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Permanent Encapsulation or Host–Guest Behavior of Aromatic Molecules in Hexanuclear Arene Ruthenium Prisms

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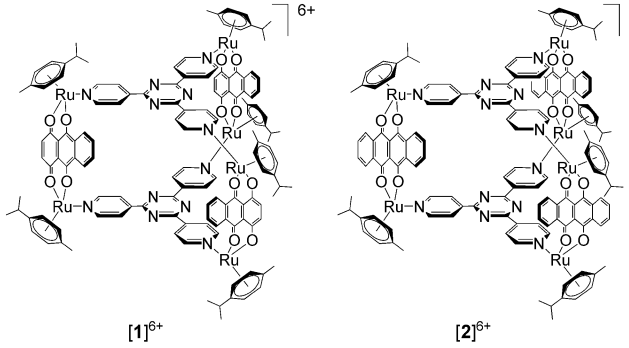
Cationic arene ruthenium metallaprisms of the general formula $[Ru_6(p\text{-cymene})_6(tpt)_2(OO\cap OO)_3]^{6+}$ {tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine; $OO\cap OO$ = 9,10-dioxo-9,10-dihydroanthracene-1,4-diolato [**1**]$^{6+}$, 6,11-dioxo-6,11-dihydronaphthacene-5,12-diolato [**2**]$^{6+}$} have been obtained from the corresponding dinuclear arene ruthenium complexes $[Ru_2(p\text{-cymene})_2(OO\cap OO)Cl_2]$ by reaction with tpt and silver trifluoromethanesulfonate. Aromatic molecules (phenanthrene, pyrene, triphenylene, coronene) present during the synthesis of these metallaprisms are permanently encapsulated to give carceplex systems. All empty cages ([**1**]$^{6+}$ and [**2**]$^{6+}$) and carceplex systems ([guest⊂**1**]$^{6+}$ and [guest⊂**2**]$^{6+}$) were isolated in good yield as trifluoromethanesulfonate salts and characterized by NMR, UV, and IR spectroscopy. The host–guest properties of [**1**]$^{6+}$ and [**2**]$^{6+}$ were studied in solution in the presence of small aromatic molecules (phenanthrene and pyrene). The stability constant of association (K_a) was estimated by NMR spectroscopy for the following host–guest systems: [phenanthrene⊂**1**]$^{6+}$, [pyrene⊂**1**]$^{6+}$ and [phenanthrene⊂**2**]$^{6+}$, [pyrene⊂**2**]$^{6+}$. All K_a values were found to be larger than 2.0×10^4 M^{-1} for these host–guest systems ([D$_3$]acetonitrile, 21 °C).

Introduction

The encapsulation of appropriately sized, shaped, and functionalized guest molecules into self-assembling supramolecular capsules has received considerable attention, especially as a model for substrate recognition by enzymes.[1] In the case of 3D coordination cages, a number of different models have been reported in the literature over the past few years. Nitrate encapsulation, both in the solid state and in solution, by a cationic trigonal prismatic host has been reported by Stang.[2] Entrapment of sizeable neutral molecules, including *o*-carborane and adamantane, by a water-soluble truncated tetrahedral capsule has been described by Fujita.[3] The host property of these systems and of other 3D self-assembled aggregates has been largely demonstrated[4] and potential uses are still in development.

Thus, in 2008, we reported the ability of hexacationic metallaprism $[Ru_6(p\text{-cymene})_6(tpt)_2(dobq)_3]^{6+}$ [tpt = 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine; dobq = 3,6-dioxocyclohexa-1,4-diene-1,4-diolato] to permanently encapsulate square-planar complexes[5] and aromatic molecules.[6] Last year, the facility to permanently encapsulate large planar molecules as well as to allow host–guest chemistry to take place with smaller aromatic molecules was demonstrated with a slightly more spacious metallaprism: $[Ru_6(p\text{-cymene})_6(tpt)_2(donq)_3]^{6+}$ (donq = 5,8-dioxo-5,8-dihydronaphthalene-1,4-diolato).[7]

We have now extended these previous studies to two others cationic hexanuclear metallaprisms: $[Ru_6(p\text{-cymene})_6(tpt)_2(doaq)_3]^{6+}$ ([**1**]$^{6+}$; doaq = 9,10-dioxo-9,10-dihydroanthracene-1,4-diolato) and $[Ru_6(p\text{-cymene})_6(tpt)_2(dotq)_3]^{6+}$ ([**2**]$^{6+}$; dotq = 6,11-dioxo-6,11-dihydronaphthacene-5,12-diolato). Their aptitude to permanently encapsulate or to temporary host aromatic molecules, according to the size of the guest molecule, has been studied in solution, and the corresponding binding constant of association for the host–guest systems has been estimated.



Results and Discussion

Hexacationic metallaprisms **1** and **2** were synthesized by following a one-step strategy. The corresponding dinuclear arene ruthenium complex $[Ru_2(p\text{-cymene})_2(doaq)Cl_2]$[8] or $[Ru_2(p\text{-cymene})_2(dotq)Cl_2]$[9] reacts in methanol at room temperature in the presence of silver trifluoromethanesulfonate (halide scavenger) with tpt (donor ligand) to give the

