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# An aggregation-induced emission luminophore with multi-stimuli single- and two-photon fluorescence switching and large two-photon absorption cross section†

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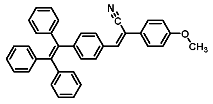
**A novel aggregation- and crystallization-induced emission luminophore (ENPOMe) containing tetraphenylethene and acrylonitrile moieties with high fluorescence efficiency ($\Phi_F$ of up to 0.85) has been easily synthesized. ENPOMe has an exceptionally large two-photon absorption cross section ($\sigma$) of 5548 GM, and exhibits striking multi-stimuli-responsive single- and two-photon fluorescence switching with excellent reversibility in the solid state.**



**Scheme 1** Chemical structure of ENPOMe.

Stimuli-responsive fluorescence switching, which can be achieved by controlling the structure of molecular assemblies with external stimuli, has attracted considerable interest, because of its significant applications in the fields of memory devices, photomodulation, information displays, and sensors.[1] However, like many common organic luminescent materials, fluorescence-switching dyes exhibit fluorescence quenching at high concentrations or in the solid state. This phenomenon is notoriously known as aggregation-caused quenching (ACQ).[2]

Several anti-ACQ materials were reported by Tang *et al.*[3] and Park *et al.*[4] in 2001 and 2002, respectively. These substances are called aggregation-induced emission (AIE) or crystallization-induced emission enhancement (CIEE) compounds.[5] Recently, several AIE compounds were reported to have fluorescence switching properties.[6] Fluorescence-switching materials with two-photon absorption (TPA) are more attractive than conventional single-photon absorption switching dyes because of their unique advantages. These advantages include highly spatially confined excitation, intrinsic three-dimensional (3-D) resolution, and negligible background fluorescence. These properties are extremely important in numerous applications such as 3-D optical data storage, sensing, and imaging.[7] However, creating such stimuli-responsive fluorescence-switching materials, which combine excellent reversibility, high two-photon fluorescence (TPF), and large TPA cross section, is challenging.

In this study, we try to develop a novel two-photon excited fluorescence-switching compound with AIE and CIEE properties (ENPOMe, Scheme 1). Since molecules with a D–A–D structure will have higher $\sigma$, an electron acceptor (cyano group) was introduced into the molecule between tetraphenylethene and methylphenate.[8] Furthermore, aromatic-substituted acrylonitrile derivatives[4,9] and tetraphenylethene derivatives[10] have been proved to be AIE active, respectively. We believe the molecule containing tetraphenylethene and aromatic-substituted acrylonitrile moieties will possess strong TPF emission.

Aggregation-induced emission: the ENPOMe molecules were genuinely dissolved in tetrahydrofuran (THF) and almost no signal was detected from the dilute ENPOMe solution in THF, as shown in Fig. S1 (ESI†). Fluorescence intensity remained very low in aqueous mixtures with water fraction less than 80%, but increased swiftly with the water fraction above 80%. Compared with the pure THF dilute solution, the fluorescence intensity enhancement of the water–THF mixture with 98% water fraction reached 192-fold. UV-visible spectra of ENPOMe (Fig. S2, ESI†) corresponded well to the fluorescence spectral changes and suggested nanoparticle formation in the mixture solvent. The results indicate that the emission intensity of ENPOMe is enhanced by nanoaggregation and thus ENPOMe is AIE-active.

TPA properties: the quadratic dependence of fluorescence intensity *versus* incident laser power was checked to investigate

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whether the ENPOMe luminophore has TPA properties. The results are shown in Fig. S3 (ESI†). The experimental regression coefficient of ENPOMe was estimated to be about 2.03, indicating that no saturation occurred in the experimental laser power. Thus, fluorescence arose from a TPA process.[11] ENPOMe has an exceptionally large $\sigma$ of 5548 GM when excited by a laser pulse at 740 nm. This $\sigma$ is larger than most of the representative materials.[12] The large $\sigma$ of ENPOMe is attributed to the intermolecular charge transfer from the tetraphenylethene and methylphenate to the electron-drawing cyano group. Fig. S4 (ESI†) shows the quantum mechanical simulation carried out by Gaussian 03W with B3LYP/6-31G(d).[13] Most of the electrons of tetraphenylethene and methylphenate transferred to the cyano group at the lowest unoccupied molecular orbital (LUMO), further confirming the aforementioned hypothesis. Fig. S5 (ESI†) shows the TPF emission spectra of the dilute solutions of ENPOMe in water–THF mixtures with different water fractions, which are similar to SPF. Most TPA dyes are hydrophobic and suffer from the ACQ when dispersed in water. Thus, the unique TPF-AIE properties, as well as the large $\sigma$, endow ENPOMe with attractive advantages in practical applications such as biological imaging, especially for two-photon microscopy.[7c,14]

