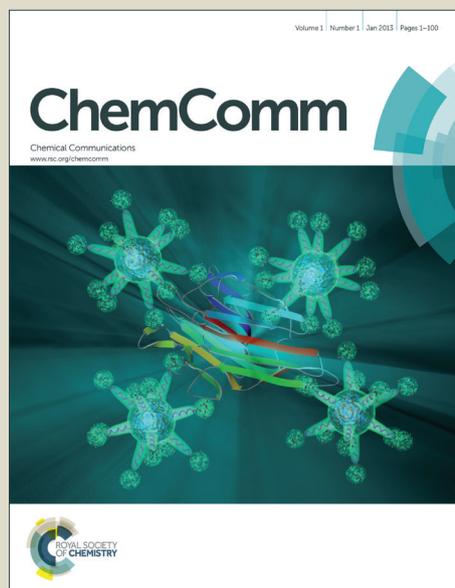


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An AIE-active boron-difluoride complex: multi-stimuli-responsive fluorescence and application for data security protection

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A novel AIE-active boron-difluoride complex (PTZ) was synthesized and exhibits multi-stimuli responsive characteristics. Its colours and emissions can be switched by mechanical grinding, organic solvent vapours and acid/base vapours. This complex can be utilized in data encryption and decryption based on the protonation-deprotonation control.

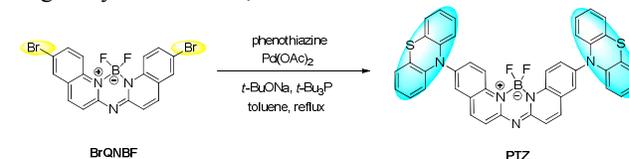
Smart luminescent materials have attracted considerable attention due to their stimuli responsive emission changing characteristic and broad applications in the fields of optical data recording, data security and data protection.¹ Based on the aggregation induced emission (AIE)² effect, some materials exhibit particular stimuli luminescent response, such as mechano-responsive fluorochromes and vapor-responsive fluorochromes. Because their relative loose structure arrangement could be easily destroyed by the external stimulus, the luminescence shows swiftable emissions.³ To date, most of the AIE-active stimuli-responsive materials reported are based on the tetraphenylethene core structure.⁴ It remains great challenges in the development of new AIE-active material with multi-stimuli-responsive materials, especially for data recording and security protection.

Boron-difluoride complexes have been extensively studied because of strong ground-state absorption in visible region, high photoluminescence quantum yield and excellent chemical stability.⁵ Besides, the phenothiazine chromophore with a twisted bowl-shaped configuration has been proved an excellent building block for AIE-active molecules.⁶ It could be reasonable to build a twisted molecule, which use boron-difluoride structure as main structure and motif phenothiazine by single bond, and could qualify AIE characteristic. We believe this molecule could be a candidate for multi-stimuli-responsive luminescent material.

In this work, we prove structure design strategy and report a new boron-difluoride complex (PTZ) containing a planar aza-boron-diquinomethene (aza-BODIQU) core structure and two *N*-substituted phenothiazine chromophores (Scheme 1). This novel complex displays AIE characteristic, multi-stimuli responsive fluorescent properties in the aggregate state.

Furthermore, it can be applied to realize data encryption and decryption based on the protonation-deprotonation effect.

Complex PTZ was simply synthesized by one-step Buchwald-Hartwig coupling reaction (Scheme 1). The synthetic routes and detailed procedure are provided in ESI.† Its structure was determined by ¹H NMR, ¹³C NMR and ¹⁹F NMR as well as single-crystal structure, which all show satisfied results.



Scheme 1. Synthesis of PTZ.

PTZ shows a weak blue emission at $\lambda_{max} = 450$ nm and 480 nm in tetrahydrofuran (THF) (Fig. 1a). However, when H₂O was added into the THF solution of PTZ in a fraction of 70% (v/v%), as shown in Fig. 1b, the emission significantly red-shifted ($\lambda_{max} = 550$ nm), and the intensity dramatically increased. Furthermore, its solid powder exhibits a strong yellow emission at $\lambda_{max} = 540$ nm with tailed spectra in the region of 550-650 nm (Fig. 2b). All these indicate PTZ is a very typical AIE-active complex.

