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Supplementary Material

A Novel Imidazophenazine-Based Stimuli Responsive Chemosensor for Highly Selective and Sensitive Fluorescence Detection of CN^-

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Contents

1. Materials and methods

All reagents and materials were commercially available at analytical grade and were used without further purification. The anions were used as the tetrabutylammonium (TBA) salts, which were purchased from Alfa Aesar and used as received. Double distilled water was used throughout the experiment. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrouorophotometer. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. ^{1}H NMR spectra was recorded on a Mercury-600 BB spectrometer at 600 MHz. Electrospray ionization mass spectra (ESI-MS) was measured on an Agilent 1100 LC-MSD-Trap-VL system. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected).

2. General procedure

2.1 General procedure for UV-vis and fluorescence spectra experiments

The solution of sensor **S** (2.0×10^{-4} M) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. The DMSO solutions of each anions (1.0×10^{-2} M) were prepared, via tetrabutylammonium salts of anions (I^-, Br^-, Cl^-, F^-, $H_2PO_4^-$,CH_3COO^-, ClO_4^- , and HSO_4^-) and sodium salt of anions (CN^-, SCN^-). All the UV-vis experiments were carried out in DMSO/H_2O (v:v = 7:3) solution on a Shimadzu UV-2550 spectrometer. Any change in the UV-vis spectra of the synthesized compounds was recorded on addition of salts while keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments. All the fluorescence spectra experiments were carried out in DMSO/H_2O (v:v = 7:3) solution on a Shimadzu RF-5301PC spectrometer. The fluorescence spectra were obtained by excitation at 470 nm. Any change in the fluorescence spectra of the synthesized compounds was recorded upon the addition of salts while keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments.

2.2 General procedure for ^{1}H NMR titrations

The **S** (1.0×10^{-2} mol/L) was dissolved in the DMSO-d_6 (0.5 ml) , then a series of different equivalents of CN^- were added into the solution of **S** and recorded their ^{1}H NMR respectively. All the solutions were mixed directly in NMR tube.

2.3 General procedure for preparation of CN^- test paper

The filter paper were first immersed in diluted hydrochloric acid solution, then washed with double distilled water to neutrality and dried in vacuum. The filter paper were cut into paper pieces with length of about 4 cm and width of about 2 cm. Next, the prepared paper pieces were immersed in the solution of sensor **S** (0.01 M) in DMSO, then dried in vacuum. It was found that the test strips appeared red color in visible light and red fluorescence under the UV-lamp.

