

## **Supramolecular polymerization based on metalation of porphyrin nanosheets in aqueous media**

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## Materials and method

Unless otherwise noted, reagents and solvents were purchased from commercial suppliers without further purification. Air- and/or water-sensitive reactions were conducted under argon atmosphere using dry solvents. Compound **3**<sup>1</sup> was synthesized according to reported procedures. The 5,10,15,20-tetrakis(4-hydroxyphenyl)-21*H*,23*H*-porphyrin (compound **S1**) was purchased from Aldrich.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DX 300, Bruker DX 500 (300 MHz, 500 MHz) spectrometer. All chemical shifts are reported in parts per million (ppm) from tetramethylsilane (0 ppm for <sup>1</sup>H) or residual CHCl<sub>3</sub> (77 ppm for <sup>13</sup>C) as an internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained using a Bruker (autoflex maX). Ultraviolet-visible absorption spectra were recorded using a quartz cuvette of 1.0 or 0.2 cm path length on a Jasco V-750 spectrophotometer equipped with a Jasco ETCS-761 cell holder for temperature control. Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer Nano Zs instrument. Atomic force microscopy (AFM) was performed on a XE-100 and a PPP-NCHR 10 M cantilever (Park systems) atomic force microscope under ambient conditions in the scan assist analysis. AFM images were analyzed with ImageJ.

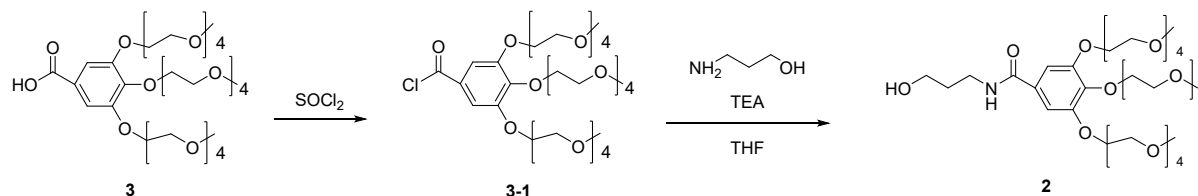
**Preparation of seeds.** The seeds were prepared by applying sonication to aqueous solution of **1**<sub>Zn</sub> at low temperature. The **1**<sub>Zn</sub> seed was obtained via sonication at 5 °C for 10 min (3 ml, 20 μM). By applying sonication, SPs fragmented into short pieces with relatively narrow area distribution were obtained, which was confirmed through analysis of AFM images, as shown in figure 5 and Figure S18.

**Extended Nanosheets.** The nanosheets **1**<sub>Zn</sub> was synthesized via seeded growth living CDSA method. The solution of **1**<sub>Zn</sub> seed was carefully placed on top of solution of **1**<sub>Free</sub> in quartz cuvette, these solutions were mixed in seed/nanoparticles ratios of 1:1, 1:2 and 1:3, respectively. The mixture was shaken for few second and then aged for 24h at 55°C under stirring at 400 rpm. The resulting solutions were spin coated on a Mica substrate for AFM observation to confirmed that *A<sub>n</sub>* is proportional to the [nanoparticles]/ [seed] ratio, as shown in Figure 5(i-iv), and Figure S18.

**Preparation of AFM samples.** 15 μL of the solution was used for spin casting samples on the substrates (MICA and HOPG) using spin coater. The coating duration was 30 second at 500 RPM and 2 min at 2000 RPM.

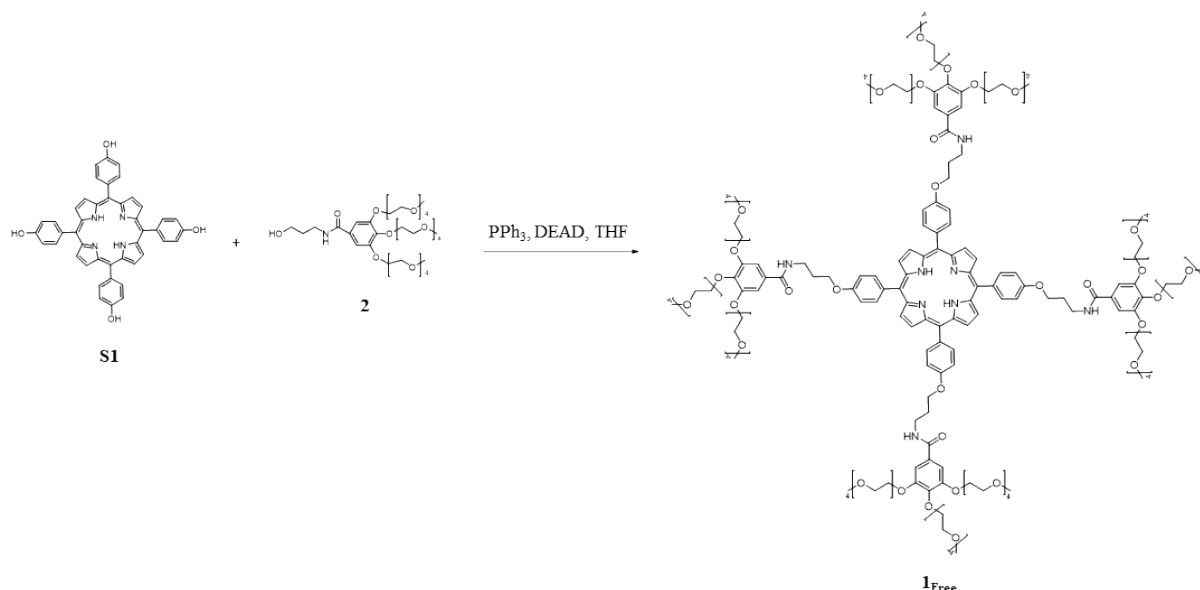
## Synthesis and characterization

### Synthesis of **2**



Compound **3** (4 g, 5.4mmol) was dissolved in Thionyl chloride (about 5mL) and stirred for 5h in room temperature to get **3-1**. Compound **3-1**(4g, 5.27mmol) in dry tetrahydrofuran (THF) (20mL) was added dropwise to a solution of 3-amino-1-propanol (0.5mL, 5.68mmol) and triethylamine (1mL, 6.48mmol) in dry THF (30mL) at 0 °C under an argon atmosphere. The mixture was stirred for overnight, and then the reaction mixture was added  $\text{NaHCO}_3$  and extracted with chloroform. The solvent was evaporated, the liquid material was purified through column chromatography ( $\text{SiO}_2$ ;  $\text{CHCl}_3/\text{MeOH}$ , from 1:0 to 10:1 in volume) to yield compound **2** yellow liquid (3.23g, 75%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.73 (2H, m,  $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ ), 3.31 (9H, t), 3.48 (4H, m,  $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ ), 3.65 (36H, m,  $\text{CH}_3-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_3-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 3.78 (6H, m,  $\text{CH}_3-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_3-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 4.15 (6H, m,  $\text{CH}_3-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_3-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 7.10 (2H, s, phenyl-H), 7.33(1H, m, NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.32, 151.96, 141.06, 128.94, 106.99, 71.91, 71.50, 71.46, 70.21, 70.17, 70.13, 70.06, 69.28, 63.63, 59.41, 58.59, 58.56, 36.93, 31.53. ESI-MS  $\text{C}_{37}\text{H}_{67}\text{NO}_{17}$   $[\text{M}+\text{Na}]^+$ :  $m/z = 797.411$ ; found : 820.67.

