Supporting Information

Isophthalate-Based Room Temperature Phosphorescence: from Small Molecule to Side-Chain Jacketed Liquid Crystalline Polymer

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1. Experiment section

Reagents and materials
Unless other noted, all reagents and solvents used in the experiments were obtained from commercial sources without further purification. Tetrahydrofuran (THF) and dichloromethane (DCM) were dried over CaH$_2$ and distilled before use.

Instruments and measurements
Nuclear magnetic resonance (\textsuperscript{1}H NMR, 400 MHz) spectra were obtained on a Bruker ARX400 spectrometer. Chemical shift was relative to tetramethylsilane (TMS) as the internal standard.
Mass spectra were obtained on a Bruker Solarix XR mass spectrometer.
Elemental analyses were performed on a Vario EL elementar.
Gel permeation chromatography (GPC) was carried out on a Waters 515 GPC instrument using THF as an eluent. The GPC calibration curve was obtained with linear polystyrene standards.
UV-visible absorption spectra were obtained on the spectrophotometer with the type of Lambda35 and UV3600Plus.
Steady-state fluorescence/phosphorescence spectra, lifetime and photoluminescence quantum yields were obtained on Edinburgh FLS980 fluorescence spectrophotometer equipped with a xenon lamp, a microsecond flash-lamp and an integrating sphere, respectively.
Differential scanning calorimetry (DSC) curves were obtained on TA Q100 with a mechanical refrigerator. The sample was encapsulated in a hermetically sealed aluminum pan, with a typical sample weight of 3-5 mg.
Single-crystal X-ray diffraction (XRD) data were collected in a XtaLAB PRO 007HF(Mo) diffractometer.
Two-dimensional (2D) XRD patterns were obtained on Ganesha system(SAXSLAB, U.S) equipped with a multilayer focused Cu Ka radiation as the X-ray source (Genix3D Cu ULD) and a semiconductor detector (Pilatus 100 K, DECTRIS, Swiss).
The luminescent photos and videos were taken by a Cannon EOS 80D camera.

Synthesis and Characterization
The chemical structures and synthetic routes of DDIP-H, DDIP-Br, DDIP-CH₃, DDIP-CH=CH₂ and polymer Poly-1 are shown in Scheme S1. The experimental details are described as follows.

**Scheme S1.** Synthetic routes to (a) DDIP-H, (b) DDIP-Br, (c) DDIP-CH₃, (d) DDIP-CH=CH₂ and (e) Poly-1.

**Synthesis of DDIP-H**
To a solution of isophthalic acid (1.66 g, 0.01 mol) in dimethylformamide (DMF) (40 mL) was added potassium bicarbonate (KHCO₃, 2 g, 0.02 mol) and stirred at room temperature to form potassium salt. Then 1-bromodecane (5.31 g, 0.024 mol) was added and the mixture was stirred at 90 °C for 12 h. The reaction mixture was cooled to room temperature, poured into 250 mL water and extracted with ethyl acetate. After drying with anhydrous sodium sulfate (Na₂SO₄), filtration and removing the solvent, the crude product was purified by column chromatography using petroleum ether/ethyl acetate (15/1, v/v) as the eluent. Didecyl isophthalate (DDIP-H) was obtained as colorless liquid in yield of 80%. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.69 (s, 1H), 8.22 (dd, J = 7.8, 1.6 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 4.34 (t, J = 6.7 Hz, 4H), 1.86 - 1.71 (m, 4H), 1.52 - 1.16 (m, 28H), 0.88 (t, J = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 165.90, 133.66, 130.96, 130.65, 128.52, 65.52, 31.90, 29.55, 29.32, 29.29, 28.70, 26.03, 22.69, 14.12. Anal. calcd for C₂₈H₄₆O₄: C, 75.29; H, 10.38. Found: C, 74.91; H, 10.62. Melt point of DDIP-H crystal: 1.0 - 10.2 °C.

