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# Building Symmetric Two-Dimensional Two-Photon Materials

Ajit Bhaskar,[†] Ramakrishna Guda,[†] Michael M. Haley,[‡] and Theodore Goodson III*,[†]
*Department of Chemistry and Department of Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, and Department of Chemistry and the Materials Science Institute, University of Oregon, Eugene, Oregon 97403*

Received April 18, 2006; E-mail: tgoodson@umich.edu

Multi-chromophore structures composed of repeat building block molecules have now been applied to the discovery of new electronic and optical materials.[1−4] Most recently in the area of nonlinear optics, organic multi-chromophore systems such as organic dendrimers have been utilized for two-photon absorption (TPA) effects which may have applications in optical limiting, imaging, and photodynamic therapy.[5] A major advantage of the organic branched structure originates from the intramolecular interactions in the multi-chromophore system, leading to enhanced two-photon cross sections.[5] Other multi-chromophore assemblies have also been prepared, including novel multi-annulene systems.[6−11] These systems show a wide range of molecular symmetries as well as strong intramolecular coupling. Two-dimensional systems such as these may offer a novel avenue for creating useful TPA materials. The construction of different multi-annulene molecules allows for the investigation of the influence of symmetry on the characteristics of the ground and excited states that are accessible by one- and two-photon processes. This ultimately gives information regarding the mechanism of the large TPA effect found in some of these systems.

Shown in Figure 1 are the molecular structures of the multi-annulene systems studied. The fundamental building block molecule is a diphenylbutadiyne (DPB), and the triangle-shaped molecule (**1**) can be considered as a repeat unit for the larger annulene systems (**3**−**6**). The synthesis of these particular annulenes has been reported previously.[10,11] The molecules display a wide range of different molecular symmetries despite containing the same building block.

In a recent report,[6] the linear optical spectra of the building block molecule **1** were investigated experimentally and calculated by computational methods. It was found that the fundamental excitation was a $\pi$-to-$\pi^*$ transition with vibronic contributions observed in the case of the "closed" annulene systems.[6] Optical absorption and fluorescence properties of all the annulenes have been investigated (see Supporting Information). Within the set of annulenes, one finds a relatively large shift in absorption maximum from the "triangle" (**1**) to the "radiation symbol" compound (**6**). The emission results also show interesting characteristics, such as the large shift in emission maximum for annulene **6** in comparison to other annulenes.

The TPA cross sections ($\delta$) of annulenes **1**−**6** were determined by the method of degenerate two-photon excited fluorescence.[12] These measurements were carried out with femtosecond pulses delivered from an optical parametric amplifier. Spectral measurements of the TPA cross sections were carried out in order to observe the values close to and far from the maximum. As shown in Figure 2, **6** has the largest TPA cross section, and the others follow in the order of **3**, **4**, **5**, **2**, and **1**.

