Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information

Supramolecular squares of dirhodium(II) tetracarboxylate: Combining carboxylate-exchange and metal-ligand coordination for self-assembly**

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1. Experimental details

- Synthesis

- UV Spectrophotometric Titrations

- Cyclic Voltammetry Studies

- Crystallography

2. Figures

1. Experimental details

- *Synthesis*

All chemicals were obtained from Aldrich and Strem and were used without further purification. Silica gel (70–230 mesh) for flash-column chromatography was purchased from Aldrich. Preparative TLC plates (Silica Gel GF, 1000 micron, 20×20 cm) were purchased from Analtech. All ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) at room temperature. Chemical shifts are given with respect to tetramethylsilane. High resolution mass spectra were obtained on a QSTAR XL (AB/MSD Sciex) instrument on an ESI positive mode by the Mass Spectrometry Laboratory, University of Geneva. MALDI-TOF mass spectra were carried out by Mass Spectrometry Laboratory, University of Geneva. Microanalyses were performed at the Microchemical Laboratory of the University of Geneva.

Compound **1**:

Dirhodium tetraacetate (0.5 g, 1.13 mmol) and 3,5-di-*tert*-butylbenzoic acid (2.12 g, 9.05 mmol) in toluene (40 mL) was refluxed overnight with a Dean-Stark apparatus. The solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography using $CHCl_3$ as eluant to afford compound **1** as a green solid. The compound **1** was highly soluble in a range of common organic solvents including $CHCl_3$, CH_2Cl_2, benzene and toluene, as well as coordinating solvents such as DMF, THF and acetone. Yield: 1.29 g (quantitative). ^{1}H NMR ($CDCl_3$): δ 7.81 (d, *J*= 1.9 Hz, 8H, Ar*H*), 7.47 (t, *J*= 1.9 Hz, 4H, Ar*H*), 1.28 (s, C(C*H*$_3$)$_3$, 72H). MALDI-TOF calcd. 1138.4, found 1138.4. λ_{max} ($CHCl_3$)/nm 437, 619 (log [ε/$M^{-1}cm^{-1}$] 176.4, 308.8). Anal. calc. for $C_{60}H_{84}O_8Rh_2$: C 63.26; H 7.43%. Found C 63.26; H 7.60%.

Compound **2**:

To dirhodium tetracarboxylate **1** (0.1 g, 0.088 mmol) in toluene (10 mL) was added isonicotinic acid (0.011 g, 0.088 mmol). The reaction was heated under reflux overnight and the solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography using $CHCl_3$ as eluent to afford the product **2** as a green solid. Yield: 0.075 g (83 %). Crystals of **2** suitable for X-ray crystallographic analysis were obtained by slow diffusion of toluene into a

chloroform solution of the complex. ^{1}H NMR ($CDCl_3$): δ 9.48 (d, *J*= 6.4 Hz, 2H, Py*H*), 8.40 (d, *J*= 6.4 Hz, 2H, Py*H*), 7.79 (d, *J*= 1.9 Hz, 2H, Ar*H*), 7.70 (d, *J*= 1.9 Hz, 4H, Ar*H*), 7.46 (t, *J*= 1.9 Hz, 1H, Ar*H*), 7.41 (t, *J*= 1.9 Hz, 2H, Ar*H*), 1.28 (s, 18H, C(CH_3)$_3$), 1.20 (s, 36H, C(CH_3)$_3$). MALDI-TOF calcd. 4109.20, found 4109.24. λ_{max} ($CHCl_3$)/nm 561 ([ε/$M^{-1}cm^{-1}$] 1398.6). Anal. calc. for $C_{204}H_{268}N_4O_{32}Rh_8$: C 59.59, H 6.57, N 1.36%. Found C 59.63, H 6.72, N 1.34%.

Compound **3**:

To dirhodium tetracarboxylate **1** (0.05 g, 0.044 mmol) in benzene (10 mL) was added 4-(pyridin-4-yl)benzoic acid (0.009 g, 0.044 mmol). The reaction was heated under reflux overnight and the solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography using $CHCl_3$ as eluent to afford the product **3** as a green solid. Yield: 0.019 g (39 %). ^{1}H NMR ($CDCl_3$): δ 9.54 (d, *J*= 6.4 Hz, 2H, Py*H*), 8.28 (d, *J*= 8.4 Hz, 2H, Ar*H*), 8.09 (d, *J*= 6.4 Hz, 2H, Py*H*), 7.85 (d, *J*= 8.4 Hz, 2H, Ar*H*), 7.81 (d, *J*= 1.9 Hz, 2H, Ar*H*), 7.78 (d, *J*= 1.9 Hz, 4H, Ar*H*), 7.46 (br s, 1H, Ar*H*), 7.42 (br s, 2H, Ar*H*), 1.29 (s, 18H, C(CH_3)$_3$), 1.24 (s, 36H, C(CH_3)$_3$). MALDI-TOF calcd. 4413.32, found 4416.02. λ_{max} ($CHCl_3$)/nm 562 ([ε/$M^{-1}cm^{-1}$] 1481.1). Anal. calc. for $C_{228}H_{284}N_4O_{32}Rh_8$: C 62.01, H 6.48, N 1.27%. Found C 61.61, H 6.62, N 1.20%.

Compound **4**:

Dirhodium tetracarboxylate **1** (0.05 g, 0.044 mmol) in $CHCl_3$ (5 mL) was added methyl isonicotinate (0.009 g, 0.044 mmol) and the reaction mixture was stirred for 5 mins. The solvent was removed under reduced pressure and the product **4** was dried under vacuum. Yield: 45 mg (Quantitative). ^{1}H NMR ($CDCl_3$): δ 9.65 (d, *J*= 6.4 Hz, 2H, Py*H*), 8.43 (d, *J*= 6.4 Hz, 2H, Py*H*), 7.74 (d, *J*= 1.9 Hz, 8H, Ar*H*), 7.42 (t, *J*= 1.9 Hz, 4H, Ar*H*), 4.15 (s, 3H, OCH_3), 1.26 (s, 72H, C(CH_3)$_3$); λ_{max} ($CHCl_3$)/nm 387, 564 ([ε/M^{-1} cm^{-1}] 2836.5, 400.2); MALDI-TOF calcd. 1275.5; found 1275.8; elemental analysis for $C_{67}H_{91}NO_{10}Rh_2$: calcd, C 63.05, H 7.19, N 1.10; found C 62.94, H 7.16, N 1.04.

