Supporting Information

Synthesis and Characterization of Large Stokes-shifted Fluorescent Imide and Polyimides Bearing 2-(2'-Hydroxyphenyl)benzothiazole Moieties

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1 Materials

3,5-Dibromo-2-hydroxybenzaldehyde (BIDE, 98%), 2-aminobenzenethiol (Energy, 97%), silver nitrate ($AgNO_3$, Aladdin, 99.8%), dimethyl sulfate (BIDE, 98%), (4-aminophenyl)boronic acid hydrochloride (SUMMEDCHEM, 98%), potassium carbonate (K_2CO_3, Aladdin, 98%), tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$, BIDE, 98%), dimethyl sulfoxide (DMSO, Macklin, 99.8%), acetone (AC, Macklin, 99.8%), tetrahydrofuran (THF, Macklin, 99.8%) N,N-dimethylformamide (DMF, Macklin, 99.8%), and N-methyl-2-pyrrolidinone (NMP, J&K, 99.5%) were used as received. 2-(2'-Hydroxyphenyl)benzothiazole (HBT, Aladdin, 98%) was purified by recrystallization from ethyl alcohol. 4,4'-Oxydianiline (ODA) was purified by vacuum sublimation. 1,2,4,5-Cyclohexanetetracarboxylic dianhydride (HPMDA) and dicyclohexyl-3,4,3',4'-tetracarboxylic dianhydride (HBPDA) were purified by recrystallization from acetic anhydride.

2 Synthesis

2.4.1 Synthesis of 2-(benzo[d]thiazol-2-yl)-4,6-dibromophenol (DBrHBT)

3,5-Dibromo-2-hydroxybenzaldehyde (2.78 g, 10 mmol) and 2-aminobenzenethiol (1.25 g, 10 mmol) were dissolved in 50 ml anhydrous DMSO. Subsequently, $AgNO_3$ (0.0120 g, 0.10 mmol) was added under argon condition. Then the mixture was stirred at room temperature for 5 h (monitored by TLC). The mixture was diluted by dichloromethane three times and washed with brine. The organic layers were dried over Na_2SO_4, filtered and evaporated in a vacuum. The pure product (2.23 g, 60%) was obtained by silica-gel column chromatography (CH_2Cl_2: hexane = 3: 2). ^{1}H NMR (400 MHz, Chloroform-d) δ 13.47 (s, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 1.2 Hz, 2H), 7.54 (t, J = 7.7 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H). HR-MS (APCI, m/z): [M]+ calcd for $C_{13}H_8Br_2NOS$: 385.1. Found: 383.8687.

2.4.2 Synthesis of 2-(3,5-dibromo-2-methoxyphenyl)benzo[d]thiazole (DBrMBT)

DBrHBT (2.68 g, 7.0 mmol) was dispersed into 30 ml dry acetone containing powdered anhydrous K_2CO_3 and dimethyl sulfate. The mixture was stirred under argon condition at 60 ℃ for 5 h (monitored by TLC). After cooling to room temperature, the dry acetone was evaporated under reduced pressure. The pure product (2.50 g, 90%) was obtained by recrystallization in ethanol. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.61 (d, J = 2.5 Hz, 1H), 8.13 (dt, J = 8.1, 1.0 Hz, 1H), 7.98 (ddd, J = 7.9, 1.3, 0.7 Hz, 1H), 7.82 (d, J = 2.4 Hz, 1H), 7.56 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.46 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 3.99 (s, 3H). HR-MS (APCI, m/z): [M]+ calcd for $C_{13}H_{10}O_2Br_2NS$: 399.1. Found: 398.3311.

