

Electronic Supplementary Information

Achieving crystal-induced room temperature phosphorescence and reversible photochromic properties by strong intermolecular interactions

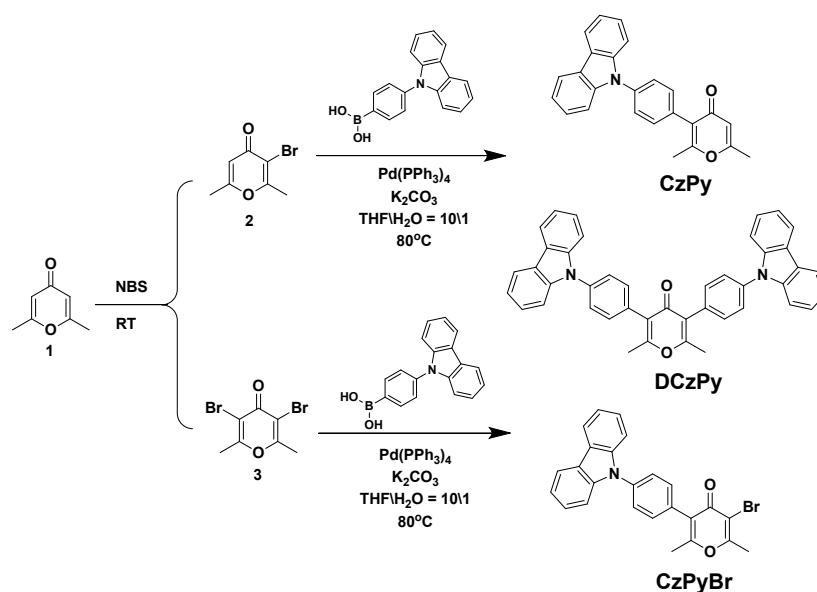
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Contents



Scheme S1 Synthetic route of the target compounds.

1. Experimental

Measurements and materials

NMR spectra were determined on a Bruker DRX 500 NMR spectrometer using deuterated chloroform as a solvent and trimethylsilane as a reference. HRMS-ESI mass spectra were conducted on a Hitachi Nano Frontier LD spectrometer. The elemental analysis was determined on an Elementar Vario MICRO analyzer. UV-vis absorption spectra were performed with a UV-3600 Shimadzu spectrophotometer. Fluorescence spectra were performed with a HITACHI F-7000 fluorometer. Phosphorescence spectra were measured by using FLS920 lifetime and steady state spectrometer. Solid-state emission quantum yields (Φ_F) were collected by using FluoroMax-4 (Horiba Jobin Yvon) fluorimeter equipped with integrated sphere. XRD curves were recorded using an Empyrean X-ray diffraction instrument. The X-ray crystallographic analyses were conducted on a Bruker SMART II CCD area detector. 2,6-Dimethyl-4H-pyran-4-one (1), (4-(9H-carbazol-9-yl)phenyl)boronic acid, benzophenone, and *N*-bromosuccinimide (NBS) were commercially available and used directly.

Synthesis of 3-Bromo-2,6-dimethyl-4H-pyran-4-one (2) and 3,5-Dibromo-2,6-dimethyl-4H-pyran-4-one (3)

The solution of NBS (1.42 g, 8 mmol) in dry DMF (10 mL) was slowly added to the solution of compound 1 in dry DMF (20 mL). The mixture was stirred at room temperature for 24 h and then poured into 100 mL water. The mixture was extracted three times with dichloromethane. Anhydrous sodium sulfate was added to dry the organic phase and then the organic solvent was evaporated by decompression. The residue was passed through a silica gel column

chromatography (petroleum ether/ethyl acetate = 1:10, v : v) to afford compound **2** and compound **3**, respectively.

3-Bromo-2,6-dimethyl-4H-pyran-4-one (2): White solid (0.52 g, 32% yield). ¹H NMR (500 MHz, CDCl₃) δ: 6.155 (s, 1H), 2.501 (s, 3H), 2.260 (s, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 173.7, 164.9, 163.5, 113.9, 112.0, 20.6, 19.5 ppm.

3,5-Dibromo-2,6-dimethyl-4H-pyran-4-one (3): White solid (1.21 g, 54% yield). ¹H NMR (500 MHz, CDCl₃) δ: 2.522 (s, 6H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 168.3, 162.8, 111.4, 20.5 ppm.

Synthesis of pyranone-carbazole compounds

General procedure: A mixture of compound **2**/compound **3** (12.0 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (10.0 mmol), Pd(PPh₃)₄ (5.0 mol%), and K₂CO₃ (5.0 mol%) were dissolved in 10.0 mL of THF and 1.0 mL of water. The mixture was stirred for 24 h at 80°C under nitrogen atmosphere. The solvent was removed under reduced pressure, and then the residue were purified by column chromatography (petroleum ether/ethyl acetate = 1:20, v : v) to afford the pure **CzPy/DCzPy/CzPyBr**.

3-(4-(9H-Carbazol-9-yl)phenyl)-2,6-dimethyl-4H-pyran-4-one (CzPy). White solid (3.91 g, 89% yield). ¹H NMR (500 MHz, CDCl₃) δ: 8.152 (d, *J* = 8.0 Hz, 2H), 7.636 (d, *J* = 8.5 Hz, 2H), 7.503 (q, *J* = 8.5 Hz, 4H), 7.425 (t, *J* = 7 Hz, 2H) 7.298 (t, *J* = 7 Hz, 2H) 6.271 (s, 1H) 2.324 (d, *J* = 3 Hz, 6H) ppm. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₂₅H₂₀NO₂, 366.1494; found, 366.1496. Anal. Calcd for C₂₅H₁₉NO₂: C, 82.17; H, 5.24; N, 3.83. Found: C, 82.43; H, 5.27; N, 3.81.

3-(4-(9H-Carbazol-9-yl)phenyl)-5-bromo-2,6-dimethyl-4H-pyran-4-one (CzPyBr). White solid (2.50 g, 47% yield). ¹H NMR (500 MHz, CDCl₃) δ: 8.153 (d, *J* = 7.5 Hz, 2H), 7.638 (d, *J* = 8.5 Hz, 2H), 7.500 (q, *J* = 6 Hz, 4H), 7.425 (t, *J* = 7.5 Hz, 2H) 7.301 (t, *J* = 7.5 Hz, 2H), 2.591 (s, 3H), 2.351 (s, 3H) ppm. δ: 172.3, 162.8, 162.0, 140.7, 137.5, 131.8, 131.2, 126.7, 125.9, 124.3, 123.5, 120.3, 120.0, 113.9, 109.9, 20.7, 18.6 ppm. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₂₅H₁₉BrNO₂, 444.0594; found, 444.0595. Anal. Calcd for C₂₅H₁₈BrNO₂: C, 67.58; H, 4.08; N, 3.15. Found: C, 67.29; H, 4.10; N, 3.13.

3,5-Bis(4-(9H-carbazol-9-yl)phenyl)-2,6-dimethyl-4H-pyran-4-one (DCzPy). White solid (2.40 g, 40% yield). ¹H NMR (500 MHz, CDCl₃) δ: 8.159 (d, *J* = 8 Hz, 4H), 7.653 (d, *J* = 8.5 Hz, 4H), 7.580 (d, *J* = 8 Hz, 4H), 7.509 (d, *J* = 8.5 Hz, 4H), 7.428 (t, *J* = 7 Hz, 4H), 7.303 (t, *J* = 7.5 Hz, 4H), 2.45 (s, 6H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 176.7, 162.2, 140.8, 137.2, 131.9, 131.7, 126.7, 125.9, 123.4, 120.2, 120.0, 109.1, 19.0 ppm. HRMS (ESI) *m/z*: [M+H]⁺ C₄₃H₃₁N₂O₂, 607.2394; found, 607.2380. Anal. Calcd for C₄₃H₃₀N₂O₂: C, 85.12; H, 4.98; N, 4.62. Found: C, 85.43; H, 5.01; N, 4.60.

2. Calculation method

The density functional theory (DFT) method at the level of b3lyp/6-31G* was used to restrictively optimize (only optimize H atoms, and other atoms based on the single crystal structures) the monomer and dimer of samples. The excited energies were calculated by the time-dependent density functional theory (TD-DFT) method. All the calculations were performed within Gaussian 09 software package. At the same level, the SOCs between singlet and triplet states are given by PySOC [1] and atomic integrals in PySOC are calculated from MolSOC code developed by Sandro Giuseppe Chiodo et al [2].

