Endowing hexaphenylsilole with chemical sensory and biological probing properties by attaching amino pendants to the silolyl core

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Abstract

Hexaphenylsilole (HPS) was functionalized by two amino (A_2) groups, giving a new silole derivative of 1,1-bis[4-(diethylaminomethyl)phenyl]-2,3,4,5-tetraphenylsilole (A_2HPS) that is capable of detecting explosives, biomacromolecules and pH changes. A_2HPS is nonemissive when molecularly dissolved but becomes highly luminescent when aggregated. The emission of its nanoaggregates is quenched by picric acid with a high K_{sv} value ($\sim1.7 \times 10^5$ M^{-1}). A_2HPS can dissolve in acidic aqueous media, due to the transformation of its amino groups to ammonium-salts. The resultant nonemissive aqueous solution is turned on by increasing its pH value or adding protein or DNA.

1. Introduction

Much research effort has been devoted to the development of stimuli-responsive materials owing to their potential applications as chemosensors and bioprobes in environmental protection and biological research [1–10]. Of particular interest are those materials whose light emissions can be enhanced/quenched and/or red/blue-shifted in the presence of analytes because the luminescence-based process enjoys such advantages as high sensitivity, low background noise, and wide dynamic working range [8–13]. Many chromophoric dyes are highly emissive in the solution state but become weakly emissive or even nonluminescent when dispersed in aqueous media or fabricated into thin films due to aggregate formation [14]. This problem must be solved, because luminophores are commonly used in aqueous media for biological and environmental applications and as thin solid films in electronic and optical devices such as organic light-emitting diodes (OLEDs).

We have recently discovered a novel phenomenon of aggregation-induced emission (AIE): a series of nonemissive molecules, such as siloles, pyrans, fulvenes and tetraphenylethylenes, are induced to emit intensely by aggregate formation [15–20]. The AIE effect greatly boosts fluorescence quantum yields (Φ_Fs) of the molecules (up to $\sim$950-fold) [17,21], turning them from faint fluorophores into strong emitters. Utilizing the unique AIE effect, we have fabricated silole-based OLEDs, which luminesce brilliantly (with luminance up to 55 880 cd/m^2) and efficiently (with external quantum efficiency up to 8%) [22]. Siloles have also been used as electron-transport materials in the construction of OLEDs [23]. The possibility of utilizing siloles as sensory materials has, however, been rarely

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explored. In this work, we designed and synthesized a silole derivative by attaching two amino (A_2) groups to the 1,1-positions of hexaphenylsilole (HPS), which is abbreviated as A_2HPS in this Letter. The amino groups confer functionality and hydrophilicity on the molecule, enabling it to work as a chemosensor and bioprobe for the detection of warfare explosives, pH changes, and biological macromolecules.

2. Experimental

The detailed synthetic procedures and characterization data of A_2HPS are given in the Appendix (see Supplementary data). Absorption spectra were recorded on a Milton Roy Spectronic 3000. Emission spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The Φ_F values were measured using the literature procedures [24], using 9,10-diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) as standard. Particle sizes of the A_2HPS nanoaggregates were measured on a Beckman Coulter Delsa 440SX zeta potential analyzer.

3. Results and discussion

A_2HPS was synthesized by desalt coupling (S1): reaction of 1,1-dichlorotetraphenylsilole [21] with *p*-lithiobenzyldiethylamine yielded the HPS derivative, which was thoroughly purified and fully characterized (Supplementary data). A_2HPS is soluble in common organic solvents such as acetonitrile, chloroform, and tetrahydrofuran (THF) but insoluble in water.

When a dilute acetonitrile solution of A_2HPS is excited at 370 nm, almost no luminescence signals are recorded by the spectrofluorometer (Supplementary data, Fig. S1). A_2HPS is thus nonemissive when it is molecularly dissolved in its good solvent. When large amounts of water are added into the solution, the mixtures become highly luminescent. Water is a non-solvent of A_2HPS and the dye molecules

must have aggregated in the aqueous media. The solutions are, however, macroscopically homogenous with no precipitate, suggesting that the aggregates are nano-sized. The Φ_F value is boosted from 0.2% in pure acetonitrile to 28% and 39% in the acetonitrile/water mixtures with water fractions of 90% and 99%, respectively. Evidently, A_2HPS, like its parent HPS, is AIE-active.

