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# Solvent effect on two-photon absorption (TPA) of three novel dyes with large TPA cross-section and red emission

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## ARTICLE INFO

## ABSTRACT

Three novel organic dyes containing 2,6-dicarbonyl-pyridine as the central electron acceptor with different end-caped amino groups as donors in the D-π-A-π-D arrangement are designed and synthesized. All three molecules exhibit large TPA cross-sections ($\delta > 1000$ GM). The cooperative effects of donor strength, conjugation length and solvent polarity on the TPA activity are studied. The conjugated system plays an important role on the enhancement of $\delta$ in the highly polar solvent, while donor strength has more impact on TPA properties. The influence of the solvent polarity on TPA properties is studied by two-photon excited fluorescence (TPEF) measurement. The result shows a nonmonotonic relationship between the TPA cross-section and the solvent, and the maximum of $\delta$ is found in solvents with moderate polarity. The $\delta$ of molecules with stronger donor reaches the maximum in more polar solvents. The highest $\delta$ is found to be 5250 GM in CHCl$_3$. All compounds exhibit large Stokes shifts due to the strong intramolecular charge transfer (ICT) effect.

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## 1. Introduction

TPA which is defined as the simultaneous absorption of a pair of photons during the excitation of a molecule was first predicted by M. Göppert-Mayer [1]. In the last decade, the design and synthesis of new organic molecules exhibiting large TPA cross-section have attracted much attention for their potential application in three-dimensional (3D) imaging [2–8], optical data storage [9,10], 3D micro-fabrication [11,12] and optical limiting [13–15]. On one hand, in the practical application, it requires lower excitation energy for decreasing the photo-induced damage and sometimes lower concentration of the TPA chromophores. Thus, the efficient fluorescent molecules with large $\delta$ are demanded [16]. However, the conventional one-photon absorption (OPA) fluorescent molecules such as rhodamine, fluorescein and cyanine dyes usually exhibit small TPA cross-sections ($\delta < 100$ GM) or poor photostability [17,18]. Recently, a variety of compounds exhibiting large TPA cross-sections ($\delta$) have been synthesized and the relationships between their

structures and TPA properties have been investigated [19–24]. Some primary principles for the enhancement of $\delta$ have been summarized such as long π-conjugated chains which lead to large conjugation system, strong donor (D) and acceptor (A) groups at the center or ends of the molecules which ensure efficient polarization [25]. It has also been reported that solvent polarity can also affect the TPA properties [21,26–31]. Nevertheless, when such factors function together, things are getting complicated and the reports on such coactions are still scarce [32]. On the other hand, the TPA molecules with red emission are badly needed especially in the biological imaging area, because their longer emission wavelength implies less background interference and damage to the sample [33,34].

Comparing with the dipolar molecules bearing a D-π-A structure, quadrupolar molecules with structures of D-π-A-π-D or A-π-D-π-A are usually considered to be more effectively polarized resulting in larger transition moment and higher TPA induced fluorescence [24,35,36]. Besides, such molecules often have enhanced ICT effect and large Stokes shift, which makes the realization of red emission possible [37,38].

Herein, the TPA properties of three novel chromophores containing 2,6-dicarbonyl-pyridine as the electron acceptor with three different end capped electron donors in the D-π-A-π-D molecular

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arrangement are reported. We investigate these molecules with different donor strength and conjugated system size in four solvents with different polarities to explore the cooperative influence of the factors mentioned above on the δ. These molecules exhibit large δ and regular relationship with the selected variables. The red emission is also obtained, indicating a successful design strategy and offering potential opportunities for compounds with large δ and efficient red emission.

## 2. Experimental section

### 2.1. Materials and measurements

All of the material for synthesis were purchased from Aladdin and used as received without further purification. ^{1}H NMR spectra were obtained using a Bruker Avance DMX500 spectrometer with tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed using a Thermo Finnigan Flash EA1112 microelemental analyzer. Differential scanning calorimetry (DSC) was performed on a Netzsch Instruments 200 F3 at a heating rate of 10 K min$^{-1}$ under nitrogen atmosphere. Thermogravimetric analysis (TGA) was obtained using a Netszch TGA209F3 with a heating rate of 10 K min$^{-1}$ in nitrogen. UV–visible absorption spectra were obtained using a Perkin–Elmer Lambda 20 spectrophotometer. Fluorescence emission spectra were obtained on a F4600 fluorescence spectrophotometer. The quantum yields ($\Phi$) were determined by comparison with fluorescein as a reference described in the literature [39] according to the following equation:

$$\Phi_s = \frac{I_s}{I_r}\frac{A_r}{A_s}\frac{c_r}{c_s}\frac{n_s^2}{n_r^2}\Phi_r \tag{1}$$

where subscripts s, t refer to the sample and the reference respectively, $I$ is the integrated fluorescence intensity, $A$ is the absorbance at the selected wavelength, $c$ is the concentration and $n$ is the refractive index of the solvents [40].