Reference

- [1] X. Gao, S. M. Bai, D. Fazzi, T. Niehaus, M. Barbatti and W. Thiel. *J. Chem. Theory. Comput.*, **2017**, 13, 515-524.
- [2] S. G. Chiodo, M. Leopoldini. *Computer Physics Communications*. **2014**, 185, 676-683.

3. Figures and tables

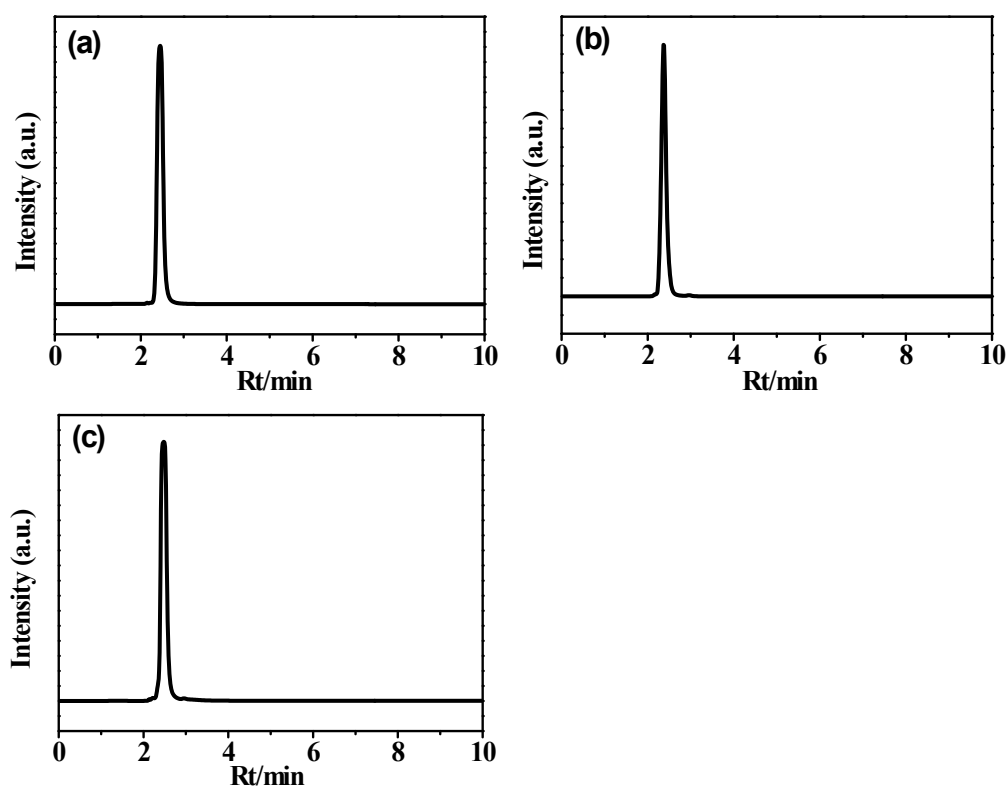


Fig. S1 HPLC spectra of CzPy (a), DCzPy (b), and CzPyBr (c). (Acetonitrile as Acetonitrile as mobile phase).

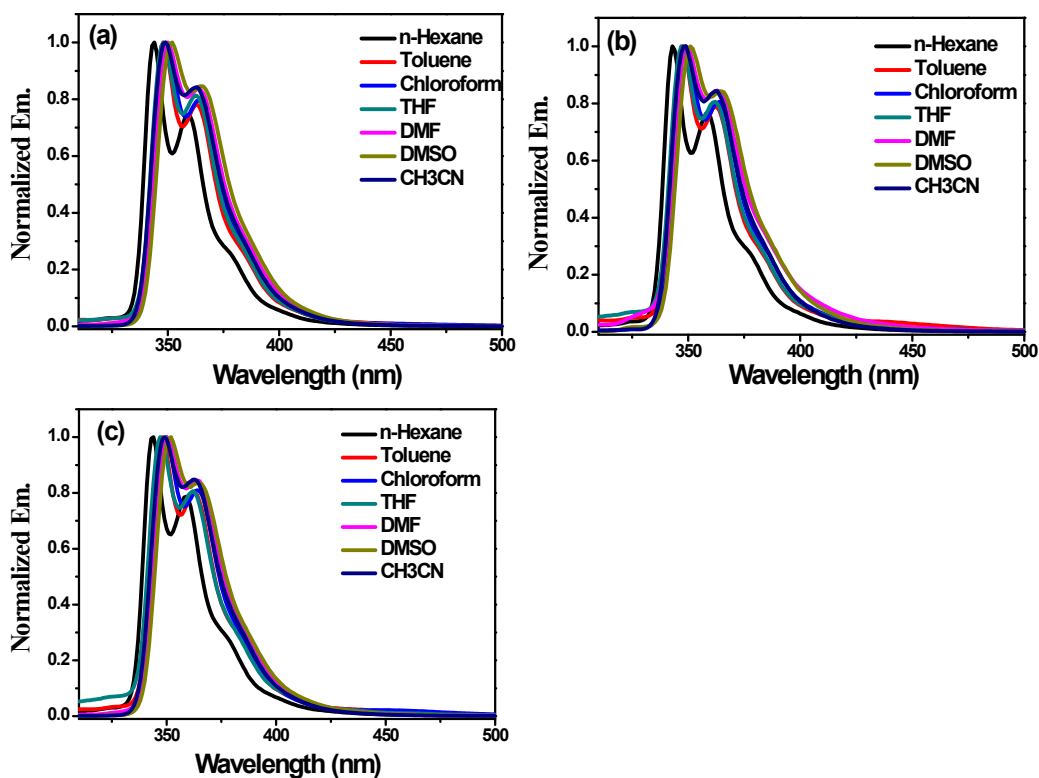


Fig. S2 The fluorescence spectra of CzPy (a), DCzPy (b), and CzPyBr (c) in different solvents.

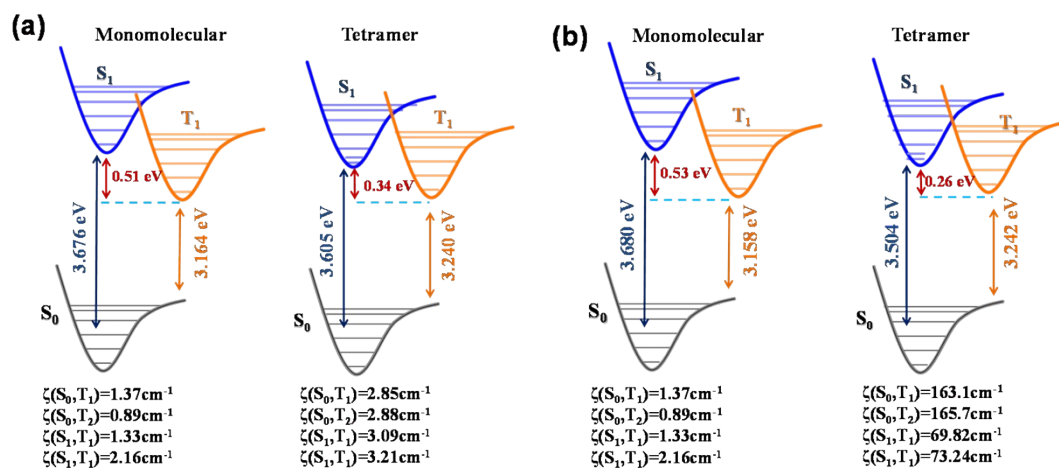


Fig. S3 (a) Energy levels and SOC of the monomolecular and tetramer of DCzPy. (b) Energy levels and SOC of the monomolecular and tetramer of CzPyBr.

