Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supporting Information

Giant oligomeric porous cage-based molecules

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Table of contents

S1. Materials

Rhodium acetate was purchased from Acros Organics. Tetrabutylammonium fluoride (TBAF) 1.0 M in THF, anhydrous $MgSO_4$, NaOH, Na_2CO_3, anhydrous $CuSO_4$, sodium ascorbate, 1,3,5-benzenetricarboxylic acid, $SOCl_2$, 2-(trimethylsilyl)ethanol, NH_4Cl, 1-hydroxybenzotriazole (HOBt), hexafluorophosphate benzotriazole tetramethyl uranium (HBTU), N,N-diisopropylethylamine (DIPEA), isophthaloyl chloride, Cu wire and anhydrous pyridine were purchased from Sigma-Aldrich. NH_2-PEG_{38}-N_3, NH_2-PEG_{38}-Alkyne and tris-hydroxypropyltriazolylmethylamine (THPTA) were purchased from BroadPharm. NH_2-PEG_6-Alkyne was purchased from Biopharma PEG. All deuterated solvents were purchased from Eurisotop. Solvents at HPLC grade were purchased from Fischer Chemicals

Ultraviolet-Visible (UV–Vis) spectra were measured using an Thermo Scientific™ NanoDrop 2000 at room temperature (*ca.* 25 °C).

Proton Nuclear Magnetic Resonance (NMR) spectra were acquired using Bruker AVANCE 500 NMR spectrometer operating at 500.13 MHz and equipped with a cryoprobe z-gradient inverse probe head capable of producing gradients in the z direction with a maximum strength of 53.5 G cm^{-1} and a Bruker Ascend 300 MHz at "Servei de Resonància Magnètica Nuclear" from Autonomous University of Barcelona (UAB). Chemical shifts (δ) for ^{1}H-NMR spectra are reported in parts per million (ppm) and relative to the solvent residual peak.

Diffusion Ordered NMR Spectroscopy (DOSY) spectra were acquired using Bruker AVANCE 500 NMR spectrometer operating at 500.13 MHz and equipped with a cryoprobe z-gradient inverse probe head capable of producing gradients in the z direction with a maximum strength of 53.5 G cm^{-1} at "Servei de Resonància Magnètica Nuclear" from Autonomous University of Barcelona (UAB).

Heteronuclear Single Quantum Correlation Spectroscopy (HSQC) spectra were acquired using Bruker AVANCE 500 NMR spectrometer operating at 500.13 MHz and equipped with a cryoprobe z-gradient inverse probe head capable of producing gradients in the z direction with a maximum strength of 53.5 G cm^{-1} and a Bruker Ascend 300 MHz at "Servei de Resonància Magnètica Nuclear" from Autonomous University of Barcelona (UAB).

Mass Spectroscopy (MALDI-TOF) measurements were performed using a 4800 Plus MALDI TOF/TOF (ABSCIEX – 2010). $(COOH)_1$-RhMOP, $(N_3)_1$-RhMOP, $(Alkyne)_1$-RhMOP, $Rh_2(PEG_6\text{-}Alkyne)_4$, $(Alkyne)_{24}$-RhMOP and MOP-satellite were analysed in positive mode. Deprotected $(N_3)_1$-RhMOP, deprotected $(Alkyne)_1$-RhMOP, MOP-dimer and MOP-tetramer were analysed in negative mode. Trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as ionization matrix in the case of $(COOH)_1$-RhMOP, $(N_3)_1$-RhMOP, $(Alkyne)_1$-RhMOP, $Rh_2(PEG_6\text{-}Alkyne)_4$ and $(Alkyne)_{24}$-RhMOP. Sinapinic acid was used as a matrix in the case of deprotected $(N_3)_1$-RhMOP, deprotected $(Alkyne)_1$-RhMOP, MOP-dimer, MOP-tetramer and MOP-satellite.

Volumetric CO_2 isotherms were collected at 200 K using an ASAP 2460 (Micromeritics). Temperature for CO_2 isotherms measurement was controlled by a chiller.

Supercritical CO_2 drying was performed using a Laboratory Supercritical Fluid Equipment SFE 15 mL (Extratex Supercritical Fluid Innovation, France).

Z-potential measurements were carried out using a Malvern Zetasizer Nano ZS. Prior to Z-potential measurements, a standard solution with a zeta-potential of −42 ± 6 mV was measured to ensure correct calibration.

Dynamic light scattering (DLS) measurements were carried out using a Zetasizer Nano Zs.

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed in an external company, Leitat, in an ICP-MS triple quadrupole Agilent 8900 ICP-QQQ. 5 mg of sample were digested with 4 mL of concentrated ultrapure nitric acid (HNO_3 70%) in an analytical microwave at 250 °C. Subsequently, the digestion residue obtained was suitably diluted to analyse the elements of interest by ICP-MS. The quantification was performed by interpolation on a calibration curve prepared from commercial standards of the elements of interest.

S2. Synthetic procedures

Synthesis of $(COOH)_1$-RhMOP: $COOTSE_{24}$-RhMOP was synthesised following the reported procedure.[1] Then, tetrabutylammonium fluoride in THF (1 M, 16.0 µL, 16.0 µmol) was added into a THF solution (3 mL) of the synthesized $COOTSE_{24}$-RhMOP (100.0 mg, 10.1 µmol). The resulting solution was kept under stirring overnight, leading to the formation of a green solution. $(COOH)_1$-RhMOP was precipitated by adding 3 mL of HCl 0.3 M to the green solution. The resulting green precipitate was washed twice with 2 mL HCl 0.3 M and twice with 2 mL H_2O. Finally, the green solid was lyophilized (yield = 95%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.02 (s, 207 H, $-CH_3$); 1.07 (t, 46 H, $-CH_2-$); 4.27 (t, 46 H, $-CH_2-$); 8.59 (broad, 72 H, -CH-) ppm.

Synthesis of $(N_3)_1$-RhMOP: HOBt (0.53 mg, 4.0 µmol), HBTU (1.9 mg, 5.0 µmol) and DIPEA (0.87 µL, 5.0 µmol) were added into a DMF solution (800 µL) containing $(COOH)_1$-RhMOP (20.0 mg, 2.0 µmol) under stirring. After 30 minutes, NH_2-PEG_{38}-N_3 (7.42 mg, 4.0 µmol) was added to the solution. The resulting mixture was stirred overnight. Afterwards, 1 mL of HCl 0.3 M was added to the green solution to induce the precipitation of $(N_3)_1$-RhMOP as a green powder. This powder was washed twice with HCl 0.3 M (1 mL), twice with H_2O (1 mL) and three times with THF:Et_2O (1:2, 2 mL). Finally, the green solid (yield = 93%) was dried under air and stored at -2ºC. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = -0.17 (s, 207 H, $-CH_3$); 0.87 (broad, 46 H, $-CH_2-$); 3.45 (s, 156 H, $-CH_2-$) 4.08 (broad, 46 H, $-CH_2-$); 8.59 (broad, 72 H, -CH-) ppm.

Synthesis of deprotected $(N_3)_1$-RhMOP: The 23 protected carboxylic groups of $(N_3)_1$-RhMOP were deprotected by dissolving $(N_3)_1$-RhMOP (20.0 mg, 1.7 µmol) in 1 mL of THF and subsequently adding 2 molar equivalents of TBAF 1 M solution in THF (346.5 µL, 346.5 µmol). The solution was maintained under stirring overnight. Afterwards, the THF was evaporated and the resultant green solid was washed twice with HCl 0.3 M (1 mL), twice with H_2O (1 mL) and three times with THF:Et_2O (1:2, 2 mL). The obtained solid was finally dried under air (yield = 96%). ^{1}H-NMR (300 MHz, D_2O): δ = 3.35 (broad, 156 H, $-CH_2-$); 8.33 (broad, 48 H, -CH-); 8.70 (broad, 24 H, -CH-) ppm.

Synthesis of $(Alkyne)_1$-RhMOP: HOBt (0.53 mg, 4.0 µmol), HBTU (1.9 mg, 5.0 µmol) and DIPEA (0.87 µL, 5.0 µmol) were added into a DMF solution (800 µL) containing $(COOH)_1$-RhMOP (20.0 mg, 2.0 µmol) under stirring. After 30 minutes, NH_2-PEG_{38}-Alkyne (7.42 mg, 4.0 µmol) was added to this solution. The resulting mixture was stirred overnight. Afterwards, 1 mL of HCl 0.3 M was added to the green solution to induce the precipitation of $(Alkyne)_1$-RhMOP as a green powder. This powder was washed twice with HCl 0.3 M (1 mL), twice with H_2O (1 mL) and three times with THF:Et_2O (1:2, 2 mL). Finally, the green solid was dried under air and kept at -2ºC (yield = 93%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = -0.17 (s, 207 H, $-CH_3$); 0.87 (broad, 46 H, $-CH_2-$); 3.45 (s, 156 H, $-CH_2-$) 4.08 (broad, 46 H, $-CH_2-$); 8.59 (broad, 72 H, -CH-) ppm.

Synthesis of deprotected $(Alkyne)_1$-RhMOP: The 23 protected carboxylic groups of $(Alkyne)_1$-RhMOP were deprotected by dissolving $(Alkyne)_1$- RhMOP (20.0 mg, 1.7 µmol) in 1 mL of THF and subsequently adding 2 molar equivalents of TBAF 1 M solution in THF (346.5 µL, 346.5 µmol). The solution was maintained under stirring overnight. Afterwards, the THF was evaporated and the resultant green solid was washed twice with HCl 0.3 M (1 mL), twice with H_2O (1 mL) and three times with THF:Et_2O (1:2, 2 mL). The obtained solid was dried under air (yield = 94%). ^{1}H-NMR (300 MHz, D_2O): δ = 3.35 (broad, 156 H, $-CH_2-$); 8.33 (broad, 48 H, -CH-); 8.70 (broad, 24 H, -CH-) ppm.

Control experiments:

1) **Reaction with 5 mol. eqs. of NH_2-PEG_{38}-N_3:** HOBt (1.32 mg, 10.0 µmol), HBTU (4.75 mg, 12.5 µmol) and DIPEA (2.17 µL, 12.5 µmol) were added into a DMF solution (800 µL) containing $(COOH)_1$-RhMOP (20.0 mg, 2.0 µmol) under stirring. After 30 minutes, NH_2-PEG_{38}- N_3 (18.5 mg, 10.0 µmol) was added to the solution. The resulting mixture was stirred overnight. Afterwards, 1 mL of HCl 0.3 M was added to the green solution to induce the precipitation of $(N_3)_1$-RhMOP as a green powder. This powder was washed twice with HCl 0.3 M (1 mL), twice with H_2O (1 mL) and three times with THF:Et_2O (1:2, 2 mL). Finally, the green solid (yield ≈ 91%) was dried under air and stored at -2ºC.
2) **Synthesis of $(COOH)_2$-RhMOP:** Tetrabutylammonium fluoride in THF (1 M, 10.0 µL, 10.0 µmol) was added into a THF solution (3 mL) of the synthesized $COOTSE_{24}$-RhMOP (50.0 mg, 5.0 µmol). The resulting solution was kept under stirring overnight, leading to the formation of a green solution. $(COOH)_2$-RhMOP was precipitated by adding 3 mL of HCl 0.3 M to the green solution. The resulting green precipitate was washed twice with 2 mL HCl 0.3 M and twice with 2 mL H_2O. Finally, the green solid was lyophilized.
3) **Synthesis of $(COOH)_3$-RhMOP:** Tetrabutylammonium fluoride in THF (1 M, 15.0 µL, 15.0 µmol) was added into a THF solution (3 mL) of the synthesized $COOTSE_{24}$-RhMOP (50.0 mg, 5.0 µmol). The resulting solution was kept under stirring overnight, leading to the formation of a green solution. $(COOH)_3$-RhMOP was precipitated by adding 3 mL of HCl 0.3 M to the green solution. The resulting green precipitate was washed twice with 2 mL HCl 0.3 M and twice with 2 mL H_2O. Finally, the green solid was lyophilized.
4) **Synthesis of $(N_3)_x$-RhMOP:** Once the deprotected products were obtained, $(COOH)_2$-RhMOP (20.0 mg, 2.0 µmol) or $(COOH)_3$-RhMOP (20.0 mg, 2.0 µmol) was dissolved in DMF (800 µL). To this solution HOBt (1.32 mg, 10.0 µmol), HBTU (4.75 mg, 12.5 µmol) and DIPEA (2.17 µL, 12.5 µmol) were added under stirring. After 30 minutes, NH_2-PEG_{38}- N_3 (18.5 mg, 10.0 µmol) was added to the solution. The resulting mixture was stirred overnight. Afterwards, 1 mL of HCl 0.3 M was added to the green solution to induce the precipitation of $(N_3)_x$-RhMOP as a green powder. This powder was washed twice with HCl 0.3 M (1 mL), twice with H_2O (1 mL) and three times with THF:Et_2O (1:2, 2 mL). Finally, the green solid was dried under air and stored at -2ºC.

Synthesis of MOP-dimer: The synthesis of the MOP-dimer was performed in two steps. In the first step, $(N_3)_1$-RhMOP (10.0 mg, 0.9 µmol) and $(Alkyne)_1$-RhMOP (10.0 mg, 0.9 µmol) were dissolved in 1 mL mixture of CH_2Cl_2:DMF (1:1). To this mixture, five consecutive additions of $CuSO_4$ (20 µL, 0.3 M in H_2O) and sodium ascorbate (20 µL, 0.9 M in H_2O) were done over a period of 1.25 hours.[2] Once the additions were finished, the mixture was kept under vigorously stirring overnight. Afterwards, the mixture was extracted twice with HCl 0.3 M (1 mL) and twice with H_2O (1 mL). Finally, the organic phase was evaporated to obtain a green solid.

In the second step, the previously obtained green solid (17.5 mg) was dissolved in 1 mL of THF. Then, an excess of 1 M TBAF solution in THF (64.6 µL, 64.6 µmol) was added to the solution, which was kept under stirring overnight. Afterwards, the THF was evaporated and the obtained green solid was washed twice with HCl 0.3 M (1 mL), twice with H_2O (1 mL) and three times with MeOH (2 mL). The resultant solid was dried under open air. Finally, the product was further purified by washing it three times with basic methanol (43.0 mM NaOH in MeOH, 2 mL), twice with H_2O (1 mL) and three times with MeOH (2 mL). The final product was dried under air (yield = 74%). ^{1}H-NMR (300 MHz, D_2O): δ = 3.53 (broad, 312 H, -CH_2-); 8.39 (broad, 96 H, -CH-); 8.81 (broad, 48 H, -CH-) ppm.

Synthesis of the 4-c cluster $Rh_2(PEG_6\text{-Alkyne})_4$: Initially, $Rh_2(bdc)_4$ was synthesised following a reported procedure.[3] Then, HOBt (9.5 mg, 70 µmol), HBTU (34.1 mg, 90 µmol) and DIPEA (15.7 µL, 90 µmol) were added into a DMF solution (0.2 mL) containing the synthesized $Rh_2(bdc)_4$ (10.0 mg, 11 µmol) under stirring. After 30 minutes, NH_2-PEG_6-Alkyne (28.7 mg, 90 µmol) was added into this solution, which was stirred overnight. Afterwards, the propargyl-PEG-complex was isolated by precipitation with Et_2O and recovered through centrifugation. Subsequently, the isolated product was washed five times with Et_2O (10 mL) and dissolved in H_2O (5 mL). The solution was extracted twice with CH_2Cl_2 (5 mL). Then, CH_2Cl_2 (5 mL) and MeOH (5mL) were added to the aqueous solution. The presence of MeOH in the mixture induced the transfer of the product from the aqueous phase to the organic phase. Finally, the CH_2Cl_2 was evaporated to obtain the 4-c cluster $Rh_2(PEG_6\text{-Alkyne})$ as a green solid (yield = 63 %). ^{1}H-NMR (300 MHz, MeOD): δ = 2. 86 (t, 1 H, -CH); 2.58 (m, 24 H, -CH_2-); 4.17 (d, 2 H, -CH_2-); 7.43 (t, 1 H, -CH-); 7.87 (d, 1 H, -CH-); 8.08 (d, 1 H, -CH-); 8.36 (s, 1 H, -CH-) ppm.

Synthesis of MOP-tetramer: This synthesis was performed in two steps. Firstly, $(N_3)_1$-RhMOP (20.7 mg, 1.8 µmol) and $Rh_2(PEG\text{-Alkyne})_4$ (0.1 mg, $4.8x10^{-2}$ µmol) were dissolved in 1 mL mixture of CH_2Cl_2:DMF (1:1). Then, $CuSO_4$ (18 µL, 0.3 M in H_2O) and sodium ascorbate (18 µL, 0.9 M in H_2O) were added to the resulting solution while stirring. After ten minutes of reaction, 5 pieces of copper wire of *ca.* 2 mg were added. The reaction mixture was kept under vigorous stirring for 48 hours. Afterwards, the mixture was extracted twice with HCl 0.3 M (1 mL) and twice with H_2O (1 mL). Finally, the organic phase was evaporated to obtain a green solid.

In the second step, the previously obtained green solid (19.4 mg) was dissolved in 1 mL of THF. Then, an excess of 1 M TBAF solution in THF (123.3 µL, 123.3 µmol) was added to the solution, which was kept stirring overnight. Afterwards, the THF was evaporated and the green solid was washed twice with HCl 0.3 M (1 mL) and twice with H_2O (1 mL). Then, the green solid was dissolved in basic water (pH ≈ 12) and the solution was filtered using a centrifugal filter with a molecular weight cut-off of 30 kDa. The centrifugal process was repeated 5 times (50 mL of water used in total). The obtained concentrated solution from the filter was precipitated by adding 1 mL of HCl 0.3 M. The collected green solid was then washed twice with H_2O (2 mL) and three times with MeOH (2 mL). The obtained solid was dried under open air (yield = 75%). ^{1}H-NMR (300 MHz, D_2O): δ = 3.45 (broad, 736 H, -CH_2-); 8.39 (broad, 208 H, -CH-); 8.81 (broad, 96 H, -CH-) ppm.

Synthesis of $(Alkyne)_{24}$-RhMOP: $COOH_{24}$-RhMOP was synthesised following the reported procedure.[1] Then, HOBt (8.6 mg, 63.8 µmol), HBTU (24.2 mg, 63.8 µmol) and DIPEA (11.1 µL, 63.8 µmol) were added into a DMF solution (2mL) containing (20.0 mg, 2.7 µmol) under stirring. After 30 minutes of reaction, NH_2-PEG_6-Alkyne (40.8 mg, 127.9 µmol) was added into the solution, which was stirred overnight. Afterwards, Et_2O (15 mL) was added to precipitate the product. The obtained solid was solubilized in H_2O (15 mL) and filtered with a centrifugal filter with a molecular weight cut-off of 10 kDa. This process was repeated three times using in total 45 mL of H_2O. The concentrated solution obtained from the filter (*ca.* 1 mL) was extracted with CH_2Cl_2 (1mL). Then, CH_2Cl_2 (1 mL) and MeOH (1 mL) were added to the concentrated aqueous solution, and the product was transferred to the chlorinated organic phase. Finally, the CH_2Cl_2 was evaporated to obtain $(Alkyne)_{24}$-RhMOP as a green solid (yield = 50%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.56 (broad, 576 H, -CH_2-); 4.10 (broad, 48 H, -CH_2-); 8.28 (broad, 48H, -CH-); 8.73 (broad, 24 H, -CH-) ppm.

Synthesis of MOP-satellite: This synthesis was performed in two steps. In the first step, $(N_3)_1$-RhMOP (37.6 mg, 3.3 µmol) and $(Alkyne)_{24}$-RhMOP (0.1mg, $1.4x10^{-2}$ µmol) were dissolved in 2

mL mixture of CH_2Cl_2:DMF (1:1). While stirring, 20 µL of an aqueous solution containing $CuSO_4$ (0.03 mg, 0.19 µmol) and THPTA (0.35 mg, 0.81 µmol) were added to the solution containing both $(N_3)_1$-TSE_{23}RhMOP and $(Alkyne)_{24}$-RhMOP. Finally, sodium ascorbate (20 µL, 0.3 M in H_2O) and five pieces of copper wire of an approximate weight of 2 mg were added to the reaction mixture. The reaction was kept under stirring for 7 days. Afterwards, the mixture was extracted twice with HCl 0.3 M (1 mL) and twice with H_2O (1 mL). The organic phase was kept and loaded with fresh catalysts to perform another reaction cycle. To this end, 1 mL of DMF and an aqueous solution containing $CuSO_4$ (0.03 mg, 0.19 µmol) and THPTA (0.35 mg, 0.81 µmol) were added to the organic phase. This mixture was kept stirring for another 7 days. Once the reaction was completed, the mixture was extracted twice with HCl 0.3 M (1 mL) and twice with H_2O (1 mL). Finally, the organic phase was evaporated to obtain a green solid.

In the second step, the previously obtained green solid (35.5 mg) was dissolved in 1 mL of THF. Then, an excess of TBAF 1 M in THF (82.0 µL, 82.0 µmol) was added to the solution, which was kept under stirring overnight. Afterwards, the resultant product was isolated by evaporating the THF and the obtained green solid was washed twice with HCl 0.3 M (1 mL) and twice with H_2O (1 mL). Then, this solid was dissolved in basic water (pH ≈ 12) and the solution was filtered using a centrifugal filter with a molecular weight cut-off of 50 kDa. The centrifugal process was repeated over five times (50 mL of water used as total). The final product was isolated by precipitation using 1 mL of HCl 0.3 M, and the green solid was washed twice with H_2O (2 mL) and three times with MeOH (2 mL). The obtained solid was dried under air (yield = 75%). ^{1}H-NMR (300 MHz, D_2O): δ = 3.45 (broad, 1952 H, -CH_2-); 8.39 (broad, 528 H, -CH-); 8.81 (broad, 264 H, -CH-) ppm.

Acid digestions: $(N_3)_1$-RhMOP, $(Alkyne)_1$-RhMOP, deprotected $(N_3)_1$-RhMOP, deprotected $(Alkyne)_1$-RhMOP and MOP-dimer were digested as follows. 5 mg of the corresponding solid sample were suspended in 0.5 mL of MeOD-d_4 containing 20 µL of DCl (2 % in D_2O:MeOD-d_4, 1:10). The mixture was heated at 65ºC overnight.

$(COOH)_1$-RhMOP and $(Alkyne)_{24}$-RhMOP were digested as follows. 5 mg of the corresponding sample were suspended in 0.5 mL of DMSO-d_6 containing 10 µL of DCl (20 % in D_2O). The resulting mixture was heated at 100ºC for 2 hours.

Samples activation: All samples were activated following this procedure. Solvent exchange with MeOH was performed during 1 week to 45 mg of sample. Finally, all solvent was removed through super critical CO_2 drying.

S3. Characterization

S3.1. $(COOH)_1$-RhMOP

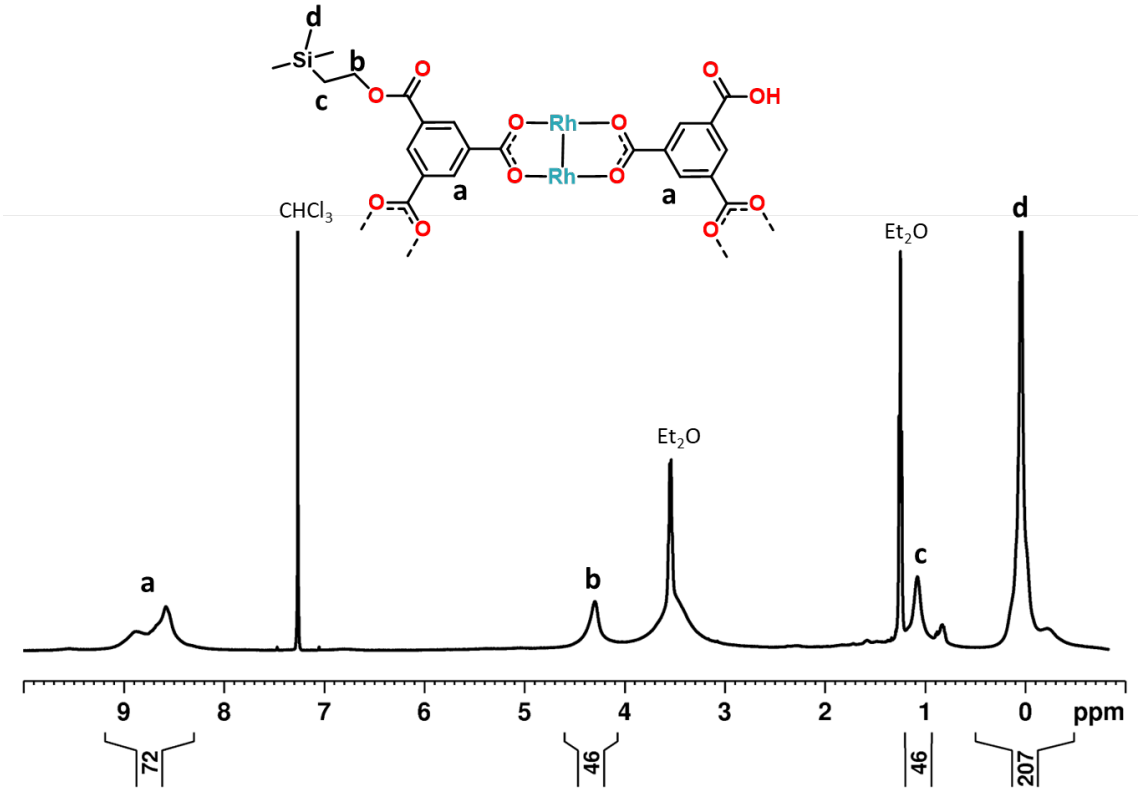

Figure S1. ^{1}H-NMR (500 MHz, 25ºC) spectrum of $(COOH)_1$-RhMOP in $CDCl_3$. Note that the relative integrations of the protons ascribed to the MOP core (*a*) and the aliphatic signals form the COOTSE group (*b,c* and *d*) correspond to the expected value for the proposed formula; that is, for each MOP core (24 COOTSE-BDC ligands: 72 aromatic protons *a*), there are 23 TSE protecting groups (46 protons *b* and *c* and 207 protons *d*).

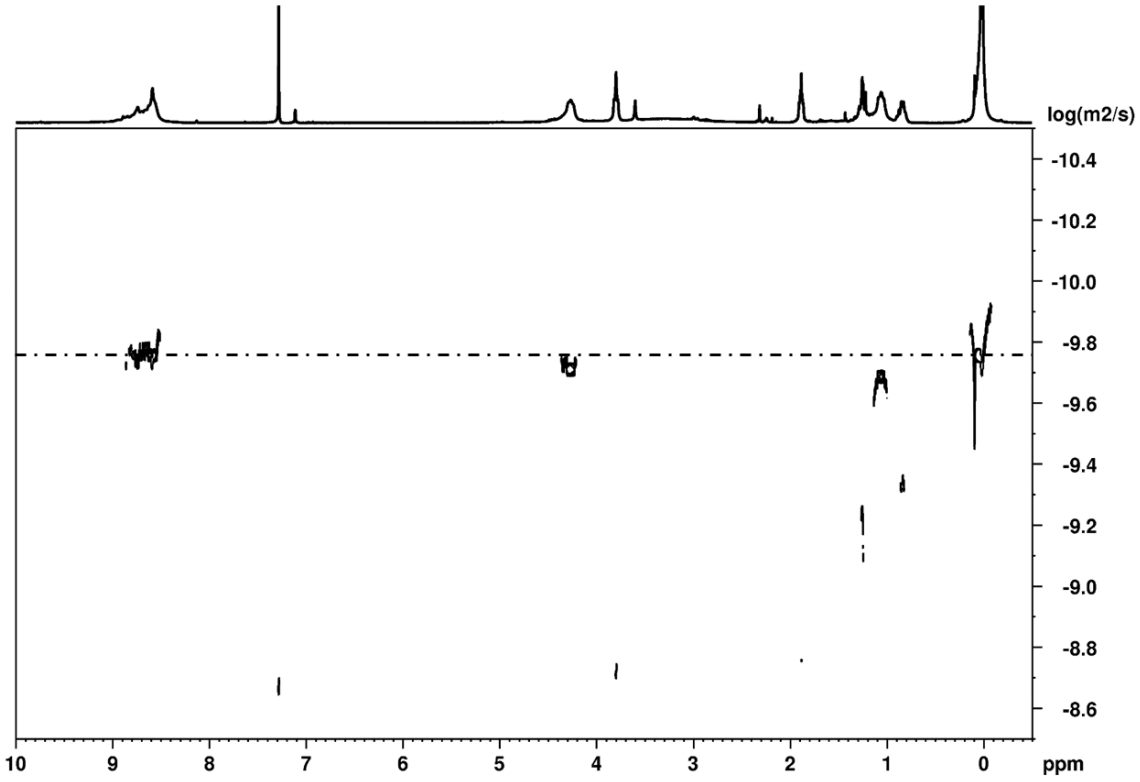

Figure S2. DOSY-NMR (300 MHz, 25ºC) spectrum of $(COOH)_1$-RhMOP in $CDCl_3$. The same diffusion coefficient ($D \approx 1.9 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$) is identified for the aromatic signals ascribed to the MOP core and the aliphatic signals assigned to the protecting groups, which confirms that both moieties belong to the same molecule. The diffusion coefficient of the residual $CHCl_3$ ($D \approx 2.3 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$) was used as internal reference.

