Supporting Information

for

Manipulation of Self-Assembled Nanostructure Dimensions in

Molecular Janus Particles

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Contents

Experimental Section

Chemicals and Solvents.

T8 aminopropylheptaisobutyl-POSS (**BPOSS-NH$_2$**, 97+%, Hybrid Plastics), T8 octavinyl-POSS (VPOSS, 97+%, Hybrid Plastics), sodium tungstate dehydrate (99%, Alfa Aesar), sodium phosphate dibasic dehydrate (99%, Acros Organics), hydrochloric acid (36%, Alfa Aesar), phosphoric acid (85%, Sigma-Aldrich), glacial acetic acid (99.5%, Sigma-Aldrich), potassium chloride (99%, Sigma-Aldrich), acrylic acid (99.5%, Acros Organics), tin(II) chloride anhydrous (98%, Alfa Aesar), *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ, 99+%, Alfa Aesar), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Sigma-Aldrich), tetrabutylammonium bromide (TBABr, 99.0+%, Sigma-Aldrich), 2-(Boc-amino)ethanethiol (97%, Sigma-Aldrich), maleic anhydride (98+%, Alfa Aesar), *β*-alanine (99%, TCI America), cyclohexanethiol (97%, Sigma-Aldrich), 3-mercaptopropyltrimethoxysilane (96%, TCI America), and triethylamine (TEA, 99.5+%, Sigma-Aldrich) were used as received. Acetonitrile (ACN, Fisher Scientific), chloroform (Fisher Scientific), dichloromethane (DCM, Fisher Scientific), tetrahydrofuran (THF, Fisher Scientific), *N,N*-dimethylformamide (DMF, anhydrous 99.8%, Sigma-Aldrich), ethyl acetate (EA, Fisher Scientific), and hexanes (Hex, Fisher Scientific) were used as received unless otherwise stated. 3-Maleimidopropionyl chloride, mono- and tri-lacunary Keggin POM derivatives, i.e., (TBA)$_4$[PW$_{11}$O$_{39}$(SnCH$_2$CH$_2$COOH)] (KPOM-COOH) and (TBA)$_3$[PW$_{11}$O$_{40}$(SiCH$_2$CH$_2$CH$_2$SH)$_2$] (KPOM-2SH), were prepared according to the corresponding literatures.[S1,2] Silica gel (Sorbent Technologies Inc., 230-400 mesh) was activated by heating to 140 °C for 12 h before use.

Instrumentation and Characterization

Nuclear Magnetic Resonance Spectroscopy. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of the products were obtained in CDCl$_3$ (99.8% deuterium, Cambridge Isotope Laboratories) or acetonitrile-d_3 (99.9 % deuterium, Cambridge Isotope Laboratories) using a Varian NMRS 500 spectrometer equipped with an auto-sampling robot at 30 °C. The ^{1}H NMR spectra were referenced to the residual proton impurities in CDCl$_3$ at δ = 7.27 ppm

or in acetonitrile-d_3 at δ = 1.94 ppm. The ^{13}C NMR spectra were referenced to ^{13}CDCl$_3$ at δ = 77.00 ppm or to ^{13}CD$_3$CN at δ = 1.79 ppm. The ^{31}P NMR spectra were referenced by external 85% phosphoric acid at δ = 0 ppm.

Fourier-transform Infrared (FTIR) Spectroscopy. Infrared spectra of the samples were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by the potassium bromide (KBr) tableting method. The data were processed using the Win-IR software.

Matrix-assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) Mass Spectroscopy. MALDI-TOF mass spectra were recorded on a Bruker Ultraflex III TOF/TOF mass spectrometer (Bruker Daltonics) equipped with a Nd:YAG laser emitting at 355 nm. T*rans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, 99%, Aldrich) was used as the matrix compound, which was dissolved in CHCl$_3$ at a concentration of 20.0 mg/mL. There is no need to add ionizing agent because the POM clusters possess several positive tetrabutylammonium counter ions. The sample was prepared by depositing 0.5 µL matrix solution on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 µL of sample solution on a spot of dried matrix, and adding another 0.5 µL matrix solution on top of the dried sample. Mass spectra were measured in the reflection mode, and the mass scale was calibrated externally with a PMMA or PS standard with similar molecular weights to those of the samples under consideration. Data analyses were conducted with the Bruker's flex Analysis software.

Density Measurement. Density of **KPOM-BPOSS** was determined using a Guy-Lussac type specific gravity bottle (10 mL) at room temperature. A mixture of tetrachloromethane/hexane solution was used to find the density of the 3D polycrystals.

Synthesis of BPOSS-Maleimide. To a 250 mL round-bottomed flask equipped with a magnetic stirring bar were added **BPOSS-NH$_2$** (2.00 g, 2.29 mmol) and 3-maleimidopropionyl chloride (486 mg, 2.50 mmol), followed by the addition of 50 mL freshly dried CH$_2$Cl$_2$ and 100 μL triethylamine. The mixture was further stirred at room temperature for 2 h to complete the reaction. After that, the solution was washed with water (3 × 30 mL) and brine, dried over Na$_2$SO$_4$, and evaporated *in vacuo*. The residue was purified by flash column

chromatography on silica gel with the mixture of hexanes/ethyl acetate (v/v = 4/1 to 2/1) as the gradient eluent

to afford the product as a white solid (2.15 g). Yield: 92%. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, see Fig. S1a): δ

6.70 (s, -CO-C*H*=C*H*-CO-, 2H), 5.55 (t, -CO-N*H*-CH$_2$CH$_2$-, 1H), 3.84 (t, -CO-N(CO)-C*H$_2$*CH$_2$-, 2H), 3.23 (m,

-CO-NH-C*H$_2$*CH$_2$-, 2H), 2.51 (t, -CO-N(CO)-CH$_2$C*H$_2$*-CONH-, 2H), 1.85 (m, -Si-CH$_2$-C*H*(CH$_3$)-CH$_3$, 7H),

1.64 (m, -Si-CH$_2$-C*H$_2$*-CH$_2$-NHCO-, 2H), 0.96 (m, -Si-CH$_2$-CH(C*H$_3$*)-C*H$_3$*, 42H), 0.61 (m, -Si-C*H$_2$*-CH$_2$-CH$_2$-

NHCO- and -Si-C*H$_2$*-CH(CH$_3$)-CH$_3$, 16H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, see Fig. S1b): δ 170.4, 169.1,

134.1, 41.8, 34.7, 34.3, 25.6, 23.8, 22.9, 22.5, 9.4. FT-IR (KBr) v (cm^{-1}): 3311, 2956, 2872, 1499, 1466, 1365,

1332, 1229, 1105 (Si-O-Si asymmetric stretching), 953, 838, 744, 615, 563, 481. MS (MALDI-TOF, *m/z,* see

Fig. S1c):calc. for [M+Na]$^+$ (C$_{38}$H$_{76}$N$_2$O$_{15}$Si$_8$Na): 1047.3, found 1047.3.