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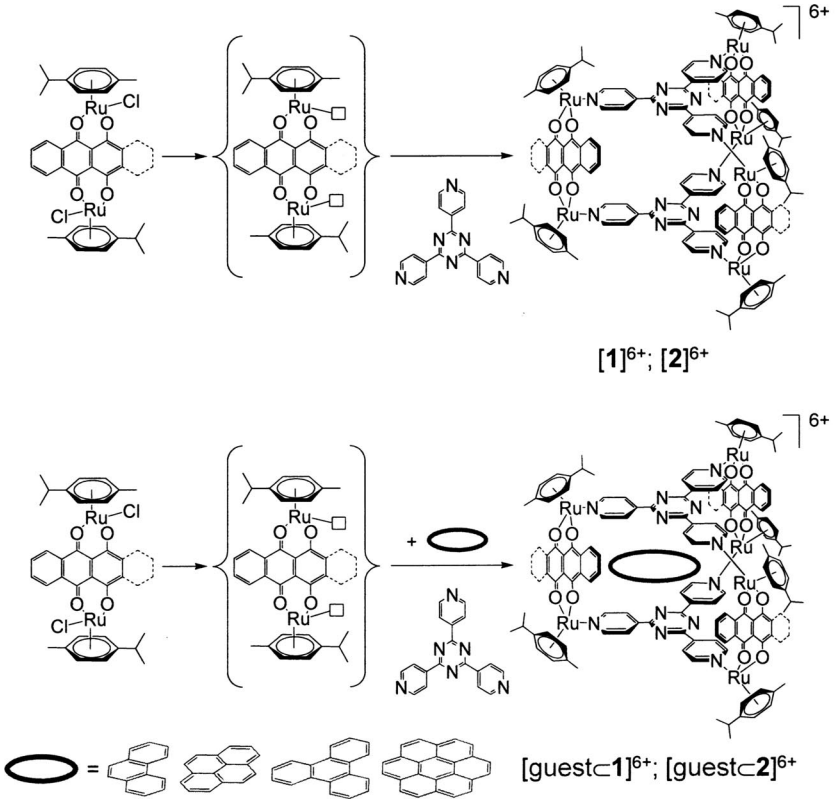
metallahexanuclear cation $[\mathbf{1}]^{6+}$ or $[\mathbf{2}]^{6+}$ isolated as the trifluoromethanesulfonate salt in good yield (≈80%, Scheme 1). The addition of one equivalent of phenanthrene, pyrene, triphenylene, or coronene leads to the direct encapsulation of the aromatic molecule in the metallaprism, following the same procedure but with a slightly better yield (≈85%), possibly due to the template effect (Scheme 1).

The infrared spectra of **1** and **2** are dominated by absorptions of the coordinated quinonato ligands, which are only slightly shifted relative to those of the free ligands. In addition to these signals, strong absorptions due to the stretching vibrations of the trifluoromethanesulfonate anions [1260 (s), 1030 (s), 638 (m) cm^{-1}] are also observed in the infrared spectra of the salts $[\mathbf{1}][CF_3SO_3]_6$ and $[\mathbf{2}][CF_3SO_3]_6$. In the cases of the $[guest\subset\mathbf{1}]^{6+}$ and $[guest\subset\mathbf{2}]^{6+}$ systems, additional absorptions due to the guest molecule are observed, and in particular a signal at around 1500 cm^{-1} assigned to valence vibrations of aromatic Csp^2–Csp^2. The electronic absorption spectra of metallaprisms **1** and **2** are characterized by an intense high-energy band centered at around 320 nm, which is assigned to a ligand-localized or intraligand $\pi \rightarrow \pi^*$ transition as well as broad low-energy bands associated to metal-to-ligand charge transfer (MLCT) transitions.

The ^1H NMR spectra of **1** and **2** show two doublets due to the tpt protons with an upfield shift of the signals relative to the signals of the free tpt molecule in $[D_6]$acetone. Similarly, the proton signals of the 9,10-dioxo-9,10-dihydroanthracene-1,4-diolato and 6,11-dioxo-6,11-dihydronaphthacene-5,12-diolato bridging ligands in metallaprisms **1** and **2** are shifted downfield relative to those of their parent complexes $[Ru_2(p\text{-cymene})_2(doaq)Cl_2]$ and $[Ru_2(p\text{-cymene})_2(dotq)Cl_2]$,[8,9] whereas the methyl, isopropyl, and phenyl signals of the *p*-cymene ligands remain almost unchanged.

To further study the structural behavior of cationic metallaprisms **1** and **2** in solution, ^1H NMR enantiodifferentiation in $[D_6]$acetone was achieved in the presence of the NMR chiral solvating agent *Λ*-TRISPHAT [TRISPHAT = tris(tetrachlorobenzenediolato)phosphate(V)].[10] Upon gradual addition of *Λ*-TRISPHAT (0.1–5.0 equiv.) to a $[D_6]$-acetone solution of metallaprism **1** or **2**, rapid and effective splitting of all signals of the metallaprisms is observed (see baseline-to-baseline separation of the *p*-cymene proton signals of **2** in Figure 1). This NMR enantiodifferentiation confirms the expected helical chirality of metallaprisms **1** and **2**, which was already observed for similar metalla-assemblies.[11]

The formation of $[guest\subset\mathbf{1}]^{6+}$ and $[guest\subset\mathbf{2}]^{6+}$ can be easily monitored by NMR spectroscopy. 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 doaq and dotq 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 prisms are not significantly affected by the presence of a guest molecule in the cavities of $[\mathbf{1}]^{6+}$ and $[\mathbf{2}]^{6+}$ (Figure 2).



Scheme 1. Syntheses of $[\mathbf{1}]^{6+}$ and $[\mathbf{2}]^{6+}$ (top) and of $[guest\subset\mathbf{1}]^{6+}$ and $[guest\subset\mathbf{2}]^{6+}$ (bottom).

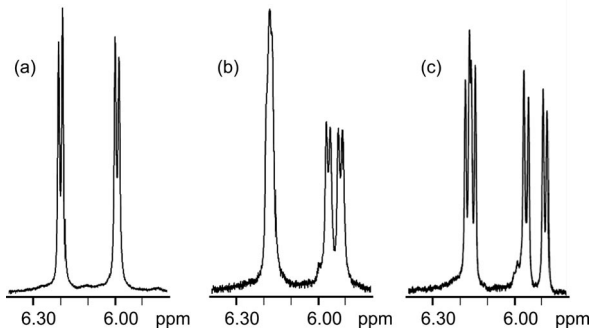


Figure 1. Splitting of *p*-cymene proton signals of metallaprism $[\mathbf{2}][CF_3SO_3]_6$ upon addition of *Λ*-TRISPHAT in [D$_6$]acetone at 21 °C: (a) $[\mathbf{2}]^{6+}$ (4.0 mM), (b) $[\mathbf{2}]^{6+}$ + *Λ*-TRISPHAT (2.0 equiv.), and (c) $[\mathbf{2}]^{6+}$ + *Λ*-TRISPHAT (5.0 equiv.).

