In- and Out-of-Cavity Interactions by Modulating the Size of Ruthenium Metallarectangles

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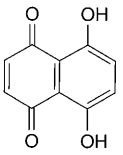
Dedicated to Professor *Georg Süss-Fink* on the occasion of his 60th birthday

Cationic (arene)ruthenium-based tetranuclear complexes of the general formula $[Ru_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-}N\cap N)_2(\mu\text{-}OO\cap OO)_2]^{4+}$ were obtained from the dinuclear (arene)ruthenium complexes $[Ru_2(\eta^6\text{-}p\text{-cymene})_2(\mu\text{-}OO\cap OO)_2Cl_2]$ (*p*-cymene = 1-methyl-4-(1-methylethyl)benzene, $OO\cap OO$ = 5,8-dihydroxy-1,4-naphthoquinonato(2−), 9,10-dihydroxy-1,4-anthraquinonato(2−), or 6,11-dihydroxynaphthacene-5,12-dionato(2−)) by reaction with pyrazine or bipyridine linkers ($N\cap N$ = pyrazine, 4,4′-bipyridine, 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine]) in the presence of silver trifluoromethanesulfonate (CF_3SO_3Ag) (*Scheme*). All complexes **4**–**12** were isolated in good yield as $CF_3SO_3^-$ salts, and characterized by NMR and IR spectroscopy. The host–guest properties of the metallarectangles incorporating 4,4′-bipyridine and (4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine] linkers were studied in solution by means of multiple NMR experiments (1D, ROESY, and DOSY). The largest metallarectangles **10**–**12** incorporating (4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine] linkers are able to host an anthracene, pyrene, perylene, or coronene molecule in their cavity, while the medium-size metallarectangles **7**–**9** incorporating 4,4′-bipyridine linkers are only able to encapsulate anthracene. However, out-of-cavity interactions are observed between these 4,4′-bipyridine-containing rectangles and pyrene, perylene, or coronene. In contrast, the small pyrazine-containing metallarectangles **4**–**6** show no interaction in solution with this series of planar aromatic molecules.

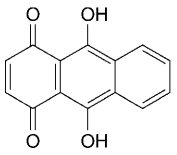
Introduction. – Half-sandwich complexes of ruthenium (Ru) and to a lesser extent osmium (Os) have received considerable attention, especially as catalysts [1], as biological agents [2], and recently as building blocks in supramolecular chemistry [3]. Their ability to generate a pre-organized arrangement with appropriate multidentate bridging ligands and rigid linkers have allowed the controlled formation of various supramolecular constructions, such as metallacycles [4], metallarectangles [5], metallaprisms [6], and metallacubes [7].

In coordination and organometallic chemistry, quinones are attracting a lot of interest [8]. Their numerous applications in organic chemistry [9], physical chemistry [10], and biology [11] are well known, and moreover, these multifunctional ligands are becoming popular for the synthesis of complexes with (η^6-arene)ruthenium units [12]. The commercially available quinone derivatives, 5,8-dihydroxy-1,4-naphthoquinone (H_2dhnq), 9,10-dihydroxy-1,4-anthraquinone (H_2dhaq), and 6,11-dihydroxynaphthacene-5,12-dione (H_2dhtq) have been used to form dinuclear species with Ru metals [13]. However, the corresponding dinuclear complexes incorporating [Ru(η^6-arene)]

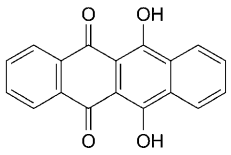
units remain scarce in the literature, and only $[Ru_2(\eta^6\text{-}p\text{-cymene})_2\{\mu\text{-}[5,8\text{-di(hydroxy-}\kappa O)\text{-}1,4\text{-naphthoquinonato}(2-)\text{-}\kappa O^1:\kappa O^4]\}Cl_2]$ [14] and $[Ru_2(\eta^6\text{-}p\text{-cymene})_2\{\mu\text{-}[9,10\text{-di(hydroxy-}\kappa O)\text{-}1,4\text{-anthraquinonato}(2-)\text{-}\kappa O^1:\kappa O^4]\}Cl_2]$ have been synthesized so far [15] (*p*-cymene = 1-methyl-4-(1-methylethyl)benzene).



H_2dhnq



H_2dhaq

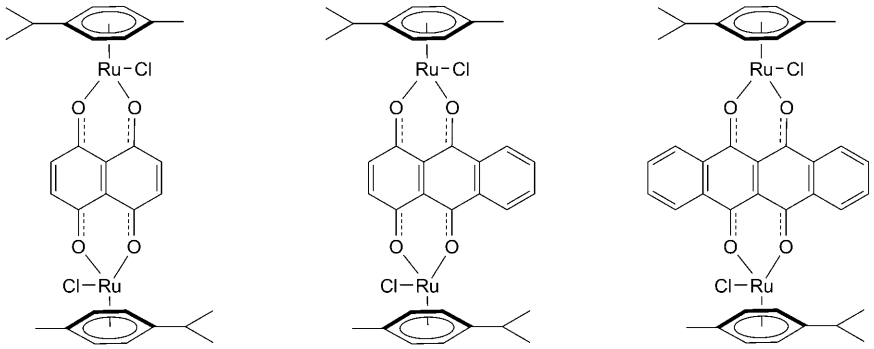


H_2dhtq

Recently, we reported the synthesis of a series of cationic tetranuclear metallarectangles of the general formula $[Ru_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-}N\cap N)_2\{\mu\text{-}[5,8\text{-di(hydroxy-}\kappa O)\text{-}1,4\text{-naphthoquinonato}(2-)\text{-}\kappa O^1:\kappa O^4]\}_2]^{4+}$ ($N\cap N$ = pyrazine, 4,4′-bipyridine, 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine]). The ability of these metallarectangles to host pyrene in solution was studied [16]. In the case of $[Ru_4(\eta^6\text{-}p\text{-cymene})_4[\mu\text{-(pyrazine-}\kappa N^1:\kappa N^4)]_2\{\mu\text{-}[5,8\text{-di(hydroxy-}\kappa O)\text{-}1,4\text{-naphthoquinonato}(2-)\text{-}\kappa O^1:\kappa O^4]\}_2]^{4+}$ **4**, no interaction between the metallarectangle and pyrene was observed. However, in the case of $[Ru_4(\eta^6\text{-}p\text{-cymene})_4[\mu\text{-}(4,4'\text{-bipyridine-}\kappa N^1:\kappa N^{1'})]_2\{\mu\text{-}[5,8\text{-di(hydroxy-}\kappa O)\text{-}1,4\text{-naphthoquinonato}(2-)\text{-}\kappa O^1:\kappa O^4]\}_2]^{4+}$ **7**, interactions occurred on the outside of the rectangular assembly, while in $[Ru_4(\eta^6\text{-}p\text{-cymene})_4\{\mu\text{-}\{4,4'\text{-}[(1E)\text{-ethene-1,2-diyl]bis-[pyridine]-}\kappa N^1:\kappa N^{1'}\}\}_2\{\mu\text{-}[5,8\text{-di(hydroxy-}\kappa O)\text{-}1,4\text{-naphthoquinonato}(2-)\text{-}\kappa O^1:\kappa O^4]\}_2]^{4+}$ **10**, the pyrene molecule was found inside the hydrophobic cavity of the metallarectangle, thus giving rise to a host–guest system. We now extended this study to three other guest molecules, anthracene, perylene, and coronene, with not only the already known 5,8-dihydroxy-1,4-naphthoquinonato(2−) containing metallarectangles but as well with 9,10-dihydroxy-1,4-anthraquinonato(2−) and 6,11-dihydroxynaphthacene-5,12-dionato(2−) bridging ligands, thus generating the cationic tetranuclear metallarectangles $[Ru_4(\eta^6\text{-}p\text{-cymene})_4(\mu\text{-}N\cap N)_2(\mu\text{-}OO\cap OO)_2]^{4+}$ ($OO\cap OO$ = 9,10-dihydroxy-1,4-anthraquinonato(2−), 6,11-dihydroxynaphthacene-5,12-dionato(2−); $N\cap N$ = pyrazine, 4,4′-bipyridine, 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine]).

