A solution-processable near-infrared thermally activated fluorescent dye with a fused aromatic acceptor and aggregation induced emission behavior

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Synthesis

General

NMR spectra were recorded on a 400 MHz Avance III HD Spectrometer, 400 MHz Smart Probe Spectrometer or a 500 MHz DCH Cryoprobe Spectrometer in the stated solvent using residual protic solvent as the internal standard. ¹H NMR chemical shifts are reported to the nearest 0.01 ppm. The coupling constants (J) are measured in Hertz. ¹³C NMR spectra were recorded in the stated solvent using the residual protic solvent as the internal standard. ¹³C NMR chemical shifts are reported to the nearest 0.1 ppm. Mass spectra were obtained using a Waters LCT, Finnigan MAT 900XP or Waters MALDI micro MX spectrometer at the Department of Chemistry, University of Cambridge. Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser. Thermal gravimetric analysis was run under a nitrogen atmosphere at a rate of 10 °C min⁻¹ using a Mettler Toledo TGA/DSC 2 instrument at a gas flow of 125 cm³min⁻¹. Thin layer chromatography (TLC) was carried out on silica gel and visualized using UV light (254, 365 nm). Flash chromatography was carried out on a Biotage® Isolera automated flash chromatography machine on 60 micron silica gel cartridges purchased from Biotage[®]. Cyclic voltammetry was recorded using a Princeton Applied Research VersaSTAT 3. A glassy carbon disk, Pt wire, and Ag/Ag+ (AgNO₃ in acetonitrile) were used as the working, counter, and reference electrodes, respectively. Measurements were corrected to the ferrocene/ferrocenium redox couple as an internal standard. Tetrahydrofuran was used as the solvent with an analyte molarity of ca. 10⁻⁵ M in the presence of 10⁻¹ M *n*-Bu₄NPF₆ as a supporting electrolyte. Solutions were degassed with Ar and experiments run under a blanket of Ar.

Chemicals

All commercial chemicals were of ≥95% purity and were used as received without further purification. Anhydrous solvents were purchased from Sigma Aldrich or Acros Organics and used as received.

Procedures



2. Bromotriphenylamine **1** (10.0 g, 30.8 mmol, 1.00 eq.) was combined in an oven dried flask with AlCl₃ (12.3 g, 9.22 mmol, 0.30 eq.) which was subsequently evacuated and backfilled with argon three times. Anhydrous CS₂ (100 mL) was added and the reaction mixture was cooled in an ice bath before the dropwise addition of benzoyl chloride (9.54 g/ 7.90 mL, 67.9 mmol, 2.20 eq.). The reaction mixture was stirred in the ice bath and allowed to warm to room temperature overnight. It was then poured onto a mixture of ice and 1 M HCl (*ca.* 500 mL) and concentrated under reduced pressure to remove the majority of the CS₂. The residue was extracted with DCM (3 × 150 mL) and the extracts were combined, dried over MgSO₄, filtered and the solvent removed under reduced pressure. This afforded a green semi-solid which as triturated with hexane and collected by filtration. Recrystallisation from ethanol (250 mL, reflux \rightarrow r.t.) afforded yellow/ gold crystals of **2** (6.90 g, 13.0 mmol, 42%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.81 – 7.75 (m, 8H), 7.60 – 7.55 (m, 2H), 7.51 – 7.46 (m, 6H), 7.18 – 7.13

(m, 4H), 7.11 – 7.07 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 195.3, 150.4, 145.2, 138.0, 133.2, 132.3, 132.2, 129.9, 128.4, 128.1 (2C), 122.7, 118.6; HRMS (ASAP): *m/z* 531.0815 [M⁺]. Calcd. for C₃₂H₂₂NO₂⁷⁹Br⁺: 531.0828.



