Electronic Supplementary Information For

# Metal−Organic Polyhedra Crosslinked Supramolecular Polymeric Elastomers

Jun Zhao, Lin Cheng, Kai Liu, Zhaoming Zhang, Wei Yu, and Xuzhou Yan*

School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Email: xzyan@sjtu.edu.cn

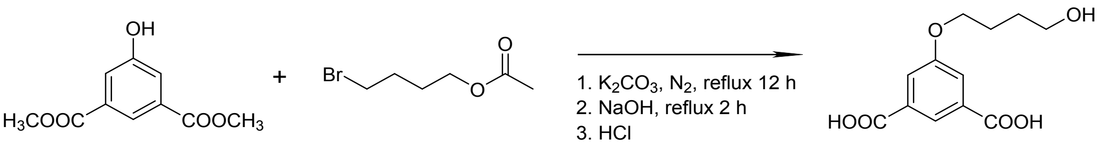
## 1. Details on experimental methods

**General:** Rhodium acetate, 4-bromobutyl acetate, dimethyl 5-hydroxyisophthalate, 5-hydroxy-1,3-benzenedicarboxylic acid, isophthalic acid, $K_2CO_3$, KI, and $Na_2CO_3$ were purchased from Sigma-Aldrich and used without further purification. Polytetramethylene glycol (PTMG, $M_n$ = 1000 g mol$^{-1}$), isophorone diisocyanate (IPDI), 1,4-butanediol (BDO) were purchased from Sigma-Aldrich and dried under vacuum at 90 °C before use. Dibutyltin dilaurate (DBTDL) catalyst was purchased from Alfa Aesar. *N,N*-Dimethylacetamide (DMA, Shanghai Titan Scientific Co. Ltd, China) was dried by $CaH_2$ and distilled under vacuum before use. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). The ligand **B**[S1], Rh-based MOPs-**1–3**[S2] and prepolymer[S3] were prepared according to the published procedures. $^1$H NMR spectra were recorded on a Bruker AVANCE III HD 400. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF) was measured on a MALDI Mass Spectrometer MALDI-7090 with *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix material. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed on a TALOS F200X. The film was sectioned into a specimen in thickness of 100 nm with liquid nitrogen refrigeration by a Leica EM UC7 Ultramicrotome and the sample was further loaded on the copper mesh. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) mapping were collected by a Nova NanoSEM 450 field emission scanning electron microscope. The sample was treated with conductive coating before test. UV-vis absorption spectra were collected on a Lambda 750S Spectrometer. Thermal gravimetric analysis was performed on a TA Q5000IR. The stress-strain tests were taken with an INSTRON 3343 universal mechanical test machine. Rheological experiments were carried out using a TA Instruments ARES G2 stress-controlled rheometer with an 8 mm parallel plate attachment.

*Film preparation for mechanical property test*: For tensile tests, the small rectangular specimens with the width of 4.0 mm and thickness of 0.30 mm was cut from the as-prepared fresh ElastoMOP films; For rheological tests, the small round specimens were prepared from the ElastoMOP films as well.

*Demonstration of the vapor-responsive actuators*: The specimens cut from the ElastoMOP-**3** film with the size of 30 × 2.0 × 0.34 mm (length × width × thickness) were exposed to the dichloromethane vapor inside a glass beaker at 20 °C. The vapor-responsive actuation behavior (bending) happened immediately. Then the specimens were put back to the air for shape recovery. The whole process was recorded by a GoPro sports camera for further analysis. For the biomimetic stimulus-responsive behavior, a specimen shaped like the *mimosa* leaf was made from the original ElastoMOP-**3** film. We followed the above-mentioned procedure to imitate the behavior of the *mimosa* leaf.

## 2. Synthesis of 5-(4-hydroxybutoxy)-1,3-benzenedicarboxylic acid (Ligand B)



To 100 mL of $CH_3CN$ solvent, dimethyl-5-hydroxyisophthalate (2.66 g, 12.7 mmol), 4-bromobutyl acetate (3.70 g, 19.0 mmol) and potassium carbonate (10.5 g, 75.9 mmol) were added. The mixture was purged with nitrogen for 15 min followed by stirring and refluxing at 90 °C under nitrogen for 12 h. The resulting mixture was filtered and the filtrate was further dried under vacuum. Then, the residuum was hydrolyzed by NaOH in the solution of 4:1 EtOH/$H_2O$ (150 mL). Finally, after removing the EtOH of the mixture, 1.00 mol/L of HCl was added to the mixture and the precipitate appeared. After filtering and drying, the target product was collected (2.96 g, 92%). $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K) $\delta$ 13.26 (s, 2H), 8.07 (t, $J$ = 1.4 Hz, 1H), 7.63 (d, $J$ = 1.4 Hz, 2H), 4.45 (s, 1H), 4.09 (t, $J$ = 6.5 Hz, 2H), 3.46 (t, $J$ = 5.2 Hz, 2H), 1.81-1.74 (m, 2H), 1.61-1.54 (m, 2H).

