Electronic Supporting Information

Unprecedented Observation and Characterization of Sulfur-Centred Bifurcated Hydrogen Bonds

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Experimental

General. Unless otherwise noted, all chemicals were purchased and used without further purification, and all NMR experiments were measured on a JNM-ECZ600R/S3 (Jeol, Japan) (600 MHz) using CD_3CN as the solvent. Chemical shifts for ^1H NMR were referred to internal Me_4Si (0 ppm) as the standard. The Fourier-transform infrared (FT-IR) transmission spectra were measured by liquid-film method on a spectrometer (Thermofisher, IS50, USA) in the range of 4000-400 cm^{-1}. It has a resolution of 4 cm^{-1}, and each spectrum was an average of 64 scans. Geometry optimizations and single-point energies calculations in the ground state were using the DFT method with the B3LYP exchange-correlation functional in combination with the all-electron 6-311++G** basis set. The nature of all stationary points was confirmed by harmonic vibrational frequency analysis. Gibbs free energies of all optimized structures were calculated at 298.15 K and 1 atm. All DFT calculations were carried out using the GAUSSIAN09 package.

1. Variable-temperature NMR experiments (Figure 2 in the text).

Detailed procedure: A mixture of phenol (**1a**) (0.057 mmol, 5.3 mg, 5 μL) and CD_3CN (500 μL) was prepared as the test sample. Then the sample was measured on a JNM-ECZ600R/S3 (Jeol, Japan) (600 MHz) at 25 °C. Diphenyl sulfide **2a** (0.057 mmol, 10.6 mg) was added to the above-mentioned mixtrue, and then variable-temperature NMR experiments (25, 35, 45, 55, 65 and 75 °C) were conducted.

Results:

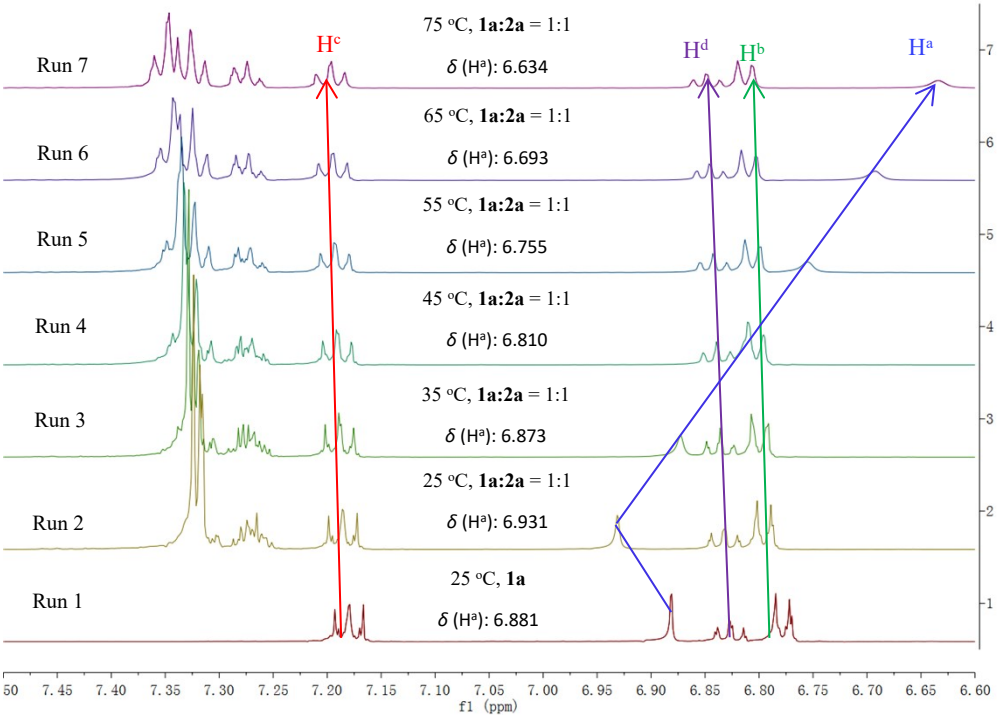


Figure S1 Variable-temperature NMR experiments

Conclusion: According to the figure S1, the O-H···S H-bond was possibly formed between phenol (**1a**) and diphenyl sulfide (**2a**)

2. Determination of stoichiometry between phenol (Host) and Ph_2S (Guest) studied by Job's plot experiments (Figure 3 in the text)

Detailed procedure: A stock solvent of phenol **1a** (1.75 mmol, 165.0 mg, 154 μL) in 3346 μL CD_3CN was prepared and the concentration of phenol **1a** is 0.50 mmol/mL. A stock solvent of diphenyl sulfide **2a** (1.75 mmol, 326.0 mg, 293 μL) in 3207 μL CD_3CN was prepared and the concentration of diphenyl sulfide **2a** is 0.50 mmol/mL. The solutions of the phenol **1a** (Host) and diphenyl sulfide **2a** (Guest) were mixed to NMR tubes according to certain proportions (Table S1). The chemical shift of OH in free phenol host is 6.981. Then the host-guest binding interactions was studied by the Job's plot method at 293 K.

