

Supporting information

A Highly Efficient Thermally Activated Delayed Fluorescence Emitter Based on 5H-benzo[d]benzo[4,5]imidazo[1,2-a]imidazole Donor

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Experimental Section

General Methods

The chemicals and solvents were procured from commercial suppliers and were used as received. All reactions were carried out in an inert nitrogen atmosphere. Column chromatography with 100–200 mesh silica as a stationary phase was used to purify the compound. A 500 MHz NMR spectrometer was used to record the ^1H and ^{13}C NMR and the chemical shift values are expressed in terms of tetramethylsilane (0.00 ppm). The absorption and emission measurements were recorded with a UV-vis spectrophotometer. The absolute PLQYs of 20 wt% emitter doped film in a DPEPO host were measured using a calibrated integrating sphere connected to a spectrofluorometer. The 20 wt% emitter doped DPEPO film were used to collect transient PL data. Electrochemical measurements were collected on a CHI electrochemical analyzer with a conventional three electrode configuration containing a glassy carbon working electrode, a platinum wire auxiliary electrode, and a non-aqueous Ag/AgNO₃ acetonitrile reference electrode. An Fc/Fc⁺ internal standard was used to calibrate the peak potentials. Theoretical calculations were performed using DFT computational on the Gaussian 16 program package.¹

Synthesis

N-(2-bromophenyl)-1H-benzo[d]imidazol-2-amine

2-Chlorobenzimidazole (1.0 g, 6.55 mmol) and 2-bromoaniline (1.41 g, 6.55 mmol) were dissolved in N-methylpyrrolidone (NMP, 6 ml) at room temperature (RT). Methanesulfonic acid (0.79 g; 0.53 mL, 7.86 mmol) was added dropwise over ca. 0.5 h. The resulting suspension was heated at 100 °C and stirred until the complete conversion of 2-chlorobenzimidazole. The reaction mixture is then cooled to RT, diluted with water (20 mL), and neutralized with 30 wt-% aqueous sodium hydroxide. The reaction mass was then extracted with dichloromethane (20 ml) three time. The organic layer was dried over MgSO₄ and the solvent was evaporated on the rotary vacuum evaporator to give a crude sticky mass. This sticky mass was stirred with diethyl ether at RT and filtered to give N-(2-bromophenyl)-1H-benzo[d]imidazol-2-amine (1.66 g, 87.83%) which was obtained as an off-white amorphous solid.

5H-benzo[d]benzo[4,5]imidazo[1,2-a]imidazole (1)

N-(2-bromophenyl)-1H-benzo[d]imidazol-2-amine (1.0 g, 3.47 mmol) was dissolved in 10 ml dimethylformamide. Cesium carbonate (1.7 g, 5.21 mmol) and copper(II) bromide (0.078 g, 0.35 mmol) were added to the solution. The resulting suspension was heated to 130°C and stirred overnight. The reaction mixture is then cooled to RT and diluted with water. The precipitated reaction product was isolated by filtration, washed thoroughly with water, and dried under a vacuum at 65°C. 5H-benzo[d]benzo[4,5]imidazo[1,2-a]imidazole (0.583 g, 81.08%) was obtained as an off-white amorphous solid which was further purified by vacuum train sublimation.

^1H NMR (500 MHz, CDCl₃, δ ppm): δ 12.00 (s, 1H), 8.06 (d, $J = 7.3$ Hz, 2H), 7.46 (d, $J = 7.8$ Hz, 2H), 7.26 (t, $J = 8.3$ Hz, 2H), 7.20 (t, $J = 8.1$ Hz, 2H). MS (APCI) m/z 208.44 [(M + H)⁺]. Calculated for C₁₃H₉N₃: 207.08

5-(4,6-Diphenyl-1,3,5-triazin-2-yl)-2-fluorobenzonitrile (2)

Intermediate **2** was synthesized according to the procedure reported in previously published work from our group.²

2-(5H-benzo[d]benzo[4,5]imidazo[1,2-a]imidazol-5-yl)-5-(4,6-diphenyl-1,3,5-triazin-2-yl)benzonitrile (BzITz)

5H-benzo[d]benzo[4,5]imidazo[1,2-a]imidazole (1.0g, 4.83 mmol) was dissolved in 5ml NMP. To the above suspension K_3PO_4 (2.05g, 9.65mmol) was added and stirred for 15 min. Afterwards, 5-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-fluorobenzonitrile (1.7g, 4.83 mmol) in NMP (5 ml) was added dropwise to the above suspension. The resulting mixture was refluxed overnight. The reaction mixture is then cooled to RT and diluted with water. The crude precipitated reaction product was isolated by filtration, washed thoroughly with water, and dried under a vacuum at 65°C. The crude mixture was purified by column chromatography using dichloromethane as eluent to give BzITz (0.65 g, 42.48%) as a bright yellow amorphous powder.

