Communications

Fluorescence of Radical Ions in Liquid Solution: Wurster's Blue as a Case Study[**]

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Radical ions are involved in many crucial chemical reactions,[1,2] and they have thus been extensively studied over the years. However, their excited-state properties are still mostly unknown.[3] Only a very few of them have been reported to fluoresce,[4–6] making the detection of electronically excited radical ions extremely difficult. The lack of emission is usually explained by a very efficient internal conversion favored by a small energy gap between the first electronic excited state (D_1) and the ground state (D_0), and/or by the presence of D_2/D_1 and D_1/D_0 conical intersections (CI).[6,7] To gain insight into the origin of this phenomenon, we have studied the excited-state dynamics of the N,N,N',N'-tetramethyl-p-phenylenediamine radical cation, commonly known as Wurster's blue (WB) by using a combination of femtosecond spectroscopy and quantum-mechanical calculations.

WB not only has a long history in science and technology,[8–10] but it is also one of the few radical ions reported with low-temperature fluorescence.[11] Moreover, WB is a mixed-valence compound of the type $[M\text{-}B\text{-}M]^+$, and the displacement of electron density, associated with the first charge-resonance electronic transition, makes it an ideal system for studying photoinduced intramolecular charge transfer.[12,13]

At room temperature, WB stationary fluorescence cannot be detected in liquid solutions or in a solid polymer film. However, an emission band that is a mirror image of the absorption band becomes apparent below about 120 K (Figure 1 a,b) and the temperature dependence of its intensity is identical in both media. This dramatic variation can be accounted for by the temperature dependence of the fluorescence lifetime. It amounts to 650 ps at 82 K, whereas
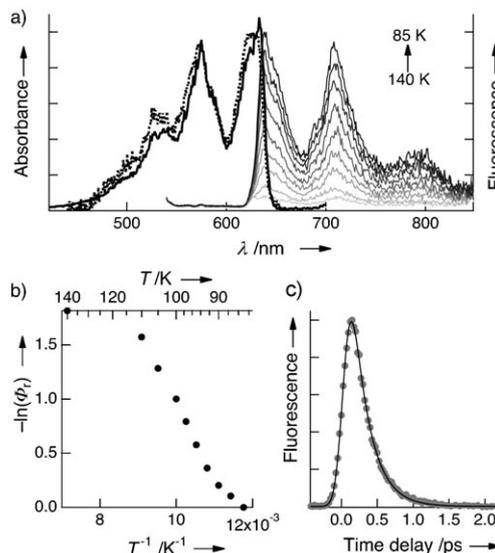
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Figure 1. a) Absorption (•••••) and fluorescence excitation spectra (——) at 85 K, and fluorescence spectra at various temperatures for WB in 1:1 methanol/ethanol. b) Temperature dependence of the relative fluorescence quantum yield ($\Phi_r = 1$ at 85 K) and c) time profile of the fluorescence intensity at 710 nm measured in D_2O at room temperature.

femtosecond resolution was required to detect fluorescence at room temperature. In the latter case, the fluorescence lifetime is 210 fs in acetonitrile and 240 fs in water (Figure 1 c; Supporting Information, Table S2). From these values and using the Strickler–Berg relationship, the fluorescence quantum yield varies from about 0.02 at 82 K to less than 10^{-5} at room temperature.

Transient absorption measurements upon $D_1 \leftarrow D_0$ excitation of WB in 12 solvents of different polarity and viscosity have been carried out to obtain a complete picture of the deactivation pathway of the excited-state population (Figure 2). These spectra reveal that the optically generated D_1 state population, identified by the stimulated emission band above 700 nm, decays directly to the D_0 ground state with a 200–300 fs time constant in all solvents investigated (Supporting Information, Table S3), which is in agreement with the fluorescence lifetime. This process is so fast that the D_0 ground state appears at first to be vibrationally hot. This can be seen in the transient spectra by the positive band above 620 nm, that is, on the low-energy side of the absorption band of the thermally equilibrated D_0 state. The decay of the hot band is accompanied by a shift to lower wavelengths. The dynamics of this process can be satisfactorily reproduced by a biexponential function. The short, almost solvent independent, circa 300 fs time constant, is most probably due to

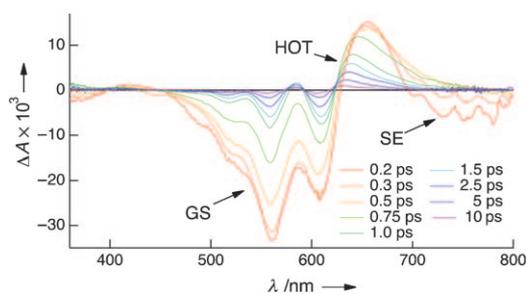**4496** *Angew. Chem. Int. Ed.* **2011**, *50*, 4496–4498

Figure 2. Transient absorption spectra recorded at different time delays after 610 nm excitation of WB in water at room temperature. GS = ground-state depletion, HOT = hot ground-state absorption, SE = stimulated emission.

