

Synthesis and Characterization of New Y-shaped Fluorophores with an Imidazole Core

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Abstract Four new y-shaped fluorophores of 4- {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]-1-H-imidazole-2-yl}benzotrinitrile **1a**, 2-phenyl- {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]-1-H-imidazole} **1b**, 2- (9-anthryl)- {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl] }-1-H-imidazole **1c** and 2- (4-nitrophenyl) – {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl] -1-H-imidazole **1d** which bear an imidazole core, were synthesized for the first time via intermediate 1,6-Bis(2,4,6-trimethoxyphenyl)hexa-1,5-diene-3,4-dione with different aldehydes. The structures of the new derivatives were confirmed by ¹H NMR, ¹³C NMR and FT-IR. The optical properties such as absorption and emission maxima, Stokes' shift and quantum yield values were investigated in solvents of toluene, tetrahydrofuran and acetonitrile. The products show intense emission maxima in the range of 440–630 nm. The imidazole derivatives exhibited excellent photostabilities.

Keywords Imidazole · Fluorophores · Y-shaped molecules · Quantum yield

Introduction

Second-order nonlinear optical (NLO) materials have been advancing for a few decades as a promising field with important applications in the domain of opto-electronics and photonics [1–16]. Organic NLO molecules have proven to be of great interest in recent years due to their extremely large optical nonlinearities as compared to most of the inorganic crystals that are transparent in the visible region [15]. One of

the major challenges in the area of organic NLO molecules is to design and synthesize second-order NLO chromophores which, simultaneously, exhibit large hyperpolarizability (β), good optical transparency and high thermal stability. Most attempts to design molecules with large β have relied upon end capping an optimal π -conjugated bridge with different donors and acceptors [16]. However, this enhancement of β is always accompanied with a red-shift in the λ_{\max} peak, which is so-called nonlinearity-transparency trade-off. Y-shaped chromophores show improved trade-off compared to classical one-dimensional dipolar chromophores, due to the contribution of the large, off-diagonal β tensorial components.

The emergence of applications of two-photon technology to up-converted lasing, optical power limiting, photodynamic therapy and generation of singlet oxygen, three-dimensional micro-fabrication and data storage, and three-dimensional fluorescence microscopy, has drawn an increasing interest in the design and development of two-photon absorbing molecules with large nonlinear absorptivity to generate a high-energy excited state with relatively low laser energy [1, 3, 8, 10]. The new structure–property correlation is being sought to establish guidance for molecular design since the ability of organic molecules to simultaneously absorb two photons to reach the excited state depends on molecular structures. Several strategies based on schemes such as D- π -D, D- π -A- π -D, and A- π -D- π -A (D: electron donating group, A: electron accepting group, and π : conjugated pathway) have been found to enhance the δ value, the two-photon absorptivity [4, 5, 10]. In the comparison with single-photon fluorescent probes, two photon fluorescent probes excited in the near infrared (NIR) region show very low background light, weak photo damage, highly transmission at the low incident intensity [10, 11]. These characters can make such two-photon chromophores suitably act as fluorescent labels in bio imagine, and the cases of two-

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photon excited fluorescence sensors for ions have been reported [8, 10].

In order to be compatible with existing semiconductor processing technology, organic NLO chromophores for device application are required to be highly thermally stable for sustaining the processing and operating temperatures [7]. Heterocyclic imidazoles based on NLO chromophores have received increasing interest due to their excellent thermal stability, improved molecular nonlinearity and high solubility [1,6,8–11].

We report here the synthesis of four new Y-shaped derivatives of 4- {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]-1-H-imidazole-2-yl}benzonitrile **1a**, 2-phenyl-{4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]-1-H-imidazole} **1b**, 2-(9-anthryl)-{4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]-1-H-imidazole} **1c** and 2-(4-nitrophenyl)-{4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]-1-H-imidazole} **1d**, having an imidazole core. Their optical properties such as absorption maxima, fluorescence emission maxima, Stokes' shifts, singlet energies, fluorescence quantum yield values and photostabilities in tetrahydrofuran, toluene and acetonitrile were also investigated.