Result:

Table S1. Experimental results of Job's Plot method (**Host: phenol; Guest: Ph_2S**).

Entry	Guest (μL)	Host (μL)	Mole fraction Host (X_{1a})	δ (-OH of **Host**) (ppm)	$\Delta\delta$ (ppm)	$X_{1a}*\Delta\delta$
1	0	500	1	6.981	0	0
2	50	450	0.9	6.979	0.002	0.0031
3	100	400	0.8	6.975	0.006	0.0062
4	150	350	0.7	6.973	0.008	0.0069
5	200	300	0.6	6.969	0.012	0.008
6	225	275	0.55	6.966	0.015	0.0081
7	250	250	0.5	6.964	0.017	0.0085
8	275	225	0.45	6.963	0.018	0.00825
9	300	200	0.4	6.961	0.02	0.0072
10	350	150	0.3	6.958	0.023	0.0056
11	400	100	0.2	6.95	0.031	0.0048
12	450	50	0.1	6.95	0.031	0.0018

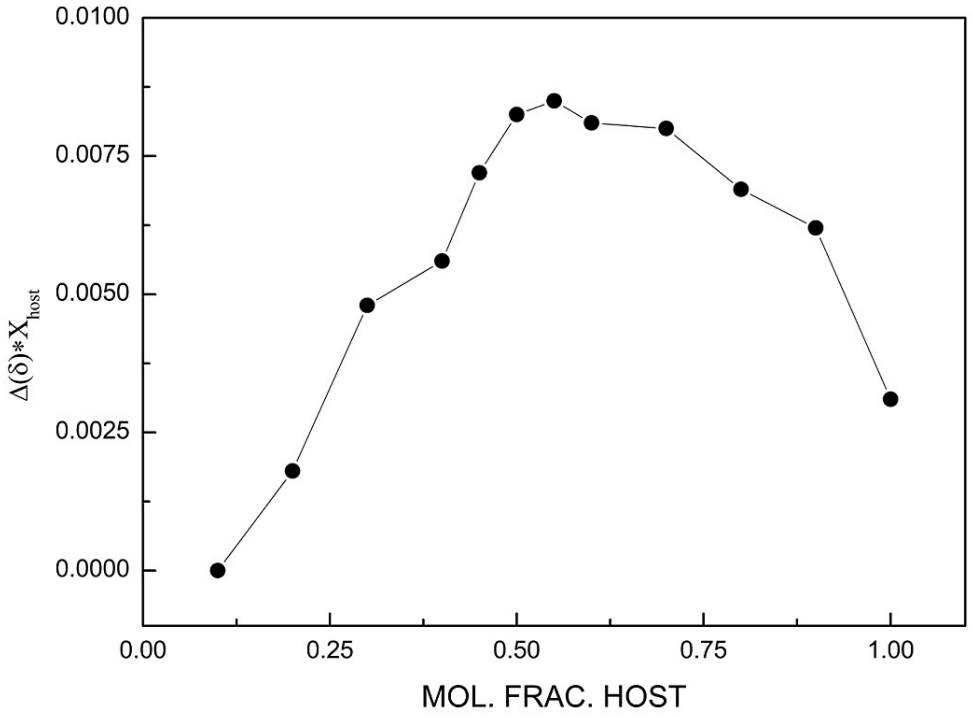


Figure S2. Job's plot

Conclusion: The maximum on the Job plot for Phenol (**1a**) is at X_{1a} = 0.55 (Figure S6), suggesting that both 1:1 and 2:1 binding complexes were possibly formed from phenol (**1a**) and diphenyl sulfide (**2a**)

3. Determination of stoichiometry between Phenol (Host) and Ph_2S (Guest) studied by ^1H NMR titration experiments (Figure 4 in the text)

Detailed procedure: phenol **1a** (0.114 mmol, 10.7 mg, 10μL) was dissolved in 490 μL CD_3CN and the concentration is 0.228 mmol/mL. Certain amount of diphenyl sulfide (**2a**) was added to the above solution according to table S2.

Result:

Table S2. ^1H NMR titration experiments

Entry	Concentration of **phenol** (mol/L)	Total Vol. (μL)	Concentration of **Ph_2S** (mol/L)	Equiv. of **Ph_2S**	δ (-OH of **phenol**) (ppm)
1	0.227	502	0.0238	0.105	6.916
2	0.226	504	0.0474	0.210	6.924
3	0.225	506	0.0708	0.315	6.93
4	0.224	508	0.0941	0.420	6.934
5	0.223	510	0.117	0.525	6.94
6	0.222	512	0.140	0.630	6.947
7	0.221	514	0.162	0.735	6.953
8	0.220	516	0.185	0.840	6.959
9	0.219	518	0.207	0.945	6.965
10	0.218	520	0.229	1.05	6.975
11	0.217	522.5	0.257	1.18	6.979
12	0.216	525	0.284	1.31	6.985
13	0.215	527.5	0.311	1.44	6.988
14	0.214	530	0.338	1.57	6.994
15	0.213	532.5	0.364	1.70	6.998
16	0.212	535	0.391	1.83	7.004
17	0.210	540	0.442	2.10	7.011
18	0.208	545	0.493	2.36	7.018
19	0.207	550	0.543	2.62	7.025
20	0.205	555	0.592	2.88	7.034
21	0.201	565	0.687	3.41	7.043
22	0.198	575	0.779	3.93	7.053
23	0.191	595	0.954	4.98	7.072

