Host–Guest Chemistry in the Hexanuclear (Arene)ruthenium Metalla-Prismatic Cage [Ru$_6$(*p*-cymene)$_6$(tpt)$_2$(dhnq)$_3$]$^{6+}$

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A large cationic triangular metalla-prism, [Ru$_6$(*p*-cymene)$_6$-(tpt)$_2$(dhnq)$_3$]$^{6+}$ ([**1**]$^{6+}$), incorporating (*p*-cymene)ruthenium building blocks, bridged by 5,8-dihydroxy-1,4-naphthoquinonato (dhnq) ligands, and connected by two 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt) subunits, allows encapsulation of various guest molecules. This cationic cage, isolated as its triflate salt, possesses a portal size smaller than its cavity, thus allowing both, permanent and temporary encapsulation of guest molecules. The host–guest properties of [**1**]$^{6+}$ have been studied in solution in the presence of planar molecules [phenanthrene, pyrene, (pyren-1-ylmethyl)amine, Pt(acac)$_2$, triphenylene]. The stability constant of association (K_a) was estimated by NMR spectroscopy for the following host–guest systems: [pyrene⊂**1**]$^{6+}$, [phenanthrene⊂**1**]$^{6+}$ and [(pyren-1-ylmethyl)amine⊂**1**]$^{6+}$. All K_a values were found to be larger than 2.4×10^4 M^{-1} for these host–guest systems ([D$_3$]acetonitrile, 21 °C). The other two synthesised complexes, [Pt(acac)$_2$⊂**1**]$^{6+}$ and [triphenylene⊂**1**]$^{6+}$, were shown to act as carceplexes only.

Introduction

In large three-dimensional assemblies, a cavity capable of accommodating guest molecules does not guarantee host–guest chemistry; access to the cavity is, however, essential for the host–guest process to take place. Therefore, in order to generate an efficient host–guest system, sufficient cavity size and portal size of the host are equally important, unless the cage possesses the ability to assemble–disassemble at will in solution. In recent years, coordination-driven self-assembly has been extensively employed to generate discrete three-dimensional structures in which guest molecules have been encapsulated. This approach, pioneered by the groups of Fujita[1] and Stang,[2] and employed by others,[3] has produced many examples showing host–guest properties. Last year we showed that the hexacationic metalla-prism [Ru$_6$(*p*-cymene)$_6$(tpt)$_2$(dhbq)$_3$]$^{6+}$ [tpt = 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine; dhbq = 2,5-dihydroxybenzoquinonato] possesses a cavity ($7.8 \times 11.7 \times 11.7$ Å^3) large enough to permanently encapsulate square-planar complexes[4] and aromatic molecules.[5]

In these structurally nonlabile systems the portal size was too small or too rigid to let the encapsulated compound escape. Moreover, all attempts at introducing a guest into the empty cavity of [Ru$_6$(*p*-cymene)$_6$(tpt)$_2$(dhbq)$_3$]$^{6+}$ failed, and therefore no host–guest properties were observed with these hexacationic metalla-prismatic cages. They seem to act only as carceplex systems.[4,5]
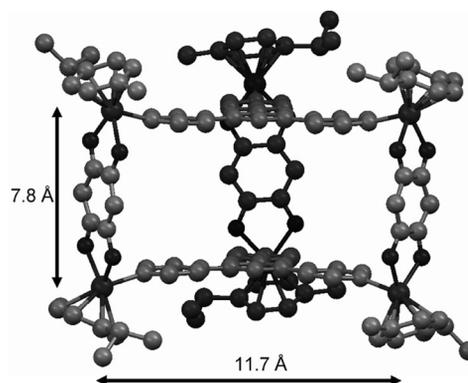
Herein we report the synthesis and characterisation of a slightly more spacious cationic hexanuclear metalla-prism [Ru$_6$(*p*-cymene)$_6$(tpt)$_2$(dhnq)$_3$]$^{6+}$ ([**1**]$^{6+}$), which incorporates the same (*p*-cymene)ruthenium building blocks connected by two tpt subunits, however with 5,8-dihydroxy-1,4-naphthoquinonato (dhnq) as bridging ligands, see Scheme 1. This new metalla-prism with a slightly larger portal size as compared to [Ru$_6$(*p*-cymene)$_6$(tpt)$_2$(dhbq)$_3$]$^{6+}$ possesses the ability to permanently encapsulate large planar molecules as well as to allow host–guest chemistry to take place with small aromatic molecules.