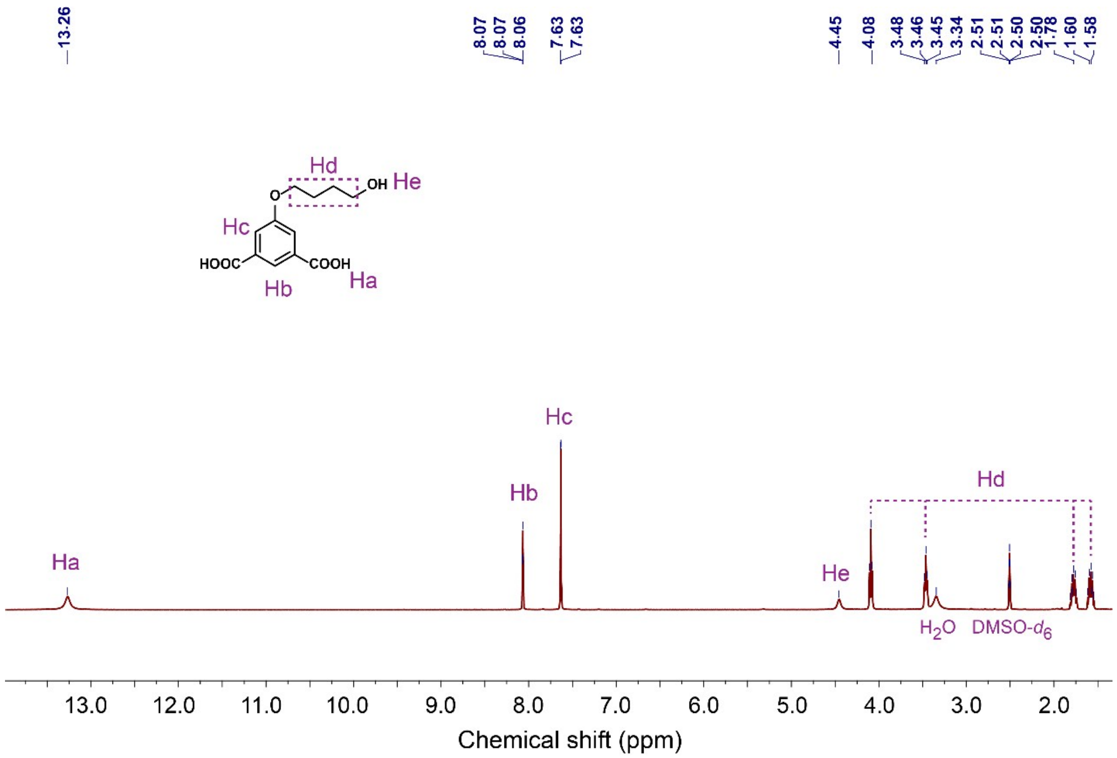
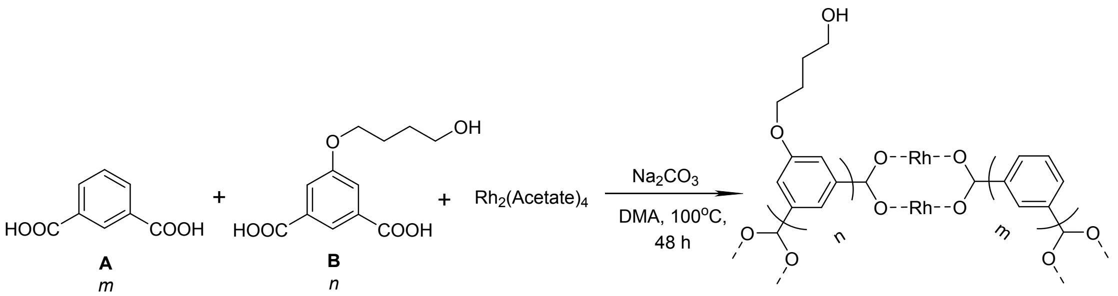


**Figure S1.** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of the 5-(4-hydroxybutoxy)-1,3-benzenedicarboxylic acid (**B**).

