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Encapsulation of Photosensitizers in Hexa- and Octanuclear Organometallic Cages: Synthesis and Characterization of Carceplex and Host−Guest Systems in Solution

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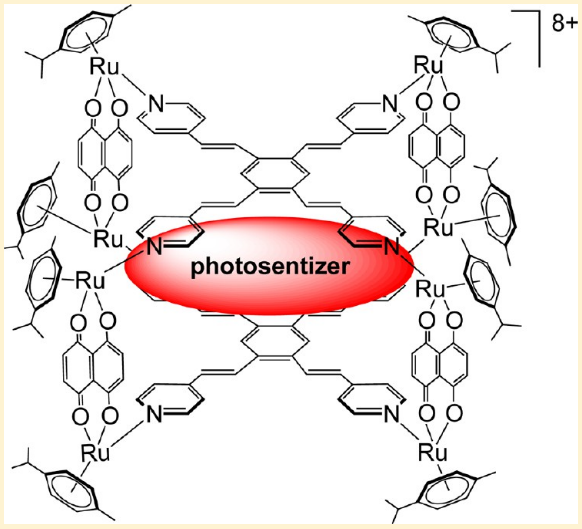
Supporting Information



ABSTRACT: Cationic arene ruthenium assemblies of the general formulas $[\mathrm{Ru_6}(p\text{-cymene})_6(\text{tris-pvb})_2(\mu_2\text{-Cl})_6]^{6+}$, $[\mathrm{Ru_6}(p\text{-cymene})_6(\text{tris-pvb})_2(\mathrm{OO{\cap}OO})_3]^{6+}$ (tris-pvb = 1,3,5-tris{2-(pyridin-4-yl)-vinyl}benzene), and $[\mathrm{Ru_8}(p\text{-cymene})_8(\mathrm{NN{\cap}NN})_2(\mathrm{OO{\cap}OO})_4]^{8+}$ (NN∩NN = 1,2,4,5-tetrakis{2-(pyridin-4-yl)vinyl}benzene, 1,2,4,5-tetrakis{2-(pyridin-4-yl)ethynyl}benzene) have been obtained from the corresponding dinuclear arene ruthenium complexes $[\mathrm{Ru_2}(p\text{-cymene})_2(\mu\text{-Cl})_2\mathrm{Cl_2}]$ and $[\mathrm{Ru_2}(p\text{-cymene})_2(\mathrm{OO{\cap}OO})\mathrm{Cl_2}]$ (OO∩OO = oxalato, 2,5-dioxido-1,4-benzoquinonato, 2,5-dichloro-1,4-benzoquinonato, 5,8-dioxido-1,4-naphthoquinonato, 5,8-dioxido-1,4-anthraquinonato, 6,11-dioxido-5,12-naphthacenedionato) by reaction with the multidentate ligands and silver trifluoromethanesulfonate. These cationic hexa- and octanuclear cages have been isolated and characterized as their triflate salts. Addition of coronene during the synthesis of the large hexanuclear assemblies leads to the direct encapsulation of coronene in the cavity of the trigonal-prismatic complexes. Photosensitizers such as porphin, phthalocyanine, and Zn-phthalocyanine present during the synthesis of these metalla-cages are encapsulated in five of these arene ruthenium complexes to give photosensitizer-encapsulated systems. The host−guest properties of these systems were studied in solution by DOSY, 2D NOESY and 2D ROESY NMR spectroscopy. The H···H distances between guests and selected metalla-cages were estimated by 2D ROESY NMR spectroscopy and modelization. NMR analyzes indicate that the guest photosensitizers are completely encapsulated in two of these metalla-cages, while in the three other ruthenium cages NMR spectra reveal an equilibrium between empty and filled cages.

■ INTRODUCTION

The concept of drug delivery has stimulated considerable research activities in order to optimize the therapy[1] and especially the photodynamic therapy (PDT) of cancer.[2] Indeed, due to the low selectivity of many photosensitizers for cancer cells and their poor solubility in water, the development of a vector-mediated selective drug delivery strategy is a major challenge in PDT. Photosensitizer delivery vectors such as gold nanoparticles,[3] liposome,[4] and even viruses[5] have been developed to improve the selective accumulation of the photoactive compound in tumor cells. However, the missing photoprotection of the photosensitizer molecules toward unexpected activation can cause undesired skin lesions, which is the main side effect of PDT and therefore a limitation of these drug delivery vectors.

In recent years, a new type of drug delivery system based on cationic arene ruthenium cages that are water-soluble as the triflate salts has been developed in our group.[6] These arene ruthenium cage systems have been used to encapsulate cytotoxic[7] as well as photoactive[8] molecules in order to transport these molecules into cancer cells. These large organometallic cages are expected to selectively target cancer cells according to the enhanced permeability and retention effect (EPR effect).[9] Moreover, the photoactivity of the hydrophobic photosensitizers is inhibited by their encapsulation in these metalla-cages, thus potentially avoiding the side effect of skin photosensitivity. As we demonstrated previously,[8] the encapsulated porphin molecules (Figure 1) show no singlet oxygen production in ethanol/DMSO, as opposed to free porphin, which leads after excitation at 414 nm to a singlet oxygen quantum yield of 97% relative to Rose Bengal. Arene ruthenium metalla-cages are known for their adaptable cavity[10] and their host−guest properties,[11] which precondition them as versatile drug delivery systems.

In this study, we report an extension of our previous work by the synthesis of new hexa- and octanuclear arene ruthenium cages of the general formulas $[\mathrm{Ru_6}(p\text{-cymene})_6(\text{tris-pvb})_2(\mu_2\text{-}$

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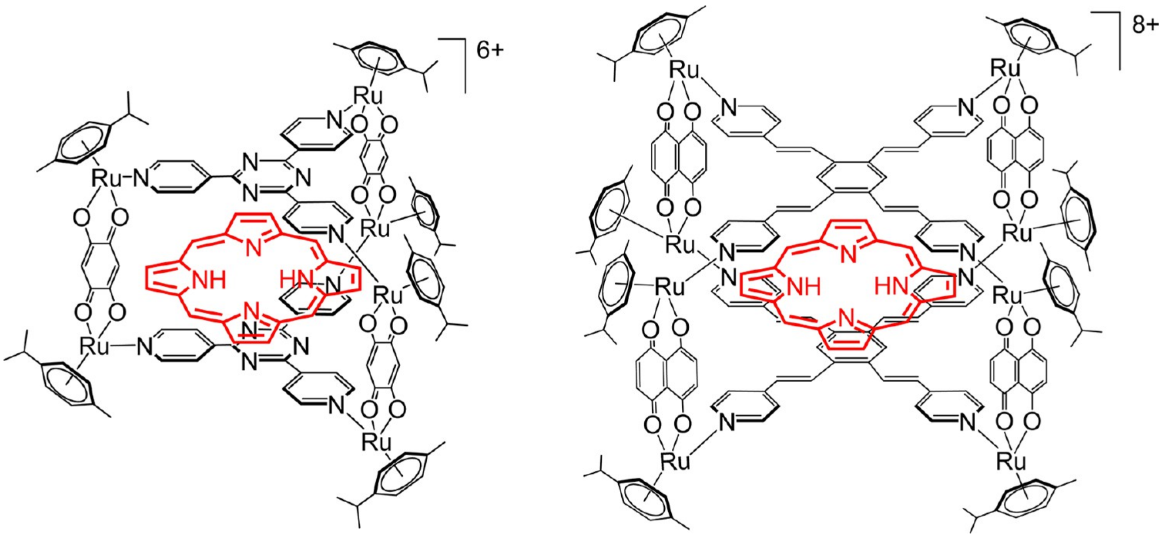
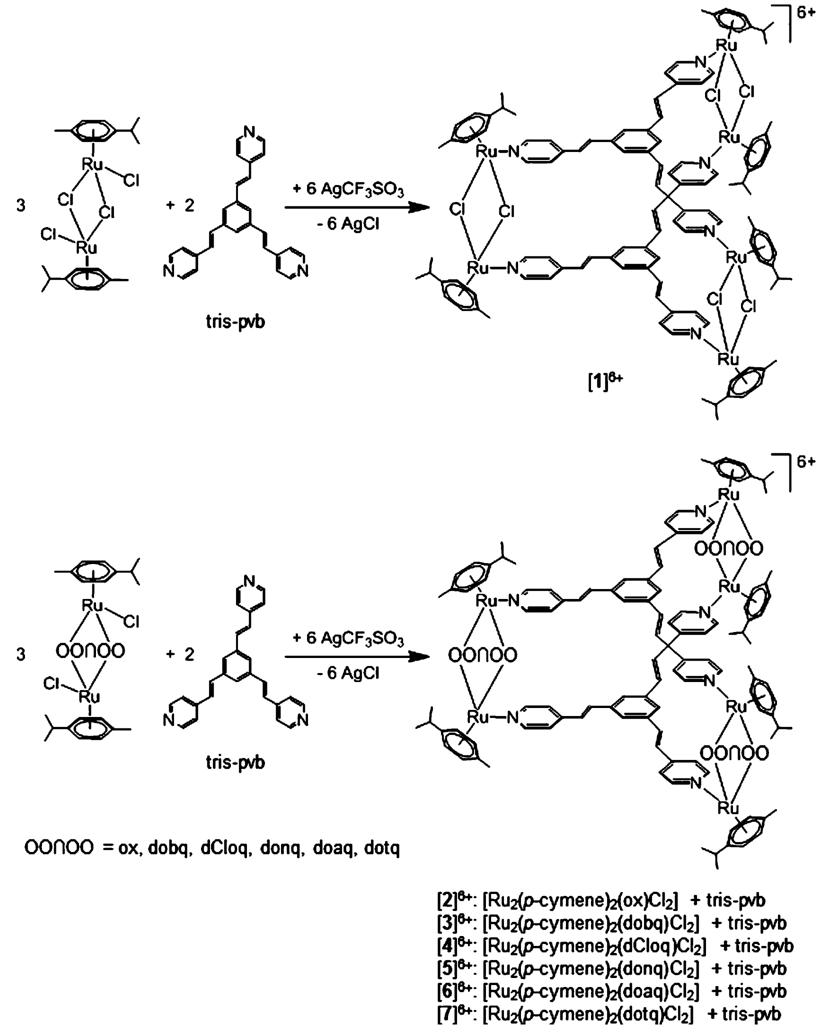


Figure 1. Porphin molecules encapsulated in hexa- and octanuclear arene ruthenium cages.[8]

Scheme 1. Synthesis of Hexanuclear Metalla-Assemblies Isolated as their Trifluoromethanesulfonate Salts

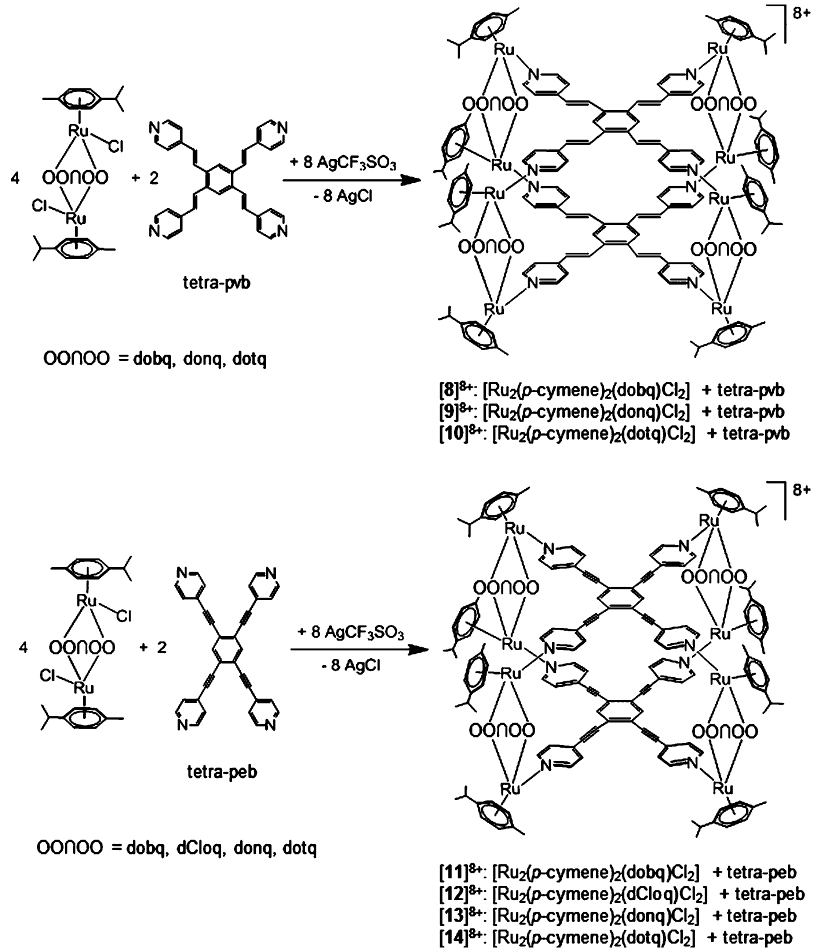


OO∩OO = ox, dobq, dCloq, donq, doaq, dotq

[2]$^{6+}$: [Ru$_2$(p-cymene)$_2$(ox)Cl$_2$] + tris-pvb
[3]$^{6+}$: [Ru$_2$(p-cymene)$_2$(dobq)Cl$_2$] + tris-pvb
[4]$^{6+}$: [Ru$_2$(p-cymene)$_2$(dCloq)Cl$_2$] + tris-pvb
[5]$^{6+}$: [Ru$_2$(p-cymene)$_2$(donq)Cl$_2$] + tris-pvb
[6]$^{6+}$: [Ru$_2$(p-cymene)$_2$(doaq)Cl$_2$] + tris-pvb
[7]$^{6+}$: [Ru$_2$(p-cymene)$_2$(dotq)Cl$_2$] + tris-pvb

Cl)$_6$]$^{6+}$, [Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(OO∩OO)$_3$]$^{6+}$, and [Ru$_8$(p-cymene)$_8$(NN∩NN)$_2$(OO∩OO)$_4$]$^{8+}$, isolated and characterized as the triflate salts, the abbreviations being tris-pvb = 1,3,5-tris{2-(pyridin-4-yl)vinyl}benzene, NN∩NN = 1,2,4,5-tetrakis{2-(pyridin-4-yl)vinyl}benzene (tetra-pvb), 1,2,4,5-tetrakis{2-(pyridin-4-yl)ethynyl}benzene (tetra-peb), OO∩OO = oxalato (ox), 2,5-dioxido-1,4-benzoquinonato (dobq), 2,5-dichloro-1,4-benzoquinonato (dCloq), 5,8-dioxi-

Scheme 2. Synthesis of Octanuclear Metalla-Assemblies Isolated as their Trifluoromethanesulfonate Salts



do-1,4-naphthoquinonato (donq), 5,8-dioxido-1,4-anthraquinonato (doaq), 6,11-dioxido-5,12-naphthacenedionato (dotq). The photosensitizers porphin, phthalocyanine, and Zn-phthalocyanine have been successfully encapsulated in five of the new organometallic cages. The host−guest properties of these systems were studied by various NMR experiments, with the aim of developing new drug delivery systems and improving the photodynamic properties.

■ RESULTS AND DISCUSSION

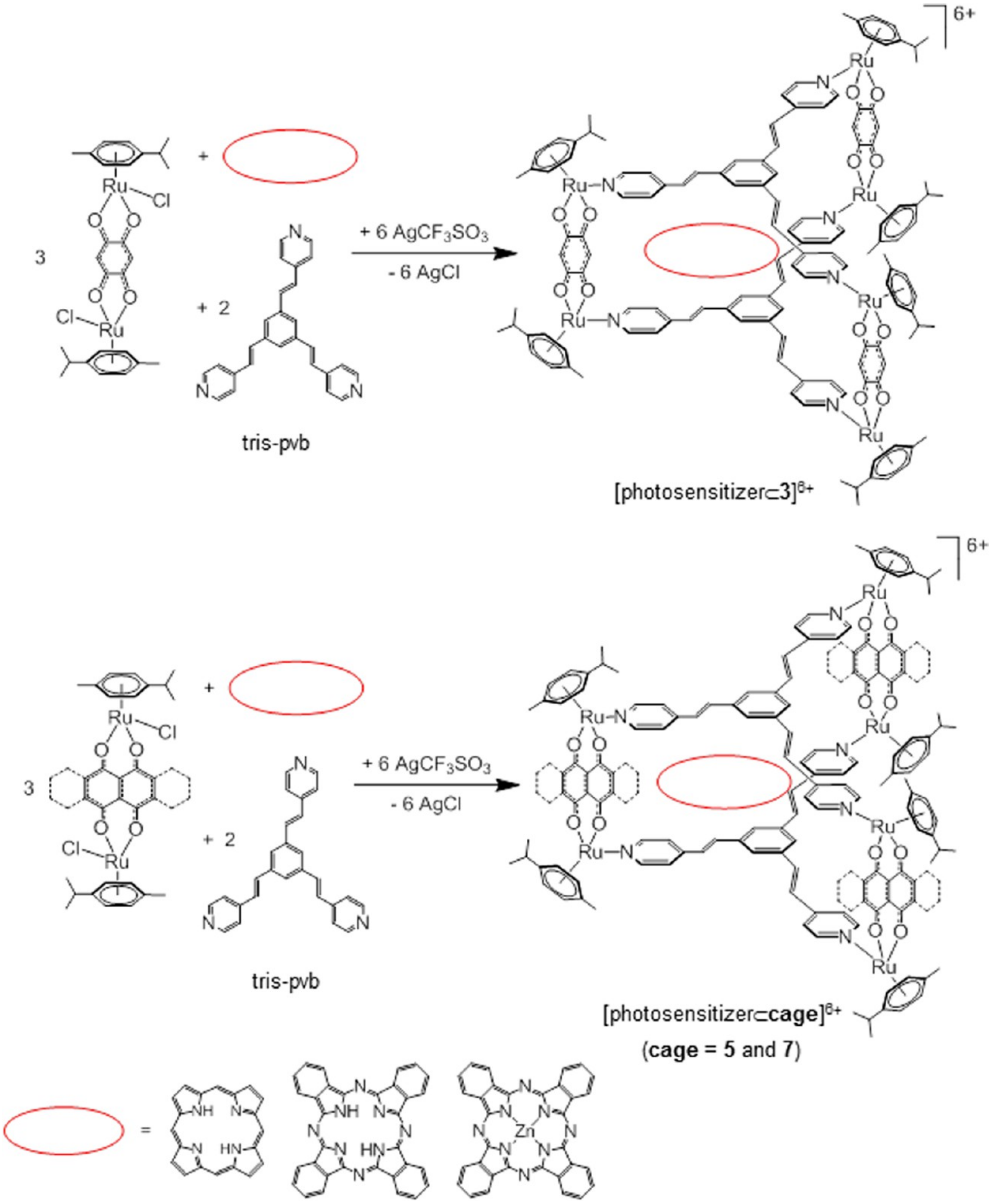
The synthesis of the arene ruthenium metalla-assemblies follows the same two-step strategy as in our previous work[6−8] and consists of reacting the dinuclear molecular clips $[Ru_2(p\text{-cymene})_2(\mu\text{-Cl})_2Cl_2]$, $[Ru_2(p\text{-cymene})_2(ox)Cl_2]$, $[Ru_2(p\text{-cymene})_2(dobq)Cl_2]$, $[Ru_2(p\text{-cymene})_2(dCloq)Cl_2]$, $[Ru_2(p\text{-cymene})_2(donq)Cl_2]$, $[Ru_2(p\text{-cymene})_2(doaq)Cl_2]$, and $[Ru_2(p\text{-cymene})_2(dotq)Cl_2]$ with the NN∩NN multidentate ligands (tris-pvb, tetra-pvb, and tetra-peb) in methanol in the presence of silver trifluoromethanesulfonate (halide scavenger). The silver chloride formed can be eliminated by filtration, and the resulting cationic *p*-cymene metalla-assemblies can be isolated as the trifluoromethanesulfonate salts in good yield (Schemes 1 and 2).

