

Supporting Information for

Colorimetric and Ratiometric Fluorescent Chemosensor Based on Diketopyrrolopyrrole (DPP) for Selective Detection of Thiols: An Experimental and Theoretical Study

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Experimental Section

General

The ground state structure of complexes were optimized using density functional theory (DFT)¹ with B3LYP functional and 6-31G(d)/LanL2DZ basis set. The excited state related calculations were carried out with the Time dependent density functional theory (TD-DFT) with the optimized structure of the ground state (DFT 6-31G(d)/LanL2DZ) There are no imaginary frequencies in frequency analysis of all calculated structures, therefore each calculated structure express an energy minimum. All these calculations were performed in Gaussian 09.²

Reference:

1. Hohenberg P, Kohn W. *Phys. Rev.* 1964; **136**: B864.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian 09 Revision A.1, Gaussian Inc., Wallingford CT, 2009.

zjz110615-1r 299 (4.984) Cm (299:311-85:114)

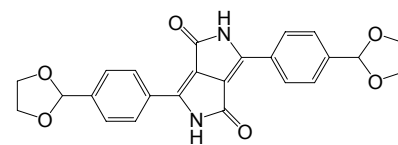
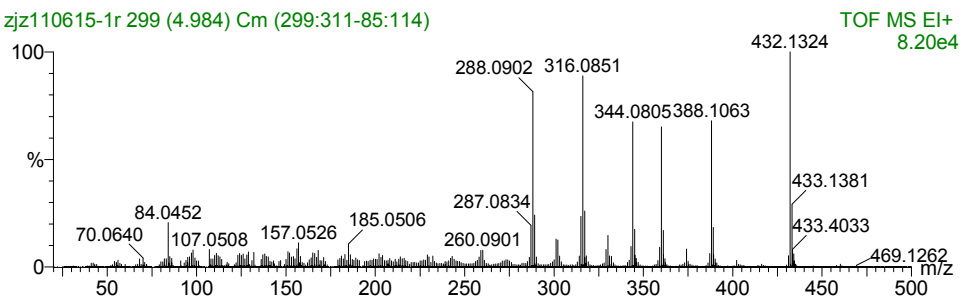


Figure S1. TOF HRMS EI of 4.

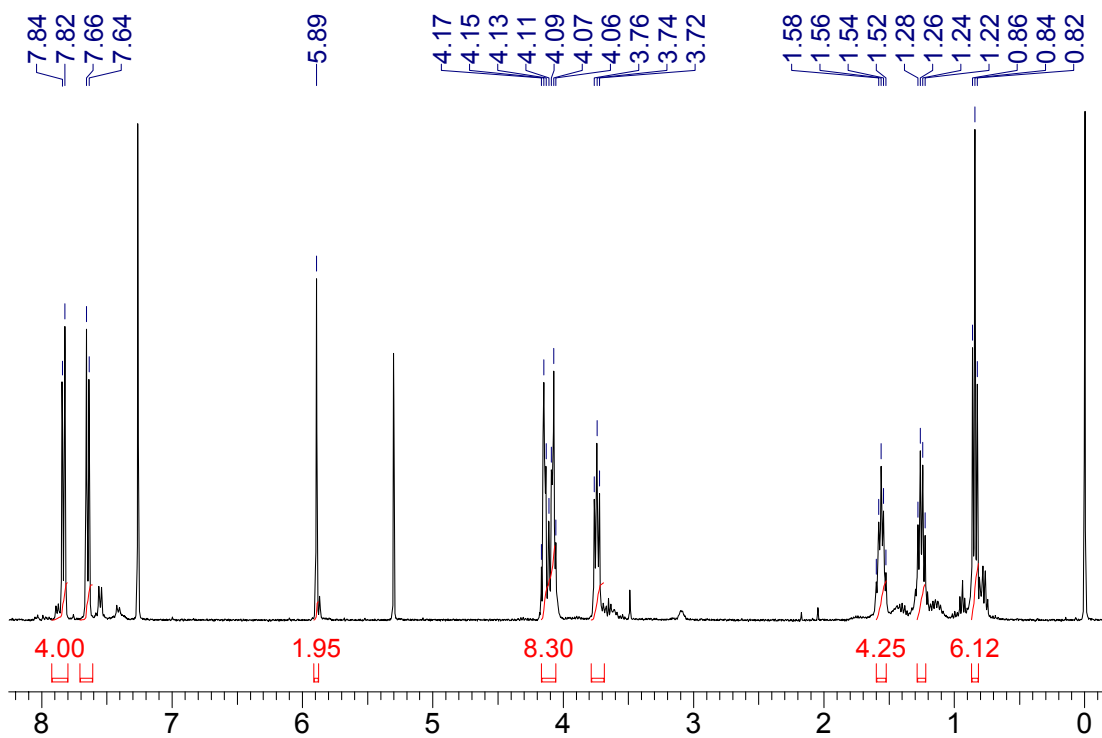


Figure S2. ^1H NMR of 3 (CDCl_3 , 400 MHz).

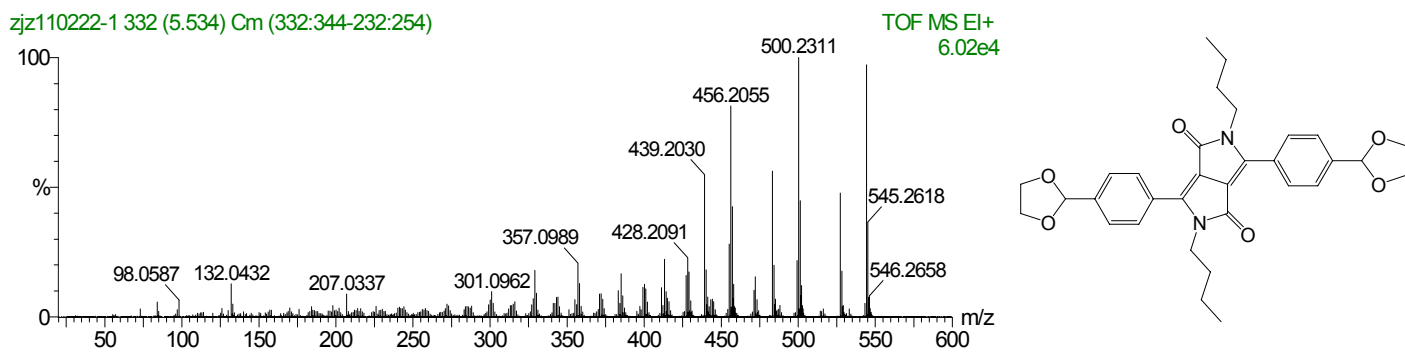


Figure S3. TOF HRMS EI of **3**.

