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Supporting Information

Excited state managing molecular design platform of blue thermally activated delayed fluorescence emitters by π linker engineering

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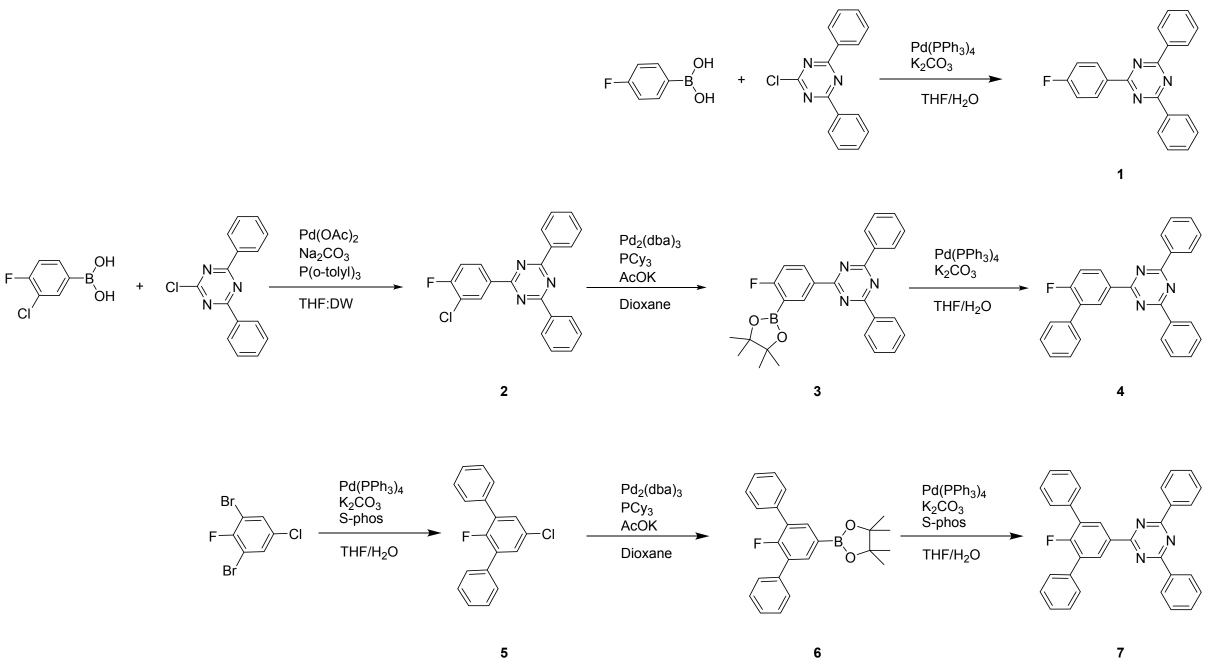
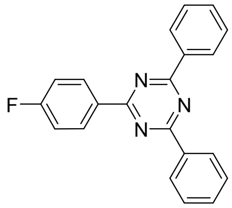


Scheme S1. Synthetic route of fluoro intermediates of TADF emitters.

Pd(II) and phosphine ligands were used to selectively couple the boronic acid with 2-positioned chloride triazine, and only 2hr of reaction time proceeded to minimize side reactions, resulting in a high yield of 94% of compound **2**, borylation was carried out at the chloro position provided compound **3**. Suzuki-Miyaura cross-coupling reaction was finally carried out with a bromobenzene with the use of a Pd catalyst in the general same manner as compuound **1** in 83% yield. **1PCTrz** was synthesized through S_NAr reaction between **4** and N-carbazolylcarbazole with Cs_2CO_3 in anhydrous *N,N*- dimethylformamide. For the synthesis of the final target **2PCTrz**, a different additive was put into reaction mixture for cross-coupling reaction. The placement of diphenyl attached at the triazine unit in **2PCTrz** would require compound **5** and **7**. Ligand S-phos was added to the general Suzuki reaction conditions to increase the reaction yield by lowering the activation energy. Accordingly, the reaction yield was found to be increased to 93%. The following the same procedure as that used for the synthesis of **CTrz** and **1PCTrz**, using **7** and *N*-carbazolylcarbazole were synthesized **2PCTrz**. Detailed synthesis of fluoro intermediates of the TADF emitters explained below.