Two-photon excited fluorescence emission spectra were noted on a USB2000 and the pump laser beam came from a Coherent Chameleon Ultra II laser system at the pulse duration of 140 fs, a repetition rate of 80 MHz. Samples were dissolved in toluene, THF, chloroform and dichloromethane respectively at the concentration of $2.0 \times 10^{-3}$ M. The two-photon excited fluorescence spectra were recorded by using fluorescein as reference [41]. The two-photon excited fluorescence intensity of samples and reference were measured at the same condition (input power 400 mW, scan to average = 4, boxcar width = 10) [17,42].

### 2.2. Synthesis of compounds MePy, EtPy and PhPy

The mixture of piperidine (2 mL) and acetate acid (1 mL) was added to a solution of 2,6-diethanone-pyridine (0.33 g, 2 mmol) and 4-(dimethylamino)benzaldehyde (0.75 g, 5 mmol) in chloroform (10 mL). The reaction mixture was refluxed for 24 h at 80 °C. After cooling to rt., the mixture was washed twice by water (50 mL × 2). The organic phase was collected and then dried with MgSO$_4$. The solvent was removed under reduced pressure. The remaining black oil was purified by chromatography (CH$_2$Cl$_2$) to yield orange solid MePy (0.52 g, 61%). EtPy and PhPy are synthesized in the same procedure.

MePy: m.p.: 228.8 °C; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 8.33$ (d, $J$(H,H) = 7.7Hz, 2H), 8.27 (d, $J$(H,H) = 15.9Hz, 2H), 8.02 (t, $J$(H,H) = 7.9Hz, 3H), 7.69 (d, $J$(H,H) = 8.85Hz, 4H), 6.73 (d, $J$(H,H) = 8.85Hz, 4H), 3.07 (s, 12H); ^{13}C NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 40.5, 112.3, 116.2, 123.7, 125.4, 131.0, 146.0, 152.3, 154.0$; MS-ESI theoretical: $m/z$ [M + H]$^+$ = 426.2, found: 426.2; elemental analysis cacld (%) for C$_{27}$H$_{27}$N$_3$O$_2$: C, 76.21; H, 6.40; N, 9.87; found: C, 75.83; H, 6.36; N, 9.73.

EtPy: m.p.: 235.0 °C; ^{1}H NMR (500MHZ, CDCl$_3$, 25 °C, TMS): $\delta = 8.33$ (d, $J$(H,H) = 7.7Hz, 2H), 8.25 (d, $J$(H,H) = 15.8Hz, 2H), 8.01 (t, $J$(H,H) = 7.9Hz, 3H), 7.67 (d, $J$(H,H) = 8.9Hz, 4H), 6.78 (d, $J$(H,H) = 8.9Hz, 4H), 3.44 (m, $J$(H,H) = 7.1Hz, 8H), 1.22 (t, $J$(H,H) = 7.1Hz, 12H); ^{13}C NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 12.8, 44.7, 111.5, 115.3, 122.5, 125.2, 131.3, 138.0, 146.1, 150.0, 154.0, 188.7$; MS-ESI theoretical: $m/z$ [M + H]$^+$ = 482.3, found: 482.3; elemental analysis cacld (%) for C$_{31}$H$_{35}$N$_3$O$_2$: C,77.31; H,7.32; N, 8.72; found: C,77.25; H, 7.37; N, 8.71.

PhPy: m.p.: 251.5 °C; ^{1}H NMR (500MHZ, CDCl$_3$, 25 °C, TMS): $\delta = 8.34$ (d, $J$(H,H) = 7.8Hz, 2H), 8.26 (d, $J$(H,H) = 16.0Hz, 2H), 8.04 (d, $J$(H,H) = 7.7Hz, 1H), 7.97 (d, $J$(H,H) = 15.9Hz, 2H), 7.57 (d, $J$(H,H) = 8.7Hz, 4H), 7.27 (m, $J$(H,H) = 7.6Hz, .8H), 7.12 (m, $J$(H,H) = 8.5Hz, 8H), 7.07 (d, $J$(H,H) = 7.4Hz, 4H), 7.00 (d, $J$(H,H) = 8.6Hz, 4H); ^{13}C NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 118.41, 121.6, 124.1, 125.4, 125.7, 128.2, 129.5, 130.1, 138.1, 145.1, 146.8, 150.5, 153.7, 188.9$; MS-ESI theoretical: $m/z$ [M + Na]$^+$ = 696.3, found: 696.3; elemental analysis cacld (%) for C$_{47}$H$_{35}$N$_3$O$_2$: C, 83.78; H, 5.24; N, 6.24; found: C, 83.64; H,5.16; N,6.09.

