Supporting Information

Photoresponsive Chiral Nanotubes of Achiral Amphiphilic Azobenzene

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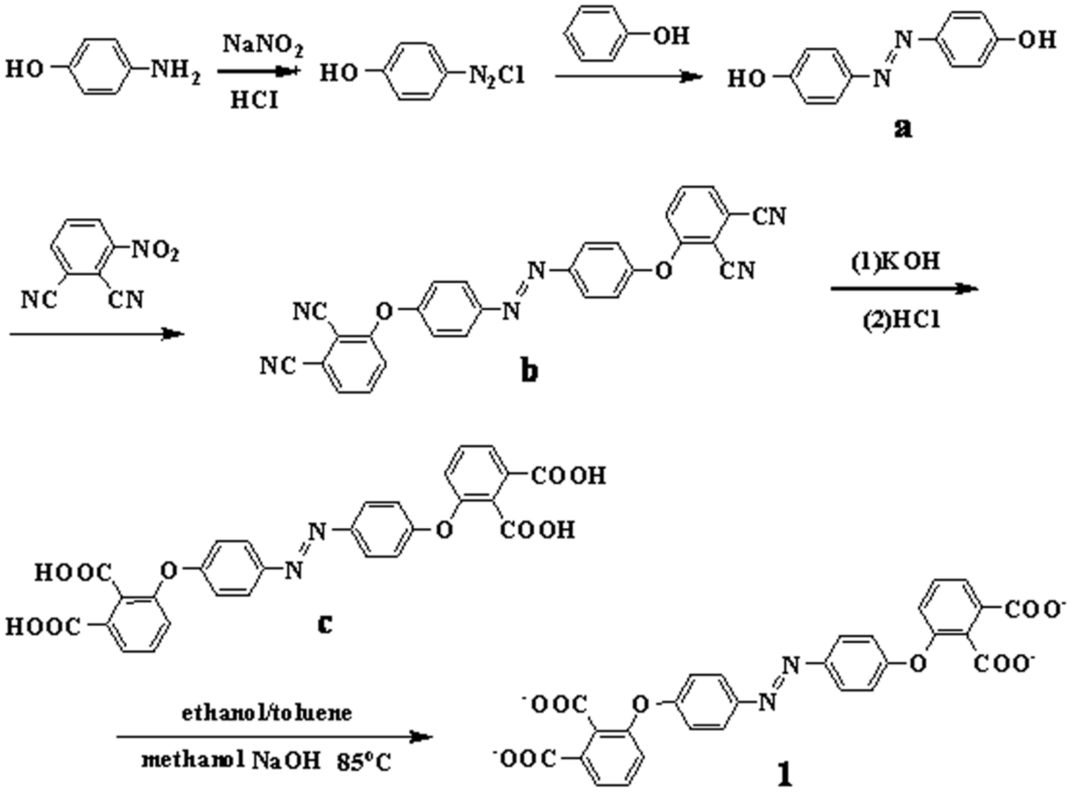
1. Experimental

1.1 Synthesis of 4,4-di(2,3- dicarboxylphenoxyl) azobenzene 1



Scheme S1. Synthesis of the amphiphilic molecule **1**.

The synthesis route was depicted in Scheme S1. The procedures are as follows:

4,4-dihydroxy azobenzene a.