2.4.3 Synthesis of 4,4''-diamino-5'-(benzo[d]thiazol-2-yl)-[1,1':3',1''-terphenyl]-4'-ol (HBTN)

DBrHBT (2.68 g, 7 mmol) and (4-aminophenyl)boronic acid hydrochloride (2.18 g, 21 mmol) were dissolved in 100 ml THF, subsequently, 2 M aqueous K_2CO_3 solution (20 mL) was added. Then $Pd(PPh_3)_4$ (catalytic amount) was added under argon condition. The mixture was stirred at 88 ℃ for 48 h (monitored by TLC). After cooling to room temperature, the mixture was washed with brine, then concentrated. The pure product (2.28 g, 80%) was obtained by silica-gel column chromatography with dichloromethane as an eluent. ^{1}H NMR (400 MHz, DMSO-d6) δ 12.57 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 1.9 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.57-7.50 (m, 2H), 7.42 (d, J = 8.0 Hz, 4H), 6.67 (td, J = 8.2, 1.7 Hz, 4H), 5.22 (s, 4H). ^{13}C NMR (151 MHz, DMSO-d6) δ 169.85, 153.10, 151.61, 148.62, 148.56, 133.41, 132.98, 131.49, 131.01, 130.47, 127.53, 127.46, 127.13, 126.35, 125.07, 123.25, 122.75, 122.41, 117.35, 114.82, 113.97. FTIR (KBr): 3349 cm^{-1} (-NH_2 stretching vibration). HR-MS (APCI, m/z): [M]+ calcd for $C_{25}H_{19}N_3OS$: 409.5. Found: 410.1320.

2.4.4 Synthesis of 5'-(benzo[d]thiazol-2-yl)-4'-methoxy-[1,1':3',1''-terphenyl]-4,4''-diamine (MBTN)

DBrMBT (2.78 g, 7.0 mmol) and (4-aminophenyl)boronic acid hydrochloride (2.18 g, 21 mmol) were dissolved in 100 ml THF, subsequently, 2 M aqueous K_2CO_3 solution (20 mL) was added. Then $Pd(PPh_3)_4$ (catalytic amount) was added under argon condition. The mixture was stirred at 88 ℃ for 48 h (monitored by TLC). After cooling to room temperature, the mixture was washed with brine, then concentrated. The pure product (2.20 g, 82%) was obtained by silica-gel column chromatography with dichloromethane as an eluent. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.45 (d, J = 2.5 Hz, 1H), 8.18 – 8.11 (m, 2H), 7.61–7.53 (m, 2H), 7.50–7.44 (m, 3H), 7.42–7.38 (m, 2H), 6.74–6.67 (m, 4H), 5.29 (d, J = 10.8 Hz, 4H), 3.48 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d6) δ 163.08, 154.16, 152.20, 148.98, 148.94, 137.70, 136.37, 136.17, 130.72, 129.86, 129.26, 127.74, 126.94, 126.81, 126.75, 125.65, 124.88, 123.49, 123.13, 122.37, 114.81, 114.44, 114.42, 60.32. FTIR (KBr): 3334 cm^{-1} (-NH_2 stretching). HR-MS (APCI, m/z): [M]+ calcd for $C_{26}H_{21}BrN_3OS$: 423.5. Found: 424.1479.

2.4.5 Synthesis of 2,2'-(5'-(benzo[d]thiazol-2-yl)-4'-hydroxy-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(hexahydro-1H-isoindole-1,3(2H)-dione)(HBTN-MC)

HBTN (0.50 g, 1.2 mmol) and hexahydroisobenzofuran-1,3-dione (0.55 g, 3.6 mmol) were dissolved in 30 mL acetic acid, and sodium acetate trihydrate (0.35 g, 3.6 mmol) was added as catalyst. The mixture was stirred at 150 ℃ for 5 h under argon condition (monitored by TLC). After cooling to room temperature, the mixture was poured into 350 ml cold water. The

