

Supporting Information

Thermally Activated Delayed Fluorescence Amorphous Molecular Materials for High-Performance Organic Light-Emitting Diodes

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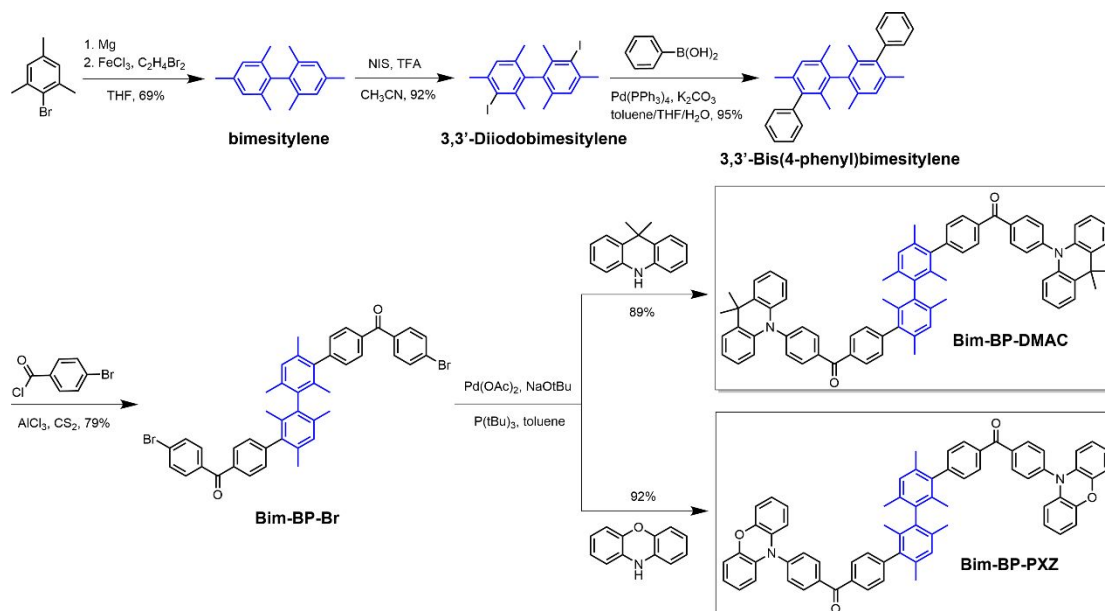
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Contents

1. Synthesis of Materials
2. Computational Methodology and Results
3. Photophysical Properties
4. Thermogravimetric Analysis
5. Atomic Force Microscopy (AFM) images
6. Device performance
7. NMR Spectra
8. Mass spectra
9. Reference

1. Synthesis of Materials



Scheme S1. Synthetic route of Bim-BP-DMAC and Bim-BP-PXZ.

1.1. Synthesis of bimesitylene^[1]

Under nitrogen protection, a mixture of magnesium powders (2.55 g, 105 mmol) and dry THF (120 mL) in a 250 mL oven-dried flask was heated to reflux, to which mesityl bromide (19.9 g, 100 mmol) was then added dropwise. The resulting solution was refluxed for 8 h. After this, a solution of iron chloride (1.62 g, 10 mmol) in 1,2-dibromoethane (6.5 mL, 75 mmol) and THF (20 mL) was added dropwise to the reaction flask, and the resulting mixture was refluxed for another 5 h. After cooling to room temperature, the reaction mixture was quenched with dilute hydrochloric acid (2%, 50 mL). The solution was extracted several times with ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄, and then the solvent was removed. The residue was purified by column chromatography over silica gel using petroleum ether as the eluent to afford the product as colorless block crystals (8.2g, yield: 69%). ¹H NMR (500 MHz, Chloroform-*d*) δ 6.93 (s, 4H), 2.33 (s, 6H), 1.86 (s, 12H).

1.2. Synthesis of 3,3'-Diiodobimesitylene^[2]

NIS (4.95 g, 22 mmol) followed by TFA (0.5 mL) was added to a solution of bimesitylene (2.38 g, 10 mmol) in dry CH₃CN (50 mL) at 0 °C, and then the mixture was stirred overnight at room temperature. Subsequently, the solvent was removed by vacuum-rotary evaporation. The resulting mixture was extracted with CH₂Cl₂ and then washed with aqueous NaHCO₃ solution and brine, respectively. After being dried over anhydrous Na₂SO₄, the crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the product as a white solid (4.5 g, yield: 92%). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.04 (s, 2H), 2.49 (s, 6H), 2.08 (s, 6H), 1.79 (s, 6H).

1.3. Synthesis of 3,3'-Bis(4-phenyl)bimesitylene^[3]

A 150 mL pressure tube was charged with 3,3'-diiodobimesitylene (1.96 g, 4 mmol), phenylboronic acid (1.47 g, 12 mmol), Pd(PPh₃)₄ (0.277 g, 0.24 mmol), toluene (20 mL), THF (10 mL), and 2 M K₂CO₃ solution (10 mL). After being evacuated under vacuum and purged with dry nitrogen for three times, the pressure tube was capped tightly. The reaction mixture was stirring at 90 °C for 24 h. Subsequently, the reaction mixture was cooled to room temperature and extracted three times with ethyl acetate. The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the product as a white solid (1.48 g, yield: 95%). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.44-7.37 (m, 4H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.16 (dd, *J* = 14.6, 7.5 Hz, 4H), 7.05 (s, 2H), 2.03 (s, 6H), 1.95 (s, 6H), 1.62 (s, 6H).

1.4. Synthesis of Bim-BP-Br

A mixture of anhydrous AlCl₃ (0.96 g, 7.2 mmol) and 3,3'-Bis(4-phenyl)bimesitylene (1.18 g, 3 mmol) in CS₂ (40 mL) were cooled to 0 °C, and then 4-bromobenzoyl

chloride (1.45 g, 6.6 mmol) was added into the mixture slowly. The resulting mixture was then reflux (50 °C) for 12 h. At the end of this period, the reaction mixture was poured into crushed ice and extracted several times with CH₂Cl₂. The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄, and then the solvent was removed. The residue was purified by column chromatography over silica gel using ethyl acetate and petroleum ether mixture (EA:PE=1:50) as the eluent to afford the product as a white solid (1.8 g, yield: 79%). ¹H NMR (500 MHz, Chloroform-d) δ 7.73 (d, J = 8.2 Hz, 4H), 7.62 (d, J = 8.6 Hz, 4H), 7.44 (t, J = 7.9 Hz, 4H), 7.36 (t, J = 7.4 Hz, 2H), 7.18 (s, 4H), 1.84-1.70 (m, 18H).

1.5. Synthesis of Bim-BP-DMAC

A mixture of **Bim-BP-Br** (0.757, 1 mmol), 9,9-dimethyl-9,10-dihydroacridine (0.314 g, 1.5 mmol), tri-tert-butylphosphine tetrafluoroborate (0.029 g, 0.1 mmol), sodium tert-butoxide (0.29 g, 3 mmol), palladium acetate (0.022 g, 0.1 mmol) and dry toluene was refluxed at 90 °C under N₂ for 18 h. After cooling to room temperature, the solvent was removed by vacuum-rotary evaporation. The mixture was then extracted several times with CH₂Cl₂. The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄. The residue was purified by column chromatography over silica gel using ethyl acetate and petroleum ether mixture (EA:PE=1:50) as the eluent to afford the product as a pale-yellow solid (0.9 g, yield: 89%). ¹H NMR (400 MHz, Chloroform-d) δ 8.08 (s, 4H), 7.45 (s, 12H), 7.35 (s, 2H), 7.21 (s, 4H), 6.98 (s, 8H), 6.34 (s, 4H), 1.91 (s, 10H), 1.75 (s, 5H), 1.66 (s, 12H), 1.59 (s, 3H). MS (m/z): [M+Na]⁺ calcd. for C₇₄H₆₄N₂O₂Na, 1035.4865; found, 1035.4858. Anal. calcd. for C₇₄H₆₄N₂O₂: C, 87.71; H, 6.37; N, 2.76. Found: C, 87.71; H, 6.15; N, 2.86.

