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

Marcus Halik,* Wim Wenseleers,a,b Cara Grasso,a Francesco Stellacci,c Egbert Zojer,c Stephen Barlow,c Jean-Luc Brédas,a Joseph W. Perry*a and Seth R. Marderab

a Department of Chemistry, University of Arizona, Tucson AZ 85721, USA
b Physics Department, University of Antwerp, Universiteitsplein 1, B-2610 Antwerpen, Belgium
c Institut für Festkörperphysik, Technische Universität Graz, Petersgasse 16, A-8010 Graz, Austria
d Optical Sciences Center, University of Arizona, Tucson AZ 85721, USA. E-mail: smarder@u.arizona.edu; jwperry@u.arizona.edu

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, optical limiting, and 3D microfabrication. The advantages of two-photon-induced processes over analogous one-photon processes are that excitation can 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). Previous studies of simple D–π–A chromophores have shown the 1,3,2-(2H)-dioxaborine moiety to be a potent π-acceptor, when attached to a π-system through its 4-position. Dioxaborines (DOB) 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 diketionate part of the molecule (computational work indicates a broadly similar picture with a net partial negative charge on the BF2O2 portion of the molecule and a partial positive charge on the unsaturated carbon atoms of the diketone). Here we report on the TPA properties and use of A–D–A (1 and 2) and A–D–D–A (3) chromophores in which the acceptors are DOBs. Diacetyl-substituted conjugated molecules were either obtained commercially or prepared from the appropriate D-system using standard Friedel–Crafts conditions. Compounds 1–3 (Scheme 1) were synthesised from reaction of the appropriate diacetyl species with BF3·2AcOH and the appropriate carboxylic anhydride, in analogy to a literature procedure, and were characterised by elemental analysis, mass spectrometry, and 1H and 13C NMR spectroscopy (see ESI†).

Table 1. The main peaks in the TPA spectra of the bis-DOB compounds were measured using the two-photon fluorescence method, and the 10,000× energy was used for the bis-DOB compounds to compare with the other TPA chromophores of similar conjugation length and A–D–A systems through its 4-position. 8

<table>
<thead>
<tr>
<th>Compound</th>
<th>λmax(1)/nm</th>
<th>λmax(2)/nm</th>
<th>δmax/GM</th>
<th>δmax(calc)/nm</th>
<th>E2/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>373</td>
<td>700</td>
<td>13</td>
<td>653</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>414</td>
<td>700</td>
<td>13</td>
<td>653</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>422</td>
<td>700</td>
<td>13</td>
<td>653</td>
<td>29</td>
</tr>
</tbody>
</table>

† 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/‡ Present address: Department of Materials Science and Engineering, MIT, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA.

Table 1. Experimental (CH2Cl2) and calculated optical data, and electrochemical data (MeCN, 0.1 M [Bu4N][PF6], 50 mV s−1), for bis(dioxaborines)

† 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/‡ Present address: Department of Materials Science and Engineering, MIT, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA.

![Scheme 1](Image)
210 GM. 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 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 \( \Delta \) 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. Here the first excited state of the chromophore should be capable of reducing silver ions to the metal (first excited state of the chromophore should be capable of reducing silver ions to the metal (first excited state of the chromophore should be capable of reducing silver ions to the metal (first excited state of the chromophore should be capable of reducing silver ions to the metal (first excited state of the chromophore should be capable of reducing silver ions to the metal (first excited state of the chromophore should be capable of reducing silver ions to the metal (first excited state of the chromophore should be capable of reducing silver ions to the metal), as well as for Ag + /Ag is 0.04 and 0.41 V vs. FeCP + /FeCP 2 in MeCN and THF respectively), but it is important that the ground state does not contain free electron transfer thermally. This second condition is not met by electron-rich donor-substituted systems (e.g. E[M\textit{M}'] for E=4,4' bis(di-n-butylamino)stilbene is \(-0.04\) V in THF and so its ground-state will be oxidised by Ag\textsuperscript{+}), but the ground states of 1–3 are inert to Ag\textsuperscript{+} (no molecular oxidations are observed electrochemically in MeCN). The potential for oxidation of the excited state, i.e. the M\textit{M}' couple, depends on the LUMO energy of the molecule and is anticipated to be similar to, although less reducing than, the M\textit{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\textsuperscript{+}. 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-ethylcarbazoleAgBF\textsubscript{4}/silver nanoparticle\textquotesingle s) 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. \(^{5}\) 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.

To summarise, we have found bis-DOB-substituted \( \pi \)-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 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).

Notes and references