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Imidazole-based solid-state fluorophores with combined ESIPT and AIE features as self-absorption-free non-doped emitters for electroluminescent devices



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ABSTRACT

Excited-state intramolecular proton transfer (ESIPT) fluorophores with an eye-catching aspect of a large Stokes shift in optical properties have been exceptionally considered as prime candidates for numerous applications. Nevertheless, as non-doped emitters for electroluminescent devices, the device performance is still far behind the traditional fluorescence emitters. Herein, two imidazole-based ESIPT-aggregate induced emission (AIE) fluorophores (**HITPE** and **HPITPE**) are designed and synthesized by covalently linked the ESIPT cores of 2-(2-hydroxyphenyl)-1,4,5-triphenylimidazole (HI) and 2-(2-hydroxylphenyl)-1-phenylphenanthroimidazole (HPI) with AIE-active luminogen of tetraphenylethene (TPE) at 5-position of the 2-hydroxyphenyl unit. The ESIPT, AIE, and photophysical properties are theoretically and experimentally studied. Both molecules display ESIPT and AIE characters with intense sky-blue/green-blue color emissions from a pure keto form in the solid-state and photoluminescence quantum yields of 57–64%. They possess high thermal and electrochemical stabilities. They are successfully fabricated as non-doped emitters in organic light-emitting diodes (OLED), and all devices exhibit strong keto-form emissions with low turn-on voltages (3.0–3.2 V). Especially, **HPITPE**-based OLED achieves a high luminance of 10680 cd m⁻², LE value of 3.67 cd A⁻¹, and external quantum efficiency (EQE) of 3.26% with a slight efficiency roll-off. Importantly, this represents an advance in the development of ESIPT molecules as a non-doped emitter for fluorescent OLEDs.

1. Introduction

In the last recent years, excited-state intramolecular proton transfer (ESIPT) molecules [1–3] have drawn extensive attention experimentally and theoretically owing to their unique assets of large Stokes shift (~600–12000 cm⁻¹) [2], multiple emissions [4,5], an ultrafast process [6], and spectral sensitivity to the surrounding environment [7,8]. All these desirable properties make ESIPT chromophores leading candidates for several applications such as fluorescence imaging and sensor [9,10], molecular logic gates [11], UV absorbers [12], solid-state emitters [13, 14], white-light emissions [15–17], and newer arenas of biotechnology [18] and photophysical dynamics studies [19]. In general, during the

ESIPT process, the ground state enol form (E) is photoexcited to an excited enol (E*), which undergoes energy relaxation *via* tautomerization, in which an excited state enol tautomer (E*) is rapidly transformed to its excited state keto tautomer (K*), stimulating by a proton transfer within an intramolecular hydrogen bonding site. Soon after decaying radiatively back to its electronic ground state (K), a reverse proton transfer happens to generate the original enol tautomer (E). Such remarkable molecular geometry and electronic changes initiated by ESIPT result in a unique fluorescence emission with a large Stokes shift, which has triggered broad interest in the field of optoelectronic devices and laser applications [20–23]. In particular, ESIPT fluorophores as light-emitting materials for organic light-emitting diodes (OLEDs)

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would make a perfect counterpart since the absence of spectral overlap between absorption and emission, unlike most organic fluorophores, can help to avoid unwanted self-reabsorption and inner-filter effects, leading to improved electroluminescence and efficiency. Despite this fact, the practical utilization of ESIPT molecules in OLEDs is still not successful. Most of the reported ESIPT emitter-based OLEDs demonstrated low external quantum efficiencies (EQE) [17,24-26]. This could result from many issues such as very low photoluminescence (PL) quantum yields (Φ_{PL}) due to a strong fluorescence quenching induced by molecular aggregation and low charge mobilities in the solid-state as well as short fluorescence lifetimes. To improve the performance of ESIPT-OLEDs, Adachi and co-workers [27] and Yang and co-workers [28] have found thermally activated delayed fluorescence (TADF)-featured ESIPT materials. These compounds exhibited ESIPT and TADF emissions with improved Φ_{PI} values and fluorescence lifetimes. Additionally, these TADF emitters need to be doped into suitable host materials. By the TADF emission channel, the OLEDs based on these ESIPT-based TADF emitters ($\sim 6-10$ wt%) doped in a suitable host matrix realized high external quantum efficiencies (EQE) ranging from 7.1% to 23.9%. You and co-workers also developed 2-(2'-hydroxyphenyl)oxazole-based ESIPT molecules, whose enol tautomer possesses a highly hybridized local and charge transfer (HLCT) excited state character. The OLED using this material 2-7 wt% doped in 3,3'-(9H-fluorene-9,9-diyl)bis (9-phenyl-9H-carbazole) (CBZ2-F1) exhibited green-white electroluminescence with EQE up to 6% due to the synergistic combination of the ESIPT and HLCT [15]. Although these signs of progress for good ESIPT emitters, careful control of dopant concentration is required to avoid unsaturated emissions resulting from ineffective energy transfer in these devices, and meanwhile, doping can also greatly limit the repeatability of devices with identical performances in a mass-production process. Hence, it is necessary to explore fluorescence quenching-free pure ESIPT emitting materials, showing high Φ_{PL} in the solid-state and improved hole-transporting ability for non-doped OLEDs.

