

Pure Branch Effect on the Optical Properties of Novel Conjugated Derivatives

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(Received March 3, 2010; CL-100198; E-mail: hrli@cqu.edu.cn)

Pure cooperative branch effects on one- and two-photon optical properties of conjugated derivatives are presented. AM1 calculations demonstrate that the electron density distribution of the frontier orbital and the dipole moment changes of the derivatives are related to the number of branches. The theoretical results show that not only the energy level of the frontier orbital could be mediated by the number of branches, but the HOMO–LUMO gap could be regulated.

Owing to wide applications such as two-photon fluorescence sensors,¹ two-photon biomarkers,² two-photon imaging reagents,³ two-photon photodynamic therapy,⁴ and nonlinear optical materials,⁵ development of highly fluorescent and two-photon absorption dyes is a significantly important topic. Many branched compounds characterized with conjugated structures containing various electron-donating or -accepting groups have been reported, and one- and two-photon characteristics were found to be related to the molecular structures.⁶ While to date, pure branch effects on the optical properties of conjugated derivatives have not been studied well. Such investigation is very necessary because it could help us in the development of novel nonlinear optical materials. This letter presents our recent endeavors on the revealing pure branch effects on optical properties of organic compounds. For this purpose, three conjugated derivatives including 4-styryltriphenylamine (**C1**); 4,4'-distyryltriphenylamine (**C2**); 4,4',4''-tristyryltriphenylamine (**C3**) (Figure 1) are developed. Obviously, no electron-donating or -accepting groups are located in the branches, thus the substituent effects could be eliminated.

C1, **C2**, and **C3** were synthesized via routine routes.⁷ **C2** and **C3** are first reported in this letter. Figure 2a shows that the UV–vis absorption spectroscopy of the derivatives displays gradual red-shift in the order of **C1** < **C2** < **C3**. This implies that the extent of internal charge transfer is related to the number of branches in the ground state. Interesting, the optical density of the derivatives increases with the number of branch. **C1**, **C2**, and **C3** are characterized with D– π , D–(π)₂, D–(π)₃ respectively, which results in a cooperative effect on the optical properties of the derivatives. The maximal absorption wavelength of **C3** is 6 nm longer than that of **C2**, and 27 nm longer than that of **C1** in benzene (Table 1). It also suggests the ratio of the molar

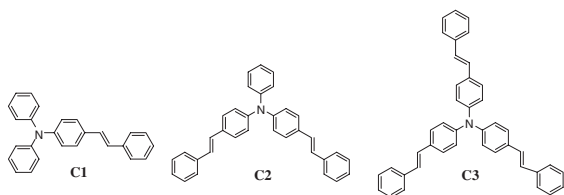


Figure 1. Chemical structures of **C1**, **C2**, and **C3**.

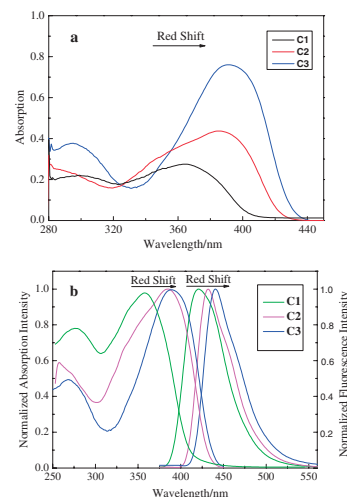


Figure 2. Typical UV–visible absorption and fluorescence spectroscopy of **C1** to **C3** in benzene. (a) Real absorption spectroscopy and (b) normalized absorption and emission spectroscopy.

extinction coefficients of **C1**, **C2**, and **C3** is close to the ratio of the number of branches, namely 1:2:3. The derivatives exhibit remarkably strong fluorescence emission in various solvents with high fluorescent quantum yields. Figure 2b shows a gradual red-shift for the maximal fluorescence wavelength as **C1** < **C2** < **C3**. This indicates that the order of the extent of internal charge transfer is **C1** < **C2** < **C3** in the excited state. As compared with the emission maxima of the derivatives in benzene, they shift to longer wavelength in ethyl acetate (EtOAc) which is ascribed to more internal charge transfer (π , π^*) transition in the excited state in polar solvents.