The addition of 1 equiv of coronene during the synthesis of the hexanuclear complexes $[\mathbf{3}]^{6+}$−$[\mathbf{7}]^{6+}$ leads to the direct encapsulation of the guest molecule in the cavity of the trigonal-prismatic complexes. The smaller hexanuclear assemblies $[\mathbf{1}]^{6+}$ and $[\mathbf{2}]^{6+}$ do not have a large enough cavity to allow the encapsulation of coronene. Using the same method, porphin, phthalocyanine, and Zn-phthalocyanine are also encapsulated in the cavity of the cages $[\mathbf{3}]^{6+}$, $[\mathbf{5}]^{6+}$, $[\mathbf{7}]^{6+}$, $[\mathbf{9}]^{8+}$, and $[\mathbf{13}]^{8+}$ (Schemes 3 and 4). However, these photosensitizers are completely encapsulated only in the cavity of the hexanuclear cage $[\mathbf{3}]^{6+}$ and the octanuclear cage $[\mathbf{9}]^{8+}$; in the hexanuclear cages $[\mathbf{5}]^{6+}$ and $[\mathbf{7}]^{6+}$, the NMR spectra reveal an equilibrium between empty and filled cages. In the case of the octanuclear cage $[\mathbf{13}]^{8+}$, only phthalocyanine and Zn-phthalocyanine are encapsulated, likewise showing an equilibrium between empty and filled cages. The octanuclear cage $[\mathbf{13}]^{8+}$ seems to be less flexible than the octanuclear cage $[\mathbf{9}]^{8+}$; therefore, it cannot withhold the small porphin in a stable fashion.

The infrared spectra of all compounds exhibit a strong absorption around 1260 cm^{-1} due to the stretching vibrations C_{sp^3}−F of the trifluoromethanesulfonate anions, together with an absorption due to the stretching vibrations C_{sp^2}−H of the NN∩NN ligands around 3070 cm^{-1}. In addition to these absorptions, strong characteristic C=O stretching vibration bands are observed for complexes $[\mathbf{2}]^{6+}$−$[\mathbf{14}]^{8+}$. In particular, bands around 1630 cm^{-1} are due to the oxalato ligand and the bands at 1525 and 1500 cm^{-1} are caused by the dobq and dCloq ligands, respectively, while absorptions around 1540 cm^{-1} are due to the donq, doaq, and dotq ligands.

The electronic absorption spectra of the metalla-cages are characterized by an intense high-energy band centered at around 340 nm, which is assigned to a ligand-localized or

Scheme 3. Encapsulation of Photosensitizer Molecules in Hexanuclear Metalla-Cages



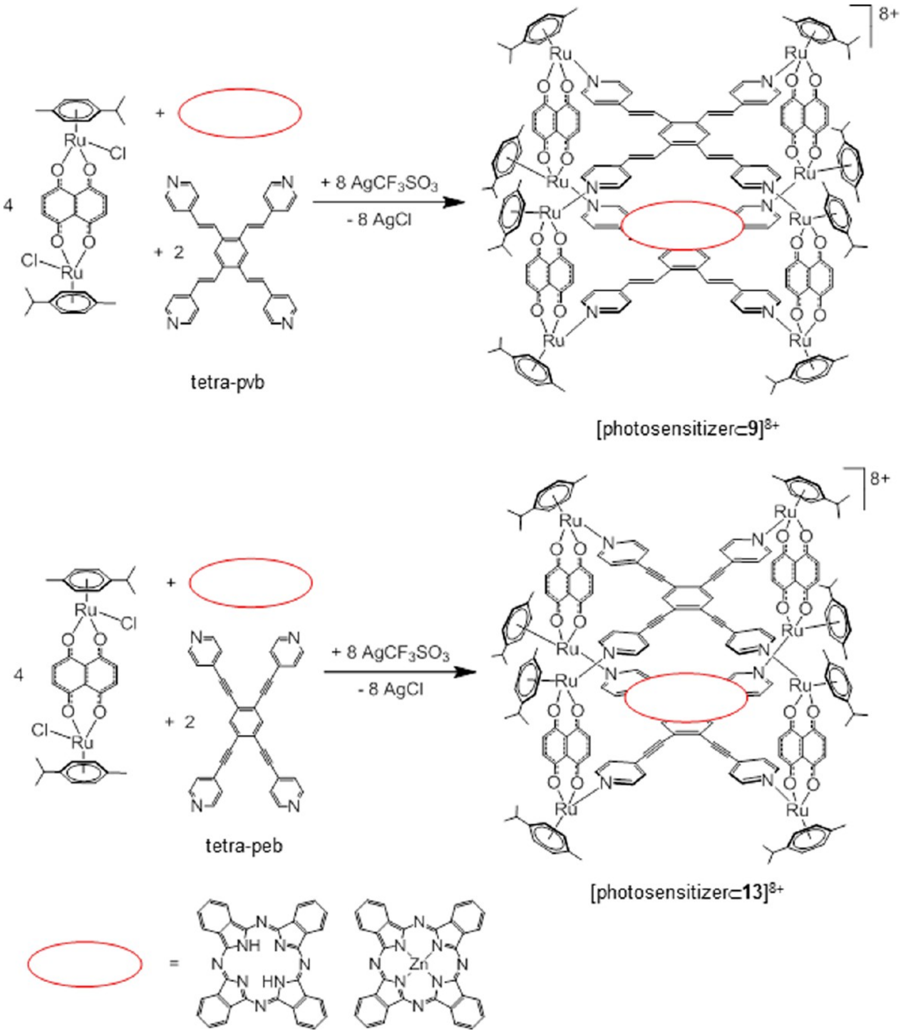
intraligand $\pi \rightarrow \pi^*$ transition as well as broad low-energy bands related to metal-to-ligand charge transfer (MLCT) transitions. In the case of the systems [porphin⊂**cage**]$^{6+}$, an additional band caused by the characteristic absorption of porphin is observed at around 395 nm (Figure 2). Similarly, the systems [Zn-phthalocyanine⊂**cage**]$^{6+}$ and [Zn-phthalocyanine⊂**cage**]$^{8+}$ show an absorption around 690 nm due to Zn-phthalocyanine. Finally, for the systems [phthalocyanine⊂**cage**]$^{6+}$ and [phthalocyanine⊂**cage**]$^{8+}$, two absorptions around 670 and 710 nm are identified.

The formation of the systems [photosensitizer⊂**cage**]$^{n+}$ (n = 6, 8; **cage** = **3**, **5**, **7**, **9**, **13**) can be followed by ^{1}H NMR spectroscopy. During the formation of these systems, the signals associated with the different pyridyl, vinyl, and benzene protons of the tris-pvb, tetra-pvb, and tetra-peb panels are shifted upfield, while the signals of the ligands dobq, donq, and dotq are shifted downfield in comparison to the protons of the empty host complexes. On the other hand, the signals corresponding to the *p*-cymene ligands, due to their localization in the periphery of the metalla-assemblies, are not affected by the presence of a guest molecule in the cavity.

The ^{1}H NMR spectrum of the system [Zn-phthalocyanine⊂**9**]$^{8+}$ shows that the signals associated with the pyridyl protons (H$_\beta$) of the tetra-pvb ligand are shifted upfield by 0.6 ppm, as compared to the corresponding signals for the empty cage (Figure 3). Similarly, the signals of the vinyl (H$_A$ and H$_B$) and benzene (H$_C$) protons are shifted upfield by as much as 3.2 ppm, relative to those of the empty cage [**9**]$^{8+}$. The signals of the donq ligands are shifted downfield by ca. 0.4 ppm, while the *p*-cymene proton signals do not shift but split in some cases.

The 2D ROESY and 2D NOESY experiments confirm the encapsulation of photosensitizers in the cavity of the metalla-cages [**3**]$^{6+}$, [**5**]$^{6+}$, [**7**]$^{6+}$, [**9**]$^{8+}$, and [**13**]$^{8+}$ (Figures 4 and 5 and Figures S1−S3 (Supporting Information)). 2D nuclear Overhauser effect spectroscopy (NOESY), rotational frame nuclear Overhauser effect spectroscopy (ROESY), and diffusion

Scheme 4. Encapsulation of Phthalocyanine Derivatives in Octanuclear Metalla-Cages



ordered spectroscopy (DOSY) are powerful NMR techniques for investigating in solution the behavior of chemical complexes large molecular weights. For example, the 2D ROESY spectra of the system [phthalocyanine⊂**3**]$^{6+}$ clearly show a strong nuclear Overhauser effect of the aromatic phthalocyanine protons with the pyridyl protons (H_α and H_β) and vinyl protons (H_A and H_B) of the tris-pvb ligands, together with a weaker ROE signal between these phthalocyanine protons and the vinyl dobq ligand protons (H_{dobq}) (Figure 4). Moreover, ROEs between the NH phthalocyanine protons and the vinyl protons of the tris-pvb ligands (H_A and H_B) are observed. Thus, interactions between phthalocyanine and the dobq molecular clip as well as between phthalocyanine and the tris-pvb panels are clearly established. Since no interaction between phthalocyanine and the *p*-cymene ligands is observed, we can conclude that the photosensitizer guest molecule is in fact encapsulated inside the cavity of the host complex [**3**]$^{6+}$.

In these large systems, ROESY experiments perform better than NOESY experiments for determining close intramolecular and intermolecular interactions. The [photosensitizer⊂**cage**]$^{n+}$ systems have a molecular weight >3800, and the $\omega\tau_c$ value for such systems is close to 1.12 (where ω is the proton Larmor frequency and τ_c is the tumbling correlation time), where the NOE effect crosses the null point. Therefore, the NOE cross peaks are weak, can possess opposite signs, or can even be absent. This behavior can be seen in the 2D NOESY spectrum of the [porphin⊂**5**]$^{6+}$ system (Figure 5), in which both positive and negative NOE peaks are observed. Positive NOEs between the signals associated to the porphin protons and those of the donq ligands as well as between the porphin protons and those of the tris-pvb panels are indicative of a fast motion of the porphin molecule inside the cavity of [**5**]$^{6+}$ (Figure 5). In the case of phthalocyanine and Zn-phthalocyanine, this fast motion is not observed due to a significantly lower mobility of these larger photosensitizers in the cavity. Moreover, rapid rotation of the *p*-cymene moiety is also observed, as inferred from the positive NOEs between the *p*-cymene signals and those of the tris-pvb panels and the donq ligands. The correlation time of these fast internal motions has to be faster than the overall tumbling correlation time.

Thanks to the 2D ROESY measurements, approximate distances between protons of the photosensitizers and those of the cages were estimated for the two systems [Zn-phthalocyanine⊂**13**]$^{8+}$ and [phthalocyanine⊂**3**]$^{6+}$ (Tables 1 and 2). The 2D ROESY experiments were recorded with a spin-lock time of 300 ms. Under these conditions, only direct ROE cross peaks were observed and no three spin effect cross peaks were detected. Therefore, the ROE cross peaks represent genuine close intermolecular interactions between the phthalocyanine and the cage. The size of the complex allows

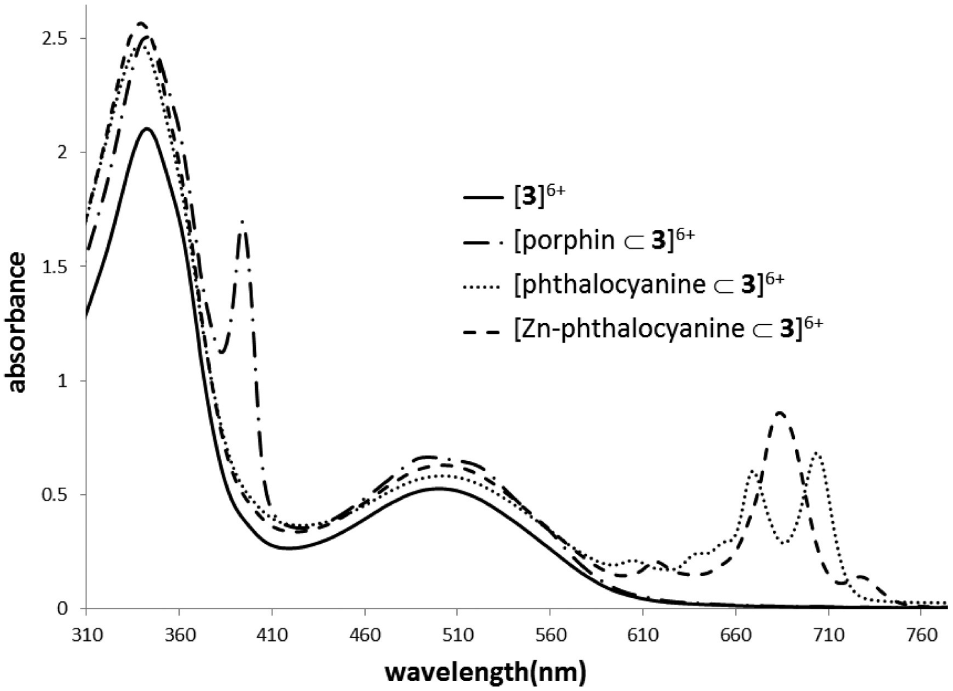


Figure 2. UV–visible spectra of the [photosensitizer⊂**3**]$^{6+}$ systems (1.0×10^{-5} M in CH_2Cl_2).

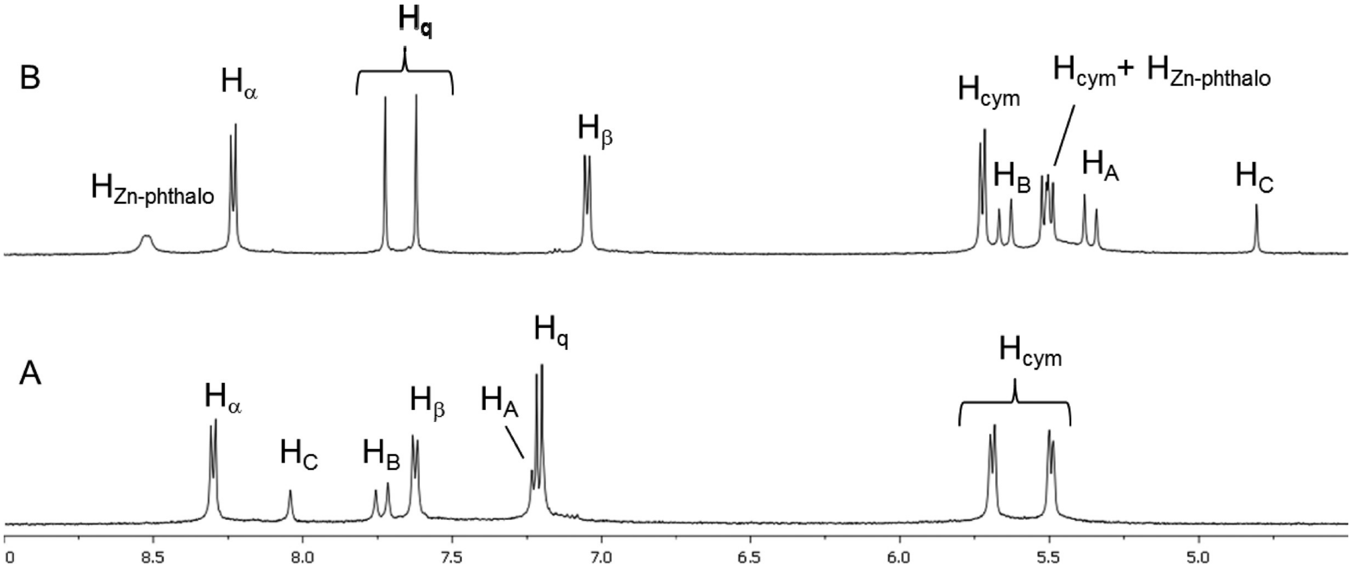


Figure 3. ^{1}H NMR comparison spectra of the empty cage [**9**]$^{8+}$ (A) and the system [Zn-phthalocyanine⊂**9**]$^{8+}$ (B) (in CD_3CN at 25 °C).

an estimation of 4.5 Å for the upper limit of the distances that can be detected. The derived distances have a high standard deviation (0.5 Å) for the complex [Zn-phthalocyanine⊂**13**]$^{8+}$ due to the broadness of the NMR signals, whereas for the system [phthalocyanine⊂**3**]$^{6+}$ the standard deviation for the estimated distances is 0.25 Å. Thus, the estimated distance (d) between the protons $H2_{\text{Zn-phthalo}}$ of the Zn-phthalocyanine and the protons H_{donq} of the molecular clip is approximately 4 Å (3.5 Å < d < 4.5 Å). Roughly, the same distances are calculated between the $H2_{\text{Zn-phthalo}}$ protons and the two different protons H_α and H_β of the tetra-peb panels. The protons $H1_{\text{Zn-phthalo}}$ of the photosensitizer show only one correlation with the protons H_β of the tetra-peb of the cage, and the distance with these protons is evaluated to be about 3.3 Å.

The 2D ROESY spectra of the system [phthalocyanine⊂**3**]$^{6+}$ show that the protons $H1_{\text{phthalo}}$ of the photosensitizer are close to the protons H_β and $H_{A/B}$ of the tris-pvb at a distance ranging from 3.2 to 4.0 Å. The longer distances between the $H1_{\text{phthalo}}$ protons and the H_α and H_C protons of the panels are evaluated to be approximately 4.4 and 4.5 Å, respectively. Moreover, the protons $H2_{\text{phthalo}}$ of the phthalocyanine seem to be at equivalent distances from the protons H_α and H_β of the tris-pvb panels at about 3.9 Å and near the protons H_{dobq} of the molecular clip at a distance of 4.1 Å. The NH protons of the phthalocyanine are also close to the protons H_C and $H_{A/B}$ at distances between 3.2 and 4.0 Å.

