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New Heterocycle-Based Organic Molecule with Two-Photon Induced Blue Fluorescent Emission

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A new heterocycle-based quadrupolar molecule containing 2,5-diphenyl-1,3,4-oxadiazole as the π-centre and two carbazoles as end units has been synthesized. It exhibits two-photon induced blue emission, and its two-photon absorption cross section in the femtosecond region is measured to be 239×10^{-50} cm^4 s photon^{-1} at a wavelength of 788 nm.

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Research into molecular two-photon absorption (TPA) has drawn growing interest recently, because of potential applications such as three-dimensional (3D) optical data storage, micro- and nano-manufacture, two-photon laser scanning fluorescence microscopy, two-photon up-converted lasing, and photodynamic therapy.[1–4] Among these applications, two-photon induced fluorescence (TPIF) has gained popularity, especially with the biology community, because it has many advantages. Molecular excitation by the simultaneous absorption of two low-energy photons leads to highly confined excitation and intrinsic 3D resolution, as well as an increased penetration depth in tissue. It has become clear that the development of TPIF microscopy would greatly benefit from the design and synthesis of efficient fluorophores with large TPA cross sections (σ_2) and desired emitting characteristics. Until now, many organic compounds have been synthesized for this application.[5–8] However, the emitting wavelengths of these reported molecules are mostly in the range 500–700 nm and the study of the TPIF molecules with efficient two-photon induced blue emission is still lacking. This seriously restricts the development of multi-channel TPIF microscopy. Thus, it is essential to develop compounds with large σ_2 and efficient two-photon induced blue emission.

The most extensively investigated TPA molecules have the general structures of donor–bridge–acceptor (D–π–A) dipoles,[6–8] donor–bridge–donor (D–π–D) or acceptor–bridge–acceptor (A–π–A) quadrupoles,[5,9–12] and octupoles.[13,14] For those molecules with the comparative π-system, quadrupoles are reported to exhibit larger σ_2 and blue-shift emission relative to dipolar compounds.[15] The results of structure-property relationship studies reveal that quadrupolar molecules are likely to display large σ_2 values in relation to a symmetrical charge transfer between the periphery and the centre of the molecule.[9–12] Increasing the donor/acceptor strength of quadrupolar molecules, lengthening the conjugated system, or enhancing the intramolecular charge transfer by forming either D–π–A–π–D or A–π–D–π–A frameworks, would significantly increase the σ_2 values.[9–12] However, this effect unfortunately often leads to red-shifted emission and decreased fluorescence quantum yield.[5]

Within this work, the merits of quadrupolar molecules were used to design and synthesize a new TPA molecule (**3**) with efficient two-photon induced blue fluorescent emission. Semi-coplanar 2,5-diphenyl-1,3,4-oxadiazole was selected as the π-centre, which was symmetrically terminated with *N*-hexadecylcarbazol-3-yl groups. 1,3,4-Oxadiazole and carbazole fragments are often used in highly emissive materials.[16–19] They are both π-deficient and π-excessive heterocyclic compounds, and are also often used as moderate acceptor and donor moieties, respectively, in TPA chromophores.[15,20–22] This work presents 2,5-diphenyl-1,3,4-oxadiazole to be a π-center in the quadrupolar TPA molecules for the first time. The electron-deficient heterocycle can promote symmetrical charge transfer, which increases the σ_2 value. The twist conformation of 2,5-diphenyl-1,3,4-oxadiazole leads to a blue-shift in the emitting wavelength of the molecule. Further, the moderate electron-pulling ability of the carbazole fragments is also responsible for blue-shift emission. The long alkyl chains on the 9-position of carbazole groups are beneficial because they increase the solubility of the compound.

The compound **3** was synthesized from 2,5-bis(4-xylylenediethylphosphonate)phenyl-1,3,4-oxadiazole **2** and *N*-hexadecylcarbazole-3-carbaldehyde through the Wittig–Horner reaction (Scheme 1), and has been characterized by ^{1}H NMR, FTIR, and elemental analysis.

