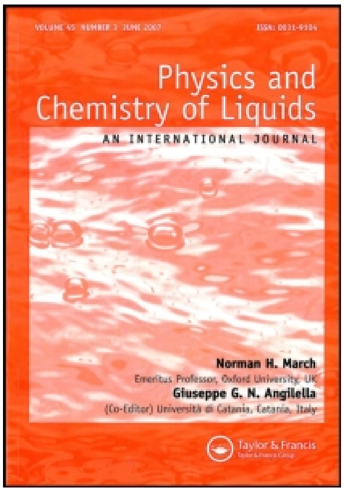

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Facile synthesis, optical properties and theoretical calculation of a novel bent-shaped two-photon absorption chromophore

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A novel bent-shaped derivative, 2-thiomethyl-4,6-*bis*(4-*N*,*N*-methylaminostyryl) pyrimidine (TMAP) has been successfully synthesised and fully characterised by elemental analysis, IR, ^{1}H NMR and MS. The molecule possesses D–π–A–π–D structures. Dimethylamino is used as the donor (D), and the pyrimidine ring is used as the acceptor (A). One- and two-photon absorption and fluorescence in various solvents were experimentally investigated. The chromophore shows intense single-photon excited fluorescence (SPEF) and two-photon excited fluorescence (TPEF) in a wide spectral range, with the spectral peak position of the SPEF being basically the same as that of the TPEF. The chromophore combines well with peak TPA cross-sections (up to 352.0 GM) and broad TPA bands throughout the whole 700–900 nm range and high-fluorescence quantum yields could thus be obtained. The theoretical and experimental studies indicate the charge transfer from donor to acceptor.

Keywords: synthesis; theoretical calculation; bent-shaped; two-photon absorption

1. Introduction

Molecular two-photon absorption (TPA) has attracted growing interest over recent years owing to its application in various fields, such as two-photon excited fluorescence (TPEF) microscopy [1], three-dimensional optical data storage [2,3], microfabrication [4], two-photon up-converted lasing [5], high-resolution three-dimensional imaging of biological systems [6], photon dynamic therapy [7], and so forth. To fully realise these applications, an intense worldwide effort has been focused on the research of design organic materials with high-TPA cross-section (δ) at desirable wavelengths [8–13]. Marder, Perry and Webb found that *bis*(styryl)benzene derivatives with donor–acceptor–donor (D–A–D) and acceptor–donor–acceptor (A–D–A) structural motifs, which are rod-like quadrupolar molecules, show exceptionally large TPA cross-sections [8,13]. Some studies showed that the bent-shaped quadrupolar molecule two-photon absorbing chromophores exhibit large TPA cross-sections [14,15].

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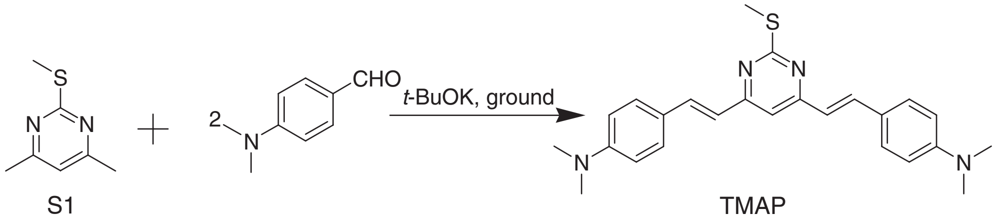

Scheme 1. Synthesis of TMAP.

Bent-shaped molecules can develop more polar structures than rod-like molecules, even if the molecules are achiral. Their unique properties result from restricted molecular rotation around the long axis. Spontaneous electric polarisation of bent-core materials is usually higher than polarisation of rod-like materials. Most of the synthesised bent-shaped molecules are imine derivatives [16] that show poor chemical stability at elevated temperature, and under an electric field or light illumination. Mongin *et al.* [17] showed that a bent-shaped quadrupolar structure significantly increases the TPA cross-section in comparison to a rod-like counterpart of chromophores with biphenyl or fluorine central units.