1.6. Synthesis of Bim-BP-PXZ

A procedure similar to that used for Bim-BP-DMAC was followed but with 10H-phenoxazine instead of 9,9-dimethyl-9,10-dihydroacridine. The product was obtained as a yellow solid in a yield of 92%. ¹H NMR (400 MHz, Chloroform-d) δ 8.07 (d, J = 7.1 Hz, 4H), 7.45 (s, 8H), 7.36 (d, J = 8.7 Hz, 2H), 7.20 (s, 4H), 6.75-6.56 (m, 12H),

5.98 (s, 4H), 1.88 (s, 11H), 1.75 (s, 5H), 1.57 (s, 2H). MS (m/z): $[M+Na]^+$ calcd. for $C_{68}H_{52}N_2O_4Na$, 983.3825; found, 983.3819. Anal. calcd. for $C_{68}H_{52}N_2O_4$: C, 84.97; H, 5.45; N, 2.91. Found: C, 84.97; H, 5.41; N, 3.02.

2. Computational Methodology and Results

All the calculations were carried out using the Gaussian 09 program package^[4]. The density functional theory (DFT) calculations at the PEB0/6-311G (d, p) level were used to optimize the ground state geometries of the investigated compounds. Time-dependent density functional theory (TD-DFT) calculations were performed at the same level using the optimized ground state geometries. The spin-orbit couplings were calculated at PBE0/DKH by ORCA. The electron density diagrams of molecular orbitals were generated using GaussView program. The partition orbital composition was analyzed by using the Multiwfn 2.4 program^[5].

Table S1. Calculated energy levels of the excited states and spin-orbit couplings.

Compd	S ₁ /S ₂ [eV]	T ₁ /T ₂ [eV]	T ₃ /T ₄ [eV]	SOC _{S1-T1} [cm ⁻¹]	SOC _{S1-T2} [cm ⁻¹]	SOC _{S1-T3} [cm ⁻¹]	SOC _{S1-T4} [cm ⁻¹]
Bim-BP- DMAC	2.7005 /2.7006	2.6880 /2.6880	2.9020 /2.9020	0.047	0.030	0.357	0.877
Bim-BP- PXZ	2.4500 /2.4561	2.3931 /2.4018	2.7653 /2.7667	0.030	0.222	0.993	0.130

3. Photophysical Properties

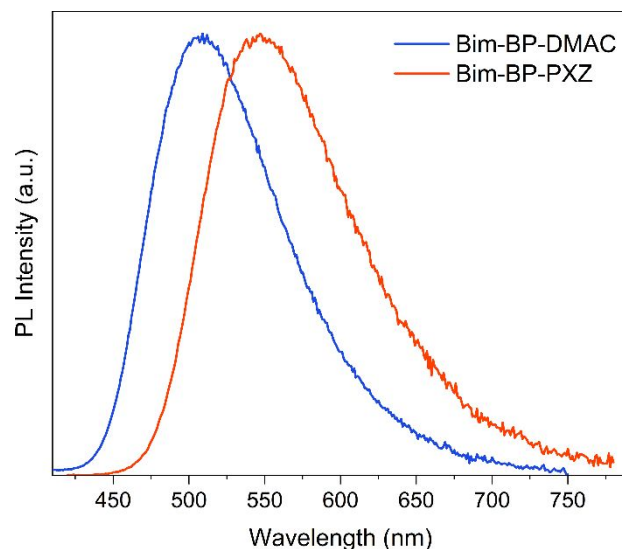


Figure S1. Steady-state photoluminescence spectra of Bim-BP-DMAC and Bim-BP-PXZ in 20 wt%-doped BCPO film at room temperature ($\lambda_{\text{ex}} = 340$ nm).

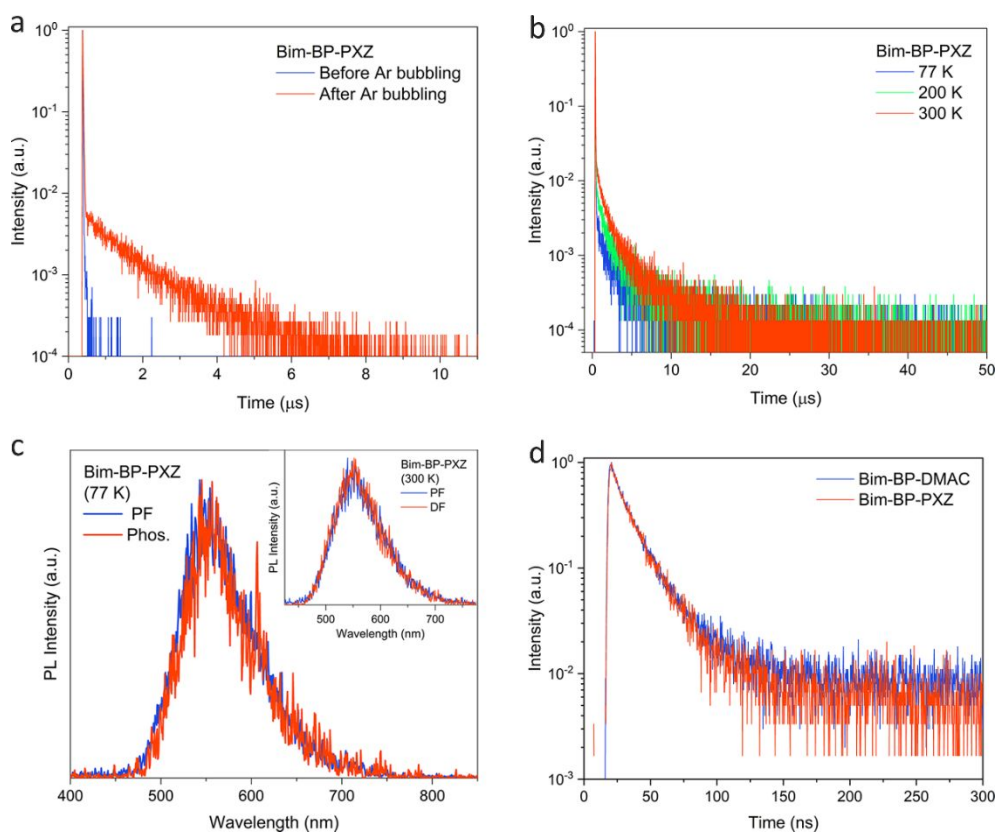


Figure S2. (a) Transient PL decay curves of Bim-BP-PXZ in toluene solution at room temperature before and after Ar gas bubbling for 10 min; (b) Transient PL decay curves of Bim-BP-PXZ in 20 wt%-doped BCPO film at different temperatures; (c) Time resolved PL spectra of Bim-BP-PXZ in 20 wt%-doped BCPO film at 77 K and 300 K (the inset); (d) Transient PL decay curves (with 0-300 ns time range) of Bim-BP-DMAC and Bim-BP-PXZ in 20 wt%-doped BCPO film at room temperature.

