

Supporting Information

A Strategy for Achieving Efficient Electroluminescence with Reduced Efficiency Roll-off: Enhancement of Hot Excitons Spin Mixing and Restriction of Internal Conversion by Twisted Structure Regulation from Anthracene Derivative

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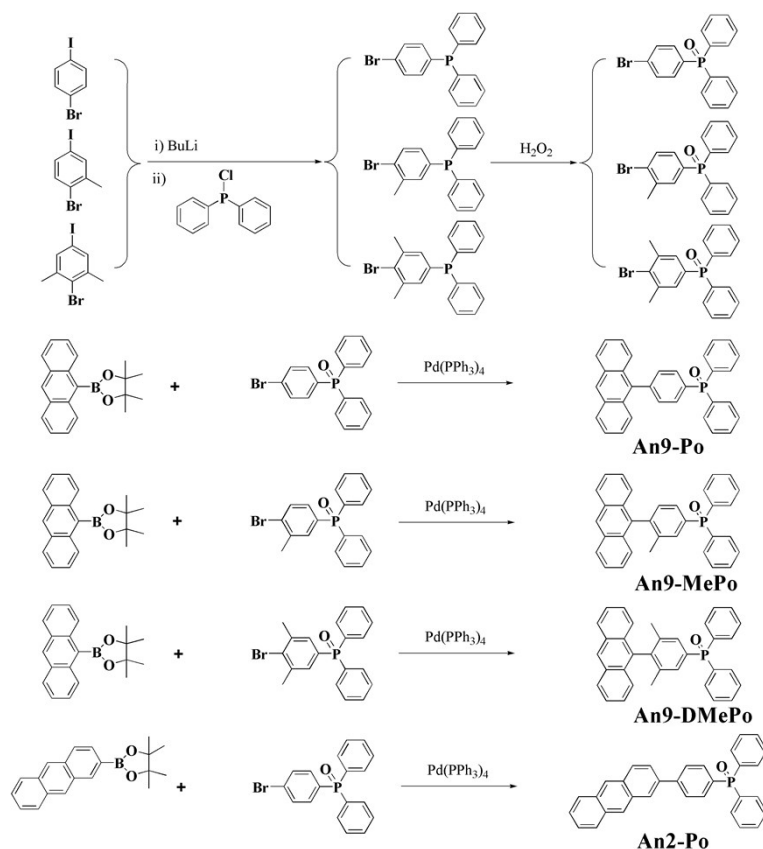
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Scheme 1 Molecular structures and the synthetic routes to An9-Po, An9-MePo, An9-DMePo and An2-Po.

Synthesis of 1-Bromo-4-(diphenyl-phosphinoyl)-benzene: Under the N₂ atmosphere, 1-Bromo-4-iodo-benzene (2.32g, 8.20 mmol) were dissolved in anhydrous tetrahydrofuran (50 mL). The solution was cooled to -78 °C and added *n*-BuLi (3.96 mL, 9.90 mmol, 2.5 M in hexane). After stirred for 45 min, chlorodiphenylphosphine (1.49 mL, 8.20 mmol) was added to the mixture and reacted at room temperature overnight. Dilute hydrochloric acid was added to the mixture to adjust pH value to *ca.* 7.0 and the mixture was extracted with CH₂Cl₂ (3 × 15 mL), the organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was re-dissolved in tetrahydrofuran (50 mL), H₂O₂ (10 mL, 30%) was added to the solution dropwise. After react at rt. for 2 h, the mixture was extracted with CH₂Cl₂ (3 × 15 mL), the organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. Then, the residue was purified by column chromatography over silica gel using CH₂Cl₂/EtOAc (6:1 v/v) as the eluent.

