

Supporting INFO

A two-step ICT process for solvatochromic betaine pyridinium revealed by ultrafast spectroscopy, Multivariate Curve Resolution, and TDDFT calculations.

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I. Electrochemical measurements of SBPa

From a thermodynamical point of view, the extrapolated Weller expression,¹⁻³ gives the efficiency of photoinduced ET through the determination of the free energy of reaction. This equation in the case of ACN (representative case) reduces to:

$$\Delta G_{ET}^0(eV) = [E_{ox}(D) - E_{red}(A)] - E_{00} - 0.06 \quad (1)$$

In this equation, E_{00} is the pure electronic transition energy, generally deduced from the intersection of the lowest energy absorption band and the emission band. As we will see, we cannot proceed by this way for **SBPa** since different excited states are involved in the two transitions. Consequently, E_{00} will be approximated as the average between the top and right bandfoot position of the absorption band; in ACN $E_{00} \approx 2.75$ eV. Moreover in the above equation, the value of $E_{ox} - E_{red}$ can be determined from the cyclic voltammogram of **SBPa** (Figure SI.1). The cathodic part of this voltammogram shows the irreversible reduction of **SBPa**. The corresponding potential has a value of ca. -1.39 V/SCE, which is close to the reduction potential of the pyridinium group⁴ (-1.21 V/SCE). At high potential, **SBPa** shows an irreversible oxidation wave with a maximum located at 0.11 V/SCE that should be ascribed to the oxidation of the anionic part of the chromophore (benzopyrazole moiety). Accordingly, a $E_{ox} - E_{red}$ value of 1.51 eV is estimated, which leads to a $\Delta G_{ET}^0(eV) = -1.3$ eV in ACN. This manifestly negative value reveals the exothermic character of the photoinduced charge transfer and confirms thus that the CT reaction occurs spontaneously in the excited state.

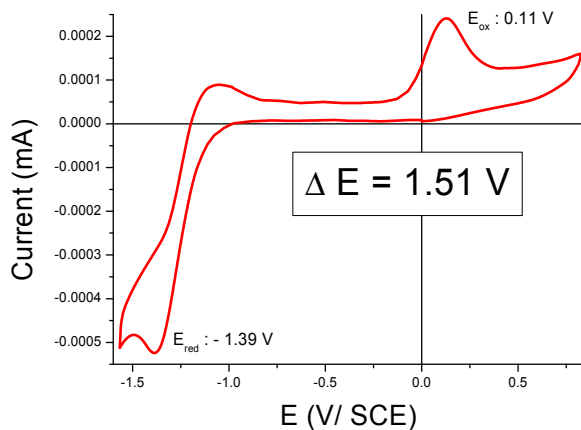


Figure SI.1. Cyclic voltammogram of **SBPa** in ACN ($\sim 10^{-3}$ M) with 0.1 M n-BuF₄ as electrolyte support.

II. Global fitting of figure 4 (SBPa/ACN).

Table SI1. Preexponential factors deduced from global fits of data in Figure 3 d-e

	415 nm	485 nm	600 nm	700 nm
$\tau_1 = 110$ fs	0.029	-0.145	-0.069	0.14
$\tau_2 = 290$ fs	0.011	0.032	-0.015	-0.041
$\tau_3 = 5$ ps	-0.039	0.005	-0.08	-0.0003
$\tau_4 = 128$ ps	-0.14	0.046	0.055	-0.030