Results and Discussion. – The synthesis of cationic tetranuclear metallarectangles involves the dinuclear (η^6-arene)ruthenium precursors $[Ru_2(\eta^6\text{-}p\text{-cymene})_2(\mu\text{-}OO\cap OO)_2Cl_2]$ **1**–**3**. Whereas the syntheses of the dinuclear metallaclips **1** [14] and **2** [15] have already been reported, the synthesis of $[Ru_2(\eta^6\text{-}p\text{-cymene})_2\{\mu\text{-}[6,11\text{-di(hydroxy-}\kappa O)\text{naphthacene-}5,12\text{-dionato}(2-)\text{-}\kappa O^5:\kappa O^{12}]\}Cl_2]$ (**3**) is new. Complex **3** is characterized by NMR, UV/VIS, and IR spectroscopy. As expected, the ^{1}H-NMR spectra of **3** show two *doublet*s at δ(H) 8.50 and 7.72 corresponding to the H-atoms of the 6,11-dihydroxynaphthacene-5,12-dionato(2−) bridging ligand along with the signals associated with the η^6-*p*-cymene ligands.

These dinuclear bridged (η^6-arene)ruthenium complexes **1**–**3** react in MeOH at room temperature in the presence of CF_3SO_3Ag (halide scavenger) with different $N\cap N$ donor ligands ($N\cap N$ = pyrazine, 4,4′-bipyridine, 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyr-



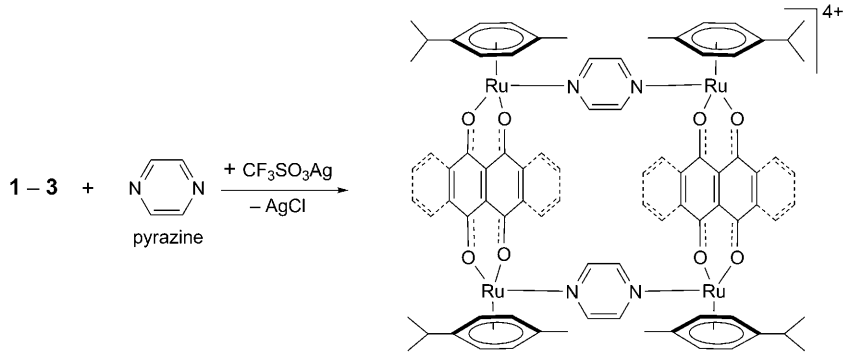
idine]) to give the cationic tetranuclear metallarectangles **4**–**12** which are isolated as $CF_3SO_3^-$ salts (*Scheme*).

The ^{1}H-NMR spectra of **4**–**6** display a *s* due to the pyrazine H-atoms. Unlike free pyrazine, where the H-atom signal is found at δ(H) 8.57 in CD_3CN, the corresponding signal of **4**–**6** appears slightly shifted upfield at δ(H) 8.46. The ^{1}H-NMR spectra of **7**–**9** show two *doublet*s due to the 4,4′-bipyridine H-atoms with an upfield shift $\Delta\delta$ of *ca.* 0.2 as compared with the free 4,4′-bipyridine in CD_3CN. The same upfield shift $\Delta\delta$ of *ca.* 0.2 is observed for the H-atoms of the 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine] linkers in complexes **10**–**12**. Upon formation of the cationic tetranuclear metallarectangles, the Me and i-Pr signals of the η^6-*p*-cymene ligands in **4**–**12** remain almost unchanged as compared to those of complexes **1**–**3**, while the aromatic H-atoms of the η^6-*p*-cymene ligands are slightly shifted downfield. Similarly, the H-atom signals of the bridging 5,8-dihydroxy-1,4-naphthoquinonato(2–), 9,10-dihydroxy-1,4-anthraquinonato(2–), and 6,11-dihydroxynaphthacene-5,12-dionato(2–) ligands in all metallarectangles **4**–**12** are shifted downfield as compared to their parent complexes **1**–**3**.

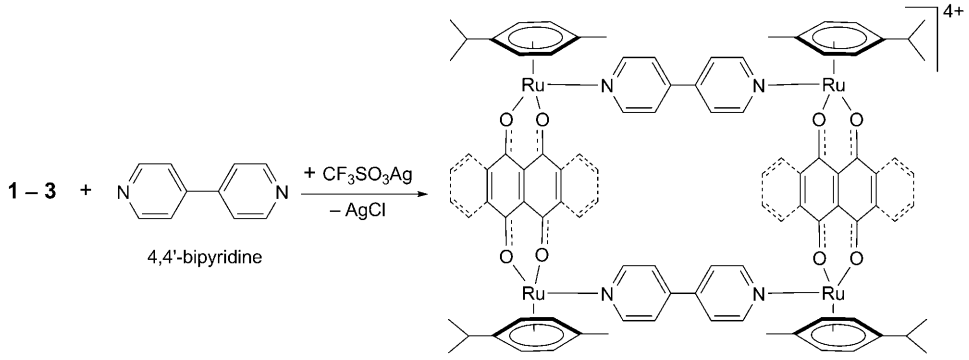
In the metallarectangles **5**, **8**, and **11**, the asymmetry of the 9,10-dihydroxy-1,4-anthraquinonato(2–) bridging ligand allows the formation of two isomers. Indeed, the presence of two isomers is quite obvious in the case of **5** in which two distinct sets of signals for the 9,10-dihydroxy-1,4-anthraquinonato(2–) ligands are observed in the ^{1}H-NMR spectrum (CD_3CN). However, the signals of the η^6-*p*-cymene and pyrazine ligands remain equivalent despite the presence of these two isomers **5** and **5′** (*Fig. 1*). In the case of **8** and **11**, in which the two 9,10-dihydroxy-1,4-anthraquinonato(2–) bridges are far away from each other, only the *singulet* of the 9,10-dihydroxy-1,4-anthraquinonato(2–) ligands is observed as nonequivalent signals. All other signals show no sign of the presence of the two isomers and give rise to only one set of signals for both isomers.

The IR spectra of **4**–**12** are dominated by absorptions of the coordinated $N \cap N$ and $OO \cap OO$ ligands which are only slightly shifted as compared to the IR absorptions of the free ligands. In addition to the $N \cap N$ and $OO \cap OO$ signals, strong absorptions due to the stretching vibrations of the $CF_3SO_3^-$ anions (1260*s*, 1030*s*, and 638*m* cm^{-1}) are also observed in the IR spectra of the salts [**4**–**12**] $[CF_3SO_3]_4$. The electronic absorption spectra of the metallarectangles **4**–**12** are characterized by an intense high-

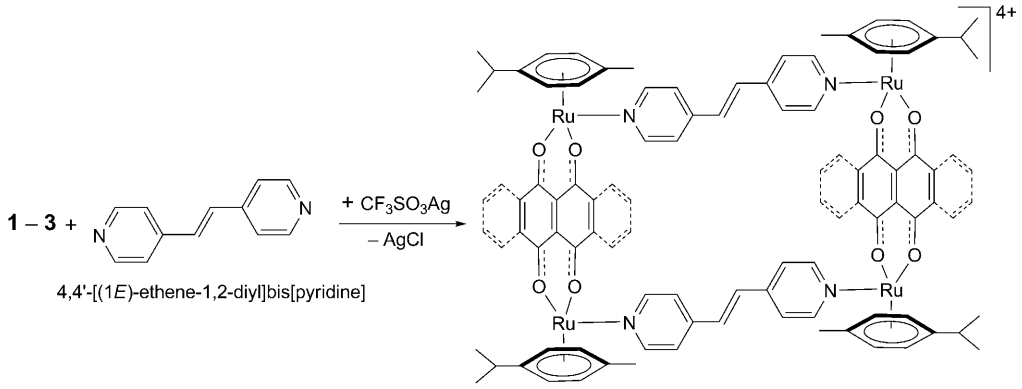
Scheme



4 5,8-dihydroxy-1,4-naphthoquinonato(2–)
5 9,10-dihydroxy-1,4-anthraquinonato(2–)
6 6,11-dihydroxynaphthacene-5,12-dionato(2–)



7 5,8-dihydroxy-1,4-naphthoquinonato(2–)
8 9,10-dihydroxy-1,4-anthraquinonato(2–)
9 6,11-dihydroxynaphthacene-5,12-dionato(2–)



10 5,8-dihydroxy-1,4-naphthoquinonato(2–)
11 9,10-dihydroxy-1,4-anthraquinonato(2–)
12 6,11-dihydroxynaphthacene-5,12-dionato(2–)

