Contents lists available at ScienceDirect

# Dyes and Pigments



# Design, synthesis, photophysical properties and intrinsic mechanism of two difluoroboron $\beta$ -diketonate complexes with TPE and *N*-alkyl pyrrole units



PIGMENTS

Wenjing Liu<sup>b</sup>, Yongtao Wang<sup>a,\*</sup>, Guixian Ge<sup>b,\*\*</sup>, Lei Ma<sup>c,\*\*\*</sup>, Litong Ren<sup>b</sup>, Yan Zhang<sup>b</sup>

<sup>a</sup> College of Chemistry and Bioengineering, Guilin University of Technology, Guilin, 541006, PR China

<sup>b</sup> School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi, 832003,

<sup>c</sup> Tianjin International Center for Nanoparticles and Nanosystem, Tianjin University, Tianjin, 300072, PR China

#### ARTICLE INFO

Keywords: Aggregation-induced emission Mechanochromism Multi-emission Boron complex Pyrrole

## ABSTRACT

It is a hot topic to furnish aggregation-caused quenching luminogens with aggregation-induced emission (AIE) active units and explore their optical properties and inherent mechanism. In this paper, two newly designed and synthesized difluoroboron  $\beta$ -diketonate complexes (**TPE-BF<sub>2</sub>-2AP** and **TPE-BF<sub>2</sub>-2MP**) with tetra (phenyl) ethylene (TPE) and *N*-alkyl pyrrole unit exhibit solvatochromism, AIE and mechanochromic properties. Although the alkyl substituents with slight difference, **TPE-BF<sub>2</sub>-2AP** relative to **TPE-BF<sub>2</sub>-2MP** show distinct increased stokes shift and red shifted fluorescence emission in organic solvents. More interestingly, single crystal analysis reveals that **TPE-BF<sub>2</sub>-2MP** forms head-to-head anti-parallel stacking, while **TPE-BF<sub>2</sub>-2AP** adopts a scarce head-to-head cross non-parallel stacking, leading to enhanced quantum efficiency from 0.24 to 0.34 before/after grinding, and blue shifted fluorescence emission compared with **TPE-BF<sub>2</sub>-2MP** in aggregated states and crystalline states. In addition, the two luminogens exhibit multi-state emission properties by grinding, solvent fumigation and heating due to incomplete transformation between amorphous and crystalline state.

# 1. Introduction

Fluorescent dyes with AIE activity have already become an important tool for bioimaging and sensors [1-4]. Different from traditional fluorophores easily suffering from aggregation-caused quenching (ACO) effect. AIE-active luminogens emit strong fluorescence in aggregated states instead of solution. Thereby, some AIE-active luminogens are valuable for turn-on probes [5-7] because of binding between luminogens and ions or biomolecules producing aggregation, which can reduce auto-fluorescence background of biomolecules. Furthermore, AIEE-active nanoparticles formed in aqueous solution are beneficial to intracellular endocytosis, directly used as bioimaging can avoid the steps of washing [8]. Moreover, most of AIE-active luminogens are generally furnished with propeller-like units resulting in loose packing in the solid state and rotatable C–C bonds in solution [9–11]. Under the action of mechanical force such as grinding or scraping, the luminogens exhibit mechanochromic properties due to collapse of loose packing. Furthermore, shift and intensity changes of emission wavelength are usually related to molecular stacking before/after mechanical force [12–14]. However, the unclear understanding of their inherent mechanism limits the design and development of high contrast mechanochromic materials. As viscosity or temperature, surrounding medium inhibit or enhance rotation of C–C bonds leading to a change in the fluorescence intensity. Together with the mentioned above, AIE-active luminogens are fascinating, and design, synthesis and photo-physical properties of AIE-active fluorescent dyes with novel structure have become a research focus.

