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Intramolecular hydrogen bond-enhanced electroluminescent performance of hybridized local and charge transfer (HLCT) excited state blue emissive materials

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The hybridized local and charge-transfer (HLCT) excited state is a successful strategy to produce both high external and internal quantum efficiency. Based on HLCT scheme, two isomeric donor-acceptor (D-A) type excited state intramolecular proton transfer (ESIPT) chromophore of o-hydroxyphenyl phenanthroimidazole (HPI)-based emissive molecules (**mTAHPI** and **pTAHPI**) and its OH protected derivative (**pTAPI**) were designed and explored for organic light-emitting diodes (OLEDs). The photophysical study and density functional theory (DFT) calculations revealed that all molecules possessed the HLCT excited state characters without exhibiting ESIPT photophysical properties, whereas the nuclear magnetic resonance spectroscopy, single-crystal and physical properties analyses discovered the existence of strong intramolecular H-bond and intermolecular interactions in both **mTAHPI** and **pTAHPI**. Consequently, their OLEDs displayed blue emissions with a narrow full width at half maximum (65-68 nm) and achieved excellent electroluminescent (EL) performance with a low turn-on voltage of 2.8 V. Particularly, **pTAHPI**-based device showed the highest maximum external quantum efficiency (EQE) of 8.13% with an ultra-high brightness of 18100 cd m⁻². The maximum singlet exciton utilization efficiency (n_s) of the device was estimated to be as high as 94%, which is among the best results of blue electroluminescence to our knowledge.

Introduction

Over the past few decades, we have seen a tremendous progress in the development of organic light-emitting diode (OLED) science and technology.¹ Many groups have exerted much effort to improve the OLED efficiency from the points of view of both new material designs and device architectures.² Nowadays, OLEDs have been demonstrated to be successful in the market, including uses in TVs, monitors, smartphones, wearable devices and lighting. Still, the future retains even better potential for this technology as it can offer an utterly new generation of low-cost, lightweight, and flexible electronic devices. For such applications, external quantum efficiency (EQE) is one of the vital parameters for OLEDs. Based on spinstatistics theorem OLEDs using fluorescent materials are restricted to the theoretical internal quantum efficiency (IQE) of

25% and the remaining 75% of the electronically excited states generally relax via non-radiative decay processes during electroluminescence. Accordingly, the highest theoretical EQE is limited to only about 5%, assuming a light out-coupling constant of \sim 20% in devices, which is a major inadequacy for industrial applications.³ To attain OLEDs with EQEs exceeding the spin-statistical limit, triplet excitons have been utilized. It has been shown that electro-phosphorescent OLEDs (PhOLEDs), utilizing organometallic phosphors of heavy transition metals, can produce a 100% IQE.⁴ However, they have some serious drawbacks such as toxicity of these metals and their rarity, fabrication cost and device stability of the blue devices. Besides, many efforts have been also made to utilize triplet excitons to enlarge the theoretical IQE of fluorescent materials such as triplet-triplet annihilation (TTA),^{2d,5} thermally activated delayed fluorescence (TADF),^{2b,6} and hybridized local and chargetransfer (HLCT) technologies,^{1f,7} but TTA process has a 62.5% upper limit of singlet exciton utilization efficiency (n_s) and TADF devices suffer from serious roll-off at high current density due to the long-lived first triplet excited state (T₁) excitons in TADF materials. Hence, HLCT materials holding nondelayed fluorescent mechanism and the maximum η_s approaching nearly 100% have been the first option for the development of a new generation of organic electroluminescent materials.7b,8 Moreover, being different from phosphorescent materials, OLEDs based on HLCT mechanism are cheaper and sufficient for full-color display especially blue.^{2b,9} The HLCT excited state has contemporaneous reactions of local emission (LE) and excited-

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state intramolecular charge transfer (CT). Molecules showing HLCT states generally hold the donor-acceptor (D-A) type structure, beneficial to the balanced charge injection and charge transport. The essential energy level structure of a large energy separation between the T₁ and T₂ states, together with a small energy gap between T_2 and singlet state (S_m , $m \ge 1$) nicely fosters the singlet exciton fraction via reverse intersystem crossing (RISC) along the hot exciton channel. As a result, all the excitons are nearly utilized giving rise to the improvement in the efficiency of fluorescent OLEDs, but also can usefully conceal the build-up of long-lifetime T₁ exciton, relieving the triplet-triplet concentration quenching. During the past few years, numbers of fluorophores harnessing HLCT excited states have been synthesized by coupling different donor and acceptor pairs^{2e,7b,10} and the extremely enhanced electroluminescence (EL) efficiencies or EQEs have been realized.¹ In many cases, the LE state component has a large oscillator strength from overlap of electron and hole wave functions and donates to the absolute fluorescence quantum yield (Φ_{Pl}) enhancement, however, the CT state still triggers wider emission.¹¹ Therefore, more sophisticated molecular designs aiming at balanced LE and CT components to accomplish golden combination between optical properties and η_{s} of the HLCT-state-based emitters are required. Herein, we report new D-A type HLCT molecules, namely mTAHPI, pTAHPI and pTAPI, featuring excited-state intramolecular proton

(ESIPT) of transfer moiety o-hydroxyphenyl phenanthroimidazole (HPI)¹² and its O-benzyl-protected derivative (PI) as the A part and triphenylamine (TPA) as the D part of the molecules (Scheme 1). In this design, anthracene was inserted between HPI and TPA moieties to enhance a deep blue emission of the target molecules. Anthracene is one of the polyaromatic chromophores that have been utilized intensively to construct deep blue emissive molecules and successfully applied as emitters in OLEDs, owing to its intrinsically wide energy band gap, outstanding thermal and electrochemical stabilities, and high Φ_{PL} as well as ease of chemical modification and low-cost which is extremely vital in development of emissive materials for a practical application to date.13 In order to optimize the LE and CT components in the molecules, TPAanthracene moiety was linked to HPI/PI units at different positions. Actually, these HLCT compounds delivered blue emission property without exhibiting ESIPT photophysical properties in solution and film state. Crucially, the -OH of the HPI unit instigated abundant intramolecular H-bond and intermolecular interactions in mTAHPI and pTAHPI, which thus showed narrower photoluminescence (PL) and electroluminescence (EL) emissions as compared to pTAPI. The OLED device based on pTAHPI attained an EQE of 8.13% (>2.5 times enhancement compared with a pTAPI-based device) with an ultra-high brightness 18100 cd m⁻², narrow emission (FHWM = 68 nm) and η_s value as high as 94%.



Scheme 1 Synthesis of HPI derivatives mTAHPI, pTAHPI and pTAPI.

Results and discussion

The target two isomeric o-hydroxyphenyl phenanthroimidazole (HPI) derivatives **mTAHPI** and **pTAHPI** and its O-benzyl (Bn)-protected derivative **pTAPI** were synthesized as described in Scheme 1. First, the anthracene borolane **3** was prepared by mono coupling of 9-10-dibromoanthracene **1** with

4-(diphenylamino)phenylboronic acid followed by borolylation of the resulting bromoanthracene 2 with bis(pinacolato)diboron catalysed by Pd(dppf)₂Cl₂/KOAc. Second, the two isomers of bromo phenanthroimidazole intermediates 5 and 6 were formed via an acid catalysed onepot multi-component condensation reaction of phenanthrenedione, aniline, ammonium acetate and the corresponding bromosalicylaldehyde. Finally, Suzuki coupling

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reaction of borolane **3** with either bromo phenanthroimidazoles **5** or **6** afforded the related **pTAHPI** and **mTAHPI** as pale-yellow solids in good yields. To evaluate the existence and effect of ESIPT process in HPI moiety of the molecules, **pTAHPI** was then reacted with benzyl bromo in the presence of KOH to give the O-benzyl-protected **pTAPI** in 89% yield. All compounds were fully characterized by standard spectroscopic techniques and the results agreed with their expected chemical structures. As shown in Fig. S1 (ESI⁺), each ¹H-NMR spectrum of both **pTAHPI** and **mTAHPI** detected a characteristic hydrogen-bonded OH proton signal at exceptionally down-fields of 14.26 and 13.52 ppm, respectively, indicating the presence of a six-membered ring intramolecular hydrogen-bond system between -OH and - C=N- units (Scheme 1) when they were dissolved in chloroform-*d* solution.

