Electronic Supplementary Information for

Morphology control on fluorescent metallacycle−cored supramolecular polymers

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Table of Contents (36 Pages)

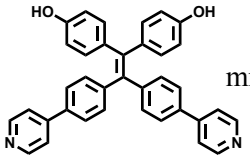
Section A. Materials/General Methods/Instrumentation

1. *Materials/General Methods/Instrumentation*

All reagents and deuterated solvents were commercially available and used without further purification. Compounds **5**[1] and **7**[2] were synthesized according to the published procedure. NMR spectra were recorded on a Bruker Avance 400 MHz or 600 MHz spectrometer. ^{1}H NMR chemical shifts were recorded relative to residual solvent signals, and $^{31}P\{^{1}H\}$ NMR chemical shifts were referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. The UV-vis experiments were conducted on a Lambda 950 absorption spectrophotometer. The fluorescent experiments were conducted on a Hitachi F-7100 fluorescence spectrophotometer. Scanning electron microscope (SEM) investigations were carried out on a Gemini SEM 500 instrument. Transmission electron microscopy (TEM) investigations were carried out on a JEOL JEM-F200(HR) instrument. Confocal laser scanning microscopy (CLSM) was performed with a Zeiss LSM 710 confocal microscope using a 63× objective.

Section B. Synthetic Procedures and Characterization Data

1. Synthesis of compound ***5***



4,4'-[2,2-Bis(4-bromophenyl)ethenylidene]bis[phenol] (522mg, 1.00 mmol), pyridin-4-ylboronic acid (492 mg, 4.00 mmol), K_2CO_3 (829 mg, 6.00 mmol) and Pd $(PPh_3)_4$ (116 mg, 0.10 mmol) were added to a mixture of toluene (28.0 ml), ethanol (7.0 mL) and water (7.0 mL). The reaction mixture was stirred at 80 ℃ for 48 h under nitrogen atmosphere. After cooling to room temperature, the product was concentrated to give a residue which was purified by flash column chromatography with dichloromethane/methanol (20:1, v/v) as the eluent to afford compound **4** (351 mg, 68 %) as yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6, 295 K) 9.40 (s, 2H), 8.58 (d, J = 6.1 Hz, 4H), 7.66 (dd, J = 9.9, 7.3 Hz, 8H), 7.10 (d, J = 8.3 Hz, 4H), 6.81 (d, J = 8.5 Hz, 4H), 6.53 (d, J = 8.6 Hz, 4H). The NMR spectrum matches well with the reported data.[1]

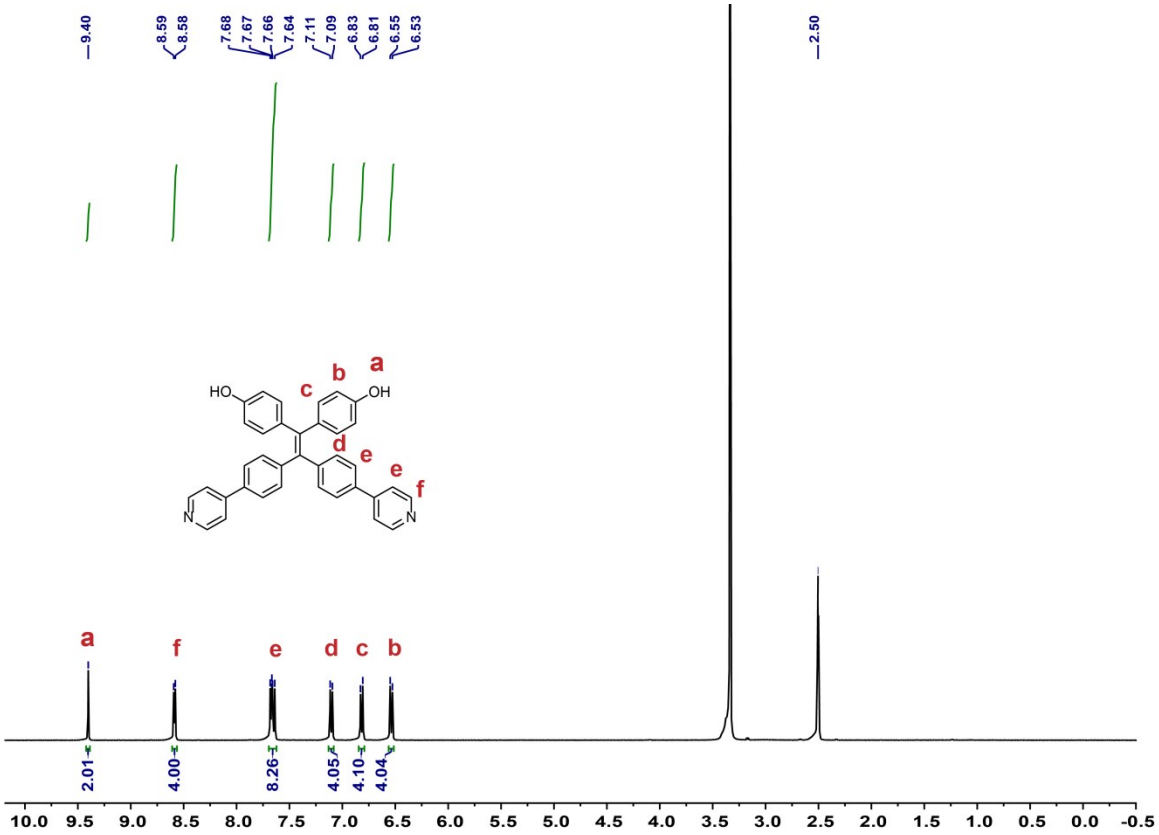
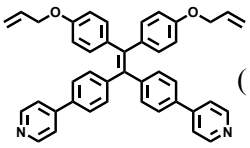


Fig. S1 ^{1}HNMR spectrum (400 MHz, DMSO-d_6, 295K) recorded for **5**.

2. Synthesis of compound ***6***



To compound **5** (100 mg, 0.193 mmol)) in a 100ml Schlenk flask, NaH (14.0 mg, 0.578 mmol) in DMF (30ml) was added. The whole system was stirred for 30 min and then allyl bromide (51.3 mg, 0.424 mmol) in DMF (5 ml) was added drop wisely in an ice bath. The reaction mixture was slowly restored to room temperature and reacted for 12h. The crude product was purified by flash column chromatography (CH_2Cl_2:CH_3OH = 30:1) to give compound **6** (78.5 mg, 67.97%) as a cyan solid. ^{1}H NMR (600 MHz, DMSO-d_6, 295 K) 8.66–8.55 (m, 4H), 7.73–7.61 (m, 8H), 7.13 (d, J = 8.4 Hz, 4H), 6.93 (d, J = 8.7 Hz, 4H), 6.76 (d, J = 8.8 Hz, 4H), 5.99 (m, 4H), 5.36 (dd, J = 17.3, 1.7 Hz, 4H), 5.27–5.18 (m, 4H), 4.48 (d, J = 5.3 Hz, 4H).

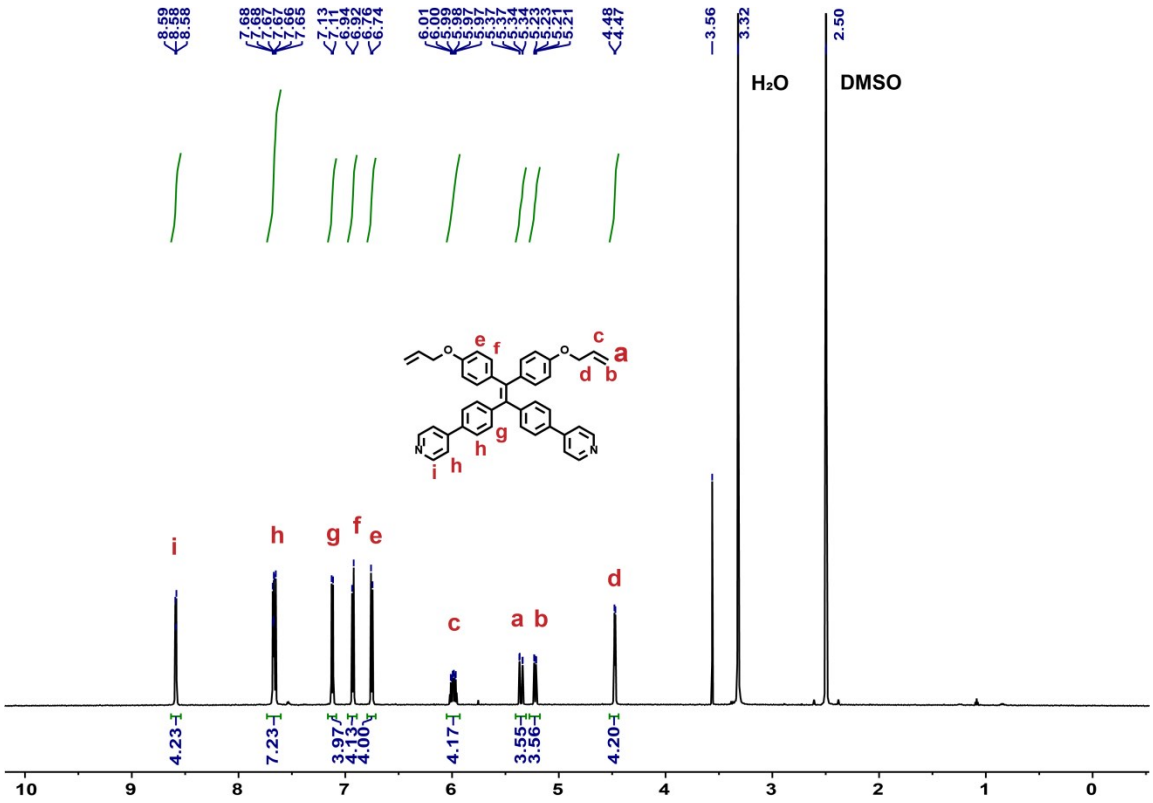


Fig. S2 ^{1}HNMR spectrum (600 MHz, DMSO-d_6, 295K) recorded for **6**.

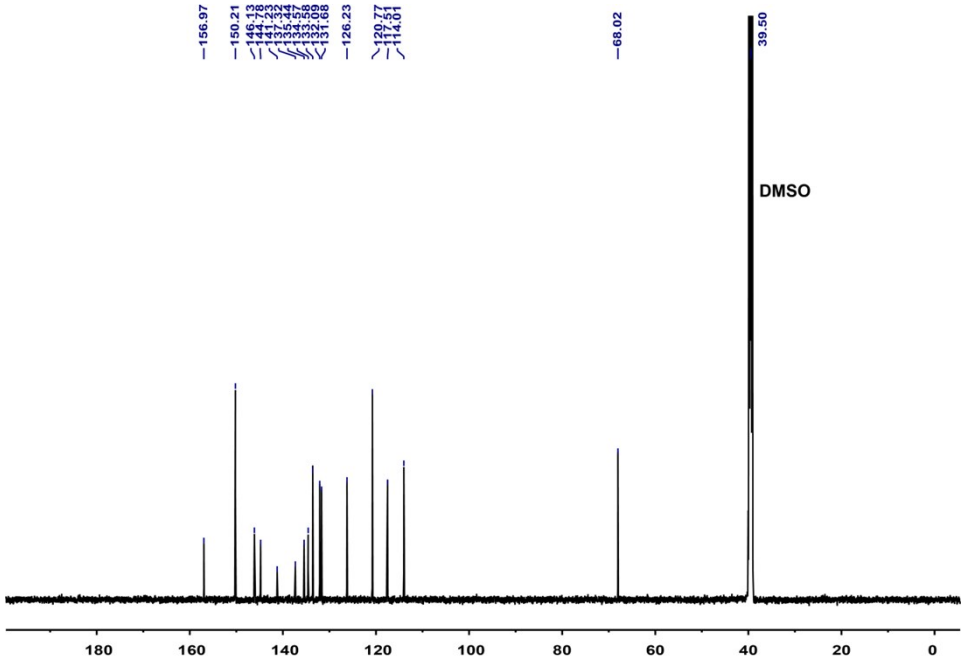


Fig. S3 Partial ^{13}C NMR (100 MHz, DMSO-d_6, 295 K) spectrum recorded for ligand **6**.

3. Synthesis of compound 7

Compound **7** was synthesized according to literature procedure. The ^{1}H NMR and ^{31}P NMR of compound **7** matches well with the reported data.[2]

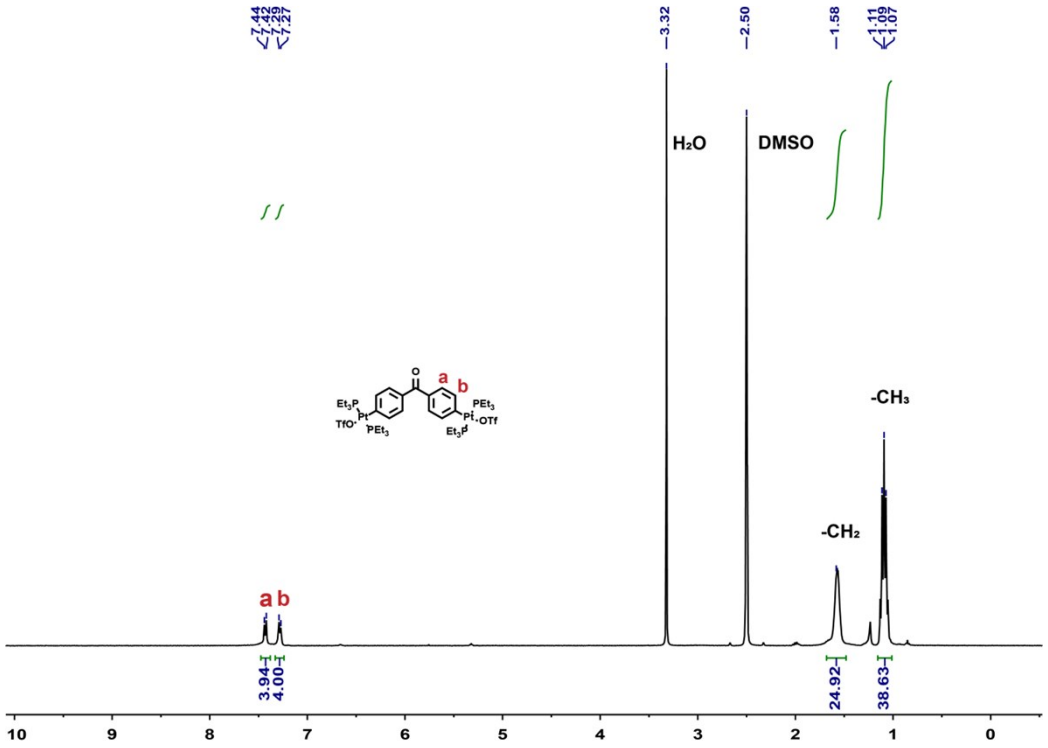


Fig. S4 ^{1}HNMR spectrum (400 MHz, DMSO-d_6, 295K) recorded for **7**

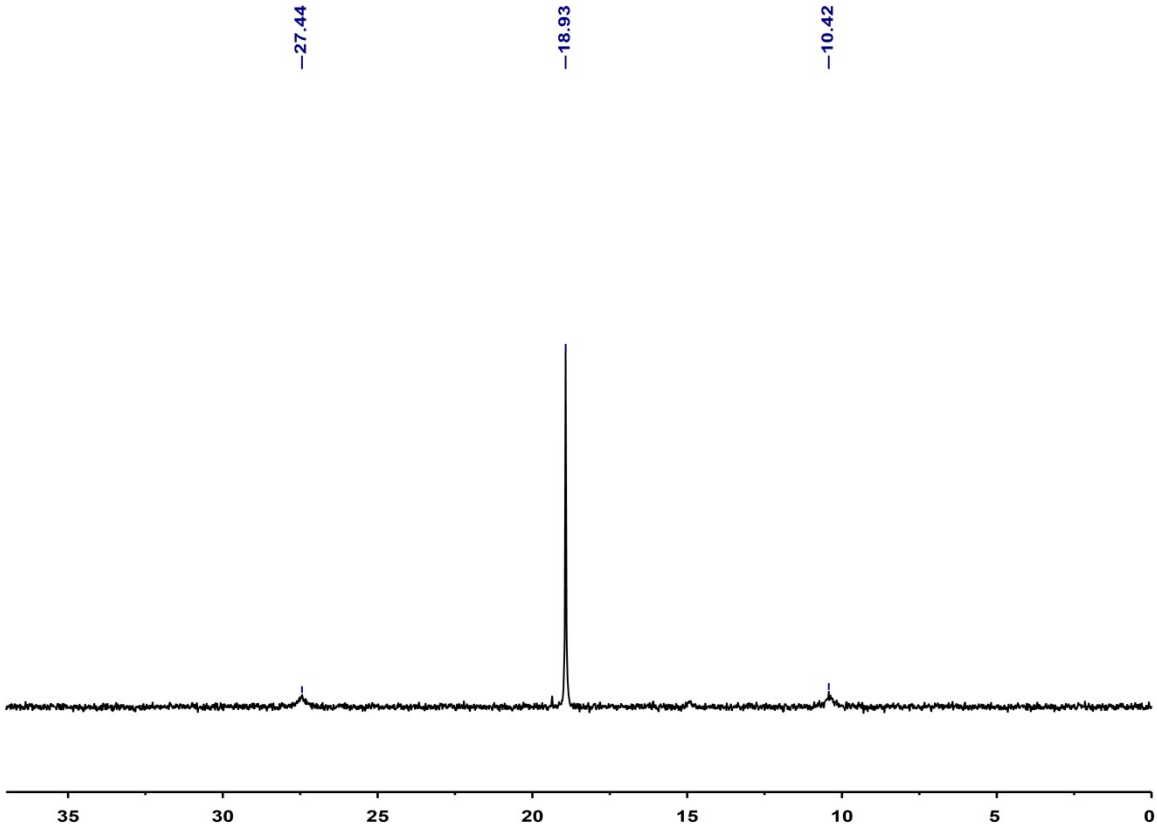
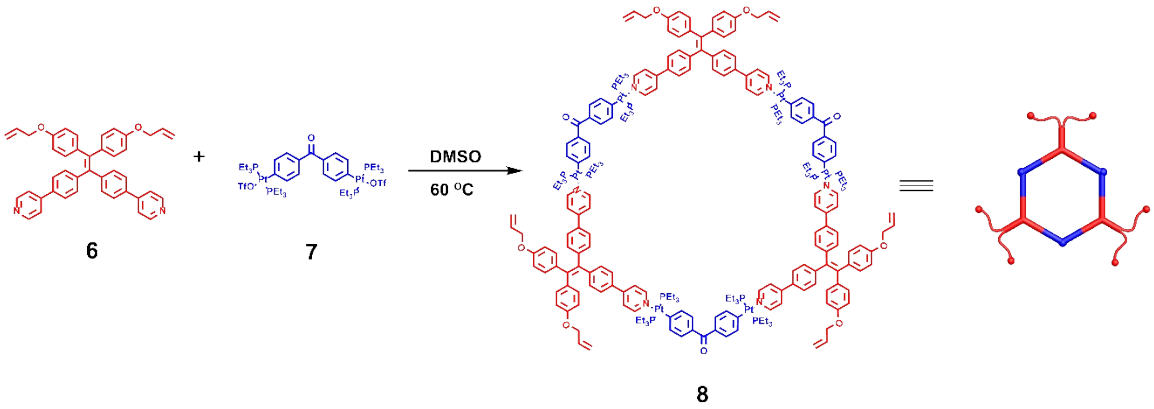


Fig. S5 Partial $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, DMSO-d_6, 295K) recorded for **7**.

