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## Introduction

Sulfur mustard (**SM**, or mustard gas) is a severe vesicant that can induce grievous blisters on the skin and mucous membranes and, in extreme circumstances, lead to death.<sup>1-5</sup> SM is also an alkylating agent that could react with the guanine nucleotide in DNA, and thus results in carcinogenic, mutagenic and teratogenic effects with long-term exposure.<sup>6,7</sup> As a notorious class of chemical warfare agent (CWA), **SM** has caused millions of casualties since its first military use in World War I, as well as in the Iran–Iraq War in the 1980s.<sup>8–12</sup> Although **SM** has been banned by international organizations, large amounts of **SM** are still stockpiled or dumped into the sea, which may cause serious health and environmental problems over

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# Mercaptomethylphenyl-modified tetraphenylethene as a multifunctional luminophor: stimuli-responsive luminescence color switching and AIE-active chemdosimeter for sulfur mustard simulants<sup>†</sup>

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As a commonly known chemical warfare agent, sulfur mustard (SM) is a severe vesicant that can induce grievous blisters on the skin and mucous membranes. Because the onset of SM toxicity is fast, a rapid, sensitive, and accurate method for the detection of SM is necessary. However, designing an effective detection method for SM is challenging because SM does not have any traditional molecular recognition sites. In this study, a fluorescence probe for the detection of SM and an SM simulant (2-chloroethyl ethyl sulfide, CEES) was developed based on the reaction of benzenemethanethiol with the analytes. A non-emissive mercaptomethylphenyl-modified tetraphenylethene (TPE) probe was designed and synthesized. This probe can emit strong fluorescence upon reacting with CEES for 5 minutes in an aqueous solution in the presence of metal ions due to the formation of a sandwich-type complex, which can effectively restrict the rotation of the phenyl rings of TPE. Furthermore, this procedure exhibited high sensitivity for analytes and can be applied to the detection of CEES in soil. As a TPE derivative, this probe also exhibited a reversible solid-state luminescence color switching between blue emission (467 nm) in the crystal state and green emission (516 nm) in the amorphous state upon fuming, grinding and heating. These results indicate that S4 has potential as a multifunctional material of a "smart" luminophor and an AIE-active fluorescent probe for SM.

time.<sup>13–15</sup> More importantly, due to the lack of effective treatments for **SM**-induced injury and its easy preparation and low cost, **SM** is increasingly considered a terrorist threat to humankind and homeland security. Therefore, it is of great importance and interest to develop simple yet effective detection systems for this chemical.

Arising from the serious threat of SM, many efforts have been devoted to the development of detection techniques against SM over the past few years, including gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), and GC-MS combined with some other enrichment technologies.<sup>16-23</sup> However, the disadvantages of these methods are very distinct, and they are usually costly, have poor selectivity, and are susceptible to the environment. In comparison with these instrumental analysis systems, methods based on colorimetry or fluorometry are much simpler, cost-effective, and easy to operate.<sup>24-26</sup> However, due to the relatively low reactivity and the absence of any traditional molecular recognition sites of SM, the design and development of chromogenic and fluorogenic detection systems are quite challenging.<sup>27</sup> To date, there are only a few elegant optical probes for successful detection of SM and its simulants. For example, Kumar and Anslyn reported a

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turn-on fluorescent sensor for SM simulants by using a metal-ion indicator displacement assay in 2013.28 This chemosensor can selectively detect SM simulants at low millimolar levels but requires an intermediary step of capping the reporter before detection. Pardasani et al. developed a rhodamine-based fluorescence turn-on probe for SM utilizing a tandem S-alkylation followed by desulfurization reaction of rhodamine-thioamide with **SM**.<sup>29,30</sup> Wolfbeis *et al.* developed a test strip for colorimetric detection of gaseous SM based on the degradation of SM by the enzyme haloalkane dehalogenase, which could change the local pH and was thus detected by pH indicators incorporated in the strips.<sup>31</sup> In spite of the sensitivity and rapidity of these methods, some drawbacks still exist, such as the requirement of capping the indicator and the complex synthetic procedures. The development of new colorimetry or fluorometry-based detection systems that meet the criteria of simplicity, rapidity, and on-site analysis of SM is still highly desired.

