Mulliken–Hush analysis of a bis(triarylamine) mixed-valence system with a N···N distance of 28.7 Å†

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An organic mixed valence compound with a spacer length of 25 unsaturated bonds separating two amine redox centres was synthesised and the electron transfer behaviour was investigated in the context of a Mulliken–Hush analysis in order to estimate the longest redox centre separation for which an intervalence charge transfer band can be observed.

Mixed valence (MV) compounds which consist of two equivalent redox centres bridged by an unsaturated spacer play a dominant role for the investigation of basic charge transfer processes in small molecular model compounds.[1–3] In these MV radical ions one usually considers the so called intervalence charge transfer band (IV-CT) which originates from an optically induced charge transfer from one charged redox centre to the neutral other one. This IV-CT band can be analysed by the generalised *Mulliken–Hush* (GMH) theory[4,5] in order to evaluate the electronic coupling V between the two diabatic (noninteracting) states (green potentials in Fig. 1) in which the charge is localised at either redox centre.

While the IV-CT band analysis is straightforward for bis(triarylamine) radical cation MV systems exhibiting strong coupling, it is normally very complicated for weakly coupled systems (*e.g.* in cases where the redox centres are separated by a large spacer) due to the fact that absorption bands resulting from a hole transfer from one redox centre to the bridge unit (triarylamine to bridge bands) superpose the IV-CT band.[6–8] As can be seen from Fig. 1, this band is the more red shifted the more stabilised the hole at the bridge is. Furthermore, the relatively weak intensity of the IV-CT bands of these MV compounds complicates the analysis. Thus, no MV compound with a distance of more than 25.0 Å between two redox centres[9] has been investigated by optical methods and the electronic coupling evaluated, to the best of our knowledge. In order to explore the longest separation of redox centres that will allow the analysis of the associated IV-CT band by a *Mulliken–Hush* analysis we present in this communication the synthesis of the bis(triarylamine) MV compounds **1a** and **1b** in which the distance between the amine centres are 28.7 Å. By using cyano-substituted benzenes in **1b** as electron deficient spacer units we raise the energy of the local bridge state to minimise the overlap of the bridge band and the IV-CT band (Fig. 1).

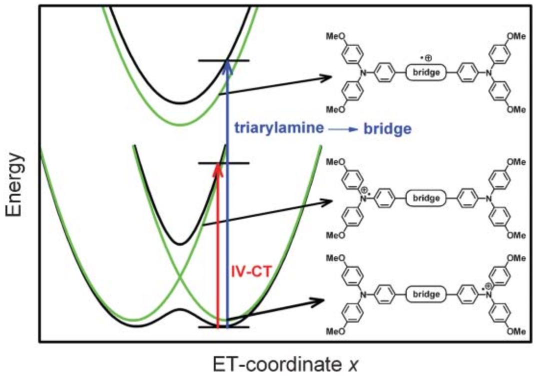
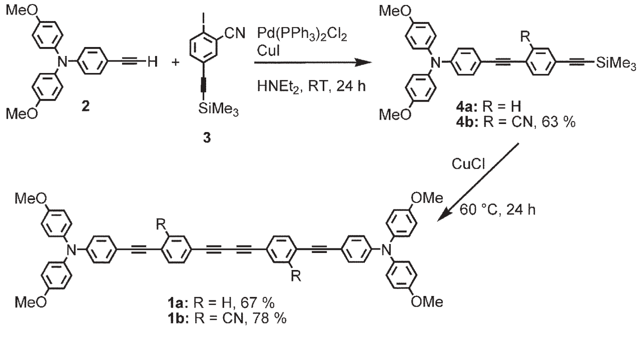


Fig. 1 Adiabatic (black lines) and diabatic (green lines) states within a three level model projected on one dimension.

Compound **1b** was synthesised starting from the terminal alkyne **2**[10] and benzonitrile **3**[11] by a Pd-catalysed *Hagihara–Sonogashira* coupling reaction[12,13] to obtain the precursor **4b** which could be directly transferred to the desired product by a new *Hay* coupling reaction[14] in good yield. In the same way bis(triarylamine) **1a** was synthesised starting from silane **4a**[16] (Scheme 1).

