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Supramolecular Chemistry

Using a Hydrogen-Bonded Rosette-Type Scaffold to Generate Heteronuclear Metalla-Assemblies

Fan Zhang[a] and Bruno Therrien*[a]

Abstract: Pyridyl-functionalized melamine (MEpy) and barbituric acid (BApy) derivatives have been designed to generate rosette-type structures with multiple coordination sites. The introduction of a pyridyl group on both components (MEpy and BApy) allows coordination of metals at the periphery of the $(MEpy)_3$•$(BApy)_3$ rosette. Dichloro *para*-cymene ruthenium and dichloro pentamethylcyclopentadienyl rhodium units were inserted to generate the heteronuclear rosettes, $(MEpyRu)_3$•$(BApyRh)_3$ and $(MEpyRh)_3$•$(BApyRu)_3$, respectively. Both rosettes were characterized by spectroscopic methods and their behavior in solution was studied.

Introduction

Rosette-type structures can be designed using hydrogen bonds.[1] Among these 2D hydrogen-bonded assemblies, the most studied system remains the pair involving melamine (ME) and barbituric acid (BA).[2] In such ME–BA systems, the formation of discrete $(ME)_3$•$(BA)_3$ rosettes over polymeric $(ME)_n$•$(BA)_n$ tape-like structures is controlled by thermodynamic parameters.[3] Introduction of bulky substituents on either the ME or BA units reduces the planarity of the hydrogen-bonded assemblies (rosette and tape-like), thus favoring the crystallization of the rosette-type structure.[3,4]

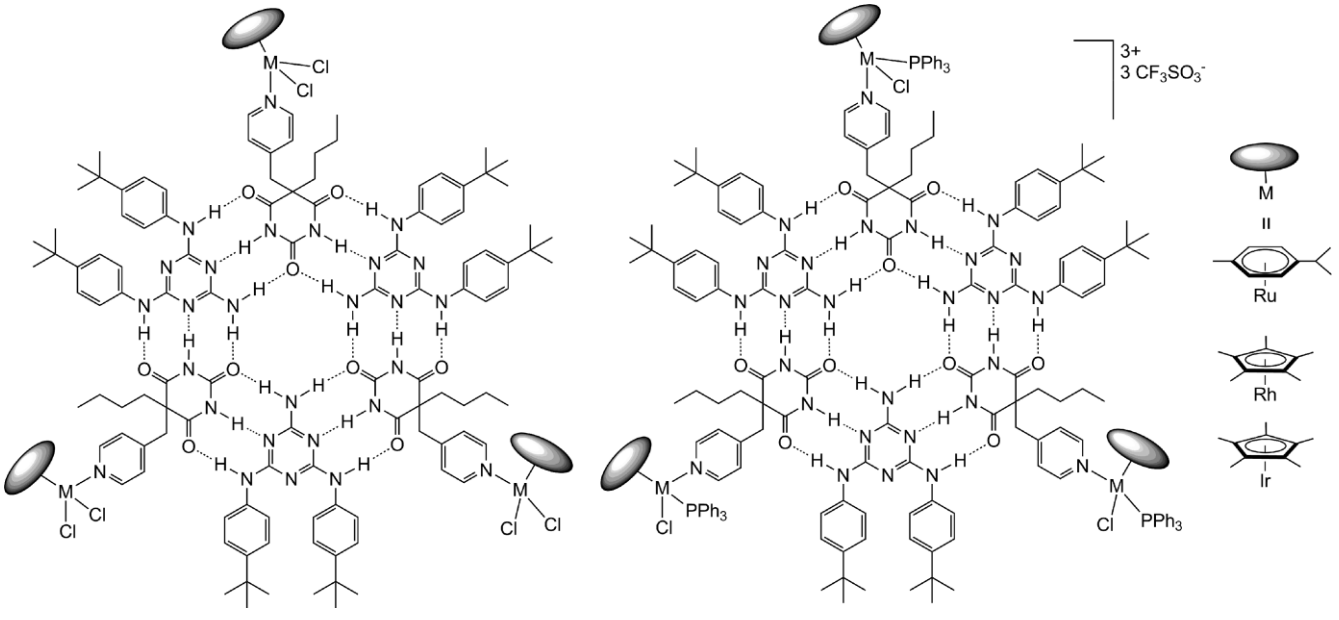


Figure 1. Molecular structures of neutral (left) and ionic (right) hexameric rosettes incorporating three piano-stool complexes.[5]

Last year, we used a pyridyl-containing barbituric acid derivative, 5-butyl-5-(pyridin-4-ylmethyl)pyrimidine-2,4,6-trione (BApy),[5] in combination with *N*,*N*′-bis(4-*tert*-butylphenyl)mel-

[a] *Institute of Chemistry, University of Neuchatel, Avenue de Bellevaux 51, 2000 Neuchatel, Switzerland*
E-mail: bruno.therrien@unine.ch
https://www.unine.ch/chim/home.html
ORCID(s) from the author(s) for this article is/are available on the WWW under https://doi.org/10.1002/ejic.201800135.

amine (ME),[4] to generate a $(ME)_3$•$(BApy)_3$ rosette structure with three coordination sites at the periphery of the hexameric rosette.[5] Arene ruthenium and cyclopentadienyl rhodium and iridium piano-stool complexes were coordinated to the rosette, giving rise to neutral and cationic trinuclear systems (Figure 1).

With the view of increasing the nuclearity of these systems and generating heteronuclear rosette-type assemblies, a pyridyl group has now been introduced to the melamine unit, thus providing six coordination sites to the $(MEpy)_3$•$(BApy)_3$ rosette. Coordination of piano-stool complexes on the MEpy and BApy units, prior to the formation of the rosette, allows controlled formation of the desired heteronuclear system. These hexameric hexanuclear metalla-assemblies show good stability in solution, as demonstrated by various NMR spectroscopic experiments.

Results and Discussion

5-Butyl-5-(pyridin-4-ylmethyl)pyrimidine-2,4,6-trione (BApy)[5] and *N*-(4-*tert*-butylphenyl)-*N*′-(pyridin-4-ylmethyl)melamine (MEpy)[6] have been prepared according to published methods. The pyridyl-containing derivatives react with the dinuclear complexes $[Ru(cym)Cl_2]_2$ (cym = *p*-cymene) and $[Rh(Cp^*)Cl_2]_2$ (Cp^* = pentamethylcyclopentadienyl) to give the corresponding mononuclear piano-stool complexes (MEpyRu), (MEpyRh), (BApyRu), and (BApyRh) (see Figure 2). As often encountered in such neutral dichloro piano-stool complexes,[7] a peak corresponding to the cationic $[M - Cl]^+$ species is observed in their ESI mass spectrum (positive mode).

As previously shown,[5] trinuclear systems can be prepared by mixing a metal-containing unit with the corresponding metal-free component (Scheme 1), thus giving rise to four trinuclear rosettes; $(MEpy)_3$•$(BApyRu)_3$, $(MEpyRu)_3$•$(BApy)_3$, $(MEpy)_3$•$(BApyRh)_3$, and $(MEpyRh)_3$•$(BApy)_3$. As in the $(ME)_3$•$(BApyRu)_3$ rosette,[5] the diffusion coefficient of these trinuclear systems is about 4×10^{-10} m^2 s^{-1}, which corresponds to a hydrodynamic radius (R_H) of more than 10 Å.

From these trinuclear systems, $(MEpy)_3$•$(BApyRu)_3$, $(MEpyRu)_3$•$(BApy)_3$, $(MEpy)_3$•$(BApyRh)_3$, and $(MEpyRh)_3$•$(BApy)_3$, hexameric hexanuclear assemblies can be obtained by the addition of 1.5 equivalents of $[Ru(cym)Cl_2]_2$ or $[Rh(Cp^*)Cl_2]_2$ (Path A, Scheme 2). The same hexanuclear rosettes can also be prepared by mixing in chloroform equimolar amounts of the mononuclear piano-stool complexes (MEpyM) and (BApyM′) (Path B, Scheme 2). Both strategies provide the desired hexanuclear rosette $(MEpyRu)_3$•$(BApyRh)_3$ and $(MEpyRh)_3$•$(BApyRu)_3$ in excellent yield (ca. 90 %).