Compound **5**:

Dirhodium tetracarboxylate **1** (0.05 g, 0.044 mmol) in $CHCl_3$ (5 mL) was added methyl 4-(pyridin-4-yl)benzoate (0.009 g, 0.044 mmol) and the reaction mixture was stirred for 5 mins. The solvent was removed under reduced pressure and the product **5** was dried under vacuum. Yield: 0.048 g (quantitative). ^{1}H NMR ($CDCl_3$): δ 9.58 (d, *J*= 6.4 Hz, 2H, Py*H*), 8.32 (d, *J*= 8.4 Hz, 2H, Py*H*), 8.10 (d, *J*= 6.4 Hz, 2H, Py*H*), 8.01 (d, *J*= 8.4 Hz, 2H, Py*H*), 7.77 (d, *J*= 1.9 Hz, 8H, Ar*H*), 7.43 (t, *J*= 1.9 Hz, 4H, Ar*H*), 4.03 (s, 3H, OCH_3), 1.27 (s, 72H, C(CH_3)$_3$). λ_{max} ($CHCl_3$)/nm 362, 570 ([ε/$M^{-1}cm^{-1}$] 4337.7, 413). MALDI-TOF calcd. 1351.5, found 1351.3; elemental analysis for $C_{73}H_{95}NO_{10}Rh_2$: C 64.83, H 7.08, N 1.04%. Found C 64.36, H 7.15, N 0.91%.

Scrambling reaction with 2,6-diphenylisonicotinic acid (see Figure S7)

Dirhodium tetracarboxylate **1** (0.05 g, 0.044 mmol) in toluene (5 mL) was added 2,6-diphenylisonicotinic acid (0.012 g, 0.044 mmol). The reaction mixture was refluxed overnight and the solvent was removed under vacuum. The reaction was purified by preparative TLC using CH_2Cl_2/hexane (2/1) as the eluent to afford five products.

Dirhodium tetra-(3,5-di-tert-butylbenzoate). **("A_4" product)** Yield: 0.009 g (18%). ^{1}H NMR ($CDCl_3$): δ 7.81 (d, *J*= 1.9 Hz, 8H, Ar*H*), 7.47 (t, *J*= 1.9 Hz, 4H, Ar*H*), 1.28 (s, C(CH_3)$_3$, 72H). HR ESI $[M+NH_4]^+$ calcd. 1156.4614, found 1156.4605. λ_{max} ($CHCl_3$)/nm 437, 619 (log [ε/$M^{-1}cm^{-1}$] 176.4, 308.8). Anal. calc. for $C_{60}H_{84}O_8Rh_2$: C 63.26; H 7.43%. Found C 63.26; H 7.60%.

Dirhodium tri-(3,5-di-tert-butylbenzoate)-mono-(2,6-diphenylisonicotinate). **("A_3B" product)** Yield: 0.013 g (25%). ^{1}H NMR ($CDCl_3$): δ 8.19 (s, 2H, Ar*H*), 8.16–8.11 (m, 4H, Ar*H*), 7.85–7.81 (m, 6H, Ar*H*), 7.52–7.38 (m, 9H, Ar*H*), 1.28 (s, 18H, C(CH_3)$_3$), 1.27 (s, 36H, C(CH_3)$_3$). HR ESI $[M+H]^+$ calcd. 1180.3675, found 1180.3641. λ_{max} ($CHCl_3$)/nm 609 ([ε/$M^{-1}cm^{-1}$] 322). Anal. calc. for $C_{63}H_{75}NO_8Rh_2$: C 64.12, H 6.41, N 1.19%. Found C 64.00, H 6.49, N 1.01%.

Dirhodium di-(3,5-di-tert-butylbenzoate)-di-(2,6-diphenylisonicotinate). **(Mixture of "A_2B_2" *cis*/*trans* products)** Yield: 0.010 g (20%). HR ESI $[M+H]^+$ calcd. 1221.3002, found 1221.3058. Anal. calc. for $C_{66}H_{66}N_2O_8Rh_2.2CH_3OH$: C 63.53, H 5.81, N 2.18%. Found C 63.86, H 5.66, N 2.48%.

Dirhodium mono-(3,5-di-tert-butylbenzoate)-tri-(2,6-diphenylisonicotinate). **("AB_3" product)** Yield: 0.002 g (4%). ^{1}H NMR ($CDCl_3$): δ 8.21 (s, 4H, Ar*H*), 8.20 (s, 2H, Ar*H*), 8.15–8.11 (m, 12H, Ar*H*), 7.87 (d, *J*= 1.9 Hz, 2H, Ar*H*), 7.52 (t, *J*= 1.9 Hz, 1H, Ar*H*), 7.50–7.36 (m, 18H, Ar*H*), 1.28 (s, 18H, C(CH_3)$_3$). HR ESI $[M+H]^+$ calcd. 1262.2328, found 1262.2453. λ_{max} ($CHCl_3$)/nm 600 ([ε/$M^{-1}cm^{-1}$] 314). Anal. calc. for $C_{69}H_{57}N_3O_8Rh_8$: C 65.67, H 4.55, N 3.33%. Found C 65.43, H 4.32, N 3.05%.

- UV Spectrophotometric Titrations

Monomer Titrations. Spectrophotometric titrations in the UV range were recorded in solution with a Perkin-Lambda 5 spectrophotometer interfaced to a PC and using a probe of 1.0 cm path length. Automated titrations were carried out at 25°C using a Metrohm burette with a 5 mL syringe and were performed by the addition of 0.1 mL aliquots of the respective ligand solution (5.0 mM) to the monomer solution (5.0 mL, 1.0 mM). The solvent used for all systems was chloroform. A total volume of 7.0 mL was added with UV spectra recorded after each addition between 440-700 nm at 1 nm intervals. The titration cell (20 mL) was stirred by a magnetic stirrer throughout the titration.

