Supporting Information for

Organic Nanosheets with Charged Surface: Two Dimensional Self-Assembly of a Non-Symmetric Bis-acylurea with Pyridyl End Group

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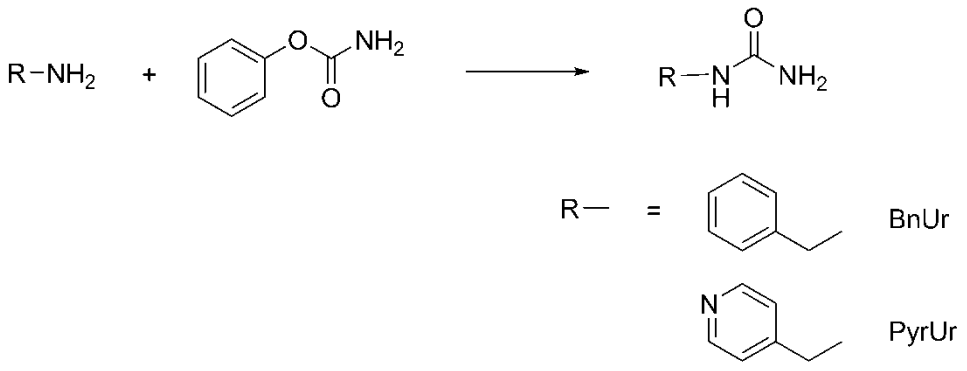
1. Synthesis of **PyrC8Bn**

(1) Ureas



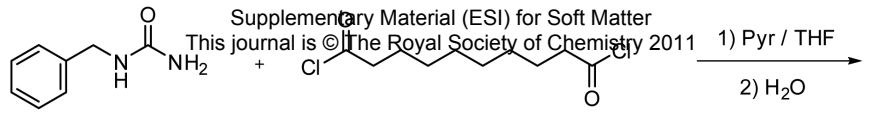
Synthesis of Benzylurea, **BnUr**.

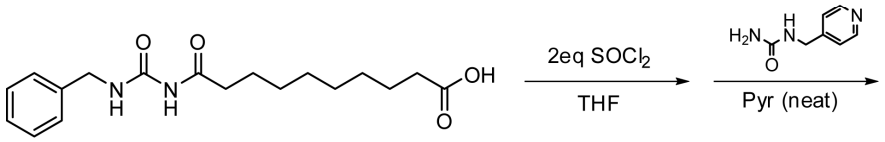
To a stirred mixture of benzylamine (10 mmol, 1.09 mL) and phenyl carbamate (10 mmol, 1.37 g) in THF (100 mL), 2.8 mL of triethylamine (20 mmol) was added under argon atmosphere. After stirring at 60 ^{o}C for 16 h, volatiles were evaporated under reduced pressure. Crude white solids were purified by recrystallization in a mixture of ethylacetate and n-hexane, to give 1.4 g of white crystals (100%). ^{1}H NMR (300 MHz, D_6-acetone): δ = 4.30 (d, 2H), 5.13 (br, 2H), 6.01 (br, 1H), 7.15-7.35 (m, ar, 5H).

Synthesis of 4-Picolylurea, **PyrUr**.

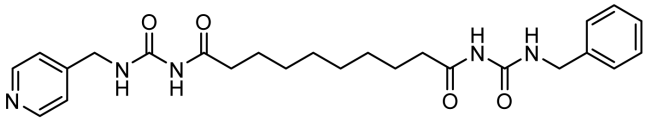
To a stirred mixture of 4-picolylamine (10 mmol, 1.02 mL) and phenyl carbamate (10 mmol, 1.37 g) in THF (100 mL), 1.62 mL of pyridine (20 mmol) was added under argon atmosphere. After stirring at 60 ^{o}C for 20 h, volatiles were evaporated under reduced pressure. Crude white solids were filtered and washed thoroughly with ethylacetate. After drying overnight in vacuum, 1.1 g of white powder was obtained. (73%). ^{1}H NMR (300 MHz, D_4-methanol): δ = 4.40 (s, 2H), 7.40 (d, 2H), 8.50 (d, 2H).

