

A new building block, bis(thiophene vinyl)-pyrimidine, for constructing excellent two-photon absorption materials: synthesis, crystal structure and properties†

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Two new molecules (**Py1** and **Py2**) of D- π -A- π -D motif, where the - π -A- π - moiety is bis(thiophene vinyl)-pyrimidine as a building block, have been designed and synthesized *via* the Knoevenagel and Suzuki coupling reactions. The X-ray single crystal structure analysis of **Py1** showed good coplanarity in the whole building block. Their two-photon absorption (2PA) properties were measured by two-photon induced fluorescence techniques with a mode-locked Ti: sapphire pulsed laser in the range of 700–940 nm. Both **Py1** and **Py2** exhibited large cross-section values of 1702 and 1879 GM, respectively, no matter whether the peripheral donor is weak or strong. The results demonstrate that bis(thiophene vinyl)-pyrimidine is a new building block for constructing molecules with effective 2PA.

1. Introduction

Two-photon absorption (2PA) is defined as the electronic excitation of a molecule induced by a simultaneous absorption of a pair of photons of the same or different energy.¹ It was predicted theoretically by Maria Göppert-Mayer in 1931,² and was demonstrated experimentally in 1961,³ soon after the invention of the laser. Over recent years, molecular 2PA has attracted great interest owing to the potential applications including optical limiting, optical data storage, up converted lasing, fluorescence microscopy, and microfabrication,^{4–10} that have stimulated the designing of materials with specific 2PA performance. In this context, organic compounds have presented great possibilities due to their flexibility in terms of structural engineering, allowing the development of molecules with tunable optical nonlinearities in accord with the target applications.¹¹ To date, some efficient molecular design strategies were put forward to provide guidelines on the development of organic conjugated molecules with improved 2PA. Three main classes of molecules were found to be potential 2PA chromophores: dipolar type with a donor- π bridge-acceptor (D- π -A) motif,^{12–15} quadrupolar type with a D- π -D, A- π -A, D- π -A- π -D or A- π -D- π -A motif,^{16–18} and octupolar type with three-branched dipoles.^{19,20} Indeed, symmetrical quadrupolar structures have experimentally and theoretically demonstrated enhanced 2PA cross sections that are approximately an order of magnitude greater than those of

dipolar analogues.^{21–24} In addition, quadrupolar compounds have higher fluorescence quantum yields relative to corresponding dipolar compounds, most likely due to cancellation of D-A dipoles which otherwise would tend to induce charge transfer quenching of fluorescence.²⁵ What is more, in quadrupolar systems, D- π -D and D- π -A- π -D structures are generally more effective for 2PA than A- π -A and A- π -D- π -A systems.²⁶ Therefore, we focus on the design and synthesis of molecules with D- π -A- π -D structures to gain high 2PA materials in this paper.

Our group²⁷ and Z. Huang's group²⁸ have reported some 2PA molecules based on a pyrimidine core (Fig. 1a), with cross-section (δ) values of about 300–700 GM, where the conjugation bridge is a styryl unit. On the other hand, thiophene as an electron-rich moiety has been widely used in organic semiconductors, which have shown good chemical stability and

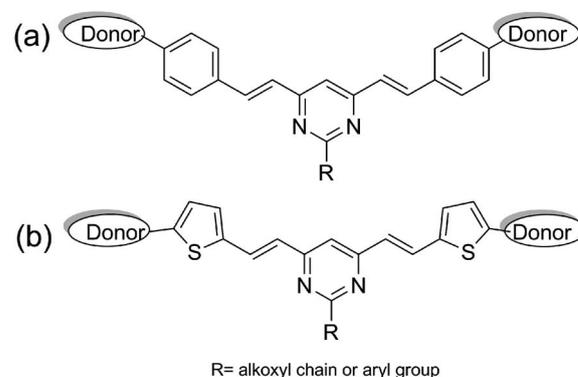


Fig. 1 Structure of pyrimidine-based chromophores: (a) reported in the literature; (b) reported in this paper.