Tetramer Titrations. Spectrophotometric titrations in the UV range were recorded in solution with a Perkin-Lambda 5 spectrophotometer interfaced to a PC and using a probe of 1.0 cm path length. Automated titrations were carried out at 25°C using a Metrohm burette with a 5 mL syringe and were performed by the addition of 0.5 mL aliquots of the respective ligand solution (0.10 mM) to the tetramer solution (5.0 mL, 0.30 mM). The solvent used for all systems was chloroform. A total volume of 50.0 mL was added with UV spectra recorded after each addition between 440-700 nm at 1 nm intervals. The titration cell (20 mL) was stirred by a magnetic stirrer throughout the titration.

Data Treatment. The spectra obtained were analyzed using a non-linear least-squares method to fit an equilibrium model to the observed multi-wavelength data.[1, 2]

1 S. E. Norman, 'Chemical Process Analysis: Chemometrics; Instrument Control; Applications in Equilibrium and Kinetic Investigations', PhD thesis, University of Newcastle, Newcastle, Australia, 2008.

2 H. Gampp, M. Maeder, C. J. Meyer, and A. D. Zuberbühler, *Talanta*, 1985, **32**, 257.

- ***Cyclic Voltammetry Studies***

The electrochemical studies in 5 mL of CH_2Cl_2/NBu_4PF_6 (0.1 M) were performed with a 3-electrodes cell (Working electrode: vitreous C, Reference electrode: Ag, Counter electrode: Ag). The potential of the cell was controlled by an Epsilon (Bioanalytical Systems, Inc.) potentiostat monitored by a computer. Ferrocene was added at the end of each experiment to determine redox potential values. The redox couple Fc^+/Fc, in these conditions, presents a peak difference ΔE_p ($E_{pa} - E_{pc}$) of 75 mV. The redox potential of ferrocene was determined vs. SCE (0.40 V) in $MeCN/NBu_4PF_6$.

For the complexes studied, the linearity of the plot of anodic peak current i_{pa} depending on the square root of scan rate, $v^{1/2}$, indicates a diffusion-controlled process. For the same concentration (1 mM) at a given scan rate (0.1 V/s), the anodic peak intensities for small and large tetramers complexes are respectively 3 and 3.5 times higher than that observed for the parent monomer complex $[Rh_2(O_2C(tBu_2Ph))_4]$ (Figure S12). This result can be explained by taking into account both the number of electrons exchanged during the redox process (n = 4) and the diffusion coefficient of electroactive species.

The diffusion coefficient of compounds **1**–**3** were deduced from the Randles-Sevcik equation and linear regression. The results are in agreement with those obtained by ^1H DOSY NMR experiments in that the tetrameric derivatives have lower diffusion coefficients compared to the monomeric complex (Figure S13). In the case of the tetrameric species, the differences obtained with ^1H DOSY NMR experiments can be explained by slower electron transfer occurring during the redox process (low k_0) and/or the existence of weak communication between the dirhodium centers within the tetramer, thus reducing the intensity of real systems.

Table S1. UV-Vis and electrochemical data for compounds **1** to **5**.

Complex	λ_{max} (ε/$M^{-1}.cm^{-1}$)[a]	$E_{1/2}$/V *vs.* Fc (ΔE_p/mV)[b]
Compound **1**	619 (308.8)	0.78 (135)
Small tetramer **2**	561 (1398.6)	0.79 (215)
Large tetramer **3**	562 (1481.1)	0.69 (160)
Mono-adduct **4**	564 (400.2)	0.69 (125)
Mono-adduct **5**	570 (413)	0.66 (110)

[a] λ_{max} values for the $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition, solvent $CHCl_3$. [b] solvent CH_2Cl_2 with 0.1 M NBu_4PF_6, v = 0.1 $V.s^{-1}$, vitreous carbon working electrode.

- Crystallography

Crystal data for **1**, $C_{128.5}H_{192}Cl_{1.5}O_{20.19}Rh_4$, monoclinic, space group $P2_{1/n}$, T = 200(2) K, a = 18.0308(6) Å, b = 27.2458(7) Å, c = 28.0382(8) Å, α = 90°, β = 91.860(2)°, γ = 90°, V = 13766.9(7) $Å^3$, Z = 4, ρ = 1.218 $g.cm^{-3}$, reflections collected 117384, independent reflections 32925 (R_{int} = 0.0546), 1144 parameters, R_1 = 0.0724 for I > 2sigma(I) and wR_2 = 0.1973 for all data. For **2**, $C_{59}H_{78}NO_{9.5}Rh_2$, cubic, space group Ia-3d, T = 180(2) K, a = b = c =59.616(3) Å, α = β = γ = 90°, V = 211879(17) $Å^3$, Z = 96, ρ = 0.872 $g.cm^{-3}$, reflections collected 128659, independent reflections 8666 (R_{int} = 0.2164), 596 parameters, R_1 = 0.1141 for I > 2sigma(I) and wR_2 = 0.2877 for all data.

Comment on structure **1**. There are two rhodium dimers in the asymmetric unit. The methyl of the tert-butyl parts show important disorder and are refined isotropically. Several attempts to model this disorder anisotropically or with multiple moieties with partial occupancies didn't improve the convergence. The rhodium coordination sphere is filled with an ethanol molecule. Some parts of these solvent molecules show disorder (large anisotropic displacement parameters). Modeling this positional disorder with two partially occupied molecules didn't improve the refinement. The void between the two dimers is partially occupied by a water molecule. Hydrogen atoms of the water molecule were not located.

