

Supporting Information  
to  
“Computational Investigation of Explicit  
Solvent Effects and Specific Interactions of  
Hydroxypyrene Photoacids in Acetone,  
DMSO, and Water”

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# Re-Assessing the Method Performance for Photoacid B

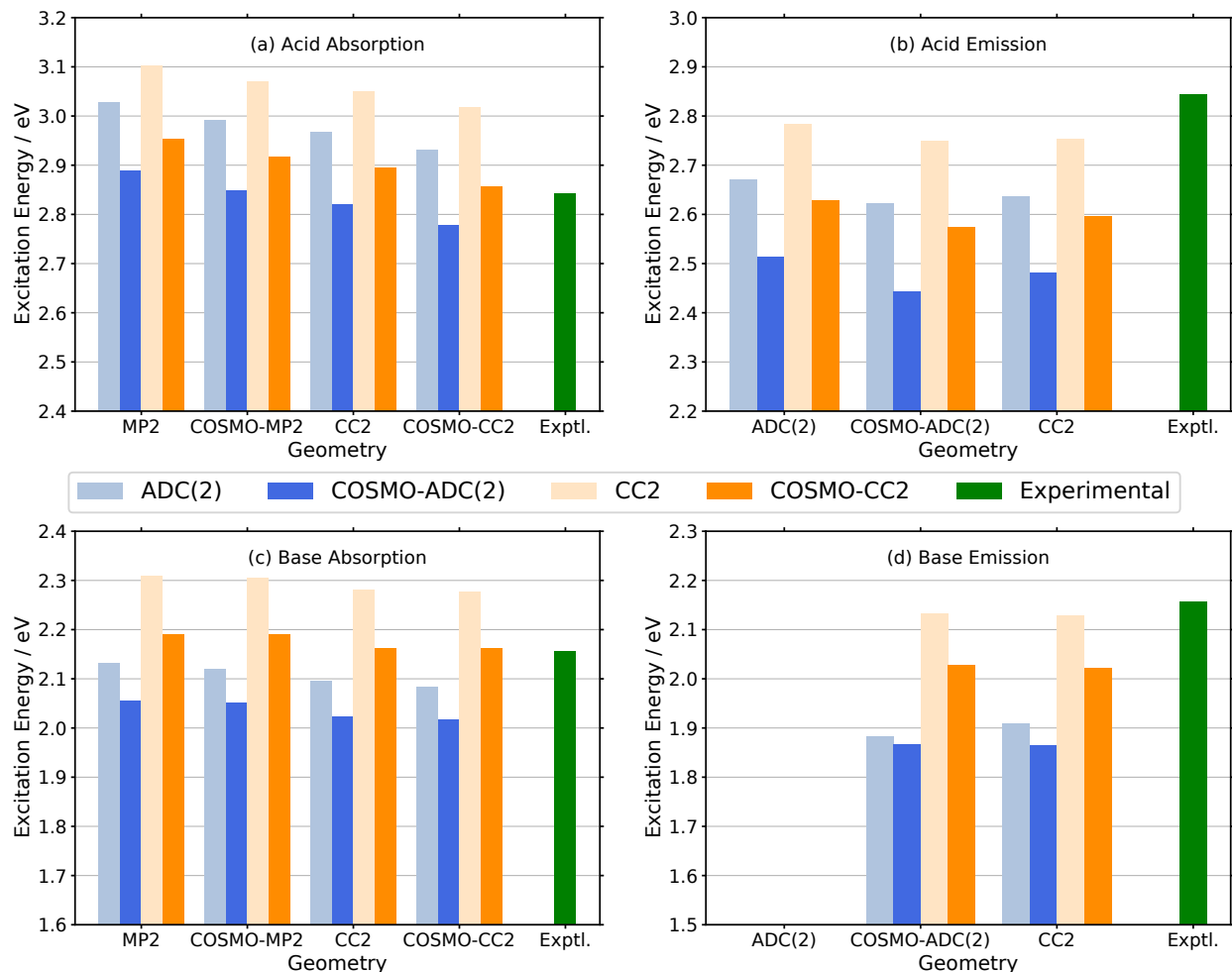


Figure S1: **Disentangling structural and energetic effects of the solvent and methods on the electronic excitation energies.** Comparison of absorption (left) and emission (right) energies in eV at different combinations of methods for the equilibrium structures (horizontal axis; groups) and for the calculation of the electronic excitation energies (vertical axis; colored bars) of the acid (top) and base (bottom) species of photoacid **B**. Structures were optimized in the cc-pVDZ basis set and excitation energies were subsequently calculated in the aug-cc-pVDZ basis set. Experimental values (band maxima) taken from Ref. 1 are included for comparison. The results at the gas-phase ADC(2)  $S_1$  geometry of the base in (d) are not included due to nonphysically low values.

**Table S1: Numerical values for Fig. S1.** Comparison of vertical electronic excitation energies in eV for the first transition with different combinations of equilibrium structures for  $S_0$  or  $S_1$  (rows) and methods for the calculation of the electronic excitation energy (columns) of the protonated and deprotonated species of photoacid **F**. For comparison, the experimental results (band maxima) from Ref. 1 are from top to bottom: 2.844 eV, 2.551 eV, 2.156 eV, 2.141 eV.

		<b>Excitation Energies</b>			