## 3. Synthesis of Rh-based metal-organic polyhedra (MOPs) with different amounts of hydroxyl groups



MOP-**1**, *m* = 16, *n* = 8
MOP-**2**, *m* = 8, *n* = 16
MOP-**3**, *m* = 0 , *n* = 24

The typical synthetic procedure of the Rh-based MOPs was reported by Furukawa and *co*-workers.[S2] Specifically, in this work, Rh-based hydroxyl groups-functionalized MOPs were synthesized with isophthalic acid (marked as **A**) and 5-(4-hydroxybutoxy) -1,3-benzenedicarboxylic acid (marked as **B**) in the presence of $Rh_2(OAc)_4$. The detailed compositions of the reactants are listed in Table S1. Herein the precursors were added into 8.0 mL *N*,*N*-dimethylacetamide (DMA) solution. The mixture was heated at 100 °C for 48 h, and then the dark green solution was filtered and the filtrate was dried under vacuum. The residuum was washed with MeOH and acetone to produce dark green powder which was denoted as MOP-**1**, MOP-**2**, and MOP-**3**, respectively.

**Table S1.** The detailed compositions of reactants for synthesis MOPs.

| **Sample Name** | **Reactant** | **Dosages (g)** | **mM** |
|---|---|---|---|
| MOP-**1** | **A** | 0.106 | 0.640 |
| | **B** | 0.081 | 0.320 |
| | $Rh_2$(acetate)$_4$ | 0.177 | 0.400 |
| | $Na_2CO_3$ | 0.106 | 1.00 |
| MOP-**2** | **A** | 0.053 | 0.320 |
| | **B** | 0.163 | 0.640 |
| | $Rh_2$(acetate)$_4$ | 0.177 | 0.400 |
| | $Na_2CO_3$ | 0.106 | 1.00 |
| MOP-**3** | **A** | – | – |
| | **B** | 0.244 | 0.960 |
| | $Rh_2$(acetate)$_4$ | 0.177 | 0.400 |
| | $Na_2CO_3$ | 0.106 | 1.00 |

