Supplementary Material (ESI) for *PCCP*

SUPPORTING INFORMATION
for

Characterization of radical intermediates in laccase-mediator systems. A multifrequency EPR, ENDOR and DFT/PCM investigation

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Table 1S DFT/PCM computed g- and hf- tensor principal components for VIO neutral and cation radicals

VIO radical	g_i	A_i (N7)	A_i (H1)	A_i(H3)	A_i (N3)	A_i (N1)	A_i (H7)
		mT	*mT*	*mT*	*mT*	*mT*	*mT*
DFT							
Neutral radical							
Vacuo							
*uB3LYP/6-31G**							
x	2.0064	2.619	-0.030	0.129	0.256	-0.022	
y	2.0028	2.469	-0.030	0.164	0.267	-0.014	
z	2.0019	4.346	0.035	0.263	0.341	-0.007	
uB3LYP/EPRII							
x	2.0065	2.614	-0.030	0.132	0.310	-0.018	
y	2.0034	2.445	-0.031	0.166	0.319	-0.009	
z	2.0019	4.390	0.035	0.264	0.394	-0.003	
uB3LYP/TZVP							
x	2.0067	2.561	-0.029	0.114	0.308	-0.020	
y	2.0028	2.397	-0.030	0.148	0.316	-0.010	
z	2.0018	4.453	0.036	0.245	0.394	-0.003	
*PBE0/6-31G**							
x	2.0064	2.618	-0.030	0.134	0.246	-0.023	
y	2.0026	2.437	-0.030	0.166	0.526	-0.015	
z	2.0018	4.311	0.034	0.262	3.238	-0.008	
PBE0/EPRII							
x	2.0065	2.603	-0.029	0.135	0.296	-0.020	
y	2.0027	2.405	-0.030	0.167	0.304	-0.011	
z	2.0018	4.347	0.034	0.261	0.377	-0.005	
PBE0/TZVP							
x	2.0067	2.558	-0.030	0.120	0.295	-0.020	
y	2.0026	2.363	-0.030	0.152	0.302	-0.011	
z	2.0018	4.395	0.034	0.245	0.377	-0.005	
PCM							
*uB3LYP/631G**							
x	2.0064	2.612	-0.028	0.129	0.236	-0.024	
y	2.0032	2.445	-0.028	0.166	0.246	-0.014	
z	2.0020	4.345	0.037	0.262	0.324	-0.007	
uB3LYP/EPRII							
x	2.0065	2.614	-0.028	0.134	0.286	-0.020	
y	2.0034	2.430	-0.029	0.171	0.297	-0.009	
z	2.0020	4.402	0.037	0.266	0.376	-0.003	
uB3LYP/TZVP							
x	2.0067	2.568	-0.028	0.134	0.283	-0.021	
y	2.0033	2.382	-0.029	0.171	0.293	-0.009	
z	2.0019	4.469	0.037	0.266	0.375	-0.003	

uB3LYP/mixed basis set[a]							
x	2.0064	2.503	-0.029	0.139	0.232	-0.023	
y	2.0032	2.336	-0.030	0.177	0.241	-0.013	
z	2.0020	4.233	0.036	0.272	0.320	-0.006	
*PBE0/6-31G**							
x	2.0064	2.617	-0.028	0.132	0.224	-0.025	
y	2.0029	2.417	-0.028	0.168	0.233	-0.014	
z	2.0020	4.315	0.036	0.261	0.308	-0.008	
PBE0/EPRII							
x	2.0065	2.614	-0.028	0.135	0.273	-0.022	
y	2.0031	2.394	-0.028	0.172	0.283	-0.011	
z	2.0020	4.364	0.036	0.262	0.360	-0.004	
PBE0/TZVP							
x	2.0066	2.569	-0.028	0.121	0.281	-0.022	
y	2.0029	2.350	-0.028	0.158	0.336	-0.011	
z	2.0020	4.413	0.036	0.248	0.359	-0.005	
*QCISD/6-31G**							
x	—	2.721	-0.019	0.111	0.177	-0.033	
y	—	2.353	-0.017	0.137	0.194	-0.013	
z	—	4.180	0.038	0.217	0.254	-0.007	
Explicit water molecules[b] *uB3LYP/6-31G**							
x	2.0060	3.105	-0.028	0.116	0.167	-0.018	
y	2.0022	2.962	-0.027	0.151	0.180	-0.012	
z	2.0015	5.026	0.040	0.238	0.252	-0.005	
*Explicit water molecules +PCM uB3LYP/6-31G**							
x	2.0060	3.055	-0.028	0.113	0.176	-0.019	
y	2.0022	2.905	-0.027	0.150	0.187	-0.012	
z	2.0016	4.970	0.040	0.239	0.261	-0.006	
Radical cation *uB3LYP/6-31G**							
x	2.0037	1.095	-0.003	0.088	0.102	-0.154	0.855
y	2.0103	1.042	-0.109	-0.133	0.055	-0.133	0.722
z	2.0091	1.785	0.044	0.259	0.427	-0.031	1.703