Currently, some boron complexes bearing bidentate (N, O, N, N and O, O) ligands show outstanding photophysical and photochemical properties. Recently, Wang et al. [15] reported three boron complexes possessing room temperature phosphorescence under visible and near-infrared (NIR)-light excitation by taking advantage of spin-orbital coupling of heavy atom (Br and I) and intramolecular charge transfer (ICT) effect between carbazole and difluoroboron unit. A series of BF<sub>2</sub>-anchored acylhydrozones are prepared by one-pot two-step reaction, and they exhibit remarkable AIE activities and reversible photo-isomerization [16]. In our previous research [17–19], three series of difluoroboron complexes have been designed and synthesized by

https://doi.org/10.1016/j.dyepig.2019.107704

Received 13 April 2019; Received in revised form 30 June 2019; Accepted 7 July 2019 Available online 08 July 2019 0143-7208/ © 2019 Elsevier Ltd. All rights reserved.



PR China

<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author.

<sup>\*\*\*</sup> Corresponding author.

E-mail addresses: wyt\_shzu@163.com (Y. Wang), geguixian@126.com (G. Ge), maleixinjiang@gmail.com (L. Ma).



Fig. 1. The molecular structures and emission maxima of reported  $\beta$ -diketonate boron complex in THF-H<sub>2</sub>O mixtures (water fraction = 90%).

assembling tetraphenyl ethylene (TPE) and halogen atom, alkoxybenzene, aromatic amines (As shown in Fig. 1). The luminogens except TPE-BF2-DMeA not only have desired AIE activities, but also show high-contrast mechanochromism, polymorphism-dependent fluorescence and even multi-state emission properties. Compared with TPE-BF2-H, the emission maxima of TPE-BF2-OHe, TPE-BF2-ONo and TPE-**BF<sub>2</sub>-DBeA** shift to short wavelength in THF/H<sub>2</sub>O (Volume ratio = 1:9) solution, which is attributed to reduction of environmental polarity caused by benzyl and long alkoxy chains, while the rest complexes show red-shifted fluorescence emission in aggregation state due to electron effect and extended conjugation by alkoxy, N-substituent groups and halogen atom. However, emission maxima of the complexes are still unable to meet the needs of bioimaging. To expand the application range of the chromophores, it is essential to extend conjugation or enhance ICT effect by developing boron complex with red shifted fluorescence emission.

Pyrrole is the fundamental structural unit of heme, chlorophyll, bile pigments and some enzymes, and they show excellent physiological activities and drug functions [20,21]. Meanwhile, pyrrole in comparison with benzene is an electron-rich  $6\pi$  aromatic systems, inferring a stronger electron-donating ability. Furthermore, single crystal analysis display BF2 ring and its 1, 3-disubstituted benzenes tend to planar configuration in  $\beta$ -diketonate boron complex [22,23]. This planar structure easily leads to fluorescence quenching due to  $\pi$ - $\pi$  stacking in solid state. Furnishing boron complex with TPE and N-alkylpyrrole are expected to obtain AIE activity and bathochromic emission. Meanwhile, optical properties of luminogens in aggregated state are closely related to the intermolecular stacking and arrangement, while simply alkyl chain modification has exhibited a significant regulatory effect on intermolecular stacking and arrangement. Therefore, TPE-BF2-2AP and TPE-BF<sub>2</sub>-2MP were designed and synthesized (Scheme 1). Both of them show solvatochromism, AIEE and mechanochromic properties, further,

their optical properties and intrinsic mechanism are analyzed and discussed in detail.

