Supporting Information

Phenanthro[9,10-*d*]triazole and imidazole Derivatives: High Triplet Energy Host Materials for Blue Phosphorescent Organic Light Emitting Devices

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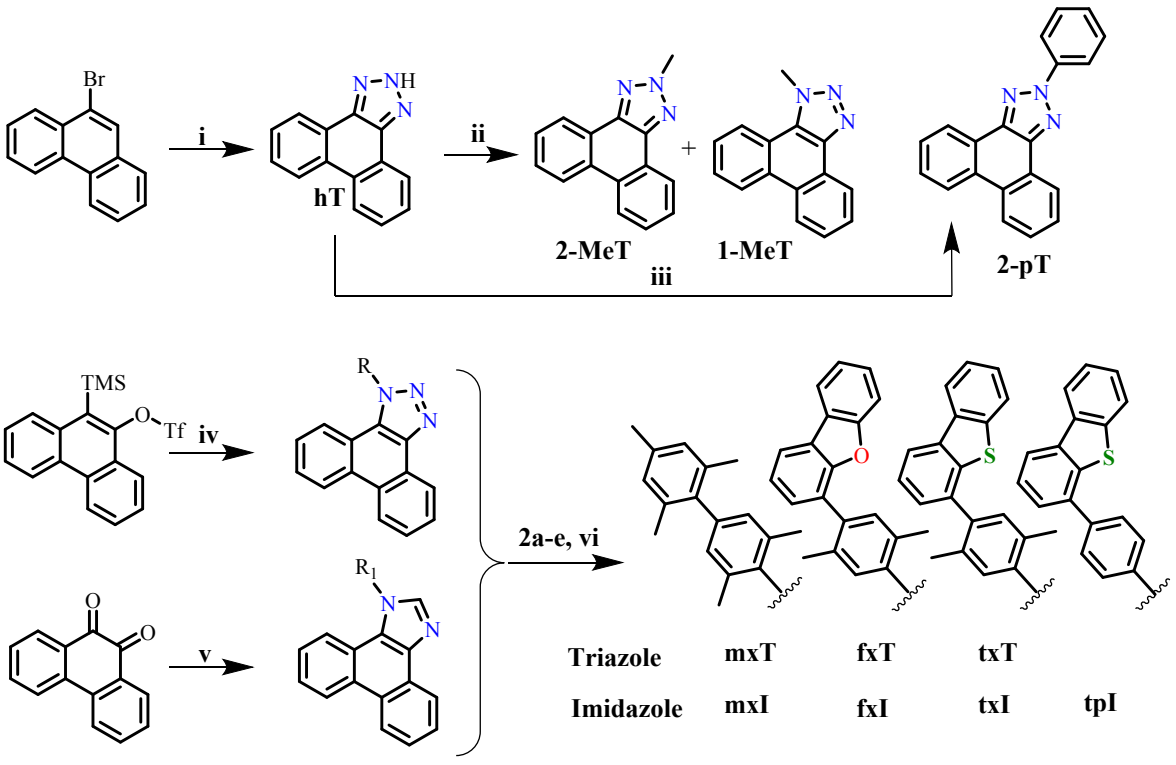
Contents

1. Synthesis

All commercial reagents and solvents are purchased from Sigma Aldrich, Matrix Scientific and Ark Pharm and are used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on Varian 400 NMR spectrometer and referenced to residual protons in the deuterated chloroform ($CDCl_3$) solvent.

Synthesis of Phenanthro[9,10-d]triazole (**hT**)

To a solution of 9-bromophenanthrene (15.0g, 58.4mmol) in 265 ml of dry dimethyl sulfoxide were added dry potassium *t*-butoxide (19.6g, 175.0mmol) and sodium azide (7.58g, 116.7mmol). The reaction mixture was stirred at room temperature under nitrogen atmosphere for 12 hours. The reaction mixture was poured into 500 ml of 1M HCl to form off-white precipitate. The precipitate is filtered and further washed with cold acetone. The residue is dried under *vacuo* to yield off-white solid (7.05 g, 32 mmol, 55%):



R = Phenyl	**1-pT**	2,6-Xylyl	**1-xT**	R_1 = Methyl	**MeI**	2,6-Xylyl 4-Br	(**2c**)
Tolyl	**1-tT**	2,6-Xylyl 4-Br	(**2a**)	Phenyl	**pI**	2,5-Xylyl 4-Br	(**2d**)
Mesityl	**mT**	2,5-Xylyl 4-Br	(**2b**)	Mesityl	**mI**	Phenyl-Br	(**2e**)

Scheme S1: i: NaN_3, K-tBuO, DMSO rt. 12 h. ii: MeI, K_2CO_3, DMF, rt. iii: PhI, $Fe(acac)_3$, CuO, DMF, 100°C, 30 h. iv: RN_3, CsF, MeCN, rt. 30 h. v: R_1NH_2, Formaldehyde, NH_2OAc, Acetic acid, 100°C, 4 h. vi: $ArylB(OH)_2$, K_2CO_3, Toluene/Water (2/1), 110°C, 12-48 h.

Synthesis of 1-methyl-phenanthro[9,10-d]triazole (1-MeT) and 2-methyl-phenanthro[9,10-d]triazole (2-MeT)

To solution of ***hT*** (4.46g, 20.3mmol) in DMF (15 mL) was added K_2CO_3 (5.62g, 40.8 mmol) followed by methyl iodide (2.89g, 20.3 mmol). The resulting mixture was stirred for 12 hours at room temperature. Upon the completion of the reaction, DCM (50 mL) and water (50 mL) were added, and the layers were separated. The aqueous layer was further extracted with dichloromethane. The organic layer was dry over Na_2SO_4 and concentrated to dryness. The residue was purified by chromatography on silica gel (eluting with a mixture of ethyl acetate and hexane) to give **2-MeT** as yellow solid (2.1 g, 9.00 mmol, 44%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 – 8.56 (m, 1H), 8.50 – 8.45 (m, 1H), 7.69 – 7.58 (m, 2H), 4.52 (d, *J* = 1.0 Hz, 2H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 141.16, 130.30, 127.60, 127.57, 124.50, 123.66, 123.42, 77.29, 77.17, 76.97, 76.65, 42.66. (Found: C, 77.12; H, 4.73; N, 17.59. Calc. for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01%).

and **1-MeT** as brown solid (1.2 g, 5.14 mmol, 25%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (ddd, *J* = 7.8, 2.9, 1.5 Hz, 1H), 8.70 – 8.62 (m, 1H), 8.58 – 8.51 (m, 1H), 8.30 – 8.23 (m, 1H), 7.73 – 7.61 (m, 4H), 4.63 (d, *J* = 5.9 Hz, 3H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 142.05, 130.80, 128.67, 128.36, 128.07, 127.50, 127.28, 126.92, 125.01, 124.41, 123.23, 122.87, 122.30, 120.74, 77.32, 77.00, 76.68, 38.24. (Found: C, 76.81; H, 4.82; N, 17.14. Calc. for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01%).

Synthesis of 2-phenyl-2H-phenanthro[9,10-d][1,2,3]triazole (2-pT)

In a 3-necked round bottomed flask Fe(acac)$_3$ (966 mg, 2.74 mmol), CuO (72.56 mg, 0.2 mmol), phenanthro[9,10-*d*]triazole (2.00 g, 9.12 mmol), and Cs_2CO_3 (5.94 g, 18.24 mmol). Iodobenzene (1.86 g, 9.12 mmol) and anhydrous DMF (10 mL) were added to the flask. The reaction mixture was heated to 90^{o}C and stirred for 30 h under nitrogen. After cooling to room temperature, the mixture was diluted with dichloromethane and filtered. The filtrate was washed twice with water, and the combined aqueous phases were extracted twice with dichloromethane. The organic layers were combined, dried over Na_2SO_4, and concentrated to yield the crude product, which was further purified by silica gel chromatography (7:3 hexanes/EtAc) to yield 2-phenyl-2H-phenanthro[9,10-d][1,2,3]triazole (1) as puffy solid (2.10g g, 7.11 mmol, 78%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 – 8.52 (m, 4H), 8.42 – 8.36 (m, 2H), 7.71 – 7.62 (m, 4H), 7.60 – 7.52 (m, 2H), 7.45 – 7.38 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.14, 140.40, 130.77, 129.35, 128.07, 127.91, 127.69, 124.45, 123.96, 123.72, 119.72, 77.30, 76.98, 76.66. (Found: C, 81.64; H, 4.56; N, 13.78. Calc. for $C_{20}H_{13}N_3$: C, 81.34; H, 4.44; N, 14.23%).

Synthesis of 9-Hydroxyphenanthrene.

In a dry 1000 ml one-necked round bottom flask, 9-bromophenanthrene (15.0g, 58.3 mmol) was dissolved in 120 ml tetrahydrofuran and cooled down to -78^{o}C. n-butyl lithium (4.48g, 70.0mmol, 2.5 M) was added dropwise to the reaction mixture under nitrogen. The reaction mixture was stirred at -78^{o}C for 30 minutes followed by dropwise addition of trimethyl borate (7.27g, 70.0mmol) in 50 ml tetrahydrofuran. The reaction mixture is stirred at -5^{o}C for 1 hour and then recooled to -10^{o}C. Glacial acetic acid (5.3 ml) was added followed by a solution of 30% aqueous hydrogen peroxide (6.6 ml) in water (6.0 ml) while maintaining the solution at -10^{o}C. The resulting solution was allowed to warm to room temperature while stirring for an additional 40 min. Saturated aqueous ammonium chloride solution was added (100 ml) followed by tetrahydrofuran (50 ml), and the organic layer was separated. The organic layer was washed with saturated aqueous

sodium bicarbonate solution (100 ml), water (100 ml), and brine (3 × 100 ml), dried with sodium sulfate, and filtered. The residue was purified by chromatography on silica gel (eluting with a mixture of ethyl acetate and hexane) to give white powder (9.5 g, 49 mmol, 84%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.29 (s, 1H), 8.69 (dddd, J = 41.0, 8.1, 1.3, 0.6 Hz, 2H), 8.29 – 8.15 (m, 1H), 7.76 – 7.54 (m, 3H), 7.44 (dddd, J = 28.7, 8.3, 7.0, 1.4 Hz, 2H), 7.04 (s, 1H).