*4. Self-assembly of hexagonal metallacycle **8***



Compound **6** (2.00 mg, 0.00334 mmol) and compound **7** (4.80 mg, 0.00334mmol) were dissolved in DMSO in a 5 mL vial. The whole system was stirred at 60℃ for 24 h. The solution was filtered and the solvent was removed by nitrogen flow. The orange solid **8** (6.26 mg, 92 %) was gained by recrystallization through dichloromethane/diethyl ether twice. ^{1}H NMR (400 MHz, DMSO-d_6, 295K) 8.78 (s, 12H), 8.06 (s, 12H), 7.87 (d, J = 7.8 Hz, 12H), 7.68–7.38 (m, 26H), 7.21 (s, 12H), 6.98 (d, J = 6.6 Hz, 12H), 6.80 (d, J = 8.7 Hz, 12H), 6.02 (m, 7H), 5.38 (d, J = 18.9 Hz, 7H), 5.33 – 5.19 (m, 7H), 4.52 (s, 12H), 1.29 (m, 72H), 1.09 (m, 108H). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 295 K) δ (ppm): 13.18 ppm (s, ^{195}Pt satellites, $^{1}J_{Pt–P}$ = 2647.08 Hz). ESI-TOF-MS: m/z 820.7321 [**8** – 6OTf]$^{6+}$, 1014.6749 [**8** – 5OTf]$^{5+}$, 1305.5957 [**8** – 4OTf]$^{4+}$, 1790.4800 [**8** – 3OTf]$^{3+}$.

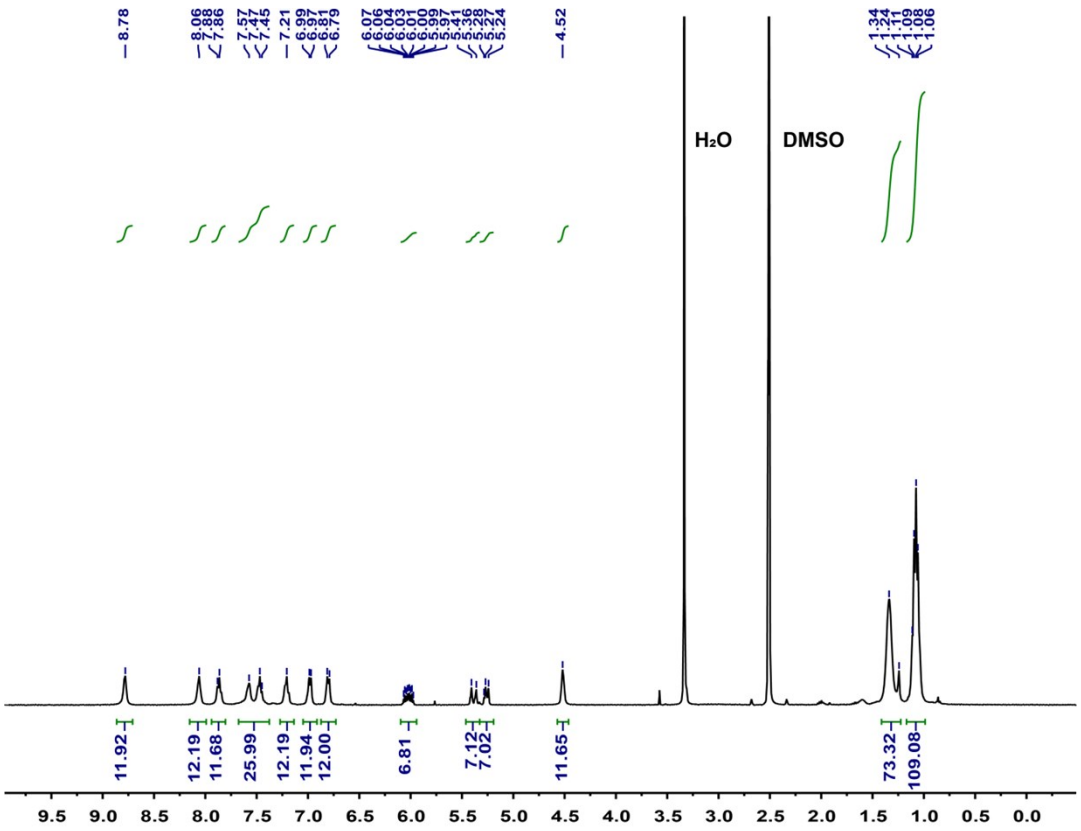


Fig. S6 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 295K) recorded for **8**.

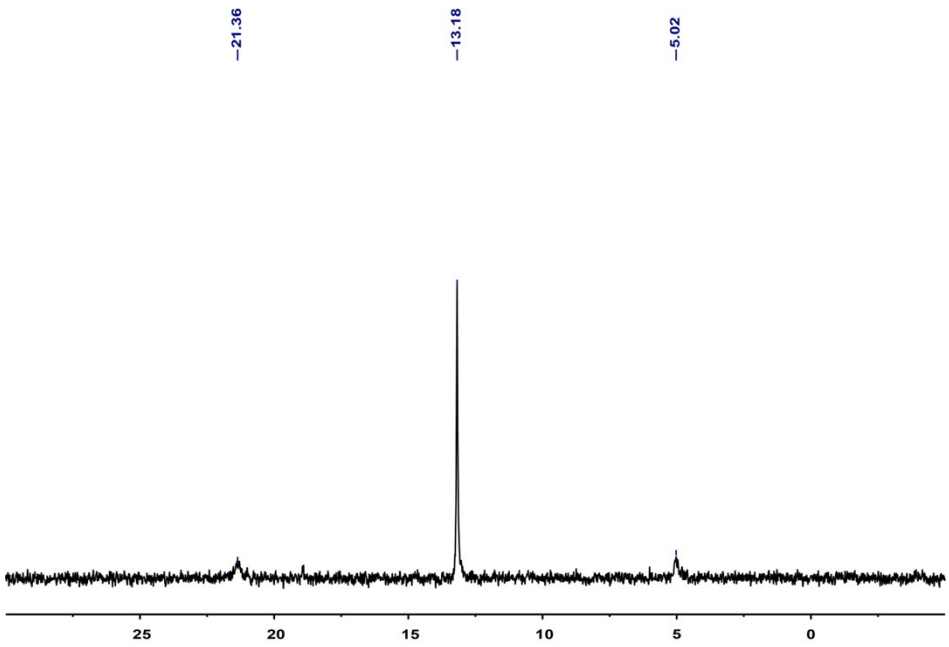


Fig. S7 Partial $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, DMSO-d_6, 295K) recorded for **8**.

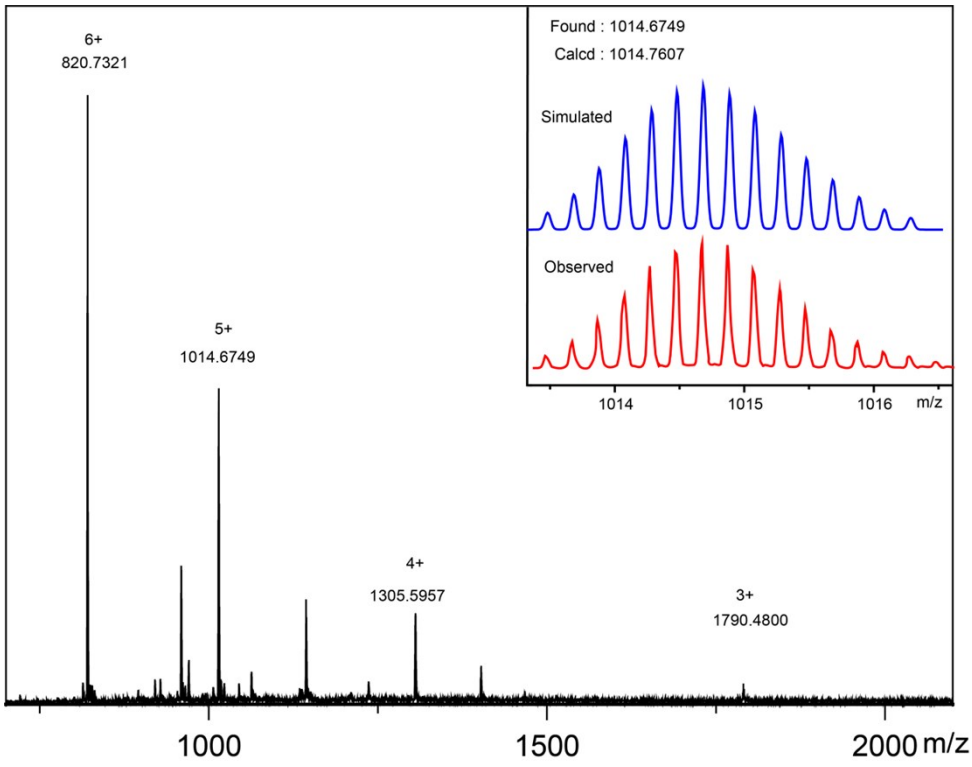
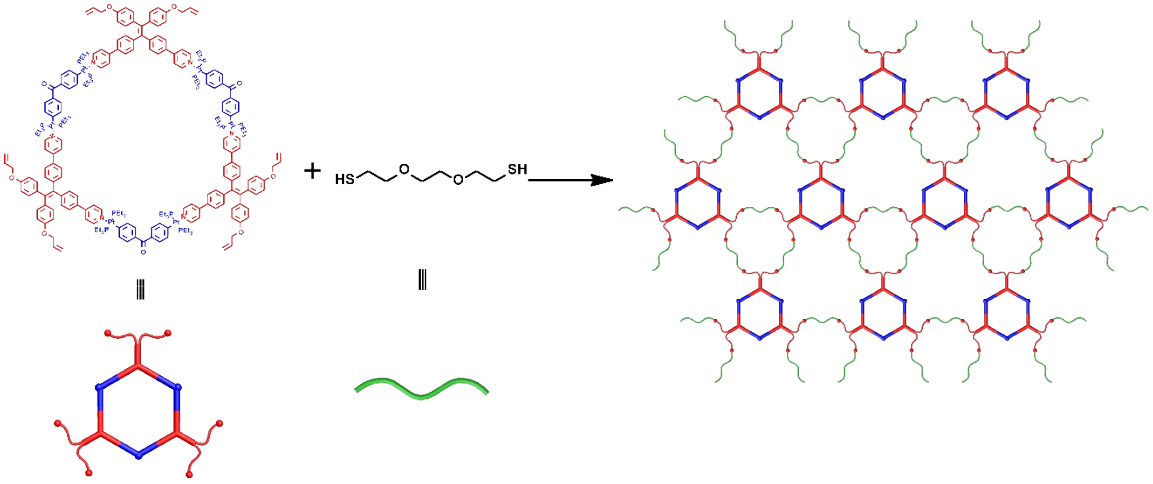


Fig. S8 ESI-TOF-MS of metallacycle **8**. Experimental (red) and calculated (blue) spectra of [**8** - 5OTf]$^{5+}$.

*5. Synthesis of polymer **1***



8 **linker 1** **polymer 1**

Metallacycle **8** (13.6 mg,0.00234 mmol), linker **1** (1.28 mg, 0.701 mmol) and a catalytic amount of 2,2-dimethoxy-2-phenylacetophenone (DMPA) (1.56mg, 0.0078mmol) were added in methanol or THF (10 mL). The reaction mixture was stirred at room temperature upon the irradiation of 365nm UV light for 16 h. After the reaction, the solvent was removed and the light-yellow solid polymer **1** (13.98 mg, 94 %) was gained by recrystallization through dichloromethane/diethyl ether twice. ^{1}H NMR (400 MHz, DMSO-d_6, 295K) 8.83–8.73 (m, 12H), 8.12–8.01 (m, 12H), 7.93–7.83 (m, 11H), 7.58 (s, 12H), 7.51–7.44 (m, 13H), 7.26–7.17 (m, 12H), 7.02–6.93 (m, 13H), 6.78 (s, 12H), 3.97 (s, 12H), 2.65 (s, 26H), 1.93 (s, 13H), 1.43–1.25 (m, 73H), 1.12 – 0.99 (m, 119H). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 295 K) δ (ppm): 13.19 ppm (s, ^{195}Pt satellites,$^{1}J_{Pt-P}$ = 2651.94 Hz).

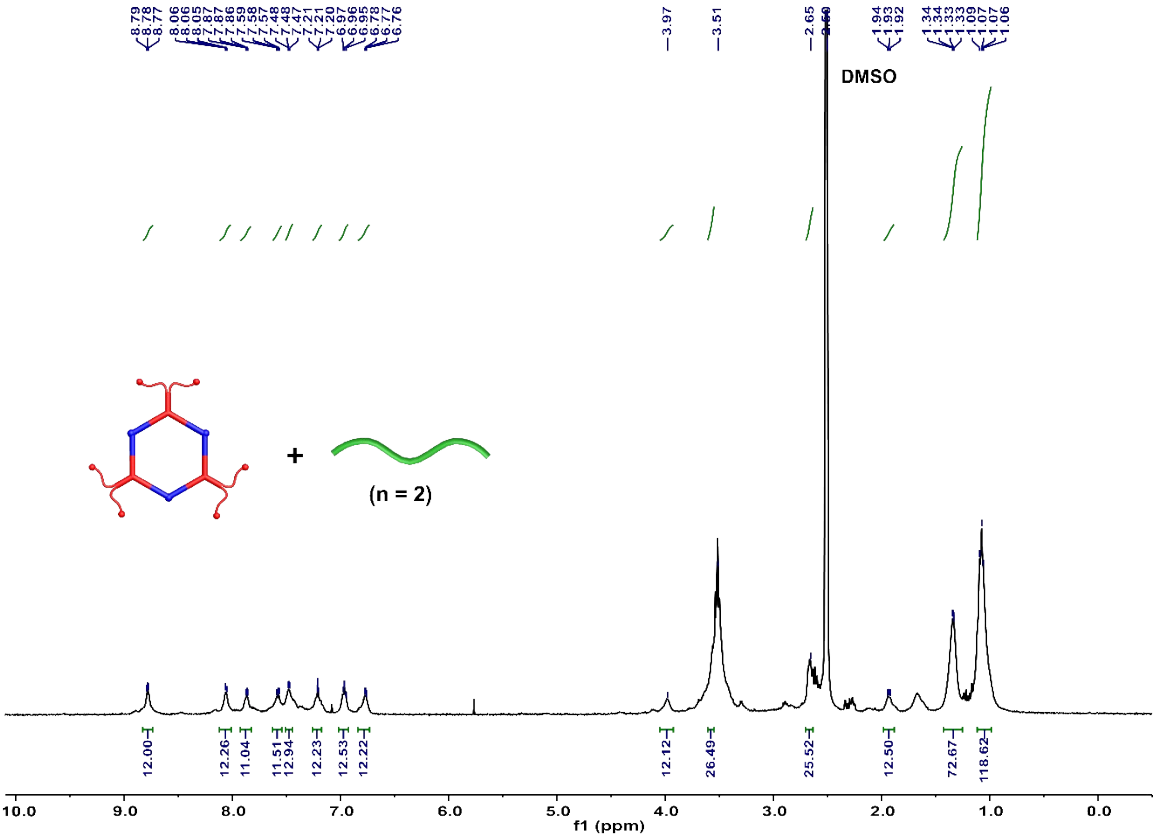


Fig. S9 [1]HNMR spectrum (400 MHz, DMSO-d_6, 295K) recorded for polymer **1**.

