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1. Materials and Methods

General. All commercially available reagents and solvents were reagent grade and used without further purification. Column chromatography was performed using 63–210 µm silica gel. All the solvents for the preparation of the assemblies were spectral grade and used without further purification. Preparative gel permeation chromatography (GPC) was performed on a recycling preparative HPLC (LC-9225NEXT, Japan Analytical Industry) equipped with GPC columns JAIGEL-1H + 2H). ^{1}H and ^{13}C NMR spectra were recorded on Bruker-AVANCE III-400M and JEOL JNM-ECS 500 NMR spectrometers and chemical shifts are reported in parts per million (ppm, δ) with the signal of tetramethylsilane (TMS) as internal standard. ESI-MS spectra were measured on an Exactive (Thermo Scientific). UV/Vis absorption spectra were recorded on JASCO V-760 spectrophotometer with a Peltier device temperature-control unit using a screw-capped quartz cuvette of 1.0-mm path length. Fourier transform infrared (FT-IR) spectra were recorded on JASCO FT/IR-4600 spectrometer. Dynamic light scattering (DLS) measurements were conducted on Zetasizer Nano (Malvern Instruments) using noninvasive backscattering (NIBS) technology under 4.0-mW He-Ne laser (λ = 633 nm). The scattering angle was set at 173°. Atomic force microscopy (AFM) images were acquired under ambient conditions using a Multimode 8 Nanoscope V (Bruker AXS) in Scanasyst mode (cantilever: SCANASYST-AIR; spring constant = 0.9 N/m; frequency = 70 kHz). The samples were prepared by spin coating aliquots of the assembling solution onto freshly cleaved highly-oriented pyrolytic graphite (HOPG, 5 mm × 5 mm). SEM images were acquired on JSM-6510 scanning electron microscopy. The samples were prepared by drop-casting aggregate solutions on a silicon substrate, dried under vacuum for 24 h, and sputtered with Pt using JFC-1600 (JEOL) Auto Fine Coater before observation.

X-ray diffraction (XRD) analysis of precipitates. XRD patterns of bulk samples were measured using 0.154-nm X-ray (CuKα-beam) in the transparent mode using NANO-Viewer (Rigaku Corp.) equipped with a Pilatus 100K (Dectris) detector. The scattering angle (2θ) and the position of the incident X-ray beam on the detectors were calibrated using several orders of layer reflections from silver behenate (d = 58.380 Å). The sample-to-detector distances were 69 cm for **2** and 7.6 cm for **3**, respectively. The obtained diffraction patterns were integrated along the Debye–Scherrer ring to afford 1D intensity data using 2DP software (Rigaku Corp.)

Calculation of α_{agg}: Degree of aggregation (α_{agg}) was calculated from molar extinction coefficient (ε) at 354 nm for **2**, and at 355 nm for **3** in temperature-dependent UV/Vis spectra, based on following equation (S1):

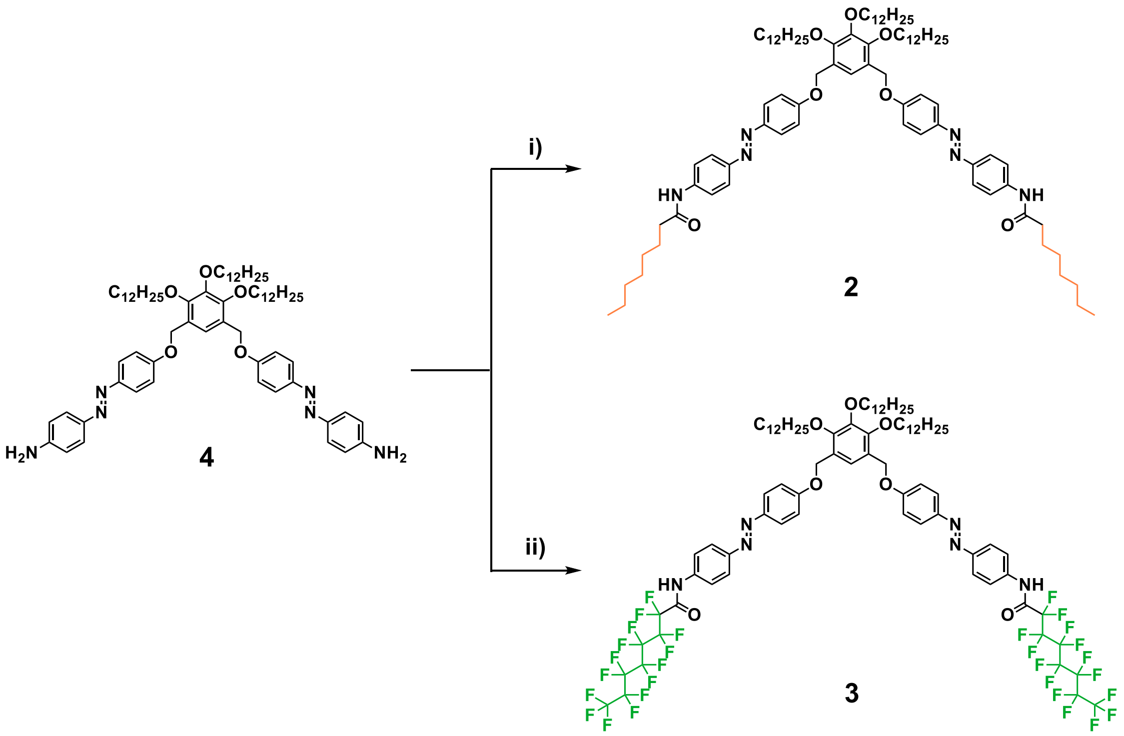
$$\alpha_{\mathrm{agg}} = \frac{\varepsilon_{\mathrm{max}} - \varepsilon}{\varepsilon_{\mathrm{max}} - \varepsilon_{\mathrm{min}}} \qquad \text{S1}$$