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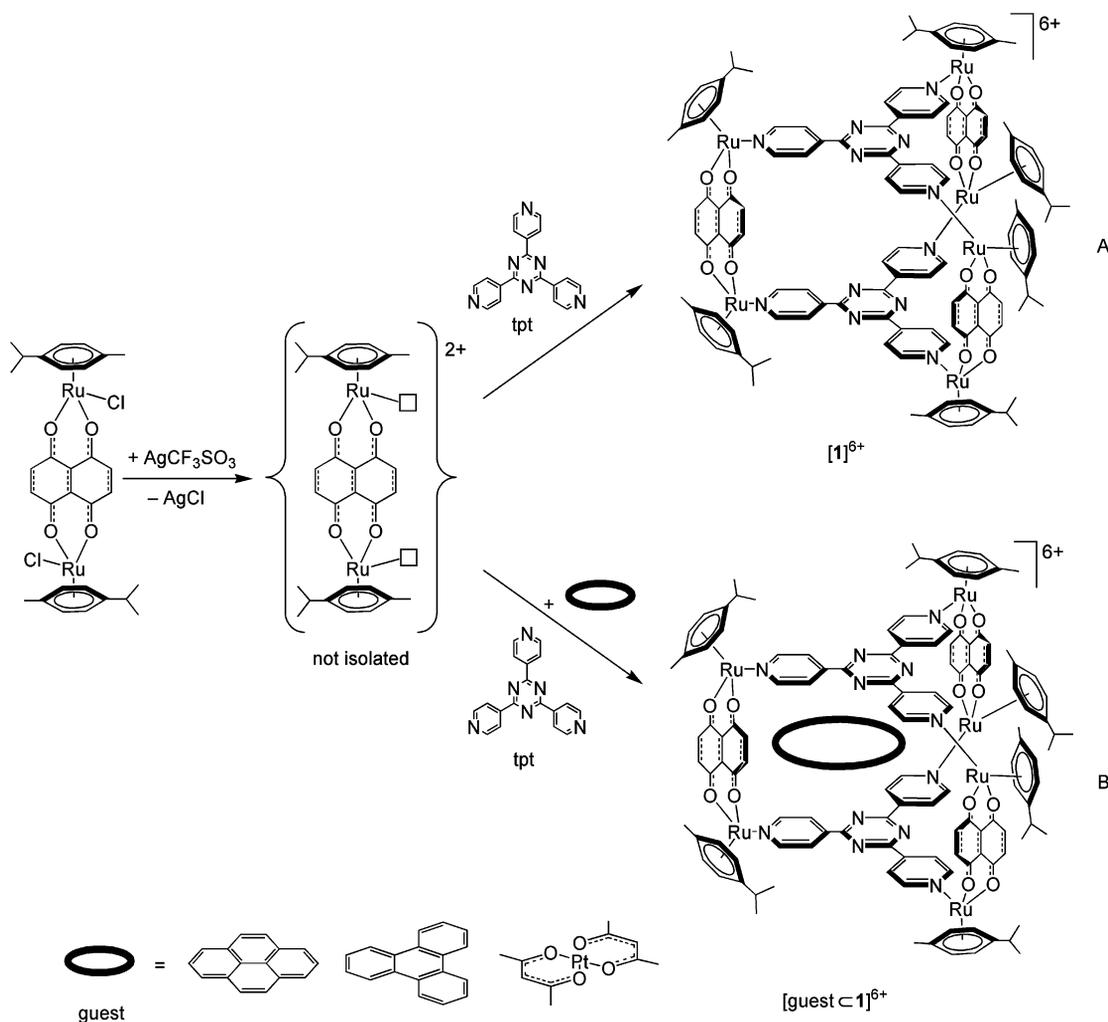
Scheme 1. Synthesis of [1][CF₃SO₃]₆ (route A) and [guest⊂1][CF₃SO₃]₆ (route B).

Results and Discussion

The hexanuclear cation $[Ru_6(p\text{-cymene})_6(tpt)_2(dhnq)_3]^{6+}$ ($[1]^{6+}$) was prepared according to a two-step strategy in which the new dinuclear complex $[Ru_2(p\text{-cymene})_2(dhnq)\text{-}Cl_2]$ was used as a metal clip (Scheme 1, route A). The coordinatively unsaturated intermediate formed upon addition of $AgCF_3SO_3$ (not isolated) allows the $Ru_2(p\text{-cymene})_2\text{-}(dhnq)^{2+}$ units to adopt a *syn* geometry upon coordination to the pyridyl groups of the tpt panels. The resulting hexacationic complex was isolated in good yield (ca. 80%) and characterised as its triflate salt ($[1][CF_3SO_3]_6$). The cavity of $[1]^{6+}$ is estimated by molecular modelling to be approximately $8.4 \times 11.7 \times 11.7$ Å, whereas the portal size is expected to be ca. 8.4×7.7 Å.

