Supporting Information

Experimental study and quantum chemical calculation of free radical reactions in ciprofloxacin degradation during UV/chlorine oxidation process

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Supporting Tables

Table S1 The minima points for the ESP (surface electrostatic potential)

Number	a.u.	eV	Kcal/mol	**X/Y/Z coordinate(Angstrom)**		
1	-0.03933855	-1.070456	-24.685334	-6.464935	-0.495447	-1.640649
2	0.01858337	0.505679	11.661250	-5.775873	-1.030268	2.984008
3	0.02487289	0.676826	15.607989	-5.283681	3.352858	0.528981
4	-0.00887714	-0.241559	-5.570494	-2.758436	0.484231	1.950898
5	-0.02013389	-0.547871	-12.634220	-2.042388	-4.096568	-1.558495
6	0.00040833	0.011111	0.256231	-0.853350	-0.300517	2.049892
7	0.04426785	1.204590	27.778521	-0.954540	3.303702	0.935578
8	0.00534718	0.145504	3.355408	-0.578581	-0.006982	-1.926315
9	0.01083212	0.294757	6.797261	1.268424	4.858961	-1.912045
10	0.02192754	0.596679	13.759748	2.801367	3.524688	1.552337
11	-0.05341862	-1.453594	-33.520716	2.942127	-4.290243	-0.524275
12	-0.00434543	-0.118245	-2.726798	3.920273	0.261579	-1.795763
13	-0.08089184	-2.201179	-50.760437	7.421622	0.219604	0.386739

Table S2 The maxima points for the ESP (surface electrostatic potential)

Number	a.u.	eV	Kcal/mol	**X/Y/Z coordinate(Angstrom)**		
1	0.0599530	1.631407	37.621171	-7.696407	1.287014	0.935578
2	0.03038998	0.826953	19.070018	-6.971218	-2.153540	1.732115
3	0.03611646	0.982779	22.663439	-5.378990	3.337930	-1.578014
4	0.01501371	0.408544	9.421252	-5.048030	-2.747738	-1.247053
5	0.02791050	0.759483	17.514117	-3.534505	-2.655884	2.242741
6	0.05283103	1.437605	33.152001	-1.807043	2.694795	0.384606
7	0.05231153	1.423469	32.826005	-1.410161	4.661453	0.076599
8	0.00397413	0.108142	2.493805	-0.379206	-1.106734	1.683164
9	0.00610176	0.166037	3.828916	-0.203089	-0.419157	-1.820692
10	0.04317969	1.174979	27.095686	0.138939	2.332586	-2.833089
11	0.05184611	1.410805	32.533955	0.040231	3.667190	2.249090
12	0.05394388	1.467888	33.850325	0.309666	4.405711	1.143800
13	0.01952648	0.531342	12.253059	0.374313	-4.401641	-0.587306
14	0.04727929	1.286535	29.668224	1.629319	5.625803	1.182088
15	0.01793821	0.488123	11.256403	1.769642	0.100524	1.876268
16	0.01906005	0.518650	11.960373	1.873762	0.484970	-1.612831
17	0.03700032	1.006830	23.218073	2.030501	2.344713	-1.843325
18	0.03907204	1.063204	24.518094	3.476711	3.016425	-1.825935
19	0.00158502	0.043131	0.994616	3.883638	-1.615226	1.588356
20	0.03538103	0.962767	22.201950	3.890073	3.141564	0.673043
21	0.00206084	0.056078	1.293200	4.129317	-1.099396	-1.603366
22	0.00670996	0.182587	4.210567	4.939966	-3.416862	-0.328646

Table S3 The minima points for the ALIE (average local ionization energy)

