Organometallic boxes built from 5,10,15,20-tetra(4-pyridyl)porphyrin panels and hydroxyquinonato-bridged diruthenium clips

Nicolas P.E. Barry, Padavattan Govindaswamy, Julien Furrer, Georg Süss-Fink, Bruno Therrien *

Institut de Chimie, Université de Neuchâtel, Case, postale 158, CH-2009 Neuchâtel, Switzerland

ABSTRACT

Self-assembly of 5,10,15,20-tetra(4-pyridyl)porphyrin (tpp-H_2) tetradentate panels with dinuclear arene ruthenium clips [$Ru_2(\eta^6$-arene$)_2$(dhbq)Cl_2] (arene = C_6H_5Me, p-$Pr^iC_6H_4Me$, C_6Me_6; dhbq = 2,5-dihydroxy-1,4-benzoquinonato) affords the cationic organometallic boxes [$Ru_8(\eta^6$-$C_6H_5Me)_8$(tpp-$H_2)_2$(dhbq)$_4$]$^{8+}$ ([**1**]$^{8+}$), [$Ru_8(\eta^6$-p-$Pr^iC_6H_4Me)_8$(tpp-$H_2)_2$(dhbq)$_4$]$^{8+}$ ([**2**]$^{8+}$) and [$Ru_8(\eta^6$-$C_6Me_6)_8$(tpp-$H_2)_2$(dhbq)$_4$]$^{8+}$ ([**3**]$^{8+}$). These octanuclear cations have been isolated as their triflate salts and characterised by mass spectrometry, NMR and IR spectroscopy. The molecular structure of these systems was deduced by one-dimensional and two-dimensional NMR experiments (ROESY, COSY, HSQC).

Keywords: Bridging ligands Arene ligands Ruthenium Supramolecular chemistry Cage compounds

Organometallic half-sandwich complexes of Ru(II), Rh(III) and Ir(III) are becoming more and more popular as versatile building blocks in supramolecular chemistry. The lability of the ligands opposite to the inert η^6-arene ligand can generate a pre-organised arrangement that allows the controlled formation of supramolecular assemblies. These three facial coordination sites have been extensively exploited to build up rectangles, macrocycles and cages [1–9].

Recently we used arene ruthenium complexes as building blocks for the assembly of a series of cationic triangular metallo-prisms containing bridging chloro [10], oxalato [11] and 2,5-dihydroxy-1,4-benzoquinonato [12] ligands connected by 2,4,6-tri(pyridyl)-1,3,5-triazine subunits. Herein we report the synthesis and characterisation of three rectangular metallo-prismatic cations incorporating arene ruthenium building blocks (arene = C_6H_5Me, p-$Pr^iC_6H_4Me$, C_6Me_6), bridged by 2,5-dihydroxy-1,4-benzoquinonato (dhbq) ligands, and connected by 5,10,15,20-tetra(4-pyridyl)porphyrin (tpp-H_2) tetrapodal ligands.

The dinuclear arene ruthenium complexes [Ru(η^6-arene)Cl_2]$_2$ (arene = C_6H_5Me, p-$Pr^iC_6H_4Me$, C_6Me_6) react in methanol with 2,5-dihydroxy-1,4-benzoquinone (dhbq-H_2) to form in good yield the dinuclear complexes [$Ru_2(\eta^6$-$C_6H_5Me)_2$(dhbq)Cl_2] [13], [Ru_2-(η^6-p-$Pr^iC_6H_4Me)_2$(dhbq)Cl_2] [12a] and [$Ru_2(\eta^6$-$C_6Me_6)_2$(dhbq)-Cl_2] [12c], respectively. Addition of silver triflate to these dinuclear clips in the presence of 5,10,15,20-tetra(4-pyridyl)porphyrin (tpp-H_2) leads to the connection of two tetradentate panels, affording

the octanuclear metallo-prismatic cations [$Ru_8(\eta^6$-$C_6H_5Me)_8$(tpp-$H_2)_2$(dhbq)$_4$]$^{8+}$ ([**1**]$^{8+}$), [$Ru_8(\eta^6$-p-$Pr^iC_6H_4Me)_8$(tpp-$H_2)_2$(dhbq)$_4$]$^{8+}$ ([**2**]$^{8+}$) and [$Ru_8(\eta^6$-$C_6Me_6)_8$(tpp-$H_2)_2$(dhbq)$_4$]$^{8+}$ ([**3**]$^{8+}$) in good yield ($\approx$80%), see Scheme 1. These rectangular prismatic cations are isolated as their trifluoromethanesulfonate salt [14].