Finally, the encapsulation of the photosensitizers within the metalla-assemblies [**3**]$^{6+}$, [**5**]$^{6+}$, [**7**]$^{6+}$, [**9**]$^{8+}$, and [**13**]$^{8+}$ was further studied by DOSY measurements (Figure 6 and Figures

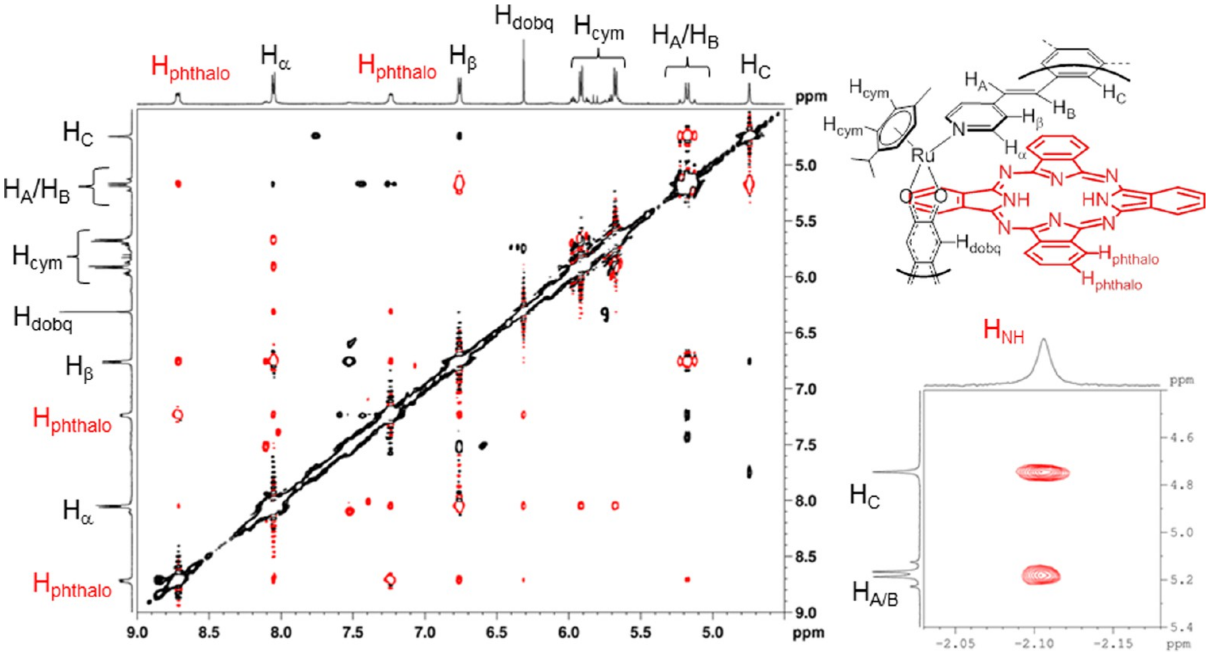


Figure 4. 2D ROESY spectrum of the system [phthalocyanine⊂3]$^{6+}$ (in CD_3CN at 25 °C) and assignment of the aromatic protons.

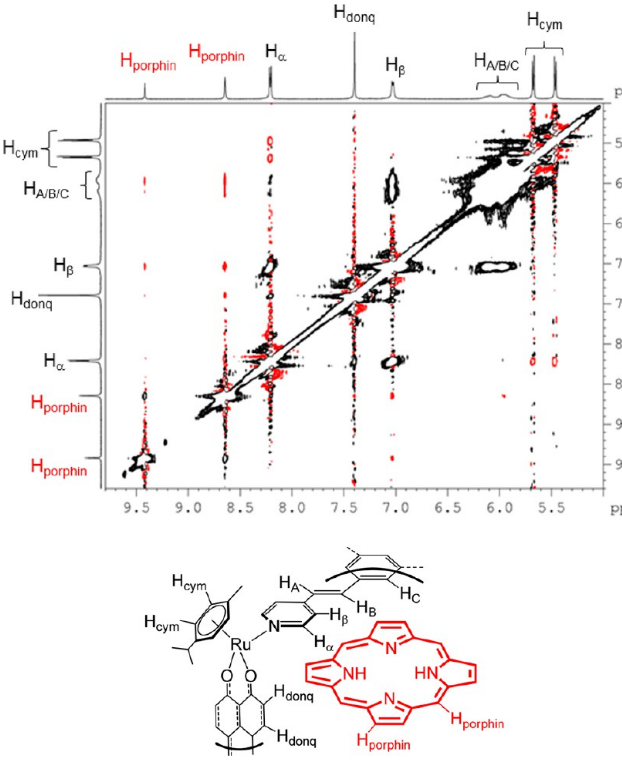


Figure 5. 2D NOESY spectrum of the system [porphin⊂5]$^{6+}$ (in CD_3CN at 25 °C) and assignment of the aromatic protons.

S4−S8 (Supporting Information)), which confirm the encapsulation of the photosensitizer guest molecules inside the cavity of the host metalla-cages. The DOSY experiments were recorded in CD_3CN and at 25 °C for all of the samples using the pulsed gradient stimulated echo pulse sequence. The DOSY spectra of the systems [phthalocyanine⊂**9**]$^{8+}$ and [Zn-phthalocyanine⊂**9**]$^{8+}$ show at ~4.5 × 10^{-10} m^2 s^{-1} almost equivalent diffusion coefficients in comparison to the empty cage [**9**]$^{8+}$, suggesting that the photosensitizers diffuse at the same rate (within the experimental error) as the host metalla-cages. The diffusion coefficient D is given by the Stokes−Einstein equation:

$$D = \frac{kT}{6\pi\eta r}$$

where k is the Boltzmann constant, T is the temperature, η is the solvent viscosity, and r is the hydrodynamic radius of the compound. It is worth noting that, upon encapsulation of the guest in the metalla-cages, there is no significant change of the hydrodynamic radius of the metalla-cages. This results in similar diffusion coefficients for both the empty and filled metalla-cages, despite their different molecular weights.

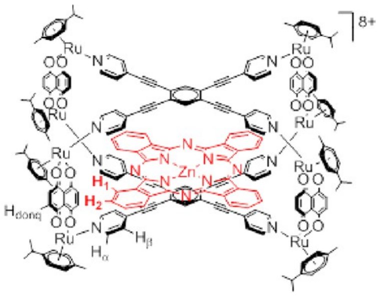
The H···H distances estimated by 2D ROESY measurements were also confirmed by modelization of the [photosensitizer⊂**cage**]$^{n+}$ systems using Chem3D software.[13] For example, in the [phthalocyanine⊂**13**]$^{8+}$ system (Figure 7), the distance between the planes of the phthalocyanine guest molecule and the tetra-peb panels is estimated at ~3.6 Å, and the distance between the NH protons of the phthalocyanine and the protons of the benzene moieties is expected to be 3.8 Å. Overall, the metrical parameters obtained by modelization fit well with those estimated by 2D ROESY measurements, thus further confirming the formation of the [photosensitizer⊂**cage**]$^{n+}$ systems.

■ EXPERIMENTAL SECTION

General Considerations. [Ru_2(*p*-cymene)$_2$(μ-Cl)$_2Cl_2$],[14] [Ru_2(*p*-cymene)$_2$(ox)Cl_2],[15] [Ru_2(*p*-cymene)$_2$(dobq)Cl_2],[7a] [Ru_2(*p*-cymene)$_2$(dCloq)Cl_2],[6a] [Ru_2(*p*-cymene)$_2$(donq)Cl_2],[6b] [Ru_2(*p*-cymene)$_2$(doaq)Cl_2],[16] [Ru_2(*p*-cymene)$_2$(dotq)Cl_2],[17] 1,3,5-tris{2-(4-pyridyl)vinyl}benzene (tris-pvb),[18] 1,2,4,5-tetrakis{2-(4-pyridyl)-vinyl}benzene (tetra-pvb),[18] and 1,2,4,5-tetrakis{2-(4-pyridyl)-ethynyl}benzene (tetra-peb)[18] were prepared according to published methods. Porphin, phthalocyanines, and all other reagents were commercially available (Sigma-Aldrich, Frontier Scientific) and used as received. The ^1H, $^{13}C\{^1H\}$, ^1H 2D DOSY, ^1H 2D ROESY, and ^1H 2D NOESY NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 25 °C by using the residual protonated solvent as

Table 1. Estimated H···H Distances of the System [Zn-phthalocyanine⊂13]$^{8+}$ from 2D ROESY Measurements[a]

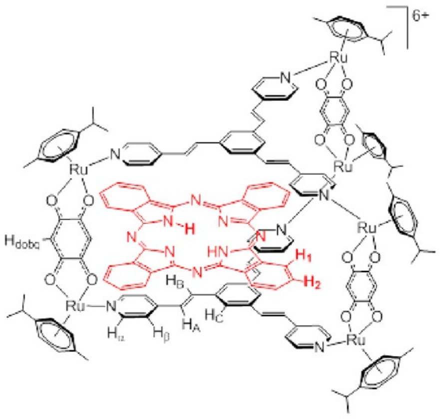
Protons concerned	Distance (Å)	SD (Å)
$H1_{Zn\text{-}phthalo}/H_{\beta}$	3.3	±0.5
$H2_{Zn\text{-}phthalo}/H_{donq}$	4.0	±0.5
$H2_{Zn\text{-}phthalo}/H_{\alpha}$	4.0	±0.5
$H2_{Zn\text{-}phthalo}/H_{\beta}$	4.0	±0.5



[a]See Figure S2 (Supporting Information).

Table 2. Estimated H···H Distances of the System [Phthalocyanine⊂3]$^{6+}$ from 2D ROESY Measurements[a]

Protons concerned	Distance (Å)	SD (Å)
$H1_{phthalo}/H_{\alpha}$	4.4	±0.25
$H1_{phthalo}/H_{\beta}$	3.5	±0.25
$H1_{phthalo}/H_{A/B}$	3.8	±0.25
$H1_{phthalo}/H_{C}$	4.5	±0.25
$H2_{phthalo}/H_{\alpha}$	3.9	±0.25
$H2_{phthalo}/H_{\beta}$	3.9	±0.25
$H2_{phthalo}/H_{dobq}$	4.1	±0.25
$NH_{phthalo}/H_{C}$	3.5	±0.25
$NH_{phthalo}/H_{A/B}$	3.7	±0.25



[a]See Figure 4.

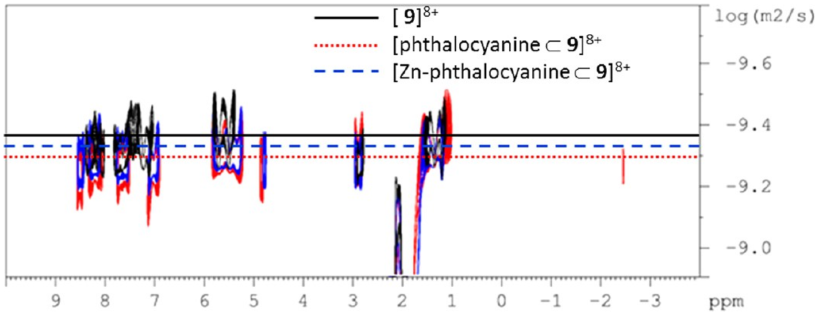


Figure 6. Superposition of the DOSY spectra of the empty metalla-cage [**9**]$^{8+}$, [phthalocyanine⊂**9**]$^{8+}$, and [Zn-phthalocyanine⊂**9**]$^{8+}$ (in CD_3CN at 25 °C).

internal standard. The 2D ROESY and NOESY experiments were recorded with 8 or 16 scans for each of the 400 t_1 increments. The duration of the spin-lock time in the ROESY and the mixing time in the NOESY experiments were 0.3 and 0.4 s, respectively. The spin lock in the ROESY was performed with a train of 180 (x) − 180 ($-x$) pulses for reducing the TOCSY magnetization transfer.[19] The data were multiplied with a cosine window function in both dimensions prior to Fourier transformation and zero-filled to 2048 and 1024 points in ω_2 and ω_1 dimensions, respectively. The 2D DOSY experiments were recorded using the pulsed gradient stimulated echo sequence[20] and bipolar gradients for reducing eddy currents.[21] The strength of the gradients was incremented from 2% (first value) to 95% (last value) in 32 or 64 regular steps. Typically 8 or 16 scans were recorded for each increment. The data were multiplied with exponential window functions prior to Fourier transformations. The DOSY software module of the Bruker Topspin program was used for processing the data in the F_1 dimension. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer FTIR 1720 X spectrometer. UV−visible absorption spectra were recorded on an Uvikon 930 spectrophotometer using precision cells made of quartz (1 cm). Electrospray ionization mass spectra were recorded in positive-ion mode with a Bruker FTMS 4.7T BioAPEX II mass spectrometer (University of Fribourg, Fribourg, Switzerland). Microanalyzes were performed by the Mikroelementarisches Laboratorium, ETH Zürich (Zürich, Switzerland). Atom labeling for characterization data is given in Chart 1.

Synthesis of Metalla-Prisms [1]$^{6+}$–[7]$^{6+}$: General Procedure. A mixture of 1.5 equiv of molecular clip ([Ru_2(p-cymene)$_2$(μ-Cl)$_2$$Cl_2$], 55.1 mg; [$Ru_2$($p$-cymene)$_2(ox)Cl_2$], 56.7 mg; [$Ru_2$($p$-cymene)$_2$(dobq)$Cl_2$], 61.2 mg; [$Ru_2$($p$-cymene)$_2$(dCloq)$Cl_2$], 67.4 mg; [$Ru_2$($p$-cymene)$_2$(donq)$Cl_2$], 65.7 mg; [$Ru_2$($p$-cymene)$_2$(doaq)-$Cl_2$], 70.2 mg; [$Ru_2$($p$-cymene)$_2$(dotq)$Cl_2$], 74.7 mg; 0.09 mmol), 3 equiv of Ag(CF_3SO_3) (46.2 mg, 0.18 mmol), and 1 equiv of tris-pvb (23.2 mg, 0.06 mmol) in MeOH (20 mL) was stirred at reflux for 24 h

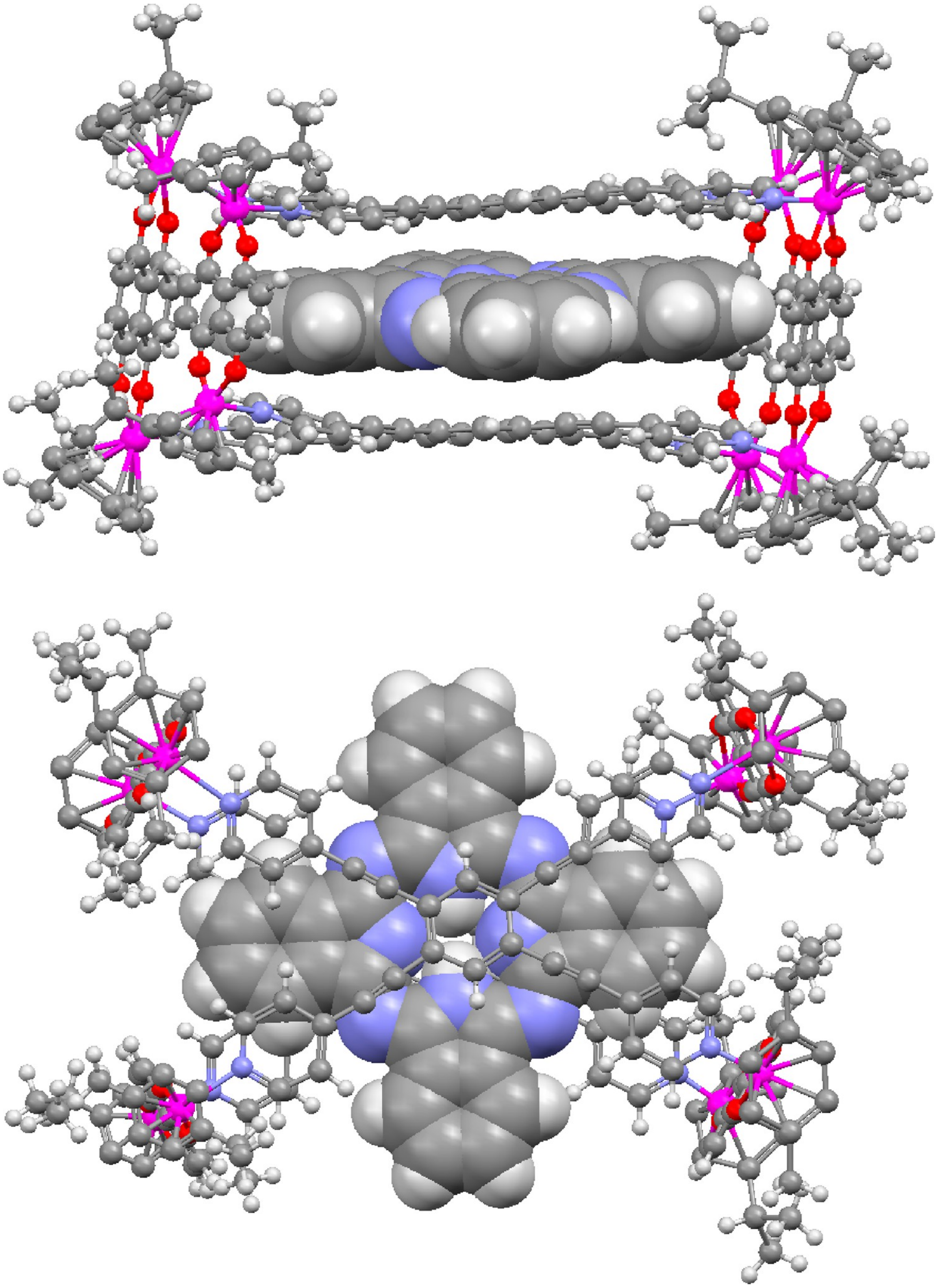
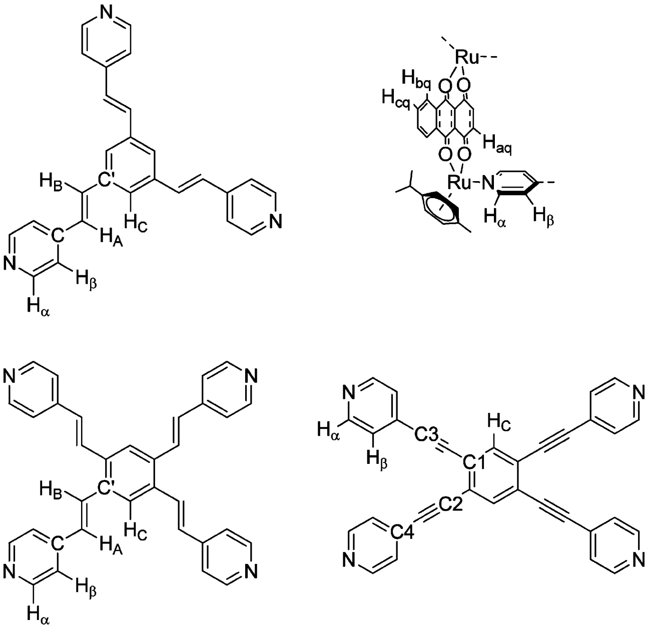


Figure 7. Chem 3D model of [phthalocyanine⊂**13**]$^{8+}$: side and top views.

and then filtered. The solvent was removed, and the dark residue was dissolved in CH_2Cl_2/CH_3CN (1/1, 3 mL), before slowly adding diethyl ether to precipitate a dark red, dark purple, or dark green solid. The solid was filtered, washed with diethyl ether, and dried under vacuum.

