

Two-photon absorption properties of hexa-substituted benzene derivatives. Comparison between dipolar and octupolar molecules†

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Hexa-substituted benzene derivatives show larger two-photon cross sections than the corresponding dipolar counterparts and the largest values of $\delta_{\max} = 2000 \text{ GM}$ and $\delta_{\max}/\text{MW} = 2.25 \text{ GM g}^{-1}$ have been obtained with a compound having $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ bonds in the conjugation bridge.

During the last decade, there has been rapid progress in the development of efficient two-photon materials for possible applications in optical limiting,¹ 3D microfabrication,² and multiphoton microscopy.^{3,4} A variety of donor–bridge–acceptor (D– π –A) dipoles, donor–bridge–donor (D– π –D) quadruples, octupoles, multi-branched molecules, and organometallic compounds have been developed, and their structure–property relationships were investigated to develop organic materials with large two-photon absorption (TPA) cross-sections.⁵ The results of these studies reveal that the TPA cross section increases with the donor–acceptor strength, conjugation length, and the planarity of the π -center.

Recently, we reported that the first hyperpolarizabilities of the 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives are larger than those of the corresponding dipolar molecules, presumably due to the efficient π -orbital overlap between the three dipolar units sharing the central phenyl group.⁶ We also reported that there is a qualitative linear relationship between the first hyperpolarizabilities and two-photon cross sections of octupolar molecules.⁷ This suggests an interesting possibility that the two-photon cross section of the octupolar molecules may be higher than those for the corresponding dipolar analogues. Therefore, it seemed interesting to compare the TPA properties of the two types of molecules.

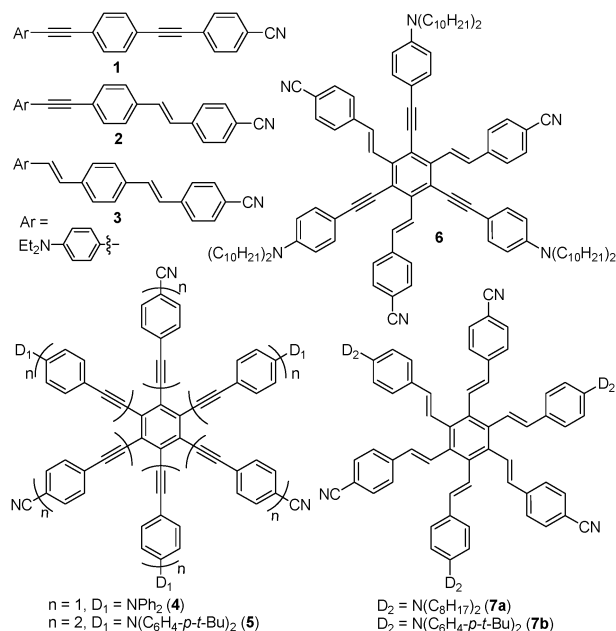
In this work, we have studied one- and two-photon absorption properties of a series of donor–acceptor substituted dipolar compounds (**1–3**) and their octupolar analogues (**4–7**) (Scheme 1). The effects of conjugation bridge, conjugation length, donor, and molecular symmetry on the one- and two-photon absorption properties of **1–7** have been studied. From these results, the structural motifs that induce large TPA cross sections have been elucidated.

Compounds **1–5** were available from previous studies.^{6,8} Synthesis of **6** and **7** is summarized in Scheme 2. To synthesize **6**, **A** was subjected to the Horner–Wittig reaction with

p-cyanobenzaldehyde to obtain **C**. Coupling between **C** and 4-(didecylamino)phenylacetylene under the Sonogashira condition produced **6**. Compound **7** was prepared from **B** by two consecutive Horner–Wittig reactions. To obtain **7a** and **7b**, **D** was brominated and phosphorylated to afford **E**, which was then reacted with *N,N*-dioctylaminobenzaldehyde and 4-[bis-(*p*-*tert*-butylphenyl)amino]benzaldehyde, respectively, under Horner–Wittig conditions. All compounds were unambiguously characterized by NMR and elemental analysis (see ESI†).

The λ_{\max} of **1–3** increased gradually in the order, **1** < **2** < **3**, as the $\text{C}\equiv\text{C}$ bond in the conjugation bridge is systematically replaced by the $\text{C}=\text{C}$ bond (Table 1). This indicates a more efficient intramolecular charge transfer (ICT) in this order, and that the $\text{C}=\text{C}$ bond is more effective conjugation bridge than the $\text{C}\equiv\text{C}$ bond.