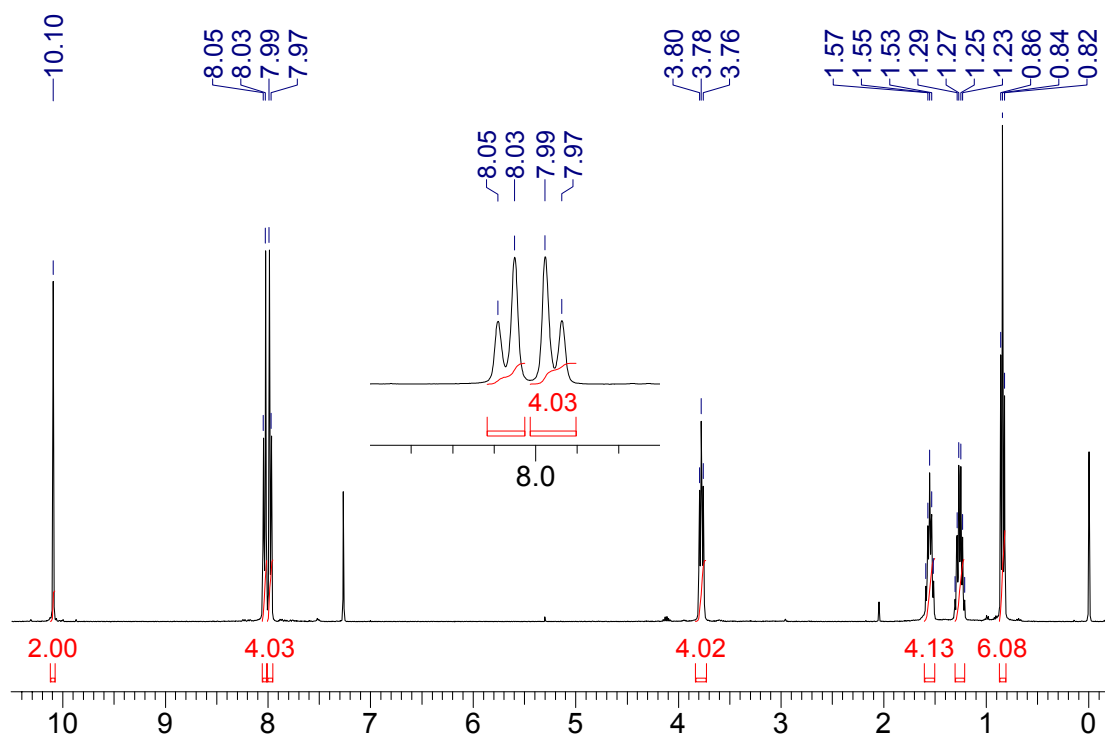


Figure S4. ^1H NMR of **2** (CDCl_3 , 400 MHz).

zjz110222-4 416 (6.933) Cm (416:425-143:174)

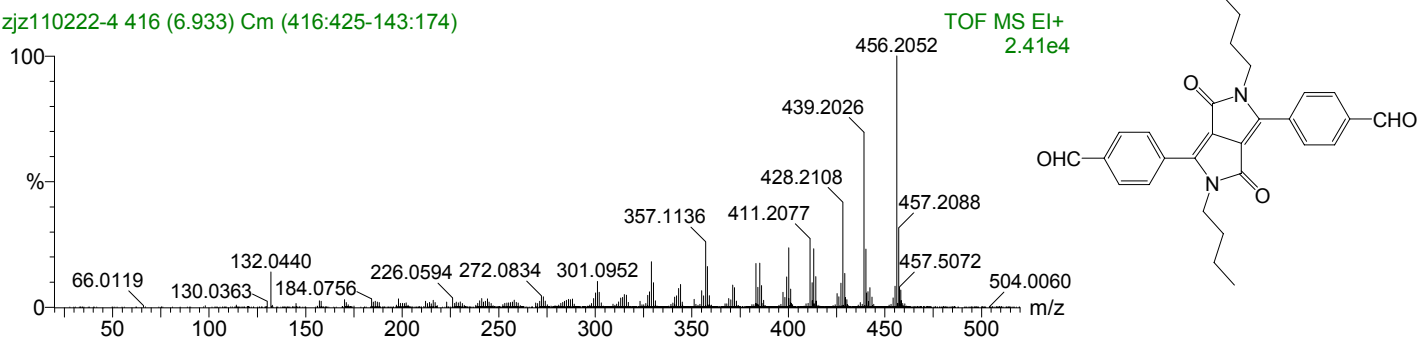


Figure S5. TOF HRMS EI of 2.