3. n-BuLi (1.6 M in hexane, 16.8 mL, 26.9 mmol, 2.20 eq.) was added dropwise to a solution of diphenylmethane (4.72 g, 28.1 mmol, 2.30 eq.) in dry THF (250 mL) under argon at room temperature. The mixture was stirred at room temperature for 30 min before it was cooled to -78 °C and 2 (6.50 g, 12.2 mmol, 1.00 eq.) was added in a single portion. The reaction mixture was allowed to warm to room temperature overnight before it was quenched with satd. NH₄Cl solution (300 mL) and extracted with DCM (3 \times 100 mL). The extracts were combined, dried over MgSO₄, filtered and the solvent removed under reduced pressure. The residue was dissolved in toluene (250 mL) with p-TSA (200 mg) and heated to reflux overnight under air. The reaction mixture was cooled to room temperature, the solvent removed under reduced pressure and the residue purified by flash chromatography on silica gel (eluent: gradient 5 \rightarrow 30% vol. DCM in hexane with 1% NEt₃ to elute the product **3**, followed by 55% vol. DCM in hexane with 1% NEt₃ to elute mono-reacted intermediate **3 int**). After trituration with methanol, filtration and drying under suction, **3** was obtained as a light yellow powder (1.54 g, 1.85 mmol, 15%). The recovered 3 int (4.5 g, 6.59 mmol, 54%) was subjected to the same reaction conditions again with diphenylmethane (3.55 g, 21.2 mmol) and n-BuLi (1.6 M in hexane, 12.4 mL, 19.8 mmol) in THF (200 mL), followed by dehydration in toluene (250 mL) with p-TSA (200 mg). A second portion of **3** was obtained after the same purification procedure (4.48 g, 5.38 mmol. Total yield = 6.02 g, 7.23 mmol, 59%).

3. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.28 (d, *J* = 8.8 Hz, 2H), 7.13 – 7.01 (m, 30H), 6.88 – 6.81 (m, 6H), 6.73 (d, *J* = 8.6 Hz, 4H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 146.7, 145.3, 144.1, 143.8, 143.6, 140.9, 140.7, 138.7, 132.4, 132.1, 131.5, 131.5, 131.5, 127.8, 127.8, 127.7, 126.6, 126.5, 126.5, 125.3, 123.3, 114.9; HRMS (ASAP): *m/z* 831.2475 [M⁺]. Calcd. for C₅₈H₄₂N⁷⁹Br⁺: 831.2495.

3 int. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.78 – 7.74 (m, 2H), 7.71 – 7.67 (m, 2H), 7.56 (dd, J = 8.5, 6.3 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.15 – 6.94 (m, 21H), 6.86 (d, J = 8.6 Hz, 2H).



4. Prepared based on a literature procedure for an analogue.¹ 3 (2.00 g, 2.40 mmol, 1.00 eq.), B₂pin₂ (640 mg, 2.52 mmol, 1.05 eq.), KOAc (636 mg, 6.48 mmol, 2.70 eq.) and Pd(dppf)Cl₂ (53 mg, 72.0 μmol, 3%) were combined in an oven dried flask which was subsequently evacuated and backfilled with

argon three times. Dry, degassed dioxane (50 mL) was added and the reaction mixture was heated in a 90 °C oil bath overnight. The reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: gradient $0 \rightarrow 30\%$ vol. DCM in hexane to elute unreacted starting material followed by 50% vol. DCM in hexane to elute **4**.). After trituration with methanol, filtration and drying under suction, **4** was obtained as a yellow powder (1.27 g, 14.4 mmol, 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.6 Hz, 2H), 7.14 – 7.00 (m, 30H), 6.91 (d, J = 8.6 Hz, 2H), 6.88 – 6.84 (m, 4H), 6.78 – 6.74 (m, 4H), 1.34 (d, J = 7.1 Hz, 12H); ¹³C NMR (176 MHz, CDCl₃) δ (ppm) = 150.3, 145.4, 144.1, 143.9, 143.6, 140.9, 140.8, 138.9, 135.8, 132.3, 131.5, 131.5 (4C), 127.8, 127.8, 127.7, 126.6, 123.9, 122.0, 83.7, 25.0; HRMS (ASAP): m/z 880.4297 [M–H⁺]. Calcd. for C₆₄H₅₅BNO₂⁷⁹Br⁺: 880.4326.



