RESEARCH ARTICLE

Endowing imidazole derivatives with thermally activated delayed fluorescence and aggregation-induced emission properties for highly efficient non-doped organic light-emitting diodes

Ge Yang | You Ran | Yimin Wu | Minqi Chen | Zhengyang Bin | Jingsong You

Abstract
The development and enrichment of high-performance organic fluorophores that simultaneously possess thermally activated delayed fluorescence (TADF) and aggregation-induced emission (AIE) properties is going pursued but remains a great challenge due to severe exciton quenching. Herein, a systematical investigation on imidazole moiety has successfully given rise to a series of highly efficient imidazole-based TADF-AIE luminogens for the first time. The attachment of two cyano functionalities on imidazole moiety can significantly increase the electron-withdrawing ability, so as to realize TADF emissions with small singlet-triplet energy gaps ($\Delta E_{ST}$) values. Meanwhile, the installation of a steric hindrance group at N1 position of imidazole moiety can twist the geometry between imidazole and phenyl bridge, thus transforming imidazole derivative from an aggregation-caused quenching emitter into an AIE luminogen. Consequently, the non-doped organic light-emitting diodes (OLEDs) utilizing these TADF-AIE luminogens as emitters exhibit outstanding sky-blue and green emissions, with external quantum efficiency (EQE) as high as 20.0% and low efficiency roll-off (EQE at 1000 cd m$^{-2}$, 16.1%). These values represent the state-of-the-art performance for all imidazole-based OLED devices, which illustrates the significant potential of imidazole derivatives in assembling high-performance OLEDs.

KEYWORDS
aggregation-induced emission, imidazole, non-doped OLEDs, thermally activated delayed fluorescence

1 | INTRODUCTION

Since 1987, organic light-emitting diodes (OLEDs) have triggered a great deal of research and have been widely used in displays, such as mobile phone and television.[1] In OLEDs, to suppress aggregation-caused quenching (ACQ) effect, the emitting layer (EML) is always based on doped materials consisting of host and dopant.[2] This doped EML needs complicated co-evaporation process, which leads to high fabrication cost. As is known, due to the simplified fabrication process, non-doped OLEDs are considered as competitive candidates for future OLEDs applications.[3] However, up to now, the external quantum efficiency (EQE) of non-doped OLEDs is significantly lower than that of doped OLEDs. Especially at high exciton concentration, non-doped OLEDs face severe exciton quenching thus significant efficiency roll-off.[4]

Recently, organic fluorophores those simultaneously possess thermally activated delayed fluorescence (TADF) and aggregation induced emission (AIE) properties have been widely used as emitters in high-performance non-doped OLEDs.[5] For one aspect, TADF materials can utilize both of singlet and triplet excitons owing to the small singlet and triplet energy gap ($\Delta E_{ST}$), thus potentially achieving 100% internal quantum efficiency, and meanwhile, TADF materials intrinsically possess bipolar transporting property that is beneficial for carrier recombination, thus potentially achieving high EQE and low efficiency roll-off. For the other aspect, AIE luminogens can efficiently overcome the drawbacks of ACQ effect in the aggregated states, thus significantly reducing exciton quenching in non-doped OLEDs.[6] Accordingly, using TADF-AIE luminogen as emitters, the EQEs of non-doped OLEDs have been rapidly improved. In 2020, our group has developed a novel
heptagonal diimide acceptor (N-(4-(tert-butyl)phenyl)-1,1'-biphenyl-2,2'-dicarboximide, BPI).[7] The well-balanced rotatability and rigidity of BPI skeleton endows BPI-based TADF-AIE luminogen with excellent external quantum efficiency (EQE) as high as 24.7% and impressively low efficiency roll-off as small as 1% at 1000 cd m$^{-2}$. Undoubtedly, the development and enrichment of high-performance TADF-AIE luminogens is urgently needed to promote future application of non-doped OLEDs.

Herein, we have demonstrated that the attachment of two cyano groups on imidazole moiety can significantly increase the electron-withdrawing ability, so as to achieve TADF property, and meanwhile the installation of a methyl or phenyl group at N1 position of imidazole moiety can twist the geometry, thus achieving AIE property (Figure 1A). As a result, a series of highly efficient imidazole-based TADF-AIE luminogens have been developed for the first time. The corresponding non-doped OLEDs devices exhibit outstanding EQE as high as 20% and low efficiency roll-off (EQE at 1000 cd m$^{-2}$, 16.1%), representing the state-of-the-art performance for all imidazole-based OLEDs (Table S2).