3. Experimental Section

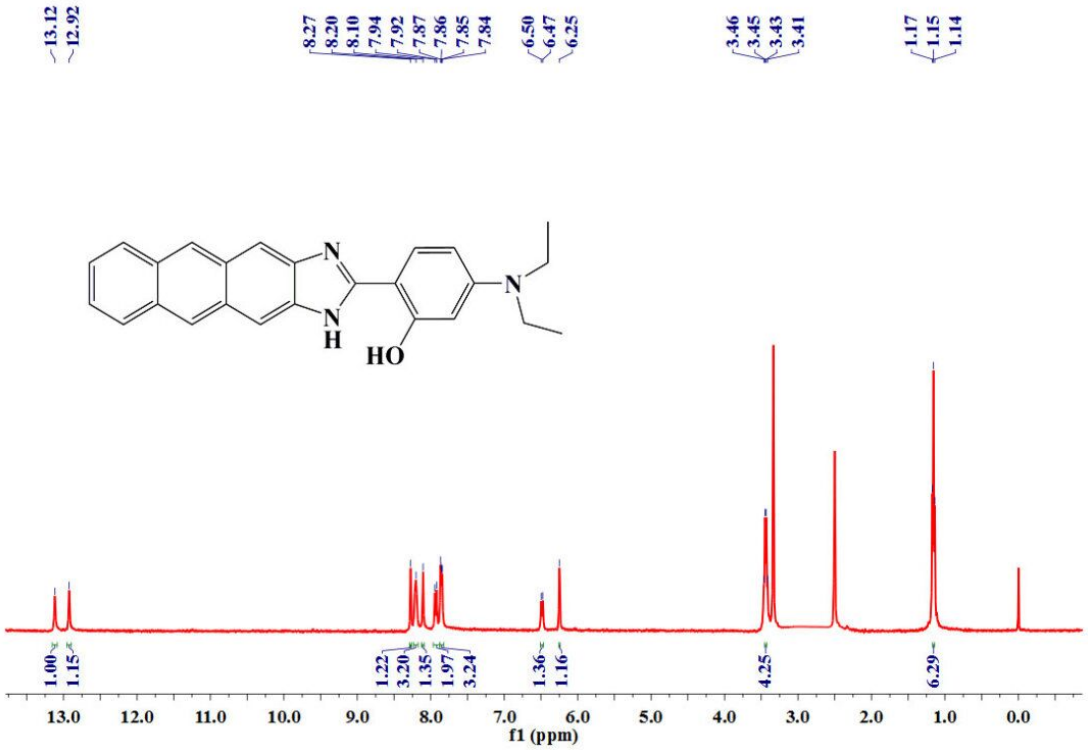

Fig. S1 ^{1}H NMR spectra of **S**.

