Electronic Supplementary Information (ESI)

Photocontrolled Reversible Conversion of Lamellar Supramolecular Assembly Based on Cucurbiturils and Naphthalenediimide Derivative

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1. General information.

Materials.

All reagents were commercially available and used without further purification, unless otherwise noted. Compounds S1, S2 and S3 were synthesized according to the previous reports¹⁻³. Solvent were dried according to procedures described in the literature. Column chromatography was performed on silica gel (200-300 mesh). All experiments were performed in deionized water at 25 °C unless noted otherwise.

Measurements.

¹H NMR and ¹³C NMR spectroscopic data were recorded on a Bruker AVANCE AV400 (400 and 100 MHz). Signal positions were reported in part per million (ppm) relative to the residual solvent peaks or to the peak of Si(CH₃)₄ used as an internal standard. The residual ¹H peak of deuterated solvent appeared at 4.79 ppm in D₂O, 7.26 ppm in CDCl₃, 2.50 ppm in d_6 -DMSO. High-resolution mass spectra were performed on an Agilent 6520 Q-TOF LC/MS with ESI ionization or Varian 7.0T FTMS with MALDI. UV/vis spectra were recorded in a quartz cell (light path 10 mm) on a Thermo Scientific EVOLUTION 300 spectrophotometer equipped with a HAAKE SC 100 temperature controller to keep the temperature at 25 °C. The sample for TEM measurement was prepared by dropping the solution onto a copper grid and then air-dried. The samples were examined by a high-resolution TEM (Tecnai G2 F20 microscope, FEI) equipped with a CCD camera (Orius 832, Gatan) operating at an accelerating voltage of 200 kV.

2. Synthetic procedures.



Figure S1. Synthetic route of compounds S1.

Synthesis of S1

3-bromopropylamine hydrobromide (1.39 g, 6.40 mmol) was added to the solution of 4,4'-bipyridyl (9.98 g, 64.00 mmol) in acetonitrile (100 ml) and refluxed for 1.5 h, then a large amount of precipitation appeared. After cooling, filtered and washed thoroughly with acetonitrile, the product **S1** was obtained as white solid (1.44 g, 60%). ¹H NMR (400 MHz, *d*₆-DMSO, 25 °C) δ 9.26 (d, *J* = 6.0 Hz, 2H), 8.89 (d, *J* = 5.1 Hz, 2H), 8.70 (d, *J* = 6.1 Hz, 2H), 8.06 (d, *J* = 4.8 Hz, 2H), 7.84 (s, 3H), 4.73 (t, *J* = 6.3 Hz, 2H), 2.89 (s, 2H), 2.25 (m, 2H). ¹³C NMR (100 MHz, *d*₆-DMSO, 25 °C) δ 152.31, 151.01, 145.40, 140.80, 125.53, 121.87, 57.35, 35.60, 28.59. HRMS (ESI) for C₁₃H₁₇Br₂N₃: calcd. [M-HBr-Br]⁺: 214.1344, found: 214.1341.



Figure S2. Synthetic route of compounds C4-NDI-MV.

Synthesis of S2

A 30 ml DMF solution of n-butylamine (7 mL, 5.16 g, 70.60 mmol) was added dropwise into the solution of 1,4,5,8-Naphthalenetetracarboxylic dianhydride (19.25 g, 71.80 mmol) in 400 ml DMF under the environment of nitrogen protection. The reaction was heated to 120 °C for 24 h, and then cooled in the freezer for 1 h. The precipitate was filtered off and purified with flash column chromatography (CH₂Cl₂) to afford **S2** as white powder (8.67 g, 38 %). ¹H NMR (400 MHz, d_6 -DMSO, 25 °C) δ 8.70 (m, 4H), 4.06 (t, J = 7.2 Hz, 2H), 1.73 (m, 2H), 1.38 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ 162.23, 158.86, 133.17, 131.21, 128.87, 127.95, 126.86, 122.81, 40.98, 30.09, 20.32, 13.78. HRMS (ESI) for C₁₈H₁₃NO₅: calcd. [M+H]⁺: 324.0871, found: 324.0868.

