

## Supporting Information

# **Cylindrical NIR-Responsive Metallopolymer Containing Möbius Metalla-aromatics**

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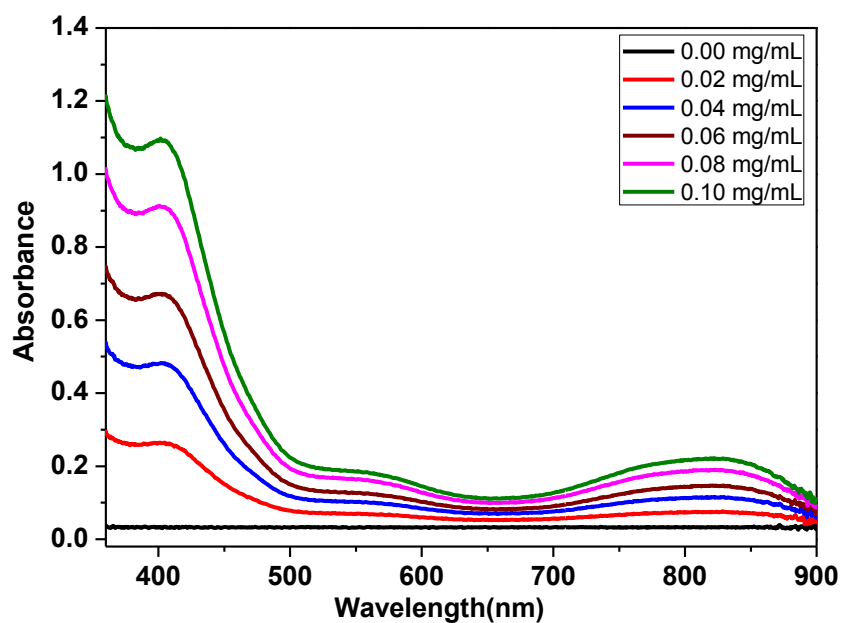
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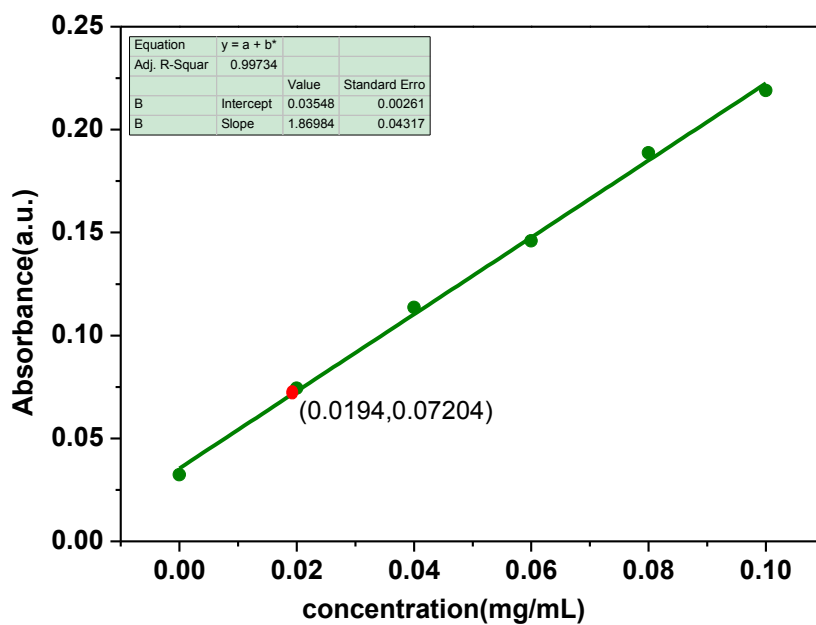
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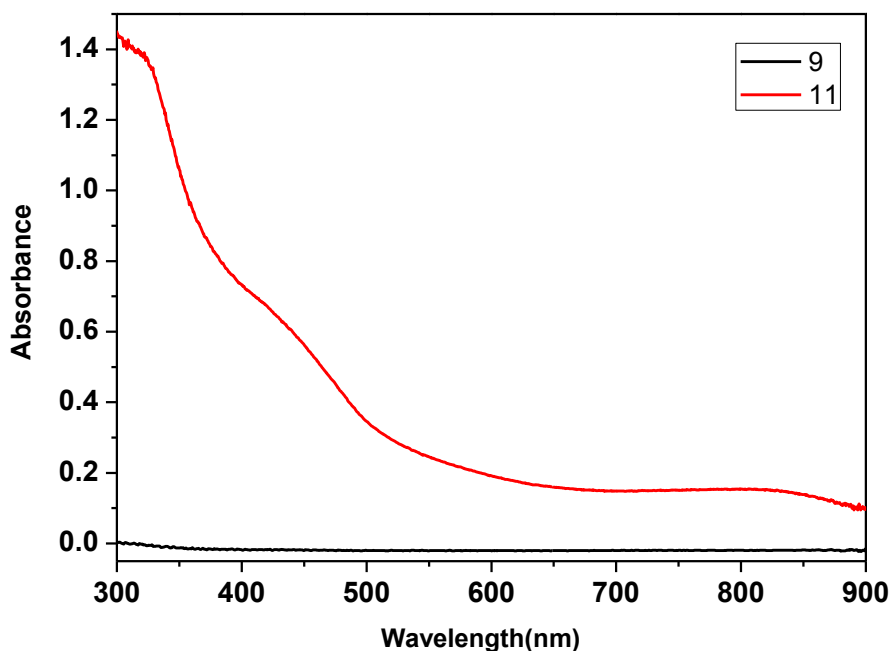
## 1. Supplementary Figures