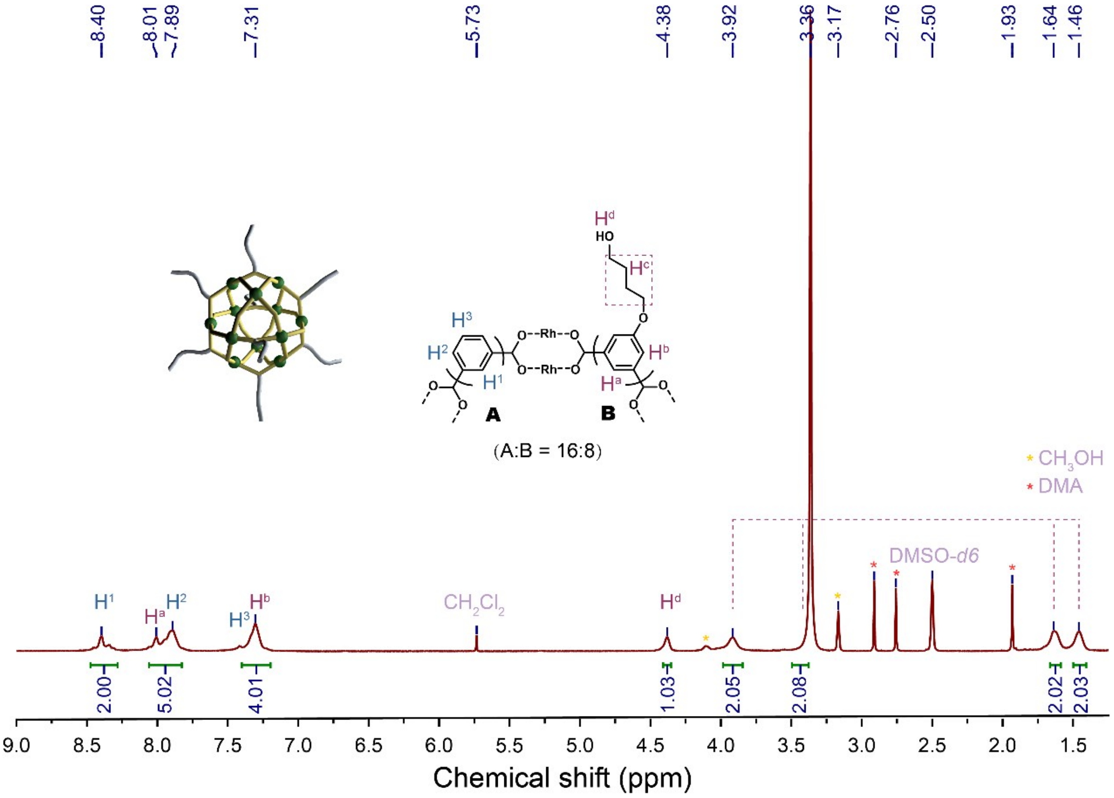


**Figure S2.** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of the MOP-**1**.

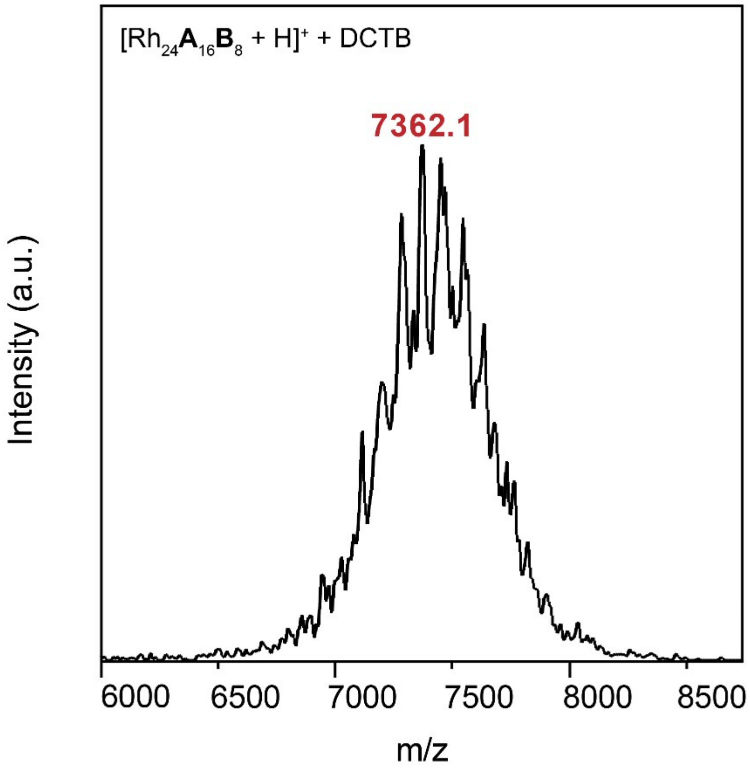


**Figure S3.** MALDI-TOF spectrum of the MOP-**1**. The molecular weight corresponding to the formula $[Rh_{24}(bdc)_{16}(butylhydroxy\text{-}bdc)_8 + H]^+$ + DCTB has been highlighted: expected = 7361.6; found = 7362.1.