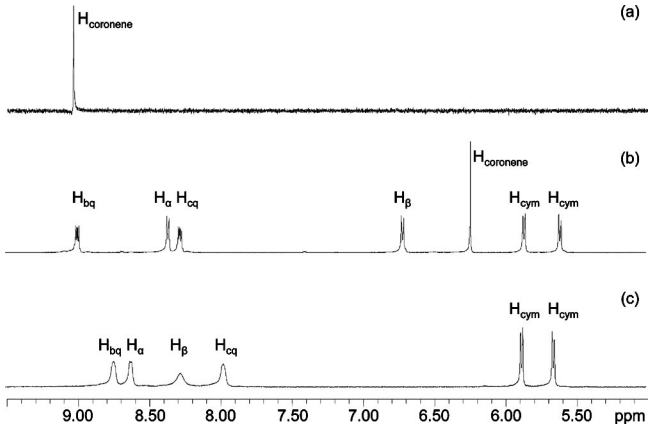


Figure 2. ^{1}H NMR spectra (400 MHz, [D$_3$]acetonitrile) of free coronene (a), [coronene⊂**2**][CF$_3$SO$_3$]$_6$ (b), and [**2**][CF$_3$SO$_3$]$_6$ (c).

^{1}H ROESY experiments confirm the encapsulation of aromatic molecules (phenanthrene, pyrene, triphenylene, and coronene) in metallaprisms **1** and **2**. For example, the ^{1}H ROESY spectrum of [coronene⊂**2**]$^{6+}$ shows a strong nuclear Overhauser effect between the irradiated coronene and tpt protons (H_α & H_β). Moreover a weak nuclear Overhauser interaction with the protons of the quinonato bridges (H_{bq} & H_{cq}) is as well observed (Figure 3).

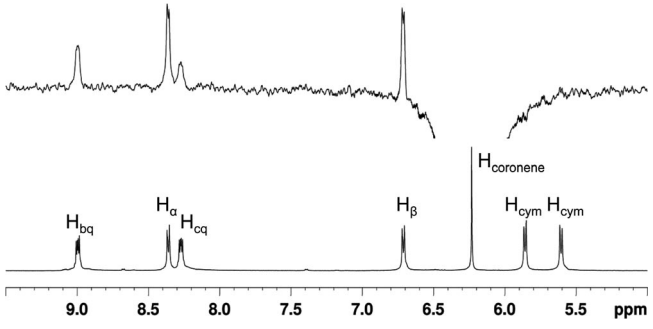


Figure 3. 1D ^{1}H ROESY spectrum (21 °C, [D$_3$]acetonitrile) of [coronene⊂**2**]$^{6+}$ (top). ^{1}H NMR spectrum of [coronene⊂**2**]-[CF$_3$SO$_3$]$_6$ (bottom).

To evaluate these metallacages as potential host–guest systems, we first studied the stability of all systems in solution (water, toluene, acetonitrile) at room and elevated temperatures. Complexes [triphenylene⊂**1**]$^{6+}$, [triphenylene⊂**2**]$^{6+}$, [coronene⊂**1**]$^{6+}$, and [coronene⊂**2**]$^{6+}$ show no degradation of the cages or leaching of the guests in all solvents tested, even at reflux for 24 h. However, [phenanthrene⊂**1**]$^{6+}$, [phenanthrene⊂**2**]$^{6+}$, [pyrene⊂**1**]$^{6+}$, and [pyrene⊂**2**]$^{6+}$ show rapid loss of their guest molecules in [D$_8$]toluene at 80 °C, whereas these systems remain intact in acetonitrile and water. Therefore, we decided to further study the host–guest chemistry of metallaprisms [**1**]$^{6+}$ and [**2**]$^{6+}$ in acetonitrile solution by using NMR spectroscopy. Upon gradual addition of guest (either phenanthrene or pyrene, 0.1–3.0 equiv.) to a [D$_3$]acetonitrile solution of the metallaprism ([**1**][CF$_3$SO$_3$]$_6$ or [**2**][CF$_3$SO$_3$]$_6$, 4.0 mM), the ^{1}H NMR spectra show displacement of the chemical shifts of the signals for some protons of the host and of the guest. The broadening and chemical shifts of the signals clearly support rapid inclusion of pyrene in the hydrophobic cavity of [**2**]$^{6+}$, as previously observed in analogous systems.[7] A plot of these chemical shift changes ($\Delta\delta$) for the H_β proton of the tpt ligands versus the molar ratio of pyrene/[**2**]$^{6+}$ indicates the stoichiometry of host–guest formation (Figure 4). The plot shows unambiguously the formation of a 1:1 host–guest system for which an association constant of 2.23×10^4 M^{-1} is calculated by the nonlinear least-square fitting program winEQNMR2 (Table 1).[12]

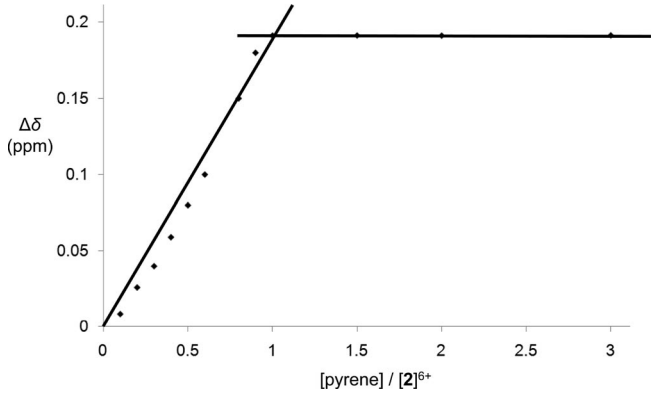


Figure 4. ^{1}H NMR chemical shift changes for the H_β proton of the tpt ligands vs. the molar ratio of pyrene/[**2**]$^{6+}$ in [D$_3$]acetonitrile at 21 °C.

Table 1. Association constants and free energies for the encapsulation of phenanthrene and pyrene in [**1**]$^{6+}$and [**2**]$^{6+}$ ([D$_3$]acetonitrile at 21 °C, 4.0 mM concentration of [**1**]$^{6+}$ and [**2**]$^{6+}$).