**Synthesis of DDIP-Br**
To a solution of 5-bromoisophthalic acid (2.45 g, 0.01 mol) in dimethylformamide (DMF) (40 mL) was added potassium bicarbonate (KHCO₃, 2 g, 0.02 mol) and stirred at room temperature to form potassium salt. Then 1-bromodecane (5.31 g, 0.024 mol) was added and the mixture was stirred at 90 °C for 12 h. The reaction mixture was cooled to room
temperature, poured into 250 mL water and extracted with ethyl acetate. After drying with anhydrous sodium sulfate (Na₂SO₄), filtration and removing the solvent, the crude product was purified by column chromatography using petroleum ether/ethyl acetate (15/1, v/v) as the eluent. Didecyl 5-bromoisophthalate (DDIP-Br) was obtained as white solid in yield of 75%.

1H NMR (400 MHz, CDCl₃, ppm) δ 8.59 (t, J = 1.5 Hz, 1H), 8.33 (d, J = 1.5 Hz, 2H), 4.34 (t, J = 6.8 Hz, 4H), 1.84 - 1.72 (m, 4H), 1.47 - 1.20 (m, 28H), 0.88 (t, J = 6.8 Hz, 6H). 13C NMR (100 MHz, CDCl₃, ppm) δ 164.62, 136.47, 132.70, 129.21, 122.49, 65.97, 31.90, 29.55, 29.52, 29.31, 29.27, 28.64, 25.97, 22.69, 14.12. HRMS, m/z: [M+H]+ calcd for C₂₉H₄₆BrO₄ 525.2574; found: 525.25796. Anal. calcd for C₂₉H₄₅BrO₄: C, 63.99; H, 8.63. Found: C, 64.12; H, 8.84. Melt point of DDIP-Br crystal: 39.7 - 42.4 °C.

Synthesis of DDIP-CH₃

To a solution of 5-methylisophthalic acid (1.80 g, 0.01 mol) in dimethylformamide (DMF) (40 mL) was added potassium bicarbonate (KHCO₃, 2 g, 0.02 mol) and stirred at room temperature to form potassium salt. Then 1-bromodecane (5.31 g, 0.024 mol) was added and the mixture was stirred at 90 °C for 12 h. The reaction mixture was cooled to room temperature, poured into 250 mL water and extracted with ethyl acetate. After drying with anhydrous sodium sulfate (Na₂SO₄), filtration and removing the solvent, the crude product was purified by column chromatography using petroleum ether/ethyl acetate (15/1, v/v) as the eluent. Didecyl 5-methylisophthalate (DDIP-CH₃) was obtained as white solid in yield of 82%. 1H NMR (400 MHz, CDCl₃, ppm) δ 8.48 (t, J = 1.5 Hz, 1H), 8.03 (d, J = 0.8 Hz, 2H), 4.33 (t, J = 6.7 Hz, 4H), 2.46 (s, 3H), 1.93 - 1.68 (m, 4H), 1.52 - 1.17 (m, 28H), 0.88 (t, J = 6.9 Hz, 6H). 13C NMR (100 MHz, CDCl₃) δ 165.90, 133.66, 130.96, 130.65, 128.52, 65.52, 31.90, 29.55, 29.32, 29.29, 28.70, 26.03, 22.69, 14.12. HRMS, m/z: [M+H]+ calcd for C₂₉H₄₉BrO₄ 461.36254; found: 461.36276. Anal. calcd for C₂₉H₄₉BrO₄: C, 75.61; H, 10.50. Found: C, 75.74; H, 10.56. Melt point of DDIP-CH₃ crystal: 26.5 - 31.4 °C.

Synthesis of DDIP-CH=CH₂

To a solution of 5-vinylisophthalic acid (1.92 g, 0.01 mol) in dimethylformamide (DMF) (40 mL) was added potassium bicarbonate (KHCO₃, 2 g, 0.02 mol) and stirred at room temperature to form potassium salt. Then 1-bromodecane (5.31 g, 0.024 mol) was added and the mixture was stirred at 90 °C for 12 h. The reaction mixture was cooled to room temperature, poured into 250 mL water and extracted with ethyl acetate. After drying with anhydrous sodium sulfate (Na₂SO₄), filtration and removing the solvent, the crude product was purified by column chromatography using petroleum ether/ethyl acetate (15/1, v/v) as the eluent. Didecyl 5-vinylisophthalate (DDIP-CH=CH₂) was obtained as white solid in yield of
60%. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 8.55 (t, $J = 1.5$ Hz, 1H), 8.24 (d, $J = 1.4$ Hz, 2H), 6.79 (dd, $J = 17.6$, 10.9 Hz, 1H), 5.91 (d, $J = 17.6$ Hz, 1H), 5.41 (d, $J = 10.9$ Hz, 1H), 4.35 (t, $J = 6.7$ Hz, 4H), 1.89 - 1.72 (m, 4H), 1.61 - 1.17 (m, 28H), 0.88 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 165.90, 133.66, 130.96, 130.65, 128.52, 65.52, 31.90, 29.55, 29.32, 29.29, 28.70, 26.03, 22.69, 14.12. HRMS, m/z: [M+H]$^+$ calcd for C$_{30}$H$_{49}$O$_4$ 473.36254; found: 473.36267. Anal. calcd for C$_{30}$H$_{48}$O$_4$: C, 76.23; H, 10.24. Found: C, 76.36; H, 10.47.

