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2,6-Bis[4-(*p*-dihexylaminostyryl)styryl]anthracene Derivatives with Large Two-Photon Cross Sections

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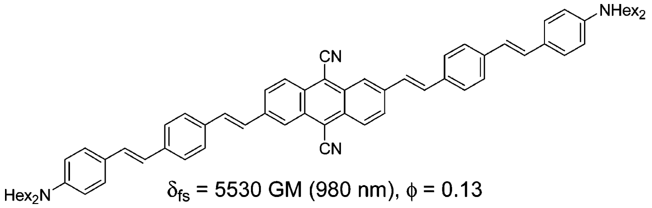
ABSTRACT



Anthracene derivatives with a variety of donor–acceptor substituents have been synthesized and shown to exhibit large two-photon cross sections over a wide range of wavelengths.

There is much interest in the development of organic materials exhibiting large two-photon (TPA) cross sections (δ_{TPA}) for possible applications in a number of new areas, including the fluorescence imaging of biological samples, optical limiting, photodynamic therapy, and three-dimensional optical data storage and microfabrication.[1−14] The most extensively investigated structural motifs are donor−bridge−acceptor (D−π−A) dipoles, donor−bridge−donor (D−π−D) quadrupoles, multibranched compounds, dendrimers, octupoles, and porphyrin.[15−20] The results of these studies reveal that δ_{TPA} increases with the donor/acceptor strength, conjugation length, and planarity of the π-center. Among the most extensively utilized π-centers are benzene, biphenyl, fluorene, dithieniothiophene, and dihydrophenathrene. Very recently, we reported that 2,6-bis(styryl)anthracene derivatives show large two-photon cross sections, demonstrating the utility of the anthracene as an efficient π-center for the two-photon chromophore.[18f]

In this work, we have synthesized a series of 2,6-bis[4-(*p*-dihexylaminostyryl)styryl]anthracene derivatives **1**−**5** with

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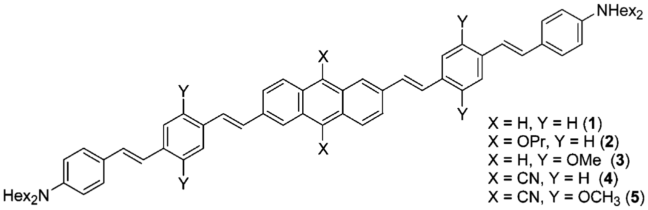
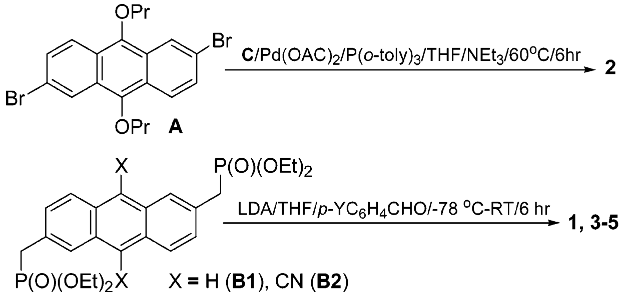


Figure 1.

a variety of donor−acceptor substituents (Figure 1) and measured the δ_{TPA} values by using the femtosecond (fs) fluorescence method. We were interested in learning whether the presence of additional donors and extended conjugation would significantly enhance the two-photon cross section. Dihexylamino group has been employed as the terminal donor to improve the solubility. We now report that **1**−**5** show large two-photon cross sections over a wide range of wavelengths.

Scheme 1



Synthesis of **1**−**5** is shown in Scheme 1. Sandmeyer reaction of 2,6-diaminoanthraquinone followed by the reductive alkylation afforded **A** in 67% overall yield. Compound **2** was synthesized by Heck coupling between **A** and 4-(*p*-dihexylaminostyryl)styrene (**C**). To prepare **1** and **3**−**5**, **B1** and **B2** were reacted with appropriate benzaldehyde derivatives. The structures of **1**−**5** were unambiguously characterized by ^{1}H and ^{13}C NMR and elemental analysis (see Supporting Information).