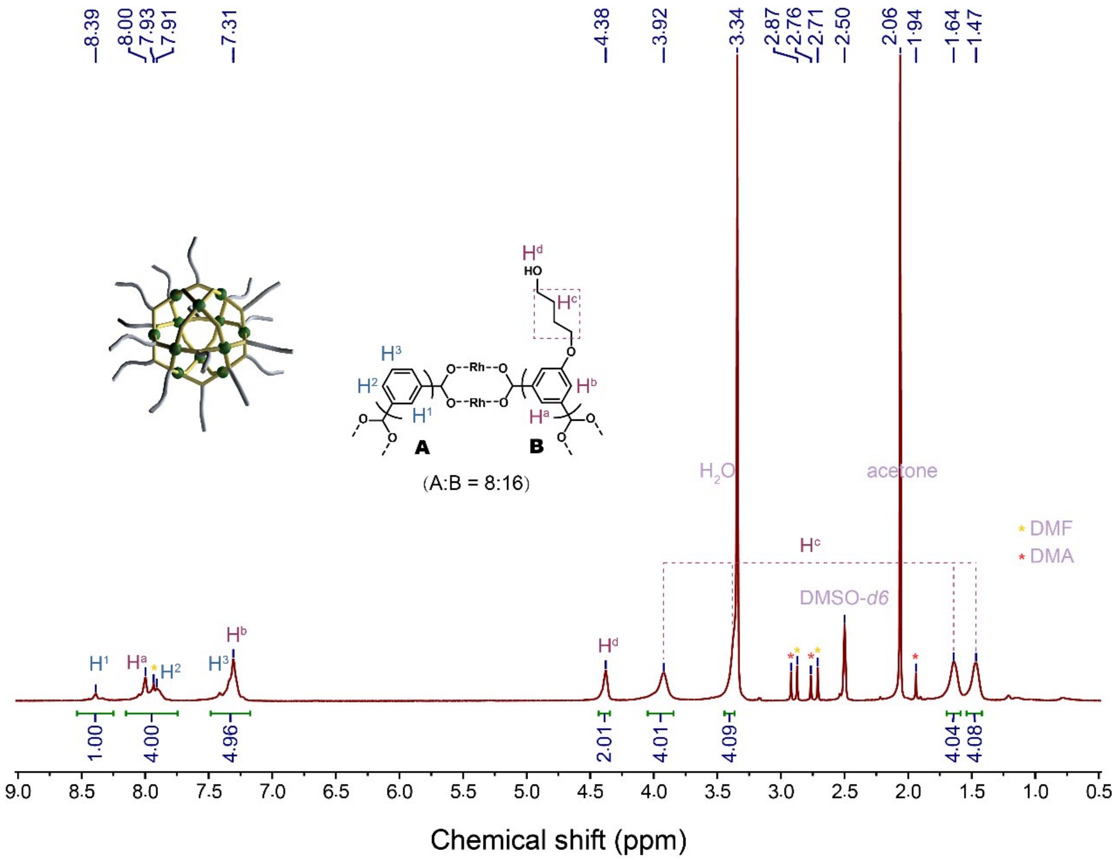


**Figure S4.** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of the MOP-**2**.

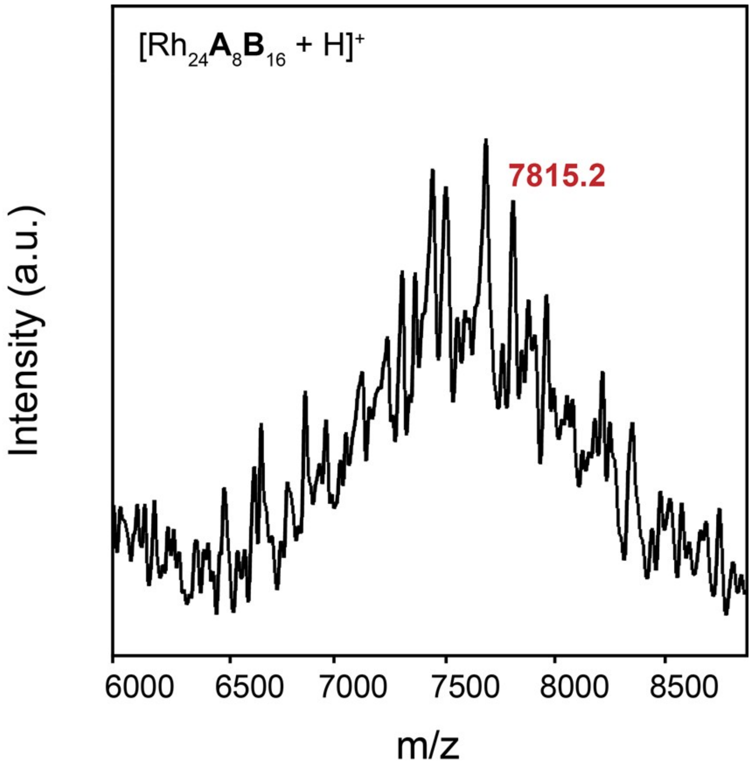


**Figure S5.** MALDI-TOF spectrum of the MOP-**2**. The molecular weight corresponding to the formula $[Rh_{24}(bdc)_8(butylhydroxy\text{-}bdc)_{16} + H]^+$ has been highlighted: expected = 7815.8; found = 7815.2.

