Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

SUPPORTING INFORMATION

Tailoring the HSO_4^- anion hybrid receptor based on phenazine derivative

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The general procedure for fluorescence spectra experiments

The solution of sensor PD (2.0×10^{-5} M) in DMSO/ethaonal (1:4,v/v) was prepared and stored in a dry atmosphere. The solution was used for all specification studies, all analytical substrates (1.0×10^{-2} M) were prepared in deionized water with HEPES buffer solutions (pH=7.2). All fluorescence spectra were performed in DMSO/ethanol/H_2O (1:8:1,v/v/v) solution via Shimadzu RF-5301 spectrometer.

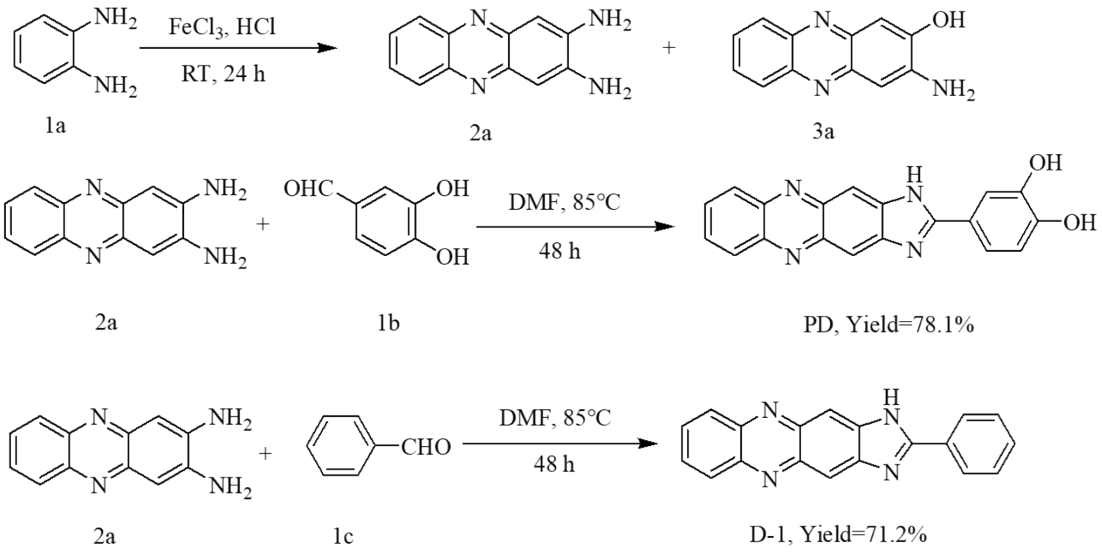
Preparation of Starting Materials

o-phenylenediamine(1a), 3,4-dihydroxybenzaldehyde(1b) and benzaldehyde (1c) were commercially available. 2,3-diamino-phenazine 2a and 3a was prepared according to literature[1].

Synthesis compound PD and D-1

Intermediate(2a) 2,3-diamino-phenazine (0.42g, 2mmol), 3,4-dihydroxybenzaldehyde (0.35g, 2.5mmol) and acetic acid (1-2mL) as the catalyst were mixed in hot absolute DMF (20 mL).The solution was mechanically stirred for 24 hours under continuous refluxing conditions, then the dark brown precipitate was achieved by filtrating the mixture after cooling to room temperature, finally alternately washed with hot absolute ethanol and deionized water five times, then recrystallized with DMF/H_2O(5:3,v/v) to get dark brown powdery product compound PD. The

control compounds D-1 was synthesized according to the reported literature[2,3]. The synthetic diagram could be shown in Scheme S1.



Scheme S1 Synthesis of compound PD and control compound D-1

Solvent screening

At firstly, we investigated the various solvent effect on the fluorescence intensity and lifetime of the PD, including water, methanol, ethanol, acetone, dichloromethane (DCM), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), ethyl acetate, and acetonitrile. As shown in Fig. S1, the PD (2.0×10^{-4} M) could completely dissolve in Dimethyl sulfoxide and N, N-Dimethyl acrylamide and partly dissolve in other different solvent together with some apparent precipitation. It is a pity that no fluorescence also been found in the water and dichloromethane (DCM) solvent. However, the maximum fluorescence emission intensity and the longer fluorescence lifetime of the PD appeared in the ethanol solvent as shown in Fig.S 2. According to the previous research works, taking the preferable solubility and fluorescence

characteristic into consideration to choose the ethanol as the solvent under the help of DMSO as the solubilizer. In view of water system could be beneficial to the interaction between the receptor and anions, the results suggested that with the water content increasing, the fluorescence emission intensity at 535 nm reduced gradually. The emission intensity was maximized when the water content reached 10%. Finally, we selected the minimal integer fraction DMSO/ethanol/H_2O (1:8:1 v/v/v) system as the optimal mixed solvent as shown in Fig.S3. Hence, we carried out a series of experiments in DMSO/ethanol/H2O (1:8:1 v/v/v) HEPES buffered solution (pH 7. 2).