By using the free online tool, BindFit, which is available at http://supramolecular.org, our ^1H NMR titration experimental data were fitting with 1:1, 1:2 and 2:1 models and the links and figures are listed as below:

1:1 model

http://app.supramolecular.org/bindfit/view/1055db3a-f95b-4d05-bd5e-1121343e79b1

1:2 model

http://app.supramolecular.org/bindfit/view/f702cb8f-41c0-42ec-9cf9-e851ea600321

2:1 model

http://app.supramolecular.org/bindfit/view/4262ee35-bab1-4d3b-bae9-91e9ea9c38ea

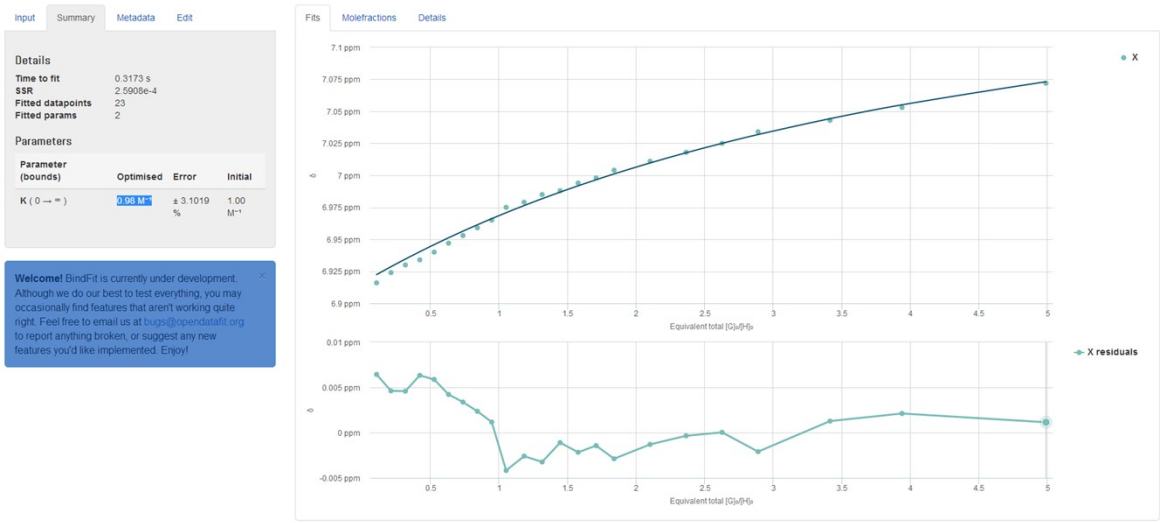


Figure S3 fitting curve of ^{1}H NMR titration experiments by 1:1 model

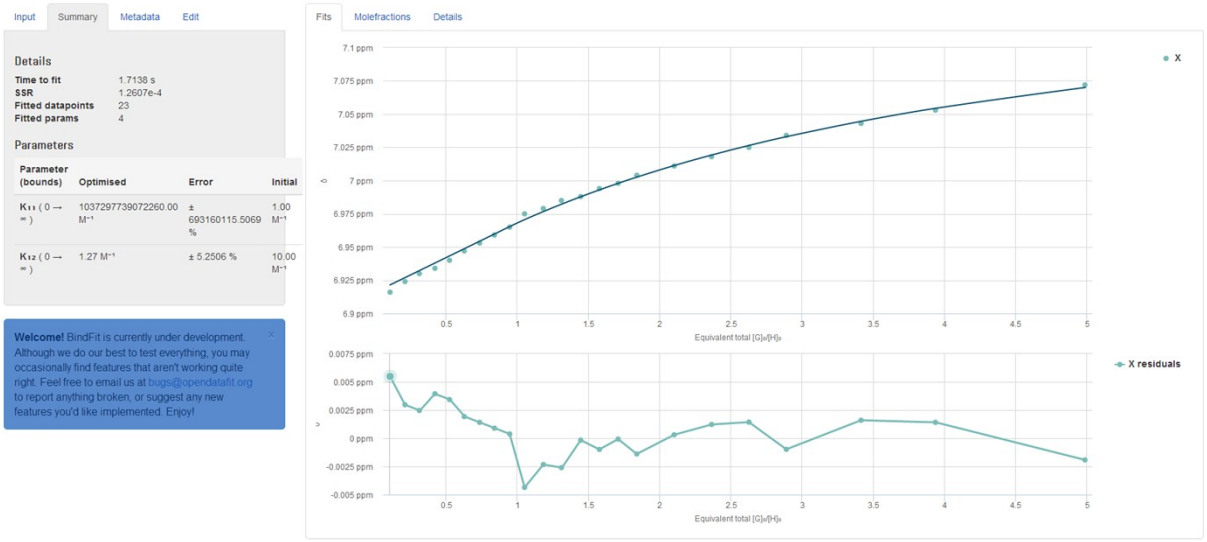


Figure S4 fitting curve of ^{1}H NMR titration experiments by 1:2 model

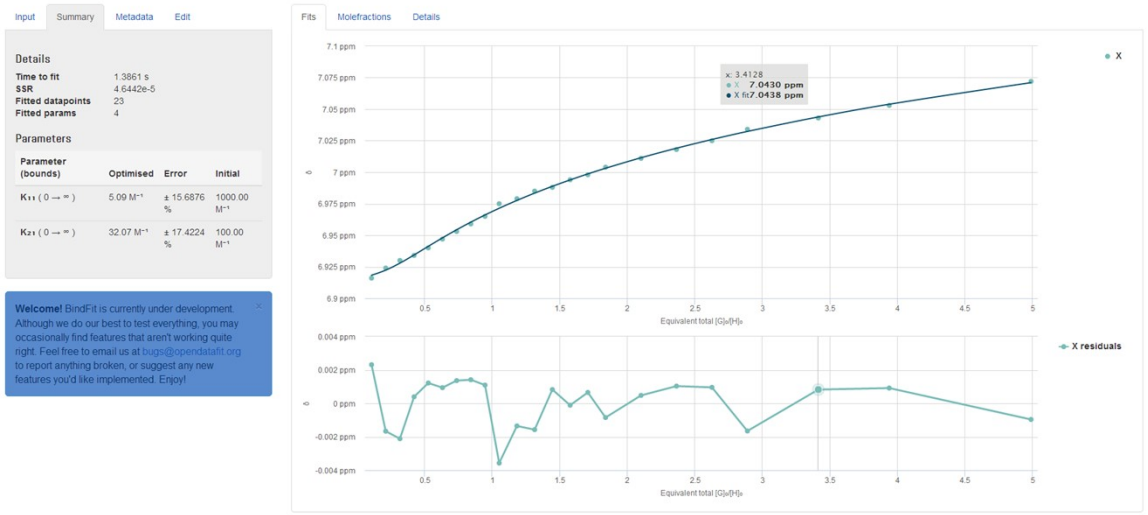


Figure S5 fitting curve of ^{1}H NMR titration experiments by 2:1 model

Table S3 Binding constants obtained by using BindFit.

Filter model	*Ka* (M^{-1})	
	K_1	K_2
NMR 1:1	0.98±3.10%	
NMR 1:2	1037297739072260.00 ±693160115.5069%	1.27±5.2506%
NMR 2:1	5.09±15.68%	32.07±17.42%

Conclusion:

As shown in figures S3 and S4, fitting of the titration data with a simple 1:1 or 1:2 model doesn't provide a good match between the calculated and experimental data and the systematic distribution of residuals indicates the incorrectness of this model. When the data were fitted with a 2:1 model, a perfect match was obtained with stochastic residuals of very low values (Figure S5). Besides, the binding constants of 1:2 model have large error while that of 2:1 model is rational and effective. Within the error boundaries, an $\alpha = 4K_2/K_1 = 25.2 >> 1$ was obtained, indicating the presence of a positive cooperativity in this system and the formation of both 1:1 and 2:1 binding complex.[1] Moreover, the formation of a 2:1 complex is more favourable over the formation of a 1:1 complex

1. P. Thordarson, *Chem. Soc. Rev*., 2011, **40**, 1305

4. DOSY NMR experiments (Figure 6 in the text).

Detailed procedure: Two samples were prepared. **Sample 1**: a mixture of phenol **1a** (0.057 mmol, 5.3 mg, 5 μL) and CD_3CN (500 μL); **Sample 2**: a mixture of phenol **1a** (0.057 mmol, 5.3 mg, 5 μL), diphenyl sulfide **2a** (0.0285 mmol, 5.3 mg) and CD_3CN (500 μL). Then the DOSY NMR spectra were recorded by using a simple Carr-Purcell spin-echo sequence (diffusion time = 0.10 s, FG pulse width = 0.0011 s, relaxation time = 7 s, points =16, BASE = 2, and scans = 8) at 298K.

