SUPPORTING INFORMATION

Electronic spectrum and characterization of diabatic potential energy surfaces for thiophenol

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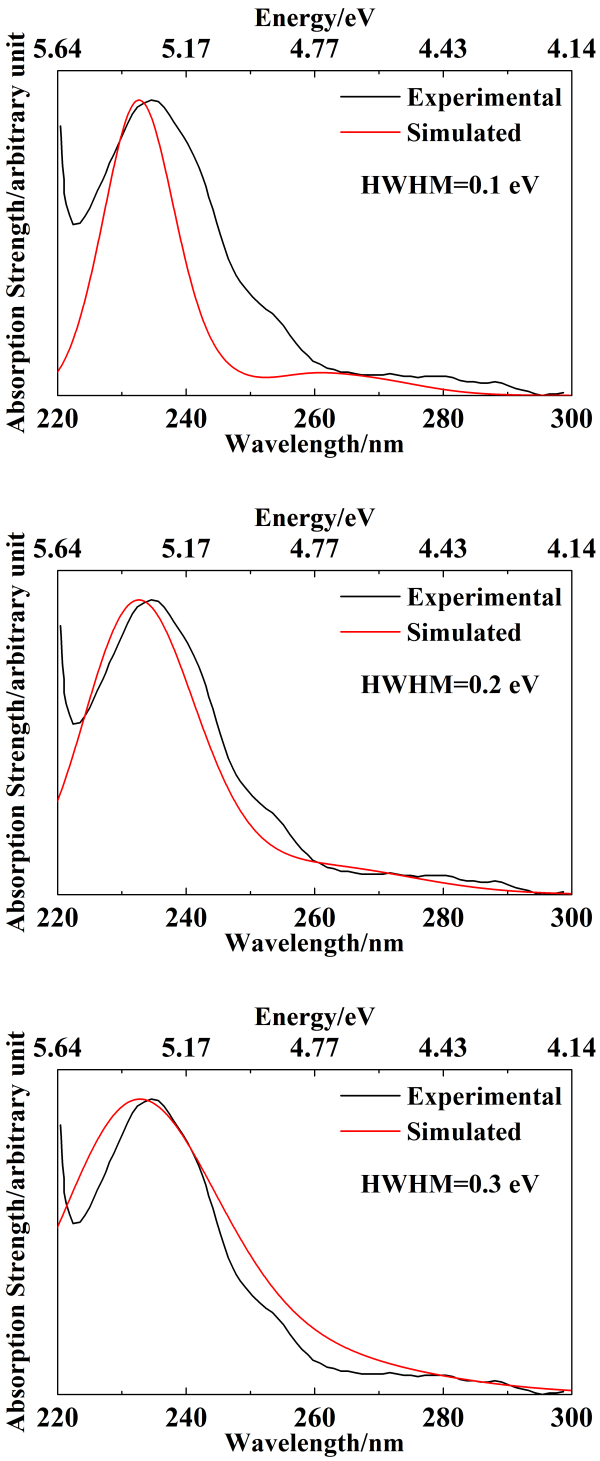

Fig. S1. Experimental absorption spectrum taken in *n*-hexane (data from Fig. 5 of I. S. Lim, J. S. Lim, Y. S. Lee and S. K. Kim, *J. Chem. Phys.*, 2007, **126**, 34306 compared to simulated spectra with vertical excitation energies and oscillator strengths calculated by TDA-τ-HCTHhyb/def-TZVP in the gas phase and broadened using Gaussian functions with three choices of half width at half maximum HWMH parameter.

