European Journal of Inorganic Chemistry

Supporting Information

Synthesis, Characterization, and Singlet Oxygen Sensitization by Antimony (III/V) Corrole Complexes

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Table S1 Crystallographic data for **3** and **4**.

compound code	**3**	**4**
molecular formula	$C_{45}H_{27}N_6O_2Sb$	$C_{90}H_{54}N_{12}O_6Sb_2$
Fw	805.47	1642.97
Radiation	Mo *K*α	Mo *K*α
Crystal symmetry	Triclinic	Triclinic
space group	P-1	P-1
a(Å)	8.5792(3)	8.8254(2)
b(Å)	14.8700(7)	15.4901(4)
c(Å)	16.8362(6)	17.9596(5)
a(deg)	105.402(4)	111.704(2)
β(deg)	101.476(3)	90.938(2)
g(deg)	94.698(3)	100.056(2)
V(Å^3)	2008.56(14)	2237.28(10)
Z	2	2
μ (mm^{-1})	0.731	0.659
T(K)	100	100
D_{calcd} (g cm^{-3})	1.332	1.219
2θ range (deg)	6.534 to 53.466	6.71 to 54.206
e data (R_{int})	8447 (0.0971)	9807 (0.0902)
R1 ($I>2\sigma(I)$)	0.0757	0.0362
WR2 (all data)	0.2113	0.0844
GOF	1.101	1.043
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	5.052, -1.476	1.152, -1.051

To estimate the quantum yield of the population of the luminescent singlet excited state of dioxygen {$\Phi(^1O_2)$}, a comparison of luminescence of $^1O_2$ at 1270 nm of the sample of interest (x) and a suitable standard (st) were recorded for iso absorbing chloroform solution at the excitation wavelength. [1] The unknown value of $\Phi(^1O_2)$ can be determined by means of the following equation:

$$\Phi(^1O_2)_x = \Phi(^1O_2)_{st} \times (I_x/I_{st})$$

where I_x and I_{st} are the luminescence intensity at 1270 nm for the sample of interest (x) and the standard (st).

Table S2 Quantum yield of singlet oxygen production.

compound	$\Phi(^1O_2)$
1	15%
2	40%
3	34%
4	69%

[1] Y. Rio, G. Accorsi, H. Nierengarten, C. Bourgogne, J.-M. Strub, A. Van Dorsselaer, N. Armaroli, J.-F. Nierengarten, *Tetrahedron* **2003**, *59*, 3833-3844.

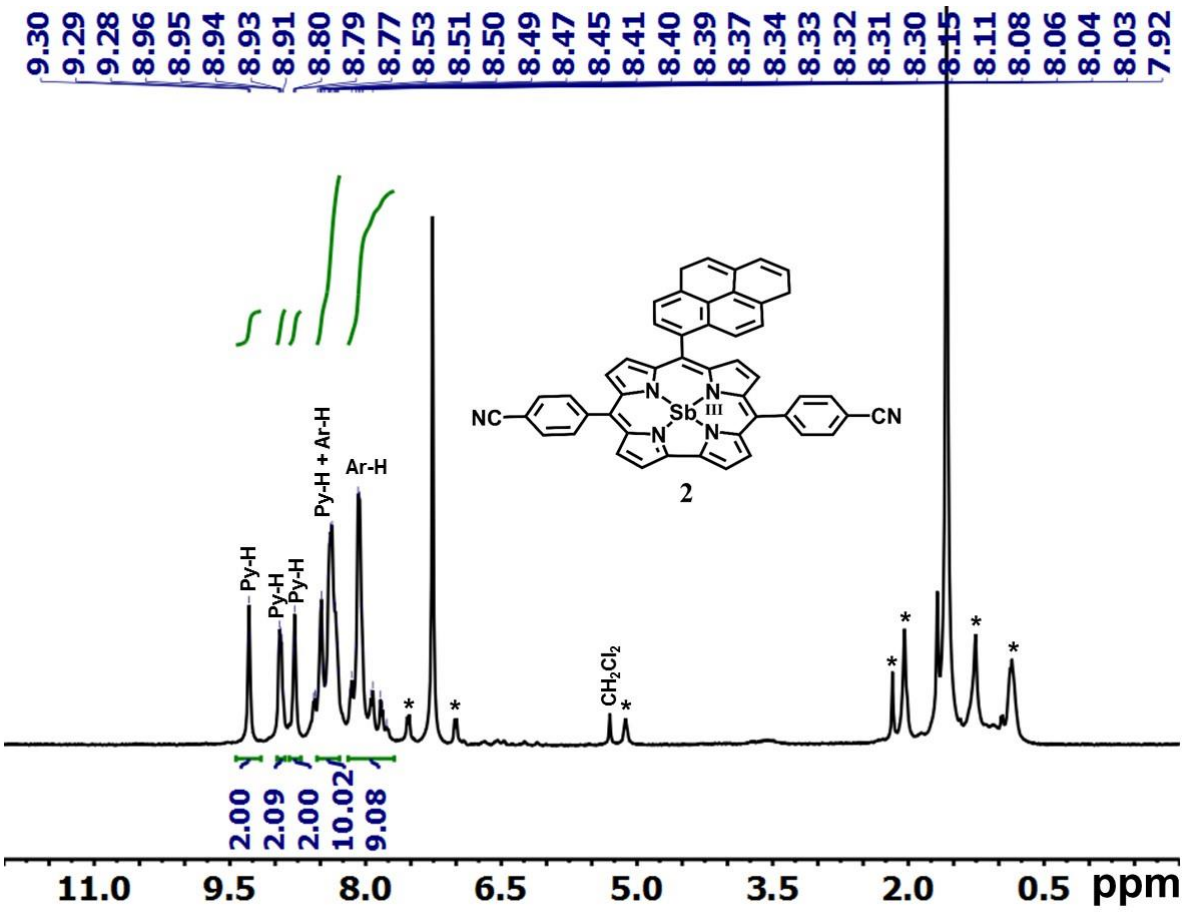

Figure S1 ^{1}H NMR spectrum of **2** in $CDCl_3$.

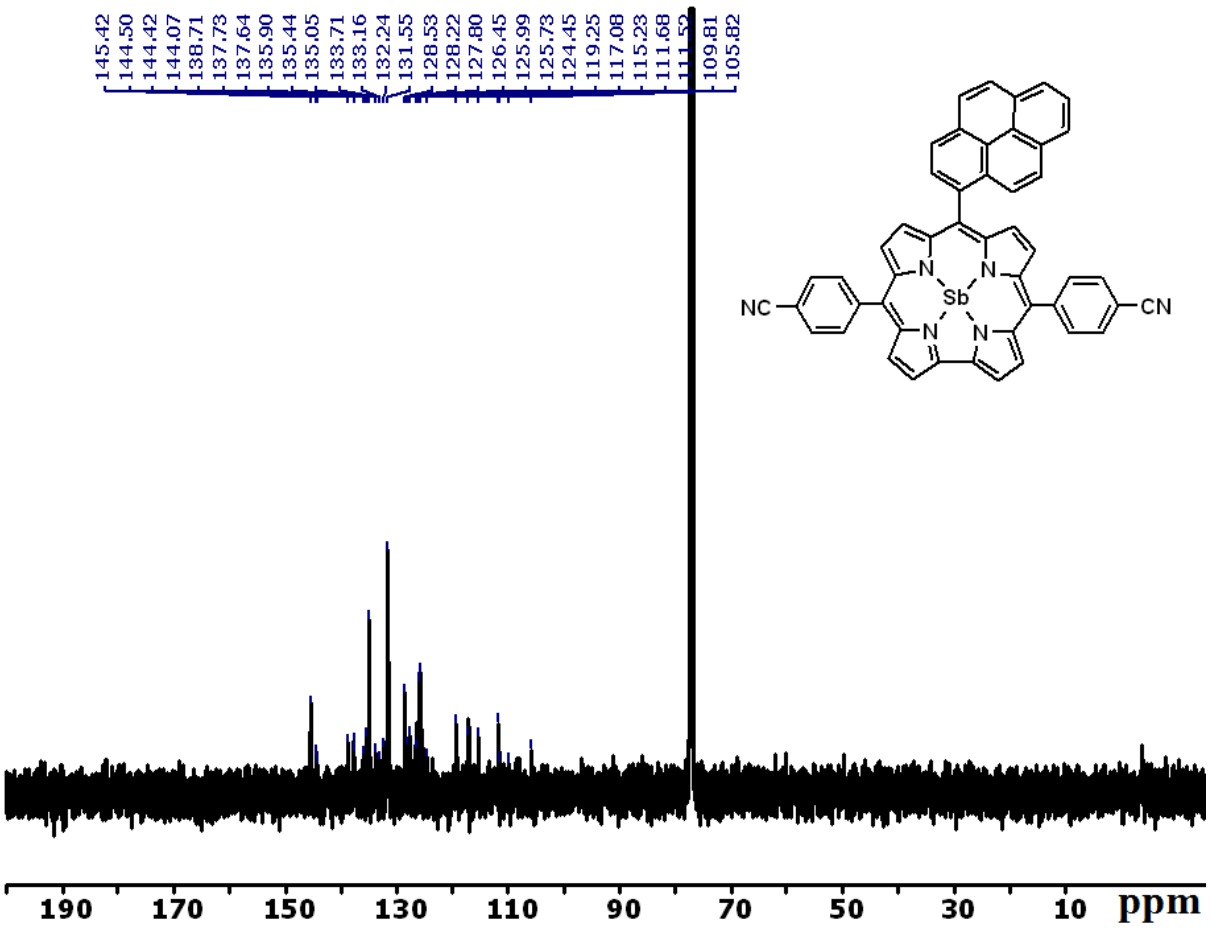

Figure S2 ^{13}C NMR spectrum of **2** in $CDCl_3$.

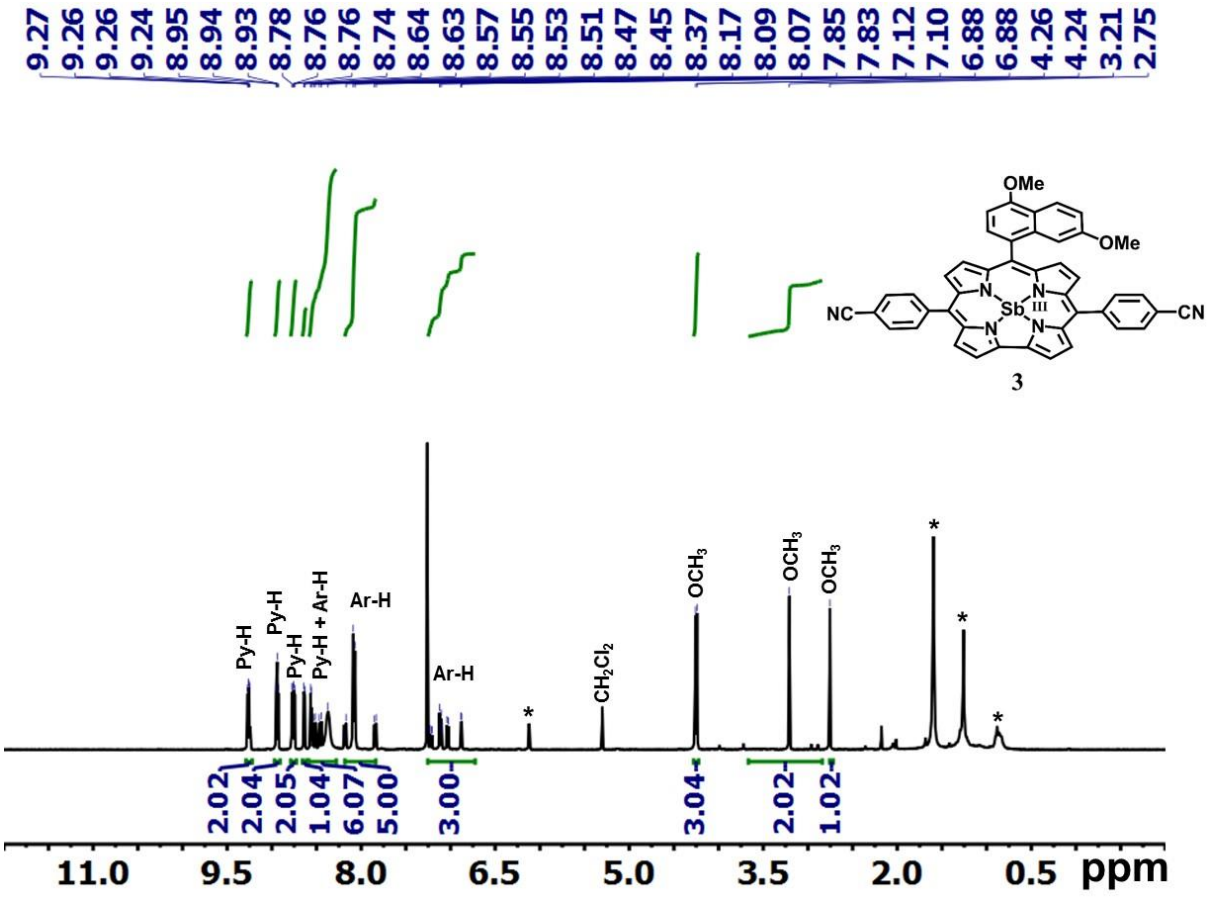

Figure S3 ^{1}H NMR spectrum of **3** in $CDCl_3$.