wherein $\varepsilon_{\mathrm{max}}$ is the molar extinction coefficient of fully aggregated state estimated from the spectra at 20 °C ($\alpha_{\mathrm{agg}} = 1$), and $\varepsilon_{\mathrm{min}}$ is the molar extinction coefficient of fully monomeric state estimated from the spectra at 90 °C ($\alpha_{\mathrm{agg}} = 0$).

Photoirradiation Experiments: Photoirradiation experiments were performed using 365 nm UV light (LED lamp, 17 mW/cm^2) and 470 nm visible light (LED lamp, 18 mW/cm^2). Sample solutions in a 1 mm-path length quartz cuvette or vial were placed at the distance of 3 cm from the light source.

2. Synthesis and Characterization

Azobenzene dyads **2** and **3** were synthesized according to Scheme S1. Compound **4** was prepared according to a reported procedure.[S1]



Scheme S1. Reagents and condition: i) *n*-octanoic acid, *N,N′*-dicyclohexylcarbodiimide (DCC), *N,N′*-dimethyl-4-aminopyridine (DMAP), CH_2Cl_2, 0 °C → r.t.; ii) 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoyl chloride, *N,N‘*-diisopropylethylamine (DIPEA), CH_2Cl_2, −40 °C → r.t.

Compound 2: Compound **4** (68 mg, 0.063 mmol), *n*-octanoic acid (37 mg, 0.18 mmol) and DMAP (5 mg, 0.04 mmol) were dissolved in 3 mL of CH_2Cl_2 at 0 °C under N_2 atmosphere. To this mixture, DCC (37 mg, 0.18 mmol) was added and the mixture was stirred for 20 h at room temperature. The reaction mixture was diluted with $CHCl_3$ and washed with aqueous HCl (2 M) solution, saturated aqueous $NaHCO_3$ solution and then brine. The organic layer was dried over Na_2SO_4, filtrated, and evaporated to dryness. The residue was purified by column chromatography over silica gel (eluent: $CHCl_3$:EtOAc = 10:1) and further purified by GPC (eluent: $CHCl_3$) to give **2** as orange solid (41 mg, 49% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 7.82$ (d, $J = 9.0$ Hz, 4H), 7.81 (d, $J = 8.8$ Hz, 4H), 7.62 (d, $J = 8.7$ Hz, 4H), 7.41 (brs, 2H), 7.24 (s, 1H), 7.00 (dd, $J = 2.1, 9.0$ Hz, 4H), 5.13

(s, 4H), 4.08 (t, J = 6.7 Hz, 4H), 4.03 (t, J = 6.3 Hz, 2H), 2.41 (t, J = 7.4 Hz, 4H), 1.78–1.72 (m, 10H), 1.48–1.23 (m, 70H), 0.91–0.85 (m, 15H).

^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ = 171.77, 161.10, 151.94, 149.21, 147.15, 145.87, 139.96, 129.83, 125.51, 124.65, 123.68, 120.07, 115.08, 74.32, 73.82, 65.64, 37.98, 32.03, 31.78, 30.52, 30.49, 29.84, 29.80, 29.78, 29.74, 29.67, 29.63, 29.48, 29.46, 29.36, 29.16, 29.14, 22.80, 22.78, 22.71, 14.21, 14.16.

HRMS (ESI): *m/z* calcd for $C_{84}H_{129}O_7N_6$ 1333.9917 $[M+H]^+$, found 1333.9915.

Compound 3: Compound **4** (122 mg, 0.113 mmol) and DIPEA (93 mg, 0.72 mmol) were dissolved in 10 mL of CH_2Cl_2 at −40 °C under N_2 atmosphere. To this mixture, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoyl chloride (174 mg, 0.402 mmol) was added dropwise and stirred for 0.5 h at −40 °C. This mixture was gradually warmed to 0 °C over 1.5 h and stirred for 24 h at room temperature. The reaction mixture was diluted with $CHCl_3$ and washed with aqueous HCl (2 M) aqueous solution, saturated aqueous $NaHCO_3$ solution and then brine. The organic layer was dried over Na_2SO_4, filtrated, and evaporated to dryness. The residue was purified by column chromatography over silica gel (eluent: $CHCl_3$:*n*-hexane = 8:1) and further purified by GPC (eluent: $CHCl_3$) to give **3** as orange solid (161 mg, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 8.16 (brs, 2H), 7.88 (dd, J = 1.9, 8.7 Hz, 4H), 7.83 (dd, J = 2.0, 9.0 Hz, 4H), 7.67 (dd, J = 2.0, 8.9 Hz, 4H), 7.21 (s, 1H), 7.00 (dd, J = 2.0, 8.8 Hz, 4H) 5.15 (s, 4H), 4.09 (t, J = 6.5 Hz, 4H), 4.03 (t, J = 6.7 Hz, 2H), 1.78–1.73 (m, 6H), 1.48–1.22 (m, 54H), 0.89–0.84 (m, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, 60 °C): δ = 161.60, 151.86, 150.93, 147.21, 145.77, 136.56, 125.43, 124.84, 123.76, 121.12, 115.25, 74.25, 73.83, 65.75, 31.94, 31.92, 30.48, 30.42, 29.72, 29.68, 29.64, 29.59, 29.54, 29.35, 29.32, 26.23, 26.20, 22.65, 22.63, 13.96.

