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View Article Online View Journal | View Issue Synthesis and application of reversible fluorescent photochromic molecules based on

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Tetraphenylethylene-naphthopyran (TPE-NP) and tetraphenylethylene-spirooxazine (TPE-SO) with conjugated photochromic groups and fluorophores were designed and synthesized. Both of them exhibit the

comprehensive effects of aggregation-induced emission (AIE) and photochromism while different photochromic groups lead to a unique photochromic rate and fluorescence intensity. Among them, TPE-NP

has significant photochromic and fluorescence effects with good stability. Therefore, it could be used as an

anti-counterfeiting ink and is expected to be used in fluorescence switches in the future.

tetraphenylethylene and photochromic groups[†]

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Introduction

Since the first discovery of photochromism¹ in 1867 by Fritsche,² great progress has been made in the research of organic and inorganic photochromic materials. Research on various organic photochromic systems such as diarylethene,³ spiropyran,⁴ spirooxazine,⁴ fulgide,⁵ and azobenzene⁶ gradually emerged. Naphthopyrans (NPs) are well known as an important class of organic photochromic compound because of their ease of preparation, high coloration, rapid color reversibility and good fatigue resistance.^{7–9} Spirooxazine compounds have special photochromic properties; in particular, their two isomers have outstanding fatigue resistance.

In most research regarding luminescence as a detection or readout signal, the photochromism is investigated in solution.¹⁰ However, optoelectronic applications of photo-switches often require the photoswitch to be in a solid or aggregated state.¹¹ The primary challenge in solid-state photoswitches concerns tight molecular packing in aggregated molecules, which will impede the *cis-trans* transformation.¹² Thus, providing a large free volume in the solid state is vital to promote effective photoswitching. Recently, tetraphenyl-ethylene (TPE)¹³ and its derivatives with a twisted π -conjugated structure have attracted substantial research interest. It's highly 3D structure avoids strong intermolecular π - π stacking; this particular phenomenon is aggregation-induced

emission (AIE).^{14–17} TPE-based materials are easy to synthesize and modify, and exhibit high AIE effect values (the extent of the emission enhancement) and excellent solid-state fluorescence.

Therefore, the combination of photochromic molecules with TPE is envisioned to achieve a new type of multi-responsive luminescent material. Qi *et al.* reported multicolored tunable emission anti-counterfeiting inks and super-resolution imaging agents by blending spiropyran-functionalized with a distyryl-anthracene derivative.¹² Li *et al.* conjugated dithienylethene and tetraphenylethene as a novel switchable fluorescent material, which has potential for utilization in localization-based super-resolution imaging as an alternative optical nanoimaging agent.¹⁸ Therefore, it can be imagined that the conjugation of TPE with naphthopyran or spirooxazine by a covalent bond will enhance their performance and extend their application fields.

Inspired by the above design strategy, we synthesized two new molecules (TPE-NP and TPE-SO) through covalent connection (Scheme 1). TPE-NP and TPE-SO show distinct photochromic and AIE properties. These molecules not only can emit bright fluorescence, but also demonstrate reversible solid-state luminescence switching under alternating UV light and visible light treatment.

Results and discussion

Design and synthesis

TPE-NP and TPE-SO were synthesized by a series of chemical reactions according to Scheme 1. The detailed synthetic procedure and characterization are described in the Experimental section and $ESI.^{\dagger}$

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Aggregation-induced emission properties

TPE-NP and TPE-SO are two potential fluorophores because of the large Stokes shift (TPE-NP: λ_{abs} = 360 nm, λ_{em} = 480 nm. TPE-SO: λ_{abs} = 350 nm, λ_{em} = 475 nm). The AIE properties of TPE-NP and TPE-SO were measured in their THF/water solution and shown in Fig. 1. When the water fraction (f_w) is lower than 70%, the PL curve is almost parallel to the horizontal coordinate, which indicated that there is no emission in pure THF solution. However, when a large amount (>70%) of water (a poor solvent) was added to its THF solution, the peak of TPE-NP at 480 nm and the peak of TPE-SO at 475 nm can be clearly found. The mechanism for this AIE phenomenon has been thoroughly studied and the increased fluorescence intensity attributed to the formation of molecular aggregates, in which the intramolecular free rotation has been blocked. In the meantime, the fluorescence intensity of TPE-SO was significantly higher than that of TPE-NP by comparing the fluorescence spectra and fluorescence images of the two molecules.

Photochromic properties in the solution state

Similar to the reported spirooxazine and naphthopyran molecular switches, their isomerization can be triggered by



Fig. 1 (a and b) Fluorescent images of TPE-NP and TPE-SO, respectively, in different water fraction (f_w) mixtures under 365 nm UV illumination. (c and d) Fluorescence spectra of TPE-NP and TPE-SO (10^{-5} M), respectively, in THF/H₂O mixtures with different f_w values.