Synthesis of CPOSS-NH$_2$. T8 VPOSS (500 mg, 0.790 mmol) and 2-(Boc-amino)ethanethiol (13.2 mg,

0.112 mmol) were dissolved in 5 mL chloroform, followed by adding 2 wt% DMPA. After irradiation under a

365 nm UV lamp at room temperature for 15 min, cyclohexanethiol (1508 mg, 13.0 mmol) was added into the

solution, followed by another 30 min UV irradiation to fully consume the vinyl groups. The crude product was

purified by flash column chromatography on silica gel using ethyl acetate/hexanes = 6/1 (v/v) as the eluent to

afford **CPOSS-NHBoc** as a light-yellow liquid. **CPOSS-NH$_2$** was obtained by treating **CPOSS-NHBoc** with

trifluoroacetic acid in dichloromethane (20 mL), and deprotonated by washing with saturated NaHCO$_3$ aqueous

solution (3 × 20 mL). The organic phase was collected and dehydrated with anhydrous Na$_2$SO$_4$, followed by

evaporating *in vacuo* to afford the product as a colorless liquid (300 mg). Overall yield: 25%. ^{1}H NMR (CDCl$_3$,

500 MHz, ppm, see Fig. S2a): δ 3.09 (t, -S-CH$_2$C*H$_2$*-NH$_2$, 2H), 2.82 (t, -S-C*H$_2$*CH$_2$-NH$_2$, 2H), 2.63 (m, -CH$_2$-

C*H$_2$*-S-C*H*(-CH$_2$-)-, 21H and -CH$_2$C*H$_2$*-S-CH$_2$CH$_2$NH$_2$, 2H), 1.31-1.95 (m, CH$_2$s on cyclohexyl groups, 70H),

1.01 (m, -Si-C*H$_2$*CH$_2$-, 16H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, see Fig. S2b): δ 43.3, 33.6, 26.1, 25.9, 24.0,

13.4. FT-IR (KBr) v (cm^{-1}): 2927, 2855, 1687, 1448, 1281, 1265, 1204, 1180, 1115, 1108, 799, 689. MS

(MALDI-TOF, *m/z,* see Fig. S2c):calc. for [M+Na]$^+$ (C$_{60}$H$_{115}$NO$_{12}$S$_8$Si$_8$Na): 1544.4, found 1544.3.

Synthesis of KPOM-BPOSS ((NBu)$_4$[PW$_{11}$O$_{39}$SnC$_2$H$_4$CONH-BPOSS]). The synthesis is based on a reported procedure with modifications.[S3] **KPOM-COOH** (767 mg, 0.200 mmol) and EEDQ (74.2 mg, 0.300 mmol) were dissolved in 10 mL acetonitrile by vigorously stirring at 80 °C for 15 min. To the resulting solution was added T8 **BPOSS-NH$_2$** (400 mg, 0.46 mmol) dissolved in 10 mL freshly distilled anhydrous THF in a single portion. The reaction mixture was refluxing at 80 °C overnight. After that, the solvent was evaporated *in vacuo*, and the residue was dissolved in acetonitrile (20 mL) and washed with hexanes (3 × 20 mL). Precipitation of the concentrated acetonitrile solution into water followed by vacuum filtering afforded **KPOM-BPOSS** as a white powder (861 mg). Yield: 91%. ^{1}H NMR (CD$_3$CN, 500 MHz, ppm, see Fig. S3a): δ 6.56 (t, -N*H*CO-, 1H), 3.16-3.20 (m, -NC*H$_2$*CH$_2$CH$_2$CH$_3$, 32H and -C*H$_2$*NHCO-, 2H), 2.50 (t, -SnCH$_2$C*H$_2$*-, 2H), 1.92 (m, -SiCH$_2$C*H*-, 7H), 1.69 (m, -NCH$_2$C*H$_2$*CH$_2$CH$_3$, 32H), 1.44 (m, -NCH$_2$CH$_2$C*H$_2$*CH$_3$, 32H), 1.04 (m, -NCH$_2$CH$_2$C*H$_2$*CH$_3$, 48H and -Si-CH$_2$-CH(C*H$_3$*)-CH$_3$, 42H), 0.62 (m, -Si-C*H$_2$*-CH$_2$-CH$_2$-NHCO- and -Si-C*H$_2$*-CH(CH$_3$)-CH$_3$, 16H). ^{13}C NMR (CD$_3$CN, 125 MHz, ppm, see Fig. S3b): δ 58.4, 25.0, 23.8, 23.5, 22.1, 19.4, 12.9. ^{31}P NMR (CD$_3$CN, 200 MHz, ppm, see Fig. 1a): δ -11.7. FT-IR (KBr) v (cm^{-1}): 2958, 2873, 1666, 1483, 1467, 1333, 1229, 1107, 1066, 961, 885, 803, 742. MS (MALDI-TOF, *m/z*, see Fig. 1b): calc. for [M+TBA]$^+$ (C$_{114}$H$_{254}$N$_6$O$_{52}$PSi$_8$SnW$_{11}$): 4937.9, found 4937.9.