As the molecular structure is changed from **1** to **4**, λ_{\max} is red shifted by 61 nm, indicating that ICT increases significantly as the three dipolar units share the central phenyl group as the conjugation path. Also, the molar extinction coefficient (ϵ) increases by 3-fold from **1** to **4** (Table 1). When the conjugation length was increased from **4** to **5**, the λ_{\max} decreased with a concomitant increase in the localized band (Fig. S1†), probably because the extended conjugation with the poorly conjugating $\text{C}\equiv\text{C}$ bonds inhibited the ICT.⁶

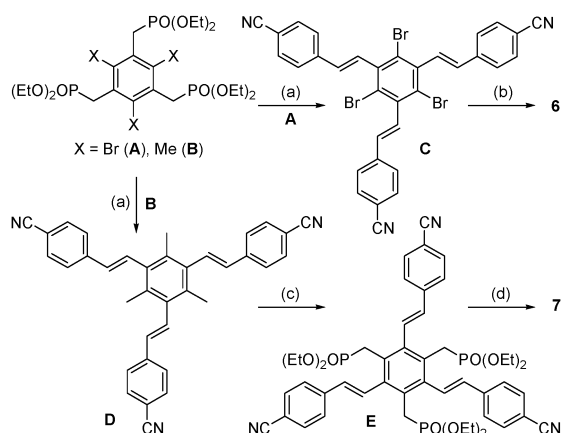


Scheme 1 Structures of dipolar (**1–3**) and octupolar molecules (**4–7**) used in this study.

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Scheme 2 Synthesis of **6** and **7**. Reagents and conditions: (a) 4-cyano-benzaldehyde/LDA/THF, 24 h; (b) 4-(didecylamino) phenylacetylene/Pd₂Cl₂(PPh₃)₂/CuI/Et₃N/THF–DMF, 100 °C, 36 h; (c) (i) NBS/BPO/CCl₄, 90 °C, 36 h; (ii) P(OEt)₃/toluene, 160 °C, 5 h; (d) *N,N*-dioctylaminobenzaldehyde (for **7a**) or 4-[bis-(*p*-*tert*-butylphenyl)amino]benzaldehyde (for **7b**)/LDA/THF, 24 h.

Table 1 Photophysical data of **1–7**^a

Cpd	λ_{\max} (10 ⁻⁴ ϵ) ^b	λ_{fl}^c	$\Delta\nu^d$	Φ^e	$\lambda_{\max}^{(2)}$ ^f	δ_{\max}^g	$\delta_{\max}/\text{MW}^h$
1	384 (3.05)	440	3314	1.00	780	300	0.87
2	393 (4.66)	499	5405	0.72	800	540	1.55
3	418 (3.93)	498	3843	0.71	820	450	1.28
4	445 (9.93)	512	2941	1.00	840	820	0.93
5	379 (17.2)	502	6465	0.74	800	1940	1.31
6	420 (8.46)	542	5359	0.21	820	2000	2.25
7a	402 (8.17)	526	5864	0.11	780	1550	1.73
7b	405 (8.34)	523	5571	0.13	800	1620	1.81

^a In toluene. ^b λ_{\max} of the one-photon absorption spectra in nm. The numbers in the parentheses are molar extinction coefficient in M⁻¹ cm⁻¹. ^c λ_{\max} of the one-photon fluorescence spectra in nm. ^d Stokes shift in cm⁻¹. ^e Fluorescence quantum yield, $\pm 10\%$. ^f λ_{\max} of the two-photon absorption spectra in nm. ^g Two-photon absorptivity in 10⁻⁵⁰ cm⁴ s per photon (GM), $\pm 15\%$. ^h The molecular weight (MW) was calculated by assuming that NR₂ = NMe₂. The unit is GM.

Interestingly, the λ_{\max} decreases in the order, **4** > **6** > **7**, as the conjugation bridges in the octupoles are sequentially changed from a C≡C to C=C bond (Table 1), despite the fact that C=C is a more efficient conjugation bridge than C≡C. This may be due to the steric hindrance between the vinylic C–H (=C–H) bonds and C≡C or =C–H bonds in the neighboring conjugation bridges, which may have distorted the structure and hampered the ICT.

The fluorescence spectra for most of the compounds show single peaks, indicating that the emission occurs from the lowest excited state with the largest oscillator strength. All of the compounds show large Stokes shifts ranging from 2941 for **4** to 6465 cm⁻¹ for **5**. The fluorescence quantum yields range from 1.0 for **1** and **4** to 0.11 for **7a**. The much smaller quantum yield for **7a** and **7b** may be due to the much lower energy of the emitting states, which may facilitate the nonradiative pathways.

