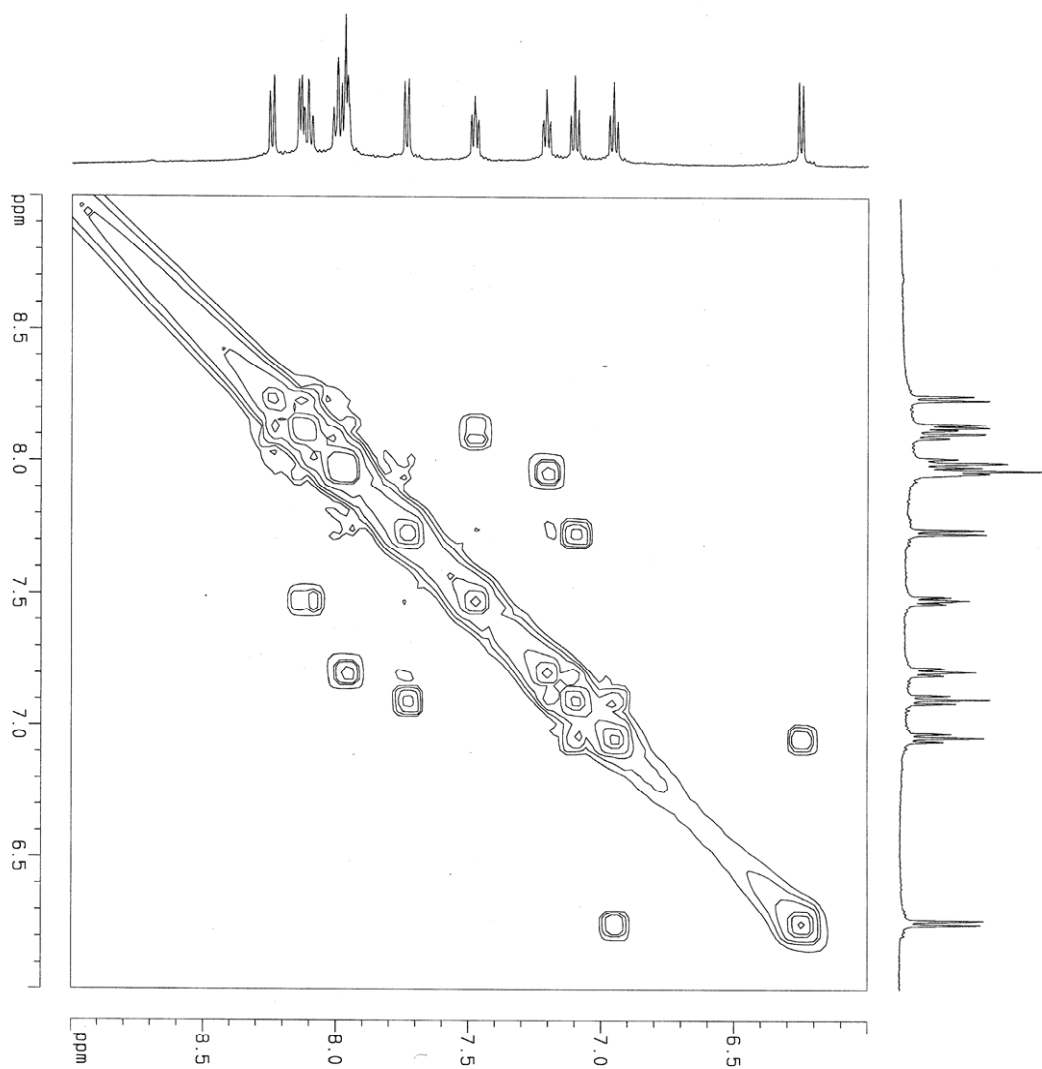
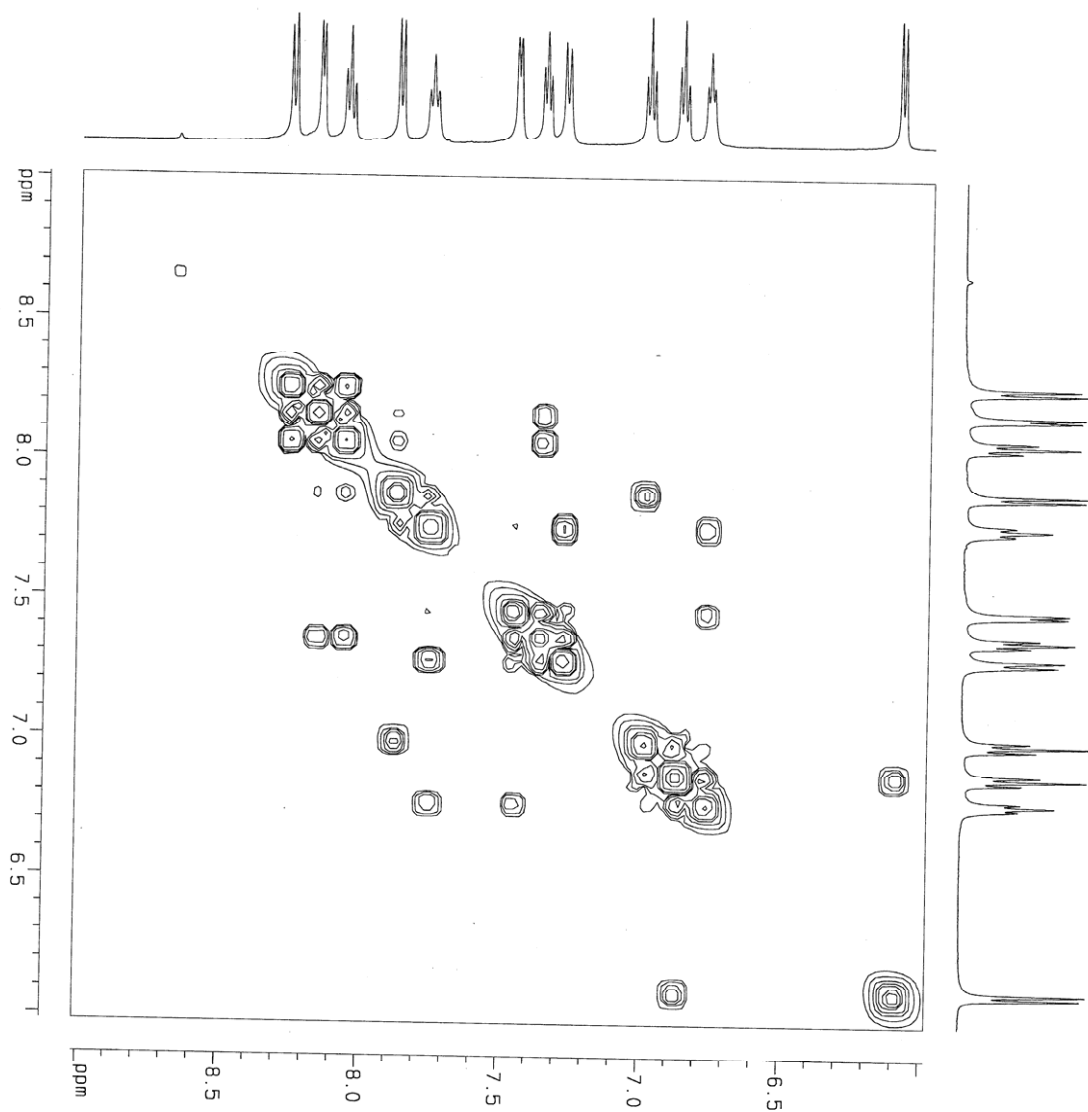


