

Electrochemical, thermal, and photophysical properties of novel two-photon absorption chromophores

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Electrochemical, thermal, and photophysical properties of novel two- (BPODPA), four- (BBPOPA), and six-branch (TBPOA) triphenylamine chromophores are studied. The decomposition temperature of chromophores reaches 373 – 412 °C. The electrochemical properties is explored by cyclic voltammetry. The ionization potential of chromophores is in the range of 5.14 – 5.18 eV. Excitation at 400 nm reveals emission peaks at 483 – 487 nm and the fluorescence quantum yields are 0.73 – 0.75 in CH₂Cl₂. Two-photon absorption (TPA) properties of chromophores are measured by nonlinear transmission method. The maximum TPA cross-section values are measured at 758 nm to be 20369 GM (1 GM=10⁻⁵⁰ cm⁴·s/photon) for TBPOA, 7024 GM for BBPOPA, and 1227 GM for BPODPA, respectively. When pumped with 800-nm laser irradiation, chromophores show strong two-photon excited blue-green fluorescence at 502 – 518 nm. These results provide a basis for understanding the electronic and optical properties of the conjugated multi-branch chromophore in terms of the underlying molecular and electronic structures.

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Organic multi-branch systems have been utilized for two-photon absorption (TPA) effects which may have applications in optical power limiting, two-photon fluorescence imaging, three-dimensional optical data storage, frequency-upconverted lasing, and two-photon photodynamic therapy^[1,2]. A major advantage of the multi-branch structure originates from the intra-molecular coupling and cooperative enhancement of TPA. This enhancement is correlated to intra-molecular interactions that occur between the branches and the center of the molecules. Increasing the extent of charge transfer from the ends to the middle results in a large increase of TPA cross-section value^[3–6].

In this letter, we report the electrochemical, thermal, photophysical, and TPA properties of multi-branch chromophores N,N,N-tris[4-{2-(3,5-di-{5-[4-(*tert*-butyl)phenyl]-1,3,4-oxadiazol-2-yl}phenyl)-1-ethenyl}phenyl] amine (TBPOA), N,N-bis[4-{2-(3,5-di-{5-[4-(*tert*-butyl)phenyl]-1,3,4-oxadiazol-2-yl}phenyl)-1-ethenyl}phenyl]-N-phenylamine (BBPOPA), N-[4-{2-(3,5-di-{5-[4-(*tert*-butyl)phenyl]-1,3,4-oxadiazol-2-yl}phenyl)-1-ethenyl}phenyl]-N, N-diphenylamine (BPODPA). Figure 1 shows the molecular structures of these multi-branch chromophores. The fundamental building block molecule is 3,5-di-{5-[4-(*tert*-butyl)phenyl]-1,3,4-oxadiazol-2-yl}-styrene (BPO), which can be

considered as a repeat unit for triphenylamine core and N-coupling center.

TBPOA, BBPOPA, and BPODPA are multi-armed chromophores which involve linkage of one, two, and three BPO bis-branch repeat units through the electron-donating trigonal triphenylamine. The coupling center of these compounds is nitrogen atom. Compared with one-dimensional molecules, multi-branch chromophores have appeared to show promising properties. A butyl moiety is attached to the end of each arm to induce the optical transparency as well as the good solubility to various organic solvents.

The behaviours of chromophores under heating were determined by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. The samples were heated in a pan at a rate of 10 °C/min to give the decomposition temperature (*T*_d). *T*_d values reached 373 – 412 °C, which are reported in Table 1. The chromophores show relatively higher thermal stability. The six-branch chromophore TBPOA exhibits a slightly higher *T*_d compared with two-branch BPODPA.

The electrochemical properties of multi-branch chromophores were obtained by cyclic voltammetry, the results are given in Table 1 and Fig. 2. The ionization potential *I*_p and electron affinity *E*_a of chromophores were estimated by using the following relations: [*E*_{onset}]^{ox} = *I*_p – 4.46 and *E*_a = *I*_p – *E*_g, where [*E*_{onset}]^{ox} is the onset potential for the oxidation of chromophores versus saturated calomel electrode (SCE), and the band gap energy (*E*_g) was determined from the onset point of the absorption spectrum^[7]. TBPOA exhibits slightly lower band gap energy and ionization potential compared with BPODPA and BBPOPA.

