

Amino-substituted spirothiopyran as an initiator for self-assembly of gold nanoparticles

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Electronic Supplementary Information (ESI†)

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DTITLE ST-NH2 Proton-1-11&u.als
COMNT single_pulse
DATIM 2013-12-17 13:31:22
OBNUC 1H
EXMOD proton.fxp
OBFREQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 15.0000 sec
PWL 5.00 usec
IRNUC 1H
CTEMP 30.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 38

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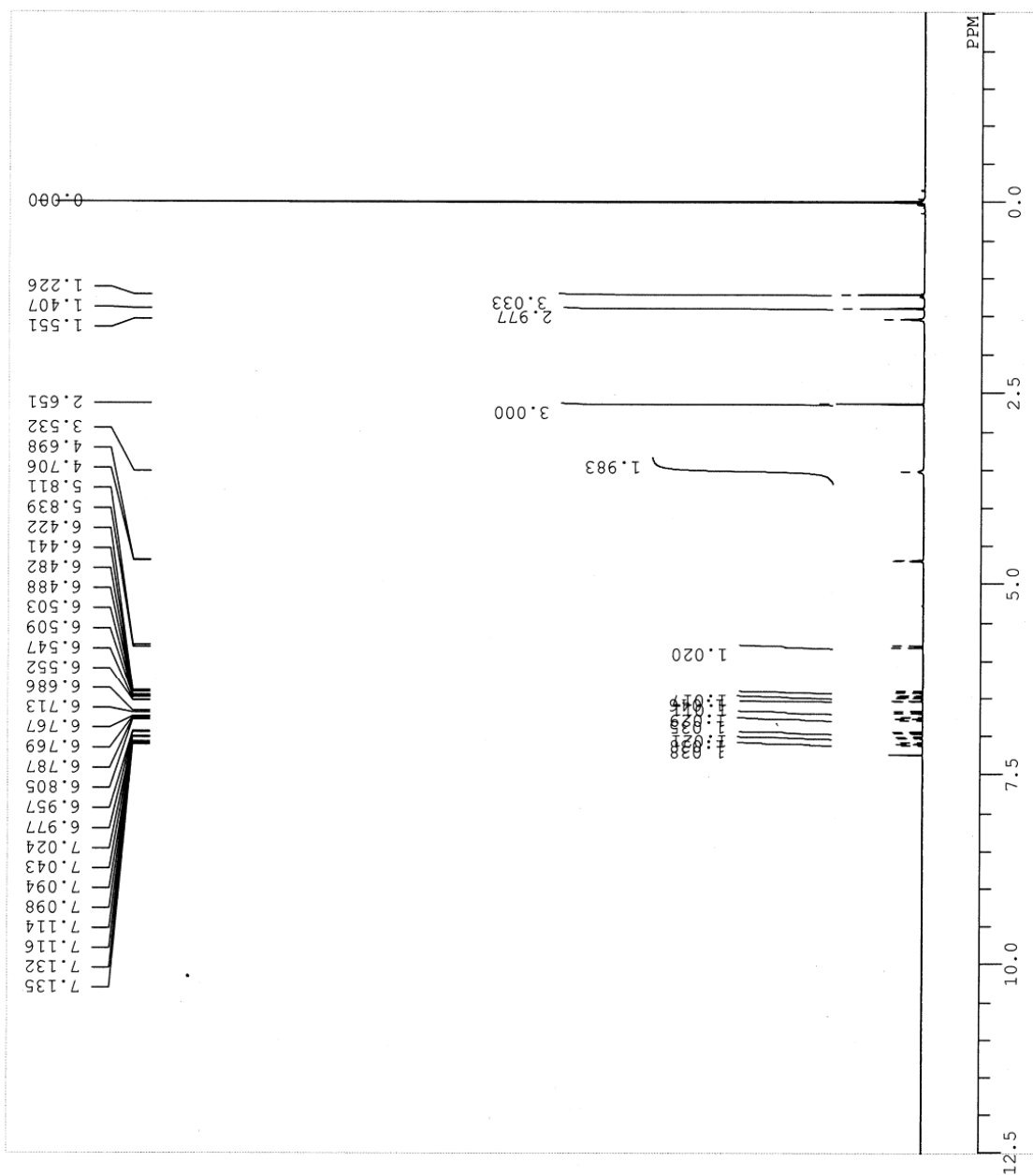
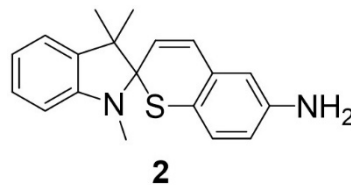


