

# Sequential Proton Coupled Electron Transfer (PCET): Dynamics Observed over 8 Orders of Magnitude in Time.

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*KEYWORDS Pump-probe spectroscopy; action spectroscopy; photo-triggered charge transfer; electron and proton transfer; tryptophan-containing peptide; metal-peptide complex*

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## SUPPORTING INFORMATION

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### Supplementary Tables

Tables below list atomic charges used for simulations performed within this work (Table S1 and S2), and energy/coordinates of reactant, product and transition state on the optimized proton transfer pathway (Table S3).

**Table S1. Tryptophan atomic charges\*.**

Trp	HF/6-31G(d) <sup>a</sup>	CHARMM <sup>b</sup>	CHARMM <sup>*c</sup>	Trp-	HF/6-31G(d) <sup>a</sup>	CHARMM <sup>*c</sup>	Trp+	HF/6-31G(d) <sup>a</sup>	CHARMM <sup>*c</sup>
CB	-0.39	-0.18	-0.24	CB	-0.35	-0.245	CB	-0.46	-0.26
HB1	0.12	0.09	0.12	HB1	0.07	0.09	HB1	0.19	0.17
HB2	0.12	0.09	0.12	HB2	0.08	0.09	HB2	0.16	0.17
CG	0.09	-0.03	0.06	CG	-0.06	-0.07	CG	0.24	0.28
CD1	-0.22	0.04	-0.12	CD1	0.02	-0.16	CD1	0.2	0.2
HD1	0.21	0.12	0.18	HD1	0.1	0.08	HD1	0.2	0.25
NE1	-0.45	-0.61	-0.6	NE1	-0.76	-0.85	NE1	-0.49	-0.64
HE1	0.4	0.38	0.4				HE1	0.45	0.57
CE2	0.23	0.13	0.13	CE2	0.44	0.195	CE2	0.38	0.38
CD2	0.05	-0.02	-0.05	CD2	-0.05	-0.13	CD2	-0.11	-0.11
CE3	-0.18	-0.12	-0.18	CE3	-0.2	-0.2	CE3	-0.04	-0.13
HE3	0.17	0.12	0.18	HE3	0.14	0.2	HE3	0.17	0.13
CZ3	-0.24	-0.12	-0.18	CZ3	-0.29	-0.2	CZ3	-0.2	-0.13
HZ3	0.16	0.12	0.18	HZ3	0.13	0.2	HZ3	0.19	0.13
CZ2	-0.32	-0.12	-0.18	CZ2	-0.32	-0.2	CZ2	-0.29	-0.13
HZ2	0.18	0.12	0.18	HZ2	0.14	0.2	HZ2	0.22	0.13
CH2	-0.07	-0.12	-0.18	CH2	-0.18	-0.2	CH2	0.03	-0.13
HH2	0.14	0.12	0.18	HH2	0.11	0.2	HH2	0.16	0.13

\* All charges are given in units of e. <sup>a</sup>from HF/6-31G(d) ESP fits, <sup>b</sup>from CHARMM 22 parameter set and <sup>c</sup>the corresponding adjusted ESP CHARMM\* charges.

**Table S2. Histidine atomic charges\*.**

His	HF/6-31G(d) <sup>a</sup>	CHARMM <sup>b</sup>	CHARMM* <sup>c</sup>	His <sup>+</sup>	HF/6-31G(d) <sup>a</sup>	CHARMM <sup>b</sup>	CHARMM* <sup>c</sup>
CB	-0.39	-0.09	-0.16	CB	-0.39	-0.05	-0.20
HB1	0.15	0.09	0.14	HB1	0.16	0.09	0.16
HB2	0.13	0.09	0.14	HB2	0.18	0.09	0.16
ND1	-0.41	-0.36	-0.41	ND1	-0.25	-0.51	-0.35
HD1	0.36	0.32	0.33	HD1	0.41	0.44	0.41
CG	0.20	-0.05	-0.04	CE1	0.08	0.32	0.16
CE1	0.23	0.25	0.24	HE1	0.26	0.18	0.26
HE1	0.12	0.13	0.13	CG	0.25	0.19	0.25
NE2	-0.51	-0.70	-0.71	NE2	-0.19	-0.51	-0.33
				HE2	0.41	0.44	0.41
CD2	-0.03	0.22	0.20	CD2	-0.20	0.19	-0.10
HD2	0.15	0.10	0.15	HD2	0.27	0.13	0.17

\* All charges are given in units of e. <sup>a</sup>from HF/6-31G(d) ESP fits, <sup>b</sup>from CHARMM 22 parameter set and <sup>c</sup>the corresponding adjusted ESP CHARMM\* charges.