4-Aminophenol (5 g, 0.046 mol) was added to the hydrochloric acid solution (20%, 23 ml), which was stirred until it was dissolved. The water solution (15 ml) of sodium nitrite (3.3 g, 0.0478 mol) was added dropwisely to the above solution within 1 h and then stirred for another 30 minutes. The temperature of the whole process was kept at 2 °C. Phenol (4.35 g, 0.0463mol) and sodium hydroxide (1.85 g, 0.0463mol) were dissolved in water (50 ml), and added dropwisely to the above diazonium salt solution within 1 h with the pH value maintained at about 8 and the temperature kept under 2 °C. The reaction was completed after stirring for another 3 h at 2 °C. After stewing at room temperature for 24h, black product was precipitated, and was chromatographed on silica gel using hexane and acetone (v/v = 1/2) as eluent. The second fraction was collected and evaporated, giving yellow solid (4.9g) with yield of 49.89%. ^{1}H NMR (Acetone, 300 MHz), δ (ppm): 8.94 (s, 2 H, *H*O), 7.82-7.77 (d, 4 H, *Ar*), 7.01-6.96 (d, 4 H, *Ar*), MS: *m/z* 2123.0666 [M-H]$^+$.

4,4-di(2,3- dicyanophenoxyl) azobenzene b.

4,4-dihydroxy azobenzene (0.62 g 0.0029 mol) and sodium carbonate (0.636 g, 0.006 mol) were dissolved in DMF (30 ml) and was stirred at 60 °C for 30 min. 2,3-dicyano nitrobenzene (1.038 g, 0.006 mol) was added to the above solution, which was then heated and stirred at 80°C for 28 h. After the reaction completed, solution was cooled down to the room temperature and was poured into the water to get the yellow precipitate. The precipitate gathered by filtering and washed with water and acetone in turn. Finally, dried product (0.735g) was obtained with yield of 54.4%. ^{1}H NMR (DMSO, 300 MHz), δ (ppm): 8.04-8.01 (d, 4 H, azo*benzene ring*), 7.96-7.92 (m, 2 H, *benzene ring*), 7.89-7.87 (d, 2 H, *benzene ring*), 7.54-7.50 (d, 2 H, *benzene ring*), 7.46-7.43 (d, 4 H, azo*benzene ring*), MS: *m/z* 467.1251. $[M+H]^+$.

4,4-di(2,3- dicarboxylphenoxyl) azobenzene c.

4,4-di(2,3-dicyanophenoxyl) azobenzene (0.139 g, 0.298 mmol) and potassium hydroxide (0.2 g, 3.58 mmol) were added to the mixed solvents of ethanol and H_2O (v/v = 1/1) and stirred at 90°C for 45 h until the solution became clear. After then, solution was filtered to remove the small amount of the impurity. The pH value of the filtrate was adjusted to 5 and the precipitate was obtained. After filtering, washing with water and drying, product (0.146 g) with yield of 90.7% was obtained. ^{1}H NMR (300 MHz, DMSO), δ (ppm): 7.87-7.85 (d, 4H, azo*benzene ring*), 7.79-7.77 (d, 2 H, *benzene ring*), 7.51-7.45 (m, 2 H, *benzene ring*), 7.28-7.26 (d, 2H, *benzene ring*), 7.05-7.02 (d, 2H, azo*benzene ring*). MS: *m/z* 542.1221.

Azobenzene aromatic acid sodium salt 1.

4,4-di(2,3- dicarboxylphenoxyl) azobenzene (0.7 g, 1.3 mmol) was added to the mixed solvents of ethanol (27 ml) and toluene (3 ml). And it was heated to reflux at 85°C for 1h. Then the methanol solution (15 ml) of sodium hydroxide (0.265 g) was added to the above solution and heated to reflux at 85°C for another 12 h. Yellow precipitate appeared and gathered by filtering. The final product (0.852g) was obtained after washed with ethanol. The yield is 81.8%. ^{1}H NMR (300 MHz, D_2O), δ (ppm): 7.76 (d, 4H), 7.46 (d, 2 H), 7.29 (m, 2 H), 7.08 (d, 6H). MS: *m/z* 631.2488. $[M+H]^+$.