<b>Geometries</b>		<b>ADC(2)</b>	<b>COSMO-ADC(2)</b>	<b>CC2</b>	<b>COSMO-CC2</b>
		<b>Acid</b>			
$S_0$	MP2	3.028	2.888	3.103	2.954
	COSMO-MP2	2.992	2.848	3.070	2.916
	CC2	2.968	2.821	3.050	2.896
	COSMO-CC2	2.932	2.779	3.018	2.858
$S_1$	ADC(2)	2.670	2.514	2.784	2.629
	COSMO-ADC(2)	2.621	2.442	2.749	2.573
	CC2	2.636	2.480	2.752	2.597
		<b>Base</b>			
$S_0$	MP2	2.133	2.055	2.309	2.190
	COSMO-MP2	2.121	2.051	2.305	2.191
	CC2	2.097	2.023	2.282	2.163
	COSMO-CC2	2.083	2.017	2.277	2.162
$S_1$	ADC(2)	0.573	1.410	1.061	1.462
	COSMO-ADC(2)	1.883	1.867	2.132	2.027
	CC2	1.909	1.864	2.129	2.022

## Comparison of Photoacids A–F in Implicit Acetone

**Table S2: Numerical values for Fig. 3.** Comparison of vertical electronic excitation energies in eV for the first transition calculated of the acid and base form of the photoacids A–F in acetone. Absorption energies were calculated at the COSMO-MP2/cc-pVDZ  $S_0$  geometry, while emission energies were calculated at the COSMO-ADC(2)/cc-pVDZ  $S_1$  geometry; both either with COSMO-ADC(2) or COSMO-CC2 in the aug-cc-pVDZ basis set. In addition, COSMO-CC2/aug-cc-pVDZ absorption energies were also calculated at the re-optimized COSMO-CC2  $S_0$  geometry. Experimental values (band maxima) are taken from Ref. 2.