## Synthesis of **1<sub>Free</sub>**

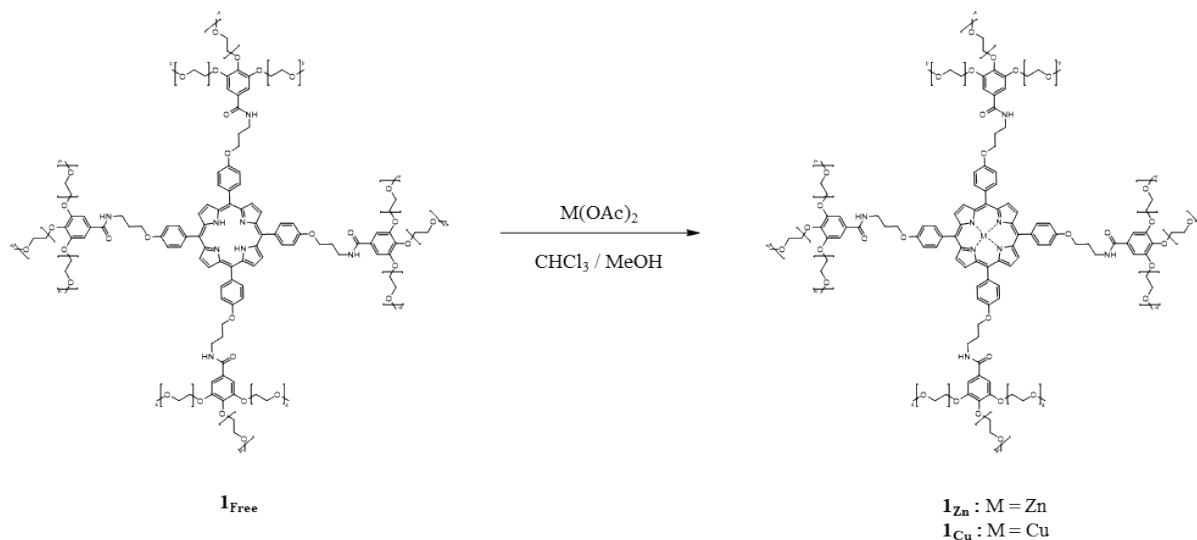


Compound **S1** (100mg, 0.147mmol), Compound **2** (10eq, 1.17g, 1.47mmol) and  $\text{PPh}_3$  (10eq, 358mg, 1.47mmol) were dissolved in THF (3mL). Diethyl azodicarboxylate (DEAD) (534 $\mu\text{L}$  of 40wt% toluene solution: 0.8mmol) was slowly added to the solution at 0 °C. The reaction mixture was stirred at 50 °C for 24h under an argon atmosphere. After cooling to room temperature, the reaction mixture was evaporated and the resultant residue was purified through column chromatography ( $\text{SiO}_2$ ,  $\text{CHCl}_3/\text{MeOH}$ , 1:0 to 10:1 volume) and SEC (bio-beads S-X1, DCM,  $\phi$  22 mm  $\times$  100 cm) to yield Compound **1<sub>Free</sub>** as purple waxy solid (156 mg, 28%).

Anal. calcd. for  $\text{C}_{192}\text{H}_{290}\text{N}_8\text{O}_{68}$ : C, 60.71; H, 7.70; N, 2.95. Found: C, 61.71; H, 7.72; N, 2.90.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  -2.76 (2H, s, NH), 1.25 (8H, d,  $J = 4.4$  Hz, -NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-), 2.34 (8H, m, -NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-), 3.34 (36H, d,  $J = 10.3$  Hz, CH<sub>3</sub>-), 3.44-3.69 (144H, m, CH<sub>3</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-), 3.78-3.85 (24H, m, CH<sub>3</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.19-4.26 (24H, m, CH<sub>3</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.41 (8H, t,  $J = 5.8$  Hz, -NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-) 6.97 (4H, t,  $J = 5.6$  Hz, -NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-), 7.20 (8H, s, C<sub>6</sub>H<sub>2</sub>), 7.30 (8H, d,  $J = 8.6$  Hz, phenyl-H), 8.13 (8H, d,  $J = 8.6$  Hz, phenyl-H), 8.84 (8H, s,  $\beta$ -pyrrole-H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.96, 158.36, 152.23, 141.18, 135.40, 134.51, 129.64, 119.47, 112.52, 107.20, 72.14, 71.64, 71.59, 70.38, 70.35, 70.32, 70.29, 70.27, 70.23, 70.20, 70.18, 70.13, 69.50, 68.86, 66.38, 58.71, 37.82, 29.20, 0.80. MALDI-TOF mass ( $\alpha$ -Cyano-4-hydroxycinnamic acid): calcd. for  $\text{C}_{192}\text{H}_{290}\text{N}_8\text{O}_{68} [\text{M}]^+$ :  $m/z = 3797.955$ ; found: 3797.1853.

## Synthesis of **1<sub>Zn</sub>** and **1<sub>Cu</sub>**

### Synthesis of **1<sub>Zn</sub>**



To a  $\text{CHCl}_3$  solution (2mL) of compound **1<sub>Free</sub>** (50mg, 0.013mmol),  $\text{Zn(OAc)}_2$  (10eq, 24mg, 0.13mmol) in MeOH (1mL) was added, and the mixture was stirred for 3 h at 50 °C under an argon atmosphere. After cooling to room temperature, the solvents were evaporated, and the resultant residue was purified through column chromatography ( $\text{SiO}_2$ ,  $\text{CHCl}_3/\text{MeOH}$ , 1:0 to 10:1 volume) to yield compound **1<sub>Zn</sub>** as purple waxy solid (46mg, 90%).

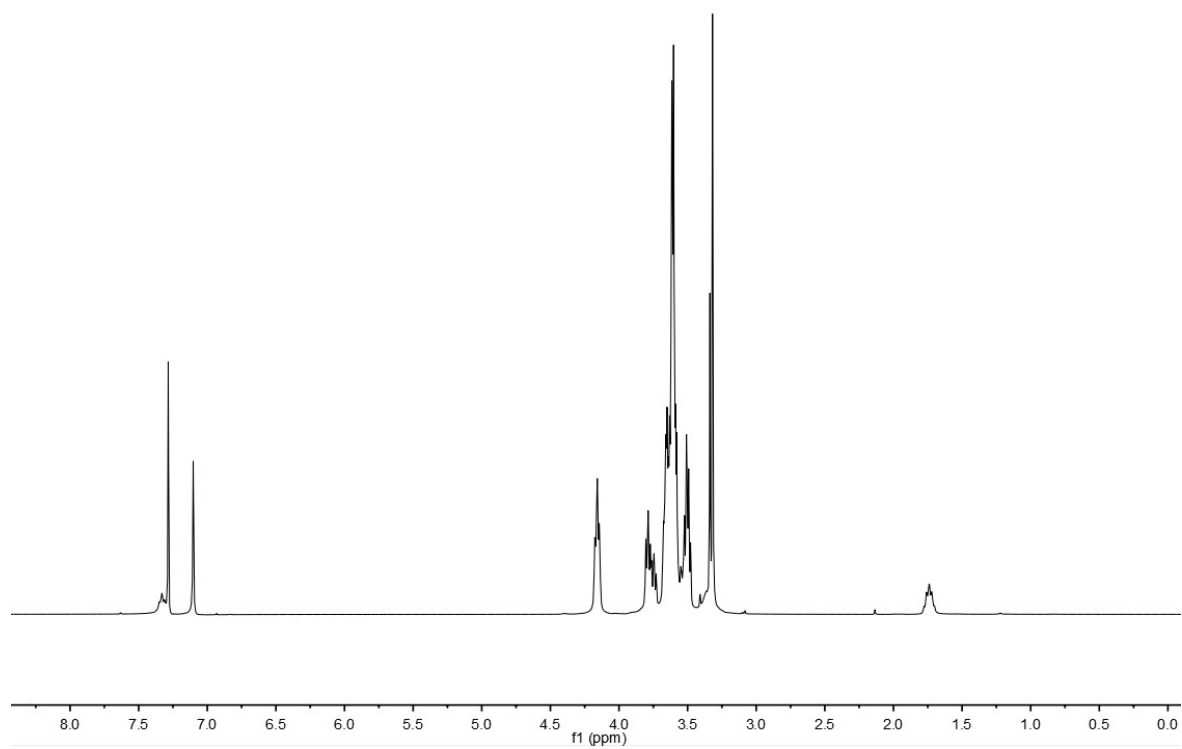
Anal.calcd. for  $\text{C}_{192}\text{H}_{288}\text{N}_8\text{O}_{68}\text{Zn}$ : C, 59.72; H, 7.52; N, 2.90; Found: C, 59.47; H, 7.62; N, 2.73;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.24 (8H, d,  $J = 8.1$  Hz, -NH- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -O-), 2.29 (8H, t,  $J = 6.1$  Hz, -NH- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -O-), 3.10 (36H, m,  $\text{CH}_3$ -), 3.21-3.65 (144H, m,  $\text{CH}_3$ -O-( $\text{CH}_2$ - $\text{CH}_2$ -O) $_3$ - $\text{CH}_2$ - $\text{CH}_2$ -O-), 3.74-3.80 (24H, m,  $\text{CH}_3$ -O-( $\text{CH}_2$ - $\text{CH}_2$ -O) $_3$ - $\text{CH}_2$ - $\text{CH}_2$ -O-), 4.16-4.22 (24H, m,  $\text{CH}_3$ -O-( $\text{CH}_2$ - $\text{CH}_2$ -O) $_3$ - $\text{CH}_2$ - $\text{CH}_2$ -O-), 4.38 (8H, t,  $J = 5.3$  Hz, -NH- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -O-) 7.08 (4H, d,  $J = 5.7$  Hz, -NH- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -O-), 7.15 (8H, s,  $\text{C}_6\text{H}_2$ ), 7.26 (8H, d,  $J = 4.1$  Hz, phenyl-H), 8.10 (8H, d,  $J = 7.9$  Hz phenyl-H), 8.80 (8H, s,  $\beta$ -pyrrole-H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.96, 158.36, 152.23, 141.18, 135.40, 134.51, 129.64, 119.47, 112.52, 107.20, 72.14, 71.64, 71.59, 70.38, 70.35, 70.32, 70.29, 70.27, 70.23, 70.20, 70.18, 70.13, 69.50, 68.86, 66.38, 58.71, 37.82, 29.20, 0.80. MALDI-TOF mass (( $\alpha$ -Cyano-4-hydroxycinnamic acid): calcd. for  $\text{C}_{192}\text{H}_{288}\text{N}_8\text{O}_{68}\text{Zn}[\text{M}]^+$ :  $m/z = 3859.868$ ; found : 3859.5015