The assembly of $[1]^{6+}$ can also be achieved in the presence of only 1 equiv. of various planar molecules such as $Pt(acac)_2$ (acac = acetylacetonato), triphenylene or pyrene to give the guest-encapsulated systems ($[guest⊂1]^{6+}$) without affecting the overall yield (Scheme 1, route B). These complexes were as well isolated as triflate salts and characterised on the basis of elemental analysis, ^1H NMR, IR and

UV/Vis spectroscopy. Their infrared spectra are dominated by absorptions of the coordinated tpt and dhnq ligands, which are only slightly shifted as compared to the free ligands. In addition to these signals, strong absorptions attributed to the triflate anions are observed in the infrared spectra. The UV/Vis spectra of $[1][CF_3SO_3]_6$ and $[guest⊂1][CF_3SO_3]_6$ in acetone (see Supporting Information) show intense high-energy bands at 310 nm assigned to the interligand π-stacking interactions[6] and broad low-energy bands at 440 nm associated to metal-to-ligand charge transfer (MLCT) transition.[7]

The formation of $[1]^{6+}$ and $[guest⊂1]^{6+}$ can be easily monitored by NMR spectroscopy, and their molecular structures were established by one-dimensional ^1H ROESY experiments. The signals of the different protons of the guest molecule as well as those of the pyridyl protons of the tpt panels are shifted upfield upon formation of the host–guest system, whereas the signals of the C*H* protons of the dhnq bridging ligands are shifted downfield. On the other hand, the signals of the protons of the *p*-cymene ligands located at the periphery of the prism are not significantly affected by the presence of a guest molecule in the

cavity of $[\mathbf{1}]^{6+}$. In the ^{1}H NMR spectrum of [Pt-(acac)$_2$⊂$\mathbf{1}$]$^{6+}$ the CH and CH_3 signals of the acetylacetato ligands are shifted upfield by about 1.7 ppm relative to those of the free complex in CD$_3$CN, whereas in the ^{195}Pt NMR spectrum the platinum signal is shifted downfield (δ = –392.6 ppm) by approximately 33 ppm upon encapsulation {δ[Pt(acac)$_2$] = –425.8 ppm in CD$_3$CN at 21 °C}. In the ^{1}H NMR spectra of [pyrene⊂$\mathbf{1}$]$^{6+}$ and [triphenylene-⊂$\mathbf{1}$]$^{6+}$ the signals of the CH protons of the encapsulated aromatic compounds are all shifted upfield relative to those of the free molecule in CD$_3$CN, the chemical shifts being similar to those observed in [pyrene⊂Ru$_6$(p-cymene)$_6$(tpt)$_2$-(dhbq)$_3$]$^{6+}$ and [triphenylene⊂Ru$_6$(p-cymene)$_6$(tpt)$_2$-(dhbq)$_3$]$^{6+}$.[5] One-dimensional ^{1}H ROESY experiments confirm the molecular structure of these cationic [guest-⊂$\mathbf{1}$]$^{6+}$ systems. For example, in [triphenylene⊂$\mathbf{1}$]$^{6+}$, intense cross-peaks are observed between the protons of the encapsulated aromatic compound (H$_g$ and H$_{g'}$) and the protons of the cationic cage (H$_\alpha$, H$_\beta$, H$_{cym}$ and H$_q$) in close proximity (Figure 1).

