Electrochemical deposition of a semiconducting gold dithiolene complex with NIR absorption

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Contents **Page**

^{1}H NMR spectra

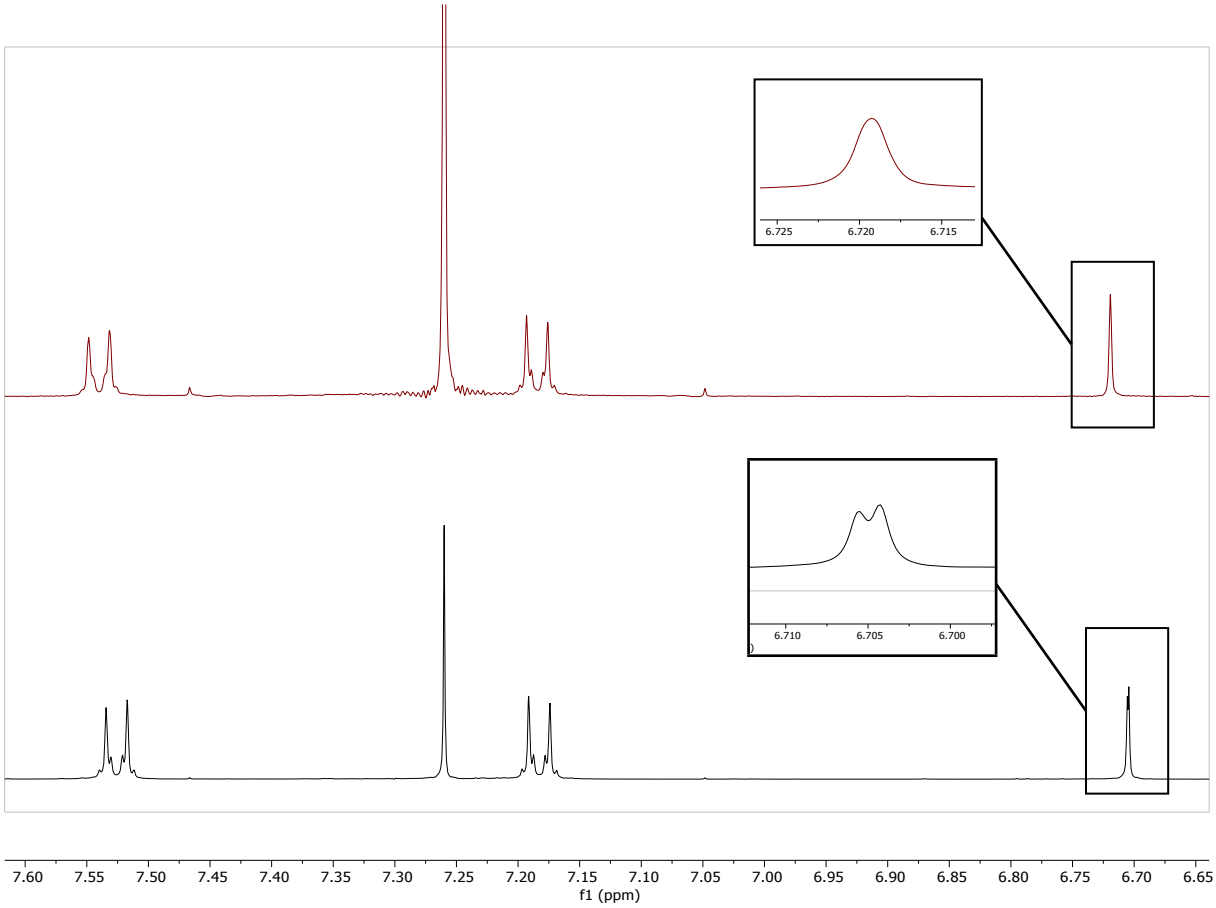

Figure S1: *TOP: ^{1}H NMR spectrum of pure isomer* ***NBu$_4$·[1-i]****. BOTTOM: ^{1}H NMR spectrum of the mixture of cis and trans isomers of* ***NBu$_4$·[1]****. Both spectra recorded in $CDCl_3$ at room temperature.*

Powder diffraction pattern

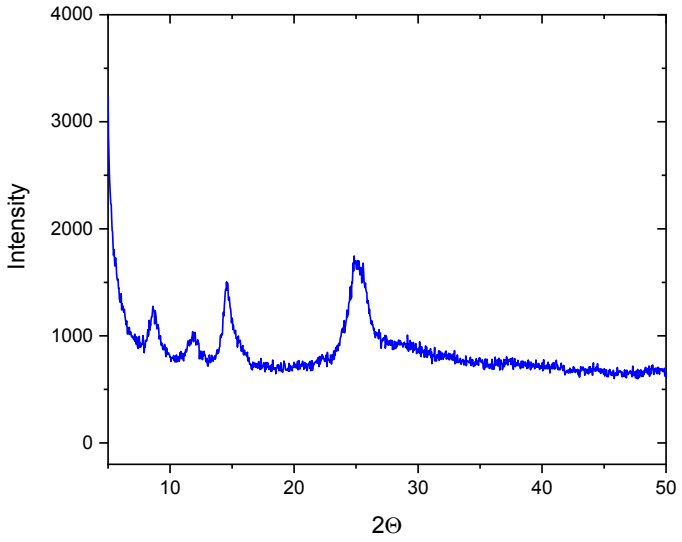

Figure S2: *Powder X-Ray diffraction (PXRD) pattern of* ***2****.*

Cyclic Voltammetry

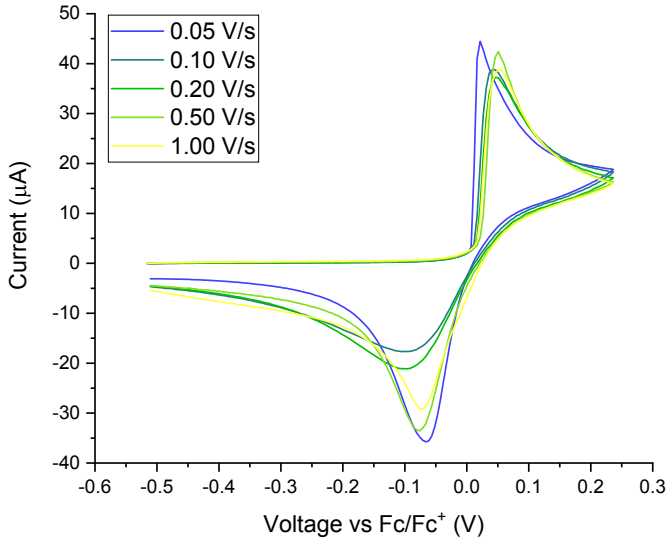

Figure S3: *Cyclic voltammograms of* ***NBu$_4$·[1-i]*** *with varying scan rates, at RT in acetonitrile with 0.1M [TBA][PF$_6$] as the supporting electrolyte.*

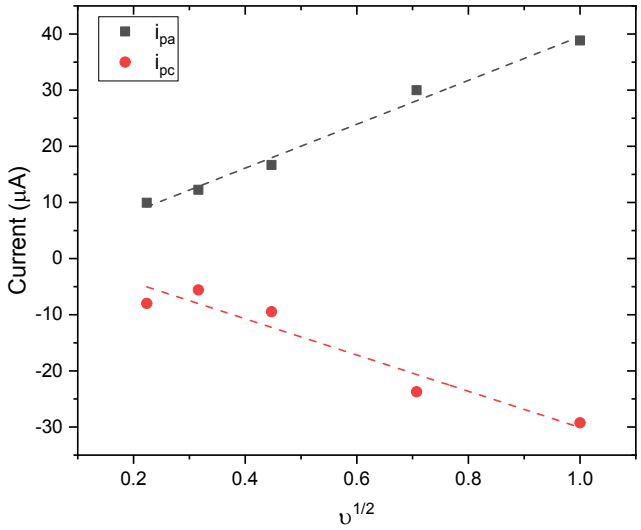

Figure S4: *Randles-Sevaik plot for the first oxidation of* ***NBu$_4$·[1-i]****.*