### 2. Results and discussion

#### 2.1. Solvatochromism

As shown in Fig. 2 and Table S1, with the increase of solvent polarity from hexane, tetrahydrofuran (THF) to dimethyl sulfoxide (DMSO), the bathochromic-shift of absorption maxima does not exceed 13 nm for TPE-BF<sub>2</sub>-2AP and TPE-BF<sub>2</sub>-2MP, however, their fluorescence emission peaks exhibit significant 113 nm and 142 nm red shifts respectively, accompanied by observable color changes on direct observation, indicating the easily polarized excited-state relative to the ground-state. Compared with THF solution, the two dyes show redshifted fluorescence emission in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solution, which is attributed to solvation effects of CH<sub>2</sub>Cl<sub>2</sub>. Furthermore, relative fluorescence quantum yields ( $\Phi_F$ ) of two dyes are determined by using quinine sulphate as a standard in various solvents. The  $\Phi_{\rm F}$  of **TPE-BF**<sub>2</sub>-**2MP** decreased in turn with increasing solvent polarity due to D (TPE unit)-A (dioxaborine ring)-D' (N-methyl pyrrole)-type asymmetric molecule with ICT effect, while TPE-BF<sub>2</sub>-2AP shows the abnormal  $\Phi_F$  in DMSO solution possibly due to increased viscosity for DMSO and itself extended alkyl chain. However, as a whole the two chromophores have inferior  $\Phi_F$  and emit faint fluorescence in solution due to non-radiative energy dissipation induced by rotation and vibration of C-C single bonds. In addition, TPE-BF2-2AP show larger stokes shift than TPE-BF2-2MP in Hexane, DCM and THF (Table S1) possibly due to increased electron-donating ability of allyl group, which is desirable for biomarker by decreasing of re-absorption of emission.



Scheme 1. Synthetic routes of TPE-BF2-2AP and TPE-BF2-2MP.



**Fig. 2.** Normalized UV–vis absorption spectra and fluorescence spectra of (A) **TPE-BF<sub>2</sub>-2MP**, (C) **TPE-BF<sub>2</sub>-2AP** in various solvents. Photographs coupled with the fluorescence quantum yields of (B) **TPE-BF<sub>2</sub>-2MP**, (D) **TPE-BF<sub>2</sub>-2AP** in different solvents under 365 nm UV illumination (Solution concentration: 10 μM). Excitation wavelength: 410 nm.

### 2.2. Aggregation induced emission

TPEDKBF<sub>2</sub>Ca, TPEDKBF<sub>2</sub>DMeA and TPEDKBF<sub>2</sub>DBeA all have the same TPE, BF<sub>2</sub> units and different arylamine units (Fig. 1), however, the small differences result in the presentation of AIE, ACQ and dual-state emission characteristics in turn. A consequence of the high-contrast fluorescence emission means that it is difficult to set AIE properties of TPE-BF2-2MP and TPE-BF2-2AP in advance. Fortunately, both show significant AIE effects. As the volume fraction of water (f<sub>w</sub>) increases, the fluorescence emission of TPE-BF2-2MP in solution gradually increases from  $f_w = 70\%$  to  $f_w = 95\%$ , and reaches the strongest at  $f_w = 95\%$  (Fig. 3A and B), while emission intensity of TPE-BF<sub>2</sub>-2AP decreased at  $f_w = 95\%$  due to decreased solubility, which should be attributed to increased hydrophobicity of allyl compared with methyl (Fig. 2C and D). Viscosity experiments based on different ratios of glycerol and DMSO further confirm that the mechanism of AIE lies in the inhibition of the rotation and vibration of intramolecular C-C single bonds (Fig. S1). The fluorescence emission intensity of TPE-BF2-2MP continuously enhances with the increase of viscosity, however, an abnormal phenomenon is also observed in glycerol/DMSO mixture at fraction of glycerol ( $f_g$ ) of 95% for TPE-BF<sub>2</sub>-2AP, and the reduction of emission intensity mainly is related to different states of aggregation with similar situation to  $f_w = 95\%$ . Then, laser particle size analyzer is used to characterize the aggregated particles of TPE-BF2-2AP at  $f_{\rm w}$  = 70, 80 and 95% after an overnight stay. By contrast, nanoparticles at  $f_w = 80\%$  reveal the maximum particle radius with an average size of  $\sim\!5000\,\mathrm{nm},$  when  $f_\mathrm{w}$  increases to 95%, nanoparticles become larger at

