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Dyes and Pigments 75 (2007) 641–646
DYES and PIGMENTS
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Synthesis and two-photon absorption properties of 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles

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Received 30 June 2006; accepted 11 July 2006
Available online 8 September 2006

Abstract

Two symmetrical 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles that exhibit strong two-photon absorption and enhanced two-photon excited fluorescence were designed and synthesized based on ''push-core-pull-core-push'' molecules built from embedding electron-transporting 1,3,4-oxadiazole in aromatic conjugated system through Wittig–Horner reaction. Pumped by nanosecond laser at 800 nm, strong up-conversion emissions with the central wavelength at 507 nm (green) of 2,5-bis[4-(2-*N*,*N*-diphenylaminostyryl)phenyl]-1,3,4-oxadiazole and 475 nm (blue) of 2,5-bis[4-{2-(3-*N*-ethylcarbazolyl)vinyl}phenyl]-1,3,4-oxadiazole in the solution of $CHCl_3$ have been observed. Their two-photon absorption cross-sections obtained by nonlinear transmission method are 107×10^{-48} cm^4 s $photon^{-1}$ and 66×10^{-48} cm^4 s $photon^{-1}$. A very effective energy transfer from the excited terminal units to the π-conjugated bridging units of the 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles is the dominant contribution to the two-photon absorption.

Keywords: 1,3,4-Oxadiazole derivatives; Two-photon excited fluorescence; Two-photon absorption cross-sections

1. Introduction

Extensive research was being conducted during the past decade to develop organic materials with large two-photon absorption cross-sections owing to their wide-ranging applications such as two-photon up-conversion lasing, optical power limiting, two-photon fluorescence excitation microscopy, three-dimensional optical data storage, and photodynamic therapy [1–8]. Two-photon absorption is a nonlinear optical process wherein a molecule simultaneously absorbs two photons of energy hν (or of energy hν_1 and hν_2) to access an excited state of energy 2hν (or hν_1 + hν_2) in the presence of intense laser pulse. In recent years, a considerable amount of effort has been devoted to two-photon absorption materials and devices that produce a short wavelength emission when pumped with long wavelength. A variety of compounds including donor–bridge–acceptor (D–π–A) dipoles [9–11], donor–bridge–donor (D–π–D) quadrupoles [12–14], multibranched compounds [15–18], dendrimers, and octupoles have been synthesized and researched. A number of factors influence the TPA magnitude, among which are electronic delocalization and intramolecular charge-transfer phenomena.

It has been observed recently that symmetrical conjugated molecules with two electron-donating end groups exhibit high nonlinear absorption properties, and large two-photon absorption cross-section values, σ_2. This enhancement in σ_2 was correlated to an intramolecular charge redistribution that occurs between the ends and the center of the molecules. Increasing the conjugation length of the molecule or increasing the extent of symmetrical charge from the ends to the middle results in a large increase of σ_2 [19,20].

The aim of this paper is to investigate synthesis and TPA properties of V-style geometry D–π–A–π–D chromophores, where terminal electron-donor group is triphenylamine

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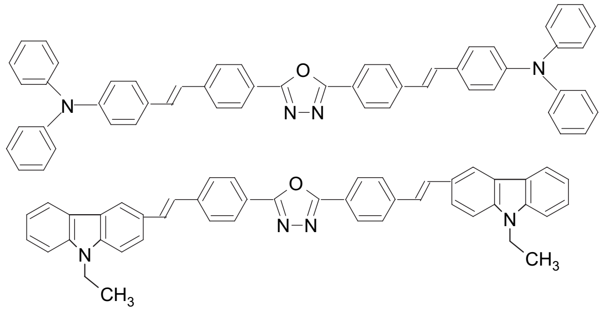
doi:10.1016/j.dyepig.2006.07.017

trigonal moiety or carbazole group, and the center of the molecules is electron-acceptor group of oxadiazole segment. In this paper, we first briefly describe the synthesis of 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles. Linear absorption and fluorescence properties of the chromophores, in particular, the solvatochromic behavior of one-photon spectra, are then thoroughly explored through experimental results. Two-photon excited fluorescence is measured and two-photon absorption cross-section evaluated.



