Electronic Structure Changes of an Aromatic Amine Photoacid along the Förster Cycle

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Contents

S1. Experimental Details
S2. Steady-State Spectroscopy
S3. Femtosecond UV/IR Pump-Probe Spectroscopy
S4. Computational Details
  S4.1. Ground state CPMD simulations.
  S4.2. Simulation of UV-vis spectra
  S4.3. Simulation of Ground and Excited State N K-edge XAS
       at TD-DFT and/or CASSCF/NEVPT2 levels of theory.

S1. Experimental Details

8-aminopyrene-1,3,6-trisulfonic acid was purchased from Chemos GmbH & Co. KG as a sodium salt and dissolved in spectroscopy grade deuterium oxide D$_2$O (Deutero GmbH) at a concentration of 50 mM. To ascertain that before electronic excitation APTS is quantitatively in either its photoacid or photobase forms, either 200 mM HCl or NaOH was added to the solution. The solution was filtered and degassed before it was injected into the experimental vacuum chamber using a liquid flatjet setup, collected in an evacuated catcher bottle and recycled. The flatjet was generated using nozzles with a 30 micrometer orifice forming a liquid sheet at flow rates between 1.5 and 1.7 ml/min.

Synchrotron radiation generated in the storage ring BESSY II and monochromatised in the beamline UE52_SGM was used to record the X-ray photon energy dependent absorption spectra with a bandwidth of 130 meV. The static spectra were recorded using a GaAsP photodiode at jet thicknesses on the order of 6 µm. The experimental scheme is discussed in detail by Ekimova et al. [1]. For the time-resolved measurements, X-ray pulses originating from the hybrid bunch in the fill pattern of the synchrotron were synchronised with a laser system used for the optical excitation of the sample operating at a repetition rate of 208 kHz. The energy density used for the excitation can be estimated to be on the order of 90 mJ cm$^{-2}$ (spotsize $\sim$ 75 x 98 µm$^2$, pulse energy $\sim$ 7.5 µJ) for 343 nm wavelength and 38 mJ cm$^{-2}$ (spotsize $\sim$ 65 x 85 µm$^2$, pulse energy $\sim$ 2.4 µJ) for 258 nm wavelength.

The intensity of the X-ray pulses, that were transmitted through the sample material, was monitored using a capped (300 nm Aluminium film) Silicon avalanche photodiode combined with a 20 dB amplifier and a boxcar integrator UHFLI of Zürich Instrument AG. The detection of X-ray pulses at a specified delay with respect to the optical excitation and an additional pulse separated by 4 microseconds allowed for a differential detection of the transiently altered X-ray absorption cross-section. Details on the measurement scheme are discussed in detail by Fondell et al. [2].


S2. Steady-State Spectroscopy

Stationary UV/Vis absorption and fluorescence spectra were recorded on a Perkin Elmer spectrometer and a JOBIN YVON Horiba Fluorolog, respectively. Steady state luminescence spectra have been acquired for a range of APTS sample concentrations (acid form, 200 mM HCl added) from 10 µM to 150 mM. Fluorescent light was detected from the front angle of a thin (1 mm) cuvette to minimize the effects of reabsorption or shifts in the region of absorption within the cuvette. This geometry in conjunction with the large Stokes shift between absorption and emission, which is characteristic for photoacids, prevents the occurrence of an internal filter effect.

As shown in Fig. S1 a maximum in fluorescence intensity is reached at an APTS concentration of 5 mM while a further increase in sample concentration reduces the luminescence yield. No new luminescence bands appear over the entire concentration range. Hence the observed trend in luminescence intensities is assumed to be mainly caused by self-quenching at higher APTS concentrations. Molecules with a pyrene core such as APTS are well-known for their tendency to form aggregates altering their photodynamics [3]. Although bringing the evenly charged sulfonate groups of APTS into close proximity seems unfavorable, aggregation has also been observed for aromatic compounds carrying charged groups in their outer periphery [4]. The Coulombic repulsion between charged parts of such molecules can be compensated by the energetically beneficial stacking between extended delocalized \( \pi \)-systems and electrostatic shielding by counter ions.