These [guest⊂$\mathbf{1}$]$^{6+}$ complexes were evaluated as potential host–guest systems. We first studied the stability of all systems in solution (water, toluene, acetonitrile) at room and elevated temperatures. Both complexes, [Pt(acac)$_2$⊂$\mathbf{1}$]$^{6+}$ and [triphenylene⊂$\mathbf{1}$]$^{6+}$, show no degradation of the cage or leaching of the guest in all solvents tested, even at reflux for 24 h. However, [pyrene⊂$\mathbf{1}$]$^{6+}$ shows rapid loss of its guest in [D$_8$]toluene at 80 °C, while this system remains intact in acetonitrile and water. Therefore, we decided to further study the host–guest chemistry of the metalla-prism $[\mathbf{1}]^{6+}$ in solution.
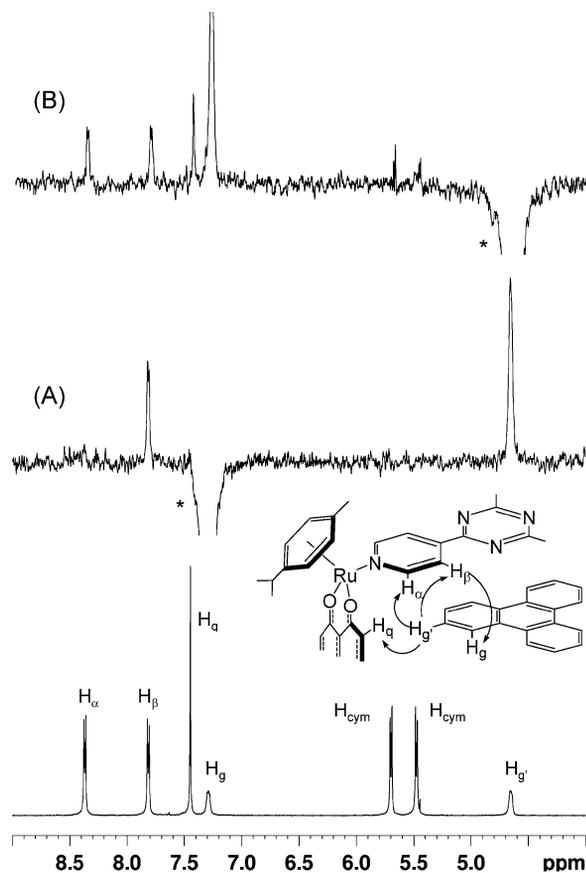
Figure 1. One-dimensional ^{1}H ROESY spectra (400 MHz, CD$_3$CN, 21 °C) of [triphenylene⊂$\mathbf{1}$]$^{6+}$ focusing on the triphenylene protons H$_g$ (A) and H$_{g'}$ (B).
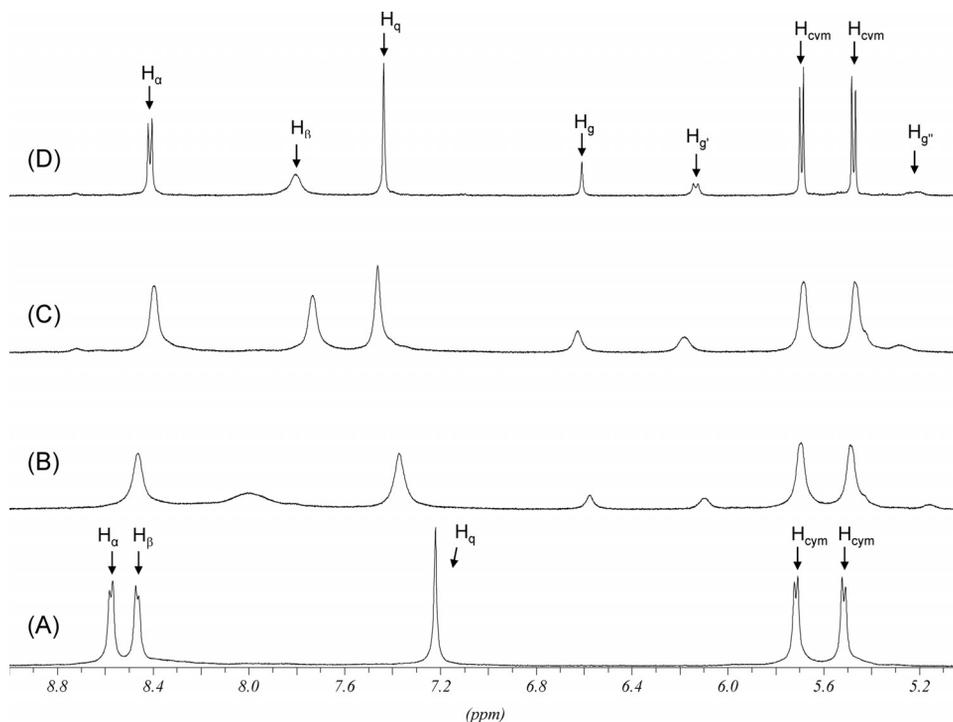
Figure 2. ^{1}H NMR titration of pyrene in a CD$_3$CN solution of [$\mathbf{1}$][CF$_3$SO$_3$]$_6$ at 21 °C, (A) $[\mathbf{1}]^{6+}$ (4.0 mM), (B) $[\mathbf{1}]^{6+}$ + 0.5 equiv. of pyrene, (C) $[\mathbf{1}]^{6+}$ + 1.0 equiv. of pyrene and (D) [pyrene⊂$\mathbf{1}$]$^{6+}$.

Figure 3. ^{1}H NMR chemical shift changes for the H$_\beta$ proton of the tpt ligands vs. the molar ratio of pyrene/[**1**]$^{6+}$ in CD$_3$CN at 21 °C.