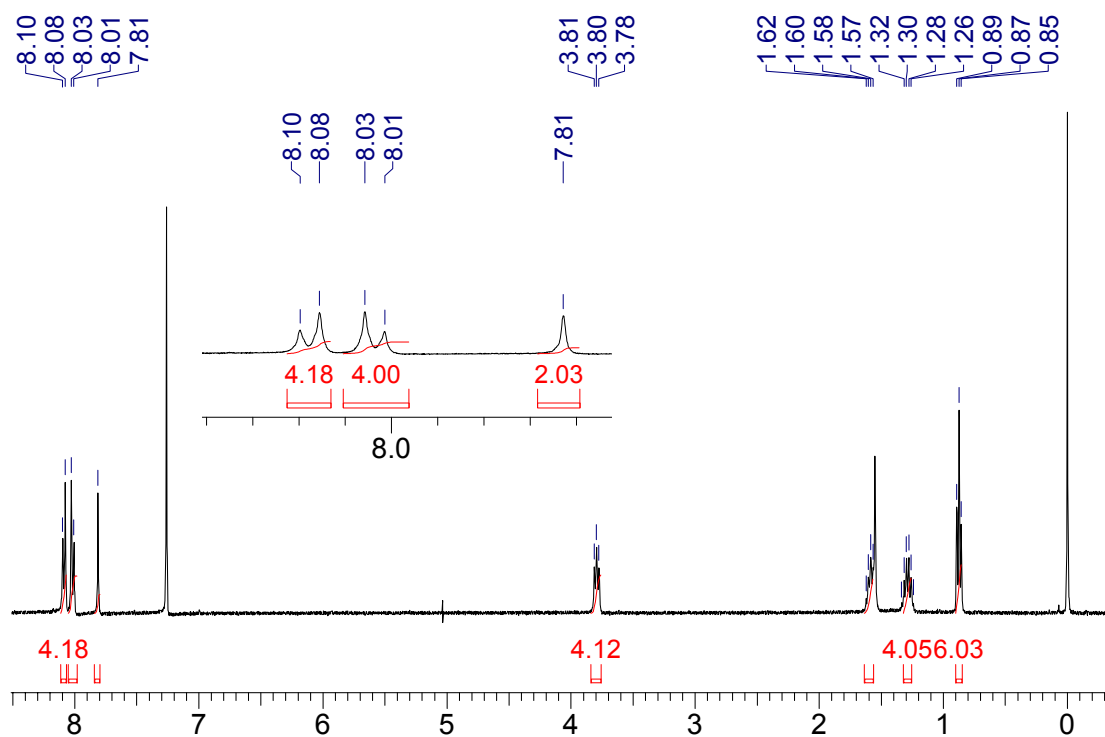


Figure S6. ^1H NMR of probe 1 (CDCl_3 , 400 MHz).

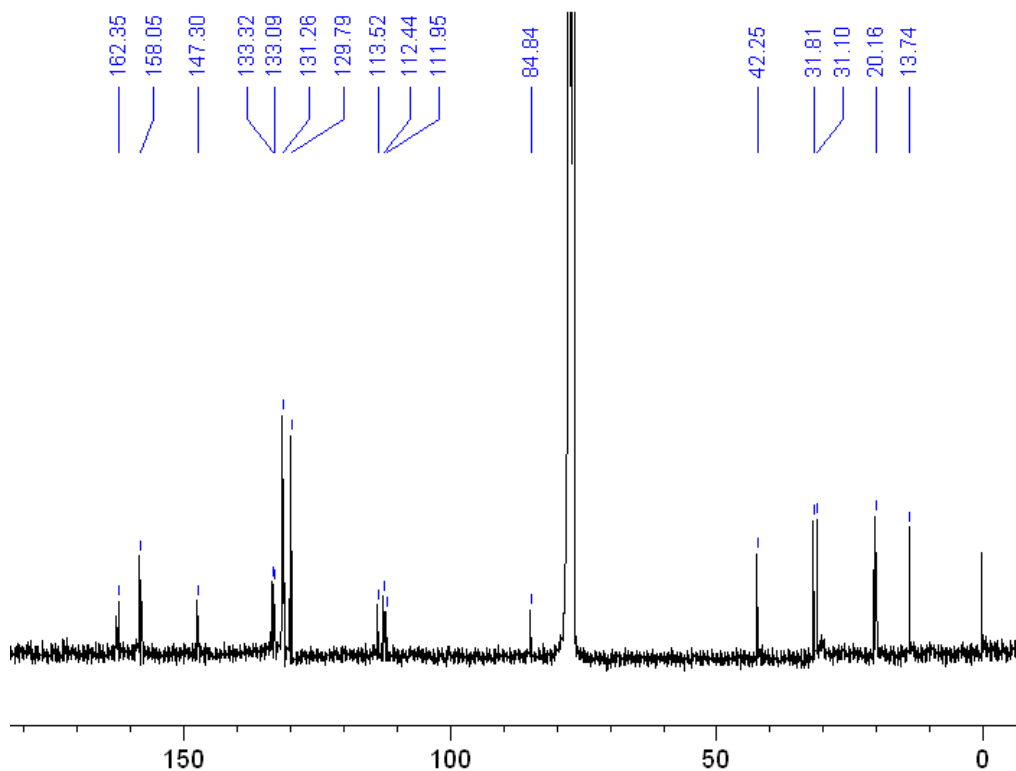
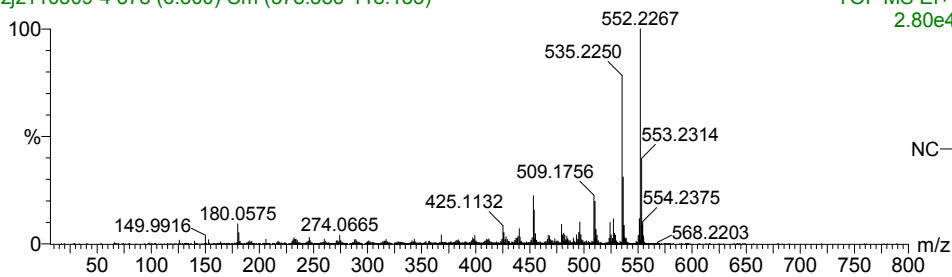


Figure S7. ^{13}C NMR of **1** (CDCl_3 , 100 MHz).

zjz110509-4 378 (6.300) Cm (378:386-118:135)



TOF MS EI+
2.80e4

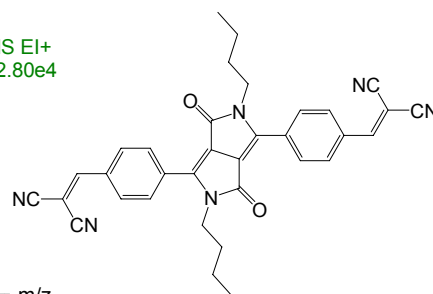


Figure S8. TOF HRMS EI of **1**.

