

Electronic Supporting Information

for

Synthesis and Piezochromic Luminescence Study of a Coumarin

Hydrozone Compound

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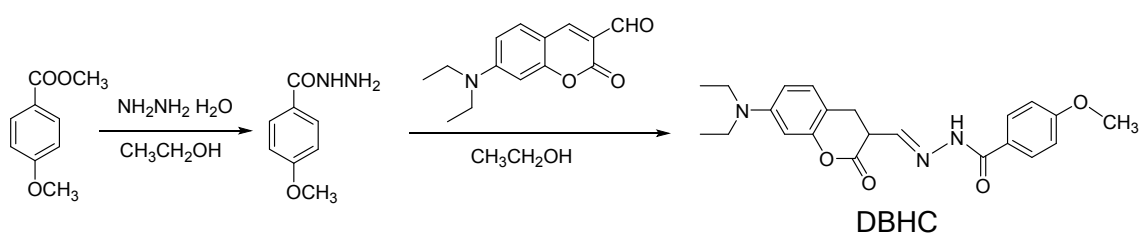
Table of Content

Contents	Pages
1. Materials and methods	S3
2. Synthesis	S3
3. Differential scanning calorimetry (DSC) measurement	S4
4. Diffuse reflectance absorption spectra	S4
5. References	S5
6. ¹HNMR and ¹³CNMR spectra	S6
7. ESI-MS spectra	S7

Materials and methods

All chemicals and reagents were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. and used without further purification. 7-diethylamino-3-formyl-coumarin was synthesized by this group previously.¹

The ¹H and ¹³C nuclear magnetic resonance (NMR) were recorded on a Bruker DRX-400AV ANCE spectrometer, DMSO-d₆ and CDCl₃ were used as solvents. Steady-state fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer. Diffuse reflectance absorption spectra of solids were recorded on a Shimadzu UV-2600 spectrophotometer. Mass spectra (EI-MS) were obtained by use of an Agilent 7890A-5975C GC-MC spectrometer. X-ray spectra were obtained on a Rigaku Ultima IV. DSC spectra were gaved on a Netzsch DSC 200 F3. Ground sample was prepared by grinding, using a mortar and pestle. The method of solvent vapor fuming treatment involves filling the ground sample on a grooved glass, which was then placed in a large beaker saturated with dichloromethane (DCM) for 5min at room temperature. Thermal annealing of DBHC was obtained by heating the ground solid for 10min at 170 °C. Solid-state fluorescence quantum efficiency was measured with an integrating sphere (Edinburgh Instrument FLS920), with a 420 nm Xe light as the excitation source. The instrument measurement error range is about ±3%.



Scheme S1. Synthesis method of **DBHC**.

Synthesis

4-methoxybenzylidenehydrazine was synthesized according to the reference with a minor modification.² Methyl 4-methoxybenzoate 0.26 g (1.5 mmol) and 80% hydrazine hydrate 0.451 g (9 mmol) in 15 mL ethanol were heated under reflux for 12 h in a flask. After cooled to room temperature, the solvent was removed under vacuum. Petroleum ether was added into the mixture and the precipitate was collected. The crude product was obtained by suction filtering, ethanol washing and drying (0.20 g, 77% yield). ¹H

NMR (400 MHz, CDCl_3): δ (ppm) = 7.72 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H).

Analytically calculated for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$: C, 57.82; H, 6.07; N, 16.86%. Found: C, 57.80; H, 6.02; N, 16.95%. EI-MS: m/z : calcd: 167.0820. Found: 167.0826 $[\text{M}+1]^+$.

7-diethylamino-3-[4'-(methoxy)benzoylhydrazone]methylcoumarin (**DBHC**) was synthesized according to the reference with a minor modification.³ 7-diethylamino-3-formyl-coumarine 0.51 g (2.08 mmol) and 4-methoxybenzoyl hydrazine 0.264 g (1.6 mmol) were stirred at 80 °C for 5 h in 20 mL ethanol. Then cooled to room temperature, the solute is deposited. The residue was purified by suction filtering, ethanol washing and drying (0.55 g, 88% yield). ^1H NMR (400 MHz, DMSO-d_6) δ (ppm)=11.77 (s, 1H), 8.49 (s, 1H), 8.36 (s, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 8.8 Hz, 2H), 6.77 (dd, J = 4.0 Hz, 1H), 6.58 (d, J = 4.0 Hz, 1H), 3.83 (s, 3H), 3.47 (q, J = 6.0 Hz, 4H), 1.14 (t, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 164.75, 163.61, 159.23, 154.02, 141.14, 133.56, 128.14, 116.45, 115.51, 112.47, 110.84, 99.17, 58.17, 46.98, 15.11. Analytically calculated for $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_4$: C, 67.16; H, 5.89; N, 10.68%. Found: C, 67.11; H, 5.83; N, 10.74%. EI-MS: m/z : calcd: 394.1767. Found: 394.1774 $[\text{M}+1]^+$.