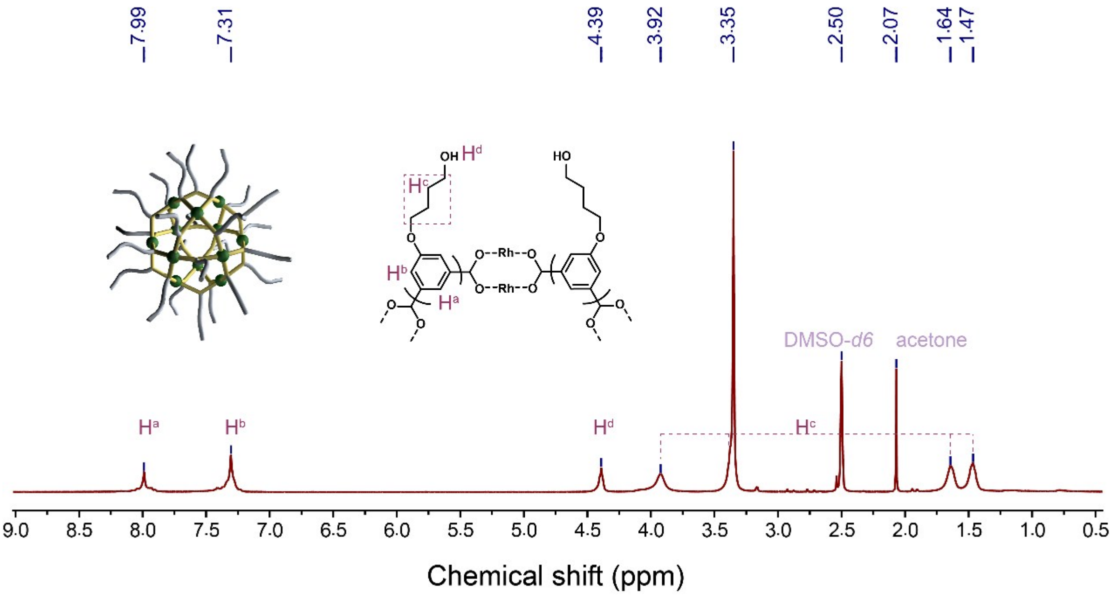


**Figure S6.** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of the MOP-**3**.

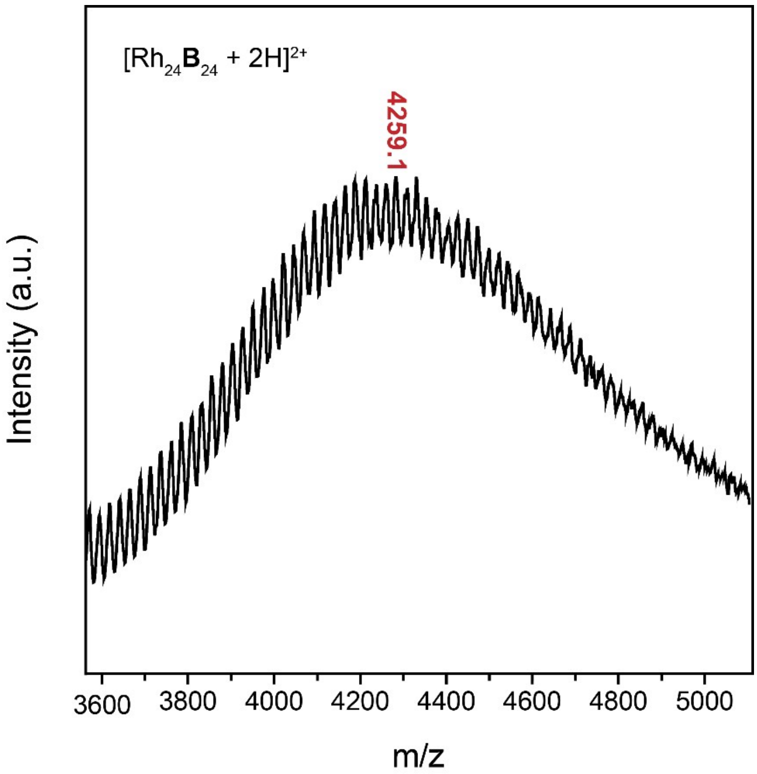
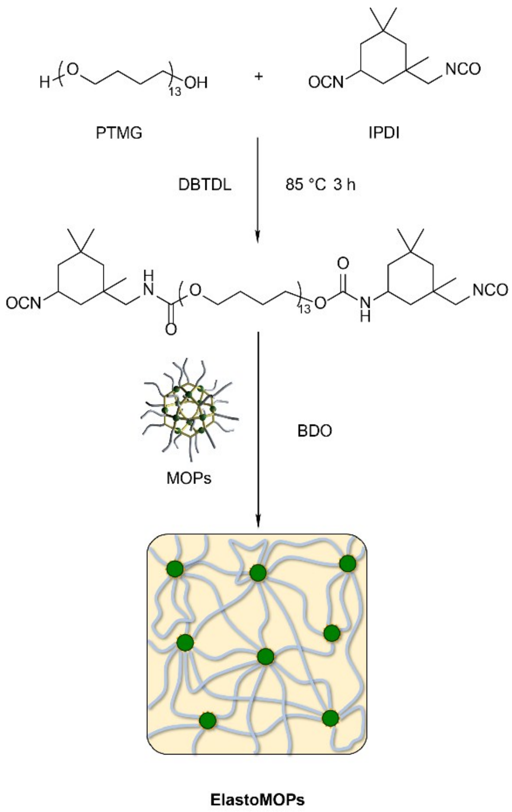


**Figure S7.** MALDI-TOF spectrum of the MOP-**3**. The molecular weight corresponding to the formula [Rh$_{24}$(butylhydroxy-bdc)$_{24}$ + 2H]$^{2+}$ has been highlighted: expected = 4260.6; found = 4259.1.

## 4. Synthesis of the ElastoMOPs



**Scheme S1.** Synthetic route of the ElastoMOPs via condensation polymerization.

*Synthesis of the prepolymer*. In a 100 mL three-necked flask equipped with mechanical stirrer were added PTMG (3.00 g, 3.00 mmol) and IPDI (1.33 g, 6.00 mmol) under nitrogen atmosphere. Three drops of DBTDL catalyst was then added and the resultant mixture was kept stirring at 85 °C for 3 h to yield the prepolymer. Afterwards, 5.0 mL of dry DMA was added to dissolve the prepolymer.