HRMS (ESI): *m/z* calcd for $C_{84}H_{99}O_7N_6F_{30}$ 1873.7091 $[M+H]^+$, found 1873.7054.

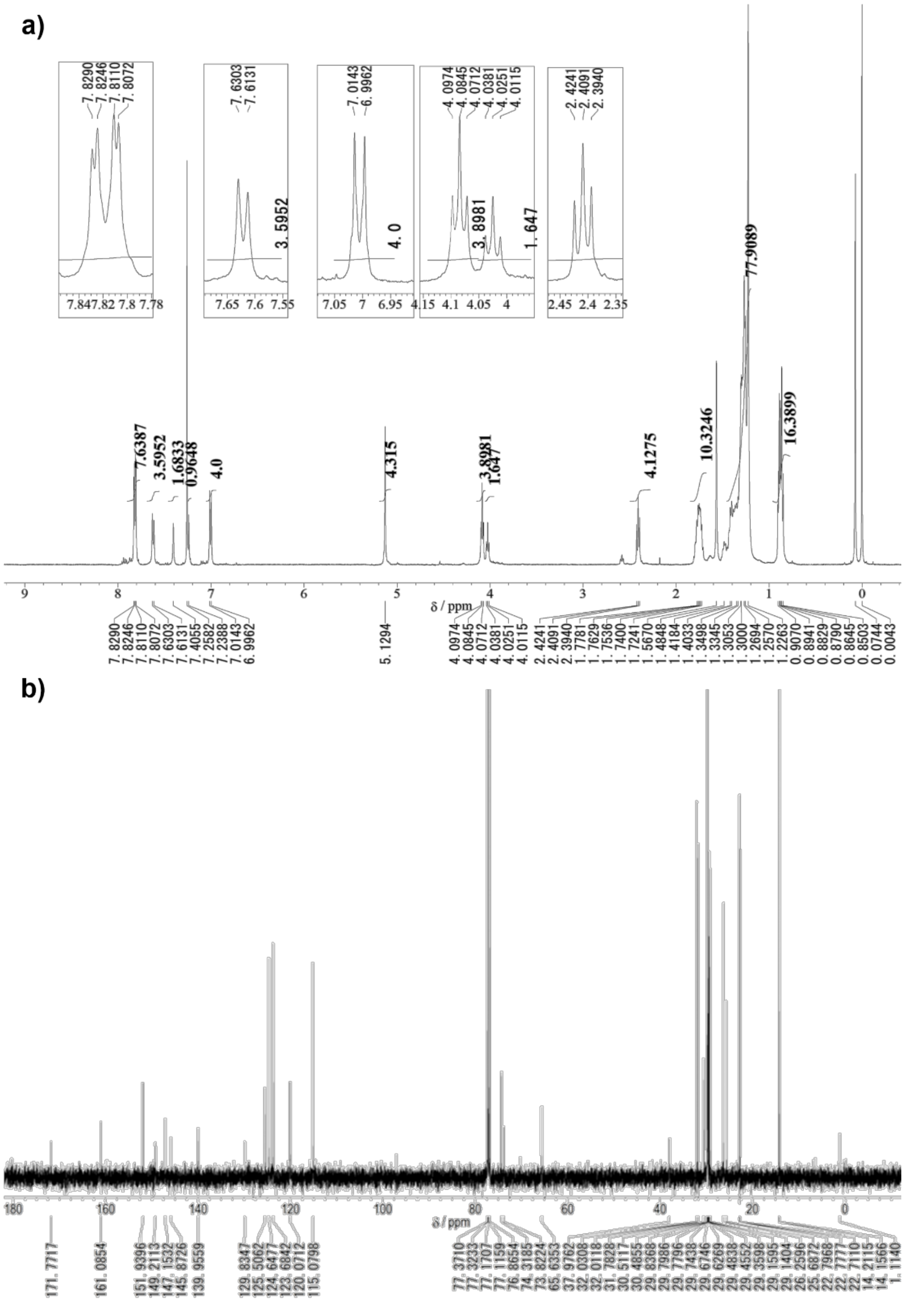


Chart S1. a) ^{1}H and b) ^{13}C NMR spectra of **2** in $CDCl_3$.