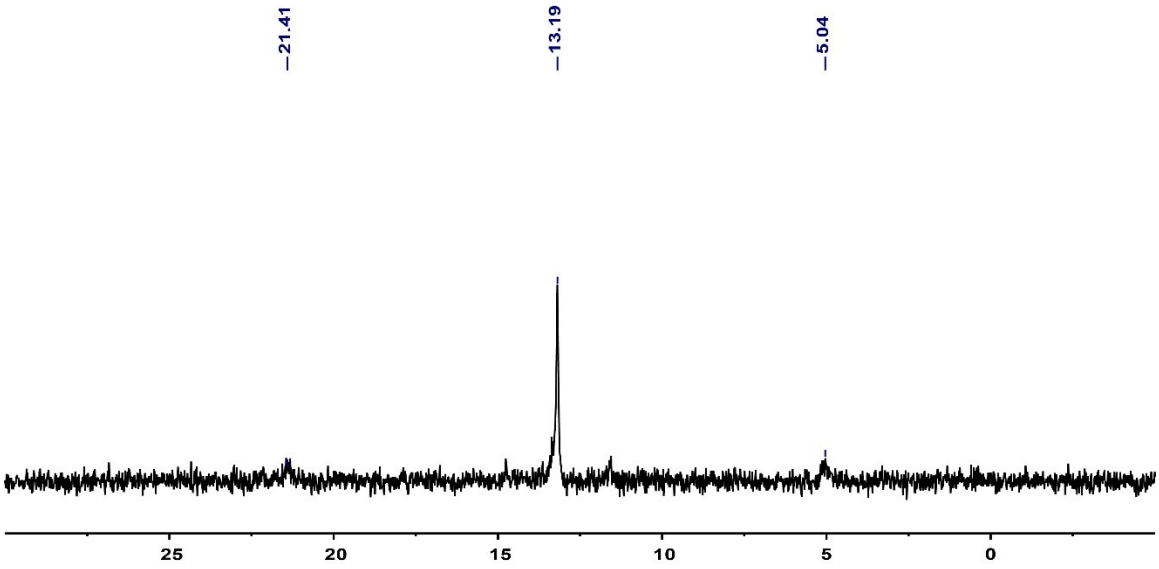


Fig. S10 Partial $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, DMSO-d_6, 295K) recorded for polymer **1**.

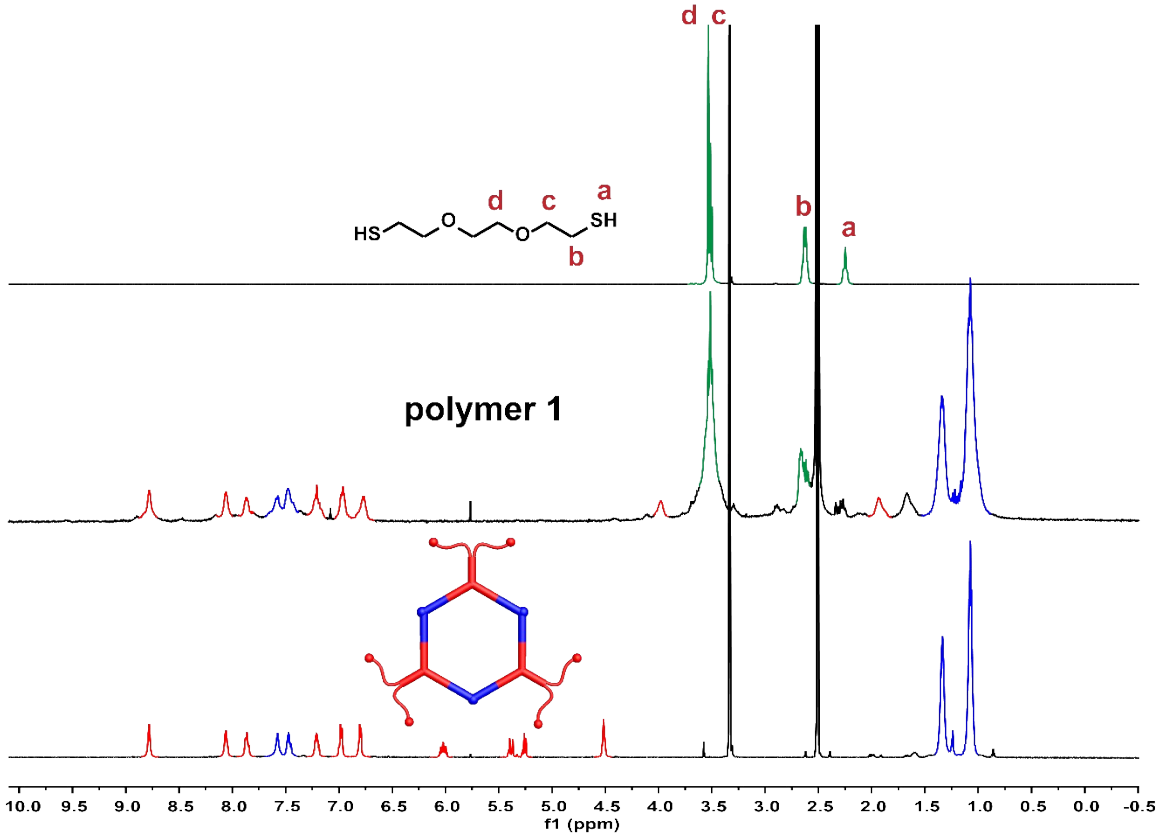
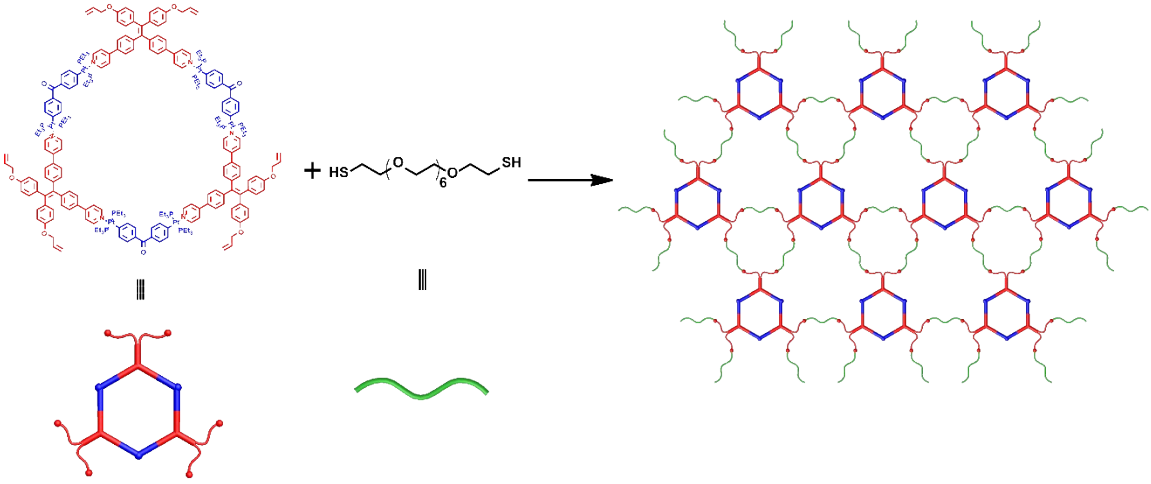


Fig. S11 ^{1}H NMR spectra (400 MHz, DMSO-d_6, 295 K) recorded for metallacycle **8** (bottom), linker **1** (top), and polymer **1** (middle).

*6. Synthesis of polymer **2***



Metallacycle **8** (13.6 mg,0.00234 mmol), linker **2** (2.80 mg, 0.701 mmol) and a catalytic amount of 2,2-dimethoxy-2-phenylacetophenone (DMPA) (1.56mg, 0.0078mmol) were added in methanol or THF (10 mL). The reaction mixture was stirred at room temperature upon the irradiation of 365nm UV for 16h. After the reaction, the solvent was removed and the light-yellow solid polymer **2** (15.80 mg, 96 %) was gained by recrystallization through dichloromethane/diethyl ether twice. ^{1}H NMR (400 MHz, DMSO-d_6, 295K) 8.92–8.74 (m, 14H), 8.11–7.97 (m, 10H), 7.95–7.80 (m, 12H), 7.58 (s, 13H), 7.53–7.42 (m, 15H), 7.31–7.15 (m, 14H), 7.09–6.90 (m, 13H), 6.76 (d, J = 5.6 Hz, 11H), 3.98 (d, J = 6.6 Hz, 14H), 3.57 (s, 78H), 2.68 (dd, J = 28.3, 4.4 Hz, 28H), 2.02–1.89 (m, 13H), 1.47–1.23 (m, 75H), 1.20–0.88 (m, 124H). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 295 K) δ (ppm): 13.20 ppm (s, ^{195}Pt satellites, $^{1}J_{Pt-P}$ = 2640.60 Hz).

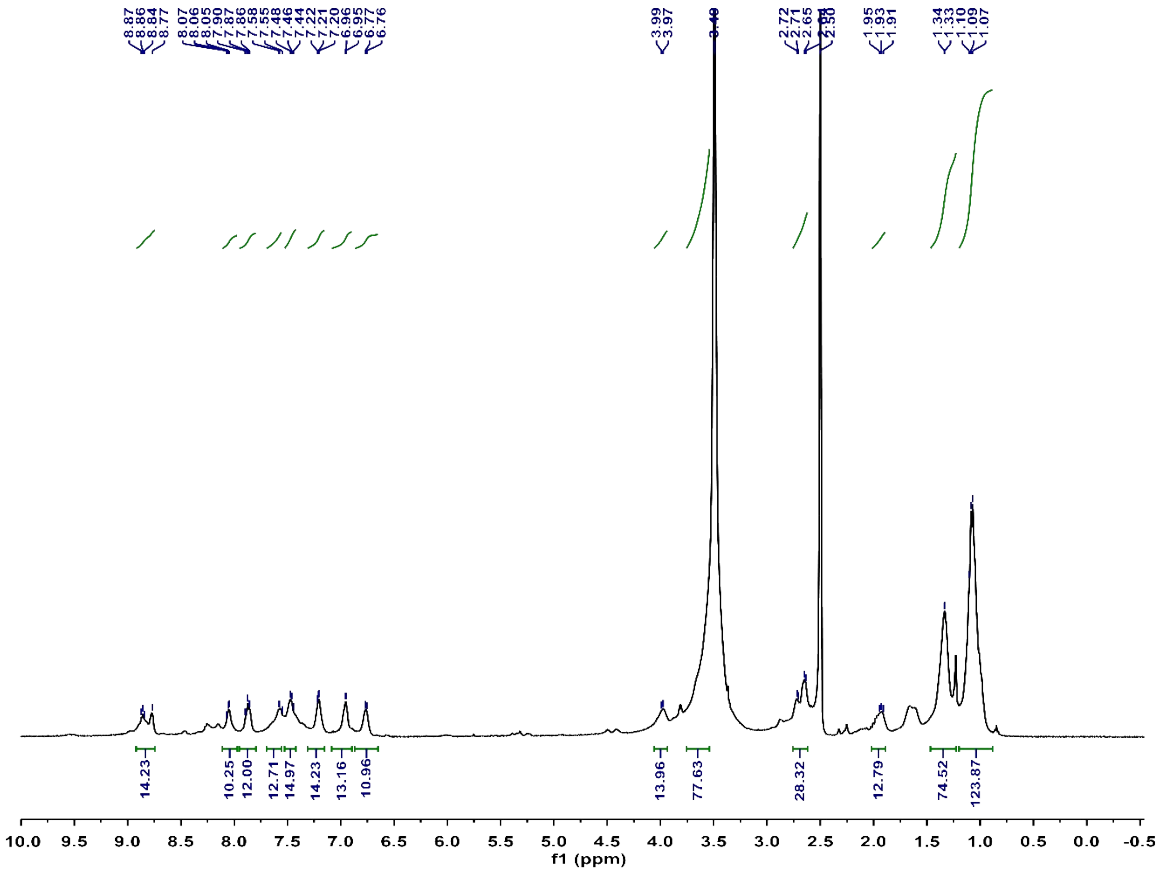


Fig. S12 ^{1}HNMR spectrum (400 MHz, DMSO-d_6, 295K) recorded for polymer **2.**

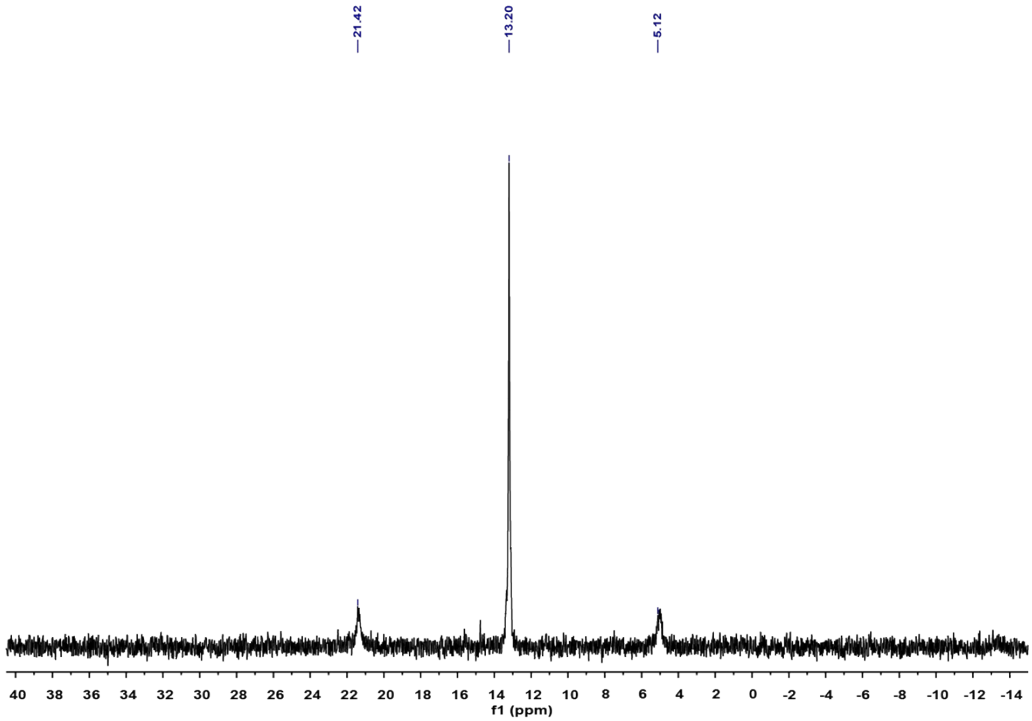


Fig. S13 Partial $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, DMSO-d_6, 295K) recorded for polymer **2**.

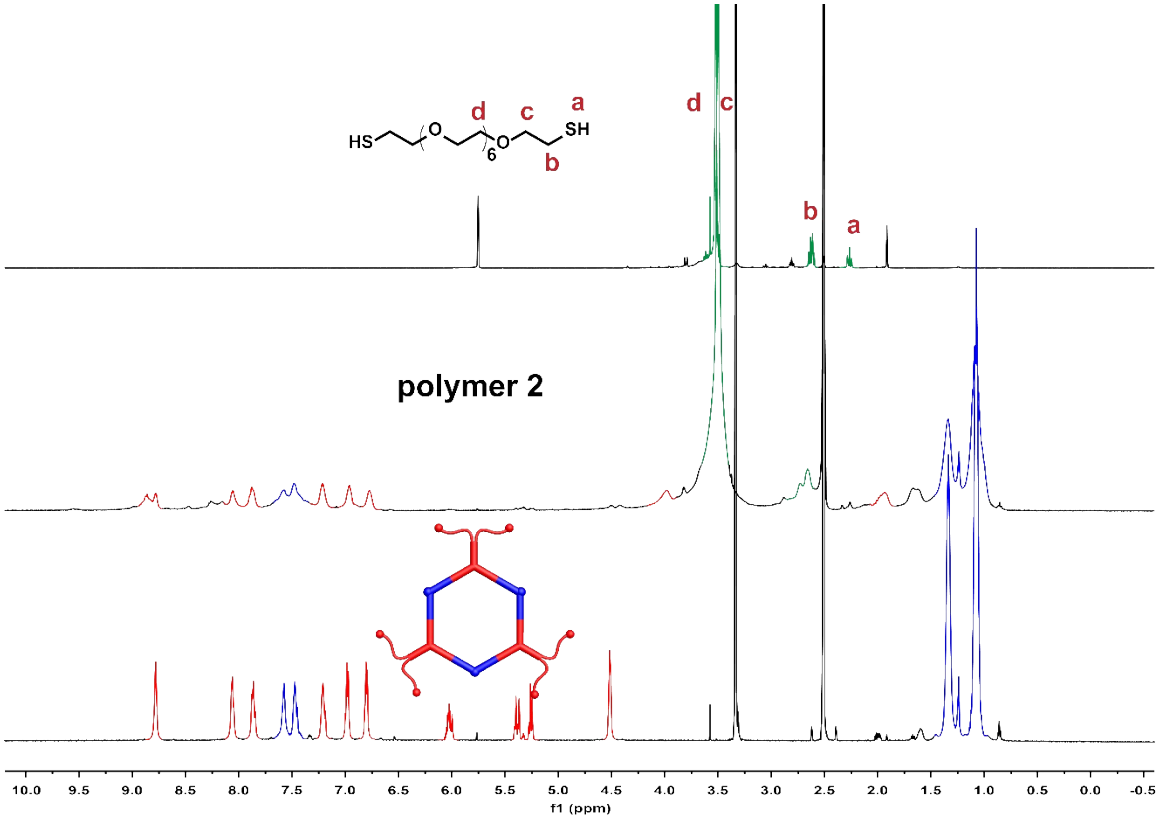
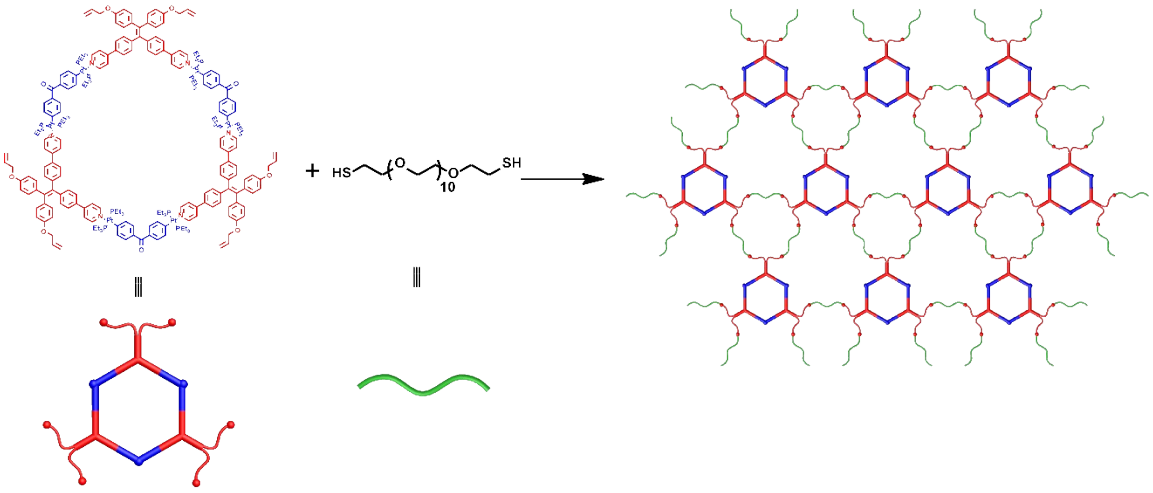


Fig. S14 ^{1}H NMR spectra (400 MHz, DMSO-d_6, 295 K) recorded for metallacycle **8** (bottom),

linker **2** (top), and polymer **2** (middle).