*[Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(μ-Cl)$_6$][CF$_3$SO$_3$]$_6$ ([**1**][CF$_3$SO$_3$]$_6$).* Yield: 60.2 mg (61%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 347 nm (ε = 1.61×10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3067 (m, aromatic, C–H), 1262 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.72 (d, ^3J = 6.7 Hz, 12H, H_α), 7.96 (s, 6H, H_C), 7.68 (d, ^3J = 6.7 Hz, 12H, H_β), 7.66 (d, ^3J = 16.4 Hz, 6H, H_B), 7.45 (d, ^3J = 16.4 Hz, 6H, H_A), 5.83 (d, ^3J = 6.1 Hz, 6H, $H_{p\text{-cym}}$), 5.79 (d, ^3J = 6.1 Hz, 6H, $H_{p\text{-cym}}$), 5.61 (d, ^3J = 6.1 Hz, 6H, $H_{p\text{-cym}}$), 5.54 (d, ^3J = 6.1 Hz, 6H, $H_{p\text{-cym}}$), 2.87 (sept, ^3J = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.04 (s, 18H, CH_3), 1.31 (d, ^3J =

Chart 1



6.9 Hz, 36H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 155.7 (CH$_\alpha$), 148.3 (C$_{\text{tris-pvb}}$), 138.2 (C′$_{\text{tris-pvb}}$), 136.2 (CH$_B$), 128.0 (CH$_C$), 126.7 (CH$_A$), 123.6 (CH$_\beta$), 106.6 (C$_{p\text{-cym}}$), 102.1 (C$_{p\text{-cym}}$), 86.9 (CH$_{p\text{-cym}}$), 85.9 (CH$_{p\text{-cym}}$), 84.5 (CH$_{p\text{-cym}}$), 31.7 (CH(CH$_3$)$_2$), 22.3 (CH(CH$_3$)$_2$), 22.3 (CH(CH$_3$)$_2$), 18.3 (CH$_3$). MS (ESI positive mode): *m*/*z* 949.04 [**1** + 3 CF$_3$SO$_3$]$^{3+}$. Anal. Calcd for C$_{120}$H$_{126}$Cl$_6$F$_{18}$N$_6$O$_{18}$Ru$_6$S$_6$·4CH$_2$Cl$_2$: C, 40.99; H, 3.72; N, 2.31. Found: C, 40.79; H, 3.88; N, 2.51.

*[Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(ox)$_3$][CF$_3$SO$_3$]$_6$ ([**2**][CF$_3$SO$_3$]$_6$).* Yield: 62.1 mg (62%). UV–vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 346 nm (ε = 0.94 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3069 (m, aromatic, C–H), 1631 (s, oxalato, C=O), 1261 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 7.83 (d, ^3J = 6.2 Hz, 12H, H$_\alpha$), 7.61 (s, 6H, H$_C$), 7.43 (d, ^3J = 6.2 Hz, 12H, H$_\beta$), 7.39 (d, ^3J = 16.4 Hz, 6H, H$_B$), 7.24 (d, ^3J = 16.4 Hz, 6H, H$_A$), 5.80 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 5.64 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 2.79 (sept, ^3J = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 2.14 (s, 18H, CH$_3$), 1.31 (d, ^3J = 6.9 Hz, 36H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 171.0 (CO), 152.1 (CH$_\alpha$), 148.3 (C$_{\text{tris-pvb}}$), 136.5 (C′$_{\text{tris-pvb}}$), 136.5 (CH$_B$), 127.8 (CH$_C$), 125.1 (CH$_A$), 122.9 (CH$_\beta$), 102.3 (C$_{p\text{-cym}}$), 97.4 (C$_{p\text{-cym}}$), 82.0 (CH$_{p\text{-cym}}$), 81.4 (CH$_{p\text{-cym}}$), 30.9 (CH(CH$_3$)$_2$), 21.4 (CH(CH$_3$)$_2$), 17.2 (CH$_3$). MS (ESI positive mode): *m*/*z* 966.08 [**2** + 3 CF$_3$SO$_3$]$^{3+}$, 1523.12 [**2** + 4 CF$_3$SO$_3$]$^{2+}$. Anal. Calcd for C$_{126}$H$_{126}$F$_{18}$N$_6$O$_{30}$Ru$_6$S$_6$·5CH$_2$Cl$_2$: C, 41.74; H, 3.64; N, 2.23. Found: C, 41.50; H, 3.77; N, 2.44.

*[Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(dobq)$_3$][CF$_3$SO$_3$]$_6$ ([**3**][CF$_3$SO$_3$]$_6$).* Yield: 94.5 mg (90%). UV–vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 343 nm (ε = 2.10 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 502 nm (ε = 0.53 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3069 (m, aromatic, C–H), 1525 (s, dobq, C=O), 1258 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.11 (d, ^3J = 6.4 Hz, 12H, H$_\alpha$), 7.78 (s, 6H, H$_C$), 7.54 (d, ^3J = 6.4 Hz, 12H, H$_\beta$), 7.47 (d, ^3J = 16.5 Hz, 6H, H$_B$), 7.26 (d, ^3J = 16.5 Hz, 6H, H$_A$), 5.86 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 5.73 (s, 12H, H$_{\text{dobq}}$), 5.64 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 2.83 (sept, ^3J = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 2.12 (s, 18H, CH$_3$), 1.32 (d, ^3J = 6.9 Hz, 36H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 185.2 (CO), 153.7 (CH$_\alpha$), 148.5 (C$_{\text{tris-pvb}}$), 137.6 (C′$_{\text{tris-pvb}}$), 136.1 (CH$_B$), 128.2 (CH$_C$), 125.8 (CH$_A$), 123.9 (CH$_\beta$), 104.4 (C$_{p\text{-cym}}$), 102.4 (CH$_{\text{dobq}}$), 99.6 (C$_{p\text{-cym}}$), 84.5 (CH$_{p\text{-cym}}$), 82.7 (CH$_{p\text{-cym}}$), 32.0 (CH(CH$_3$)$_2$), 22.4 (CH(CH$_3$)$_2$), 18.2 (CH$_3$). MS (ESI positive mode): *m*/*z* 724.83 [**3** + 2 CF$_3$SO$_3$]$^{4+}$, 1016.43 [**3** + 3 CF$_3$SO$_3$]$^{3+}$, 1598.66 [**3** + 4 CF$_3$SO$_3$]$^{2+}$. Anal. Calcd for C$_{138}$H$_{132}$F$_{18}$N$_6$O$_{30}$Ru$_6$S$_6$·9CH$_2$Cl$_2$: C, 41.45; H, 3.55; N, 1.97. Found: C, 41.21; H, 3.68; N, 2.23.

*[Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(dCloq)$_3$][CF$_3$SO$_3$]$_6$ ([**4**][CF$_3$SO$_3$]$_6$).* Yield: 103.3 mg (93%). UV–vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 343 nm (ε = 2.13 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 520 nm (ε = 0.49 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3069 (m, aromatic, C–H), 1500 (s, dCloq, C=O), 1260 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.12 (d, ^3J = 6.3 Hz, 12H, H$_\alpha$), 7.78 (s, 6H, H$_C$), 7.55 (d, ^3J = 6.3 Hz, 12H, H$_\beta$), 7.47 (d, ^3J = 16.5 Hz, 6H, H$_B$), 7.26 (d, ^3J = 16.5 Hz, 6H, H$_A$), 5.93 (d, ^3J = 6.2 Hz, 12H, H$_{p\text{-cym}}$), 5.74 (d, ^3J = 6.2 Hz, 12H, H$_{p\text{-cym}}$), 2.88 (sept, ^3J = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 2.19 (s, 18H, CH$_3$), 1.37 (d, ^3J = 6.9 Hz, 36H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 178.7 (CO), 153.7 (CH$_\alpha$), 148.7 (C$_{\text{tris-pvb}}$), 137.6 (C′$_{\text{tris-pvb}}$), 136.3 (CH$_B$), 128.4 (CH$_C$), 125.8 (CH$_A$), 124.0 (CH$_\beta$), 107.1 (C$_{\text{dCloq}}$), 104.9 (C$_{p\text{-cym}}$), 99.4 (C$_{p\text{-cym}}$), 84.4 (CH$_{p\text{-cym}}$), 83.4 (CH$_{p\text{-cym}}$), 32.2 (CH(CH$_3$)$_2$), 22.3 (CH(CH$_3$)$_2$), 18.3 (CH$_3$). MS (ESI positive mode): *m*/*z* 776.52 [**4** + 2 CF$_3$SO$_3$]$^{4+}$, 1085.35 [**4** + 3 CF$_3$SO$_3$]$^{3+}$, 1702.49 [**4** + 4 CF$_3$SO$_3$]$^{2+}$. Anal. Calcd for C$_{138}$H$_{126}$Cl$_6$F$_{18}$N$_6$O$_{30}$Ru$_6$S$_6$·7CH$_2$Cl$_2$·CH$_3$CN: C, 40.70; H, 3.32; N, 2.26. Found: C, 40.68; H, 3.55; N, 2.28.

*[Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(donq)$_3$][CF$_3$SO$_3$]$_6$ ([**5**][CF$_3$SO$_3$]$_6$).* Yield: 96.7 mg (88%). UV–vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 337 nm (ε = 1.72 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 590 nm (ε = 0.05 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 643 nm (ε = 0.08 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 700 nm (ε = 0.09 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3059 (m, aromatic, C–H), 1535 (s, donq, C=O), 1259 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.23 (d, ^3J = 5.9 Hz, 12H, H$_\alpha$), 7.67 (s, 6H, H$_C$), 7.42 (d, ^3J = 5.9 Hz, 12H, H$_\beta$), 7.35 (d, ^3J = 16.8 Hz, 6H, H$_B$), 7.19 (s, 12H, H$_{\text{donq}}$), 7.15 (d, ^3J = 16.8 Hz, 6H, H$_A$), 5.66 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 5.46 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 2.81 (sept, ^3J = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 2.08 (s, 18H, CH$_3$), 1.30 (d, ^3J = 6.9 Hz, 36H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 171.7 (CO), 152.8 (CH$_\alpha$), 148.4 (C$_{\text{tris-pvb}}$), 138.3 (CH$_{\text{donq}}$), 137.6 (C′$_{\text{tris-pvb}}$), 135.6 (CH$_B$), 127.9 (CH$_C$), 125.8 (CH$_A$), 123.5 (CH$_\beta$), 112.3 (C$_{\text{donq}}$), 104.4 (C$_{p\text{-cym}}$), 100.1 (C$_{p\text{-cym}}$), 85.0 (CH$_{p\text{-cym}}$), 83.9 (CH$_{p\text{-cym}}$), 31.4 (CH(CH$_3$)$_2$), 22.3 (CH(CH$_3$)$_2$), 17.3 (CH$_3$). MS (ESI positive mode): *m*/*z* 1066.12 [**5** + 3 CF$_3$SO$_3$]$^{3+}$. Anal. Calcd for C$_{150}$H$_{138}$F$_{18}$N$_6$O$_{30}$Ru$_6$S$_6$·8CH$_2$Cl$_2$: C, 43.88; H, 3.59; N, 1.94. Found: C, 43.99; H, 3.57; N, 2.24.

*[Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(doaq)$_3$][CF$_3$SO$_3$]$_6$ ([**6**][CF$_3$SO$_3$]$_6$).* Yield: 86.1 mg (76%). UV–vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 338 nm (ε = 1.85 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 560 nm (ε = 0.07 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 604 nm (ε = 0.12 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 653 nm (ε = 0.14 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3066 (m, aromatic, C–H), 1538 (s, doaq, C=O), 1261 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.67 (br s, 6H, H$_{\text{bq}}$), 8.28 (br s, 12H, H$_\alpha$), 7.97 (br s, 6H, H$_{\text{cq}}$), 7.58 (br s, 6H, H$_C$), 7.37 (d, ^3J = 5.8 Hz, 12H, H$_\beta$), 7.29 (m, 6H, H$_B$), 7.25 (s, 3H, H$_{\text{aq}}$), 7.24 (s, 3H, H$_{\text{aq}}$), 7.11 (m, 6H, H$_A$), 5.77 (d, ^3J = 5.8 Hz, 6H, H$_{p\text{-cym}}$), 5.72 (d, ^3J = 5.8 Hz, 6H, H$_{p\text{-cym}}$), 5.55 (d, ^3J = 5.8 Hz, 6H, H$_{p\text{-cym}}$), 5.53 (d, ^3J = 5.8 Hz, 6H, H$_{p\text{-cym}}$), 2.87 (sept, ^3J = 6.8 Hz, 6H, CH(CH$_3$)$_2$), 2.13 (s, 18H, CH$_3$), 1.32 (d, ^3J = 6.8 Hz, 18H, CH(CH$_3$)$_2$), 1.29 (d, ^3J = 6.8 Hz, 18H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 171.4 (CO), 170.4 (CO), 152.7 (CH$_\alpha$), 148.3 (C$_{\text{tris-pvb}}$), 138.6 (CH$_{\text{aq}}$), 137.5 (C′$_{\text{tris-pvb}}$), 135.5 (CH$_B$), 134.2 (CH$_{\text{cq}}$), 134.1 (C$_q$), 128.2 (CH$_{\text{bq}}$), 127.8 (CH$_C$), 125.8 (CH$_A$), 123.5 (CH$_\beta$), 110.5 (C$_q$), 104.4 (C$_{p\text{-cym}}$), 100.2 (C$_{p\text{-cym}}$), 85.0 (CH$_{p\text{-cym}}$), 84.8 (CH$_{p\text{-cym}}$), 83.7 (CH$_{p\text{-cym}}$), 83.6 (CH$_{p\text{-cym}}$), 31.4 (CH(CH$_3$)$_2$), 22.5 (CH(CH$_3$)$_2$), 22.2 (CH(CH$_3$)$_2$), 17.6 (CH$_3$). MS (ESI positive mode): *m*/*z* 1115.80 [**6** + 3 CF$_3$SO$_3$]$^{3+}$. Anal. Calcd for C$_{162}$H$_{144}$F$_{18}$N$_6$O$_{30}$Ru$_6$S$_6$·15CH$_2$Cl$_2$·CH$_3$CN: C, 42.07; H, 3.49; N, 1.92. Found: C, 42.24; H, 3.50; N, 2.04.

*[Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(dotq)$_3$][CF$_3$SO$_3$]$_6$ ([**7**][CF$_3$SO$_3$]$_6$).* Yield: 93.3 mg (79%). UV–vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 339 nm (ε = 2.07 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 528 nm (ε = 0.08 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 567 nm (ε = 0.18 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 611 nm (ε = 0.25 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3067 (m, aromatic, C–H), 1542 (s, dotq, C=O), 1261 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.75 (dd, ^4J = 3.4 Hz, ^3J = 5.5 Hz, 12H, H$_{\text{bq}}$), 8.32 (d, ^3J = 5.4 Hz, 12H, H$_\alpha$), 7.98 (dd, ^4J = 3.4 Hz, ^3J = 5.5 Hz, 12H, H$_{\text{cq}}$), 7.46 (s, 6H, H$_C$), 7.27 (br s, 12H, H$_\beta$), 7.15 (d, ^3J = 16.0 Hz, 6H, H$_B$), 6.96 (d, ^3J = 16.0 Hz, 6H, H$_A$), 5.84 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 5.62 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 2.93 (sept, ^3J = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 2.15 (s, 18H, CH$_3$), 1.30 (d, ^3J = 6.9 Hz, 36H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR

(100 MHz, CD_3CN): δ (ppm) 170.0 (CO), 152.6 (CH_α), 148.2 ($C_{tris\text{-}pvb}$), 137.4 ($C'_{tris\text{-}pvb}$), 135.4 (CH_B), 134.7 (C_q), 133.9 (CH_{cq}), 128.2 (CH_{bq}), 127.7 (CH_C), 125.6 (CH_A), 123.4 (CH_β), 107.9 (C_q), 104.5 ($C_{p\text{-}cym}$), 100.4 ($C_{p\text{-}cym}$), 84.9 ($CH_{p\text{-}cym}$), 83.4 ($CH_{p\text{-}cym}$), 31.4 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 17.8 (CH_3). MS (ESI positive mode): *m/z* 1166.46 [**7** + 3 CF_3SO_3]$^{3+}$. Anal. Calcd for $C_{174}H_{150}F_{18}N_6O_{30}Ru_6S_6\cdot 12CH_2Cl_2$: C, 44.99; H, 3.53; N, 1.69. Found: C, 44.94; H, 3.51; N, 1.95.

Synthesis of [coronene⊂3][CF_3SO_3]$_6$–[coronene⊂7][CF_3SO_3]$_6$: General Procedure. A mixture of 3 equiv of the molecular clip [Ru_2(*p*-cymene)$_2$(dobq)Cl_2], [Ru_2(*p*-cymene)$_2$(dCloq)Cl_2], [Ru_2(*p*-cymene)$_2$(donq)Cl_2], [Ru_2(*p*-cymene)$_2$(doaq)Cl_2], or [Ru_2(*p*-cymene)$_2$(dotq)Cl_2] (0.09 mmol), 6 equiv of Ag(CF_3SO_3) (46.2 mg, 0.18 mmol), 1 equiv of coronene (9.0 mg, 0.03 mmol), and 2 equiv of tris-pvb (23.2 mg, 0.06 mmol) in MeOH (20 mL) was stirred at reflux for 24 h and then filtered. The solvent was removed, and the dark residue was dissolved in CH_2Cl_2/CH_3CN (1/1, 3 mL), before slowly adding diethyl ether to precipitate a dark red, dark purple, or dark green solid. The solid was filtered, washed with diethyl ether, and dried under vacuum.