CAT-TPE. 4 (1.26 g, 1.43 mmol, 1.10 eq.), 5-bromo-6-cyanoacenaphthenedione (374 mg, 1.30 mmol, 1.00 eq.) and Pd(PPh₃)₄ (90 mg, 0.08 mmol, 6 mol%) were combined in degassed THF (100 mL). Degassed 2 M Na₂CO₃ (10 mL) was added and the reaction was submerged in a preheated 70 °C oil bath for 4 h. The reaction mixture was cooled to room temperature and poured into a mixture of DCM (200 mL) and 1 M HCl (200 mL). The layers were separated and the aqueous layer was further extracted (2 \times 50 mL). The extracts were combined, washed with brine (50 mL), dried over MgSO₄, filtered and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: gradient $0 \rightarrow 50\%$ vol. DCM in hexane to elute residual 4, followed by 100% vol. DCM) to afford the presumed Suzuki-coupled dione intermediate (710 mg, 0.69 mmol). It was suspended in degassed acetic acid (50 mL) with diaminomaleonitrile (90 mg, 0.83 mmol) and heated to reflux overnight. The reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: gradient $0 \rightarrow 100\%$ vol. DCM in hexane). The dark band was collected, and after evaporation of the column solvent the obtained solid was refluxed in ethanol (100 mL) overnight and then recovered by hot filtration. The filtrand was washed with further boiling ethanol (3 × 50 mL) and then dried under suction to afford CAT-TPE as a dark green powder (488 mg, 0.47 mmol, 36%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.59 – 8.56 (m, 2H), 8.31 (d, J = 7.3 Hz, 1H), 7.95 (d, J = 7.3 Hz, 1H), 7.29 $(d, J = 8.6 \text{ Hz}, 2\text{H}), 7.17 - 7.01 \text{ (m, 32H)}, 6.95 - 6.88 \text{ (m, 8H)}; {}^{1}\text{H NMR} (400 \text{ MHz}, d_{s}-pyridine) \delta (ppm) =$ 8.65 (d, J = 7.2 Hz, 2H), 8.40 (d, J = 7.3 Hz, 1H), 7.93 (d, J = 7.3 Hz, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.37 - 7.11 (m, 38H); HRMS (ESI): m/z 1031.3845 [M-H⁺]. Calcd. for C₇₅H₄₇N₆: 1031.3862.



Spectrum S1. ¹H NMR spectrum of 2.

NMR spectra



S6



Spectrum S3. ¹H NMR spectrum of 3.



Spectrum S4. ¹³C NMR spectrum of 3.



Spectrum S5. ¹H NMR spectrum of 3 int.



Spectrum S6. ¹H NMR spectrum of 4.



Spectrum S7. ¹³C NMR spectrum of **4**.



Spectrum S8. ¹H NMR spectrum of **CAT-TPE** in pyridine-*d*₅.



S13

Photophysics

Sample preparation

All sample preparation was carried out in a nitrogen environment. CAT-TPE was dissolved at 70 °C overnight at 0.1 mg/mL in toluene for solution studies and 10mg/ml in chlorobenzene for film studies. Borosilicate glass substrates were pre-cleaned by sequential use of a non-ionic detergent solution, deionised water, acetone and propan-2-ol. CAT-TPE:TPBi doped films were drop-cast at 5 wt.%, 40 wt.% and 100 wt.% of CAT-TPE onto the substrates at 70 °C.

Steady-state photophysics

A Shimadzu UV-3600 Plus spectrophotometer was used to measure the steady-state absorbance of samples, which comprises a photomultiplier tube for the ultraviolet and visible regions.

Steady-state PL and PLQY measurements were performed in an integrating sphere using an Andor Shamrock spectrometer and Andor iDus CCD array and laser excitation at λ_{ex} = 405 nm. PLQY was measured and calculated according to the de Mello method.² For pristine and doped films the PLQY values were determined on triplicate samples, which were each measured twice – the quoted values are an average of six measurements. The PLQY was measured in an ambient environment then corrected by the ratio of integrated PL of linear measurements of the films in an ambient environment vs. under vacuum (Fig. S2).