**Figure S1** UV-Vis-NIR absorption spectra of **2** with different concentrations in DMF.



**Figure S2** Linear relationship between the concentrations and absorption intensities of **2** at 820 nm.

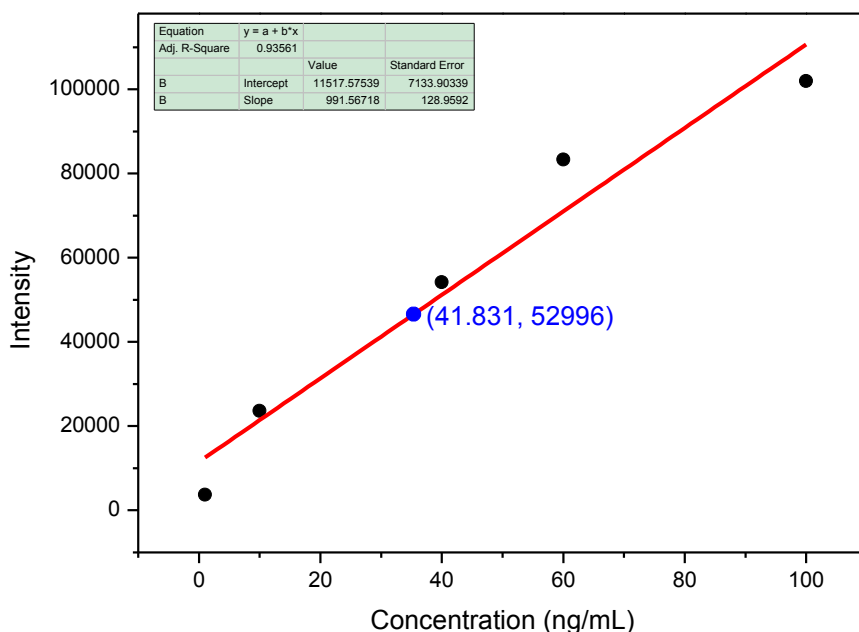


**Figure S3** UV-Vis-NIR absorption spectra of polymers **9** and **11** (0.36 mg/mL) in DMF.

Comparing the absorption of metallopolymer **11** (Figure S3) with the standard UV-Vis absorption curve of complex **2** (Figure S2), the weight ratio of **2/11** ( $M_2/M_{11}$ ) in metallopolymer **11** was:

$$M_2/M_{11} = W_2/W_{11} = 0.0194/0.36 = 0.054 = 5.4\%$$

Where  $W_2$  and  $W_{11}$  are weight concentrations of complex **2** in polymer **11** and metallopolymer **11**,  $W_2$  is calculated to be 0.0194 mg/mL by using the absorption value in Figure S3 and the standard UV-Vis absorption curve of complex **2** (Figure S2).  $M_2$  and  $M_{11}$  are weights of complex **2** and metallopolymer **11**.