Considering a model where dimers of APTS are already present in their ground state and do not fluoresce after optical excitation, the fluorescence intensity \( I \) can be described as a function of concentration as follows:

\[
I_f = K \left(1 - 10^{-A_t} \right) \cdot \frac{A_m}{A_t}
\]  

(1)

With \( A_t = A_m + A_d = (\epsilon_m c_m + \epsilon_d c_d) \cdot d \), \( A_t \) – total absorbance, \( A_m/d \) – absorbance from monomers/dimer, \( \epsilon \) - molecular extinction coefficient, \( c_m/d \) – the concentration of monomers/dimers respectively, whose ratio can be expressed by the dimerization constant \( K_d = \frac{c_d}{c_m} \) and \( d \) – the thickness of the cuvette. \( K \) is a proportionality constant taking into account the fluorescence quantum yield and instrumental characteristics such as the collection efficiency of emitted luminescence. The resulting poor match with the experimental data (Fig. S1b) indicates that a model purely based on a static quenching mechanism is insufficient. Additional, dynamic quenching processes such as energy transfer from excited monomers to dimers and/or exciplex formation must be considered. While the shown luminescence measurements alone do not allow for an in depth analysis of the more complex self-quenching mechanism, the overall fluorescence decrease is well described by a single exponential:

\[
I_f = K \cdot \left(1 - 10^{-\alpha c_d} \right) \cdot e^{-k c}
\]  

(2)

**Figure S1:** a) Luminescence spectra of APTS in its acid form (200 mM HCl added) excited at 343 nm and b) integrated luminescence intensities as a function of APTS concentration. The dashed red line corresponds to a static quenching model described by Eq.1.
S3. Femtosecond UV/IR Pump-Probe Spectroscopy

Ultrafast UV pump/mid-IR probe spectroscopy was carried out as described previously [3]. One fraction of the laser output (800 nm, 50 fs, 1 kHz) from a regenerative Ti:Sapphire amplifier system (Spitfire Pro XP, Spectra Physics) was used to generate the UV excitation beam in a commercial optical parametric amplifier (TOPAS-C, Light Conversion) and send over a delay stage. Prior to being focused onto the sample the pump pulses were temporally stretched by propagation through a cuvette filled with water resulting in a pump-probe cross-correlation of approx. 350 fs. To avoid contributions of rotational diffusion the polarization between pump and probe was set to the magic angle (54.7°) throughout the measurements. The spot size of the focused pump beam (1.5 µm, Ø: 200 µm) at the sample position was kept larger than that of the probe beam to ensure homogeneous illumination conditions. For the generation of the tunable mid-IR probe pulses a second part of the laser output was sent into a home-built double-pass OPA followed by detection frequency mixing of signal and idler. Using a ZnSe wedge the DFG beam was split into a probe and reference beam, focused onto the sample by an off-axis parabolic mirror, dispersed in a polychromator (2 cm⁻¹ resolution between 1400-1700 cm⁻¹) and detected by a HgCdTe double array detector (Infrared Associates MCT-6400) cooled by liquid N₂. The sample was circulated through a flow cell (1 mm CaF₂ windows, spacing of 100 µm) and kept in an environment purged with N₂ to avoid absorption of mid-IR pulses by CO₂ and H₂O.

Femtosecond UV/mid-IR probe spectroscopy has proven to be an effective tool for studying the dynamics associated with the phenomenon of photoactivity and has previously been applied to the hydroxy-photoacid HPTS [6], which is closely related to APTS. Upon UV excitation, HPTS was found to undergo a deuteron transfer in 250 ps followed by the radiative decay of the excited base form in about 5 ns [7]. Transient changes in the fingerprint region of APTS after excitation at 330 nm are shown in Fig. S2 for three different sample concentrations. The associated dynamics are analyzed using a kinetic model based on Eq. 3 and summarized in Tables S1 and S2. At the lowest concentration of 10 mM a feature exhibiting two maxima at 1497 cm⁻¹ and 1510 cm⁻¹ rises with a time constant of 170 ps. Within the experimentally accessible time range it only slightly decreases in intensity with a time constant of 5 ns. Given the striking similarities with the photokinetics of HPTS, it is reasonable to assign these two strongest features at 1497 cm⁻¹ and 1510 cm⁻¹ to the excited base form of APTS, which is formed from the initially excited photoacid by deuteron transfer in 170 ps. The ensuing decay of the excited base form by fluorescence leads to the appearance of ground states features of the APTS base form at 1521, 1587, 1607 and 1617 cm⁻¹. A clear signature of the excited photoacid form which is expected at early delays is not present in the spectra. It should be noted that already in the static IR spectra the cross sections for vibrational transitions in the fingerprint region are on average almost four times higher for the base form than for the photoacid form. Small transient changes may not be resolved properly if they fall below 0.1 mOD.