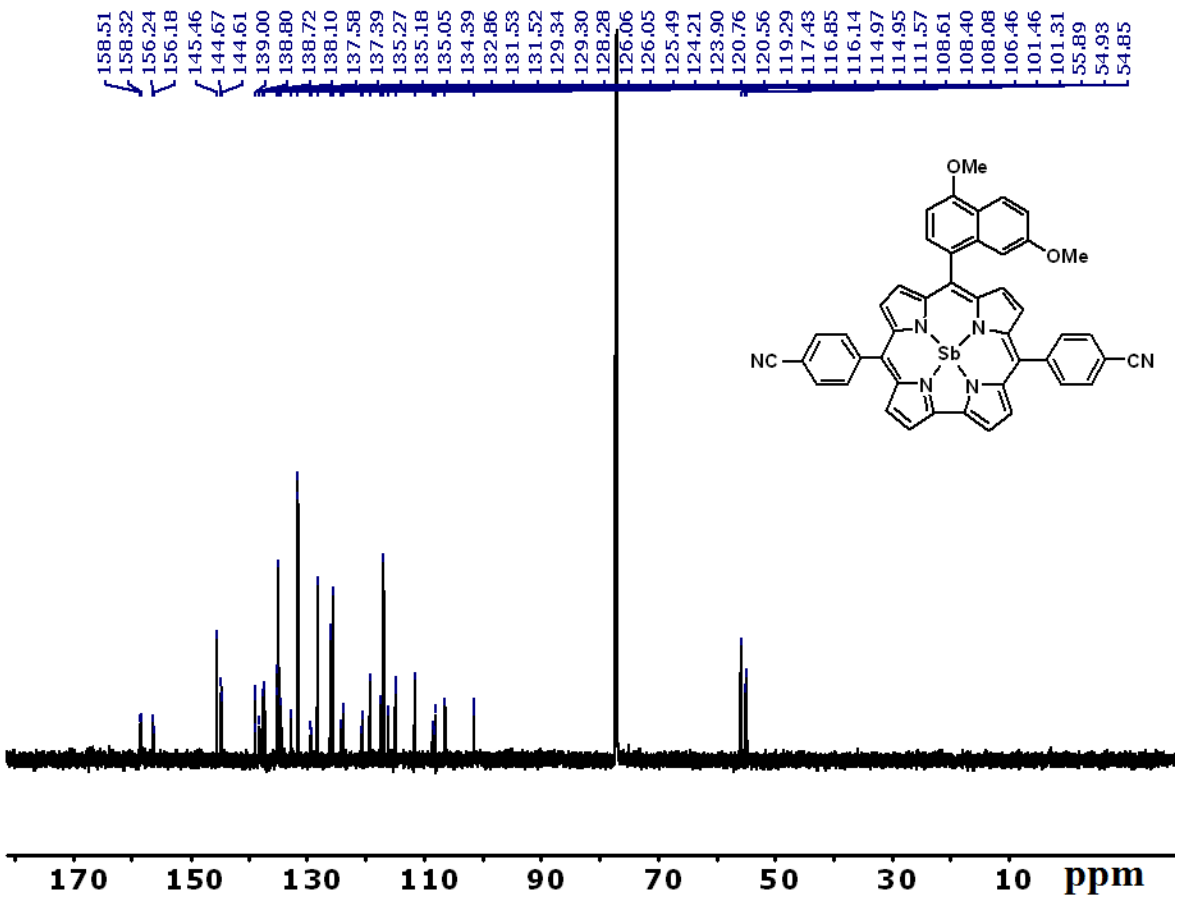

Figure S4 ^{13}C NMR spectrum of **3** in $CDCl_3$.

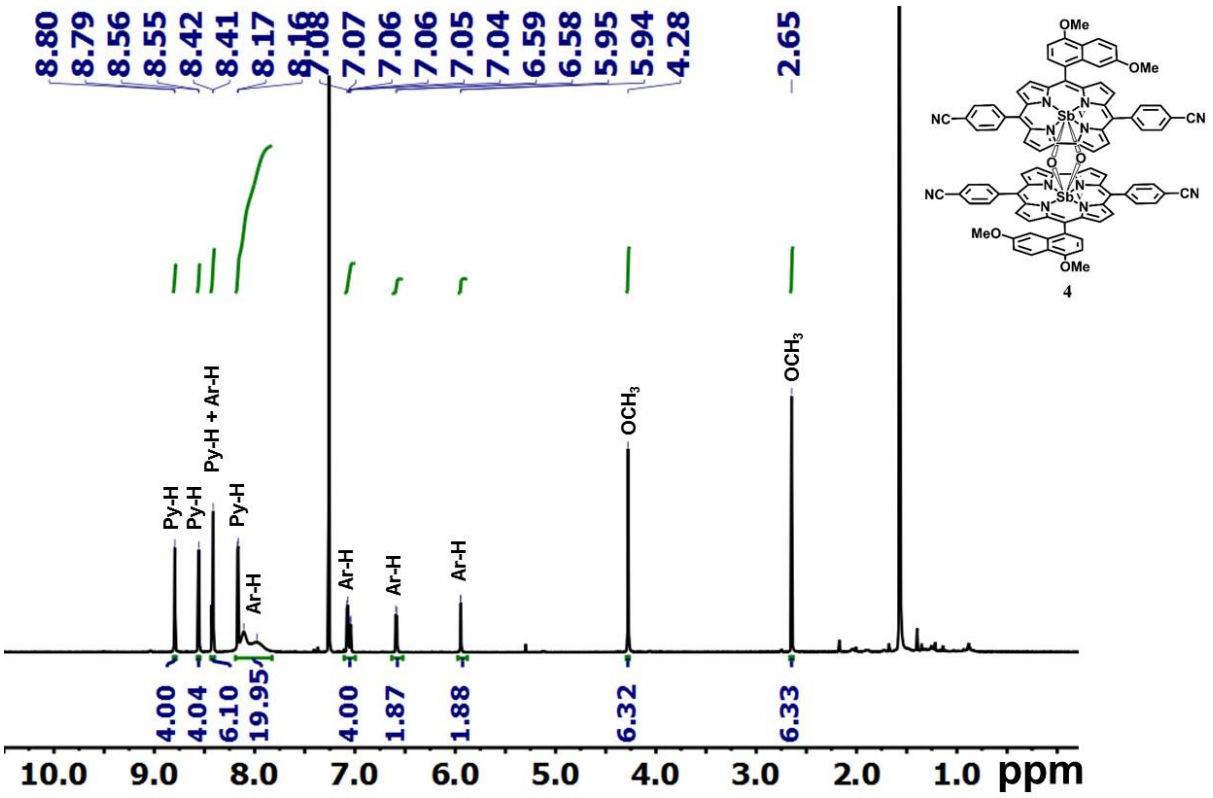

Figure S5 ^{1}H NMR spectrum of **4** in $CDCl_3$.

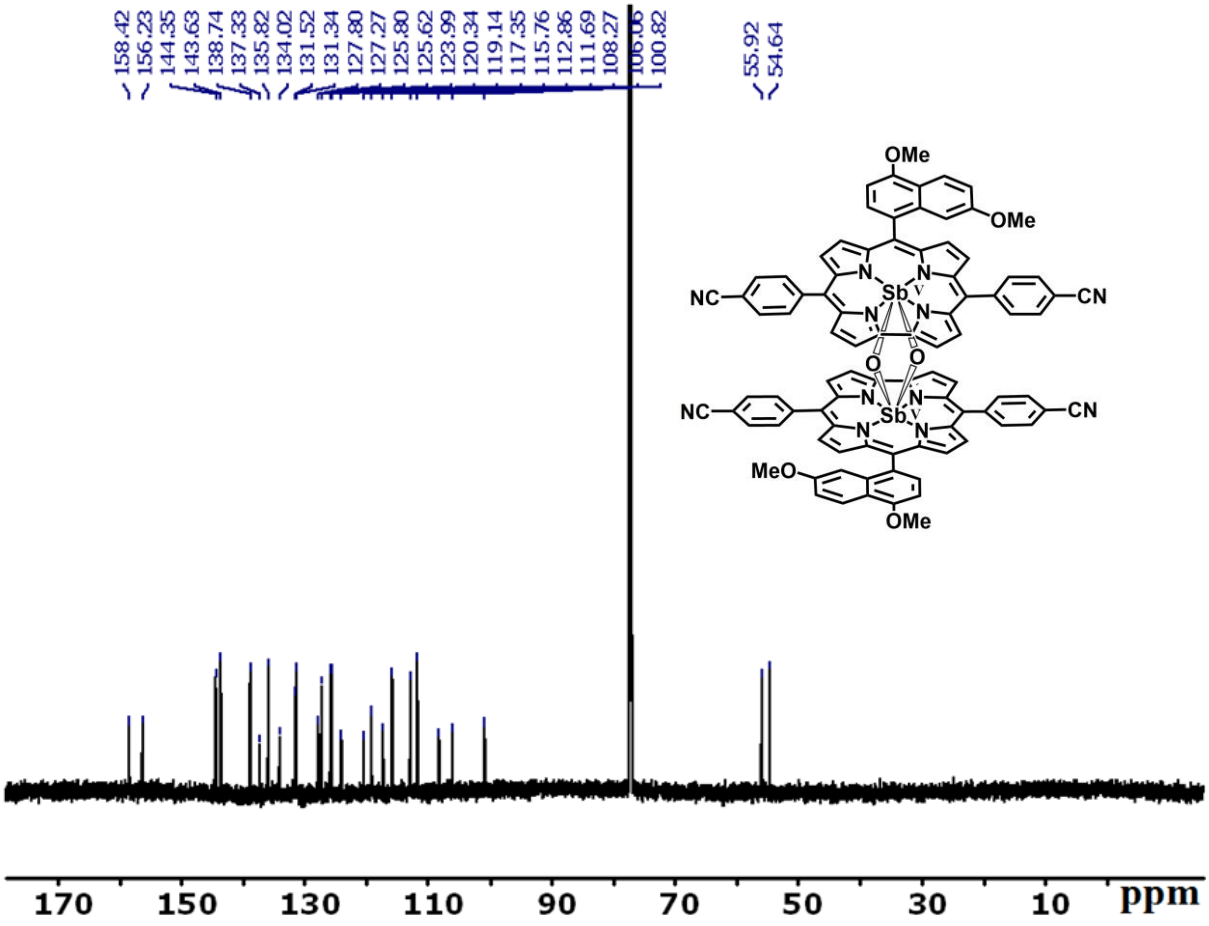

Figure S6 ^{13}C NMR spectrum of **4** in $CDCl_3$.

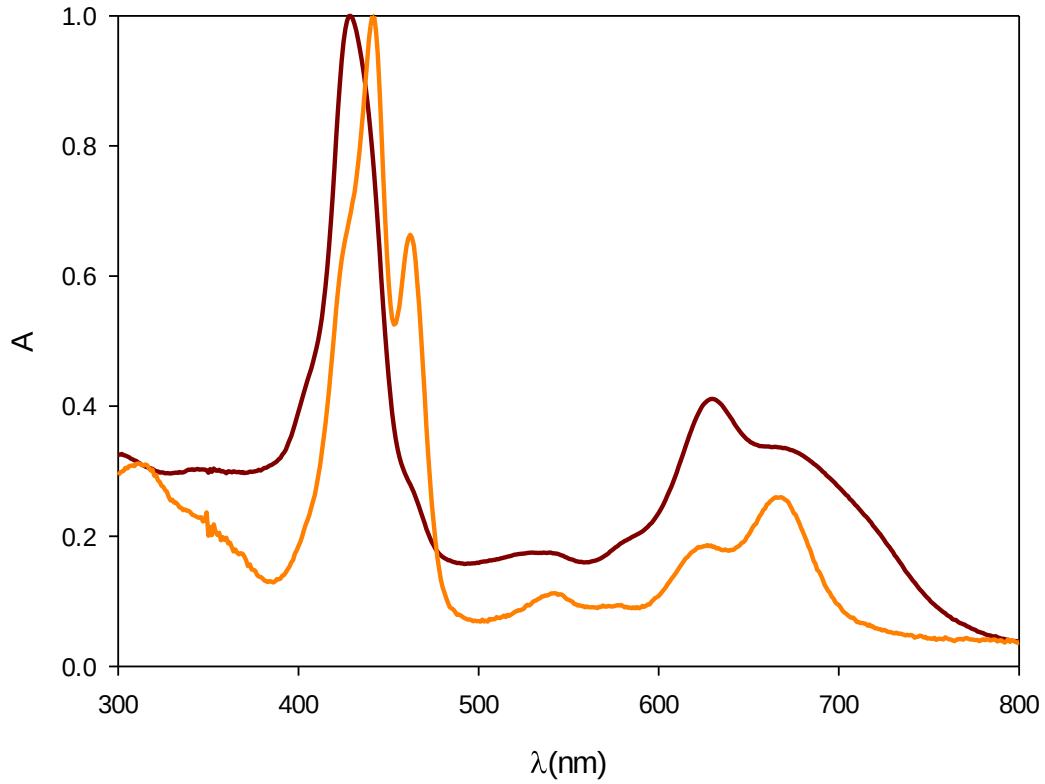

Figure S7 Absorption spectra of compounds **1** (dark red line) and after four days (orange line) in $CHCl_3$ solution at 298 K