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charge transport ability. In addition, it is easy to modify the thiophene unit by common chemical means to give various derivatives. As a result, in this paper we replace the styryl unit with a thiophene vinyl, and thus a new building block for 2PA materials is obtained, as shown in Fig. 1b. Thiophene is a five-membered ring, so there will be less steric hindrance and better planarity when terminal donors are connected to the central bis(thiophene vinyl)-pyrimidine moiety to shape conjugated molecules, compared to the reported bis(styryl)-pyrimidine based compounds. A hexyl group was introduced into the pyrimidine unit in order to increase the solubility of the molecule. Two representative molecules, **Py1** and **Py2**, with a weak and strong donor respectively, were synthesized and studied here. Both of them showed much larger cross-sections compared to the similar bis(styryl)-pyrimidine based molecules when measured by a two-photon induced fluorescence technique.

2. Experimental

2.1 Materials

THF was dried over and distilled from K–Na alloy under an atmosphere of argon. Compounds **1**,^{29,30} **2**,³¹ **4**,³² and **5**³³ were synthesized according to the literature. Other reagents were commercially obtained from Sinopharm Chemical Reagent Co. (Shanghai, China).

2.2 Instruments

¹H NMR and ¹³C NMR spectra were measured on a MECUYR-VX300 spectrometer. Elemental analysis of carbon, hydrogen, and nitrogen was performed on a Vario EL III microanalyzer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C min⁻¹ from 30 to 500 °C. The single crystal data were collected using a Bruker SMART Diffractometer equipped with a CCD detector (graphite-monochromated Mo-K α radiation λ = 0.71073 Å) at 298(2) K. Cyclic voltammetry (CV) was carried out in nitrogen purged anhydrous CH₂Cl₂ solution at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consisted of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s⁻¹. Formal potentials were calculated as the average of cyclic voltammetric anodic and cathodic peaks. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. Two-photon excited fluorescence was measured using a mode-locked Ti: sapphire femtosecond pulsed laser (Chameleon Ultra II, Coherent Inc.). The pulse width and repetition rate were 140 fs and 80 MHz, respectively.

2.3 Synthetic procedures

2.3.1 4,6-Bis(E)-2-(5-bromothiophen-2-yl)vinyl)-2-(hexyloxy)-pyrimidine (M). A mixture of Compounds **1** (1.52 g, 9.53 mmol) and **2** (4 g, 20.9 mmol) in 50 mL of ethanol was stirred under argon at room temperature for 0.5 h. Hydrochloric acid (4 mL, 3.0 mol L⁻¹) was added stepwise to the reaction mixture which was then refluxed for 48 h. The solvent was neutralized with 0.5 mol L⁻¹ sodium carbonate, and then the solution was filtrated. The residue was washed by water, ethanol and ethylether in turn. After drying in a vacuum, the crude product (Compound **3**) was used in the next reaction without further purification.

Compound **3** (1.4 g, 2.98 mmol), n-hexyl bromide (0.6 mL, 4.2 mmol) and K₂CO₃ (2 g, 15 mmol) were dissolved in 30 mL of DMF, and the mixture was stirred under argon at 80 °C for 24 h. After the reaction, the solution was poured into water and extracted with CH₂Cl₂ three times. The combined organic phase was dried over Na₂SO₄. When the solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether, 1/2) to give the product **M** as a yellow solid. Yield: 1.0 g, 61%. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 7.93 (d, J = 15.6 Hz, 2H), 7.02–6.97 (m, 4H), 6.75 (s, 1H), 6.67 (d, J = 15.3 Hz, 2H), 4.44 (t, J = 6.6 Hz, 2H), 1.89–1.82 (m, 2H), 1.52 (m, 2H), 1.37 (m, 4H), 0.91 (m, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ [ppm]: 165.1, 164.1, 142.7, 130.8, 129.3, 128.7, 125.0, 114.4, 111.1, 67.4, 31.5, 28.8, 25.6, 22.5, 13.9. Anal. Calcd for C₂₂H₂₂Br₂N₂OS₂: C, 47.66; H, 4.00; N, 5.05. Found: C, 47.88; H, 3.77; N, 5.03.