1H NMR (500 MHz, $CDCl_3$, δ ppm): δ 9.44 (d, $J = 2.1$ Hz, 1H), 9.27 (dd, $J = 8.4, 2.0$ Hz, 1H), 8.82 (dd, $J = 8.4, 1.3$ Hz, 4H), 8.32 – 8.24 (m, 3H), 7.73 (t, $J = 7.3$ Hz, 2H), 7.70 – 7.61 (m, 5H), 7.49 (dd, $J = 16.7, 8.1$ Hz, 2H), 7.42 (d, $J = 7.8$ Hz, 1H), 7.37 – 7.28 (m, 2H).

MS (HR-FAB) m/z Found: 540.19 $[(M + H)^+]$. Calculated for $C_{35}H_{21}N_7$: 539.19

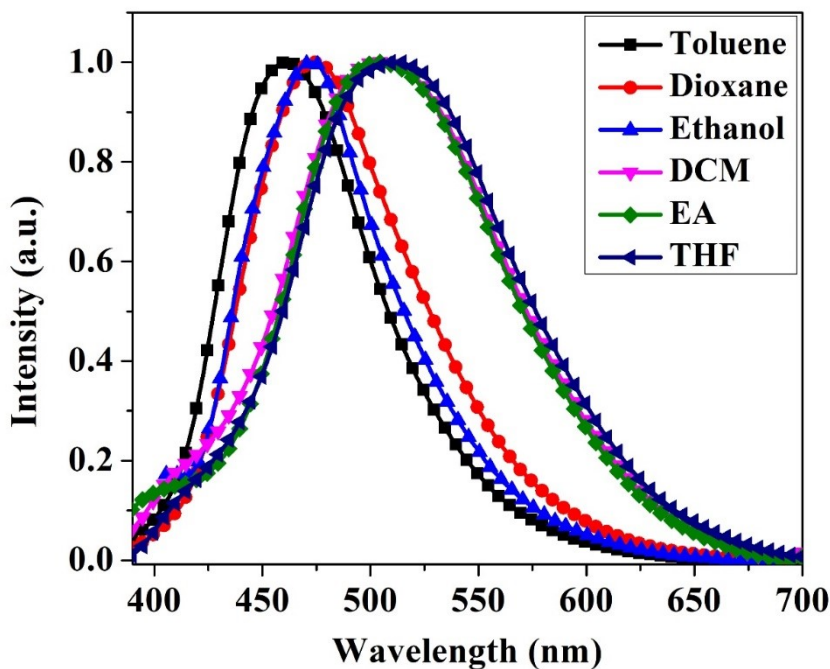


Figure S1. Solvatochromism study of the emitter in solvents of varying polarities.