The molecular structure of the hexameric hexanuclear rosettes $(MEpyRu)_3$•$(BApyRh)_3$, and $(MEpyRh)_3$•$(BApyRu)_3$ was confirmed by infrared and NMR spectroscopy. Upon formation of six triple ME–BA hydrogen bonds (N–H···O, N···H–N, N–H···O), the stretching vibrations of N–H broadened and shifted by almost 200 cm^{-1} in the infrared spectra, as compared with pure MEpy and BApy. The ^1H NMR spectra also support the formation of the hexameric hexanuclear structure: Other than the expected *p*-cymene and pentamethylcyclopentadienyl signals, broad signals corresponding to the NH and NH_2 groups are observed (see Experimental Section). As illustrated in Figure 3, the protons involved in the hydrogen-bonded network are shifted downfield when an equimolar amount of the mononuclear complexes (MEpyRh and BApyRu) are mixed in $[D_1]$-chloroform. And the general broadening of the signals can be attributed to the presence of multiple isomers obtained when the rosette structure is formed; these isomers cannot be identified due to the complexity of the system.

As deduced by DOSY NMR spectroscopy, the average hydrodynamic radius of the hexameric hexanuclear rosettes is 12.4 Å, which is slightly larger than those found for the trinuclear species $(MEpy)_3$•$(BApyRu)_3$, $(MEpyRu)_3$•$(BApy)_3$, $(MEpy)_3$•$(BApyRh)_3$, and $(MEpyRh)_3$•$(BApy)_3$. Moreover, 2D NMR spectroscopy also confirms the presence of hydrogen-bond interactions between the MEpy and BApy units. In the NOESY spectrum of $(MEpy)_3$•$(BApyRu)_3$ (Figure 4), cross peaks between the protons

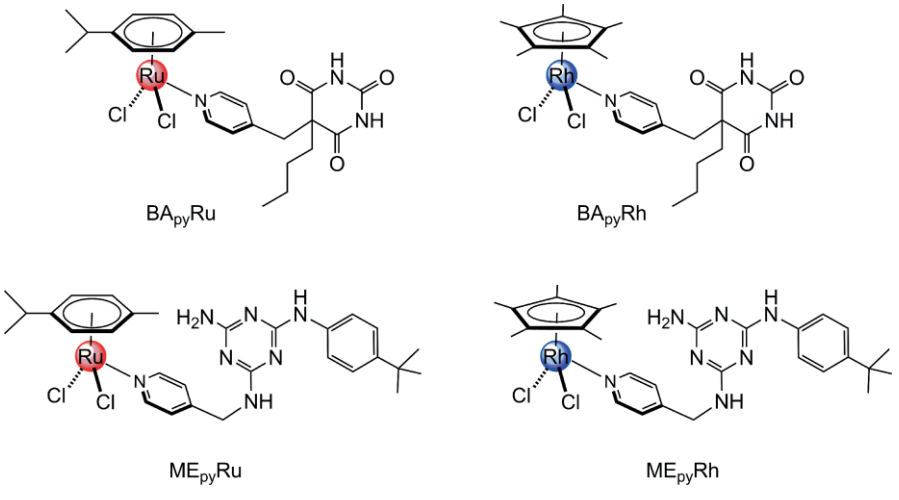
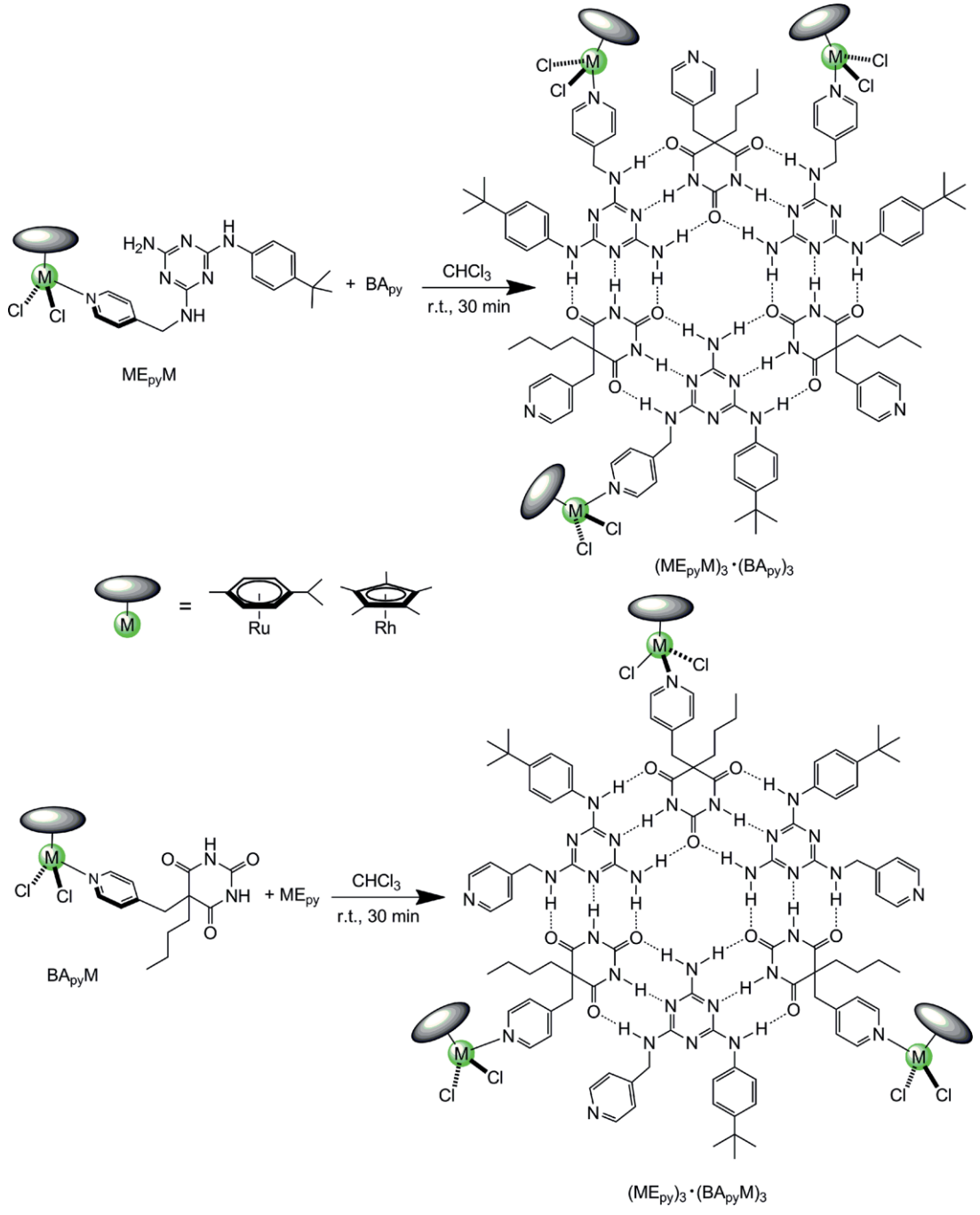


Figure 2. Mononuclear piano-stool complexes (BApyRu), (MEpyRu), (BApyRh), and (MEpyRh).