Synthesis of 10-Bromo-9-phenanthrol: is prepared from literature procedure without modification.[1]
A solution of NBS (5.6 g, 31.7 mmol) in methylene chloride (280 mL) was added dropwise over 1 hour to a solution of 9-phenanthrol (5.6 g, 28.8 mmol) and *i*-Pr_2-NH (0.4 ml, 2.88 mmol) in methylene chloride. After addition was complete, the mixture was stirred at room temperature for 1 h, poured on H_2O, and acidified to pH 1 by careful addition of concentrated H_2SO_4. The resulting mixture was extracted with CH_2Cl_2, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography of the residue (SiO_2, 1:3 AcOEt/hexane) afforded a white solid (5.9 g, 75%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 – 8.53 (m, 2H), 8.37 (ddd, J = 7.8, 1.6, 0.6 Hz, 1H), 8.19 – 8.07 (m, 1H), 7.78 – 7.45 (m, 4H), 6.29 (s, 1H).

*Synthesis of 10-Trimethylsilylphenanthryl 9-Trifluoromethanesulfonate***:** is prepared from literature procedure without modification.[1]
n-BuLi (11.2 mL, 2.50 M, 27.80 mmol) was added dropwise to a solution of 10-Bromo-9-phenanthrol (5.10 g, 18.6 mmol) in THF (250 mL) cooled to -78 °C. After stirring at -78 °C for 15 min, TMSCl (3.78 mL, 29.8 mmol) was added, the cooling bath was removed, and stirring was kept for 10 min at room temperature. The mixture was again cooled to -78 °C, *n*-BuLi (7.44 mL, 2.50 M, 18.6 mmol) was added dropwise, stirring was kept up at -78 °C for 15 min, and TMSCl (3.78 mL, 29.8 mmol) was added. Stirring at room temperature was kept up overnight, H_2O (300 mL) was added, and the resulting mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude intermediate, which was taken to the next step without further purification. To a solution of this crude residue in Et_2O (250 mL) at 0 °C, *n*-BuLi (16.80 mL, 2.50 M, 42.0 mmol) was dropwise added. The mixture was stirred at room temperature for 4 h and cooled again to 0 °C, and then Tf_2O (13.4 mL, 79.7 mmol) was added. Stirring was kept for 40 min, and then saturated aqueous $NaHCO_3$ (300 mL) was added. The mixture was extracted with Et_2O, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; hexane) to afford yellow viscous oil (9.6 g, 46%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 – 8.51 (m, 1H), 8.27 – 8.00 (m, 1H), 7.86 – 7.43 (m, 2H), 0.59 (d, J = 1.5 Hz, 4H).

Synthesis of aryl azides: Aryl azides are from literature procedure without modification.[2]

Azidobenzene, 2-azido-1,3,5-trimethylbenzene, 1-azido-2-methylbenzene, 2-azido-1,3-dimethylbenzene, 2-azido-5-bromo-1,3-dimethylbenzene have all been reported and are prepared from reference 2 without modification.[2-5]

1-azido-4-bromo-2,5-dimethylbenzene:

Yellow liquid/solid (1.58 g, 7.00 mmol, 70%): ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.40 (s, 1H), 7.17 (s, 1H), 2.37 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, acetone) δ 137.70, 136.56, 134.17, 128.86, 120.32, 119.42, 21.46, 15.55.

[3+2] Cycloaddition of Aryl Azides to benzynes and product characterization.

General procedure: to a solution of benzyne precursor (5.02 mmol, 1 equiv) and azide (6.02 mmol, 1.2 equiv) in dry MeCN (30 mL) was added CsF (1.52 mmol, 2.0 equiv). The reaction vial was sealed, and the reaction mixture stirred at room temperature for 24 h before being poured into saturated aqueous $NaHCO_3$. The resulting mixture was extracted with EtOAc or DCM, and the combined organic layers were dried over $MgSO_4$ and evaporated. The residue was purified by silica gel chromatography (hexane/EtOAc, 70/30).

1-phenyl-1H-phenanthro[9,10-*d*][1,2,3]triazole: (1-pT)

White solid (200 mg, 0.68 mmol, 62%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.90 (ddd, *J* = 7.9, 1.5, 0.7 Hz, 1H), 8.74 (ddd, *J* = 8.3, 1.2, 0.6 Hz, 1H), 8.66 (ddd, *J* = 8.2, 1.3, 0.7 Hz, 1H), 7.83 – 7.74 (m, 1H), 7.78 – 7.62 (m, 7H), 7.63 (ddd, *J* = 8.2, 1.4, 0.7 Hz, 1H), 7.50 – 7.36 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.55, 138.04, 131.17, 130.46, 129.89, 129.03, 128.99, 128.21, 127.84, 127.15, 127.01, 126.93, 124.94, 124.32, 123.34, 123.14, 122.86, 120.30.

1-(o-tolyl)-1H-phenanthro[9,10-*d*][1,2,3]triazole (1-tT)

White solid (490 mg, 1.58 mmol, 50%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.92 – 8.87 (m, 1H), 8.73 (ddd, *J* = 8.3, 1.1, 0.6 Hz, 1H), 8.66 (ddt, *J* = 8.2, 1.1, 0.6 Hz, 1H), 7.78 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 7.71 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.54 – 7.48 (m, 3H), 7.41 – 7.32 (m, 2H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.28, 137.14, 136.15, 131.50, 131.04, 130.88, 129.27, 128.96, 128.21, 127.84, 127.82, 127.45, 127.35, 127.09, 125.05, 124.22, 123.36, 123.07, 122.09, 120.42, 77.29, 76.97, 76.66, 17.34.

1-(2,6-dimethylphenyl)-1H-phenanthro[9,10-*d*][1,2,3]triazole (xT)

White solid (250 mg, 0.77 mmol, 74%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 (dt, *J* = 7.9, 1.9 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 7.82 – 7.61 (m, 3H), 7.48 (td, *J* = 7.8, 1.9 Hz, 1H), 7.42 – 7.22 (m, 4H), 1.94 (d, *J* = 1.8 Hz, 6H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.38, 136.43, 136.35, 130.98, 130.60, 128.98, 128.91, 128.83, 128.23, 127.88, 127.64, 127.09, 125.13, 124.20, 123.39, 123.00, 121.51, 120.47, 77.30, 76.98, 76.66, 17.51.

1-mesityl-1H-phenanthro[9,10-*d*][1,2,3]triazole (mT)

White solid (1.2 g, 3.56 mmol, 71%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.92 – 8.87 (m, 1H), 8.72 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.66 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.78 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 7.68 (dddd, *J* = 21.8, 8.4, 7.1, 1.5 Hz, 2H), 7.40 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.33 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.13 (s, 2H), 2.46 (s, 3H), 1.89 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.33, 140.61, 135.97, 133.80, 130.93, 129.59, 128.96, 128.91, 128.19, 127.80, 127.59, 127.02, 125.18, 124.14, 123.37, 122.98, 121.56, 120.58, 77.30, 76.98, 76.66, 21.34, 17.42. (Found: C, 81.80; H, 5.72; N, 12.16. Calc. for $C_{23}H_{19}N_3$: C, 81.87; H, 5.68; N, 12.45%).

1-(4-bromo-2,6-dimethylphenyl)-1H-phenanthro[9,10-*d*][1,2,3]triazole (2a)

White solid (1.4 g, 3.48 mmol, 68%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89 (ddt, *J* = 7.9, 1.5, 0.7 Hz, 1H), 8.74 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.70 – 8.62 (m, 1H), 7.79 (ddt, *J* = 7.9, 7.0, 1.0 Hz, 1H), 7.71 (dddt, *J* = 16.8, 8.2, 7.1, 1.0 Hz, 2H), 7.51 (q, *J* = 0.8 Hz, 2H), 7.44 (ddt, *J* = 8.1, 7.1,

1.0 Hz, 1H), 7.33 – 7.27 (m, 1H), 1.92 (q, *J* = 0.8 Hz, 6H), 1.56 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.57, 135.49, 131.85, 131.06, 128.98, 128.32, 128.09, 127.78, 127.23, 124.99, 124.53, 124.32, 123.40, 123.01, 121.36, 120.20, 77.29, 77.18, 76.97, 76.65, 17.42.

1-(4-bromo-2,5-dimethylphenyl)-1H-phenanthro[9,10-*d*][1,2,3]triazole (2b)
White solid (3.22 g, 8.00 mmol, 56%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 – 8.85 (m, 1H), 8.73 (dt, *J* = 8.4, 0.7 Hz, 1H), 8.66 (ddd, *J* = 8.0, 1.3, 0.7 Hz, 1H), 7.78 (ddt, *J* = 7.9, 7.0, 1.0 Hz, 1H), 7.74 – 7.63 (m, 3H), 7.47 – 7.37 (m, 3H), 2.52 – 2.36 (m, 3H), 2.01 – 1.87 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.30, 137.52, 136.15, 135.10, 134.94, 131.07, 129.65, 128.95, 128.27, 127.99, 127.48, 127.22, 127.18, 124.94, 124.30, 123.38, 123.08, 122.02, 120.23, 77.29, 77.18, 76.97, 76.65, 22.50, 16.70.