The ^{1}H NMR spectra of **1, 2** and **3** display a similar signal pattern for the tpp-H_2 protons. Interestingly, diastereotopic protons are observed upon formation of the cationic cages, suggesting a tilt of the bi-metallic clips, thus introducing helical-type chirality [15]. A similar chiral conformation was observed in the oxalato-bridged analogous cage [$Ru_8(\eta^6$-p-$Pr^iC_6H_4Me)_8$(tpp-$H_2)_2(C_2O_4)_4$]$^{8+}$, for which a racemic mixture of two helical isomers was found in the crystal [16]. Surprisingly, in this oxalato-bridged analogue, the NH signal of the tpp-H_2 panels is found unchanged, as compared to free tpp-H_2 at $\delta = -3.1$ ppm, while in the cage molecules **1–3** this signal is strongly shifted upfield to $\delta \approx -7.0$ ppm. Moreover, in the oxalato-bridged analogue, the CH and CH_3 signals of the p-cymene ligands are superimposed at $\delta = 3.35$ ppm, while in **2** the two signals are well separated at $\delta = 3.13$ (CH) and 2.43 (CH_3), respectively.

Multiple one-dimensional and two-dimensional NMR experiments (ROESY, COSY, HSQC) allow the complete assignment of the proton signals of the cages **1–3**. Fig. 1 shows the two-dimensional ^{1}H COSY spectrum of the pyridyl and pyrrole region of the tpp-H_2 panels in **2**. Strong cross-peaks attributed to ^3J H–H coupling together with weak cross-peaks for ^4J coupling constant allow the assignment of two distinct series of pyridyl and pyrrole protons, identified as H and H′, respectively. The assignment is further confirmed by one-dimensional ^{1}H ROESY experiments in which strong cross-peaks are observed between H_q (dhbq protons)

* Corresponding author. Tel.: +41 32 718 24 99; fax: +41 32 718 25 11.
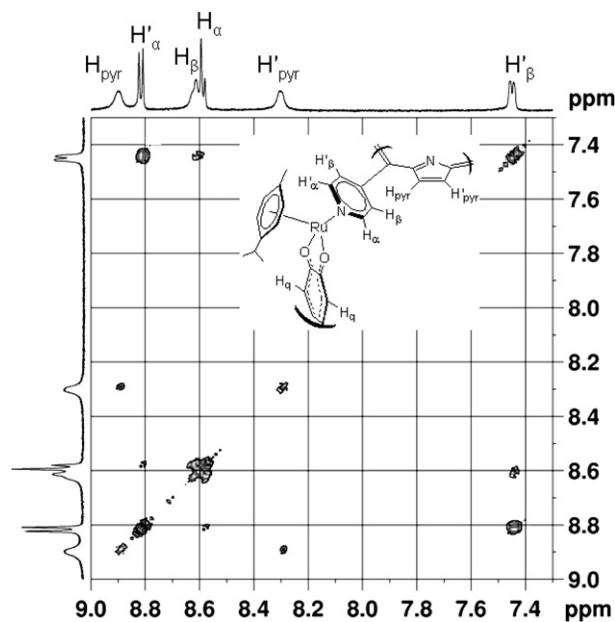*E-mail address:* bruno.therrien@unine.ch (B. Therrien).
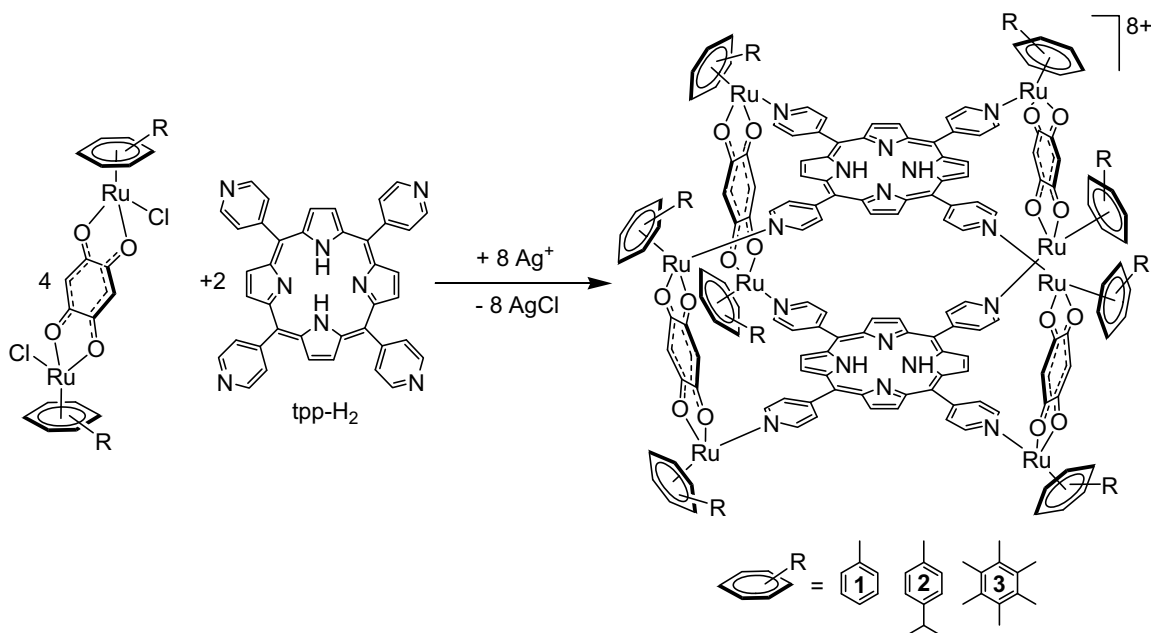
Scheme 1.