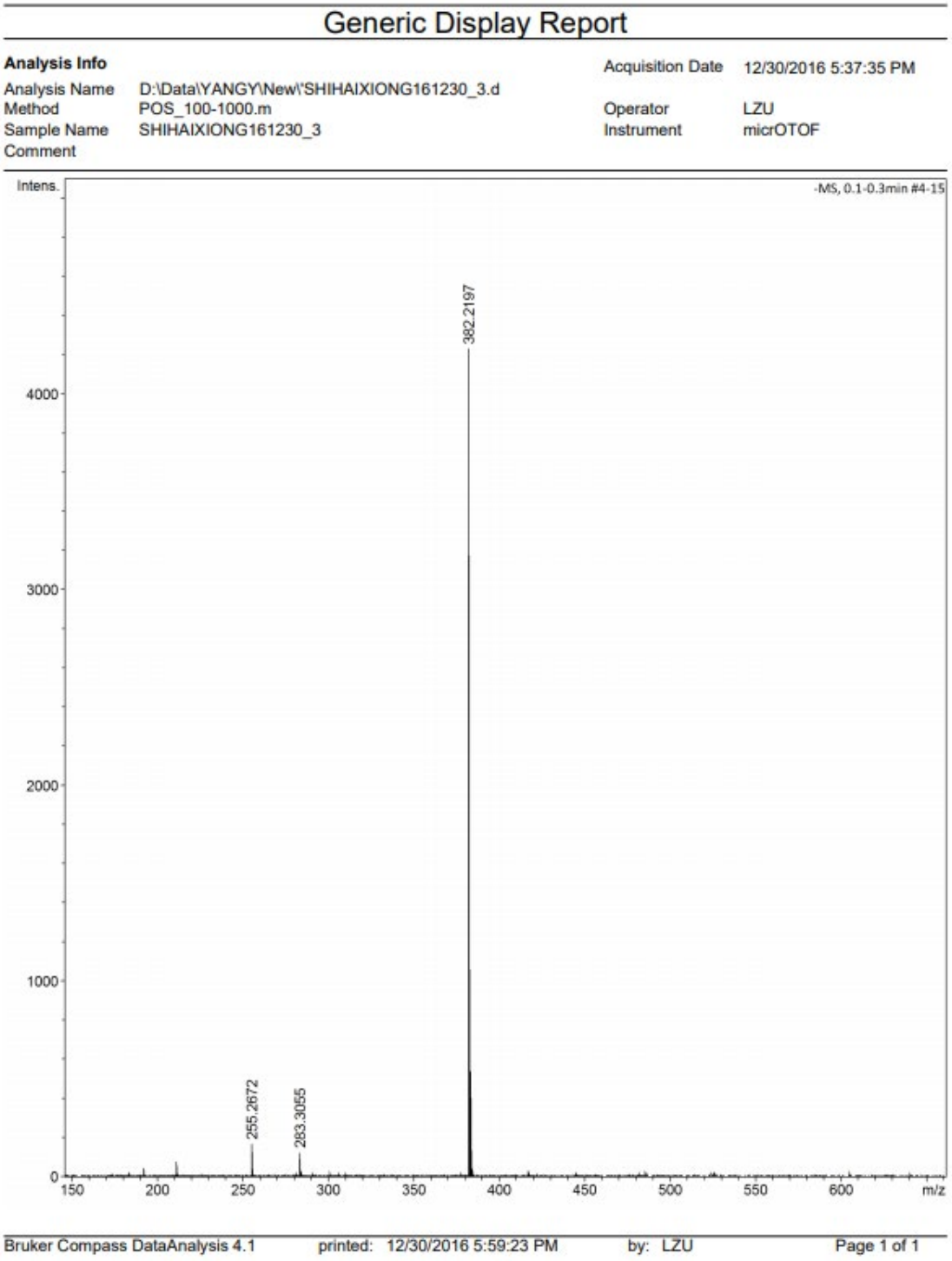

Fig. S2 ESI-MS spectrum of **S**.

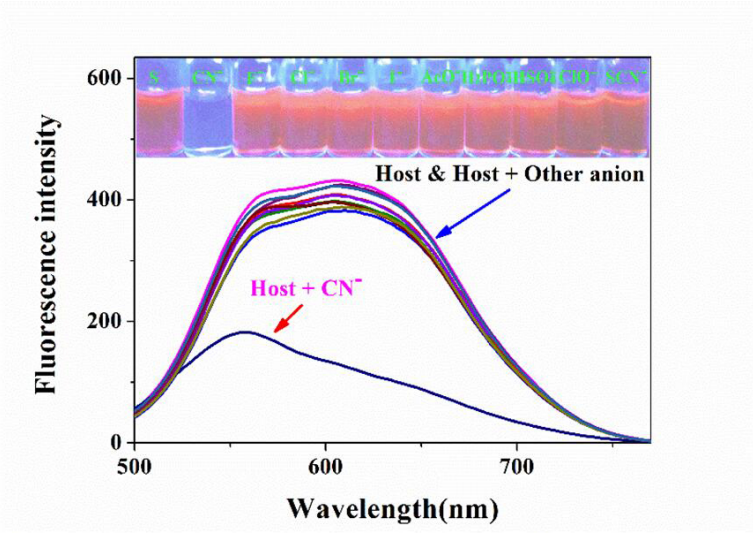

Fig. S3 Fluorescence spectra of **S** (20 uM) upon addition of various anions in DMSO / H_2O (v: v = 7: 3) solution. Inset shows the fluorescence color changes is observed for **S** upon the addition of 50 equiv. of various anions.

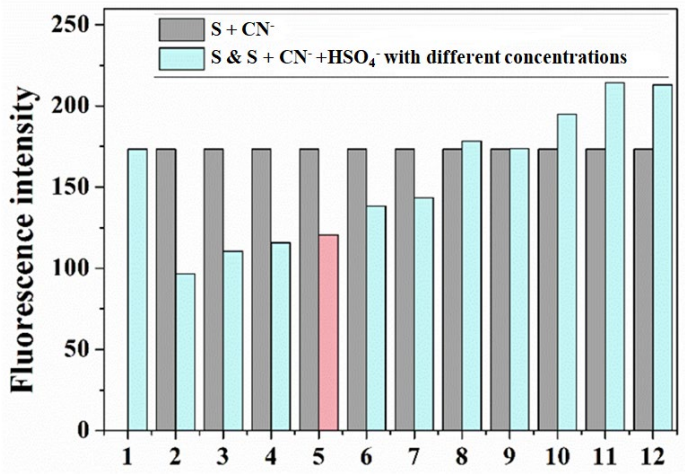

Fig. S4 Fluorescence of the sensor **S** (20 uM) and CN^- (50 equiv.) in the presence of different concentrations of HSO_4^- in DMSO/H_2O (v:v = 7:3) solution. From 1 to 12: **S** , **S** + CN^- , **S** + CN^- + 10% HSO_4^- , **S** + CN^- + 20% HSO_4^- , **S** + CN^- + 30% HSO_4^- , **S** + CN^- + 40% HSO_4^- , **S** + CN^- + 50% HSO_4^- , **S** + CN^- + 60% HSO_4^- , **S** + CN^- + 70% HSO_4^- , **S** + CN^- + 80% HSO_4^- , **S** + CN^- + 90% HSO_4^- , **S** + CN^- + 100% HSO_4^- , respectively.