Experimental

General

All solvents were of analytical grade and purchased from Merck (Darmstadt, Germany), Fluka (Buchs, Switzerland), and Riedel (Seelze, Germany). All melting points were measured in sealed tubes using an electrothermal digital melting points apparatus (Southend, UK) and are uncorrected. Infrared spectra were recorded on a Perkin Emler (Massachusetts, USA) FTIR infrared spectrometer (spectrum BX-II). ¹H-NMR and ¹³C-NMR spectra were recorded on Bruker AC500 (500 MHz) (Coventry, UK). Ultra performance liquid chromatography coupled to mass spectrometry detection (UPLC-MS) was performed with a Waters Alliance systems (gradient mixtures of acetonitrile/water) equipped with Acquity UPLC columns. The Waters systems consisted of a Waters Separations Module 2695, a Waters Diode Array detector 996, a LCT Premier XE mass spectrometer, and a Waters Mass Detector ZQ 2000. Analytical and preparative thin layer chromatography (TLC) were carried out using silica gel 60F₂₅₄ (Merck). Column chromatography was carried out by using 70–230 mesh silica gel (0.063–0.2 mm, Merck). UV/visible absorption spectra were recorded with Shimadzu UV-1601 spectrophotometer (Tokyo, Japan). All fluorescence measurements were undertaken by using Varian-Carry Eclipse spectrofluorimeter (Mulgrave, Australia). 1-hydroxypyrene-3,6,8-trisulfonate trisodium salt (HPTS) purchased from Fluka was used as reference standard for fluorescence quantum yield calculations of **1a–d**.

Synthesis

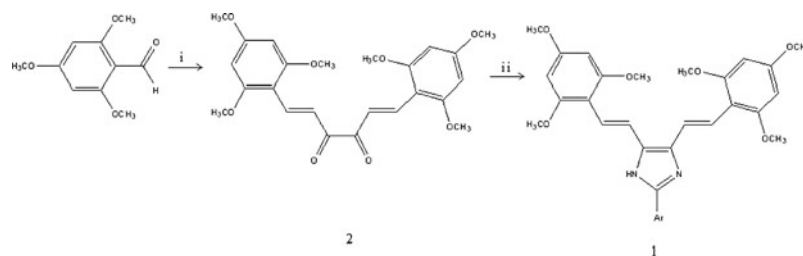
1,6-Bis(2,4,6-trimethoxyphenyl)hexa-1,5-diene-3,4-dione (**2**). 2,3-butanedione (0.36 ml, 5 mmol) was added to the methanol (20 ml) solution of 2,4,6-trimethoxybenzaldehyde (2 g, 10 mmol). Then, piperidine (0.56 ml, 5.56 mmol) and glacial acetic acid (0.32 ml, 5.55 mmol) were added as catalyst to the stirred mixture. The mixture was refluxed for 6 h under nitrogen atmosphere, during which orange crystals started to form. After cooling to room temperature, the crystals were filtered and washed with methanol for several times to obtain the title compound with a yield of 30 %; mp 223–224 °C; FT-IR (KBr): ν_{\max} 1650, 1551, 1207 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 3.88 (s, 6H), 3.90 (s, 12 H), 6.33 (s, 4H), 7.38 (d, *J*=8.3 Hz, 2H), 8.02 (d, *J*=8.3 Hz, 2H); ¹³C NMR (500 MHz, DMSO-d₆): δ 53.7, 56.4, 91.4, 105.1, 119.6, 138.3, 161.9, 164.2, 193.2; HRMS (ESI-TOF): *m/z* Anal. Calcd. for C₂₄H₂₇O₈ (M⁺ + H)=443.1706; Found: 443.1712.

General methods for the synthesis of **1a–d** Glacial acetic acid (1.91 ml) and **2** (0.1 g, 0.23 mmol) were added to a 50 mL round bottom flask. The mixture was allowed to stir at room temperature until the entire solid was dissolved. Aldehyde (0.23 mmol) was then added, followed by the addition of ammonium acetate (0.28 g, 3.6 mmol). The reaction mixture was magnetically stirred at 118 °C under nitrogen atmosphere for 6 h and then cooled to room temperature. The mixture was poured into 19.1 ml of ice water and neutralized by 10% of sodium carbonate solution to a pH 6.5–7.0. The formed precipitate was filtered and washed with water for several times. Then redissolved in ethyl acetate and purified by column chromatography using ethyl acetate / hexane as eluent.