Synthesis of **S3**

S1 (937.8 mg, 2.50 mmol), **S2** (646.6 mg, 2.00 mmol) and DIPEA (323.1 mg, 2.50 mmol) was dissolved in a 1:1 mixture solution of water/n-

propanol (200 ml), and then heated to 95 °C for 48 h. After concentration pressure, the remained solid was washed under reduced by dichloromethane thoroughly, and then dispersed into large amount of acetonitrile. Filter undissolved substance and concentrate the acetonitrile solution under reduced pressure to afford S3 as an off-white solid (479.6 mg, 40%). ¹H NMR (400 MHz, d_6 -DMSO, 25 °C) δ 9.24 (d, J = 5.9 Hz, 2H), 8.86 (s, 2H), 8.70 (s, 4H), 8.64 (d, J = 5.7 Hz, 2H), 8.02 (s, 2H), 4.76 (s, 2H), 4.22 (s, 2H), 4.08 (s, 2H), 2.42 (s, 2H), 1.66 (s, 2H), 1.36 (m, 2H), 0.94 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, d_6 -DMSO, 25 °C) δ 162.98, 162.52, 152.25, 150.97, 145.40, 140.69, 130.43, 126.37, 126.26, 126.19, 126.06, 125.26, 121.80, 58.50, 37.14, 29.72, 29.53, 19.77, 13.67. HRMS (ESI) for $C_{31}H_{27}BrN_4O_4$: calcd. [M-Br]⁺: 519.2032, found: 519.2032.

Synthesis of C4-NDI-MV

S3 (299.2 mg, 0.50 mmol) was dissolved in DMF (10 mL), then iodomethane (0.31 ml, 706.7 mg, 5.00 mmol) was added under the environment of nitrogen protection at 120 °C for 12 h. The reaction mixture was poured into 50 mL diethyl ether, and then the precipitate was collected by filtration, washed with diethyl ether for several times, dried overnight in a vacuum to give product **C4-NDI-MV** as orange solid (333.6 mg, 90%). ¹H NMR (400 MHz, D₂O, 25 °C) δ 9.21 (d, *J* = 6.5 Hz, 2H), 9.03 (d, *J* = 6.3 Hz, 2H), 8.62 (m, 4H), 8.55 (d, *J* = 6.7 Hz, 2H), 8.49

(d, J = 6.8 Hz, 2H), 4.90 (m, 2H), 4.48 (s, 3H), 4.27 (s, 2H), 4.07 (d, J = 6.9 Hz, 2H), 2.58 (s, 2H), 1.65 (s, 2H), 1.37 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, d_6 -DMSO, 25 °C) δ 163.60, 163.12, 149.03, 148.54, 147.14, 146.41, 131.00, 130.94, 126.96, 126.93, 126.90, 126.80, 126.68, 126.53, 59.49, 48.53, 37.61, 30.42, 30.06, 20.28, 14.21. HRMS (MALDI-TOF) for C₃₂H₃₀BrIN₄O₄: calcd. [M-Br-I]⁺: 534.2267, found: 534.2265.

3. Characterization of C4-NDI-MV and precursors.

7.84 7.87 7.87 7.84 8.87 8.71 8.69 8.05 8.05 7.84



-4.73 -4.73 -4.71 -4.71 -4.71 -2.33 -2.33 -2.27 -2.27 -2.25

Figure S3. ¹H NMR spectrum (400 MHz, d_6 -DMSO, 25 °C) of S1.



Figure S4. ¹³C NMR spectrum (100 MHz, d_6 -DMSO, 25 °C) of S1.



Figure S5. HRMS spectrum of S1 ($C_{13}H_{17}Br_2N_3$). The peak at m/z 214.1341 is assigned to [M-HBr-Br]⁺, calcd.: 214.1344.



Figure S7. ¹³C NMR spectrum (100 MHz, CDCl₃, 25 °C) of S2.



Figure S8. HRMS spectrum of S2 ($C_{18}H_{13}NO_5$). The peak at m/z 324.0868 is assigned to [M+H]⁺, calcd.: 324.0871.

9.25 9.25 8.70 8.65 8.63 8.63 A.76 4.02 4.08 4.08 2.42 7.1.41 1.1.40 1.1.40 0.09 0.09 0.03



Figure S9. ¹H NMR spectrum (400 MHz, d_6 -DMSO, 25 °C) of S3.



