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Supersensitive detection of explosives by recyclable AIE luminogen-functionalized mesoporous materials†

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Mesoporous SBA-15 functionalized with aggregation-induced emission (AIE) luminogens serves as an efficient and recyclable fluorescent sensor for the detection of picric acid (PA), with a quenching constant of up to 2.5×10^5 M^{-1} in a water solution, presenting a new model for the supersensitive detection of explosives.

Explosives detection in groundwater or seawater has become an increasingly important and urgent issue in modern society due to its antiterrorism applications in both national security and environmental protection.[1] So far many real time analytical methods have been used for the detection of explosives, such as gas chromatography, ion mobility spectrometry, Raman spectroscopy, fluorescence spectroscopy and so on.[2] Among these techniques, fluorescence sensing of explosives by harnessing organic dyes has drawn much more attention because it is more simple, sensitive, and cost-effective.[3] However, traditional fluorescent dyes often suffer from the aggregation-caused quenching (ACQ) effect when dispersed in poor solvent or incorporated into solid matrix materials, resulting in drastically negative effects on the efficiency and sensitivity of the sensors.[4] Recently, a group of molecules nonemissive in solution have been found to luminesce intensively upon molecular aggregation, showing an exotic aggregation-induced emission (AIE) characteristic.[5] Restriction of intramolecular rotation is proposed as the main cause for this phenomenon.[6] Due to their emission turn-on nature, instead of quenching, AIE-active materials have found tremendous uses such as efficient electroluminescent materials, sensitive chemosenors and bioprobes.[7] In particular, some materials based on AIE luminogens show amplified sensing performance for explosive detection in the aggregate state.[8] For example, AIE-active hyperbranched

conjugated polymers and inorganic–organic hybrid polymers have been reported with good sensing performance.[9] However, most of them can only be dispersed in mixed solutions, thus limiting their explosive detection in water solutions. There is still a large amount of room for improvement in terms of sensitivity and applicability.

Ordered mesoporous materials with a high pore volume and a large surface area have been widely used in various fields such as catalysis, separation, and adsorption.[10] Many of these applications are built on the unique character that mesoporous materials can rapidly associate analytes inside the pores *via* physical diffusion and/or chemical interaction.[11] In this regard, fluorophore-functionalized mesoporous materials can potentially serve as a new generation of fluorescent chemo-/bio-sensor with remarkable sensitivity. From the structural point of view, the pore size generally lies in the working distances of photoinduced electron transfer and/or energy transfer.[12] Photophysically, the analytes in the pores can efficiently interact with the fluorophores in/on the pore wall, leading to a dramatically enhanced sensing performance. However, a high density of conventional fluorophores anchored to the pore wall may lead to the ACQ problem, which has been a hurdle to fluorescence sensing.[13] In this context, the construct of an AIE luminogen-mesoporous material is an ideal choice to serve the sensing purpose.

Recently, we developed a strategy to introduce the AIE luminogen tetraphenylethene (TPE) into mesoporous silica SBA-15 *via* covalent chemical bonding.[14] The TPE-functionalized mesoporous materials were demonstrated to be excellent fluorescence probes for potential applications in drug delivery. In this work, we expand on our previous findings and apply AIE luminogen-functionalized mesoporous materials to the detection of explosives with the nitroaromatic compound 2,4,6-trinitrophenol (picric acid, PA) as a model. Such materials show supersensitive fluorescence quenching to PA in aqueous solution owing to photoinduced electron transfer and/or energy transfer. Importantly, this probe is recyclable after washing with proper solvents, thus proving it to be a promising candidate for practical explosive detection in an environmentally friendly manner.

Amine-modified mesoporous SBA-15 and 1,2-bis[4-(bromomethyl)phenyl]-1,2-diphenylethene (BTPE) were prepared according to the published procedures.[15] Different amounts of BTPE were grafted onto the amine-modified mesoporous

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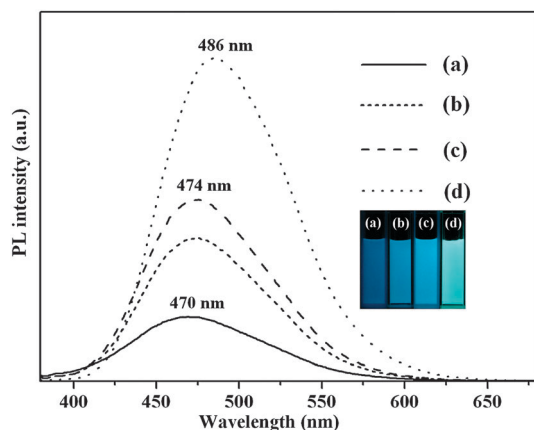
Fig. 1 Fluorescence spectra of (a) SNF-1; (b) SNF-2; (c) SNF-3; (d) SNF-4 in THF–water solutions ($1:9$ v v^{-1}). Excitation wavelength: 360 nm. The photographs were taken under UV light illumination (365 nm).