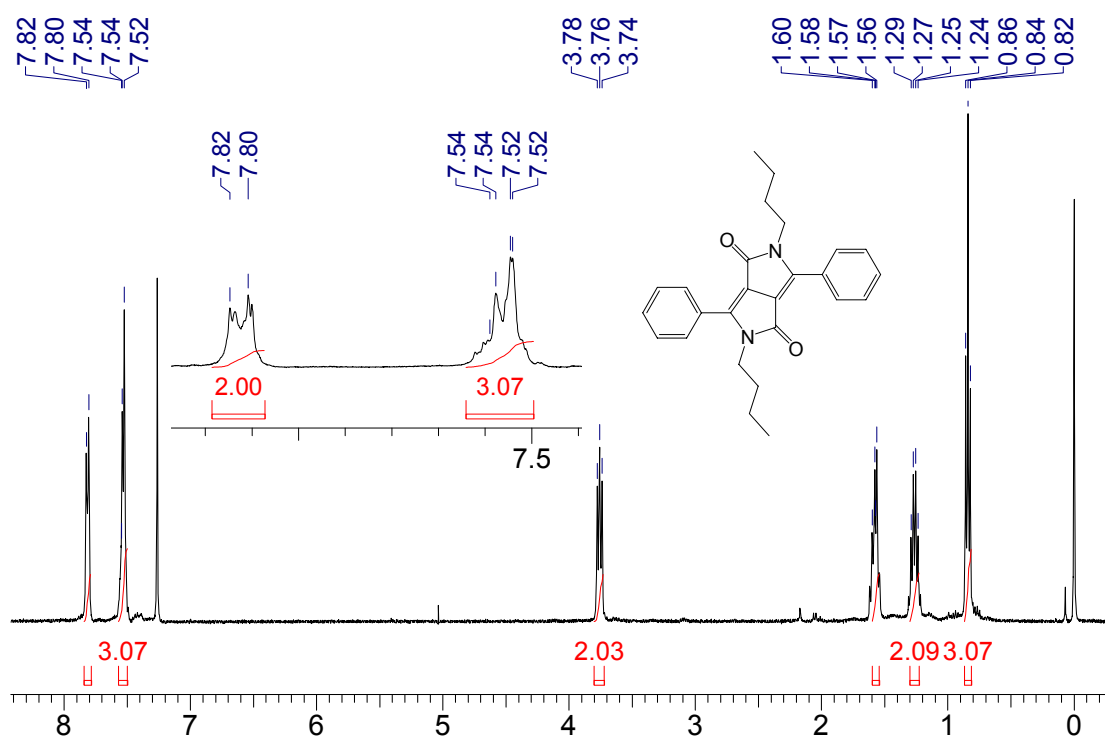


Figure S9. ¹H NMR of DPP (CDCl₃, 400 MHz).

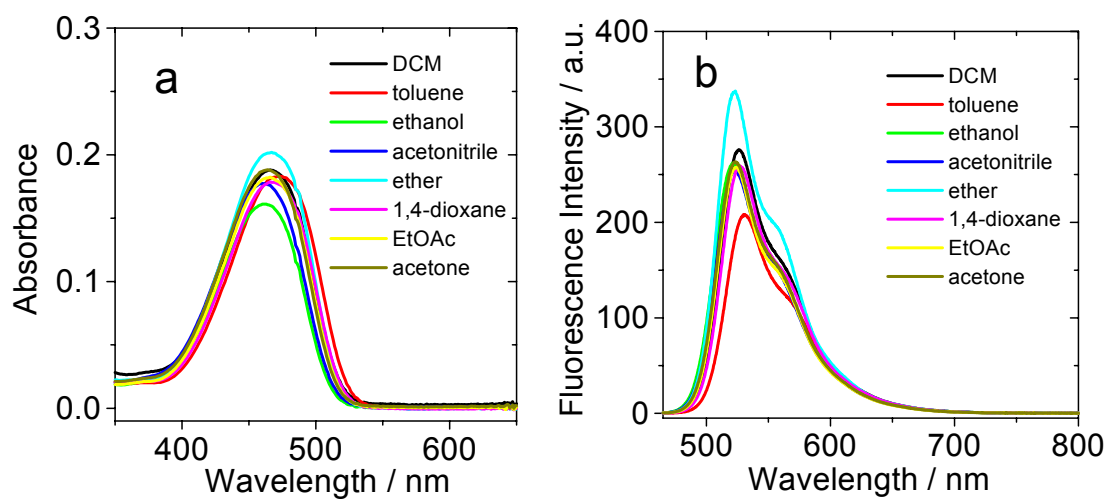


Figure S10. (a) UV-vis absorption and (b) fluorescence spectra of DPP in the other solvents. $c(\text{DPP}) = 1.0 \times 10^{-5}$ mol/L.

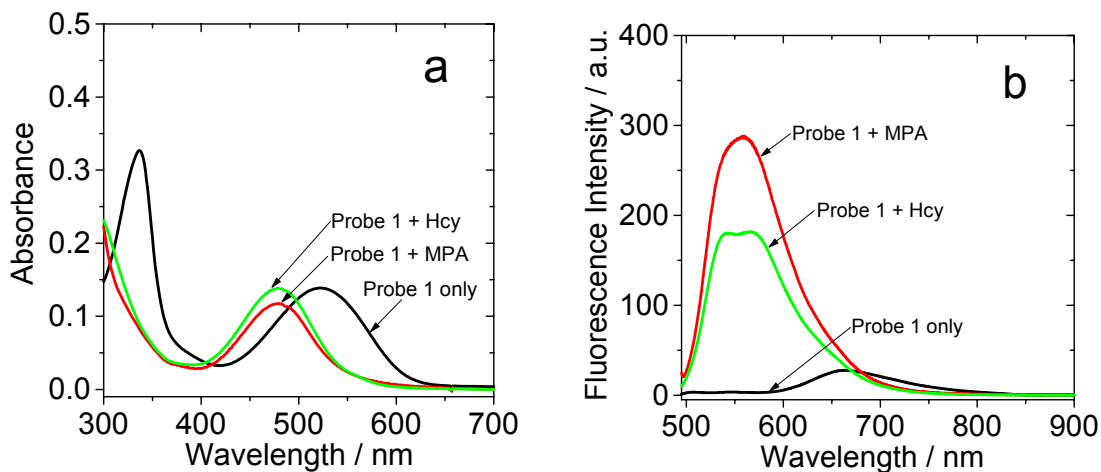


Figure S11. (a) UV-vis absorption and (b) fluorescence spectra of **1** before and after addition of 3-mercaptopropionic acid (MPA) or DL-homocysteine (Hcy). In mixed solvent of CH₃CN/H₂O (4:1, v/v). c (Probe **1**) = 1.0×10^{-5} mol/L, c (3-mercaptopropionic acid or DL-homocysteine) = 2.0×10^{-3} mol/L, 37 °C.