## Synthesis of **1**<sub>Cu</sub>

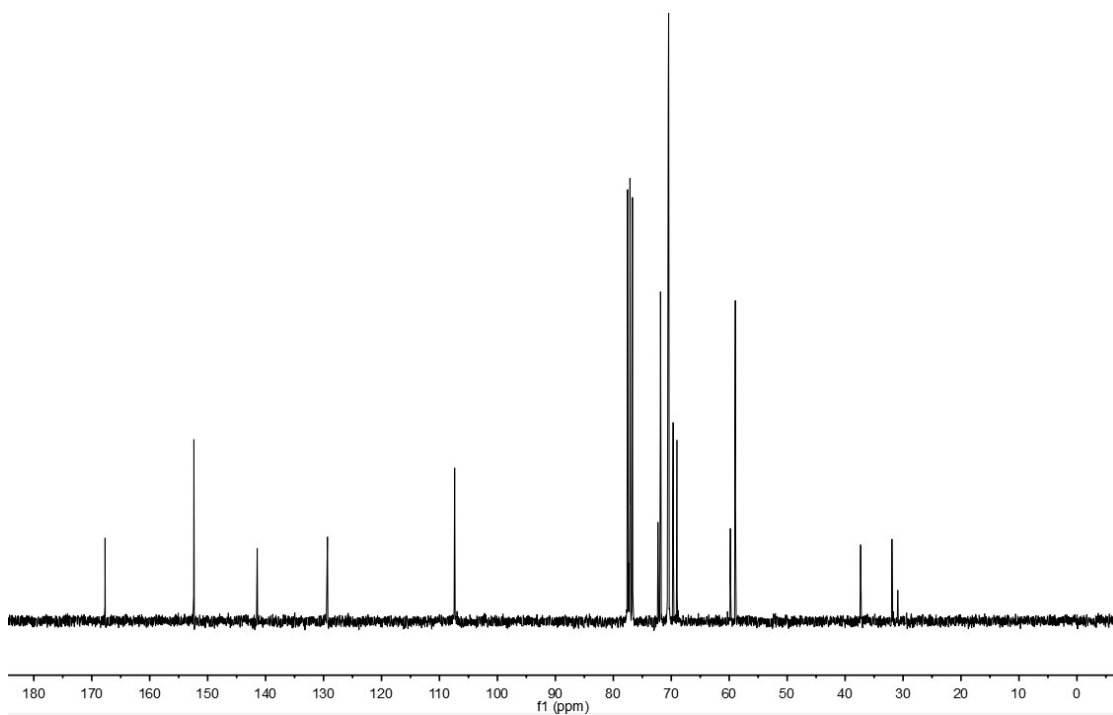
To a CHCl<sub>3</sub> solution (2mL) of compound **1**<sub>Free</sub> (50mg, 0.013mmol), Cu(OAc)<sub>2</sub> (10eq, 24mg, 0.13mmol) in MeOH (1mL) was added, and the mixture was stirred for 3 h at 50 °C under an argon atmosphere. After cooling to room temperature, the solvents were evaporated, and the resultant residue was purified through column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>/MeOH, 1:0 to 10:1 volume) to yield compound **1**<sub>Cu</sub> as red solid (45mg, 90%). The paramagnetic nature of the copper ion hindered NMR characterization of **4**<sub>Cu</sub> compound.

Anal.calcd. for C<sub>192</sub>H<sub>288</sub>N<sub>8</sub>O<sub>68</sub>Cu: C, 59.74; H, 7.52; N, 2.90; Found: C, 60.74; H, 8.52; N, 2.70; MALDI-TOF mass (( $\alpha$ -Cyano-4-hydroxycinnamic acid): calcd. for C<sub>192</sub>H<sub>288</sub>N<sub>8</sub>O<sub>68</sub>Cu [M]<sup>+</sup>: m/z =3858.869; found : 3858.1677

