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Electronic Supplementary Information

Mechanochromic asymmetric sulfone derivatives for efficient blue organic light-emitting diodes

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CONTENTS

SI-1. General Procedures

^{1}HNMR and ^{13}CNMR measurements were recorded with a Varian Gemin-400 spectrometer. Mass spectra were performed with a PE SCIEX APIMS spectrometer. Absorption and photoluminescence spectra were determined with a Perkin-Elmer Lambda 2SUV-Vis spectrophotometer and a Perkin-Elmer LS50B Luminescence spectrophotometer. Density functional theory (DFT) B3LYP/6-31G (d) was used to optimize the structure. Theoretical calculation of the compound was carried out using the Gaussian03 program. Cyclic voltammetry was performed on a BAS 100 B/W electrochemical analyser. The electrolytic cell is constructed a glassy carbon working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel electrode (SCE) as the reference electrode were employed. The ferrocene/ferrocenium couple was used as the internal standard. 0.10 M TBAPF$_6$ was used as the supporting electrolyte and DCM as the solvent, respectively. Thermal gravity analysis (TGA) and differential scanning calorimetry (DSC) measurements were recorded with a TA Instrument TGAQ50 and a TA Instrument DSC2910 respectively. Diffraction Gemini E equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd) at room temperature. The crystal structures were solved by direct methods (SHELXTL-97), all non-hydrogen atoms were refined with anisotropic thermal parameters.

SI-2. Synthesis

A two-steps synthetic route was showed in **Scheme S1,** and all the compounds have a good yield, the final product chemical structure was fully confirmed by mass spectrometry, ^{1}HNMR and ^{13}CNMR spectrometry. The starting material 1 and 4was prepared as reported previously.[1]

9-(4-((4-bromophenyl)sulfonyl)phenyl)-9*H*-carbazole (3)

The 1, 4,4'-sulfonylbis(bromobenzene), (2.5 g, 6.6 mmol), 2, 9*H*-carbazole, (0.55 g, 3.3 mmol), iodide copper (0.04 g, 0.2 mmol), 18-Crown-6 (0.08 g, 0.3 mmol), anhydrous potassium carbonate (1.13 g, 8.2mmol) were added into 15 mL of DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone) and heated to 120 ºC for 24 h with stirring. Then the reaction mixture was poured into water and extracted with dichloromethane. The organic phase was combined and dried over magnesium sulfate. After the solvent was removed, the product was purified by column chromatography silica gel. (1.08 g ,48%).

2-(4'-((4-(9H-carbazol-9-yl)phenyl)sulfonyl)-[1,1'-biphenyl]-4-yl)-1-(4-(tert-butyl)phenyl)-1*H*-phenanthro[9,10-*d*]imidazole (5)