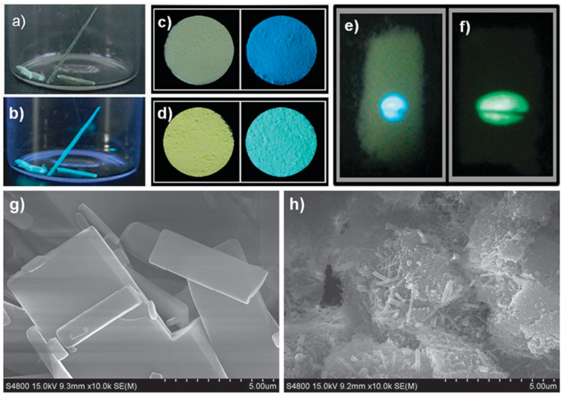

**Fig. 1** ENPOMe crystals obtained from methanol/acetonitrile under (a) ambient light and (b) UV light with an excitation of 365 nm; (c) as-synthesized sample of ENPOMe under ambient light (left) and UV light with an excitation of 365 nm (right); (d) ground sample of ENPOMe under ambient light (left) and UV light with an excitation of 365 nm (right); (e) as-synthesized sample and (f) ground sample of ENPOMe illuminated by a 740 nm laser pulse; (g) SEM of the as-synthesized sample; and (h) ground sample of ENPOMe.

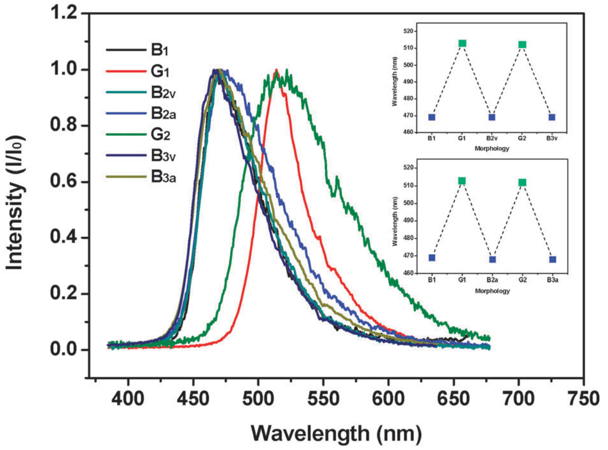

**Fig. 2** TPF spectra of ENPOMe: ($B_1$) as-synthesized sample; ($G_1$) ground sample; ($B_{2v}$) fumed sample (ground sample in dichloromethane vapor for five minutes); ($B_{2a}$) annealed sample (The ground sample was homoiothermal at 140 °C for ten minutes and cooled down at room temperature.); ($G_2$) re-ground sample; ($B_{3v}$) re-fumed sample; ($B_{3a}$) re-annealed sample. The insets depict the reversibility of the TPF wavelengths of ENPOMe: by grinding–fuming treatments (top); and by grinding–annealing treatments (down).