Up to now, a large number of molecules possessing ESIPT have been established and are broadly explored, including the derivatives of benzophenones [29], anthraquinones [30], benzotriazoles [31], 2-(2'-hy droxyphenyl)-1,4,5-triphenyl-1H-imidazoles [32,33], 2-(2'-hydroxyphenyl)phenanthrol imidazoles [32,34,35], N-salicylideneanilines [36], quinolones [37], quinoxalines [38], flavones [39,40], 2-(2'-hydroxyphenyl)benzimidazoles [41,42], 2-(2'-hydroxyphenyl)

benzoxazoles [43,44], 2-(2'-hydroxyphenyl)benzothiazoles [45–47], and imidazo[1,2-a]pyridines [48-50]. Among them, the imidazole, containing electron-deficient five-membered heterocycle ring, has also been broadly employed as a building block for assembling effective emitters for OLEDs because of its decent Φ_{PL} and charge transport properties [51-57]. In this work, we report new imidazole-based ESIP-T-aggregate induced emission (AIE) molecules, namely HITPE and HPITPE (Scheme 1), as efficient ESIPT non-doped emitters for electroluminescent devices. In this design, ESIPT cores of 2-(2-hydroxyphenyl)-1,4,5-triphenylimidazole (HI) and 2-(2-hydroxylphenyl)-1phenylphenanthroimidazole (HPI) are directly attached by AIE-active luminogen of tetraphenylethene (TPE) at 5-position of the 2-hydroxyphenyl unit in order to enhance the solid-state fluorescence efficiency of common ESIPT molecule to a higher solid-state fluorescence AIE-ESIPT fluorophore. AIE is an unusual photophysical phenomenon where the light emission of a fluorogen in the aggregated state is higher than in the solution due to intramolecular rigidification upon aggregation, reducing the excited energy loss due to a free-rotation [58,59]. The application of this phenomenon was enormously advanced, as witnessed by an incredible number of AIE molecules developed [60-62]. Several AIE derivatives have been effectively applied as non-doped emitters in OLED devices, which accomplished great EL performances [60,63-70]. It is envisioned that a combination of the self-absorption-free emission feature of the ESIPT unit and the solid-state fluorescence enhancement feature of the AIE unit would bring about even better non-doped emitting materials for OLEDs. Indisputably, these newly synthesized ESIPT-AIE molecules demonstrated high fluorescence efficiency in the solid-state with a pure keto tautomer emission and superior hole mobility. The non-doped OLEDs based on HPITPE attained a high brightness of 10680 cd m⁻², a luminance efficiency of 3.67 cd A⁻¹, and a low turn-on voltage of 3.0 V.

2. Experimental

2.1. Materials and methods

All reagents were purchased from suppliers and used without further purifications. ¹H NMR and ¹³C NMR spectra: Bruker AVANCE III HD 600 (600 MHz-¹H, 151 MHz-¹³C) using CDCl₃ as a solvent. High-resolution mass analysis: Bruker LC-Quadrupole-Time-of-Flight Tandem Mass



Scheme 1. Synthesis of imidazole derivatives (HITPE and HPITPE).

spectrometer. UV-Vis spectra: Perkin Elmer Lambda 1050 UV/Vis/NIR spectrometer. Steady-state fluorescence, phosphorescence and lifetime: Edinburgh Instruments FLS980 Spectrometer. Absolute photoluminescence quantum yield (Φ_{PI}): Edinburgh Instruments FLS980 Spectrometer integrated with a calibrated integrating sphere. Differential scanning calorimetry (DSC)/Thermogravimetric analysis (TGA): PerkinElmer DSC-8500 and Perkin-Elmer TGA Pyris 1 instrument operated at a heating rate of 10 °C min⁻¹ under N₂ flow. Electrochemical analyses: Autolab PGSTA101 equipped with three-electrode setups (Pt, glassy carbon, and Ag/AgCl electrode) in CH₂Cl₂ containing n-Bu₄NPF₆ (0.1 M) as a supporting electrolyte at a scan rate of 50 mV s⁻¹. Melting points: Krüss KSP1N melting point meter and the data were uncorrected. Single-crystal X-ray diffraction (SC XRD): Bruker D8 Venture singlecrystal diffractometer at 110 K (Mo K $\alpha = 0.7107$ Å). The crystal refinement was calculated and illustrated using APEX3, PLATON, OLEX1.2, and MERCURY3 software. Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC 2059961 and 2061555 of HPITPE and HITPE contains the supplementary crystallographic data including the structure factors, respectively. This data can be obtained free of charge via www.ccdc.cam.ac.uk.

Quantum chemical calculation: Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) using the Gaussian 09 package with PBE0/6-31G(d,p) level of theory.

2.2. Device fabrication and testing

Non-doped OLEDs with configuration of ITO/MoO₃ (6 nm)/NPB (80 nm)/EML (40 nm)/TPBi (45 nm)/LiF (0.5 nm)/Al (100 nm) were fabricated on patterned ITO glass substrates (12 Ω sq⁻¹). The substrates were pre-cleaned thoroughly and placed under UV/O3 treatment for 30 min. Then 6 nm thick molybdenum oxide (MoO₃), 80 nm thick of NPB (N,N-di-1-naphthyl-N,N-diphenylbenzidine), 40 nm thick of HPITPE and HITPE as EML, 45 nm thick of TPBi (2,2',2"-(1,3,5-Benzinetriyl)-tris (1-phenyl-1-H-benzimidazole)), 0.5 nm thick of LiF, and 100 nm thick of aluminum layers were subsequently deposited at a thermal evaporation rate of 0.2–1.0 Å s⁻¹, from low-temperature evaporation sources using a Kurt J. Lasker mini SPECTROS 100 thin film deposition system under a base pressure 5×10^{-6} mbar to form an active diode area of 4 mm². The film thickness was monitored using a quartz oscillator thickness sensor. The hole- and electron-only devices were also fabricated in similar manners. Current density-voltage-luminance (J-V-L) characteristics were analyzed instantaneously using a Keithley 2400 source meter and a Hamamatsu Photonics PMA-12 multi-channel analyzer. The absolute external quantum efficiency (EQE) was measured by Hamamatsu Photonics C9920-12 External Quantum Efficiency Measurement System utilizing an integrating sphere. All devices were unencapsulated and measured under an ambient atmosphere at room temperature.

