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Photodissociation of Leucine-Enkephalin protonated peptide: an experimental and theoretical perspective.

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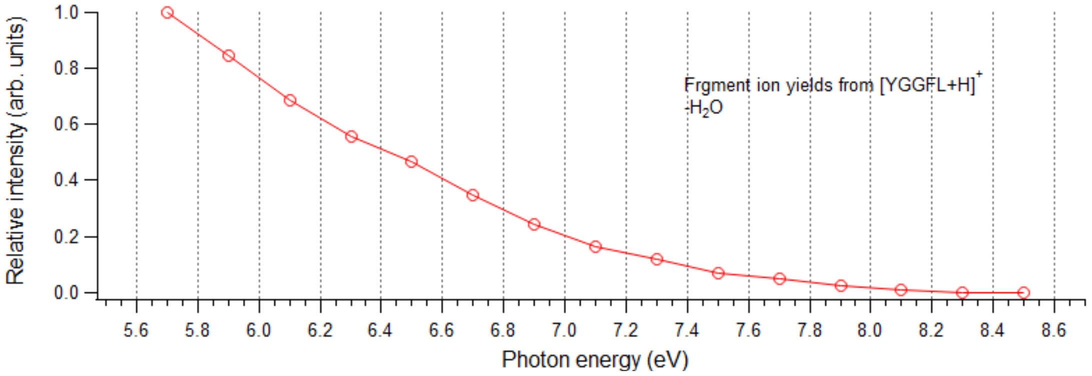
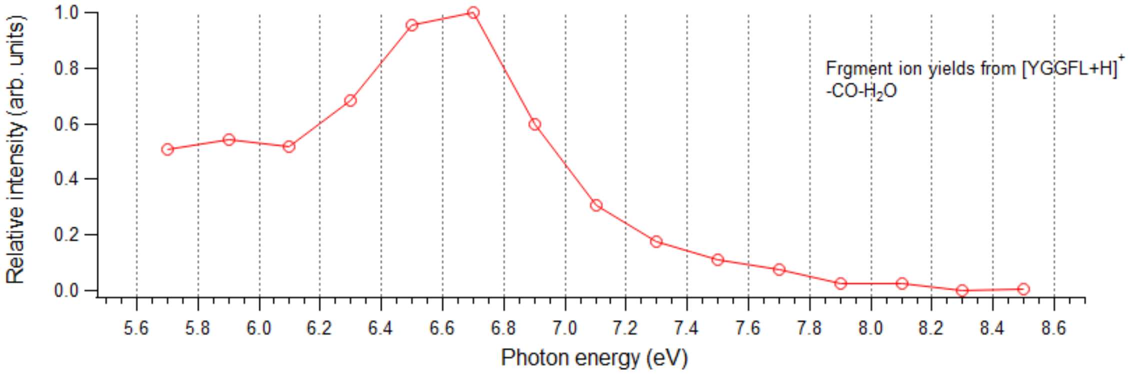
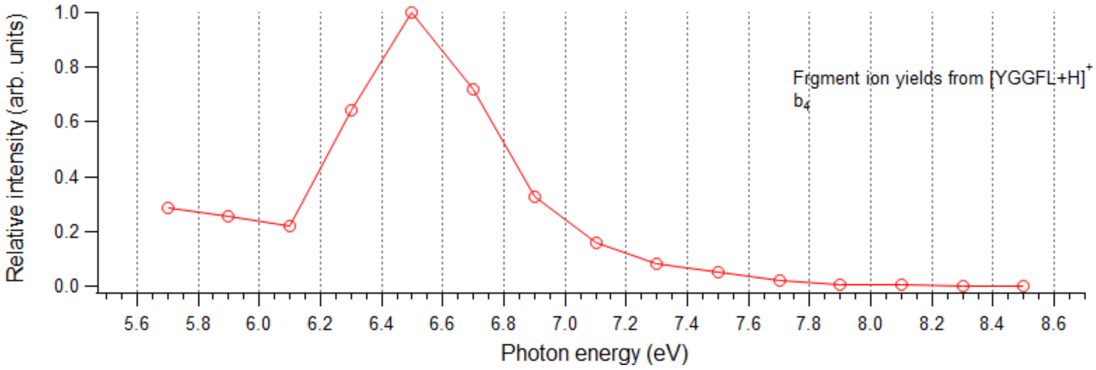
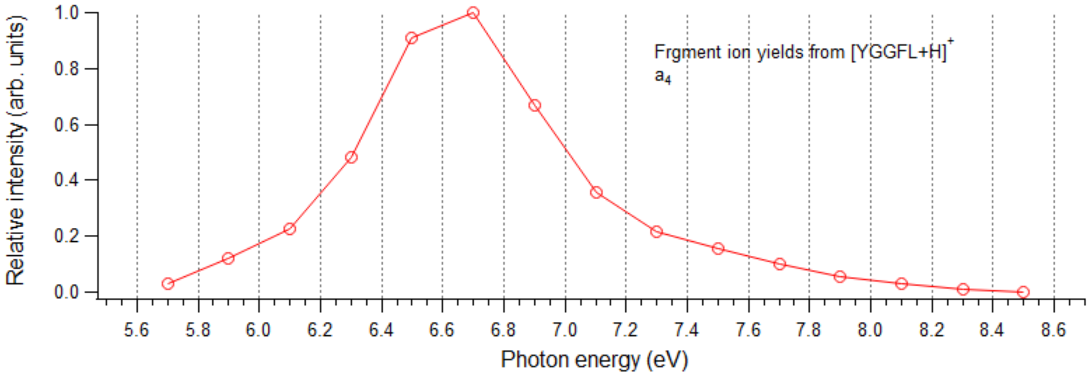
SUPPORTING INFORMATION

