Supporting Information

Unusual Mechanohypsochromic Luminescence and Unique Bidirectional Thermofluorochromism of Long-Alkylated Simple DPP Dyes

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Supporting Materials and Methods

Experimental Section

Materials

N,*N*-dimethylformamide (DMF) were distillated over calcium hydride before use. Pigment Red 254 (3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4(*2H,5H*)-dione), $C_{14}H_{29}Br$, C_4H_9Br and K_2CO_3 were purchased from Energy Chemical Ltd. Shanghai, China, without further purification. Dichloromethane (DCM), acetone, ether, isopropyl ether, butyl ether, hexane, ethyl acetate (EA), trichloromethane ($CHCl_3$), acetonitrile (CH_3CN), toluene (PhMe), tetrahydrofuran (THF) and other solvents are analytical grade and obtained from commercially available resources.

Measurements

^1H and ^{13}C NMR spectra were measured by a Bruker–AC500 spectrometer (500 MHZ) using tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as a solvent. The elemental analysis was carried out with Perkin–Elmer 2400. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFRTM plus instrument. UV–visible absorption spectra was respectively recorded on Hitachi U-4100 spectrophotometer, and the fluorescence emission spectra was measured by Hitachi F-4600 spectrophotometer. Powder X-ray diffraction (PXRD) experiments were performed with a Powder X-ray Diffractometry (INCA Energy, Oxford Instruments) with operating at 3 kW. Differential scanning calorimetry (DSC) curves were recorded on a Netzsch DSC (204F1) at a heating (or cooling) rate of 10 ^{o}C /min. Polarizing microscope images were recorded using a cross-polarized optical microscopy (OLYMPUS BX51). The samples were prepared on quartz plate at 25℃.

The solution fluorescence quantum yields (Φ) were determined by the dilute solution method with fluorescein solution in water (pH = 11) as the reference. The solid fluorescence efficiencies were performed with FLS980 Spectrometer. Grinding and stimulus-recovering experiments: Pristine solids were ground on glass plate using a metal spatula at room temperature. The heat treatments of the solid sample was placed into the oven with the certain temperature for the given time, and then cooled to room temperature before the measurements. The fuming experiment was conducted in a beaker containing a small amount of dichloromethane, and the sample was put above the DCM level at room temperature. The pressing experiment is conducted at room temperature using an IR pellet press (1 min at 1500 psi). Crystalline-state PL efficiencies were measured on an integrating sphere (C-701, Labsphere) with a 325 nm Xe light as the excitation source, and the laser was introduced into the sphere through the optical fiber. Single crystals of the compounds were slowly prepared by simple vapor-diffusion method from the dichloromethane−methanol system at room temperature under rigorous exclusion of light. Single crystals of BDPP and TDPP were obtained from the mixture of methanol and dichloromethane (V/V=1/1) and the mixture of methanol and chloroform (V/V=2:1), respectively. The single crystal X-ray diffraction experiment of BDPP was carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo Kα and Control Software using RAPID AUTO at 293(±2) °C. The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS v.5.1 programs, respectively. The space groups were determined from the systematic absences, and their correctness was confirmed by successful solution and refinement of structures. TDPP single crystal was carried out on a Rigaku XtaLABP200 System diffractometer at –123(±2) °C. Crystallographic data for BDPP and TDPP structures reported in this paper have been deposited as CIF files into the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 1497296 and 1497297.

Synthesis

1,4-Diketo-2,5-ditetradecyl-3,6-di(p-chlorophenyl)pyrrolo[3,4,c]pyrrole (TDPP). K_2CO_3 (1.2 g, 3 mmol) and 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4(*2H,5H*)-dione (1.0 g, 2.8 mmol) in 50 mL anhydrous DMF were stirred for 1 h at 120 ^{o}C under nitrogen atmosphere. Then $C_{14}H_{29}Br$ (3.9 g, 14.0 mmol, in 5 mL DMF) was slowly added to the flask. The reaction mixture was kept for 24 h at 130 ^{o}C. The mixture was extracted with dichloromethane after being cooled to room temperature. The organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The crude product was purified by a silica column chromatography using petroleum ether/CH_2Cl_2 (1/1, v/v) as the eluent. A crimson crystalline solid was obtained (630 mg, yield 30%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.756 (d, 4H), 7.522 (d, 4H), 3.724 (t, 4H), 1.540 (m, 4H), 1.195-1.247 (m, 44H), 0.878 (t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 162.46, 147.35, 137.35, 129.99, 129.29, 126.57, 109.97, 41.92, 31.92, 29.63, 29.42, 29.03, 26.92, 26.69, 22.68, 14.11. MS (ESI): MW 749.95, m/z 749.93 (M^+). Anal. Calcd. for $C_{46}H_{66}Cl_2N_2O_2$: C, 73.67; H, 8.87; N, 3.74; O, 4.27; Cl, 9.45. Found: C, 74.01; H, 8.79; N, 3.63.