2.3. Material synthesis

2-(2-Hydroxy-5-bromophenyl)-1,4,5-triphenylimidazole (4) and 2-(2-Hydroxyl-5-bromophenyl)-1-phenylphenanthroimidazole (5): To a solution of compounds 2 (500 mg, 2.38 mmol) or 3 (496 mg, 2.38 mmol), 1 (478 mg, 2.38 mmol) in glacial acetic acid (30 ml) was added with dropwise of aniline (0.33 ml, 3.57 mmol). After that, ammonium acetate (550 mg, 7.14 mmol) was added. The reaction mixture was then stirred at reflux for 12 h. After being cooled down to room temperature, it was poured into ice water (100 ml). The white solid was filtered and dried in a vacuum, and then it was further purified by silica gel column chromatography eluting with CH_2Cl_2 /hexane (1/4 v/v).

4 as white solids (667 mg, 60%). ¹H NMR (600 MHz, CDCl₃) δ 13.58 (s, 1H), 7.55–7.50 (m, 2H), 7.49–7.40 (m, 3H), 7.32–7.18 (m, 9H), 7.18–7.13 (m, 2H), 6.95 (d, J = 8.8 Hz, 1H), 6.55 (d, J = 2.4 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 157.54, 143.65, 136.65, 135.40, 132.85, 132.45, 131.30, 130.81, 129.83, 129.59, 129.52, 128.62, 128.54, 128.53, 128.35, 127.21, 126.95, 119.40, 114.52, 109.59; HRMS (APCI)

m/z: calcd. for C₂₇H₁₉BrN₂O (M+): 466.0681, found: 467.0765.

5 as light-green solids (609 mg, 55%). ¹H NMR (600 MHz, CDCl₃) δ 13.92 (s, 1H), 8.77 (d, J = 8.3 Hz, 1H), 8.70 (dd, J = 13.8, 8.1 Hz, 2H), 7.83 (t, J = 7.5 Hz, 1H), 7.81–7.74 (m, 3H), 7.69 (t, J = 7.7 Hz, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.7 Hz, 1H), 7.30–7.25 (m, 2H), 7.13 (d, J = 8.3 Hz, 1H), 7.00 (d, J = 8.7 Hz, 1H), 6.74 (d, J = 2.4 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 158.28, 147.08, 138.62, 134.38, 133.23, 131.10, 130.96, 129.68, 128.88, 128.68, 128.56, 127.61, 127.17, 126.65, 126.26, 125.69, 125.56, 124.24, 123.28, 122.57, 122.50, 120.98, 119.72, 114.58, 109.74; HRMS (APCI) m/z: calcd. for C₂₇H₁₇BrN₂O (M+): 464.0524, found: 465.0844.

4,4,5,5-Tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2dioxaborolane (7): A mixture of 1 (1.0 g, 2.43 mmol), bis(pinacolato) diboron (926 mg, 3.65 mmol), K_2CO_3 (1.7 g, 12.15 mmol), $Pd(dppf)_2Cl_2$ (98 mg, 0.12 mmol) and toluene (50 ml) was degassed with N₂ for 15 min. The reaction mixture was heated at 110 °C under an N₂ atmosphere for 24 h. The mixture was cooled to room temperature and then was extracted with CH_2Cl_2 (3 \times 50 ml). The combined organic layer was washed with water (100 ml), brine solution (100 ml), dried over anhydrous Na₂SO₄, filtered, and concentrated to dryness. The crude product was purified by silica gel column chromatography eluting with CH_2Cl_2 /hexane (1/3 v/v) to give white solids (780 mg, 70%). ¹H NMR (600 MHz, CDCl₃) δ 7.53 (d, J = 7.6 Hz, 2H), 7.08 (s, 9H), 7.05–6.97 (m, 8H), 1.31 (s, 12H); ¹³C NMR (151 MHz, CDCl₃) δ 146.76, 143.70, 143.60, 143.53, 141.39, 140.87, 134.09, 131.35, 131.32, 131.30, 130.68, 127.72, 127.62, 126.51, 126.44, 126.42, 83.69, 24.89; HRMS (APCI) *m*/*z*: calcd. for C₃₂H₃₁BO₂ (M+): 458.2417, found: 458.1652.

2-(4-Hydroxy-4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-3-yl)-1,4,5-triphenylimidazole (HITPE) and 2-(4-methyl-4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-3-yl)-1-phenyl-1H-phenanthro [9,10-d] imidazole (HPITPE): A mixture of 4 (200 mg, 0.43 mmol) or 5 (200 mg, 0.43 mmol), 2 (298 mg, 0.65 mmol), Pd(PPh₃)₄ (26 mg, 0.022 mmol), 2 M Na₂CO₃ aqueous solution (5 ml) in THF (25 ml) was degassed with N₂ for 15 min. The reaction mixture was heated at reflux under N₂ atmosphere for 24 h and then cooled down to room temperature. The resulting mixture was extracted with CH₂Cl₂ (3 × 50 ml). The combined organic layer was washed with water (100 ml), brine solution (100 ml), dried over anhydrous Na₂SO₄, filtered, and concentrated to dryness. The crude product was purified by silica gel column chromatography eluting with CH₂Cl₂/hexane (1/4 v/v) followed by recrystal-

lization in a mixture of CH₂Cl₂/MeOH. HITPE as in white solids (201 mg, 65%). m.p. = 276–277 °C; ¹H NMR (600 MHz, CDCl₃) δ 13.41 (s, 1H), 7.48 (d, J = 7.8 Hz, 2H), 7.32–7.27 (m, 3H), 7.24 (t, J = 7.5 Hz, 1H), 7.22–7.18 (m, 5H), 7.18–7.13 (m, 5H), 7.10 (d, J = 8.3 Hz, 2H), 7.07–6.99 (m, 10H), 6.98–6.91 (m, 6H), 6.79 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 2.2 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 158.00, 144.88, 143.87, 143.83, 143.69, 141.71, 140.89, 140.56, 138.00, 137.41, 135.28, 133.07, 131.49, 131.41, 131.37, 131.34, 131.33, 130.51, 129.92, 129.83, 129.79, 129.23, 128.80, 128.49, 128.31, 128.05, 127.68, 127.62, 127.06, 126.93, 126.43, 126.37, 126.32, 125.03, 124.53, 117.94, 112.99; HRMS (APCI) m/z: calcd. for C₅₃H₃₈BrN₂O (M+): 718.2984, found: 719.2821.