PCM							
*uB3LYP/6-31G**							
x	2.0096	1.004	-0.001	0.080	-0.028	-0.165	0.728
y	2.0090	0.962	-0.119	-0.144	0.017	-0.143	0.599
z	2.0038	1.641	0.045	0.244	0.337	-0.030	1.538

[a]EPRII on H1 and H3, 6-31G* on the others
[b]See Figure 1S below

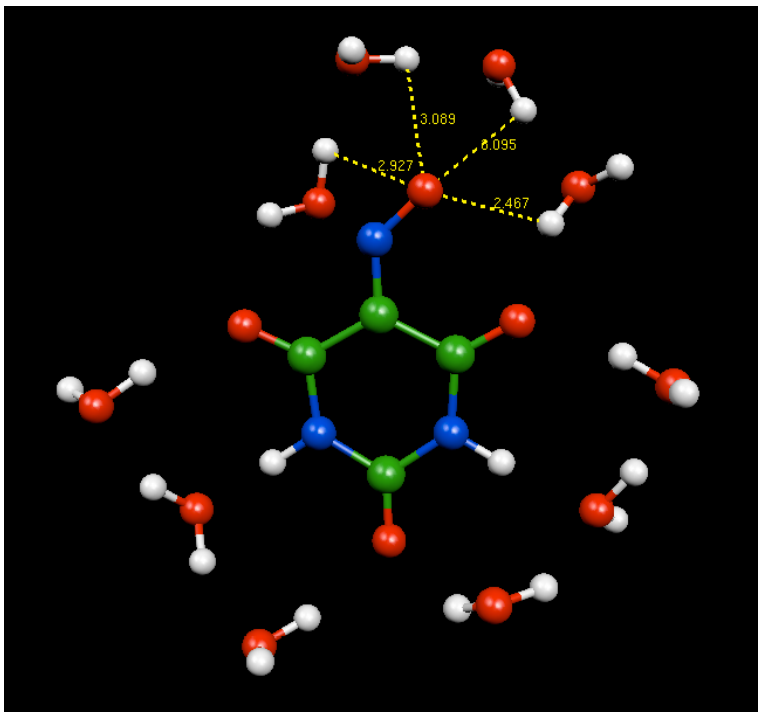

Figure 1S Molecular representation of a small cluster consisting of the VIO neutral radical in the presence of 10 water molecules optimized at the DFT level via explicit solvent molecules.

