# 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-$\pi$-A-$\pi$-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 $\pi$-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-$\pi$-A structure, quadrupolar molecules with structures of D-$\pi$-A-$\pi$-D or A-$\pi$-D-$\pi$-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-$\pi$-A-$\pi$-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 $\delta$. These molecules exhibit large $\delta$ 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 $\delta$ 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-$\pi$-A-$\pi$-D which is appropriate for effective ICT effect. Although
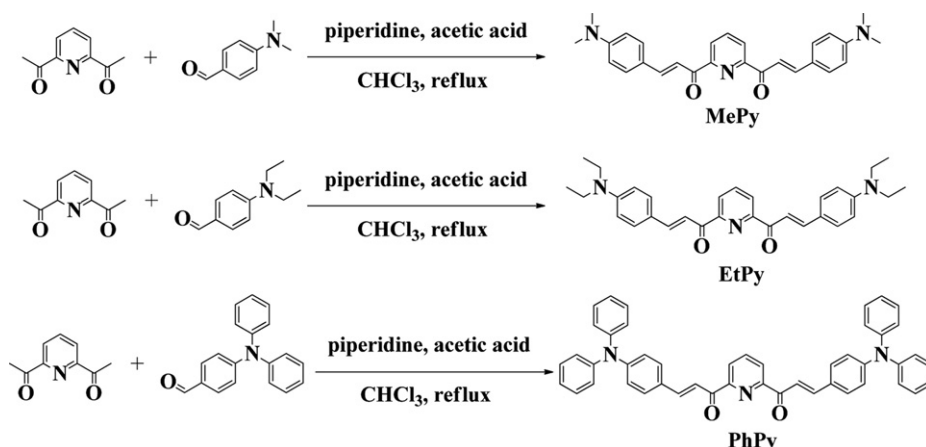


**Scheme 1.** Synthesis of MePy, EtPy and PhPy.