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Solid-State Fluorophore Based on π-Extended Heteroaromatic Acceptor: Polymorphism, Mechanochromic Luminescence and Electroluminescence

Bin Huang^{a,b,*}, Xiaomin Gu^a, Yan Feng^a, Ying Zhang^a, Dawei Jiang^a, Wen-Cheng

Chen^{b, c,}*, Gu Dai^a, Yigang Ji^a, Qiang Zhao^a, and Chun-Sing Lee^{b,*}

^a College of Life Sciences and Chemistry, Jiangsu Key Laboratory of Biofunctional Molecule, Institute of New Materials for Vehicles, Jiangsu Second Normal University, Nanjing, 210013, P. R. China

^b Center of Super-Diamond and Advanced Films (COSDAF) and Department of

Chemistry, City University of Hong Kong, Hong Kong SAR, P. R. China

^c School of Chemical Engineering and Light Industry, Guangdong University of

Technology, Guangzhou, 510006, P. R. China

Correspondent Author: Bin Huang; Wen-Cheng Chen; Chun-Sing Lee

material, ABSTRACT: А novel light-emitting 4-(4-diphenylaminophenyl)benzo[d,e]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (4-TPA-BBI) is synthesized and 4-TPA-BBI exhibits excellent characterized. polymorphism, mechanochromic luminescence (MCL) and electroluminescence properties. It can form three different aggregate species: yellow rod-like crystal (Y-crystal), orange needle-like crystal (Ocrystal) and red solid (R-solid). It is observed that Y-crystal can be reversibly changed to R-solid upon external stimuli, while O-crystal can be irreversibly transformed to R-solid via sublimation under vacuum. Crystallographic and photophysical studies indicate that Y-crystal featuring loose molecular packing demonstrates a high photoluminescence quantum yield (Φ_{PL} ~1) and obvious MCL property, while the compactly packed O-crystal shows a lower $\Phi_{\rm PL}$ of 0.646 with negligible MCL. A non-doped light-emitting device

based on 4-TPA-BBI as an emitter exhibits bright orange emission with a peak at 588 nm, a high external quantum efficiency of 4.4% and a maximum luminance of 22470 cd m^{-2} .

KEYWORDS: polymorphism, mechanochromic luminescence, electroluminescence, triphenylamine, benzo[*d*,*e*]benzo[4,5]imidazo[2,1-*a*]isoquinolin-7-one, emitter

INTRODUCTION

In recent years, highly emissive solid-state organic materials have received increasing attention due to their potential applications in sensors, optoelectronic devices etc.¹⁻⁵ Tuning the luminescence properties of organic materials is also very important for practical applications.⁶⁻⁸ One feasible strategy for achieving efficient and tunable luminescence is to develop new light-emitting molecular structures or to decorate the known luminescent skeletons through chemical modifications.⁹⁻¹⁰ Alternatively, manipulation of molecular aggregation states is believed to be efficient for fine-tuning the emission properties without any chemical reactions, especially for the solid-state luminophores. In comparison with the former, the

latter has the advantage of facile preparation and low pollution.¹¹ Moreover, the study of the influence of aggregation state on luminescence properties helps us to further understand the structure-property relationship.

Mechanochromic luminescent (MCL) emitters which show reversible color switching upon external stimuli have aroused increasing interest in recent years.¹² They often display polymorphism and multiple molecular packing arrangements, which are considered to be the main reason for the MCL behavior, are potential materials to be used in solid-state sensors, optoelectronic devices, and security inks.¹³⁻¹⁵ Up till now, although some MCL-active luminophores have been reported, the underlying MCL mechanism at the molecular level remains unclear.¹⁶⁻²⁹ Generally, the solid-state emission of a luminophore depends on many factors, such as molecular conformation, intermolecular interaction and packing or their combination. Therefore, the development of polymorphdependent MCL materials with tunable and predicable crystal structures facilitates the elaboration of the MCL mechanism. In 2015 and 2016, Chi's group and Li's group reported two tetraphenylethene derivatives P4TA and TMPE with two polymorphs, respectively.³⁰⁻³¹ Different conformations and intermolecular interactions in the crystals account for their similar

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MCL behavior. Very recently, Tian's group reported another MCL material APMOB and revealed the influence of the molecular conformation and π - π stacking interactions on the photophysical properties.³² However, so far MCL materials showing more than one single crystal structures remain limited.¹⁴ It is thus important to enrich the library of polymorph-dependent MCL materials and unveil how aggregates influence MCL. On the other hand, for EL application an efficient OLED often need a highly emissive solid thin film as the emissive layer. However, most MCL materials show strong emission in crystal but low efficiency in film; therefore, efficient non-doped OLEDs based on polymorph-dependent MCL materials remain limited.¹⁴

Benzo[*d*,*e*]benzo[4,5]imidazo[2,1-*a*]isoquinolin-7-one (BBI) is a novel heteroaromatic building block for organic optoelectronics application.³³ BBI has a π -extended conjugated skeleton ensuring high photoluminescence quantum yield (Φ_{PL}) and can be used as an electron acceptor to construct bipolar donor-acceptor (D-A) emitters because of its electron-withdrawing carbonyl group.³³ More importantly, the heteroaromatic framework with nitrogen and oxygen atom can provide abundant intermolecularly interacting sites (such as forming intermolecular N···H or O···H bonds) to manipulate aggregation states for realizing polymorphism and MCL.³⁴