Photofragment Partial Ion Yields (PIY)









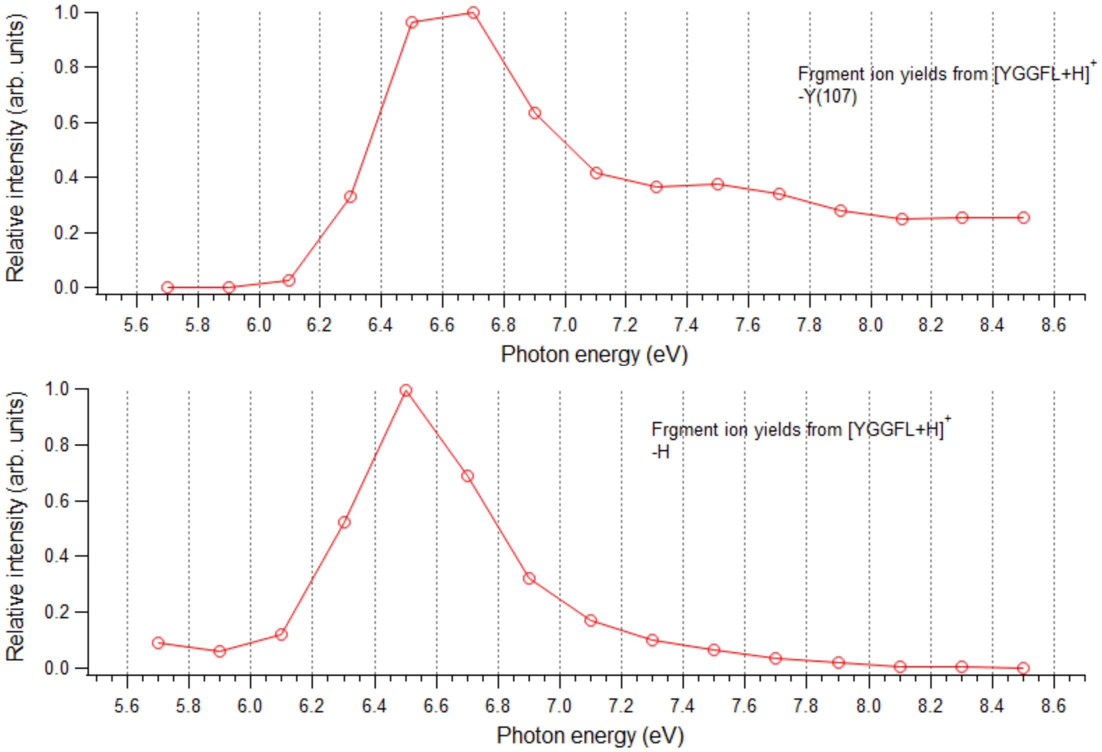


Figure S1. Selected experimental partial ion yields for protonated leucine-enkephalin peptide.