As shown in Fig. 1c, PTZ exhibits switched emission in THF/water mixture solutions with different water fractions (*fw*, the volume percentage of water in THF/water mixtures), which directly elucidate the AIE process. When the *fw* was below 50%, the weak blue emission with λ_{max} at 480 nm was gradually quenched. Meanwhile, when H₂O fraction was over 60% in the mixed solvent, the complexes aggregated and the emission intensity faded up. When the *fw* further increased to 70-80%, the emission of solutions red-shifted to 540 nm and the intensity increased. When the *fw* increased to 90%, the emission of solutions further red-shifted to 610 nm, which increased by *ca.* 2.4 fold intensity. These results can infer that two phenothiazine chromophores dynamically rotate against the aza-BODIQU core on the single bond axes in diluted THF solution, which leading to a weak emission. When small

fraction of water exists ($f_w \leq 50\%$), twisted intramolecular charge transfer (TICT) activity dominates the emission intensity and quenches the blue light emission. When large amount of water is added ($f_w \geq 60\%$), the emission red-shifted to 540 nm because the molecules tend to aggregate and form nanoparticles by the intermolecular C-H...F and C-H... π interaction, which restricts the radiationless relaxation channel and opens the radiative decay pathway, thus the intensity increased.^{2c,2d} When the water content is further increased to 90%, the coplanarity and π -conjugation of molecules are further enhanced by the enhanced π - π interaction between neighbour, then the emission red-shifted to 610 nm. As seen from Fig. 1c, the emission colours of PTZ were tuned from blue, yellow to red. Its average particle diameter in the THF-H₂O (1:9, v/v) mixture is *ca.* 184 nm (Fig. S6). Based on the concentration dependence study (Fig. S7), PTZ shows increasing emission intensity from 1.25 μ M to 15.0 μ M concentration of THF/H₂O mixture (1:9, v/v); the AIE emission could still be observed at 2.5 μ M by naked eyes under the irradiation at 365 nm. The AIE phenomenon has also been demonstrated in DMSO-H₂O system (Fig. S8). All these results proved PTZ a switched AIE-active molecule with enhanced photoluminescence (PL) intensity.

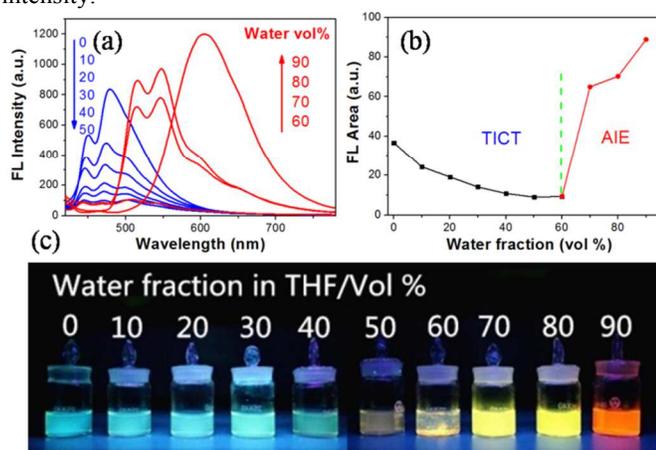


Fig. 1 (a) The fluorescence spectra of PTZ in THF-H₂O with different H₂O fractions (vol, 0-90%). (b) Plots of fluorescent areas of PTZ versus water fraction in THF-H₂O. (c) The digital photos of PTZ in THF-H₂O under irradiation of UV lamp at 365 nm.

