Supporting Information

Benzothiophene Based Semi-Bis-Chalcone as Photo-Luminescent Chemo-Sensor with Real Time Hydrazine Sensing and DFT Studies

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General Information and Material:

All the chemicals were obtained from Sigma–Aldrich and were used without further purification. Solvents were dried over molecular sieves if necessary. The ^{1}H, H-H Cosy and HERTCORE NMR spectra were recorded in $CDCl_3$ or DMSO-*d6* at room temperature using a Bruker AVANCE III 500 MHz (AV 500) multi nuclei solution NMR Spectrometer, TMS was used as internal reference, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad, app = apparent), coupling constants (J; Hz), and assignment. ^{13}C and DEPT-135 NMR spectra were measured on Bruker AVANCE III 125 MHz (AV 125) with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. Infrared (IR) spectra were recorded neat by ATR on a Thermo Nicolet iS50 FT–IR spectrometer and are reported in cm^{-1}. HR–MS data were obtained in methanol, with Thermo Scientific Orbitrap Elite Mass spectrometer. Melting point is measured by open capillary method using Sigma Melting Point Apparatus. Single crystal structural data were recorded on Bruker Kappa APEXII. High performance liquid chromatography (HPLC) was performed on JASCO instruments at 210 nm using 4.6 mm x 25 cm Daicel CHIRALCEL OJ-H. Optical rotations were measured on a Rudolph Autopol IV digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. The products were purified by recrystallization or column chromatography silica gel 60 (Merck, 230-400 mesh).

Spectral data:

(1*E*,4*E*)-1,5-bis(benzo[*b*]thiophen-2-yl)penta-1,4-dien-3-one (SBC 3a)

Yellow solid; Yield 80 %; M.P. 152-160 ^{0}C; IR (ν, cm^{-1}): 825 (C-S), 1100 (C-C), 1600 (C=C), 1789 (C=O), 3025 (C-H); ^{1}H NMR (500 MHz, $CDCl_3$) δppm: 7.965 (d, *J*=15.5 Hz, 2H), 7.817 (dd, *J*=16.0, 7.5 Hz, 4H), 7.574 (s, 2H), 7.417-7.386 (m, 4H), 6.905 (d, *J*=15.5 Hz, 2H), ^{13}C NMR (125MHz, $CDCl_3$) δppm: 187.46, 140.22, 139.75, 136.56, 130.00, 126.61, 125.02, 124.61, 122.58; HRMS (ESI; Ion Trap) m/z: [M+H] Calculated. ($C_{21}H_{15}OS_2$) 347.0712, Observed: 347.0716.

(1*E*,4*E*)-1,5-bis(benzo[*b*]thiophen-3-yl)penta-1,4-dien-3-one (SBC 3b)

Yellow solid; Yield 85 %; M.P. 158-160 ^{0}C; IR (ν, cm-1): 814 (C-S), 1100 (C-C), 1621 (C=C), 1762 (C=O), 2914 (C-H); ^{1}H NMR (500 MHz, $CDCl_3$) δppm: 7.729 (d, *J*=15.5 Hz, 1H), 7.637 (d, *J*=8.5, 2H), 7.598-7.534 (m, 3H), 7.467 (s, 1H), 7.411-7.371 (m, 2H), 7.318 (d, *J*=9.5, 1H), 7.071 (d, *J*=16, 2H), 6.687 (d, *J*=16, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δppm: 188.85, 143.33, 143.04, 142.92, 140.16, 133.82, 128.96, 128.81, 127.95, 127.65, 127.36, 127.09, 125.38; HRMS (ESI; Ion Trap) m/z: [M+H] Calculated ($C_{21}H_{15}OS_2$) 347.0730, Observed: 347.0736.