*7. Synthesis of polymer **3***



Metallacycle **8** (13.6 mg,0.00234 mmol), linker **3** (4.67 mg, 0.701 mmol) and a catalytic amount of 2,2-dimethoxy-2-phenylacetophenone (DMPA) (1.56mg, 0.0078mmol) were added in methanol or THF (10 mL). The reaction mixture was stirred at room temperature upon the irradiation of 365nm UV light for 16 h. After the reaction, the solvent was removed and the light-yellow solid polymer **3** (17.10 mg, 96 %) was gained by recrystallization through dichloromethane/diethyl ether twice. ^{1}H NMR (400 MHz, DMSO-d_6, 295K) 9.00–8.85 (m, 11H), 8.29–8.15 (m, 15H), 8.02 (d, J = 2.8 Hz, 12H), 7.60 (d, J = 8.2 Hz, 12H), 7.49 (d, J = 8.7 Hz, 10H), 7.20 (s, 5H), 7.07 (s, 4H), 6.94 (s, 4H), 3.59–3.45 (m, 133H), 2.70 (s, 25H), 2.03 (s, 14H), 1.51–1.23 (m, 71H), 1.24–0.67 (m, 113H). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 295 K) δ (ppm): 13.19 ppm (s, ^{195}Pt satellites,$^{1}J_{Pt-P}$ = 2638.90 Hz).

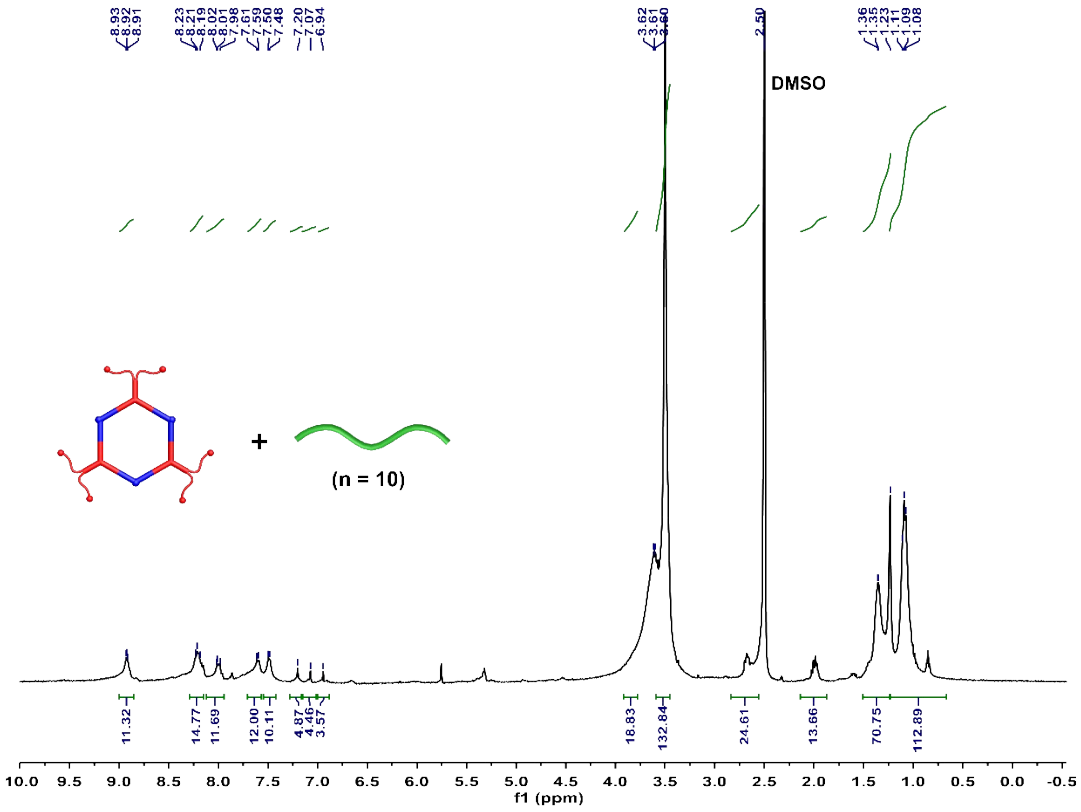


Fig. S15 ^{1}HNMR spectrum (400 MHz, DMSO-d_6, 295K) recorded for polymer **3**

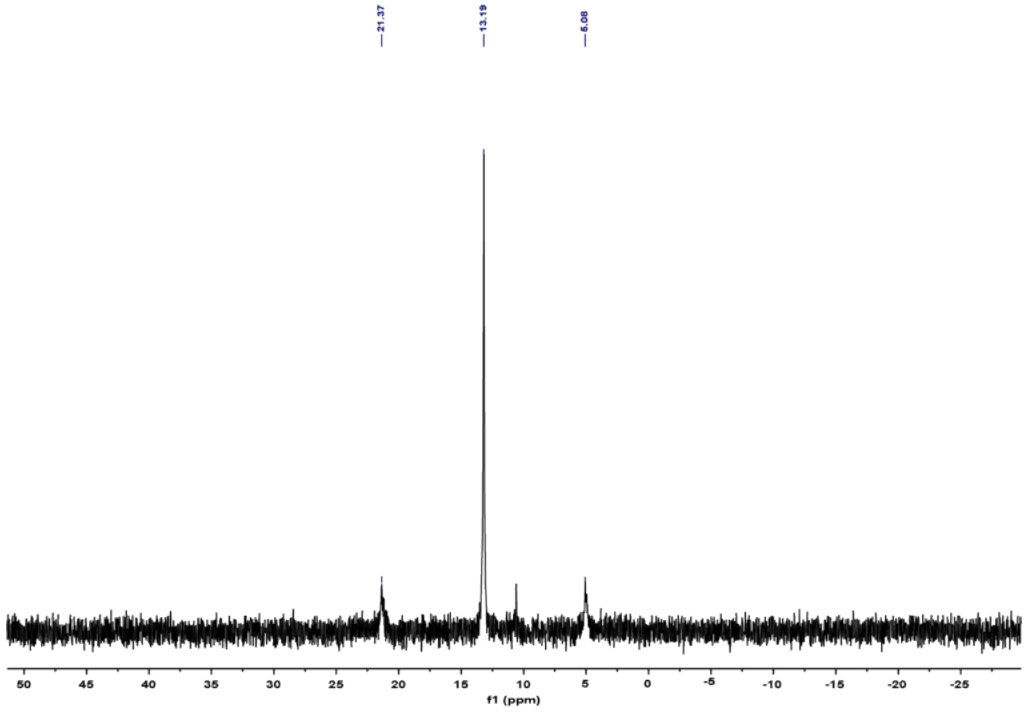


Fig. S16 Partial ^{31}P{^{1}H} NMR spectrum (162 MHz, DMSO-d_6, 295K) recorded for polymer **3**.

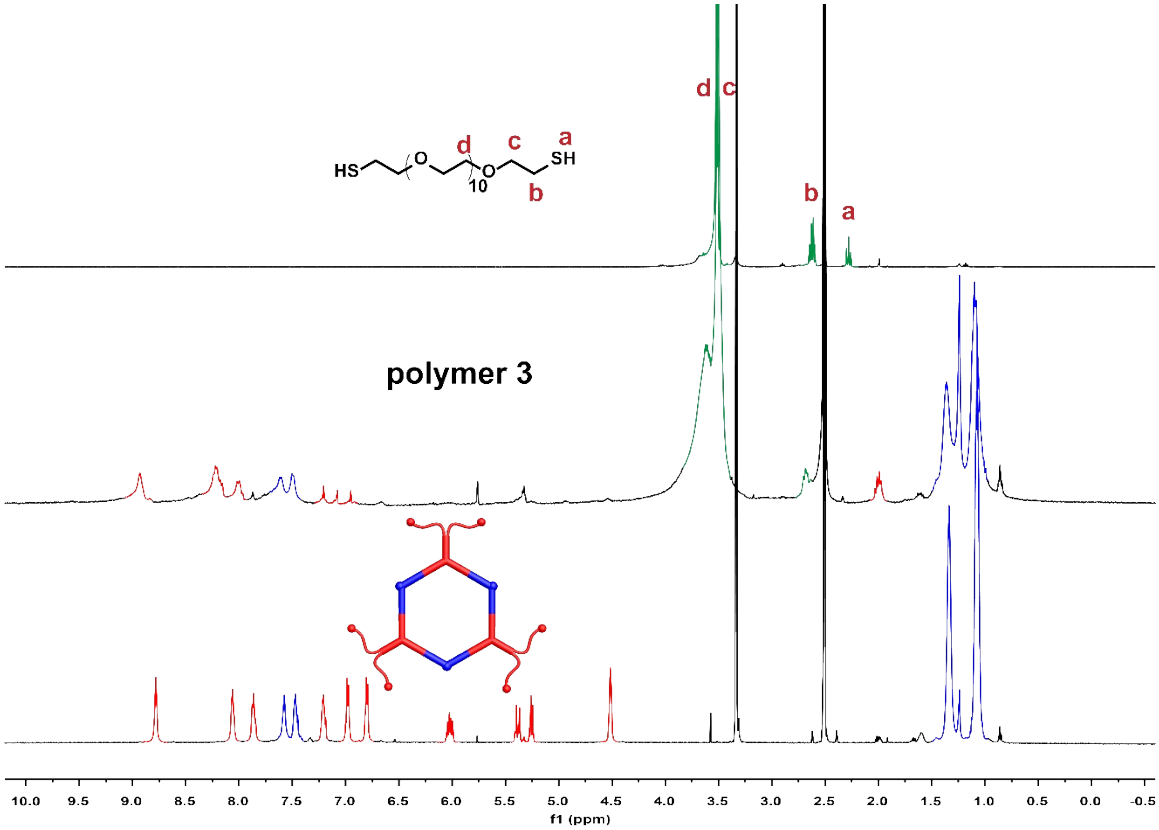
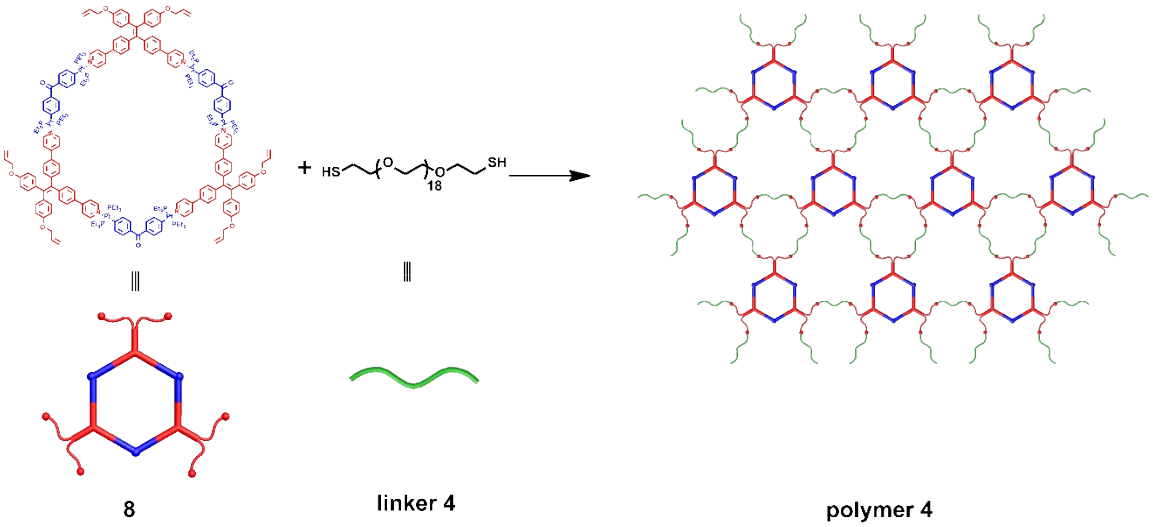


Fig. S17 ^{1}H NMR spectra (400 MHz, DMSO-d_6, 295 K) recorded for metallacycle **8** (bottom), linker **3** (top), and polymer **3** (middle).

*8. Synthesis of polymer **4***



Metallacycle **8** (13.6 mg,0.00234 mmol), linker **4** (7.01 mg, 0.701 mmol) and a catalytic amount of 2,2-dimethoxy-2-phenylacetophenone (DMPA) (1.56mg, 0.0078mmol) were added in methanol or THF (10 mL). The reaction mixture was stirred at room temperature upon the irradiation of 365nm UV light for 16 h. After the reaction, the solvent was removed and the light-yellow solid polymer **4** (18.96 mg, 92 %) was gained by recrystallization through dichloromethane/diethyl ether twice. ^{1}H NMR (400 MHz, DMSO-d_6, 295K) 8.92 (s, 13H), 8.21 (dd, J = 5.7, 2.2 Hz, 13H), 8.06–7.91 (m, 13H), 7.60 (s, 13H), 7.49 (s, 12H), 7.21 (s, 4H), 7.08 (s, 3H), 6.95 (s, 3H), 3.99–3.83 (m, 29H), 3.50 (s, 239H), 2.77–2.60 (m, 7H), 2.12–1.81 (m, 13H), 1.52–1.22 (m, 80H), 1.22–0.80 (m, 133H). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 295 K) δ (ppm): 13.19 ppm (s, ^{195}Pt satellites, $^{1}J_{Pt-P}$ = 2647.08 Hz).

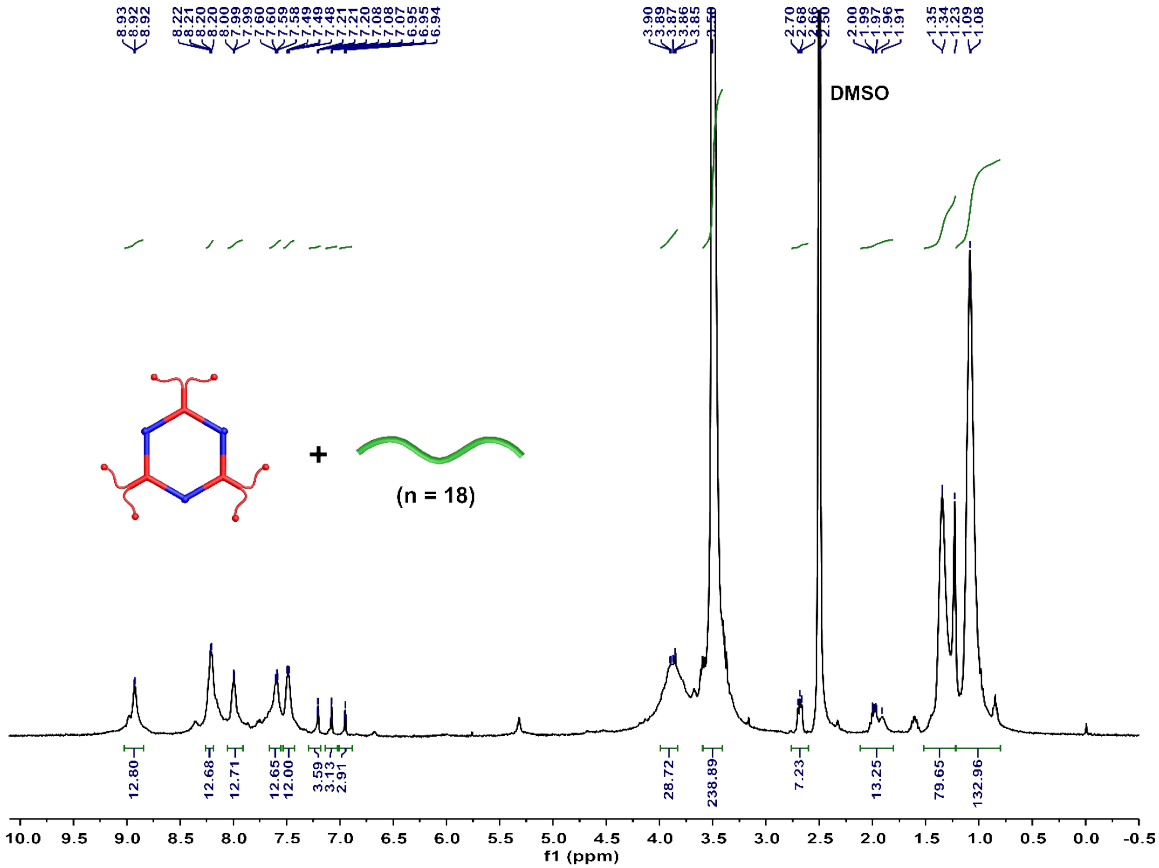


Fig. S18 ^{1}HNMR spectrum (400 MHz, DMSO-d_6, 295K) recorded for polymer **4**.