III. Femtosecond transient absorption signal of SBPa in EtOH.

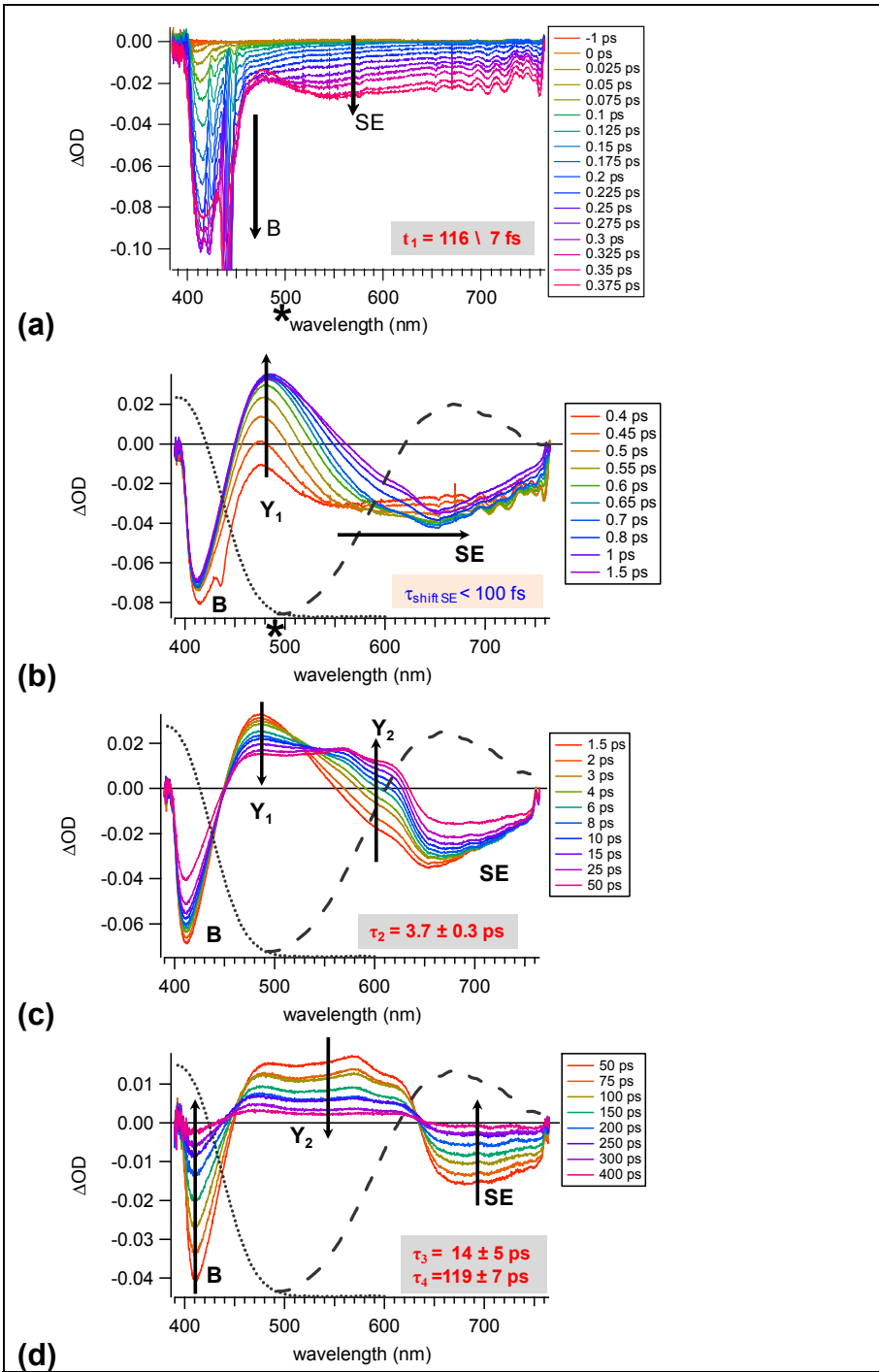


Figure SI.2 Femtosecond transient absorption spectra of **SBPa** in EtOH following 390 nm excitation: a) 0-0.4 ps range (growth of the SE band), b) 0.4-1.5 ps range (growth of excited-state absorption and red-shift of the SE band), c) 1.5-50 ps range (ICT dynamics), and d) 50-400 ps range (decay of all signals). The stationary absorption (dotted line) and emission (dashed line) spectra are also shown for comparison. The star indicates a stimulated Raman peak of the solvent. Pump-probe correlation time: $\tau = 190$ fs

IV. Femtosecond transient absorption signal of Br₂SBPa.

To better identify the presence of excited triplet state, we investigated a **SBPa** derivative, **Br₂SBPa**, substituted by two bromine atoms, for which notable enhancement of the quantum yield of triplet state formation via intersystem crossing (ISC) is expected through heavy atom effect.

