Supplementary Information

Exploring Mechanism of Generating Spin-Orbital Coupling through Donor-Acceptor Design to Realize Spin Flipping in Thermally Activated Delayed Fluorescence

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Supplementary Figures

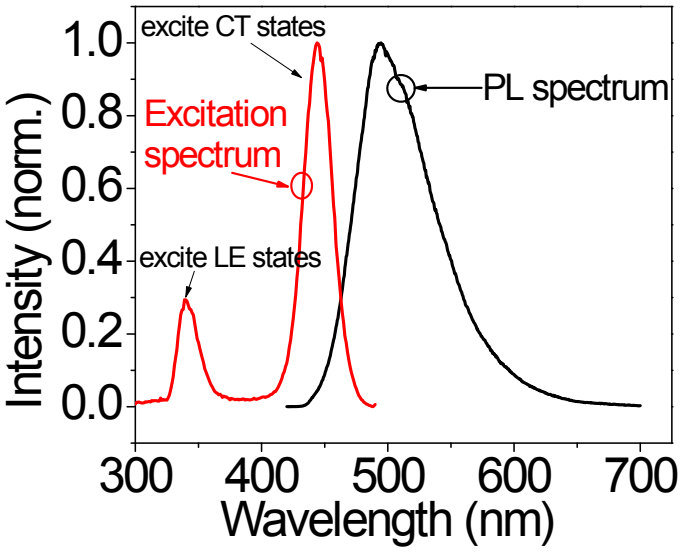


Figure S1. Excitation and PL spectrum for DMAC-TRZ toluene solution. The excitation spectrum is measured by recording the PL peak intensity at 495 nm as the function of the excitation wavelength. PL spectrum is recorded by using 405 nm wavelength excitation. There are two excitation peaks corresponding to localized states excitation and CT states excitation, respectively. The directly excitation of CT states gives stronger emission compared with localized states excitation.

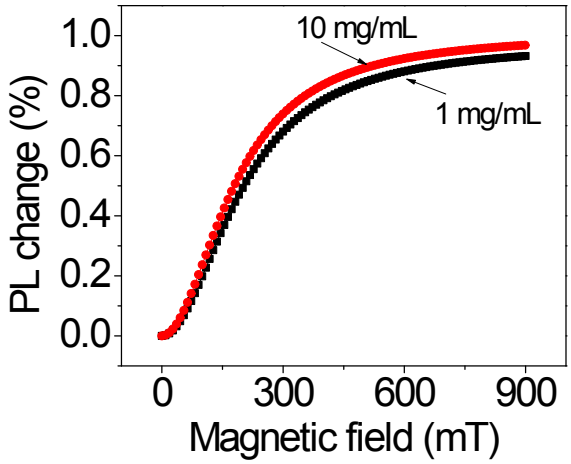


Figure S2. Magneto-PL of DMAC-TRZ in toluene solutions under 405 nm laser excitation with different concentrations. The concentration of the DMAC-TRZ does not have a significant influence on the spin mixing since it is very difficult to form intermolecular interactions between TADF molecules in solution.