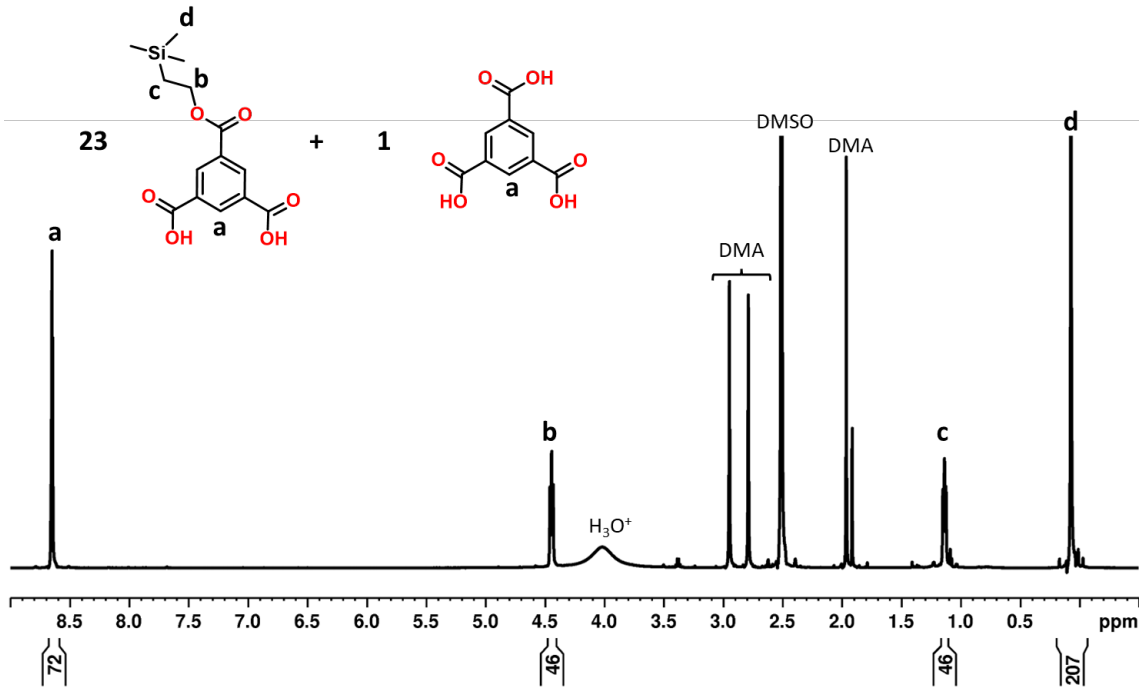

Figure S3. ^{1}H-NMR (300 MHz, 25ºC) spectrum of $(COOH)_1$-RhMOP digested in DMSO-d_6 under acidic conditions (DCl 20 %, 100 ºC, overnight). The analysis of the relative integrations in the spectrum of the digested sample confirms the expected value for the proposed formula; that is, for each MOP core (24 COOTSE-BDC ligands: 72 aromatic protons *a*), there are 23 TSE protecting groups (46 protons *b* and *c* and 207 protons *d*).

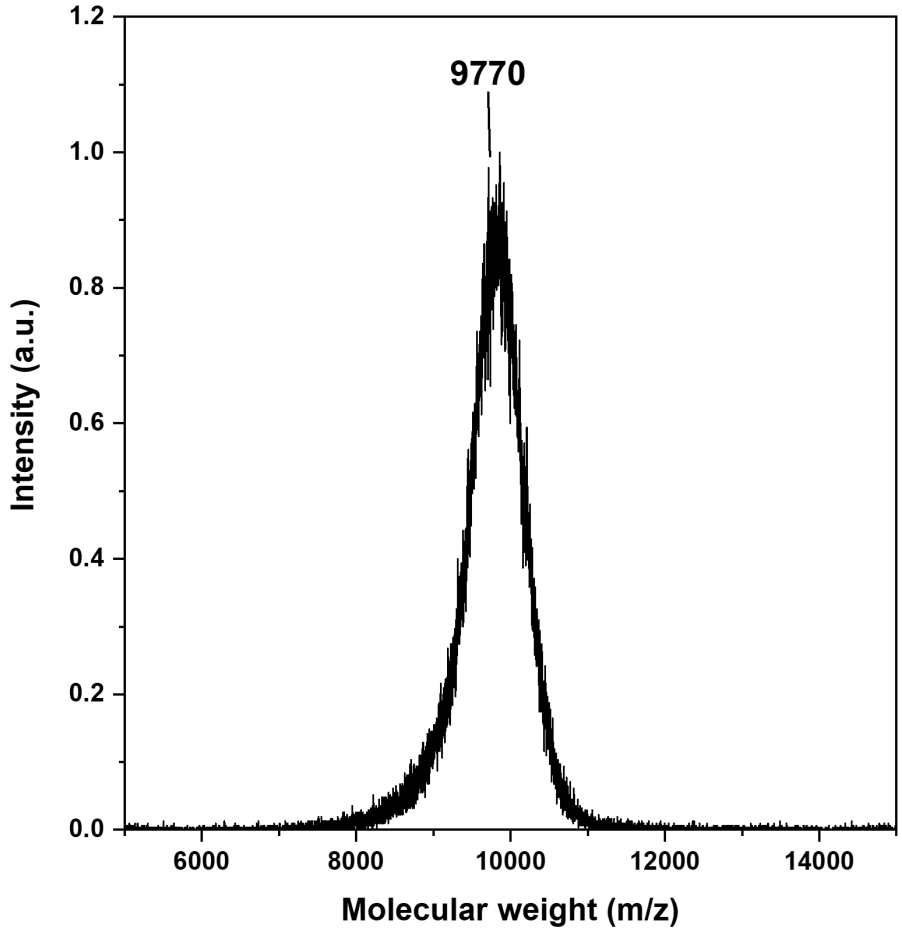

Figure S4. MALDI-TOF spectrum of $(COOH)_1$-RhMOP in DMF. The highlighted mass corresponds to the molecular formula of $[(COOTSE\text{-}BDC)_{23}(BTC)_1Rh_{24} + H^+]^{+\cdot}2H_2O$. Expected m/z = 9776 g/mol; found m/z = 9770 g/mol.

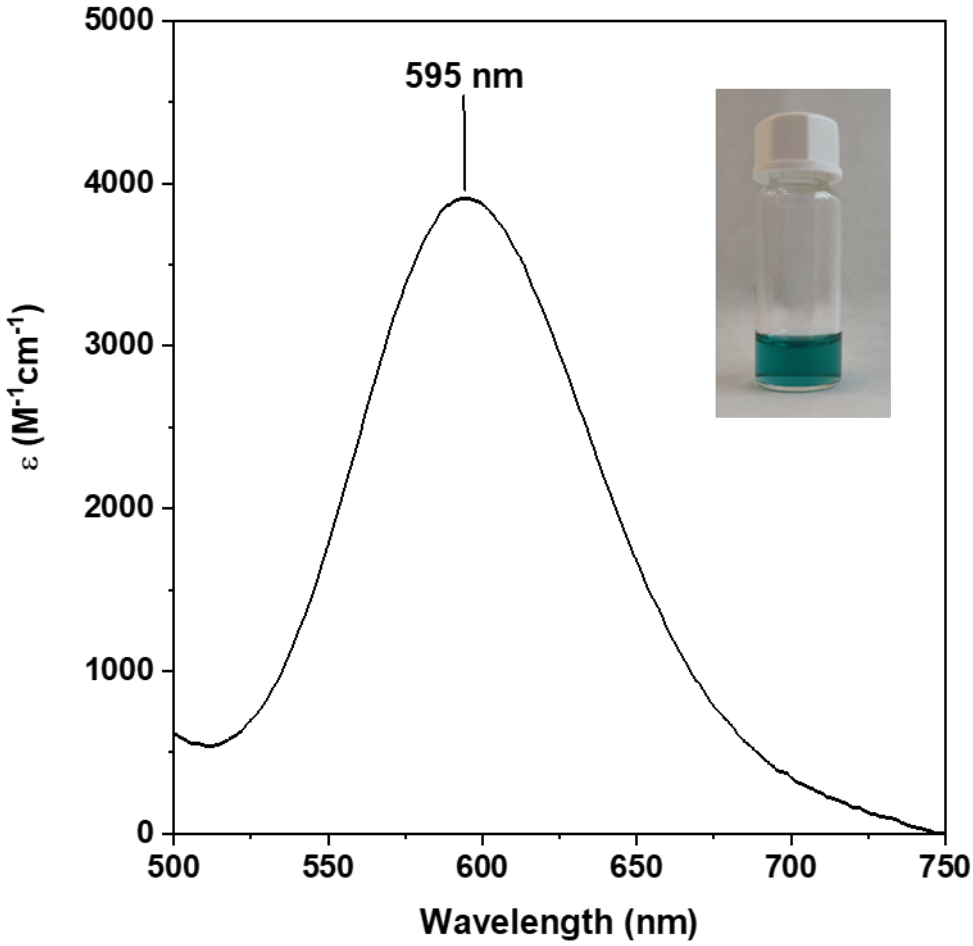

Figure S5. UV-Vis spectrum of $(COOH)_1$-RhMOP in DMF with a concentration of 0.2 mM. λ_{max} is centered at 595 nm, thus confirming the integrity of the Rh (II) paddlewheel after the monodeprotection procedure.

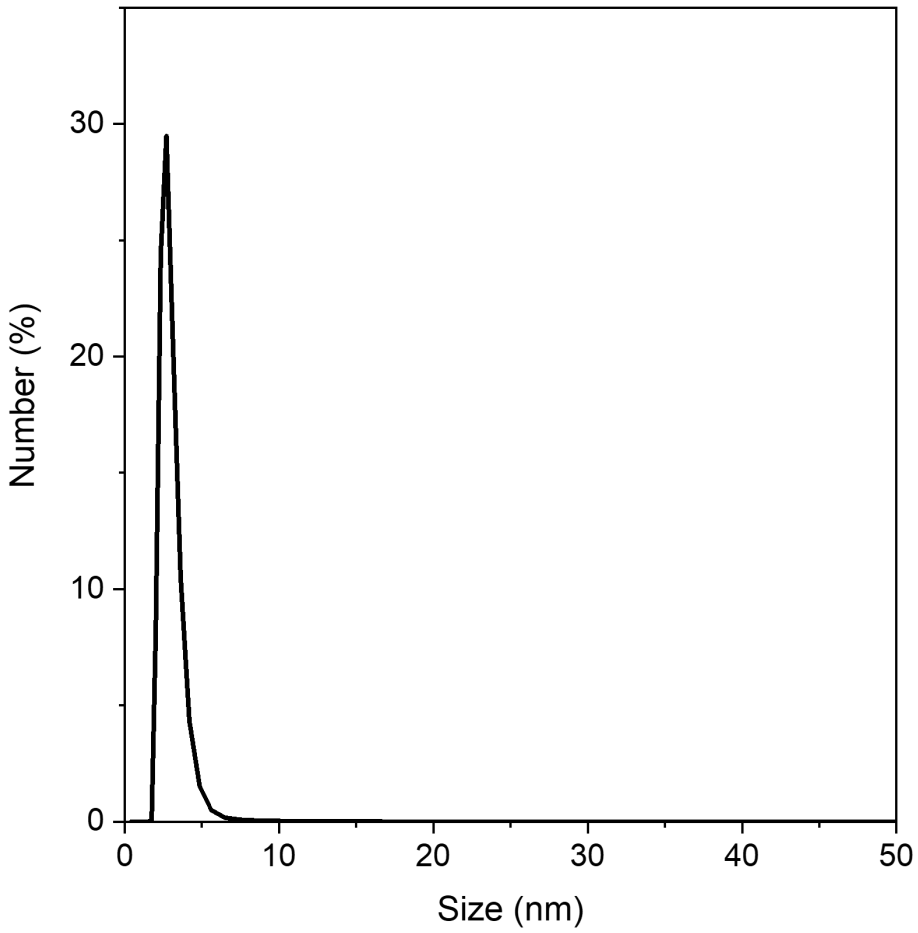

Figure S6. DLS spectrum of $(COOH)_1$-RhMOP in DMF with a concentration of 0.3 mM. The average diameter was found to be 3.0 ± 0.5 nm.

S3.2. $(N_3)_1$-RhMOP

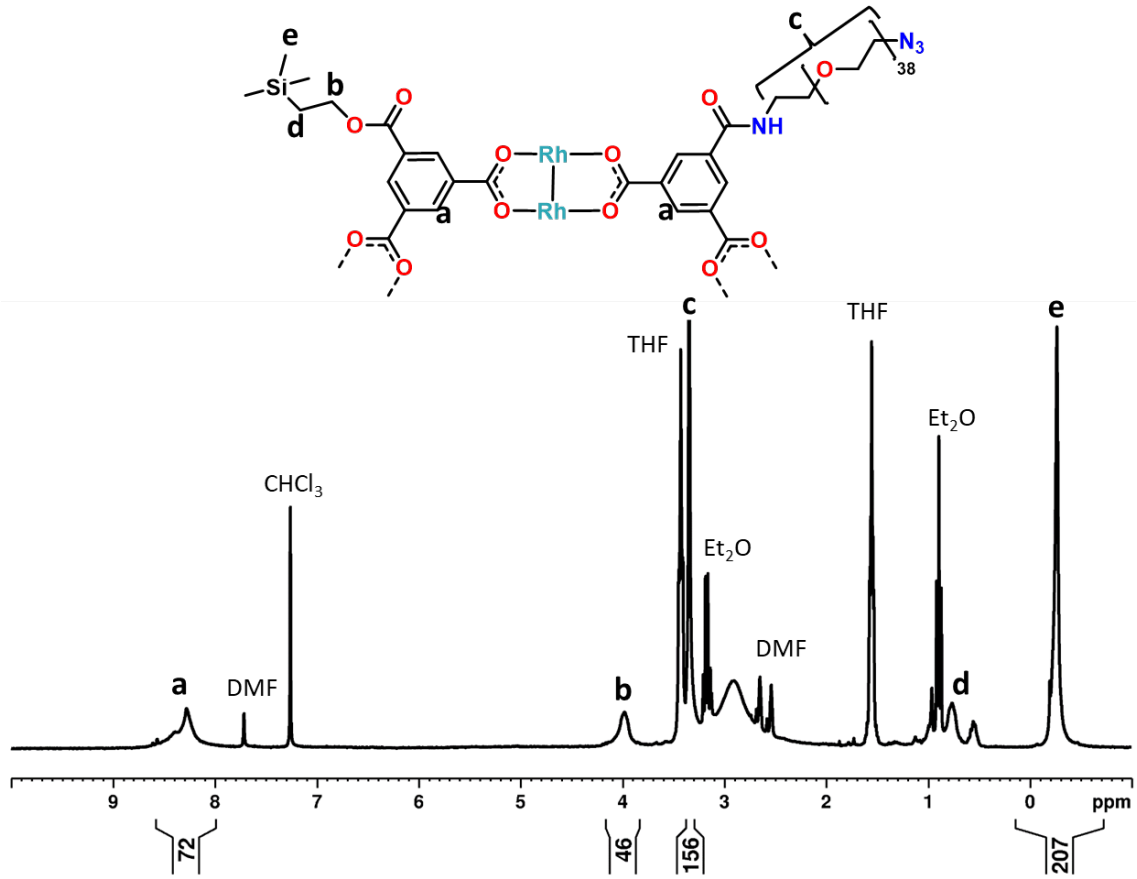

Figure S7. ^{1}H-NMR spectrum (300 MHz, 25ºC) of $(N_3)_1$-RhMOP in $CDCl_3$. Note that the relative integrations of the protons ascribed to the MOP core (*a*) and the aliphatic signals form the PEG chain (*c*) and TSE protecting group (*b* and *e*) correspond to the expected value for the proposed formula; that is, for each MOP core (24 functionalized BDC ligands: 72 aromatic protons *a*), there are 23 TSE protecting groups (46 protons *b* and 207 protons *e*) and a single PEG chain with *ca.* 156 aliphatic protons *c*.

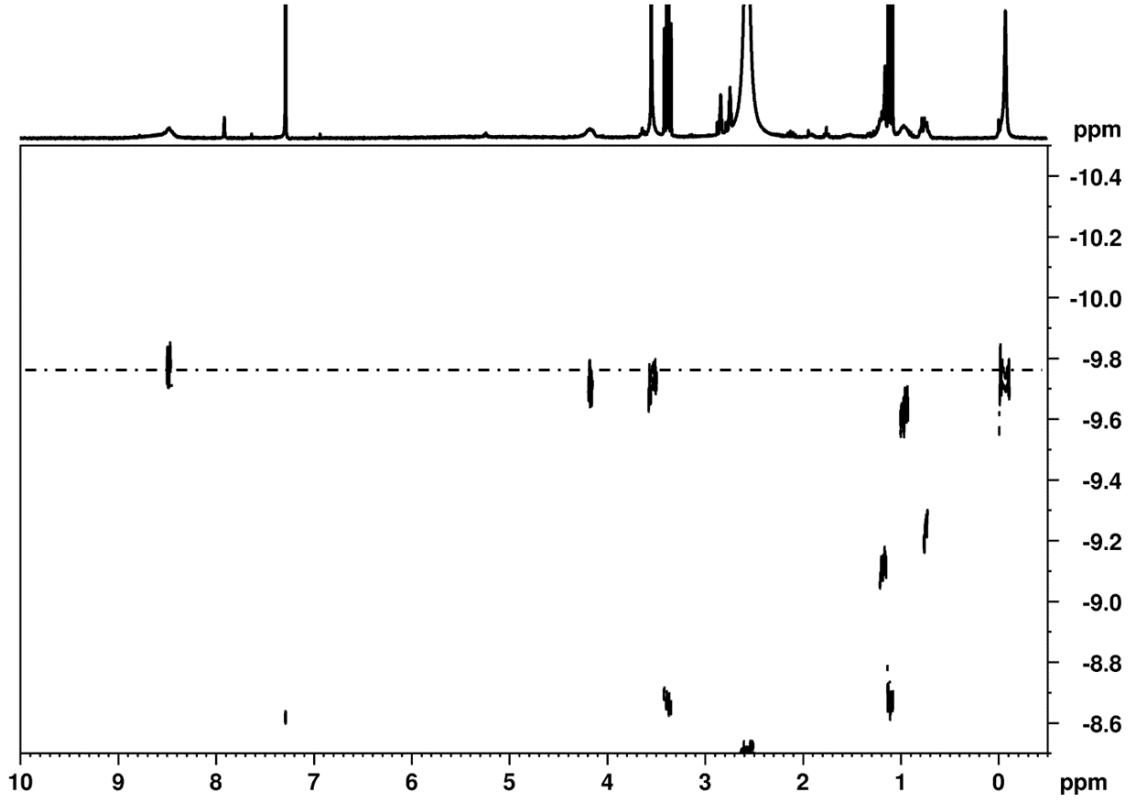

Figure S8. DOSY-NMR (300 MHz, 25ºC) spectrum of $(N_3)_1$-RhMOP in $CDCl_3$. The same diffusion coefficient ($D \approx 1.8 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$) is identified for the aromatic signals of the core of the Rh-MOP and the aliphatic signals from the COOTSE groups and the ones from the PEG, which evidences that all belong to the same molecule. The diffusion coefficient of the residual $CHCl_3$ ($D \approx 2.3 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$) was used as internal reference.

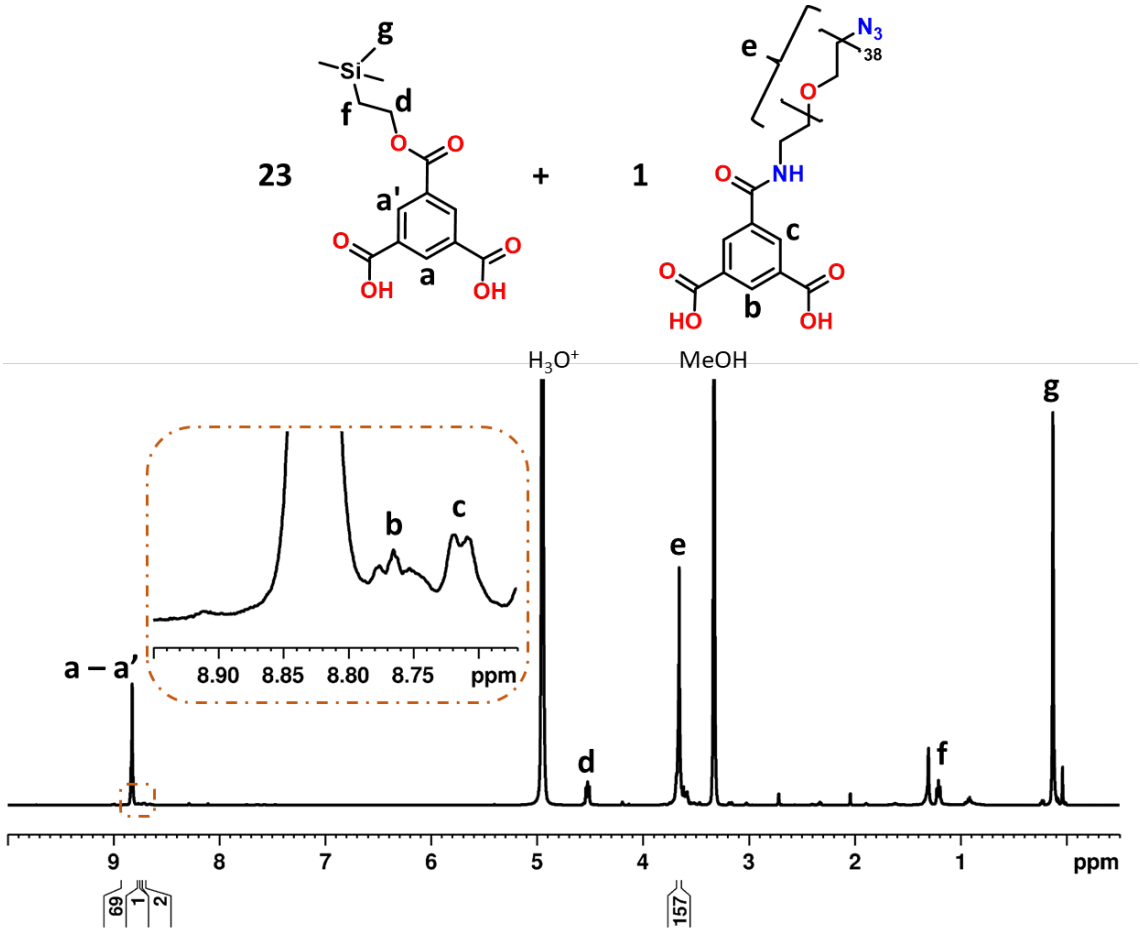

Figure S9. ^{1}H-NMR spectrum (500 MHz, 25ºC) of the digested $(N_3)_1$-RhMOP in MeOD under acidic conditions (DCl 2 %, 65º C, overnight). The appearance of the new aromatic signals (*b* and *c*) confirms the formation of the amide bond. The analysis of the relative integrations in the spectrum of the digested sample confirms the expected ratio of COOTSE-BDC:PEG-functionalized ligand of 23:1. Note that the peaks at 4.27, 1.07 and 0.13 ppm (protons *d*, *f* and *g* respectively) could not be integrated due to the hydrolysis of the COOTSE ester under the required acidic MeOD conditions for the digestion. Signal of protons *a* and *a'* was used to determine the ligand ratio.

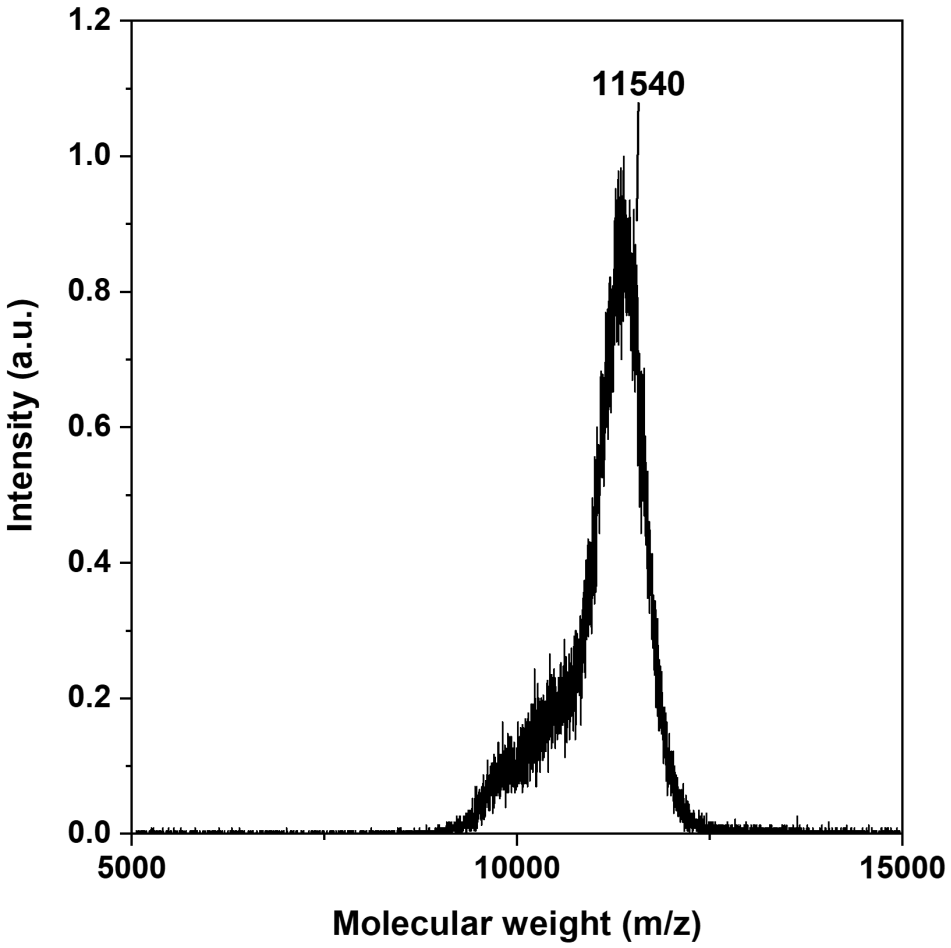

Figure S10. MALDI-TOF spectrum of $(N_3)_1$-RhMOP in DMF. The highlighted mass corresponds to the molecular formula $[(COOTSE\text{-}DC)_{23}(N_3\text{-}PEG_{38}\text{-}BDC)_1Rh_{24}+H^+]^+$. Expected: m/z = 11544 ± 370 g/mol; found: m/z = 11540 g/mol.

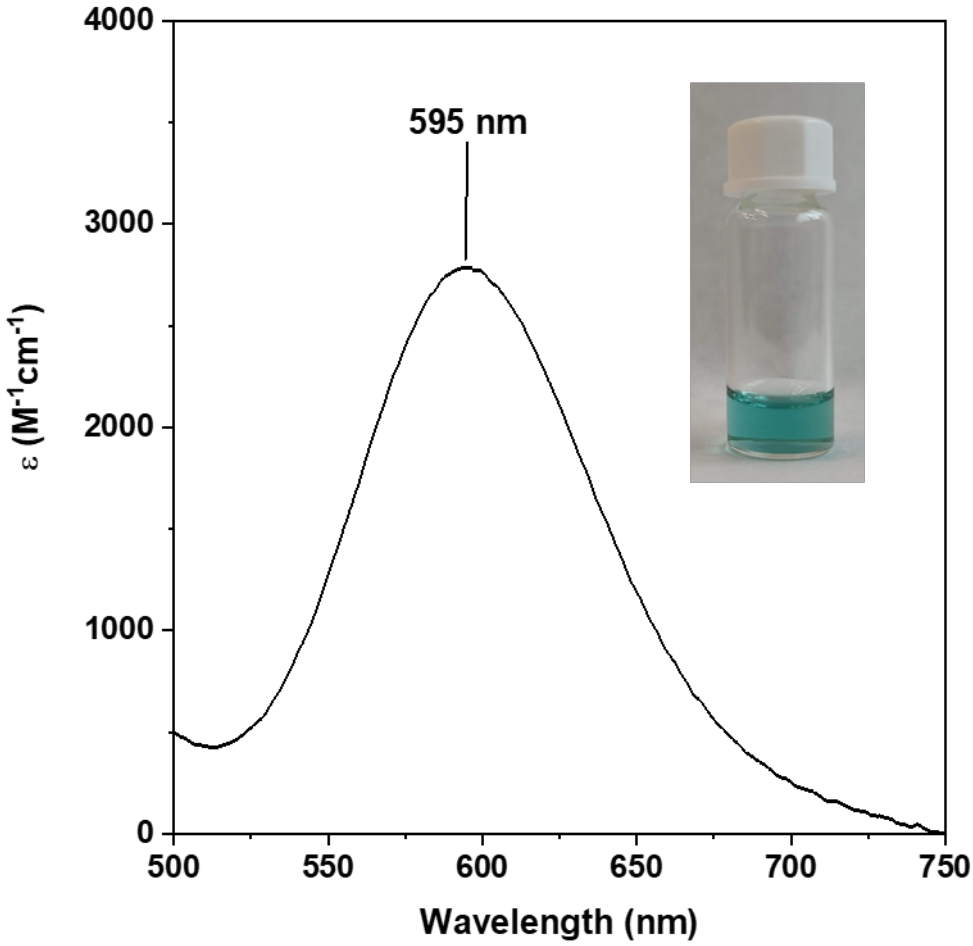

Figure S11. UV-Vis spectrum of $(N_3)_1$-RhMOP in DMF with a concentration of 0.2 mM. λ_{max} is centered at 595 nm, confirming that the Rh(II) paddlewheel is maintained after the amide formation and that there is not remaining coordinated N-containing reactants and reagents (*i.e.* NH_2-PEG_{38}-N_3, HOBt, HBTU, DIPEA).

