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Bis(dioxaborine) compounds with large two-photon cross sections, and their use in the photodeposition of silver†

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Received (in Cambridge, UK) 25th March 2003, Accepted 24th April 2003
First published as an Advance Article on the web 21st May 2003

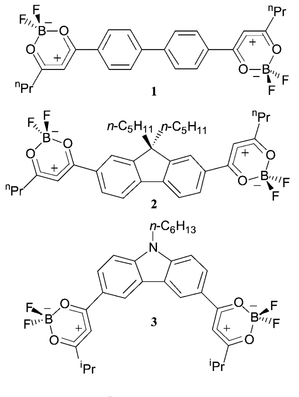
Compounds in which two dioxaborines are linked by a conjugated bridge exhibit high two-photon cross sections and can be used as sensitisers for the photodeposition of metallic silver lines.

Two-photon excitation can be utilised for a variety of applications including 3D fluorescence microscopy,[1] optical limiting,[2] and 3D microfabrication.[3–5] The advantages of two-photon-induced processes over analogous one-photon processes are that excitation may be carried out with sub-diffraction-limited 3D resolution, and at depth in optically dense media. However, to fully exploit the greater potential of two-photon-induced processes, chromophores with high two-photon absorption (TPA) cross sections, δ, are required. Recent structure–property studies have shown that π-systems, symmetrically substituted with donors (D) and/or acceptors (A), can have large TPA cross sections (δ).[6,7]

Previous studies of simple D–π–A chromophores have shown the 1,3,2-(2*H*)-dioxaborine moiety to be a potent π-acceptor, when attached to a π-system through its 4-position.[8] Dioxaborines (DOBs) are heterocycles which can be regarded as β-diketonate complexes of boron dihalides, dicarboxylates or dialkoxides. As shown in Scheme 1, the boron carries a formal negative charge, with a positive charge in the diketonate part of the molecule (computational work indicates a broadly similar picture with a net partial negative charge on the BF_2O_2 portion of the molecule and a partial positive charge on the unsaturated carbon atoms of the diketonate). Here we report on the TPA properties and use of A–π–A (**1** and **2**) and A–D–A (**3**) chromophores in which the acceptors are DOBs.

Diacetyl-substituted conjugated molecules were either obtained commercially or prepared from the appropriate π-system using standard Friedel–Crafts conditions. Compounds **1**–**3** (Scheme 1) were synthesised from reaction of the appropriate diacetyl species with $BF_3{\cdot}2AcOH$ and the appropriate carboxylic anhydride, in analogy to a literature procedure,[9] and were characterised by elemental analysis, mass spectrometry, and ^1H and ^{13}C NMR spectroscopy (see ESI†).

TPA spectra were measured for the bis-DOBs using the two-photon fluorescence method;[10,11,]† optical data are compared in Table 1. The main peaks in the TPA spectra of **1** and **2** occur at substantially less than twice the wavelength of the one-photon maximum, indicating that the most strongly allowed two-photon transition takes place to a state higher in energy to that populated in the one-photon transition, consistent with the mutually exclusive selection rules for centrosymmetric systems (at least some conformations of **1** and **2** are approximately centrosymmetric). A minor peak seen at longer wavelength in the TPA spectrum of **1** (700 nm ≡ transition energy of 3.54 eV) is much closer in energy to the main one-photon state (3.32 eV). The $\delta_{\max}$ values for the main peaks compare favourably with other TPA chromophores of similar conjugation length and $\lambda^{(2)}_{\max}$; for example, the D–π–D chromophore *E*-4,4′-bis(di-*n*-butylamino)stilbene is characterised by $\lambda^{(2)}_{\max}$ = 605 nm; $\delta_{\max}$ =



Scheme 1

Table 1 Experimental (CH_2Cl_2) and calculated optical data, and electrochemical data (MeCN, 0.1 M [$^nBu_4N$][PF_6], 50 mV s^{-1}), for bis(dioxaborines)

Compound	$\lambda^{(1)}_{\max}$ [a]/nm	η[b]	$\lambda^{(2)}_{\max}$ [c]/nm	$\delta_{\max}$/GM[d]	$\lambda^{(2;\,calc)}_{\max}$ [c]/nm	$\delta^{(calc)}_{\max}$/GM	$E_{\frac{1}{2}}$[e]/V
1	373	0.68	700	13	653	29	−1.29[g]
			588	433	535	547	
2	414	0.72	[f]	[f]	661	66	−1.31[h]
			612	489	567	522	
3	422	0.65	840	71	738	36	−1.50, −1.72[i]
					689	61	
			ca. 710	*ca*. 530	577	301	
			585	243	496	97	

[a] One-photon absorption maximum. [b] Fluorescence quantum yield. [c] Two-photon absorption maxima. [d] 1 GM = 10^{-50} cm^4 s photon^{-1}. [e] Half-wave potential for reduction to anion and/or dianion *vs*. $FeCp_2^+/FeCp_2$. [f] Long-wavelength range not studied. [g] Reversible 2e reduction ($E_{ox} - E_{red}$ = 48 mV). [h] Reversible, presumably two overlapping 1e reductions ($E_{ox} - E_{red}$ = 99 mV). [i] Successive 1e reductions, not fully reversible (I_{ox}/I_{red} = *ca*. 0.3).

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† Electronic supplementary information (ESI) available: synthesis and characterisation details for **1–3**, details for the two-photon measurements, for the methodology used in the quantum chemical simulations, and for the silver photodeposition. See http://www.rsc.org/suppdata/cc/b3/b303135g/

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DOI: 10.1039/b303135g

210 GM.[6] The A–D–A chromophore **3** has more complex one- and two-photon spectra (Fig. 1), due to its more effectively broken symmetry.