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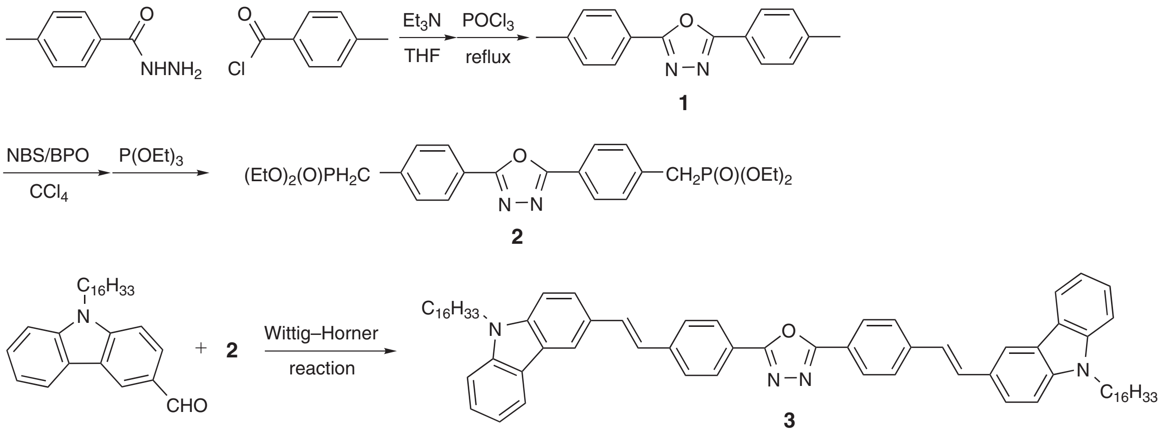

Scheme 1. Synthetic route for molecule **3**.

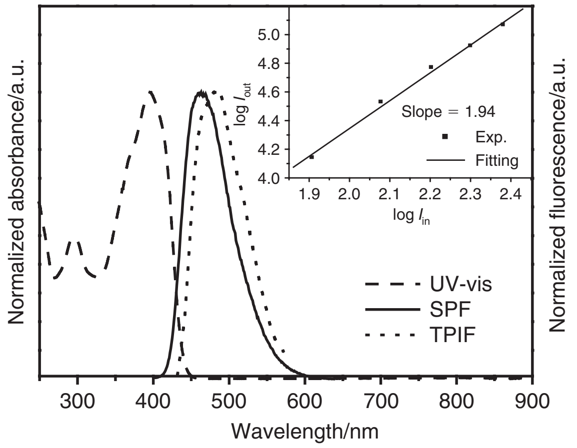

Fig. 1. Normalized one-photon absorption and single-photon fluorescence (SPF) emission spectra, and TPIF spectrum of **3** in $CHCl_3$. Inset: the intensity of up-converted emission vs the intensity of two-photon excitation at 788 nm for **3**.

The one-photon absorption and emission spectra of **3** in chloroform ($\sim 10^{-5}$ mol L^{-1}) are shown in Fig. 1. Its linear optical absorption and emission maxima, λ_{max}^{abs} and λ_{max}^{spf}, are located around 395 and 463 nm, respectively. The quantum yield (Φ_f) of **3** was measured to be 51% by the optically dilute measurement method using quinine sulfate (Φ_f assumed to be 54.6% in 1.0 mol L^{-1} H_2SO_4) as the reference.[23]

As shown in Fig. 1, molecule **3** in chloroform (10^{-4} mol L^{-1}) emits blue up-converted fluorescence when excited by a femtosecond laser at a wavelength of 788 nm. The profile of the up-converted fluorescent spectrum of **3** is similar to its single-photon fluorescence (SPF) spectrum. The peak position is red-shifted ($\sim$17 nm) relative to the peak value of SPF spectrum due to the re-absorption effect.[24] This result is similar to the reported trend.[8,25]

Molecule **3** has no linear optical absorption between 500 and 900 nm (Fig. 1), which implies that up-converted fluorescence can be induced by TPA. The dependence of the up-converted fluorescence intensity on the excitation intensity of **3** was also examined, as illustrated in the inset of Fig. 1. The slope is approximately 2. Therefore, the emission intensity is a function of the square of the laser power. This result indicates that the up-converted fluorescence observed is induced by a two-photon excitation process.

The TPA cross sections (σ_2) of the compounds were determined by the TPIF measurement technique and Eqn (1)[26]

$$\sigma_{2s} = \sigma_{2r}(F_s/F_r)(\Phi_r/\Phi_s)(c_r/c_s)(n_r/n_s) \qquad (1)$$

where the subscripts 's' and 'r' refer to the sample and reference molecules, respectively. F is the integrated fluorescence intensity measured at the same power of the excitation beam, and Φ is the fluorescence quantum yield. The number density of the molecules in the solution was denoted as c, n is the refractive index, and σ_{2r} is the TPA cross section of the reference molecule. In this experiment, fluorescein was selected as reference molecule (10^{-5} mol L^{-1} in 0.1 mol L^{-1} NaOH) and its σ_2 value was assumed to be 37 GM (1 GM = 10^{-50} cm^4 s $photon^{-1}$) at a wavelength of 788 nm, which was taken from the literature.[26]

Table 1 shows the photophysical properties of **3** compared to those of two-photon induced blue emissive fluorophores reported.