Single crystal structure has been employed to study luminescence properties in the solid state. Red block crystals were obtained by slow evaporation of mixture solvent (*n*-hexane/chloroform) at room temperature. The bowl-shaped *N*-substituted phenothiazine rings are almost vertically twisted from the planar aza-BODIQU core (Fig. S9b), which implies a highly twisted conformation exist in the single crystal of the complex. This crystal belongs to the triclinic space with a *P*-1 group. The complexes adopt a stacking mode of H-type aggregation along *a* axis via intermolecular C-H...F, π - π and C-H... π interaction, and the vertical distance between them was measured to be 3.51 Å. These interactions between complexes induced the red-shifted emission of crystal with $\lambda_{max} = 625$ nm. Meanwhile, another polymorph of yellow

crystals with $\lambda_{max} = 548$ nm were also obtained (Fig. S11). Unfortunately, the size of yellow crystals obtained is too small which are not suitable for X-ray structural analysis. However, it still provides a piece of evidence that PTZ can form two or even more different aggregation structures with various emissions in solid state.

Based on these AIE effect, the mechanofluorochromism property of PTZ has been investigated. As shown in Fig. 2a, PTZ is yellow powder with bright fluorescence ($\lambda_{max} = 540$ nm) (PTZ-Y) under 365 nm UV light. After simply grinding, orange powder with red fluorescent ($\lambda_{max} = 635$ nm) (PTZ-R) was obtained (Fig. 2a, 2b). It indicates that the grinding treatment has induced a spectral red-shift of *ca.* 95 nm. To check the reversibility of the piezochromic effect observed for PTZ powder, the ground powder was exposed to CH₂Cl₂ vapour (PTZ-R-CH₂Cl₂), the colour and emission were recovered (Fig. 2b). In order to gain further insight into piezochromic phenomenon of the PTZ powder, powder X-ray diffraction (XRD) are conducted (Fig. 2c). The diffraction pattern of the initial powder exhibits sharp and intense reflections which are consistent with the simulated XRD pattern from the powder of PTZ-Y, which indicated that the aggregate was well ordered in crystalline state. After grinding, although some of the resolvable peaks of the ground sample are consistent with those of the unground sample, they are weaker in intensity and have broader peak shapes, suggesting that the initial aggregation state was changed into an amorphous state by grinding. When ground sample was fumed with solvent vapour, sharp and intense peaks reappeared, which implied that the crystalline state was recovered through molecular repacking. From these results, we can infer that the twisted conformation of PTZ molecules and weak π - π interactions make the molecular packing relatively loose, with the crystalline structure in low lattice energy and formation of cavities. Upon mechanical grinding, the crystals are easy to be destroyed, then the PTZ molecules are packed in close proximity through π - π stacking interaction to form an aggregate in the amorphous phase.³ Thus, the significant red-shift of the emission are caused by the smaller band gap induced by the increased π - π interaction, the increasing of excimer coupling, as well as the increased orbital overlap between neighboring molecules.⁷ All these data suggest PTZ is a very promising piezochromic material.

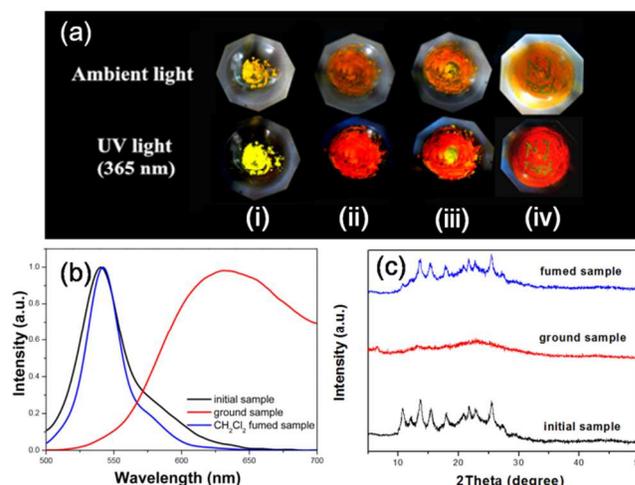


Fig. 2 (a) Photographic images of **PTZ** in response to mechanical grinding under the irradiation of ambient light and UV light at 365 nm: (i) crystalline sample, (ii) ground sample, (iii) ground sample upon addition of a drop of CH_2Cl_2 , and (iv) the letters of "NJ Tech" were written on the ground sample via capillary gla tube with CH_2Cl_2 . (b) Emission spectra of the corresponding samples. (c) XRD patterns of the corresponding samples.

