Supplementary Material (ESI) for *PCCP*

Photodegradation Mechanism of the Common Non-Steroid Anti-Inflammatory Drug Diclofenac and its Carbazole Photoproduct

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Supporting Information

Table S1: Mulliken atomic charges (B3LYP/6-31G(d,p) level) for selected atoms in different intermediates of the photodegradation mechanism shown in Fig. 2. For atomic labeling see Fig. 1.

system	C_1	C_2	C_8	C_{10}	N_9	O_{19}	O_{20}	H_{18}	H_{21}	Cl_{16}
A (singlet)	0.586	-0.322	0.250	0.316	-0.699	-0.469	0.469	0.308	0.326	
$\mathbf{A}^{\bullet -}$(doublet)[a]	0.556		0.260	0.235	-0.651	-0.487	-0.486	0.286	0.303	-0.313
$\mathbf{A}^{\bullet +}$ (doublet)	0.614	-0.352	0.266	0.297	-0.615	-0.475	-0.438	0.355	0.355	
$^3\mathbf{A}$ (triplet)	0.592	-0.341	0.261	0.340	-0.647	-0.470	-0.464	0.322	0.331	-0.222
$\mathbf{A}^-$ (singlet)	0.555	-0.326	0.251	0.351	-0.739	-0.614	-0.571	0.388		
$^3\mathbf{A}^-$ (triplet)	0.566	-0.334	0.302	0.285	-0.660	-0.517	-0.493	0.381		-0.576
B (singlet)	0.584	-0.308	0.259	0.330	-0.721	-0.471	-0.469	0.291	0.328	
$\mathbf{B}^{\bullet -}$(doublet)	0.540	-0.276	0.246	0.327	-0.722	-0.517	-0.502	0.272	0.299	
$\mathbf{B}^{\bullet +}$ (doublet)	0.610	-0.340	0.254	0.336	-0.656	-0.482	-0.438	0.339	0.355	
$^3\mathbf{B}$ (triplet)	0.579	-0.300	0.283	0.359	-0.710	-0.475	-0.470	0.295	0.327	
$\mathbf{B}^-$ (singlet)	0.554	-0.322	0.203	0.340	-0.733	-0.617	-0.567	0.376		
$^3\mathbf{B}^-$ (triplet)	0.569	-0.333	0.241	0.331	-0.686	-0.555	-0.522	0.305		
^{3}**C** (triplet)	0.741	-0.322	0.212		-0.714	-0.375	-0.343	0.276		
C(singlet)	0.551	-0.318	0.200	0.306	-0.715	-0.624	-0.577	0.334		
D(singlet)	0.317	-0.271	0.212	0.315	-0.713	-0.621	-0.580	0.340		
$^1\mathbf{E}^{*-}$(singlet)		-0.457	0.121	0.349	-0.706			0.251		
$^3\mathbf{E}^{*-}$(triplet)		-0.343	0.195	0.339	-0.731			0.238		
E(singlet)		-0.394	0.251	0.337	-0.729			0.267		
F(singlet)[b]		-0.268	0.255	0.333	-0.735			0.274		
G (singlet)[c]			0.258	0.338	-0.739			0.265		

[a] the charge of "Cl_{17}" atom = -0.710
[b] the charge of "O" of -CHO group = -0.421
[c] the charge of "O" of –OH group = -0.543 and "H" = 0.313