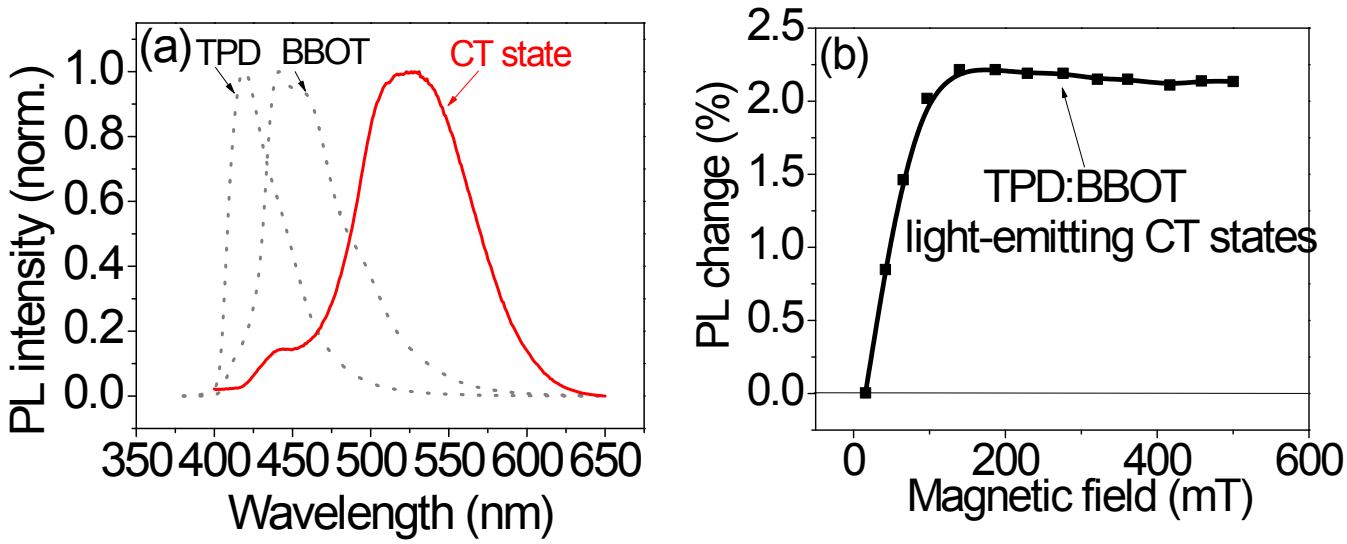
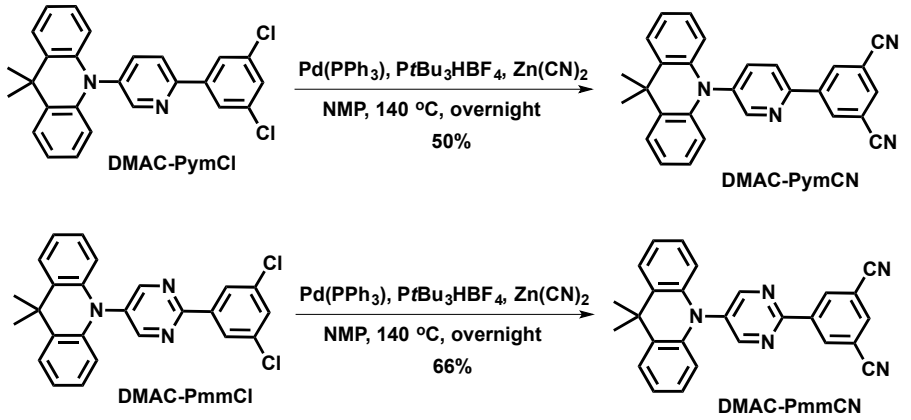


Figure S3. (a) PL spectra for pristine TPD, pristine BBOT, and TPD:BBOT (1:1) in toluene solution. (b) Magneto-PL from TPD:BBOT light-emitting charge-transfer states occurring in spin-orbital coupling regime (>10 mT).

Synthesis procedure of DMAC-PymCN and DMAC-PmmCN:



5-(5-(9,9-dimethylacridin-10(9*H*)-yl)pyridin-2-yl)isophthalonitrile (DMAC-PymCN):

A mixture of 10-(6-(3,5-dichlorophenyl)pyridin-3-yl)-9,9-dimethyl-9,10-dihydroacridine (**DMAC-PymCl**) (0.431 g, 1 mmol), $Zn(CN)_2$ (0.164 g, 1.4 mmol), $Pd(PPh_3)_4$ (0.462 g, 0.4 mmol) and P*t*Bu_3HBF_4 (0.239 g, 0.8 mmol) in dry NMP (10 mL) was heated to 140 °C for overnight under an argon atmosphere. After cooling to room temperature, the reaction was extracted with EA and water. The organic layer was dried over anhydrous $MgSO_4$, and concentrated to give the crude product which was then purified by column chromatography (SiO_2, CH_2Cl_2/Hexane = 1/1) to afford **DMAC-PymCN** as a yellow solid (0.208 g, 50%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.70 (s, 6 H), 6.28-6.31 (m, 2 H), 6.98-7.01 (m, 4 H), 7.50-7.52 (m, 2 H), 7.92 (dd, *J* = 2.6, 8.2 Hz, 1 H), 8.03 (t, *J* = 1.4 Hz, 1 H), 8.08 (dd, *J* = 1.0, 8.2 Hz, 1 H), 8.69 (d, *J* = 1.6 Hz, 2 H), 8.72 (dd, *J* = 1.4, 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 31.3, 36.6, 114.6, 115.3, 117.3, 122.0, 122.7, 126.1127.1, 131.5, 134.9, 135.9, 139.1, 141.1, 141.2, 141.6, 152.3, 153.6. HRMS (m/z, ESI, $[M+H]^+$) calcd. for $C_{28}H_{21}N_4$ 413.1760, found 413.1739.

5-(5-(9,9-dimethylacridin-10(9*H*)-yl)pyrimidin-2-yl)isophthalonitrile (DMAC-PmmCN):

A mixture of 10-(2-(3,5-dichlorophenyl)pyrimidin-5-yl)-9,9-dimethyl-9,10-dihydroacridine (**DMAC-PmmCl**) (0.346 g, 0.8 mmol), $Zn(CN)_2$ (0.132 g, 1.12 mmol), $Pd(PPh_3)_4$ (0.37 g, 0.32 mmol) and P*t*Bu_3HBF_4 (0.186 g, 0.64 mmol) in dry NMP (8 mL) was heated to 140 °C for overnight under an argon atmosphere. After cooling to room temperature, the reaction was extracted with EA and water. The organic layer was dried over anhydrous $MgSO_4$, and concentrated to give the crude product which was then purified by column chromatography (SiO_2, CH_2Cl_2/ Hexane = 1/1) to afford **DMAC-PmmCN** as a yellow solid (0.199 g, 66%). ^{1}H

