High two-photon cross-sections in bis(diarylaminostyryl) chromophores with electron-rich heterocycle and bis(heterocycle)vinylene bridges†

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Received (in Cambridge, UK) 14th December 2006, Accepted 8th January 2007
First published as an Advance Article on the web 26th January 2007
DOI: 10.1039/b618265h

Chromophores in which vinylene units and either pyrrole or dialkoxythiophene groups form the bridge between two diarylaminophenyl groups exhibit two-photon cross-sections of 1000–5000 GM at 600–650 nm.

The applications of two-photon absorption (2PA), ranging from 3D fluorescence imaging, nonlinear optical transmission, and 3D microfabrication, have motivated recent interest in the development of new chromophores with large 2PA cross-sections, δ.[1] To realize the full potential of these applications it is necessary to develop more complete structure-property relationships for δ. Several classes of organic molecules have been investigated including quadrupolar π-systems with donor end groups (D–π–D);[2] species such as D–π–D bis(styryl)benzenes exhibit peak δ values at least an order of magnitude larger than their unsubstituted counterparts. δ can be increased further and the 2PA band can be red-shifted when the π bridge is elongated or acceptor-substituted (D–A–D). Here we report on the 2PA properties of 2,5-bis[4-(diarylamino)styryl]thiophenes, a 2,5-bis[4-(diarylamino)styryl]pyrrole (D–D′–D, **1**, **3**, **5**, Fig. 1),[3] and of extended chromophores with additional heterocycle–vinylene units in the bridge (D–D′–D′–D, **2**, **4**, **6**) and compare them to those of the previously investigated chromophore **7**.[2a,c]

The 2PA spectra were determined by two-photon-induced fluorescence (for lower photon energies) and Z-scan (for higher photon energies) and are shown for some of the compounds in Fig. 2. **1–6** all show moderate (<1000 GM; 1 GM = 1 × 10^{-50} cm^4 s $photon^{-1}$ $molecule^{-1}$) 2PA in the 3.0–3.5 eV state-energy range (*i.e.*, corresponding to absorption of photons of energy 1.5–1.75 eV, equivalent to a wavelength of 700–830 nm), with distinct maxima resolvable for most cases, but only a shoulder observed for **2**. As previously reported,[2a,c] **7** also shows a well-defined moderate peak in δ in this region. For compounds **2–6** a more intense (>1000 GM) 2PA feature is observed at higher energy (state energy >3.5 eV; photon energy >1.75 eV; photon wavelength <700 nm). For **1** and **7** only the onset of a high-energy peak is seen in the energy range studied. We note that, as with 1PA (see ESI†), the 2PA peaks of the pyrrole-bridged compounds are blue-shifted

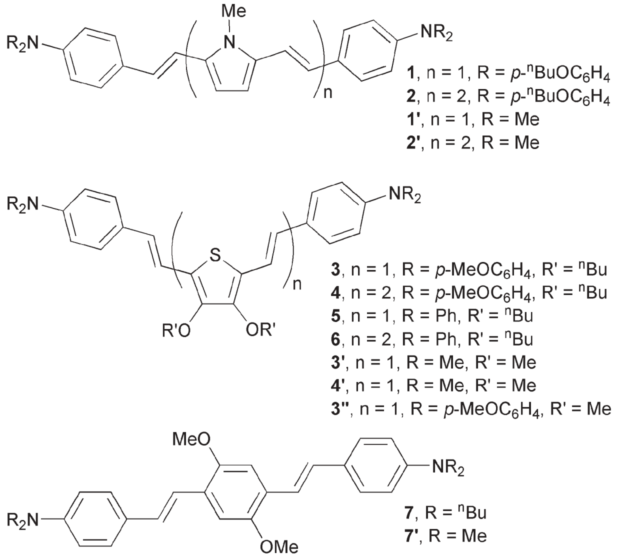

Fig. 1 Structures of **1–7** and model compounds **1′–4′**, **7′** and **3″**.