		<b>Photoacids</b>					
<b>Level</b>		<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>	<b>F</b>
		<b>Acid</b>					
<b>S<sub>0</sub></b>	COSMO-ADC(2)//COSMO-MP2	2.912	2.848	2.927	2.898	2.987	2.983
	COSMO-CC2//COSMO-MP2	2.970	2.916	2.977	2.951	3.033	3.029
	COSMO-CC2//COSMO-CC2	2.920	2.858	2.935	2.905	2.989	2.989
	Experiment	2.883	2.831	2.904	2.938	2.945	2.945
<b>S<sub>1</sub></b>	COSMO-ADC(2)//COSMO-ADC(2)	2.483	2.428	2.535	2.500	2.598	2.588
	COSMO-CC2//COSMO-ADC(2)	2.603	2.561	2.652	2.621	2.714	2.698
	Experiment	2.605	2.551	2.684	2.713	2.719	2.719
		<b>Base</b>					
<b>S<sub>0</sub></b>	COSMO-ADC(2)//COSMO-MP2	2.130	2.048	2.121	2.126	2.206	2.190
	COSMO-CC2//COSMO-MP2	2.263	2.189	2.249	2.258	2.326	2.310
	COSMO-CC2//COSMO-CC2	2.235	2.153	2.224	2.231	2.298	2.281
	Experiment	2.187	2.156	2.183	2.242	2.450	2.234
<b>S<sub>1</sub></b>	COSMO-ADC(2)//COSMO-ADC(2)	1.928	1.851	1.958	1.962	2.048	2.017
	COSMO-CC2//COSMO-ADC(2)	2.080	2.011	2.100	2.108	2.186	2.152
	Experiment	2.168	2.141	2.160	2.191	2.309	2.194

**Table S3: Supplement to Tab. 3.**  $\Delta pK_a$  based on the Förster cycle using either absorption, emission, or averaged excitation energies calculated with COSMO-ADC(2) and COSMO-CC2 at the COSMO-MP2 ( $S_0$ ) or COSMO-ADC(2) ( $S_1$ ) geometries (cf. Tab. S2) and the experimental results (taken from Ref. 2). For absorption, COSMO-CC2 absorption energies at the COSMO-CC2  $S_0$  geometry are additionally included.

		<b>Photoacids</b>					
	<b>Level</b>	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>	<b>F</b>
<b>Absorption</b>	COSMO-ADC(2)//COSMO-MP2	-13.2	-13.5	-13.6	-13.1	-13.2	-13.4
	COSMO-CC2//COSMO-MP2	-12.0	-12.3	-12.3	-11.7	-11.9	-12.2
	COSMO-CC2//COSMO-CC2	-11.6	-11.9	-12.0	-11.4	-11.7	-12.0
	Experimental	-11.8	-11.4	-12.2	-11.8	-8.4	-12.0
<b>Emission</b>	COSMO-ADC(2)//COSMO-ADC(2)	-9.4	-9.7	-9.8	-9.1	-9.3	-9.7
	COSMO-CC2//COSMO-ADC(2)	-8.8	-9.3	-9.3	-8.7	-8.9	-9.2
	Experimental	-7.4	-6.9	-8.9	-8.8	-6.9	-8.9
<b>Averaged</b>	COSMO-ADC(2)	-11.3	-11.6	-11.7	-11.1	-11.2	-11.5
	COSMO-CC2	-10.4	-10.8	-10.8	-10.2	-10.4	-10.7
	Experimental	-9.6	-9.2	-10.5	-10.3	-7.6	-10.4

# Explicit Solvent Effects in Acetone and DMSO

**Table S4: Solvatochromic shifts and resulting  $\Delta pK_a$  due to explicit solvent in the first solvation shell of photoacids **A** and **F** in the solvents acetone and DMSO.**

Comparison of calculated UV/Vis absorption (ROH, RO<sup>-</sup>) and fluorescence emission energies (ROH\*, RO<sup>-\*</sup>) in eV of the acid and base species of the two photoacids. Results are given for the structures without explicit solvent in purely implicit solution and with one explicit solvent molecule. Absorption and emission energies were calculated using COSMO-CC2/aug-cc-pVDZ at the COSMO-MP2/cc-pVDZ and COSMO-ADC(2)/cc-pVDZ geometries, respectively. Experimental results are taken from Refs. 2 and 3 for acetone and DMSO, respectively. For the deprotonated species (RO<sup>-</sup>, RO<sup>-\*</sup>), the results with explicit solvent are not calculated (labeled ‘n.a.’) due to the weak HB donation of these solvents, which has shown little effect on the transition energies for photoacid **B** (cf. Tab. 5). For the calculation of  $\Delta pK_a$ , the corresponding RO<sup>-</sup>/RO<sup>-\*</sup> results in implicit solution have thus been used.