Results:

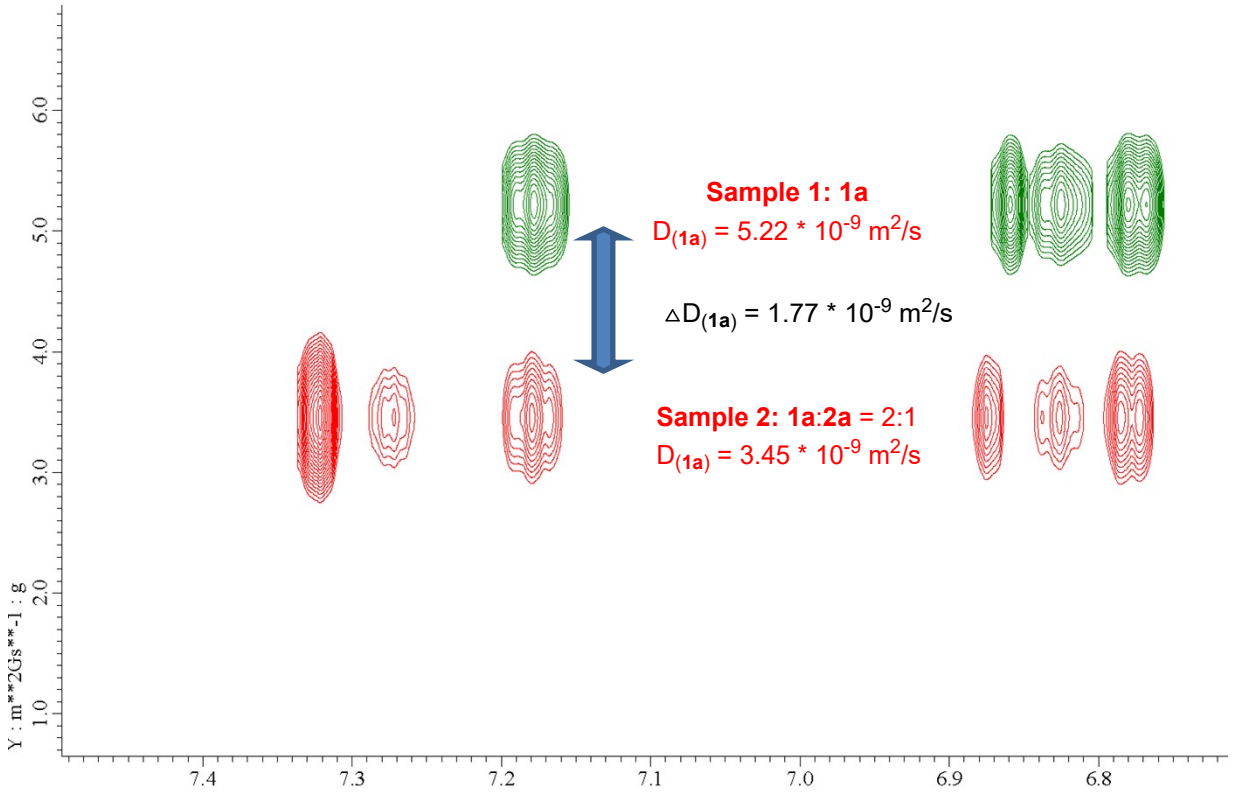


Figure S6 The DOSY NMR experiment

Conclusion: The diffusion coefficient of phenol (**1a**) significantly decreased from $5.22*10^{-9}$ m^2/s to $3.45*10^{-9}$ m^2/s, when 0.5 equiv. diphenyl sulfide (**2a**) was added, suggesting that a much bigger binding species might be formed from phenol (**1a**) and diphenyl sulfide (**2a**) *via* H-bonding. The mixture of 1.0 equiv. phenol (**1a**) and 0.5 equiv. diphenyl sulfide (**2a**) could give a clear and simple DOSY spectrum (Figures S6), suggesting that a single binding specie is formed and the binding stoichiometry between phenol (**1a**) and diphenyl sulfide (**2a**) may be 2:1.

5. FT-IR experiments (Figures 7-8 in the text).

Detailed procedure: A mixture of phenol **1a** and diphenyl sulfide (**2a**) or dipropyl sulfide (**2b**) was prepared according to table S4, and then the mixture was directly analyzed on a IR spectrometer (Thermofisher, IS50, USA) in the range of 4000-400 cm^{-1}.

Result:

Table S4. The preparation of test samples

	1：2 (mol)	**1a**/uL	**2a**/uL	**2b**/uL
1	1:0	100		
2	0:1		100	
3	0:1			100
4	1:0.25	87.9	41.8	
5	1:0.5	87.9	83.7	
6	1:1	87.9	167.4	
7	1:1.5	87.9	251.0	
8	1:0.25	87.9		35.6
9	1:0.5	87.9		71.2
10	1:1	87.9		142.5
11	1:1.5	87.9		213.7

