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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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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], multi-branched 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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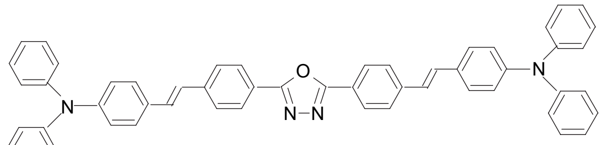
trigonal moiety or carbazole group, and the center of the molecules is electron-acceptor group of oxadiazole segment. In this paper, we first briefly describe the synthesis of 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles. Linear absorption and fluorescence properties of the chromophores, in particular, 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.



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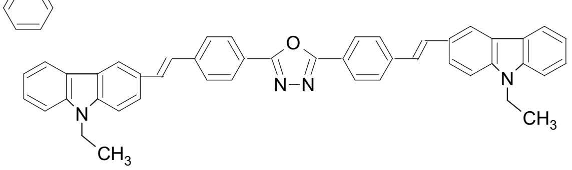

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2. Experimental

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**)

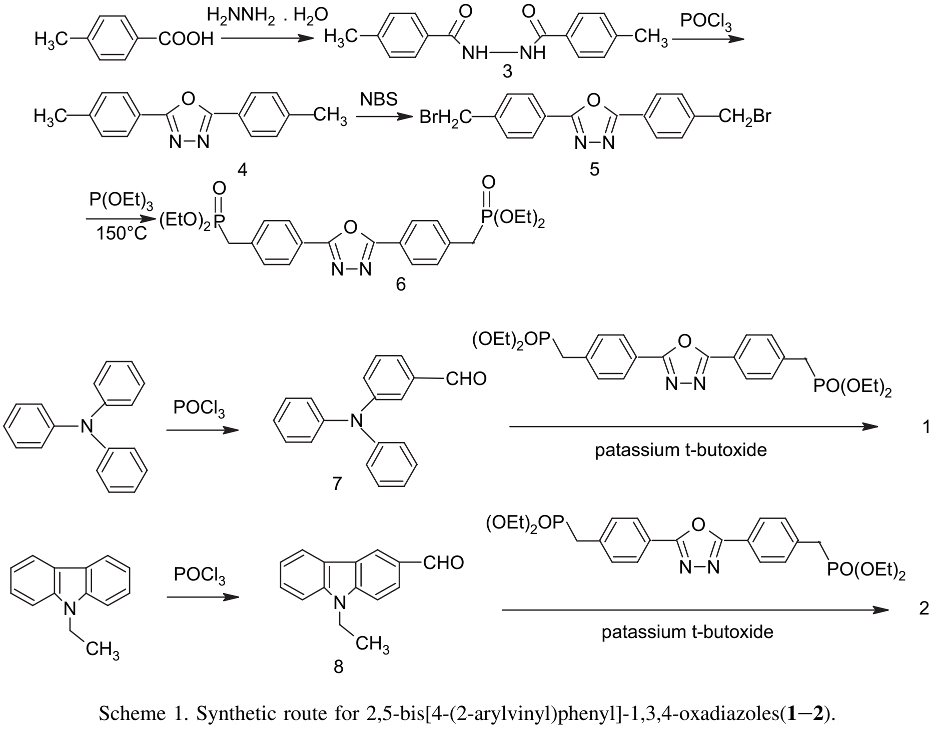
A mixture of 4-methylbenzoic acid 13.6 g (0.1 mol), polyphosphoric acid 50 mL and hydrazine hydrate 5 g (0.05 mol) was stirred for 10 h at 130 °C temperature under nitrogen atmosphere. The mixture was poured into ice water. This was then neutralized, filtered and washed with water and dilute sodium carbonate 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 $\mathrm{cm^{-1}}$; ^{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 $\mathrm{cm^{-1}}$; ^{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**).