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## COMMUNICATION

## Small molecules based on diphenylamine and carbazole with large two-photon absorption cross sections and extraordinary AIEE properties

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Accepted 00th January 2012Guojian Tian,<sup>a</sup> Wei Huang,<sup>a</sup> Shengyun Cai,<sup>a</sup> Haitao Zhou,<sup>a</sup> Bo Li,<sup>b</sup> Qiaochun Wang<sup>a</sup> and Jianhua Su<sup>\*a</sup>

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**Two simple small molecules based on diphenylamine (T1) and carbazole (T2) have been synthesized for two-photon absorption materials. Both dyes exhibit extraordinary aggregation-induced emission enhancement (AIEE) properties and high corresponding quantum efficiencies of 11.5 % and 16.0 %. The value of the two-photon absorption cross-section for T1 is 1240 GM.**

The emergence of the two-photon absorption (2PA) materials has opened up a new avenue for scientists to research the progressive field such as two-photon dynamic therapy, up-converted lasing,<sup>1</sup> optical power limiting materials,<sup>2</sup> two-photon microscopy and bioimaging. Nowadays, a series of novel organic fluorophores with large 2PA cross-sections ( $\sigma$ ) and good processabilities have emerged.<sup>3</sup> The structures of organic fluorophores include asymmetrical donor- $\pi$ -bridge-acceptor (D- $\pi$ -A), symmetrical donor- $\pi$ -bridge-donor (D- $\pi$ -D), and donor- $\pi$ -bridge-acceptor- $\pi$ -bridge-acceptor- $\pi$ -bridge-donor (D- $\pi$ -A- $\pi$ -A- $\pi$ -D). The 2PA cross section is connected with the intramolecular charge transfer from the donor to the  $\pi$ -bridge. Moreover, the solvent polarity, molecular coplanarity, and hydrogen-bonding can also intensify the 2PA cross-section.<sup>4</sup>

However, most 2PA dyes are soluble in organic solvent, but their fluorescence will be lost in aqueous media, due to self-aggregation driven by limited solubility as well as  $\pi$ - $\pi$  interactions.<sup>5</sup> It is restricted that their biophotonic applications in aqueous media for those highly efficient 2PA materials. So to investigate the 2PA dyes that can be soluble or dispersible in water and remain highly fluorescent in aqueous media is considerable. Recently, Tang and co-workers observed that some fluorophores have enhanced emission in aggregation, namely aggregation-induced emission (AIE). They deduced that the mechanism of AIE was restricted intramolecular vibrational and rotational motions (RIR) in the aggregated solid.<sup>6</sup> This phenomenon offered a new path for the materials with large 2PA cross sections. Prasad and co-workers studied some dyes with aggregation-enhanced fluorescence and two-photon absorption properties.<sup>7</sup> Tang and co-workers also investigated some organic molecules and polymers displaying 2PA and AIE properties.<sup>6</sup>

It is well known that triphenylamine and carbazole with excellent electron-donating and transporting capabilities have been widely used in optical and electroactive materials.<sup>8</sup> Owing to the special propeller starburst molecular structure of triphenylamine, which has aroused great interest and become the focus of progressive research in 2PA field. Furthermore, cyano-substituted materials exhibit excellent optical and electrical properties due to their favorable electron affinities.<sup>9</sup> In this work, considering to extend  $\pi$ -conjugation length largely and facilitate the effect of intramolecular charge transfer efficiently would enlarge the 2PA cross section,<sup>10</sup> we design two simple small molecule with diphenylamine and carbazole as the donor and two-cyano group as the acceptor. In view of the effective intramolecular charge transfer (ICT) effect and the molecule structure of this two dyes, excellent 2PA values and favorable AIEE properties can be anticipated.

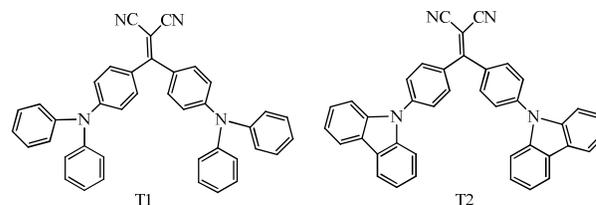


Fig. 1 Molecular structures of T1-T2.

