

## 2,6-Bis(styryl)anthracene derivatives with large two-photon cross-sections†

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The first synthesis of 2,6-bis(styryl)anthracene derivatives with very large two-photon cross sections is reported.

Organic nonlinear optical materials exhibiting large two-photon absorption (TPA) cross sections ( $\delta_{\text{TPA}}$ ) are of considerable interest for applications in a number of new areas including three dimensional fluorescence imaging, optical limiting, photodynamic therapy, and three dimensional optical data storage and microfabrication.<sup>1–14</sup> A variety of compounds including donor–bridge–acceptor (D– $\pi$ –A) dipoles, donor–bridge–donor (D– $\pi$ –D) quadrupoles, multi-branched compounds, dendrimers, and octupoles have been synthesized and their structure–property relationships established.<sup>15–22</sup> The results reveal that that  $\delta_{\text{TPA}}$  increases with the donor/acceptor strength, conjugation length, and planarity of the  $\pi$ -center. Among the most extensively utilized  $\pi$ -centers are benzene, biphenyl, fluorene, dithienothiophene, and dihydrophenanthrene.

We thought that anthracene might be a useful  $\pi$ -center not only because it is an excellent fluorophore but also because its derivatives have been extensively used as fluorescence sensors. Hence, if such derivatives with large  $\delta_{\text{TPA}}$  are synthesized, it might be possible to develop two-photon sensors for biological applications. However, there has been no report regarding the TPA properties of such compounds. In this work, we have synthesized a series of 2,6-bis(styryl)anthracene derivatives (**1–3**) and measured their  $\delta_{\text{TPA}}$  by two-photon induced fluorescence. We now report that these compounds show among the largest TPA cross-sections ever reported.

Synthesis of **1–3** is shown in Scheme 1. The reaction between 2,6-dimethylanthraquinone (**A**) and *p*-cyanophenyllithium at  $-60$  °C produced 9,10-bis(*p*-cyanophenyl)-2,6-dimethylanthracene (**B**) in 56% yield. Reduction of **A** afforded 2,6-dimethylanthracene (**C**) in 73% yield. Bromination of **C** followed by cyanation produced 9,10-dicyano-2,6-dimethylanthracene (**D**) in 75% yield. To prepare **E**, **B–D** were reacted with NBS and then treated with  $\text{P}(\text{OEt})_3$ . Compounds **1–3** were synthesized by the condensation between the phosphonate ylids and benzaldehyde derivatives as shown in Scheme 1. The structures of **1–3** were unambiguously characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, and elemental analysis.

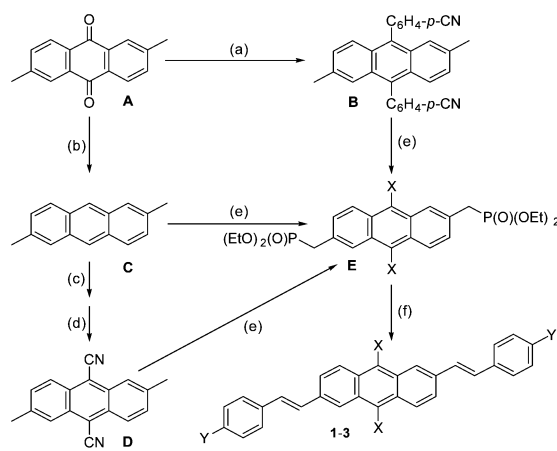
The two-photon cross section  $\delta$  was measured by using the two-photon-induced fluorescence measurement technique with eqn. (1), where the subscripts *s* and *r* stand for the sample and reference molecules.<sup>8b</sup> The intensity of the signal collected by a PMT detector was denoted as *S*.  $\Phi$  is the fluorescence quantum yield.  $\phi$  is the overall fluorescence collection efficiency of the experimental apparatus. The number density of the molecules in solution was denoted as *c*.  $\delta_r$  is the TPA cross section of the reference molecule.

$$\delta = \frac{S_s \Phi_s \phi_s c_r}{S_r \Phi_r \phi_r c_s} \delta_r \quad (1)$$

† Electronic supplementary information (ESI) available: synthesis details; measurement of two-photon cross-sections. See <http://www.rsc.org/suppdata/cc/b3/b309124d/>

