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ESI for: First-principle investigation of the double ES-IPT process in a thiophene-based dye.†

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S1 Geometries

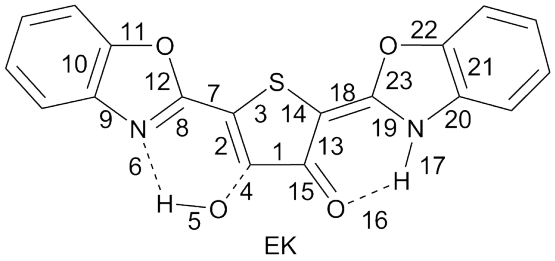

Fig. S1 Bond labels of the Enol-Keto BBTP form. Labels are identical for EE and KK.

Table S1 Bond lengths of the GS and ES of EE optimised with B3LYP, M06-2X, ωB97X-D, and CC2. All the optimisations are performed in gas phase and use the cc-pVTZ basis set. The C_{2v} symmetry is used in all cases except B3LYP/TD-DFT that leads a C_s structure. See Figure S1 for labels.

		GS				ES			
		B3LYP	M06-2X	ωB97X-D	CC2	B3LYP	M06-2X	ωB97X-D	CC2
1	C-C	1.424	1.427	1.427	1.410	1.392	1.384	1.383	1.380
2	C-C	1.385	1.374	1.375	1.390	1.422	1.422	1.423	1.428
3	C-S	1.743	1.730	1.730	1.727	1.766	1.753	1.754	1.753
4	C-O	1.334	1.331	1.327	1.334	1.337	1.332	1.328	1.333
5	O-H	0.984	0.977	0.978	0.991	0.984	0.979	0.980	0.996
6	H-N	1.898	1.942	1.898	1.822	1.891	1.915	1.876	1.785
7	C-C	1.423	1.430	1.429	1.410	1.388	1.387	1.387	1.371
8	C-N	1.307	1.298	1.298	1.317	1.337	1.331	1.331	1.354
9	N-C	1.389	1.391	1.389	1.383	1.363	1.361	1.361	1.355
10	C-C	1.397	1.392	1.389	1.396	1.414	1.409	1.405	1.414
11	C-O	1.376	1.369	1.368	1.374	1.368	1.360	1.367	1.365
12	O-C	1.366	1.355	1.351	1.368	1.381	1.371	1.367	1.386

Table S2 Bond lengths of EK* and KK* optimised with B3LYP, M06-2X, ωB97X-D, and CC2. All the optimisations are in gas phase and use the cc-pVTZ atomic basis set. See Figure S1 for labels.

		EK*				KK*			
		B3LYP	M06-2X	ωB97X-D	CC2	B3LYP	M06-2X	ωB97X-D	CC2
1	C-C	1.452	1.447	1.447	1.415	1.485	1.477	1.474	1.458
2	C-C	1.394	1.394	1.399	1.401	1.458	1.464	1.464	1.462
3	C-S	1.757	1.740	1.734	1.768	1.738	1.719	1.719	1.714
4	C-O	1.327	1.321	1.315	1.343	1.244	1.236	1.238	1.266
5	O-H	0.994	0.987	0.990	0.996	1.972	1.978	1.959	1.780
6	H-N	1.843	1.876	1.830	1.812	1.021	1.020	1.019	1.039
7	C-C	1.400	1.402	1.401	1.381	1.371	1.364	1.364	1.369
8	C-N	1.329	1.317	1.317	1.337	1.361	1.358	1.357	1.357
9	N-C	1.375	1.381	1.381	1.374	1.380	1.380	1.378	1.371
10	C-C	1.405	1.398	1.394	1.403	1.397	1.394	1.391	1.397
11	C-O	1.378	1.372	1.371	1.374	1.386	1.378	1.377	1.383
12	O-C	1.379	1.365	1.361	1.385	1.365	1.357	1.354	1.366
13	C-C	1.467	1.472	1.466	1.485	1.458	1.464	1.464	1.462
14	C-S	1.720	1.701	1.705	1.696	1.738	1.719	1.719	1.714
15	C-O	1.242	1.236	1.238	1.269	1.244	1.236	1.238	1.266
16	O-H	2.002	2.006	1.998	1.776	1.972	1.978	1.959	1.780
17	H-N	1.019	1.019	1.017	1.040	1.021	1.020	1.019	1.039
18	C-C	1.377	1.373	1.372	1.378	1.371	1.364	1.364	1.369
19	C-N	1.359	1.357	1.357	1.355	1.361	1.358	1.357	1.357
20	N-C	1.380	1.379	1.377	1.367	1.380	1.380	1.378	1.371
21	C-C	1.397	1.394	1.391	1.398	1.397	1.394	1.391	1.397
22	C-O	1.385	1.377	1.376	1.379	1.386	1.378	1.377	1.383
23	O-C	1.360	1.335	1.352	1.362	1.365	1.357	1.354	1.366

Table S3 Bond length of EE* optimised with TD-DFT/6-31G(d) in gas and solution (LR and VEM-UD), with both M06-2X and ωB97X-D. See Figure S1 for labels.