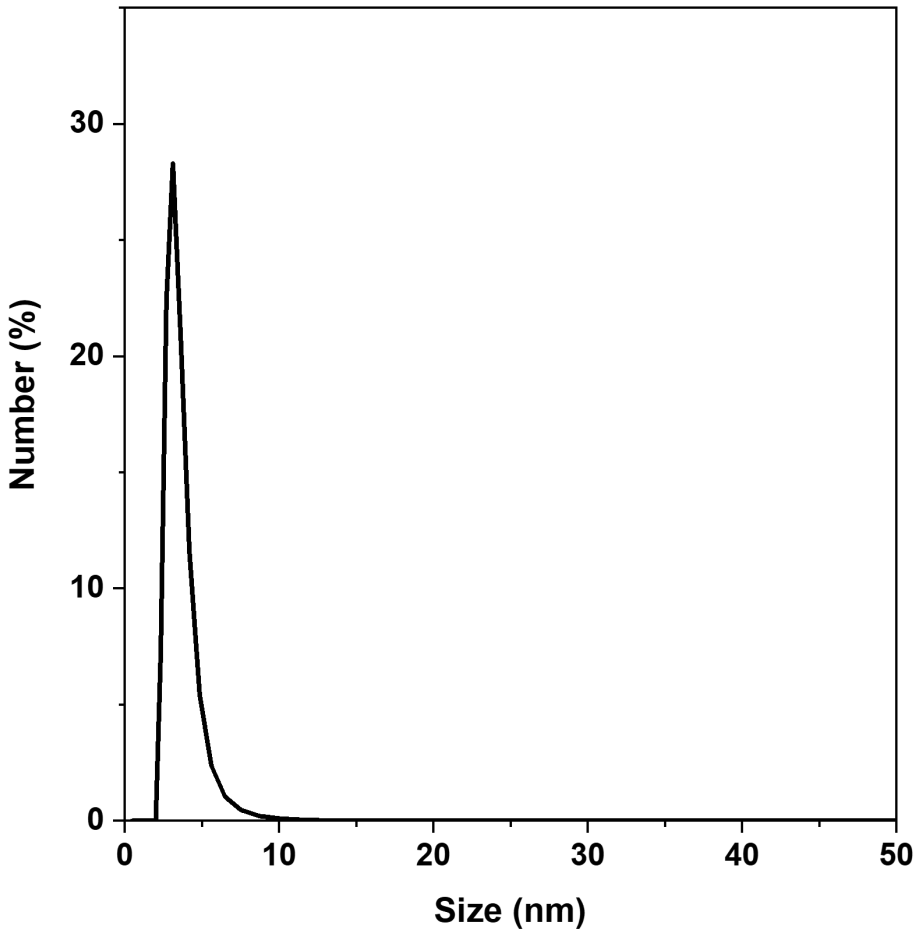

Figure S12. DLS spectrum of $(N_3)_1$-RhMOP in DMF with a concentration of 0.3 mM. The average diameter was found to be 2.6 ± 0.9 nm.

S3.3. (Alkyne)$_1$-RhMOP

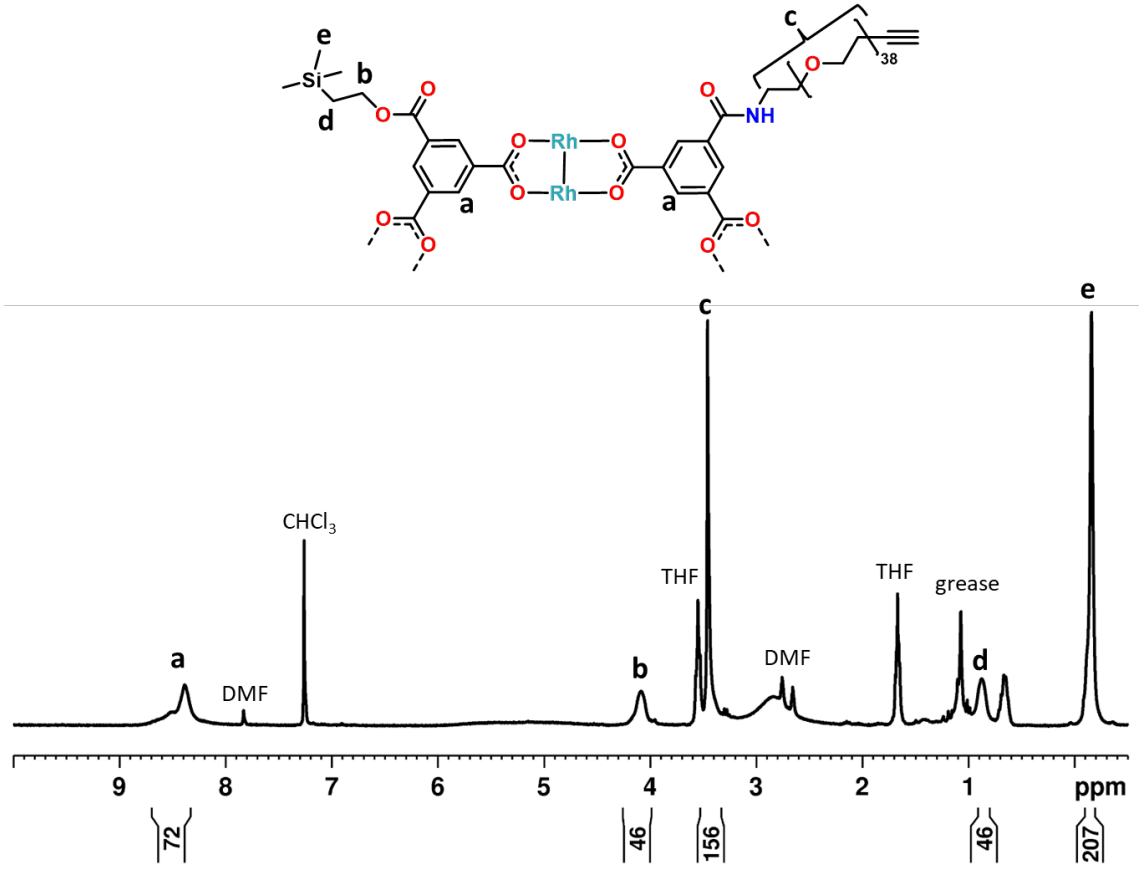

Figure S13. ^{1}H-NMR spectrum (300 MHz, 25ºC) of (Alkyne)$_1$-RhMOP in $CDCl_3$. Note that the relative integrations of the protons ascribed to the MOP core (*a*) and the and the aliphatic signals form the PEG chain (*c*) and TSE protecting group (*b* and *e*) correspond to the expected value for the proposed formula; that is, for each MOP core (24 COOTSE-BDC ligands with 72 aromatic protons *a*), there are 23 TSE protecting groups (46 protons *b* and 207 protons *e*) and a single PEG chain with *ca*. 156 aliphatic protons *c*.

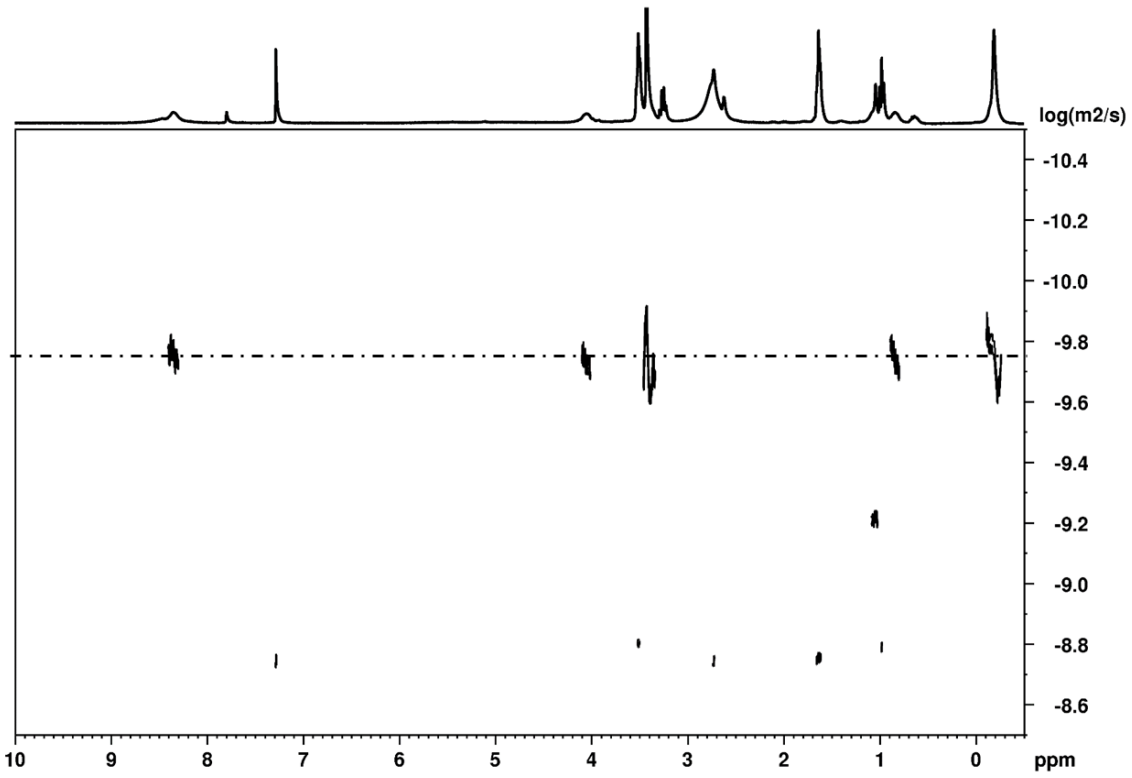

Figure S14. DOSY-NMR (300 MHz, 25ºC) spectrum of $(Alkyne)_1$-RhMOP in $CDCl_3$. The same diffusion coefficient ($D \approx 1.7 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$) is identified for the aromatic signals of the core of the Rh-MOP and the aliphatic signals from the COOTSE groups and the ones form the PEG, which evidences that all belong to the same molecular entity. The diffusion coefficient of the remaining $CHCl_3$ ($D \approx 2.3 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$) was used as internal reference.

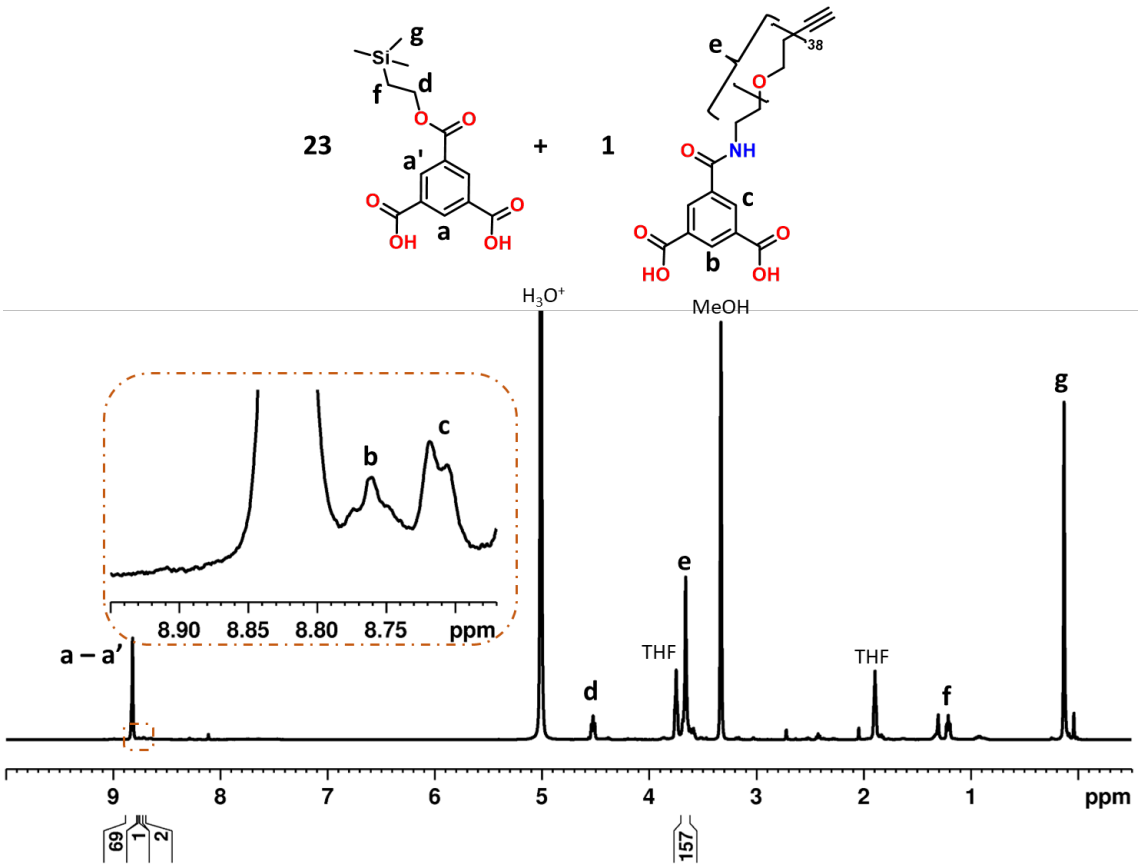

Figure S15. ^{1}H-NMR spectrum (500 MHz, 25ºC) of the digested (Alkyne)$_1$-RhMOP in MeOD under acidic conditions (DCl 2%, 65ºC, overnight). The appearance of the new aromatic signals (*b* and *c*) confirms the formation of the amide bond. The acidic digestion of (Alkyne)$_1$-RhMOP should release 23 protected ligands and 1 PEG-functionalized BDC ligand per MOP. The analysis of the relative integrations in the spectrum of the digested sample confirm the expected ratio of COOTSE-BDC:PEG-functionalized ligand of 23:1. Note that the peaks at 4.27, 1.07 and 0.13 ppm (protons *d*, *f* and *g* respectively) could not be integrated due to the hydrolysis of the COOTSE ester under the acidic MeOD conditions employed for the digestion. Proton *a* was employed to determine the ligand ratio.

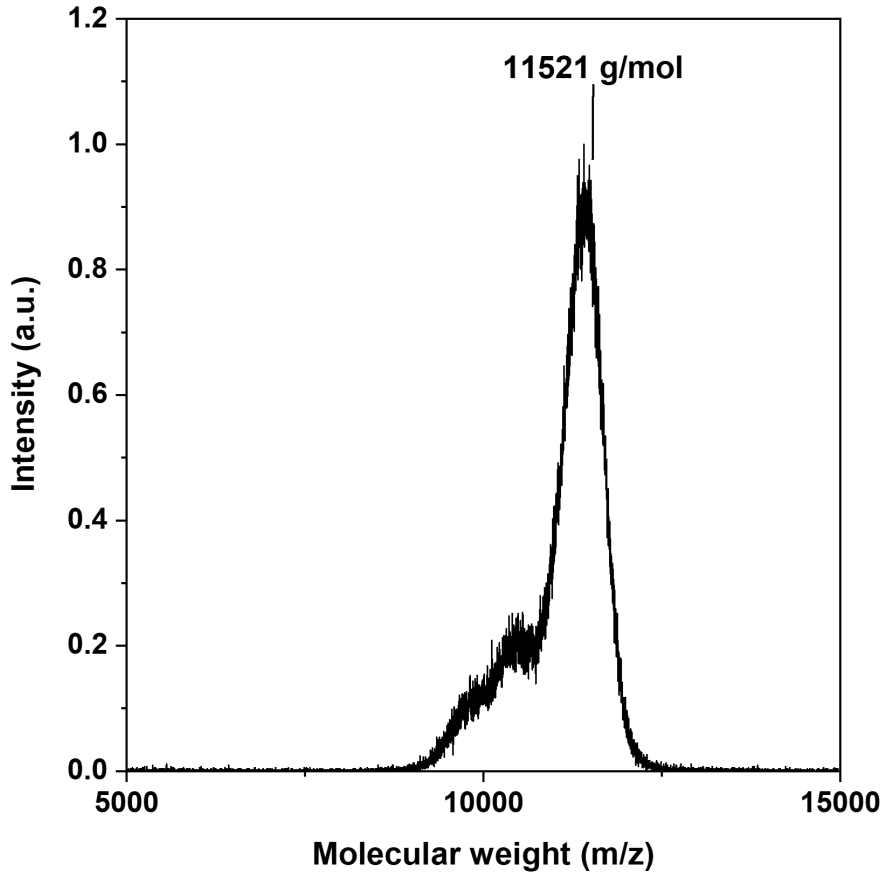

Figure S16. MALDI-TOF spectrum of $(Alkyne)_1$-RhMOP in DMF. The highlighted mass corresponds to the molecular formula of $[(COOTSE\text{-}BDC)_{23}(Alkyne\text{-}PEG_{38}\text{-}BDC)_1Rh_{24}+H^+]^+$. Expected: m/z = 11521 ± 480 g/mol; found: m/z = weight 11521 g/mol.

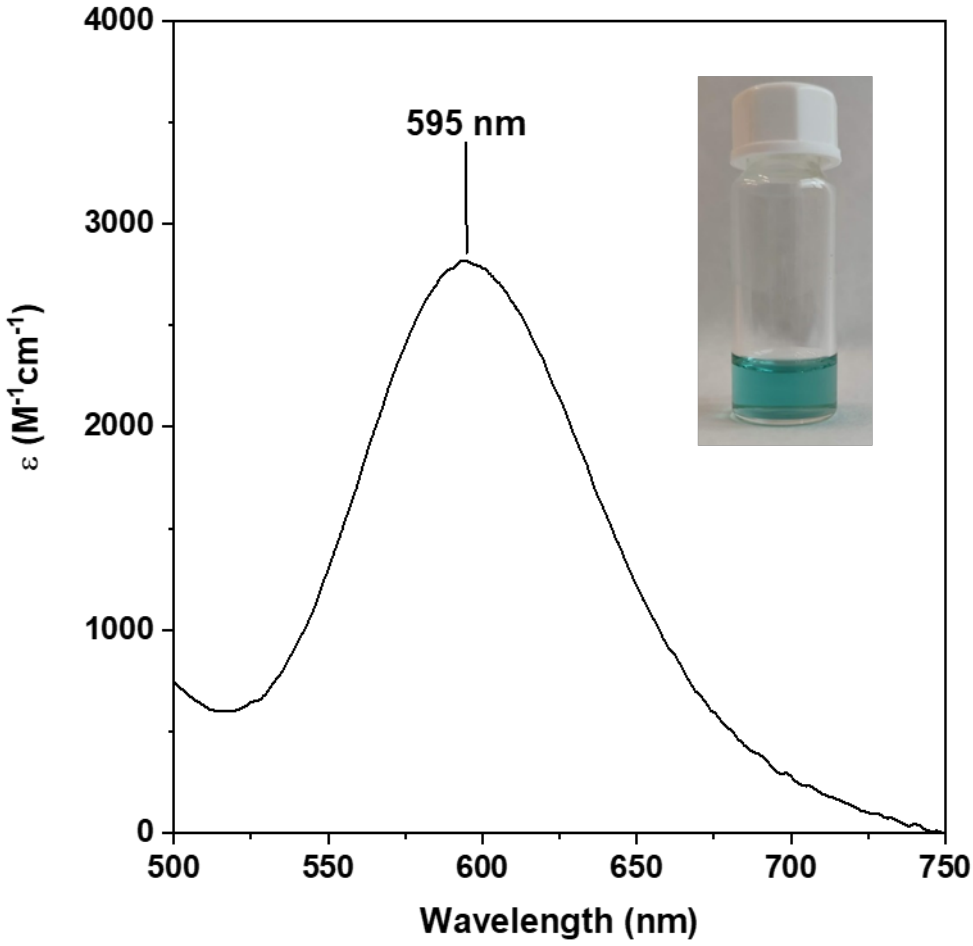

Figure S17. UV-Vis spectrum of $(Alkyne)_1$-RhMOP in DMF with a concentration of 0.2 mM. λ_{max} is centered at 595 nm, confirming that the Rh(II) paddlewheel is maintained after the amide formation and that there is not remaining coordinated N-containing reactants (*i.e.* NH_2-PEG_{38}-N_3, HOBt, HBTU, DIPEA).

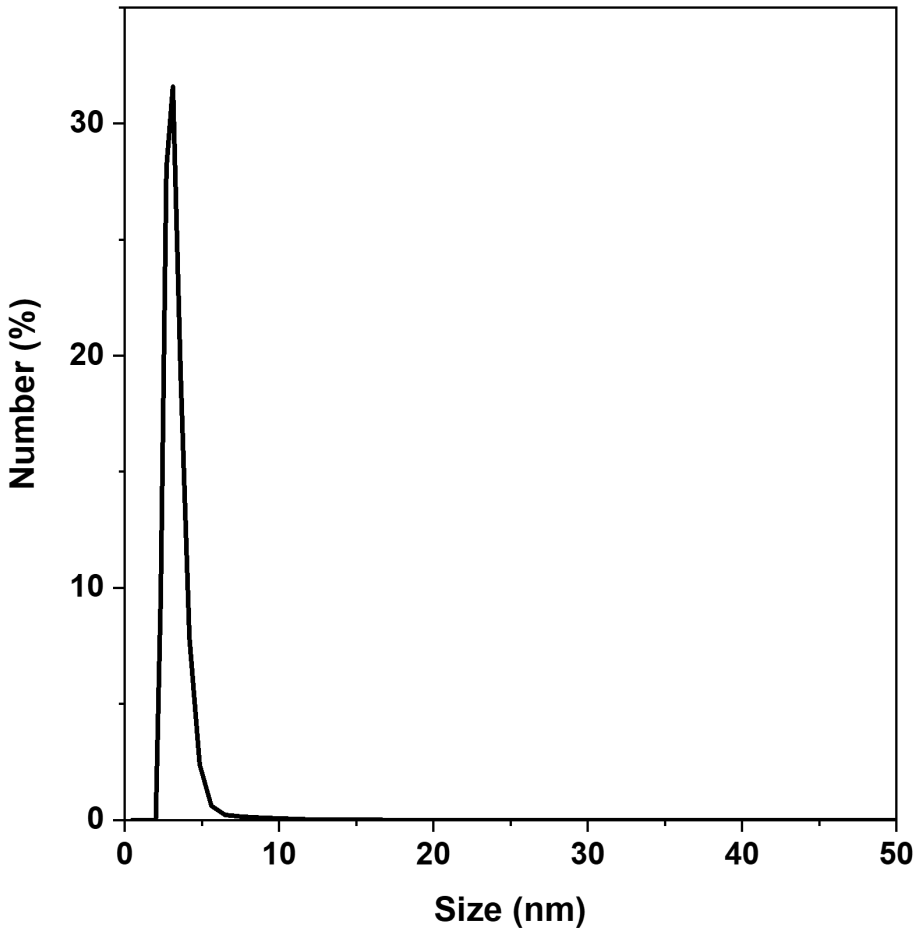

Figure S18. DLS spectrum of $(Alkyne)_1$-RhMOP in DMF with a concentration of 0.3 mM. The average diameter was found to be 3.3 ± 0.6 nm.

S3.4. Deprotected $(N_3)_1$-RhMOP

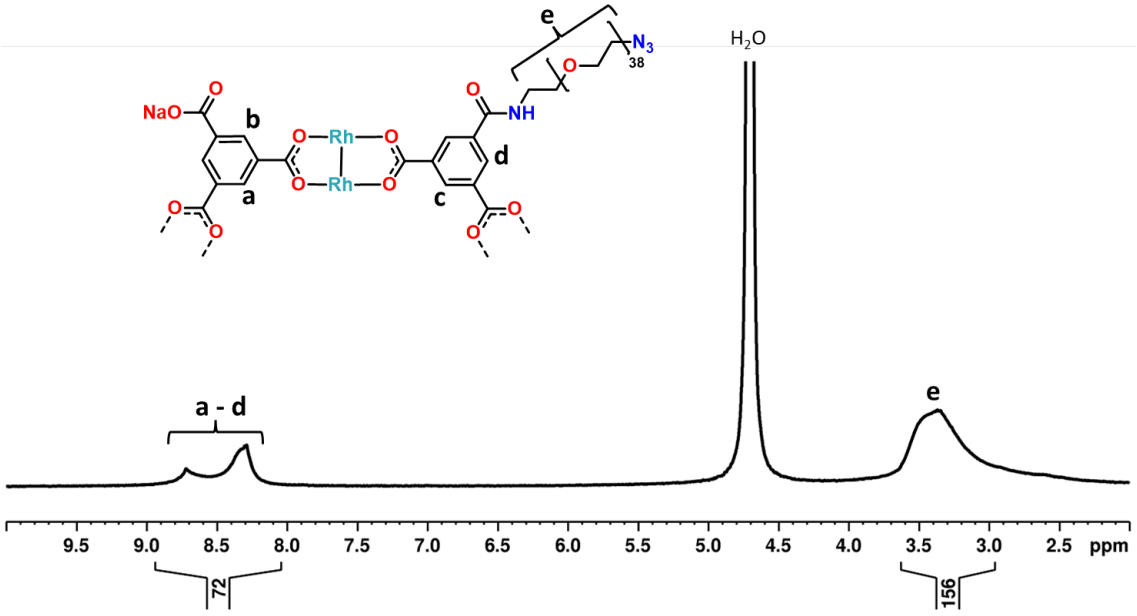

Figure S19. ^{1}H-NMR spectrum (300 MHz, 25ºC) of deprotected $(N_3)_1$-RhMOP in basic D_2O (pD ≈ 12). Note that, under basic conditions, the surface carboxylic groups are deprotonated affording solubility in water. The relative integrations of the protons ascribed to the MOP core (*a*-*d*) and the aliphatic signals form the PEG chain (*e*) correspond to the expected value for the proposed formula. That is, for each MOP core (24 functionalized BDC ligands with 72 aromatic protons *a*-*d*), there is a single PEG chain with *ca.* 156 aliphatic protons *e*.

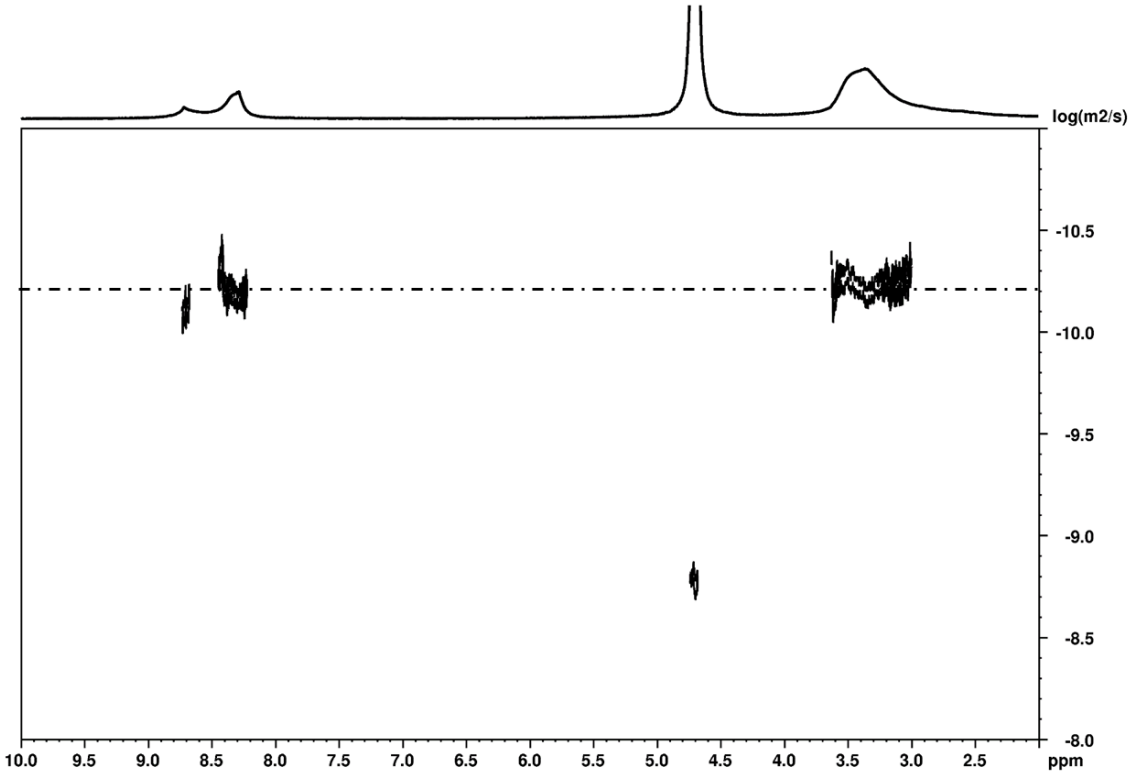

Figure S20. DOSY-NMR (300 MHz, 25ºC) spectrum of the deprotected $(N_3)_1$-RhMOP in D_2O (pD ≈ 12). The same diffusion coefficient (D = 6.6· 10^{-10} $m^2 \cdot s^{-1}$) is identified for the aromatic signals that correspond to the MOP and for the PEG, demonstrating that all belongs to the same molecule. The diffusion coefficient of the remaining H_2O (D ≈ 2.3 · 10^{-9} $m^2 \cdot s^{-1}$) was used as internal reference.