Synthesis of KPOM-CPOSS ((NBu)$_4$[PW$_{11}$O$_{39}$SnC$_2$H$_4$CONH-CPOSS]). KPOM-COOH (500 mg, 0.130 mmol) and EEDQ (48.2 mg, 0.195 mmol) were dissolved in 10 mL acetonitrile by vigorously stirring at 80 °C for 15 min. To the resulting solution was added T8 **CPOSS-NH$_2$** (804 mg, 0.529 mmol) dissolved in 10 mL freshly distilled anhydrous THF in a single portion. The reaction mixture was refluxing at 80 °C overnight. After that, the solvent was evaporated *in vacuo*, and the residue was dissolved in acetonitrile (20 mL) and washed with cyclohexane (3 × 20 mL). Precipitation of the concentrated acetonitrile solution into water followed by vacuum filtering afforded **KPOM-CPOSS** as a white powder (619 mg). Yield: 89%. ^{1}H NMR (CD$_3$CN, 500 MHz, ppm, see Fig. S4a): δ 6.71 (t, -N*H*CO-, 1H), 3.36 (m,-C*H$_2$*NHCO-, 2H), 3.18 (m, -NC*H$_2$*CH$_2$CH$_2$CH$_3$, 32H), 2.68 (m, -CH$_2$-C*H$_2$*-S-C*H*(-CH$_2$-)-, 21H and -CH$_2$C*H$_2$*-S-CH$_2$CH$_2$NHCO-, 2H), 2.56

(m, -SnCH$_2$C*H$_2$*-, 2H), 1.98-1.77 (m, CH$_2$s on cyclohexyl groups), 1.71 (m, -NCH$_2$C*H$_2$*CH$_2$CH$_3$, 32H), 1.46 (m, -NCH$_2$CH$_2$C*H$_2$*CH$_3$, 32H), 1.35 (m, CH$_2$s on cyclohexyl groups), 1.00-1.20 (m, -NCH$_2$CH$_2$C*H$_2$*CH$_3$, 48H, and -Si-C*H$_2$*-, 16H). ^{13}C NMR (CD$_3$CN, 125 MHz, ppm, see Fig. S4b): δ 58.4, 42.9, 33.5, 25.9, 23.5, 22.1, 19.4, 13.0. ^{31}P NMR (CD$_3$CN, 200 MHz, ppm, see Fig. 1a): δ -12.1. FT-IR (KBr) v (cm^{-1}): 2959, 2933, 2872, 2857, 1675, 1482, 1446, 1385, 1280, 1181, 1125, 1064, 1007, 962, 886, 830, 794, 717. MS (MALDI-TOF, *m/z*, see Fig. 1b): calc. for [M+TBA]$^+$ (C$_{143}$H$_{298}$N$_6$O$_{52}$PS$_{10}$Si$_8$SnW$_{11}$): 5587.1, found 5587.1.

Synthesis of KPOM-2BPOSS ((NBu)$_3$[PW$_{11}$O$_{39}$(SiC$_3$H$_6$S-BPOSS)$_2$O]). BPOSS-Maleimide (235 mg, 0.230 mmol) and **KPOM-2SH** (278 mg, 0.077 mmol) were separately dissolved in 5 mL THF and 5 mL acetonitrile respectively. The two solutions were mixed, followed by adding a catalytic amount of triethylamine (10 μL). After stirring the mixture at room temperature for 24 h, the solvent was removed *in vacuo*. The residue was purified by flash column chromatography on silica gel with the mixture of dichloromethane/tetrahydrofuran (v/v = 8/1 to 2/1) as the eluent to afford the product as a yellow-white powder (370 mg). Yield: 85%. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, see Fig. S5a): δ 5.75 (t, -N*H*CO-, 2H), 3.98 (s, -S-C*H*(CH$_2$-)-CO-, 2H), 3.79 (t, -CO-N(CO-)-C*H$_2$*CH$_2$-, 4H), 3.00-3.40 (m, -S-CH(C*H$_2$*-)-CO-, 2H; -NC*H$_2$*CH$_2$CH$_2$CH$_3$, 24H, and -CONH-C*H$_2$*CH$_2$-, 4H), 2.80 (m, -S-CH(C*H$_2$*-)-CO-, 2H), 2.50-2.58 (m, -CH$_2$-C*H$_2$*-S-CH(CH$_2$-)-, 4H and -CH$_2$-C*H$_2$*-CONH-, 4H), 2.02 (m, -CONH-CH$_2$-C*H$_2$*-, 4H), 1.87 (m, -SiCH$_2$C*H*(CH$_3$)-, 14H), 1.71 (m, -NCH$_2$C*H$_2$*CH$_2$CH$_3$, 24H), 1.55 (m, -NCH$_2$CH$_2$C*H$_2$*CH$_3$, 24H), 0.96-1.05 (t, -NCH$_2$CH$_2$CH$_2$C*H$_3$*, 36H and -SiCH$_2$CH(C*H$_3$*)-C*H$_3$*, 84H), 0.59 (t, -Si-C*H$_2$*-, 36H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, see Fig. S5b): δ 58.9, 42.0, 30.3, 25.7, 23.8, 22.5, 19.8, 13.8, 9.5. ^{31}P NMR (DMSO-d$_6$, 200 MHz, ppm, see Fig. 1a): δ -14.7. FT-IR (KBr) v (cm^{-1}): 2956, 2927, 2874, 1707, 1460, 1401, 1366, 1230, 1109, 1036, 964, 871, 827, 744. MS (MALDI-TOF, *m/z,* see Fig. 1b**Error! Reference source not found.**): calc. for [M+TBA]$^+$ (C$_{146}$H$_{310}$N$_8$O$_{70}$PS$_2$Si$_{18}$W$_{11}$): 5920.6, found 5920.5.