Fig. 1. ^{1}H COSY NMR spectrum of cation **2** in CD$_3$CN, showing the pyridyl and pyrrole region of the tpp-H$_2$ panels.

and the two diastereotopic H$_\alpha$ of the unsymmetrical pyridyl groups (H$_\alpha$ and H'_α) [17].

The infrared spectra of **1–3** are dominated by absorptions of the 5,10,15,20-tetra(4-pyridyl)porphyrin (tpp-H$_2$) and 2,5-dihydroxy-1,4-benzoquinonato (dhbq) ligands [19]. In addition to the tpp-H$_2$ and dhbq bands, strong absorptions attributed to the triflate anions are observed in the infrared spectra of [**1**][CF$_3$SO$_3$]$_8$, [**2**][CF$_3$SO$_3$]$_8$ and [**3**][CF$_3$SO$_3$]$_8$ [1260(s), 1031(s), 638(s) cm^{-1}]

[20]. Under conditions of electrospray mass spectrometry, the cages **1–3** show a remarkable stability. The ESI-MS spectra of **1–3** show peaks corresponding to [**1** + (CF$_3$SO$_3$)$_4$]$^{4+}$, [**2** + (CF$_3$SO$_3$)$_4$]$^{4+}$ and [**3** + (CF$_3$SO$_3$)$_4$]$^{4+}$ at m/z 983.0, 1067.3 and 1123.3, respectively [21]. These peaks can be assigned unambiguously on the basis of their characteristic Ru$_8$ isotope pattern. Furthermore, in the ESI-MS spectra of **1** and **2**, the second major peak corresponding to [**1** + (CF$_3$SO$_3$)$_5$]$^{3+}$ and [**2** + (CF$_3$SO$_3$)$_5$]$^{3+}$ is observed at m/z 1359.3 and 1472.5, respectively. Fig. 2 shows the ESI-MS spectrum of [**1**][CF$_3$SO$_3$]$_8$ in acetonitrile.