UV light. Therefore, the isomerizations of TPE-NP and TPE-SO in dichloromethane were measured. It was easy to find from the UV/vis absorption of TPE-NP and TPE-SO in Fig. 2, that the two compounds can undergo reversible photoisomerization between their unconjugated closed form (CF) isomer and conjugated open form (OF) isomer under the irradiation of a 365 nm ultraviolet lamp. The absorption peak at 362 nm for TPE-NP-CF (tetraphenylethylene-naphthopyran-closed form) gradually decreased and a new absorption peak at 490 nm assigned to the OF appeared and increased with exposure duration (Fig. 2a). It is clearly seen that the absorption peak at 292 nm and 354 nm for TPE-SO-CF gradually decreased and a new absorption peak at 466 nm assigned to the OF appeared and increased under continuous UV irradiation (Fig. 2b). The OF absorption peak of TPE-NP (484 nm) has an obvious redshift compared with the OF absorption peak of TPE-SO (466 nm), which implies that the TPE-NP-OF has a better π -conjugated effect than that of TPE-SO-OF (tetraphenylethylene-spirooxazineopen form). Interestingly, TPE-NP can much more easily undergo photoisomerism compared to TPE-SO, because TPE-NP can achieve the maximum ring-open ratio after 10 s UV irradiation, whereas TPE-SO needs nearly 24 min. Thus, the different linking groups between NP and SO will lead to the different photochromic behaviors and capacity. The reason may be that the worse π -conjugation between TPE and spirooxazine-OF in TPE-SO-OF (tetraphenylethylene-naphthopyran-open form) reduces the



Fig. 2 Time-dependent UV/vis absorption spectra of (a) TPE-NP and (b) TPE-SO (10^{-5} M) in dichloromethane recorded under 365 nm handheld ultraviolet lamp irradiation.





stability of the SO moiety by aggregating the positive charge of the nitrogen cation of indoline and makes photochromism more difficult.¹⁹ In contrast, TPE-NP-OF has good stability and is prone to photochromism.

Scheme 2 illustrates the photochromism of TPE-NP and the mechanisms of solution quenching and enhanced solid state fluorescence. Non-radiative decay occurs due to the free internal motions of molecules in solution, resulting in quenching and non-fluorescence. Conversely, the solid state results in restriction of intramolecular rotations (RIR) of the molecules, and subsequent enhanced emission.²⁰ After transformation into the opened form, the new peak at around 480 nm in the absorption spectra overlaps with the TPE emission and energy transfer occurs, which leads to the quenching of the emission. This process can explain the "on-state" and "off-state" phenomenon in the solid state of TPE-NP-OF and TPE-NP-CF. Photos of the two isomeric forms of the solid state (Fig. 3) show changes in color and fluorescence in the open and closed forms. TPE-NP-CF appears yellow-green (Fig. 3a) under visible light. After 40 s UV (365 nm) irradiation, TPE-NP-CF isomerized to TPE-NP-OF, which is yellow-brown (Fig. 3b) under visible light and bright blue-white (Fig. 3c) under a 365 nm hand-held ultraviolet lamp.

Photoswitchable patterns

We applied TPE-NP as an anti-counterfeiting ink due to its good photochromic properties. Firstly, the TLC plate was dipped into TPE-NP solution, and after drying in the surrounding environment, nothing could be found on the TLC paper under visible light (Fig. 4a), whereas it showed blue-green fluorescence under 365 nm hand-held UV lamp irradiation (Fig. 4b). Next, the TLC paper was covered by a plate with a hollow out "USTB", and then the hollowed out part was exposed to UV light (365 nm) for 40 s. A pale brown pattern could be observed on the TLC paper



Fig. 3 Photos of TPE-NP-CF and TPE-NP-OF powders in visible and under UV light (365 nm) against a white background. (a) Photograph under visible light for TPE-NP-CF, (b) photograph under visible light for TPE-NP-OF, and (c) fluorescence image of TPE-NP-CF and TPE-NP-OF.



Fig. 4 Illustration of TPE-NP as an anti-counterfeiting ink on a TLC plate printed with "USTB". (a) The unprinted image taken under visible light, and (b) its fluorescence image. (c) The printed image taken under visible light after 40 s UV irradiation, and (d) its fluorescence image.

