‖ Sensors

Effect of the Counterion on Light Emission: A Displacement Strategy to Change the Emission Behaviour from Aggregation-Caused Quenching to Aggregation-Induced Emission and to Construct Sensitive Fluorescent Sensors for Hg^{2+} Detection

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Abstract: In this paper, a simple strategy to change the emission behaviour of luminogenic materials was developed. Tetraphenylethene (TPE)-functionalised benzothiazolium salts with different counteranions (TPEBe—X; X = I−, ClO_4^- and PF_6^-) were designed and synthesised. All the luminogens show weak red emission in the solution state that originates from intramolecular charge transfer from TPE to the benzothiazolium unit. Whereas aggregate formation enhances the light emission of TPEBe—ClO_4 and TPEBe—PF_6, that of TPEBe—I is quenched, thus demonstrating the phenomena of aggregation-induced emission and aggregation-caused quenching. TPEBe—I works as a light-up fluorescent sensor for Hg^{2+} in aqueous solution with high sensitivity and specificity owing to the elimination of the emission quenching effect of the iodide ion by the formation of HgI_2 as well as the induction in aggregate formation by the complexation of Hg^{2+} with the S atom of the benzothiazolium unit of TPEBe—I. A solid film of TPEBe—I was prepared that can monitor the level of Hg^{2+} in aqueous solution with a detection limit of 1 μM.

Introduction

The development of efficient luminescent materials in the aggregated or solid state is a topic of current interest on account of their potential applications in the fields of electronics, optics and biological sciences.[1] In response to this demand, scientists have prepared a large number and a wide variety of fluorescent materials. Whereas they are highly emissive in the solution state, they become weakly emissive or even non-emissive when aggregated in the condensed phase. This aggregation-caused quenching (ACQ) effect has significantly limited the high-tech application of conventional fluorophores.[2] Various physical and chemical methods have been utilised to mitigate aggregate formation but have met with little success as they are working against the natural process.[3] In 2001, we observed a phenomenon of aggregation-induced emission (AIE) in some propeller-shaped molecules that is the exact opposite of the ACQ effect.[4] These luminogens are non-emissive in the solution state, but are induced to emit intensely upon aggregate formation. Such a discovery has attracted much interest and many research groups in the world are now conducting AIE research.[5–7] Their enthusiastic research efforts have led to the generation of new AIE fluorogens and exploration of new technological applications. Incorporation of an AIE unit into ACQ fluorophores has solved their ACQ problem and at the same time imparted them with AIE characteristics without causing any adverse effects, thus demonstrating a novel approach to widen the family of AIE luminogens with desirable properties.[8, 9]

Sensitive and specific sensors for Hg^{2+} detection are in great demand because of the serious deleterious effects of mercury on the environment and human health.[10] To date, a variety of fluorescent Hg^{2+} sensors have been developed from conventional fluorophores based on the mechanism of fluorescence resonance energy transfer,[11] photoinduced electron transfer[12] and intramolecular charge transfer.[13] AIE luminogens have also been utilised as sensory materials for Hg^{2+} detection.[14,15]

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Upon complexation with Hg^{2+}, the intramolecular rotation of the sensor is restricted, which blocks the non-radiative relaxation channel and thus converts the luminogens into strong emitters. Since most AIE luminogens are hydrophobic in nature and emit efficiently in the aggregated state, to maximise the sensitivity, the detection is normally carried out in pure organic solvent that is miscible with the aqueous Hg^{2+} solution. Development of water-soluble AIE luminogens might solve such problem, but it is not easy from the synthetic point of view. On the other hand, for practical application, it is preferable to perform the Hg^{2+} detection on a solid support because it requires no expensive spectrofluorometer and is thus simple and convenient. Unfortunately, such sensing systems are rare.