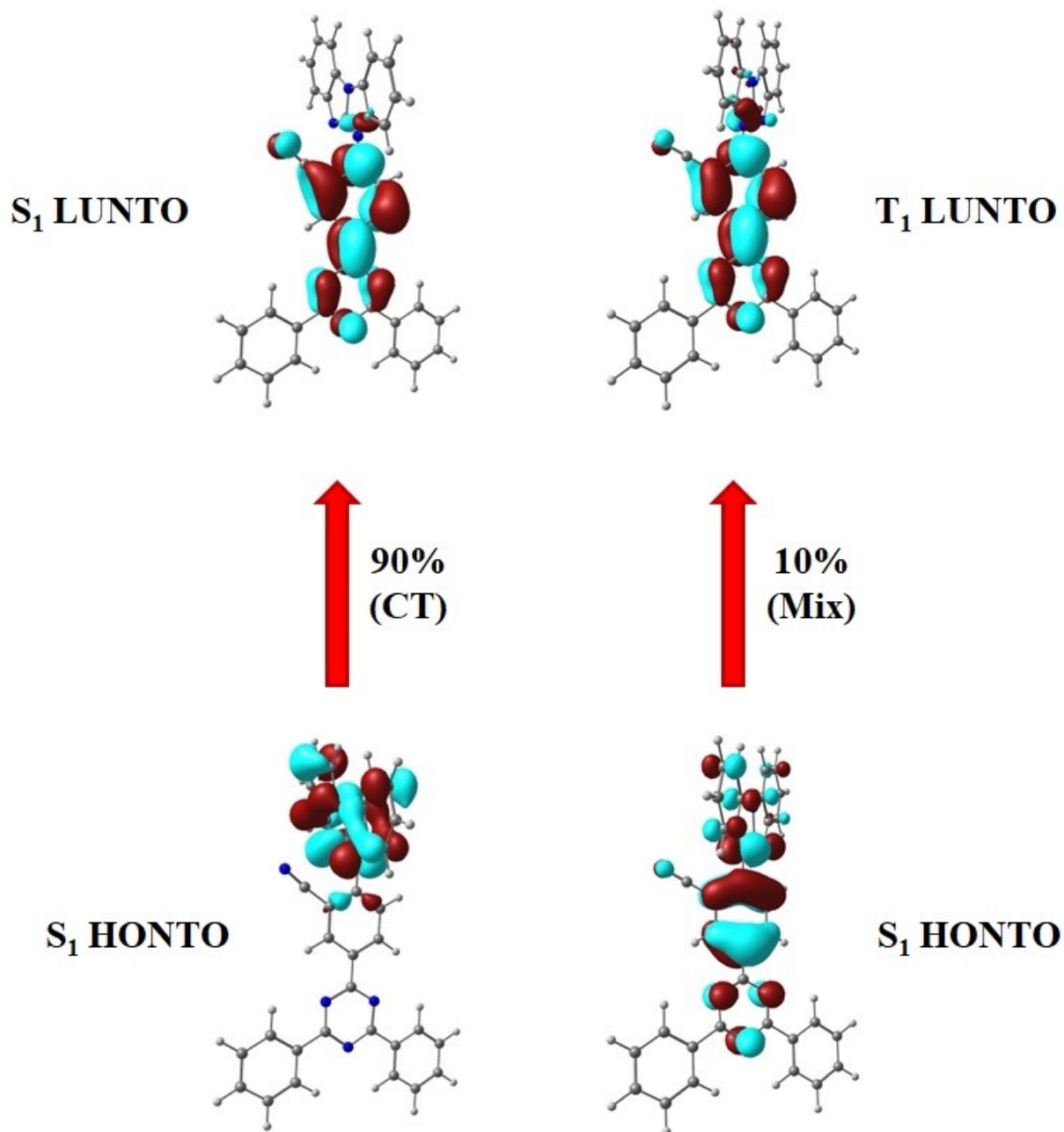


Figure S2. The natural transition orbital (NTO) distributions in singlet and excited states of the emitter.