S.1 Functional and basis set evaluation

We computed Leu-Enk-H$^+$ absorption spectrum with eight different functionals belonging to three different families (all in combination with cc-pVDZ basis set) for assessing their performance (Figure S1). For the experimental spectrum, we only have data in the 5.7-8.5 eV region. There is one band that appears at 6.7 eV. (See figure 3 of main text).

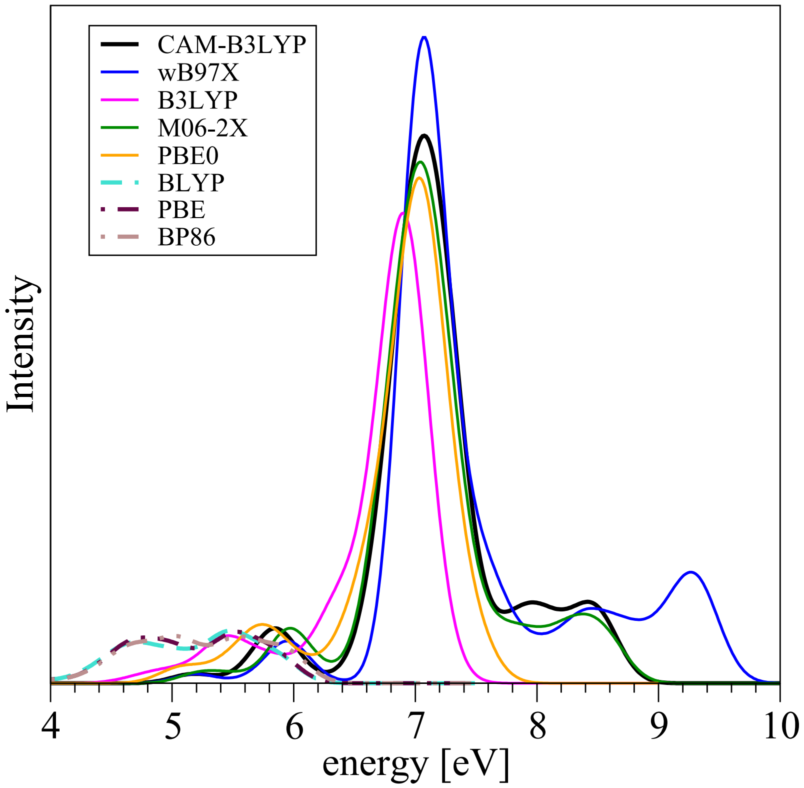


Figure S2: TD-DFT computed LeuEnkH$^+$ absorption spectra, with different functionals and cc-pVDZ basis set.

The group of LD/GGA (BP86, PBEPBE and BLYP) clearly fail to reproduce the spectra. They all render a similar spectrum with two overlapping bands of similar intensity, centered around 4.7 eV and 5.5eV.

The group of hybrid functionals (B3LYP, M06-2X, PBE0). B3LYP and PBE0 yield spectra very similar in shape, with a small band at 5.45 and 5.76 and a second, high intensity band at 6.90 and 7.00 eV. M06-2X shows these two bands also, slightly shifted to the blue (5.96 and 7.00) and a third one appearing at 8.41 eV.

Long-range corrected (LC) (CAM-B3LYP and wB97X) slightly differ in their shape. In particular in the high energy region. Both show a low intensity band at 5.85 and 5.95, respectively. A second band, the most intense one, centered at 7 eV in both bases. Cam-b3lyp displays two overlapping bands of low intensity at 7.94 and 8.44 eV while for wB972X this two bands are displaced to the blue, appearing at 8.44 and 9.29 eV, with the second slightly higher in intensity.

All the computed spectra appear shifted to the blue compared to the experimental. There is not a clear choice comparing to the experimental data, all hybrid and long-range corrected show a main band as the experimental one. Long-range corrected functionals are better suited charge transfer excitations, that might be relevant in our study. Between the two LC tested, we chose cam-B3LYP since it is faster and has shown good performance in treating such kind of extended pi systems.