2.3.2 Synthesis of Py1. Compound **M** (0.2 g, 0.36 mmol), **4** (0.16 g, 0.76 mmol) and Pd (PPh₃)₄ (18 mg, 2 mol %) were mixed in a Schlenk tube (50 mL), which was then filled with argon under vacuum line. 2 mL of aqueous solution of K₂CO₃ (2 mol L⁻¹) and 10 mL of THF were added to the mixture by syringe. The reaction was carried out at 65 °C for 24 h. After the reaction cooled to room temperature, it was poured into water, and extracted with chloroform. The organic phase was collected and dried over Na₂SO₄. When the solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether, 1/2) and then recrystallized in dichloromethane and petroleum to give the product **Py1** as a deep yellow solid. Yield: 0.16 g, 80%. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 8.01 (d, J = 15.6 Hz, 2H), 7.26–7.24 (m, 4H), 7.14–7.13 (m, 4H), 7.06–7.05 (m, 2H), 6.77–6.72 (m, 3H), 4.45 (t, J = 7.2 Hz, 2H), 1.90–1.85 (m, 2H), 1.57 (m, 2H), 1.38 (m, 4H), 0.92 (m, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ [ppm]: 165.5, 164.5, 140.3, 139.0, 137.2, 130.7, 129.5, 128.2, 125.3, 124.8, 124.5, 111.5, 67.7, 31.8, 29.2, 26.0, 22.8, 14.3. Anal. Calcd for C₃₀H₂₈N₂OS₄: C, 64.25; H, 5.03; N, 5.00. Found: C, 64.01; H, 4.77; N, 4.84.

2.3.3 Synthesis of Py2. Compound **Py2** was obtained by the same procedure as that for **Py1** except that Compound **5** (0.28 g, 0.76 mmol) was used as one reactant. The product was purified by column chromatography (silica gel, CHCl₃/petroleum ether, 1/1) and then recrystallized in chloroform and ethanol to give the product **Py2** as a red solid. Yield: 0.27 g, 85%. ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 8.01 (d, J = 15.9 Hz, 2H), 7.48 (d, J = 8.1 Hz, 4H), 7.31–7.26 (m, 10H), 7.17–7.06 (m, 18H), 6.78–6.73 (m, 3H), 4.46 (t, J = 6.9 Hz, 2H), 1.90–1.85 (m, 2H), 1.56 (m, 2H), 1.38

(m, 4H), 0.92 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ [ppm]: 164.8, 160.7, 148.1, 147.5, 146.2, 140.0, 131.2, 130.1, 129.6, 127.8, 126.9, 125.0, 124.4, 123.6, 123.4, 123.2, 111.2, 67.7, 31.9, 29.2, 26.0, 22.9, 14.3. Anal. Calcd for $\text{C}_{58}\text{H}_{50}\text{N}_4\text{OS}_2$: C, 78.88; H, 5.71; N, 6.34. Found: C, 79.28; H, 6.07; N, 6.26.

3. Results and discussion

3.1 Synthesis and characterization

The synthetic routes of the new compounds are illustrated in Scheme 1. The pyrimidine ring of Compound **1** is electron-deficient, so the methyl groups connected to the ring are highly reactive. As a result, Compound **3** was easily obtained by the Knoevenagel reaction. The poor solubility of **3** in common solvents makes it hard to purify. Therefore the crude product of **3** was directly used in the next step without further purification, and an n-hexyl group was connected to the pyrimidine core by nucleophilic substitution to give monomer **M** in good yield. **Py1** and **Py2** were obtained by the Suzuki coupling reaction with $\text{Pd}(\text{PPh}_3)_4$ as catalyst and K_2CO_3 as base in the solvent of THF/ H_2O at 65°C for 24 h. The X-ray single crystal structure of **Py1** was determined. The new compounds were fully characterized by ^1H -NMR, ^{13}C -NMR, and elemental analysis. The thermal properties of the two compounds were evaluated by TGA. As shown in Fig. 2, excellent thermal stabilities were manifested in