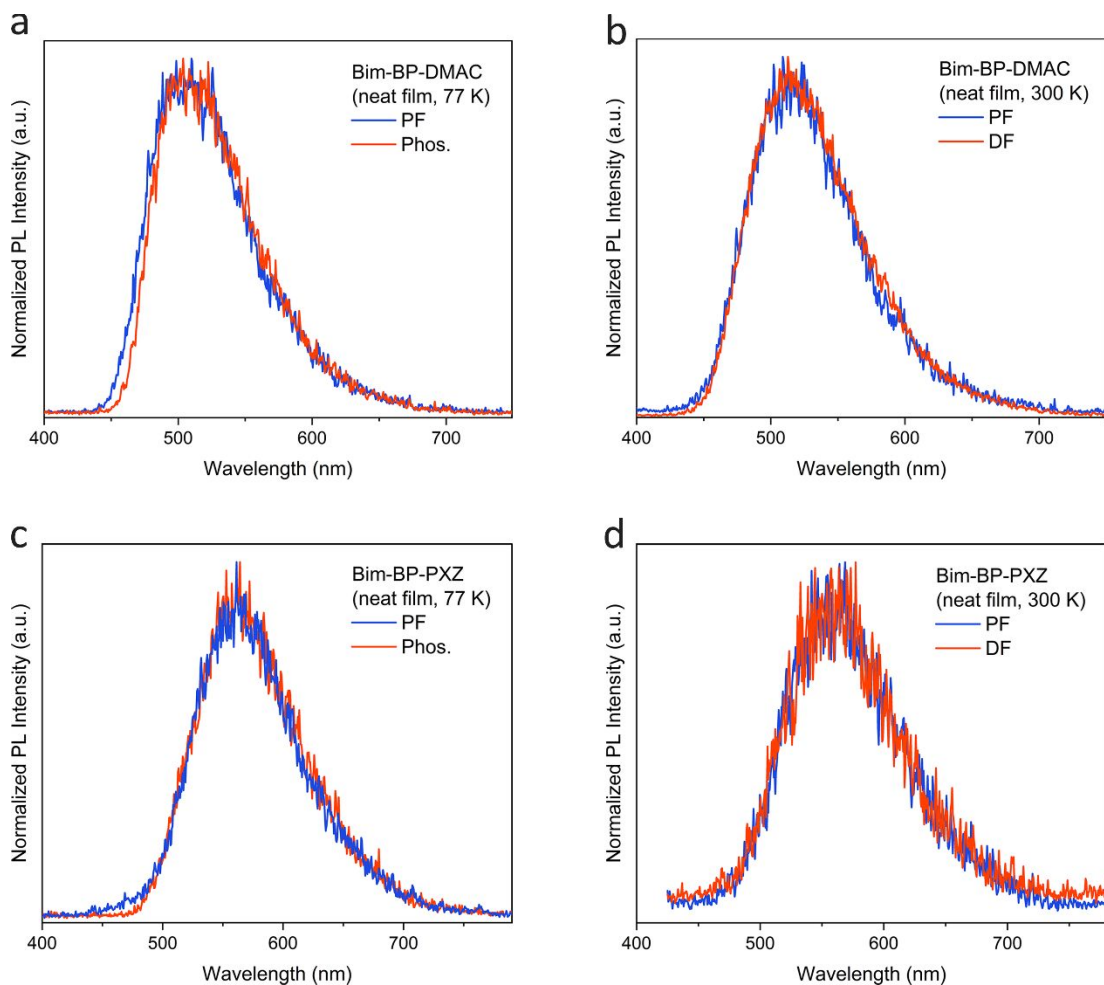


Figure S3. (a) Time resolved PL spectra of Bim-BP-DMAC in neat film at 77 K; (b) Time resolved PL spectra of Bim-BP-DMAC in neat film at 300 K; (c) Time resolved PL spectra of Bim-BP-PXZ in neat film at 77 K; (d) Time resolved PL spectra of Bim-BP-PXZ in neat film at 300 K. PF: prompt fluorescence; DF: delayed fluorescence; Phos.: phosphorescence.

Table S2. Energy levels and energy gaps of S_1 and T_1 states determined in doped films and neat films.

Compound	in 20 wt%-doped BCPO film			in neat film		
	E_{S1}^a	E_{T1}^b	ΔE_{ST}	E_{S1}^a	E_{T1}^b	ΔE_{ST}
	[eV]	[eV]	[eV]	[eV]	[eV]	[eV]
Bim-BP-DMAC	2.83	2.78	0.05	2.78	2.72	0.06
Bim-BP-PXZ	2.60	2.57	0.03	2.58	2.55	0.03

a) Evaluated from the onset of prompt fluorescence spectra recorded at 77 K; b) Evaluated from the onset of phosphorescence spectra recorded at 77 K.

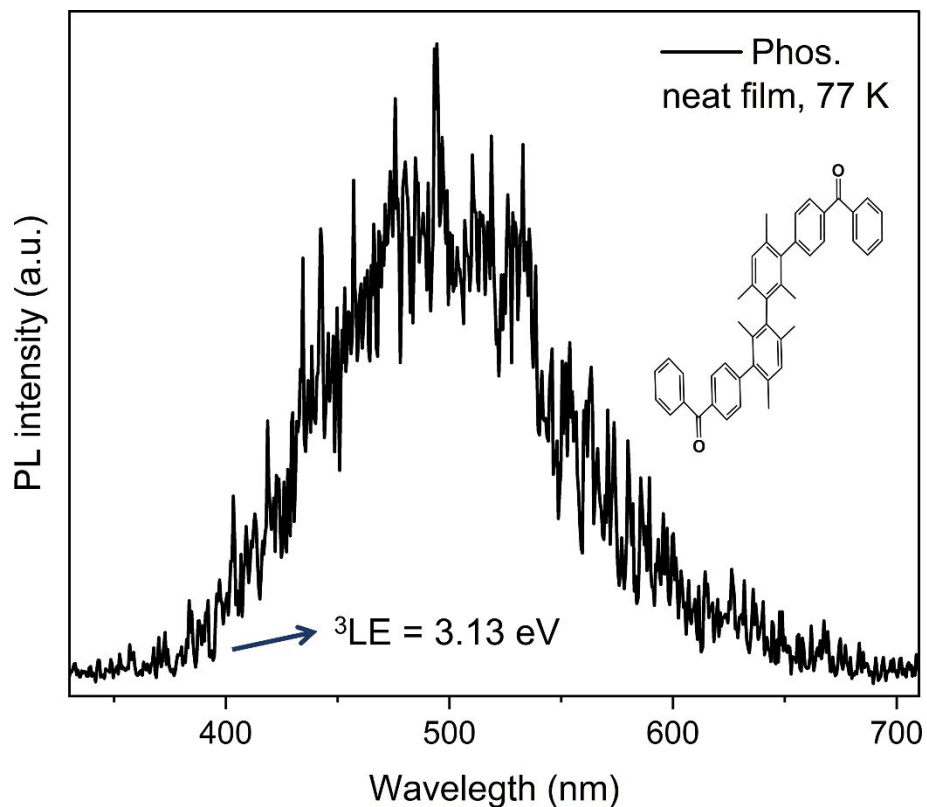


Figure S4. Phosphorescence spectra of Bim-BP fragment in neat film at 77 K.

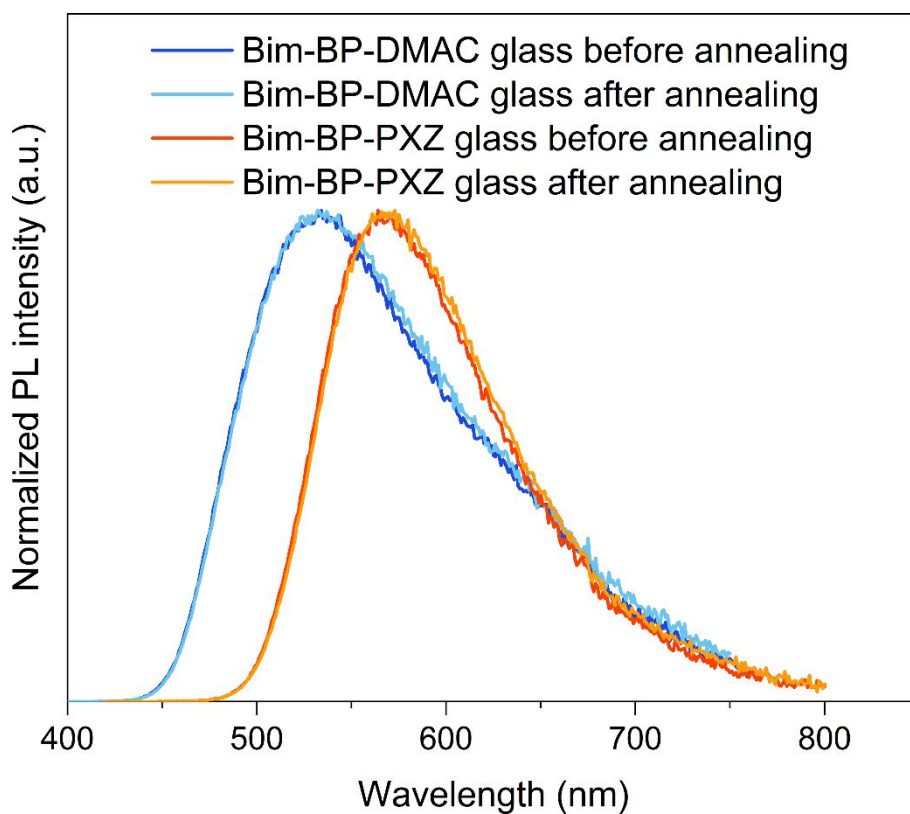


Figure S5. Steady-state photoluminescence spectra of Bim-BP-DMAC and Bim-BP-PXZ before and after annealing (heat treatment at 185 °C under Ar atmosphere for 30 min).