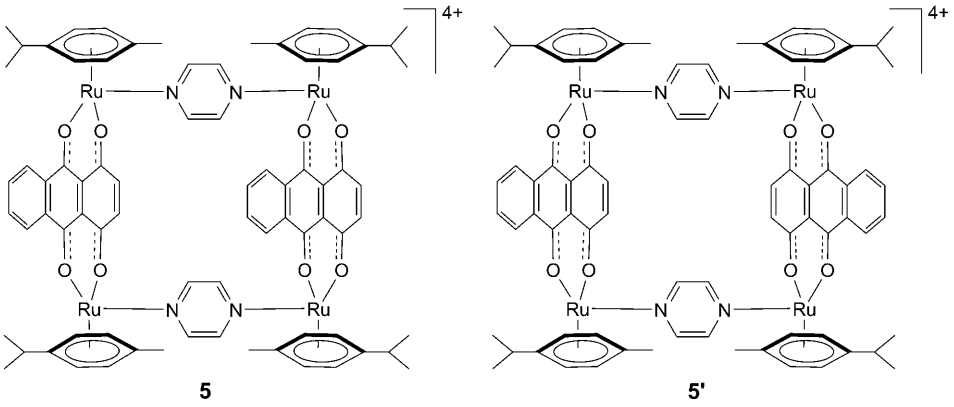


Fig. 1. *Schematic representation of the two isomers of* **5**

energy band centered at 320 nm, which is assigned to ligand-localized or intra-ligand $\pi \rightarrow \pi^*$ transition as well as broad low-energy bands associated to metal-to-ligand charge-transfer (MLCT) transitions. In **1**–**3**, only one MLCT band is found at *ca.* 600 nm, while in metallarectangles **4**–**12**, an additional band centered at *ca.* 400 nm is observed as well (*Fig. 2*).

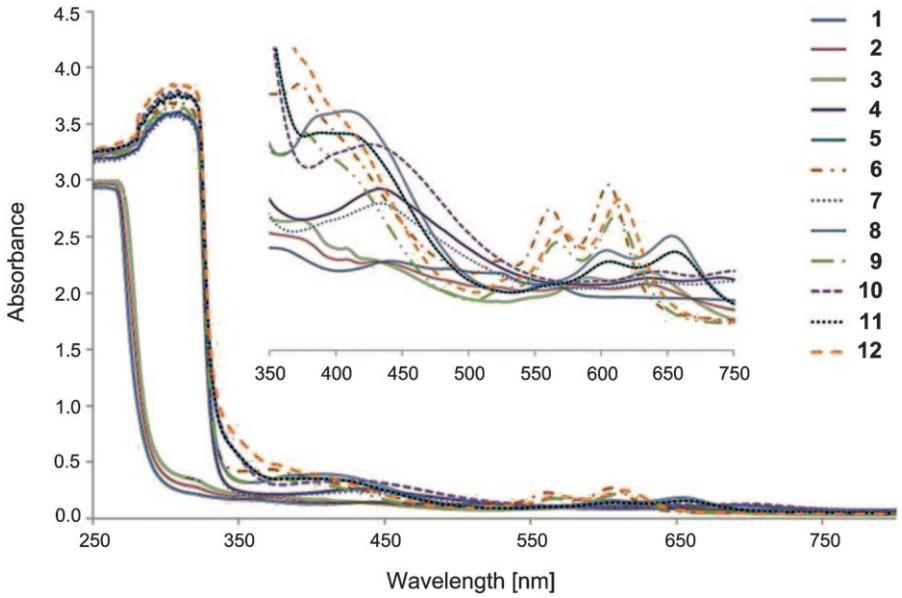


Fig. 2. UV/VIS *Spectra of* **1**–**12** (10^{-5} M) *in* CH_2Cl_2

As we were unable to grow crystals for X-ray measurements, the cavity sizes of the different metallarectangles were estimated by molecular modeling and from analogous

structures incorporating the same bridging and connecting ligands. The pyrazine series possess a cavity of *ca.* 8.4 × 7.0 Å^2 (Ru-to-Ru edges), while the cavity sizes of the 4,4′-bipyridine and 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine] series are expected to be *ca.* 8.4 × 11.2 and 8.4 × 13.6 Å^2, respectively (*Fig. 3*).

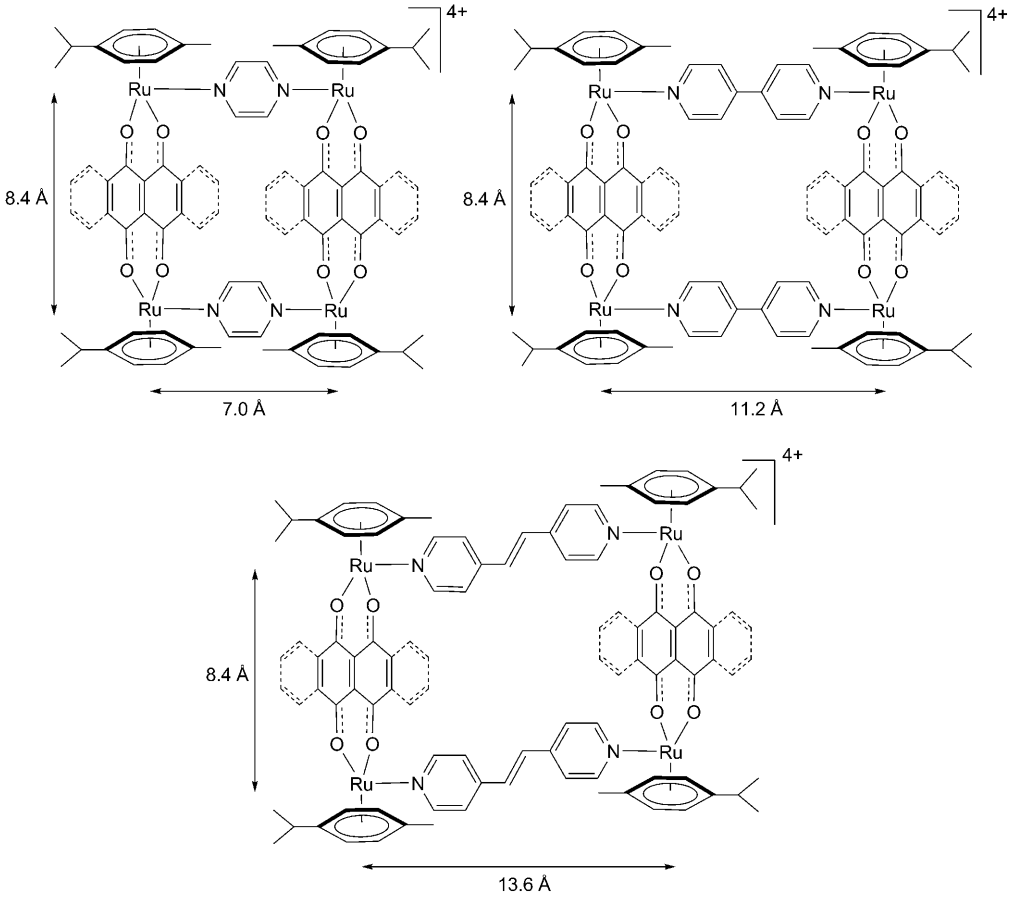


Fig. 3. *Estimated cavity size of the different metallarectangles*

To study the ability of the hydrophobic cavity of the metallarectangles **4**–**12** to encapsulate guest molecules in solution, we performed various NMR experiments. ^{1}H-NMR Spectra of 1:1 mixtures of metallarectangles with planar aromatic molecules (pyrene, anthracene, perylene, and coronene) were measured. In the case of the pyrazine-containing metallarectangles **4**–**6**, no shifts of the chemical shifts were observed for the H-atoms of the host and of the aromatic molecule in CD_3CN. The result is quite different with the larger metallarectangles **7**–**12** in which some H-atoms of the rectangle and of the aromatic molecule are shifted as compared to their initial ^{1}H-NMR spectra (*Fig. 4*). Consequently, these observations prompted us to further investigate the hosting potential of the metallarectangles **7**–**12** in solution by diffusion-

ordered NMR spectroscopy (DOSY). DOSY Measurement is a powerful tool for studying host–guest association in solution [17]. The diffusion coefficient depends on the shape and size of the molecules. Therefore, in a host–guest system in which 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. On the other hand, in a host–guest system in which the guest interacts with the host but not in a guest ⊂ host fashion, the host and the guest will keep their individual diffusion coefficients.