4-{4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]-1-H-imidazole-2-yl}benzonitrile (**1a**) Yield 49 %; mp 174 °C; FT-IR (KBr): ν_{\max} 3204, 2223, 1630, 1454, 1328, 1204, cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): 3.84 (s, 6H), 3.84 (s, 12H), 6.56 (s, 4H), 7.33 (d, *J*=8.3 Hz, 2H), 7.48 (d, *J*=3.4 Hz, 2H), 7.51 (d, *J*=3.4 Hz, 2H), 7.58 (d, *J*=8.3 Hz, 2H), 12.65 (s, 1H); ¹³C NMR (500 MHz, DMSO-d₆): δ 55.2, 55.8, 91.2, 105.2, 118.1, 119.1, 123.6, 125.7, 130.8, 132.4, 132.8, 144.4, 149.7, 159.1, 161.9; HRMS (ESI-TOF): *m/z* Anal. Calcd. for C₃₂H₃₂N₃O₆ (M⁺ + H)=554.2291; Found: 554.2354.

2-phenyl-{4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]-1-H-imidazole} (**1b**) Yield 78 %; mp 135 °C; FT-IR (KBr): ν_{\max} 3200, 1602, 1454, 1327, 1203; ¹H NMR (500 MHz, DMSO-d₆): 3.83 (s, 6H), 3.91 (s, 12H), 6.32 (s, 4H), 7.27 (d, *J*=8.2 Hz, 2H), 7.41–7.38 (m, 5H), 7.51 (d, *J*=4.4 Hz, 2H), 12.36 (s, 1H); ¹³C NMR (500 MHz, DMSO-d₆): δ 55.2, 55.9, 91.2, 117.4, 125.5, 126.4, 127.6, 128.2, 128.5, 130.4, 136.1, 146.4, 158.1, 163.3; HRMS (ESI-TOF): *m/z* Anal. Calcd. for C₃₁H₃₃N₂O₆ (M⁺ + H)=529.2339; Found: 529.2189.

Scheme 1 Synthesis of **1a-d**. i) butane-2,3-dione, piperidine; ii) ArCHO, NH₄Ac, glacial HAC



	1a	1b	1c	1d
Ar				

2- (9-anthryl)-{4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]}-1-H-imidazole (**1c**) Yield 62 %; mp 159 °C; FT-IR (KBr): ν_{\max} 3250, 1602, 1454, 1329, 1203; ¹H NMR (500 MHz, DMSO-d₆): 3.82 (s, 6H), 3.87 (s, 12H), 6.56 (s, 4H), 7.15 (d, *J*=8.8 Hz, 2H), 7.64-7.50 (m, 9H), 7.76 (d, *J*=4.01 Hz, 2H), 12.75 (s, 1H); ¹³C NMR (500 MHz, DMSO-d₆): δ 55.3, 55.8, 91.1, 117.1, 125.6, 126.0, 126.6, 126.7, 126.8, 128.0, 128.4, 129.1, 130.7, 130.9, 139.3, 144.5, 159.0, 159.8; HRMS (ESI-TOF): *m/z* Anal. Calcd. for C₃₉H₃₇N₂O₆ (M⁺ + H)=629.2652; Found: 629.2784.

2- (4-nitrophenyl) - {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]}-1-H-imidazole (**1d**) mp 145 °C; FT-IR (KBr): ν_{\max} 3200, 1690, 1513, 1454, 1326, 1203, cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 3.841(s, 6H), 3.92 (s, 12 H), 6.56 (s, 4H), 7.37 (d, *J*=8.3 Hz, 2H), 7.50 (d, *J*=3.5 Hz, 2H), 7.53 (d, *J*=3.6 Hz, 2H), 7.60 (d, *J*=8.2 Hz, 2H), 12.78 (s, 1H); ¹³C NMR (500 MHz, DMSO-d₆): δ 55.4, 55.9, 91.2, 107.3, 124.2, 126.0, 131.3, 135.9, 140.7 144.1, 149.7, 159.0, 159.8, 160.5; HRMS (ESI-TOF): *m/z* Anal.