yellowish precipitate was collected and the pure product (0.65 g, 80%) was obtained by silica-gel column chromatography with dichloromethane as an eluent. ^{1}H NMR (400 MHz, DMSO-d6) δ 13.02 (s, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.15 (dd, J = 5.1, 2.8 Hz, 2H), 7.96–7.83 (m, 5H), 7.63 (t, J = 7.7 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.46–7.35 (m, 4H), 3.16 (t, J = 5.3 Hz, 4H), 1.82 (d, J = 20.7 Hz, 8H), 1.44 (s, 8H). 13C NMR (151 MHz, DMSO-d6) δ 179.15, 179.11, 169.21, 154.59, 151.40, 139.15, 137.35, 133.14, 132.80, 132.28, 132.22, 132.02, 130.41, 130.35, 127.93, 127.67, 127.56, 127.17, 126.61, 126.56, 122.88, 122.55, 118.00, 23.86, 21.97. FTIR (KBr): 3483 cm^{-1} (-OH stretching), 1778 cm^{-1} and 1709 cm^{-1} (C=O stretching). HR-MS (APCI, m/z): [M]+ calcd for $C_{41}H_{35}N_3O_5S$: 681.8. Found: 682.2382.

2.4.6 Synthesis of 2,2'-(5'-(benzo[d]thiazol-2-yl)-4'-methoxy-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(hexahydro-1H-isoindole-1,3(2H)-dione (MBTN-MC)

MBTN (0.51 g, 1.2 mmol) and hexahydroisobenzofuran-1,3-dione (0.55 g, 3.6 mmol) were dissolved in 30 mL acetic acid, and sodium acetate trihydrate (0.35 g, 3.6 mmol) was added as catalyst. The mixture was stirred at 150 ℃ for 5 h under argon condition (monitored by TLC). After cooling to room temperature, the mixture was poured into 350 ml cold water. The white precipitate was collected and the pure product (0.67 g, 80%) was obtained by silica-gel column chromatography with dichloromethane as an eluent. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.78 (d, J = 2.4 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.85–7.79 (m, 4H), 7.70 (d, J = 2.3 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.49–7.40 (m, 5H), 3.56 (s, 3H), 3.08 (dt, J = 6.9, 4.8 Hz, 4H), 1.96 (d, J = 12.0 Hz, 8H), 1.55 (h, J = 3.2 Hz, 8H). ^{13}C NMR (151 MHz, DMSO-d6) δ 179.08, 179.06, 162.31, 155.69, 152.18, 139.05, 137.25, 136.60, 136.20, 135.61, 132.71, 132.66, 129.86, 127.99, 127.83, 127.60, 127.42, 127.00, 126.76, 125.95, 123.32, 122.53, 61.31, 23.86, 21.97. FTIR (KBr): 1793 cm^{-1} and 1704 cm^{-1} (C=O stretching). HR-MS (APCI, m/z): [M]+ calcd for $C_{42}H_{37}N_3O_5S$: 695.8. Found: 696.2527.

2.4.7 Synthesis of the polyimides

All the polyimides were synthesized by one-step method. The HPHBTNms PI polymers were prepared by condensation of two diamines (HBTN and ODA) with commercial dianhydride 1,2,4,5cyclohexanetetracarboxylic dianhydride (HPMDA) with the feed molar ratios of 6:94:100 (HPHBTN6), 10:90:100 (HPHBTN10). The HBHBTNms PI polymers were prepared by condensation of two diamines (HBTN and ODA) with commercial dianhydride dicyclohexyl-3,4,3',4'-tetracarboxylic dianhydride (HBMDA) with the feed molar ratios of 6:94:100 (HBHBTN6), 10:90:100(HBHBTN10). HPHBTN6 was used as an example to illustrate the general synthetic procedure. To the solution of ODA (0.9486 g, 4.7 mmol) and HBTN (0.1238 g, 0.3 mmol) in 5 ml anhydrous NMP, HPMDA (1.1297 g, 5.0 mmol) was added in one portion. After stirring at room temperature overnight, benzoic acid (0.0310 g, 0.25 mmol) was added and the reaction system stirred at 80 ℃ for 2 h. Then the reaction system was stirred at 180 ℃ for 6 h. After cooling to room temperature, the resulting polymer was precipitated in ethanol, washed with ethanol and dried in a vacuum oven at 70 ℃ for 24 h. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.28 (d, J = 8.8 Hz, 3H), 7.18–7.10 (m, 3H), 4.36 (t, J = 5.1 Hz, 1H), 3.45 (qd, J = 7.0, 5.0 Hz, 1H), 3.25–3.15 (m, 4H), 2.32–2.22 (m, 2H), 2.00–1.94 (m, 2H), 1.06 (t, J = 7.0 Hz, 2H).