Recently, we have exploited a D-A type MCL molecule 3-TPA-BBI by employing triphenylamine (TPA) and BBI as the D and the A moieties, respectively.³⁴ 3-TPA-BBI can form two aggregates and its photoluminescence (PL) can be reversibly switched between orange and yellow upon external stimuli. Unfortunately, we failed to obtained more than one type of single crystal of 3-TPA-BBI for illustrating the underlying MCL mechanism. Herein, an isomer of 3-TPA-BBI, 4-(4-diphenylaminophenyl)-benzo[*d*,*e*]benzo[4,5]imidazo[2,1-*a*]isoquinolin-7-

one (4-TPA-BBI) is synthesized and characterized. 4-TPA-BBI is a versatile fluorophore

that exhibits polymorphism, high-contrast MCL and efficient electroluminescence (EL) properties. Two types of single crystals (Y- and O-crystal) of 4-TPA-BBI have been obtained and the crystallographic study indicates that Y-crystal with weak π - π interaction and low intermolecular overlap exhibits a respectably high Φ_{PL} approaching unity and high-contrast MCL property, while O-crystal with strong π - π interaction and high intermolecular overlap displays a lower Φ_{PL} of 0.646 and negligible MCL. Importantly, the 4-TPA-BBI's thin film displays a high Φ_{PL} of 0.723. A non-doped organic light-emitting device (OLED) with 4-TPA-BBI as an emissive layer exhibits orange EL with a decent external quantum efficiency (EQE) of 4.4% and a high maximum luminance of 22470 cd m⁻².

EXPERIMENTAL SECTION

General information. All reagents and solvents were purchased from commercial sources and used as received without further purification. A mixture of 3-bromobenzo[*d*,*e*]benzo[4,5]imidazo[2,1-*a*]isoquinolin-7-one (3-Br-BBI) and 4-

bromobenzo[d,e]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (4-Br-BBI) was obtained according to the reported method and used for the next step without separation.³³ ¹H and ¹³C NMR spectra were recorded on a Bruker AV 300 NMR spectrometer. Si(CH₃)₄ was used as the internal standard. Mass spectra were measured with a Thermo Electron Corporation Finnigan LTQ mass spectrometer. The UV-vis absorption spectra were measured on a UV-vis spectrophotometer (Agilent 8453). The PL properties were measured with an Edinburgh FLS980 spectrophotometer. The X-ray diffraction (XRD) measurements were obtained through a diffractormeter (Ultima IV) with an X-ray source of Cu Ka at 40 kV and 40 mA, at a scan rate of 2° (20) per min. Single crystal XRD measurements were carried out on a single crystal X-ray diffractometer (Oxford Gemeni S Ultra) with Cu Ka radiation. CCDC 1963811 (Y-crystal) and 11963810 (O-crystal) contain the supplementary crystallographic data for this paper.³⁵

All DFT calculations were performed using Gaussian 09 program package.³⁶ The molecular models were selected from the single crystal structures. The molecular structures of 4-TPA-BBI monomers at ground state were optimized at the B3LYP/6-

31G(d) level.³⁷ In view of the intermolecular interactions, the molecular structures at ground state of 4-TPA-BBI dimers were further calculated with M062X/6-31G(d).³⁸ The excitation energies in the singlet and triplet states were obtained using TD-DFT method based on the optimized molecular structures at ground state.³⁷

Synthesis of 4-TPA-BBI. A mixture of 3-Br-BBI/4-Br-BBI (10 mmol), 4-(diphenylamino)phenyl boronic acid (10 mmol) in 100 mL of toluene and 40 mL of ethanol, K_2CO_3 aqueous solution (2.0 M, 10 mL) was added in a three-necked flask. After purging with N₂ for 10 min, Pd(PPh₃)₄ (1 mmol) was added. Then the reaction mixture was refluxed under N₂ for 24 h. After cooling to room temperature, the mixture was poured into 100 mL water, and extracted with dichloromethane (DCM) (2 × 100 mL). The combined organic layer was washed with saturated NaCl aqueous solution (2 × 40 mL), dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v:v = 10:1) as eluent to afford 3-TPA-BBI ($R_{\rm f}$ = 0.21) and 4-TPA-BBI ($R_{\rm f}$ = 0.16) with

yields of 21.5% and 30%, respectively. The structure analysis of 4-TPA-BBI is shown in Table S1.

Different aggregates of 4-TPA-BBI. The block-shaped yellow crystals (Y-crystal) of 4-TPA-BBI were grown from DCM/ethanol (v:v = 1:1) solution by slow evaporation at room temperature. The needle-like orange crystals (O-crystal) were grown from DCM/hexane (v:v = 1:1) solution by slow evaporation at room temperature. The red solid (R-soid) is obtained by sublimating the as-prepared powder or crystalline samples at 170 °C under high vacuum (10⁻⁶ Torr).

Device fabrication and performance measurement. Before device fabrication, indiumtin oxide (ITO)-coated glass substrates were cleaned with detergent and dried carefully and treated by UV ozone for 20 min. Then the samples were transferred into an evaporation chamber with a base vacuum of 5×10^{-7} Torr. Subsequently, the holeinjection material 4,4'-cyclohexylidenebis[N,N-bis(p-tolyl)aniline (TAPC), hole-transporting

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material 4,4',4''-tris(carbazol-9-yl)-triphenylamine (TCTA), the exciton blocking material 1,3-di(9/-/carbazol-9-yl)benzene (mCP), the emitter 4-TPA-BBI, and electrontransporting material 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-*1*/-/benzimidazole) (TPBI) were deposited in sequence via thermal evaporation at a rate of 1.0 Å s⁻¹. Finally, LiF and Al were deposited at rates of 0.1 and 5 Å s⁻¹, respectively. The current-voltage characteristics of the device are characterized with a Keithley 2400 Sourcemeter. The electroluminescent spectra, luminance, and Commission Internationale de l'Éclairage (CIE) color coordinates were obtained with a Spectrascan PR650 photometer.