Fig. S1 ¹H NMR chart of **2** (CDCl₃, 400 MHz)

DFILE ST-NH2_Carbon-1-ii.als
 COMNT single_pulse decoupled gate
 DATIM 2013-12-18 15:22:19
 OBNUC 13C
 EXMOD carbon_jxp
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 26214
 FREQU 25125.63 Hz
 SCANS 1024
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PUL 2.87 usec
 IRNUC 1H
 CTEMP 30.0 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 Hz
 RGAIN 50

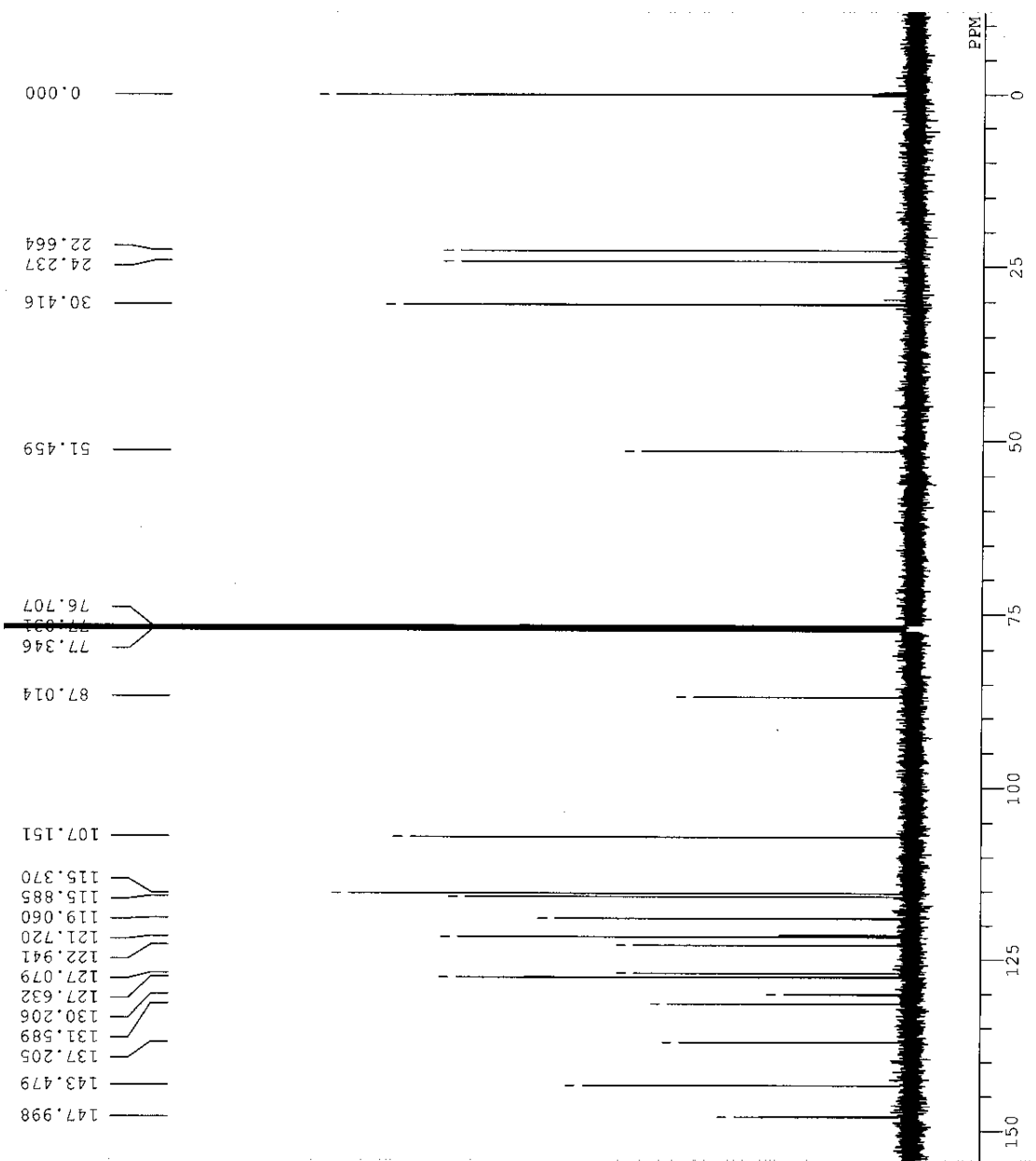
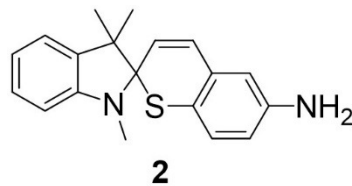