In this context, we have implemented a molecular-engineering approach towards the bent-core quadrupolar molecule with large TPA cross-section. By following the route for molecular TPA optimisation proposed by Marder and collaborators [8,13], we focused on the optimisation of quasi-one-dimensional quadrupolar systems, that is, symmetrical conjugated molecules bearing two electron-releasing (D) or electron-withdrawing (A) end groups [18–20]. The structure was built from symmetrical grafting onto a conjugated core of two elongated conjugated rods bearing either a D or A end-group. The central building blocks were selected as more or less rigid units that may assist quadrupolar intramolecular charge transfer (CT) by acting as an acceptor core. We selected 2-thiomethyl-4,6-dimethylpyrimidine central units, which allow the tuning of the electronic delocalisation along the conjugated backbone in the ground state by modulation of the twist angle between the two halves of the molecules [21]. It should be noted that pyrimidine derivatives have been intensively investigated as electroluminescent materials in the past [21,22] owing to the planarity they provide. By applying solvent-free reaction, a novel bent-shaped TPA chromophore based on pyrimidine has been prepared (Scheme 1). These solvent-free reactions are important not only for their efficiency and simplicity, but also because they are green and sustainable procedures, which is very important for large-scale production. The optical properties and the calculated TPA cross-section of the chromophore have been systematically investigated. The novel chromophore possesses potential application prospects due to their simple preparation and efficient initiating properties.

2. Experimental

2.1. *Instrument*

All chemicals used were of analytical grade. The solvents were purified by conventional methods before use. Elemental analyses were performed with a Perkin–Elmer 240B instrument. Mass spectrum was determined with a Micromass GCT-MS (EI source). IR spectra were recorded on a NEXUS 870 (Nicolet) spectrophotometer in the

4000–400 cm^{-1} region with samples prepared as KBr pellets. ^{1}H NMR spectrum was obtained on a Bruker Avance 400 NMR spectrometer in CDCl$_3$ solution (TMS as internal standard in NMR). Electronic spectra were recorded on a UV-3600 spectrophotometer. The one-photon fluorescence spectra measurement is performed with use of an F-2500 Spectro-fluorophotome. Spectra are recorded between 400 and 800 nm using a photomultiplier tube as detector. The TPEF spectra were measured using a mode-locked Ti: sapphire laser (Coherent Mira900F) as a pump source, with pulse duration of 200 fs, a repetition rate of 76 MHz and a single-scan streak camera (Hamamastu Model C5680-01) as the recorder, together with a monochromator.

2.2. *Synthesis*

The synthetic route of 2-thiomethyl-4,6-*bis*(4-*N*,*N*-methylaminostyryl)pyrimidine (TMAP) is described in Scheme 1.

TMAP: At room temperature, *t*-BuOK (5.6 g, 50 mmol) was placed into a dry mortar and milled to very small size, then S1 (1.54 g, 10 mmol) and *N*,*N*-methylaminobenzaldehyde (3.28 g, 22 mmol) were added and mixed. The mixture was milled vigorously for about 20 min. The mixture became sticky and was then continuously milled for 10 min. After completion of the reaction (monitored by TLC), the mixture was dispersed in 100 mL methanol. The residual solid was filtered and recrystallised from anhydrous dichloromethane/methanol, to give pale-yellow micro-crystals TMAP (3.01 g, yield 72%). Anal. Calcd for $C_{25}H_{28}N_4S$: C, 72.08; H, 6.77; N, 13.45. Found: C, 72.15; H, 6.59; N, 13.49%. IR (KBr, cm^{-1}) selected bands: 2971 (w), 2921(w), 1600 (m), 1556 (s), 1147 (m), 671 (w), 524 (w). ^{1}H NMR: (400 MHz, CDCl$_3$), δ (ppm): 2.67 (s, 3H), 3.02 (s, 12H), 6.70 (d, $J = 8.8$ Hz, 4H), 6.79 (d, $J = 16.0$ Hz, 2H), 6.85 (s, 1H), 7.49 (d, $J = 8.8$ Hz, 4H), 7.80 (d, $J = 16.0$ Hz, 2H). MS, *m*/*z* (%): 416.16 ([M$^+$], 100).