High pressure conductivity

Compressed pellet geometry

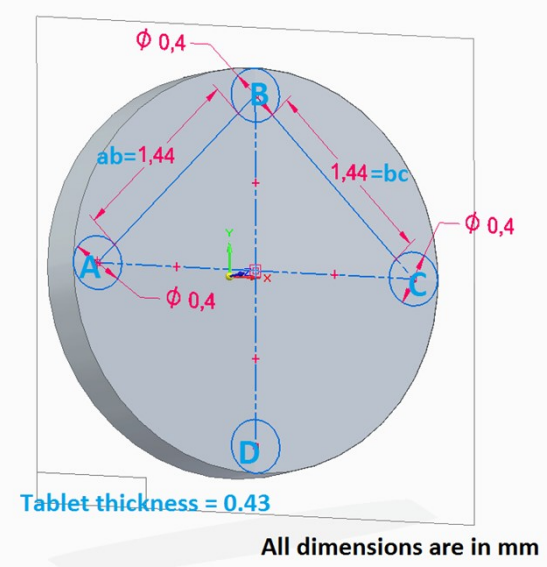

Figure S5: *Geometry of the compressed pellet of* ***2*** *showing the location of the four contact wires (A-D).*

The optimal thickness of the compressed pellet was calculated according to the Montgomery method.[1] For contacts spaced 1.44 mm apart (diagonally) this results in a thickness (E) of 0.43 mm. To convert resistance into resistivity the following formula is used:

$$\rho = H * E * R$$

where the value of H = 4.531 for contacts were ab=bc; this value was taken from the Montgomery method.[1]

*Pellet preparation (*Figure S6*):* Copper wires are attached using silver paint and silver epoxy. Paraffin was added on top of the pellet to prevent pellet and contact damage in a high pressure environment. The pellet-sensor assembly is placed into a high pressure piston cylinder cell, using Daphne Oil as the pressure medium. The pressure on the sample could then be modified by placing the piston cylinder cell into a hydraulic press. The pressure inside the cell was measured using the resistance of manganin wire which was present inside the sample chamber. Once the piston cylinder cell is assembled, the Manganin sensor is calibrated, by measuring its resistance, R_0, at atmospheric pressure. This allows for the resistance of the coil to be converted into pressure using the following equation:

$$P(GPa) = \frac{\frac{R}{R_0} - 1}{0.0234}$$

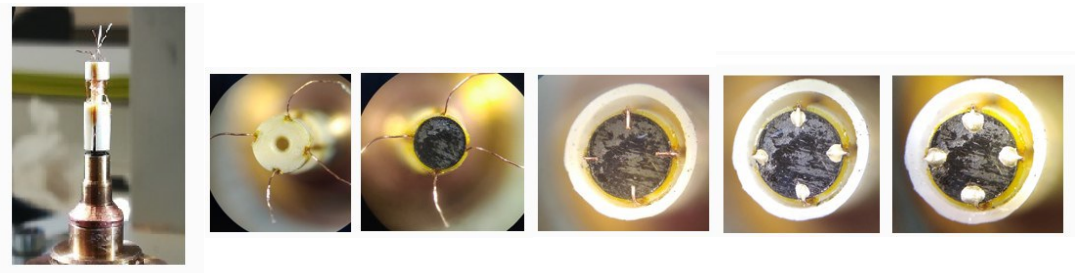

Figure S6: *Stages of the sample mounting process*

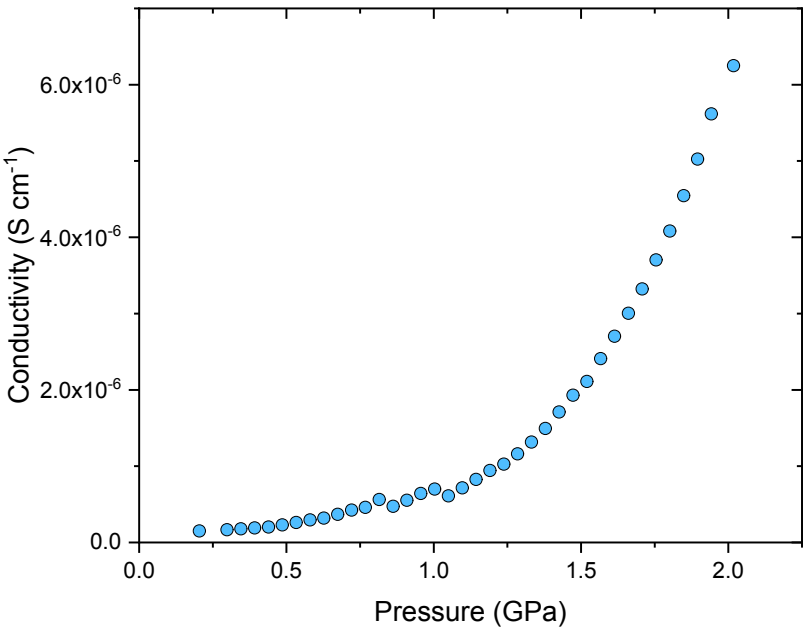

Figure S7: *Pressure dependent conductivity of a compressed pellet of* ***2.***

(TD-)DFT calculations

Optimisations with the B3LYP functional

Table S1: *MO energies and % MO contributions from key groups for* ***[trans-1]***$^-$ *optimised with B3LYP functional. 'Ditholene core' refers to the C, S and H atoms included on the chelate ring. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

Orbital No.		Energy (eV)	Ditholene core	'Rest of ligand'	Au
118	L+5	1.63	61	38	1
117	L+4	1.41	4	95	0
116	L+3	1.4	0	100	0
115	L+2	1.16	23	77	0
114	L+1	1.15	26	73	1
113	LUMO	-0.39	73	5	22
112	HOMO	-2.28	88	9	3
111	H-1	-2.88	83	12	5
110	H-2	-3.75	82	10	8
109	H-3	-3.92	84	15	1
108	H-4	-4.12	87	6	7
107	H-5	-4.48	80	2	18

Table S2: *MO energies and % MO contributions from key groups for* ***[cis-1]***$^-$ *optimised with B3LYP functional. 'Ditholene core' refers to the C, S and H atoms included on the chelate ring. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

Orbital No.		Energy (eV)	Ditholene core	'Rest of ligand'	Au
118	L+5	2.2	0	99	1
117	L+4	1.82	2	97	1
116	L+3	1.81	2	98	0
115	L+2	1.56	25	75	0
114	L+1	1.51	25	74	1
113	LUMO	-0.23	76	3	21
112	HOMO	-2.07	90	7	3
111	H-1	-2.66	83	11	6
110	H-2	-3.57	85	7	8
109	H-3	-3.7	84	15	1
108	H-4	-3.95	88	3	8
107	H-5	-4.28	80	8	12

Table S3: *MO energies and % MO contributions from key groups for trans-**2** optimised with the B3LYP functional. 'Ditholene core' refers to the C, S and H atoms included on the chelate ring. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