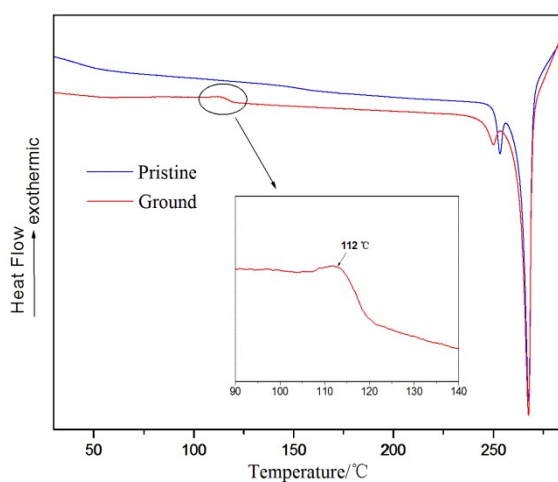


Figure S1. DSC curves of pristine sample and ground sample.

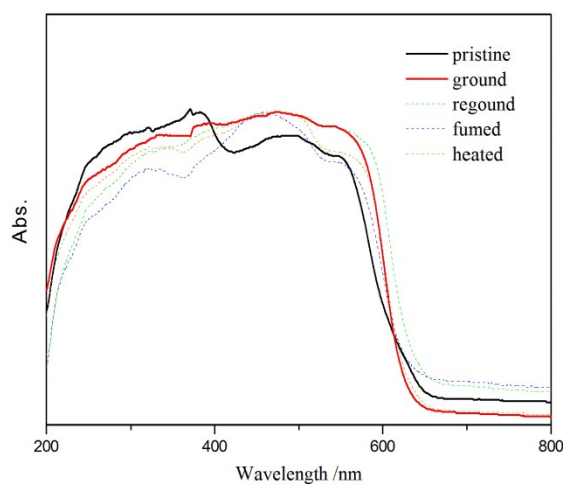


Figure S2. Diffuse reflectance absorption spectra of DBHC in solid states.

References:

- 1 L. M. Zhu, J. Yang, Q. S. Wang, L. T. Zeng, *Journal of Luminescence*, 2014, **148** 161.
- 2 K. M. Khan, M. Rasheed, Z. Ullah, S. Hayat, F. Kaukab, M.I. Choudhary, *Bioorganic & Medicinal Chemistry*, 2003, **11**, 1381.
- 3 D. C. Guo, P. L. Wu, H. Tan, L. Xia, W. H. Zhou, *Journal of Luminescence*, 2011, **131**, 1272.

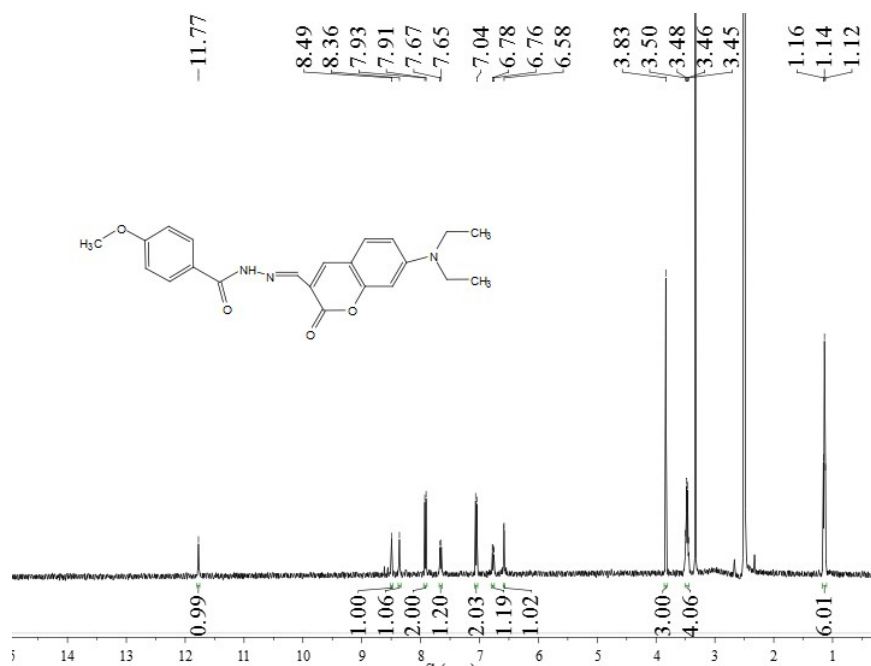


Figure S3. ¹H NMR spectra of DBHC in DMSO-d₆.