General Procedure for Condensation reaction.
A mixture of phenanthrene-9,10-dione (48.03 mmol, 1 equiv), mesityl amine (57.63 mmol, 1.2 equiv), formaldehyde (48.03 mmol, 1 equiv) and ammonium acetate (96.05 mmol, 2 equiv) in glacial acetic acid (550 mL) was refluxed for 3 h. The solvent is evaporated to dryness and the crude is extracted with saturated aqueous $NaHCO_3$ and CH_2Cl_2. The organics were combined and dried over Na_2SO_4. The crude was purified by silica gel chromatography (hexane/EtOAc, 60/40) followed by sublimation to give pure products.

1-methyl-1H-phenanthro[9,10-*d*]imidazole (MeI)
Yellow solid (600 mg, 0.95 mmol, 59%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 – 8.74 (m, 1H), 8.67 (dtd, *J* = 7.7, 1.4, 0.6 Hz, 2H), 8.37 – 8.29 (m, 1H), 7.89 – 7.77 (m, 1H), 7.69 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 7.66 – 7.55 (m, 3H), 4.28 (d, *J* = 0.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.04, 138.55, 129.00, 127.93, 127.48, 127.29, 126.64, 125.95, 125.38, 125.05, 124.98, 124.30, 123.51, 123.06, 122.31, 120.59, 109.98, 77.30, 77.19, 76.98, 76.66, 35.60. (Found: C, 82.72; H, 5.22; N, 11.87. Calc. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06%).

1-phenyl-1H-phenanthro[9,10-*d*]imidazole (pI)
White solid (220 mg, 0.75 mmol, 5%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.77 – 7.69 (m, 1H), 7.66 – 7.56 (m, 4H), 7.55 – 7.46 (m, 3H), 7.40 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.32 – 7.25 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.70, 137.86, 137.72, 129.93, 129.79, 129.59, 129.19, 128.29, 127.39, 127.22, 126.32, 126.29, 125.66, 125.22, 124.08, 123.15, 122.69, 122.53, 121.16, 77.39, 77.08, 76.76. (Found: C, 86.01; H, 4.98; N, 9.53. Calc. for $C_{21}H_{14}N_2$: C, 85.69; H, 4.79; N, 9.52%).

1-mesityl-1H-phenanthro[9,10-*d*]imidazole (mI)
White solid (10.2g , 30.32 mmol, 71%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 – 8.73 (m, 2H), 8.72 – 8.68 (m, 1H), 7.83 (s, 1H), 7.74 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.64 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.31 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.19 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.13 – 7.08 (m, 2H), 2.45 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.68, 139.69, 137.88, 136.25, 133.40, 129.54, 128.96, 128.20, 127.55, 127.36, 126.90, 125.53, 125.46, 125.17, 123.91, 123.26, 123.16, 122.30, 119.65, 77.32, 77.21, 77.00, 76.69, 21.25, 17.66. (Found: C, 85.91; H, 5.99; N, 8.28. Calc. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33%).

1-(4-bromo-2,6-dimethylphenyl)-1H-phenanthro[9,10-*d*]imidazole (2c)
White solid (1.25 g, 3.11 mmol, 22%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 – 8.68 (m, 3H), 7.92 (s, 1H), 7.77 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 7.67 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.57 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.37 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.17 (dd, *J* = 8.2, 1.3 Hz, 1H), 1.98 (d, *J* = 0.6 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.43, 140.27, 138.77, 137.48, 135.04, 131.84, 129.16, 128.35, 127.61, 127.18, 127.04, 125.86, 125.58, 125.24, 124.11, 123.70, 123.22, 122.83, 122.46, 119.40, 20.91, 17.65, 17.42.

1-(4-bromo-2,5-dimethylphenyl)-1H-phenanthro[9,10-*d*]imidazole (2d)
White solid (5.50 g, 13.71 mmol, 46%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 – 8.74 (m, 2H), 8.71 (ddt, *J* = 8.9, 1.2, 0.6 Hz, 1H), 8.00 (s, 1H), 7.77 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.68 (s, 1H), 7.73 – 7.63 (m, 1H), 7.58 (ddt, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.31 – 7.23 (m, 1H), 2.49 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 175.70, 141.04, 137.50, 137.11, 135.77, 135.51, 134.88, 129.89, 129.15, 128.34, 127.58, 126.94, 126.90, 126.41, 126.16, 125.84, 125.53, 124.09, 123.20, 122.76, 122.55, 120.08, 22.50, 16.83.

1-(4-bromophenyl)-1H-phenanthro[9,10-*d*]imidazole (2e)
White solid (10.05 g, 26.9 mmol, 56 ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 10.0 Hz, 1H), 8.71 (dd, *J* = 8.1, 6.0 Hz, 2H), 8.01 (d, *J* = 0.8 Hz, 1H), 7.76 (m, 3H), 7.66 (dd, *J* = 10.8, 0.8 Hz, 1H), 7.56 (t, *J* = 0.0 Hz, 1H), 7.45 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 141.66, 137.88, 136.73, 133.22, 132.88, 129.30, 128.77, 128.36, 127.52, 127.02, 126.45, 125.85, 125.45, 124.22, 123.67, 123.17, 122.55, 122.45, 121.03.

General Procedure for Suzuki Coupling:
In a one-necked RBF, add Pd(PPh$_3$)$_4$ in glovebox the bromide, boronic acid and K$_2$CO$_3$ are added outside glovebox quickly to minimize the amount of time Pd(PPh$_3$)$_4$ is exposed to air. The flask is equipped with condenser and stirrer bar. The flask is then filled and evacuated 3 times. Toluene/Water is added via cannula transfer and the reaction mixture is stirred at 110^{o}C for 48 h. The reaction mixture is extracted with water and the organic layer is dried with Na$_2$SO$_4$. The crude residue was purified by column chromatography (silica), using gradient of ethyl acetate in hexane, yielding **1**

1-(2',3,4',5,6'-pentamethyl-[1,1'-biphenyl]-4-yl)-1H-phenanthro[9,10-*d*][1,2,3]triazole (mxT)
White solid (1.00 g, 2.26 mmol, 91%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.95 – 8.90 (m, 1H), 8.75 (d, *J* = 8.4 Hz, 1H), 8.71 – 8.66 (m, 1H), 7.80 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.70 (dddd, *J* = 22.1, 8.4, 7.0, 1.6 Hz, 2H), 7.38 (ddt, *J* = 7.8, 6.9, 0.9 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.12 (s, 2H), 7.00 (s, 2H), 2.36 (s, 3H), 2.18 (s, 3H), 2.14 (s, 3H), 1.97 (s, 6H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 143.86, 141.46, 137.85, 137.01, 136.58, 135.79, 135.26, 134.81, 131.06, 129.84, 129.01, 128.88, 128.27, 128.11, 127.88, 127.50, 127.12, 125.16, 124.27, 123.42, 123.01, 121.37, 120.51, 21.05, 20.86, 20.60, 17.58. (Found: C, 84.64; H, 6.36; N, 9.55. Calc. for C$_{31}$H$_{27}$N$_3$: C, 84.32; H, 6.16; N, 9.52%).

1-(2',3,4',5,6'-pentamethyl-[1,1'-biphenyl]-4-yl)-1H-phenanthro[9,10-*d*]imidazole (mxI)
White solid (1.20 g, 2.72 mmol, 90%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (t, *J* = 9.1, 8.0 Hz, 2H), 8.73 (d, *J* = 9.1 Hz, 1H), 7.78 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.67 (ddd, *J* = 8.4, 7.0, 1.5

Hz, 1H), 7.56 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.33 – 7.24 (m, 2H), 7.18 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.11 (s, 2H), 7.01 (d, *J* = 6.5 Hz, 2H), 2.38 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 143.06, 140.26, 137.90, 137.01, 136.76, 135.57, 135.47, 134.40, 129.82, 129.12, 128.29, 128.21, 127.48, 127.4126.77, 125.62, 125.40, 125.27, 124.04, 123.21, 123.15, 122.39, 119.51, 21.06, 20.85, 20.59, 17.84. (Found: C, 88.10; H, 6.43; N, 6.36. Calc. for $C_{32}H_{28}N_2$: C, 87.24; H, 6.41; N, 6.36%).

1-(4-(dibenzo[b,d]furan-4-yl)-2,5-dimethylphenyl)-1H-phenanthro[9,10-*d*][1,2,3]triazole (fxT)

White solid (1.20 g, 2.45 mmol, 82%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.95 – 8.90 (m, 1H), 8.79 – 8.74 (m, 1H), 8.71 – 8.66 (m, 1H), 8.06 – 8.00 (m, 2H), 7.80 (ddd, *J* = 8.0, 7.1, 1.2 Hz, 1H), 7.72 (tdd, *J* = 8.3, 7.1, 1.5 Hz, 2H), 7.68 – 7.63 (m, 1H), 7.60 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.55 – 7.44 (m, 6H), 7.39 (td, *J* = 7.5, 1.0 Hz, 1H), 2.32 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 156.21, 153.43, 141.30, 139.28, 136.61, 136.58, 133.32, 132.98, 131.07, 129.36, 129.20, 128.99, 128.23, 128.18, 127.89, 127.51, 127.38, 127.09, 125.12, 124.97, 124.47, 124.24, 124.19, 123.39, 123.10, 122.90, 122.39, 120.78, 120.54, 120.26, 111.87, 77.30, 77.19, 76.98, 76.66, 19.81, 16.96. (Found: C, 83.68; H, 4.79; N, 8.48; O, 3.05. Calc. for $C_{34}H_{23}N_3O$: C, 83.41; H, 4.74; N, 8.58; O, 3.27%).