3 NMR Spectrum for the Synthesized Compounds

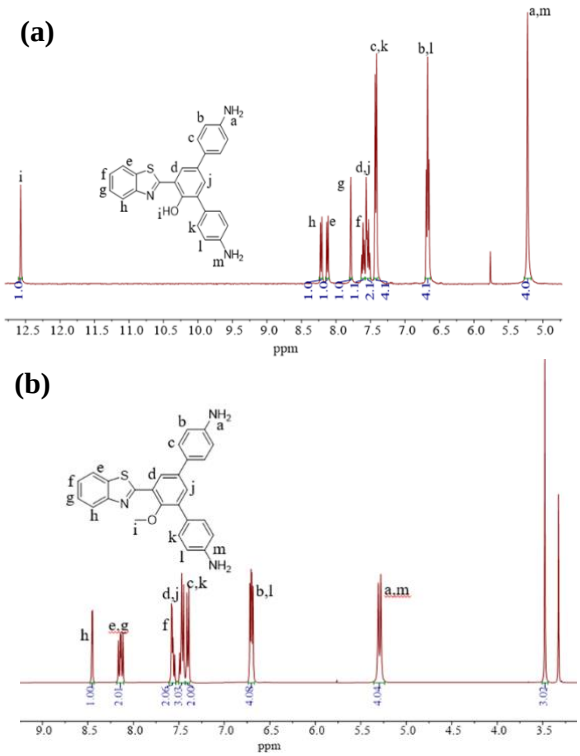

Figure S1. ^{1}H NMR spectrum for diamines HBTN (a) and MBTN (b).

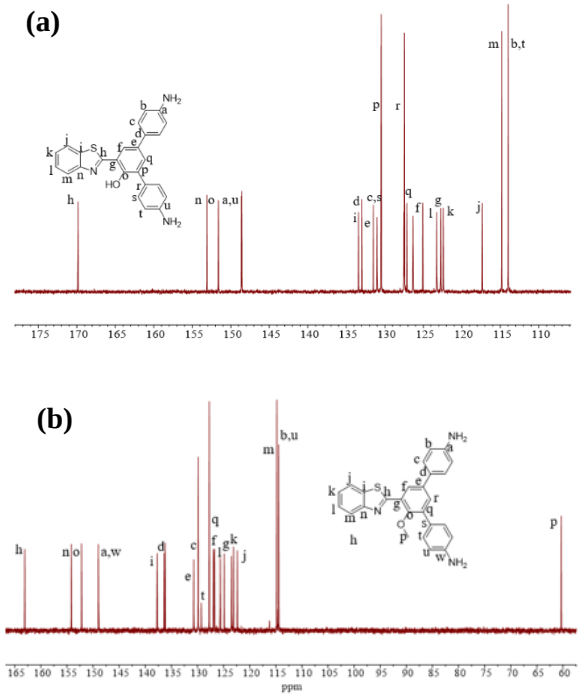

Figure S2. ^{13}C NMR spectrum for diamines HBTN (a) and MBTN (b).