It should be realized that the existence of intramolecular Hbonding in both pTAHPI and mTAHPI can promote the proton transfer through a characteristic four-level photocycle (5- or 6membered cyclic transition state) resulting in ESIPT process occurring in the molecules.14 Many HPI moiety contained molecules have been observed to exhibit ESIPT via a strong intramolecular hydrogen bond between its OH proton donor and -C=N- proton acceptor.^{12,15} However, it has been reported that the introduction of an electron-donating triphenylamine (TPA) group into the side of oxazole of 2-12'hydroxyphenyl)oxazoles and side of azole of 2-(2hydroxyphenyl)-azoles (a class of typical ESIPT molecules) can lead to a sole enol-form emission in PL spectra with different polar solutions, and the ESIPT keto-form emission is suppressed completely.¹⁶ The TPA bearing 2-(2'-hydroxyphenyl)oxazoles displayed a deep-blue enol-form emission in both PL and EL spectra with narrow emission spectra owing to the absence of the keto-form emission at the long wavelength region.^{16a} Thus, it is noteworthy to gain a theoretical understanding of the ESIPT process in HPI moiety of mTAHPI and pTAHPI. Accordingly, the ground-state potential energy curves (GS-PECs) and excitedstate potential energy curves (ES-PECs) of the proton transfer (PT) coordinates in gas phase as a function of the O-H bond length were constructed using the CAM-B3LYP/6-31G(d,p) approach.17 This approach has been utilized and proven to be reliable in providing qualitative energetic pathways for the PT process.¹⁸ As depicted in Fig. 1a, all molecules exhibited high energy barriers in both ground-state (12.46-12.65 kcal/mol) and excited-state (9.23-12.55 kcal/mol), suggesting that the PT process in mTAHPI and pTAHPI is unlikely to occur both in the S_0 and S_1 states. The optimized structures of **mTAHPI** and pTAHPI in the ground state reveal a nearly planar conformation between phenol and five-membered imidazole ring with small dihedral angles (ϕ) of 6-10°, which could be the result of a strong intramolecular H-bond formed between the two units (Fig. 2). On the other hand, without the ability to form intramolecular hydrogen bond the O-benzyl-protected phenol of pTAPI aligns almost perpendicular to the plane of five-membered imidazole ring with ϕ of 84°. The calculated intramolecular H-bond (N···H) distance of **mTAHPI** are shortened from 1.656 Å in the S₀ state to 1.638 Å in the S₁ state, while there is no obvious difference in the N···H distances of the S_0 and S_1 states of **pTAHPI** (Table S1, ESI⁺), suggesting that the intramolecular H-bond of mTAHPI becomes strengthened upon photoexcitation. Accordingly, if there is ESIPT process taking place in both molecules, mTAHPI will be more susceptible to ESIPT than pTAHPI. In addition, the simulated enol absorption and enol emission spectra based on the vertical electronic transition computed by using TD-CAM-B3LYP/6-31G(d,p) basis set¹⁷ (Fig. 1b) were in good agreement with the experimental results. As shown in Fig. 2, for all molecules, the highest occupied molecular orbitals (HOMO) are fully delocalized over TPA and anthracene moieties, while the lowest unoccupied molecular orbitals (LUMO) are mainly localized on the anthracene unit with little distribution on the adjacent phenyl rings. Therefore, the HOMO and LUMO distributions hold a large overlap over the anthracene moiety, which is rather beneficial for boosting the LE component and enhancing the photoluminescence (PL) efficiency of these molecules.19

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Fig. 1 a) Calculated potential energy curves in the S_0 and S_1 and b) simulated enol absorption and enol emission spectra of mTAHPI and pTAHPI computed at TD-CAM-B3LYP/6-31G(d,p) level.



Fig. 2 The optimized structures with dihedral angles and HOMO-LUMO orbitals of mTAHPI, pTAHPI and pTAHPI computed at TD-CAM-B3LYP/6-31G(d,p) level.

The UV-vis absorption and photoluminescence (PL) spectra of **mTAHPI**, **pTAHPI** and **pTAPI** measured in dilute toluene solutions and neat films are shown in Fig. 3a, and the characteristics are summarized in Table 1. Their absorption bands in the short-wavelength region (<350 nm) were corresponded to the π - π * transition or the n- π * transition of triarylamine and aromatics, and the typical absorptive bands of anthracene, while the longest wavelength absorption at ~377 nm might derive from an intramolecular charge transfer (ICT) transition from donor to acceptor. The compounds exhibited

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strong blue emission in the solution with maximum emission bands in the rage of 453-459 nm with the Φ_{PL} measured by integrating sphere to be as high as 76-89%. The PL spectrum of **pTAHPI** was found to match well with PL of its OH-protected derivative **pTAPI**. Meanwhile, the stokes shifts between the absorption and PL spectra of **mTAHPI** and **pTAHPI** were calculated to be 78-86 nm, which are far too low for ESIPT molecules.^{14a,20} A partial overlap of the absorption and PL spectra was also observed in both cases. These results confirm that no ESIPT take place in **mTAHPI** and **pTAHPI** and their PL emissions are enol emission, consistent well with the DFT findings. In the neat films, the PL spectra of **mTAHPI**, **pTAHPI** and **pTAPI** were somewhat red shifted relative to their toluene solutions (Fig. 3a) as well as their Φ_{PL} values significantly dropping to 13-21%, indicating that intermolecular π - π interactions exist in the film state causing a strong fluorescence quenching. Such intermolecular aggregations have been detected in several anthracene derivatives.²¹ The Φ_{PL} values of the molecules in film states could be improved by doping in 4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) film. With the optimum doping concentration of 20wt% the Φ_{PL} values of **mTAHPI**, **pTAHPI** and **pTAPI** in doped films were evaluated to be 46%, 43% and 45% respectively. As shown in Fig. S2 (ESI⁺), the PL spectra of the doped films are slightly blue shifted as compared to the neat films with no emission peaks of the CBP host matrix being spotted, indicating a complete energy transfer from the CBP host to the dopants.

Table 1 Key physical data of the synthesized compounds.												
Compd	λ _{abs} ^a (nm)	λ _{PL} (nm) solº/film ^b /dfilm ^c	Stokes shift (nm)ª	τ ^d (ns) ^b	⊕ _{PL} (%) ^e solª/film ^b /dfilm ^c /solid ^f	T _g /T _m /T _{5d} (°C) ^g	Eg ^{opt} (eV) ^h	HOMO/LUMO (eV) ⁱ				
mTAHPI	367	453/465/462	86	<1	89/13/46/38	-/293/501	2.73	-5.70/-2.97				
рТАНРІ	374	459/477/468	85	1	87/16/43/28	-/325/513	2.72	-5.64/-2.92				
pTAPI	378	456/474/462	78	2	76/21/45/20	150/-/370	2.97	-5.64/-2.87				

^{*a*} Measured in solution of toluene. ^{*b*} Measured in thin film coated on fused silica substrates. ^{*c*} Measured in 20 wt% doped CBP thin film coated on fused silica substrates. ^{*d*} Transient PL decay life time of the thin films. ^{*e*} Absolute PL quantum yield evaluated using an integrating sphere. ^{*f*} Obtained from solid powders. ^{*g*} Measured by DSC (2nd scan) and TGA under N₂ flow. ^{*h*}Estimated from absorption onset in thin film: $E_{g}^{opt} = 1240/\lambda_{onset}$. ^{*i*} HOMO measured by AC-2 of neat film and LUMO = HOMO + E_{g}^{opt} .



