Electronic Supplementary Information (ESI)

Photocontrolled morphological conversion and chiral transfer of snowflake-like supramolecular assembly based on azobenzene-bridged bis(dibenzo-24-crown-8) and a cholesterol derivative

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Experimental Section

Instrumentation and methods

All the reagents and solvents were commercially available and used as received without further purification. The precursor 4-chloromethylene dibenzo-24-crown-8 ether was prepared according to literature procedures. Column chromatography was performed on silica gel (200-300 mesh). NMR spectra were recorded on Bruker AV400 instrument at 25 °C and chemical shifts were recorded in parts per million (ppm). Electrospray ionization (ESI) mass spectra were measured on a Q-TOF LC-MS. High-resolution matrix-assisted laser desorption/ionization spectra (HR-MALDI) were measured on a Varian 7.0T FT-MS. The UV light irradiation experiment was carried out using a ZF-7A lamp (365 nm, 8 W), and the visible light irradiation experiment ($\lambda > 420$ nm) was carried out using a CEL HXF300 xenon lamp with cutoff filter. UV/vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. The sample for TEM measurements was prepared by dropping the solution onto a copper grid. The grid was 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 with a CCD camera (Orius 832, Gatan) operating at an accelerating voltage of 200Kv. The molecular packing model of supramolecular assemblies voltage of 200 kV. CD spectra were collected on a JASCO J-715 Circular Dichroism spectroimeter.
Scheme S1. Synthetic route of 1 and 2.
Synthesis of azobenzene-bridged bis(dibenzo-24-crown-8) (1).

4,4'-Dihydroxyazobenzene (60.46 mg, 0.28 mmol) was added to a stirred solution of 4-chloromethylenedibenzo-24-crown-8 ether (350 mg, 0.7 mmol) in acetone (80 ml), to which K$_2$CO$_3$ (681.16 mg, 4.94 mmol) was added under argon at room temperature. The mixture was stirred under reflux for 7 days. After cooling to room temperature, the mixture was filtered and the filtrate was evaporated under reduced pressure to remove acetone. The residue was dissolved in chloroform (50 ml) and washed with water (2 × 50 ml), dried with anhydrous MgSO$_4$ and evaporated to a yellow residue which was purified by silica gel column chromatography using chloroform-methanol solution (v/v = 200:1) as eluent to give azobenzene-bridged bis(dibenzo-24-crown-8) (123.8 mg) as a yellow powder (yield 38.97 %).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J = 8.7$ Hz, 4H), 7.05 (d, $J = 8.8$ Hz, 4H), 6.97 (d, $J = 5.1$ Hz, 4H), 6.88 (s, 10H), 5.03 (s, 4H), 4.16 (s, 16H), 3.92 (s, 16H), 3.83 (s, 16H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 159.70, 148.01, 147.86, 147.82, 146.12, 128.44, 123.30, 120.37, 119.79, 114.03, 112.97, 112.70, 112.47, 70.26, 69.17, 68.43, 68.34. MALDI-MS for 1 (C$_{62}$H$_{74}$N$_2$O$_{18}$): calcd. [M+Na$^+$]: 1157.4834, found: 1157.4833.

Synthesis of cholesteryl aldehyde benzoate (3).

4-Formylbenzoic acid (555 mg, 3.7 mmol), cholesterol (1.43 g, 3.7 mmol), DMAP (0.23 g, 1.9 mmol) and DCC (0.84 g, 4.07 mmol) were dissolved in chloroform (100 ml). The mixture was stirred 4 h under argon at room temperature. The mixture was evaporated under reduced pressure to remove chloroform. The residue was purified by silica gel column chromatography using petroleum ether-chloroform (v/v = 5:3) as eluent to give product (1.13 g) as a white solid (yield 58.9%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.09 (s, 1H), 8.17 (d, $J = 7.6$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 2H), 5.42 (s, 1H), 4.89 (s, 1H), 2.46 (d, $J = 7.6$ Hz, 2H), 2.00 (s, 3H), 1.85-1.71 (m, 3H), 1.62-1.44 (m, 7H), 1.38-1.29 (m, 4H), 1.17-1.05 (m, 9H), 0.99 (d, $J = 7.0$ Hz, 3H), 0.91 (d, $J = 6.2$ Hz, 3H), 0.86 (d, $J = 6.1$ Hz, 6H), 0.681 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 190.54, 163.86, 138.38, 138.04, 134.83, 129.11, 128.39, 122.00, 74.35, 55.69, 55.18, 49.06, 38.52, 36.00, 34.79, 30.93, 30.88, 27.22, 27.00, 26.84, 22.85, 21.80, 21.56, 20.06, 18.35, 17.73, 10.86.
Synthesis of methylenebenzylamine benzoic acid cholesterylamine (4).
Cholesteryl aldehyde benzoate (0.518 g, 1 mmol), benzylamine (0.13 g, 1.2 mmol) and triethylamine (0.24 g, 4 mmol) were dissolved in methanol and chloroform. The mixture was stirred under reflux for 1 day under argon. After cooling to room temperature, the sodium borohydride (0.61 g, 16 mmol) was added to the reaction system under ice bath conditions. Then the mixture was stirred 24 h under argon at room temperature. Then water was added to stop the reaction. After the solution was concentrated, the residue was dissolved with CH$_2$Cl$_2$ (50 ml) and washed with H$_2$O (2 × 50 ml). The organic phase was dried by MgSO$_4$ and evaporated off. Then the residue was purified by column chromatography using chloroform as eluent to give product (0.41 g) as a white solid (yield 68.8%). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.02 (d, $J$ = 8.0 Hz, 2H), 7.42 (d, $J$ = 8.0 Hz, 2H), 7.34 (d, $J$ = 4.2 Hz, 5H), 5.44 (s, 1H), 4.87 (s, 1H), 3.83 (d, $J$ = 24.7 Hz, 4H), 2.48 (d, $J$ = 7.7 Hz, 2H), 2.10-1.95 (m, 3H), 1.84-1.69 (m, 3H), 1.65-1.44 (m, 7H), 1.43-1.32 (m, 4H), 1.19-1.07 (m, 9H), 1.05-0.99 (m, 3H), 0.95 (d, $J$ = 6.3 Hz, 3H), 0.89 (d, $J$ = 6.1 Hz, 6H), 0.71 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 165.91, 145.51, 140.08, 139.70, 129.73, 129.58, 128.47, 128.17, 127.92, 127.08, 122.78, 74.52, 56.73, 56.20, 53.17, 52.79, 50.09, 42.37, 39.80, 39.58, 38.29, 37.10, 36.69, 36.25, 35.86, 31.99, 31.93, 28.30, 28.06, 27.96, 24.35, 23.91, 22.90, 22.64, 21.11, 19.44, 18.79, 11.93.