It is well known that in coordinating solvents ligand exchange can occur with arene ruthenium complexes [10]. In order to examine the stability of the rectangular metallo-prism **2** in solution, we recorded the ^{1}H NMR spectra in various deuterated solvents {CD$_2$Cl$_2$, (CD$_3$)$_2$CO, CD$_3$CN, (CD$_3$)$_2$SO} with different coordinating ability. At room temperature and even elevated temperature, ^{1}H NMR experiments for **2** in dichloromethane-d_2, acetone-d_6 and acetonitrile-d_3 showed no signal changes which could indicate the cleavage of the hydroxyquinonato bridges or the presence of free tpp-H$_2$ molecules. However, in dimethylsulfoxide-d_6 at 40 °C, compound [**2**][CF$_3$SO$_3$]$_8$ shows an additional new set of signals clearly attributed to the different components of the cage after decomplexation: doublets at 9.0 ppm and 8.2 ppm corresponding to H$_\alpha$ and H$_\beta$ of the uncoordinated tpp-H$_2$ pyridyl protons as well as a singlet at 8.9 ppm for the pyrrolyl protons; the NH signal at −7.0 ppm being replaced by a new singlet at −3.0 ppm. The decomplexation is complete and irreversible at 60 °C, as shown by ^{1}H NMR.

In conclusion, we have shown a simple and straightforward synthesis of hydroxyquinonato-bridged arene ruthenium rectangular metallo-prisms using tetradentate porphyrin panels. The organometallic boxes **1–3** possess helical chirality, as demonstrated by NMR spectroscopy. These data are in agreement with the analogous compound [Ru$_8$(η^6-p-Pr^{i}C$_6$H$_4$Me)$_8$(tpp-H$_2$)$_2$(C$_2$O$_4$)$_4$][CF$_3$SO$_3$]$_8$, for which a chiral deformed cubic structure was confirmed by single-crystal X-ray structure analysis [16].
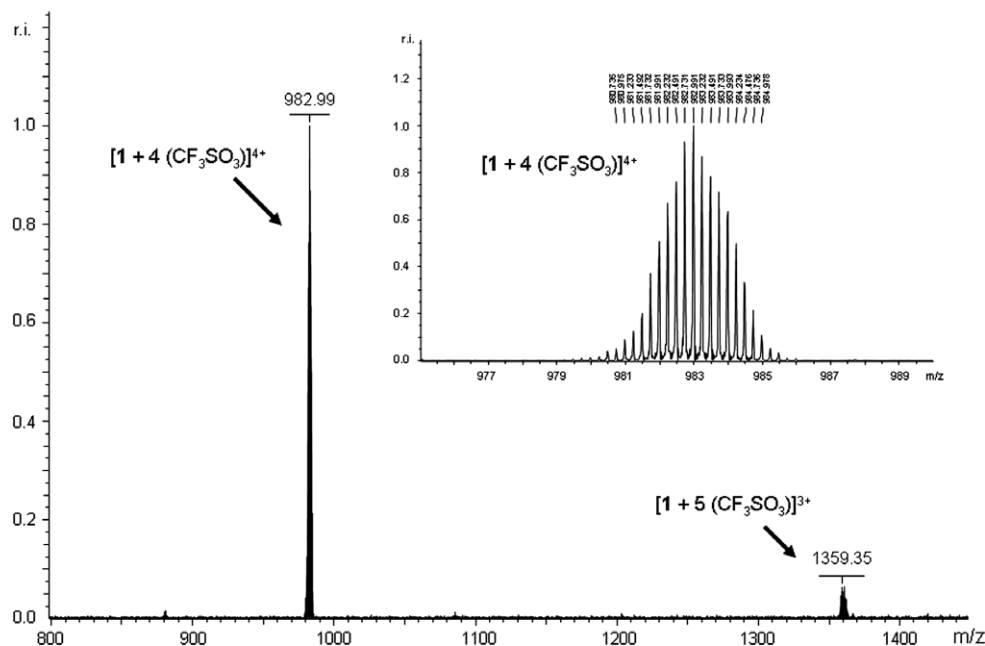
Fig. 2. ESI-MS of [**1**][CF$_3$SO$_3$]$_8$.