Orbital No.		Energy (eV)	Ditholene core	'Rest of ligand'	Au		Energy (eV)	Ditholene core	'Rest of ligand'	Au
117	L+4 (α)	-1.2	3	96	0	L+5 (β)	-1.18	3	96	0
116	L+3 (α)	-1.2	5	95	1	L+4 (β)	-1.19	5	95	1
115	L+2 (α)	-1.74	38	62	0	L+3 (β)	-1.61	33	67	0
114	L+1 (α)	-1.79	42	58	1	L+2 (β)	-1.66	37	62	1
113	LUMO (α)	-4.06	71	7	23	L+1 (β)	-3.99	71	7	22
112	HOMO (α)	-6.02	85	12	3	LUMO (β)	-4.78	88	9	3
111	H-1 (α)	-6.48	69	28	4	HOMO (β)	-5.94	78	17	6
110	H-2 (α)	-7.28	32	65	4	H-1 (β)	-7.09	46	49	4
109	H-3 (α)	-7.42	39	58	3	H-2 (β)	-7.2	47	51	2
108	H-4 (α)	-7.76	22	76	2	H-3 (β)	-7.64	58	37	5

Table S4: *MO energies and % MO contributions from key groups for cis-**2** optimised with the B3LYP functional. 'Ditholene core' refers to the C, S and H atoms included on the chelate ring. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

Orbital No.		Energy (eV)	Ditholene core	'Rest of ligand'	Au		Energy (eV)	Ditholene core	'Rest of ligand'	Au
117	L+4 (α)	-0.76	2	97	1	L+5 (β)	-0.75	2	97	1
116	L+3 (α)	-0.77	3	96	1	L+4 (β)	-0.76	3	96	1
115	L+2 (α)	-1.35	41	59	0	L+3 (β)	-1.19	35	65	0
114	L+1 (α)	-1.43	42	57	1	L+2 (β)	-1.29	36	63	1
113	LUMO (α)	-3.8	76	3	21	L+1 (β)	-3.73	76	3	21
112	HOMO (α)	-5.68	86	11	3	LUMO (β)	-4.43	90	8	3
111	H-1 (α)	-6.19	68	28	4	HOMO (β)	-5.64	76	17	6
110	H-2 (α)	-7.03	21	77	2	H-1 (β)	-6.9	26	73	1
109	H-3 (α)	-7.19	40	57	4	H-2 (β)	-7	40	56	4
108	H-4 (α)	-7.52	9	90	1	H-3 (β)	-7.49	29	68	3

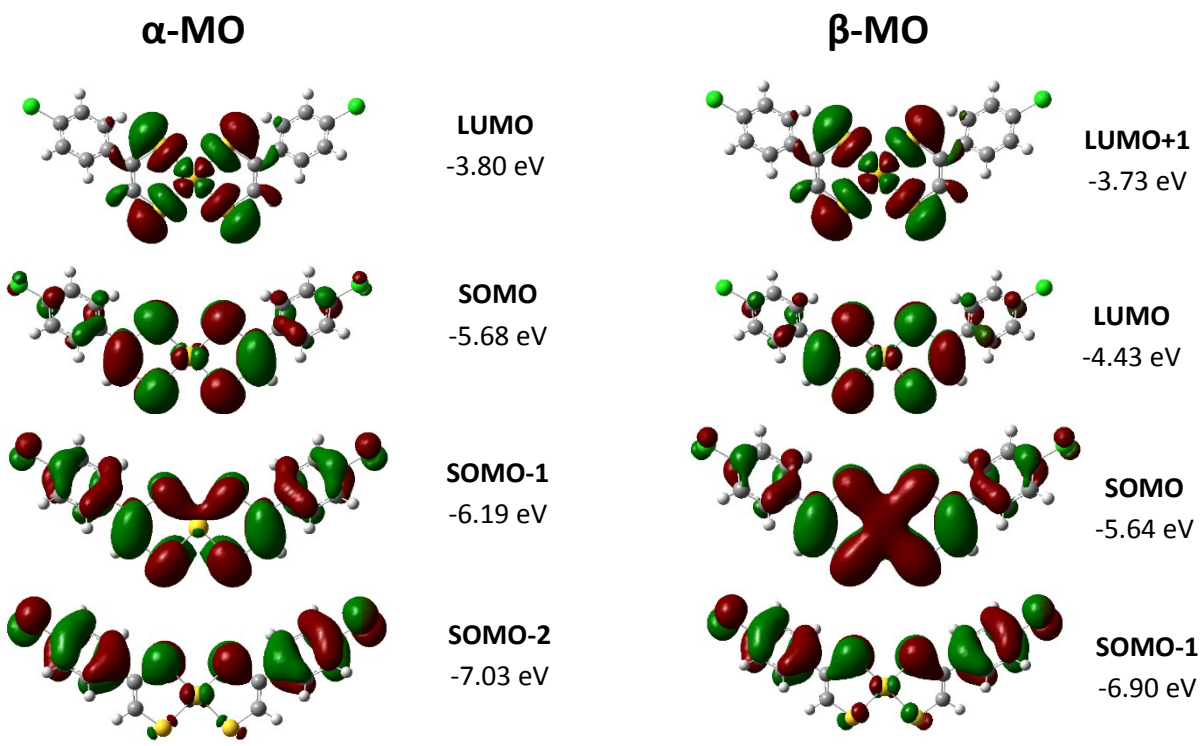

Figure S8: *Frontier molecular orbitals of cis-**2** (B3LYP functional, isocontour set at 0.02000).*

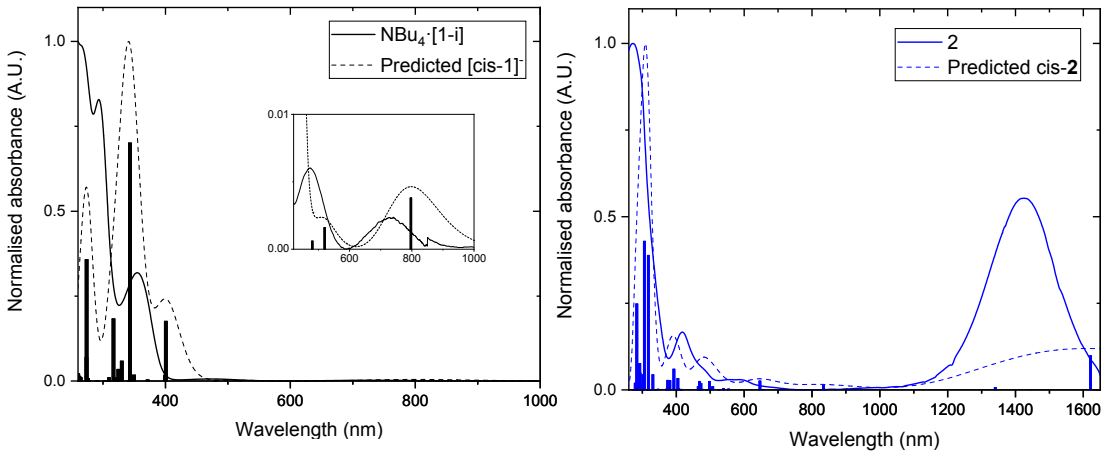

Figure S9:: *Simulated and experimental UV/Vis/NIR spectra of LEFT: **NBu$_4$·[1-i]** and **[cis-1]$^-$** and RIGHT: **2** and cis-**2** based on TD-DFT calculations. The predicted spectrum is shown in dashed lines, and the experimental spectra in solid lines.*

Table S5: *Energy and composition of TD-DFT calculated singlet-singlet transitions of* ***[trans-1]***$^{-}$ *optimised with the B3LYP functional*