Calcd. for C₃₁H₃₂N₃O₈ (M⁺ + H)=574.2189; Found: 574.2299.

Results and Discussion

Scheme 1 describes the synthesis of 4- {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]}-1-H-imidazole-2-yl} benzonitrile **1a**, 2-phenyl- {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]}-1-H-imidazole **1b**, 2- (9-anthryl)- {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]}-1-H-imidazole **1c** and 2- (4-nitrophenyl) - {4,5-[2,2'-Bis(2,4,6-trimethoxyphenyl)vinyl]}-1-H-imidazole **1d**, with a yield from 49 to 86 %, via intermediate 1,6-Bis(2,4,6-trimethoxyphenyl)hexa-1,5-diene-3,4-dione **2**, which was obtained by the reaction of 2,3-butanedione with 2,4,6- trimethoxybenzaldehyde. The structures of **2** and **1a-d** were confirmed by ¹H and ¹³C NMR, FT-IR and UPLC.

Next, the optical properties of **1a-d** were investigated (Table 1, Figs. 1, 2 and 3). The absorption maxima of **1a-**

Table 1 Absorption and fluorescence emission data for compounds **1a-d** maximum absorption wavelengths ($\lambda_{\max}^{\text{abs}}$, nm), maximum emission wavelengths ($\lambda_{\max}^{\text{em}}$, nm), molar extinction coefficients (ϵ , l mol⁻¹ cm⁻¹), Stokes' shifts, $\Delta\lambda$ (nm), singlet energies, E_s (kcal mol⁻¹), and fluorescence quantum yields, Φ in toluene, tetrahydrofuran, and acetonitrile

Compound	Solvent	$\lambda_{\max}^{\text{abs}}$	ϵ_{\max}	$\lambda_{\max}^{\text{em}}$	$\Delta\lambda$	E_s	Φ
1a	Toluene	336	9600	486	150	58.7	0.1295
	Tetrahydrofuran	383	20300	519	136	55.0	0.3888
	Acetonitrile	382	18200	547	165	52.2	0.2577
1b	Toluene	340	13400	440	100	64.8	0.3169
	Tetrahydrofuran	375	18800	466	91	61.2	0.5420
	Acetonitrile	356	20000	462	106	61.8	0.5731
1c	Toluene	385	18300	579	194	49.3	0.1281
	Tetrahydrofuran	383	31800	589	206	48.4	0.0301
	Acetonitrile	382	23000	452	70	63.1	0.0115
1d	Toluene	391	8800	630	239	45.3	0.0123
	Tetrahydrofuran	388	32600	445	57	64.1	0.0073
	Acetonitrile	386	29700	445	59	64.1	0.0061