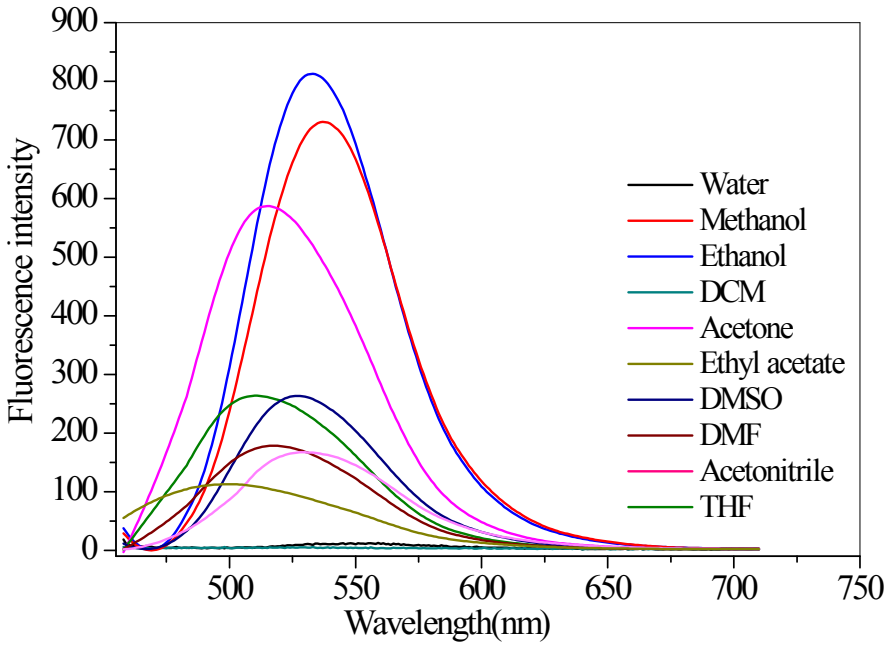


Figure S1The response fluorescence intensity PD (20 μM) were present in diffrent solvent solution.Insert : Dissolve situation of PD appeared in various solvent.

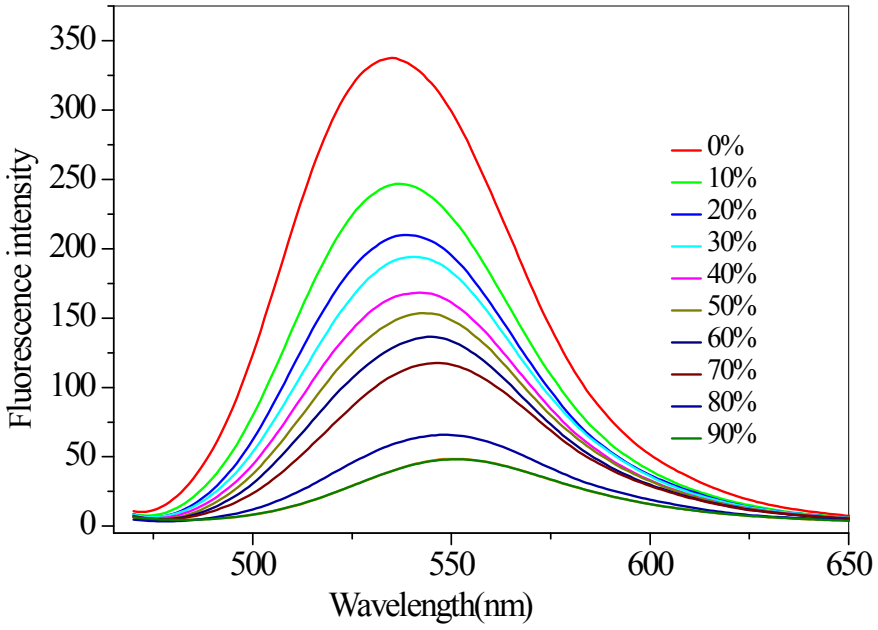


Figure S 2 The response fluorescence intensity PD (20 μM) at different water volume fractions (Vol%)Insert From 1 to 10:0,10%,20%,30%,40%,50%,60%,70%,80%,90%.

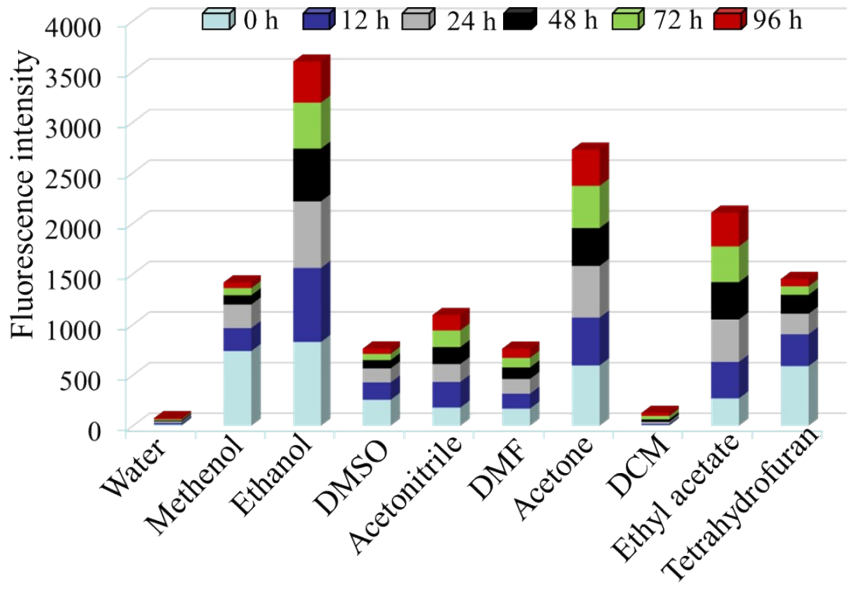


Fig S3. Fluorescence response of the PD (2.0×10^{-4} M) in the presence of various solvent and different times (Ex = 450 nm, 0 h,12 h,24 h,48 h,72 h,96 h)