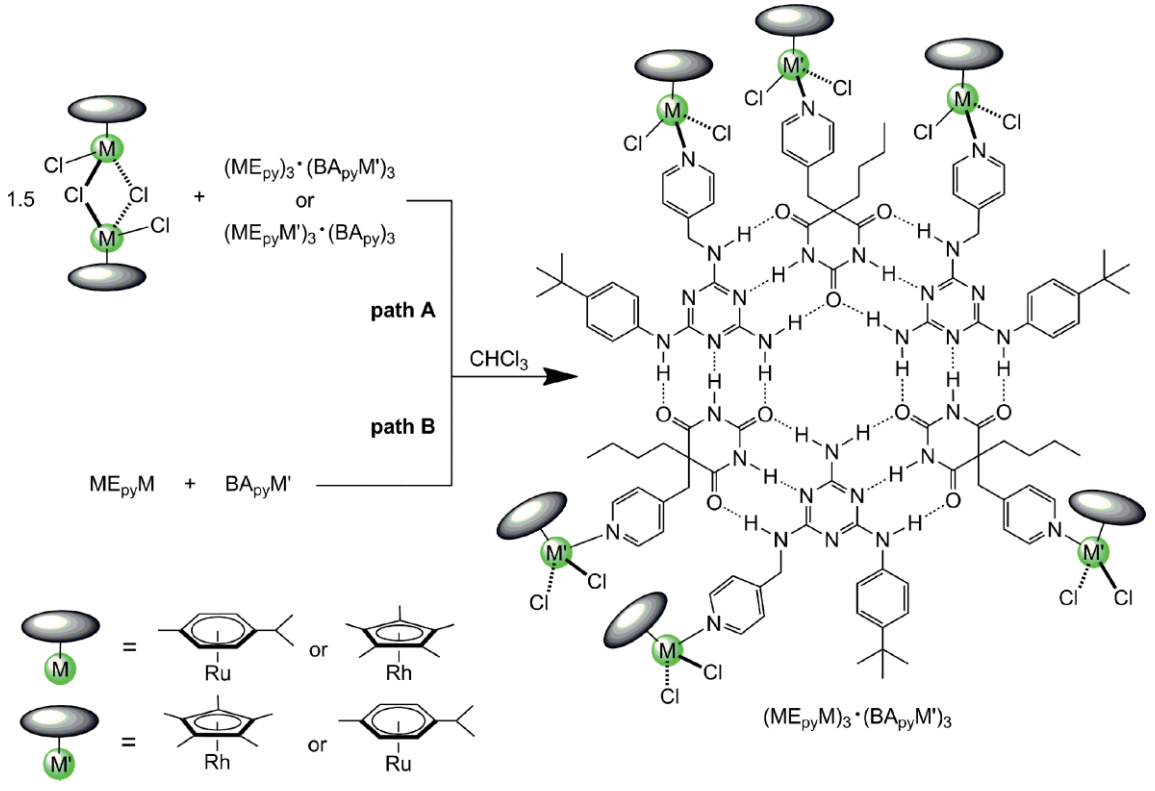
Scheme 1. Synthesis of trinuclear rosette-type assemblies.

of the NH groups of BApyRu and the protons of the NH_2 and NH groups of MEpy are observed.

The electrospray ionization mass spectra (ESI-MS) of the hexameric hexanuclear rosettes show, in both cases, a parent peak at 580.9 *m/z*, together with other metal-containing fragments of lower intensities. This main peak corresponds to the trichlorido-bridged dinuclear complex $[Rh_2(Cp^*)_2(\mu\text{-}Cl)_3]^+$, a cationic trichlorido-bridged dinuclear complex that is often produced upon decomposition of piano-stool complexes.[8] The decomposition occurs during the ionization process, as the ^1H NMR spectra of the rosettes in $[D_1]$chloroform suggest high stability in solution.

The solution stability of piano-stool complexes is crucial for various applications.[9] It is well known that chloro ligands of piano-stool complexes are easily exchanged by water (aquation) or by other coordinating solvent molecules.[10] Moreover, even monodentate pyridyl-based ligands can be removed from the coordination sphere and replaced by dmso molecules.[11] Therefore, the stability in solution of the mononuclear pyridyl-based complexes and of the rosettes was evaluated.

The mononuclear pyridyl-based complexes are stable in solution for weeks as demonstrated by ^1H NMR spectroscopic experiments. Similarly, when the hexanuclear rosettes, $(MEpyRu)_3$·



Scheme 2. Synthesis of hexanuclear rosette-type assemblies (paths A and B).

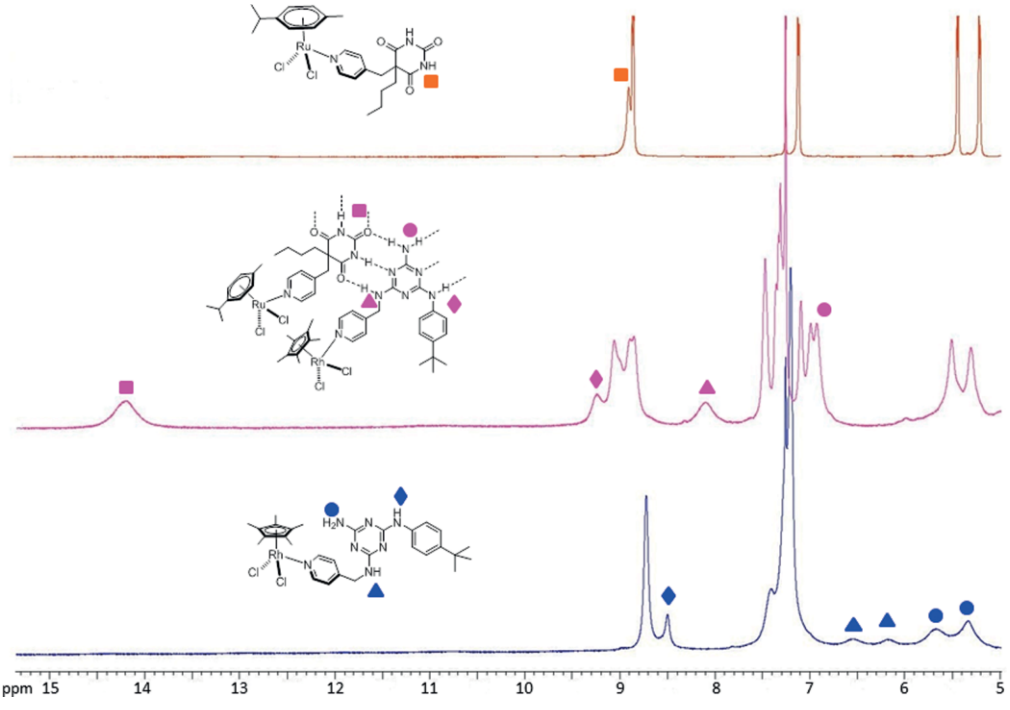


Figure 3. ^{1}H NMR spectra of BApyRu (top), $(MEpyRh)_3$·$(BApyRu)_3$ (middle), and MEpyRh (bottom), with an emphasis on the chemical shifts of the different N–H protons ($CDCl_3$, 25 °C).

$(BApyRh)_3$ and $(MEpyRh)_3$·$(BApyRu)_3$, are left in [D_1]chloroform for a long period of time (up to two weeks), all signals remain intact (chemical shift and integration), and no additional signals are observed (Figure 5).

As previously discussed, all ^{1}H NMR spectra suggest that the rosette-type assemblies were stable at room temperature in [D_1]chloroform (Figure 5). Therefore, to determine the effect of temperature on the stability of the rosettes in solution,

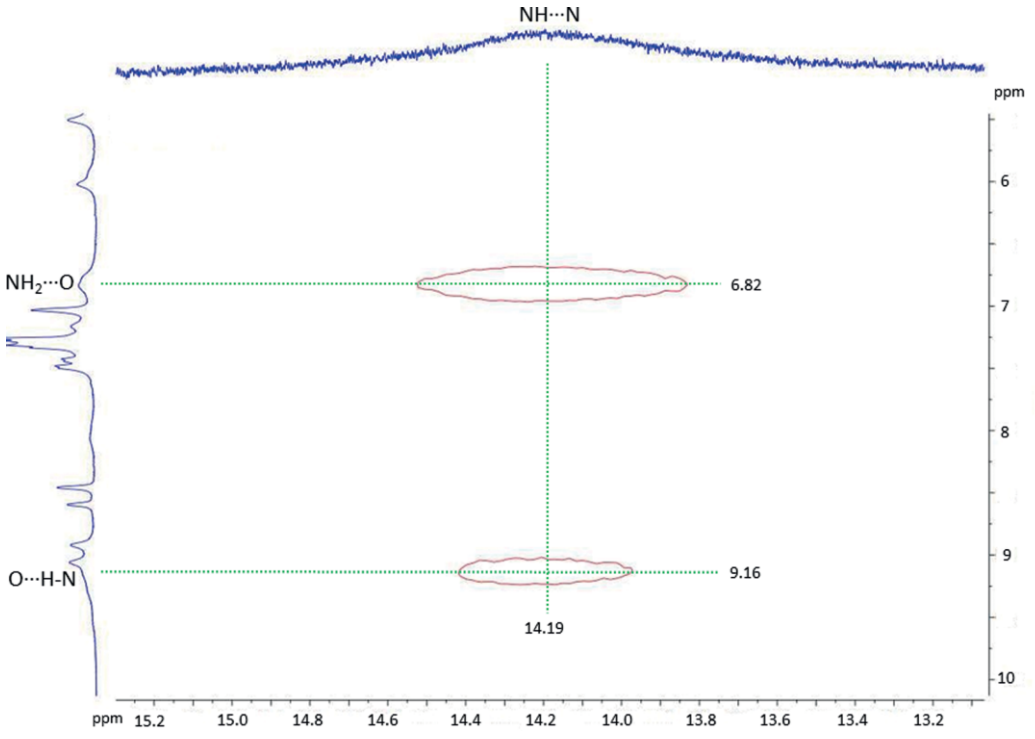


Figure 4. NOESY spectrum of $(MEpy)_3$•$(BApyRu)_3$, showing the N–H hydrogen-bond cross peaks ($CDCl_3$, 25 °C).