To gain insight into the origin of the observed TPA spectra, we performed quantum-chemical simulations using the perturbative Sum-Over-States (SOS) approach[12] including the coupling between the 300 lowest lying excited states. To account for the much larger width of the TPA peaks experimentally observed for molecules **1** and **2**, the calculated TPA spectra were convoluted with a Gaussian function in order to reproduce the experimental full width at half maximum.† The quantum-chemical simulations fully reproduce the experimental finding of a weak and a strong two-photon transition for **1** and **2**, as well as three TPA maxima in the investigated wavelength range for molecule **3** (with the calculated peaks containing contributions from several excited states). A detailed analysis of the nature of the TPA-allowed states in **1** and **2** shows that their description is dominated by the same excited determinants. The large difference in the $\delta_{\max}$ values between the two peaks can be explained as a consequence of a correlation-induced oscillator strength redistribution from the lower lying to the higher lying excited state (we have previously discussed similar effects in D- and A-substituted stilbene-based TPA dyes in ref. 13). The situation becomes significantly more complex in molecule **3**, in which transition dipoles and dipole moment changes parallel and perpendicular to the molecular axis are coupled, resulting in several channels contributing to the TPA cross-section for each excited state and, thus, in a breakdown of simple two-, or three-state models aimed at describing TPA processes within a perturbative description.

The bis-DOB TPA chromophores are attractive for certain applications, such as the photodeposition of silver.[5] Here the first excited state of the chromophore should be capable of reducing silver ions to the metal ($E_{\frac{1}{2}}$ for Ag^+/Ag is 0.04 and 0.41 V *vs.* $FeCp_2^+/FeCp_2$ in MeCN and THF respectively),[14] but it is important that the ground state does not undergo electron transfer thermally. This second condition is not met by electron-rich donor-substituted systems (*e.g.* $E_{\frac{1}{2}}[\mathbf{M}^+/\mathbf{M}]$ for *E*-4,4′-bis(di-*n*-butylamino)stilbene is −0.04 V in THF[3] and so its ground-state will be oxidised by Ag^+), but the ground states of **1–3** are inert to Ag^+ (no molecular oxidations are observed electrochemically in MeCN). The potential for oxidation of the excited state, *i.e.* the $\mathbf{M}^+/\mathbf{M}^*$ couple, depends on the LUMO energy of the molecule and is anticipated to be similar to, although less reducing than, the $\mathbf{M}/\mathbf{M}^-$ potentials which we have investigated by cyclic voltammetry. As shown in Table 1, the molecular reductions of **1–3** fall in the range −1.29 to −1.50 V, showing that the LUMO energies are sufficiently high that the excited molecule can transfer an electron from this orbital to Ag^+. We have investigated the use of **3** for the photodeposition of silver and have found that it is highly miscible with poly(*N*-vinylcarbazole) (PVK) and can be incorporated in composite matrices (dye/PVK/*N*-ethylcarbazole/$AgBF_4$/silver nanoparticles) for two-photon silver deposition at much higher levels ($\leq$13% by weight) than the bis-aldehyde dye we previously utilised in ref. 5 ($\leq$6%). **3** also has the effect of plasticising the composite and, therefore, allows reduction of the added *N*-ethylcarbazole plasticiser content from 33 to 17%. We have indeed been able to fabricate structures based upon metallic silver lines using **3** as the TPA dye.† The laser power threshold at which writing became possible in a sample containing 4% **3** was similar to that for a sample containing 6% of the dye used in ref. 5.

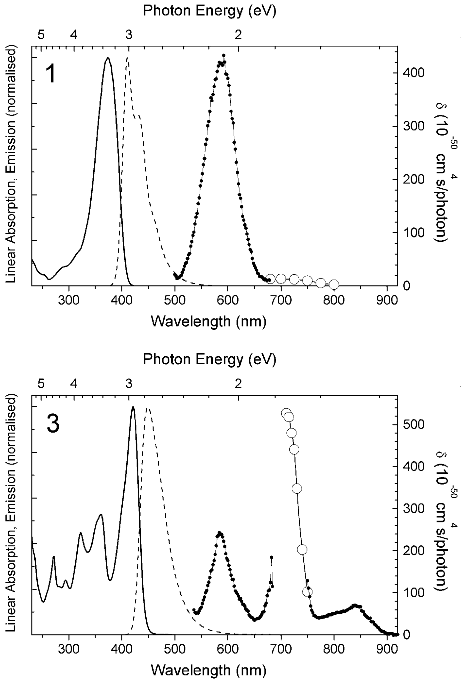

Fig. 1 Spectra of **1** and **3** in dichloromethane: one-photon absorption (solid line), fluorescence (dashed), and two-photon absorption as measured with fs (open circles) and ns (full circles) pulses.

To summarise, we have found bis-DOB-substituted π-systems to be effective TPA materials. Their electron-deficient character suggests applications for which donor-substituted dyes are unsuitable; indeed, we have shown one example to be effective for the two-photon photoreduction of silver ions. Moreover, the high fluorescence quantum yields of **1–3** suggest possible uses in other TPA applications.

Support from NSF (through the STC for Materials and Devices for Information Technology — DMR-0120967 — and through CHE-0107105), the AFOSR (F49620-02-1-0358 and F49620-99-1-0161), the Deutsche Forschungsgemeinschaft, the University of Arizona Photonics Initiative, the IBM SUR program, and the W. M. Keck Foundation (for instrumentation used in this research) is gratefully acknowledged. W. W. is a Postdoctoral Fellow of the Fund for Scientific Research, Flanders (Belgium). (FWO — Vlaanderen).

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