In this paper, we report a simple strategy to tune the emission behaviour of a tetraphenylethene (TPE)-functionalised benzothiazolium salt (TPEBe—X; Scheme 1). By varying the counteranion from I^- to ClO_4^- or PF_6^-, TPEBe—X changes its

TPEBe-X (X = I, ClO_4, and PF_6)
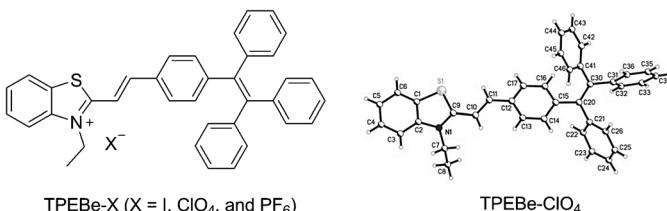
TPEBe-ClO_4

Scheme 1. Structure of TPEBe—X and ORTEP drawing of TPEBe—ClO_4. Anions are omitted for clarity.

emission behaviour from ACQ to AIE. Addition of Hg^{2+} into the aqueous solution of TPEBe—I enhances the light emission by 80-fold, which suggests that it is an excellent fluorescent Hg^{2+} sensor with high sensitivity and selectivity. The sensing process can also be performed in solid film with a detection limit of 1 μM, thereby demonstrating the use of AIE compounds for Hg^{2+} detection in real-world conditions.

Results and Discussion

The TPE-functionalised benzothiazolium salts (TPEBe—I, TPEBe—ClO_4 and TPEBe—PF_6) were prepared according to the synthetic routes shown in Scheme S1 of the Supporting Information. Whereas TPEBe—I and TPE—ClO_4 are new compounds, TPEBe—PF_6 was prepared in our previous work.[16] Briefly, the coupling reaction of 3-ethyl-2-methyl-1,3-benzothiazol-3-ium iodide and 4-(1,2,2-triphenylvinyl)benzaldehyde in ethanol heated at reflux generated TPEBe—I in a high yield, which underwent counteranion exchange in the presence of sodium perchlorate and potassium hexafluorophosphate, respectively, to give TPEBe—ClO_4 and TPEBe—PF_6. All the final products were characterised by ^1H and ^{13}C NMR and mass spectroscopies, from which satisfactory results corresponding to their molecular structures were obtained (see the Supporting Information for details). Single crystals of TPEBe—ClO_4 were grown by slow evaporation of its dichloromethane/ethanol mixture and analysed crystallographically. The ORTEP drawing is shown in Scheme 1, and the crys-
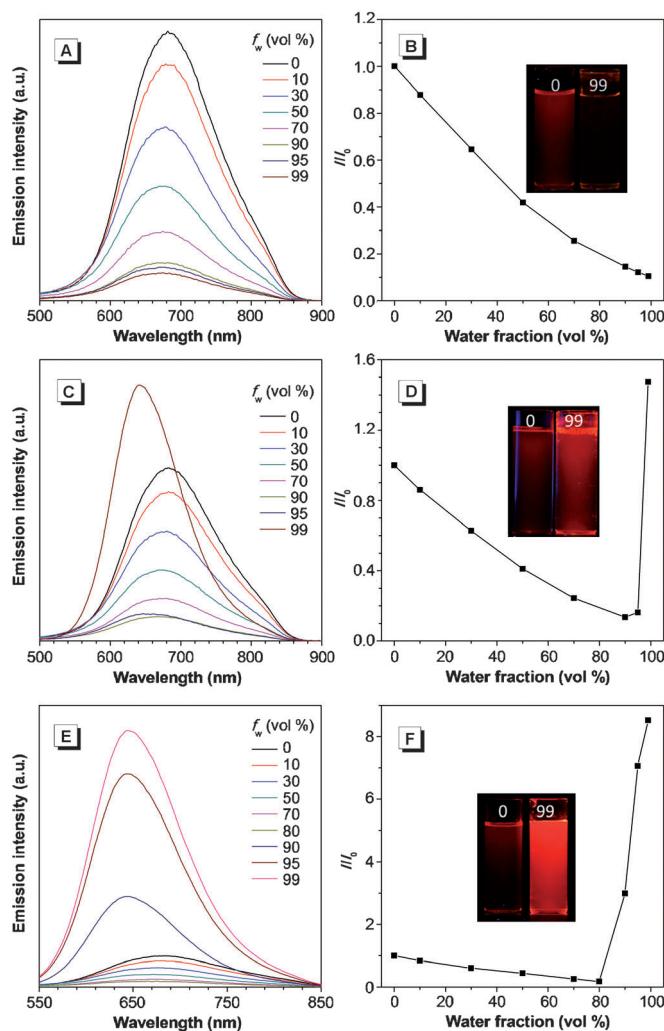
Figure 1. Emission spectra of A) TPEBe—I, C) TPEBe—ClO_4 and E) TPEBe—PF_6 in DMSO and DMSO/water mixtures with different water fractions (f_w). Plots of relative emission intensity (I/I_0) versus the composition of the aqueous mixtures of B) TPEBe—I, D) TPEBe—ClO_4 and F) TPEBe—PF_6; I_0 = emission intensity in pure DMSO solution. Solution concentration: 20 μM; excitation wavelength: 420 nm. Inset: Photographs of B) TPEBe—I, D) TPEBe—ClO_4 and F) TPEBe—PF_6 in DMSO/water mixtures with f_w values of 0 and 99 vol% under 365 nm UV irradiation.

tal data are summarised in Table S1 of the Supporting Information.