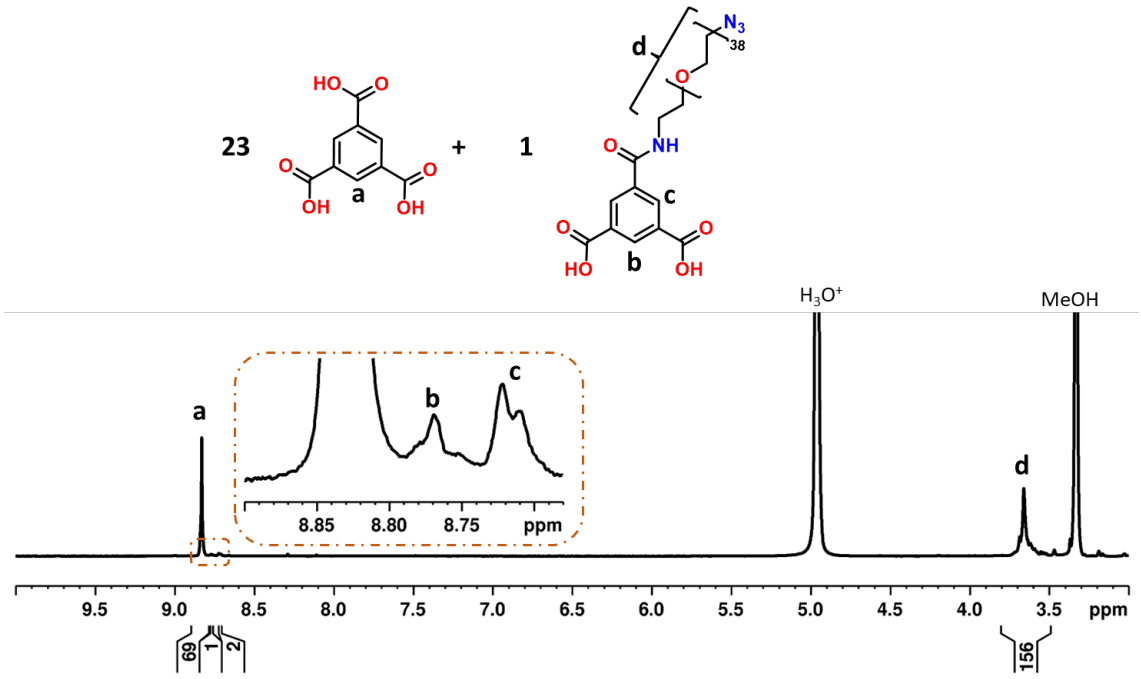

Figure S21. ^{1}H-NMR spectrum (500 MHz, 25ºC) of the digested deprotected $(N_3)_1$-RhMOP in MeOD under acidic conditions (DCl 2%, 65 ºC, overnight). The analysis of the relative integrations in the spectrum of the digested sample confirms the expected ratio of BTC:PEG-functionalized ligand of 23:1.

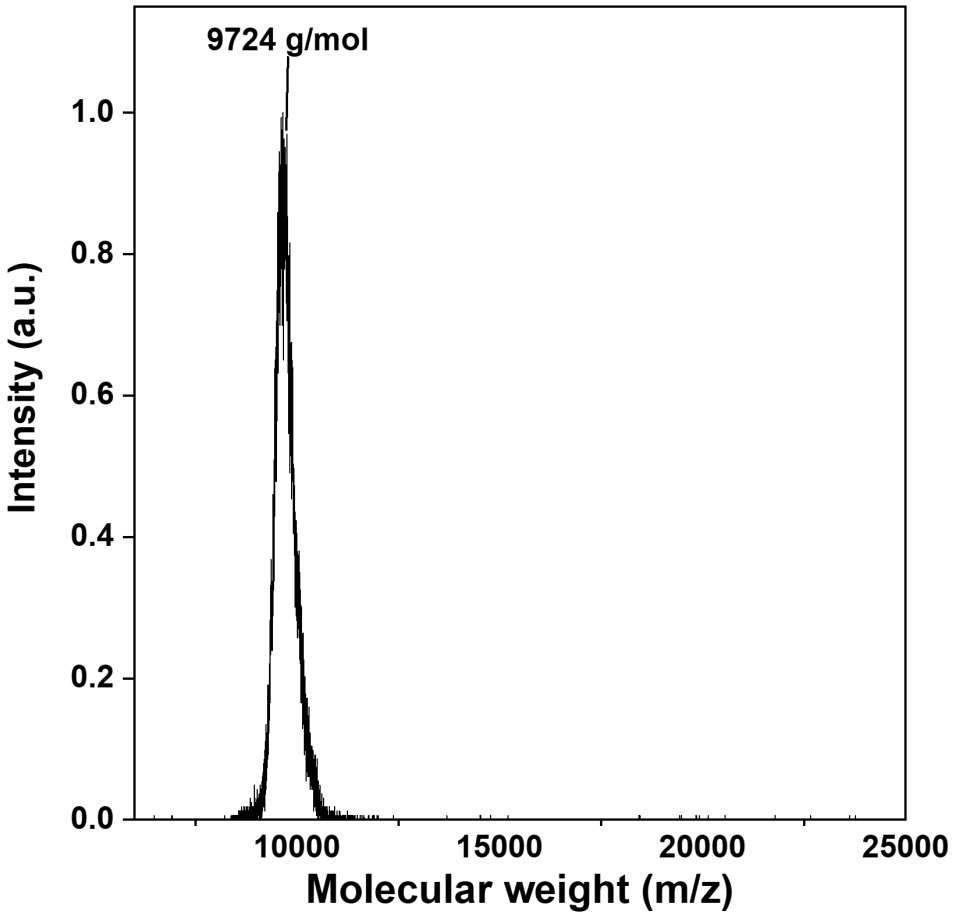

Figure S22. MALDI-TOF spectrum of the deprotected $(N_3)_1$-RhMOP in basic H_2O. The highlighted mass corresponds to the molecular formula of $[(COONa\text{-}BDC)_{23}((N_3)\text{-}PEG_{38}\text{-}BDC)_1Rh_{24}\text{-}Na^+]^-$. Expected m/z = 9726 ± 370 g/mol; found m/z = 9724 g/mol.

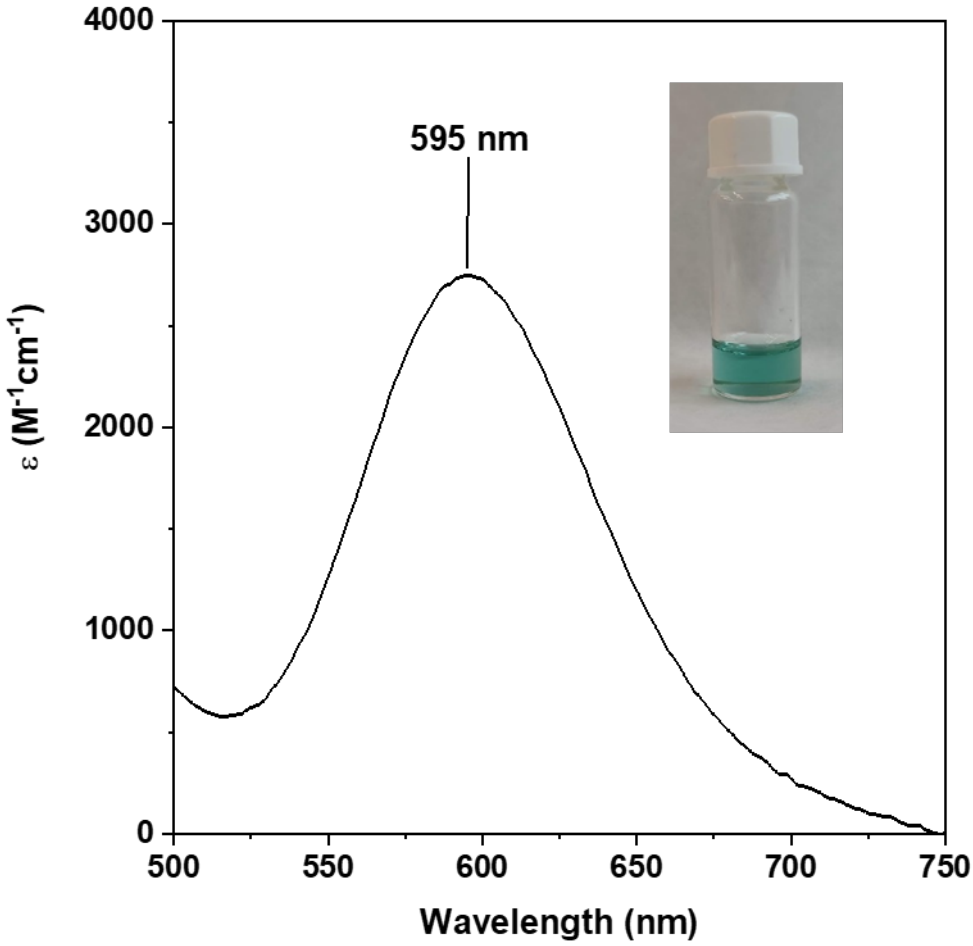

Figure S23. UV-Vis spectrum of the deprotected $(N_3)_1$-RhMOP in DMF with a concentration of 0.2 mM. λ_{max} is centered at 595 nm, confirming that the Rh(II) paddlewheel is maintained and that there is not remaining coordinated N-containing reactants (*i.e.* NH_2-PEG_{38}-N_3).

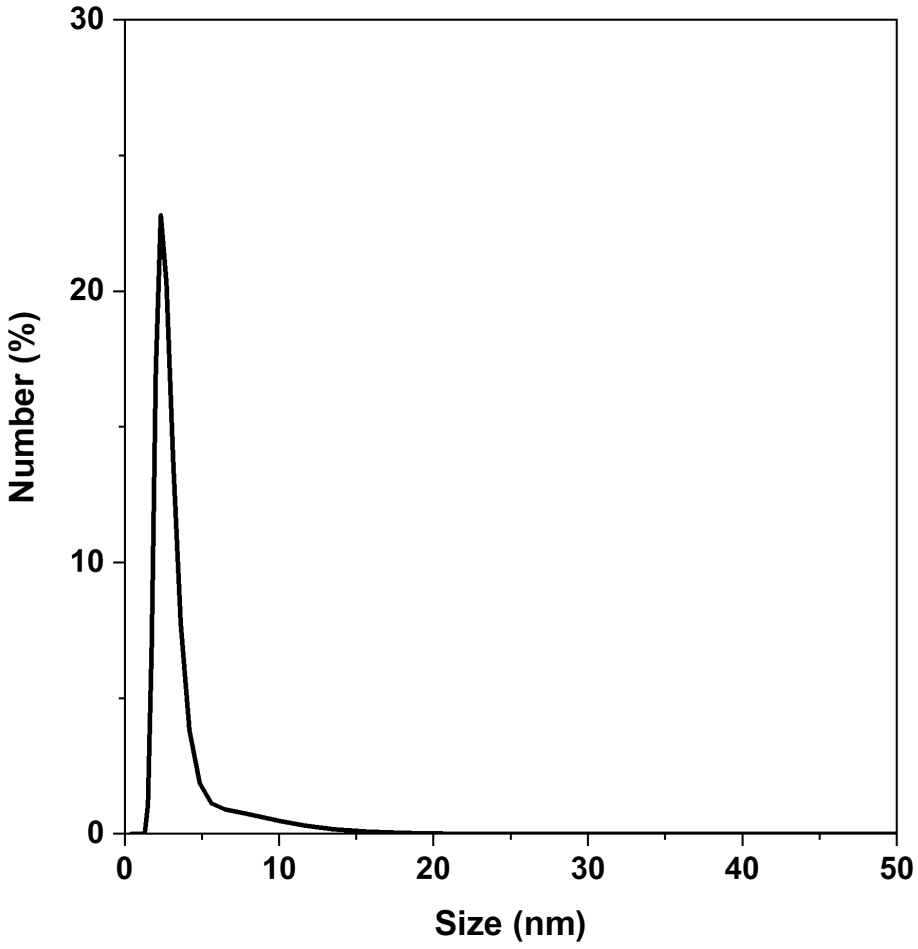

Figure S24. DLS spectrum of the deprotected $(N_3)_1$-RhMOP in DMF with a concentration of 0.3 mM. The average diameter was found to be 2.6 ± 0.2 nm.

S3.5. Deprotected (Alkyne)$_1$-RhMOP

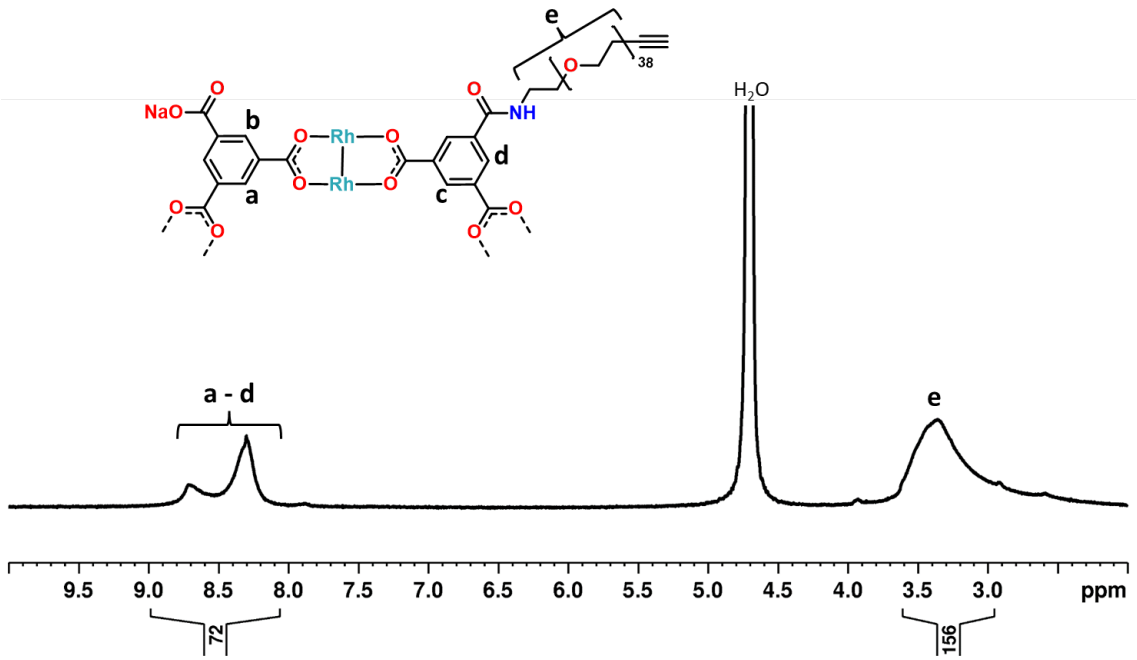

Figure S25. ^{1}H-NMR spectrum (300 MHz, 25ºC) of the deprotected (Alkyne)$_1$-RhMOP in basic D_2O (pD ≈ 12). Note that under basic conditions the surface carboxylic groups are deprotonated affording solubility in water. The relative integrations of the protons ascribed to the MOP core (*a*-*d*) and the aliphatic signals form the PEG chain (*e*) correspond to the expected value for the proposed formula; that is, for each MOP core (24 functionalized BDC ligands with 72 aromatic protons *a*-*d*), there is a single PEG chain with *ca.* 156 aliphatic protons *e*.

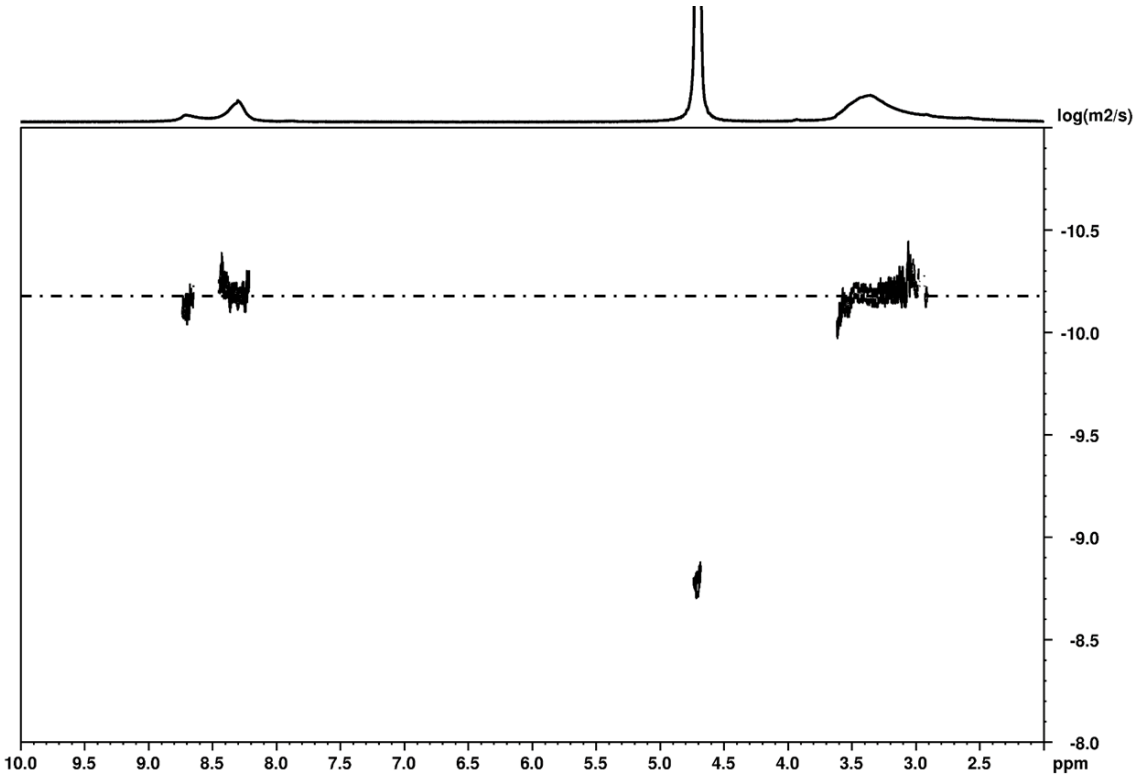

Figure S26. DOSY-NMR (300 MHz, 25ºC) spectrum of the deprotected $(Alkyne)_1$-RhMOP in D_2O (pD ≈ 12). The same diffusion coefficient ($D \approx 6.9 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$) is identified for the aromatic signals that correspond to the MOP and for the PEG, demonstrating that all belongs to the same molecular entity. The diffusion coefficient of the remaining H_2O ($D \approx 2.3 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$) was used as internal reference.

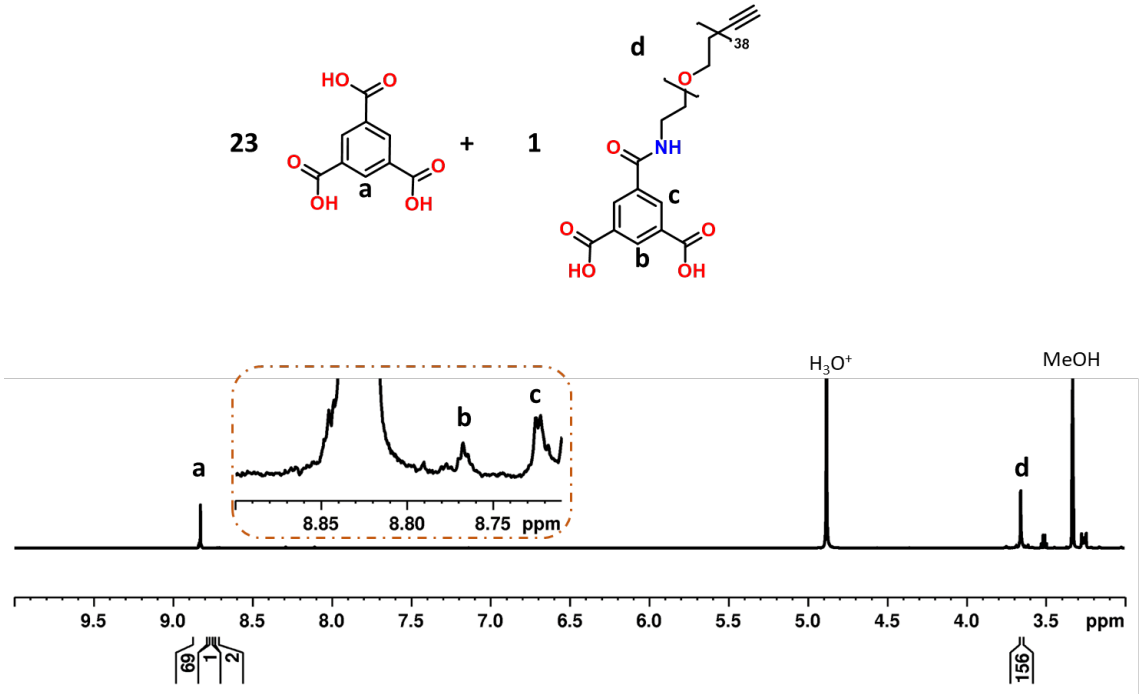

Figure S27. ^{1}H-NMR spectrum (500 MHz, 25ºC) of the digested deprotected $(Alkyne)_1$-RhMOP in MeOD under acidic conditions (DCl 2%, 65 ºC, overnight). The analysis of the relative integrations in the spectrum of the digested sample confirms the expected ratio of BTC:PEG-functionalized ligand of 23:1.

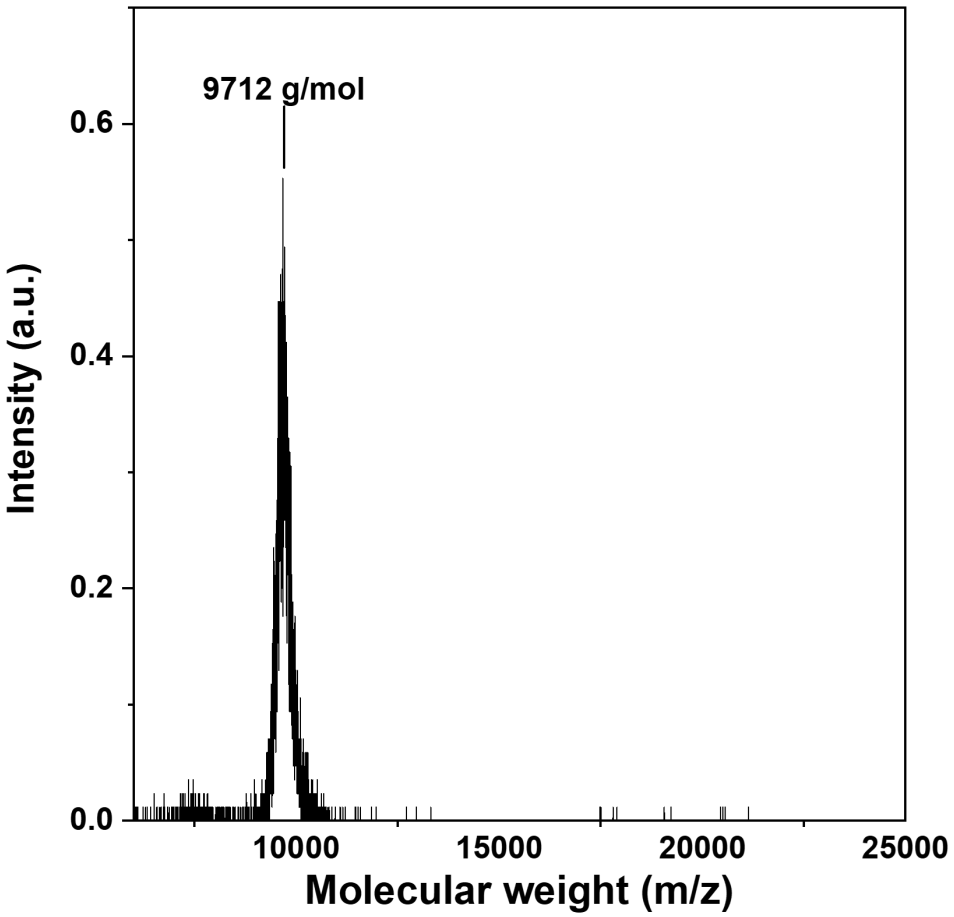

Figure S28. MALDI-TOF spectrum of the deprotected $(Alkyne)_1$-RhMOP in basic H_2O. The highlighted mass corresponds to the molecular formula of $[(COONa\text{-}BDC)_{23}(Alkyne\text{-}PEG_{38}\text{-}BDC)_1Rh_{24}\text{-}Na^+]^-$. Expected m/z = 9706 ± 480 g/mol; found m/z = 9712 g/mol.

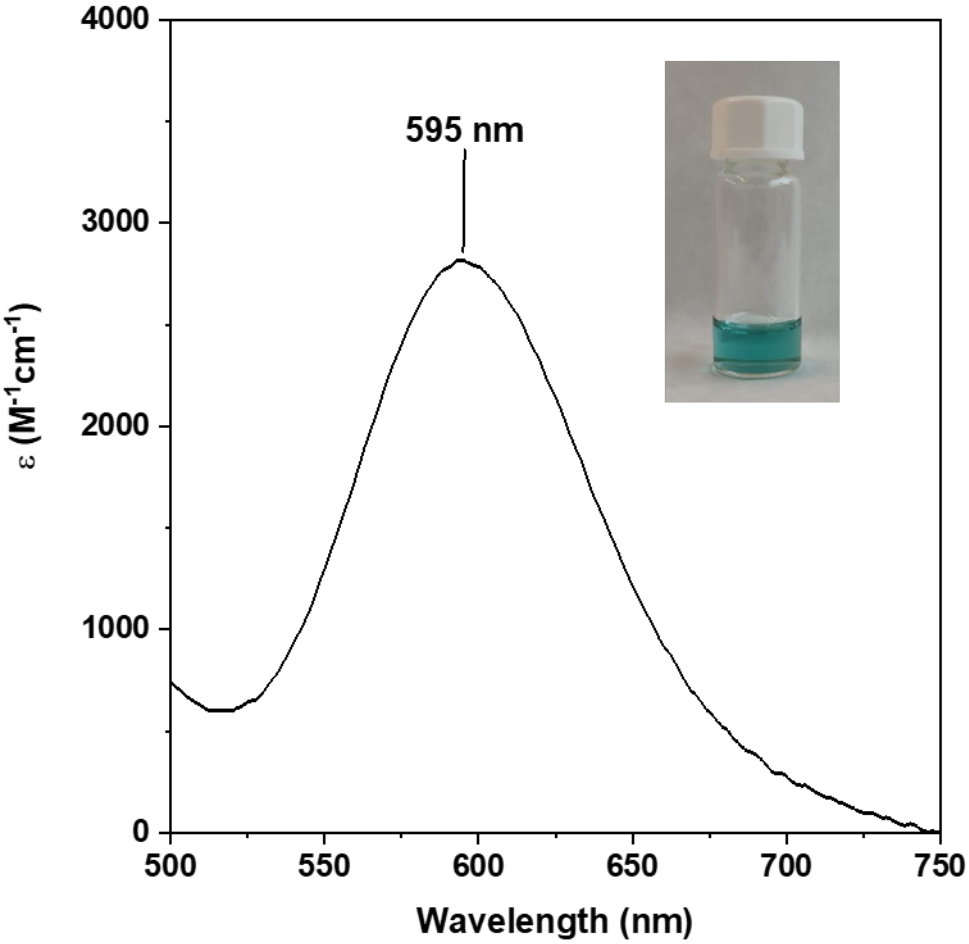

Figure S29. UV-Vis spectrum of the deprotected $(Alkyne)_1$-RhMOP in DMF with a concentration of 0.2 mM. λ_{max} is centered at 595 nm, confirming that the Rh(II) paddlewheel is maintained and that there is not remaining coordinated N-containing reactants (*i.e.* NH_2-PEG_{38}-Alkyne).

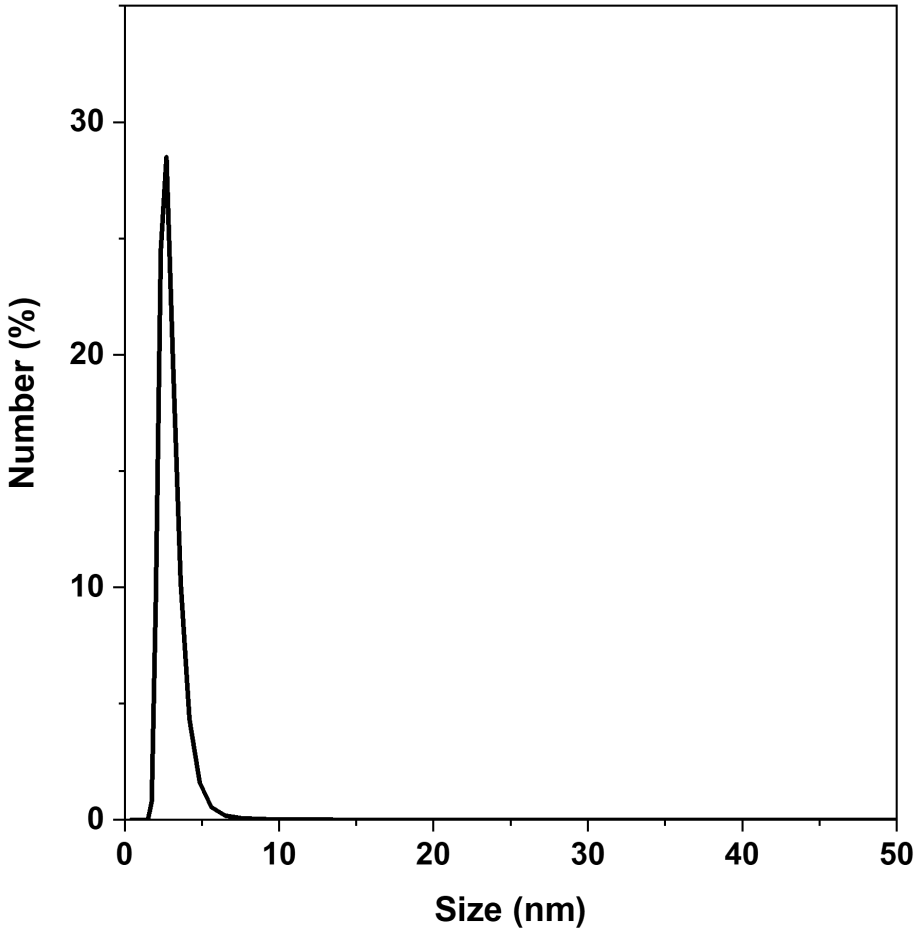

Figure S30. DLS spectrum of the deprotected $(Alkyne)_1$-RhMOP in DMF with a concentration of 0.3 mM. The average diameter was found to be 2.3 ± 0.3 nm.