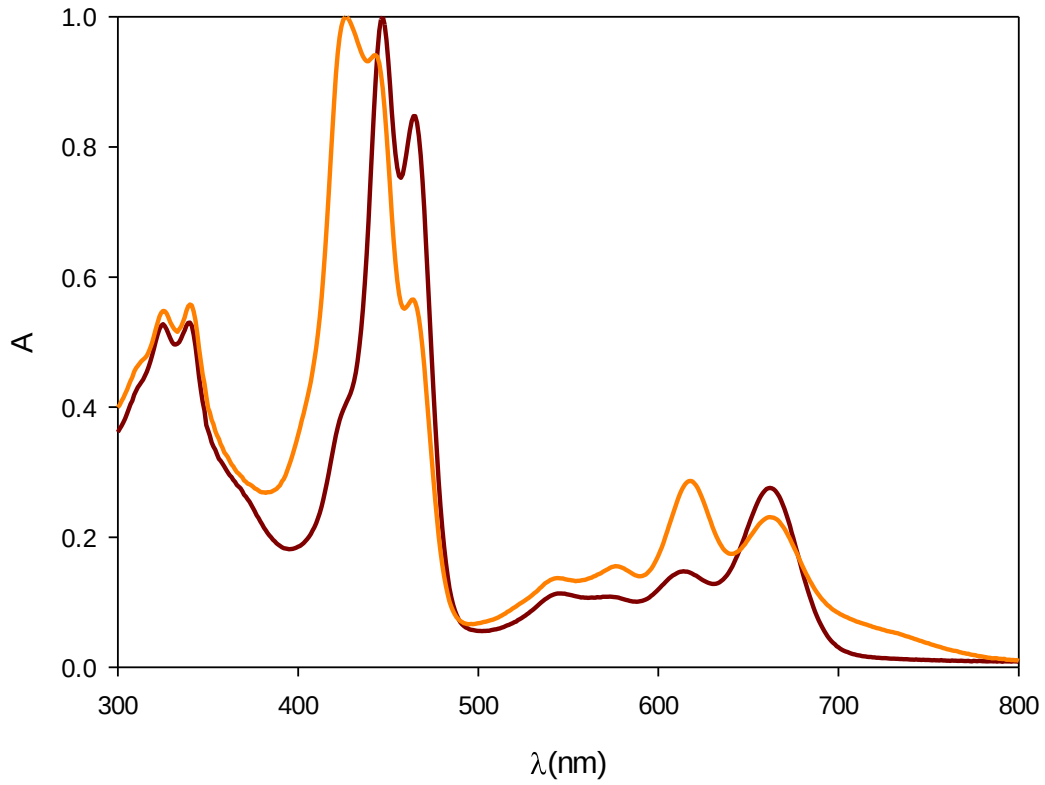

Figure S8 Absorption spectra of compounds **2** (dark red line) and after four days (orange line) in $CHCl_3$ solution at 298 K

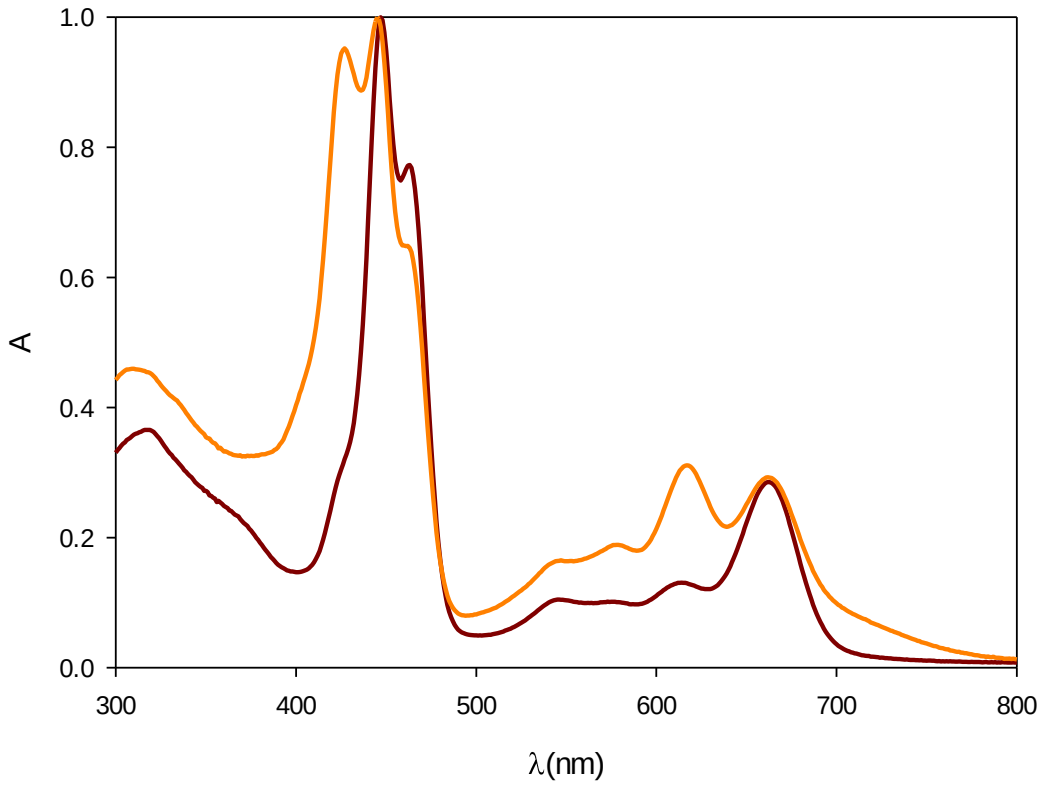

Figure S9 Absorption spectra of compounds **3** (dark red line) and after four days (orange line) in $CHCl_3$ solution at 298 K

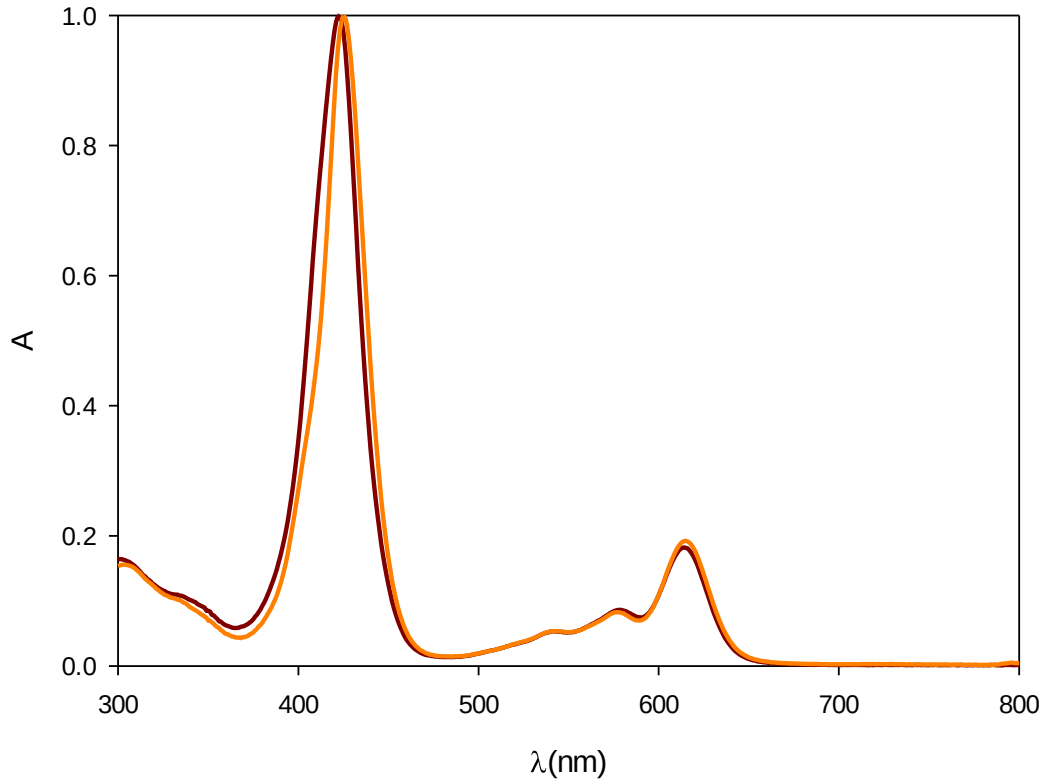

Figure S10 Absorption spectra of compounds **4** (dark red line) and after four days (orange line) in $CHCl_3$ solution at 298 K

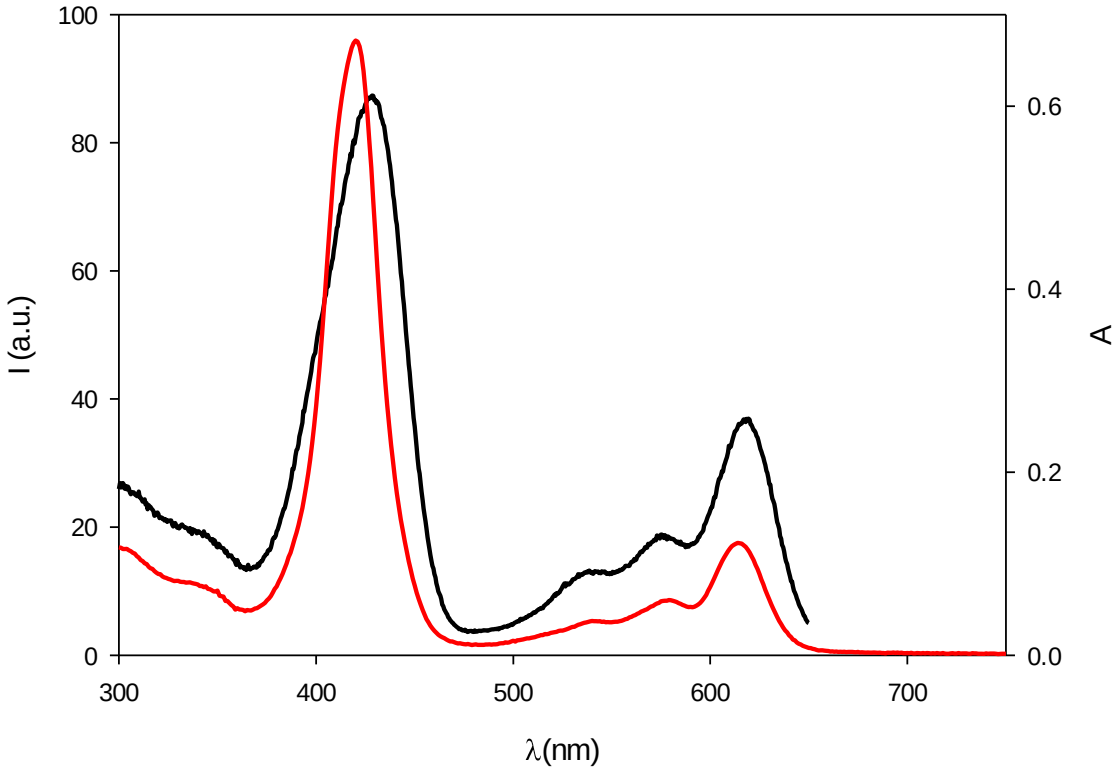

Figure S11 Absorption (red line) and excitation spectra (black line) of compounds **4** in $CHCl_3$ solution at 298 K. λ_{em}=700 nm

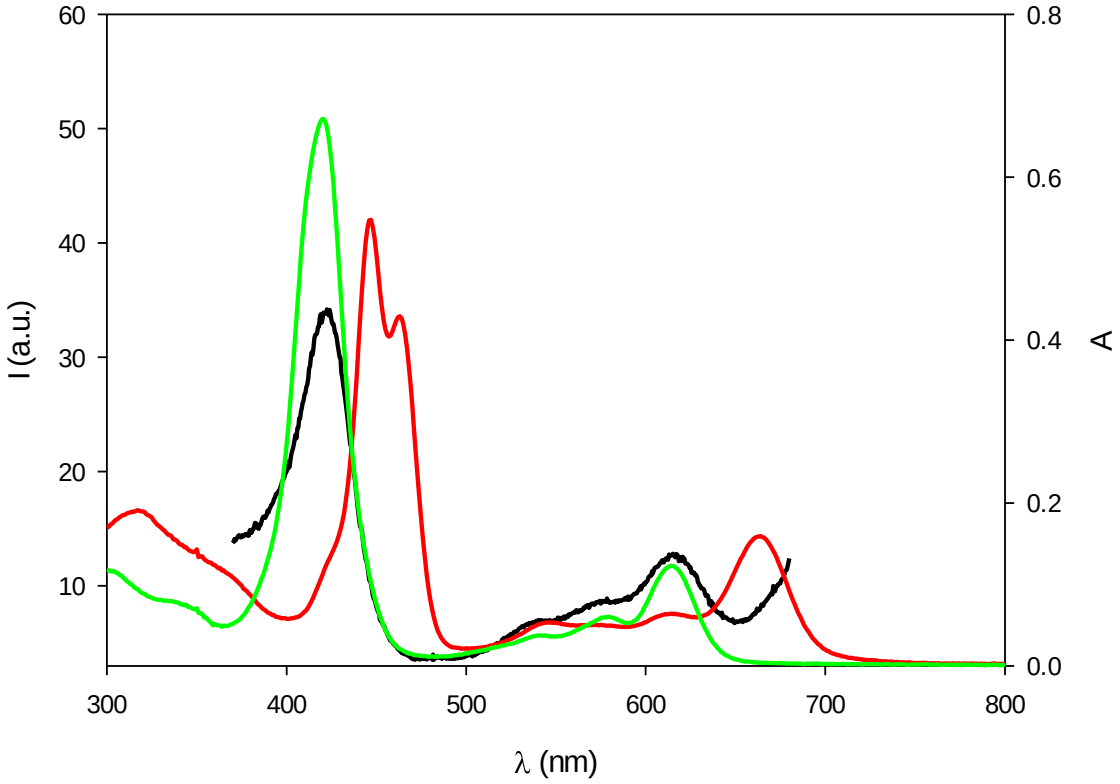

Figure S12 Absorption (red line), excitation spectra (black line) of compounds **3** and absorption spectra of compound **4** (green line) in $CHCl_3$ solution at 298 K. λ_{em}=680 nm