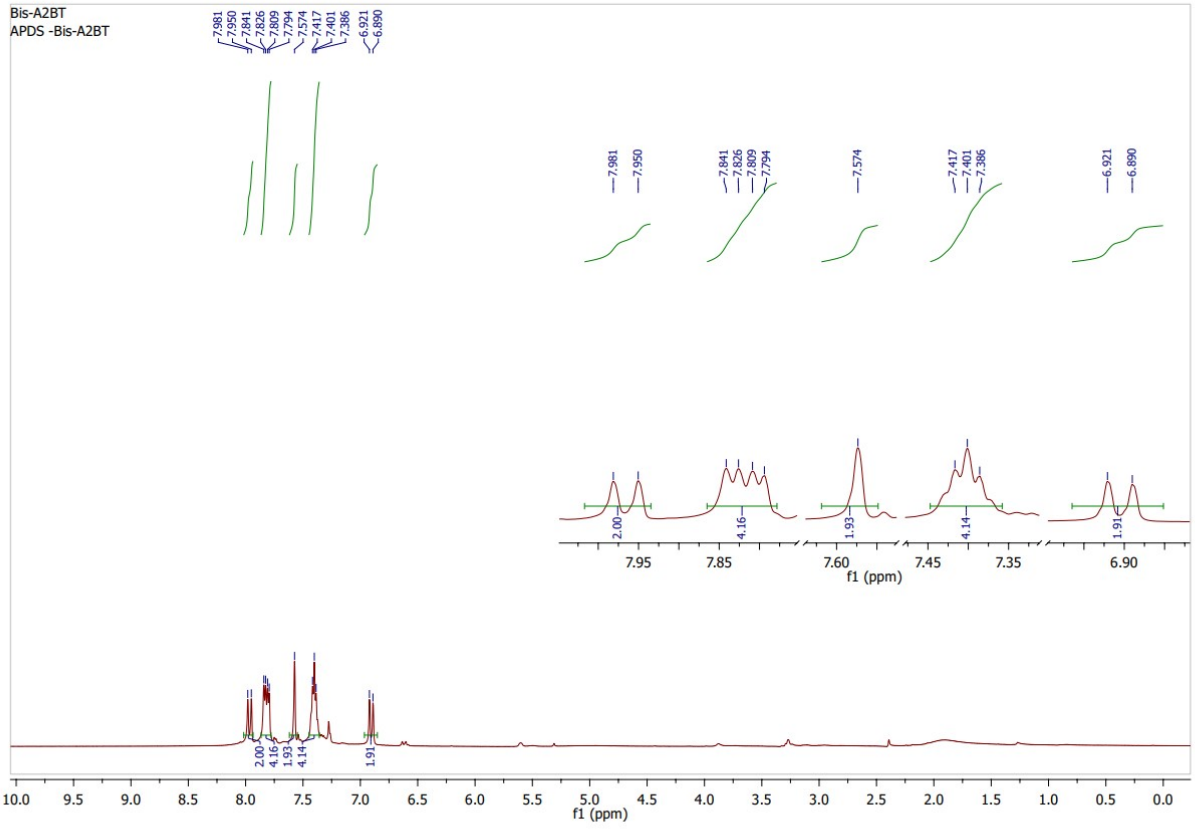


Figure S1. ^{1}H NMR Spectra of SBC **3a**

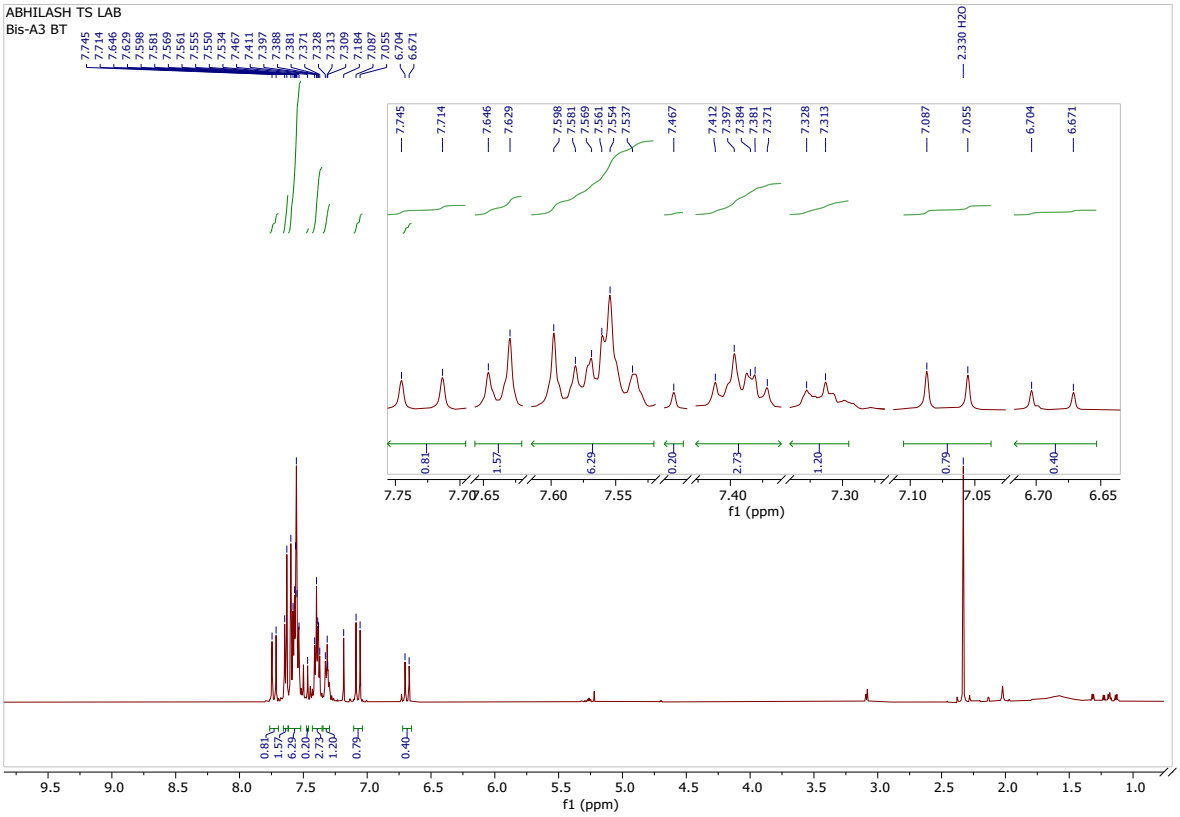


Figure S2. ^{1}H NMR Spectra of SBC **3b**

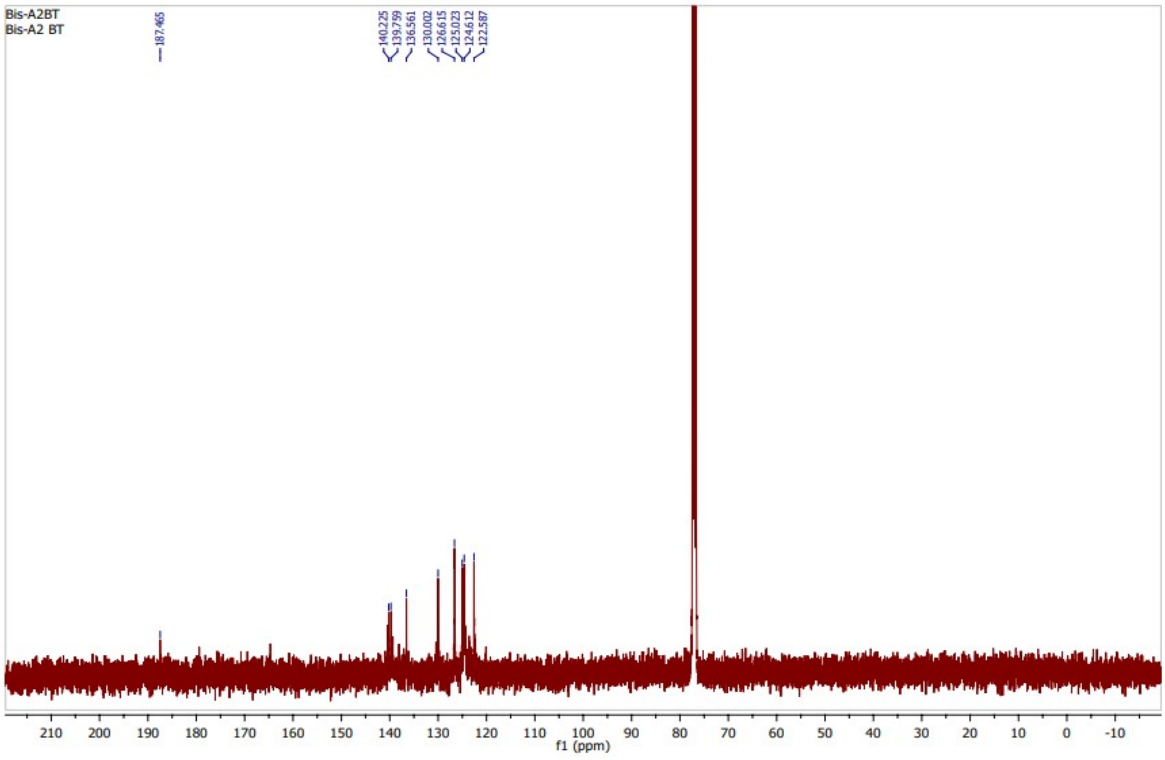


Figure S3. ^{13}C NMR Spectra of SBC **3a**

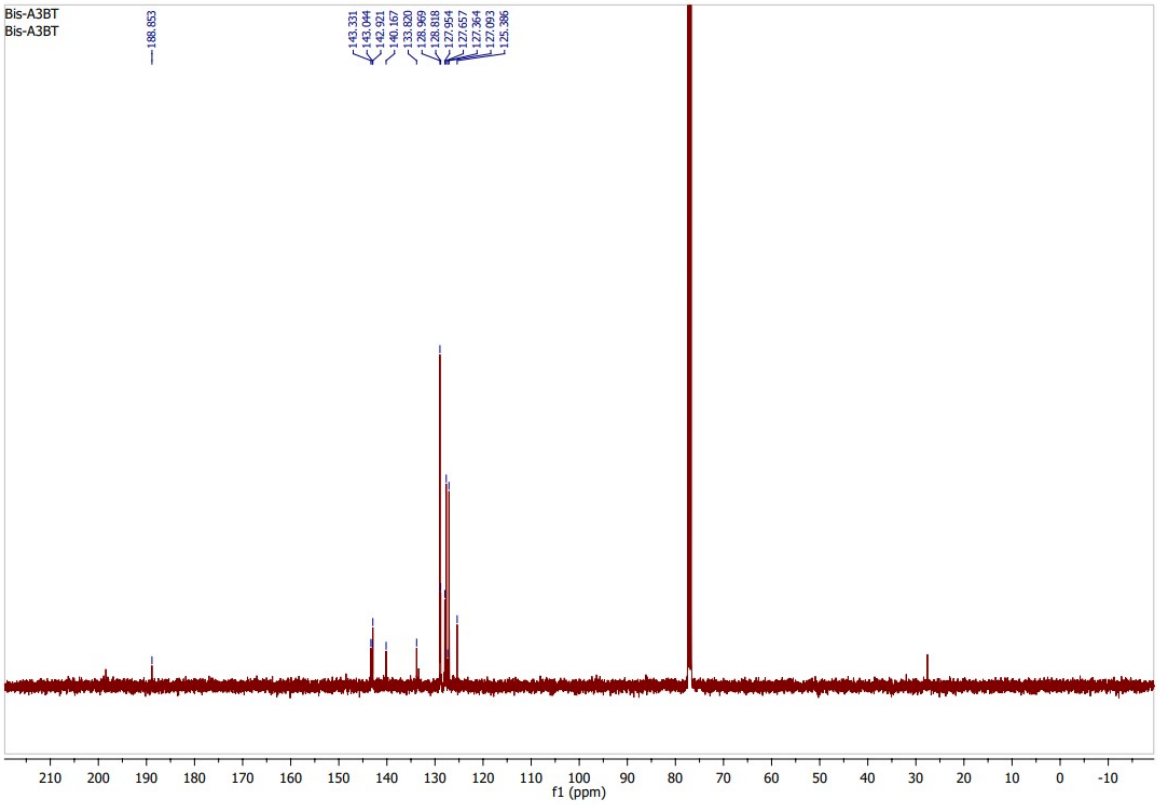