2. Experimental

2.1. Materials

Triphenylamine was purchased from Acros Organics. Potassium *tert*-butoxide and triethyl phosphite were commercially available. Triethyl phosphite was distilled carefully before use. Potassium *tert*-butoxide was prepared before use. All solvents were of anhydrous grade after further purification (Scheme 1).

2.2. Synthesis

2.2.1. 1,2-Bis(4-methylbenzoyl)-hydrazine (**3**)

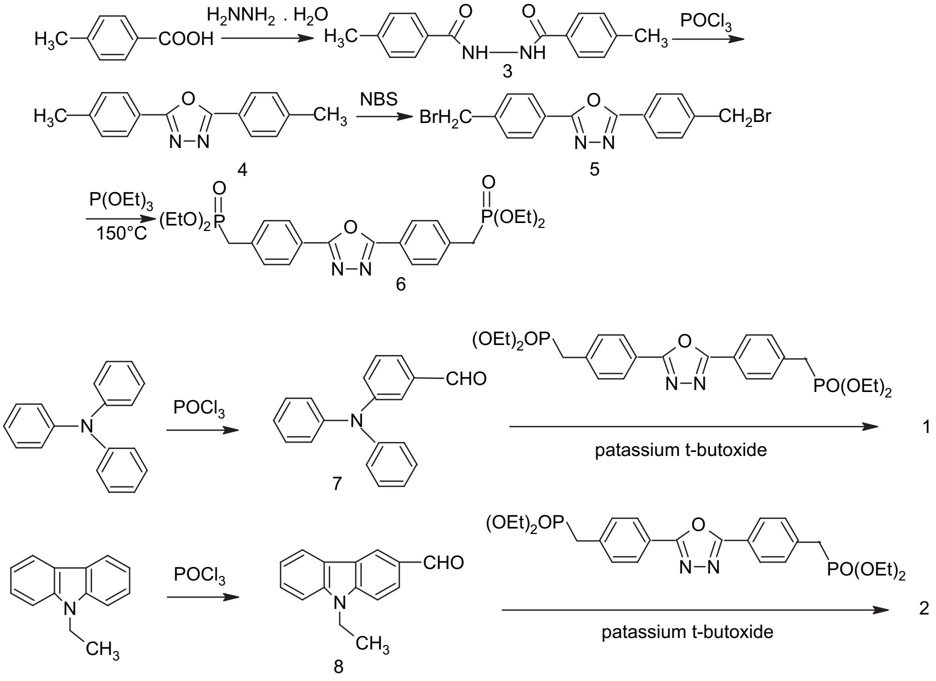
A mixture of 4-methylbenzoic acid 13.6 g (0.1 mol), polyphosphoric acid 50 mL and hydrazine hydrate 5 g (0.05 mol) was stirred for 10 h at 130 °C temperature under nitrogen atmosphere. The mixture was poured into ice water. This was then neutralized, filtered and washed with water and dilute sodium carbonate solution repeatedly. White crystals (**3**) were obtained after recrystallization in ethanol with 85% yield. m.p. 243–245 °C; IR ν: 3510, 3350, 1667, 1606 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ: 2.35 (s, 6H, CH_3), 7.32 (d, 4H, ph-H), 7.81 (d, 4H, ph-H), 10.35 (s, 2H, NH).

2.2.2. 2,5-Bis(4-methylphenyl)-1,3,4-oxadiazole (**4**)

Compound **3,** 12.5 g (0.047 mol), and 150 mL $POCl_3$ were added to a flask and refluxed for 8 h under nitrogen atmosphere; this was then cooled to room temperature. The reaction mixture was slowly poured into ice water and neutralized with dilute sodium carbonate solution. Then the precipitate was filtered and dried after washing with water. Compound **4** was obtained as brown needle crystals recrystallized from chloroform/methanol (1:1) with 77.2% yield. m.p. 172–173 °C; IR ν: 3043, 2922, 2856, 1553, 1446, 1612, 1350, 1176 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ: 2.43 (s, 6H, CH_3), 7.32 (d, 4H, ph-H), 8.05 (d, 4H, ph-H).