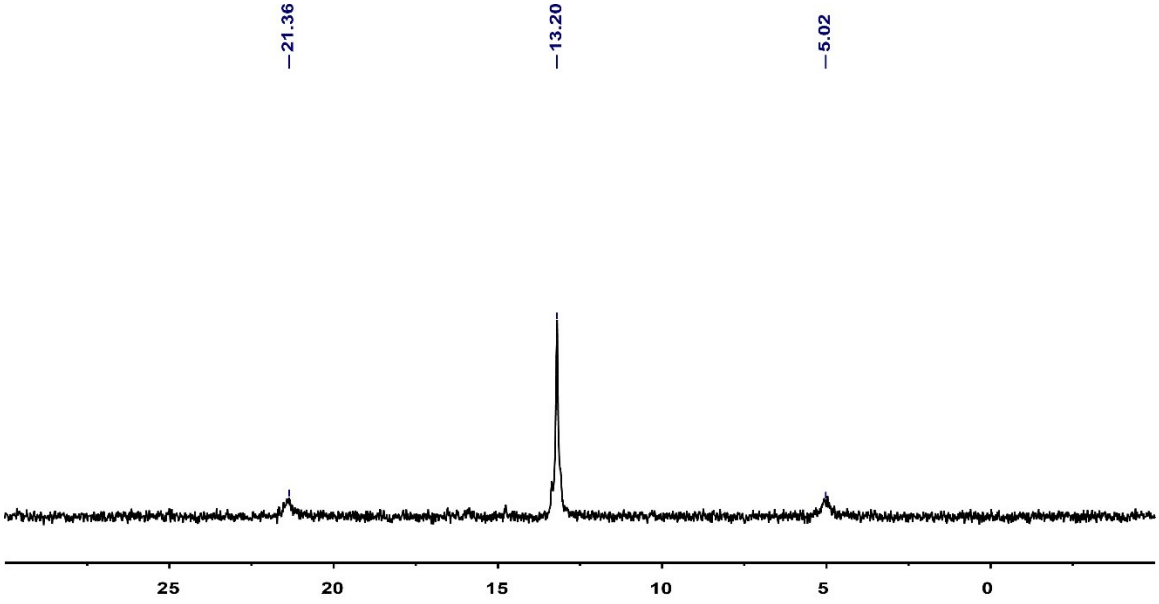


Fig. S19 Partial ^{31}P{^{1}H} NMR spectrum (162 MHz, DMSO-d_6, 295K) recorded for polymer **4**.

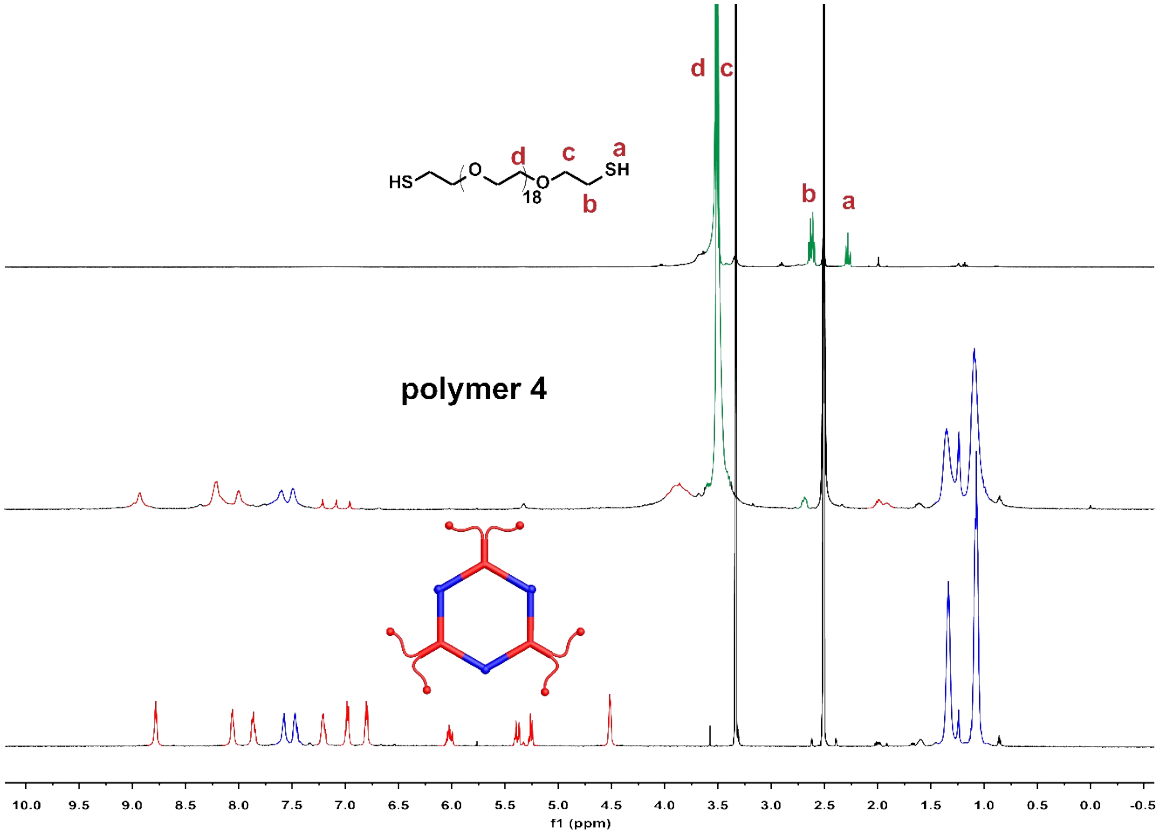


Fig. S20 ^{1}H NMR spectra (400 MHz, DMSO-d_6, 295 K) recorded for metallacycle **8** (bottom), linker **4** (top), and polymer **4** (middle).

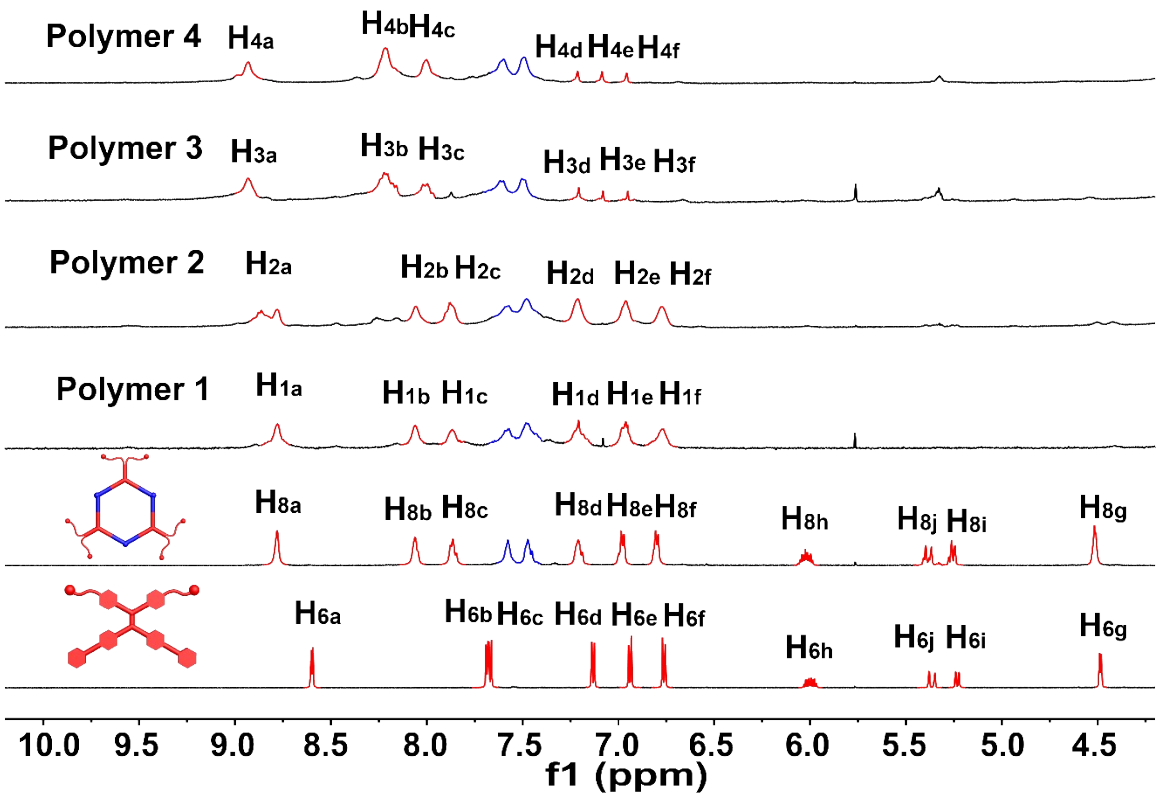


Fig. S21 Partial ^{1}H NMR spectra (DMSO-d_6, 295 K) of ligand **6**, platinum acceptor **7**, hexagonal Pt (II) metallacycle **8**, polymers **1**-**4**. The peaks for protons of ligand **6** and platinum acceptor **7** are marked in red and blue respectively.

Section C. Absorption and emission data and SEM, TEM, AFM and CLSM images

*1. UV/vis absorption and fluorescence spectra of ligand **6**, metallacycle **8**, polymers **1-4**.*

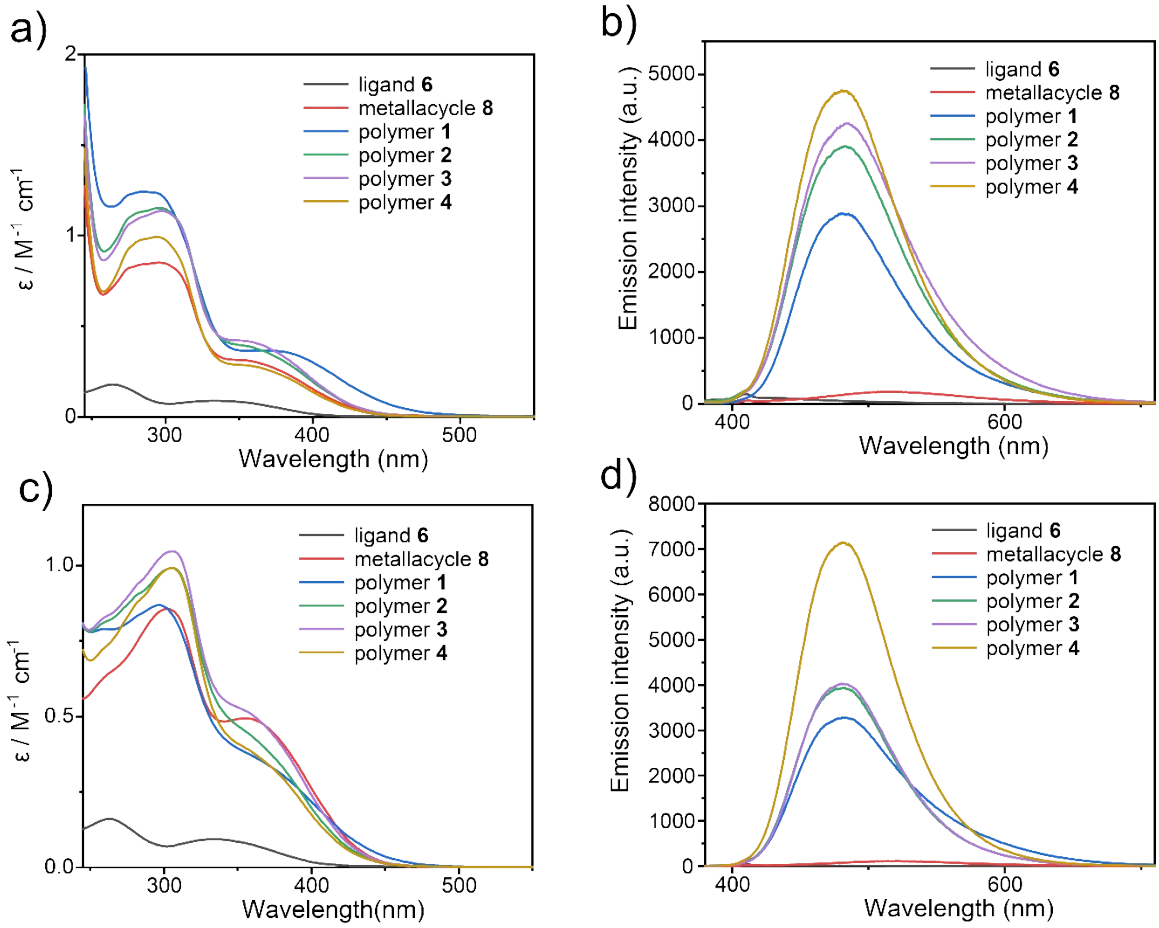


Fig. S22 (a, c) UV-Vis absorption spectra of ligand **6**, hexagonal **8**, polymers **1-4** in tetrahydrofuran and methanol, respectively. (b, d) Fluorescence spectra of ligand **6**, hexagonal **8** and polymers **1-4** in tetrahydrofuran and methanol, respectively. (λ_{ex} = 365 nm); All of the concentrations are 10.0 μmol/L; monomer concentration was used for polymers **1-4**.

*2. SEM, TEM, AFM and CLSM images of polymer **1** in methanol*

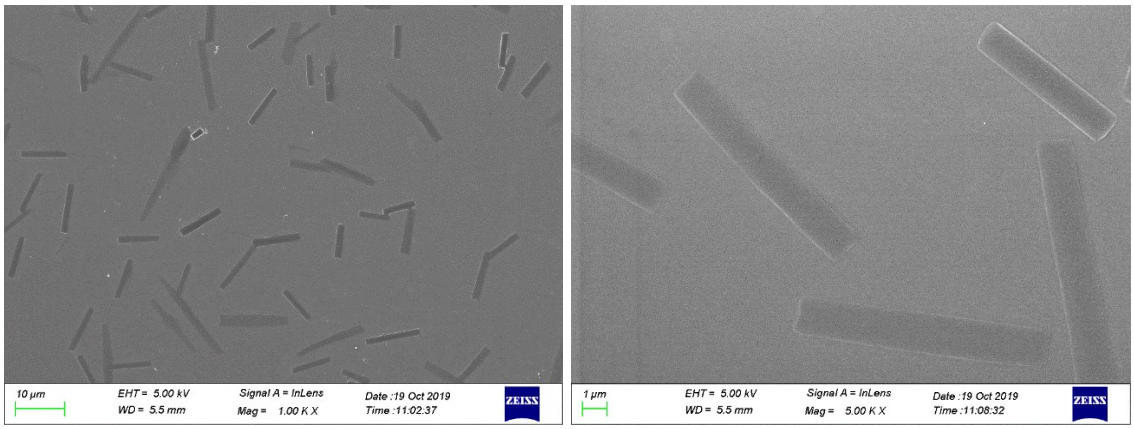


Fig. S23 SEM images of polymer **1** in methanol at the concentration of 10.0 µmol/L (monomer concentration).

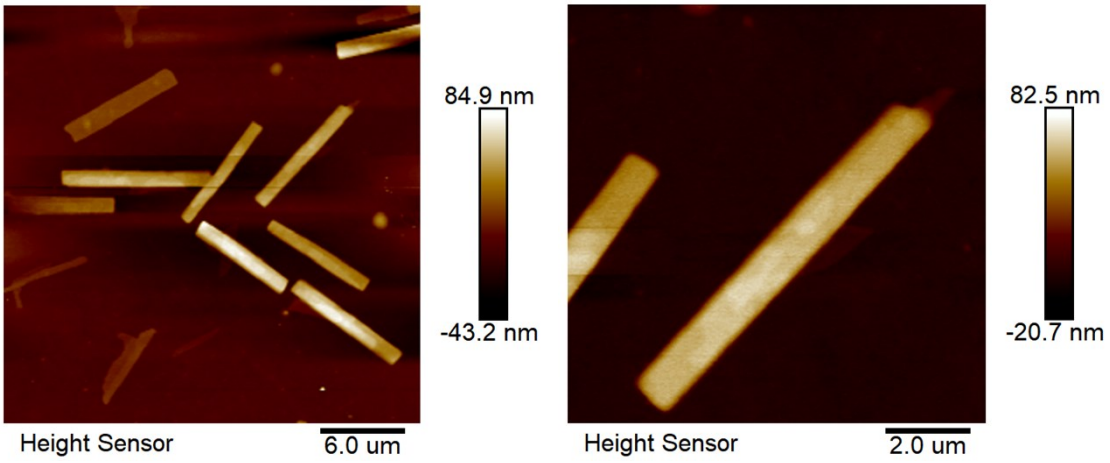


Fig. S24 AFM images of polymer **1** in methanol at the concentration of 10.0 µmol/L (monomer concentration).