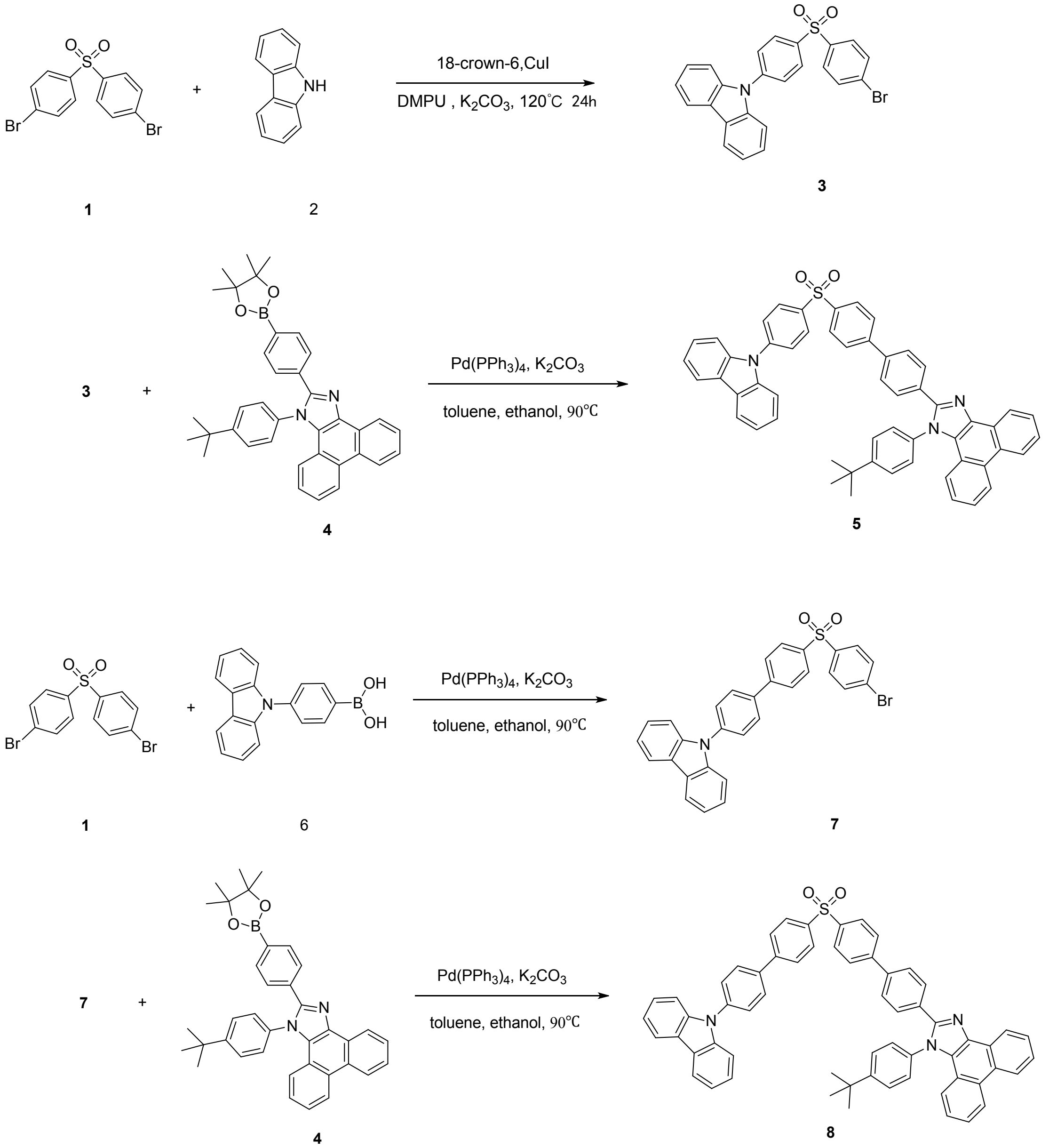
The compound 3 (1 g, 2.16 mmol), the compound 4 (1.40 g, 2.6 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol), and K_2CO_3 aqueous (2 M, 5 mL) in toluene (20 mL) and ethanol (4 mL) was heated to reflux in a nitrogen atmosphere for 24 h. The solution was cooled to room temperature and extracted with dichloromethane. The extracts were dried with anhydrous Na_2SO_4 and concentrated by rotary evaporation. The residue was further purified by column chromatography (using CH_2Cl_2) as fluent to get pure white powder (1.12 g, 63%).^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.81 (d, J = 8.1 Hz, 1H), 8.76 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 8.7 Hz, 2H), 8.12 (dd, J = 17.4, 8.0 Hz, 4H), 7.88 – 7.66 (m, 10H), 7.63 (d, J = 7.9 Hz, 3H), 7.53 – 7.39 (m, 6H), 7.32 (dd, J = 10.8, 4.0 Hz, 3H), 7.20 (d, J = 7.9 Hz, 1H), 1.46 (s, 10H).^{13}C NMR (101 MHz, CD_2Cl_2) δ 140.19, 133.47, 129.79, 129.51, 128.48, 128.33, 127.90, 127.19, 126.96, 126.24, 125.62, 123.96, 123.14, 120.80, 120.33, 118.68, 109.61, 34.92, 31.09.MS (ESI) (m/z): Calculated for $C_{55}H_{41}N_3O_2S$: 808.00 Found $[M\text{-}Cz+H]^+$: 643.2404.(Cz is carbazole)

