Supporting Information

Tricolor Fluorescence Switching in a Single Component Mechanochromic Molecular Material

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Experimental Section

Material synthesis. DDDCS was synthesized according to the procedure shown in Scheme S1. All chemicals were purchased commercially, and used without further purification.

4-Dodecyloxy-benzaldehyde. K₂CO₃ (6.79 g, 49.1 mmol) and KI (catalytic amount) were added to a solution of 4-hydroxybenzaldehyde (5.00 g, 40.9 mmol) in dry DMF (10 mL), and the mixture was stirred at 80 °C. 1-Bromododecane (11.8 mL, 49.1 mmol) was slowly dropped into the mixture. The reaction lasted overnight. After cooling to room temperature, the mixture was poured into brine and extracted with dichloromethane. The organic phase was dried over MgSO₄ and the solvent was evaporated in vacuo. The product (8.54 g, 72 %) was obtained by column chromatogra-phy using ethyl acetate and n-hexane (1:10 v/v). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 9.88 (s, 1H, -CHO), 7.83 (d, 2H, Ar-H), 6.99 (d, 2H, Ar-H), 4.04 (t, 2H, -OCH₂), 1.81 (p, 2H, -CH₂), 1.46 (p, 2H, -CH₂), 1.26 (m, 16H, -CH₂), 0.88 (t, 3H, -CH₃).

(2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-(4-tris(dodecyloxy)phenyl)acrylonitrile) (DDDCS). The mixture of 4-Dodecyloxy-benzaldehyde (2.00 g, 6.89 mmol) and (4-cyanomethyl-phenyl)-acetonitrile (0.807 g, 3.44 mmol) in tert-butyl alcohol (20 mL) was stirred at 50 °C. Tetrabutylammonium hydroxide (TBAH, 1 M solution in methanol, 0.689 mL) was slowly dropped into the mixture and stirred for 2 hours. The resulting precipitate was filtered and purified by column chromatography using dichloromethane. DDDCS bulk powder (1.57 g,

65%) was obtained by reprecipitation from ethanol solution. ¹H NMR (300 MHz, CDCl₃) δ [ppm]: 7.90 (d, 4H, Ar-H), 7.71 (s, 4H, Ar-H), 7.51 (s, 2H, Vinyl-H) 6.98 (d, 4H, Ar-H), 4.03 (t, 4H, -OCH2), 1.81 (p, 4H, -CH2), 1.47 (p, 4H, -CH2), 1.27 (m, 32H, -CH2), 0.89 (t, 6H, -CH3). ¹³C NMR (500 MHz, CDCl₃) δ [ppm]: 161.54, 142.47, 135.33, 131.61, 126.42, 126.28, 118.55, 115.15, 107.57, 77.48, 77.22, 76.97, 68.50, 32.14, 29.88, 29.87, 29.82, 29.79, 29.59, 29.58, 29.34, 26.22, 22.91, 14.35. m/z (FAB, positive) Calcd for C₄₈H₆₄N₂O₂, 700.50; Found, 700.4980. Anal. Calcd for C₄₈H₆₄N₂O₂: C, 82.24; H, 9.20; N, 4.00. Found: C, 82.24; H, 9.19; N, 3.99.



Scheme S1. Synthetic scheme of DDDCS.

Sample Preparation. DDDCS nanoparticles were obtained by a simple reprecipitation method from DDDCS solution in THF ($1 \times 10^{-3} \text{ mol/L}$) by injection of water in 2 : 98 volume fraction. B state powder was prepared by heating to 110 °C (3 min; Hot plate), O state was prepared by exposing to dichloromethane (5 min), and G state were prepared by grinding.

Spectroscopic Characterization. ¹H NMR spectra were recorded on a Bruker, Avance-300 (300 MHz) in CDCl₃ solution. Mass spectra were measured using a JEOL, JMS-600W mass spectrometer. Elemental analyses were carried out using a CE instruments, EA1110 elemental analyzer. UV-visible absorption spectra were recorded on a Shimazu, UV-1650 PC spectrometer. Photoluminescence emission spectra was obtained using a Photo Technology International, Felix32 QM-40 and a Varian, Cary Eclipse Fluorescence spectrophotometer. The absolute photoluminescence quantum efficiency was measured using an integrating sphere (Lasphere Co., 600 diameter). Time-resolved fluorescence lifetime experiments were performed by the time-correlated single photon counting (TCSPC) technique with a FluoTime200 spectrometer (PicoQuant) equipped with a PicoHarp300 TCSPC board (PicoQuant) and a PMA182 photomultiplier (PicoQuant). The excitation source was a 377 nm picoseconds pulsed diode laser (PicoQuant, LDH375) driven by a PDL800-D driver (PicoQuant) with fwhm ~70 ps. The decay time fitting procedure was carried out with the IRF by using a Fluofit software (PicoQuant). The smallest residual value was controlled during the fitting and simulation.

X-ray and Thermal Analysis. XRD measurements were performed on a X-ray Diffractometer (Bruker, Germany), operating at 3 kW. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC7.



Fig. S1. Normalized photoluminescence spectra ($\lambda_{ex} = 360 \text{ nm}$) of DDDCS in THF solution (c = 2 x 10⁻⁵ mol/L, blue line) and DDDCS suspension in THF/water mixture (c = 2 x 10⁻⁵ mol/L, orange line).



Fig. S2. PL spectra of DDDCS powder (O, solvent-vapor annealed sample; B, thermal annealed sample; G, smeared sample). Processing cycle : $O1 \rightarrow G1 \rightarrow O2 \rightarrow G2 \rightarrow B1 \rightarrow G3 \rightarrow B2 \rightarrow G4 \rightarrow O3 \rightarrow G5$.



Fig. S3. First heating DSC curve and photo images of DDDCS under UV light.



Fig. S4. POM image of the DDDCS LC phase at 150 °C.



Fig. S5. Changes in fluorescence decay profile of different stimuli treated DDDCS. B state (A_1 = 160 Cnts, τ_1 = 14.3 ns, A_2 = 11813 Cnts, τ_2 = 3.9 ns), O state (A_1 = 125 Cnts, τ_1 = 57.4 ns, A_2 = 17379 Cnts, τ_2 = 14.1 ns, A_3 = -7888 Cnts, τ_3 = 3.7 ns), G state (A_1 = 3201 Cnts, τ_1 = 16.9 ns, A_2 = 4812 Cnts, τ_2 = 7.0 ns, A_3 = 6358 Cnts, τ_3 =

1.3 ns).