The one-photon absorption spectra of T1-T2 in THF were shown in Fig. 2 (ESI<sup>†</sup>). The absorption maxima ( $\lambda_{\text{max}}$ ) of T1-T2 located at 438 nm, 404 nm, respectively. It was obviously shown that the  $\lambda_{\text{max}}$  of T1 was red shifted by 34 nm than that of T2, which was coincide with that the electron-donating ability of diphenylamine was stronger than that of carbazole. To investigate the effect of the solvent polarity on this two compounds, Fig. 3 (ESI<sup>†</sup>) showed the solvent effect behaviour of T1-T2. The emission spectra of T1-T2 were made by increasing the polarity from cyclohexane to ethanol. It was a positive solvent effect based on the emission spectra, for example, the emission peak of T1 located at 494 nm in cyclohexane undergo a red shift to 631 nm in ethanol. This phenomenon was similar for T2 that from 481 nm in cyclohexane to 600 nm in ethanol. So the intramolecular charge transfer (ICT) effect of T1 was stronger than

that of **T2**. From the above, an obvious ICT effect lied in this two compounds.

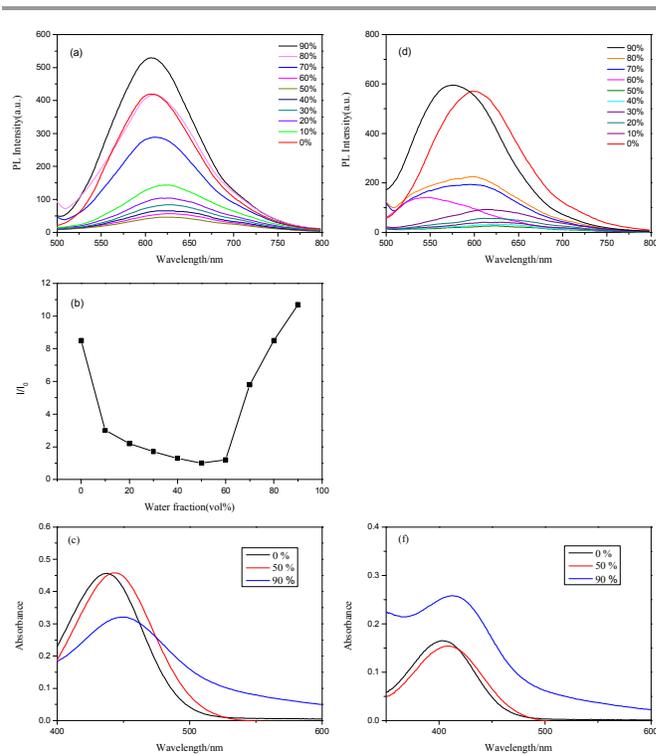
The compounds **T1-T2** can be dissolved by the common organic solvent such as THF and dichloromethane, but not water. To explore the AIEE attributes of **T1-T2**, we use anhydrous THF and water as the good solvent and the poor solvent, respectively. The method to disperse **T1-T2** by the primary way, adding different amounts of water to the anhydrous THF solution and making the water fraction ( $f_w$ ) at 0 - 90 %. Fig. 4 (a, d) showed the corresponding emission spectra of **T1-T2** at a concentration of  $1.0 \times 10^{-5}$  M. As gradual addition of water amounts into the anhydrous THF solution, the fluorescence intensities of **T1** in the THF/water mixtures were obviously quenched at the initial stage from  $f_w = 0\%$  to  $f_w = 50\%$ . Meanwhile, the  $\lambda_{\max}$  of emission spectrum of **T1** in the solvent mixture was red shifted by 27 nm from  $f_w = 0\%$  to  $f_w = 50\%$ . Since **T1** was a donor-acceptor fluorogen, this phenomena indicated a typical intramolecular charge transfer (ICT) effect, as a consequence with the increase in solvent polarity. Upon further addition of water amounts into the solvent mixture, the **T1** molecules become nano-aggregated, and their fluorescence intensity dramatically recovered and heightened with increasing  $f_w$  from 50 % to 90 %. However, the  $\lambda_{\max}$  of emission spectrum of **T1** in the solvent mixture was blue shifted by 25 nm from  $f_w = 50\%$  to  $f_w = 90\%$ . Apparently, the emission of **T1** was induced by aggregation, and displaying the AIEE feature (Figure 4a). As a result, both the effect of ICT and AIEE could be suited to **T1**.<sup>11</sup>

Moreover, firstly the reduced and red-shifted phenomena and then become enhanced and blue-shifted emissions along with aggregation for the emission spectra of **T1**, compared to the dyes in the solution, the possible reason lied in the dye crystallization in the solid film.<sup>12</sup> Fig. 4c showed the absorption of **T1** when  $f_w = 0\%$ ,  $f_w = 50\%$  and  $f_w = 90\%$ . Compared to the fluorescence intensity, the absorption spectra of **T1** that from the molecule's nano-aggregated state was red-shifted and widened. A quantitative graph of the AIEE process could be work out by measuring the change of the PL spectra with different  $f_w$ . As to **T1**, the fluorescence reached to its maximum when the  $f_w$  at 90 %, while the weakest fluorescence at 50 % with a 10.7-fold reduction and the intensity was increasing at 0 % with an 8.5-fold increase in the  $I/I_0$  ratio (Fig. 4b), respectively. Fig. 5(b, **T1**) showed the scanning electron microscopy (SEM) image of **T1**. It showed that a nano-aggregated structure has formed in the mixture with a high water content.