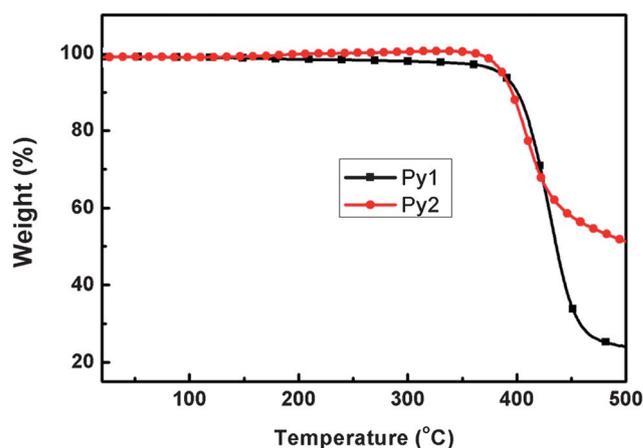
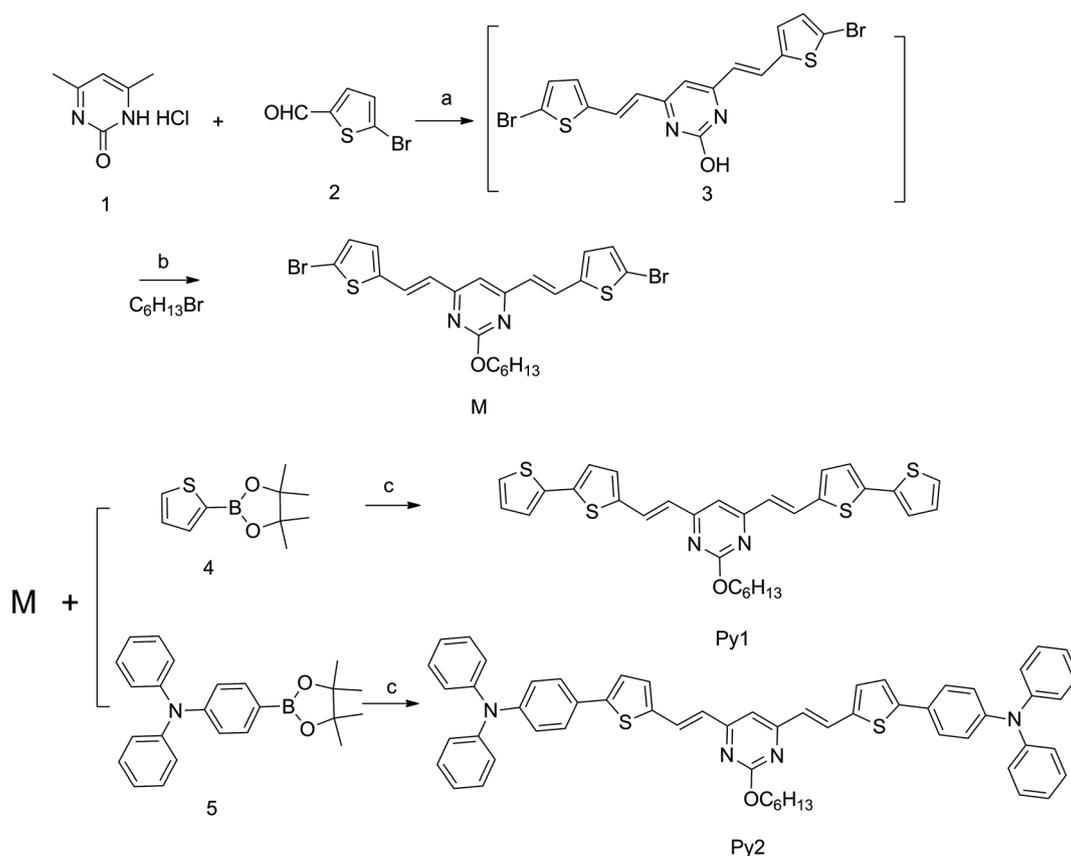


Fig. 2 TGA plots of **Py1** and **Py2** with a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 atmosphere.

their TGA profiles showing a decomposition temperature of about 385°C (5% weight loss) for both molecules.

