# Electronic Supplementary Information

## Combining the qualities of carbazole and tetraphenyl silane in a desirable main chain for thermally activated delayed fluorescence polymers

Xiang Zhou,[a] Manli Huang,[a] Xuan Zeng,[a] Tianheng Chen,[a] Guohua Xie,[a] Xiaojun Yin [b] and Chuluo Yang*[ab]

[a.]Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China

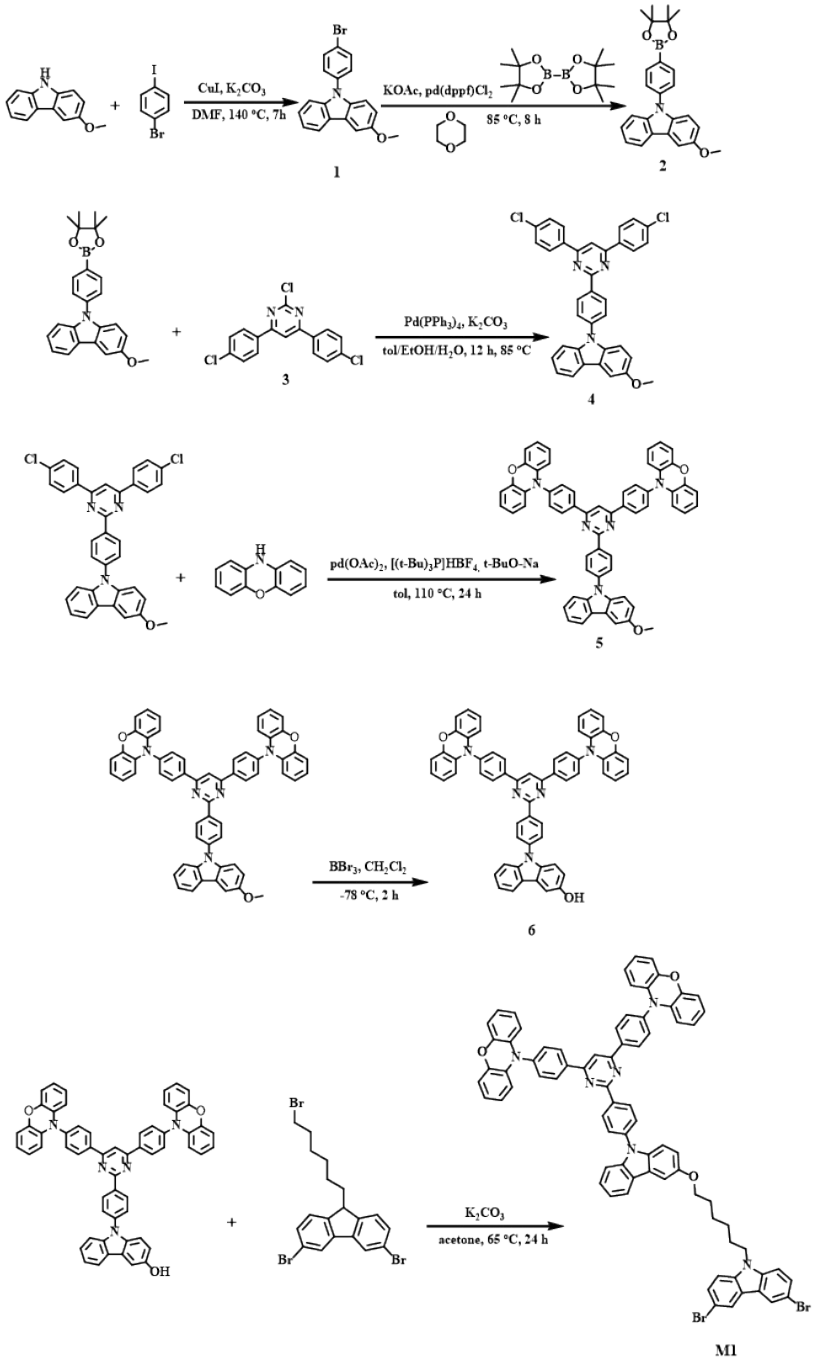
E-mail: clyang@whu.edu.cn

[b.]Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

## Experimental

**General Information:** All reagents and solvents were purchased from commercial sources. In addition, tetrahydrofuran and toluene were dried by sodium-potassium alloy. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded by Bruker Advanced II (400 MHz) spectrometers using $CDCl_3$ as solvent and tetramethyl silane as the internal standards. High resolution mass spectra (HRMS) were recorded using a Thermo Scientific LTQ Orbitrap XL mass spectrometer with an electrospray ionization (ESI) source. Mass spectra were measured by a Bruker BIFLEX III TOF mass spectrometer. Gel permeation chromatography (GPC) was carried out on a Waters 2690 D system using a refractive detector and THF as the eluent. UV-vis absorption spectra were performed

on a Shimadzu UV-2700 spectrophotometer. PL spectra were collected on a Hitachi F-4600 fluorescence spectrophotometer. The transient photoluminescence decay curves were measured by a single photo counting spectrometer from Edinburgh Instruments (FLS920). Absolute PLQYs were obtained using a Quantaurus-QY measurement system (C9920-02, Hamamatsu Photonics) and all the samples were excited at their maximum absorption wavelength. The calculations were carried out with the Gaussian 16 code. All the molecules were optimized in their ground