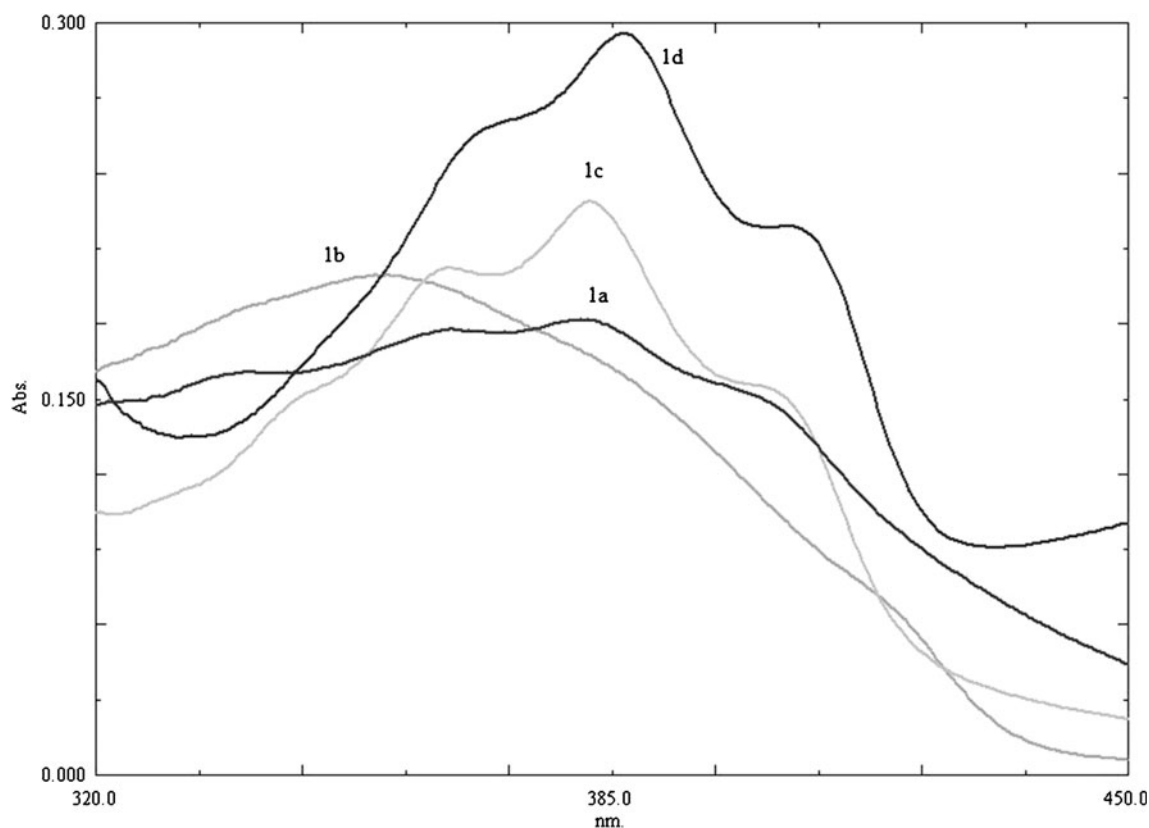


Fig. 1 Absorption spectra of **1a-d** in acetonitrile

d were observed in the 336–391 nm range. Figure 1 shows the absorption spectra of **1a-d** in acetonitrile. In the absorption maxima of **1a** and **1b** bathochromic shifts were observed as the solvent polarity increases, while in the absorption maxima of **1c** and **1d** there are slight hypsochromic shifts indicating that the absorption maxima were not affected so much by solvent polarity for **1c** and **1d** (Fig. 1). While **1a** and **1b** show the longest wavelength absorption maxima in tetrahydrofuran, **1c** and **1d** show the longest wavelength absorption maxima in toluene (Table 1). Among all the derivatives **1**, **1d** has the longest absorption maxima at

391 nm (in toluene). This can be attributed to the enhanced conjugation of **1d** due to the strong electron accepting nitro group.

The maximum emission wavelengths of **1a-d** are in the range of 440–630 nm as summarized in Table 1. Figure 2 depicts the fluorescence spectra of **1a-d** in toluene. In fluorescence maxima of **1a** and **1b** bathochromic shifts were observed as the solvent polarity is increased, while for **1c** and **1d** dramatical hypsochromic shifts were observed as the solvent polarity is increased. Among all the derivatives **1**, **1d** has the longest absorption maxima at 630 nm (in toluene)

