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Axial and peripheral tetraarylethylene-modified subphthalocyanines with distinctive fluorescent performances

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ABSTRACT

Special aromatic structure and unique geometric characteristics make subphthalocyanines possess distinctive electronic structures and physicochemical properties. In this paper, tetraarylethylenes with aggregation-induced emission were introduced to subphthalocyanine macrocycles at the axial direction and the periphery to improve the fluorescence emission properties. Results show that the modification at the two different positions of the subphthalocyanines has different effects on regulating the fluorescence performances. The subphthalocyanine modified axially by tetraphenylethylene shows outstanding fluorescence resonance energy transfer (FRET) phenomenon, and the modification on the periphery of subphthalocyanine is conducive to enhance the fluorescence intensity. These distinctive performances have the potential applications in fluorescence sensor and probe.

Introduction

Subphthalocyanine with a highly polarized π-conjugated system and noncentrosymmetric cone-shaped structure has become a promising building blocks for studying nonlinear optical materials in recent years [1–3]. It has electron-rich feature and strong absorption and emission in the visible light region, so it is expected to be widely applied in the fields of organic semiconductors [4], solar cell [5], sensors and optical information storage media [6,7]. At the same time, it has also been used as an excellent building unit for asymmetric phthalocyanine synthesis and catalytic degradation because of the characteristic of easy ring opening and the twisted structure [8–19]. Moreover, some subphthalocyanine derivatives are considered as promising fluorescent probes, which emit strong near infrared fluorescence in solution. However, with the increasing of the concentration in solution, especially in the solid state and aggregation state, it often shows aggregation-induced quenching (ACQ), which undoubtedly limits its practical application. In order to overcome the ACQ effect, it is an effective protocol to incorporate fluorescent functional groups with aggregation-induced emission (AIE), such as tetraarylethylene, which is one of the outstanding representatives of luminogenic materials with aggregation-induced emission [20–24]. Moreover, there is significant overlap between the emission spectrum of tetraphenylethylene and the excitation spectrum of subphthalocyanine according to the reported literature, which makes them have the possibility of fluorescence resonance energy transfer (FRET) [25]. Recently, a considerable number of controlled AIE materials containing AIE donors and tunable acceptors have been reported, which could produce energy transfer reaction utilizing aggregation-induced emission [26–32]. Inspired by the AIE and FRET mechanism, herein we try to introduce tetraphenylethylene functional groups at the different positions of subphthalocyanine to regulate its fluorescent performances in solid or aggregation state, and the target compounds **SubPc-1** and **SubPc-2** have been obtained by modifying at the axial and peripheral positions of the subphthalocyanines. The structures of the new subphthalocyanines were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectrometry, and the distinctive fluorescent properties were studied in detail.

Results and discussion

*Synthesis of axial tetraphenylethylene-substituted **SubPc-1** and peripheral substituted **SubPc-2***

The synthetic routes of the two target compounds were summarized in scheme 1. Intermediate **SubPc-0** and tetraphenylethylene derivatives **1** and **2** were firstly prepared according to literature procedures [33–35]. With them in hand, **SubPc-1** was then synthesized by the axial substitution reaction between the hydroxyl-tetraphenylethylene **1** and subphthalocyanine **SubPc-0**

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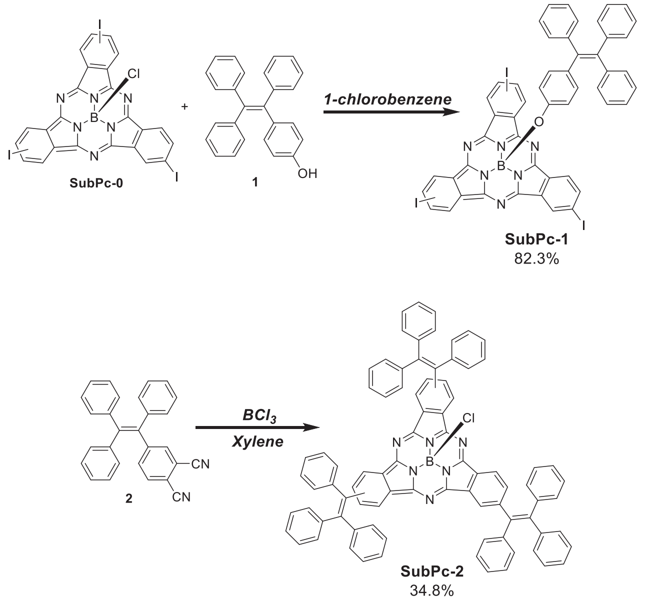

Scheme 1. The synthesis of the tetraarylethylene-modified subphthalocyanines.

in 1-chlorobenzene under high temperature conditions. **SubPc-2** was obtained by the cyclization of tetraphenylethylene-dinitrile derivative **2** using boron trichloride as a template in xylene solvent. The synthesis and characterization of all the intermediates were described in detail in the Supporting Information.