**Table S3. Reactant, Product and Transition State structures coordinates.**

		Transition state (1 imaginary freq. : -729.8099 cm <sup>-1</sup> ) E(UB3LYP) = -1915.33265 a.u.			Reactant E(UB3LYP) = - 1915.35625 a.u.			Product E(UB3LYP) = - 1915.33655 a.u.		
1	C	-1.505079	-0.889602	-0.62265	-1.669591	-1.322998	-0.823885	-0.972773	-1.601058	-0.407487
2	C	-2.813515	-1.147606	-0.940932	-3.028293	-1.416259	-0.99791	-2.331784	-1.738343	-0.528097
3	N	-2.965629	-2.516251	-0.813682	-3.336446	-2.734761	-0.728565	-2.594888	-3.093796	-0.425885
4	C	-1.784686	-3.043241	-0.440693	-2.189792	-3.378926	-0.416809	-1.447207	-3.75569	-0.261114
5	N	-0.874537	-2.081488	-0.317675	-1.152934	-2.553562	-0.466936	-0.449743	-2.869597	-0.250224
6	C	-3.963265	-0.278094	-1.317707	-4.086979	-0.426702	-1.352337	-3.399561	-0.724164	-0.793409
7	C	-5.109319	-0.294437	-0.234222	-5.081305	-0.149549	-0.162862	-4.64633	-0.777176	0.165449
8	N	-6.390631	-0.674472	-0.781346	-6.460084	-0.408377	-0.509158	-5.835264	-1.333919	-0.450061
9	C	-6.631176	-1.946686	-1.180415	-6.915732	-1.668549	-0.712641	-6.074046	-2.650596	-0.63554
10	C	-8.0191	-2.247258	-1.701991	-8.394591	-1.817131	-0.998899	-7.440838	-3.020805	-1.165278
11	C	-5.223775	1.109345	0.368054	-4.97596	1.31426	0.291246	-5.013156	0.669789	0.564584
12	O	-6.076965	1.905219	-0.008233	-5.87874	2.122946	0.10164	-5.973509	1.239327	0.058609
13	N	-4.247761	1.386295	1.267563	-3.791023	1.624317	0.868788	-4.165369	1.23996	1.454358
14	C	-3.840718	2.733557	1.615402	-3.404895	2.975174	1.207868	-4.067639	2.678088	1.624598
15	C	-2.308854	2.719522	1.698552	-1.881106	2.99992	1.355454	-2.586198	3.05546	1.496546
16	O	-1.709662	1.691996	2.004926	-1.238797	1.948811	1.453678	-1.715651	2.198932	1.693254
17	N	-1.676911	3.900639	1.467413	-1.304189	4.21991	1.40171	-2.302842	4.336794	1.190539
18	C	-0.234482	3.929769	1.382187	0.113998	4.411087	1.705512	-0.934191	4.858713	1.165566
19	C	0.296248	3.287902	0.082087	1.066395	4.214999	0.509655	-0.139023	4.544707	-0.120178
20	O	-0.442643	2.861297	-0.796054	1.758945	5.130671	0.089219	0.276866	5.438815	-0.842605
21	N	1.658679	3.285877	-0.003486	1.07429	2.949649	-0.006931	0.075789	3.215987	-0.343412
22	C	2.353791	2.619091	-1.080867	2.019386	2.569841	-1.027756	0.902079	2.75022	-1.442182
23	C	3.401633	1.655128	-0.515754	2.902922	1.408771	-0.560618	1.862654	1.682548	-0.914563
24	O	3.547617	1.488933	0.690574	2.55914	0.645818	0.344564	1.434198	0.699418	-0.299482
25	N	4.148113	0.996727	-1.451696	4.065353	1.245699	-1.24078	3.17613	1.891864	-1.154453
26	C	5.314674	0.226268	-1.071464	5.082264	0.296447	-0.851494	4.250839	1.115403	-0.564586
27	C	6.421159	0.545655	-2.098869	6.390169	0.779749	-1.521403	5.465923	2.067172	-0.498496
28	O	6.125112	0.950006	-3.215081	6.349544	1.504411	-2.504585	5.52918	3.055312	-1.215102
29	C	5.050123	-1.32154	-1.090532	4.79174	-1.178887	-1.317458	4.634246	-0.181791	-1.382976
30	C	3.861793	-1.719311	-0.286207	3.66836	-1.831142	-0.590296	3.994176	-1.410299	-0.833622
31	C	3.770894	-2.100592	1.085274	3.697554	-2.520971	0.66002	4.494545	-2.28464	0.178533
32	C	2.391226	-2.325403	1.354218	2.368476	-2.942721	0.932797	3.437473	-3.200273	0.458746