1,4-Diketo-2,5-dibutyl-3,6-di(p-chlorophenyl)pyrrolo[3,4,c]pyrrole (BDPP) was synthesized by the same procedure as described for TDPP. K_2CO_3 (1.2 g, 3 mmol) and 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1.0 g, 2.8 mmol) in 50 mL anhydrous DMF were stirred for 1 h at 120 ^{o}C under nitrogen atmosphere. Then $C_{14}H_{29}Br$ (1.9 g, 14.0 mmol, in 5 mL DMF) was slowly added to the flask. The reaction mixture was kept for 24 h at 130 ^{o}C. The mixture was extracted with dichloromethane after being cooled to room temperature. The organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The crude product was purified by a silica column chromatography using petroleum ether/CH_2Cl_2 (1/1, v/v) as the eluent. A red crystalline solid was obtained (580 mg, yield 44%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.756 (d, 4H), 7.522 (d, 4H), 3.724 (t, 4H), 1.502 (m, 4H), 1.263 (m, 4H), 0.878 (t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 162.26, 147.27, 137.22, 129.93, 129.04, 126.23, 109.74, 41.62, 28.74, 22.02, 13.74. Anal. Calcd. for $C_{26}H_{26}Cl_2N_2O_2$: C, 66.53; H, 5.58; Cl, 15.11; N, 5.97; O, 6.82. Found: C, 66.48; H, 5.60; N, 6.03.

Supporting Figures

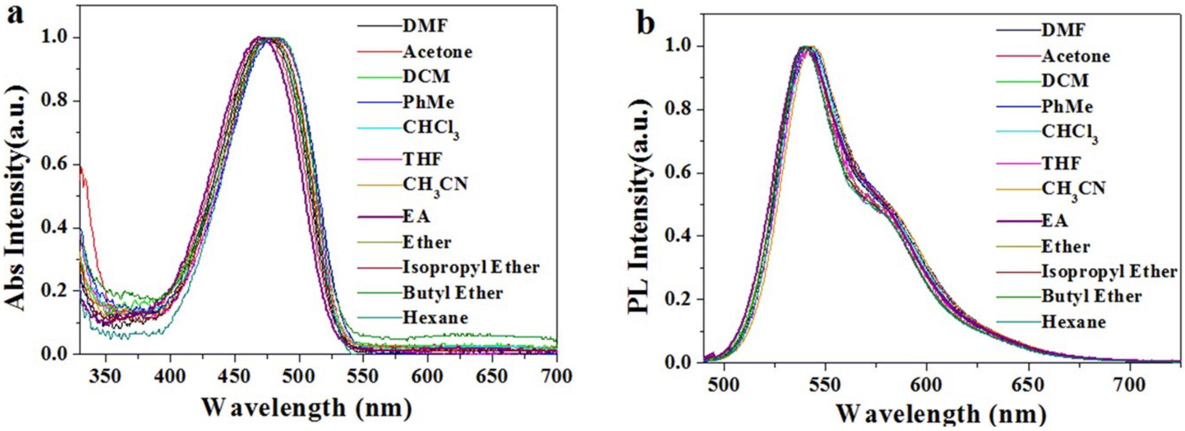

Figure S1a. The absorption (a) and emission spectra (b) of TDPP in different solvents at 1 × 10^{-5} M. The spectra are excited at 480 nm.