Complex	$K_a \times 10^4$ M^{-1}	$\Delta G°$ (kcal mol^{-1})
[phenanthrene⊂**1**]$^{6+}$	2.05 ± 0.7	–5.88 ± 0.2
[pyrene⊂**1**]$^{6+}$	2.01 ± 0.4	–5.87 ± 0.1
[phenanthrene⊂**2**]$^{6+}$	2.90 ± 0.9	–6.08 ± 0.2
[pyrene⊂**2**]$^{6+}$	2.23 ± 0.5	–5.93 ± 0.6

Finally, DOSY measurements were performed to complete the host–guest studies. This powerful tool for studying host–guest association in solution is based on diffusion coefficients that depend on the shape and size of the mole-

cules.[13] Thus, if the guest and the host keep their individual diffusion coefficients, there is no guest⊂host adduct. However, if the guest is perfectly encapsulated in the cavity of the host without significantly affecting the size and shape of the host, the diffusion coefficient of the guest⊂host adduct will be almost identical to the diffusion coefficient of the host alone. DOSY spectra of $[\mathbf{2}]^{6+}$ and [phenanthrene⊂$\mathbf{2}$]$^{6+}$ show diffusion coefficients that are almost equivalent with values at around 5.6×10^{-10} m^{2}s^{-1}, thus confirming the encapsulation of phenanthrene in the hydrophobic cavity of $[\mathbf{2}]^{6+}$ and the formation of a [phenanthrene⊂$\mathbf{2}$]$^{6+}$ adduct, without radical modification of the shape of $[\mathbf{2}]^{6+}$ (Figure 5).

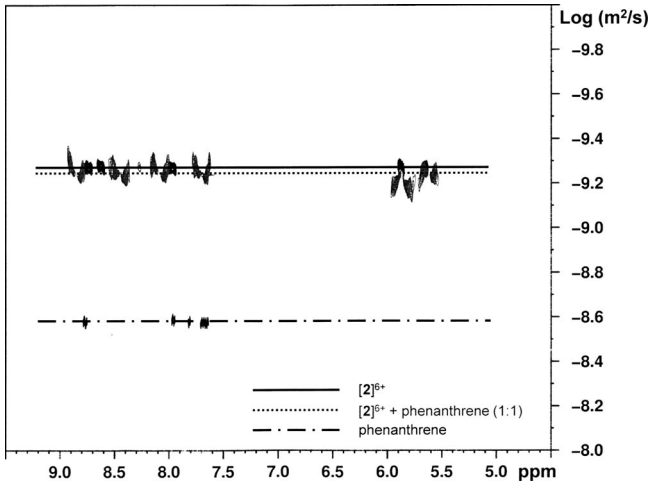


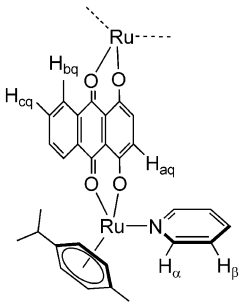
Figure 5. DOSY ^{1}H NMR spectra of phenanthrene, $[\mathbf{2}]^{6+}$, and $[\mathbf{2}]^{6+}$ + phenanthrene (1 equiv.) at 21 °C in [D$_3$]acetonitrile.

Conclusions

We have described two new cationic metallaprisms with different portal sizes that, in solution, are both able to allow small aromatic molecules to enter and leave the hydrophobic cavity. However, for larger aromatic molecules capable of fitting into the cavity but too large to exit the portal of the cage, permanent encapsulation was observed, thus giving rise to stable carceplex systems. Association constants in all host–guest systems were found to be around 2.5×10^4 M^{-1}, thus suggesting that the difference in the portal size in those two metallaprisms does not affect the dynamic host–guest equilibrium in solution.

Experimental Section

General: [Ru$_2$(*p*-cymene)$_2$(doaq)Cl$_2$],[8] [Ru$_2$(*p*-cymene)$_2$(dotq)Cl$_2$],[9] and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt)[14] were prepared according to published methods. *Λ*-TRISPHAT tetrabutylammonium salt and all other reagents were commercially available (Sigma–Aldrich) and used as received. ^{1}H, ^{13}C{^{1}H}, ^{1}H DOSY, and ^{1}H ROESY NMR spectra were recorded with a Bruker AvanceII 400 spectrometer by using the residual protonated solvent as internal standard. Infrared spectra were recorded as KBr pellets with a Perkin–Elmer FTIR 1720X spectrometer. UV/Vis absorption spectra were recorded with a Uvikon 930 spectrometer by using precision cells made of quartz (1 cm). Elemental analyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland).



Syntheses of [1][CF$_3$SO$_3$]$_6$ and [2][CF$_3$SO$_3$]$_6$: A mixture of [Ru$_2$(*p*-cymene)$_2$(*OO*∩*OO*)Cl$_2$] (*OO*∩*OO* = 9,10-dioxo-9,10-dihydroanthracene-1,4-diolato, 50.0 mg, 0.064 mmol; *OO*∩*OO* = 6,11-dioxo-6,11-dihydronaphthacene-5,12-diolato, 53.3 mg; 0.064 mmol), $AgCF_3SO_3$ (33.0 mg, 0.128 mmol), and tpt (13.4 mg, 0.043 mmol) in MeOH (20 mL) was heated under reflux for 24 h and then filtered. The solvent was removed, and the dark residue was dissolved in CH_2Cl_2 (3 mL). Diethyl ether was added to precipitate a dark green solid. The solid was filtered and dried under vacuum.