33	N	1.656557	-2.099245	0.171976	1.557396	-2.537171	-0.141751	2.313873	-2.917437	-0.35446
34	C	2.509747	-1.746219	-0.773364	2.302284	-1.888415	-1.022475	2.660683	-1.890783	-1.10293
35	C	4.712751	-2.274828	2.113196	4.717089	-2.830934	1.577046	5.716008	-2.390507	0.862417
36	C	4.260388	-2.660458	3.380438	4.384844	-3.534133	2.73734	5.862442	-3.400338	1.8199
37	C	2.899807	-2.86781	3.620164	3.06393	-3.926324	2.984151	4.813703	-4.286414	2.086239
38	C	1.935334	-2.70167	2.599317	2.025722	-3.636378	2.075347	3.581486	-4.196456	1.402957
39	O	-5.760055	-2.827007	-1.115223	-6.16418	-2.65234	-0.666831	-5.232741	-3.52986	-0.383777
40	H	-7.937731	-2.676444	-2.705064	-8.926468	-0.862831	-1.038802	-8.073351	-2.155412	-1.378116
41	H	-8.668007	-1.368123	-1.737328	-8.842684	-2.443601	-0.221225	-7.940787	-3.65574	-0.426935
42	H	-8.480063	-3.004961	-1.060496	-8.521787	-2.340794	-1.951082	-7.320401	-3.615093	-2.075805
43	H	-7.078562	0.066962	-0.862416	-7.068547	0.40403	-0.523671	-6.550267	-0.638444	-0.650281
44	H	-4.84263	-1.014684	0.546751	-4.80457	-0.801259	0.67426	-4.395568	-1.358277	1.060643
45	H	-3.88261	-2.966157	-0.931453	-4.306761	-3.066827	-0.705812	-3.575491	-3.458713	-0.4172
46	H	-3.598155	0.740313	-1.478473	-3.609092	0.502773	-1.675755	-2.924491	0.259415	-0.730323
47	H	-4.394038	-0.612414	-2.266528	-4.674648	-0.789641	-2.201079	-3.770314	-0.824772	-1.820228
48	H	-0.994556	0.062962	-0.581553	-1.04051	-0.448557	-0.918967	-0.337605	-0.722978	-0.410548
49	H	-1.617083	-4.09712	-0.273353	-2.148774	-4.429729	-0.167681	-1.346014	-4.824592	-0.153472
50	H	-3.540466	0.688837	1.481029	-3.063029	0.928558	1.000061	-3.321112	0.747946	1.732414
51	H	-4.244229	3.041021	2.590303	-3.860625	3.299876	2.154596	-4.428721	2.986185	2.615075
52	H	-4.223685	3.432646	0.86565	-3.749438	3.671439	0.434455	-4.697031	3.166625	0.875297
53	H	-2.19051	4.631592	0.993756	-1.87209	5.04185	1.244884	-3.057919	4.96925	0.96085
54	H	0.176392	3.389823	2.240925	0.387787	3.716359	2.507003	-0.401	4.454961	2.032753
55	H	0.104954	4.968462	1.444027	0.25587	5.433001	2.057007	-0.979702	5.944301	1.249834
56	H	2.195752	3.403396	0.848236	0.55166	2.226237	0.480745	-0.265972	2.540041	0.335872
57	H	1.612104	2.082361	-1.681801	1.508618	2.259276	-1.952415	0.292571	2.29507	-2.236365
58	H	2.846304	3.342473	-1.746495	2.616536	3.454883	-1.266104	1.410799	3.61896	-1.865886
59	H	4.1607	1.308854	-2.420311	4.355547	1.889697	-1.973512	3.496152	2.750549	-1.59773
60	H	5.59904	0.523033	-0.057286	5.173606	0.296619	0.241214	3.950081	0.815457	0.44502
61	H	5.949552	-1.830543	-0.727206	5.709636	-1.758714	-1.167351	5.722913	-0.298407	-1.365096
62	H	4.905088	-1.620596	-2.135385	4.595329	-1.151791	-2.394367	4.343339	-0.012476	-2.424627
63	H	2.175038	-1.5209	-1.778822	1.876788	-1.484135	-1.931774	1.974857	-1.4559	-1.820451
64	H	0.455628	-2.151247	-0.006205	0.489886	-2.657569	-0.226123	0.589135	-3.073177	-0.204988
65	H	5.772448	-2.117259	1.934586	5.746276	-2.53835	1.390416	6.541149	-1.715635	0.646757
66	H	0.880433	-2.861243	2.798158	1.004824	-3.946194	2.273007	2.777144	-4.894603	1.614114
67	H	4.97367	-2.799682	4.186121	5.158789	-3.782102	3.456235	6.800317	-3.502927	2.356563
68	H	2.570191	-3.164713	4.610914	2.829877	-4.47138	3.893227	4.949418	-5.06522	2.830687
69	N	7.691908	0.281216	-1.704098	7.540993	0.296569	-0.986694	6.454655	1.689266	0.354339
70	H	8.441842	0.505795	-2.34603	8.411975	0.634619	-1.377222	7.245819	2.312015	0.458328
71	H	7.933845	0.130046	-0.735607	7.573899	-0.105562	-0.061008	6.297836	1.005588	1.081014

