

Supporting Information

Photo-induced fiber-vesicle morphological change in an organogel based on azophenyl hydrazide derivative

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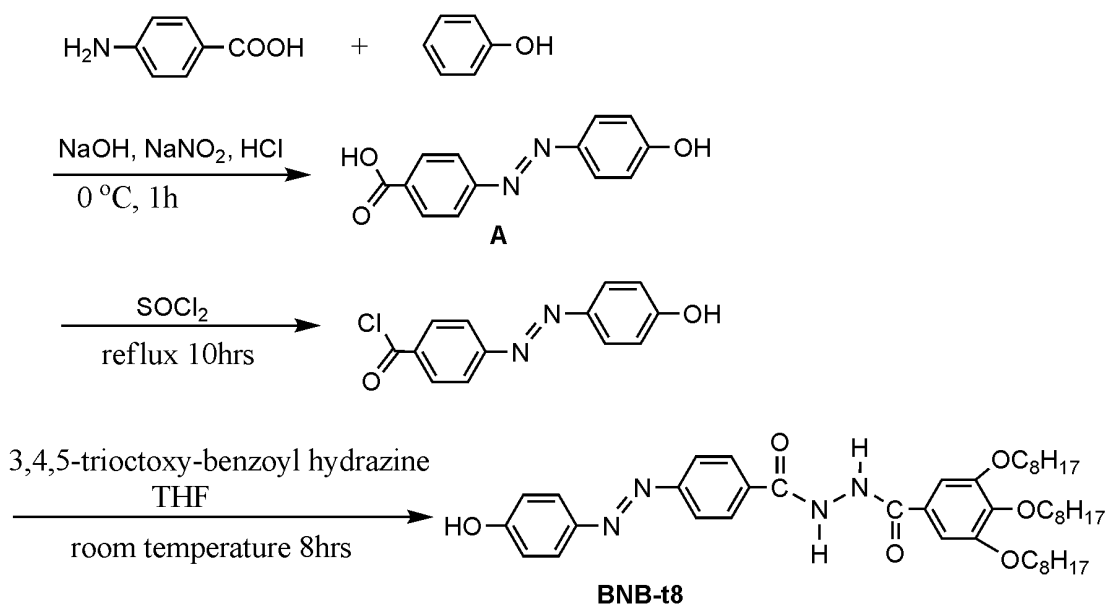
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1. Experimental Section

1.1 Synthesis

Scheme S1. Synthetic route for BNB-t8



The compound,

N-(3,4,5-octanoxyphenyl)-N'-4-[(4-hydroxyphenyl)azophenyl]

benzohydrazide (BNB-t8), was synthesized through the route shown in

Scheme S1.

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1.1.1 Synthesis of 4-(4'-hydroxyphenyl)azobenzoic acid (**A**) 4-aminobenzoic acid (6.58 g, 0.048 mol) was dissolved in 40 mL 15% NaOH aqueous. NaNO₂ (3.32 g, 0.048 mol) dissolved in water (24 mL), was added to the solution and kept in the ice bath at 0 °C. 1 mol L⁻¹ aqueous HCl (20 mL) was added dropwise to the mixture. Phenol (4.71 g, 0.05 mol) was dissolved in ethanol and was added dropwise to the above mixture, pH value was adjusted to 8-9. The resulted mixture was allowed to stir for 1h at 0 °C and then pH value of the reaction mixture was adjusted to 1-2. The precipitated crude product was heated up to 90-100 °C, filtered, washed with water and recrystallized from anhydrous ethanol; yield 78%.

¹H NMR (300 MHz, DMSO-*d*₆), (ppm, from TMS): 12.96 (s, H), 10.48 (s, H), 8.10 (d, 2H, J=9.0), 7.84-7.90 (m, 4H), 6.97 (d, 2H, J=9.0).

FT-IR (KBr, pellet, cm⁻¹): 3429, 1682, 1591, 1501, 1468, 1423, 1384, 1290, 1243, 1142, 1102, 1009, 866, 841, 721, 692.