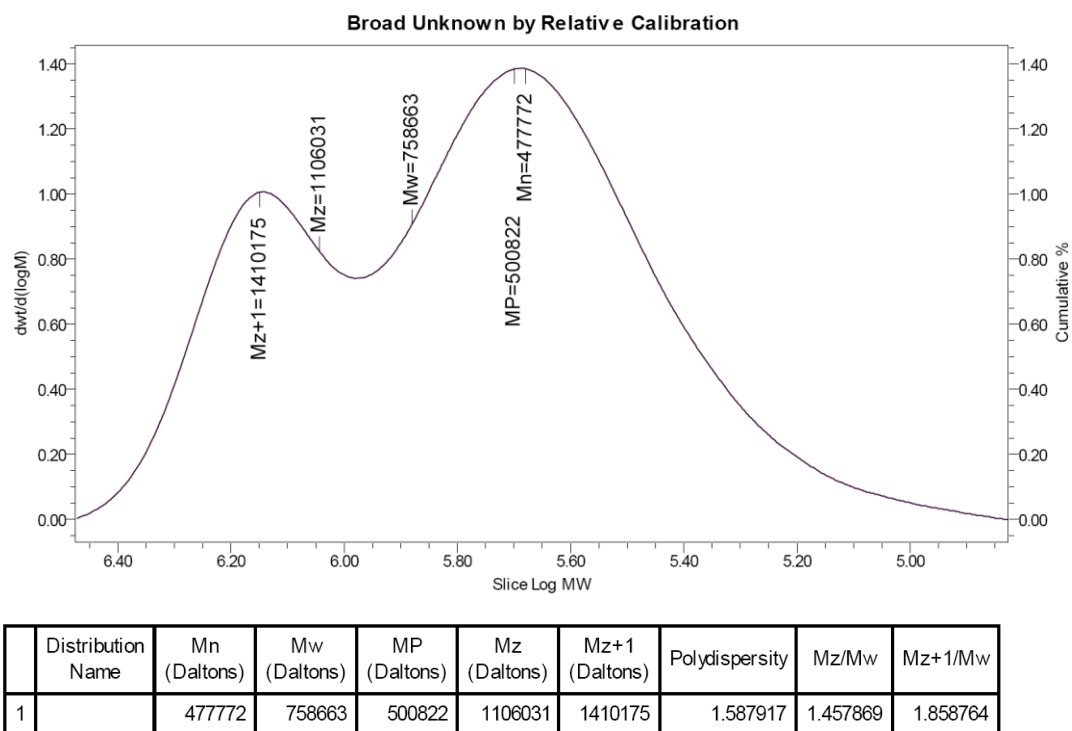


**Figure S4** The linear relationship between the concentrations and intensities of **Os** determined by ICP-MS.

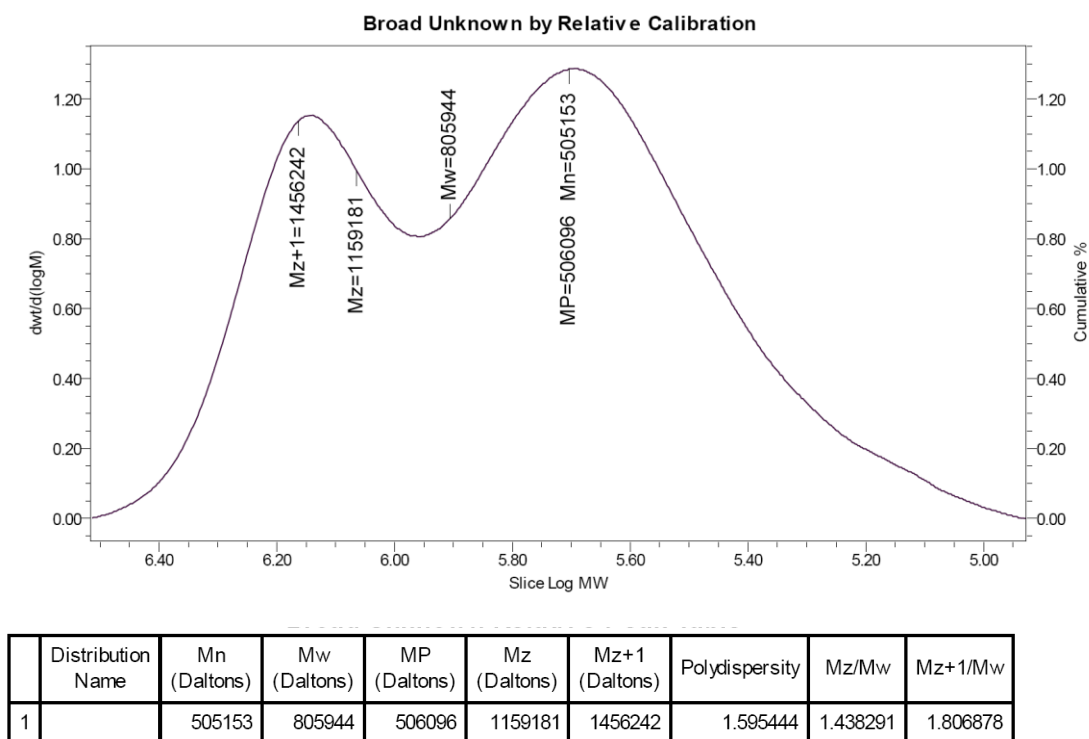
Comparing the intensity of metallopolymer **11** (6000 ng/mL) with the standard curve of **Os** (Figure S4) determined by ICP-MS, the weight ratio of **2/11** ( $M_2/M_{11}$ ) in metallopolymer **11** was:

$$M_2/M_{11} = W_2/W_{11} = (W_{Os} \times [M_2]/[M_{Os}])/W_{11} = (34.594 \times 1435/190)/6000 = 0.044 = 4.4\%$$