As shown in Figure 1, photoexcitation of the dilute solutions of all the luminogens in dimethylsulfoxide (DMSO) induces a red emission peak at 682 nm that originated from the intramolecular charge transfer (ICT) from the electron-donating TPE group to the electron-accepting benzothiazolium unit. The fluorescence quantum yield (Φ_F) using 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (Φ_F = 82% in dimethylformamide) as standard is all equal to approximately 2.00%, presumably due to the ICT effect as well as active intramolecular rotation, which consumes the energy of the excitons through the non-radiative relaxation channel. The emission was further weakened upon addition of water into the solution as the ICT effect becomes intensified by increasing the polarity of the solvent mixture. The higher the water content, the

lower the light emission (Figure 1B, D and F). Interestingly, starting from a water fraction of 90 and 80%, respectively, the TPEBe–ClO_4 and TPEBe–PF_6 solutions become emissive again, whereas that of TPEBe–I remains weakly fluorescent. At 99% aqueous solution, almost no light was emitted from the aqueous mixture of TPEBe–I, and the appearance of the solution changes from red in pure DMSO to dark in 99% aqueous mixture under 365 nm UV illumination (inset in Figure 1B). In contrast, the aqueous mixtures of TPEBe–ClO_4 and TPEBe–PF_6 show stronger emission peaks at 643 nm than their pure DMSO solutions. Clearly, TPEBe–I demonstrates an ACQ phenomenon, whereas TPEBe–ClO_4 and TPEBe–PF_6 are AIE-active. The Φ_F values of their powders determined by a calibrated integrating sphere are approximately 0.01, 8.20 and 9.48%, with lifetimes of approximately 76 ps, 1.23 ns and 0.84 ns, respectively, thus substantiating the conclusion stated above.

The luminogens must aggregate in aqueous mixture with a large amount of water on account of their poor solubility in water. However, all the solutions are homogeneous without precipitates, which reveals that the formed particles are of nanodimensions. This is indeed the case, as revealed by the existence of nanoparticles with average sizes of approximately 50–100 nm in 99% aqueous mixture by TEM analysis (Figure S1 in the Supporting Information). The emission spectra of thin films of the luminogens are illustrated in Figure S2 of the Supporting Information. The spectrum of TPEBe–I is basically a flat line parallel to the abscissa. However, intense emission signals with peaks at 650 nm are recorded in TPEBe–ClO_4 and TPEBe–PF_6. When observed under 365 nm UV irradiation, the thin film of TPEBe–I appears black, whereas those of TPEBe–ClO_4 and TPEBe–PF_6 show strong red emission. Such a distinctly different appearance allows easy differentiation of TPEBe–I among the luminogens by the naked eye.

It is noteworthy that all the luminogens possess the same cationic unit. Thus, the counteranion should play a key role in their different emission behaviours in the condensed phase. Iodine is a well-known effective fluorescent quencher due to its heavy-atom effect, which helps to accelerate the rate of intersystem crossing and hence promote non-radiative relaxation by colliding with the luminogenic molecules.[17] In the solution state, the TPEBe–I molecules exist in the form of solvent-separated ion pairs. Such a structure possesses a low rate of colliding, and thus the quenching effect of I^- is disabled.[18] In the condensed phase, however, the drastic collision between the iodide ion and the cationic unit in the state of closely contacting ion pairs has annihilated the excitons, thus rendering TPEBe–I non-emissive in the aggregated or solid state. Changing the counteranion to ClO_4^- or PF_6^- alters the emission behaviour in the solution state only a little, but recovers the intrinsic AIE characteristic of the TPE unit of TPEBe–ClO_4 and TPEBe–PF_6 in the condensed phase. Clearly, this displacement strategy of counterion provides a simple and novel route for changing the emission behaviour of a luminogen from ACQ into AIE. According to previous reports[19] as well as crystal structure of TPEBe–ClO_4 and TPEBe–PF_6,[16] the size of the ClO_4^- or PF_6^- and its interaction with the cationic unit seems to exert a strong influence on the emission efficiency of the

corresponding luminogens (TPEBe–ClO_4 or TPEBe–PF_6) in the aggregated state. Therefore this simple strategy provides an opportunity to generate AIE luminogens with efficient solid-state light emission.