Figures

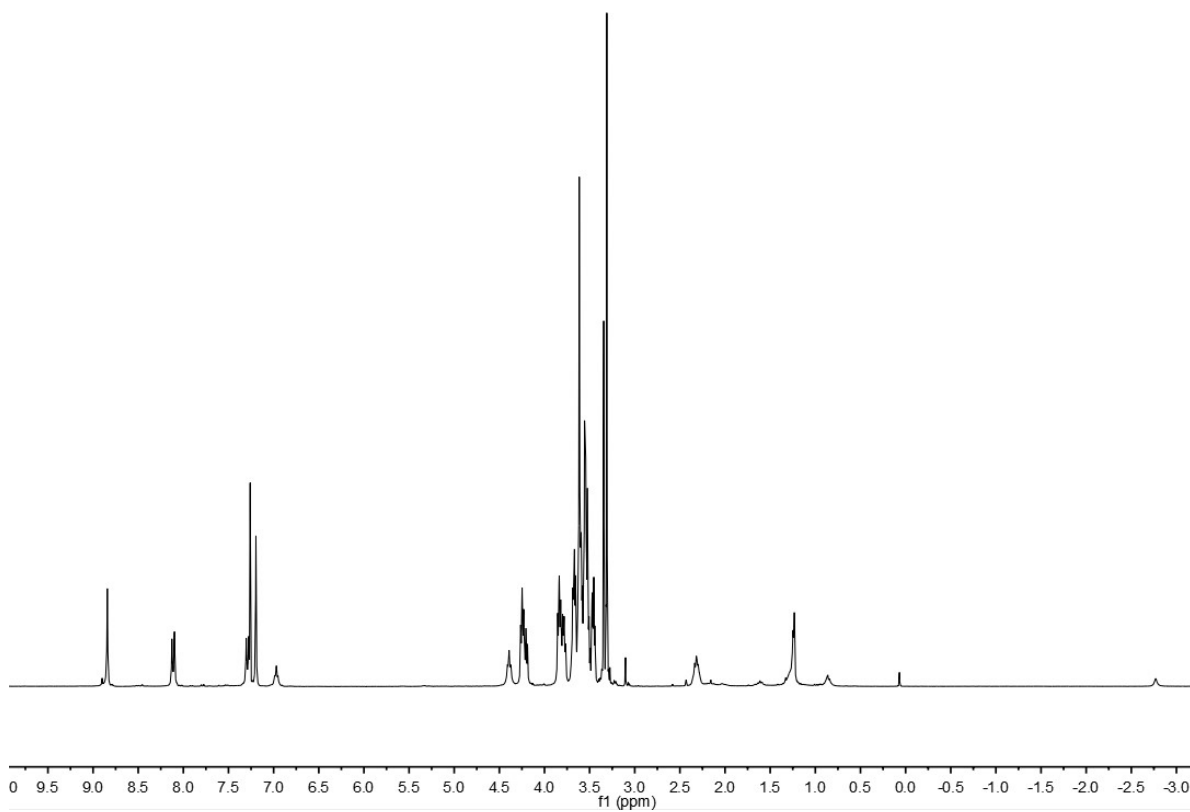


**Figure S1.** <sup>1</sup>H NMR spectrum of Compound **2** in CDCl<sub>3</sub> at 298K.

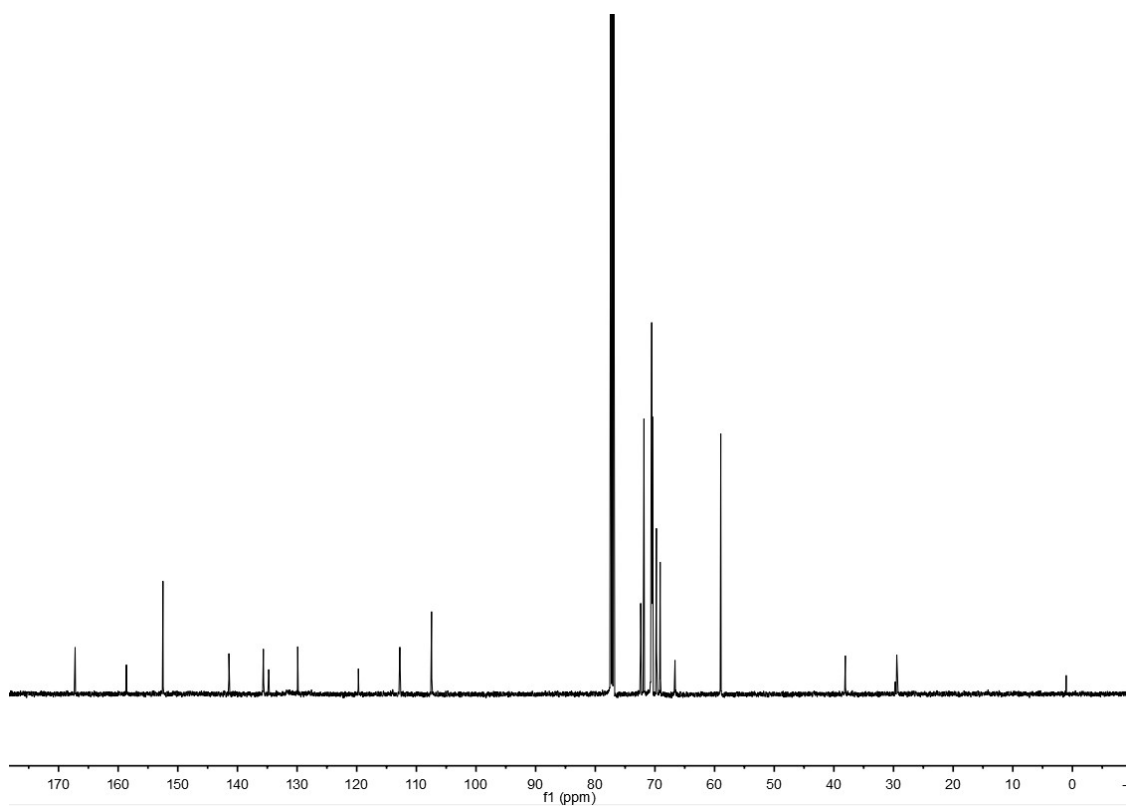


**Figure S2.**  $^{13}\text{C}$  NMR spectrum of Compound **2** in  $\text{CDCl}_3$  at 298K.

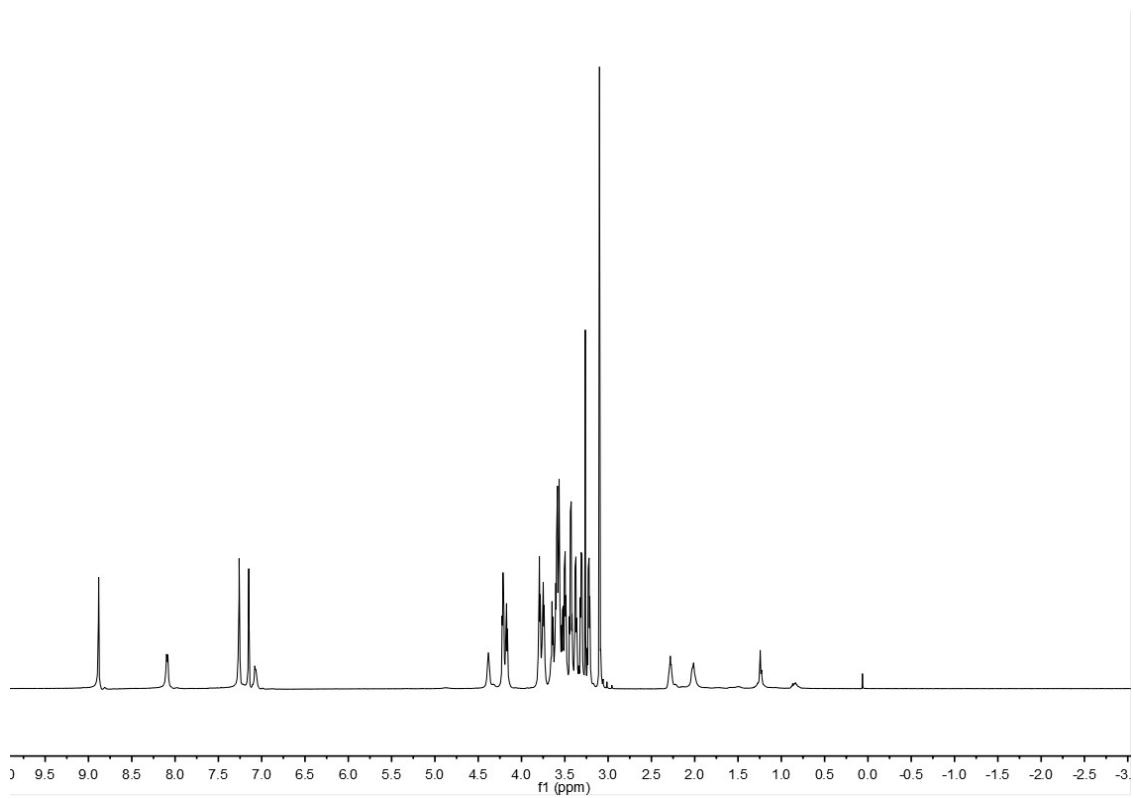




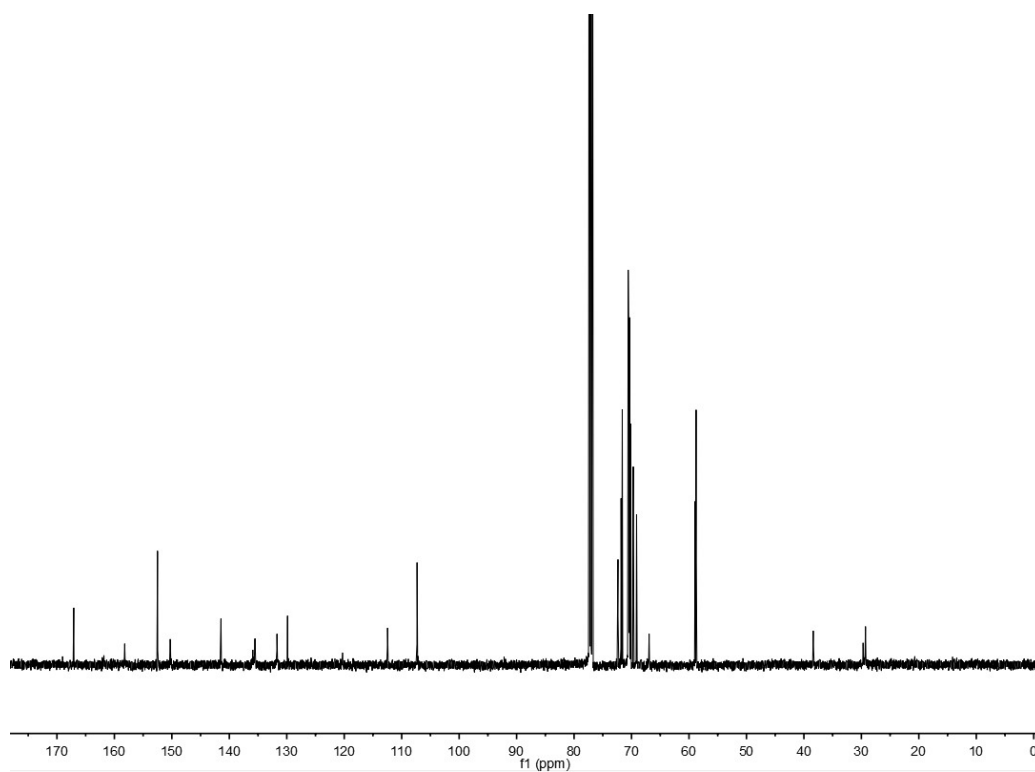