(Fig. 4c) under visible light, and this effect was mainly caused by photochromism. It could also be found that the hollowed out part was black (Fig. 4d) but the other part hadn't changed under UV light, as in the case described in Fig. 4c, and all these phenomena could be explained by Scheme 2. In addition, these changes can easily be observed with the naked eye, and the printed pattern could be restored to its original state under ambient conditions for 20 s. This color reversibility could be repeated many times. What's more, the corresponding fluorescence image showed clearer signals than the visual photo of TPE-NP in this process. The good solid-state photochromic properties of TPE-NP make it a promising anti-counterfeiting ink with either visual color or emission changes.

Conclusions

In summary, we report a photochromic naphthopyranfunctionalized tetraphenylethylene derivative, TPE-NP, and spirooxazine-functionalized tetraphenylethylene derivative, TPE-SO. Both of them could photoswitch in absorption and fluorescence under alternating UV/visible treatment. A comparison of the two molecules indicates that the different linking groups between TPE and the photochromic groups will result in different π -conjugate systems, which eventually produce different photochromic and fluorescence properties. This reversible fluorescence switch for TPE-NP and TPE-SO may have great potential for applications such as anti-counterfeiting inks and fluorescence sensors.

Experimental section

Materials

Dimethylacetamide (DMAc) were distilled under vacuum from phosphorus pentoxide. Pyridinium 4-toluenesulfonate (PPTS), 6-bromo-2-naphthol, bromotriphenylethylene, 1,1-diphenyl-2propyne-1-ol trimethyl orthoformate, 4-vinylphenylboronic acid 6-bromo-2-naphthol, indoline, tetrabutylammonium bromide (TBAB), palladium acetate ($Pd(OAc)_2$) and tetrakis(triphenylphosphine) palladium $Pd(PPh_3)_4$ were purchased from Energy Chemical, and all the other chemicals were purchased from BeiJing Chemical Works and used as received without further purification.

Instruments

¹H NMR spectra were recorded on a 500 MHz BRAKER AVANCE III HD NMR spectrometer, by using CDCl₃ as the solvent and tetramethylsilane (TMS) as an internal standard (d = 0.00 ppm). MALDI-TOF MS was performed by an Agilent 1290-microTOF Q II. UV/vis spectra were recorded in a quartz cuvette on a JASCO V-570 spectrophotometer. Fluorescence spectra were recorded using a Shimadzu RF-5301 PC spectrometer.

Synthesis and characterization

Tetraphenylethene-naphthopyran (TPE-NP) and tetraphenylethenedpirooxazine (TPE-SO) were prepared according to the synthetic routes shown in Scheme 1. Compounds **1–4** were synthesized according to the literature method.^{21–24}

8-Bromo-3,3-diphenyl-3*H*-benzo[*f*]chromene (1). 6-Bromo-2naphthol (1 mmol) and 1,1-diphenyl-2-propyne-1-ol (1.1 mmol) in the presence of PPTS (0.05 mmol) and trimethyl orthoformate (2 mmol) in 1,2-dichloroethane (5 mL) were refluxed for 3.5 h. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with CH_2Cl_2/n -hexane (v/v = 1:2) as an eluent to give a faint white powder with 90% yield. ¹H NMR (500 MHz, CDCl₃, TMS): δ = 7.87–7.88(d, 1H), 7.82–7.84(d, 1H), 7.57–7.58(d, 1H), 7.53– 7.54(dd, 1H), 7.50–7.52(m, 4H), 7.34–7.37(m, 4H), 7.29– 7.31(m, 1H), 7.28–7.29(m, 1H), 7.23–7.26(t, 2H), 6.31–6.32(d, 1H). HRMS (MALDI-TOF MS): m/z (C₂₅H₁₇BrO) calculated: 412.1, found: 412.2.

4-(1,2,2-Triphenylvinyl)benzaldehyde (2). Bromotriphenylethylene (2.01 g, 6 mmol) and 4-vinylphenylboronic acid (1.33 g, 9 mmol) were dissolved in a mixture of toluene (40 mL), TBAB (0.19 g, 0.6 mmol) and 1.2 M potassium carbonate aqueous solution (10 mL). The mixture was stirred at room temperature for 0.5 h under N₂ gas followed by adding Pd(PPh₃)₄ (60 mg, 5.3×10^{-3} mmol) and then heated to 90 °C for 24 h. After that the mixture was poured into water and extracted three times with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After moving the solvent under reduced pressure, the residue was chromatographed on a silica gel column with CH₂Cl₂/*n*-hexane (v/v = 1:2) as an eluent to give a faint white powder with 90% yield. ¹H NMR (500 MHz, CDCl₃, TMS): δ = 7.17–7.18(d, 2H), 7.11–7.14(m, 9H), 7.04–7.08(m, 6H), 6.99–7.01(d, 2H), 6.61–6.67(dd, 1H), 5.67–5.71(d, 1H), 5.19–5.22(d, 1H), 5.19–5.22(d, 1H). HRMS (MALDI-TOF MS): *m*/*z* (C₂₈H₂₂) calculated: 358.2, found: 358.3.