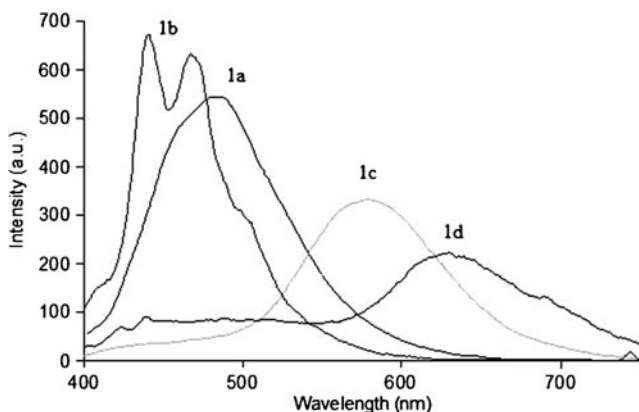


Fig. 2 Emission spectra of **1a-d** in toluene

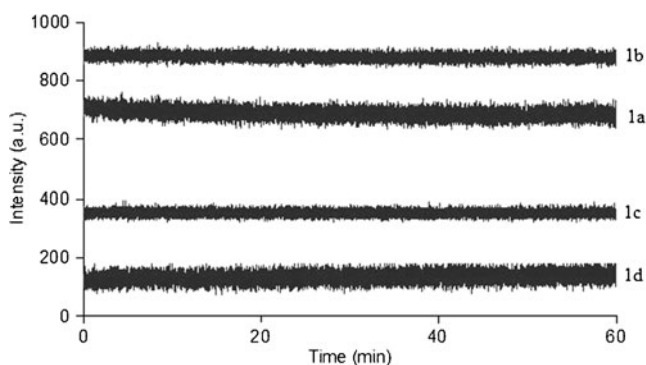


Fig. 3 The photostability test results of **1a-d** in tetrahydrofuran after 1 h of monitoring

(Table 1, Fig. 2). This can be attributed to the enhanced conjugation of **1d** due to the strong electron accepting nitro group. Thus, also the largest Stokes' shift value is observed for **1d** as 239 nm (in toluene) among the derivatives **1** (Table 1). The Stokes' shift values for **1a** and **1b** increase slightly as the solvent polarity is increased according to the results obtained for toluene and acetonitrile, while the Stokes' shift values for **1c** and **1d** decrease dramatically as the solvent polarity increases according to the results obtained for toluene and acetonitrile. The high Stokes' shift values observed for **1a-d**, confers the advantage of better spectral resolution in emission based studies and is a desired property in commercially important fluorophores.

The quantum yield values of the synthesized compounds were also investigated. HPTS was used as reference quantum yield standard $\lambda_{\text{ex}}=400$ nm, quantum yield=1. Fluorescence quantum yields (Φ_F) were determined by the formula [17]:

$$\Phi = \Phi_{\text{std}} \times (F A_{\text{std}} \eta^2) / (F_{\text{std}} A \eta_{\text{std}}^2)$$

where F and F_{std} are the areas under the fluorescence emission curves of the samples and the standard, respectively. A and A_{std} are the respective absorbance of the samples and standard at the excitation wavelength, respectively, and η and η_{std} the refractive indices of solvents used for the samples and standard, respectively. **1a** and **1b** have promising quantum yield values up to 0.5731 and the fluorescent efficiencies are enhanced in polar solvents (Table 1). In addition, the highest quantum yield values were observed for **1b** indicating that the introduction of a phenyl group drastically increase the quantum yield value. For **1c** and **1d**, quantum yield values decreased, indicating that the introduction of an anthryl and nitro moieties onto Y-shaped molecules skeleton decreased the quantum yield values. For **1c** and **1d** quantum yield values decreased as the solvent polarity increased. This can be attributed to the fact that highly polar solvents provide **1c** and **1d** freedom to rotate and vibrate which can be possible sources of the non-radiative transitions.

The photostabilities of **1a-d** were recorded with a steady-state spectrofluorimeter in toluene, tetrahydrofuran and acetonitrile (Fig. 3). The data were acquired at their maximum emission wavelengths after exposure to xenon arc lamp for 1 h monitoring. All derivatives exhibited excellent photostability in three of the solvents studied.

Conclusion

In summary, we achieved four new Y-shaped fluorophores with emission maxima in the range of 440 – 630 nm. **1a** and

1b exhibited promising fluorescent efficiency, while **1c** and **1d** which contain anthryl and nitro moieties exhibited low fluorescent ability. All derivatives displayed large Stokes' shift values and excellent photostabilities. The remarkable photophysical properties of the derivatives **1a-b**, would make them candidates for the development of fluorescent sensors for different applications.