1-(4-(dibenzo[b,d]furan-4-yl)-2,5-dimethylphenyl)-1H-phenanthro[9,10-*d*]imidazole (fxI)

White solid (1.52 g, 3.11 mmol, 83%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 – 8.78 (m, 3H), 8.74 (d, *J* = 8.8 Hz, 2H), 8.10 (s, 1H), 8.08 – 8.01 (m, 3H), 7.78 (ddd, *J* = 15.2, 12.0, 7.4 Hz, 1H), 7.69 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.54 – 7.37 (m, 5H).
^{13}C NMR (101 MHz, cdcl$_3$) δ 156.20, 153.42, 141.06, 138.47, 137.43, 136.53, 136.51, 136.27, 133.46, 133.23, 129.50, 129.12, 128.25, 127.46, 127.41, 127.39, 127.28, 126.83, 126.40, 125.66, 125.34, 124.93, 124.49, 124.21, 124.03, 123.18, 123.09, 123.07, 122.94, 122.54, 120.80, 120.43, 120.26, 111.86, 19.82, 17.10. (Found: C, 86.48; H, 4.91; N, 5.65; O, 2.96. Calc. for $C_{35}H_{24}N_2O$: C, 86.04; H, 4.95; N, 5.73; O, 3.27%).

1-(4-(dibenzo[b,d]thiophen-4-yl)-2,5-dimethylphenyl)-1H-phenanthro[9,10-*d*][1,2,3]triazole (txT)

White solid (1.26 g, 3.13 mmol, 82%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.96 – 8.89 (m, 1H), 8.79 – 8.74 (m, 1H), 8.72 – 8.67 (m, 1H), 8.23 (dt, *J* = 7.9, 1.3 Hz, 2H), 7.90 – 7.84 (m, 1H), 7.80 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.64 – 7.40 (m, 8H), 2.26 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 142.69, 141.32, 136.74, 135.95, 135.89, 135.80, 135.53, 133.41, 132.41, 131.10, 129.52, 129.37, 129.01, 128.24, 127.92, 127.53, 127.12, 127.10, 126.95, 125.09, 124.79, 124.54, 124.27, 123.41, 123.10, 122.81, 122.24, 121.88, 120.83, 120.50, 100.38, 77.30, 77.19, 76.99, 76.67, 19.40, 16.91. (Found: C, 80.95; H, 4.54; N, 8.05; S, 6.31. Calc. for $C_{34}H_{23}N_3S$: C, 80.76; H, 4.59; N, 8.31; S, 6.34%).

1-(4-(dibenzo[b,d]thiophen-4-yl)-2,5-dimethylphenyl)-1H-phenanthro[9,10-*d*]imidazole (txI)

White solid (1.58 g, 3.13 mmol, 84%): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 8.27 – 8.16 (m, 3H), 7.86 (t, *J* = 4.2 Hz, 1H), 7.79 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.69 (ddd, *J* = 8.5, 7.0, 1.4 Hz, 1H), 7.62 (td, *J* = 7.8, 2.7 Hz, 2H), 7.54 – 7.37 (m, 7H), 2.19 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 142.35,

139.53, 136.13, 135.92, 135.81, 135.37, 133.67, 132.47, 129.62, 129.37, 128.51, 127.76, 127.06, 127.00, 126.21, 125.81, 124.84, 124.60, 124.13, 123.21, 122.93, 122.77, 122.62, 121.92, 120.89, 120.34, 77.30, 77.19, 76.99, 76.67, 19.41, 17.02. (Found: C, 83.70; H, 4.82; N, 5.49; S, 6.45. Calc. for $C_{35}H_{24}N_2S$: C, 83.30; H, 4.79; N, 5.55; S, 6.35%).

1-(4-(dibenzo[b,d]thiophen-4-yl)phenyl)-1H-phenanthro[9,10-*d*]imidazole (tpI)
White solid (10.20 g, 21.4 mmol, 80 %): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (ddd, *J* = 10.6, 8.1, 4.4 Hz, 2H), 8.74 (dd, *J* = 9.1, 5.2 Hz, 2H), 8.29 – 8.21 (m, 2H), 8.13 (s, 1H), 8.06 – 8.01 (m, 2H), 7.92 – 7.86 (m, 2H), 7.81 – 7.57 (m, 6H), 7.56 – 7.48 (m, 2H), 7.43 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 141.99, 141.72, 139.32, 138.46, 138.00, 137.25, 136.57, 135.67, 135.42, 129.81, 129.31, 128.38, 127.56, 127.47, 127.23, 127.11, 127.03, 126.44, 126.35, 125.76, 125.35, 125.32, 124.65, 124.18, 123.18, 122.71, 122.68, 122.60, 121.87, 121.31, 121.22

2. Photophysical measurements and spectra

UV–visible spectra were recorded on a Hewlett–Packard 4853 diode array spectrometer. Steady state photoluminescent spectra were measured using a QuantaMaster Photon Technology International phosphorescence/fluorescence spectrofluorometer, whereas gated phosphorescence was measured on the same instrument using a Xe flash lamp with 40 μs delay. Photoluminescent quantum yield (PLQY) measurements were carried out using a Hamamatsu C9920 system equipped with a Xe lamp, calibrated integrating sphere and model C10027 photonic multi-channel analyzer (PMA). Photophysical measurements were carried out in 2-methyltetrahydrofuran (2-MeTHF). Samples were deoxygenated by bubbling N_2 in a quartz cuvette fitted with a Teflon stopcock. Spin-coated films were prepared on quartz substrates, and photoluminescence quantum yield (PLQY) measurements were done under nitrogen atmosphere.

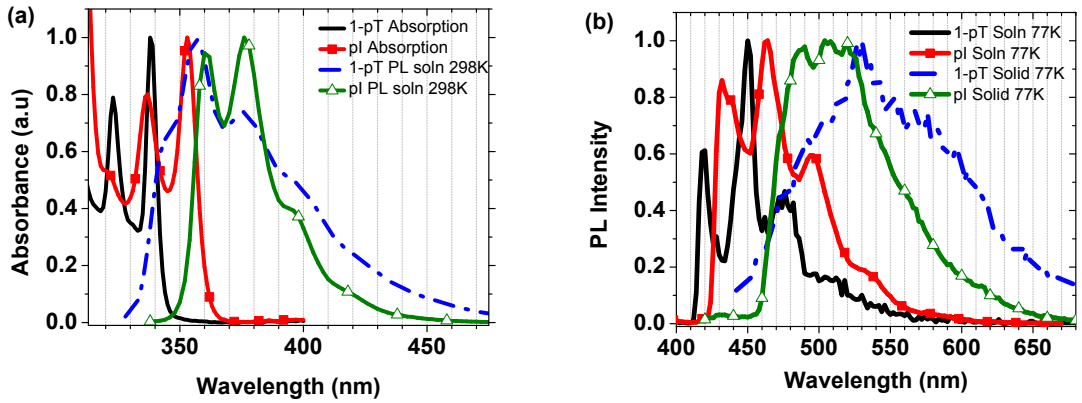


Fig. S1. (a) Absorption spectra and normalized emission spectra in 2-MeTHF at 298K. (b) Normalized emission spectra in 2-MeTHF and neat solid at 77K.

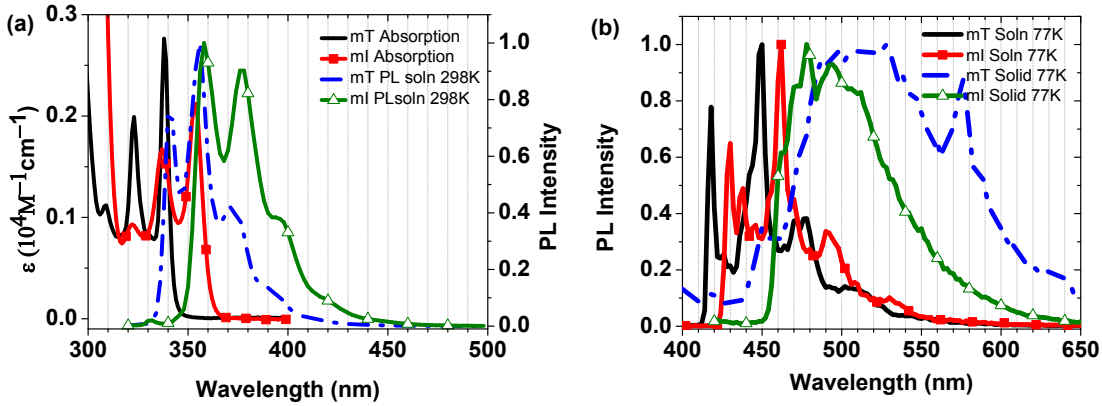


Fig. S2. (a) Absorption spectra and normalized emission spectra in 2-MeTHF at 298K. (b) Normalized emission spectra in 2-MeTHF and neat solid at 77K.

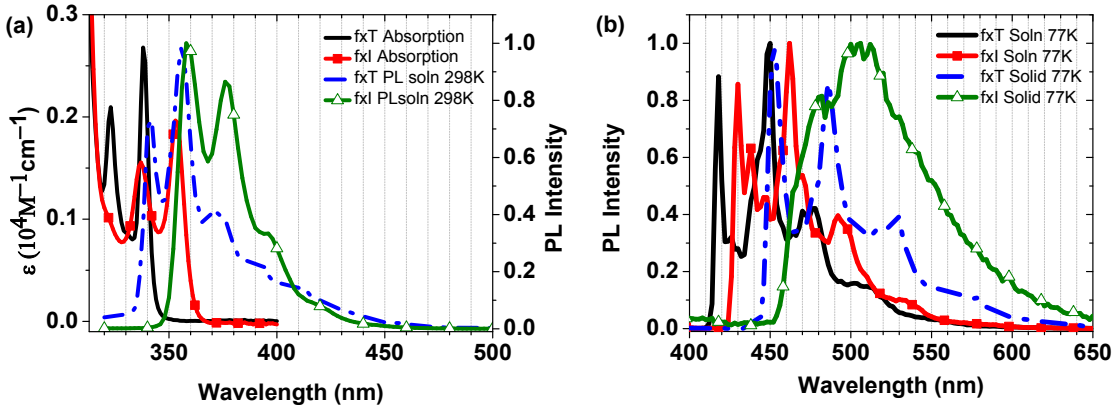


Fig. S3. (a) Absorption spectra and normalized emission spectra in 2-MeTHF at 298K. (b) Normalized emission spectra in 2-MeTHF and neat solid at 77K.