NMR (400 MHz, CD_2Cl_2): δ = 1.70 (s, 6 H), 6.36-6.38 (m, 2 H), 7.04-7.06 (m, 4 H), 7.52-7.54 (m, 2 H), 8.09 (t, *J* = 1.6 Hz, 1 H), 8.94 (s, 2 H), 9.10 (d, *J* = 1.2 Hz, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 31.0, 36.8, 115.1, 115.2, 117.3, 122.8, 126.3, 127.2, 132.5, 136.1, 137.1, 137.4, 140.2, 140.8, 159.6, 160.5. HRMS (m/z, MALDI, $[M+H]^+$) calcd. for $C_{27}H_{20}N_5$ 414.1713, found 414.1738.

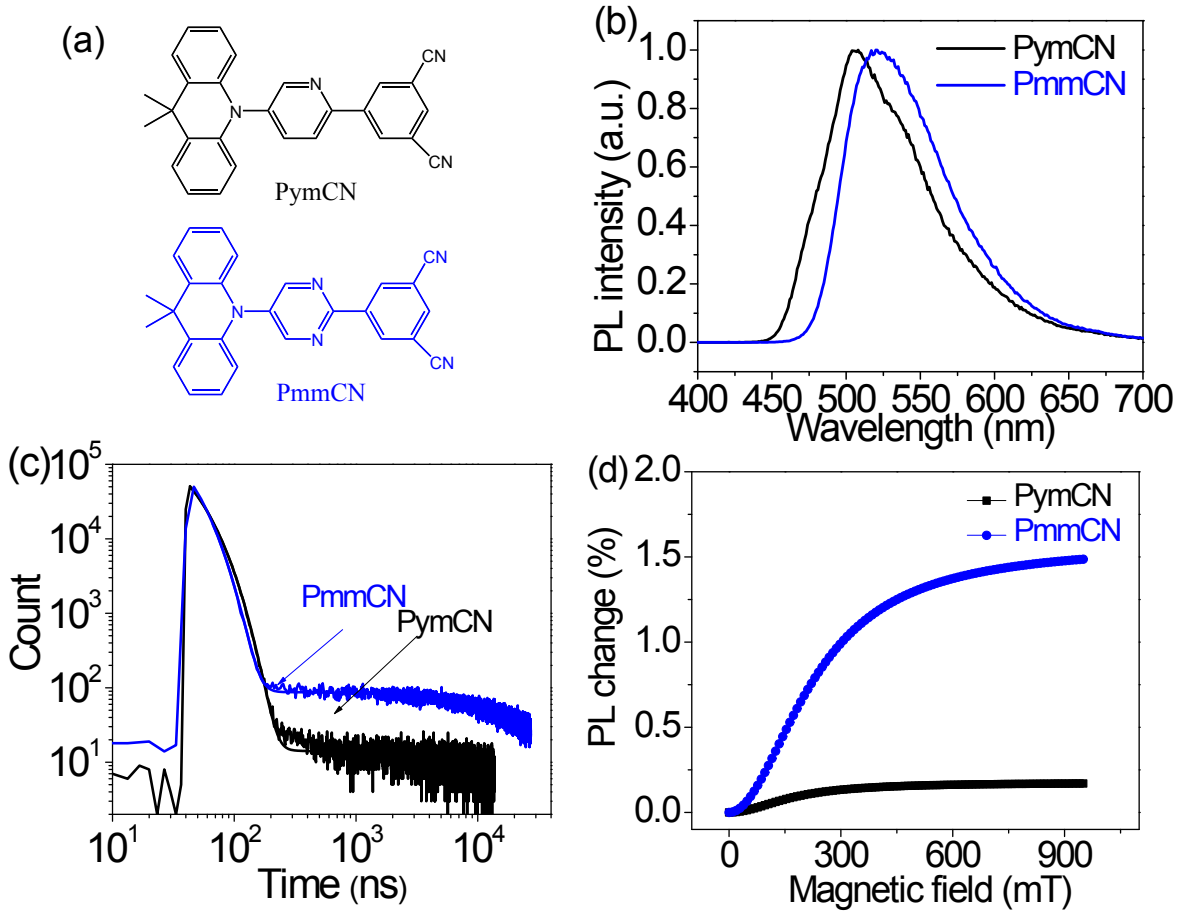


Figure S4. Magneto-optical studies on TADF molecule DMAC-PymCN and DMAC-PmmCN. (a) Molecular structure of DMAC-PymCN and DMAC-PmmCN; (b) PL spectra, (c) PL decay curves, and (d) magneto-PL of DMAC-PymCN and DMAC-PmmCN molecules in toluene solution (1 mg/mL) under 405nm laser excitation.