Figure 3. a) Geometrical parameters of the ground-state minimum (D_0 min) and first excited-state minimum (D_1 min), and the D_1/D_0 conical intersection (CI) calculated for the gas (in italics) and solution phases. b) Linearly interpolated D_1 state paths connecting the D_1 min and D_1/D_0 CI in the gas phase and in methanol.[17]

intramolecular vibrational relaxation, whereas the longer time constant, ranging from 3 to 7 ps depending on the solvent (Supporting Information, Table S3), can be ascribed to vibrational cooling.[14] After this process, the negative transient band between 500 and 620 nm owing the depletion of the ground-state population has totally vanished.

This ultrafast D_1–D_0 internal conversion cannot be simply explained in terms of the energy gap law, as the 2 eV D_1–D_0 gap of WB is similar to the S_1–S_0 gap of many closed-shell molecules with nanosecond fluorescence lifetimes. This, together with the non-Arrhenius temperature dependence of the fluorescence intensity point to the involvement of a CI in the ultrafast relaxation of WB excited state. To identify the relevant modes associated with this process, a search for the CI connecting the D_1 and D_0 states was performed. The computational details for the different methods used in this work are given in the Supporting Information.

The gas-phase equilibrium geometry (D_0 min), optimized at the state-of-the-art CASPT2/6-31++G* level, shows a quinoid structure (Figure 3a) with the charge and unpaired electron localized on the two C−N bonds, in agreement with experimental data and previous calculations.[15,16] The D_1 equilibrium structure (D_1 min) has π–π* character, with the charge and the unpaired electron delocalized on the phenyl ring.

Both the computed vertical absorption $\lambda_{abs} = 600$ nm and emission energies $\lambda_{fl} = 623$ nm agree well with the experiment (Supporting Information, Table S4). To our knowledge, this is the first model of an organic mixed-valence compound with quantitatively reproduced experimental λ_{max} value for both absorption and emission.

Given the high computational cost of numerical CASPT2 gradients, the D_1 energy profile of gas-phase WB was scanned along selected coordinates (Figure 3b) using quantum mechanics (QM) at the CASPT2//CASSCF/6-31G* level for the gas-phase, and hybrid quantum mechanics/molecular mechanics (QM/MM) with CASPT2//CASSCF/6-31G*/ AMBER protocol for the solvent shell (methanol). The solvent can partially rearrange on a sub-picosecond reaction timescale, therefore we performed QM/MM calculations for two limiting cases: with relaxed and fixed (at the D_0 configuration) solvent shells.

As shown in Figure 3b, the D_1/D_0 CI (Supporting Information, Figure S5A), located 10–15 kcal mol⁻¹ below
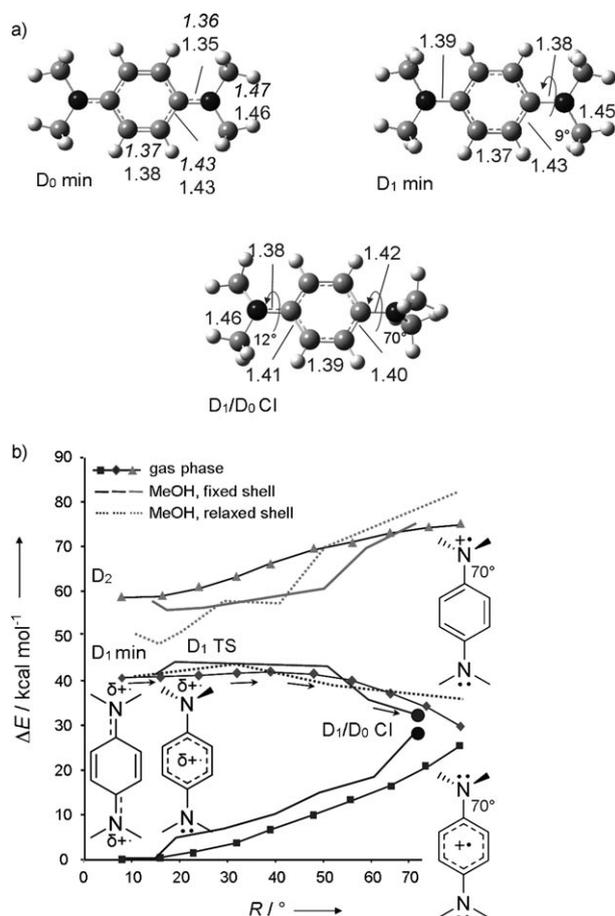
D_1 min, can in all cases be reached by twisting one of the C−N bonds. In solution, the path to the CI features a barrier of ≤ 3 kcal mol⁻¹,[17] corresponding to the D_1 TS structure with a C−N bond distorted by 20⁰. Initially, the D_1 state relaxation of WB is dominated by the bond stretch altering the quinoid geometry, which has the unpaired electron and the positive charge on the C−N groups, into a structure with both the electron and the hole delocalized on the phenyl ring. A coupled increase in the bond stretch and C−N twisting induces a further change: the unpaired electron and the positive charge localize on the twisting dimethylamino group (NMe_2). Upon decay and relaxation to the D_0 state, progressive planarization reconstitutes the original quinoid situation in which both C−N bonds hold the unpaired electron and the positive charge.