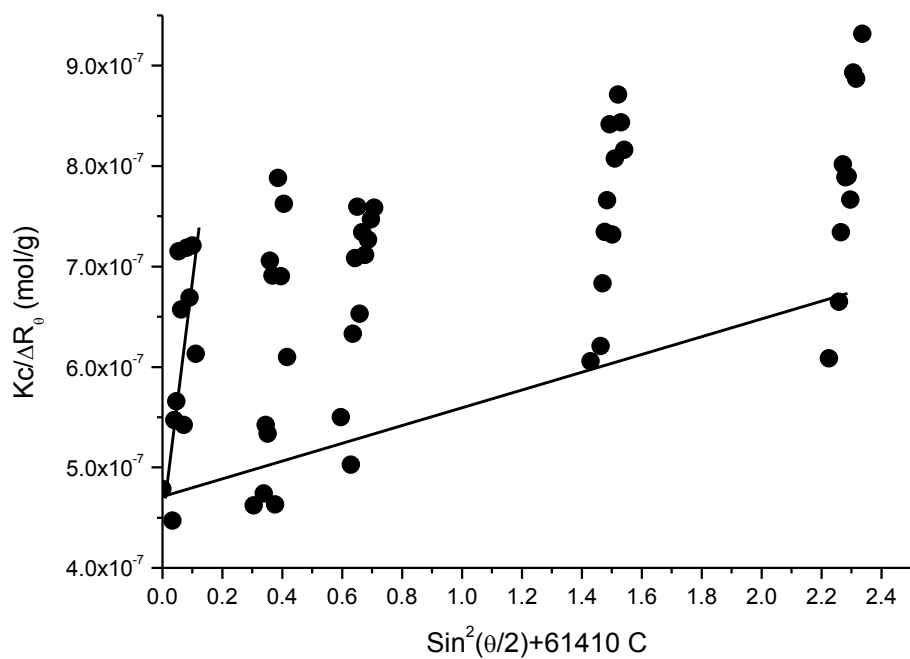
Where  $W_2$ ,  $W_{11}$  and  $W_{Os}$  are weight concentrations of complex **2** in polymer **11**, metallopolymer **11**, and **Os** in metallopolymer **11**.  $W_{Os}$  was calculated to be 34.594 ppb by using the intensity value of **Os** in metallopolymer **11** (6000 ppb) and the standard curve of **Os** (Figure S4).  $[M_2]$  and  $[M_{Os}]$  are molecular weights of complex **2** and **Os**.