Figure 3 presents TPA emission of the derivatives under 700 nm Ti:sapphire laser in benzene. Clearly, the maximal TPA emission exhibits gradual red-shift in the order of **C1** → **C2** → **C3**. Furthermore, it shows that the maximal TPA emission of **C2** exhibits red-shift with the increasing polarity of the solvents (from benzene to EtOAc). TPA cross sections of the derivatives were determined by fluorescence.⁷ The order of the maximal TPA emission wavelength and TPA cross section of the derivatives are the same order as **C3** > **C2** > **C1**,⁷ clearly reflecting pure branch effects on two-photon optical properties. Herein, **C2** was used as an example to check the relationship between TPA emission intensity and the pumped powers, which follows well the square law in the excitation laser wavelength at 800 nm. The slope of 1.916 confirms that the derivative has excellent two-photon absorption.⁷ We shall point out that the TPA optical parameters of **C1** measured in this letter are very close to reported data.⁸ We further determined TPA cross

Table 1. One- and two-photon optical properties of the derivatives⁷

Derivatives	$\lambda_{\text{abs}}^{\text{OPA}}/\text{nm}$		$\varepsilon/10^{-5} \text{ L mol}^{-1} \text{ cm}^{-1}$		$\lambda_{\text{em}}^{\text{OPF}}/\text{nm}$		Φ		$\lambda_{\text{em}}^{\text{TPA}}/\text{nm}$	$\sigma^{\text{TPA}}/\text{GM}^{\text{a}}$	
	Benzene	EtOAc	Benzene	EtOAc	Benzene	EtOAc	Benzene	EtOAc	EtOAc	Benzene	EtOAc
C1	363	358	0.28	0.32	418	434	0.75	0.89	438	46.6	51.5
C2	384	379	0.44	0.51	430	444	0.86	0.76	443	218.6	263.0
C3	390	386	0.76	0.96	439	451	0.67	0.60	467	254.0	271.8

^aGM = $10^{-50} \text{ cm}^4 \text{ s/photom}$.

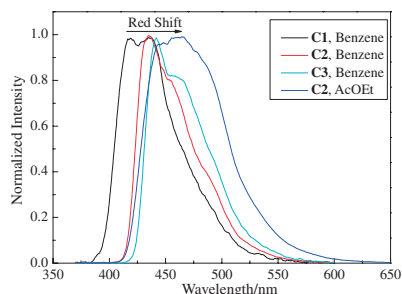


Figure 3. Normalized two-photon induced up-conversion fluorescence emission of **C1** to **C3** in solvents excited by 700 nm Ti:sapphire laser.

sections of the derivatives by tuning laser wavelength from 700 to 880 nm at intervals of 20 nm. It is interesting to observe that the maximal TPA emission of the derivatives is independent of the excited wavelength and it is almost identical to one-photon fluorescence wavelength, which implies that one-photon and two-photon excited fluorescence spectroscopy could originate from a similar excited state. The derivatives have the TPA cross sections in the order of **C3** > **C2** > **C1** at most laser frequencies,⁷ which reveals further the branch cooperative effects on the two-photon optical properties. The larger absorption coefficients and TPA crossing sections of **C2** and **C3** could be explained in terms of exciton coupling effects (namely interaction between transition dipoles) caused by the branches.⁹ The vectorial combination between transition dipole moments along the styryl moieties results in the enhancement of one and two optical parameters.

We utilized AM1 calculations to determine further the frontier orbitals of the derivatives.⁷ For the HOMO orbital of the derivatives, the electron density is mainly distributed around the triphenylamine core, while for the LUMO orbital of the derivatives, the majority of the electron density distribution is located at stilbene part. Obviously, the order of the charge delocalization extent in the LUMO is **C3** > **C2** > **C1**.⁷ The dipole moment changes between the excited state and ground state are calculated, which is in the order of **C3** > **C2** > **C1**.⁷ The energy levels of frontier orbitals are also calculated. HOMO–LUMO gap is in the order of **C1** > **C2** > **C3**.⁷ The results show that not only the electron density distribution of the frontier orbitals and the dipole moment changes between the excited state and the ground state could be tuned by the number of branches, but the HOMO–LUMO energy gaps of the derivatives could be regulated. The calculation explains well the gradual red-shift of absorption and fluorescence spectroscopy of **C1**, **C2**, and **C3**. This also explains why the maximal TPA

fluorescence wavelength and TPA cross section of these compounds are related to the number of branches. Our calculations also confirm the existence of very small energy range between the rotational conformers around the conjugated single bond between phenylamine and styryl group for each derivative respectively (the maximum difference is about 10 kJ mol^{-1}) and the difference of electronic properties in frontier orbitals of the conformers is negligible.⁷

To summarize, this letter describes strong evidence that one- and two-photon optical properties of conjugated derivatives are affected by the number of branches. The geometry optimization demonstrates that the electron density distribution of the frontier orbitals, the dipole moment changes and HOMO–LUMO gaps of the derivatives could be mediated by the number of branches. These could be the fundamental reasons for branch effects on the optical properties of the derivatives.

The authors appreciate NSFC (Nos. 20776165, 20702065, and 20872184) and (Nos. CSTC 2009BB4216 and CSTC 2008BA4020). Thank Mrs. Wang C for the suggestion on the calculation.

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