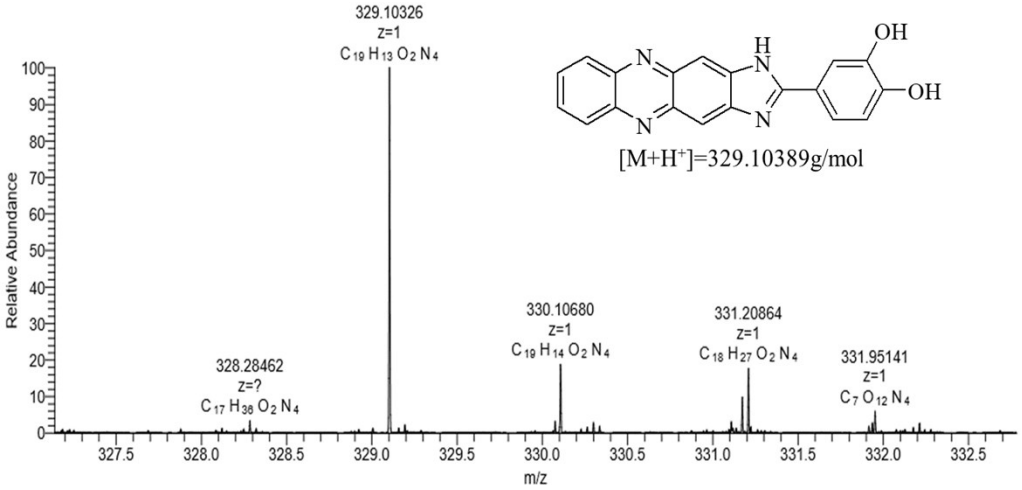


Figure S4 The ESI-MS of PD: [M+H+] = 329.10326 (ESI-MS m/z: [M+H+] Calcd for C19H12N4O2 329.10389; Found 329.10326)

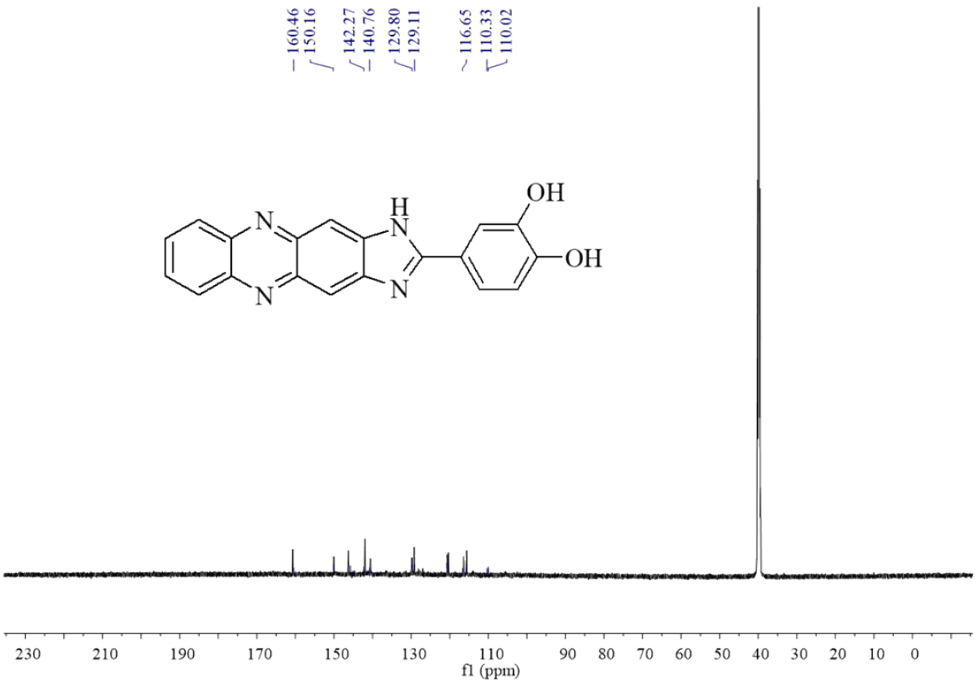


Figure S5 ^{13}C NMR spectrum (150 MHz, DMSO-d_6, 293 K) of PD

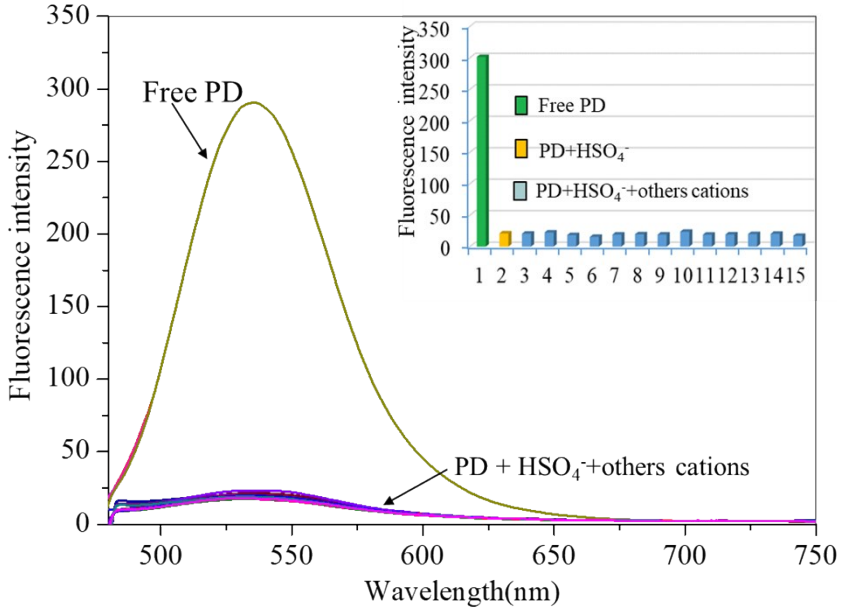


Fig S6. Fluorescence response of the PD-HSO_4^- in the presence of various caions. From 1 to 15: PD, PD-HSO_4^-, Zn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Ba^{2+}, Cr^{3+}in three solvent system DMSO/Ethanol/H_2O (1:8:1, v/v/v) solution