1.1.2 Synthesis of

N-(3,4,5-octanoxyphenyl)-N'-4-[(4-hydroxyphenyl)azophenyl]

benzohydrazide (**BNB-t8**) 4-(4'-hydroxyphenyl)azobenzoic acid (**A** 1.46 g, 0.006 mol) and thionyl chloride (50 mL) were refluxed for 10 h. 4-(4'-hydroxyphenyl)azobenzoic acid chloride was collected after removing unreacted thionyl chloride. 4-(4'-hydroxyphenyl)azobenzoic acid chloride was dissolved in tetrahydrofuran, 3,4,5-trioctoxy-benzoyl hydrazine¹ was added slowly, and the resulting mixture was stirred for 8 h. The resulted reaction

mixture was poured into an excess of ice water, and the precipitate was recrystallized from tetrahydrofuran.

^1H NMR (300MHz, DMSO- d_6), (ppm, from TMS): 10.61 (s, 1H), 10.43 (s, 1H), 10.42 (s, 1H), 8.08 (d, 2H, $J=8.4$), 7.92 (d, 2H, $J=8.3$), 7.85 (d, 2H, $J=8.6$), 7.23 (s, 2H), 6.96 (d, 2H, $J=8.7$), 4.04-3.90 (m, 6H), 1.79-1.60 (m, 6H), 1.45-1.27 (m, 30H), 0.86-0.84 (m, 9H).

^{13}C NMR (300MHz, DMSO- d_6), (ppm): 165.16, 161.42, 153.90, 152.23, 145.26, 140.24, 133.67, 128.58, 127.10, 125.07, 121.89, 115.92, 105.92, 72.38, 68.45, 31.15, 31.09, 29.67, 28.73, 25.47, 21.94, 13.73.

FT-IR (KBr, pellet, cm^{-1}): 3339, 3237, 2952, 2925, 2855, 1675, 1657, 1606, 1584, 1503, 1466, 1428, 1391, 1329, 1275, 1232, 1187, 1138, 1116, 857, 839, 763, 696.

Elemental analysis: calculated for $\text{C}_{44}\text{H}_{64}\text{N}_4\text{O}_6$ (%): C, 70.94; H, 8.66; N, 7.52. Found: C, 71.00; H, 8.93; N, 7.65.

MALDI-TOF MS: m/z : calculated for: 746.5, found: 746.8.

