

A brand-new type of excited-state proton transfer (ESIPT) molecule
based on sulfoxide/sulfenic acid tautomerism

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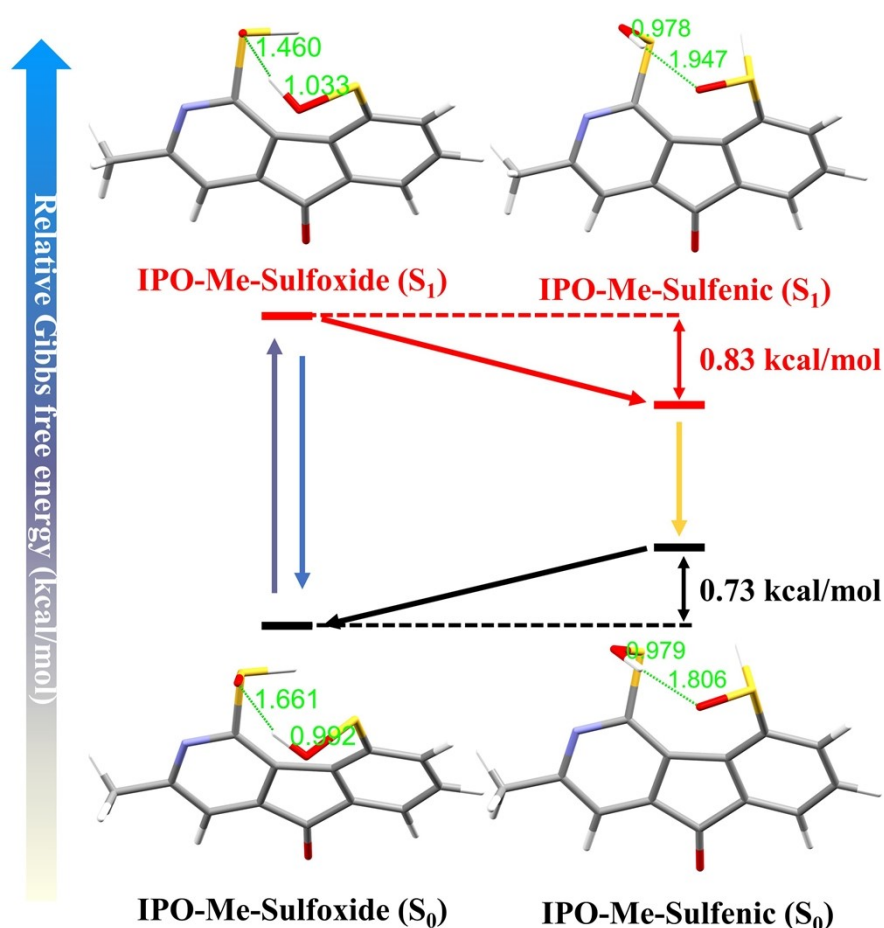


Fig. S1. The stable conformers for the ground state (bottom) and first excited singlet state (top) of IPO-Me were obtained by using the M06-2X/6-311++G(d,p) method in acetonitrile.

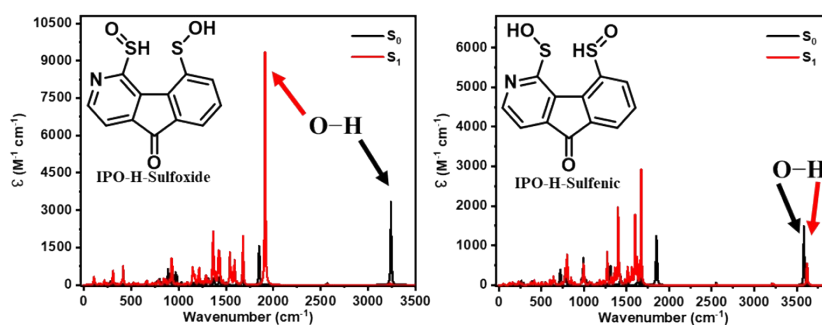


Fig. S2. The calculated infrared spectrum of IPO-H in the ground and first excited singlet states using the M06-2X/6-311++G(d,p) method in dichloromethane.