S3.6. Control experiments

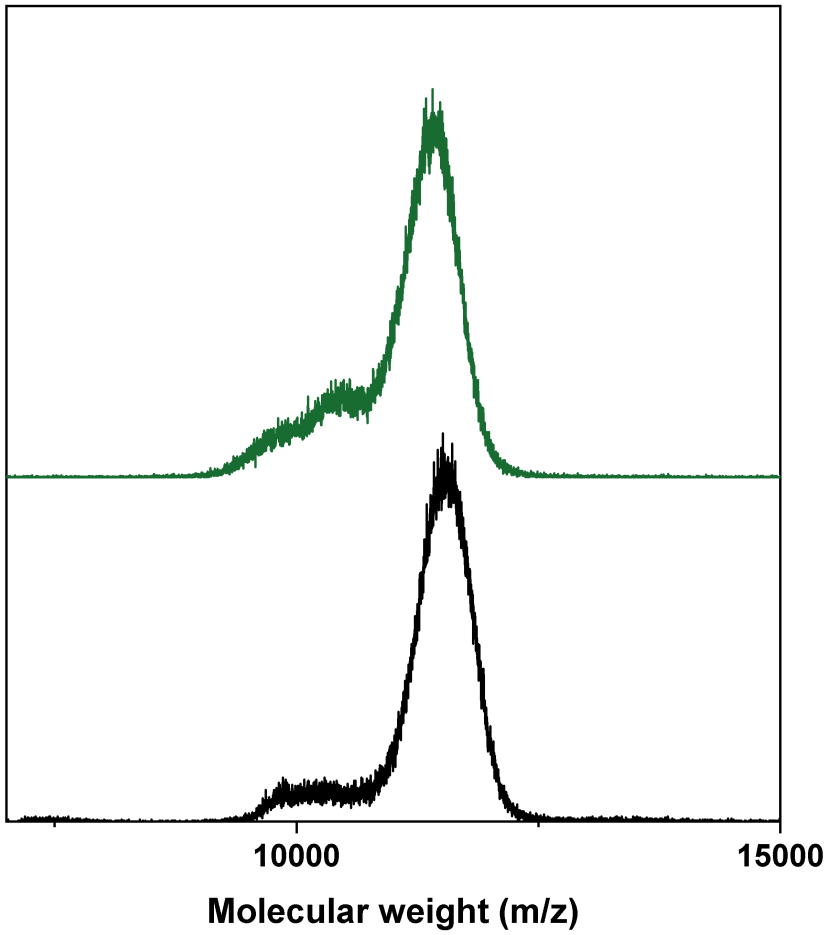

Figure S31. MALDI-TOF spectra comparison between $(N_3)_1$-RhMOP obtained through the reaction of $(COOH)_1$-RhMOP with 2 mol. eqs. of NH_2-PEG_{38}-N_3 (green, top) or 5 mol. eqs. of NH_2-PEG_{38}-N_3 (black, bottom).

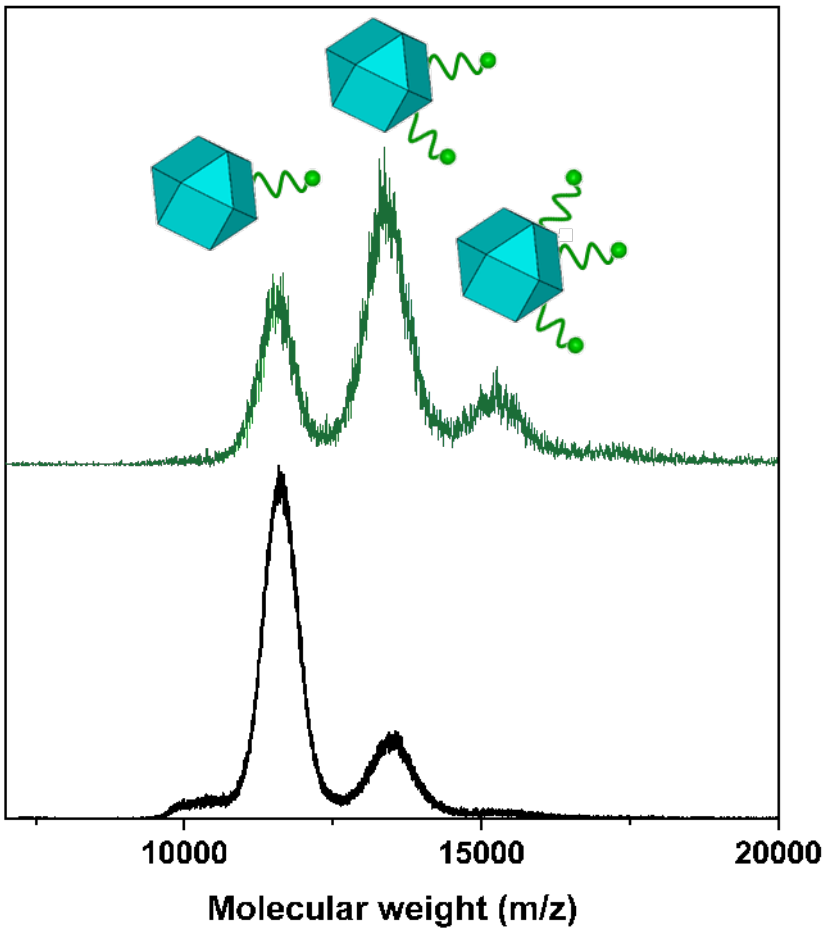

Figure S32. MALDI-TOF spectra of the products obtained after reacting 5 mol. eq. of NH_2-PEG_{38}-N_3 with TSE-protected Rh-MOPs treated with 3 mol. eq. of TBAF (black) and 5 mol. eq. of TBAF (green).

S3.7. MOP-dimer

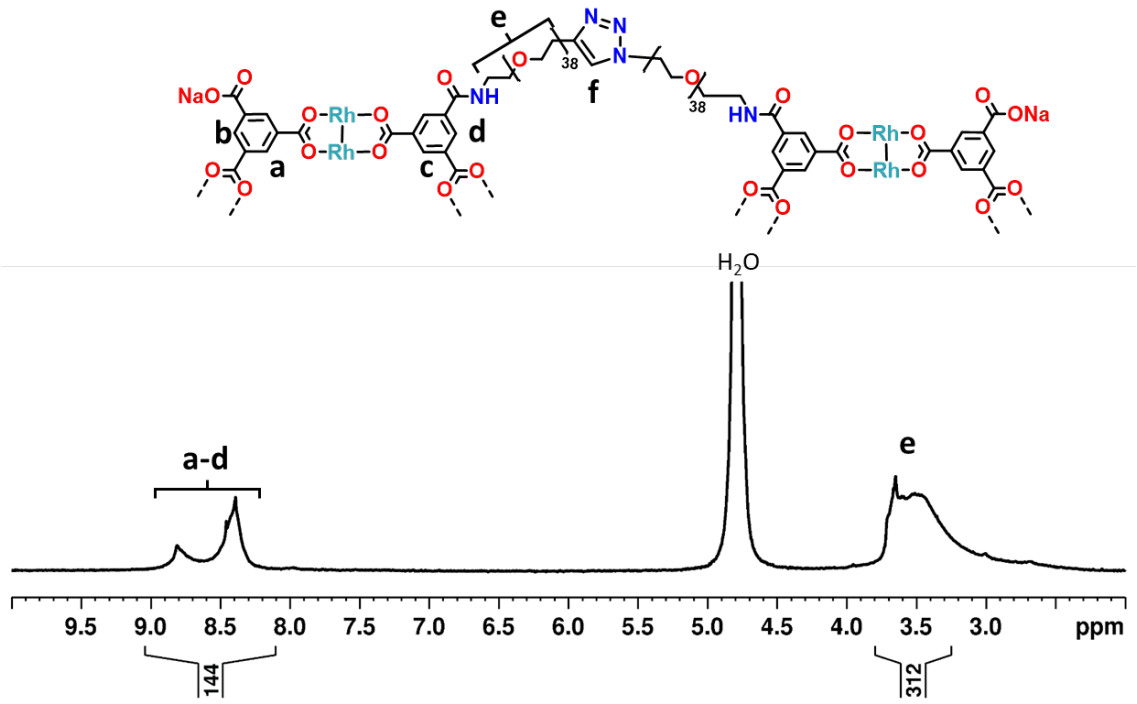

Figure S33. ^{1}H-NMR spectrum (300 MHz, 25ºC) of MOP-dimer in D_2O (pD ≈ 12). Note that under basic conditions the surface carboxylic groups are deprotonated affording solubility in water. The relative integrations of the protons ascribed to the MOP core (*a-d*) and the aliphatic signals form the PEG chain (e) correspond to the expected value for the proposed formula; that is, for each dimer, there are 2 MOPs with 144 aromatic protons (a-d) and a single PEG chain linking them with *ca.* 312 aliphatic protons (*e*).

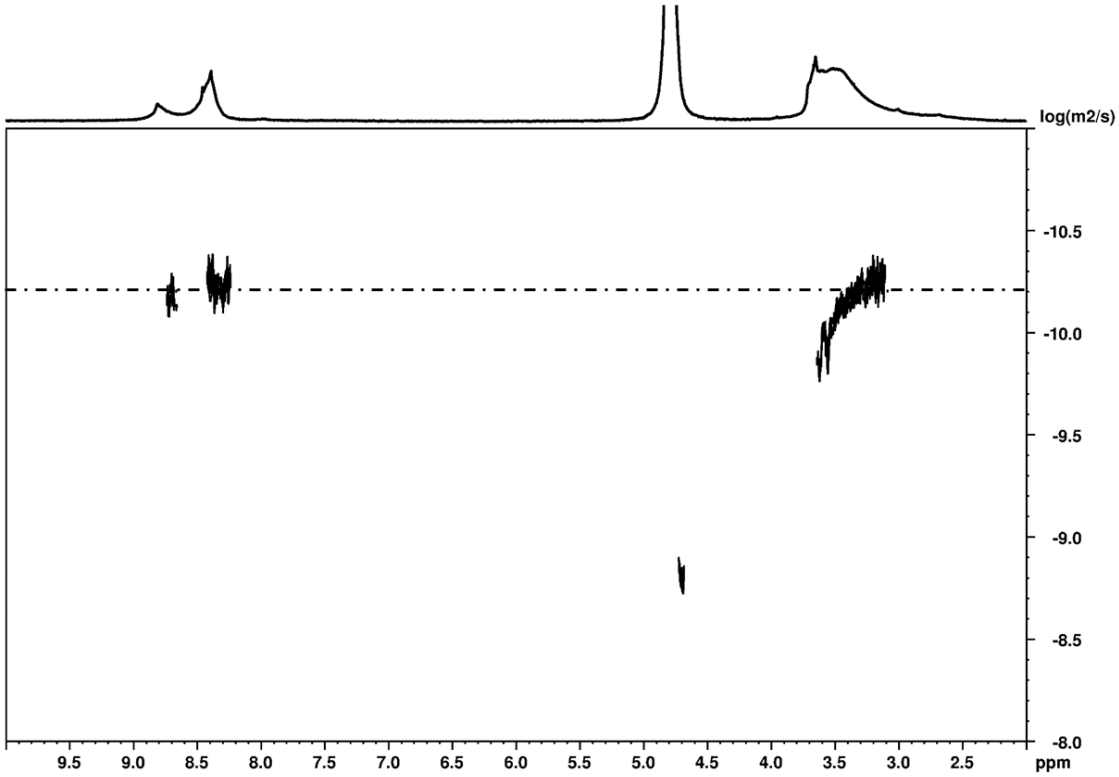

Figure S34. DOSY-NMR (300 MHz, 25ºC) spectrum of the MOP-dimer in basic D_2O (pD ≈ 12). The same diffusion coefficient (D ≈ 6.2· 10^{-10} $m^2 \cdot s^{-1}$) is identified for the aromatic signals that correspond to the MOP and for the PEG, demonstrating that all belongs to the same molecule. The diffusion coefficient of the residual H_2O (D ≈ 2.3 · 10^{-9} $m^2 \cdot s^{-1}$) was used as internal reference.

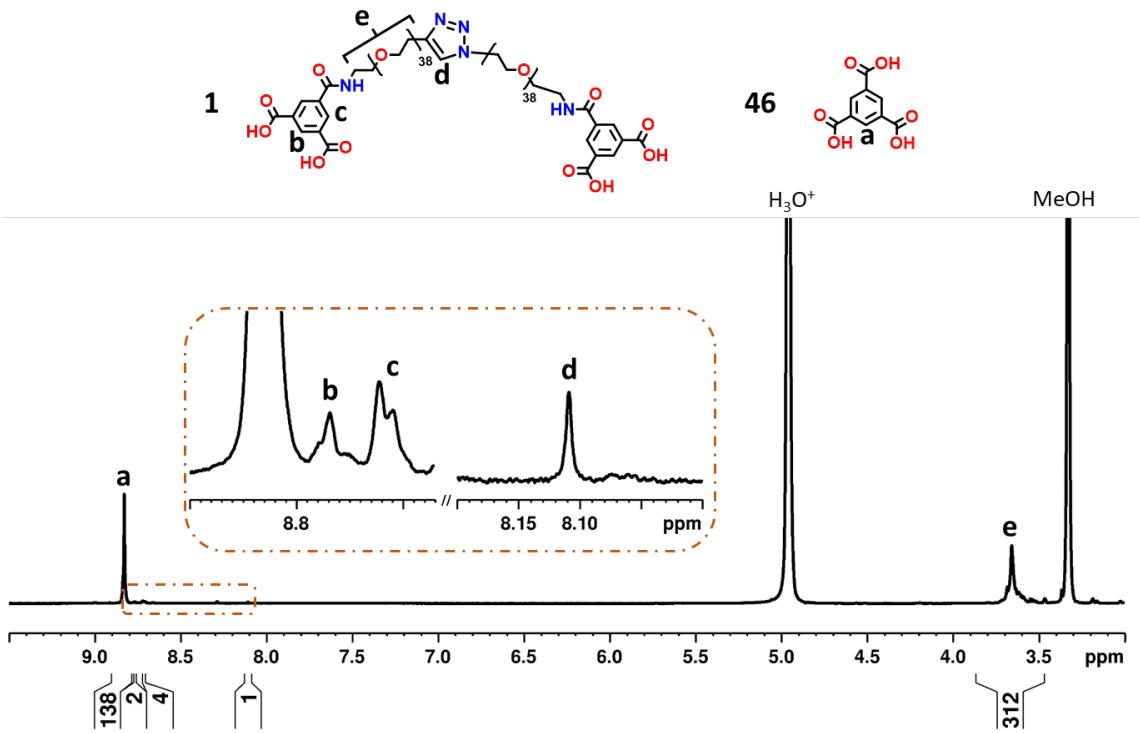

Figure S35. ^{1}H-NMR spectrum (500 MHz, 25ºC) of the digested MOP-dimer in MeOD under acidic conditions (DCl 2 %, 65º C, overnight). The appearance of a singlet at 8.11 ppm (proton *d*) confirms the formation of the triazole ring. The acidic digestion of the dimer should release 46 trimesic ligands (138 protons) and one molecule consisting of two functionalized BDC linkers bridged by a PEG chain (*ca.* 312 aliphatic protons). The analysis of the relative integrations in the spectrum of the digested sample confirms the expected ratio of BTC ligand:bridged functionalized BDC ligand of 46:1.

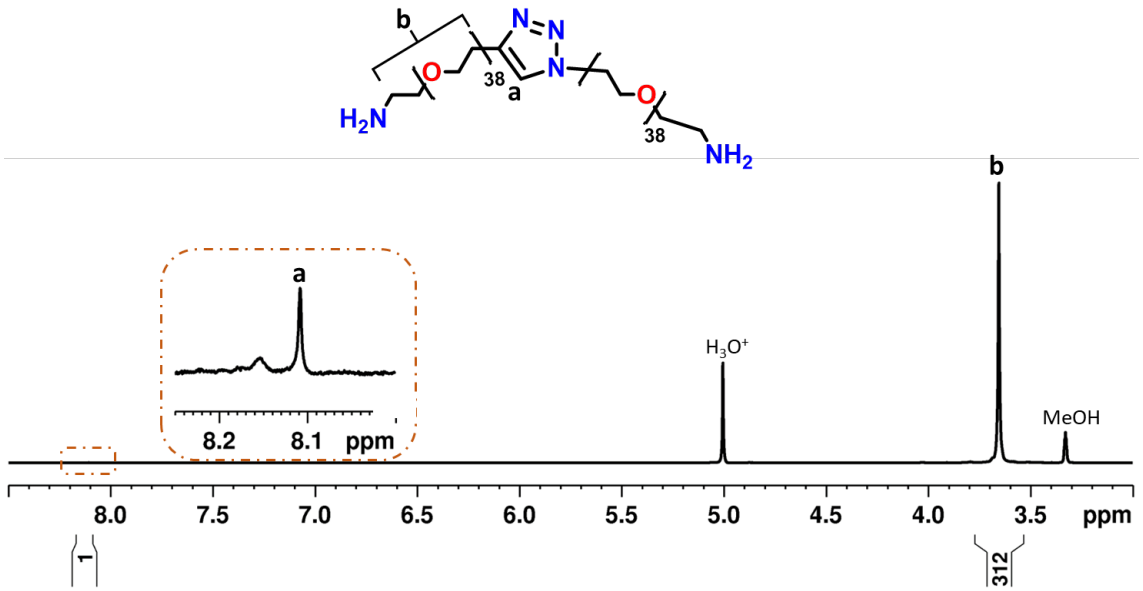

Figure S36. ^{1}H-NMR spectrum (500 MHz, 25ºC) of the digested product obtained after a blank click reaction between NH_2-PEG_{38}-(N_3) and NH_2-PEG_{38}-Alkyne. Digestion carried out in MeOD under acidic conditions (DCl 2 %, 65º C, overnight). A singlet appearing at 8.11 ppm can be ascribed to the triazole ring (a), as in the case of the spectrum of the digested MOP – dimer (Figure S33).

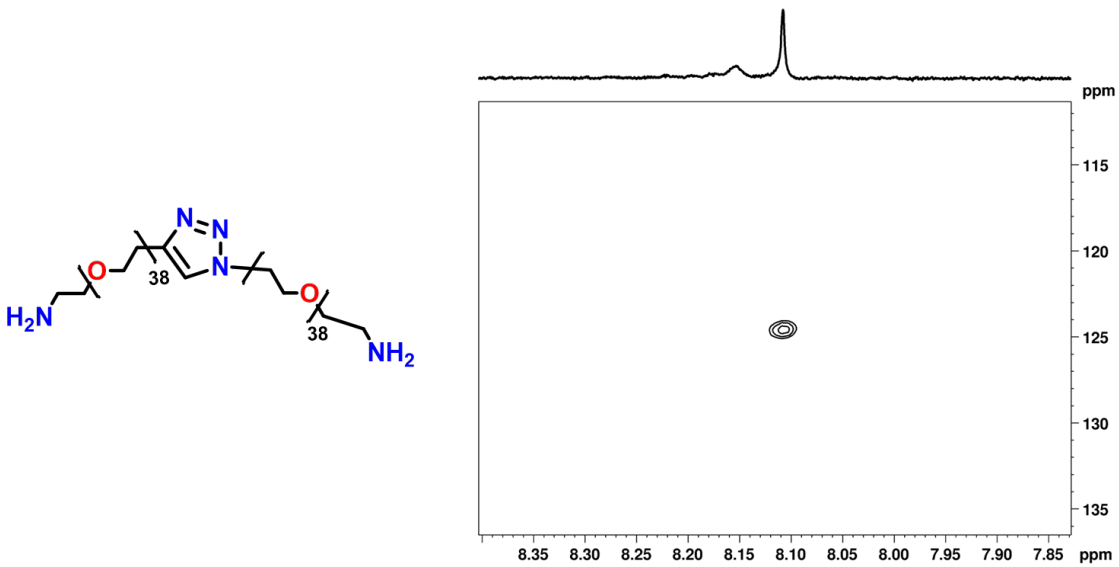

Figure S37. ^{1}H-^{13}C- HSQC spectrum (500 MHz, 25ºC) of the product obtained after a blank click reaction between NH_2-PEG_{38}-N_3 and NH_2-PEG_{38}-Alkyne. The correlation of the proton *a* at 8.11 ppm with a carbon at 124 ppm, which is in agreement with the expected chemical shift for an aromatic triazole carbon,[2] further confirms the assignment of proton *a* to the triazole ring.

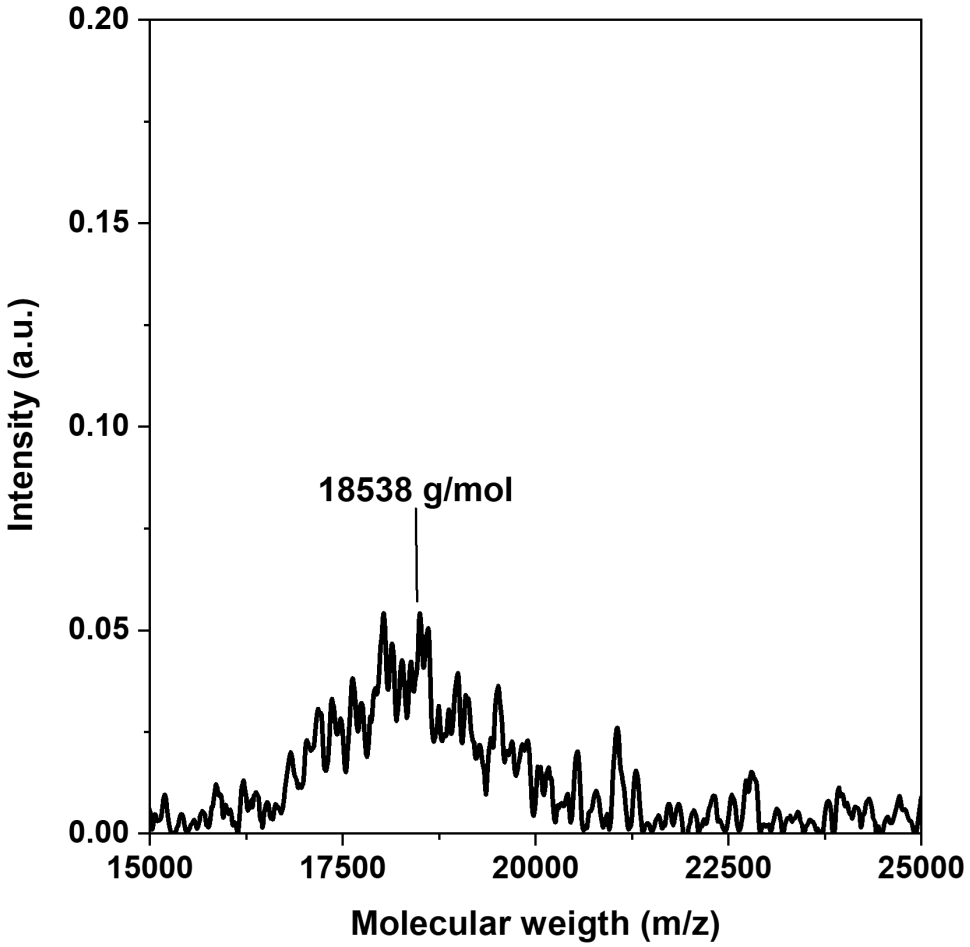

Figure S38. MALDI-TOF spectra of MOP-dimer in DMF. The highlighted mass corresponds to the molecular formula of $[(COOH\text{-}BDC)_{46}(BDC\text{-}PEG_{38}\text{-}1H\text{-}1,2,3\text{-}triazol\text{-}4\text{-}yl\text{-}PEG_{38}\text{-}BDC)_1Rh_{48}\text{-}H^+]^-\cdot DMF$. Expected m/z = 18539 ± 850 g/mol; found m/z = 18538 g/mol.

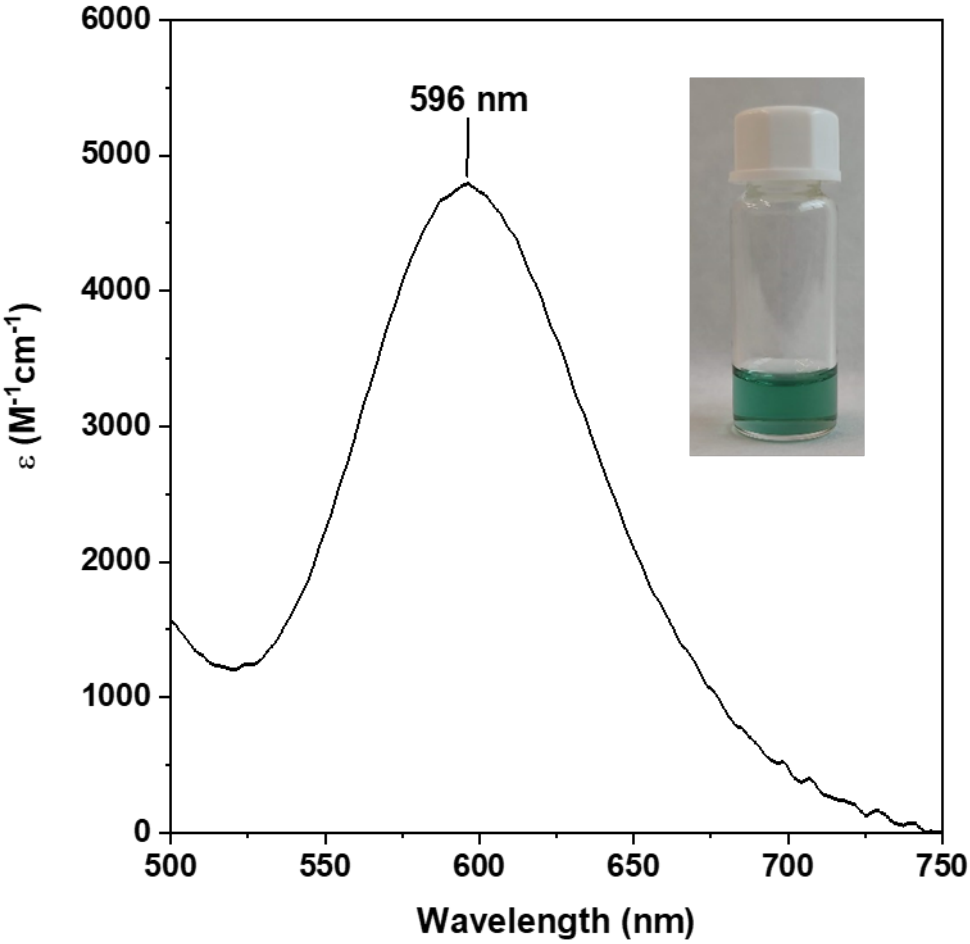

Figure S39. UV-Vis spectrum of MOP-dimer in DMF with a concentration of 0.2 mM. λ_{max} is centered at 596 nm, confirming that the Rh(II) paddlewheel is maintained and that it is not coordinated to N-containing reagents (i. e. *i.e.* NH_2-PEG_{38}-Alkyne) or the triazole moiety present in the product.