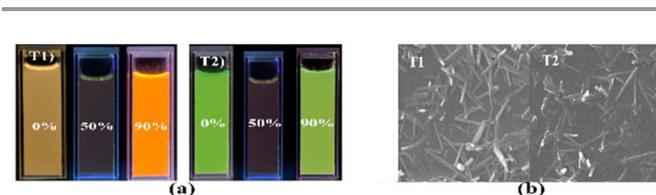
The compounds **T1-T2** emit different one-photon fluorescence with different ratios of THF and water. Fig. 5(a) showed the one-photon emission images in different water fractions ( $f_w$ ) of solution. Slight emission was observed at  $f_w = 50\%$ , but intensified dramatically when  $f_w = 0\%$  and  $f_w = 90\%$ , which was coincide with the AIEE phenomenon. The different pH values in the solution had no effect on the one-photon fluorescence Fig. 9 (ESI†).

Similar phenomenon was observed for **T2**. The PL intensity was weakest at  $f_w = 50\%$ , and when the  $f_w = 90\%$  and  $f_w = 0\%$ , which given a strong luminescence with a 19-fold and 18.6-fold increase, respectively (Fig. 4e). Fig. 5(b, **T2**) showed the scanning electron microscopy (SEM) image of **T2**.

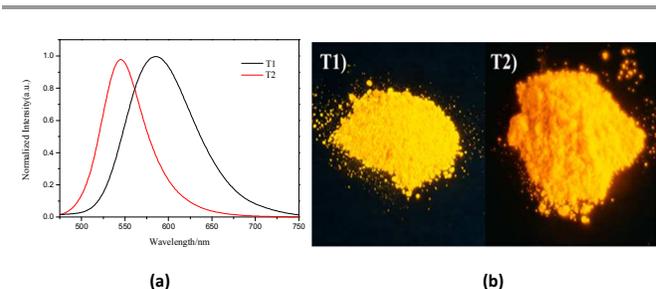
The lively picture of the solid powders could also prove the effect of AIEE property, where they show yellow and deep yellow fluorescence emission (Fig. 6). To quantitatively evaluate the AIEE property of the fluorescent materials, the emission spectra and quantum efficiencies of the solid powders were investigated. The dyes (**T1-T2**) exhibited emission peak at 586 nm and 545 nm and the quantum efficiencies were pitched on 11.5 % and 16.0 %, respectively. Such high quantum efficiencies of the solids indicated that they had great prospects in OLED applications.<sup>13</sup>



**Fig. 4** (a, d) The PL spectra of **T1-T2**, in different water fractions ( $f_w$ ); Excitation wavelength: 443 nm (**T1**), 409 nm (**T2**). (b, e) Plots of  $(I/I_0)$  values versus water content of the solvent mixture for **T1-T2**, where  $I_0$  is the PL intensity in  $f_w = 50\%$ . (c, f) Absorptions of **T1-T2** in THF and water where  $f_w = 0\%$ ,  $f_w = 50\%$  and  $f_w = 90\%$  at a concentration of  $1.0 \times 10^{-5}$  M.



**Fig. 5** (a) The one-photon fluorescence (OPF) emission photos of  $1.0 \times 10^{-5}$  M of **T1-T2**, respectively, in different ratios of water and THF; Excitation wavelength: 365 nm. (b) The SEM images of **T1-T2** nano-aggregates prepared in  $f_w = 90\%$  at concentrations of  $1.0 \times 10^{-3}$  M.



**Fig. 6** (a) The solid powder emission spectra of **T1-T2**; Excitation wavelength: 443 nm (**T1**), 409 nm (**T2**). (b) The images of **T1-T2** as solid powders under 365 nm UV light illumination.

The 2PA cross sections of **T1-T2** were measured by a previously described method that the femtosecond open-aperture Z-scan technique, Fig. 7a and b showed the data fitting of the open-aperture Z-scan. The 2PA cross section ( $\sigma$ ) can be calculated by the equation of  $\sigma = hv\beta/N_0$ , in which  $N_0 = N_A C$  is the number density of the

absorption centers,  $N_A$  is the Avogadro constant and  $C$  represents the solute molar concentration.<sup>14</sup> The values of the 2PA at the wavelength of 800 nm for **T1-T2** were 1420 GM and 802 GM in chloroform, respectively. While in dichloromethane, the values of 2PA for both dyes become small in Fig. 8(ESI<sup>†</sup>), which were 457 GM and 210 GM respectively. It was noteworthy that solvent effect had a significant influence on the 2PA cross section, the value in chloroform was bigger than that in dichloromethane. As the solvent polarity increased, consistent with more pronounced ICT in the excited state, larger changes were produced by solvent stabilization. The correlation between the solvent effect and the 2PA cross section value was complicated and had not made very clear by far, which may related to the solute-solvent interactions, solubility and the solvent polarity.<sup>15</sup>