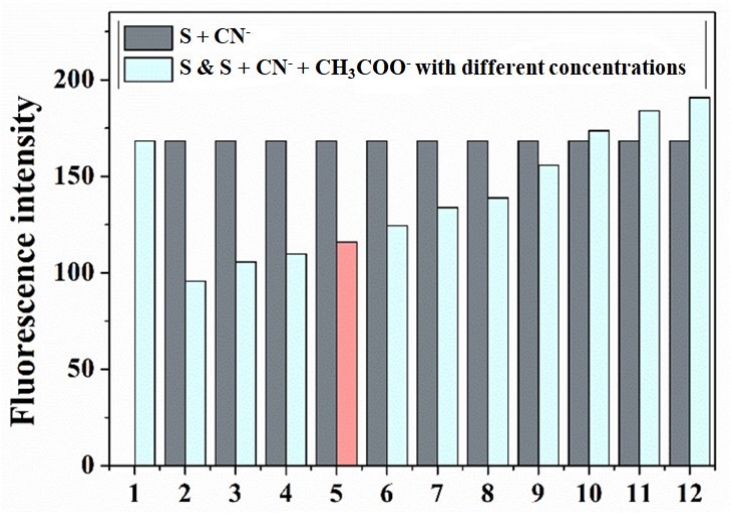

Fig. S5 Fluorescence of the sensor **S** (2×10^{-5} M) and CN^- (50 equiv.) in the presence of different concentrations of AcO^- in DMSO/H_2O (v:v = 7:3) solution. From 1 to 12: **S** , **S** + AcO^- , **S** + CN^- + 10% AcO^- , **S** + CN^- + 20% AcO^- , **S** + CN^- + 30% AcO^-, **S** + CN^- + 40% AcO^-, **S** + CN^- + 50% AcO^- , **S** + CN^- + 60% AcO^- , **S** + CN^- + 70% AcO^- , **S** + CN^- + 80% AcO^-, **S** + CN^- + 90% AcO^- , **S** + CN^- + 100% AcO^- , respectively.

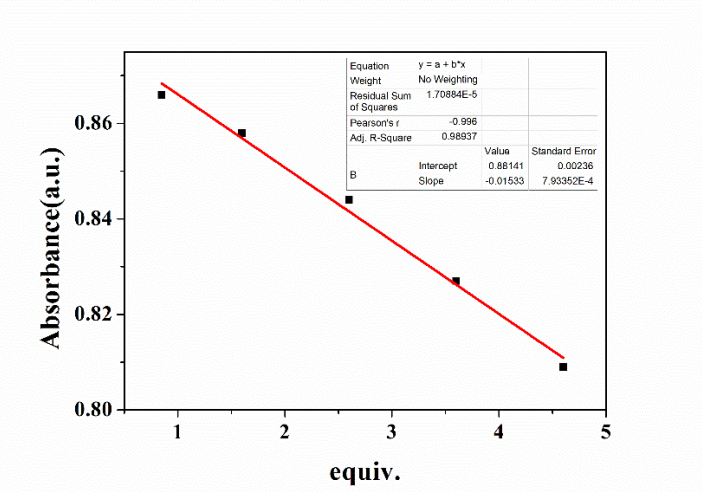

Fig. S6 Absorbance versus concentration plot of **S** (20 uM) upon the addition of various concentrations of CN^- to **S** in DMSO/H_2O (7:3, v/v) solution.

Linear Equation: $Y = -0.0153 \times X + 0.8814$

$R^2 = 0.98937$

$S = 0.0153 \times 10^6$

$$\delta = \sqrt{\frac{\sum\left(A_0 - A_1\right)^2}{N-1}} = 0.0011 \ (N = 20)$$

$$K = 3$$

$$LOD = K \times \delta / S = 2.16 \times 10^{-7}\ M$$

$\mathbf{A_0}$ is the absorbance intensity of **S**; $\mathbf{A_1}$ is the absorption intensity of **S** in the presence of CN^- (0.1 M) in DMSO/H_2O (7:3, v/v) solution.