## Supplementary Figures

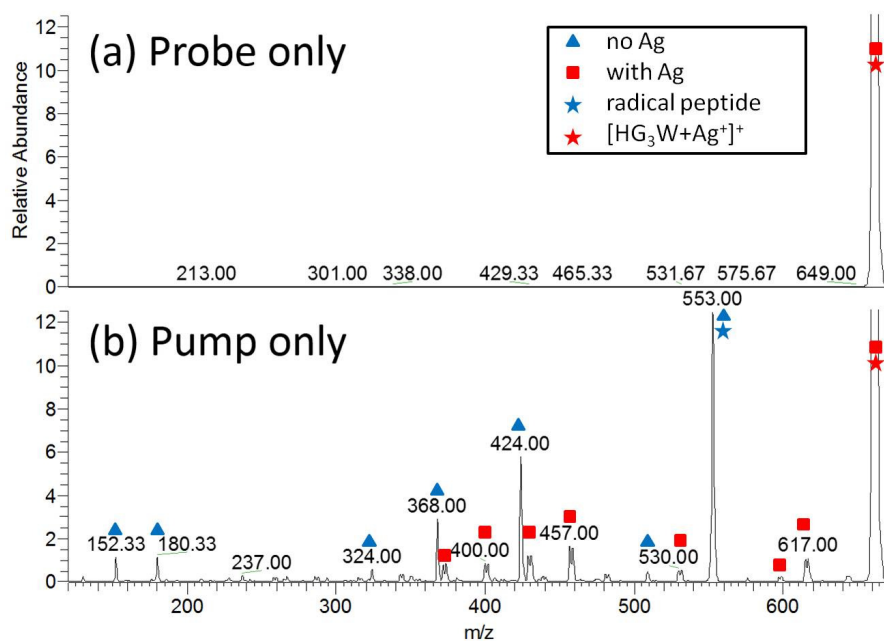


Figure S1. Typical photo-fragmentation mass spectra of [HG<sub>3</sub>W+Ag]<sup>+</sup> after a single pulse of either probe laser at 580 nm (a) or pump laser at 266 nm (b). Both laser pulse energies are identical to the one used for pump-probe experiments. Relative abundances (in %) are normalized to the metal complex intensity in each spectrum. Pump beam generates mostly Ag-free fragments (blue triangle) and to a lesser extent silver containing fragments (red square). Both ion families are readily identified based on the silver-specific isotopic pattern. Probe has comparatively no effect.

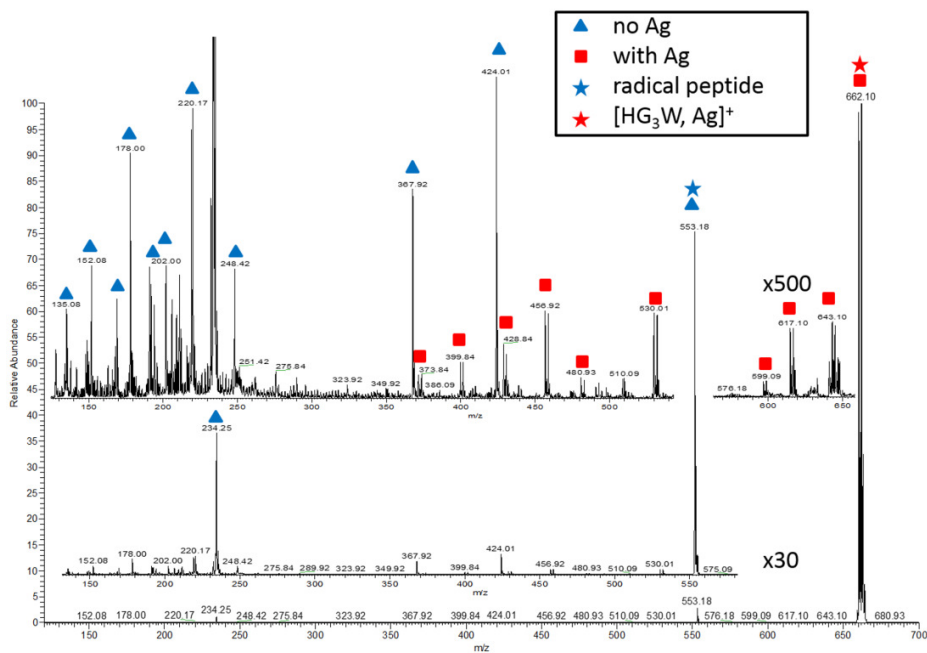


Figure S2. Typical mass spectrum after photo-fragmentation of  $[\text{HG}_3\text{W}+\text{Ag}]^+$  after pump and probe irradiation (mass spectra obtained for different pump-probe delays were averaged). Parent silver complex dissociates into silver-containing (red square) and silver-free (blue triangle) ions. Both ion families are readily identified based on the silver-specific isotopic pattern.

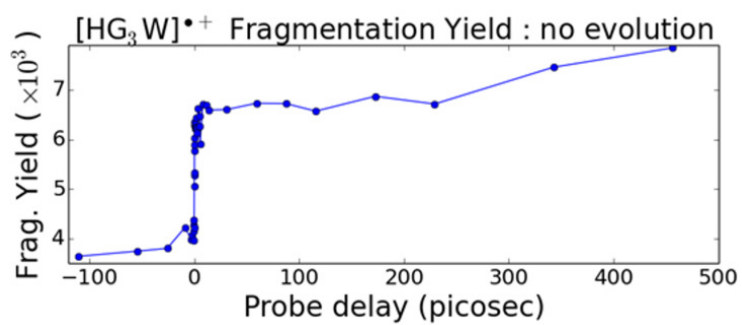


Figure S3. Evolution of radical peptide [HG<sub>3</sub>W]<sup>•+</sup> FY as a function of the pump-probe delay. Fragmentation yield of radical peptide exhibits a step-like behavior within the boundaries of the ultrafast experiment (<500 ps). Prior to pump, the peptide is not radical and does not absorb the probe laser. After pump and charge transfer, a radical is formed on tryptophan and displays higher absorption properties. FY is constant after radical formation, which indicates that the timescale is too short to observe proton transfer.