*[coronene⊂Ru_6(p-cymene)$_6$(tris-pvb)$_2$(dobq)$_3$][CF_3SO_3]$_6$ ([coronene⊂**3**][CF_3SO_3]$_6$).* Yield: 97.0 mg (85%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 344 nm ($\varepsilon = 1.84 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 502 nm ($\varepsilon = 0.47 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3069 (m, aromatic, C–H), 1524 (s, dobq, C═O), 1258 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.11 (d, ^3J = 5.8 Hz, 12H, H_α), 8.06 (s, 12H, H_{cor}), 7.33 (d, ^3J = 5.8 Hz, 12H, H_β), 6.80 (m, 12H, $H_{B/C}$), 6.60 (m, 12H, H_A), 5.89 (s, 6H, H_{dobq}), 5.88 (d, ^3J = 6.1 Hz, 12H, $H_{p\text{-}cym}$), 5.66 (d, ^3J = 6.1 Hz, 12H, $H_{p\text{-}cym}$), 2.84 (sept, ^3J = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.12 (s, 18H, CH_3), 1.33 (d, ^3J = 6.9 Hz, 36H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 185.2 (CO), 153.6 (CH_α), 148.4 ($C_{tris\text{-}pvb}$), 136.3 ($C'_{tris\text{-}pvb}$), 135.5 (CH_B), 129.0 (C_{cor}), 127.3 (CH_C), 126.6 (CH_{cor}), 124.8 (CH_A), 123.7 (CH_β), 122.8 (C_{cor}), 104.5 ($C_{p\text{-}cym}$), 102.5 (CH_{dobq}), 99.6 ($C_{p\text{-}cym}$), 85.5 ($CH_{p\text{-}cym}$), 82.7 ($CH_{p\text{-}cym}$), 32.0 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 18.2 (CH_3). MS (ESI positive mode): *m/z* 724.83 [**3** + 2 CF_3SO_3]$^{4+}$, 1016.42 [**3** + 3 CF_3SO_3]$^{3+}$. Anal. Calcd for $C_{162}H_{144}F_{18}N_6O_{30}Ru_6S_6\cdot 6CH_2Cl_2\cdot CH_3CN$: C, 46.98; H, 3.69; N, 2.26. Found: C, 46.95; H, 3.98; N, 2.34.

*[coronene⊂Ru_6(p-cymene)$_6$(tris-pvb)$_2$(dCloq)$_3$][CF_3SO_3]$_6$ ([coronene⊂**4**][CF_3SO_3]$_6$).* Yield: 103.1 mg (86%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 342 nm ($\varepsilon = 2.61 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 518 nm ($\varepsilon = 0.59 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C–H), 1500 (s, dCloq, C═O), 1260 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.11 (d, ^3J = 6.4 Hz, 12H, H_α), 8.03 (s, 12H, H_{cor}), 7.37 (d, ^3J = 6.4 Hz, 12H, H_β), 6.96 (m, 12H, $H_{B/C}$), 6.74 (m, 6H, H_A), 5.95 (d, ^3J = 6.3 Hz, 12H, $H_{p\text{-}cym}$), 5.75 (d, ^3J = 6.3 Hz, 12H, $H_{p\text{-}cym}$), 2.89 (sept, ^3J = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.19 (s, 18H, CH_3), 1.38 (d, ^3J = 6.9 Hz, 36H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 178.7 (CO), 153.6 (CH_α), 148.5 ($C_{tris\text{-}pvb}$), 136.4 ($C'_{tris\text{-}pvb}$), 135.7 (CH_B), 128.9 (C_{cor}), 127.4 (CH_C), 126.5 (CH_{cor}), 124.8 (CH_A), 123.8 (CH_β), 122.8 (C_{cor}), 107.2 (C_{dCloq}), 104.9 ($C_{p\text{-}cym}$), 99.4 ($C_{p\text{-}cym}$), 84.4 ($CH_{p\text{-}cym}$), 83.4 ($CH_{p\text{-}cym}$), 32.2 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$), 18.3 (CH_3). MS (ESI positive mode): *m/z* 776.52 [**4** + 2 CF_3SO_3]$^{4+}$, 851.72 [coronene + **4** + 2 CF_3SO_3]$^{4+}$, 1085.35 [**4** + 3 CF_3SO_3]$^{3+}$. Anal. Calcd for $C_{162}H_{138}Cl_6F_{18}N_6O_{30}Ru_6S_6\cdot 8CH_2Cl_2\cdot CH_3CN$: C, 43.74; H, 3.35; N, 2.08. Found: C, 43.69; H, 3.67; N, 2.18.

*[coronene⊂Ru_6(p-cymene)$_6$(tris-pvb)$_2$(donq)$_3$][CF_3SO_3]$_6$ ([coronene⊂**5**][CF_3SO_3]$_6$).* Yield: 96.0 mg (81%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 337 nm ($\varepsilon = 1.91 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 588 nm ($\varepsilon = 0.10 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 643 nm ($\varepsilon = 0.10 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 702 nm ($\varepsilon = 0.10 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3053 (m, aromatic, C–H), 1535 (s, donq, C═O), 1259 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.23 (d, ^3J = 6.1 Hz, 12H, H_α), 7.83 (s, 6H, H_C), 7.29 (d, ^3J = 6.1 Hz, 12H, H_β), 7.26 (s, 12H, H_{donq}), 7.12 (m, 12H, H_{cor}), 6.96 (m, 6H, H_B), 6.78 (m, 6H, H_A), 5.67 (d, ^3J = 6.1 Hz, 12H, $H_{p\text{-}cym}$), 5.46 (d, ^3J = 6.1 Hz, 12H, $H_{p\text{-}cym}$), 2.82 (sept, ^3J = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.08 (s, 18H, CH_3), 1.31 (d, ^3J = 6.9 Hz, 36H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 171.8 (CO), 152.8 (CH_α), 148.3 ($C_{tris\text{-}pvb}$), 138.5 (CH_{donq}), 137.0 ($C'_{tris\text{-}pvb}$), 135.4 (CH_B), 128.9 (C_{cor}), 127.4 (CH_{cor}), 126.4 (CH_C), 125.3 (CH_A), 123.5 (CH_β), 122.8 (C_{cor}), 112.5 (C_{donq}), 104.5 ($C_{p\text{-}cym}$), 100.2 ($C_{p\text{-}cym}$), 85.1 ($CH_{p\text{-}cym}$), 84.0 ($CH_{p\text{-}cym}$), 31.5 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 17.3 (CH_3). MS (ESI positive mode): *m/z* 1066.12 [**5** + 3 CF_3SO_3]$^{3+}$. Anal. Calcd for $C_{174}H_{150}F_{18}N_6O_{30}Ru_6S_6\cdot 15CH_2Cl_2\cdot 2CH_3CN$: C, 43.72; H, 3.54; N, 2.11. Found: C, 43.61; H, 3.51; N, 2.08.

*[coronene⊂Ru_6(p-cymene)$_6$(tris-pvb)$_2$(doaq)$_3$][CF_3SO_3]$_6$ ([coronene⊂**6**][CF_3SO_3]$_6$).* Yield: 80.8 mg (66%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 338 nm ($\varepsilon = 2.13 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 560 nm ($\varepsilon = 0.08 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 603 nm ($\varepsilon = 0.13 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 653 nm ($\varepsilon = 0.17 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3064 (m, aromatic, C–H), 1538 (s, doaq, C═O), 1261 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.74 (m, 6H, H_{bq}), 8.26 (dd, ^3J = 7.0 Hz, ^3J = 13.7 Hz, 12H, H_α), 8.04 (m, 6H, H_{cq}), 7.64 (s, 12H, H_{cor}), 7.34 (s, 12H, H_{aq}), 7.17 (m, 12H, H_β), 6.66 (m, 18H, $H_{A/B/C}$), 5.78 (dd, ^3J = 2.7 Hz, ^3J = 5.4 Hz, 6H, $H_{p\text{-}cym}$), 5.72 (dd, ^3J = 2.7 Hz, ^3J = 5.4 Hz, 6H, $H_{p\text{-}cym}$), 5.56 (dd, ^3J = 2.7 Hz, ^3J = 5.4 Hz, 6H, $H_{p\text{-}cym}$), 5.53 (dd, ^3J = 2.7 Hz, ^3J = 5.4 Hz, 6H, $H_{p\text{-}cym}$), 2.88 (sept, ^3J = 6.8 Hz, 6H, $CH(CH_3)_2$), 2.12 (s, 18H, CH_3), 1.33 (d, ^3J = 6.8 Hz, 18H, $CH(CH_3)_2$), 1.30 (d, ^3J = 6.8 Hz, 18H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 171.4 (CO), 170.6 (CO), 152.6 (CH_α), 148.1 ($C_{tris\text{-}pvb}$), 138.8 (CH_{aq}), 136.5 ($C'_{tris\text{-}pvb}$), 135.1 (CH_B), 134.3 (CH_{cq}), 134.1 (C_q), 128.7 (C_{cor}), 128.3 (CH_{bq}), 127.1 (CH_C), 126.1 (CH_{cor}), 124.9 (CH_A), 123.3 (CH_β), 122.6 (C_{cor}), 110.6 (C_q), 104.4 ($C_{p\text{-}cym}$), 100.2 ($C_{p\text{-}cym}$), 85.0 ($CH_{p\text{-}cym}$), 84.8 ($CH_{p\text{-}cym}$), 83.7 ($CH_{p\text{-}cym}$), 83.6 ($CH_{p\text{-}cym}$), 31.4 ($CH(CH_3)_2$), 22.5 ($CH(CH_3)_2$), 22.2 ($CH(CH_3)_2$), 17.6 (CH_3). MS (ESI positive mode): *m/z* 800.11 [**6** + 2 CF_3SO_3]$^{4+}$, 1115.79 [**6** + 3 CF_3SO_3]$^{3+}$. Anal. Calcd for $C_{186}H_{156}F_{18}N_6O_{30}Ru_6S_6\cdot 7CH_2Cl_2$: C, 49.42; H, 3.65; N, 1.79. Found: C, 49.70; H, 3.84; N, 2.10.

*[coronene⊂Ru_6(p-cymene)$_6$(tris-pvb)$_2$(dotq)$_3$][CF_3SO_3]$_6$ ([coronene⊂**7**][CF_3SO_3]$_6$).* Yield: 108.2 mg (85%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 338 nm ($\varepsilon = 2.27 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 528 nm ($\varepsilon = 0.09 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 567 nm ($\varepsilon = 0.20 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 611 nm ($\varepsilon = 0.27 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3064 (m, aromatic, C–H), 1543 (s, dotq, C═O), 1260 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.82 (dd, ^4J = 3.4 Hz, ^3J = 5.8 Hz, 12H, H_{bq}), 8.29 (d, ^3J = 6.1 Hz, 12H, H_α), 8.06 (dd, ^4J = 3.4 Hz, ^3J = 5.8 Hz, 12H, H_{cq}), 7.50 (s, 6H, H_{cor}), 7.02 (br s, 12H, H_β), 6.48 (br s, 12H, H_B/H_C), 6.27 (br s, 6H, H_A), 5.84 (d, ^3J = 6.2 Hz, 12H, $H_{p\text{-}cym}$), 5.62 (d, ^3J = 6.2 Hz, 12H, $H_{p\text{-}cym}$), 2.94 (sept, ^3J = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.09 (s, 18H, CH_3), 1.31 (d, ^3J = 6.9 Hz, 36H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 170.1 (CO), 152.4 (CH_α), 148.0 ($C_{tris\text{-}pvb}$), 136.1 ($C'_{tris\text{-}pvb}$), 134.9 (CH_B), 134.7 (C_q), 134.0 (CH_{cq}), 128.6 (C_{cor}), 128.3 (CH_{bq}), 126.7 (CH_C), 126.0 (CH_{cor}), 124.6 (CH_A), 123.2 (CH_β), 122.5 (C_{cor}), 108.1 (C_q), 104.5 ($C_{p\text{-}cym}$), 100.4 ($C_{p\text{-}cym}$), 84.9 ($CH_{p\text{-}cym}$), 83.4 ($CH_{p\text{-}cym}$), 31.4 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 17.8 (CH_3). MS (ESI positive mode): *m/z* 1166.46 [**7** + 3 CF_3SO_3]$^{3+}$. Anal. Calcd for $C_{198}H_{162}F_{18}N_6O_{30}Ru_6S_6\cdot 9CH_2Cl_2$: C, 49.62; H, 3.62; N, 1.68. Found: C, 49.84; H, 3.92; N, 1.99.

Synthesis of [photosensitizer⊂3][CF_3SO_3]$_6$, [photosensitizer⊂5][CF_3SO_3]$_6$, and [photosensitizer⊂7][CF_3SO_3]$_6$: General Procedure. A mixture of 3 equiv of molecular clip ([Ru_2(*p*-cymene)$_2$(dobq)Cl_2], 61.2 mg; [Ru_2(*p*-cymene)$_2$(donq)Cl_2], 65.7 mg; [Ru_2(*p*-cymene)$_2$(dotq)Cl_2], 74.7 mg; 0.09 mmol), 6 equiv of Ag(CF_3SO_3) (46.2 mg, 0.18 mmol), 1 equiv of photosensitizer (porphin, 9.4 mg; phthalocyanine, 15.4 mg; Zn-phthalocyanine, 17.3 mg; 0.03 mmol), and 2 equiv of tris-pvb (23.2 mg, 0.06 mmol) in MeOH (20 mL) was stirred at reflux for 24 h and then filtered. The solvent was removed, and the dark residue was dissolved in CH_2Cl_2/CH_3CN (1/1, 3 mL), before slowly adding diethyl ether to precipitate a dark solid. The solid was filtered, washed with diethyl ether, and dried under vacuum.

*[porphin⊂Ru_6(p-cymene)$_6$(tris-pvb)$_2$(dobq)$_3$][CF_3SO_3]$_6$ ([porphin⊂**3**][CF_3SO_3]$_6$).* Yield: 104.0 mg (91%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 345 nm ($\varepsilon = 2.49 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 395 nm ($\varepsilon = 1.68 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 494 nm ($\varepsilon = 0.66 \times 10^5$ M^{-1} cm^{-1}), λ_{max}

520 nm ($\varepsilon = 0.63 \times 10^{5}$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3069 (m, aromatic, C–H), 1524 (s, dobq, C=O), 1257 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 9.56 (s, 4H, H$_{\text{porphin}}$), 8.76 (s, 8H, H$_{\text{porphin}}$), 8.12 (d, $^{3}J = 5.7$ Hz, 12H, H$_\alpha$), 7.22 (d, $^{3}J = 5.7$ Hz, 12H, H$_\beta$), 6.32 (br s, 6H, H$_{\text{B}}$), 6.16 (br s, 12H, H$_{\text{A/C}}$), 5.97 (s, 6H, H$_{\text{dobq}}$), 5.89 (d, $^{3}J = 6.0$ Hz, 12H, H$_{p\text{-cym}}$), 5.66 (d, $^{3}J = 6.0$ Hz, 12H, H$_{p\text{-cym}}$), 2.85 (sept, $^{3}J = 6.9$ Hz, 6H, CH(CH$_3$)$_2$), 2.12 (s, 18H, CH$_3$), 1.34 (d, $^{3}J = 6.9$ Hz, 36H, CH(CH_3)$_2$), −5.24 (s, 2H, NH). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 185.5 (CO), 153.6 (CH$_\alpha$), 148.3 (C$_{\text{tris-pvb}}$), 135.2 (CH$_{\text{B}}$), 131.8 (C$_{\text{porphin}}$), 130.6 (CH$_{\text{porphin}}$), 124.5 (CH$_{\text{A/C}}$), 123.7 (CH$_\beta$), 104.7 (CH$_{\text{porphin}}$), 104.6 (C$_{p\text{-cym}}$), 102.7 (CH$_{\text{dobq}}$), 99.6 (C$_{p\text{-cym}}$), 84.5 (CH$_{p\text{-cym}}$), 82.8 (CH$_{p\text{-cym}}$), 32.1 (CH(CH$_3$)$_2$), 22.4 (CH(CH$_3$)$_2$), 18.2 (CH$_3$). MS (ESI positive mode): m/z 724.83 [**3** + 2 CF$_3$SO$_3$]$^{4+}$, 1016.43 [**3** + 3 CF$_3$SO$_3$]$^{3+}$. Anal. Calcd for C$_{158}$H$_{146}$F$_{18}$N$_{10}$O$_{30}$Ru$_6$S$_6$·7CH$_2$Cl$_2$·2Et$_2$O: C, 45.68; H, 3.99; N, 3.08. Found: C, 45.70; H, 4.10; N, 3.00.

*[phthalocyanine⊂Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(dobq)$_3$][CF$_3$SO$_3$]$_6$ ([phthalocyanine⊂**3**][CF$_3$SO$_3$]$_6$).* Yield: 109.1 mg (91%). UV–vis (1.0×10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 340 nm ($\varepsilon = 2.47 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 505 nm ($\varepsilon = 0.58 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 606 nm ($\varepsilon = 0.21 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 641 nm ($\varepsilon = 0.24 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 656 nm ($\varepsilon = 0.30 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 670 nm ($\varepsilon = 0.60 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 704 nm ($\varepsilon = 0.68 \times 10^{5}$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3072 (m, aromatic, C–H), 1520 (s, dobq, C=O), 1258 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.71 (dd, $^{4}J = 2.9$ Hz, $^{3}J = 5.6$ Hz, 8H, H$_{\text{phthalocyanine}}$), 8.05 (d, $^{3}J = 6.6$ Hz, 12H, H$_\alpha$), 7.24 (dd, $^{4}J = 2.9$ Hz, $^{3}J = 5.6$ Hz, 8H, H$_{\text{phthalocyanine}}$), 6.76 (d, $^{3}J = 6.6$ Hz, 12H, H$_\beta$), 6.31 (s, 6H, H$_{\text{dobq}}$), 5.91 (d, $^{3}J = 6.3$ Hz, 12H, H$_{p\text{-cym}}$), 5.67 (d, $^{3}J = 6.3$ Hz, 12H, H$_{p\text{-cym}}$), 5.20 (d, $^{3}J = 16.4$ Hz, 6H, H$_{\text{B}}$), 5.14 (d, $^{3}J = 16.4$ Hz, 6H, H$_{\text{A}}$), 4.74 (s, 6H, H$_{\text{C}}$), 2.87 (sept, $^{3}J = 6.9$ Hz, 6H, CH(CH$_3$)$_2$), 2.11 (s, 18H, CH$_3$), 1.36 (d, $^{3}J = 6.9$ Hz, 36H, CH(CH_3)$_2$), −2.11 (s, 2H, NH). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 185.3 (CO), 153.1 (CH$_\alpha$), 147.6 (C$_{\text{tris-pvb}}$), 137.5 (C$_{\text{phthalocyanine}}$), 133.7 (C′$_{\text{tris-pvb}}$), 132.9 (CH$_{\text{B}}$), 130.7 (CH$_{\text{phthalocyanine}}$), 124.3 (CH$_{\text{C}}$), 123.5 (CH$_\beta$), 123.3 (CH$_{\text{A}}$), 123.1 (CH$_{\text{phthalocyanine}}$), 104.6 (C$_{p\text{-cym}}$), 102.8 (CH$_{\text{dobq}}$), 99.7 (C$_{p\text{-cym}}$), 84.5 (CH$_{p\text{-cym}}$), 82.8 (CH$_{p\text{-cym}}$), 32.1 (CH(CH$_3$)$_2$), 22.4 (CH(CH$_3$)$_2$), 18.2 (CH$_3$). MS (ESI positive mode): m/z 514.17 phthalocyanine, 724.83 [**3** + 2 CF$_3$SO$_3$]$^{4+}$, 1016.43 [**3** + 3 CF$_3$SO$_3$]$^{3+}$, 1598.18 [**3** + 4 CF$_3$SO$_3$]$^{2+}$. Anal. Calcd for C$_{170}$H$_{150}$F$_{18}$N$_{14}$O$_{30}$Ru$_6$S$_6$·9CH$_2$Cl$_2$: C, 45.03; H, 3.55; N, 4.11. Found: C, 45.00; H, 3.76; N, 4.10.