state ($S_0$) at the DFT level of theory using the B3LYP hybrid functional and the def2-SVP basis set. The density functional dispersion correction was conducted by Grimme's D3 version with Becke-Johnson damping function. The excitation energies the $S_1$ and$T_1$ state were calculated by employing the gap-tuned range-separated LC-ω*PBE functional with the def2-SVP basis set.




**Scheme S1.** Synthetic Routes of the monomers.

**monomer synthesis:** 3-methoxy-9*H*-carbazole, 2-chloro-4,6-bis(4-chlorophenyl)pyrimidine, 3,6-dibromo-9-(6-bromohexyl)-9*H*-carbazole, 9-(6-(9*H*-carbazol-9-yl)hexyl)-3,6-dibromo-9*H*-carbazole (M2) and diphenylbis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (M3) were synthesized according to the literature methods.[1-5]

**9-(4-bromophenyl)-3-methoxy-9*H*-carbazole (1).** In a twin-neck round bottom flask, 3-methoxy-9*H*-carbazole (1.7 g, 8.6 mmol), 1-bromo-4-iodobenzene (2.5 g, 8.6 mmol), copper (I) iodide (0.163 g, 0.86 mmol) and potassium carbonate (1.78 g, 13 mmol) were dissolved in dry DMF (30 mL) under argon atmosphere. After stirring at 140 ℃ for 7 hours, the reaction mixture was poured into water (300 mL) and extracted with 100 mL $CH_2Cl_2$ for three times. Then the combined organic phases were dried over $Na_2SO_4$. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum ether/$CH_2Cl_2$ v/v 2:1) to give white powder (2.4 g, 80%). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.47-7.34 (m, 4H), 7.32-7.24 (m, 3H), 7.05 (d, *J* = 8.9 Hz, 1H), 3.95 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.40, 140.95, 137.02, 135.46, 133.08, 128.49, 126.08, 123.81, 123.38, 120.54, 120.29, 119.83, 115.01, 110.34, 109.67, 103.20, 56.01. HRMS (ESI) m/z calcd for $C_{19}H_{15}BrNO^+$ $(M+H)^+$ 352.03315, found 352.03329.