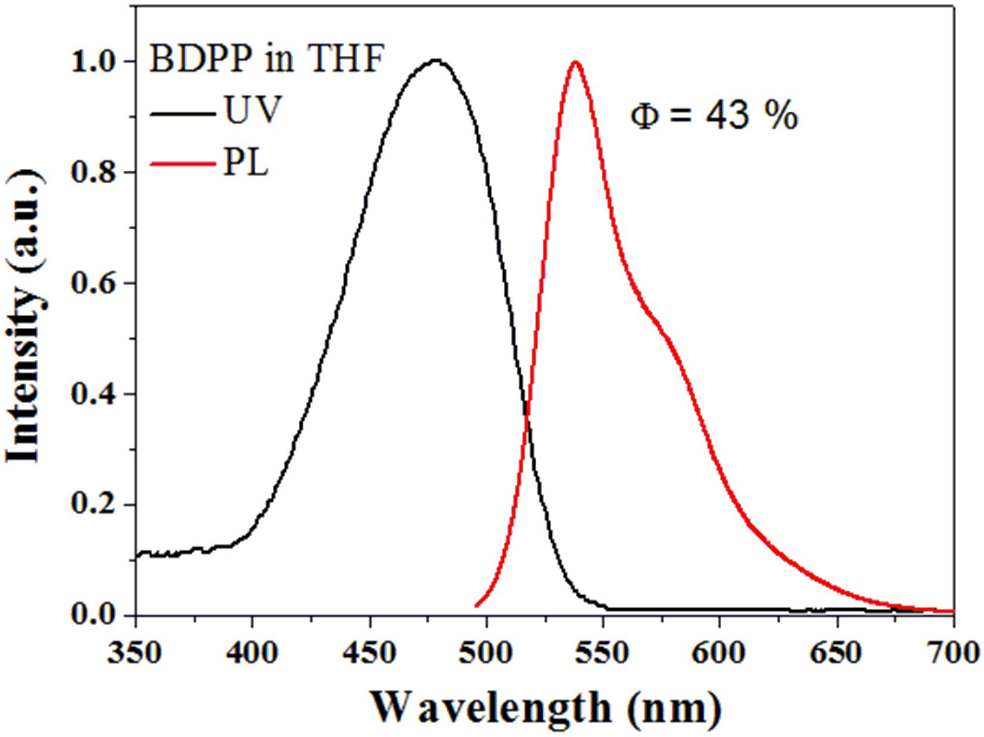

Figure S1b. The absorption and emission spectra of BDPP in THF at 1 × 10^{-5} M. The spectra are excited at 480 nm.

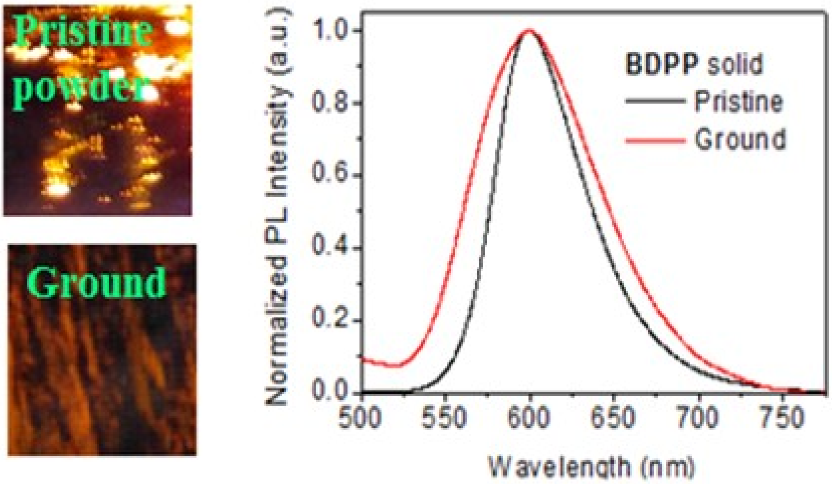

Figure S2. The fluorescence images and emission spectra of BDPP solid before and after mechanical grinding. The spectra are excited at 480 nm.

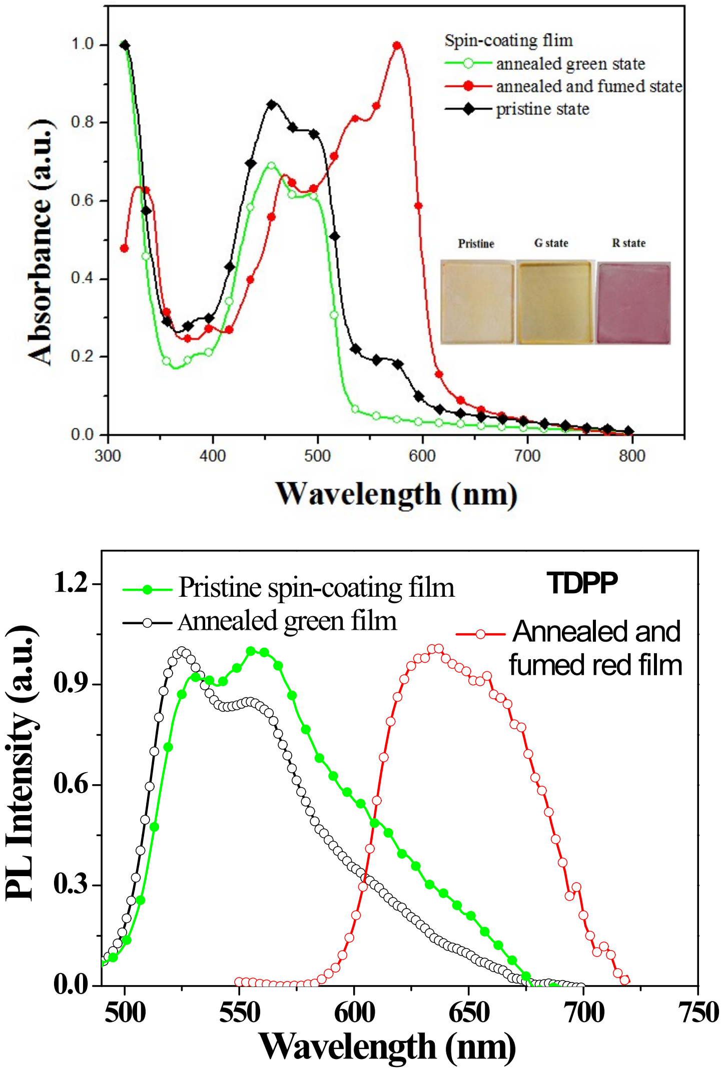

Figure S3a. The absorption spectra (top) of spin-coating TDPP films, respectively annealed green state or G state、annealed and fumed stated or R state 、pristine state or Y state, (Insert: Images of films in natural light). And emission (bottom) spectra of spin-coating and annealed (or fumed) TDPP films. The emission spectra are excited at 480 nm.