Figure S4. ^{13}C NMR Spectra of SBC **3b**

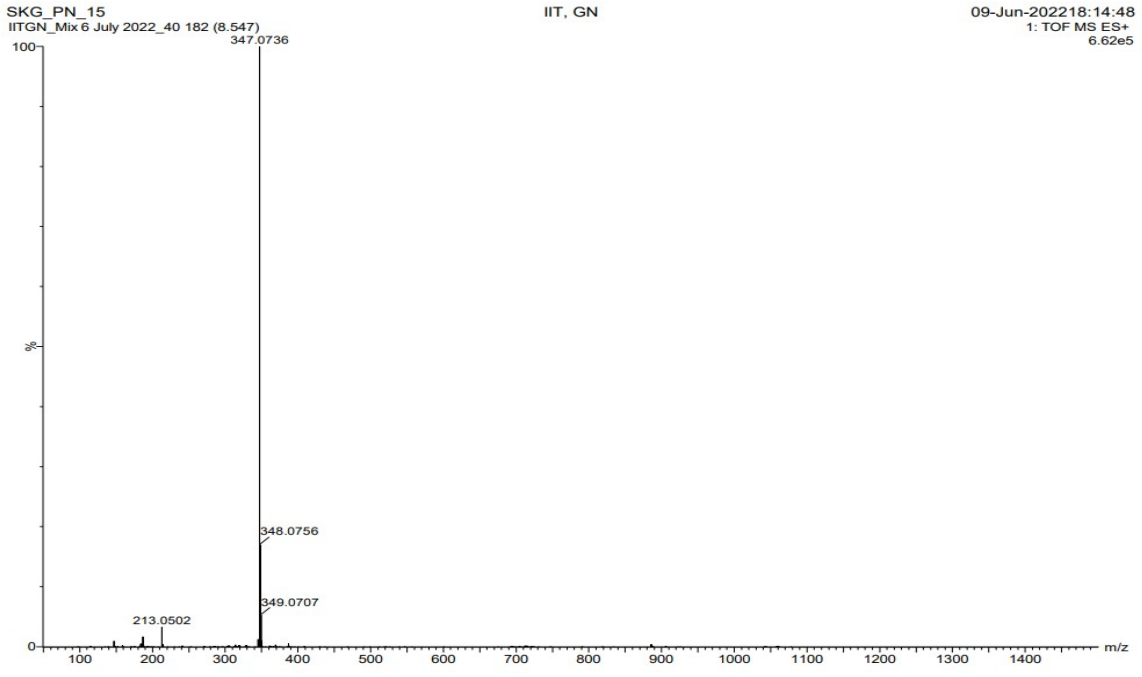


Figure S5. HRMS Spectra of SBC **3a**

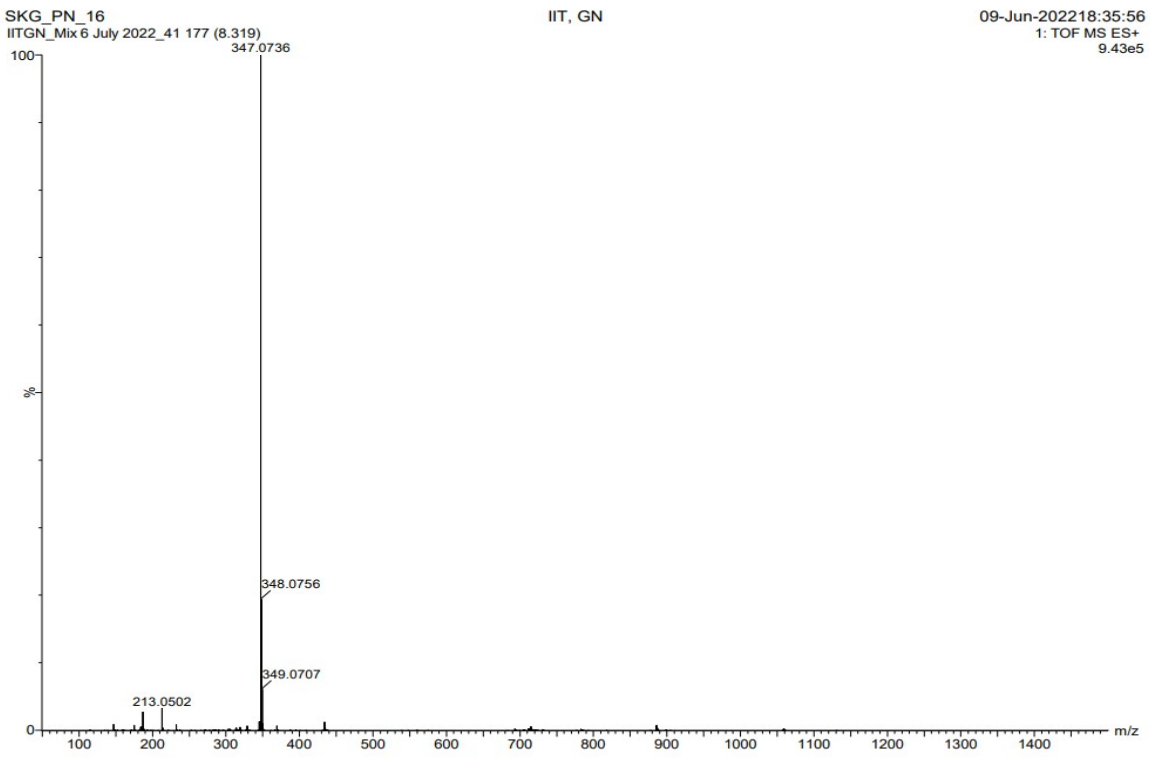


Figure S6. HRMS Spectra of SBC **3b**

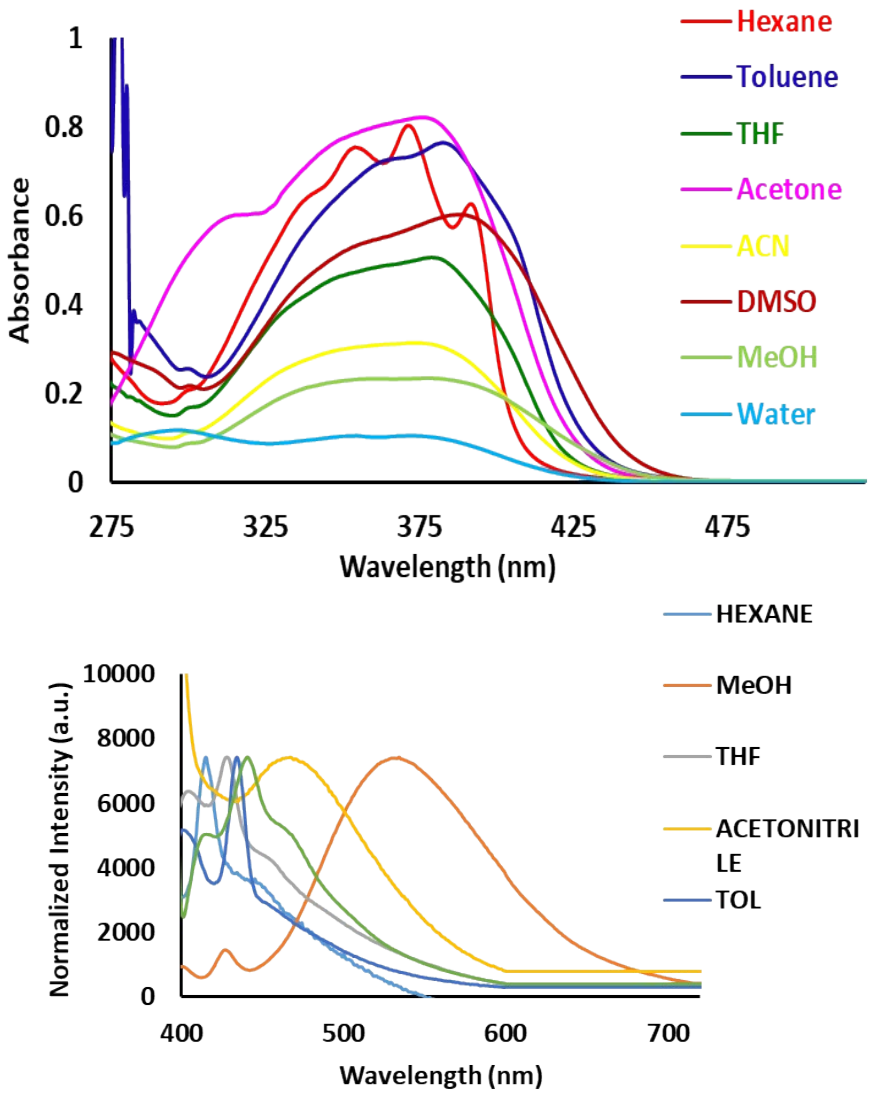


Figure S7. UV-Vis absorption and Fluorescence