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Supporting Information

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Phenoxyl Radicals Hydrogen-Bonded to Imidazolium - Analogues of Tyrosyl D$^{\bullet}$ of Photosystem II: High-Field EPR and DFT Studies**

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Figure SI1. W-band EPR spectra of $[^{PhOMe}LH]^{\bullet+}$ (top) and $[^{Ph}LH]^{\bullet+}$ (bottom). In each case, the experimental spectrum was measured for the electrochemically generated $[^{R}LH]^{\bullet+}$ (1 mM) in CH_2Cl_2 at 80 K and the simulated spectrum was obtained using the parameters shown in Table 1.

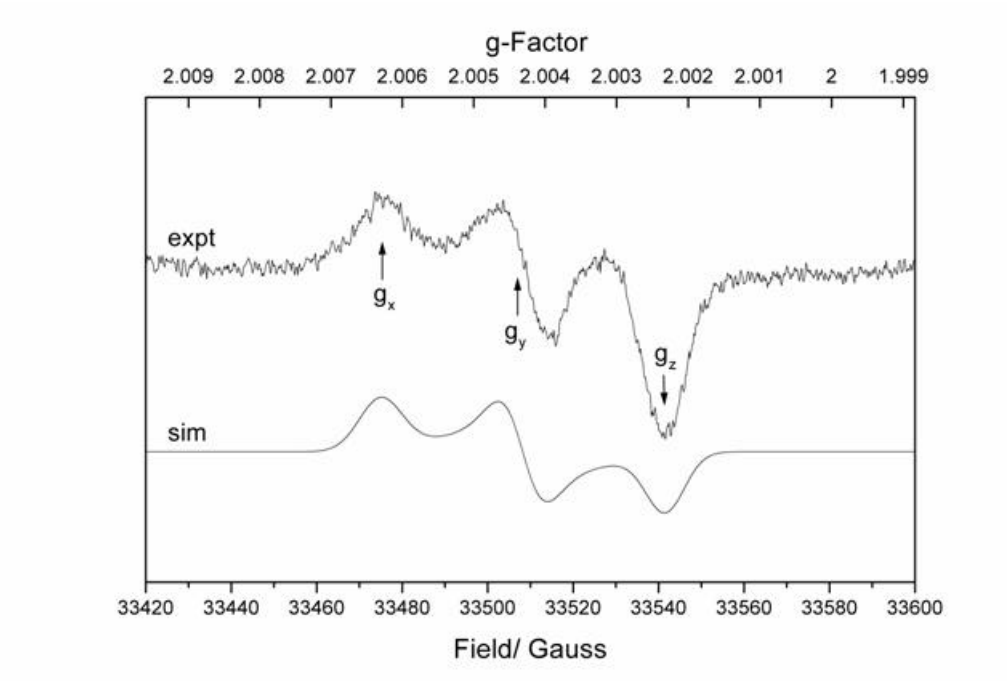
Table SI1. A comparison of the bond lengths calculated for the optimized structure of ^{R}LH (R = Ph, PhOMe, or Bz) with those determined by X-ray crystallography.[6]

Table SI2. Bond lengths calculated for the optimized structures of $[^{R}LH_O]^{\bullet+}$ and $[^{R}LH_N]^{\bullet+}$ (R = Ph, PhOMe, or Bz).

Table SI3. Structural parameters (distance/Å; angle/^{o}) calculated for the intramolecular hydrogen bond in $[^{R}LH_O]^{\bullet+}$ (O-H···N) and $[^{R}LH_N]^{\bullet+}$ (O···H-N) (R = Ph, PhOMe, or Bz).

Figure SI2. (a) Singly occupied molecular orbital (SOMO) of $[^{Ph}LH_O]^{\bullet+}$ and $[^{Ph}LH_N]^{\bullet+}$ (top) and $[^{PhOMe}LH_O]^{\bullet+}$ and $[^{PhOMe}LH_N]^{\bullet+}$ (bottom); (b) non-zero spin populations (???>0.01) for $[^{Ph}LH_O]^{\bullet+}$ and $[^{Ph}LH_N]^{\bullet+}$ (top) and $[^{PhOMe}LH_O]^{\bullet+}$ and $[^{PhOMe}LH_N]^{\bullet+}$ (bottom).