Fig. S2 ^{13}C NMR chart of **2** (CDCl_3 , 101 MHz)

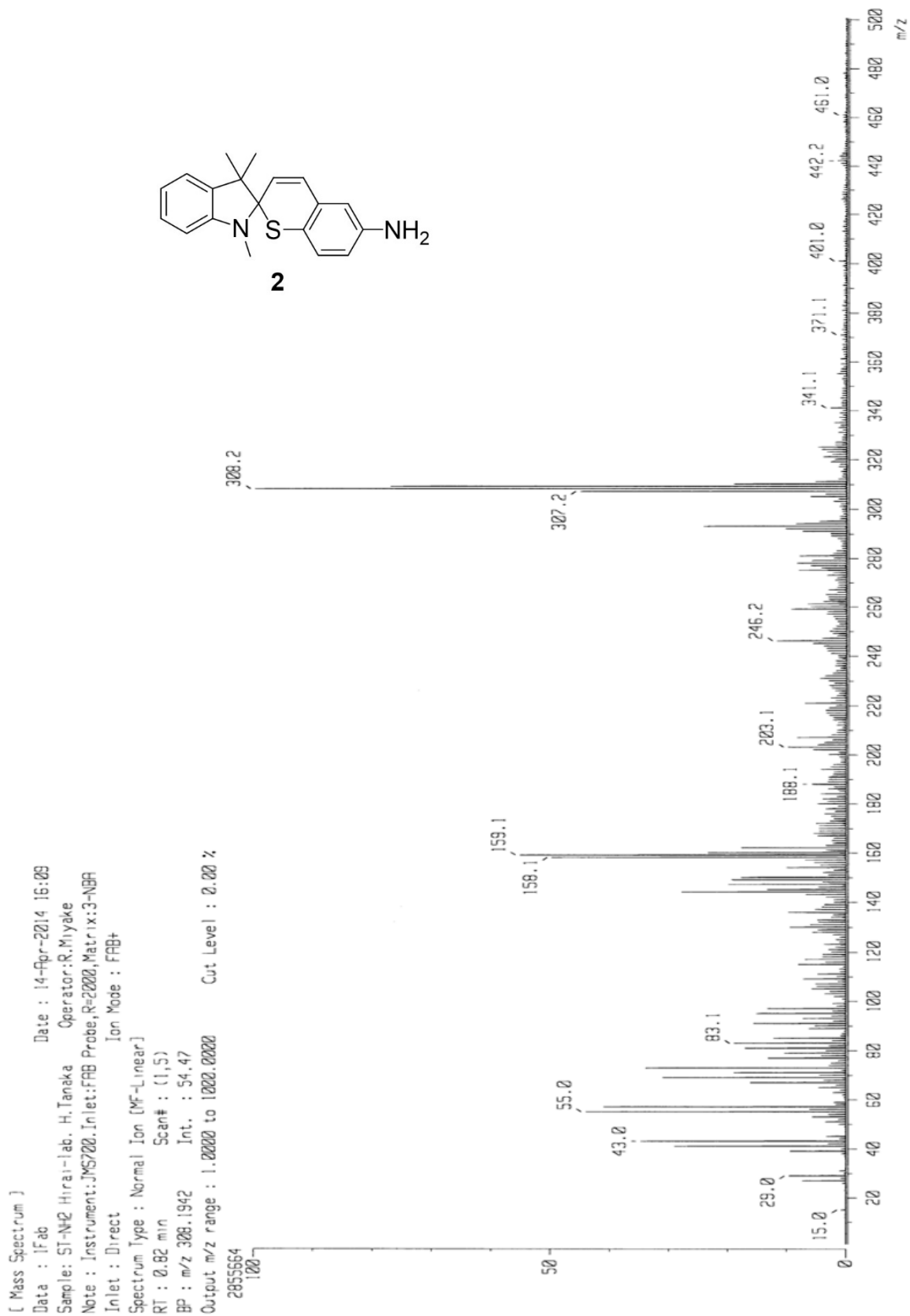


Fig. S3 FAB-MS chart of 2.

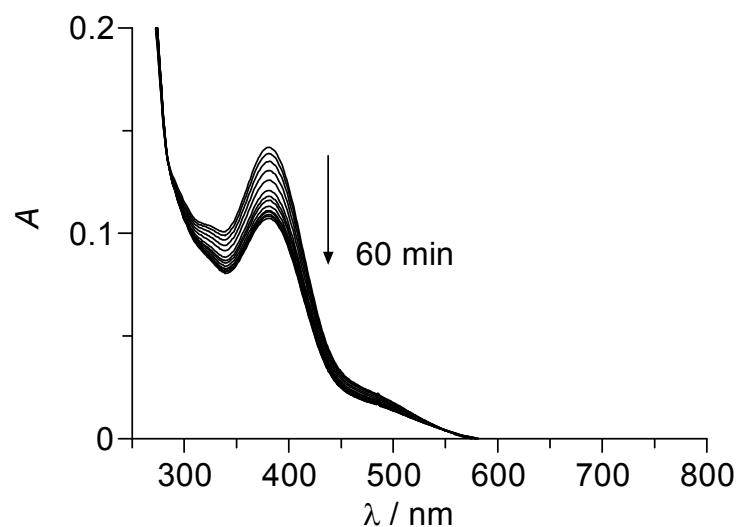


Fig. S4 Change in absorption spectra of the solution containing the MC form of **2** (20 μM) during visible light irradiation (490 nm) for 60 min at 25 °C.