The study of the host–guest properties of [**1**][CF$_3$SO$_3$]$_6$ was carried out in acetonitrile solution by using NMR spectroscopy. Upon gradual addition of pyrene (0.1–3.0 equiv.) to a CD$_3$CN solution of [**1**][CF$_3$SO$_3$]$_6$ (4.0 mM), the ^{1}H NMR spectra show displacement of the chemical shifts of the signa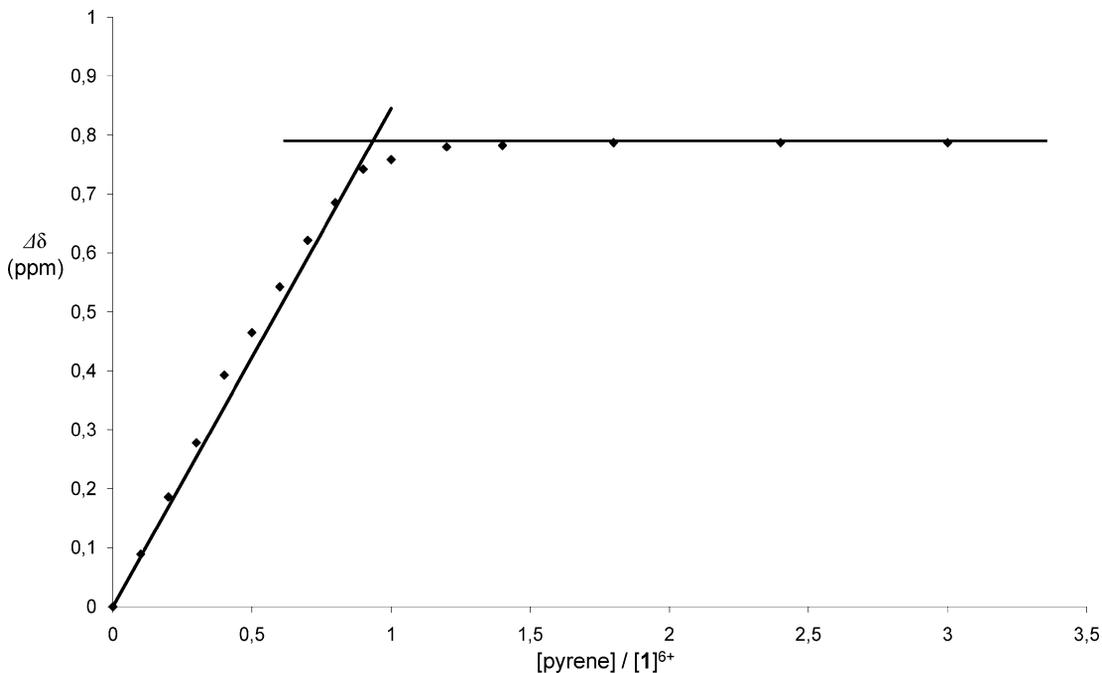ls for some protons of the host and of the guest. Parts of the ^{1}H NMR spectra obtained from the titration experiments with pyrene at 21 °C in [D$_3$]acetonitrile are shown in Figure 2. The broadening and chemical shift of the signals clearly support a rapid inclusion of pyrene in the hydrophobic cavity of [**1**]$^{6+}$. Moreover, after addition of exactly 1 equiv. of pyrene, all chemical shifts of the cage and of the pyrene molecule are identical to those found in the isolated host–guest system [pyrene⊂**1**]$^{6+}$ (Scheme 1, route B).

A plot of these chemical shift changes ($\Delta\delta$) for the H$_\beta$ proton of the tpt ligands vs. the molar ratio of pyrene/cage [**1**]$^{6+}$ (Figure 3) indicates the stoichiometry of host–guest formation, and from this plot the stability constants of association can be estimated (Table 1). The plot shows unambiguously the formation of a 1:1 host–guest system for which an association constant of $4.6 \pm 0.6 \times 10^4$ M^{-1} was calculated by the general expression of K_a.[8] Similarly, by assuming a 1:1 system and using the $\Delta\delta$ value at known guest/host molar ratio with help of the nonlinear least-square fitting program winEQNMR2,[9] an association constant of $4.0 \pm 1.7 \times 10^4$ M^{-1} was found. Both methods give – within experimental errors – the same association constant. The binding free energies ($\Delta G°$) for the [guest⊂**1**]$^{6+}$ systems are determined from the corresponding association constants obtained at 21 °C in [D$_3$]acetonitrile. In all cases a $\Delta G°$ value of approximately –6.2 kcal mol^{-1} is observed.

The host–guest properties of [**1**][CF$_3$SO$_3$]$_6$ were further studied with two more guest molecules, phenanthrene and

Table 1. Association constants and free energies for the encapsulation of pyrene, phenanthrene and (pyren-1-ylmethyl)amine in [**1**]$^{6+}$ (CD$_3$CN at 21 °C, 4.0 mM concentration of [**1**]$^{6+}$).

Guest	K_a [10^4 M^{-1}]	$\Delta G°$ [kcal mol^{-1}]
Pyrene[a]	4.6 ± 0.6	-6.35 ± 0.08
Pyrene[b]	4.0 ± 1.7	-6.28 ± 0.33
Phenanthrene[a]	2.4 ± 0.5	-5.96 ± 0.07
Phenanthrene[b]	2.9 ± 1.1	-6.08 ± 0.20
(Pyren-1-ylmethyl)amine[a]	4.1 ± 0.2	-6.29 ± 0.02
(Pyren-1-ylmethyl)amine[b]	4.1 ± 1.6	-6.29 ± 0.30

[a] Determined by the general expression of K_a.[8] [b] Determined by a computational method using winEQNMR2.[9]

(pyren-1-ylmethyl)amine hydrochloride. Titration experiments ([D$_3$]acetonitrile, 21 °C) for these aromatic molecules in the presence of [**1**]$^{6+}$ (4.0 mM) gave similar association constants and free energy changes (Table 1). The data support the formation of a 1:1 host–guest system in which the pyrenyl moiety of (pyren-1-ylmethyl)amine as well as the phenanthrene molecule are strongly encapsulated between the two tpt units of the metalla-prism. The association constant for the encapsulation of phenanthrene within the cavity of [**1**]$^{6+}$ is slightly smaller than those found for [pyrene⊂**1**]$^{6+}$ and [(pyren-1-ylmethyl)amine⊂**1**]$^{6+}$. This decrease of the association constant is consistent with a diminution of the aromatic surface of the guest molecule, thus reducing the ability to form π–π interactions between phenanthrene and the tpt panels as compared to pyrene.