high water ratio and result in precipitation, as a result similar particle size distribution between  $f_w = 70\%$  and 95% can be observed, which is responsible for the decrease of fluorescence intensity (Fig. S2). The scanning electron microscope (SEM) further provides information on nano-assembly of TPE-BF<sub>2</sub>-2AP formed at  $f_{\rm w}$  = 80%, 90% and 95% without stay overnight (Fig. S3), among of them, nanoparticles at  $f_{\rm w} = 95\%$  have the largest particle size subsequently inducing precipitation, whereas particle sizes of  $f_{\rm w}$  = 90% are the smallest due to the formation of large numbers of crystal nucleus. More interesting, TPE-BF2-2MP compared with TPE-BF2-2AP provides bathochromic fluorescence emission at  $f_w = 95\%$ , which is the opposite of what happens in solution. It is inferred that the two dyes may have different intermolecular packing in aggregated state. The AIE absorption tests (Fig. S4) indicate maximum absorption wavelength of two dyes can be divided into four sections with the increase of  $f_w$  from 0 to 90%, including rapid blue shift, slow red shift, rapid red shift and rapid blue shift. When a small amount of water is added, hydrogen bonding between water and dyes reduces energy-loss of relaxation process, resulting in blue shift of fluorescence emission; further increase of water content provides a more polar environment, thereby enhances ICT effect and leads red shift of fluorescence emission; with the formation of aggregated nanoparticles, intermolecular J-type stacking cause absorption redshift, but further aggregation provides a hydrophobic nonpolar environment for the luminescence center, which promotes blue-shifted fluorescence emission. The emission maxima of TPE-BF2-**2MP** obviously exceeds 600 nm at  $f_w = 90\%$ , which presents tiny red shift compared with TPE-BF2-Ca (590 nm) and TPE-BF2-Br (593 nm).



**Fig. 3.** Fluorescence emission spectra of (A) **TPE-BF<sub>2</sub>-2MP**, (C) **TPE-BF<sub>2</sub>-2AP** in the THF/water mixtures with different fractions of water. Solution concentration: 10 μM. Chart of relationship between FL peak intensity and water fraction for (B) **TPE-BF<sub>2</sub>-2MP**, (D) **TPE-BF<sub>2</sub>-2AP**. Excitation wavelength: 430 nm. Solution concentration: 10 μM. Inset: Photographs in THF/water mixtures with different fractions of water under 365 nm UV illumination.

However, the D-A-D' type complex still shows weaker ICT effect in contrast with D-A type boron complexes reported by hao et al. [24,25], among of them, emission maxima of some AIE-active dyes even exceed 700 nm.

#### 2.3. Mechanochromic properties

To investigate the mechanochromic behavior of TPE-BF2-2MP and TPE-BF<sub>2</sub>-2AP, fluorescence emission spectra of two dyes in different solid states are tested and compared by grinding, heating and solvent fuming. As shown in Fig. 4 and Fig. 5, TPE-BF<sub>2</sub>-2MP exhibits bathochromic emission maxima compared with TPE-BF2-2AP in the crystalline state, which is similar to aggregated state in THF/H<sub>2</sub>O solution. Further, the distinct mechanochromism is present in TPE-BF<sub>2</sub>-2MP and TPE-BF<sub>2</sub>-2AP. After gentle grinding, hypsochromic fluorescence emission can be observed for both luminogens. The phenomenon is interpreted as "disaggregation" or altered "electron delocalization" and band gap, in other words, grinding leads to inverse processes of aggregation and reduces particle diameter, which leads to a shorter fluorescence wavelength [26,27]. On the contrary, the hard ground samples experience bathochromic emission wavelength due to the compression of molecular spacing, thereby excimer resulted from  $\pi$ - $\pi$ stacking might be present and act as energy trap to collect all the