2.2.3. 2,5-Bis(4-bromomethylphenyl)-1,3,4-oxadiazole (**5**)

Compound **4,** 6 g (0.024 mol), was dissolved in fresh distilled carbon tetrachloride, then 5 g (0.028 mol) of *N*-bromosuccinimide (NBS) and 1 g (0.004 mol) of benzoyl peroxide as a catalyst were added. The mixture was refluxed for 6 h



Scheme 1. Synthetic route for 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles(**1–2**).

under nitrogen atmosphere. The precipitate was filtered and dried after washing with water. The crude product was obtained as white needle crystals recrystallized from tetrahydrogenfuran/ethanol (1:1) with 65% yield. m.p. 226–227 °C; IR ν: 3050, 1600, 1552, 1494, 1347, 1226, 598 cm^{-1}; ^1H NMR (DMSO-d_6) δ: 4.80 (s, 4H, CH_2Br), 7.72 (d, 4H, ph-H), 8.15 (d, 4H, ph-H).

2.2.4. 2,5-Bis(4-methylphenyl)-1,3,4-oxadiazole phosphonate (**6**)

The mixture of 15 mL (0.09 mol) of triethyl phosphite and 3 g (0.07 mol) of compound **5** was stirred at 150 °C for 6 h. Unreacted triethyl phosphite was removed by distillation; the residue was poured into 15 mL oil ether. The precipitate was filtered and dried, then the crude product was obtained as white needle crystals recrystallized from ethyl acetate/oil ether (1:3) with 83% yield. m.p. 136–138 °C; IR ν: 2981, 2910, 1635, 1501, 1446, 1343, 1256, 1066, 790 cm^{-1}; ^1H NMR (DMSO-d_6) δ: 1.18 (t, 12H, CH_3), 3.45–3.70 (m, 8H, $POCH_2$), 7.50 (d, 4H, ph-H), 8.10 (d, 4H, ph-H).

2.2.5. 2,5-Bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles (**1–2**)

2,5-Bis[4-(2-*N*,*N*-diphenylaminostyryl)phenyl]-1,3,4-oxadiazole (**1**) was prepared as follows. A mixture of 1 g (0.036 mol) of 4-diphenylamino-benzaldehyde and 1 g (0.026 mol) of compound **6** was dissolved in 5 mL THF. Potassium *tert*-butoxide, 0.6 g (0.057 mol), was dissolved in THF and added dropwise to the reaction mixture with stirring. The mixture was refluxed for 12 h under nitrogen atmosphere. The precipitate was filtered and washed after pouring into ethanol. Then the crude product was obtained as yellow crystals recrystallized from ethanol with 80% yield. m.p. 256–257 °C; IR ν: 3026, 1602, 1589, 1508, 1490, 1326, 1291, 1176, 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.03 (d, 2H, –CH=CH–), 7.19 (d, 2H, –CH=CH–), 7.07–7.10 (m, 10H, ph-H), 7.14–7.16 (m, 4H, ph-H), 7.30 (d, 4H, ph-H), 7.43 (d, 4H, ph-H), 7.65 (d, 4H, ph-H), 8.13 (d, 4H, ph-H).

The Synthesis of 2,5-bis[4-{2-(3-*N*-ethylcarbazolyl) vinyl}phenyl]-1,3,4-oxadiazole (**2**) was similar to that of **1**. Bright yellow crystals, yield 75%. m.p. > 300 °C; IR ν: 2972, 1627, 1593, 1501, 1470, 1323, 1242, 1176, 968 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.47 (t, 6H, CH_3), 4.39–4.43 (m, 4H, $-CH_2-$), 7.20 (d, 2H, –CH=CH–), 7.31 (d, 2H, –CH=CH–), 7.43–7.45 (m, 4H, carbazole-H), 7.50–7.54 (m, 4H, carbazole-H), 7.72 (d, 4H, carbazole-H), 8.16 (d, 8H, ph-H), 8.30 (s, 2H, carbazole-H).