The molar absorptivity spectra for **1**−**5** in toluene are displayed in Figure 2. The peak positions of absorption and emission spectra are summarized in Table 1. Interestingly, $\lambda_{\max}^{(1)}$ of **1** and **4** are blue shifted by approximately 30−50 nm from those of the corresponding 2,6-bis(*p*-dihexylaminostyryl)anthracene derivatives (**D** and **E**), despite the extended conjugation (Table 1).[18f] This could be explained, if the structures of **1**−**5** are significantly distorted to hinder the effective conjugation. In addition, there are several peaks near $\lambda_{\max}^{(1)}$ in the absorption spectra. This indicates an

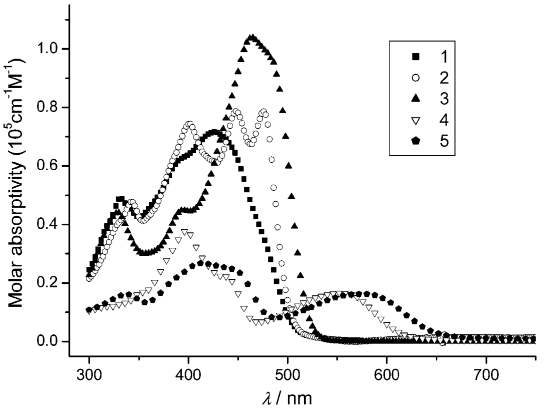


Figure 2. Molar absorptivity spectra of **1**−**5** in toluene.

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Table 1. One- and Two-Photon Properties of 1−5 in Toluene

compd	$\lambda_{max}^{(1)}$ [a]	$\lambda_{max}^{\{fl\}}$ [b]	$\Delta\tilde{\nu}$ [c]	Φ [d]	$\lambda_{max}^{(2)}$ [e]	δ_{max} [f]
D[g,h]	455	487	1444	0.78	800	1100[i]
E[h,j]	587	656	1792	0.11	990	2290[i]
1	427	503	3540	0.64	800	1140
2	448	497	2200	0.75	770	1810
	476	526	2000		800	1900
3	465	527	2530	0.66	770	2580
	478	551	2770		800	2490
4	531	650	3450	0.13	980	5530
5	575	678	2640	0.064	980	3650

[a] λ_{max} of the one-photon absorption spectra in nm. [b] λ_{max} of the one-photon fluorescence spectra in nm. [c] Stokes shift in cm^{-1}. [d] Fluorescence quantum yield. [e] λ_{max} of the two-photon excitation spectra in nm. [f] Peak two-photon absorptivity in 10^{-50} cm^4 s $photon^{-1}$ (GM) measured by fs pulses except otherwise noted. [g] 2,6-Bis(*p*-dihexylamino)anthracene. [h] Reference 18f. [i] δ_{max} measured by ns pulses. [j] 9,10-Dicyano-2,6-bis(*p*-dihexylaminostyryl)anthracene.

increased number of one-photon-allowed states near the lowest energy Franck−Condon states. If the structure is distorted, the intramolecular charge transfer (ICT) would be significantly inhibited, which would in turn increase the probability of the localized absorption.

The absorption spectra show a systematic bathochromic shift in the order **1** < **2** < **3** < **4** < **5**. The $\lambda_{max}^{(1)}$ is shifted to a longer wavelength as the 9,10-substituent is changed from H to OPr to CN, i.e., **1** < **2** < **4**, and as Y is changed to a stronger donor, i.e., **1** < **3** and **4** < **5**. This indicates that the energy gap between the ground and Franck−Condon states decreases as the conjugation is extended by the substituent regardless of whether it is electron donating or withdrawing. Furthermore, the charge-transfer bands for **4** and **5** are virtually separated from the shorter wavelength bands. This suggests a significant ICT from the donor to the acceptor.

The fluorescence spectra of **1**−**5** are displayed in Figure 3. As observed in the absorption spectra, the emission spectra of **2** and **3** show shoulders, indicating the existence of more than one emitting state. This is again due to the distorted structure. The much larger Stokes shifts for **1** and **4** than for **D** and **E** provide evidence supporting this explanation (Table 1). Because the excited-state structure is expected to be more stretched than the ground-state structure, the difference between the two structures, and hence the Stokes shift, should be larger for more distorted compounds.