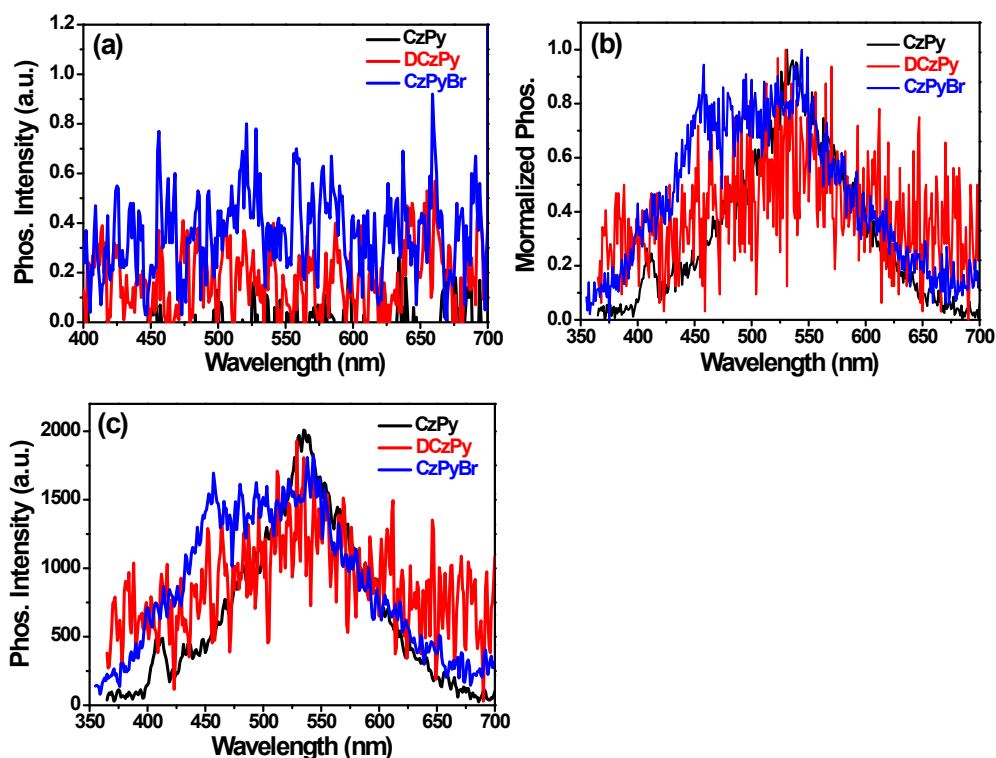


Fig. S4 (a) Phosphorescence emissions of the three compounds in solution (THF as solvent, 1.0×10^{-5} mol/L). (b) Phosphorescence emissions of the three compounds in amorphous state. (c) Phosphorescence emission of three compounds in amorphous state under nitrogen atmosphere.

Table S1 Crystal data and details of collection and refinement for **CzPy**, **DCzPy**, and **CzPyBr**

	CzPy	DCzPy	CzPyBr
CCDC (no.)	2018726	2018727	2018725
Empirical formula	$C_{25}H_{19}NO_2$	$C_{43}H_{30}N_2O_2$	$C_{25}H_{18}BrNO_2$
Formula weight	365.41	606.69	444.31
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Trigonal	Monoclinic	Monoclinic
Space group	$R\bar{3}c:H$	$P2(1)/c$	$P2(1)/n$
<i>Z</i>	18	4	4
D_{calcd} [Mg/m^3]	1.322	1.287	1.489
<i>F</i> (000)	3456	1272	904
θ range [$^\circ$]	2.47-25.99	2.82-25.50	2.38-26.00
R_1 [$I > 2\sigma(I)$]	0.0355	0.0503	0.0477
wR_2 [$I > 2\sigma(I)$]	0.0734	0.1110	0.1208
<i>a</i> [\AA]	33.0425(9)	9.8491(8)	8.0234(3)
<i>b</i> [\AA]	33.0425(9)	21.1814(12)	17.1521(6)
<i>c</i> [\AA]	8.7370(13)	15.1737(10)	14.4245(6)
α [deg]	90	90	90
β [deg]	90	98.426(2)	93.059(2)
γ [deg]	120	90	90
V [\AA^3]	8261.1(13)	3131.3(4)	1982.24(13)

GOF	1.081	1.029	1.038
R(int)	0.0524	0.0398	0.0367
No. of reflcns collected	40683	15032	19746
No. of unique reflcns	3611	5792	3887
R_1 (all data)	0.0462	0.0890	0.0708
wR_2 (all data)	0.0794	0.1368	0.1346

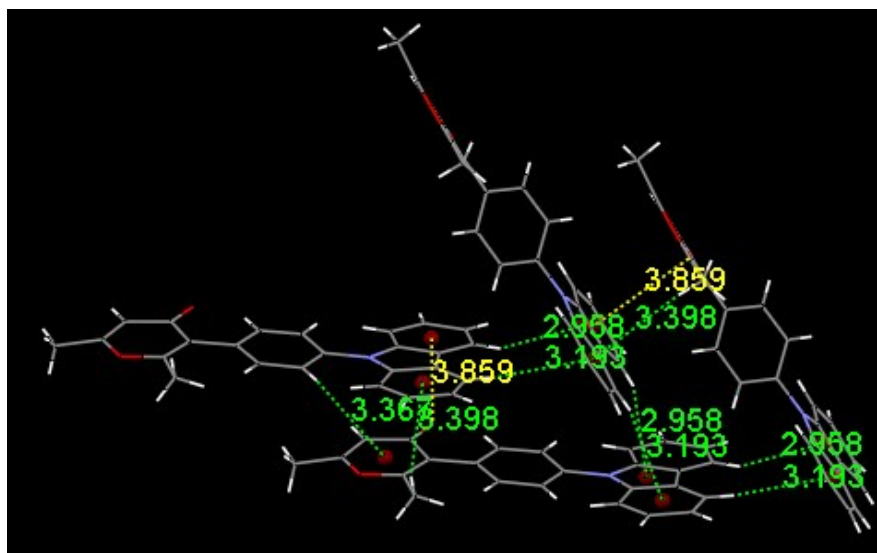


Fig. S5 The distances of the C-H... π (green line) and C-H...O (yellow line) interactions of CzPy.

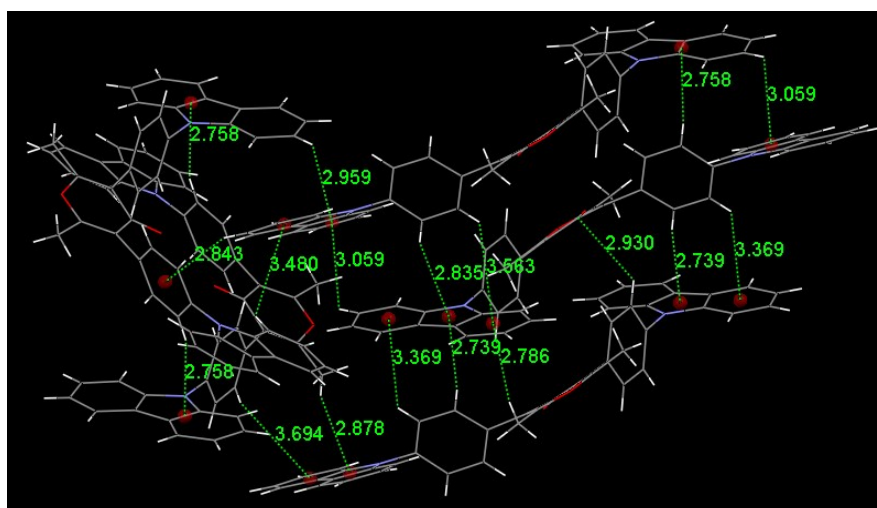


Fig. S6 The distances of the C-H... π (green line) interactions of DCzPy.

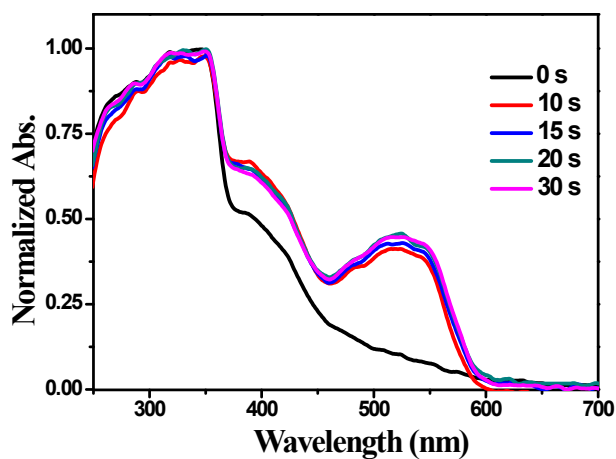


Fig. S7 Time-dependent solid-state UV-vis absorption spectra changes of the crystalline **CzPyBr** upon UV-light irradiation (360 nm) with increasing time.