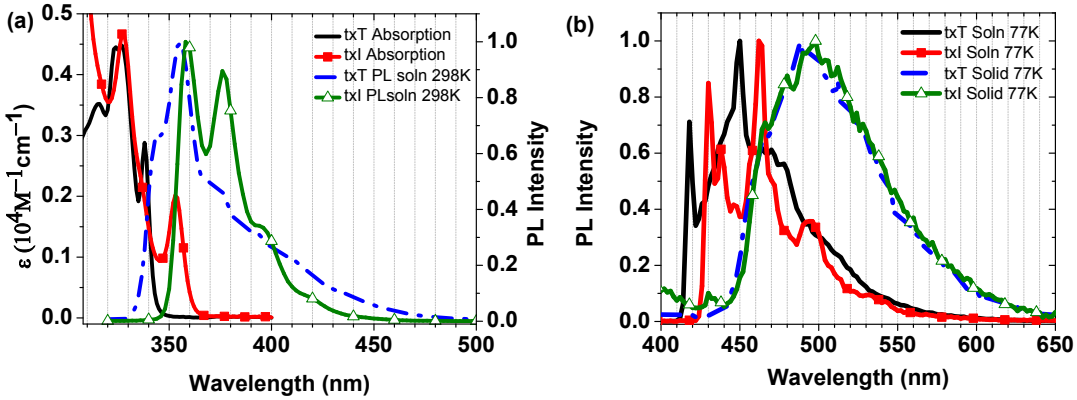


Fig. S4. (a) Absorption spectra and normalized emission spectra in 2-MeTHF at 298K. (b) Normalized emission spectra in 2-MeTHF and neat solid at 77K.

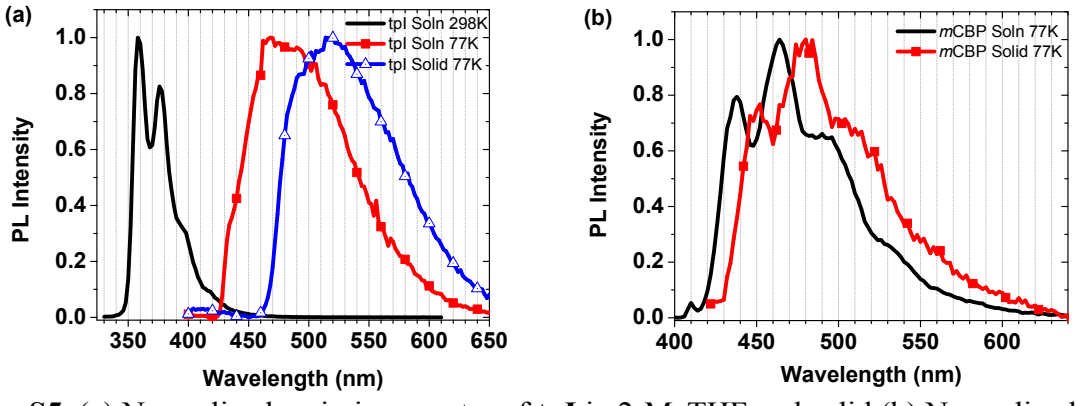


Fig. S5. (a) Normalized emission spectra of **tpI** in 2-MeTHF and solid (b) Normalized emission spectra of *m*CBP measured in 2-MeTHF and solid.

3. Thermal measurements and properties

Thermogravimetric analysis (TGA) measurements were performed on a NETZSCH STA 449F3 thermogravimeter by measuring weight loss while heating at a rate of 10°C min^{-1} under nitrogen. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC 8000 with CLN2 instrument at a heating rate of 10°C min^{-1} under nitrogen atmosphere.

