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A DFT/TDDFT Study of the Excited State Intramolecular Proton Transfer Based Sensing Mechanism for the Aqueous Fluoride Chemosensor BTTPB

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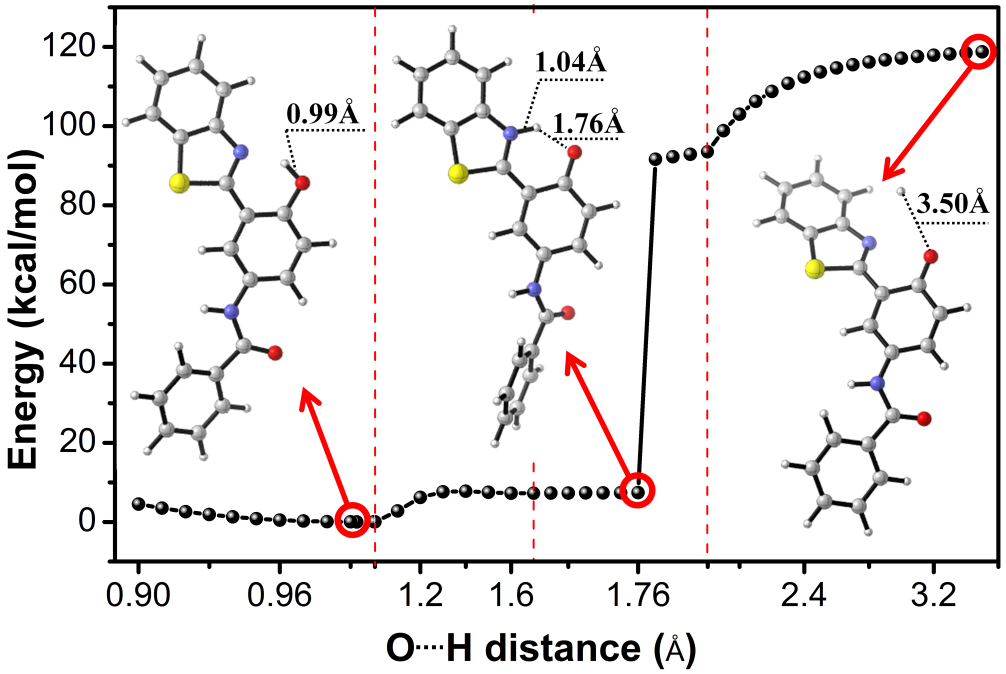

Fig.S1 Potential energy curve for **3-BTHPB**$^-$ and H^+, which is the function of O···H distance in ground state (The energy is the electronic energy obtained at DFT/B3LYP/TZVP level with IEF-PCM water, ε=78.4).

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Table S1 Comparison of experimental[1] and calculated electronic transitions for **BTTPB** at the TDDFT/B3LYP/TZVP level.

Theoretical data					Experimental data
Electronic transition	Energy (nm/eV)	*f*	Contrib.	CI	Absorbance band (nm)
$S_0 \rightarrow S_1$	328 (3.78)	0.1571	H→L	0.88	~335
$S_0 \rightarrow S_2$	309 (4.02)	0.5433	H→L	0.89	
$S_0 \rightarrow S_3$	280 (4.23)	0.0307	H-1→L	0.36	
			H-2→L	0.46	
$S_0 \rightarrow S_4$	279 (4.44)	0.0105	H→L+2	0.93	
$S_0 \rightarrow S_5$	274 (4.53)	0.3686	H-1→L	0.45	
			H-2→L	0.40	
$S_0 \rightarrow S_6$	267 (4.65)	0.0740	H→L+3	0.50	

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Table S2 Comparison of experimental[1] and calculated electronic transitions for **3-BTHPB** at the TDDFT/B3LYP/TZVP level.

Theoretical data					Experimental data
Electronic transition	Energy (nm/eV)	*f*	Contrib.	CI	Absorbance band (nm)
$S_0 \rightarrow S_1$	368(3.37)	0.3000	H→L	0.97	~360
$S_0 \rightarrow S_2$	312 (3.98)	0.5043	H→L+1	0.93	
$S_0 \rightarrow S_3$	304 (4.08)	0.1908	H-1→L	0.70	
$S_0 \rightarrow S_4$	293 (4.23)	0.3173	H-2→L	0.71	
$S_0 \rightarrow S_5$	265 (4.68)	0.0031	H-3→L+1	0.40	
			H-5→L+1	0.31	
$S_0 \rightarrow S_6$	263 (4.72)	0.0029	H-3→L	0.82	

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Table S3 Comparison of experimental[1] and calculated electronic transition $S_0 \rightarrow S_1$ for **BTTPB** with different functionals (at the TDDFT/B3LYP/TZVP and TDDFT/CAM-B3LYP/TZVP levels).

Theoretical data					Experimental data
Functional	Energy (nm/eV)	*f*	Contrib.	CI	Absorbance band (nm)
B3LYP	328 (3.78)	0.1571	H→L	0.88	~335
CAM-B3LYP	278 (4.47)	0.2046	H→L	0.64	

Table S4 Comparison of experimental[1] and calculated electronic transition $S_0 \rightarrow S_1$ for **3-BTHPB** with different functionals (at the TDDFT/B3LYP/TZVP and TDDFT/CAM-B3LYP/TZVP levels).