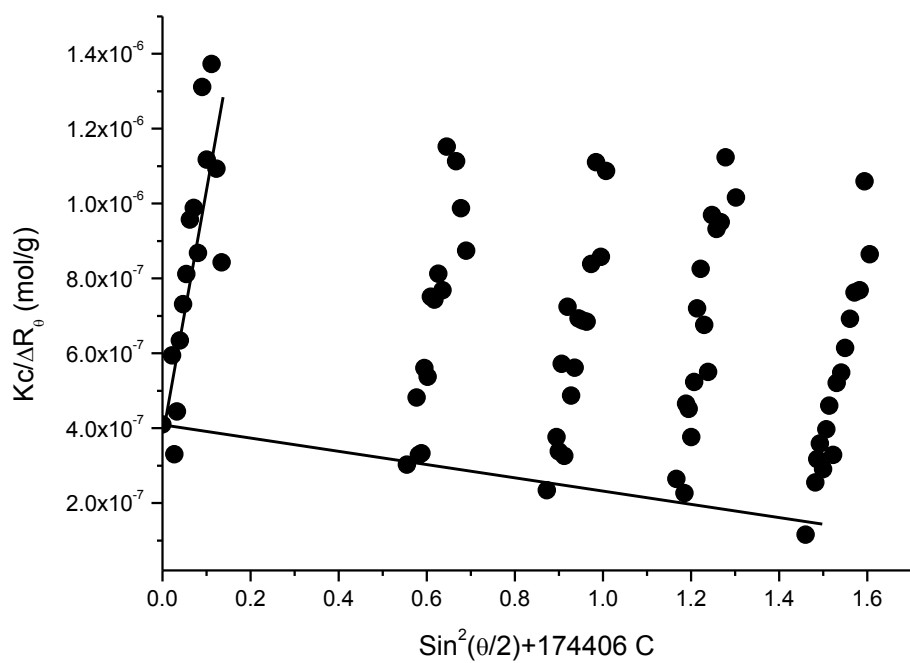
**Figure S5** Molecular weight and its distribution of polymer **9** determined by GPC in DMF relative to narrow molecular weight polystyrenes.