[1][CF$_3$SO$_3$]$_6$: Yield: 59 mg (76%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon\times10^4$, M^{-1}cm^{-1}) = 372 (4.3), 401 (4.0), 552 (1.3), 601 (1.9), 648 (2.2) nm. IR (KBr): $\tilde{\nu}$ = 3065 (w, CH_{aryl}), 1539 (s, C=O), 1261 (s, CF_3) cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN): δ = 8.70 (m, 3 H, H$_{bq}$), 8.66 (m, 3 H, H$_{bq}$), 8.61 (dd, $^3J_{H,H}$ = 6.0 Hz, 6 H, H$_\alpha$), 8.59 (dd, 6 H, H$_\alpha$), 8.38 (dd, $^3J_{H,H}$ = 5.8 Hz, 6 H, H$_\beta$), 8.35 (dd, 6 H, H$_\beta$), 7.99 (m, 3 H, H$_{cq}$), 7.95 (m, 3 H, H$_{cq}$), 7.27 (d, $^3J_{H,H}$ = 4.1 Hz, 3 H, H$_{aq}$), 7.23 (d, 3 H, H$_{aq}$), 5.81 (m, 6 H, H$_{cym}$), 5.75 (m, 6 H, H$_{cym}$), 5.58 (m, 12 H, H$_{cym}$), 2.89 [sept, $^3J_{H,H}$ = 6.7 Hz, 6 H, C*H*(CH$_3$)$_2$], 2.12 (m, 18 H, CH$_3$), 1.31 [m, 36 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ = 171.5 (*C*O), 170.6 (*C*$_{tpt}$), 170.5 (*C*O), 154.2 (*C*H$_\alpha$), 145.1 (*C*$_{tpt}$), 138.7 (*C*H$_{aq}$), 134.4 (*C*H$_{cq}$), 134.0 (*C*$_q$), 128.3 (*C*H$_{bq}$), 124.9 (*C*H$_\beta$), 110.7 (*C*$_q$), 104.8 (*C*$_{cym}$), 100.6 (*C*$_{cym}$), 85.3 (*C*H$_{cym}$), 85.0 (*C*H$_{cym}$), 83.9 (*C*H$_{cym}$), 83.8 (*C*H$_{cym}$), 31.4 [*C*H(CH$_3$)$_2$], 22.5 [CH(*C*H$_3$)$_2$], 22.3 [CH(*C*H$_3$)$_2$], 17.6 (*C*H$_3$) ppm. $C_{144}H_{126}F_{18}N_{12}O_{30}Ru_6S_6$ (3645.5): calcd. C 47.44, H 3.48, N 4.61; found C 47.51, H 3.60, N 4.63.

[2][CF$_3$SO$_3$]$_6$: Yield: 62 mg (77%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon\times10^4$, M^{-1}cm^{-1}) = 370 (4.2), 398 (3.4), 558 (1.0), 602 (1.9), 650 (2.0) nm. IR (KBr): $\tilde{\nu}$ = 3070 (w, CH_{aryl}), 1540 (s, C=O), 1260 (s, CF_3) cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN): δ = 8.74 (br., 12 H, H$_{bq}$), 8.62 (br., 12 H, H$_\alpha$), 8.27 (br., 12 H, H$_\beta$), 7.97 (br., 12 H, H$_{cq}$), 5.88 (d, $^3J_{H,H}$ = 6.3 Hz, 12 H, H$_{cym}$), 5.66 (d, 12 H, H$_{cym}$), 2.93 [sept, $^3J_{H,H}$ = 6.9 Hz, 6 H, C*H*(CH$_3$)$_2$], 2.13 (s, 18 H, CH$_3$), 1.30 [d, 36 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ = 170.5 (*C*$_{tpt}$), 170.0 (*C*O), 154.1 (*C*H$_\alpha$), 145.0 (*C*$_{tpt}$), 134.6 (*C*$_q$), 134.1 (*C*H$_{cq}$), 128.2 (*C*H$_{bq}$), 124.9 (*C*H$_\beta$), 108.1 (*C*$_q$), 104.9 (*C*$_{cym}$), 100.7 (*C*$_{cym}$), 85.1 (*C*H$_{cym}$), 83.6 (*C*H$_{cym}$), 31.5 [*C*H(CH$_3$)$_2$], 22.5 [CH(*C*H$_3$)$_2$], 17.8 (*C*H$_3$) ppm. $C_{156}H_{132}F_{18}N_{12}O_{30}Ru_6S_6$ (3795.6): calcd. C 49.36, H 3.51, N 4.43; found C 49.88, H 3.70, N 4.44.

Syntheses of [Guest⊂1][CF$_3$SO$_3$]$_6$ and [Guest⊂2][CF$_3$SO$_3$]$_6$: To a mixture of [Ru$_2$(*p*-cymene)$_2$(*OO*∩*OO*)Cl$_2$] (*OO*∩*OO* = 9,10-dioxo-9,10-dihydroanthracene-1,4-diolato, 50.0 mg, 0.064 mmol; *OO*∩*OO* = 6,11-dioxo-6,11-dihydronaphthacene-5,12-diolato, 53.3 mg, 0.064 mmol) and $AgCF_3SO_3$ (33.0 mg, 0.128 mmol) in MeOH (20 mL) was added tpt (13.4 mg, 0.043 mmol) and the aromatic guest molecule (phenanthrene 4.1 mg, 0.023 mmol; pyrene

4.7 mg, 0.023 mmol; triphenylene 5.3 mg, 0.023 mmol; coronene 6.9 mg, 0.023 mmol). The mixture was stirred at reflux for 24 h and then filtered. The solvent was removed, and the dark residue was dissolved in CH_2Cl_2 (3 mL). Diethyl ether was added to precipitate a dark green solid. The solid was filtered and dried under vacuum.