RESULTS AND DISCUSSION

Photophysical Properties of 4-TPA-BBI in Solvents. 4-TPA-BBI shows distinctive photophysical properties in solvents with different polarities. Figure 1a shows the photographs of 4-TPA-BBI in various solvents under daylight (upper panel) and daylight plus 365-nm UV excitation (bottom panel). UV-vis absorption spectra of 4-TPA-BBI in solvents with varying polarity are shown in Figure 1b. In DCM, 4-TPA-BBI shows two absorption bands at 298 and 439 nm (Figure 2b), which can be ascribed to π - π * transition and intramolecular charge transfer (ICT), respectively. The absorption spectra of 4-TPA-BBI exhibit insignificant change upon increasing solvent polarity.

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In sharp contrast, the PL spectra show obvious variation upon increasing solvent polarity. As shown in Figure 1c and Table 1, 4-TPA-BBI in non-polar hexane shows cyan emission peaking at 487 nm with a small Stokes shift (Δv) of 2885 cm⁻¹, while the emission peak of 4-TPA-BBI markedly red-shifted to 623 nm in polar DCM with a dramatically increased Δv of 6728 cm⁻¹. These results indicate that the excited state of 4-TPA-BBI can be stabilized in polar solvents, implying typical ICT characteristics. The change in dipole moment between S₁ and S₀ upon excitation ($\Delta \mu$) is analyzed using the following Lippert-Mataga Eq. (1)³⁹⁻⁴⁰:

$$\Delta v = v_a - v_f = \left(2\Delta\mu^2 / hca^3\right)\Delta f(\varepsilon, n) + A$$
(1);

where, $\Delta f(\varepsilon, n)$ is calculated from Eq. (2):

$$\Delta f(\varepsilon, n) = \left[(\varepsilon - 1)/(2\varepsilon + 1) \right] - \left[(n^2 - 1)/(2n^2 + 1) \right]$$
(2).

Here, *h* is the Plank's constant (6.6 × 10⁻³⁴ J s⁻¹), *c* is the velocity of light in the vacuum ($3.0 \times 10^8 \text{ m s}^{-1}$), *a* is the Onsagar cavity radius, *n* and *e* are the reflective index and the static dielectric constant of the solvents, respectively. The slope value is calculated to be 11714 cm⁻¹. Because 3-TPA-BBI and 4-TPA-BBI have similar structures, the calculated *a* of 4-TPA-BBI is estimated to be 0.9575 nm, which is comparable to that of 3-TPA-BBI.³⁴ Accordingly, the $\Delta\mu$ value of 4-TPA-BBI is calculated

to be 30.4 D (Figure 1d), which is similar to the $\Delta\mu$ value 3-TPA-BBI (33.8 D).³⁴ The large $\Delta\mu$ value suggests an efficient ICT between the donor TPA and the acceptor BBI within the molecular framework.⁴¹

Polymorphism and MCL. Through controlling the precipitation conditions, 4-TPA-BBI can form three different aggregated solid states: Y-crystal, O-crystal and R-solid (Figure 2a). Among them, Y-crystal can be changed to R-solid via sublimation under high vacuum, and R-solid can be transformed back to Y-crystal form upon heating (150 °C, 5 s) or fuming with hexane vapor. The reversible transformation between Y-crystal and Rsolid in response to external stimuli indicates the obvious MCL property of 4-TPA-BBI. In comparison, O-crystal can be changed into R-solid via sublimation under high vacuum, but R-solid cannot be directly recovered to O-crystal upon external stimuli. It seems like that the O-crystal can be regarded as a metastable state between Y-crystal and R-solid. The different MCL features of the two crystals might be attributed to different molecular conformations and intermolecular interactions (vide infra).

As shown in Figure 2b and Table 2, the three aggregates of 4-TPA-BBI exhibit broad fluorescence with PL peaks at 553 nm (Y-crystal), 576 nm (O-crystal), and 595 nm (R-solid), respectively. Absolute Φ_{PL} values of the three aggregates were also measured (Table 2).

 Compared with O-crystal and R-solid, Y-crystal exhibits a high $\Phi_{PL} \sim 1$, which may be attributed to the suppressed non-radiative transition without any strong intermolecular interactions. To better understand the PL characteristics of 4-TPA-BBI, transient PL decays were investigated (Figure 2c and Table 2). All the three aggregates of 4-TPA-BBI exhibit short-lived nanosecondscaled lifetimes. Among them, Y-crystal exhibits the largest radiation rate constant of 1.3×10^8 s⁻¹.