excitons, leading to red-shifted fluorescence emission, accompanied by reduced absolute quantum yield ( $\Phi_F$ ) for TPE-BF<sub>2</sub>-2MP from 0.23 to 0.13 and elevated  $\Phi_F$  for TPE-BF<sub>2</sub>-2AP from 0.24 to 0.34, further, emission enhancement is rather scarce and valuable relative to the opposite behavior after grinding (Table S2). More importantly, TPE-BF2-2MP and TPE-BF2-2AP exhibit multi-state emission properties because the ground samples can't return to emission of pristine crystals by heating and solvent fuming. To explore the intrinsic mechanism of mechanochromism, we carried out analysis of X-ray diffraction (XRD), differential scanning calorimeter (DSC) analysis and fluorescence lifetime. XRD spectrum indicate ground samples have a more amorphous characteristic, while ground samples after heating and fumigation are crystalline based on diffuse changes of reflections, therefore, mechanochromism of the two dyes are attributed to incomplete transformation between amorphous and crystalline state. Moreover, amorphous forms of the ground samples are metastable and reverts to the crystalline state by heating and fuming, which can be judged from cold-crystallization peaks of DSC curves at 131 °C and 110 °C (Fig. 5E). The fluorescence lifetime measurements (Fig. S5 and Tables S3-6) indicate that the fluorescence decay curves of two dyes consisted of three exponential components before/after grinding. A short lifetime (1.53 ns) with a component of 41% and two long (4.05 ns and 17.08 ns) lifetimes are observed with components of 52% and 7% in turn for TPE-BF<sub>2</sub>-2MP in



Fig. 4. Photographic Schematic illustration for the MCL behavior of organic dyes images of TPE-BF<sub>2</sub>-2MP and TPE-BF<sub>2</sub>-2AP in different solid states under natural light and UV light (365 nm).

crystalline state, which means that they have multiple decay pathways. After grinding, the fluorescence average lifetime of TPE-BF2-2MP is prolonged from 4.42 ns to 6.34 ns, accompanied by the increase of longlived components from 52% to 60% and from 7% to 9% respectively and the decrease of fast component from 41% to 31%. Similar situation happened to TPE-BF2-2AP, which indicates that grinding alters the fluorescence emission channels of the two complexes. The radiation decay rate (K<sub>r</sub>) of **TPE-BF<sub>2</sub>-2MP** are  $5.2 \times 10^7 \text{ s}^{-1}$  (K<sub>r</sub> =  $\Phi/\tau$ ,  $\tau$  is defined as the average life) and  $2.0 \times 10^7 \, \text{s}^{-1}$  respectively before/after grinding, and  $9.1 \times 10^7 \text{ s}^{-1}$  and  $5.9 \times 10^7 \text{ s}^{-1}$  for **TPE-BF**<sub>2</sub>-2AP, while non-radiation decay rate (K\_nr) of  $\text{TPE-BF}_2\text{-}2\text{MP}$  are up to  $1.7\times10^8\,\text{s}^{-1}$  $(K_{nr} = (1-\Phi)/\tau)$  and  $1.4 \times 10^8 \text{ s}^{-1}$  respectively before/after grinding,  $2.9 \times 10^8 \text{ s}^{-1}$  and  $1.2 \times 10^8 \text{ s}^{-1}$  for **TPE-BF<sub>2</sub>-2AP**. Obviously, grinding results in simultaneous reduction of both Kr and Knr, while the enhanced  $\Phi_F$  of TPE-BF<sub>2</sub>-2AP in comparison with TPE-BF<sub>2</sub>-2MP is attributed to increased Kr and reduced Knr after grinding.