	Solvents					
	Acetone			DMSO		
	Photoacid A					
	Impl.	Expl.	Exptl.	Impl.	Expl.	Exptl.
ROH	2.970	2.977	2.883	2.938	2.829	2.818
RO <sup>-</sup>	2.263	(n.a.)	2.187	2.229	(n.a.)	2.183
$\Delta pK_a$ (abs.)	-12.0	-12.1	-11.8	-12.0	-10.1	-10.7
ROH*	2.603	2.566	2.605	2.605	2.440	—
RO <sup>-*</sup>	2.080	(n.a.)	2.168	2.078	(n.a.)	2.160
$\Delta pK_a$ (em.)	-8.8	-8.2	-7.4	-8.9	-6.1	—
$\Delta pK_a$ (ave.)	-10.4	-10.1	-9.6	-10.4	-8.1	—
	Photoacid F					
	Impl.	Expl.	Exptl.	Impl.	Expl.	Exptl.
ROH	3.029	3.030	2.945	2.999	2.930	2.877
RO <sup>-</sup>	2.310	(n.a.)	2.234	2.283	(n.a.)	2.238
$\Delta pK_a$ (abs.)	-12.2	-12.2	-12.0	-12.1	-10.9	-10.8
ROH*	2.698	2.611	2.719	2.655	2.557	2.599
RO <sup>-*</sup>	2.152	(n.a.)	2.194	2.129	(n.a.)	2.194
$\Delta pK_a$ (em.)	-9.2	-7.8	-8.9	-8.9	-7.2	-6.8
$\Delta pK_a$ (ave.)	-10.7	-10.0	-10.4	-10.5	-9.1	-8.8

# Specific Photoacid-Base Interactions

**Table S5: Effect of specific photoacid-base interactions on the spectral properties of photoacid **B** in acetone.** Comparison of calculated UV/Vis absorption (ROH) and fluorescence emission energies (ROH\*) in eV (nm) for complexes of the protonated and deprotonated species of photoacid **B** with different bases. The HB role of the base is specified as acceptor (HB-A) or donor (HB-D).

	Acetone	H <sub>2</sub> O		(H <sub>2</sub> O) <sub>2</sub>	
	(HB-A)	HB-D	HB-A	HB-D	HB-A
<b>ROH</b>	2.837 (437.0)	2.915 (425.3)	2.786 (445.0)	2.913 (425.6)	2.759 (449.4)
<b>ROH*</b>	2.481 (499.7)	2.602 (476.5)	2.479 (500.1)	2.604 (476.1)	2.450 (506.1)
<b>RO<sup>-</sup></b>	2.187 (566.9)	2.229 (556.2)	—	2.215 (559.7)	—
<b>RO<sup>-*</sup></b>	2.020 (613.8)	2.068 (599.5)	—	2.046 (606.0)	—

## References

- (1) Sülzner, N.; Geissler, B.; Grandjean, A.; Jung, G.; Nuernberger, P. Excited-State Proton Transfer Dynamics of a Super-Photoacid in Acetone-Water Mixtures. *ChemPhotoChem* **2022**, *6*, e202200041.
- (2) Spies, C.; Finkler, B.; Acar, N.; Jung, G. Solvatochromism of pyranine-derived photoacids. *Physical Chemistry Chemical Physics* **2013**, *15*, 19893.
- (3) Finkler, B.; Spies, C.; Vester, M.; Walte, F.; Omlor, K.; Riemann, I.; Zimmer, M.; Stracke, F.; Gerhards, M.; Jung, G. Highly Photostable “Super”-Photoacids for Ultra-sensitive Fluorescence Spectroscopy. *Photochemical & Photobiological Sciences* **2014**, *13*, 548.