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Four new two-photon polymerization initiators with varying donor and conjugated bridge: Synthesis and two-photon activity

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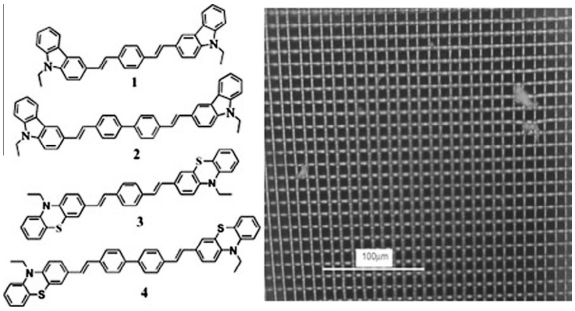
HIGHLIGHTS

- We have synthesized four D–π–D dyes with two-photon absorption.
- Four dyes contain phenothiazines/carbazoles with styrene/biphenylethyne as bridge.
- Photophysical properties of four dyes were investigated.
- Donors have larger contribution to σ value than that of conjugated bridge.
- Four dyes can be used as organic two-photon photopolymerization initiators.

GRAPHICAL ABSTRACT

A new series of dumbbell-shaped bis-carbazoles and bis-phenothiazines chromophores (**1**, **2**, **3** and **4**) constructed with styrene or biphenylethyne as the π-bridge have been synthesized and characterized. Experimental results revealed that extending conjugated chain and introducing donors have substantial effect on their photophysical properties. Compared with extending conjugated chain, enhancing electron-donating ability play a major role in enlarging two-photon absorption cross-sections (σ). Moreover, those four chromophores can be used as effectively organic two-photon photopolymerization initiators.



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ABSTRACT

A specific series of dumbbell-shaped bis-carbazoles or bis-phenothiazines dyes (**1**, **2**, **3** and **4**) constructed with styrene or biphenylethyne as the π-bridge have been synthesized and characterized. Detailed spectral properties including linear absorption, one and two-photon fluorescence properties were investigated. The results show that extending conjugated chain and introducing donors have substantial effect on their photophysical properties. Among them, two-photon absorption cross sections (σ) of the four dyes in DMF determined by the Z-scan technique are successively increased from **1** to **4** with enhancing electron-donating ability and extending conjugated chain, but electron-donating ability has larger contribution to the σ values than extending conjugated chain based on the comparison of small molecules (D–π–D). Two-photon initiation polymerization (TPIP) microfabrication experiments have been carried out using compound **4** as an initiator under irradiation of 200 fs, 76 MHz femtosecond laser at 760 nm. The results confirm that the four dyes can be effectively used as organic two-photon photopolymerization initiators.

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Introduction

Two-photon excitation of fluorophores results from the simultaneous absorption of two photons. The excitation process has a number of unique advantages, such as reduced specimen photodamage, enhanced penetration depth and high spatial resolution in three dimensions and has made possible the development of three-dimensional fluorescence imaging and photodynamic therapy [1–7], 3D microfabrication [8,9], optical data storage [10,11] and optical limiting [12]. In fact, these applications are limited due to the lack of dyes with a large σ value and facile synthetic method.

Over the past twenty years, numerous organic dyes with large two-photon absorption (TPA) cross-sections and high photochemical quantum yield (Φ) having a general structure of the types D–π–D, A–π–A, D–π–A (A: an acceptor group, D: a donating group, and π: a conjugating moiety) have been investigated both experimentally and theoretically in order to understand their structure–property relationships. Generally, there are several essential parameters are required for two-photon dyes [13–20], namely (i) increasing the strength of the donor and acceptor (ii) changing the character of the conjugated bridge (iii) increasing the planarity of the chromophores and (iv) extending length of the mobile π-bridge.

Although great progresses in the study of these materials have been made, more and further investigations are still needed. In order to systematically increase the two-photon cross section and tune the position of the two-photon absorption peak, the design of new materials must combine improved two-photon absorption with other molecular properties, such as high fluorescence quantum yield, efficient intersystem crossing, and low oxidation potential, which make them suitable for the given applications. Our group has made great efforts to develop a series of two-photon active dyes bearing heteroaromatic-based derivatives [21–24].