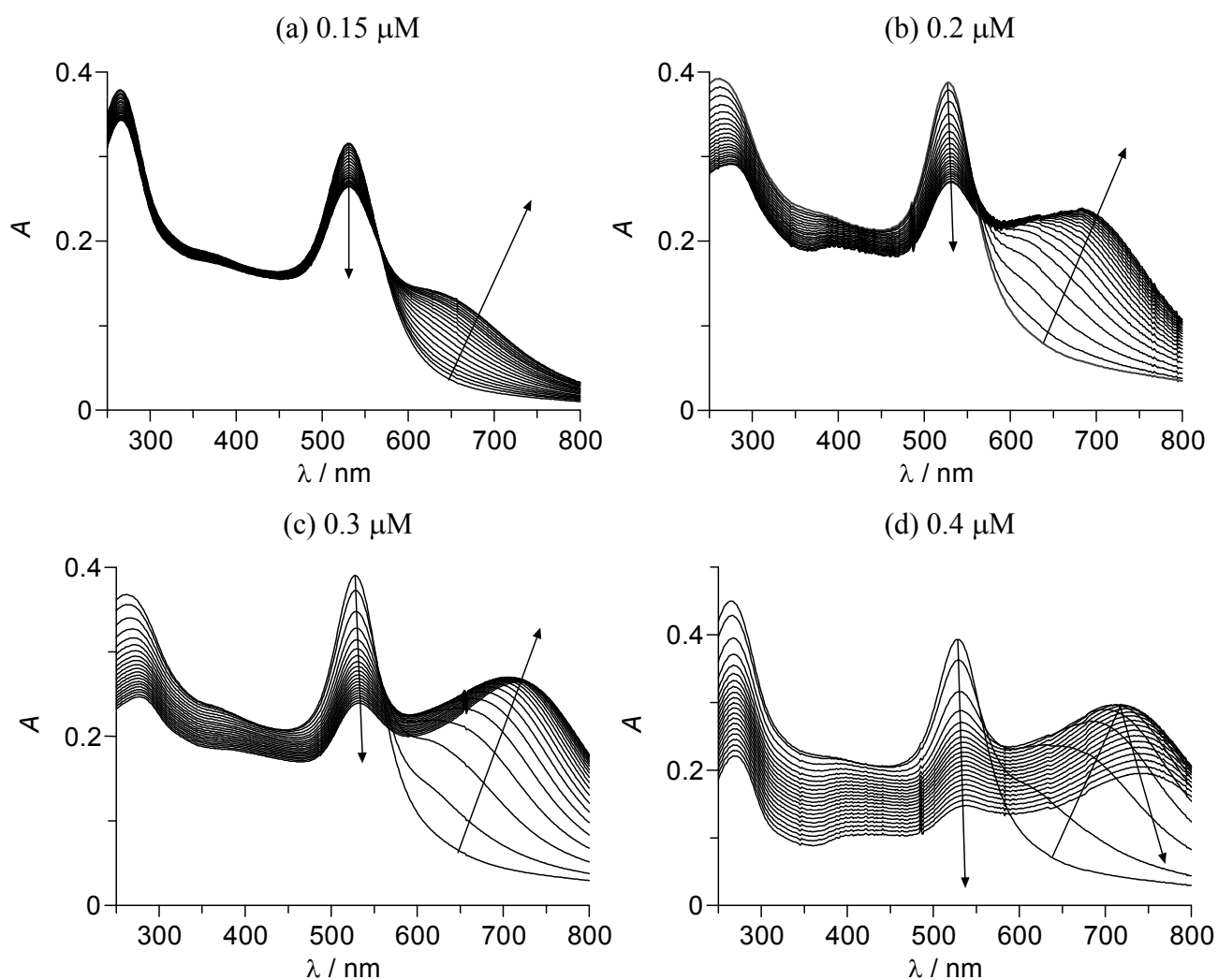


Fig. S5 Absorption spectra of the solution containing AuNPs (0.12 nM) stabilized with 4.8 mM GABA during stirring with different amount of **2** in the dark condition.

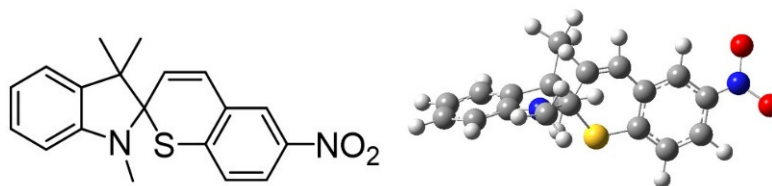
Table S1 Calculated electronic excitation properties for the SP and MC forms of **2**.^[a]

Species	CIC ^[b]	$E / \text{eV} [\lambda / \text{nm}]$	μ / Debye			f	
			μ_x	μ_y	μ_z		μ_{tot}
$S_0 \rightarrow S_1$	HOMO \rightarrow LUMO (0.659)	3.3747 [367.39]	-0.536	0.705	1.262	0.08	0.0304
$S_0 \rightarrow S_2$	HOMO-1 \rightarrow LUMO (0.691)	3.5742 [346.89]	0.069	0.066	0.585	0.01	0.0048
$S_0 \rightarrow S_3$	HOMO \rightarrow LUMO+2 (0.480)	4.4515 [278.52]	-0.251	-0.116	0.006	0.00	0.0013