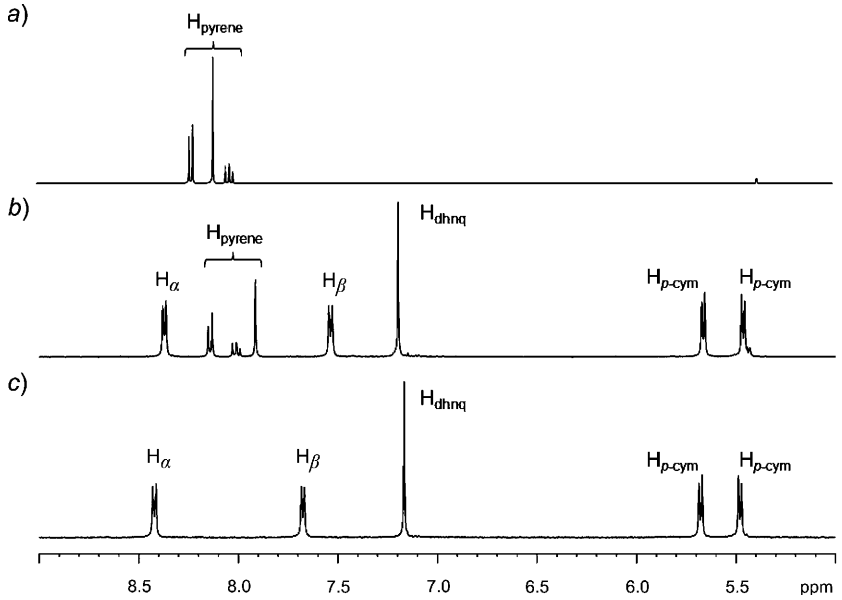


Fig. 4. *^{1}H-NMR Spectra* (25°, CD_3CN) a) *of pyrene,* b) *pyrene +1 equiv. of* **7**, *and* c) *of* **7**

Room-temperature DOSY measurements of the 4,4′-bipyridine-containing metallarectangles **7**–**9** in the presence of anthracene, pyrene, perylene, and coronene suggest out-of-cavity interactions between the different rectangles and the aromatic molecules. However, at −40°, the same DOSY experiment with anthracene and metallarectangle **7** clearly shows that anthracene diffuses at almost the same coefficient as the host (*Fig. 5*), thus supporting an in-cavity location of anthracene. To confirm this assumption, a ROESY (rotating-frame NOE spectroscopy) measurement at −40° was performed (*Fig. 5*). The ^{1}H-ROESY shows that some H-atoms of anthracene are in close proximity to the H-atoms of the 5,8-dihydroxy-1,4-naphthoquinonato(2−) and 4,4′-bipyridine ligands which confirms, together with the DOSY experiment at −40°, the presence of anthracene in the cavity of **7**. All other aromatic molecules (pyrene, perylene, and coronene) do not show in-cavity interactions with metallarectangles **7**–**9**, even at low temperature, which fit with out-of-cavity interactions. In contrast, 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine]-containing metallarectangles **10**–**12** show in-cavity interactions with these large planar aromatic molecules.

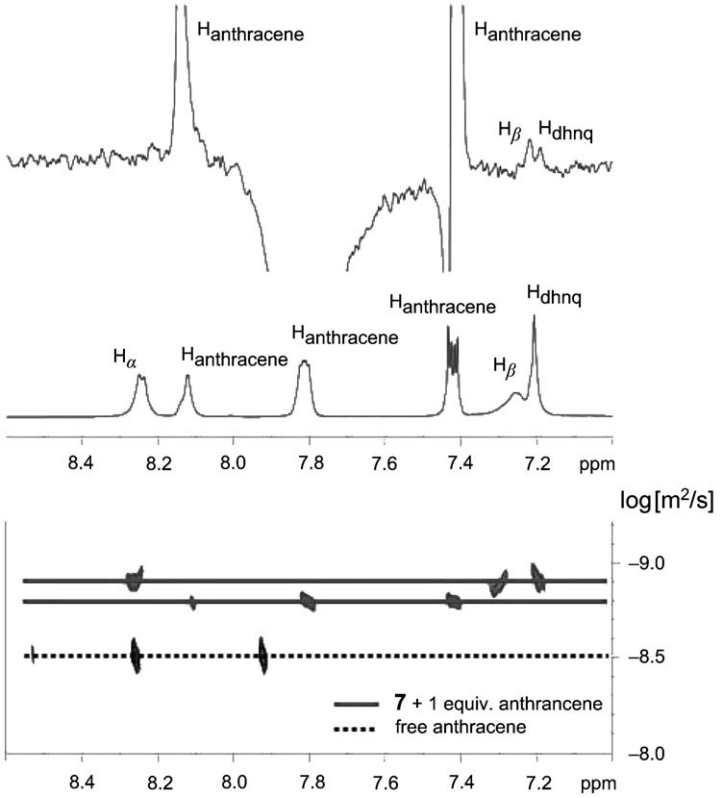


Fig. 5. *DOSY* (bottom) *and ROESY* (top) *NMR plots of* **7** + 1 *equiv. of anthracene at* $-40°$ (CD_3CN)

DOSY Experiments of anthracene with metallarectangles **10**–**12** show both in-cavity and out-of-cavity interactions at room temperature, as opposed to pyrene, perylene, and coronene for which in-cavity interaction dominates. As an example, the DOSY spectra of coronene, metallarectangle **10** and a 1:1 mixture of coronene, and **10** in CD_3CN at room temperature are presented in *Fig. 6*. These experiments clearly show that at room temperature, coronene/**10** 1:1 and **10** possess almost identical diffusion coefficients, which confirm the encapsulation of coronene in the hydrophobic cavity of **10** and the formation of a coronene ⊂ **10** adduct.

In summary, ^{1}H-NMR, DOSY and ROESY studies revealed that no meaningful interaction occurs between the pyrazine-containing metallarectangles **4**–**6** and planar aromatic molecules, while out-of-cavity interactions are prevailing in the case of the 4,4′-bipyridine-containing metallarectangles **7**–**9**, with the exception of anthracene which can do both in-cavity and out-of-cavity interactions with these metallarectangles. On the other hand, in-cavity interactions take place for the 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine]-containing metallarectangles **10**–**12**, thus giving rise to guest ⊂ host systems.

Therefore, to gain further information on the hosting ability of **10**–**12** in solution, a series of ^{1}H-NMR titration in CD_3CN solution with pyrene, perylene, and coronene

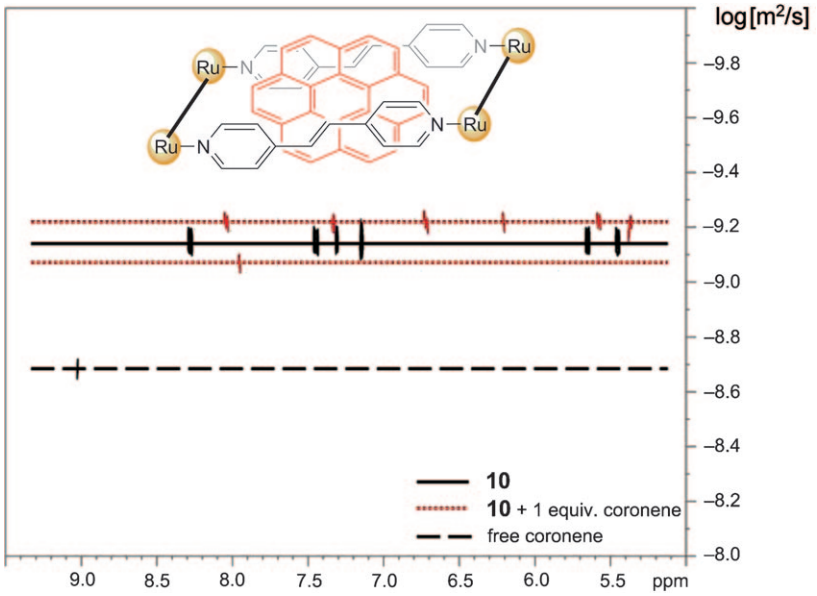


Fig. 6. *DOSY ^{1}H-NMR plots* (25°, CD_3CN) *of coronene,* **10**, *and* **10** + 1 *equiv. of coronene*

was performed. Upon gradual addition of guest molecule (0.0 – 20.0 equiv. of pyrene, perylene, or coronene) to a CD_3CN solution of metallarectangles **10** – **12** (4.0 mM), ^{1}H-NMR spectra were recorded. Then, the chemical-shift changes ($\Delta\delta$) of one chosen signal of the metallarectangles **10** – **12** (*e.g.*, of the ethenediyl moiety) *vs.* the molar ratio of the guest to the metallarectangle were plotted (*Fig. 7*). Considering the DOSY experiments reported previously, and accordingly assuming a 1 : 1 system, and by using the $\Delta\delta$ value at known guest/host molar ratio with the help of the nonlinear least-square fitting program winEQNMR2 [18], the stability constants of association (K_a) together with the free energies (ΔG°) were estimated (*Table*). The estimated stability constants are comprised between 52000 M^{-1} and 69000 M^{-1}, which imply a relatively strong affinity between the host and the guest – metallarectangle and aromatic molecules –