Hg^{2+} is known to show a high affinity toward the iodide ion.[20] With this in mind, it is envisioned that Hg^{2+} can displace the cationic unit of TPEBe–I, and the removal of the iodide ion might affect the optical properties of the luminogen. Given such a possibility, we thus tested the response of TPEBe–I to the presence of Hg^{2+} in aqueous buffer solution (pH 7.4, 20 mM 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES) buffer with 1% DMSO) by both UV/Vis and fluorescence spectroscopies. Each sample was measured per minute. As shown in Figure 2, upon gradual addition of Hg^{2+} into the
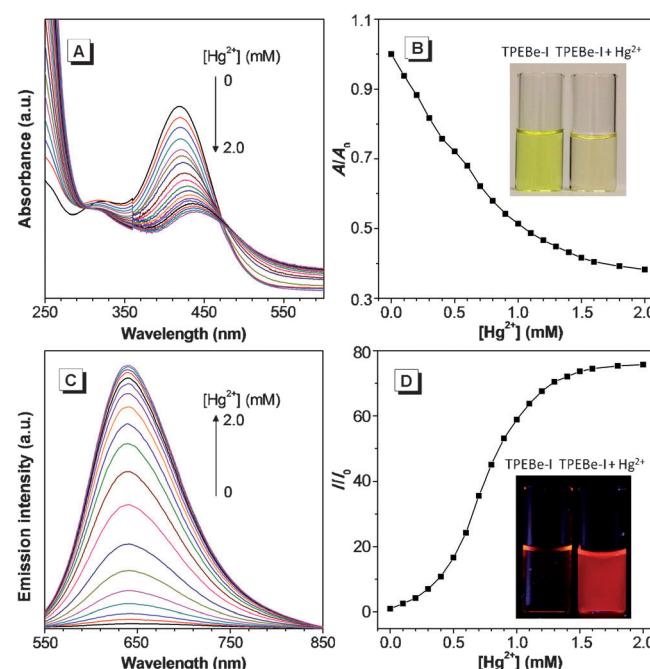
Figure 2. A) UV/Vis and C) emission spectra of TPEBe–I in aqueous buffer solutions (pH 7.4, 20 mM HEPES buffer with 1% DMSO) with different concentrations of Hg^{2+} (0–2.0 mM). B) Plot of relative absorbance (A/A_0) and D) emission intensity (I/I_0) versus the Hg^{2+} concentration. A_0 = absorbance at 420 nm in the absence of Hg^{2+}; I_0 = the emission intensity at 640 nm in the absence of Hg^{2+}. Inset: Photographs of TPEBe–I in aqueous buffer with [Hg^{2+}] of 0 and 2.0 mM taken under B) daylight and D) 365 nm UV illumination. Solution concentration: 20 μM; excitation wavelength: 480 nm.