**Figure S3.** <sup>1</sup>H NMR spectrum of **1<sub>free</sub>** in CDCl<sub>3</sub> at 298K.



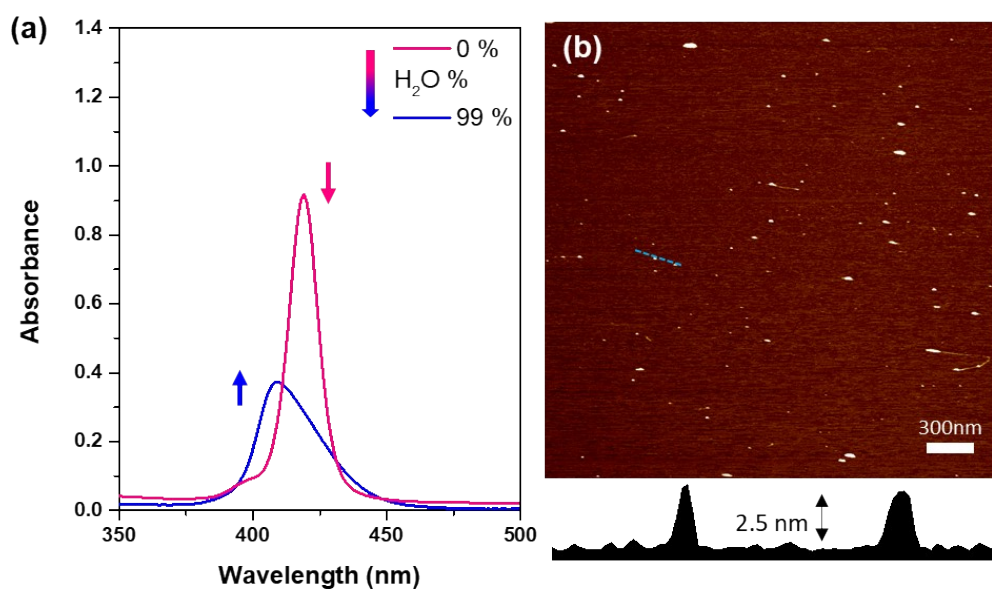
**Figure S4.**  $^{13}\text{C}$  NMR spectrum of  $\mathbf{1}_{\text{free}}$  in  $\text{CDCl}_3$  at 298K.



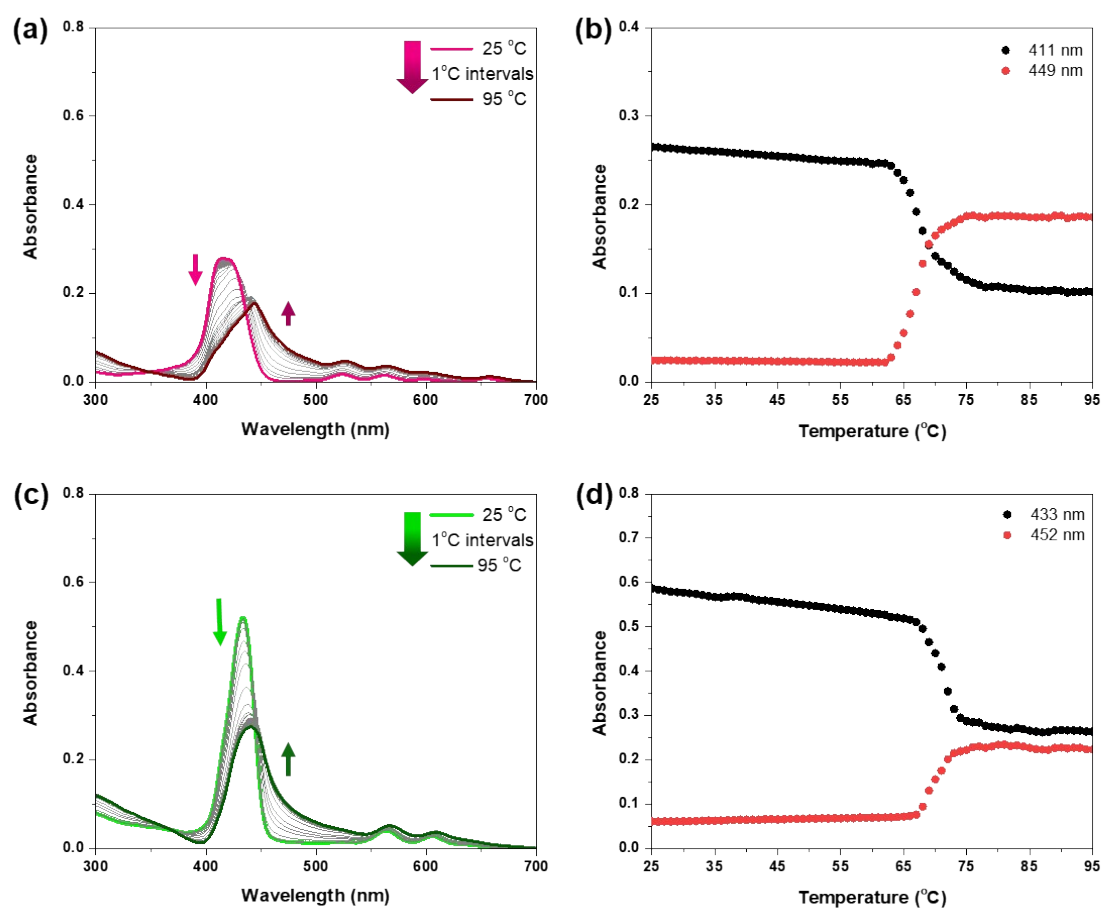
**Figure S5.**  $^1\text{H}$  NMR spectrum of  $1_{\text{zn}}$  in  $\text{CDCl}_3$  at 298K.