Table. *Stability Constants and Free Energies for the Encapsulation of Pyrene, Perylene, and Coronene in Metallarectangles* **10** – **12** (CD_3CN at 25°, 4.0 mM of host)

Guest ⊂ host	K_a [10^4 M^{-1}]	ΔG° [kcal mol^{-1}]
Pyrene ⊂ **10**	5.8 ± 0.9	– 6.48 ± 0.05
Perylene ⊂ **10**	5.5 ± 0.4	– 6.46 ± 0.02
Coronene ⊂ **10**	6.9 ± 0.6	– 6.60 ± 0.02
Pyrene ⊂ **11**	6.8 ± 0.8	– 6.59 ± 0.04
Perylene ⊂ **11**	5.7 ± 0.5	– 6.47 ± 0.02
Coronene ⊂ **11**	5.6 ± 0.7	– 6.47 ± 0.02
Pyrene ⊂ **12**	5.2 ± 0.9	– 6.43 ± 0.02
Perylene ⊂ **12**	5.6 ± 0.4	– 6.47 ± 0.02
Coronene ⊂ **12**	6.2 ± 0.7	– 6.53 ± 0.04

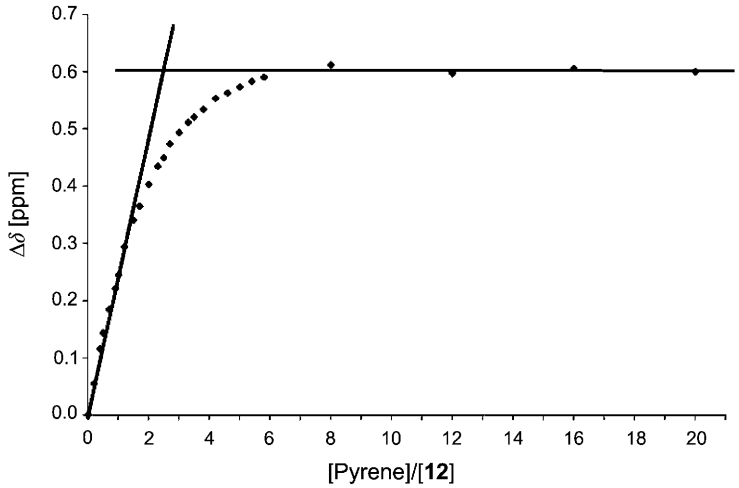


Fig. 7. *^{1}H-NMR Chemical-shift changes $\Delta\delta$* (25°, CD_3CN) *of the H-atoms of the ethenediyl moiety of* **12** *upon addition of pyrene to* **12**

which, however, suggest no selectivities or preferences by the metallarectangle among these guests (pyrene, perylene, and coronene). This nonspecificity of the metallarectangles **10**–**12** for these planar aromatic molecules in MeCN was further confirmed by a competition experiment in which a 1:1:1:1 mixture of pyrene, perylene, coronene, and **10** was involved. A ^{1}H-DOSY experiment shows that the three potential guest molecules are competing equally for the hydrophobic cavity of **10**, which is not surprising given their comparable stability constants.

To conclude these host–guest studies, we performed a fluorescence-emission titration of perylene with metallarectangle **10**. Perylene has been intensively used as fluorescent probe, and its basic fluorescence is well documented [19]. The fluorescence quenching of perylene *via* exciplex formation [20] or energy transfer [21] in solution has been also studied in detail, and we propose here to see whether or not such quenching by encapsulation of perylene inside the cavity of a metallarectangle **10** occurred. The emission spectra of a CH_2Cl_2 solution of perylene (10^{-7} M, 350 nm as excitation wavelength) upon gradual addition of metallarectangle **10** (0.0–10 equiv.) were recorded (*Fig. 8*). A quenching of the perylene fluorescence is clearly observed when **10** is added. This quenching of the fluorescence of perylene can be explained by two effects. Firstly, as the guest goes into the cavity of the metallarectangle **10**, there is a loss of excitation energy received by the guest molecule: a part of the energy can be absorbed by the metallarectangle and consequently, the perylene molecule encapsulated in the metallarectangle is less excited and, therefore, cannot reemit the same energy as compared to its free state. Secondly, the quenching can result from energy transfer from perylene to metallarectangle **10**. Indeed, due to a good spectral overlap of absorbance of metallarectangle **10** with the perylene emission, energy transfer can spontaneously take place (*Fig. 9*), thus leading to a decrease in the emission energy of perylene and ultimately to fluorescence quenching [22].

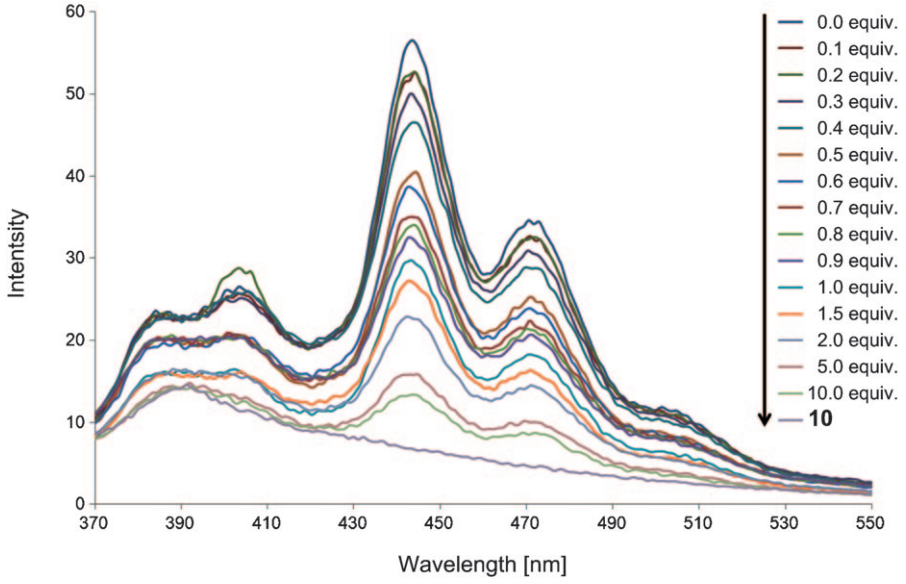


Fig. 8. *Fluorescence-emission titration of perylene* (10^{-7} M in CH_2Cl_2) *by metallarectangle* **10** (excitation wavelength 350 nm)

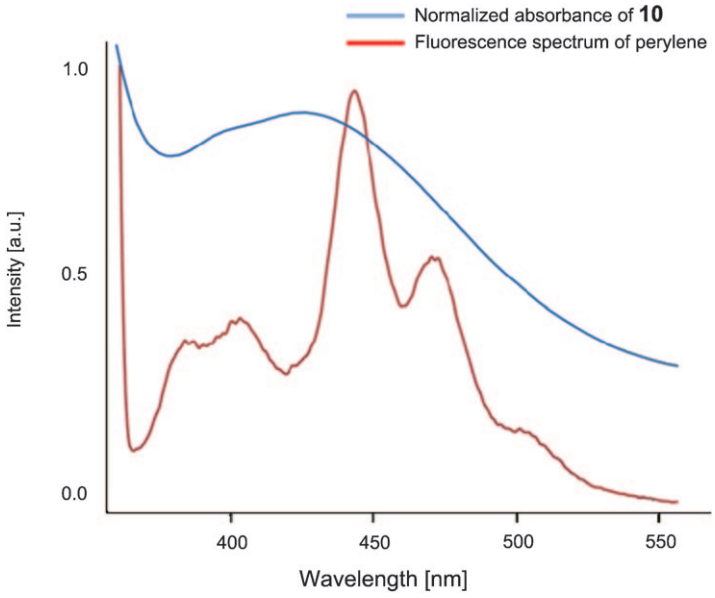


Fig. 9. *Normalized absorbance spectrum of metallarectangle* **10** *and fluorescence spectrum of perylene*