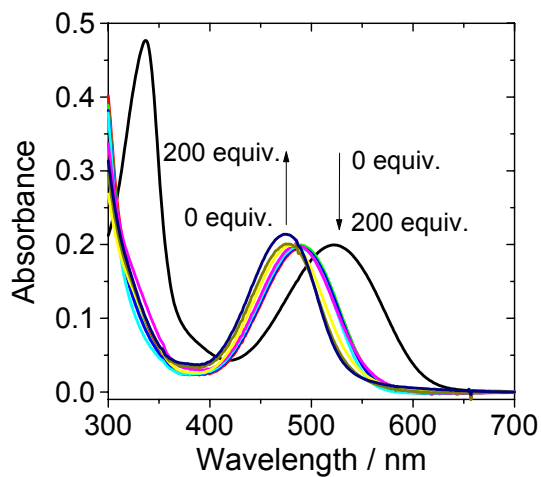


Figure S12. UV-vis absorption of probe **1** after addition of different concentration of L-cysteine after 300 min. In mixed solvent of CH₃CN/H₂O (4:1, v/v). c (Probe **1**) = 1.0×10^{-5} mol dm⁻³, 37 °C.

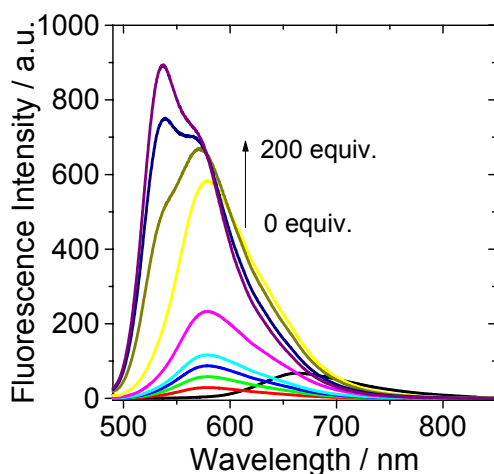


Figure S13. fluorescence spectra of probe **1** after addition of different concentration of L-cysteine ($\lambda_{\text{ex}} = 490 \text{ nm}$) after 300 min. In mixed solvent of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v). c (Probe **1**) = $1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $37 \text{ }^\circ\text{C}$.

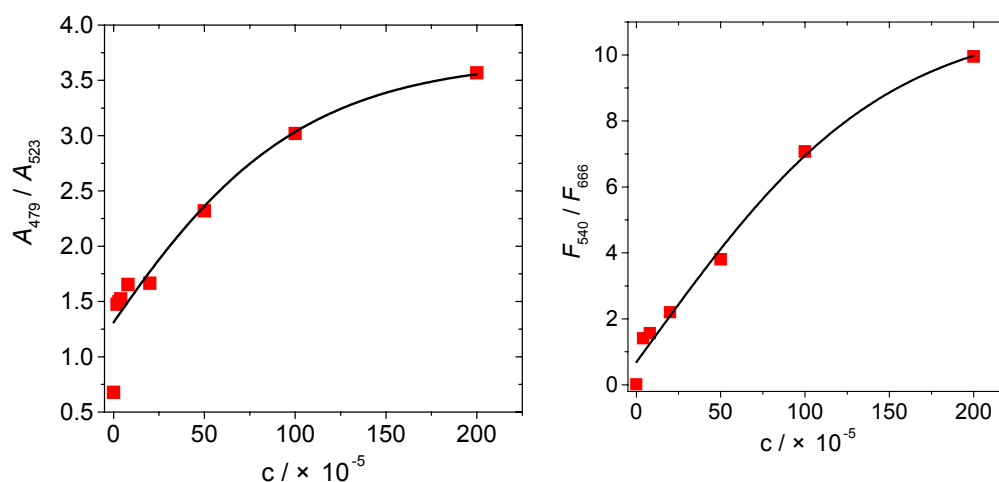


Figure S14. Ratiometric and colorimetric responses of the probe **1** to cysteine. (a) Quantified by the absorption data. $A_{479 \text{ nm}}/A_{523 \text{ nm}}$ of probe **1** before and after addition of different concentration of L-cysteine after 300 min. In mixed solvent of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v). c (Probe **1**) = $1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $37 \text{ }^\circ\text{C}$. (b) Fluorescence ratiometric response ($F_{540 \text{ nm}}/F_{666 \text{ nm}}$) of probe **1** after addition of different concentration of L-cysteine ($\lambda_{\text{ex}} = 490 \text{ nm}$) after 300 min. In mixed solvent of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1, v/v). c (Probe **1**) = $1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $37 \text{ }^\circ\text{C}$.

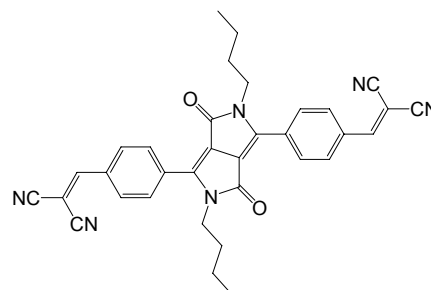
Z-matrix, number of imaginary frequencies and total energy of the compounds (there are no imaginary frequencies for all the structures).

Compound 1 ground state configuration (DFT B3LYP 6-31G(d))

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.63370400	-1.65887500	-0.32233100
C	-1.53871800	-0.84063900	-0.11328500
C	-0.66958900	0.23202800	0.05039200
C	0.66959500	-0.23191900	-0.05016300
C	-0.63366700	1.65897700	0.32263100
C	1.53873300	0.84074000	0.11338800
O	-1.50752000	2.50085200	0.50748400
O	1.50757100	-2.50068800	-0.50739000
N	0.76293000	1.97245600	0.34112500
N	-0.76289000	-1.97234300	-0.34102400
C	1.19545200	3.30835600	0.73348000
H	1.42082600	3.93438900	-0.13572900
H	0.36864600	3.76473200	1.27943800
H	2.07208800	3.25002200	1.38061900
C	-1.19532800	-3.30816300	-0.73377700
H	-0.36854100	-3.76430300	-1.27996100
H	-2.07202100	-3.24969300	-1.38081900
H	-1.42057400	-3.93449300	0.13525300
C	-2.99748700	-0.83040000	-0.03113100
C	-3.74529800	-1.93965700	0.41265800
C	-3.69041900	0.35430600	-0.36775400
C	-5.12685000	-1.86599000	0.49911400
H	-3.25172000	-2.85058200	0.72482600
C	-5.07063600	0.42303200	-0.28945100
H	-3.13325800	1.22795400	-0.68274400
C	-5.82539500	-0.69116700	0.14283400
H	-5.68218900	-2.72904700	0.85414800
H	-5.55942200	1.34825500	-0.56626800
C	2.99752100	0.83048000	0.03120800
C	3.74530400	1.93958800	-0.41301000
C	3.69046000	-0.35411300	0.36816300
C	5.12684100	1.86586900	-0.49960000
H	3.25170300	2.85042100	-0.72541200
C	5.07068600	-0.42288500	0.28972200
H	3.13332400	-1.22764500	0.68350800
C	5.82539300	0.69114900	-0.14303500
H	5.68215900	2.72878600	-0.85501300
H	5.55947000	-1.34804000	0.56675700