Figure. SI1.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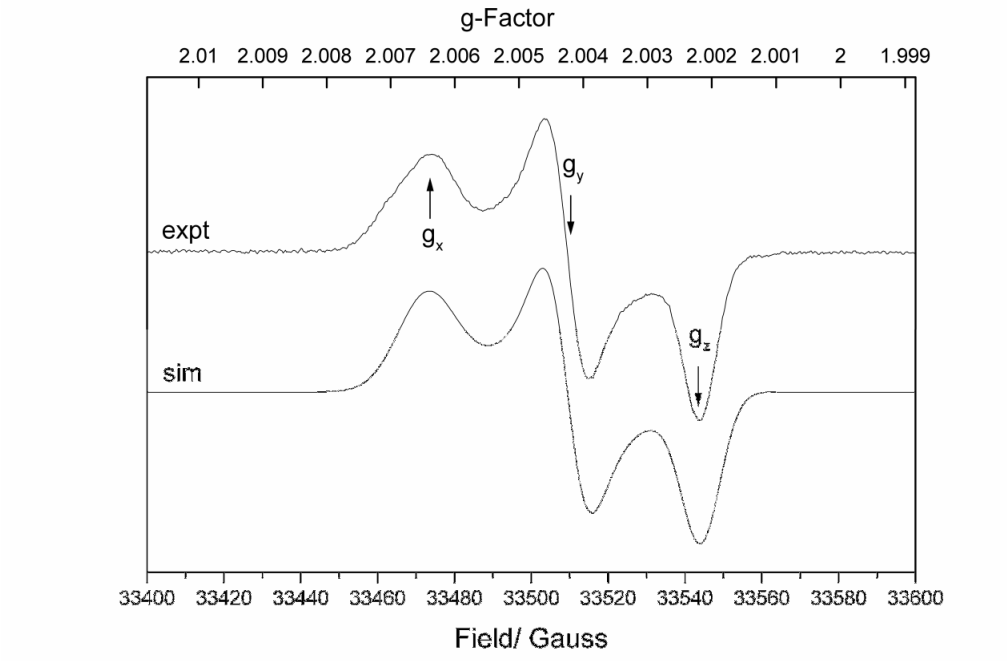
Field/ Gauss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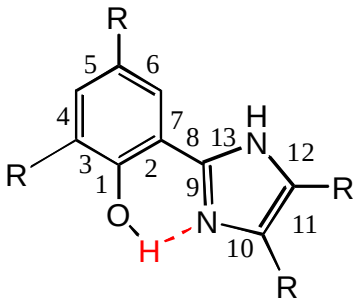
Field/ Gauss