### Supplementary Information

S<sub>1</sub> COSY of (1)



S<sub>2</sub> COSY of (2)



S<sub>3</sub> DFT (B3PW91) Optimized Geometry of (1) in XYZ Format

Rh	0.167520313	0.036939486	-0.000731344
N	-1.071881811	1.019246256	-1.344140575
C	0.543582450	1.926630421	0.535447870
N	1.576310008	-0.774127356	1.283769976
N	-0.368869453	-2.071344146	-0.599153569
N	-1.614296109	-0.115913058	1.403152551
C	1.785952738	0.193135389	-1.163194989
C	-1.785996028	0.432530301	-2.317436353
C	-1.127426484	2.369322908	-1.179682422
C	1.437499835	2.372856693	1.512139571
C	-0.248988560	2.887364042	-0.134599913
C	2.851270901	-0.772049036	0.804984586
C	1.315892856	-1.273267414	2.501640618
C	-1.608285114	-2.593255261	-0.521485246
C	0.611437547	-2.847735449	-1.086311813
C	-1.648160096	0.716107668	2.455878947
C	-2.727079096	-0.819239599	1.118923033
C	2.984398743	-0.249810368	-0.552094481
C	1.851503338	0.672536052	-2.473217054
C	-1.958549885	3.136722863	-2.005526252
C	-2.619804130	1.143718447	-3.166701615
C	-0.153421707	4.248068184	0.192760052
C	1.529915732	3.730148818	1.831776178
C	2.306272450	-1.780417031	3.328430475
C	3.892737817	-1.267138968	1.601194390
C	0.412182709	-4.162962004	-1.494045574
C	-1.893671289	-3.898979483	-0.934973177
C	-3.900277503	-0.692397813	1.869989368
C	-2.767017149	0.875992194	3.268267552
C	3.065552841	0.706738967	-3.162015282
C	4.202001068	-0.210735365	-1.250278638
H	-1.666589212	-0.640032806	-2.418168757
H	2.077540964	1.668870319	2.036351556
H	0.957157130	1.031606614	-2.972952675
H	0.276149145	-1.256410823	2.807386743
H	1.589020346	-2.384120309	-1.162581659
H	-0.742886270	1.286617231	2.636381468
C	-2.791517890	-1.806745266	-0.015702851
C	-2.710366088	2.525416153	-2.997873333
C	0.732444801	4.669161534	1.176614005
C	3.623047315	-1.768095354	2.865921948
C	-0.867499749	-4.701972360	-1.417834992
C	-3.921388019	0.162158984	2.965579536
C	4.242739977	0.267840834	-2.552870082
H	-3.178047047	0.623696492	-3.937580750
H	-0.765474596	4.986218107	-0.318927625
H	-2.004169701	4.211533054	-1.871498435
H	2.234100686	4.055754705	2.593737116
H	3.093353600	1.084165339	-4.181386322
H	5.121283716	-0.552935536	-0.782015044
H	4.909308532	-1.255615936	1.224514167
H	2.048717175	-2.170902785	4.307094194
H	1.250686001	-4.740185597	-1.870391784
H	-2.915594726	-4.254773272	-0.871403069
H	-2.724210996	1.558484488	4.111105572
H	-4.769601048	-1.269703113	1.576869248
O	-3.889346207	-2.092402261	-0.464416418

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H	-3.353651619	3.119905609	-3.640234324
H	0.807173284	5.723429554	1.426501391
H	5.185163140	0.300459872	-3.091609837
H	4.429701034	-2.149439252	3.485482140
H	-1.065820238	-5.722239424	-1.732899018
H	-4.819698165	0.267628716	3.566844492

S<sub>4</sub> DFT (B3PW91) Optimized Geometry of (2) in XYZ Format

Rh	0.07336407	-0.03460061	-0.00918780
N	-1.33512588	-0.69505698	1.36049184
C	-0.14733366	-1.91187980	-0.65688857
C	1.62705042	-0.73961329	1.03085310
N	1.59408047	0.42426908	-1.33710299
N	-1.63905834	0.75769141	-1.27254209
N	0.20730638	2.08829178	0.76327615
C	-1.76315918	-1.97205030	1.16447646
C	-1.81693049	0.02493168	2.38472910
C	0.50627457	-2.52570459	-1.72853186
C	-1.12570822	-2.65647479	0.04337856
C	2.87769603	-0.58336833	0.38454517
C	1.60889037	-1.33066907	2.29628739
C	1.42774475	1.03943947	-2.51752541
C	2.83935109	0.05632773	-0.92788399
C	-2.37267871	1.83047176	-0.94741496
C	-2.06150814	-0.00439329	-2.30572050
C	-0.77871218	2.99271741	0.67664981
C	1.35409340	2.46252891	1.36943311
C	-2.76504492	-0.47137157	3.26618064
C	-2.72537265	-2.52241818	2.02114743
C	-1.43671662	-3.96951828	-0.33997712
C	0.19294543	-3.83447902	-2.10451311
C	2.79234249	-1.74863736	2.90803732
C	4.06381717	-1.00609985	1.00519973
C	3.94433610	0.31221014	-1.75036785
C	2.48534809	1.31825685	-3.36956142
C	-3.21515679	0.24369954	-3.02601325
C	-3.56786732	2.14818095	-1.62198552
C	1.55769885	3.70983069	1.93121700
C	-0.65378627	4.28451209	1.22306401
N	-2.00123334	2.67962611	0.08956962
H	2.12325398	1.69954564	1.41159549
H	0.66908116	-1.47673808	2.82021090
H	0.40862317	1.30732287	-2.77193748
H	1.27275539	-1.99204653	-2.28328219
H	-1.41024195	1.02319910	2.49567983
H	-1.43520848	-0.86012850	-2.53409824
C	-3.23004965	-1.77263557	3.07277419
C	-0.77968243	-4.55805520	-1.41313055
C	4.02132500	-1.58852646	2.26491343
C	3.76941202	0.94115646	-2.97401246
C	-3.99278973	1.34590236	-2.66293049
C	0.52000928	4.64152830	1.85936668
H	2.50055505	3.94087859	2.41453412
H	-1.47150132	4.99412771	1.12959729
H	2.75432528	-2.20681968	3.89348113
H	5.02344525	-0.88435015	0.50942048
H	4.93524666	0.01382800	-1.42713649
H	0.71670197	-4.29318863	-2.93987076
H	2.30257654	1.81509284	-4.31633434
H	-2.19160290	-4.53966449	0.19528490
H	-3.06656888	-3.53917308	1.86288671
H	-3.12152403	0.14625668	4.08360277
H	-2.67787303	3.41835119	0.22404718
H	-4.13974328	3.02463092	-1.32900648
H	-3.49942829	-0.41331482	-3.84055201

