# Supporting Information

## A Facile Way to Obtain Near-Infrared Room-Temperature Phosphorescent Soft Materials based on Bodipy Dyes

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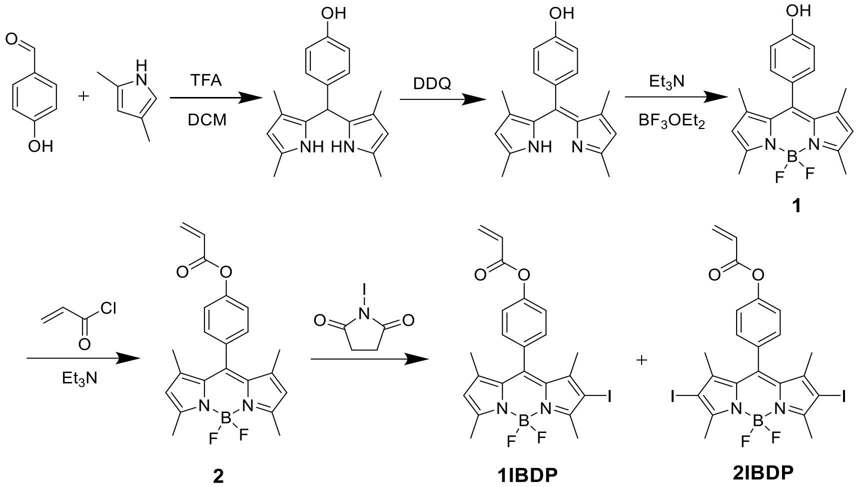
## Experimental Procedures

**Materials:** All reagents used in this research work were commercially available. AIBN (2,2'-azobis(2-methylpropionitrile)) was used after recrystallization in ethanol and the other reagents were all used without further purification. Solvents were purified according to standard laboratory methods. The in-termediates were confirmed by $^{1}$H NMR, $^{13}$C NMR and high resolution ESI mass spectroscopy. The solid polymers were characterized by aqueous gel permeation chromatography.

**Characterization**: $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Brüker AV-400 spectrometer with chemical shifts reported as ppm. The electronic spray ionization (ESI) high-resolution mass spectra were tested on a Waters LCT Premier XE spectrometer. UV-Vis spectra were done on a UV-2550 UV-Vis spectrophotometer and a Varian Lambda 950. Photoluminescence spectra and phosphorescence lifetimes were obtained on a Varian Cary Eclipse spectrophotometer and a Horiba Fluoremax-4 spectrofluorometer. Phosphorescence and delayed fluorescence were recorded in a delayed mode (delay time = 0.1 ms, gate time = 2.0 ms) on the Varian Cary Eclipse spectrophotometer. Quantum yields were measured by using an integrating sphere on a HAMAMATSU Quantaurus-QY C11347-11. Powder X-ray diffraction (XRD) was performed on a D/max2550V. Aqueous gel permeation chromatography (GPC) was measured on a Waters 2695. Rheological properties were measured using a TA Discovery HR-3 rheometer. Photographs were taken with a digital camera.