Results and Discussion

Crystal structure determination of KPOM-BPOSS. Selected area electron diffraction (SAED) patterns from the multiple-layer stacked lamellae are shown in Fig. 2d and Fig. S6a. Detailed analysis of the

SAED patterns gives rise to two perpendicular reciprocal axes. Assuming that this ED pattern is obtained along the [001] zone, it should represent a 2D rectangular unit cell with dimensions of $a = 2.68$ nm and $b = 1.38$ nm in the correlated real space. Since none of the three strong diffraction peaks with the q ratios of 1:2:3 observed in the SAXS and WAXD patterns in Fig. 2a corresponds to any of the diffraction spots in the a^*b^* plane in Fig. 2d, we deduce that these three strong diffraction peaks must be located along the c^* axis and thus, may be indexed as the (001), (002) and (003) diffractions, respectively. To prove this deduction, tilted SAED experiments were performed. After the single crystal was tilted 34° along the proposed b^*-axis, a set of new diffraction spots appeared (see Fig. S6b). This set of new diffractions that is perpendicular to the b^*-axis could be identified as (202) using the proposed unit cell parameters. A simple geometry relation can thus be built to calculate the β^* angle between c^* and a^*, which is 90°. Moreover, in Fig. S6b, the projection of c^* on the new zone is perpendicular to b^*, indicating that the α^* angle between c^* and b^* is also 90°. Therefore, based on the combined SAED, WAXD and SAXS experimental results, the **KPOM-BPOSS** crystal structure can be determined as an orthorhombic unit cell with the dimensions of $a = 2.68$ nm, $b = 1.38$ nm and $c = 4.06$ nm. Density measurements give rise to a statistic value of 2.02 ± 0.01 g/cm^3, implying that there are four molecules in each unit cell, which results in a calculated density of 2.04 g/cm^3 ($Z = 4$). The major diffraction peaks in WAXD patterns can thus be indexed, as summarized in Table S1.
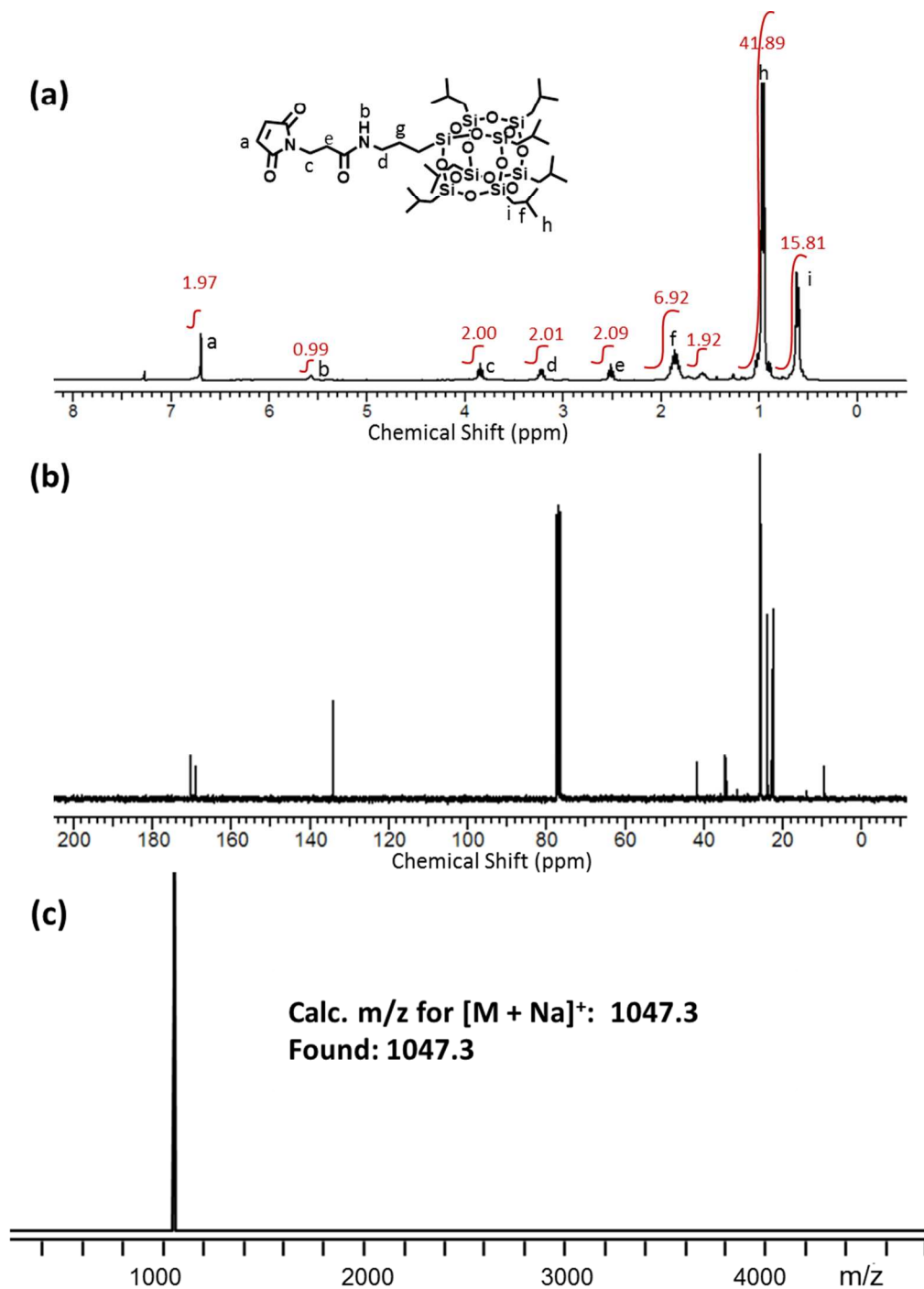
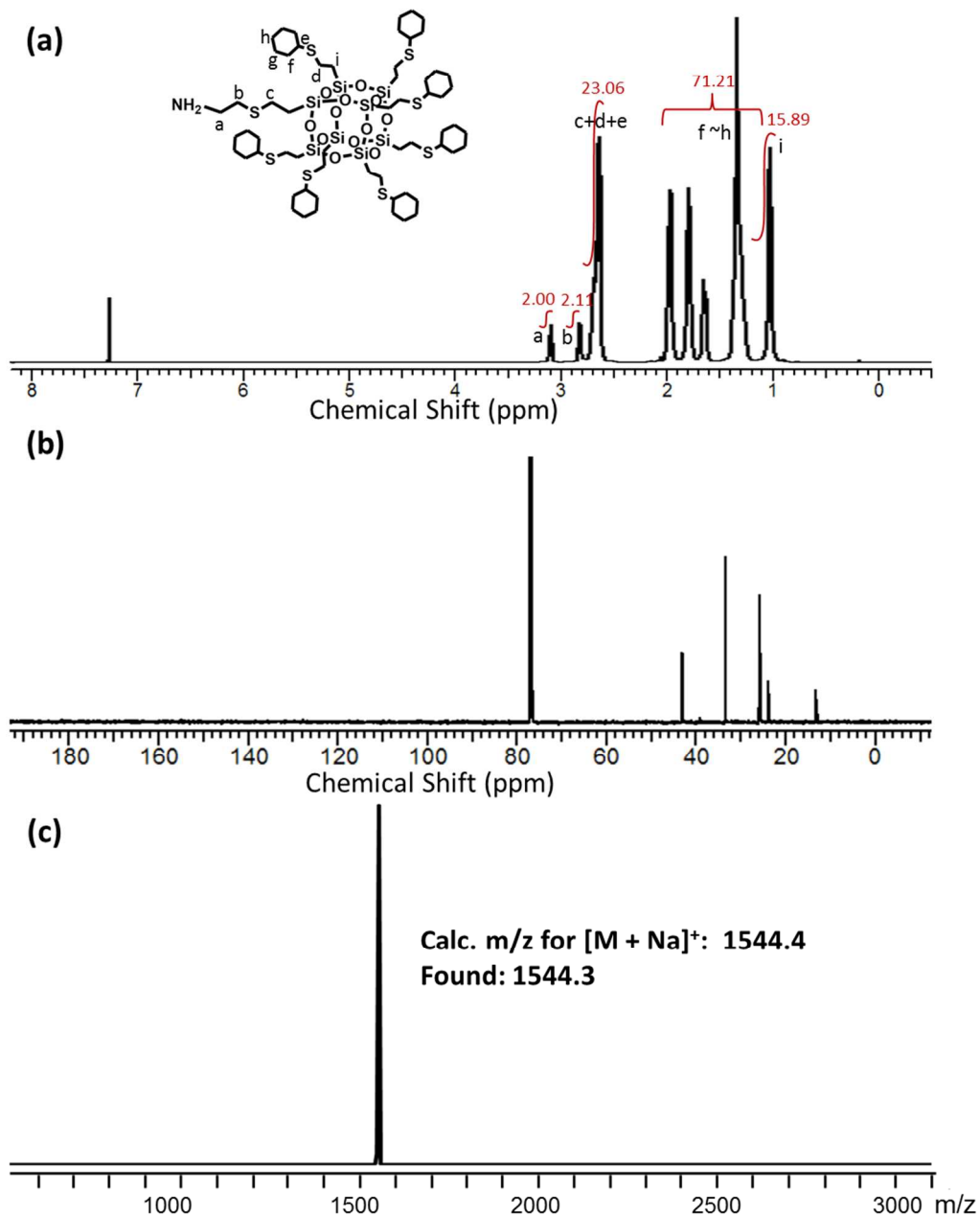Fig. S1. (a)^{1}H NMR, (b) ^{13}C NMR, and (c) MALDI-TOF mass spectra of **BPOSS-Maleimide**.