Using the same conditions as for the BESSY experiments, i.e. a concentration of 50 mM of APTS, changes in the reaction rates can be observed compared to the more dilute sample solution. Deuteron transfer from the excited photoacid now proceeds on a shorter time scale of 140 ps. The lifetime of the excited base features at 1497 cm⁻¹ and 1510 cm⁻¹ has visibly shortened to 1.2 ns as well. This is accompanied by more pronounced signatures of the base form in its ground state at long delay times. Significant self-quenching has been observed in the luminescence measurements (Fig. S1) and the measured lifetime shortening confirms the dynamic nature of the fluorescence quenching mechanism. Since the transient spectrum still contains mainly spectral features corresponding to the ground state and excited base form of APTS, it is assumed that the quenching process leads to a faster non-radiative transition back to the APTS base ground state.

When approaching the solubility limit of APTS in water at a concentration of 150 mM, a new intense feature between 1530 cm⁻¹ and 1570 cm⁻¹ is present already at earliest delays. It is characterized by a fast initial decay with a time constant of 40 ps as shown by the green curve in Fig.2b. While the additional increase in concentration further shortened the time scale for the deuteron transfer to 80 ps and the fluorescence lifetime to 800 ps, the fast 40 ps component also plays a role in the fast population of APTS base ground state features.

These results show that only at the highest concentration the interaction between individual molecules begins to dominate and drastically alter the photochemistry of APTS, presumably by the formation of dimeric or higher oligomeric aggregates.

The experimental data were analyzed using the standard model for a consecutive reaction A → B → C with an additional exponential term to account for the decay of dimeric/oligomeric APTS. The kinetics for four representative traces were globally fit, with coefficients corresponding to the ground state base and the dimer population limited to only suitable traces. Note that at a concentration of 150 mM the early rise of ground state base population is linked to the decay of dimers by using a negative coefficient c₂.

\[
\begin{align*}
\text{(Acid)} & \xrightarrow{hν} \text{Acid}^* \xrightarrow{t_1} \text{Base}^* \xrightarrow{t_2} \text{Base} \\
\Delta A &= c_1[\text{Base}^*] + c_2[\text{Base}] + c_3[\text{Dimer}^*] + y_0 \\
\text{[Base]} &= \frac{1}{t_2} \frac{[\text{Acid}^*]_0}{1 - \frac{1}{\tau_1}} \left( e^{-\frac{t_1}{\tau_1}} - e^{-\frac{t_2}{\tau_2}} \right) \tag{3.1} \\
\text{[Base]} &= \left[1 + \frac{1}{t_1} e^{-\frac{t_1}{\tau_1}} - \frac{1}{t_2} e^{-\frac{t_2}{\tau_2}} \right] \frac{1}{\tau_1} \frac{[\text{Dimer}^*]_0}{1 - \frac{1}{\tau_1}} \tag{3.2} \\
\text{[Dimer]} &= [\text{Dimer}^*]_0 e^{-\frac{t_2}{\tau_2}} \tag{3.3}
\end{align*}
\]
Figure S2: a) Transient IR spectra of APTS in its acid form (200 mM HCl added) recorded after electronic excitation at 330 nm with static IR spectra of base (blue) and acid (red) shown in the middle and b) selected kinetic traces for features assigned to the excited base form (red), ground state base form (blue, orange) and APTS dimers/multimers (green). Solid lines represent best fits to a kinetic model as described by Eq.3 yielding time constants listed in Table S1.