By considering the quinoline and phenothiazine rings in the structure of **PTZ**, the molecule is a Lewis base that can be protonated by an acid. Therefore, prepared filter paper of complex **PTZ** was employed for acid stimuli-responsive experiments. The **PTZ** test paper shows strong yellow fluorescence under 365 nm UV light (Fig. S16). After exposing in hydrochloride (HCl) vapour, the fluorescence of **PTZ** was quenched immediately. Then fuming this test paper with triethylamine (TEA) for 30s, the original bright yellow fluorescence could be observed again. This cycle can be repeated for more than three times (Fig. S17). The emission of **PTZ** in the presence of acid (such as HCl and TFA) and the base (such as NaOH) in different solutions have also been studied (Fig. S18-20). The emission was quenched immediately after adding excess acid, and then recovered by adding excess base.

To further understand the protonation effect, UV-vis absorptions of **PTZ** and **PTZ-HCl** in solution and solid state have been studied (Fig. S21-22). The absorption of **PTZ** in *n*-hexane exhibits fine structure with a maximum band at 445 nm, which blue-shifted to 429 nm in methanol. The absorption is attributed to π - π^* transition localized on the conjugated aromatic system, which is also supported by its minor solvatochromic effect (Fig. S4).

Upon titration of **PTZ** solution in THF with hydrochloric acid (37%, w/w), no obvious change can be observed (Fig. S21). However, in solid state, the absorption of **PTZ** fumed by HCl vapour for 5 min (**PTZ-HCl**) exhibits a 28 nm red-shift compared to its original form (Fig. S22). When fumed by HCl vapour, the chemical shifts in ^1H NMR spectra reveal the changing of electron density on aromatic hydrogen atoms, which further confirms the protonation of **PTZ** (Fig. S23). All these results demonstrate that complex **PTZ** could be a potential acid and base stimuli-responsive on/off sensor.

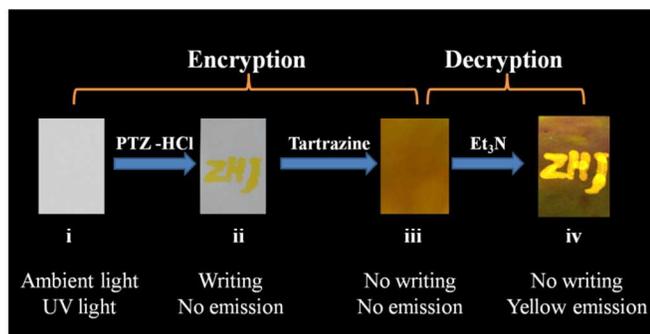


Fig. 3. Photographic images of information encryption and decryption.

According to these significant fluorescence switching features, a new technology for information encryption and decryption was

designed. **PTZ-HCl** was used as cryptographic ink, while the dye tartrazine (Scheme S2) was used to form the 'security paper'. The tartrazine was selected to provide background colour, because its bright lemon yellow colour can cover 'writing' under both of ambient light and UV light, as well as its acid and alkali resistance. In the encryption stage, characters 'ZHJ' were written on a filter paper by using **PTZ-HCl** ink, then the paper was immersed into tartrazine solution for 20s and dried at room temperature. So the 'writing' was hidden by tartrazine and could not be observed neither under ambient light nor UV light. In decryption stage, the yellow fluorescence of the characters 'ZHJ' can be revealed clearly after exposing the test paper to TEA vapour for 10 min. We envision that this protonation-deprotonation stimuli luminescent materials have potential applications in data security protection.

In summary, we demonstrated an AIE-active boron-difluoride complex **PTZ** with multi-stimuli-responsive features. This complex shows switched emission ranging from blue, yellow to red in THF/water mixture solutions. In addition, its colours and emissions can be switched by multiple external stimuli including grinding, organic solvent vapours, as well as acid and base vapours. The fumigation with HCl/TEA vapours of **PTZ** exhibits an off/on switching fluorescence effect. Based on the protonation-deprotonation stimuli luminescent property of **PTZ**, a simple, convenient and efficient technology for data encryption and decryption was designed. All these comprehensive investigations suggest that complex **PTZ** is a very promising candidate for the applications in sensing, detection and security protection.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, synthetic procedure, calculation, photophysical studies and crystallographic data in CIF. See DOI: 10.1039/c000000x/

