

## An anionic organic mixed-valence system with a remarkably well-resolved vibrational structure in its intervalence band

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**The reduction of a phenylene-bridged bis(dioxaborine) affords a strongly delocalised organic mixed-valence system; for the first time details of the vibrations coupled to the electron transfer have been extracted from the intervalence band.**

Transition-metal mixed-valence (MV) compounds have played an important role in the study of intramolecular electron transfer.<sup>1</sup> More recently, organic MV systems<sup>2</sup> have attracted increasing attention due to their structural tunability, their tendency to exhibit rather strong coupling, and the insight they provide into the properties of advanced materials. In the course of our investigations of 2,2-difluoro-1,3,2-(2*H*)-dioxaborines as charge-transport materials, we investigated the MV properties of [1]<sup>-</sup> (Scheme 1) to gain insight into the degree of delocalisation possible in dioxaborine-based systems and its impact on the transport properties. Here we report the results of experimental and quantum-mechanical studies of [1]<sup>-</sup>.

Compound **1** was synthesized as previously described.<sup>3</sup> Cyclic voltammetry in CH<sub>3</sub>CN–0.1 M [nBu<sub>4</sub>N][PF<sub>6</sub>] reveals two successive reversible reductions at –970 and –1180 mV vs. ferrocenium–ferrocene, suggesting that both [1]<sup>-</sup> and [1]<sup>2-</sup> might be accessible *via* chemical reduction.

Chemical reduction to [1]<sup>-</sup> was achieved by addition of a sub-stoichiometric portion of a dry CH<sub>3</sub>CN or tetrahydrofuran (THF) solution of cobaltocene (the cobaltocenium–cobaltocene couple is at –1310 mV vs. ferrocenium–ferrocene in CH<sub>3</sub>CN<sup>4</sup>) to a dry CH<sub>3</sub>CN or THF solution of **1** under nitrogen. Electronic spectra in the two solvents were almost identical (Fig. 1). For both, a low-energy structured band with λ<sub>max</sub> = 920 nm (1.35 eV; 10870 cm<sup>-1</sup>) and ε<sub>max</sub> = ca. 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> was observed and assigned to the intervalence charge-transfer (IVCT) band of the mixed-valence [1]<sup>-</sup> anion (the lowest energy absorption maximum of neutral **1** is at 365 nm, that of the cobaltocenium cation is at 405 nm, and no low-energy bands were observed for a mononuclear dioxaborine radical anion<sup>5</sup>). A second structured band at 491 nm (2.53 eV; 20370 cm<sup>-1</sup>) is also attributable to [1]<sup>-</sup>.

We also generated [1]<sup>2-</sup> by addition of excess cobaltocene to **1** in CH<sub>3</sub>CN; the lowest energy feature (besides the weak and poorly resolved d–d transitions of excess cobaltocene<sup>6</sup>) was a structured peak with a maximum at 459 nm. Addition of excess **1** to this solution led to the appearance of the structured bands

at 920 and 491 nm, indicating that reduction to the dianion is chemically reversible and that the band at 459 nm is attributable to [1]<sup>2-</sup>. This further supports the assignment of the 920 nm peak as the IVCT transition of [1]<sup>-</sup>.

The observed vibrational fine structure in the IVCT band, along with the absence of solvent dependence, strongly points towards the assignment of [1]<sup>-</sup> to Robin and Day's class III;<sup>7</sup> most IVCT bands are featureless with vibrational structure only seen in a few cases of class-III systems.<sup>2c,e,f</sup> The maximum energy of the IVCT band, *E*<sub>op</sub>, in a class-III system is a direct measure of electronic coupling between redox sites *via* *H*<sub>ab</sub> = *E*<sub>op</sub>/2;<sup>8</sup> this equation indicates *H*<sub>ab</sub> = 0.68 eV for [1]<sup>-</sup>. This value can be compared with that for other *p*-phenylene-bridged MV systems; *H*<sub>AB</sub> is intermediate between the values found in cationic class-III diamine species (1.01 and 0.75 eV)<sup>2c</sup> and that found for a cationic class-II bis(hydrazine) derivative (0.22 eV).<sup>2d</sup> *H*<sub>AB</sub> for [1]<sup>-</sup> is larger than in previously studied examples of organic MV anions with bridges of comparable length (*H*<sub>AB</sub> = 0.40 and 0.46 eV for class III anions in which two quinone rings are fused to a common benzene moiety;<sup>9</sup> *H*<sub>AB</sub> = ca. 0.02–0.05 for several class II triarylmethyl radical/triarylmethanide species<sup>10,11</sup>) and almost as large as that in a small anion in which two quinones are directly fused (0.69 eV).<sup>9</sup>