## 3. Results and discussion

### 3.1. Design and synthesis

To obtain the desired compounds, we adopt the structure of D-π-A-π-D which is appropriate for effective ICT effect. Although
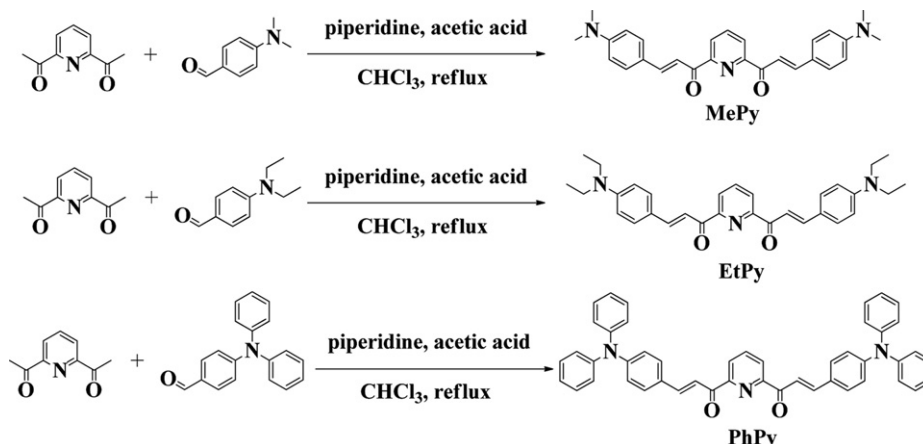


**Scheme 1.** Synthesis of MePy, EtPy and PhPy.

larger Stokes shift could also be realized by enlarging the conjugated system of the molecules, bulky conjugated chains may lower the solubility and decrease the interactions between the donor and the acceptor groups, leading to the reduction of ICT effect. Therefore, we choose the way of strengthening the donor and acceptor groups. 2, 6-(dicarbonyl)pyridine is selected as the central acceptor group because of the strong electron-withdrawing ability of both carbonyl and pyridine [43]. Dimethylamine, diethylamine and diphenylamine are chosen as end capped donor group because of their excellent photostability and the capability of enhancing fluorescence and Stokes shift. And most importantly, they have the same structure but minor difference in the donor strength and conjugated length. The phenyl groups of diphenylamine provide both larger conjugated length leading to the enhancement of the molecule's TPA activity and the damping effect on the donor strength which may weaken its TPA response. While dimethylamine and diethylamine possess stronger electron-donating ability as well as minor conjugated system compared with diphenylamine. These regular differences may interact with solvent polarity and generate regular variations. Combining the chosen donor and acceptor group with styrene as the conjugated bridge, three new compounds, 2,6-bis(4-dimethylaminostyrylcarbonyl) pyridine (MePy), 2,6-bis(4-diethylaminostyrylcarbonyl)pyridine (EtPy) and 2,6-bis(4-diphenylaminostyrylcarbonyl)pyridine (PhPy) are designed.

These three compounds were all synthesized via Knoevenagel reaction as described in the Scheme 1. The structures of PhPy and its derivatives were confirmed by $^1$H NMR and elemental analysis. The decomposition temperature ($T_d$) of PhPy and its derivatives are almost the same (334—335 °C), while their melting temperatures exhibit minor differences, which may be ascribed to the different end capped group.