XRD patterns of 4-TPA-BBI in different solid states are shown in Figure 2d. The different XRD patterns confirm the three different aggregate states. Because of their well-ordered crystalline structures, the Y-crystal and O-crystal show strong and evident diffraction peaks. In contrast, the R-solid show weak diffraction patterns, suggesting its disordered amorphous nature. After heating at 150 °C for 5 s or fuming with hexane vapor, R-solid was transformed to Y-crystal via an amorphous-crystalline phase transformation process, which is confirmed by the similar XRD patterns of the heated Rsolid and the Y-crystal. Note that Y-crystal has two sharp peaks at $2\theta 4.7^{\circ}$ and 13.8° while the heated R-solid has only one sharp peak at $2\theta 4.7^{\circ}$, indicating that the Y-crystal grown from organic solution by slow evaporation has more ordered structure than the heated Rsolid by quickly thermal treatment. The subtle difference in ordered structure between

Y-crystal and the heated R-solid may cause different intermolecular interactions, which

should be responsible for the red-shifted PL emission (562 nm, Figure 2b) of the heated R-solid compared with that of Y-crystal (553 nm, Figure 2b). We consider that the heat energy forces the molecules in the Y-crystal lattice to experience a re-arrangement process. In this case, the BBI π -extended moleties are likely to pack more compactly, like the case of O-crystal, to reach a more stabilized state, leading to the red-shifted emission. In addition, upon repeated treatment by heating or fuming with hexane and scratching (Figure S1), we found that the PL emission of R-solid can be changed between orange and yellow emission with good reversibility and repeatability. The versatility of the MCL of 4-TPA-BBI is further demonstrated. A 20-nm neat thin-film was prepared by thermal evaporation at a rate of 1.0 Å s⁻¹. As shown in Figure 2e, the film emits orange fluorescence with λ_{PL} of 583 nm and Φ_{PL} of 0.723. After heating at 150 °C for 5 s, the emission color of the film is switched to green ($\Phi_{PL} = 0.802$, $\lambda_{PL} = 541$ nm). Next, a capital letter "M" was written on the film by a slight touch with a cotton swab. The scratched area is changed to give orange emission, showing highcontrast MCL property. After fuming with hexane vapor, the emission switch back to green again (Φ_{PL} = 0.748, λ_{PL} = 536 nm). The results indicate that the emission color of the film can

be reversibly changed in response to external stimulus.

Crystallographic study. To investigate the mechanism of the MCL behaviors of 4-TPA-BBI, the single-crystal structures of Y-crystal and O-crystal were measured. Interestingly, both Y-crystal and O-crystal are monoclinic with space groups P2₁/c (Table 3), but exhibit different molecular configuration with the D-A dihedral angles between the adjacent phenyl planes of 54.23° and 42.35° for Y-crystal and O-crystal, respectively (Figure 3a-b).

In the Y-crystal, the two neighboring molecules adopt a face-to-tail stacking arrangement along *b*-axis. The adjacent BBI rings exhibit a small interlayer overlap of approximately 20% with a centroid-centroid (C_g - C_g) distance of 3.649 Å. These weak π - π interactions in the Y-crystal are beneficial to inhibiting non-radiative transition, which can explain the observed high Φ_{PL} . Meanwhile, the low overlap and long C_g - C_g distance induce a loose packing (the V_{cell} of Y-crystal is 2604.3(9) Å³ (Z = 4) as shown in Table 3), and the molecular packing is easy to be disturbed, resulting in evident MCL upon stimulus.

In the case of O-crystal, the neighboring molecules show similar stacking mode along *c*-

axis. However, the Cg-Cg distance between two adjacent BBI rings is shortened to 3.584

Å. Notably, the interlayer overlaps between two parallel BBI planes increases to ~70%. Compared with Y-crystal, these stronger π - π interactions in O-crystal induce red-shift PL emission and decreased Φ_{PL} value. In addition, the shorter C_g-C_g distance and the enhanced intermolecular overlap in O-crystal lead to a more compact packing. Therefore, the V_{cell} of O-crystal decreases to 2509.0(5) Å³ (Z = 4), comparing to that of 2604.3(9) Å³ (Z = 4) in Y-crystal, as shown in Table 3. It is believed that compact packing along with stronger π - π interactions can lead to a less stable aggregation state.³² By comparing the single crystal structures of Y-crystal and O-crystal, the molecular packing may account for the significantly different MCL behavior of the two crystals.

Theoretical Calculations. To further clarify the influence of packing modes on the emissions of the different polymorphs, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations based on the single crystals were carried out. As shown in Figure 4, the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the 4-TPA-BBI monomers in different states are almost the same, which agree well with the theoretically optimized geometry. All the calculated S₁ values (2.47 eV) of the monomers are comparable, which cannot explain the emission variation of Y-crystal

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and O-crystal. The results indicate that the conformation change between Y-crystal and O-crystal has negligible influence on the emission properties. As mentioned above, intermolecular interactions in the crystals may have prominent influence on the emissions. Therefore, dimer models of Y-crystal and O-crystal are selected. As shown in Figure 4 and Table 4, the dimers exhibit lower excited state energies in comparison with the monomers. Meanwhile, due to the enhanced intermolecular interactions, the dimer of O-crystal (2.20 eV) have smaller calculated S_1 values than that of the dimer of Y-crystal (2.40 eV), which agree well with the experimental results that O-crystal has a red-shifted PL emission.

Electroluminescence Performance. To investigate the EL performance of 4-TPA-BBI, we fabricated an OLED with a configuration of ITO/TAPC (50 nm)/TCTA (20 nm)/mCP (10 nm)/4-TPA-BBI (20 nm)/TPBI (50 nm)/LiF (1 nm)/Al (100 nm). The EL characteristics of the device are shown in Figure 5. The non-doped OLED exhibits orange emission with a peak at 588 nm and the CIE coordinate of (0.55, 0.45), which is slightly red-shifted compared to the corresponding PL spectrum of the neat film. The OLED shows a low turn-on voltage of 3.0 V, a maximum current efficiency of 10.4 cd A⁻¹, a peak external quantum efficiency (EQE) of 4.4%, and a maximum luminance of 22470 cd m⁻². The performance of this OLED is comparable with the non-doped OLEDs based on other MCL emitters.^{3, 42} It is worth

noting that the EQE roll-off of the device is small. The EQE remains 4.2% at 5000 cd m⁻ ², corresponding to 95% of the maximum EQE.