In 2001, Tang and co-workers reported an abnormal emission phenomenon called "aggregation-induced emission" (AIE), in which a series of silole molecules were found to be non-luminescent in solution but emissive in the solid state.<sup>32</sup> Since this pioneering work, luminescent materials with AIE attributes have received extensive interest due to their promising applications in the fields of organic light-emitting diodes, luminescent sensors, biomedical imaging and stimuli-responsive "smart" materials.<sup>33–43</sup> For sensing applications, AIE fluorogens were typically engineered to dissolve in aqueous media, in which the molecules would show extremely weak fluorescence.<sup>44</sup> When target analytes were introduced, the specific interactions between the AIE fluorogens and the analytes could light up the fluorescence. Compared with conventional fluorophore based probes, AIE-based probes afford much higher photo-stability and signal reliability, as AIE signals are produced only when the intramolecular rotations are restricted. The last few years have witnessed the continual emergence of various AIE-based chemo- and bio-sensors for the assays of pH, amines, ions, peptides, proteins, nucleic acids, etc.<sup>45-49</sup> However, to the best of our knowledge, a fluorescence probe based on AIE molecules for SM has not been reported.

Tetraphenylethene (TPE), as a star AIE molecule, has been widely studied for the construction of new AIE materials as well as AIE-based probes due to a number of advantages, such as its high efficiency of solid-state emission, simple synthesis, and easy functionalization.<sup>50-52</sup> In this study, the TPE system is adopted to discover a novel metal ion coordination assisted AIE-active probe for selective fluorescence turn-on detection of SM and its simulant. In our detection system, TPE was functionalized with benzenemethanethiol groups to obtain the TPE-derived molecule (Scheme 1), 1,1,2,2-tetrakis(2'-(ethylthio)propyl-[1,1'biphenyl]-4-yl)-ethene (S4). This compound could react with SM and its stimulant, 2-chloroethyl ethyl sulfide (CEES), to generate strong green AIE signals. The detection process was proven to be simple, rapid and selective for SM and the SM simulant. In addition, as a TPE derivative, compound S4 exhibited reversible solid-state luminescence color switching between blue emission (467 nm) in the crystal state and green emission

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Scheme 1 The synthetic routes of compound S4.

(516 nm) in the amorphous state upon fuming, grinding and heating. This paper also presents the study of stimuliresponsive luminescence color switching of **S4**. The results indicate that **S4** has multi-potential as a "smart" material or an AIE-active fluorescent probe for **SM**.

### **Experimental sections**

#### Synthesis and characterization

Tetrabromo-tetraphenylethene (1) was synthesized according to the literature method.<sup>50</sup> Suzuki coupling reaction was used to prepare the intermediate product tetra(*o*-tolyl)tetraphenylethene (2) *via* reacting 1 with *o*-tolylboronic acid. The reaction of 2 with NBS in the presence of AIBN gave tetra(2-(bromomethyl)phenyl)-tetraphenylethene (3). The title compound tetra(mercaptomethyl)phenyl-tetraphenylethene (S4) was ultimately obtained through the reaction of 3 with thiourea followed by base hydrolysis and treatment with acid. Details of the synthesis, purification and single-crystal preparation processes, along with <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy data, mass spectrometry results, elemental analysis characterization and X-ray single crystal structure, can be found in the ESI.<sup>†</sup>

#### Spectroscopic characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance spectrometer (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C) in CDCl<sub>3</sub>. Element analyses (C, H) were performed using a German Vario EL III elemental analyzer. Mass analyses were performed using an Agilent 5973N MSD Spectrometer. UV-visible absorption spectra for the solutions were recorded using a Shimadzu UV-2550 spectrometer. Photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301PC fluorescence spectrometer. The fluorescence quantum yield ( $\Phi$ ) in solution was determined using rhodamine B in ethanol as a reference according to a previously reported method. Quantum yields of the solid-state powder were determined with a PTI C-701 calibrated integrating sphere system. Steady-state fluorescence spectra and decay curves were obtained using an Edinburgh FLS920 fluorescence spectrometer and a time-correlated single

#### Single-crystal X-ray diffraction

The single crystal of **S4** was obtained through slow diffusion of its tetrahydrofuran (THF) solution for several days at room temperature. The data collection was performed without any inert gas protection at room temperature on a Bruker SMART APEX-II CCD area detector using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data reduction and integration and global unit cell refinements were performed using the INTEGRATE program of the APEX2 software package. Semiempirical absorption corrections were applied using the SCALE program for the area detector. The structure was solved by direct methods and refined using the full-matrix least-squares methods on  $F^2$  using SHELX.