2 RESULTS AND DISCUSSION

The molecular structures of the designed cyan-substituted imidazole acceptors (CNIM, CNIB, and CNBIM) and the corresponding TADF materials (DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM) are illustrated in Figure 1B,C. The density functional theory (DFT) and time-dependent DFT calculation with the B3LYP function and the 6–31+G(d) basis are used to optimize the geometry in the ground state and calculate the energy level alignment of the frontier molecular orbitals. As shown in Figure 1B, introducing two cyano groups on imidazole and benzimidazole groups

FIGURE 1 (A) The molecular design concept of imidazole-based thermally activated delayed fluorescence-aggregation-induced emission (TADF-AIE) luminogen. (B) Energy level of imidazole derivatives. (C) Molecular structures, calculated FMOs distributions, and energy levels of DMAC-CNIM, DMAC-CNIB and DMAC-CNBIM. (D) Synthetic routes to DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM
can significantly decrease the lowest unoccupied molecular orbital (LUMO) energy levels, which indicates the largely enhanced electron-withdrawing ability of cyan-substituted imidazole groups. Incorporation with 9,9-dimethyl-9,10-dihydroacridine (DMAC) donors, the target molecules all exhibit well-separated highest occupied molecular orbital (HOMO) and LUMO distributions, resulting in the small singlet–triplet energy gaps ($\Delta E_{ST}$) of 0.034 eV, 0.009 eV, 0.007 eV for DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM, respectively (Figure 1C).

The synthetic routes to DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM are shown in Figure 1D. Firstly, the condensation reactions between dianimonomaleonitrile derivatives and 4-(9,9-dimethylacridin-10(9H)-yl)benzaldehyde are carried out to rapidly construct dicyanimidazole skeletons (DMAC-CNIH and DMAC-CNBIH). Then, the N-methylation and N-phenylation reactions are successfully used to afford the target molecules (DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM) in good yields.

The molecular structures and the packing patterns of DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM are investigated by their crystal analysis, as shown in Figure 2. The three molecules exhibit similar molecular geometries with large dihedral angles between phenyl bridges and DMAC donors (80.1°, 87.8°, and 83.2° for DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM, respectively) and relatively smaller dihedral angles between phenyl bridges and imidazole acceptors (36.2°, 24.2°, and 46.5° for DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM, respectively). The highly twisted conformation is beneficial to separate the HOMO and LUMO distributions, thus potentially leading to small $\Delta E_{ST}$ values, as calculated (Figure 1C). Furthermore, the deeper crystal analysis reveals that the packing patterns of three isomers are considerably different. In DMAC-CNIM crystal, the phenyl group on N1 position brings significant steric hindrance to inhibit the formation of continuous imidazole packing frameworks. Therefore, only isolated $\pi$-$\pi$ bonding interactions between imidazole skeletons (3.64 Å) are found. This packing mode is more favorable for the transport of holes than that of electrons (Figure S1). As for DMAC-CNIM, the phenyl group on N1 position is replaced by methyl group, which is found to form strong C-H-$\cdots$$\pi$ bonding interaction (2.93 Å) with cyano group. Accordingly, the DMAC-CNIM molecules pack together to form a 3D supramolecular framework via $\pi$-$\pi$ bonding interaction between imidazole skeletons and C-H-$\cdots$$\pi$ bonding interactions between methyl and cyano groups. This packing mode significantly narrows the gap between electron and hole transporting properties, which leads to a relatively more balanced bipolar transporting property of DMAC-CNIM than that of DMAC-CNIB (Figure S1). Moreover, a more compact packing mode that possesses C-H-$\cdots$N hydrogen bonding interaction (3.32 Å) besides $\pi$-$\pi$ and C-H-$\cdots$$\pi$ bonding interactions (2.83 Å) is found in DMAC-CNBIM crystal. Crucially, this packing mode gives a well-balanced hole and electron transporting properties (Figure S1), which is beneficial to assemble high-performance non-doped OLED devices.[7,9]