### 3.2. Linear photophysical properties

Fig. 1 shows the one-photon absorption and fluorescence emission spectra of MePy, EtPy and PhPy in solvents with different polarity respectively, and the main linear photophysical parameters are listed in Table 1. With the increase of the solvent polarity: toluene (33.9) < THF (37.4) < CHCl$_3$ (39.1) < CH$_2$Cl$_2$ (40.7) [44], the absorption and the corresponding fluorescence emission spectra of MePy, EtPy and PhPy red shift. Comparing the absorption spectra of these compounds, some similarity can be found. All of the spectra have the similar profile except slight red shifts with the increase of the solvent polarity. For MePy, EtPy and PhPy dissolved in the same solvent, the absorption peak wavelength is in the order of PhPy > EtPy > MePy. The fluorescence emission spectra of these compounds have the same tendency except that the red shifts of PhPy are larger. Large Stokes shifts are found in all the compounds which is attributed to the ($\pi \to \pi^*$) transition of the conjugated system of the D-$\pi$-A-$\pi$-D structure strengthened by the strong donor and acceptor groups. Although the donor of PhPy is weaker than the other two counterparts, PhPy has an even larger Stokes shift (166 nm in CH$_2$Cl$_2$). Considering the enlarged conjugated system of PhPy due to the end capped phenyl groups which may result in larger Stokes shift than the other molecules, it can be speculated that the conjugation length plays an important role in the enhancement of solvatochromism. For the same reason, the fluorescent quantum yields of PhPy in different solvent also have an apparent enhancement (Table 1). In addition, molar extinction coefficients ($\varepsilon$) of MePy, EtPy and PhPy are almost independent to solvent polarity, while for the same solvent, $\varepsilon$ of PhPy is considerably lower than those of MePy and EtPy, suggesting that the donor strength affects the absorption ability of molecules with this structure more intensely than other factors.
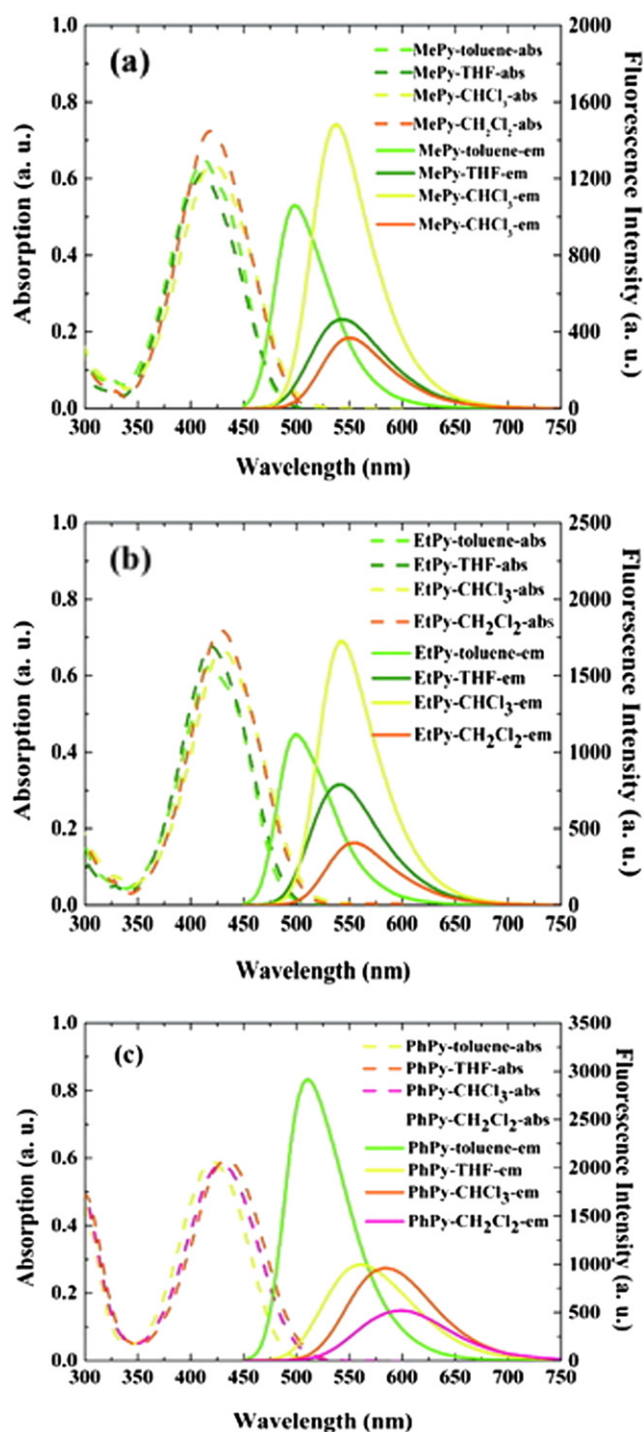


**Fig. 1.** Absorption and fluorescent emission spectra of MePy (a), EtPy (b) and PhPy (c) in toluene, THF, CHCl$_3$ and CH$_2$Cl$_2$ with concentration of $1 \times 10^{-5}$ M.