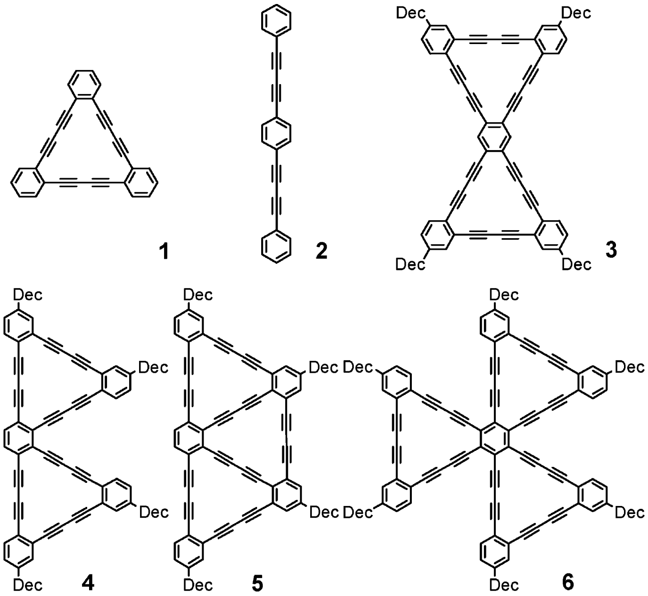

***Figure 1.*** Structures of molecules investigated in this report.

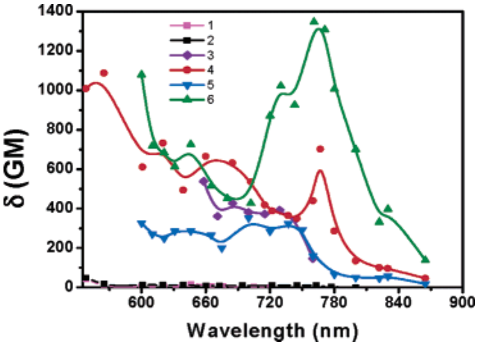

***Figure 2.*** Degenerate TPA cross sections of molecules **1**−**6**.

***Table 1.*** Linear and Nonlinear Optical Properties of the Investigated Annulenes[a]

| molecule (symmetry) | $\delta_{max}$ (GM) | $\delta'$ (per $\pi$ e$^-$) | $[E_{ge} - E_{ge'}]/2$ | $M_{ge}$ (D) | $M_{ee'}$ (D) |
|---|---|---|---|---|---|
| **1** ($C_{3h}$) | 11.5 | 0.4 | | 11.8 | 4.7 |
| **2** ($D_{\infty h}$) | 17 | 0.65 | 1.55 | 11.7 | 4.9 |
| **3** ($D_{2h}$) | 701 | 13 | 1.27 | 19.3 | 4.5 |
| **4** ($C_{2v}$) | 393 | 7.3 | 1.27 | 18.9 | 4.3 |
| **5** ($C_{2v}$) | 353 | 6.1 | 1.18 | 18.3 | 3.7 |
| **6** ($D_{3h}$) | 1346 | 17.3 | 1.17 | 17.6 | 6.0 |

[a] Here, $\delta_{max}$ is the maximum TPA cross section, $\delta'$ represents the TPA cross section per unit $\pi$-electron, and $E_{ge}$, $E_{ge'}$ are the energy differences corresponding to one-photon and two-photon maxima.

One might suggest that this order is similar to that of the increase in chromophore density (or number of $\pi$-electrons). However, calculation of the ratio of cross section to the number of $\pi$-electrons ($\delta'$) does not agree with this assumption (Table 1). One finds the largest ratio for **6**, followed by **3**. In fact, $\delta'$ for **6** is almost 2 orders of magnitude larger than that of **1**, which is thought to be the basic building block molecule for the closed systems. This suggests that molecules with relatively poor TPA cross sections may be used as

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[†] University of Michigan.
[‡] University of Oregon.

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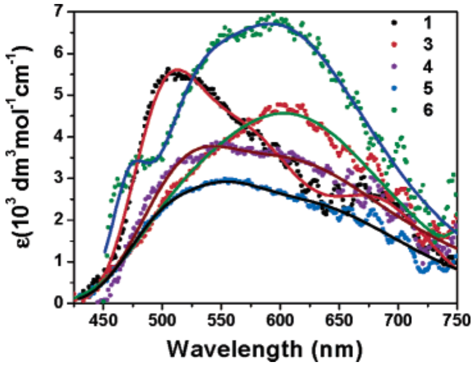

***Figure 3.*** Transient absorption spectra of the compounds **1**, **3**−**6** at a time delay of 150 fs after excitation at 370 nm. Solid lines are the Gaussian (three) fit of the ESA spectra.

building blocks for larger systems with larger TPA cross sections beyond the additive property of just increasing the chromophore density. It should also be noted that, for **3** and **5**, there is an increase in $\delta'$ by a factor of 2 in favor of **3**. This is surprising, as **5** clearly has the larger chromophore density. The observations on $\delta'$ suggest that molecules possessing higher symmetry give rise to larger TPA cross sections. Indeed, the TPA properties of the annulene systems may be adjusted by changing the molecular symmetry, as described above.

