Electronic Supporting Information

Supramolecular Hybrids Based on Ru(II) Porphyrin and Octahedral Mo(II) Iodide Cluster

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1. Ru(II)CO porphyrin building block

1.1. Characterization of RuDTolP(CO)H₂O

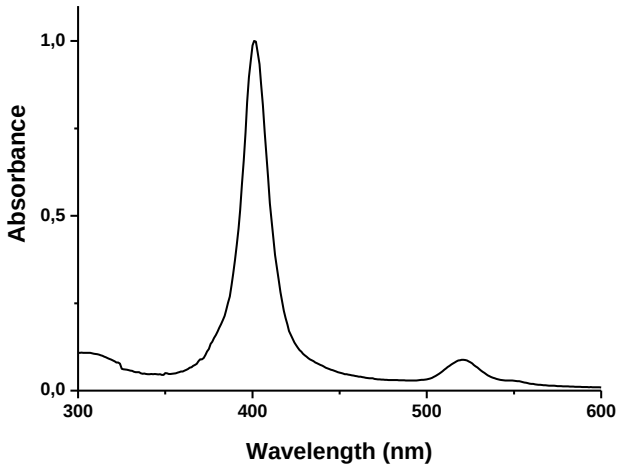


Fig. S1 UV-Vis spectrum of **RuDTolP(CO)L** (L= H_2O/solvent) in $CHCl_3$.

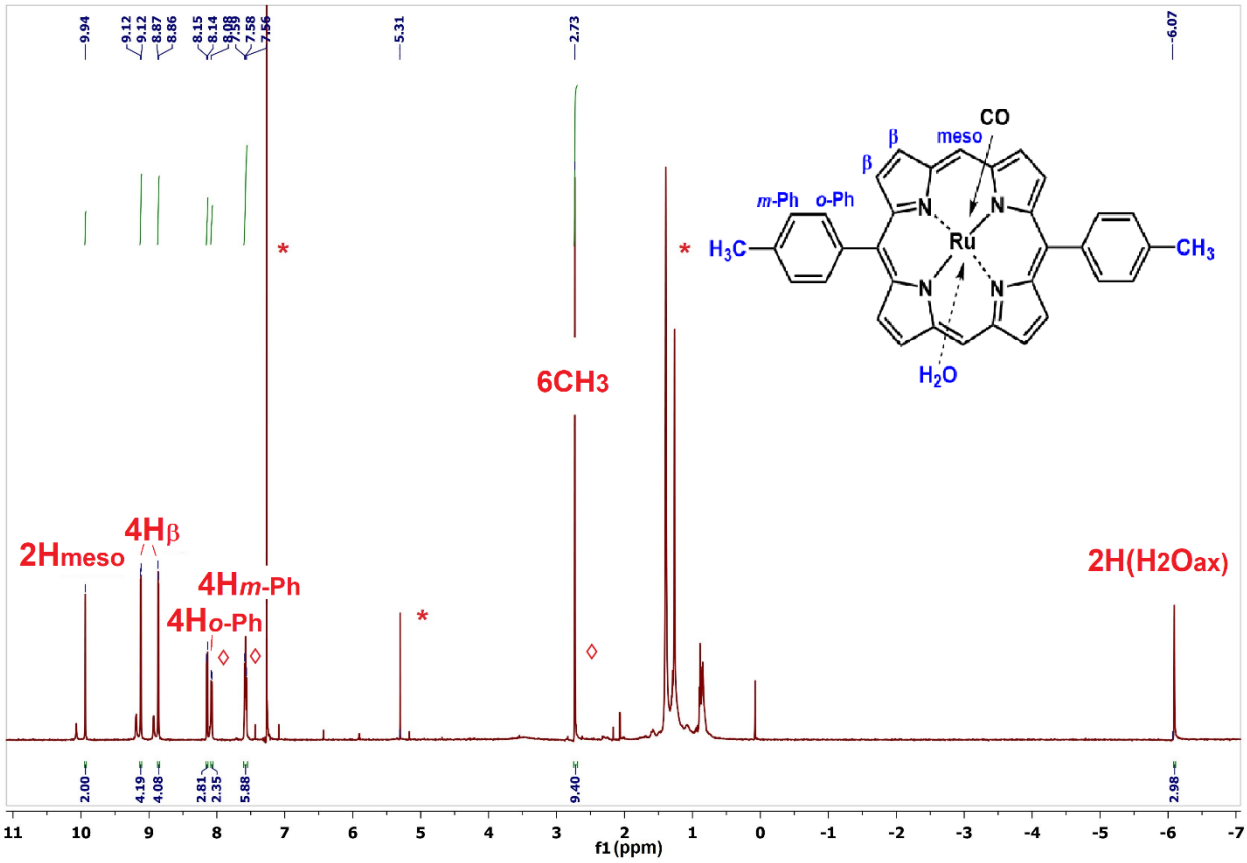


Fig. S2 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 303 K) of **RuDTolP(CO)H₂O**. Solvent peaks are indicated with * (δ_H 7.28 ppm – $CHCl_3$, δ_H 5.30 ppm – CH_2Cl_2, δ_H 1.56 ppm – H_2O). The indicated with ◊ integrals are overestimated as these signals are overlapped with those of the second porphyrin **RuDTolP(CO)L** (L = solvent).

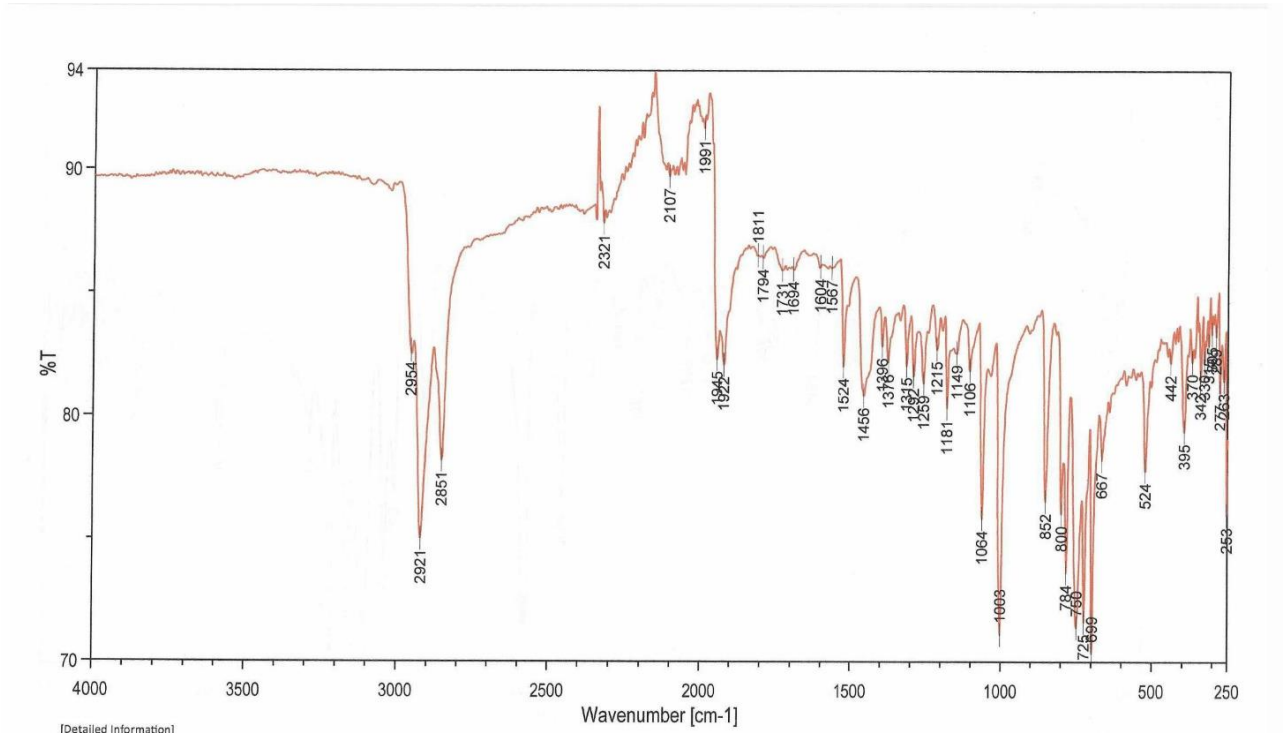


Fig. S3 FT-IR spectrum of **RuDTolP(CO)L** (L= H_2O/solvent).

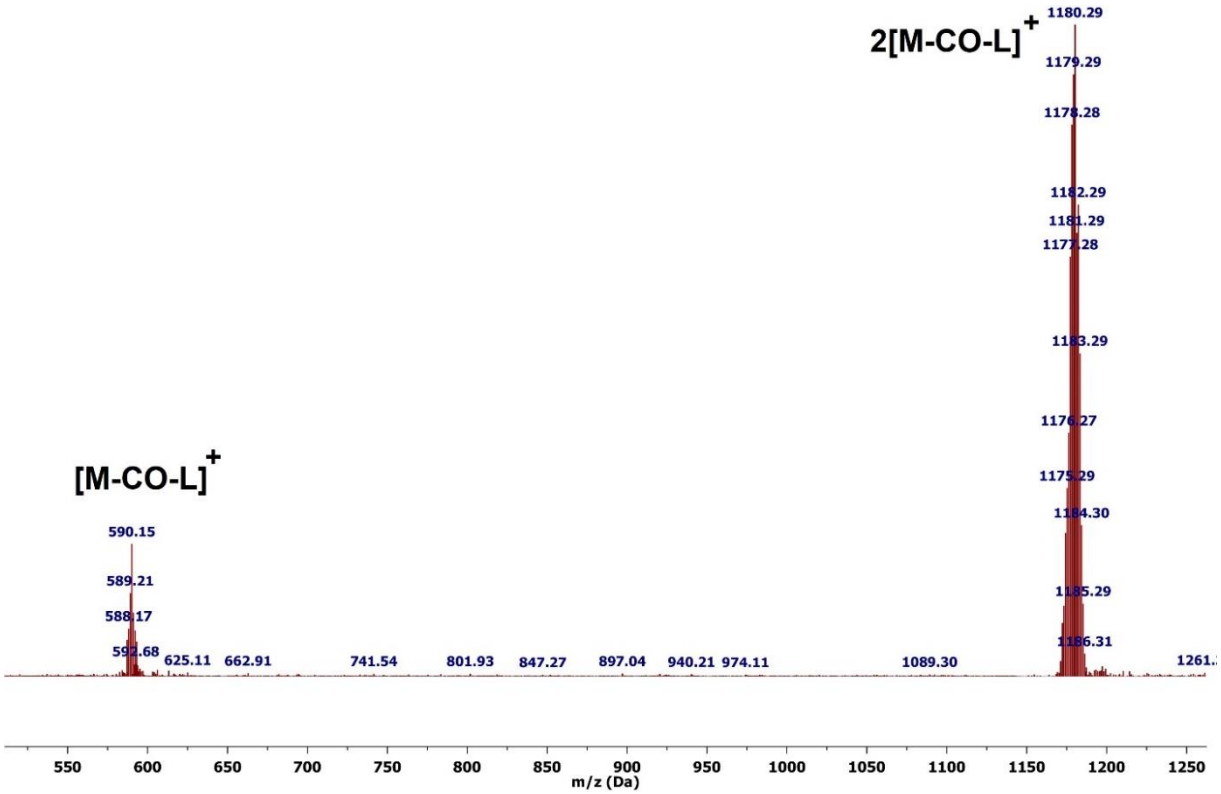


Fig. S4 MALDI TOF mass spectrum of **RuDTolP(CO)L** (L= H_2O/solvent).

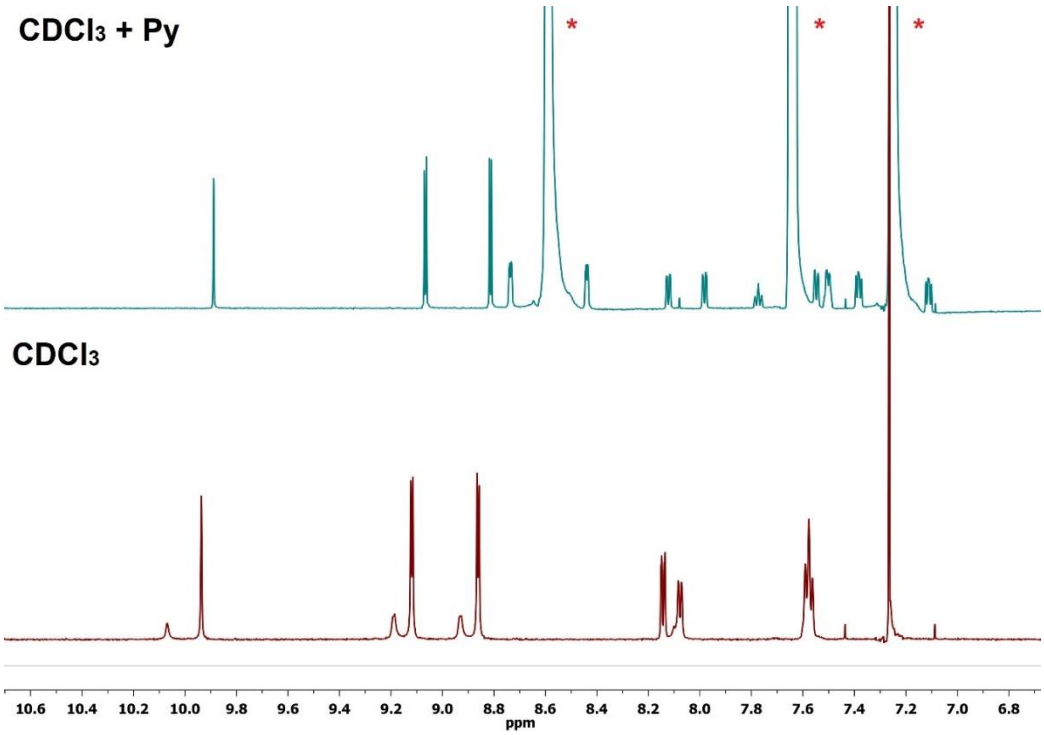


Fig. S5 ^{1}H NMR spectra ($CDCl_3$, 600 MHz, 303 K) of **RuDTolP(CO)L** (L= H_2O/solvent) (aromatic range). Solvent peaks are indicated with * (δ_H 7.28 ppm – $CHCl_3$, δ_H 8.62, 7.68, 7.29 ppm – pyridine).

1.2. Characterization of RuDTolP(CO)Py

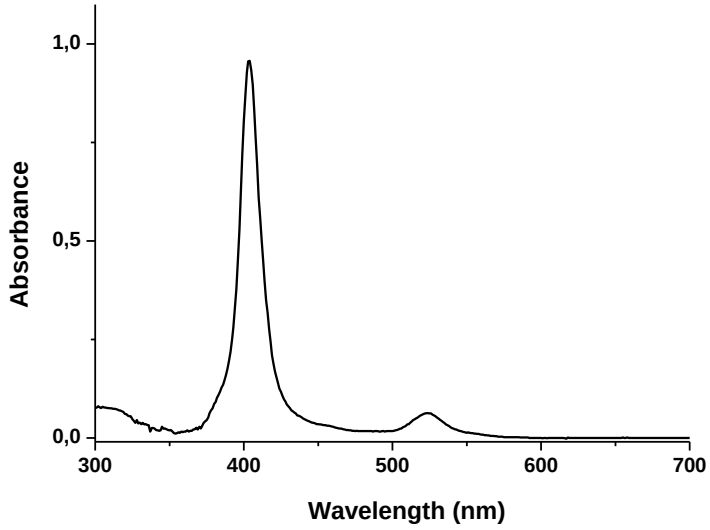


Fig. S6 UV-Vis spectrum of **RuDTolP(CO)Py** in $CHCl_3$.

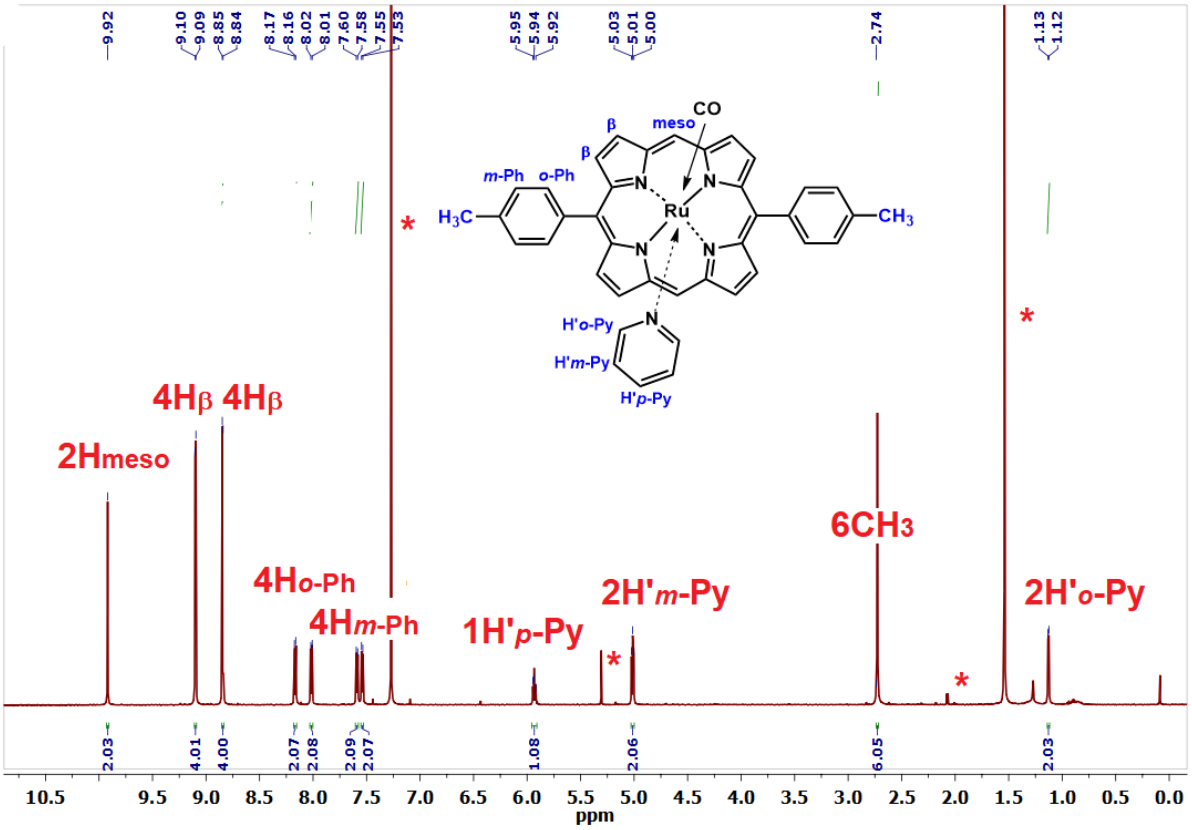


Fig. S7 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 303 K) of **RuDTolP(CO)Py**. Solvent peaks are indicated with * (δ_H 7.28 ppm – $CHCl_3$, δ_H 5.30 ppm- CH_2Cl_2, δ_H 1.56 ppm – H_2O).

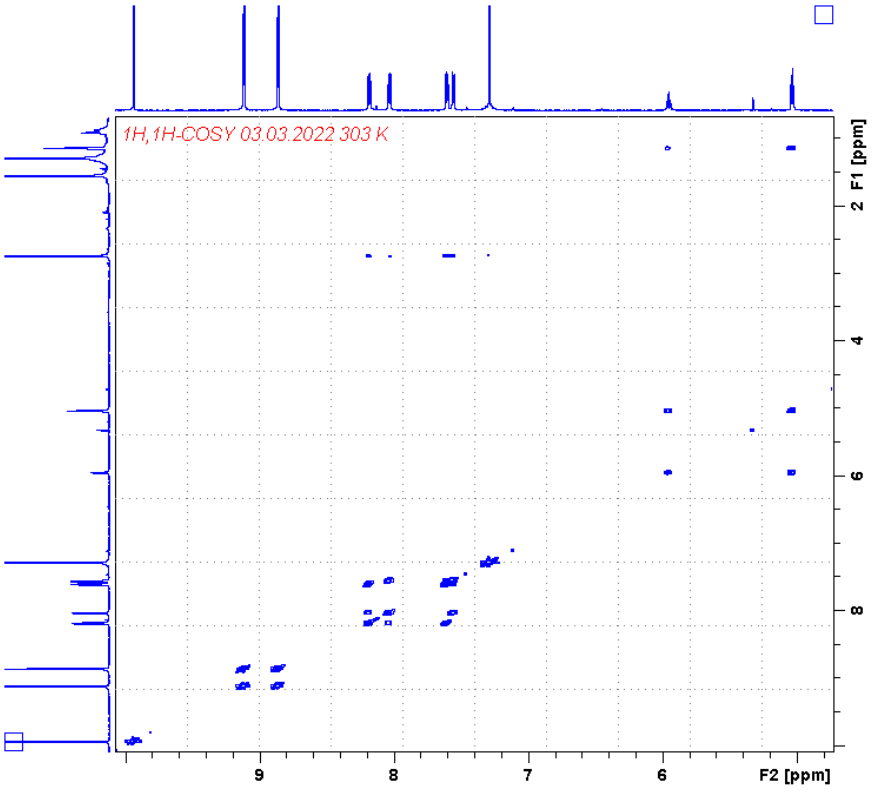


Fig. S8 ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 600 MHz, 303 K) of **RuDTolP(CO)Py.**

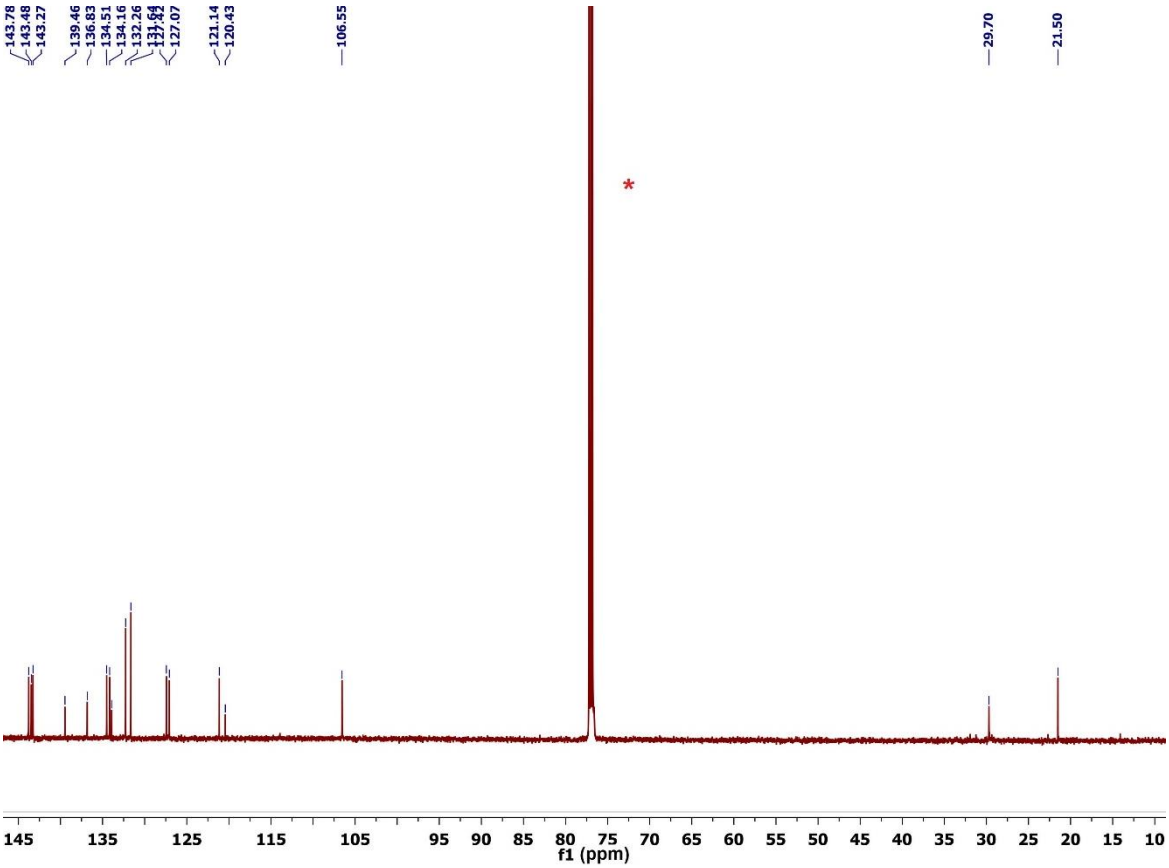


Fig. S9 ^{13}C NMR spectrum ($CDCl_3$, 600 MHz, 303 K) of **RuDTolP(CO)Py**. Solvent peak is indicated with * (δ_c 77.21 ppm – $CHCl_3$).

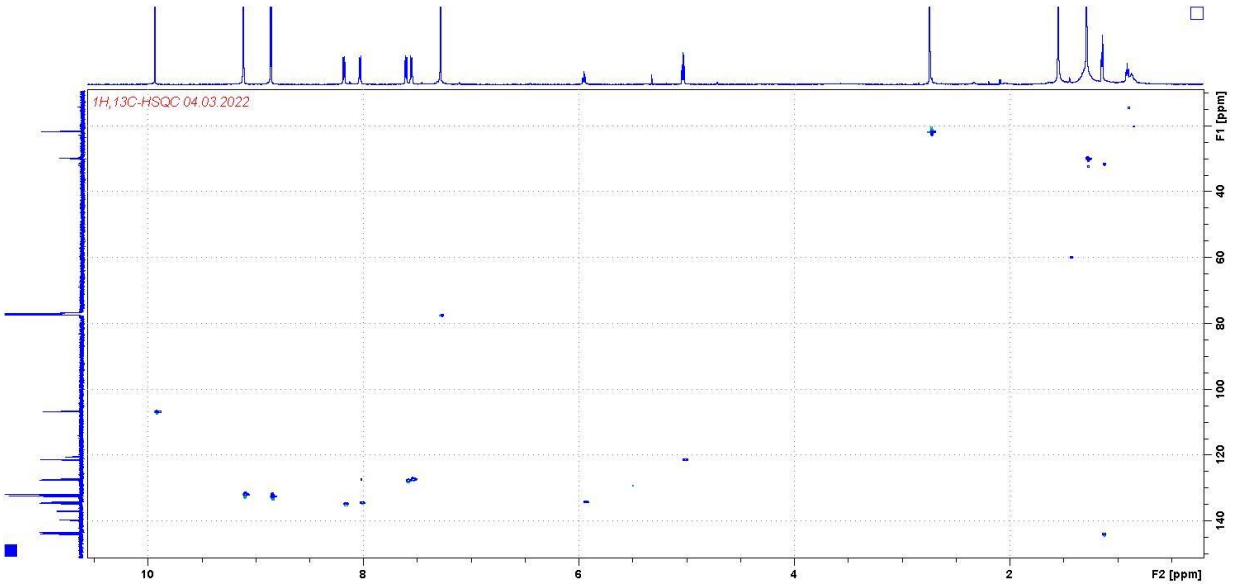


Fig. S10 ^{1}H-^{13}C HSQC spectrum ($CDCl_3$, 600 MHz, 303 K) of **RuDTolP(CO)Py**.