3. Results and discussion

3.1. *Theoretical calculation*

The TPA cross-section which can be directly comparable with the experimental measurement is defined as

$$\sigma_{tp} = \frac{4\pi^2 a_0^5 \alpha}{15 c_0} \frac{\omega^2 g(\omega)}{\Gamma_{\mathrm{f}}} \delta_{tp}. \tag{1}$$

Here α_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, ω is the photon energy of the incident light, $g(\omega)$ denotes the spectral line profile and Γ_{f} is the lifetime broadening of the final state, which is assumed to be 0.1eV [23]. δ_{tp} is written as follows [24]:

$$\delta_{tp} = \sum_{\alpha\beta} \left[F \times S_{\alpha\alpha} S_{\beta\beta}^* + G \times S_{\alpha\beta} S_{\alpha\beta}^* + H \times S_{\alpha\beta} S_{\beta\alpha}^* \right], \tag{2}$$

where *F*, *G* and *H* are coefficients dependent on polarisation of the light. $S_{\alpha\beta}$ is the TPA transition matrix element for the two-photon resonant absorption of identical energy, and can be written as [25]:

$$S_{\alpha\beta} = \sum_j \left[\frac{\langle 0|\mu_\alpha|j\rangle\langle j|\mu_\beta|f\rangle}{\omega_j - \omega_f/2} + \frac{\langle 0|\mu_\beta|j\rangle\langle j|\mu_\alpha|f\rangle}{\omega_j - \omega_f/2} \right], \tag{3}$$

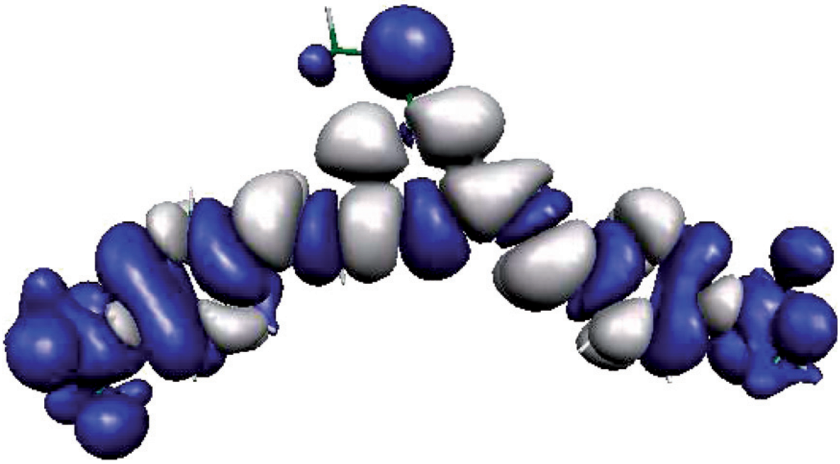

Figure 1. Density difference between the CT and ground states of TMAP in the gas phase. The blue and grey parts represent the electron loss and gain, respectively, upon excitation (colour online).

where $\alpha, \beta \in (x, y, z)$, ω_j and ω_f are the excitation frequency for the intermediate state $|j\rangle$ and the final state $|f\rangle$, respectively.

The most straightforward approach to analyse optical properties of molecules is the response theory [26], which can provide an analytical solution for the TPA cross-section. The equilibrium geometries of molecules in gas phase are optimised by use of the Gaussian package (GAUSSIAN-98, http://www.gaussian.com) at the hybrid density functional theory (DFT/B3LYP) level with a 6-31G* basis set. The TPA properties are calculated by use of the response theory at DFT level implemented in DALTON (http://www.kjemi.uio.no/software/dalton/) [27]. The optimal two-photon excitation (TPE) wavelength for TMAP is 790 nm. The energy gap of the TPA band is 3.34 eV. The largest calculated TPA cross-section of TMAP is 964.7 GM ($1\,\mathrm{GM} = 10^{-50}\,\mathrm{cm}^4\,\mathrm{s\,photon}^{-1}$). In order to demonstrate the CT process, we tried to make a theoretical investigation. Our *ab initio* calculation at the time-dependent hybrid density functional theory B3LYP level coded in the GAUSSIAN package for TMAP showed that the first excited state is the CT state. We have plotted the charge density difference between the ground state and CT state for TMAP in the gas phase (Figure 1), which is visualised by use of the MOLEKEL program (http://www.cscs.ch/molekel/). The blue and grey parts represent the electron gain and loss, respectively (colour online). It can be seen that upon excitation, charge is mainly transferred from two branches to the third branch. From Figure 1, it can be seen that upon excitation, charges are mainly transferred from the donor side to the acceptor side. In the CT state, there are more electrons on the acceptor side, indicating that the molecule could be giving away its electron to initiate the reaction. However, whether the photo-induced electron-transfer reaction can be energetically feasible needs to be further theoretically investigated.