The cyclic voltammogram (CV) of **1b** in 0.1 M tetrabutylammonium hexafluorophosphate (TBAH)–CH_2Cl_2 solution shows four oxidation processes. The first two processes are reversible but not resolved (digital simulations yields E^1_{Ox} = 330 mV and E^2_{Ox} = 385 mV; for comparison, the statistical value for two noninteracting redox centres ΔE = 35.6 mV) and can be assigned to the oxidation of both triarylamine centres. The third and fourth processes ($E^{3/4}_{\mathrm{Ox}} \approx$ 1000 mV) are also not resolved but are irreversible (CV and digital simulation are shown in Supporting Information†). For a more detailed study of the ET behaviour we performed a UV/Vis/NIR-monitored chemical oxidation of **1b** in dichloromethane by a stepwise addition of a $SbCl_5$–CH_2Cl_2 solution (1.0 mM) (Fig. 2).



Scheme 1 Synthesis of compounds **1a** and **1b**.

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† Electronic supplementary information (ESI) available: synthesis and spectral data of compounds **1a**, **1b** and **4b**, CV of **1b** and digital simulation. See DOI: 10.1039/b604603g

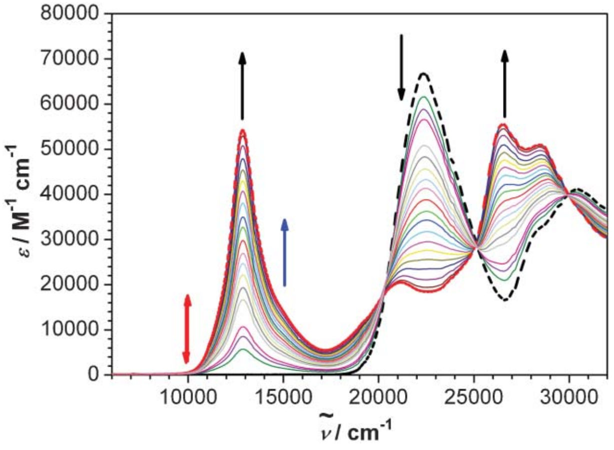

Fig. 2 Chemical oxidation of **1b** (dashed black line) to the dication $\mathbf{1b}^{2+}$ (dashed red line) in dichloromethane by stepwise addition of a $SbCl_5$–CH_2Cl_2 solution (1.0 mM). Further addition of the oxidant causes no more change of the spectrum.

As expected, a band A at around 23 000 cm^{-1} which is typical of a triarylamine system decreases with proceeding oxidation while in the same way a new intense band at 13 000 cm^{-1} increases which is associated whith a π–π* transition of the dianisylphenylamine radical cations.[16] This band also shows a shoulder at *ca.* 14 000 cm^{-1} which we assign to a hole transfer from the triarylamine centre to the bridge unit. Owing to the electron withdrawing nitrile substituents this band is at distinctly higher energy than in **1a** (Fig. 3) or any other analogous triarylamine systems where the bridge is electron rich.[6,8,16] Even more interesting is the observation of a weak and broad absorption band at about 10 000 cm^{-1} which partially overlaps with the red edge of the π–π* transition band. With proceeding oxidation of **1b**, this band first increases as the monocation $\mathbf{1b}^{+}$ is mainly generated and decreases at further oxidation to the dication $\mathbf{1b}^{2+}$ (Fig. 4). This behaviour proves the 10 000 cm^{-1} band to be an IV-CT band associated with an optically induced hole transfer from one triarylamine to the other.[1]