C	-7.26751800	-0.73039800	0.26491500
H	-7.66120500	-1.67752100	0.62455500
C	7.26750000	0.73018900	-0.26535000
H	7.66119500	1.67712600	-0.62549600
C	-8.22387800	0.21643300	0.00732600
C	8.22381400	-0.21657600	-0.00745300
C	-7.98710000	1.54229000	-0.47473200
N	-7.83658300	2.62818100	-0.86638000
C	-9.60344500	-0.10515400	0.22661100
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ΓΓ

SCF Done: E(RB3LYP) = -1555.51801177 a.u.

Number of Imaginary frequencies: 0

Compound 1 excited state configuration (TDDFT B3LYP 6-31G(d))

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.63149500	-1.66029600	-0.26541400
C	-1.55888400	-0.89288300	-0.07052900
C	-0.65564900	0.22023600	0.04222200
C	0.65568300	-0.21993800	-0.04232800
C	-0.63145300	1.66059700	0.26529500
C	1.55892900	0.89316700	0.07045000
O	-1.51006600	2.49263900	0.44186700
O	1.51012300	-2.49234400	-0.44188500
N	0.76419800	2.00021000	0.25465500
N	-0.76415000	-1.99992800	-0.25466000
C	1.15738600	3.36891500	0.57664000
H	1.40772400	3.93342300	-0.32587100
H	0.29924100	3.84164700	1.05425500
H	2.00565200	3.36518400	1.26260600
C	-1.15737600	-3.36866600	-0.57645600
H	-0.29928100	-3.84146100	-1.05409700
H	-2.00570900	-3.36499800	-1.26234000
H	-1.40764300	-3.93306900	0.32614100

C	-2.99118100	-0.87592300	0.00795400
C	-3.77656500	-2.01537300	0.34124200
C	-3.68078300	0.34693200	-0.23443500
C	-5.15077900	-1.93095100	0.40190600
H	-3.30834800	-2.95448700	0.59985800
C	-5.05593400	0.42116900	-0.18769300
H	-3.11588100	1.24175800	-0.46288000
C	-5.84228600	-0.71992000	0.12712600
H	-5.72196400	-2.81340800	0.67550100
H	-5.52841300	1.37271400	-0.39537400
C	2.99123000	0.87612100	-0.00800300
C	3.77673300	2.01547300	-0.34135900
C	3.68071300	-0.34679400	0.23442300
C	5.15093800	1.93091100	-0.40200600
H	3.30862200	2.95461200	-0.60006100
C	5.05585600	-0.42117100	0.18770100
H	3.11571700	-1.24155700	0.46288700
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H	5.72221300	2.81329400	-0.67565000
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C	7.27381100	0.74989600	-0.20529700
H	7.69306800	1.71498300	-0.47758000
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C	8.22023800	-0.23818400	0.00741000
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N	7.78273100	-2.70140000	0.68322500
C	9.60413600	0.08071600	-0.14663300
N	10.73487400	0.33623200	-0.27132300

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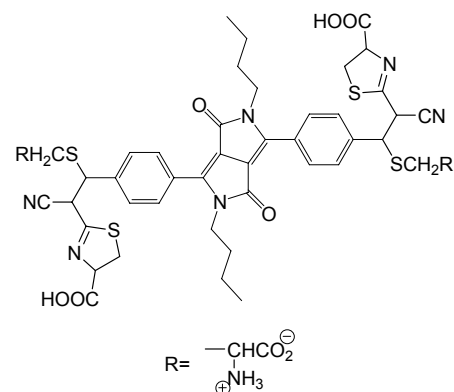
Number of Imaginary frequencies: 0

Compound 1-Cys adduct ground state configuration (DFT B3LYP 6-31G(d))

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-0.52768642	2.21783581	0.54604721
C	1.35769656	0.88232946	0.20844254
C	0.24007437	0.10343496	-0.05385240
C	-0.93568161	0.88298288	0.15574075
C	-0.16757935	-1.23062313	-0.44741511
C	-2.05293834	0.10684338	-0.11705702
O	0.45252448	-2.25673032	-0.72001753
O	-1.14792878	3.24329627	0.82104637
N	-1.59839113	-1.16018398	-0.47366448
N	0.90349885	2.14866362	0.56781471
C	-2.37625797	-2.37268503	-0.69023455
H	-2.70607548	-2.46601926	-1.73015481
H	-1.72484909	-3.21720897	-0.46026433
H	-3.24559613	-2.39007136	-0.03070412
C	1.68137980	3.36065630	0.78644911
H	1.02316838	4.20528990	0.57752120
H	2.53982903	3.38980799	0.11300464
H	2.02771446	3.44224527	1.82196369
C	2.76669506	0.48978131	0.14365919
C	3.75370919	1.03515025	0.98403894
C	3.15471359	-0.50689508	-0.77535811
C	5.07890778	0.61318387	0.89796760
H	3.49409929	1.77244073	1.73349234
C	4.47811598	-0.91564674	-0.86111546
H	2.41140563	-0.96084273	-1.41986338
C	5.46670648	-0.36321647	-0.03069483
H	5.80383578	1.06467422	1.56782319
H	4.75205534	-1.67661978	-1.58702711
C	-3.46160722	0.50447610	-0.07875502
C	-4.43156657	-0.03929629	-0.94376121
C	-3.86197966	1.51360878	0.81821282
C	-5.75120471	0.39874200	-0.90093872
H	-4.15495079	-0.78072018	-1.68320214
C	-5.18525529	1.93929182	0.86063679
H	-3.12909223	1.97609774	1.46867113
H	-6.47191824	-0.01713453	-1.59734249
H	-5.46893833	2.71707490	1.56525632
C	6.89094476	-0.86679816	-0.15575305
S	7.23918440	-2.31808409	0.94865503
C	7.09881061	-1.61838251	2.63079507
H	7.21547372	-2.46630361	3.31059065
H	7.89293580	-0.89520421	2.83346971
H	6.11766985	-1.16701859	2.79518823



