Unique Piezochromic Fluorescence Behavior of Organic

Crystal of Carbazole-substituted CNDSB

Cunfang Feng, Kai Wang, Yuanxiang Xu, Liqun Liu, Bo Zou, Ping Lu

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depressurizing process.

1. Experimental Section

All the reagents and solvents used for the syntheses were purchased from Aldrich or Acros and used as received. The reactions were performed under a dry nitrogen atmosphere. The NMR spectra were recorded on AVANCE 500 spectrometer at 298 K by utilizing deuterated chloroform (CDCl₃) or deuterated dimethyl sulfoxide (DMSO) as solvents and tetramethylsilane (TMS) as internal standard. The elemental analysis were performed by a Flash EA 1112, CHNS-O elemental analysis instrument. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFRTM plus were recorded on a UV-3100 instrument. UV-vis absorption spectra spectrophotometer. Fluorescence measurements were carried out with a RF-5301PC. The differential scanning calorimetry (DSC) analysis was determined using a NETZSCH (DSC-204) instrument at 10 °C min⁻¹ under nitrogen flushing. Highcarried out using pressure experiments were а diamond anvil cell (DAC). The culet diameter of the diamond anvils was 0.5 mm. T301 stainless steel gaskets were preindented to a thickness of 60 µm, and center holes of 0.16 mm were drilled for the sample. The ruby chip was used for pressure determination using the standard ruby fluorescent technique. Silicone oil was used as the pressure-transmitting medium. All experiments were performed at room temperature. High-pressure Raman spectra were recorded using a spectrometer (iHR 550, Horiba Jobin Yvon) equipped with the liquid nitrogen cooled CCD (Symphony II, Horiba Jobin Yvon). The 785 nm single mode laser was excite the sample and the output power utilized to was 50 mW. The in situ PL measurements under high pressure were performed on a QE65000 spectrometer (produced by Ocean Optics Inc.) in the reflection mode. The 355 nm line of a violet diode laser with a spot size of 20 mm and a power of 10 mW was used as the excitation source. The DAC containing the sample was put on a Nikon fluorescence microscope to focus the laser on the sample. Optical photographs of the were obtained using compressed samples an imaging camera (Canon EOS 5D Mark II) equipped on the fluorescence microscope. A screwdriven diamond anvil cell was used to perform the high pressure studies. The loading force is applied to the diamond anvils through the lever arm when the spring washers are compressed by the turn of the screws. As a result, the pressure in sample chamber will be gradually increased, which can be monitored by ruby fluorescence peaks. When the pressure reached to the highest pressure we studied, we can reverse rotate the screws to reduce the applied force on diamond anvil cell and the corresponding pressure in sample chamber. The high pressure on sample will be completely moved after the deformation of spring washers restored.

Measurements of the single crystal of CzCNDSB were performed on a Rigaku R-AXIS RAPID diffractometer equipped with a graphite monochromated Mo-Ka radiation source. The diffraction data were collected at room temperatures. The structure was determined using direct methods with the SHELXL-97 software programme. X-ray diffraction of powder was carried out with a Rigaku Smart Lab (3) diffractometer. The sample placed on a glass plate (glass thickness: 0.05 mm) was irradiated by CuKα radiation source (voltage: 40 kV; current: 30 mA).



Synthesis of 4-(9H-Carbazol-9-yl)benzaldehyde (1)

2.

Carbazole (3 g, 17.9 mmol), 4-bromobenzaldehyde (3.3 g, 17.9 mmol), potassium carbonate (3.72 g, 26.9 mmol), copper iodide (0.4 g, 2.1 mmol) and 18-crown-6 (0.33 g, 1.3 mmol) were refluxed in 1,2-dichlorobenzene (18 mL) for 48 h. And then, the mixture was cooled and acidified with 20% aqueous HCl (30 mL) and extracted with chloroform. The solvent was evaporated by rotary evaporation under vacuum and the product was purified by column chromatography using dichloromethane/petroleum ether (1:1, v/v) as the eluent, which gave the compound 1 (3.9 g) as a white powder. Yield: 82%. ¹H NMR (500 MHz, DMSO): δ 10.15 (s, 1H), 8.29 (d, J = 7.7 Hz, 2H), 8.22 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.51 – 7.45 (t, 2H), 7.36 (t, J = 10.9 Hz, 2H).