No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	1280.564	0	HOMO->LUMO (100%)	
2	771.9101	0.0041	H-1->LUMO (99%)	
3	515.3768	0	H-2->LUMO (99%)	
4	471.172	0.0026	H-3->LUMO (96%)	H-4->LUMO (2%)
5	424.2257	0.1793	HOMO->L+2 (88%)	H-5->LUMO (9%), H-1->L+1 (2%)
6	418.1451	0	HOMO->L+1 (97%)	
7	394.8415	0.0164	HOMO->L+3 (94%)	H-1->L+4 (5%)
8	394.3392	0	HOMO->L+4 (93%)	H-1->L+3 (5%)
9	356.7069	0.0195	H-5->LUMO (26%), H-1->L+1 (55%)	HOMO->L+2 (8%), HOMO->L+5 (9%)
10	354.4026	0	HOMO->L+6 (92%)	H-1->L+5 (3%), HOMO->L+7 (2%)
11	353.4831	0.0424	HOMO->L+5 (84%)	H-5->LUMO (3%), H-1->L+1 (6%), H-1->L+6 (3%)
12	346.6344	0.8552	H-4->LUMO (74%)	H-7->LUMO (3%), H-5->LUMO (7%), H-3->LUMO (3%), H-1->L+1 (6%)
13	344.5537	0	H-6->LUMO (22%), H-1->L+2 (72%)	
14	341.526	0	H-6->LUMO (73%), H-1->L+2 (21%)	
15	325.1277	0.0052	H-1->L+4 (85%)	H-7->LUMO (3%), H-5->LUMO (3%), HOMO->L+3 (5%)
16	325.0936	0	H-1->L+3 (92%)	HOMO->L+4 (5%)
17	324.0993	0	HOMO->L+7 (86%)	H-1->L+8 (2%), HOMO->L+6 (3%), HOMO->L+10 (3%), HOMO->L+11 (3%)
18	323.0185	0.0187	HOMO->L+8 (83%)	H-5->LUMO (4%), H-1->L+1 (2%), H-1->L+7 (3%)
19	321.2192	0.1015	H-7->LUMO (40%), H-5->LUMO (26%), H-1->L+1 (16%)	HOMO->L+8 (5%), HOMO->L+17 (2%)
20	320.3064	0.048	H-7->LUMO (50%), H-5->LUMO (12%), H-4->LUMO (10%)	H-1->L+1 (8%), H-1->L+4 (8%), HOMO->L+8 (4%)
21	309.8675	0	H-10->LUMO (81%)	H-8->LUMO (4%), H-1->L+2 (3%)
22	300.5167	0.0008	H-1->L+6 (91%)	HOMO->L+5 (3%)
23	300.473	0	H-1->L+5 (90%)	HOMO->L+6 (3%), HOMO->L+11 (3%)
24	296.4427	0	HOMO->L+10 (37%), HOMO->L+11 (45%)	H-1->L+5 (3%), HOMO->L+7 (7%), HOMO->L+16 (2%)
25	291.2752	0.0043	HOMO->L+9 (84%)	H-1->L+10 (4%), HOMO->L+8 (2%), HOMO->L+12 (3%)
26	287.5996	0	HOMO->L+10 (44%), HOMO->L+11 (34%)	H-8->LUMO (2%), H-2->L+1 (4%), H-1->L+9 (3%), HOMO->L+13 (2%), HOMO->L+15 (3%), HOMO->L+16 (2%)
27	286.3376	0.1925	H-9->LUMO (41%), H-3->L+1 (12%), H-2->L+2 (41%)	
28	286.0338	0	H-8->LUMO (54%), H-2->L+1 (26%)	H-10->LUMO (6%), H-3->L+2 (5%), HOMO->L+10 (4%)

29	283.5156	0.2234	H-9->LUMO (58%), H-2->L+2 (30%)	H-3->L+1 (7%)
30	283.0948	0	H-8->LUMO (38%), H-2->L+1 (50%)	H-3->L+2 (7%)
31	279.401	0	H-1->L+8 (10%), HOMO->L+13 (63%), HOMO->L+15 (16%)	HOMO->L+19 (3%)
32	278.6851	0.01	H-1->L+7 (65%), HOMO->L+12 (18%)	H-1->L+11 (5%), HOMO->L+8 (3%), HOMO->L+9 (6%)
33	277.2455	0	H-1->L+8 (81%)	HOMO->L+10 (3%), HOMO->L+13 (5%), HOMO->L+15 (4%)
34	275.4959	0.0018	H-1->L+7 (25%), HOMO->L+12 (65%)	
35	271.8952	0.0047	H-3->L+4 (22%), H-2->L+3 (67%)	HOMO->L+12 (3%)
36	271.8058	0	H-3->L+3 (24%), H-2->L+4 (67%)	H-3->L+2 (2%)
37	269.3727	0.0417	H-3->L+1 (73%), H-2->L+2 (19%)	H-4->L+1 (4%)
38	268.4687	0	H-3->L+2 (77%), H-2->L+1 (14%)	H-4->L+2 (2%)
39	266.0548	0	H-14->LUMO (20%), H-12->LUMO (13%), H-11->LUMO (58%)	H-4->L+2 (4%)
40	264.9405	0.0046	H-4->L+1 (93%)	
41	263.6167	0	H-4->L+2 (90%)	H-3->L+2 (3%)
42	262.2339	0.0064	HOMO->L+14 (83%)	H-1->L+11 (4%), HOMO->L+21 (3%)
43	262.1009	0	HOMO->L+13 (19%), HOMO->L+15 (47%), HOMO->L+16 (10%)	H-1->L+9 (2%), H-1->L+12 (3%), HOMO->L+11 (4%), HOMO->L+19 (4%)
44	258.5158	0	H-14->LUMO (16%), H-12->LUMO (45%), H-11->LUMO (34%)	
45	255.9647	0.0158	H-1->L+10 (38%), H-1->L+11 (38%)	H-2->L+5 (3%), H-1->L+7 (2%), H-1->L+13 (2%), H-1->L+16 (2%), HOMO->L+12 (5%), HOMO->L+14 (2%)
46	253.7176	0	H-1->L+9 (21%), HOMO->L+15 (15%), HOMO->L+16 (46%)	H-1->L+12 (3%), HOMO->L+13 (3%)
47	253.1633	0	H-3->L+3 (12%), H-3->L+5 (17%), H-2->L+6 (53%)	H-2->L+4 (6%)
48	252.869	0	H-3->L+3 (57%), H-2->L+4 (20%), H-2->L+6 (12%)	H-3->L+5 (3%)
49	252.8174	0.0049	H-3->L+4 (68%), H-2->L+3 (25%)	
50	252.7092	0.0094	H-3->L+6 (20%), H-2->L+5 (63%)	H-6->L+5 (2%), H-1->L+10 (6%)

Table S6: *Energy and composition of TD-DFT calculated singlet-singlet transitions of* ***[cis-1]***$^{-}$ *optimised with the B3LYP functional*