3.2. *Linear absorption and one-photon excited fluorescence*

The linear optical properties for TMAP in different solvents are listed in Table 1. We observe that the chromophore displays an intense absorption in the near UV–visible

Table 1. Single-photon-related photophysical properties of the chromophore TMAP in several different polar solvents.

Compound	Solvents	$\lambda_{\max}^{(1a)}$ (nm)[a]	$\lambda_{\max}^{(1f)}$ (nm)[b]	Φ[c]	$\Delta\nu$ (cm^{-1})[d]
TMAP	Toluene	428	486	0.65	3586
	Ethyl acetate	428	522	0.60	2376
	Ethanol	434	556	0.23	1856
	Acetonitrile	434	562	0.25	1905
	DMF	440	564	0.21	2001

Notes: [a]Peak position of the longest absorption band. [b]Peak position of SPEF, excited at the absorption maximum. [c]Quantun yields determined by using Rhodamine B as standard. [d]Stokes' shift.

blue region. Its absorption and emission range can be tuned by playing on the polarity of solvents. In addition, the chromophore exhibits good fluorescence quantum yields in different polar solvents. The absorption maxima of the chromophores is located around 430 nm in five solvents, respectively. The one-photon absorption and fluorescence spectra of TMAP are shown in Figure 2. The concentration of the solution was 1.0×10^{-6} mol L^{-1}. One can also observe that the relative fluorescence intensities of TMAP show significant differences among the different solvents, as shown in Figure 2(b). This result suggests that solvents have influence on the values of the energy gap between the ground state and the first excited state in the linear emission process, which is similar to the result obtained in linear absorption studies. This can be attributed to the fact that the excited state may possess higher polarity than that of the ground state, since there is strong dipole–dipole interaction between the solute and solvent. In all the five solvents, TMAP shows significant charge redistribution, which indicates that the lone pair of electrons is largely delocalised into the large π-system in the excited state. But with the increasing polarity of the solvent, the SPEF spectra show remarkable bathochromic shifts. The quantum yields (Φ) of TMAP in different solvents were determined by using Rhodamine B as the standard. Upon increasing the solvent polarity, the fluorescence quantum yield drops significantly. This spectroscopic behaviour reflects the intramolecular CT character of the S_1 state [12,28–30], and is strongly supported by a theoretical calculation on the molecular orbital.

In order to further demonstrate the influence of solvents on fluorescence, Table 1 lists the Stokes' shift of the chromophore in solvents with different polarity. Stokes' shift is defined as the loss of energy between absorption and re-emission of light, which is the result of several dynamic processes. These processes include losses due to dissipation of vibrational energy, redistribution of electrons in the surrounding solvent molecules induced by the altered dipole moment of the excited chromophore, reorientation of the solvent molecules around the excited state dipole, and specific interactions between the chromophore and the solvent or solutes. The Lippert equation is the most widely used equation to describe the effects of the physical properties of the solvent on the emission spectra of chromophore [31]:

$$\Delta\nu = \nu_{\text{abs}} - \nu_{\text{em}} = (2/cha^3)\Delta f(\mu_e - \mu_g)^2 + \text{const.}$$

In this equation, *h* is Planck's constant, *c* is the speed of light and *a* is the radius of the cavity in which the chromophore resides. The wavenumbers of the absorption and