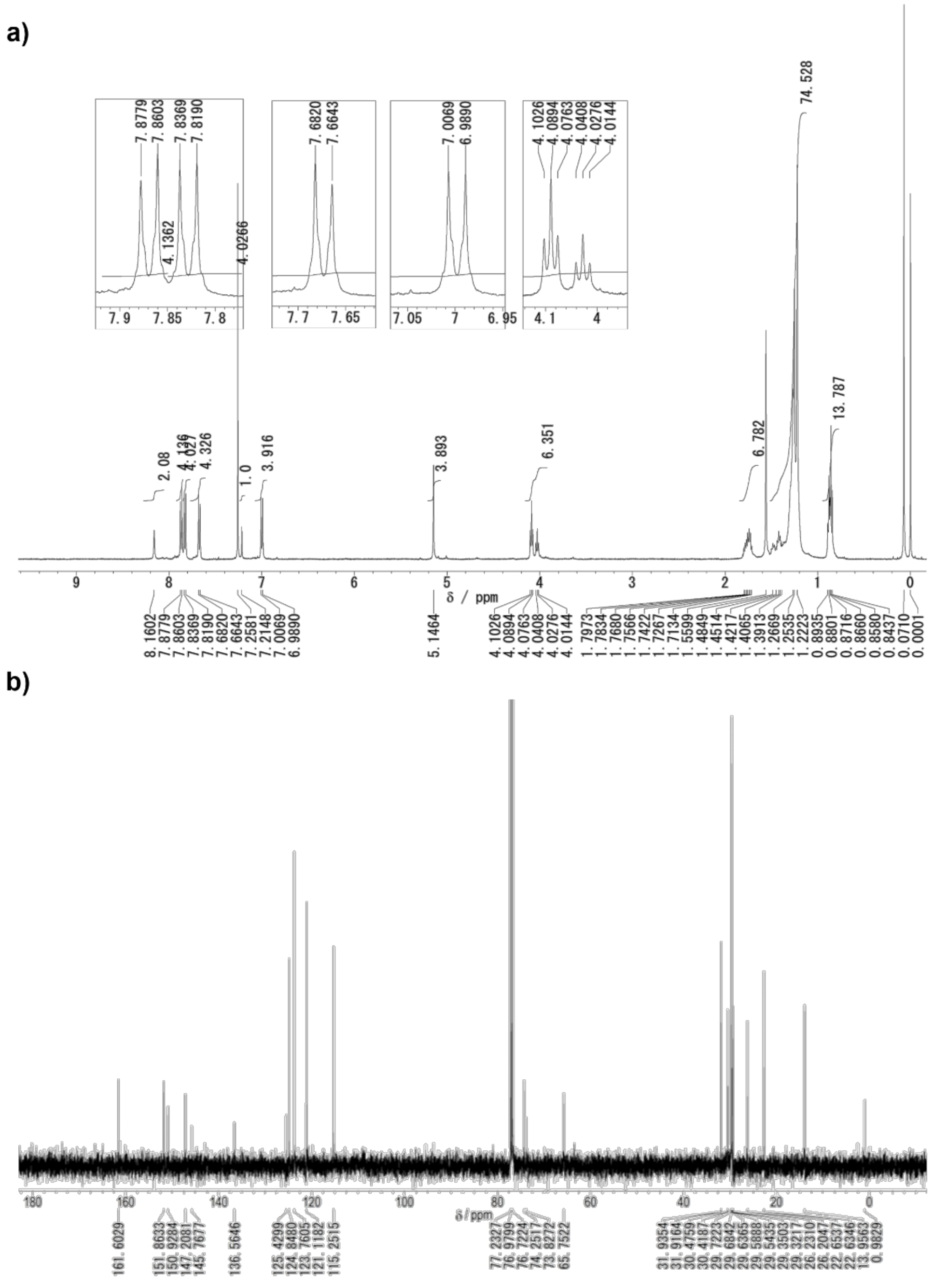


Chart S2. a) ^{1}H and b) ^{13}C NMR spectra of **3** in CDCl$_3$.

3. Supporting Figures

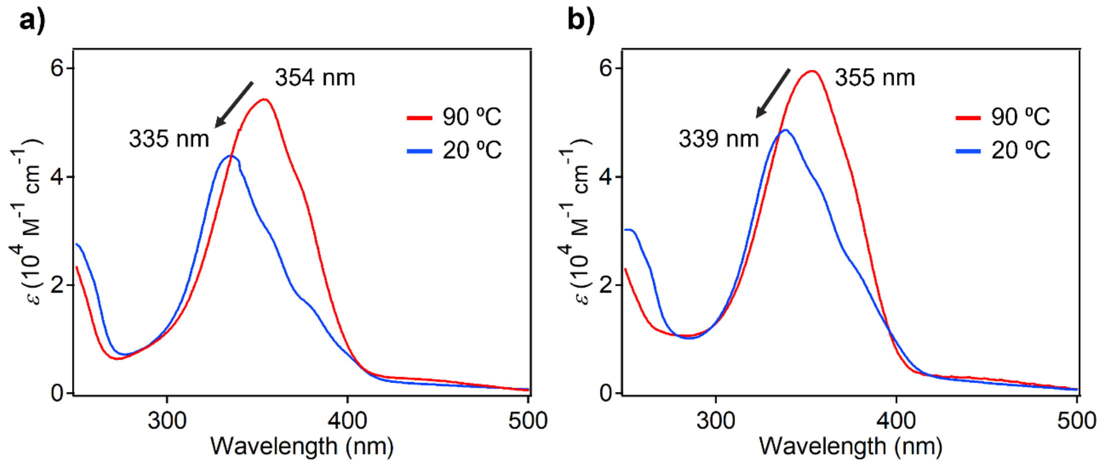


Figure S1. a,b) UV/Vis absorption spectra of a) **2** and b) **3** in MCH (c = 100 μM) upon cooling from 90 °C (red spectra) to 20 °C (blue spectra) at a rate of 1 °C/min.