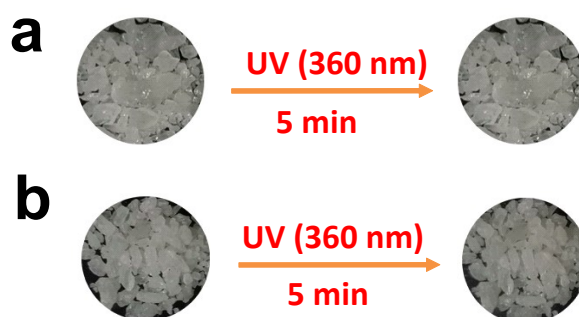


Fig. S8 The pictures of the crystalline samples of **CzPy** (a) and **DCzPy** (b) before and after the UV light irradiation (360 nm) under natural light.

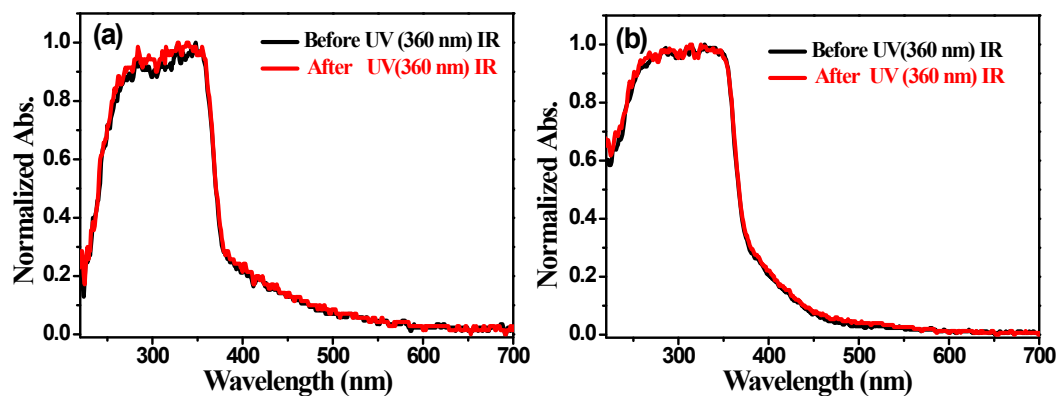


Fig. S9 Absorption spectra of the crystalline samples of **CzPy** (a) and **DCzPy** (b) before and after UV light irradiation (IR).

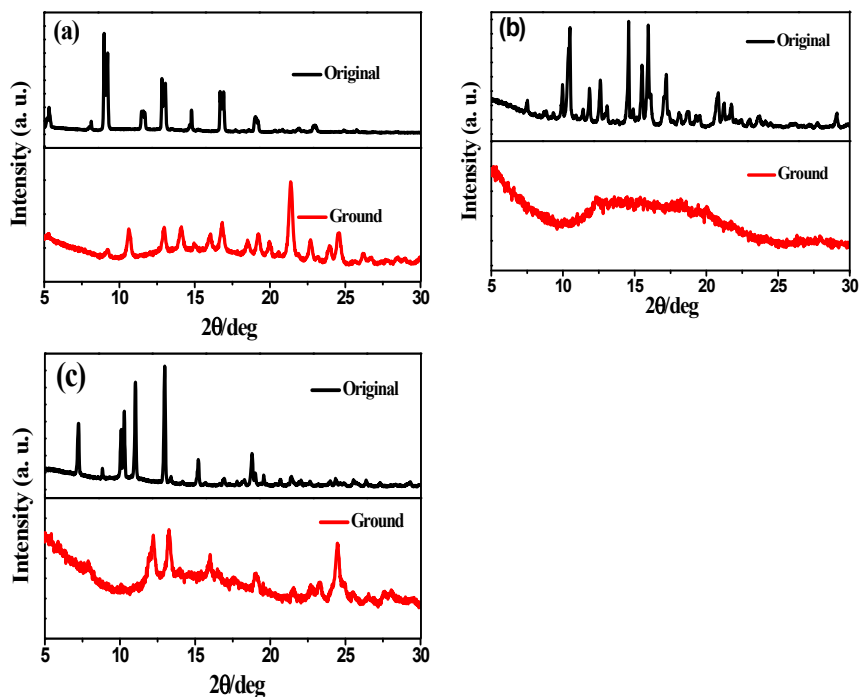


Fig. S10 (a) XRD curves of the crystalline sample of CzPy before and after grinding. (b) XRD curves of the crystalline sample of DCzPy before and after grinding. (c) XRD curves of the crystalline sample of CzPyBr before and after grinding.

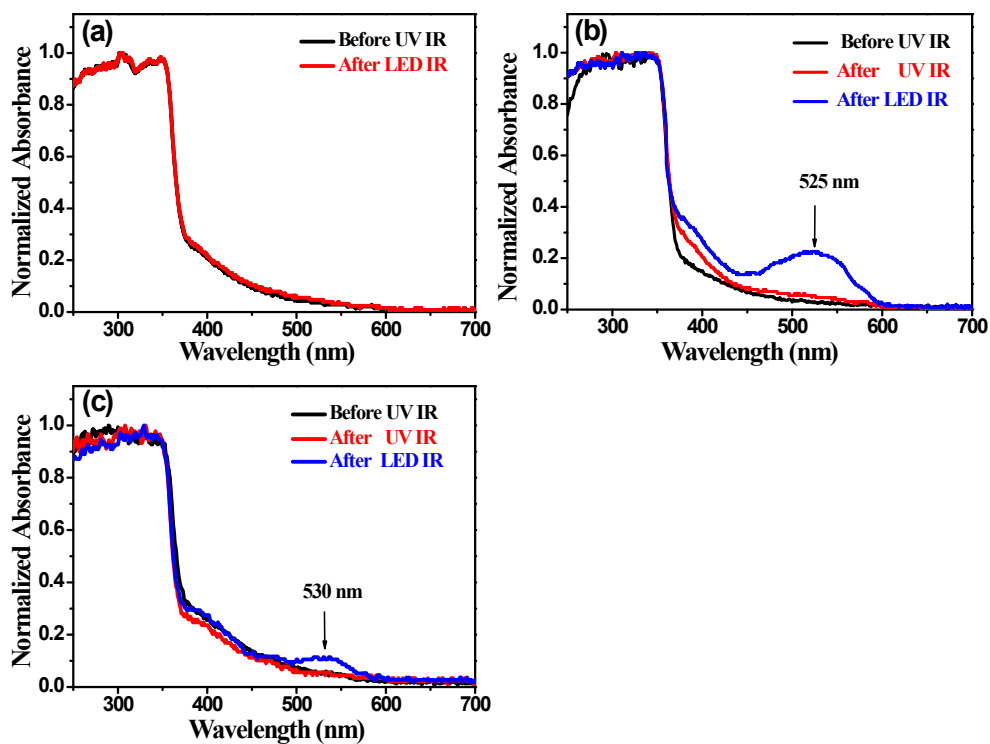


Fig. S11 The absorption spectra of the ground samples of CzPy (a), DCzPy (b), and CzPyBr (c) before and before and after different light irradiation (IR).

Table S2 The color coordinates (CIELAB) of the solid-state samples of the pyranone-carbazole compounds before and after UV light irradiation (IR).

Samples	Original crystalline CzPyBr	UV light IR crystalline CzPyBr	Original Ground DCzPy	UV light IR Ground DCzPy
L	77	46	76	44
a	-3	38	-4	35
b	21	25	20	26

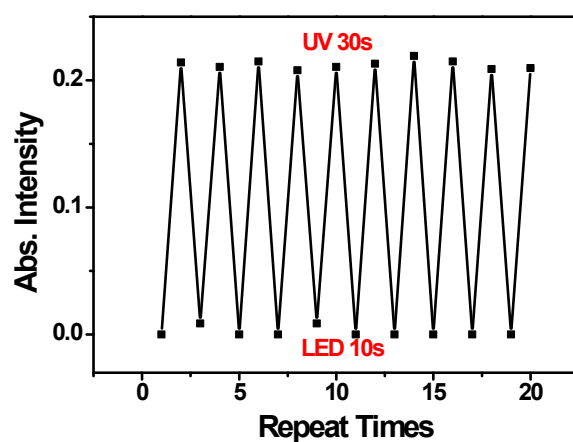


Fig. S12 Recycling of the photochromic process of the ground sample of DCzPy exposure to UV-light (365 nm) and LED-light for 30 s and 10 s, respectively.