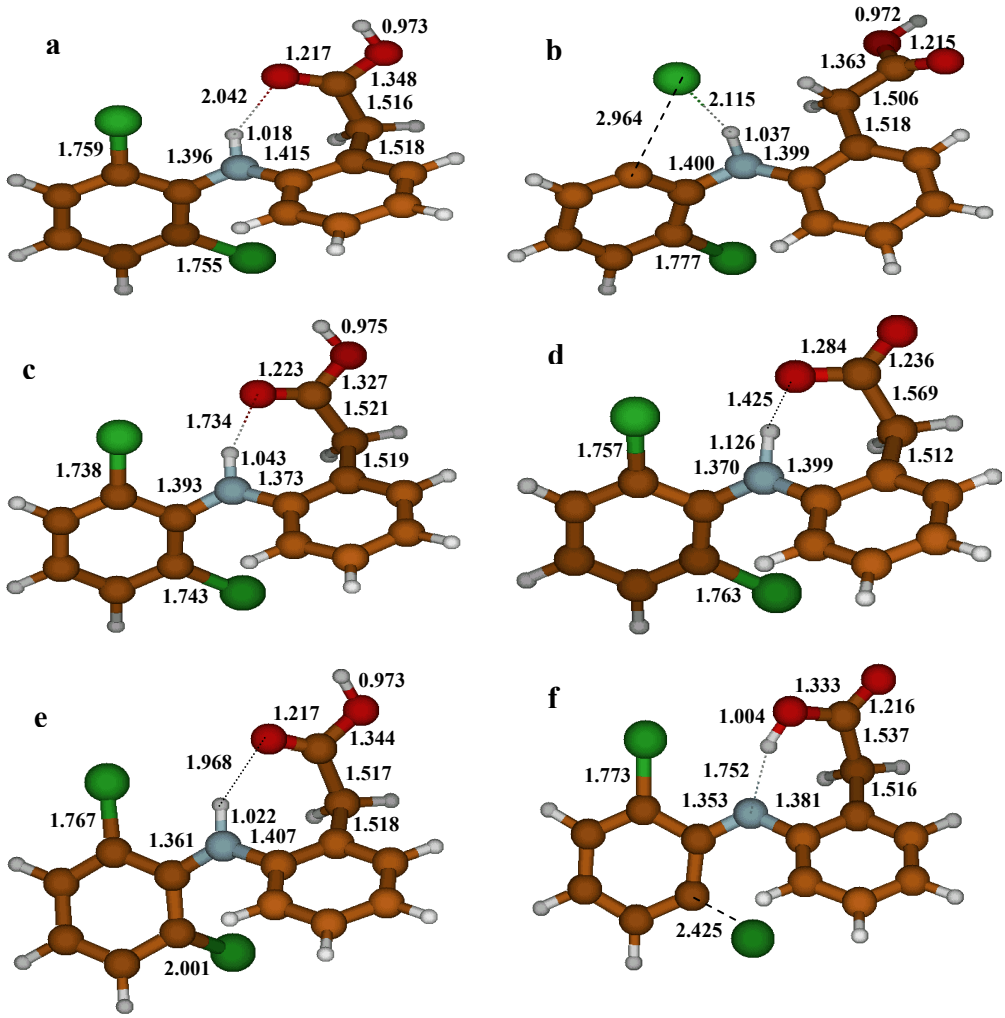

Figure S1. B3LYP/6-31G(d,p) optimized structures DF; (a) neutral ground state (**A**), (b) radical anion ($\mathbf{A}^{\bullet-}$), (c) radical cation ($\mathbf{A}^{\bullet+}$), (d) deprotonated acid ($\mathbf{A}^{-}$), (e) neutral triplet state ($^{3}\mathbf{A}$) and (f) deprotonated triplet state ($^{3}\mathbf{A}^{-}$).