2.3. Characterizations

Chemical structures were identified by Fourier transform infrared spectra (FT-IR) and ^1H NMR spectra. FT-IR spectra were recorded on a Nicolet 750 series in the region of 4000–400 cm^{-1} using KBr pellets. ^1H NMR measurements were determined with a Brucker 500 MHz apparatus, with TMS (tetramethyl silane) as internal standard. Linear optical properties were measured by a Shimadzu UV-2201 UV–vis spectra and an Edingburgh FLS920 fluorescence spectra in solution.

Nonlinear absorption phenomena were investigated by a direct nonlinear transmission (NLT) method [21–24]. First, two-photon excitation spectra for photoluminescence were measured to locate the effective TPA resonance. Then, intensity-dependent transmission was measured at the resonance wavelength using the laser pulses with 6-ns duration. The laser beam passed through a 1-cm path quartz cuvette filled with the solution and the intensities of transmitted beam were measured as a function of incident intensity. For two-photon absorption cross-section measurements, a 1-cm path length solution sample was placed near the focal plane to create a greater nonlinear transmission change.

3. Results and discussion

3.1. Linear optical properties of chromophores

Possible solvent influence on the linear absorption behavior is investigated. The one-photon absorption spectra of **1–2** in four different solvents, $CHCl_3$, THF, CH_2Cl_2, DMF, at a concentration of 10^{-5} M are shown in Fig. 1. It is noted that there is no absorption in the range from 450 to 900 nm, as presented in Fig. 1. The absorption band at about 220–320 nm is assigned to absorption of the phenylene ring, whereas the longer wavelength region absorption band is attributed to a charge-transfer band of the chromophores. The maximum peaks of one-photon absorption corresponding to the CT bands are at 408 nm for **1** and at 393 nm for **2** in THF. The maximum molar extinction coefficients of the two chromophores in THF are 1.58×10^5 cm^{-1} M^{-1} and 0.86×10^5 cm^{-1} M^{-1} for **1** and **2**, respectively. The absorption spectra shown in Fig. 1 are measured for samples of equal concentrations. The absorption maxima and shapes of the chromophore **1** exhibited weak solvent polarity dependencies. For chromophore **2**, a red shift is observed with the increase of solvent polarity.

The emission spectra using the same excitation wavelength of 380 nm for chromophores **1–2** in $CHCl_3$ and THF at a concentration of 10^{-5} M are shown in Fig. 2. In $CHCl_3$, the fluorescence of **1** is strong, in the green region, with a peak at 507 nm, and chromophore **2** exhibits a weak emission at 475 nm in the blue region. The single-photon fluorescence spectra of chromophores all show sensitivity to the solvent polarity. For the emission peaks of **1** and **2**, a red shift is observed with the increase of solvent polarity.

3.2. Nonlinear optical properties of chromophores

Figs. 3 and 4 show that the maximum peaks of one-photon and two-photon fluorescence are at 502 nm and 507 nm for chromophore **1** and at 466 nm and 475 nm for chromophore **2** in $CHCl_3$. The green fluorescence of **1** and the blue fluorescence of **2** were obtained. As shown, the central wavelengths for one-photon and two-photon fluorescence are almost the same, although they are obtained by different excitation mode and wavelength. The one-photon fluorescence excitation