Yellow solid was obtained (2.25 g, 76.8%). ¹H NMR (400 MHz, CDCl₃, δ): 7.65–7.62 (m, 3H), 7.61–7.56 (m, 3H), 7.55–7.49 (m, 4H), 7.46–7.42 (m, 4H). ¹³C NMR (100 MHz, CDCl₃, δ): 133.72, 133.61, 132.66, 132.35, 132.25, 132.23, 132.13, 132.03, 131.95, 131.83, 131.61, 131.32, 128.76, 128.64, 127.26, 127.23. ³¹P NMR (161.9 MHz, CDCl₃, δ): 28.97. Anal. Calcd for C₁₈H₁₄BrPO: C, 60.50; H, 3.92. Found: C, 60.47; H, 3.88.

Synthesis of 4-Bromo-3-methyl-phenyl)-diphenyl-phosphane: Under the N₂ atmosphere, 1-Bromo-4-iodo-2-methyl-benzene (2.44g, 8.20 mmol) were dissolved in anhydrous tetrahydrofuran (50 mL). The solution was cooled to □78 °C and added *n*-BuLi (3.96 mL, 9.90 mmol, 2.5 M in hexane). After stirred for 45 min, chlorodiphenylphosphine (1.49 mL, 8.20 mmol) was added to the mixture and reacted at room temperature overnight. Dilute hydrochloric acid was added to the mixture to adjust pH value to *ca.* 7.0 and the mixture was extracted with CH₂Cl₂ (3 × 15 mL), the organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was re-dissolved in tetrahydrofuran (50 mL), H₂O₂ (10 mL, 30%) was added to the solution dropwise. After react at rt. for 2 h, the mixture was extracted with CH₂Cl₂ (3 × 15 mL), the organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. Then, the residue was purified by column chromatography over silica gel using CH₂Cl₂/EtOAc (6:1 v/v) as the eluent. White solid was obtained (2.04 g, 67.1%). ¹H NMR (400 MHz, CDCl₃, δ): 7.67 – 7.59 (m, 6H), 7.55 (td, *J* = 7.6, 1.6 Hz, 2H), 7.48 – 7.44 (m, 4H), 7.25 – 7.20 (m, 1H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 138.74, 138.62, 134.11, 134.01, 132.60, 132.55, 132.43, 132.10, 132.07, 132.03, 131.93, 131.57, 131.14, 130.71, 130.60, 129.62, 128.62, 128.50, 22.95. ³¹P NMR (162 MHz, CDCl₃, δ): 28.66. Calcd for C₁₉H₁₆BrPO: C, 61.46; H, 4.31. Found: C, 61.39; H, 4.26.

Synthesis of 2-Bromo-5-(diphenyl-phosphinoyl)-1,3-dimethyl-benzene: Under the N₂ atmosphere, 2-Bromo-5-iodo-1,3-dimethyl-benzene (2.56g, 8.20 mmol) were dissolved in anhydrous tetrahydrofuran (50 mL). The solution was cooled to □78 °C

and added *n*-BuLi (3.96 mL, 9.90 mmol, 2.5 M in hexane). After stirred for 45 min, chlorodiphenylphosphine (1.49 mL, 8.20 mmol) was added to the mixture and reacted at room temperature overnight. Dilute hydrochloric acid was added to the mixture to adjust pH value to *ca.* 7.0 and the mixture was extracted with CH₂Cl₂ (3 × 15 mL), the organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was re-dissolved in tetrahydrofuran (50 mL), H₂O₂ (10 mL, 30%) was added to the solution dropwise. After react at rt. for 2 h, the mixture was extracted with CH₂Cl₂ (3 × 15 mL), the organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. Then, the residue was purified by column chromatography over silica gel using CH₂Cl₂/EtOAc (6:1 v/v) as the eluent. White solid was obtained (2.27 g, 71.9%). ¹H NMR (400 MHz, CDCl₃, δ): 7.67 – 7.62 (m, 4H), 7.57 – 7.52 (m, 2H), 7.48 – 7.44 (m, 4H), 7.35 (d, *J* = 12.0 Hz, 2H), 2.40 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 139.04, 138.91, 132.86, 132.36, 132.10, 132.06, 132.04, 132.00, 131.82, 131.36, 131.26, 130.28, 128.63, 128.51, 24.03. ³¹P NMR (162 MHz, CDCl₃, δ): 28.38. Calcd for C₂₀H₁₈BrPO: C, 62.34; H, 4.68. Found: C, 62.29; H, 4.65.