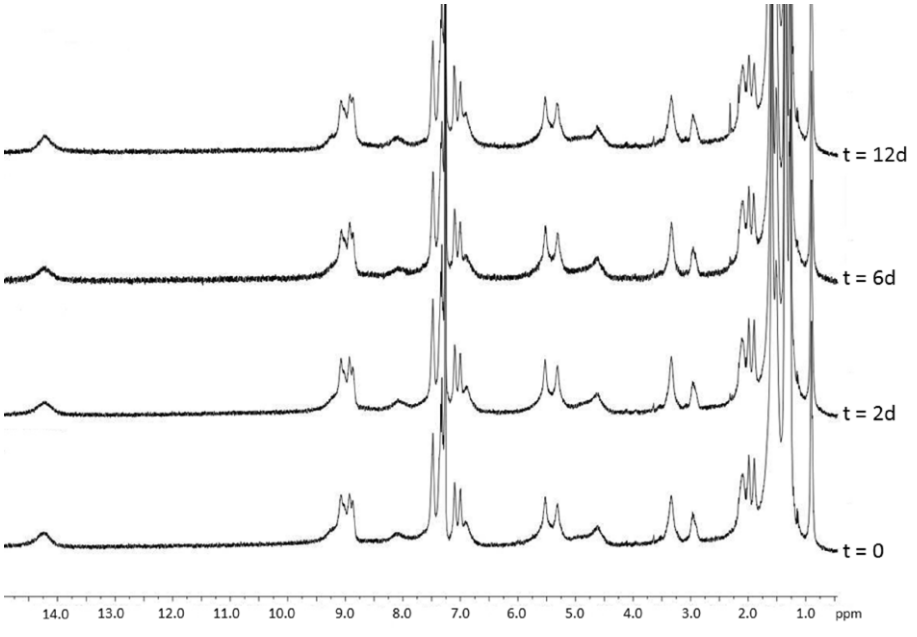


Figure 5. Evolution of the ^1H NMR spectra of $(MEpyRh)_3$•$(BApyRu)_3$ over a period of 12 days ($CDCl_3$, 25 °C).

$(MEpy)_3$•$(BApyRu)_3$ was solubilized in 1,1,2,2-$[D_2]$tetrachloroethane, and the sample heated to 120 °C (Figure 6). Interestingly, the signal from the NH protons involved in the hydrogen-bonded network at δ = 14.25 ppm, remains visible up to 70 °C. However, a significant chemical shift is observed around 50 °C, suggesting disassembly of the rosette.

The temperature-dependence experiment provides thermodynamic data on the system.[12] An equilibrium constant of

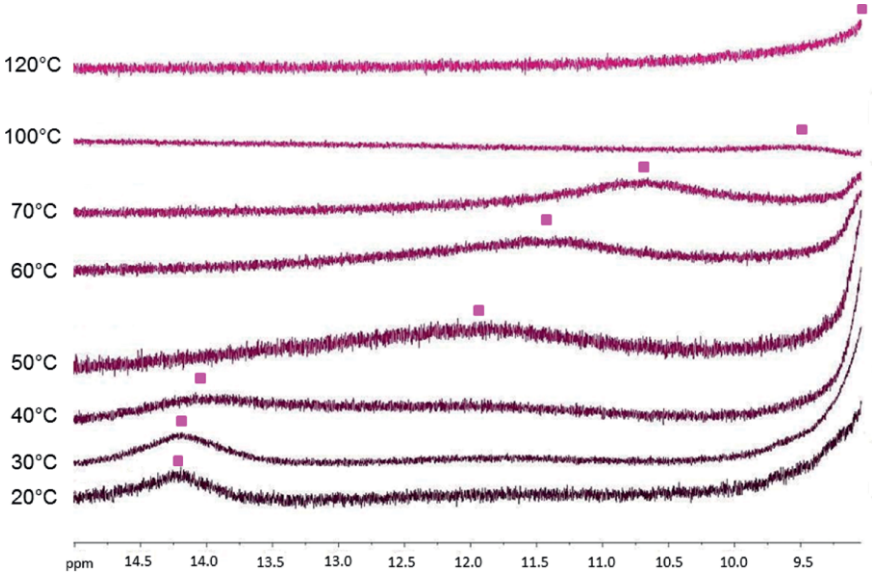


Figure 6. Temperature dependence of the proton NMR chemical shift of the NH proton (■) of BApyRu in the rosette $(MEpy)_3$•$(BApyRu)_3$ (1,1,2,2-[D_2]tetrachloroethane).

4400 s^{-1} is associated with the assembly–disassembly process, which corresponds to a chemical stability for the supramolecular rosette structure of approximately 13.5 kJ. This value is in agreement with those found by Timmerman, de Jong et al. for analogous $(ME)_3$•$(BA)_3$ rosettes.[3]

Conclusions

In conclusion, two heterohexanuclear and four homotrinuclear rosette-type assemblies have been prepared and characterized. The combination of pyridyl-functionalized melamine and barbituric acid derivatives allows a controlled synthesis of the designed heteronuclear systems. The rosette-type assemblies are stable in solution at room temperature, showing an equilibrium constant of 4400 s^{-1} and a stability constant of approximately 13.5 kJ in 1,1,2,2-[D_2]tetrachloroethane. In the future, we would like to insert additional complexity to such supramolecular assemblies, and expand, in a controlled manner, the system to the third dimension.

Experimental Section

Materials and Methods: All solvents were dried before use following standard procedures and all reactions were manipulated under an inert atmosphere. 5-Butyl-5-(pyridin-4-ylmethyl)pyrimidine-2,4,6-trione (BApy),[5] *N*-(4-*tert*-butylphenyl)-*N*′-(pyridin-4-ylmethyl)-melamine (MEpy),[6] $[Ru(cym)Cl_2]_2$,[13] $[Rh(Cp^*)Cl_2]_2$,[14] BApyRu[5], and BApyRh[5] were prepared according to published methods. All other reagents were commercially available and used as received. NMR spectra were recorded with a Bruker Avance II 400 spectrometer. DOSY experiments were conducted using standard parameters,[15] while the corresponding diffusion coefficients were calculated by the Stokes-Einstein equation.[12] UV/Visible absorption spectra were recorded with a Perkin–Elmer UV/Visible spectrophotometer. Infrared spectra were recorded with a Perkin–Elmer FTIR spectrometer. Electrospray mass spectra were obtained in the positive mode with an LCQ Finnigan mass spectrometer (University of Fribourg, Switzerland). Microanalyses were carried out by the Mikroelementaranalytisches Laoratorium (ETH Zürich, Switzerland).

Synthesis and Characterization

MEpyRu and MEpyRh: A mixture of MEpy (91.3 mg, 0.26 mmol) and $[Ru(cym)Cl_2]_2$ (80.0 mg, 0.13 mmol) or $[Rh(Cp^*)Cl_2]_2$ (80.7 mg, 0.13 mmol) in dry tetrahydrofuran (7 mL) was stirred at 25 °C for 16 h. The solvent was then evaporated. The residue was solubilized in chloroform (2 mL) and pentane was added to precipitate the product, giving the desired solid after filtration.