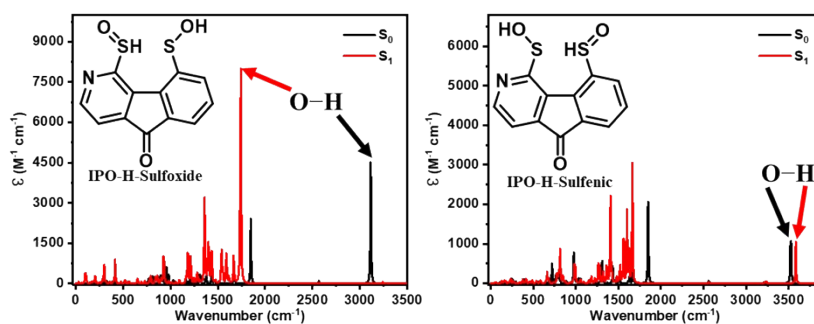


Fig. S3. The calculated infrared spectrum of IPO-H in the ground and first excited singlet states using the M06-2X/def2-TZVP method in acetonitrile.

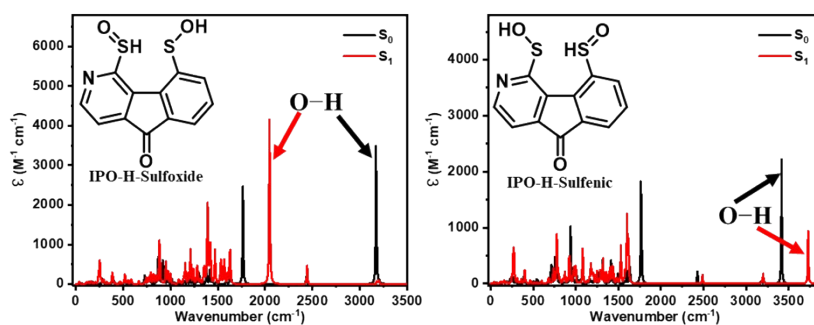


Fig. S4. The calculated infrared spectrum of IPO-H in the ground and first excited states using the B3LYP/6-311++G(d,p) method in acetonitrile.

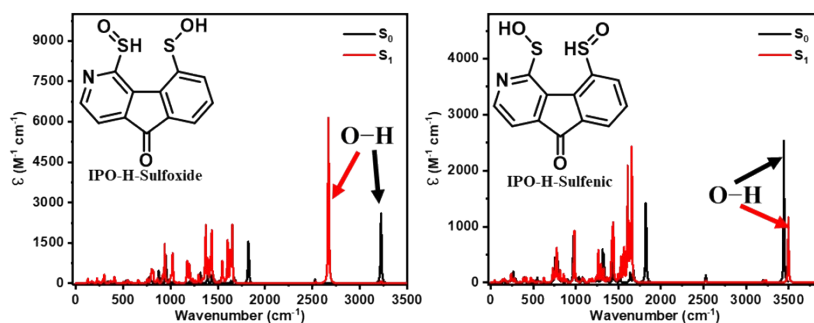


Fig. S5. The calculated infrared spectrum of IPO-H in the ground and first excited singlet states using the CAM-B3LYP/6-311++G(d,p) method in acetonitrile.

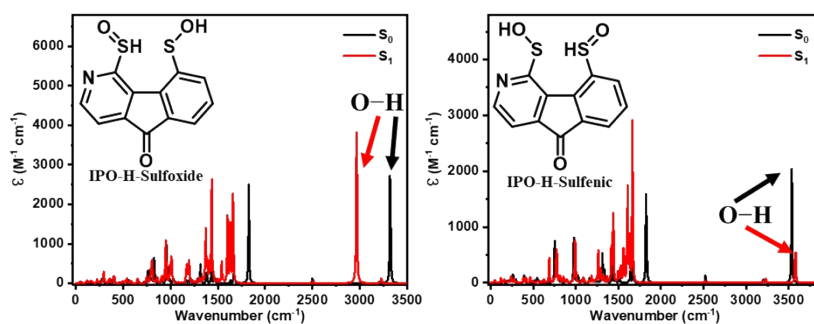


Fig. S6. The calculated infrared spectrum of IPO-H in the ground and first excited singlet states using the ω B97X-D/6-311++G(d,p) method in acetonitrile.