[Phenanthrene⊂1][CF_3SO_3]$_6$: Yield: 68 mg (84%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon\times10^4$, $M^{-1}cm^{-1}$) = 373 (4.0), 399 (3.8), 554 (1.3), 601 (1.8), 648 (2.1) nm. IR (KBr): $\tilde{\nu}$ = 3068 (w, CH_{aryl}), 1539 (s, C=O), 1262 (s, CF_3) cm^{-1}. ^1H NMR (400 MHz, CD_3CN): δ = 8.74 (m, 3 H, H_{bq}), 8.70 (m, 3 H, H_{bq}), 8.56 (dd, $^3J_{H,H}$ = 6.3 Hz, 6 H, H_α), 8.53 (dd, 6 H, H_α), 8.19 (m, 12 H, H_β), 8.02 (m, 6 H, H_{cq}), 7.41 (m, 2 H, $H_{phenanthrene}$), 7.33 (d, $^3J_{H,H}$ = 3.7 Hz, 3 H, H_{aq}), 7.29 (d, 3 H, H_{aq}), 6.91 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, $H_{phenanthrene}$), 5.81 (m, 6 H, H_{cym}), 5.75 (m, 6 H, H_{cym}), 5.63 (m, 2 H, $H_{phenanthrene}$), 5.57 (m, 12 H, H_{cym}), 5.20 (m, 2 H, $H_{phenanthrene}$), 4.50 (dd, 2 H, $H_{phenanthrene}$), 2.89 [sept, $^3J_{H,H}$ = 6.5 Hz, 6 H, C*H*$(CH_3)_2$], 2.11 (m, 18 H, CH_3), 1.32 [m, 36 H, CH(C*H*$_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 171.5 (*C*O), 170.6 (*C*O), 170.3 (C_{tpt}), 154.0 (*C*H$_\alpha$), 145.0 (C_{tpt}), 138.8 (*C*H$_{aq}$), 134.5 (*C*H$_{cq}$), 134.1 (C_q), 128.4 (*C*H$_{bq}$), 124.8 (*C*H$_\beta$), 110.6 (C_q), 104.8 (C_{cym}), 100.7 (C_{cym}), 85.3 (*C*H$_{cym}$), 85.0 (*C*H$_{cym}$), 83.9 (*C*H$_{cym}$), 83.8 (*C*H$_{cym}$), 31.5 [*C*H$(CH_3)_2$], 22.5 [CH(*C*H$_3)_2$], 22.3 [CH(*C*H$_3)_2$], 17.6 (*C*H$_3$) ppm. $C_{158}H_{136}F_{18}N_{12}O_{30}Ru_6S_6$ (3823.7): calcd. C 49.63, H 3.59, N 4.40; found C 49.77, H 3.72, N 4.45.

[Pyrene⊂1][CF_3SO_3]$_6$: Yield: 68 mg (83%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon\times10^4$, $M^{-1}cm^{-1}$) = 321 (7.1), 337 (6.9), 374 (4.3), 402 (4.1), 554 (1.3), 601 (1.9), 649 (2.3) nm. IR (KBr): $\tilde{\nu}$ = 3064 (w, CH_{aryl}), 1539 (s, C=O), 1260 (s, CF_3) cm^{-1}. ^1H NMR (400 MHz, CD_3CN): δ = 8.79 (m, 6 H, H_{bq}), 8.48 (m, 12 H, H_α), 8.10 (m, 6 H, H_{cq}), 7.95 (m, 12 H, H_β), 7.42 (m, 6 H, H_{aq}), 6.16 (m, 4 H, H_{pyrene}), 5.81 (m, 6 H, H_{cym}), 5.75 (m, 6 H, H_{cym}), 5.65 (br., 2 H, H_{pyrene}), 5.56 (m, 12 H, H_{cym}), 5.00 (m, 4 H, H_{pyrene}), 2.89 [sept, $^3J_{H,H}$ = 6.7 Hz, 6 H, C*H*$(CH_3)_2$], 2.09 (m, 18 H, CH_3), 1.32 [m, 36 H, CH(C*H*$_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 171.5 (*C*O), 170.7 (*C*O), 169.9 (C_{tpt}), 153.7 (*C*H$_\alpha$), 144.3 (C_{tpt}), 139.0 (*C*H$_{aq}$), 134.7 (*C*H$_{cq}$), 134.2 (C_q), 129.9 (*C*H$_{pyrene}$), 128.4 (*C*H$_{bq}$), 127.1 (*C*H$_{pyrene}$), 125.1 (*C*H$_{pyrene}$), 124.5 (*C*H$_\beta$), 110.7 (C_q), 104.8 (C_{cym}), 100.7 (C_{cym}), 85.7 (*C*H$_{cym}$), 85.2 (*C*H$_{cym}$), 83.8 (*C*H$_{cym}$), 83.1 (*C*H$_{cym}$), 31.4 [*C*H$(CH_3)_2$], 22.4 [CH(*C*H$_3)_2$], 17.6 (*C*H$_3$) ppm. $C_{160}H_{136}F_{18}N_{12}O_{30}Ru_6S_6$ (3847.7): calcd. C 49.95, H 3.56, N 4.37; found C 49.98, H 3.74, N 4.42.

[Triphenylene⊂1][CF_3SO_3]$_6$: Yield: 72 mg (84%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon\times10^4$, $M^{-1}cm^{-1}$) = 380 (3.8), 415 (4.0), 550 (0.9), 612 (1.5), 659 (1.9) nm. IR (KBr): $\tilde{\nu}$ = 3060 (w, CH_{aryl}), 1539 (s, C=O), 1260 (s, CF_3) cm^{-1}. ^1H NMR (400 MHz, CD_3CN): δ = 8.82 (m, 6 H, H_{bq}), 8.38 (dd, $^3J_{H,H}$ = 6.3 Hz, 6 H, H_α), 8.29 (dd, 6 H, H_α), 8.28 (m, 6 H, H_{cq}), 7.71 (br., 3 H, H_{aq}), 7.69 (d, $^3J_{H,H}$ = 2.5 Hz, 3 H, H_{aq}), 6.92 (dd, $^3J_{H,H}$ = 6.6 Hz, 6 H, H_β), 6.79 (dd, 6 H, H_β), 6.58 (m, 6 H, $H_{triphenylene}$), 5.78 (m, 6 H, H_{cym}), 5.74 (m, 6 H, H_{cym}), 5.63 (m, 12 H, H_{cym}), 4.44 (m, 6 H, $H_{triphenylene}$), 2.88 [sept, $^3J_{H,H}$ = 6.4 Hz, 6 H, C*H*$(CH_3)_2$], 2.04 (m, 18 H, CH_3), 1.29 [m, 36 H, CH(C*H*$_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 171.3 (*C*O), 171.1 (*C*O), 166.0 (C_{tpt}), 152.0 (*C*H$_\alpha$), 142.4 (C_{tpt}), 138.5 (*C*H$_{aq}$), 134.6 (*C*H$_{cq}$), 132.2 (C_q), 128.4 ($C_{triphenylene}$), 128.1 (*C*H$_{bq}$), 127.1 (*C*H$_{triphenylene}$), 122.4 (*C*H$_{triphenylene}$), 120.2 (*C*H$_\beta$), 108.9 (C_q), 103.2 (C_{cym}), 100.1 (C_{cym}), 86.4 (*C*H$_{cym}$), 86.1 (*C*H$_{cym}$), 83.0 (*C*H$_{cym}$), 82.9 (*C*H$_{cym}$), 30.4 [*C*H$(CH_3)_2$], 21.6 [CH(*C*H$_3)_2$], 21.4 [CH(*C*H$_3)_2$], 16.9 (*C*H$_3$) ppm. $C_{162}H_{138}F_{18}N_{12}O_{30}Ru_6S_6$ (3873.8): calcd. C 50.23, H 3.59, N 4.34; found C 50.45, H 3.73, N 4.43.