$S_0 \rightarrow S_4$	HOMO \rightarrow LUMO+1 (0.482)	4.5404 [273.07]	1.119	0.412	-0.529	0.07	0.0293
$S_0 \rightarrow S_5$	HOMO-1 \rightarrow LUMO+1 (0.491)	4.5667 [271.50]	-1.357	-0.431	0.637	0.11	0.0421
$S_0 \rightarrow S_6$	HOMO \rightarrow LUMO+3 (0.495)	4.7975 [258.44]	1.900	0.672	0.672	0.21	0.0821
<hr/>							
$S_0 \rightarrow S_1$	HOMO \rightarrow LUMO (0.604)	1.6298 [760.75]	5.017	2.127	-0.001	0.47	0.1835
$S_0 \rightarrow S_2$	HOMO-1 \rightarrow LUMO (0.695)	1.8293 [677.76]	0.006	0.000	0.020	0.00	0.0000
$S_0 \rightarrow S_3$	HOMO-2 \rightarrow LUMO (0.614)	3.0205 [410.47]	-7.693	-0.421	-0.002	1.73	0.6799
$S_0 \rightarrow S_4$	HOMO-3 \rightarrow LUMO (0.636)	3.2582 [380.52]	-3.177	1.450	0.002	0.38	0.1507