Number	a.u.	eV	Kcal/mol	**X/Y/Z coordinate(Angstrom)**		
1	0.48599004	13.224461	304.963608	-7.003254	-2.260632	1.351728
2	0.49395472	13.441192	309.961529	-6.678605	1.520749	1.662295
3	0.33781143	9.192316	211.980048	-6.336166	-0.453118	-1.708323
4	0.49006044	13.335223	307.517824	-5.833765	3.050139	-1.723507
5	0.36983685	10.063773	232.076323	-3.026852	0.755136	1.888097
6	0.49463931	13.459820	310.391116	-2.920827	-2.470144	2.150175
7	0.59185051	16.105071	371.392116	-2.220439	-3.203110	-2.119888
8	0.59191134	16.106727	371.430288	-2.010024	-4.062635	0.634876
9	0.52559906	14.302278	329.818668	-1.500080	4.732171	-0.441555
10	0.39747102	10.815737	249.417043	-0.711405	0.207633	2.148944
11	0.39736497	10.812851	249.350492	-0.756540	0.807106	-1.934704
12	0.41128011	11.191501	258.082383	-0.407204	-2.448366	1.707623
13	0.41551961	11.306863	260.742708	-0.438518	-1.732422	-2.251276
14	0.51271341	13.951642	321.732795	0.203830	2.946749	2.669679
15	0.41566166	11.310729	260.831848	1.130862	-1.200119	1.942107
16	0.41490243	11.290069	260.355425	1.182228	-0.670942	-2.083634
17	0.48090136	13.085992	301.770413	1.164667	4.849871	-1.927820
18	0.44357848	12.070384	278.349935	2.095913	-3.668644	0.935578
19	0.44322869	12.060866	278.130437	2.190666	-3.265884	-1.765200
20	0.52646922	14.325956	330.364700	2.349426	5.823253	0.846858
21	0.50016539	13.610192	313.858786	2.831733	3.240669	1.561258
22	0.39297279	10.693334	246.594357	3.158900	-0.357088	2.192558
23	0.39436848	10.731312	247.470163	3.397659	0.191978	-1.897380
24	0.52983610	14.417573	332.477451	3.705900	3.462312	-1.704938
25	0.44083041	11.995606	276.625494	5.062152	1.321691	1.951851
26	0.44123831	12.006705	276.881453	5.181582	1.757571	-0.958510
27	0.45332671	12.335647	284.467044	6.007463	-2.155228	1.665802
28	0.45330960	12.335182	284.456307	6.130615	-1.644847	-1.647786
29	0.39871082	10.849473	250.195027	7.288456	-0.238361	0.302269

Table S4 The maxima points for the ALIE (average local ionization energy)