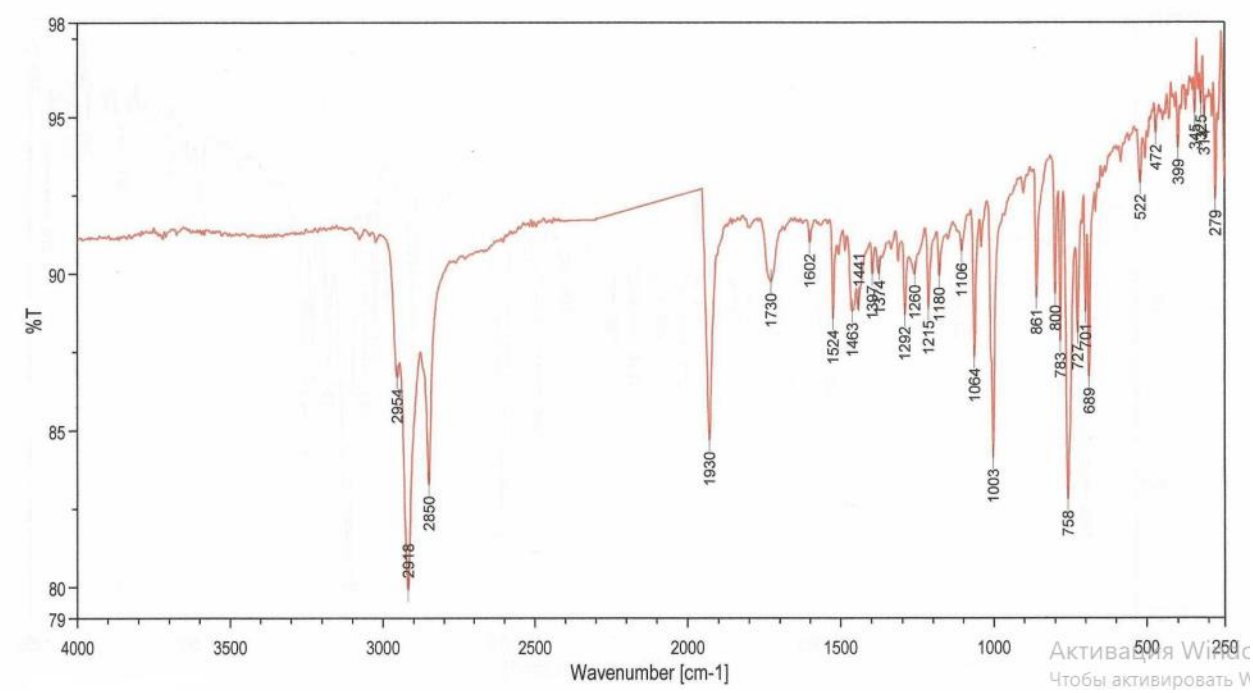


Fig. S11 FT-IR spectrum of **RuDTolP(CO)Py**.

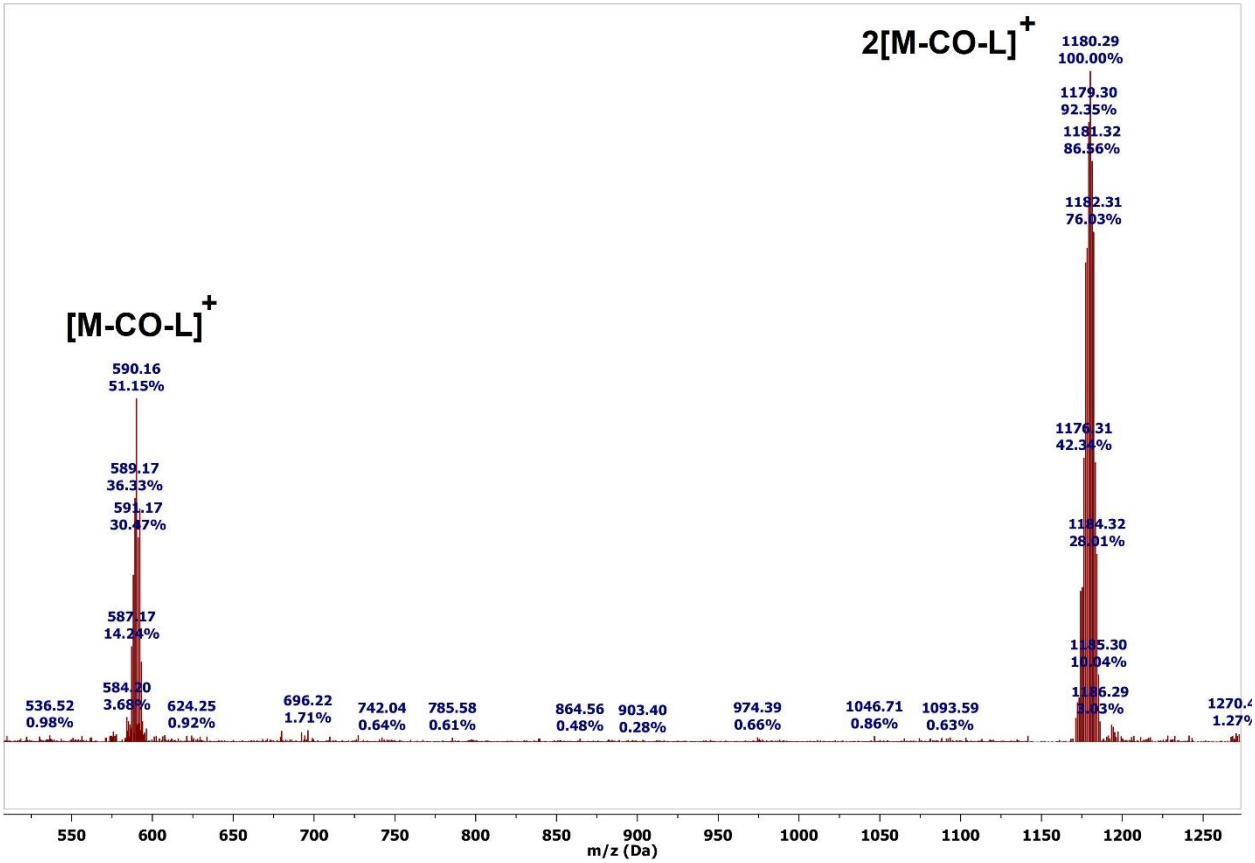


Fig. S12 MALDI TOF mass spectrum of **RuDTolP(CO)Py**.

2. Cluster–Ru(II)Porphyrin complexes

2.1. HRMS (ESI) spectra

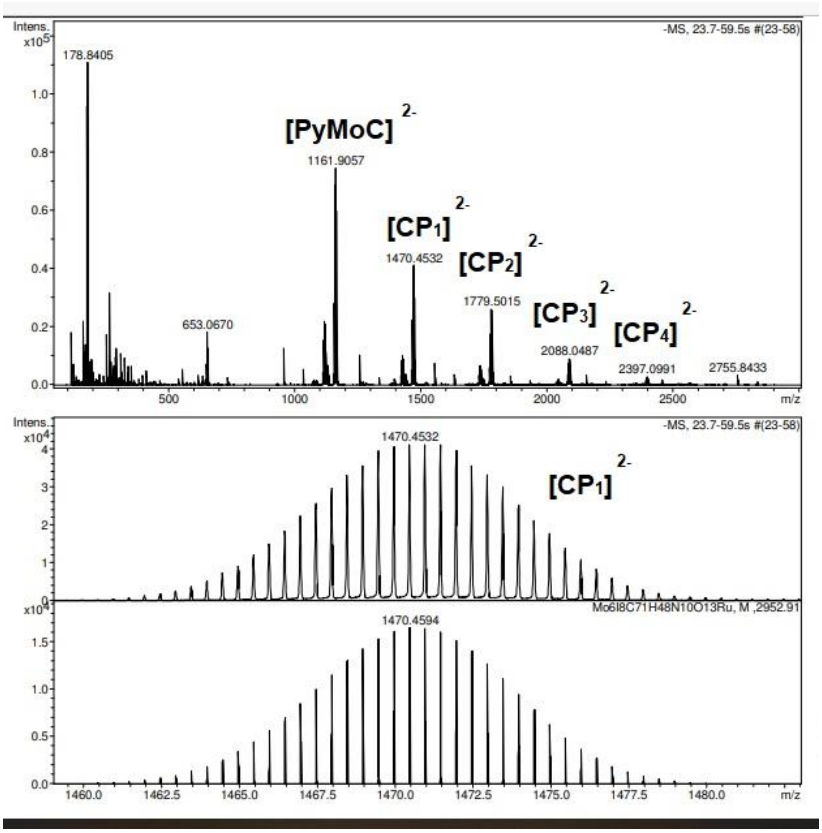


Fig. S13 HRMS (ESI) spectrum of cluster—porphyrin mixture with C:P molar ratio equal to 1:1 in $CHCl_3$.

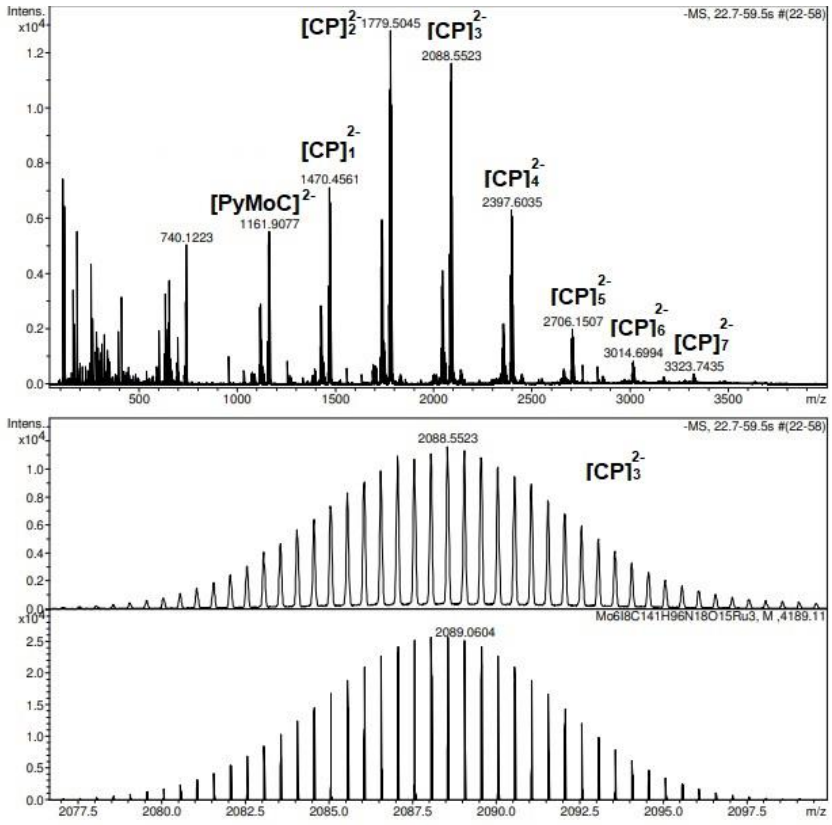


Fig. S14 HRMS (ESI) spectrum of cluster—porphyrin mixture with C:P molar ratio equal to 1:3 in $CHCl_3$.

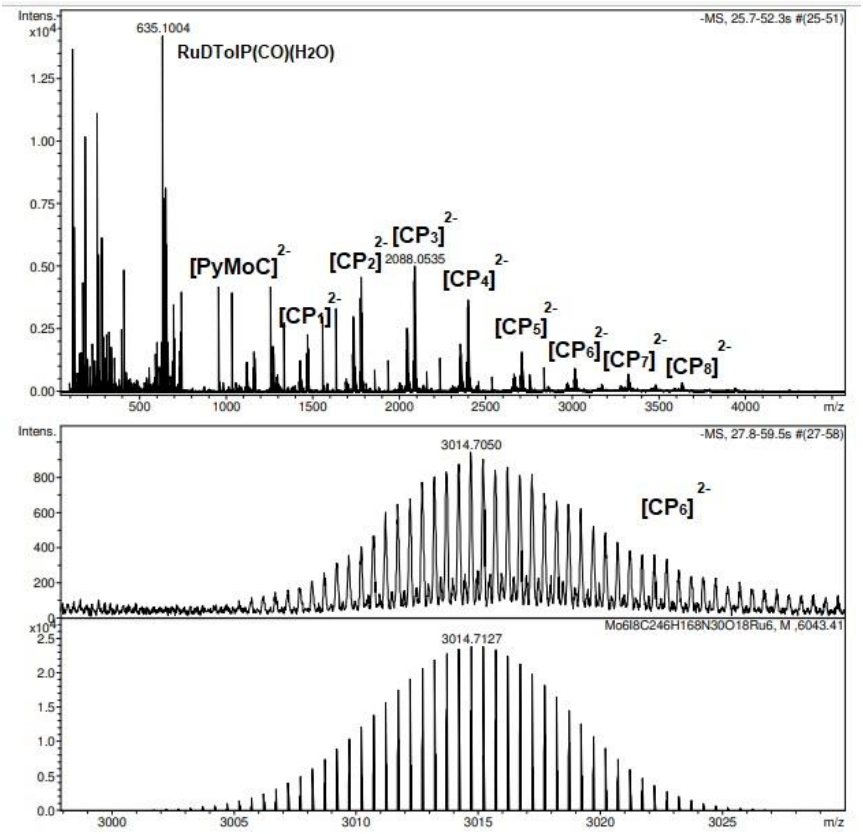


Fig. S15 HRMS (ESI) spectrum of cluster—porphyrin mixture with C:P molar ratio equal to 1:6 in $CHCl_3$.

2.2.UV-Vis spectroscopy

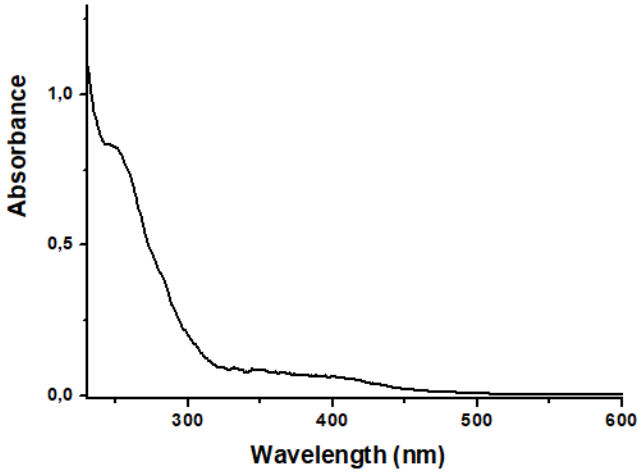


Fig. S16 UV-Vis spectrum of **PyMoC** in CH_2Cl_2.

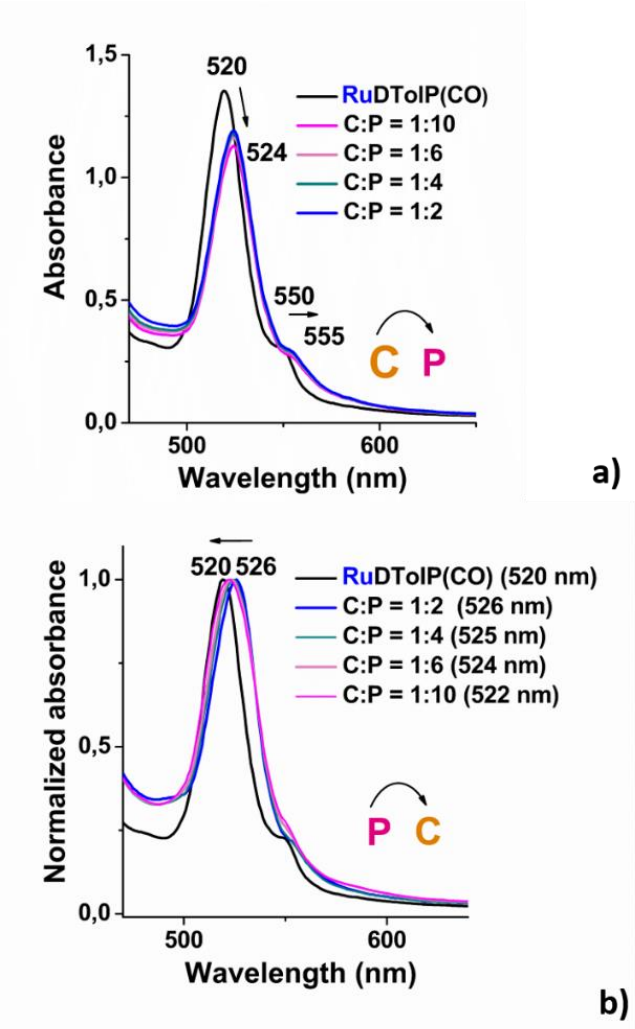


Fig. S 17 UV-Vis spectral changes at 298 K observed upon stepwise addition of the **PyMoC** ($4.6x10^{-4}$ M) solution to **RuDTolP(CO)H_2O** (10^{-4} M) solution in CH_2Cl_2 to achieve the cluster amount 0.10, 0.17, 0.25 and 0.50 equiv. relative to the amount of porphyrin, which corresponds to the C:P molar ratio equal to 1:10, 1:6, 1:4, 1:2 (a); reverse stepwise addition of the **RuDTolP(CO)H_2O** ($5x10^{-3}$ M) solution to **PyMoC** ($2.05x10^{-5}$ M) solution in CH_2Cl_2 (b).

2.3. NMR spectroscopy

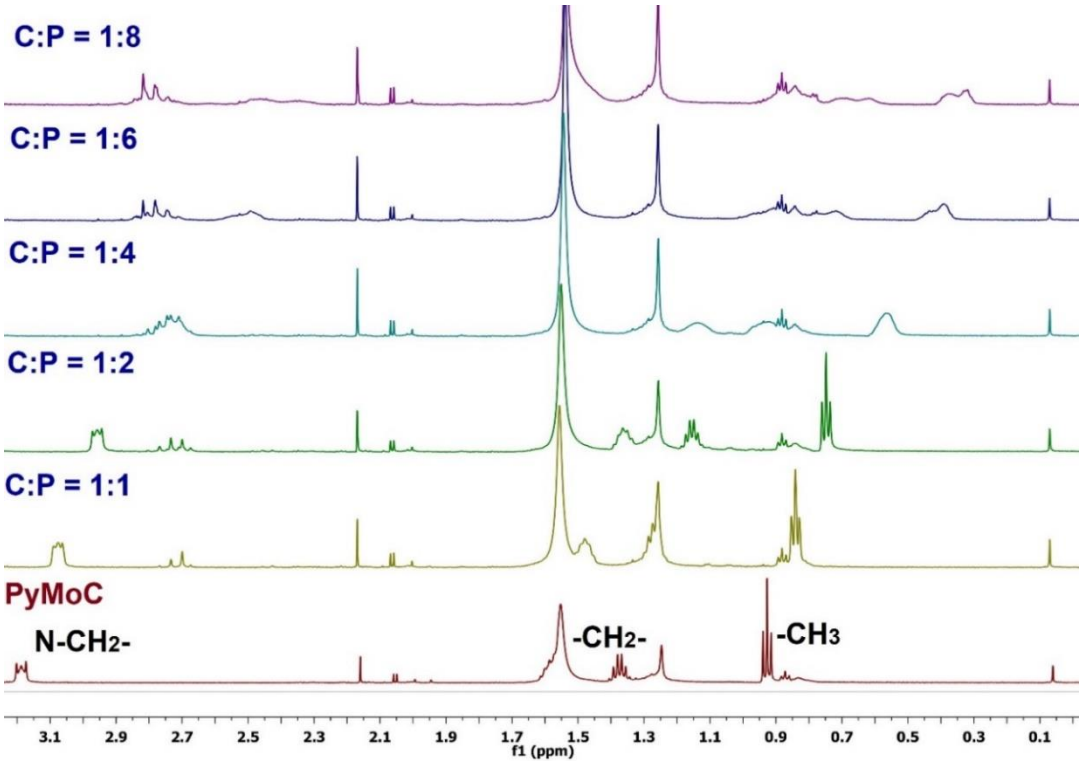


Fig. S18 ^{1}H NMR spectra ($CDCl_3$, 600 MHz, 303 K, aliphatic region) of **PyMoC** ($5x10^{-4}$ M) upon titration with **RuDTolP(CO)H$_2$O** ($4x10^{-3}$ M).

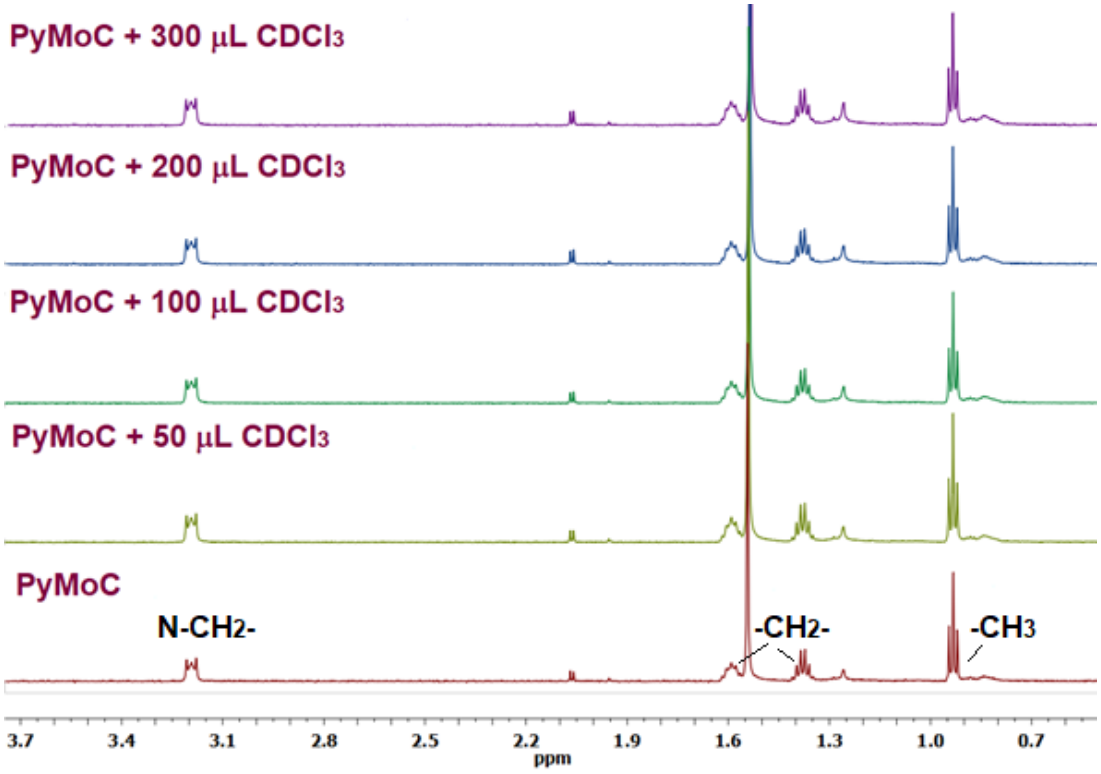


Fig. S19 ^{1}H NMR spectra ($CDCl_3$, 600 MHz, 303 K, aliphatic region) of **PyMoC** ($5x10^{-4}$ M) upon dilution with $CDCl_3$. The volumes of the added solvent are the same as those used for the above-mentioned titration (Fig. S18).

Downfield shifts of the signals from Bu_4N^+ during titration were observed (Fig. S18, S19). This can be attributed to the effect of the ring currents of the porphyrin macrocycle and proves that the Bu_4N^+ cations in a nonpolar $CDCl_3$ solution are arranged near the periphery of **RuDTolP(CO)** molecules. A similar conclusion about the association between the cationic and anionic components in $CDCl_3$ is reached from DOSY experiments (see below). The same effect was detected for the zinc analogue and discussed in detail in our previous paper[1].

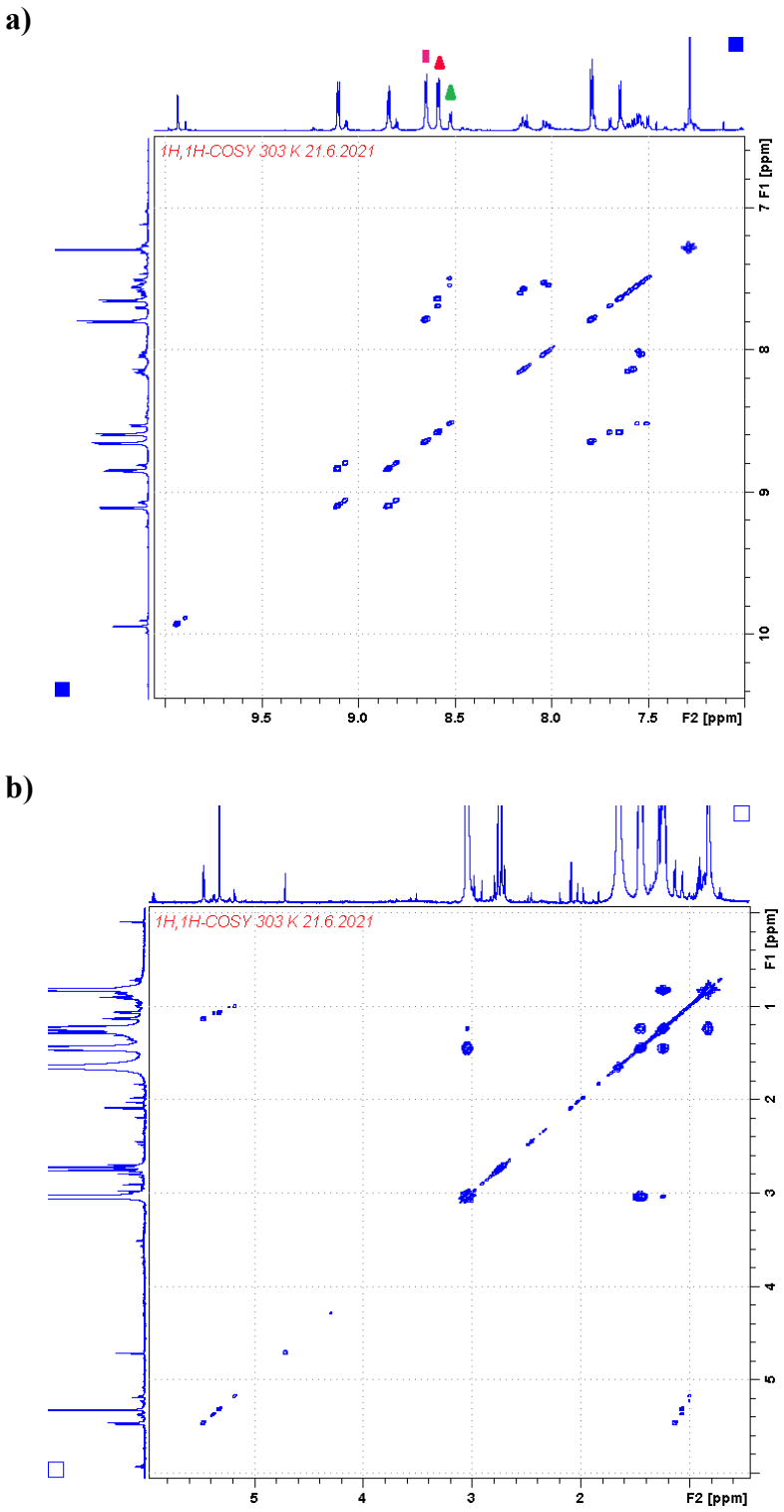


Fig. S20 ^1H-^1H COSY NMR spectrum ($CDCl_3$, 600 MHz, 303 K) of cluster—porphyrin mixture (C:P = 1:1): aromatic region **(a)** labeling of $\mathbf{H_o}$ protons, used hereinafter for the assignment of NMR spectra of cluster and supramolecular assemblies according to Table S1, aliphatic region **(b)**.