Conclusions

We have described a new cationic metalla-prism, which possesses a portal size large enough to allow small planar aromatic molecules to enter and exit the hydrophobic cavity

of the cage, thus giving rise to host–guest chemistry in solution. However, for planar molecules capable of fitting into the cavity, but that are too large to pass through the portal of the cage, permanent encapsulation was observed, thus giving rise to stable carceplex systems.

Experimental Section

General: 2,4,6-Tris(4-pyridyl)-1,3,5-triazine (tpt)[10] and [Ru(*p*-cymene)Cl$_2$]$_2$[11] were prepared according to published methods. All other reagents were commercially available (Sigma–Aldrich) and used as received. The ^{1}H, ^{13}C{^{1}H} and ^{1}H ROESY NMR spectra were recorded with a Bruker AMX 400 spectrometer by using the residual protonated solvent as internal standard. Infrared spectra were recorded as KBr pellets with a Perkin–Elmer FTIR 1720 X spectrometer. UV/Vis absorption spectra were recorded with an Uvikon 930 spectrophotometer by using precision cells made of quartz (1 cm). Elemental analyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland).

[Ru$_2$(*p*-cymene)$_2$(dhnq)Cl$_2$]: A mixture of [Ru(*p*-cymene)Cl$_2$]$_2$ (145.0 mg, 0.23 mmol), CH$_3$COONa (38.4 mg, 0.46 mmol) and 5,8-dihydroxy-1,4-naphthoquinone (44.5 mg, 0.23 mmol) in ethanol (25 mL) was stirred at reflux for 24 h. Then the dark precipitate was filtered off, washed with ethanol, water, acetone, diethyl ether and pentane and dried under vacuum to afford a green solid. Yield 154 mg (92%). UV/Vis [1.0×10^{-5} M, (CH$_3$)$_2$CO]: λ_{max} (ε) = 354 (0.17×10^5), 439 (0.15×10^5), 483 (0.13×10^5), 520 (0.13×10^5), 562 (0.11×10^5), 719 (0.08×10^5 M^{-1} cm^{-1}) nm. IR (KBr): ṽ = 3071 (w, CH$_{aryl}$), 1535 (s, C=O), 1268 (s, CH$_3$) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.98 (s, 4 H, H$_q$), 5.50 (d, $^3J_{H,H}$ = 6.7 Hz, 4 H, H$_{cym}$), 5.23 (d, $^3J_{H,H}$ = 6.7 Hz, 4 H, H$_{cym}$), 2.87 [sept, $^3J_{H,H}$ = 5.9 Hz, 2 H, CH(CH$_3$)$_2$], 2.16 (s, 6 H, CH$_3$), 1.58 [d, $^3J_{H,H}$ = 5.9 Hz, 12 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 170.9 (*CO*), 137.0 (*CH*$_q$), 111.9 (*C*$_q$), 100.3 (*C*$_{cym}$), 98.0 (*C*$_{cym}$), 82.8 (*CH*$_{cym}$), 79.6 (*CH*$_{cym}$), 30.7 [*CH*(CH$_3$)$_2$], 22.4 [CH(*CH$_3$*)$_2$], 17.9 (*CH$_3$*) ppm. C$_{30}$H$_{32}$Cl$_2$O$_4$Ru$_2$ (729.6): calcd. C 49.38, H 4.42; found C 49.39, H 4.37.