6-Bromo-1-nitro naphthalen-2-ol (3). 6-Bromo-2-naphthol (0.50 g, 2.24 mmol), NaOH (90 mg, 2.24 mmol) in water (10 mL), NaNO₂ (0.16 g, 2.24 mmol), and H_2SO_4 (0.16 mL, 2.91 mmol) were reacted at 0 °C for 1 h. A solid precipitate was obtained and column chromatography (SiO₂; EtOAc:hexane, 1:20) gave 5 g as a yellow solid (0.41 g, 73%). The relevant characterization is consistent with the literature.

8'-Bromo-1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-*b*]-[1,4]oxazine] (4). Indoline (0.940 mL, 5.31 mmol) and 6-bromo-1-nitro naphthalen-2-ol (1.323 g, 5.29 mmol) in ACN (50 mL). The solution was refluxed for 24 h before being concentrated *in vacuo*. Purification by column chromatography (95:5, hexanes: EtOAc) afforded the desired spiropyran as a yellow amorphous solid (0.818 g, 47%). ¹H NMR (500 MHz, CDCl₃, TMS): δ = 8.45–8.47(d, 1H), 7.92(d, 1H), 7.77(s, 1H), 7.66– 7.67(dd, 1H), 7.58–7.60(d, 1H), 7.25–7.28(m, 1H), 7.10–7.12(d, 1H), 7.05–7.06(d,1H), 6.92–6.94(t, 1H), 6.60–6.61(d, 1H), 2.78(s, 3H), 1.38(s, 3H), 1.37(s, 3H). HRMS (MALDI-TOF MS): *m/z* (C₂₂H₁₉BrN₂O) calculated: 406.1, found: 406.1.

Synthesis of TPE-SO

1-(4-Vinylphenyl)-l,2,2-triphenylethylene (1 mmol, 0.36 g), 8'bromo-1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazine] $(1 \text{ mmol}, 0.35 \text{ g}), K_3 PO_4$ (3 mmol, 0.65 g), and Pd(OAc)₂ as the catalyst (200 mg) were dissolved in dry DMAc (5 mL). The reaction mixture was heated to 110 °C in an oil bath and stirred for 24 h under a N₂ atmosphere. After being cooled to room temperature, the reaction mixture was poured into water and filtered to get the precipitated solid. The product was chromatographed on a silica gel column with petroleum ether/ethyl acetate (50:1 v/v) to give TPE-SO as a yellow solid (0.13 g, 20%). ¹H NMR (500 MHz, CDCl₃, TMS): $\delta = 8.53-8.56(d, 1H)$, 7.95(d, 1H), 7.88-7.91(dd, 1H), 7.77-7.80(d, 1H), 7.69-7.71(d, 1H), 7.31-7.33(d, 2H), 7.21(s, 1H), 7.20(s,1H), 7.02-7.16(m, 20H), 6.84-6.88(t, 3H), 6.70-6.72(d, 1H), 4.56(s, 1H), 2.90(s, 3H), 1.64(s, 3H), 1.03(s, 3H). HRMS (MALDI-TOF MS): m/z (C₅₀H₄₀N₂O) calculated: 684.3, found: 683.3 [M - 1].

Synthesis of TPE-NP

1-(4-Vinylphenyl)-l,2,2-triphenylethylene (1 mmol, 0.36 g), 8-bromo-3,3-diphenyl-3*H*-benzo[*f*]chromene (1 mmol, 0.35 g), K_3PO_4 (3 mmol, 0.65 g), and Pd(OAc)₂ as the catalyst (200 mg) were dissolved in dry DMAc (5 mL). The reaction mixture was heated to 110 °C in an oil bath and stirred for 24 h under a N_2 atmosphere. After being cooled to room temperature, the reaction mixture was poured into water and filtered to get the precipitated solid. The product was chromatographed on a silica gel column with petroleum ether/ethyl acetate (50:1 v/v) to give TPE-NP as a yellow solid (0.25 g, 39%). ¹H NMR (500 MHz, CDCl₃, TMS): δ = 7.98-8.00(d, 1H), 7.92(d, 1H), 7.75-7.77(d, 1H), 7.66-7.68(d, 1H), 7.59-7.60(d, 1H), 7.36-7.39(t, 3H), 7.29-7.33(m, 8H), 7.21-7.24(d, 1H), 7.05-7.16(m, 17H), 6.76(s, 1H), 5.71(s, 1H). HRMS (MALDI-TOF MS): *m/z* (C₅₃H₃₈O) calculated: 690.3, found: 689.8.

Conflicts of interest

There are no conflicts to declare.

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