The ^{1}H NMR spectra of the equimolar composition contain two sets of signals from porphyrins, H_{Py} signals from uncoordinated cluster groups (H_o 8.3—8.7 ppm, H_m 7.3—7.8 ppm) and new upfield shifted signals in the ranges 5.0—5.6 and 1.0—1.2 ppm, which can be attributed to the H_{Py} of coordinated moieties because they lie within the shielding cone of the Ru(II) porphyrin ring[2]. All the signals, including partially overlapped H_{Py} and H_{Ph} signals in the range 7.3—7.8 ppm and signals in the range 1.0—1.2 ppm masked by Bu_4N^+ signals, have been completely assigned from ^{1}H-^{1}H COSY spectra (Fig. S20). The protons of the coordinated pyridyl moieties are considerably shielded because of the ring current over the porphyrin macrocycle: $\Delta\delta$ = –7.83 ppm for the H'$_o$ protons adjacent to the bound nitrogen atom of the cluster pyridyl moiety and $\Delta\delta$ = –3.02 ppm for H'$_m$ protons, which are more distant from the porphyrin core. The observed upfield shift is comparable to that in other axially bound pyridyl ligands[3-5]. A careful analysis of proton resonances from coordinated and uncoordinated pyridyl units demonstrates that at the cluster—porphyrin molar ratio 1:1 four species are present in $CDCl_3$ solution. One of them is unreacted **PyMoC** cluster and the other three are hybrid **CP$_n$** complexes with increasing number of coordinated porphyrin molecules (Fig. S20).

It should be noted that the coordination of Ru(II) porphyrin leads to the loss of equivalence of the pyridyl protons, which is observed as the appearance of additional signals (their number exceeds the number of possible **CP$_n$** species) for both bound and free Py moieties, especially for the *meta* protons (Fig. S20, S26 and S27). This observation can be rationalized assuming that the effect of the "trans" partner on a given Py moiety in the cluster is responsible for changes in the shielding of the Py protons. In **CP$_n$** assemblies, three types of trans Py…Mo_6I_8…Py ordinates are possible: two unbound Py moieties Py…Mo_6I_8…Py, bound and unbound trans-partners Ru-Py…Mo_6I_8…Py, and two bound trans-partners Ru-Py…Mo_6I_8…Py-Ru. Thus, two separate signals from unbound Py protons and two separate signals from bound Py protons can be observed for each **CP$_n$** hybrid. The relative intensities of these signals are consistent with the number of coordinates of a definite type, including the existence of geometrical isomers (see Table S1). For example, the **CP$_1$** complex contains two types of uncoordinated Py moieties: four of them are located at two Py…Mo_6I_8…Py trans-ordinates, and one group is located trans to the bound Py moiety. These groups give rise to the signals of *meta*-protons at 7.65 and 7.71 ppm, respectively, with the relative intensities 1:4. The **CP$_2$** complex exists as two geometrical isomers, *trans*-**CP$_2$** and *cis*-**CP$_2$**, in the 1 : 4 ratio. In the *trans*-isomer, there are four equivalent unbound Py moieties; in the *cis*-isomer, there is one trans-ordinate containing two similar moieties. This gives 1 × 4 + 4 × 2 = 12 unbound moieties of one type. In addition, the *cis*-isomer also contains two unbound Py moieties located at the mixed trans-ordinates: 4 × 2 = 8. Both types of moieties are responsible for the signals of *meta* protons at 7.50 and 7.56 ppm, respectively, and the relative intensities of these signals should be 4 : 3, which is consistent with the experimental data. The **CP$_2$** isomers also contain coordinated Py moieties: two of them at the Ru-Py…Mo_6I_8…Py-Ru ordinate in the *trans*-isomer (1 × 2 = 2) and two moieties are at the mixed ordinates in the *cis*-isomer (4 × 2 = 8). This gives the relative intensities of the corresponding signals (5.52 and 5.46 ppm) 1 : 4 which is consistent with the observed intensities. Results of analogous calculations for all complexes are presented in Table S1.

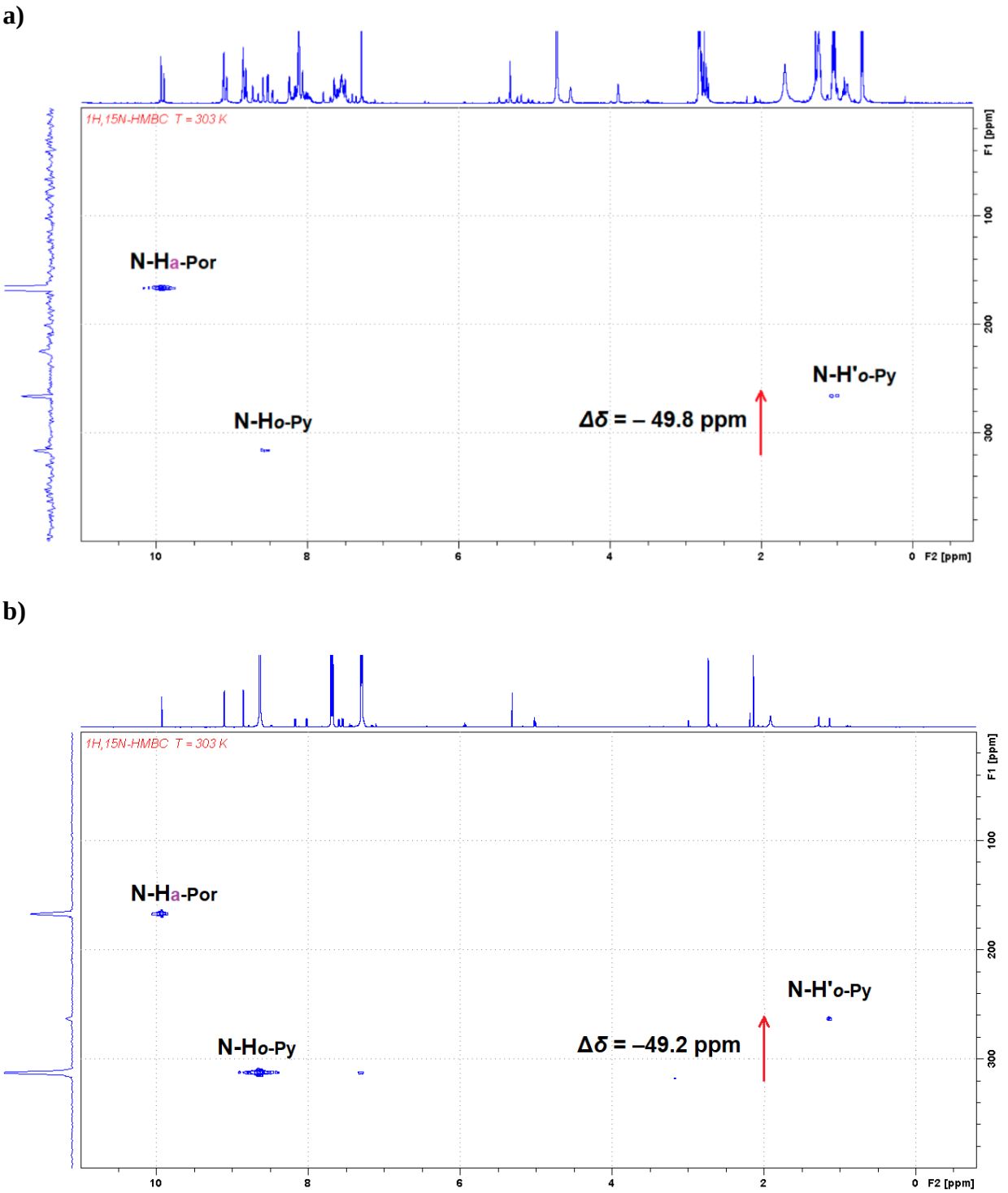


Fig. S21 ^{1}H-^{15}N HMBC NMR spectra ($CDCl_3$, 600 MHz, 303 K) of cluster:porphyrin mixture with C:P molar ratio equal to 1:2 **(a)**; of **RuDTolP(CO)Py** in the presence of Py excess **(b)**; assignment of the protons according to Fig. 4 in main text.

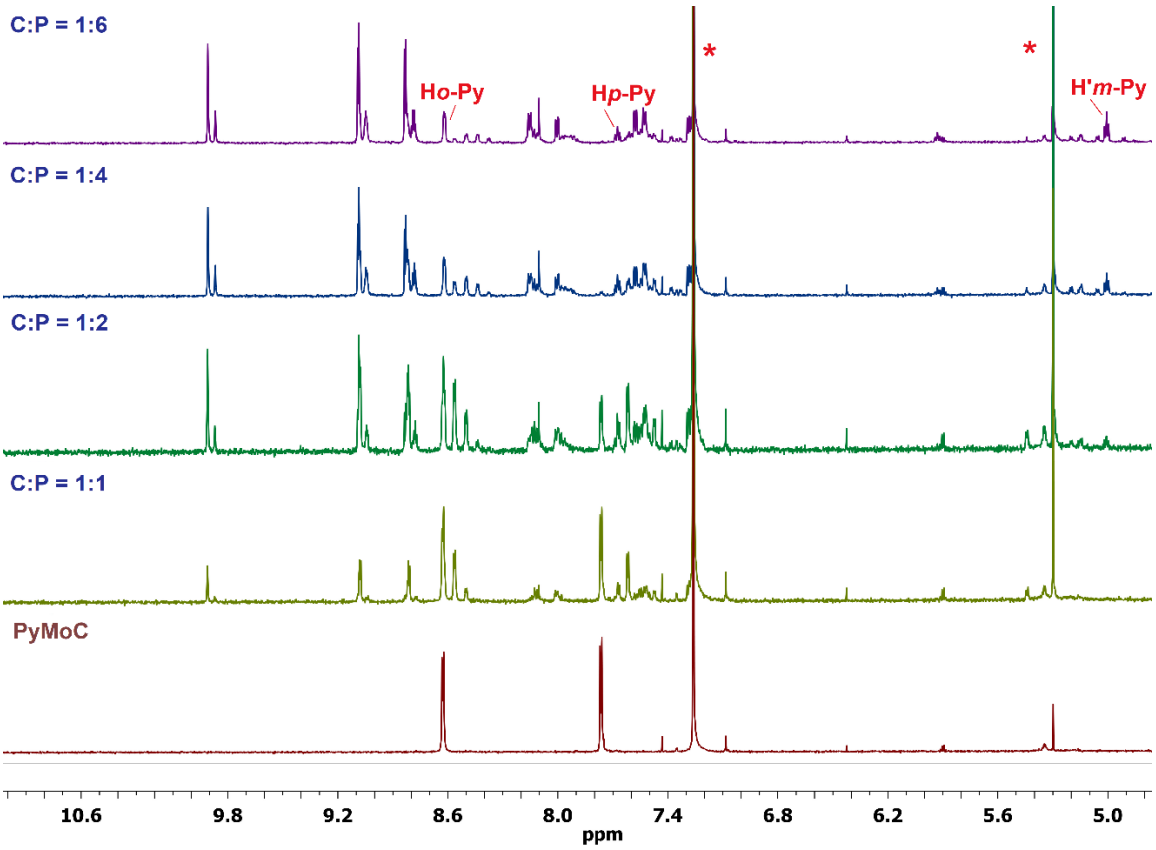


Fig. S22 ^{1}H NMR spectra ($CDCl_3$, 600 MHz, 303 K, aromatic region) of **PyMoC** ($5x10^{-4}$ M) upon titration with **RuDTolP(CO)Py** ($8x10^{-3}$ M); assignment of the protons according to Fig. S7. Solvent peaks are indicated with * (δ_H 7.28 ppm – $CHCl_3$, δ_H 5.30 ppm- CH_2Cl_2).

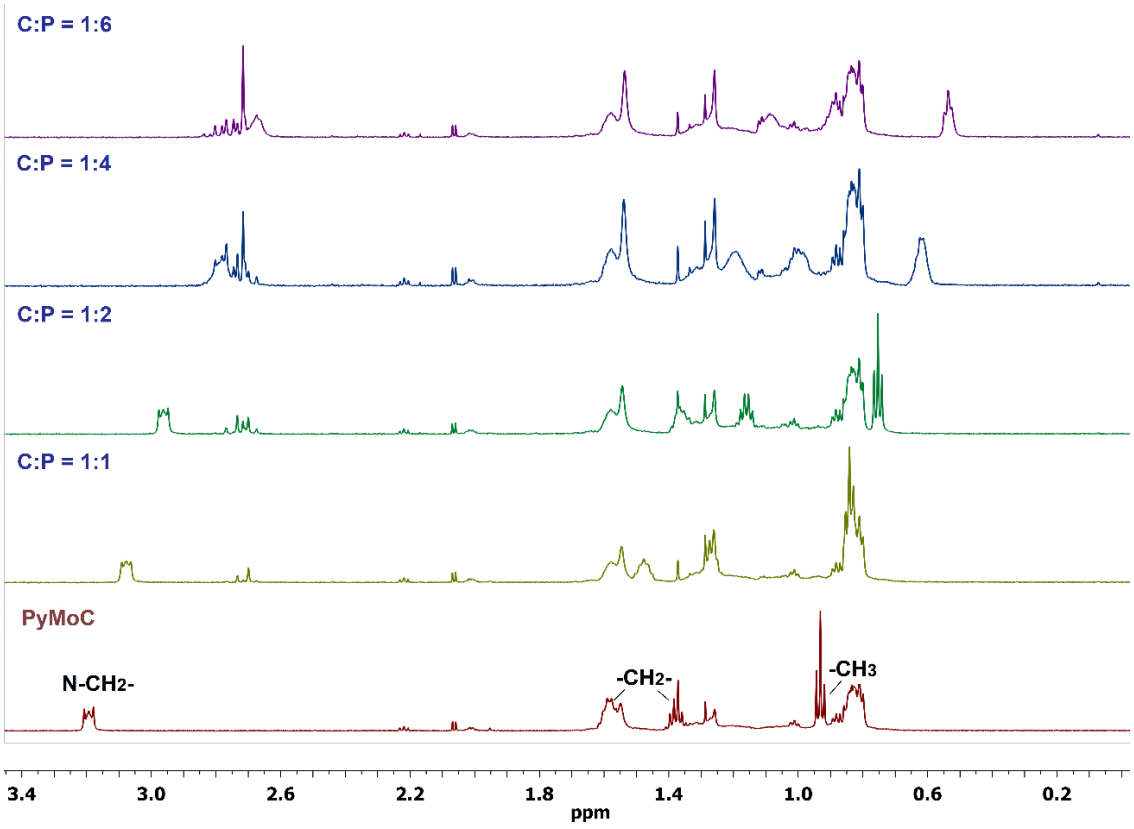


Fig. S23 ^{1}H NMR spectra ($CDCl_3$, 600 MHz, 303 K, aliphatic region) of **PyMoC** ($5x10^{-4}$ M) upon titration with **RuDTolP(CO)Py** ($8x10^{-3}$ M).

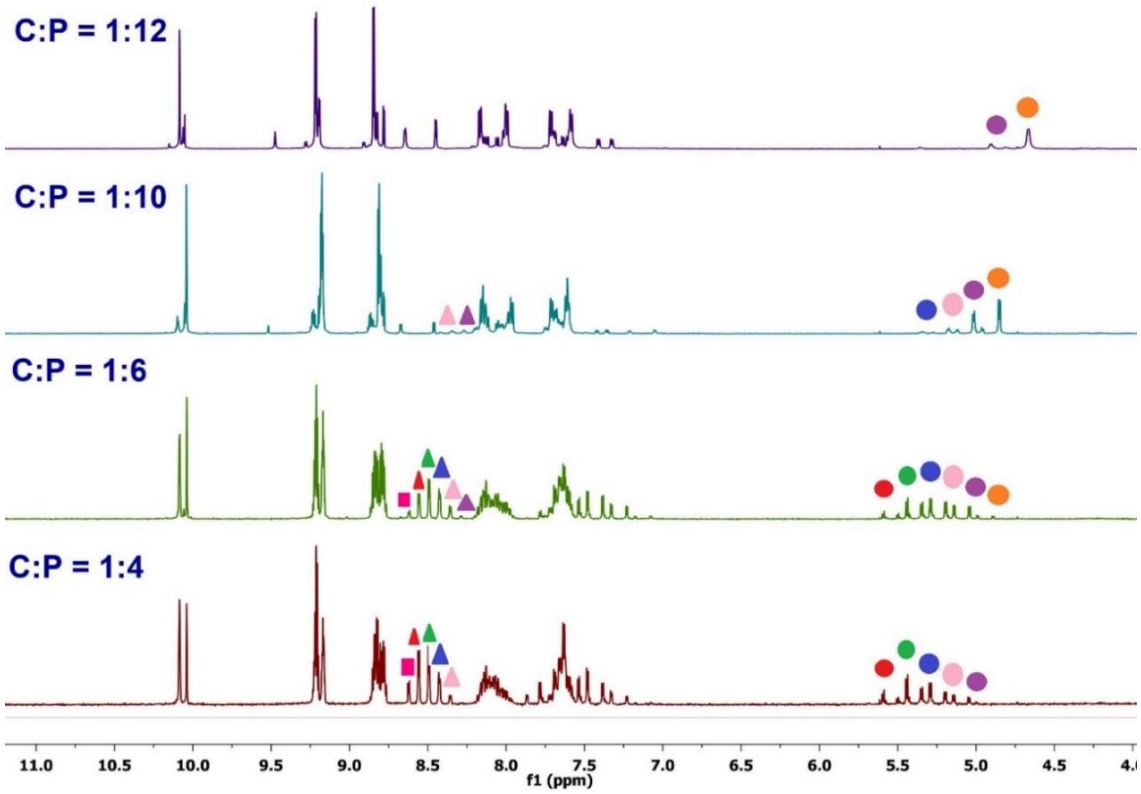


Fig. S24 Changes in ^{1}H NMR spectra (acetone-d_6, 600 MHz, 303 K) of cluster—porphyrin mixtures with different molar C:P ratios, aromatic region; labeling of $\mathbf{H}_o$ and $\mathbf{H'}_m$ protons, used hereinafter for the assignment of NMR spectra of cluster and supramolecular assemblies according to Table S1.

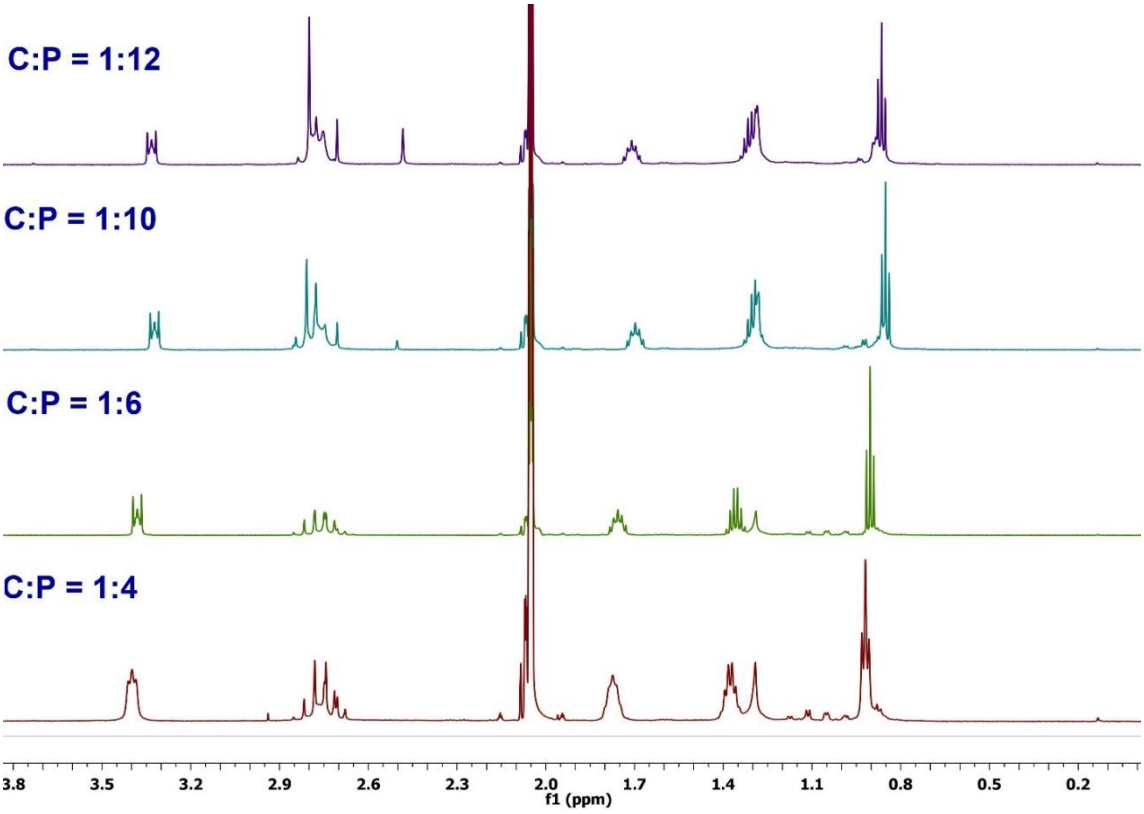


Fig. S25 Changes in ^{1}H NMR spectra (acetone-d_6, 600 MHz, 303 K) of cluster−porphyrin mixtures with different molar C:P ratios, aliphatic region.

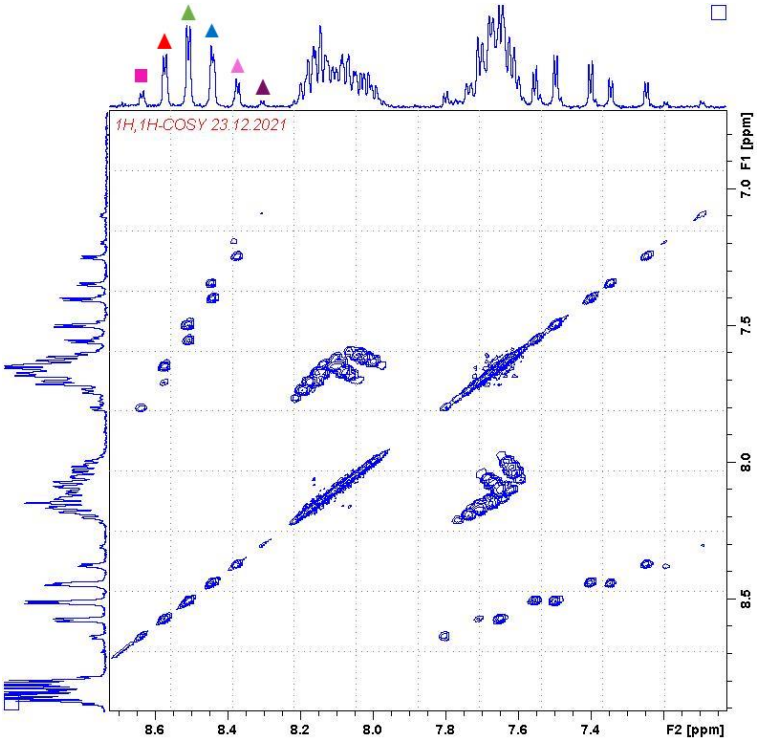


Fig. S26 ^{1}H-^{1}H COSY spectrum (acetone-d_6, 600 MHz, 303 K) of **PyMoC** + 6 equiv. **RuDTolP(CO)H_2O** after heating at 45 °C for 2 h, aromatic region; labeling of **H_o** protons, used hereinafter for the assignment of NMR spectra of cluster and supramolecular assemblies according to Table S1.

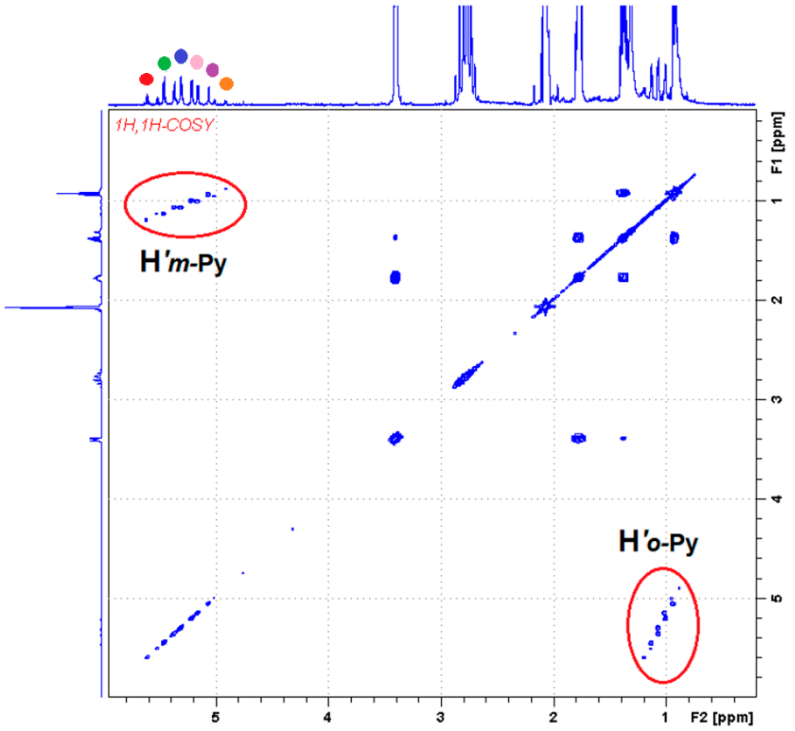
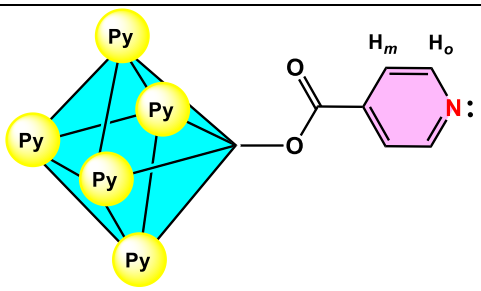
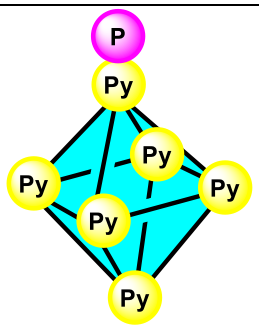
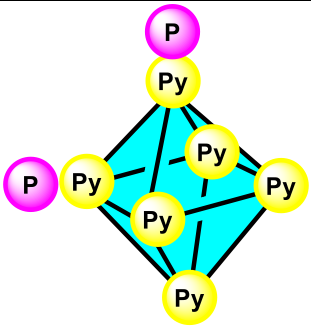
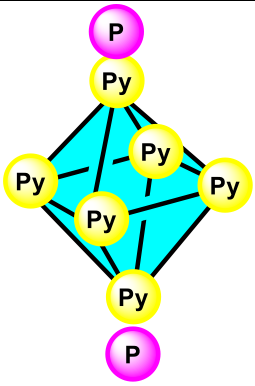
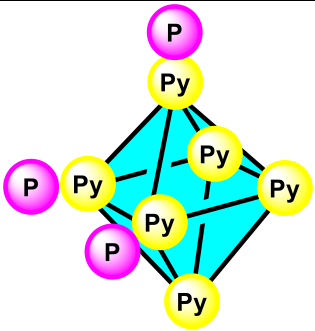
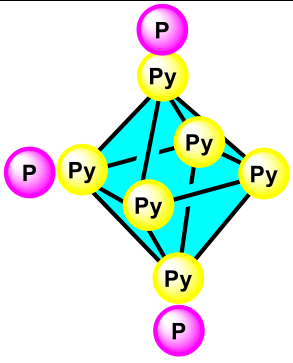
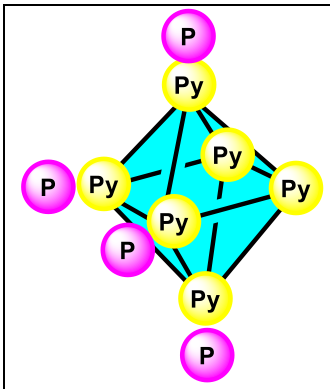
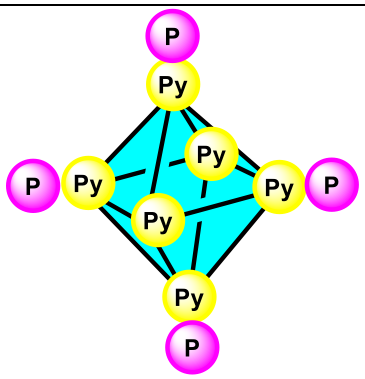
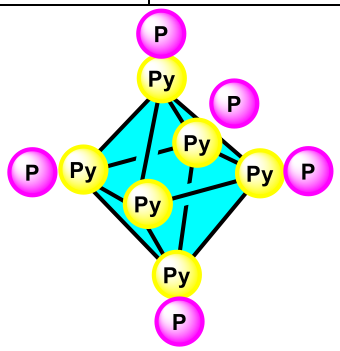
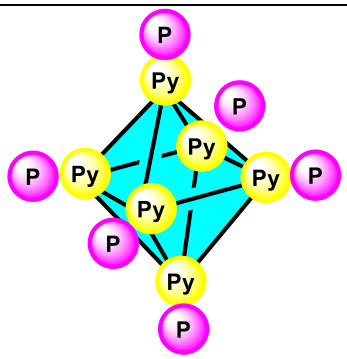


Fig. S27 ^{1}H-^{1}H COSY NMR spectrum (acetone-d_6, 600 MHz, 303 K) of **PyMoC** + 6 equiv. **RuDTolP(CO)H_2O** after heating at 45 °C for 2 h, aliphatic region, zoom; labeling of **H'*m*** protons, used hereinafter for the assignment of NMR spectra of supramolecular assemblies according to Table S1.