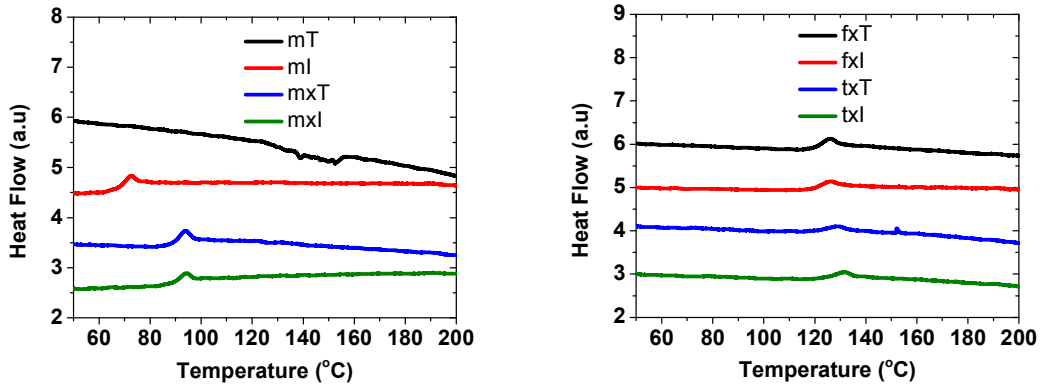


Fig. S6. DSC Curves of phenanthro[9,10-*d*]triazoles/imidazoles

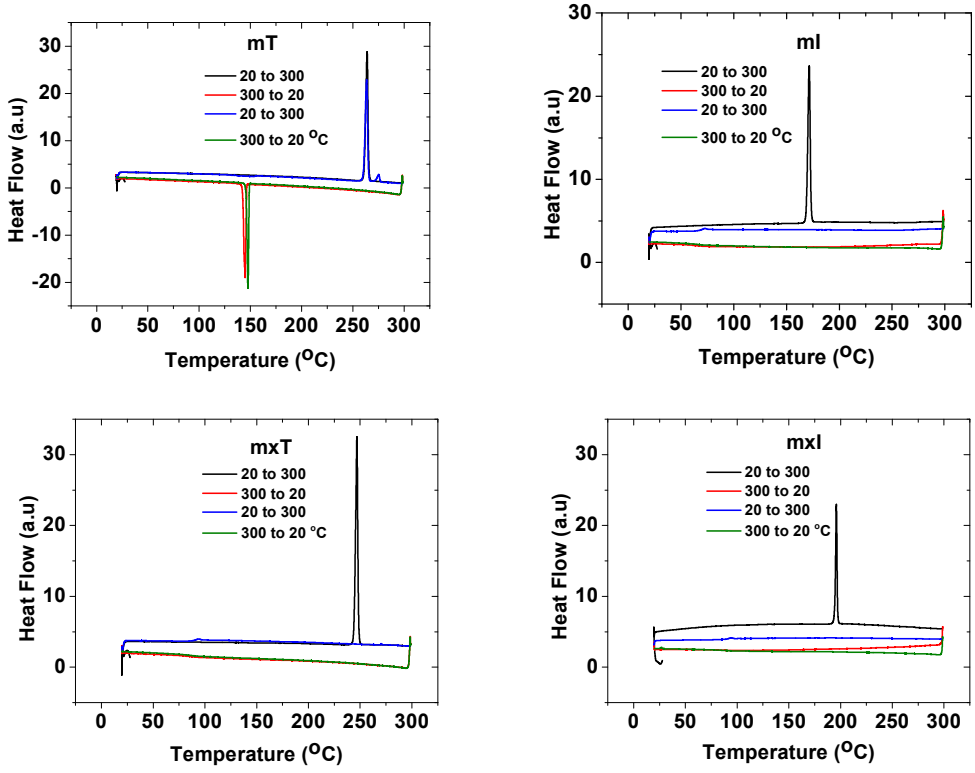


Fig. S7. DSC Heating curves of phenanthro[9,10-*d*]triazoles/imidazoles

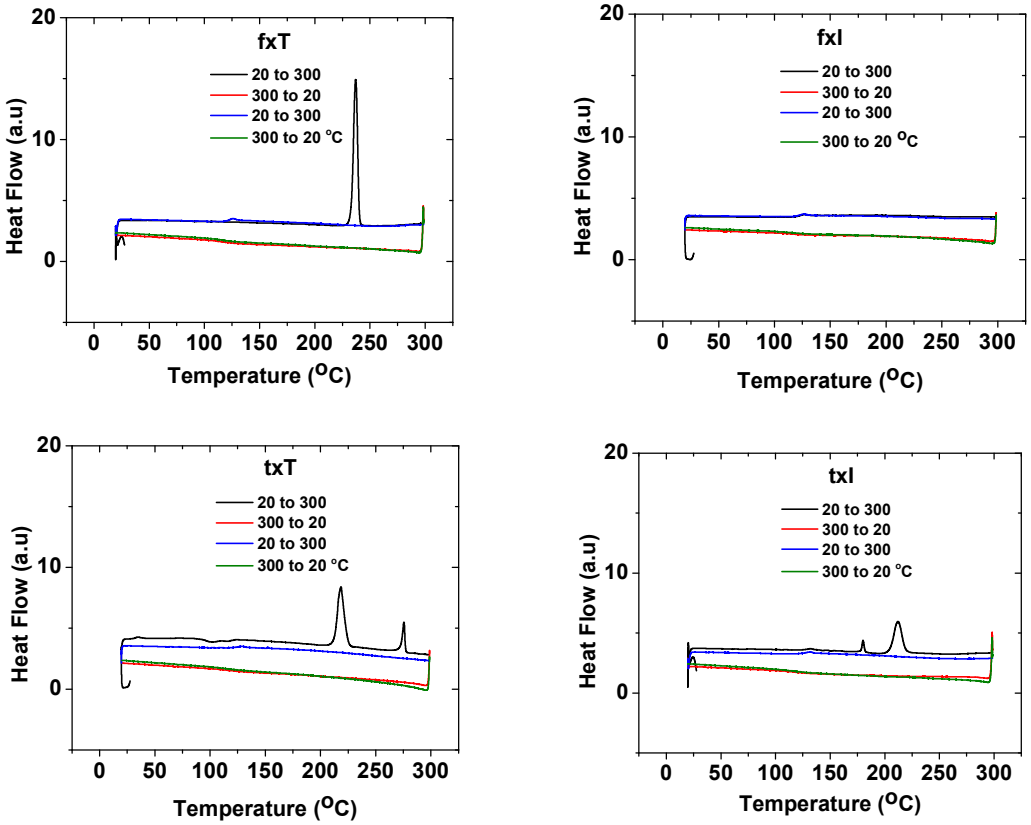


Fig. S8. DSC Heating curves of phenanthro[9,10-*d*]triazoles/imidazoles

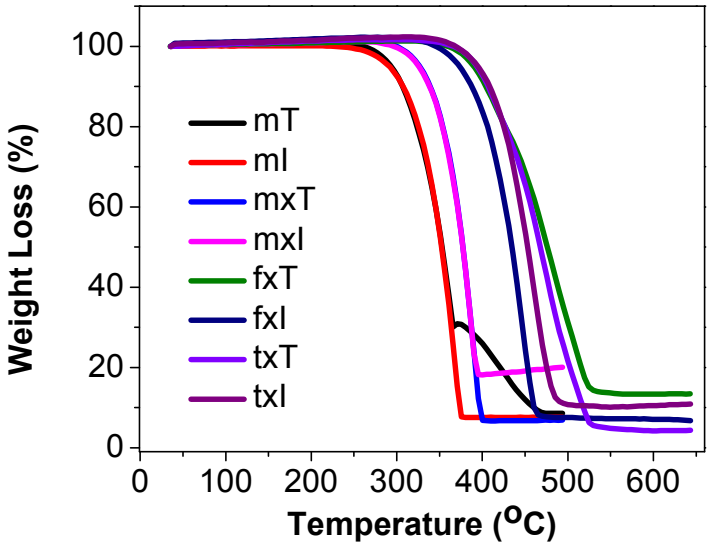


Fig. S9. TGA curves of phenanthro[9,10-*d*]triazoles/imidazoles

4. Electrochemical measurements and data

Cyclic voltammetry and differential pulse voltammetry were performed using a VersaSTAT 3 potentiostat. Anhydrous acetonitrile (Aldrich) solvent was used under nitrogen atmosphere with 0.1 M tetra(*n*-butyl)-ammonium hexafluorophosphate (TBAF) as the supporting electrolyte. A Ag wire was used as the pseudo reference electrode, a Pt wire as the counter electrode, and a glassy carbon rod working electrode. The redox potentials are based on the values from differential pulsed voltammetry measurements and are reported relative to the ferrocenium/ferrocene (Cp_2Fe^+/Cp_2Fe) redox couple used as an internal reference, whereas electrochemical reversibility was studied using cyclic voltammetry.

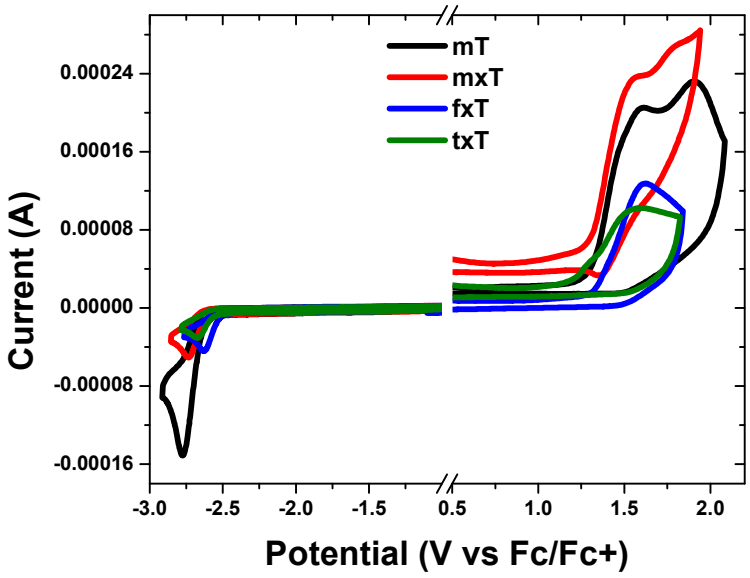


Fig. S10. Cyclic voltammetry curves of phenanthro[9,10-*d*]triazoles

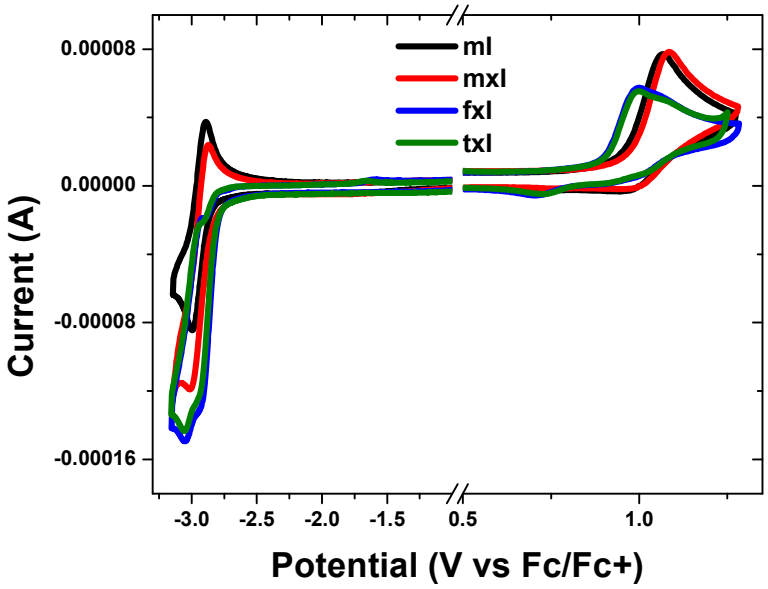


Fig. S11. Cyclic voltammetry curves of phenanthro[9,10-*d*]imidazoles

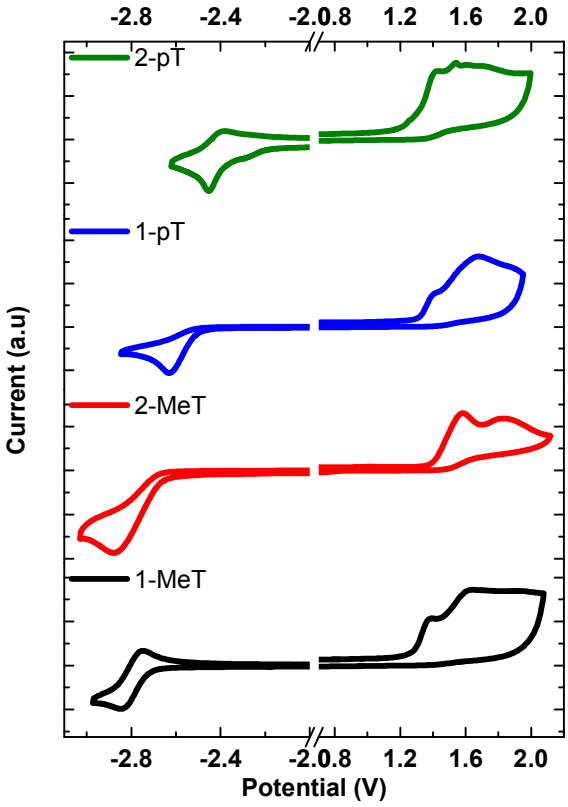


Fig. S12. Cyclic voltammetry curves of phenanthro[9,10-*d*]triazoles

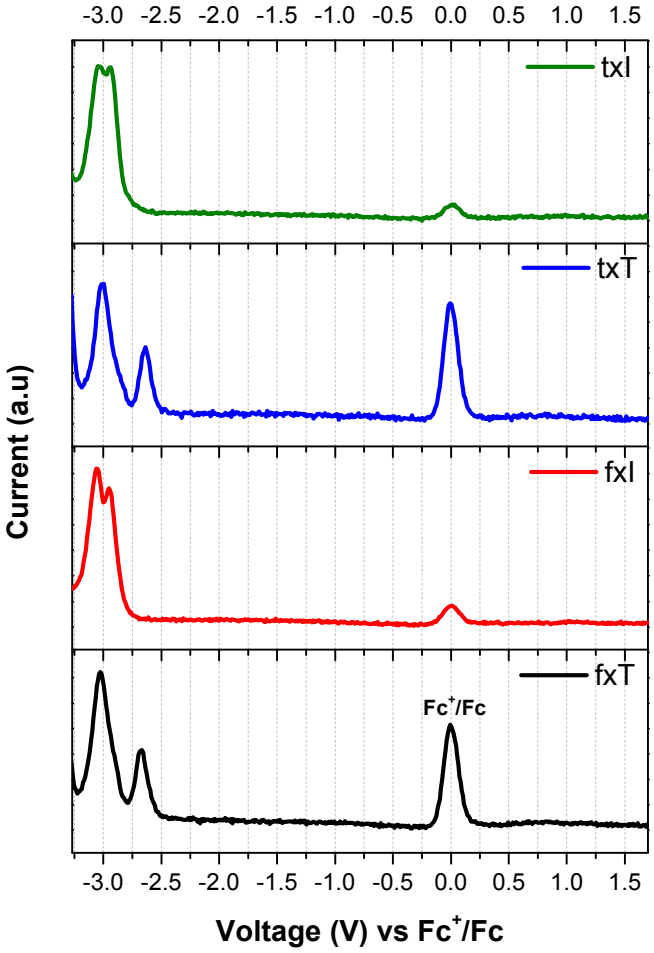


Fig. S13. DPV data of selected phenanthro[9,10-*d*]triazoles/imidazoles

5. Computational modeling

Calculations were performed using Jaguar 8.4 (release 12) software package on the Schrödinger Material Science Suite (v2017-2). Gas phase geometry optimization was obtained using B3LYP functional with the LACVP** basis set. The HOMO and LUMO energies were determined using minimized singlet geometries to approximate the ground state, whereas the triplet excited state is calculated using self-consistent field method (ΔSCF) by taking the difference between lowest singlet and triplet excited states.