Comment on structure **2**. Due to the poor quality of crystals combined with huge unit cell, the quality of the data set is quite low. We had to perform the data collection with IP – crystal distance = 190mm and despite a long exposure time per image, intensities of reflexions at high angle are low. The resolution is then limited (> 1Å). One quarter of the tetramer is found in the asymmetric unit, with two distinct solvate toluene molecules each having occupancy fixed to 0.5. A water molecule was found in the difference Fourrier map with occupancy fixed to 0.5. The tert-butyl groups are all disordered (rotation axe). Disorder were modelled by splitting each Tert-butyl group over two sites (occupancies were refined and all of them converged near ~0.5) and therefore were refined isotropically. One methanol molecule completes the coordination sphere of the external rhodium atom (but we didn't refine or calculate the H atoms). There is no classical hydrogen bond found in the structure.

2. Figures

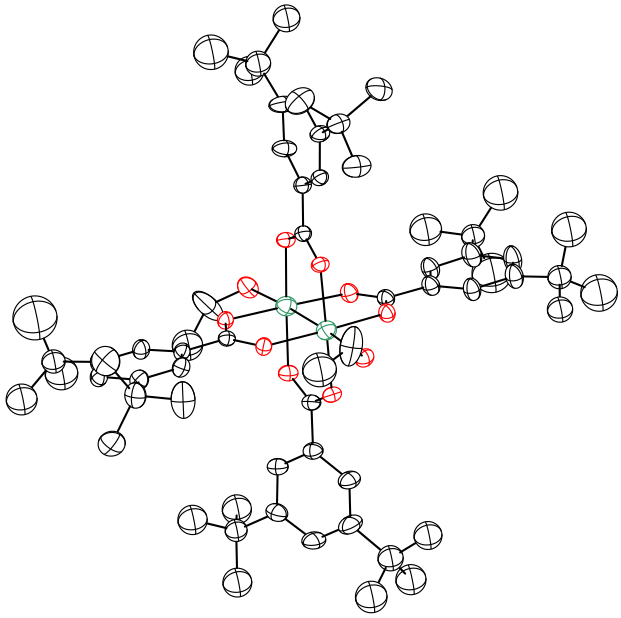


Figure S1. ORTEP representation (30 % probability) of dirhodium complex **1**. (Key: Rh green, O red, C black)

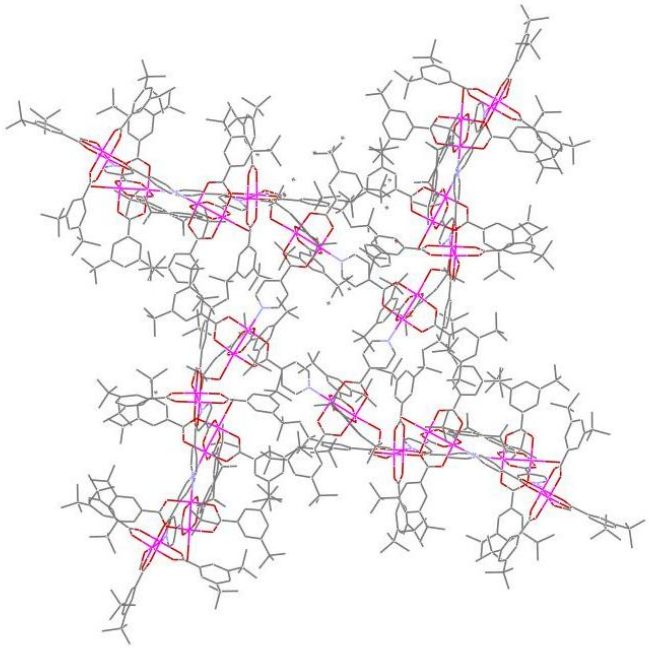


Figure S2. Crystal structure packing of the small tetramer **2**.

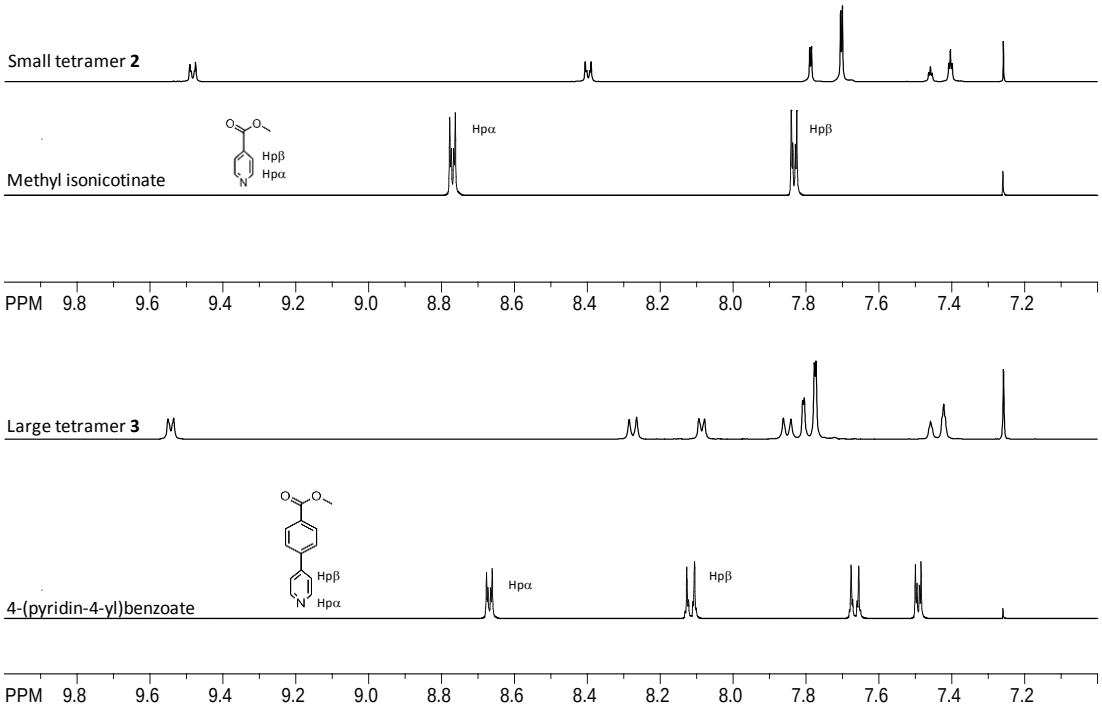


Figure S3. ^{1}H NMR spectra in $CDCl_3$ of small and large tetramers **2** and **3** compared with the free ligands methyl isonicotinate and 4-(pyridin-4-yl)benzoate.