**3-methoxy-9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole (2).** In a twin-neck round bottom flask, 1 (840 mg, 2.4 mmol), potassium acetate (941 mg, 9.6 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (700 mg, 2.4 mmol) and [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (82 mg, 0.1 mmol) were dissolved in dry 1,4-dioxacyclohexane (25 mL) under argon atmosphere. After stirring at 85 ℃ for 8 hours, the reaction mixture was poured into water (300 mL) and extracted with 100 mL $CH_2Cl_2$ for three times. Then the combined organic phases were dried over $Na_2SO_4$. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum ether/$CH_2Cl_2$ v/v 3:1) to give

white powder (800 mg, 85%). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 20.7, 8.0 Hz, 3H), 7.59 (dd, *J* = 8.6, 5.4 Hz, 3H), 7.48-7.34 (m, 3H), 7.28 (s, 1H), 7.24 (s, 1H), 7.04 (d, *J* = 11.4 Hz, 1H), 3.95 (s, 3H), 1.40 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.37, 140.95, 140.60, 136.38, 135.49, 126.00, 125.82, 124.01, 123.42, 120.28, 119.73, 114.96, 110.67, 109.98, 103.16, 84.09, 56.12, 24.95.. HRMS (ESI) m/z calcd for $C_{25}H_{27}BNO_3^+$ $(M+H)^+$ 400.20785, found 400.20792.

**9-(4-(4,6-bis(4-chlorophenyl)pyrimidin-2-yl)phenyl)-3-methoxy-9*H*-carbazole (3).** In a twin-neck round bottom flask, **2** (1.0 g, 2.5 mmol), 2-chloro-4,6-bis(4-chlorophenyl)pyrimidine (840 mg, 2.5 mmol), tetrakis(triphenylphosphine)palladium (20 mg) and potassium carbonate (1.0 g, 7.5 mmol) were dissolved in the mix solvent of toluene (24 mL), ethanol (8 mL) and distilled water (4 mL) under argon atmosphere. After stirring at 85 ℃ for 24 hours, the mixture was cooled to room temperature and poured into water (300 mL) and extracted with 100 mL $CH_2Cl_2$ for three times. Then the combined organic phases were dried over $Na_2SO_4$. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum ether/$CH_2Cl_2$ v/v 3:2) to give green solid (1.3 g, 90%). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 8.6 Hz, 2H), 8.28 (d, *J* = 8.7 Hz, 4H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.99 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.63 (s, 1H), 7.60-7.39 (m, 7H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 3.97 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.03, 163.93, 154.48, 140.95, 140.34, 137.32, 136.36, 135.65, 135.47, 130.06, 129.30, 128.61, 126.51, 126.11, 124.14, 123.54, 120.37, 119.88, 115.06, 110.76, 110.05, 109.81, 103.21, 56.13. HRMS (ESI) m/z calcd for $C_{35}H_{24}Cl_2N_3O^+$ $(M+H)^+$ 572.12909, found 572.12933.

**10,10'-((2-(4-(3-methoxy-9*H*-carbazol-9-yl)phenyl)pyrimidine-4,6-diyl)bis(4,1-phenylene))bis(10*H*-phenoxazine) (4).** In a twin-neck round bottom flask, **3** (670 mg, 1.17 mmol), 10*H*-phenoxazine (641 mg, 3.5 mmol), palladium acetate (15.8 mg, 0.07 mmol), tri-tert-butylphosphine tetrafluoroborate (61 mg, 0.21 mmol) and sodiumt-butoxide (337 mg, 3.51 mmol) were dissolved in toluene (20 mL) under argon atmosphere. After stirring at 110 ℃ for 24 hours, the mixture was cooled to room temperature and poured into water (300 mL) and extracted with 100 mL $CH_2Cl_2$ for three times. Then the combined organic phases were dried over $Na_2SO_4$. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum ether/$CH_2Cl_2$ v/v 1:1) to give yellow solid (900 mg, 89%). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 8.6 Hz, 2H), 8.58 (d, *J* = 8.5 Hz, 4H), 8.18 (s, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.66-7.53 (m, 6H), 7.51-7.39 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.69 (m, 12H), 6.06 (d, *J* = 7.8 Hz, 4H), 3.97 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.96, 154.10, 143.67, 141.91, 141.54, 141.01, 140.42, 137.09, 136.32, 135.47, 133.85, 131.69, 129.72, 126.39, 125.80, 124.10, 122.72, 121.82, 120.24, 119.96, 119.62, 115.49, 114.89, 112.93, 110.52, 109.85, 103.29, 58.12. HRMS (ESI) m/z calcd for $C_{59}H_{40}N_5O_3^+$ $(M+H)^+$ 866.31257, found 866.31219.