## Synthetic routes

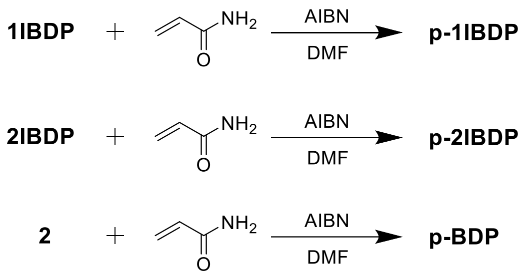


**Scheme S1**. Preparation routine of 1IBDP and 2IBDP.

**Synthesis of Compound 1**. Compound 1 was synthesized according to literature procedure with same structure.[S1]

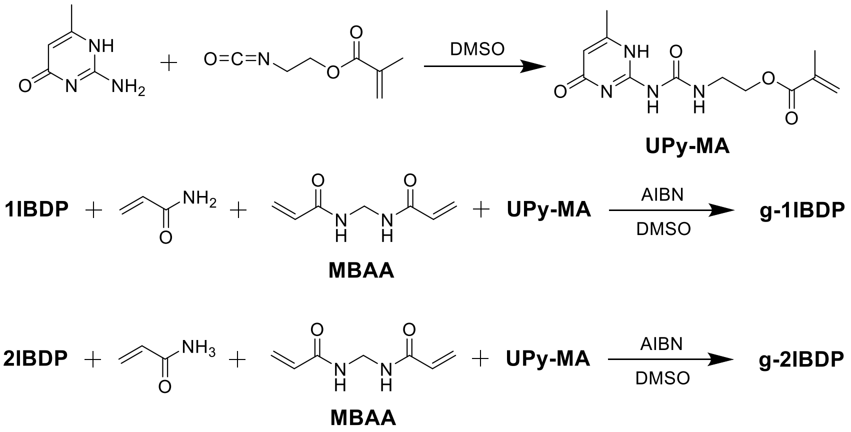
**Synthesis of Compound 2**. Compound 1 (250 mg, 0.74 mmol, 1 eq) and trimethylamine (0.15 mL, 1.11 mmol, 1.5 eq) were firstly dissolved in dried dichloromethane under argon atmosphere and cooled with ice-water bath. Acryloyl chloride (0.071 mL, 0.89 mmol, 1.2 eq) was then added dropwise with a syringe. The mixture was stirred at 0 $^{o}$C for 30 mins and room temperature for 9 hours. After reaction, the solution was washed with $H_2O$ (3×15 mL) and brine (3×15 mL). The obtained organic phase was dried with anhydrous $Na_2SO_4$ and concentrated to give a red solid, which was purified by column chromatography (petroleum ether/ dichloromethane, 1/2) (236 mg, 82% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 2.8 Hz, 4H), 6.65 (d, J = 16.2 Hz, 1H), 6.35 (dd, J = 16.2 Hz, 10.4 Hz, 1H), 6.07 (d, J = 10.4 Hz, 1H), 5.99 (s, 2H), 2.56 (s, 6H), 1.44 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.11, 154.65, 150.10, 142.07, 139.59, 132.01, 131.44, 130.40, 128.13, 126.63, 121.43, 120.31, 28.66, 13.50. HR-ESI-MS m/z: $[M+H]^+$ calculated for $C_{22}H_{22}BF_2N_2O_2$ 395.1742; found, 395.1738.

**Synthesis of 1IBDP and 2IBDP**. Compound 2 (200 mg, 0.51 mmol, 1 eq) and N-iodosuccinimide (288 mg, 1.28 mmol, 2.5 eq) were dissolved in dried dichloromethane. After stirring at room temperature for 5 hours, the solution was washed with $H_2O$ (3×15 mL) and brine (2×15 mL). The organic phase was dried with anhydrous $Na_2SO_4$ and concentrated to give a mixture of 1IBDP and 2IBDP. Column chromatography were used to separate them (petroleum ether/ dichloromethane, 2/1). 1IBDP (145 mg, 55% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 1.7 Hz, 4H), 6.66 (d, J = 17.3 Hz, 1H), 6.36 (dd, J = 17.3, 10.4 Hz, 1H), 6.07 (d, J = 10.4 Hz, 1H), 6.06 (s, 1H) 2.64 (s, 3H), 2.57 (s, 3H), 1.45 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.11, 158.06, 154.81, 151.35, 145.13, 140.43, 133.18, 132.31, 129.13, 127.65, 122.68, 122.48, 16.86, 15.83, 14.81. HR-ESI-MS m/z: $[M+K]^+$ calculated for $C_{22}H_{20}BF_2IN_2O_2K$ 559.0268; found, 559.0278. 2IBDP (115 mg, 35% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 4H), 6.66 (d, J = 17.3, 1H), 6.36 (dd, J = 17.3 Hz, 10.4 Hz, 1H), 6.08 (d, J = 10.4, 1H), 2.65 (s, 6H), 1.45 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.04, 157.05, 151.55, 145.34, 140.30, 133.27, 132.18, 131.35, 129.06, 127.60, 122.87, 85.89, 29.73, 17.19, 16.08. HR-ESI-MS m/z: $[M-H]^-$ calculated for $C_{22}H_{18}BF_2I_2N_2O_2$ 644.9519; found, 644.9523.