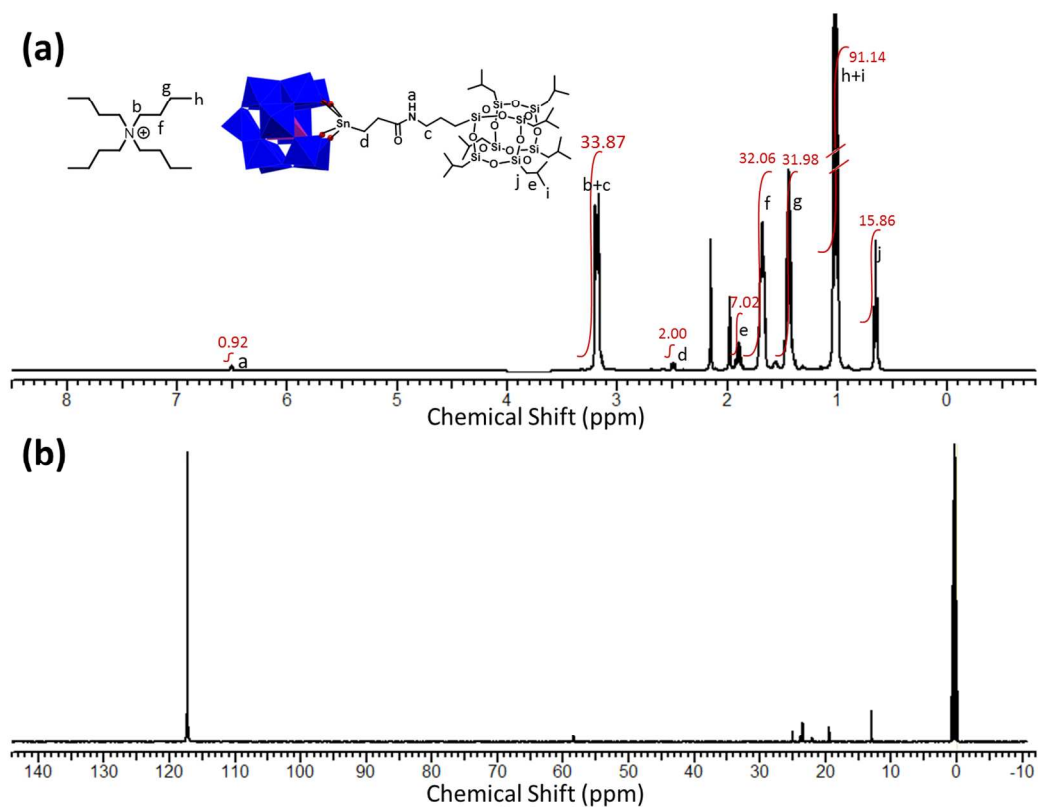Fig. S2. (a)^{1}H NMR, (b) ^{13}C NMR, and (c) MALDI-TOF mass spectra of **CPOSS-NH₂**.