The TADF and AIE properties of DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM are further investigated, and the performances are summarized in Table 1. As shown in ultraviolet (UV)-via absorption spectra (Figure 3A), the three molecules all exhibit absorption peaks at long wavelength region from 350 nm to 450 nm, which are attributed to the charge-transfer transitions from DMAC donors to imidazole acceptors. Compared with DMAC-CNIM, DMAC-CNIB with a phenyl substitution on N1 position and DMAC-CNBIM with a fused phenyl group on imidazole skeleton both show significantly red-shifted emissions, which is mainly attributed to the more extended LUMO distributions when phenyl groups are introduced (Figure 1C). According to the onset wavelengths of room-temperature photoluminescence spectra (RTPL) and low-temperature photoluminescence spectra (LTPL) measured at 77 K after 10 ms decay, the singlets energies ($E_S$) and triplet energies ($E_T$) of DMAC-CNIM, DMAC-CNIB and DMAC-CNBIM are measured and their $\Delta E_{ST}$ values are further calculated to be 0.11 eV, 0.06 eV and 0.06 eV, respectively. The small $\Delta E_{ST}$ values demonstrate that DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM all possess TADF properties. Subsequently, the AIE properties of these compounds are investigated by measuring the RTPL spectra of these compounds in mixed tetrahydrofuran (THF)/water solutions with different water fraction ($f_w$) from 0% to 90% (Figure 3B). To gain insight into the AIE mechanism, DMAC-CNIH is also synthesized for comparison. In the absence of a steric hindrance group at the N1 position of imidazole moiety, DMAC-CNIH prefers
a planar geometry between imidazole moiety and phenyl bridge with strong N-H⋯N intermolecular hydrogen bonding interaction (Figure S2), which leads to severe ACQ effect (Figure 3B). Herein, by simply introducing a steric hindrance group at the N1 position of imidazole acceptor, we have successfully transformed DMAC-CNIH from an ACQ molecule into an AIE luminogen. As shown in Figure 3B, when aggregated, DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM all exhibit significant AIE properties, which is most pronounced in the case of DMAC-CNBIM. The AIE properties lead to significantly higher photoluminescence yields (PLQYs) from solutions (9.9% for DMAC-CNIM, 14.3% for DMAC-CNIB, and 20.6% for DMAC-CNBIB) to films (81.7% for DMAC-CNIM, 60.2% for DMAC-CNIB, and 92.3% for DMAC-CNBIM), which is beneficial for assembling high-performance non-doped devices. From solutions to films, the delayed component ratios (Rd) are significantly increased for DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM, but considerably decreased for DMAC-CNIH (Figure 3C), which further demonstrates that DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM are TADF-AIE luminogens while DMAC-CNIH is an ACQ molecule.

Prior to the study of electroluminescence (EL) performance for DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM, the thermal and electrochemical properties are investigated by using thermogravimetric analysis (TGA) and cyclic voltammetry (CV). The TGA curves shown in Figure S3A reveal these compounds are all thermally stable with thermal decomposition (T_d) corresponding to 5% weight loss) values of 321, 331, and 368°C for DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM, respectively. According to the CV curves shown in Figure S3B, the HOMO energy levels are calculated from oxidative potentials, which are −2.12, −2.07, and −2.13 eV for DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM, respectively. The morphologies of DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM films are measured by atomic force microscope, which indicates that all the films prepared by conventional thermal deposition method under a high vacuum chamber are flat with root-mean-square (r.m.s) values as small as 0.74 nm (Figure S5). Utilizing DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM as emitters in the EML, non-doped OLED devices are assembled, and the optimized device structure is ITO/TAPC (25 nm)/TCTA (8 nm)/EML (35 nm)/TmPyPb (55 nm)/LiF (0.8 nm)/Al (100 nm), where TAPC, TCTA, and TmPyPb represent 1,1′-bis(di-4-tolylaminophenyl) cyclohexane, 4,4′,4′′-tris(carbazol–9-yl)triphenylene and 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene, respectively. The energy diagrams of related materials used in OLED devices are summarized in Figure 4A, and the molecular structures are shown in Figure 4B. The EL performances are shown in Figure 4C-E and summarized in Table 1. The OLEDs based on DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM display sky-blue and green emission with emission peaks at 491, 510, and 520 nm, respectively. The corresponding OLEDs all exhibit low turn-on voltages at around 2.7 V, and the maximum external quantum efficiencies (EQE_max) are 15.3%, 13.7%, and 20.0% for DMAC-CNIM-, DMAC-CNIB-, and DMAC-CNBIM-based OLEDs, respectively. Notably, the light-emitting performance of DMAC-CNBIM-based device is significantly better than DMAC-CNIM-based and DMAC-CNIB-based devices, which is possibly due to the higher PLQY and the most balanced bipolar transporting property. Moreover, DMAC-CNBIM-based OLEDs also exhibit low efficiency roll-off. For example, when the luminance is increased to 1000 cd m−2, the EQE still maintains 16.1%. These values represent the state-of-the-art high-performance for all imidazole-based OLEDs (Table S2).
FIGURE 3  (A) Normalized UV/vis absorption spectra, photoluminescence spectra measured at room-temperature (room-temperature photoluminescence [RTPL]) and photoluminescence spectra measured at 77 K after 10 ms decay (low-temperature photoluminescence [LTPL]) of DMAC-CNIH, DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM in dilute toluene solution at 10-5 M. (B) RTPL of DMAC-CNIH, DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM in THF/H2O solution with different water fractions ($f_w$). (C) Transient photoluminescence decay of DMAC-CNIH, DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM in THF solution and neat film. Inset in (B): Photographs of DMAC-CNIH, DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM in THF/water mixtures ($f_w = 0$ and 90%) under 365 nm excitation