Carbazole and phenothiazine commercial available are well-known heterocyclic dyes with electron-rich nitrogen or sulfur heteroatoms, exhibiting good optical properties [25–28]. Based on molecular designing consideration, the carbazolyl and phenothiazinyl were introduced to the target molecules as electron donors and styrene or biphenylethyne as the conjugated chain (Scheme 1 is placed in supporting information). Herein, we designed and synthesized four novel heteroaromatic-based TPA dyes with dumbbell-shape (D–π–D) by solvent-free Wittig reaction, and investigated the influence of donors (phenothiazine or carbazole) and the conjugated frame on TPA properties, The results reveal that compared with extending conjugated chain, enhancing electron-donating ability play a major role in enlarging two-photon absorption cross-sections (σ) and those four dyes exhibit highly efficient two-photon initiated polymerization abilities.

Experimental

Materials and methods

All materials and methods in the article have been shown in the supporting information.

Synthesis

The synthetic route and general procedure are were placed in the supporting information, respectively. Four target dyes **1**–**4** were synthesized by solvent-free Witting reaction. The intermediates **a**–**d** were synthesized with reference to the reported methods [29].

Results and discussion

Linear absorption spectra

The photophysical properties for all dyes were summarized in Table 1. The linear absorption spectra were measured in different solvents such as Benzene, CH_2Cl_2, Benzyl alcohol and DMF ($c = 1 \times 10^{-5}$ mol L^{-1}). From Fig. 1, there is no obvious linear absorption in the spectral range of 450–800 nm. Moreover, the absorption spectrum of each dye exhibits two bands, the one centered in the region 298–318 nm due to non-directional π–$\pi*$ excitation, and the other centered at 330–380 nm, corresponding to intramolecular charge transfer (ICT) excitation [30]. The former band remains relatively constant with the chain extension/donor change from **1** to **3** compared to the absorption of **4**. Whereas the latter band shows obvious red shift from **1** to **4**, which can be explained by extending the conjugation length *via* the insertion of a benzene ring between the two donors such as **2** and **4** compared with **1** and **3**, respectively. On the other hand, the absorption peaks of **3** and **4** (containing phenothiazine group) are red-shifted about 35 nm relative to those of their analogues of carbazole group for **1** and **2** because the lone pair electrons of sulfur atom from phenothiazine delocalize into two benzene rings, which form p–π conjugated bond and hence there is some double-bond character in the bonds of the molecule, resulting in red-shift. In other words it suggested that electron-donating abilities of phenothiazine group is stronger than that of carbazole group. The results seem similar to those of the reported molecules [31]. Furthermore, the absorption bands of the four dyes show no specific solvatochromism, indicating that the surrounding solvent molecules have little influence on the π–$\pi*$ transition energy of the dye molecules (see Table 1).

Single-photon excited fluorescence (SPEF) and quantum yield

One-photon excited fluorescence (SPEF) spectra were measured at the same concentration as those of the linear absorption spectra and the maxima wavelength display in the blue–green spectra range (seen Table 1). From Fig. 2, one can see that under identical experimental conditions, SPEF spectra showed a similar trend with the linear absorption spectra. The spectra of **1**–**4** exhibit a large red-shifted with changing conjugation length/donor group (D). As

Table 1
Photophysical data of four target dyes in different solvents.

Molecule	Solvent	λ^{a}_{max}	$\lambda^{SPEF,b}_{max}$	Φ [c]	τ [d]	$\lambda^{TPEF,e}_{max}$
1	Benzene	298, 332	394	0.74	3.22	
	CH_2Cl_2	299, 329	396	0.72	2.55	417
	Benzyl alcohol	300, 331	401	0.63	2.31	410
	DMF	299, 330	397	0.75	2.59	419
2	Benzene	300, 343	426	0.75	0.80	
	CH_2Cl_2	302, 341	430	0.65	0.58	436
	Benzyl alcohol	302, 345	432	0.61	0.76	421
	DMF	300, 343	423	0.73	0.78	441
3	Benzene	298, 357	475	0.63	3.48	
	CH_2Cl_2	300, 358	502	0.64	4.85	498
	Benzyl alcohol	298, 361	500	0.52	5.29	438
	DMF	298, 362	506	0.66	5.34	505
4	Benzene	316, 376	496	0.58	3.06	
	CH_2Cl_2	318, 377	514	0.56	4.43	520
	Benzyl alcohol	315, 381	516	0.47	4.59	525
	DMF	318, 380	519	0.61	4.47	537

[a] λ_{max} of the absorption spectra in nm.
[b] λ_{max} of the one-photon fluorescence spectra in nm.
[c] Fluorescence quantum yield.
[d] The lifetime of one-photon fluorescence in ns.
[e] λ_{max} of the two-photon fluorescence spectra in nm.