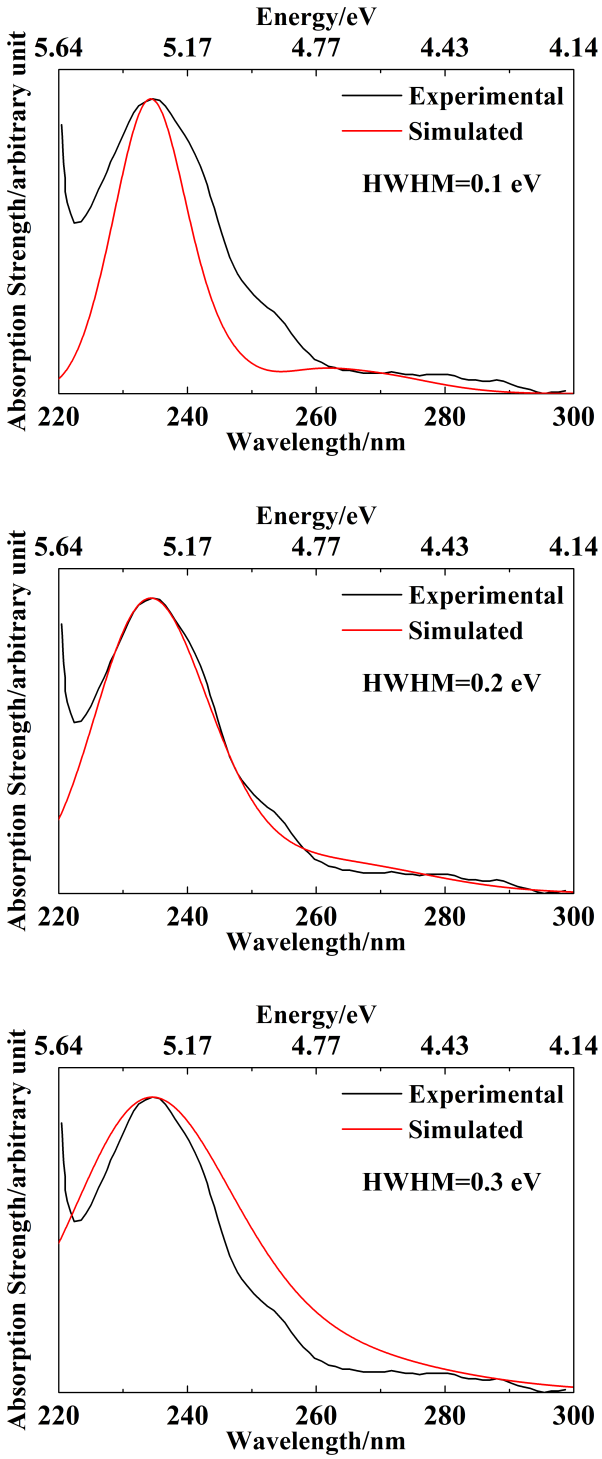

Fig. S2. Experimental absorption spectrum taken in *n*-hexane (data from Fig. 5 of I. S. Lim, J. S. Lim, Y. S. Lee and S. K. Kim, *J. Chem. Phys.*, 2007, **126**, 34306 compared to simulated spectra with vertical excitation energies and oscillator strengths calculated by TDA-τ-HCTHhyb/def-TZVP using state-specific corrected linear response for solvation effects with the SMD solvation model in *n*-hexane and broadened using Gaussian functions with three choices of half width at half maximum HWMH parameter.

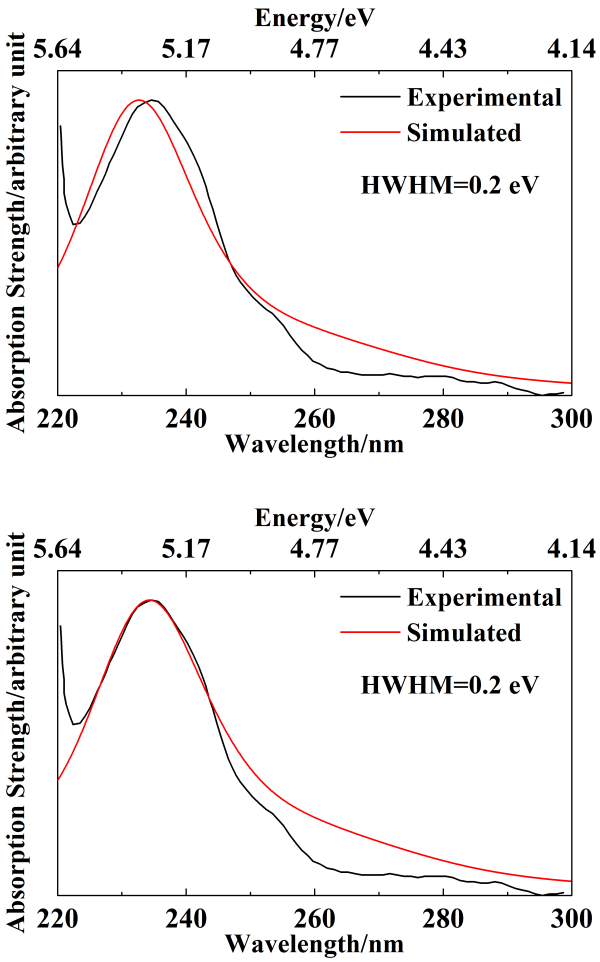

Fig. S3. Experimental absorption spectrum taken in *n*-hexane (data from Fig. 5 of I. S. Lim, J. S. Lim, Y. S. Lee and S. K. Kim, *J. Chem. Phys.*, 2007, **126**, 34306 compared to simulated spectra with vertical excitation energies and oscillator strengths calculated by TDA-τ-HCTHhyb/def-TZVP: (a) gas-phase simulation; (b) liquid-phase simulation calculated using state-specific corrected linear response with the SMD solvation model in *n*-hexane, and broadened using Gaussian functions with HWHM = 0.2 eV.