**Scheme S2.** Preparation routine of p-1IBDP, p-2IBDP and p-BDP.

**Synthesis of p-1IBDP, p-2IBDP and p-BDP**. These polymers were prepared by copolymerization of 1IBDP/2IBDP/**2** (1 eq) and acrylamide (100 eq) by radical polymerization with AIBN (0.1 eq) as the radical initiator at 70 °C under argon atmosphere in 1.5 mL DMF for 15 h. The precipitated solid was repeatedly washed with methanol to give p-1IBDP, p-2IBDP and p-BDP. GPC ($H_2O$, p-1IBDP): Mn (PDI) = 9547 Da (3.49); GPC ($H_2O$, p-2IBDP): Mn (PDI) = 5987 Da (2.52); GPC ($H_2O$, p-IBDP): Mn (PDI) = 7441 Da (3.05).



**Scheme S3.** Preparation routine of g-1IBDP and g-2IBDP.

**Synthesis of UPy-MA**. UPy-MA was synthesized according to literature procedure with same structure.[S2]

**Synthesis of g-1IBDP and g-2IBDP**. G-1IBDP and g-2IBDP were prepared by copolymerization of 1IBDP/2IBDP (1 eq), acrylamide (100 eq), MBAA (2 eq) and UPy-MA (2.5 eq) by radical polymerization with AIBN (0.1 eq) as the radical initiator at 70 °C under argon atmosphere in 1.3 mL DMSO. Gels were directly obtained after 24 h and washed with $H_2O$ to remove the residual DMSO.

## PHOTOPHYSICAL PROPERTIES

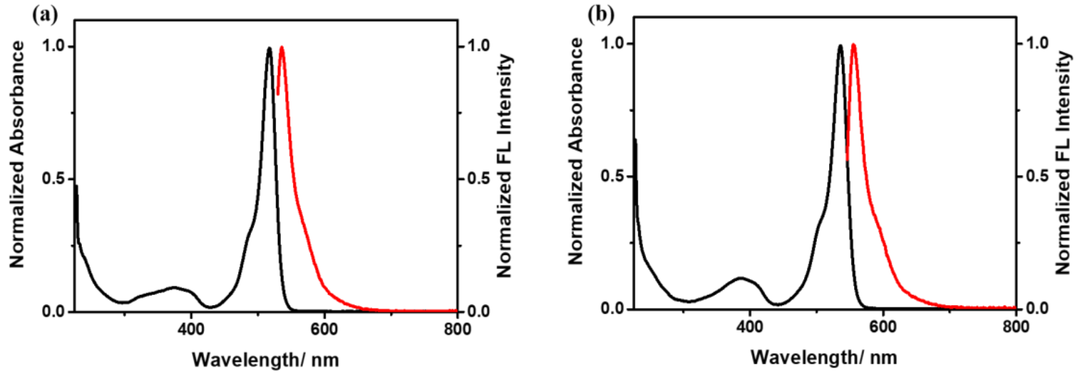


**Figure S1.** Normalized UV-Vis absorption spectra (black line) and fluorescence (red line) of (a) 1IBDP and (b) 2IBDP in dichloromethane. (c = $10^{-5}$ mol/L, $\lambda_{ex1}$ = 518 nm, $\lambda_{ex2}$ = 535 nm).