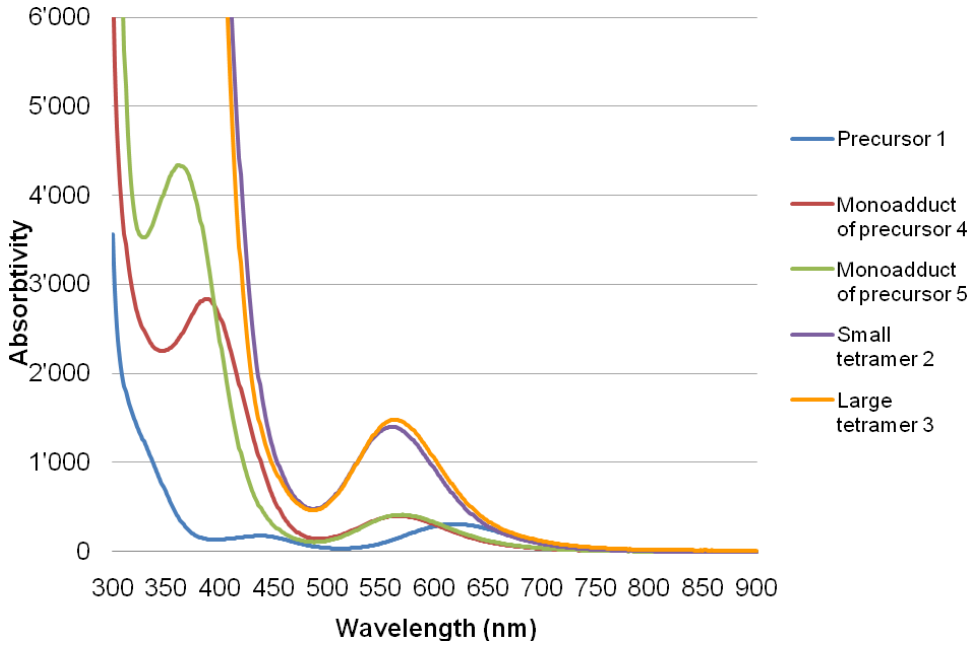


Figure S4. Electronic spectra of **1–5** showing the hypsochromic shift of the $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition band after axial coordination of pyridyl groups on one Rh atom.

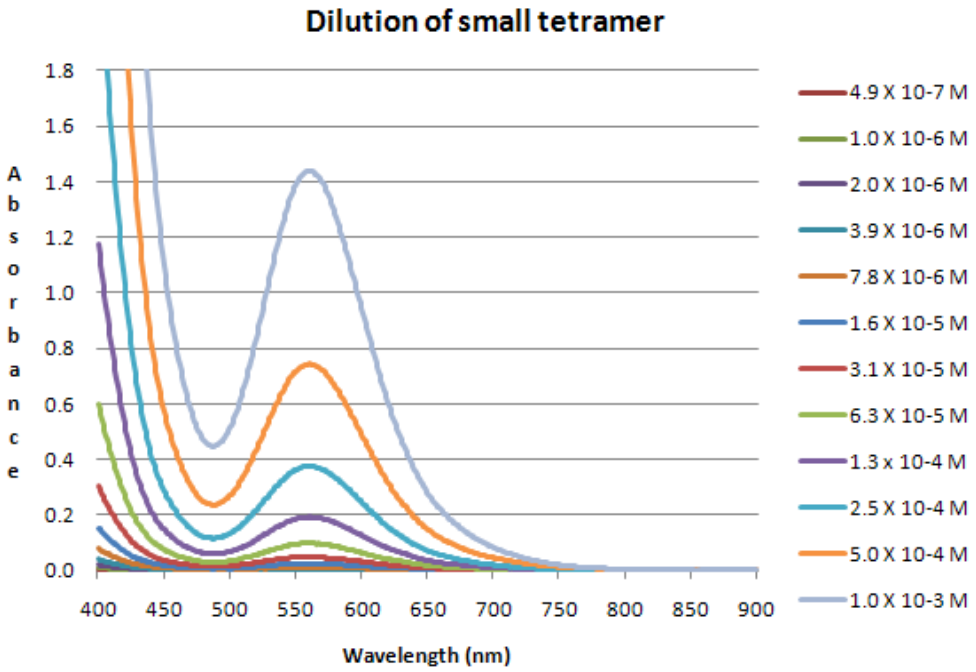


Figure S5. Dilution experiments on the small tetramer **2** carried out in $CHCl_3$. Concentration range from 1.0×10^{-3} M to 4.9×10^{-7} M.