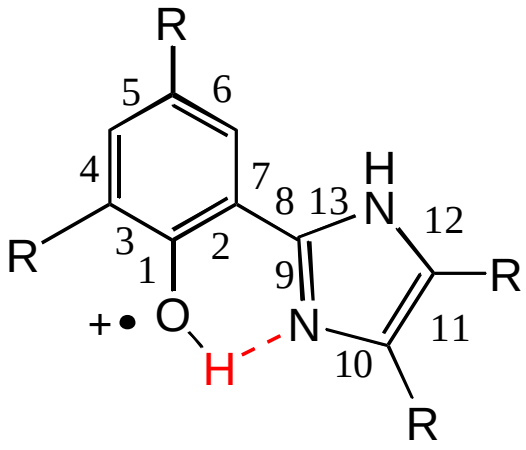
Table SI1



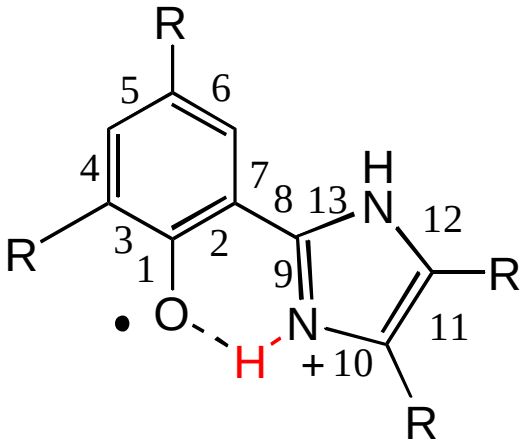
	Calcd bond length /Å			Expt bond length /Å		
bonds	^{Ph}LH	^{PhOMe}LH	^{Bz}LH	^{Ph}LH	^{PhOMe}LH	^{Bz}LH *
1	1.354	1.354	1.350	1.368(2)	1.348(6)	1.366(2); 1.378(2)
2	1.424	1.425	1.426	1.407(2)	1.398(8)	1.404(2); 1.398(2)
3	1.424	1.424	1.425	1.402(2)	1.408(8)	1.409(2); 1.414(3)
4	1.397	1.397	1.396	1.405(2)	1.406(8)	1.390(2); 1.387(2)
5	1.412	1.412	1.413	1.403(2)	1.409(9)	1.401(2); 1.407(3)
6	1.390	1.391	1.389	1.384(2)	1.378(8)	1.383(2); 1.376(2)
7	1.411	1.410	1.411	1.399(2)	1.406(7)	1.402(2);1.403(2)
8	1.454	1.454	1.438	1.462(2)	1.460(7)	1.459(2); 1.460(2)
9	1.339	1.339	1.338	1.339(2)	1.330(7)	1.329(2); 1.328(2)
10	1.383	1.385	1.386	1.385(2)	1.383(7)	1.392(2); 1.391(2)
11	1.398	1.398	1.421	1.382(2)	1.362(8)	1.407(2); 1.400(3)
12	1.392	1.394	1.388	1.380(2)	1.387(7)	1.386(2); 1.381(2)
13	1.371	1.371	1.384	1.360(2)	1.359(7)	1.358(2); 1.363(2)

*Two molecules are present in the asymmetric unit

Table SI2



$[^{R}LH_{O}]^{\bullet+}$



$[^{R}LH_{N}]^{\bullet+}$

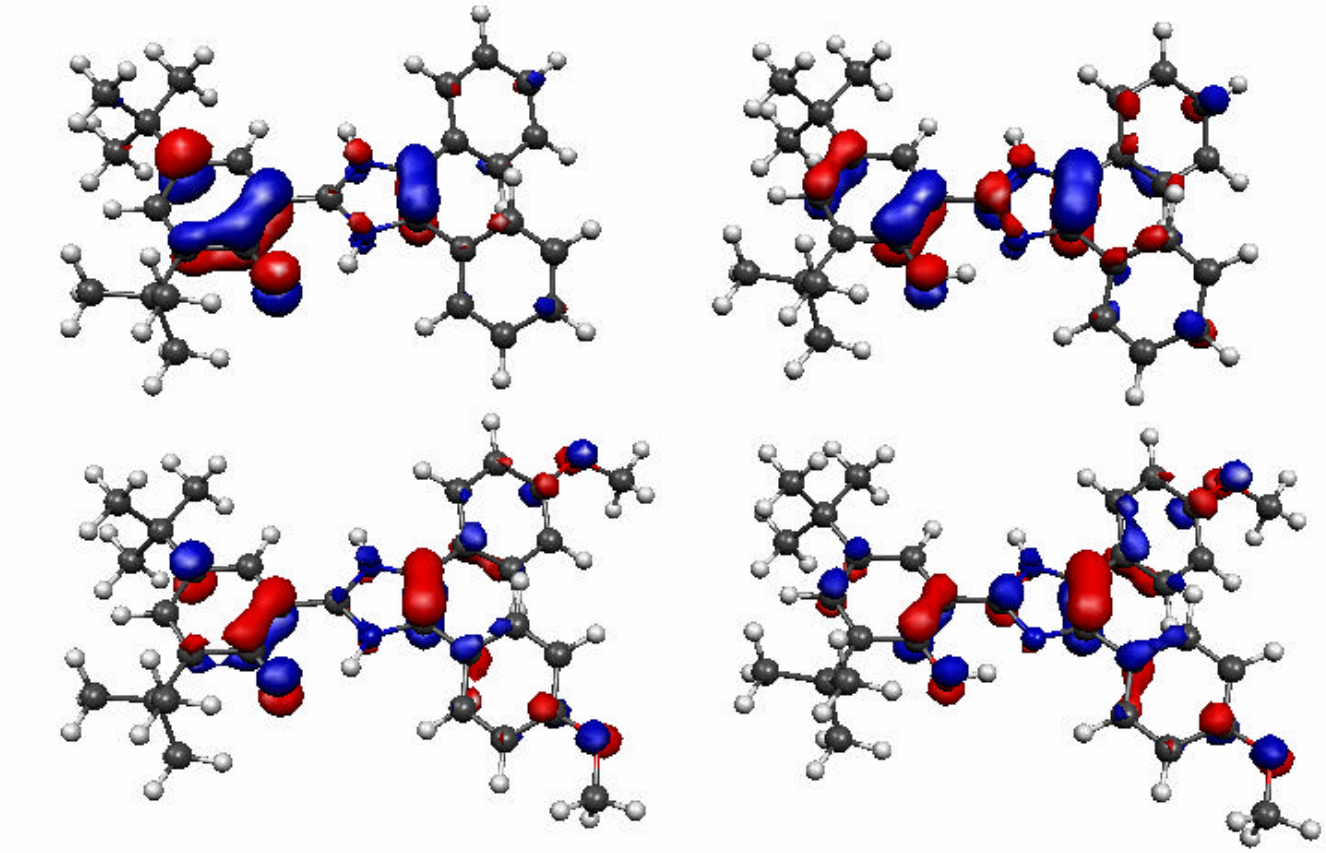
	$[^{R}LH_{O}]^{\bullet+}$			$[^{R}LH_{N}]^{\bullet+}$		
Bond	$[^{Ph}LH]^{\bullet+}$	$[^{PhOMe}LH]^{\bullet+}$	$[^{Bz}LH]^{\bullet+}$	$[^{Ph}LH]^{\bullet+}$	$[^{PhOMe}LH]^{\bullet+}$	$[^{Bz}LH]^{\bullet+}$
1	1.332	1.343	1.307	1.265	1.270	1.261
2	1.449	1.440	1.466	1.481	1.479	1.481
3	1.430	1.426	1.447	1.472	1.468	1.478
4	1.388	1.392	1.381	1.380	1.380	1.381
5	1.428	1.423	1.432	1.429	1.431	1.425
6	1.384	1.384	1.397	1.399	1.392	1.407
7	1.413	1.416	1.397	1.398	1.406	1.392
8	1.431	1.435	1.437	1.433	1.427	1.442
9	1.350	1.347	1.348	1.354	1.355	1.354
10	1.360	1.366	1.371	1.378	1.378	1.383
11	1.438	1.439	1.434	1.405	1.413	1.418
12	1.367	1.373	1.378	1.383	1.384	1.387
13	1.377	1.377	1.373	1.360	1.363	1.361