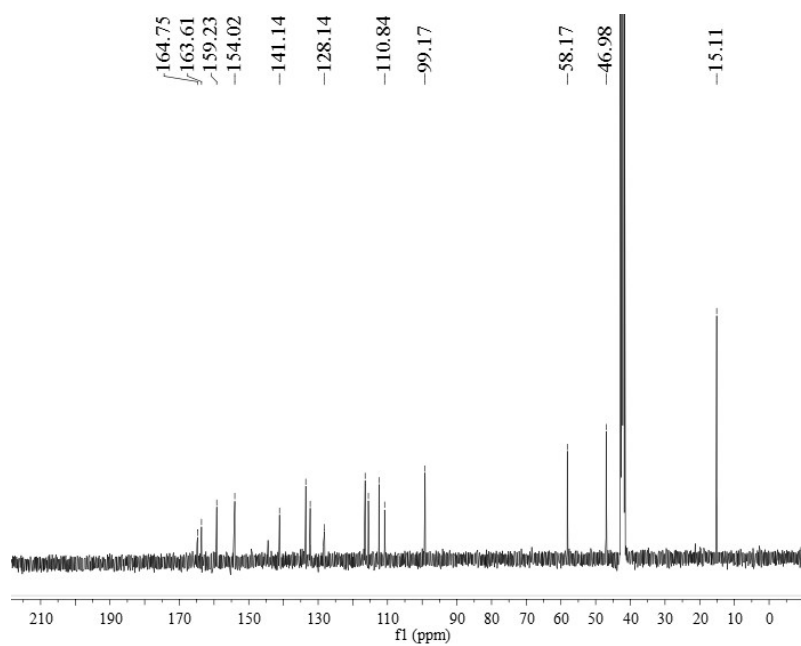


Figure S4. ¹³C NMR spectra of DBHC in DMSO-d₆.

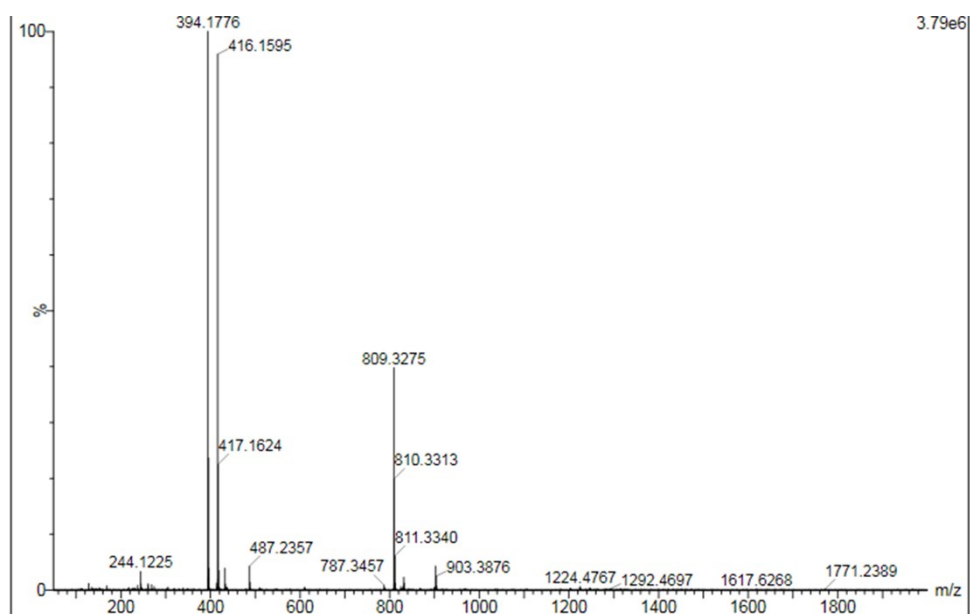


Figure S5. ESI-MS spectra of DBHC.