Conclusion. – This study reveals that tetranuclear (arene)ruthenium complexes containing $OO \cap OO$-bridges (5,8-dihydroxy-1,4-anthraquinonato(2 –), 9,10-dihy-

droxy-1,4-anthraquinonato(2−), and 6,11-dihydroxynaphthacene-5,12-dionato(2−)) and $N \cap N$-linkers (pyrazine, 4,4′-bipyridine, 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine]) can be designed to accommodate guest molecules inside their cavity. Various NMR experiments showed that the small pyrazine-containing metallarectangles **4**–**6** do not interact with planar aromatic molecules (anthracene, pyrene, perylene, and coronene), while the more spacious 4,4′-bipyridine and 4,4′-[(1*E*)-ethene-1,2-diyl]bis[pyridine]-containing metallarectangles **7**–**12** give both in-cavity and out-of-cavity interactions with these aromatic molecules. Encapsulation of perylene in the hydrophobic cavity of **10** strongly quenches the fluorescence of perylene in solution, which confirms the great potential of such metallarectangles for applications in host–guest chemistry.

We thank *Johnson Matthey Research Center* for a generous loan of ruthenium chloride hydrate.

Experimental Part

General. The [Ru(η^6-*p*-cymene)Cl_2]$_2$ [23], the dinuclear [Ru(arene)]complexes [Ru_2(η^6-*p*-cymene)$_2$(μ-*OO* ∩ *OO*)Cl_2] **1** and **2** (*OO* ∩ *OO* = 5,8-dihydroxy-1,4-naphthoquinonato(2−) [14], 9,10-dihydroxy-1,4-anthraquinonato(2−) [15]) and the metallarectangles **4**, **7**, and **10** [16] were prepared according to published methods. All other reagents were commercially available (*Sigma–Aldrich*) and used as received. UV/VIS Spectra: *Uvikon-930* spectrophotometer; precision cells made of quartz (1 cm); λ_{max} (ε [$M^{-1} \cdot cm^{-1}$]) in nm. Fluorescence spectra: *Perkin-Elmer-LS50B* luminescence spectrometer; precision cells made of quartz (1 cm). IR Spectra: *Perkin-Elmer-1720X* FT-IR spectrometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C{^{1}H}-NMR Spectra and ^{1}H-ROESY: *Bruker-Avance II-400* spectrometer; residual protonated solvent as internal standard ($CDCl_3$: δ(H) 7.26; CD_3CN: δ(H) 1.94), *J* in Hz. Microanalyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva, Switzerland.

DOSY-NMR Experiments. For all DOSY experiments, the temp. was regulated at 298 or 233 K, the airflow was increased to 670 $l \cdot min^{-1}$, and the NMR tube was not spun. The diffusion NMR experiments were performed with a standard pulsed-gradient stimulated echo (LED-PFGSTE) sequence and a bipolar gradient [17]. DOSY Spectra were generated by using the TopSpin 2.0 software package (*Bruker*). Experimental parameters were $\Delta = 50.0$ ms (diffusion delay), $\tau = 1.0$ ms (gradient recovery delay), and $Te = 5.0$ ms (eddy current recovery delay). For each data set, 4096 complex points were collected, and the gradient dimension was sampled by means of 16 experiments in which the gradient strength was linearly incremented from 1.0 to 50.8 $G \cdot cm^{-1}$. The gradient duration $\delta/2$ was adjusted to observe a near-complete signal loss at 50.8 $G \cdot cm^{-1}$. Typically, the $\delta/2$ delay was chosen in the 1.2–2.0 ms range. A 1.0 s recycle delay was used between scans for data shown. For each data set, the spectral axis was processed with an exponential function (3–5 Hz line broadening), and *Fourier* transform was applied to obtain 4096 real points. The DOSY reconstruction was realized with 256 points in the diffusion dimension. The number of scans ranged from 8 to 64 and was adapted to each sample. The experimental time ranged from 4 to 30 min.

ROESY-NMR Experiments. For the ROESY experiment shown, the temp. was regulated at 233 K, and the NMR tube was not spun. The ROESY experiment was performed by means of a gradient-selected ROESY [24], with the Tr-ROESY scheme [25] for efficient TOCSY transfer suppression. Experimental parameters were $\tau_m = 200$ ms (mixing time), $\delta = 500$ μs (gradient length), $G_0 = 1.0$ $G \cdot cm^{-1}$, $G_1 = 3.0$ $G \cdot cm^{-1}$, $G_2 = 6.0$ $G \cdot cm^{-1}$ (gradient strength), and $\tau_p = 100$ ms (selective pulse, Seduce-1). A total of 8192 complex points were collected. A 3 s recycle delay was used. The spectral axis was processed with an exponential function (3 Hz line broadening), and *Fourier* transform was applied to obtain 8192 real points. The number of scans was 1024 and the experimental time *ca.* 90 min.

*Dinuclear Metallaclip: Dichloro{μ-[6,11-di(hydroxy-*κ*O)naphthacene-5,12-dionato(2−)-*κ*O^5:*κ*O^{12}]}bis[1,2,3,4,5,6-*η*)-1-methyl-4-(1-methylethyl)benzene]diruthenium* (**3**). A mixture of [Ru(η^6-*p*-cymene)Cl_2]$_2$ (145.0 mg, 0.23 mmol), anh. AcONa (38.4 mg, 0.46 mmol), and 6,11-dihydroxynaphtha-

cene-5,12-dione (66.8 mg, 0.23 mmol) in EtOH (25 ml) is stirred under reflux for 24 h. Then the precipitate is filtered and washed with EtOH, H_2O, acetone, Et_2O, and pentane: **3** (177 mg, 93%). Blue solid. UV/VIS ($1.0 \cdot 10^{-5}$ M, acetone): 326 ($3.06 \cdot 10^4$), 384 ($2.04 \cdot 10^4$), 416 ($1.02 \cdot 10^4$), 594 ($1.19 \cdot 10^4$), 648 ($0.16 \cdot 10^4$). IR: 3055*w* ($\nu_{C_{sp^2}-H}$), 1546*s* ($\nu_{C=O}$), 850*s* ($\delta_{C_{sp^2}-H}$). ^{1}H-NMR (400 MHz, $CDCl_3$): 8.50 (*d*, ^3J = 8.1, 4 H_{dhtq}); 7.72 (*d*, ^3J = 8.1, 4 H_{dhtq}); 5.68 (*d*, ^3J = 5.4, 4 $H_{p\text{-cym}}$); 5.33 (*d*, ^3J = 5.4, 4 $H_{p\text{-cym}}$); 3.06 (*sept.*, ^3J = 3.0, 2 Me_2CH); 2.42 (*s*, 2 Me); 1.57 (*d*, 2 Me_2CH). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.4 (CO); 134.5 (CH_{dhtq}); 131.1 (CH_{dhtq}); 126.8 (C_{dhtq}); 99.8 ($C_{p\text{-cym}}$); 97.4 ($C_{p\text{-cym}}$); 83.1 ($CH_{p\text{-cym}}$); 79.3 ($CH_{p\text{-cym}}$); 30.9 (Me_2CH); 18.0 (Me). Anal. calc. for $C_{38}H_{36}Cl_2O_4Ru_2$ (829.75): C 55.01, H 4.37; found: C 55.98, H 4.98.

Metallarectangles **4**–**12**: *General Procedure.* A mixture of 1 equiv. of **1**–**3** (0.21 mmol), 2 equiv. of CF_3SO_3Ag (0.43 mmol), and 1 equiv. of the corresponding $N \cap N$ linker (0.21 mmol) in MeOH (40 ml) is stirred at 60° for 24 h, and then the soln. is filtered to remove AgCl. The solvent is evaporated, and the residue is taken up in CH_2Cl_2 (3 ml). Then Et_2O is added to precipitate the products as green or blue solids.