The efficient emission of A_2HPS in the aggregate state spurred us to explore its potential application as a chemosensor. Nitroaromatics such as 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), and picric acid (PA) are warfare explosives and are important chemical species to detect in mine fields and munitions remediation sites [25,26]. Oligo(tetraphenylsilole) nanoparticles suspended in THF/water mixtures have been used to detect TNT [27]. Due to the commercial unavailability of DNT and TNT, we used PA as a model explosive in this study.

To a solution of A_2HPS in 1.5 mL of THF, 150 mL of water is rapidly added. The mixture is shaken vigorously, giving an emissive aggregate suspension of A_2HPS in the aqueous mixture with an average particle size of ~270 nm (S2). The emission of the nanoaggregates is weakened when PA is added into the suspension and is almost completely quenched in the presence of a large amount of PA (5 µg/mL; Fig. 1a). The Stern–Volmer plot gives a quenching constant (K_{sv}) of 1.67×10^5 M^{-1} with a R^2 value of 0.9930 in the [PA] range of 0–7.2 µM. The response of HPS, the parent form of A_2HPS, to PA is tested as a control. Similar to the A_2HPS nanoaggregates, the emission of HPS nanoaggregates also becomes weaker in the presence of PA. However, different from A_2HPS, even at a high dose of PA (e.g., 10 µg/mL), the HPS aggregates are still emissive, indicating that A_2HPS is a better chemosensor. The sensitivity of HPS to PA has been enhanced by the amination reaction and may be further improved by appropriate structural modifications.

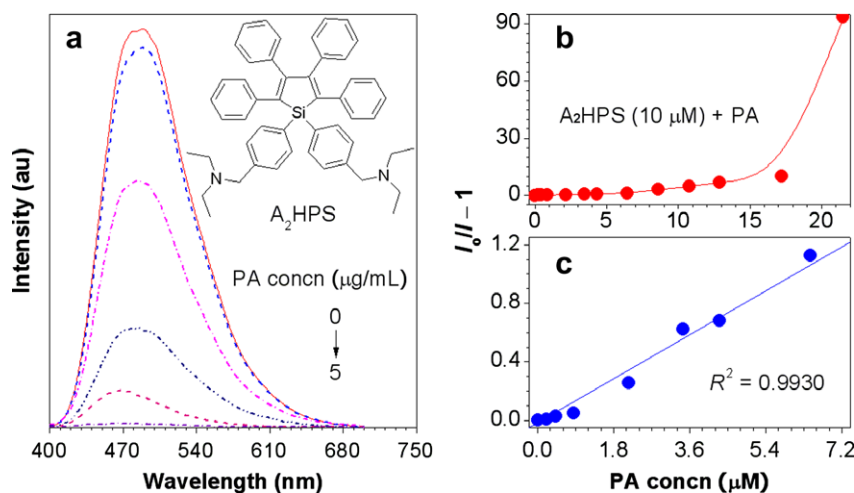As mentioned above, A_2HPS is insoluble in water. However, after adding a small amount of sulfuric acid, A_2HPS

Fig. 1. (a) Emission spectra of A_2HPS in THF/H$_2$O mixtures (1:100 v/v) containing different amounts of PA. (b) Plot of emission intensity vs. PA concentration. (c) Linear region of the ($I_0/I - 1$)–[PA] plot in panel b. Concentration of A_2HPS: 10 µM. Excitation wavelength: 370 nm.

dissolves readily in the acidified water because of the transformation of its tertiary amino groups to ammonium-salts. The aqueous solution is nonluminescent because the salt molecules are genuinely dissolved in the acidic medium. What will happen if the acid is neutralized by a base such as potassium hydroxide? The emission intensity remains unchanged when the pH value is increased from 2 to 5.4 by the addition of aqueous KOH solutions but starts to swiftly increase afterward (Fig. 2). At a pH value of 6.35, the emission is >150-fold stronger than that at pH = 2. This is easy to understand. At a low pH, the dye molecules exist in an ammonium-salt form and are thus dissolved in water. When the pH value exceeds 5.4, the dye molecules are converted back to their amine forms. The decrease in the hydrophilicity induces the molecules to aggregate in the aqueous medium, thus turning their emissions on.