ACQ and AIEE properties of the titled compounds

FRET (fluorescence resonance energy transfer) is a photophysical process in which the excited fluorescence donor transfers its excitation energy to the acceptor through long-distance dipole–dipole interaction. In order to apply the FRET mechanism to the intelligent regulation of fluorescent molecules, we designed and prepared the compound **SubPc-1** by axially linking subphthalocyanine **SubPc-0** with tetraphenylethylene **1** through an oxygen atom, and its fluorescence performances caused by fluorescence resonance energy transfer were further analyzed.

Fig. 1a shows a normalized comparison between the emission spectrum of tetraphenylethylene **1** and the excitation spectrum of subphthalocyanine precursor **SubPc-0**, from which we can find there is obvious overlap. According to the basic principle of FRET, in this case, the emission light generated by the excitation of the tetraphenylethylene can be further used as an excitation light to excite the fluorescence of the subphthalocyanine unit. It means that if the two structural units are connected in a non-conjugated way in a system and the distance is appropriate, the two units may undergo this kind of energy transfer (Fig. 1b).

Because the absorptions of tetraphenylethylenes and subphthalocyanines are often strong at the B band but weak at Q band around 480 nm (Fig. S1), 270 nm and 480 nm light are selected as excitation light to observe and compare the different changes in fluorescence between the unsubstituted subphthalocyanine intermediate **SubPc-0** and the target subphthalocyanine axially substituted with tetraphenylethylene **SubPc-1**. Result shows that substituted **SubPc-1** performs remarkable fluorescence resonance energy transfer as expected.

We first studied the fluorescence emission behavior of reference compound, **SubPc-0**. Fig. 2 shows the changes in fluorescence intensity of the unsubstituted subphthalocyanine precursor **SubPc-0** with different water content in THF solution. Under the excitation of 480 nm light source, the THF solution of subphthalocyanine **SubPc-0** emitted significant fluorescence at around 610 nm, but the fluorescence intensity reduced slowly after adding water-the poor solvent for subphthalocyanine. When the water content was increased to 60%, the fluorescence was greatly quenched. The fluorescence could hardly detect when the water content was increased to 90%. It was a typical aggregation-induced quenching (ACQ) phenomenon.

Then 270 nm was also chosen as excitation wavelength for comparison. It was found that the fluorescence of the subphthalocyanine **SubPc-0** was very weak even in the 100% THF solvent. As the water content increased, the fluorescence intensity of the subphthalocyanine also reduced to almost 0 (Fig. S2**).**

Comparing the fluorescence emission of the unsubstituted subphthalocyanine **SubPc-0** under the excitation of these two different light sources (480 nm and 270 nm), it can be found that in the neat THF solution, the fluorescence emission intensity