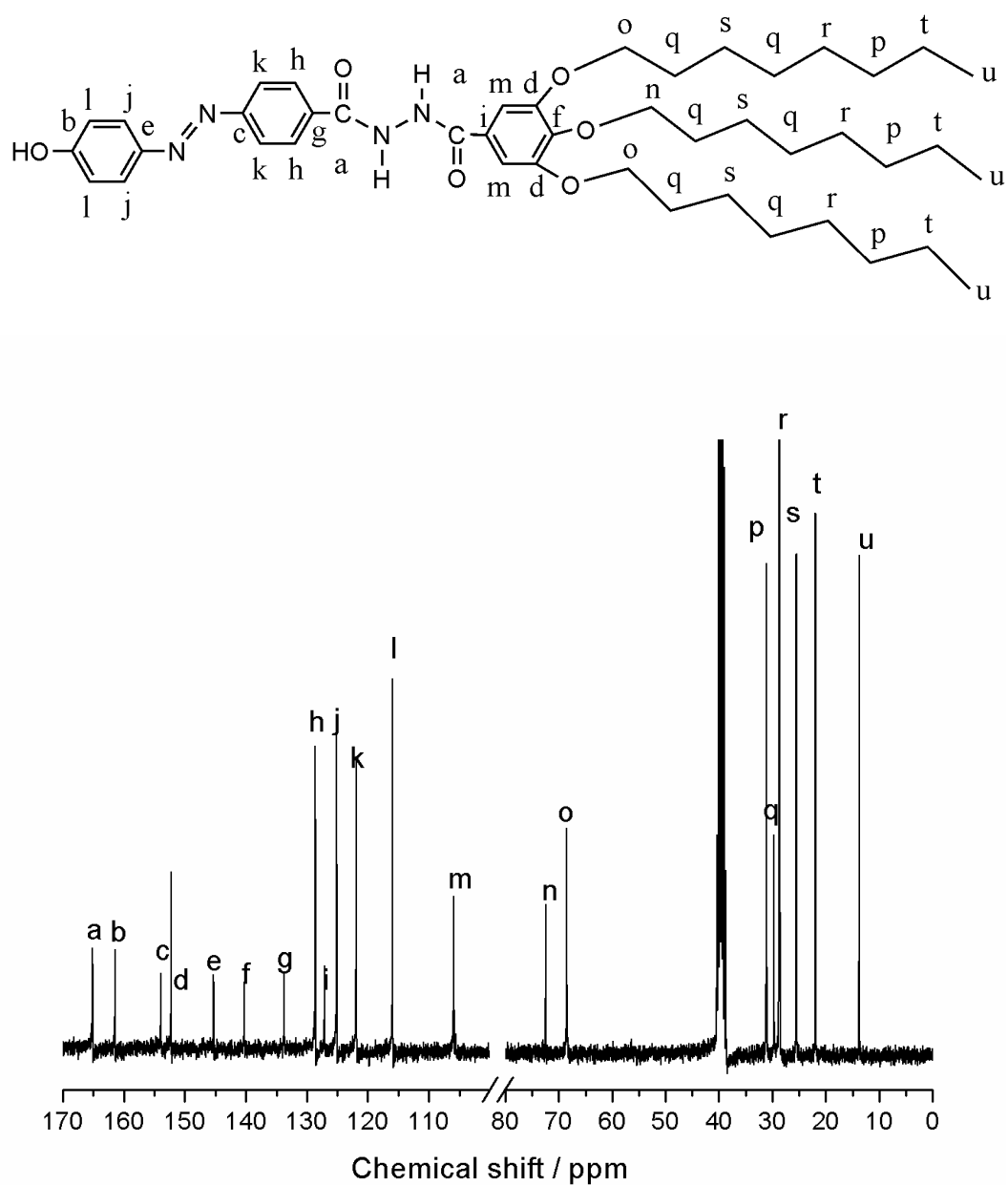


Fig. S1 ¹³C NMR spectra (δ 0-170 ppm region shown; DMSO; 300MHz) of BNB-t8.

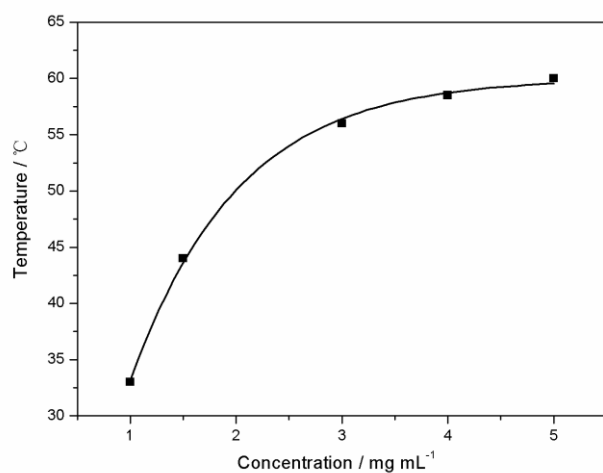


Fig. S2 Concentration-dependent melting temperature of BNB-t8 gels in chloroform.

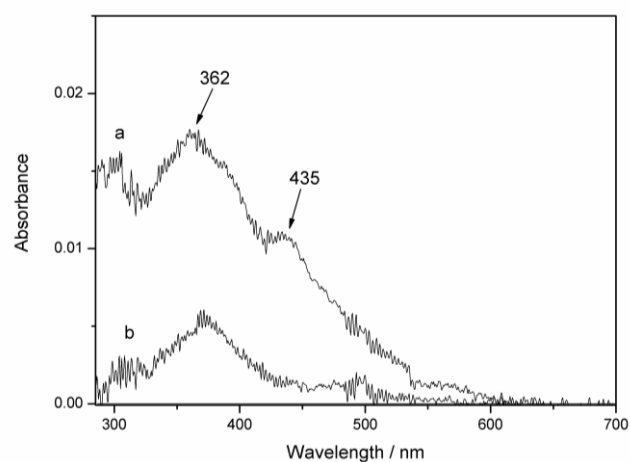


Fig. S3 UV-vis spectra of (a) the precipitate developed from the gel in chloroform under the irradiation of 365 nm light and (b) xerogel from BNB-t8 in chloroform at room temperature.

1 Y. D. Zhang, K. G. Jespersen, M. Kempe, J. A. Kornfield, S. Barlow, B. Kippelen, S. R. Marder, *Langmuir*, 2003, **19**, 6534.