The two-photon cross section (δ_{TPA}) was measured by the two-photon-induced fluorescence measurement technique using the femto-second (fs) laser pulses as described before.⁹

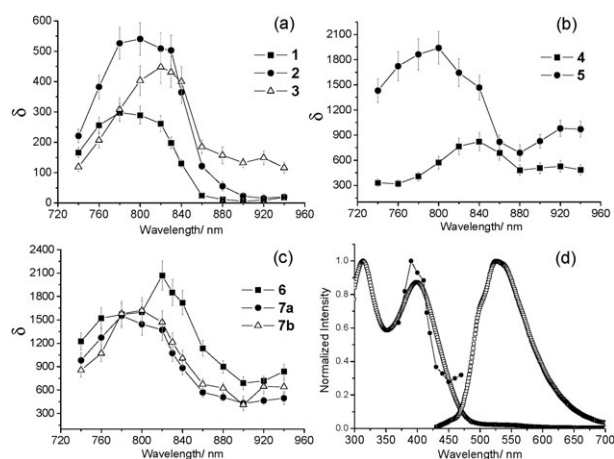


Fig. 1 (a–c) Two-photon excitation spectra of **1–7** in toluene. (d) Normalized one-photon absorption (○), emission (□), and two-photon excitation (●) spectra for **7a** in toluene. The two-photon spectrum is plotted against half the wavelength (twice the photon energy).

As shown in Fig. S2,[†] the output intensity of two-photon excited fluorescence is linearly dependent on the square of the input laser intensity, thereby confirming the occurrence of nonlinear absorption.

All compounds show large two-photon cross sections in the range of 300–2000 GM at 780–840 nm (Fig. 1, Table 1). The normalized one-photon absorption and two-photon excitation spectra show that $\lambda_{\max}^{(2)}/2$ of all compounds are located at nearly the same wavelengths as the absorption maxima (Fig. 1d and S3[†]). This is consistent with the prediction that the two-photon allowed states of the dipolar and octupolar molecules are similar to those of the one-photon allowed states.^{5,10}

The δ_{\max} and δ_{\max}/MW values increase in the order, **1** < **3** < **2**, as the conjugation bridge is changed systematically from C≡C to C=C. The increase in these values from **1** to **2** can be attributed to the enhanced ICT, while the small decrease from **2** to **3** is attributed to the distorted structure of **3** (Fig. 1, Table 1). It is to be noted that the structures of **1–3** are gradually more distorted in the order, **1** < **2** < **3**.⁶ This result indicates the importance of optimizing the ICT and planarity to design efficient TPA materials.

When the molecular structure was changed from **1** to **4**, the δ_{\max} value increased by 2.7-fold with large increases in λ_{\max} and ϵ values. However, the values of δ_{\max}/MW for **1** and **4** are almost the same, indicating negligible enhancement effect. On the other hand, when the conjugation bridge was changed from C≡C (**4**) to C=C (**6**) the δ_{\max} and δ_{\max}/MW values increased dramatically to 2000 GM and 2.25 GM g⁻¹, respectively, which are comparable to the most efficient TPA materials in the literature.⁵ A further change in the conjugation bridge from C≡C (**6**) to C=C (**7a**), however, caused a slight decrease in both values, which are in between those for **4** and **6**, probably because of the distorted structure (*vide supra*). In addition, the δ_{\max}/MW values of **6** and **7a** are larger than those for **2** and **3**, indicating the onset of the enhancement effect. Interestingly, the combination of C≡C and C=C bonds in the conjugation bridge appears to be most effective in enhancing the TPA properties of octupoles (**4–7**) and dipoles (**1–3**).

When the conjugation length was increased from **4** to **5**, δ_{\max} and δ_{\max}/MW values increased by 2.4-fold and 40%, respectively, indicating significant enhancement effect (Table 1). However, the change of the donor from NR₂ to NAr₂ increased the δ_{\max} value only slightly.

To conclude, we have studied one- and two-photon spectroscopic properties of a series of hexa-substituted benzene derivatives having styryl or phenylethynyl group as the substituent and their dipolar analogues. When the C≡C bond in the conjugation bridge was systematically replaced by the C=C bond, the λ_{\max} of the dipoles increased gradually, whereas those of octupoles decreased, probably because of the distorted structure. Except for **4**, the δ_{\max}/MW values of the octupoles were always larger than those for the corresponding dipoles. For both dipoles and octupoles, the largest δ_{\max}/MW values were determined for compounds (**2** and **6**) having C≡C and C=C bonds in the conjugation bridge. This result provides a useful guideline for the design of efficient TPA materials.

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