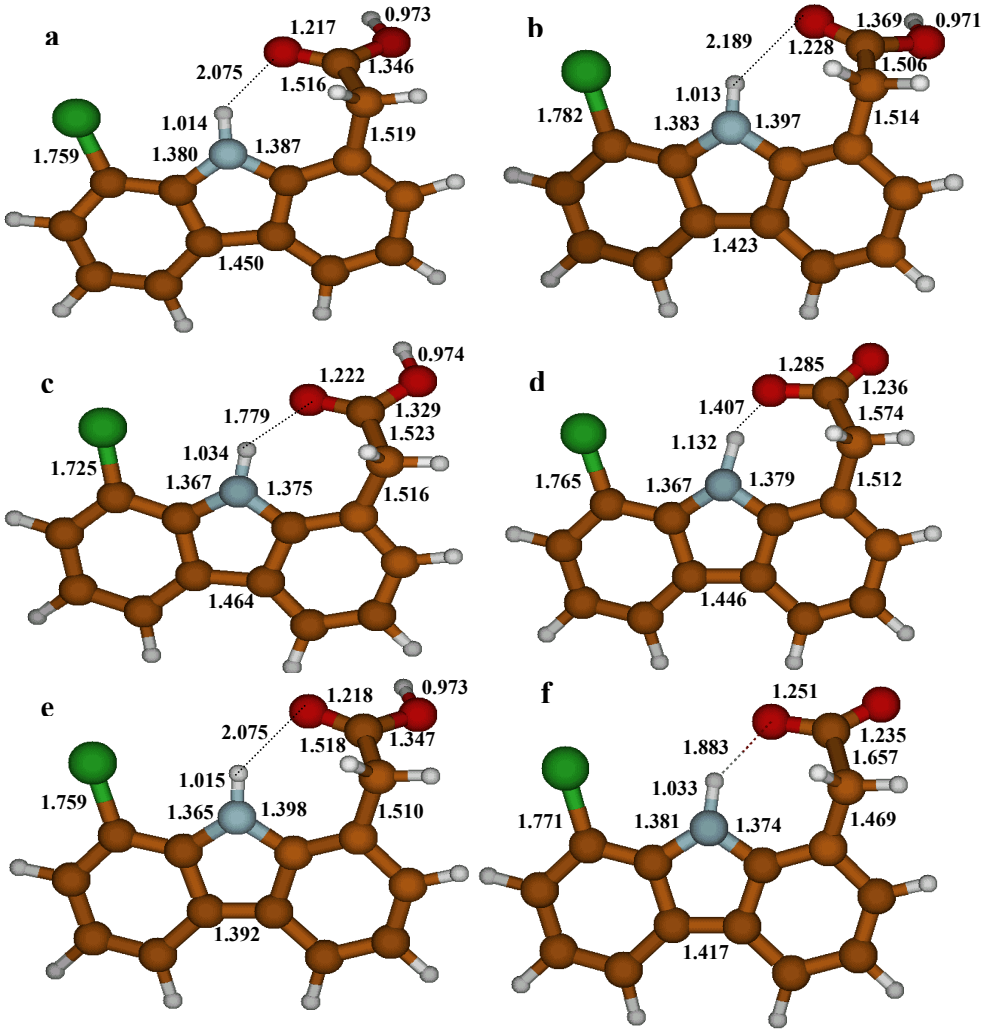

Figure S2. B3LYP/6-31G(d,p) optimized structures of CCA; (a) neutral ground state (**B**), (b) radical anion ($\mathbf{B}^{\bullet-}$), (c) radical cation ($\mathbf{B}^{\bullet+}$), (d) deprotonated acid ($\mathbf{B}^{-}$), (e) neutral triplet state ($^{3}\mathbf{B}$) and (f) deprotonated triplet state ($^{3}\mathbf{B}^{-}$).

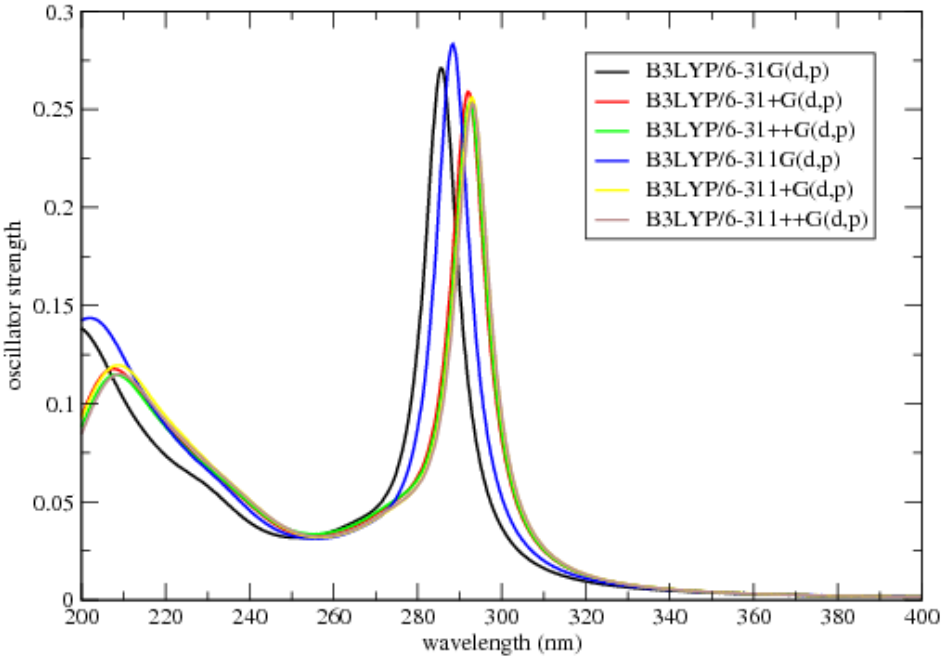

Figure S3. Absorption spectra of neutral Dichlofenac, computed with different basis sets, with and without diffuse functions, in the TD-DFT framework.