**9-(4-(4,6-bis(4-(10*H*-phenoxazin-10-yl)phenyl)pyrimidin-2-yl)phenyl)-9*H*-carbazol-3-ol (5).** In a Schlenk flask, boron tribromide (0.6 mL, 6 mmol) was added dropwise to a stirring mixture of **4** (1.0 g, 1.2 mmol) in dry $CH_2Cl_2$ (15 mL) at -78 ℃ under argon atmosphere. After stirring for 2 hours at this temperature, the reaction mixture was slowly warmed to room temperature and stirred for 12 hours. Then the

reaction mixture was poured slowly into a large amount of cold methanol to provide precipitation. After filtration, the residue was dried under vacuum at 70 ℃ to give a light yellow powder (900 mg, 90%).$^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.04-8.91 (m, 2H), 8.58 (d, *J* = 8.5 Hz, 4H), 8.18 (s, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.83-7.71 (m, 2H), 7.67-7.49 (m, 6H), 7.44 (m, 2H), 7.37-7.28 (m, 1H), 7.00 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.69 (m, 12H), 6.06 (dd, *J* = 7.8, 1.5 Hz, 4H), 4.75 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.38, 149.93, 143.99, 142.88, 141.71, 141.09, 140.46, 137.36, 136.32, 134.88, 134.02, 131.60, 130.13, 129.58, 127.54, 126.57, 125.31, 124.50, 124.48, 123.99, 123.34, 121.71, 119.92, 115.68, 113.31, 110.69, 110.00. HRMS (ESI) m/z calcd for $C_{58}H_{38}N_5O_3^+$ $(M+H)^+$ 852.29692, found 852.29718.

**10,10'-((2-(4-(3-((6-(3,6-dibromo-9*H*-carbazol-9-yl)hexyl)oxy)-9*H*-carbazol-9-yl)phenyl)pyrimidine-4,6-diyl)bis(4,1-phenylene))bis(10*H*-phenoxazine) (M1).** In a twin-neck round bottom flask, 6 (900 mg, 1.1 mmol), 3,6-dibromo-9-(6-bromohexyl)-9*H*-carbazole (537 mg, 1.1 mmol) and potassium carbonate (152 mg, 1.1 mmol) were dissolved in acetone (10 mL). After stirring at 65 ℃ for 24 hours, the mixture was cooled to room temperature and poured into water (300 mL) and extracted with 100 mL $CH_2Cl_2$ for three times. Then the combined organic phases were dried over $Na_2SO_4$. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum ether/$CH_2Cl_2$ v/v 1:1) to give yellow solid (1.2 g, 80%). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 6.8 Hz, 2H), 8.58 (d, *J* = 8.6 Hz, 4H), 8.20-8.06 (m, 4H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.64-7.51 (m, 8H), 7.45 (dd, *J* = 16.9, 8.6 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 1H), 6.76-6.60 (m, 13H), 6.06 (d, *J* = 9.3 Hz,

4H), 4.28 (t, $J$ = 7.1 Hz, 2H), 4.07 (t, $J$ = 6.2 Hz, 2H), 1.93-1.69 (m, 4H), 0.92-0.80 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.36, 153.77, 152.27, 147.92, 145.97, 145.28, 143.85, 141.64, 140.85, 139.76, 139.20, 137.34, 136.19, 135.55, 134.06, 133.70, 131.46, 130.10, 129.96, 129.11, 126.53, 126.03, 124.17, 123.34, 121.61, 120.24, 119.88, 115.64, 113.31, 111.88, 110.73, 104.35, 103.88, 68.45, 58.59, 43.18, 28.81, 18.44. MS (MALDI-TOF, m/z): [$M^+$] calcd for $C_{76}H_{54}Br_2N_6O_3$ 1259.1, found 1258.6.