To explain the dominance of $\delta'$ for **3** and **6** in comparison to the other annulenes studied, we have considered a simplified sum-over-states formalism for the expression of the TPA cross sections,[2]

$$\delta \propto \sum_{e'} (M_{ge}^2 M_{ee'}^2)/([E_{ge} - E_{ge'}/2]^2 \Gamma) \qquad (1)$$

Here, $M_{ij}$ is the transition dipole moment from state $i$ to state $j$, and $E_{ij}$ is the energy difference between these states. $\Gamma$ is the damping factor. From steady-state absorption measurements, we have determined $M_{ge}$ using eq 2 (below), and the corresponding values are given in Table 1. It can be observed from the table that the results for the $M_{ge}$ calculations did not follow the same sequence of increase in $\delta'$ that has been observed from the TPA measurements. Thus, it is suggested that the oscillator strength of this particular transition is not the only determining factor which dictates the increase in the $\delta$ of the annulenes studied here. However, estimates of the magnitude of $M_{ee'}$ for the different annulenes did show a trend similar to that of the TPA cross-section measurements. Ultrafast transient absorption spectroscopy has been employed to determine the magnitude of $M_{ee'}$. We have measured the excited-state extinction coefficients under actinometric conditions for all the compounds. Shown in Figure 3 are the excited-state absorption (ESA) spectra (extinction coefficient versus wavelength) of the investigated molecules at the time delay of 150 fs (immediately after photoexcitation at 370 nm).

It can be observed from Figure 3 that annulene **6** has the highest excited-state extinction coefficient, while annulene **5** shows the lowest. Excited-state transition dipole moments ($M_{ee'}$) have been determined using the following expression:

$$M_{ij}^2 = (1500 \ln(10)\hbar cn)/(2\pi^2 N_A) \int (\epsilon(\bar{\nu}))/(\bar{\nu})\, d\bar{\nu} \qquad (2)$$

Here, $N_A$ is Avogadro's number, $c$ is the velocity of light, and $\epsilon$ is the extinction coefficient of the singlet state. As the ESA represents $S_1$-to-$S_n$ transitions, the observed ESA has been best fit with Gaussians, and we have determined the area under the curve to calculate the excited-state transition dipole moment. The corresponding $M_{ee'}$ values for different molecules are provided in Table 1. It can be noted from the table that $M_{ee'}$ is highest for **6**, followed by **3**, **4**, and **5**. Relative estimates of the TPA cross sections have been made using eq 1, with the data presented in Table 1. Within the sequence of **5**, **4**, **3**, and **6**, respective estimated ratios of cross sections ($\delta_{\text{molecule}}/\delta_{\mathbf{5}}$) of 1, 1.24, 1.43, and 2.4 closely followed the experimentally observed ratios ($\delta'_{\text{molecule}}/\delta'_{\mathbf{5}}$) of 1, 1.2, 2.14, and 2.84. The observed low excited-state transition dipole moment for the **5** can be ascribed to the presence of an additional meta-conjugation unit, which localizes the conjugation.[13] Thus, we are able to successfully predict the trend observed in experimental TPA cross sections using the optical absorption and femtosecond transient absorption measurements. It has been shown here that **6**, the molecule with highest order of symmetry, has a large TPA cross section by virtue of an enhanced $M_{ee'}$.

In conclusion, we have investigated new multi-chromophore symmetric annulenes for TPA properties important for optical applications. It is found that the increase in chromophore density is not the determining factor which governs the magnitude of the cross sections of these systems. The annulenes with high symmetry were observed to have a large ratio of the TPA cross section to the number of $\pi$-electrons. Linear and nonlinear optical measurements have shown that the increase in symmetry of the annulene systems enhances the TPA cross sections by virtue of higher excited-state transition dipole moments. These new annulene systems offer a new avenue toward increasing the two-photon cross section with identical building block chromophores but with different macromolecular symmetries. Furthermore, if we substitute donor and acceptor groups for the case of **1**, we observe almost 2 orders of magnitude enhancement in TPA cross section (Supporting Information). Large TPA cross sections can be realized if donor−acceptor groups (to increase intramolecular charge transfer) are substituted in larger annulene[14] systems.

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**Supporting Information Available:** Absorption and emission spectra of all the molecules, transient absorption measurements, complete ref 2, and details of all experimental techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

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