Both ultrafast spectroscopic data and computational results give a consistent picture of WB dynamics (Figure 4). Upon optical population of the D_1 state at room temperature, geometrical deformation of the benzene ring and C−N bonds and torsion around a single C−N bond bring WB to the D_0 state in about 200 fs via the 60/70° D_1/D_0 CI. The calculations show that the solvent cavity is large enough to accommodate
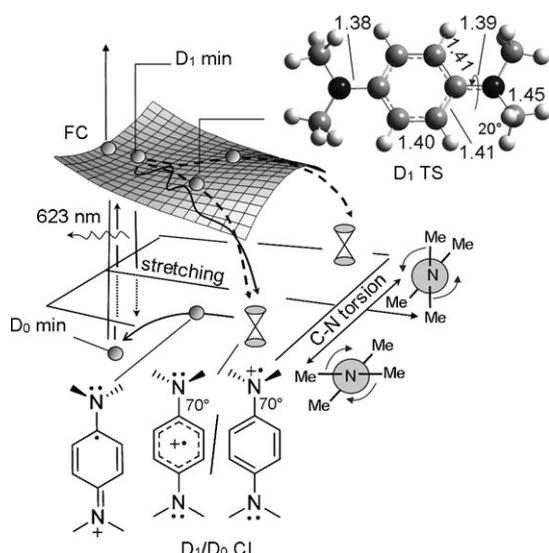
Figure 4. Representation of the D_1 potential energy surface in methanol along the two coordinates responsible for ultrafast radiationless deactivation of WB (stretching and C—N torsion). Two paths from D_1 min drive the system to the corresponding D_1/D_0 CIs through the mirror-image transition structures (D_1 TS).[18] D_0 relaxation involves the formation of a quinoid transient species (bottom left resonance formula) with a partially twisted NMe_2 group. This species was identified by analysis of the CI branching plane (Supporting Information, Figure S6).

such a twist without significant friction. The energy barrier controlling the accessibility of the CI is reached from D_1 min upon only 10° distortion of the C—N bond. The thermally equilibrated ground-state population is then restored within a few picoseconds upon intra- and intermolecular vibrational relaxation. The whole process is associated with an electron transfer from the nitrogen centers to the phenyl ring and back. As the temperature is lowered, the $\leq 3\ \text{kcal mol}^{-1}$ barrier, located on the way to the CI, comes into play and the lifetime of the D_1 state becomes long enough for fluorescence to be a competing deactivation pathway.

The hypotheses proposed until now to explain the absence of fluorescence of open-shell radical ions, namely a small D_1–D_0 gap and the involvement of the D_2 state, do not hold for WB. Although a gas-phase D_2/D_1 CI is accessible upon deformation of the phenyl ring, it lies $13.5\ \text{kcal mol}^{-1}$ above the D_1 min and is unlikely to be reached on an ultrafast timescale (Supporting Information, Figure S4). Instead, the deactivation of the D_1 state population is associated with an initial charge transfer from the NMe_2 groups to the benzene ring. This is followed by a localization of the electron and hole on the twisting NMe_2 group via further bond stretching and

C—N bond torsion. Upon decay at the D_1/D_0 CI, the charge goes back to the phenyl ring and during the D_0 relaxation moves first to the in-plane (conjugated) NMe_2 group (Figure 4 and Supporting Information, Figure S6) and, after planarization of the twisted NMe_2 group, to the original D_0 min symmetric distribution. Further studies with other radical ions are required to see if the behavior found for WB is more general.

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[17] The calculations were performed in the gas phase with constrained benzene ring bond lengths and dihedral angles for twisting about the C—N bond, and in solution with fixed dihedral angles only (see also the Supporting Information for details).
[18] D_1 TS was not located as a first-order saddle point, due to the extreme flatness of the CASSCF D_1 state PES, but rather was approximated as a maximum of the corresponding energy profile. The latter results from a linear interpolation between the D_1 min and the D_1/D_0 CI (see Figure 3B and the Supporting Information).