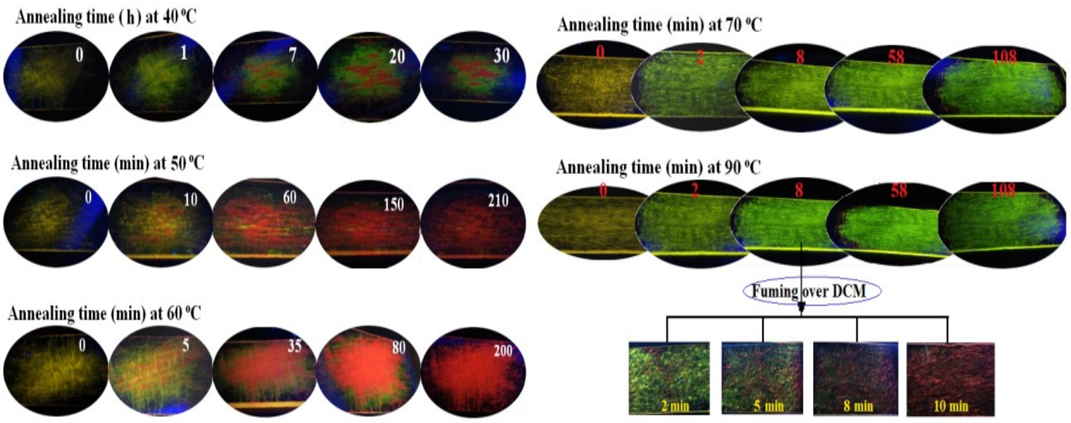

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Figure S3b. Fluorescence images of ground TDPP solid upon heat annealing for the given time on a glass plate at different temperature.

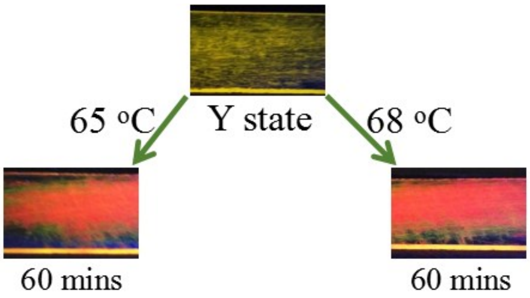

Figure S3c. Fluorescence images of TDPP Y state sample upon heat annealing for the given time on a glassplate at 65 and 68 ^{o}C temperature.