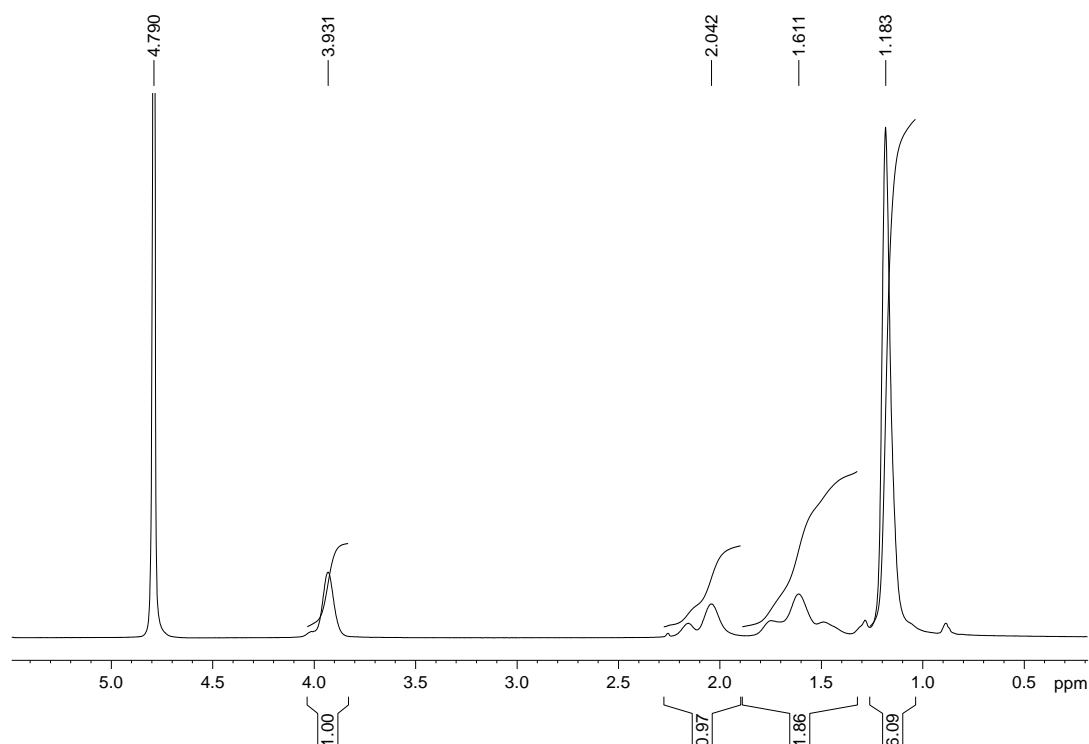
**Figure S6** Molecular weight and its distribution of metallopolymer **11** determined by GPC in DMF relative to narrow molecular weight polystyrenes.



**Figure S7** Zimm plot of polymer **9**.



**Figure S8** Zimm plot of metallopolymer **11**.



**Figure S9** The  $^1\text{H}$  NMR (500.2 MHz,  $\text{D}_2\text{O}$ ) spectrum for polymer **9**.

## 2. Experimental Procedures

### General information

All syntheses were carried out under an inert atmosphere (argon) using standard Schlenk techniques unless otherwise stated. The complex **2**,<sup>1</sup> and macroinitiator **7** (PEG2000)<sup>2,3</sup> were synthesized according to previously published literatures. The other reagents and solvents were used as purchased from commercial sources without further purification. The NMR spectrum was collected on a Bruker AV-500 spectrometer (500 MHz) at room temperature.  $^1\text{H}$  NMR chemical shifts ( $\delta$ ) is relative to tetramethylsilane. Absorption spectra were recorded on a Shimadzu UV2550 UV–Vis spectrophotometer. For stable Os isotope analysis, an ELAN DRC II ICPMS (PerkinElmer, SCIEX, Canada) equipped with a concentric pneumatic nebulizer and a cyclonic spray chamber was used. The ICP/MS operational parameters were as follows: nebulizer Ar gas, 0.88 L/min; auxiliary Ar gas, 1.0 L/min; plasma Ar gas, 15

L/min; RF power, 1200 W; dwell time, 100 ms; lens voltage, 7.2 V. Parameters such as Ar nebulizer gas flow and lens voltage were optimized daily to obtain the best sensitivity with ELAN DRC II Setup/Stab/Masscal Solution. Infrared (IR) spectra were recorded using a Nicolet 380. The relative molecular weights and molecular weight distribution were determined by gel permeation chromatography (GPC). The GPC system (Waters Breeze HPLC Series) was equipped with a refractive-index detector and gel columns (Waters Styragel HT 3, HT 4, HT 5 and HT 6) maintained at 80 °C. LiBr/DMF (50 mmol/mL) solution was used as the eluent at a flow rate of 1.0 mL/min. The gel columns were calibrated with narrow-molecular-weight polystyrene standards ( $PDI \leq 1.05$ , Shoko, Japan). The laser used in photothermal experiments was the STL808T1-15W fiber-coupled laser system (Stone Company) and the temperature data were collected by FLIR A35 FOV 24 thermal imaging camera. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-1400 at an accelerating voltage of 100 kV. Standard Laser Light Scattering (LLS) spectrometer (BI-200SM) equipped with a BI-9000 AT digital time correlator (Brookhaven Instruments, Inc.) and a Mini-L30 diode laser (30 mW, 637 nm) as the light source were used. The refractive index increment ( $d_n/d_c$ ) was measured using a BI-DNDC differential refractometer.