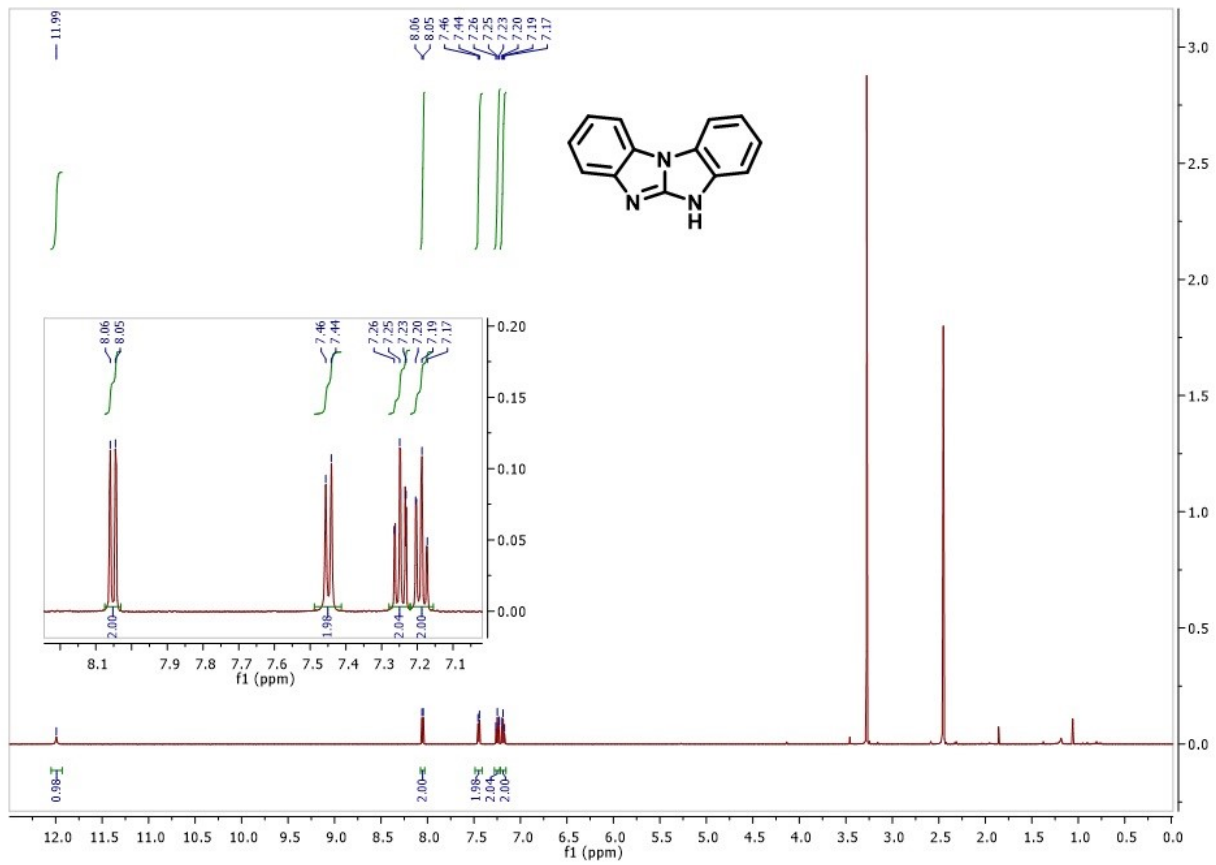
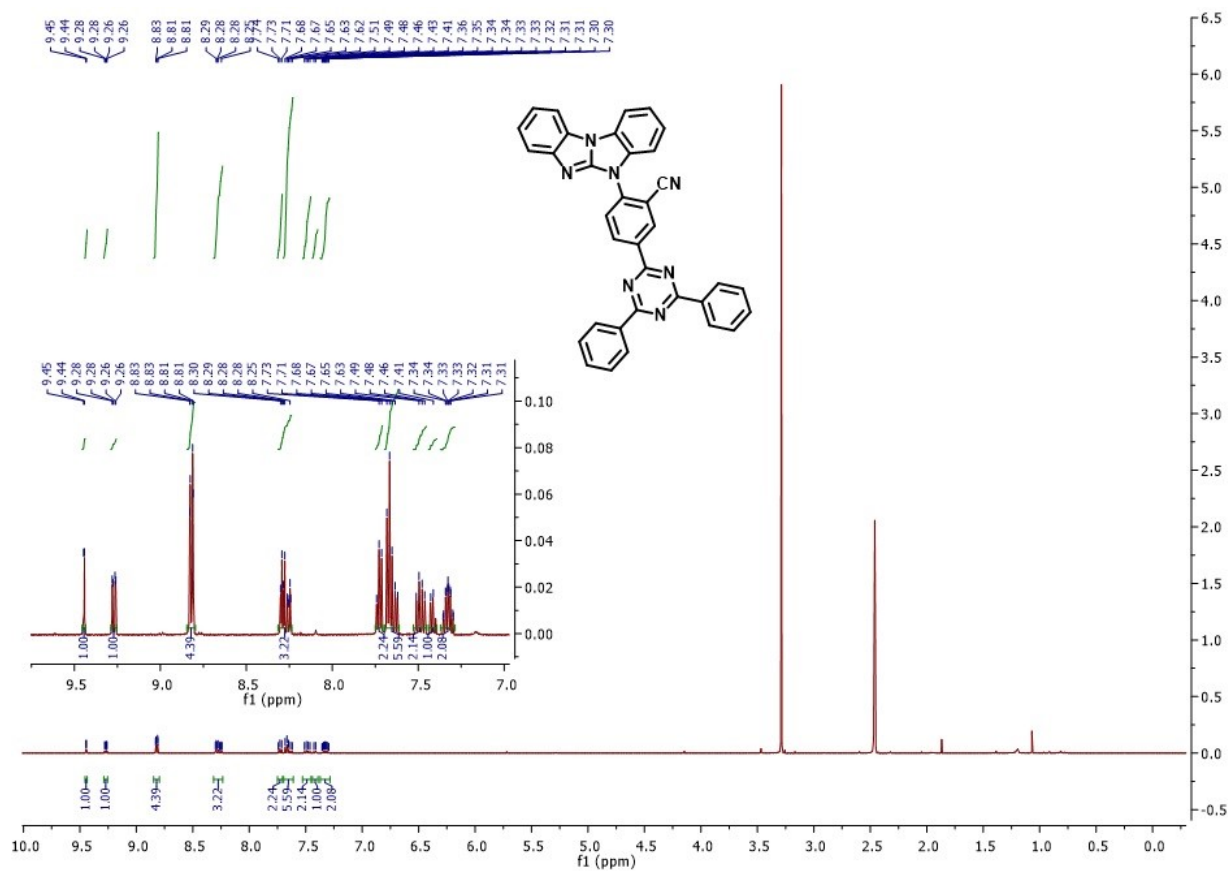
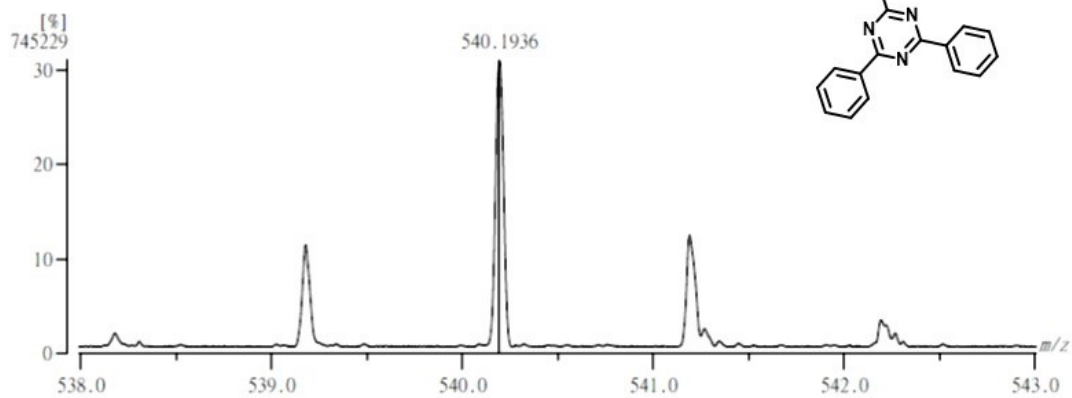