References

[1] R.H. Fish, Bioorganometallics, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006. p. 321 and references therein.
[2] [a] H. Yan, G. Süss-Fink, A. Neels, H. Stoeckli-Evans, J. Chem. Soc.; Dalton Trans. (1997) 4345;
[b] P. Govindaswamy, D. Linder, J. Lacour, G. Süss-Fink, B. Therrien, Dalton Trans. (2007) 4457;
[c] P. Govindaswamy, G. Süss-Fink, B. Therrien, Inorg. Chem. Commun. 10 (2007) 1489.
[3] [a] S. Korn, W.S. Sheldrick, J. Chem. Soc.; Dalton Trans. (1997) 2191;
[b] S. Korn, W.S. Sheldrick, Inorg. Chim. Acta 254 (1997) 85;
[c] P. Annen, S. Schildberg, W.S. Sheldrick, Inorg. Chim. Acta 307 (2000) 115.
[4] [a] K. Severin, Chem. Commun. (2006) 3859. and references therein;
[b] C. Olivier, Z. Grote, E. Solari, R. Scopelliti, K. Severin, Chem. Commun. (2007) 4000;
[c] Z. Grote, H.-D. Wizemann, R. Scopelliti, K. Severin, Z. Anorg. Allg. Chem. 633 (2007) 858;
[d] Z. Grote, R. Scopelliti, K. Severin, Eur. J. Inorg. Chem. (2007) 694;
[e] C. Olivier, E. Solari, R. Scopelliti, K. Severin, Inorg. Chem. 47 (2008) 4454.
[5] [a] H. Suzuki, N. Tajima, K. Tatsumi, Y. Yamamoto, Chem. Commun. (2000) 1801;
[b] Y. Yamamoto, H. Suzuki, N. Tajima, K. Tatsumi, Chem. Eur. J. 8 (2002) 372.
[6] [a] K. Yamanari, S. Yamamoto, R. Ito, Y. Kushi, A. Fuyuhiro, N. Kubota, T. Fukuo, R. Arakawa, Angew. Chem. Int. Ed. 40 (2001) 2268;
[b] K. Yamanari, R. Ito, S. Yamamoto, T. Konno, A. Fuyuhiro, K. Fujioka, R. Arakawa, Inorg. Chem. 41 (2002) 6824.
[7] J.L. Boyer, M.L. Kuhlman, T.B. Rauchfuss, Acc. Chem. Res. 40 (2007) 233. and references therein.
[8] W.S. Han, S.W. Lee, Dalton Trans. (2004) 1656.
[9] [a] Y.-F. Han, Y.-J. Lin, W.-G. Jia, L.-H. Weng, G.-X. Jin, Organometallics 26 (2007) 5848;
[b] Y.-F. Han, W.-G. Jia, Y.-J. Lin, G.-X. Jin, J. Organomet. Chem. 693 (2008) 546;
[c] Y.-F. Han, Y.-B. Huang, Y.-J. Lin, G.-X. Jin, Organometallics 27 (2008) 961;
[d] Y.-F. Han, Y.-J. Lin, W.-G. Jia, G.-L. Wang, G.-X. Jin, Chem. Commun. (2008) 1807.
[10] P. Govindaswamy, G. Süss-Fink, B. Therrien, Organometallics 26 (2007) 915.
[11] P. Govindaswamy, D. Linder, J. Lacour, G. Süss-Fink, B. Therrien, Chem. Commun. (2006) 4691.
[12] [a] B. Therrien, G. Süss-Fink, P. Govindaswamy, A.K. Renfrew, P.J. Dyson, Angew. Chem. Int. Ed. Engl. 47 (2008) 3773;
[b] P. Govindaswamy, J. Furrer, G. Süss-Fink, B. Therrien, Z. Anorg. Allg. Chem. 634 (2008) 1349;
[c] J. Mattsson, P. Govindaswamy, J. Furrer, Y. Sei, K. Yamaguchi, G. Süss-Fink, B. Therrien, Organometallics (2008), doi:10.1021/om800419s.