Figure S10. ¹³C NMR spectrum (100 MHz, d_6 -DMSO, 25 °C) of S3.



Figure S11. HRMS spectrum of S3 ($C_{31}H_{27}BrN_4O_4$). The peak at m/z 519.2032 is assigned to [M-Br]⁺, calcd.: 519.2032.



Figure S12. ¹H NMR spectrum (400 MHz, D_2O , 25 °C) of C4-NDI-



Figure S13. ¹³C NMR spectrum (100 MHz, d_6 -DMSO, 25 °C) of C4-

NDI-MV.



Figure S14. MALDI-TOF-HRMS spectrum of S3 ($C_{32}H_{30}BrIN_4O_4$). The peak at m/z 534.2265 is assigned to [M-Br-I]⁺, calcd.: 534.2267.

4. XRD pattern of C4-NDI-MV



Figure S15. XRD pattern of self-assembly formed by C4-NDI-MV



5. Job's plot of C4-NDI-MVCCB[7]

Figure S16. UV/vis spectra of C4-NDI-MV \subset CB[7] complex ([C4-NDI-MV] + [CB[7]] = 0.02 mM) with the molar ratio of C4-NDI-MV = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 in aqueous solution, measured in a 10 mm quartz cell. Inset: Job's plot showing the 1:1 stoichiometry of the complex between C4-NDI-MV and CB[7], where ΔA means the absorbance difference value with free C4-NDI-MV under the same concentration at 261 nm.

6. Job's plot of C4-NDI-MV⊂CB[8]



Figure S17. UV/vis spectra of C4-NDI-MV \subset CB[8] complex ([C4-NDI-MV] + [CB[8]] = 0.02 mM) with the molar ratio of C4-NDI-MV = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 in aqueous solution, measured in a 10 mm quartz cell. Inset: Job's plot showing the 1:1 stoichiometry of the complex between C4-NDI-MV and CB[8], where ΔA means the absorbance difference value with free C4-NDI-MV under the same concentration at 261 nm.

7. MALDI-TOF HRMS spectra



Figure S18. MALDI-TOF-HRMS spectrum of C4-NDI-MV⊂CB[7]



Figure S19. MALDI-TOF-HRMS spectrum of C4-NDI-MV⊂CB[8]

8. Association constant of C4-NDI-MVCCB[7]



Figure S20. UV/vis spectral changes of C4-NDI-MV upon addition of CB[7] in water ([C4-NDI-MV] = 2×10^{-5} M, [CB[7]] = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.4, 2.8, 3.2, 3.6 and 4.0×10^{-5} M, respectively). Inset: The nonlinear least-squares analysis of absorbance at 270 nm to calculate the K_a value for C4-NDI-MV⊂CB[7] complex.

9. Association constant of C4-NDI-MVCCB[8]



Figure S21. UV/vis spectral changes of C4-NDI-MV upon addition of CB[8] in water ([C4-NDI-MV] = 1×10^{-5} M, [CB[8]] = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.4, 1.7 and 2.0×10^{-5} M, respectively). Inset: The nonlinear least-squares analysis of absorbance at 270 nm to calculate the K_a value for C4-NDI-MV_CCB[8] complex.

10. TEM of disassembly of C4-NDI-MV⊂CB[7]



Figure S22. TEM image of C4-NDI-MV \subset CB[7] after adding α -CD ([C4-NDI-MV] = [CB[7]] = [α -CD] = 0.03 mM).

11. Absorption spectra of **Azo⊂α-CD** by alternate irradiation with UV and visible light



Figure S23. Absorption spectra of **Azo⊂α-CD** in water after UV irradiation at 365 nm, Inset: Absorbance changes at 333 nm versus irradiation time.



Figure S24. Cycling of the photocontrolled *trans* and *cis* isomerization of **Azo** $\sub{\alpha}$ -**CD** ([**Azo**] = [α -**CD**] = 0.05 mM) by alternate irradiation with UV and visible light at 25 °C

12. Absorption spectra of the four-component by irradiation with UV light



Figure S25. Absorption spectra of a four-component mixture of after UV irradiation at 365 nm ([C4-NDI-MV] = [CB[7]] = [Azo] = $[\alpha$ -CD] = 0.05 mM), Inset: Absorbance changes at 340 nm versus irradiation time.