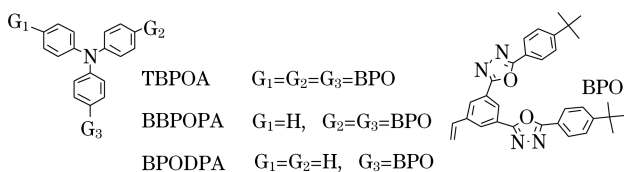


Fig. 1. Chemical structures of chromophores.

Table 1. Photophysical and Electrochemical Properties of Chromophores

	$\lambda_{\max,UV}$ (nm)	ε ($\times 10^4$ M $^{-1}$ · cm $^{-1}$)	λ_{em} (nm)	Φ	T_d (°C)	I_p (eV)	E_a (eV)	E_g (eV)	σ_2 (GM)
BPODPA	295/390	13.87/4.56	486	0.74	373	5.18	2.32	2.86	20369
BBPOPA	295/398	17.02/5.15	483	0.75	412	5.15	2.37	2.78	7024
TBPOA	295/408	17.26/5.96	487	0.73	398	5.14	2.41	2.73	1227
BPO	295	15.08	360	0.35	375	—	—	—	—

$\lambda_{\max,UV}$: maximum absorption wavelength; ε : maximum molar extinction coefficient; λ_{em} : emission wavelength; Φ : fluorescence quantum yield; σ_2 : TPA cross section. 1 M=1 mol/L; 1 GM= 10^{-50} cm 4 ·s/photon.

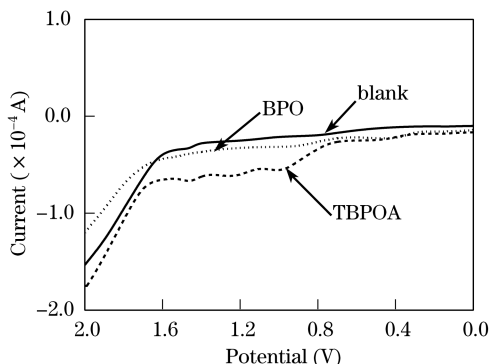


Fig. 2. Cyclic voltammogram curve of chromophores in CH_2Cl_2 (10^{-3} mol/L).

The ultraviolet (UV)/visible absorption spectra of the three chromophores in dichloromethane solution displayed a maximum absorption peak at 390–408 nm (Fig. 3), which were ascribed to the $\pi - \pi^*$ electron transition of the entire conjugated backbone. A bathochromic shift was observed with increasing conjugated arms. The maximum absorption of branched compound BPO was observed at 295 nm. Excitation at 400 nm revealed emission peaks at 483–487 nm in the blue-green region and the fluorescence quantum yields were 0.73–0.75 in CH_2Cl_2 . The emission of branched compound BPO was observed at 360 nm (Fig. 4). Results on the optical properties and molecular orbital energy levels of chromophores are summarized in Table 1.

The very strong frequency-upconverted fluorescence emission can be observed from chromophores solution excited with a Nd:YAG-pumped dye laser (Continuum PR II8010) at the wavelength of 800 nm in CH_2Cl_2 at a concentration of 10^{-2} mol/L. Figure 5 shows that the maximum peaks of two-photon excited fluorescence in CH_2Cl_2 are at 502 nm for BPODPA, 515 nm for BBPOPA, and 518 nm for TBPOA, respectively. The red-shift for two-photon fluorescence, in comparison with the corresponding single-photon fluorescence, can be explained by the re-absorption.

The TPA cross-section values of compounds were investigated by a direct nonlinear transmission (NLT) method^[7,8]. The excitation sources were a Q-switched and frequency-doubled Nd:YAG laser and an optical parameter amplifier (OPA) system, the latter produced 8 ns pulse width, 500–900 nm wavelength laser output with a repetition rate of 10 Hz.

The TPA cross-section values were measured at 758 nm

to be 20369 GM for TBPOA, 7024 GM for BBPOPA, and 1227 GM for BPODPA, respectively (Fig. 6).