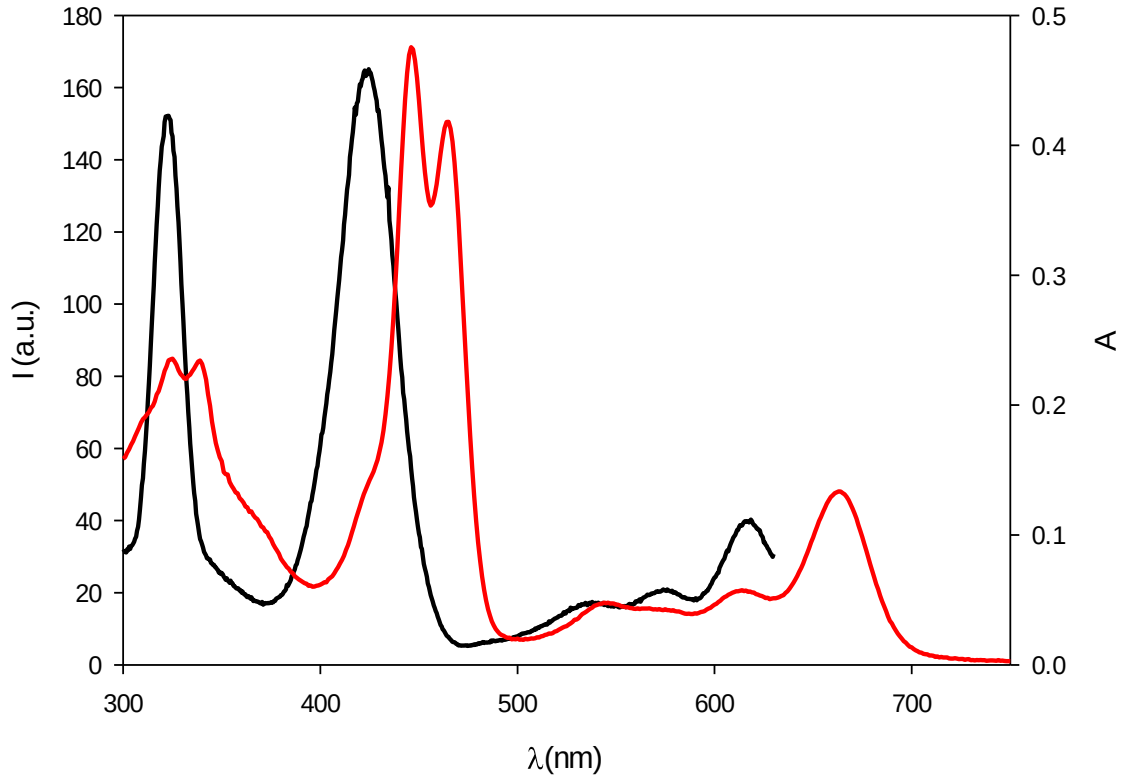

Figure S13 Absorption (red line) and excitation spectra (black line) of compounds **2** in $CHCl_3$ solution at 298 K. λ_{em}=700 nm

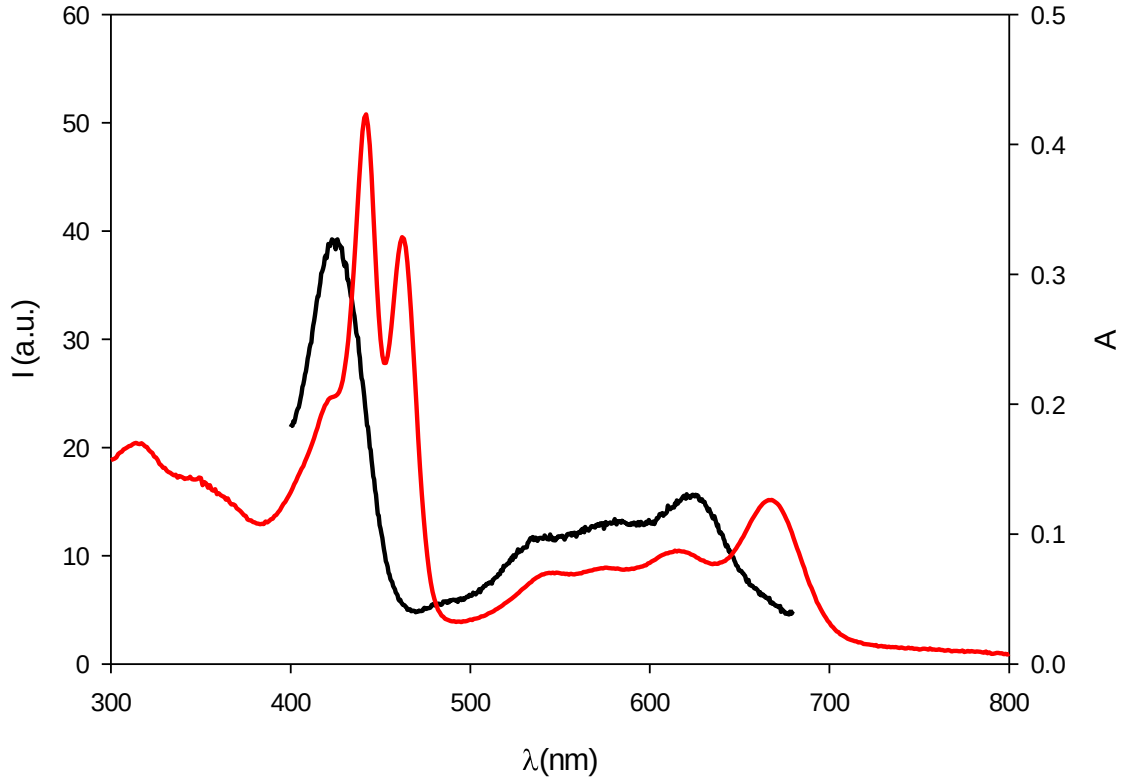

Figure S14 Absorption (red line) and excitation spectra (black line) of compounds **1** in $CHCl_3$ solution at 298 K. λ_{em}=700 nm

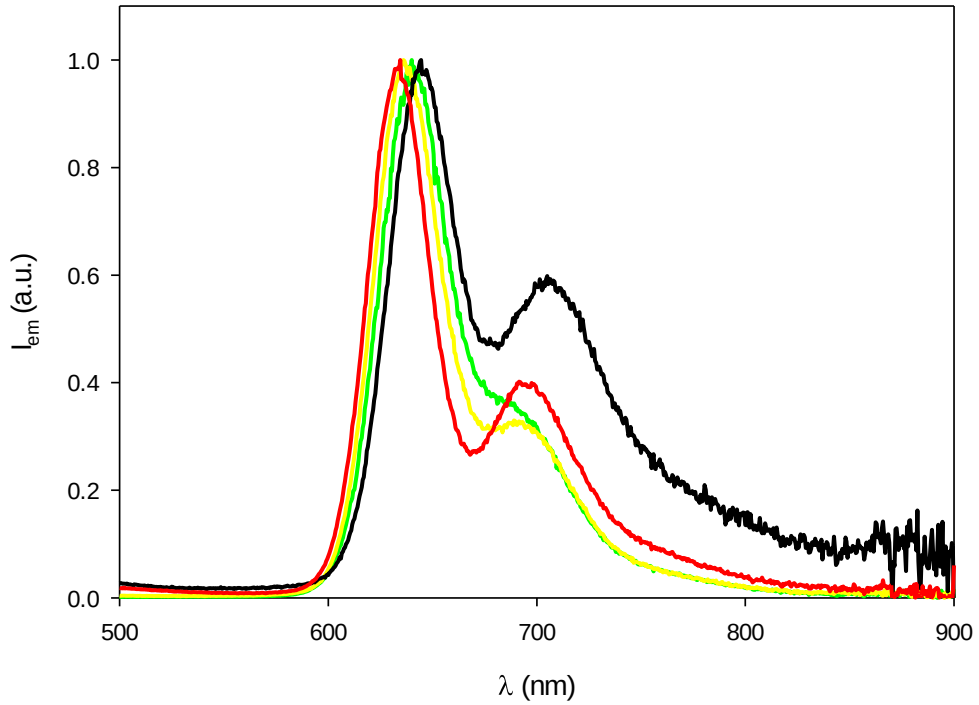

Figure S15 Emission spectra of compounds **1** (black line), **2** (red line), **3** (yellow line), **4** (green line) in $CHCl_3$ solution at 298 K. λ_{exc}= 430 nm

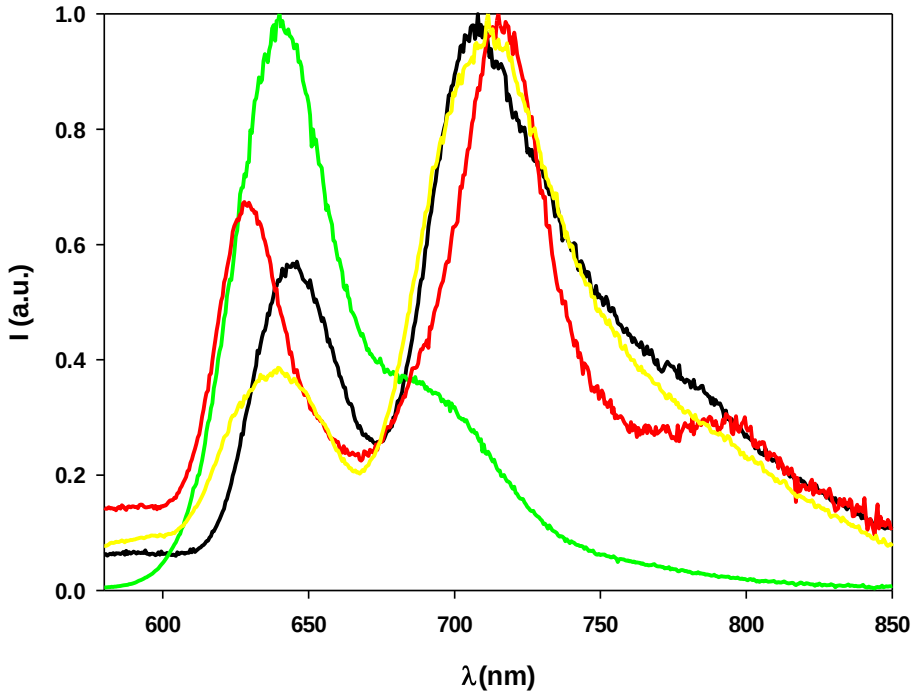

Figure S16 Emission spectra of **1** (black line), **2** (red line), **3** (yellow line), **4** (green line) in CH_2Cl_2/MeOH 1:1 a rigid matrix at 77 k. λ_{exc}= 430 nm

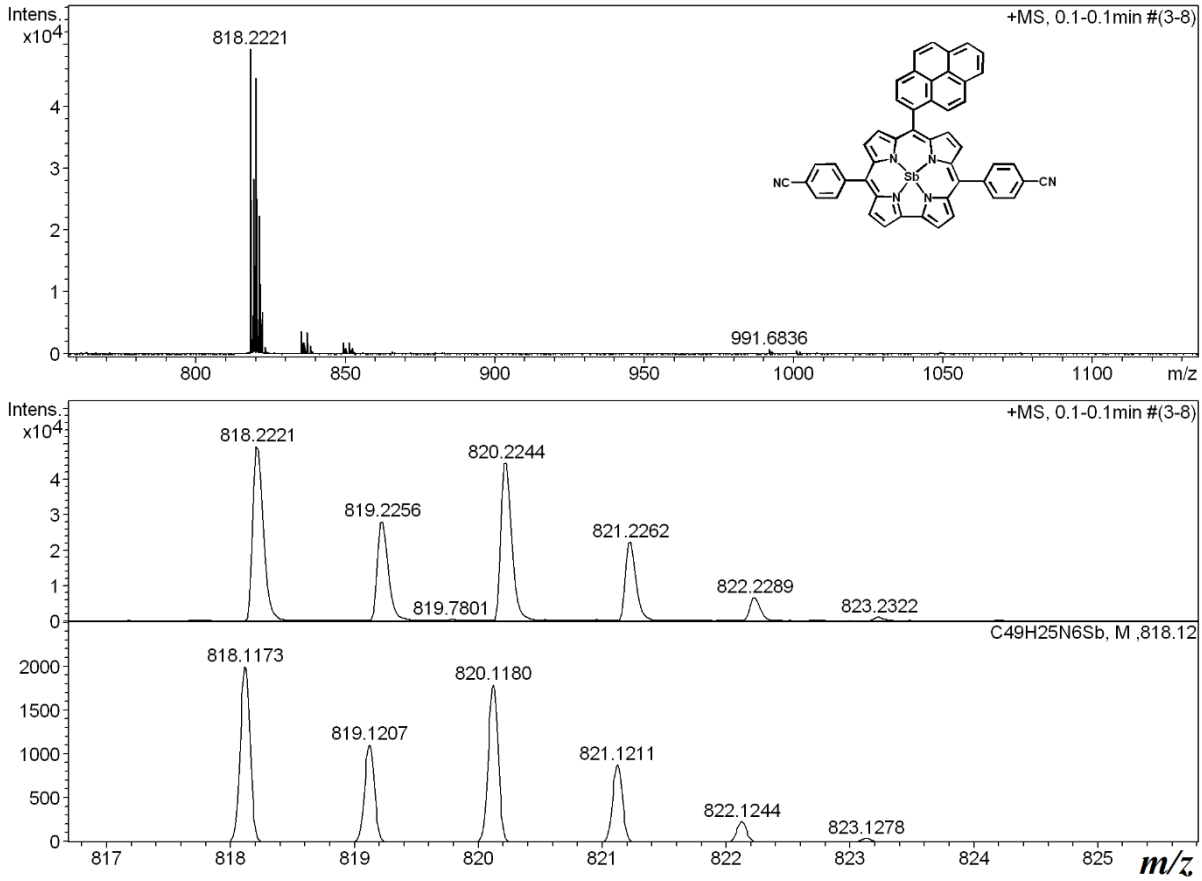

Figure S17 ESI−MS spectrum of **2** in CH_3CN shows the measured spectrum with an isotopic distribution pattern.