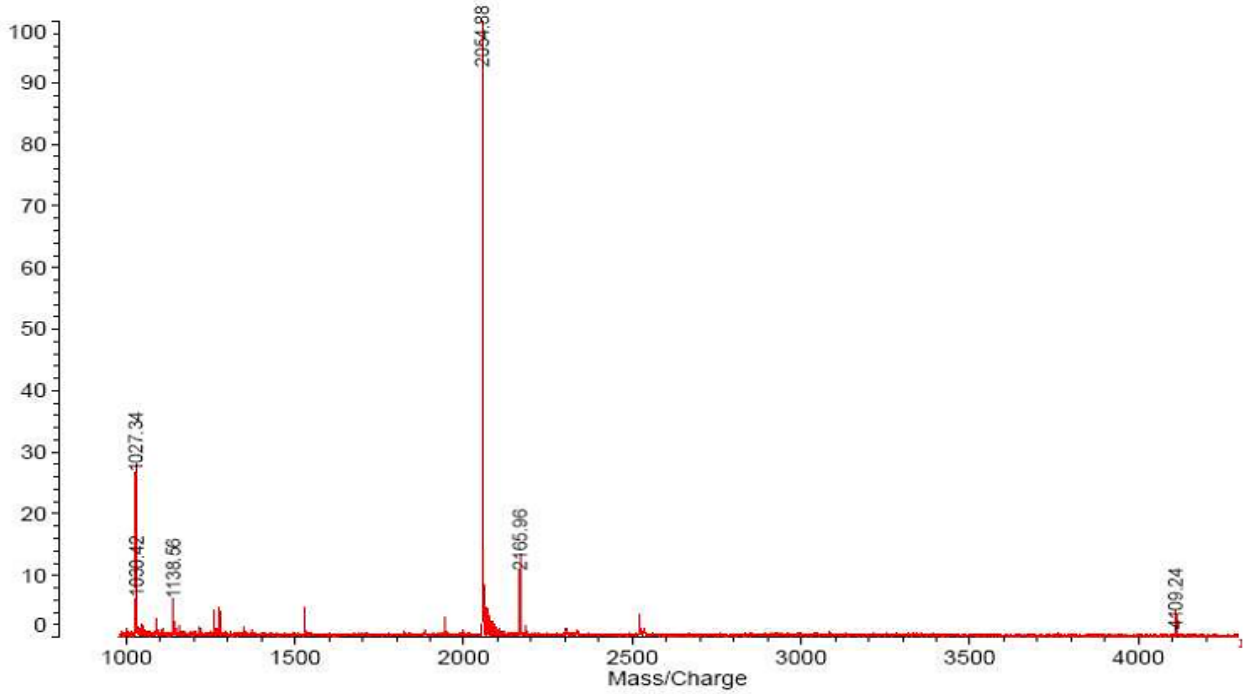


Figure S6. MALDI-TOF spectrum of the small tetramer **2**.

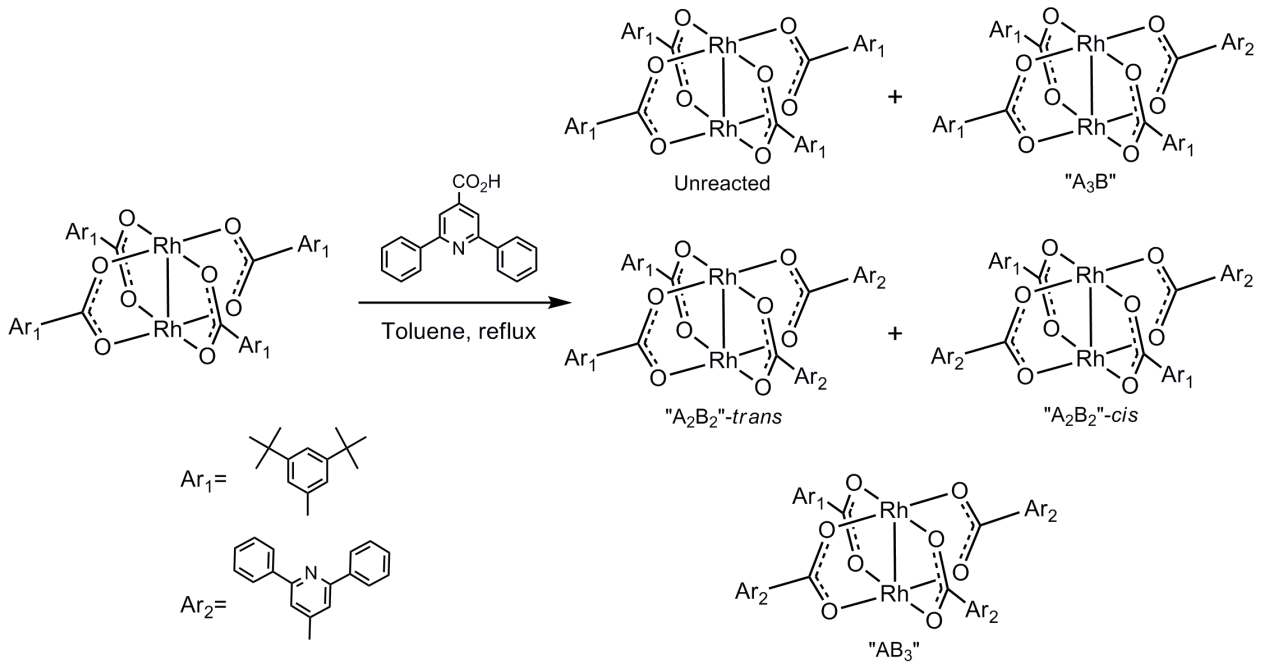


Figure S7. The scrambling reaction of compound **1** with 2,6-diphenylisonicotinic acid.

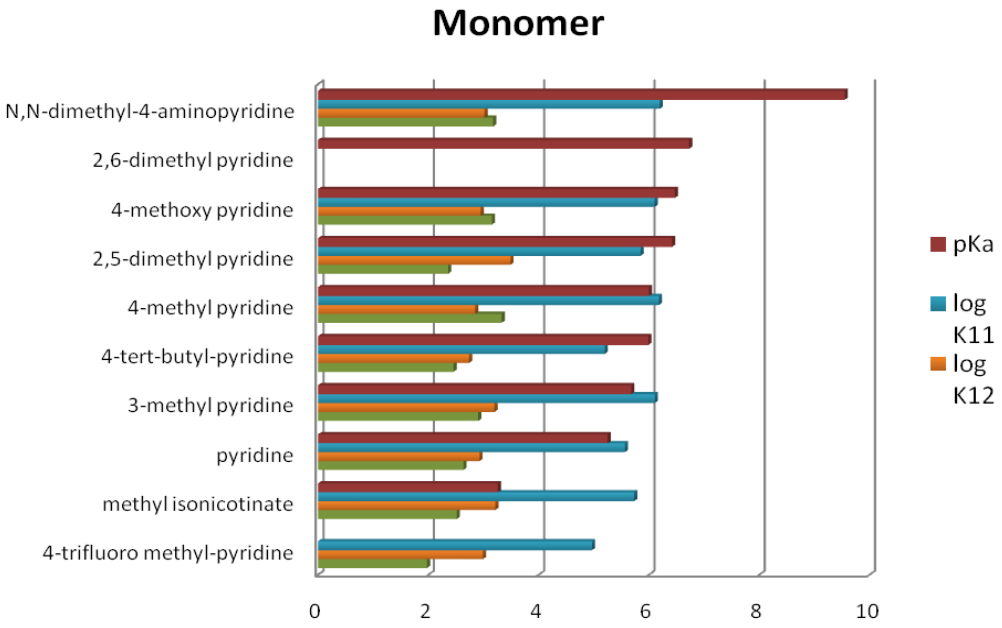


Figure S8. Spectrophotometric titrations in $CHCl_3$ of various linker molecules with compound **1**.