3.1 Analysis of rate constants

Rate constants of the investigated compounds in 20 wt% BCPO films at room temperature are determined from the measured quantum yields and lifetimes of the prompt fluorescence (PF) and delayed fluorescence (DF) components according to equations S1-S6^[6].

$$k_{PF} = \frac{1}{\tau_{PF}} \quad \text{Equation S1}$$

$$k_{DF} = \frac{1}{\tau_{DF}} \quad \text{Equation S2}$$

$$k_{RISC} = \frac{k_{PF} + k_{DF}}{2} - \sqrt{\left(\frac{k_{PF} + k_{DF}}{2}\right)^2 - k_{PF}k_{DF}\left(1 + \frac{\phi_{DF}}{\phi_{PF}}\right)} \quad \text{Equation S3}$$

$$k_{ISC} = \frac{k_{PF}k_{DF}\phi_{DF}}{k_{RISC} \phi_{PF}} \quad \text{Equation S4}$$

$$k_r^S \approx \frac{k_{PF}k_{DF}}{k_{RISC}}\phi_{PL} \quad \text{Equation S5}$$

$$k_{nr}^S \approx \frac{k_{PF}k_{DF}}{k_{RISC}}(1 - \phi_{PL}) \quad \text{Equation S6}$$

4. Thermogravimetric Analysis

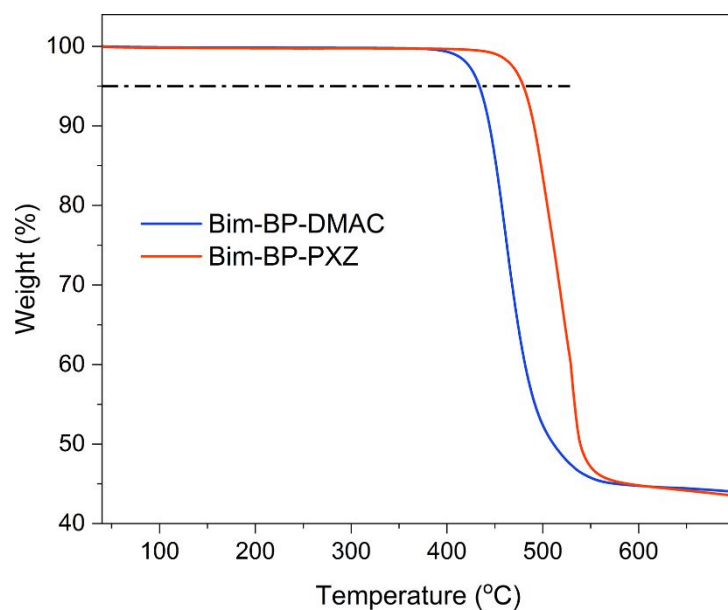


Figure S6. TGA curves of Bim-BP-DMAC and Bim-BP-PXZ. The black dashed line marks 95% of the original sample weight.

5. Atomic Force Microscopy (AFM) images

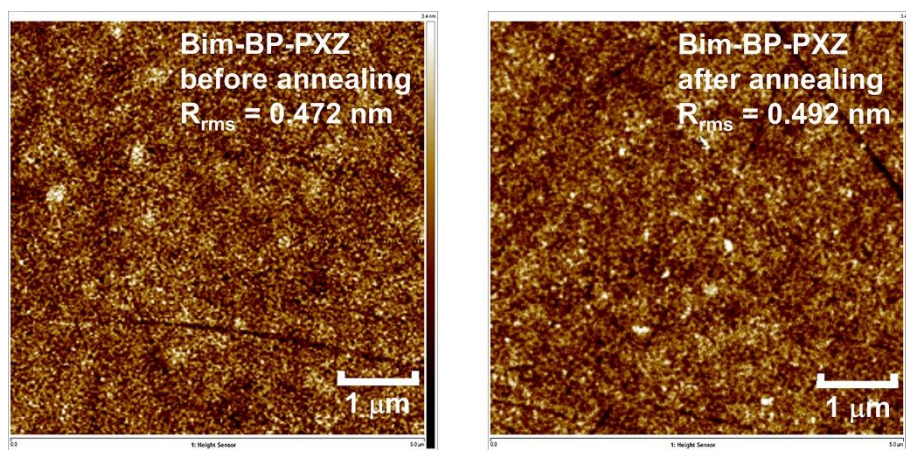


Figure S7. AFM images ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of the surface morphology of vacuum-deposited neat film of Bim-BP-PXZ before and after annealing (heat treatment at $120\ ^\circ\text{C}$ under Argon atmosphere for 30 min).

6. Device performance

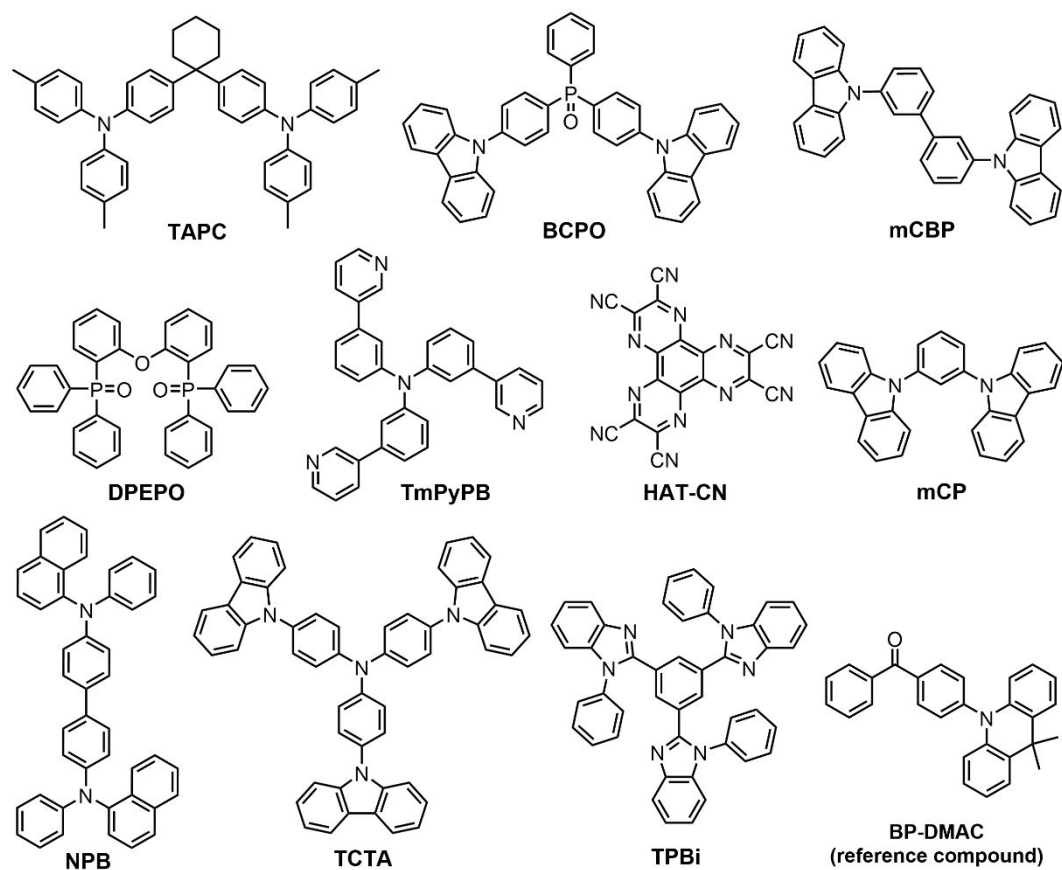


Figure S8. Molecular structures of the functional materials used in the OLEDs.