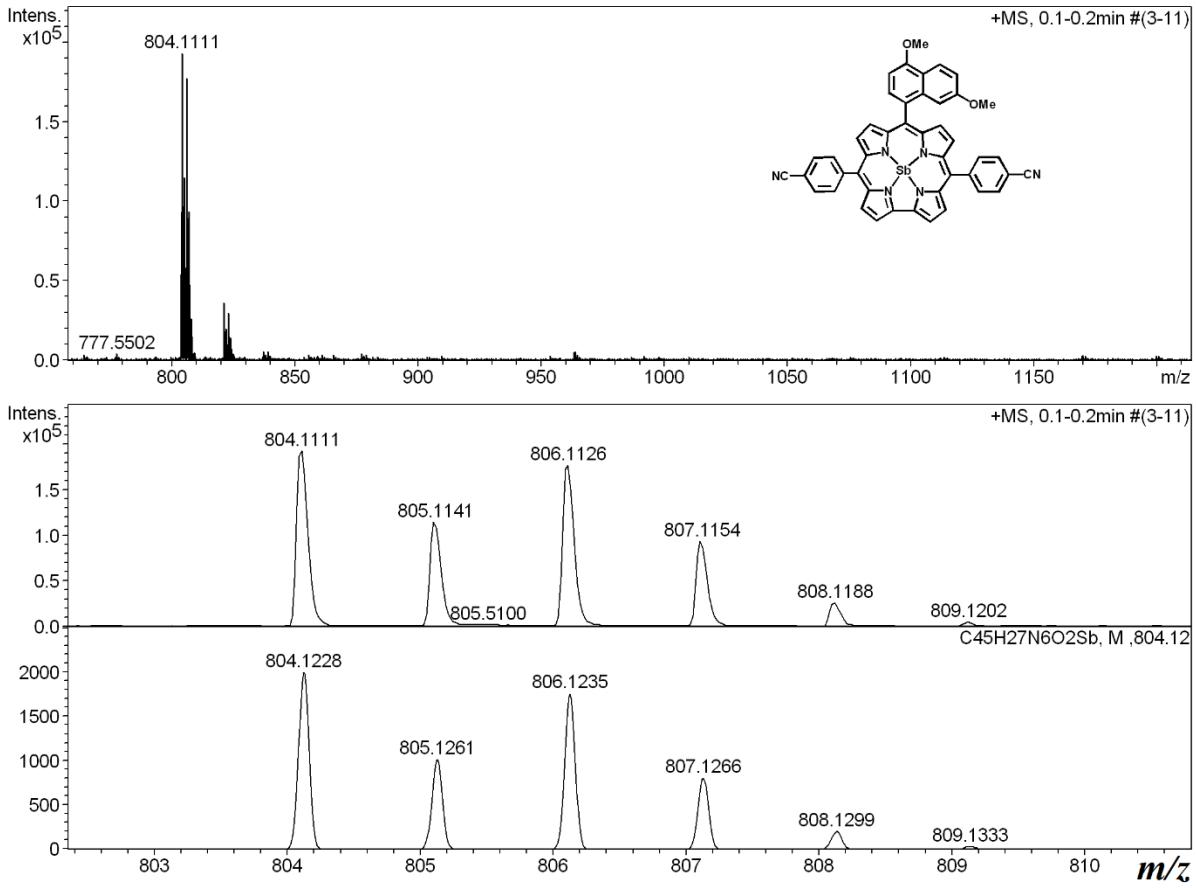

Figure S18 ESI−MS spectrum of **3** in CH_3CN shows the measured spectrum with an isotopic distribution pattern.

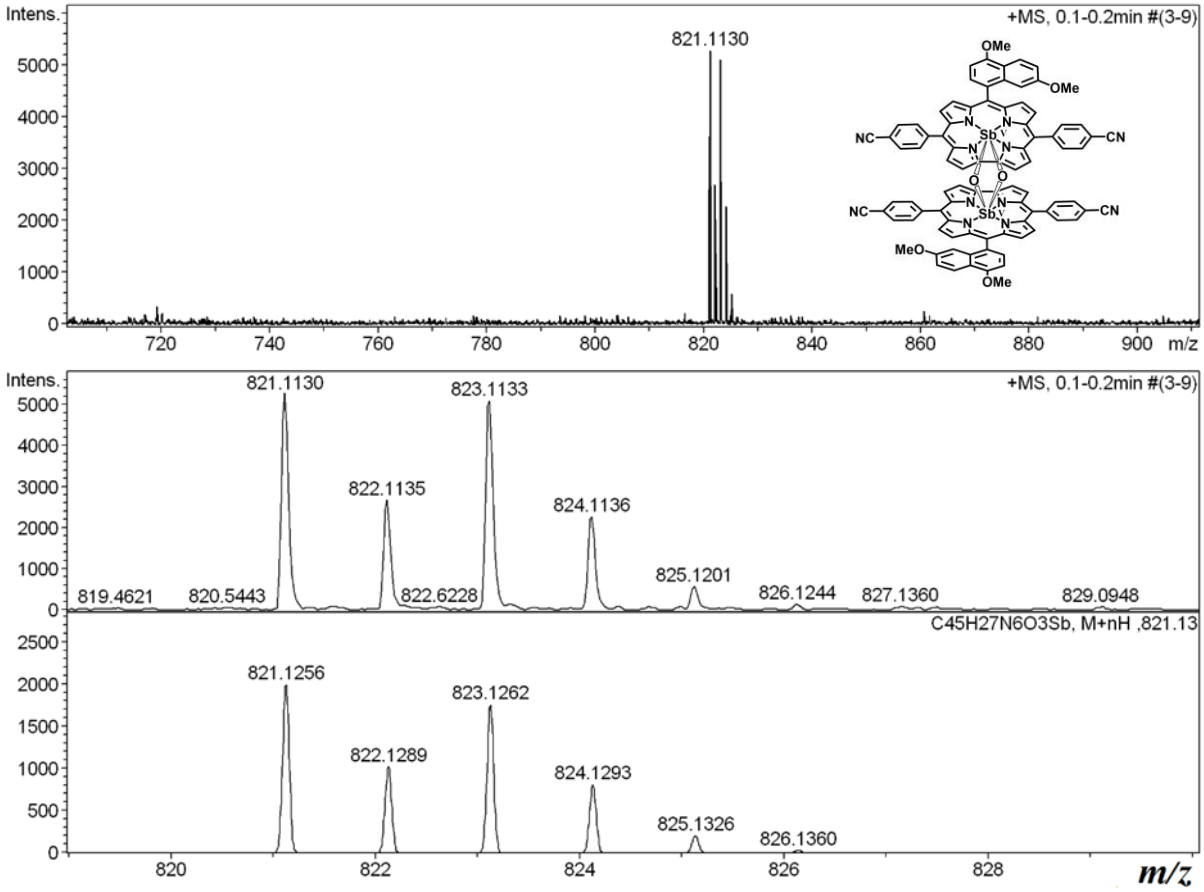

Figure S19 ESI−MS spectrum of **4** in CH_3CN shows the measured spectrum with an isotopic distribution pattern.

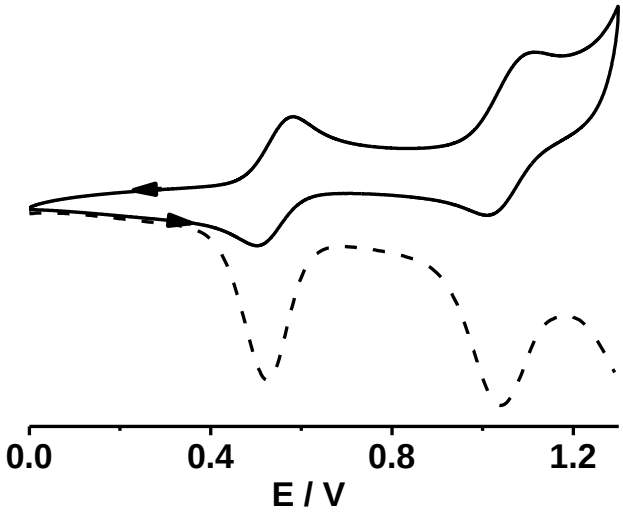

Figure S20 Cyclic voltammograms and differential pulse voltammograms of **2** in CH_2Cl_2. The potentials are vs. Ag/AgCl.

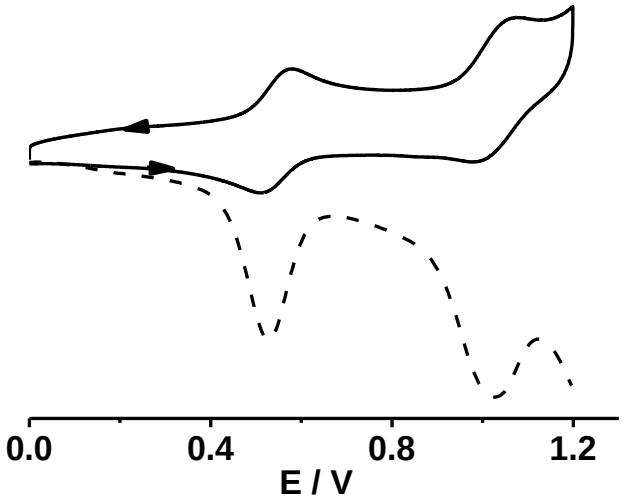

Figure S21 Cyclic voltammograms and differential pulse voltammograms of **3** in CH_2Cl_2. The potentials are vs. Ag/AgCl.

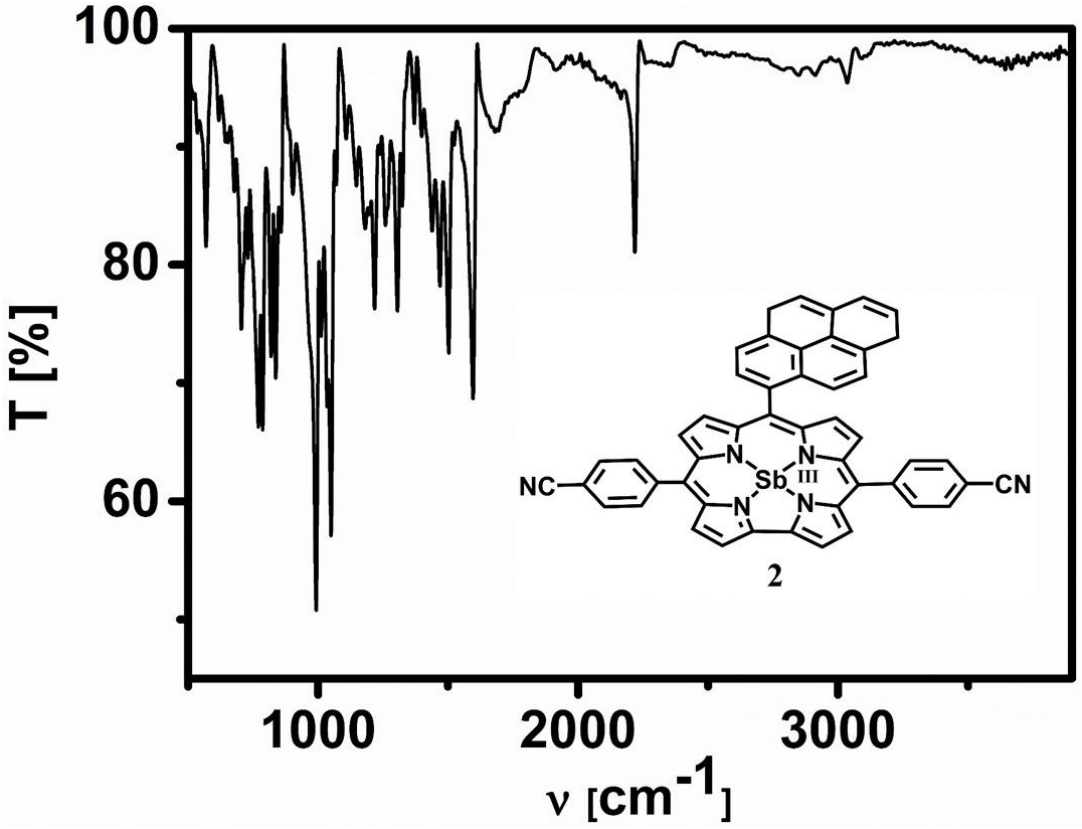

Figure S22 FT IR spectra of **2** as KBr Pellet.