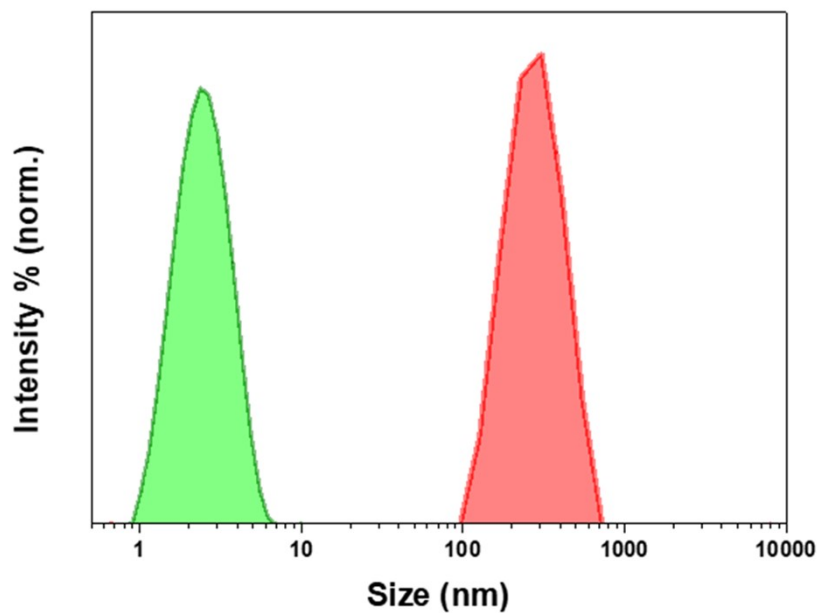
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of  $\mathbf{1}_{\text{zn}}$  in  $\text{CDCl}_3$  at 298K.



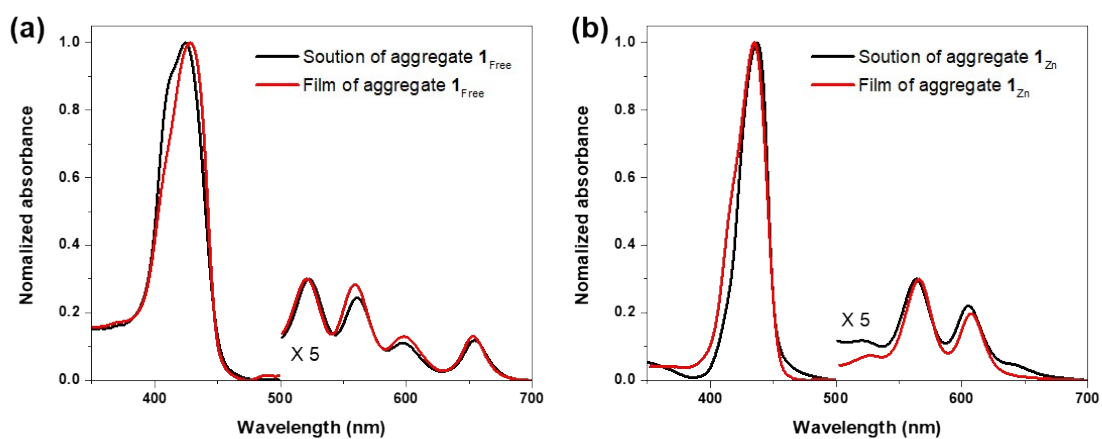
**Figure S7. Self-assembling behavior of  $1_{Cu}$  in tetrahydrofuran (THF) and water ( $H_2O$ ) solvent mixture.** (a) Absorption spectra of  $1_{Cu}$  in THF/  $H_2O$  mixed solvents:  $[1_{Cu}] = 20 \mu M$ . (b) Top, AFM image of nanoparticle on mica substrate; scale bar, 300nm. Bottom, height profile of  $1_{Cu}$  obtained across blue line.



**Figure S8. Self-assembling behavior of  $1_{\text{Free}}$  and  $1_{\text{Zn}}$  in THF/H<sub>2</sub>O (1:99)** (a) Temperature-dependent absorption spectra of  $1_{\text{Free}}$  observed upon heating process:  $[1_{\text{Free}}] = 20 \mu\text{M}$ . (b) Change in the absorbance at 411 nm, 449 nm as a function of temperature: the disassembling process of H-aggregate formation. (c) Temperature-dependent absorption spectra of  $1_{\text{Zn}}$  observed upon heating process:  $[1_{\text{Zn}}] = 20 \mu\text{M}$ . (d) Change in the absorbance at 433 nm, 452 nm as a function of temperature: the disassembling process of J-aggregate formation.

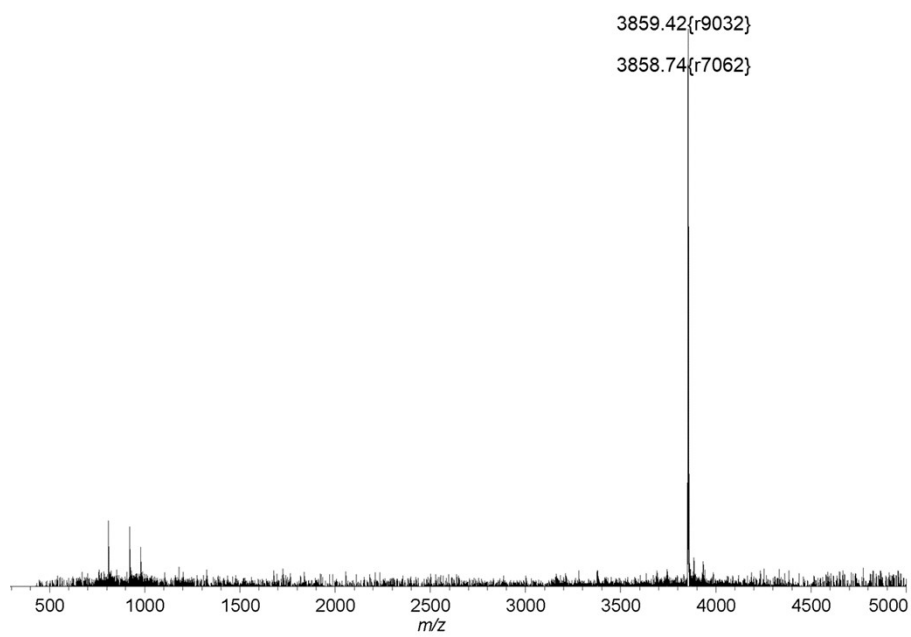


**Figure S9.** Size distribution DLS data of nanoparticles  $\mathbf{1}_{\text{Free}}$  (green line) and nanosheets  $\mathbf{1}_{\text{Zn}}$  (red line).

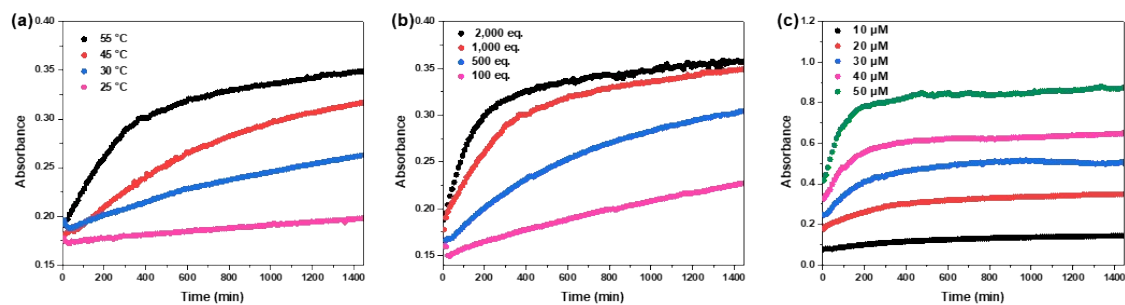


**Figure S10. Self-assembling behavior of  $1_{Free}$  and  $1_{Zn}$  in solution and solid state** (a) Absorption spectra of  $1_{Free}$  in solution (black) and thin film (red). (b) Absorption spectra of  $1_{Zn}$  in solution (black) and thin film (red); absorption spectra in thin films spin-casted from the aggregate solutions.