Basis set

Once the functional is chosen, we tested different basis set using CAM-B3LYP, Figure S2.

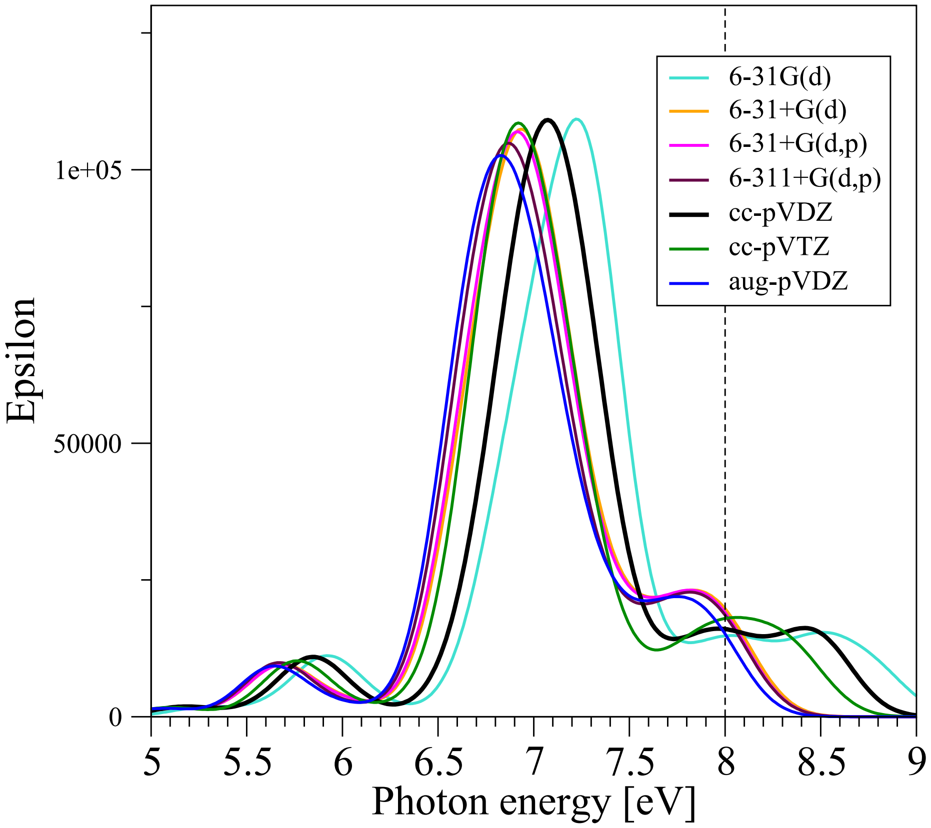


Figure S3: TD-DFT computed LeuEnkH$^+$ absorption spectra, with CAM-B3LYP and different basis sets.

The increase of the basis set causes a red shift of the spectra, as well as the inclusion of diffuse functions. We chose cc-pVDZ basis set as a good compromise between accuracy and computational cost.

S.2. Explanation of the theoretical protocol used.

1. The Franck-Condon (FC) principle is based upon the fact that electronic transitions occur vertically in potential energy diagrams. This means than when going from the ground state (GS) to the excited state (ES), the electrons will move much more quickly than the nuclei. Therefore, right after the molecule absorbs the photon, the nuclei will remain in the same place, but the electronic distributions might be different. Therefore, after the vertical transition the molecule is in a non-equilibrium geometry of the SX excited state. So, once the molecule has absorbed the photon and the electrons redistributed themselves, the nuclei will in turn evolve to their new equilibrium positions, the nuclear coordinates will change adopting a new equilibrium geometry.

   In other words, the FC region is the region around which the molecule oscillates when it absorbs light. Thus, when we refer to the FC region, we mean the region of the PES defined by the ground state minimum of the molecule.

2. The oscillator strength (*f*) is a quantity that expresses the probability of absorption (or emission) of electromagnetic radiation between two energy levels. It is proportional to the transition dipole moment. The larger *f* is for a given transition, the greater the probability of that transition happening, and therefore the probability of the final state (excited state) becoming populated. Transitions with large oscillator strengths are called bright transitions. On the contrary, transitions with f = 0 (or very low) are not allowed (or have a very low probability) and are called dark transitions.