3.2 Single crystal structure features of **Py1**

The X-ray single crystal structure of **Py1** is shown in Fig. 3.³⁴ Two double bonds connecting the thiophene and pyrimidine unit are both in the *trans*-configuration, which favors the building



Scheme 1 The synthetic routes of **Py1** and **Py2**. Conditions (a) EtOH, HCl (3M), reflux, 12 h; (b) $\text{C}_6\text{H}_{13}\text{Br}$, DMF, K_2CO_3 , 80°C , 24 h; (c) $\text{Pd}(\text{PPh}_3)_4$, THF, K_2CO_3 (2M, aq), 65°C , 24 h.

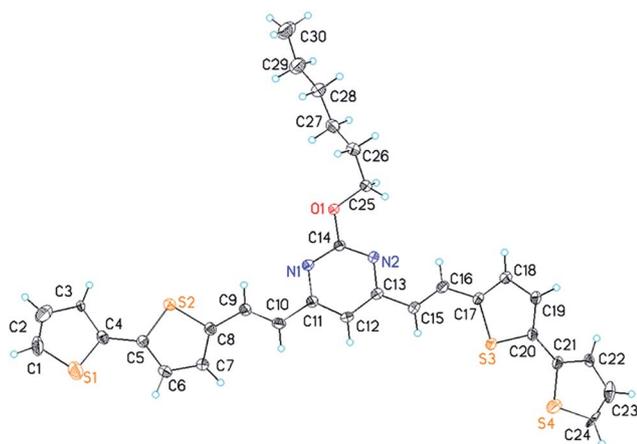


Fig. 3 Single crystal structure plot of **Py1**.

block, bis(thiophene vinyl)-pyrimidine, aligning in almost the same plane with small dihedral angles. The dihedral angles between the terminal thiophene groups and the building block are also small with a value of about 8° , indicating that it is effective for the building block to be modified and produce various planar molecules. The alkyl chain is spread out, and does not affect the conjugation degree of the compound. As a result, the building block shows good conjugation and coplanarity, which can be beneficial to π -delocalization of the system and lead to large 2PA cross-sections. It may also imply that the building block is useful for constructing some semiconducting materials for organic thin-film transistors (OTFTs) and polymer solar cells (PSCs) where a coplanar $-\pi-A-\pi-$ bridge is necessary.

3.3 Linear absorption and single-photon-excited fluorescence

The normalized single-photon absorption and emission spectra of the compounds in chloroform are presented in Fig. 4, and the spectroscopic properties are summarized in Table 1. Owing to the intramolecular charge transfer (ICT) from the peripheral donors to the central pyrimidine acceptors, two molecules covered a wide absorption range. The absorption maximum of

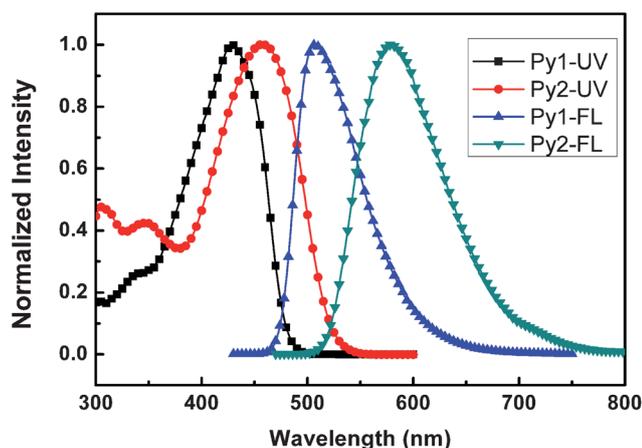


Fig. 4 UV-Vis absorption and single-photon fluorescence spectra of **Py1** and **Py2** in chloroform.