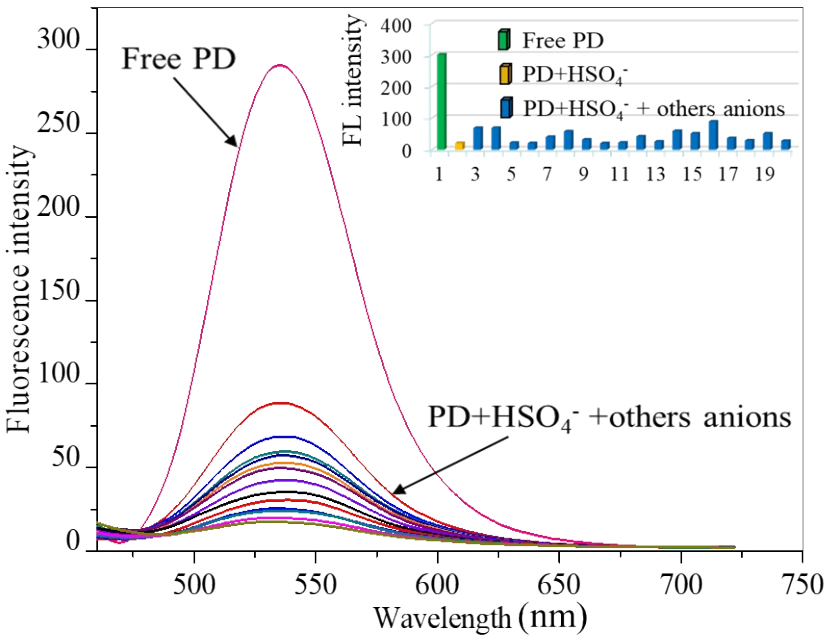


Fig S7. Fluorescence response of the PD- HSO_4^- in the presence of various anions. From1 to 20: PD, PD-HSO_4^-, PD, ClO_4^-, HSO_4^-, F^-, Cl^-, Br^-, I^-, CH_3COO^-, $H_2PO_4^-$, CN^-,SCN^-,

NO_3^-,SO_3^{2-},NO_2^-,$P_2O_7^{4-}$,PO_4^{3-},$C_2O_4^{2-}$,$S_2O_3^{2-}$,CO_3^{2-},HPO_4^{2-})in in three solvent system DMSO/Ethanol/H_2O (1:8:1, v/v/v) solution

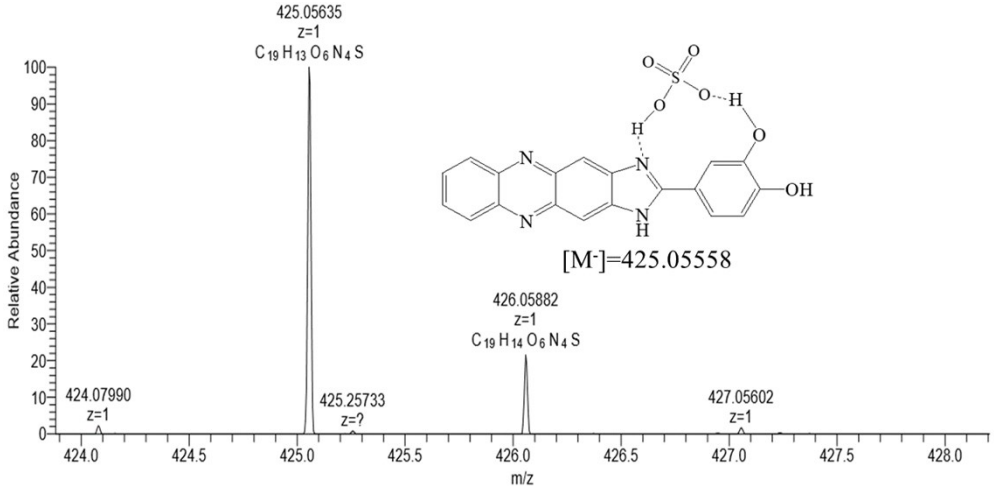


Fig. S8 ESI-MS of PD-HSO_4^- [M^-]=425.05635 (ESI-MS m/z: [M^-]Calcd for $C_{19}H_{13}N_4O_6S$ 425.05558; Found 425.05635)