HPITPE as light-yellow solids (170 mg, 55%). m.p. = 324-325 °C; ¹H NMR (600 MHz, CDCl₃) δ 13.91 (s, 1H), 8.80 (d, J = 8.3 Hz, 1H), 8.74 (d, J = 8.0 Hz, 2H), 7.80 (t, J = 7.5 Hz, 1H), 7.75–7.66 (m, 6H), 7.56 (t, J =7.7 Hz, 1H), 7.46 (dd, J = 8.5, 2.3 Hz, 1H), 7.29 (t, J = 9.1 Hz, 1H), 7.24–7.18 (m, 3H), 7.18 (s, 1H), 7.17–7.12 (m, 7H), 7.12–7.05 (m, 6H), 7.04 (d, J = 2.2 Hz, 1H), 6.96 (d, J = 8.3 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 158.75, 148.32, 143.95, 143.84, 143.70, 141.88, 140.96, 140.57, 139.35, 137.99, 134.48, 131.56, 131.45, 131.42, 131.35, 131.09, 130.62, 130.17, 129.56, 129.12, 128.89, 128.48, 127.74, 127.66, 127.55, 127.05, 126.55, 126.48, 126.42, 126.37, 126.11, 125.81, 125.33, 125.19, 124.74, 124.22, 123.24, 122.62, 120.92, 118.31, 113.12; HRMS (APCI) *m/z*: calcd. for C₅₃H₃₆BrN₂O (M+): 716.2828, found: 717.2771.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 describes the synthesis of the designed imidazole-based EIPT-AIE molecules (HITPE and HPITPE). Firstly, two imidazolebased ESIPT intermediates of 2-(2-hydroxy-5-bromophenyl)-1,4,5-triphenylimidazole (HI) (4) and 2-(2-hydroxyl-5-bromophenyl)-1-phenylphenanthroimidazole (HPI) (5) were prepared by the acid-catalyzed one-pot multicomponent condensation reactions of benzil (2) or phenanthrenedione (3), aniline, bromosalicylaldehyde, and ammonium acetate. Then bromotetraphenylethene (TPE) (6) was converted to its boronate derivatives 2 through the Pd(dppf)₂Cl₂-catalyzed borylation with bis(pinacolato)diboron. Finally, Suzuki cross-coupling reactions of the two components of the imidazole intermediates (4 or 5) with the borolane 2 in the catalytic system of Pd(PPh₃)₄/Na₂CO₃ afforded the target HITPE and HPITPE as white and light-yellow solids in good yields, respectively. All compounds were explicitly characterized by standard spectroscopic methods (¹H NMR, ¹³C NMR, and HRMS), and the results agreed with their chemical structures. The ¹H NMR spectra of both HITPE and HPITPE displayed a signal at high chemical shifts (13.41–13.91 ppm) of the –OH proton, suggesting the presence of a sixmembered ring of intramolecular H-bond between -OH and -C=N imidazole moieties when these molecules were dissolved in chloroformd solution. The structures of HITPE and HPITPE were able to be verified by single-crystal X-ray diffraction.

3.2. Crystal structures

The suitable crystals of **HPITPE** and **HITPE** for single-crystal X-ray diffraction studies were obtained during the co-solvent recrystallization from CH₂Cl₂/CH₃OH and CH₂Cl₂/hexane at the ambient conditions, respectively, which were refined and formed in a triclinic crystal system with *P*–1 space group (Fig. 1a and Table S1). Furthermore, the intramolecular hydrogen bonding of O–H…N in **HPITPE** and **HITPE** were observed with distances of 1.736 and 1.845 Å, respectively, which were verified the ESIPT effect in both molecules. From the crystal packing point of view, both crystals were principally ensembled with edge-to-face C–H… π interaction of the aromatic moieties with no evidence of π – π stacking (Fig. 1b and S1-2). However, the **HPITPE** crystal structure



presented its unique molecular arrangement compared with HITPE. HITPE unveiled the molecular arrangement mainly with intermolecular C–H··· π interactions among the phenyl groups on the TPE and imidazole units. Each hydrogen atom of the C–H $\cdots\pi$ bond contacted only a centroid per atom with a distance between 2.5 and 2.8 Å. Contrarywise, the phenyl units in HPITPE were affiliated with the phenanthroline planes, existing intermolecular C–H $\cdots\pi$ interactions along the a-axis direction with the multiple centroid contacts with the distance of 2.9-3.0 Å (Fig. 1b). Both crystal configuration in HITPE and HPITPE with C–H $\cdots\pi$ interactions limited the molecular vibration and TPE unit's rotation restriction that could lower the non-radiative decay and increase the aggregation-induced emission effect [60]. However, the HPITPE crystal arrangement presented a higher centroid-per-hydrogen atom of C–H $\cdots\pi$ interactions than HITPE. Additionally, the continuous $C-H\cdots\pi$ edge-to-face orientations of HPITPE presented the preferred electron hopping direction that could also influence high electron transportation in the solid-state while the C–H $\cdots\pi$ interaction of **HPITPE** crystal was intermittent [71]. These two reasons may be offered the outstanding OLED performances for HPITPE in terms of high external quantum efficiency and charge mobility.