3 | CONCLUSIONS

In conclusions, a series of novel and highly efficient imidazole-based luminogens have been developed and systematically investigated. Among the all, DMAC-CNBIM, which features a methyl-sustituted imidazole skeleton with a fused phthalonitrile group as the acceptor, acquires a significant TADF property and a mostly pronounced AIE property. Moreover, the unique packing pattern also endows DMAC-CNBIM with a well-balanced bipolar transporting property. As a whole, the corresponding non-doped OLEDs device utilizing DMAC-CNBIM as the emitter represents the state-of-the-art performance for all imidazole-based OLEDs. This work exemplifies the great potential of cyano-fused
strategy in TADF design and also the significant substitution effect on ACQ/AIE properties.

ACKNOWLEDGMENTS
We acknowledge financial support from the National NSF of China (grant numbers: 22031007 and 22005204) and the Sichuan Science and Technology Program (grant numbers: 2020YJ0245 and 2020YJ0302). We also thank the Comprehensive Training Platform Specialized Laboratory, College of Chemistry, Sichuan University.

CONFLICT OF INTEREST
The authors declare that there is no conflict of interest.

DATA AVAILABILITY STATEMENT
Supporting data are available from authors upon reasonable request.

ORCID
Zhengyang Bin https://orcid.org/0000-0001-6216-7234
Jingsong You https://orcid.org/0000-0002-0493-2388

REFERENCES
1. a) C. W. Tang, S. A. VanSlyke, Appl. Phys. Lett. 1987, 51, 913. b) M. A. Baldo, M. E. Thompson, S. R. Forrest, Nature 2000, 402, 750. c) S. Y. Lee, T. Yasuda, H. Nomura, C. Adachi, Appl. Phys. Lett. 2012, 101, 093306. d) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Nature 2012, 492, 234. e) S.-J. Zou, Y. Shen, F.-M. Xie, J.-D. Chen, Y.-Q. Li, J.-X. Tang, Mater. Chem. Front. 2020, 4, 788.
2. a) S. Y. Byeon, D. R. Lee, K. S. Yook, J. Y. Lee, Adv. Mater. 2019, 31, 1803714. b) W. Liang, Y. Yang, M. Yang, M. Zhang, C. Li, Y. Ran, J. Lan, Z. Bin, J. You, Angew. Chem. Int. Ed. 2021, 60, 3493. c) Y. Ran, G. Yang, Y. Liu, W. Han, G. Guo, R. Su, Z. Bin, J. You, Mater. Horiz. 2021, 8, 2025. d) T. Liu, X. Chen, J. Chen, Z. Zhao, W. Wei, Z. Mao, W. Wu, S. Jiao, Y. Liu, Z. Yang, Z. Chi, Chem. Sci. 2021, 12, 5171. e) Y. Hu, Y. Zhang, W. Han, J. Li, X. Pu, D. Wu, Z. Bin, J. You, Chem. Eng. J. 2022, 428, 131186.
3. J. Guo, Z. Zhao, B. Z. Tang, Adv. Opt. Mater. 2018, 6, 1800264.
4. a) J. Guo, X.-L. Li, H. Nie, W. Luo, S. Gan, S. Hu, R. Hu, A. Qin, Z. Zhao, S.-J. Su, B. Z. Tang, Adv. Funct. Mater. 2017, 27, 1606458. b) Y.-Z. Shi, K. Wang, X. Li, G.-L. Dai, W. Liu, K. Ke, M. Zhang, S.-L. Tao, C.-J. Zheng, X.-M. Ou, X.-H. Zhang, Angew. Chem. Int. Ed. 2018, 57, 9480. c) L. Wu, K. Wang, C. Wang, X.-C. Fan, Y.-Z. Shi, X. Zhang, S.-L. Zhang, J. Ye, C.-J. Zheng, Y.-Q. Li, J. Yu, X.-M. Ou, X.-H. Zhang, Chem. Sci. 2021, 12, 1495.
5. a) J. Mei, N. L. Leung, R. T. Kwok, J. W. Lam, B. Z. Tang, Chem. Rev. 2015, 115, 11718. b) Z. Xie, C. Chen, S. Xu, J. Li, Y. Zhan, S. Liu, J. Xu, Z. Chi, Angew. Chem. Int. Ed. 2015, 54, 7181. c) F. Rizzo, F. Cucinotta, Isr. J. Chem. 2018, 58, 874. d) H. Liu, J. Zeng, J. Guo, H. Nie, Z. Zhao, B. Z. Tang, Angew. Chem. Int. Ed. 2018, 57, 9290. e) H. Liu, J. Guo, Z. Zhao, B. Z. Tang, ChemPhotoChem 2019, 3, 993. f) Z. Zhao, H. Zhang, J. W. Lam, B. Z. Tang, Angew. Chem. Int. Ed. 2020, 59, 9888. g) J. Yang, M. Fang, Z. Li, Angew. Chem. Int. Ed. 2020, 1, 6.
6. a) R. Furue, T. Nishimoto, S. I. Park, J. Lee, T. Yasuda, Angew. Chem. Int. Ed. 2016, 55, 7171. b) Q. Zhang, S. Sun, W. Liu, P. Leng, X. Lv, Y. Wang, H. Chen, S. Ye, S. Zhuang, L. Wang, J. Mater. Chem. C 2019, 7, 9487. c) G. Xia, C. Qu, Y. Zhu, J. Ye, K. Ye, Z. Zhang, Y. Wang, Angew. Chem. Int. Ed. 2021, 60, 9598.