Table S1. ^{1}H NMR chemical shifts of H_{Py} for hybrid complexes $Mo_6I_8(Py)_6(Ru(CO)Por)_n$ (n=1-6) in 1:6 cluster—porphyrin mixture in acetone-d_6.

Hybrid species		Non-coordinated H_{Py}, ppm		Coordinated H'_{Py}, ppm	
		H_o	H_m	H'_o	H'_m
		8.64 ■	7.80		
		8.57 ▲	7.71:7.65 1:4[a]	1.20	5.61 ●
CP_1					
		8.51 ▲	7.56:7.50 3:4[a]	1.13	5.52:5.46 1:4[a] ●
***cis*-CP_2**	***trans*-CP_2**				
		8.44 ▲	7.40:7.35 3:2[a]	1.07	5.36:5.31 2:3[a] ●
***fac* -CP_3**	***mer* -CP_3**				

		8.37 ▲	7.25:7.20 4:1[a]	1.00	5.21:5.16 3:2[a] ●
***cis*-CP$_4$**	***trans*-CP$_4$**				
		8.30 ▲	7.10	0.93	5.06:5.01 4:1[a] ●
CP$_5$					
				0.87	4.91 ●
CP$_6$					

[a] The relative intensities of the signals for *meta*-protons given in the table are consistent with the number of identical free and bound Py moieties located at trans-ordinates of a definite type in the **CP$_n$** complexes, including the geometrical isomers (see above for details).

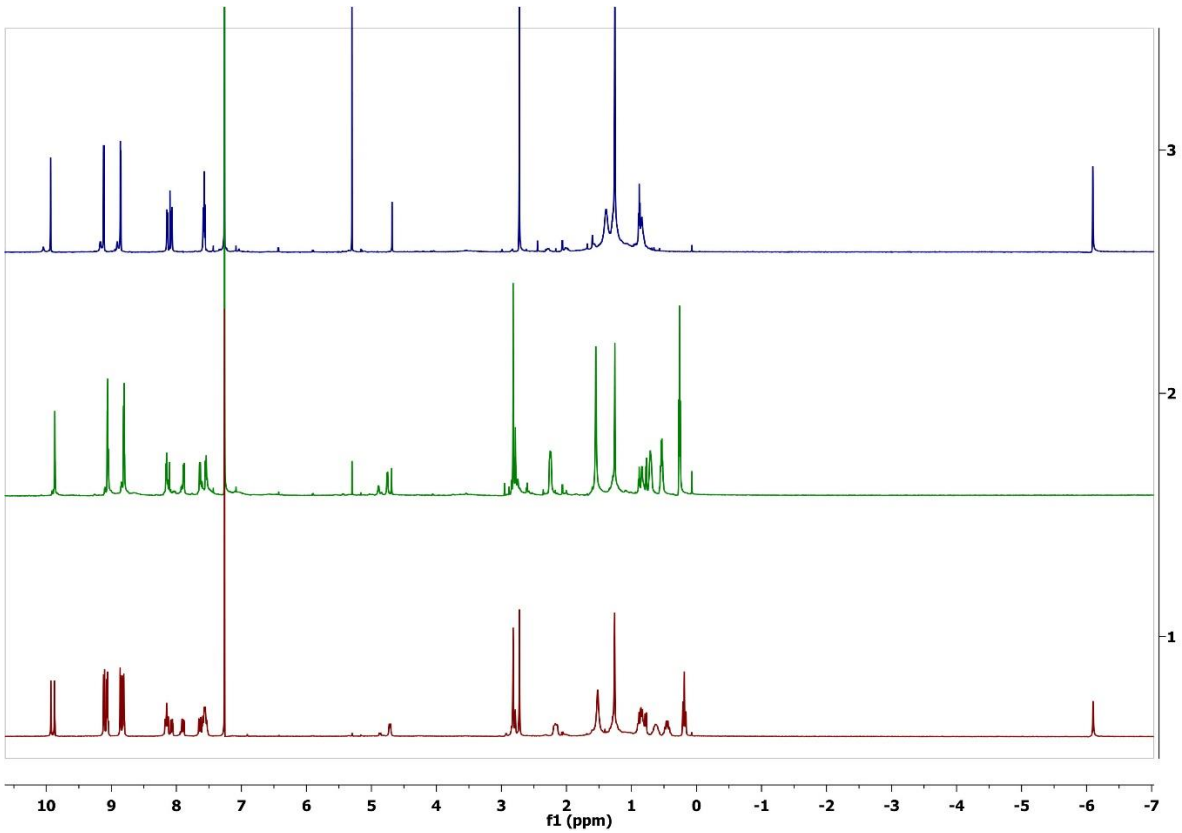


Fig. S28 ^{1}H NMR spectra ($CDCl_3$, 600 MHz, 303 K) of cluster:porphyrin mixture with C:P molar ratio equal to 1:12 (bottom), hybrid complexes $Mo_6I_8(Py)_6(Ru(CO)Por)_{5,6}$ (middle) and **RuDTolP(CO)H$_2$O** (top), separated by gel-filtration (Bio-Beads S-X1), eluent CH_2Cl_2.

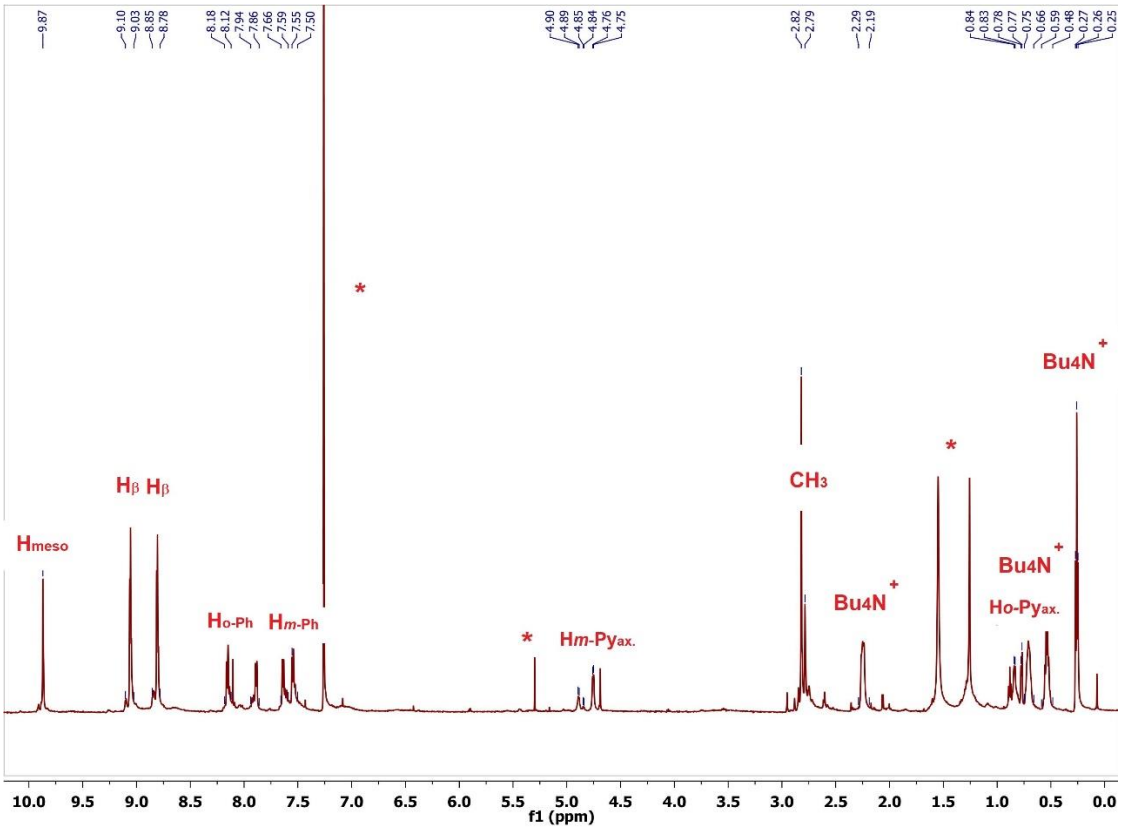


Fig. S29 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 303 K) of hybrid complexes $Mo_6I_8(Py)_6(Ru(CO)Por)_5(Bu_4N)_2$ and $Mo_6I_8(Py)_6(Ru(CO)Por)_6(Bu_4N)_2$. Solvent peaks are indicated with * (δ_H 7.28 ppm – $CHCl_3$, δ_H 5.30 ppm – CH_2Cl_2, δ_H 1.56 ppm – H_2O).

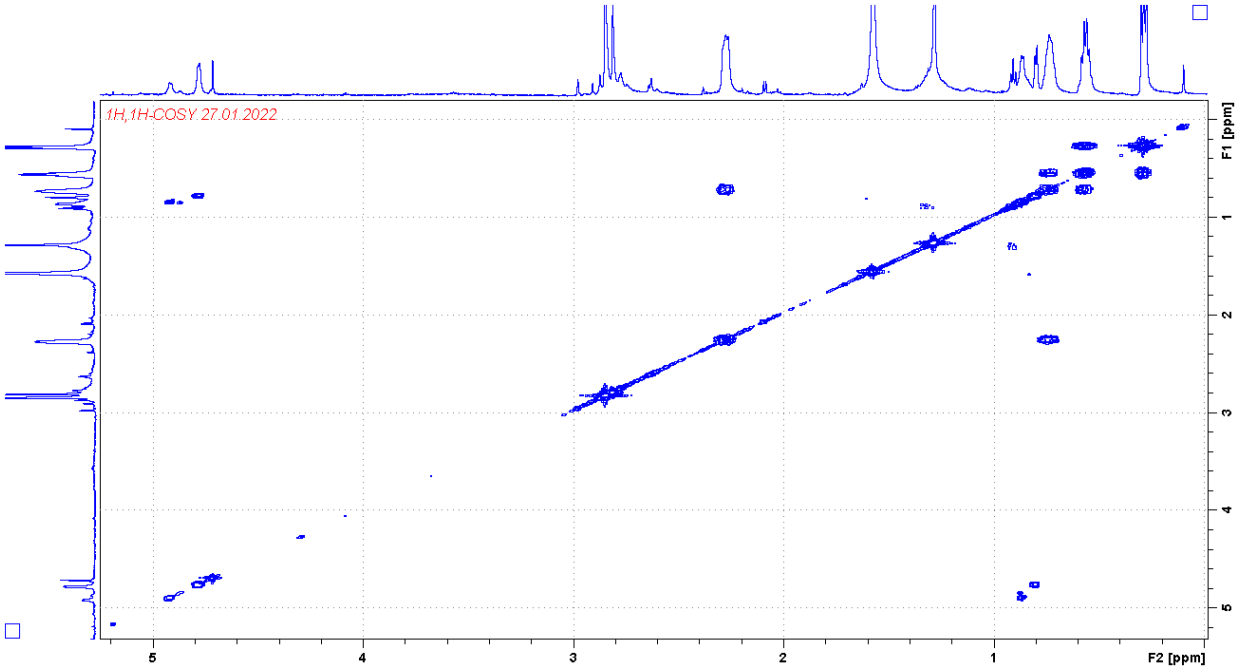


Fig. S30 ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 600 MHz, 303 K) of hybrid complexes $Mo_6I_8(Py)_6(Ru(CO)Por)_5(Bu_4N)_2$ and $Mo_6I_8(Py)_6(Ru(CO)Por)_6(Bu_4N)_2$., aliphatic region.

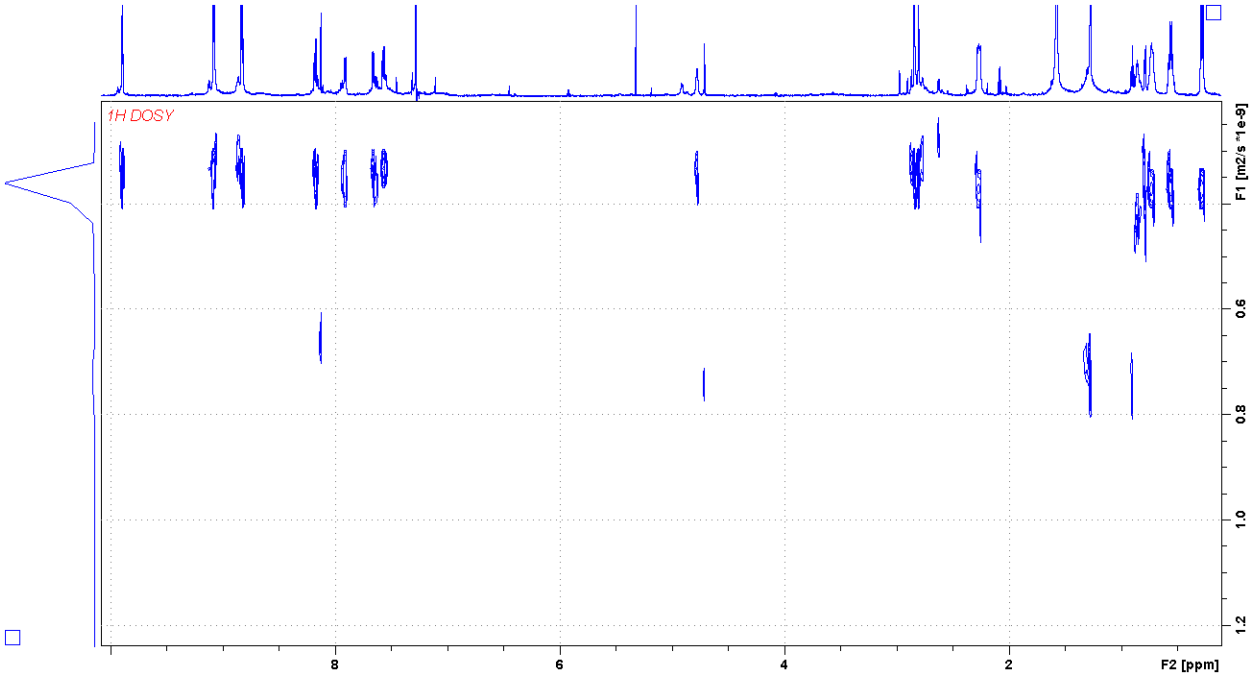


Fig. S31 DOSY ^{1}H NMR spectra ($CDCl_3$, 600 MHz, 303 K) of hybrid complexes $Mo_6I_8(Py)_6(Ru(CO)Por)_5(Bu_4N)_2$ and $Mo_6I_8(Py)_6(Ru(CO)Por)_6(Bu_4N)_2$.

2.3.1. DOSY Experiments

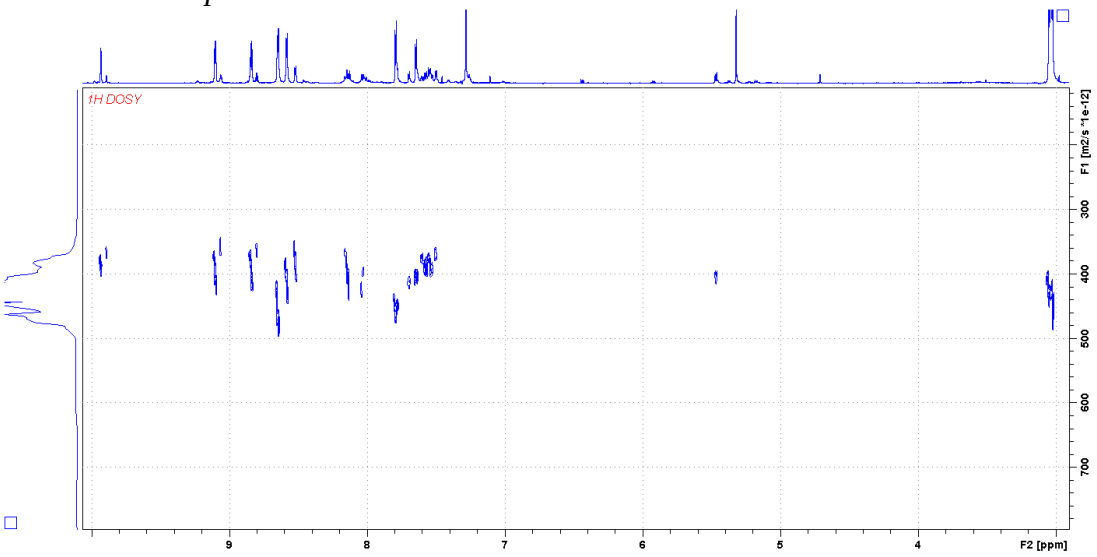


Fig. S32 DOSY ^{1}H NMR spectra ($CDCl_3$, 600 MHz, 303 K) of 1:1 cluster—porphyrin mixture.

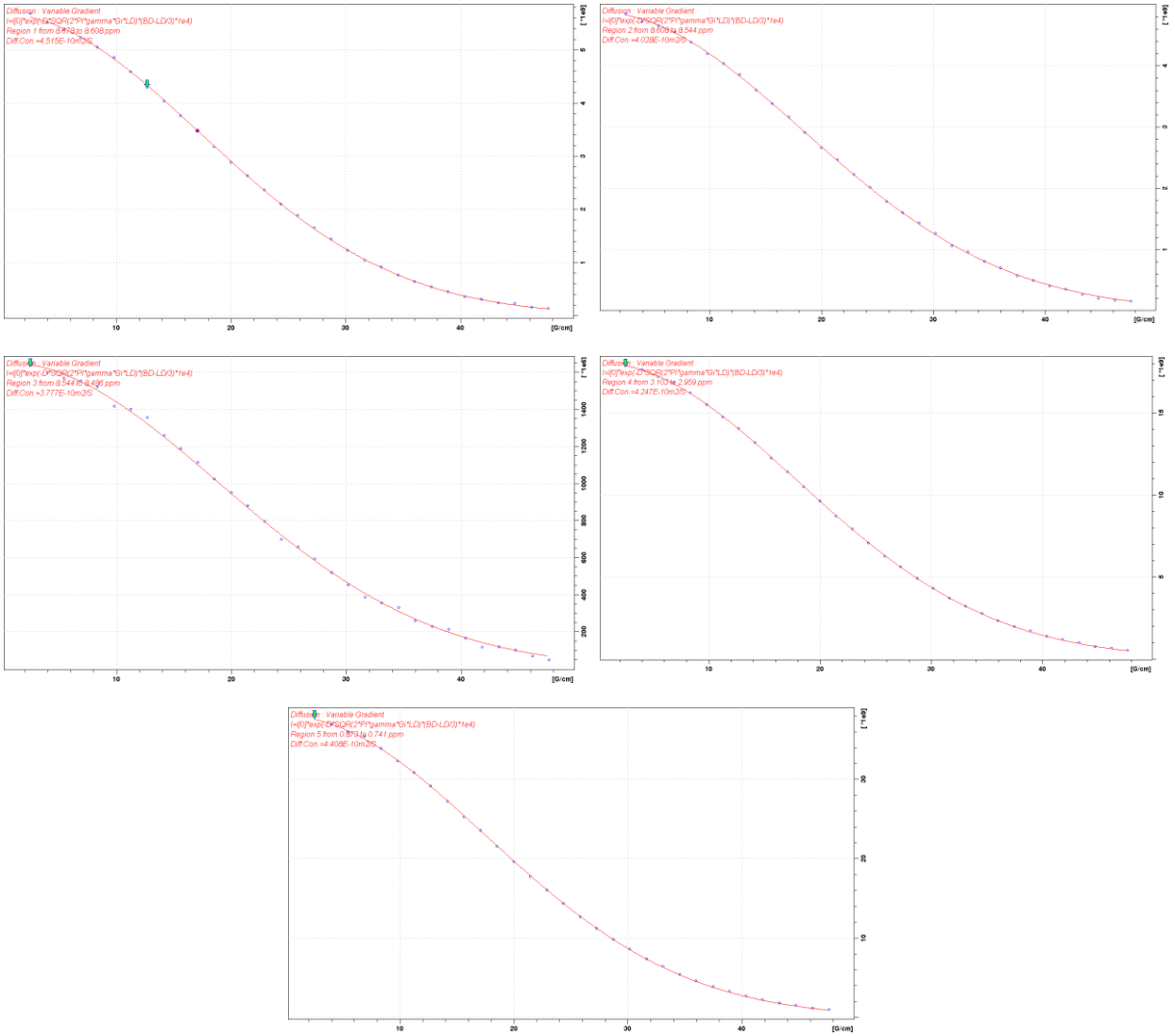


Fig. S33 Echo damping as a function of gradient strength g for the non-coordinated H*o*-Py signals of **PyMoC**, **CP$_1$** and **CP$_2$** and for **NCH$_2$-** and **-CH$_3$** of **Bu$_4$N$^+$** in 1:1 cluster:porphyrin mixture in $CDCl_3$. *Measurement conditions:* diffusion time, 140 ms; gradient pulse duration, 1950 μs.

Molecular weights (M) of assemblies (Figure S32 and S34) have been estimated using the fact that the ratio of the diffusion coefficients of two different molecular species (D_1/D_2) is inversely proportional to the square root or to the cube root of their molecular weights M_2/M_1 for rod-like and spherical molecules, respectively[6]:

$$\sqrt[3]{\frac{M_2}{M_1}} \leq \frac{D_1}{D_2} \leq \sqrt{\frac{M_2}{M_1}}$$

Comparison of the ratios of experimental diffusion coefficients and cubic or square roots of the ratios of theoretical molecular weights when different **CP_n** species are used as reference ones (Tables S2 and S3) shows a good match between them. The most pronounced discrepancy between the corresponding values is observed when the cluster molecule is used as a reference for estimating the molecular weights of hybrid complexes, which indicates that the binding of the first porphyrin molecule to the cluster core leads to a considerable change in the shape of the resulting species compared to that of the initial **PyMoC**; therefore, we believe that it is more correct to evaluate the molecular weights using neighboring hybrid species as reference molecules.

Table S2. Experimental diffusion coefficients (*Ds*) of **PyMoC** and hybrid complexes $Mo_6I_8(Py)_6(Ru(CO)Porph)_{1,2}$ in 1:1 cluster—porphyrin mixture in $CDCl_3$ according DOSY-NMR data.

Species	D_s, m^2s^{-1} [a]	M_{theor}, Da [b]
PyMoC	$4.52x10^{-10}$	2807
CP_1	$4.03x10^{-10}$	3425
CP_2	$3.78x10^{-10}$	4042
Bu_4N^+ (CH_3-)	$4.41x10^{-10}$	
Bu_4N^+ (NCH_2-)	$4.25\ x10^{-10}$	

$\sqrt[3]{\frac{M_{CPm}}{M_{CPn}}}$	$\frac{D_{CPn}}{D_{CPm}}$	$\sqrt{\frac{M_{CPm}}{M_{CPn}}}$
n = 0, **m** = 1		
1.07	1.12	1.10
n = 0, **m** = 2		
1.13	1.2	1.19
n = 1, **m** = 2		
1.06	1.07	1.08

[a] The D_s values determined for non-coordinated H_o-*Py* of the cluster and hybrid complexes.
[b] Molecular weight M_{theor} was calculated for $Mo_6I_8(Py)_6(Ru(CO)Por)_n](Bu_4N)_2$ (n=0-2).

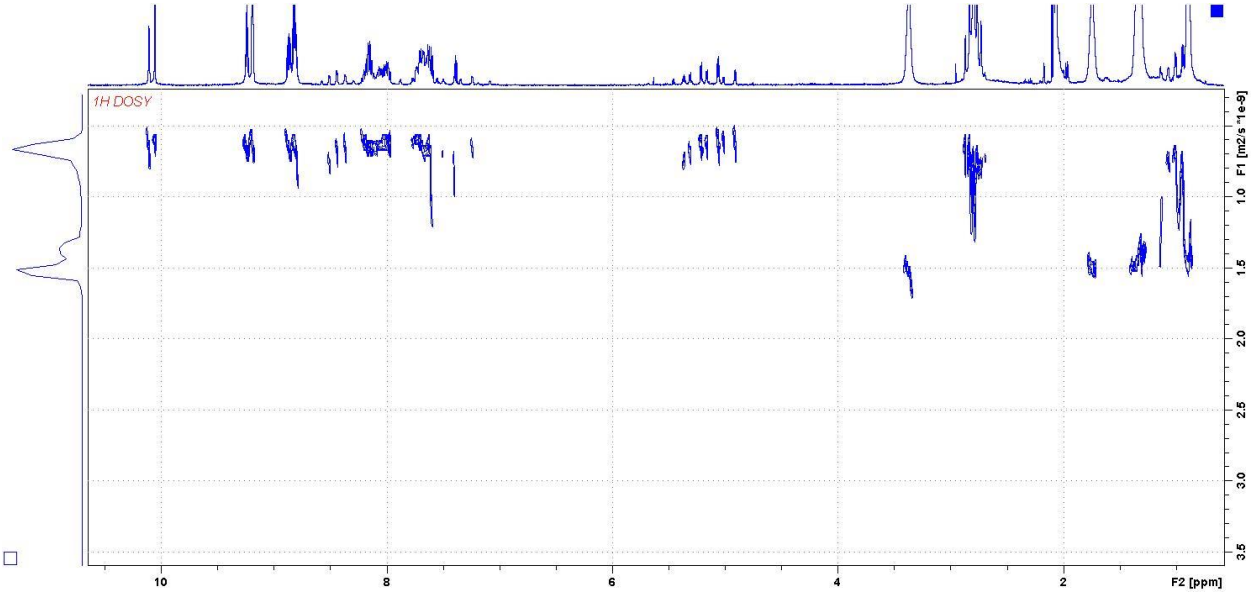


Fig. S34 DOSY ^{1}H NMR spectrum (acetone-d_6, 600 MHz, 303 K) of 1:7 cluster—porphyrin mixture.