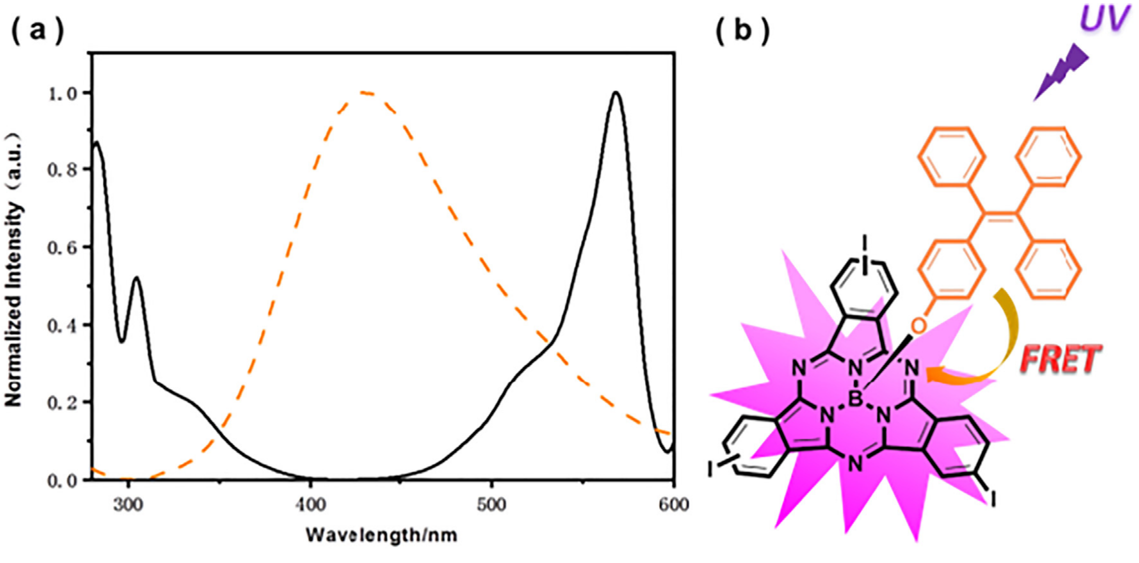

Fig. 1. (a) Overlap between the fluorescence spectrum of tetraphenylethylene 1 (– – –) in the aggregate state and the excitation spectrum of subphthalocyanine SubPc-0 (—) in THF; (b) The schematic diagram of FRET process in **SubPc-1**.

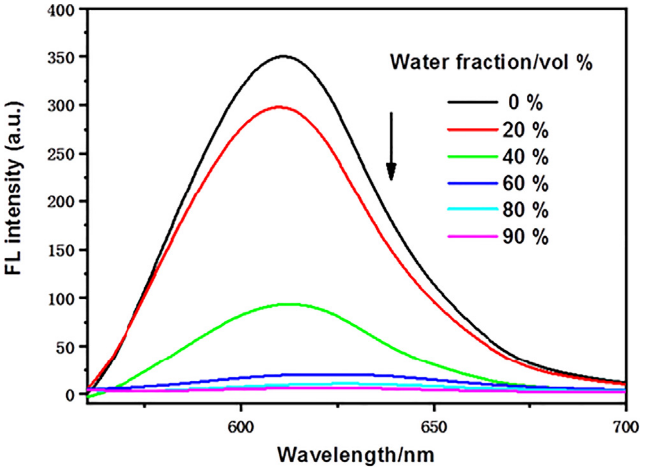

Fig. 2. The fluorescence spectra of SubPc-0/ THF solution (5 × 10^{-6} M) with different water contents (λ_{ex} = 480 nm).

generated by excitation at 480 nm is significantly higher than that generated by excitation at 270 nm. It shows that ultraviolet light (270 nm) as the subphthalocyanine excitation light source is obviously not as efficient as the light source in the visible light region (480 nm), and in comparison, it can even be ignored.

When axial tetraphenylethylene-substituted **SubPc-1** was selected to study the fluorescence emission under the two excitation wavelengths, it showed totally different phenomenon from aforementioned **SubPc-0**. In the THF solution, the fluorescence intensity of the compound **SubPc-1** is weaker than that of **SubPc-0** under the exciting light of 270 nm and 480 nm. It may be because the axial substituent of **SubPc-1** caused the molecular structure looser and increased the chances to dissipate excited state energy through intra-molecular rotation.

However, when adding water to the THF solution, the fluorescence emission of **SubPc-1** (excited by the 270 nm light) continuously enhanced with the increase of water content, as shown in Fig. 3a. This behavior is contrary to that under the excitation of 480 nm light. It showed obviously fluorescence quenching upon excitation with the light of 480 nm when adding water to the THF solution of **SubPc-1** (Fig. 3b).

Judging from the fluorescence quenching behavior of unsubstituted **SubPc-0** both at the excitation of 480 nm and 270 nm, even if the axial substitution in **SubPc-1** might increase the inter-molecular spacing and weaken the degree of aggregation, the fluorescence quenching is unavoidable when excited by 480 nm light, as shown in Fig. 3b. Therefore, the fluorescence enhancement of **SubPc-1** under the excitation of 270 nm light should be attributed to the FRET. It is to say that, with the excitation of 270 nm light, the axial unconjugated tetraphenylethylene unit in **SubPc-1** can emit fluorescence at the range of 300–600 nm, which can be used as the exciting light for subphthalocyanine unit (Fig. 1b). It is well known that tetraphenylethylene shows prominent aggregation-induced luminescence at around 300–600 nm [24,36–38]. With the adding of water content and the formation of the aggregation state, the fluorescence emitted by the tetraphenylethylene unit increases significantly (Fig. S3), which means that the intensity of the efficient exciting light around 480 nm for subphthalocyanine will enhance accordingly. Therefore, compound **SubPc-1** exhibits the distinctive aggregation-induced emission enhancement (AIEE) phenomenon through the action of fluorescence resonance energy transfer (Fig. S4). The excitation spectra of two target compounds with different water contents also confirmed the occurrence of energy transfer (Fig. S5).