#### Powder X-ray diffraction and thermal analysis

For phase identification, powder X-ray diffraction (XRD) patterns were recorded at room temperature with a Bruker AXS X-ray powder diffractometer using Cu K $\alpha$  radiation. The data were recorded in the  $2\theta$  mode with a step size of  $0.02626^{\circ}$ . Differential scanning calorimetry (DSC) measurements were performed to enable a better understanding of the phase transitions, and the curves were obtained with a NETZSCH thermal analyzer (DSC 204 F1) at heating and cooling rates of 10 K min<sup>-1</sup> under a N<sub>2</sub> atmosphere.

### **Results and discussion**

#### Design criteria

Designing a fluorescence detection method for SM is challenging because SM does not have any traditional molecular recognition sites. Furthermore, SM is not a particularly good electrophile compared to a simple primary alkyl halide and is difficult to react with any sensor molecules in common solvents. Recently, studies have found that the chlorine atoms in SM are reactive with good nucleophiles in basic medium and can form three-membered cationic sulfonium heterocycles, which can greatly enhance the electrophilicity of SM.<sup>28</sup> On the basis of this finding, the Anslyn group designed a dithiol derivative with a benzenemethanethiol structure, which can react with SM in hot water at pH 9 to form a podand and ultimately reached for the detection of SM through an optical technique.<sup>28,53</sup> Inspired by this promising reaction, we realized that, when connecting benzenemethanethiol with the TPE moiety, the tetrathiol compound would be a multi-site reactant for SM. The reaction of the tetrathiol compound S4 with the target analyte SM will give a sulfur-based podand molecule L with four open chains, which are excellent receptors for some metal ions, e.g. Hg<sup>2+</sup> and Cd<sup>2+</sup>. As illustrated in Scheme 2, in the presence of metal ions, it is expected that the metal ions can be chelated by two stagger sulfur-based chains and then sandwiched by two podand molecules (L). The face-to-face molecular stacking will ultimately lock the TPE moieties to restrict the rotation of the phenyl rings of TPE and result in an AIE-active fluorescence enhancement in comparison with the non-emissive probe **S4**.

illustration of the fluorescent enhancement induced by the metal ion-

#### Detection of mustard simulant

coordination

In the current study, we chose 2-chloroethyl ethyl sulfide (CEES), an SM simulant, which is known as "half mustard", as the analyte. CEES has the relevant chemical properties of the real agent without its associated toxicological properties. CEES has a relatively high  $LD_{50}$  of 252 mg kg<sup>-1</sup> (rat oral) in comparison with that of SM (2.4 mg kg<sup>-1</sup>), and is an appropriate substitute of SM for studies with an academic setting.<sup>54</sup>

As expected, probe S4 displayed almost no emission in dilute solution. When an excess of CEES (15 equivalents) was added to the probe solution of S4 in a mixture of DMSO and sodium bicarbonate/sodium hydroxide buffer (1:1 vol, pH = 9)and reacted at 80 °C for 5 minutes, the fluorescence intensity showed medium enhancement. This phenomenon is due largely to the resulting long open chains which decelerate (or partially restrict) the rotation of the phenyl rings of TPE. The formation of the product L(X = H) was confirmed by mass spectrometry (see Fig. S7 in the ESI<sup>+</sup>). The next aim was to choose the metal ion and determine the required concentration of metal ion that saturates the fluorescent enhancement. We firstly determined the fluorescence change of L in response to different metal ions, including Hg<sup>2+</sup>, Ag<sup>+</sup>, Al<sup>3+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup> and Zn<sup>2+</sup>. The results manifested that Hg<sup>2+</sup> and Cd<sup>2+</sup> can cause obvious fluorescent enhancement of L (see Fig. S1 in the ESI<sup>†</sup>), and Hg<sup>2+</sup> was ultimately selected as the assistant ion. Toward this end, fluorescence titration was carried out for the quantitative determination of HgCl<sub>2</sub> in the achieved system containing L. As shown in Fig. 1a, the fluorescence emission of the mixed solution was gradually increased with an increase in the concentration of Hg<sup>2+</sup>, and became saturated with the addition of five equivalents of  $\mathrm{Hg}^{2+}$  (5  $\mu$ M). After confirming the required equivalents of Hg<sup>2+</sup>, we went on to explore the detection of CEES. In this process, S4 in the mixture of DMSO and buffer (1:1 vol) containing five equivalents of HgCl<sub>2</sub> was allowed to