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Energy in hartrees, Cartesian coordinates in Å, and frequencies in cm^{-1} of the S_0 thiophenol optimized by M06-2X/aug-cc-pVTZ

-630.419110

C	-1.19371600	-1.58393600	0.00000000
C	-1.20130400	-0.19810100	0.00000000
C	0.00000000	0.50576800	0.00000000
C	1.20403900	-0.19117700	0.00000000
C	1.20204300	-1.57789800	0.00000000
C	0.00622000	-2.28135500	0.00000000
H	-2.13305100	-2.11987800	0.00000000
H	-2.14015600	0.33998400	0.00000000
H	2.14265100	0.34666700	0.00000000
H	2.14420600	-2.10902600	0.00000000
H	0.00928800	-3.36208000	0.00000000
H	1.23499500	2.49352600	0.00000000
S	-0.08510100	2.27318800	0.00000000

178	209	279	406	419	479	629	691	
715	760	864	929	934	998	1012	1019	
1061	1114	1137	1174	1208	1306	1354	1488	
1524	1648	1660	2738	3196	3200	3211	3216	3229

Energy in hartrees, Cartesian coordinates in Å, and frequencies in cm^{-1} of the S_0 thiophenoxyl optimized by M06-2X/aug-cc-pVTZ

-629.775728

C	-1.19822600	-1.53251400	0.00000000
C	-1.20600300	-0.14631700	0.00000000
C	0.00000000	0.55209000	0.00000000
C	1.20599700	-0.14632700	0.00000000
C	1.19821300	-1.53252500	0.00000000
C	-0.00000900	-2.23244500	0.00000000
H	-2.13875600	-2.06642600	0.00000000
H	-2.14363000	0.39329600	0.00000000
H	2.14363100	0.39327600	0.00000000
H	2.13874500	-2.06643200	0.00000000
H	-0.00002100	-3.31308600	0.00000000
S	0.00001200	2.30547500	0.00000000

183	248	418	421	477	626	704	716
758	864	926	1000	1015	1016	1060	1107
1126	1173	1206	1288	1348	1474	1515	1636
1654	3197	3201	3211	3217	3229		

Energy in hartrees, Cartesian coordinates in Å, and frequencies in cm^{-1} of the S_0 thiophenol optimized by CASSCF(12,11)/MG3S

-628.428206

C	-0.00117316	0.50216329	0.00000000
C	1.20516598	-0.19421969	0.00000000
C	-1.20507634	-0.20214134	0.00000000
C	1.20424759	-1.58538306	0.00000000
H	2.13804722	0.33527514	0.00000000
S	-0.08381797	2.30345988	0.00000000
C	-1.19846272	-1.59146941	0.00000000
H	-2.13828063	0.32813150	0.00000000
C	0.00543422	-2.28954268	0.00000000
H	2.13881469	-2.11285329	0.00000000
H	1.24665773	2.52861261	0.00000000
H	-2.12996912	-2.12415147	0.00000000
H	0.00852669	-3.36219954	0.00000000

65	190	283	416	429	494	663	716	
730	768	866	928	938	998	1017	1058	
1099	1151	1166	1178	1276	1306	1450	1569	
1621	1704	1720	2645	3314	3319	3330	3337	3347

Energy in hartrees, Cartesian coordinates in Å, and frequencies in cm^{-1} of the S_1 thiophenol optimized by CASSCF(12,11)/MG3S

-628.256213

C	-0.0012220651	0.5293807028	0.0000000000
C	1.2461159732	-0.1730190450	0.0000000000
C	-1.2442813750	-0.1803898715	0.0000000000
C	1.2404456835	-1.6023759363	0.0000000000
H	2.1719286853	0.3633811342	0.0000000000
S	-0.0838750279	2.2981296255	0.0000000000
C	-1.2350243923	-1.6099249423	0.0000000000
H	-2.1701346147	0.3573227120	0.0000000000
C	0.0045849108	-2.3096557367	0.0000000000
H	2.1668748374	-2.1389431580	0.0000000000
H	1.2454624260	2.5332140750	0.0000000000
H	-2.1590517287	-2.1502674837	0.0000000000
H	0.0082906875	-3.3811700761	0.0000000000

109	160	267	279	373	386	505	548	
567	582	636	646	698	748	925	977	
1016	1028	1125	1241	1252	1407	1502	1544	
1630	1650	1809	2643	3337	3347	3352	3361	3370

Energy in hartrees, Cartesian coordinates in Å, and frequencies in cm^{-1} of the S_0 thiophenol optimized by M06-L/def-TZVP

-630.477020

C	-1.20540200	-1.57833400	0.00000000
C	-1.20664600	-0.19344100	0.00000000
C	0.00000000	0.50433200	0.00000000
C	1.20084900	-0.20151200	0.00000000
C	1.18944000	-1.58728000	0.00000000
C	-0.01019900	-2.28335300	0.00000000
H	-2.14941000	-2.10906900	0.00000000
H	-2.14407000	0.34904300	0.00000000
H	2.14425200	0.33108100	0.00000000
H	2.12991800	-2.12447000	0.00000000
H	-0.01386500	-3.36546600	0.00000000
H	1.26615700	2.47443700	0.00000000
S	-0.06507800	2.28012300	0.00000000

178	207	273	406	416	467	635	661	
713	730	839	882	922	957	975	1023	
1056	1113	1123	1186	1211	1341	1369	1484	
1517	1627	1642	2717	3171	3176	3186	3191	3204