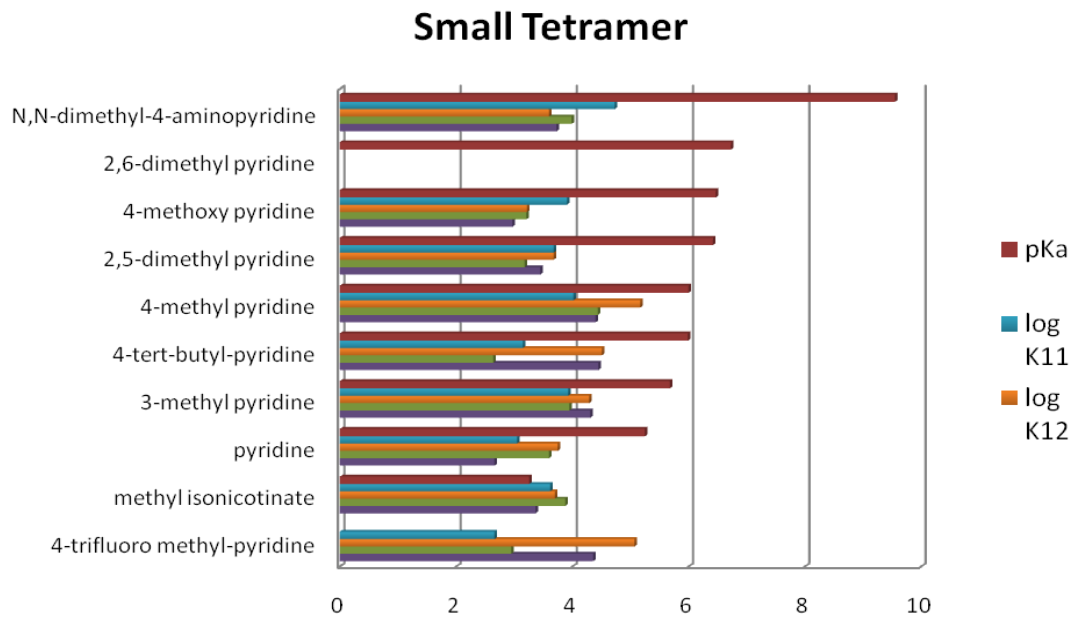


Figure S9. Spectrophotometric titrations in $CHCl_3$ of various linker molecules with small tetramer **2**.

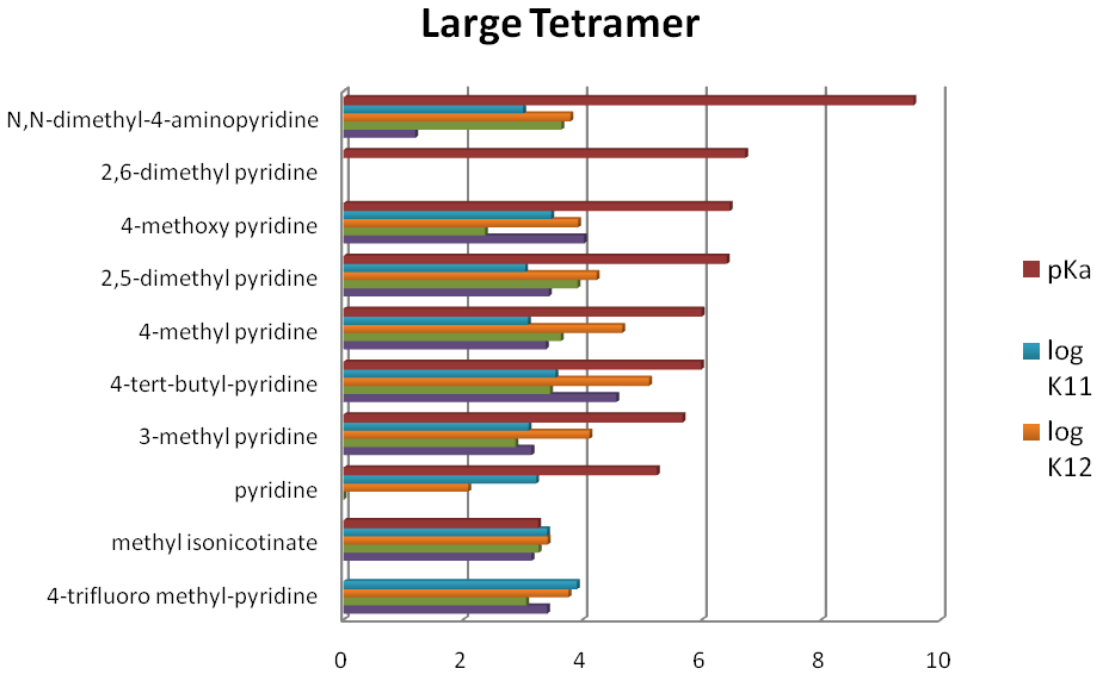


Figure S10. Spectrophotometric titrations in $CHCl_3$ of various linker molecules with large tetramer **3**.