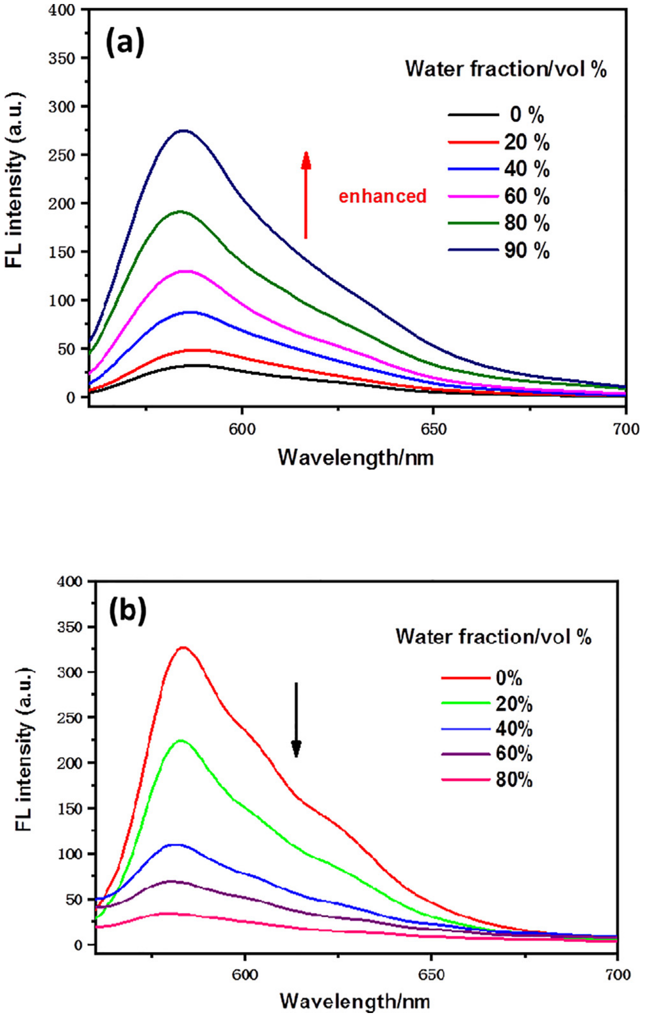

Fig. 3. The fluorescence spectra of SubPc-1 / THF solution (5 × 10^{-6} M) with different water content under 270 nm (a) and 480 nm (b) excitation.

In order to further investigate the effect of the substituent of tetraphenylethylene at different positions, three tetraphenylethylenes were bonded to the peripheral of the subphthalocyanine to obtain **SubPc-2**. Its fluorescent behavior was also examined and compared with unsubstituted **SubPc-0**.

Results show that the fluorescence behavior of **SubPc-2** is consistent with that of **SubPc-0** in the H_2O-THF mixed solution. It also shows obvious fluorescence quenching with the increase of water content (Fig. 4). However, in the neat THF solution (5 × 10^{-6} M), it is found that the peripherally substituted **SubPc-2** has a significant increase in fluorescence intensity compared with **SubPc-0**. Through the comparative study of the ultraviolet absorption spectra (Fig. S6), it is found that the absorption peak of the compound **SubPc-2** in the ultraviolet region has significantly enhanced compared with that of the **SubPc-0** and the overall red shift phenomenon has occurred, which indicates that the tetraphenylethylene units modified on the periphery of **SubPc-2** have further increased the degree of π-π conjugation. The possible reason for this fluorescence enhancement phenomenon may be due to the increase in molecular conjugation, which increases the probability of $\pi^* \rightarrow \pi$ transition between the lowest excited singlet state (S1) and the ground state (S0). This experimental result shows that the modification with tetraphenylethylene on the periphery of the subphthalocyanine can enhance efficiently the fluorescence

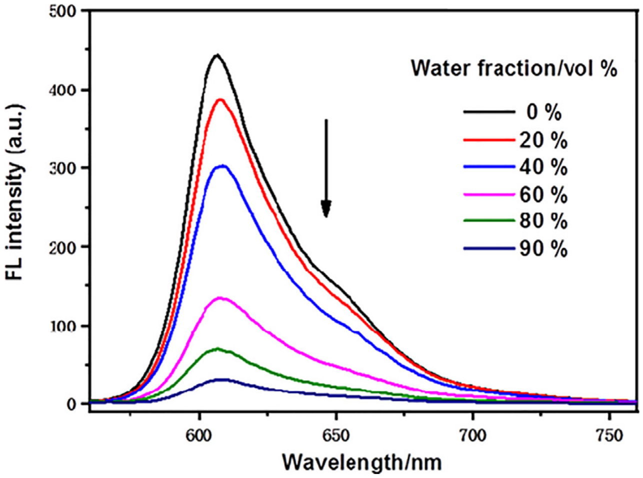

Fig. 4. The fluorescence spectra of SubPc-2/THF solution (5×10^{-6} M) with different water content under the exciting light of 480 nm.

intensity of the subphthalocyanine molecule, but cannot overcome the problem of fluorescence quenching in the aggregate state.