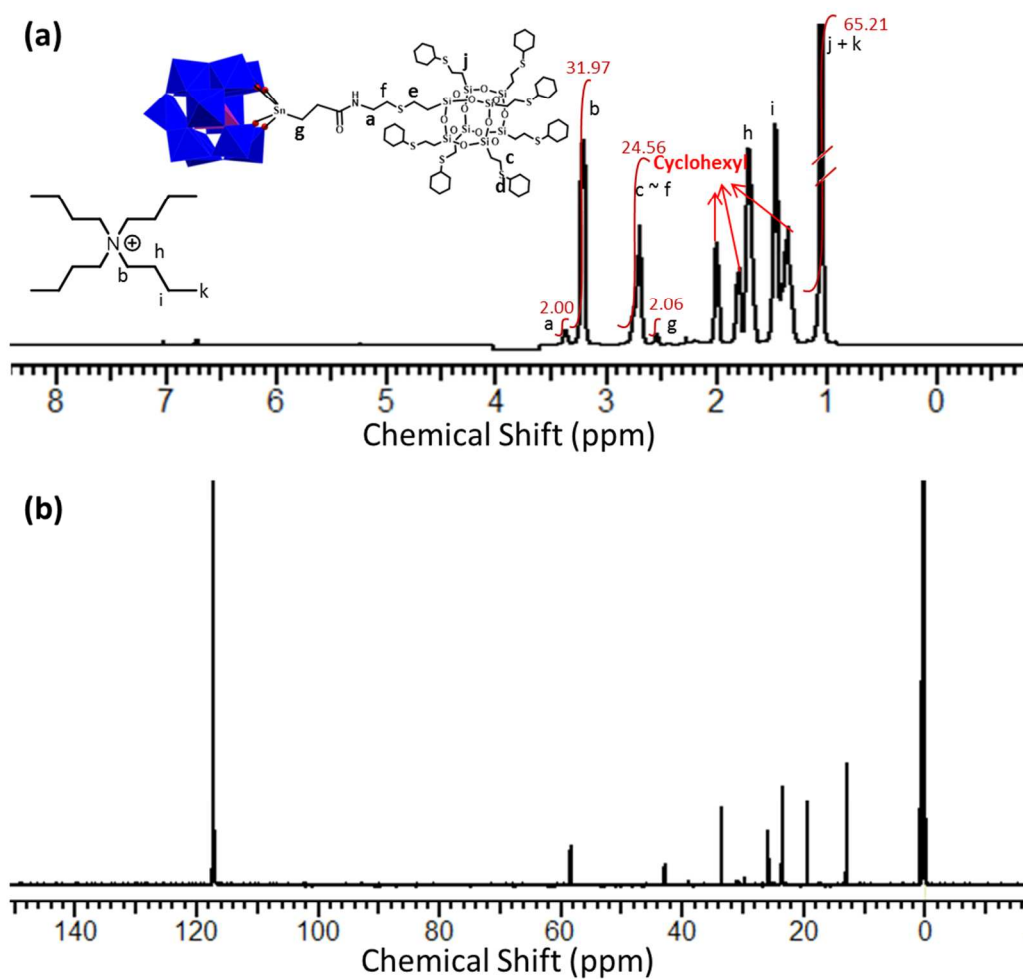Fig. S3. (a)^{1}H NMR and (b) ^{13}C NMR of **KPOM-BPOSS**.

Fig. S4. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **KPOM-CPOSS**.
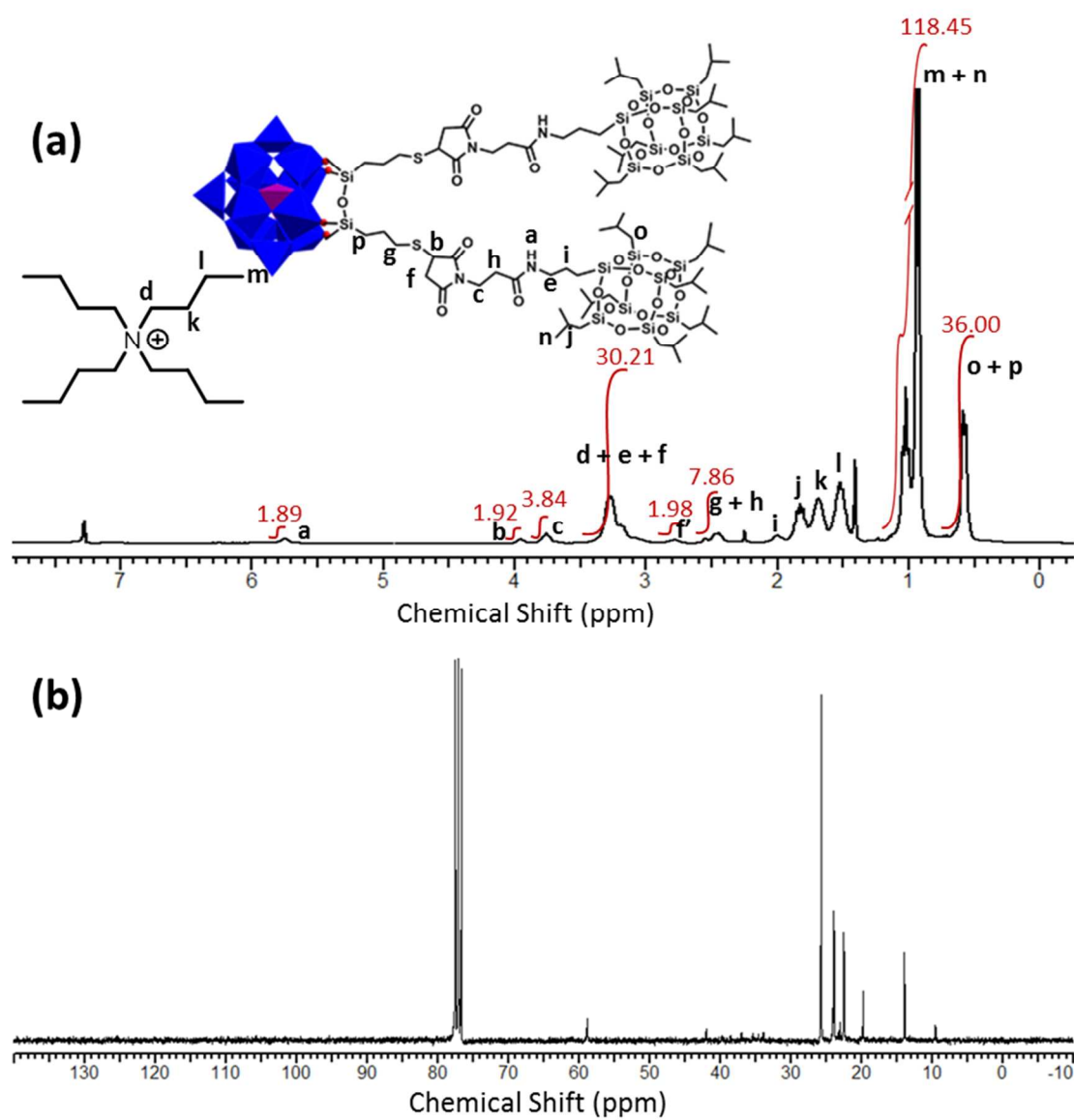
Fig. S5. (a)^{1}H NMR and (b) ^{13}C NMR spectra of **KPOM-2BPOSS**.
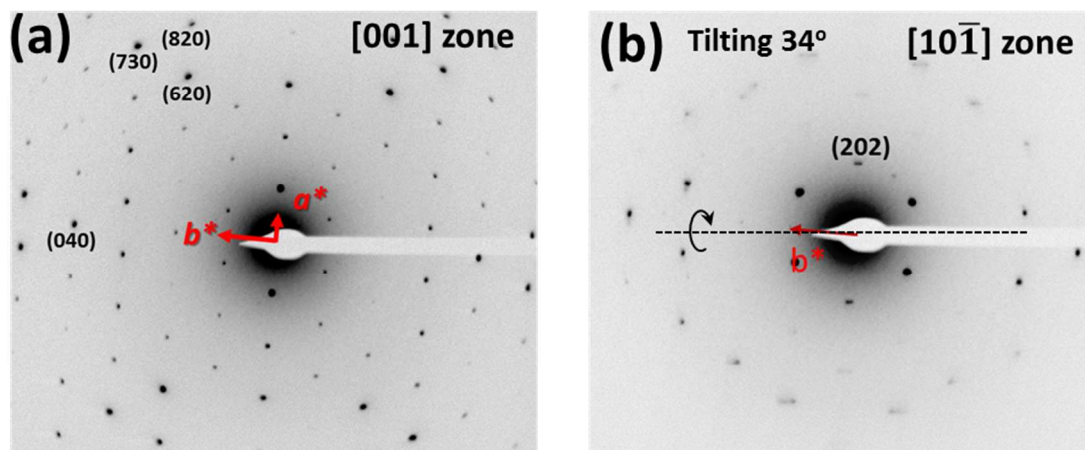
Fig. S6. (a) SAED pattern of the stacked lamellar crystals of **KPOM-BPOSS**. (b) SAED pattern obtained by tilting 34° along the *b** axis from the diffraction pattern in (a). The dashed line represents the tilting axis.