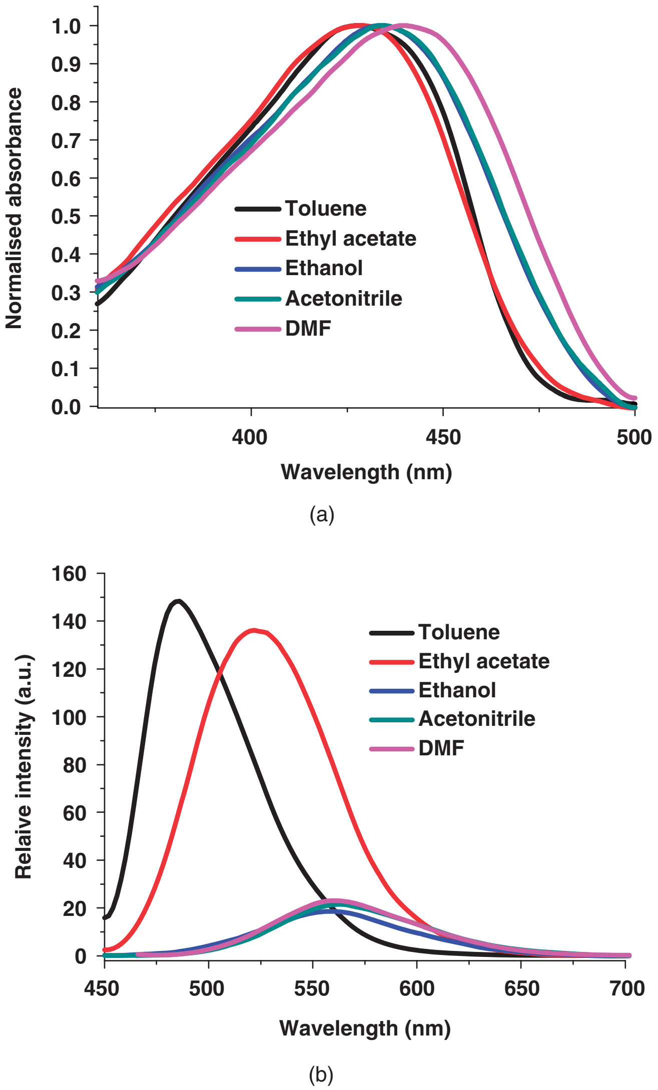

Figure 2. One-photon absorption (a) and fluorescence (b) spectra of TMAP in different solvents.

emission are ν_a and ν_f (in cm^{-1}). In aprotic solvents, Stokes' shifts are approximately proportional to the orientational polarisability. Obvious shifts, larger than expected, are found in protic solvents, even though hydrogen bonds between the chromophores and the protic solvents [32,33].

3.3. *Two-photon excited fluorescence*

As shown in Figure 3, the emission intensity of TMAP was investigated at 800 nm. The linear dependence on the square of input laser power suggests that it is a TPE mechanism. Detailed experiments reveal that from 700 to 900 nm the peak position in the TPEF spectra

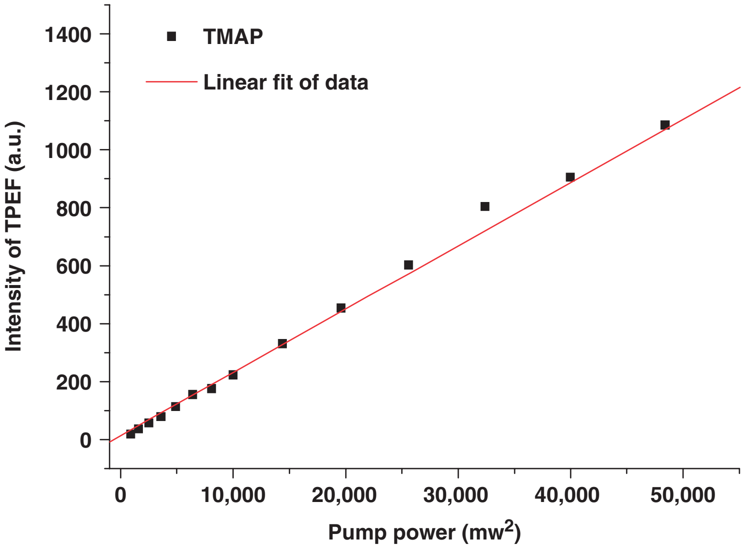

Figure 3. Output fluorescence intensity (I_{out}) *vs*. the square of input laser power $(I_{\mathrm{in}})^2$ for TMAP in acetonitrile. Excitation carried out at 800 nm, with $C = 1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$.

of the chromophore is independent of the excitation wavelengths, but the emission intensities of TPEF are dependent over that range (700–900 nm).

