

SUPPORTING INFORMATION

Thermal Stability and Structural Characterization of Organic/Inorganic Hybrid Nonlinear Optical Material Containing Two-Dimensional Chromophore

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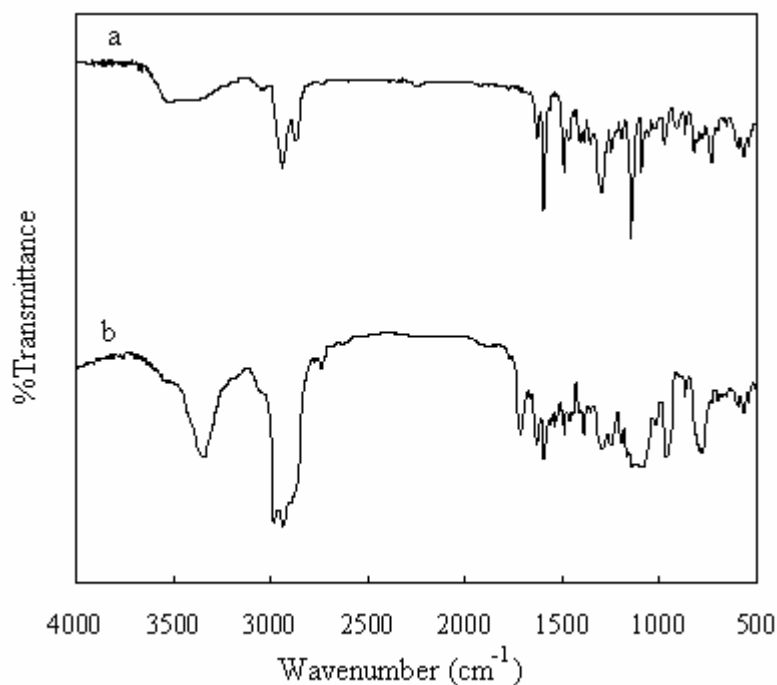


Figure S1. FT-IR spectra of (a) Cz2PhSO₂OH and (b) Cz2PhSO₂OH-TES

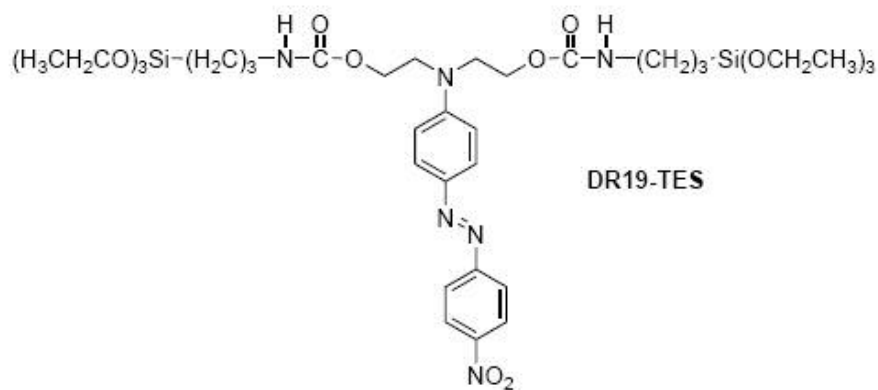
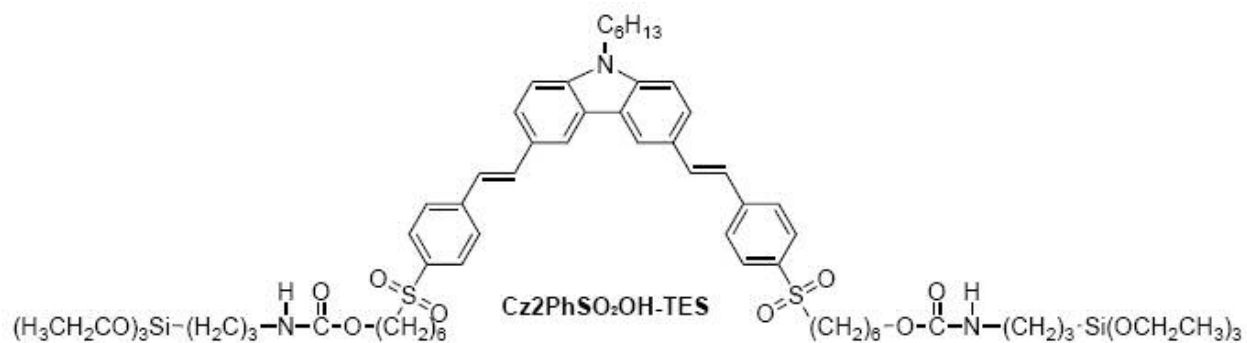