Number	a.u.	eV	Kcal/mol	X/Y/Z coordinate(Angstrom)		
1	0.61215194	16.657501	384.131462	-7.440958	-0.359414	0.812695
2	0.61359565	16.696787	385.037405	-6.938375	1.869109	-0.491512
3	0.54423999	14.809523	341.516034	-6.137685	-1.831851	-0.333076
4	0.55932506	15.220009	350.982070	-5.626673	1.428669	1.951881
5	0.54598507	14.857009	342.611088	-5.461904	1.177641	-2.084270
6	0.59585611	16.214069	373.905666	-5.038844	-2.844388	0.829743
7	0.59255878	16.124344	371.836558	-4.863348	-2.025111	2.306337
8	0.60260829	16.397805	378.142727	-3.907365	2.213326	-2.139793
9	0.59798156	16.271906	375.239411	-3.783978	3.067238	-0.634108
10	0.54215033	14.752661	340.204751	-3.188885	-0.885020	2.203310
11	0.67823793	18.455793	425.601086	-3.042765	-4.035968	-0.844460
12	0.61510155	16.737764	385.982376	-2.538663	-1.827152	-1.803845
13	0.54436627	14.812959	341.595277	-2.571896	2.255004	0.502885
14	0.53280387	14.498331	334.339756	-2.189717	0.533917	-2.239485
15	0.61280518	16.675277	384.541377	-2.080635	-2.258473	-2.089735
16	0.61136963	16.636214	383.640557	-1.824598	-3.316828	1.110387
17	0.56544107	15.386434	354.819924	-0.973943	3.663719	-2.035478
18	0.50969695	13.869559	319.839930	-0.219020	-1.095508	1.678852
19	0.50827350	13.830825	318.946705	-0.127850	-0.572318	-1.840108
20	0.64716352	17.610215	406.101579	0.404690	4.496872	1.099238
21	0.59057585	16.070386	370.592250	1.030017	1.508159	2.205604
22	0.55477173	15.096106	348.124809	1.704821	0.194365	1.913908
23	0.54976890	14.959972	344.985479	1.886966	0.595670	-1.619838
24	0.58444447	15.903543	366.744747	1.951320	2.398287	-1.921979
25	0.51562585	14.030893	323.560380	2.131488	-2.152638	1.612286
26	0.51475925	14.007312	323.016580	2.402929	-1.517625	-1.969891
27	0.56494049	15.372813	354.505808	3.119573	5.102359	-0.863624
28	0.54639868	14.868264	342.870637	3.696400	-4.110025	-0.464763
29	0.54555579	14.845328	342.341711	3.748194	2.450081	1.676427
30	0.54016853	14.698733	338.961154	4.019594	-1.829761	1.475785
31	0.54016853	14.698733	338.961156	4.170758	-1.360774	-1.553456
32	0.54650623	14.871191	342.938124	4.188115	2.699719	-0.450429
33	0.54621458	14.863255	342.755110	4.874036	-0.976507	1.905752
34	0.54594649	14.855959	342.586882	4.951261	-0.465577	-1.628261
35	0.63145673	17.182811	396.245410	5.201425	-3.379083	-0.290867
36	0.52391574	14.256472	328.762367	6.583473	2.004461	0.632065

Table S5 Hirshfeld charges, condensed Fukui functions and condensed dual descriptors of ciprofloxacin