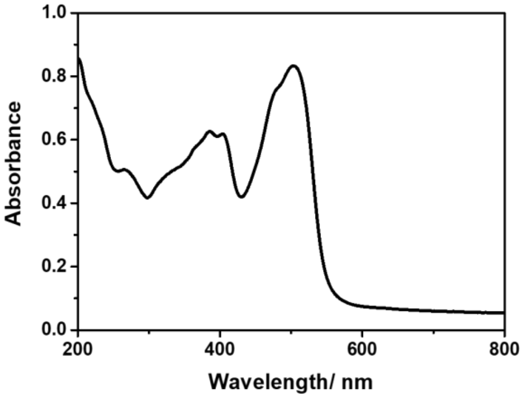


**Figure S2.** UV-Vis absorption spectra of p-BDP in amorphous solid state.

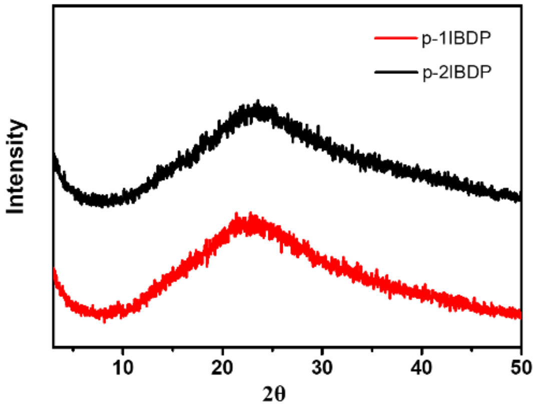


**Figure S3.** X-ray diffraction (XRD) patterns of p-1IBDP and p-2IBDP.

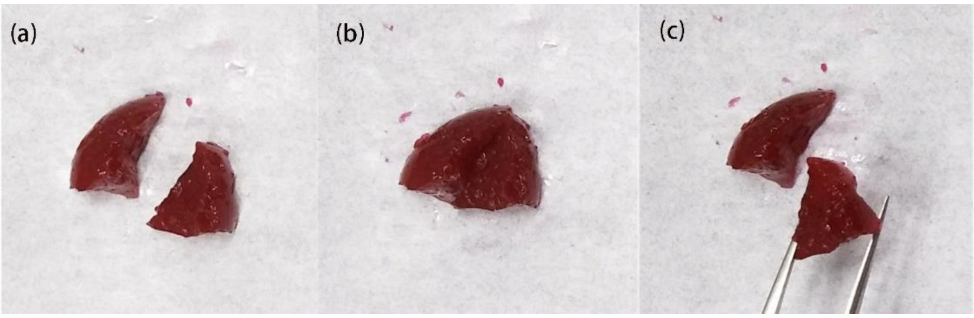


**Figure S4.** (a) Two pieces of reference gels composed of 2IBDP, acrylamide and MBAA (1:100:2). (b) The two pieces were put together. (c) The two pieces were easily separated by tweezers after being put together for 24 hours.

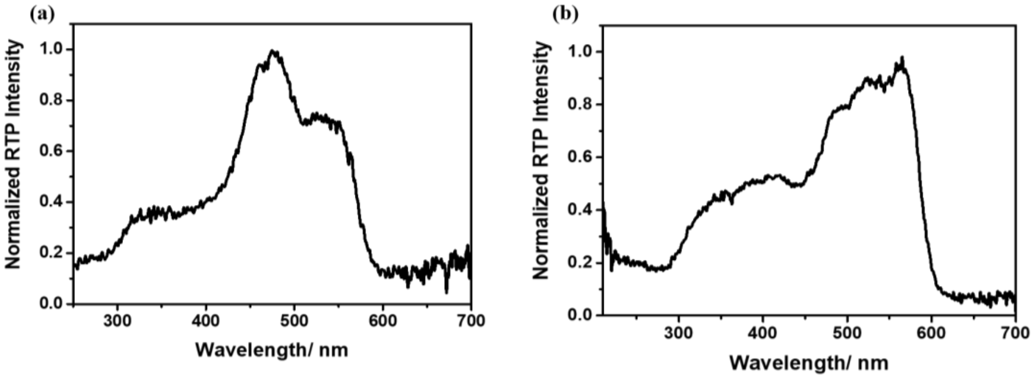


**Figure S5.** Excitation spectra of (a) g-1IBDP and (b) g-2IBDP ($\lambda_{em}$ = 775 nm).

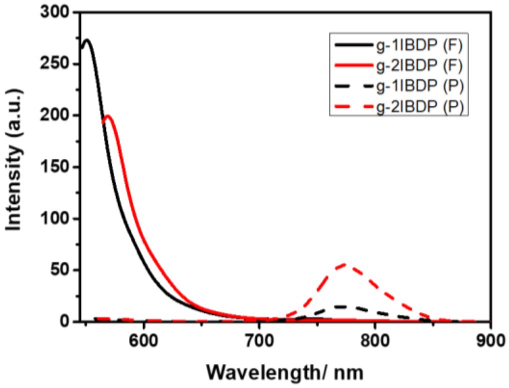


**Figure S6.** Fluorescence and RTP emission of g-1IBDP and g-2IBDP ($\lambda_{ex1}$ = 520 nm, $\lambda_{ex2}$ = 540 nm).

## REFERENCES

(S1) N. G. Patil, N. B. Basutkar, A. V. Ambade, *Chem. Commun.*, 2015, **51**, 17708-17711.

(S2) X. Chang, Y. Geng, H. Cao, J. Zhou, Y. Tian, G. Shan, Y. Bao, Z. L. Wu, P. Pan, *Macromol. Rapid. Commun.*, 2018, **39**, 1700806.