Melt point of DDIP-CH=CH$_2$ crystal: 40.7 - 44.5 °C.

**Synthesis of Poly-1**

To a solution of **DDIP-CH=CH$_2$** (200 mg, 0.423 mmol) in THF (1 mL) in a spherical polymerization tube was added azobisisobutyronitrile (AIBN) (0.344 mg, 0.0021 mmol). After three freeze-pump-thaw cycles, the polymerization tube was sealed under vacuum and inserted into an oil bath at 70 °C. After 12 h, the polymerization process was stopped. The polymer was diluted with THF and precipitated in methanol to obtain a crude polymer. The crude product was redissolved in 5 mL of THF and reprecipitated twice with methanol. Then the resultant polymer was dried under vacuum for 24 h. **Poly-1** was obtained as white solid in yield of 80%. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.85 (br, 1H), 6.85 (br, 2H), 4.05 (br, 4H), 1.55 (br, 4H), 1.27 (br, 28H), 0.88 (t, $J = 6.5$ Hz, 6H).

**Theoretical calculation**

Time-dependent density functional theory (TD-DFT) calculations were performed on Gaussian 09 program (Revision e01).

The ground state ($S_0$) geometries were optimized with the Becke's three-parameter exchange functional along with the Lee Yang Parr's correlation functional (B3LYP) using 6-31G** basis sets.

The excitation energies in the singlet states were obtained using the TD-DFT method based on an optimized molecular structure at ground state. The excitation energies in the triplet states were obtained using the TD-DFT method based on an optimized molecular structure at excited state.

For crystal state, the computational models were built from the single crystal structures. Solid state effect was considered through the combined quantum mechanics and molecular mechanics (QM/MM) theory with two-layer ONIOM method. A model containing 41 molecules arranged in experimental structures were used. The molecule in center was chosen as QM molecule and simulated by B3LYP method, whereas the remaining molecules around were calculated by universal force field (UFF) to simulate the crystal environment.
Figure S1. QM/MM model taking DDIP-Br as an example: one central QM molecule for high layer and the surrounding MM molecules for low layer.

Computer simulation
Molecular modeling was performed using Materials Studio software package5.0 (Accelrys Software Inc.). Each chain in the double-chain column of Poly-1 was built by 30 repeating units through head-to-tail arrangement. Geometry optimization followed by energy minimization of chains were carried out through the Forcite module with the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. The convergence level for optimization was set to be ultrafine.
2. NMR data of small molecules of isothphalate

Figure S2. $^1$H NMR and $^{13}$C NMR spectra of DDIP-H in CDCl$_3$. 
Figure S3. $^1$H NMR and $^{13}$C NMR spectra of DDIP-Br in CDCl$_3$. 
Figure S4. $^1$H NMR and $^{13}$C NMR spectra of DDIP-CH$_3$ in CDCl$_3$. 
Figure S5. $^1$H NMR and $^{13}$C NMR spectra of DDIP-CH=CH$_2$ in CDCl$_3$. 
3. Data of molecular characterization and phase behavior of Poly-1

**Figure S6.** $^1$H NMR spectrum of Poly-1 in CDCl$_3$.

**Table S1.** Molecular Weight and Polydispersity of Poly-1.

| Sample | $M_n$ ($\times 10^4$ g/mol) | $M_w$ ($\times 10^4$ g/mol) | PDI   |
|--------|-----------------------------|-----------------------------|-------|
| Poly-1 | 9.3                         | 19.9                        | 2.14  |

**Figure S7.** Set of DSC traces of Poly-1 recorded upon cooling and subsequent heating at different rates.
Figure S8. 1D XRD profiles of Poly-1 recorded during (a) heating and (b) cooling.