### 3.3. Nonlinear photophysical properties

In order to determine the two-photon absorption efficiency of these compounds, two-photon fluorescent emission spectra and $\delta$ of the novel dyes were obtained by the TPEF measurement in toluene, THF, CHCl$_3$ and CH$_2$Cl$_2$, as shown in Fig. 2 $\delta$ and other nonlinear photophysical parameters were included in Table 2. Unlike the one-photon absorption coefficients, the TPA cross-sections of MePy, EtPy and PhPy vary significantly with the increase of the solvent polarity. From Fig. 3, one may also find

**Table 1**
Linear photophysical properties of PhPy and its derivatives.[a]

| | $\varepsilon^b \times 10^4 L \cdot mol^{-1} \cdot cm^{-1}$ | | | $\tau^c$, ns | | | $\Phi^d$, % | | | Stokes shift, nm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | MePy | EtPy | PhPy | MePy | EtPy | PhPy | MePy | EtPy | PhPy | MePy | EtPy | PhPy |
| toluene | 6.26 | 6.42 | 5.95 | 2.57 | 2.69 | 3.86 | 9.2 | 10.8 | 29.8 | 87 | 81 | 87 |
| THF | 6.14 | 6.76 | 5.92 | 1.39 | 1.31 | 2.41 | 4.2 | 4.6 | 8.9 | 119 | 115 | 140 |
| CHCl$_3$ | 7.18 | 7.24 | 5.81 | 1.57 | 2.63 | 3.30 | 8.2 | 10.1 | 14.4 | 129 | 121 | 155 |
| CH$_2$Cl$_2$ | 6.40 | 6.66 | 5.95 | 1.32 | 1.11 | 2.11 | 3.4 | 1.7 | 8.2 | 131 | 127 | 166 |

[a] All the compounds were dissolved in solvents at the concentration of $1 \times 10^{-5}$ M.
[b] The molar absorption coefficient of PhPy and its derivatives.
[c] The lifetime of PhPy and its derivatives.
[d] Fluorescence quantum yield of PhPy and its derivatives excited at the respective maximum absorption wavelengths. These data were obtained using fluorescein ($\Phi = 0.95$ in 0.01 M NaOH) as the reference.

drastic solvatochromism in all the three compounds with the same tendency as one-photon excited fluorescence by changing the solvent polarity. PhPy shows the largest Stokes shift in CH$_2$Cl$_2$ and exhibits red emission. As a representative example for all the compounds studied in this work, intensive green fluorescence is observed with PhPy in the low polarity solvent toluene and red emission fluorescence in the highly polar CH$_2$Cl$_2$. Besides, compared with the corresponding one-photon fluorescence, all the two-photon excited fluorescence spectra of the three compounds have the same shape and peak wavelength, suggesting that the one- and two -photon induced fluorescence originates from the same excited state, which allows us to calculate some crucial nonlinear photophysical parameters of these molecules as shown in Table 2.

By using the three state model based on the sum-over-state (SOS) [45–48], the $\delta$ at the maximum can be expressed by equation (1)

$$\delta^{peak} = \frac{4\pi^2 L^4}{5\hbar c^2 n^2} \frac{E_{ge'}}{\Gamma_{ge}} \frac{M_{ge}^2 M_{ee'}^2}{(E_{ge} - E_{ge'}/2)^2} \tag{2}$$

where $M_{ij}$ is the transition dipole moment and $E_{ij}$ for the excitation energy between $i$ state and $j$ state, and $\Gamma_{ij}$ is the corresponding damping factor ($ij$ = g, e, e', where g is the ground state, e is the one-photon-allowed excited state, and e' is the two-photon-allowed excited state). $h$ is the Plank's constant divided by $2\pi$, $c$ is the speed of light in the vacuum, $n$ is the refractive index of the solvent, and $L$ is the Lorentz field correction, $L = (n^2 + 2)/3$.

The transition dipole moment Mge (in Debye units) can be calculated from equation (2) by integrating the absorption band [49]:

$$M_{ge} = \left[ \frac{1}{nf(n)} \frac{2303}{8\pi} \frac{3hc}{N_A} \int \frac{\varepsilon(\nu)}{\nu} d\nu \right]^{1/2} \tag{3}$$

where $n$ is the refractive index of the solvent, $h$ is the Planck constant, $c$ is the speed of light, $N_A$ is Avogadro's number, $\varepsilon(\nu)$ is the extinction coefficient and $\nu$ is the optical frequency in wavenumber.