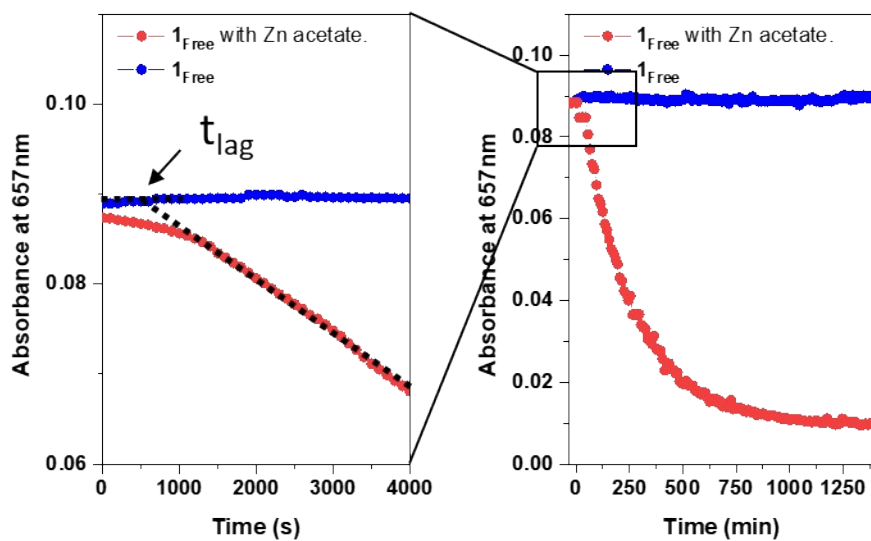




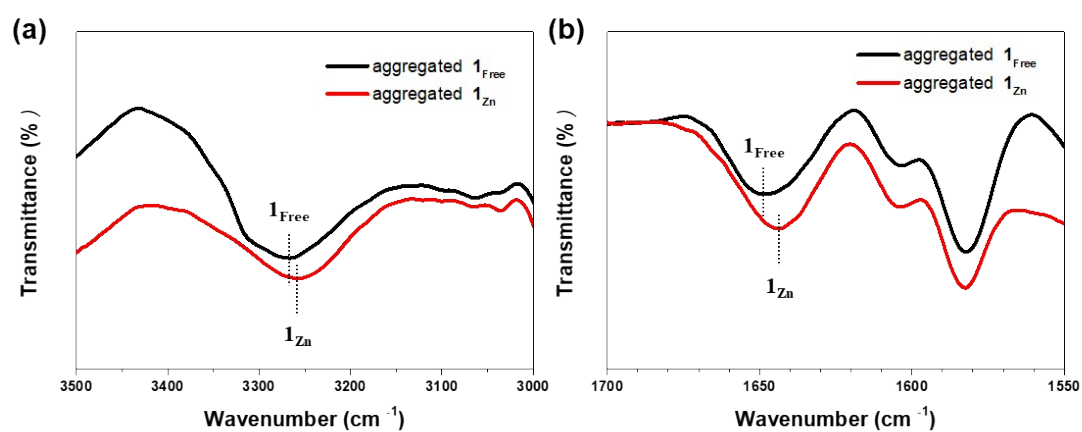
**Figure S11.** MALDI-TOF spectrum of **1<sub>Free</sub>** with Zn(II) ion.



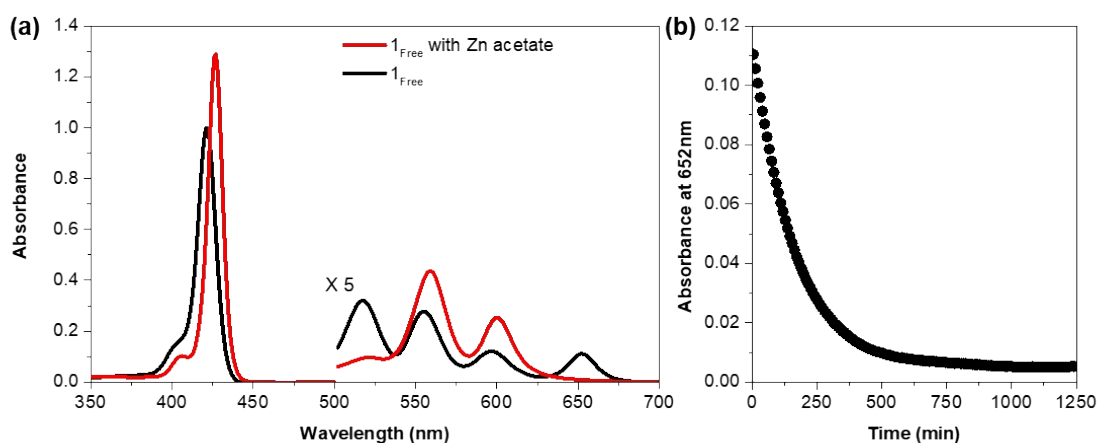
**Figure S12. Kinetic profiles of  $1_{\text{Free}}$  with Zn ions ( $\text{Zn}(\text{OAc})_2$ ) for metalation** Change in the absorption at 566 nm as a function of time during the transformation from nanoparticles  $1_{\text{Free}}$  to nanosheets  $1_{\text{Zn}}$  (a) at different temperatures in the presence of Zn ions (1,000 eq.), (b) various equivalents of Zn ions at 55 °C, and (c) at different concentration of  $1_{\text{Free}}$  in the presence of Zn ions (1,000 eq.) at 55 °C.



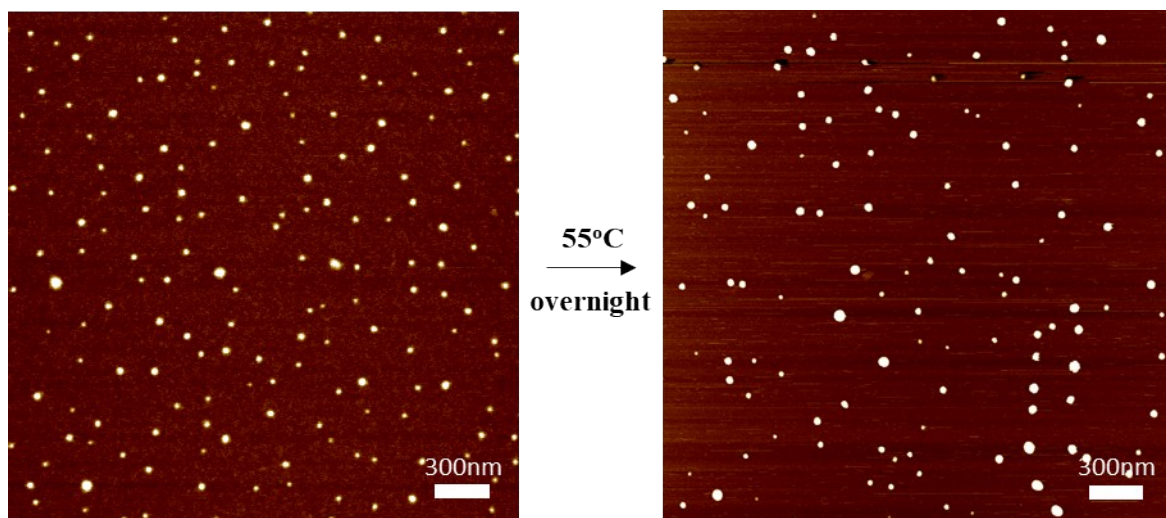
**Figure S13. Kinetic profile** Change in the absorption at 657 nm as a function of time during the transformation from nanoparticles  $1_{\text{Free}}$  (20  $\mu\text{M}$ ) to nanosheets  $1_{\text{Zn}}$  in the presence of Zn ions (1,000 eq.) at 55  $^{\circ}\text{C}$ ; the data points at kinetic profile (0 – 4000 sec) were fitted by simple linear regression, the  $t_{\text{lag}}$  (lag time) were then determined from the intersection point of these two lines.