   We used *f* as a guide to select which states are preferentially populated after light absorption and most probable to initiate a photochemical pathway.

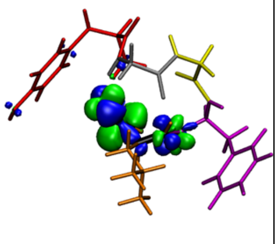
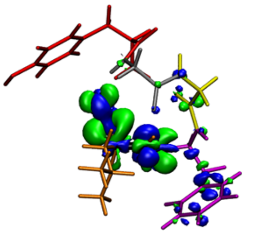
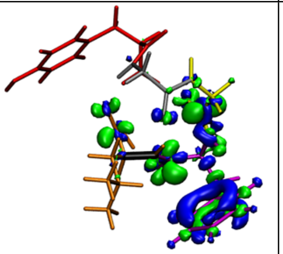
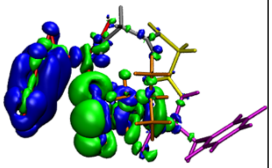
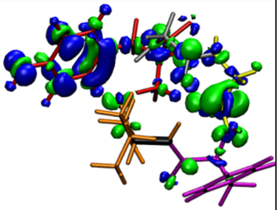
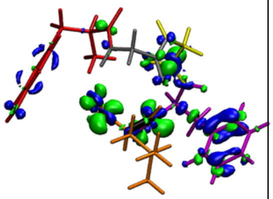
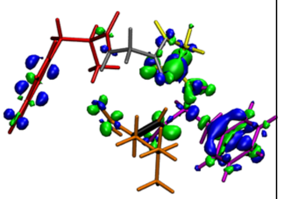
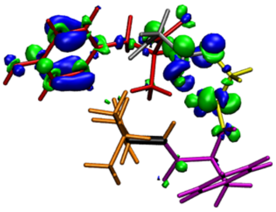
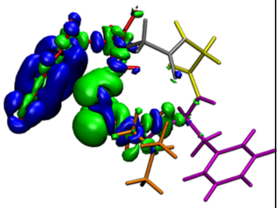
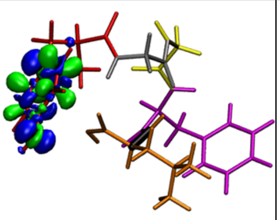
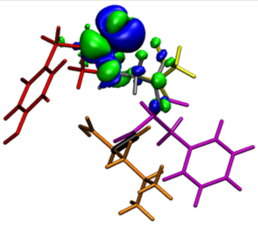
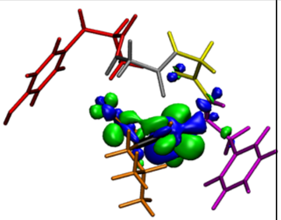
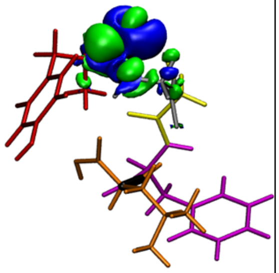
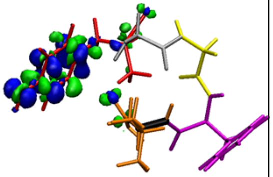
So, the standard procedure is to consider the lowest brightest singlet states in the FC region and then characterize their potential energy surface. For completeness, sometimes the same is done with the dark states, but we would like to emphasize that only considering the birth ones means in our case to optimize 22 states. We also consider that if a dark state presents a very stable minimum, it could be reached from our calculations.