spectra of SBC **3a** in different solvents with 5μM concentration

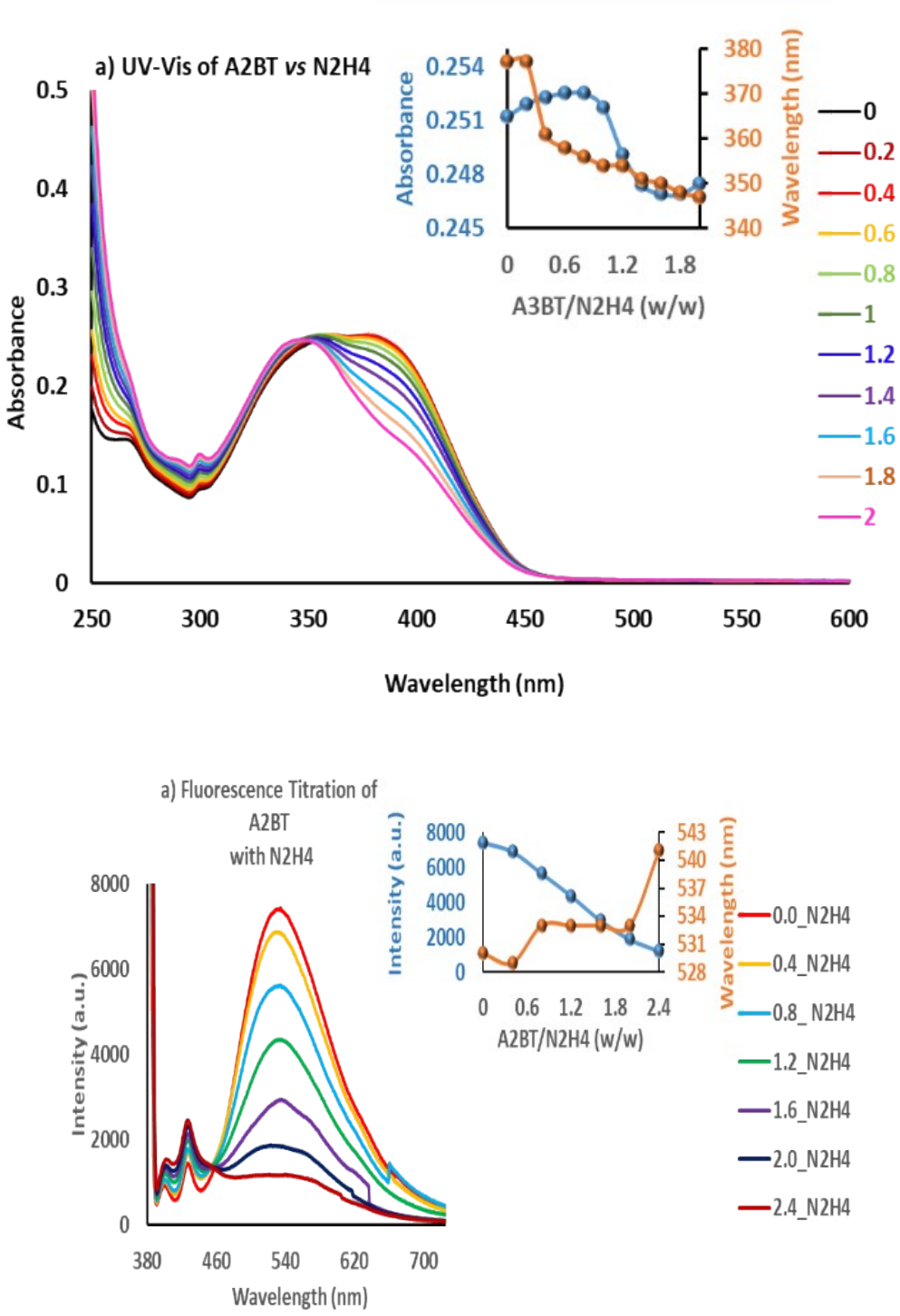


Figure S8. UV–Vis absorption and Fluorescence spectra of the 5 μM SBC **3a** solution in MeOH after addition of hydrazine. In inset represented hydrazine molar ratio *vs* absorbance and emission