Table SI3

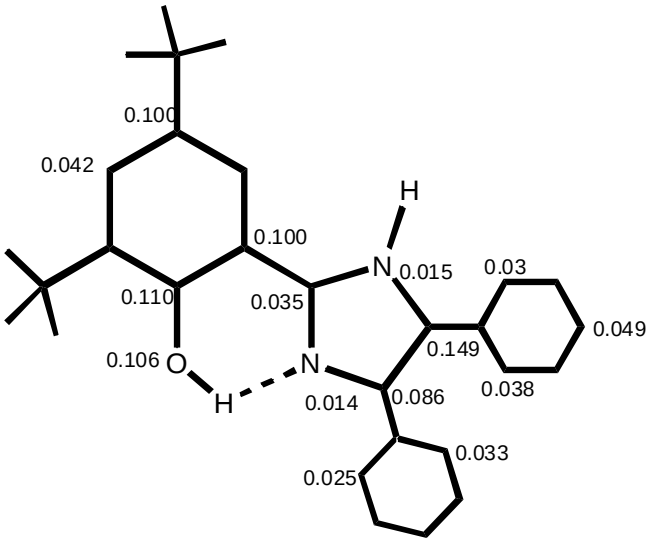
Cation	O-H	O···N	N···H	<O-H···N>	C-O
$[^{Ph}LH_O]^{\bullet+}$	1.032	2.548	1.600	150.3	1.332
$[^{PhOMe}LH_O]^{\bullet}$	1.024	2.563	1.623	150.4	1.343
$[^{Bz}LH_O]^{\bullet+}$	1.102	2.462	1.435	151.8	1.307
	O···H	O···N	N-H	<O···H-N>	
$[^{Ph}LH_N]^{\bullet+}$	1.832	2.603	1.036	128.1	1.265
$[^{PhOMe}LH_N]^{\bullet}$	1.781	2.582	1.041	130.5	1.270
$[^{Bz}LH_N]^{\bullet+}$	1.867	2.621	1.032	127.0	1.261