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H	0.62936761	5.63539247	2.28355989
H	4.93878184	-1.91824346	2.74357079
H	4.62485510	1.13723785	-3.61413089
H	-1.01972335	-5.57573731	-1.70682133
H	-3.97282089	-2.19943355	3.74071845
H	-4.91152902	1.58145593	-3.19219264

S<sub>5</sub> Frontier Orbitals of (1) and Their Composition (H=HOMO, L=LUMO, L+1=LUMO+1, etc.)

Orbital	<i>E</i> (eV)	Rh %	dpk %	ppy	
				phenyl %	pyridyl %
L+9	-2.54	28.7	9.3	56.7	5.3
L+8	-3.08	50.7	3.6	19.6	26.1
L+7	-3.55	0.6	63.1	5.1	31.1
L+6	-3.58	0.6	36.1	6.8	56.4
L+5	-3.67	2.1	10.5	13.2	74.2
L+4	-4.04	1.6	85.8	0.9	11.7
L+3	-4.12	1.2	43.5	14.4	40.9
L+2	-4.20	3.6	45.4	13.0	38.1
L+1	-4.25	4.4	13.4	23.5	58.7
L	-5.46	0.9	97.8	0.2	1.0
H	-8.42	30.5	1.5	56.9	11.1
H-1	-8.69	1.9	1.6	74.6	22.0
H-2	-8.95	6.3	0.7	76.7	16.4
H-3	-9.03	3.7	1.9	84.3	10.0
H-4	-9.47	70.4	3.6	9.8	16.3
H-5	-9.52	70.0	5.2	8.5	16.3
H-6	-9.95	6.9	65.7	26.4	1.0
H-7	-10.09	19.6	17.5	60.4	2.4
H-8	-10.31	5.2	79.2	13.0	2.7
H-9	-10.51	13.4	66.4	14.9	5.3

S<sub>6</sub> Frontier Orbitals of (2) and Their Composition (H=HOMO, L=LUMO, L+1=LUMO+1, etc.)

Orbital	<i>E</i> (eV)	Rh %	HDP A %	ppy	
				phenyl %	pyridyl %
L+9	-2.39	27.3	10.1	57.7	4.8
L+8	-2.65	5.9	89.3	1.6	3.2
L+7	-2.91	47.7	7.8	19.7	24.8
L+6	-3.44	1.3	1.3	10.6	86.8
L+5	-3.47	0.1	97.9	0.7	1.3
L+4	-3.54	2.0	8.5	13.5	76.1
L+3	-3.88	1.7	86.4	0.5	11.4
L+2	-4.01	2.6	13.1	20.9	63.3
L+1	-4.08	3.5	13.3	23.9	59.2
L	-4.12	2.7	77.8	5.4	14.1
H	-8.26	32.3	2.4	55.1	10.3
H-1	-8.56	2.0	1.3	75.5	21.2
H-2	-8.82	6.8	1.4	75.3	16.5
H-3	-8.90	7.2	6.1	77.4	9.4
H-4	-8.94	10.6	75.8	10.5	3.0
H-5	-9.28	70.3	4.1	10.3	15.3
H-6	-9.40	57.6	21.5	7.0	13.8
H-7	-9.97	19.9	15.9	61.8	2.5
H-8	-10.01	15.2	34.3	48.1	2.5
H-9	-10.41	32.7	7.4	31.0	28.9