4. Additional photophysical properties of DDIP-H, DDIP-Br, DDIP-CH₃, DDIP-CH=CH₂ and Poly-1 in solution and in solid state

Figure S9. Normalized UV-Visible spectra of DDIP-Br, DDIP-CH₃, DDIP-CH=CH₂ and Poly-1 in DCM (a) and solid state (b) at RT.
Figure S10. Normalized photoluminescence spectra of DDIP-Br, DDIP-CH₃, DDIP-CH=CH₂ and Poly-1 in (a) DCM and (b) solid state at RT. The excitation wavelength is 280 nm.

Figure S11. Normalized excitation spectra of DDIP-Br, DDIP-CH₃, DDIP-CH=CH₂ and Poly-1 in (a) DCM and (b) solid state at RT. The emission wavelengths of DDIP-Br, DDIP-CH₃, DDIP-CH=CH₂ and Poly-1 in DCM solution are 319, 312, 343 and 388 nm, respectively. The emission wavelengths of DDIP-Br, DDIP-CH₃, DDIP-CH=CH₂ and Poly-1 in solid state are 329, 313, 347 and 389 nm, respectively.
Figure S12. Normalized phosphorescence excitation (a), emission (b) spectra and the corresponding lifetimes (c) of DDIP-Br, DDIP-CH$_3$, DDIP-CH=CH$_2$ and Poly-1 in solid state at RT. In (a), the emission wavelengths of DDIP-Br, DDIP-CH$_3$, DDIP-CH=CH$_2$ and Poly-1 are 520, 505, 610 and 550 nm, respectively. In (b), for DDIP-Br and DDIP-CH$_3$, the excitation wavelength is 320 nm. For DDIP-CH=CH$_2$, the excitation wavelength is 345 nm. For Poly-1, the excitation wavelength is 365 nm. The delayed time is 5 ms.
**Figure S13.** Normalized phosphorescence spectra (a) and the corresponding lifetimes (b) of DDIP-Br, DDIP-CH₃, DDIP-CH=CH₂ and Poly-1 in DCM solution at 77 K. The excitation wavelength is 280 nm. The delayed time is 5 ms.

**Figure S14.** Phosphorescence spectra of DDIP-Br measured during heating. The excitation wavelength is 320 nm. The delayed time is 5 ms.
Figure S15. Phosphorescence spectra of DDIP-CH$_3$ measured during heating. The excitation wavelength is 320 nm. The delayed time is 5 ms.

Figure S16. Phosphorescence spectra of DDIP-CH=CH$_2$ measured during heating. The excitation wavelength is 345 nm. The delayed time is 5 ms.
Figure S17. Normalized fluorescence excitation (a) and emission (b) spectra of Poly-1 in solid state at RT. In a), the black and red lines are the excitation spectra with emission wavelengths of 389 and 470 nm. In b), the black and red lines are the emission spectra with excitation wavelengths of 280 and 365 nm.

Figure S18. Photographs of DDIP-Br, DDIP-CH$_3$ and DDIP-CH=CH$_2$ taken under room light, before and after turning-off the 365 nm UV-irritation under ambient conditions.
Figure S19. (a) Normalized photoluminescence spectra of DDIP-H under different conditions. Including fluorescence of DCM solution at 293 K (black line, excited at 280 nm), phosphorescence of DCM solution at 77 K (green line, excited at 280 nm, \( t_d = 5 \) ms), photoluminescence of crystal at 293 K (red line, excited at 280 nm) and phosphorescence of crystal at 263 K (blue line, excited at 320 nm, \( t_d = 5 \) ms). (b) Phosphorescence lifetime of DDIP-H in crystal at 263 K.

Figure S20. (a) Photoluminescence and (b) phosphorescence spectra of Poly-1 during heating. The excitation wavelength is 365 nm.
Figure S21. Photoluminescence and phosphorescence spectra of Poly-2. Including photoluminescence (black line, excited at 280 nm) and phosphorescence (red line, excited at 365 nm, \( t_d = 0.5 \text{ ms} \)) at 293 K.

5. Single crystal data

Figure S22. Single-crystal structure and molecular packing of DDIP-CH₃.
Figure S23. Single-crystal structure and molecular packing of DDIP-CH=CH₂.