CONCLUSIONS

In conclusion, we have developed a solid-state emitter 4-TPA-BBI which exhibits polymorphism, high-contrast MCL and decent EL properties. 4-TPA-BBI can form two types of single crystals with different photophysical properties. Change of molecular packing is responsible for the significantly different MCL behaviors: Y-crystal with a loose packing exhibits a high $\Phi_{PL} \sim 1$ and evident MCL, while O-crystal with a compact packing shows a moderate Φ_{PL} and insignificant MCL. This work may help us to understand the underlying MCL and provide a guideline for further design of MCL emitters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

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Maximum PL emission of 4-TPA-BBI (R-solid) upon repeated treatment by heating and scratching; maximum PL emission of 4-TPA-BBI (R-solid) upon repeated treatment by fuming with hexane and scratching; normalized EL spectra of the device; the structure analysis of 4-TPA-BBI (PDF) Accession Codes CCDC 1963811 (Y-crystal) and 11963810 (O-crystal) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Correspondent Authors

*E-mail: huangbinhb31@sina.com

*E-mail: wencchen@gdut.edu.cn

*E-mail: apcslee@cityu.edu.hk

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REFERENCES:

Nakanotani, H.; Higuchi, T.; Furukawa, T.; Masui, K.; Morimoto, K.; Numata, M.; Tanaka,
 H.; Sagara, Y.; Yasuda, T.; Adachi, C. High Efficiency Organic Light Emitting Diodes with
 Fluorescent Emitters. *Nat. Commun.*, **2014**, *5*, 4016-4022.

(2) Tao, Y.; Yuan, K.; Chen, T.; Xu, P.; Li, H.; Chen, R.; Zheng, C.; Zhang, L.; Huang, W.

Thermally Activated Delayed Fluorescence Materials Towards the Breakthrough of Organoelectronics. *Adv. Mater.*, **2014**, *26*, 7931-7958.

(3) Yang, Z.; Mao, Z.; Xie, Z.; Zhang, Y.; Liu, S.; Xu, J.; Chi, Z.; Aldred, M. P. Recent Advances in Organic Thermally Activated Delayed Fluorescence Materials. *Chem. Soc. Rev.*, **2017**, *46*, 915-1016.

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(4) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Tang, B. Z.; Chen, H.; Qiu, C.; Kwok, H.

S.; Zhan, X.; Liu, Y.; Zhu, D. Aggregation-induced Emission of 1-Methyl-1,2,3,4,5-

pentaphenylsilole. Chem. Commun., 2001, 18, 1740-1741.

(5) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. Aggregation-induced emission. *Chem. Soc. Rev.*, **2011**, 40, 5361-5388.

(6) Zhang, Q.; Kuwabara, H.; Potscavage, W.; Huang, S.; Hatae, Y.; Shibata, T.; Adachi, C. Anthraquinone-based Intramolecular Charge-transfer Compounds: Computational Molecular Design, Thermally Activated Delayed Fluorescence, and Highly Efficient Red Electroluminescence. *J. Am. Chem. Soc.*, **2014**, 136, 18070-18081.

(7) Xu, S.; Liu, T.; Mu, Y.; Wang, Y.; Chi, Z.; Lo, C.; Liu, S.; Zhang, Y.; Lien, A.; Xu, J. An Organic Molecule with Asymmetric Structure Exhibiting Aggregation-Induced Emission, Delayed Fluorescence, and Mechanoluminescence. *Angew. Chem. Int. Ed.*, **2015**, *54*, 874-878.

(8) Li, Q.; Li, Z. The Strong Light-Emission Materials in the Aggregated State: What Happens from a Single Molecule to the Collective Group. *Adv. Sci.*, **2017**, *4*, 1600484.

(9) Zhang Y, Yang H, Ma H, Bian G, Zang Q, Sun J, Zhang, C.; An, Z.; Wong W.-Y. Excitation Wavelength Dependent Fluorescence of an ESIPT Triazole Derivative for Amine Sensing and Anti-counterfeiting Applications. *Angew. Chem. Int. Ed.*, **2019**, 58, 8773-8778.

(10) Zheng, W.; Zhao, Y.; Zhuang, W.-H.; Wu, J.-J.; Wang, F.-Z.; Li, C.-H.; Zuo, J.-L.
Phthalorubines: Fused-ring Compounds Synthesized from Phthalonitrile. *Angew. Chem. Int. Ed.*, 2018, *57*, 15384-15389.

(11) Dong, Y.; Xu, B.; Zhang, J.; Tan, X.; Wang, L.; Chen, J.; Lv, H.; Wen, S.; Li, B.; Ye, L.;
Zou, B.; Tian, W. Piezochromic Luminescence Based on the Molecular Aggregation of 9,10-Bis((*E*)-2-(pyrid-2-yl)vinyl)anthracene. *Angew. Chem. Int. Ed.*, **2012**, *51*, 10782-10785.

(12) Sagara, Y.; Kato, T. Mechanically Induced Luminescence Changes in Molecular Assemblies. *Nat. Chem.*, **2009**, *1*, 605-610.

(13) Chi, Z.; Zhang, X.; Xu, B.; Zhou, X.; Ma, C.; Zhang, Y.; Liu, S.; Xu, J. Recent Advances in Organic Mechanofluorochromic Materials. *Chem. Soc. Rev.*, **2012**, *41*, 3878-3896.