H	7.01087675	-1.31622852	-1.14580450
C	-6.15279039	1.38508524	0.00982674
C	-7.58984990	1.87006506	0.11330487
H	-7.58466026	2.83906918	0.62195036
C	7.97060901	0.25479516	-0.01137034
H	7.91473229	0.70512917	0.98433902
C	7.72318462	1.32615763	-0.99145226
N	7.52980341	2.16160138	-1.77380629
S	-8.42031030	2.16023372	-1.51662371
C	-7.53130527	3.68265170	-2.00420401
H	-6.46020067	3.49531333	-2.11384680
H	-7.94131683	3.98203238	-2.97189905
H	-7.69895423	4.48542889	-1.28104541
C	-8.45661704	0.93948309	1.03648672
H	-7.91983769	0.88449001	1.99053275
C	-9.76399685	1.55093386	1.32332901
N	-10.78345407	2.03972714	1.58484441
C	-8.65736758	-0.47876497	0.51285199
N	-9.40424300	-0.73793782	-0.48299310
S	-7.83500168	-1.82899599	1.34501460
C	-8.35404535	-2.93514398	-0.02972846
H	-8.66080194	-3.90509839	0.36256803
H	-7.50834718	-3.07278448	-0.70598091
C	-9.51367918	-2.16998104	-0.73921757
H	-9.46236524	-2.35864926	-1.81554138
C	-10.88264856	-2.66181261	-0.25283798
O	-11.63419572	-2.05464888	0.47606825
O	-11.13228697	-3.89567091	-0.73269023
H	-11.99107306	-4.18706720	-0.36887155
C	9.39853842	-0.25337782	-0.14805346
N	10.22481795	-0.15353269	0.81297862
S	9.94856874	-0.99227762	-1.68544315
C	11.48018291	-1.53163992	-0.81917550
H	12.34189816	-1.41501720	-1.47699910
H	11.37634569	-2.58335582	-0.54625523
C	11.55592342	-0.63249106	0.45149708
H	11.97492120	-1.21394292	1.27805680
C	12.47760773	0.57170407	0.22467502
O	12.11867331	1.71615617	0.06256051
O	13.76531765	0.17632813	0.20131776
H	14.31344410	0.96334217	0.01431355

1 4 1.5 8 2.0 10 1.0

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SCF Done: E(RB3LYP) = -3763.72723698 a.u.

Number of Imaginary frequencies: 0

Compound 1-Cys adduct excited state configuration (TDDFT B3LYP 6-31G(d))

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-0.54020100	2.14397400	0.69701500
C	1.38491900	0.87713700	0.31731100
C	0.22674000	0.13105500	-0.10993200
C	-0.93188200	0.86146200	0.13347700
C	-0.16310800	-1.15501000	-0.66426300

C	-2.08974800	0.11332000	-0.29413200
O	0.47870700	-2.15278500	-0.99586600
O	-1.18013900	3.14026300	1.03683900
N	-1.58690500	-1.08727700	-0.76760000
N	0.88318800	2.07419100	0.80069000
C	-2.31613900	-2.28334300	-1.17062700
H	-2.66155800	-2.21542900	-2.20676200
H	-1.62019000	-3.11906800	-1.09376500
H	-3.16782300	-2.45062100	-0.50864100
C	1.61529000	3.26574700	1.21141200
H	0.92019400	4.10307600	1.14570200
H	2.46426000	3.43821400	0.54704800
H	1.96567000	3.18742200	2.24514300
C	2.76085400	0.48293300	0.26784600
C	3.79180700	1.07385700	1.05156100
C	3.14769200	-0.57532800	-0.60743200
C	5.11013200	0.65745300	0.94083100
H	3.56157300	1.83627200	1.78238500
C	4.46667900	-0.97319900	-0.71085600
H	2.39421000	-1.07689000	-1.20265000
C	5.48587300	-0.36382300	0.04820000
H	5.84981800	1.14521400	1.56846100
H	4.72301900	-1.77426900	-1.39986200
C	-3.46541400	0.51300200	-0.26463000
C	-4.49031100	-0.08844500	-1.05206300
C	-3.85384500	1.59712700	0.57466700
C	-5.80336900	0.34455900	-0.97601300
H	-4.25315600	-0.86669000	-1.76373500
C	-5.17275700	2.01393800	0.64204400
H	-3.10319700	2.11535400	1.15951700
H	-6.54812500	-0.11888100	-1.61528600
H	-5.42947200	2.84196900	1.29866300
C	6.90357800	-0.86141400	-0.09757500
S	7.28632300	-2.28493100	1.04452600
C	7.19921700	-1.52907100	2.70585100
H	7.31389200	-2.35580200	3.41160500
H	8.01218400	-0.81607200	2.86559000
H	6.23120500	-1.05214800	2.87625900
H	7.00465600	-1.34240800	-1.07506400
C	-6.18163000	1.39182300	-0.11587700
C	-7.61155500	1.87252700	0.01462700
H	-7.59790800	2.86048200	0.48575400
C	7.98466000	0.26331300	-0.00744700
H	7.94641800	0.74422100	0.97467600
C	7.71647400	1.30340200	-1.01535500
N	7.50988500	2.11463200	-1.81965200