Fig. 3 a) The absorption and fluorescence spectra in toluene solution (solid line) and in neat films (dashed line) coated on fused silica substrates. b) PL spectra in various polarity solvents. c) linear fitting of the Lippert–Mataga plots (Δf , orientation polarizability of solvent media; $\upsilon_a - \upsilon_r$, Stokes shift a: absorption; f: fluorescence). d) Transient PL decay spectra in in various polarity solvents.

To further investigate the photophysical properties and fluorescent characteristics of **mTAHPI**, **pTAHPI** and **pTAPI**, the absorption and PL spectra in various solvent systems were thoroughly evaluated. This solvatochromic experiment is generally used to inspect the excited state properties for CTstate molecule.^{7b,22} As depicted in Fig. 3b, from low-polarity hexane to high-polarity acetonitrile, all molecules show large

solvatochromic shifts of 89-105 nm from blue to orange. In addition, their PL spectra in low-polarity hexane reveal mild vibronic structures and then the PL spectra gradually broaden and become structureless with the increasing of solvent polarity. Furthermore, the correlation between the Stokes shift (v_a-v_f) against the solvent orientational polarizability (Δf) was plotted and linear fitted according to Lippert-Mataga equation (Table S2, ESI⁺). The dipole moment (μ_e) of the excited state, describing the variation of excited state of the molecules, can be estimated from the slope of the Lippert-Mataga plots. The ground-state dipole moments (μ_g) were estimated using DFT at the level of B3LYP/6-31G(d,p) to be 5.00 D, 4.89 D and 3.21 D for mTAHPI, pTAHPI and pTAPI, respectively. As shown in Fig. 3c, all molecules displayed to two different fitted slopes in lowpolarity and high-polarity regions, and accordingly two μ_{e} values were calculated to be 17.30 D and 31.31 D for mTAHPI, 17.60 D and 32.09 D for pTAHPI and 16.29 D and 31.77 D for pTAPI. These results signify the coexistence of CT and LE components, which are consistent with the description of HLCT state.²³ In other words, mTAHPI, pTAHPI and pTAPI possess HLCT character. The HLCT is a valuable excited state which originates from a state-mixing of the weak binding energy of CT state and large radiative transition rate of LE state.7b,8b The presence of HLCT state could ensure a relatively high photoluminescence (PL) efficiency and a large fraction of singlet exciton generation in electroluminescence (EL).²⁴ Notably, both μ_g and μ_e values of mTAHPI and pTAHPI are bit higher than pTAPI in both highpolarity or low-polarity regions, which could be the effect of the intramolecular H-bonding in mTAHPI and pTAHPI. This could influence the properties of mTAHPI and pTAHPI in solution and thin film when compared with pTAPI. As listed in Table S2, all molecules showed high Φ_{PL} in different solutions. Generally, the

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molecules based on CT state always show low radiative transition rate and poor PL efficiency, which is mainly caused by the spatially separated transition orbital of CT state, as well as the CT state being a dark state in solutions with high polarity.²⁵ However, their high Φ_{PL} values (60-82%) in polar solutions (acetone and acetonitrile) are the indication of the highly statemixed CT and LE states (or HLCT) in the molecules. Further study by time-resolved fluorescence spectroscopy revealed fluorescence traces of **mTAHPI**, **pTAHPI** and **pTAPI** with a single-exponential decay in different solvent polarities (Fig. 3d), verifying that fluorescence evolves from only one excited state and HLCT state was supposed to be formed rather than a simple mixture of the LE and CT states.

To inspect the excited-state properties and confirm the HLCT character of **mTAHPI**, **pTAHPI** and **pTAPI**, the quantified natural transition orbitals (NTOs) of $S_0 \rightarrow S_1$ were calculated using the TDA-B3LYP/6-31G(d,p) method based on the optimized lowest singlet excited state geometry.¹⁷ In all molecules, the spatial distributions of holes and particles were

similar and NTOs of $S_0 \rightarrow S_1$ clearly displayed the HLCT transition characteristics (Fig. 4a) as it is comprised of both LE and CT transitions. The hole is mainly distributed on the TPA and anthracene, while the particle is largely spread over the anthracene with a slight residue on the phenyl of TPA and phenol of HPI. The hole and particle distributions are totally overlapped on the anthracene ring, indicating the LE-like transition, whereas the hole and particle distributions do not overlap on the entire TPA unit, indicating a CT-like transition. As is evident from the energy landscape plots (Fig. 4b), in all cases the energy gaps between the S_1 and T_2 states (<0.08 eV) are substantially narrower than that between T_2 and T_1 states (>1.25 eV), indicating that the RISC rate (k_{RISC}) from the T2 to S_1 state should be higher than the internal conversion rate (k_{ICT}) from the T_2 to T_1 states, giving rise to a possibly hot-exciton channel for the RISC of the $T_2 \rightarrow S_1$ process according to the El-Sayed rule.²⁶ Therefore, when the triplet excitons relax to the lowest vibration level of T₁, some of them can be converted to singlet excitons through the $T_2 \rightarrow S_1$ channel.



Fig. 4 a) Natural transition orbitals (NTOs) of $S_0 \rightarrow S_1$ transition (*f* represents the oscillator strength. The percentage indicates the possibility of the transition) and b) the energy landscape of singlet and triplet excited states obtained from TDA-B3LYP/6-31G(d,p) calculations.

The presence of intramolecular H-bond and its impact on molecular interactions, crystallinity, morphology and thermal stability of the materials were investigated. The single crystal of mTAHPI was successfully grown from a mixture of dichloromethane:hexane and examined by single crystal X-ray diffraction (SCXRD). The crystallographic data are given in the Supporting Information (Table S3, ESI⁺). As shown in Fig. 5a, the molecular structure shows the intramolecular H-bonding of O1—H1…N3 with the distance of 1.879 Å, indicating strong Hbonds. The strong intramolecular H-bonds bring about a relatively small ϕ of 12.9° between phenol and five-membered imidazole ring as compared to that between phenol and anthracene ring (66.1°), resulting in a high degree of planarity in o-hydroxyphenyl phenanthroimidazole (HPI) plane. The crystal packing shows the intermolecular interactions and stacking in a face-to-face manner, observing between the anthracene units with the centroid-centroid distances of 4.024 Å (Fig. 5a, highlighted in red color). These separations are close to an effective intermolecular interaction distance (3.7 Å), signaling the strong π - π stacking which could trigger a serious fluorescence aggregation-caused quenching, giving rise to low

PL efficiency in neat film state of the molecule. The packing interactions are also observed through edge-to-face C-H···π interactions between the phenyl group of imidazole unit and phenanthrene ring center, and among the triphenylamine units (with molecular distances of 2.622-2.780 Å) (Fig. 5a, highlighted in green and yellow colors, respectively). Moreover, such strong interactions may rigidify the molecular structure for efficient radiative transition and narrow emission spectrum.19 Accordingly, the Φ_{PL} values of **mTAHPI** and **pTAHPI** in solid powder were recorded to be somewhat higher than pTAPI. The crystallinity of these as-synthesized mTAHPI, pTAHPI and pTAPI solid powders was further evaluated by powder x-ray diffraction (PXRD). As illustrated in Fig. 5b, the PXRD profile of mTAHPI reveals amounts of intense diffraction peaks, indicating the presence of a long-range ordered structure and crystalline behavior of the material. The XRD pattern of pTAHPI was roughly similar to that of mTAHPI but with relatively lower peak intensity, while that of pTAPI displayed strong diffraction peak at low 20 value of 7.66° with few low-intensity peaks at higher 20. Hence, pTAPI was suspected to have a less crystallinity or molecular interactions when compared to mTAHPI and pTAHPI.