(14) Ubba, E.; Tao, Y.; Yang, Z.; Zhao, J.; Wang L.; Chi, Z. Organic Mechanoluminescence with Aggregation-Induced Emission. *Chem.-Asian J.*, **2018**, *13*, 3106-3121.

(15) Di, B.; Chen, Y. Recent Progress in Organic Mechanoluminescent Materials. *Chin. Chem. Lett.*, **2018**, *29*, 245-251.

(16) Sagara, Y.; Mutai, T.; Yoshikawa, I.; Araki, K. Material Design for PiezochromicLuminescence: Hydrogen-Bond-Directed Assemblies of a Pyrene Derivative. *J. Am. Chem. Soc.*, **2007**, *129*, 1520-1521.

(17) Zhang, G.; Lu, J.; Sabat, M.; Fraser, C. L. Polymorphism and Reversible Mechanochromic Luminescence for Solid-State Difluoroboron Avobenzone. *J. Am. Chem. Soc.*, **2010**, *132*, 2160-2162.

(18) Yuan, W. Z.; Tan, Y.; Gong, Y.; Lu, P.; Lam, J. W. Y.; Shen, X. Y.; Feng, C.; Sung, H. H-Y.; Lu, Y.; Williams, I. D.; Sun, J. Z.; Zhang Y.; Tang, B. Z. Synergy between Twisted Conformation and Effective Intermolecular Interactions: Strategy for Efficient Mechanochromic Luminogens with High Contrast. *Adv. Mater.*, **2013**, *25*, 2837-2843.

(19) Gong, Y.; Tan, Y.; Liu, J.; P. Lu, C. Feng, W. Z. Yuan, Y. Lu, J. Z. Sun, He, G.; Zhang, Y. Twisted D-π-A Solid Emitters: Efficient Emission and High Contrast Mechanochromism. *Chem. Commun.*, **2013**, *49*, 4009-4011.

(20) Gong, Y.; Zhang, Y.; Yuan, W. Z.; Sun, J. Z.; Zhang, Y. D-A Solid Emitter with Crowded and Remarkably Twisted Conformations Exhibiting Multifunctionality and Multicolor Mechanochromism. *J. Phys. Chem. C* **2014**, *118*, 10998-11005.

(21) Jadhav, T.; Choi, J. M.; Shinde, J.; Lee, J. Y.; Misra, R. Mechanochromism and Electroluminescence in Positional Isomers of Tetraphenylethylene Substituted Phenanthroimidazoles. *J. Mater. Chem. C* 2017, *5*, 6014-6020.

(22) Yang, J.; Gao, X.; Xie, Z.; Gong, Y.; Fang, M.; Peng, Q.; Chi, Z.; Li, Z. Elucidating the Excited State of Mechanoluminescence in Organic Luminogens with Room-Temperature Phosphorescence. *Angew. Chem. Int. Ed.*, **2017**, *56*, 15299-15303.

(23) Huang, B.; Li, Z.; Yang, H.; Hu, D.; Wu, W.; Feng, Y.; Jiang, W.; Lin, B.; Sun, Y. Bicolour Electroluminescence of 2-(Carbazol-9-yl)anthraquinone Based on a Solution Process. *J. Mater. Chem. C* 2017, *5*, 12031-12034.

(24) Gong, Y.; Zhang, P.; Gu, Y.; Wang, J.; Han, M.; Chen, C.; Zhan, X.; Xie, Z.; Zou, B.; Peng, Q.; Chi, Z.; Li, Z. The Influence of Molecular Packing on the Emissive Behavior of Pyrene Derivatives: Mechanoluminescence and Mechanochromism. *Adv. Opt. Mater.*, **2018**, *6*, 1800198.

Crystal Growth & Design

(25) Yang, J.; Qin, J.; Geng, P.; Wang, J.; Fang M.; Li, Z. Molecular Conformation-Dependent Mechanoluminescence: Same Mechanical Stimulus but Different Emissive Color over Time. *Angew. Chem. Int. Ed.*, **2018**, *57*, 16407-16411.

(26) Wu, X.; Guo, J.; Cao, Y.; Zhao, J.; Jia, W.; Chen, Y.; Jia, D. Mechanically Triggered Reversible Stepwise Tricolor Switching and Thermochromism of Anthracene-o-Carborane Dyad. *Chem. Sci.*, **2018**, *9*, 5270-5277.

(27) Huang, B.; Chen, W.-C.; Li, Z.; Zhang, J.; Zhao, W.; Feng, Y.; Tang, B. Z.; Lee, C.-S. Manipulation of Molecular Aggregation States to Realize Polymorphism, AIE, MCL, and TADF in a Single Molecule. *Angew. Chem. Int. Ed.*, **2018**, *57*, 12473-12477.

(28) Isayama, K.; Aizawa, N.; Kim, J. Y.; Yasuda, T. Modulating Photo- and Electroluminescence in a Stimuli-Responsive π -Conjugated Donor-Acceptor Molecular System. *Angew. Chem. Int. Ed.*, **2018**, *57*, 11982-11986.

(29) Chen, Y.; Wang, S.; Wu, X.; Xu, Y.; Li, H.; Liu, Y.; Tong, H.; Wang, L. Triazatruxene-Based Small Molecules with Thermally Activated Delayed Fluorescence, Aggregation-Induced Emission and Mechanochromic Luminescence Properties for Solution-Processable Nondoped OLEDs. J. Mater. Chem. C 2018, 6, 12503-12508.