S	-8.48790500	2.09743800	-1.60581200
C	-7.61383600	3.59797500	-2.18015500
H	-6.54504000	3.40721300	-2.30460300
H	-8.04558100	3.85344100	-3.15098000
H	-7.76740100	4.43185300	-1.48973800
C	-8.45993800	0.97994700	0.99538800
H	-7.90687000	0.97423300	1.94155900
C	-9.76566300	1.59798800	1.27514300
N	-10.78187800	2.09706600	1.53039300
C	-8.66071000	-0.46263700	0.54575300
N	-9.43226800	-0.77851500	-0.41443000
S	-7.80165200	-1.76246700	1.42069900
C	-8.34616500	-2.93977800	0.11679100
H	-8.62838400	-3.89335200	0.56375000
H	-7.51921400	-3.09940300	-0.57768600
C	-9.53626100	-2.22291900	-0.59163900
H	-9.52005500	-2.46841900	-1.65762400
C	-10.88333000	-2.69889000	-0.03298900
O	-11.61991800	-2.05634700	0.68072200
O	-11.13246900	-3.96230400	-0.42907300
H	-11.97634900	-4.23942300	-0.02187900
C	9.41074500	-0.24705500	-0.15426400
N	10.25344900	-0.12049800	0.78928600
S	9.93514500	-1.02768000	-1.67992800
C	11.48145700	-1.54338300	-0.82541600
H	12.33187300	-1.44462800	-1.50071600
H	11.38281200	-2.58739400	-0.52253800
C	11.57809100	-0.61071300	0.41945400
H	12.00921600	-1.17104900	1.25429800
C	12.49822600	0.58535700	0.14808300
O	12.13926400	1.72667700	-0.03481200
O	13.78453600	0.18619200	0.11245000
H	14.33118500	0.96714300	-0.10225900

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 83 84 1.0
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SCF Done: E(RB3LYP) = -3763.72022650 a.u.

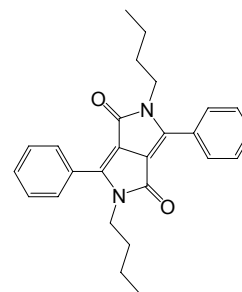
Number of Imaginary frequencies: 0

Compound DPP ground state configuration (DFT B3LYP 6-31G(d))

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-0.60250670	-0.38225286	0.01590751
C	0.60250392	0.38226728	-0.01593701
C	-1.68990236	0.47509243	-0.06066368
C	1.68989814	-0.47507768	0.06065555
C	-3.11546424	0.13796599	-0.03222488
C	-3.53303843	-1.09519442	-0.57258843
C	-4.08092331	0.97894479	0.55549510
C	-4.87592892	-1.46098217	-0.54563153
H	-2.79820476	-1.76445359	-1.00477130
C	-5.42229707	0.60252220	0.58645607
H	-3.78435671	1.91199049	1.01960988
C	-5.82669893	-0.61289815	0.02946472



H	-5.18152488	-2.41072928	-0.97517704
H	-6.15127313	1.25968631	1.05163618
H	-6.87393134	-0.90069408	0.05000996
C	3.11546202	-0.13796160	0.03222843
C	4.08091927	-0.97896828	-0.55545324
C	3.53304305	1.09520425	0.57257419
C	5.42229829	-0.60256348	-0.58640225
H	3.78434736	-1.91202489	-1.01954420
C	4.87593848	1.46097457	0.54562868
H	2.79821163	1.76448153	1.00473264
C	5.82670650	0.61286569	-0.02943463
H	6.15127356	-1.25974932	-1.05155300
H	5.18154003	2.41072716	0.97515816
H	6.87394298	0.90064754	-0.04996957
C	-0.24579470	-1.78064005	0.14416721
C	0.24579055	1.78065450	-0.14419517
O	-0.90341214	-2.81639070	0.22960179
O	0.90340688	2.81640651	-0.22962170
N	1.18747831	-1.77050770	0.15797615
C	1.91577619	-3.00376932	0.42217358
H	2.27214151	-3.47398389	-0.50030442
H	2.76458087	-2.81077332	1.08050781
H	1.22101022	-3.68931881	0.90990607
N	-1.18748225	1.77052312	-0.15799117
C	-1.91577558	3.00378739	-0.42218962
H	-2.76458660	2.81079317	-1.08051597
H	-2.27212921	3.47401106	0.50028821
H	-1.22100894	3.68932891	-0.90993254

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2 4 2.0 28 1.0

3 5 1.0 36 1.0

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37 38 1.0 39 1.0 40 1.0
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SCF Done: E(RB3LYP) = -1031.74500983 a.u.

Number of Imaginary frequencies: 0

compound DPP excited state configuration (TDDFT B3LYP 6-31G(d))

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.58751200	0.37343000	0.00181100
C	-0.58752300	-0.37338000	-0.00187000
C	1.73376100	-0.50248600	-0.03555300
C	-1.73377400	0.50253100	0.03552100
C	3.12427100	-0.15042800	-0.00821800
C	3.50672100	1.17490500	-0.36966700
C	4.16207900	-1.04532600	0.38251200
C	4.83917000	1.56018400	-0.36937300
H	2.74134300	1.89278600	-0.63950900
C	5.49037300	-0.64210600	0.38124300
H	3.92592400	-2.04176700	0.73011300
C	5.84592300	0.65704500	-0.00314100
H	5.09916500	2.57479400	-0.65918900
H	6.25754800	-1.34511400	0.69416000
H	6.88806200	0.96280400	-0.00642900
C	-3.12427800	0.15044000	0.00821000

C	-4.16212800	1.04529400	-0.38251400
C	-3.50667100	-1.17491000	0.36965400
C	-5.49040600	0.64202000	-0.38122700
H	-3.92602300	2.04174000	-0.73013100
C	-4.83910500	-1.56024300	0.36938000
H	-2.74125900	-1.89276300	0.63947900
C	-5.84589900	-0.65714400	0.00316400
H	-6.25761300	1.34499500	-0.69413900
H	-5.09905400	-2.57486600	0.65919400
H	-6.88802600	-0.96294600	0.00646300
C	0.22390600	1.77770100	0.09384800
C	-0.22391900	-1.77765000	-0.09392600
O	0.88935700	2.81245200	0.17730000
O	-0.88937500	-2.81240400	-0.17731100
N	-1.20524600	1.78214200	0.08736900
C	-1.90305900	3.04240100	0.30780200
H	-2.30997200	3.44713500	-0.62418700
H	-2.70956000	2.90798900	1.03113800
H	-1.16929200	3.74779300	0.69877100
N	1.20523200	-1.78209500	-0.08737200
C	1.90306800	-3.04236000	-0.30770400
H	2.70961300	-2.90797100	-1.03099400
H	2.30992800	-3.44704800	0.62432900
H	1.16933100	-3.74777500	-0.69868700

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SCF Done: E(RB3LYP) = -1031.73812451 a.u.

Number of Imaginary frequencies: 0