3.3. Photophysical properties

The photophysical studies of these new ESIPT-AIE molecules were performed both in the solutions and solid-states (thin-film and solid powder), as summarized in Table 1. In the toluene solution, the molecules were mainly absorbed in the UV region, with the lowest energy absorption band located at 336 nm for HITPE and 371 nm for HPITPE (Fig. 2a), which could be assigned to the π - π * transition. From the frontier molecular orbitals simulated at the DFT/B3LYP/6-31G(d,p) level of theory (Fig. 4), it is possible to identify that this transition involves moving electrons from the imidazole-TPE moiety to the TPE. The red-shift of the HPITPE absorption band compared to HITPE could be ascribed to the more extended π -conjugation in the phenanthroimidazole moiety of HPITPE than the triphenylimidazole one of HITPE. Both molecules exhibited long wavelength emissions peaked at 503 and 514 nm (Fig. 2a). The Stokes shifts between the absorption and emission spectra were verified to be 147-172 nm (Table 1), with no spectral overlap between the two curves being detected, indicating that all molecules displayed ESIPT characteristics. The photoluminescence

Fig. 1. a) X-ray molecular structures **HPITPE** and **HITPE** with dihedral angles and the thermal ellipsoids drawn at the 50% probability level at 100 K. H-bonds were illustrated as orange dash lines. b) Crystal packing of **HPITPE** and **HITPE**. The C-H··· π interactions were highlighted as yellow dash line, and all hydrogen atoms without intermolecular C-H··· π bonding were omitted for clarity. Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC 2059961 (**HPITPE**) and 2061555 (**HITPE**) contains the supplementary crystallographic data including the structure factors, respectively. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk.

Table 1

Key optical, physical and electronic data.

Compd	λ_{abs} (nm) sol ^a / film ^b	λ_{em} (nm) sol ^a / film ^b	Stokes shift (nm) sol ^a /film ^b	$\Phi_{ m PL}$ (%) ^c sol ^a / solid ^d	$\tau^e~(ns)~sol^a/\\film^b$	$T_c/T_m/T_{5d}^f$ (°C)	$\begin{array}{c} E_{1/2} \ \nu s \ Ag/Ag_+ \\ (V)^g \end{array}$	E ^{opt} (eV) ^h	HOMO/LUMO (eV) ⁱ
HITPE	298, 331/296, 336	503/497	172/161	1/57	0.4/1.3	-/276/475	1.09,1.34	3.15	-5.79/-2.64
HPITEP	316, 367/325, 373	514/509	147/136	5/64	0.4/0.9	203/323/ 492	1.14,1.33	3.09	-5.64/-2.55

^a Measured in toluene solution (1.7 \times 10⁻⁵ M).

^b Measured as neat films spin-coated on fused silica substrates.

^c Absolute PL quantum yield measured using an integrating sphere.

^d Measured as a solid powder.

e Transient PL decay time.

 $^{\rm f}\,$ Recorded by DSC and TGA at a heating rate of 10 $^{\circ}\text{C}\,\text{min}^{-1}$ under N_2 flow.

^g Performed in CH₂Cl₂ solution containing *n*-Bu₄NPF₆ as a supporting electrolyte at a scan rate of 50 mV s⁻¹ under argon atmosphere.

^h Estimated from UV–Vis absorption onset: $E_g^{opt} = 1240/\lambda_{onset}$.

ⁱ HOMO deduced from oxidation onset (E_{onset}^{ox}) of the CV plots: HOMO = -(4.44 + E_{onset}^{ox}) and LUMO = HOMO + E_{z}^{opt} .



Fig. 2. a) UV–Vis absorption and PL spectra in toluene solution (1.7×10^{-5} M). b) PL spectra of **HPITPE** in various solvent polarities. c) Lippert-Mataga correlation between the Strokes shift and solvent orientation polarizability (Δf). d) Transient PL decay spectra in toluene solution and neat film cast on fused silica substrates.

(PL) in toluene was a pure keto tautomer emission because of a complete ESIPT process. As shown in Fig. 2b and S3, both molecules in polar aprotic solvents (toluene, xylene, and tetrahydrofuran (THF)) exhibit a pure keto emission, whereas, in a high polarity index solvent like acetonitrile (ACN), a dual emission from both an enol and keto forms is observed in all cases. A high polarity of the nitrile group in acetonitrile stabilizes the enol form through $C = N \cdots H - O$ intermolecular hydrogen bonding in both the ground and excited states [72], which leads to a

weakened proton-transfer rate. This behavior has been observed in some ESIPT molecules in high polarity solvents in which the enol emission is usually enhanced [73-75]. In order to quantify the solvatochromic effect induced by the solvents of different polarities, the Lippert-Mataga (LM) correlations [76,77] between the Strokes shifts and solvent orientation polarizability (Δf) were constructed and are presented in Fig. 2c. A nearly constant correlation between the Stokes shift and solvent polarity suggests minimum intramolecular charge transfer in the molecules [78, 78].



Fig. 3. a) PL spectra and b) relative PL intensity of **HPITPE** in THF/water mixtures with different water fractions (f_w) (Inset: fluorescent photographs of **HPITPE** in THF ($f_w = 0\%$) and a THF/water mixture with $f_w = 90\%$. c) Photographs of solid powders under ambient light and UV light illumination at 325 nm. d) UV–Vis absorption and PL spectra of neat films cast on fused silica substrates (Insert: photographs of the neat films under UV light illumination at 325 nm.



Fig. 4. a) Optimized structures, frontier orbital distributions, and energy levels of the molecules computed at PBE0/6-31G(d,p) level. b) Simulated UV–Vis absorption and emission spectra and c) plots of potential energy (PCE) versus O–H bond length in a frequency range from 0.9 Å to 1.8 Å of the molecules in the S_0 and S_1 states computed by TDDFT/PBE0/6-31G(d,p) function.