9-(4'-((4-bromophenyl)sulfonyl)-[1,1'-biphenyl]-4-yl)-9*H*-carbazole (7)

The compound 1 (2.5 g, 6.6 mmol), the compound 6 (1.26 g, 4.4 mmol), $Pd(PPh_3)_4$ (0.25 g, 0.22 mmol), and K_2CO_3 aqueous (2 M, 5 mL) in toluene (20 mL) and ethanol (4 mL) was heated to reflux in a nitrogen atmosphere for 24 h. The solution was cooled to room temperature and extracted with dichloromethane. The extracts were dried with anhydrous Na_2SO_4 and concentrated by rotary evaporation. The residue was further purified by column chromatography to get pure white powder (1.4 g, 58%).

2-(4'-((4'-(9*H*-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)sulfonyl)-[1,1'-biphenyl]-4-yl)-1-(4-(*tert*-butyl)phenyl)-1*H*-phenanthro[9,10-*d*]imidazole(8)

The synthetic procedures were similar to the compound 5 (1.4 g, 70%).^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.79 (d, J = 8.8 Hz, 1H), 8.74 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 7.8 Hz, 2H), 8.08 (dd, J = 12.7, 8.4 Hz, 4H), 7.86 (dd, J = 8.4, 5.1 Hz, 4H), 7.79 (d, J = 8.3 Hz, 5H), 7.73 – 7.64 (m, 5H), 7.59 (d, J = 8.1 Hz, 3H), 7.49 (d, J = 8.1 Hz, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 3H), 7.21 (d, J = 7.5 Hz, 1H), 1.46 (s, 9H).^{13}C NMR (75 MHz, CD_2Cl_2) δ 154.08, 145.63, 141.08, 140.99, 138.46, 136.38, 130.10, 129.55, 129.22, 128.85, 128.66, 128.59, 128.37, 128.24, 127.79, 127.69, 127.65, 127.60, 127.37, 126.71, 126.42, 125.94, 125.35, 125.33, 124.38, 123.88, 123.56, 122.84, 121.39, 120.64, 120.54, 110.10, 35.27, 31.50.MS (ESI) (m/z): Calculated for $C_{61}H_{45}N_3O_2S$: 884.09 Found$[M+K]^+$:922.0013.



Scheme S1 The molecular structure and synthetic route of **PSC** and **PSBC**

SI-3. Electrochemical cyclic voltammetry (CV)