SBA-15 (SN) *via* chemical bonding according to the procedure described in our previous work[14] with a slight modification (Scheme S1, ESI†). The contents of TPE loaded into the mesoporous materials determined by elemental analysis were 0.031, 0.042, 0.067, and 0.110 mmol g^{-1}, the resulting materials were denoted as SNF-1, -2, -3 and -4, respectively. It was noticed that SNF-4 could not be well dispersed in the water solution owing to its hydrophobic surface property. The emission spectra of the SNFs in the THF–water solutions ($1:9$ v v^{-1}) are shown in Fig. 1, and the photoluminescence (PL) intensity is enhanced with the increasing loading amounts of TPE. In addition, the emission peaks of the SNFs show a red shift from 470 nm to 486 nm. This is probably due to more and more amino groups in the materials that might be protonated[16] as the reaction proceeds. The two-dimensional hexagonal mesostructure of the SNFs was confirmed by transmission electron microscopy (TEM) (Fig. S1, ESI†) and small-angle powder X-ray diffraction (XRD) (Fig. S2, ESI†). The BET surface areas, pore volumes and pore size distributions measured by N$_2$ adsorption–desorption of the SNFs are presented in Table S1 and Fig. S3 (ESI†).

We took commercially available picric acid (PA), as a model for the explosive detection. The fluorescence changes of SNF-1, -2 and -3 in response to different amounts of PA in a water solution have been studied. Their PL intensity decreases significantly with the increasing loading amount of PA (Fig. S4–6, ESI†). Fig. 2A shows the fluorescence emission spectra of SNF-3 with the addition of different amounts of PA in water solution. The PL quenching can be clearly discerned at a [PA] level as low as 1.7 μM or 0.4 ppm. When the PA concentration is increased to 49 μM, it shows almost no luminescence in the fluorescence image. The Stern–Volmer plots of relative PL intensity (I_0/I) of SNF-1, -2, and -3 *versus* PA concentration are shown in Fig. 2B to further quantify the quenching efficiency, where I_0 and I are the PL intensities of the SNFs before and after adding PA, respectively. It is notable that the I_0/I *versus* [PA] plots bend upwards instead of being linear lines, which may be due to the emission of SNFs being quenched by a static quenching or with the participation of a dynamic quenching.[17] The Stern–Volmer curves in the water solution of SNF-1, -2 and -3 can be well fitted to the exponential equations of $I_0/I = 2.8e^{51334[PA]} - 1.8$, $I_0/I = 3.0e^{62784[PA]} - 2.0$ and
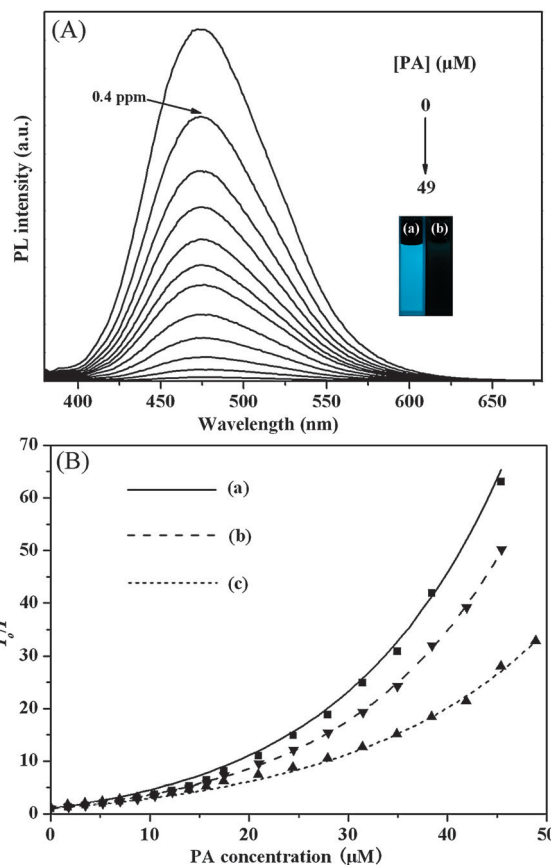

Fig. 2 (A) Fluorescence emission spectra of SNF-3 with the addition of different amounts of PA in water solution. (B) Stern–Volmer plots of I_0/I *versus* [PA] in water (a) SNF-3; (b) SNF-2; (c) SNF-1. The photographs of SNF-3 in the water solution with [PA] of 0 and 49 μM are taken under UV light illumination (365 nm). SNF-3 concentration: 1 mg mL^{-1}; excitation wavelength: 360 nm.