79]. A further study by time-resolved fluorescence spectroscopy revealed that PL decay spectra of **HPITPE** and **HITPE** in toluene solution and neat film displayed a single-exponential decay with short lifetimes (τ) of 0.4–1.2 ns as shown in Fig. 2d (Table 1), confirming that their PL

emissions originate from the singlet state.

The AIE properties of **HPITPE** and **HITPE** were analyzed by monitoring their PL emissions in THF/water mixtures with different water fractions (f_w), enabling a fine-tuning of the solvent polarity and the degree of solute aggregation, as described in Fig. 3a and S4. In a pure THF solution, both molecules exhibited weak green fluorescence with an emission maximum at 505 nm for HPITPE and 502 nm for HITPE. With the gradual increase of the water content in the mixture ($f_w < 80\%$), the emission of the HPITPE solutions slowly increased, while the emission of the HITPE solutions stayed silent and was almost unchanged in profile (Fig. 3b and S4). At $f_{\rm W} = 90\%$, the emission is noticeably enhanced, showing an apparent AIE effect. In addition, the emission maximum is blue-shifted of 3-6 nm relative to pure THF. The emission intensities at $f_{\rm W} = 90\%$ are 10-fold (HPITPE) and 50-fold (HITPE) higher than that in pure THF solutions. These data reveal that these molecules are ESIPT fluorophores having a stronger AIE effect. The fluorescence quantum yield (Φ_{PL}) provides a quantitative measure of the AIE effect. The absolute $\Phi_{PL, sol}$ values of HPITPE and HITPE in THF were as low as 5% and 1%, while their absolute $\Phi_{\text{PL}, \text{ solid}}$ values in the solid states reached 64% and 57%, respectively (Table 1). As shown in Fig. 3c, the solid powders of HPITPE and HITPE are strongly fluorescence under a handheld UV lamp. After covalent incorporation of TPE, both HPITPE and HITPE enjoy >16% enhancement in solid-state emission efficiency compared to their related parents HPI (34%) and HI (35%) [32]. Their corresponding AIE factors defined by Φ_{PL} solid/ Φ_{PL} sol are ~13 and ~57, indicating more significant AIE effect of HITPE. Meanwhile, no apparent PL spectral shifts and enol emissions were noticed from solution to solid-state (Fig. 3d), dismissing the possibility of π - π stacking interactions and incomplete ESIPT process taking place in the aggregate state. Accordingly, these newly design ESIPT-AIE molecules are more suitable to serve as an emitter for electroluminescent devices.

3.4. Theoretical calculations

The proton transferability and property of **HPITPE** and **HITPE** were theoretically studied in the gas phase using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods

operated with Gaussian 09 package using the PBE0/6-31G(d,p) basis set [80]. The results are presented in Fig. 4, and key data are listed in Table S2-3. As shown in Fig. 4a, the optimized geometries of the molecules in enol form at the ground state (S_0) in the gas phase reveal a nearly planar conformation of the 2-(imidazole-2-yl)phenol moieties with small dihedral angles (ϕ) of 12–17° between the phenol and five-membered imidazole ring, which could derive from a durable intramolecular H-bond formed between them. The TPE unit was about 34-36° twisted out of the plane of 2-(imidazole-2-yl)phenol. The H-bond lengths (N···H–O) of HPITPE and HITPE in the S₀ state were changed from 1.644 to 1.680 Å to 1.630 and 1.674 Å in the excited state (S_1) (Table S2). In the meanwhile, their torsion angles (NC1C2C3O) were also reduced from 12 to 17° in the S_0 state to 10 and 16° in the S_1 state, respectively. Accordingly, their intramolecular H-bonds (N---H-O) are strengthened in the S₁ state, which could enhance the probability of ESIPT. The frontier molecular orbitals (mainly the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)) were calculated and analyzed to gain insight into the charge distribution and charge transfer in the molecules. The calculated electronic transition peaks, oscillator strengths, and molecular orbitals (MO) contribution are given in Table S3. As depicted in Fig. 4a, in the LUMO levels of both molecules, the excited electrons are localized mainly on the TPE moiety and a tiny on the 2-(imidazole-2-yl)phenol unit, while in their HOMO levels, the ground state electrons are delocalized over the whole molecule. The electron densities of HOMO and LUMO orbitals display π and π^* characters, respectively. In both cases, the main contribution of the electronic transition is the HOMO \rightarrow LUMO and their MO contributions are in the range of 77-89% with the oscillator strengths (f) of 0.737–0.757. Fig. 5b shows the simulated absorption and emission spectra of HPITPE and HITPE with wavelengths ranging from 250 nm to 700 nm. The peaks of calculated absorption spectra and keto-form emission spectra are located at 346 and 344 nm, and 509 and 502 nm, respectively, which are in accordance with the experimental



Fig. 5. a) DSC and TGA thermograms recorded at a heating rate of 10 $^{\circ}$ C min⁻¹. b) CV traces measured at a scan rate of 50 mV s⁻¹. Current density–voltage (*J–V*) characteristics c) of the electron-only devices (EOD) and d) of the hole-only devices (HOD).

results (Table 1). This consistency certifies the effectiveness of the theoretical method utilized in the present work. For clear evidence of the OH group's proton migration process to the N atom, the potential energy curves (PEC) as a function of O1–H1 bond length ranging from 0.9 Å to 1.8 Å of **HPITPE** and **HITPE** in the S₀ and S₁ states were constructed. As illustrated in Fig. 4c, it can be seen that, in the S₀ state, both molecules showed high potential barriers for the proton transfer of 12.45–12.61 kcal mol⁻¹, while, in the S₁ state, the moderate potential barriers of 9.13–9.30 kcal mol⁻¹ were observed. Hence, the transfer of proton in the S₀ state is difficult to occur due to high potential barriers (>10 kcal mol⁻¹), while the proton transfer process in the S₁ state should be possible with low to moderate potential barriers. Moreover, the proton transfer process in **HITPE** could be easier proceeded than in **HPITPE** since its potential barrier of proton transfer in the S₁ state (9.13 kcal mol⁻¹) was smaller than those of **HPITPE** (9.30 kcal mol⁻¹).