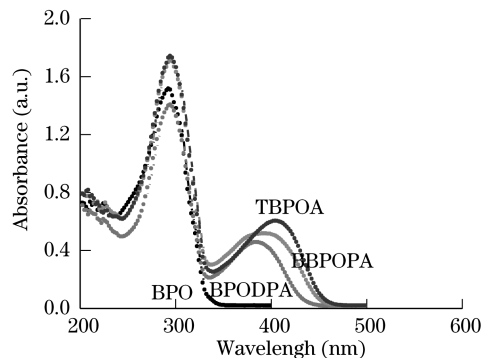


Fig. 3. Absorption spectra of chromophores in CH_2Cl_2 at the concentration of 1.0×10^{-5} mol/L.

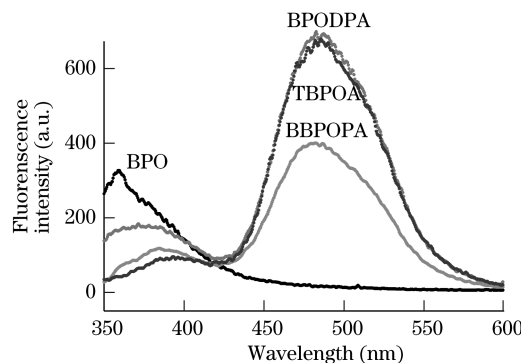


Fig. 4. Fluorescence spectra of chromophores in CH_2Cl_2 at the concentration of 1.0×10^{-5} mol/L.

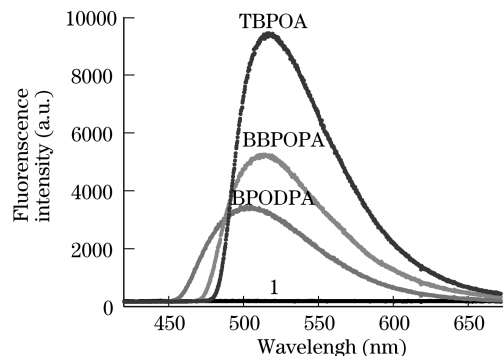


Fig. 5. Two-photon fluorescence of chromophores at 1.0×10^{-2} mol/L in CH_2Cl_2 .

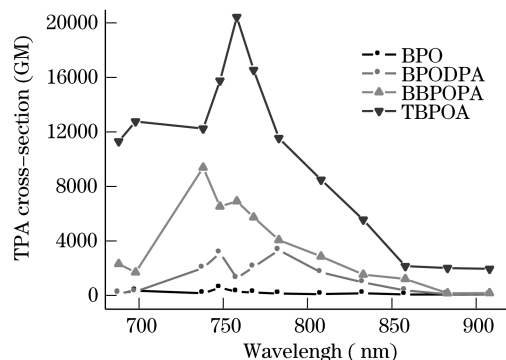


Fig. 6. TPA cross-sections of chromophores from 575 to 490 nm in CH_2Cl_2 .

The large amplified TPA responses shown by multi-branch chromophores are related to the interaction between the branched dipolar unities and the nitrogen-coupling center. We observe that the three-branch compound leads to a larger cooperative effect than the analogous two-branch systems. This suggests that further TPA enhancement could be achieved in multi-branch systems built from a core. The electronic push-pull structures in the arm and their cooperative effect help the extended charge transfer for TPA. Not only dipolar interactions but also coherent interactions are important in defining the total coupling and hence the TPA properties of multi-branch structures.

In conclusion, electrochemical, thermal, and photo-physical properties of novel multi-branch triphenylamine chromophores are studied. The ionization potential of chromophores is in the range of 5.14 – 5.18 eV. The decomposition temperature of chromophores reaches 373 – 412 °C. Excitation at 400 nm reveals emission peaks at 483 – 487 nm and fluorescence quantum yields are

0.73 – 0.75 in CH_2Cl_2 . The maximum TPA cross-section value is measured at 758 nm to be 20369 GM. The TPA enhancement could be achieved in multi-branch systems built from a core. This enhancement is correlated to an intra-molecular charge redistribution that occurs between the ends and the center of the molecules.

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