



New conjugated organic dyes with various electron donors: One- and two-photon excited fluorescence, and bioimaging



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ABSTRACT

Six new fluorescent donor- π bridge-acceptor (D- π -A) structural molecules with various electron donors were synthesized and fully characterized. Influence of electron-donating strength on optical properties was investigated by the systematic alteration of the electron donors. The optical properties of the dyes were successfully tuned by choosing different electron donors. All the dyes in solution show strong one-photon excited fluorescence (OPEF) and high quantum yield. With increasing electron-donating strength of donors, dye **5** with diphenylamine and dye **6** with (4,4'-diethoxyphenyl)amino substituents, exhibit strong two-photon excited fluorescence (TPEF), and the large two-photon absorption (TPA) cross-section values are 1378 GM for **5** and 1654 GM for **6**. The structure–property relationships were detailed through quantum chemical calculations and X-ray crystallography. The results of living cell imaging experiments show the values of them in one- or two-photon fluorescence microscopy bioimaging applications.

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1. Introduction

Conjugated organic molecules with large delocalized π -electron systems continue to be the subject of very active research due to their potential applications as one- or two-photon optical materials in several areas such as fluorescence imaging, photodynamic therapy, photoswitching devices and 3-D data storage [1–14]. Organic molecules that can be used for such applications are expected to have high fluorescence quantum yield and large two-photon absorption cross-section values. However, the relatively low quantum yield and small two-photon absorption cross-section values of the materials often limit their widespread utility [15–18]. Therefore, extensive efforts have been concentrated on the synthesis of dyes with high fluorescence quantum yield and large two-photon cross-sections. The two-photon absorbing organic materials with large two-photon absorption are particularly attractive due to the advantages of two-photon absorption processes [19]. It is well known that TPA cross-section can be increased either by an enhancement of the conjugation length as well as the coplanarity of

the π -center, or by an appropriate combination of electron donors and acceptors. The molecules with D- π -A structure often have two-photon fluorescence property. It has been well-established that increasing the electron-donating strength of terminal groups and extending conjugation, can exert significant influence on enhancement of TPA cross-section due to the highly extended π -conjugation [20]. Recently, remarkable progress in the design and synthesis of organic dyes with very high TPA cross sections (>1000 GM) has been reported [21].

Dipyridyl has been widely used as electron acceptor group to design optical materials, due to its electron-deficient nature of the heterocycle, excellent optical property, good thermal and chemical stabilities, as well as excellent metal cation coordination ability [22]. Our group has reported a series of TPA pyridine or bipyridine derivatives and the corresponding complexes [23]. As continuous efforts to explore new molecules with high fluorescence quantum yield and large TPA cross section values, 2,2-bipyridyl group as electron acceptor moiety is incorporated into various electron donors through a π -conjugating spacer, we obtained six dyes with excellent optical properties. The adopted electron donors are imidazole (**D1**), triazole (**D2**), carbazole (**D3**), anthracene (**D4**), diphenylamine (**D5**), and (4,4'-diethoxyphenyl)amino (**D6**), whose electron-donating strength increases in the order of

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D6 > D5 > D3 > D4 > D1 > D2. By using the different electron donors, the one- and two-photon fluorescence properties of the dyes have been successfully tuned. All the compounds have high fluorescence quantum yield. With increasing electron-donating strength of donors, **5** and **6** exhibit excellent two-photon excited fluorescence with the maximum TPA cross-section values of 1378 GM for **5** and 1654 GM for **6**, which are relatively large compared to those reported and the commercial fluorophores, such as rhodamine B [24].

The molecular structures for the dyes (**1–6**) are shown in Scheme 1. All the compounds can be obtained in high yield and exhibit a simple preparation and purification at lower cost. In addition, the simple modification of molecular structure by introducing a benzene ring into the six position of pyridyl may produce a steric hindrance, which is expected to suppress molecular internal rotation to some extent and prevent the intermolecular $\pi \cdots \pi$ interactions between the coplanar conjugated backbones. Finally, dyes **1–6** are NNC-cyclometalated ligands, which are suitable for preparing cyclometalated platinum(II) and ruthenium(II) complexes for use in dye-sensitized solar cells or luminophores [25], and the related studies are currently underway in our group.

