Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

A theoretical exploration on electronically excited states of protonated furan and thiophene

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This supplementary file contains five Tables:

Table SM1: Comparison the geometry parameters of neutral furan and thiophen with corresponding gas phase experimental results (presented in braket).

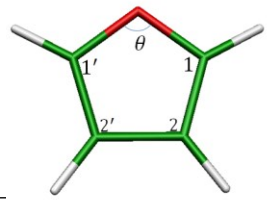
Table SM2: xyz coordinates revealed to the ground optimized geometry of neutral/protonated of furan and thiophene.

Table SM3: Vertical transition energies of neutral and protonated furan [$FC1H^+$] , computed at the CC2/aug-cc-pVDZ level of theory.

Table SM4: Vertical transition energies of neutral and protonated thiophene [$TC1H^+$] , computed at the CC2/aug-cc-pVDZ level of theory.

Table SM5: Basis set effect on the vertical and adiabatic transition energies of S_2-S_0 and S_1-S_0 of neutral Furan and Thiophene.

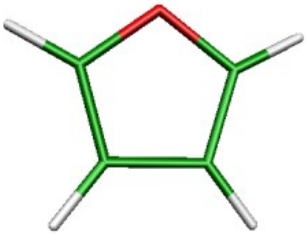
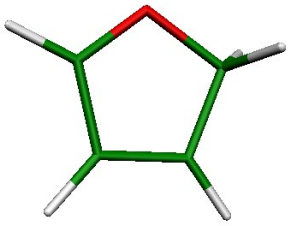
Table SM1

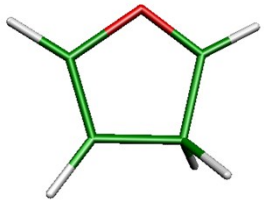
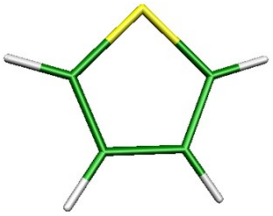
	Furan		Thiophene	
	aug-cc-pVDZ	cc-pVDZ	aug-cc-pVDZ	cc-pVDZ
r(X–C1)/Å	1.372 [1.362]*	1.364	1.730 [1.714]**	1.726
r(C1–C2)/Å	1.380 [1.360]	1.378	1.392 [1.369]	1.388
r(C2–C2')/Å	1.438 [1.430]	1.436	1.427 [1.423]	1.427
r(C1–H1)/Å	1.087 [1.075]	1.088	1.090 [1.077]	1.081
r(C2–H2)/Å	1.088 [1.076]	1.089	1.092 [1.080]	1.093
θ1(C1'-X-C1)	106.9 [106.3]	106.8	92.1 [92.1]	92.0
θ2(X-C1-C2)	110.4 [110.4]	110.8	111.5 [111.2]	111.6
θ3(C1-C2-C2')	106.1 [106.3]	105.8	112.5 [112.2]	112.4
θ4(X –C1-H1)	115.8 [115.5]	115.8	120.0 [119.5]	120.3
θ5(C2'-C2-H2)	127.9 [127.5]	127.9	124.6 [124.1]	124.5

**The experimental values have been adopted from: B. Bsreg et al J. Mol. Spect., 1962, 9, 124-129*

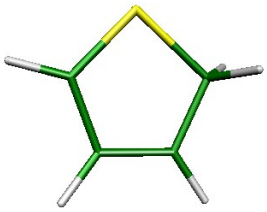
***The experimental values have been adopted from: B. Bsreg et al J. Mol. Spect., 1961, 7, 58-63.*

Table SM2

Neutral Furan			
C	-1.29638	-0.49545	-0.00002
C	-1.29646	0.94226	0.00002
C	0.02904	-0.87849	0.00002
C	0.02892	1.32544	-0.00001
O	0.84582	0.22352	0.00003
H	-2.15559	-1.16335	-0.00010
H	-2.15574	1.61006	0.00010
H	0.53281	-1.84132	0.00004
H	0.53259	2.28833	-0.00008
			
FC1H$^+$			
C	-1.39833	-0.37925	0.01631
C	-1.36822	0.99426	0.02622
C	-0.00630	-0.88829	-0.02699
C	0.01949	1.34702	-0.01017
O	0.81828	0.33109	-0.04067
H	-2.28022	-1.02369	0.03610
H	-2.20031	1.69644	0.05516
H	0.48827	2.33585	-0.01567
H	0.30321	-1.46156	0.86284
H	0.25212	-1.44688	-0.94213
			