Synthesis of 9-[4-(Diphenyl-phosphinoyl)-phenyl]-anthracene (An9-Po): Under the N₂ atmosphere, 4-Bromo-3-methyl-phenyl)-diphenyl-phosphane (1.79g, 5 mmol), 9-Anthraceneboronic acid (1.22g, 5.5 mmol) and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) were added to a flask containing THF (50 mL) and aqueous solution of Na₂CO₃ (2.0 M, 25 mL). The reaction mixture was heated at 110 °C and stirred for 24 h under a nitrogen atmosphere. After it was cooled to room temperature, the reaction mixture was extracted with CH₂Cl₂. All the organic phase was combined and dried with anhydrous MgSO₄. Then, the solvent was removed in vacuum and the resultant residue was purified by column chromatography using a proper petroleum ether/CH₂Cl₂ eluent system to give the target product (White solid, 1.86 g, 81.9%). ¹H NMR (400 MHz, CDCl₃, δ): 8.53 (s, 1H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.90 – 7.81 (m, 6H), 7.62 – 7.60 (m, 2H), 7.58 – 7.53 (m, 7H), 7.49 – 7.45 (m, 3H), 7.40 – 7.36 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 142.95, 132.87, 132.28, 132.22, 132.18, 132.12, 132.09, 132.01,

131.91, 131.83, 131.57, 131.52, 131.45, 131.24, 131.21, 131.00, 129.83, 128.69, 128.57, 128.42, 127.16, 126.29, 125.71, 125.20. ³¹P NMR (162 MHz, CDCl₃, δ): 29.49. Anal. Calcd for C₃₂H₂₃PO: C, 84.58; H, 5.07. Found: C, 84.49; H, 5.05.

Synthesis of 9-[4-(Diphenyl-phosphinoyl)-2-methyl-phenyl]-anthracene (An9-MePo): Under the N₂ atmosphere, 4-Bromo-3-methyl-phenyl)-diphenyl-phosphane (1.86g, 5 mmol), 9-Anthraceneboronic acid (1.22g, 5.5 mmol) and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) were added to a flask containing THF (50 mL) and aqueous solution of Na₂CO₃ (2.0 M, 25 mL). The reaction mixture was heated at 110 °C and stirred for 24 h under a nitrogen atmosphere. After it was cooled to room temperature, the reaction mixture was extracted with CH₂Cl₂. All the organic phase was combined and dried with anhydrous MgSO₄. Then, the solvent was removed in vacuum and the resultant residue was purified by column chromatography using a proper petroleum ether/CH₂Cl₂ eluent system to give the target product (White solid, 1.85 g, 78.9%). ¹H NMR (400 MHz, CDCl₃, δ): 8.52 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.86 – 7.81 (m, 5H), 7.61 – 7.53 (m, 6H), 7.49 – 7.44 (m, 5H), 7.39 – 7.33 (m, 3H), 1.87 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 142.51, 142.48, 138.79, 138.67, 134.78, 133.61, 133.52, 133.02, 132.97, 132.51, 132.21, 132.11, 132.00, 131.29, 131.25, 129.54, 129.50, 129.43, 128.63, 128.55, 128.52, 128.40, 126.91, 125.96, 125.81, 125.23, 19.77. ³¹P NMR (162 MHz, CDCl₃, δ): 29.53. Anal. Calcd for C₃₃H₂₅PO: C, 84.62; H, 5.34. Found: C, 84.53; H, 5.39.