aqueous solution of TPEBe–I, the absorption peak at approximately 420 nm became weaker progressively and shifted slightly to the redder region. Meanwhile, a level-off absorption tail appears at the longer-wavelength region, thus revealing the formation of aggregates.[5] The solution colour also changes from yellow into colourless, thereby allowing rapid detection of Hg^{2+} in aqueous solution by the naked eye. Correspondingly, the emission of TPEBe–I is turned on in the presence of Hg^{2+} (Figure 2C). At an Hg^{2+} concentration of 2.0 mM, the emission intensity is 80-fold higher than that of aqueous buffer without metal ions. When observed under 365 nm UV illumination, the original non-emissive solution now shows in-
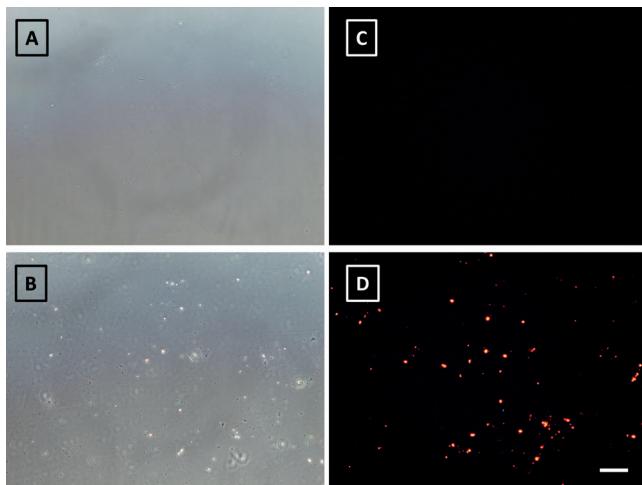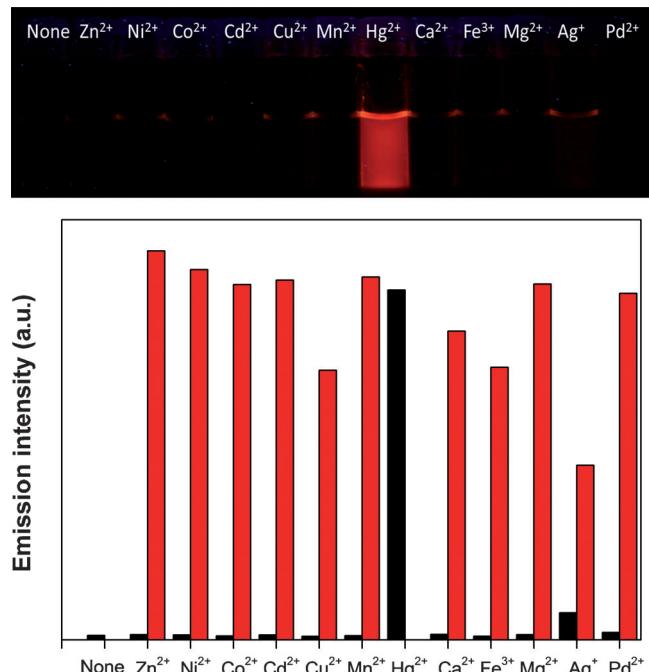
Figure 3. A, B) Bright-field and C, D) fluorescent images of TPEBe–I (20 μM) in aqueous buffer solutions with A, C) 0 and 2.0 mM B, D) of Hg^{2+}. Scale bar: 100 μm.

Figure 4. Top: Photographs of TPEBe–I in aqueous buffer solutions (20 μM) with various metal ions (2.0 mM) taken under 365 nm UV illumination. Bottom: Emission response of TPEBe–I to various metal ions. Black bars represent the addition of different metal ions (2.0 mM) to the aqueous solution of TPEBe–I, whereas the red bars represent the subsequent addition of Hg^{2+} (2.0 mM) to the solution containing a specific metal ion. Excitation wavelength: 480 nm; emission wavelength: 640 nm.

tense red fluorescence, thereby enabling TPEBe–I to serve as a "light-up" fluorescent sensor for Hg^{2+} detection with a detection limit of 1 mM in aqueous solution.

The Hg^{2+} sensing process was also examined under a fluorescent microscope. As depicted in Figure 3A and B, nearly no emissive particles are observed in the pure buffer solution of TPEBe–I. Addition of Hg^{2+} (2.0 mM) into the solution resulted in the formation of more and larger particles with red emission (Figure 3B and D). This result shows that Hg^{2+} induces the aggregate formation of TPEBe–I.

Excepting sensitivity, a fluorescent sensor should possess an excellent selectivity for its targeting analyte. Thus, the fluorescence response of TPEBe–I to various metal ions including Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Hg^{2+}, Ca^{2+}, Fe^{3+}, Mg^{2+}, Ag^{+} and Pd^{2+} was carried out under the same experimental conditions. The results show that none of these ions causes a noticeable change in the emission of TPEBe–I (Figure 4 and Figure S3 in the Supporting Information), thus indicating that TPEBe–I possesses a higher selectivity to Hg^{2+} than other metal ions. The interference of various metal ions on the sensing process was also tested. Even when the buffer solutions contained the same amount of other metal cations (2.0 mM), a similar extent of emission enhancement was observed, thus verifying the high anti-interference of the present Hg^{2+} sensor. Relative to the previous sensor for Hg^{2+} based on the AIE mechanism,[15] TPEBe–I exhibits high sensitivity and water compatibility.