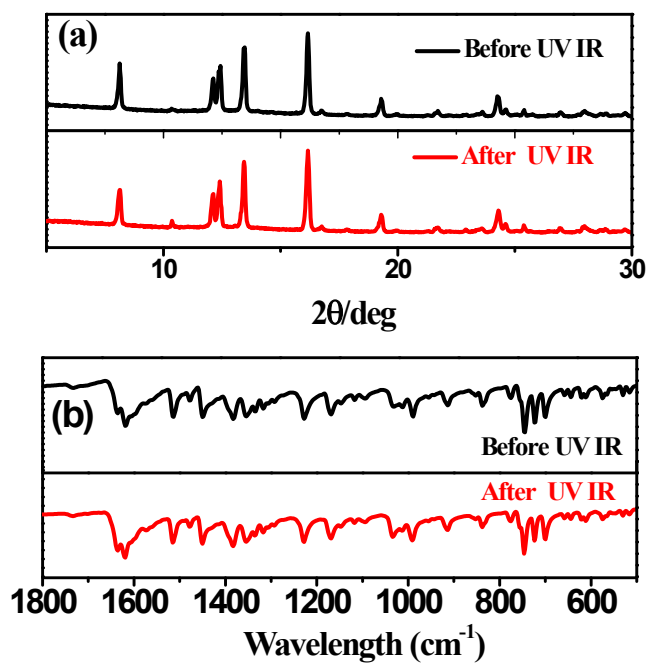


Fig. S13 (a) XRD curves of crystal CzPyBr before and after UV light (360 nm) irradiation. (b) Infrared spectra of crystal CzPyBr before and after UV light (360 nm) irradiation.

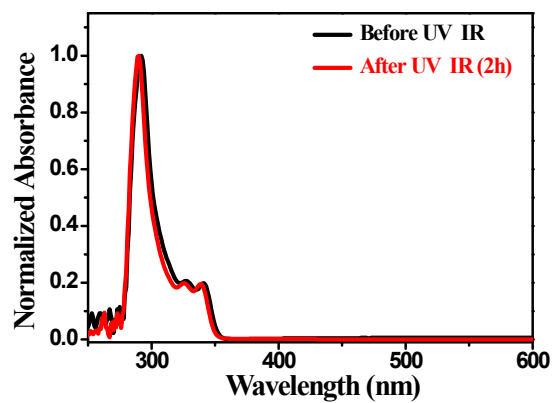


Fig. S14 Absorption spectra of CzPyBr in THF solution before and after UV light irradiation.

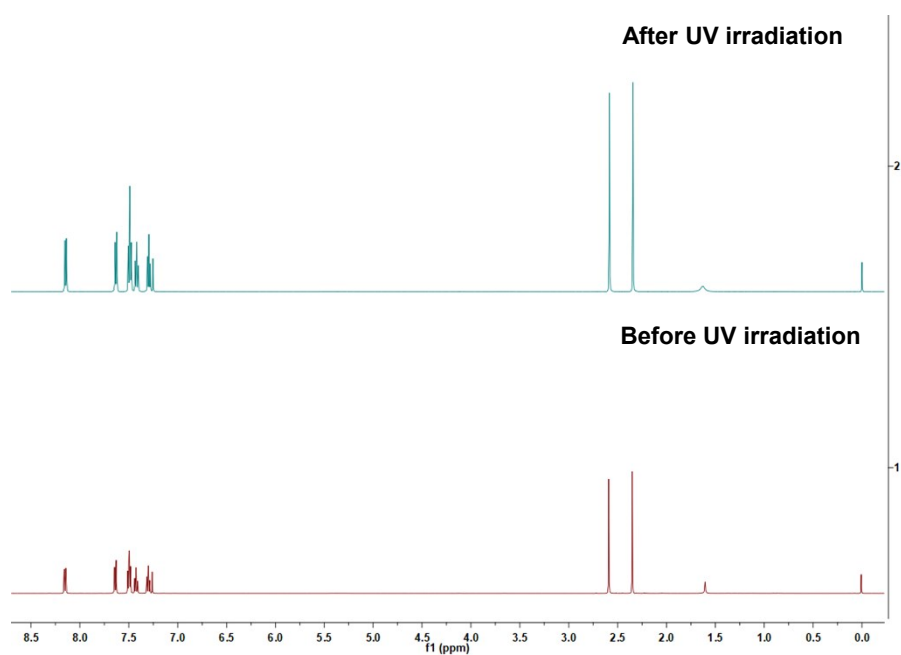


Fig. S15 The ¹H NMR spectra (CDCl₃, 500 MHz) of CzPyBr before and after UV light irradiation.

4. NMR Spectra

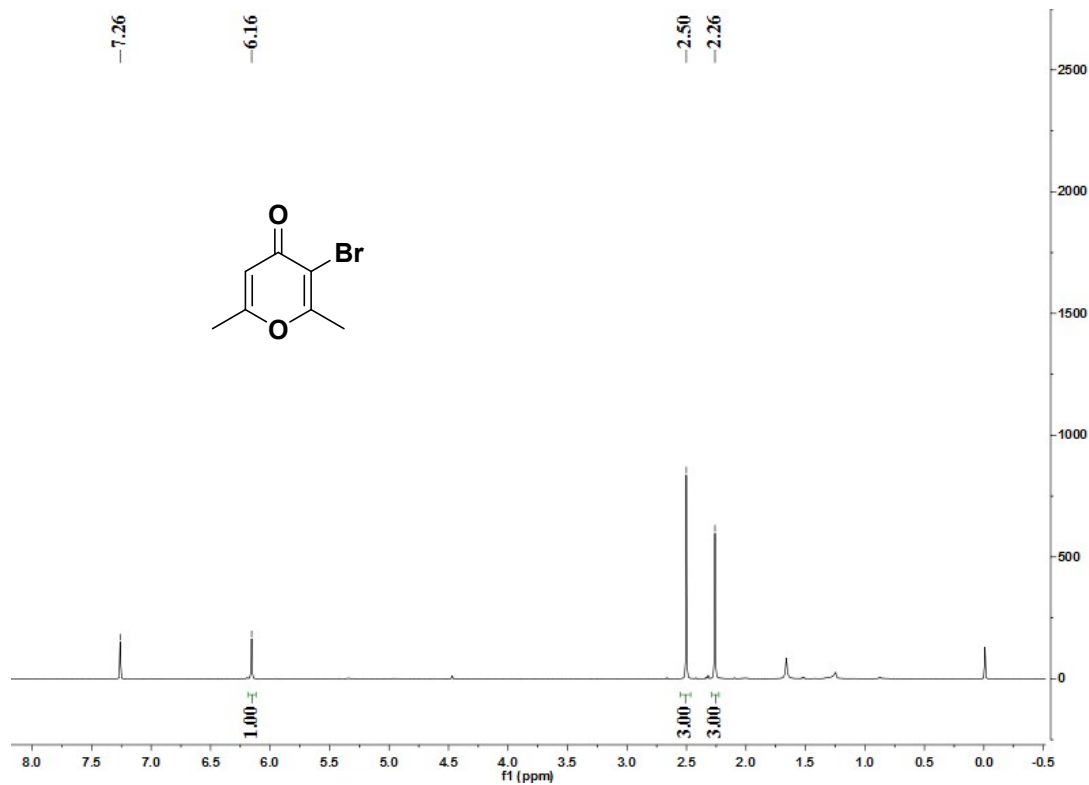


Fig. S16 ¹H NMR of compound 2 (CDCl₃, 500 MHz).