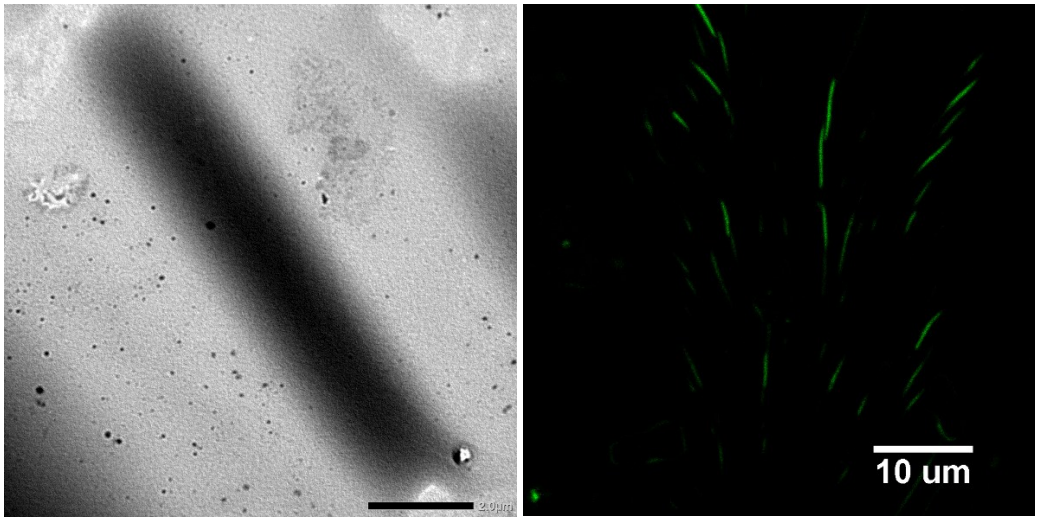


Fig. S25 TEM and LSCM (laser confocal scanning microscopy) images of polymer **1** in methanol at the concentration of 10 μmol/L (monomer concentration).

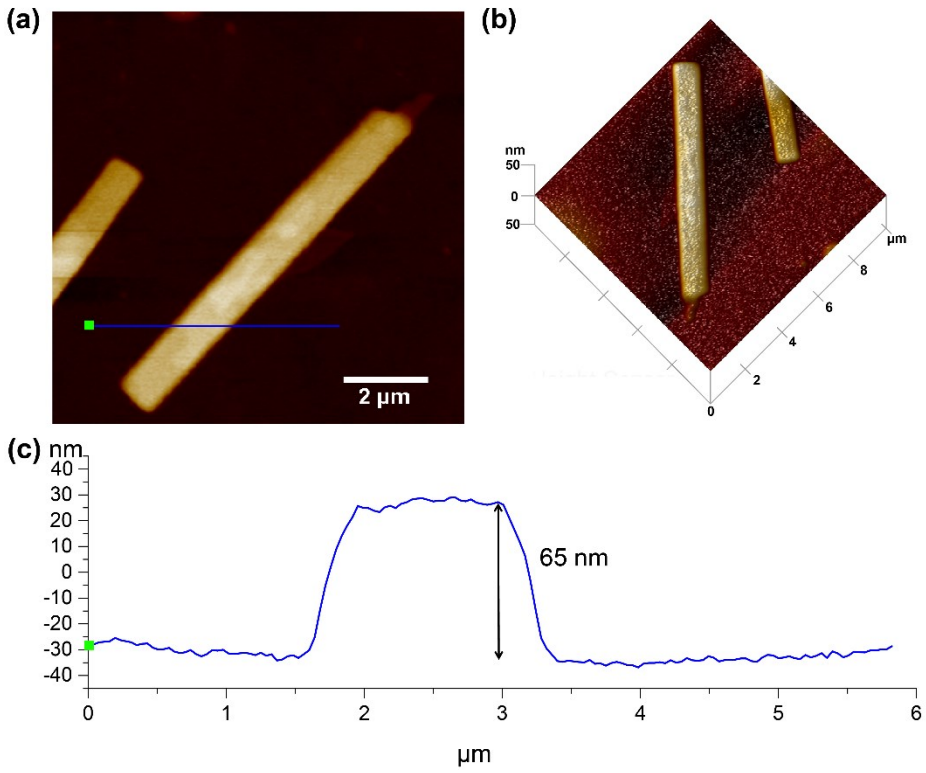


Fig. S26 AFM images of two−dimensional polymer rectangle nanosheets, (a) and (b) is two−dimensional and three−dimensional figure, respectively. (c) is the height analysis of the selected part.

*3. SEM, TEM, AFM and CLSM images of polymer **2** in methanol*

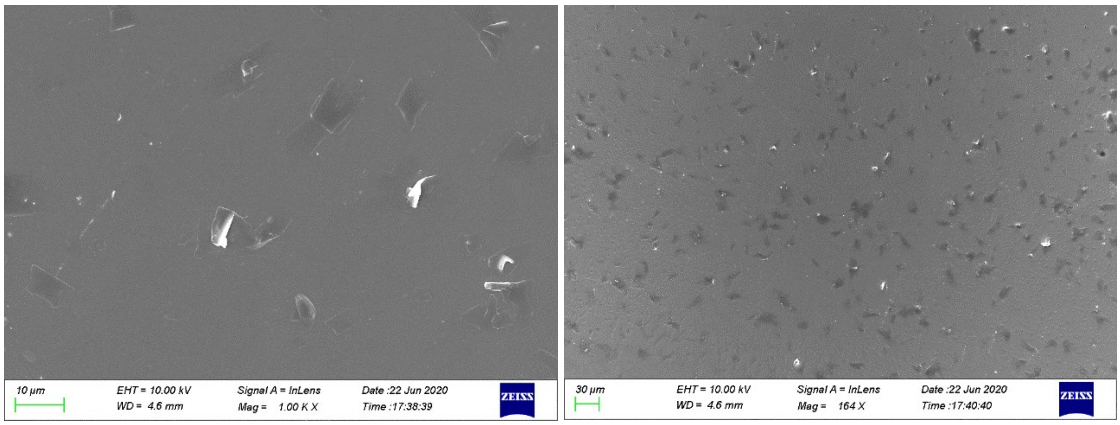


Fig. S27 SEM images of polymer **2** in methanol at the concentration of 10 μmol/L (monomer concentration).

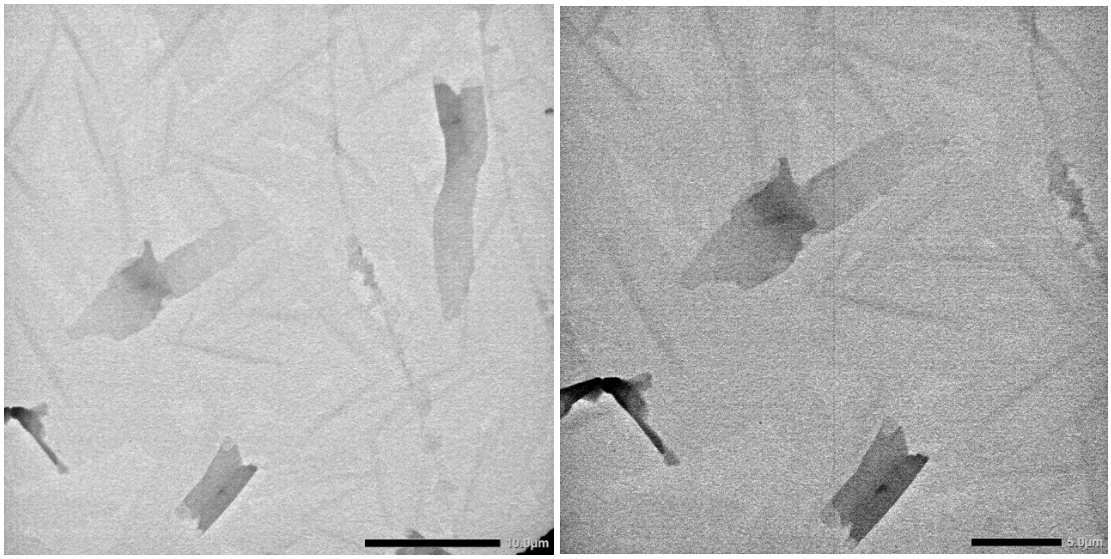


Fig. S28 TEM images of polymer **2** in methanol at the concentration of 10 μmol/L (monomer concentration).

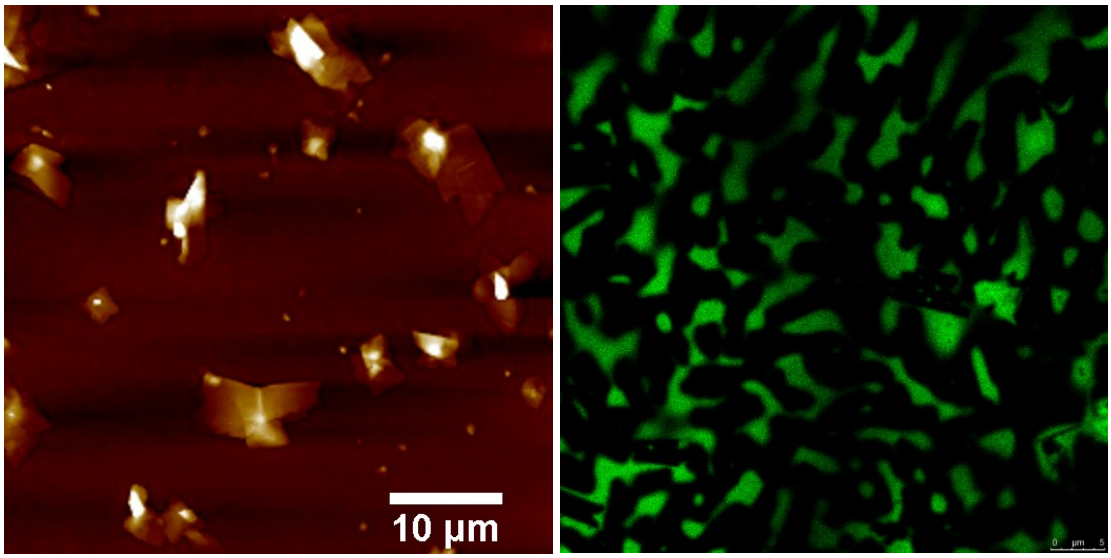


Fig. S29 AFM and CLSM (confocal laser scanning microscopy) images of polymer **2** in methanol at the concentration of 10 µmol/L (monomer concentration).

*4. SEM, TEM, AFM and CLSM images of polymer **3** in methanol*

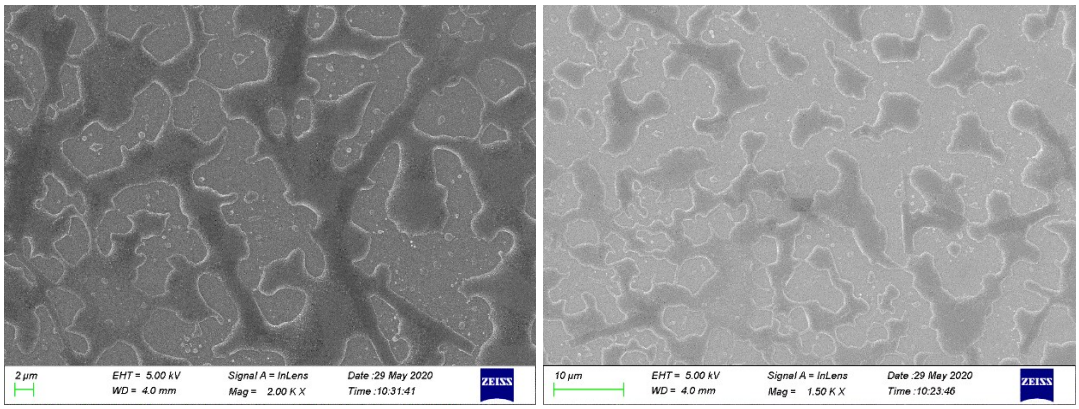


Fig. S30 SEM images of polymer **3** in methanol at the concentration of 10 µmol/L (monomer concentration).

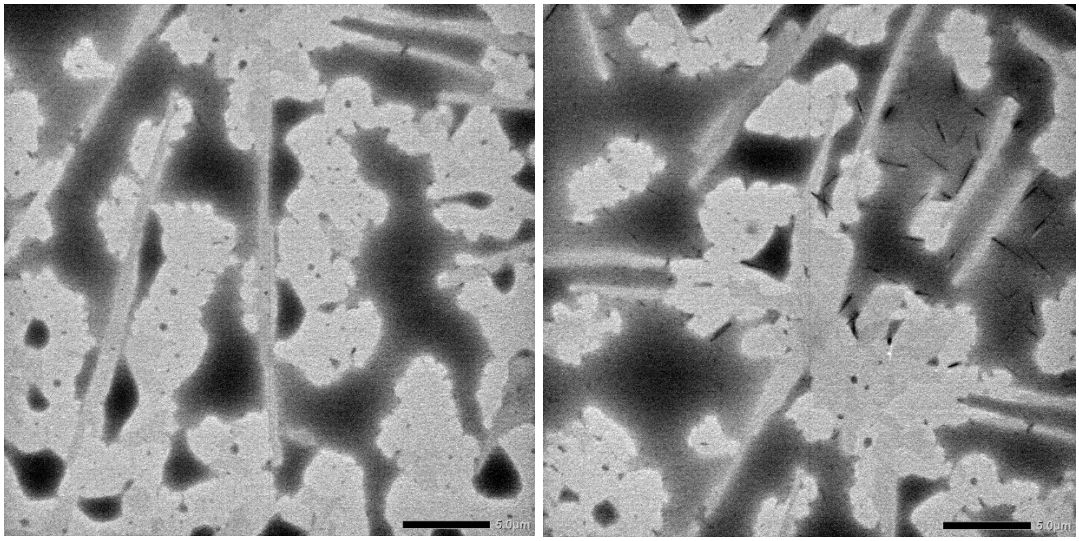


Fig. S31 TEM images of polymer **3** in methanol at the concentration of 10 μmol/L (monomer concentration).

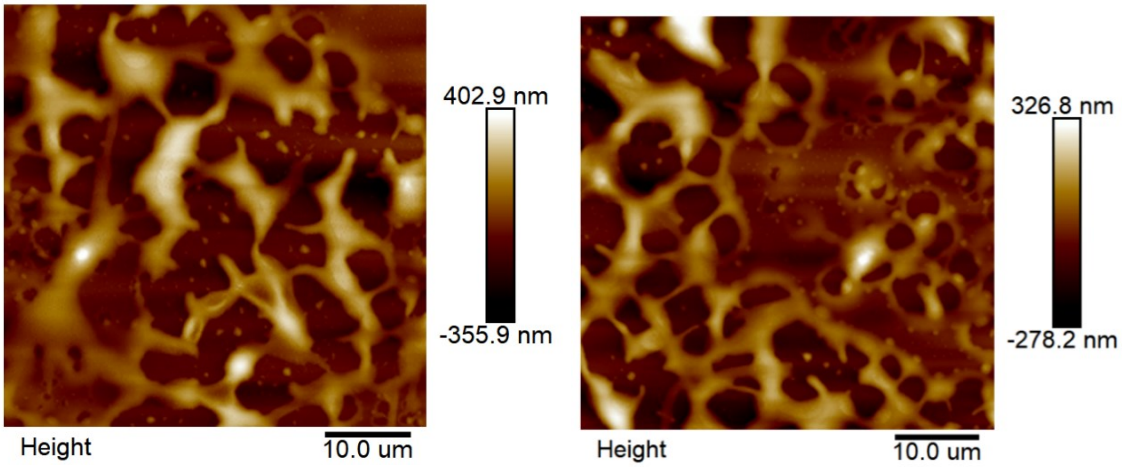


Fig. S32 AFM images of polymer **3** in methanol at the concentration of 10 μmol/L (monomer concentration).

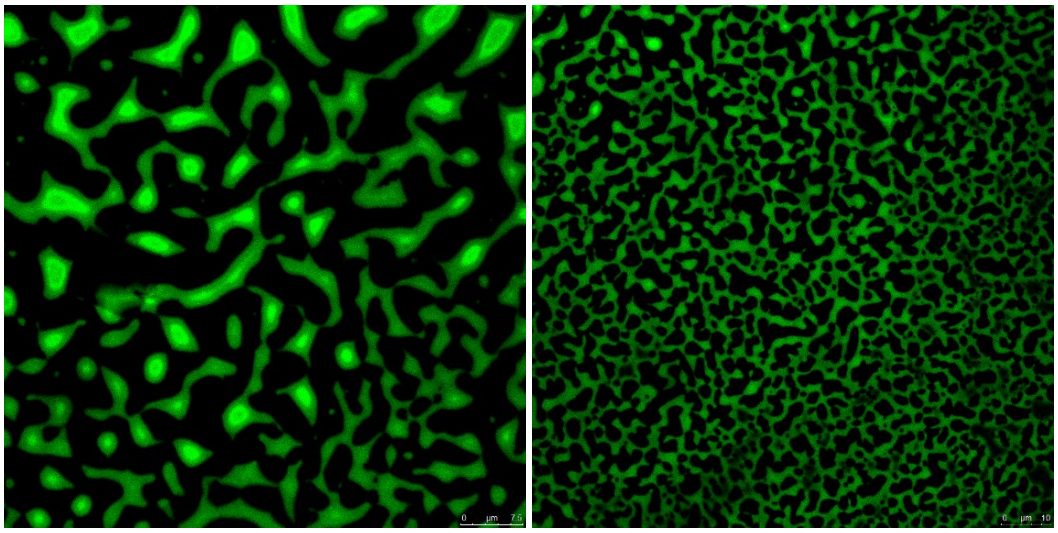


Fig. S33 CLSM (confocal laser scanning microscopy) images of polymer **3** in methanol at the concentration of 10 μmol/L (monomer concentration).