MEpyRu: Orange solid. Yield = 89 % (0.15 g, 0.23 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (br., 2 H, $CH_{Py}N$), 7.40 (br., 2 H, $CH_{ar}CC$), 7.22 (br., 2 H, $CH_{ar}CN$), 7.13 (br., 2 H, $CH_{Py}C$), 5.38 (br., 2 H, CH_{cym}), 5.15 (br., 2 H, CH_{cym}), 4.45 (br., 2 H, CH_2), 2.89 (br., 1 H, CH), 1.90 (br., 3 H, CH_3C_{cym}), 1.26 [s, 9 H, $C(CH_3)_3$], 1.22 [m, 6 H, $(CH_3)_2CH$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.73 (CNHCH$_2$), 165.53 (CNH_2), 163.74 (CNHC), 154.40 ($CH_{Py}N$), 151.63 (C_{Py}), 146.13 ($C_{ar}C$), 136.07 ($C_{ar}NH$), 125.62 ($CH_{ar}CN$), 123.32 ($CH_{Py}C$), 120.54 ($CH_{ar}CC$), 103.33 ($C_{cym}CH$), 97.24 ($C_{cym}CH_3$), 83.04 (CH_{cym}), 82.10 (CH_{cym}), 43.07 (CH_2), 34.39 [$C(CH_3)_3$], 31.57 [$C(CH_3)_3$], 30.75 (CH), 22.41 [$(CH_3)_2CH$], 18.24 (CH_3C_{cym}) ppm. UV/Vis ($CHCl_3$, 5.0×10^{-5} M): λ_{max} (ε) = 267 (2.49×10^4), 422 (7.48×10^2 M^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3311 (br., NH), 2960 (br., CH aromatic), 1590 (s, C⋯N), 1567 (s, C=N), 1497 (s, CN), 1412 (s, C⋯C) cm^{-1}. D ($CDCl_3$): 5.0×10^{-10} m^2 s^{-1}. ESI-MS: m/z = 620.1 $[M - Cl]^+$. $C_{29}H_{37}Cl_2N_7Ru$•H_2O (673.7): calcd. C 51.71, H 5.84, N 14.55; found C 51.20, H 5.72, N 14.12.

MEpyRh: Dark orange solid. Yield = 94 % (0.16 g, 0.25 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (br., 2 H, $CH_{Py}N$), 8.51 (br., 1 H, NHC_{ar}), 7.42 (br., 2 H, $CH_{ar}CC$), 7.21 (br., 4 H, $CH_{ar}CN$, and $CH_{Py}C$), 6.25 (br., 1 H, $NHCH_2$), 5.46 (br., 2 H, NH_2), 4.47 (br., 2 H, CH_2), 1.47 (s, 15 H, $CH_3C_{cp^*}$), 1.27 (s, 9 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.97 (CNHCH$_2$), 166.22 (CNH_2), 164.41 (CNHC), 152.90 ($CH_{Py}N$), 152.17 (C_{Py}), 145.98 ($C_{ar}C$), 136.31 ($C_{ar}NH$), 125.59 ($CH_{ar}CN$), 123.97 ($CH_{Py}C$), 120.33 ($CH_{ar}CC$), 94.13 (C_{cp^*}), 43.27 (CH_2), 34.36 [$C(CH_3)_3$], 31.55 [$C(CH_3)_3$], 8.92 ($CH_3C_{cp^*}$) ppm. UV/Vis ($CHCl_3$, 5.0×10^{-5} M): λ_{max} (ε) = 265 (2.95×10^4), 407 (2.78×10^3 M^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3310 (br., NH), 2961 (br., CH aromatic), 1597 (s, C⋯N), 1568 (s, C=N), 1504 (s, CN), 1414 (s, C⋯C) cm^{-1}. D ($CDCl_3$): 7.2×10^{-10} m^2 s^{-1}. ESI-

MS: *m/z* = 622.1 [M – Cl]$^+$. $C_{29}H_{38}Cl_2N_7Rh{\cdot}2H_2O$ (694.5): calcd. C 50.15, H 6.10, N 14.12; found C 49.76, H 5.88, N 13.31.

(MEpy)$_3$·(BApy)$_3$: A mixture of BApy (39.4 mg, 0.14 mmol) and MEpy (50.0 mg, 0.14 mmol) in dry chloroform (1 mL) was stirred at 25 °C for 30 min. Pentane was then added to precipitate the product as a white solid. Yield = 89 % (79.6 mg, 0.04 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.59 (br., 6 H, NH···N), 9.19 (br., 3 H, O···HN), 8.61 (d, $^3J_{H,H}$ = 3.3 Hz, 6 H, $CH_{Py\ ME}N$), 8.46 (d, $^3J_{H,H}$ = 3.1 Hz, 6 H, $CH_{Py\ BA}N$), 8.03 (br., 3 H, O···HN), 7.48 (d, $^3J_{H,H}$ = 7.7 Hz, 6 H, $CH_{ar}CC$), 7.29 (d, $^3J_{H,H}$ = 3.3 Hz, 6 H, $CH_{Py\ ME}C$), 7.26 (d, $^3J_{H,H}$ = 7.7 Hz, 6 H, $CH_{ar}CN$), 7.00 (d, $^3J_{H,H}$ = 3.1 Hz, 6 H, $CH_{Py\ BA}C$), 6.74 (br., 6 H, NH_2···O), 4.69 (s, 6 H, $CH_{2\ ME}$), 3.28 (s, 6 H, $CH_{2\ BA}$), 2.14 (s, 6 H, CH_2C_{BA}), 1.33 [s, 27 H, $C(CH_3)_3$], 1.30 (m, 12 H, CH_2 and CH_2CH_3), 0.90 (t, $^3J_{H,H}$ = 6.4 Hz, 9 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.67 (CO), 166.00 (*C*NHCH$_2$), 165.67 (CNH_2), 163.58 (*C*NHC), 152.28 (HNCONH), 150.34 ($CH_{Py\ BA}N$), 149.91 ($CH_{Py\ ME}N$), 148.98 ($C_{Py\ ME}$), 146.21 ($C_{ar}C$), 144.02 ($C_{Py\ BA}$), 136.55 ($C_{ar}NH$), 125.54 ($CH_{ar}CN$), 124.74 ($CH_{Py\ BA}C$), 122.35 ($CH_{Py\ ME}C$), 120.75 ($CH_{ar}CC$), 57.73 (C_{BA}), 43.97 ($CH_{2\ ME}$), 42.87 ($CH_{2\ BA}$), 40.04 (CH_2C_{BA}), 34.46 [*C*(CH$_3$)$_3$], 31.60 [C(*C*H$_3$)$_3$], 27.12 (CH_2), 22.73 (CH_2CH_3), 13.80 (CH_3) ppm. UV/Vis ($CHCl_3$, 1.0 × 10^{-5} M): λ_{max} (ε) = 265 (8.00 × 10^4 M^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3344 (br., NH), 2961 (br., CH aromatic), 1720 (s, NH), 1685 (s, C=O), 1602 (s, C···N), 1571 (s, C=N), 1520 (s, CN), 1411 (s, C···C) cm^{-1}. *D* ($CDCl_3$): 4.0 × 10^{-10} m^2 s^{-1}. $C_{99}H_{120}N_{30}O_9{\cdot}H_2O$ (1892.3): calcd. C 62.84, H 6.50, N 22.21; found C 62.18, H 6.36, N 21.24.

(MEpy)$_3$·(BApyRu)$_3$ and (MEpy)$_3$·(BApyRh)$_3$: A mixture of (BApyRu) (50.0 mg, 0.09 mmol) or (BApyRh) (50.3 mg; 0.09 mmol) and MEpy (30.1 mg, 0.09 mmol) in dry chloroform (1 mL) was stirred at 25 °C for 30 min. Pentane was then added to precipitate the product.