Synthesis of 9-[4-(Diphenyl-phosphinoyl)-2,6-dimethyl-phenyl]-anthracene (An9-DMePo): Under the N₂ atmosphere, 2-Bromo-5-(diphenyl-phosphinoyl)-1,3-dimethyl-benzene (1.93g, 5 mmol), 9-Anthraceneboronic acid (1.22g, 5.5 mmol) and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) were added to a flask containing THF (50 mL) and aqueous solution of Na₂CO₃ (2.0 M, 25 mL). The reaction mixture was heated at 110 °C and stirred for 24 h under a nitrogen atmosphere. After it was cooled to room temperature, the reaction mixture was extracted with CH₂Cl₂. All the organic phase was combined and dried with anhydrous MgSO₄. Then, the solvent was removed in vacuum and the resultant residue was purified by column chromatography using a

proper petroleum ether/CH₂Cl₂ eluent system to give the target product (White solid, 1.83 g, 75.9%). ¹H NMR (400 MHz, CDCl₃, δ): 7.67 – 7.62 (m, 6H), 7.57 – 7.53 (m, 3H), 7.48 – 7.43 (m, 8H), 7.36 – 7.31 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 2.40 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 138.97, 138.85, 134.44, 134.37, 132.72, 132.34, 132.31, 132.01, 131.98, 131.92, 131.68, 131.28, 131.18, 130.15, 130.02, 128.57, 128.44, 128.09, 127.97, 127.87, 127.82, 127.75, 23.97. ³¹P NMR (162 MHz, CDCl₃, δ): 28.76. Anal. Calcd for C₃₄H₂₇PO: C, 84.65; H, 5.60. Found: C, 84.69; H, 5.67.

Synthesis of 2-[4-(Diphenyl-phosphinoyl)-phenyl]-anthracene (An2-Po): Under the N₂ atmosphere, 4-Bromo-3-methyl-phenyl)-diphenyl-phosphane (1.79g, 5 mmol), 2-Anthraceneboronic acid (1.22g, 5.5 mmol) and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) were added to a flask containing THF (50 mL) and aqueous solution of Na₂CO₃ (2.0 M, 25 mL). The reaction mixture was heated at 110 °C and stirred for 24 h under a nitrogen atmosphere. After it was cooled to room temperature, the reaction mixture was extracted with CH₂Cl₂. All the organic phase was combined and dried with anhydrous MgSO₄. Then, the solvent was removed in vacuum and the resultant residue was purified by column chromatography using a proper petroleum ether/CH₂Cl₂ eluent system to give the target product (White solid, 1.90 g, 83.9%). ¹H NMR (400 MHz, CDCl₃, δ): 8.49 (s, 1H), 8.45 (s, 1H), 8.24 (s, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 8.02 (m, 2H), 7.88 – 7.86 (m, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.72 (m, 5H), 7.60 – 7.56 (m, 2H), 7.53 – 7.48 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 136.44, 132.77, 132.67, 132.18, 132.14, 132.08, 132.00, 131.98, 131.61, 130.99, 129.11, 128.62, 128.50, 128.22, 128.18, 127.40, 127.27, 126.90, 126.47, 126.12, 125.69, 124.91. ³¹P NMR (162 MHz, CDCl₃, δ): 29.05. Anal. Calcd for C₃₂H₂₃PO: C, 84.58; H, 5.07. Found: C, 84.52; H, 5.10.

The solvatochromic Lippert-Mataga model

We used the Lippert-Mataga equation, which describes the interactions between the solvent and the dipole moment of solute to estimate the dipole moments of S₁ state:

$$hc(\nu_a - \nu_f) = hc(\nu_a^0 - \nu_f^0) - \frac{2(\mu_e - \mu_g)^2}{a_0^3} f(\varepsilon, n)$$