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To investigate morphology and thermal stability of the materials, thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out (Fig. 5c, Table 1). The decomposition temperatures (T_{5d}, at 5% weight loss) of mTAHPI and pTAHPI were over 500 °C, which is much higher than that of pTAPI (370 °C), indicating the superior thermal stability of mTAHPI and pTAHPI over pTAPI. Also, mTAHPI and pTAHPI exhibited high melting temperatures (T_m) of 293 °C and 325 °C, while for **pTAPI** only glass transition temperature (T_g) was detected to be 150 °C. Furthermore, mTAHPI and pTAHPI showed high T_{5d} and crystalline structure resulting from the existence of strong intramolecular H-bond and intermolecular interactions in the molecules, while pTAPI had a morphology of amorphous solid. The high T_{5d} and T_m have proved that the compounds possess good thermal stability which is an essential aspect for device fabrication by thermal evaporation as well as for achieving a good device performance,²⁷ since they can endure high temperatures and would not decompose during device fabrication process under vacuum thermal deposition.

Electrochemical behaviours of mTAHPI, pTAHPI and pTAPI were investigated using cyclic voltammetry (CV) in dichloromethane solutions in the presence of *n*-Bu₄NPF₆ as a supporting electrolyte (Fig. S3, ESI+). All molecules exhibited good electrochemical stability and reversibility, as their repeated CV scans demonstrated unchanged CV traces. This implied that the highly reactive radical cations of TPAanthracene formed during the first oxidation ($E_{1/2} \sim 0.98$ V) were fairly stable to an oxidative coupling dimerization on the surface of a working electrode, believably due to an effective π -electron delocalization between TPA and anthracene units.13d,28 The HOMO energy levels of the materials in thin film were determined by photoelectron yield spectroscopy (AC-2) in air (Fig. S4, ESI⁺). The LUMO energy levels were deduced from the HOMO and optical band gaps (Egopt) by using the equation of LUMO = HOMO + E_g^{opt} . The corresponding HOMO/LUMO levels for mTAHPI, pTAHPI and pTAPI were estimated to be -5.70/-2.97 eV, -5.64/-2.92 eV and -5.64/-2.87 eV, respectively (Table 1).



To explore the effect of molecular structure on the EL properties of the designed HPI derivatives, the optimized OLED devices with mTAHPI, pTAHPI and pTAPI as the emitters were fabricated with configuration of ITO/PEDOT:PSS:Nf (40 nm)/emitter 20wt% in CBP (40 nm)/TmPyPb (30 nm)/LiF (0.5 nm)/Al (100 nm) (Fig. 6c, insert). With a view to simplify the device structure while at the same time maintaining high-Nafion (Nf) efficiency, doped poly(3,4ethylenedioxythiophene):poly(4-styrene sulfonate (PEDOT:PSS) with ratio of 1:4 was applied as hole injection layers (HIL) with a work function of 5.50 eV (Fig. 6a and S4, ESI⁺). It has been reported that the work function of PEDOT:PSS as HIL can be fine-tuned by mixing with Nafion in different rations.²⁹ An appropriate match between the work functions of HIL and HOMO level of emissive layer (EML) can reduce the charge injection barrier between the two layers, giving rise to a better charge carrier balance within the EML caused by the efficient hole injection from HIL to EML.³⁰ The high electron mobility and suitable LUMO level (-2.73 eV) of 1,3,5-tris(3-pyridyl-3phenyl)benzene (TmPyPb) was employed as electron transporting layer (ETL). The optimized energy band alignment of the device would facilitate hole/electron accumulation and confine exciton recombination zone within the EML.³¹ As EML, in order to reach their optimal PL efficiency, different host materials and doping concentrations were tried to reach the best performances of the devices. Successfully, the emitters were doped in CBP at 20 wt%. The characteristic curves and device data are shown in Fig. 6b-e and Table 2. As depicted in Fig. 6e and the insert photo, the mTAHPI, pTAHPI and pTAPI based OLEDs exhibited strong blue emission colours with the EL emission peaks at 463, 472 and 467 nm and Commission Internationale de l'Eclairage (CIE) coordinates of (0.14, 0.17), (0.15, 0.23) and (0.19, 0.25), respectively. Moreover, the mTAHPI- and pTAHPI-devices showed EL spectra with the full width half maximum (FWHM) values of 65-68 nm, which are relatively narrower than that of **pTAPI** device. This might be a result of strong H-bonding interactions which stiffen the molecular structure to generate narrow emission. EL spectra of all devices fitted well with their PL spectra in the thin film without emission peaks of TmPyPB (470 nm)³² and CBP (390 nm)³³ at lower wavelengths. Notably, these EL were unchanged under the applied voltages ranging from 6 V to 10 V (Fig. S5, ESI⁺), implying effective charge injection and recombination in the EML, and excimer emission as well as exciplex emission from EML/TmPyPB interface being efficiently suppressed. All three devices had low turn-on voltages of 2.8-3.2 V at 1 cd m⁻², indicating the effective charge injection and transfer of the devices. Considering that these molecules possess D-A properties, a host containing electron donor unit may also contribute to the balanced transportation of carriers. Among them, pTAHPI-based device delivered the best overall EL

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Fig. 5 a) Crystal structure packing of mTAHPI. Intramolecular hydrogen bonding of $\mathsf{O}_1\text{-}\mathsf{H}_1\cdots\mathsf{N}_3$ and intermolecular interactions showing $\pi\text{-}\pi$ facial stacking of anthracene, C-H···π stacking between phenyl ring and phenanthroimidazole unit of HPI and C-H··· π stacking of TPA group are highlighted in magenta, red, green, and vellow, respectively. The distances are given in Å, b) Powder x-ray diffraction patterns of solid samples. c) DSC (2nd heating scan) and TGA thermograms.

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performance, where the maximum external quantum efficiency (EQE_{max}) was as high as 8.13%, and corresponding current efficiency (CE) and power efficiency (PE) were 12.43 cd A⁻¹ and 10.39 lm W⁻¹, respectively. The device produced an ultra-high brightness of 18100 cd m⁻². The **mTAHPI**-based device also achieved good EL efficiency, together with luminance maximum of 13630 cd m⁻² and EQE, CE and PE of 6.73%, 9.78 cd A⁻¹ and 8.10 lm W⁻¹, respectively. While the OH-protected derivative pTAPI-based device exhibited a relatively poor results in all device parameters. Both pTAHPI- and mTAHPI-based devices also showed better efficiency roll-off at high luminance than pTAPI-based device. Remarkably, the EQE_{max} (6.73-8.13%) of surpassing the theoretical upper limit (5%) of fluorescent materials of the devices based on pTAHPI and mTAHPI and their superior EL results as compared to **pTAPI** could be accredited to the combined effects of the H-bond interactions, the HLCT character and optimized device structure. The possible RISC process from upper excited states could somewhat boost up the EQE, while H-bond interactions could partially reduce the unavoidable excited state geometric relaxation, giving rise to a narrow EL emission and high efficiency.^{16a} In addition, the results of hole-only devices (ITO/NPB (10 nm)/EML 20% doped in CBP (90 nm)/NPB (10 nm)/Al (100 nm), Fig. 6f, insert) demonstrated that pTAHPI and mTAHPI possessed better hole transporting ability than pTAPI (Table 1). As illustrated in Fig. 6f, at the same voltage pTAHPI and mTAHPI possess relatively

higher and faster currents for holes when compared to **pTAPI** counterpart. Consequently, the hole mobilities for **mTAHPI**, **pTAHPI** and **pTAPI** were calculated by combining the Mott-Gurney equation and Frenkel effect³⁴ to be 3.99 x 10⁻⁶, 4.33 x 10⁻⁶ and 1.02 x 10⁻⁷ cm² V⁻¹s⁻¹, respectively. It is known that high mobility emitter could contribute to widen the recombination zone in the emissive layer and result in long device lifetime as well as low driving voltages.³⁵ Besides, the singlet exciton utilization efficiency (η_s) of the EL device was calculated