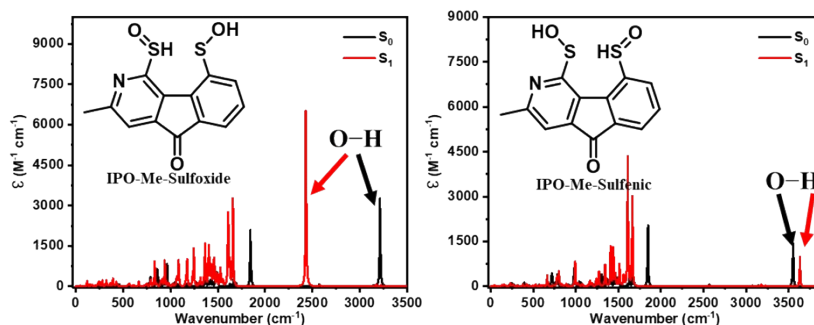


Fig. S7. The calculated infrared spectrum of IPO-Me in the ground and first excited singlet states using the M06-2X/6-311++G(d,p) method in acetonitrile.

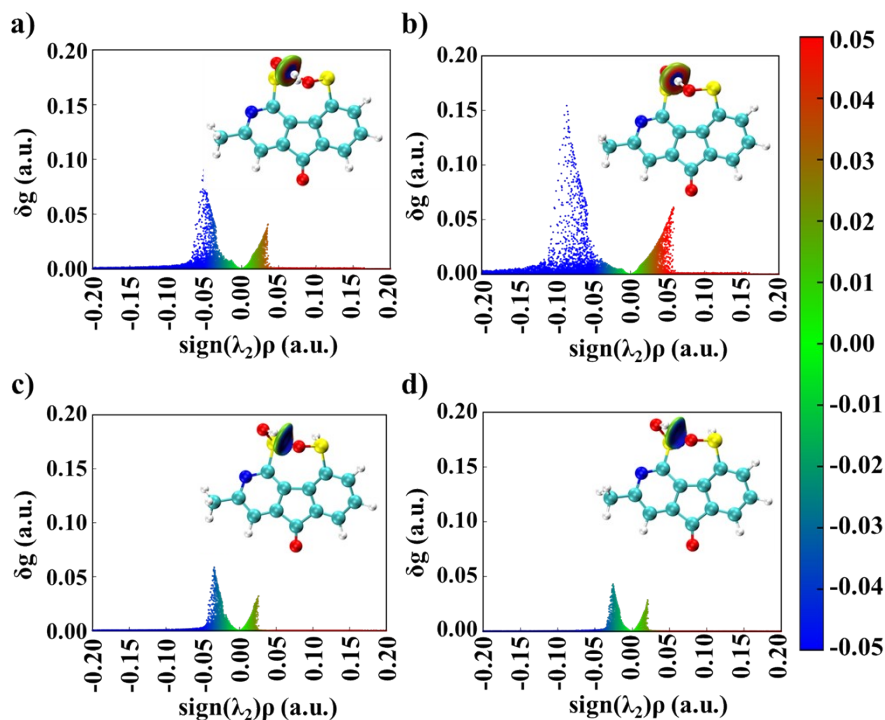


Fig. S8. The scatter plots of the $\text{sign}(\lambda_2)\rho$ versus δg and isosurface density (inset) for the IPO-Me compounds at M06-2X/6-311++G(d,p) method in acetonitrile. The ground state (a), first excited singlet state (b) for IPO-Me-Sulfoxide and ground state (c), first excited singlet state (d) for IPO-Me-Sulfenic.