Table 2S DFT/PCM computed g- and hf- tensor principal components for ABTS cation radical

ABTS radical	**g_i**[a]	**A_i (N2,2')**	**A_i(N3,3')**	**A_i(H4,4')**	**A_i(H5,5')**	**A_i(H7,7')**	**A_i (Ha 10,10')**[h]	**A_i (Hb 10,10')**[h]
		mT	*mT*	*mT*	*mT*	*mT*	*mT*	*mT*
DFT *Trans- radical cation*[c]								
Vacuo								
*uB3LYP/6-31G**								
iso	2.0072	0.338	0.295	-0.052	-0.051	0.060	0.190	0.115
x	2.0118	0.971	0.743	0.001	0.008	0.104	0.265	0.200
y	2.0059	0.027	0.075	-0.070	-0.078	0.047	0.163	0.103
z	2.0039	0.017	0.068	-0.087	-0.084	0.030	0.140	0.042
uB3LYP/EPRII[d]								
iso	2.0054	0.254	0.262	-0.055	-0.044	-0.058	0.202	0.119
x	2.0062	0.945	0.742	-0.001	0.015	0.014	0.279	0.208
y	2.0061	-0.086	0.025	-0.075	-0.070	0.044	0.176	0.105
z	2.0041	-0.096	0.018	-0.089	-0.077	0.027	0.151	0.045
uB3LYP/TZVP								
iso	2.0056	0.231	0.237	-0.051	-0.042	0.057	0.189	0.110
x	2.0062	0.950	0.726	0.002	-0.016	0.102	0.266	0.198
y	2.0064	-0.123	-0.004	-0.070	-0.068	0.043	0.162	0.096
z	2.0041	-0.134	-0.011	-0.084	-0.074	0.024	0.138	0.035
*PBE0/6-31G**								
iso	2.0052	0.379	0.336	-0.066	-0.039	0.085	0.201	0.122
x	2.0061	1.053	0.805	-0.011	0.015	0.136	0.279	0.212
y	2.0056	0.047	0.105	-0.088	-0.064	0.064	0.174	0.109
z	2.0039	0.036	0.097	-0.100	-0.067	0.054	0.150	0.046
PBE0/EPRII[d]								
iso	2.0048	0.267	0.299	-0.067	-0.032	0.079	0.209	0.124
x	2.0062	0.997	0.800	-0.010	-0.022	0.132	0.287	0.217
y	2.0041	-0.092	0.052	-0.091	-0.057	0.057	0.182	0.108
z	2.0042	-0.104	0.045	-0.100	-0.060	0.047	0.157	0.047

PBE0/TZVP								
iso	2.0049	0.243	0.272	-0.063	-0.030	0.078	0.198	0.116
x	2.0065	0.995	0.778	-0.008	-0.022	0.131	0.277	0.209
y	2.0041	-0.127	0.023	-0.086	-0.055	0.058	0.170	0.101
z	2.0042	-0.139	0.015	-0.096	-0.057	0.045	0.146	0.049
PCM								
*uB3LYP/6-31G**								
iso	2.0042	0.392	0.318	-0.087	0.007	0.054	0.222	0.122
x	2.0066	1.137	0.800	-0.028	0.035	0.099	0.307	0.225
y	2.0038	0.026	0.081	-0.115	0.001	0.038	0.192	0.103
z	2.0022	0.013	0.073	-0.119	-0.015	0.024	0.168	0.038
uB3LYP/EPRII[d]								
iso	2.0043	0.285	0.274	-0.086	0.008	0.048	0.233	0.125
x	2.0068	1.081	0.779	-0.026	0.036	0.093	0.317	0.229
y	2.0039	-0.106	0.025	-0.114	0.003	0.033	0.204	0.104
z	2.0022	-0.119	0.017	-0.117	-0.014	0.018	0.179	0.041
uB3LYP/TZVP								
iso	2.0044	0.259	0.247	-0.080	0.008	0.046	0.217	0.113
x	2.0074	1.086	-0.761	-0.023	0.035	0.091	0.302	0.217
y	2.0040	-0.148	-0.006	-0.107	0.003	0.031	0.187	0.093
z	2.0022	-0.162	-0.014	-0.111	-0.014	0.015	0.163	0.030
*PBE0/6-31G**								
iso	2.0042	0.424	0.352	-0.106	0.024	0.073	0.228	0.127
x	2.0067	1.192	0.845	-0.044	0.047	0.052	0.313	0.232
y	2.0038	0.032	0.109	-0.135	0.023	0.043	0.198	0.107
z	2.0022	-0.047	0.100	-0.138	0.002	0.073	0.173	0.042
PBE0/EPRII[d]								
iso	2.0043	0.290	0.306	-0.100	0.023	0.064	0.235	0.127
x	2.0069	1.111	0.823	-0.038	0.046	0.115	0.319	0.235
y	2.0039	-0.112	0.051	-0.129	0.022	0.044	0.207	0.105
z	2.0022	-0.127	0.043	-0.134	0.001	0.034	0.180	0.043
PBE0/TZVP								
iso	2.0045	0.264	0.278	-0.097	0.023	0.064	0.223	0.118