3.5. Thermal, electrochemical, and charge-carrier properties

The thermal properties of **HPITPE** and **HITPE** were examined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Fig. 5a, the decomposed temperatures at 5% weight loss (T_{5d}) are observed to be well over 475 °C, ensuring that these compounds could withstand heating in a vacuum chamber during OLED fabrication. Their DSC thermograms reveal melting temperatures (T_m) higher than 276 °C (Table 1), indicating that all compounds possess good thermal stability despite the relatively low molecular weight, which is a very desirable feature for OLED's stability [81,82].

The electrochemical behavior of HPITPE and HITPE was investigated by cyclic voltammetry (CV) to estimate the redox potentials and HOMO-LUMO energy levels of each molecule. The experiments were carried out in a CH₂Cl₂ solution containing 0.1 M n-Bu₄NPF₆ as a supporting electrolyte under an argon atmosphere, and the results are depicted in Fig. 5b. The CV voltammograms HPITPE and HITPE showed an irreversible oxidation wave at 1.14 and 1.09 V followed by a quasireversible oxidation couple at half-wave potential $(E_{1/2})$ of 1.33 and 1.34 V, respectively (Table 1). Under these experimental conditions, no obvious reduction process was found in both cases. The first oxidation wave could be attributed to the oxidation of the whole conjugated molecular structure, and the second oxidation wave could be associated with the TPE unit [83]. On the basis of the onset potentials of oxidation, the HOMO levels of HPITPE and HITPE were estimated to be -5.64 and -5.79 eV, respectively. From the HOMOs and the optical band gap energies (E^{opt}_o) deduced from the onset of UV-vis absorption spectra, the LUMO levels of HPITPE and HITPE were calculated to be -2.55 and -2.64 eV, respectively (Table 1.)

To further evaluate the charge-carrier properties of two compounds, the hole-only and electron-only devices (HOD and EOD) were fabricated with the structures of ITO/MoO₃ (10 nm)/HPITPE or HITPE (70 nm)/MoO₃ (10 nm)/Al (100 nm) and ITO/TPBi (30 nm)/HPITPE or HITPE (70 nm)/TPBi (30 nm)/LiF (0.5 nm)/Al (100 nm), respectively. In these devices, MoO₃ and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) layers were utilized to block electron and hole injection from the cathode and anode, respectively [84,85]. The electron/hole motilities of each compound were measured by means of the space-charge-limited current (SCLC) method and extracted by fitting the J-V curves in the SCLC regime using the following equation [86].

$$\mathbf{J} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{(V_{app} - V_{bi})^2}{d^3}$$

where J is the current density in the SCLC regime, V_{app} is the applied voltage, V_{bi} is the built-in voltage, ε_0 is the permittivity of free space (8.854 × 10⁻¹² F m⁻¹), ε_r is the relative dielectric constant of the thin film that is assumed to be 3 (a typical value for an organic semiconductor) [86], μ is the electron/hole mobility, and d is the film thickness. As illustrated in Fig. 5c and d, both compounds exhibit a

somewhat better hole-carrier property than electron-carrier property. The hole mobility of **HPITPE** $(2.27 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ was calculated to be about 16 times higher than that of **HITPE** $(1.38 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$, which likely benefit from its π - π stacking and strongly interacting solid-state structure, facilitating charge hopping between the adjacent molecules and thus enhanced charge mobility. The higher hole mobility of **HPITPE** than **HITPE** was also observed in other derivatives of 1, 2-diphenyl-1H-phenanthro[9,10-d]imidazole and 1,2,4,5-tetraphenyl-1H-imidazole cores [53,87]. It is well known that a carrier mobility emitter could contribute to widen the recombination zone in the EML and bring about a longer device lifetime as well as lower driving voltages [88]. Hence, it is assumed that the **HPITPE**-based blue OLEDs should possess better performance.