[Coronene⊂1][CF_3SO_3]$_6$: Yield: 72 mg (86%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon\times10^4$, $M^{-1}cm^{-1}$) = 385 (3.9), 409 (3.9), 555 (0.8), 609 (1.5), 654 (1.8) nm. IR (KBr): $\tilde{\nu}$ = 3062 (w, CH_{aryl}), 1539 (s, C=O), 1261 (s, CF_3) cm^{-1}. ^1H NMR (400 MHz, CD_3CN): δ = 8.95 (m, 6 H, H_{bq}), 8.35 (dd, $^3J_{H,H}$ = 6.4 Hz, 6 H, H_α), 8.30 (dd, 6 H, H_α), 8.29 (m, 6 H, H_{cq}), 7.70 (br., 3 H, H_{aq}), 7.67 (d, $^3J_{H,H}$ = 2.4 Hz, 3 H, H_{aq}), 6.86 (dd, $^3J_{H,H}$ = 6.4 Hz, 6 H, H_β), 6.77 (dd, 6 H, H_β), 6.59 (s, 12 H, $H_{coronene}$), 5.80 (m, 6 H, H_{cym}), 5.71 (m, 6 H, H_{cym}), 5.53 (m, 12 H, H_{cym}), 2.88 [sept, $^3J_{H,H}$ = 6.4 Hz, 6 H, C*H*$(CH_3)_2$], 2.05 (m, 18 H, CH_3), 1.31 [m, 36 H, CH(C*H*$_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 170.2 (*C*O), 170.1 (*C*O), 166.1 (C_{tpt}), 152.2 (*C*H$_\alpha$), 142.0 (C_{tpt}), 138.4 (*C*H$_{aq}$), 134.1 (*C*H$_{cq}$), 133.3 (C_q), 127.8 (*C*H$_{bq}$), 127.2 ($C_{coronene}$), 125.2 (*C*H$_{coronene}$), 122.6 (*C*H$_\beta$), 120.4 ($C_{coronene}$), 109.7 (C_q), 103.9 (C_{cym}), 99.8 (C_{cym}), 84.5 (*C*H$_{cym}$), 84.1 (*C*H$_{cym}$), 83.0 (*C*H$_{cym}$), 82.9 (*C*H$_{cym}$), 30.6 [*C*H$(CH_3)_2$], 21.6 [CH(*C*H$_3)_2$], 21.4 [CH(*C*H$_3)_2$], 16.7 (*C*H$_3$) ppm. $C_{168}H_{138}F_{18}N_{12}O_{30}Ru_6S_6$ (3945.8): calcd. C 51.09, H 3.62, N 4.25; found C 51.14, H 3.53, N 4.26.

[Phenanthrene⊂2][CF_3SO_3]$_6$: Yield: 70 mg (83%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon\times10^4$, $M^{-1}cm^{-1}$) = 354 (6.3), 368 (6.2), 523 (1.7), 563 (2.7), 607 (3.4) nm. IR (KBr): $\tilde{\nu}$ = 3070 (w, CH_{aryl}), 1544 (s, C=O), 1259 (s, CF_3) cm^{-1}. ^1H NMR (400 MHz, CD_3CN): δ = 8.78 (dd, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 3.4 Hz, 12 H, H_{bq}), 8.54 (d, $^3J_{H,H}$ = 6.4 Hz, 12 H, H_α), 8.01 (m, 24 H, H_β and H_{cq}), 6.73 (br., 2 H, $H_{phenanthrene}$), 5.87 (d, $^3J_{H,H}$ = 6.3 Hz, 12 H, H_{cym}), 5.75 (br., 2 H, $H_{phenanthrene}$), 5.63 (d, 12 H, H_{cym}), 5.56 (br., 2 H, $H_{phenanthrene}$), 5.16 (br., 2 H, $H_{phenanthrene}$), 4.63 (br., 2 H, $H_{phenanthrene}$), 2.93 [sept, $^3J_{H,H}$ = 6.9 Hz, 6 H, C*H*$(CH_3)_2$], 2.11 (s, 18 H, CH_3), 1.30 [d, 36 H, CH(C*H*$_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 168.7 (*C*O), 166.2 (C_{tpt}), 152.5 (*C*H$_\alpha$), 141.0 (C_{tpt}), 133.3 (C_q), 132.9 (*C*H$_{cq}$), 127.0 (*C*H$_{bq}$), 123.4 (*C*H$_\beta$), 106.7 (C_q), 103.5 (C_{cym}), 99.4 (C_{cym}), 83.9 (*C*H$_{cym}$), 82.3 (*C*H$_{cym}$), 30.1 [*C*H$(CH_3)_2$], 21.2 [CH(*C*H$_3)_2$] 16.5 (*C*H$_3$) ppm. $C_{170}H_{142}F_{18}N_{12}O_{30}Ru_6S_6$ (3973.8): calcd. C 51.33, H 3.70, N 4.22; found C 51.38, H 3.60, N 4.23.