### **Synthesis of cylindrical polymer 9:**

An ampule charged with macroinitiator **7** (20 mg), tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>TREN, 10  $\mu$ L), *N*-isopropylacrylamide (NIPAM, 5.0 g), and acetone (10 mL) was deaerated by three freeze–pump–thaw cycles in liquid N<sub>2</sub> and then sealed. A copper wire (L = 6 cm) was added to the mixture under argon atmosphere. The reaction mixture was stirred at room temperature for 12 h; then, 100 mL diethyl ether was slowly poured into the mixture to give a white precipitate, which was collected by filtration. The crude product was further purified by re-dissolving in acetone (10 mL) and poured into diethyl ether (100 mL) to give a white solid. The pure sample



was thus obtained by repeating this procedure several times. Finally, the product was dried under vacuum to give polymer **9** as a white solid. Yield: 3.3 g, 66%. <sup>1</sup>H NMR (500.2 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 3.39 (br, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.04 (br, 1H, –CH<sub>2</sub>CH–), 1.61 (br, 2H, –CH<sub>2</sub>CH–), 1.18 (br, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). GPC, *M*<sub>w</sub>: 758663 g/mol; *M*<sub>w</sub>/*M*<sub>n</sub>: 1.59. SLS, *M*<sub>w</sub>: (2.08 ± 0.32) × 10<sup>6</sup> g/mol.

#### **Synthesis of cylindrical polymer 10:**

Cylindrical polymer **9** (1.0 g) and sodium azide (200 mg,) were dissolved in DMF (10 mL). The reaction mixture was stirred for 48 h at room temperature. After removing DMF under vacuum, the residue was redissolved with THF and passed through a neutral alumina column to remove residual sodium salt. The filtrate was concentrated by rotary evaporation, and precipitated in 100 mL of diethyl ether. The precipitate was filtered, washed by diethyl ether and dried overnight in vacuum oven. Yield: 855 mg, 85%. The azide functionality was verified by FT-IR. Cylindrical polymer **10** displayed the characteristic stretching band of N<sub>3</sub>, which appeared at 2026 cm<sup>-1</sup> in the FT-IR spectrum.

#### **Synthesis of cylindrical metallopolymer 11:**

A mixture of cylindrical polymer **10** (300 mg), complex **2** (50 mg), CuSO<sub>4</sub> (20 mg), and sodium ascorbate (20 mg) was dissolved in DMF (5 mL). The reaction mixture was stirred at room temperature for 12 h. After removing DMF under vacuum, the residue was redissolved with THF and passed through a neutral alumina column. The filtrate was concentrated by rotary evaporation and precipitated in 30 mL of diethyl ether. The product was further purified by re-dissolving in THF (5 mL) and poured into diethyl ether (30 mL) to give a light-yellow solid. The precipitate was filtered and dried overnight in vacuum oven. Yield: 285 mg, 90%. GPC, *M*<sub>w</sub>: 805944 g/mol; *M*<sub>w</sub>/*M*<sub>n</sub>: 1.60. SLS, *M*<sub>w</sub>: (2.44 ± 0.74) × 10<sup>6</sup> g/mol.

### 3. References

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3. Xu, H.; Xu, Y.; Pang, X.; He, Y.; Jung, J.; Xia, H.; Lin, Z. A General Route to Nanocrystal Kebabs Periodically Assembled on Stretched Flexible Polymer Shish. *Sci. Adv.* **2015**, 1, e1500025.