Table S3. Experimental diffusion coefficients (*Ds*) of **PyMoC** and hybrid complexes $Mo_6I_8(Py)_6(Ru(CO)Por)_n$ (n=2-6) in 1:7 cluster—porphyrin mixture in acetone-d_6 according DOSY-NMR data.

Species	D_s, m^2/s	M_{theor}, Da[c]
CP_2	$7.10x10^{-10}$ [a]	3558
CP_3	$6.35x10^{-10}$ [a]	4176
CP_4	$5.92x10^{-10}$ [b]	4794
CP_5	$5.63x10^{-10}$ [b]	5412
CP_6	$5.48x10^{-10}$ [b]	6029
Bu_4N^+ (-NCH_2-)	$1.54 x10^{-9}$	-

$\sqrt[3]{\frac{M_{CPm}}{M_{CPn}}}$	$\frac{D_{CPn}}{D_{CPm}}$	$\sqrt{\frac{M_{CPm}}{M_{CPn}}}$
n = 2, **m** = 3		
1.05	1.12	1.08
n = 3, **m** = 4		
1.05	1.07	1.07
n = 4, **m** = 5		
1.04	1.05	1.06
n = 5, **m** = 6		
1.04	1.03	1.05

[a] The D_s values determined for non-coordinated H*o-Py* of the cluster and hybrid complexes.
[b] The D_s values determined for coordinated H'*m-Py* of hybrid complexes.
[c] Molecular weight M_{theor} was calculated for $[Mo_6I_8(Py)_6(Ru(CO)Por)_n]^{2-}$ (n=1-6).

2.4.FT-IR spectra

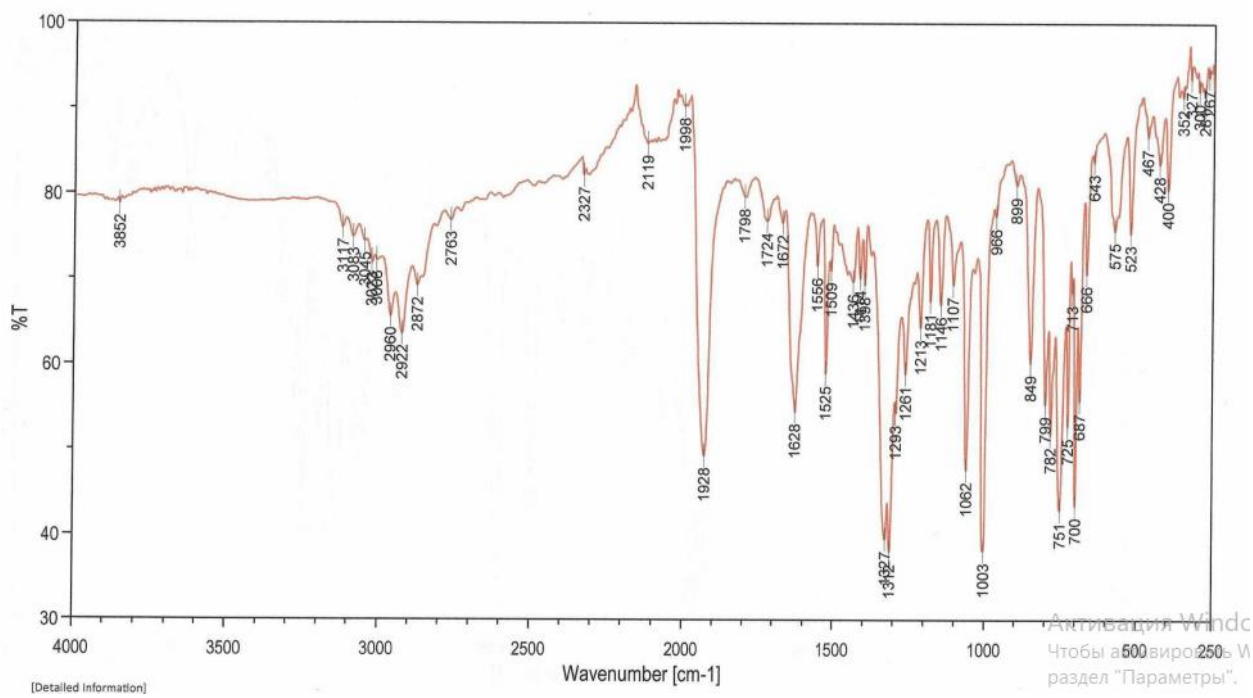


Fig. S35 FT-IR spectrum of hybrid complexes $Mo_6I_8(Py)_6(Ru(CO)Por)_5(Bu_4N)_2$ and $Mo_6I_8(Py)_6(Ru(CO)Por)_6(Bu_4N)_2$.

2.5. Single-Crystal X-ray Analysis

Table S4. Crystal data and structure refinement for **RuDTolP(CO)H_2O** and **RuDTolP(CO)Py**.

Identification code	**RuDTolP(CO)H_2O**	**RuDTolP(CO)Py**
CCDC number	2173217	2173218
Empirical formula	$C_{37}H_{26}Cl_6N_4O_2Ru$	$C_{41.5}H_{29}Cl_{4.49}D_{1.16}N_5ORu$
Formula weight	872.39	876.26
Temperature/K	140(2)	100(2)
Crystal system	monoclinic	trigonal
Space group	C2/c	R-3c
a/Å	21.6281(11)	15.1883(4)
b/Å	9.4437(4)	15.1883(4)
c/Å	19.2876(9)	85.428(4)
α/°	90	90
β/°	114.1080(10)	90
γ/°	90	120
Volume/$Å^3$	3595.9(3)	17066.7(11)
Z	4	18
$\rho_{calc}g/cm^3$	1.611	1.535
μ/mm^{-1}	0.923	0.771
F(000)	1752.0	7965.0
Crystal size/mm^3	0.2 × 0.2 × 0.02	0.36 × 0.2 × 0.16
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.126 to 55.132	4.914 to 61.108
Index ranges	$-28 \le h \le 28$, $-12 \le k \le 12$, $-25 \le l \le 25$	$-17 \le h \le 21$, $-21 \le k \le 18$, $-116 \le l \le 121$
Reflections collected	19912	74663
Independent reflections	4143 [R_{int} = 0.0545, R_{sigma} = 0.0551]	5828 [R_{int} = 0.0696, R_{sigma} = 0.0341]
Data/restraints/parameters	4143/0/272	5828/0/278
Goodness-of-fit on F^2	1.033	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.0831	R_1 = 0.0637, wR_2 = 0.1614
Final R indexes [all data]	R_1 = 0.0616, wR_2 = 0.0902	R_1 = 0.0768, wR_2 = 0.1712
Largest diff. peak/hole / e $Å^{-3}$	0.48/-0.76	2.85/-2.84

Table S5. Bond lengths for **RuDTolP(CO)H_2O**.

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Ru(1)	N(1)^1	2.053(2)		C(3)	C(4)	1.444(4)
Ru(1)	N(1)	2.053(2)		C(3)	C(2)	1.352(4)
Ru(1)	N(2)	2.055(2)		C(10)	C(1)^1	1.401(4)
Ru(1)	N(2)^1	2.055(2)		C(10)	C(9)	1.409(4)
Ru(1)	O(2)	2.090(4)		C(5)	C(4)	1.385(4)
Ru(1)	C(18)	1.988(5)		C(5)	C(6)	1.394(4)
Ru(1)	C(18A)	2.090(4)		C(6)	C(7)	1.445(4)

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ru(1)	O(2A)	1.988(5)		C(8)	C(9)	1.430(4)
Cl(02)	C(19)	1.760(5)		C(8)	C(7)	1.354(4)
Cl(03)	C(19)	1.762(5)		C(1)	C(2)	1.451(3)
Cl(04)	C(19)	1.760(5)		C(17)	C(16)	1.386(4)
N(1)	C(4)	1.372(3)		C(12)	C(13)	1.385(4)
N(1)	C(1)	1.375(3)		C(16)	C(14)	1.381(4)
N(2)	C(6)	1.373(3)		C(13)	C(14)	1.384(4)
N(2)	C(9)	1.376(3)		C(14)	C(15)	1.515(4)
C(18)	O(1)	1.077(5)		Cl(1)	C(19A)	1.745(18)
C(11)	C(10)	1.503(4)		C(19A)	Cl(3)	1.721(17)
C(11)	C(17)	1.392(4)		C(19A)	Cl(4)	1.727(19)
C(11)	C(12)	1.390(4)		O(1A)	C(18A)	1.034(8)

[1]1-X,+Y,3/2-Z

Table S6. Bond angles for **RuDTolP(CO)H_2O**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N(1)[1]	Ru(1)	N(1)	179.45(12)		C(1)[1]	C(10)	C(11)	116.9(2)
N(1)	Ru(1)	N(2)	91.18(8)		C(1)[1]	C(10)	C(9)	125.2(2)
N(1)[1]	Ru(1)	N(2)[1]	91.18(8)		C(9)	C(10)	C(11)	117.8(2)
N(1)[1]	Ru(1)	N(2)	88.80(8)		C(4)	C(5)	C(6)	127.6(2)
N(1)	Ru(1)	N(2)[1]	88.81(8)		N(1)	C(4)	C(3)	109.1(2)
N(1)[1]	Ru(1)	O(2)	89.73(6)		N(1)	C(4)	C(5)	125.6(2)
N(1)	Ru(1)	O(2)	89.73(6)		C(5)	C(4)	C(3)	125.3(2)
N(1)[1]	Ru(1)	C(18A)	89.73(6)		N(2)	C(6)	C(5)	125.4(3)
N(1)	Ru(1)	C(18A)	89.73(6)		N(2)	C(6)	C(7)	109.4(2)
N(2)	Ru(1)	N(2)[1]	176.92(12)		C(5)	C(6)	C(7)	125.3(2)
N(2)[1]	Ru(1)	O(2)	88.46(6)		C(7)	C(8)	C(9)	108.1(2)
N(2)	Ru(1)	O(2)	88.46(6)		N(1)	C(1)	C(10)[1]	125.8(2)
N(2)	Ru(1)	C(18A)	88.46(6)		N(1)	C(1)	C(2)	108.7(2)
N(2)[1]	Ru(1)	C(18A)	88.46(6)		C(10)[1]	C(1)	C(2)	125.5(2)
C(18)	Ru(1)	N(1)[1]	90.27(6)		C(16)	C(17)	C(11)	120.8(3)
C(18)	Ru(1)	N(1)	90.27(6)		C(13)	C(12)	C(11)	121.0(3)
C(18)	Ru(1)	N(2)	91.54(6)		C(3)	C(2)	C(1)	107.3(2)
C(18)	Ru(1)	N(2)[1]	91.54(6)		C(14)	C(16)	C(17)	121.3(3)
C(18)	Ru(1)	O(2)	180.0		N(2)	C(9)	C(10)	124.8(2)
O(2A)	Ru(1)	N(1)	90.27(6)		N(2)	C(9)	C(8)	109.1(2)
O(2A)	Ru(1)	N(2)	91.54(6)		C(10)	C(9)	C(8)	126.1(2)
O(2A)	Ru(1)	C(18A)	180.0		C(14)	C(13)	C(12)	121.2(3)
C(4)	N(1)	Ru(1)	125.16(18)		C(8)	C(7)	C(6)	106.5(2)
C(4)	N(1)	C(1)	107.5(2)		C(16)	C(14)	C(13)	118.0(3)
C(1)	N(1)	Ru(1)	127.35(17)		C(16)	C(14)	C(15)	121.2(3)
C(6)	N(2)	Ru(1)	125.10(18)		C(13)	C(14)	C(15)	120.8(3)
C(6)	N(2)	C(9)	106.9(2)		Cl(02)	C(19)	Cl(03)	110.2(3)

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C(9)	N(2)	Ru(1)	127.97(17)		Cl(02)	C(19)	Cl(04)	109.1(2)
O(1)	C(18)	Ru(1)	180.0		Cl(04)	C(19)	Cl(03)	110.9(3)
C(17)	C(11)	C(10)	121.6(2)		Cl(3)	C(19A)	Cl(1)	107.3(9)
C(12)	C(11)	C(10)	120.7(3)		Cl(3)	C(19A)	Cl(4)	104.3(10)
C(12)	C(11)	C(17)	117.7(3)		Cl(4)	C(19A)	Cl(1)	107.8(9)
C(2)	C(3)	C(4)	107.4(2)		O(1A)	C(18A)	Ru(1)	180.0

[1]1-X,+Y,3/2-Z

Table S7. Bond lengths for **RuDTolP(CO)Py**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ru1	N1[1]	2.052(3)		C14	C16	1.402(6)
Ru1	N1	2.052(3)		C14	C16A	1.62(2)
Ru1	N2[1]	2.052(3)		C14	C13A	1.30(3)
Ru1	N2	2.052(3)		C16	C17	1.400(6)
Ru1	N3	2.200(4)		C16A	C17A	1.40(3)
Ru1	C18	1.830(5)		C19	C20	1.396(5)
O1	C18	1.157(7)		C20	C21	1.385(4)
N1	C1	1.372(5)		Cl1	C22	1.762(4)
N1	C4	1.378(4)		C22	D22	0.9800
N2	C6	1.384(4)		Cl2	C24	1.753(5)
N2	C9	1.361(5)		Cl2A	C24	2.09(3)
N3	C19[1]	1.345(4)		C24	D24	0.9800
N3	C19	1.345(4)		C24	D24A	0.9800
C1	C2	1.445(5)		Cl3	C25[2]	1.599(19)
C1	C10[1]	1.393(5)		Cl3	C25[3]	1.704(18)
C2	C3	1.348(6)		Cl3	C25	1.599(19)
C3	C4	1.456(5)		Cl3	C25[4]	1.704(18)
C4	C5	1.395(5)		Cl3	C25[5]	1.704(18)
C5	C6	1.395(5)		Cl3	C25[6]	1.599(19)
C5	C11	1.499(4)		Cl4	Cl4[4]	2.302(6)
C6	C7	1.448(5)		Cl4	Cl4[5]	2.302(6)
C7	C8	1.349(6)		Cl4	C25	1.78(2)
C8	C9	1.442(5)		Cl4	C25[6]	2.25(2)
C9	C10	1.394(5)		Cl4	C25[5]	1.553(19)
C11	C12	1.379(6)		C25	C25[5]	0.810(17)
C11	C17	1.406(5)		C25	C25[3]	1.61(3)
C11	C17A	1.53(2)		C25	C25[2]	1.39(3)
C11	C12A	1.30(3)		C25	C25[6]	1.39(3)
C12	C13	1.391(6)		C25	C25[4]	0.810(17)
C13	C14	1.364(7)		C12A	C13A	1.44(4)
C14	C15	1.518(5)				

[1]1/3-Y+X,2/3-Y,7/6-Z; [2]-Y,+X-Y,+Z; [3]-X,-Y,1-Z; [4]-Y+X,+X,1-Z; [5]+Y,-X+Y,1-Z; [6]+Y-X,-X,+Z

Table S8. Bond angles for **RuDTolP(CO)Py**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ru1	N1^{1}	175.89(16)		C20	C21	C20^{1}	118.1(5)
N1^{1}	Ru1	N3	87.94(8)		Cl1^{2}	C22	Cl1	112.3(3)
N1	Ru1	N3	87.94(8)		Cl1^{3}	C22	Cl1	112.3(3)
N2	Ru1	N1	88.57(12)		Cl1^{3}	C22	Cl1^{2}	112.3(3)
N2^{1}	Ru1	N1^{1}	88.59(12)		Cl1^{2}	C22	D22	106.5
N2^{1}	Ru1	N1	91.29(12)		Cl1	C22	D22	106.5
N2	Ru1	N1^{1}	91.29(12)		Cl1^{3}	C22	D22	106.5
N2	Ru1	N2^{1}	176.36(16)		Cl2^{4}	C24	Cl2^{5}	108.1(3)
N2^{1}	Ru1	N3	88.18(8)		Cl2^{4}	C24	Cl2	108.1(3)
N2	Ru1	N3	88.18(8)		Cl2	C24	Cl2^{5}	108.1(3)
C18	Ru1	N1^{1}	92.06(8)		Cl2	C24	Cl2A^{4}	74.1(9)
C18	Ru1	N1	92.06(8)		Cl2^{5}	C24	Cl2A^{5}	36.5(9)
C18	Ru1	N2	91.82(8)		Cl2^{4}	C24	Cl2A^{5}	74.1(9)
C18	Ru1	N2^{1}	91.82(8)		Cl2^{4}	C24	Cl2A^{4}	36.5(9)
C18	Ru1	N3	180.0		Cl2	C24	Cl2A^{5}	132.5(9)
C1	N1	Ru1	125.0(2)		Cl2^{5}	C24	Cl2A^{4}	132.4(9)
C1	N1	C4	107.5(3)		Cl2^{5}	C24	D24	110.8
C4	N1	Ru1	127.4(3)		Cl2	C24	D24	110.8
C6	N2	Ru1	127.2(3)		Cl2^{4}	C24	D24	110.8
C9	N2	Ru1	125.3(2)		Cl2A^{4}	C24	Cl2A	106.5(9)
C9	N2	C6	107.4(3)		Cl2A^{5}	C24	Cl2A	106.5(8)
C19	N3	Ru1	121.3(2)		Cl2A^{4}	C24	D24A	112.3
C19^{1}	N3	Ru1	121.3(2)		Cl2A^{5}	C24	D24A	112.3
C19	N3	C19^{1}	117.4(4)		Cl2A	C24	D24A	112.3
N1	C1	C2	109.3(3)		C25^{6}	Cl3	C25^{7}	48.0(10)
N1	C1	C10^{1}	125.5(3)		C25	Cl3	C25^{8}	28.2(4)
C10^{1}	C1	C2	125.3(4)		C25^{9}	Cl3	C25^{8}	58.1(10)
C3	C2	C1	107.2(4)		C25^{8}	Cl3	C25^{7}	48.0(10)
C2	C3	C4	107.7(3)		C25	Cl3	C25^{7}	28.2(4)
N1	C4	C3	108.3(3)		C25^{9}	Cl3	C25	51.4(10)
N1	C4	C5	125.7(3)		C25^{10}	Cl3	C25^{9}	51.4(10)
C5	C4	C3	126.0(3)		C25^{10}	Cl3	C25^{7}	58.1(10)
C4	C5	C6	124.9(3)		C25^{10}	Cl3	C25	51.4(10)
C4	C5	C11	117.6(3)		C25^{10}	Cl3	C25^{8}	28.2(4)
C6	C5	C11	117.4(3)		C25^{9}	Cl3	C25^{7}	28.2(4)
N2	C6	C5	125.7(3)		Cl4^{8}	Cl4	Cl4^{7}	118.55(12)
N2	C6	C7	108.3(3)		C25^{7}	Cl4	Cl4^{7}	50.6(8)
C5	C6	C7	126.0(3)		C25^{9}	Cl4	Cl4^{7}	39.8(4)
C8	C7	C6	107.5(3)		C25	Cl4	Cl4^{7}	77.5(6)
C7	C8	C9	107.2(4)		C25^{7}	Cl4	C25^{9}	12.5(9)
N2	C9	C8	109.5(3)		C25	Cl4	C25^{9}	38.0(10)
N2	C9	C10	125.6(3)		C25^{7}	Cl4	C25	27.0(8)

Table S8. Bond angles for **RuDTolP(CO)Py**							
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Angle/°**
C10	C9	C8	124.9(4)		Cl3	C25	Cl3[6] 121.9(10)
C1[1]	C10	C9	127.3(4)		Cl3	C25	Cl4[10] 84.3(9)
C5	C11	C17A	115.2(8)		Cl3[6]	C25	Cl4[10] 88.1(9)
C12	C11	C5	121.4(3)		Cl3	C25	Cl4 102.1(11)
C12	C11	C17	117.6(3)		Cl3[6]	C25	Cl4 105.8(11)
C17	C11	C5	120.8(3)		Cl3	C25	C25[6] 64.2(12)
C12A	C11	C5	122.4(13)		Cl4[8]	C25	Cl3 123.8(13)
C12A	C11	C17A	116.0(15)		Cl4[8]	C25	Cl4 87.1(8)
C11	C12	C13	121.4(4)		C25[9]	C25	Cl3 64.3(5)
C14	C13	C12	121.5(4)		C25[7]	C25	Cl3 83(2)
C13	C14	C15	121.3(4)		C25[10]	C25	Cl3 64.3(5)
C13	C14	C16	118.3(4)		C25[8]	C25	Cl3 83(2)
C15	C14	C16A	116.6(8)		C25[6]	C25	Cl4 120(2)
C16	C14	C15	120.3(4)		C25[9]	C25	Cl4 90(2)
C13A	C14	C15	122.8(14)		C25[10]	C25	Cl4 150(2)
C13A	C14	C16A	112.2(15)		C25[7]	C25	Cl4 61(2)
C17	C16	C14	120.4(4)		C25[8]	C25	Cl4 174(3)
C17A	C16A	C14	115.4(16)		C25[7]	C25	C25[8] 117.8(14)
C16	C17	C11	120.4(4)		C25[7]	C25	C25[9] 31.1(7)
C16A	C17A	C11	118.3(16)		C25[8]	C25	C25[9] 90.00(3)
O1	C18	Ru1	180.0		C11	C12A	C13A 122(2)
N3	C19	C20	122.9(3)		C14	C13A	C12A 122(3)
C21	C20	C19	119.4(3)				

[1]1/3-Y+X,2/3-Y,7/6-Z; [2]1-Y,1+X-Y,+Z; [3]+Y-X,1-X,+Z; [4]1-Y,+X-Y,+Z; [5]1+Y-X,1-X,+Z; [6]-X,-Y,1-Z; [7]+Y,-X+Y,1-Z; [8]-Y+X,+X,1-Z; [9]+Y-X,-X,+Z; [10]-Y,+X-Y,+Z

In both complexes, the ruthenium porphyrin unit has a typical geometry where the metal ion is located inside the porphyrin ring and adopts a usual octahedral geometry by coordinating a carbonyl ligand and a water or pyridine molecule in the remaining axial position (Table S9). The bond distances Ru–N(Por) span a narrow range of 2.052(3)–2.055(2) Å (Table S9), which is close to bond lengths found in other ruthenium porphyrins[7,8]. The carbonyl ligand is coordinated in a linear fashion, the Ru-C(CO)-O(CO) angle being 180° for both complexes. Curiously, the Ru–C distance is 1.988(5) Å for **RuDTolP(CO)H_2O** but only 1.830(5) Å for **RuDTolP(CO)Py**. The Ru-CO distance in the pyridine adduct is in fact close to that in Ru(TPP)(CO)(Py) (1.838 Å) [7]. In the aqua complex, the Ru–C bond is elongated due to mutual disorder of CO and H_2O ligands over two positions with 0.64 and 0.36 occupancies, and is close to the distance found in Ru(TCPP)(CO)(AcPy) (1.982 Å) [8]. The Ru-N(py) distance is non-exceptional, being equal to 2.200(4) Å [9,10]. The deviation of Ru from the N_4 porphyrin plane is 0.032(1) Å for **RuDTolP(CO)H_2O** and 0.069(2) Å for **RuDTolP(CO)Py**. The porphyrin macrocycles are almost flat, and the root mean square deviation (RMSD) from the mean plane of the 24-atom core of the porphyrin (N_4C_{20}) does not exceed 0.056 Å and 0.064 Å for aqua and pyridine complexes, respectively. A slight elongation along the 5,15-axis in both compounds can be observed, which

is a common motif in the 5,15-porphyrins [11,12]. The $C_5 \cdot\cdot C_{15}$ distance is 6.949(6) Å vs. 6.811(6) Å for $C_{10} \cdot\cdot C_{20}$ in **RuDTolP(CO)H$_2$O** and 6.951(7) Å vs. 6.794(8) Å in **RuDTolP(CO)Py**.

Table S9. Selected bond distances (Å) and angles (°) of **RuDTolP(CO)H$_2$O** and **RuDTolP(CO)Py**

	RuDTolP(CO)H$_2$O	**RuDTolP(CO)Py**
Ru1–N1	2.053(2)	2.052(3)
Ru1–N2	2.055(2)	2.052(3)
Ru–C(CO)	1.988(5)	1.830(5)
C(CO)–O(CO)	1.077(5)	1.157(7)
Ru–N(Py)	–	2.200(4)
Ru–O(H$_2$O)	2.090(4)	–
Ru deviation from N_4 plane	0.032(1)	0.069(2)
RMSD from N_4C_{20} plane	0.056	0.064

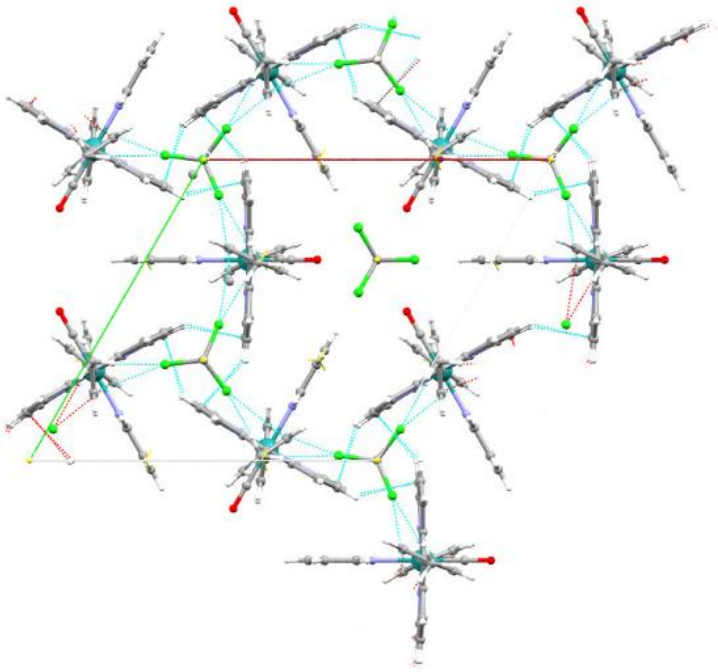
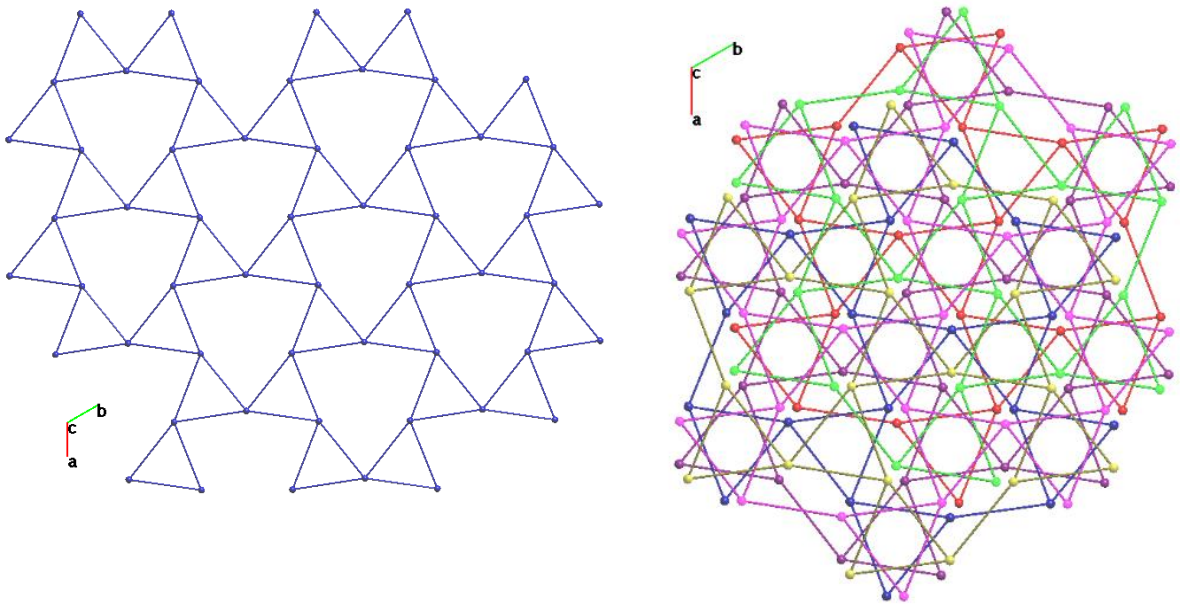


Fig. S36 Crystal packing of **RuDTolP(CO)Py**, view along *c* direction. Blue dotted lines show C–H$\cdot\cdot$ π contacts between porphyrin molecules [C$\cdots$C distances span 3.586–3.663 Å] and contacts with chloroform molecules.



a b

Fig. S37 Crystal packing of **RuDTolP(CO)Py**, simplified using ToposPro,[13] each porphyrin is simplified to the dot in its center of mass, lines show the closest contacts between adjacent molecules. One layer in *ab* plane *(a)*, seven layers in the unit cell, which are stacked with rotation (*b*), each layer is shown by different color.