Figure S3. ¹H NMR of Intermediate 1.



. Figure S4. ¹H NMR of BzITz.

[Mass Spectrum]
 Data : FAB-D116 Date : 20-Jan-2022 16:47
 RT : 0.08 min Scan# : (3.29)
 Elements : C 100/0, H 100/0, N 10/0
 Mass Tolerance : 20ppm, 5mmu if m/z < 250, 20mmu if m/z > 1000
 Unsaturation (U.S.) : -0.5 - 40.0



	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	540.1936	30.99	+10.7 / +5.8	32.0	C43 H24
2			-0.1 / -0.1	28.5	C35 H22 N7

. Figure S5. HRMS of BzITz.

References

- 1 S. Y. Byeon, J. Kim, D. R. Lee, S. H. Han, S. R. Forrest and J. Y. Lee, Nearly 100% Horizontal Dipole Orientation and Upconversion Efficiency in Blue Thermally Activated Delayed Fluorescent Emitters, *Adv. Opt. Mater.*, 2018, **6**, 1–6.
- 2 R. K. Konidena, K. H. Lee, J. Y. Lee and W. P. Hong, Triggering Thermally Activated Delayed Fluorescence by Managing the Heteroatom in Donor Scaffolds: Intriguing Photophysical and Electroluminescence Properties, *Chem. - An Asian J.*, 2019, **14**, 2251–2258.