[Pyrene⊂2][CF_3SO_3]$_6$: Yield: 75 mg (84%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon\times10^4$, $M^{-1}cm^{-1}$) = 350 (6.1), 362 (6.2), 522 (1.6), 565 (2.6), 609 (3.6) nm. IR (KBr): $\tilde{\nu}$ = 3070 (w, CH_{aryl}), 1540 (s, C=O), 1260 (s, CF_3) cm^{-1}. ^1H NMR (400 MHz, CD_3CN): δ = 8.80 (dd, $^3J_{H,H}$ = 6.3 Hz, $^4J_{H,H}$ = 3.2 Hz, 12 H, H_{bq}), 8.50 (d, $^3J_{H,H}$ = 6.5 Hz, 12 H, H_α), 8.01 (m, 24 H, H_β and H_{cq}), 6.14 (m, 4 H, H_{pyrene}), 5.90 (d, $^3J_{H,H}$ = 6.2 Hz, 12 H, H_{cym}), 5.70 (br., 2 H, H_{pyrene}), 5.60 (d, 12 H, H_{cym}), 5.05 (m, 4 H, H_{pyrene}), 2.94 [sept, $^3J_{H,H}$ = 6.9 Hz, 6 H, C*H*$(CH_3)_2$], 2.10 (s, 18 H, CH_3), 1.29 [d, 36 H, CH(C*H*$_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 170.1 (*C*O), 165.8 (C_{tpt}), 152.4 (*C*H$_\alpha$), 141.2 (C_{tpt}), 133.1 (C_q), 132.6 (*C*H$_{cq}$), 129.7 (*C*H$_{pyrene}$), 127.4 (*C*H$_{pyrene}$), 127.0 (*C*H$_{bq}$), 125.3 (*C*H$_{pyrene}$), 123.0 (*C*H$_\beta$), 106.8 (C_q), 103.4 (C_{cym}), 99.2 (C_{cym}), 83.6 (*C*H$_{cym}$), 82.1 (*C*H$_{cym}$), 29.9 [*C*H$(CH_3)_2$], 19.2 [CH(*C*H$_3)_2$] 16.8 (*C*H$_3$) ppm. $C_{172}H_{142}F_{18}N_{12}O_{30}Ru_6S_6$ (3997.8): calcd. C 51.67, H 3.68, N 4.20; found C 51.96, H 3.90, N 4.28.

[Triphenylene⊂2][CF_3SO_3]$_6$: Yield: 75 mg (87%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon\times10^4$, $M^{-1}cm^{-1}$) = 351 (6.3), 368 (6.1), 526 (1.5), 564 (2.5), 608 (3.3) nm. IR (KBr): $\tilde{\nu}$ = 3069 (w, CH_{aryl}), 1543 (s, C=O), 1259 (s, CF_3) cm^{-1}. ^1H NMR (400 MHz, CD_3CN): δ = 8.86 (m, 12 H, H_{bq}), 8.42 (d, $^3J_{H,H}$ = 5.7 Hz, 12 H, H_α), 8.12 (m, 12 H, H_{cq}), 7.58 (d, 12 H, H_β), 6.58 (m, 6 H, $H_{triphenylene}$), 5.87 (d, $^3J_{H,H}$ = 5.9 Hz, 12 H, H_{cym}), 5.61 (d, 12 H, H_{cym}), 4.41 (m, 6 H, $H_{triphenylene}$), 2.92 [sept, $^3J_{H,H}$ = 6.9 Hz, 6 H, C*H*$(CH_3)_2$], 2.06 (s, 18 H, CH_3), 1.29 [d, 36 H, CH(C*H*$_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 170.2 (*C*O), 168.6 (C_{tpt}), 153.0 (*C*H$_\alpha$), 143.9 (C_{tpt}), 134.6 (*C*H$_{cq}$), 134.4 (C_q), 128.5 ($C_{triphenylene}$), 128.5 (*C*H$_{bq}$), 126.4 (*C*H$_{triphenylene}$), 124.4 (*C*H$_\beta$), 122.9 (*C*H$_{triphenylene}$), 107.8 (C_q), 104.8 (C_{cym}), 100.8 (C_{cym}), 85.3 (*C*H$_{cym}$), 83.5 (*C*H$_{cym}$),

31.5 [*C*H(CH$_3$)$_2$], 22.5 [CH(*C*H$_3$)$_2$], 17.8 (*C*H$_3$) ppm. $C_{174}H_{144}F_{18}N_{12}O_{30}Ru_6S_6$ (4023.9): calcd. C 51.94, H 3.61, N 4.23; found C 51.92, H 3.71, N 4.18.

[Coronene⊂2][CF$_3$SO$_3$]$_6$: Yield: 71 mg (81%). UV/Vis (1.0×10^{-5} M, CH_2Cl_2): λ ($\varepsilon \times 10^4$, $M^{-1}cm^{-1}$) = 305 (17.2), 343 (8.7), 372 (5.8), 568 (2.3), 611 (3.0) nm. IR (KBr): $\tilde{\nu}$ = 3064 (w, CH_{aryl}), 1544 (s, C=O), 1261 (s, CF_3) cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN): δ = 8.99 (dd, $^3J_{H,H}$ = 5.9 Hz, $^4J_{H,H}$ = 3.4 Hz, 12 H, H_{bq}), 8.36 (d, $^3J_{H,H}$ = 6.5 Hz, 12 H, H_α), 8.27 (dd, 12 H, H_{cq}), 6.71 (d, 12 H, H_β), 6.23 (s, 12 H, $H_{coronene}$), 5.86 (d, $^3J_{H,H}$ = 6.1 Hz, 12 H, H_{cym}), 5.60 (d, 12 H, H_{cym}), 2.93 [sept, $^3J_{H,H}$ = 6.9 Hz, 6 H, C*H*(CH$_3$)$_2$], 2.05 (s, 18 H, CH$_3$), 1.31 [d, 36 H, CH(C*H*$_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 169.9 (*C*O), 166.0 (C_{tpt}), 152.1 (*C*H$_\alpha$), 141.8 (C_{tpt}), 133.9 (C_q), 133.8 (*C*H$_{cq}$), 127.7 (*C*H$_{bq}$), 127.0 ($C_{coronene}$), 124.9 (*C*H$_{coronene}$), 122.5 (*C*H$_\beta$), 120.2 ($C_{coronene}$), 107.1 (C_q), 104.0 (C_{cym}), 99.8 (C_{cym}), 84.2 (*C*H$_{cym}$), 82.7 (*C*H$_{cym}$), 30.6 [*C*H(CH$_3$)$_2$], 21.6 [CH(*C*H$_3$)$_2$], 16.9 (*C*H$_3$) ppm. $C_{180}H_{144}F_{18}N_{12}O_{30}Ru_6S_6$ (4095.9): calcd. C 52.78, H 3.54, N 4.10; found C 52.91, H 3.72, N 4.12.

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