*The fluorescence quantum yields of **SubPc-1** and **SubPc-2***

In order to further quantitatively compare the fluorescence changes before and after modification with tetraphenylethylenes on the periphery and axial direction of the subphthalocyanines. The ethanol solutions of **SubPc-0**, **SubPc-1** and **SubPc-2** were measured for fluorescence quantum yields with rhodamine 6G as a reference. The following Eq. (1) was used to calculate the fluorescence quantum yield [39].

$$\varnothing F = \varnothing F(\mathrm{Std}) \frac{F \cdot A_{Std} \cdot n^2}{F_{Std} \cdot A \cdot {n_{Std}}^2} \tag{1}$$

Among them, $\varnothing F(\mathrm{Std})$ is the standard fluorescence quantum yield of the reference substance, and the reference substance here is rhodamine 6G ($\varnothing F = 0.94$ in ethanol [40]). F and F_{Std} represent the integrated areas under the fluorescence emission curves of the samples and the reference substance, respectively. A and A_{Std} are the corresponding absorbance of the sample and the reference substance at their respective excitation wavelengths. n^2 and n^2_{Std} are the refractive index of the sample and the reference substance in the solvent respectively. In order to simplify the calculation, we adjusted the concentrations to make the absorption curves of three target products and rhodamine 6G intersect at about 488 nm, and used it as the excitation wavelength for the measurement of fluorescence quantum yield.

The maximum absorption wavelength and maximum emission wavelength of **SubPc-0** in ethanol solution are 569 nm and 584 nm, respectively, and its fluorescence quantum yield is 2.2%, as shown in Table 1. After it was modified with tetraphenylethylene in the axial direction, the degree of molecular conjugation did not change. Therefore, the maximum absorption wavelength and fluorescence maximum emission wavelength of the compound **SubPc-1** had little difference from that of **SubPc-0**. However, the fluorescence emission of **SubPc-1** reduced, and the quantum yield was only 0.6%. The reason might be that the spatial structure of the subphthalocyanine after the axial substitution became looser, and the degree of freedom of the molecule increased, so that the energy of the excited state could be released through the movement of the molecule to undergo a non-radiative transition back to the ground state. When the periphery of **SubPc-0** is modified with tetraphenylethylenes, **SubPc-2** has an obvious red shift in the maximum absorption and emission wavelengths due to the increase in molecular conjugation and electron cloud density, and the fluorescence quantum yield reaches 13.7%, which shows significant enhancement. These data indicate that the modification of AIE units such as tetraphenylethene on the different position of subphthalocyanine is closely related to their photophysical properties.

Table 1
Photophysical properties of SubPc-0, SubPc-1 and SubPc-2 in ethanol solution (T: 25 °C).

Compound	λ_{abs}/nm	λem max/nm	Φ_f (%)
SubPc-0	569	584	2.2
SubPc-1	568	582	0.6
SubPc-2	589	615	13.7

(λ_{abs}: absorption wavelength; λ_{em} max: maximum emission wavelength; Φ_f : fluorescence quantum yield).

Conclusions

In this paper, two novel subphthalocyanines, **SubPc-1** and **SubPc-2**, were constructed by modifying tetraarylethylenes at the axial and peripheral positions, respectively. Their fluorescent performances at different conditions were focused on. The experimental results showed that the subphthalocyanine **SubPc-1** with the axial substituent of aggregation-induced emission (AIE) exhibited typical aggregation-induced quenching (ACQ) phenomenon when excited at 480 nm, but performed significant aggregation-induced emission enhancement (AIEE) when the excitation wavelength changed to the excitation wavelength of the tetraarylethylene unit (270 nm), which was attributed to the fluorescence resonance energy transfer. In addition, the peripherally modified subphthalocyanine **SubPc-2** did not exhibit any aggregation-induced-emission properties, but the fluorescence intensity of the whole molecule enhanced significantly in neat THF solution. Such new subphthalocyanine molecules are expected to be used in the fluorescence probe and fluorescence detection materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2021.153096.

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