[1][CF$_3$SO$_3$]$_6$: A mixture of Ag(CF$_3$SO$_3$) (72 mg, 0.28 mmol) and [Ru$_2$(*p*-cymene)$_2$(dhnq)Cl$_2$] (100 mg, 0.14 mmol) in CH$_2$Cl$_2$ (30 mL) was stirred at room temperature for 3 h, then filtered. To the green filtrate, tpt (29 mg, 0.09 mmol) was added. The solution was refluxed for 15 h, and then the solvent was removed. The residue was dissolved in CH$_2$Cl$_2$ (3 mL), and diethyl ether was slowly added to precipitate the green solid, which was filtered and dried under vacuum. Yield 130 mg (80%). UV/Vis [1.0×10^{-5} M, (CH$_3$)$_2$-CO]: λ_{max} (ε) = 308 (3.93×10^5), 437 (0.53×10^5), 643 (0.18×10^5), 700 (0.19×10^5 M^{-1} cm^{-1}) nm. IR (KBr): ṽ = 3064 (w, CH$_{aryl}$), 1536 (s, C=O), 1259 (s, CF$_3$) cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 8.58 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, H$_\alpha$), 8.47 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, H$_\beta$), 7.22 (s, 12 H, H$_q$), 5.73 (d, $^3J_{H,H}$ = 5.9 Hz, 12 H, H$_{cym}$), 5.52 (d, $^3J_{H,H}$ = 5.9 Hz, 12 H, H$_{cym}$), 2.85 [sept, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH(CH$_3$)$_2$], 2.10 (s, 18 H, CH$_3$), 1.33 [d, $^3J_{H,H}$ = 7.2 Hz, 36 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ = 171.8 (*CO*), 170.7 (*C*$_{tpt}$), 154.3 (*CH*$_\alpha$), 145.2 (*C*$_{tpt}$), 138.4 (*CH*$_q$), 125.0 (*CH*$_\beta$), 112.5 (*C*$_q$), 104.9 (*C*$_{cym}$), 100.5 (*C*$_{cym}$), 85.2 (*CH*$_{cym}$), 84.2 (*CH*$_{cym}$), 31.5 [*CH*(CH$_3$)$_2$], 23.1 [CH(*CH$_3$*)$_2$], 22.3 [CH(*CH$_3$*)$_2$], 17.3 (*CH$_3$*) ppm. C$_{132}$H$_{120}$F$_{18}$N$_{12}$O$_{30}$Ru$_6$S$_6$ (3495.2): calcd. C 45.32, H 3.43, N 4.81; found C 45.10, H 3.44, N 4.65.

[pyrene⊂1][CF$_3$SO$_3$]$_6$: A mixture of Ag(CF$_3$SO$_3$) (72 mg, 0.28 mmol) and [Ru$_2$(*p*-cymene)$_2$(dhnq)Cl$_2$] (100 mg, 0.14 mmol) in CH$_2$Cl$_2$ (30 mL) was stirred at room temperature for 3 h, then filtered. To the green filtrate, tpt (29 mg, 0.09 mmol) and pyrene (9.2 mg, 0.04 mmol) were added. The residue was dissolved in CH$_2$Cl$_2$ (3 mL), and diethyl ether was slowly added to precipitate the green solid, which was filtered and dried under vacuum. Yield: 123 mg (83%). UV/Vis [1.0×10^{-5} M, (CH$_3$)$_2$CO]: λ_{max} (ε) = 308 (3.92×10^5), 334 (1.21×10^5), 437 (0.47×10^5), 643 (0.16×10^5), 700 (0.16×10^5 M^{-1} cm^{-1}) nm. IR (KBr): ṽ = 3062 (w, CH$_{aryl}$), 1537 (s, C=O), 1260 (s, CF$_3$), 713 (w, C=C) cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 8.41 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, H$_\alpha$), 7.81 (m, 12 H, H$_\beta$), 7.44 (s, 12 H, H$_q$), 6.61 (m, 4 H, H$_g$), 6.14 (m, 4 H, H$_{g'}$), 5.69 (d, $^3J_{H,H}$ = 5.7 Hz, 12 H, H$_{cym}$), 5.47 (d, $^3J_{H,H}$ = 5.7 Hz, 12 H, H$_{cym}$), 5.20 (m, 2 H, H$_{g''}$), 2.83 [sept, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(CH$_3$)$_2$], 2.09 (s, 18 H, CH$_3$), 1.32 [d, $^3J_{H,H}$ = 6.8 Hz, 36 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ = 171.8 (*CO*), 170.7 (*C*$_{tpt}$), 154.3 (*CH*$_\alpha$), 145.2 (*C*$_{tpt}$), 138.4 (*CH*$_q$), 130.0 (*C*$_{pyrene}$), 127.5 (*CH*$_{pyrene}$), 126.1 (*CH*$_{pyrene}$), 125.5 (*C*$_{pyrene}$), 125.0 (*CH*$_\beta$), 112.5 (*C*$_q$), 104.9 (*C*$_{cym}$), 100.5 (*C*$_{cym}$), 85.2 (*CH*$_{cym}$), 84.2 (*CH*$_{cym}$), 31.5 [*CH*(CH$_3$)$_2$], 23.1 [CH(*CH$_3$*)$_2$], 22.3 [CH(*CH$_3$*)$_2$], 17.3 (*CH$_3$*) ppm. C$_{148}$H$_{130}$F$_{18}$N$_{12}$O$_{30}$Ru$_6$S$_6$ (3697.5): calcd. C 48.04, H 3.52, N 4.54; found C 48.10, H 3.55, N 4.50.