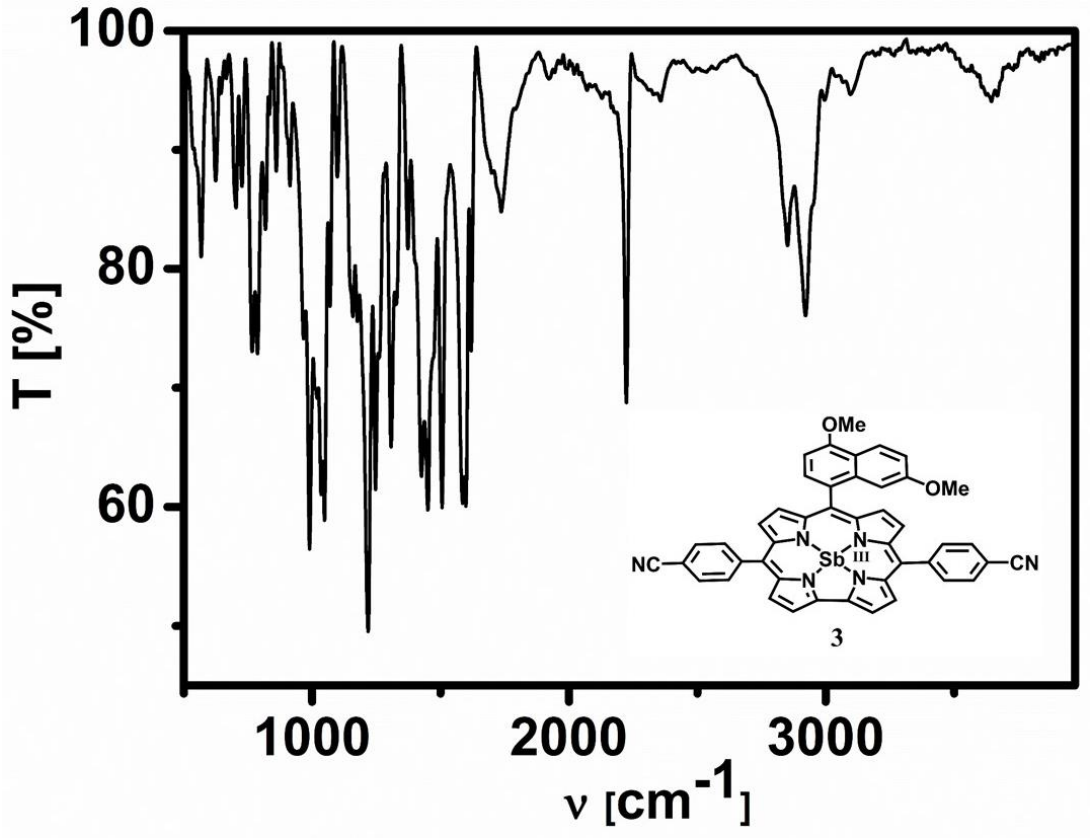

Figure S23 FT IR spectra of **3** as KBr Pellet.

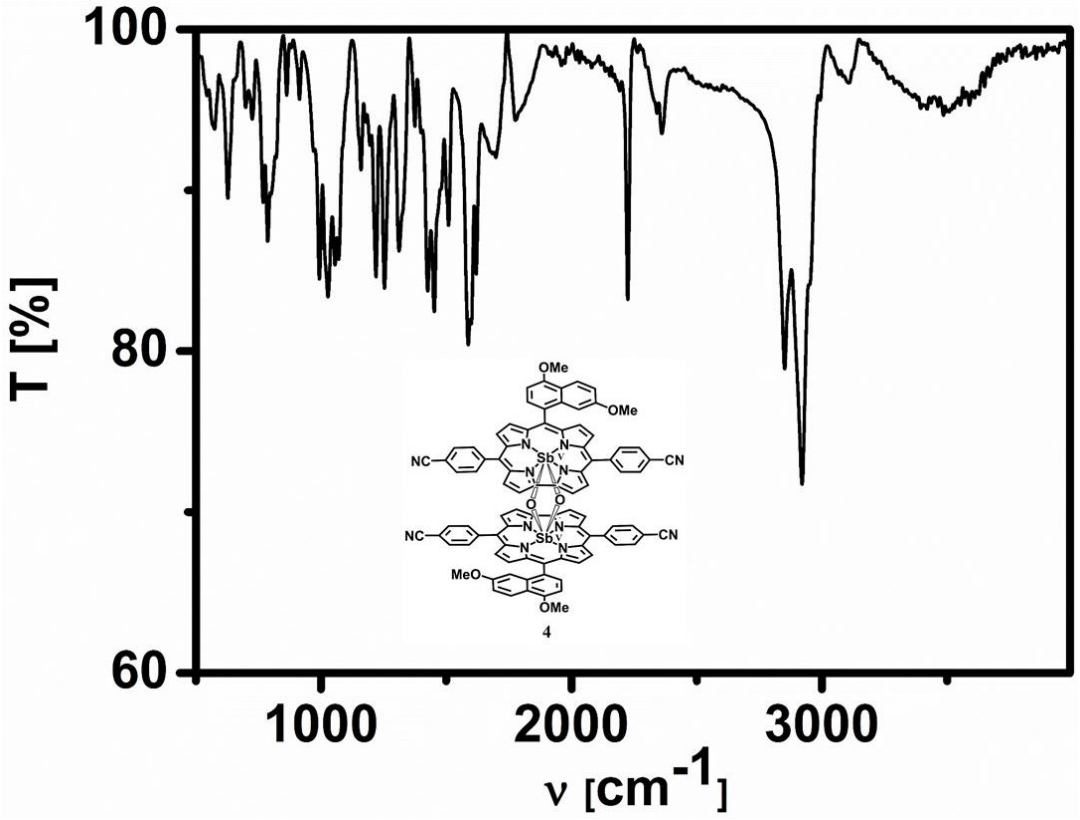

Figure S24 FT IR spectra of **4** as KBr Pellet.

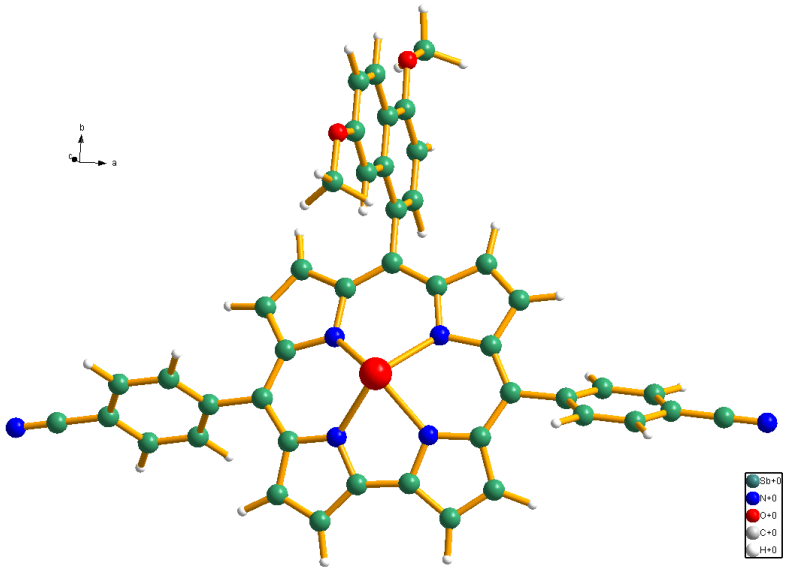

Figure S25 DFT-optimized geometry of **3** using the 6-311G (d, p) basis set.

Table S3 TD-DFT Calculated Electronic Transitions for **3**.

State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital contributions[a]
S1	2.052	604.06	0.2987	HOMO->LUMO (88%)
S2	2.254	550.059	0.0027	HOMO-1->LUMO (49%) HOMO->LUMO+1 (50%)
S3	2.647	468.35	0.0527	HOMO-2->LUMO (88%)
S4	2.777	446.44	0.5322	HOMO-2->LUMO (11%) HOMO-1->LUMO (37%) HOMO->LUMO+1 (40%)
S5	2.870	431.89	0.6755	HOMO-1->LUMO+1 (66%) HOMO->LUMO+3 (10%)
S6	2.978	416.27	0.0855	HOMO-2->LUMO+1 (72%) HOMO->LUMO+2 (22%)

S7	3.028	409.38	0.0804	HOMO-2->LUMO+1 (13%) HOMO->LUMO+2 (65%)
S8	3.065	404.47	0.068	HOMO-1->LUMO+1 (12%), HOMO->LUMO+3 (72%)
S9	3.337	371.48	0.0028	HOMO-3->LUMO (97%)
S10	3.347	370.38	0.0289	HOMO-1->LUMO+2 (92%)
S11	3.376	367.23	0.055	HOMO-1->LUMO+3 (92%)
S12	3.437	360.63	0.0003	HOMO->LUMO+4 (99%)
S13	3.626	341.86	0.4692	HOMO-4->LUMO (86%)
S14	3.659	338.81	0.0083	HOMO-5->LUMO (96%)
S15	3.236	335.46	0.0121	HOMO-3->LUMO+1 (97%)
S16	3.703	334.80	0.0082	HOMO->LUMO+5 (82%)
S17	3.723	332.95	0.0019	HOMO->LUMO+5 (10%) HOMO->LUMO+6 (88%)

S18	3.802	326.10	0.0027	HOMO-2->LUMO+2 (99%)
S19	3.827	323.95	0.0097	HOMO-2->LUMO+3 (76%) HOMO-1->LUMO+4 (19%)
S20	3.832	323.54	0.0093	HOMO-2->LUMO+3 (22%) HOMO-1->LUMO+4 (74%)
S21	3.846	322.36	0.0621	HOMO->LUMO+7 (78%)
S22	3.952	313.70	0.0134	HOMO-7->LUMO (82%)
S23	3.992	310.55	0.1081	HOMO-8->LUMO (11%) HOMO-6->LUMO (37%) HOMO-4->LUMO+1 (30%)
S24	4.030	307.59	0.2237	HOMO-6->LUMO (21%) HOMO-2->LUMO+4 (62%)
S25	4.067	304.85	0.0177	HOMO-1->LUMO+5 (86%)
S26	4.084	303.51	0.0146	HOMO-1->LUMO+6 (89%)
S27	4.108	301.74	0.1561	HOMO-6->LUMO (25%) HOMO-4->LUMO+1 (32%) HOMO-2->LUMO+4 (14%)

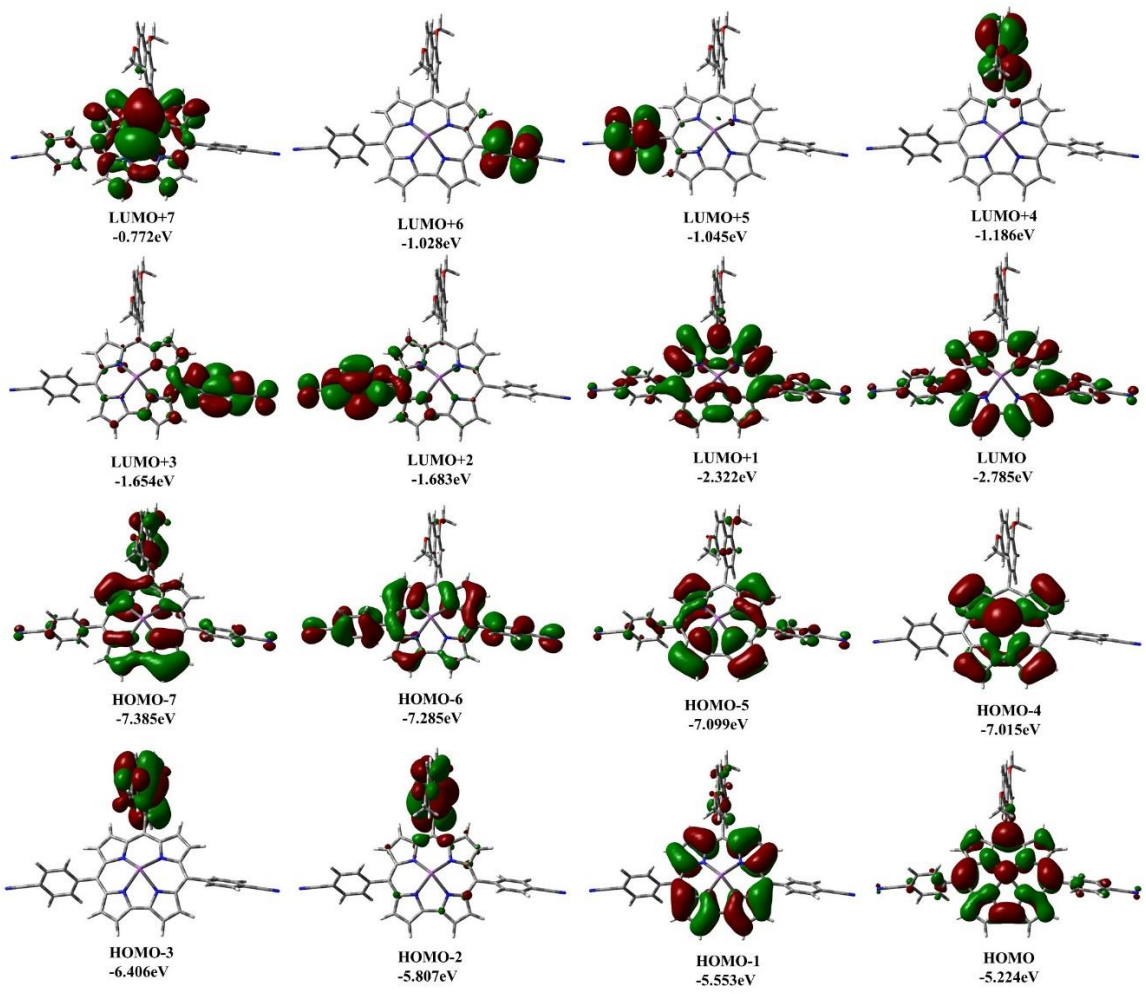

Figure S26 Selected frontier MOs and orbital energies of corrolato antimony(III), **3**.