TABLE 2 Summary of electroluminescence (EL) characteristics for devices of DMAC-CNIM, DMAC-CNIB, and DMAC-CNBIM

| EML      | $E_{\text{Lpeak}}$ (nm) | $V_{\text{on}}$(V) | EQE$_{\text{max}}$ (%) | PE$_{\text{max}}$ (lm W$^{-1}$) | CIE $x$, $y$ | EQE (%) | PE (lm W$^{-1}$) |
|----------|--------------------------|-------------------|------------------------|-------------------------------|-------------|----------|------------------|
| DMAC-CNIM| 491                      | 2.8               | 15.3                   | 36.8                          | (0.18, 0.33)| 7.1       | 9.9              |
| DMAC-CNIB| 510                      | 2.7               | 13.7                   | 43.8                          | (0.25, 0.50)| 7.9       | 13.9             |
| DMAC-CNBIM| 520                    | 2.6               | 20.0                   | 61.1                          | (0.30, 0.53)| 16.1      | 35.7             |

Abbreviations: EML, emitting layer; $E_{\text{Lpeak}}$, electroluminescent peak; $V_{\text{on}}$, turn-on voltage; EQE$_{\text{max}}$, maximum external quantum efficiency; PE$_{\text{max}}$, maximum Power efficiency; CIE, Commission Internationale de l’Eclairage coordinates; EQE, external quantum efficiency; PE, power efficiency.
7. Z. Huang, Z. Bin, R. Su, F. Yang, J. Lan, J. You, Angew. Chem. Int. Ed. 2020, 59, 9992.
8. CCDC 2088596 for DMAC-CNIM, 2088599 for DMAC-CNIB, 2088605 for DMAC-CNBIM and 2106520 for DMAC-CNIH contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
9. L. Dan, J. Wei, W. Tian, W. Jiang, Y. Sun, Z. Zhao, B. Z. Tang, Chem. Sci. 2020, 11, 7194.
10. a) J. Huang, H. Nie, J. Zeng, Z. Zhuang, S. Gan, Y. Cai, J. Guo, S.-J. Su, Z. Zhao, B. Z. Tang, Angew. Chem. Int. Ed. 2017, 56, 12971. b) J. Guo, J. Fan, L. Lin, J. Zeng, H. Liu, C.-K. Wang, Z. Zhao, B. Z. Tang, Adv. Sci. 2019, 6, 1801629.

**SUPPORTING INFORMATION**
Additional supporting information may be found in the online version of the article at the publisher’s website.

*How to cite this article:* G. Yang, Y. Ran, Y. Wu, M. Chen, Z. Bin, J. You, Aggregate 2022, 3, e127. https://doi.org/10.1002/agt2.127