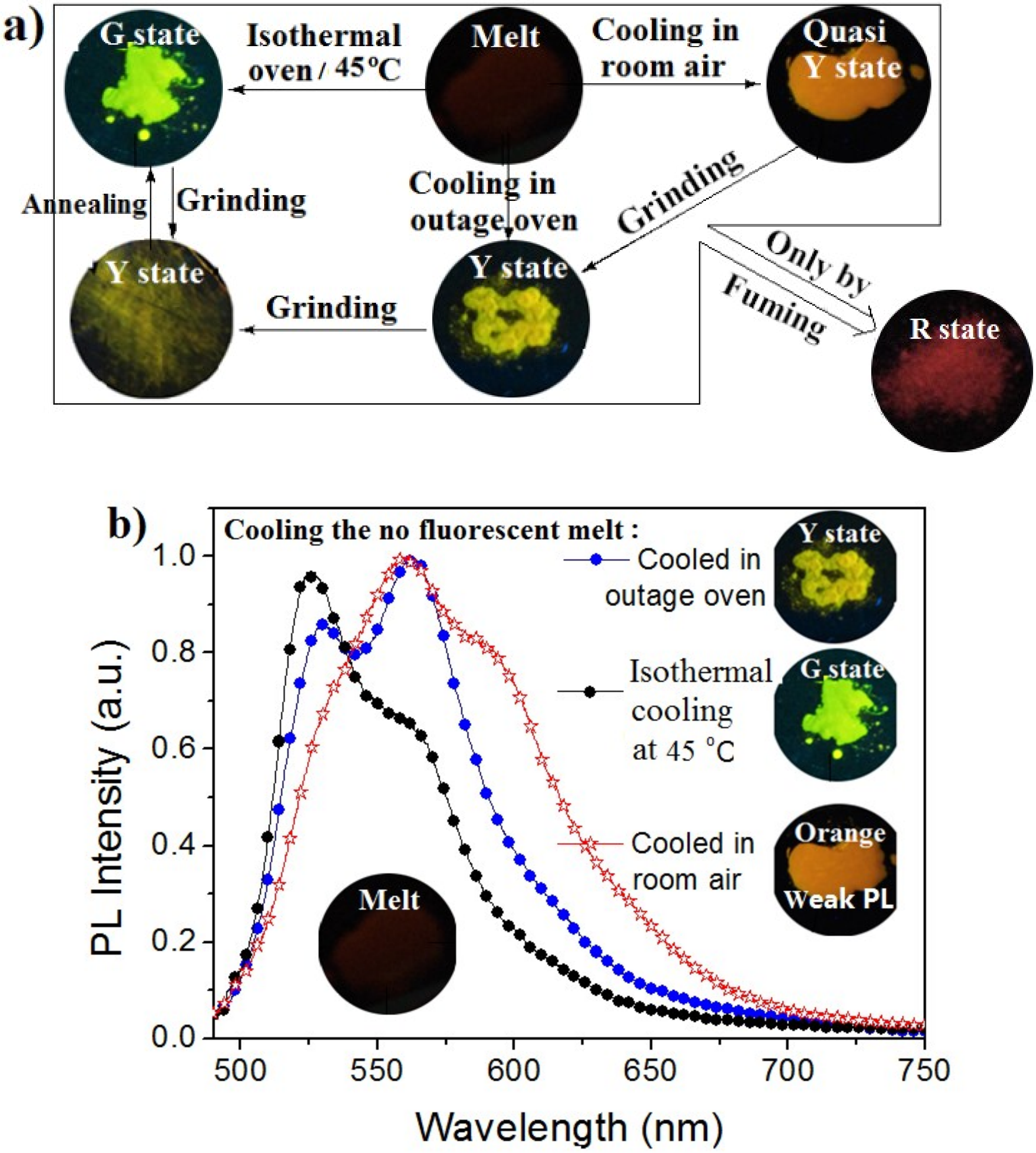

Figure S4. (a) The fluorescence emission spectra of TDPP solids obtained under different cooling conditions and (b) the stimuli responsive behaviors of the cooled melts. The spectra are excited at 480 nm.

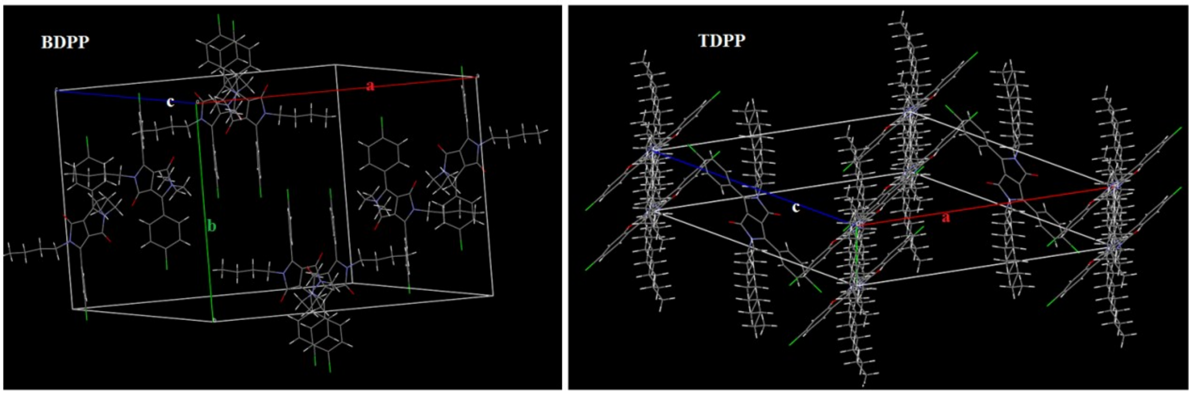

Figure S5a. Molecular packing structures of BDPP (left) and TDPP (right).

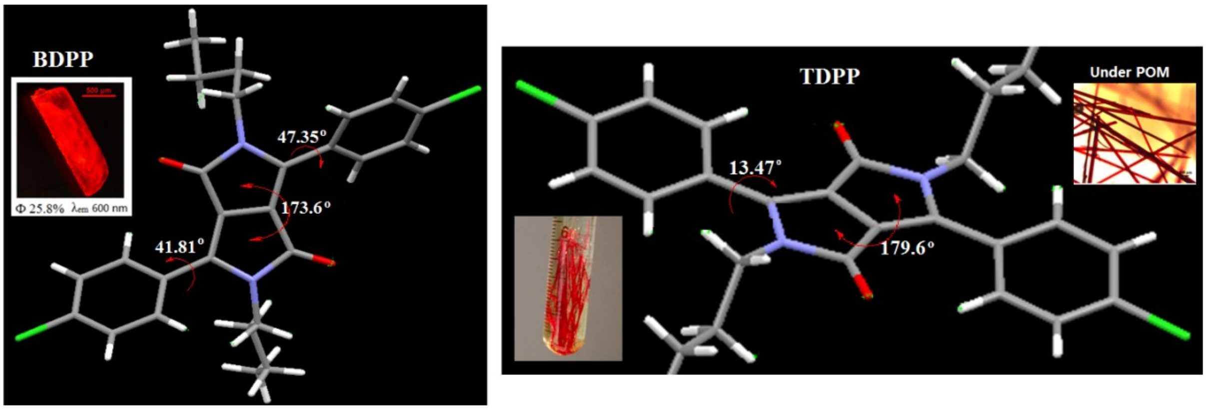

Figure S5b. Molecular π-backbone conformations of BDPP (left) and TDPP (right). The insets are the corresponding single crystal photos.