(MEpy)$_3$·(BApyRu)$_3$: Yellow solid. Yield = 89 % (71.3 mg, 0.03 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.26 (br., 6 H, NH···N), 9.26 (br., 3 H, O···HN), 9.07 (br., 3 H, $CH_{Py\ ME}N$), 8.92 (br., 3 H, $CH_{Py\ BA}N$), 8.60 (br., 3 H, $CH_{Py\ ME}$'N), 8.47 (br., 3 H, $CH_{Py\ BA}$'N), 8.10 (br., 3 H, O···H'N), 7.48 (dd, $^3J_{H,H}$ = 7.7 Hz, 6 H, $CH_{ar}CC$), 7.34 (dd, $^3J_{H,H}$ = 7.7 Hz, 6 H, $CH_{ar}CN$), 7.29 (br., 6 H, $CH_{Py\ ME}C$), 7.03 (br., 6 H, $CH_{Py\ BA}C$), 6.84 (br., 3 H, NH_2···O), 6.02 (br., 3 H, NH_2'···O), 5.52 (br., 6 H, CH_{cym}), 5.30 (br., 6 H, CH_{cym}), 4.68 (br., 6 H, $CH_{2\ ME}$), 3.30 (br., 6 H, $CH_{2\ BA}$), 2.97 (m, 3 H, CH), 2.15 (br., 3 H, CH_2C_{BA}), 2.10 (br., 3 H, CH_2'C_{BA}), 1.95 (m, 9 H, CH_3C_{cym}), 1.36 [br, 27 H, $C(CH_3)_3$], 1.32 (m, 12 H, CH_2 and CH_2CH_3), 1.28 [m, 18 H, $(CH_3)_2CH$], 0.89 (t, $^3J_{H,H}$ = 6.6 Hz, 9 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.81 (CO), 165.84 (*C*NHCH$_2$), 165.54 (CNH_2), 165.41 (CNH_2'), 163.43 (*C*NHC), 155.27 ($CH_{Py\ BA}N$), 154.91 ($CH_{Py\ ME}N$), 152.63 (HNCONH), 151.53 (HNC'ONH), 150.36 ($CH_{Py\ BA}$'N), 149.93 ($CH_{Py\ ME}$'N), 148.88 ($C_{Py\ ME}$), 146.55 ($C_{ar}C$), 146.23 (C_{ar}'C), 143.96 ($C_{Py\ BA}$), 136.65 ($C_{ar}NH$), 136.44 (C_{ar}'NH), 125.92 ($CH_{Py\ BA}C$), 125.53 ($CH_{ar}CN$), 124.71 ($CH_{Py\ BA}$'C), 122.73 ($CH_{Py\ ME}C$), 122.35 ($CH_{Py\ ME}$'C), 120.77 ($CH_{ar}CC$), 120.63 (CH_{ar}'CC), 103.33 ($C_{cym}CH$), 97.36 ($C_{cym}CH_3$), 83.35 (CH_{cym}), 81.93 (CH_{cym}), 57.68 (C_{BA}), 57.40 (C_{BA}'), 43.97 ($CH_{2\ ME}$), 43.37 ($CH_{2\ ME}$'), 43.35 ($CH_{2\ BA}$), 42.76 ($CH_{2\ BA}$'), 39.99 (CH_2C_{BA}), 34.50 [*C*(CH$_3$)$_3$], 34.44 [*C*'(CH$_3$)$_3$], 31.67 [C(*C*H$_3$)$_3$], 31.58 [C(*C*'H$_3$)$_3$], 30.84 (CH), 27.07 (CH_2), 26.69 (CH_2'), 22.68 (CH_2CH_3), 22.50 [$(CH_3)_2CH$], 18.40 (CH_3C_{cym}), 18.19 (CH_3'C_{cym}), 13.79 (CH_3) ppm. UV/Vis ($CHCl_3$, 1.0 × 10^{-5} M): λ_{max} (ε) = 267 (8.55 × 10^4), 413 (2.67 × 10^3 M^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3326 (br., NH), 2961 (br., CH aromatic), 1725 (s, NH), 1698 (s, C=O), 1601 (s, C···N), 1570 (s, C=N), 1512 (s, CN), 1413 (s, C···C) cm^{-1}. *D* ($CDCl_3$): 3.9 × 10^{-10} m^2 s^{-1}. $C_{129}H_{162}Cl_6N_{30}O_9Ru_3{\cdot}3H_2O$ (2846.9): calcd. C 54.43, H 5.95, N 14.76; found C 53.47, H 5.82, N 13.89.

(MEpy)$_3$·(BApyRh)$_3$: Orange solid, yield 89 % (71.5 mg, 0.03 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.17 (br., 6 H, NH···N), 9.20 (br., 3 H, O···HN), 8.96 (br., 3 H, $CH_{Py\ ME}N$), 8.83 (br., 3 H, $CH_{Py\ BA}N$), 8.61 (br., 3 H, $CH_{Py\ ME}$'N), 8.46 (br., 3 H, $CH_{Py\ BA}$'N), 8.06 (br., 3 H, O···H'N), 7.46 (br., 6 H, $CH_{ar}CC$), 7.32 (br., 6 H, $CH_{Py\ ME}C$), 7.29 (br., 6 H, $CH_{ar}CN$), 7.08 (br., 3 H, $CH_{Py\ BA}C$), 7.01 (br., 3 H, $CH_{Py\ BA}$'C), 6.83 (br., 3 H, NH_2···O), 4.69 (br., 6 H, $CH_{2\ ME}$), 3.29 (br., 6 H, $CH_{2\ BA}$), 2.13 (br., 6 H, CH_2C_{BA}), 1.53 (m, 45 H, CH_3C_{cp*}), 1.33 [br, 27 H, $C(CH_3)_3$], 1.30 (m, 12 H, CH_2 and CH_2CH_3), 0.89 (t, $^3J_{H,H}$ = 6.4 Hz, 9 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.01 (CO), 165.53 (*C*NHCH$_2$), 165.28 (CNH_2), 163.26 (*C*NHC), 153.73 ($CH_{Py\ BA}N$), 153.33 ($CH_{Py\ ME}N$), 152.90 (HNCONH), 151.55 (HNC'ONH), 150.27 ($CH_{Py\ BA}$'N), 149.56 ($CH_{Py\ ME}$'N), 149.25 ($C_{Py\ ME}$), 146.80 ($C_{ar}C$), 146.31 (C_{ar}'C), 144.03 ($C_{Py\ BA}$), 136.47 ($C_{ar}NH$), 136.30 (C_{ar}'NH), 126.56 ($CH_{Py\ BA}C$), 125.51 ($CH_{ar}CN$), 124.70 ($CH_{Py\ BA}$'C), 123.73 ($CH_{Py\ ME}C$), 122.44 ($CH_{Py\ ME}$'C), 120.80 ($CH_{ar}CC$), 120.66 (CH_{ar}'CC), 94.16 (C_{cp*}), 57.62 (C_{BA}), 57.45 (C_{BA}'), 43.97 ($CH_{2\ ME}$), 43.61 ($CH_{2\ ME}$'), 42.72 ($CH_{2\ BA}$), 41.06 ($CH_{2\ BA}$'), 39.95 (CH_2C_{BA}), 34.44 [*C*(CH$_3$)$_3$], 31.57 [C(*C*H$_3$)$_3$], 27.04 (CH_2), 26.82 (CH_2'), 22.61 (CH_2CH_3), 13.78 (CH_3), 8.99 (CH_3C_{cp*}), 8.90 (CH_3'C_{cp*}) ppm. UV/Vis ($CHCl_3$, 1.0 × 10^{-5} M): λ_{max} (ε) = 265 (1.02 × 10^5), 402 (8.59 × 10^3 M^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3327 (br., NH), 2960 (br., CH aromatic), 1726 (s, NH), 1698 (s, C=O), 1601 (s, C···N), 1570 (s, C=N), 1512 (s, CN), 1413 (s, C···C) cm^{-1}. *D* ($CDCl_3$): 3.9 × 10^{-10} m^2 s^{-1}. $C_{129}H_{165}Cl_6N_{30}O_9Rh_3{\cdot}3H_2O$ (2855.4): calcd. C 54.26, H 6.04, N 14.72; found C 53.42, H 6.07, N 14.46.

(MEpyRu)$_3$·(BApy)$_3$ and (MEpyRh)$_3$·(BApy)$_3$: A mixture of BApy (30.0 mg, 0.11 mmol) and (MEpyRu) (71.4 mg, 0.11 mmol) or (MEpyRh) (71.8 mg, 0.11 mmol) in dry chloroform (1 mL) was stirred at 25 °C for 30 min. Pentane was then added to precipitate the corresponding product.