Take differential on both sides of the above equation, we got

$$\mu_e = \mu_g + \left\{ \frac{hca_0^3}{2} \cdot \left[\frac{d(\nu_a - \nu_f)}{df(\varepsilon, n)} \right] \right\}^{1/2}$$

where h is the Plank constant, c is the light speed in vacuum, $f(\varepsilon, n)$ is the orientational polarizability of solvents, $\nu_a^0 - \nu_f^0$ is the Stokes shifts when f is zero, μ_e and μ_g are dipole moments of excited-state and ground-state, respectively; a_0 is the solvent Onsager cavity radius, derived from the Avogadro number (N), molecular weight (M), and density ($d=1.0 \text{ g/cm}^3$); ε is the solvent dielectric constant and n is the solvent refractive index; μ_g of An9-Po, An9-MePo, An9-DmePo and An2-Po could be estimated from density-functional-theory (DFT) calculation at the level of B3LYP/6-31g(d,p) from Gaussian09 package, which gave μ_g of 4.1 D, 4.5 D, 4.3 D and 4.3 D, respectively. $f(\varepsilon, n)$ and a_0 can be calculated as follows:

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \quad a_0 = \left(\frac{3M}{4N\pi d} \right)^{1/3}$$

The detailed data are listed in Table S1. For An9-Po, An9-MePo, An9-DmePo and An2-Po, the μ_e was estimated to be 6.5 D (slope value of ≈ 646 , $R= 0.80$), 6.9 D (slope value of ≈ 628 , $R= 0.64$), 6.2 D (slope value of ≈ 373 , $R= 0.55$) and 8.9 D (slope value of ≈ 2283 , $R= 0.85$), respectively.

Table S1. The data about absorption and emission peak positions of An9-Po, An9-MePo, An9-DmePo and An2-Po in different solvents.

Solvents	ε	n	$f(\varepsilon, n)$	An9-Po			An9-MePo			An9-DmePo			An2-Po		
				λ_a	λ_f	$\nu_a - \nu_f$	λ_a	λ_f	$\nu_a - \nu_f$	λ_a	λ_f	$\nu_a - \nu_f$	λ_a	λ_f	$\nu_a - \nu_f$
				(n)	(n)	(cm ⁻¹)	(n)	(n)	(cm ⁻¹)	(n)	(n)	(cm ⁻¹)	(n)	(n)	(cm ⁻¹)

				m)	m)	l)	m)	m)		m)	m)	l)	m)	m)	l)
Hexane	1.9	1.37	0.001	38	42	2277	38	41	1761	24	41	1722	38	42	2010
		5	2	5	2		5	3		1	2	2	9	2	
Toluene	2.3	1.49	0.014	38	42	2445	38	41	2051	24	41	1745	38	43	2505
	8	4		5	5		5	8		1	6	6	9	1	
Triethylamin e	2.4	1.40	0.048	38	43	2879	38	41	1878	24	41	1739	38	43	2928
	2	1		5	3		5	5		1	5	8	9	9	
Butyl ether	3.0	1.39	0.096	38	42	2277	38	41	1819	24	41	1733	38	42	2178
	8	9		5	2		5	4		1	4	9	9	5	
Isopropyl ether	3.8	1.36	0.145	38	42	2333	38	41	1819	24	41	1728	38	42	2288
	8	8		5	3		5	4		1	3	1	9	7	
Ethyl ether	4.3	1.35	0.167	38	42	2266	38	41	1878	24	41	1728	39	42	2331
	4	2		6	3		5	5		1	3	1	0	9	
Ethyl acetate	6.0	1.37	0.200	38	42	2322	38	41	1811	24	41	1733	39	43	2385
	2	2		6	4		6	5		1	4	9	0	0	
Tetrahydrofu ran	7.5	1.40	0.210	38	42	2322	38	41	1926	24	41	1739	39	43	2546
	8	7		6	4		6	7		1	5	8	0	3	
dichlorometh ane	8.9	1.42	0.217	38	42	2378	38	41	1984	24	41	1745	39	43	2439
	3	4		6	5		6	8		1	6	6	0	1	
Acetone	20.	1.35	0.284	38	42	2433	38	41	2041	24	41	1739	39	43	2546
	7	9		6	6		6	9		1	5	8	0	3	
Acetonitrile	37.	1.34	0.305	38	42	2476	38	42	2154	24	41	1751	39	43	2758
	5	4		7	8		6	1		1	7	3	0	7	