Theoretical data					Experimental data
Functional	Energy (nm/eV)	*f*	Contrib.	CI	Absorbance band (nm)
B3LYP	368(3.37)	0.3000	H→L	0.97	~360
CAM-B3LYP	321 (3.86)	0.3900	H→L	0.93	

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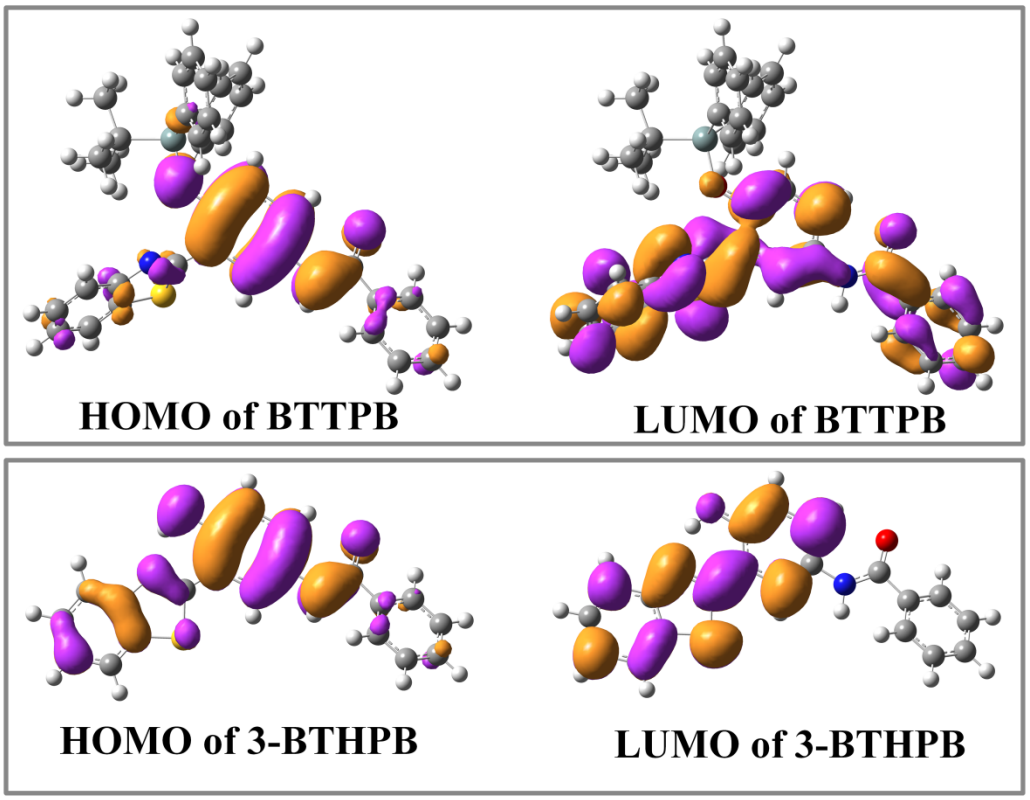

Fig.S2 The calculated frontier molecular orbitals HOMO and LUMO for **BTTPB** and **3-BTHPB** at the DFT/CAM-B3LYP/TZVP level.

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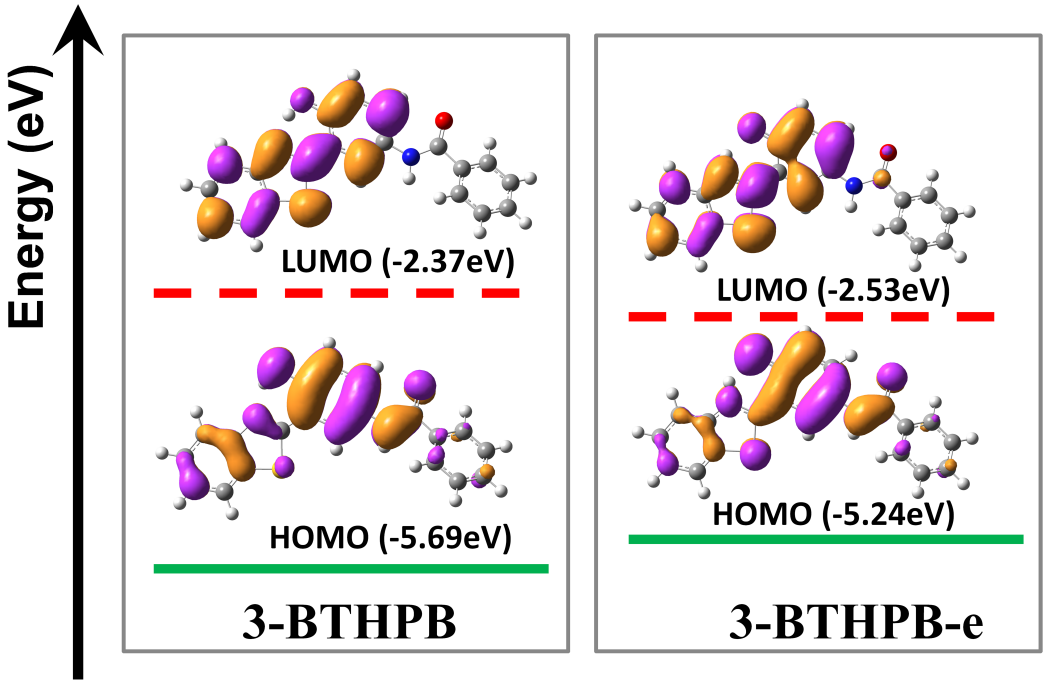

Fig.S3 Calculated frontier molecular orbitals HOMO and LUMO for **3-BTHPB** (enol form) and **3-BTHPB-e** (keto form).

Reference:

1. R. Hu, J. A. Feng, D. H. Hu, S. Q. Wang, S. Y. Li, Y. Li and G. Q. Yang, *Angew. Chem., Int. Ed.*, 2010, **49**, 4915-4918.