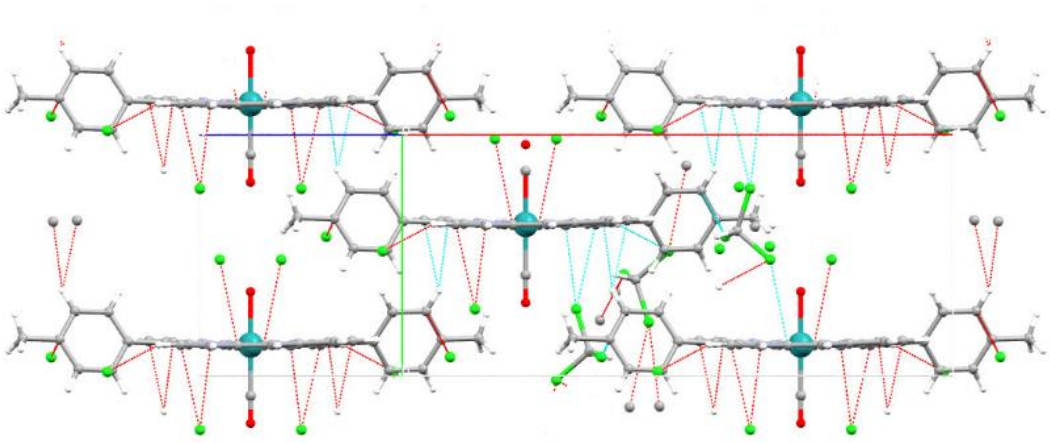


Fig. S38 Crystal packing of **RuDTolP(CO)H_2O**. Blue dotted lines show C−H·· π contacts between tolyl substituent and porphyrin core of adjacent molecule [C··C distances span 3.558−3.802 Å].

Table S10. Crystal data and structure refinement for **CP_6** and **CP_{6+2}**.

Identification code	**CP_6**	**CP_{6+2}**
Empirical formula	$C_{246}H_{168}I_8Mo_6N_{30}O_{18}Ru_6$	$C_{360}H_{286}D_{24}I_8Mo_6N_{40}O_{26}Ru_8$
CCDC number	2173541	2173542
Formula weight	6029.35	8036.01
Temperature/K	100(2)	140(2)
Crystal system	monoclinic	triclinic
Space group	C2/m	P-1
a/Å	27.408(6)	21.1183(7)
b/Å	27.031(5)	22.5011(7)
c/Å	22.388(5)	24.4219(8)

α/°	90	110.2710(10)
β/°	108.56(3)	109.4890(10)
γ/°	90	99.2040(10)
Volume/Å^3	15723(6)	9751.6(6)
Z	2	1
ρ_{calc}g/cm^3	1.274	1.368
μ/mm^{-1}	1.519	1.179
F(000)	5876.0	3986.0
Crystal size/mm^3	0.1 × 0.1 × 0.03	0.4 × 0.3 × 0.25
Radiation	synchrotron (λ = 0.745)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.0 to 53.3	2.456 to 50.7
Index ranges	-33 ≤ h ≤ 33, -32 ≤ k ≤ 32, -26 ≤ l ≤ 26	-25 ≤ h ≤ 25, -27 ≤ k ≤ 27, -29 ≤ l ≤ 29
Reflections collected	86656	164344
Independent reflections	14685 [R_{int} = 0.0639, R_{sigma} = 0.0411]	35665 [R_{int} = 0.0662, R_{sigma} = 0.0707]
Data/restraints/parameters	14685/16/712	35665/130/2009
Goodness-of-fit on F^2	1.038	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0621, wR_2 = 0.1841	R_1 = 0.0783, wR_2 = 0.2172
Final R indexes [all data]	R_1 = 0.1078, wR_2 = 0.2160	R_1 = 0.1387, wR_2 = 0.2802
Largest diff. peak/hole / e Å^{-3}	1.19/-0.79	2.73/-1.48

Table S11. Bond lengths for **CP$_6$**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
I2	Mo2	2.7491(13)		C8	C7	1.508(18)
I2	Mo1	2.7526(10)		C64	C63	1.354(14)
I2	Mo1^1	2.7526(10)		C64	C63^1	1.353(14)
I3	Mo2	2.7978(13)		C26	C25	1.504(17)
I3	Mo1^2	2.7903(12)		C26	C27	1.343(18)
I3	Mo1^3	2.7903(13)		C35	C36	1.3900
I1	Mo2	2.7777(10)		C35	C41	1.3900
I1	Mo1^3	2.8087(11)		C35	C34	1.485(10)
I1	Mo1	2.7918(12)		C36	C37	1.3900
Mo2	Mo1	2.6638(13)		C37	C38	1.3900
Mo2	Mo1^3	2.6582(11)		C38	C40	1.3900
Mo2	Mo1^2	2.6582(11)		C38	C39	1.590(14)
Mo2	Mo1^1	2.6638(13)		C40	C41	1.3900
Mo2	O3	2.097(7)		C10	C9	1.379(14)
Ru1	N5	2.061(7)		C61	C62	1.397(16)
Ru1	N6	2.032(8)		C61	C60	1.460(16)
Ru1	N1	2.168(8)		C6	C5	1.414(15)
Ru1	N4	2.044(8)		C25	C17	1.360(16)
Ru1	N3	2.054(9)		C17	C16	1.403(16)
Ru1	C00Q	1.810(14)		C17	C18	1.537(15)

Table S11. Bond lengths for **CP$_6$**						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Mo1	Mo1^{3}	2.6601(14)		C45	C46	1.365(14)
Mo1	Mo1^{1}	2.643(2)		C45	C44	1.438(15)
Mo1	O1	2.116(7)		C63	C62	1.480(18)
Ru2	N8	2.007(14)		C4	C3	1.410(15)
Ru2	N8^{1}	2.007(14)		C27	C28	1.486(15)
Ru2	N2	2.166(10)		C34	C42	1.377(12)
Ru2	N7^{1}	2.105(13)		C34	C33	1.411(14)
Ru2	N7	2.105(13)		C43	C42	1.462(14)
Ru2	C01R	1.829(14)		C43	C44	1.402(15)
O3	C7	1.194(14)		C29	C28	1.369(15)
O6	C01R	1.170(14)		C48	C49	1.45(2)
N8	C63	1.381(13)		C52	C60	1.416(18)
N8	C60	1.484(19)		C52	C51	1.363(19)
O1	C1	1.190(14)		C52	C53	1.480(18)
C47	C48	1.492(19)		C46	C13	1.402(17)
C47	C48^{1}	1.492(19)		C33	C32	1.455(14)
O5	C00Q	1.172(13)		C16	C15	1.468(17)
N5	C30	1.400(13)		C23	C21	1.37(2)
N5	C33	1.372(12)		C23	C24	1.364(18)
O2	C1	1.277(14)		C50	C49	1.31(2)
N6	C45	1.377(12)		C50	C51	1.417(18)
N6	C42	1.382(11)		C18	C19	1.363(18)
N1	C4	1.353(13)		C18	C24	1.38(2)
N1	C5	1.372(12)		C13	C14	1.464(17)
C30	C29	1.377(14)		C32	C31	1.368(15)
C30	C31	1.429(14)		C12	C11	1.398(17)
N2	C10	1.313(13)		C21	C20	1.38(2)
N2	C11	1.322(15)		C21	C22	1.594(19)
N7	C48	1.386(15)		C20	C19	1.436(16)
N7	C51	1.423(19)		C57	C56	1.56(2)
N4	C25	1.418(12)		C7	O4^{1}	1.435(17)
N4	C28	1.388(13)		C7	O4	1.435(17)
C2	C1	1.487(15)		C15	C14	1.348(19)
C2	C6	1.368(14)		C53	C59	1.3900
C2	C3	1.404(13)		C53	C54	1.3900
N3	C16	1.399(13)		C59	C58	1.3900
N3	C13	1.368(16)		C58	C56	1.3900
C8	C9	1.355(16)		C56	C55	1.3900
C8	C12	1.403(15)		C55	C54	1.3900

^{1}+X,1-Y,+Z; ^{2}1-X,1-Y,1-Z; ^{3}1-X,+Y,1-Z

Table S12. Bond angles for **CP_6**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Mo2	I2	Mo1	57.92(3)		C29	C30	N5	123.9(10)
Mo2	I2	$Mo1^{1}$	57.92(3)		C29	C30	C31	126.5(11)
Mo1	I2	$Mo1^{1}$	57.39(4)		C10	N2	Ru2	122.1(8)
$Mo1^{2}$	I3	Mo2	56.81(3)		C10	N2	C11	117.6(10)
$Mo1^{3}$	I3	Mo2	56.81(3)		C11	N2	Ru2	120.2(7)
$Mo1^{2}$	I3	$Mo1^{3}$	56.54(4)		C48	N7	Ru2	125.5(15)
Mo2	I1	$Mo1^{2}$	56.82(3)		C48	N7	C51	105.3(15)
Mo2	I1	Mo1	57.15(3)		C51	N7	Ru2	129.1(9)
Mo1	I1	$Mo1^{2}$	56.72(3)		C25	N4	Ru1	126.2(7)
I2	Mo2	I3	176.91(4)		C28	N4	Ru1	126.0(7)
I2	Mo2	I1	89.47(2)		C28	N4	C25	107.8(9)
I2	Mo2	$I1^{1}$	89.47(2)		C6	C2	C1	117.2(10)
I1	Mo2	I3	90.42(2)		C6	C2	C3	120.4(11)
$I1^{1}$	Mo2	I3	90.42(2)		C3	C2	C1	122.3(11)
I1	Mo2	$I1^{1}$	175.71(4)		C16	N3	Ru1	127.9(8)
$Mo1^{2}$	Mo2	I2	121.08(4)		C13	N3	Ru1	125.3(7)
Mo1	Mo2	I2	61.11(3)		C13	N3	C16	106.8(9)
$Mo1^{3}$	Mo2	I2	121.08(4)		C9	C8	C12	117.0(10)
$Mo1^{1}$	Mo2	I2	61.11(3)		C9	C8	C7	123.2(10)
$Mo1^{3}$	Mo2	I3	61.45(3)		C12	C8	C7	119.8(12)
$Mo1^{1}$	Mo2	I3	121.42(4)		$C63^{1}$	C64	C63	126(2)
Mo1	Mo2	I3	121.42(4)		O5	C00Q	Ru1	178.8(11)
$Mo1^{2}$	Mo2	I3	61.45(3)		C27	C26	C25	107.4(12)
$Mo1^{3}$	Mo2	$I1^{1}$	62.18(3)		C36	C35	C41	120.0
Mo1	Mo2	I1	61.69(3)		C36	C35	C34	116.8(7)
$Mo1^{2}$	Mo2	$I1^{1}$	121.80(3)		C41	C35	C34	123.1(7)
$Mo1^{1}$	Mo2	$I1^{1}$	61.70(3)		C37	C36	C35	120.0
$Mo1^{2}$	Mo2	I1	62.18(3)		C36	C37	C38	120.0
$Mo1^{1}$	Mo2	I1	121.16(4)		C37	C38	C40	120.0
$Mo1^{3}$	Mo2	I1	121.80(3)		C37	C38	C39	124.3(11)
Mo1	Mo2	$I1^{1}$	121.16(4)		C40	C38	C39	115.6(11)
$Mo1^{3}$	Mo2	$Mo1^{1}$	59.98(3)		C41	C40	C38	120.0
$Mo1^{3}$	Mo2	Mo1	89.60(4)		C40	C41	C35	120.0
Mo1	Mo2	$Mo1^{1}$	59.49(5)		N2	C10	C9	122.9(11)
$Mo1^{2}$	Mo2	$Mo1^{1}$	89.60(4)		C62	C61	C60	106.0(14)
$Mo1^{2}$	Mo2	Mo1	59.98(3)		O1	C1	O2	129.1(13)
$Mo1^{2}$	Mo2	$Mo1^{3}$	59.63(4)		O1	C1	C2	116.1(12)
O3	Mo2	I2	91.7(2)		O2	C1	C2	114.0(12)
O3	Mo2	I3	85.2(2)		C2	C6	C5	118.6(10)
O3	Mo2	I1	87.94(2)		C8	C9	C10	121.0(10)
O3	Mo2	$I1^{1}$	87.94(2)		N4	C25	C26	107.4(11)
O3	Mo2	$Mo1^{1}$	137.35(14)		C17	C25	N4	126.2(11)
O3	Mo2	$Mo1^{3}$	132.98(15)		C17	C25	C26	126.3(12)

Table S12. Bond angles for **CP_6**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O3	Mo2	$Mo1^2$	132.98(15)		C25	C17	C16	126.6(11)
O3	Mo2	Mo1	137.34(14)		C25	C17	C18	117.3(12)
N5	Ru1	N1	87.5(3)		C16	C17	C18	116.0(11)
N6	Ru1	N5	88.4(3)		N6	C45	C44	110.7(9)
N6	Ru1	N1	86.2(3)		C46	C45	N6	126.7(10)
N6	Ru1	N4	173.7(3)		C46	C45	C44	122.5(11)
N6	Ru1	N3	91.0(4)		N8	C63	C62	109.3(14)
N4	Ru1	N5	91.0(3)		C64	C63	N8	124.8(19)
N4	Ru1	N1	87.5(3)		C64	C63	C62	125.3(13)
N4	Ru1	N3	89.2(4)		N1	C4	C3	125.2(10)
N3	Ru1	N5	175.8(4)		C26	C27	C28	108.6(12)
N3	Ru1	N1	88.3(4)		C42	C34	C35	118.3(9)
C00Q	Ru1	N5	93.0(4)		C42	C34	C33	123.5(9)
C00Q	Ru1	N6	92.3(4)		C33	C34	C35	118.2(9)
C00Q	Ru1	N1	178.4(4)		C44	C43	C42	107.6(10)
C00Q	Ru1	N4	94.0(4)		C28	C29	C30	129.7(11)
C00Q	Ru1	N3	91.2(4)		N6	C42	C43	108.1(8)
I2	Mo1	$I3^3$	90.20(3)		C34	C42	N6	127.6(9)
I2	Mo1	I1	89.10(3)		C34	C42	C43	124.0(10)
I2	Mo1	$I1^2$	177.12(4)		N7	C48	C47	120(2)
$I3^3$	Mo1	I1	175.72(4)		N7	C48	C49	112.0(18)
$I3^3$	Mo1	$I1^2$	89.94(3)		C49	C48	C47	127.1(13)
I1	Mo1	$I1^2$	90.55(4)		C61	C62	C63	109.3(11)
$Mo2^3$	Mo1	I2	121.48(4)		C60	C52	C53	119.8(13)
Mo2	Mo1	I2	60.97(3)		C51	C52	C60	124.5(18)
$Mo2^3$	Mo1	$I3^3$	61.73(3)		C51	C52	C53	115.6(14)
Mo2	Mo1	$I3^3$	121.96(4)		N1	C5	C6	123.4(10)
Mo2	Mo1	I1	61.16(3)		C45	C46	C13	126.5(11)
$Mo2^3$	Mo1	I1	122.07(3)		C43	C44	C45	105.6(11)
$Mo2^3$	Mo1	$I1^2$	61.00(3)		N5	C33	C34	125.4(9)
Mo2	Mo1	$I1^2$	121.22(3)		N5	C33	C32	108.7(10)
$Mo2^3$	Mo1	Mo2	90.40(4)		C34	C33	C32	125.8(10)
$Mo2^3$	Mo1	$Mo1^2$	60.12(3)		N3	C16	C17	123.8(11)
$Mo1^2$	Mo1	I2	120.87(4)		N3	C16	C15	108.8(11)
$Mo1^1$	Mo1	I2	61.31(2)		C17	C16	C15	127.3(11)
$Mo1^2$	Mo1	$I3^3$	121.84(4)		C24	C23	C21	126(2)
$Mo1^1$	Mo1	$I3^3$	61.73(2)		C49	C50	C51	115(2)
$Mo1^2$	Mo1	I1	61.96(3)		C19	C18	C17	121.4(14)
$Mo1^2$	Mo1	$I1^2$	61.32(3)		C19	C18	C24	120.9(12)
$Mo1^1$	Mo1	I1	121.39(3)		C24	C18	C17	117.6(14)
$Mo1^1$	Mo1	$I1^2$	121.18(3)		N3	C13	C46	125.4(10)
$Mo1^1$	Mo1	Mo2	60.25(2)		N3	C13	C14	109.5(12)
$Mo1^1$	Mo1	$Mo2^3$	60.18(2)		C46	C13	C14	125.1(14)

Table S12. Bond angles for **CP_6**								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
Mo1[2]	Mo1	Mo2	59.91(3)		C2	C3	C4	116.7(11)
Mo1[1]	Mo1	Mo1[2]	89.998(1)		C31	C32	C33	107.2(10)
O1	Mo1	I2	92.57(18)		O6	C01R	Ru2	177.4(12)
O1	Mo1	I3[3]	88.33(18)		C11	C12	C8	117.9(12)
O1	Mo1	I1[2]	84.55(18)		C23	C21	C20	116.7(15)
O1	Mo1	I1	87.48(18)		C23	C21	C22	118.6(19)
O1	Mo1	Mo2	137.17(17)		C20	C21	C22	124.1(17)
O1	Mo1	Mo2[3]	132.25(17)		C21	C20	C19	118.9(15)
O1	Mo1	Mo1[2]	131.83(18)		N4	C28	C27	108.5(10)
O1	Mo1	Mo1[1]	138.07(18)		C29	C28	N4	124.0(10)
N8	Ru2	N8[1]	88.1(8)		C29	C28	C27	127.4(12)
N8[1]	Ru2	N2	87.2(3)		C50	C49	C48	102.2(12)
N8	Ru2	N2	87.2(3)		C18	C19	C20	120.4(15)
N8	Ru2	N7	88.5(5)		C32	C31	C30	107.9(10)
N8[1]	Ru2	N7[1]	88.5(5)		N2	C11	C12	123.6(10)
N8	Ru2	N7[1]	173.6(4)		O3	C7	C8	114.0(13)
N8[1]	Ru2	N7	173.6(4)		O3	C7	O4[1]	117.1(10)
N7[1]	Ru2	N2	87.2(3)		O3	C7	O4	117.1(10)
N7	Ru2	N2	87.2(3)		O4	C7	C8	112.5(9)
N7[1]	Ru2	N7	94.4(8)		O4[1]	C7	C8	112.5(9)
C01R	Ru2	N8	92.1(4)		O4	C7	O4[1]	79.3(17)
C01R	Ru2	N8[1]	92.1(4)		C61	C60	N8	109.1(12)
C01R	Ru2	N2	178.9(5)		C52	C60	N8	127.1(13)
C01R	Ru2	N7	93.5(4)		C52	C60	C61	123.6(17)
C01R	Ru2	N7[1]	93.5(4)		C52	C51	N7	124.4(16)
C7	O3	Mo2	137.1(9)		C52	C51	C50	131(2)
C63	N8	Ru2	127.6(14)		C50	C51	N7	104.9(15)
C63	N8	C60	106.0(14)		C23	C24	C18	116.5(17)
C60	N8	Ru2	126.2(7)		C14	C15	C16	107.0(12)
C1	O1	Mo1	134.6(9)		C15	C14	C13	107.7(14)
C48[1]	C47	C48	133.7(19)		C59	C53	C52	119.1(9)
C30	N5	Ru1	124.5(7)		C59	C53	C54	120.0
C33	N5	Ru1	127.8(7)		C54	C53	C52	120.9(9)
C33	N5	C30	107.5(8)		C58	C59	C53	120.0
C45	N6	Ru1	125.1(7)		C59	C58	C56	120.0
C45	N6	C42	107.9(8)		C58	C56	C57	124.2(12)
C42	N6	Ru1	126.9(7)		C58	C56	C55	120.0
C4	N1	Ru1	121.9(7)		C55	C56	C57	115.7(12)
C4	N1	C5	115.4(10)		C56	C55	C54	120.0
C5	N1	Ru1	122.1(8)		C55	C54	C53	120.0
N5	C30	C31	108.6(10)					

[1]+X,1-Y,+Z; [2]1-X,+Y,1-Z; [3]1-X,1-Y,1-Z

Table S13. Bond lengths for **CP_{6+2}**						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
I1	Mo1	2.7811(12)		C222	C223	1.33(3)
I1	Mo2	2.7919(11)		C223	C224	1.42(2)
I1	Mo3	2.7838(12)		C224	C225	1.29(3)
I2	Mo1	2.7643(11)		C225	C226	1.55(3)
I2	Mo2	2.7441(10)		C226	C227	1.30(3)
I2	$Mo3^1$	2.7697(12)		C227	C228	1.52(2)
I3	$Mo1^1$	2.8031(11)		C228	C229	1.34(3)
I3	Mo2	2.7898(11)		C228	C234	1.31(3)
I3	$Mo3^1$	2.8042(10)		C229	C230	1.40(3)
I4	Mo1	2.7626(12)		C230	C231	1.34(4)
I4	$Mo2^1$	2.7734(10)		C231	C232	1.59(3)
I4	$Mo3^1$	2.7782(10)		C231	C233	1.38(4)
Ru11	N11	2.187(8)		C233	C234	1.39(3)
Ru11	N12	2.048(10)		C301	C302	1.43(3)
Ru11	N13	2.046(9)		C301	C327	1.42(3)
Ru11	N14	2.035(9)		C302	C303	1.29(3)
Ru11	N15	2.049(9)		C303	C304	1.42(2)
Ru11	C11	1.814(12)		C304	C305	1.41(2)
Ru21	N21	2.158(11)		C305	C306	1.408(18)
Ru21	N22	2.045(14)		C306	C307	1.408(19)
Ru21	N23	2.055(10)		C307	C308	1.318(18)
Ru21	N24	2.020(12)		C308	C309	1.429(19)
Ru21	N25	2.061(12)		C309	C310	1.397(18)
Ru21	C21	1.830(15)		C310	C311	1.514(15)
Ru31	N31	2.167(9)		C310	C318	1.379(17)
Ru31	N32	2.046(14)		C311	C312	1.372(16)
Ru31	N33	2.065(11)		C311	C317	1.388(16)
Ru31	N34	2.046(11)		C312	C313	1.380(16)
Ru31	N35	2.065(13)		C313	C314	1.381(17)
Ru31	C31	1.818(13)		C314	C315	1.516(16)
Mo1	Mo2	2.6712(11)		C314	C316	1.353(17)
Mo1	$Mo2^1$	2.6777(13)		C316	C317	1.388(16)
Mo1	Mo3	2.6685(11)		C318	C319	1.467(18)
Mo1	$Mo3^1$	2.6587(11)		C319	C320	1.337(18)
Mo1	O11	2.111(7)		C320	C321	1.45(2)
Mo2	$Mo3^1$	2.6732(13)		C321	C322	1.401(18)
Mo2	Mo3	2.6634(12)		C322	C323	1.40(2)
Mo2	O21	2.120(8)		C323	C324	1.47(2)
Mo3	O31	2.103(7)		C324	C325	1.34(3)
O11	C20	1.262(12)		C325	C326	1.41(3)
O12	C20	1.228(13)		C326	C327	1.39(3)
O13	C11	1.179(14)		C327	C328	1.509(19)
O21	C27	1.274(16)		C328	C329	1.40(3)

Table S13. Bond lengths for **CP_{6+2}**						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
O22	C27	1.221(17)		C328	C334	1.36(3)
O23	C21	1.141(15)		C329	C330	1.39(2)
O31	C37	1.254(12)		C330	C331	1.42(5)
O32	C37	1.255(12)		C331	C332	1.52(2)
O33	C31	1.167(14)		C331	C333	1.43(5)
N11	C13	1.342(13)		C333	C334	1.46(2)
N11	C14	1.333(13)		Ru41	O41	2.199(8)
N12	C101	1.406(15)		Ru41	N41	2.074(10)
N12	C104	1.374(15)		Ru41	N42	2.057(10)
N13	C106	1.375(14)		Ru41	N43	2.051(9)
N13	C109	1.375(14)		Ru41	N44	2.034(10)
N14	C118	1.395(13)		Ru41	C41	1.785(13)
N14	C121	1.387(13)		O42	C41	1.174(14)
N15	C123	1.386(15)		N41	C401	1.355(16)
N15	C126	1.390(15)		N41	C404	1.366(17)
N21	C23	1.346(18)		N42	C406	1.371(15)
N21	C24	1.355(16)		N42	C409	1.372(14)
N22	C201	1.403(19)		N43	C418	1.378(14)
N22	C204	1.31(2)		N43	C421	1.371(14)
N23	C206	1.363(17)		N44	C423	1.364(15)
N23	C209	1.400(15)		N44	C426	1.394(15)
N24	C218	1.404(15)		C401	C402	1.433(19)
N24	C221	1.395(17)		C401	C427	1.407(19)
N25	C223	1.37(2)		C402	C403	1.33(2)
N25	C226	1.39(2)		C403	C404	1.431(18)
N31	C33	1.331(14)		C404	C405	1.37(2)
N31	C34	1.350(14)		C405	C406	1.398(18)
N32	C301	1.397(18)		C406	C407	1.434(19)
N32	C304	1.34(2)		C407	C408	1.356(19)
N33	C306	1.375(18)		C408	C409	1.443(17)
N33	C309	1.380(14)		C409	C410	1.406(16)
N34	C318	1.382(14)		C410	C411	1.494(16)
N34	C321	1.371(16)		C410	C418	1.400(15)
N35	C323	1.34(2)		C411	C412	1.420(16)
N35	C326	1.360(18)		C411	C417	1.380(17)
C12	C13	1.376(13)		C412	C413	1.385(17)
C12	C16	1.388(14)		C413	C414	1.377(19)
C14	C15	1.370(14)		C414	C415	1.510(17)
C15	C16	1.387(14)		C414	C416	1.397(19)
C16	C20	1.525(13)		C416	C417	1.383(17)
C22	C23	1.39(2)		C418	C419	1.433(15)
C22	C26	1.41(2)		C419	C420	1.343(15)
C24	C25	1.380(18)		C420	C421	1.459(15)