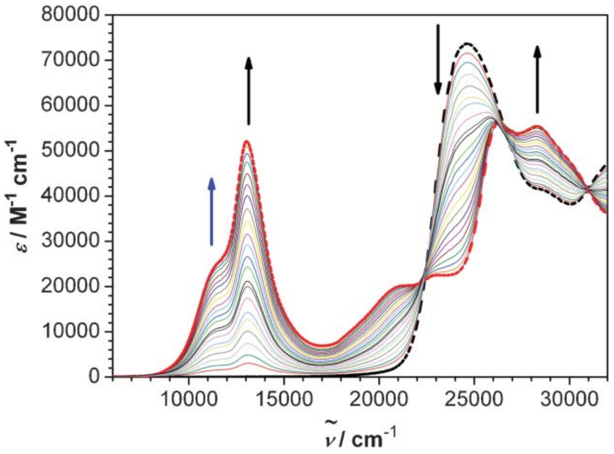

Fig. 3 Chemical oxidation of **1a** (dashed black line) to the dication $\mathbf{1a}^{2+}$ (dashed red line) in dichloromethane by stepwise addition of a $SbCl_5$–CH_2Cl_2 solution (1.0 mM). Further addition of the oxidant causes no more change of the spectrum.

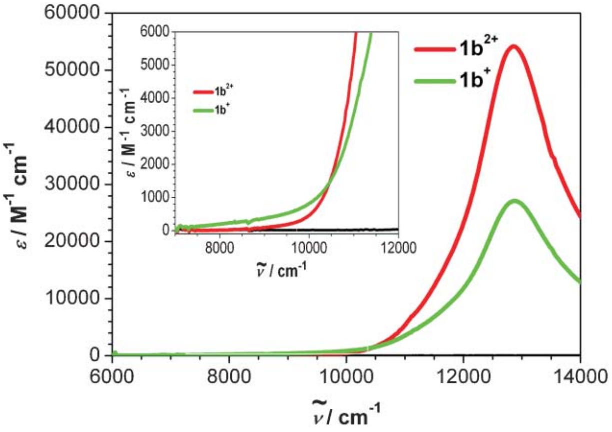

Fig. 4 Vis/NIR spectra of $\mathbf{1b}^{+}$ and $\mathbf{1b}^{2+}$ in dichloromethane.[17]

For comparison, the chemical oxidation of **1a** in dichloromethane is shown in Fig. 3. It is obvious that an analysis of the IV-CT band is only possible when the bridge band is blue shifted and the overlap with the IV-CT band is minimised. The data of the bands of **1a** and **1b** observed during the chemical oxidation are summarised in Table 1.

In order to investigate the IV-CT band in the context of a *Mulliken–Hush* analysis we extracted[17] the spectrum of pure $\mathbf{1b}^{+}$ from the redox titration of **1b** and fitted both the π–π* transition band and the IV-CT band with four Gaussian functions (Fig. 5).

From this fit we determined the parameters of the IV-CT band of $\mathbf{1b}^{+}$ ($\tilde{\nu}_{max}$ = 11 790 cm^{-1}, ε = 990 M^{-1} cm^{-1}, $\tilde{\nu}_{1/2}$ = 4060 cm^{-1}).

$$V_{12} = \frac{\mu_{ag}\tilde{\nu}_{max}}{\Delta\mu_{12}} \qquad (1)$$

$$\Delta\mu_{12} = \sqrt{\Delta\mu_{ag}^2 + 4\mu_{ag}^2} \quad \text{with} \quad \Delta\mu_{ag} = e \times r \qquad (2)$$

For the evaluation of the electronic coupling V_{12} by eqn (1) (where μ_{ag} = 1.98 D is the transition dipole moment of the IV-CT band) the diabatic dipole moment difference $\Delta\mu_{ag}$ is needed which we calculated by eqn (2) from the diabatic quantity $\Delta\mu_{ag}$ which is the diabatic dipole moment difference. In order to get a reliable value of $\Delta\mu_{ag}$ we performed an AM1-CI optimisation† of $\mathbf{1b}^{+}$ which yields $\Delta\mu_{ag}$ = 122.8 D. The computed dipole moment also shows that the effective ET distance *r* is about 90% of the often used N···N distance of the neutral compound.