No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	1345.315	0.0001	HOMO->LUMO (100%)	
2	797.121	0.0038	H-1->LUMO (99%)	
3	519.8717	0.0016	H-2->LUMO (99%)	
4	480.1495	0.0006	H-3->LUMO (97%)	
5	400.6858	0.1759	HOMO->L+1 (97%)	
6	399.3564	0.0169	H-5->LUMO (16%), HOMO->L+2 (80%)	H-1->L+1 (2%)
7	372.1908	0.0017	HOMO->L+3 (94%)	H-1->L+4 (5%)
8	371.4771	0.0033	HOMO->L+4 (93%)	H-1->L+3 (6%)
9	349.734	0.0175	H-6->LUMO (23%), H-5->LUMO (38%), H-1->L+1 (23%), HOMO->L+2 (12%)	
10	343.0569	0.7011	H-7->LUMO (14%), H-4->LUMO (70%)	H-1->L+2 (9%), HOMO->L+9 (2%)
11	341.3098	0.0011	H-6->LUMO (67%), H-1->L+1 (22%)	H-5->LUMO (4%), HOMO->L+2 (4%)
12	330.0876	0.0586	H-7->LUMO (48%), H-1->L+2 (46%)	
13	324.5914	0.0342	H-10->LUMO (11%), H-7->LUMO (33%), H-4->LUMO (17%), H-1->L+2 (26%)	HOMO->L+5 (7%)
14	322.0536	0.0083	HOMO->L+5 (86%)	H-1->L+2 (6%), H-1->L+6 (3%)
15	321.3191	0.0084	HOMO->L+6 (88%)	H-5->LUMO (3%), H-1->L+1 (3%), H-1->L+5 (4%)
16	316.7225	0.1831	H-5->LUMO (29%), H-1->L+1 (46%)	H-6->LUMO (4%), HOMO->L+6 (6%), HOMO->L+11 (2%)
17	309.4267	0.0096	H-1->L+3 (91%)	HOMO->L+4 (6%)
18	309.1567	0.0003	H-1->L+4 (91%)	HOMO->L+3 (6%)
19	303.2214	0.001	H-10->LUMO (73%), H-1->L+2 (10%)	H-14->LUMO (2%), HOMO->L+8 (2%)
20	291.0495	0.0013	H-9->LUMO (22%), H-8->LUMO (76%)	
21	290.6947	0	H-9->LUMO (73%), H-8->LUMO (21%)	H-10->LUMO (4%)
22	277.7424	0.0009	H-1->L+5 (91%)	HOMO->L+6 (5%)
23	277.6491	0.0016	H-1->L+6 (46%), HOMO->L+7 (49%)	
24	276.1648	0.0072	H-1->L+6 (43%), HOMO->L+7 (46%)	H-2->L+2 (2%), HOMO->L+5 (4%)
25	273.6958	0.3576	H-3->L+1 (30%), H-2->L+2 (58%)	H-1->L+6 (4%)
26	273.4966	0.0697	H-3->L+2 (11%), H-2->L+1 (80%)	H-1->L+5 (2%)
27	264.2403	0.0095	H-11->LUMO (94%)	
28	262.1729	0.0141	HOMO->L+8 (83%)	HOMO->L+9 (3%), HOMO->L+13 (6%)
29	260.3343	0.0212	H-3->L+1 (62%), H-2->L+2 (35%)	

30	260.1103	0.0026	H-3->L+4 (27%), H-2->L+3 (59%)	H-4->L+1 (3%), H-3->L+2 (2%)
31	259.8705	0.008	H-3->L+3 (31%), H-2->L+4 (62%)	
32	258.0531	0.0209	H-3->L+2 (79%), H-2->L+1 (11%)	H-4->L+1 (2%), H-2->L+3 (3%)
33	256.6376	0.0001	H-12->LUMO (88%)	H-21->LUMO (2%), H-18->LUMO (3%), H-6->LUMO (2%)
34	256.2981	0.002	H-14->LUMO (67%), H-13->LUMO (17%)	H-17->LUMO (7%)
35	255.4111	0.0084	H-4->L+1 (92%)	H-3->L+2 (3%)
36	252.3594	0.0014	H-4->L+2 (93%)	HOMO->L+9 (2%)
37	248.7794	0.0008	HOMO->L+9 (29%), HOMO->L+10 (62%)	HOMO->L+13 (3%)
38	244.0009	0.0592	HOMO->L+9 (42%), HOMO->L+10 (26%)	H-17->LUMO (5%), H-5->L+1 (6%), H-4->LUMO (2%), H-3->L+3 (7%), H-2->L+4 (3%)
39	243.785	0.0164	H-3->L+4 (26%), H-2->L+3 (14%), H-1->L+7 (37%)	H-1->L+8 (4%), HOMO->L+11 (7%), HOMO->L+12 (6%), HOMO->L+14 (3%)
40	243.603	0.0085	H-3->L+3 (54%), H-2->L+4 (32%)	HOMO->L+9 (6%)
41	243.4547	0.0172	H-3->L+4 (36%), H-2->L+3 (19%), H-1->L+7 (29%)	HOMO->L+11 (2%), HOMO->L+12 (5%)
42	240.2655	0.0071	H-5->L+1 (84%)	H-6->L+1 (3%), HOMO->L+9 (3%)
43	238.2113	0.004	H-14->LUMO (11%), H-13->LUMO (75%)	H-19->LUMO (3%), H-5->L+1 (2%)
44	237.7773	0.001	H-5->L+2 (87%)	H-6->L+2 (4%)
45	236.3855	0.0004	H-4->L+3 (11%), H-3->L+6 (25%), H-2->L+5 (45%)	H-7->L+5 (3%), H-6->L+6 (3%), H-1->L+7 (2%), H-1->L+8 (2%), HOMO->L+12 (3%)
46	236.2639	0.0023	H-4->L+3 (69%), HOMO->L+12 (10%)	H-5->L+4 (3%), H-2->L+5 (3%), H-1->L+8 (4%)
47	236.1334	0.0038	H-3->L+5 (35%), H-2->L+6 (51%)	H-7->L+6 (4%), H-6->L+5 (4%)
48	235.9267	0.0042	H-1->L+7 (12%), HOMO->L+11 (22%), HOMO->L+12 (41%)	H-4->L+3 (7%), H-3->L+6 (4%), H-2->L+5 (7%), H-1->L+8 (2%)
49	235.689	0.0025	H-4->L+4 (83%)	H-5->L+3 (4%)
50	234.0428	0.0546	H-1->L+7 (14%), H-1->L+8 (46%)	H-5->L+2 (3%), H-1->L+13 (6%), HOMO->L+11 (9%), HOMO->L+14 (8%)

Table S7: *Energy and composition of TD-DFT calculated doublet-doublet transitions of trans-**2** optimised with the B3LYP functional*