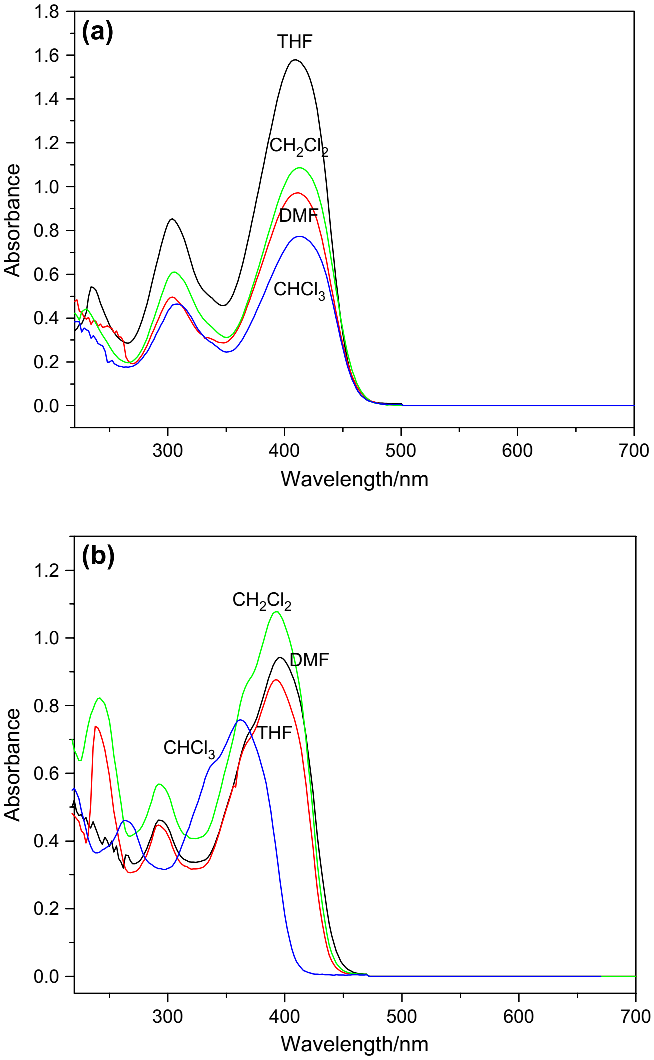


Fig. 1. UV absorption spectra for (a) chromophore **1** and (b) chromophore **2** at 1.0×10^{-5} mol dm^{-3} in different solvents.

wavelength is 380 nm and the two-photon fluorescence is by a Q-switched and frequency-doubled Nd:YAG laser at 800 nm. And the red shift for two-photon fluorescence, in comparison with corresponding one-photon fluorescence, can explain the re-absorption.

3.3. Two-photon absorption cross-sections

The two-photon properties of chromophores are investigated with an IR dye laser pumped by a Q-switched and frequency-doubled Nd:YAG laser. The basic parameters of this dye laser output are 800 nm wavelength, 6 ns pulse width, and 1–2 mJ pulse energy. Fig. 5 shows the optical power limiting measured by the NLT method at the maximum wavelength of two-photon-induced fluorescence excitation. It is seen that the intensity of the transmitted laser beam (I) increased nonlinearly as that of the incident laser beam (I_0) increased. The nonlinear absorption coefficient is obtained by fitting the experimental data with Eq. (1) [21–24]