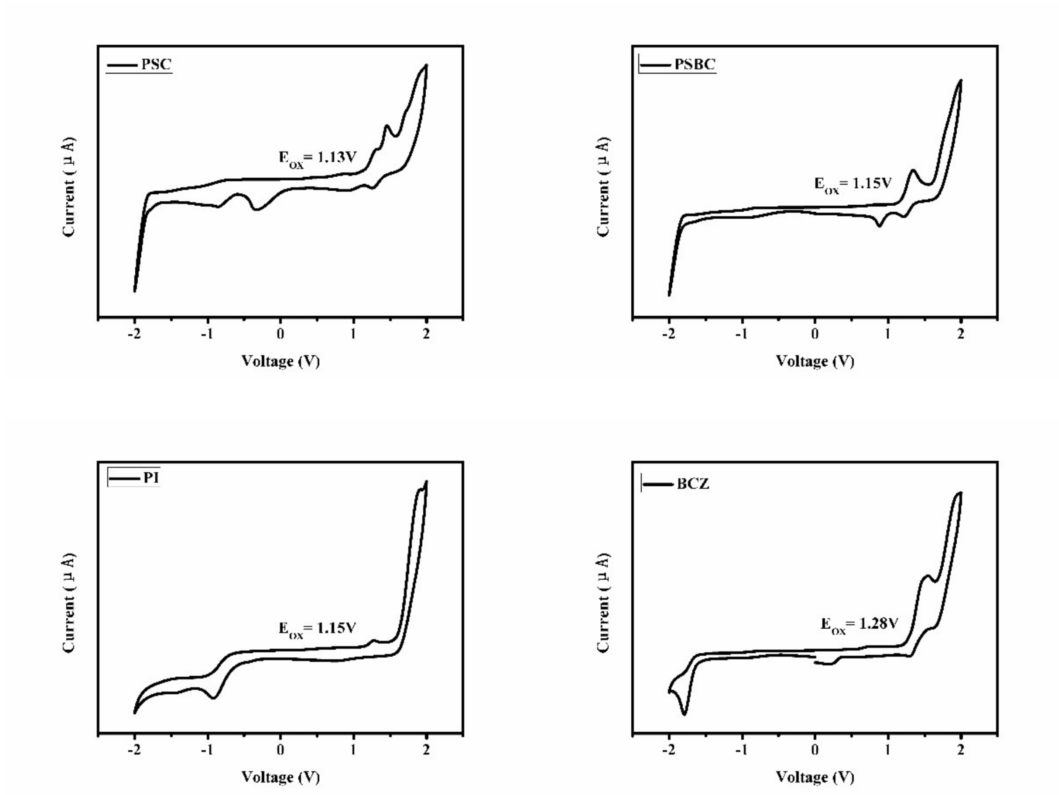


Figure S1. Cyclic voltammograms of **PSC**, **PSBC**, **PI** and **BCZ** in CH_2Cl_2.

SI-4. Lippert-Mataga calculation

One reliable way to explore the influence of solvent environment on the optical property of our compounds can be understood using the Lippert-Mataga equation, [2] a model that describes the interactions between the solvent and the dipole moment of solute:

$$\mathrm{hc}(\upsilon_a\text{-}\upsilon_f) = \mathrm{hc}(\upsilon_a^0\text{-}\upsilon_f^0) + \frac{2(\mu_e - \mu_o)^2}{a^3}\mathrm{f}(\varepsilon, \mathrm{n})$$

where Δf is the orientational polarizability of solvents, μ_e is the excited-state dipole moment, μ_o is the ground-state dipole moment; ε and n are the solvent dielectric and the solvent refractive index, respectively; a is the solvent cavity (Onsager) radius, derived from the Avogadro number (N), molecular weight (M), and density (d=1.0 g/cm^3); f(ε,n) and a can be calculated respectively as follows:

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \quad a = \left(\frac{3M}{4N\pi d}\right)^{1/3}$$

Figure 6. (a) and (b) show the linear Lippert-Mataga plots with the slope values of 13050 cm^{-1} (R ≈ 0.90) for PSC and 15029 cm^{-1} (R ≈ 0.95) for PSBC.

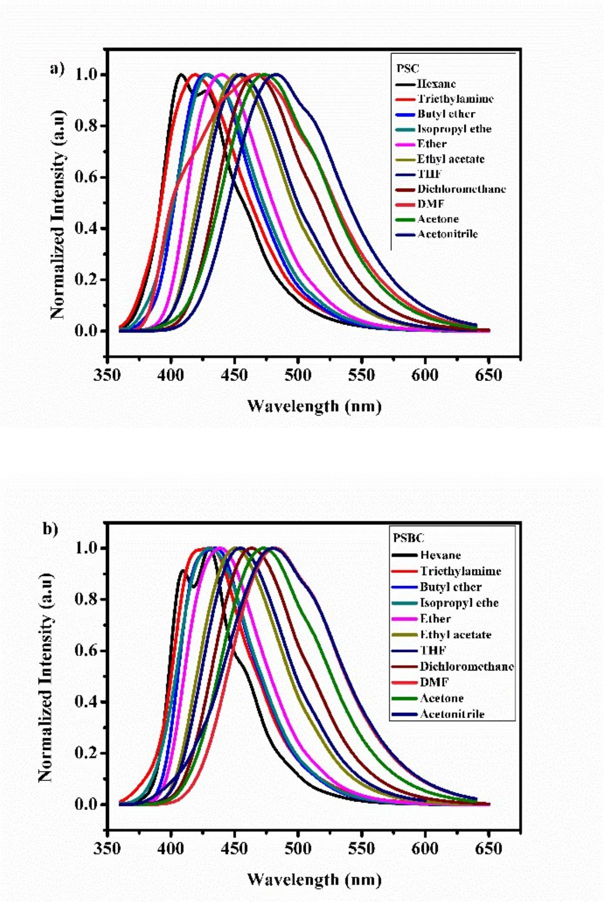


Figure S2. PL spectra of **PSC** and **PSBC** in solvents of different polarities.