#### 2.4. Crystal structures and theoretical calculation

To better understand optical properties of the two boron complexes, vellow granular crystal TPE-BF2-2MP (CCDC 1909832) and yellow needle crystal TPE-BF2-2AP (CCDC 1909833) were cultured by slow diffusion of n-hexane into a saturated CH<sub>2</sub>Cl<sub>2</sub> solution of complexes. As shown in Fig. 6A and D, two compounds contain multiple intermolecular hydrogen bonds and weak interactions such as C-H...F, C-H···C and C···C, leading to twisted and rigid molecular conformations. Methyl linked on nitrogen and pyrrole ring are in the same plane, while allyl group is almost perpendicular to pyrrole ring. Therefore, the dihedral angle between ring A and B barely changed for two dyes with the increase of steric hindrance of allyl group, furthermore, the dihedral angles between ring B and C are 27.46° for TPE-BF2-2MP and 7.37° for TPE-BF<sub>2</sub>-2AP. Obviously, TPE-BF<sub>2</sub>-2MP with N-methyl substitute has the more twisted conformation than TPE-BF<sub>2</sub>-2AP in crystalline state, which narrows molecular band gap, and leads to red-shifted fluorescence emission for TPE-BF2-2MP. In addition, two complexes adopt obviously distinct molecular packing. TPE-BF2-2AP along the b-axis presents scarce cross non-parallel stacking with 4.322 Å centroid to centroid (Cg-Cg) distances between intermolecular -BF2 planes, along the a-axis, TPE-BF2-2MP adopts anti-parallel head-to-head stacking with 3.783 Å distances, resulting in extended conjugation and redshifted fluorescence emission compared with that of TPE-BF2-2AP. Even so, they has almost the same  $\Phi_{\rm F}$ . On the one hand,  $\pi$ - $\pi$  staking is not observed in the two crystals. On the other hand, TPE-BF2-2MP (1.308 gcm<sup>-3</sup>) relative to TPE-BF<sub>2</sub>-2AP (1.276 gcm<sup>-3</sup>) have higher crystalline density, which can enhance fluorescence emission by inhibiting the rotation of C–C bonds, thereby offset efficiency decline due to red shift of emission wavelength. Theoretical calculations revealed the electrons of TPE-BF2-2MP in its HOMO and LUMO orbitals are distributed in the whole molecule except methyl, furthermore, the electron cloud density of HOMO is mainly located on the pyrrole and boron heterocycles moiety, whereas the electron cloud density of LUMO is mainly distributed on TPE unit, outlining the obvious shift of electron cloud density, which is attributed to pyrrole is stronger electron donor compared with TPE (Fig. 7). Similar situation happens in TPE-BF<sub>2</sub>-2AP, moreover, TPE-BF2-2AP has the more obvious ICT effect, increased HOMO, LUMO and energy gap compared with TPE-BF<sub>2</sub>-2MP, which is consistent with experimental results. However, quantum efficiency of ground samples are difficult to predict based on the high-contrast molecular packing of crystals. The tighter stacking induced by grinding is conducive to restricting the rotation and vibration of molecular bonds and reducing non-radiation loss, but after ordered molecular arrangement, intermolecular hydrogen bonds and weak interactions are destroyed,  $\pi$ - $\pi$  stacking is prone to occur due to compressed molecular spacing and intermolecular slip, which causes reduction of quantum efficiency. At last, it's also worth mentioning that the different stacking modes endow TPE-BF2-2AP slightly higher mechanochromic contrast in comparison to TPE-BF<sub>2</sub>-2MP.

#### 3. Conclusions

In summary, **TPE-BF<sub>2</sub>-2MP** and **TPE-BF<sub>2</sub>-2AP** were designed and synthesized by assembling difluoroboron  $\beta$ -diketonate complexs with



Fig. 5. The emission spectra of TPE-BF<sub>2</sub>-2MP (A) and TPE-BF<sub>2</sub>-2AP (C), excitation wavelength: 420 nm; and XRD patterns of TPE-BF<sub>2</sub>-2MP (F) and TPE-BF<sub>2</sub>-2AP (G) in various solid states. (Slightly heated: heating the lightly ground powder). (E) DSC thermograms of the two crystals in different state.

TPE unit and *N*-methyl or *N*-allyl pyrrole. The two luminogens exhibit solvatochromism, AIE and irreversible mechanochromic properties. In various solvents, **TPE-BF<sub>2</sub>-2AP** show red shifted fluorescence emission and the large stokes shift compared with **TPE-BF<sub>2</sub>-2MP** possibly due to stronger electron donating ability for allyl. Contrary to monomolecular dispersion, **TPE-BF<sub>2</sub>-2AP** in comparison to **TPE-BF<sub>2</sub>-2MP** displays blue shifted fluorescence emission in crystalline and aggregated states. Single crystal X-ray analysis indicated **TPE-BF<sub>2</sub>-2MP** and **TPE-BF<sub>2</sub>-2AP** form head-to-head anti-parallel stacking and cross non-parallel stacking respectively. The anti-parallel stacking mode leads to deteriorating



Fig. 6. Single crystal structure and conformation with hydrogen bond and weak interaction sites, intermolecular stacking modes ignoring hydrogen atoms (A–C) TPE-BF<sub>2</sub>-2MP, (D–F) TPE-BF<sub>2</sub>-2AP.