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	Δf	Electro-philicity	Nucleo-philicity	s^-	s^+	s_0	s^+/s^-	s^-/s^+
F1	-0.08	-0.1095	-0.0614	0.0187	0.0295	0.0241	0.0108	0.03712	0.03274	0.0700	0.1107	0.0904	1.5811	0.6325
O2	-0.3018	-0.4018	-0.2596	0.0422	0.1	0.0711	0.0578	0.12587	0.07405	0.1584	0.3755	0.267	2.3704	0.4219
O3	-0.139	-0.1589	-0.127	0.012	0.0199	0.016	0.0079	0.02511	0.02106	0.0451	0.0749	0.06	1.6624	0.6015
O4	-0.3366	-0.3772	-0.3103	0.0263	0.0407	0.0335	0.0143	0.05118	0.0462	0.0988	0.1527	0.1258	1.5448	0.6473
N5	0.0013	-0.0226	0.0047	0.0034	0.024	0.0137	0.0206	0.03018	0.00599	0.0128	0.09	0.0514	7.0253	0.1423
N6	-0.0849	-0.0923	0.1083	0.1932	0.0074	0.1003	-0.1857	0.00934	0.33906	0.7253	0.0279	0.3766	0.0384	26.0287
N7	-0.1686	-0.1732	-0.1463	0.0223	0.0046	0.0135	-0.0178	0.00576	0.0392	0.0839	0.0172	0.0505	0.2049	4.8814
C8	0.0193	0.0196	0.0162	-0.0031	-0.0003	-0.0017	0.0028	-0.00037	-0.00548	-0.0117	-0.0011	-0.0064	0.0953	10.4948
C9	-0.0715	-0.0818	-0.0731	-0.0016	0.0103	0.0043	0.0119	0.01295	-0.00279	-0.006	0.0386	0.0163	-6.472	-0.1545
C10	-0.0574	-0.0746	-0.0432	0.0142	0.0173	0.0157	0.0031	0.02175	0.02487	0.0532	0.0649	0.059	1.2197	0.8198
C11	0.0471	0.0296	0.0669	0.0198	0.0175	0.0187	-0.0023	0.02208	0.03476	0.0744	0.0659	0.0701	0.8857	1.129
C12	0.0661	-0.0073	0.079	0.0129	0.0734	0.0432	0.0605	0.0924	0.02266	0.0485	0.2756	0.1621	5.6856	0.1759
C13	-0.0217	-0.042	0.0141	0.0358	0.0203	0.028	-0.0155	0.02553	0.06281	0.1344	0.0762	0.1053	0.5668	1.7643
C14	-0.0559	-0.1144	-0.0369	0.019	0.0585	0.0387	0.0395	0.07361	0.03327	0.0712	0.2196	0.1454	3.0857	0.3241
C15	0.0454	-0.0199	0.0348	-0.0106	0.0653	0.0274	0.0759	0.08224	-0.01857	-0.0397	0.2453	0.1028	-6.1765	-0.1619
C16	-0.0041	-0.0095	0.0252	0.0293	0.0054	0.0173	-0.0239	0.00674	0.05143	0.11	0.0201	0.0651	0.1828	5.4704
C17	-0.005	-0.01	0.0254	0.0304	0.0051	0.0177	-0.0253	0.00637	0.05334	0.1141	0.019	0.0665	0.1664	6.0082
C18	-0.0565	-0.0776	-0.0426	0.0139	0.0211	0.0175	0.0073	0.02662	0.02432	0.052	0.0794	0.0657	1.5264	0.6551
C19	0.1028	0.0297	0.1131	0.0103	0.0731	0.0417	0.0627	0.09197	0.01813	0.0388	0.2744	0.1566	7.0744	0.1414
C20	-0.0053	-0.0127	0.0072	0.0125	0.0074	0.01	-0.005	0.00937	0.02188	0.0468	0.0279	0.0374	0.5969	1.6753
C21	-0.0034	-0.0109	0.0092	0.0127	0.0075	0.0101	-0.0052	0.00944	0.02223	0.0475	0.0282	0.0379	0.5924	1.6881
C22	-0.0348	-0.1083	-0.0076	0.0272	0.0735	0.0503	0.0463	0.09251	0.04773	0.1021	0.276	0.189	2.7026	0.37
C23	0.0934	0.0612	0.1142	0.0208	0.0322	0.0265	0.0114	0.04052	0.03658	0.0783	0.1209	0.0996	1.5447	0.6474
C24	0.1889	0.1808	0.1936	0.0047	0.0081	0.0064	0.0034	0.01014	0.00825	0.0176	0.0302	0.0239	1.7139	0.5835