Bis{μ-[9,10-di(hydroxy-κO)anthracene-1,4-dionato(2−)-κO^1:κO^4]tetrakis[(1,2,3,4,5,6-η)-1-methyl-4-(1-methylethyl)benzene]bis[μ-(pyrazine-κN^1:κN^4)]tetraruthenium 1,1,1-Trifluoromethanesulfonate (1:4) ([**5**] $[CF_3SO_3]_4$): Yield 169 mg (74%). UV/VIS ($1.0 \cdot 10^{-5}$ M, acetone): 304 ($3.52 \cdot 10^5$), 442 ($0.25 \cdot 10^5$), 625 ($0.12 \cdot 10^5$), 696 ($0.11 \cdot 10^5$). IR: 3055*w* ($\nu_{C_{sp^2}-H}$), 1546*s* ($\nu_{C=O}$), 1261*s* ($\nu_{C_{sp^3}-F}$), 850*s* ($\delta_{C_{sp^2}-H}$). ^{1}H-NMR (400 MHz, CD_3CN): 8.82 (*d*, ^3J = 8.5, 2 H_{dhaq}); 8.59 (*d*, ^3J = 7.9, 2 $H_{dhaq'}$); 8.58 (*s*, 8 $H_{pyrazine}$); 7.93 (*d*, ^3J = 8.5, 2 H_{dhaq}); 7.82 (*d*, ^3J = 7.9, 2 $H_{dhaq'}$); 7.17 (*s*, 2 H_{dhaq}); 7.05 (*s*, 2 $H_{dhaq'}$); 5.91 (*d*, ^3J = 5.6, 4 $H_{p\text{-cym}}$); 5.86 (*d*, ^3J = 5.6, 4 $H_{p\text{-cym}}$); 5.80–5.84 (*m*, 8 $H_{p\text{-cym}}$); 2.82 (*sept.*, ^3J = 2.9, 4 Me_2CH); 2.13 (*s*, 4 Me); 1.45 (*d*, ^3J = 2.9, 4 Me_2CH). ^{13}C-NMR (100 MHz, CD_3CN): 172.3 (CO); 171.2 (CO); 145.7 ($CH_{pyrazine}$); 139.2 (CH_{dhaq}); 132.7 (CH_{dhaq}); 133.3 (C_{dhaq}); 133.0 (C_{dhaq}); 128.1 (CH_{dhaq}); 104.2 ($C_{p\text{-cym}}$); 100.1 ($C_{p\text{-cym}}$); 85.9 ($CH_{p\text{-cym}}$); 85.1 ($CH_{p\text{-cym}}$); 83.2 ($CH_{p\text{-cym}}$); 83.8 ($CH_{p\text{-cym}}$); 31.5 (Me_2CH); 22.7 (Me_2CH); 17.6 (Me). Anal. calc. for $C_{80}H_{76}F_{12}N_4O_{20}Ru_4S_4$ (2173.41): C 44.21, H 3.52, N 2.58; found: C 43.05, H 3.22, N 2.41.

Bis{μ-[6,11-di(hydroxy-κO)naphthacene-5,12-dionato(2−)-κO^5:κO^{12}]tetrakis[(1,2,3,4,5,6-η)-1-methyl-4-(1-methylethyl)benzene]bis[μ-(pyrazine-κN^1:κN^4)]tetraruthenium 1,1,1-Trifluoromethanesulfonate (1:4) ([**6**] $[CF_3SO_3]_4$): Yield 178 mg (73%). UV/VIS ($1.0 \cdot 10^{-5}$ M, acetone): 312 ($3.68 \cdot 10^5$), 380 ($0.42 \cdot 10^5$), 530 ($0.14 \cdot 10^5$), 568 ($0.21 \cdot 10^5$), 613 ($0.24 \cdot 10^5$). IR: 3060*w* ($\nu_{C_{sp^2}-H}$), 1542*s* ($\nu_{C=O}$), 1260*s* ($\nu_{C_{sp^3}-F}$), 850*s* ($\delta_{C_{sp^2}-H}$). ^{1}H-NMR (400 MHz, CD_3CN): 8.57 (*d*, ^3J = 8.4, 8 H_{dhtq}); 8.47 (*s*, 8 $H_{pyrazine}$); 7.82 (*d*, ^3J = 8.4, 8 H_{dhtq}); 5.90 (*d*, ^3J = 5.8, 8 $H_{p\text{-cym}}$); 5.76 (*d*, ^3J = 5.8, 8 $H_{p\text{-cym}}$); 2.93 (*sept.*, ^3J = 3.0, 4 Me_2CH); 2.16 (*s*, 4 Me); 1.29 (*d*, ^3J = 3.0, 4 Me_2CH). ^{13}C-NMR (100 MHz, CD_3CN): 169.9 (CO); 149.4 ($CH_{pyrazine}$); 134.2 (CH_{dhtq}); 128.4 (CH_{dhtq}); 107.8 (C_{dhtq}); 107.8 ($C_{p\text{-cym}}$); 106.1 ($C_{p\text{-cym}}$); 100.7 (C_{dhtq}); 84.6 ($CH_{p\text{-cym}}$); 84.5 ($CH_{p\text{-cym}}$); 31.3 (Me_2CH); 22.4 (Me_2CH); 17.8 (Me). Anal. calc. for $C_{88}H_{80}F_{12}N_4O_{20}Ru_4S_4$ (2273.50): C 46.49, H 3.52, N 2.46; found: C 47.65, H 3.78, N 2.80.

[Bis[μ-(4,4′-bipyridine-κN^1:κN$^{1'}$)]bis{μ-[9,10-di(hydroxy-κO)anthracene-1,4-dionato(2−)-κO^1:κO^4]}-tetrakis[(1,2,3,4,5,6-η)-1-methyl-4-(1-methylethyl)benzene]tetraruthenium 1,1,1-Trifluoromethanesulfonate (1:4) ([**8**] $[CF_3SO_3]_4$): Yield 192 mg (77%). UV/VIS ($1.0 \cdot 10^{-5}$ M, acetone): 312 ($3.58 \cdot 10^5$), 418 ($0.39 \cdot 10^5$), 608 ($0.16 \cdot 10^5$), 658 ($0.18 \cdot 10^5$). IR: 3069*w* ($\nu_{C_{sp^2}-H}$), 1539*s* ($\nu_{C=O}$), 1260*s* ($\nu_{C_{sp^3}-F}$), 850*s* ($\delta_{C_{sp^2}-H}$). ^{1}H-NMR (400 MHz, CD_3CN): 8.60–8.64 (*m*, 4 H_{dhaq} + $H_{dhaq'}$); 8.46 (*d*, ^3J = 8.6, 8 H_α); 7.91–7.95 (*m*, 4 H_{dhaq} + $H_{dhaq'}$); 7.60 (*d*, ^3J = 8.6, 8 H_β); 7.21 (*s*, 2 H_{dhaq}); 7.20 (*s*, 2 $H_{dhaq'}$); 5.78 (*d*, ^3J = 5.8, 4 $H_{p\text{-cym}}$); 5.73 (*d*, ^3J = 5.8, 4 $H_{p\text{-cym}}$); 5.54–5.58 (*m*, 8 $H_{p\text{-cym}}$); 2.85 (*sept.*, ^3J = 2.8, 4 Me_2CH); 2.11 (*s*, 4 Me); 1.30 (*d*, ^3J = 2.8, 4 Me_2CH). ^{13}C-NMR (100 MHz, CD_3CN): 171.2 (CO); 170.3 (CO); 153.8 (CH_α); 145.7 (C_{bpy}); 138.7 (CH_{dhaq}); 134.4 (CH_{dhaq}); 134.0 (C_{dhaq}); 133.9 (C_{dhaq}); 128.3 (CH_{dhaq}); 123.9 (CH_β); 104.6 ($C_{p\text{-cym}}$); 100.5 ($C_{p\text{-cym}}$); 85.2 ($CH_{p\text{-cym}}$); 84.9 ($CH_{p\text{-cym}}$); 83.7 ($CH_{p\text{-cym}}$); 83.7 ($CH_{p\text{-cym}}$); 31.4 (Me_2CH); 22.5 (Me_2CH); 17.6 (Me). Anal. calc. for $C_{92}H_{84}F_{12}N_4O_{20}Ru_4S_4$ (2325.55): C 47.52, H 3.61, N 2.41; found: C 45.48, H 3.27, N 2.21.