(2) Synthesis of **PyrC8Bn**





BnC8OH



PyrC8Bn

Synthesis of **BnC8OH**

To a stirred mixture of benzylurea (5 mmol, 0.75 g) and pyridine (15 mmol, 1.21 mL) in dry THF (100 mL) at room temperature, sebacoyl chloride (5 mmol, 1.10 mL) was added dropwise under argon atmosphere. After stirring for 16 h, H_2O (50 mmol, 0.9 mL) was added, and then stirred for another 30 min. Using rotary evaporation, volatiles were evaporated, and the crude white solids were filtered and washed thoroughly with hot ethanol (60 ^{o}C). The filtered solids were determined to be disubstituted bis-acylurea, **BnC8Bn**, using ^{1}H NMR. The collected filtrate was concentrated in vacuum, and the white solids were washed thoroughly with boiling water and dried in vacuum to afford 0.58 g (35%) of white solids. ^{1}H NMR (300 MHz, D_6-DMSO): δ = 1.10-1.30 (br, 8H), 1.30-1.60 (br, 4H), 2.17 (t, 2H), 2.27 (t, 2H), 4.35 (d, 2H), 7.15-7.40 (ar, 5H), 8.77 (t, 1H), 10.34 (s, 1H), 11.98 (br, 1H).

Synthesis of **PyrC8Bn**.

To a dispersed solution of **BnC8OH** (0.5 mmol, 167 mg) in THF (5 mL) at room temperature under argon atmosphere, thionyl chloride (1 mmol, 0.072 mL) was added using a syringe. After stirring for 2 h, volatiles were evaporated in vacuum. Into the reaction flask, 4-picolylurea (1 mmol, 151 mg) was transferred, and the reaction flask was purged by several cycles of evacuation and refilling with argon. To the flask, pyridine (10 mL) was added through a septum with use of syringe, then the reaction

mixture was stirred at 75 ^{o}C. After 16 h, volatiles were evaporated, and the crude yellowish solids were recrystallized from a hot dilute solution of ethanol to give 80 mg (34%) of white solids. ^{1}H NMR (400 MHz, D_6-DMSO, 60 ^{o}C): δ = 1.15-1.40 (br, 8H), 1.45-1.65 (br, 4H), 2.20-2.35 (m, 4H), 4.30-4.45 (m, 4H), 7.15-7.40 (ar, 7H), 8.51 (br, ar, 2H), 8.69 (br, 1H), 8.79 (br, 1H), 10.15 (br, 1H), 10.21 (br, 1H). ^{13}C NMR (400 MHz, D_6-DMSO, 60 ^{o}C): δ = 24.86, 28.88, 28.94, 36.24, 42.23, 43.10, 122.57, 127.38, 127.66, 128.84, 139.71, 149.21, 149.78, 153.89, 175.56. MS (ESI, m/z) $[M+H]^+$ 468.25 (100%), 469.27 (17%), $[M+Na]^+$ 490.25 (9%).