		M06-2X			ωB97X-D		
		gas	LR	VEM-UD	gas	LR	VEM-UD
1	C-C	1.391	1.385	1.395	1.390	1.385	1.389
2	C-C	1.425	1.428	1.410	1.427	1.430	1.427
3	C-S	1.761	1.760	1.758	1.763	1.762	1.762
4	C-O	1.333	1.337	1.349	1.334	1.335	1.335
5	O-H	0.986	0.986	0.984	0.986	0.986	0.987
6	H-N	1.911	1.910	1.923	1.881	1.879	1.875
7	C-C	1.391	1.386	1.403	1.391	1.387	1.389
8	C-N	1.335	1.338	1.327	1.336	1.339	1.337
9	N-C	1.364	1.361	1.376	1.365	1.363	1.365
10	C-C	1.414	1.416	1.407	1.410	1.412	1.411
11	C-O	1.362	1.362	1.368	1.363	1.363	1.364
12	O-C	1.372	1.372	1.371	1.370	1.370	1.369
13	C-C	1.425	1.428	1.436	1.427	1.430	1.427
14	C-S	1.761	1.760	1.765	1.763	1.762	1.762
15	C-O	1.333	1.337	1.325	1.334	1.335	1.335
16	O-H	0.986	0.986	0.989	0.986	0.986	0.987
17	H-N	1.911	1.910	1.881	1.881	1.879	1.875
18	C-C	1.391	1.386	1.372	1.391	1.387	1.389
19	C-N	1.335	1.338	1.356	1.336	1.339	1.337
20	N-C	1.364	1.361	1.349	1.365	1.363	1.365
21	C-C	1.414	1.416	1.428	1.410	1.412	1.411
22	C-O	1.362	1.362	1.365	1.363	1.363	1.364
23	O-C	1.372	1.372	1.369	1.370	1.370	1.369

Table S4 Bond lengths of EK* optimised with TD-DFT/6-31G(d) in gas and solution (LR and VEM-UD) with both M06-2X and ωB97X-D. See Figure S1 for labels.

		M06-2X			ωB97X-D		
		gas	LR	VEM-UD	gas	LR	VEM-UD
1	C-C	1.448	1.439	1.445	1.450	1.440	1.443
2	C-C	1.395	1.390	1.383	1.401	1.395	1.388
3	C-S	1.759	1.774	1.801	1.751	1.770	1.797
4	C-O	1.328	1.339	1.346	1.323	1.335	1.341
5	O-H	0.991	0.987	0.988	0.994	0.989	0.989
6	H-N	1.895	1.929	1.928	1.848	1.886	1.887
7	C-C	1.404	1.402	1.396	1.403	1.401	1.393
8	C-N	1.321	1.321	1.337	1.322	1.322	1.336
9	N-C	1.382	1.384	1.374	1.384	1.386	1.379
10	C-C	1.403	1.403	1.409	1.400	1.400	1.404
11	C-O	1.374	1.373	1.371	1.375	1.374	1.373
12	O-C	1.368	1.369	1.379	1.365	1.366	1.375
13	C-C	1.483	1.488	1.500	1.477	1.485	1.495
14	C-S	1.708	1.707	1.716	1.712	1.706	1.712
15	C-O	1.241	1.245	1.231	1.244	1.247	1.235
16	O-H	1.977	2.031	2.069	1.977	2.022	2.049
17	H-N	1.024	1.022	1.020	1.023	1.021	1.019
18	C-C	1.377	1.384	1.374	1.377	1.385	1.379
19	C-N	1.360	1.357	1.354	1.361	1.356	1.352
20	N-C	1.380	1.377	1.381	1.381	1.378	1.383
21	C-C	1.400	1.402	1.399	1.397	1.399	1.395
22	C-O	1.377	1.374	1.375	1.379	1.376	1.379
23	O-C	1.356	1.353	1.349	1.355	1.351	1.346

Table S5 Bond length of KK* optimised with TD-DFT/6-31G(d) in gas and solution (LR and VEM-UD) with both M06-2X and ωB97X-D. See Figure S1 for labels.