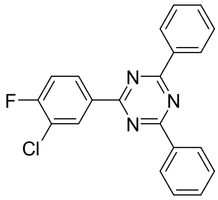
2-(4-Fluorophenyl)-4,6-diphenyl-1,3,5-triazine (1)



1

A mixture of (4-fluorophenyl)boronic acid (2.74 g, 19.61 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (5.0 g, 18.68 mmol) and tetrakis(triphenylphosphine)palladium(0) (1.08 g, 0.93 mmol, 5 mol %) in 30 mL of anhydrous tetrahydrofuran was refluxed under argon for 4 h. To the reaction mixture was slowly added a solution of potassium carbonate (5.16 g, 37.35 mmol) in 30 mL of water. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/n-hexane (1/1) and 5.09 g (83 %) of 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (**1**) was obtained a white solid.

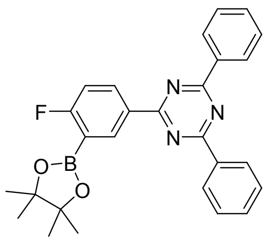
2-(3-chloro-4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (2)



2

A mixture of (3-chloro-4-fluorophenyl)boronic acid (14.70 g, 84.32 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (21.5 g, 80.31 mmol), tris(o-tolyl)phosphine (0.98g, 3.21 mmol) and palladium(II)acetate (0.36 g, 1.61 mmol, 2 mol %) in 190 mL of anhydrous tetrahydrofuran was refluxed under argon for 2 h. To the reaction mixture was slowly added a solution of sodium carbonate (12.77 g, 120.46 mmol) in 85 mL of water. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/n-hexane (1/1) and recrystallized in ethyl acetate to give 27.43 g (94 %) of 2-(3-chloro-4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (**2**) was obtained a white solid.

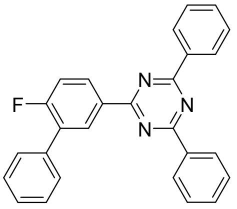
2-(2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4,6-diphenyl-1,3,5-triazine (3)



3

2-(3-Chloro-4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (**2**) (28.1g, 77.67 mmol), bis(pinacolato)diboron (39.45 g, 155.33 mmol), potassium acetate (22.87 g, 233.00 mmol), tricyclohexylphosphine (2.187 g, 7.77 mmol) and tris(dibenzylideneacetone)dipalladium(0) (7.11 g, 7.77 mmol) were dissolved in 1,4-dioxane (155 mL) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h. The mixture was filtered, diluted with ethyl acetate, and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated with a rotary evaporator. The crude product was purified by column chromatography by dichloromethane/n-hexane (1/1) and the dried under vacuum to give 2-(2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4,6-diphenyl-1,3,5-triazine (**3**) (32.40 g, 92 %).

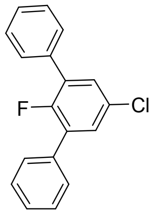
2-(6-Fluoro-[1,1'-biphenyl]-3-yl)-4,6-diphenyl-1,3,5-triazine (4)



4

A solution of bromobenzene (4.6g, 29.30 mmol), 2-(2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4,6-diphenyl-1,3,5-triazine (**3**) (19.92g, 43.95 mmol), potassium carbonate (8.09g, 58.59 mmol) in tetrahydrofuran (60 mL), and water (30 mL) was stirred under nitrogen for 30 min. After addition of tetrakis(triphenylphosphine)palladium(0) (0.68g, 0.59 mmol) to the solution, it was stirred at 80°C under nitrogen for 3 h. After cooling, the solution was evaporated, and toluene was added. The organic phase was washed with water, dried over anhydrous $MgSO_4$, and then filtered. Evaporation of the filtrate gave the crude product, which was purified by column chromatography using a dichloromethane/n-hexane(1/2) to give compound **4** as a white yellow powder (9.29 g, 79 %).