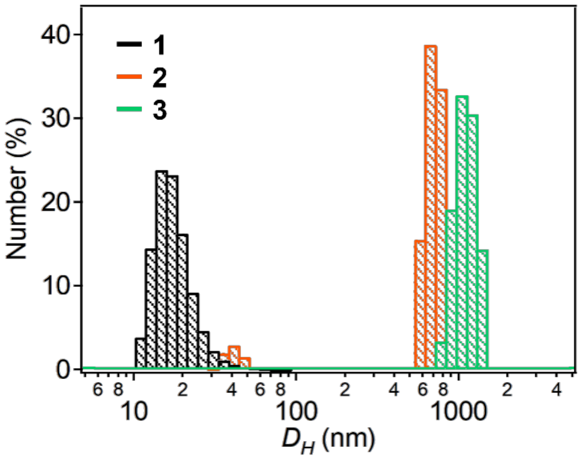


Figure S2. DLS size distribution of **1** (black bars), **2** (orange bars) and **3** (green bars) in MCH (c = 100 μM) at 20 °C.

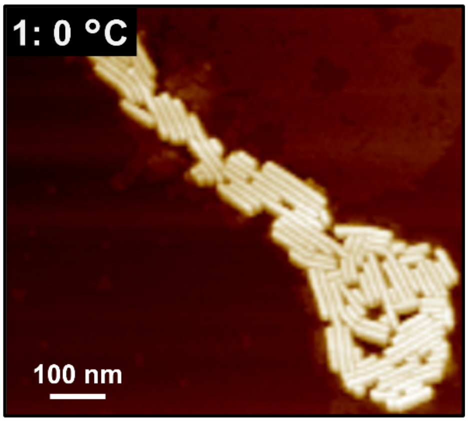


Figure S3. AFM image of nanotubes of **1** obtained by cooling its MCH solution (*c* = 100 μM) from 90 °C to 0 °C at a rate of 1 °C/min.

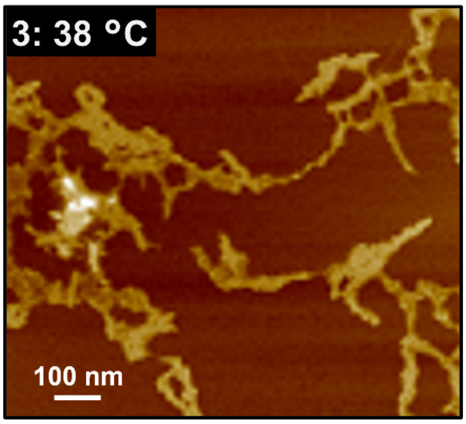


Figure S4. AFM image of amorphous aggregates of **3** obtained by cooling its MCH solution (*c* = 100 μM) from 90 °C to 38 °C at a rate of 1 °C/min.

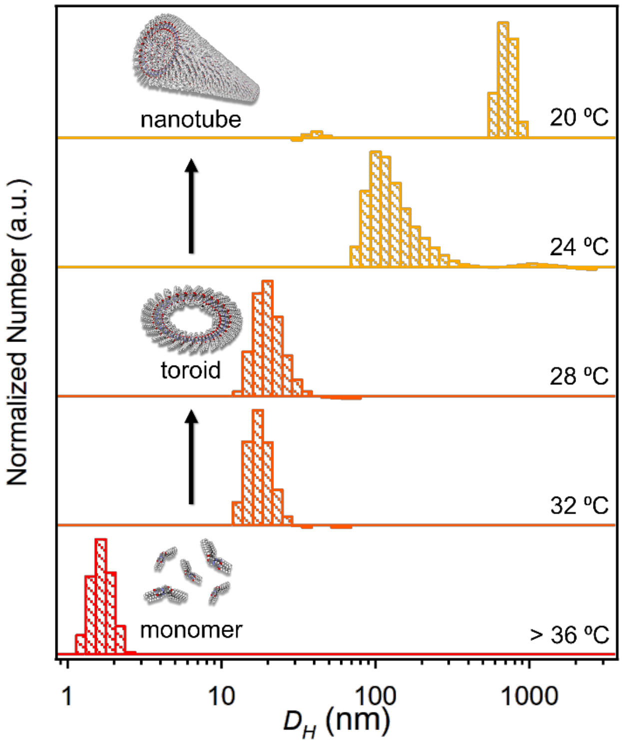


Figure S5. DLS size distribution of **2** in MCH solution (c = 100 μM) between 36 °C to 20 °C.