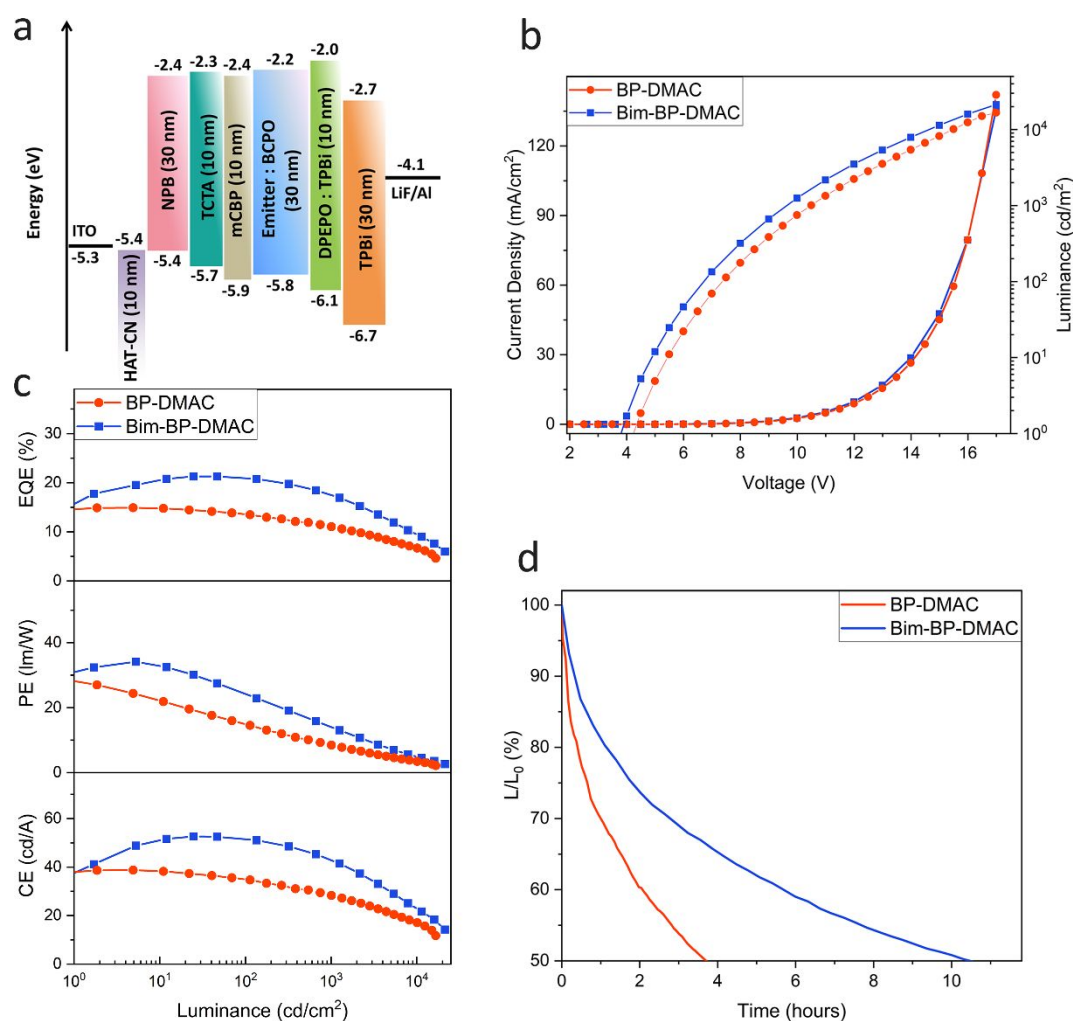


Figure S9. The structure and device performances of lifetime devices based on Bim-BP-DMAC and the reference compound BP-DMAC (20wt%). (a) Energy level diagram; (b) Current density-luminance-voltage (J-V-L) characteristics; (c) External quantum efficiency, power efficiency and current efficiency versus luminance characteristics; (d) Device operating lifetime curves (initial luminance: 500 cd/m²).

Table S3. EL performance of the lifetime OLEDs based on Bim-BP-DMAC and the reference compound BP-DMAC.

Device	V_{on}^a	L_{max}^b	CE	PE	EQE	$CIE_{1931}(x,y)^c$	T_{50}^d
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	[V]	[cd/m ²]	[cd/A]	[lm/W]	[%]		[h]
Bim-BP-DMAC	3.80	21272	52.7	34.1	21.3	(0.23, 0.42)	10.4
BP-DMAC	4.25	16650	38.7	29.3	14.9	(0.24, 0.45)	3.7

a) turn-on voltage taken at 1 cd/m²; b) the maximum luminance; c) CIE 1931 coordinates; d) Device operating lifetime (initial luminance: 500 cd/m²).

7. NMR Spectra

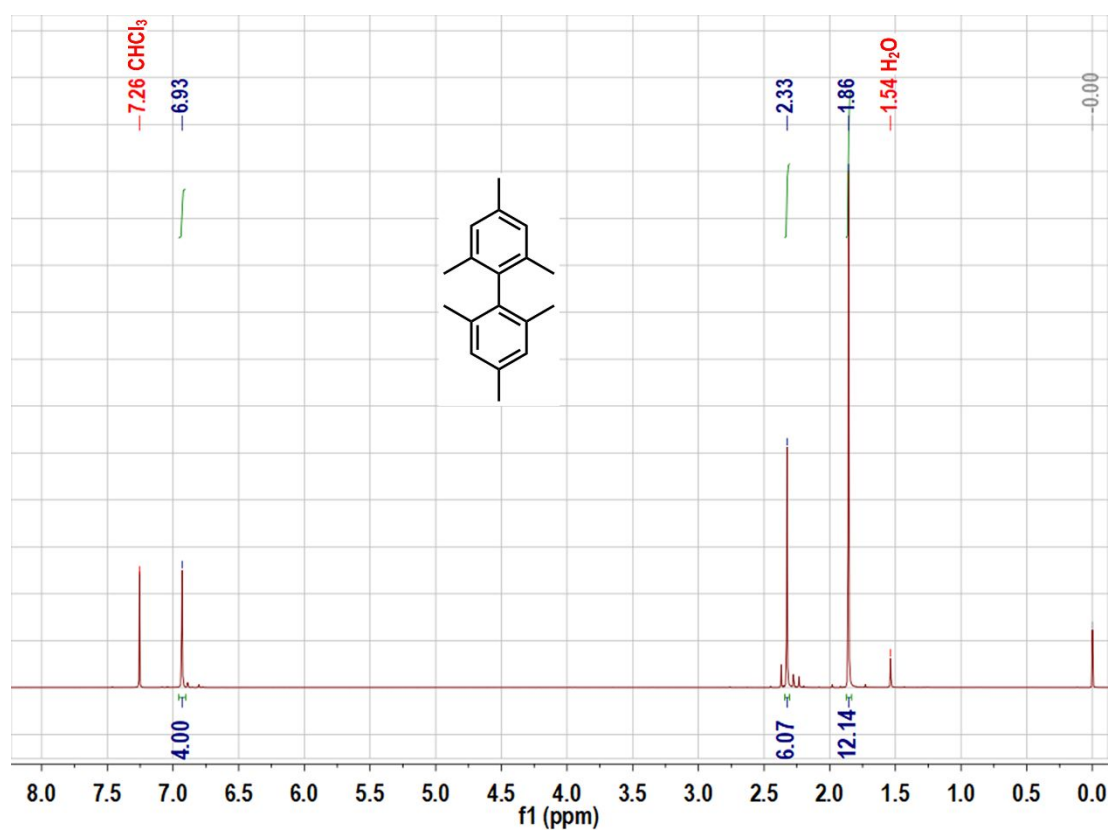


Figure S10. ¹H-NMR spectrum of bimesitylene (500 MHz, CDCl₃).