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$$\eta_s = EQE/(\Phi_{PL} \times \eta_{rec} \times \eta_{out}) \tag{1}$$

according to the equation (1),³⁶

where η_{rec} is the electron-hole recombination efficiency which can be counted as 100% in a suitable device; η_{out} is the outcoupling efficiency which is approximately 20% for glass substrates; Φ_{PL} is the fluorescence quantum yield of the emitters in corresponding solid state. Thus, the η_s values for the devices based on **mTAHPI** and **pTAHPI** were calculated to be 73% and 94% according to Equation (1), which are far beyond the limitation of 25% for fluorescent materials, while the calculated η_s value for **pTAPI** was to be as low as 34% (Table 2). In this regard, both **mTAHPI** and **pTAHPI** may achieve the optimum hybrid excited stated between LE and CT components and the hydroxyl group or H-bonding present in their molecular structures is supposed to provide conditions for increased CT process in the excited state and balance LE and CT components.



Fig. 6 a) Energy level diagram of the OLEDs. b) Current density-voltage-luminance (J-V-L) plots, c) external quantum efficiency-current density (EQE-J) plots (insert: schematic structure of the OLEDs), d) luminance efficiency-power efficiency-current density (LE-PE-J) plots and e) electroluminescence (EL) spectra (insert: image of blue OLED) of the devices. f) Current density-voltage (J-V) plots of the hole only devices (insert: structure of hole only devices).

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Table 2 Electroluminescent data of solution-processed devices. ^o													
EML	Hole mobility	Von	λ_{EL}	L _{max}	EQE/LE/PE (%, cd A ⁻¹ , lm W ⁻¹) ^c		CIE	FHWM	ηs				
	(cm² 以-1 s-1) ^b	(V)	(nm)	(cd m ⁻²)	maximum	@ 1000 cd m ⁻²	(x, y)	(nm)	(%) ^d				
mTAHPI	3.99 x 10 ⁻⁶	2.8	463	13630	6.73/9.78/8.10	2.92/4.05/2.05	0.14, 0.17	65	73				
pTAHPI	4.33 x 10 ⁻⁶	2.8	472	18100	8.13/12.43/10.39	3.33/5.60/3.05	0.15, 0.23	68	94				
pTAPI	1.02 x 10 ⁻⁷	3.2	467	3358	3.13/5.34/4.72	0.69/1.18/0.96	0.19, 0.25	77	34				
•													

^a ITO/PEDOT:PSS:Nf (40 nm)/EML 20% doped in CBP (40 nm)/TmPyPb (30 nm)/LiF (0.5 nm):Al (100 nm). ^b ITO/NBP (10 nm)/ EML 20% doped in CBP (90 nm)/NBP (10 nm)/Al (100 nm). ^c External quantum efficiency/luminance efficiency/power efficiency. ^d Singlet exciton utilization efficiency.

Experimental

Materials and methods: All reagents and solvents were without further purification. All NMR spectra were recorded on Bruker Ascend III HD (600 MHz) spectrometer using CDCl₃ as a solvent in all cases. High resolution mass analysis was performed on Bruker LC-QTOF-MS/MS. UV-Visible spectra were recorded on Perkin Elmer Lambda 1050 UV/Vis/NIR spectrometer. Fluorescence emission spectra and photoluminescence decay profiles were measured using Edinburgh Instruments FLS980 spectrometer. Absolute fluorescence quantum yield $(\Phi_{\mbox{\scriptsize F}})$ was measured by integrating sphere on Edinburgh Instruments FLS 980. Electrochemical analysis was operated on Autolab PGSTA101 with three electrode system fitted with a Pt as counter electrode, a glassy carbon as working electrode and an Ag/AgCl as reference electrode at scan rate of 50 mV s⁻¹ by using TBAPF₆ as electrolyte under argon. HOMO of samples in film states are measured by Riken-Keiki ultraviolet photoelectron spectrometer AC-2 in air. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were done on PerkinElmer DSC-8500 and Perkin–Elmer TGA Pyris 1 instrument, respectively, under nitrogen gas flow with heating rate of 10 °C min⁻¹. Melting points were measured using a Krüss KSP1N melting point meter and are uncorrected. Powder XRD patterns were collected using a Bruker D8 ADVANCE diffractometer at 40 kV, 40 mA for Cu K α , (λ = 1.5418 Å) from two theta of 2 to 40° with a step size of 0.01° and scanning rate of 0.6° min⁻¹. Single crystals data were collected on a Bruker D8 Venture diffractometer using φ and ω scans with Mo K radiation at 298 K. The crystal structures were solved with the ShelXT and OLEX2 programs using Levenberg-Marquardt minimization method. The crystal data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif (CCDC: 2007054).

All quantum chemical calculations were performed using the Gaussian 09 package.¹⁷ The ground state geometries, HOMO and LUMO distributions, and HOMO, LUMO energy levels were calculated by B3LYP/6-31G(d,p) level of theory in CH_2Cl_2 solvent. On the basis of the optimized configuration of the ground state (S₀), the high excitation energy levels of singlet and triplet states were computed by TDA-B3LYP/6-31G(d,p) method. Natural transition orbitals (NTOs) were evaluated for the S₁ states. In order to gain further insights into the ESIPT character, potential energy curves were constructed using CAM-B3LYP with 6-31G(d,p) theoretical level and the simulated enol optical spectra were computed at TD-CAM-B3LYP/6-31G(d,p) level.

Device fabrication and measurements: The patterned indium tin oxide (ITO) glass substrates with a sheet resistance of 12 Ω sq⁻¹ were thoroughly cleaned by successive ultrasonic treatment in Liquinox detergent, deionized water, acetone, and isopropanol and brew with nitrogen for drying. The cleaned ITO was then treated by UV ozone for 15 min, then a 40 nm hole iniection laver (poly(3,4-ethylenedioxythiophene:poly(4styrene sulfonate) (PEDOT:PSS, CLEVIOSTM P VP AI 4083) and Nafion in a ratio 1:4 (v/v) was spin coated above ITO at a spin speed of 5000 rpm for 30 s and dried at 120 °C for 30 min. A 40 nm thick EML and CBP layer was deposited simultaneously at an thermal evaporation rate of 0.8 Å s⁻¹ and 0.2 Å s⁻¹, respectively, from low temperature evaporation sources using a Kurt J. Lasker mini SPECTROS 100 thin film deposition system under a base pressure of 5 x 10⁻⁶ mbar to form an active diode area of 4 mm². The film thickness was monitored using a guartz oscillator thickness sensor. A 30 nm thick TmPyPb, 0.5 nm thick LiF and 150 nm thick aluminium layers were subsequently deposited. The hole-only devices were also fabricated as mentioned above. Current density-voltage-luminescence (J-V-L) characteristics were measured simultaneously using a Keithley 2400 source meter and a Hamamatsu Photonics PMA-12 multi-channel analyzer. The absolute external quantum efficiency (EQE) of OLED devices was obtained by Hamamatsu Photonics C9920-12 External Quantum Efficiency Measurement System utilizing an integrating sphere under ambient atmosphere at room temperature.