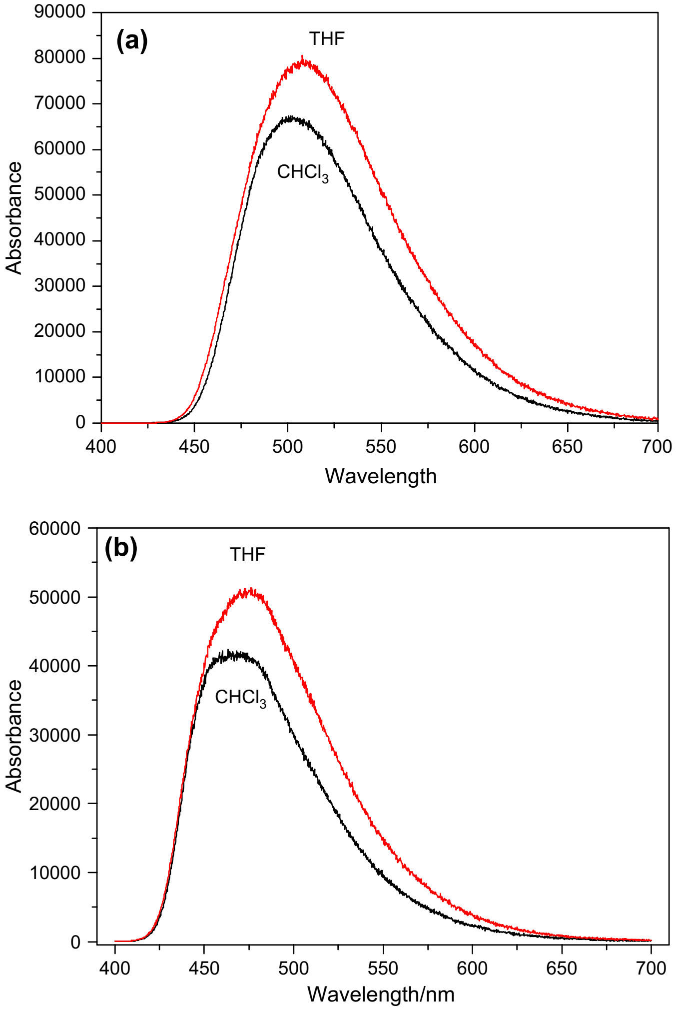


Fig. 2. Single-photon excited fluorescence (SPEF) of (a) chromophore **1** and (b) chromophore **2** at 1.0×10^{-5} mol dm^{-3} in CHCl$_3$ and THF.

$$I = \frac{I_0}{1 + I_0 L \beta} \tag{1}$$

where L is the thickness of the sample and β is the nonlinear absorption coefficient, which is related to the effective TPA molecular cross-section as follows:

$$\sigma_2 = \mathrm{h}\nu\beta/N_0 \tag{2}$$

Here N_0 is the molecular density in the ground state, hν is the energy of the incident photon, and σ_2 is in units of cm^4 s.

The two-photon absorption cross-section values are measured to be 1.07×10^{-46} cm^4 s for chromophore **1** and 0.66×10^{-46} cm^4 s for chromophore **2** (within our experimental error of ±15%).

It is reasonable to limit a sum-over-states expansion to three closest energy levels (three level model), namely, the ground state (index 0), two-photon excited state (f), and a main intermediate electronic state (i), then the peak cross-section can be expressed as [25]

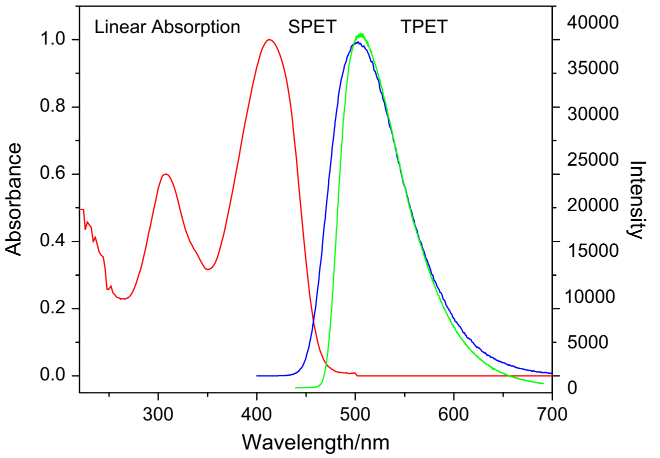


Fig. 3. UV absorption spectra and one-photon fluorescence at 1.0×10^{-5} mol dm^{-3}, and two-photon excited fluorescence (TPEF) at 1.0×10^{-2} mol dm^{-3} of chromophore **1** in $CHCl_3$.

$$\sigma_2 \propto \frac{\left(E_{f0}/2\right)^2 M_{i0}^2 M_{fi}^2}{\left(E_{i0} - E_{f0}/2\right)^2 \Gamma_{f0}} \tag{3}$$

Here Γ_{f0} is the linewidth of the two-photon transition, and E_{nm} are M_{nm} are the energy difference and the transition dipole moment between the states n and m, respectively.