Solvents	**Δ*f***	**PSC**			**PSBC**		
		ν_a (nm)	ν_f (nm)	ν_a-ν_f (cm^{-1})	ν_a (nm)	ν_f (nm)	ν_a-ν_f (cm^{-1})
Hexane	0.0012	338	408	6166.6	340	430	6155.95
Trimethylamine	0.048	337	419	5807.24	340	430	6155.95
Butyl ether	0.096	338	429	6166.6	340	435	6423.26
Isopropyl ether	0.145	338	427	6275.78	340	430	6155.95
Ether	0.167	337	440	6946.32	340	438	6580.71
Ethyl acetate	0.2	337	451	7500.64	340	450	7189.54

THF	0.21	339	455	7520.5	340	454	7385.33
Dichloromethane	0.217	340	466	7952.53	341	463	7727.24
DMF	0.276	340	468	8044.24	342	482	8492.88
Acetone	0.284	340	473	8270.12	340	472	8225.32
Acetonitrile	0.305	339	483	8794.61	340	480	8578.43

Table S1. Solvatochromic UV-PL data for Lippert-Mataga model

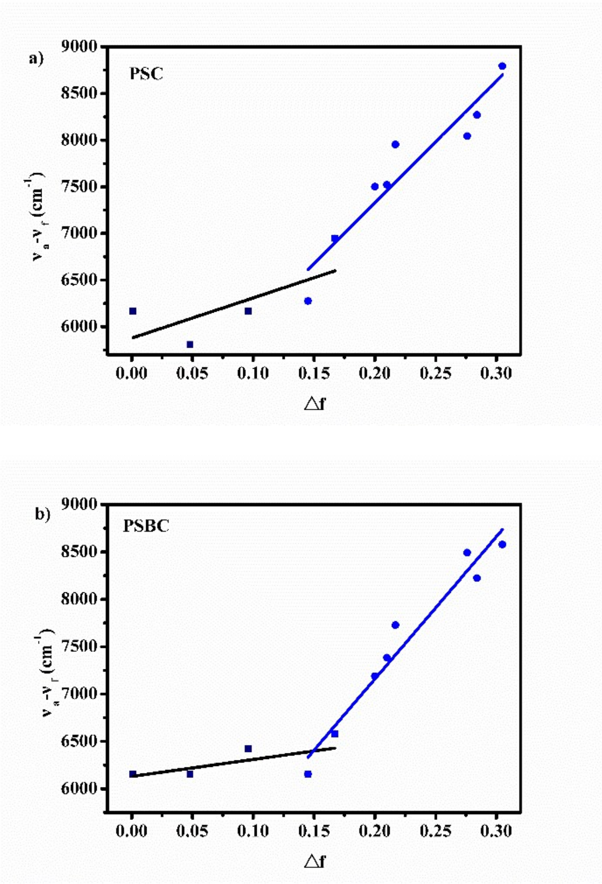
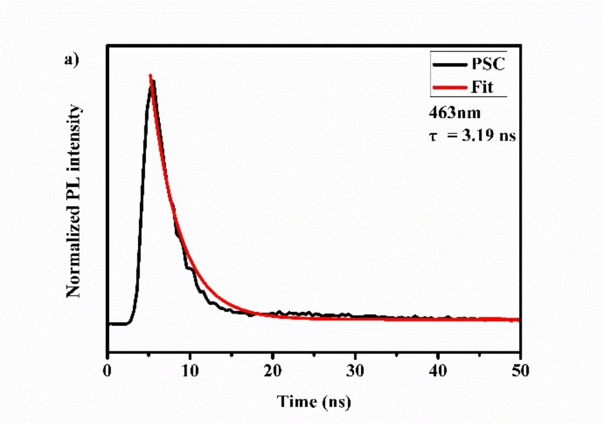


Figure S3. Solvatochromic Lippert–Mataga models of **PSC** and **PSBC**.