Multi-stimuli-responsive fluorescence switching: the as-synthesized ENPOMe compound exhibits strong blue-light TPF ($B_1$-form, $\lambda_{max}$ = 469 nm) in the solid state (Fig. 1a–f and 2). However, when the sample was ground, the color changed from light green to greenish-yellow, and the maximum TPF wavelength shifted bathochromically to 513 nm ($G_1$-form). Aside from the red-shift of $\lambda_{max}$, the fluorescence efficiency of ENPOMe decreased from 0.85 in $B_1$-form to 0.66 in $G_1$-form. Differential scanning calorimetry (DSC) was performed for $B_1$ and $G_1$, and the results are shown in Fig. S6 (ESI†). An exothermal peak at around 82 °C is observed in the DSC thermogram of $G_1$. This peak is absent in the DSC curve of $B_1$. The ground sample, $G_1$-form, is metastable and can crystallize promptly upon heating. The crystalline sample ($B_{2a}$) from $G_1$ exhibits a melting point at around 171 °C and a TPF $\lambda_{max}$ at 470 nm (Fig. 2), which are equal to those of the pristine sample, $B_1$. Thus, the ground sample can revert back to the original state, and the TPF can exhibit hypochromic shift back to blue. The treatments of grinding and annealing were repeated beginning with $B_{2a}$. The results are similar to the first round, thus further confirming the excellent reversibility of TPF between green and blue light, which correspond to the crystalline B-form and metastable G-form, respectively. The melting peak of $G_1$ is obviously higher than the exothermal peak, implying that $B_1$ crystals are destroyed and partially changed into an amorphous state by grinding. Aside from annealing, solvent-vapor-induced crystallized samples ($B_{2v}$ and $B_{3v}$) are obtained from the ground samples ($G_1$ and $G_2$). The properties of the crystallized samples are similar to that of the initial sample, suggesting that both annealing and vapor-inducement can promptly revert TPF from green light to blue light. Fig. 1g and h show the typical scanning electron microscopy (SEM) images of $B_1$ and $G_1$. The sample $B_1$ of ENPOMe is formed by crystals with a smooth surface and a rectangular shape with different lengths that result in the blue-light emission of TPF. Whereas the $G_1$-form is rough and the crystals are destroyed, breaking into small pieces or even becoming amorphous. This process leads to the green-light emission of TPF. Time-resolved emission decay was also carried out (Fig. S7, ESI†). The $B_1$ of ENPOMe has only one lifetime (1.48 ns), whereas $G_1$ has two ($\tau_1$ = 1.54 ns, $\tau_2$ = 2.66 ns), indicating that $G_1$ exhibits two decay pathways. Considering that the $\tau_1$ of $G_1$ is close to the $B_1$ lifetime, then the $\tau_2$ of $G_1$ may belong to the amorphous state of ENPOMe. The results of powder X-ray diffraction (XRD) of ENPOMe samples show that ENPOMe exhibits different molecular aggregation structures before and after grinding (Fig. S8, ESI†). The XRD results demonstrated that the B-form samples were well-ordered microcrystalline-like structures and the G-form samples were metastable amorphous states. Thus, TPF reversibility for ENPOMe is ascribed to amorphization and crystallization upon the grinding–annealing (or fuming) process. ENPOMe is proven to be CIEE-active because the crystallinity and fluorescence efficiency of the B-form are higher than those of the G-form. Although several luminophores have been reported to exhibit morphology-dependent fluorescence, compounds showing large differences in fluorescence efficiency with the CIEE effect, as well as the TPF emission color, have not yet been reported. SPF and TPF spectra of ENPOMe in B-form and G-form are shown in Fig. S9 (ESI†). The $\lambda_{\max}$ of SPF in $B_1$ and $G_1$ is located at 469 and 512 nm, respectively, under 370 nm excitation by a xenon lamp. This finding agrees well with TPF. The good match between single- and two-photon excitation fluorescence suggests that the emission results from the same excited state without regard to different excitation modes. The reversibility between B-forms and G-forms in SPF is similar to that in TPF (Fig. S10, ESI†), demonstrating that ENPOMe can be switched by both SPF and TPF.

Fig. S11 (ESI†) shows the molecular packing structures of the ENPOMe single crystal (four molecules per unit cell; crystal data summarized in Table S1, ESI†) demonstrated by single crystal X-ray diffraction. ENPOMe crystallizes layer-by-layer when assisted by weak C–H···π interaction. The molecules in the crystal are arranged in slip-stack order along the long *c*-axis with a pitch angle of 71.4°. Molecules form antiparallel coupling in the same layer, and establish efficient tail-to-tail interaction with adjacent molecules by C–H···N and C–H···O hydrogen bonds. These bonds are more robust than the C–H···π interactions of the interlayer. Thus, the molecules will first slip along the *c*-axis when triggered by an external pressure, and then the crystal will crack. Furthermore, numerous cavities are found in each layer, indicating that ENPOMe affords loose-packing patterns in its crystals. Geometry of isolated free molecules of ENPOMe in the ground state was obtained by simulation based on B3LYP/6-31G(d) using Gaussian 03W (Fig. S12 and Table S2, ESI†) to validate the piezofluorochromism mechanism. The dihedral angles of A–D and D–F pairs in the simulated molecule are 75.2° and 5.7°, respectively, which are 5.3° and 8.7° lower than those in the crystal. Thus, the twist stress of the molecules in the crystals is greater, and readily released when triggered by external pressure, which leads to the planarization of the molecular conformation, an extension of molecular conjugation, and a bathochromic shift of both SPF and TPF spectra.

In summary, we have easily synthesized and fully characterized a novel AIE- and CIEE-active luminophore constituted by tetraphenylethene and acrylonitrile (ENPOMe) with high fluorescence ($\Phi_F$ of up to 0.85). ENPOMe has an exceptionally large TPA cross section of 5548 GM. The as-synthesized sample exhibits striking multi-stimuli-responsive SPF and TPF switching with excellent reversibility in the solid state. The unique reversibility of TPF makes ENPOMe a promising material for 3-D optical data storage or sensing.

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