S<sub>7</sub> Complete Listing of TD-DFT Calculated Singlet Excited States of (1) at B3PW91 Level

#	(eV)	(nm)	(f)	(Assignment; H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
1	2.37	523.6	0.0065	H→L (+98%)
2	2.71	456.8	0.0030	H-1→L (+98%)
3	2.99	414.3	0.0020	H-2→L (+97%)
4	3.05	406.3	0.0022	H-3→L (+89%)
5	3.26	380.4	0.0015	H-6→L (15%), H-4→L (+74%)
6	3.31	374.5	0.0039	H-6→L (+43%), H-4→L (+23%)
7	3.36	369.2	0.0154	H-5→L (+84%)
8	3.43	362.0	0.0364	H→L+1 (+90%)
9	3.52	352.8	0.0015	H→L+2 (+86%)
10	3.65	340.1	0.0081	H→L+3 (+88%)
11	3.75	330.5	0.0081	H→L+4 (+92%)
12	3.84	323.1	0.0058	H-1→L+1 (+87%)
13	3.89	318.7	0.0275	H-1→L+2 (+80%)
14	3.96	313.4	0.0068	H-7→L (+89%)
15	4.01	309.0	0.0105	H-1→L+3 (+75%)
16	4.02	308.8	0.0197	H-8→L (+62%), H-6→L (17%)
17	4.05	306.1	0.0045	H→L+5 (22%), H→L+8 (+47%)
18	4.08	303.6	0.0188	H-2→L+1 (+21%), H→L+5 (+43%), H→L+8 (+18%)
19	4.10	302.7	0.0018	H-1→L+4 (+82%)
20	4.14	299.4	0.0302	H-2→L+1 (+56%), H→L+5 (17%)
21	4.17	297.6	0.0146	H-3→L+2 (13%), H-2→L+2 (+39%), H→L+6 (10%)
22	4.17	297.2	0.0171	H-3→L+1 (+22%), H-3→L+2 (11%), H→L+6 (+30%)
23	4.19	296.2	0.0121	H-3→L+2 (+15%), H-2→L+2 (+23%), H→L+6 (+14%)
24	4.23	293.2	0.0319	H-3→L+1 (+38%), H→L+6 (14%)
25	4.27	290.4	0.0035	H→L+6 (16%), H→L+7 (+69%)
26	4.28	289.6	0.0138	H-2→L+3 (+60%)
27	4.30	288.2	0.0227	H-4→L+2 (16%), H-4→L+8 (+27%), H-2→L+3 (12%)
28	4.32	286.8	0.0021	H-3→L+2 (+22%), H-3→L+3 (+39%), H-2→L+4 (25%)
29	4.34	285.6	0.0472	H-5→L+8 (+15%), H-3→L+2 (+16%), H-2→L+4 (+12%)
30	4.36	284.5	0.0101	H-4→L+1 (+63%), H-3→L+3 (+10%)
31	4.41	281.4	0.0152	H-3→L+3 (+20%), H-2→L+4 (+48%)
32	4.44	279.3	0.0120	H-10→L (14%), H-9→L (11%), H-5→L+1 (+23%), H-1→L+5 (+10%)
33	4.45	278.8	0.0060	H-10→L (+18%), H-9→L (+30%), H-5→L+1 (+12%), H-1→L+5 (+16%)
34	4.47	277.6	0.0064	H-5→L+1 (+15%), H-3→L+4 (+56%)
35	4.47	277.3	0.0444	H-13→L (+17%), H-9→L (10%), H-1→L+5 (+23%)
36	4.49	276.2	0.0580	H-13→L (13%), H-3→L+4 (+18%), H-1→L+5 (+12%)
37	4.54	272.9	0.0251	H-4→L+3 (22%), H-1→L+6 (+29%)
38	4.57	271.2	0.0086	H-12→L (13%), H-10→L (+35%), H-4→L+3 (+13%)
39	4.59	270.1	0.0013	H-4→L+2 (10%), H→L+9 (+33%)
40	4.59	270.0	0.0198	H-5→L+2 (10%), H-4→L+3 (+16%), H→L+9 (+23%)
41	4.60	269.3	0.0072	H-1→L+6 (21%), H-1→L+7 (+41%)
42	4.62	268.5	0.0179	H-5→L+3 (+15%), H-4→L+2 (11%), H-1→L+7 (+22%)
43	4.64	267.5	0.0561	H-5→L+2 (+27%), H-5→L+3 (+19%), H-2→L+5 (11%)
44	4.67	265.3	0.0494	H-5→L+3 (+26%), H-1→L+6 (10%), H-1→L+7 (11%)
45	4.71	263.1	0.0197	H-11→L (+29%), H-4→L+4 (+51%)
46	4.73	262.3	0.0274	H-13→L (+11%), H-11→L (+35%), H-4→L+4 (31%)
47	4.74	261.6	0.0245	H-2→L+5 (+15%), H-1→L+8 (+55%)
48	4.76	260.2	0.0161	H-13→L (13%), H-12→L (+43%), H-5→L+4 (22%), H-2→L+5 (+10%)
49	4.78	259.3	0.0405	H-12→L (+13%), H-5→L+4 (+24%), H-2→L+5 (11%)
50	4.80	258.1	0.0145	H-5→L+4 (+30%), H-3→L+5 (24%)