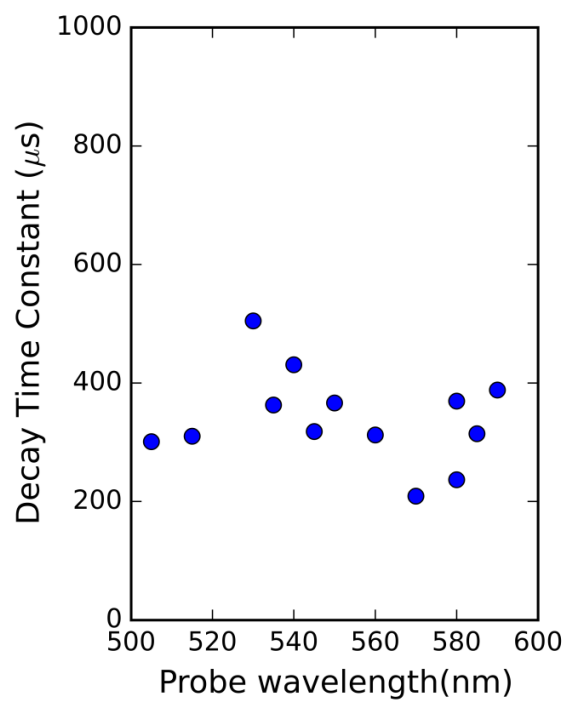


Figure S4. Time constant for proton transfer in  $[\text{HG}_3\text{W}]^{2+}$  evaluated at different probe wavelengths.

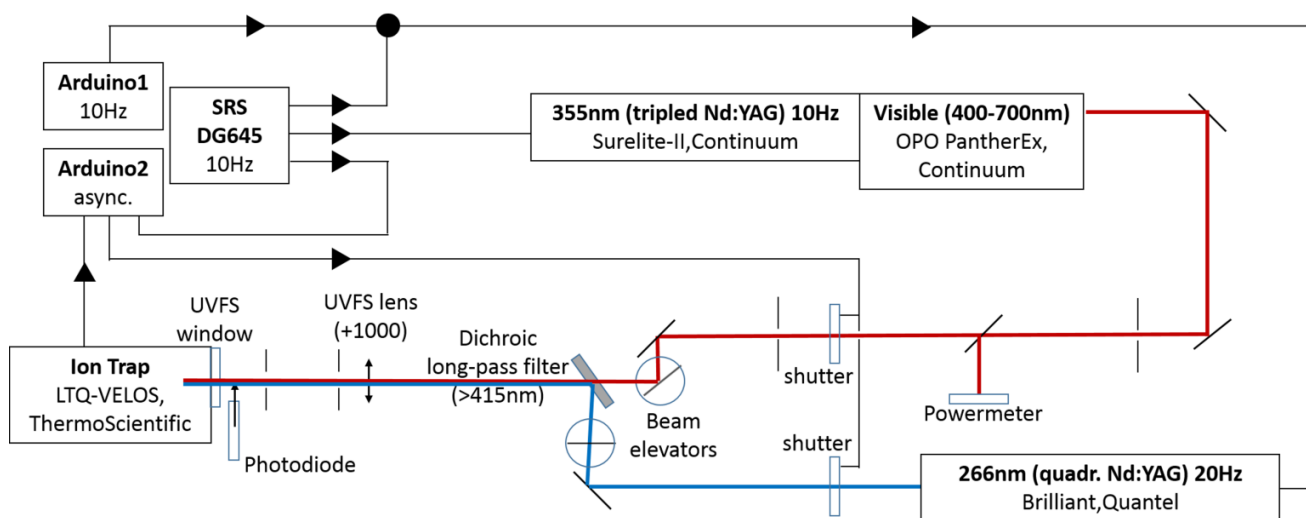


Figure S5. Setup for the nanosecond pump-probe delay experiments.