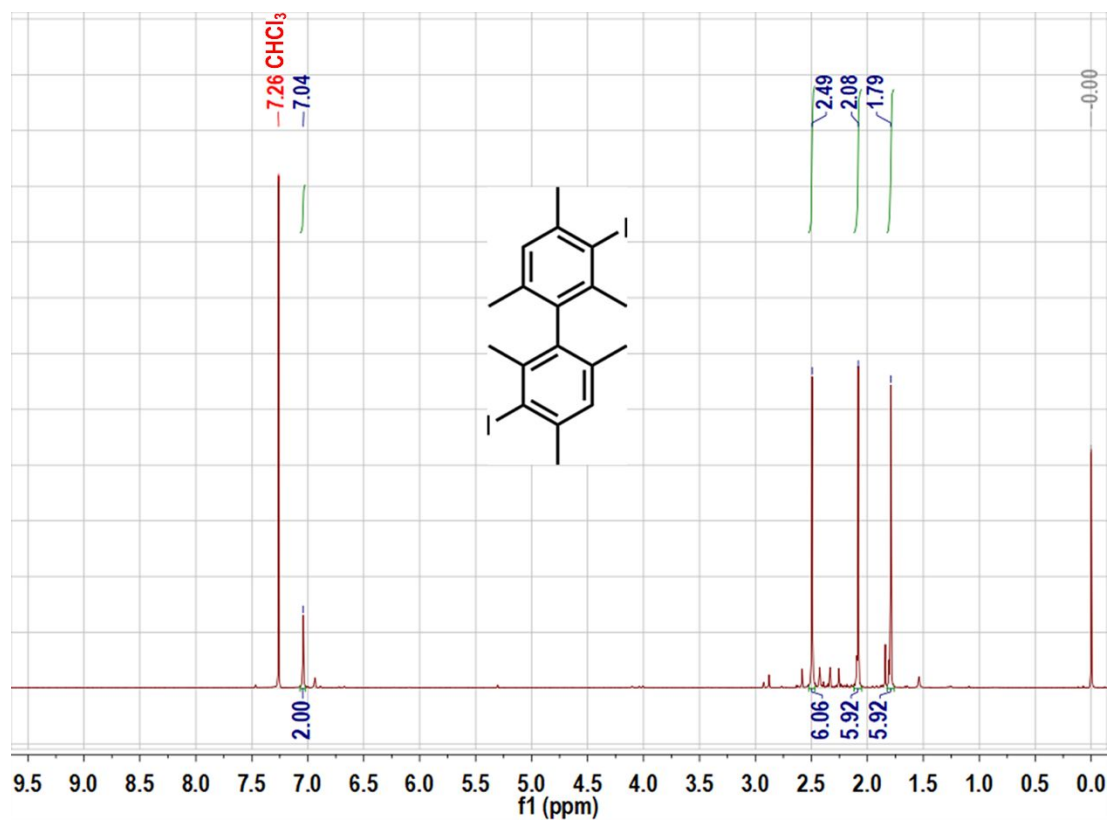


Figure S11. ¹H-NMR spectrum of 3,3'-Diiodobimesitylene (500 MHz, CDCl₃).

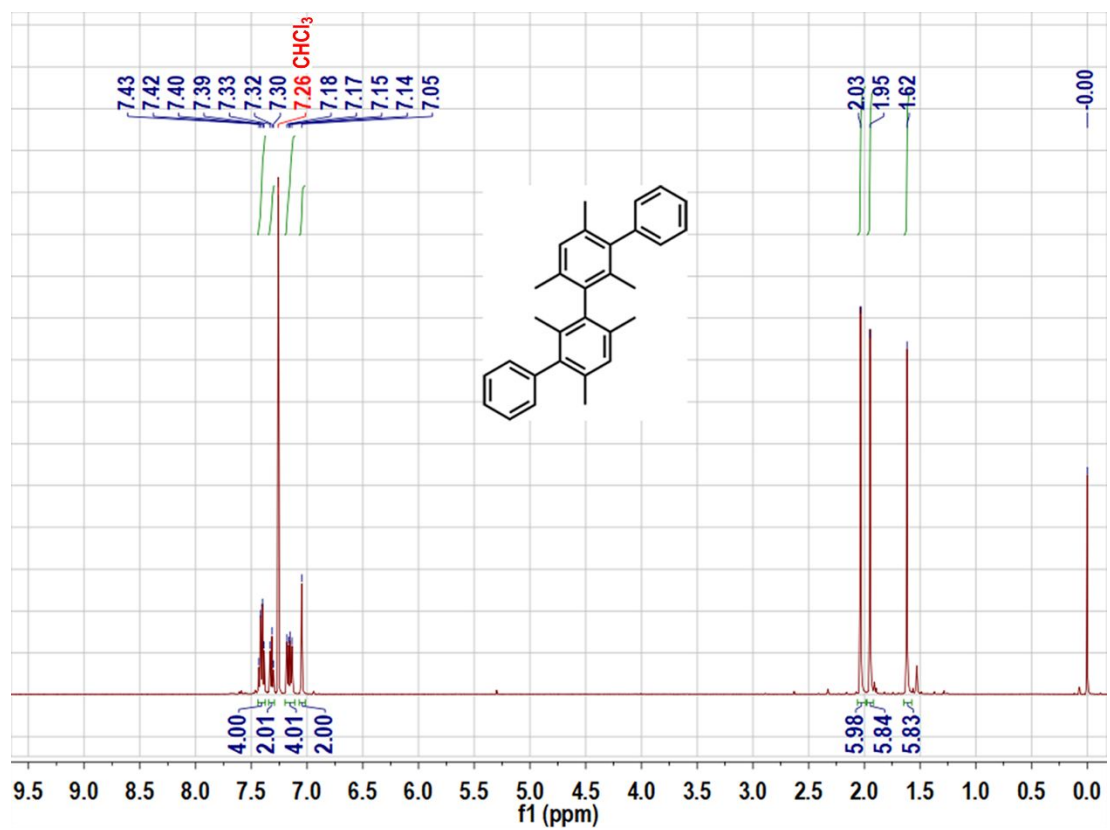


Figure S12. ¹H-NMR spectrum of 3,3'-Bis(4-phenyl)bimesitylene (500MHz, CDCl₃).