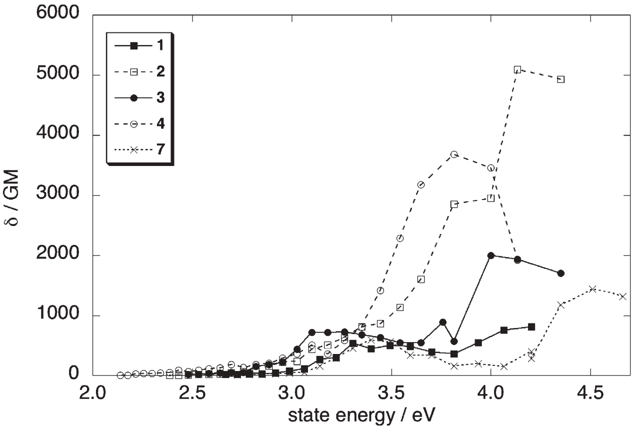

Fig. 2 Two-photon spectra of **1–4** and **7** in THF.

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† Electronic supplementary information (ESI) available: Experimental details for synthesis, 2PA measurements and calculations; characterizing data including electrochemical and spectroscopic data; 2PA spectra for **1–7** with data points acquired by Z-scan and two-photon fluorescence differentiated. See DOI: 10.1039/b618265h

relative to the corresponding dialkoxythiophene species, and those of the n = 2 molecules are red-shifted relative to their n = 1 analogs. The R = Ph compounds, **5** and **6**, show similar 1PA and 2PA spectra to the R = p-MeOC$_6$H$_4$ chromophores, **3** and **4**, respectively (see ESI†).

For (approximately) centrosymmetric systems, the cross-section for 2PA from the ground state, g, into a state, e′, is often dominated by three-state terms of the form

$$\delta_{\mathrm{e}',\text{3-state}} \propto E_{\mathrm{ge}'}^2 \frac{M_{\mathrm{ge}}^2 M_{\mathrm{ee}'}^2}{(E_{\mathrm{ge}} - (E_{\mathrm{ge}'}/2))^2} \tag{1}$$

where E and M are energies and transition dipole moments respectively, and where the e subscript denotes an intermediate 1PA-allowed state.[4] Quantum-chemical calculations on the model compounds (Fig. 1) were used to obtain values of δ (obtained including the 50 lowest singlet excited states in the perturbative description, see ESI†) and of the quantities entering eqn (1) (see Table 1) for the lowest lying 2PA states. The calculated δ values are in qualitative agreement with experiment. In all cases, there is a strong 2PA peak in the high-energy region; the magnitude of δ is also consistent, considering the significantly larger peak-widths in the experimental data (*ca.* 0.6 eV compared to 0.2 eV for calculations; see ESI†). The theoretical results show several weaker 2PA-active states in the 3.0–3.5 state-energy eV region, consistent with the measured low-energy 2PA profiles; however, δ for these features is underestimated in the calculations. In part this can be attributed to replacing the terminal aryl with methyl groups (**3′** *vs.* **3″**). We also cannot exclude additional vibrational channels contributing to the overall magnitude of those maxima. Such contributions have been discussed before[5] and have also been identified as being responsible for deviations between theory and experiment for relatively weak 2PA features.[6] The trends in the energies of the 1PA- and 2PA-active states for the different compounds are well reproduced by the calculations; typically for the methodology used,[6] the absolute values of the excited-state energies are, however, somewhat overestimated. Calculations also suggest that the onset we seen in the high-energy region for **1** and **7** are tails of strong 2PA peaks similar to those seen for **2–6**.