1.2 Preparation of Aqueous Dispersion of Self-Assemblies.

The azobenzene aromatic acid sodium salt **1** (6 mg) was dissolved into pure deionized water (18 ml) at room temperature. The solution was acidified by adding certain amount of HCl (1.2×10^{-1} mol•L^{-1}) until the pH reached to 2.77. Then red precipitate was formed slowly. After the dispersion was standing for 20 minutes, the nanotubes with nanoribbons were formed as proved by TEM observation. After incubation of the aggregates for more than 7 days, large amount of nanotubes with uniform diameter and length of more than 30 micrometers were obtained. The aggregates can be transferred and casted onto a copper grid by pipetting, and air-dried at ambient condition for more than 7 days before the electron microscopy characterization. Each of the morphologies of the assembled structures can stand for more than 1 month.

2. Results

2.1 pH titration profile with NaOH standard solution.

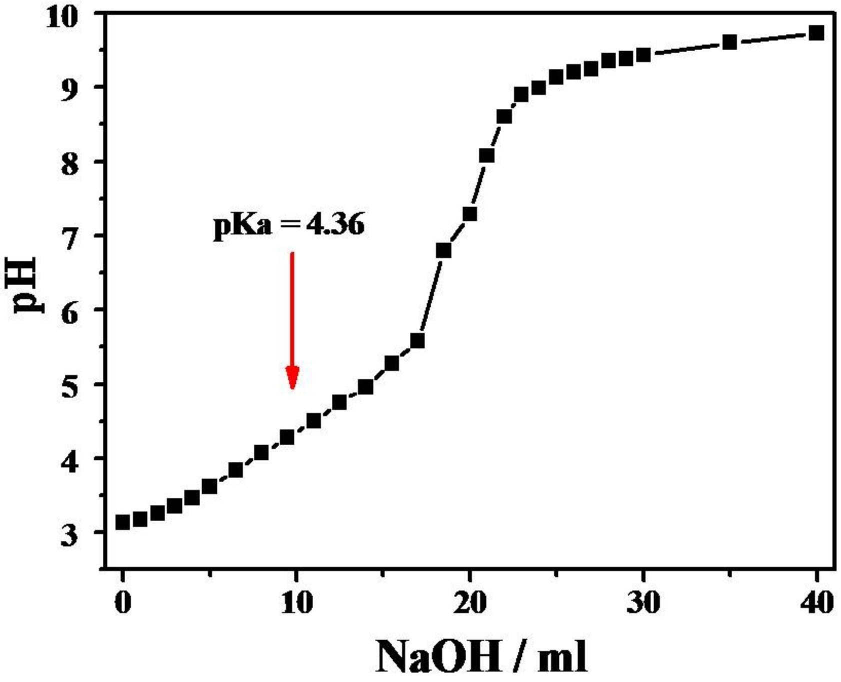


Figure S1. pH titration profile of the bolaamphiphile azobenzene (0.01058 mmol) with NaOH (2.12 mM) standard solution.

2.2 ^{1}H NMR spectroscopy of the photoisomerization of the amphiphilic azobenzene.