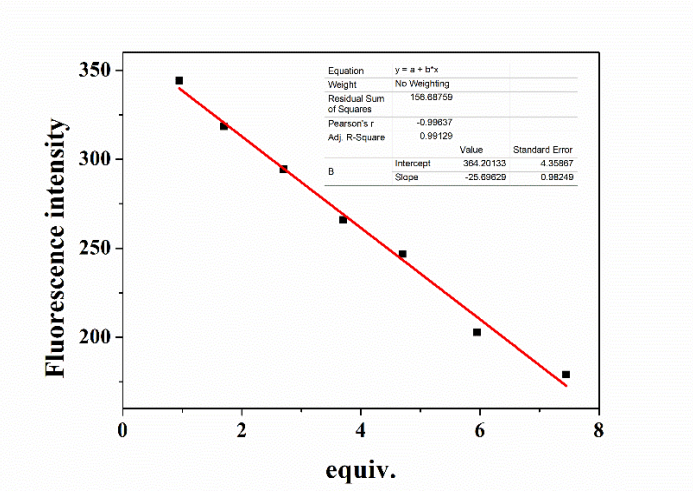

Fig. S7 Fluorescence intensity versus concentration plot of **S** (20 uM) upon the addition of various concentrations of CN^- to **S** in DMSO/H_2O (7:3, v/v) solution.

Linear Equation: $$Y = -26.6963 \times X - 242.778$$

$$R^2 = 0.99129$$

$$S = 26.6963 \times 10^6$$

$$\delta = \sqrt{\frac{\sum\left(F_0 - F_1\right)^2}{N-1}} = 1.7274\ (N = 20)$$

$$K = 3$$

$$LOD = K \times \delta / S = 1.94 \times 10^{-7}\ M$$

$\mathbf{F_0}$ is the absorbance intensity of **S**; $\mathbf{F_1}$ is the absorption intensity of **S** in the presence of CN^- (0.1 M) in DMSO/H_2O (7:3, v/v) solution.

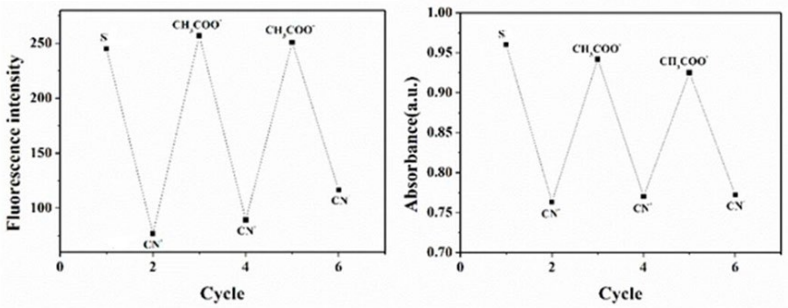

Fig. S8 Fluorescence intensity (left) and reversible switching cycles of absorbance intensity (right)

by alternate addition of CN^- and CH_3COO^- in DMSO/H_2O (v:v = 7:3) solution.

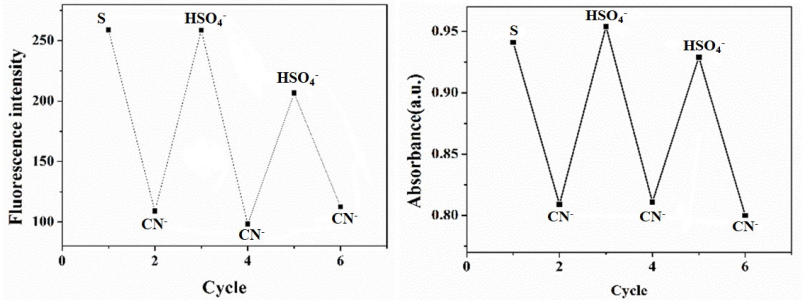

Fig. S9 Fluorescence intensity (left) and reversible switching cycles of absorbance intensity (right) by alternate addition of CN^- and HSO_4^- in DMSO/H_2O (v:v = 7:3) solution.