It has been reported that strong donors within the symmetric molecules could enhances the ICT effect, bringing a large breaking of the alternant symmetry, causing an enhancement of the
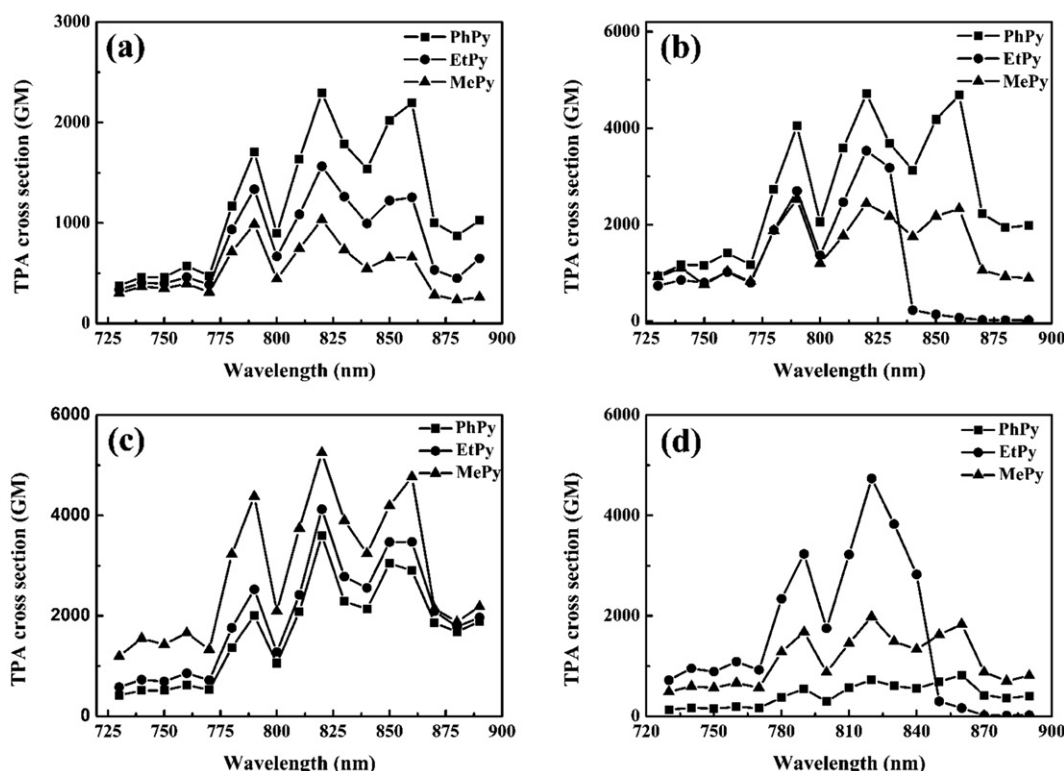


**Fig. 2.** TPA cross-section of MePy, EtPy and PhPy in toluene (a), THF (b), CHCl$_3$ (c) and CH$_2$Cl$_2$ (d) at the concentration of $2 \times 10^{-3}$ M.

**Table 2**
Experimental one- and two-photon photophysical properties of MePy, EtPy and PhPy in different solvents.

| Sample | Solvent | $E_{ge}$[a], eV | $E_{ge'}$[b], eV | $\Delta E$[c], eV | $M_{ge}$[d], D | $M_{ee'}$[e], D | $\lambda_{max}$[f], nm | $\delta$[g], GM |
|---|---|---|---|---|---|---|---|---|
| MePy | toluene | 3.01 | 3.03 | 1.50 | 9.13 | 33.91 | 820 | 1033 |
|  | THF | 3.02 | 3.03 | 1.51 | 10.09 | 47.38 | 820 | 2439 |
|  | CHCl$_3$ | 2.96 | 3.03 | 1.45 | 10.73 | 62.86 | 820 | 5250 |
|  | CH$_2$Cl$_2$ | 2.95 | 3.03 | 1.44 | 11.10 | 37.18 | 820 | 1984 |
| EtPy | toluene | 2.97 | 3.03 | 1.46 | 10.24 | 36.15 | 820 | 1564 |
|  | THF | 2.96 | 3.03 | 1.45 | 10.49 | 52.74 | 820 | 3531 |
|  | CHCl$_3$ | 2.89 | 3.03 | 1.38 | 10.82 | 48.33 | 820 | 3475 |
|  | CH$_2$Cl$_2$ | 2.89 | 3.03 | 1.37 | 10.99 | 55.28 | 820 | 4743 |
| PhPy | toluene | 2.93 | 3.03 | 1.42 | 9.70 | 45.09 | 820 | 2294 |
|  | THF | 2.95 | 3.03 | 1.44 | 9.77 | 65.08 | 820 | 4711 |
|  | CHCl$_3$ | 2.89 | 3.03 | 1.38 | 10.11 | 47.27 | 820 | 2904 |
|  | CH$_2$Cl$_2$ | 2.86 | 3.03 | 1.35 | 10.01 | 23.23 | 820 | 721 |