(30) Xu, B.; He, J.; Mu, Y.; Zhu, Q.; Wu, S.; Wang, Y.; Zhang, Y.; Jin, C.; Lo, C.; Chi, Z.; Lien, A.; Liu, S.; Xu, J. Very Bright Mechanoluminescence and Remarkable Mechanochromism Using a Tetraphenylethene Derivative with Aggregation-induced Emission. *Chem. Sci.* **2015**, *6*, 3236-3241.

(31) Wang, C.; Xu, B.; Li, M.; Chi, Z.; Xie, Y.; Li, Q. A Stable Tetraphenylethene Derivative: Aggregation-induced Emission, Different Crystalline Polymorphs, and Totally Different Mechanoluminescence Properties. *Mater. Horiz.*, **2016**, *3*, 220-225.

(32) Jiang, S.; Wang, J.; Qi, Q.; Qian, J.; Xu, B.; Li, F.; Zhou, Q.; Tian, W. Organic Polymorphs with Fluorescence Switching: Direct Evidence for Mechanical and Thermal Modulation of Excited State. *Chem. Commun.*, **2019**, *55*, 3749-3752.

(33) Jiang, W.; Tang, J.; Qi, Q.; Wu, W.; Sun, Y.; Fu, D. An Experimental and Computational Study of Intramolecular Charge Transfer: Diarylamino Derivatives of 7*H*-Benzimidazo(2,1-*a*)benz(*d*,*e*)isoquinolin-7-ones. *Dyes Pigm.*, **2009**, *80*, 279-286.

(34) Huang, B.; Jiang, D.; Feng, Y.; Chen, W-C.; Zhang, Y.; Cao, C.; Shen, D.; Ji, Y.; Wang, C.; Lee, C.-S. Mechanochromic Luminescence and Color-tunable Light-emitting Devices of Triphenylamine Functionalized Benzo[*d*,*e*]benzo[4,5]imidazo[2,1-*a*]isoquinolin-7-one. *J. Mater. Chem. C* **2019**, *7*, 9808-9812.

(35) CCDC 1963811 (Y-crystal) and 1963810 (O-crystal) contain the supplementary

crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

(36) Gaussian 09 (Revision A.01), Gaussian, Inc., Wallingford, CT, 2009.

(37) Lee, S. Y.; Yasuda, T, Yang, Y. S.; Zhang, Q.; Adachi, C. Luminous Butterflies: Efficient Exciton Harvesting by Benzophenone Derivatives for Full-color Delayed Fluorescence OLEDs. *Angew. Chem. Int. Ed.*, **2014**, *53*, 6402-6406.

(38) Cai, S.; Shi, H.; Li, J.; Gu, L.; Ni, Y.; Cheng, Z.; Wang, S.; Xiong, W.; Li, L.; An, Z.; Huang, W. Visible-light-excited Ultralong Organic Phosphorescence by Manipulating Intermolecular Interactions. *Adv. Mater.*, **2018**, *29*, 1701244.

(39) Sumalekshmy, S.; Gopidas, K. R. Photoinduced Intramolecular Charge Transfer in Donor-Acceptor Substituted Tetrahydropyrenes. *J. Phys. Chem. B* **2004**, *108*, 3705-3712.

(40) Mataga, N.; Kaifu Y.; Koizumi, M. Solvent Effects Upon Fluorescence Spectra and the Dipole moments of Excited Molecules. *Bull. Chem. Soc. Jpn.*, **1956**, *29*, 465-471.

(41) Sk, B.; Khodia, S.; Patra, A. T and V-shaped Donor-Acceptor-Donor Molecules Involving Pyridoquinoxaline: Large Stokes Shift, Environment-Sensitive Tunable Emission and Temperature-induced Fluorochromism. *Chem. Commun.*, **2018**, *54*, 1786-1789.

(42) Ruan, Z.; Li, L.; Wang, C.; Xie, Y.; Hu, Q.; Peng, Q.; Ye, S.; Li, Q.; Li Z. Tetraphenylcyclopentadiene Derivatives: Aggregation Induced Emission, Adjustable Luminescence from Green to Blue, Efficient Undoped OLED Performance and Good Mechanochromic Properties. *Small*, **2016**, *12*, 6623-6632.



Scheme 1. Synthesis route of 4-TPA-BBI.



Figure 1. (a) The photographs of 4-TPA-BBI in various solvents under daylight (upper panel) and daylight plus 365 nm UV excition (bottom panel); (b) UV-vis absorption spectra of 4-TPA-BBI in various solvents; (c) PL spectra of 4-TPA-BBI in various solvents; (d) Lippert-Mataga plots of 4-TPA-BBI.



Figure 2. (a) Photographs of the three solid states of 4-TPA-BBI under the 365 nm UV excitation; (b) PL spectra of 4-TPA-BBI in different aggregation states; (c) PL decay curves of 4-TPA-BBI in different aggregation states; (d) XRD spectra of 4-TPA-BBI in different solid states; (e) the fluorescence image of a 4-TPA-BBI film on quartz under the 365 nm UV lamp.



Figure 3. (a) The single crystal structure of the Y-crystal; (b) the single crystal structure of the O-crystal; (c) molecular interactions (upper panel) and overlap (along the b axis, bottom panel) of the Y-crystal; (d) molecular interactions (upper panel) and overlap (along the c axis, bottom panel) of the O-crystal. (Hydrogen atoms have been omitted for clarity)



Figure 4. Calculated energy levels for 4-TPA-BBI monomers and dimers selected from single crystals.



Figure 5. (a) Luminance-voltage-current density curve; (b) luminance-EQE characteristics of the device.