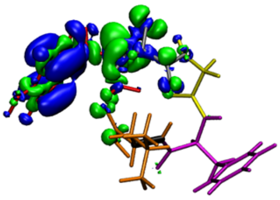
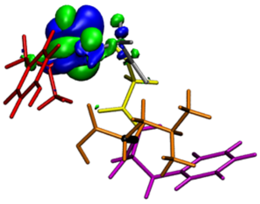
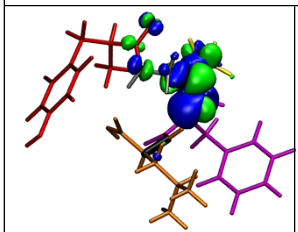
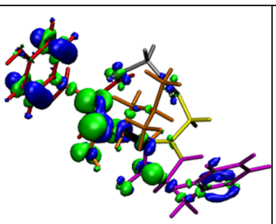
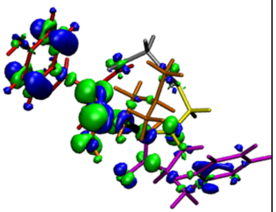
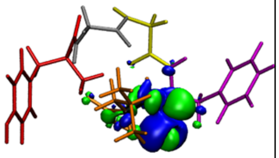
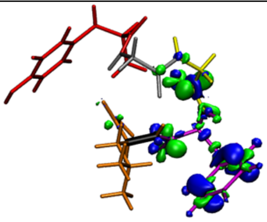
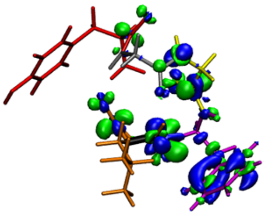
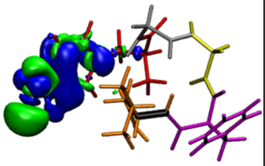
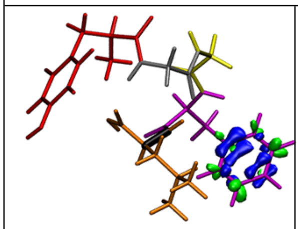
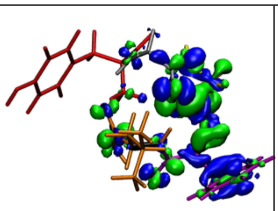
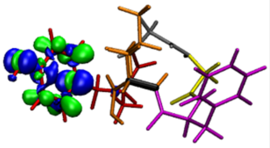
S.3. Franck-Condon states and S_1 minima

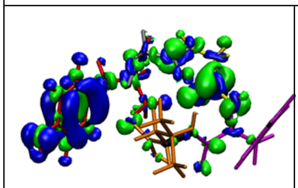
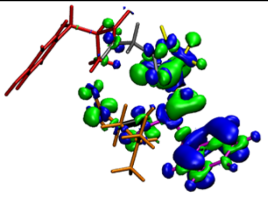
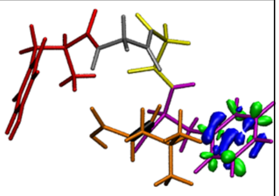
Table S1: Characteristics of the brightest excited states (f > 0.05) up to 8 eV and the S_1 minimum they reach upon optimization. For comparison, all the states below S_6 are included independently of their f.

Franck-Condon				**Optimized minima**			
Excited State	**Familiy**	**Vertical [eV]**	**f=**	**Family**	**Adiabatic [eV]**	**Vertical [eV]**	**f=**
S_1	F1	5.17	0.0267	min3-PB1	4.80	3.75	0.0005
S_2	F2	5.48	0.0008	min7-phenol	4.99	4.82	0.0337
S_3	PB1	5.54	0.0054	min3-PB1	4.80	3.75	0.0005
S_4	PB2	5.62	0.0106	min5-PB4	4.88	3.67	0.0011
S_5	PB4	5.76	0.0099	min3-PB1	4.80	3.75	0.0005
S_6	COOH	5.80	0.0315	min1-HT	3.69	0.99	0.0001
S_7	F1	5.87	**0.1142**	min3-PB1	4.80	3.75	0.0005
S_{14}	F3	6.76	0.0784	min1-HT	3.69	0.99	0.0001
S_{16}	F3	6.87	**0.4199**	min1-HT	3.69	0.99	0.0001
S_{17}	F4	6.94	0.0823	min2-HT	4.32	2.19	0.0003
S_{18}	F4	6.97	0.069	min8-phenyl	5.33	5.19	0.012
S_{19}	F4	6.97	**0.1033**	min1-HT	3.69	0.99	0.0001
S_{20}	F5	7.03	**0.1388**	min1-HT	3.69	0.99	0.0001
S_{21}	F5	7.06	**0.3066**	min1-HT	3.69	0.99	0.0001
S_{22}	F6	7.10	**0.1575**	min5-PB4	4.88	3.67	0.0011
S_{23}	F6	7.11	**0.1969**	min5-PB4	4.88	3.67	0.0011
S_{25}	F3	7.17	0.0563	min7-phenol	4.99	4.82	0.0337
S_{27}	F3	7.24	**0.1467**	min6-phenol	4.95	1.00	0.0000
S_{28}	F3	7.26	**0.3207**	min5-PB4	4.88	3.67	0.0011
S_{29}	F4	7.28	0.0717	min4-PB1	4.84	3.75	0.0017
S_{30}	F3	7.35	0.0743	min8-phenyl	5.33	5.19	0.0012