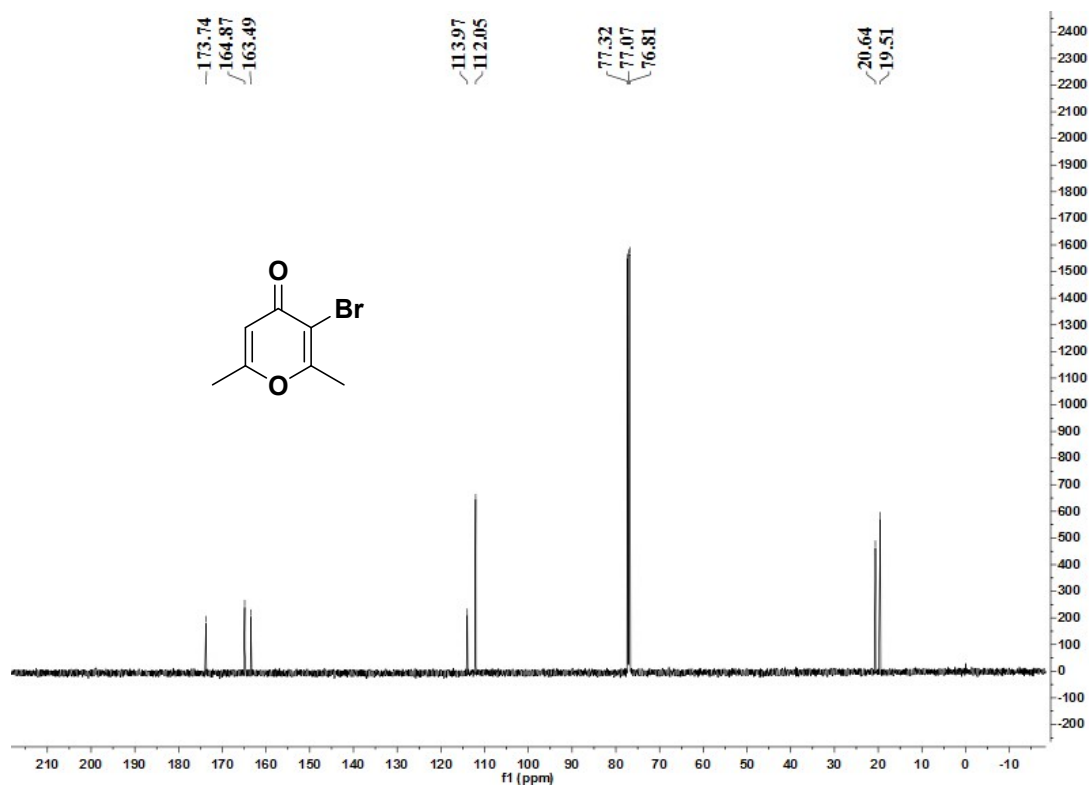


Fig. S17 ¹³C NMR of compound 2 (CDCl₃, 125 MHz).

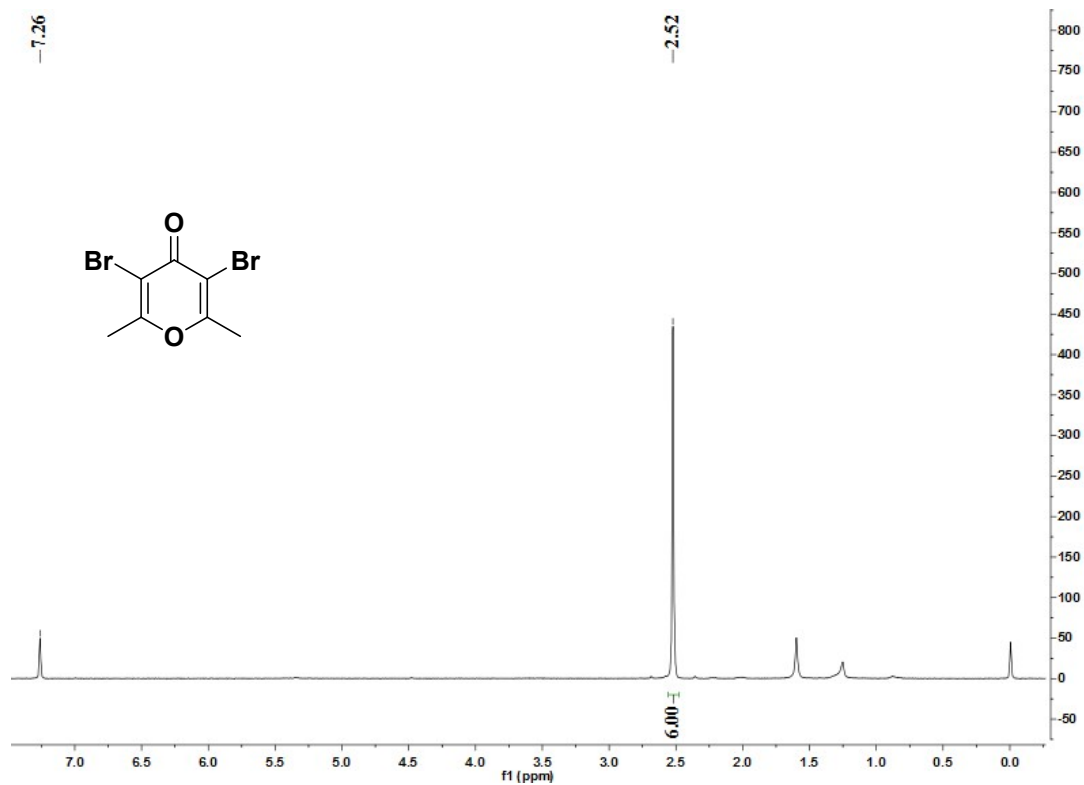


Fig. S18 ¹H NMR of compound 3 (CDCl₃, 500 MHz).

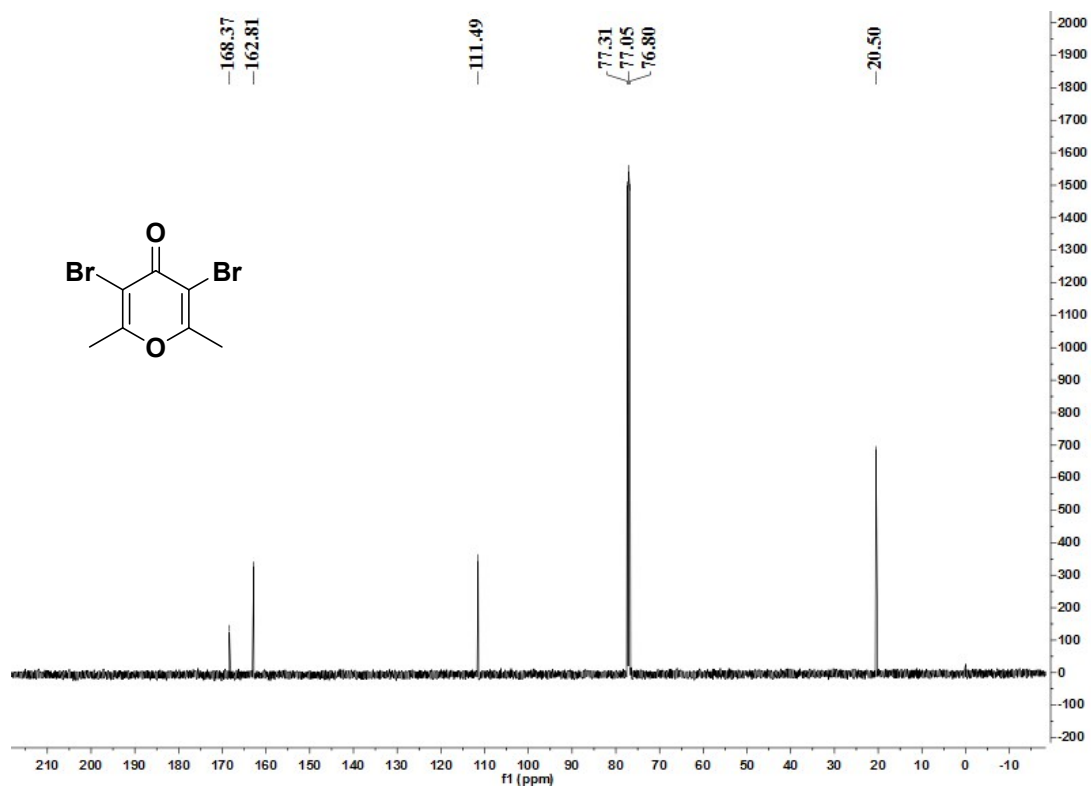


Fig. S19 ¹³C NMR of compound 3 (CDCl₃, 125 MHz).