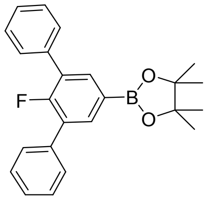
5'-Chloro-2'-fluoro-1,1':3',1''-terphenyl (5)



5

A mixture of phenylboronic acid (63.43 g, 520.22 mmol), 1,3-dibromo-5-chloro-2-fluorobenzene (50.00 g, 173.41 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-phos, 14.24g, 34.68 mmol) and tetrakis(triphenylphosphine)palladium(0) (20.04 g, 17.34 mmol, 10 mol %) in 300 mL of anhydrous tetrahydrofuran was refluxed under argon for 16 h. To the reaction mixture was slowly added a solution of potassium carbonate (95.87 g, 693.63 mmol) in 300 mL of water. After allowing it to cool to ambient temperature, the reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/n-hexane (1/1). Recrystallization was carried out using n-hexane only, and was rapidly formed by lowering the temperature below 5 °C using an ice bath. A large amount of white solid of 5'-chloro-2'-fluoro-1,1':3',1''-terphenyl (**5**) were obtained in 83% yield.

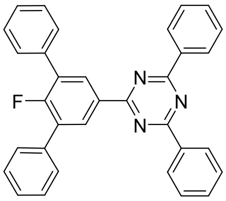
2-(2'-Fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



6

5'-Chloro-2'-fluoro-1,1':3',1''-terphenyl (**5**) (40.66g, 143.81 mmol), bis(pinacolato)diboron (54.78 g, 215.71 mmol), potassium acetate (35.29 g, 359.52 mmol), tricyclohexylphosphine (4.03 g, 14.38 mmol) and tris(dibenzylideneacetone)dipalladium(0) (13.17 g, 14.38 mmol) were dissolved in 1,4-dioxane (290 mL) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 20 h. The mixture was filtered, diluted with toluene, and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated with a rotary evaporator. The crude product was purified by column chromatography by dichloromethane/n-hexane (2/3) and the dried under vacuum to give 2-(2'-fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6**) (47.0 g, 87 %).

2-(2'-Fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,6-diphenyl-1,3,5-triazine (7)



7

A mixture 2-(2'-fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6) (30.20 g, 80.68 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (18.0 g, 67.23 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-phos, 5.52 g, 13.45 mmol) and tetrakis(triphenylphosphine)palladium(0) (3.89 g, 3.36 mmol, 5 mol %) in 110 mL of anhydrous tetrahydrofuran was refluxed under argon for 19 h. To the reaction mixture was slowly added a solution of potassium carbonate (18.59 g, 134.47 mmol) in 110 mL of water. After allowing it to cool to ambient temperature, the reaction mixture was extracted with toluene and water. The organic layer was evaporated with a rotary evaporator. The product was purified by column chromatography using dichloromethane/n-hexane (1/1) and 30.0 g (93 %) of 2-(2'-fluoro-[1,1':3',1''-terphenyl]-5'-yl)-4,6-diphenyl-1,3,5-triazine (**7**) was obtained a white solid.

Table S1. Calculated values of material properties of TADF emitters

TADF emitter	Overlap (S1)	Overlap (T1)	ΔE_{ST} (eV)	Reorganization energy (eV)	SOC matrix element (cm^{-1})	k_{RISC} ($10^5 s^{-1}$)
CTrz	0.22	0.68	0.24	0.253	0.289	0.646
1PCTrz	0.17	0.61	0.16	0.180	0.204	1.29
2PCTrz	0.14	0.53	0.11	0.118	0.217	7.59