Synthesis of mTAHPI and pTAHPI: A mixture of 5 or 6 (200 mg, 0.43 mmol), 3 (284 mg, 0.52 mmol), Pd(PPh₃)₄ (50 mg, 0.043 mmol), 2M Na₂CO₃ aqueous solution (10 ml) and THF (30 ml)

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was degassed with nitrogen for 15 min while stirring. Then the stirring reaction was heated and refluxed under nitrogen atmosphere for 24 h. The mixture was cooled to room temperature after confirming consumption of the starting materials by TLC in 30% v/v CH₂Cl₂-hexane. Then the mixture was added with brine solution (30 ml) and extracted with CH₂Cl₂ (3 x 30 ml). The organic extract was washed with water (50 ml), dried over anhydrous Na2SO4, filtered, concentrated under reduced pressure, and finally purified by silica gel column chromatography eluting with 30% v/v CH₂Cl₂-hexane. The product was recrystallized in CH₂Cl₂-MeHO.

mTAHPI as light-yellow solids (71%). M.p = 302-303 °C; ¹H NMR (600 MHz, CDCl₃) δ = 13.52 (s, 1H), 8.80 (d, J = 7.8 Hz, 1H), 8.77 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 3H), 7.71 (t, J = 7.8 Hz, 1H), 7.53 (d, J = 7.8 Hz, 4H), 7.50 (t, J = 7.8 Hz, 1H), 7.41 – 7.32 (m, 11H), 7.29 (t, J = 9.0 Hz, 9H), 7.21 (t, J = 7.8 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 7.09 (t, J = 7.2 Hz, 2H), 7.06 (d, J = 8.4 Hz, 1H), 6.92 (s, 1H); 13 C NMR (151 MHz, CDCl₃) δ = 158.29, 148.54, 147.84, 147.16, 138.66, 136.72, 136.22, 134.88, 134.05, $132.72,\,132.21,\,132.09,\,130.71,\,130.17,\,130.04,\,129.97,\,129.60,$ 129.53, 129.39, 128.66, 128.58, 128.52, 127.56, 127.32, 127.13, 126.90, 126.52, 126.11, 125.98, 125.30, 124.84, 124.78, 124.68, 124.17, 123.25, 123.20, 123.10, 123.08, 122.67, 122.66, 120.93, 117.89, 113.17; HRMS (APCI): *m/z* clacd. for C₅₉H₃₉N₃O (M+): 805.3093, found: 806.2729 (MH+).

pTAHPI as light-yellow solids (76%). M.p = 331-332 °C; ¹H NMR (600 MHz, CDCl₃) δ = 14.27 (s, 1H), 8.81 (d, J = 7.8 Hz, 1H), 8.78 (d, J = 8.4 Hz, 1H), 8.75 (d, J = 8.4 Hz, 1H), 7.85 - 7.75 (m, 10H), 7.72 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.40 - 7.27 (m, 18H), 7.09 (t, J = 6.6 Hz, 2H), 7.08 (d, J = 7.2, 1H), 6.95 (d, J = 7.8 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) $\delta =$ 159.36, 148.51, 147.84, 147.17, 139.19, 136.01, 134.52, 132.62, 132.18, 132.07, 131.05, 130.76, 130.04, 129.61, 129.56, 129.39, 129.17, 128.56, 127.60, 127.18, 127.04, 126.92, 126.61, 126.15, 125.86, 125.76, 125.34, 125.06, 124.98, 124.70, 124.25, 123.27, 123.14, 123.09, 122.67, 121.50, 121.13, 120.94, 112.40. HRMS (APCI): *m*/*z* clacd. for C₅₉H₃₉N₃O (M+): 805.3093, found: 806.1889 (MH+).

Synthesis of pTAPI: A solution of pTAHPI (50 mg, 0.06 mmol) in anhydrous DMF (20 ml) was stirred and cooled down to 0 °C for 10 min. KOH (9 mg, 0.16 mmol) was added into the mixture and stirred continuously for another 30 min. The reaction was set under room temperature for 12h after adding benzyl bromide (16 mg, 0.09 mmol). The consumption of the starting materials was confirmed by TLC in 50% v/v CH₂Cl₂-hexane before termination of reaction. Then the mixture was added to brine solution (20 ml) and extracted with CH₂Cl₂ (3 x 30 ml). The organic extract was washed with water (50 ml), dried over anhydrous Na2SO4, filtered, concentrated under reduced pressure and finally purified by silica gel column chromatography eluting with 30% v/v CH₂Cl₂-hexane. The product was recrystallized in CH₂Cl₂-MeOH to give light-yellow solids (40 mg, 70%). M.p = 310-311 °C; ¹H NMR (600 MHz, CDCl₃) δ = 8.98 (d, J = 7.8 Hz, 1H), 8.81 (d, J = 8.4 Hz, 1H), 8.76 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.79 (t, J = 7.2 Hz, 1H), 7.74 (d, J = 7.2 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.53 (q, J = 7.2 Hz, 2H), 7.47 (t, J = 7.8 Hz, 2H), 7.44 - 7.27 (m,

21H), 7.17 (s, 4H), 7.12 (d, J = 8.4 Hz, 1H), 7.09 (t, J = 7.2 Hz, 2H), 6.95 (s, 1H), 4.86 (s, 2H); ¹³C NMR (151 MHz, CDCl₃) δ = 155.66, 148.47, 146.48, 145.92, 140.97, 136.93, 136.27, 136.02, 135.00, 134.70, 131.43, 131.11, 130.78, 130.73, 128.69, 128.29, 128.08, 127.85, 127.70, 127.68, 127.64, 127.07, 126.91, 126.38, 126.18, 126.07, 125.98, 125.78, 125.72, 125.38, 124.86, 124.13, 123.88, 123.69, 123.51, 123.41, 122.76, 122.40, 121.81, 121.75, 121.73, 121.54, 119.77, 118.65, 114.15, 68.77. HRMS (APCI): m/z clacd. for C₆₆H₄₅N₃O: 895.3563 (M+), found: 896.3590 (MH+).