1 (a) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, 2002, 420, 759; (b) A. Kishimura, T. Yamashita, K. Yamaguchi and T. Aida, *Nat. Mater.*, 2005, 4, 546; (c) Y. Che, X. Yang and L. Zang, *Chem. Commun.*, 2008, 1413; (d) H. B. Sun, S. J. Liu, W. P. Lin, K. Y. Zhang, W. Lv, X. Huang, F. W. Huo, H. R. Yang, G. Jenkins, Q. Zhang and W. Huang, *Nat. Comm.*, 2013, 5, 3601.

2 (a) J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740; (b) B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, 124, 14410; (c) J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. Zhu and B. Z. Tang, *Chem. Mater.* 2003, 15, 1535; (d) J. Mei, Y. N. Hong, J. W. Y. Lam, A. J.

- Qin, Y. H. Tang and B. T. Tang, *Adv. Mater.*, 2014, DOI: 10.1002/adma.201401356.
- 3 (a) Z. G. Chi, X. Q. Zhang, B. J. Xu, X. Zhou, C. P. Ma, Y. Zhang, S. W. Liu and J. R. Xu, *Chem. Soc. Rev.*, 2012, **41**, 3878; (b) X. Q. Zhang, Z. G. Chi, H. Y. Li, B. J. Xu, X. F. Li, W. Zhou, S. W. Liu, Y. Zhang and J. R. Xu, *Chem.-Asian J.*, 2011, **6**, 808; (c) H. Y. Li, X. Q. Zhang, Z. G. Chi, B. J. Xu, W. Zhou, S. W. Liu, Y. Zhang and J. R. Xu, *Org. Lett.*, 2011, **13**, 556.
- 4 (a) Q. Qi, J. Zhang, B. J. Xu, B. Li, S. X. Zhang, and W. J. Tian, *J. Phys. Chem. C*, 2013, **117**, 24997; (b) X. Q. Zhang, Z. G. Chi, B. J. Xu, B. Chen, X. Zhou, Y. Zhang, S. W. Liu, and J. R. Xu, *J. Mater. Chem.*, 2012, **22**, 18505; (c) C. Li, X. Luo, W. Zhao, C. Li, Z. Liu, Z. Bo, Y. Dong, Y. Dong, and B. Z. Tang, *New J. Chem.*, 2013, **37**, 1696; (d) X. Luo, W. Zhao, J. Shi, C. Li, Z. Liu, Z. Bo, Y. Q. Dong, and B. Z. Tang, *J. Phys. Chem. C*, 2012, **116**, 21967; (e) X. Luo, J. Li, C. Li, L. Heng, Y. Q. Dong, Z. Liu, Z. Bo and B. Z. Tang, *Adv. Mater.*, 2011, **23**, 3261.
- 5 (a) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891; (b) N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.*, 2012, **41**, 1130; (c) G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem. Int. Ed.*, 2008, **47**, 1184; (d) S. Atilgan, Z. Ekmekci, A. L. Dogan, D. Guc and E. U. Akkaya, *Chem. Commun.*, 2006, 4398; (e) S. Erbas, A. Gorgulu, M. Kocakusakogullari and E. U. Akkaya, *Chem. Commun.*, 2009, 4956; (f) N. Adarsh, R. R. Avirah, D. Ramaiah, *Org. Lett.*, 2010, **12**, 5720.
- 6 M. Zheng, M. X. Sun, Y. P. Li, J. F. Wang, L. Y. Bu, S. F. Xue and W. J. Yang, *Dyes and Pigments*, 2014, **103**, 29.
- 7 (a) C. Kittel, *Introduction to Solid State Physics*, Wiley, New York, 1996; (b) Y. J. Dong, B. Xu, J. B. Zhang, X. Tan, L. J. Wang, J. L. Chen, H. G. Lv, S. P. Wen, B. Li, L. Ye, B. Zou and W. J. Tian, *Angew. Chem., Int. Ed.*, 2012, **51**, 10782.