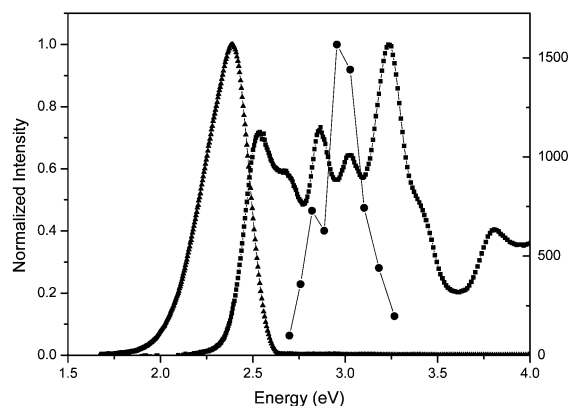
The normalized one-photon absorption and fluorescence spectra as well as the two-photon induced fluorescence excitation spectra for **3a** are shown in Fig. 1. The corresponding spectroscopic parameters are reported in Table 1.

The lowest energy one-photon absorption maxima ( $\lambda_{\text{max}}^{(1)}$ ) for **1–3** are red shifted by approximately 80–210 nm from that of anthracene ( $\lambda_{\text{max}}^{(1)} = 378$  nm). Moreover,  $\lambda_{\text{max}}^{(1)}$  gradually increases with a stronger donor/acceptor, *i.e.*,  $\text{NAr}_2 < \text{NHex}_2$  and  $\mathbf{1} < \mathbf{3} < \mathbf{2}$  (Table 1). Interestingly, the lowest energy bands for **2a,b** are virtually separated from the higher energy bands. This suggests a significant intramolecular charge transfer (ICT)



X = H (**1**), CN (**2**), *p*-CNC<sub>6</sub>H<sub>4</sub> (**3**) Y = NHex<sub>2</sub> (**a**), N(C<sub>6</sub>H<sub>4</sub>-*p*-*t*-Bu)<sub>2</sub> (**b**), NPh<sub>2</sub> (**b'**)

**Scheme 1** Reagents and conditions: (a) i: *p*-CNC<sub>6</sub>H<sub>4</sub>Br/BuLi/THF/ $-78$  °C–RT/5 h; ii: Zn/AcOH/120 °C/3 h; (b) HgCl<sub>2</sub>/Al/CCl<sub>4</sub>/cyclohexanol/85 °C/48 h; (c) Br<sub>2</sub>/CCl<sub>4</sub>/0 °C/5 h; (d) CuCN/pyridine/220 °C/4 h; (e) i: NBS/BPO/benzene/reflux/3 h; ii:  $\text{P}(\text{OEt})_3$ /reflux/12 h; (f) LDA/THF/*p*-YC<sub>6</sub>H<sub>4</sub>CHO/ $-78$  °C–RT/6 h.



**Fig. 1** Normalized one-photon emission (▲, excitation at 488 nm), absorption (■) spectra and two-photon excitation spectrum (●) for **3a** in toluene. The two-photon spectrum is plotted as a function of total transition energy (twice the photon energy).

**Table 1** One- and two-photon properties of **1–3**

	$\lambda_{\max}^{(1)a}$	$\lambda_{\max}^{(1)b}$	$\Delta V_{ST}^c$	$\Phi^d$	$\lambda_{\max}^{(2)e}$	$\delta_{\max}^f$	$\Phi\delta_{\max}^g$
<b>1a</b>	455	487	1444	0.78	800	1100	850
<b>1b</b>	454	479	1450	0.82	820	1340	1100
<b>2a</b>	587	656	1792	0.11	990	2290	250
<b>2b</b>	566	635	1920	0.15	990	2490	370
<b>3a</b>	488	535	1800	0.64	840	1570	1000
<b>3b'</b>	474	509	1451	0.84	820	1760	1480

<sup>a</sup>  $\lambda_{\max}^{(1)}$  of the one-photon absorption spectra in nm. <sup>b</sup>  $\lambda_{\max}^{(1)}$  of the one-photon fluorescence spectra in nm. <sup>c</sup> Stokes shift in  $\text{cm}^{-1}$  ( $1/\lambda_{\max}^{(1)} - 1/\lambda_{\max}^{(1)}$ ). <sup>d</sup> Fluorescence quantum yield. <sup>e</sup>  $\lambda_{\max}^{(2)}$  of the two-photon absorption spectra in nm. <sup>f</sup> The peak two-photon absorptivity in GM. <sup>g</sup> TPF action cross section.

between the donor/acceptor. A similar trend is observed in the fluorescence spectra, *i.e.*, larger bathochromic shift with a stronger donor/acceptor. This indicates a significant stabilization of the emitting states by the substituents, and provides additional evidence for the ICT. Also, the Stokes shift increases with a stronger acceptor, although it is relatively insensitive to the variation of the donors. As expected, the fluorescence quantum yields are always higher when  $\text{NAr}_2$  is the donor.