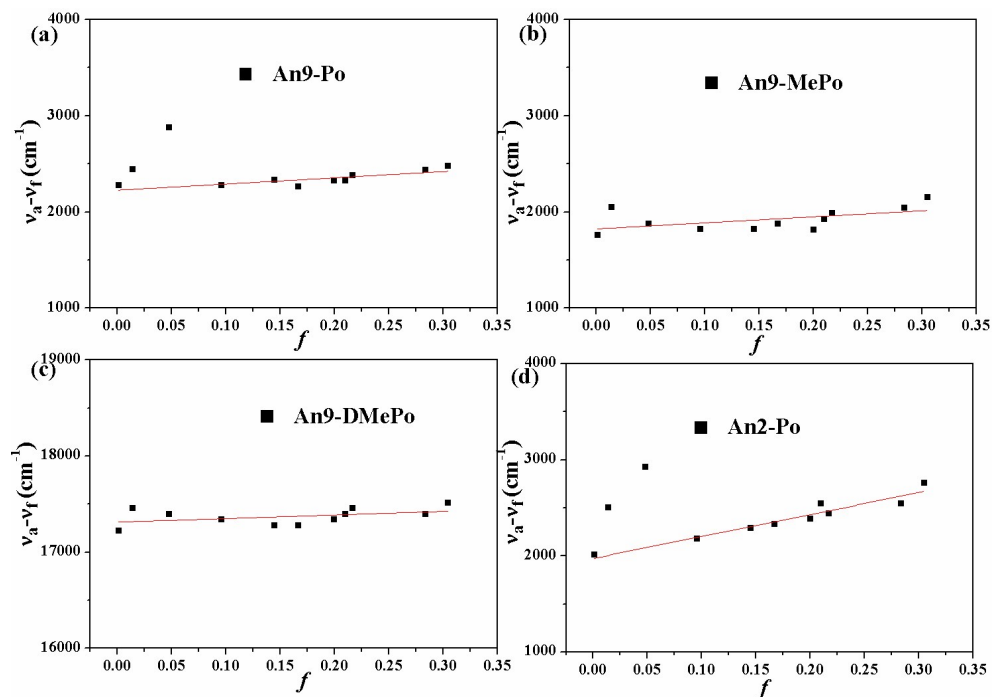


Fig. S1 (a) Linear correlation of orientation polarization ($f(\varepsilon, n)$) of solvent media with the Stokes shift ($\nu_a - \nu_f$) for An9-Po. (b) Linear correlation of orientation polarization ($f(\varepsilon, n)$) of solvent media with the Stokes shift ($\nu_a - \nu_f$) for An9-MePo. (c) Linear correlation of orientation polarization ($f(\varepsilon, n)$) of solvent media with the Stokes shift ($\nu_a - \nu_f$) for An9-DMePo. (d) Linear correlation of orientation polarization ($f(\varepsilon, n)$) of solvent media with the Stokes shift ($\nu_a - \nu_f$) for An2-Po.

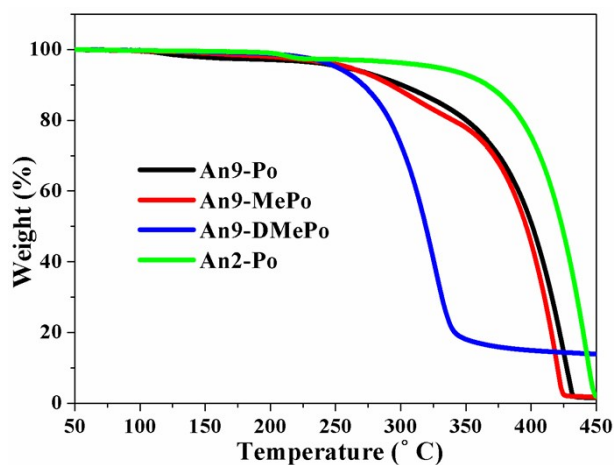


Fig. S2 Thermogravimetric analyses of An9-Po, An9-MePo, An9-DMePo and An2-Po at a heating rate of 20 K min⁻¹.