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Fig. 1 (a) Fluorescence titration of a reaction solution of S4 ( $1.0 \mu$ M) and 15 equivalents of CEES with increasing concentrations of Hg<sup>2+</sup>. (b) Fluorescence titration of a mixed solution of S4 and five equivalents of Hg<sup>2+</sup> with increasing concentrations of CEES, inset: colorimetric response of the solution with sequential addition of CEES from left to right. (c) The relationship of the fluorescence intensity of S4 at 482 nm and CEES concentration in the presence and absence of Hg<sup>2+</sup> respectively. (d) Reaction-time profiles: the fluorescence intensity of the reaction solution of S4 (5.0  $\mu$ M) with 10 equivalents of CEES in the presence of five equivalents of Hg<sup>2+</sup> at 482 nm *versus* time (within 7 minutes).

react with CEES with varied equivalents from 1 to 15 at 80 °C for 5 minutes and then the fluorescence spectrum of each solution was subsequently recorded. As shown in Fig. 1b, the solutions containing excess of nine equivalents of CEES exhibited maximum fluorescence intensity, which was approximately 30-fold higher than that of the solution without CEES. The fluorescence intensity of the probe solution increased gradually and showed good linearity with the concentration of CEES. The detection limit of the probe for CEES is about 1.10 µM based on a signal-to-noise ratio (S/N) of 3 under such test conditions, which is much lower than the lethal dose (Fig. S2 in the ESI<sup>+</sup>). Moreover, a visual fluorescent boost of the S4 solution can be readily observed by the naked eye after reacting with CEES, which suggests that S4 can be utilized as a convenient probe for naked eye detection of CEES (inset in Fig. 1b). As a control, we also inspected the fluorescence response of S4 to CEES in the absence of metal ions  $(Hg^{2+})$ , showing that the fluorescence enhancement was rather limited under such conditions (Fig. 1c). The results indicate that the ion-coordinationinduced sandwich-type structure plays a crucial role in the fluorescence enhancement during the process of CEES detection. In addition, we further studied the response time. The fluorescence intensity of S4 treated with nine equivalents of CEES reached a maximal value within about 5 minutes (Fig. 1d), which indicated that probe S4 could rapidly monitor

**CEES.** The reaction in this sensing process needed to be heated at 80  $^{\circ}$ C, which is one downside of this detection method. It is one of our aims to improve the reaction conditions and decrease the reaction temperature in our follow-on work.

Next, we investigated the selectivity of **S4** for **CEES** by testing the potential interfering agents like alkyl halides (butyl iodide, butyl bromide) and the oxy derivative of mustard (bis-(2chloroethyl) ether, 2-chloroethyl ethyl ether) using the same protocol. No evident fluorescence enhancement was observed (Fig. 2), which indicated that the halogens in simple alkyl halides and the oxy derivative of mustard are not as reactive as that in **CEES**. In addition, when **CEES** was added to the solution of **S4** containing all the above potential interfering agents, fluorescence enhancement appeared, indicating that these species do not interfere with the detection of **CEES**.