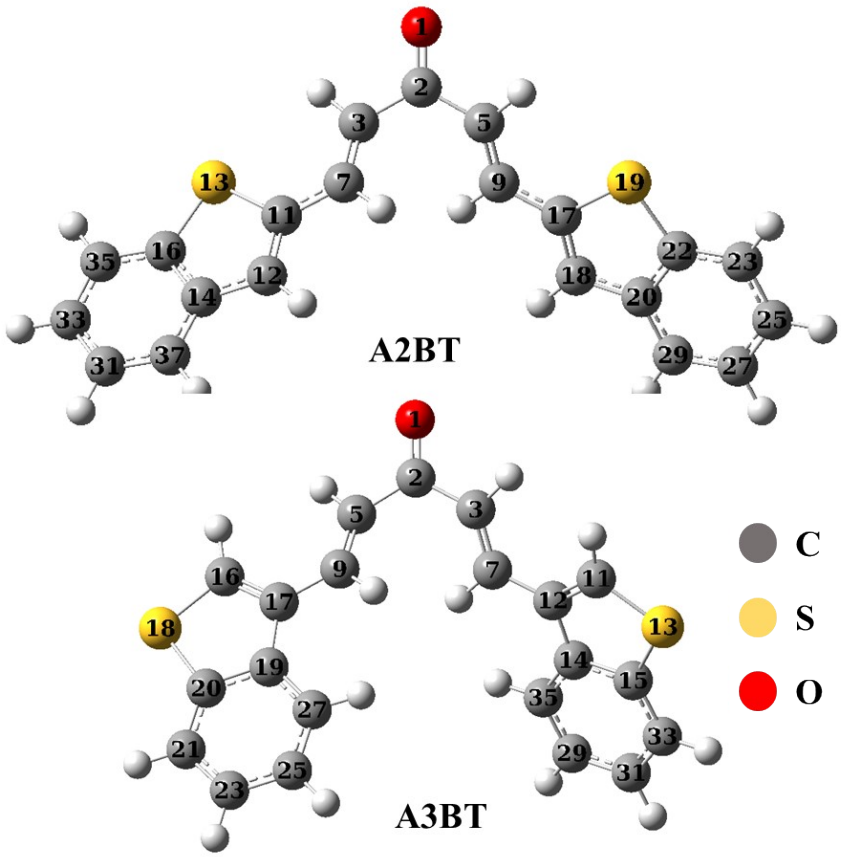
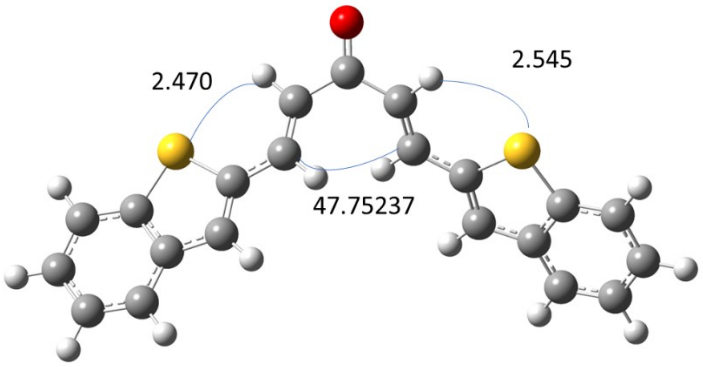
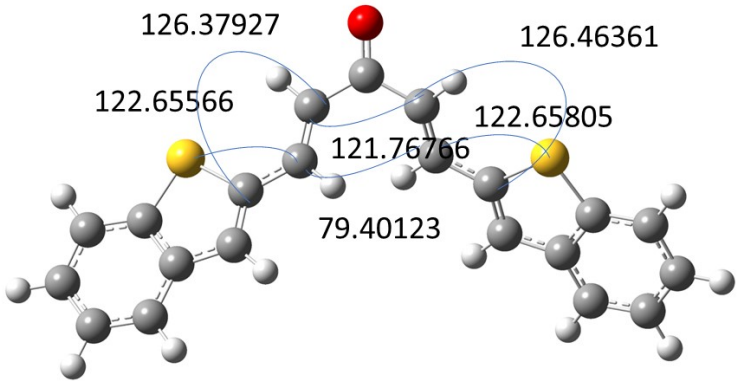
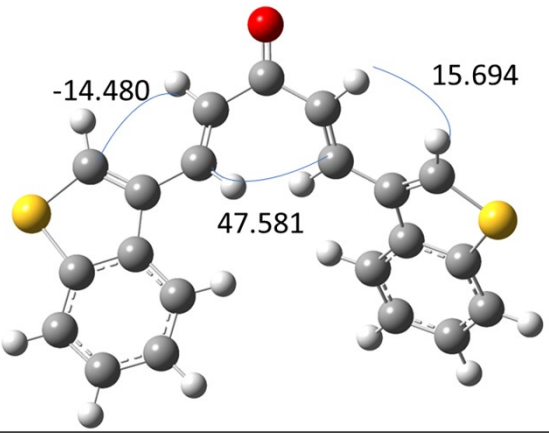
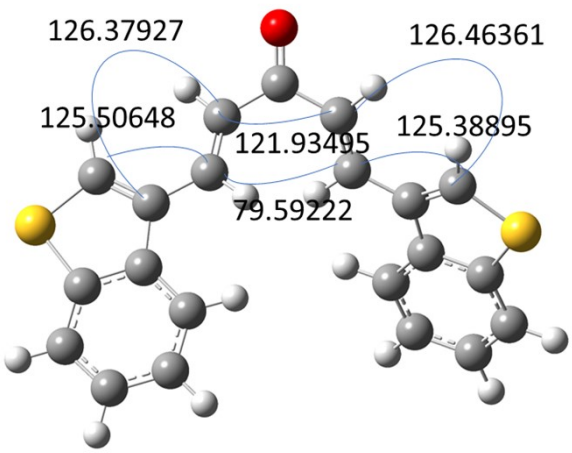


Figure S9. Optimized structures of **SBC 3a** and **3b** with respective atom labelling

Table S1. The calculated bond angles and their dihedral angles of SBC **3a** and **3b**.