First, knowing that **Br₂SBPa** is a solvatochromic molecule, we checked by TDDFT calculation that the electronic transitions are the same as for the **SBPa** molecule (not shown). Then, femtosecond transient absorption spectra were recorded in the 0.8–500 ps temporal window after 390 nm excitation (figure SI.3). The data show the evolution from a broad absorption band centred near 480 nm to a new band peaking near 450 nm with a characteristic time of $\tau_T = 31$ ps. The final band, abbreviated as band T, is stable between 200 and 500 ps. Finally, nanosecond flash photolysis measurements show the decay of band T with a kinetics notably shortened in the presence of air, which provides clear evidence for the assignment of band T to the lowest triplet state T₁.

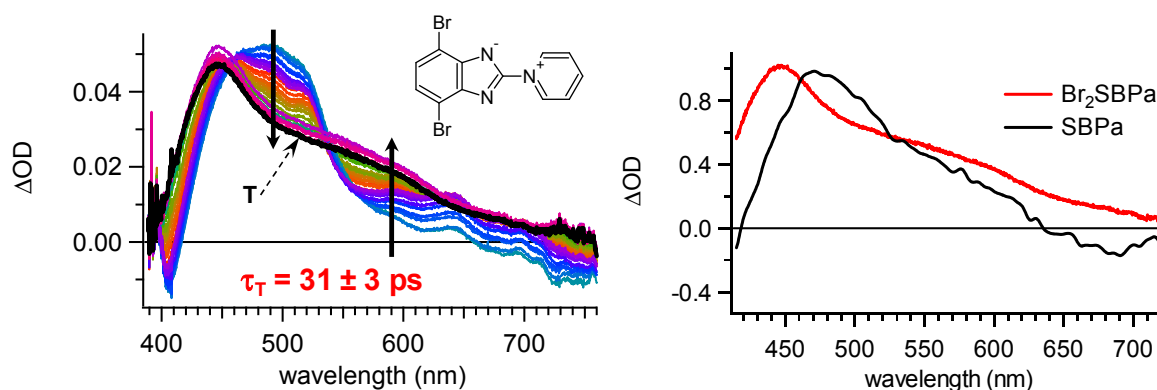


Figure SI.3 (left) Femtosecond transient absorption spectra of **Br₂SBPa** in ACN between 0.8 and 500 ps (the thick black line is the final signal); (right) Comparison of the 500 ps transient absorption spectra observed for **SBPa** and **Br₂SBPa** in ACN.

The residual signal observed at the end of the femtosecond transient absorption evolution of **Br₂SBPa** is comparable to that obtained for **SBPa** (see fig SI.3), despite a small shift of the band maxima because the overlapped bleaching band is red-shifted in **SBPa** compared to its position in **Br₂SBPa**. This analogy allows us ascribing with certainty the **SBPa** residual spectrum observed at 500 ps to the triplet T₁ state. As expected from the heavy atom effect, the intensity of the T₁ state spectrum is much higher for **Br₂SBPa** than for **SBPa**. Owing to this large intensity, the rise of the T₁ state absorption is clearly observed in the spectra and the corresponding time constant measured. In the case of **SBPa**, the residual spectrum characterizing the T₁ state is so weak that its rising dynamics is not observed (Figure 4). An important question concerns thus the identity of the excited singlet state that is the precursor of the triplet state in the case of **SBPa**. Two hypotheses can be considered:

- The S₁(CT) state characterized by a decay time constant of $\tau_3 = 5$ ps
- The emissive S₁(E) state characterized by a decay time constant of $\tau_4 = 128$ ps

Since the heavy atom effect is expected to favour the ISC process, the triplet state formation is likely occurring with higher rate constant in **Br₂SBPa** than in **SBPa**. Therefore a characteristic time longer than $\tau_T = 31$ ps can be assumed for the formation of T₁ in **SBPa**, which strongly suggests that the precursor of T₁ must be the S₁(E) state.