x	2.0072	1.107	0.800	-0.037	0.046	0.114	0.308	0.225
y	2.0040	-0.150	0.021	-0.124	0.023	0.044	0.193	0.096
z	2.0022	-0.166	0.012	-0.129	0.001	0.032	0.168	0.033

DFT
Cis- radical cation[c]

PCM

*uB3LYP/6-31G**		**A_i (N2)**					
iso	2.0047	0.402	0.309	-0.085	0.006	0.051	0.217	0.117
x	2.0069	1.152	0.779	-0.027	0.034	0.095	0.300	0.218
			0.078	-0.111	0.000	0.035	0.188	0.099
			0.070	-0.116	-0.015	0.022	0.163	0.035
y	2.0051	0.035	0.284	-0.054	-0.027	0.029	0.202	0.109
z	2.0022	0.020	0.693	-0.004	0.016	0.072	0.306	0.183
			0.083	-0.072	-0.047	0.016	0.205	0.091
			0.076	-0.087	-0.049	0.000	0.095	0.053
		Ai (N2')						
iso		0.413						
x		1.148						
y		0.052						
z		0.038						

[c]See Figure 2S below
[d]EPRII basis set on C,H,N,O mixed with the 6-31G* on S

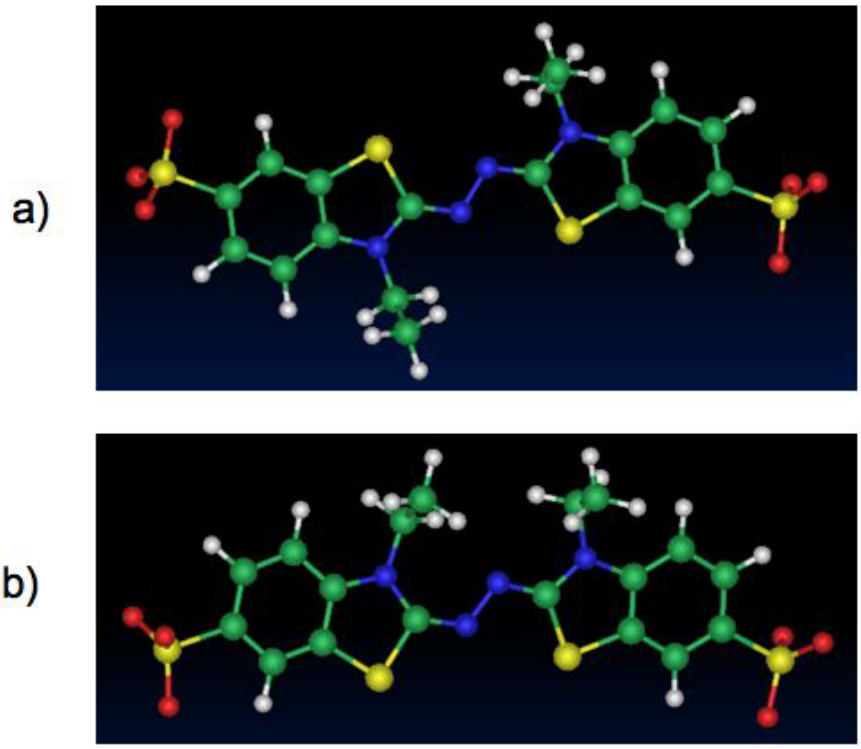

Figure 2S Molecular structure of (a) trans- and (b) cis- ABTS radical cation optimized at the DFT level.