*[Zn-phthalocyanine⊂Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(dobq)$_3$][CF$_3$SO$_3$]$_6$ ([Zn-phthalocyanine⊂**3**][CF$_3$SO$_3$]$_6$).* Yield: 110.1 mg (90%). UV–vis (1.0×10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 340 nm ($\varepsilon = 2.57 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 505 nm ($\varepsilon = 0.63 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 618 nm ($\varepsilon = 0.20 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 685 nm ($\varepsilon = 0.86 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 729 nm ($\varepsilon = 0.14 \times 10^{5}$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3064 (m, aromatic, C–H), 1523 (s, dobq, C=O), 1258 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.71 (br s, 8H, H$_{\text{Zn-phthalocyanine}}$), 8.08 (d, $^{3}J = 4.2$ Hz, 12H, H$_\alpha$), 7.23 (br s, 8H, H$_{\text{Zn-phthalocyanine}}$), 6.79 (br s, 12H, H$_\beta$), 6.32 (s, 6H, H$_{\text{dobq}}$), 5.91 (d, $^{3}J = 5.9$ Hz, 12H, H$_{p\text{-cym}}$), 5.68 (d, $^{3}J = 5.9$ Hz, 12H, H$_{p\text{-cym}}$), 5.22 (d, $^{3}J = 16.0$ Hz, 6H, H$_{\text{B}}$), 5.10 (d, $^{3}J = 16.0$ Hz, 6H, H$_{\text{A}}$), 4.66 (s, 6H, H$_{\text{C}}$), 2.87 (sept, $^{3}J = 6.8$ Hz, 6H, CH(CH$_3$)$_2$), 2.12 (s, 18H, CH$_3$), 1.35 (d, $^{3}J = 6.8$ Hz, 36H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 185.7 (CO), 153.2 (CH$_\alpha$), 147.4 (C$_{\text{tris-pvb}}$), 139.1 (C$_{\text{Zn-phthalocyanine}}$), 134.3 (C′$_{\text{tris-pvb}}$), 132.4 (CH$_{\text{B}}$), 130.4 (CH$_{\text{Zn-phthalocyanine}}$), 124.9 (CH$_{\text{A}}$), 123.8 (CH$_{\text{C}}$), 123.7 (CH$_\beta$), 123.0 (CH$_{\text{Zn-phthalocyanine}}$), 104.6 (C$_{p\text{-cym}}$), 102.8 (CH$_{\text{dobq}}$), 99.7 (C$_{p\text{-cym}}$), 84.5 (CH$_{p\text{-cym}}$), 82.8 (CH$_{p\text{-cym}}$), 32.1 (CH(CH$_3$)$_2$), 22.4 (CH(CH$_3$)$_2$), 18.2 (CH$_3$). MS (ESI positive mode): m/z 576.08 Zn-phthalocyanine, 724.83 [**3** + 2 CF$_3$SO$_3$]$^{4+}$, 869.36 [Zn-phthalocyanine + **3** + 2 CF$_3$SO$_3$]$^{4+}$, 1016.43 [**3** + 3 CF$_3$SO$_3$]$^{3+}$. Anal. Calcd for C$_{170}$H$_{148}$F$_{18}$N$_{14}$O$_{30}$Ru$_6$S$_6$Zn·7CH$_2$Cl$_2$·4Et$_2$O: C, 46.69; H, 4.10; N, 3.95. Found: C, 46.77; H, 3.90; N, 3.74.

*[porphin⊂Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(donq)$_3$][CF$_3$SO$_3$]$_6$ ([porphin⊂**5**][CF$_3$SO$_3$]$_6$).* Yield: 79.2 mg (67%). UV–vis (1.0×10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 338 nm ($\varepsilon = 3.07 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 393 nm ($\varepsilon = 2.62 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 488 nm ($\varepsilon = 0.38 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 563 nm ($\varepsilon = 0.11 \times 10^{5}$ M^{-1}· cm^{-1}), $\lambda_{\max}$ 645 nm ($\varepsilon = 0.13 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 703 nm ($\varepsilon = 0.14 \times 10^{5}$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C–H), 1537 (s, dobq, C=O), 1260 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 9.40 (s, 4H, H$_{\text{porphin}}$), 8.63 (s, 8H, H$_{\text{porphin}}$), 8.21 (d, $^{3}J = 5.9$ Hz, 12H, H$_\alpha$), 7.39 (s, 12H, H$_{\text{donq}}$), 7.03 (d, $^{3}J = 5.9$ Hz, 12H, H$_\beta$), 6.12 (br s, 6H, H$_{\text{B}}$), 5.98 (br s, 12H, H$_{\text{A/C}}$), 5.67 (d, $^{3}J = 6.1$ Hz, 12H, H$_{p\text{-cym}}$), 5.46 (d, $^{3}J = 6.1$ Hz, 12H, H$_{p\text{-cym}}$), 2.83 (sept, $^{3}J = 7.0$ Hz, 6H, CH(CH$_3$)$_2$), 2.08 (s, 18H, CH$_3$), 1.32 (d, $^{3}J = 7.0$ Hz, 36H, CH(CH_3)$_2$), −5.16 (s, 2H, NH). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 171.9 (CO), 152.6 (CH$_\alpha$), 147.9 (C$_{\text{tris-pvb}}$), 138.6 (CH$_{\text{donq}}$), 135.5 (C′$_{\text{tris-pvb}}$), 134.6 (CH$_{\text{B}}$), 131.8 (CH$_{\text{porphin}}$), 126.2 (CH$_{\text{C}}$), 124.4 (CH$_{\text{A}}$), 123.3 (CH$_\beta$), 112.6 (C$_{\text{donq}}$), 104.5 (C$_{p\text{-cym}}$), 104.4 (CH$_{\text{porphin}}$), 100.2 (C$_{p\text{-cym}}$), 85.1 (CH$_{p\text{-cym}}$), 84.0 (CH$_{p\text{-cym}}$), 31.4 (CH(CH$_3$)$_2$), 22.3 (CH(CH$_3$)$_2$), 17.3 (CH$_3$). MS (ESI positive mode): m/z 1066.12 [**5** + 3 CF$_3$SO$_3$]$^{3+}$, 1673.75 [**5** + 4 CF$_3$SO$_3$]$^{2+}$. Anal. Calcd for C$_{170}$H$_{152}$F$_{18}$N$_{10}$O$_{30}$Ru$_6$S$_6$·3CH$_2$Cl$_2$·Et$_2$O: C, 49.62; H, 3.95; N, 3.27. Found: C, 49.53; H, 4.21; N, 3.09.

*[phthalocyanine⊂Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(donq)$_3$][CF$_3$SO$_3$]$_6$ ([phthalocyanine⊂**5**][CF$_3$SO$_3$]$_6$).* Yield: 84.7 mg (70%) ([phthalocyanine⊂**5**] 75%, [**5**] 25%, determined by ^{1}H NMR). UV–vis (1.0×10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 337 nm ($\varepsilon = 2.56 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 609 nm ($\varepsilon = 0.21 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 641 nm ($\varepsilon = 0.31 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 656 nm ($\varepsilon = 0.38 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 669 nm ($\varepsilon = 0.59 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 704 nm ($\varepsilon = 0.66 \times 10^{5}$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C–H), 1534 (s, donq, C=O), 1259 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.56 (dd, $^{4}J = 2.9$ Hz, $^{3}J = 5.5$ Hz, 8H, H$_{\text{phthalocyanine}}$), 8.16 (d, $^{3}J = 5.7$ Hz, 12H, H$_\alpha$), 7.61 (s, 12H, H$_{\text{donq}}$), 6.93 (dd, $^{4}J = 2.9$ Hz, $^{3}J = 5.5$ Hz, 8H, H$_{\text{phthalocyanine}}$), 6.66 (d, $^{3}J = 5.7$ Hz, 12H, H$_\beta$), 5.69 (d, $^{3}J = 5.9$ Hz, 12H, H$_{p\text{-cym}}$), 5.47 (d, $^{3}J = 5.9$ Hz, 12H, H$_{p\text{-cym}}$), 5.15 (d, $^{3}J = 16.4$ Hz, 6H, H$_{\text{B}}$), 5.09 (d, $^{3}J = 16.4$ Hz, 6H, H$_{\text{A}}$), 4.68 (s, 6H, H$_{\text{C}}$), 2.85 (sept, $^{3}J = 7.0$ Hz, 6H, CH(CH$_3$)$_2$), 2.07 (s, 18H, CH$_3$), 1.33 (d, $^{3}J = 7.0$ Hz, 36H, CH(CH_3)$_2$), −2.14 (s, 2H, NH). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 172.1 (CO), 152.2 (CH$_\alpha$), 147.4 (C$_{\text{tris-pvb}}$), 138.8 (CH$_{\text{donq}}$), 137.7 (C$_{\text{phthalocyanine}}$), 133.7 (C′$_{\text{tris-pvb}}$), 132.4 (CH$_{\text{B}}$), 130.4 (CH$_{\text{phthalocyanine}}$), 124.1 (CH$_{\text{C}}$), 123.4 (CH$_{\text{phthalocyanine}}$), 123.0 (CH$_\beta$), 123.0 (CH$_{\text{A}}$), 112.6 (C$_{\text{donq}}$), 104.6 (C$_{p\text{-cym}}$), 100.3 (C$_{p\text{-cym}}$), 85.2 (CH$_{p\text{-cym}}$), 84.0 (CH$_{p\text{-cym}}$), 31.5 (CH(CH$_3$)$_2$), 22.4 (CH(CH$_3$)$_2$), 17.3 (CH$_3$). Due to the equilibrium between empty and filled complexes in solution, which does not allow the isolation of a single product, the molecular mass and the elemental composition were not determined.

*[Zn-phthalocyanine⊂Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(donq)$_3$][CF$_3$SO$_3$]$_6$ ([Zn-phthalocyanine⊂**5**][CF$_3$SO$_3$]$_6$).* Yield: 88.2 mg (70%). Due to the broadness of the signal, the equilibrium between empty and filled cages has not been determined by ^{1}H NMR. UV–vis (1.0×10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 336 nm ($\varepsilon = 2.60 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 619 nm ($\varepsilon = 0.25 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 654 nm ($\varepsilon = 0.25 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 686 nm ($\varepsilon = 1.02 \times 10^{5}$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C–H), 1537 (s, donq, C=O), 1259 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.53 (br s, 8H, H$_{\text{Zn-phthalocyanine}}$), 8.20 (d, $^{3}J = 5.8$ Hz, 12H, H$_\alpha$), 7.42 (br s, 12H, H$_{\text{donq}}$), 6.94 (br s, 8H, H$_{\text{Zn-phthalocyanine}}$), 5.68 (d, $^{3}J = 6.2$ Hz, 12H, H$_{p\text{-cym}}$), 5.47 (d, $^{3}J = 6.2$ Hz, 12H, H$_{p\text{-cym}}$), 2.83 (sept, $^{3}J = 7.0$ Hz, 6H, CH(CH$_3$)$_2$), 2.08 (s, 18H, CH$_3$), 1.32 (d, $^{3}J = 7.0$ Hz, 36H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 171.9 (CO), 153.7 (C$_{\text{Zn-phthalocyanine}}$), 152.5 (CH$_\alpha$), 147.7 (C$_{\text{tris-pvb}}$), 139.1 (C$_{\text{Zn-phthalocyanine}}$), 138.5 (CH$_{\text{donq}}$), 129.8 (CH$_{\text{Zn-phthalocyanine}}$), 122.8 (CH$_{\text{Zn-phthalocyanine}}$), 122.8 (CH$_\beta$), 112.4 (C$_{\text{donq}}$), 104.5 (C$_{p\text{-cym}}$), 100.2 (C$_{p\text{-cym}}$), 85.1 (CH$_{p\text{-cym}}$), 84.0 (CH$_{p\text{-cym}}$), 31.4 (CH(CH$_3$)$_2$), 22.3 (CH(CH$_3$)$_2$), 17.3 (CH$_3$). Due to the equilibrium between empty and filled complexes in solution, which does not allow the isolation of a single product, the molecular mass and the elemental composition were not determined.

*[porphin⊂Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(dotq)$_3$][CF$_3$SO$_3$]$_6$ ([porphin⊂**7**][CF$_3$SO$_3$]$_6$).* Yield: 106.1 mg (83%). UV–vis (1.0×10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 339 nm ($\varepsilon = 2.70 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 393 nm ($\varepsilon = 2.29 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 489 nm ($\varepsilon = 0.16 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 526 nm ($\varepsilon = 0.12 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 567 nm ($\varepsilon = 0.27 \times 10^{5}$ M^{-1} cm^{-1}), $\lambda_{\max}$ 612 nm ($\varepsilon = 0.33 \times 10^{5}$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C–H), 1542 (s, dobq, C=O), 1260 (s, triflate, C–F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 9.11 (s, 4H, H$_{\text{porphin}}$), 8.88 (br s, 12H, H$_{\text{bq}}$), 8.26 (d, $^{3}J = 5.7$ Hz, 12H, H$_\alpha$), 8.26 (s, 8H, H$_{\text{porphin}}$), 8.11 (br s, 12H, H$_{\text{cq}}$), 6.79 (br s, 12H, H$_\beta$), 5.85 (d, $^{3}J = 6.0$ Hz, 12H,

H$_{p\text{-cym}}$), 5.61 (d, ^3J = 6.0 Hz, 12H, H$_{p\text{-cym}}$), 2.95 (sept, ^3J = 6.9 Hz, 6H, C*H*(CH$_3$)$_2$), 2.12 (s, 18H, CH$_3$), 1.32 (d, ^3J = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$), −5.22 (s, 2H, NH). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 170.2 (CO), 152.4 (CH$_\alpha$), 147.8 (C$_{\text{tris-pvb}}$),142.5 (C$_{\text{porphin}}$), 134.9 (C$_{\text{dotq}}$), 134.1 (CH$_{\text{cq}}$), 128.4 (CH$_{\text{bq}}$), 123.1 (CH$_\beta$), 108.2 (C$_{\text{dotq}}$), 104.6 (C$_{p\text{-cym}}$), 104.0 (CH$_{\text{porphin}}$), 100.4 (C$_{p\text{-cym}}$), 84.9 (CH$_{p\text{-cym}}$), 83.4 (CH$_{p\text{-cym}}$), 31.4 (CH(CH$_3$)$_2$), 22.5 (CH(CH$_3$)$_2$), 17.8 (CH$_3$). MS (ESI positive mode): m/z 1166.46 [7 + 3 CF$_3$SO$_3$]$^{3+}$, 1824.64 [7 + 4 CF$_3$SO$_3$]$^{2+}$. Anal. Calcd for C$_{194}$H$_{164}$F$_{18}$N$_{10}$O$_{30}$Ru$_6$S$_6$·2CH$_2$Cl$_2$·3Et$_2$O: C, 53.03; H, 4.26; N, 2.96. Found: C, 52.99; H, 4.16; N, 2.75.

*[phthalocyanine⊂Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(dotq)$_3$][CF$_3$SO$_3$]$_6$ ([phthalocyanine⊂**7**][CF$_3$SO$_3$]$_6$).* Yield: 98.7 mg (78%) ([phthalocyanine⊂7] 54%, [7] 46%, determined by ^{1}H NMR). UV−vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 336 nm (ε = 3.08 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 530 nm (ε = 0.12 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 569 nm (ε = 0.27 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 611 nm (ε = 0.46 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 638 nm (ε = 0.33 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 654 nm (ε = 0.26 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 670 nm (ε = 0.61 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 705 nm (ε = 0.71 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C−H), 1542 (s, dotq, C═O), 1260 (s, triflate, C−F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 9.00 (dd, ^4J = 3.4 Hz, ^3J = 6.1 Hz, 12H, H$_{\text{bq}}$), 8.26 (dd, ^4J = 3.4 Hz, ^3J = 6.1 Hz, 12H, H$_{\text{cq}}$), 8.25 (d, ^3J = 6.2 Hz, 12H, H$_\alpha$), 8.15 (dd, ^4J = 3.0 Hz, ^3J = 5.5 Hz, 8H, H$_{\text{phthalocyanine}}$), 6.49 (d, ^3J = 6.2 Hz, 12H, H$_\beta$), 6.33 (dd, ^4J = 3.0 Hz, ^3J = 5.5 Hz, 8H, H$_{\text{phthalocyanine}}$), 5.86 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 5.61 (d, ^3J = 6.1 Hz, 12H, H$_{p\text{-cym}}$), 4.97 (d, ^3J = 16.4 Hz, 6H, H$_B$), 4.92 (d, ^3J = 16.4 Hz, 6H, H$_A$), 4.49 (s, 6H, H$_C$), 2.96 (sept, ^3J = 6.9 Hz, 6H, C*H*(CH$_3$)$_2$), 2.09 (s, 18H, CH$_3$), 1.33 (d, ^3J = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$), −2.37 (s, 2H, NH). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 170.4 (CO), 152.1 (CH$_\alpha$), 147.3 (C$_{\text{tris-pvb}}$), 137.4 (C$_{\text{phthalocyanine}}$), 135.0 (C$_{\text{dotq}}$), 134.4 (CH$_{\text{cq}}$), 133.5 (C$'_{\text{tris-pvb}}$), 132.3 (CH$_B$), 129.9 (CH$_{\text{phthalocyanine}}$), 128.6 (CH$_{\text{bq}}$), 124.0 (CH$_C$), 123.2 (CH$_A$), 122.9 (CH$_\beta$), 122.7 (CH$_{\text{phthalocyanine}}$), 108.1 (C$_{\text{dotq}}$), 104.6 (C$_{p\text{-cym}}$), 100.4 (C$_{p\text{-cym}}$), 85.0 (CH$_{p\text{-cym}}$), 83.4 (CH$_{p\text{-cym}}$), 31.5 (CH(CH$_3$)$_2$), 22.5 (CH(CH$_3$)$_2$), 17.9 (CH$_3$). Due to the equilibrium between empty and filled complexes in solution, which does not allow the isolation of a single product, the molecular mass and the elemental composition were not determined.