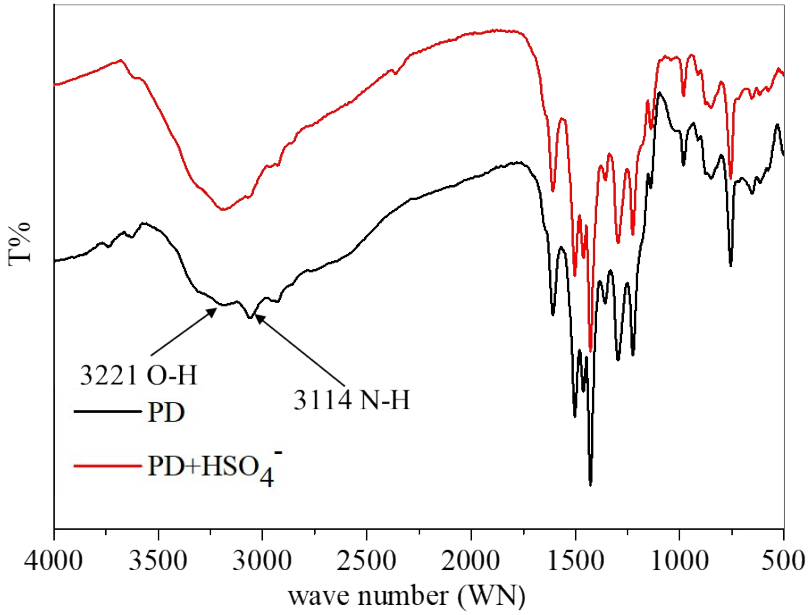


Fig S9 IR spectrum of PD-HSO_4^- complex

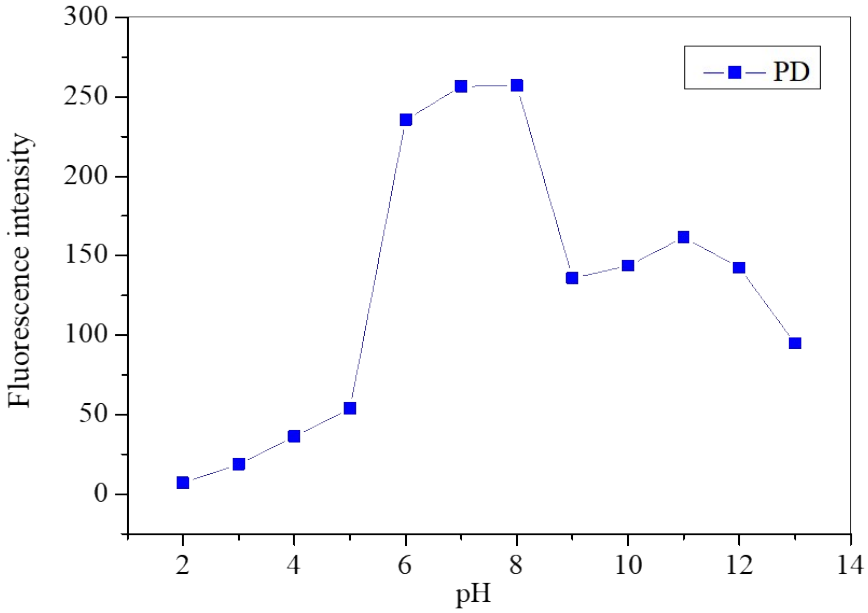


Fig S10 The pH-Dependent fluorescence responses of PD (2×10^{-5} M) (pH from 1 to 13).