Table S2: Electronic densities for the brightest excited states (f> 0.05) at the Franck-Condon region for [YGGFL+H]$^+$. They are grouped based on the minimum reached after optimization of the FC excited state, shown in the last column (geometry and electronic density difference for the S_1 minima, and relative energies). Note, that the last minima is at the S_2 excited state surface.

FC region			**Optimized S_1 minima**
 S_6-CO$_2$H	 S_{14}-F3	 S_{16}-F3	 **Min1-HT** **0.00eV**
 S_{19}-F4	 S_{20}-F5	 S_{21}-F5	
 S_{17}-F4			 **Min2-HT** **0.63eV**
 S_1 -F1	 S_3-PB1	 S_5-PB4	 **Min3-PB1** **1.11eV**
 S_7-F1			

FC region			Optimized S_1 minima
 S_{29}-F4			 **Min4-PB1** **1.15eV**
 S_4-PB2	 S_{22}-F6	 S_{23}-F6	 **Min5-PB4** **1.19eV**
 S_{28}-F3			
 S_{27}-F3			 **Min6-phenol** **1.26eV**
 S_2-F2	 S_{25}-F3		 **Min7-phenol** **1.30eV**

FC region			Optimized S_1 minima
 S_{18} -F4	 S_{30}-F3		 **Min8-phenyl** **1.65eV- S_2**

S4. Spin-orbit coupling and T_1 calculations.

In tables S3 to S10 we reported the vertical energies and spin-orbit coupling (cm^{-1}) terms computed at the TDA CAM-B3LYP/cc-pVDZ level of theory for the eight minima reported in the main text. Spin Orbit Coupling (SOC) terms have been estimated using the single particle Breit–Pauli operator with an effective charge approximation as implemented in the PySOC Code (ref 69). Highlighted in green are all the states below S_1 minimum and up to 0.5 eV over it.

Table S3: min1 SOC (cm^{-1}) terms and vertical energies (eV).

ee	**Vertical energy**	**SOC**
T1	0.9877	0.01842
S1	**0.9945**	
T2	2.4455	0.5019

Table S4: min2 SOC (cm^{-1}) terms and vertical energies (eV).

Ee	**Vertical energy**	**SOC**
T1	2.0932	0.45257
S1	**2.1859**	
T2	3.0578	8.23827
T3	3.1776	1.71617
T4	3.4816	10.01797

Table S5: min3 SOC (cm^{-1}) terms and vertical energies (eV).

ee	**Vertical energy**	**SOC**
T1	2.884	39.75559
T2	3.1997	11.01356
T3	3.516	0.80708
T4	3.5549	0.00044
S1	**3.7527**	
T5	4.1145	0.75858
T6	4.5809	2.04187

Table S6: min4 SOC (cm^{-1}) terms and vertical energies (eV).

ee	**Vertical energy**	**SOC**
T1	2.9727	42.01945
T2	3.1829	9.27501
T3	3.5178	1.14948
T4	3.5546	0.00194
S1	**3.7551**	
T5	4.1572	0.32198
T6	4.5626	1.1174

Table S7: min5 SOC (cm^{-1}) terms and vertical energies (eV).