We also examined the possibility of utilizing A_2HPS as a bioprobe for detecting biomacromolecules. The buffer solution (pH = 2) of A_2HPS emits only a faint light at 496 nm (Fig. 3). Upon addition of bovine serum albumin (BSA),

the dye solution becomes emissive. The emission intensity is increased progressively with an increase in BSA concentration and a 52-fold increase in the emission intensity is achieved at a BSA concentration of 500 μg/mL. A_2HPS is thus an excellent 'light-up' biosensor for the protein detection, whose sensitivity is higher than those of the tetraphenylethylene-based bioprobes developed in our previous study [9].

The effect of DNA is even more pronounced. The emission of A_2HPS is turned on when herring sperm (hs) DNA is added to its buffer solution (Fig. 4). The intensity is monotonically increased with an increase in the DNA concentration. At the same concentrations, the $(I/I_0 - 1)$ values are higher than those induced by BSA (cf., Fig. 3), indicating that A_2HPS is a more sensitive probe for DNA detection. The linear range of $I/I_0 - 1$ vs. [hs DNA] plot is as wide as 0–100 μg/mL, with a correlation coefficient as high as 0.997.

Our previous work reveals that the AIE effect is caused by the restriction of intramolecular rotations (RIR) of the
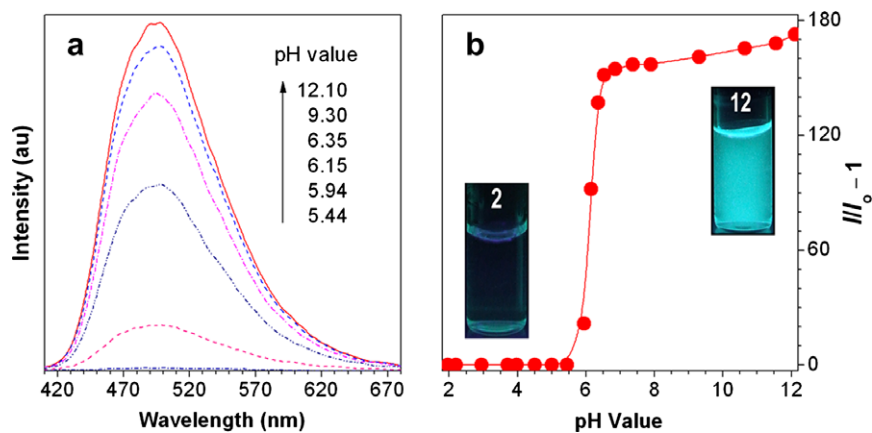

Fig. 2. (a) Emission spectra of A_2HPS in aqueous mixtures at different pH values and (b) plot of $I_0/I - 1$ vs. pH value. Inset: Photographs of A_2HPS solutions at pH 2 and 12 taken under the illumination of a UV lamp. Concentration of A_2HPS: 10 μM. Excitation wavelength: 370 nm.
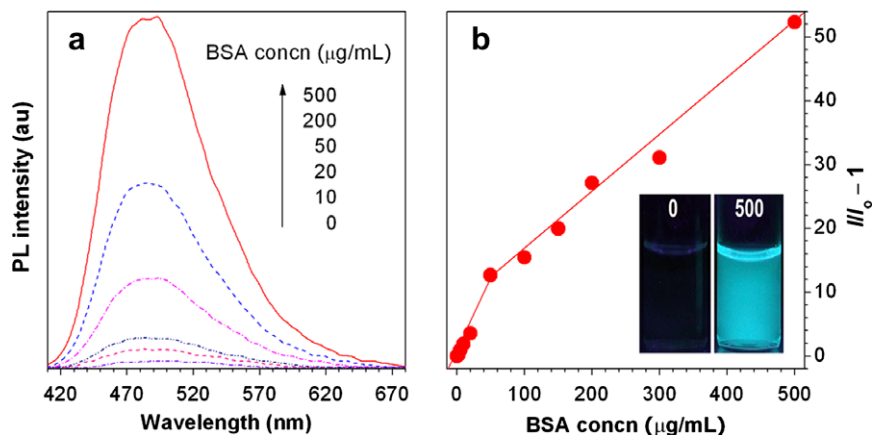