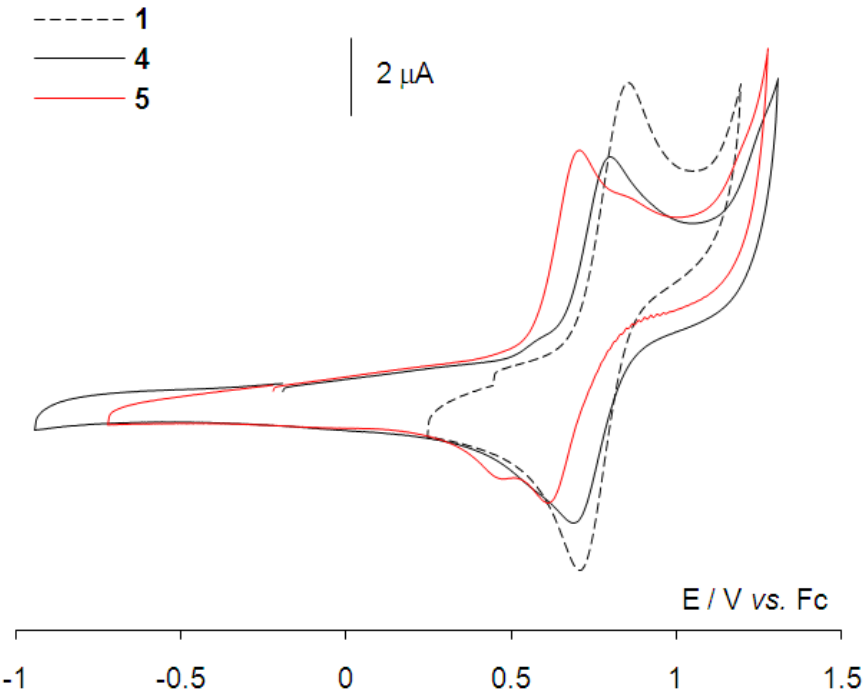


Figure S11. Cyclic voltammetries of monomer complexes **1**, **4** and **5**, 1mM in CH_2Cl_2 with 0.1 M NBu_4PF_6, v = 0.1 $V.s^{-1}$, at vitreous carbon electrode.

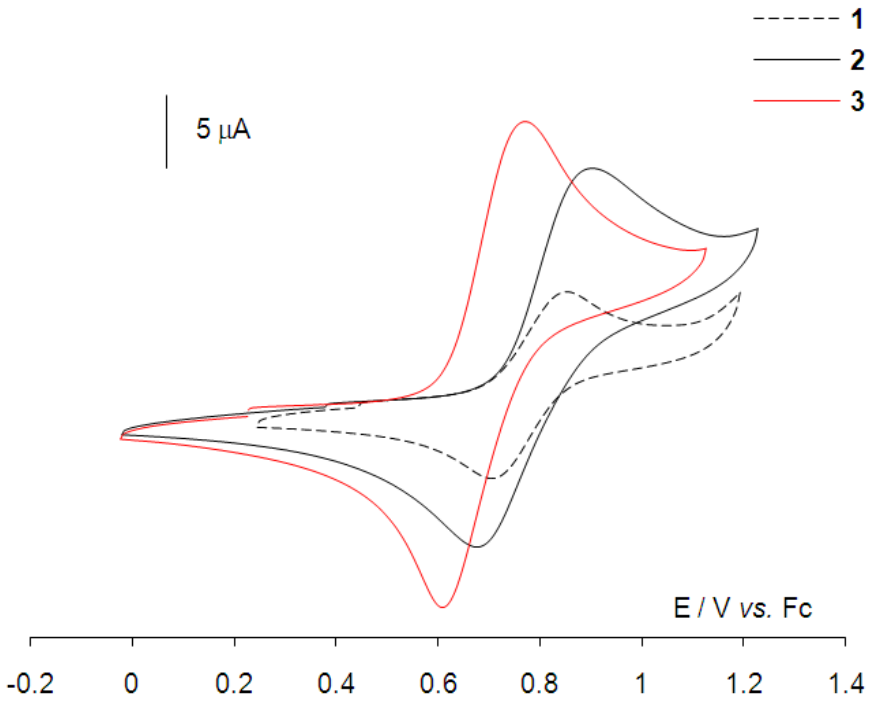
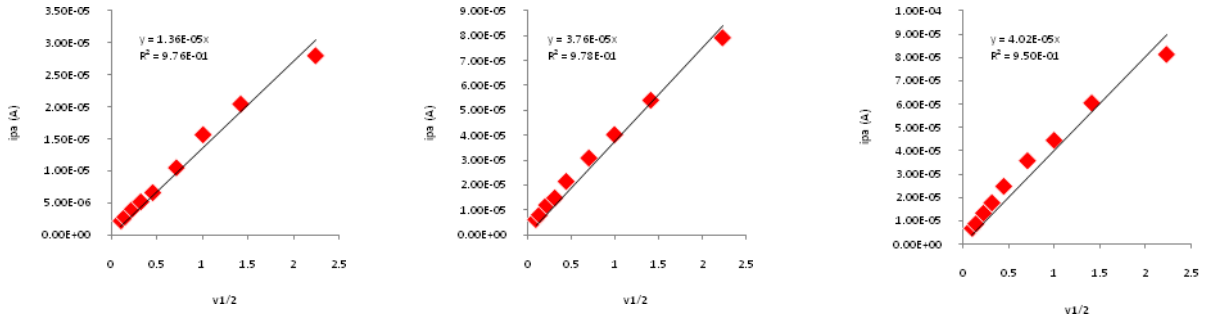


Figure S12. Cyclic voltammetries of molecules **1**, **2** and **3**, 1mM in CH_2Cl_2 with 0.1 M NBu_4PF_6, v = 0.1 $V.s^{-1}$, at vitreous carbon electrode.



Monomer	**Small tetramer**	**Large tetramer**
D (VC) = $1.6.10^{-11}$ $m^2.s^{-1}$	D (VC) = $1.9.10^{-12}$ $m^2.s^{-1}$	D (VC) = $2.2.10^{-12}$ $m^2.s^{-1}$
D (DOSY) = $6.5.10^{-10}$ $m^2.s^{-1}$	D (DOSY) = $4.4.10^{-10}$ $m^2.s^{-1}$	D (DOSY) = $3.6.10^{-10}$ $m^2.s^{-1}$

Figure S13. Determination of diffusion coefficients for compounds **1**, **2** and **3** by linear regression of $i_{pa} = f(v^{1/2})$, comparison with the diffusion coefficients obtained by DOSY spectroscopy.