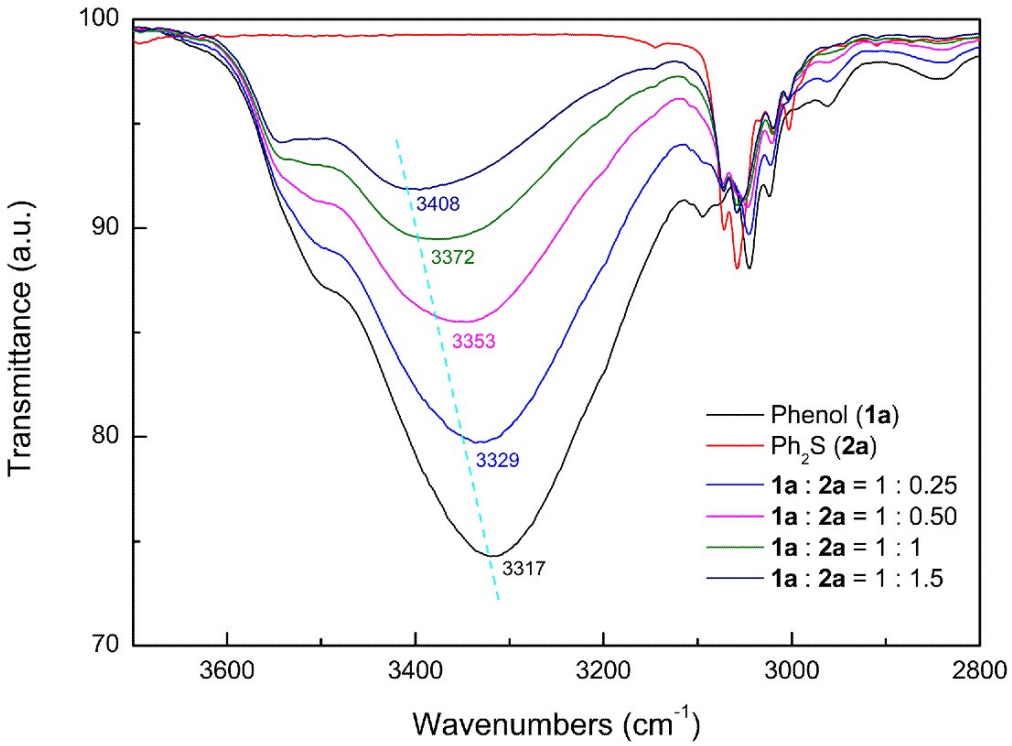


Figure S7 The IR experiments of phenol (**1a**) and diphenyl sulfide (**2a**)

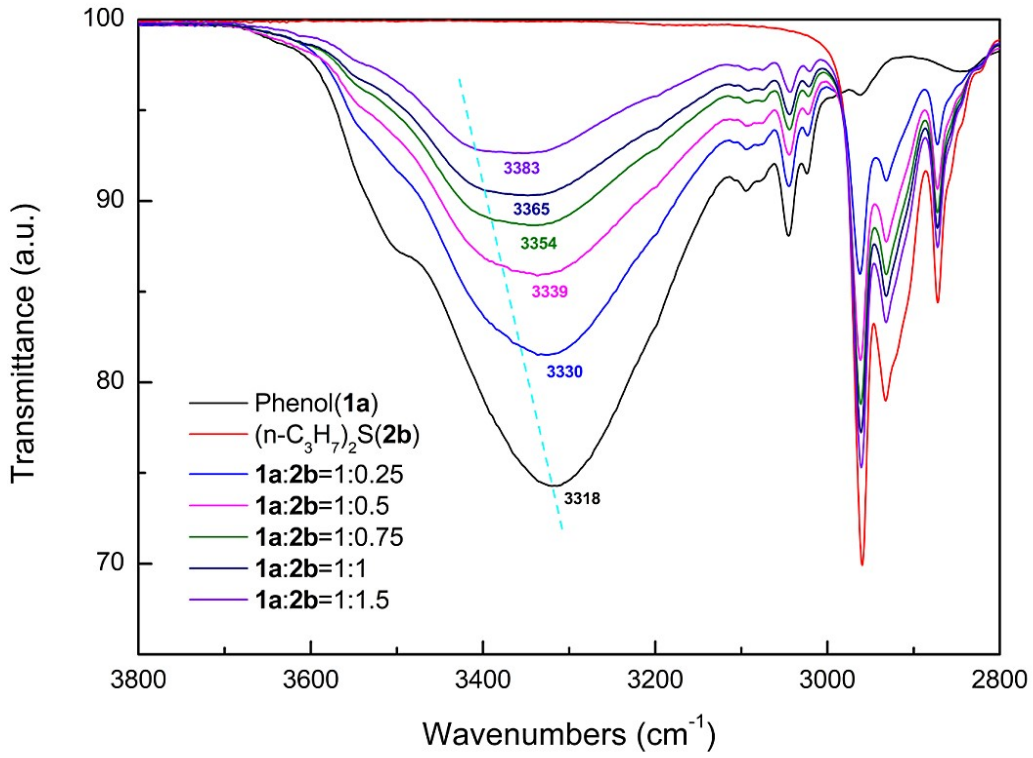
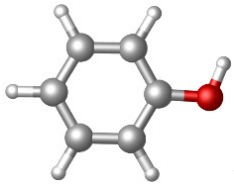
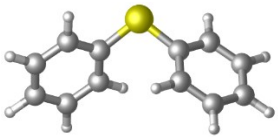
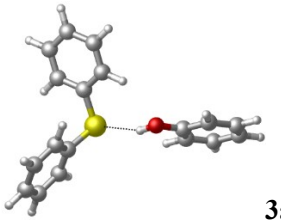
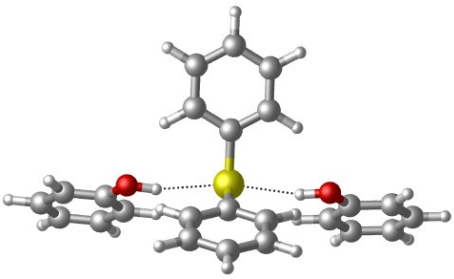