*5. SEM, TEM, AFM and CLSM images of polymer **4** in methanol*

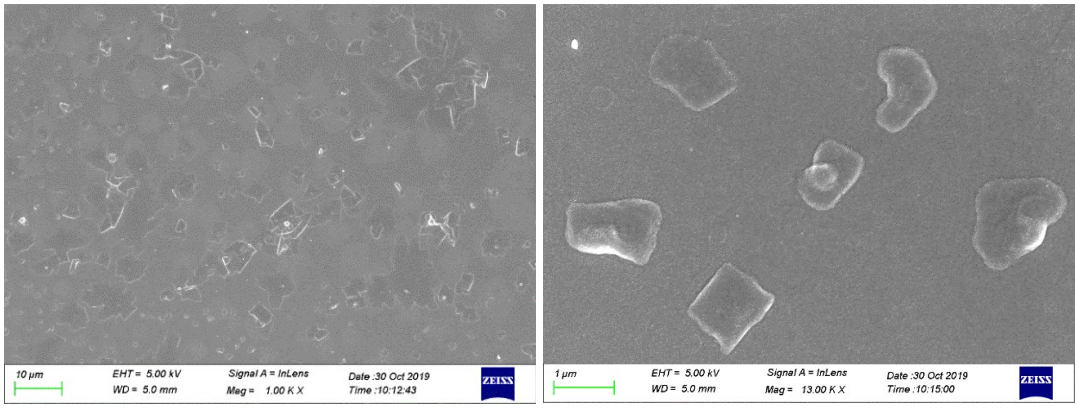


Fig. S34 SEM images of polymer **4** in methanol at the concentration of 10 μmol/L (monomer concentration).

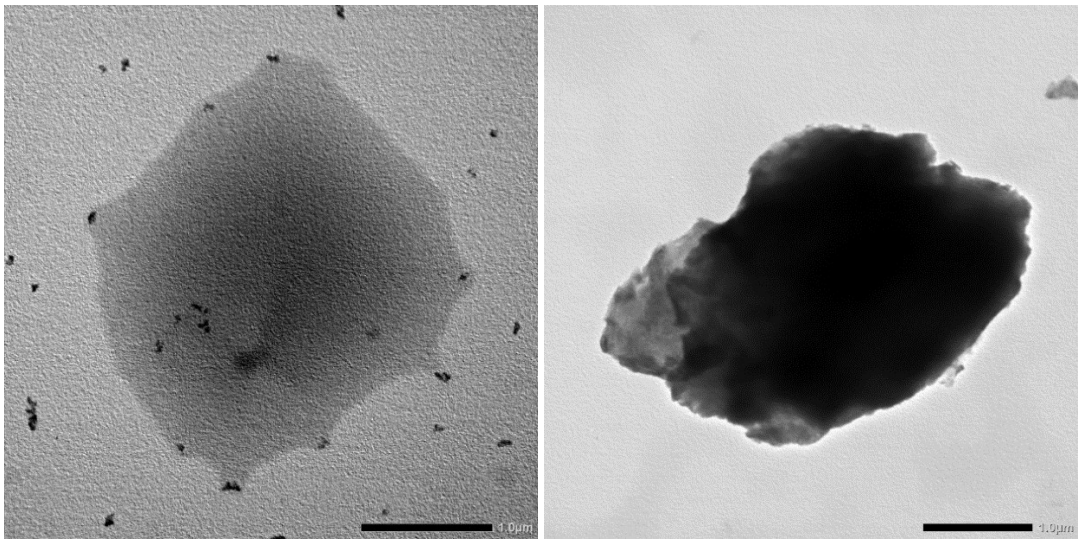


Fig. S35 TEM images of polymer **4** in methanol at the concentration of 10 μmol/L (monomer concentration).

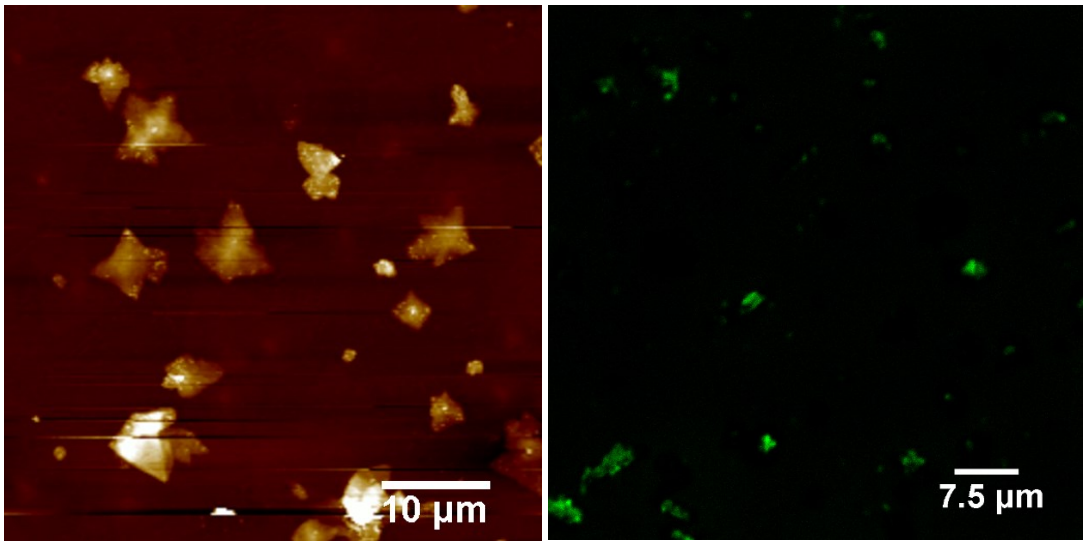


Fig. S36 AFM and CLSM (confocal laser scanning microscopy) images of polymer **4** in methanol at the concentration of 10 μmol/L (monomer concentration).

*6. SEM, TEM, AFM and CLSM images of polymer **1** in THF*

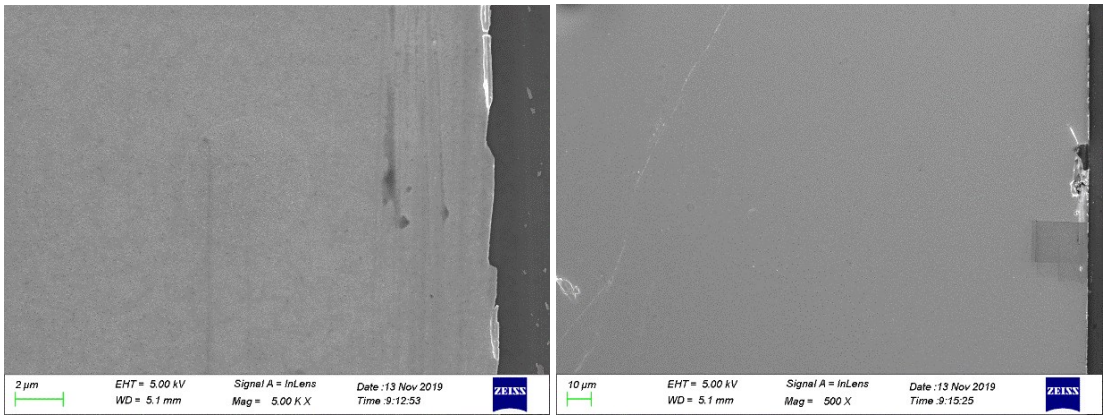


Fig. S37 SEM images of polymer **1** in THF at the concentration of 20 μmol/L (monomer concentration).

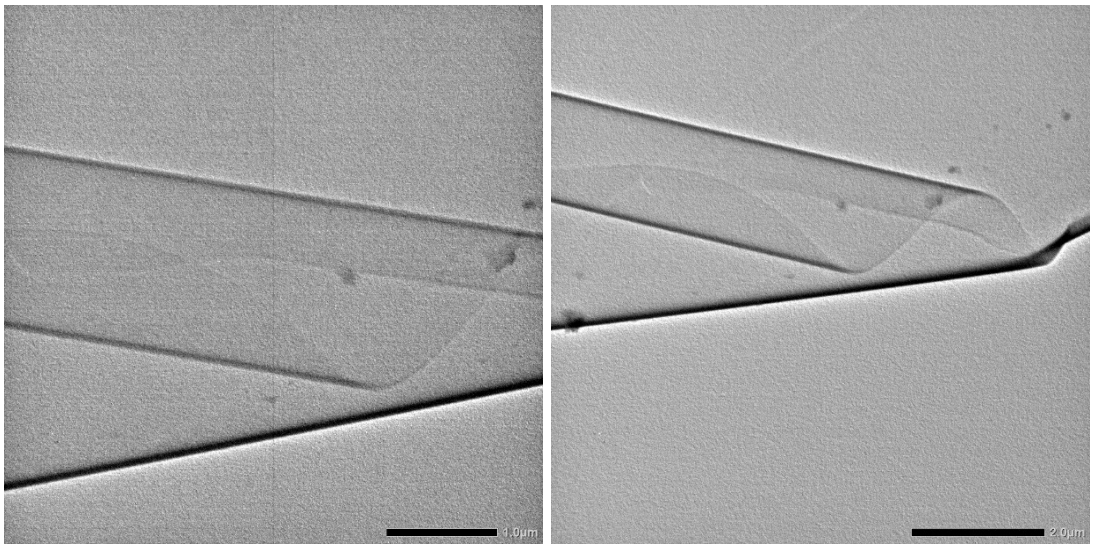


Fig. S38 TEM images of polymer **1** in THF at the concentration of 20 μmol/L (monomer concentration).

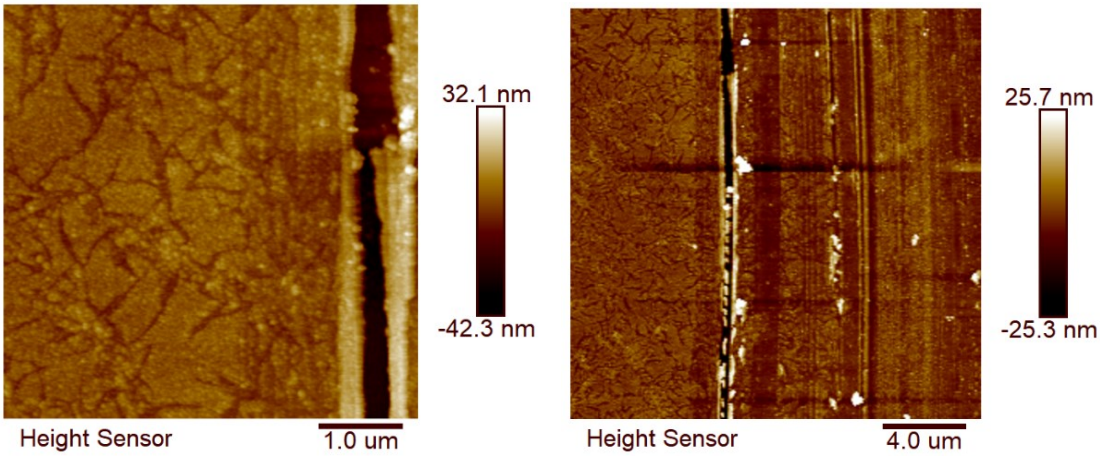


Fig. S39 AFM images of polymer **1** in THF at the concentration of 20 μmol/L (monomer concentration).

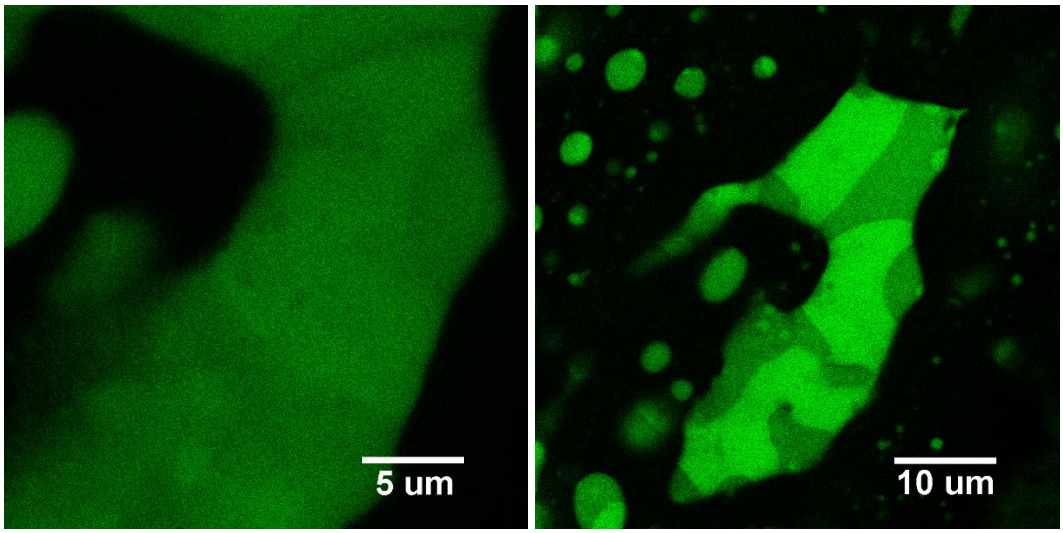


Fig. S40 CLSM (confocal laser scanning microscopy) images of polymer **1** in THF at the concentration of 20 μmol/L (monomer concentration).

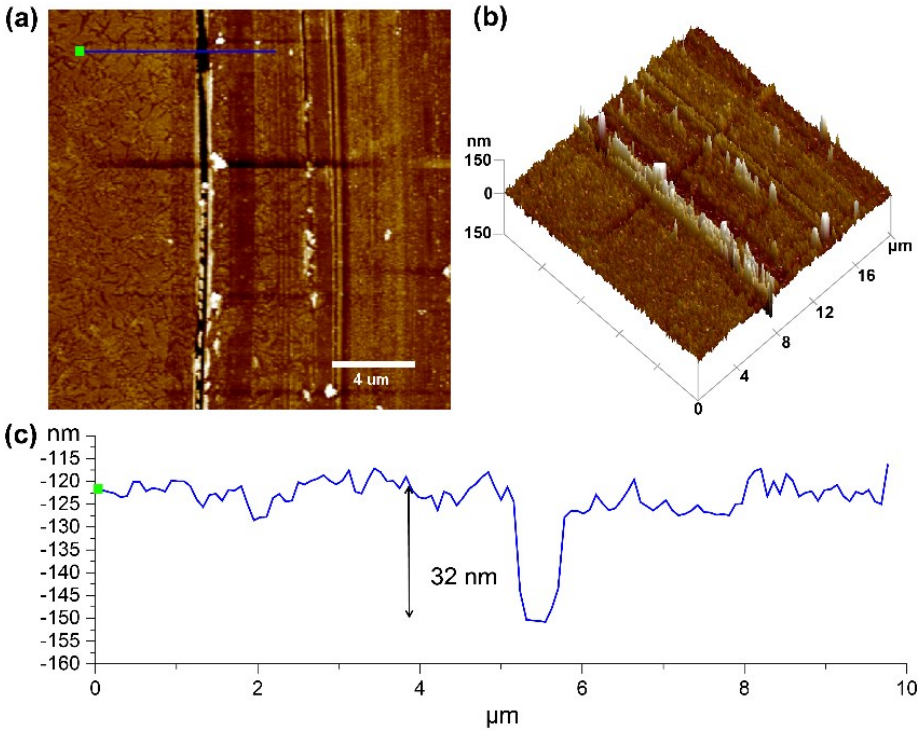


Fig. S41 AFM images of two−dimensional polymer films (a) and (b) is two−dimensional and three−dimensional figure, respectively. (c) is the height analysis of the selected part.

*7. SEM, TEM, AFM and CLSM images of polymer **2** in THF*

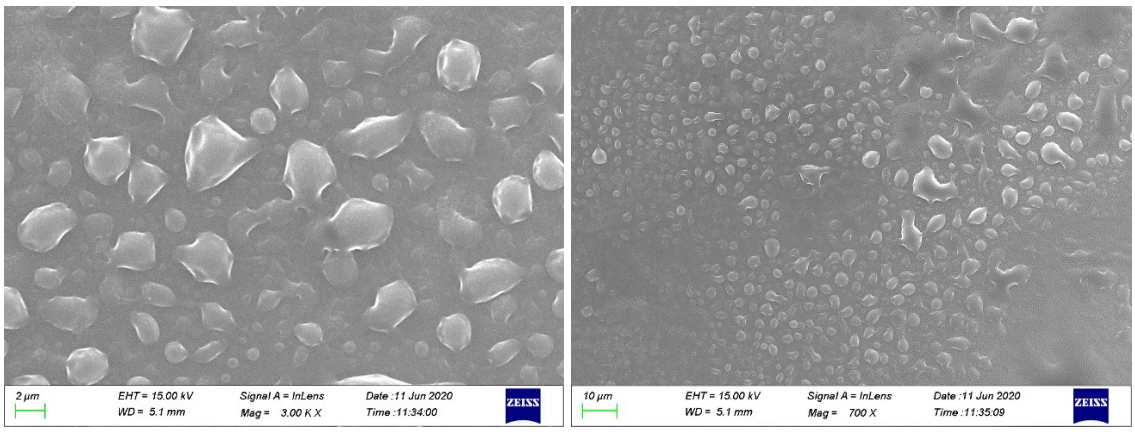


Fig. S42 SEM images of polymer **2** in THF at the concentration of 10 μmol/L (monomer concentration).