Table S1: Lifetimes derived from UV pump/mid-IR probe experiments of APTS in its acid form (200 mM HCl added) using a kinetic model based on Eq. 3

|       | $\tau_1$: proton transfer A*→B* | $\tau_2$: relaxation B*→B | $\tau_3$: relaxation dimer* |
|-------|---------------------------------|---------------------------|-----------------------------|
| 10 mM | 166 ± 4 ps                      | 5100 ± 600 ps             | 16 ± 5 ps                   |
| 50 mM | 138 ± 2 ps                      | 1240 ± 30 ps              | 21 ± 2 ps                   |
| 150 mM| 84 ± 4 ps                       | 810 ± 40 ps               | 38.4 ± 0.7 ps               |

Table S2: Amplitudes from fitting Eq. 3 to the experimental data for four kinetic traces

| Amplitude $c_1$ | Amplitude $c_2$ | Amplitude $c_3$ |
|-----------------|-----------------|-----------------|
| 1497 cm$^{-1}$  | 0.92 / 1.29 / 0.46 | - / - / -       |
| 1520 cm$^{-1}$  | 0.18 / 0.27 / -  | 0.29 / 0.45 / 0.36 | - / - / -0.22 |
| 1540 cm$^{-1}$  | 0.33 / 0.40 / 0.25 | - / - / -       | 0.07 / 0.23 / 0.79 |
| 1606 cm$^{-1}$  | 0.21 / 0.22 / -  | 0.28 / 0.27 / 0.32 | - / - / -0.15 |
S4. Computational Details

S4.1. Ground state CPMD simulations.

Ab-initio molecular dynamics (AIMD) simulations were carried on the NVT ensemble [9] at 300 K for ~40 ps in the CPMD software [9] on both the acid and base form in its ground state in aqueous solution, after 10 ps equilibration. The Car-Parrinello algorithm was used with a time step of 5 a.u. and a fictitious electron mass of 800 a.u. combined with deuterium of all hydrogens in the system. We used a gradient-corrected (BLYP) functional [10] with an empirical addition of van der Waals interactions [11] and norm-conserving pseudopotentials [12], expressed in the Kleinman-Bylander form [13]. The plane-wave expansion of the Kohn-Sham orbitals, calculated at the Gamma point only, had an energy cut-off of 70 Ry. The pseudo-potentials for C, N, O and S were of Martin-Troullier type 11 and were non-local in the l = 0 (C, N, O) and l = 0, 1 (S) channels. For hydrogen, we used a local pseudo-potential parameterized with one Gaussian. Due to the limited sampling, the counter ions were neglected and an orthorhombic simulation cell with non-cubic shape a = b = 1.3746**c was used to accommodate the APTS molecules solvated in 200 H$_2$O molecules. The orientation of the normal of the APTS molecule along the c axis was maintained by fixing the z coordinate of carbon atoms (C6, C10, C14, C18) to be in the ab plane. The AIMD simulation was initialization from 1 ns force field simulations with the Amber 1994 force field [14], in which the cell parameters (a$_{cell}$ = 19.429 Å and a$_{cell}$ = 19.525 Å) were determined in the NPT ensemble in the M.DynaMix code [15].

S4.2. Simulation of UV-vis spectra

The UV-vis spectra and N K edge spectra were determined for single configurations of the acid and base forms of the APTS molecule in aqueous solution. From the AIMD simulations, one of the snapshots i.e. one configuration from the AIMD simulation was taken from each of the forms. The large number of water molecules, required to properly hydrate APTS in the AIMD simulation, made it impossible to treat the system with accurate quantum chemical techniques for spectrum simulations, for example TD-DFT/CAM-BLYP [16] and CASSCF/NEVPT2 [17]. Hence, we created a truncated system by restricting the number of water molecules surrounding the main molecule. Only water molecules directly interacting with the functional groups in the acid and base forms of APTS were included. To compensate for the truncation, a surrounding polarizable continuum model was added.