To check the effect of pH on the sensing property of TPEBe–I, we studied its emission in buffer solutions with different pH in the absence and presence of Hg^{2+} (Figure S4 in the Supporting Information). TPEBe–I shows relatively stronger emission in acidic buffer solution (pH < 7) without Hg^{2+}, presumably due to the removal of iodide ion by their combination with the proton in the medium. At pH > 7, the solution only emits a faint light due to the quenching effect of the iodide ion. Addition of Hg^{2+} into the basic aqueous solution enhanced the light emission but the extent was smaller than that

under acidic conditions. At pH 11, the non-fluorescent TPEBe–I solution alters little, even upon addition of Hg^{2+}. The formation of Hg(OH)$_2$ in strong basic buffer reduces the amount of free Hg^{2+} in solution and thus led to no emission enhancement. In addition, according to the previous report,[21] TPEBe–I undergoes hydrolysis in the presence of OH$^-$ ion, thus making it incapable of sensing Hg^{2+}. Through the above investigation, it becomes clear that TPEBe–I exhibits satisfactory sensing ability at neutral pH, thereby enabling it to work under a physiological environment.

The Hg^{2+} sensing can also be performed in the solid state. Thin solid films of TPEBe–I were prepared by drop-casting its solution in dichloromethane (2.0 mM, 10 μL) on cover glasses followed by drying in air for 10 min. Aqueous solutions that contained different Hg^{2+} concentrations (5.0 μL) were then dropped onto the films. After being kept at room temperature for 30 min, photographs of the tested films were taken under 365 nm UV irradiation. As shown in Figure 5, the spots on the TPEBe–I films that contained Hg^{2+} showed red light with varying degree, whereas the untreated parts remained dark. The large contrast between the two portions enabled a detection limit down to 1 μM ($\approx$ 200 ppm), which is 100-fold lower than the value in aqueous solution. This provides an effective and convenient tool for tracking the level of Hg^{2+} in aqueous solution for real-world applications. To the best of our knowledge, this is the first example of utilising a solid film for detecting Hg^{2+} in aqueous solution based on the AIE mechanism.
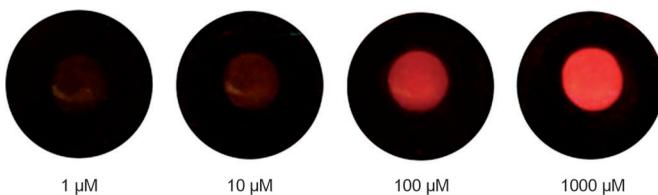
Figure 5. Photographs of thin films of TPEBe—I containing different concentrations of Hg^{2+} (5.0 μL) in aqueous solution taken under 365 nm UV illumination.

For the purpose of mechanistic understanding, the emission response of TPEBe—ClO_4 to Hg^{2+} was also investigated. Addition of Hg^{2+} into the aqueous buffer solution of TPEBe—ClO_4 gave a similar change in the UV/Vis spectrum to that in TPEBe—I. Simultaneously, the emission of TPEBe—ClO_4 is enhanced progressively as the amount of Hg^{2+} increases. It is noteworthy that at the same Hg^{2+} concentration, the magnitude of emission enhancement in TPEBe—ClO_4 is lower than TPEBe—I owing to the stronger fluorescence background of the former dye molecule. This result implies that the stronger emission response or higher sensitivity of TPEBe—I to Hg^{2+} stems from the presence of iodide ion. It also suggests that the cationic unit of the luminogens plays a role in the Hg^{2+}-induced emission enhancement. Except for its high affinity to the iodide ion, Hg^{2+} is a well-known thiophilic metal ion and can interact preferentially with a soft base such as S atom on the basis of Pearson's hard/soft acid/base theory.[22] The coordination of Hg^{2+} with the S atom of the benzothiazolium unit of TPEBe—I and TPEBe—ClO_4 generates complexes with even worse solubility in aqueous buffer. This induces aggregate formation and hence enhances the light of the luminogens.