SI-5. Time-resolved emission decays



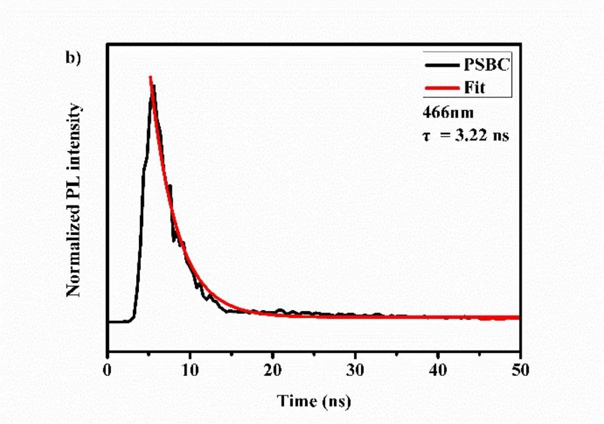


Figure S4. Decay profile of **PSC** and **PSBC** in THF

SI-6. Mechanochromic properties

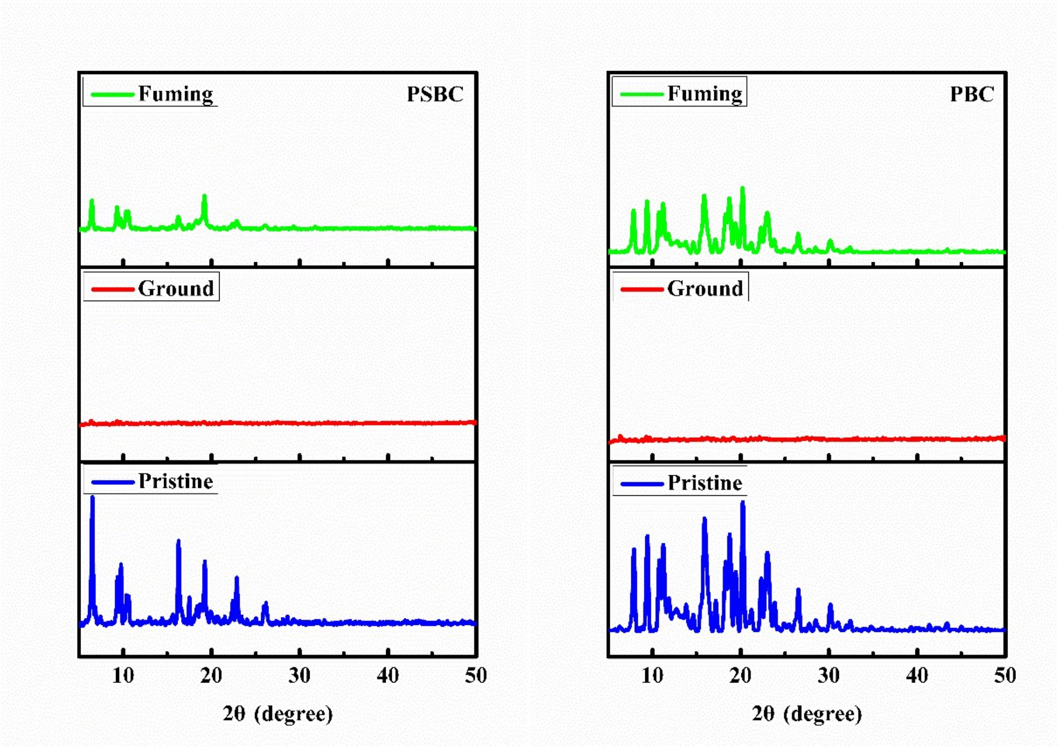


Figure S5. XRD diffract grams of as pristine, ground and solvent fumed powders of **PSC** and

PSBC.