Here, we report synthesis and optical properties (linear and nonlinear) of the six organic compounds, together with quantum-chemical calculation and X-ray crystallography for discussion on the correlation between molecular structures and spectral properties. One- and two-photon fluorescence cell imaging experiment indicated the suitability of them for this potential application.

2. Experimental section

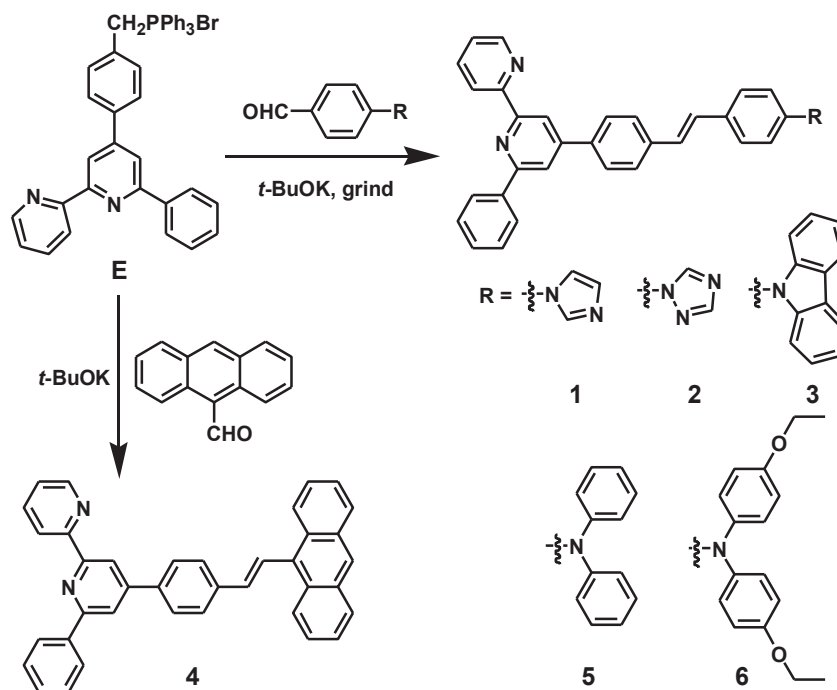
2.1. General procedures

All commercially available chemicals are of analytical grade. Every solvent was purified as conventional methods beforehand. Elemental analyses were carried out on Perkin–Elmer 240 analyzer. IR spectra were recorded with a Nicolet FT-IR NEXUS 870 spectrometer (KBr discs) in the 4000–400 cm^{-1} region. ^1H and ^{13}C NMR

spectra were recorded on a Bruker AV 400 spectrometer using CDCl_3 or $(\text{CD}_3)_2\text{SO}$ as solvent. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm) and coupling constants in Hz. Splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). The mass spectra were obtained on a Bruker Autoflex III smartbeam mass spectrometer and an LTQ-Orbitrap XL mass spectrometer. The X-ray diffraction measurements were performed on a CCD area detector using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) at 298 (2) K. Intensity data were collected in the variable ω -scan mode. The structures were solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with SHELXTL-97 program package. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 931,717(for **2**), 938,586(for **3**), 921,209(for **4**), 928,376(for **5**).

2.2. Optical measurements

The one-photon absorption (OPA) spectra were recorded on an SPECORD S600 spectrophotometer. The one-photon excited fluorescence spectra measurements were performed using a Hitachi F-7000 fluorescence spectrophotometer. In the measurements of emission and excitation spectra, the pass width is 5 nm for all compounds. OPA and OPEF of compounds **1–6** were measured in five organic solvents of different polarities with the concentration of $1.0 \times 10^{-5} \text{ mol L}^{-1}$. The quartz cuvettes used are of 1 cm path length. The absolute fluorescence quantum yield (Φ) values were determined using an integrating sphere. For time-resolved fluorescence measurements, the fluorescence signals were collimated and focused onto the entrance slit of a monochromator with the output plane equipped with a photomultiplier tube (HORIBA HuoroMax-4P). The decays were analyzed by 'least-squares'. The quality of the exponential fits was evaluated by the goodness of fit (χ^2).



Scheme 1. Synthetic routes to target compounds **1–6**.

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