Ee	**Vertical energy**	**SOC**
T1	3.0737	26.12196
T2	3.2305	29.1501
T3	3.5192	0.0144
T4	3.5564	0.26525
S1	**3.6715**	
T5	4.1447	0.00996
T6	4.6064	0.01845

Table S8: min6 SOC (cm^{-1}) terms and vertical energies (eV).

min6	**Vertical energy**	**SOC**
S0	0	
T1	-1.916	26.01919
T2	0.6234	0.40502
S1	**0.9991**	
T3	3.2498	2.16563
S2	3.2982	
T4	3.3151	

Table S9: min7 SOC (cm^{-1}) terms and vertical energies (eV).

ee	**Vertical energy**	**SOC**
T1	3.2437	1.27001
T2	3.5539	0.00049
T3	3.7292	0.10663
T4	4.3667	0.0289
T5	4.738	0.00164
T6	4.7662	0.29641
T7	4.7705	0.00481
S1	**4.817**	
T8	5.0135	0.22231
T9	5.0141	0.17335
T10	5.0762	0.05137
T11	5.106	0.0045
T12	5.1702	0.34386
T13	5.2068	0.13813
T14	5.3035	1.03726
T15	5.3133	0.1287
T16	5.3844	0.23768

Table S10: min8 SOC (cm^{-1}) terms and vertical energies (eV).

ee	**Vertical energy**	**SOC**
T1	3.1226	1.35904
T2	3.5215	0.00555
T3	4.1473	0.00101
T4	4.4538	0.02303
T5	4.504	0.04925
T6	4.6058	0.00075
T7	4.7539	0.00737
T8	4.8712	0.02136
T9	4.9955	0.33421
T10	5.0252	0.00563
T11	5.082	0.0817
S1	5.1569	
T12	5.1705	0.146
S2	**5.1932**	
T13	5.2083	0.29296
T14	5.3107	0.20427
T15	5.3737	0.11249
T16	5.3969	0.01355
T17	5.5001	0.20258

Table S11: Relative energies after optimization in T_1 surface of the S_1 minima structure we high SOC. Energies are relative to the ground state starting minimum, min0. Optimization were performed at DFT CAM-B3LYP/cc-pVDZ level of theory.

Starting Structure	**Rel. Energy [eV]**
Min3	3.92
Min3	3.94*
Min4	4.08**
Min5	4.20
Min9-HT-PB4	3.85
Min6	4.04

*Optimization considering the first two excited singlets and triplets and using TDA.

** Not converged

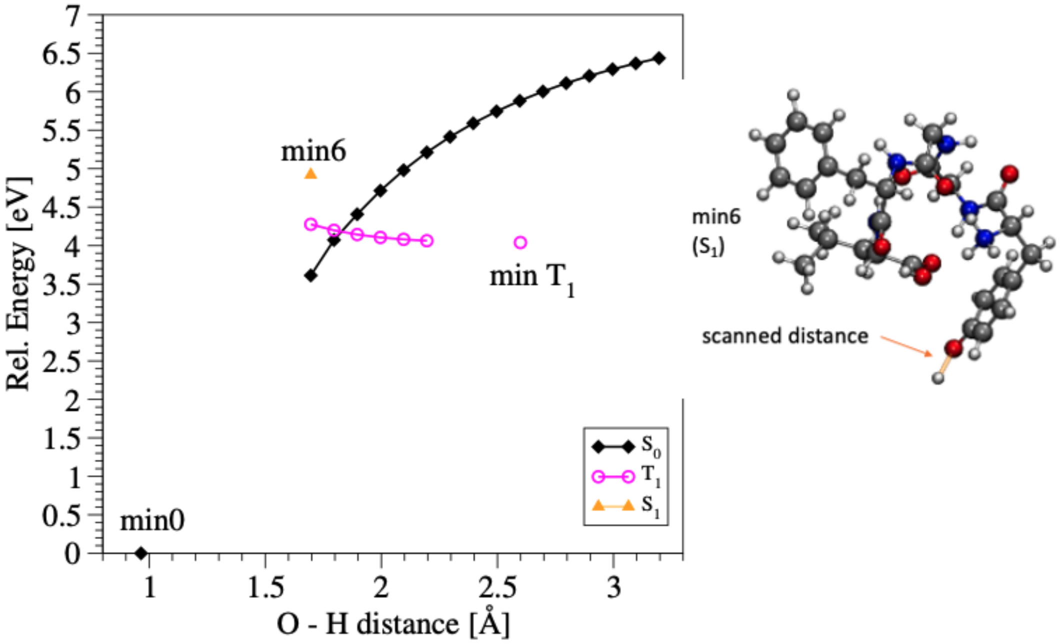


Figure S4: Scan of the phenol's hydroxyl O-H distance in the S_0 and T_1 PES to explain H loss mechanism.