The energy of the IV-CT band $\tilde{\nu}_{max}$ which corresponds (exactly within a two-level approximation with parabolic potentials) to the Marcus reorganisation energy λ is significantly higher than for corresponding bis(triarylamine) radical cations with shorter spacer units. In fact we discovered that in such systems λ passes through a minimum when plotted against the length of the spacer, and for MV systems with bridge units composed of more than ten bonds λ steadily increases.[2] An increase of the reorganisation energy with increasing redox centre separation is due to the dominating solvent reorganisation contribution according to the Born model.[19] Furthermore, the high energy value of $\tilde{\nu}_{max}$ in $\mathbf{1b}^{+}$ is also confirmed by the results of the AM1-CI calculation which yields 10 040 cm^{-1}.

With the above mentioned data we calculated the electronic coupling V_{12} = 190 cm^{-1} by eqn (2). Current investigations about

Table 1 Absorption maxima and extinction coefficients of the bands in the UV/Vis/NIR spectra of neutral compounds **1a** and **1b**, the monocation **1b**$^+$ and dications **1a**$^{2+}$ and **1b**$^{2+}$

$\tilde{\nu}_{max}$/cm^{-1} [ε/M^{-1} cm^{-1}]	Band A (neutral triarylamine)	π–π*-transition	Bridge band
1b	22 300 [66 700]	—	—
1a	24 600 [73 700]	—	—
1b^{+a}	—	12 800 [19 900]	14 100 [10 200]
1b^{2+b}	—	12 800 [44 500]	14 300 [17 900]
1a^{2+b}	—	13 200 [45 000]	11 500 [22 400]

[a] Data obtained from a fit of the spectra of the monocation **1b**$^+$ with four gaussian functions.[17] [b] Data of the bands for the dications **1a**$^{2+}$ and **1b**$^{2+}$ were obtained from a fit of the observed bands assigned to a π–π*-transition and a hole transfer from one redox centre to the bridge unit by three gaussian functions.[18]

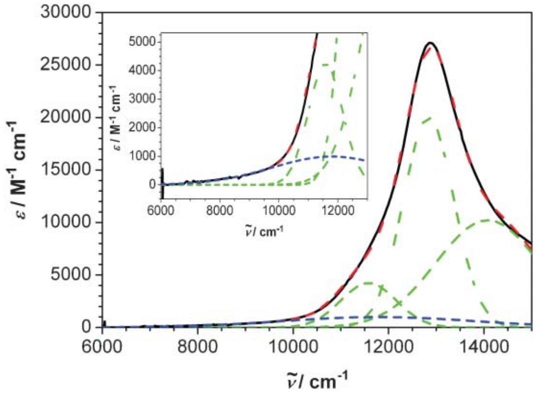

Fig. 5 Fit of the IV-CT band and the π–π* absorption band (red) with four Gaussian functions (green and blue).[18] The blue Gaussian function represents the IV-CT band.

the trends of V_{12} depending on the N···N distance in bis(triarylamines) with unsaturated spacer units anticipate a somewhat higher value for $V_{1/2}$ ($V_{1/2} \approx$ 400–500 cm^{-1}) for **1b**$^+$. The lower value evaluated for **1b**$^+$ might be due to increasing formation of unfavourable conformers about the triple bond axes.[20]

In summary, our strategy to build up a spacer with electron deficient units to raise the energy of the bridge state and to avoid an overlap of the bridge band and the IV-CT band was successful. In this way, we were able to determine the ET parameters of the organic MV compound **1b**$^+$ with a spacer unit consisting of 25 unsaturated bonds, the longest separation of redox centres for which an IV-CT band has ever been observed. A rather weak electronic interaction of both triarylamine units was ascertained by a *Mulliken–Hush* analysis of the IV-CT band. AM1-CI calculations are in agreement with the experimental results and also show that the charge in **1b**$^+$ is localised on the triarylamine centres. We anticipate that in cases where the total reorganisation energy is even lower than in the present case, and consequently the IV-CT band is at lower energy, one could observe an IV-CT band for a compound with an even longer redox centre separation.

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18 We fitted the spectrum of the dication **1b**$^{2+}$ with three Gaussian functions, one representing the bridge band, and two representing the π–π*-transition. The spectrum of the monocation **1b**$^{+17}$ was fitted with an additional Gaussian function for the IV-CT band. In this fit the energies of the three Gaussians were kept at almost the same energy as in **1b**$^{2+}$.
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