Table S1. Summary of experimental and calculated crystallographic parameters of **KPOM-BPOSS** crystals.

No.	(*hkl*)	2θ (deg)		d-spacing (Å)	
		Exptl[a]	Calc[b]	Exptl[a]	Calc[b]
1	(001)	2.17	2.17	40.6	40.6
2	(002)	4.35	4.35	20.3	20.3
3	(200), (003)	6.54,6.59	6.54,6.59	13.4, 13.5	13.4, 13.5
4	(110)	7.24	7.24	12.2	12.2
5	(004)	8.57	8.66	10.3	10.2
6	(310)	11.80	11.80	7.49	7.49
7	(020)	12.77	12.81	6.92	6.90
8	(130)	19.53	19.57	4.54	4.53
9	(602)	20.34	20.34	4.36	4.36
10	(330)	21.65	21.70	4.10	4.09
11	(620)	23.44	23.70	3.79	3.75
12	(710)	24.02	24.02	3.70	3.70
13	(530)	25.27	25.49	3.52	3.49
14	(440)	29.25	29.15	3.05	3.06
15	(730)	30.16	30.26	2.96	2.95
16	(150)	32.52	32.52	2.75	2.75
17	(0016)	35.44	35.29	2.53	2.54

Note: [a] Experimental values observed in both WAXD and SAED data. [b] Calculated based on the orthorhombic unit cell of a = 2.68 nm, b = 1.38 nm and c = 4.06 nm.
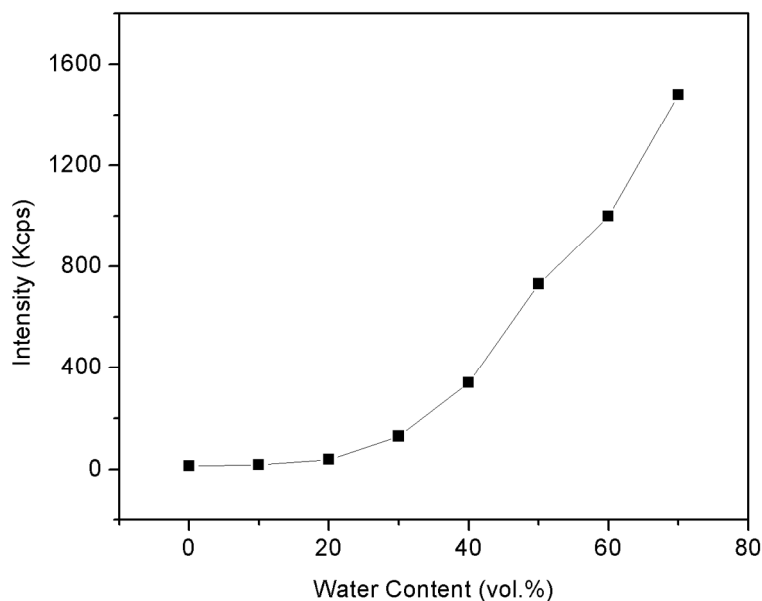
Fig. S7. Light scattering intensity versus water content in the acetonitrile/water system with an initial concentration of 0.1 wt% **KPOM-BPOSS** in acetonitrile.
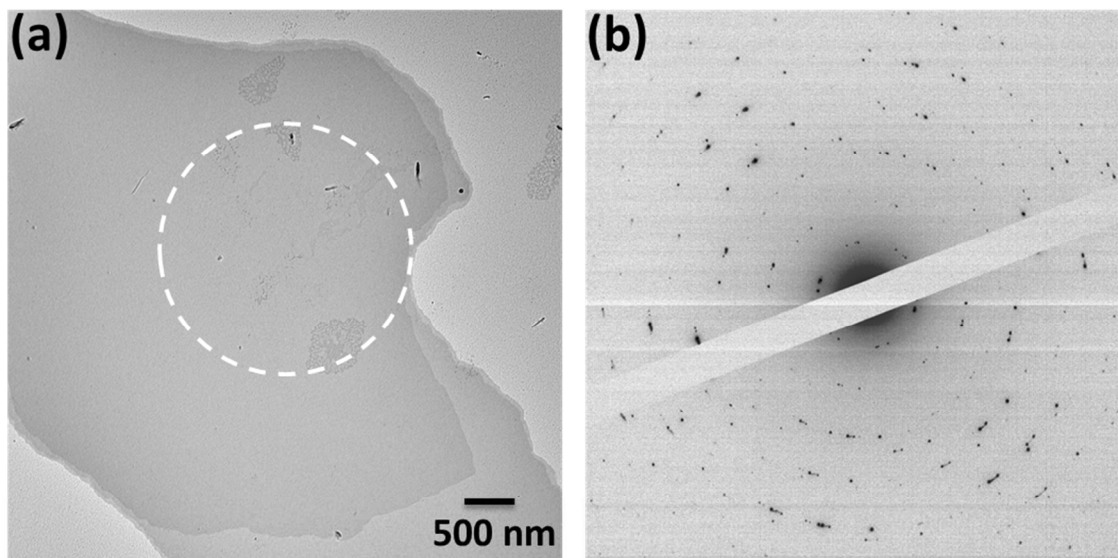