Synthesis of (2z,2'z)-2,2'-(1,4-phenylene)bis(3-(4-(9H-carbazol-9-yl)phenyl) acrylonitrile) (CzCNDSB)

The mixture of 4-(9H-Carbazol-9-yl)benzaldehyde (542.6 mg, 2 mmol), 1, 4phenylenediacetonitrile (156.2 mg, 1 mmol), tert-butyl alcohol (10 mL) and THF (5 mL) was stirred at 46 °C for 30 min. Then, potassium tert-butoxide (1 M solution in tetrahydrofuran, 0.25 mL) and tetrabutylammonium hydroxide (TBAH, 1 M solution in methanol, 0.25 mL) were added, and the mixture was stirred for 30 minutes. The resulting precipitate was filtered and purified by column chromatography using dichloromethane as eluent to give CzCNDSB as a green yellow powder (500 mg). Yield: 70%. ¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, J = 8.5 Hz, 4H), 8.19 (d, J = 7.7 Hz, 4H), 7.89 (s, 4H), 7.79 (d, J = 8.5 Hz, 4H), 7.76 (s, 2H), 7.56 (d, J = 8.2 Hz, 4H), 7.50 – 7.46 (m, 4H), 7.36 (t, J = 7.4 Hz, 4H). ¹³C NMR (126 MHz, CDCl₃, δ): 141.57, 140.26, 140.02, 135.22, 132.02, 131.11, 127.02, 126.70, 126.19, 123.77, 120.60, 120.49, 117.71, 109.86, 109.74. IR (KBr, v, cm⁻¹): 3043, 2216, 1625, 1595, 1515, 1477, 1421, 1361,1333, 1319, 1261, 1223, 1168, 1118, 1016, 996, 916, 839, 832, 750, 722, 621, 534, 422. MS: Calcd for C₄₈H₃₀N₄: 662.25, Found: 662.81. Elemental analysis (Calcd., Found for C₄₈H₃₀N₄): C (86.98, 86.91), H (4.56, 4.55), N (8.45, 8.46).

2.2 ¹H NMR spectra of CzCNDSB



Figure S1. ¹H NMR spectra of CzCNDSB before UV irradiation (a) and after UV irradiation for 30 min (b).

3. Thermal properties of CzCNDSB



Figure S2. Thermal properties of CzCNDSB, (a) The TGA graph of CzCNDSB (heating rate: 10 °C/min under nitrogen flushing), (b) DSC graph of CzCNDSB (the second heating circulation, heating rate: 10° C/min under nitrogen flushing).

4. Crystal data and structure refinement of CzCNDSB

 Table S1. Crystal data and structure refinement of CzCNDSB crystal

Identification code	CzCNDSB
Chemical formula	$C_{48}H_{30}N_4$
Formula weight	662.76
T/K	293
Crystal system	Trigonal
space group	R-3
a/Å	30.549(5)
b/Å	30.549(5)
c/Å	11.026(5)
$\alpha/^{\circ}$	90
β/°	90
$\gamma/^{\circ}$	120
V/Å ³	8911(5)
Z	9
Density/g/cm ³	1.112
M(Mo Kα)/mm ⁻¹	0.066
θ range/°	1.33-27.470
Reflections collected	4512
Independent reflections	2708
GOF	1.055
$R_1[I > 2\sigma(I)]$	0.0639



Figure S3. The ellipsoid structure figure of CzCNDSB.

5. Piezochromic properties



Figure S4. Fluorescent spectra and PXRD patterns of CzCNDSB, (a) Fluorescent spectra of grinding, solution fuming (CH₂Cl₂), annealing (150 °C for 10 min) and as prepared samples of CzCNDSB, (b) their corresponding XRD diffraction graphs (range of scanning angle: 2° - 40° , rate: 0.02 degree/min).

6. In situ Raman spectra in high pressure experiment



Figure S5. Raman spectra of C_Z CNDSB crystal at ambient conditions and the assignments of Raman peaks.

Table S2. The peak assignment of raman spectra

Vibration mode	Wavelength (cm ⁻¹)
-CN stretching vibration	2217
-C=C stretching vibration	1627
Benzene ring vibration	1590, 1582, 1556
Carbazole ring vibration	1455, 1425
Para-benzene ring vibration	1205, 640
Para-benzene –C-H out of plane wag mode	942, 831, 788
-C=C out-of-plane vibration	820
external molds	115, 103, 89



Figure S6. Raman spectra of CzCNDSB crystal, (a) Raman spetra at pressurizing process, (b) depressurizing process. Excited by 671 nm, laser power: 2 mW.



Figure S7. Frequency shifts of major Raman peaks of CzCNDSB as a function of pressure.



Figure S8. (a) PL spectra of CzCNDSB:KBr (weight ratio of 1:10) during pressurizing process, (b) during depressurizing process, (c) Images of mixture in DAC during pressurizing and depressurizing cycle; excited by laser ($\lambda_{ex} = 355$ nm).



Figure S9. The wavelength change of CzCNDSB in repeat pressurizing and depressurizing process.