Table S2. Single crystals data of DDIP-Br, DDIP-CH₃ and DDIP-CH=CH₂.

| Name          | DDIP-Br                  | DDIP-CH₃                  | DDIP-CH=CH₂                |
|---------------|--------------------------|---------------------------|----------------------------|
| Formula       | C₂₈ H₄₃ Br O₄            | C₂₉ H₄₈ O₄                | C₃₀ H₄₈ O₄                 |
| Wavelength (Å) | 0.71073                  | 0.71073                   | 0.71073                    |
| Space Group   | P -1                     | P -1                      | P -1                       |
| a             | 8.4088(4)                | a 8.4972(3)               | a 8.7036(1)                |
| b             | 9.2855(4)                | b 18.0564(8)              | b 9.2765(1)                |
| c             | 19.2276(8)               | c 19.8354(8)              | c 18.379(2)                |
| Cell Angles (°) | β 78.169(4)         | β 82.890(3)               | β 78.319(1)                |
|               | γ 67.826(4)               | γ 79.624(3)               | γ 76.418(1)                |
| Cell Volume (Å³) | 1359.83(1)              | 2744.89(2)                | 1412.3(3)                  |
| Z             | 2                        | 4                         | 2                          |
| Density (g/cm³) | 1.284                    | 1.115                     | 1.417                      |
| F (000)       | 560                      | 1016                      | 616                        |
| h max, k max, l max | 10, 12, 24              | 11, 23, 25                | 11, 12, 23                 |
| CCDC Number   | 1887457                  | 1887456                   |                            |
6. Time-dependent density functional theory (TD-DFT) calculations

Figure S24. The energy level diagrams of DDIP-CH$_3$ in gas a) and crystal b).

Figure S25. The energy level diagrams of DDIP-CH=CH$_2$ in gas a) and crystal b).

Table S3. Energy levels of DDIP-Br, DDIP-CH$_3$ and DDIP-CH=CH$_2$ in gas state from TD-DFT calculation.

| Compound  | DDIP-Br | DDIP-CH$_3$ | DDIP-CH=CH$_2$ |
|-----------|---------|-------------|----------------|
| S$_1$-S$_0$ (eV) | 4.17    | 4.27        | 3.82           |
| T$_1$-S$_0$ (eV) | 2.68    | 2.56        | 1.87           |
| T$_2$-S$_0$ (eV) | 3.43    | 3.77        | 3.26           |
| T$_3$-S$_0$ (eV) | 3.94    | 3.93        | 3.61           |
| T$_4$-S$_0$ (eV) | 3.99    | 4.04        | 4.09           |
| T$_5$-S$_0$ (eV) | 4.20    | 4.32        | 4.29           |
| T$_6$-S$_0$ (eV) | 4.44    | 4.58        | 4.30           |
Table S4. Energy levels of DDIP-Br, DDIP-CH₃ and DDIP-CH=CH₂ in crystal state from QM/MM method.

| Compound | DDIP-Br (eV) | DDIP-CH₃ (eV) | DDIP-CH=CH₂ (eV) |
|----------|--------------|---------------|------------------|
| S₁-S₀    | 4.10         | 4.26          | 3.71             |
| T₁-S₀    | 2.60         | 2.55          | 1.62             |
| T₂-S₀    | 3.66         | 3.76          | 3.19             |
| T₃-S₀    | 3.86         | 3.93          | 3.66             |
| T₄-S₀    | 3.97         | 4.07          | 4.01             |
| T₅-S₀    | 4.25         | 4.32          | 4.24             |
| T₆-S₀    | 4.52         | 4.58          | 4.33             |

7. Complementary videos

**Video S1.** DDIP-Br in crystal was white under incandescent light. When excited with a 365 nm UV lamp, it emitted blue-violet light. After the switch off of UV lamp, a green afterglow was clearly observed by the naked eye.

**Video S2.** DDIP-CH₃ in crystal was white under incandescent light. When excited with a 365 nm UV lamp, it emitted blue light. After the switch off of UV lamp, a green afterglow was clearly observed by the naked eye.

**Video S3.** DDIP-CH=CH₂ in crystal was white under incandescent light. When excited with a 365 nm UV lamp, it emitted blue-violet light. After the switch off of UV lamp, a red afterglow was clearly observed by the naked eye.