*Synthesis of ElastoMOP-**1***. MOP-**1** (320 mg, 0.0450 mmol) in 15.0 mL of dry DMA was added to the prepolymer solution and kept stirring for 40 min at 90 °C. Then BDO (254 mg, 2.82 mmol) dissolved in 5.0 mL of DMA was then dropwise added into the mixture. Different amounts of BDO was accordingly adjusted in order to keep the NCO/OH = 1 for the ElastoMOPs. After fully stirring the mixture for 30 min, the mixture was poured into a PTFE plate which was subsequently put in a vacuum oven at 90 °C for 12 h to allow the reaction to complete. Then the resulting dark green transparent ElastoMOP-**1** film was obtained.

*Synthesis of ElastoMOP-**2***. MOP-**2** (352 mg, 0.0450 mmol) in 15.0 mL of dry DMA was added to the prepolymer solution and kept stirring for 40 min at 90 °C. Then BDO (238 mg, 2.64 mmol) dissolved in 5.0 mL of DMA was then dropwise added into the mixture. After fully stirring the mixture for 30 min, the mixture was poured into a PTFE plate which was subsequently put in a vacuum oven at 90 °C for 12 h to allow the reaction to complete. Then the resulting dark green transparent ElastoMOP-**2** film was obtained.

*Synthesis of ElastoMOP-3*. MOP-**3** (384 mg, 0.0450 mmol) in 15.0 mL of dry DMA was added to the prepolymer solution and kept stirring for 40 min at 90 °C. Then BDO (222 mg, 2.46 mmol) dissolved in 5.0 mL of DMA was then dropwise added into the mixture. After fully stirring the mixture for 30 min, the mixture was poured into a PTFE plate which was subsequently put in a vacuum oven at 90 °C for 12 h to allow the reaction to complete. Then the resulting dark green transparent ElastoMOP-**3** film was obtained.

**Table S2.** The compositions ElastoMOPs-**1**−**3**.

| **Sample name** | **MOPs, wt %** | **IPDI, wt %** | **PTMG, wt %** | **BDO, wt %** |
|---|---|---|---|---|
| ElastoMOP-**1** | 6.53 | 27.1 | 61.2 | 5.18 |
| ElastoMOP-**2** | 7.15 | 27.0 | 61.0 | 4.84 |
| ElastoMOP-**3** | 7.78 | 26.9 | 60.8 | 4.50 |

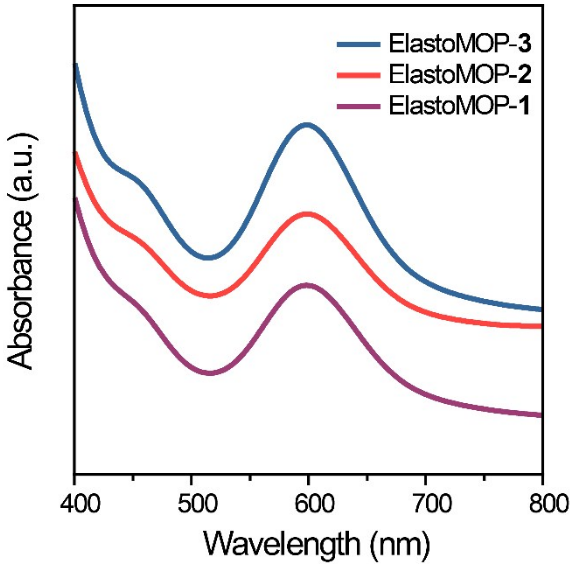


**Figure S8.** UV-vis spectra of the ElastoMOP films. The $\lambda_{\max}$ centered at 599 nm and the second peaks centered at 450 nm confirm the presence of the dirhodium paddlewheels.

