Supplementary Information

2,3-Dimethylindole as Donor for Novel Thermally Activated

Delayed Fluorescence Emitters

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General experimental information

All reagents for synthesis were purchased from Energy Chemical Co. and used as received without further purification. Detailed synthetic routes of the objective compounds are outlined in the synthesis section. ¹H and ¹³C NMR spectra were recorded on Bruker 500M spectrometer. Mass spectra were obtained using a Waters SQII mass detector. TGA figures were undertaken by using a Netzsch TG 209 unit under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 209 under N2 flow at a heating and cooling rate of 10 °C min⁻¹. CV was performed on a CHI600D electrochemical workstation with a Pt working electrode and a Pt wire counter electrode at a scanning rate of 100 mV s⁻¹ against a Ag/Ag⁺ (0.1 m of AgNO₃ in acetonitrile) reference electrode with a nitrogen-saturated anhydrous acetonitrile solution of 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate. UV-vis absorption spectra were measured by using a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Photoluminescence spectra were measured by using a Horiba Fluorolog luminescence spectrometer. PLOYs of the doped films were measured by using an integrating sphere on a Hamamatsu absolute PL quantumyield spectrometer C11347. Transient PL was measured with an Edinburgh FL920 fluorescence spectrophotometer. The wavelength of exciting light source was 295 nm, while emissions corresponding to doped DPEPO films' PL peaks were collected for DMI-Tz and BDMI-Tz, respectively.

Theoretical Calculation

All of the simulations were performed using the Gaussian 09_B01 program package ⁽¹⁾. Density functional theory (DFT) calculations were performed at the B3LYP/6-31G (d) and TD-B3LYP/6-31G* level to investigate DMI-Tz and BDMI-Tz's ground states geometries, FMOs distributions and energy level, oscillator strength, as well as energy of excited state at molecular level.

Synthesis



Scheme S1. Synthetic routes of DMI-Tz and BDMI-Tz

Synthesis of **DMI-Tz**: 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (3 mmol, 1.16 g), 2,3-dimethyl-1*H*-indole (3.5 mmol, 0.51 g) and cesium carbonate (6 mmol, 1.95 g) were added into 50 mL of *N*,*N*-dimethylformamide (DMF). The mixture was heated to 150 °C and stirred overnight. Then the reaction mixture was poured into 300 mL of water and extracted with dichloromethane (100 mL × 3). The organic phase was combined and dried over magnesium sulfate. After the solvent was removed, the product was purified through column chromatography on silica gel to afford the target compound as light green solid (1.15 g, yield: 81%). Highly purified product was then obtained via vacuum sublimation. MS (APCI⁺, m/Z): calcd. for C₃₁H₂₄N₄: 452.2; found: 453.2. Anal. calcd. for C₃₁H₂₄N₄: C 82.27, H 5.35, N 12.38; found: C 82.30, H 5.42, N 12.41. ¹H-NMR (500 MHz, CDCl₃, δ): 8.95 (d, *J* = 8.3 Hz, 2H), 8.88 (d, *J* = 6.5 Hz, 4H), 7.68-7.56 (m, 9H), 7.28-7.26 (m, 1H), 7.17 (pd, *J* = 7.0, 1.4 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H). ¹³C-NMR (126 MHz, CDCl₃, δ): 171.81, 171.05, 142.18, 136.97, 136.16, 135.01, 132.66, 132.49, 130.15, 129.18, 129.02, 128.71, 127.80, 121.54, 119.91, 118.07, 109.81, 109.08, 11.18, 8.91.

Synthesis of **BDMI-Tz**: This compound was synthesized according to the procedure as described above for the synthesis of **DMI-Tz** by combining 2,4-bis(4-bromophenyl)-6-phenyl-1,3,5-triazine (2 mmol, 0.93 g) and 2,3-dimethyl-1*H*-indole (4.4 mmol, 0.64 g), giving a light green solid in 84% yield. Highly purified product was then obtained via vacuum sublimation. MS (APCI⁺, m/Z): calcd. for C₄₁H₃₃N₅: 595.3; found: 596.3. Anal. calcd. for C₄₁H₃₃N₅: C 82.66, H 5.58, N 11.76; found: C 82.72, H 5.64, N 11.79. ¹H-NMR (500 MHz, CDCl₃, δ): 9.00 (d, *J* = 7.3 Hz, 4H), 8.88 (d, *J* = 7.5 Hz, 2H), 7.73-7.55 (m, 9H), 7.32 (d, *J* = 6.7 Hz, 2H), 7.21 (dd, *J* = 7.6, 3.6 Hz, 4H), 2.40 (s, 6H), 2.38 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃, δ): 171.92, 171.16, 142.33, 136.98, 136.07, 134.86, 132.83, 132.48, 130.21, 129.24, 129.09, 128.80, 127.83, 121.62, 120.00, 118.14, 109.83, 109.20, 11.24, 8.97.

Device Fabrication and Characterization

The substrates were cleaned with ultra-purified water and then dry-cleaned for 10 min by exposure to UV-ozone. Then the organic layers, LiF and Al were vacuum deposited successively (10^{-5} Pa). Deposition rates are 1 Å s⁻¹ for organic materials except light emitting dopant, 0.1 Å s⁻¹ for LiF, and 1.5 Å s⁻¹ for Al, respectively. EL spectra and luminance were taken by using an Photo Research PR-655 spectroradiometer. The current density–voltage characteristic was measured by using a Keithley source measure unit 2400.



Figure S1. (a) Differential scanning calorimetry (DSC) and (b) thermogravimetric analysis (TGA) thermograms of DMI-Tz and BDMI-Tz.



Figure S2. Low temperature PL spectra of DMI-Tz (top) and BDMI-Tz (bottom) in toluene solution at 77 K.

References:

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