No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	1789.352	0.0949	HOMO(B)->LUMO(B) (97%)	
2	1309.646	0	HOMO(A)->LUMO(A) (98%)	
3	1282.816	0.0043	HOMO(B)->L+1(B) (96%)	H-1(A)->LUMO(A) (2%)
4	814.4531	0.0112	H-1(A)->LUMO(A) (91%)	H-3(A)->LUMO(A) (3%), HOMO(B)->L+1(B) (3%)
5	747.7486	0	H-1(B)->LUMO(B) (92%)	H-3(B)->LUMO(B) (6%)
6	719.625	0.0222	H-2(B)->LUMO(B) (90%)	H-9(A)->LUMO(A) (2%), H-7(B)->LUMO(B) (2%), H-5(B)->LUMO(B) (2%)
7	620.9144	0.0047	H-7(B)->LUMO(B) (19%), H-4(B)->LUMO(B) (77%)	H-1(A)->LUMO(A) (2%)
8	593.1974	0	H-2(A)->LUMO(A) (10%), H-3(B)->L+1(B) (15%), H-1(B)->L+1(B) (68%)	H-6(A)->LUMO(A) (6%)
9	561.5226	0	H-3(B)->LUMO(B) (90%)	H-1(B)->LUMO(B) (6%)
10	559.546	0.0016	H-3(A)->LUMO(A) (15%), H-2(B)->L+1(B) (54%)	H-8(A)->LUMO(A) (5%), H-7(A)->LUMO(A) (3%), H-4(A)->LUMO(A) (3%), H-8(B)->LUMO(B) (3%), H-7(B)->L+1(B) (8%), H-5(B)->L+1(B) (5%)
11	543.3852	0.0242	H-8(B)->LUMO(B) (27%), H-7(B)->LUMO(B) (25%), H-5(B)->LUMO(B) (24%)	H-7(A)->LUMO(A) (3%), H-4(A)->LUMO(A) (2%), H-7(B)->L+1(B) (3%), H-4(B)->LUMO(B) (6%), H-4(B)->L+1(B) (4%), H-2(B)->LUMO(B) (3%)
12	534.1153	0.0178	H-7(A)->LUMO(A) (19%), H-4(A)->LUMO(A) (10%), H-5(B)->LUMO(B) (12%), H-4(B)->L+1(B) (32%), H-2(B)->L+1(B) (10%)	H-7(B)->LUMO(B) (4%), H-7(B)->L+1(B) (8%)
13	517.2042	0.0134	H-8(B)->LUMO(B) (51%), H-5(B)->LUMO(B) (28%)	H-3(A)->LUMO(A) (3%), H-4(B)->L+1(B) (5%), H-2(B)->LUMO(B) (2%), H-2(B)->L+1(B) (8%)
14	508.9663	0	H-6(A)->LUMO(A) (16%), H-2(A)->LUMO(A) (67%), H-1(B)->L+1(B) (14%)	
15	495.6394	0	H-6(B)->LUMO(B) (99%)	
16	489.3212	0.0006	H-7(B)->LUMO(B) (43%), H-5(B)->LUMO(B) (30%), H-4(B)->LUMO(B) (10%)	H-3(A)->LUMO(A) (3%), H-8(B)->LUMO(B) (9%)
17	471.8713	0.0297	H-9(A)->LUMO(A) (16%), H-3(A)->LUMO(A) (34%), H-8(B)->L+1(B) (21%)	H-7(A)->LUMO(A) (4%), H-8(B)->LUMO(B) (6%), H-7(B)->LUMO(B) (4%), H-7(B)->L+1(B) (4%), H-2(B)->L+1(B) (4%)
18	458.9627	0.023	H-9(A)->LUMO(A) (21%), H-8(A)->LUMO(A) (12%), H-3(A)->LUMO(A) (26%), H-8(B)->L+1(B) (22%)	H-7(A)->LUMO(A) (2%), H-4(A)->LUMO(A) (2%), H-8(B)->LUMO(B) (2%), H-7(B)->L+1(B) (2%), H-4(B)->L+1(B) (2%), H-2(B)->L+1(B) (5%)
19	437.6582	0	H-6(A)->LUMO(A) (13%), H-3(B)->L+1(B) (60%), H-1(B)->L+1(B) (14%)	H-2(A)->LUMO(A) (5%), H-11(B)->L+1(B) (2%)
20	419.5317	0.0017	H-1(A)->L+1(A) (15%), HOMO(A)->L+2(A) (24%), HOMO(B)->L+2(B) (24%)	H-9(A)->LUMO(A) (3%), H-4(A)->LUMO(A) (2%), H-7(B)->L+1(B) (2%), H-5(B)->L+1(B) (9%), H-4(B)->L+1(B) (4%), H-2(B)->L+1(B) (2%), H-1(B)->L+3(B) (2%)
21	413.0741	0	H-1(A)->L+2(A) (16%), HOMO(A)->L+1(A) (32%), HOMO(B)->L+3(B) (30%)	H-3(B)->L+1(B) (4%), H-1(B)->L+2(B) (2%)
22	412.5518	0	H-6(A)->LUMO(A) (61%), H-2(A)->LUMO(A) (15%), H-3(B)->L+1(B) (17%)	H-5(A)->LUMO(A) (2%)
23	407.2934	0.0385	H-5(B)->L+1(B) (27%), H-4(B)->L+1(B) (14%), H-2(B)->L+1(B)	H-9(A)->LUMO(A) (2%), H-8(A)->LUMO(A) (3%), H-4(A)->LUMO(A) (2%), H-1(A)-

			(12%)	>L+1(A) (4%), HOMO(A)->L+2(A) (7%), H-8(B)->L+1(B) (6%), H-7(B)->L+1(B) (9%), HOMO(B)->L+2(B) (8%)
24	389.1531	0.0509	H-8(A)->LUMO(A) (61%), H-7(A)->LUMO(A) (12%), H-3(A)->LUMO(A) (10%)	H-9(A)->LUMO(A) (2%), H-4(B)->L+1(B) (8%)
25	380.1913	0.0001	H-5(A)->LUMO(A) (85%)	H-6(A)->LUMO(A) (2%), H-6(B)->L+1(B) (9%)
26	379.4002	0.0338	H-7(A)->LUMO(A) (20%), H-4(A)->LUMO(A) (69%)	H-8(A)->LUMO(A) (4%)
27	373.3676	0.025	H-7(B)->L+1(B) (23%), H-5(B)->L+1(B) (52%), H-4(B)->L+1(B) (18%)	
28	372.6046	0.0001	H-5(A)->LUMO(A) (10%), H-6(B)->L+1(B) (86%)	H-12(B)->LUMO(B) (2%)
29	369.4844	0	H-12(B)->LUMO(B) (90%)	H-11(B)->LUMO(B) (4%), H-9(B)->LUMO(B) (2%), H-6(B)->L+1(B) (2%)
30	347.1294	0.1269	H-9(A)->LUMO(A) (23%), HOMO(A)->L+2(A) (17%), H-8(B)->L+1(B) (22%), HOMO(B)->L+2(B) (27%)	
31	340.7376	0	H-11(B)->LUMO(B) (74%), H-9(B)->LUMO(B) (11%)	H-15(B)->LUMO(B) (5%), H-12(B)->LUMO(B) (5%)
32	338.8843	0	H-13(A)->LUMO(A) (14%), H-12(A)->LUMO(A) (39%), H-12(B)->L+1(B) (39%)	
33	333.7214	0	HOMO(A)->L+1(A) (31%)	H-5(A)->L+3(A) (3%), H-4(A)->L+4(A) (2%), H-3(A)->L+2(A) (7%), H-2(A)->L+1(A) (9%), H-1(A)->L+2(A) (2%), H-12(B)->L+1(B) (4%), H-6(B)->L+4(B) (4%), H-5(B)->L+5(B) (2%), H-2(B)->L+3(B) (6%), H-1(B)->L+2(B) (6%), HOMO(B)->L+3(B) (4%), HOMO(B)->L+12(B) (2%)
34	330.9246	0.0236	H-10(B)->LUMO(B) (93%)	H-13(B)->LUMO(B) (3%)
35	330.2898	0	H-11(B)->LUMO(B) (13%), H-9(B)->LUMO(B) (83%)	H-14(B)->LUMO(B) (3%)
36	329.8856	0.022	H-2(A)->L+2(A) (10%), H-2(B)->L+2(B) (10%), HOMO(B)->L+2(B) (11%)	H-5(A)->L+4(A) (6%), H-4(A)->L+3(A) (4%), H-3(A)->L+1(A) (8%), H-1(A)->L+1(A) (3%), HOMO(A)->L+2(A) (2%), HOMO(A)->L+10(A) (2%), H-13(B)->LUMO(B) (2%), H-6(B)->L+5(B) (5%), H-5(B)->L+4(B) (3%), H-3(B)->L+3(B) (2%), H-1(B)->L+3(B) (9%)
37	326.0425	0.5051	H-7(A)->LUMO(A) (14%), H-13(B)->LUMO(B) (35%), H-7(B)->L+1(B) (17%)	H-9(A)->LUMO(A) (2%), H-8(A)->LUMO(A) (4%), H-4(A)->LUMO(A) (3%), H-16(B)->LUMO(B) (4%), H-10(B)->LUMO(B) (6%), H-8(B)->L+1(B) (2%), H-4(B)->L+1(B) (4%), HOMO(B)->LUMO(B) (2%)
38	322.3048	0	HOMO(A)->L+1(A) (15%), HOMO(B)->L+3(B) (45%)	H-12(A)->LUMO(A) (2%), H-5(A)->L+3(A) (2%), H-4(A)->L+4(A) (2%), H-3(A)->L+2(A) (2%), H-2(A)->L+1(A) (2%), H-12(B)->L+1(B) (4%), H-6(B)->L+4(B) (2%), H-2(B)->L+3(B) (5%), H-1(B)->L+2(B) (4%)
39	319.9757	0	H-14(B)->LUMO(B) (93%)	H-15(B)->LUMO(B) (2%), H-9(B)->LUMO(B) (2%)
40	314.7286	0.3239	HOMO(A)->L+2(A) (14%), H-13(B)->LUMO(B) (41%)	H-9(A)->LUMO(A) (5%), H-7(A)->LUMO(A) (7%), H-4(A)->LUMO(A) (2%), H-8(B)->L+1(B) (5%), H-7(B)->L+1(B) (7%), H-4(B)->L+1(B) (2%), HOMO(B)->L+2(B) (4%)
41	309.5194	0.0001	H-1(A)->L+4(A) (12%), HOMO(A)->L+3(A) (33%), HOMO(B)->L+5(B) (35%)	H-2(A)->L+3(A) (2%), H-2(B)->L+5(B) (2%), H-1(B)->L+4(B) (3%), HOMO(B)->L+4(B) (2%)
42	309.4499	0.0083	H-1(A)->L+3(A) (12%), HOMO(A)->L+4(A) (27%), HOMO(B)->L+4(B) (41%)	H-2(A)->L+4(A) (2%), H-2(B)->L+4(B) (2%), H-1(B)->L+5(B) (3%), HOMO(B)->L+5(B) (2%)
43	305.3723	0.0864	H-1(A)->L+1(A) (23%), HOMO(A)->L+2(A) (31%)	H-9(A)->LUMO(A) (5%), H-8(A)->LUMO(A) (2%), H-7(A)->LUMO(A) (5%), H-13(B)->LUMO(B) (9%), H-8(B)->L+1(B) (5%), H-7(B)->L+1(B) (5%), HOMO(B)->L+2(B) (2%)
44	302.2088	0	H-12(A)->LUMO(A) (20%), H-1(A)->L+2(A) (16%), HOMO(A)->L+1(A) (13%), H-12(B)->L+1(B) (30%)	H-13(A)->LUMO(A) (6%), HOMO(A)->L+7(A) (2%)