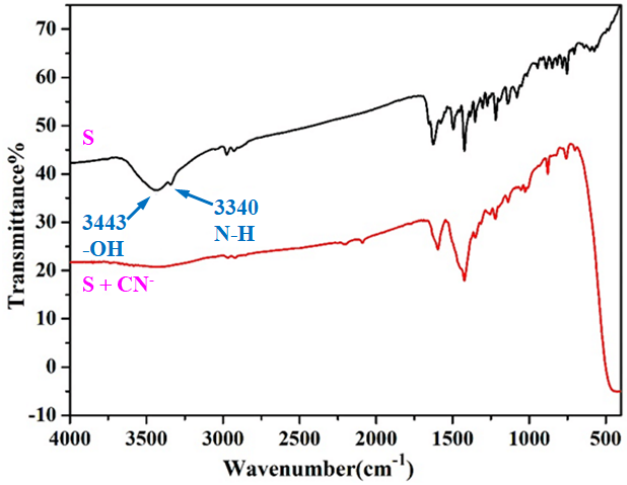

Fig. S10 FT-IR spectra of sensor **S** and **S**-CN^-.

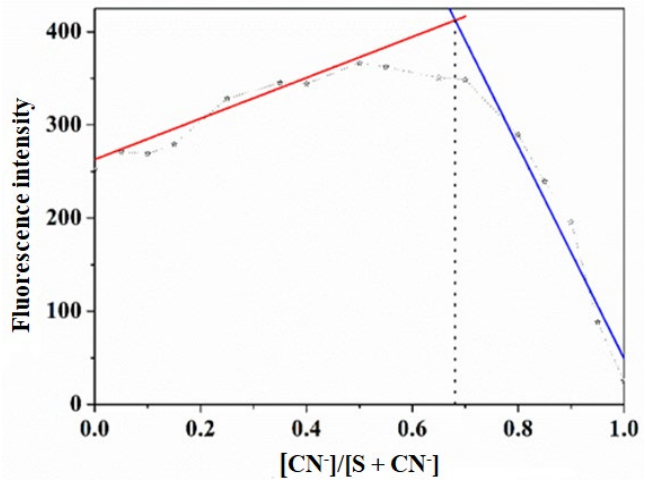

Fig. S11 The Job's plot of sensor **S** on addition of CN^- in DMSO/H_2O (v:v = 7:3) solution.

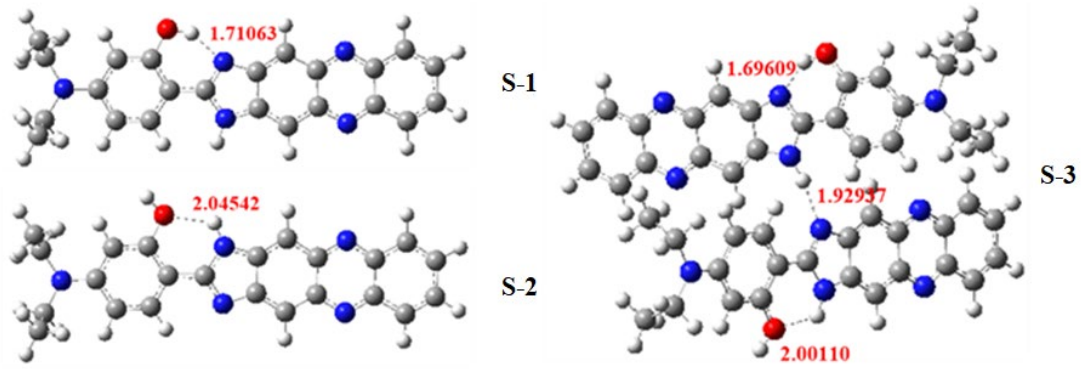

Fig. S12 Optimized structures of **S-1**, **S-2** and **S-3**.

Table S1 The energy of **S-1**, **S-2** and **S-3**.

Energy of Structures	E（a.u.）	H（a.u.）	G（a.u.）
S-1	-1237.7041	-1237.6792	-1237.7589
S-2	-1237.7532	-1237.7285	-1237.8076
S-3	-2475.5116	-2475.4611	-2475.6041