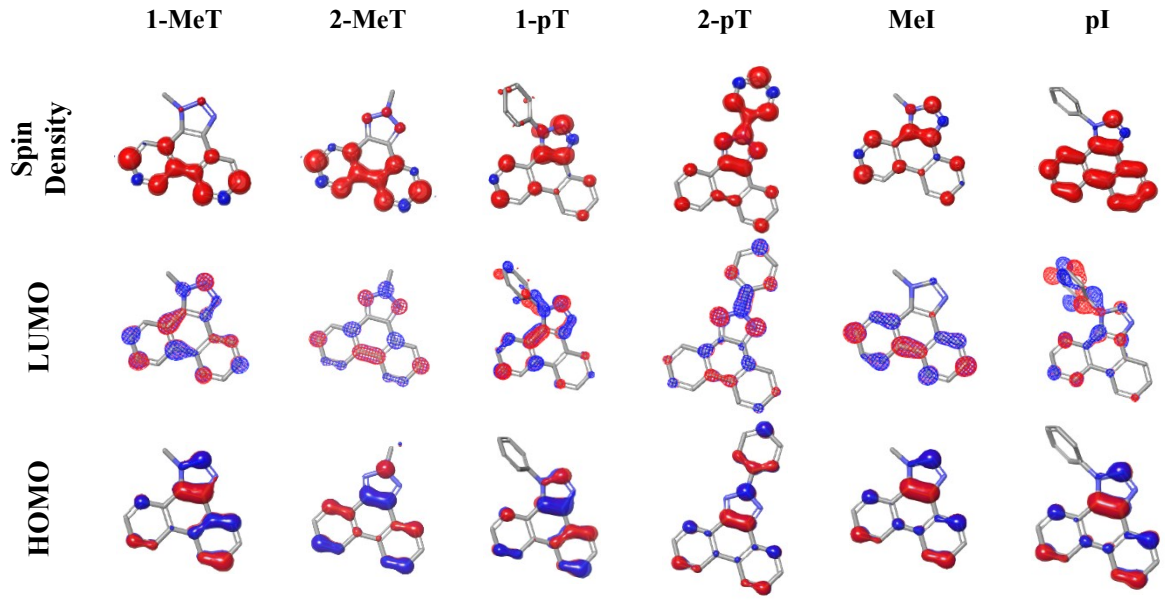


Fig. S14. Molecular orbital representation of phenanthro[9,10-*d*]triazoles and phenanthro[9,10-*d*]imidazoles

Table S1. Triplet energies of host materials

Compound	E_T (eV)		ΔT_1 (eV)[c]
	Solution[a]	Solid[b]	
1-MeT	2.97	2.66	0.30
2-MeT	2.97	2.64	0.33
MeI	2.91	2.70	0.21
tpI	2.88	2.64	0.24
***m*CBP**	2.93	2.86	0.07

[a]Gated phosphorescence with 40 μS delay measured in 2-MeTHF at 77K. [b]Gated phosphorescence with 40 μS delay measured as a neat powder. [c]Difference between triplet in solution and neat solid. All the triplet energies are obtained from the onset spectra. The onset was chosen as the wavelength when the PL intensity reaches 0.2 with the peak normalized to 1.0.

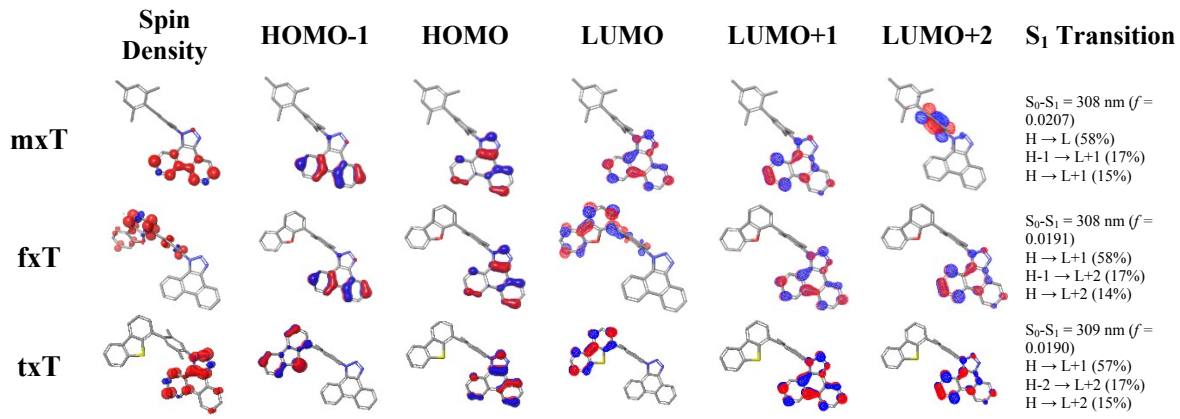


Fig. S15. Molecular orbital representation of phenanthro[9,10-*d*]triazoles (H = HOMO, L = LUMO)

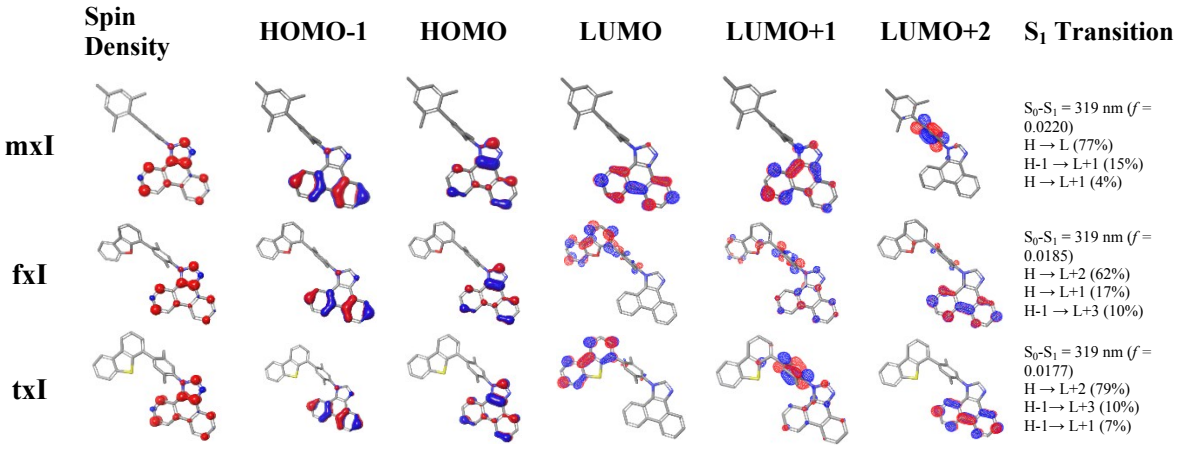


Fig. S16. Molecular orbital representation of phenanthro[9,10-*d*]imidazoles (H = HOMO, L = LUMO)

6. OLED Fabrication and Studies

Glass substrates with pre-patterned, 1 mm wide indium tin oxide (ITO) stripes were cleaned by sequential sonication in tergitol, deionized water, acetone, and isopropanol, followed by 15 min UV ozone exposure. Organic materials and metals were deposited at rates of 0.5-2 Å/s through shadow masks in a vacuum thermal evaporator with a base pressure of 10^{-7} Torr. A separate shadow mask was used to deposit 1 mm wide stripes of 100 nm thick Al films perpendicular to the ITO stripes to form the cathode, resulting in 2 mm^2 device area. The device structure is: glass substrate / 70 nm ITO / 5 nm dipyrazino[2,3,-f:20,30-h]quinoxaline 2,3,6,7,10,11-hexacarbonitrile (HATCN) / 40 nm 4,4′-cyclohexylidenebis [N,N-bis(4-methylphenyl)benzenamine] (TAPC) / 10 nm N,N'-dicarbazolyl-3,5-benzene (*m*CP)/8 vol% FIrpic:Host / 45 nm BP4mPy / 1.5 nm 8-hydroxyquinolinato lithium (LiQ) / 100 nm Al. The host is either 3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl (*m*CBP), 2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine (26DCzppy) or one of the phenanthro-imidazole/triazole compounds.

A semiconductor parameter analyzer (HP4156A) and a calibrated large area photodiode that collected all light exiting the glass substrate were used to measure the *J-V*-luminance characteristics. The device spectra were measured using a fiber-coupled spectrometer. All devices were packaged under dry nitrogen prior to testing.