FC2H+			
O	0.79187	0.28836	0.00333
C	0.01035	1.29793	0.06080
C	-1.40756	0.90254	0.06874
C	-1.31205	-0.59294	0.00148
C	-0.00653	-0.92627	-0.03574
H	0.47326	2.28873	0.09621
H	-2.14894	-1.28986	-0.01433
H	0.58888	-1.83440	-0.08543
H	-1.93974	1.37253	-0.78359
H	-1.90454	1.29339	0.98056
			
Thiophene			
C	2.34434	0.06353	0.00165
C	3.73014	0.19117	-0.00663
C	4.15196	1.55424	-0.00485
C	3.08047	2.44229	0.00482
S	1.56532	1.60788	0.01162
H	1.74681	-0.84827	0.00242
H	4.40555	-0.66703	-0.01372
H	5.19405	1.88096	-0.01048
H	3.10237	3.53221	0.00817
			

TC1H+			
C	2.90100	2.57452	0.11834
S	1.39960	1.56880	0.36461
C	2.26242	0.14920	0.20137
C	3.66765	0.30607	-0.03766
C	4.02807	1.63256	-0.08492
H	5.04462	1.99973	-0.25511
H	4.34325	-0.54236	-0.16267
H	1.73866	-0.81002	0.28069
H	2.73046	3.23570	-0.75333
H	3.03226	3.21681	1.01067



TC2H+			
C	2.75485	2.54864	0.14859
S	1.39389	1.62363	0.30588
C	2.27389	0.09437	0.17554
C	3.61101	0.30713	0.01155
C	3.98905	1.74800	-0.01651
H	4.33872	-0.50170	-0.09024
H	1.71732	-0.84256	0.23233
H	2.68973	3.64095	0.17144
H	4.71698	2.01182	0.78064
H	4.49756	2.03472	-0.96222

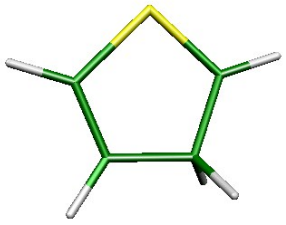


Table SM3

state	Energy (eV)	oscillator strengths	configuration
Furan			
S_1 ($^1A_2$)	5.86	0.0000	(π_1/ σ_1*) 45.3%
S_2 ($^1B_1$)	6.31	0.1849	(π_1/ π_1*) 73.6%
S_3 ($^1B_2$)	6.38	0.0414	(π_1/ σ_3*)84.5%
S_4 ($^1A_2$)	6.55	0.0000	(π_1/ σ_5*) 84.1%
S_5 ($^1A_1$)	6.60	0.0001	(π_2/ π_1*) 24.7%
[FC1H$^+$]			
S_1 ($^1A'$)	5.34	0.1382	)89.3% (π_1/ π_1*
S_2 ($^1A''$)	6.41	0.0015	(σ_1/ π_1*)84.3%
S_3 ($^1A''$)	7.42	0.0002	(σ_2/ π_1*)87.1%
S_4 ($^1A'$)	7.61	0.1283	(π_2/ π_1*)89.0%
S_5 ($^1A''$)	8.10	0.0015	(σ_3/ π_1*)89.4%

Table SM4:

state	Energy (eV)	oscillator strengths	configuration
Thiophene			
S_1 ($^1A_1$)	5.67	0.0731	(π_1/ π_1*)70.2%
S_2 ($^1A_2$)	5.87	0.0000	(π_1/ σ_1*)82.7%
S_3 ($^1B_1$)	5.97	0.1079	(π_2/ π_1*)85.7%
S_4 ($^1B_2$)	6.04	0.0191	(π_2/ σ_3*)43.0%
S_5 ($^1B_2$)	6.38	0.0007	(π_1/ σ_1*)77.9%
[TC1H+]			
S_1 ($^1A'$)	4.35	0.1370	(π_1/ π_1*)93.8%
S_2 ($^1A''$)	5.72	0.0020	)97.2%(σ_1/ π_1*
S_3 ($^1A'$)	6.31	0.0811	(π_2/ π_1*)85.0%
S_4 ($^1A''$)	7.03	0.0000	(σ_2/ π_1*)57.3%
S_5 ($^1A''$)	7.05	0.0004	(π_1/σ_1*)21.3%

Table SM5

Molecule	Basis Set	Vertical transition energy/ev	Oscillator strength	Adiabatic transition energy/ev
Furan S_2-S_0	aug-cc-pVDZ	6.31	0.1849	5.96
	aug-cc-pVTZ	6.39	0.1853	6.02
	aug-cc-pVQZ	6.41	0.1850	6.03
Thiophene S_1-S_0	aug-cc-pVDZ	5.67	0.0731	5.45
	aug-cc-pVTZ	5.74	0.0727	5.52
	aug-cc-pVQZ	5.75	0.0717	5.53