[Bis[μ-(4,4′-bipyridine-κN^1:κN$^{1'}$)]bis{μ-[6,11-di(hydroxy-κO)naphthacene-5,12-dionato(2−)-κO^5:κO^{12}]}tetrakis[(1,2,3,4,5,6-η)-1-methyl-4-(1-methylethyl)benzene]tetraruthenium 1,1,1-Trifluoromethanesulfonate (1:4) ([**9**] $[CF_3SO_3]_4$): Yield 211 mg (81%). UV/VIS ($1.0 \cdot 10^{-5}$ M, acetone): 312 ($3.58 \cdot 10^5$), 384 ($0.34 \cdot 10^5$), 533 ($0.14 \cdot 10^5$), 573 ($0.19 \cdot 10^5$), 618 ($0.20 \cdot 10^5$). IR: 3071*w* ($\nu_{C_{sp^2}-H}$), 1543*s* ($\nu_{C=O}$), 1262*s* ($\nu_{C_{sp^3}-F}$), 850*s* ($\delta_{C_{sp^2}-H}$). ^{1}H-NMR (400 MHz, CD_3CN): 8.69 (*d*, ^3J = 8.6, 8 H_{dhtq}); 7.93 (*d*, ^3J = 7.9, 8 H_α); 7.57 (*d*, ^3J = 7.9, 8 H_β); 7.52 (*d*, ^3J = 8.6, 8 H_{dhtq}); 5.85 (*d*, ^3J = 5.8, 8 $H_{p\text{-cym}}$); 5.63 (*d*, ^3J = 5.8, 8 $H_{p\text{-cym}}$); 2.88 (*sept.*, ^3J = 2.9, 4 Me_2CH); 2.16 (*s*, 4 Me); 1.37 (*d*, ^3J = 2.9, 4 Me_2CH). ^{13}C-NMR (100 MHz, CD_3CN):

170.0 (CO); 153.7 (CH_{α}); 134.5 (C_{bpy}); 134.0 (CH_{dhtq}); 128.2 (CH_{β}); 123.9 (CH_{dhtq}); 108.0 (C_{dhtq}); 104.7 ($C_{p\text{-cym}}$); 100.7 ($C_{p\text{-cym}}$); 85.1 ($CH_{p\text{-cym}}$); 83.5 ($CH_{p\text{-cym}}$); 31.4 (Me_2CH); 22.4 (Me_2CH); 17.8 (Me). Anal. calc. for $C_{100}H_{88}F_{12}N_4O_{20}Ru_4S_4$ (2425.64): C 49.52, H 3.63, N 2.31; found: C 51.20, H 3.75, N 2.80.

Bis{μ-[9,10-di(hydroxy-κO)anthracene-1,4-dionato(2−)-κO^1:κO^4]}bis{μ-[4,4′-[(1E)-ethene-1,2-diyl]-bis[pyridine]-κN^1:κN$^{1'}$}}tetrakis[(1,2,3,4,5,6-η)-1-methyl-4-(1-methylethyl)benzene]tetraruthenium 1,1,1-Trifluoromethanesulfonate (1:4) ([**11**] $[CF_3SO_3]_4$): Yield 189 mg (74%). UV/VIS ($1.0\cdot10^{-5}$ M, acetone): 313 ($3.75\cdot10^5$), 416 ($0.35\cdot10^5$), 608 ($0.14\cdot10^5$), 658 ($0.16\cdot10^5$). IR: 3068*w* ($\nu_{C_{sp^2}-H}$), 1538*s* ($\nu_{C=O}$), 1260*s* ($\nu_{C_{sp^3}-F}$), 850*s* ($\delta_{C_{sp^2}-H}$). ^{1}H-NMR (400 MHz, CD_3CN): 8.60–8.66 (*m*, 4 H_{dhaq} + $H_{dhaq'}$); 8.33 (*d*, ^3J = 8.4, 8 H_{α}); 7.90–7.94 (*m*, 4 H_{dhaq} + $H_{dhaq'}$); 7.38 (*d*, ^3J = 8.4, 8 H_{β}); 7.23 (*s*, 4 $H_{C=C}$); 7.18 (*s*, 2 H_{dhaq}); 7.17 (*s*, 2 $H_{dhaq'}$); 5.76 (*d*, ^3J = 5.6, 4 $H_{p\text{-cym}}$); 5.69 (*d*, ^3J = 5.6, 4 $H_{p\text{-cym}}$); 5.53 (*d*, ^3J = 5.6, 4 $H_{p\text{-cym}}$); 5.51 (*d*, ^3J = 5.6, 4 $H_{p\text{-cym}}$); 2.85 (*sept.*, ^3J = 2.8, 4 Me_2CH); 2.11 (*s*, 4 Me); 1.29 (*d*, ^3J = 2.8, 4 Me_2CH). ^{13}C-NMR (100 MHz, CD_3CN): 171.3 (CO); 170.4 (CO); 153.1 (CH_{α}); 146.8 (C_{ethene}); 138.6 (CH_{dhaq}); 134.2 (CH_{dhaq}); 134.1 (C_{dhaq}); 132.0 (C_{dhaq}); 128.3 (CH_{dhaq}); 128.2 (CH=CH); 124.1 (CH_{β}); 110.6 (CF_3); 104.5 ($C_{p\text{-cym}}$); 100.3 ($C_{p\text{-cym}}$); 85.1 ($CH_{p\text{-cym}}$); 84.8 ($CH_{p\text{-cym}}$); 83.8 ($CH_{p\text{-cym}}$); 83.7 ($CH_{p\text{-cym}}$); 31.4 (Me_2CH); 22.5 (Me_2CH); 17.6 (Me). Anal. calc. for $C_{96}H_{88}F_{12}N_4O_{20}Ru_4S_4$ (2377.61): C 48.50, H 3.70, N 2.35; found: C 46.87, H 3.96, N 2.62.

Bis{μ-[6,11-di(hydroxy-κO)naphthacene-5,12-dionato(2−)-κO^5:κO^{12}]}bis{μ-[4,4′-[(1E)-ethene-1,2-diyl]bis[pyridine]-κN^1:κN$^{1'}$}}tetrakis[(1,2,3,4,5,6-η)-1-methyl-4-(1-methylethyl)benzene]tetraruthenium 1,1,1-Trifluoromethanesulfonate (1:4) ([**12**] $[CF_3SO_3]_4$): Yield 199 mg (75%). UV/VIS ($1.0\cdot10^{-5}$ M, acetone): 315 ($3.84\cdot10^5$), 382 ($0.46\cdot10^5$), 531 ($0.12\cdot10^5$), 570 ($0.20\cdot10^5$), 618 ($0.24\cdot10^5$). IR: 3070*w* ($\nu_{C_{sp^2}-H}$), 1543*s* ($\nu_{C=O}$), 1259*s* ($\nu_{C_{sp^3}-F}$), 850*s* ($\delta_{C_{sp^2}-H}$). ^{1}H-NMR (400 MHz, CD_3CN): 8.69 (*d*, ^3J = 8.6, 8 H_{dhtq}); 8.37 (*d*, ^3J = 7.9, 8 H_{α}); 7.92 (*d*, ^3J = 8.6, 8 H_{dhtq}); 7.30 (*d*, ^3J = 7.9, 8 H_{β}); 7.14 (*s*, 4 $H_{C=C}$); 5.81 (*d*, ^3J = 5.6, 8 $H_{p\text{-cym}}$); 5.60 (*d*, ^3J = 5.6, 8 $H_{p\text{-cym}}$); 2.90 (*sept.*, ^3J = 2.9, 4 Me_2CH); 2.13 (*s*, 4 Me); 1.28 (*d*, ^3J = 2.9, 4 Me_2CH). ^{13}C-NMR (100 MHz, CD_3CN): 170.4 (CO); 153.0 (CH_{α}); 146.8 ($C_{ethylene}$); 134.6 (CH_{dhtq}); 133.9 (C_{dhtq}); 133.8 (C_{dhtq}); 131.9 (CH_{dhtq}); 128.1 (CH=CH); 124.1 (CH_{β}); 100.4 ($C_{p\text{-cym}}$); 84.9 ($CH_{p\text{-cym}}$); 83.5 ($CH_{p\text{-cym}}$); 31.4 (Me_2CH); 22.5 (Me_2CH); 17.9 (Me). Anal. calc. for $C_{104}H_{92}F_{12}N_4O_{20}Ru_4S_4$ (2477.69): C 50.41, H 3.71, N 2.26; found: C 48.22, H 3.51, N 2.38.

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Received November 30, 2009