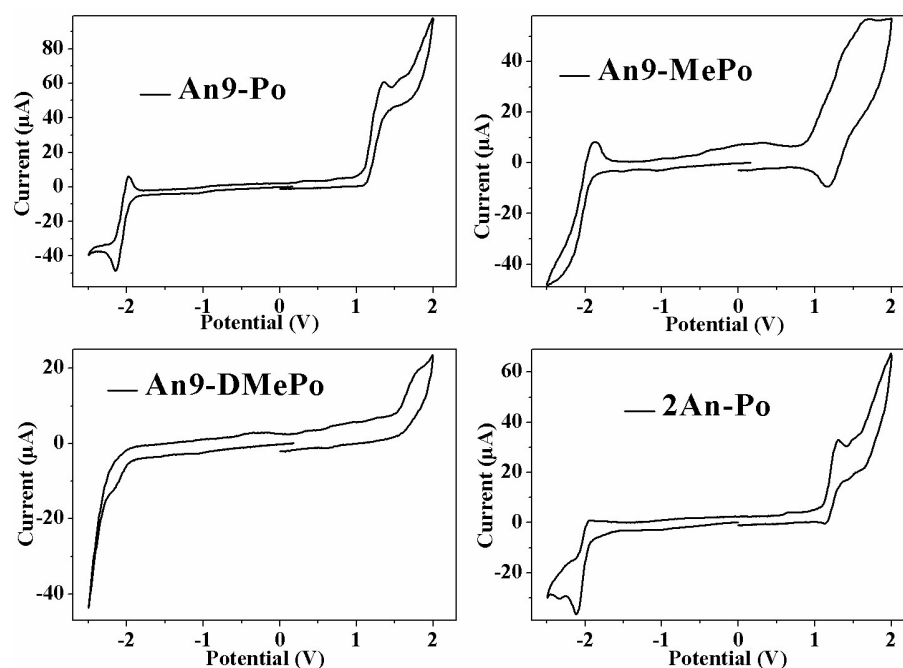
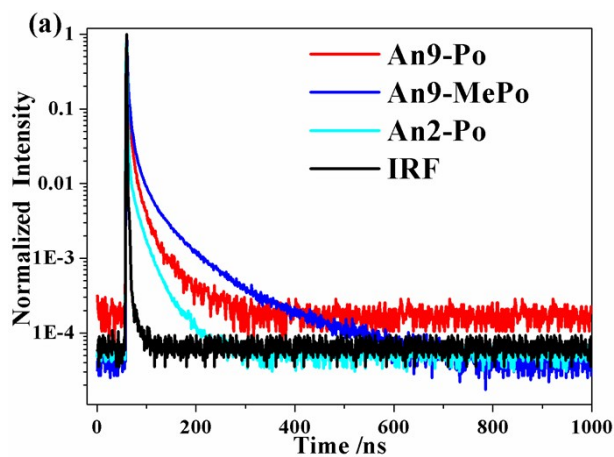


Fig. S3 The cyclic voltammetry characteristics of An9-Po, An9-MePo, An9-DMePo and An2-Po.



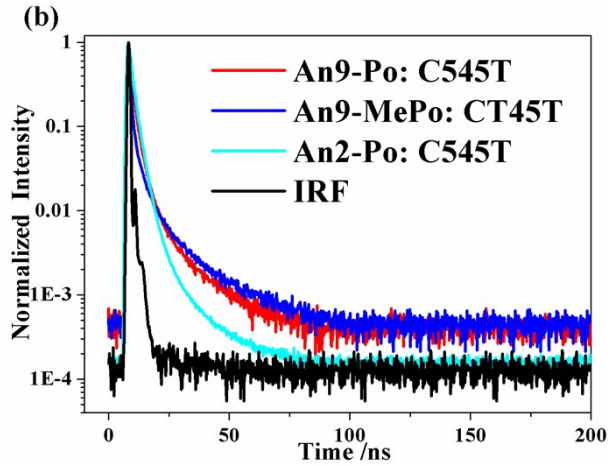


Fig. S4 (a) Lifetime measurement of An9-Po, An9-MePo and An2-Po in thin film. (b) Lifetime measurement of 1 wt% An9-Po: C545T, An9-MePo: C545T and An2-Po: C545T in thin film.