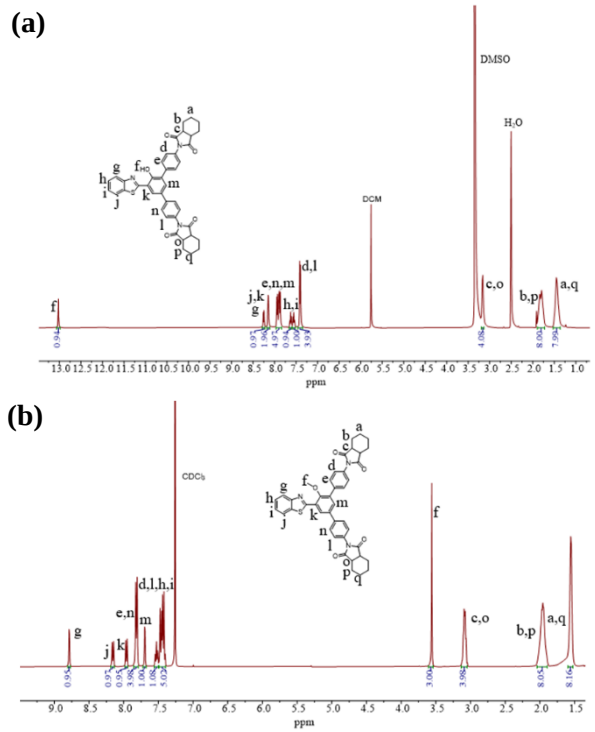

Figure S3. ^{1}H NMR spectrum for imides HBTN-MC (a) and MBTN-MC (b).

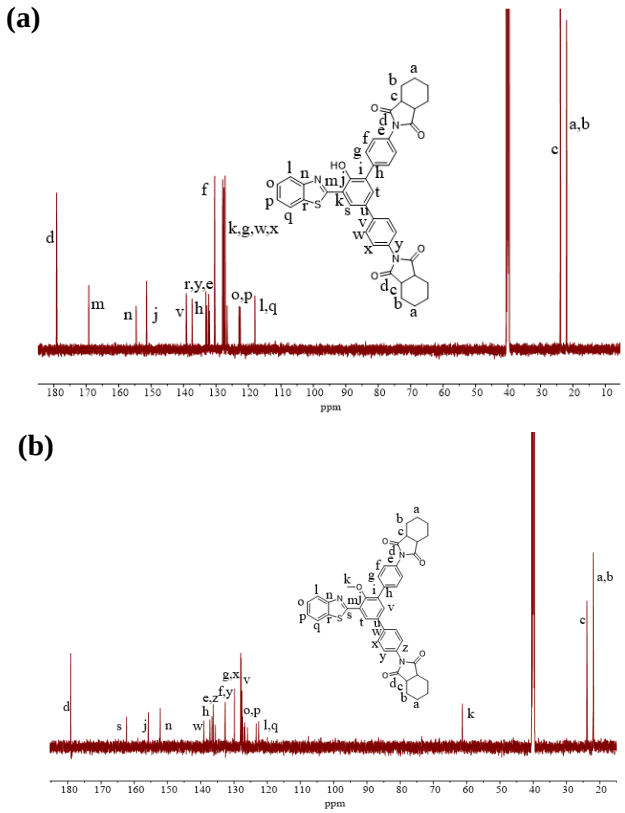

Figure S4. ^{13}C NMR spectrum for imides HBTN-MC (a) and MBTN-MC (b).

4 FT-IR Spectrum for diamides and imides

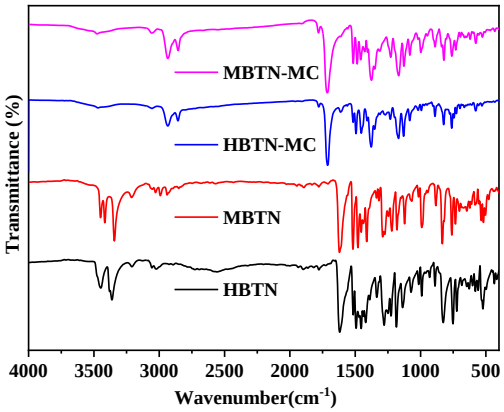

Figure S5. FT-IR spectrum for diamides (HBTN and MBTN) and imides (HBTN-MC and MBTN-MC).