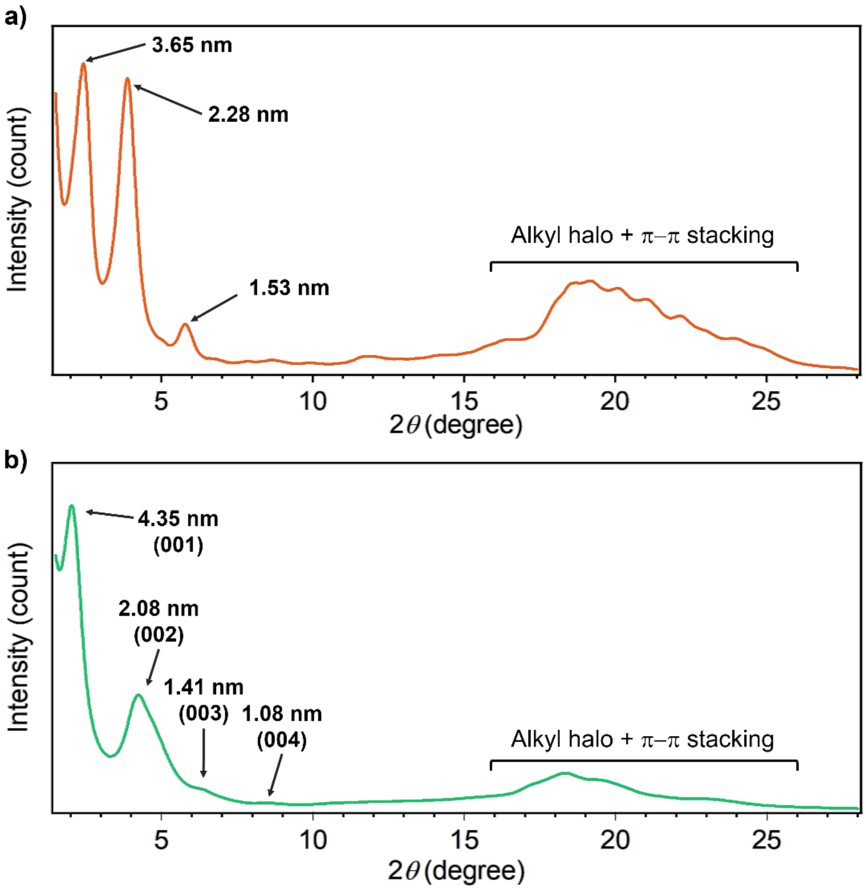


Figure S6. Additional XRD patterns of precipitated a) **2** and b) **3**.

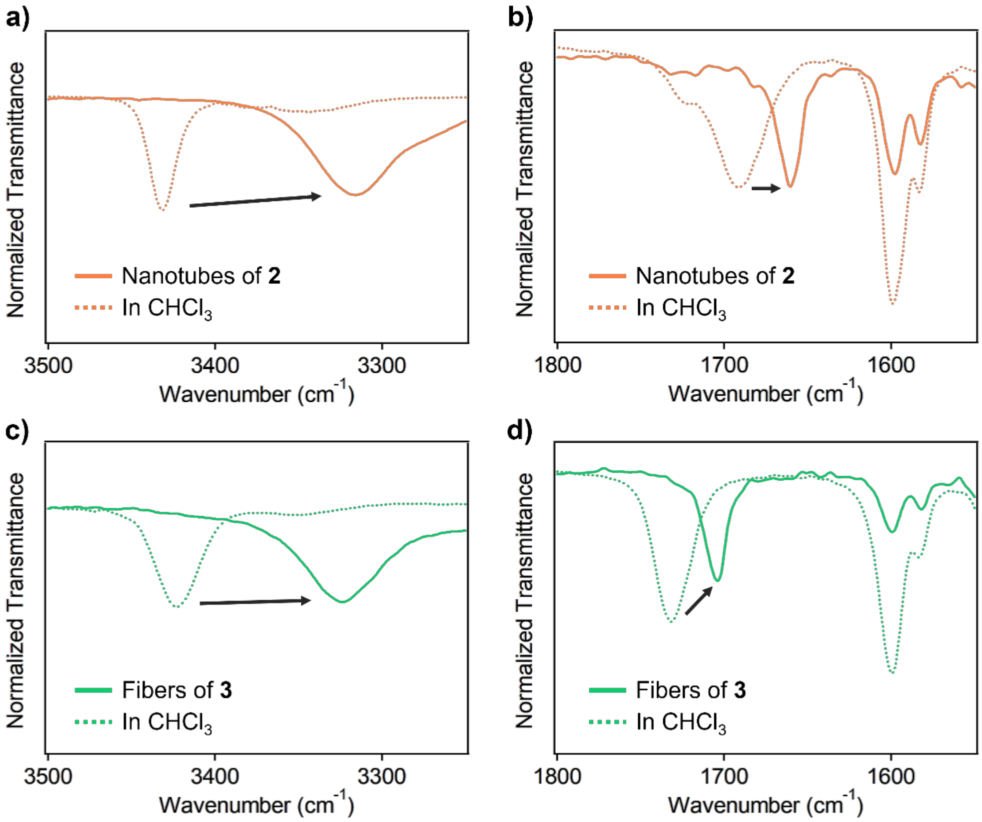


Figure S7. FT-IR spectra of a,b) nanotubes of **2** and c,d) fibers of **3** in the dried state (solid lines) and monomeric state in $CHCl_3$ (*c* = 1 mM, dashed lines) at 20 °C, respectively. The spectra display a,c) N-H stretching bands and b,d) carbonyl (C=O) stretching bands of amide groups, respectively.