IV. Comparison of τ_2 and $\langle\tau_{\text{solv}}\rangle$

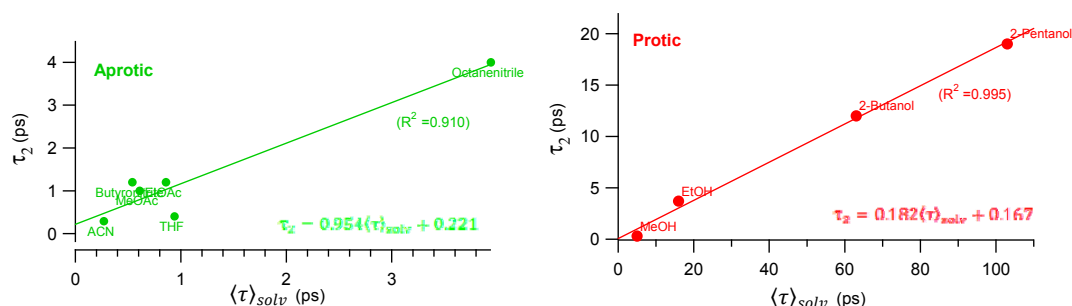


Figure SI.4. Plots of the SPBa time constant τ_2 as a function of the average solvation time $\langle\tau\rangle_{\text{solv}}$ and best linear fits for aprotic (left panel) and protic (right panel) solvents.

V. TwSBPa molecule

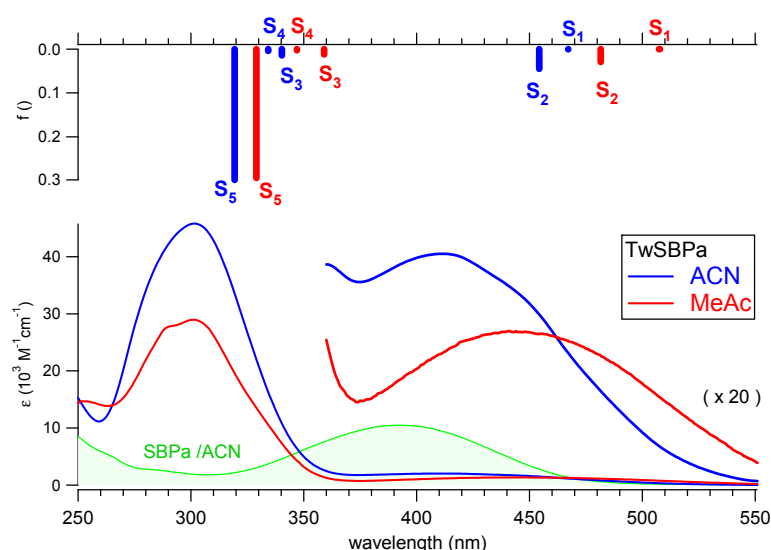


Figure SI.5. Stationary absorption spectra of TwSBPa in ACN (blue trace) and MethylAcetate (red trace), as compared with the SBPa spectrum in ACN (green trace). The inset shows an expansion of the 340-550 nm region. PCM-TDDFT position (PBE0/6-311++G(d,p)//PBE0/6-311++G(d,p)) and electronic oscillator strengths for vertical transitions up to S_5 are also given for TwSBPa (upper graph).

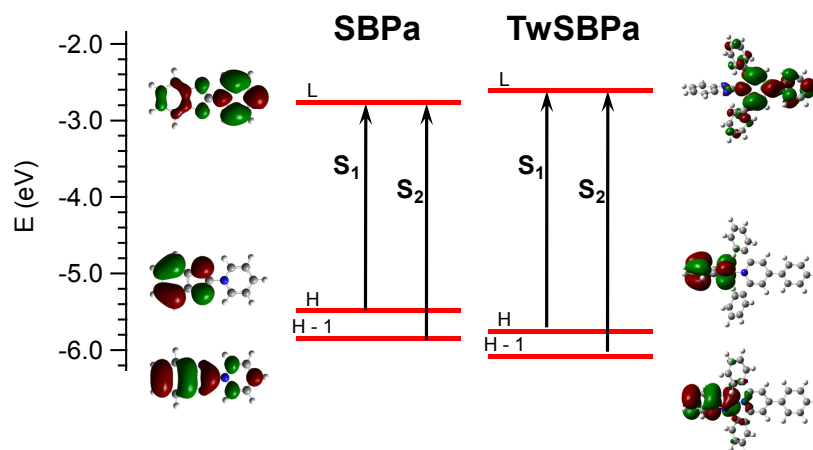


Figure SI.6 Molecular orbital representation of the H-1, H and L orbitals (PCM-PBE0/6-311++G(d,p) in ACN) for the TwSBPa and SBPa molecules.

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