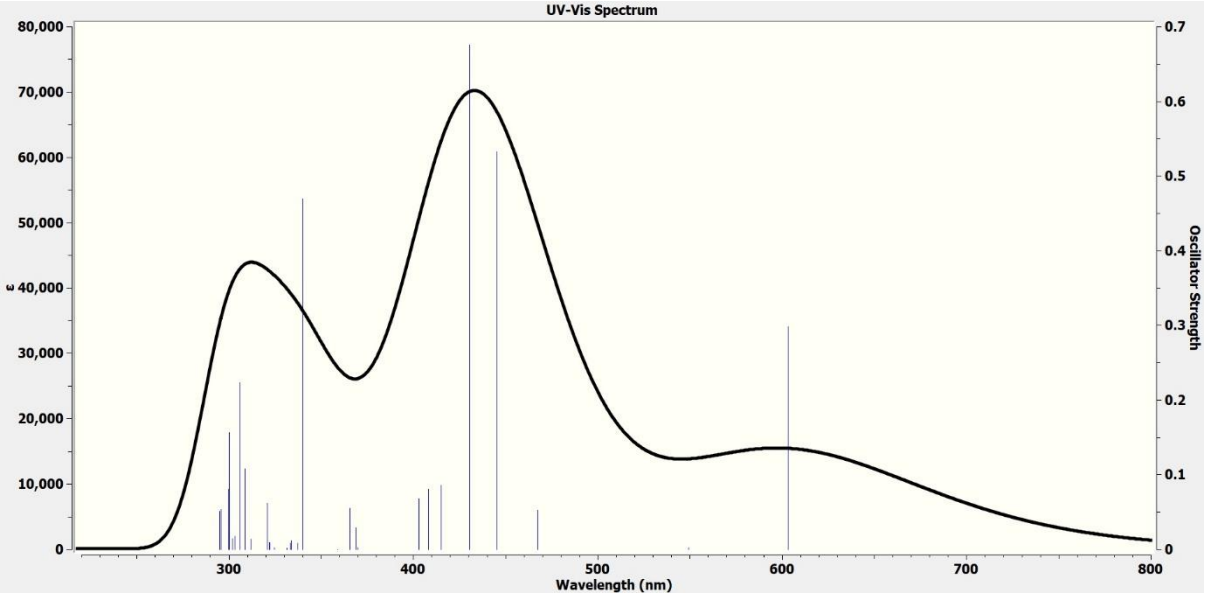

Figure S27 TD-DFT-based electronic absorption spectra of **3.**

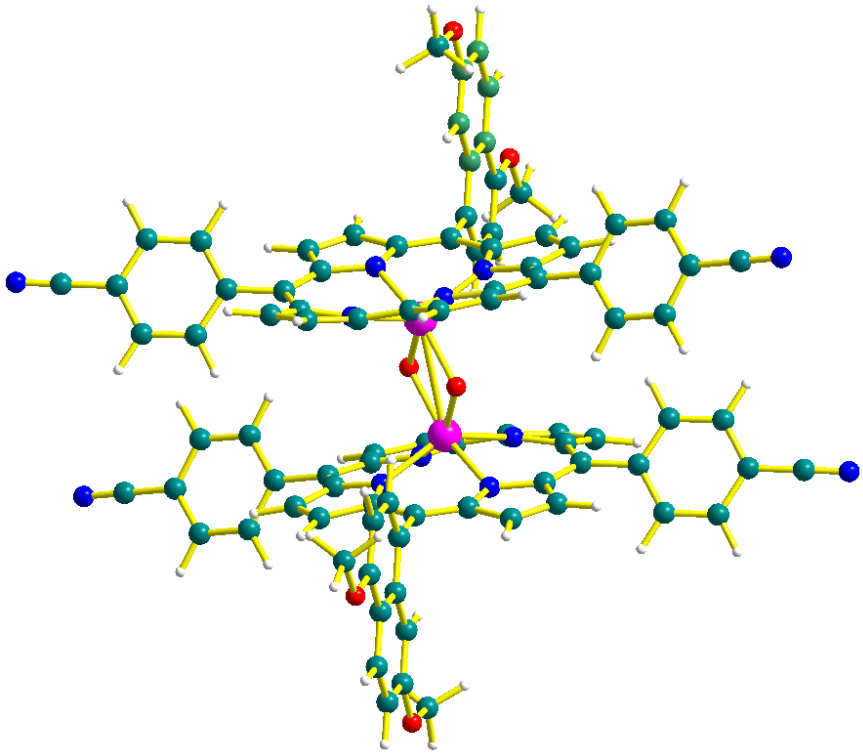

Figure S28 DFT-optimized geometry of **4** using the 6-311G (d, p) basis set.

Table S4 TD-DFT Calculated Electronic Transitions for **4.**

State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Orbital contributions[a]
S1	2.182	568.02	0.0817	HOMO-1->LUMO (14%) HOMO->LUMO+1 (82%)
S2	2.269	546.35	0.3409	HOMO-1->LUMO (74%)
S3	2.330	531.93	0.0284	HOMO-3->LUMO (35%) HOMO-2->LUMO+1 (28%) HOMO-1->LUMO+2 (14%) HOMO->LUMO+3 (21%)
S4	2.398	516.96	0.0046	HOMO-3->LUMO (46%) HOMO-2->LUMO+1 (52%)
S5	2.578	480.87	0.0267	HOMO-5->LUMO (58%) HOMO-4->LUMO+1 (32%)
S6	2.641	469.33	0.0081	HOMO-1->LUMO+2 (49%) HOMO->LUMO+3 (48%)
S7	2.684	461.83	0.0005	HOMO-5->LUMO (35%) HOMO-4->LUMO+1 (63%)
S8	2.836	437.09	0.0123	HOMO-3->LUMO+2 (58%), HOMO-2->LUMO+3 (35%)

S9	2.853	434.55	0.0901	HOMO->LUMO+4 (65%)
S10	2.861	433.22	0.1044	HOMO-5->LUMO+2 (30%) HOMO-4->LUMO+3 (23%) HOMO-2->LUMO+3 (18%) HOMO->LUMO+4 (18%)
S11	3.062	404.88	0.8751	HOMO-1->LUMO+2 (21%) HOMO->LUMO+3 (14%)
S12	3.097	400.24	1.0237	HOMO-2->LUMO+4 (30%)
S13	3.109	398.74	0.9183	HOMO-2->LUMO+4 (35%)
S14	3.160	392.33	0.0013	HOMO-5->LUMO+2 (43%) HOMO-4->LUMO+3 (55%)
S15	3.236	383.05	0.0297	HOMO-7->LUMO (62%) HOMO-6->LUMO+1 (30%)

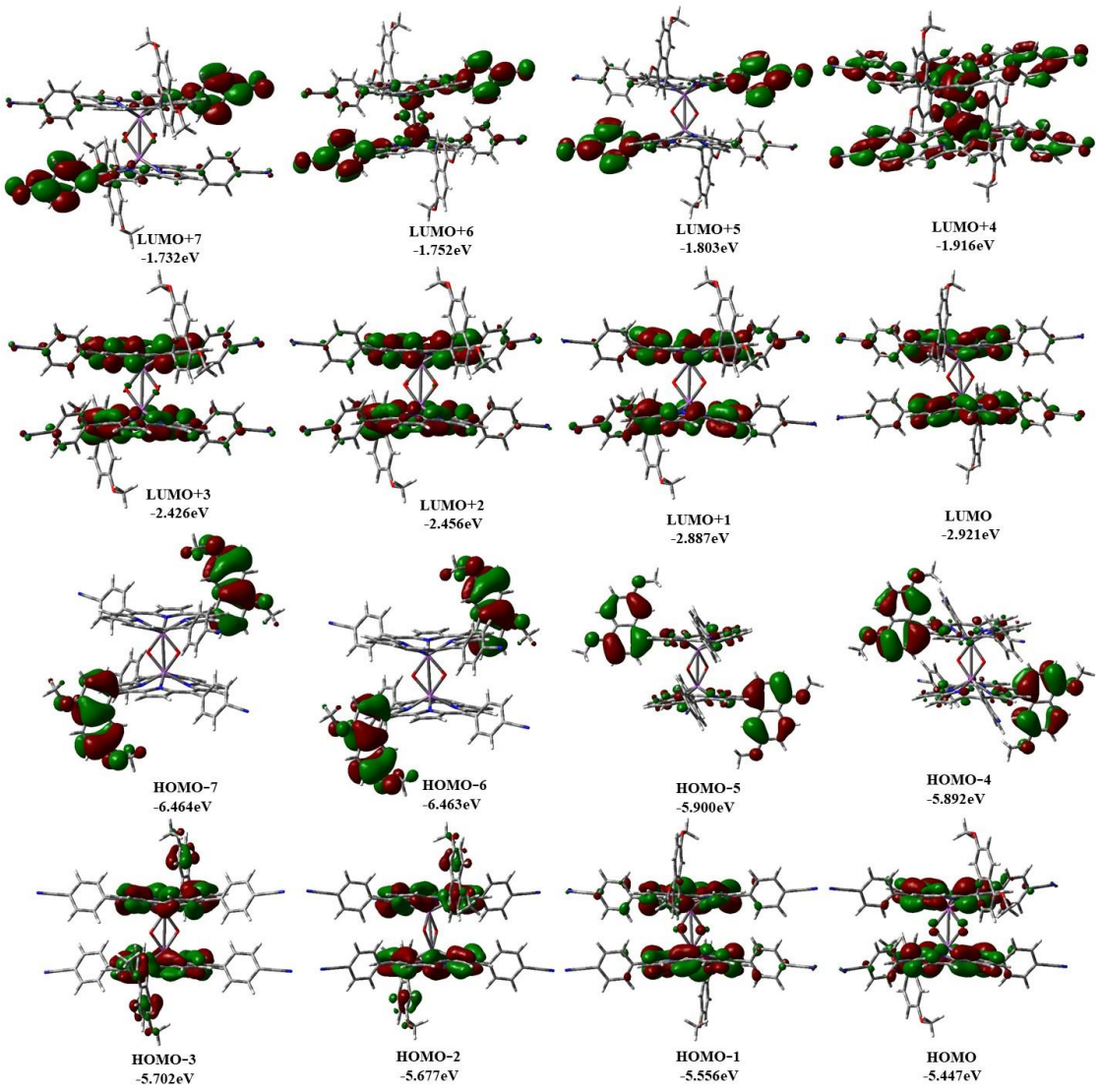

Figure S29 Composition and Energies of Selected Molecular Orbitals of **4**.