Fig. 7. B3LYP/6-31G (d,p) calculated molecular orbital amplitude plots of HOMO and LUMO levels for TPE-BF<sub>2</sub>-2MP and TPE-BF<sub>2</sub>-2AP.

quantum efficiency for ground **TPE-BF<sub>2</sub>-2MP**, while cross non-parallel stacking mode endows **TPE-BF<sub>2</sub>-2AP** with enhanced quantum efficiency from 0.24 to 0.34 after grinding. Further, the two boron complexes exhibit multi-state emission properties by grinding, solvent fumigation and heating due to incomplete transformation between amorphous and crystalline state. Last but not least, the small structure modification on pyrrole can remarkably adjust the molecular packing and optical properties of luminogens, thereby endow luminogens with a larger Stokes shift and higher mechanochromic contrast, which are important for bioimaging and sensors.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21766030, 21566034, 21403144 and 11464038). This paper is completed under the guidance of associate professor Yongtao Wang.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2019.107704.

#### References

[1] Wu W, Ye S, Huang L, Xiao L, Fu Y, Huang Q, et al. A conjugated hyperbranched polymer constructed from carbazole and tetraphenylethylene moieties: convenient synthesis through one-pot "A2 + B4" Suzuki polymerization, aggregation-induced enhanced emission, and application as explosive chemosensors and PLEDs. J Mater Chem 2012;22(13):6374.

- [2] Zhang X, Chi Z, Xu B, Chen C, Zhou X, Zhang Y, et al. End-group effects of piezofluorochromic aggregation-induced enhanced emission compounds containing distyrylanthracene. J Mater Chem 2012;22(35):18505–13.
- [3] Kim HJ, Heo CH, Kim HM. Benzimidazole-based ratiometric two-photon fluorescent probes for acidic pH in live cells and tissues. J Am Chem Soc 2013:135(47):17969–77.
- [4] Li K, Zhang Y, Qiao B, Tao F, Li T, Ding Y, et al. Facile fabrication of AIE/AIEEactive fluorescent nanoparticles based on barbituric for cell imaging applications. RSC Adv 2017;7(48):30229–41.
- [5] Shan Y, Yao W, Liang Z, Zhu L, Yang S, Ruan Z. Reaction-based AIEE-active conjugated polymer as fluorescent turn on probe for mercury ions with good sensing performance. Dyes Pigments 2018;156:1–7.
- [6] Puri P, Kumar G, Paul K, Luxami V. Self-agglomerated crystalline needles harnessing ESIPT and AIEE features for the 'turn-on' fluorescence detection of Al3+ ions. New J Chem 2018;42(23):18550–8.
- [7] Shellaiah M, Simon T, Srinivasadesikan V, Lin C-M, Sun KW, Ko F-H, et al. Novel pyrene containing monomeric and dimeric supramolecular AIEE active nano-probes utilized in selective "off-on" trivalent metal and highly acidic pH sensing with live cell applications. J Mater Chem C 2016;4(10):2056–71.
- [8] Pramanik S, Bhalla V, Kim HM, Singh H, Lee HW, Kumar M. A hexaphenylbenzene based AIEE active two photon probe for the detection of hydrogen sulfide with tunable self-assembly in aqueous media and application in live cell imaging. Chem Commun (Camb) 2015;51(85):15570–3.
- [9] Hong Y, Lam JWY, Tang BZ. Aggregation-induced emission. Chem Soc Rev 2011;40(11):5361–88.
- [10] Luo J, Xie Z, Lam JWY, Cheng L, Tang BZ, Chen H, et al. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. Chem Commun 2001(18):1740–1.
- [11] Huang W, Wang H, Sun L, Li B, Su J, Tian H. Propeller-like D–π–A architectures: bright solid emitters with AIEE activity and large two-photon absorption. J Mater Chem C 2014;2(33):6843–9.
- [12] Sagara Y, Kato T. Mechanically induced luminescence changes in molecular assemblies. Nat Chem 2009;1(8):605–10.
- [13] Zhang X, Chi Z, Zhang Y, Liu S, Xu J. Recent advances in mechanochromic luminescent metal complexes. J Mater Chem C 2013;1(21):3376.
- [14] Sagara Y, Yamane S, Mitani M, Weder C, Kato T. Mechanoresponsive luminescent molecular assemblies: an emerging class of materials. Adv Mater 2016;28(6):1073–95.
- [15] Wang XF, Xiao H, Chen PZ, Yang QZ, Chen B, Tung CH, et al. Pure Organic room temperature phosphorescence from excited dimers in self-assembled nanoparticles under visible and near-infrared irradiation in water. J Am Chem Soc 2019;141(12):5045–50.
- [16] Yu C, Hao E, Fang X, Wu Q, Wang L, Li J, et al. AIE-active difluoroboronated acylhydrozone dyes (BOAHY) emitting across the entire visible region and their photo-switching properties. J Mater Chem C 2019;7(11):3269–77.
- [17] Qi Y, Wang Y, Yu Y, Liu Z, Zhang Y, Du G, et al. High-contrast mechanochromism and polymorphism-dependent fluorescence of difluoroboron  $\beta$ -diketonate complexes based on the effects of AIEE and halogen. RSC Adv 2016;6(40):33755–62.
- [18] Qi Y, Liu W, Wang Y, Ma L, Yu Y, Zhang Y, et al. The inherent mechanism of mechanochromism under different stress: electron cloud density distribution, J-type stacking, pore structure and collapse of J-type stacking. New J Chem 2018;42(14):11373–80.
- [19] Qi Y, Wang Y, Ge G, Liu Z, Yu Y, Xue M. Multi-state emission properties and the inherent mechanism of D–A–D type asymmetric organic boron complexes. J Mater Chem C 2017;5(42):11030–8.
- [20] Okner R, Shaulov Y, Tal N, Favaro G, Domb AJ, Mandler D. Electropolymerized tricopolymer based on N-pyrrole derivatives as a primer coating for improving the performance of a drug-eluting stent. ACS Appl Mater Interfaces 2009;1(4):758–67.
- [21] Yu Z, Pandian GN, Hidaka T, Sugiyama H. Therapeutic gene regulation using