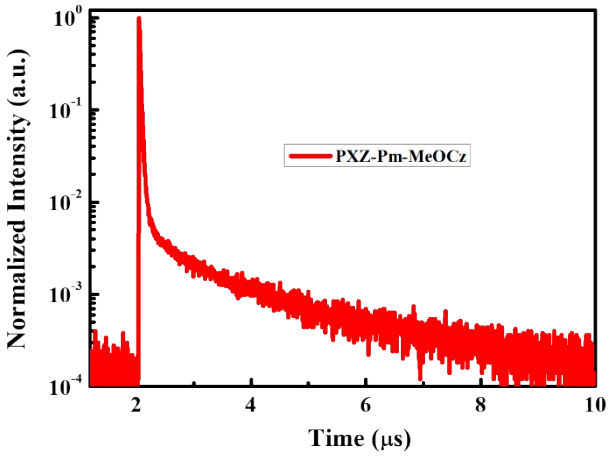



**Figure S1.** Transient PL decay spectra of TADF unit PXZ-Pm-MeOCz in the neat film at 300K.

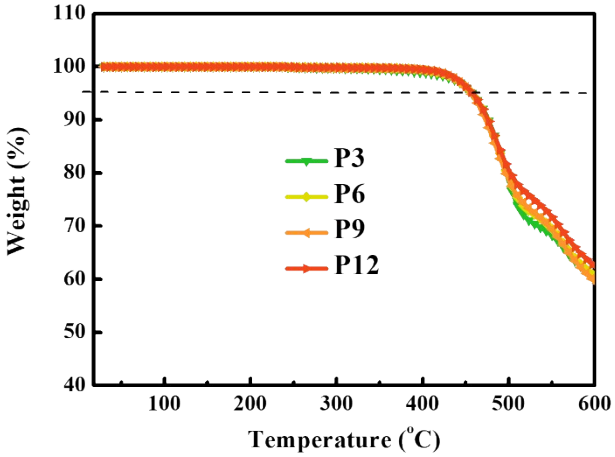



**Figure S2.** TGA traces of P3, P6, P9 and P12 recorded at a heating rate of 10 °C min$^{-1}$.

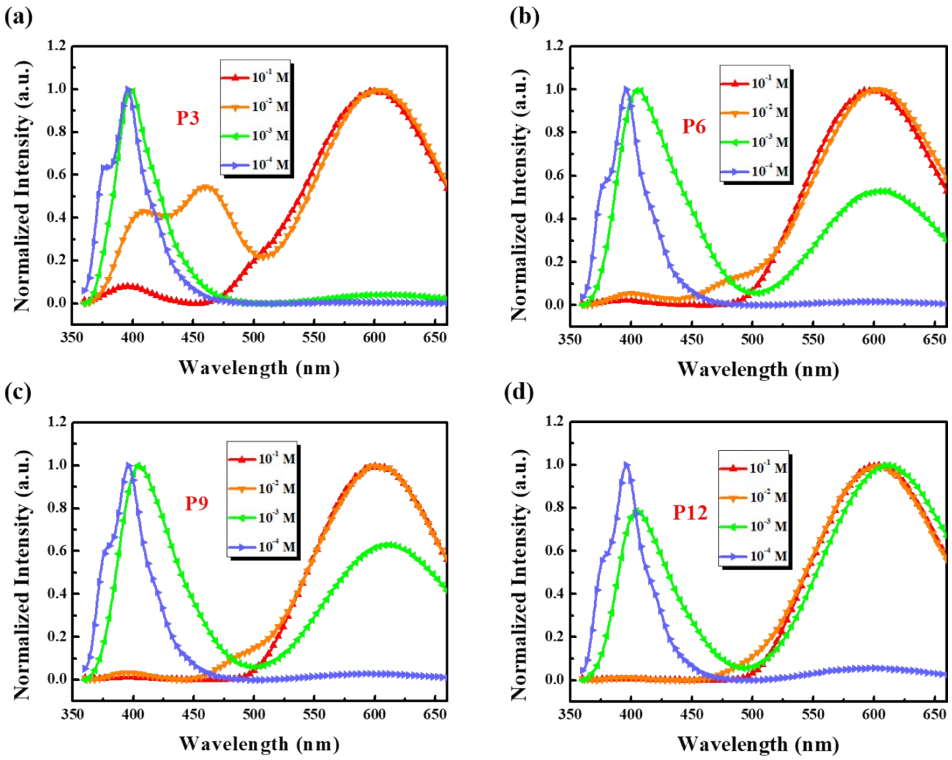