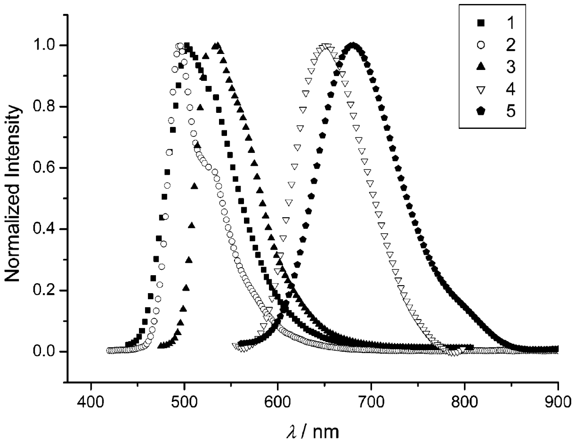

Figure 3. Normalized fluorescence spectra of **1**−**5** in toluene.

Overall, $\lambda_{max}^{\{fl\}}$ shows a parallel increase with $\lambda_{max}^{(1)}$ (Table 1). This means that the energy gap between the ground and lowest excited state monotonically decreases as the extent of charge transfer of the electronic ground state increases. All of the compounds show large Stokes shifts ranging from 2000 for **2** to 3540 cm^{-1} for **1**. The Stokes shifts are significantly smaller for compounds with OR groups, i.e., **2**,**3** < **1** and **5** < **4**, probably because the emitting states are destabilized by these substituents. The fluorescence quantum yields range from 0.75 for **2** to 0.064 for **5** and decrease as the extent of charge transfer increases. The much smaller quantum yields for **4** and **5** 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 determined by the two-photon-induced fluorescence measurement technique as described previously.[15b,18c] To avoid possible complications due to the excited-state excitation, we have used femtosecond (fs) laser pulses. The pulse width and repetition rate of the laser are 160 fs and 1 kHz, respectively (see Supporting Information). As shown in Figure 4, the output intensity of two-photon excited fluorescence is linearly dependent on the square of the input laser intensity, indicating the occurrence of nonlinear absorption.

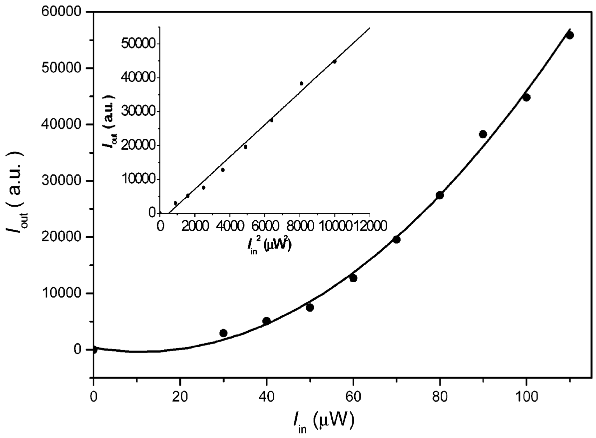

Figure 4. Dependence of output fluorescence intensity (I_{out}) of compound **1** in toluene on the input laser power (I_{in}). The insert shows the linear dependence of I_{out} on I_{in}^2 (800 nm, 1 kHz, τ = 160 fs).

The two-photon excitation spectra for **1**−**5** are displayed in Figure 5. Table 1 shows that $\lambda_{max}^{(2)}$ of **1**−**3** appear at 770−800 nm. This turns out to be very important for practical applications, because the most common source for the two-photon excitation is the Ti/Sapphire laser, which emits an

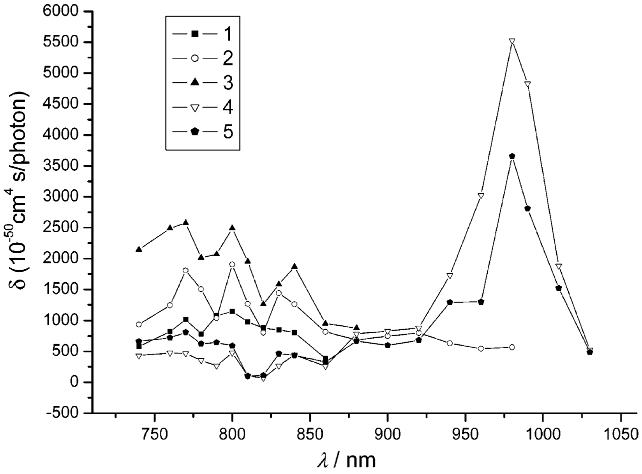

Figure 5. Two-photon excitation spectra of **1**−**5** in toluene.

intense beam at around 800 nm. Moreover, $\lambda_{max}^{(2)}$ increases dramatically to 990 nm when strongly electron-withdrawing CN groups are attached at the 9,10-positions (Table 1). This suggests an interesting possibility that the wavelength of the maximum two-photon cross section could be tuned by using an appropriate donor−acceptor substituent.