SBC 3a	
Dihedral angle	
Bond angle	
SBC 3b	
Dihedral angle	
Bond angle	

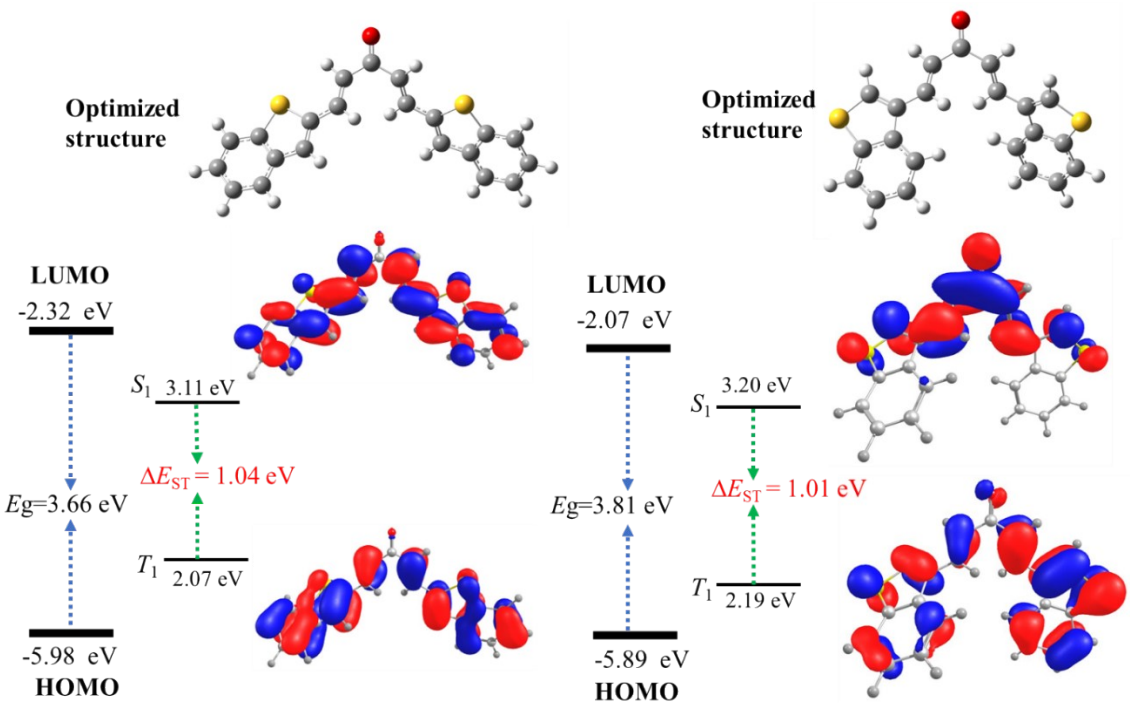


Figure S10. Frontier molecular orbital of the SBC **3a** and **3b** with respective electronic distribution of HOMO-LUMO in gas phase.

Table S2. SBC 3a energy, wavelength and their oscillation with along major contribution in solvent and Gas phase.

Solvent				
State	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Major contribs**
Singlet				
S_1	25204.19344	396.759373547	0.6728	HOMO->LUMO (98%)
S_2	26372.09232	379.188722634	0.0621	H-4->LUMO (58%), H-1->LUMO (36%)
S_3	27240.75744	367.096987741	0.0785	H-4->LUMO (25%), H-3->LUMO (24%), H-1->LUMO (47%)
S_4	28188.46544	354.755033447	0.1293	H-2->LUMO (96%)
S_5	29003.8976	344.781247607	0.0292	H-4->LUMO (12%), H-3->LUMO (69%)
S_6	31963.9728	312.852224677	0.3747	H-1->L+1 (97%)
S_7	32945.55632	303.531071167	0.4682	HOMO->L+1 (81%)
S_8	34116.68144	293.111744106	0.0552	H-3->L+1 (92%)
S_9	34348.16416	291.136374958	0.0436	H-2->L+1 (89%)
S_{10}	36208.09152	276.181361132	0.0156	H-4->L+1 (95%)
Triplet	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Major contribs**
T_1	16971.63552	589.218404332	0.0	H-1->LUMO (64%), HOMO->L+1 (23%)
T_2	17563.65056	569.357717852	0.0	H-1->L+1 (23%), HOMO->LUMO (69%)
T_3	22840.97264	437.809727178	0.0	H-4->LUMO (73%), H-3->LUMO (11%)
T_4	24914.6384	401.370465003	0.0	H-4->LUMO (13%), H-3->LUMO (59%), H-2->L+1 (14%)
T_5	25016.26496	399.739929841	0.0	H-3->L+1 (15%), H-2->LUMO (76%)
T_6	27037.50432	369.856621441	0.0	H-1->LUMO (25%), HOMO->L+1 (52%)
T_7	28049.73712	356.509580008	0.0	H-1->L+1 (58%), HOMO->LUMO (26%)
T_8	30137.92096	331.807891237	0.0	H-6->L+1 (12%), H-5->LUMO (25%)
T_9	30392.79392	329.025361285	0.0	H-6->LUMO (18%), H-5->L+1 (13%), H-3->L+3 (10%)
T_{10}	32297.08208	309.625494193	0.0	H-2->L+1 (59%)
Gas				
Singlet	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Major contribs**
S_1	25104.98656	398.3272	0.0086	H-4->LUMO (77%), H-1->LUMO (12%)
S_2	26245.4624	381.0182	0.5067	HOMO->LUMO (97%)
S_3	27792.44448	359.81	0.0764	H-2->LUMO (23%), H-1->LUMO (65%)

S_4	28835.32656	346.7968	0.1118	H-3->LUMO (96%)
S_5	29464.44336	339.3921	0.0111	H-4->LUMO (13%), H-2->LUMO (64%), HOMO->L+1 (13%)
S_6	31888.96272	313.5881	0.4131	H-1->L+1 (89%)
S_7	33697.27024	296.7599	0.263	H-3->L+1 (27%), HOMO->L+1 (55%)
S_8	33835.192	295.5503	0.0058	H-4->L+1 (20%), H-2->L+1 (70%)
S_9	34671.59472	288.4205	0.1447	H-3->L+1 (66%), HOMO->L+1 (22%)
S_{10}	34813.54928	287.2445	0.0782	H-4->L+1 (72%), H-2->L+1 (22%)
Triplet	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Major contribs**
T_1	16737.73312	597.452470314	0.0	H-1->LUMO (66%), HOMO->L+1 (22%)
T_2	17770.12992	562.742087144	0.0	H-1->L+1 (26%), HOMO->LUMO (66%)
T_3	21415.78112	466.945377522	0.0	H-4->LUMO (75%)
T_4	24996.10096	400.062394371	0.0	H-4->LUMO (11%), H-3->L+1 (13%), H-2->LUMO (57%)
T_5	25324.37088	394.876541944	0.0	H-3->LUMO (73%), H-2->L+1 (18%)
T_6	27178.65232	367.935830013	0.0	H-1->LUMO (23%), HOMO->L+1 (49%)
T_7	28187.65888	354.765184387	0.0	H-1->L+1 (59%), HOMO->LUMO (28%)
T_8	30222.60976	330.878110111	0.0	H-6->L+1 (12%), H-5->LUMO (22%), H-3->L+3 (10%)
T_9	30294.3936	330.09408051	0.0	H-6->LUMO (16%), H-5->L+1 (12%), H-2->L+3 (11%)
T_{10}	32330.9576	309.301076811	0.0	H-3->L+1 (50%)

Table S3. SBC 3b energy, wavelength and their oscillation with along major contribution in solvent and Gas phase.