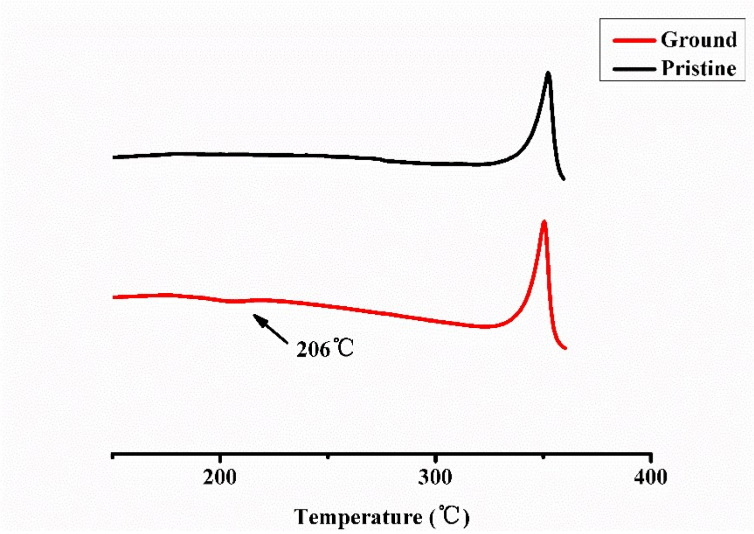


Figure S6. DSC profiles of **PSC** with an exothermic peak in the cycling of ground powder.

SI-7. Device fabrication and measurement

Pre-patterned indium tin oxide (ITO) glass substrates with asheet resistance of 15 Ω per square were cleaned with isopropyl alcohol and Decon 90 solution, then rinsed in deionized waterand dried in an oven. After a 15 min UV-ozone treatment, theITO substrates were immediately transferred into a deposition chamber with a base pressure of 5×10^{-7} torr for organic and cathode depositions. Organic materials were deposited viathermal deposition at a rate of 1 Å s^{-1}, while the cathodes were completed via deposition of LiF (0.1– 0.2 Å s^{-1}) and Al (5– 6 Å s^{-1}) successively. Electroluminescent spectra and the corresponding (CIE) coordinates were measured with a Spectrascan PR650 photometer. Current–voltage–luminance (*J*–*V*–*L*) characteristics were recorded with a Keithley 2400 Sourcemeter under ambient atmosphere without device encapsulation.