Figure S8 The IR experiments of phenol (**1a**) and dipropyl sulfide (**2b**)

Conclusion: An obvious blue shift was observed when certain amount of diphenyl sulfide (**2a**) or dipropyl sulfide (**2b**) was added to the pure phenol (**1a**), suggesting that the blue shift effect is ascribed to the formation of S···H-O H-bond between phenol (**1a**) and a thioether. Therefore, the possible л-л stacking interaction between phenol (**1a**) and diphenyl sulfide (**2a**) is excluded.

6. DFT calculation (Figure 9 in the text).

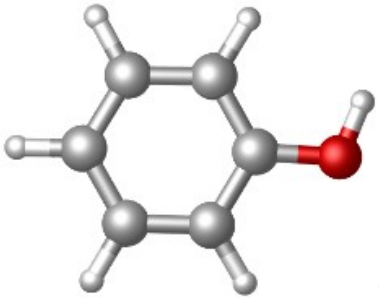
Structures	E_0	H_{298}	G_{298}	TCGFE
 **1a**	-307.454788	-307.448231	-307.483846	0.074885
 **2a**	-861.448107	-861.436384	-861.487308	0.142198
 **3a**	-1168.908104	-- 1168.888730	-1168.962383	0.232296
 **4a**	-1476.366782	-1476.340774	-1476.431934	0.326837

E_0: Sum of electronic and zero-point Energies

H_{298}: Sum of electronic and thermal Enthalpies

G_{298}: Sum of electronic and thermal Free Energies

TCGFE: Thermal correction to Gibbs Free Energy



1a

Standard orientation:

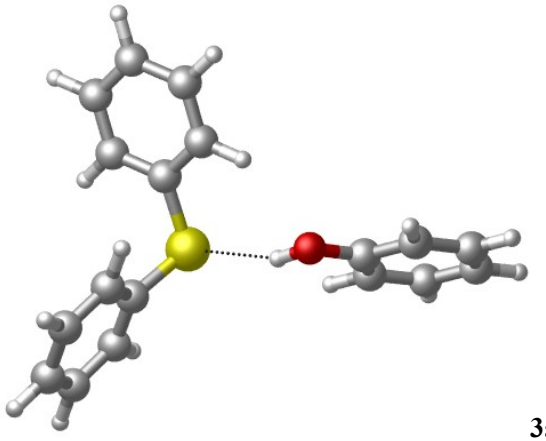
Center Number	Atomic Number	Coordinates Type	(Angstroms) X	Y	Z
1	6	0	-1.169707	-1.188851	-0.000001
2	6	0	0.220923	-1.221513	0.000000
3	6	0	0.938101	-0.023991	0.000000
4	6	0	0.262669	1.197721	0.000000

5	6	0	-1.131319	1.217197	0.000000
6	6	0	-1.855164	0.027125	0.000000
7	1	0	-1.721929	-2.122027	-0.000001
8	1	0	0.764036	-2.158818	-0.000001
9	1	0	0.822822	2.128442	-0.000001
10	1	0	-1.649060	2.169872	0.000001
11	1	0	-2.938347	0.045590	0.000001
12	8	0	2.305329	-0.110342	-0.000002
13	1	0	2.686830	0.773548	0.000012

2a

Standard orientation:

Center	Atomic	Coordinates	(Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-2.603095	-1.377891	-0.984245
2	6	0	-1.458383	-0.588437	-0.927459
3	6	0	-1.409318	0.507432	-0.058704
4	6	0	-2.518481	0.811236	0.735996
5	6	0	-3.670069	0.028704	0.656403
6	6	0	-3.714568	-1.070233	-0.198071
7	1	0	-2.631540	-2.229056	-1.655607
8	1	0	-0.605092	-0.821329	-1.552869
9	1	0	-2.475927	1.652901	1.417534
10	1	0	-4.526322	0.273438	1.274984
11	1	0	-4.606513	-1.683735	-0.252197
12	6	0	1.409309	0.507484	0.058705
13	6	0	2.518315	0.811083	-0.736290
14	6	0	1.458549	-0.588148	0.927751
15	6	0	3.669926	0.028580	-0.656704
16	1	0	2.475619	1.652566	-1.418043
17	6	0	2.603276	-1.377578	0.984534
18	1	0	0.605377	-0.820869	1.553386
19	6	0	3.714595	-1.070121	0.198062
20	1	0	4.526062	0.273151	-1.275512
21	1	0	2.631860	-2.228560	1.656124
22	1	0	4.606558	-1.683598	0.252188
23	16	0	-0.000026	1.617652	0.000008



3a

Standard orientation:

Center Number	Atomic Number	Coordinates Type	(Angstroms) X	Y	Z
1	6	0	-4.031108	2.347852	-0.329791
2	6	0	-3.254379	1.278496	-0.764898
3	6	0	-1.875389	1.280273	-0.530083
4	6	0	-1.276329	2.360032	0.122717
5	6	0	-2.061069	3.436973	0.538153
6	6	0	-3.435919	3.431280	0.318535
7	1	0	-5.100506	2.340928	-0.508505
8	1	0	-3.712870	0.444610	-1.282801
9	1	0	-0.209860	2.358359	0.314084
10	1	0	-1.592798	4.273933	1.043641
11	1	0	-4.043067	4.266469	0.648668
12	6	0	-1.473782	-1.503446	-0.264097
13	6	0	-1.565682	-2.707174	-0.967292
14	6	0	-1.798717	-1.460509	1.094523
15	6	0	-1.975057	-3.866282	-0.309114
16	1	0	-1.326283	-2.734558	-2.024141
17	6	0	-2.225386	-2.618838	1.738336
18	1	0	-1.719942	-0.530143	1.643625
19	6	0	-2.310513	-3.824883	1.042159
20	1	0	-2.042887	-4.797776	-0.859779
21	1	0	-2.481175	-2.579830	2.791295
22	1	0	-2.636989	-4.724751	1.550498
23	16	0	-0.847619	-0.063881	-1.147218
24	6	0	5.505089	0.686147	0.789247
25	6	0	4.183870	0.985859	1.104932
26	6	0	3.149181	0.480013	0.313612
27	6	0	3.446277	-0.324306	-0.790160
28	6	0	4.774405	-0.617332	-1.095840
29	6	0	5.810916	-0.116002	-0.311399
30	1	0	6.302044	1.082680	1.408818
31	1	0	3.935141	1.606338	1.957694

32	1	0	2.642899	-0.716424	-1.405167
33	1	0	4.995316	-1.242038	-1.954404
34	1	0	6.841797	-0.346410	-0.552658
35	8	0	1.870498	0.804777	0.665653
36	1	0	1.228658	0.393588	0.062155

4a

Standard orientation:

Center Number	Atomic Number	Coordinates Type	(Angstroms) X	Y	Z
1	6	0	-1.232803	-2.506567	3.283169
2	6	0	-1.229861	-1.814327	2.073385
3	6	0	-0.013288	-1.453557	1.488549
4	6	0	1.194307	-1.768154	2.116825
5	6	0	1.179897	-2.459636	3.327204
6	6	0	-0.030640	-2.830566	3.909835
7	1	0	-2.176918	-2.786837	3.736340
8	1	0	-2.165200	-1.553363	1.592993
9	1	0	2.135893	-1.473935	1.668914
10	1	0	2.117093	-2.703798	3.814366
11	1	0	-0.037424	-3.366576	4.852160
12	6	0	0.006217	-1.819620	-1.323682
13	6	0	-1.202337	-2.293276	-1.840356
14	6	0	1.222460	-2.312362	-1.803296
15	6	0	-1.189164	-3.275451	-2.829450
16	1	0	-2.143759	-1.897373	-1.478784
17	6	0	1.224144	-3.294653	-2.792199
18	1	0	2.158378	-1.930856	-1.413078
19	6	0	0.021132	-3.777671	-3.304369
20	1	0	-2.127008	-3.643039	-3.230206
21	1	0	2.167901	-3.677247	-3.163981
22	1	0	0.026957	-4.539853	-4.075317
23	16	0	-0.002870	-0.518566	-0.063407
24	6	0	6.034932	2.509599	-0.118943
25	6	0	5.336275	1.306633	-0.105380
26	6	0	3.939991	1.316363	-0.137755

27	6	0	3.251065	2.530947	-0.183779
28	6	0	3.962750	3.729524	-0.196664
29	6	0	5.355545	3.727921	-0.164293
30	1	0	7.118997	2.494296	-0.093891
31	1	0	5.853694	0.355269	-0.070119
32	1	0	2.166067	2.537065	-0.209222
33	1	0	3.420576	4.668003	-0.232448
34	1	0	5.904719	4.661825	-0.174630
35	8	0	3.299588	0.108064	-0.121406
36	1	0	2.335035	0.224476	-0.142715
37	6	0	-6.025412	2.526747	-0.147746
38	6	0	-5.333377	1.319898	-0.155829
39	6	0	-3.936694	1.322535	-0.161467
40	6	0	-3.240782	2.534046	-0.159160
41	6	0	-3.945865	3.736545	-0.150742
42	6	0	-5.339014	3.741977	-0.144872
43	1	0	-7.109823	2.516936	-0.143558
44	1	0	-5.856327	0.370911	-0.158173
45	1	0	-2.155485	2.534689	-0.164051
46	1	0	-3.398256	4.672552	-0.148757
47	1	0	-5.883059	4.678914	-0.138384
48	8	0	-3.302783	0.110776	-0.168611
49	1	0	-2.337440	0.222911	-0.166726