45	293.3704	0	HOMO(A)->L+3(A) (39%), HOMO(B)->L+5(B) (44%)	H-1(A)->L+2(A) (2%), H-1(A)->L+4(A) (3%)
46	292.8576	0.0165	HOMO(A)->L+4(A) (44%), HOMO(B)->L+4(B) (42%)	H-1(A)->L+3(A) (6%)
47	292.2019	0	H-15(B)->L+1(B) (10%), H-11(B)->L+1(B) (52%)	H-16(A)->LUMO(A) (3%), H-13(A)->LUMO(A) (5%), H-12(A)->LUMO(A) (3%), H-15(B)->LUMO(B) (4%), H-12(B)->L+1(B) (6%), H-9(B)->L+1(B) (3%)
48	289.9401	0	H-18(B)->LUMO(B) (16%), H-15(B)->LUMO(B) (60%)	H-1(A)->L+2(A) (6%), H-20(B)->LUMO(B) (2%), H-11(B)->LUMO(B) (3%), H-11(B)->L+1(B) (2%)
49	289.1895	0.0083	H-1(A)->L+2(A) (41%), HOMO(B)->L+3(B) (10%)	H-13(A)->LUMO(A) (4%), H-12(A)->LUMO(A) (4%), H-1(A)->L+1(A) (2%), HOMO(A)->L+3(A) (3%), H-18(B)->LUMO(B) (2%), H-15(B)->LUMO(B) (5%), H-12(B)->L+1(B) (6%), H-11(B)->L+1(B) (5%), HOMO(B)->L+5(B) (2%), HOMO(B)->L+12(B) (2%)
50	289.0883	0.1873	H-1(A)->L+1(A) (38%), HOMO(B)->L+2(B) (15%)	H-9(A)->LUMO(A) (7%), H-8(A)->LUMO(A) (2%), H-7(A)->LUMO(A) (2%), H-1(A)->L+2(A) (2%), H-8(B)->L+1(B) (7%), H-7(B)->L+1(B) (3%), HOMO(B)->L+4(B) (2%), HOMO(B)->L+8(B) (2%), HOMO(B)->L+9(B) (5%)

Table S8: *Energy and composition of TD-DFT calculated singlet-singlet transitions of* ***cis-2*** *optimised with the B3LYP functional*

No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	1621.344	0.0985	HOMO(B)->LUMO(B) (96%)	HOMO(B)->L+1(B) (2%)
2	1442.515	0.0001	HOMO(A)->LUMO(A) (99%)	
3	1340.37	0.0066	HOMO(B)->L+1(B) (95%)	H-1(A)->LUMO(A) (2%), HOMO(B)->LUMO(B) (2%)
4	833.8435	0.0128	H-1(A)->LUMO(A) (93%)	H-3(A)->LUMO(A) (3%), HOMO(B)->L+1(B) (2%)
5	655.8969	0.0012	H-1(B)->LUMO(B) (94%)	H-6(B)->LUMO(B) (3%)
6	646.5592	0.0254	H-2(B)->LUMO(B) (93%)	H-7(B)->LUMO(B) (2%), H-5(B)->LUMO(B) (3%)
7	554.2432	0.0026	H-7(B)->LUMO(B) (23%), H-5(B)->LUMO(B) (18%), H-3(B)->LUMO(B) (54%)	
8	539.2024	0.0039	H-3(A)->LUMO(A) (13%), H-5(B)->L+1(B) (11%), H-2(B)->L+1(B) (60%)	H-7(A)->LUMO(A) (5%), H-7(B)->L+1(B) (4%), H-3(B)->LUMO(B) (2%), H-3(B)->L+1(B) (2%)
9	526.4051	0.0004	H-2(A)->LUMO(A) (17%), H-6(B)->L+1(B) (10%), H-1(B)->L+1(B) (64%)	H-9(A)->LUMO(A) (3%), H-8(B)->LUMO(B) (2%)
10	507.155	0.009	H-6(B)->LUMO(B) (79%)	H-8(A)->LUMO(A) (5%), H-2(A)->LUMO(A) (6%), H-8(B)->LUMO(B) (3%), H-1(B)->LUMO(B) (3%), H-1(B)->L+1(B) (2%)
11	501.2095	0.0024	H-7(A)->LUMO(A) (12%), H-6(A)->LUMO(A) (19%), H-7(B)->L+1(B) (21%), H-3(B)->L+1(B) (22%)	H-4(A)->LUMO(A) (7%), H-3(A)->LUMO(A) (4%), H-5(B)->LUMO(B) (2%), H-5(B)->L+1(B) (9%), H-3(B)->LUMO(B) (2%)
12	497.6087	0.0242	H-7(B)->LUMO(B) (17%), H-5(B)->LUMO(B) (68%)	H-3(B)->LUMO(B) (5%), H-2(B)->LUMO(B) (4%)
13	489.3984	0.0009	H-8(B)->LUMO(B) (43%), H-4(B)->LUMO(B) (36%)	H-2(A)->LUMO(A) (9%), H-1(B)->L+1(B) (9%)
14	476.954	0.0016	H-2(A)->LUMO(A) (19%), H-8(B)->LUMO(B) (11%), H-4(B)->LUMO(B) (58%)	H-1(B)->L+1(B) (7%)
15	472.3567	0.0185	H-6(A)->LUMO(A) (13%), H-3(A)->LUMO(A) (39%), H-7(B)->LUMO(B) (13%), H-3(B)->LUMO(B) (15%), H-2(B)->L+1(B) (11%)	H-5(B)->LUMO(B) (4%)
16	468.6076	0.0244	H-3(A)->LUMO(A) (19%), H-7(B)->LUMO(B) (44%), H-3(B)->LUMO(B) (21%)	H-6(A)->LUMO(A) (5%), H-5(B)->LUMO(B) (2%), H-2(B)->L+1(B) (4%)
17	464.6561	0.0094	H-2(A)->LUMO(A) (38%), H-8(B)->LUMO(B) (38%)	H-8(B)->L+1(B) (2%), H-6(B)->LUMO(B) (9%), H-4(B)->LUMO(B) (5%), H-1(B)->L+1(B) (4%)
18	439.6759	0.0001	H-8(A)->LUMO(A) (41%), H-8(B)->L+1(B) (43%)	H-2(A)->LUMO(A) (3%), H-6(B)->L+1(B) (9%)
19	416.1381	0.0011	H-1(A)->L+1(A) (12%), HOMO(A)->L+2(A) (21%), H-6(B)->L+1(B) (24%), HOMO(B)->L+2(B) (20%)	H-9(A)->LUMO(A) (3%), H-8(A)->LUMO(A) (2%), H-1(B)->L+1(B) (3%), H-1(B)->L+3(B) (2%)
20	414.2195	0.0006	HOMO(A)->L+1(A) (18%), H-5(B)->L+1(B) (23%), HOMO(B)->L+3(B) (14%)	H-7(A)->LUMO(A) (5%), H-6(A)->LUMO(A) (2%), H-4(A)->LUMO(A) (3%), H-3(A)->LUMO(A) (2%), H-1(A)->L+2(A) (8%), H-7(B)->L+1(B) (7%), H-2(B)->L+1(B) (7%), H-1(B)->L+2(B) (2%)
21	407.4273	0.0031	HOMO(A)->L+2(A) (11%), H-6(B)->L+1(B) (43%), H-1(B)->L+1(B) (10%), HOMO(B)->L+2(B) (13%)	H-9(A)->LUMO(A) (5%), H-1(A)->L+1(A) (6%), H-8(B)->L+1(B) (5%)
22	404.5425	0.0327	HOMO(A)->L+1(A) (20%), H-5(B)->L+1(B) (22%), H-2(B)->L+1(B) (10%), HOMO(B)->L+3(B) (15%)	H-7(A)->LUMO(A) (6%), H-3(A)->LUMO(A) (2%), H-1(A)->L+2(A) (8%), H-7(B)->L+1(B) (8%), H-3(B)->L+1(B) (2%)