Fig. 1 shows that the two-photon allowed states for **3a** are located at somewhat higher energy than the ICT bands. Moreover, values of  $\lambda_{\max}^{(2)}$  for **1–3** increase with the electron-withdrawing ability of the 9,10-substituents (Table 1). This indicates an interesting possibility that the wavelength of the maximum two-photon cross section could be tuned by using appropriate substituents. Interestingly,  $\lambda_{\max}^{(2)}$  for **1** and **3** appear near 800 nm. This turns out to be very important for practical applications, because most TPF microscopy uses a visible beam with a wavelength around 800 nm.

The  $\delta_{\max}$  value of **1a** is 1100 GM ( $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$ ), which is somewhat larger than those for the closely-related 1,4-bis(*p*-dibutylaminoethyl)benzene and 4,4'-bis[4-(*p*-dihexylaminophenylethynyl)styryl]biphenyl. The value increases approximately two-fold when CN groups are bound to the 9,10-position (**2a,b**).<sup>8b,9b</sup> Note that **2a,b** show large bathochromic shifts in the absorption spectra and large Stokes shifts (Table 1). The acceptor groups 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 is, the higher the probability of the excitation will be. This result underlines the importance of ICT to obtain TPA chromophores with large  $\delta_{\max}$ . On the other hand, the values of  $\Phi\delta_{\max}$ , the two-photon fluorescence action cross-section, for **2a,b** are smaller than those of **1a,b** because of the smaller fluorescence quantum yields.

Optimization of  $\Phi\delta_{\max}$  has been accomplished by using *p*-cyanophenyl groups at the 9,10-positions. Hence,  $\delta_{\max}$  values of **3a,b'** are 1570–1760 GM, which are among the largest values reported in the literature.<sup>‡</sup> Also, the fluorescence quantum yields are relatively high, hence large  $\Phi\delta_{\max}$ . Finally,  $\lambda_{\max}^{(2)}$  values of **3a,b'** are 840 and 820 nm, respectively, which are close to 800 nm. Therefore, **3a,b** may be useful for applications that use two-photon excited fluorescence. It should be noted that  $\delta_{\max}$  and  $\Phi\delta_{\max}$  are always larger when  $\text{NAr}_2$  is used as the donor. The special effect of  $\text{NAr}_2$  donor has been previously reported.<sup>8</sup>

In conclusion, we have synthesized a series of 2,6-bis(styryl)anthracene derivatives with large  $\delta_{\max}$ ,  $\lambda_{\max}^{(2)}$  and  $\delta_{\max}$  increase with stronger acceptors at the 9,10-positions. Both  $\lambda_{\max}^{(2)}$  and  $\Phi\delta_{\max}$  have been optimized by introducing donor-substituted styryl and *p*-cyanophenyl groups at the 2,6- and 9,10-positions, respectively. These molecules may ultimately find useful applications as two-photon materials.

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## Notes and references

‡ The most efficient two-photon chromophores with very large two-photon cross-sections measured by the two-photon fluorescence method are 2,5-dicyano-1,4-bis(*p*-diphenylaminoethyl)benzene ( $\lambda_{\max}^{(2)} = 835 \text{ nm}$ ,  $\delta_{\max} = 1940 \text{ GM}$ ),<sup>8a</sup> dihydrophenanthrene derivatives ( $\lambda_{\max}^{(2)} = 740 \text{ nm}$ ,  $\delta_{\max} = 3760 \text{ GM}$ ),<sup>9a</sup> and 4,4',4''-tris{[2,5-dicyano-4-(*p*-diphenylaminoethyl)styryl]triphenylamine} ( $\lambda_{\max}^{(2)} = 840 \text{ nm}$ ,  $\delta_{\max} = 5030 \text{ GM}$ ).<sup>12e</sup>

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