SI-8. Device architectures

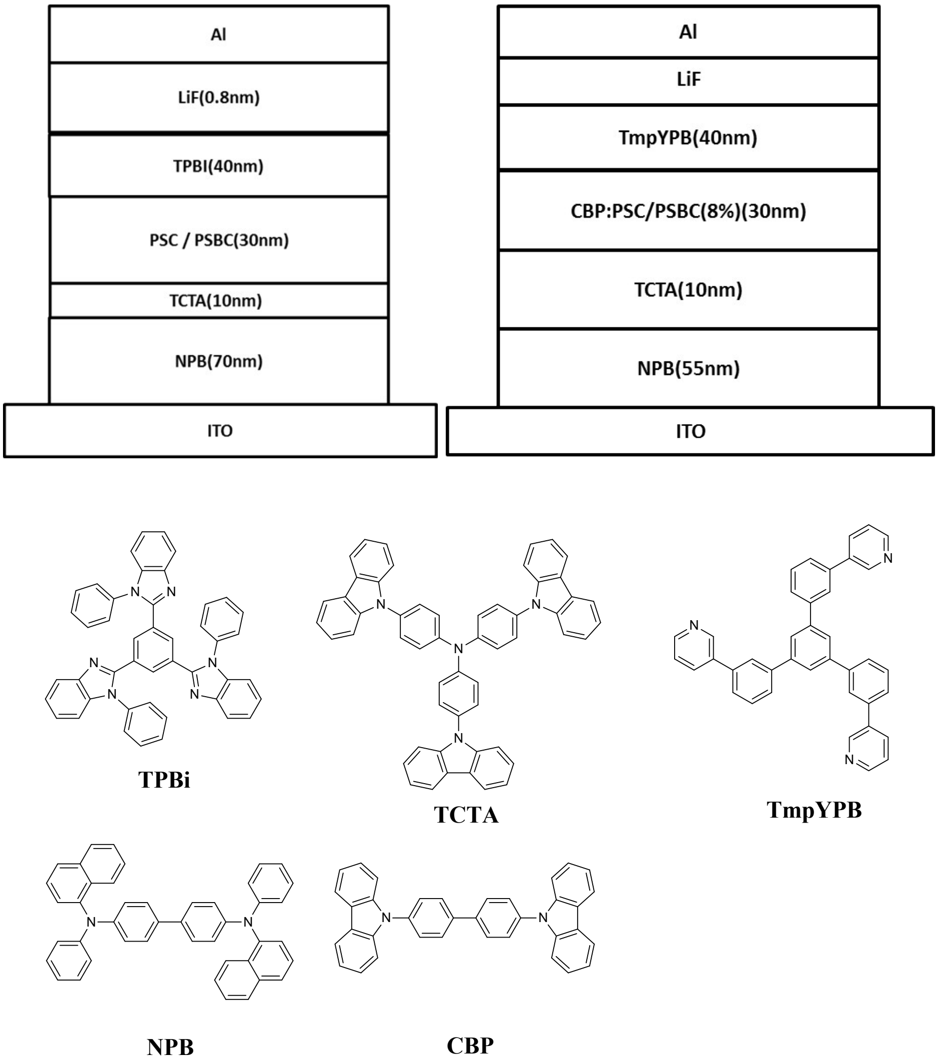
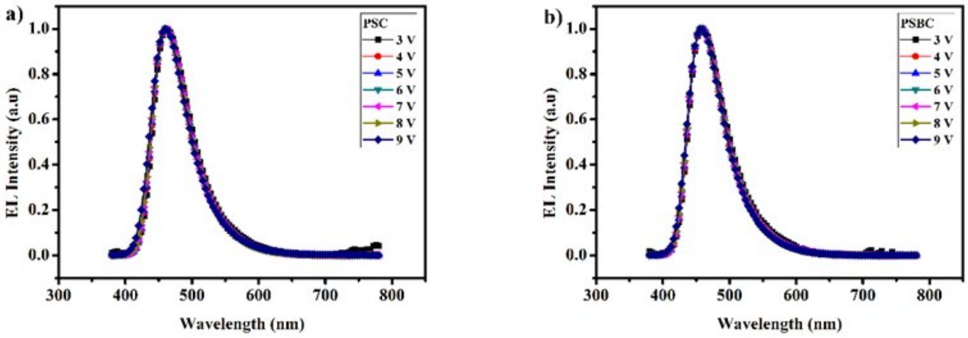


Figure S7. The nondoped and doped device architectures

SI-9. The EL spectra of all devices at different voltages

Nondoped devices



Doped devices

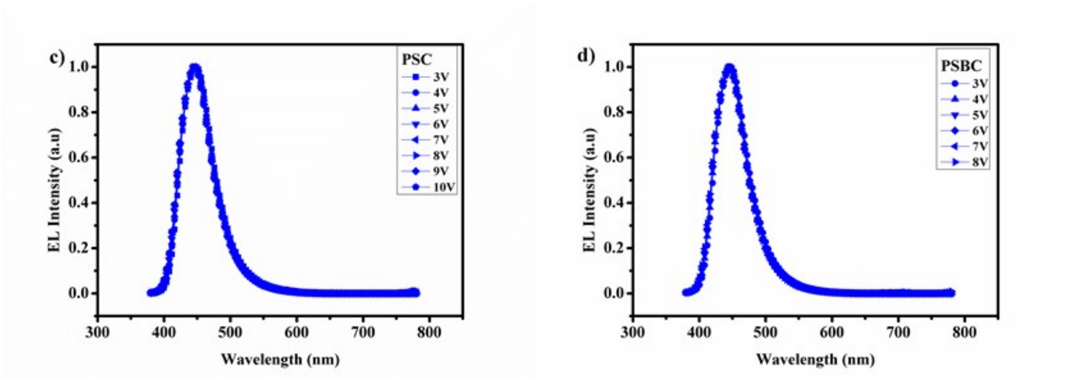


Figure S8. The EL spectra of the nondoped devices and doped devices

Reference

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2 Z. R. Grabowski, K. Rotkiewicz, W. Rettig, *Chem. Rev.*, 2003, **103**, 3899.