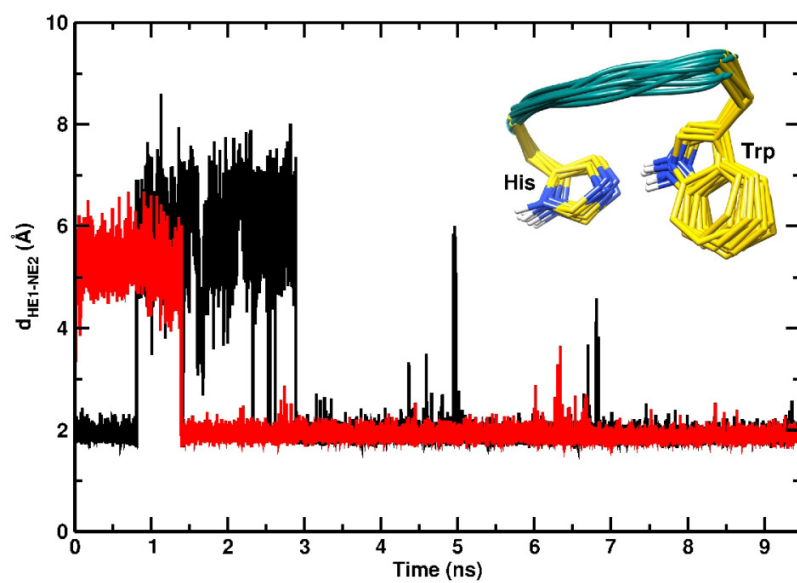


Figure S6 – Time history of the indoleNH-imidazoleN distance (HE1Trp—NE2His) distance in  $[\text{HG}_3\text{W}]^{**}$  for two 10 ns MD simulations starting from an extended peptide structure. The inset shows a superposition of instantaneous configurations.

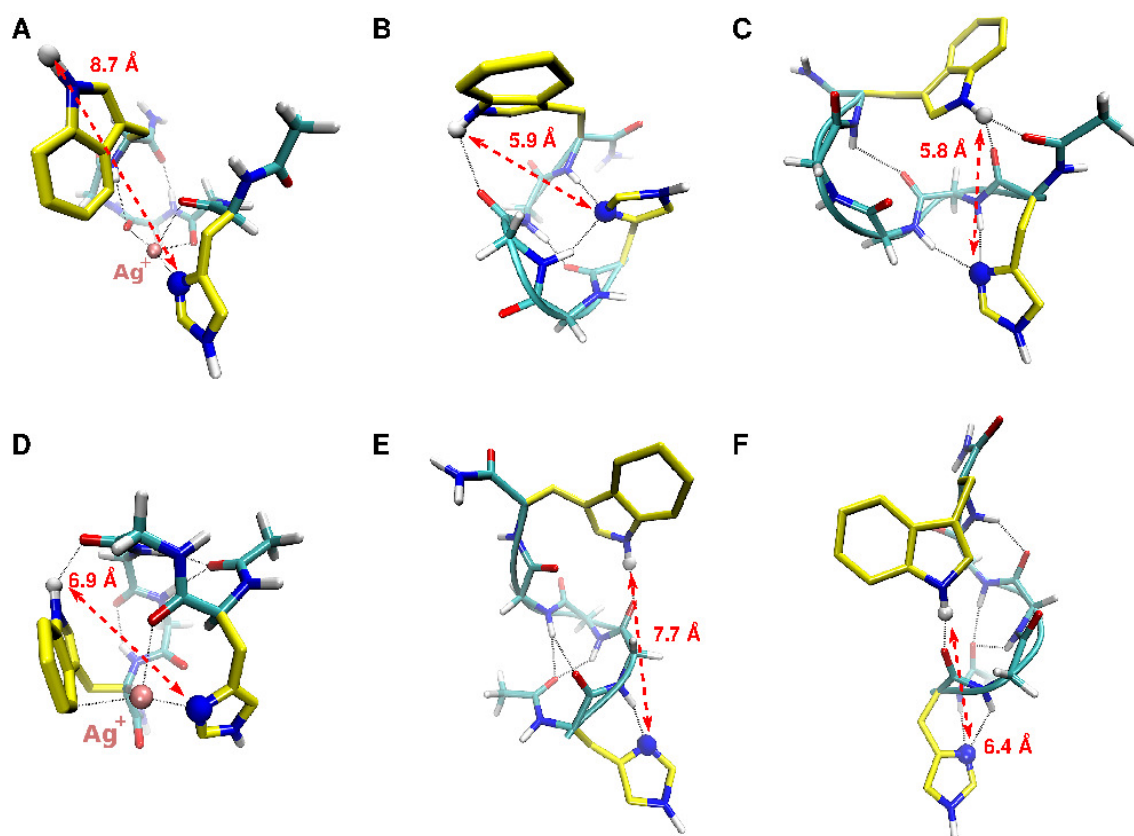


Figure S7 – Structures of HG<sub>3</sub>W peptide. (A, D) Lowest energy structures obtained for the [Ag+HG<sub>3</sub>W]<sup>+</sup> complex (ref33 in MS). Typical hindered structures at equilibrium obtained for HG<sub>3</sub>W<sup>++</sup> after silver has been removed from structure A (B, C) or from structure D (E, F). Dashed red lines indicate the indoleNH to imidazoleN distances. H atom on indoleN and N atom on imidazole are highlighted by vdW representations.