**Figure S3.** PL spectra of (a) P3, (b) P6, (c) P9 and (d) P12 in THF solutions with different concentration.

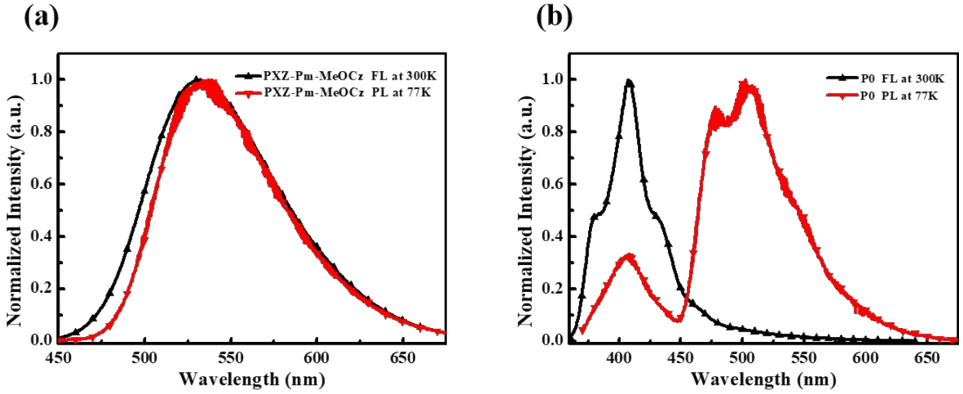



**Figure S4.** Fluorescence spectra (black line) and phosphorescence spectra (red line) of (a) PXZ-Pm-MeOCz and (b) P0 in the neat film.