Table 1 One- and two-photon properties of the 2PA dyes

Compound	λ_{abs} (nm) ^a	λ_{PL} (nm) ^b	$\Delta\nu$ (cm ⁻¹) ^c	Φ^d	λ_{2PA} (nm) ^e	δ_{max}^f (GM)	δ_{max}^g (MW)
Py1	428	507	3640	0.10	810	1702	3.47
Py2	459	579	4515	0.50	820	1879	2.31

^a The absorption maxima in the one-photon absorption spectrum. ^b The emission maxima in the one-photon fluorescence spectrum. ^c Stokes shift ($\Delta\nu = 1/\lambda_{\text{abs}} - 1/\lambda_{\text{PL}}$). ^d Fluorescent quantum yield in chloroform. ^e Wavelength of maximum 2PA cross-sections. ^f The peak of 2PA cross-section in 10^{-50} cm⁴ s photon⁻¹ (GM). ^g

Py2 was 31 nm red-shifted compared to that of **Py1**, because the terminal triphenylamine unit in **Py2** was a stronger donor than the thiophene unit in **Py1** leading to more effective ICT in the D- π -A- π -D system. This phenomenon was also verified in their fluorescence spectra, where the emission maximum of **Py2** was 72 nm red-shifted. The fluorescent quantum yields of the two compounds were measured in chloroform with fluorescein (in 0.1 M NaOH) as the reference molecule. The values are 0.10 for **Py1** and 0.50 for **Py2**, so a two-photon induced fluorescence technique method can be used to study their 2PA properties.

3.4 Electrochemical behaviors

Cyclic voltammetry was employed to investigate the redox behaviors of the chromophores and estimate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. Fig. 5 shows the cyclic voltammograms of the two compounds in 0.1 mol L⁻¹ Bu₄NPF₆ CH₂Cl₂ solution. All reported potentials were calibrated against the ferrocene/ferrocenium (Fc/Fc⁺) couple, which was used as the internal standard. The HOMO energies were estimated to be -5.20 and -5.10 eV for **Py1** and **Py2**, respectively, according to the equation $\text{HOMO} = -(E_{\text{onset}}^{\text{ox}} + 4.8)$ eV.^{35,36} **Py2** showed a higher HOMO energy level owing to its more electron donating property of the terminal triphenylamine unit. The LUMO energies were estimated from the optical band gaps and the HOMO levels. The data are summarized in Table 2.

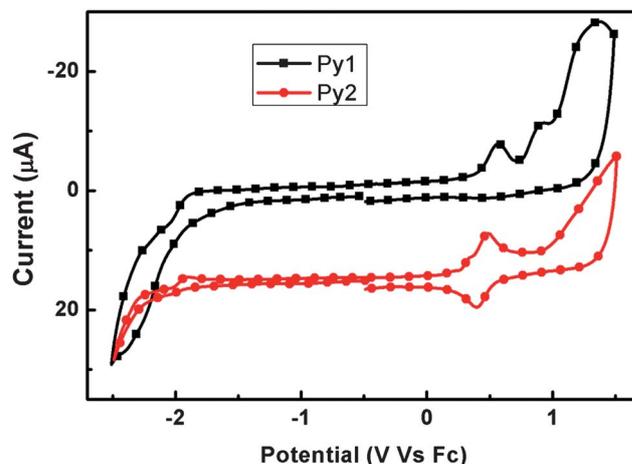


Fig. 5 The cyclic voltammograms of **Py1** and **Py2** in CH₂Cl₂ solution.

Table 2 Energy levels of **Py1** and **Py2**

	$E_{\text{onset}}^{\text{ox}}$ (V)	HOMO (eV)	LUMO (eV)	$E_{\text{g}}^{\text{opt}}$ (eV) ^a
Py1	0.4	-5.20	-2.61	2.59
Py2	0.3	-5.10	-2.72	2.38

^a $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$ (eV), wherein λ_{onset} is the wavelength of its onset absorption edge in the longer wavelength direction.

3.5 2PA properties

The 2PA behaviour of **Py1** and **Py2** were measured by a two-photon induced fluorescence technique in chloroform, which is direct and very convenient. In order to eliminate contributions from the excited-state absorption, a femtosecond (~140 fs) pulsed laser was used for the measurement. A well characterized 2PA chromophore, Rhodamine B (1.0×10^{-4} M in EtOH), was used as a reference.