[a] Transition energy between ground state and one-photon-allowed excited state.
[b] Transition energy between ground state and two-photon-allowed excited state.
[c] Detuning energy $\Delta E \equiv E_{ge} - 1/2E_{ge'}$.
[d] Transition dipole moment between ground state and one-photon-allowed excited state.
[e] Transition dipole moment between one- and two-photon-allowed excited states calculated from equation (1).
[f] Maximum of TPA absorption spectra.
[g] Maximum of the TPA cross-section.

transition dipole moment between excited states ($M_{ee'}$) which result in large TPA activity [50,51] and in low polar toluene and THF, EtPy has a much stronger TPA fluorescence response than that of MePy due to its stronger donor groups. However, also in toluene and THF, PhPy exhibit larger TPA cross-sections than EtPy and MePy, which should be due to the effect of its larger conjugated system, indicating that enlarging the conjugation size may have greater impact on the TPA activity than the strength of donors in the solvents with low polarity. Nevertheless, in CHCl$_3$ and CH$_2$Cl$_2$, the TPA cross-sections of PhPy are lower than that of EtPy and MePy, suggesting the donor strength has more influence than the size of conjugated system. The $M_{ee'}$ of the compounds also exhibit the same tendency. The changes of the influences on TPA activity between donor strength and the conjugated size in solvents with different polarity reveal that the solvent polarity could have significant impact on the TPA cross-sections by affecting the ICT efficiency.

Unlike the one-photon absorption spectra, the different polarities of solvents result in different molecular energy level configuration, thus leading to a large variation of $\delta$ values of the same molecule in different solvents (Table 2 and Fig. 4). Split peaks are observed in all the three molecules, which have been reported previously [52] and explained for the molecular rotation due to high input laser pulse [53]. The highest $\delta$ values of MePy and PhPy are found to be 4711 GM and 5250 GM in THF and CHCl$_3$ respectively, neither in toluene nor CH$_2$Cl$_2$, indicating that the solvent polarity has a complicated influence on the TPA activity. By comparing the TPA cross-sections of MePy and PhPy in the selected solvents, some regularity may be found. With the increase of the solvent polarity, the $\delta$ values of the two compounds increase firstly when the solvent polarity is low, and then decrease dramatically in highly polar solvents. This situation probably can be ascribed to the dilemmatic influence of solvent polarity on the ICT effect. For one hand, the ICT effect can be enhanced by solvent polarity, especially in symmetric molecules, and bring higher $\delta$ values by introducing a large symmetry breaking in the excited ICT state, for the other hand, the solvent polarity may also lower down the energy level of the ICT state and expand the energy gap between the one- and two-photon-allowed excited states, which may decrease the transition dipole moment ($M_{ee'}$), resulting in the decrease of ICT efficiency and TPA activity (Table 2). Thus the TPA cross-sections of PhPy and
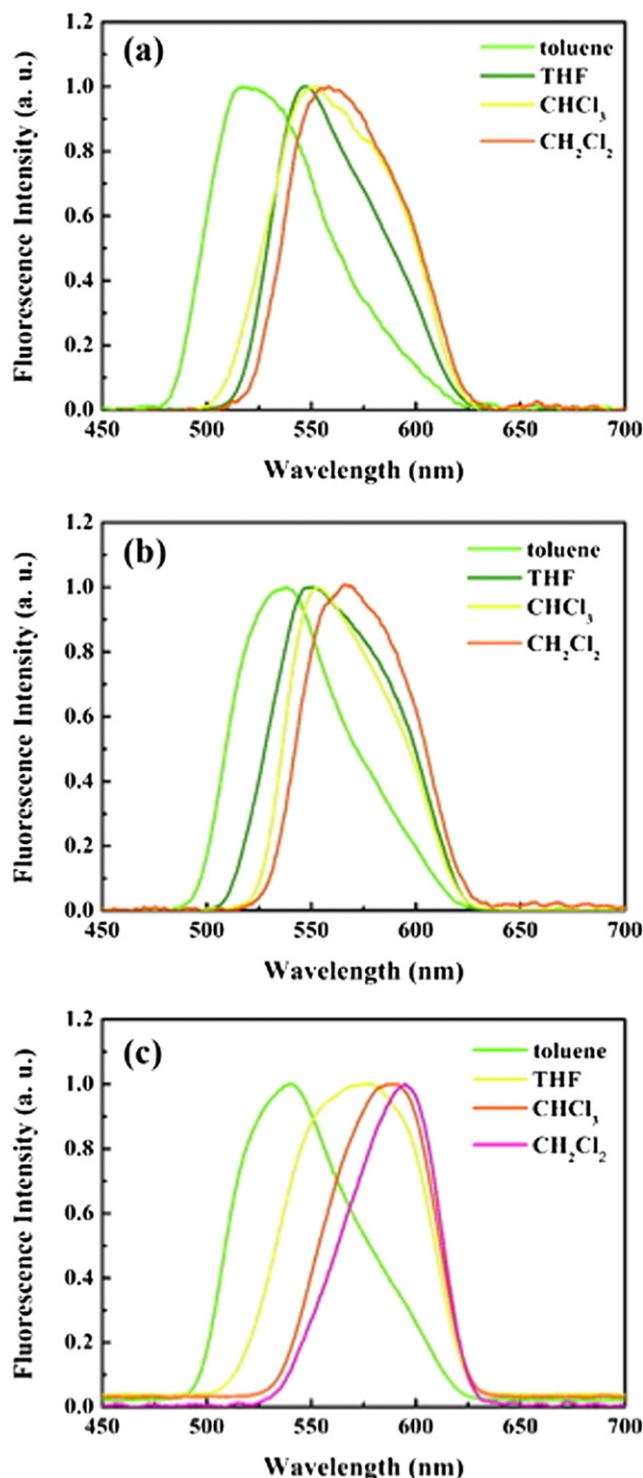