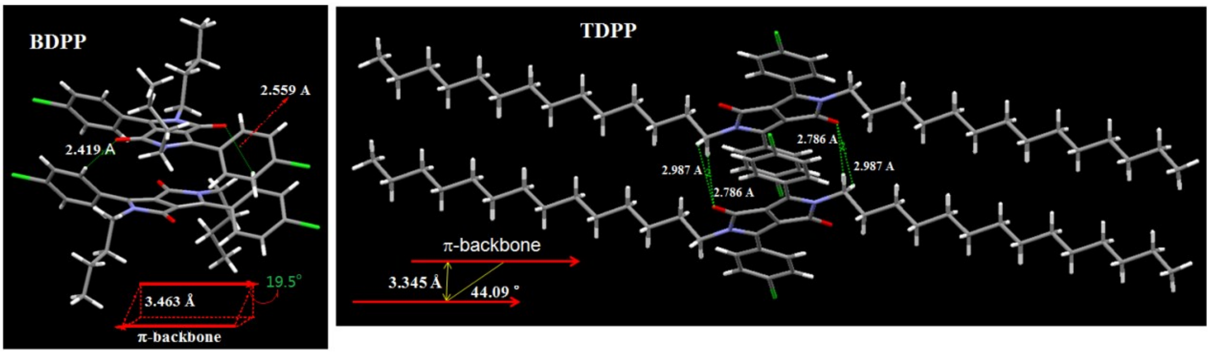

Figure S5c. Adjacent molecular packing structures and strong interactions of BDPP (left) and TDPP (right). The insets are the corresponding π-backbone packing modes.

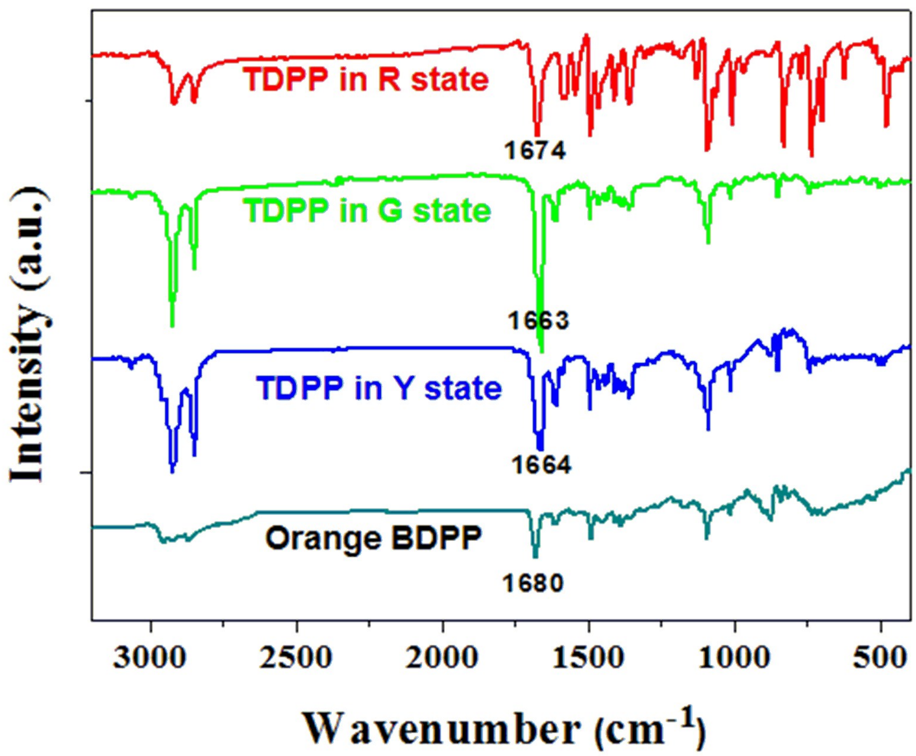

Figure S6. IR spectra of alkyl DPPs with different fluorescence colors.