Conclusions

In conclusion, we successfully synthesized and studied two isomeric D-A molecules containing ESIPT chromophore of ohydroxyphenyl phenanthroimidazole (HPI) mTAHPI and pTAHPI, and its OH protected derivative pTAPI. Their properties were systematically investigated and compared. The theoretical calculation and optical studies demonstrated that mTAHPI and pTAHPI did not show ESIPT characteristics due to high potential energy of proton transfer process in the excited state, while solvatochromic experiments proved that they exhibited an HLCT excited state, which is advantageous to the improvement of EL efficiency. Single-crystal analysis of mTAHPI revealed intramolecular H-bond and intermolecular interactions that were capable of efficiently repressing the inevitable excited state geometric relaxation. The optimized EL devices based on mTAHPI and pTAHPI showed highly efficient EL performance. Especially, pTAHPI-based device achieved an EQE of 8.13% with an ultra-high brightness 18100 cd m⁻², narrow emission (FHWM = 68 nm) and η_s value as high as 94%, while its OH protected derivative **pTAPI** demonstrated rather low EL efficiency and η_s value of 34%. These results hint that such superior EL efficiencies originate from the RISC process arising from the HLCT excited state character which is efficiently enhanced by the intramolecular H-bonding between phenol hydroxyl and phenanthroimidazole. As a result, 3a features a high PL efficiency and exhibits a high exciton utilization efficiency of nearly 100% with EQE up to 7.1% in OLEDs. The results of this work have demonstrated that HPI-based D-A materials are good fluorescent emitters for blue OLEDs and provided a useful guide in the future for designing efficient electroluminescent materials for high-efficiency and high color purity OLEDs by taking advantage of intramolecular H-bond interaction and the HLCT excited state.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- (a) C. W. Tang and S. A. Vanslyke, Appl. Phys. Lett., 1987, 51, 1 913; (b) P. Funchien, P. Chasing, T. Sudyoadsuk and V. Promarak, Chem. Commun., 2020, 56, 6305; (c) M. Godumala, S. Choi, M. J. Cho and D. H. Choi, J. Mater. Chem. C, 2019, 7, 2172; (d) J. H. Lee, C. H. Chen, P. H. Lee, H. Y. Lin, M. K. Leung, T. L. Chiu and C. F. Lin, J. Mater. Chem. C, 2019, 7, 5874; (e) X. Lv, M. Sun, L. Xu, R. Wang, H. Zhou, Y. Pan, S. Zhang, Q. Sun, S. Xue and W. Yang, Chem. Sci., 2020, 5058; (f) S. Kim, H. J. Kwon, S. Lee, H. Shim, Y. Chun, W. Choi, J. Kwack, D. Han, M. Song, S. Kim, S. Mohammadi, I. Kee and S. Y. Lee, Adv. Mater., 2011, 23, 3511; (g) W. Zeng, H. Y. Lai, W. K. Lee, M. Jiao, Y. J. Shiu, C. Zhong, S. Gong, T. Zhou, G. Xie, M. Sarma, K. T. Wong, C. C. Wu and C. Yang, Adv. Mater., 2018, 30, 1704961; (h) Y. Yin, M. U. Ali, W. Xie, H. Yang and H. Meng, Mater. Chem. Front., 2019, 3, 970.
- 2 (a) M. Y. Wong and E. Zysman-Colman, Adv. Mater., 2017, 29, 1605444; (b) A. Maheshwaran, V. G. Sree, H. Y. Park, H. Kim, S. H. Han, J. Y. Lee and S. H. Jin, Adv. Funct. Mater., 2018, 28, 1802945; (c) J. Tagare and S. Vaidyanathan, J. Mater. Chem. C, 2018, 6, 10138; (d) Y. Xu, X. Liang, X. Zhou, P. Yuan, J. Zhou, C. Wang, B. Li, D. Hu, X. Qiao, X. Jiang, L. Liu, S. J. Su, D. Ma and Y. Ma, Adv. Mater., 2019, 31, 1807388; (e) Q. Wei, N. Fei, A. Islam, T. Lei, L. Hong, R. Peng, X. Fan, L. Chen, P. Gao and Z. Ge, Adv. Opt. Mater., 2018, 6, 1800512; (f) Z. Xu, B. Z. Tang, Y. Wang and D. Ma, J. Mater. Chem. C, 2020, 8, 2614.
- B. Zhao, T. Zhang, B. Chu, W. Li, Z. Su, H. Wu, X. Yan, F. Jin, Y. Gao and C. Liu, *Sci. Rep.*, 2015, 5, 10697.
- 4 (a) F. Kessler, Y. Watanabe, H. Sasabe, H. Katagiri, M. K. Nazeeruddin, M. Grätzel and J. Kido, *J. Mater. Chem. C*, 2013, 1, 1070; (b) X. Ban, K. Sun, Y. Sun, B. Huang, S. Ye, M. Yang and W. Jiang, *ACS Appl. Mater. Interfaces*, 2015, 7, 25129.
- 5 (a) H. Liu, L. Kang, J. Li, F. Liu, X. He, S. Ren, X. Tang, C. Lv and P. Lu, J. Mater. Chem. C, 2019, 7, 10273; (b) W. Liu, S. Ying, R. Guo, X. Qiao, P. Leng, Q. Zhang, Y. Wang, D. Ma and L. Wang, J. Mater. Chem. C, 2019, 7, 1014; (c) Y. J. Luo, Z. Y. Lu and Y. Huang, Chinese Chem. Lett., 2016, 27, 1223.
- (a) T. T. Bui, F. Goubard, M. Ibrahim-Ouali, D. Gigmes and F.
 Dumur, *Beilstein J. Org. Chem.*, 2018, **14**, 282; (b) Y. Liu, C. Li, Z.
 Ren, S. Yan and M. R. Bryce, *Nat. Rev. Mater.*, 2018, **3**, 18020.
- 7 (a) W. Z. Yuan, X. Bin, G. Chen, Z. He, J. Liu, H. Ma, Q. Peng, B. Wei, Y. Gong, Y. Lu, G. He and Y. Zhang, *Adv. Opt. Mater.*, 2017, 5, 1700466; (b) W. Li, Y. Pan, L. Yao, H. Liu, S. Zhang, C. Wang, F. Shen, P. Lu, B. Yang and Y. Ma, *Adv. Opt. Mater.*, 2014, 2, 892; (c) Y. Liu, H. Liu, Q. Bai, C. Du, A. Shang, D. Jiang, X. Tang and P. Lu, *ACS Appl. Mater. Interfaces*, 2020, 12, 16715.
- 8 (a) W. Li, D. Liu, F. Shen, D. Ma, Z. Wang, T. Feng, Y. Xu, B. Yang and Y. Ma, *Adv. Funct. Mater.*, 2012, 22, 2797; (b) W. Li, Y. Pan, R. Xiao, Q. Peng, S. Zhang, D. Ma, F. Li, F. Shen, Y. Wang, B. Yang and Y. Ma, *Adv. Funct. Mater.*, 2014, 24, 1609.
- 9 (a) C. Fu, S. Luo, Z. Li, X. Ai, Z. Pang, C. Li, K. Chen, L. Zhou, F. Li,
 Y. Huang and Z. Lu, *Chem. Commun.*, 2019, **55**, 6317; (b) B. Liu,
 Z. W. Yu, D. He, Z. L. Zhu, J. Zheng, Y. D. Yu, W. F. Xie, Q. X.
 Tong and C. S. Lee, *J. Mater. Chem. C*, 2017, **5**, 5402.
- 10 X. Tang, X. L. Li, H. Liu, Y. Gao, Y. Shen, S. Zhang, P. Lu, B. Yang,