Synthesis of 2.
Methylenebenzylamine benzoic acid cholesterylamine: (154.96 mg, 0.25 mmol), trifluoroacetic acid (144.98 mg, 1.25 mmol) were dissolved in chloroform. The mixture was stirred 2 h at room temperature. Then the solvent was evaporated to obtain a white solid. Then the solid was dissolved in chloroform and methional. A saturated solution of NH$_4$PF$_6$ was added to the solution until no further precipitation was observed. The precipitate was filtered off, washed with water and dried to obtain aim product as a yellow solid (119.1 mg, yield 62%). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.01 (d, $J$ = 8.2 Hz, 2H), 7.41 (d, $J$ = 8.2 Hz, 2H), 7.35 (d, $J$ = 4.4 Hz,4H) 7.30-7.27(m,1H), 5.42 (d, $J$ = 3.9 Hz, 1H), 4.90-4.81 (m, 1H), 3.868 (s, 2H), 3.808 (s, 2H), 2.46 (d, $J$ = 7.7 Hz, 2H), 2.07-1.96 (m, 3H), 1.94-1.71 (m, 3H), 1.63-1.42 (m, 7H), 1.40-1.29 (m, 4H), 1.19-1.07 (m, 9H), 1.05-0.98 (m, 3H), 0.93 (d, $J$ = 6.5 Hz, 3H),
0.88 (d, J = 1.7 Hz, 3H), 0.87 (d, J = 1.6 Hz, 3H), 0.695 (s, 3H). 13C NMR (101 MHz, CDCl3):
δ 164.85, 143.74, 138.65, 138.36, 128.71, 127.48, 127.23, 127.00, 126.20, 121.73, 73.51,
55.68, 55.13, 51.92, 51.52, 49.04, 41.31, 38.73, 38.50, 37.21, 35.64, 35.17, 34.78, 30.92,

Figure S1. 1H NMR spectrum of 1 in CDCl3, 400 MHz, 298 K.
Figure S2. $^{13}$C NMR spectrum of 1 in CDCl$_3$, 100 MHz, 298 K.

Figure S3. MADILI-TOFMS spectrum of 1 (C$_{62}$H$_{74}$N$_2$O$_{18}$): calcd. [M+Na$^+$]: 1157.4834, found: 1157.4833.
Figure S4. $^1$H NMR spectrum of 3 in CDCl$_3$, 400 MHz, 298 K.

Figure S5. $^{13}$C NMR spectrum of 3 in CDCl$_3$, 100 MHz, 298 K.
**Figure S6.** $^1$H NMR spectrum of 4 in CDCl$_3$, 400 MHz, 298 K.

**Figure S7.** $^{13}$C NMR spectrum of 4 in CDCl$_3$, 100 MHz, 298 K.
Figure S8. $^1$H NMR spectrum of 2 in CDCl$_3$, 400 MHz, 298 K.

Figure S9. $^{13}$C NMR spectrum of 2 in CDCl$_3$, 100 MHz, 298 K.
Figure S10. The ESI-MS spectrum of 2 (C_{42}H_{60}NO_{2}PF_{6}): calcd. [M–PF_{6}]: 610.4619, found: 610.4620.

Figure S11. Absorption spectra of 1 upon irradiation at 365 nm for different time in CH_{2}Cl_{2} at 298 K ([I] = 3×10^{-5} M).
Figure S12. Partial $^1$H NMR spectra (400 MHz, CDCl$_3$, 298 K) of a) trans-1, b) sample (a) irradiated with 365 nm light for 50 min, c) sample (b) irradiated with > 420 nm light for 30 min.

Figure S13. UV-vis titration spectra of trans-1 (2 × 10$^{-5}$ M) upon addition of 2 ((0-160) × 10$^{-6}$ M) in CH$_2$Cl$_2$ at 298 K, Inset: Nonlinear least squares fit of the absorption changes at 257 nm to determine the complex stability constant (K) as 13400 ± 700 M$^{-1}$. 

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Figure S14. SEM image of a) *trans*-1, b) *cis*-1, DLS data of c) *trans*-1, d) *cis*-1. All samples were prepared in CH₂Cl₂ at 298 K. ([*trans*-1] = [*cis*-1] = \(3.3 \times 10^{-4}\) M).

Scheme S2. Schematic representations of 2.
Figure S15. SEM images of 2⊂trans-1 in CH₂Cl₂ upon the irradiation of 365 nm light for a) 0 min, (2⊂trans-1) b) 50 min (2⊂cis-1) (1: 2 = 1:2, [1] = 3.3 × 10⁻⁴ M).

References