The geometry of [1]<sup>-</sup> has been optimised at the density functional theory (DFT) using B3LYP/6-31G\* level<sup>12,13</sup> for the electronic configurations corresponding to the ground state and the first excited state. The energies of the low-lying excited states have been calculated with time-dependent (TD-) DFT<sup>14,15</sup> and Zerner's intermediate neglect of differential overlap (ZINDO).<sup>16</sup> All calculations were carried out using the Gaussian98 package.<sup>17</sup>

The DFT calculations<sup>18</sup> show that *syn*- and *anti*-rotameric isomers with C<sub>2</sub> and C<sub>i</sub> symmetry, respectively, are energetically comparable. While the *anti*-rotamer is more stable in the gas phase (Δ*E* ≈ 0.03 eV), solvent polarity should play a large role in the preferred conformation because the dipole moment of the *syn* conformer is ca. 10 D greater than that of the *anti*. The

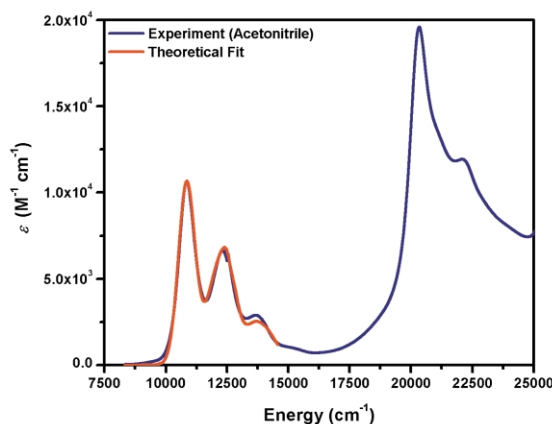
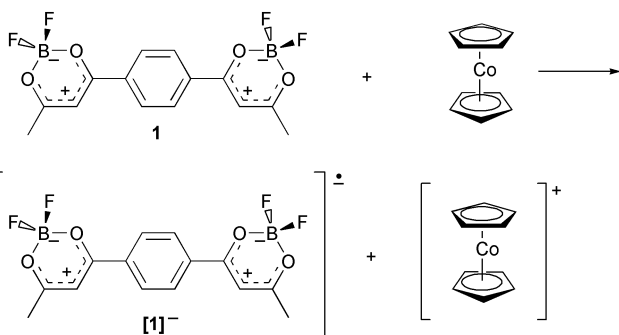


Fig. 1 Experimental absorption spectra of [1]<sup>-</sup> in CH<sub>3</sub>CN compared to a normalised vibronic fit to the low energy band.



Scheme 1 Chemical reduction of **1** using cobaltocene.

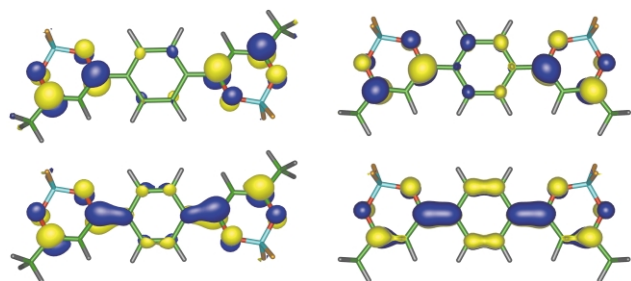
ground-state geometries of both conformers maintain planar structures with only very slight torsions ( $\sim 2^\circ$ ) between the dioxaborine rings and the central phenylene ring. Upon excitation of  $[1]^-$ , these torsions increase to  $\sim 25^\circ$  and there occurs a significant elongation (0.05 Å) of the C–C inter-ring bonds; little change occurs in the bonds to boron.