The UV-vis spectra were computed involving different degrees of solvation, i.e. obtained by truncating the number of solvent water molecules in the system. Our calculated results can be compared with experimental electronic absorption spectra we recorded for both the photoacid and conjugate photobase forms (see Fig. S3). The highest level of solvation that we used has a complete layer of water molecules around APTS, i.e. having 74 explicit water molecules in case of base form and 67 in case of acid form. For the purpose of enabling more demanding calculations, we also further truncated the explicit water solvation down to 33/34, for base/acid forms respectively, water localized around the polar group of both forms of APTS. The 74/67 H$_2$O configurations are referred to as the "full" solvation models and the 33/34 configurations are referred to as the “truncated” models. When not mentioned otherwise the truncated models are used in the presented results. For the "full" and truncated models, there was the implicit solvent model, brought by interfacing the quantum chemical computation with CPCM polar continuum model with water as solvent. Hence the presence of both explicit solvation, especially the hydrogen-bonded water molecules, along with implicit solvation, i.e., by CPCM solvent model, can be taken to be fairly as accurate as achievable by purely quantum chemical methods.

Figure S3: Comparison of experimental and TD-DFT calculated electronic absorption spectra of APTS in photoacid and conjugate photobase forms. The position of the absorption bands match well when taking into account full solvation.

S4.3. Simulation of Ground and Excited State N K-edge XAS at TD-DFT and/or CASSCF/NEVPT2 levels of theory.

However, during computation of N K-edge XAS spectra we used the truncated explicit water solvation with 33/34 water molecules, for base/acid forms, respectively, water localized around the polar group of both forms of APTS. The CPCM model of implicit solvation was present as discussed earlier. This truncation is necessary to bring down the system size further as computation of XAS at the NEVPT2 level of theory is an additionally complicated and computationally expensive task. The computations have been carried out in ORCA 4.2 program package [18]. It is noteworthy to mention here that the XAS spectra were computed at different levels of theory keeping in mind the accuracy, scope and feasibility of different theories. Cross-
In Fig. S4 we show the comparison of XAS resulting from TDDFT/CAM-B3LYP/CPCM calculations using full hydration layer models with the TZVP basis set and those resulting from the truncated hydration models with basis set def2-SVP. With this approach we can simultaneously evaluate the system size and basis set dependences on the N1s XAS of aqueous APTS at high and low pH, and conclude that there is only a weak dependence. We employed def2-SVP basis sets along with RJCOSX approximation to speed up the computation. The XAS from the S₀ state was also computed using TD-DFT with CAM-B3LYP functional. We targeted 200 states with excitation from the N 1s orbital to all the virtual states. The TD-DFT(CAM-B3LYP) simulation of XAS from S₀ state is beneficial as it spans a much larger energy window as compared to CASSCF/NEVPT2, where we can only target the pre-edge feature. Similarly, for XAS from T₁ state, DFT-ROCIS(B3LYP) functional, which is known to perform agreeably accurately for open shell systems [20] (see Fig. S5). At the TDDFT level of theory we have evaluated the sensitivity of the calculated XAS to variations in the basis set and system size, by performing calculations with a TZVP basis set on the full solvation model, and the main peak positions and overall shape of the spectra were preserved. This DFT-ROCIS(B3LYP) protocol also has the advantage for spanning a large energy window. Thus, by using these protocols we were not only able to get the N 1s pre-edge feature, but also the rising and some of the post edge features for the XAS from these two states. However, the TDDFT could not be applied to compute XAS from the excited S₁ and S₂ states and thus CASSCF/NEVPT2(6,7) level of theory was evoked. An active space of 6 electrons in 7 orbitals was used, including the N 1s orbital which was rotated into the active space (see Fig. S6 and Fig. S7). The state averaged SA-CASSCF computation was performed for 110 singlet states and the core excited states was found to start from the 106th state. NEVPT2 was performed after the converged CASSCF computation to include dynamical correlation. XAS was also computed from computed XAS from the excited S₁ and S₂ states at the NEVPT2 level of theory. In addition XAS spectra for T₁ state was also computed at the CASSCF/NEVPT2 level of theory which can be compared to the ROCIS computation, and thus validates the estimation of valence and core excited states at the CASSCF/NEVPT2 level of theory. Interestingly, it was found that XAS spectra obtained from DFT/ROCIS and CASSCF/NEVPT2 spectra for T₁ state consistently gave a single peak in the pre-edge region. This agreement with DFT/ROCIS, which very accurately produces XAS spectra of open-shell species like T₁ states, indicates towards the accuracy and sanctity of our CASSCF/NEVPT2 computation and the active space employed (see Fig. S5).