H25	0.0474	0.0297	0.0509	0.0034	0.0177	0.0106	0.0143	0.02231	0.00602	0.0129	0.0665	0.0397	5.1699	0.1934
H26	0.0474	0.0285	0.0508	0.0034	0.0189	0.0112	0.0155	0.02379	0.00604	0.0129	0.071	0.042	5.4904	0.1821
H27	0.05	0.0452	0.05	0	0.0048	0.0024	0.0047	0.00601	0.00006	0.0001	0.0179	0.009	138.2767	0.0072
H28	0.0557	0.0344	0.0685	0.0128	0.0212	0.017	0.0084	0.02673	0.02252	0.0482	0.0797	0.0639	1.6553	0.6041
H29	0.0521	0.0422	0.0607	0.0086	0.0099	0.0093	0.0013	0.0125	0.01516	0.0324	0.0373	0.0349	1.1497	0.8698
H30	0.0593	0.024	0.0708	0.0114	0.0354	0.0234	0.0239	0.04451	0.02008	0.043	0.1328	0.0879	3.0907	0.3235
H31	0.0388	0.0084	0.05	0.0111	0.0305	0.0208	0.0194	0.03837	0.01953	0.0418	0.1145	0.0781	2.7398	0.365
H32	0.0184	0.0095	0.0788	0.0604	0.0089	0.0346	-0.0515	0.01118	0.10601	0.2268	0.0334	0.1301	0.1471	6.7969
H33	0.0207	0.0146	0.0723	0.0516	0.0061	0.0289	-0.0456	0.00764	0.09064	0.1939	0.0228	0.1083	0.1175	8.5092
H34	0.0224	0.0135	0.078	0.0556	0.0089	0.0323	-0.0466	0.01127	0.09757	0.2087	0.0336	0.1212	0.161	6.2112
H35	0.0184	0.01	0.0768	0.0584	0.0084	0.0334	-0.0501	0.01053	0.10259	0.2195	0.0314	0.1254	0.1431	6.9871
H36	0.0428	0.0301	0.0689	0.0262	0.0127	0.0194	-0.0135	0.01599	0.04594	0.0983	0.0477	0.073	0.4853	2.0606
H37	0.0128	0.0033	0.0378	0.025	0.0095	0.0172	-0.0154	0.01197	0.04381	0.0937	0.0357	0.0647	0.3811	2.6241
H38	0.0431	0.0303	0.0689	0.0258	0.0128	0.0193	-0.013	0.01606	0.04523	0.0967	0.0479	0.0723	0.4951	2.02
H39	0.0137	0.0036	0.0396	0.026	0.01	0.018	-0.016	0.01262	0.0456	0.0976	0.0376	0.0676	0.3858	2.5917
H40	0.0531	0.0165	0.0736	0.0205	0.0366	0.0286	0.0161	0.04613	0.03605	0.0771	0.1376	0.1074	1.7843	0.5605
H41	0.1012	0.0872	0.1294	0.0282	0.014	0.0211	-0.0143	0.0176	0.04958	0.1061	0.0525	0.0793	0.4951	2.02
H42	0.1657	0.1547	0.1708	0.0051	0.011	0.008	0.0059	0.01385	0.00893	0.0191	0.0413	0.0302	2.1625	0.4624

Note:

q(N): Hirshfeld charges in neutral state

q(N+1): Hirshfeld charges in a positive charge state

q(N-1): Hirshfeld charges in a negative charge state

f^-: Electrophilic Fukui function

f^+: Nucleophilic Fukui function

f^0: Radical Fukui function

Δf: Condensed dual descriptors

Electrophilicity: Reduced local electrophilic index
Nucleophilicity: Reduced local nucleophilic index
s^-: Reduced local softness
s^+: Relative electrophilic index
s_0: Relative nucleophilic index
E(N): -1147.880740 a.u.
E(N+1): -1147.904551 a.u.
E(N-1): -1147.590626 a.u.
E_HOMO(N): -0.270690 a.u.
E_HOMO(N+1): 0.000470 a.u.
E_HOMO(N-1): -0.392805 a.u.
Vertical IP: 0.290115 a.u.
Vertical EA: 0.023811 a.u.
Mulliken electronegativity: 0.156963 a.u.
Chemical potential: -0.156963 a.u.
Hardness (=fundamental gap): 0.266304 a.u.
Softness: 3.755114 $a.u.^{-1}$
Electrophilicity index: 0.046258 a.u.
Nucleophilicity index: 0.064508 a.u.

Table S6 Acute and chronic toxicity ($LC_{50,}$ $EC_{50,}$ ChV) of ciprofloxacin and its intermediates predicted by ECOSAR software