(MEpyRu)$_3$·(BApy)$_3$: Yellow solid. Yield = 88 % (89.3 mg, 0.03 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.18 (br., 6 H, NH···N), 9.20 (br., 3 H, O···HN), 9.07 (br., 3 H, $CH_{Py\ ME}N$), 8.92 (br., 3 H, $CH_{Py\ BA}N$), 8.60 (br., 3 H, $CH_{Py\ ME}$'N), 8.45 (br., 3 H, $CH_{Py\ BA}$'N), 8.10 (br., 3 H, O···H'N), 7.47 (dd, $^3J_{H,H}$ = 7.9 Hz, 6 H, $CH_{ar}CC$), 7.33 (dd, $^3J_{H,H}$ = 7.9 Hz, 6 H, $CH_{ar}CN$), 7.28 (br., 6 H, $CH_{Py\ ME}C$), 7.02 (br., 6 H, $CH_{Py\ BA}C$), 6.85 (br., 3 H, NH_2···O), 6.03 (br., 3 H, NH_2'···O), 5.50 (br., 6 H, CH_{cym}), 5.30 (br., 6 H, CH_{cym}), 4.68 (br., 6 H, $CH_{2\ ME}$), 3.30 (br., 6 H, $CH_{2\ BA}$), 2.96 (m, 3 H, CH), 2.11 (br., 6 H, CH_2C_{BA}), 1.96 (m, 9 H, CH_3C_{cym}), 1.35 [br, 27 H, $C(CH_3)_3$], 1.32 (m, 12 H, CH_2 and CH_2CH_3), 1.28 [m, 18 H, $(CH_3)_2CH$], 0.88 (t, $^3J_{H,H}$ = 6.4 Hz, 9 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.83 (CO), 165.73 (*C*NHCH$_2$), 165.43 (CNH_2), 165.33 (*C*'NH_2), 163.34 (*C*NHC), 155.23 ($CH_{Py\ BA}N$), 154.87 ($CH_{Py\ ME}N$), 152.69 (HNCONH), 151.51 (HNC'ONH), 150.24 ($CH_{Py\ BA}$'N), 149.76 ($CH_{Py\ ME}$'N), 149.02 ($C_{Py\ ME}$), 146.56 ($C_{ar}C$), 146.23 (C_{ar}'C), 144.05 ($C_{Py\ BA}$), 136.59 ($C_{ar}NH$), 136.39 (C_{ar}'NH), 125.92 ($CH_{Py\ BA}C$), 125.51 ($CH_{ar}CN$), 124.73 ($CH_{Py\ BA}$'C), 122.76 ($CH_{Py\ ME}C$), 122.37 ($CH_{Py\ ME}$'C), 120.76 ($CH_{ar}CC$), 120.61 (CH_{ar}'CC), 103.30 ($C_{cym}CH$), 102.98 (C_{cym}'CH), 97.60 ($C_{cym}CH_3$), 97.36 (C_{cym}'CH_3), 83.33 (CH_{cym}), 81.93 (CH_{cym}), 57.63 (C_{BA}), 57.36 (C_{BA}'), 43.94 ($CH_{2\ ME}$), 43.35 ($CH_{2\ ME}$'), 43.34 ($CH_{2\ BA}$), 43.71 ($CH_{2\ BA}$'), 39.97 (CH_2C_{BA}), 34.47 [*C*(CH$_3$)$_3$], 34.42 [*C*'(CH$_3$)$_3$], 31.64 [C(*C*H$_3$)$_3$], 31.55 [C(*C*H$_3$')$_3$], 30.81 (CH), 27.03 (CH_2), 26.67 (CH_2'), 22.65 (CH_2CH_3), 22.57 (CH_2'CH_3), 22.47 [$(CH_3)_2CH$], 18.38 (CH_3C_{cym}), 18.18 (CH_3'C_{cym}), 13.78 (CH_3) ppm. UV/Vis ($CHCl_3$, 1.0 × 10^{-5} M): λ_{max} (ε) = 267 (9.14 × 10^4), 407 (2.55 × 10^3 M^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3324 (br., NH), 2960 (br., CH aromatic), 1725 (s, NH), 1698 (s, C=O), 1614 (s, C···N), 1570 (s, C=N), 1512 (s, CN), 1414 (s, C···C) cm^{-1}. *D* ($CDCl_3$): 3.0 × 10^{-10} m^2 s^{-1}. $C_{129}H_{162}Cl_6N_{30}O_9Ru_3{\cdot}CHCl_3{\cdot}H_2O$ (2930.2): calcd. C 53.29, H 5.68, N 14.34; found C 52.46, H 5.83, N 13.85.

(MEpyRh)$_3$·(BApy)$_3$: Orange solid. Yield = 88 % (89.5 mg, 0.03 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.15 (br., 6 H, NH···N), 9.21 (br., 3 H, O···HN), 8.96 (br., 3 H, $CH_{Py\ ME}N$), 8.83 (br., 3 H, $CH_{Py\ BA}N$), 8.61 (br., 3 H, $CH_{Py\ ME}$'N), 8.46 (br., 3 H, $CH_{Py\ BA}$'N), 8.06 (br., 3 H, O···H'N), 7.47 (br., 6 H, $CH_{ar}CC$), 7.35 (br., 6 H, $CH_{Py\ ME}C$),

7.31 (br., 6 H, $CH_{ar}CN$), 7.08 (br., 3 H, $CH_{Py\ BA}C$), 7.02 (br., 3 H, $CH_{Py\ BA}'C$), 6.85 (br., 6 H, $NH_2\cdots O$), 4.69 (br., 6 H, $CH_{2\ ME}$), 3.29 (br., 6 H, $CH_{2\ BA}$), 2.13 (br., 6 H, CH_2C_{BA}), 1.53 (m, 45 H, CH_3C_{cp*}), 1.34 [br, 27 H, $C(CH_3)_3$], 1.30 (m, 12 H, CH_2 and CH_2CH_3), 0.89 (t, $^3J_{H,H}$ = 6.4 Hz, 9 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.87 (CO), 165.69 ($CNHCH_2$), 165.39 (CNH_2), 163.32 (*C*NHC), 153.73 ($CH_{Py\ BA}N$), 153.35 ($CH_{Py\ ME}N$), 151.55 (HNCONH), 150.26 ($CH_{Py\ BA}'N$), 149.72 ($CH_{Py\ ME}'N$), 149.05 ($C_{Py\ ME}$), 146.82 ($C_{ar}C$), 146.25 ($C_{ar}'C$), 144.05 ($C_{Py\ BA}$), 136.54 ($C_{ar}NH$), 136.37 ($C_{ar}'NH$), 126.55 ($CH_{Py\ BA}C$), 125.51 ($CH_{ar}CN$), 124.70 ($CH_{Py\ BA}'C$), 123.72 ($CH_{Py\ ME}C$), 122.38 ($CH_{Py\ ME}'C$), 120.77 ($CH_{ar}CC$), 120.63 ($CH_{ar}'CC$), 94.18 (C_{cp*}), 57.63 (C_{BA}), 57.47 (C_{BA}'), 43.95 ($CH_{2\ ME}$), 43.62 ($CH_{2\ ME}'$), 42.72 ($CH_{2\ BA}$), 41.07 ($CH_{2\ BA}'$), 39.96 (CH_2C_{BA}), 34.43 [$C(CH_3)_3$], 31.58 [$C(CH_3)_3$], 27.03 (CH_2), 26.81 (CH_2'), 22.60 (CH_2CH_3), 13.78 (CH_3), 9.01 (CH_3C_{cp*}), 8.90 ($CH_3'C_{cp*}$) ppm. UV/Vis ($CHCl_3$, 1.0 × 10^{-5} M): λ_{max} (ε) = 265 (9.65 × 10^4), 403 (8.61 × 10^3 M^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3329 (br., NH), 2960 (br., CH aromatic), 1726 (s, NH), 1698 (s, C=O), 1602 (s, C⋯N), 1570 (s, C=N), 1513 (s, CN), 1414 (s, C⋯C) cm^{-1}. *D* ($CDCl_3$): 3.7 × 10^{-10} m^2 s^{-1}. $C_{129}H_{165}Cl_6N_{30}O_9Rh_3{\cdot}CHCl_3{\cdot}H_2O$ (2938.7): calcd. C 53.13, H 5.76, N 14.30; found C 52.31, H 5.90, N 13.62.

$(MEpyRh)_3{\cdot}(BApyRu)_3$ and $(MEpyRu)_3{\cdot}(BApyRh)_3$

Path A: A mixture of (BApyRu) (83.2 mg, 0.14 mmol) or (BApyRh) (83.6 mg, 0.14 mmol) and MEpy (50.0 mg, 0.14 mmol) in dry chloroform (3 mL) was stirred at 25 °C. After 30 min, $[Rh(Cp^*)Cl_2]_2$ (44.2 mg, 0.07 mmol) or $[Ru(cym)Cl_2]_2$ (43.8 mg, 0.07 mmol) was added, and the mixture was stirred at 25 °C for 16 h. The mixture was then concentrated and pentane was added to precipitate the product.

Path B: A mixture of (BApyRu) (44.2 mg, 0.08 mmol) or (BApyRh) (44.6 mg, 0.08 mmol) and (MEpyRh) (50.0 mg, 0.08 mmol) or (MEpyRu) (50.0 mg, 0.08 mmol) in dry chloroform (2 mL) was stirred at 25 °C for 30 min. Pentane was then added to precipitate the product.