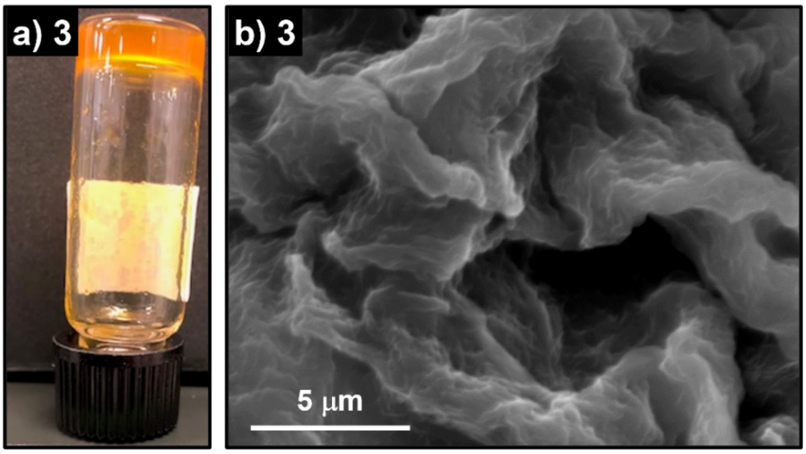


Figure S8. a) Photograph of an organogel of **3** obtained by cooling its hot MCH solution (c = 3 mM) to r.t. b) SEM image of a dried gel of **3**.

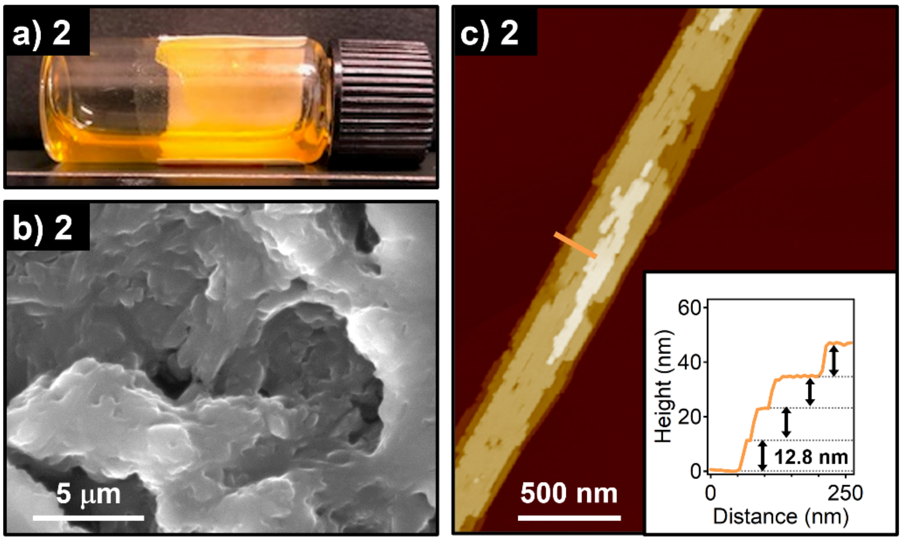


Figure S9. a) Photograph of suspension of **2** obtained by cooling its hot MCH solution (c = 10 mM) to r.t. b) SEM image of precipitate of **2**. c) AFM image of lamellarly packed nanotubes of **2**. Inset: AFM cross-sectional analysis along the orange lines in c).

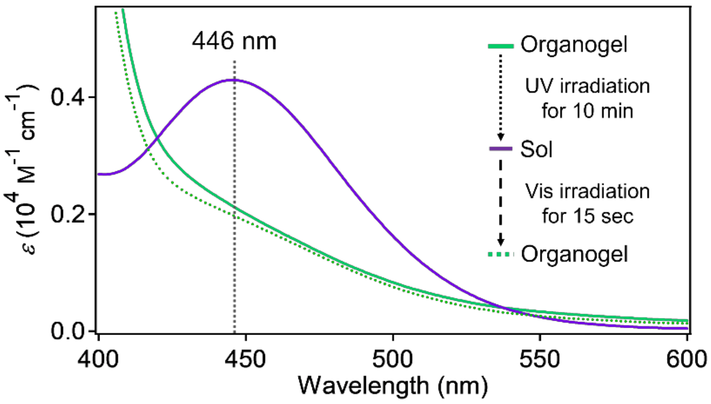


Figure S10. UV/Vis absorption spectra of **3** (c = 1.5 mM) at 20 °C in the pristine gel (green solid spectrum), in the solution obtained by irradiation of the gel with UV light for 10 min (purple solid spectrum), and in the regenerated gel obtained by irradiation of the solution with visible light for 15 sec (green dashed spectrum). The increase of the absorption intensity at 446 nm (n–π* transition of *trans*-azobenzene chromophore) on UV light irradiation (photostationary state) is 84% of that of the monomeric state in $CHCl_3$ (*trans*:*cis* = 3:97, see Figure S11), suggesting *trans:cis* ratio of 9:91.