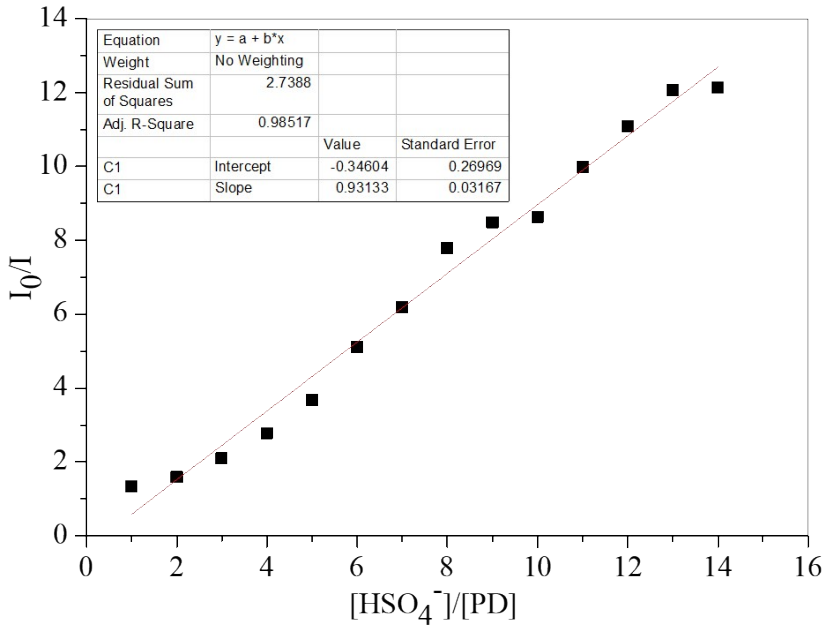


Fig S11 The linear fitting equation and the detection limit of PD to the HSO_4^-

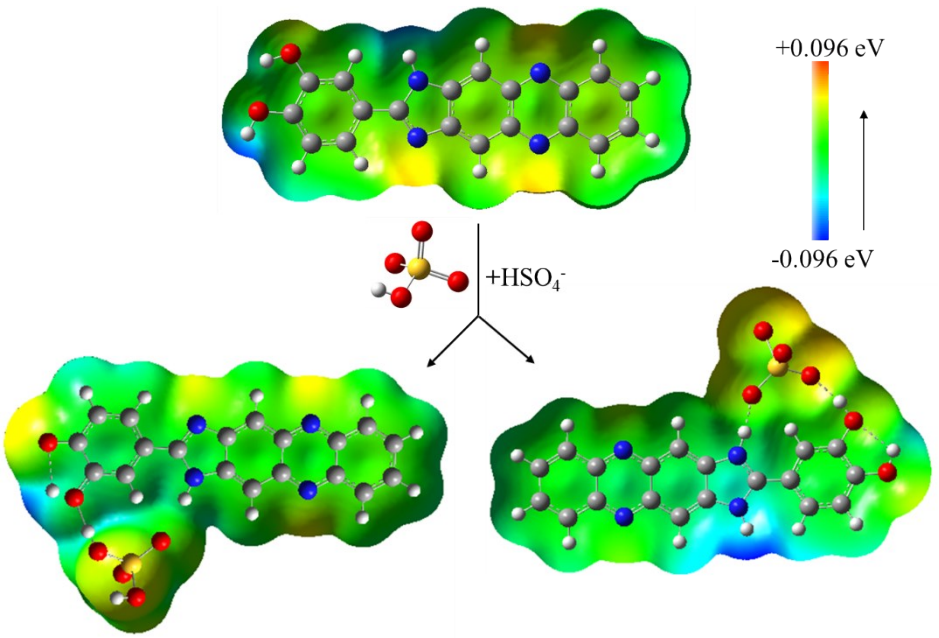


Fig S12 A diagrammatic figure of electron density distribution for model 1 (left) and model 2 (right).

Table S1 The optimization of practical orientation of the molecular structure in spatial distribution for the PD-HSO_4^-(mode 2)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.804625	1.286816	-0.010912
2	6	0	-6.500231	1.705173	-0.019335
3	6	0	-5.443493	0.745517	-0.014882
4	6	0	-5.770287	-0.664498	-0.001038
5	6	0	-7.141486	-1.059530	0.007336

6	6	0	-8.127945	-0.108545	0.002426
7	6	0	-3.509145	-1.189921	-0.004615
8	6	0	-3.180353	0.226122	-0.019162
9	6	0	-1.822826	0.654793	-0.030226
10	1	0	-1.597142	1.709858	-0.041848
11	6	0	-0.862554	-0.320884	-0.026042
12	6	0	-1.187128	-1.718113	-0.008247
13	6	0	-2.477576	-2.172263	0.001820
14	1	0	-8.606799	2.011765	-0.014242
15	1	0	-6.224613	2.749505	-0.029433
16	1	0	-7.356104	-2.118180	0.017553
17	1	0	-9.167499	-0.406218	0.008761
18	1	0	-2.757038	-3.214816	0.014337
19	7	0	-4.800387	-1.605849	0.003925
20	7	0	-4.159787	1.165171	-0.023758
21	7	0	0.536805	-0.241963	-0.032606
22	6	0	1.078733	-1.481284	-0.025141
23	7	0	0.049954	-2.386229	-0.008318
24	1	0	0.170482	-3.382162	-0.042965
25	6	0	2.485497	-1.783801	-0.023736
26	6	0	3.395930	-0.731905	-0.273996
27	6	0	2.976489	-3.078217	0.253517
28	6	0	4.755745	-0.960627	-0.211640
29	1	0	3.048314	0.256275	-0.522627
30	6	0	4.347522	-3.310450	0.286507

31	1	0	2.306013	-3.897994	0.475490
32	6	0	5.237523	-2.259518	0.059950
33	8	0	6.587336	-2.474132	0.106345
34	1	0	7.060847	-1.632827	-0.058267
35	16	0	3.118768	3.021700	0.043247
36	8	0	2.891205	4.623989	-0.518674
37	8	0	3.376969	3.596310	1.611626
38	8	0	4.402836	2.283148	-0.649821
39	1	0	4.749147	-4.288593	0.503624
40	8	0	5.728536	-0.009759	-0.398944
41	1	0	5.356010	0.911275	-0.477940
42	1	0	1.071921	0.648422	-0.024779
43	8	0	1.758285	2.119868	-0.116760

Table S2 The optimization of Standard orientation of the molecular structure in spatial distribution for the PD-HSO_4^-(mode 2)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.804625	1.286816	-0.010912
2	6	0	-6.500231	1.705173	-0.019335
3	6	0	-5.443493	0.745517	-0.014882
4	6	0	-5.770287	-0.664498	-0.001038
5	6	0	-7.141486	-1.059530	0.007336

6	6	0	-8.127945	-0.108545	0.002426
7	6	0	-3.509145	-1.189921	-0.004615
8	6	0	-3.180353	0.226122	-0.019162
9	6	0	-1.822826	0.654793	-0.030226
10	1	0	-1.597142	1.709858	-0.041848
11	6	0	-0.862554	-0.320884	-0.026042
12	6	0	-1.187128	-1.718113	-0.008247
13	6	0	-2.477576	-2.172263	0.001820
14	1	0	-8.606799	2.011765	-0.014242
15	1	0	-6.224613	2.749505	-0.029433
16	1	0	-7.356104	-2.118180	0.017553
17	1	0	-9.167499	-0.406218	0.008761
18	1	0	-2.757038	-3.214816	0.014337
19	7	0	-4.800387	-1.605849	0.003925
20	7	0	-4.159787	1.165171	-0.023758
21	7	0	0.536805	-0.241963	-0.032606
22	6	0	1.078733	-1.481284	-0.025141
23	7	0	0.049954	-2.386229	-0.008318
24	1	0	0.170482	-3.382162	-0.042965
25	6	0	2.485497	-1.783801	-0.023736
26	6	0	3.395930	-0.731905	-0.273996
27	6	0	2.976489	-3.078217	0.253517
28	6	0	4.755745	-0.960627	-0.211640
29	1	0	3.048314	0.256275	-0.522627
30	6	0	4.347522	-3.310450	0.286507