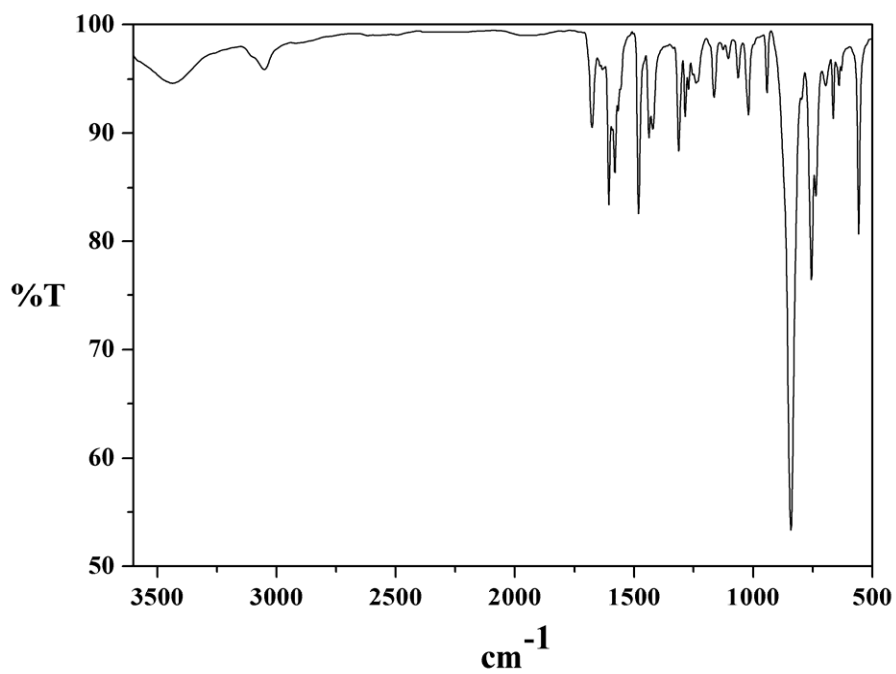


S<sub>8</sub> Complete Listing of TD-DFT Calculated Singlet Excited States of (2) at B3PW91 Level