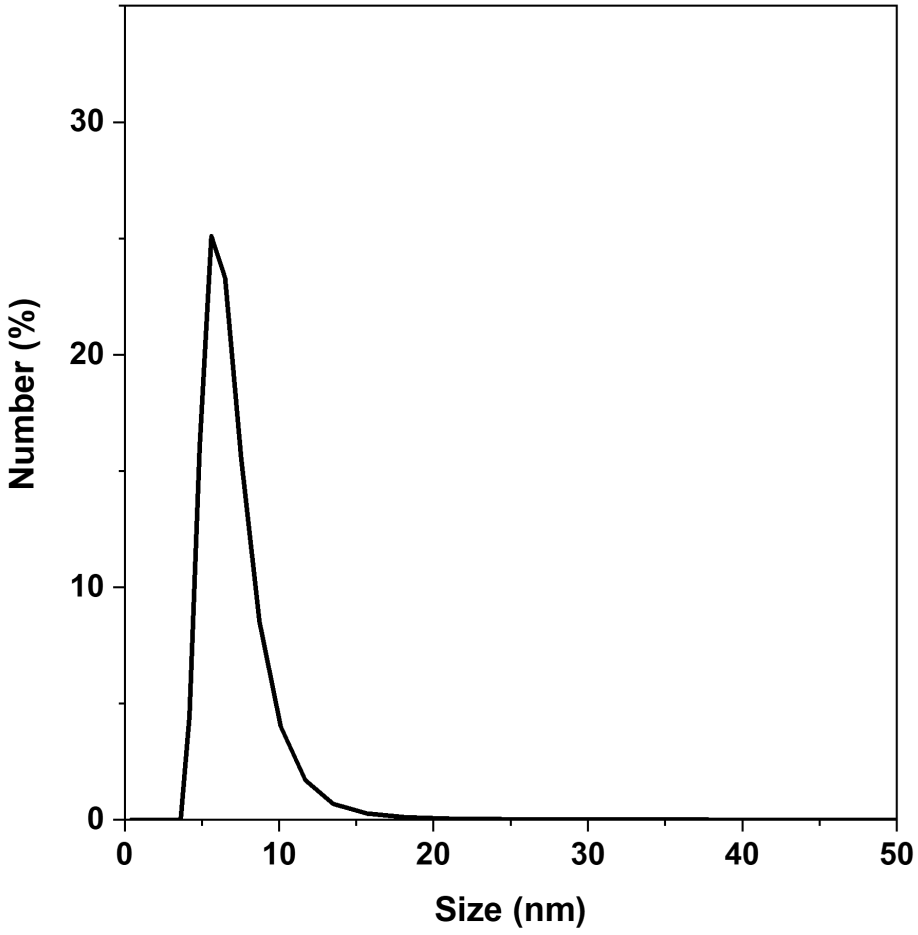

Figure S40. DLS spectrum of MOP-dimer in basic H_2O (pH ≈ 12) at a concentration of 0.3 mM. The average diameter was found to be 6.3 ± 1.1 nm.

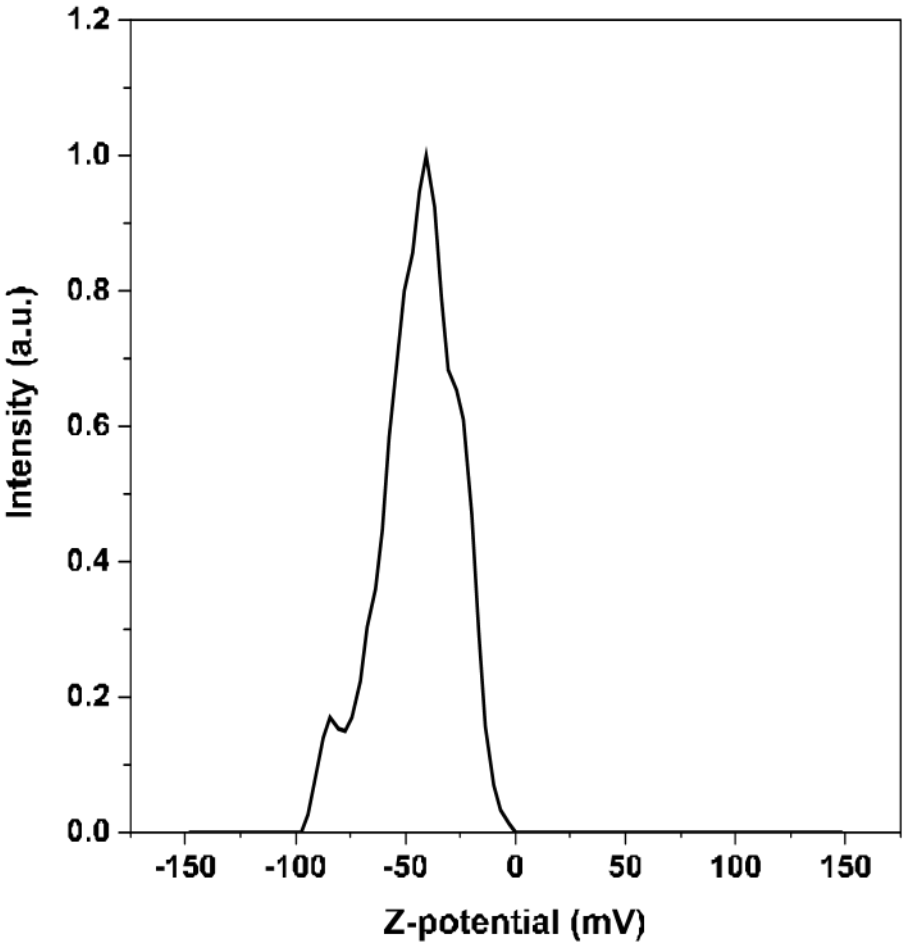

Figure S41. Z-potential distribution of MOP-dimer in basic water H_2O (pH = 12).

S3.8. 4-c cluster $Rh_2(PEG_6\text{-Alkyne})_4$

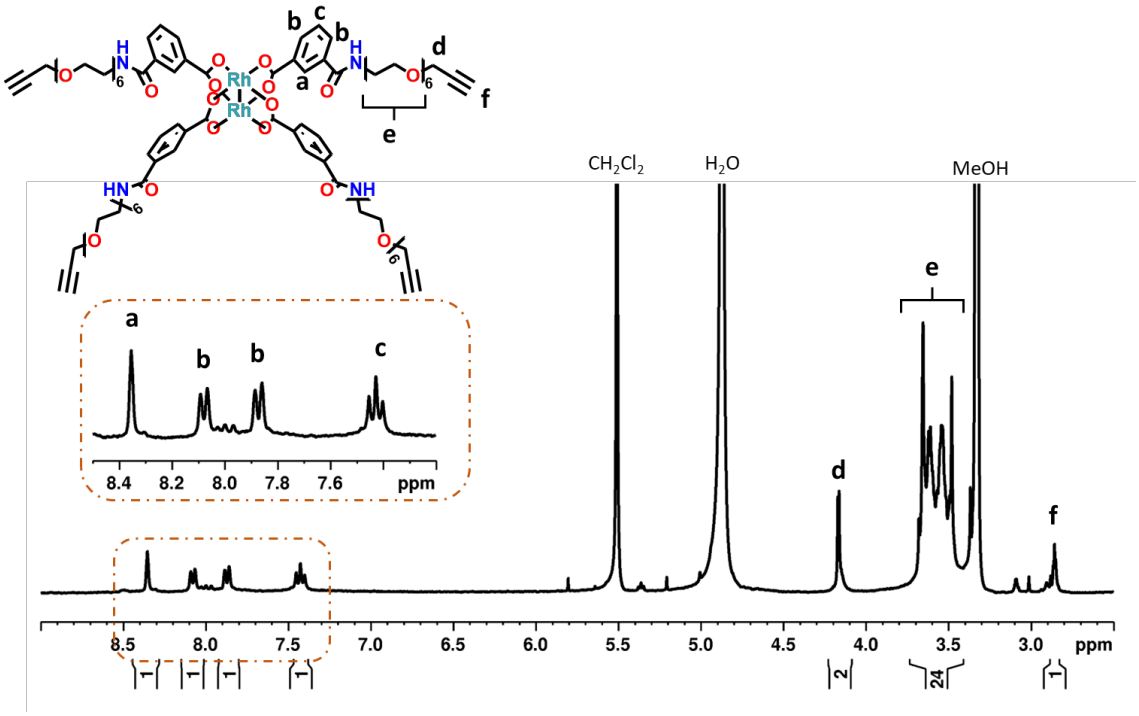

Figure S42. ^{1}H-NMR spectrum (300 MHz, 25ºC) of the 4-c $Rh_2(PEG_6\text{-Alkyne})_4$ cluster in MeOD. The correct ratio between the aromatic and the aliphatic signals confirms the successful attachment of four $NH_2\text{-}PEG_6\text{-Alkyne}$ chains to the Rh_2BDC_4 cluster.

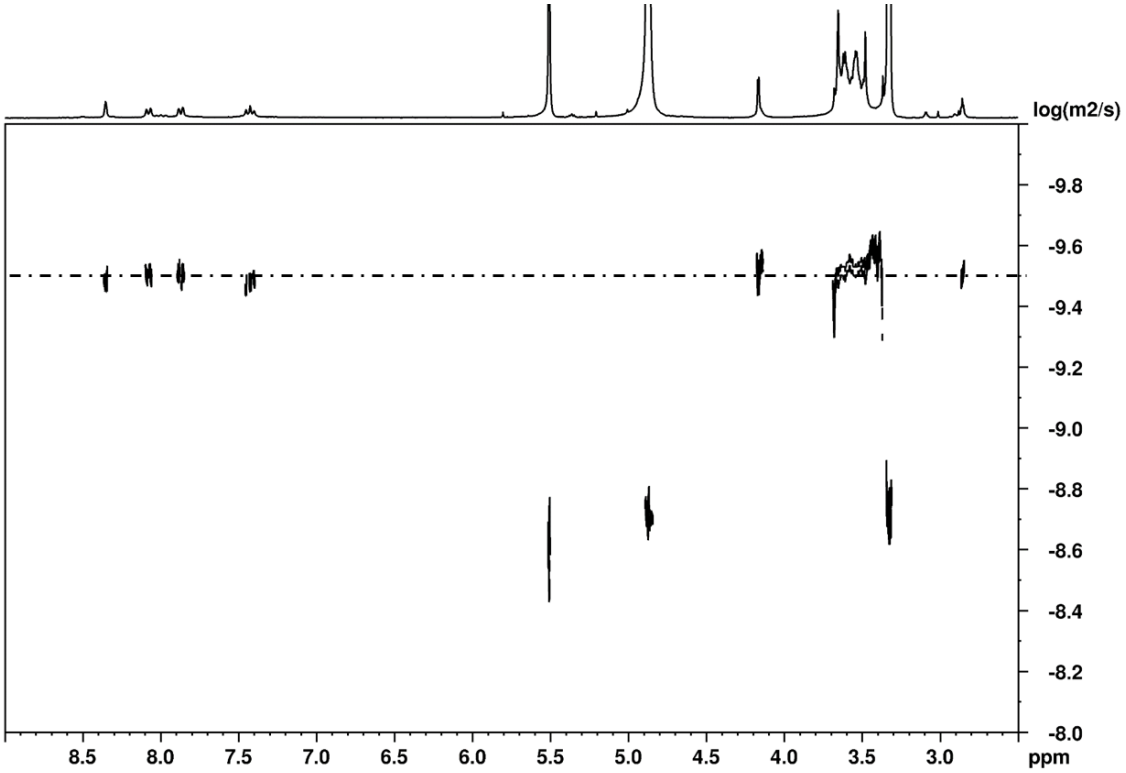

Figure S43. DOSY-NMR (300 MHz, 25ºC) spectrum of the 4-c $Rh_2(PEG_6\text{-Alkyne})_4$ cluster in MeOD. The same diffusion coefficient ($D \approx 3.1 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$) is assigned for the aromatic and aliphatic protons, demonstrating that all belongs to the same molecule. The diffusion coefficient of the residual MeOH ($D \approx 2.4 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$) was used as internal reference.

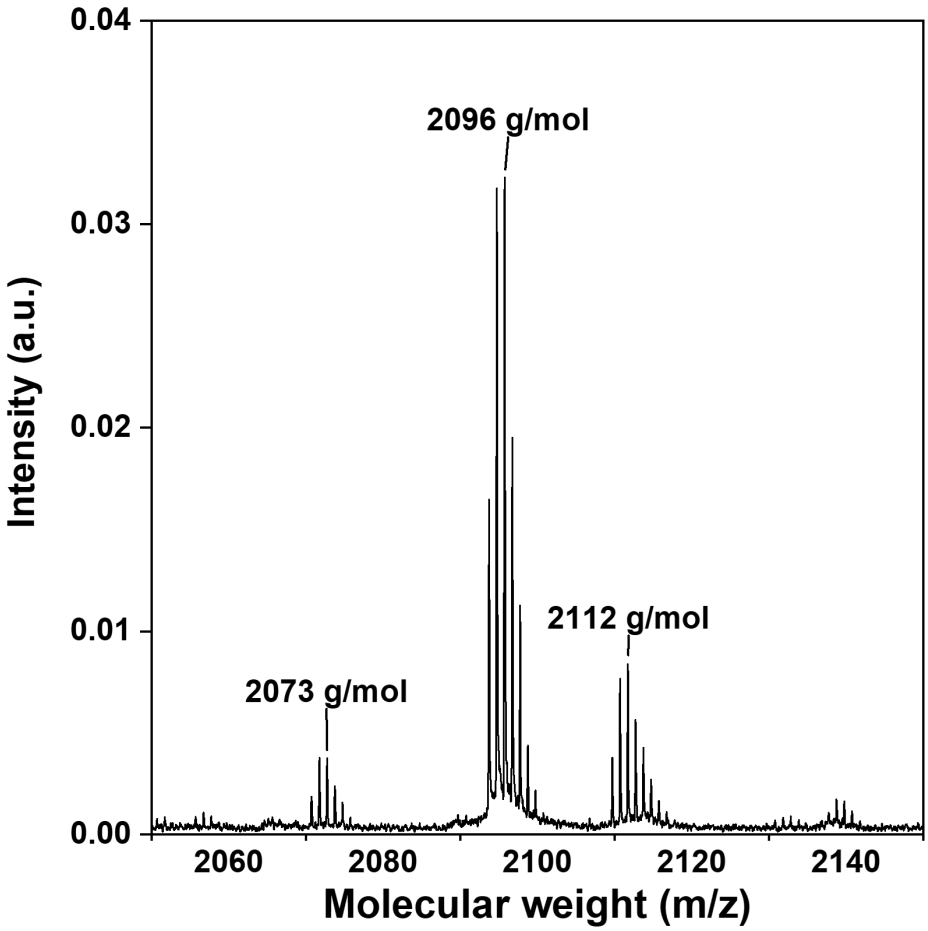

Figure S44. MALDI-TOF spectra of the 4-c $Rh_2(PEG_6\text{-Alkyne})_4$ cluster in MeOH. The highlighted mass corresponds to the molecular formula of $[(Alkyne\text{-}PEG_6\text{-}BDC)_4Rh_2 + H^+]^+ \cdot H_2O$. Expected: m/z = 2090; Found: m/z = 2096. The second peak at 2073 m/z corresponds to the loss of a water molecule (expected: m/z = 2072) whereas the peak centred at 2112 m/z corresponds to addition of a second water molecule (expected: m/z = 2108).

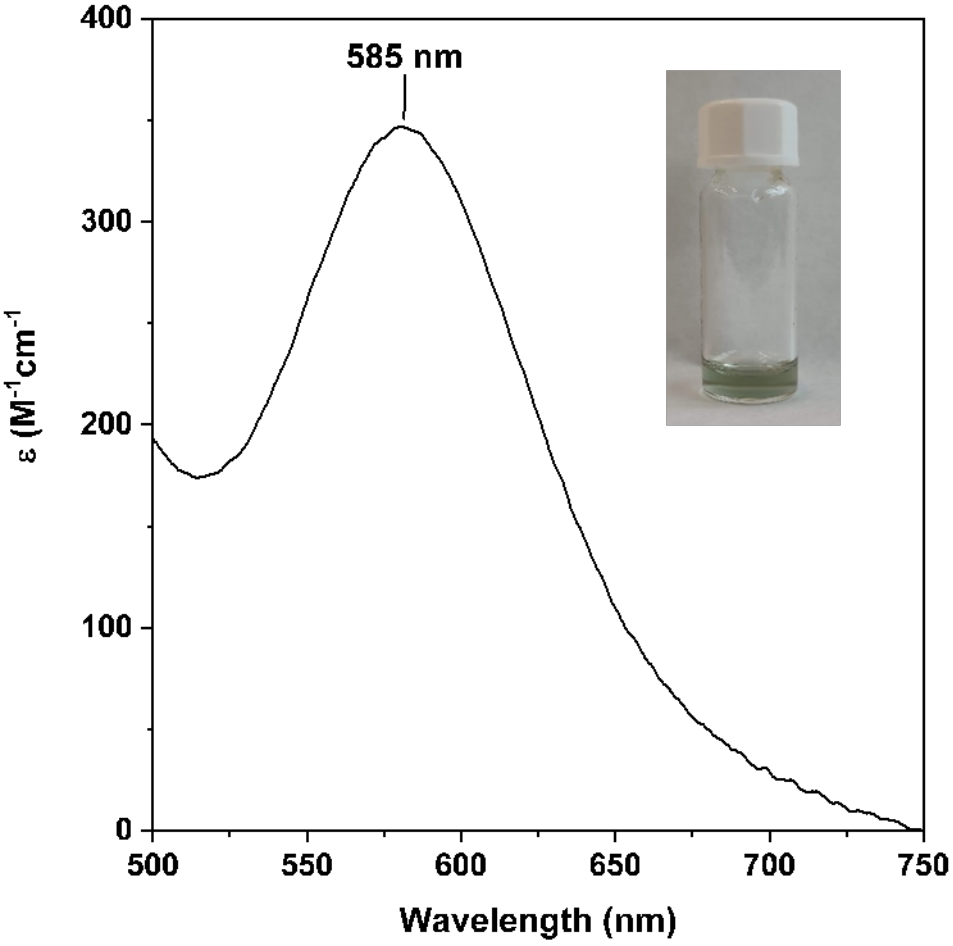

Figure S45. UV-Vis spectrum of the 4-c $Rh_2(PEG_6\text{-Alkyne})_4$ cluster in DMF with a concentration of 1.6 mM. λ_{max} is centred at 585 nm, confirming that the Rh(II) paddlewheel is maintained and that is not coordinated to remaining N-containing reactants (*i.e.* $NH_2\text{-}PEG_6\text{-Alkyne}$).

S3.9. MOP-tetramer

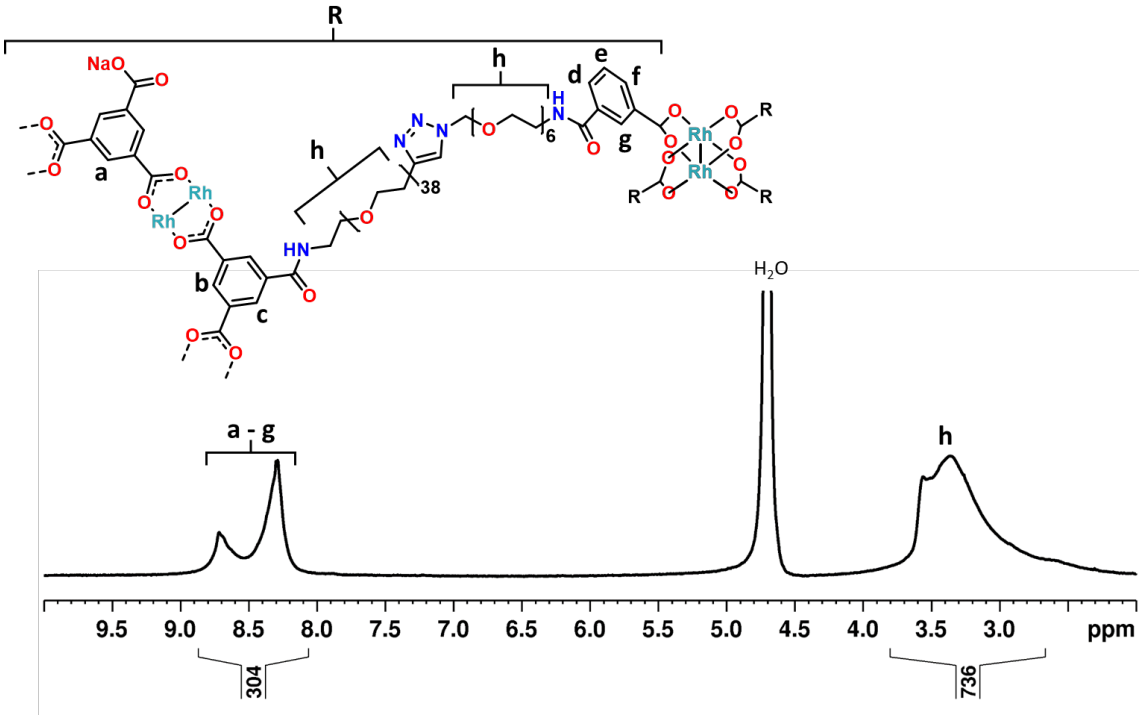

Figure S46. ^{1}H-NMR spectrum (300 MHz, 25ºC) of the MOP-tetramer in basic D_2O (pD ≈ 12). Note that, under basic conditions, the surface carboxylic groups are deprotonated affording solubility in water. The relative integrations of the protons ascribed to the MOP core and the 4-c cluster (*a*-*g*) and the aliphatic signals form the PEG chain (*h*) correspond to the expected value for the proposed formula; that is, for each MOP-tetramer, there are 4 MOPs and 1 4-c cluster that contribute with 304 aromatic protons (*a*-*g*) and four PEG chains with up to 736 aliphatic protons (*h*).

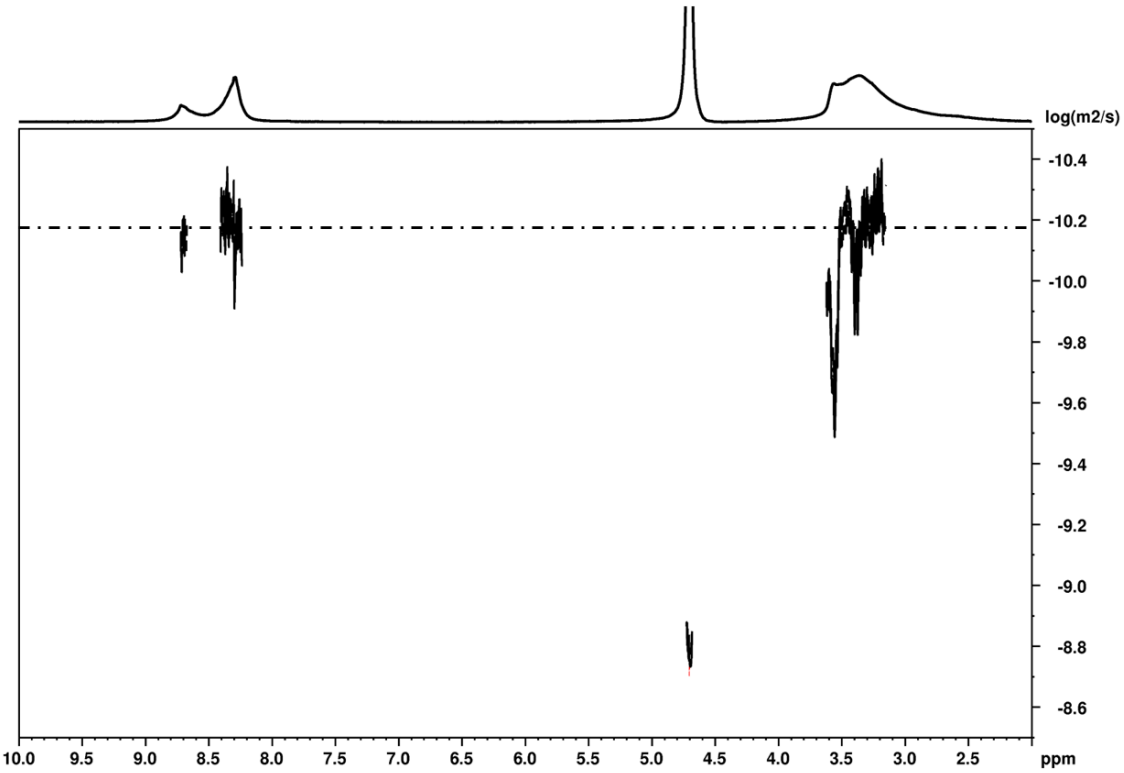

Figure S47. DOSY-NMR (300 MHz, 25ºC) spectrum of MOP-tetramer in basic D_2O (pD ≈ 12). The same diffusion coefficient (D ≈ 5.5· 10^{-10} $m^2 \cdot s^{-1}$) is identified for the aromatic signals that correspond to the MOP and for the PEG, demonstrating that all belongs to the same molecule. The diffusion coefficient of the residual H_2O (D ≈ 2.3 · 10^{-9} $m^2 \cdot s^{-1}$) was used as internal reference.

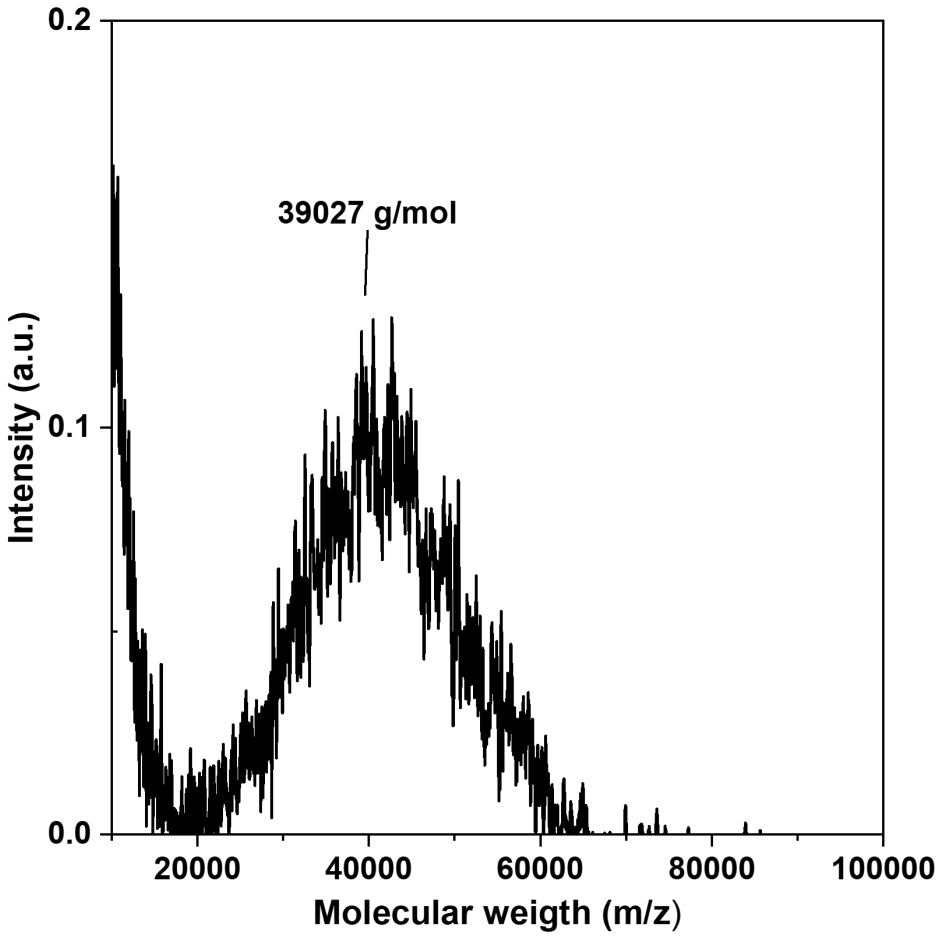

Figure S48. MALDI-TOF spectrum of the MOP-tetramer in DMF. The highlighted mass corresponds to the molecular formula of $[[(COOH\text{-}BDC)_{23}(BDC\text{-}PEG_{38}\text{-}1H\text{-}1,2,3\text{-}triazol\text{-}4\text{-}yl\text{-}PEG_6\text{-}BDC)_1Rh_{24})]_4Rh_2\text{-}H^+]^-$. Expected: m/z = 39047 ± 1480 g/mol; found: m/z = 39027 g/mol.

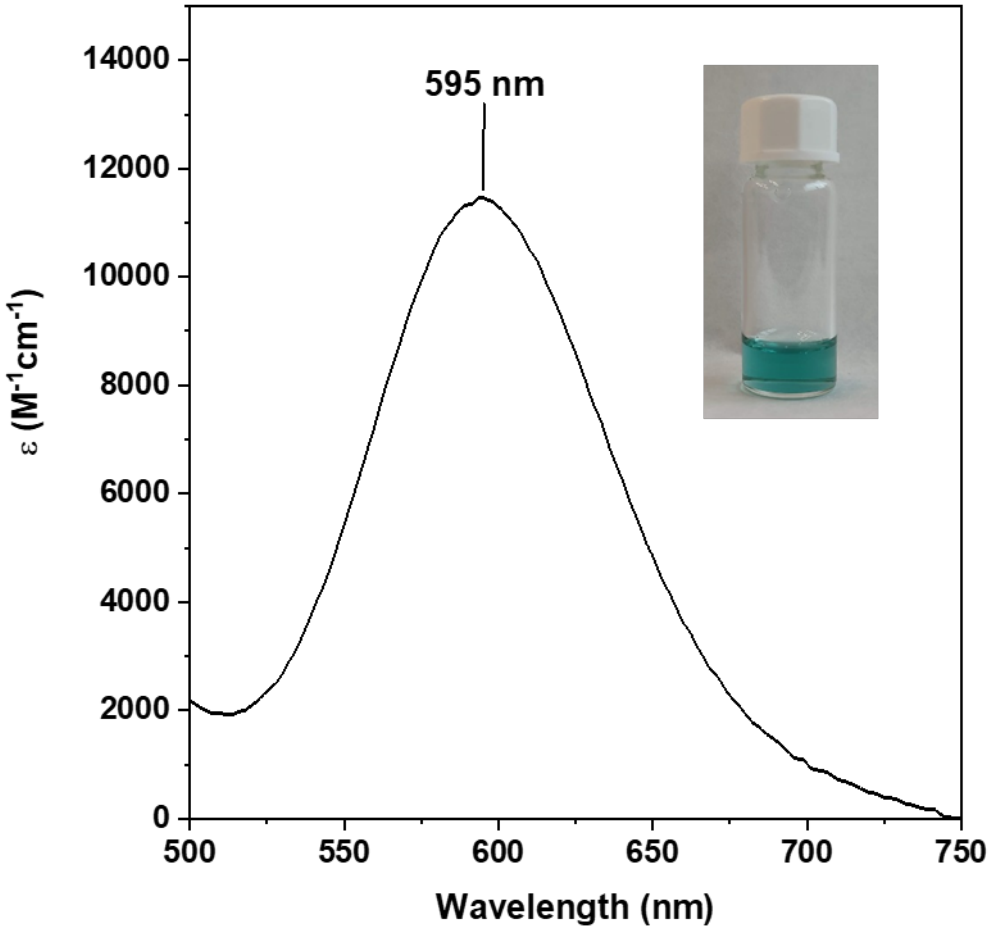

Figure S49. UV-Vis spectrum of MOP-tetramer in DMF with a concentration of 0.1 mM. λ_{max} is centered at 595 nm, confirming that the Rh(II) paddlewheel is maintained and that it is not coordinated to the triazole group present in the product.