Fig. S8. (a) BF TEM image of overlapped 2D nanosheets of **KPOM-CPOSS** obtained by slow diffusion of chloroform vapor into its methanol solution with an initial concentration of 1 wt%. (b) SAED patterns obtained from the circled area in (a) showing no crystallographic registration between the different nanosheets.
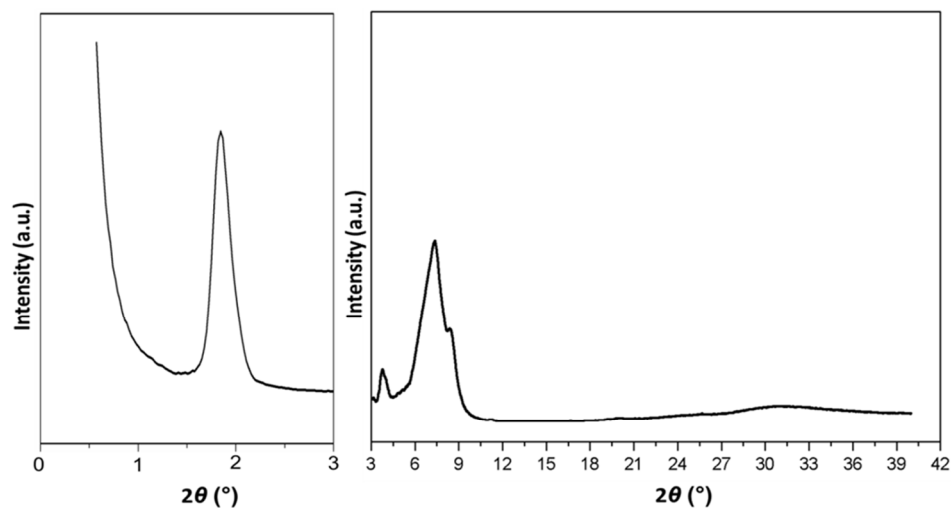
Fig. S9. Combined SAXS and WAXD profiles of the **KPOM-2BPOSS** crystalline powders obtained by slow diffusion of methanol vapor into its chloroform solution.
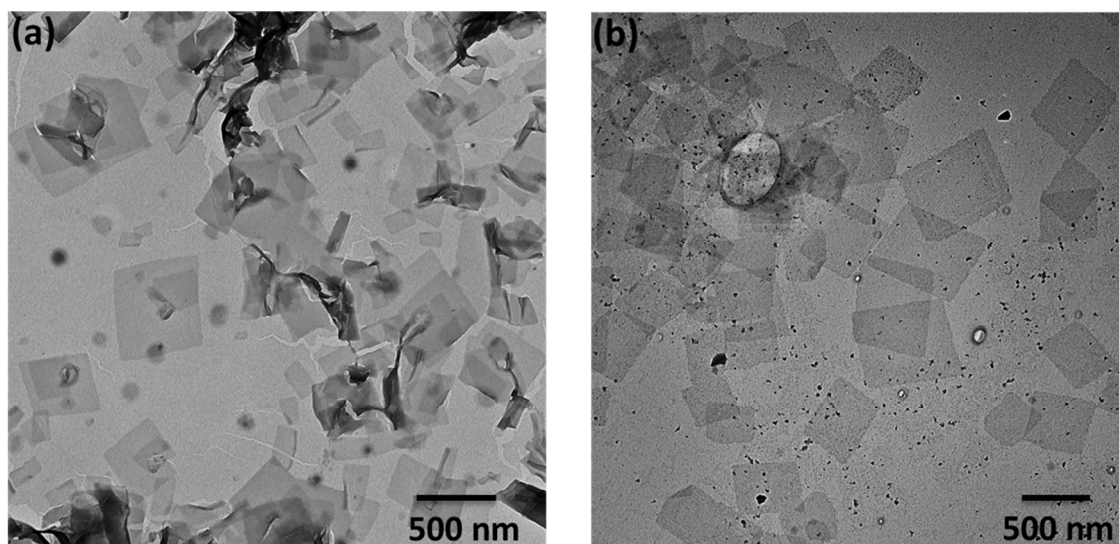

Fig. S10. BF TEM images of 2D nanosheets obtained from adding water into 0.5 wt% (a) acetone and (b) DMF solutions of **KPOM-2BPOSS**.

References

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