Solvent				
State	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Major contribs**
Singlet				
S_1	25952.68	385.3166	0.397	HOMO->LUMO (94%)
S_2	27242.37	367.0753	0.0654	H-4->LUMO (56%), H-1->LUMO (32%)
S_3	28332.84	352.9473	0.0584	H-4->LUMO (33%), H-1->LUMO (63%)
S_4	32191.42	310.6418	0.026	H-3->LUMO (61%), H-2->LUMO (22%), HOMO->L+1 (13%)
S_5	32200.29	310.5562	0.0381	H-3->LUMO (22%), H-2->LUMO (59%), H-1->L+1 (14%)
S_6	33316.57	303.1509	0.1502	H-2->LUMO (11%), H-1->L+1 (77%)
S_7	33418.2	299.2381	0.0084	HOMO->L+1 (72%)
S_8	36996.1	270.2988	0.1797	H-6->LUMO (90%)
S_9	37348.57	267.7479	0.0048	H-5->LUMO (12%), H-4->L+1 (43%), H-2->L+1 (19%)
S_{10}	37510.69	266.5907	0.0101	H-4->L+1 (35%), H-2->L+1 (10%), HOMO->L+2 (35%)
Triplet	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Major contribs**
T_1	17970.96336	556.453196174	0.0	H-1->LUMO (62%), HOMO->L+1 (20%)
T_2	18636.37536	536.585028302	0.0	H-1->L+1 (20%), HOMO->LUMO (64%)
T_3	23586.23408	423.976119548	0.0	H-4->LUMO (79%)
T_4	26689.87696	374.673889092	0.0	H-5->LUMO (12%), H-1->LUMO (11%), H-1->L+2 (16%), HOMO->L+1 (26%)
T_5	27252.04928	366.944881732	0.0	H-1->L+1 (21%), HOMO->LUMO (12%), HOMO->L+2 (22%)
T_6	29295.87232	341.345015802	0.0	H-3->LUMO (18%), H-1->LUMO (18%), HOMO->L+3 (12%)
T_7	29519.28944	338.76154168	0.0	H-3->LUMO (38%), H-2->LUMO (11%)
T_8	29816.10352	335.389229961	0.0	H-2->LUMO (49%), H-2->L+1 (14%), HOMO->L+1 (15%)
T_9	30237.9344	330.710420484	0.0	H-1->L+1 (39%), HOMO->LUMO (15%)
T_{10}	31636.50944	316.090497245	0.0	H-5->LUMO (29%)
Gas				
Singlet	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Major contribs**
S_1	25872.83	386.5058	0.0285	H-2->LUMO (71%), HOMO->LUMO (16%)
S_2	27215.75	367.4342	0.3035	H-2->LUMO (10%), HOMO->LUMO (78%)
S_3	28980.51	345.0595	0.0576	H-2->LUMO (11%), H-1->LUMO

				(77%)
S_4	32703.59	305.7768	0.1297	H-4->LUMO (11%), H-3->LUMO (23%), H-1->L+1 (50%)
S_5	32989.92	303.1229	0.0244	H-4->LUMO (40%), H-3->LUMO (25%), HOMO->L+1 (22%)
S_6	33588.38	297.722	0.0539	H-4->LUMO (24%), H-3->LUMO (36%), H-1->L+1 (25%)
S_7	33972.31	294.3574	0.0049	H-4->LUMO (19%), H-3->LUMO (10%), H-1->L+1 (10%), HOMO->L+1 (48%)
S_8	35707.22	280.0554	0.0054	H-2->L+1 (90%)
S_9	37417.12	267.2573	0.017	H-3->L+1 (23%), HOMO->L+2 (41%)
S_{10}	37605.86	265.916	0.023	H-5->LUMO (12%), H-4->L+1 (16%), H-1->L+2 (37%), HOMO->L+2 (10%)
Triplet	**Energy (cm-1)**	**Wavelength (nm)**	**Osc. Strength**	**Major contribs**
T_1	17718.51008	564.381539692	0.0	H-1->LUMO (61%), HOMO->L+1 (18%)
T_2	18790.42832	532.185846416	0.0	H-1->L+1 (21%), HOMO->LUMO (59%)
T_3	22238.47232	449.671175974	0.0	H-2->LUMO (77%)
T_4	26524.53216	377.009477101	0.0	H-5->LUMO (13%), H-1->L+2 (17%), HOMO->L+1 (25%)
T_5	27346.4168	365.678621559	0.0	H-1->L+1 (16%), H-1->L+3 (10%), HOMO->LUMO (11%), HOMO->L+2 (20%)
T_6	29529.77472	338.64125598	0.0	H-1->LUMO (14%), HOMO->L+1 (19%), HOMO->L+3 (15%)
T_7	29861.27088	334.881929178	0.0	H-4->LUMO (36%), HOMO->LUMO (10%)
T_8	30250.83936	330.569339944	0.0	H-4->LUMO (14%), H-3->LUMO (39%), H-3->L+1 (13%), HOMO->L+1 (11%)
T_9	30354.8856	329.436260501	0.0	H-4->LUMO (15%), H-3->LUMO (19%), H-1->L+1 (33%)
T_{10}	31726.84416	315.190503965	0.0	H-5->LUMO (29%)