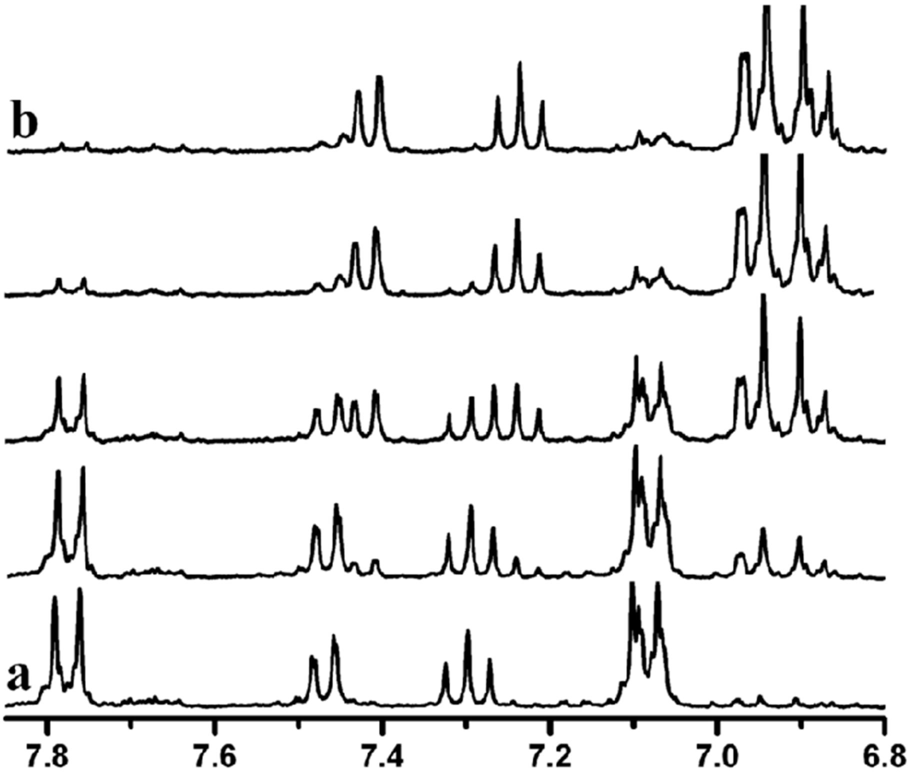


Figure S2. ^{1}HNMR spectra of the sodium salt of the amphiphilic azobenzene in D_2O before UV irradiation (a), the changes observed upon UV illumination for 0, 30, 50, 65, and 75 min (from bottom to top), respectively; and arriving at the PSS (b).