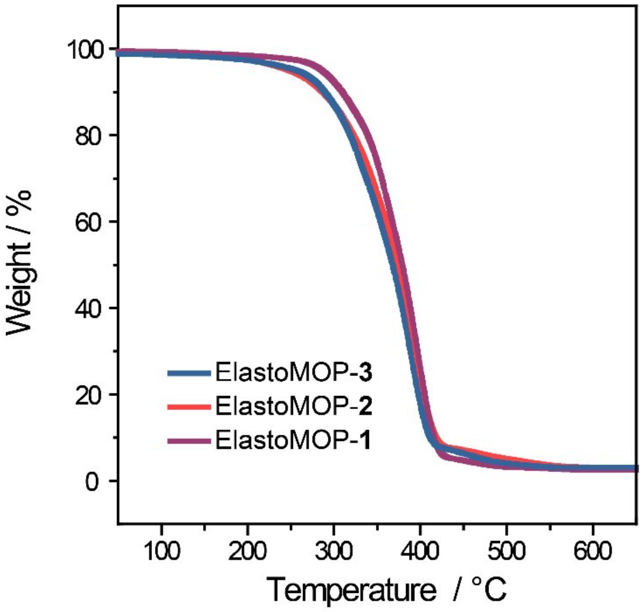


**Figure S9.** TGA curves of the ElastoMOPs-**1**−**3**.

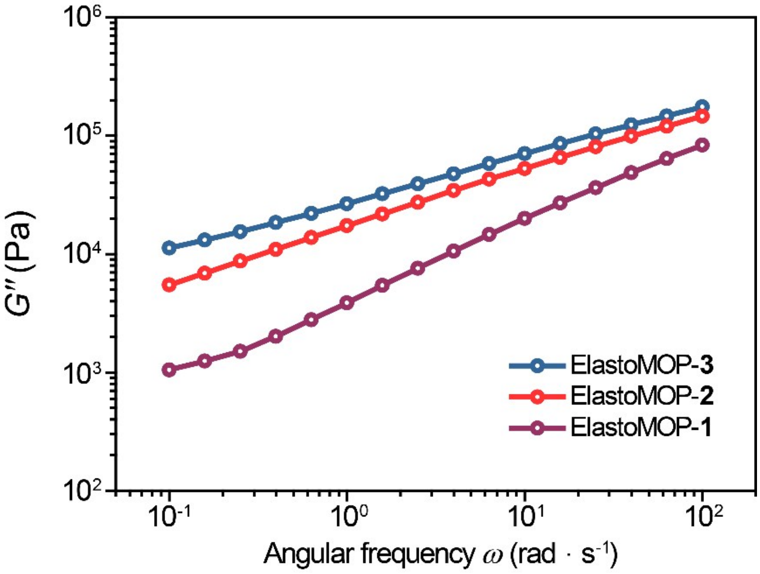


**Figure S10**. The loss moduli of the ElastoMOPs-**1**−**3** versus frequency in an oscillatory rheometry at a 5.0% strain amplitude.

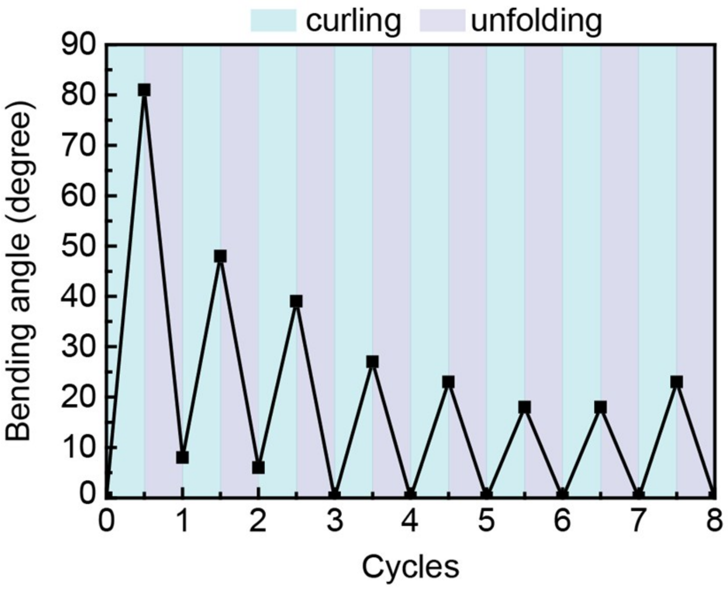


**Figure S11**. The circular deformation of the ElastoMOP-**3** specimen upon cyclic exposure to dichloromethane vapor.

## Supplementary references

S1. Varaprasad, N. S. S.; Ramakrishnan, S. Hybrasurfs-A New Class of Hyperbranched Surfactants. *Langmuir* **2018**, *34*, 11464-11472.

S2. Carné-Sánchez, A.; Albalad, J.; Grancha, T.; Imaz, I.; Juanhuix, J.; Larpent, P.; Furukawa, S.; Maspoch, D. Postsynthetic Covalent and Coordination Functionalization of Rhodium(II)-Based Metal-Organic Polyhedra. *J. Am. Chem. Soc.* **2019**, *141*, 4094-4102.

S3. Zhang, Q.; He, H.; Xi, K.; Huang, X.; Yu, X.; Jia, X. Synthesis of *N*-Phenylaminomethyl POSS and Its Utilization in Polyurethane. *Macromolecules* **2011**, *44*, 550-557.