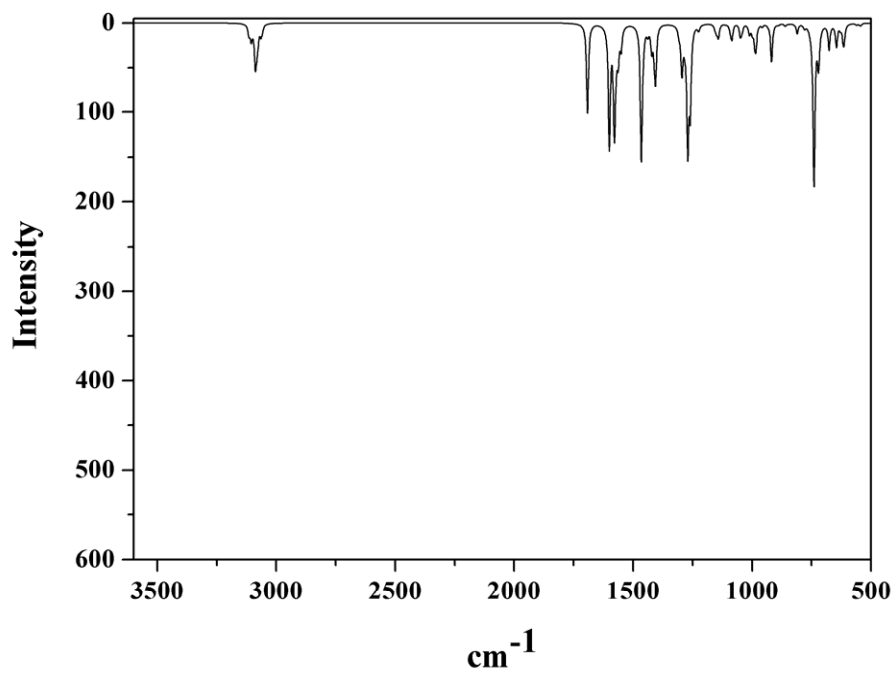
#	(eV)	(nm)	(f)	(Assignment; H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
1	3.40	364.7	0.0334	H→L (+75%), H→L+1 (+16%)
2	3.47	357.3	0.0035	H→L (14%), H→L+1 (+72%)
3	3.57	347.1	0.0043	H→L+2 (+85%)
4	3.74	331.1	0.0072	H→L+3 (+93%)
5	3.84	322.6	0.0027	H-1→L (+76%), H-1→L+1 (+11%)
6	3.88	319.5	0.0215	H-1→L+1 (+68%), H-1→L+2 (+14%)
7	3.97	312.2	0.0126	H-1→L (+10%), H-1→L+1 (11%), H-1→L+2 (+71%)
8	4.04	306.6	0.0077	H-3→L (12%), H→L+4 (+31%), H→L+7 (+30%)
9	4.05	306.5	0.0093	H→L+4 (+49%), H→L+7 (20%)
10	4.08	303.7	0.0133	H-4→L (10%), H-3→L (15%), H-3→L+1 (+19%), H-2→L (+10%)
11	4.11	302.0	0.0047	H-1→L+3 (+54%), H→L+5 (+18%), H→L+6 (13%)
12	4.12	301.0	0.0138	H-5→L (10%), H-2→L (+52%)
13	4.15	299.0	0.0060	H-2→L+1 (12%), H-1→L+3 (+14%), H→L+6 (+35%)
14	4.17	297.3	0.0014	H-3→L (21%), H-2→L+1 (+14%), H→L+6 (+27%)
15	4.17	297.2	0.0901	H-4→L (+10%), H-3→L+2 (+15%), H-2→L+1 (+29%)
16	4.20	295.1	0.0147	H-1→L+3 (15%), H→L+5 (+47%)
17	4.22	293.7	0.0165	H-3→L+1 (12%), H-3→L+2 (+13%), H-2→L+1 (12%), H-2→L+2 (+18%)
18	4.24	292.7	0.0191	H-2→L+2 (36%), H→L+5 (10%)
19	4.27	290.6	0.0461	H-4→L (+38%), H-3→L (13%), H→L+6 (10%)
20	4.28	289.7	0.0102	H-4→L+1 (+48%), H-3→L+1 (15%)
21	4.29	289.2	0.0096	H-5→L (21%), H-5→L+7 (+20%)
22	4.33	286.3	0.0101	H-5→L (+16%), H-4→L+2 (+33%), H-3→L+2 (13%)
23	4.33	286.1	0.0624	H-5→L (+12%), H-5→L+1 (+16%), H-2→L+3 (+10%), H-1→L+6 (+11%)
24	4.37	283.8	0.0166	H-4→L+2 (+23%), H-4→L+3 (11%), H-3→L+3 (18%)