*[Zn-phthalocyanine⊂Ru$_6$(p-cymene)$_6$(tris-pvb)$_2$(dotq)$_3$][CF$_3$SO$_3$]$_6$ ([Zn-phthalocyanine⊂**7**][CF$_3$SO$_3$]$_6$).* Yield: 96.0 mg (71%), ([Zn-phthalocyanine⊂ 7] 38%, [7] 62%, determined by ^{1}H NMR). UV−vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 339 nm (ε = 2.61 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 531 nm (ε = 0.12 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 571 nm (ε = 0.25 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 616 nm (ε = 0.40 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 687 nm (ε = 0.51 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C−H), 1543 (s, dotq, C═O), 1261 (s, triflate, C−F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 9.00 (br s, 12H, H$_{\text{bq}}$), 8.29 (br s, 24H, H$_{\text{cq}}$ et H$_\alpha$), 8.13 (br s, 8H, H$_{\text{Zn-phthalocyanine}}$), 6.52 (br s, 12H, H$_\beta$), 6.35 (br s, 8H, H$_{\text{Zn-phthalocyanine}}$), 5.85 (d, ^3J = 6.0 Hz, 12H, H$_{p\text{-cym}}$), 5.62 (d, ^3J = 6.0 Hz, 12H, H$_{p\text{-cym}}$), 4.97 (br s, 12H, H$_B$ et H$_A$), 4.50 (br s, 6H, H$_C$), 2.94 (sept, ^3J = 7.0 Hz, 6H, C*H*(CH$_3$)$_2$), 2.14 (s, 18H, CH$_3$), 1.31 (d, ^3J = 7.0 Hz, 36H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 170.4 (CO), 153.4 (C$_{\text{Zn-phthalocyanine}}$), 152.1 (CH$_\alpha$), 147.1 (C$_{\text{tris-pvb}}$), 138.8 (C$_{\text{Zn-phthalocyanine}}$), 134.6 (C$_{\text{dotq}}$), 133.9 (CH$_{\text{cq}}$), 131.1 (CH$_B$), 129.3 (CH$_{\text{Zn-phthalocyanine}}$), 128.2 (CH$_{\text{bq}}$), 123.9 (CH$_C$), 123.4 (CH$_A$), 123.0 (CH$_\beta$), 122.5 (CH$_{\text{Zn-phthalocyanine}}$), 107.9 (C$_{\text{dotq}}$), 104.5 (C$_{p\text{-cym}}$), 100.3 (C$_{p\text{-cym}}$), 84.9 (CH$_{p\text{-cym}}$), 83.4 (CH$_{p\text{-cym}}$), 31.4 (CH(CH$_3$)$_2$), 22.4 (CH(CH$_3$)$_2$), 17.8 (CH$_3$). Due to the equilibrium between empty and filled complexes in solution, which does not allow the isolation of a single product, the molecular mass and the elemental composition were not determined.

Synthesis of Metalla-Cubes [8]$^{8+}$–[10]$^{8+}$: General Procedure. A mixture of 2 equiv of molecular clip ([Ru$_2$(*p*-cymene)$_2$(dobq)Cl$_2$], 55.7 mg; [Ru$_2$(*p*-cymene)$_2$(donq)Cl$_2$], 60.0 mg; [Ru$_2$(*p*-cymene)$_2$(dotq)Cl$_2$], 68.0 mg; 0.082 mmol), 4 equiv of Ag(CF$_3$SO$_3$) (42.1 mg, 0.164 mmol), and 1 equiv of tetra-pvb (20.0 mg, 0.041 mmol) in MeOH (20 mL) was stirred at reflux for 24 h and then filtered. The solvent was removed, and the dark residue was dissolved in CH$_2$Cl$_2$/CH$_3$CN (1/1, 3 mL), before slowly adding diethyl ether to precipitate a dark red or dark green solid. The solid was filtered, washed with diethyl ether, and dried under vacuum.

*[Ru$_8$(p-cymene)$_8$(tetra-pvb)$_2$(dobq)$_4$][CF$_3$SO$_3$]$_8$ ([**8**][CF$_3$SO$_3$]$_8$).* Yield: 85.0 mg (90%). UV−vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 321 nm (ε = 1.34 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 505 nm (ε = 0.49 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3066 (m, aromatic, C−H), 1523 (s, dobq, C═O), 1258 (s, triflate, C−F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.02 (d, ^3J = 6.3 Hz, 16H, H$_\alpha$), 7.57 (s, 4H, H$_C$), 7.31 (d, ^3J = 6.3 Hz, 16H, H$_\beta$), 7.29 (d, ^3J = 16.1 Hz, 8H, H$_B$), 6.65 (d, ^3J = 16.1 Hz, 8H, H$_A$), 5.92 (d, ^3J = 6.2 Hz, 16H, H$_{p\text{-cym}}$), 5.72 (d, ^3J = 6.2 Hz, 16H, H$_{p\text{-cym}}$), 5.62 (s, 8H, H$_{\text{dobq}}$), 2.84 (sept, ^3J = 6.9 Hz, 8H, C*H*(CH$_3$)$_2$), 2.19 (s, 24H, CH$_3$), 1.31 (d, ^3J = 6.9 Hz, 48H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 184.4 (CO), 153.5 (CH$_\alpha$), 149.5 (C$_{\text{tetra-pvb}}$), 138.3 (C$'_{\text{tetra-pvb}}$), 138.1 (CH$_B$), 131.5 (CH$_A$), 127.1 (CH$_C$), 123.9 (CH$_\beta$), 104.3 (C$_{p\text{-cym}}$), 102.2 (CH$_{\text{dobq}}$), 99.5 (C$_{p\text{-cym}}$), 84.4 (CH$_{p\text{-cym}}$), 82.7 (CH$_{p\text{-cym}}$), 32.1 (CH(CH$_3$)$_2$), 22.4 (CH(CH$_3$)$_2$), 18.3 (CH$_3$). MS (ESI positive mode): m/z 1003.09 [8 + 4 CF$_3$SO$_3$]$^{4+}$, 1387.11 [8 + 5 CF$_3$SO$_3$]$^{3+}$. Anal. Calcd for C$_{180}$H$_{172}$F$_{24}$N$_8$O$_{40}$Ru$_8$S$_8$·3CH$_2$Cl$_2$: C, 45.20; H, 3.69; N, 2.30. Found: C, 45.04; H, 3.94; N, 2.52.

*[Ru$_8$(p-cymene)$_8$(tetra-pvb)$_2$(donq)$_4$][CF$_3$SO$_3$]$_8$ ([**9**][CF$_3$SO$_3$]$_6$).* Yield: 68 mg (69%). UV−vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 368 nm (ε = 1.83 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 645 nm (ε = 0.13 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 702 nm (ε = 0.14 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3060 (m, aromatic, C−H), 1537 (s, donq, C═O), 1260 (s, triflate, C−F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.31 (d, ^3J = 5.8 Hz, 16H, H$_\alpha$), 8.04 (s, 4H, H$_C$), 7.74 (d, ^3J = 16.2 Hz, 8H, H$_B$), 7.64 (d, ^3J = 5.8 Hz, 16H, H$_\beta$), 7.23 (s, 8H, H$_{\text{donq}}$), 7.22 (d, ^3J = 16.2 Hz, 8H, H$_A$), 7.21 (s, 8H, H$_{\text{donq}}$), 5.70 (d, ^3J = 5.7 Hz, 16H, H$_{p\text{-cym}}$), 5.50 (d, ^3J = 5.7 Hz, 16H, H$_{p\text{-cym}}$), 2.85 (sept, ^3J = 6.9 Hz, 8H, C*H*(CH$_3$)$_2$), 2.12 (s, 24H, CH$_3$), 1.33 (d, ^3J = 6.9 Hz, 48H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 171.9 (CO), 171.7 (CO), 152.9 (CH$_\alpha$), 148.3 (C$_{\text{tetra-pvb}}$), 138.4 (CH$_{\text{donq}}$), 135.8 (C$'_{\text{tetra-pvb}}$), 131.3 (CH$_B$), 128.5 (CH$_A$), 125.2 (CH$_C$), 124.2 (CH$_\beta$), 112.4 (C$_{\text{donq}}$), 104.5 (C$_{p\text{-cym}}$), 100.1 (C$_{p\text{-cym}}$), 85.1 (CH$_{p\text{-cym}}$), 85.0 (CH$_{p\text{-cym}}$), 84.1 (CH$_{p\text{-cym}}$), 31.4 (CH(CH$_3$)$_2$), 22.4 (CH(CH$_3$)$_2$), 22.3 (CH(CH$_3$)$_2$), 17.3 (CH$_3$). MS (ESI positive mode): m/z 1053.36 [9 + 4 CF$_3$SO$_3$]$^{4+}$, 1453.85 [9 + 5 CF$_3$SO$_3$]$^{3+}$. Anal. Calcd for C$_{196}$H$_{180}$F$_{24}$N$_8$O$_{40}$Ru$_8$S$_8$·8CH$_2$Cl$_2$·CH$_3$CN: C, 44.75; H, 3.63; N, 2.28. Found: C, 44.52; H, 3.51; N, 2.39.

*[Ru$_8$(p-cymene)$_8$(tetra-pvb)$_2$(dotq)$_4$][CF$_3$SO$_3$]$_8$ ([**10**][CF$_3$SO$_3$]$_8$).* Yield: 79.1 mg (74%). UV−vis (1.0 × 10^{-5} M, CH$_2$Cl$_2$): $\lambda_{\max}$ 368 nm (ε = 1.14 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 485 nm (ε = 0.12 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 522 nm (ε = 0.11 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 572 nm (ε = 0.13 × 10^5 M^{-1} cm^{-1}), $\lambda_{\max}$ 615 nm (ε = 0.18 × 10^5 M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C−H), 1543 (s, dotq, C═O), 1260 (s, triflate, C−F). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) 8.87 (dd, ^4J = 3.4 Hz, ^3J = 6.0 Hz, 8H, H$_{\text{bq}}$), 8.79 (dd, ^4J = 3.4 Hz, ^3J = 6.0 Hz, 8H, H$_{\text{bq}}$), 8.31 (d, ^3J = 6.1 Hz, 16H, H$_\alpha$), 8.19 (dd, ^4J = 3.4 Hz, ^3J = 6.0 Hz, 8H, H$_{\text{cq}}$), 8.02 (dd, ^4J = 3.4 Hz, ^3J = 6.0 Hz, 8H, H$_{\text{cq}}$), 7.26 (d, ^3J = 6.1 Hz, 16H, H$_\beta$), 7.10 (br s, 8H, H$_B$), 6.84 (br s, 2H, H$_C$), 6.61 (br s, 8H, H$_A$), 5.89 (d, ^3J = 6.0 Hz, 8H, H$_{p\text{-cym}}$), 5.88 (d, ^3J = 6.0 Hz, 8H, H$_{p\text{-cym}}$), 5.78 (br s, 2H, H$_C$), 5.66 (d, ^3J = 6.0 Hz, 8H, H$_{p\text{-cym}}$), 5.65 (d, ^3J = 6.0 Hz, 8H, H$_{p\text{-cym}}$), 2.97 (sept, ^3J = 6.9 Hz, 8H, C*H*(CH$_3$)$_2$), 2.16 (s, 24H, CH$_3$), 1.34 (d, ^3J = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 1.33 (d, ^3J = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) 170.2 (CO), 169.8 (CO), 152.5 (CH$_\alpha$), 147.9 (C$_{\text{tetra-pvb}}$), 134.8 (C$_{\text{dotq}}$), 134.7 (C$_{\text{dotq}}$), 134.0 (CH$_{\text{cq}}$), 132.0 (CH$_C$), 131.5 (C$'_{\text{tetra-pvb}}$), 130.4 (CH$_B$), 128.4 (CH$_{\text{bq}}$), 128.2 (CH$_{\text{bq}}$), 127.8 (CH$_A$), 125.4 (CH$_C$), 123.9 (CH$_\beta$), 108.0 (C$_{\text{dotq}}$), 104.5 (C$_{p\text{-cym}}$), 100.4 (C$_{p\text{-cym}}$), 85.0 (CH$_{p\text{-cym}}$), 85.0 (CH$_{p\text{-cym}}$), 83.4 (CH$_{p\text{-cym}}$), 31.4 (CH(CH$_3$)$_2$), 22.5 (CH(CH$_3$)$_2$), 17.8 (CH$_3$). MS (ESI positive mode): m/z 1153.40 [10 + 4 CF$_3$SO$_3$]$^{4+}$, 1587.82 [10 + 5 CF$_3$SO$_3$]$^{3+}$. Anal. Calcd for C$_{228}$H$_{196}$F$_{24}$N$_8$O$_{40}$Ru$_8$S$_8$: C, 52.57; H, 3.79; N, 2.15. Found: C, 52.36; H, 4.06; N, 2.21.

Synthesis of Metalla-Cubes [11]$^{8+}$–[14]$^{8+}$: General Procedure. A mixture of 2 equiv of molecular clip ([Ru$_2$(*p*-cymene)$_2$(dobq)Cl$_2$], 55.7 mg; [Ru$_2$(*p*-cymene)$_2$(dCloq)Cl$_2$], 61.4 mg; [Ru$_2$(*p*-cymene)$_2$(donq)Cl$_2$], 60.0 mg; [Ru$_2$(*p*-cymene)$_2$(dotq)-Cl$_2$], 68.0 mg; 0.082 mmol), 4 equiv of Ag(CF$_3$SO$_3$) (42.1 mg, 0.164

mmol), and 1 equiv of tetra-peb (19.8 mg, 0.041 mmol) in MeOH (20 mL) was stirred at reflux for 24 h and then filtered. The solvent was removed, and the dark residue was dissolved in CH_2Cl_2/CH_3CN (1/1, 3 mL), before slowly adding diethyl ether to precipitate a dark red, dark purple, or dark green solid. The solid was filtered, washed with diethyl ether, and dried under vacuum.

*[Ru_8(p-cymene)$_8$(tetra-peb)$_2$(dobq)$_4$][CF_3SO_3]$_8$ ([**11**][CF_3SO_3]$_8$).* Yield: 85 mg (90%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 342 nm ($\varepsilon = 2.32 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 499 nm ($\varepsilon = 0.58 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3064 (m, aromatic, C–H), 1525 (s, dobq, C═O), 1258 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.06 (d, $^3J = 5.7$ Hz, 16H, H_α), 7.84 (s, 4H, H_C), 7.38 (d, $^3J = 5.7$ Hz, 16H, H_β), 5.93 (d, $^3J = 6.1$ Hz, 16H, $H_{p\text{-cym}}$), 5.71 (d, $^3J = 6.1$ Hz, 16H, $H_{p\text{-cym}}$), 5.63 (s, 8H, H_{dobq}), 2.83 (sept, $^3J = 6.9$ Hz, 8H, $CH(CH_3)_2$), 2.17 (s, 24H, CH_3), 1.30 (d, $^3J = 6.9$ Hz, 48H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 184.2 (CO), 153.7 (CH_α), 134.0 ($C4_{tetra\text{-}peb}$), 133.3 (CH_C), 128.5 (CH_β), 126.7 ($C1_{tetra\text{-}peb}$), 104.5 ($C_{p\text{-cym}}$), 102.5 (CH_{dobq}), 99.9 ($C_{p\text{-cym}}$), 94.3 ($C2_{tetra\text{-}peb}$), 92.6 ($C3_{tetra\text{-}peb}$), 84.6 ($CH_{p\text{-cym}}$), 82.8 ($CH_{p\text{-cym}}$), 32.1 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 18.3 (CH_3). MS (ESI positive mode): m/z 1008.14 [**11** + 4 CF_3SO_3 + HCl]$^{4+}$. Anal. Calcd for $C_{180}H_{156}F_{24}N_8O_{40}Ru_8S_8\cdot 4CH_2Cl_2\cdot 4Et_2O$: C, 45.94; H, 3.93; N, 2.14. Found: C, 45.69; H, 4.11; N, 2.41.

*[Ru_8(p-cymene)$_8$(tetra-peb)$_2$(dCloq)$_4$][CF_3SO_3]$_8$ ([**12**][CF_3SO_3]$_8$).* Yield: 86 mg (86%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 317 nm ($\varepsilon = 1.44 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 522 nm ($\varepsilon = 0.57 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C–H), 1504 (s, dCloq, C═O), 1260 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.06 (d, $^3J = 5.6$ Hz, 16H, H_α), 7.84 (s, 4H, H_C), 7.41 (d, $^3J = 5.6$ Hz, 16H, H_β), 6.01 (d, $^3J = 6.1$ Hz, 16H, $H_{p\text{-cym}}$), 5.83 (d, $^3J = 6.1$ Hz, 16H, $H_{p\text{-cym}}$), 2.88 (sept, $^3J = 6.9$ Hz, 8H, $CH(CH_3)_2$), 2.24 (s, 24H, CH_3), 1.35 (d, $^3J = 6.9$ Hz, 48H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 177.8 (CO), 153.5 (CH_α), 134.4 ($C4_{tetra\text{-}peb}$), 133.5 (CH_C), 128.8 (CH_β), 126.6 ($C1_{tetra\text{-}peb}$), 107.2 (C_{dCloq}), 105.0 ($C_{p\text{-cym}}$), 99.8 ($C_{p\text{-cym}}$), 94.5 ($C2_{tetra\text{-}peb}$), 92.5 ($C3_{tetra\text{-}peb}$), 84.5 ($CH_{p\text{-cym}}$), 83.5 ($CH_{p\text{-cym}}$), 32.2 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$), 18.3 (CH_3). MS (ESI positive mode): m/z 1068.48 [**12** + 4 CF_3SO_3]$^{4+}$, 1077.05 [**12** + 4 CF_3SO_3 + HCl]$^{4+}$. Anal. Calcd for $C_{180}H_{148}Cl_8F_{24}N_8O_{40}Ru_8S_8\cdot 6CH_2Cl_2\cdot Et_2O$: C, 41.86; H, 3.14; N, 2.06. Found: C, 41.64; H, 3.43; N, 2.36.