5 Simulated IR for HBT and HBTN-MC

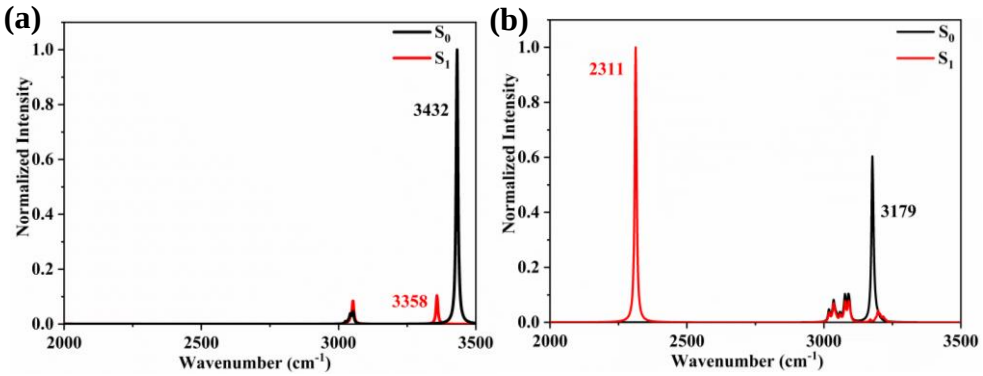

Figure S6. Simulated IR of (a) HBT and (b) HBTN-MC in the O_1-H_2 stretching band region in the S_0 and S_1 states.

6 Calculated transition wavelength and oscillator strength for HBT and HBTN-MC

Table S1 The calculated transition wavelength and oscillator strength of the keto form of HBT and HBTN-MC in the S_1 state

Compound	State	Transition wavelength (nm)	Oscillator strength (*f*)	Orbitals
HBT	Keto*-S_1	517.58	0.3510	HOMO->LUMO
	Keto*-S_2	400.83	0.0354	HOMO-1->LUMO
HBTN-MC	Keto*-S_1	573.93	0.4702	HOMO->LUMO
	Keto*-S_2	382.14	0.1535	HOMO-1->LUMO

The vertical excitation energies of S_1->S_0 for HBT (keto form) and HBTN-MC (keto form) in the dichloromethane solvent environment (with the solvation model density (SMD) implemented in the Gaussian software) were calculated by TD-DFT applying the B3LYP-D3(BJ) functional with 6-311+G (d, p) basis set, and the vertical excitation energy and oscillator strength (*f*) were obtained under the optimal structure of S_1 state

7 FT-IR Spectrum for Polyimides

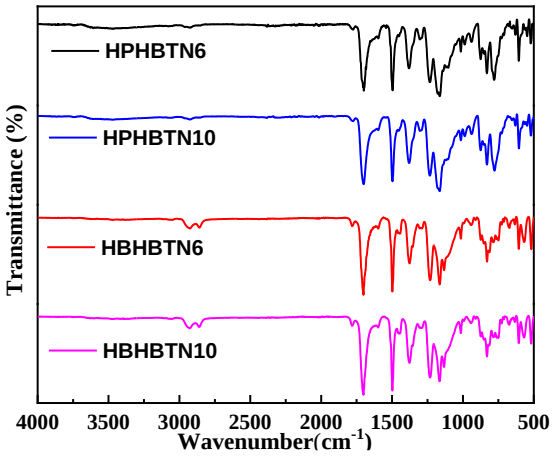

Figure S7. FT-IR spectrum for polyimides.