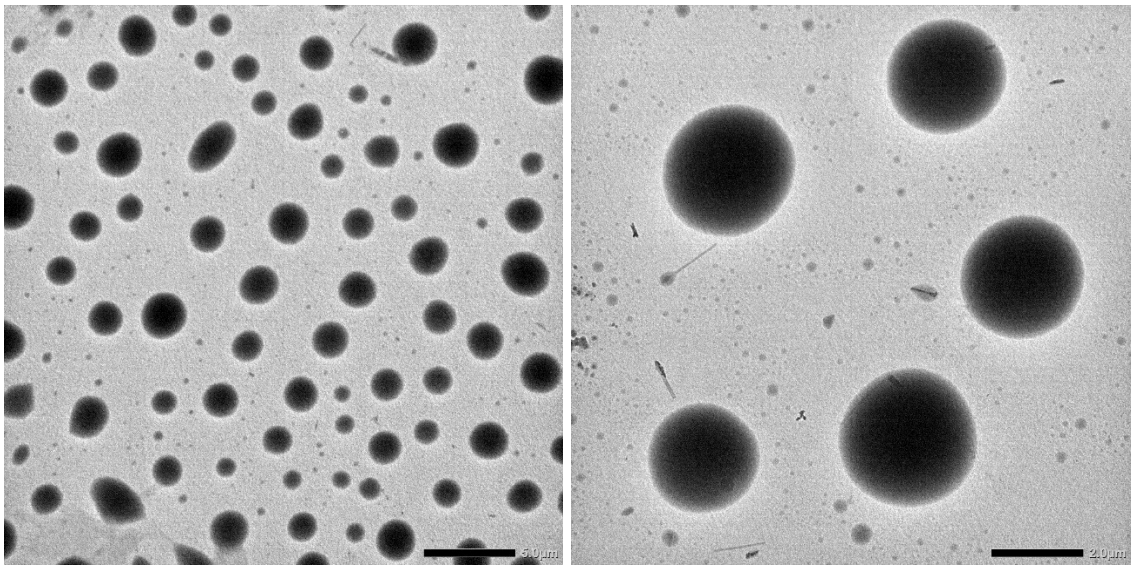


Fig. S43 TEM images of polymer **2** in THF at the concentration of 10 μmol/L (monomer concentration).

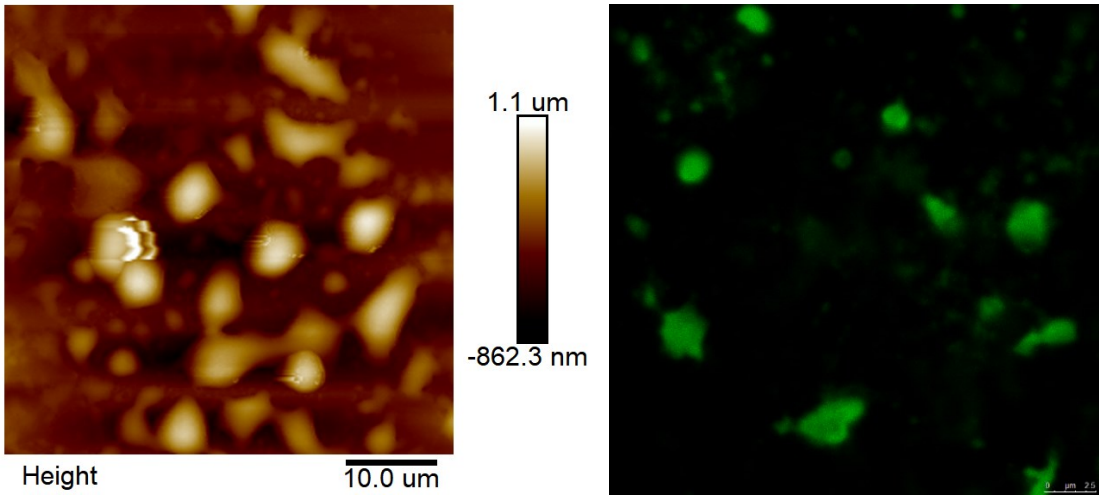


Fig. S44 AFM and CLSM (confocal laser scanning microscopy) images of polymer **2** in THF at the concentration of 10 μmol/L (monomer concentration).

*8. SEM, TEM, AFM and CLSM images of polymer **3** in THF*

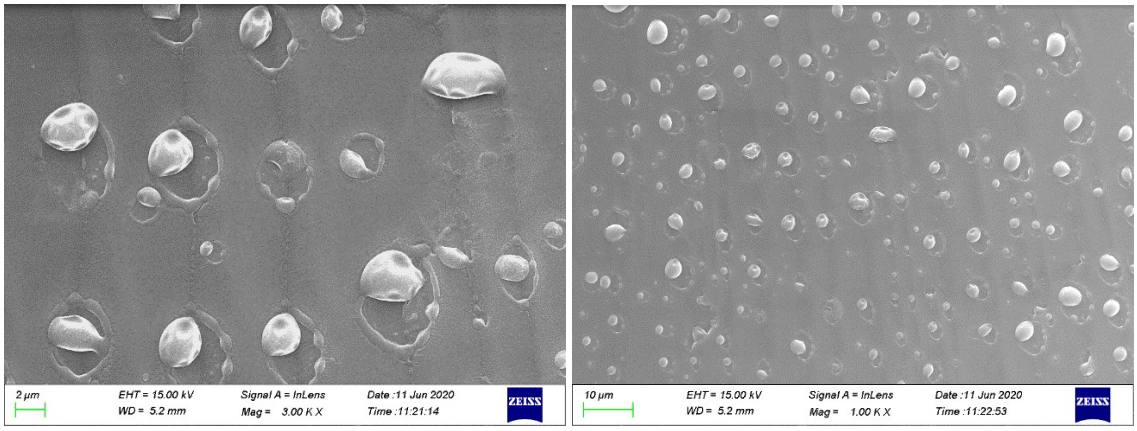


Fig. S45 SEM images of polymer **3** in THF at the concentration of 10 μmol/L (monomer concentration).

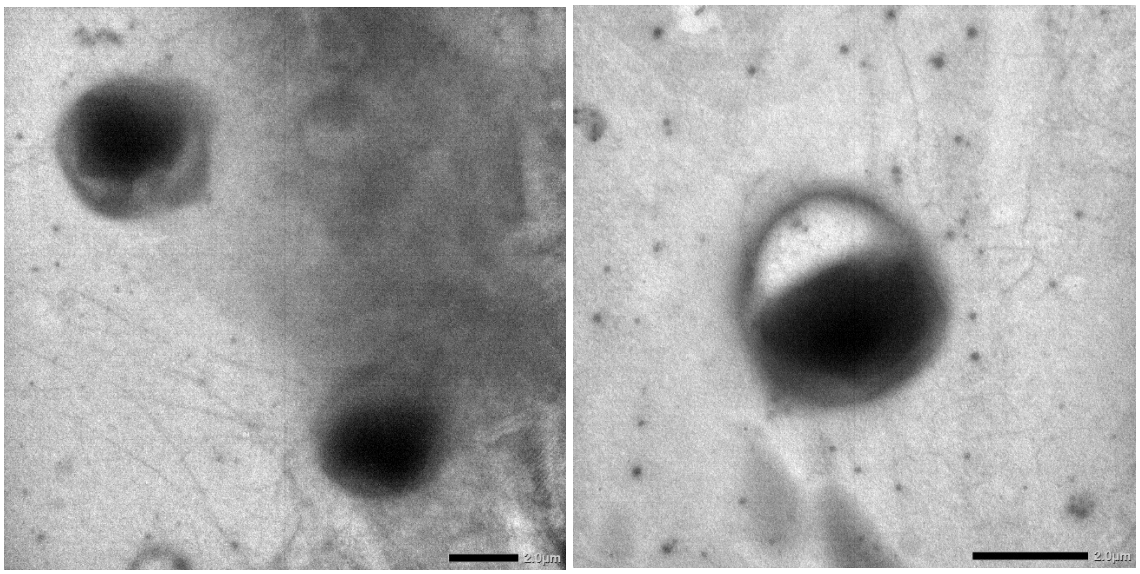


Fig. S46 TEM images of polymer **3** in THF at the concentration of 10 μmol/L (monomer concentration).

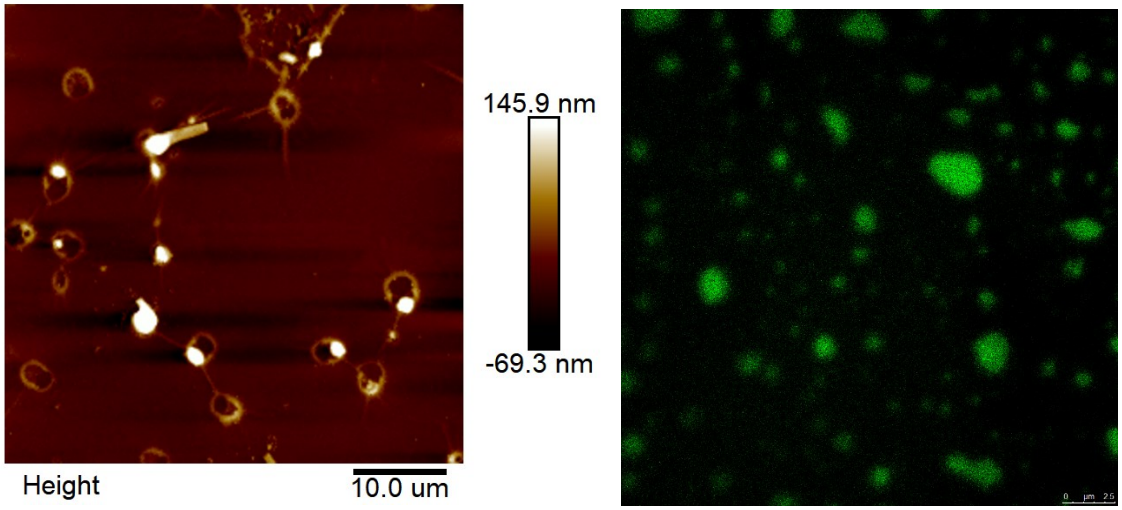


Fig. S47 AFM and CLSM (confocal laser scanning microscopy) images of polymer **3** in THF at the concentration of 10 μmol/L (monomer concentration).

*9. SEM, TEM, AFM and CLSM images of polymer **4** in THF*

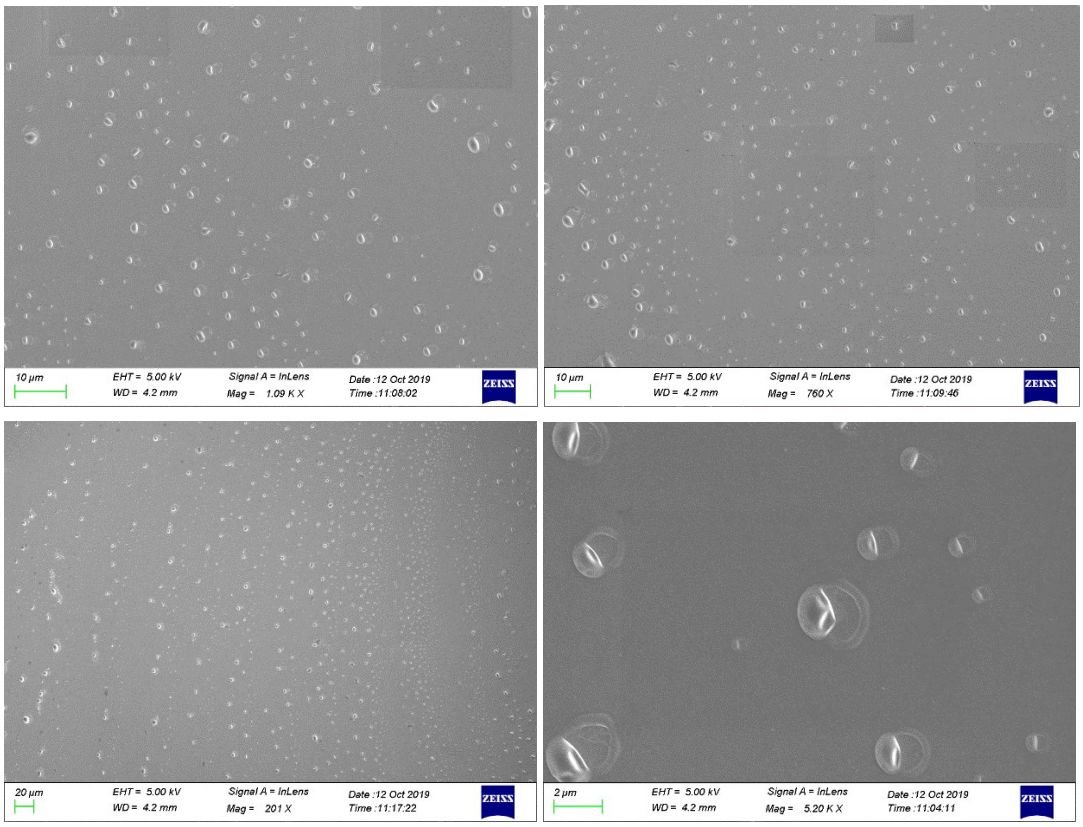


Fig. S48 SEM images of polymer **4** in THF at the concentration of 10 μmol/L (monomer concentration).

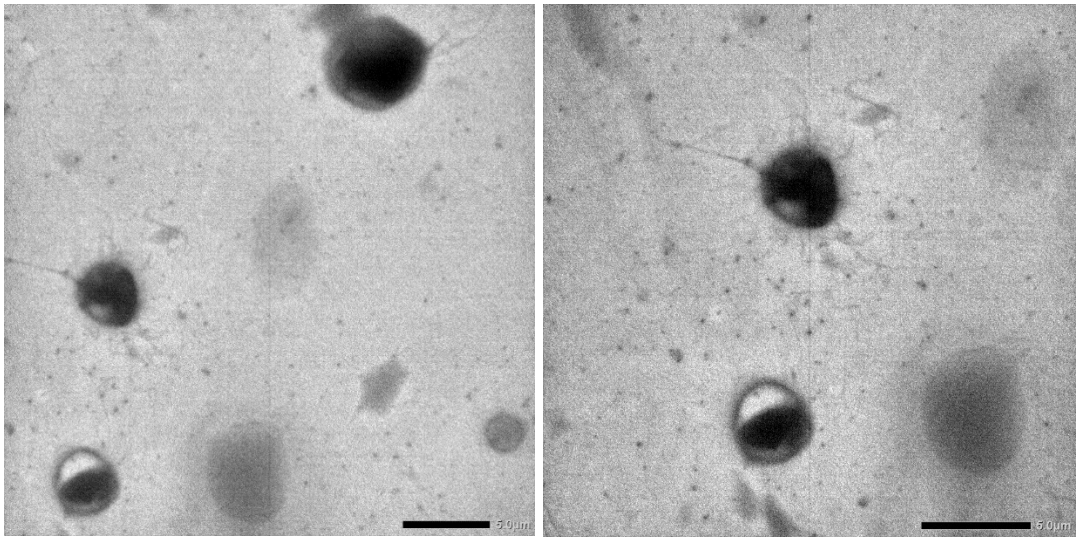


Fig. S49 TEM images of polymer **4** in THF at the concentration of 10 μmol/L (monomer concentration).

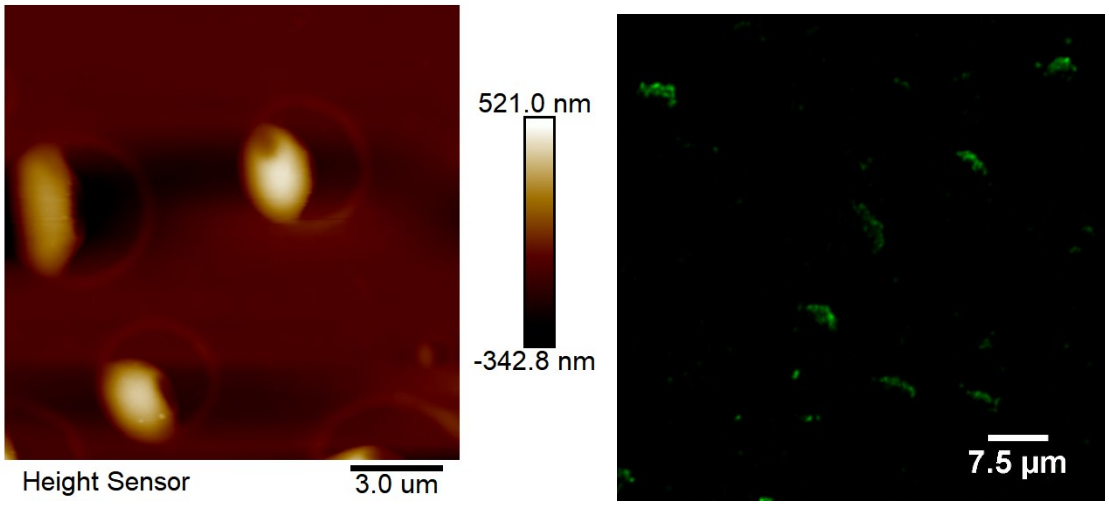


Fig. S50 AFM and CLSM (confocal laser scanning microscopy) images of polymer **4** in THF at the concentration of 10 μmol/L (monomer concentration).

Section D. References

1. Y. Fu, J. Yao, W. Xu, T. Fan, Q. He, D. Zhu, H. Cao and J. Cheng, *Polym. Chem*., 2015, **6**, 2179.

2. H.-B. Yang, K. Ghosh, B. H. Northrop, Y.-R. Zheng, M. M. Lyndon, D. C. Muddiman and P. J. Stang, *J. Am. Chem. Soc*., 2007, **129**, 14187.