Table 1 INDO/MRDCI-calculated state energies (eV) and transition dipole moments (D) for the most strongly allowed low-lying 1PA (italics, denoted e) and 2PA (denoted e′) states of **1′–4′**, **3″** and **7′**, along with calculated detuning energies (eV) and cross-sections (GM) for the 2PA states

	State	E_{ge} or $E_{\mathrm{ge}'}$[a]	$E_{\mathrm{ge}} - (E_{\mathrm{ge}'}/2)$[b]	M_{ge} or $M_{\mathrm{ee}'}$[c]	δ[d]
1′	S_1 (e)	3.41		11.3	
	S_2 (e′)	3.53	1.65	7.8	132
	S_7 (e′)	4.92	0.95	7.3	855
	S_8 (e′)	5.20	0.81	19.1	9471
2′	S_1 (e)	3.08		13.6	
	S_2 (e′)	3.33	1.42	9.5	341
	S_5 (e)	4.73	0.71	23.6	22453
3′	S_1 (e′)	3.24	1.75	5.7	50
	S_2 (e)	3.37		10.2	
	S_3 (e′)	4.19	1.27	5.5	179
	S_7 (e′)	4.79	0.98	7.0	543
	S_8 (e′)	4.94	0.90	20.2	6104
3′	S_1 (e)	3.21		11.1	
	S_2 (e′)	3.36	1.53	8.7	175
	S_3 (e′)	3.82	1.30	9.2	406
	S_6 (e′)	4.70	0.86	10.2	1643
	S_7 (e′)	4.77	0.82	18.9	6781
4′	S_1 (e′)	2.89	1.59	6.2	71
	S_2	3.04		12.1	
	S_3 (e′)	3.71	1.18	4.0	120
	S_5 (e′)	4.42	0.83	22.8	10031
7′	S_1 (e)	3.68		11.4	
	S_2 (e′)	4.11	1.62	12.0	447
	S_3 (e′)	4.31	1.52	3.7	77
	S_8 (e′)	5.50	0.93	19.9	8867

[a] E_{ge} and $E_{\mathrm{ge}'}$ for 1PA and 2PA states, respectively. [b] Detuning energy between the virtual state and the lowest energy strongly 1PA-allowed state. [c] M_{ge} and $M_{\mathrm{ee}'}$ for 1PA and 2PA states respectively, e in each case denoting the lowest energy strongly 1PA-allowed state. [d] Calculated cross-sections obtained including the 50 lowest singlet excited states in the perturbative description of δ with the term given in eqn (1) (with the lowest strongly allowed 1PA state as the intermediate state, e) making the dominant contribution (see ESI).

According to eqn (1), states with small detuning energies, $E_{\mathrm{ge}} - (E_{\mathrm{ge}'}/2)$, should exhibit strong 2PA;[7] this has been demonstrated experimentally in several classes of compounds with sharp low-energy cut-offs to 1PA and low detuning energies of 0.2–0.5 eV;[8] however, often 2PA maxima at small detuning energy will overlap with the tail of 1PA, reducing the usefulness of these systems for practical applications. In the strong high-energy peaks of the present compounds, however, the detuning energies are still relatively large (see Table 1), but the large transition dipoles, $M_{\mathrm{ee}'}$, of *ca.* 20 D obtained for the higher lying states are *ca.* 3 × larger than those into the low-energy states. These enter the expression for δ as their square (see eqn (1)), amounting to approximately an order-of-magnitude increase in δ for the high- *vs.* low-energy states. The rest of the difference results from the smaller detuning and larger energy pre-factor that always apply to high-energy peaks. In addition it is worth noting that the 1PA and 2PA absorptions of the chromophores referred to in ref. 8 are considerably red-shifted relative to those of the present chromophores.

To understand the origin of the large $M_{\mathrm{ee}'}$ values in **1–6**, it is necessary to look at the quantum-mechanical nature of the excited states (*i.e.*, their configuration interaction, CI, descriptions), which are essentially equivalent for all the molecules investigated. As a representative example, we consider **3″**: while the CI description (given for spin-adapted determinants; see ESI† for details) of the 1PA state, S$_1$, is dominated by a single determinant (H → L), the two low-energy 2PA states (S$_2$ and S$_3$) and the strong high-energy 2PA state (S$_7$) are dominated by three main determinants:

$$\mathrm{S}_2 = 0.52(\mathrm{H,H} \rightarrow \mathrm{L,L}) - 0.38(\mathrm{H} \rightarrow \mathrm{L{+}1}) - 0.42(\mathrm{H{-}1} \rightarrow \mathrm{L})$$

$$\mathrm{S}_3 = 0.67(\mathrm{H{-}1} \rightarrow \mathrm{L}) - 0.58(\mathrm{H} \rightarrow \mathrm{L{+}1})$$

$$\mathrm{S}_7 = 0.49(\mathrm{H,H} \rightarrow \mathrm{L,L}) + 0.42(\mathrm{H} \rightarrow \mathrm{L{+}1}) + 0.33(\mathrm{H{-}1} \rightarrow \mathrm{L})$$

Thus, the phases with which the doubly-excited and the two singly-excited determinants mix is different for S$_2$ and S$_7$; this mixing results in a correlation-induced redistribution of the oscillator strength between those two states, *i.e.*, the higher lying state gains transition dipole moment (and consequently 2PA cross-section) at the expense of the two lower 2PA states. A detailed theoretical discussion of this effect can be found in refs. 6 and 9. The behavior of the present D–D′–(D′)–D systems (which is similar to that calculated for stilbene)[9] is the exact opposite of what happens in D–A–D type molecules, where the breaking of that redistribution has been identified as the microscopic origin of the strong 2PA states in the low-energy region.[9] This is also evidenced by the experimental finding that here very strongly 2PA active states are found only at higher energies, while the primary advantage of the more "conventional" D–A–D systems is that there the lowest 2PA states are already characterized by high cross-sections.

It is worth noting that the heterocycles in the bridges lead to **1–6** being rather electron rich; **1** and **2** are oxidized at −0.19 and −0.37 V, respectively, *vs.* FeCp$_2^{+/0}$ and **3–6** all oxidize in the range +0.05–0.15 V (see ESI†). Excited-state potentials, $E_{1/2}^{+/*}$, can be estimated from $E_{1/2}^{+/0} - E_{0,0}$ where $E_{0,0}$ is the energy of the lowest singlet excited state (estimated from the onset of 1PA), and indicate that **1** (−2.71 V) and **2** (−2.69 V) are superior excited-state reducing agents to **7** (−2.58 V), whereas **3–6** (−2.15 to −2.35 V) are somewhat poorer than **7**. Since **7** has been shown to be a sufficiently powerful excited-state reductant to initiate the radical polymerization of acrylates, it has found application as an initiator for 2PA microfabrication.[10] The similarity of the excited-state redox potentials to that of **7**, along with the enhanced δ of the present compounds at higher energy, suggest the present compounds, particularly the more electron-rich pyrrole examples, might be useful 2PA photoinitiators.

Finally, we have performed preliminary pump–probe experiments on compound **4**; these indicate excited-state absorption at *ca.* 670 nm, a wavelength for which there is strong 2PA from the ground state (corresponding to a $E_{ge'}$ state energy of 3.7 eV), suggesting the possibility of optical pulse suppression[11] *via* a 2PA-induced excited-state absorption mechanism.[12]

In summary, we have shown that D–D′–(D′)–D chromophores can show high δ into a state with energy in the range *ca.* 3.8–4.1 eV (corresponding to photon energies of 600–650 nm), which in some cases is detuned sufficiently from double resonance that these states can be easily accessed experimentally without interference from 1PA. The high cross-sections associated with these peaks can be understood in terms of a correlation-induced redistribution of oscillator strength. The 2PA spectral features, along with the excited-state redox potentials for the present molecules, suggest potential use in 2PA microfabrication.

This material is based upon work supported in part by the STC Program of the NSF under Agreement No. DMR-0120967. We also thank the National Science Foundation (CRIF 04-43564), the AFOSR (FA95500410200), the DARPA (MORPH program, ONR N00014-04-0095), and NSF-China (Nos. 20420150034, 20433070, 10425420). We thank Greg Walker for supplying a sample of **7**.

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