2.3 Circular dichroism characterization.

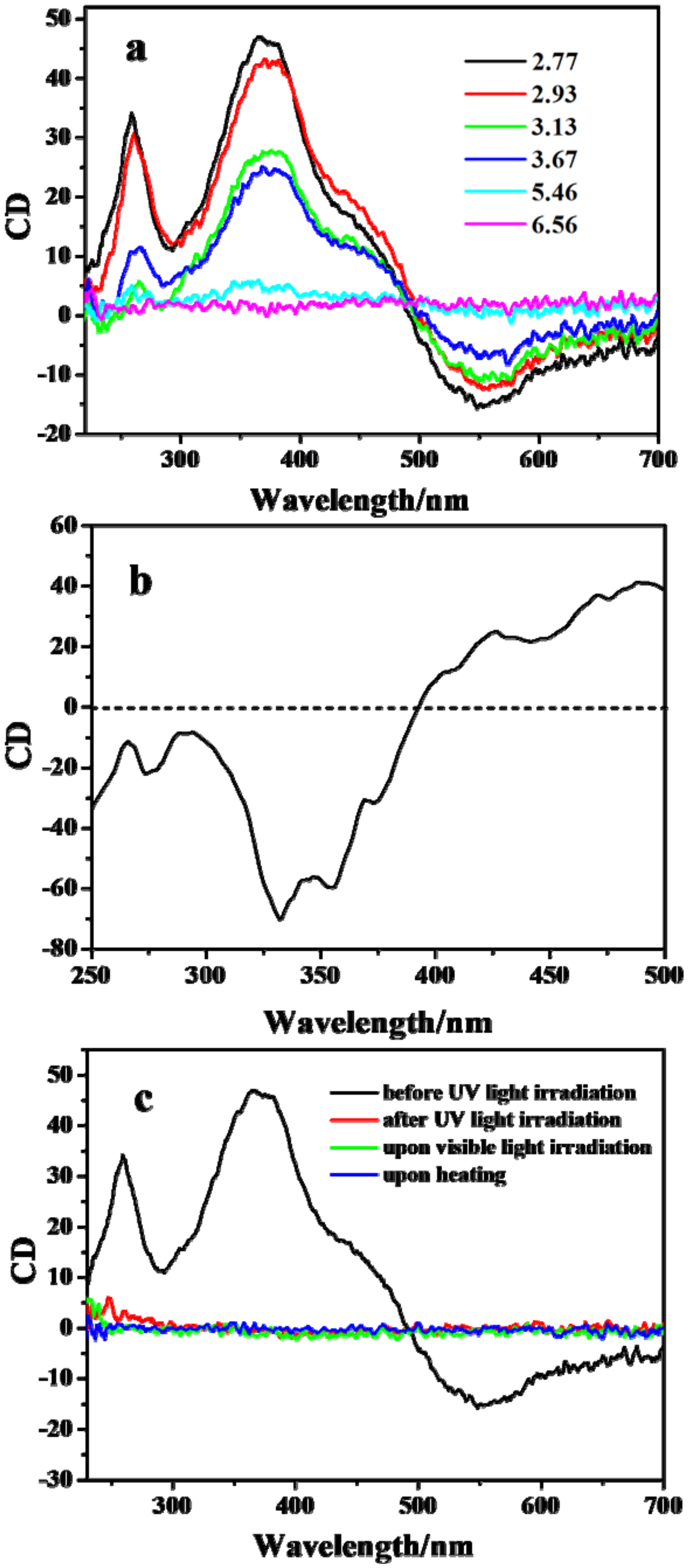


Figure S3. CD spectra of (a) the amphiphilic azobenzene suspension at different pH, (b) CD spectra of the self-assembled aggregation at pH 2.77 with inverse signals, and (c) the self-assembled suspensions upon UV irradiation, and after exposed to visible light for more than 15 min.

2.4 Characterization of nanotubes.

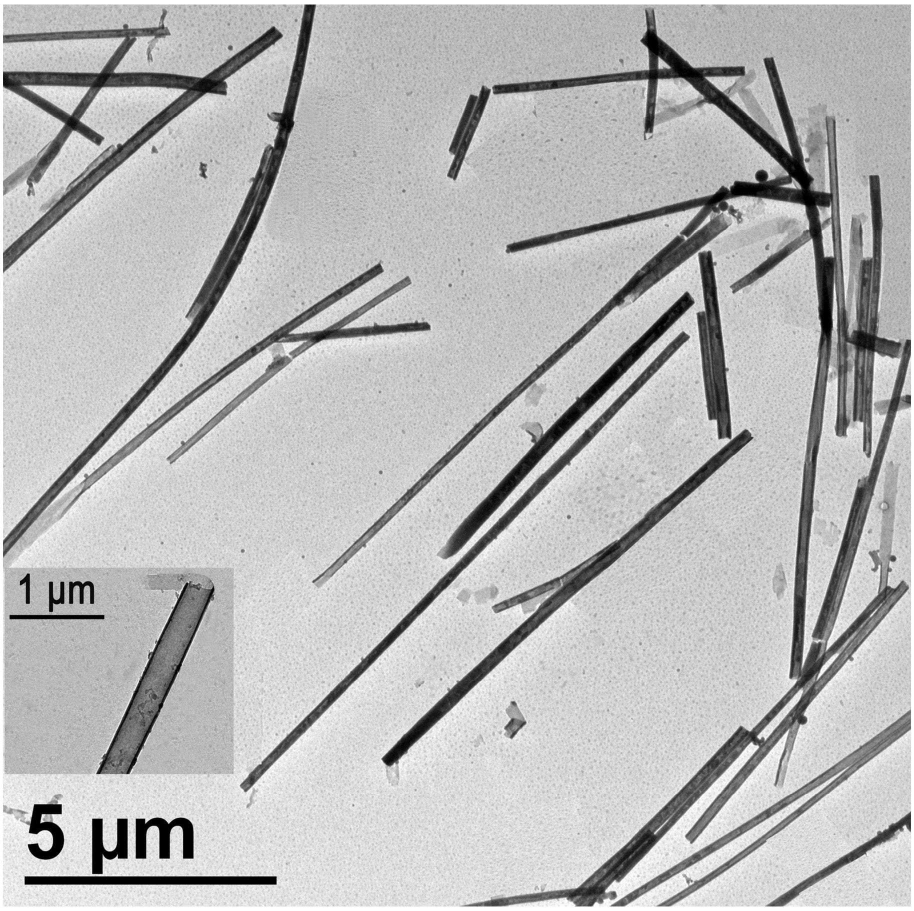


Figure S4. Transmission electron microscopy (TEM) image of the nanotubes.

