A chiral luminescent liquid crystal with a tolane unit

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Experimental Section

General information

Tetrahydrofuran was distilled from sodium benzophenone ketyl in an atmosphere of nitrogen. 1,3-Dicyclohexylcarbodiimide (DCC) was purchased from Suzhou Highfine Biotech Co., Ltd. (China). 4-Dimethylaminopyridine (DMAP) and (R)-2-octanol were obtained from J & K Scientific Ltd. (China). All other chemicals were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (China) and used as received without further purification.

FTIR spectroscopy was performed on a Nicolet 6700 spectrometer at 2 cm^{-1} resolution by averaging over 32 scans. The ^1H NMR spectrum was taken on a Varian NMR (400 MHz) spectrometer in $\text{DMSO}-d_6$ solutions using tetramethylsilane (TMS) as an internal standard at room temperature. Elemental analysis was measured on an EA-1106 instrument. UV-Vis absorption spectra were recorded on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Photoluminescence spectra were obtained on a F-2500 FL spectrophotometer. Fluorescence quantum yields (Φ_F) were determined by a comparative method and using quinine sulfate in 0.1 M H_2SO_4 ($\Phi_F = 54.6\%$) as the standard.[1] The absorbance of the solutions was maintained at 0.04–0.06 to avoid the internal filter effect. Differential scanning calorimetry (DSC) measurements were conducted on a TA-Q200 under nitrogen at $5.0\text{ }^\circ\text{C min}^{-1}$. Circular dichroism spectra were recorded in a 0.01-mm quartz cell on an AVIV-410 spectropolarimeter. For the crystalline structure of **1TC8***, all measurements were made on a Bruker APEX-II CCD X-ray diffractometer by using graphite monochromated Mo Ka ($\lambda = 0.071073\text{ nm}$) at 273 K. The structure was solved in the space group $\text{P2}_1\text{2}_1\text{2}_1$ by direct methods and refined on F^2 using full matrix least-squares methods with SHELXTL version 2008.

Synthesis

(S)-4-(Octan-2-yloxy)phenol (**1**) and 4-[(4-methoxyphenyl)ethynyl]benzoic acid (**2**) shown in Scheme 1 were prepared according to the modified methods reported in our previous work.[2,3]

Synthesis of (S)-4-(octan-2-yloxy)phenyl 4-((4-methoxyphenyl)ethynyl)benzoate (1TC8*). 1.2 g (5.4 mmol) of **1** and 1.63 g (6.5 mmol) of **2** were added into a 500-mL round-bottom flask. Then, 200 mL of distilled tetrahydrofuran was injected under N₂ to dissolve the solid, followed by the addition of 1.3 g (6.5 mmol) of DCC and appropriate DMAP. The reaction mixture was stirred at 0°C for 3 h and room temperature for another 24 h under N₂. After filtration and solvent evaporation, the crude product was purified by a silica gel column using ethyl acetate/petroleum ether (1 : 20) as eluent and recrystallization from acetone/methanol. A white solid of 1TC8* was obtained in 30.0% (0.75 g). FT-IR (KBr pellet): 3071 cm⁻¹ (C-H of the phenyl, stretching), 2956 cm⁻¹ (ν_{asC-H3}), 2866 cm⁻¹ (ν_{sC-H3}), 2923 cm⁻¹ (ν_{asC-H2}), 2854 cm⁻¹ (ν_{sC-H2}), 2206 cm⁻¹ (ν_{C≡C}), 1730 cm⁻¹ (ν_{C=O}), 1599 cm⁻¹, 1509 cm⁻¹, 1468 cm⁻¹ (ν_{Ph}). ¹H-NMR (400 MHz, DMSO-*d*₆, TMS, 25°C): δ = 0.86 (t, 3H, *J* = 6.8 Hz; CH₃CH₂-), 1.22-1.69 [m, 13H; -CH₂ CH₂ CH₂ CH₂ CH₂ CH(CH₃)-], 3.81 (s, 3H; -OCH₃), 4.39-4.47 (m, 1H; -CH₂CH), 6.98 (d, 2H, *J* = 8.8 Hz; 2,6-PhH₂OCH₃), 7.02 (d, 2H, *J* = 8.6 Hz; 3,5-PhH₂OCO), 7.19 (d, 2H, *J* = 8.8 Hz; 2,6-PhH₂OCO), 7.57 (d, 2H, *J* = 8.8 Hz; 3,5-PhH₂OCH₃), 7.73 (d, 2H, *J* = 8.4 Hz; 3,5-COOPhH₂C), 8.13 (d, 2H, *J* = 8.4 Hz; 2,6-COOPhH₂C). Elemental analysis calcd for C₃₀H₃₂O₄ (%): C, 78.30; H, 6.94. Found: C, 78.92; H, 7.06.

Scheme S1 Synthetic route to **1TC8***.

Figure S1. Photographs of ITC8* at 143°C (a) and 135°C (b) taken under UV illumination.

Figure S2. DSC curve of ITC8* in the third heating and cooling process at the rate of 5.0 °C min⁻¹.

References

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