pyrrole-imidazole polyamides. Adv Drug Deliv Rev 2019. ahead of print https://doi.org/10.1016/j.addr.2019.02.001.

- [22] Xu S, Evans RE, Liu T, Zhang G, Demas JN, Trindle CO, et al. Aromatic difluoroboron beta-diketonate complexes: effects of pi-conjugation and media on optical properties. Inorg Chem 2013;52(7):3597–610.
- [23] Morris WA, Kolpaczynska M, Fraser CL. Effects of α-substitution on mechanochromic luminescence and aggregation-induced emission of difluoroboron β-diketonate dyes. J Phys Chem C 2016;120(39):22539–48.
- [24] Yu Y, Yu C, Wu Q, Wang H, Jiao L, Wong W-Y, et al. Pure E/Z isomers of N-methylpyrrole-benzohydrazide-based BF<sub>2</sub> complexes: remarkable aggregation-crystallization, -induced emission switching properties and application in sensing

intracellular pH microenvironment. J Mater Chem C 2019;7(15):4533-42.

- [25] Yu C, Hao E, Fang X, Wu Q, Wang L, Li J, et al. AIE-active diffuoroboronated acylhydrozone dyes (BOAHY) emitting across the entire visible region and their photo-switching properties. J Mater Chem C 2019;7(11):3269–77.
- [26] Yadav P, Singh AK, Upadhyay C, Singh VP. Photoluminescence behaviour of a stimuli responsive Schiff base: aggregation induced emission and piezochromism. Dyes Pigments 2019;160:731–9.
- [27] Wang Y, Liu W, Ren l, Ge G. Deep insights into polymorphism initiated by exploring multicolor conversion materials. Mater Chem Front 2019:c9qm00293f. ahead of print.