It is known that **SM** behaves with high environmental stability and can remain active in neutral soil for as long as several weeks following deployment. With an aim to mimic real-life scenarios for on-site and off-site detection, the sensing protocol was further implemented in spiked soil samples. To determine the presence of **CEES** in soil samples, soil was spiked using a solution of **CEES** in THF. The solvent was evaporated to obtain dry soil spiked with **CEES**. The sample was then divided into two equal portions, one of them was treated with **S4** in DMSO/buffer (1:1 vol) containing five equivalents of Hg<sup>2+</sup> at



Fig. 2 Fluorescence spectra of the solutions of **S4** (5  $\mu$ M) and five equivalents of HgCl<sub>2</sub> treated with 10 equivalents of **CEES**, HCl, bis(2-chloroethyl)ether (**BCEE**), 2-chloroethyl ethyl ether (**CEEE**), butyl iodide (**BI**) and butyl bromide (**BB**), respectively, inset: colorimetric response of Hg<sup>2+</sup>-containing **S4** solution to different analytes.

80 °C. The other was treated with a solution of **S4** in a similar manner without  $Hg^{2+}$ . Meanwhile, the soil sample without spiked **CEES** was also treated with the probe solution containing  $Hg^{2+}$  as a control. As shown in Fig. 3, the solution of the unspiked soil sample exhibited almost no emission, suggesting the absence of **CEES** in the soil. A medium emissive intensity was observed for the probe solution without  $Hg^{2+}$  when treated with the spiked soil sample. While a strong fluorescence emission was observed when the spiked soil sample was treated with **S4** and  $Hg^{2+}$ . Moreover, the measured concentration of **CEES** in the spiked soil sample was consistent with the calibration curve with a 7% error, which indicates that this method can be applied in practice.

In a real-life **SM** assay, besides the sandwich-type construction containing metal ions (Scheme 2), our strategy would likely create compound **S6**, as presented in Scheme 3, by reacting **SM** with two adjacent sulfydryl groups of **S4**. The two formed macrocycles can likewise restrict the rotation of the phenyl



Fig. 3 The fluorescent responses of S4 (1  $\mu$ M) with the CEES-spiked soil sample in the presence of Hg<sup>2+</sup>, the CEES-spiked soil sample in the absence of Hg<sup>2+</sup> and unspiked soil sample, inset: the visual fluorescence color of the CEES-spiked and unspiked soil sample treated with S4 (and Hg<sup>2+</sup>).



Scheme 3 Schematic presentation of the proposed reaction between real-life agent **SM** and compound **S4**.

rings of TPE to cause fluorescence enhancement. In this model, probe **S4** can directly monitor **SM** sensitively with no need of the assistance of metal ions.

#### Stimuli-responsive luminescence switching

As a TPE derivative, the AIE properties of compound **S4** were inevitably explored. We measured the fluorescence change of **S4** in the THF/water mixed system with varied water fractions and found that not only was the fluorescence intensity of the solution enhanced with increasing water fractions, but also the fluorescence maximum of the mixture with 90 vol% water showed a 25 nm blue-shift relative to its pure THF solution (from 503 to 478 nm, Fig. S3 in the ESI†). The aggregation-induced luminous blue-shift phenomenon indicates that **S4** has the potential to be a smart luminescence switching molecule. Based on the previous studies of our group,<sup>55,56</sup> the stimuli-responsive luminescence switching properties of **S4** were therefore systematically investigated.

We first cultured the crystals of S4 through slow diffusion of its THF solution to obtain the colorless crystals B-S4, which emit intense blue fluorescence in 365 nm UV light with a high fluorescence quantum yield  $\Phi_{\rm F}$  of 47%. When fuming or smoking the lamellar blue crystals with CH<sub>2</sub>Cl<sub>2</sub> vapor, we observed that the crystals gradually turned pale green and their emissive wavelength also changed from 467 nm (blue) to 516 nm (green) with a relatively low  $\Phi_{\rm F}$  of 23% (Fig. 4a and b). Grinding the blue crystalline powder of B-S4 in an agate mortar gave a pale green powder, which exhibited a green emission (508 nm) similar to the CH2Cl2-fumed B-S4. Furthermore, the stimuliresponsive conversion from blue to green can be reversed by thermal treatment. Upon heating the CH2Cl2-fumed B-S4 samples (green fluorescence) to 97 °C using a microscopic melting-point apparatus with a heating rate of  $\sim 5 \text{ K min}^{-1}$  under ambient conditions (or directly heating the green sample at 97 °C for approximately 5 s), we observed the solid-state fluorescence switching from green to blue.