Table S13. Bond lengths for **CP_{6+2}**						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
C25	C26	1.325(17)		C421	C422	1.389(16)
C26	C27	1.520(19)		C422	C423	1.415(16)
C32	C33	1.364(16)		C423	C424	1.459(16)
C32	C36	1.384(14)		C424	C425	1.354(19)
C34	C35	1.354(15)		C425	C426	1.393(18)
C35	C36	1.388(14)		C426	C427	1.396(18)
C36	C37	1.481(14)		C427	C428	1.509(18)
C101	C102	1.441(19)		C428	C429	1.340(17)
C101	C127	1.343(18)		C428	C434	1.34(2)
C102	C103	1.364(19)		C429	C430	1.420(19)
C103	C104	1.435(18)		C430	C431	1.33(2)
C104	C105	1.396(17)		C431	C432	1.51(2)
C105	C106	1.397(18)		C431	C433	1.38(2)
C106	C107	1.431(16)		C433	C434	1.42(2)
C107	C108	1.314(17)		O1	C6	1.19(3)
C108	C109	1.449(15)		C1	D1A	0.9800
C109	C110	1.408(16)		C1	D1B	0.9800
C110	C111	1.475(16)		C1	D1C	0.9800
C110	C118	1.428(15)		C1	C6	1.52(5)
C111	C112	1.402(16)		C6	C10	1.43(4)
C111	C117	1.407(15)		C10	D10A	0.9800
C112	C113	1.376(16)		C10	D10B	0.9800
C113	C114	1.371(17)		C10	D10C	0.9800
C114	C115	1.513(18)		O2	C2	1.24(3)
C114	C116	1.380(19)		C2	C17	1.42(4)
C116	C117	1.375(17)		C2	C18	1.37(4)
C118	C119	1.408(15)		C17	D17A	0.9800
C119	C120	1.359(15)		C17	D17B	0.9800
C120	C121	1.424(16)		C17	D17C	0.9800
C121	C122	1.389(15)		C18	D18A	0.9800
C122	C123	1.399(16)		C18	D18B	0.9800
C123	C124	1.438(15)		C18	D18C	0.9800
C124	C125	1.341(18)		O5	C7	1.29(6)
C125	C126	1.437(17)		C3	D3A	0.9800
C126	C127	1.398(18)		C3	D3B	0.9800
C127	C128	1.49(2)		C3	D3C	0.9800
C128	C129	1.36(3)		C3	C7	1.47(5)
C128	C134	1.42(2)		C7	C8	1.73(8)
C129	C130	1.38(3)		O15	C5	1.19(3)
C130	C131	1.25(5)		C4	D4A	0.9800
C131	C132	1.56(3)		C4	D4B	0.9800
C131	C133	1.45(4)		C4	D4C	0.9800
C133	C134	1.40(3)		C4	C5	1.33(4)

Table S13. Bond lengths for **CP$_{6+2}$**						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
C201	C202	1.40(3)		C5	C9	1.48(4)
C201	C227	1.43(3)		C9	D9A	0.9800
C202	C203	1.33(3)		C9	D9B	0.9800
C203	C204	1.49(2)		C9	D9C	0.9800
C204	C205	1.40(2)		N51	C51	1.53(2)
C205	C206	1.37(2)		N51	C71	1.55(2)
C206	C207	1.451(18)		N51	C81	1.56(2)
C207	C208	1.350(18)		N51	C61	1.57(3)
C208	C209	1.441(17)		C51	C52	1.46(2)
C209	C210	1.376(17)		C71	C72	1.55(2)
C210	C211	1.509(16)		C81	C82	1.49(3)
C210	C218	1.393(17)		C52	C53	1.46(3)
C211	C212	1.389(17)		C62	C61	1.53(3)
C211	C217	1.375(16)		C62	C63	1.58(3)
C212	C213	1.382(17)		C73	C72	1.48(2)
C213	C214	1.404(19)		C73	C74	1.51(2)
C214	C215	1.512(18)		C63	C64	1.49(3)
C214	C216	1.401(18)		C53	C54	1.52(3)
C216	C217	1.391(16)		C84	C83	1.43(3)
C218	C219	1.436(18)		C83	C82	1.46(3)
C219	C220	1.384(18)		C8	D8A	0.9800
C220	C221	1.41(2)		C8	D8B	0.9800
C221	C222	1.410(19)		C8	D8C	0.9800

[1]1-X,1-Y,1-Z

Table S14. Bond angles for **CP$_{6+2}$**								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
Mo1	I1	Mo2	57.28(3)		C129	C128	C127	124.4(19)
Mo1	I1	Mo3	57.31(3)		C129	C128	C134	115.4(18)
Mo3	I1	Mo2	57.07(3)		C134	C128	C127	120.2(18)
Mo1	I2	Mo3[1]	57.43(3)		C128	C129	C130	127(3)
Mo2	I2	Mo1	58.01(3)		C131	C130	C129	120(4)
Mo2	I2	Mo3[1]	58.00(3)		C130	C131	C132	125(4)
Mo1[1]	I3	Mo3[1]	56.84(3)		C130	C131	C133	119(3)
Mo2	I3	Mo1[1]	57.21(3)		C133	C131	C132	116(4)
Mo2	I3	Mo3[1]	57.09(3)		C134	C133	C131	121(3)
Mo1	I4	Mo2[1]	57.85(3)		C133	C134	C128	117(2)
Mo1	I4	Mo3[1]	57.35(3)		N22	C201	C202	107.3(19)
Mo2[1]	I4	Mo3[1]	57.34(3)		N22	C201	C227	125.5(18)
N12	Ru11	N11	87.8(3)		C202	C201	C227	127.1(17)
N12	Ru11	N15	88.8(4)		C203	C202	C201	109.4(17)
N13	Ru11	N11	88.5(3)		C202	C203	C204	105.9(19)
N13	Ru11	N12	90.3(4)		N22	C204	C203	108.3(16)

Table S14. Bond angles for **CP_{6+2}**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N13	Ru11	N15	175.4(3)		N22	C204	C205	126.4(15)
N14	Ru11	N11	88.7(3)		C205	C204	C203	125.4(19)
N14	Ru11	N12	176.5(3)		C206	C205	C204	127.6(16)
N14	Ru11	N13	89.1(3)		N23	C206	C205	124.8(13)
N14	Ru11	N15	91.5(4)		N23	C206	C207	108.1(12)
N15	Ru11	N11	86.9(3)		C205	C206	C207	127.0(15)
C11	Ru11	N11	176.3(5)		C208	C207	C206	107.9(12)
C11	Ru11	N12	95.4(5)		C207	C208	C209	108.0(12)
C11	Ru11	N13	93.3(4)		N23	C209	C208	107.4(11)
C11	Ru11	N14	88.1(5)		C210	C209	N23	125.2(11)
C11	Ru11	N15	91.3(4)		C210	C209	C208	127.3(11)
N22	Ru21	N21	88.2(5)		C209	C210	C211	119.3(11)
N22	Ru21	N23	90.9(5)		C209	C210	C218	126.1(11)
N22	Ru21	N25	89.3(6)		C218	C210	C211	114.5(11)
N23	Ru21	N21	87.5(4)		C212	C211	C210	120.2(11)
N23	Ru21	N25	174.6(4)		C217	C211	C210	121.8(11)
N24	Ru21	N21	87.8(4)		C217	C211	C212	117.8(11)
N24	Ru21	N22	176.0(5)		C213	C212	C211	121.2(12)
N24	Ru21	N23	89.0(4)		C212	C213	C214	121.4(12)
N24	Ru21	N25	90.4(5)		C213	C214	C215	122.1(13)
N25	Ru21	N21	87.1(4)		C216	C214	C213	116.8(12)
C21	Ru21	N21	179.0(6)		C216	C214	C215	121.1(13)
C21	Ru21	N22	92.8(6)		C217	C216	C214	120.7(13)
C21	Ru21	N23	92.5(5)		C211	C217	C216	121.9(12)
C21	Ru21	N24	91.2(5)		N24	C218	C219	109.6(11)
C21	Ru21	N25	92.9(5)		C210	C218	N24	124.5(12)
N32	Ru31	N31	88.4(4)		C210	C218	C219	125.7(11)
N32	Ru31	N33	91.4(5)		C220	C219	C218	106.9(12)
N32	Ru31	N35	88.0(6)		C219	C220	C221	107.4(13)
N33	Ru31	N31	88.5(4)		N24	C221	C220	110.7(12)
N34	Ru31	N31	85.6(4)		N24	C221	C222	122.7(15)
N34	Ru31	N32	173.9(4)		C222	C221	C220	126.6(15)
N34	Ru31	N33	88.7(4)		C223	C222	C221	128.7(17)
N34	Ru31	N35	91.4(5)		N25	C223	C224	110.4(19)
N35	Ru31	N31	87.5(4)		C222	C223	N25	126.2(14)
N35	Ru31	N33	176.0(4)		C222	C223	C224	123(2)
C31	Ru31	N31	177.7(6)		C225	C224	C223	108(2)
C31	Ru31	N32	89.7(5)		C224	C225	C226	109.2(17)
C31	Ru31	N33	90.3(5)		N25	C226	C225	103.1(19)
C31	Ru31	N34	96.3(5)		C227	C226	N25	127.7(18)
C31	Ru31	N35	93.7(5)		C227	C226	C225	128.9(18)
I1	Mo1	$I3^1$	89.86(3)		C201	C227	C228	115(2)
I2	Mo1	I1	89.75(4)		C226	C227	C201	125.3(16)

Table S14. Bond angles for **CP_{6+2}**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
I2	Mo1	I3[1]	177.25(4)		C226	C227	C228	119(2)
I4	Mo1	I1	176.25(4)		C229	C228	C227	123(2)
I4	Mo1	I2	90.81(3)		C234	C228	C227	122.5(19)
I4	Mo1	I3[1]	89.41(3)		C234	C228	C229	112(2)
Mo2	Mo1	I1	61.56(3)		C228	C229	C230	122(3)
Mo2[1]	Mo1	I1	121.37(4)		C231	C230	C229	119(3)
Mo2	Mo1	I2	60.62(3)		C230	C231	C232	116(3)
Mo2[1]	Mo1	I2	121.27(4)		C230	C231	C233	109(3)
Mo2[1]	Mo1	I3[1]	61.14(3)		C233	C231	C232	119(3)
Mo2	Mo1	I3[1]	121.43(4)		C231	C233	C234	118(3)
Mo2	Mo1	I4	121.82(4)		C228	C234	C233	124(3)
Mo2[1]	Mo1	I4	61.28(3)		N32	C301	C302	108.6(19)
Mo2	Mo1	Mo2[1]	90.20(4)		N32	C301	C327	122.3(17)
Mo3	Mo1	I1	61.40(3)		C327	C301	C302	129.1(15)
Mo3[1]	Mo1	I1	121.76(4)		C303	C302	C301	107.3(15)
Mo3	Mo1	I2	120.45(4)		C302	C303	C304	109(2)
Mo3[1]	Mo1	I2	61.39(3)		N32	C304	C303	109.4(17)
Mo3[1]	Mo1	I3[1]	121.02(4)		N32	C304	C305	126.2(15)
Mo3	Mo1	I3[1]	61.60(3)		C305	C304	C303	124(2)
Mo3[1]	Mo1	I4	61.62(3)		C306	C305	C304	127.0(17)
Mo3	Mo1	I4	121.27(4)		N33	C306	C305	124.5(14)
Mo3[1]	Mo1	Mo2[1]	59.88(3)		N33	C306	C307	109.0(12)
Mo3	Mo1	Mo2	59.84(3)		C307	C306	C305	126.6(16)
Mo3	Mo1	Mo2[1]	60.00(3)		C308	C307	C306	107.6(14)
Mo3[1]	Mo1	Mo2	60.20(3)		C307	C308	C309	109.5(12)
Mo3[1]	Mo1	Mo3	89.74(4)		N33	C309	C308	106.7(12)
O11	Mo1	I1	88.9(2)		N33	C309	C310	124.3(12)
O11	Mo1	I2	91.78(19)		C310	C309	C308	129.0(11)
O11	Mo1	I3[1]	85.49(19)		C309	C310	C311	116.6(11)
O11	Mo1	I4	87.3(2)		C318	C310	C309	126.1(11)
O11	Mo1	Mo2[1]	132.3(2)		C318	C310	C311	117.1(11)
O11	Mo1	Mo2	137.5(2)		C312	C311	C310	119.1(10)
O11	Mo1	Mo3[1]	136.49(19)		C312	C311	C317	118.6(11)
O11	Mo1	Mo3	133.65(19)		C317	C311	C310	122.2(10)
I2	Mo2	I1	89.94(3)		C311	C312	C313	120.5(12)
I2	Mo2	I3	89.87(3)		C312	C313	C314	121.1(12)
I2	Mo2	I4[1]	176.90(4)		C313	C314	C315	120.8(12)
I3	Mo2	I1	176.82(5)		C316	C314	C313	118.1(11)
I4[1]	Mo2	I1	90.56(3)		C316	C314	C315	121.0(12)
I4[1]	Mo2	I3	89.47(3)		C314	C316	C317	121.9(12)
Mo1	Mo2	I1	61.16(3)		C311	C317	C316	119.7(12)
Mo1[1]	Mo2	I1	121.02(4)		N34	C318	C319	107.4(11)
Mo1	Mo2	I2	61.37(3)		C310	C318	N34	125.7(12)

Table S14. Bond angles for **CP_{6+2}**								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
$Mo1^1$	Mo2	I2	121.29(4)		C310	C318	C319	126.9(11)
Mo1	Mo2	I3	121.38(4)		C320	C319	C318	108.8(12)
$Mo1^1$	Mo2	I3	61.65(3)		C319	C320	C321	106.5(13)
$Mo1^1$	Mo2	$I4^1$	60.87(3)		N34	C321	C320	109.9(11)
Mo1	Mo2	$I4^1$	121.45(4)		N34	C321	C322	124.9(14)
Mo1	Mo2	$Mo1^1$	89.80(4)		C322	C321	C320	125.2(14)
Mo1	Mo2	$Mo3^1$	59.67(3)		C321	C322	C323	126.6(15)
$Mo3^1$	Mo2	I1	120.82(4)		N35	C323	C322	127.1(14)
Mo3	Mo2	I1	61.31(3)		N35	C323	C324	109.8(16)
Mo3	Mo2	I2	121.39(4)		C322	C323	C324	123.0(19)
$Mo3^1$	Mo2	I2	61.48(3)		C325	C324	C323	103.9(19)
Mo3	Mo2	I3	121.34(4)		C324	C325	C326	110.3(16)
$Mo3^1$	Mo2	I3	61.73(3)		N35	C326	C325	108.2(19)
$Mo3^1$	Mo2	$I4^1$	120.69(4)		N35	C326	C327	124.9(17)
Mo3	Mo2	$I4^1$	61.42(3)		C327	C326	C325	126.5(16)
Mo3	Mo2	Mo1	60.03(3)		C301	C327	C328	117.5(19)
$Mo3^1$	Mo2	$Mo1^1$	59.83(3)		C326	C327	C301	126.9(14)
Mo3	Mo2	$Mo1^1$	59.71(3)		C326	C327	C328	116(2)
Mo3	Mo2	$Mo3^1$	89.54(4)		C329	C328	C327	121.7(17)
O21	Mo2	I1	88.4(2)		C334	C328	C327	119.3(18)
O21	Mo2	I2	91.5(2)		C334	C328	C329	119.0(16)
O21	Mo2	I3	88.4(2)		C330	C329	C328	122(2)
O21	Mo2	$I4^1$	85.4(2)		C329	C330	C331	119(2)
O21	Mo2	Mo1	137.1(2)		C330	C331	C332	119(3)
O21	Mo2	$Mo1^1$	133.0(2)		C330	C331	C333	121.6(17)
O21	Mo2	$Mo3^1$	137.7(2)		C333	C331	C332	119(3)
O21	Mo2	Mo3	132.7(2)		C331	C333	C334	115(3)
I1	Mo3	$I3^1$	89.77(3)		C328	C334	C333	123(2)
$I2^1$	Mo3	I1	176.65(4)		N41	Ru41	O41	87.7(4)
$I2^1$	Mo3	$I3^1$	89.05(3)		N42	Ru41	O41	89.9(3)
$I2^1$	Mo3	$I4^1$	90.37(3)		N42	Ru41	N41	90.8(4)
$I4^1$	Mo3	I1	90.63(4)		N43	Ru41	O41	86.9(3)
$I4^1$	Mo3	$I3^1$	176.74(4)		N43	Ru41	N41	174.5(4)
Mo1	Mo3	I1	61.29(3)		N43	Ru41	N42	88.5(4)
$Mo1^1$	Mo3	I1	122.03(4)		N44	Ru41	O41	84.2(3)
Mo1	Mo3	$I2^1$	120.68(4)		N44	Ru41	N41	88.5(4)
$Mo1^1$	Mo3	$I2^1$	61.18(3)		N44	Ru41	N42	174.1(4)
$Mo1^1$	Mo3	$I3^1$	121.29(4)		N44	Ru41	N43	91.7(4)
Mo1	Mo3	$I3^1$	61.56(3)		C41	Ru41	O41	177.4(5)
$Mo1^1$	Mo3	$I4^1$	61.03(3)		C41	Ru41	N41	93.2(5)
Mo1	Mo3	$I4^1$	121.37(4)		C41	Ru41	N42	92.5(5)
$Mo1^1$	Mo3	Mo1	90.26(4)		C41	Ru41	N43	92.3(5)
$Mo1^1$	Mo3	$Mo2^1$	60.13(3)		C41	Ru41	N44	93.4(5)

Table S14. Bond angles for **CP_{6+2}**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Mo1	Mo3	Mo2[1]	60.17(3)		C401	N41	Ru41	127.3(9)
Mo1[1]	Mo3	Mo2	60.41(3)		C401	N41	C404	109.0(11)
Mo2[1]	Mo3	I1	121.44(4)		C404	N41	Ru41	123.6(9)
Mo2	Mo3	I1	61.62(3)		C406	N42	Ru41	125.2(8)
Mo2	Mo3	I2[1]	121.60(4)		C406	N42	C409	106.7(10)
Mo2[1]	Mo3	I2[1]	60.52(3)		C409	N42	Ru41	127.9(8)
Mo2[1]	Mo3	I3[1]	61.18(3)		C418	N43	Ru41	128.0(7)
Mo2	Mo3	I3[1]	121.68(4)		C421	N43	Ru41	124.1(7)
Mo2	Mo3	I4[1]	61.24(3)		C421	N43	C418	107.9(9)
Mo2[1]	Mo3	I4[1]	121.15(4)		C423	N44	Ru41	125.2(8)
Mo2	Mo3	Mo1	60.13(3)		C423	N44	C426	106.1(10)
Mo2	Mo3	Mo2[1]	90.47(4)		C426	N44	Ru41	128.6(8)
O31	Mo3	I1	87.7(2)		O42	C41	Ru41	179.2(12)
O31	Mo3	I2[1]	89.0(2)		N41	C401	C402	106.9(13)
O31	Mo3	I3[1]	85.7(2)		N41	C401	C427	125.4(12)
O31	Mo3	I4[1]	91.1(2)		C427	C401	C402	127.6(13)
O31	Mo3	Mo1	132.91(18)		C403	C402	C401	109.2(13)
O31	Mo3	Mo1[1]	136.78(18)		C402	C403	C404	106.6(14)
O31	Mo3	Mo2[1]	133.2(2)		N41	C404	C403	108.2(14)
O31	Mo3	Mo2	136.3(2)		N41	C404	C405	127.3(12)
C20	O11	Mo1	137.8(7)		C405	C404	C403	124.5(14)
C27	O21	Mo2	133.7(8)		C404	C405	C406	126.9(13)
C37	O31	Mo3	129.2(7)		N42	C406	C405	125.2(13)
C13	N11	Ru11	120.8(7)		N42	C406	C407	110.9(11)
C14	N11	Ru11	123.6(7)		C405	C406	C407	123.9(13)
C14	N11	C13	115.7(9)		C408	C407	C406	105.3(12)
C101	N12	Ru11	126.9(8)		C407	C408	C409	108.8(12)
C104	N12	Ru11	127.0(8)		N42	C409	C408	108.2(11)
C104	N12	C101	106.1(10)		N42	C409	C410	125.2(10)
C106	N13	Ru11	125.9(8)		C410	C409	C408	126.6(11)
C106	N13	C109	106.2(9)		C409	C410	C411	116.4(10)
C109	N13	Ru11	127.8(7)		C418	C410	C409	125.2(10)
C118	N14	Ru11	128.5(7)		C418	C410	C411	118.3(10)
C121	N14	Ru11	125.5(7)		C412	C411	C410	120.5(11)
C121	N14	C118	105.8(9)		C417	C411	C410	121.4(11)
C123	N15	Ru11	124.9(8)		C417	C411	C412	118.1(11)
C123	N15	C126	107.9(9)		C413	C412	C411	121.2(12)
C126	N15	Ru11	127.2(8)		C414	C413	C412	120.1(12)
C23	N21	Ru21	121.3(10)		C413	C414	C415	120.1(13)
C23	N21	C24	114.7(12)		C413	C414	C416	118.8(12)
C24	N21	Ru21	123.8(8)		C416	C414	C415	121.2(15)
C201	N22	Ru21	125.4(15)		C417	C416	C414	121.6(14)
C204	N22	Ru21	125.4(10)		C411	C417	C416	120.2(12)

Table S14. Bond angles for **CP_{6+2}**								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
C204	N22	C201	109.1(16)		N43	C418	C410	125.1(10)
C206	N23	Ru21	124.7(8)		N43	C418	C419	108.6(9)
C206	N23	C209	108.5(10)		C410	C418	C419	126.2(10)
C209	N23	Ru21	126.8(9)		C420	C419	C418	108.1(10)
C218	N24	Ru21	127.9(9)		C419	C420	C421	107.3(10)
C221	N24	Ru21	126.8(9)		N43	C421	C420	108.0(10)
C221	N24	C218	105.3(11)		N43	C421	C422	127.3(10)
C223	N25	Ru21	125.1(10)		C422	C421	C420	124.6(11)
C223	N25	C226	108.9(14)		C421	C422	C423	124.9(11)
C226	N25	Ru21	126.0(14)		N44	C423	C422	126.3(10)
C33	N31	Ru31	121.5(7)		N44	C423	C424	109.3(11)
C33	N31	C34	117.5(10)		C422	C423	C424	124.4(13)
C34	N31	Ru31	121.0(7)		C425	C424	C423	106.0(12)
C301	N32	Ru31	128.8(15)		C424	C425	C426	108.6(12)
C304	N32	Ru31	125.5(10)		N44	C426	C427	123.7(12)
C304	N32	C301	105.5(15)		C425	C426	N44	110.0(12)
C306	N33	Ru31	125.4(9)		C425	C426	C427	126.2(12)
C306	N33	C309	107.3(11)		C401	C427	C428	117.4(12)
C309	N33	Ru31	127.3(10)		C426	C427	C401	126.2(12)
C318	N34	Ru31	126.9(9)		C426	C427	C428	116.4(13)
C321	N34	Ru31	125.6(9)		C429	C428	C427	122.6(13)
C321	N34	C318	107.5(11)		C434	C428	C427	119.8(12)
C323	N35	Ru31	124.3(9)		C434	C428	C429	117.1(14)
C323	N35	C326	107.8(15)		C428	C429	C430	120.2(14)
C326	N35	Ru31	128.0(14)		C431	C430	C429	123.9(13)
O13	C11	Ru11	172.7(13)		C430	C431	C432	121.4(15)
C13	C12	C16	118.6(10)		C430	C431	C433	113.8(15)
N11	C13	C12	124.6(11)		C433	C431	C432	122.9(17)
N11	C14	C15	124.1(10)		C431	C433	C434	121.4(17)
C14	C15	C16	119.6(11)		C428	C434	C433	121.1(15)
C12	C16	C20	120.1(9)		D1A	C1	D1B	109.5
C15	C16	C12	117.3(9)		D1A	C1	D1C	109.5
C15	C16	C20	122.5(10)		D1B	C1	D1C	109.5
O11	C20	C16	112.1(9)		C6	C1	D1A	109.5
O12	C20	O11	129.1(9)		C6	C1	D1B	109.5
O12	C20	C16	118.7(9)		C6	C1	D1C	109.5
O23	C21	Ru21	178.3(14)		O1	C6	C1	123(3)
C23	C22	C26	120.4(14)		O1	C6	C10	122(3)
N21	C23	C22	122.4(15)		C10	C6	C1	115(3)
N21	C24	C25	124.8(12)		C6	C10	D10A	109.5
C26	C25	C24	120.2(13)		C6	C10	D10B	109.5
C22	C26	C27	120.7(13)		C6	C10	D10C	109.5
C25	C26	C22	117.0(13)		D10A	C10	D10B	109.5

Table S14. Bond angles for **CP_{6+2}**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C25	C26	C27	122.2(14)		D10A	C10	D10C	109.5
O21	C27	C26	110.6(12)		D10B	C10	D10C	109.5
O22	C27	O21	129.3(14)		O2	C2	C17	117(3)
O22	C27	C26	120.1(14)		O2	C2	C18	118(2)
O33	C31	Ru31	174.9(14)		C18	C2	C17	125(3)
C33	C32	C36	120.3(10)		C2	C17	D17A	109.5
N31	C33	C32	122.3(10)		C2	C17	D17B	109.5
N31	C34	C35	123.2(10)		C2	C17	D17C	109.5
C34	C35	C36	119.4(10)		D17A	C17	D17B	109.5
C32	C36	C35	117.2(9)		D17A	C17	D17C	109.5
C32	C36	C37	122.0(9)		D17B	C17	D17C	109.5
C35	C36	C37	120.8(9)		C2	C18	D18A	109.5
O31	C37	O32	124.3(10)		C2	C18	D18B	109.5
O31	C37	C36	116.1(9)		C2	C18	D18C	109.5
O32	C37	C36	119.5(9)		D18A	C18	D18B	109.5
N12	C101	C102	107.4(12)		D18A	C18	D18C	109.5
C127	C101	N12	125.3(13)		D18B	C18	D18C	109.5
C127	C101	C102	127.3(13)		D3A	C3	D3B	109.5
C103	C102	C101	109.9(13)		D3A	C3	D3C	109.5
C102	C103	C104	104.8(13)		D3B	C3	D3C	109.5
N12	C104	C103	111.8(11)		C7	C3	D3A	109.5
N12	C104	C105	124.3(12)		C7	C3	D3B	109.5
C105	C104	C103	124.0(13)		C7	C3	D3C	109.5
C104	C105	C106	127.1(12)		O5	C7	C3	124(5)
N13	C106	C105	125.4(11)		O5	C7	C8	126(4)
N13	C106	C107	109.6(11)		C3	C7	C8	108(4)
C105	C106	C107	125.0(11)		D4A	C4	D4B	109.5
C108	C107	C106	107.6(11)		D4A	C4	D4C	109.5
C107	C108	C109	108.2(11)		D4B	C4	D4C	109.5
N13	C109	C108	108.3(11)		C5	C4	D4A	109.5
N13	C109	C110	125.7(9)		C5	C4	D4B	109.5
C110	C109	C108	126.0(11)		C5	C4	D4C	109.5
C109	C110	C111	117.9(10)		O15	C5	C4	119(3)
C109	C110	C118	124.9(10)		O15	C5	C9	122(3)
C118	C110	C111	117.2(10)		C4	C5	C9	119(3)
C112	C111	C110	122.1(10)		C5	C9	D9A	109.5
C112	C111	C117	117.1(12)		C5	C9	D9B	109.5
C117	C111	C110	120.8(11)		C5	C9	D9C	109.5
C113	C112	C111	119.8(11)		D9A	C9	D9B	109.5
C114	C113	C112	123.1(13)		D9A	C9	D9C	109.5
C113	C114	C115	120.2(14)		D9B	C9	D9C	109.5
C113	C114	C116	117.5(12)		C51	N51	C71	111(2)
C116	C114	C115	122.3(13)		C51	N51	C81	95(2)

Table S14. Bond angles for **CP_{6+2}**								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
C117	C116	C114	121.2(12)		C51	N51	C61	108(2)
C116	C117	C111	121.3(12)		C71	N51	C81	131(2)
N14	C118	C110	123.9(10)		C71	N51	C61	102(2)
N14	C118	C119	109.2(9)		C81	N51	C61	109(2)
C119	C118	C110	126.9(10)		C52	C51	N51	115(2)
C120	C119	C118	108.5(10)		N51	C71	C72	104(2)
C119	C120	C121	106.8(10)		C82	C81	N51	114(3)
N14	C121	C120	109.7(9)		C51	C52	C53	114(2)
N14	C121	C122	125.2(11)		C61	C62	C63	105(2)
C122	C121	C120	125.1(11)		C62	C61	N51	109(3)
C121	C122	C123	127.1(11)		C72	C73	C74	110(2)
N15	C123	C122	125.4(10)		C73	C72	C71	103(2)
N15	C123	C124	108.9(11)		C64	C63	C62	110(2)
C122	C123	C124	125.6(11)		C52	C53	C54	115(3)
C125	C124	C123	106.3(11)		C84	C83	C82	115(3)
C124	C125	C126	110.4(12)		C83	C82	C81	108(2)
N15	C126	C125	106.5(11)		C7	C8	D8A	109.5
N15	C126	C127	124.6(11)		C7	C8	D8B	109.5
C127	C126	C125	129.0(12)		C7	C8	D8C	109.5
C101	C127	C126	127.1(13)		D8A	C8	D8B	109.5
C101	C127	C128	117.6(13)		D8A	C8	D8C	109.5
C126	C127	C128	115.3(12)		D8B	C8	D8C	109.5

[1]1-X,1-Y,1-Z

Table S14. Comparison of the geometry of Mo cluster complexes in several crystal structures.