References

- Feng K, Boni LD, Misoguti L, Mendonça CR, Meador M, Hsu FL, Bu XR (2004) Y-shaped two-photon absorbing molecules with an imidazole—thiazole core. *Chem Commun* 10:1178–1180
- Frederiksen PK, Jorgensen M, Ogilby PR (2001) Two-photon photosensitized production of singlet oxygen. *J Am Chem Soc* 123:1215–1221
- Belfield KD, Ren X, Van Stryland EW, Hagan DJ, Dubikovsky V, Miesak EJ (2000) Near-IR two-photon photoinitiated polymerization using a fluorone/amine initiating system. *J Am Chem Soc* 122:1217–1218
- Albota M, Beljonne D, Bredas L-J, Ehrlich JE, Fu J-Y, Heikal AA, Hess SE, Kogej T, Levin MD, Marder SR, McCord-Maughon D, Perry JW, Röckel H, Rumi M, Subramaniam G, Webb WW, Wu X-L, Xu C (1998) Design of organic molecules with large two-photon absorption cross sections. *Science* 281:1653–1656
- Rumi M, Ehrlich JE, Heikal AA, Perry JW, Barlow S, Hu Z, McCord-Maughon D, Parker TC, Röckel H, Thayumanavan S, Marder SR, Beljonne D, Bredas J-L (2000) Structure–property relationships for two-photon absorbing chromophores: bis-donor diphenylpolyene and bis(styryl)benzene derivatives. *J Am Chem Soc* 122:9500–9510
- Santos J, Mintz EA, Zehnder O, Bosshard C, Bu XR, Günter P (2001) New class of imidazoles incorporated with thiophenevinyl conjugation pathway for robust nonlinear optical chromophores. *Tetrahedron Lett* 42:805–808
- Marder SR, Perry JW (1994) Nonlinear optical polymers: discovery to market in 10 years. *Science* 263:1706–1707
- Zhang M, Li M, Li F, Cheng Y, Zhang J, Yi T, Huang C (2008) A novel y-type, two-photon active fluorophore: synthesis and application in ratiometric fluorescent sensor for fluoride anion. *Dyes Pigments* 77:408–414
- Wang J, Mason R, VanDerveer D, Feng K, Bu XR (2003) Convenient preparation of a novel class of imidazo [1,5-a] pyridines: decisive role by ammonium acetate in chemoselectivity. *J Org Chem* 68:5415–5418
- Zhang M, Li M, Zhao Q, Li F, Zhang D, Zhang J, Yi T, Huang C (2007) Novel y-type two-photon active fluorophore: synthesis and application in fluorescent sensor for cysteine and homocysteine. *Tetrahedron Lett* 48:2329–2333
- Ren J, Wang S-M, Wu L-F, Xu Z-X, Dong B-H (2008) Synthesis and properties of novel y-shaped NLO molecules containing thiazole and imidazole chromophores. *Dyes Pigments* 76:310–314
- So B-K, Lee K-S, Lee S-M, Lee MK, Lim TK (2003) Synthesis and linear/nonlinear optical properties of new polyamides with DANS chromophore and silphenylene groups. *Opt Mater* 21:87–92
- Koeckelberghs G, Sioncke S, Verbiest T, Persoons A, Samyn C (2003) Synthesis and properties of chiral helical chromophore-functionalised polybinaphthalenes for second-order nonlinear optical applications. *Polymer* 44:3785–3794

14. Heck J, Dabek S, Meyer-Friedrichsen T, Wong H (1999) Mono- and dinuclear sesquifulvalene complexes, organometallic materials with large nonlinear optical properties. *Coord Chem Rev* 190:1217–1254
15. Xie H-Q, Liu Z-H, Huang X-D, Guo J-S (2001) Synthesis and non-linear optical properties of four polyurethanes containing different chromophore groups. *Eur Polym J* 37:497–505
16. Jen AK-Y, Cai Y, Bedworth PV, Marder SR (1997) Synthesis and characterization of highly efficient and thermally stable diphenylamino-substituted thiophene stilbene chromophores for nonlinear optical applications. *Adv Mater* 9:132–135
17. Ozturk G, Förstel M, Ergun Y, Alp S, Rettig W (2008) Photophysical and complexation properties of benzenesulfonamide derivatives with different donor and acceptor moieties. *J Fluoresc* 18:1007–1019