Fig. 3. (a) Emission spectra of A_2HPS in buffer solutions (pH = 2) containing different amounts of BSA and (b) plot of $I_0/I - 1$ vs. BSA concentration. Inset: photographs of A_2HPS solutions without and with 500 μg/mL of BSA taken under illumination of a UV lamp. Concentration of A_2HPS: 10 μM. Excitation wavelength: 370 nm.
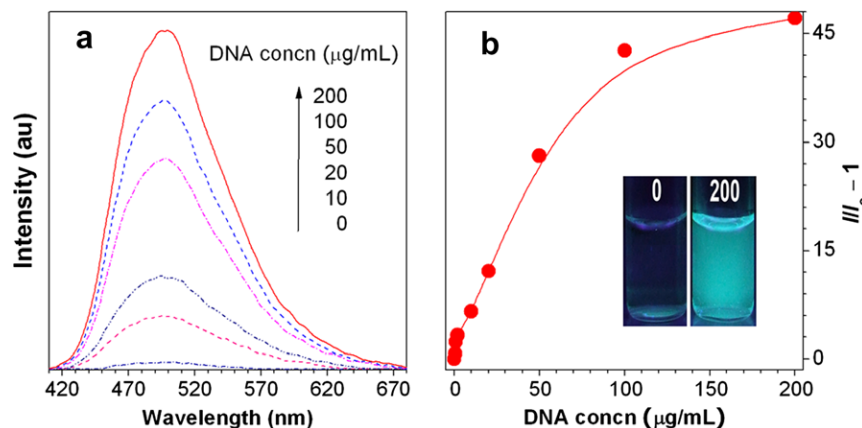
Fig. 4. (a) Emission spectra of A_2HPS in buffer solutions (pH = 2) containing different amounts of hs DNA and (b) plot of $I_0/I - 1$ vs. hs DNA concentration. Inset: photographs of A_2HPS solutions without and with 200 μg/mL of hs DNA taken under illumination of a UV lamp. Concentration of A_2HPS: 10 μM. Excitation wavelength: 370 nm.

peripheral phenyl rings of the propeller-shaped silole molecules in the aggregates [8,28]. The RIR process efficiently blocks the nonradiative channels of the dye molecules, making them highly emissive in the solid state. In the acidic buffer solutions containing the biomacromolecules, the cationic amphiphilic dye molecules may bind to the negatively charged hs DNA and enter into the hydrophobic pockets in the native folding structure of the protein via electrostatic attraction and hydrophobic effect. When docked on the surfaces of the biopolymers and in the cavities of their folding structures, the silole molecules aggregate. This suppresses the intramolecular rotations of the dye molecules, which impedes their nonradiative decays and populates their radiative transitions.

4. Conclusion

In this work, we have successfully synthesized a new silole derivative and explored its utility as a sensory material. We have found that A_2HPS is AIE-active and that the emission of its nanoaggregates is quenched by PA with a high K_{sv} value. Thanks to its tertiary amino groups, which form ammonium-salts in the acidic aqueous media, A_2HPS can function as a chemosensor and bioprobe for the detection of pH changes and biological macromolecules. It is envisioned that further structural modifications by molecular engineering endeavors will generate new AIE-active sensory materials with various emission colors and enhanced detection sensitivities.

Acknowledgements

Appendix A. Supplementary materials

Supplementary data associated with this article can be found, at <doi:10.1016/j.cplett.2007.08.030>.

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