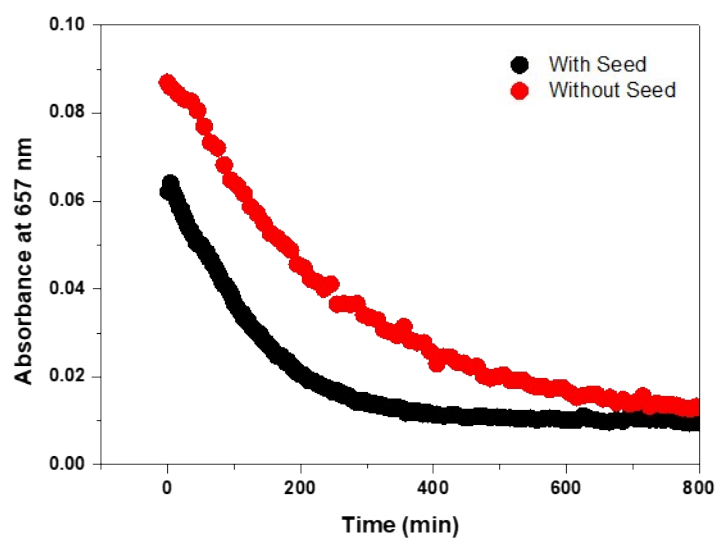
**Figure S14.** FT-IR spectra of the (a) N-H stretching vibration and (b) C=O stretching vibration for aggregated  $1_{\text{Free}}$  (black) and  $1_{\text{Zn}}$  (red).



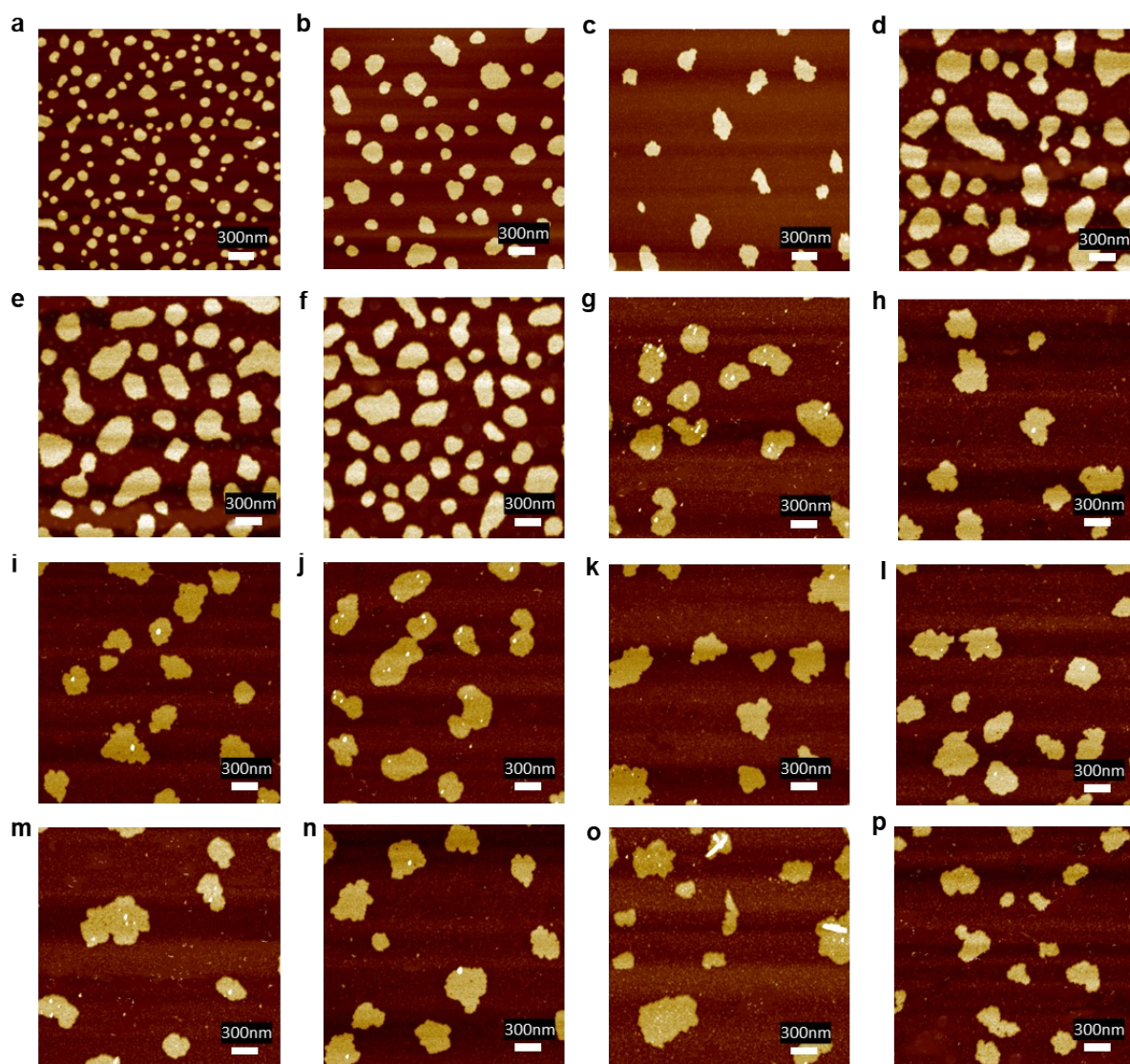
**Figure S15. Kinetic profiles of monomeric  $1_{\text{Free}}$  with Zn ions for metalation** (a) Absorption spectra of monomeric  $1_{\text{Free}}$  (black) and  $1_{\text{Free}}$  with Zn acetate (red) in THF/ H<sub>2</sub>O mixed solvent (water 40%). (b) Change in the absorption at 652 nm as a function of time during the metalation reaction from monomeric  $1_{\text{Free}}$  to  $1_{\text{Zn}}$  in the presence of Zn ions (1,000 eq.) at 55 °C; [ $1_{\text{Free}}$ ] = 20  $\mu\text{M}$ .



**Figure S16. Stability of nanoparticles** AFM images of  $\mathbf{1}_{\text{Free}}$  after overnight aged at 55°C.

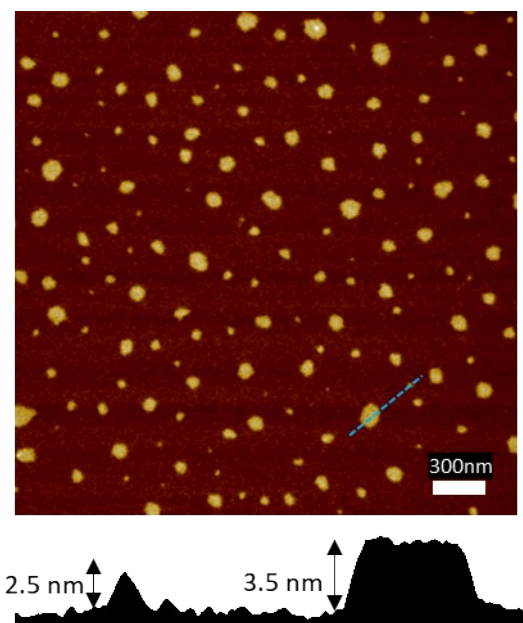


**Figure S17. Seeded living polymerization** Time course of the absorbance at 657 nm as a function of time during the transformation from nanoparticles  $\mathbf{1}_{\text{Free}}$  to nanosheets  $\mathbf{1}_{\text{Zn}}$  with seed (black line) and without seed (red line) in the presence of Zn ions (1,000 eq.) at 55 °C; the addition of seed (20  $\mu\text{M}$ ) to nanoparticle solution (20  $\mu\text{M}$ ) in the molar ratio of 1:1.



**Figure S18. Living supramolecular polymerization by seeded growth.** (a) AFM images of Seed  $1_{Zn}$ . The ratios between seed  $1_{Zn}$  (in THF/ $H_2O$ ) and nanoparticles  $1_{Free}$  (in THF/ $H_2O$ ) are 1:1 (b,c the same sample shown in Fig.5 in the main text) and 1:2 (d,e,f the same sampled shown in Fig 5 in the main text) and 1:3 (g,h,i,j,k,l,m,n,o,p the same sampled shown in Fig 5 in the main text).





**Figure S19.** AFM image of the resulting samples after living supramolecular polymerization in the absent of Zn ions; displayed the formation of nanoparticles and nanosheets.

## References

1. Wang, D. H.; Shen, Z.; Guo, M.; Cheng, S. Z. D.; Harris, F. W. Synthesis and Properties of Polyimides Containing Multiple Alkyl Side Chains. *Macromolecules* **2007**, *40* (4), 889–900.