Table S4. Molecular orbital distribution with HOMO-LUMO energy levels

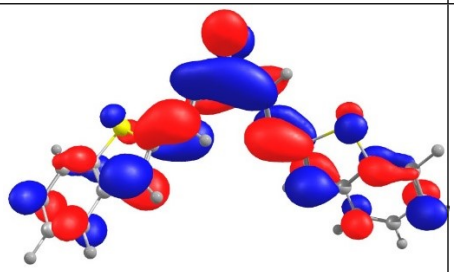
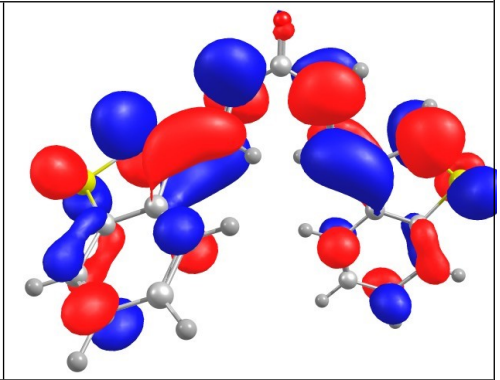
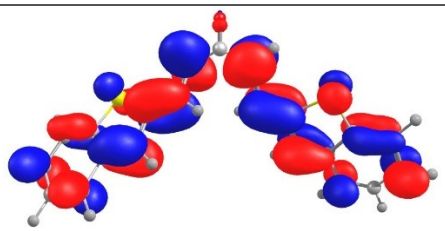
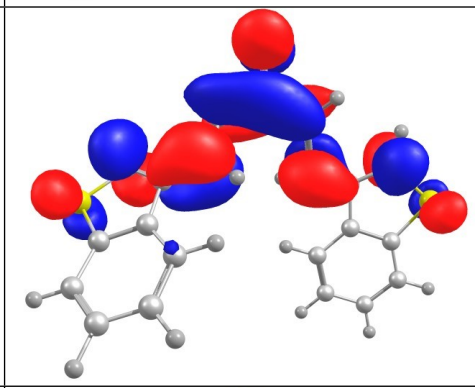
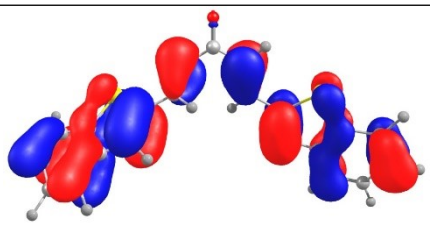
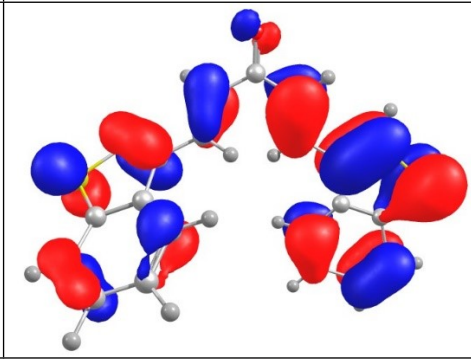
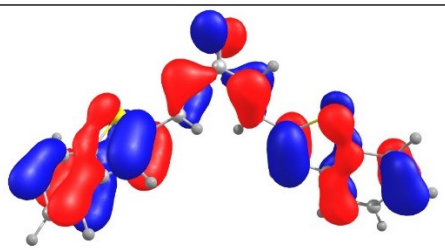
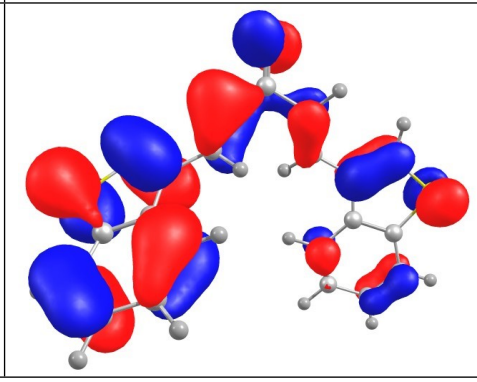
SBC 3a		SBC 3b	
LUMO+1		LUMO+1	
LUMO		LUMO	
HOMO		HOMO	
HOMO-1		HOMO-1	

Table S5. Optimized coordinates of the SBC **3a** and **3b** molecules.

SBC 3a

8	-0.608092000	0.400520000	0.210319000
6	-1.838140000	0.400071000	0.241073000
6	-2.553803000	-0.878302000	0.473249000
1	-1.939597000	-1.633186000	0.959562000
6	-2.565535000	1.677774000	0.044894000
1	-1.976878000	2.433201000	-0.471273000
6	-3.783685000	-1.186662000	0.008460000
1	-4.344433000	-0.435478000	-0.543287000
6	-3.771166000	1.985099000	0.570031000
1	-4.303157000	1.233465000	1.148969000
6	-4.457629000	-2.459565000	0.131187000
6	-5.691358000	-2.765200000	-0.383613000
16	-3.754777000	-3.833151000	1.000828000
6	-6.124172000	-4.102438000	-0.108165000
1	-6.278301000	-2.050135000	-0.950456000
6	-5.163446000	-4.821179000	0.648954000
6	-4.451462000	3.257360000	0.480755000
6	-5.657747000	3.562413000	1.057279000
16	-3.794758000	4.630888000	-0.424323000
6	-6.105061000	4.899101000	0.803254000
1	-6.214577000	2.847275000	1.653642000
6	-5.184560000	5.618052000	-0.002109000
6	-5.419456000	6.944324000	-0.374550000
1	-4.708213000	7.485266000	-0.990610000
6	-6.588883000	7.555970000	0.064949000

1	-6.789016000	8.586080000	-0.213631000
6	-7.513960000	6.859621000	0.864736000
1	-8.418642000	7.360686000	1.194938000
6	-7.281019000	5.543514000	1.234369000
1	-7.995187000	5.006954000	1.852344000
6	-7.532889000	-6.064033000	-0.099396000
1	-8.452831000	-6.565559000	-0.383522000
6	-6.567843000	-6.760202000	0.651836000
1	-6.752747000	-7.790683000	0.939418000
6	-5.378077000	-6.147908000	1.031830000
1	-4.636011000	-6.688723000	1.610513000
6	-7.320023000	-4.747484000	-0.479436000
1	-8.065089000	-4.211072000	-1.059922000

SBC 3b

8	-0.351582000	-0.355787000	0.049728000
6	-1.558907000	-0.141954000	0.158358000
6	-2.423167000	-1.180178000	0.771049000
1	-1.868361000	-1.891168000	1.378803000
6	-2.107714000	1.146751000	-0.332884000
1	-1.484031000	1.615199000	-1.091061000
6	-3.732776000	-1.369442000	0.507982000
1	-4.216981000	-0.687368000	-0.185785000
6	-3.176174000	1.792219000	0.177356000
1	-3.742225000	1.301950000	0.964713000
6	-4.276072000	-3.223921000	2.117476000
6	-4.579738000	-2.431217000	1.041127000

16	-5.506425000	-4.383109000	2.517335000
6	-5.887645000	-2.760477000	0.491655000
6	-6.516944000	-3.814089000	1.196149000
6	-2.932857000	4.042690000	-0.922435000
6	-3.645948000	3.121852000	-0.199992000
16	-3.775002000	5.537090000	-1.199022000
6	-4.957279000	3.636609000	0.168939000
6	-5.174409000	4.949569000	-0.312230000
6	-6.369577000	5.636673000	-0.080271000
1	-6.515433000	6.643323000	-0.459239000
6	-7.366102000	4.998378000	0.648363000
1	-8.301956000	5.513322000	0.842277000
6	-7.173619000	3.693370000	1.134248000
1	-7.964897000	3.210473000	1.699344000
6	-5.986692000	3.013460000	0.898289000
1	-5.858742000	2.003054000	1.274421000
6	-7.816544000	-2.668435000	-0.963473000
1	-8.334448000	-2.228847000	-1.810335000
6	-8.423903000	-3.714055000	-0.246521000
1	-9.404939000	-4.072275000	-0.542877000
6	-7.778843000	-4.297176000	0.837539000
1	-8.242777000	-5.107343000	1.391264000
6	-6.561801000	-2.194468000	-0.606093000
1	-6.103014000	-1.394070000	-1.178429000
1	-3.383843000	-3.178772000	2.726926000
1	-1.923489000	3.936209000	-1.295644000