To confirm the above speculation, the coordination process was analysed by means of ^1H NMR spectroscopy. As shown in Figure 6, addition of Hg^{2+} into the DMSO/H_2O mixture shifted the aromatic proton absorptions ($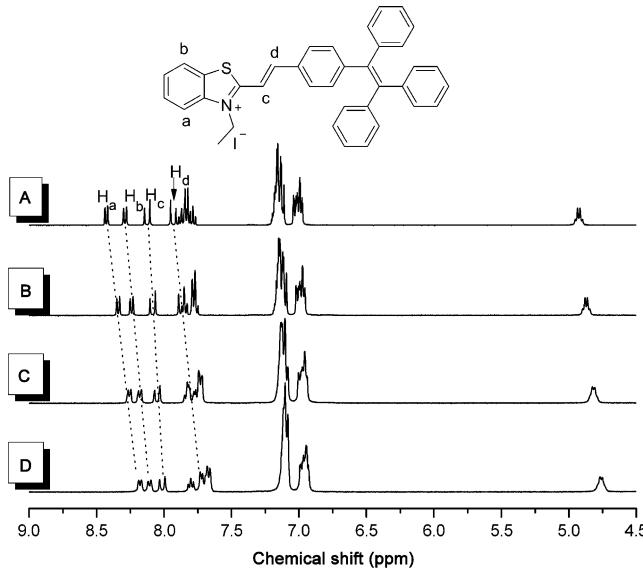H_a$, H_b, H_c, H_d) upfield. The higher the amount of Hg^{2+}, the larger the peak shift. A similar phenomenon was also observed in TPEBe—ClO_4, thereby implying that the complex is really formed through the Hg^{2+}—S interaction, which diminished the shielding effect of the thiazole ring and hence shifted the neighbouring aromatic proton resonances to higher field.

Through the above experimental results, the mechanism for the Hg^{2+} sensing is now clear and is illustrated in Figure 7.
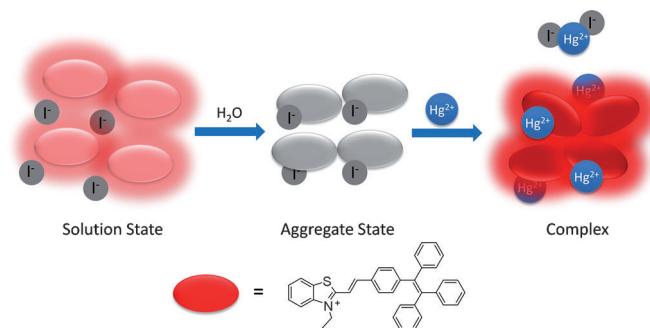
Figure 7. Schematic illustration of the mechanism for detecting Hg^{2+}.

TPEBe—I shows weak fluorescence in solution due to the ICT effect as well as intramolecular rotation of the TPE unit. Due to its hydrophobic nature, the TPEBe—I molecules aggregate in the presence of a large amount of water. The formed aggregates are non-emissive because of the formation of close-contacting ion pairs and the heavy-atom effect contributed from the iodide ion. Addition of Hg^{2+} into the aqueous solution forms HgI_2 and thus eliminates the quenching effect and induces more aggregate formation by means of its complexation with the cationic unit. These recover the light emission of the luminogen, thereby enabling it to function as an excellent "light-up" fluorescent sensor for Hg^{2+}.

Conclusion

In summary, TPE-functionalised benzothiazolium salts with different counteranions (TPEBe—X; X = I^-, ClO_4^- and PF_6^-) were designed and synthesised. All the luminogens show faint red emission in solution. Whereas aggregate formation enhanced the light emission of TPEBe—ClO_4 and TPEBe—PF_6, that of TPEBe—I is quenched owing to the heavy-atom effect of the iodide ion. TPEBe—I functions as a light-up fluorescent sensor for Hg^{2+} detection in aqueous solution with high sensitivity and specificity, which is attributed to the strong affinity of Hg^{2+} toward I^- and S atoms. A handy solid tool was prepared that can monitor the level of Hg^{2+} in aqueous solution with a detection limit of 1 μM. This work provides a novel and simple strategy to change the emission behaviour of luminogenic materials and at the same time opens a new route for detecting Hg^{2+} in aqueous solution based on the AIE mechanism.

Figure 6. ^1H NMR spectra of TPEBe—I in D_2O/DMSO mixtures with A) 0, B) 2, C) 5 and D) $HgCl_2$ (10 equiv).

Acknowledgements

Keywords: aggregation · fluorescence · iodide · mercury · sensors

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