31	1	0	2.306013	-3.897994	0.475490
32	6	0	5.237523	-2.259518	0.059950
33	8	0	6.587336	-2.474132	0.106345
34	1	0	7.060847	-1.632827	-0.058267
35	16	0	3.118768	3.021700	0.043247
36	8	0	2.891205	4.623989	-0.518674
37	8	0	3.376969	3.596310	1.611626
38	8	0	4.402836	2.283148	-0.649821
39	1	0	4.749147	-4.288593	0.503624
40	8	0	5.728536	-0.009759	-0.398944
41	1	0	5.356010	0.911275	-0.477940
42	1	0	1.071921	0.648422	-0.024779
43	8	0	1.758285	2.119868	-0.116760

Table S3 The optimization of practical orientation of the molecular structure in spatial distribution for the PD-HSO_4^-(mode 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.158675	0.184070	0.054010
2	6	0	-7.145585	1.111640	0.072815
3	6	0	-5.787314	0.681977	0.034779
4	6	0	-5.494008	-0.730707	-0.023781

5	6	0	-6.566520	-1.661084	-0.040972
6	6	0	-7.866839	-1.211589	-0.002959
7	6	0	-3.216176	-0.273048	-0.045345
8	6	0	-3.511592	1.154292	0.015455
9	6	0	-2.460272	2.104067	0.034697
10	1	0	-2.690609	3.157207	0.081430
11	6	0	-1.153709	1.630577	-0.009147
12	6	0	-0.875822	0.209336	-0.073860
13	6	0	-1.862146	-0.736757	-0.089321
14	1	0	-9.190123	0.506530	0.082789
15	1	0	-7.332827	2.174632	0.116289
16	1	0	-6.318703	-2.711485	-0.084121
17	1	0	-8.683333	-1.920245	-0.015989
18	1	0	-1.676191	-1.798923	-0.131303
19	7	0	-4.211740	-1.182155	-0.063228
20	7	0	-4.793408	1.601016	0.053907
21	7	0	0.024649	2.339985	-0.000296
22	6	0	1.013999	1.398022	-0.065133
23	7	0	0.511339	0.121581	-0.106059
24	1	0	1.057924	-0.760549	-0.140396
25	6	0	2.413298	1.729581	-0.069916
26	6	0	2.811275	3.086749	0.094951
27	6	0	3.381998	0.731646	-0.208718
28	6	0	4.158330	3.403710	0.135246
29	1	0	2.051047	3.846275	0.191157

30	6	0	4.741804	1.031052	-0.144082
31	1	0	3.093392	-0.290645	-0.382689
32	6	0	5.131715	2.399227	0.024020
33	1	0	4.472528	4.432082	0.260508
34	8	0	5.707668	0.101026	-0.224292
35	1	0	5.342240	-0.842549	-0.282698
36	8	0	6.470737	2.649078	0.068559
37	1	0	6.680762	3.592386	0.188252
38	16	0	3.259563	-2.935532	0.192833
39	8	0	3.347077	-3.244006	1.770598
40	8	0	3.109897	-4.526327	-0.684780
41	1	0	2.335329	-4.390286	-1.277108
42	8	0	4.586462	-2.236996	-0.478195
43	8	0	1.861551	-2.198457	-0.331660

Table S4 The optimization of Standard orientation of the molecular structure in spatial distribution for the PD-HSO_4^-(mode 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	8.158675	-0.184070	0.054010
2	6	0	7.145585	-1.111640	0.072815

3	6	0	5.787314	-0.681977	0.034779
4	6	0	5.494008	0.730707	-0.023781
5	6	0	6.566520	1.661084	-0.040972
6	6	0	7.866839	1.211589	-0.002959
7	6	0	3.216176	0.273048	-0.045345
8	6	0	3.511592	-1.154292	0.015455
9	6	0	2.460271	-2.104067	0.034697
10	1	0	2.690609	-3.157207	0.081430
11	6	0	1.153709	-1.630577	-0.009147
12	6	0	0.875822	-0.209336	-0.073860
13	6	0	1.862146	0.736757	-0.089321
14	1	0	9.190123	-0.506530	0.082789
15	1	0	7.332827	-2.174632	0.116289
16	1	0	6.318703	2.711485	-0.084121
17	1	0	8.683333	1.920245	-0.015989
18	1	0	1.676191	1.798923	-0.131303
19	7	0	4.211740	1.182155	-0.063228
20	7	0	4.793408	-1.601016	0.053907
21	7	0	-0.024649	-2.339985	-0.000296
22	6	0	-1.013999	-1.398022	-0.065133
23	7	0	-0.511339	-0.121581	-0.106059
24	1	0	-1.057924	0.760549	-0.140396
25	6	0	-2.413298	-1.729581	-0.069916
26	6	0	-2.811275	-3.086749	0.094951
27	6	0	-3.381998	-0.731646	-0.208718

28	6	0	-4.158330	-3.403710	0.135246
29	1	0	-2.051047	-3.846275	0.191157
30	6	0	-4.741804	-1.031052	-0.144082
31	1	0	-3.093392	0.290645	-0.382689
32	6	0	-5.131715	-2.399227	0.024020
33	1	0	-4.472528	-4.432082	0.260508
34	8	0	-5.707668	-0.101026	-0.224292
35	1	0	-5.342240	0.842549	-0.282698
36	8	0	-6.470737	-2.649078	0.068559
37	1	0	-6.680762	-3.592386	0.188252
38	16	0	-3.259563	2.935532	0.192833
39	8	0	-3.347077	3.244006	1.770598
40	8	0	-3.109897	4.526327	-0.684780
41	1	0	-2.335329	4.390286	-1.277108
42	8	0	-4.586462	2.236996	-0.478195
43	8	0	-1.861551	2.198457	-0.331660