$I_0/I = 4.1e^{62017[PA]} - 3.1$ with quenching constants of about 1.4×10^5 M^{-1}, 1.9×10^5 M^{-1} and 2.5×10^5 M^{-1}, respectively in the low concentration range. Notably, their quenching constants for PA are much higher than that of TPE itself in the THF/water mixture ($1:9$ v v^{-1}) of 3.4×10^4 M^{-1} (Fig. S7, ESI†), as well as those of other linear conjugated polysiloles reported in the literature (2×10^4 M^{-1}).[18]

The fluorescence quenching of SNF can be explained by the photoinduced electron transfer and/or energy transfer quenching mechanism,[19] as shown in Scheme 1. When PA was added to the solution of SNF, it can quickly diffuse into the pores and be effectively adsorbed around fluorophores (TPE) by the formation of a PA–amine complex *via* a acid–base interaction. The close vicinity between TPE and PA greatly facilitates the electron-transfer process and thus increases the chemosensory efficiency. On the other hand, there is an obvious spectral overlap of the absorption spectrum of PA and the emission of SNF ranging from 380–487 nm in the water solution (Fig. S8, ESI†), which allows the energy transfer from the excited state of SNF to the ground state of PA, thus further enhancing the fluorescence quenching efficiency.

The reusability of the as-prepared AIE luminogen-functionalized mesoporous material SNF-3 was further investigated. 10 mg of SNF-3 was dispersed in 10 mL of water and the fluorescence
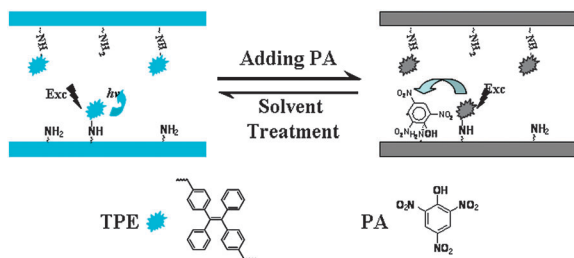
Scheme 1 The reversible fluorescence quenching mechanism of SNF with PA based on photoinduced electron transfer and/or energy transfer.
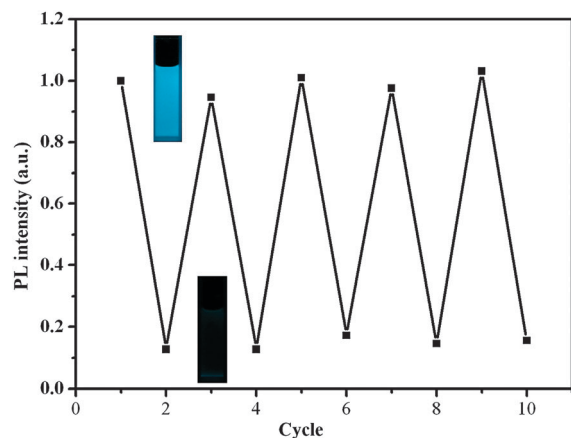

Fig. 3 The quenching and recovery test of SNF-3 in water solution. The inset shows fluorescence images in the water solution with [PA] of 0 and 0.05 mM, which are taken under UV light illumination (365 nm).

emission of the solution was recorded, then 60 μL of PA solution (8.7×10^{-3} M) was added, and the fluorescence emission of the solution was recorded again after stirring for about 1 min. Subsequently, the material was filtrated and washed with acidic THF and alkaline aqueous solution several times. After the material was completely dried, the above experimental procedure was repeated again. After five cycles of quenching and recovery, the PL intensity of the material does not change much compared with the initial state (Fig. 3), indicating that the materials can be used as environmentally friendly detectors for explosives.

In summary, we have developed an AIE luminogen-functionalized mesoporous material as a supersensitive fluorescent sensor for the detection of explosives in a water solution. The high pore volume and large surface area of the material can enhance efficient mass transport and strong interactions with the adsorbed explosive molecules. A very rapid fluorescence quenching response has been observed due to the efficient photoinduced electron transfer and/or energy transfer quenching process within the nanopore. The results show that more TPE loading can lead to higher sensing performance, with the quenching constant and the detection limit being up to 2.5×10^5 M^{-1} and 0.4 ppm, respectively. This demonstrates the advantage of AIE dyes over others. Furthermore, this sensor is recyclable by washing with

proper solvents, suggesting that it is environmentally friendly for future practical applications.

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