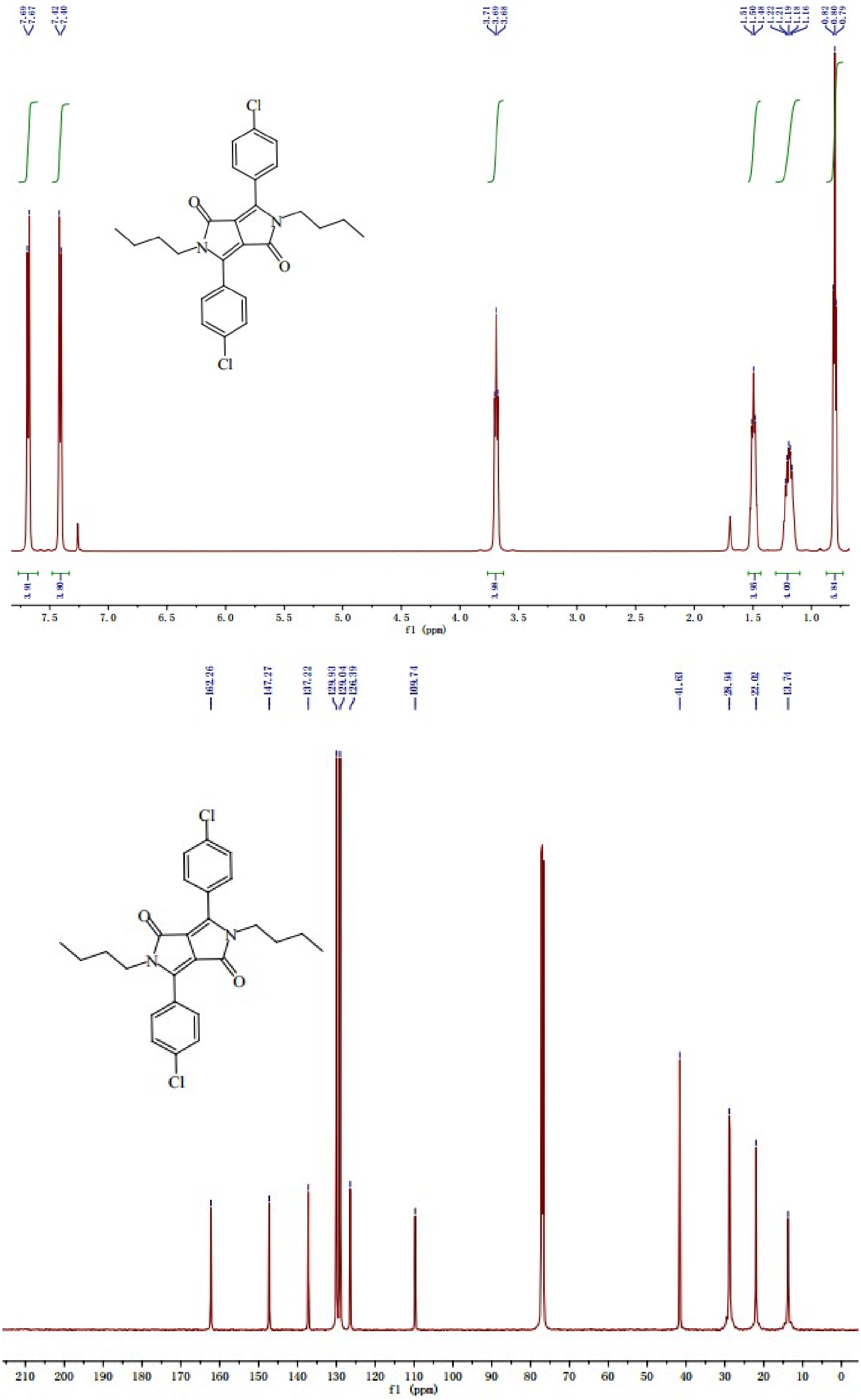

Figure S7. ^{1}H and ^{13}C NMR spectra of the compound BDPP.