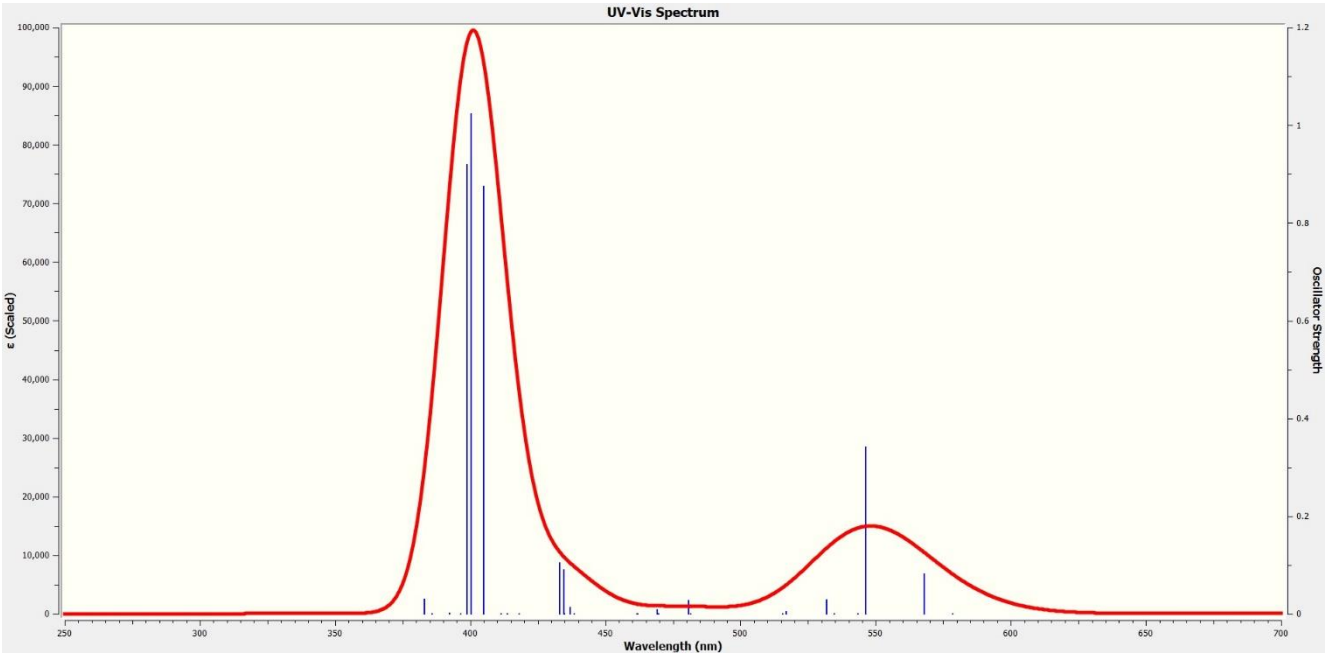

Figure S30 TD-DFT-based electronic absorption spectra of **4.**

Optimized Cartesian Co-ordinates of 10-(4,7-Di-methoxynaphthalen-1-yl)-5,15-bis(4-cyanophenyl)corrolato antimony(III), 3

Cartesian coordinates of the optimized structure (in Å). Corrolato antimony(III), **3** was optimized at the B3LYP level of theory and 6-311G (d, p) basis set. The LANL2DZ pseudopotential was used for the Sb atom.

Corrolato antimony(III), **3**

(E = -2215.9232 hartrees)

Sb	0.10200	-1.32200	1.00100
N	-1.03600	-2.94900	0.19600
N	1.46500	-0.09100	-0.11500
N	-1.39200	-0.26500	-0.12400
N	1.47700	-2.79600	0.27600
O	-0.44600	7.35000	-1.76500
O	-0.65400	4.64100	3.89600
C	-3.22600	-1.97100	-0.14800
C	1.19600	1.24100	-0.38200
C	3.51700	-1.53000	-0.06700
C	1.01100	-4.07600	0.11500
C	-2.72600	-0.65800	-0.25200
C	2.82700	-2.76000	0.07300
C	-2.38100	-3.09900	-0.00800
C	-0.40600	-4.16500	0.09100
C	-2.61900	-4.49700	-0.18100
H	-3.58000	-4.95200	-0.36500
C	-1.28800	1.07900	-0.43600
C	-2.60000	1.55600	-0.75300
H	-2.82500	2.56100	-1.07000
C	-0.08700	1.81300	-0.49300
C	-3.46900	0.50500	-0.64400
H	-4.52500	0.51400	-0.86300

C	-5.58800	-1.66100	0.64900
H	-5.20200	-1.10100	1.49200
N	10.36700	-1.92700	-0.67900
C	4.99800	-1.58800	-0.20400
C	-7.46400	-2.59500	-0.55300
C	2.12100	-4.91600	-0.14400
H	2.08400	-5.97800	-0.33200
C	3.24700	-4.10500	-0.16700
H	4.25500	-4.41300	-0.39600
C	-4.69300	-2.18600	-0.29400
C	-6.95700	-1.86000	0.52700
H	-7.63700	-1.45400	1.26600
C	2.84900	-0.29500	-0.18100
C	-0.35100	6.01500	-1.52100
C	-1.39500	-5.15100	-0.13700
H	-1.22100	-6.20700	-0.27300
C	-0.34100	4.26100	0.21500
C	2.44600	1.90600	-0.58500
H	2.55100	2.95100	-0.82800
C	-0.17700	3.27600	-0.81300
C	-0.41600	3.91000	1.59000
H	-0.34900	2.86500	1.85500
N	-10.01100	-2.97500	-0.78900
C	-6.58000	-3.12100	-1.50600
H	-6.97100	-3.67900	-2.34800
C	-0.19100	5.05100	-2.49500
H	-0.13100	5.31500	-3.54200
C	-0.42800	5.64100	-0.14500
C	3.44500	0.98000	-0.45500
H	4.50300	1.15700	-0.56100
C	9.21800	-1.85500	-0.57800
C	7.79600	-1.76700	-0.45200

C	5.64800	-1.13600	-1.36300
H	5.06100	-0.73600	-2.17900
C	5.77800	-2.14400	0.82200
H	5.29300	-2.49800	1.72300
C	-0.10700	3.69300	-2.12400
H	0.01500	2.95000	-2.90500
C	-5.21400	-2.91500	-1.37400
H	-4.54000	-3.30500	-2.12600
C	-0.57200	4.87900	2.55800
C	-0.57000	3.29800	4.35000
H	0.39200	2.84500	4.08300
H	-1.38400	2.68700	3.94300
H	-0.66000	3.34300	5.43400
C	-0.58900	6.61200	0.87800
H	-0.65400	7.65400	0.59600
C	7.15900	-2.23200	0.70700
H	7.75000	-2.65300	1.51100
C	7.02800	-1.22000	-1.49000
H	7.51600	-0.87500	-2.39300
C	-8.87300	-2.80500	-0.68400
C	-0.65900	6.24600	2.19400
H	-0.78100	6.97900	2.98300
C	-0.37900	7.80300	-3.11100
H	0.58000	7.54400	-3.57100
H	-0.47800	8.88600	-3.06500
H	-1.19600	7.38800	-3.71100

Optimized Cartesian Co-ordinates of Corrolato(oxo)antimony(V) dimer, 4

Cartesian coordinates of the optimized structure (in Å). Corrolato(oxo)antimony(V) dimer, **4** was optimized at the B3LYP level of theory and 6-311G (d, p) basis set. The LANL2DZ pseudopotential was used for the Sb atom.

Corrolato(oxo)antimony(V) dimer, **4**

(Energy= -4582.2776 hartrees)

Sb	0.96200	-0.01900	-1.25600
O	0.76100	0.79200	0.55700
N	0.36800	1.36700	-2.68700
N	0.38100	-1.13300	-2.95600
N	2.28200	-1.60800	-1.08700
N	2.70800	1.18900	-1.26500
O	8.48000	-1.17500	-2.74000
C	-0.41200	0.91500	-3.72800
C	-0.44500	-0.49800	-3.84100
C	3.77900	0.87900	-0.43500
O	8.58000	-0.88900	3.53400
C	3.41400	-1.56800	-0.28100
C	1.96900	-2.94700	-1.37100
C	0.65600	2.69900	-2.86000
C	1.01100	-3.38100	-2.30200
C	2.68400	2.57800	-1.45200
C	0.79900	-4.84300	-2.50500
C	1.73800	3.31100	-2.19100
C	2.90300	-3.74600	-0.64000
H	2.92900	-4.82400	-0.65600
C	4.11100	-0.39800	0.05000
C	0.25900	-2.48900	-3.09300
C	4.47800	2.09100	-0.14600
H	5.37300	2.15200	0.45300
C	3.77700	-2.91700	0.01300

H	4.62800	-3.20200	0.61000
C	2.19000	7.54500	-2.79800
N	2.44600	10.08600	-3.20000
C	-0.10300	3.13400	-3.98700
H	-0.08900	4.13300	-4.39500
C	-0.65300	-2.71600	-4.17000
H	-0.92900	-3.68300	-4.56200
C	-0.43200	-5.42700	-2.17500
H	-1.21200	-4.81000	-1.74600
C	-0.75500	2.03200	-4.52200
H	-1.34800	2.00700	-5.42300
C	1.91500	4.77600	-2.38000
C	3.81300	3.11700	-0.75400
H	4.07500	4.16300	-0.72500
C	0.35500	-7.58500	-2.92700
C	-1.08600	-1.48400	-4.63200
H	-1.77400	-1.30000	-5.44300
C	-0.65600	-6.78300	-2.37900
H	-1.60800	-7.22700	-2.11400
C	3.22600	6.67000	-3.15500
H	4.12900	7.06500	-3.60400
C	6.86300	-0.84800	-0.95500
H	6.02800	-0.75300	-1.63300
C	5.29600	-0.52500	0.96000
C	1.58800	-7.01000	-3.26400
H	2.36600	-7.62800	-3.69600
C	2.33000	8.95100	-3.01800
C	1.01500	7.02900	-2.23400
H	0.21600	7.70400	-1.95300
C	6.61300	-0.74400	0.44100
C	3.08500	5.30500	-2.94800
H	3.87900	4.63400	-3.25000

N	-0.05100	-10.10700	-3.33000
C	1.80200	-5.65500	-3.05400
H	2.75100	-5.21300	-3.33300
C	0.12900	-8.98000	-3.14800
C	0.88400	5.66200	-2.03300
H	-0.02300	5.27000	-1.58900
C	7.71000	-0.86500	1.34700
C	5.12200	-0.43500	2.32300
H	4.12600	-0.26500	2.71500
C	6.19700	-0.55100	3.22900
H	6.00100	-0.47100	4.29000
C	7.47400	-0.76300	2.75200
C	8.14100	-1.06200	-1.42700
C	7.45300	-1.06200	-3.71500
H	6.96700	-0.08100	-3.67300
H	6.69600	-1.84500	-3.59200
H	7.94400	-1.18200	-4.67900
C	9.01200	-1.08500	0.82600
H	9.83800	-1.17600	1.51800
C	9.22600	-1.18200	-0.52200
H	10.21500	-1.35000	-0.93000
C	8.43100	-0.79500	4.94400
H	8.03500	0.18200	5.23900
H	9.43000	-0.92100	5.35800
H	7.77600	-1.58500	5.32900
Sb	-0.96200	0.01900	1.25600
O	-0.76100	-0.79200	-0.55700
N	-0.36800	-1.36700	2.68700
N	-0.38100	1.13300	2.95600
N	-2.28200	1.60800	1.08700
N	-2.70800	-1.18900	1.26500
O	-8.48000	1.17500	2.74000

C	0.41200	-0.91500	3.72800
C	0.44500	0.49800	3.84100
C	-3.77900	-0.87900	0.43500
O	-8.58000	0.88900	-3.53400
C	-3.41400	1.56800	0.28100
C	-1.96900	2.94700	1.37100
C	-0.65500	-2.69900	2.86000
C	-1.01100	3.38100	2.30200
C	-2.68400	-2.57800	1.45200
C	-0.79900	4.84300	2.50500
C	-1.73800	-3.31100	2.19100
C	-2.90300	3.74600	0.64000
H	-2.92900	4.82400	0.65600
C	-4.11100	0.39800	-0.05000
C	-0.25900	2.49000	3.09300
C	-4.47800	-2.09100	0.14600
H	-5.37300	-2.15200	-0.45300
C	-3.77700	2.91700	-0.01300
H	-4.62800	3.20200	-0.61000
C	-2.19000	-7.54500	2.79800
N	-2.44600	-10.08600	3.20000
C	0.10300	-3.13400	3.98700
H	0.08900	-4.13300	4.39500
C	0.65300	2.71700	4.17000
H	0.92900	3.68300	4.56200
C	0.43200	5.42700	2.17500
H	1.21200	4.81000	1.74600
C	0.75500	-2.03200	4.52200
H	1.34800	-2.00700	5.42300
C	-1.91500	-4.77600	2.38000
C	-3.81300	-3.11700	0.75400
H	-4.07500	-4.16300	0.72500

C	-0.35500	7.58500	2.92700
C	1.08600	1.48400	4.63200
H	1.77400	1.30000	5.44300
C	0.65600	6.78300	2.37900
H	1.60800	7.22700	2.11400
C	-3.22600	-6.67000	3.15500
H	-4.12900	-7.06500	3.60400
C	-6.86300	0.84800	0.95500
H	-6.02800	0.75300	1.63300
C	-5.29600	0.52500	-0.96000
C	-1.58800	7.01000	3.26400
H	-2.36600	7.62800	3.69600
C	-2.33000	-8.95100	3.01800
C	-1.01500	-7.02900	2.23400
H	-0.21600	-7.70400	1.95300
C	-6.61300	0.74400	-0.44100
C	-3.08500	-5.30500	2.94800
H	-3.87900	-4.63400	3.25000
N	0.05100	10.10700	3.33000
C	-1.80200	5.65500	3.05400
H	-2.75100	5.21300	3.33300
C	-0.12900	8.98000	3.14800
C	-0.88400	-5.66200	2.03300
H	0.02300	-5.27000	1.58900
C	-7.71000	0.86500	-1.34700
C	-5.12200	0.43500	-2.32300
H	-4.12600	0.26500	-2.71500
C	-6.19700	0.55100	-3.22900
H	-6.00100	0.47100	-4.29000
C	-7.47400	0.76300	-2.75200
C	-8.14100	1.06200	1.42700
C	-7.45300	1.06200	3.71500

H	-6.96700	0.08100	3.67300
H	-6.69600	1.84500	3.59200
H	-7.94400	1.18200	4.67900
C	-9.01200	1.08500	-0.82600
H	-9.83800	1.17600	-1.51800
C	-9.22600	1.18200	0.52200
H	-10.21500	1.35000	0.93000
C	-8.43100	0.79500	-4.94400
H	-8.03500	-0.18200	-5.23900
H	-9.43000	0.92100	-5.35800
H	-7.77600	1.58500	-5.32900