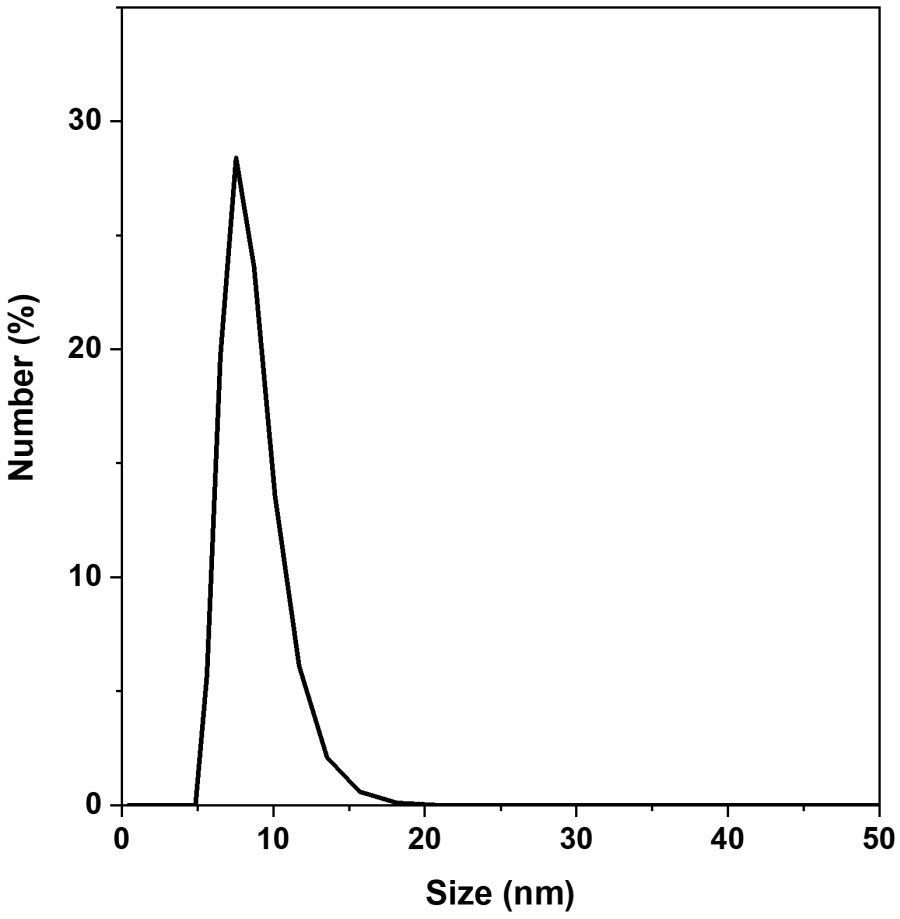

Figure S50. DLS spectrum of MOP-tetramer in basic H_2O (pH ≈ 12) at a concentration of 0.3 mM. The average diameter was found to be 7.2 ± 0.6 nm.

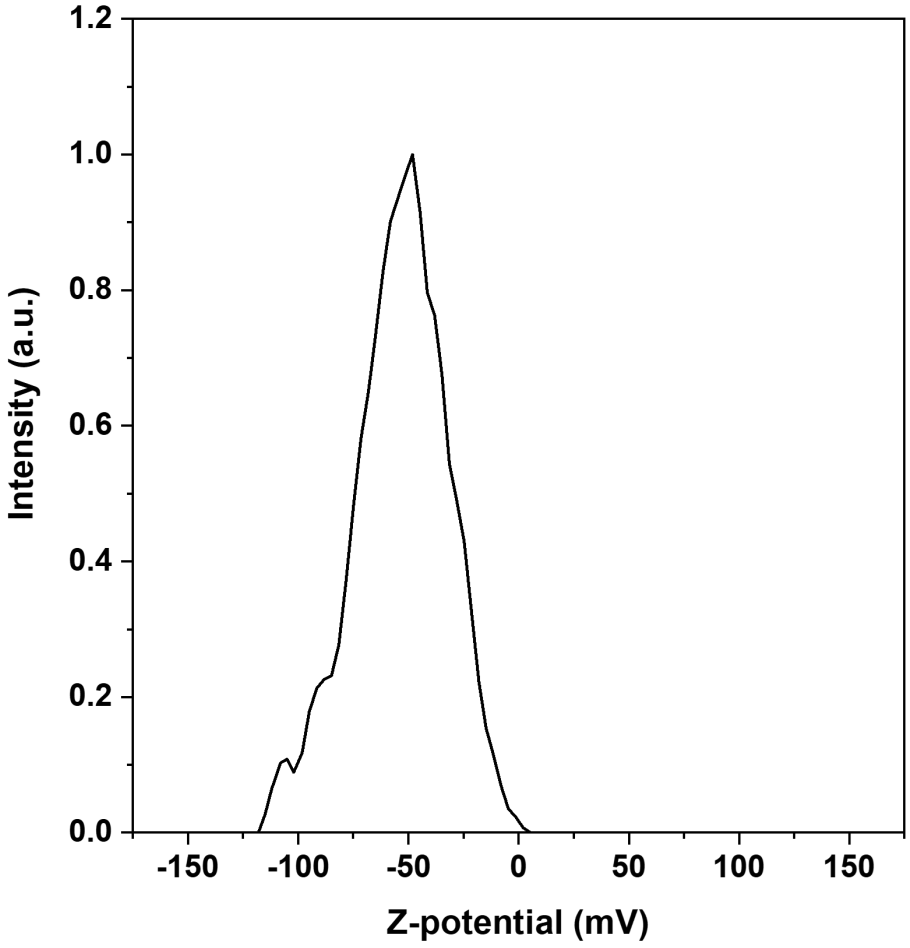

Figure S51. Z-potential distribution of MOP-tetramer in basic H_2O (pH = 12).

S3.10. (Alkyne)$_{24}$-RhMOP

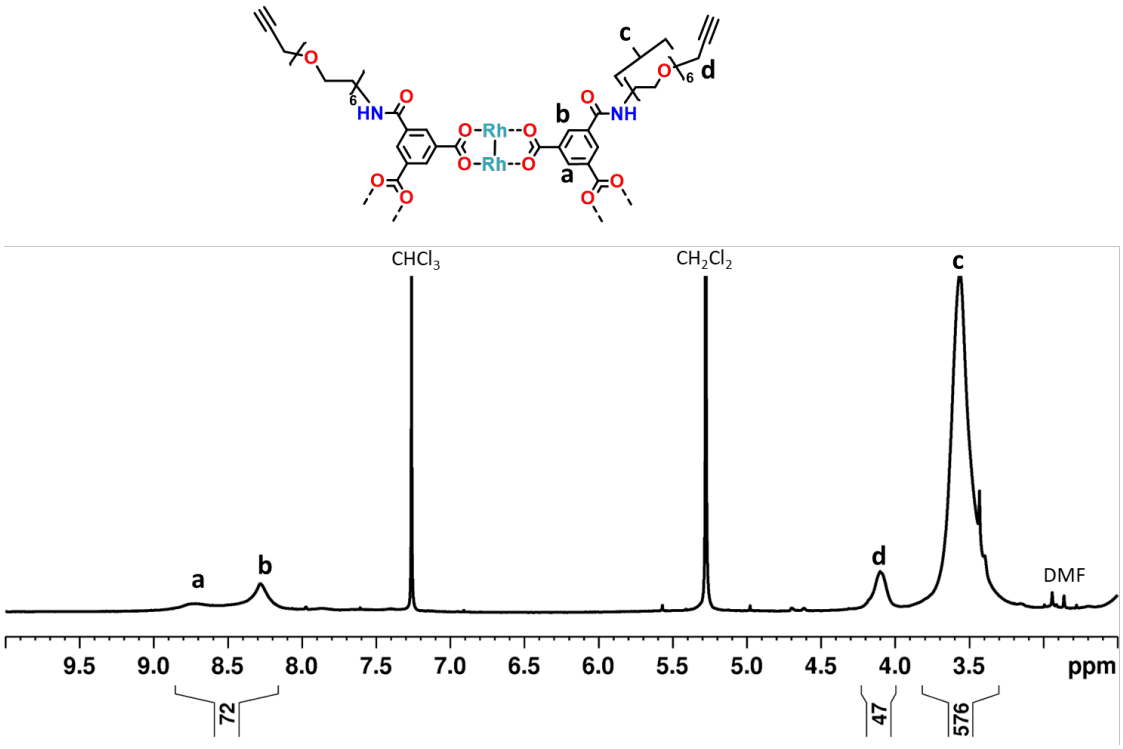

Figure S52. ^{1}H-NMR spectrum (300 MHz, 25ºC) of (Alkyne)$_{24}$-RhMOP in $CDCl_3$. The relative integrations of the protons ascribed to the MOP core (*a* and *b*) and the aliphatic signals form the PEG chain (*c*) correspond to the expected value for the proposed formula; that is, for each (Alkyne)$_{24}$-RhMOP, there are 72 aromatic protons (*a* and *b*) and *ca.* 576 aliphatic protons from the PEG chains (*c*).

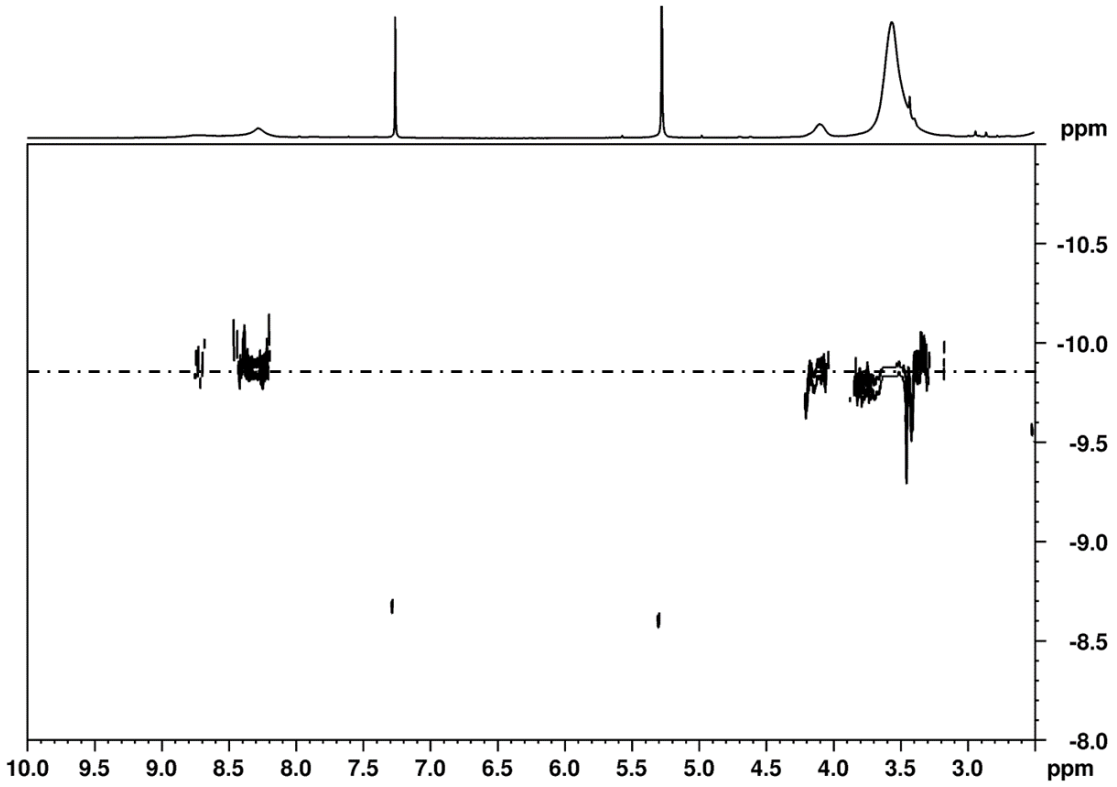

Figure S53. DOSY-NMR (300 MHz, 25ºC) spectrum of $(Alkyne)_{24}$-RhMOP in $CDCl_3$. The same diffusion coefficient ($D \approx 1.7 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$) is identified for the aromatic signals that correspond to the MOP core and for the PEG chains, demonstrating that they belong to the same molecule. The diffusion coefficient of the residual $CHCl_3$ ($D \approx 2.3 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$) was used as internal reference.

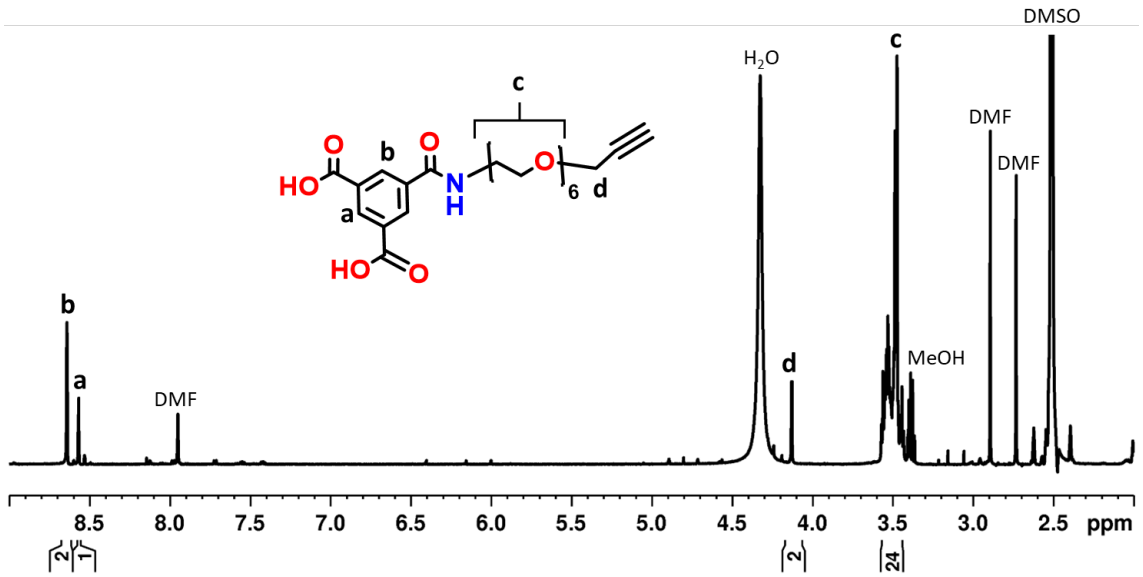

Figure S54. ^{1}H-NMR spectrum (300 MHz, 25ºC) of $(Alkyne)_{24}$-RhMOP digested in DMSO-d_6 under acidic conditions (DCl 20%, 100 ºC, 2 hours). Signals *a* and *b* confirm the formation of the amide bond, and the correct ratio between all the signals evidences the quantitative reaction. Note that the alkyne proton cannot be assigned due to its overlapping with DMF solvent signals.

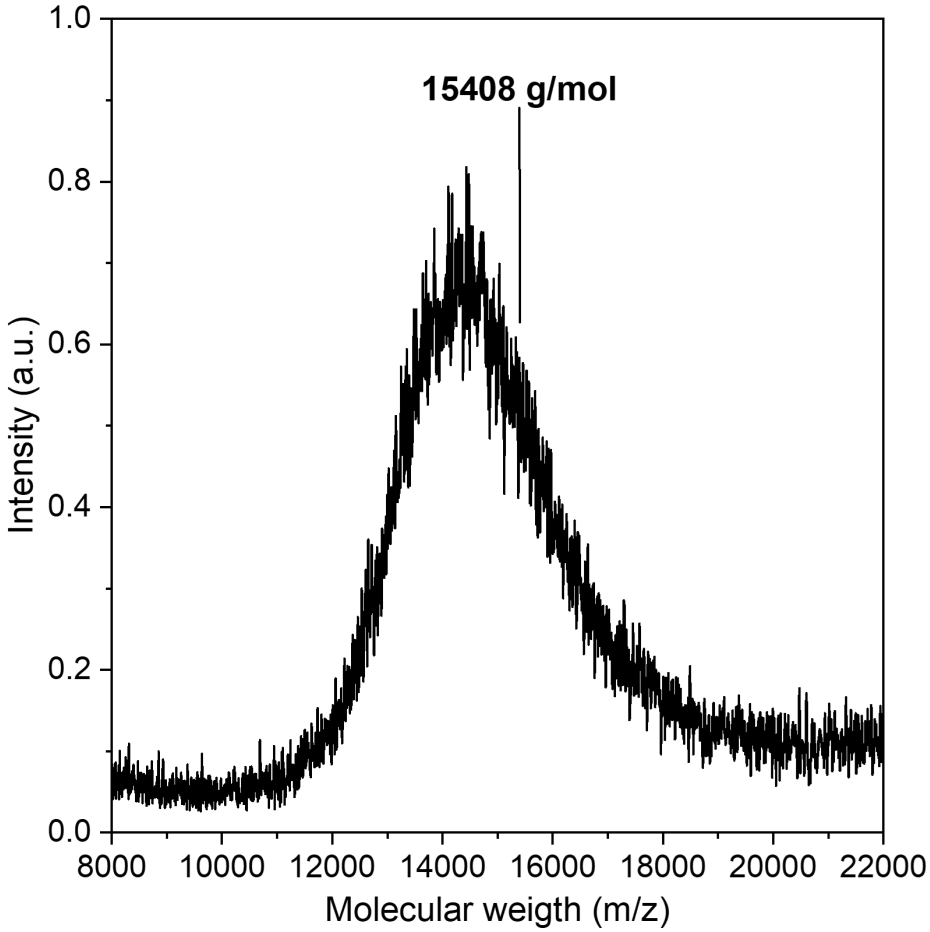

Figure S55. MALDI-TOF spectrum of $(Alkyne)_{24}$-RhMOP in $CHCl_3$. The highlighted mass corresponds to the molecular formula of $[(Alkyne\text{-}PEG_6\text{-}BDC)_{24}Rh_{24} + H^+]^+$. Expected m/z = 15408 g/mol; found m/z = 15409 g/mol.

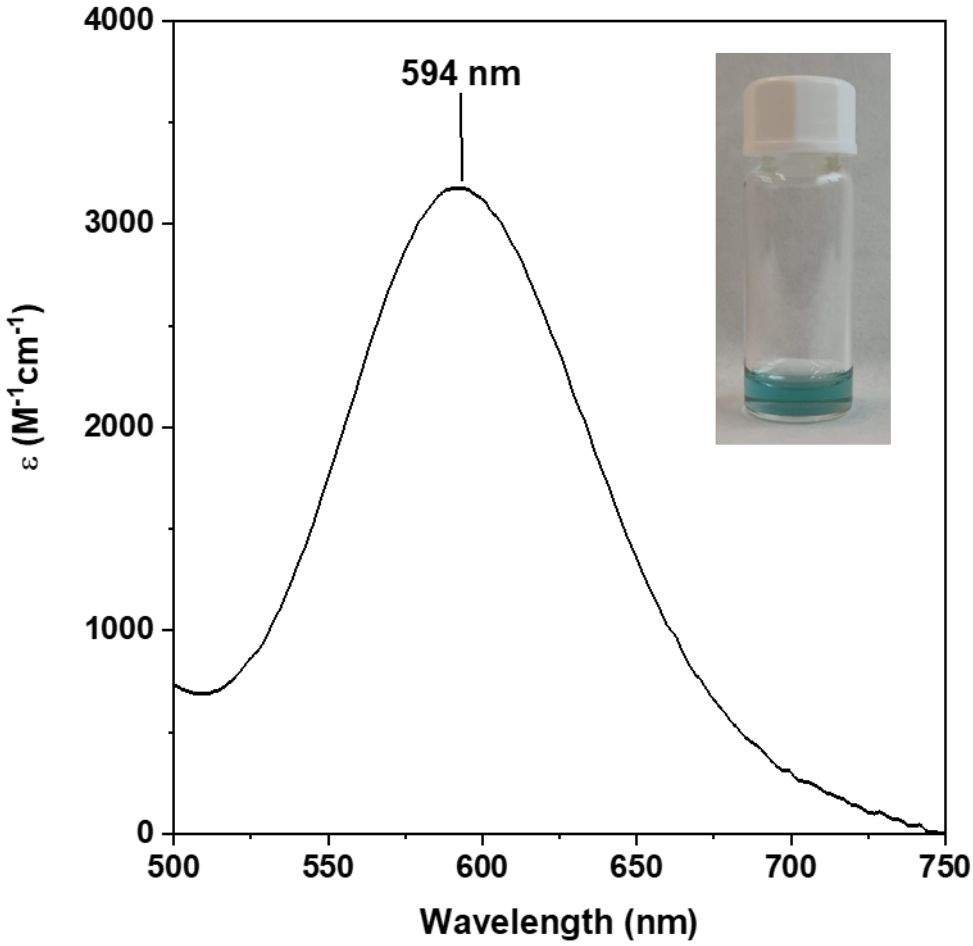

Figure S56. UV-Vis spectrum of $(Alkyne)_{24}$-RhMOP in DMF with a concentration of 2.2 mM. λ_{max} is centered at 594 nm, confirming that the Rh(II) paddlewheel is maintained and that there is not remaining N-coordinated reactants (*i.e.* NH_2-PEG_6-Alkyne, HOBt, HBTU, DIPEA).

S3.11. MOP-satellite

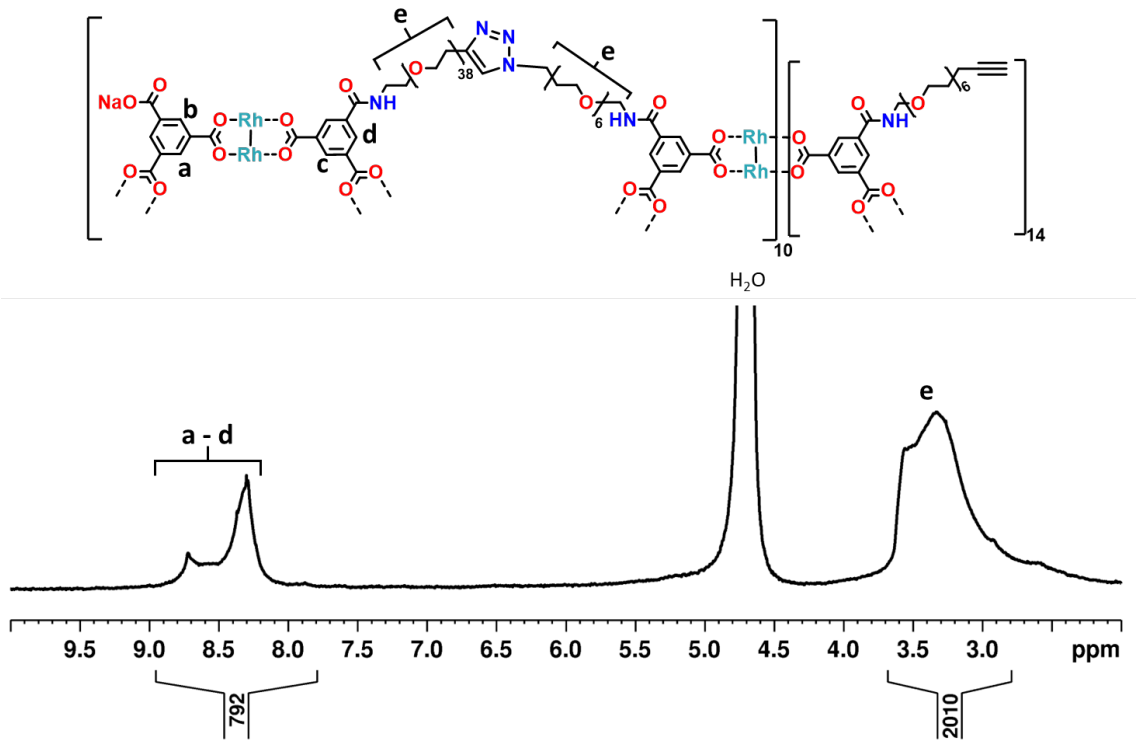

Figure S57. ^{1}H-NMR spectrum (300 MHz, 25ºC) of MOP-satellite in basic D_2O (pD ≈ 12). Note that, under basic conditions, the surface carboxylic groups are deprotonated affording solubility in water. The relative integrations of the aromatic protons ascribed to the central and peripheral MOP cores (*a* - *d*) and the aliphatic protons of the dangling and bridging PEG chains (*e*) correspond to the expected value for the proposed formula; that is, each MOP-satellite contains 11 MOPs: 1 central MOP and 11 peripheral MOPs. All these MOPs contribute with 792 aromatic protons. Regarding the PEG chains, there are two types of PEGs: 14 small alkyne terminated dangling PEG chains that are only coupled to the central MOP and that contribute with 392 aliphatic protons; and 10 bridging PEG chains that contribute with 1560 aliphatic protons. Overall, the expected ratio between aromatic to aliphatic protons is 0.41, which is very close to the experimental one (0.39).

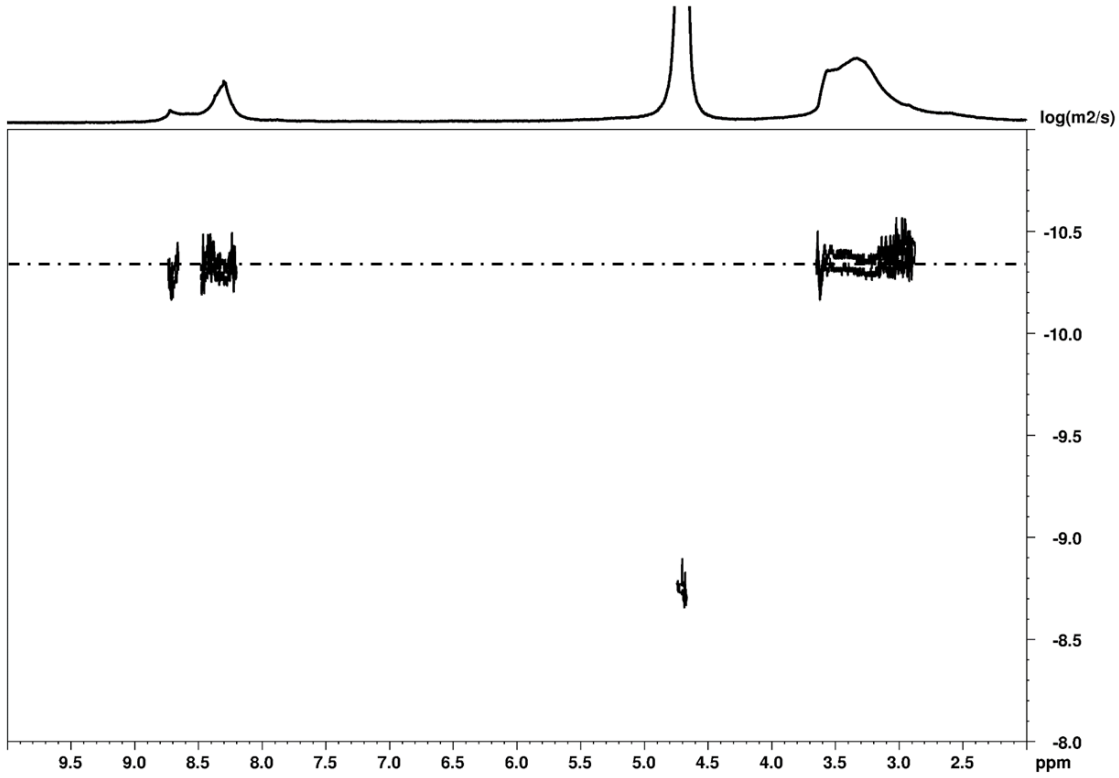

Figure S58. DOSY-NMR (300 MHz, 25ºC) spectrum of MOP-satellite in basic D_2O (pD ≈ 12). The same diffusion coefficient (D ≈ 4.7· 10^{-11} $m^2 \cdot s^{-1}$) is identified for the aromatic signals that correspond to the MOP and for the PEG, evidencing that all of them corresponds to the same molecule. The diffusion coefficient of the residual H_2O (D ≈ 2.3 · 10^{-9} $m^2 \cdot s^{-1}$) was used as internal reference.