A number of factors influence the TPA magnitude, among which are electronic delocalization and intramolecular charge-transfer phenomena. This enhancement in σ_2 is correlated to an intramolecular charge redistribution that occurs between the ends and the center of the molecules. Increasing the conjugation length of the molecule or increasing the extent of symmetrical charge from the ends to the middle results in a large increase of σ_2. Comparing the nonlinear absorption coefficients of two chromophores, we found that a very effective energy transfer from the excited terminal units to the π-conjugated bridging unit is the dominant contribution to the two-photon absorption.

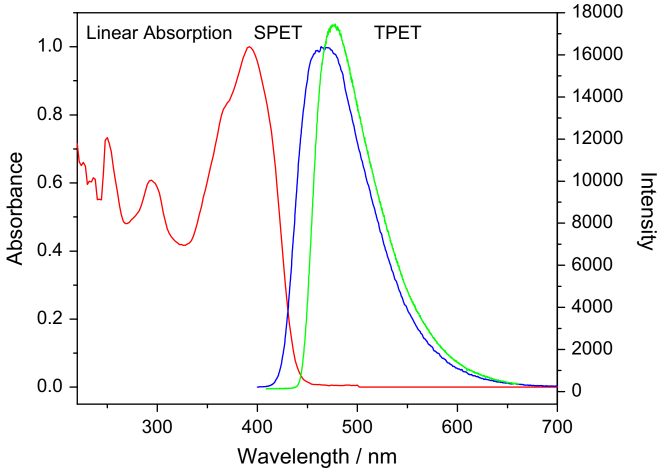


Fig. 4. UV absorption spectra and one-photon fluorescence at 1.0×10^{-5} mol dm^{-3}, and two-photon excited fluorescence (TPEF) at 1.0×10^{-2} mol dm^{-3} of chromophore **2** in $CHCl_3$.

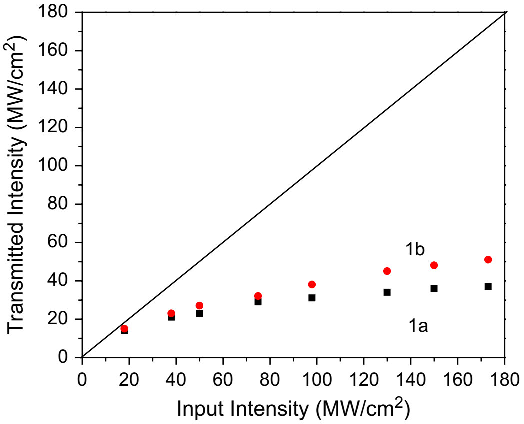


Fig. 5. The nonlinear transmission intensity vs. the input power for chromophores **1** and **2** in $CHCl_3$ at 1.0×10^{-2} mol dm^{-3}.

4. Conclusion

Two symmetrical 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles that exhibit strong two-photon absorption and enhanced two-photon excited fluorescence were designed and synthesized based on ‘‘push-core-pull-core-push’’ molecules built from embedding electron-transporting 1,3,4-oxadiazole in aromatic conjugated system through Wittig–Horner reaction. In this paper, we first briefly describe the synthesis of V-style geometry D–π–A–π–D chromophores, where terminal electron-donor group is triphenylamine trigonal moiety or carbazole group, and the center of the molecules is electron-acceptor group of oxadiazole segment. Linear absorption and fluorescence properties of the compounds, in particular, the solvatochromic behavior of one-photon spectra, are then thoroughly explored through experimental results. Two-photon excited fluorescence is measured and TPA cross-section evaluated, pumped by nanosecond laser at 800 nm, and strong up-conversion emissions with the central wavelength at 507 nm and 475 nm in the solution of $CHCl_3$ have been observed. Their two-photon absorption cross-sections obtained by nonlinear transmission method are 107×10^{-48} cm^4 s photon^{-1} and 66×10^{-48} cm^4 s photon^{-1}. Comparing the nonlinear absorption coefficients of two chromophores, we found that a very effective energy transfer from the excited terminal units to the π-conjugated bridging unit is the dominant contribution to the two-photon absorption.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (Grant No. 10374013) and the Natural Science Foundation of Southeast University (Grant No. 9207041399) for financial support.

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