*[Ru_8(p-cymene)$_8$(tetra-peb)$_2$(donq)$_4$][CF_3SO_3]$_8$ ([**13**][CF_3SO_3]$_8$).* Yield: 71 mg (72%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 308 nm ($\varepsilon = 1.62 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 389 nm ($\varepsilon = 0.44 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 431 nm ($\varepsilon = 0.41 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 650 nm ($\varepsilon = 0.12 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 701 nm ($\varepsilon = 0.14 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3059 (m, aromatic, C–H), 1535 (s, donq, C═O), 1262 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.20 (d, $^3J = 6.6$ Hz, 16H, H_α), 7.79 (s, 4H, H_C), 7.27 (d, $^3J = 6.6$ Hz, 16H, H_β), 7.09 (s, 16H, H_{donq}), 5.70 (d, $^3J = 6.2$ Hz, 16H, $H_{p\text{-cym}}$), 5.49 (d, $^3J = 6.2$ Hz, 16H, $H_{p\text{-cym}}$), 2.83 (sept, $^3J = 6.9$ Hz, 8H, $CH(CH_3)_2$), 2.12 (s, 24H, CH_3), 1.29 (d, $^3J = 6.9$ Hz, 48H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 171.1 (CO), 153.1 (CH_α), 138.3 (CH_{donq}), 133.6 ($C4_{tetra\text{-}peb}$), 133.4 (CH_C), 127.8 (CH_β), 126.5 ($C1_{tetra\text{-}peb}$), 111.7 (C_{donq}), 104.5 ($C_{p\text{-cym}}$), 100.5 ($C_{p\text{-cym}}$), 93.6 ($C2_{tetra\text{-}peb}$), 92.4 ($C3_{tetra\text{-}peb}$), 85.1 ($CH_{p\text{-cym}}$), 83.9 ($CH_{p\text{-cym}}$), 31.4 ($CH(CH_3)_2$), 22.2 ($CH(CH_3)_2$), 17.3 (CH_3). MS (ESI positive mode): m/z 1058.14 [**13** + 4 CF_3SO_3 + HCl]$^{4+}$. Anal. Calcd for $C_{196}H_{164}F_{24}N_8O_{40}Ru_8S_8\cdot 5CH_2Cl_2\cdot 2Et_2O$: C, 46.79; H, 3.64; N, 2.09. Found: C, 46.57; H, 3.90; N, 2.46.

*[Ru_8(p-cymene)$_8$(tetra-peb)$_2$(dotq)$_4$][CF_3SO_3]$_8$ ([**14**][CF_3SO_3]$_8$).* Yield: 77 mg (72%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 317 nm ($\varepsilon = 1.57 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 376 nm ($\varepsilon = 1.00 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 399 nm ($\varepsilon = 0.80 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 522 nm ($\varepsilon = 0.13 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 568 nm ($\varepsilon = 0.23 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 612 nm ($\varepsilon = 0.30 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3070 (m, aromatic, C–H), 1543 (s, dotq, C═O), 1262 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.64 (dd, $^4J = 3.3$ Hz, $^3J = 5.9$ Hz, 16H, H_{bq}), 8.24 (d, $^3J = 6.6$ Hz, 16H, H_α), 7.92 (dd, $^4J = 3.3$ Hz, $^3J = 5.9$ Hz, 16H, H_{cq}), 7.69 (s, 4H, H_C), 7.13 (d, $^3J = 6.6$ Hz, 16H, H_β), 5.89 (d, $^3J = 6.2$ Hz, 16H, $H_{p\text{-cym}}$), 5.65 (d, $^3J = 6.2$ Hz, 16H, $H_{p\text{-cym}}$), 2.98 (sept, $^3J = 6.9$ Hz, 8H, $CH(CH_3)_2$), 2.22 (s, 24H, CH_3), 1.32 (d, $^3J = 6.9$ Hz, 48H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 169.4 (CO), 152.9 (CH_α), 134.5 (C_{dotq}), 134.0 (CH_{cq}), 133.5 ($C4_{tetra\text{-}peb}$), 133.3 (CH_C), 128.0 (CH_{bq}), 127.8 (CH_β), 126.5 ($C1_{tetra\text{-}peb}$), 107.5 (C_{dotq}), 104.4 ($C_{p\text{-cym}}$), 100.7 ($C_{p\text{-cym}}$), 93.6 ($C2_{tetra\text{-}peb}$), 92.5 ($C3_{tetra\text{-}peb}$), 85.2 ($CH_{p\text{-cym}}$), 83.4 ($CH_{p\text{-cym}}$), 31.5 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 17.9 (CH_3). MS (ESI positive mode): m/z 1158.17 [**14** + 4 CF_3SO_3 + HCl]$^{4+}$, 1582.14 [**14** + 5 CF_3SO_3]$^{3+}$. Anal. Calcd for $C_{228}H_{180}F_{24}N_8O_{40}Ru_8S_8\cdot 11CH_2Cl_2\cdot Et_2O$: C, 47.06; H, 3.45; N, 1.81. Found: C, 47.00; H, 3.65; N, 1.95.

Synthesis of [photosensitizer⊂9][CF_3SO_3]$_8$ and [photosensitizer⊂13][CF_3SO_3]$_8$: General Procedure. A mixture of 4 equiv of [Ru_2(*p*-cymene)$_2$(donq)Cl_2] (60.0 mg, 0.082 mmol), 8 equiv of Ag(CF_3SO_3) (42.1 mg, 0.164 mmol), 1 equiv of photosensitizer (phthalocyanine, 10.8 mg; Zn-phthalocyanine, 12.1 mg; 0.021 mmol), and 2 equiv of tetra-pvb or tetra-peb (tetra-pvb, 20.0 mg; tetra-peb, 19.8 mg; 0.041 mmol) in MeOH (20 mL) was stirred at reflux for 24 h and then filtered. The solvent was removed, and the dark residue was dissolved in CH_2Cl_2/CH_3CN (1/1, 3 mL), before slowly adding diethyl ether to precipitate a dark green solid. The solid was filtered, washed with diethyl ether, and dried under vacuum.

*[phthalocyanine⊂Ru_8(p-cymene)$_8$(tetra-pvb)$_2$(donq)$_4$][CF_3SO_3]$_8$ ([phthalocyanine⊂**9**][CF_3SO_3]$_6$).* Yield: 82.5 mg (76%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 354 nm ($\varepsilon = 1.99 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 614 nm ($\varepsilon = 0.22 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 647 nm ($\varepsilon = 0.29 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 678 nm ($\varepsilon = 0.71 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 712 nm ($\varepsilon = 0.86 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3053 (m, aromatic, C–H), 1535 (s, donq, C═O), 1260 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.51 (d, $^3J = 7.3$ Hz, 8H, $H_{phthalocyanine}$), 8.20 (d, $^3J = 5.8$ Hz, 16H, H_α), 7.68 (s, 8H, H_{donq}), 7.58 (s, 8H, H_{donq}), 7.02 (d, $^3J = 5.8$ Hz, 16H, H_β), 5.69 (d, $^3J = 5.6$ Hz, 16H, $H_{p\text{-cym}}$), 5.67 (d, $^3J = 16.0$ Hz, 8H, H_B), 5.49 (d, $^3J = 5.6$ Hz, 8H, $H_{p\text{-cym}}$), 5.46 (d, $^3J = 5.6$ Hz, 8H, $H_{p\text{-cym}}$), 5.45 (br s, 8H, $H_{phthalocyanine}$), 5.33 (d, $^3J = 16.0$ Hz, 8H, H_A), 4.84 (s, 4H, H_C), 2.88 (sept, $^3J = 6.9$ Hz, 8H, $CH(CH_3)_2$), 2.10 (s, 24H, CH_3), 1.37 (d, $^3J = 6.9$ Hz, 24H, $CH(CH_3)_2$), 1.36 (d, $^3J = 6.9$ Hz, 24H, $CH(CH_3)_2$), −2.46 (s, 2H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 172.2 (CO), 172.0 (CO), 152.0 (CH_α), 146.6 ($C_{tetra\text{-}pvb}$), 139.0 (CH_{donq}), 138.8 (CH_{donq}), 137.4 ($C_{phthalocyanine}$), 131.4 ($C'_{tetra\text{-}pvb}$), 129.3 ($CH_{phthalocyanine}$), 126.6 (CH_B), 125.9 (CH_A), 123.9 (CH_β), 122.6 ($CH_{phthalocyanine}$), 119.9 (CH_C), 112.7 (C_{donq}), 104.7 ($C_{p\text{-cym}}$), 100.1 ($C_{p\text{-cym}}$), 85.1 ($CH_{p\text{-cym}}$), 85.0 ($CH_{p\text{-cym}}$), 84.3 ($CH_{p\text{-cym}}$), 84.2 ($CH_{p\text{-cym}}$), 31.5 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 17.3 (CH_3). MS (ESI positive mode): m/z 915.52 [phthalocyanine + **9** + 3 CF_3SO_3]$^{5+}$, 1181.91 [phthalocyanine + **9** + 4 CF_3SO_3]$^{4+}$, 1625.19 [phthalocyanine + **9** + 5 CF_3SO_3]$^{3+}$. Anal. Calcd for $C_{228}H_{198}F_{24}N_{16}O_{40}Ru_8S_8\cdot 9CH_2Cl_2$: C, 46.76; H, 3.58; N, 3.68. Found: C, 46.75; H, 3.86; N, 3.46.

*[Zn-phthalocyanine⊂Ru_8(p-cymene)$_8$(tetra-pvb)$_2$(donq)$_4$][CF_3SO_3]$_8$ ([Zn-phthalocyanine⊂**9**][CF_3SO_3]$_8$).* Yield: 79.1 mg (72%). UV–vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 343 nm ($\varepsilon = 1.22 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 411 nm ($\varepsilon = 0.73 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 626 nm ($\varepsilon = 0.20 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 666 nm ($\varepsilon = 0.20 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 694 nm ($\varepsilon = 1.02 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3059 (m, aromatic, C–H), 1537 (s, donq, C═O), 1258 (s, triflate, C–F). ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.50 (br s, 8H, $H_{Zn\text{-}phthalocyanine}$), 8.21 (d, $^3J = 5.8$ Hz, 16H, H_α), 7.69 (s, 8H, H_{donq}), 7.59 (s, 8H, H_{donq}), 7.03 (d, $^3J = 5.8$ Hz, 16H, H_β), 5.69 (d, $^3J = 6.0$ Hz, 16H, $H_{p\text{-cym}}$), 5.62 (d, $^3J = 16.1$ Hz, 8H, H_B), 5.49 (d, $^3J = 6.0$ Hz, 8H, $H_{p\text{-cym}}$), 5.47 (br s, 8H, $H_{Zn\text{-}phthalocyanine}$), 5.46 (d, $^3J = 6.0$ Hz, 8H, $H_{p\text{-cym}}$), 5.34 (d, $^3J = 16.1$ Hz, 8H, H_A), 4.78 (s, 4H, H_C), 2.89 (sept, $^3J = 6.9$ Hz, 8H, $CH(CH_3)_2$), 2.09 (s, 24H, CH_3), 1.37 (d, $^3J = 6.9$ Hz, 24H, $CH(CH_3)_2$), 1.35 (d, $^3J = 6.9$ Hz, 24H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 172.3 (CO), 172.0 (CO), 153.5 ($C_{Zn\text{-}phthalocyanine}$), 152.0 ($CH_\alpha$), 146.4 ($C_{tetra\text{-}pvb}$), 139.0 ($CH_{donq}$), 138.9 ($CH_{donq}$), 138.8 ($C_{Zn\text{-}phthalocyanine}$), 131.5 ($C'_{tetra\text{-}pvb}$), 129.0 ($CH_{Zn\text{-}phthalocyanine}$), 126.5 ($CH_B$), 126.1 ($CH_A$), 124.0 ($CH_\beta$), 122.5 ($CH_{Zn\text{-}phthalocyanine}$), 119.7 ($CH_C$), 112.8 ($C_{donq}$), 104.7 ($C_{p\text{-cym}}$), 100.2 ($C_{p\text{-cym}}$), 85.2 ($CH_{p\text{-cym}}$), 85.1 ($CH_{p\text{-cym}}$), 84.3 ($CH_{p\text{-cym}}$), 84.2 ($CH_{p\text{-cym}}$), 31.5 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$),

17.3 (CH_3). MS (ESI positive mode): *m*/*z* 1197.63 [Zn-phthalocyanine + **9** + 4 CF_3SO_3]$^{4+}$, 1646.52 [Zn-phthalocyanine + **9** + 5 CF_3SO_3]$^{3+}$. Anal. Calcd for $C_{228}H_{196}F_{24}N_{16}O_{40}Ru_8S_8Zn\cdot 7CH_2Cl_2\cdot 2CH_3CN$: C, 47.34; H, 3.59; N, 4.16. Found: C, 47.37; H, 3.90; N, 4.18.

*[phthalocyanine⊂Ru_8(p-cymene)$_8$(tetra-peb)$_2$(donq)$_4$][CF_3SO_3]$_8$ ([phthalocyanine⊂**13**][CF_3SO_3]$_8$).* Yield: 59 mg (59%) ([phthalocyanine⊂**13**] 19%, [**13**] 81%, determined by ^{1}H NMR). UV−vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 315 nm ($\varepsilon = 1.73 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 455 nm ($\varepsilon = 0.43 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 610 nm ($\varepsilon = 0.15 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 644 nm ($\varepsilon = 0.19 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 675 nm ($\varepsilon = 0.30 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 707 nm ($\varepsilon = 0.36 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3064 (m, aromatic, C−H), 1538 (s, donq, C=O), 1259 (s, triflate, C−F). ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.56 (br s, 8H, $H_{Phthalocyanine}$), 8.38 (d, ^3J = 6.4 Hz, 16H, H_α), 7.64 (s, 8H, H_{donq}), 7.62 (s, 8H, H_{donq}), 6.82 (d, ^3J = 6.4 Hz, 16H, H_β), 5.83 (br s, 8H, $H_{Phthalocyanine}$), 5.76 (d, ^3J = 6.1 Hz, 8H, $H_{p\text{-}cym}$), 5.72 (d, ^3J = 6.1 Hz, 8H, $H_{p\text{-}cym}$), 5.52 (d, ^3J = 6.1 Hz, 8H, $H_{p\text{-}cym}$), 5.49 (d, ^3J = 6.1 Hz, 8H, $H_{p\text{-}cym}$), 4.56 (s, 4H, H_C), 2.86 (sept, ^3J = 6.8 Hz, 8H, $CH(CH_3)_2$), 2.08 (s, 24H, CH_3), 1.36 (d, ^3J = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.34 (d, ^3J = 6.8 Hz, 24H, $CH(CH_3)_2$), −2.26 (s, 2H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 172.2 (CO), 171.9 (CO), 152.7 (CH_α), 139.0 (CH_{donq}), 138.9 (CH_{donq}), 134.8 (CH_C), 132.5 ($C4_{tetra\text{-}peb}$), 128.6 ($CH_{Phthalocyanine}$), 128.1 (CH_β), 122.8 ($CH_{Phthalocyanine}$), 121.7 ($C1_{tetra\text{-}peb}$), 112.4 (C_{donq}), 104.7 ($C_{p\text{-}cym}$), 100.8 ($C_{p\text{-}cym}$), 91.8 ($C3_{tetra\text{-}peb}$), 91.1 ($C2_{tetra\text{-}peb}$), 85.4 ($CH_{p\text{-}cym}$), 85.4 ($CH_{p\text{-}cym}$), 84.0 ($CH_{p\text{-}cym}$), 31.5 ($CH(CH_3)_2$), 22.5 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$), 17.3 (CH_3). Due to the equilibrium between empty and filled complexes in solution, which does not allow the isolation of a single product, the molecular mass and the elemental composition were not determined.

*[Zn-phthalocyanine⊂Ru_8(p-cymene)$_8$(tetra-peb)$_2$(donq)$_4$][CF_3SO_3]$_8$ ([Zn-phthalocyanine⊂**13**][CF_3SO_3]$_8$).* Yield: 72 mg (67%) ([Zn-phthalocyanine⊂**13**] 79%, [**13**] 21%, determined by ^{1}H NMR). UV−vis (1.0×10^{-5} M, CH_2Cl_2): λ_{max} 330 nm ($\varepsilon = 2.72 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 407 nm ($\varepsilon = 1.01 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 455 nm ($\varepsilon = 0.62 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 623 nm ($\varepsilon = 0.37 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 658 nm ($\varepsilon = 0.43 \times 10^5$ M^{-1} cm^{-1}), λ_{max} 690 nm ($\varepsilon = 1.27 \times 10^5$ M^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3064 (m, aromatic, C−H), 1537 (s, donq, C=O), 1258 (s, triflate, C−F). ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.55 (br s, 8H, $H_{Zn\text{-}phthalocyanine}$), 8.38 (d, ^3J = 6.3 Hz, 16H, H_α), 7.64 (s, 8H, H_{donq}), 7.62 (s, 8H, H_{donq}), 6.82 (d, ^3J = 6.3 Hz, 16H, H_β), 5.81 (br s, 8H, $H_{Zn\text{-}phthalocyanine}$), 5.76 (d, ^3J = 6.1 Hz, 8H, $H_{p\text{-}cym}$), 5.72 (d, ^3J = 6.1 Hz, 8H, $H_{p\text{-}cym}$), 5.52 (d, ^3J = 6.1 Hz, 8H, $H_{p\text{-}cym}$), 5.50 (d, ^3J = 6.1 Hz, 8H, $H_{p\text{-}cym}$), 4.56 (s, 4H, H_C), 2.88 (sept, ^3J = 6.8 Hz, 8H, $CH(CH_3)_2$), 2.08 (s, 24H, CH_3), 1.36 (d, ^3J = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.34 (d, ^3J = 6.8 Hz, 24H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 172.2 (CO), 172.0 (CO), 154.0 ($C_{Zn\text{-}phthalocyanine}$), 152.7 ($CH_\alpha$), 139.3 ($C_{Zn\text{-}phthalocyanine}$), 139.0 ($CH_{donq}$), 138.9 ($CH_{donq}$), 134.7 ($CH_C$), 132.5 ($C4_{tetra\text{-}peb}$), 129.3 ($CH_{Zn\text{-}phthalocyanine}$), 128.1 ($CH_\beta$), 122.7 ($CH_{Zn\text{-}phthalocyanine}$), 121.9 ($C1_{tetra\text{-}peb}$), 112.5 ($C_{donq}$), 104.7 ($C_{p\text{-}cym}$), 100.8 ($C_{p\text{-}cym}$), 92.2 ($C3_{tetra\text{-}peb}$), 90.6 ($C2_{tetra\text{-}peb}$), 85.4 ($CH_{p\text{-}cym}$), 85.4 ($CH_{p\text{-}cym}$), 84.0 ($CH_{p\text{-}cym}$), 31.5 ($CH(CH_3)_2$), 22.5 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$), 17.3 ($CH_3$). Due to the equilibrium between empty and filled complexes in solution, which does not allow the isolation of a single product, the molecular mass and the elemental composition were not determined.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving selected 2D DOSY, 2D ROESY, and 2D NOESY spectra of different empty and filled metalla-cages. This material is available free of charge via the Internet at http://pubs.acs.org.

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All authors have contributed equally to this manuscript. All authors have given approval to the final version of the manuscript before submission.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

tris-pvb, 1,3,5-tris{2-(pyridin-4-yl)vinyl}benzene; tetra-pvb, 1,2,4,5-tetrakis{2-(pyridin-4-yl)vinyl}benzene; tetra-peb, 1,2,4,5-tetrakis{2-(pyridin-4-yl)ethynyl}benzene; ox, oxalato; dobq, 2,5-dioxido-1,4-benzoquinonato; dCloq, 2,5-dichloro-1,4-benzoquinonato; donq, 5,8-dioxido-1,4-naphthoquinonato; doaq, 5,8-dioxido-1,4-anthraquinonato; dotq, 6,11-dioxido-5,12-naphthacenedionato

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