		M06-2X			ωB97X-D		
		gas	LR	VEM-UD	gas	LR	VEM-UD
1	C-C	1.479	1.476	1.484	1.476	1.474	1.479
2	C-C	1.471	1.465	1.493	1.472	1.466	1.469
3	C-S	1.728	1.727	1.710	1.730	1.728	1.738
4	C-O	1.242	1.248	1.229	1.244	1.250	1.244
5	O-H	1.975	2.046	2.066	1.964	2.036	2.084
6	H-N	1.023	1.020	1.019	1.022	1.019	1.016
7	C-C	1.367	1.371	1.372	1.366	1.371	1.363
8	C-N	1.363	1.360	1.355	1.363	1.360	1.364
9	N-C	1.382	1.383	1.386	1.382	1.383	1.384
10	C-C	1.399	1.398	1.396	1.396	1.396	1.395
11	C-O	1.379	1.380	1.380	1.380	1.381	1.382
12	O-C	1.360	1.358	1.351	1.358	1.356	1.359
13	C-C	1.471	1.465	1.442	1.472	1.466	1.469
14	C-S	1.728	1.727	1.768	1.730	1.728	1.738
15	C-O	1.242	1.248	1.255	1.244	1.250	1.244
16	O-H	2.046	2.046	2.099	2.046	2.036	2.084
17	H-N	1.023	1.020	1.017	1.022	1.019	1.016
18	C-C	1.367	1.371	1.363	1.366	1.371	1.363
19	C-N	1.363	1.360	1.374	1.363	1.360	1.364
20	N-C	1.382	1.383	1.381	1.382	1.383	1.384
21	C-C	1.399	1.398	1.401	1.396	1.396	1.395
22	C-O	1.379	1.380	1.380	1.380	1.381	1.382
23	O-C	1.360	1.358	1.370	1.358	1.356	1.359

Table S6 MAD, MSD, MaxD, and MinD in Å for the bond lengths of EE*, EK*, and KK* tautomers obtained by comparing TD-M06-2X gas, LR and VEM-UD structures.

	VEM-UD versus LR			gas versus LR			gas versus VEM-UD		
	EE*	EK*	KK*	EE*	EK*	KK*	EE*	EK*	KK*
MAD	0.010	0.014	0.012	0.002	0.014	0.015	0.010	0.007	0.012
MSD	0.000	-0.007	-0.004	0.000	-0.007	-0.007	0.000	0.004	-0.001
MaxD	0.029	0.015	0.024	0.004	0.013	0.029	0.021	0.009	0.053
MinD	-0.017	-0.092	-0.053	-0.006	-0.092	-0.091	-0.030	-0.054	-0.071

S2 Optical properties

Table S7 Emission energy (eV) from the excited-states of EE*, EK*, and KK* of BBTP, ΔE_{gas} , $\Delta E_{\text{cLR neq}}$, $\Delta E_{\text{ADC(2)}}$, and ΔE_{CC2} calculated with TD-M06-2X cLR and VEM solvent models. f are the corresponding oscillator strengths.

			cLR PCM			
	ΔE_{gas}	$\Delta E_{\text{cLR neq}}$	$\Delta E_{\text{ADC(2)}}$	ΔE_{CC2}	f cLR	f CC2
EE*	3.05	3.03	3.04	3.13	1.68	1.58
EK*	2.88	2.85	2.46	2.66	0.51	0.35
KK*	2.49	2.47	2.01	2.26	0.11	0.09
			VEM-UD			
	ΔE_{gas}	ΔE_{VEM}	$\Delta E_{\text{ADC(2)}}$	ΔE_{CC2}	f VEM	f CC2
EE*	3.06	2.84	2.82	2.93	0.91	1.55
EK*	2.86	2.55	2.13	2.34	0.26	0.38
KK*	2.49	2.21	1.75	1.99	0.06	0.10

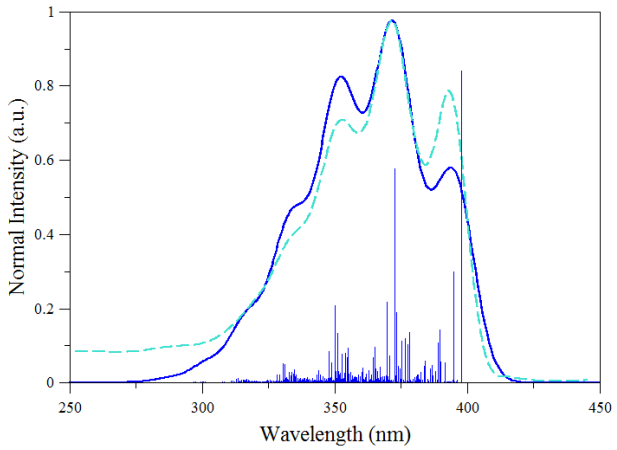

Fig. S2 Vibronic spectrum of the $S_0 \rightarrow S_1$ of EE transition with M06-2X. The theoretical spectrum is in full lines whereas the experimental is in dash lines. A Half Width of Half Maximum (HWHM) of 0.060 eV and a redshift of 0.046 eV is used to allow straight forward comparison. Experimental fluorescence is taken from Ref 1 with permission from Elsevier

Table S8 0-0 and adiabatic energies (eV) of EE* obtained with M06-2X. Energies are determined with composite approaches combining TD-DFT with cLR and VEM solvent models, with post-HF ADC(2) and CC2.

	0-0 energies		Adiabatic energies	
	cLR	VEM	cLR	VEM
TD-DFT	3.29	3.24	3.38	3.33
ADC(2)	3.09	3.03	3.18	3.12
CC2	3.16	3.10	3.25	3.20

Notes and references

1 Yongchao Hao and Yi Chen, *Dyes Pigm.*, **2016**, *129*, 186–190.