The 2PA cross-section was calculated by the following equation,³⁷ which is simplified from ref. 38 by neglecting the refractive index correction term.

$$\delta_s = \delta_r(F_s/F_r)(\Phi_r/\Phi_s)(c_r/c_s)$$

where the subscripts 's' and 'r' stand for the sample and reference molecules respectively. F is the integrated fluorescence intensity measured at the same power as the excitation beam. Φ is the fluorescence quantum yield. The number density of the molecules in the solution was denoted c . δ_r is the 2PA cross-section of the reference molecule.

Both the chromophores were stable under the test conditions, and no obvious change was observed in the UV-vis spectra after completion of the 2PA measurements. The two-photon excitation spectra of **Py1** and **Py2** in CHCl_3 (1×10^{-4} M) are displayed in Fig. 6. We tested the 2PA cross-sections from 700 nm to 940 nm with an interval of 20 or 10 nm. The cross-section values are summarized in Table 1. The 2PA cross-section per unit mass (δ/MW) is also compiled for comparison. The maximal cross-

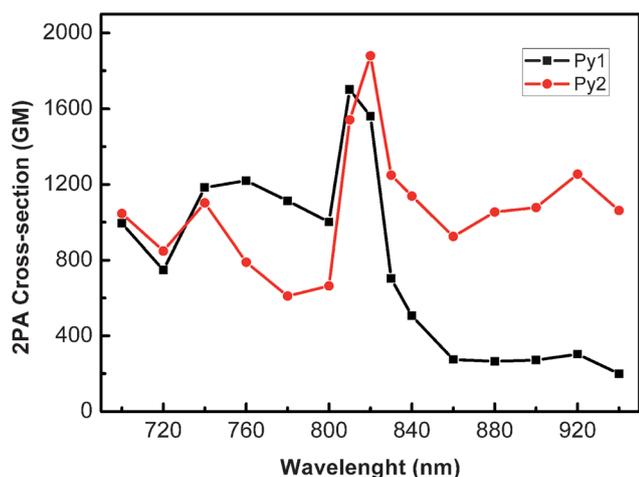


Fig. 6 Two-photon excitation spectra of **Py1** and **Py2** in CHCl_3 with $c = 1.0 \times 10^{-4}$ M.

sections of the two compounds were obtained at excitation wavelengths of 810 and 820 nm for **Py1** and **Py2**, respectively. **Py2** showed a value of 1879 GM, a little larger than that of **Py1** with a value of 1702 GM, due to the stronger electron-donating ability of triphenylamine. The δ/MW value of **Py2** was smaller than that of **Py1**, because of the larger molecular weight of **Py2**. As reported in our earlier papers,²⁷ bis(styryl)-pyrimidine based molecules, that have a similar D- π -A- π -D motif to **Py1** but with even stronger donors (diethyl amino group), showed 2PA cross-sections of only 300–700 GM. However, **Py1** with a much weaker donor (thiophene) exhibits a much larger cross-section (1702 GM), which is a twofold to fivefold increase. The results indicated that our system, using bis(thiophene vinyl)-pyrimidine based chromophores, is very effective to gain a higher 2PA performance.

4. Conclusion

We successfully synthesized two D- π -A- π -D type chromophores, **Py1** and **Py2**, constructed by a new building block, bis(thiophene vinyl)-pyrimidine, for 2PA materials. The structure of **Py1** was determined by X-ray single crystal diffraction, and it revealed that the building block showed good coplanarity, which can enhance the 2PA. As predicated, both compounds showed large cross-section values, 1702 GM for **Py1** and 1879 GM for **Py2**. The results indicate that the new building block is very useful to construct higher 2PA materials compared to the reported building block of bis(styryl)-pyrimidine. It may also imply that the building block is useful for constructing some other kinds of organic optoelectronic molecules where a strong and coplanar - π -A- π - bridge is necessary.

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