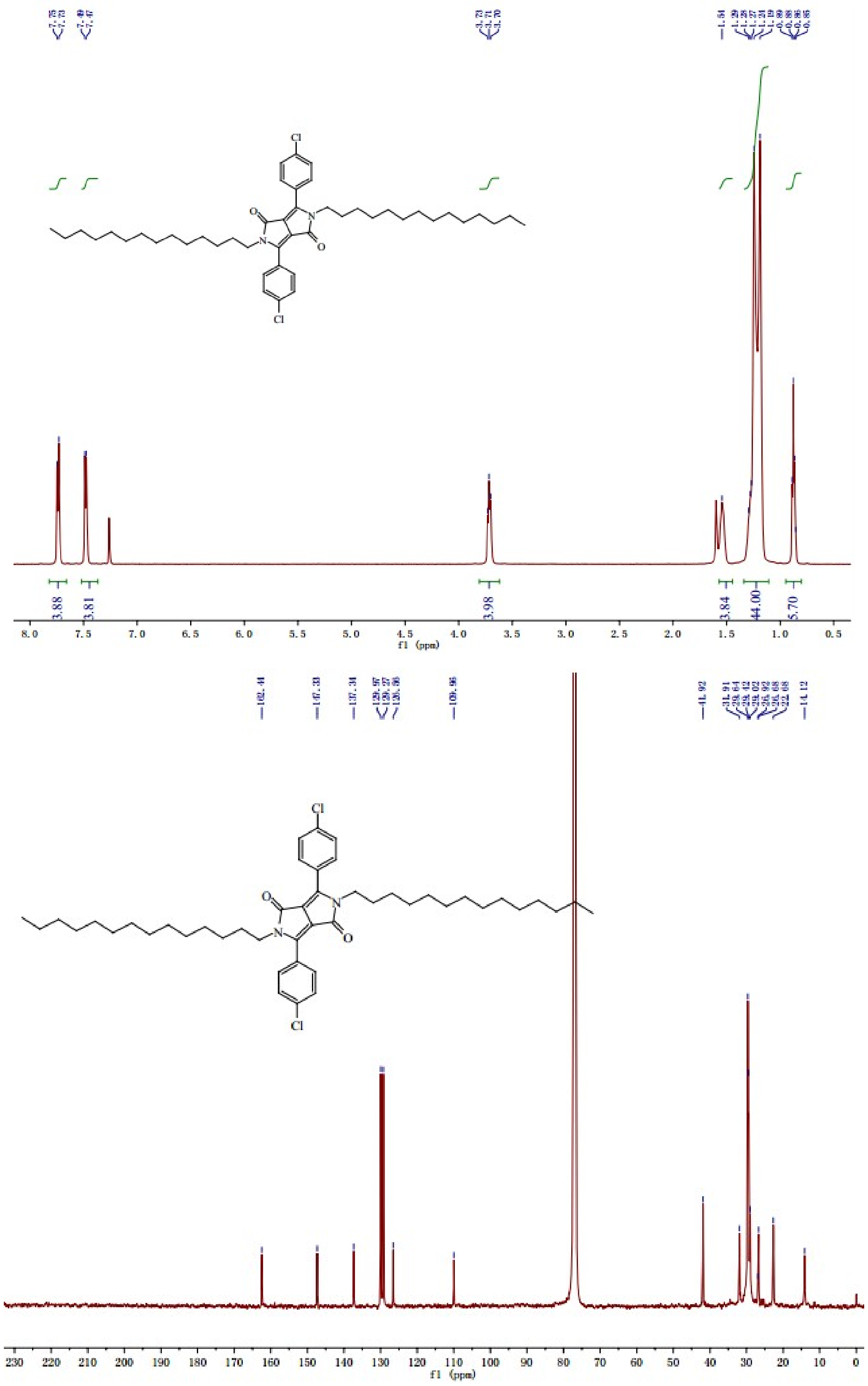

Figure S8. ^{1}H and ^{13}C NMR spectra of the compound TDPP.

Supporting Tables

Table S1 The solution fluorescence quantum yields (%) of TDPP in different solvents

Solvents	DMF	Acetone	DCM	PhMe	$CHCl_3$	THF	CH_3CN	Ethyl acetate	Ether	Hexane
fluorescence quantum yields (%)	39	41	46	38	41	46	43	47	45	38

Table S2 Crystal data and structure refinement for BDPP crystal

Compound reference	Red BDPP crystal
Chemical formula	C26 H26 Cl2 N2 O2
Formula weight	469.3
Crystal system	Monoclinic
a/Å	22.809(6)
b/ Å	17.989(4)
c/ Å	15.485(7)
β/°	131.863(3)
Unit cell volume/ Å3	4732(3)
Temperature/K	296(2)
Space group	C2/c
Z	8
Density (calculated) /g cm^{-3}	1.38
F(000)	1968.0
Theta range for data collection	2.26 to 26.00 deg.
Index ranges	-28<=h<=24, -18<=k<=22, -18<=l<=19
Reflections measured	12983
Independent reflections	4639
R_{int}	0.0267
Completeness	99. %
Absorption correction	multi-scan
Max. and min. transmission	0. 9480 and 0. 9260
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4639 / 8 / 291
Goodness-of-fit on F^2	1.052
Final R_1 values ($I > 2\sigma(I)$)	0.0586
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1359
Final R_1values (all data)	0.0816
Final $wR(F^2)$ values (all data)	0.1522
CCDC number	1497296

Table S3 Crystal data and structure refinement for TDPP crystal

Compoundreference	Red TDPP crystal
Chemical formula	C46 H66 Cl2 N2 O2
Formula weight	749.91
Crystal system	Monoclinic
a/Å	21.085(4)
b/ Å	4.8864(8)
c/ Å	21.502(4)
β/°	113.73(2)
Unit cell volume/ Å3	2028.0(6)
Temperature/K	150(2)
Space group	P21/c
Z	2
Density (calculated) /g cm^{-3}	1.228
F(000)	812
Theta range for data collection	4.14 to 67.03 deg.
Index ranges	-25<=h<=25, -4<=k<=5, -24<=l<=25
Reflections measured	10198
Independent reflections	3537
R_{int}	0.0577
Completeness	97.9 %
Absorption correction	multi-scan
Max. and min. transmission	0.8455 and 0.6513
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3537 / 0 / 236
Goodness-of-fit on F^2	1.047
Final R_1 values ($I > 2\sigma(I)$)	0.0447
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1081
Final R_1values (all data)	0.0610
Final $wR(F^2)$ values (all data)	0.1308
CCDC number	1497297