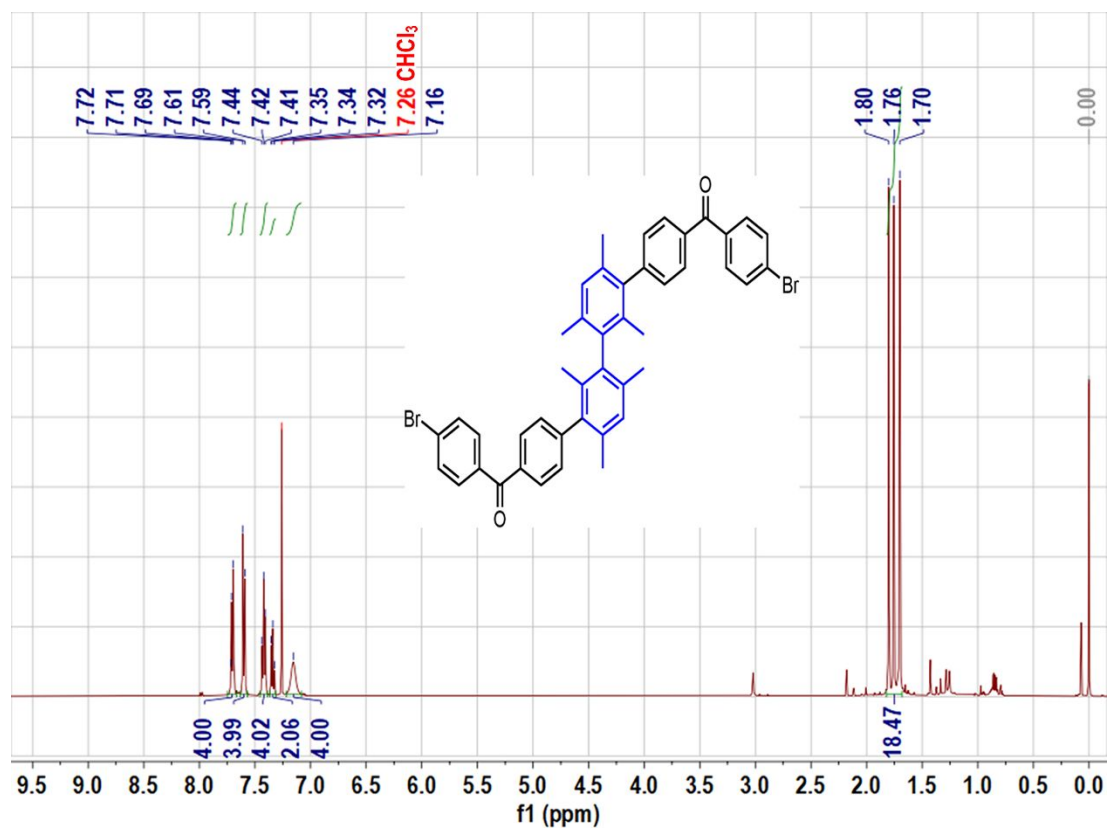


Figure S13. ¹H-NMR spectrum of Bim-BP-Br (400 MHz, CDCl₃).

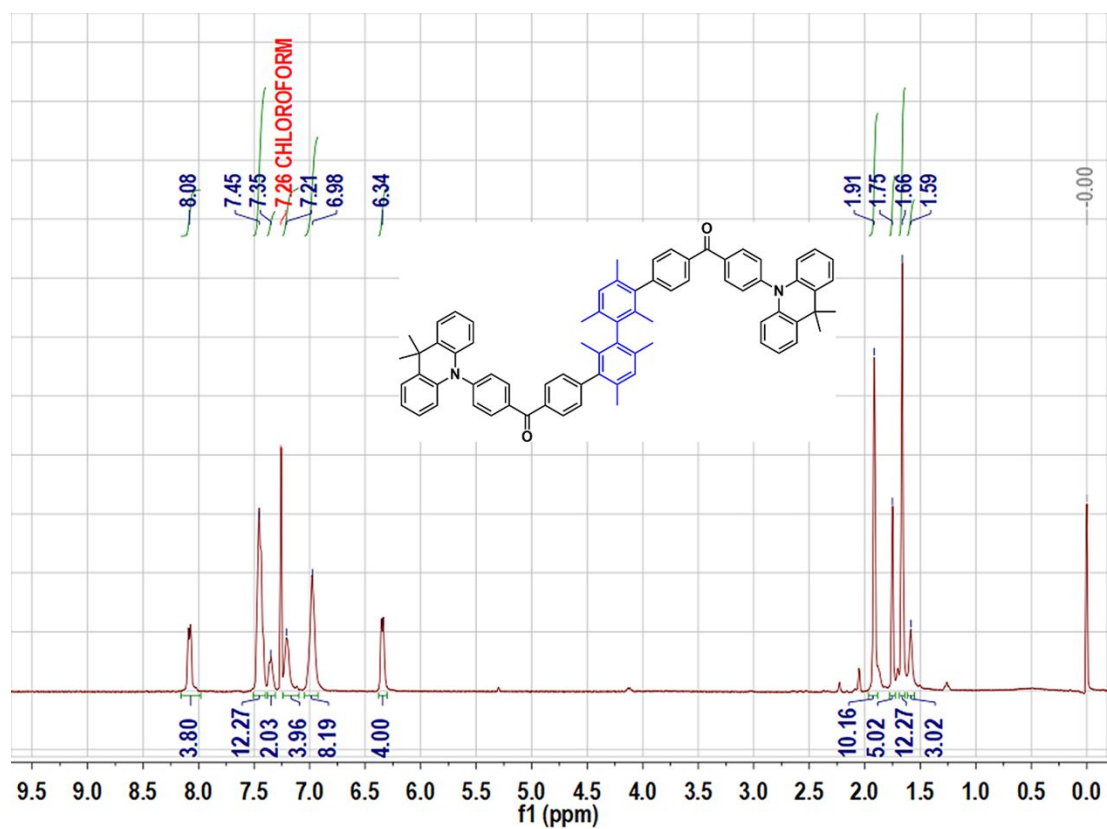


Figure S14. ¹H-NMR spectrum of Bim-BP-DMAC (400 MHz, CDCl₃).

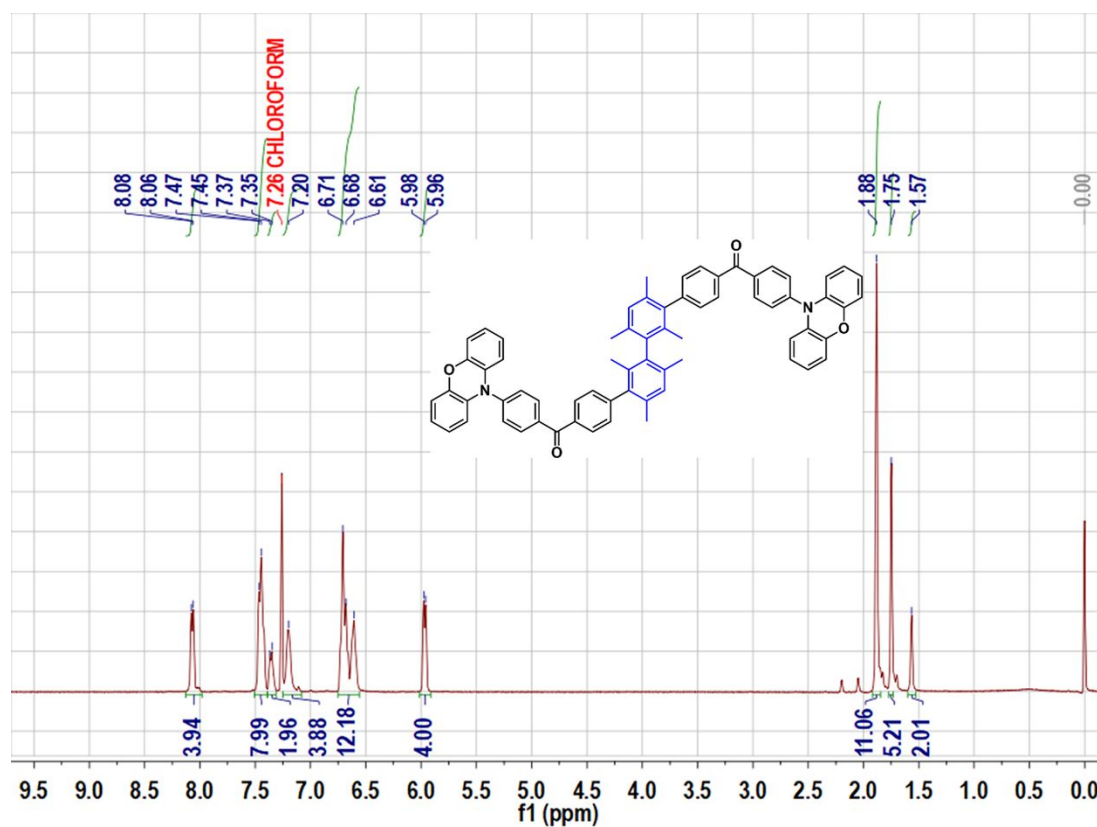


Figure S15. ¹H-NMR spectrum of Bim-BP-PXZ (400 MHz, CDCl₃).