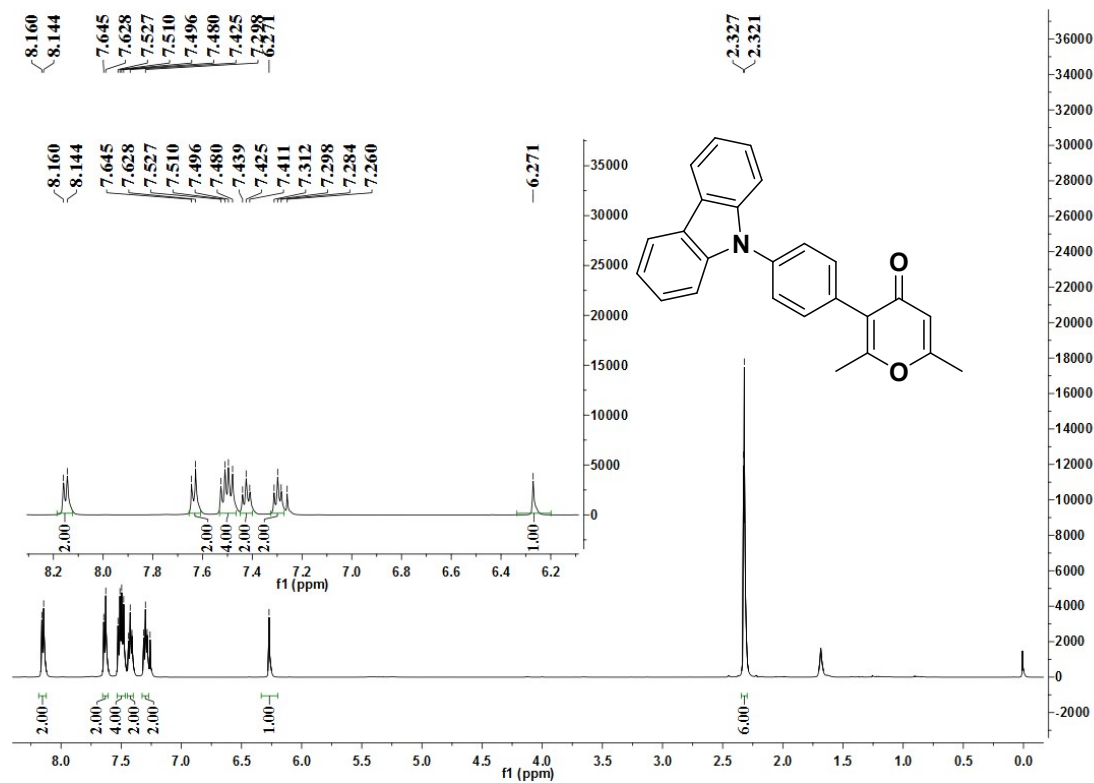


Fig. S20 ^1H NMR of compound CzPy (CDCl_3 , 500 MHz).

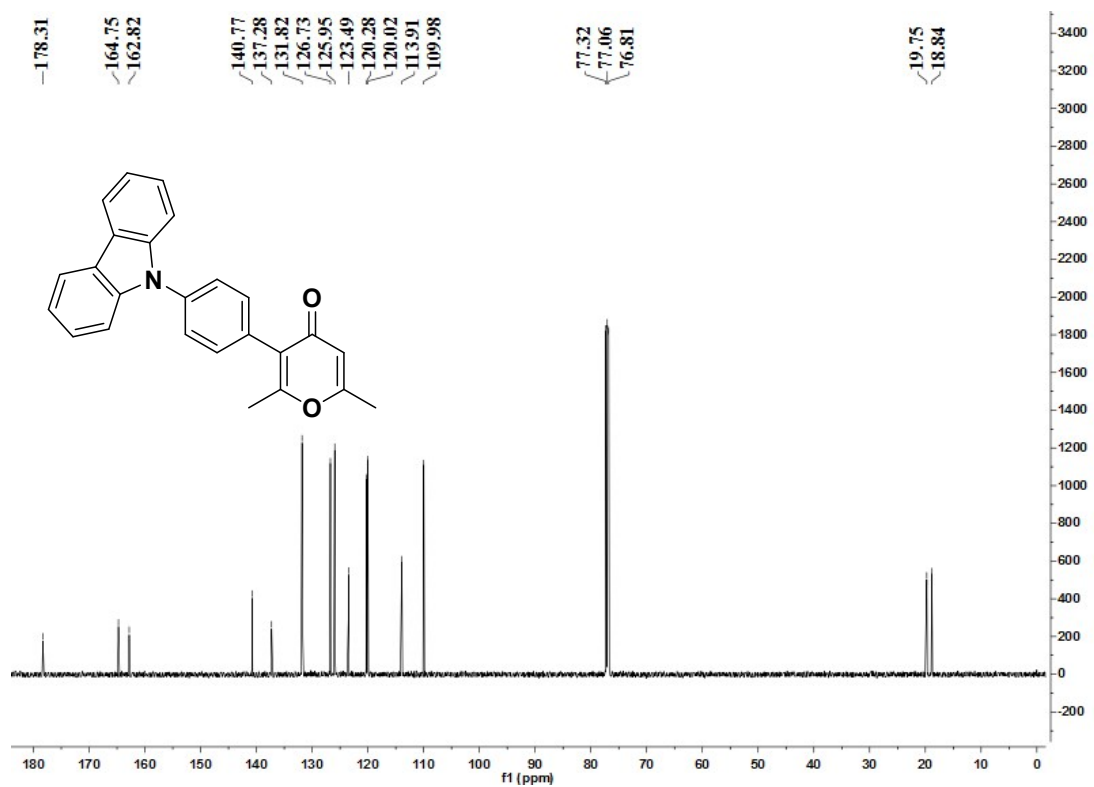


Fig. S21 ^{13}C NMR of compound CzPy (CDCl_3 , 125 MHz).

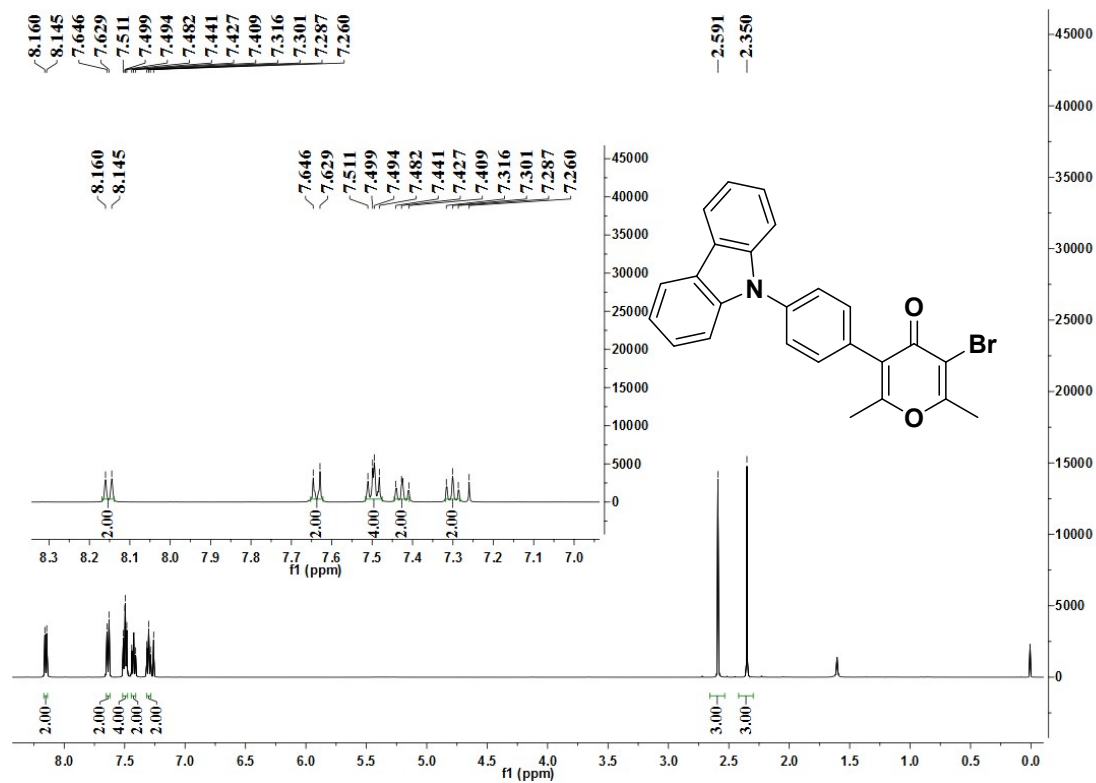


Fig. S22 ¹H NMR of compound CzPyBr (CDCl₃, 500 MHz).