S. J. Su and Y. Ma, Dye. Pigment., 2018, 149, 430.

- (a) D. Tu, P. Leong, Z. Li, R. Hu, C. Shi, K. Y. Zhang, H. Yan and Q. Zhao, *Chem. Commun.*, 2016, **52**, 12494; (b) S. Lukman, K. Chen, J. M. Hodgkiss, D. H. P. Turban, N. D. M. Hine, S. Dong, J. Wu, N. C. Greenham and A. J. Musser, *Nat. Commun.*, 2016, **7**, 13622.
- 12 (a) S. Park, J. E. Kwon and S. Y. Park, *Phys. Chem. Chem. Phys.*, 2012, 14, 8878; (b) V. S. Padalkar and S. Seki, *Chem. Soc. Rev.*, 2016, 45, 169.
- (a) J. Huang, J. H. Su and H. Tian, J. Mater. Chem., 2012, 22, 10977; (b) A. Slodek, M. Filapek, E. Schab-Balcerzak, M. Grucela, S. Kotowicz, H. Janeczek, K. Smolarek, S. Mackowski, J. G. Malecki, A. Jedrzejowska, G. Szafraniec-Gorol, A. Chrobok, B. Marcol, S. Krompiec and M. Matussek, *European J. Org. Chem.*, 2016, 2016, 4020; (c) K. Danel, T. H. Huang, J. T. Lin, Y. T. Tao and C. H. Chuen, *Chem. Mater.*, 2002, 14, 3860; (d) A.-M. Thangthong, D. Meunmart, N. Prachumrak, S. Jungsuttiwong, T. Keawin, T. Sudyoadsuk and V. Promarak, *Chem. Commun.*, 2011, 47, 7122.
- (a) K. Benelhadj, J. Massue, P. Retailleau, G. Ulrich and R.
 Ziessel, Org. Lett., 2013, 15, 2918; (b) P. Majumdar and J. Zhao,
 J. Phys. Chem. B, 2015, 119, 2384.
- K. Skonieczny, A. I. Ciuciu, E. M. Nichols, V. Hugues, M.
 Blanchard-Desce, L. Flamigni and D. T. Gryko, *J. Mater. Chem.*, 2012, 22, 20649.
- (a) B. Li, G. Tang, L. Zhou, D. Wu, J. Lan, L. Zhou, Z. Lu, and J.
 You, *Adv. Funct. Mater.*, 2017, 27, 1605245, (b) A. I. Ciuciu, K.
 Skonieczny, D. Koszelewski, D. T. Gryko and L. Flamigni, *J. Phys. Chem. C*, 2013, 117, 791.
- 17 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, 2016, Gaussian 09, Revision A.02, Gaussian, Inc., Wallin.
- (a) N. Kanlayakan, K. Kerdpol, C. Prommin, R. Salaeh, W. Chansen, C. Sattayanon and N. Kungwan, *New J. Chem.*, 2017, 41, 8761; (b) B. An, S. Feng, K. Wen, W. Wu, H. Yuan, Q. Zhu, X. Guo and J. Zhang, *Org. Electron.*, 2017, 45, 1.
- X. Qiu, Y. Xu, C. Wang, M. Hanif, J. Zhou, C. Zeng, Y. Li, Q. Jiang, R. Zhao, D. Hu and Y. Ma, *J. Mater. Chem. C*, 2019, **7**, 5461.
- 20 K. I. Sakai, S. Tsuchiya, T. Kikuchi and T. Akutagawa, *J. Mater. Chem. C*, 2016, **4**, 2011.
- (a) Y. C. Chang, S. C. Yeh, Y. H. Chen, C. T. Chen, R. H. Lee and R. J. Jeng, *Dye. Pigment.*, 2013, **99**, 577; (b) Y. H. Chen, S. L. Lin, Y. C. Chang, Y. C. Chen, J. T. Lin, R. H. Lee, W. J. Kuo and R. J. Jeng,

Journal Name

Org. Electron., 2012, 13, 43.

- 22 C. Zhou, D. Cong, Y. Gao, H. Liu, J. Li, S. Zhang, Q. Su, Q. Wu and B. Yang, *J. Phys. Chem. C*, 2018, **122**, 18376.
- 23 D. Hu, L. Yao, B. Yang and Y. Ma, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci., 2015, 373, 20140318.
- Y. Pan, J. Huang, W. Li, Y. Gao, Z. Wang, D. Yu, B. Yang and Y. Ma, *RSC Adv.*, 2017, 7, 19576.
- 25 Q. Luo, L. Li, H. Ma, C. Lv, X. Jiang, X. Gu, Z. An, B. Zou, C. Zhang and Y. Zhang, *Chem. Sci.*, 2020, **11**, 6020.
- (a) R. Chen, Y. Tang, Y. Wan, T. Chen, C. Zheng, Y. Qi, Y. Cheng and W. Huang, *Sci. Rep.*, 2017, 7, 6225; (b) N. Sharma, M. Y. Wong, D. Hall, E. Spuling, F. Tenopala-Carmona, A. Privitera, G. Copley, D. B. Cordes, A. M. Z. Slawin, C. Murawski, M. C. Gather, D. Beljonne, Y. Olivier, I. D. W. Samuel and E. Zysman-Colman, *J. Mater. Chem. C*, 2020, 8, 3773.
- 27 (a) S. Tao, Y. Zhou, C. S. Lee, S. T. Lee, D. Huang and X. Zhang, *J. Phys. Chem. C*, 2008, **112**, 14603; (b) M. G. Shin, S. O. Kim, H. T. Park, S. J. Park, H. S. Yu, Y. H. Kim and S. K. Kwon, *Dye. Pigment.*, 2012, **92**, 1075; (c) S. Ye, J. Chen, C. A. Di, Y. Liu, K. Lu, W. Wu, C. Du, Y. Liu, Z. Shuai and G. Yu, *J. Mater. Chem.*, 2010, **20**, 3186.
- N. Prachumrak, S. Namuangruk, T. Keawin, S. Jungsuttingwong,
 T. Sudyoadsuk and V. Promarak, *European J. Org. Chem.*, 2013, 3825.
- (a) J. Hossain, Q. Liu, T. Miura, K. Kasahara, D. Harada, R.
 Ishikawa, K. Ueno and H. Shirai, ACS Appl. Mater. Interfaces,
 2016, 8, 31926; (b) S. H. Kim, J. Kim, S. Nam, H. S. Lee, S. W.
 Lee and J. Jang, ACS Appl. Mater. Interfaces, 2017, 9, 12637; (c)
 A. Pachariyangkun, W. Senapak, T. Sudyoadsuk, S.
 Namuangruk and V. Promarak, Org. Electron., 2020, 85,
 105897.
- 30 R. A. K. Yadav, D. K. Dubey, S. Z. Chen, T. W. Liang and J. H. Jou, *Sci. Rep.*, 2020, **10**, 9915.
- (a) S. H. Rhee, K. B. Nam, C. S. Kim, M. Song, M. Cho, S. H. Jin and S. Y. Ryu, *ECS Solid State Lett.*, 2014, **3**, R19; (b) S. Wu, S. Li, Q. Sun, C. Huang and M. K. Fung, *Sci. Rep.*, 2016, **6**, 4.
- 32 F. X. Yu, Y. Zhang, Z. Y. Xiong, X. J. Ma, P. Chen, Z. H. Xiong and C. H. Gao, Org. Electron., 2017, 50, 480.
- 33 B. B. W. D. Andrade, J. Brooks, V. Adamovich, M. E. Thompson and S. R. Forrest, *Adv. Mater.*, 2002, 14, 1032.
- 34 Y. Li, R. G. Clevenger, L. Jin, K. V. Kilway and Z. Peng, J. Mater. Chem. C, 2014, **2**, 7180.
- 35 (a) S. W. Culligan, A. C. A. Chen, J. U. Wallace, K. P. Klubek, C.
 W. Tang and S. H. Chen, *Adv. Funct. Mater.*, 2006, **16**, 1481; (b)
 J. H. Jou, S. Kumar, M. Singh, Y. H. Chen, C. C. Chen and M. T.
 Lee, *Molecules*, 2015, **20**, 13005.
- 36 (a) J. Jayabharathi, G. Goperundevi, V. Thanikachalam and S. Panimozhi, ACS Omega, 2019, 4, 15030; (b) C. Wang, X. Li, Y. Pan, S. Zhang, L. Yao, Q. Bai, W. Li, P. Lu, B. Yang, S. Su and Y. Ma, ACS Appl. Mater. Interfaces, 2016, 8, 3041.

Graphical Abstract

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Intramolecular hydrogen bond-enhanced electroluminescent performance of hybridized local and charge transfer (HLCT) excited state blue emissive materials

Wan Li, Pongsakorn Chasing, Wachara Benchaphanthawee, Thanyarat Chawanpunyawat, Chokchai Kaiyasuan, Phattananawee Nalaoh, Nawee Kungwan, Supawadee Namuangruk, Taweesak Sudyoadsuk and Vinich Promarak*



OLED device based on o-hydroxyphenyl phenanthroimidazole (HPI)-based emissive molecules showed high maximum external quantum efficiency (EQE) of 8.13% with an ultra-high brightness of 18100 cd m⁻². The maximum singlet exciton utilization efficiency (η_s) of the device was estimated to be as high as 94%, which is among the best results of blue electroluminescence to our knowledge.