Compound	Acute Toxicity (mg·L^{-1})			Chronic Toxicity (mg·L^{-1})		
	Fish (96 h) LC_{50}	Daphnid (48 h) LC_{50}	Green Algae (96 h) EC_{50}	Fish	Daphnid	Green Algae
CIP	13100	1240	1620	1550	81.3	455
Pr364	818000	56600	137000	249000	2740	30700
Pr360	61500	6710	4830	4470	431	4950
Pr362	237000	330000	121000	194000	30500	14400
Pr344	5860	1230	485	493	102	705
Pr330	36500	3190	4880	36400	3190	4880
Pr334	68100	77100	32400	42100	8200	5070
Pr316	91600	110000	44500	61600	11300	6410
Pr307	51600	56400	24200	30400	6150	3970
Pr306	47300	4020	6470	7700	238	1680
Pr291	10300	8570	4390	4180	1130	1050
Pr288	60200	5010	8430	10500	290	2160
Pr279	217	6.28	20.6	3.76	0.068	9.69
Pr263	899	42.8	128	12.4	0.488	47.9
Pr261	4560	80.8	290	98.3	0.829	171
Pr248	1940	1230	748	545	194	256
Pr245	1130	44.9	139	16.9	0.502	56.4
Pr348	141000	11100	20800	28800	614	5120
Pr346	17400	15500	7630	7740	1950	1670

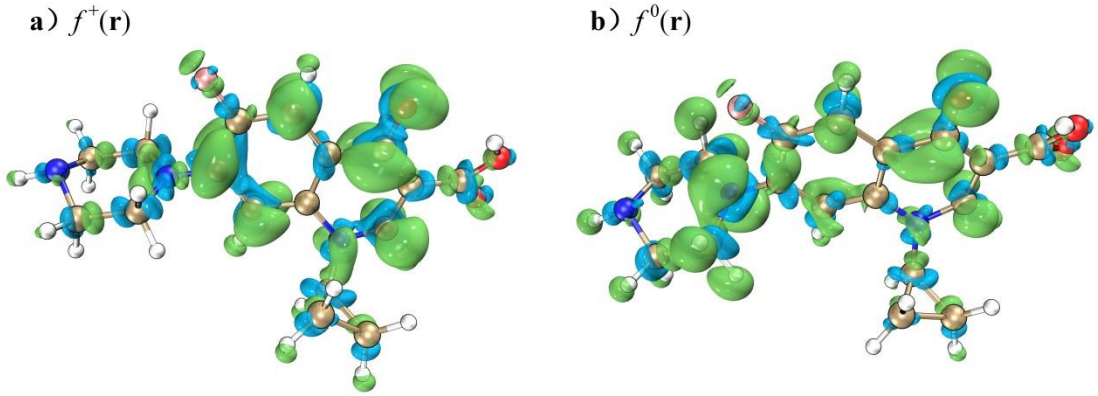

Fig. S1 Visualization of the nucleophilic Fukui function f^{+}(r) and radical Fukui function f^{0}(r) for the ciprofloxacin molecule

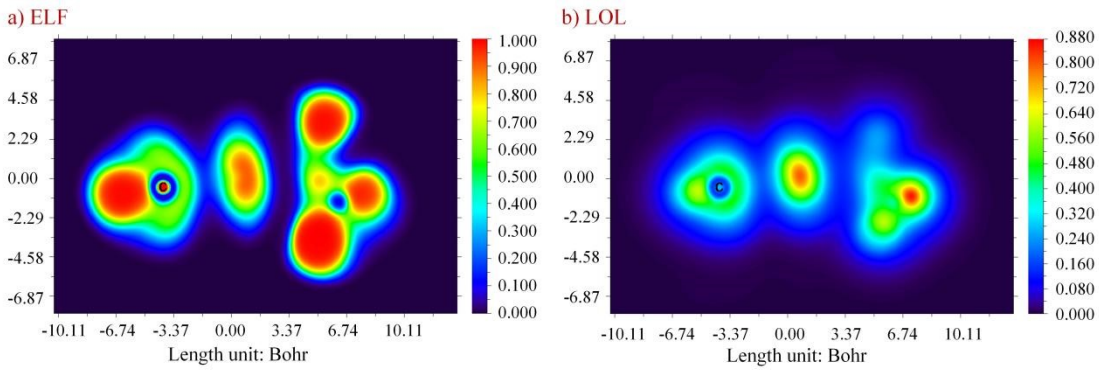

Fig.S2 Graphical representation of ELF and LOL of ciprofloxacin molec