Complex	Mo–Mo, Å	Mo–μ_3–I, Å	Mo–L, Å	Reference
CP_6 with RuDTolP(CO)	2.643(2)–2.6638(13)	2.7491(13)–2.8087(11)	*L* = C_5NH_4COO; 2.097(7)– 2.116(7)	This work
CP_{6+2} with RuDTolP(CO)	2.6587(11)–2.6780(12)	2.7447(8)–2.8043(9)	*L* = C_5NH_4COO; 2.098(6)– 2.122(7)	This work
$[\{Mo_6I_8\}L_6]^{2-}$	2.6599(7)–2.6725(8)	2.7642(7)–2.8057(7)	*L* = C_6H_5COO; 2.097(4)	[14]
PyMoC	2.6652(4)–2.6738(4)	2.7630(4)–2.8067(4)	*L* = C_5NH_4COO; 2.119(3)–2.168(3)	[1]
CP_2 with ZnDTolP	2.6570(5)–2.6774(5)	2.7728(5)–2.7937(5)	*L* = C_5NH_4COO; 2.110(3)–2.136(3)	[1]
CP_{6+2} with ZnDTolP	2.6558(16)–2.6733(16)	2.7574(15)–2.8017(15)	*L* = C_5NH_4COO; 2.074(9)–2.101(9)	[1]

In both Ru structures, **CP_6** and **CP_{6+2}**, the geometry of the $[\{Mo_6I_8\}(PyCOO)_6]^{2-}$ cluster is typical (Table S15) for such compounds, and both hybrid systems with porphyrins crystallize as a tetra-*n*-butylammonium salt. The ruthenium porphyrin also has typical geometry where the metal ion is located inside the porphyrin ring and adopts an octahedral geometry due to the axial pyridyl and CO ligands (Table S16). The Ru–N(Por) bond

distances span the range of 2.007(14)–2.105(13) Å for **CP$_6$**, and 2.029(10)–2.086(10) Å for **CP$_{6+2}$** (Table S16), which is larger than in the **RuDTolP(CO)** structures discussed above. The carbonyl ligand is coordinated to the ruthenium ion almost linearly with Ru-C(CO)-O(CO) angles of 177–179° and 174–178° for **CP$_6$** and **CP$_{6+2}$**, respectively. The Ru–C bond distances are 1.810(14)– 1.829(14) Å for **CP$_6$** and 1.827(11)–1.845(13) Å for **CP$_{6+2}$**, which is close to those in Ru(TPP)(CO)(Py) (1.838 Å)[7] and **RuDTolP(CO)Py** and in the supramolecular structures assembled by coordination of pyridine to a ruthenium porphyrin[10,15]. The Ru–N(Py) distances span 2.166(10)–2.168(8) Å in **CP$_6$** and 2.159(8)–2.192(7) Å in **CP$_{6+2}$**. They are shorter than in **RuDTolP(CO)Py** [2.200(4) Å], thus showing a stronger binding due to the influence of the electron-rich molybdenum cluster complex, which bears an overall negative charge. The deviation of the Ru atoms from the N_4 porphyrin plane is 0.093(4)–0.101(5) Å for **CP$_6$** and 0.072(5)–0.102(5) Å for **CP$_{6+2}$**. Due to the filled sixth coordination position, the ruthenium center deviates from porphyrin plane to a lesser extent than five-coordinated zinc in a similar structure[1] where the deviation reaches 0.321(8) Å. The porphyrin macrocycles are almost flat, and root mean square deviation (RMSD) from the mean plane of the 24-atom core of the porphyrin (N_4C_{20}) does not exceed 0.089 Å for **CP$_6$** and 0.105 Å for **CP$_{6+2}$**.

Table S15. Selected bond distances (Å) and angles (°) of ruthenium(II) porphyrin in the crystal structures **CP$_6$** and **CP$_{6+2}$**.

	CP$_6$		**CP$_{6+2}$**
average Ru–N(Por)	2.048, 2.056	average Ru–N(Por)	2.048, 2.057, 2.048
Ru1–N3	2.054(9)	Ru11–N12	2.054(9)
Ru1–N4	2.044(8)	Ru11–N13	2.046(7)
Ru1–N5	2.061(7)	Ru11–N14	2.043(8)
Ru1–N6	2.032(8)	Ru11–N15	2.048(7)
Ru2–N7	2.105(13)	Ru21–N22	2.065(12)
Ru2–N8	2.007(14)	Ru21–N23	2.049(8)
–	–	Ru21–N24	2.029(10)
–	–	Ru21–N25	2.086(10)
–	–	Ru31–N32	2.046(11)
–	–	Ru31–N33	2.058(9)
–	–	Ru31–N34	2.030(10)
–	–	Ru31–N35	2.059(10)
Ru–N(Py)	2.168(8), 2.166(10)	Ru–N(Py)	2.192(7), 2.162(10), 2.159(8)
Ru–C(CO)	1.810(14), 1.829(14)	Ru–C(CO)	1.827(11), 1.845(13), 1.829(12)
C(CO)–O(CO)	1.172(13), 1.170(14)	C(CO)–O(CO)	1.168(13), 1.140(14), 1.153(13)
Ru deviation from N_4 plane	0.093(4), 0.101(5)	Ru deviation from N_4 plane	0.072(5), 0.084(7), 0.091(7), 0.102(5)
RMSD from N_4C_{20} plane	0.053, 0.089	RMSD from N_4C_{20} plane	0.042, 0.077, 0.105, 0.091

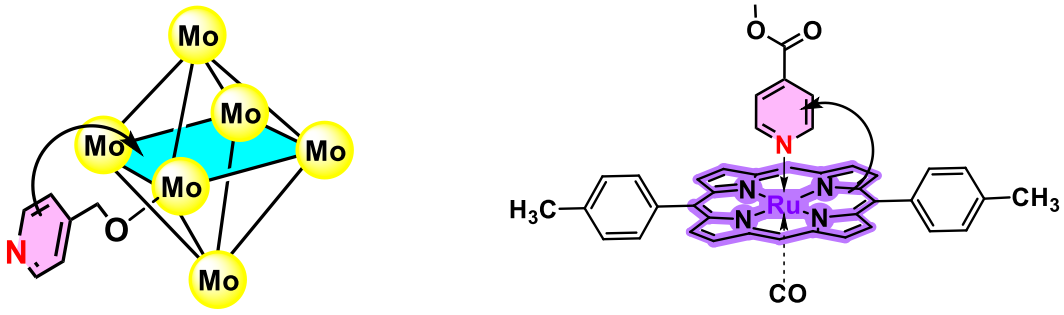
Table S16. Selected dihedral and torsion angles (°) which describe the degrees of freedom in the supramolecular structures **CP$_n$**.[a]

	CP$_6$ with RuDTolP(CO)	**CP$_{6+2}$ with RuDTolP(CO)**	**CP$_{6+2}$ with ZnDTolP**	**CP$_2$ with ZnDTolP**	**PyMoC**
(**Mo$_3$**)$_p$–(Py)$_p$	35.8(3), 44.82(3)	36.7(3), 32.6(4), 25.8(3)	7.8(3), 19.7(4), 14.5(4)	10.3(10)	7.9(1), 10.3(1), 46.5(2)
(**DTolP**)$_p$–(Ru/Zn–N(Py))$_v$	89.3(3), 89.9(4)	89.0(3), 89.7(4), 88.4(4)	89.1(5), 86.5(5), 87.2(5)	82.1(1)	–
(**DTolP**)$_p$–(Py)$_p$	83.7(3), 90.0(7)	89.9(3), 88.8(4), 89.2(4)	86.6(4), 86.9(4), 86.3(5)	69.4(1)	–
C_{Py}–N_{Py}–Zn/Ru–$C_{mesoTol}$	2.0(8), 89.96(19)	84.8(9), 9.5(13), 3.4(10)	20.1(12), 15.4(12), 50.8(18)	51.7(3)	–
Reference	This work	This work	[1]	[1]	[1]

[a] p – plane; v – vector.

In both Ru **CP$_6$** and **CP$_{6+2}$** structures there are several degrees of freedom. The first one is when the pyridyl ring rotates about the cluster, it can be characterized by the dihedral angles between Py and an adjacent Mo_3 plane (Fig. S39a). The second degree of freedom is the variation of the angle between Py-ligand and the porphyrin plane, which can differ from 90° (Fig. S39b)[16,17]. The third option is to rotate the porphyrin molecules about the pyridine moiety and change its orientation (Fig. S41). Dihedral angles that describe these degrees of freedom are summarized in Table S17.

In the crystal structure of the parent **PyMoC** cluster[1] the dihedral angles between the pyridyl rings and the Mo_3 plane vary from 7.9° to 46.5°(Fig. S40). Such a wide variation agrees with the possibility of free rotation of the pyridine fragment. When zinc porphyrins are sitting on the pyridine nitrogen, the rotation is less free due to induced steric hindrance. Accordingly, in the zinc hybrid systems the same angle varies from 7.8° to 19.7° (Table S17)[1]. Surprisingly, the rotation angle for ruthenium hybrid systems varies less but the angles are systematically larger and span the range 25.8°–44.82° for both crystal structures, **CP$_6$** and **CP$_{6+2}$**.



a) **b)**

Fig. S39 Schematic illustration of dihedral angles between Py and Mo_3 plane **(a)**, between Py-ligand and Ru(II) porphyrin plane **(b)**.

As for the angle between Py-ligand and porphyrins, the Ru–N(Py) bonds are essentially perpendicular to N_4 planes of corresponding porphyrins, and the dihedral angles between the pyridyl rings and N_4 planes are close to 90° (Table S17). Similar values were observed in the Zn

CP$_{6+2}$ structure[1], while in the Zn **CP$_2$** structure the pyridyl ring is tipped from the perpendicular position [the Ru–N(Py) bond is tilted by 7.9° from the perpendicular to N_4 plane, and the dihedral angle between the pyridyl ring and N_4 plane is 69.4°].

To compare the relative orientation of the tolyl substituted porphyrin and pyridine fragment we choose the torsion angle C_{Py}–N_{Py}–Zn/Ru–$C_{mesoTol}$ which is highlighted orange in Fig. S38 (Table S17). While the torsion angle is equal to 2.0 and 90.0° for ruthenium **CP$_6$** and 3.4, 9.5 and 84.8° for **CP$_{6+2}$**, for the zinc analogue it is equal to 15.4, 20.1 and 50.8°. These values show the differences between zinc and ruthenium **CP$_{6+2}$** complexes. The different orientation of the pyridyl plane relative to the cluster in Zn and Ru structures leads to a different twist of A_2-porphyrin for a more compact porphyrin arrangement around the cluster core.

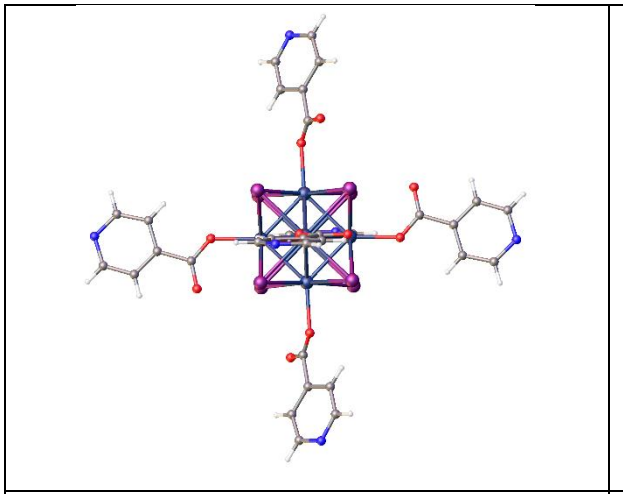
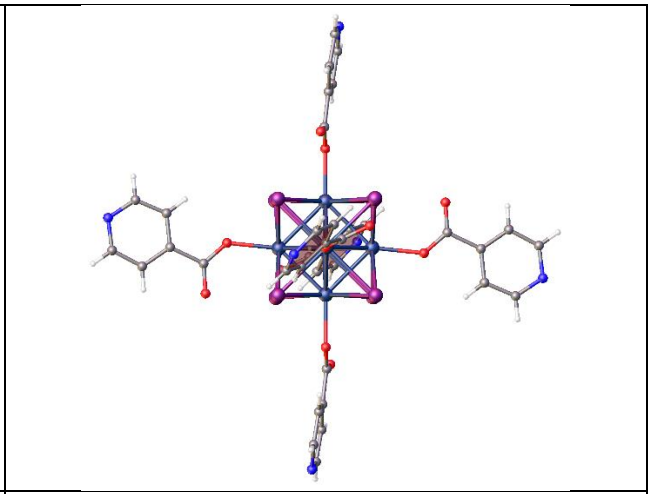
	
The lowest dihedral angle is 7.9°. Pyridine is almost in the plane Mo_3.	The highest dihedral angle is 46.5°. Pyridine is oriented in the middle between two different planes Mo_3.

Fig. S40 The dihedral angles (**Mo$_3$**)$_p$–(Py)$_p$ between the pyridyl rings and the Mo_3 plane in the crystal structure of the parent **PyMoC** cluster[1].

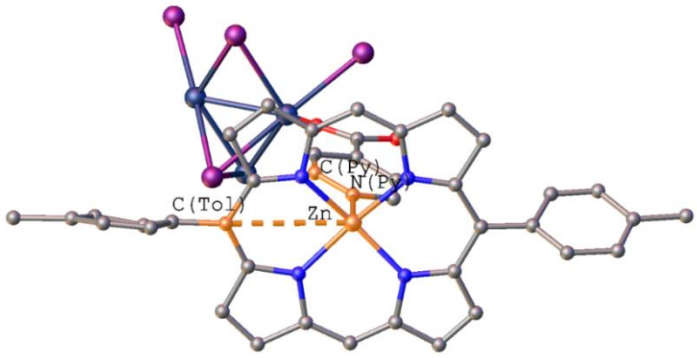


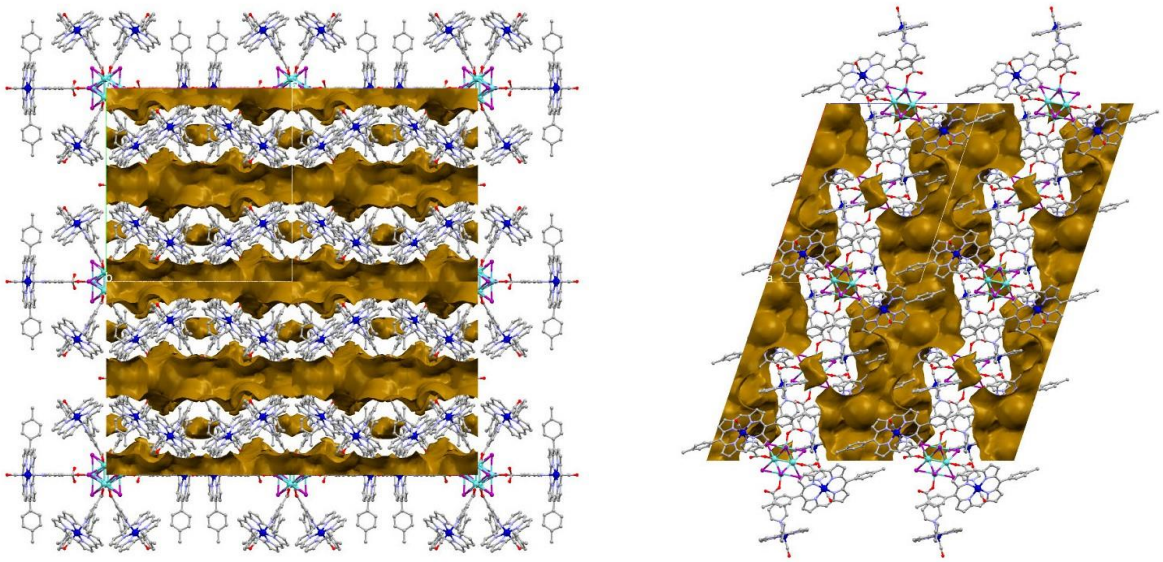
Fig. S41 The torsion angle C_{Py}–N_{Py}–Zn/Ru–$C_{mesoTol}$, which describes the porphyrin molecules rotate about pyridine moiety, is shown in orange.

Table S17. Short contacts in crystal structures **CP$_{6+2}$** and **CP$_6$** (Å) forming the packing.

Atoms D–H···A	D–H distance, Å	H···A distance, Å	D···A distance, Å	D–H–A angle, °	Type of interaction
CP$_{6+2}$					
Inside hybrid complex					
O41–H41A···O32	0.900(6)	1.797(6)	2.657(9)	159.8	H_2O(coordinated to Ru41)···O(PyCOO)
O41–H41B···O12[1]	0.900(6)	2.133(11)	2.951(14)	150.8	
C215–H21A···O42	0.98	2.64	3.60(2)	166.3	CH(Tol CH_3)···O(CO)

Weak contacts between NBu_4^+ and $PyCOO^-$					
C71–H71A···O22	0.99	2.65	3.48(2)	141.8	$CH_2(Bu_4N)\cdots O(PyCOO)$
C52–H52B···O22	0.99	2.54	3.34(2)	137.3	
Weak contacts between acetone and pyridine					
C35–H35···O15	0.95	2.55	3.43(2)	154.7	CH(Py)···O(acetone)
C4–D4A···C12	0.98	2.85	3.65(3)	138.4	CH(Me acetone)··· π (Py)
Between adjacent hybrid complexes					
Short contacts formed by CO ligand with adjacent molecules					
C203[2]–H203[2]···O13	0.95	2.69	3.48(2)	140.5	CH_β(Por)···O(CO)
C332[3]–H33A[3]···O13	0.98	2.50	3.16(2)	124.4	CH(Tol CH_3)···O(CO)
C116[4]–H116[4]···O33	0.95	2.63	3.57(1)	172.0	CH(Ph Tol)···O(CO)
CP_6					
Weak contacts forming sql 2D layers in *ab* plane					
C20[5]–H20[5]···O4	0.95	2.34	3.26(2)	162.0	C−H(Tol)···O(COO)
C57[6]–H57A[6]···C1	0.98	2.64	3.62(2)	174.1	CH(Tol CH_3)···C(COO)
C55[6]–H55[6]···C2	0.95	2.69	3.61(2)	162.5	C−H(Tol)··· π contacts between tolyl and pyridyl
C55[6]–H55[6]···C6	0.95	2.84	3.75(2)	162.1	
Contacts between layers					
C43···C45[7]	–	–	3.274(14)	–	π···π stacking between pyrrole rings of Ru1 porphyrins
C43···C44[7]	–	–	3.390(18)	–	
C44···C45[7]	–	–	3.444(16)	–	
C47…C47[8]	–	–	3.52(3)	–	C···C contacts between *meso* and β carbon atoms of Ru2 porphyrins
C49…C49[8]	–	–	3.54(3)	–	

[1]1-x,1-y,1-z; [2]+x,-1+y,+z; [3]-1+x,-1+y,-1+z; [4]1-x,-y,1-z; [5] -1/2+x,-1/2+y,+z; [6]1/2-x, 3/2-y, 1-z; [7]3/2-x,3/2-y,2-z; [8]-x,1-y,1-z.



a) **b)**

Fig. S42 The visualization of open channels in **CP_6** crystal structure, view along *c* direction **(a)** and *b* direction **(b)**. The picture was made using Mercury software.

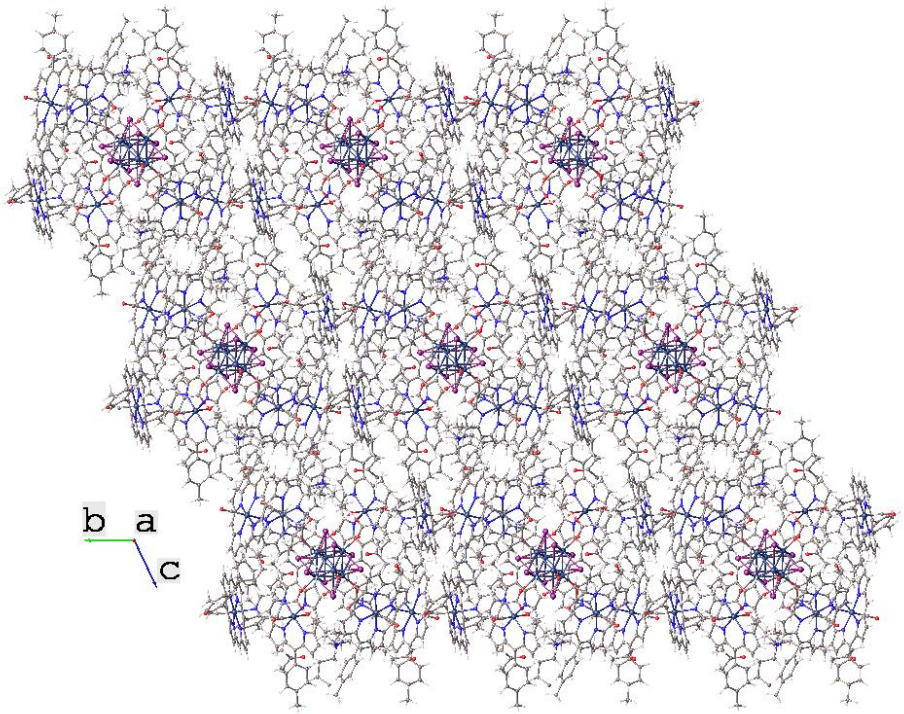


Fig. S43 The crystal packing of **CP_{6+2}**, view along *a* direction.

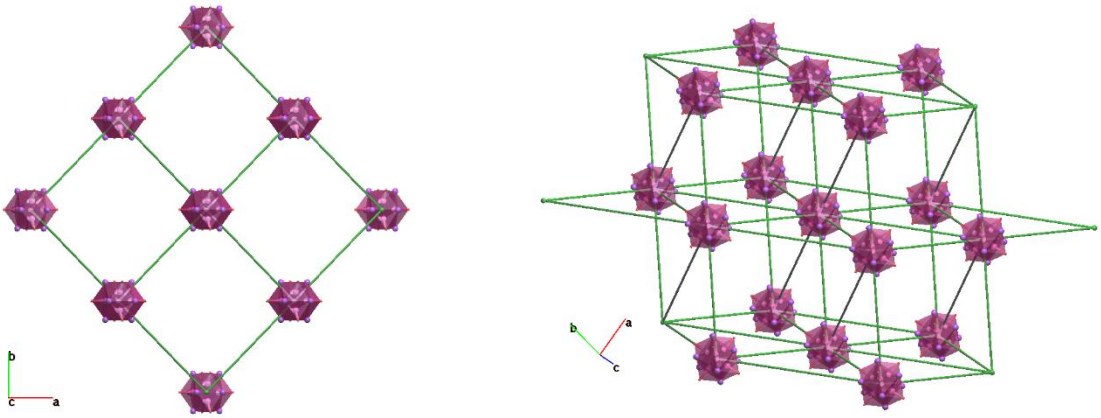


Fig. S44 The packing of **CP_6** structure, simplified using ToposPro,[13] the porphyrins are omitted for clarity and only cluster cores of hybrid spheres are shown. The closest contacts between adjacent spheres are in *ab* plane, which form the layers with **sql** topology http://rcsr.anu.edu.au/layers/sql **(a)**. The layers are placed one above another in the motive AAA along *c* axes. If the van der Waals contacts between layers are taken into account, the structure can be regarded as uninodal ten-connected 3D supramolecular framework with **bct** topology http://rcsr.anu.edu.au/nets/bct **(b)**.

2.6. Photophysical properties

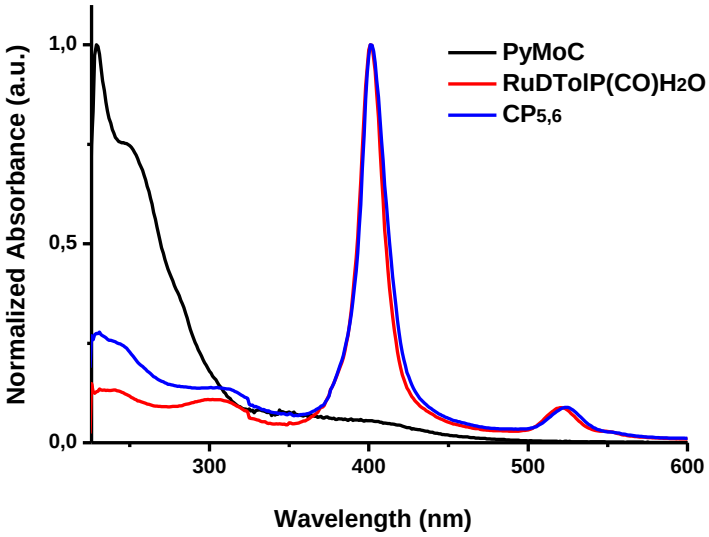


Fig. S45 UV-Vis spectrum of **PyMoC, RuDTolP(CO)H_2O** and hybrid complexes **$CP_{5,6}$** in CH_2Cl_2.

1. Volostnykh, M. V.; Mikhaylov, M.A.; Sinelshchikova, A.A.; Kirakosyan, G.A.; Martynov, A.G.; Grigoriev, M.S.; Piryazev, D.A.; Tsivadze, A.Y.; Sokolov, M.N.; Gorbunova, Y.G. *Dalt. Trans.* 2019, **48**, 1835–1842.
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