Transient & Cryogenic PL Measurements

Time-resolved PL spectra were recorded using an electrically-gated intensified charge-coupled device (ICCD) camera (Andor iStar DH740 CCI-010) connected to a calibrated grating spectrometer (Andor SR303i). Pulsed 400 nm photoexcitation was provided by second harmonic generation (SHG) in a BBO crystal from the fundamental 800 nm output (pulse width = 80 fs) of a Ti:Sapphire laser system (Spectra Physics Solstice), at a repetition rate of 1 kHz. A 425 nm long-pass filter (Thorlabs) was used to prevent scattered laser signal from entering the camera. Temporal evolution of the PL emission was obtained by stepping the ICCD gate delay with respect to the excitation pulse. The minimum gate width of the ICCD was ca. 5 ns. Time-resolved PL was carried out in under a high vacuum (10⁻⁵ mbar) to exclude oxygen and moisture from the samples unless stated otherwise that measurements were carried out under ambient conditions to demonstrate quenching of triplet contribution to luminescence. Cryogenic measurements were carried out using an Oxford Instruments Optistat Static continuous flow cryostat with liquid helium coolant, and an ITC 502 S temperature control unit. For all cryogenic measurements, the sample chamber was kept under high vacuum (10⁻⁶ mbar) to exclude oxygen and moisture from the samples.

The 1 kHz repetition rate of the laser used in this experiment precludes accurate measure of lifetimes beyond 1 ms. Prompt lifetimes were calculated by fitting a monoexponential to the early time component. Measurement of prompt lifetimes is limited by the ICCD 5 ns time step. For non-exponential luminescence decay in the solid state, a characteristic time rather than monoexponential decay time is quoted. We choose the time taken for the delayed component to reach 63% (1 - (1/e)) of the total emission integrated from the onset of delayed emission until the end of the measurement. This to allow direct comparison to lifetimes extracted from monoexponential decays.



Figure S1. Absorption spectra of **CAT-TPE** films. The bottom spectra are normalised to the intensity of the ICT band.



Figure S2. PL spectra of **CAT-TPE**/TPBi films recorded under air and vacuum to highlight quenching by oxygen.



Figure S3. Time slice PL spectra of CAT-TPE/TPBi films.



Figure S4. Plots of integrated PL intensity vs. temperature for **CAT-TPE**/ TPBi films, used to determine activation energy of TADF (E_A).

Wt.% CAT-1 in TPBi evaporated film	λ _{max} PL / nm	PLQY/ %	Wt.% CAT-TPE in TPBi drop-cast film	λ _{max} PL / nm	PLQY/ %
10	756	4.8 ± 0.1	5	752	11.3 ± 0.5
20	785	2 ± 0.05	10	784	2.7 ± 0.1
40	835	0.9 ± 0.02	40	842	0.64 ± 0.03

Table S1. PL data for CAT-TPE and CAT-1 films.

Additional AIE discussion

In THF, when excited at 400 nm weak emission is observed and the spectrum consists of two distinct bands (Figure S5, b)). The higher energy band is ascribed to local excited (LE) π – π * emission, consistent with PL data reported for the non-brominated analogue of **3** i.e. the donor moiety.³ The lower energy broad PL centred at 727 nm is assigned to CT fluorescence. Similar dual emission has been previously reported for an AIE luminogen with an ICT state.⁴ Upon increasing the water fraction, the CT band redshifts due to increased solvent polarity and aggregation (Figure S5, a), b)). The intensity of the CT band initially drops, before increasing in intensity to a value greater than that of the THF solution, with maximum CT intensity recorded at 70 vol% water. We ascribe this trend to solvent polarity quenching at lower water fractions, which gives way to AIE behaviour as the solubility of **CAT-TPE** decreases at higher water fractions (Figure S5, c)). This behaviour has been commonly reported for ICT AIE emitters.^{4–7}



Figure S5. a) Plot of charge-transfer type photoluminescence intensity vs. vol% water in THF for 100 μ M **CAT-TPE** mixtures; b) Intensity normalized PL spectra recorded for **CAT-TPE** mixtures at different vol% water (λ_{exc} = 400 nm) with charge-transfer (CT) and local excited (LE) type emission features labelled; c) A photograph of **CAT-TPE** samples at different vol% water in THF.

Electroluminescence

To demonstrate the practical potential of **CAT-TPE**, we fabricated OLED devices by solution-processing method. The champion device structure employed was: ITO / PEDOT:PSS (40nm) / PVK (10 nm) / CAT-TPE in TPBi (40 nm) / 10 wt.% TPBi:TSPO1 (10 nm) / TSPO1 (40 nm) / LiF (0.8 nm) / Al (100 nm). Fabrication of the solution-processed devices with a small molecule host is a challenging target. Many transport layers were examined, and we found that a thin layer of PVK can optimise the energy alignment and a thin layer of TSPO1 doped with 10% of TPBi improves the charge balance. For 5 wt% **CAT-TPE**, champion devices show deep-red electroluminescence (EL, $\lambda_{max} = 680$ nm, Figure S6) with a maximum external quantum efficiency (EQE) of 2.1% and small roll-off at practical brightness of 100 W/sr⁻¹m⁻². The EL spectrum remains stable even at very high voltage, without any emergence of additional high-energy peaks from host emission. We optimised the OLED device stack to achieve a charge balance and almost negligible current leakage (for current density–voltage and radiance–voltage characteristics of the devices see Figures S8 and S9).