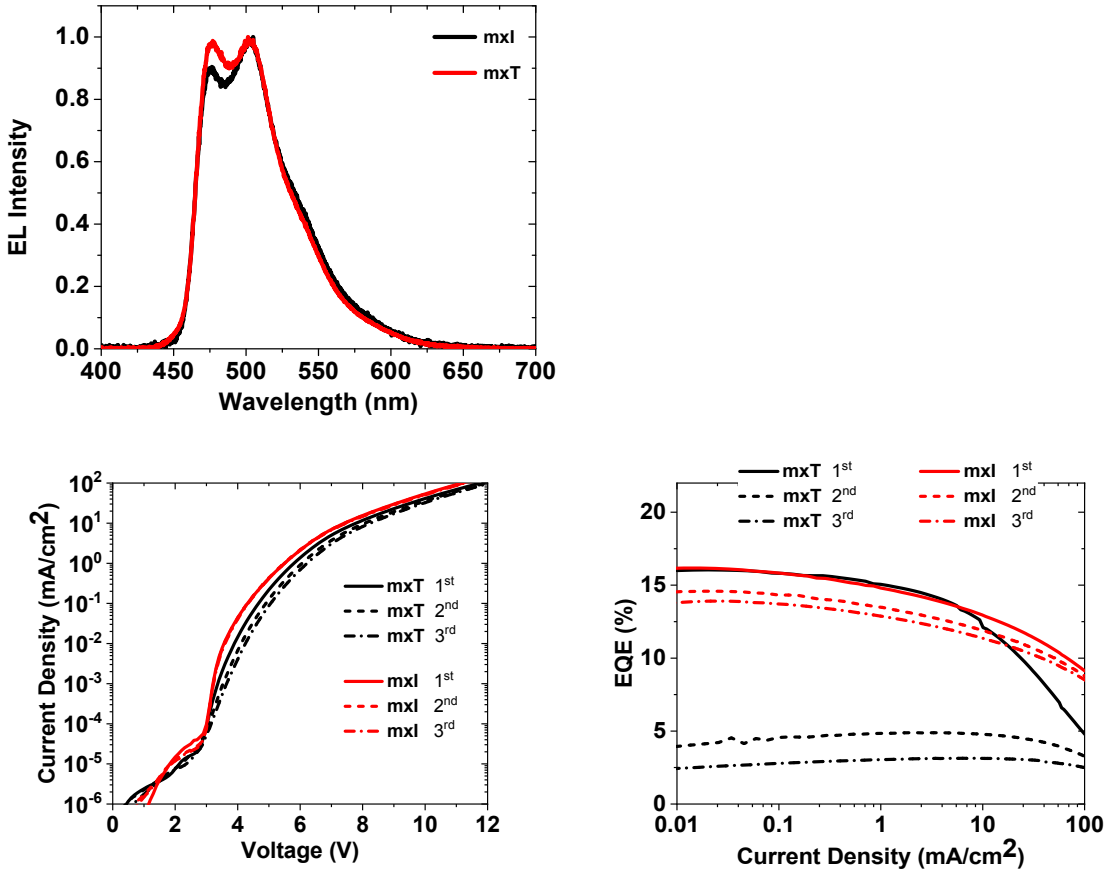


Fig. S17. Comparative OLED testing for devices with phenanthro-tirazole (**mxT**) and phenanthro-imidazole (**mxI**) host materials. The device structure used here was 70 nm ITO/5 nm HATCN/40 nm TAPC/10 nm mCP/20 nm8 vol% FIrpic:Host/45 nm BP4mPy/1.5 nm LiQ/100 nm Al). 1st, 2nd and 3rd refer to the 1st, 2nd and 3rd J-V scans of the device between 0 and 12 V (J = 0 – 100 mA/cm^2. The J-V characteristics show of the triazole become more resistive with repeated scans, while the imidazole based device J-V characteristic is unchanged. Also, the EQE values for the triazole drop markedly on the 2nd and 3rd J-V scan of the devices. The significantly higher roll-off in device efficiency for the triazole based device at J > 10 mA/cm^2 is attributed to device degradation at the higher current density. The electroluminescence (EL) spectra are nearly independent of the host material, with minor spectral differences likely caused by cavity effects on the position of the exciton formation zone.

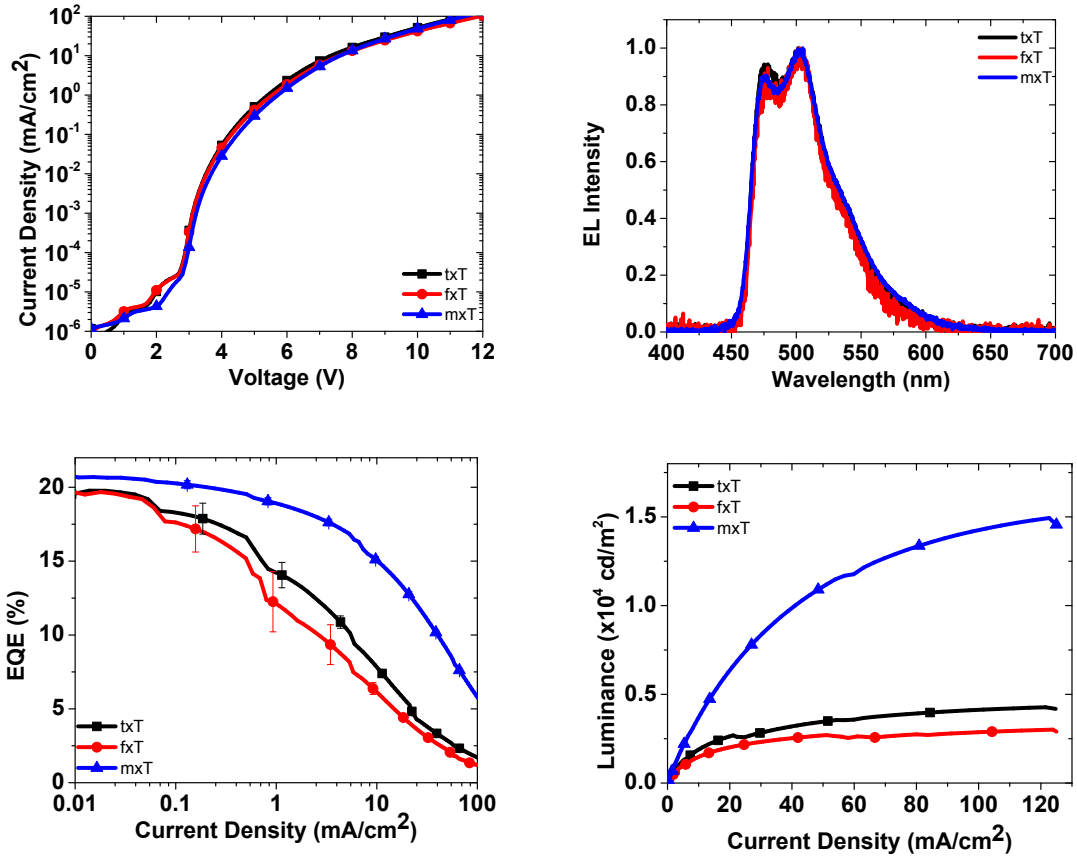


Fig. S18. OLED device characteristics of phenanthro[9,10-*d*]triazoles

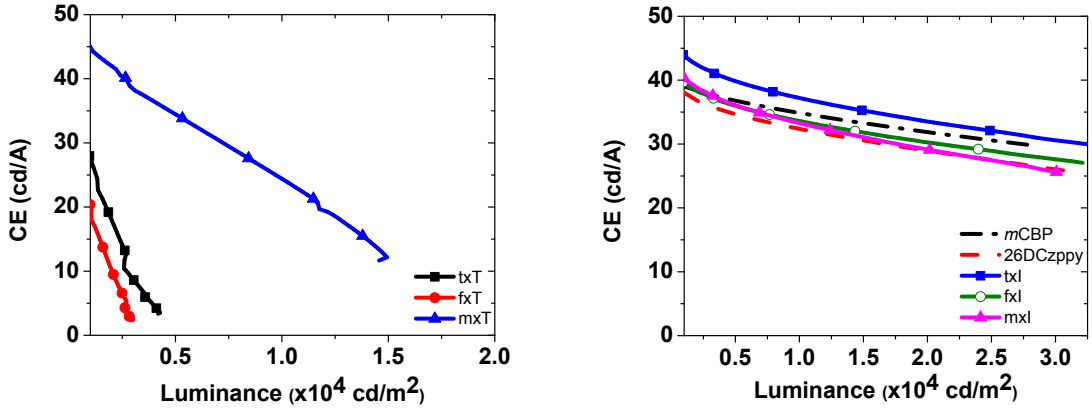


Fig. S19. Current Efficiency plot of phenanthro[9,10-*d*]triazoles and phenanthro[9,10-*d*]imidazoles

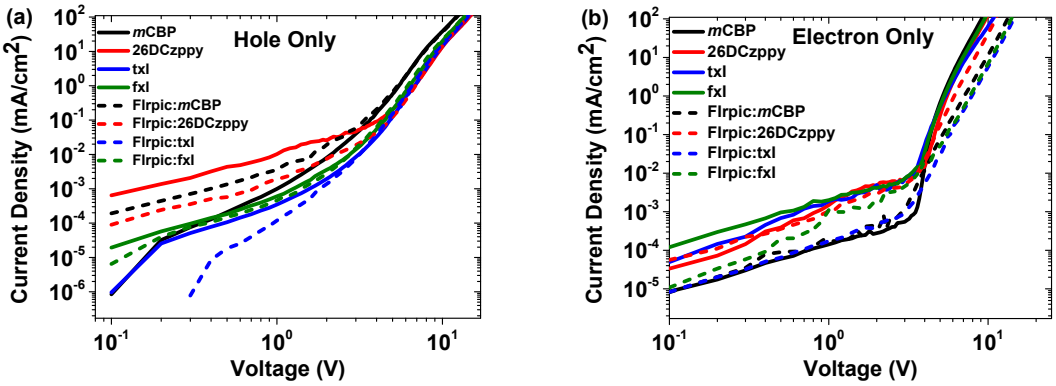


Fig. S20. (a) Hole only Structure: 20 min UV Ozone 70 nm ITO / 5 nm HATCN / 20 nm TAPC / 10 nm mCP / 20 nm 8vol% FIrpic:host or neat host / 10 nm HATCN / 100 nm Al. (b) Electron only Structure: no UV Ozone 70 nm ITO / 30 nm BP4mPy / 20 nm 8 vol% Firpic:host or neat host / 30 nm BP4mPy / 1.5 nm LiQ / 100 nm Al

7. References

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