**Fig. 3.** Normalized two-photon excited fluorescence emission spectra of MePy (a), EtPy (b) and PhPy (c) in toluene, THF, CHCl$_3$ and CH$_2$Cl$_2$ at the concentration of $2 \times 10^{-3}$ M.

MePy reach the maximum in the solvent with moderate polarity. Moreover, MePy exhibit the highest $\delta$ value in a higher polar solvent (CHCl$_3$), which could be attributed to the stronger donor end-group of MePy induced more efficient ICT effect, attesting that the solvent polarity influences the TPA properties of compounds through impacting on the ICT effect. For EtPy, with the increase of solvent polarity, the $\delta$ values increase significantly and attain the maximum in CH$_2$Cl$_2$. For the poor quantum yield of EtPy, we could not perform
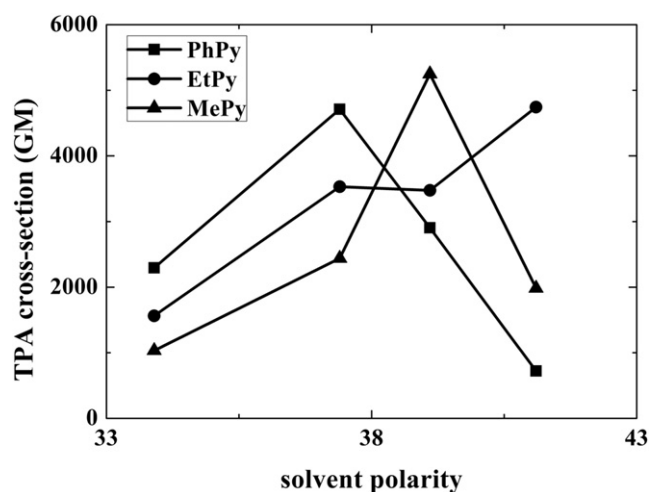
**Fig. 4.** Relationship between the maximum of TPA cross-sections and solvent polarity.

the TPEF measurement on it in higher polar solvents, but a decrease in TPA cross-section in higher polar solvent could be predicted for its same molecule structure as MePy and PhPy.

## 4. Conclusion

Three novel organic fluorescent molecules with little but significant differences were designed and synthesized and their TPA properties were studied. The results clearly show how the conjugated length, ICT efficiency and solvent polarity cooperatively tune the TPA cross-section of the organic compounds with centrosymmetric D-π-A-π-D molecular structure. The expand of conjugated system could largely enhance the TPA activities of TPA molecules in solvents with low polarity, while the donor strength plays a more important role in highly polar solvents due to the cooperative impact of environment on ICT effect. We also found that the nonmonotonic relationship between TPA cross-sections of these compounds and the solvent polarities was probably due to the double sided effect on the ICT efficiency. Moreover, these compounds show moderate fluorescent quantum yield and large Stokes shift, which suggest the potential wide application of PhPy and its derivatives in the environmental detection. The success in designing dyes with large TPA cross-sections by linking appropriate acceptor and donor group can also be a useful method for development of new TPA molecules.

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