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Table 1 Spectral properties of 4-TPA-BBI in different solvents.

Solvent	$\Delta f(\varepsilon, n)$	λ_{abs} (nm)	$\lambda_{\rm em}$ (nm)	$\Delta v (\text{cm}^{-1})$
hexane	0.001	296, 427	487	2885
toluene	0.013	299, 432	531	4316
chloroform	0.147	299, 446	604	5865
THF	0.210	295, 432	606	6646
DCM	0.217	298, 439	623	6728

	Y-crystal	O-crystal	R-solid
$\lambda_{\rm PL} ({\rm nm})$	553	576	595
$arPsi_{ ext{PL}}$	1.00	0.381	0.683
τ_1 (ns)	7.57	2.72	3.28
	(100%)	(41.90%)	(47.56%)
$\tau_2(\mathrm{ns})$	-	9.46	10.27
		(58.10%)	(52.44%)
$ au_{\mathrm{avg}}\left(\mathrm{ns}\right)$	7.57	6.16	6.20
$k_{\rm r} (10^7{ m s}^{-1})$	13.21	6.19	11.02
$k_{\rm nr} (10^7{ m s}^{-1})$	0	10.05	5.11

Table 2 PL characteristics of 4-TPA-BBI in solid state.

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			IOI T IIII DDI.
9 10		Y-crystal	O-crystal
12	Formula	C ₃₆ H ₂₃ N ₃ O	C ₃₆ H ₂₃ N ₃ O
13 14	CCDC No.	1963811	1963810
15	Formula weight	513.57	513.57
17	Space group	$P 2_1/c$	$P 2_1/c$
18 19	Temperature	293(2)	150(2)
20	Waxalangth /Å	0.71073	0.71073
21 22	wavelength /A	0./10/5	0.71075
23	Crystal system	Monoclinic	Monoclinic
24 25	a/Å	8.8030(18)	9.2158(9)
26	b/Å	7.8170(16)	16.3482(19)
27 28	$c/{ m \AA}$	37.849(8)	16.7812(19)
29	<i>a</i> /°	90.00	90.00
31	<i>Q</i> /0	90.67(3)	97.09(3)
32 33	p_{ℓ}	90.07(3)	97.09(3)
34	$\gamma/^{o}$	90.00	90.00
35	Volume/Å ³	2604.3(9)	2509.0(5)
37	Z	4	4
38 39	Calculated density /Mg m ⁻³	1 353	1 360
40	M(mm ⁻¹)	0.080	0.083
41 42	M(IIIII ⁻)	0.080	0.085
43	F(000)	1072	1072
44 45	Crystal size/mm ³	$0.10 \times 0.20 \times 0.30$	$0.20 \times 0.25 \times 0.30$
46	No. of reflns collected	4778	5087
47 48	No. of unique reflns	2029	3446
49 50	Goodness-of-fit on F ²	1.055	1.029
51	R_{1} $W_{R_{2}}[I > 2\sigma(I)]$	0.0801_0.2027	0.0866 0.1994
52 53	$\mathbf{R}_{1}, \mathbf{W}_{2} [\mathbf{P} \mathbf{Z}_{0}(\mathbf{r})]$	0.1420, 0.2105	0.0000, 0.1994
54	R_1 , wR_2 (all data)	0.1420, 0.2185	0.1281, 0.2275

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Table 4. Calculated triplet and singlet	excitation energies	(vertical transition), oscillator	strength (<i>f</i>), and
transition configurations of 4-TPA-BBI.					

compound	state	E(eV)	f	main configuration	
ground	\mathbf{S}_1	2.47	0.343	H→L	0.71
	S_2	2.94	0.216	H-1→L	0.69
	T_1	1.92	0	H-1→L	0.53
	T_2	2.37	0	H→L	0.54
YC (monomer)	\mathbf{S}_1	2.47	0.343	H→L	0.71
	S_2	2.94	0.216	H-1→L	0.69
	T_1	1.92	0	H-1→L	0.53
	T_2	2.37	0	H→L	0.54
OC (monomer)	\mathbf{S}_1	2.47	0.343	H→L	0.71
	S_2	2.97	0.241	H-1→L	0.69
	T_1	1.88	0	H-1→L	0.50
	T_2	2.43	0	H→L	0.52
YC (dimer)	\mathbf{S}_1	2.40	0	H→L	0.67
	S_2	2.51	0.578	H-1→L	0.62
	T_1	1.86	0	H→L	0.46
	T_2	1.96	0	$H \rightarrow L+1$	0.43
OC (dimer)	\mathbf{S}_1	2.20	0	H→L	0.69
	S_2	2.27	0.307	H-1→L	0.70
	T_1	1.82	0	H→L	0.50
	T_2	1.95	0	H-1→L	0.42

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Solid-State Fluorophore Based on π -Extended Heteroaromatic Acceptor: Polymorphism, Mechanochromic Luminescence and Electroluminescence

Bin Huang, Xiaomin Gu, Yan Feng, Ying Zhang, Dawei Jiang, Wen-Cheng Chen, Gu

Dai, Yigang Ji, Qiang Zhao, and Chun-Sing Lee



Synopsis

 A
 novel
 light-emitting
 material,
 4-(4-diphenylaminophenyl)

 benzo[d,e]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one is synthesized and characterized.

 This compound exhibits polymorphism, high-contrast mechanochromic luminescence

 (MCL) and electroluminescence properties. Crystallographic and photophysical studies

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indicate that change of molecular packing is responsible for the significantly different

MCL behaviors in different aggregates.