8. Mass spectra

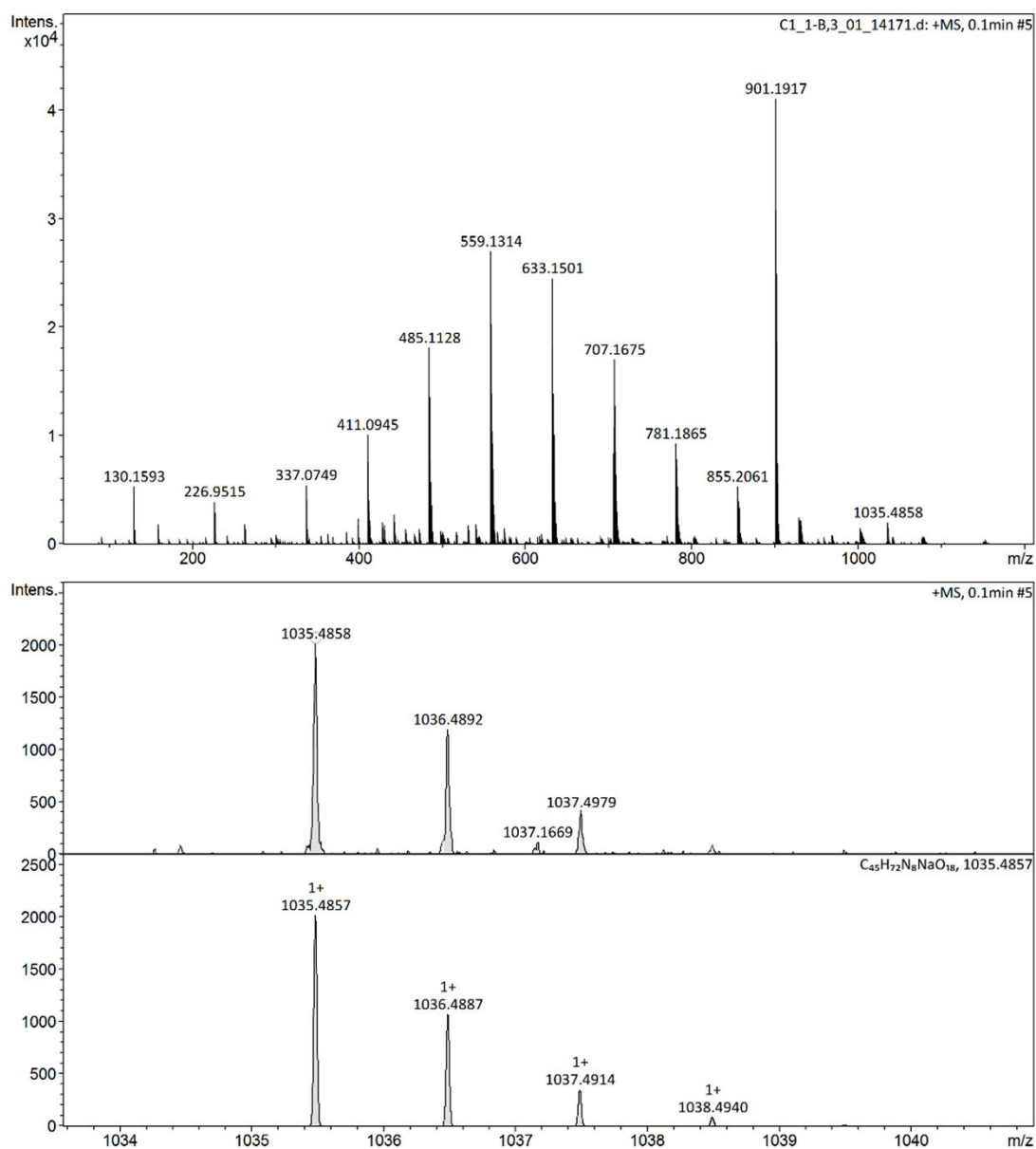


Figure S16. Mass spectrum of Bim-BP-DMAC.

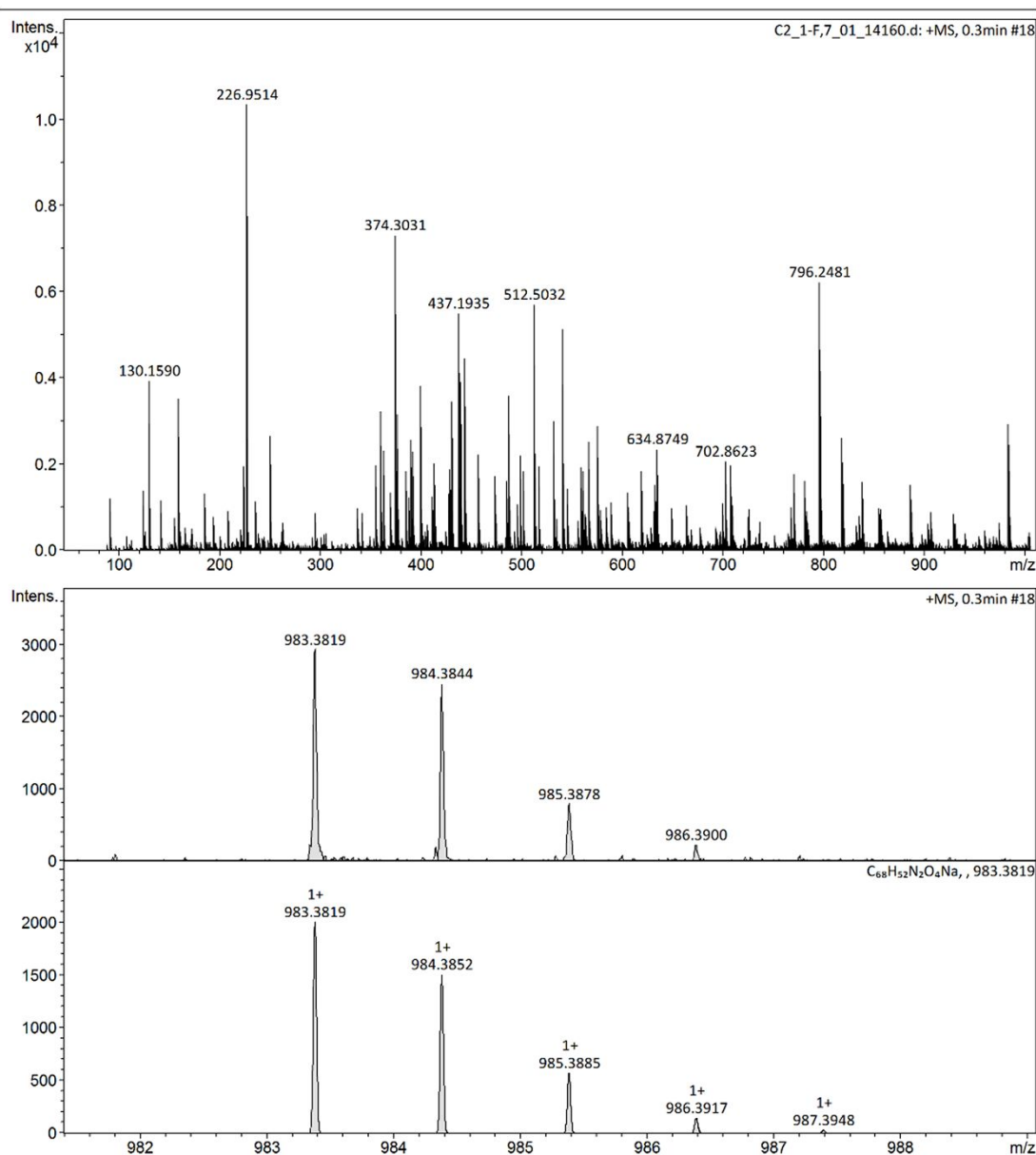


Figure S17. Mass spectrum of Bim-BP-PXZ.

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