The δ_{max} value gradually increases in the order, **1** < **2** < **3** < **4**, reaching a maximum value of 5530 GM for **4**. Because $\lambda_{max}^{(1)}$ increases in the same order, the substituents seem to stabilize the excited state more than the ground state to diminish the energy gap between the ground- and two-photon-allowed states. This would predict a larger two-photon cross section, because the smaller the energy gap, the higher the probability of the two-photon excitation.[18a−c] This result underlines the importance of ICT for obtaining a TPA chromophore with a large δ_{max}. The only exception to this trend is **5**, whose δ_{max} is smaller than that of **4**. At present, the origin of this dichotomy is not clear.

Figure 6 shows that the two-photon-allowed state of **1** is located at somewhat higher energy than the Franck−Condon state, as predicted by the symmetry.[21] A similar result is observed for all compounds (Table 1). Nevertheless, there is a significant overlap between the one- and two-photon spectra in terms of the total absorption energy. Perhaps this is why δ_{max} values of **1**−**5** are so large, because the higher the probability of the overlap between the one- and two-photon-allowed states, the larger the two-photon cross section. Moreover, the single-photon excitation fluorescence (SPEF) and two-photon excitation fluorescence (TPEF) spectra overlap with each other. This indicates that the emission occurs from the same excited states, regardless of the mode of excitation.

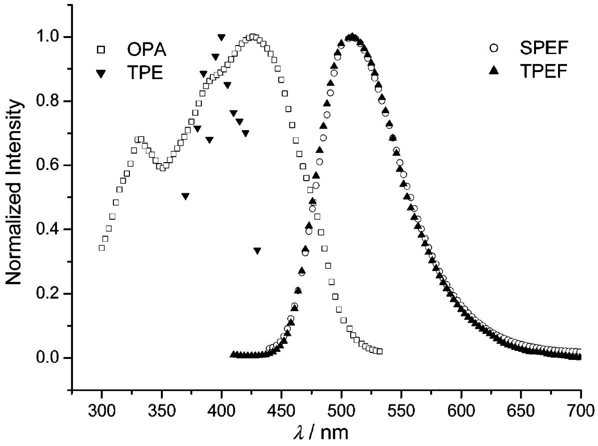

Figure 6. Normalized one-photon absorption (OPA) and two-photon excitation (TPE) spectra (left) and SPEF and TPEF spectra (right) of **1**. The two-photon spectrum is plotted against λ/2 (twice the photon energy).

It is interesting to note that the δ_{max} value of **1** is slightly larger than 1100 GM determined for **D** (Table 1).[18f] Moreover, the δ_{max} value of **4** is more than twice as large as that of **E**. The most interesting result from this study is that **1**−**5** show large TPA cross sections over a wide range of wavelengths, which will be useful for a variety of applications, including optical limiting. The results may be ascribed to the molecular size. As the molecular size increases through the extended π-conjugation, the density of states will increase, providing more effective coupling channels between the ground and two-photon-allowed states, which would in turn increase the TPA cross section over a wide range of wavelengths.

In conclusion, we have synthesized a series of 2,6-bis[4-(*p*-dihexylaminostyryl)styryl]anthracence derivatives with a large δ_{max}. The δ_{max} values increase gradually in the order **1** < **2** < **3** < **4**, reaching a maximum value of 5530 GM for **4**.[22] Moreover, **1**−**3** show large TPA cross sections over a wide range of wavelengths. These molecules may ultimately find useful applications as two-photon materials.

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Supporting Information Available: Synthesis of **1**−**5** and measurements of two-photon cross section by the fs fluorescence method. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] Most efficient TPA chromophores showing the largest TPA cross sections measured by fs fluorescence experiments are 2,7-bis{[7-(*p*-dioctylaminostryl)-9,10-dihydrophenathren-2-yl]vinyl}-9,10-dihydrophenathrene ($\lambda_{max}^{(2)}$ = 740 nm, Φ = 0.66, δ_{max} = 3760 GM)[17b] and the three-branched fluorenylene-vinylene derivative ($\lambda_{max}^{(2)}$ = 740 nm, Φ = 0.74, δ_{max} = 3660 GM).[17c]