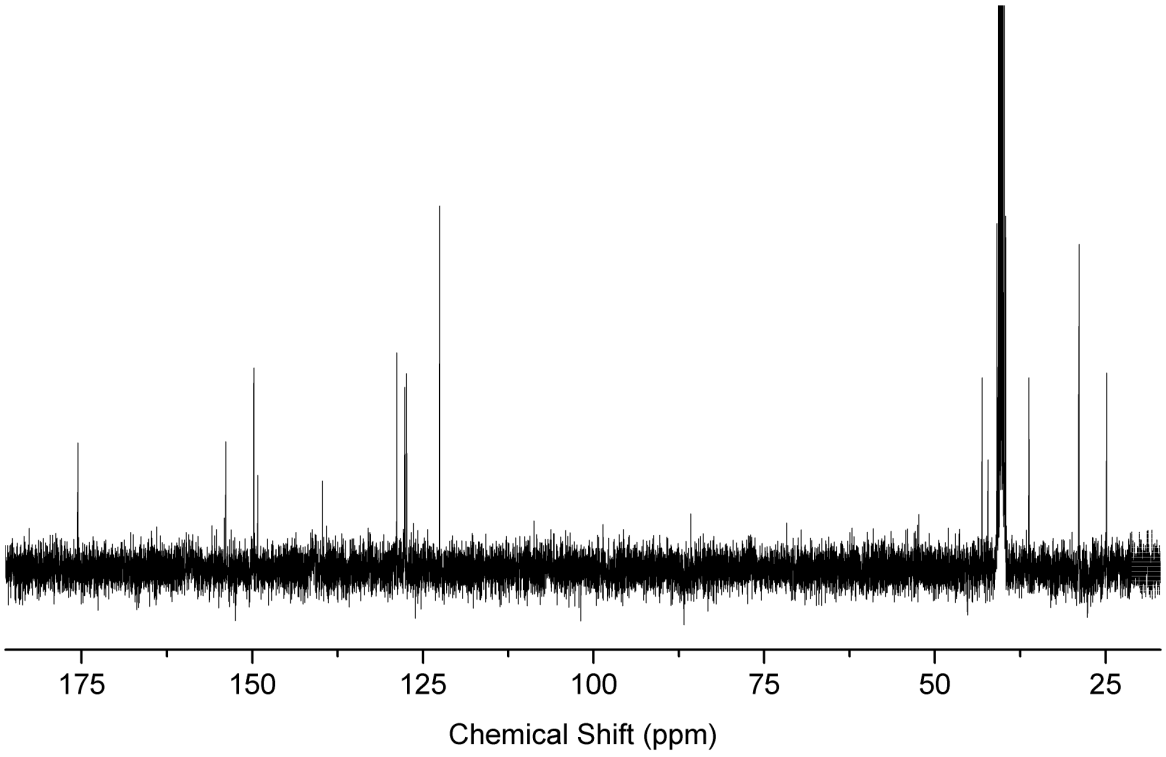


Figure S1. ^{13}C NMR spectrum of **PyrC8Bn** recorded in D_6-DMSO at 60 ^{o}C

2. Optical Micrograph of **PyrC8Bn** Nanosheets on LbL film

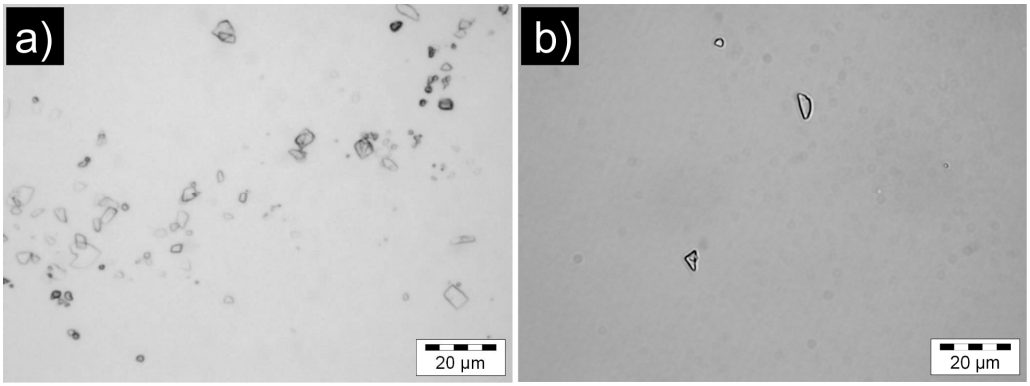


Figure S2. Optical micrograph of **PyrC8Bn** nanosheets attached on negatively charged LbL film at (a) pH 3 and (b) pH 7. The average particle densities were calculated to be 8,830 and 27.9 particles/㎟, at pH 3 and pH 7, respectively.

