%). ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.58 (d, 12H, $^3J_{H-H}$ = 6.54, H$_\alpha$), 8.10 (br, 12H, H$_\beta$), 7.14 (d, 1H, $^3J_{H-H}$ = 9.11 Hz, H$_g$) 6.98 (d, 1H, $^3J_{H-H}$ = 7.42 Hz, H$_g$), 6.92 (d, 1H, $^3J_{H-H}$ = 8.88 Hz, H$_g$), 6.33 (dd, 1H, $^3J_{H-H}$ = 7.41 Hz, H$_g$), 6.26 (br, 1H, H$_g$), 6.22 (d, 12H, $^3J_{H-H}$ = 6.31 Hz, H$_{ar}$), 6.19 (m, 1H, H$_g$) 6.16 (s, 6H, H$_q$), 6.08 (d, 1H, $^3J_{H-H}$ = 7.56 Hz, H$_g$), 6.00 (d, 12H, $^3J_{H-H}$ = 6.31 Hz, H$_{ar}$), 5.85 (d, 1H, $^3J_{H-H}$ =7.53 Hz, H$_g$), 3.8 (s, 3H, O-CH$_3$), 2.98 (sept, 6H, $^3J_{H-H}$ = 6.94 Hz, CH), 2.54 (m, 4H, C**H$_2$**CH$_2$C**H$_2$**), 2.23 (s, 18H, CH$_3$), 1.67 (m, 2H, CH$_2$C**H$_2$**CH$_2$), 1.40 (d, 36H, $^3J_{H-H}$ = 6.94 Hz, CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ (ppm) 185.19, 183.10, 168.83, 154.89, 144.39, 128.55, 127.87, 127.39, 126.73, 126.47, 125.89, 125.54, 125.25, 125.16, 124.11, 123.60, 123.18, 123.13, 120.91, 105.06, 102.93, 84.83, 83.30, 52.27, 34.26, 32.19, 26.89, 22.60, 18.22. IR (cm^{-1}): 1731(w), 1523(vs), 1376(s), 1258(s), 1159(w), 1057(w), 1030(m), 811(w), 638(m). Anal. Calcd for $C_{141}H_{132}N_{12}O_{32}F_{18}S_6Ru_6$: C, 46.43; H, 3.65; N, 4.61. Found: C, 46.11; H, 3.93; N, 4.23.

X-ray Crystallographic Study. Crystals of [pyrene⊂**1**][O$_3$SCF$_3$]$_6$and [benzo[*e*]pyrene⊂**1**][O$_3$SCF$_3$]$_6$ were mounted on a Stoe Mark II image plate diffraction system, using Mo Kα graphite-monochromated radiation, image plate distance 135 mm, 2θ range 2.4−51.3°, $D_{max}-D_{min}$ = 16.029−0.836 Å. The structures were solved by direct methods using the program SHELXS-97.[16] Refinement and all further calculations were carried out using SHELXL-97.[17] The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. Examination of the structures with PLATON[18] have revealed voids corresponding to acetone solvent molecules. Therefore, new data sets corresponding to omission of the missing solvent for both structures were generated with the SQUEEZE algorithm,[19] and the structures were refined to convergence. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. In [pyrene⊂**1**][O$_3$SCF$_3$]$_6$, the encapsulated pyrene molecule was found disordered over several positions, and therefore, multiple

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constraints where applied to generate an acceptable model, thus giving rise to a relatively high *R* factor. Crystallographic details are summarized in Table 1. Figures 5 and 6 (ORTEP[20] drawing) show selected labeling scheme for [pyrene⊂**1**][O_3SCF_3]$_6$ and [benzo[*e*]-pyrene⊂**1**][O_3SCF_3]$_6$. Figure 7 is drawn with the Accelrys DS Visualizer v1.7 software.

CCDC-685450 ([pyrene⊂**1**][O_3SCF_3]$_6$) and CCDC-662926 ([benzo[*e*]pyrene⊂**1**][O_3SCF_3]$_6$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (internat.) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk].

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Supporting Information Available: CIF files giving the X-ray crystal data, atomic coordinates, bond lengths, angles, and thermal displacement parameters for the compounds [pyrene⊂**1**][O_3SCF_3]$_6$ and [benzo[*e*]pyrene⊂**1**][O_3SCF_3]$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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