The charge distribution determined by the Mulliken population analysis indicates that the negative charge due to the excess electron is evenly distributed on the terminal dioxaborine rings in both the ground and excited states. This is consistent with a MV picture of  $[1]^-$  where each dioxaborine ring carries half a negative charge. The spin-density distribution in the excited state is also located primarily on the dioxaborine rings. However, the spin-density distribution of the ground state and the electron density of the singly occupied molecular orbital (SOMO; Fig. 2) are more extensively delocalised over the entire molecule. These results make it clear that the central phenylene ring strongly mediates the coupling between the two dioxaborine units, stabilizing a delocalised pattern in  $[1]^-$ .

The energy of the lowest optical transition of  $[1]^-$  (and the corresponding electronic coupling) has been evaluated from the energy spectrum obtained at TD-DFT and ZINDO levels and directly from the DFT calculations.<sup>19</sup> The three methods provide  $E_{op}$  energies of 1.70, 1.30 and 1.50 eV that are in reasonable agreement with the experimental value of 1.35 eV, with the best match obtained at ZINDO level. The ZINDO estimates of 3.80 and 2.80 eV for the lowest energy absorption maxima of neutral **1** and dianion  $[1]^{2-}$ , respectively, are also in good agreement with the experimental data of 3.40 and 2.70 eV.

The IVCT band of  $[1]^-$  has been analysed in the framework of a linear vibronic model that takes into account only the contribution of totally symmetric vibrations,<sup>20</sup> since these vibrations mainly contribute to the band broadening in strongly coupled MV systems.<sup>21</sup> The result of a numerical simulation is shown in Fig. 1. The reorganisation (relaxation) energy between the ground and excited states of  $[1]^-$  is dominated by a high-energy mode ( $\nu_1$ ) at  $1660\text{ cm}^{-1}$ , a frequency in the region of the C–C stretching modes of the phenylene ring; the best fit yields a contribution to the reorganisation energy of  $\lambda_1 = 0.102\text{ eV}$ . Contributions from at least two more modes can be modelled with frequencies of  $1100\text{ cm}^{-1}$  ( $\nu_2$ ) and  $140\text{ cm}^{-1}$  ( $\nu_3$ ) and with respective reorganisation energies  $\lambda_2 = 0.049$  and  $\lambda_3 = 0.029\text{ eV}$ . Experimental mode-by-mode partition of the reorganisation energy has been previously derived from resonance Raman spectroscopy.<sup>22</sup> The total reorganisation energy of 0.180 eV can be compared to values of 0.21–0.26 eV estimated for another similarly bridged species, the  $N,N,N',N'$ -tetrakis(*p*-methoxyphenyl)-*p*-phenylenediamine cation.<sup>21</sup>

In summary,  $[1]^-$  is a class-III organic MV species with a larger  $H_{AB}$  than anionic examples of comparable bridge length. The large electronic coupling suggests that conjugated polymers incorporating dioxaborine moieties could readily delocalise negative charge and, therefore, potentially act as efficient electron-transport materials. Moreover, we have described the first example of an organic MV species where details of the



**Fig. 2** The principal orbitals involved in the IVCT of  $[1]^-$ : the SOMO (below) and LUMO (above) for both the *anti*- (left) and *syn*-conformers (right), according to DFT calculations.

vibrations coupled with electron transfer have been extracted from the IVCT spectrum.

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- The difference in the excited-state energies of the *syn*- and *anti*-conformers is about 0.02 eV; for each conformer, the excited-state dipole moment is similar to that for the ground state.
- A similar procedure is commonly used to derive the reorganization energy from photoelectron spectroscopy measurements (e.g. N. E. Gruhn, D. A. da Silva Filho, T. G. Bill, M. Malagoli, V. Coropceanu, A. Kahn and J.-L. Brédas, *J. Am. Chem. Soc.*, 2002, **124**, 7918).
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