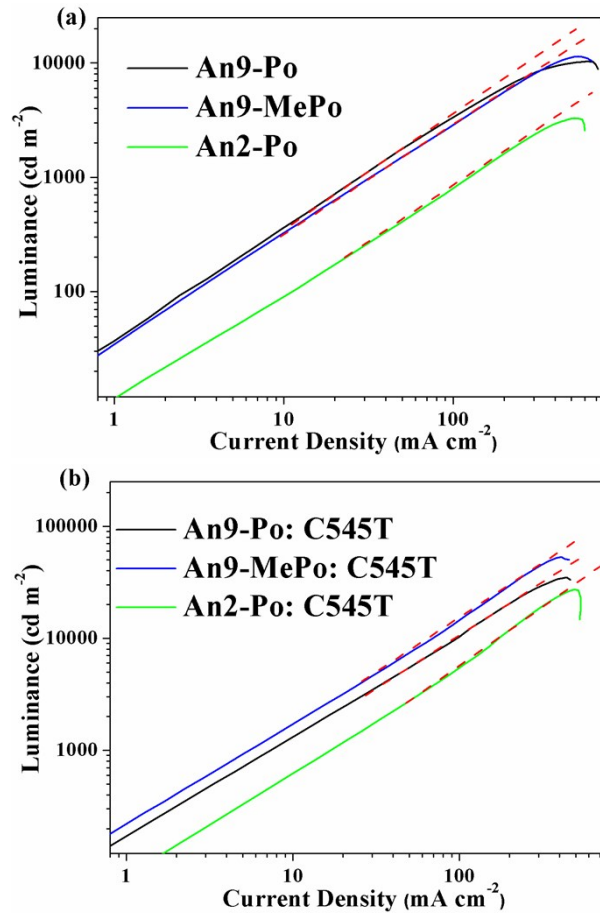


Fig. S5 (a) The current-brightness characteristic of An9-Po, An9-MePo and An2-Po nondoped devices. (b) The current-brightness characteristic of C545T doped devices with An9-Po, An9-MePo and An2-Po as host.

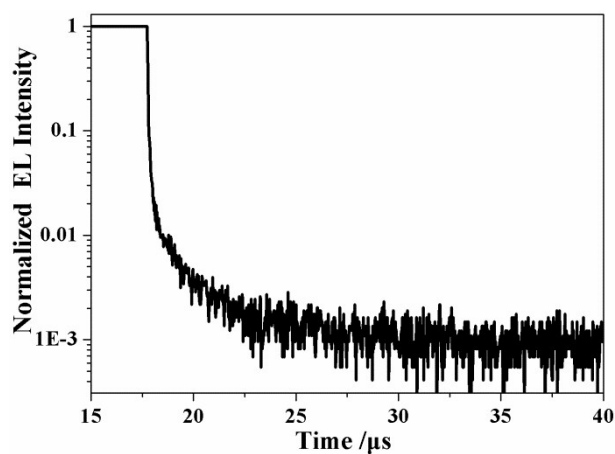


Fig. S6 Electroluminescence delay of An-MePo non-doped OLED. The measurements of the transient electroluminescence were carried out using a transient spectrometer (Edinburg FL920P), and an Agilent 8114A pulse generator (100 V/2 A) was used to generate rectangular pulse voltage with a pulse width of 15 μ s. The forward-pulse voltage was 8 V, and the baseline was -5 V to eliminate any trapped charges.