8. The excitation spectra for the polyimides

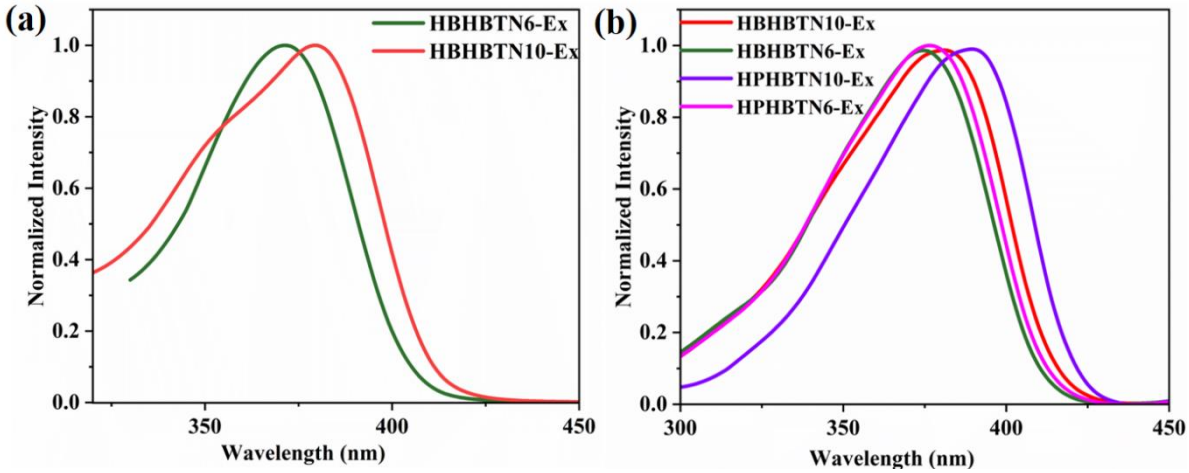

Figure S8. The excitation spectra of HBHBTNms in DCM and HBHBTNms and HPHBTNs in film state.