In order to understand the stimuli-responsive fluorescence change, we studied the phase characteristics of the relevant samples using powder XRD analysis and DSC measurements. The results indicated that the stimuli-responsive reversible fluorescence switching is derived from the stimuli-responsive reversible phase transformations between the crystal state and the amorphous state (Fig. 4c). In other words, the samples underwent a phase transformation between the crystal state and the amorphous state upon fuming, grinding, or heating, accompanying the fluorescence



Fig. 4 (a) Photographs of the crystalline phase transformation and luminescence change of S4 between blue and green upon fuming, heating, or grinding. (b) Normalized PL spectra of blue-crystal B-S4, CH<sub>2</sub>Cl<sub>2</sub> fumed B-S4, ground B-S4, and heated fumed-B-S4 (heating the green sample obtained by  $CH_2Cl_2$ -fumed blue-crystal B-S4 at 98 °C for 1 min). (c) Powder XRD profiles of the heated green S4 sample,  $CH_2Cl_2$  fumed B-S4, and blue crystal B-S4.

switching. The DSC results were consistent with the experimental phenomenon and we found that the sample of  $CH_2Cl_2$ -fumed **B-S4** displayed an exothermic peak at 97.3 °C (Fig. S5 in the ESI†).

Next, we explored the single-crystal structure of **S4** to understand the solid-state fluorescence switch. The molecular structure and packing of **S4** are shown in Fig. 5. The molecules in



Fig. 5 X-ray crystallographic packing of compound S4. (a) The single molecular structure of S4. (b) Side view of the X-ray crystallographic packing of blue crystal S4, where the layer-by-layer stacking can be clearly observed and illustration of the intermolecular C-H··· $\pi$  interactions in the crystal.

crystal B-S4 were highly twisted with a big torsion angle of the four peripheral biphenyl moieties, respectively (Fig. 5a). The crystal packing showed a typical layer-by-layer stacking characteristic, the neighboring layers were linked by weak C-H··· $\pi$  interactions (Fig. 5b), and no strong intermolecular interactions were found between molecules in the same layer. The highly twisted configuration of S4 in crystals is just attributed to the interlamellar C-H $\cdots$  $\pi$  interactions. The large torsion angle of biphenyl fragments will block intramolecular charge transfer upon excitation and enhance the energy gap between the HOMO and LUMO, ultimately leading to the blue emission of the crystal **B-S4**. In addition, the C-H $\cdots$  $\pi$  interactions also effectively restrict the rotation of the phenyl rings of S4 to result in higher fluorescence quantum yield of the crystals than that of the amorphous powder. Although the C-H··· $\pi$  interactions can facilitate molecular crystallization, they will also result in loose crystal packing due to the formation of a highly twisted molecular configuration. Such a loose crystalline structure can be readily destroyed upon external physical perturbations, which is a prerequisite for a stimuli-responsive luminescence switching molecule.

## Conclusions

In this study, we successfully designed and synthesized a mercaptomethylphenyl-modified TPE compound S4 as a fluorescence probe for SM and an SM simulant (CEES). Compound S4 exhibited almost no emission in dilute solution. However, it emitted strong fluorescence upon reacting with CEES in a hot aqueous solution in the presence of metal ions due to the formation of a sandwich-type complex, which effectively restricted the rotation of the phenyl rings of TPE. Furthermore, this procedure has high sensitivity  $(1.10 \ \mu M)$  and can be applied to the detection of CEES in soil. We anticipate that the developed protocols will be more useful and simple in the detection of real agent SM because there is no need for metal ions. On the other hand, compound S4 also exhibited reversible solid-state luminescence color switching between blue emission (467 nm) in the crystal state and green emission (516 nm) in the amorphous state upon fuming, grinding and heating. The allochroic behavior and mechanism were thoroughly explored by spectroscopy and crystal structure analysis. The results indicate that S4 has potential as a multifunctional material of a "smart" luminophor and an AIE-active fluorescent probe for SM.

## Conflicts of interest

There are no conflicts to declare.

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