25	4.40	281.5	0.0102	H-3→L+2 (12%), H-2→L+3 (+38%)
26	4.42	280.3	0.0084	H-5→L+2 (+19%), H-3→L+3 (+16%), H-2→L+3 (+24%)
27	4.46	278.3	0.0289	H-1→L+4 (+49%)
28	4.50	275.6	0.0192	H-6→L (+10%), H-5→L (17%), H-5→L+1 (+25%), H-5→L+2 (13%)
29	4.52	274.5	0.0153	H-5→L+2 (10%), H-4→L+3 (+55%), H-3→L+3 (16%)
30	4.52	274.3	0.0056	H-6→L (+24%), H-6→L+1 (+12%), H-5→L+2 (+18%), H-3→L+3 (15%)
31	4.56	272.2	0.0253	H-6→L+1 (+10%), H-1→L+5 (+22%), H-1→L+6 (17%), H→L+9 (17%)
32	4.56	271.9	0.0131	H-1→L+5 (+56%), H→L+9 (+22%)
33	4.58	271.0	0.0402	H-6→L+1 (+18%), H-1→L+5 (16%), H→L+9 (+21%)
34	4.59	270.0	0.0250	H-6→L (18%), H-6→L+2 (20%), H-1→L+6 (+24%)
35	4.63	268.0	0.0339	H-6→L+1 (+30%)
36	4.66	265.9	0.0195	H-6→L+2 (+33%), H-2→L+4 (20%), H-1→L+6 (+12%)
37	4.70	264.0	0.0092	H-5→L+3 (+72%)
38	4.76	260.5	0.0920	H-6→L+2 (10%), H-2→L+4 (30%), H-1→L+7 (+33%)
39	4.77	259.9	0.0149	H-3→L+4 (+54%), H-2→L+6 (17%)
40	4.80	258.4	0.0186	H-3→L+6 (22%), H-2→L+4 (+13%), H-1→L+7 (+44%)
41	4.83	256.7	0.0086	H-4→L+4 (30%), H-2→L+5 (+58%)
42	4.84	256.4	0.0076	H-6→L+3 (+15%), H-4→L+4 (+38%), H-2→L+5 (+12%), H-2→L+6 (+13%)
43	4.86	255.0	0.0206	H-6→L+3 (+49%), H-2→L+6 (20%)
44	4.87	254.8	0.0588	H-6→L+3 (+18%), H-3→L+6 (+13%), H-2→L+6 (+21%)
45	4.87	254.7	0.0869	H-4→L+4 (+10%), H-4→L+6 (+12%), H-3→L+6 (+25%)
46	4.89	253.4	0.1009	H-3→L+5 (+74%)
47	4.93	251.3	0.0467	H-4→L+6 (+72%), H-3→L+6 (10%)
48	4.96	250.0	0.0745	H-4→L+5 (+61%)
49	4.99	248.2	0.0376	H-7→L+1 (+40%), H-5→L+4 (+31%)
50	5.01	247.4	0.0084	H-7→L+1 (20%), H-5→L+4 (+27%), HOMO→L+8 (+20%)