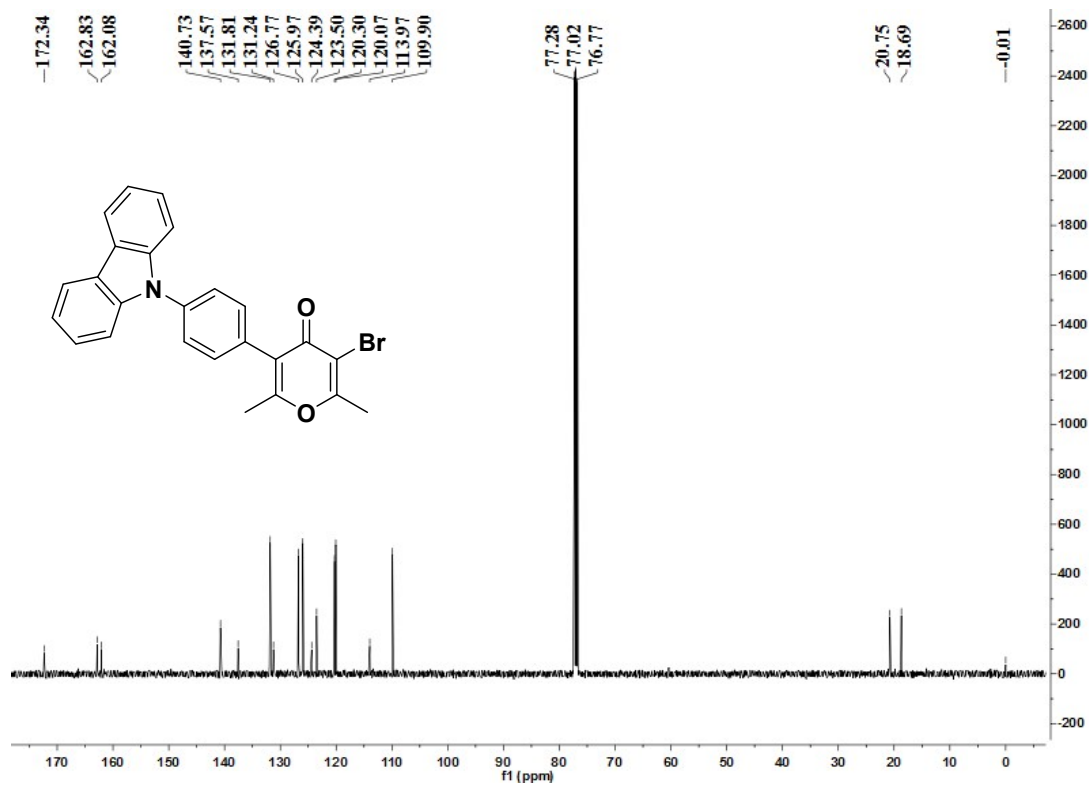


Fig. S23 ¹³C NMR of compound CzPyBr (CDCl₃, 125 MHz).

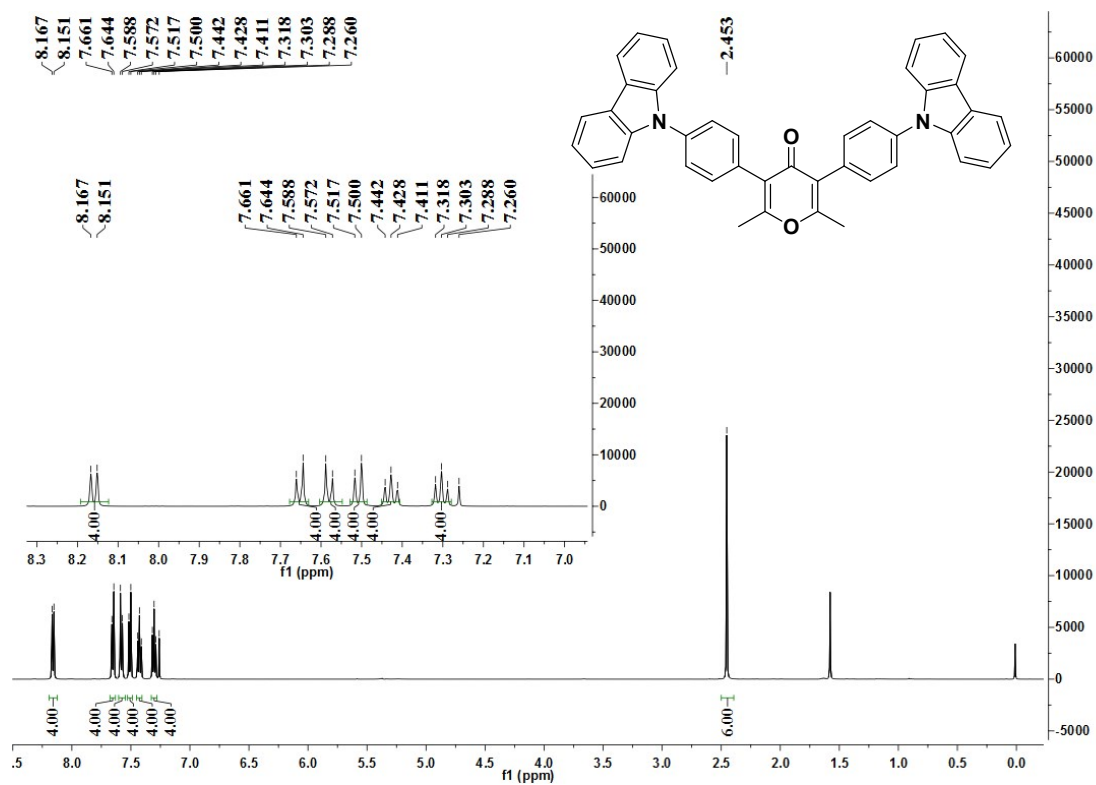


Fig. S24 ¹H NMR of compound DCzPy (CDCl₃, 500 MHz).

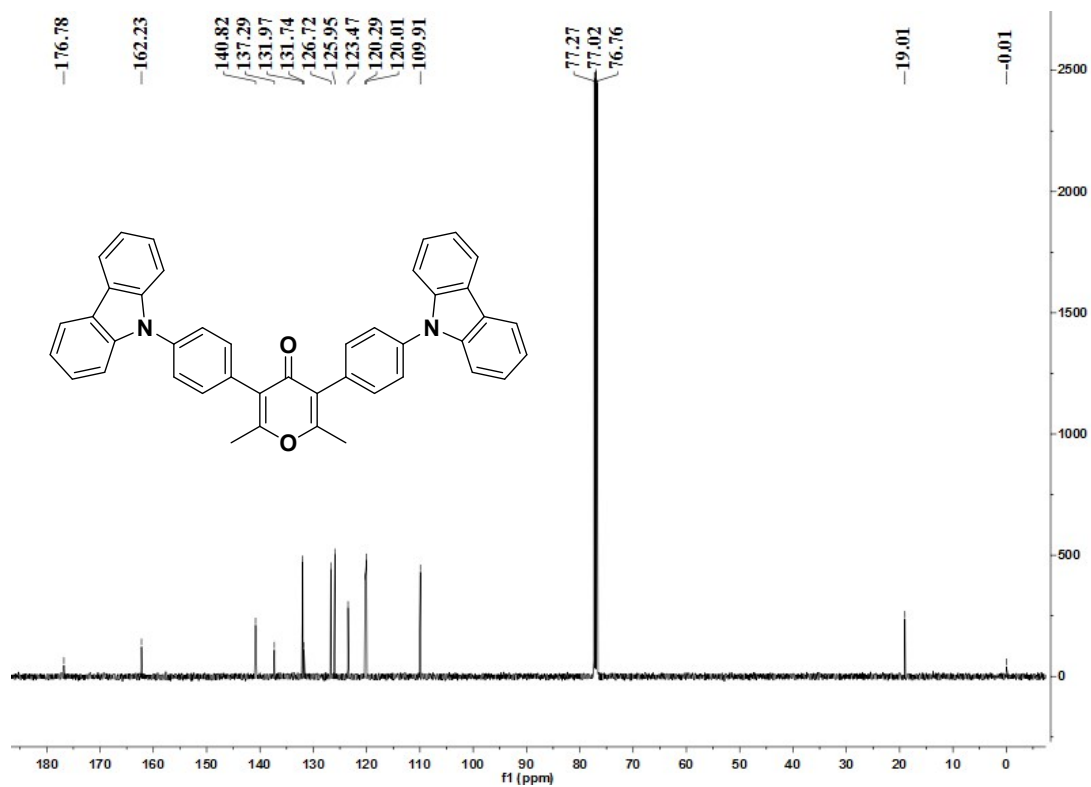


Fig. S25 ¹³C NMR of compound DCzPy (CDCl₃, 125 MHz).