[a] Calculated at the DFT level (B3LYP/6-31Gd).

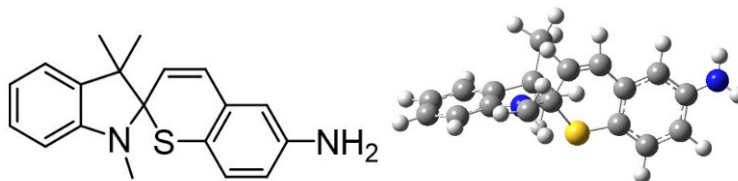
[b] CI expansion coefficients for the main orbital transitions.

Cartesian Coordinates (in Å) of **1**



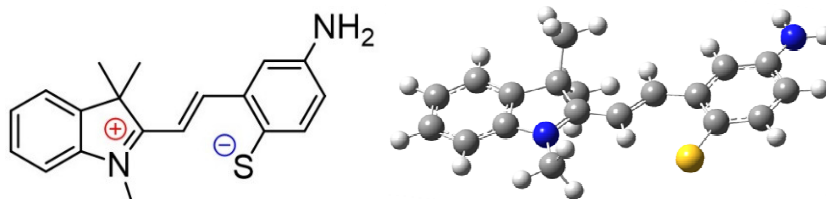
C	5.13999	-1.660764	0.422032	H	5.84551	-2.41574	0.763757
C	5.409473	-0.924193	-0.733199	H	6.326558	-1.110021	-1.290564
C	4.513341	0.047779	-1.20403	H	4.730965	0.604086	-2.112751
C	3.343249	0.259684	-0.475391	H	3.749444	-2.002293	2.049431
C	3.063028	-0.473182	0.690823	H	-1.676513	2.740231	0.675103
C	3.956629	-1.430908	1.145351	H	-1.918043	-2.329792	-1.600686
N	2.307429	1.172642	-0.724222	H	-4.34574	-2.219986	-1.098643
C	1.133575	0.754347	0.01067	H	-3.780507	1.607095	0.793219
C	1.76714	0.052458	1.290812	H	1.380667	-1.384464	2.856774
S	0.233165	-0.549784	-1.110574	H	-0.073938	-0.571027	2.271367
C	-1.467658	-0.426457	-0.67673	H	0.681736	-1.8532	1.299213
C	-1.988979	0.7047	0.000278	H	2.726049	1.938698	1.911361
C	-1.145454	1.842646	0.357054	H	1.21433	1.577477	2.775622
C	-2.325479	-1.466445	-1.077228	H	2.693617	0.675049	3.15404
C	-3.683521	-1.413445	-0.799589	H	3.137065	2.43471	-2.164193
C	-4.186232	-0.302646	-0.113506	H	2.029274	1.211841	-2.839892
C	-3.358846	0.748206	0.278166	H	1.387653	2.602035	-1.93284
C	0.88217	-1.005215	1.95756	C	0.195761	1.88787	0.308845
C	2.119717	1.137058	2.344001	H	0.693491	2.820124	0.576022
C	2.208502	1.883218	-1.987275	O	-6.033366	0.747584	0.804377
N	-5.605305	-0.236621	0.189337	O	-6.329829	-1.168672	-0.179983