The 2PA cross section of **T1** was bigger than that of **T2**, due to the ability of electron-donating group based on diphenylamine was stronger than that of carbazole. The cross sections of **T1-T2** in chloroform were quite large for 2PA dyes based on small molecules compared to those reported dyes,<sup>10(a), (b)</sup> due to its large  $\pi$ -conjugated system and the effective intramolecular charge transfer (ICT) from the donor to the acceptor, which was also in agreement with the general conclusion that enhancing the  $\pi$ -conjugated system could enlarge the value of 2PA.<sup>16</sup> So we could control the value of 2PA cross section by simply introducing different donors or acceptors, and taking the molecular structure into account.

The two-photon fluorescence (TPF) intensity could be examined the aggregation effect on the two-photon activity. Under the excitation of an 80 fs, 800 nm pulse, **T1-T2** emit yellow and deep yellow fluorescence with peaks located at 624 nm and 606 nm, respectively (Fig. 7c and d), in a mixture of THF and water ( $f_w = 50\%$  and  $f_w = 90\%$ ). Compared with the one- and two-photon excitation fluorescence, the good overlap between them indicated that the emissions resulted from the same excited state, regardless of the different mode of excitation. The two-photon emission images in different water fractions ( $f_w$ ) of solution were showed in the inside picture of Fig. 7c and d, slightly emission was observed at the  $f_w = 50\%$ . While at the  $f_w = 90\%$  the dyes irradiated yellow and deep yellow emission, when excited at 800 nm. The same phenomenon had also been seen in the one-photon emission images (Fig. 5a). Due to the limitation of our laser apparatus, just irradiation at the wavelength of 800 nm was used to carry out the two-photon excitation experiment. The 2PA cross sections of both final products would be better in other wavelengths.<sup>17</sup>

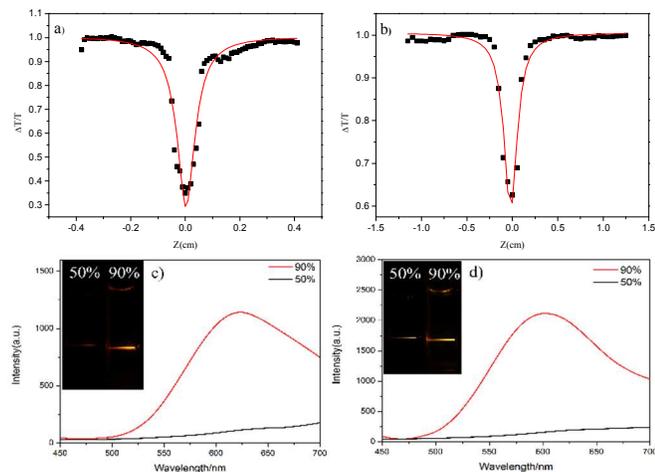


Fig. 7 a), b) The open-aperture Z-scan trace of **T1-T2** (scattered circles = experimental data, straight line = theoretical fitted data) in  $\text{CHCl}_3$ . c), d) At 800

nm excited, the TPF emission spectra of **T1-T2** in the solution 50% : 50% (v/v water / THF) and 90% : 10% (v/v water / THF) at a concentration of  $1.0 \times 10^{-5}$  M.

In summary, we have synthesized two simple small molecules **T1-T2** with large 2PA cross sections and extraordinary AIEE properties. The 2PA cross sections of **T1-T2** were 1420 GM and 802 GM in chloroform, respectively. To the best of our knowledge, the values were quite large for 2PA materials based on simple small molecules. Moreover, this two dyes exhibited particular AIEE properties with the fluorescence reached to their peak when the  $f_w$  at 90%, while the weakest fluorescence at 50% and the intensity recovered increasing to 0%. This extraordinary AIEE properties could be used in two-photon microscopy and bioimaging, which was under our further investigation. What's more, the solid fluorescence of this two compounds located at 586 nm and 545 nm and the corresponding quantum efficiencies were 11.5% and 16.0%. From the above, these excellent performances could promote them as promising materials for biophotonic applications.

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## Notes and references

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Electronic Supplementary Information (ESI) available: [The one-photon absorption of **T1-T2** in THF; The emission spectra of **T1-T2** in different solvents; The 2PA cross sections of **T1-T2** in  $\text{CH}_2\text{Cl}_2$ ; Experimental procedures for synthesis;  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, EI-TOF]; The effect of pH on the one-photon fluorescence.

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