Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Ab Initio Study on the Excited-State Proton Transfer Mechanisms for 3-hydroxy-2-(thiophen-2-yl) chromen-4-one

Huipeng Ma*[1], Jindou Huang*[2]

[1] College of Medical Laboratory Science, Dalian Medical University, Dalian 116044, China

[2]School of Physics and Materials Engineering, Dalian Nationalities University, Dalian 116600, China

*Corresponding author: Huipeng Ma, E-mail: hpma@dlmedu.edu.cn, Tel: +86-411-86110391;

Jin-Dou Huang, E-mail: jindouhuang@dicp.ac.cn, Tel: +86-411-84379236.

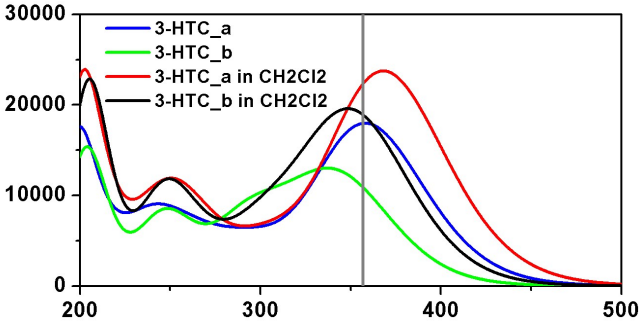

Figure S1. Calculated UV-Vis absorption spectra of 3-HTC-a and 3-HTC-b in vacuum (blue and green lines) and in CH_2Cl_2 (red and black lines) based on the optimized geometries at DFT/B3LYP-D3BJ/TZVP level.

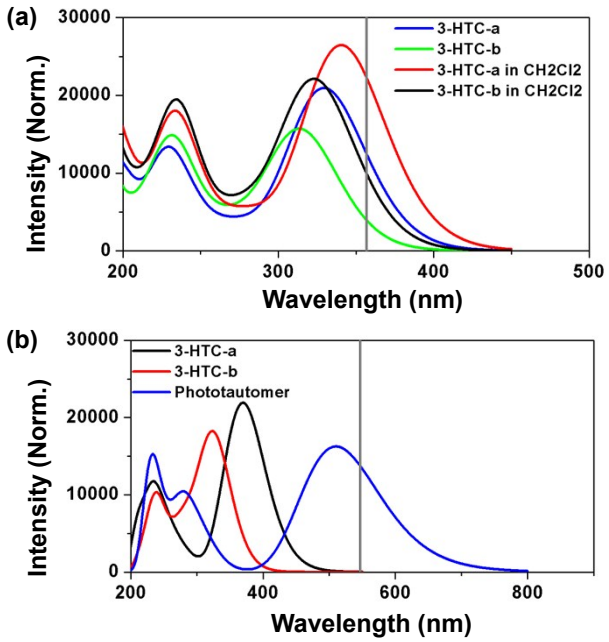

Figure S2. (a) Calculated UV-Vis absorption spectra of 3-HTC-a and 3-HTC-b in vacuum (blue and green lines) and in CH_2Cl_2 (red and black lines); and (b) the fluorescence spectra of 3-HTC-a (red line), phototautomer of 3-HTC-a (blue line), and 3-HTC-b (black line) at DFT/cam-B3LYP/def2-qzvpd level; the cross vertical line shows the experimental data in CH_2Cl_2.

Table S1 Calculated bond lengths (Å), angles and dihedral angles of 3-HTC-a and 3-HTC-b structures of the S_0 state in vacuum and in CH_2Cl_2 at DFT/B3LYP-D3BJ/TZVP level, as well as structural parameters of S_1 states in vacuum at TDDFT/cam-B3LYP/def2-qzvpd level.

Molecules	**O1-H1**		**O2-H1**		**S-H1**		**O1-H1-O2/S**		**C1-C2-C3-S**	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
3-HTC-a	0.978	0.995	2.047	1.853	3.815	3.880	117.5	123.0	0.0	0.0
3-HTC-b	0.967	0.963	3.628	3.571	2.401	2.363	126.6	124.5	27.8	15.6
3-HTC-a(CH_2Cl_2)	0.977		2.065		3.814		116.8		0.0	
3-HTC-b(CH_2Cl_2)	0.968		3.619		2.431		124.3		28.6	

Table S2. Calculated energies of 3-HTC-a and 3-HTC-b structures for the S_0 state in vacuum and in CH_2Cl_2 at DFT/B3LYP/TZVP level and DFT/B3LYP-D3BJ/TZVP level; and calculated energies of 3-HTC-a and 3-HTC-b structures for the S_1 state in vacuum at TDDFT/B3LYP/TZVP level and TDDFT/cam-B3LYP/def2-qzvpd level.

Molecules	Energy for S_0 (Hartree)		Energy for S_1 (Hartree)	
	B3LYP/TZVP	B3LYP-D3/TZVP	B3LYP/TZVP	cam-B3LYP/ Def2QZVP
3-HTC-a	-1124.3173027	-1124.3765874	-1124.3100778	-1124.0591531
3-HTC-b	-1124.3003653	-1124.3599452	-1124.28401	-1124.0394386
3-HTC-a (CH_2Cl_2)	-1124.3250677	-1124.3843362		
3-HTC-b (CH_2Cl_2)	-1124.312819	-1124.3723956		