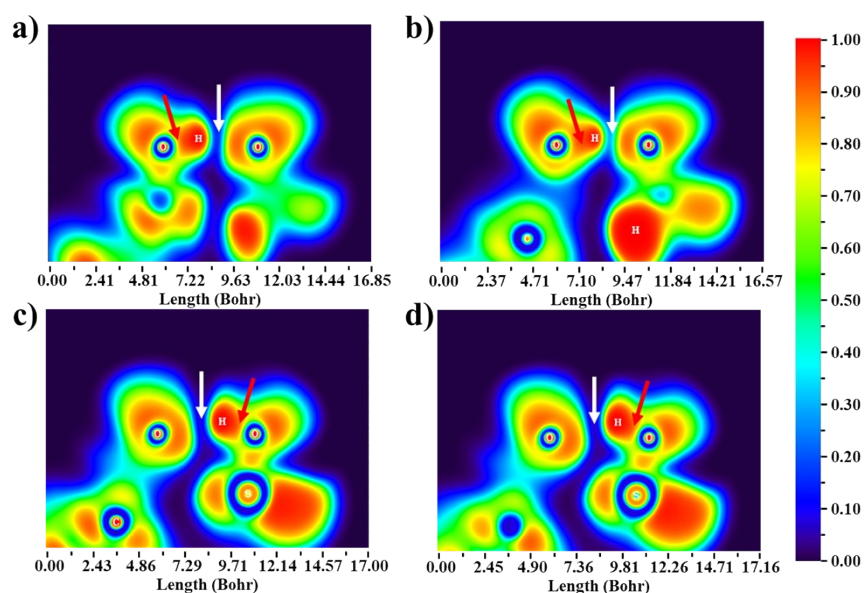


Fig. S9. ELF diagram of IPO-Me compounds in different electronic states at M06-2X/6-311++G(d,p) method in acetonitrile. The ground state (a), first excited singlet state (b) for IPO-Me-Sulfoxide and ground state (c), first excited singlet state (d) for IPO-Me-Sulfenic.

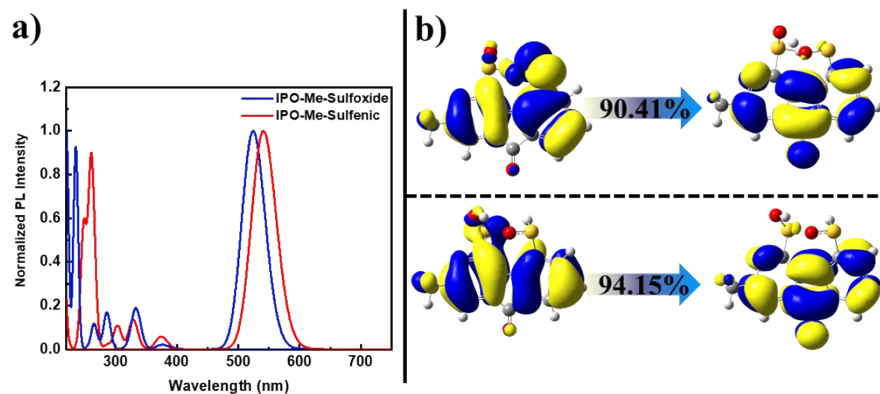


Fig. S10. Calculated (a) absorption, emission spectra ($S_1 \rightarrow S_0$), and (b) FMOs ($S_1 \rightarrow S_0$) of IPO-Me-Sulfoxide (up) and IPO-Me-Sulfenic (bottom) with STEOM-CCSD/cc-pVQZ//M06-2X/6-311++G(d,p) in acetonitrile.

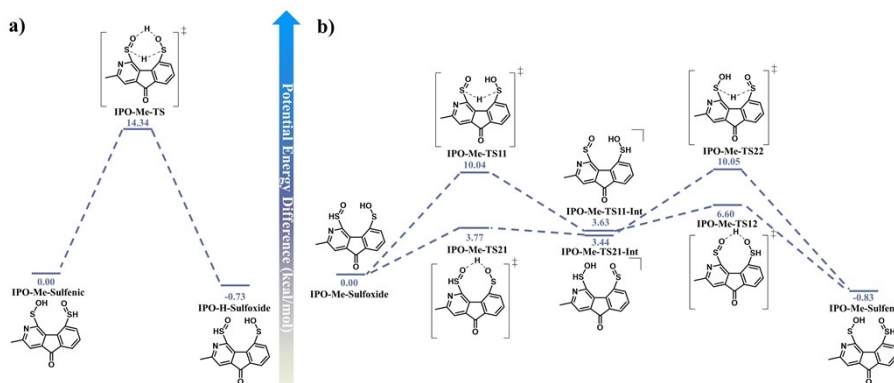


Fig. S11. The reactants, transition states, intermediates, and products of IPO-Me-Sulfoxide and IPO-Me-Sulfenic conversion in (a) ground state (CCSD/cc-pVQZ//M06-2X/6-311++G** in acetonitrile) and (b) first excited singlet state (STEOM-CCSD/cc-pVQZ//M06-2X/6-311++G** in acetonitrile).