2.5 TEM characterization of the aggregates upon light irradiation or heating

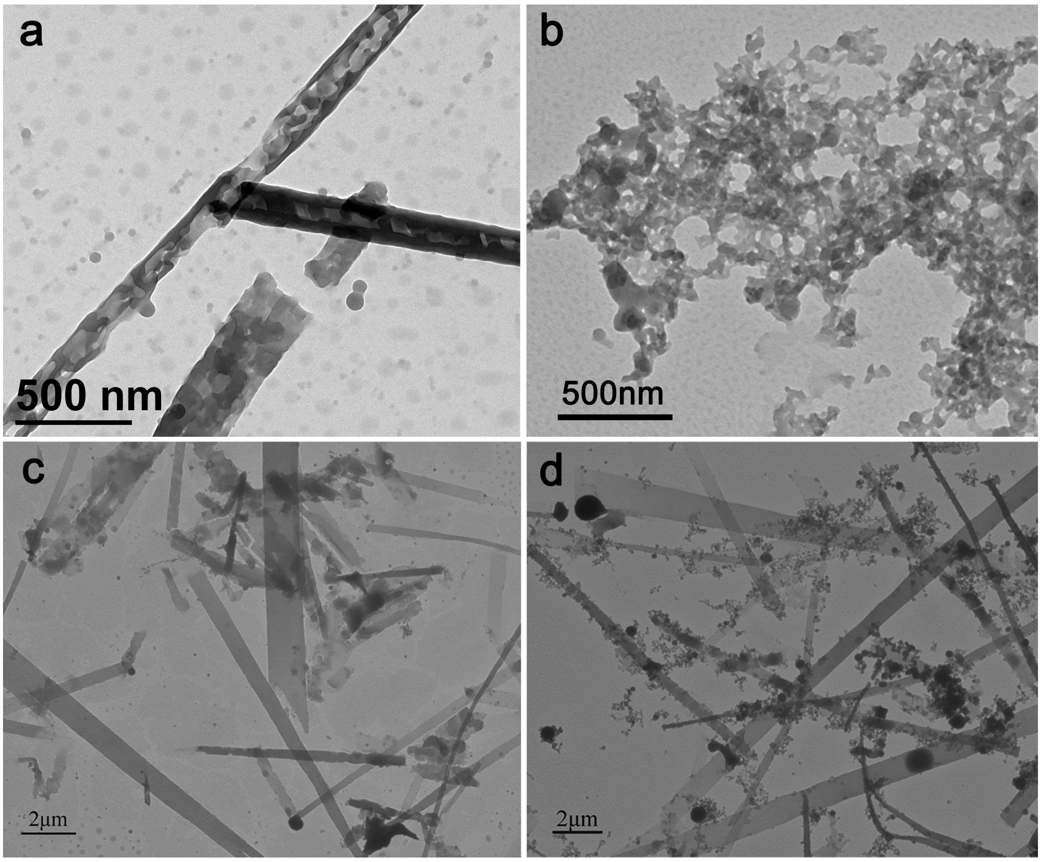


Figure S5. TEM images of the porous structure obtained by exposure of the nanotubes to UV light for 15 min (a), and for more than 2h (b); the nanobelts formed by morphological recovering from the porous nanostructures in response to visible-light (λ > 400 nm) irradiation for 2h (c), and heating at 60 °C for 1h (d).