The electronic properties like transition dipole moments (from which the dipole moment differences are derived) and electron density difference have been computed at the CASSCF level of theory. We have compiled our findings in Table S3. For reference we show in Fig. S8 the atom labelling. To make clear the more than one order of magnitude of electric dipole moment changes upon electronic excitation of 0.334 D for the photoacid and 4.701 D for the conjugate photobase forms we display Fig. 4 (f,g) on a full page size as Fig. S9.
Figure S6: Active space of the APTS R-NH$_2^+$ photoacid species used for the CASSCF/NEVP2(6,7) calculations.

Figure S7: Active space of the APTS R-NH$_2$ conjugate photobase species used for the CASSCF/NEVP2(6,7) calculations.
Figure S8: Geometry reference for charge analysis. The figure only shows base form but the atom numbers are same form for acid form with the acidic proton having label 38.

Figure S9: Electric dipole moment changes (from CASSCF(6,7) calculations) upon S0 → S1 electronic excitation in the photoacid and conjugate photobase forms. This Figure is a full page wide display of Fig. 4 (f,g) to better discern the electric dipole moment change of the photoacid form (the minor arrow is located at atom 5).
Table S3: Changes in Mulliken charges (from CASSCF(6,7) calculations) estimated for the APTS R-NH₂ conjugate photobase and R-NH₃⁺ photoacid forms.

| Atomic label(i) | Base form Atom | Base form Δq(S₁-S₀) | Acid form Atom | Acid form Δq(S₁-S₀) |
|-----------------|----------------|---------------------|----------------|---------------------|
| 1               | N              | -0.0712668          | N              | 0.000219232        |
| 2               | S              | 0.00641864          | S              | 0.00265963         |
| 3               | S              | 0.00702771          | S              | 0.00291827         |
| 4               | S              | 0.00421152          | S              | 0.00493989         |
| 5               | C              | -0.0358251          | C              | -0.0819009         |
| 6               | C              | 0.187029            | C              | -0.0390287         |
| 7               | C              | 0.0163416           | C              | 0.0183626          |
| 8               | C              | -0.0161117          | C              | 0.00803385         |
| 9               | C              | 0.0357332           | C              | -0.0477006         |
| 10              | C              | 0.1307              | C              | 0.0724864          |
| 11              | C              | -0.113034           | C              | 0.0769508          |
| 12              | C              | -0.15959            | C              | -0.0239685         |
| 13              | C              | 0.0272456           | C              | 0.0439126          |
| 14              | C              | -0.142182           | C              | 0.0633325          |
| 15              | C              | -0.00709353         | C              | -0.0686363         |
| 16              | C              | -0.0580504          | C              | 0.0143216          |
| 17              | C              | 0.0706882           | C              | 0.0269989          |
| 18              | C              | -0.167611           | C              | -0.000894249       |
| 19              | C              | 0.1094              | C              | 0.00146641         |
| 20              | C              | 0.175102            | C              | -0.0684626         |
| 21              | O              | 0.000817539         | O              | -0.00113673        |
| 22              | O              | -0.000433425        | O              | -0.00149173        |
| 23              | O              | 0.000113534         | O              | -0.000447771       |
| 24              | O              | -5.50E-05           | O              | 6.73E-05           |
| 25              | O              | -0.00024722         | O              | -0.000315525       |
| 26              | O              | 0.000301286         | O              | -0.000411755       |
| 27              | O              | -0.000375576        | O              | 0.000145514        |
| 28              | O              | -8.42E-05           | O              | -0.00074988        |
| 29              | O              | 9.29E-05            | O              | 6.46E-05           |
| 30              | H              | 3.13E-05            | H              | -0.000108046       |
| 31              | H              | -7.34E-05           | H              | -0.000219268       |
| 32              | H              | 0.000102203         | H              | 4.86E-05           |
| 33              | H              | 1.01E-05            | H              | -6.78E-05          |
| 34              | H              | -1.86E-05           | H              | -0.000220252       |
| 35              | H              | 0.000195349         | H              | 0.000168148        |
| 36              | H              | -9.91E-05           | H              | 1.88E-05           |
| 37              | H              | 9.42E-07            | H              | -2.04E-05          |
| 38              | -              | -                   | H              | -0.000282085       |
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