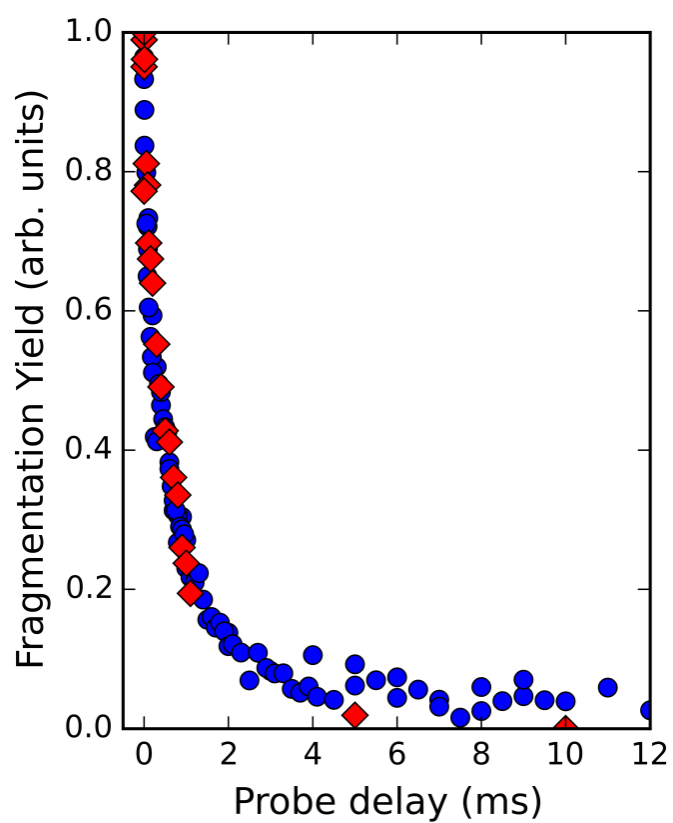


Figure S8. Evolution of  $[\text{HG}_3\text{W}]^{++}$  radical peptide fragmentation yield as a function of the pump-probe delay at probe wavelength 550 nm for the deuterated (blue circles) and the non-deuterated species (red diamond). No difference for the experimental decay rate was found for the deuterated species compared to the fully hydrogenated system which yields a primary kinetic isotope effect (KIE) close to 1.