By tuning the pump wavelengths incrementally from 700 to 900 nm, while keeping the input power fixed and then recording TPEF intensity, TPE spectra are obtained in acetonitrile with the concentration of $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$; the TPE spectra of TMAP are shown in Figure 4. The measurements were noted in the experimental section. TPEF allows direct measurement of the TPEF-action cross-section. This method has been recognised to be more reliable than non-linear transmission measurements [34]. We emphasise that experiments were conducted in the femtosecond regime, thereby preventing the contributions from linear non-resonant absorption or from excited-state absorption that are known to lead to artificially enhanced ‘effective’ TPA cross-sections if measurements are conducted in the nanosecond regime. The spectra displays one excitation peak, and this feature is similar to that observed in the linear absorption spectra, expect that the wavelengths are roughly doubled. The optimal excitation wavelength for TMAP is 790 nm. As shown in the inset of Figure 4, the peak positions of TPEF spectra of TMAP are significantly shifted compared to those of the corresponding SPEF in solution. This can be explained by the effect of reabsorption.

Two-photon absorption cross-sections (σ) have been measured using two photon-induced fluorescence techniques in acetonitrile by using the following equation [35]:

$$\delta = \delta_{\mathrm{ref}} \frac{\Phi_{\mathrm{ref}}}{\Phi} \frac{c_{\mathrm{ref}}}{c} \frac{n_{\mathrm{ref}}}{n} \frac{F}{F_{\mathrm{ref}}}.$$

Here, the subscript ‘ref’ stands for the reference molecule. δ is the 2PA cross-section value, c is the concentration of solution, n is the refractive index of the solution, F is the TPEF integral intensities of the solution emitted at the exciting wavelength and Φ is the fluorescence quantum yield. The δ_{ref} value of reference was taken from the literature.

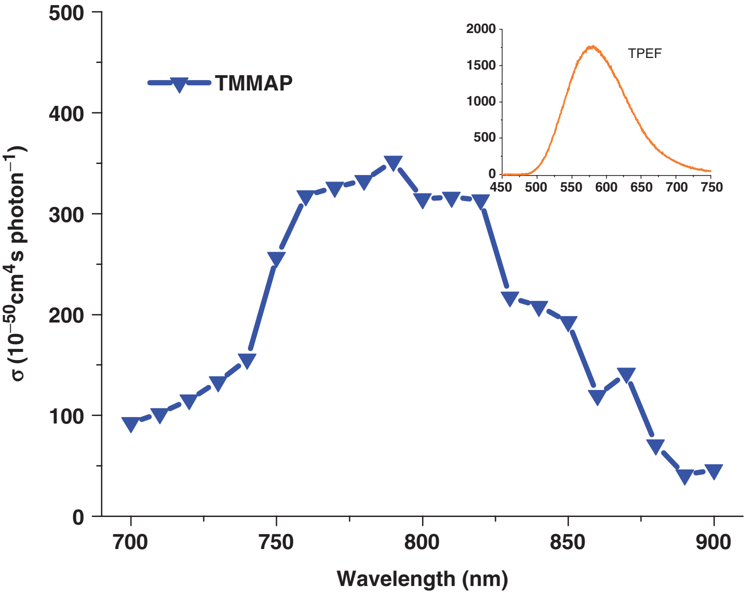

Figure 4. TPE spectra of TMAP in acetonitrile ($C = 1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$). The inset shows TPEF spectra of TMAP.

By referencing the TPA cross-section of fluorescein to the literature [36], the obtained largest TPA cross-sections of TMAP was 352.0 GM at 790 nm. Due to the ideal molecules used in the calculation, the experimental values are smaller than the calculation results.

4. Conclusions

This systematic study of the absorption, photoluminescence, TPA properties, simple preparation and theoretical calculation on the bent-shaped quadrupolar chromophore allowed us to derive structure–property relationships of great significance for both spectral tuning and amplification of the molecular TPA in the NIR spectral range. The chromophore shows good one- and two-photon excited fluorescence behaviours. The influence of solvents was studied in detail. Experimental data and theoretical calculation provide a coherent picture. With these findings, bent-shaped quadrupolar chromophores combining well-peaked TPA cross-sections (up to 352.0 GM), broad TPA bands throughout the whole 700–900 nm range and high-fluorescence quantum yields could, thus, be obtained. Such compounds are of particular interest for TPEF microscopy, as well as optical data storage in the visible and NIR regions.

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