Figure SI2

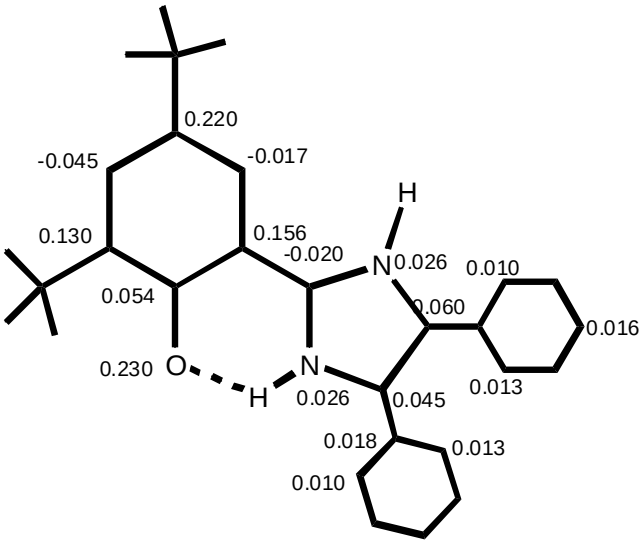
(a)



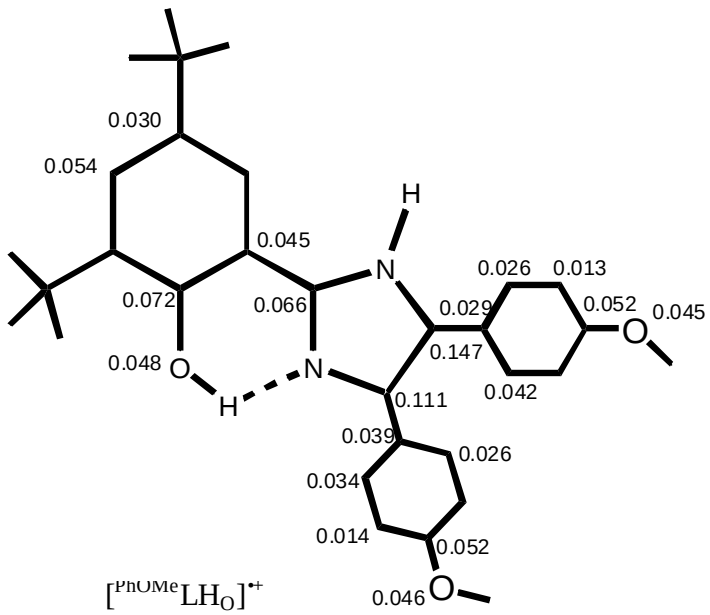
(b)



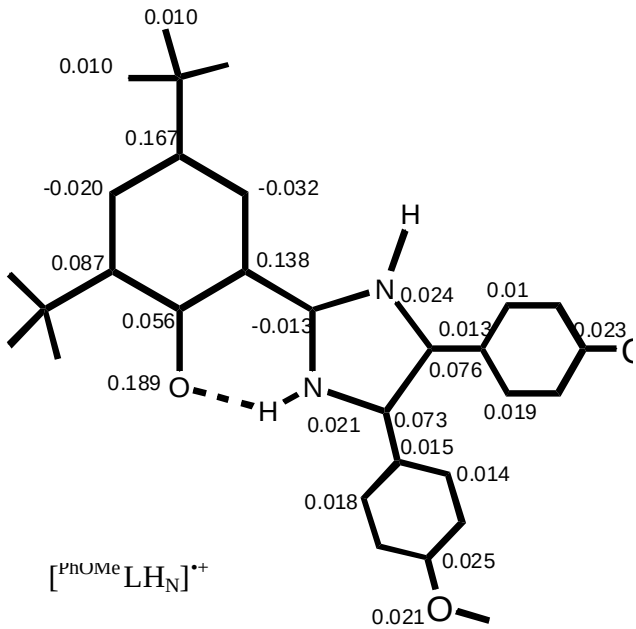
$[^{Ph}LH_O]^{\bullet+}$



$[^{Ph}LH_N]^{\bullet+}$



$[^{PhOMe}LH_O]^{\bullet+}$



$[^{PhOMe}LH_N]^{\bullet+}$