S<sub>9</sub> Comparison of Experimental IR and DFT Calculated spectrum for (1)

Experimental

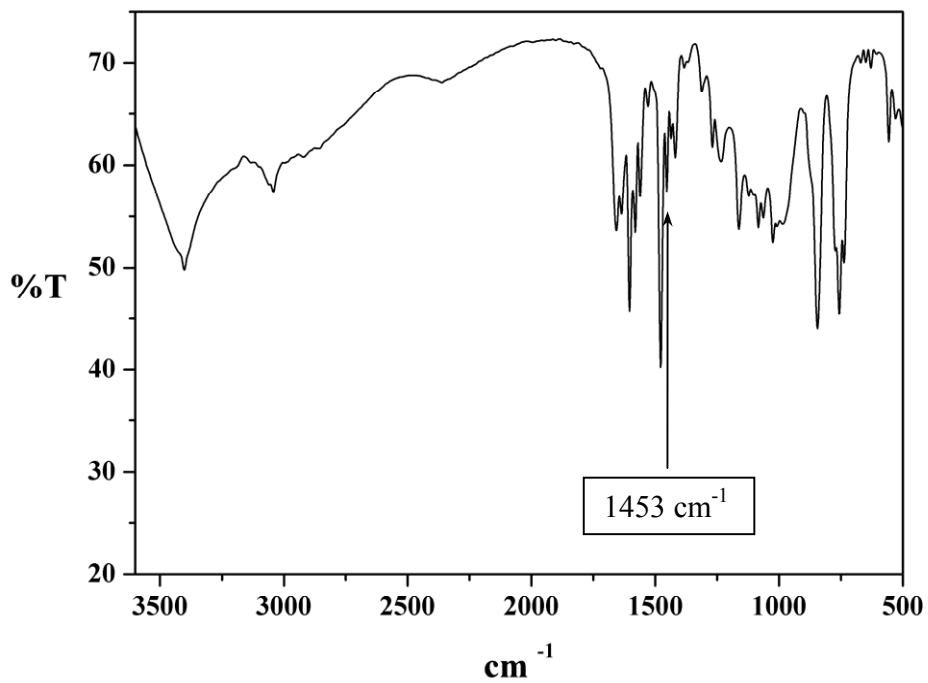


Calculated



S<sub>10</sub> Comparison of Experimental IR and DFT Calculated spectrum for (2)

Experimental



Calculated