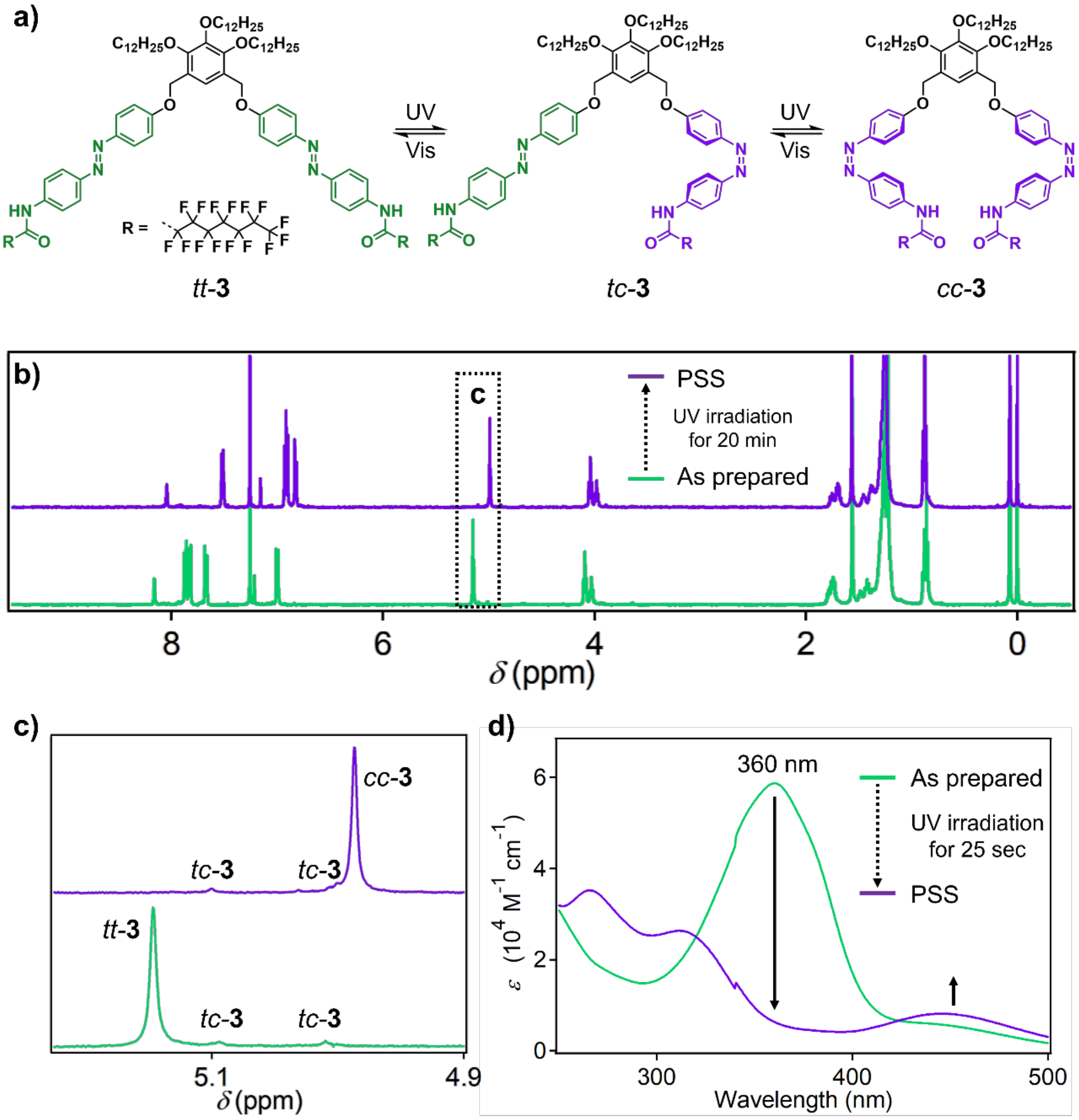


Figure S11. a) Chemical structures of *tt*-**3**, *tc*-**3** and *cc*-**3**, where *t* and *c* mean *trans*- and *cis*-azobenzene moieties, respectively. b) ^{1}H NMR spectra of **3** in CDCl$_3$ (c = 5 mM) at 20 °C before (lower green spectrum) and after irradiation with UV light for 20 min (upper purple spectrum). c) Partial ^{1}H NMR spectra of the spectra in b) wherein the integration of the benzylic proton signals of *tt*-**3**, *tc*-**3** and *cc*-**3** shows *tt*-**3**:*tc*-**3**:*cc*-**3** = 0:6:94, revealing *trans*:*cis* = 3:97. d) UV/Vis absorption spectra of **3** in CHCl$_3$ (c = 100 μM) at 20 °C before (green spectrum) and after irradiation with UV light for 25 sec (purple spectrum) to reach a photostationary state (PSS). The absorption intensity at 360 nm shows an 89% decrease upon irradiation with UV light.

Table S1. Gelation property of **3** in various organic solvents.

Solvent	**State**	**CGC (mM)**
n-octane	G	0.65
MCH	G	0.89
Toluene	G	5.5
$CHCl_3$	S	–
THF	S	–
Acetone	P	–
EtOH	P	–
MeCN	P	–

Gelation was judged after cooling a hot solution to r.t., and standing for 15 min. G = gel, S = solution, P = precipitate.

4. Supporting References

[S1] S. Yagai, M. Yamauchi, A. Kobayashi, T. Karatsu, A. Kitamura, T. Ohba and Y. Kikkawa, *J. Am. Chem. Soc.*, 2012, **134**, 18205–18208.