Recently, it has been reported that *trans*,*trans*-2-{4-[4-(*N*-carbazolyl)styryl]styryl}-1,3-benzothiazole (CSSB)[7] and *trans*-2-[*p*-formylstyryl]benzimidazole (ASBM)[8] are efficient two-photon induced blue emissive fluorophores. The σ_2 value of **3** is larger than that of these two examples (Table 1), and the quantum yield of **3** is higher than that of ASBM. However, it should be considered that the 788 nm laser source is far away from the peak position of the TPA spectra of **3**, and an enhancement of the σ_2 value is expected at optimized parameters.

In summary, a new quadrupolar TPA molecule **3** with 2,5-diphenyl-1,3,4-oxadiazole as π-centre has been synthesized. The symmetrical charge transfer of the D–π–A–π–D framework is responsible for the relatively large σ_2 value of **3**. This heterocycle-based molecule containing oxadiazole and carbazole moieties is highly emissive. The twist conformation of 2,5-diphenyl-1,3,4-oxadiazole and the nature of the moderate electron donors enable the molecule to exhibit two-photon induced blue emission.

Table 1. Photophysical properties of molecule 3 in chloroform compared to literature data of two-photon induced blue emissive fluorophores reported^{A}

Molecules	λ_{max}^{abs} [nm]	λ_{max}^{spf} [nm]	Φ_f [%]	λ_{max}^{tpf} [nm]	σ_2 [GM]^{B}
3	395	463	51	480	239
ASBM[8]	359	454	38	470	180
CSSB[7]	384	486	61	487	118

$^{A}\lambda_{max}^{abs}$, λ_{max}^{spf}, λ_{max}^{tpf}: peak wavelengths in the linear absorption, one-photon excited fluorescence and two-photon excited fluorescence spectra, respectively.
^{B}1 GM = 10^{-50} cm^{4} s photon^{-1}.

Experimental

^{1}H NMR spectra were recorded in CDCl$_3$ on a FT-NMR spectrometer (Varian Mercury VX300) operating at 298 K. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane (TMS). Elemental analysis was performed using a elemental analyzer (Carlo–Erba model 1106). Column chromatography was carried out on silica gel zcx-α (200–300 mesh). All chemicals are commercially available and were used as-received unless stated otherwise. The intermediates **1** and **2** were synthesized according to reported methods[27,28] with minor modification. The title compound **3** was prepared by the Wittig–Horner reaction by the following procedure.

N-Hexadecylcarbazole-3-carbaldehyde (168 mg, 0.4 mmol), the intermediate **2** (104 mg, 0.2 mmol), and catalyst 18-crown-6 were dissolved in anhydrous dichloromethane (50 mL), and then Bu^{t}OK powder (67 mg, 0.6 mmol) was added in portions under a nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight. Then the mixture was poured into water (20 mL), extracted with chloroform (30 mL ×3), dried with sodium sulfate, and concentrated. Purification was performed by column chromatography with chloroform as eluent. Further purification by recrystallization in ethanol/chloroform gave pure products as pale yellow *needles* (40 mg, 38%) (Found: C 84.3, H 8.7, N 4.8. Calc for $C_{74}H_{92}N_4O$: C 84.4, H 8.8, N 5.3%). δ_H (CDCl$_3$) 0.88 (t, 6H, CH$_3$), 1.25–1.35 (m, 52H, CH$_2$), 1.88 (m, 4H, CH$_2$), 4.32 (t, 4H, NCH$_2$), 7.20 (d, *J* 16.2, 2H, CH=CH), 7.26–7.30 (br, 2H, CH=CH), 7.41–7.50 (m, 8H, ArH), 7.72 (d, *J* 8.4, 6H, ArH), 8.16 (d, *J* 8.4, 6H, ArH), 8.28 (s, 2H, ArH).

UV-vis absorption spectra were recorded on a Hitachi U-3010 UV-vis spectrophotometer. Photoluminescent spectra were recorded on a Shimadzu RF-5301 fluorescence spectrophotometer.

The experimental set-up for the TPIF and TPA cross section σ_2 measurements was similar to that described by Oulianov et al.[29] The excitation source for the TPIF spectra and σ_2 measurement was a laser system (Mira 900) at 150 fs emission, 788 nm pulses at 76 MHz repetition rate. The TPIF spectrum was recorded in a direction perpendicular to the pump beam by an CCD-array spectrometer (Acton Spectrapro 2500I). The intensity of the incident beam was monitored by the detector of a power meter (Coherent, FieldMaster). The beam was focused by an $f = 150$ mm lens into the solution of the sample and was close to the TPIF-collection wall of the cell (10 mm × 10 mm) to minimize the re-absorption effect. The TPIF intensity was obtained by integrating over the entire emission range of TPIF spectrum.

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