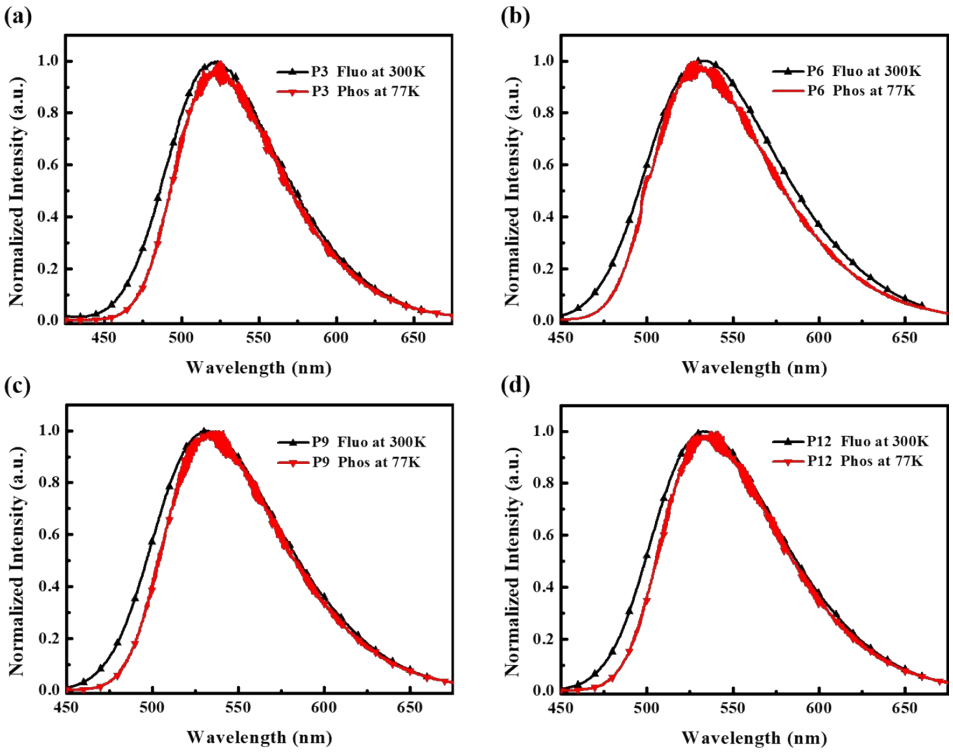



**Figure S5.** Fluorescence spectra (black line) and phosphorescence spectra (red line) of (a) P3, (b) P6, (c) P9 and (d) P12 in the neat films.

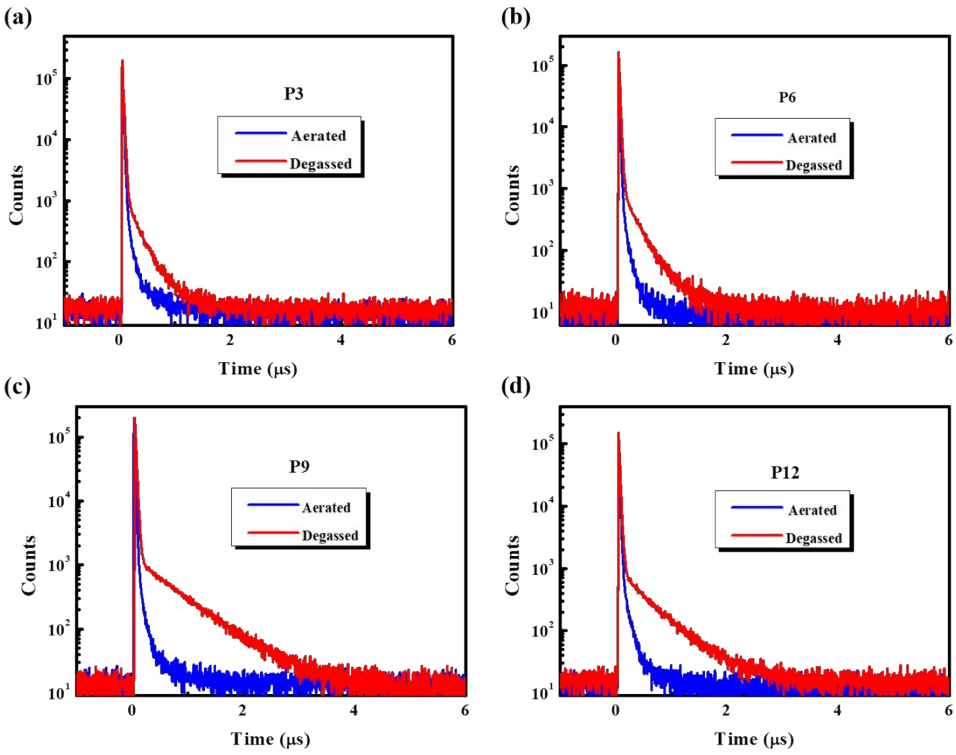



**Figure S6.** Transient PL decay spectra in degassed (red line) and aerated (blue line) THF solutions ($10^{-5}$ M) for (a) P3, (b) P6, (c) P9, and (d) P12.

**Table S1.** The calculated and experimental data of PXZ-Pm-MeOCz and P9.

| | $S_1/T_1/\Delta E_{ST}$ [eV][a)] | $S_1/T_1/\Delta E_{ST}$ [eV][b)] |
|---|---|---|
| **PXZ-Pm-MeOCz** | 2.77/2.74/0.03 | 2.62/2.55/0.07 |
| **P9** | 2.86/2.75/0.11 | 2.62/2.56/0.06 |

[a)] The theoretical data by DFT theory calculations at B3LYP-D3(BJ)/def2-SVP level;

[b)] The experimental data calculated from the peak emission of the fluorescence and phosphorescence spectra in the neat film.

## References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