Table S5 The optimization of practical orientation of the molecular structure in spatial distribution for the PD.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.804625	1.286816	-0.010912

2	6	0	-6.500231	1.705173	-0.019335
3	6	0	-5.443493	0.745517	-0.014882
4	6	0	-5.770287	-0.664498	-0.001038
5	6	0	-7.141486	-1.059530	0.007336
6	6	0	-8.127945	-0.108545	0.002426
7	6	0	-3.509145	-1.189921	-0.004615
8	6	0	-3.180353	0.226122	-0.019162
9	6	0	-1.822826	0.654793	-0.030226
10	1	0	-1.597142	1.709858	-0.041848
11	6	0	-0.862554	-0.320884	-0.026042
12	6	0	-1.187128	-1.718113	-0.008247
13	6	0	-2.477576	-2.172263	0.001820
14	1	0	-8.606799	2.011765	-0.014242
15	1	0	-6.224613	2.749505	-0.029433
16	1	0	-7.356104	-2.118180	0.017553
17	1	0	-9.167499	-0.406218	0.008761
18	1	0	-2.757038	-3.214816	0.014337
19	7	0	-4.800387	-1.605849	0.003925
20	7	0	-4.159787	1.165171	-0.023758
21	7	0	0.536805	-0.241963	-0.032606
22	6	0	1.078733	-1.481284	-0.025141
23	7	0	0.049954	-2.386229	-0.008318
24	1	0	0.170482	-3.382162	-0.042965
25	6	0	2.485497	-1.783801	-0.023736
26	6	0	3.395930	-0.731905	-0.273996

27	6	0	2.976489	-3.078217	0.253517
28	6	0	4.755745	-0.960627	-0.211640
29	1	0	3.048314	0.256275	-0.522627
30	6	0	4.347522	-3.310450	0.286507
31	1	0	2.306013	-3.897994	0.475490
32	6	0	5.237523	-2.259518	0.059950
33	8	0	6.587336	-2.474132	0.106345
34	1	0	7.060847	-1.632827	-0.058267
35	16	0	3.118768	3.021700	0.043247
36	8	0	2.891205	4.623989	-0.518674
37	8	0	3.376969	3.596310	1.611626
38	8	0	4.402836	2.283148	-0.649821
39	1	0	4.749147	-4.288593	0.503624
40	8	0	5.728536	-0.009759	-0.398944
41	1	0	5.356010	0.911275	-0.477940
42	1	0	1.071921	0.648422	-0.024779
43	8	0	1.758285	2.119868	-0.116760

Table S6 The optimization of standard orientation of the molecular structure in spatial distribution for the PD.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

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1	6	0	-7.804625	1.286816	-0.010912
2	6	0	-6.500231	1.705173	-0.019335
3	6	0	-5.443493	0.745517	-0.014882
4	6	0	-5.770287	-0.664498	-0.001038
5	6	0	-7.141486	-1.059530	0.007336
6	6	0	-8.127945	-0.108545	0.002426
7	6	0	-3.509145	-1.189921	-0.004615
8	6	0	-3.180353	0.226122	-0.019162
9	6	0	-1.822826	0.654793	-0.030226
10	1	0	-1.597142	1.709858	-0.041848
11	6	0	-0.862554	-0.320884	-0.026042
12	6	0	-1.187128	-1.718113	-0.008247
13	6	0	-2.477576	-2.172263	0.001820
14	1	0	-8.606799	2.011765	-0.014242
15	1	0	-6.224613	2.749505	-0.029433
16	1	0	-7.356104	-2.118180	0.017553
17	1	0	-9.167499	-0.406218	0.008761
18	1	0	-2.757038	-3.214816	0.014337
19	7	0	-4.800387	-1.605849	0.003925
20	7	0	-4.159787	1.165171	-0.023758
21	7	0	0.536805	-0.241963	-0.032606
22	6	0	1.078733	-1.481284	-0.025141
23	7	0	0.049954	-2.386229	-0.008318
24	1	0	0.170482	-3.382162	-0.042965

25	6	0	2.485497	-1.783801	-0.023736
26	6	0	3.395930	-0.731905	-0.273996
27	6	0	2.976489	-3.078217	0.253517
28	6	0	4.755745	-0.960627	-0.211640
29	1	0	3.048314	0.256275	-0.522627
30	6	0	4.347522	-3.310450	0.286507
31	1	0	2.306013	-3.897994	0.475490
32	6	0	5.237523	-2.259518	0.059950
33	8	0	6.587336	-2.474132	0.106345
34	1	0	7.060847	-1.632827	-0.058267
35	16	0	3.118768	3.021700	0.043247
36	8	0	2.891205	4.623989	-0.518674
37	8	0	3.376969	3.596310	1.611626
38	8	0	4.402836	2.283148	-0.649821
39	1	0	4.749147	-4.288593	0.503624
40	8	0	5.728536	-0.009759	-0.398944
41	1	0	5.356010	0.911275	-0.477940
42	1	0	1.071921	0.648422	-0.024779
43	8	0	1.758285	2.119868	-0.116760

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