[triphenylene⊂1][CF$_3$SO$_3$]$_6$: This compound was prepared according to the same procedure as described above for [pyrene⊂**1**][CF$_3$SO$_3$]$_6$ by using triphenylene (10.3 mg, 0.04 mmol). Yield 129 mg (86%). UV/Vis [1.0×10^{-5} M, (CH$_3$)$_2$CO]: λ_{max} (ε) = 308 (3.92×10^5), 437 (0.51×10^5), 643 (0.16×10^5), 700 (0.17×10^5 M^{-1} cm^{-1}) nm. IR (KBr): ṽ = 3064 (w, CH$_{aryl}$), 1536 (s, C=O), 1258 (s, CF$_3$) cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 8.36 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, H$_\alpha$), 7.82 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, H$_\beta$), 7.45 (s, 12 H, H$_q$), 7.29 (m, 6 H, H$_g$), 5.70 (d, $^3J_{H,H}$ = 6.0 Hz, 12 H, H$_{cym}$), 5.48 (d, $^3J_{H,H}$ = 6.0 Hz, 12 H, H$_{cym}$), 4.66 (m, 6 H, H$_{g'}$), 2.83 [sept, $^3J_{H,H}$ = 5.8 Hz, 6 H, CH(CH$_3$)$_2$], 2.04 (s, 18 H, CH$_3$), 1.31 [d, $^3J_{H,H}$ = 5.8 Hz, 36 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ = 170.9 (*CO*), 167.8 (*C*$_{tpt}$), 152.2 (*CH*$_\alpha$), 143.1 (*C*$_{tpt}$), 137.8 (*CH*$_q$), 128.0 (*C*$_{triphenylene}$), 125.8 (*CH*$_{triphenylene}$), 123.7 (*CH*$_\beta$), 122.5 (*CH*$_{triphenylene}$), 111.4 (*C*$_q$), 103.9 (*C*$_{cym}$), 99.8 (*C*$_{cym}$), 84.5 (*CH*$_{cym}$), 83.2 (*CH*$_{cym}$), 30.5 [*CH*(CH$_3$)$_2$], 21.5 [CH(*CH$_3$*)$_2$], 16.4 (*CH$_3$*) ppm. C$_{150}$H$_{132}$F$_{18}$N$_{12}$O$_{30}$Ru$_6$S$_6$ (3723.5): calcd. C 48.35, H 3.54, N 4.51; found C 48.10, H 3.52, N 4.45.

[Pt(acac)$_2$⊂1][CF$_3$SO$_3$]$_6$: This compound was prepared according to the same procedure as described above for [pyrene⊂**1**][CF$_3$SO$_3$]$_6$ by using Pt(acac)$_2$ (17.7 mg, 0.04 mmol). Yield 125 mg (80%). UV/Vis [1.0×10^{-5} M, (CH$_3$)$_2$CO]: λ_{max} (ε) = 308 (3.91×10^5), 437 (0.50×10^5), 643 (0.16×10^5), 700 (0.17×10^5 M^{-1} cm^{-1}) nm. IR (KBr): ṽ = 3063 (w, CH$_{aryl}$), 1533 (s, C=O), 1262 (s, CF$_3$) cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 8.58 (d, $^3J_{H,H}$ = 6.5 Hz, 12 H, H$_\alpha$), 8.36 (d, $^3J_{H,H}$ = 6.5 Hz, 12 H, H$_\beta$), 7.28 (s, 12 H, H$_q$), 5.73 (d, $^3J_{H,H}$ = 5.9 Hz, 12 H, H$_{cym}$), 5.53 (d, $^3J_{H,H}$ = 5.9 Hz, 12 H, H$_{cym}$), 3.40 (m, 2 H, CH_{acac}), 2.85 [sept, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(CH$_3$)$_2$], 2.10 (s, 18 H, CH$_3$), 1.32 [d, $^3J_{H,H}$ = 6.9 Hz, 36 H, CH(CH_3)$_2$], 0.02 (m, 12 H, CH_{3acac}) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ = 171.8 (*CO*), 170.7 (*C*$_{tpt}$), 154.3 (*CH*$_\alpha$), 145.2 (*C*$_{tpt}$), 138.4 (*CH*$_q$), 125.0 (*CH*$_\beta$), 112.5 (*C*$_q$), 104.9 (*C*$_{cym}$), 102.0 (*CH*$_{acac}$), 100.5 (*C*$_{cym}$), 85.2 (*CH*$_{cym}$), 84.2 (*CH*$_{cym}$), 31.5 [*CH*(CH$_3$)$_2$], 23.1 [CH(*CH$_3$*)$_2$], 22.3 [CH(*CH$_3$*)$_2$], 17.3 (*CH$_3$*), 15.6 (*CH$_{3acac}$*) ppm. ^{195}Pt NMR (86 MHz, CD$_3$CN): δ = –392.6 ppm. C$_{142}$H$_{134}$F$_{18}$N$_{12}$O$_{34}$PtRu$_6$S$_6$ (3888.5): calcd. C 43.83, H 3.45, N 4.32; found C 43.98, H 3.32, N 4.65.

Supporting Information (see footnote on the first page of this article): UV/Vis spectra; NMR titrations of phenanthrene and (pyren-1-ylmethyl)amine; plots of the chemical-shift changes for phenanthrene and (pyren-1-ylmethyl)amine.

Acknowledgments

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