Cartesian Coordinates (in Å) of **2** (SP)



C	4.632207	-1.613685	-0.433346	H	5.345187	-2.432939	-0.504385
C	4.902197	-0.394995	-1.058691	H	5.827811	-0.268668	-1.618795
C	3.995664	0.674552	-0.993755	H	4.214442	1.613943	-1.49607
C	2.813901	0.484689	-0.276239	H	3.228912	-2.735332	0.780308
C	2.533266	-0.737481	0.360914	H	-2.233636	2.027409	1.91717
C	3.436929	-1.785893	0.287865	H	-2.43238	-1.388479	-2.453157
N	1.771285	1.389844	-0.052228	H	-4.82898	-1.622651	-1.919171
C	0.586798	0.650552	0.356152	H	-4.300635	0.910613	1.52305
C	1.22421	-0.592457	1.123866	H	0.857724	-2.636857	1.722879
S	-0.295179	0.113899	-1.264181	H	-0.603736	-1.642891	1.657738
C	-1.993408	-0.106043	-0.774163	H	0.138708	-2.228352	0.155061
C	-2.529559	0.550506	0.353419	H	2.159823	0.730052	2.619054
C	-1.697987	1.402493	1.201428	H	0.644314	-0.021255	3.166048
C	-2.836912	-0.879957	-1.578727	H	2.12854	-0.986653	3.060143
C	-4.19123	-1.012497	-1.280008	H	2.587842	3.229766	-0.607074
C	-4.744051	-0.374667	-0.153138	H	1.56922	2.49085	-1.870027
C	-3.893988	0.403691	0.647111	H	0.823666	3.20726	-0.42297
C	0.348761	-1.848032	1.157008	C	-0.356567	1.485329	1.178553
C	1.557555	-0.183012	2.582977	H	0.136351	2.174202	1.864479
C	1.683084	2.639375	-0.786111	H	-6.481567	0.184957	0.760431
N	-6.084048	-0.563895	0.194167	H	-6.694628	-0.783812	-0.592078

Cartesian Coordinates (in Å) of 2 (MC)



C	-5.718536	-0.930191	-0.006308	H	-6.628396	-1.52745	-0.008296
C	-5.80446	0.466017	-0.007771	H	-6.780794	0.947382	-0.010991
C	-4.654342	1.263923	-0.005307	H	-4.740339	2.34797	-0.006787
C	-3.426677	0.606915	-0.001237	H	-4.408613	-2.655604	-0.001362
C	-3.322002	-0.786633	-0.000011	H	0.454869	1.583854	0.001878
C	-4.469909	-1.567862	-0.002428	H	0.98398	-1.428673	0.004329
N	-2.121399	1.15554	0.001704	H	5.275882	2.044127	-0.004823
C	-1.171818	0.194451	0.003625	H	6.5592	-0.034565	-0.007733
C	-1.854756	-1.181898	0.00416	H	2.910826	-2.296076	0.001527
C	0.192039	0.532963	0.003361	H	-0.459831	-2.280899	-1.298536
C	1.240133	-0.372822	0.003426	H	-1.735856	-1.412957	-2.17439
C	2.651639	-0.142243	0.001924	H	-2.118155	-2.903711	-1.292253
C	3.319762	1.142953	0.001362	H	-0.466401	-2.276629	1.317546
C	4.742214	1.096232	-0.003119	H	-2.125191	-2.898166	1.306681
C	5.469199	-0.074545	-0.004828	H	-1.7455	-1.404009	2.184199
C	4.823342	-1.342212	-0.003001	H	-1.257486	2.856335	0.890693
C	3.43665	-1.340866	0.000458	H	-2.773636	3.141432	0.005153
N	5.567459	-2.498225	-0.005098	H	-1.263349	2.857633	-0.891089
C	-1.513644	-1.990954	-1.271748	H	5.122186	-3.407875	-0.001691
C	-1.51984	-1.985993	1.284986	H	6.579454	-2.466428	-0.008828
C	-1.836226	2.587746	0.001538	S	2.562383	2.722701	0.001502