3. FT-IR Spectra of AuNPs functionalized by various ligands

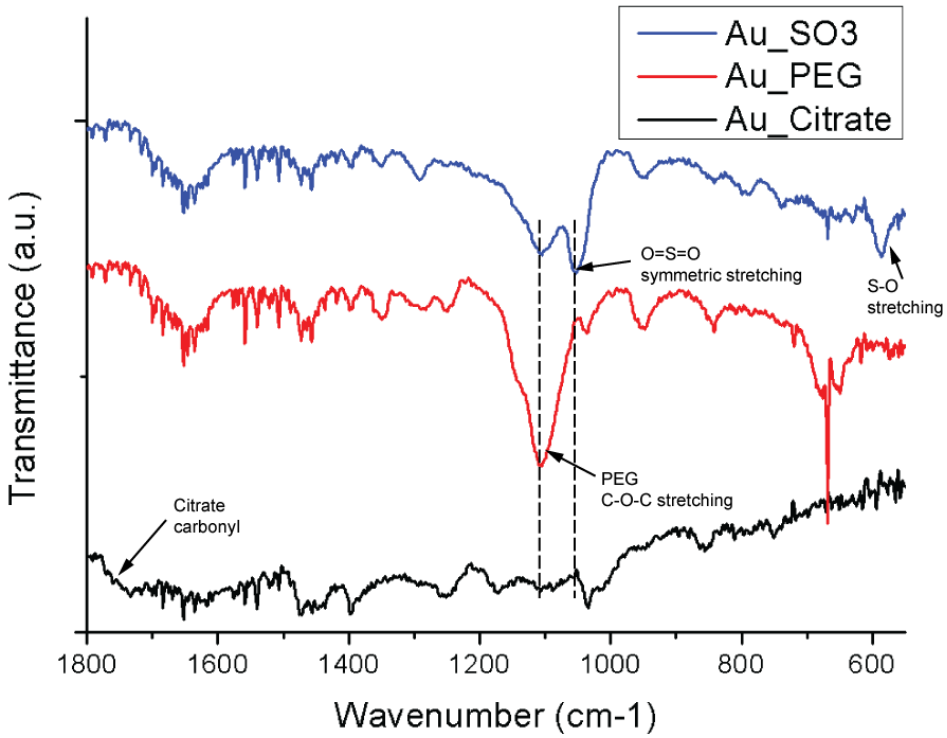


Figure S3. FT-IR spectra of AuNPs functionalized by (a) citrate anions, (b) thiolated PEG, and (c) mercaptoethanesulfonate.

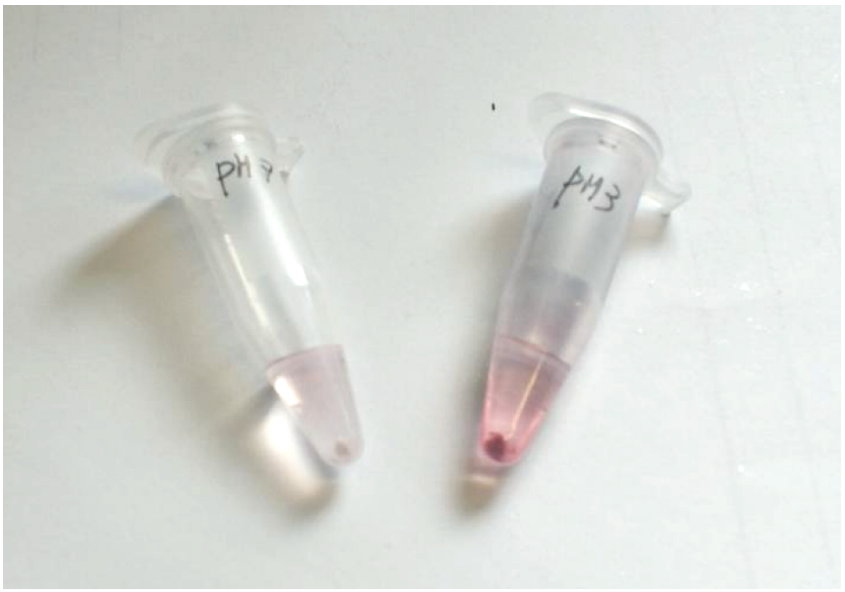


Figure S4. Suspension of AuNPs-immobilized PyrC8Bn nanosheets in H_2O. When the immobilization is performed at pH3, the color of the hybrid complex turned dark red (right), while no significant color change was observed at pH 7 (left).

5. Optical Micrograph of Spherical Hierarchical Structures of **PyrC8Bn**

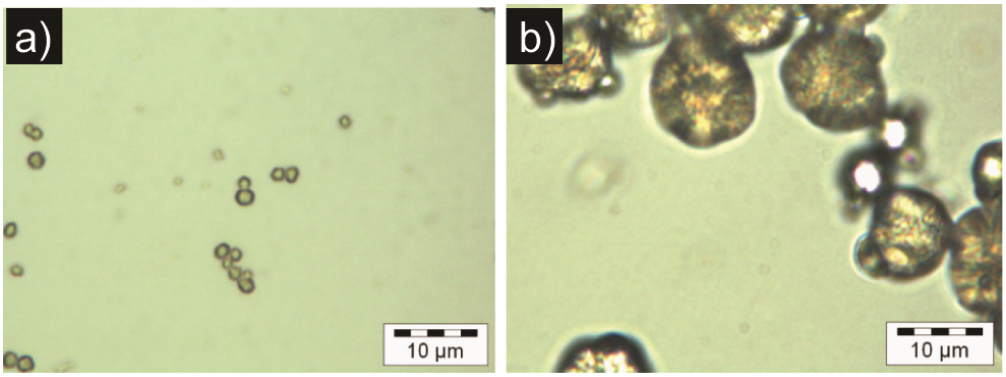


Figure S5. Optical micrographs of hierarchical microspheres of **PyrC8Bn** formed in a mixture of toluene and pyridine (15:1 v/v) by (a) quenching and (b) slow cooling.