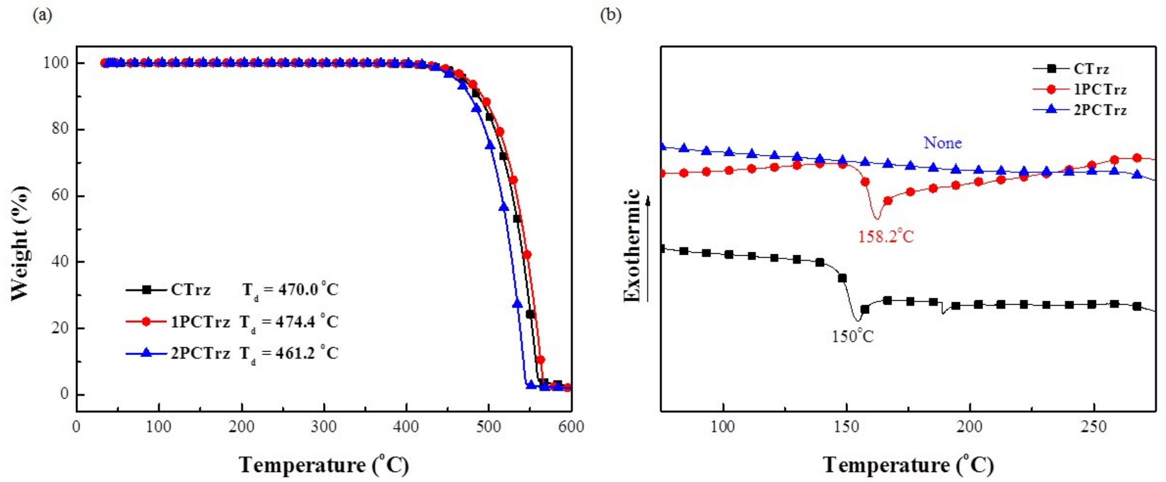


Figure S1. (a) TGA and (b) DSC traces of **CTrz**, **1PCTrz** and **2PCTrz** recorded under nitrogen at a heating rate of 10^{o}C/min.

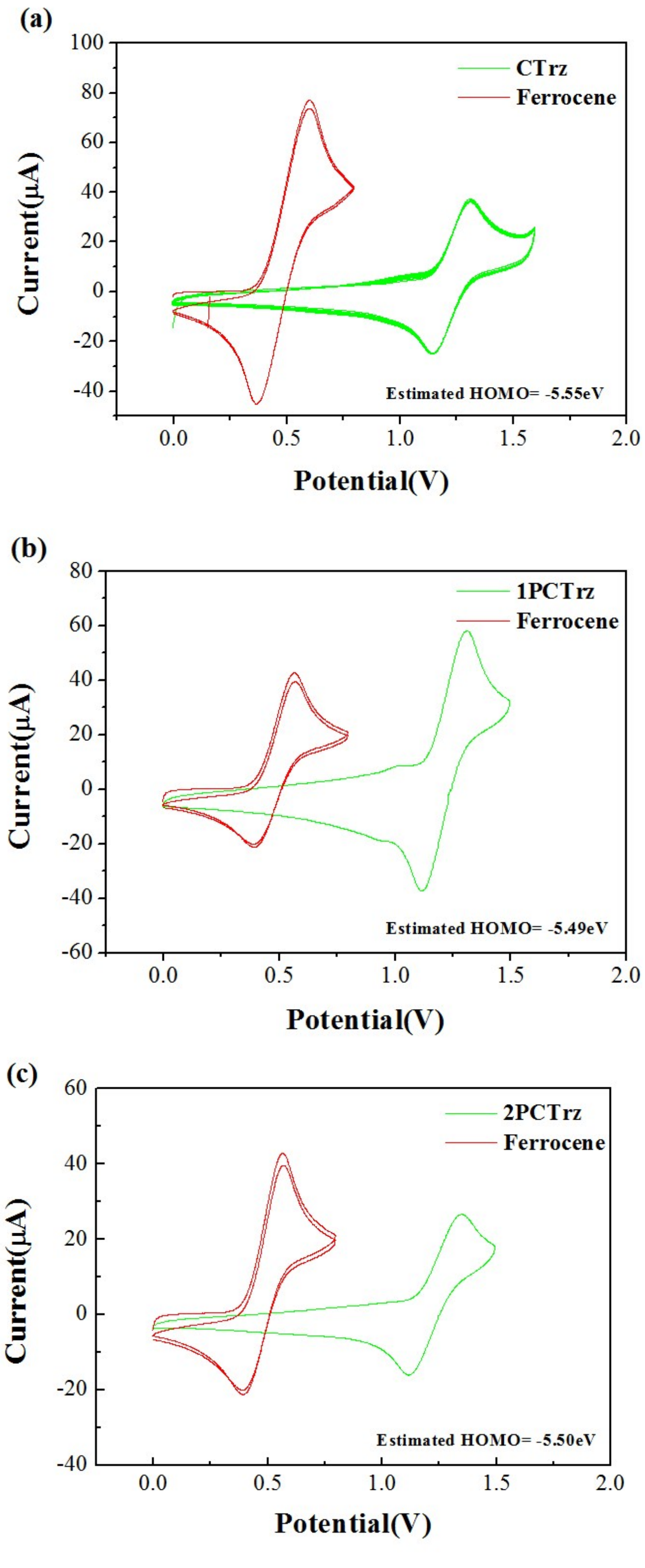


Figure S2. CV spectra of (a**) CTrz**, (b) **1PCTrz** and (c) **2PCTrz** of the TADF emitters.