Figure S2. Complete structure of Cz2PhSO₂OH-TES and DR19-TES

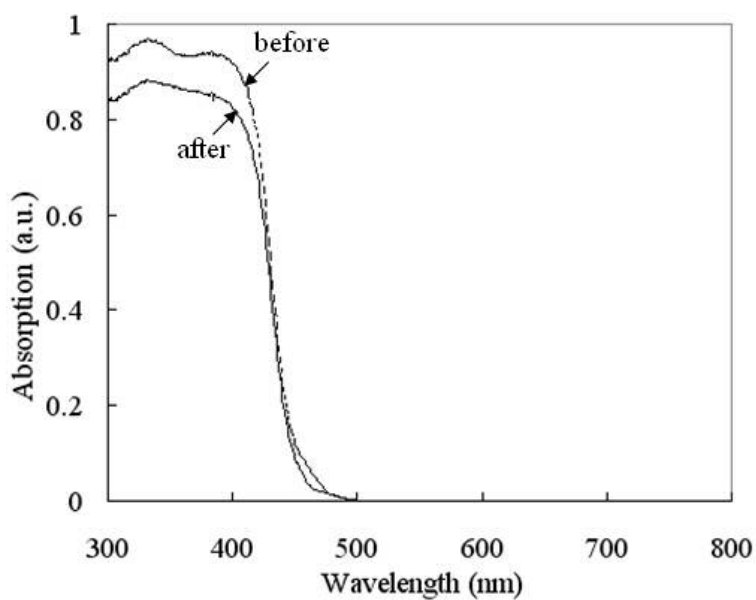


Figure S3. UV-Vis spectrum of NLO hybrid film before and after heating at 210 °C for 24 h

Synthetic route of Cz2PhSO₂OH-TES

Synthesis of 9-Hexyl-3,6-di(29-(6-hydroxyhexyl)-sulfonylphenyl)-19-ethenyl-9H-carbazole (Cz2PhSO₂OH)

Dry tetrahydrofuran (THF, 5 ml) was added to sodium hydride (NaH, 0.32 g, 60% in mineral oil, 13.5 mmol) under ice cooling. To the suspension, a mixed solution of 9-hexyl-9H-3,6-diformylcarbazole (0.5 g, 1.63 mmol) and 4-[(6-acetoxyhexyl) sulfonyl]benzyl diethylphosphate (2.34 g, 5.4 mmol) in dry THF (5 ml) was added dropwise. The reaction mixture was kept at 0 °C for 4 h under stirring. Deionized water (20 ml) was added, and THF was evaporated with an aspirator. The residue was dissolved in methanol (20 ml), and concentrated sulfuric acid (10 ml) was added dropwise at 0 °C. The solution was heated to 85 °C and refluxed for 24 h. The solution was cooled and neutralized with aqueous hydrochloric acid. The crude product was filtered. Further purification was performed by means of column chromatography (dichloromethane/acetone 1: 9). Yield: 91%. ¹H NMR (500MHz, CDCl₃, ppm): 0.81 (t, 3 H, -CH₃), 1.20-1.81 (m, 22 H, -CH₂-), 2.36 (s, 2 H, -OH), 3.04 (t, 4 H, SO₂-CH₂-), 3.52 (t, 4 H, -CH₂-OH), 4.18 (t, 2 H, -N-CH₂-), 7.07 (d, 2 H, CH=CH-PhSO₂-, J = 16.24 Hz), 7.24 (d, 4 H, ArH, meta to vinyl group), 7.30 (d, 2 H, CH=CH-PhSO₂-, J = 25.72 Hz), 7.68 (d, 6 H, ArH, meta to SO₂-and ortho to vinyl group), 7.80 (d, 4 H, ArH, ortho to SO₂-), 8.21 (s, 2 H, ArH, ortho to vinyl group).

Synthesis of Cz2PhSO₂OH-TES

Cz2PhSO₂OH (1.96g, 2.5 mmol) was placed in the flask and dissolved in the dry THF (20 ml). 3-isocyanatopropyl triethoxysilane (ICTES, 1.48g, 6 mmol) was added to the flask. The reaction mixture was stirred at 70 °C for 12 h in a nitrogen atmosphere. The crude product was recrystallized from hexane twice and dried in a vacuum oven at 25 °C for 12 h. Yield: 95%. ¹H-NMR (500MHz, CDCl₃, ppm): 0.592(m, 4H, Si-CH₂-), 0.849(m, 3H, -CH₂-CH₂-CH₃), 1.199(m, 18H, -O-CH₂-CH₃), 1.222-1.896 (m, 28H, -CH₂-), 3.04(t, 4H, -SO₂-CH₂-), 3.104(t, 4H, -CO-NH-CH₂-), 3.722(m, 4H, -CH₂-COO-), 3.988(m, 4H, -Si-O-CH₂-), 4.18 (t, 2H, -N-CH₂-), 5.278(t, 2H, -CO-NH-), 7.156(d, 2H, -CH=CH-PhSO₂-, J=16.24 Hz), 7.24 (d, 4H, ArH, meta to vinyl group), 7.30 (d, 2H, CH=CH-PhSO₂-, J=16.72 Hz), 7.68(d, 6H, ArH, meta to SO₂-and ortho to vinyl group), 7.80(d, 4H, ArH, ortho to SO₂-), 8.21(s, 2H, ArH, ortho to vinyl group)