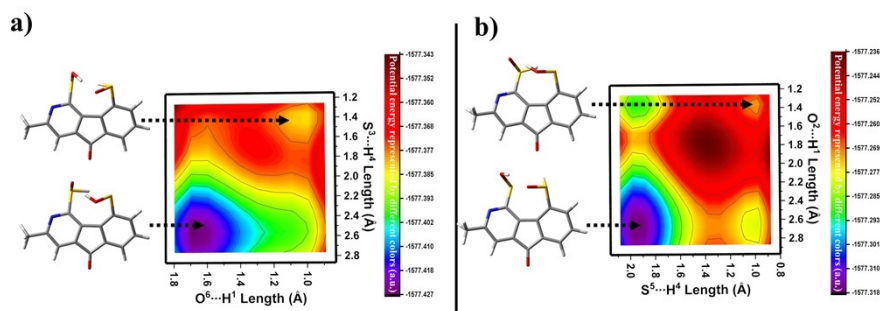


Fig. S12. Potential energy surfaces and corresponding structure of IPO-Me compounds with M06-2X/6-311++G(d,p) method in acetonitrile at (a) ground state and (b) first excited singlet state compounds with M06-2X/6-311++G(d,p) method in acetonitrile at (a) ground state and (b) first excited singlet state. 3D potential energy surface (left) and its corresponding planar projection (right).

Table S1. The S–O···H and S=O···H bond length of IPO-Me at the ground and first excited singlet states with M06-2X/6-311++G(d,p) method in acetonitrile.

Molecule	State	S–O···H (Å)	S=O···H (Å)
IPO-Me-Sulfoxide	S ₀	0.992	1.661
	S ₁	1.033	1.460
IPO-Me-Sulfenic	S ₀	0.979	1.806
	S ₁	0.978	1.947

Table S2. Calculated absorption (λ_{abs}), vertical emission wavelength (λ_{em} , S₁ → S₀), stokes shift ($\Delta\bar{\nu}$), oscillator strengths (f), charge transfer percentage (CTP) main transition orbital composition, and molecular orbital configuration coefficient (CI) of IPO-Me-Sulfoxide and IPO-Me-Sulfenic with STEOM-CCSD/cc-pVQZ//M06-2X/6-311++G(d,p) in acetonitrile.

Molecule	λ_{ex} (nm)	f_{ex}	λ_{em} (nm)	f_{em}	$\Delta\lambda$ (cm ⁻¹)	CI (S ₁ → S ₀)	CTP (%)
IPO-H-Sulfoxide	376.33	0.0041					
	333.15	0.0361					
	285.78	0.0326	524.37	0.0454	7501.92	HOMO-LUMO:90.41%	38.73
	264.84	0.0223					
IPO-H-Sulfenic	235.03	0.1788					
	374.62	0.0104					
	328.65	0.0281	541.15	0.0294	8214.55	HOMO-LUMO:94.15%	30.97
	303.10	0.0227					

259.41 0.1538

Table S3. Calculated gibbs free energy(kcal/mol) of transition state with CASSCF in acetonitrile.

Molecule	Ground state	Excited state			
		Path one ^a		Path two ^b	
		Step one	Step two	Step one	Step two
IPO-H-Sulfoxide	24.12	18.90	10.06	9.44	3.96
IPO-Me-Sulfoxide	21.27	19.75	16.75	12.29	10.70

^a path one: break the S⁵-H⁴ bond, form S³-H⁴ firstly and break the O²-H¹ bond, form O⁶-H¹ secondly, ^b path two: break the O²-H¹ bond, form O⁶-H¹ firstly and break the S⁵-H⁴ bond, form S³-H⁴ secondly.