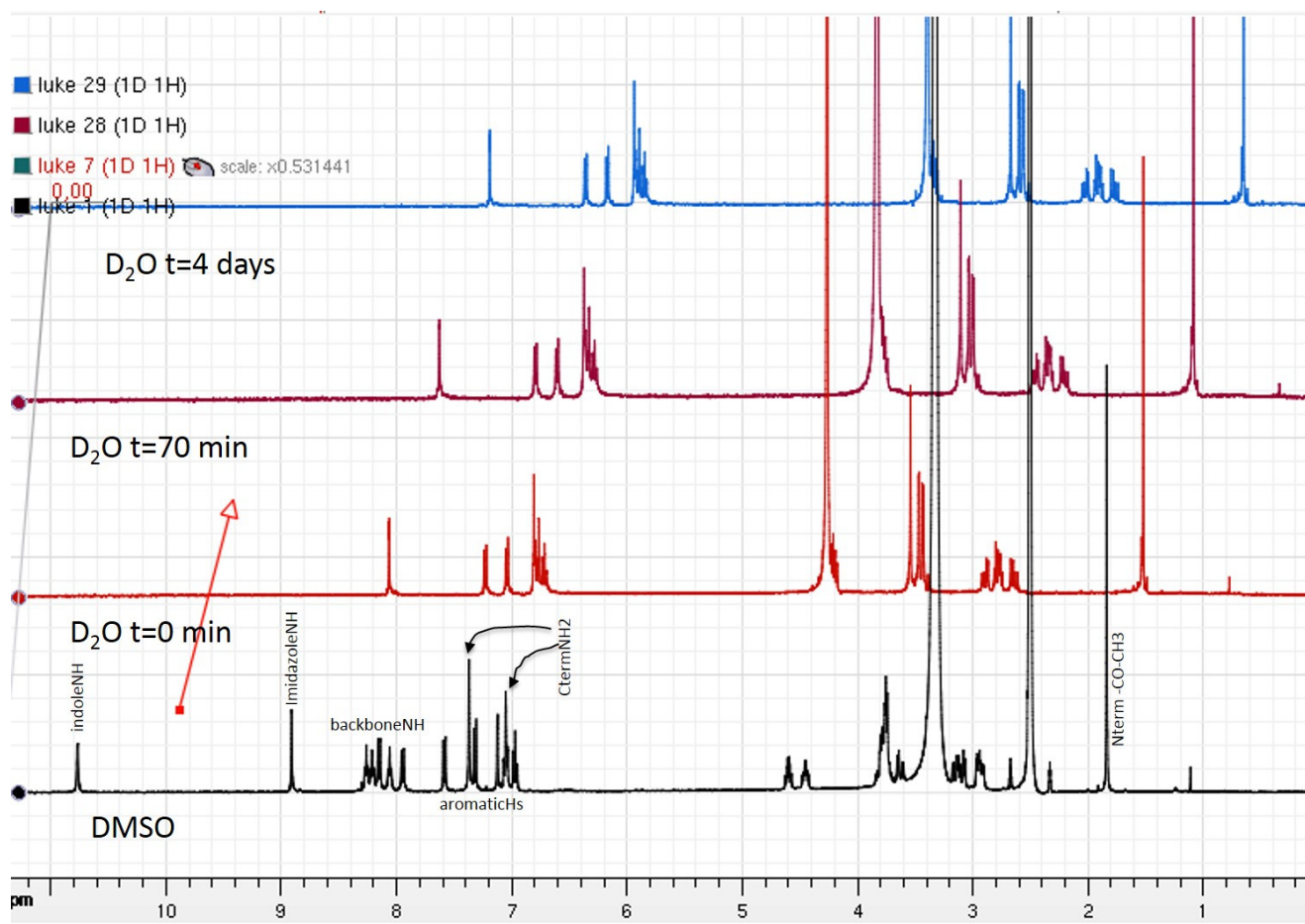


Figure S9. NMR <sup>1</sup>H spectra of HG<sub>3</sub>W in DMSO (black) and in D<sub>2</sub>O immediately after dissolution (red), and after 70 minutes (dark red) and 4 days (blue). The indoleNH is immediately exchanged with a deuterium together with all backbone NHs and the Cterm NH<sub>2</sub>.

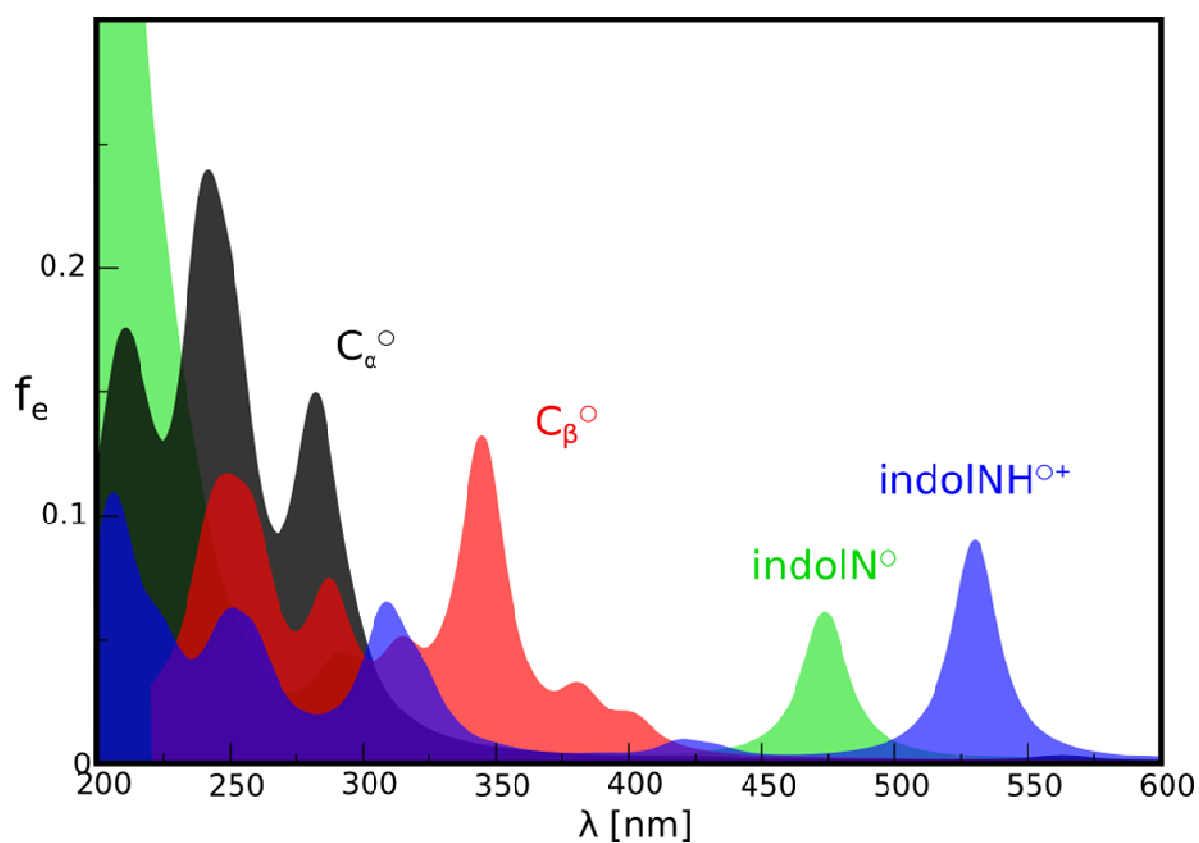


Figure S10. Absorption spectra  $f$  (oscillator strength  $f_e$ ) from TDDFT calculations for Ac-W-NH<sub>2</sub> model radicals representing the initial and potential final states of the HG<sub>3</sub>W<sup>+</sup> radical: indolNH<sup>+</sup> immediately after Ag release, and with protons translocated from C<sub>α</sub>, C<sub>β</sub> and indoleN (C<sub>α</sub><sup>o</sup>: black, C<sub>β</sub><sup>o</sup>: red, indolN<sup>o</sup>: green, respectively). Absorption lines are convoluted by Lorentzian functions with half-widths of 20 nm. Intense transitions are found in the visible range for indolNH<sup>+</sup> (490–530 nm) and indolN<sup>o</sup> (440–470 nm) which matches the steady-state spectra (Fig. 3 and ref 34 in MS). This shows that the structure after proton transfer contains an indole radical as opposed to a radical on a carbon sites (C<sub>α</sub> or C<sub>β</sub>).