3.6. Electroluminescent properties

To assess the electroluminescent (EL) performance of HPITPE and HITPE as a non-doped fluorescent emitting layer (EML) in the OLEDs, the devices with the optimized architecture of indium tin oxide (ITO)/ MoO₃ (6 nm)/NPB (80 nm)/EML (40 nm)/TPBi (45 nm)/LiF (0.5 nm):Al (100 nm) were fabricated. The device structure and energy level diagram are shown in Fig. 6a. Here, a thin buffer layer of molybdenum oxide (MoO₃) was used as a hole injection layer (HIL) to reduce the energy barrier between ITO and EML, enhancing hole injection at the interface [89–91]. It has been reported that with an optimized thickness of MoO₃ films, a significant increase in efficiency of the devices was achieved compared with the traditional ITO anode [92,93]. N,N'-Bis (naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPB) served as a hole-transporting layer (HTL). 2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) acted as an electron transport layer (ETL)/hole blocking layer (HBL). The suitable LUMO level (2.70 eV) and electron mobility $(3.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ [94] of TPBi can raise the electron injection and transportation and then charge carrier balancing in the EML, while large energy barriers between the HOMOs of the EML and TPBi (6.20 eV) help to confine hole accumulation and excitons recombination close to this interface. Fig. 6b-c shows the normalized EL spectra, current density-voltage-luminance (J-V-L) characteristics, and luminous efficiency-luminance-external quantum efficiency (LE-L-EQE) plots of the OLEDs and the key EL data of the OLEDs are listed in Table 2. Under applied bias voltage, these OLEDs started to turn on (brightness of 1 cd m⁻²) at voltages of as low as 3.0–3.2 V, indicating effective charge injection and transporting properties in the devices. As shown in Fig. 6b, the HITPE- and HPITPE-based devices emit featureless sky-blue and blue-green emission bands with the Commission Internationale de l'e'clairage (CIE) coordinates (x, y) of (0.20, 0.26) and (0.23, 0.38), respectively (Fig. S6). The EL peaks centered at 468 and 502 nm and displayed the full width at half maximum (FWHM) of 123 and 105 nm, respectively. The EL spectra of the devices matched well with the corresponding thin-film PL spectra of the emitters, showing solely keto-form emissions from the molecules. There were no emission peaks from the NPB (440 nm) [95], TPBi (~400 nm) [96], and interface exciplexes (>500 nm) [97], indicating successful recombination of the carriers (electrons and holes) in the EMLs and only emitter's emissions. The EL spectra matched well with the PL emission of the emitters indicate that emission originates from the same chromophore and suggestive that there were no strong optical cavity effects. The nearly unchanged EL spectra of all devices over the entire operating voltages, as depicted in Fig. S7, also suggest that these OLEDs have good stability during the electrical charge injection process. The ESIPT process is complete and goes on with high stability during the whole operating range of the devices. The OLED using HPITPE as an emitter attained an excellent EL performance with a maximum brightness (L_{max}) of 10680 cd m⁻², a maximum external quantum efficiency (EQE_{max}) of 3.26%, a maximum luminance efficiency (LE_{max}) of 3.67 cd A^{-1} , and a maximum power efficiency (PE_{max}) of 3.11 lm W^{-1} (Table 2). A slightly lower EL performance was achieved for HITPE-based OLED with $L_{max}\, of\, 5266 \, cd \, m^{-2}$



Fig. 6. a) The energy level diagram and device structure, b) normalized EL spectra measured at 11 V (Insert: photographs of the emissions of the OLEDs), c) current density-voltage-brightness (*J*-*V*-*L*) characteristics, and d) EQE-luminance-luminance efficiency (*EQE-L-LE*) curves of the fabricated OLEDs.

Table 2
Electroluminescent data of the fabricated OLEDs. ^a

EML	$V_{on}(V)$	λ_{EL} (nm)	L_{max} (cd m ⁻²)	J_{max} (mA cm ⁻²)	EQE _{max} (%)	LE_{max} (cd A^{-1})	PE_{max} (lm W ⁻¹)	CIE (x, y)	FWHM (nm)
HITPE	3.2	468	5266	536	2.55	2.31	1.97	0.20, 0.26	123
HPITPE	3.0	502	10680	663	3.26	3.67	3.11	0.23, 0.39	105

^a ITO/MoO₃/NPB/EML/TPBi/LiF:Al.

and EQE_{max}/LE_{max}/PE_{max} values of 2.55%/2.31 cd A⁻¹/1.97 lm W⁻¹, respectively. All devices exhibited small efficiency roll-off (Fig. 6d), which might benefit from the balanced hole and electron injection and transport devices. At luminance of 100 cd m⁻² and 1000 cd m⁻², the **HPITPE**-based device particularly, showed high EQEs(LEs) of 2.78% (2.82 cd A⁻¹) and 2.68% (2.77 cd A⁻¹), respectively. A superior EL performance of the **HPITPE** emitter could be associated with a combination of its decent Φ_{PL} and better hole mobility, ensuring a more balanced and improved recharge recombination feature within the device. To the best of our knowledge, in terms of both EL performance and brightness, the **HPITPE**-based device can be identified as one of the best ESIPT-based traditional fluorescent non-doped OLEDs reported so far.

4. Conclusions

In conclusion, two imidazole-based solid-state fluorophores (HPITPE and HITPE) with combined excited-state intramolecular proton transfer (ESIPT) and aggregate induced emission (AIE) properties were successfully designed and synthesized as self-absorption-free non-doped emitters for electroluminescent devices. The functionalization of the ESIPT cores of 2-(2-hydroxyphenyl)-1,4,5-triphenylimidazole (HI) and 2-(2-hydroxylphenyl)-1-phenylphenanthroimidazole (HPI) with AIEactive luminogen of tetraphenylethene (TPE) at 5-position of the 2hydroxyphenyl unit not only can retain the ESIPT features of the molecules but also can improve their solid-state emission due to AIE effect. Both molecules exhibited high thermal and electrochemical stabilities. In the solid-state, they showed a pronounced AIE effect and emitted intense sky blue to green-blue fluorescence from pure keto tautomer with high photoluminescence quantum yields (Φ_{PL}) of 57–64%. Due to robust intramolecular C–H··· π interactions in the solid, **HPITPE** possessed higher hole mobility. Both compounds were effectively utilized as non-doped emitters in OLEDs. These non-doped devices showed stable sky-blue and green-blue emissions, arising from pure keto-form emission of the ESIPT-AIE fluorophores, with low turn-on voltages. In particular, the **HPITPE**-based device exhibited a maximum external quantum efficiency (EQE_{max}) of 3.26% and a maximum LE_{max} of 3.67 cd A^{-1} with a slight efficiency roll-off. Our results exemplify state-of-the-art performance for ESIPT-based conventional fluorescent non-doped OLEDs. It is anticipated that this work will open up a new tactic for obtaining highly efficient OLEDs by using ESIPT-AIE molecules.

CRediT authorship contribution statement

S. P.: Investigation, data curation, and writing-original draft preparation. C. C., W. B., P. N., N. K., S. N. and T. S.: Investigation and data curation. V. P.: Supervision, funding acquisition and writing-reviewing and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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