[13] [Ru$_2$(η^6-C$_6$H$_5$Me)$_2$(dhbq)Cl$_2$]: A mixture of [Ru(η^6-C$_6$H$_5$Me)$_2$Cl$_2$]$_2$ (500 mg, 0.95 mmol) and 2,5-dihydroxy-1,4-benzoquinone (133 mg, 0.95 mmol) in MeOH (100 mL) is stirred at room temperature for 2 h, then filtered. The blood-red precipitate is filtered, washed with diethyl ether, and dried under vacuum. Yield: 452 mg (80 %). IR (cm^{-1}): 3054 (w, CH$_{aryl}$), 1506 (s, C=O), 1269 (s, CH$_3$). ^{1}H NMR (400 MHz, (CD$_3$)$_2$SO): δ (ppm) = 7.20 (m, 2H, H$_q$), 6.14 (m, 2H, H$_{ar}$), 5.70 (m, 3H, H$_{ar}$), 2.13 (s, 6H, CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, (CD$_3$)$_2$SO): δ (ppm) = 175.5 (CO), 175.2 (CO), 128.7 (CH$_{ar}$), 95.5 (CC$_q$), 89.4 (CH$_{ar}$), 84.8 (CH$_{ar}$), 82.2 (CH$_{ar}$), 16.1 (CH$_3$). Elemental Analysis (%): Calc. for C$_{20}$H$_{18}$Cl$_2$O$_4$Ru$_2$: C, 40.34; H, 3.02; Found: C, 40.57; H, 3.32.
[14] [Ru$_8$(η^6-arene)$_8$(tpp-H$_2$)$_2$(dhbq)$_4$][CF$_3$SO$_3$]$_8$: A mixture of Ag(O$_3$SCF$_3$) (165 mg, 0.64 mmol) and [Ru$_2$(η^6-arene)$_2$(dhbq)Cl$_2$] (arene = C$_6$H$_5$Me, 191 mg, 0.32 mmol; p-Pr^{i}C$_6$H$_4$Me, 218 mg, 0.32 mmol; C$_6$Me$_6$, 235 mg, 0.32 mmol) in CH$_2$Cl$_2$ (80 mL) is stirred at room temperature for 3 h, then filtered. To the red filtrate, tpp-H$_2$ (99 mg, 0.16 mmol) is added. The solution is stirred for 15 h, and then the solvent removed under vacuum. The residue is dissolved in CH$_2$Cl$_2$ (3 mL), and diethyl ether is added, and the mixture stand overnight, to precipitate the purple solid. [**1**][CF$_3$SO$_3$]$_8$: Yield: 300 mg, (83 %). IR (cm^{-1}): 3470 (m, NH), 3075 (w, CH$_{aryl}$), 1520 (s, C=O), 1260 (s, CF$_3$). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) = 8.87 (m, 16H, H$_{pyr}$ + H$'_\alpha$), 8.69 (m, 16H, H$_\alpha$ + H$_\beta$), 8.32 (m, 8H, H$'_{pyr}$), 7.45 (d, 8H, H$'_\beta$), 6.35 (m, 16H, H$_q$ + H$_{ar}$), 6.14 (m, 16H, H$_{ar}$), 5.97 (m, 16H, H$_{ar}$), 2.48 (s, 24H, CH$_3$), −6.94 (s, 4H, NH). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) = 184.3 (CO), 183.9 (CO), 152.6 (CH$'_\alpha$), 151.1 (CH$_\alpha$), 132.6 (CH$'_\beta$), 131.5 (CH$_\beta$), 123.0 (C$_{pyr}$), 120.1 (C$_{pyr}$), 101.8 (CH$_q$), 89.4 (CCH$_3$), 79.7 (CH$_{ar}$), 79.1 (CH$_{ar}$), 76.7 (CH$_{ar}$), 18.2 (CH$_3$). ESI-MS: m/z 983.0 [**1** + (CF$_3$SO$_3$)$_4$]$^{4+}$; 1359.3 [**1** + (CF$_3$SO$_3$)$_5$]$^{3+}$. Elemental Analysis (%): Calc. for C$_{168}$H$_{124}$F$_{24}$Ru$_8$N$_{16}$O$_{40}$S$_8$: C, 44.52; H, 2.74; N, 4.95; Found: C, 43.98; H, 2.33; N, 4.65.[**2**][CF$_3$SO$_3$]$_8$: Yield: 287 mg (74 %); IR (cm^{-1}): 3450 (m, NH), 3070 (w, CH$_{aryl}$), 1520 (s, C=O), 1260 (s, CF$_3$). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) = 8.89 (d, 8H, H$_{pyr}$), 8.81 (d, 8H, H$'_\alpha$), 8.59 (m, 16H, H$_\alpha$ + H$_\beta$), 8.30 (d, 8H, H$'_{pyr}$), 7.45 (d, 8H, H$'_\beta$), 6.20 (m, 16H, H$_{ar}$), 6.17 (s, 8H, H$_q$), 6.03 (m, 16H, H$_{ar}$), 3.13 (sept, 8H, CH(CH$_3$)$_2$), 2.43 (s, 24H, CH$_3$), 1.54 (m, 48H, CH(CH$_3$)$_2$), −6.96 (s, 4H, NH). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) = 184.1 (CO), 183.6 (CO), 152.4 (CH$'_\alpha$), 151.2 (CH$_\alpha$), 133.0 (CH$'_\beta$), 131.5 (CH$_\beta$), 122.8 (C$_{pyr}$), 119.6 (C$_{pyr}$), 101.9 (CH$_q$), 104.1 (CCH(CH$_3$)$_2$), 98.8 (CCH$_3$), 83.8 (CH$_{ar}$), 83.3 (CH$_{ar}$), 82.3 (CH$_{ar}$), 82.2 (CH$_{ar}$), 31.3 (CH(CH$_3$)$_2$), 21.5 (CH(CH$_3$)$_2$), 21.9 (CH(CH$_3$)$_2$), 17.5 (CH$_3$). ESI-MS: m/z 1067.3 [**2** + (CF$_3$SO$_3$)$_4$]$^{4+}$; 1472.5 [**2** + (CF$_3$SO$_3$)$_5$]$^{3+}$. Elemental Analysis (%): Calc. for C$_{192}$H$_{172}$F$_{24}$Ru$_8$N$_{16}$O$_{40}$S$_8$: C, 47.37; H, 3.54; N, 4.60; Found: C, 46.87; H, 3.11; N, 4.43. [**3**][CF$_3$SO$_3$]$_8$: Yield: 346 mg, (85 %). IR (cm^{-1}): 3430 (m, NH), 3080 (w, CH$_{aryl}$), 1520 (s, C=O), 1260 (s, CF$_3$). ^{1}H NMR (400 MHz, CD$_3$CN): δ (ppm) = 8.88 (d, 8H, H$_{pyr}$), 8.56 (m, 24H, H$'_\alpha$ + H$_\alpha$ + H$_\beta$), 8.20 (d, 8H, H$'_{pyr}$), 7.48 (d, 8H, H$'_\beta$), 6.08 (s, 8H, H$_q$), 2.52 (s, 144H, CH$_3$), −6.96 (s, 4H, NH). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ (ppm) = 184.8 (CO), 184.2 (CO), 152.2 (CH$'_\alpha$), 151.6 (CH$_\alpha$), 134.7 (CH$'_\beta$), 132.4 (CH$_\beta$), 123.8 (C$_{pyr}$), 120.6 (C$_{pyr}$), 102.9 (CH$_q$), 95.5 (CCH$_3$), 16.1 (CH$_3$). ESI-MS: m/z 1123.2 [**3** + (CF$_3$SO$_3$)$_4$]$^{4+}$. Elemental Analysis (%): Calc. for C$_{208}$H$_{204}$F$_{24}$Ru$_8$N$_{16}$O$_{40}$S$_8$: C, 49.06; H, 4.01; N, 4.40; Found: C, 48.67; H, 4.32; N, 4.51.
[15] [a] D.L. Caulder, K.N. Raymond, Acc. Chem. Res. 32 (1999) 975;
[b] D.C. Caskey, T. Yamamoto, C. Addicott, R.K. Shoemaker, J. Vacek, A.M.

Hawkridge, D.C. Muddiman, G.S. Kottas, J. Michl, P.J. Stang, J. Am. Chem. Soc. 130 (2008) 7620;

[c] B. Therrien, G. Süss-Fink, Chimia 62 (2008) 514.

[16] Y.-F. Han, Y.-J. Lin, L.-H. Weng, H. Berke, G.-X. Jin, Chem. Commun. (2008) 350.

[17] The one-dimensional ^{1}H ROESY experiments have been recorded using the MP-ROESY mixing sequence, which has shown its effectiveness with regard to TOCSY transfer suppression and cross-relaxation peak intensity enhancement [18].

[18] T.-L. Hwang, A.J. Shaka, J. Magn. Reson. 135 (1998) 280.

[19] Infrared spectra are recorded as KBr pellets on a Perkin-Elmer FTIR 1720-X spectrometer.

[20] D.H. Johnston, D.F. Shriver, Inorg. Chem. 32 (1993) 1045.

[21] Electrospray mass spectra were recorded at the University of Fribourg (Switzerland) within the group of Prof. Titus Jenny.