The electroluminescence spectrum was measured using a calibrated fibre-coupled Ocean Optics Flame spectrometer. J-V curves were measured using a Keithley 2635 source-meter. The on-axis photon flux was calculated from the output of a calibrated 1 cm² silicon photodiode positioned at a distance of 15 cm from the OLED surface. External quantum efficiency was calculated from the overlap between electroluminescence spectrum (in units of photon counts) and photodiode quantum efficiency. Radiance was calculated from the overlap between electroluminescence spectrum (in units of spectral irradiance) and photodiode responsivity. The photodiode was approximated to represent a small solid angle and the OLED was approximated as a point source. Lambertian emission was assumed.

CAT-TPE wt%	EL λ_{max} / nm	Turn on/ V	EQE max/ %	EQE at 100 W/sr ⁻¹ m ⁻² / %
5	680	12.0	2.1	1.1
10	710	8.7	1.2	0.9
15	720	8.0	0.8	0.7
Pristine	755	16.5	0.2	-

Table S2. Summary of OLED performance.



Figure S6. EL spectra of CAT-TPE OLEDs with doping concentration of 5%, 10%, 15% and pristine.



Figure S7. EQE vs. current density plots for **CAT-TPE** OLEDs with doping concentration of 5%, 10%, 15% and pristine.



Figure S8. Current density vs. voltage plots for **CAT-TPE** OLEDs with doping concentration of 5%, 10% and 15%.



Figure S9. Radiance vs. voltage plots for **CAT-TPE** OLEDs with doping concentration of 5%, 10% and 15%.



Figure S10. (a) current density vs. voltage (b) radiance vs. voltage (c) EQE vs. current density (d) EL spectra of the champion 15% **CAT-TPE**:TPBi OLED, the 15% **CAT-TPE**:TPBi OLED without PVK as the hole injection layer and the 15% **CAT-TPE**:TPBi OLED without TPBi as the electron transport layer.

The energy gap between the hole transport layer (PEDOT:PSS) and the host (TPBi) is too large to enable an efficient hole transport. Therefore, PVK is crucial here to facilitate hole injection and keep a good charge balance. As we can see from the current density vs. voltage plot, without PVK, the charge leakage before the turn-on is significant arising from an unbalanced charge carries. The purpose to add an extra TPBi layer is to improve electron transport. The combination of these transport layers can achieve an optimum electron and hole charge balance.

DFT calculations

All calculations were carried out with the Gaussian 09 package.⁸ All optimised S₀ geometries were calculated using B3LYP/6–31G^{*}.^{9–12} All S₀ geometries were true minima based on no imaginary frequencies found. Electronic structure calculations were carried out on the optimised geometries at TDA–PBE0/def2-SVP.^{13–15} The MO diagrams and orbital contributions were generated with the aid of Gabedit¹⁶ and GaussSum¹⁷ packages, respectively.



Figure S11. HOMO and LUMO plots for CAT-TPE (isovalue = 0.04).

State	Energy (eV)	Wavelength (nm)	f	Major contributors
T1	1.29	959	0	HOMO->LUMO (95%)
S1	1.37	904	0.1025	HOMO->LUMO (99%)
Т2	1.98	627	0	HOMO-1->LUMO (90%)
S2	1.98	625	0.0035	HOMO-1->LUMO (100%)

Table S3. TD-DFT data obtained for CAT-TPE.

Thermal analysis



Figure S12. (Top) TGA trace for **CAT-TPE**. 5% mass loss (T_d) occurs at 514 °C. (Bottom) DSC trace for **CAT-TPE**, glass transition temperature (T_g) = 173 °C, inset is expansion of region around T_g .