9. The transient PL decay curves for the polyimides

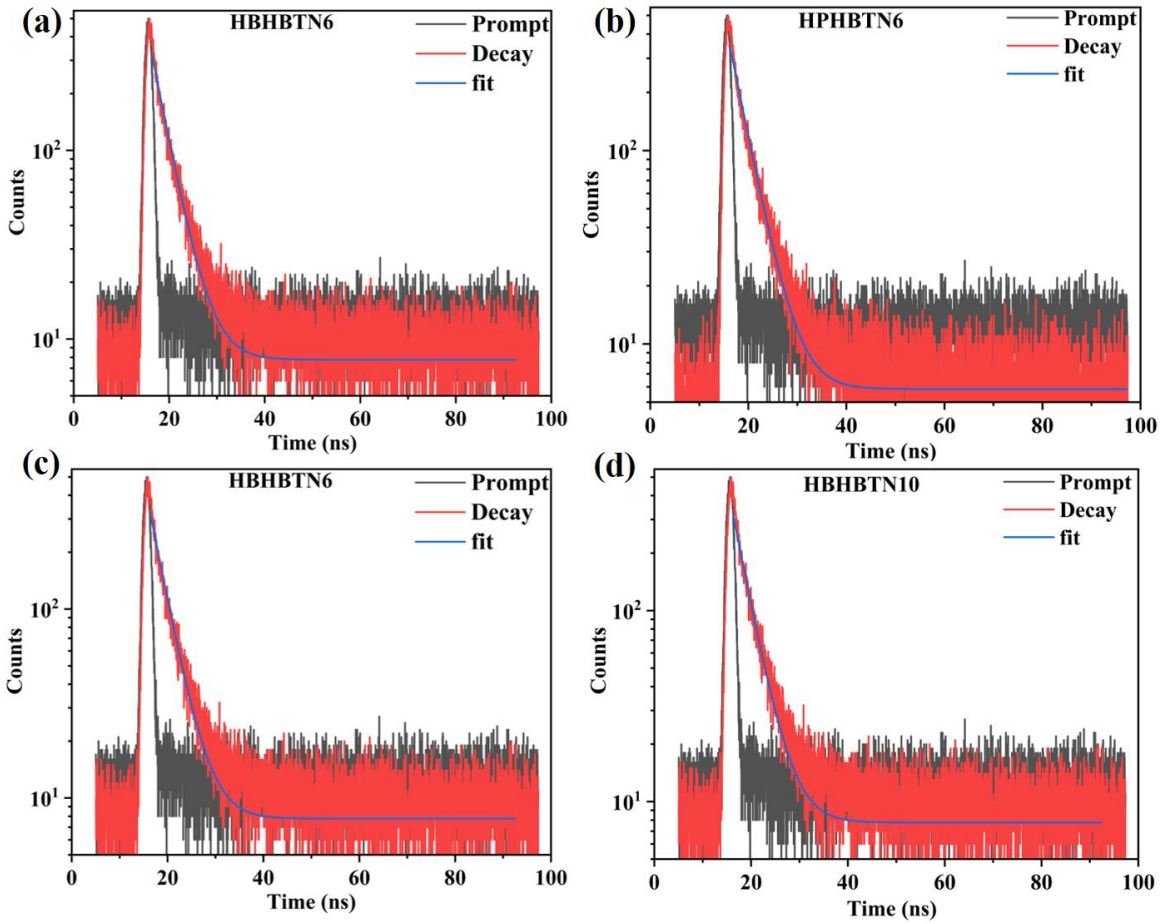

Figure S9. The transient PL decay curves of the polyimides

Table S2 The chi-square and the residuals and the values for the pre-exponential factors for all the polyimides.

Polyimides	HBHBTN6	HBHBTN10	HPHBTN6	HPHBTN10
pre-exponential factors	8.908702	7.681269	5.983029	6.33539
chi-squared Probability	1.9288E-20%	1.9288E-20%	1.9288E-20%	1.9288E-20%
Negative residuals	36.63775%	36.70089%	34.89715%	36.98243%
Residuals < 1 s.dev	63.27964%	61.57668%	62.86539%	62.42158%
Residuals < 2 s.dev	94.05205%	94.43524%	93.90112%	94.82434%
Residuals < 3 s.dev	98.3891%	99.10567%	98.98953%	98.30614%
Residuals < 4 s.dev	99.71086%	99.37065%	99.45868%	99.56085%

10 The Spectrum Comparison of LED Light, Sunlight, Excitation, and Emission of HBHBTN6

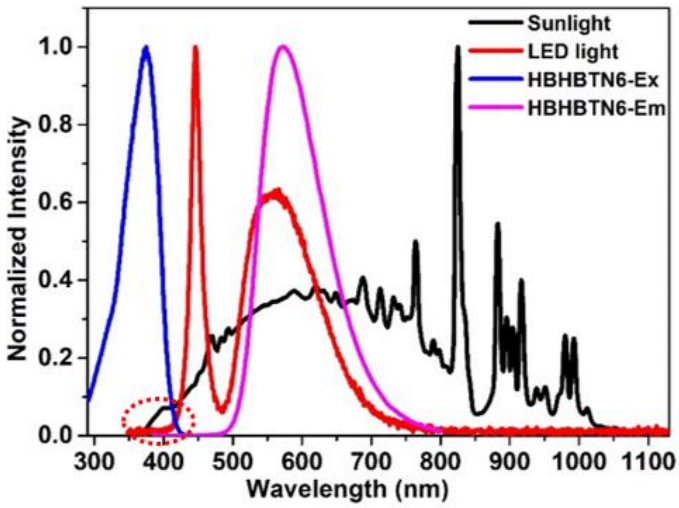

Figure S10. The spectrum comparison of LED light, sunlight, excitation, and emission of HBHBTN6.