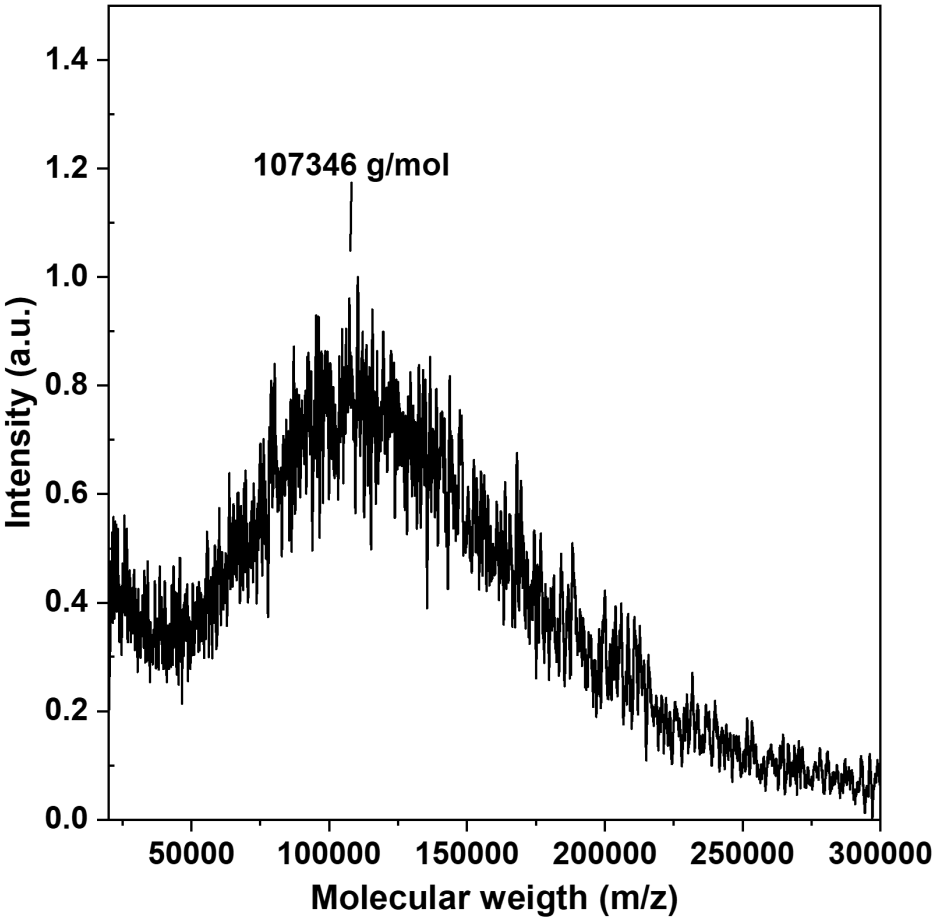

Figure S59. MALDI-TOF spectra of MOP-satellite in DMF. The highlighted mass corresponds to the molecular formula of $[[(COOH\text{-}BDC)_{23}(BDC\text{-}PEG_{38}\text{-}1H\text{-}1,2,3\text{-}triazol\text{-}4\text{-}yl\text{-}PEG_6\text{-}BDC)_1Rh_{24})_{10}(Alkyne\text{-}PEG_6\text{-}BDC)_{14}Rh_{24}]+H^+]^+$. Expected: m/z = 107678 ± 3,700 g/mol; found: m/z = 107346 g/mol.

Table S1. ICP-MS analysis of MOP-satellite. For this measurement, the MOP-satellite was incubated in basic water (pH ≈ 12) to fully deprotonate all carboxylic acids rendering an anionic MOP-satellite in which the Na(I) cations act as counterions. The sample was purified through successive washings using a centrifugal filter with a cut-off of 50 kDa to eliminate excess of Na(I) cations. The experimentally found Rh/Na molar ratio of 1.19 agrees with the expected value for a MOP-satellite with 10 peripheral MOPs (*i.e*. 230 peripheral carboxylate groups).

Rh found % (p/p)	Na found % (p/p)	Rh/Na found	Rh/Na expected
16.73	3.12	1.19	1.15

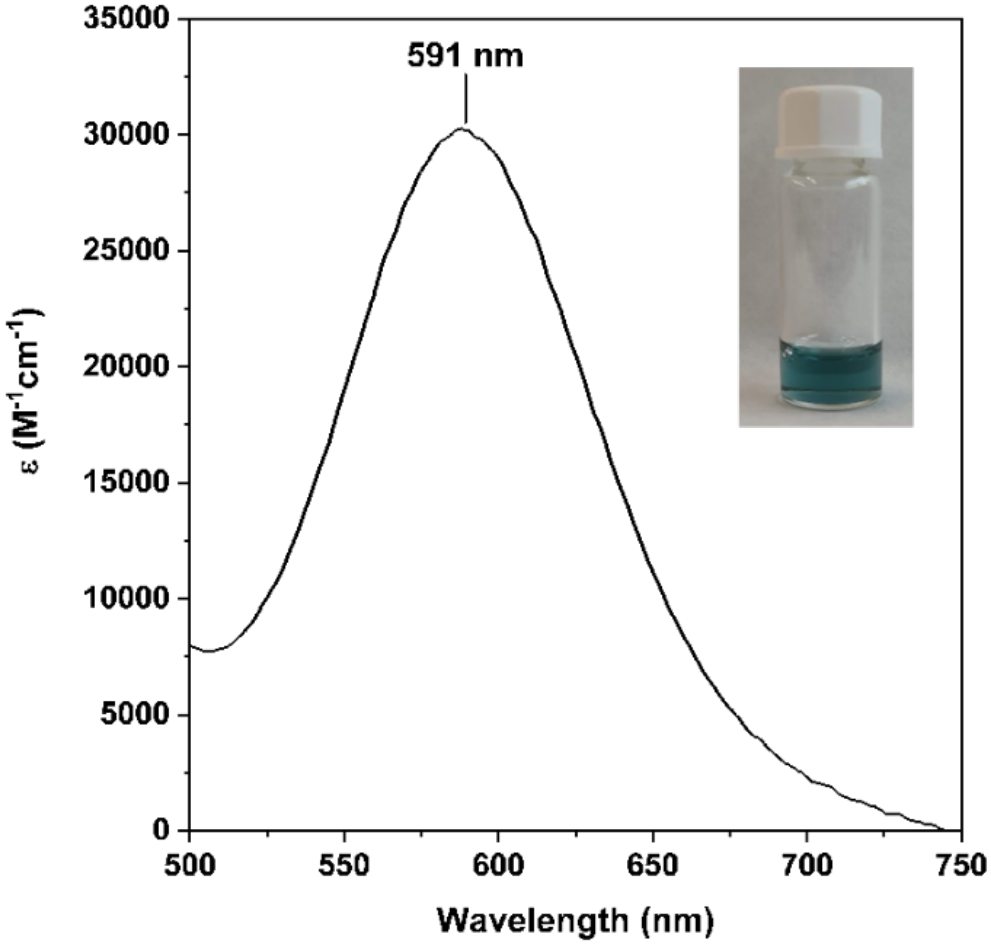

Figure S60. UV-Vis spectrum of MOP-satellite in DMF with a concentration of $3.4 \cdot 10^{-2}$ mM. λ_{max} is centered at 595 nm, confirming that the Rh(II) paddlewheel is maintained and that it is not coordinated to N-containing reagents (i. e. THPTA) or the triazole moiety present in the product.

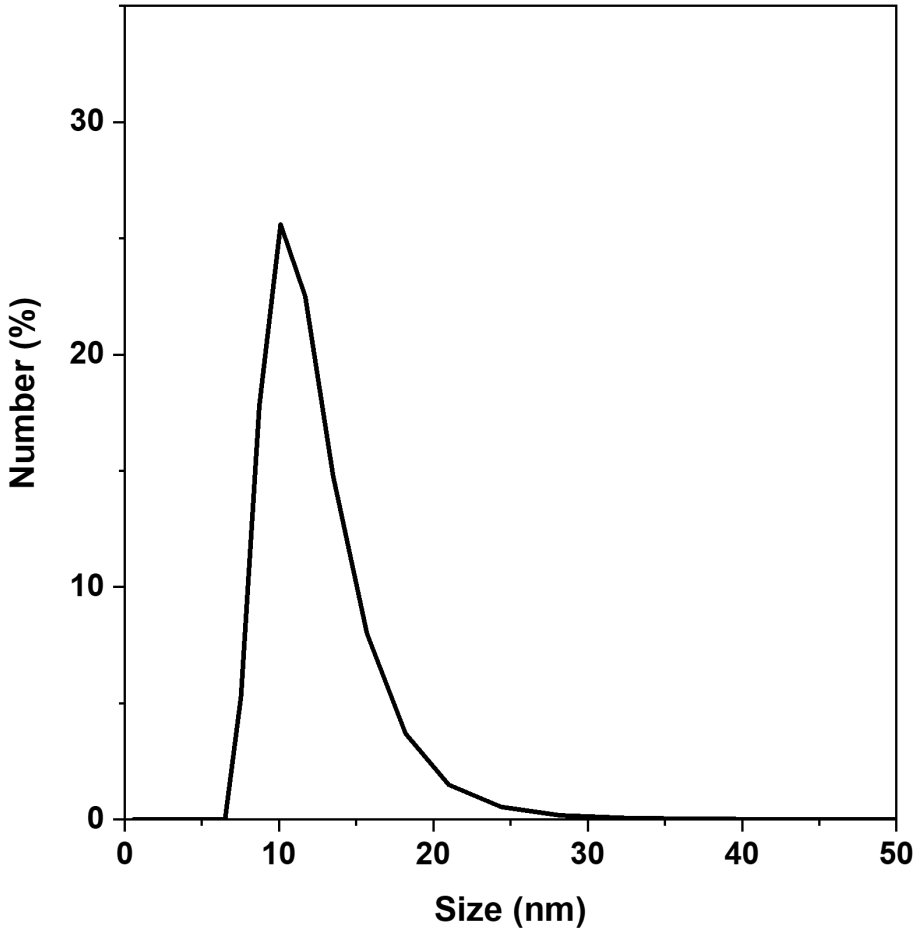

Figure S61. DLS spectrum of MOP-satellite in basic water H_2O (pH ≈ 12) with a concentration of 0.3 mM. The average size was found to be 9.6 ± 0.8 nm.

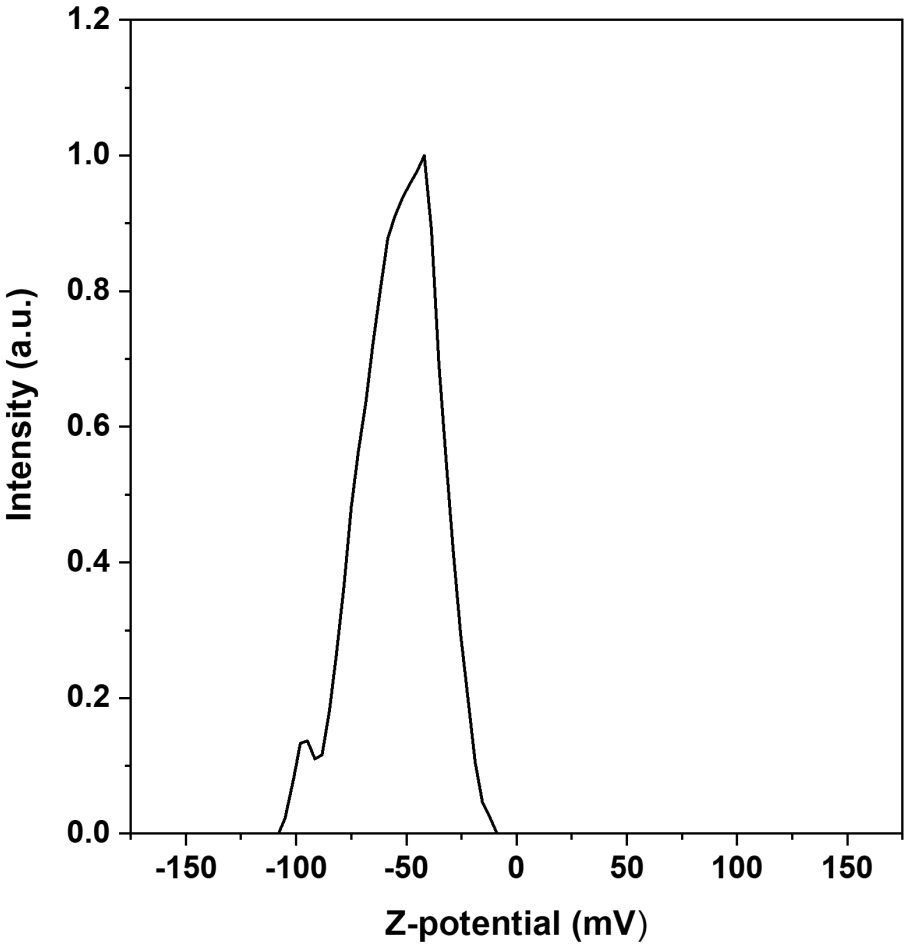

Figure S62. Z-potential distribution of MOP-satellite in basic water H_2O (pH = 12).

S3.12. Porosity measurements

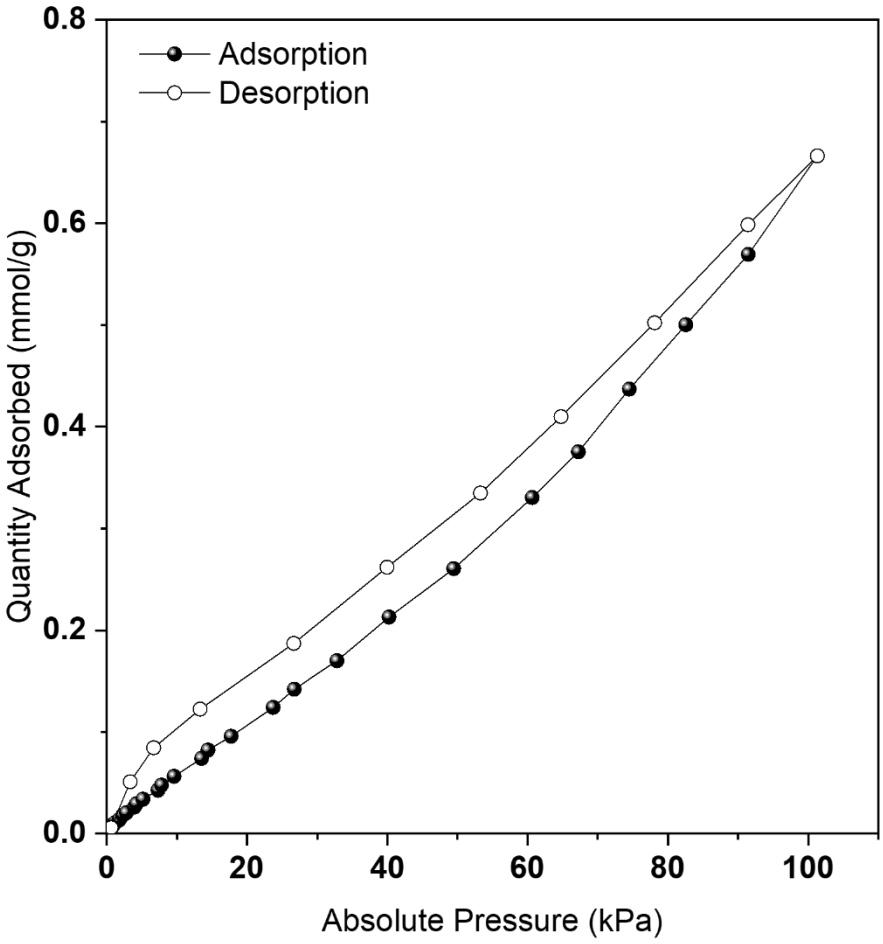

Figure S63. CO_2 adsorption isotherm at 195 K for the deprotected $(N_3)_1$-RhMOP.

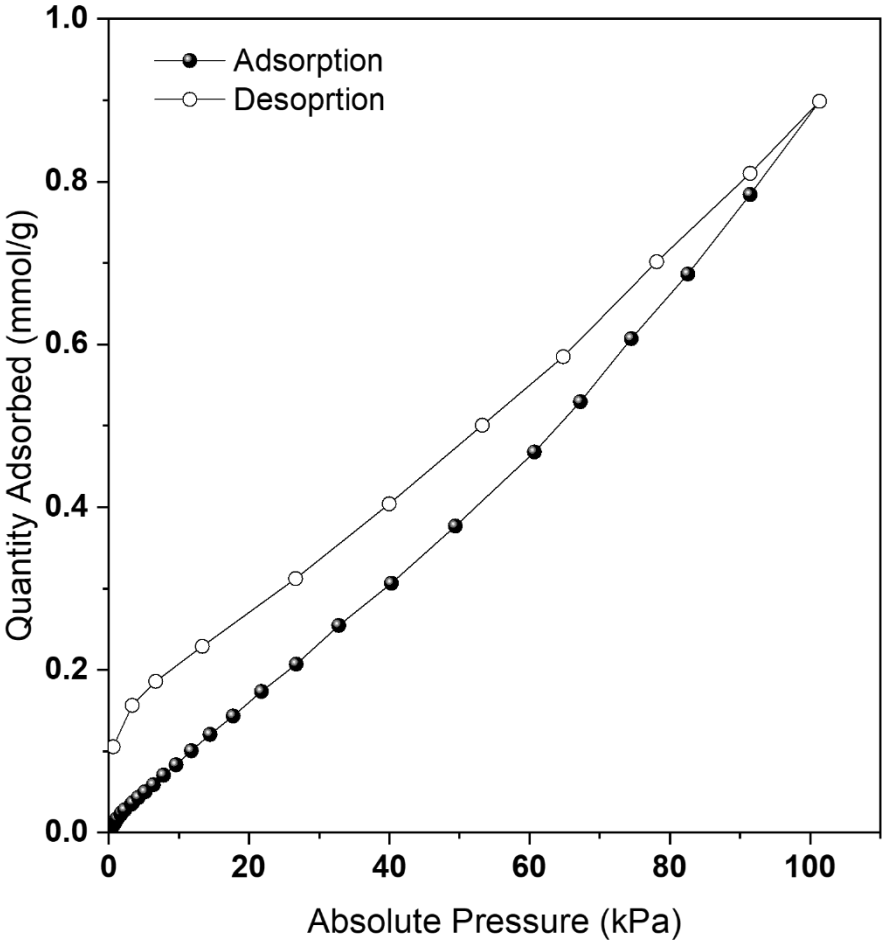

Figure S64. CO_2 adsorption isotherm at 195 K for the deprotected $(Alkyne)_1$-RhMOP.

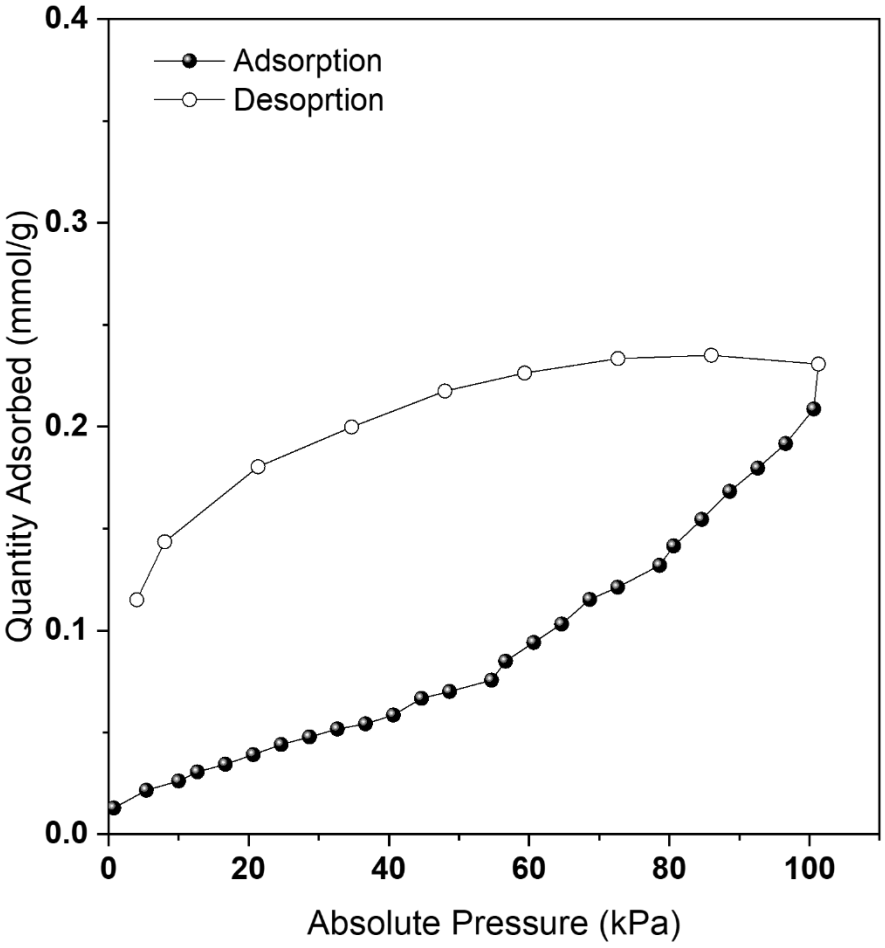

Figure S65. CO_2 adsorption isotherm at 195 K for $(Alkyne)_{24}$-RhMOP.

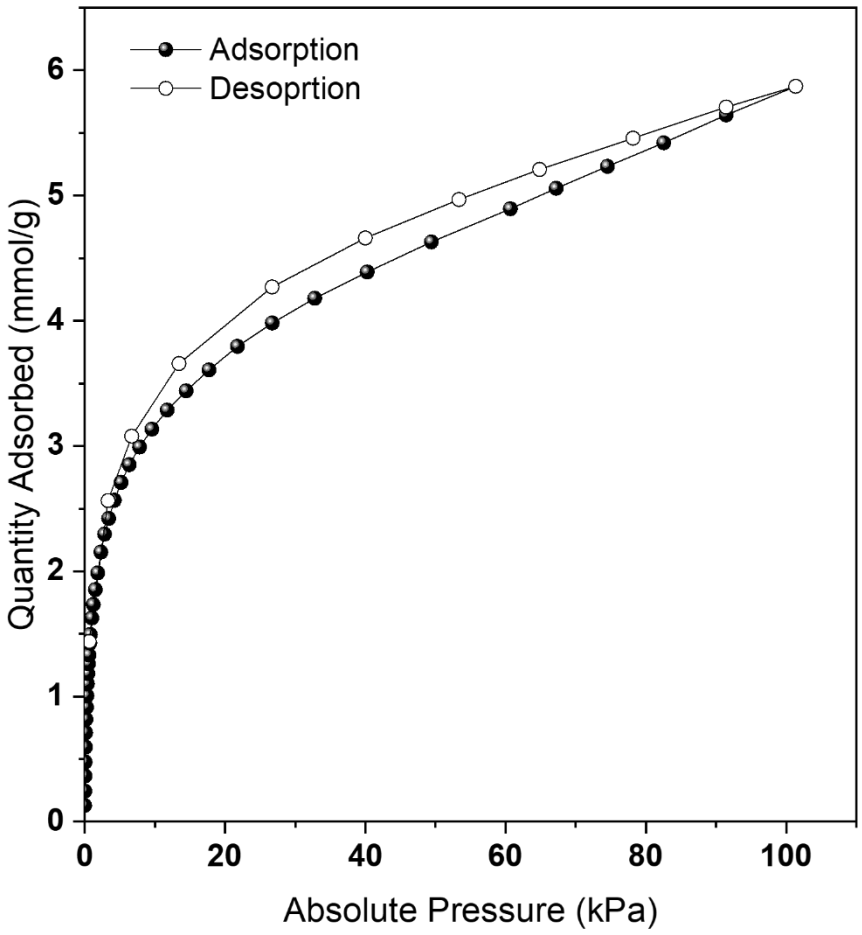

Figure S66. CO_2 adsorption isotherms at 195 K for MOP-dimer.

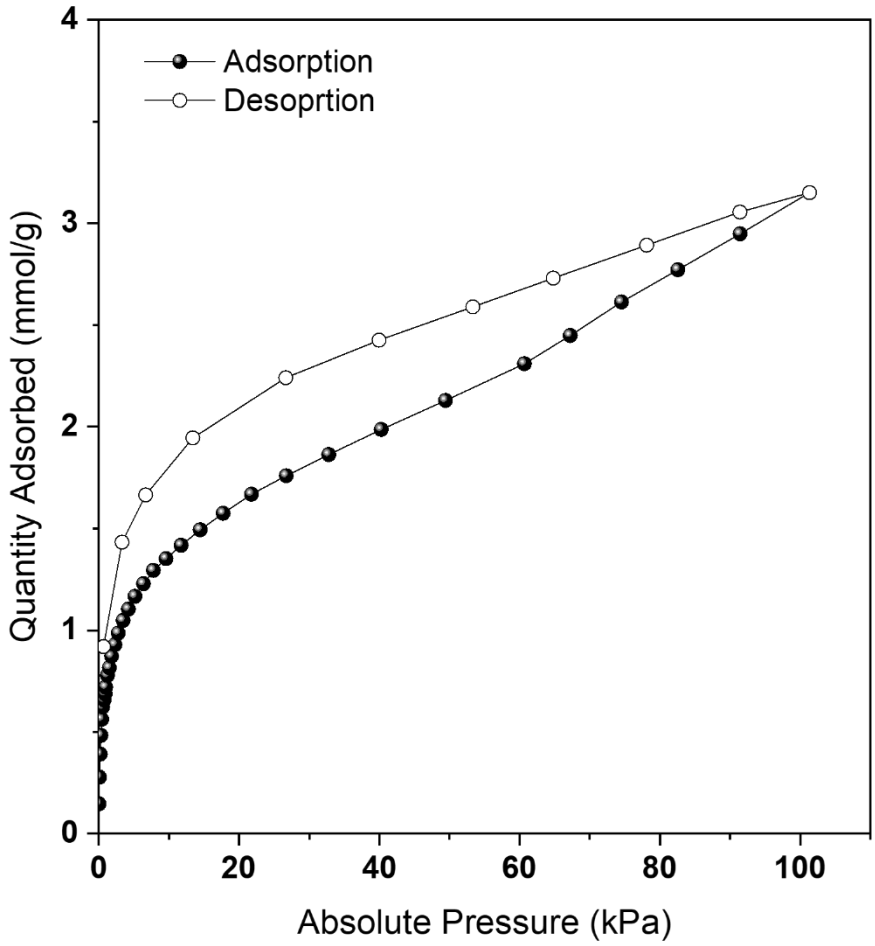

Figure S67. CO_2 adsorption isotherms at 195 K for MOP-tetramer.

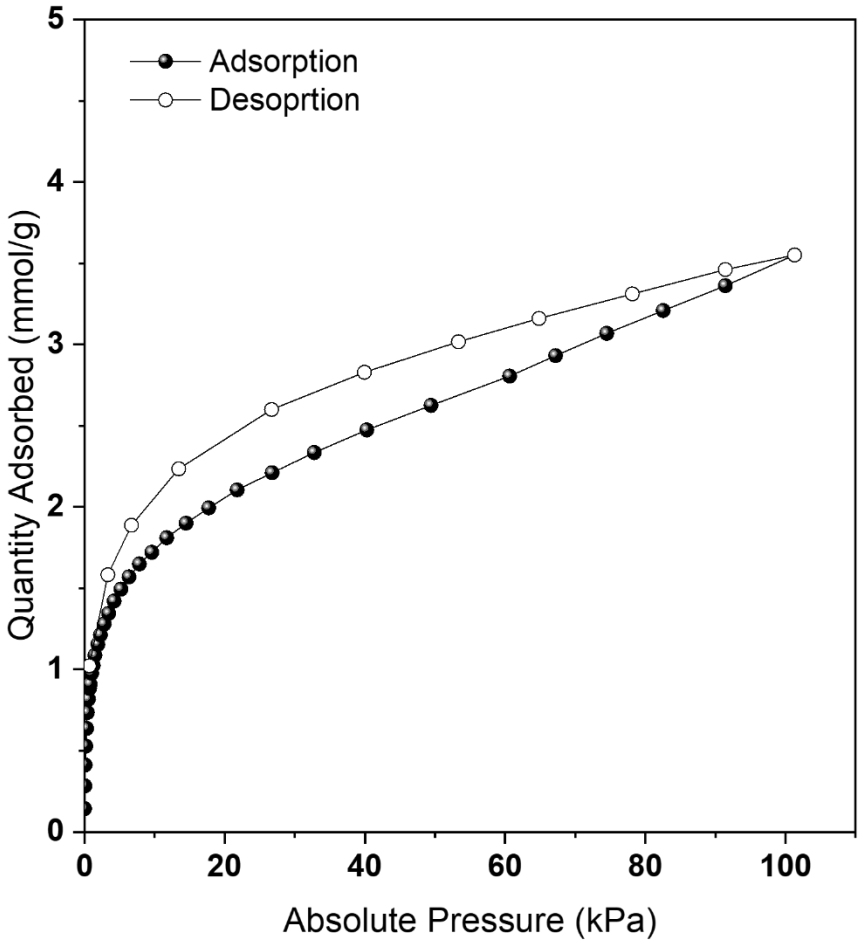

Figure S68. CO_2 adsorption isotherms at 195 K for MOP-satellite.

S4. References

1 J. Albalad, A. Carné-Sánchez, T. Grancha, L. Hernández-López and D. Maspoch, *Chem. Commun.*, 2019, **55**, 12785–12788.

2 L. Hernández-López, C. von Baeckmann, J. Martínez-Esaín, A. Cortés-Martínez, J. Faraudo, C. Caules, T. Parella, D. Maspoch and A. Carné-Sánchez, *Chem. – A Eur. J.*, , DOI:10.1002/chem.202301945.

3 C. von Baeckmann, S. Ruiz-Relaño, I. Imaz, M. Handke, J. Juanhuix, F. Gándara, A. Carné-Sanchez and D. Maspoch, *Chem. Commun.*, 2023, **59**, 3423–3426.