References

- Chini, M. K.; Mahale, R. Y.; Chatterjee, S. Effect of Heterocycles on Field-Effect Transistor Performances of Donor-Acceptor-Donor Type Small Molecules. *Chem. Phys. Lett.* 2016, 661, 107–113.
- (2) de Mello, J. C.; Wittmannn, H. F.; Friend, R. H. An Improved Experimental Determination of External Photoluminescence Quantum Efficiency. *Adv. Mater.* **1997**, *9*, 230–232.
- (3) Liu, Y.; Chen, X.; Lv, Y.; Chen, S.; Lam, J. W. Y.; Mahtab, F.; Kwok, H. S.; Tao, X.; Tang, B. Z. Systemic Studies of Tetraphenylethene-Triphenylamine Oligomers and a Polymer: Achieving Both Efficient Solid-State Emissions and Hole-Transporting Capability. *Chem. - A Eur. J.* 2012, 18, 9929–9938.
- (4) Zhang, G. F.; Aldred, M. P.; Gong, W. L.; Li, C.; Zhu, M. Q. Utilising Tetraphenylethene as a Dual Activator for Intramolecular Charge Transfer and Aggregation Induced Emission. *Chem. Commun.* 2012, 48, 7711–7713.
- (5) Funchien, P.; Chasing, P.; Promarak, V. A Highly Efficient near Infrared Organic Solid Fluorophore Based on Naphthothiadiazole Derivatives with Aggregation-Induced Emission Device †. *Chem. Commun.* **2020**, *56*, 6305–6308.
- Yang, W.; Li, C.; Zhang, M.; Zhou, W.; Xue, R.; Liu, H.; Li, Y. Charge Transfer Effect in Triphenylamine Fluorophores Containing Diphenylhydrazone. *Phys. Chem. Chem. Phys.* 2016, 18, 28052–28060.
- Yuan, W. Z.; Gong, Y.; Chen, S.; Shen, X. Y.; Lam, J. W. Y.; Lu, P.; Lu, Y.; Wang, Z.; Hu, R.; Xie, N.; Kwok, H. S.; Zhang, Y.; Sun, J. Z.; Tang, B. Z. Efficient Solid Emitters with Aggregation-Induced Emission and Intramolecular Charge Transfer Characteristics: Molecular Design, Synthesis, Photophysical Behaviors, and OLED Application. *Chem. Mater.* 2012, *24*, 1518–1528.
- (8) Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- (9) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. **1993**, *98*, 5648.
- (10) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (11) Petersson, G. A.; Al-Laham, M. A. A Complete Basis Set Model Chemistry. II. Open-Shell Systems and the Total Energies of the First-Row Atoms. J. Chem. Phys. 1991, 94, 6081–6090.
- (12) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A. A Complete Basis Set Model Chemistry. I. The Total Energies of Closed-Shell Atoms and Hydrides of the First-Row Elements. *J. Chem. Phys.* **1988**, *89*, 2193–2218.

- (13) Chen, J.-X.; Tao, W.-W.; Chen, W.-C.; Xiao, Y.-F.; Wang, K.; Cao, C.; Yu, J.; Li, S.; Geng, F.-X.; Adachi, C.; Lee, C.-S.; Zhang, X.-H. Red/Near-Infrared Thermally Activated Delayed Fluorescence OLEDs with Near 100% Internal Quantum Efficiency. *Angew. Chemie Int. Ed.* 2019, *58*, 14660–14665.
- (14) Moral, M.; Muccioli, L.; Son, W.; Olivier, Y.; Sancho-Garcia, J. C. Theoretical Rationalization of the Singlet – Triplet Gap in OLEDs Materials : Impact of Charge-Transfer Character. J. Chem. Theory Comput. 2015, 11, 168–177.
- (15) Zeng, W.; Gong, S.; Zhong, C.; Yang, C. Prediction of Oscillator Strength and Transition Dipole Moments with the Nuclear Ensemble Approach for Thermally Activated Delayed Fluorescence Emitters. J. Phys. Chem. C **2019**, *123*, 10081–10086.
- (16) Allouche, A.-R. Gabedit: A Graphical User Interface For Computational Chemistry Softwares. J. Comput. Chem. 2011, 32, 174–182.
- (17) O'Boyle, N. M.; Tenderholt, A. L.; Langner, K. M. Cclib: A Library for Package-Independent Computational Chemistry Algorithms. *J. Comput. Chem.* **2008**, *29*, 839–845.