

Photoacids: How strong can we make them?

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Since the first description of increased acidity in the excited state by Theodor Förster more than 60 years ago,^[1] photoacidity became a worthwhile phenomenon to study proton transfer reactions.^[2] Excited-state proton transfer (ESPT) is one of the few photochemical reactions which may completely proceed on the excited-state potential energy surface and, thus, can be studied by means of fluorescence spectroscopy. Especially aromatic alcohols undergo a change of the acidity upon excitation by several orders of magnitude. For example, the acidity constant pK_A of Förster's fluorescent dye hydroxypyrene-trisulfonate (HPTS, pyranine) drops from 7.3 in the ground state to 1.4 in the excited state, which enables the study of proton transfer reactions in protic solvents. Excited-state pK_A -values below 0 are mandatory for studying ESPT in aprotic solvents and are the definition of so-called super-photoacids. We recently described super-photoacidic derivatives of HPTS,^[3,4] which exhibit time constants for ESPT in protic solvents in the lower picosecond regime.^[5] The high fluorescence quantum yield and the pronounced photostability enabled measuring the kinetics of proton-photoacid recombination by a quantum-optical experiment on the single-molecule level.^[6] Subsequently, the solvent-separated ion pair and the fully-separated ion pair could be distinguished in DMSO solely by their recombination kinetics.^[7] Asymmetric substitutions of the pyrene frame led to multi-color emissive photoacids.^[8]

Recently, we started to separate the influence of the conjugated base and the surrounding solvent by investigating ternary mixtures, i.e. the photoacids, an appropriate proton acceptor and the solvent. Whereas the strongest super-photoacids known to date provided the spectroscopic signatures of the hydrogen-bonded ion pair in protic solvents,^[9] we could, yet qualitatively, isolate the influence of the solvent's dielectric constant on the extent of charge separation from the basicity of the proton acceptor (Fig. 1). Preliminary single-molecule experiments hint to persistent, local heterogeneity of the dielectric constant in pure solvents.

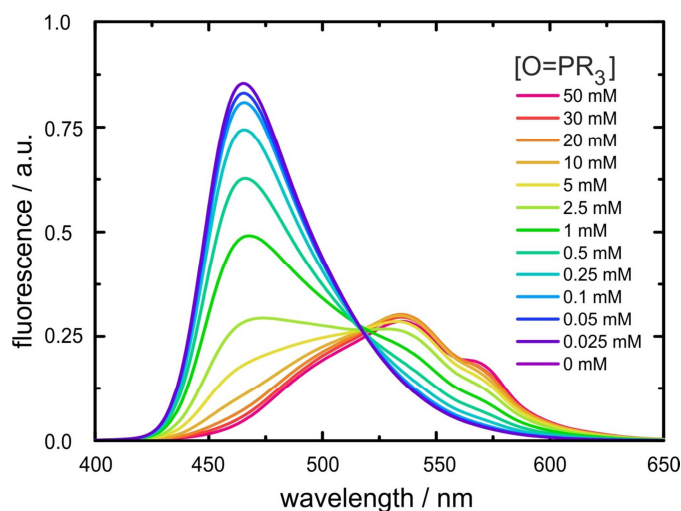


Figure 1. Emission spectra of a super-photoacid (PA, $\lambda_{em} = 460$ nm) in an inert solvent and increasing concentration of phosphine oxide (PO). The PA-PO-complex shows dual emission of the hydrogen-bonded complex at $\lambda_{em} = 480$ nm and the contact ion-pair at $\lambda_{em} = 535$ nm. Emission of the conjugated base in a solvent-separated ion pair appears as shoulder at $\lambda_{em} = 570$ nm.

Even stronger photoacids can be created if the recombination is avoided by utilizing ammonium-based photoacids, hence reaching pK_A -values close to -10 in the excited state. Our strongest photoacids exhibit ESPT in concentrated sulfuric acid as long as hydrogen sulfonate is present. In my presentation, I will present our latest finding and discuss the challenges of working with suchlike strong photoacids.

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