$(MEpyRh)_3{\cdot}(BApyRu)_3$: Orange solid, path A 93 % yield: 0.17 g, 0.04 mmol; path B 90 %: 0.16 g, 0.04 mmol. ^1H NMR (400 MHz, $CDCl_3$): δ = 14.20 (br., 6 H, NH⋯N), 9.25 (br., 3 H, O⋯HN), 9.06 (br., 6 H, $CH_{Py\ ME}N$), 8.88 (br., 6 H, $CH_{Py\ BA}N$), 8.10 (br., 3 H, O⋯H'N), 7.48 (br., 6 H, $CH_{ar}CC$), 7.34 (m, 6 H, $CH_{Py\ ME}C$), 7.32 (m, 6 H, $CH_{ar}CN$), 7.10 (br., 6 H, $CH_{Py\ BA}C$), 7.00 (br., 3 H, $NH_2\cdots O$), 6.93 (br., 3 H, $NH_2'\cdots O$), 5.51 (br., 6 H, CH_{cym}), 5.31 (br., 6 H, CH_{cym}), 4.93 (br., 3 H, $CH_{2\ ME}$), 4.58 (br., 3 H, $CH_2'_{ME}$), 3.34 (br., 6 H, $CH_{2\ BA}$), 2.94 (br., 3 H, CH), 2.09 (br., 6 H, CH_2C_{BA}), 1.94 (m, 9 H, CH_3C_{cym}), 1.54 (m, 45 H, CH_3C_{cp*}), 1.35 [m, 27 H, $C(CH_3)_3$], 1.32 (m, 12 H, CH_2 and CH_2CH_3), 1.26 [m, 18 H, $(CH_3)_2CH$], 0.89 (t, $^3J_{H,H}$ = 6.2 Hz, 9 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.93 (CO), 165.60 ($CNHCH_2$), 165.22 (CNH_2), 163.20 (*C*NHC), 155.27 ($CH_{Py\ ME}N$), 154.90 ($CH_{Py\ ME}'N$), 154.09 (HNCONH), 153.77 ($CH_{Py\ BA}N$), 153.48 ($CH_{Py\ BA}'N$), 153.11 ($C_{Py\ ME}$), 152.98 ($C_{Py\ ME}'$), 151.53 ($C_{Py\ BA}$), 151.36 ($C_{Py\ BA}'$), 146.50 ($C_{ar}C$), 146.29 ($C_{ar}'C$), 136.47 ($C_{ar}NH$), 126.52 ($CH_{Py\ BA}C$), 126.02 ($CH_{Py\ BA}'C$), 125.51 ($CH_{ar}CN$), 123.60 ($CH_{Py\ ME}C$), 122.77 ($CH_{Py\ ME}'C$), 120.64 ($CH_{ar}CC$), 103.17 ($C_{cym}CH$), 97.39 ($C_{cym}CH_3$), 94.21 (C_{cp*}), 83.48 (CH_{cym}), 82.07 (CH_{cym}), 57.44 (C_{BA}), 43.38 ($CH_{2\ ME}$), 41.67 (CH_2C_{BA}), 40.85 ($CH_{2\ BA}$), 34.46 [$C(CH_3)_3$], 31.62 [$C(CH_3)_3$], 30.81 (CH), 26.61 (CH_2), 22.55 (CH_2CH_3), 22.48 [$(CH_3)_2CH$], 18.37 (CH_3C_{cym}), 18.14 ($CH_3'C_{cym}$), 13.78 (CH_3), 9.09 (CH_3C_{cp*}), 8.95 ($CH_3'C_{cp*}$) ppm. UV/Vis ($CHCl_3$, 1.0 × 10^{-5} M): λ_{max} (ε) = 265 (1.01 × 10^5), 409 (9.97 × 10^3 M^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3318 (br., NH), 2960 (br., CH aromatic), 1726 (s, NH), 1699 (s, C=O), 1614 (s, C⋯N), 1570 (s, C=N), 1512 (s, CN), 1417 (s, C⋯C) cm^{-1}. *D* ($CDCl_3$): 3.6 × 10^{-10} m^2 s^{-1}. $C_{159}H_{207}Cl_{12}N_{30}O_9Rh_3Ru_3{\cdot}3H_2O$ (3774.0): calcd. C 50.60, H 5.69, N 11.13; found C 49.77, H 5.74, N 10.87.

$(MEpyRu)_3{\cdot}(BApyRh)_3$: Orange solid, path A 90 % yield: 0.16 g, 0.04 mmol; path B 87 %: (0.15 g, 0.04 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ = 14.22 (br., 6 H, NH⋯N), 9.25 (br., 3 H, O⋯HN), 9.08 (br., 6 H, $CH_{Py\ ME}N$), 8.86 (br., 6 H, $CH_{Py\ BA}N$), 8.11 (br., 3 H, O⋯H'N), 7.48 (br., 6 H, $CH_{ar}CC$), 7.34 (m, 6 H, $CH_{Py\ ME}C$), 7.28 (m, 6 H, $CH_{ar}CN$), 7.09 (br., 6 H, $CH_{Py\ BA}C$), 6.99 (br., 3 H, $NH_2\cdots O$), 6.92 (br., 3 H, $NH_2'\cdots O$), 5.52 (br., 6 H, CH_{cym}), 5.33 (br., 6 H, CH_{cym}), 4.96 (br., 3 H, $CH_{2\ ME}$), 4.58 (br., 3 H, $CH_2'_{ME}$), 3.34 (br., 6 H, $CH_{2\ BA}$), 2.96 (br., 3 H, CH), 2.09 (br., 6 H, CH_2C_{BA}), 1.95 (br., 9 H, CH_3C_{cym}), 1.54 (m, 45 H, CH_3C_{cp*}), 1.35 [m, 27 H, $C(CH_3)_3$], 1.32 (m, 12 H, CH_2 and CH_2CH_3), 1.27 [m, 18 H, $(CH_3)_2CH$], 0.89 (t, $^3J_{H,H}$ = 6.4 Hz, 9 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.91 (CO), 165.65 ($CNHCH_2$), 165.30 (CNH_2), 163.23 (*C*NHC), 155.22 ($CH_{Py\ ME}N$), 154.88 ($CH_{Py\ ME}'N$), 154.29 (HNCONH), 153.73 ($CH_{Py\ BA}N$), 153.46 ($CH_{Py\ BA}'N$), 153.22 ($C_{Py\ ME}$), 152.84 ($C_{Py\ ME}'$), 151.61 ($C_{Py\ BA}$), 151.39 ($C_{Py\ BA}'$), 146.47 ($C_{ar}C$), 146.23 ($C_{ar}'C$), 136.50 ($C_{ar}NH$), 126.56 ($CH_{Py\ BA}C$), 126.00 ($CH_{Py\ BA}'C$), 125.49 ($CH_{ar}CN$), 123.55 ($CH_{Py\ ME}C$), 122.72 ($CH_{Py\ ME}'C$), 120.61 ($CH_{ar}CC$), 103.14 ($C_{cym}CH$), 97.38 ($C_{cym}CH_3$), 94.20 (C_{cp*}), 83.47 (CH_{cym}), 81.81 (CH_{cym}), 57.44 (C_{BA}), 43.37 ($CH_{2\ ME}$), 41.41 (CH_2C_{BA}), 40.51 ($CH_{2\ BA}$), 34.44 [$C(CH_3)_3$], 31.59 [$C(CH_3)_3$], 30.79 (CH), 26.61 (CH_2), 22.52 (CH_2CH_3), 22.47 [$(CH_3)_2CH$], 18.33 (CH_3C_{cym}), 18.12 ($CH_3'C_{cym}$), 13.75 (CH_3), 9.07 (CH_3C_{cp*}), 8.93 ($CH_3'C_{cp*}$) ppm. UV/Vis ($CHCl_3$, 1.0 × 10^{-5} M): λ_{max} (ε) = 265 (9.77 × 10^4), 406 (9.77 × 10^3 M^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3325 (br., NH), 2960 (br., CH aromatic), 1726 (s, NH), 1699 (s, C=O), 1614 (s, C⋯N), 1570 (s, C=N), 1513 (s, CN), 1417 (s, C⋯C) cm^{-1}. *D* ($CDCl_3$): 3.0 × 10^{-10} m^2 s^{-1}. $C_{159}H_{207}Cl_{12}N_{30}O_9Rh_3Ru_3{\cdot}3H_2O$ (3774.0): calcd. C 50.60, H 5.69, N 11.13; found C 49.73, H 5.81, N 10.90.

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