23	392.8399	0.0599	H-7(A)->LUMO(A) (26%), H-6(A)->LUMO(A) (39%), H-3(A)->LUMO(A) (13%), H-5(B)->L+1(B) (11%)	H-3(B)->L+1(B) (5%), H-2(B)->L+1(B) (2%)
24	381.2318	0.0011	H-5(A)->LUMO(A) (87%)	H-8(A)->LUMO(A) (2%), H-4(B)->L+1(B) (6%)
25	380.7985	0.0269	H-4(A)->LUMO(A) (82%)	H-7(A)->LUMO(A) (9%), H-6(A)->LUMO(A) (3%), H-7(B)->L+1(B) (3%)
26	374.4954	0.0274	H-7(B)->L+1(B) (11%), H-5(B)->L+1(B) (21%), H-3(B)->L+1(B) (63%)	H-4(A)->LUMO(A) (2%)
27	374.0435	0.002	H-4(B)->L+1(B) (85%)	H-9(A)->LUMO(A) (7%), H-5(A)->LUMO(A) (6%)
28	371.4771	0.0021	H-9(A)->LUMO(A) (74%), H-6(B)->L+1(B) (10%)	H-8(A)->LUMO(A) (2%), H-5(A)->LUMO(A) (3%), H-2(A)->LUMO(A) (3%), H-4(B)->L+1(B) (4%)
29	346.2278	0.0018	H-12(B)->LUMO(B) (93%)	H-13(B)->LUMO(B) (2%), H-9(B)->LUMO(B) (4%)
30	339.4595	0.0002	H-8(A)->LUMO(A) (20%), HOMO(A)->L+2(A) (18%), H-8(B)->L+1(B) (21%), HOMO(B)->L+2(B) (21%)	H-9(A)->LUMO(A) (2%), H-3(A)->L+1(A) (3%), H-2(A)->L+2(A) (3%)
31	330.8892	0.0436	H-2(A)->L+1(A) (11%), HOMO(A)->L+1(A) (26%)	H-12(A)->LUMO(A) (2%), H-5(A)->L+3(A) (4%), H-4(A)->L+4(A) (4%), H-3(A)->L+2(A) (7%), H-1(A)->L+2(A) (2%), HOMO(A)->L+6(A) (2%), H-4(B)->L+4(B) (4%), H-3(B)->L+5(B) (3%), H-2(B)->L+3(B) (7%), H-1(B)->L+2(B) (9%), HOMO(B)->L+3(B) (4%), HOMO(B)->L+10(B) (2%)
32	325.8283	0.0001	H-2(B)->L+2(B) (11%), H-1(B)->L+3(B) (10%), HOMO(B)->L+2(B) (13%)	H-8(A)->LUMO(A) (3%), H-5(A)->L+4(A) (6%), H-4(A)->L+3(A) (5%), H-3(A)->L+1(A) (7%), H-2(A)->L+2(A) (9%), H-1(A)->L+1(A) (3%), H-1(A)->L+6(A) (2%), HOMO(A)->L+7(A) (2%), H-8(B)->L+1(B) (3%), H-4(B)->L+5(B) (5%), H-3(B)->L+4(B) (3%), HOMO(B)->L+7(B) (4%)
33	323.4398	0.0001	H-12(A)->LUMO(A) (49%), H-12(B)->L+1(B) (43%)	
34	317.493	0.3882	HOMO(A)->L+1(A) (17%), HOMO(B)->L+3(B) (44%)	H-7(A)->LUMO(A) (3%), H-5(A)->L+3(A) (2%), H-4(A)->L+4(A) (2%), H-3(A)->L+2(A) (2%), H-2(A)->L+1(A) (2%), H-1(A)->L+7(A) (2%), HOMO(A)->L+6(A) (2%), H-12(B)->L+1(B) (2%), H-7(B)->L+1(B) (5%), H-2(B)->L+3(B) (3%), H-1(B)->L+2(B) (2%)
35	317.2331	0.0001	H-11(B)->LUMO(B) (68%), H-10(B)->LUMO(B) (23%)	H-15(B)->LUMO(B) (4%)
36	312.9018	0.0004	H-9(B)->LUMO(B) (95%)	H-12(B)->LUMO(B) (3%)
37	312.3736	0	H-11(B)->LUMO(B) (21%), H-10(B)->LUMO(B) (76%)	H-14(B)->LUMO(B) (2%)
38	305.7186	0.4288	H-7(A)->LUMO(A) (17%), H-13(B)->LUMO(B) (21%), H-7(B)->L+1(B) (23%)	H-6(A)->LUMO(A) (7%), H-1(A)->L+2(A) (5%), HOMO(A)->L+1(A) (6%), H-16(B)->LUMO(B) (2%), H-3(B)->L+1(B) (2%), HOMO(B)->LUMO(B) (2%), HOMO(B)->L+3(B) (2%)
39	302.6958	0.0293	H-1(A)->L+1(A) (10%), HOMO(A)->L+2(A) (20%), HOMO(A)->L+4(A) (19%), HOMO(B)->L+4(B) (22%)	H-8(A)->LUMO(A) (4%), H-2(A)->L+4(A) (2%), H-1(A)->L+3(A) (8%), H-8(B)->L+1(B) (4%), H-1(B)->L+5(B) (3%), HOMO(B)->L+2(B) (2%)
40	302.2678	0.0008	H-1(A)->L+4(A) (13%), HOMO(A)->L+3(A) (37%), HOMO(B)->L+5(B) (33%)	H-2(A)->L+3(A) (3%), H-2(B)->L+5(B) (2%), H-1(B)->L+4(B) (4%)
41	301.6941	0.0433	H-1(A)->L+1(A) (12%), HOMO(A)->L+2(A) (24%), HOMO(A)->L+4(A) (14%), HOMO(B)->L+4(B) (16%)	H-8(A)->LUMO(A) (5%), H-1(A)->L+3(A) (5%), H-8(B)->L+1(B) (5%), H-1(B)->L+5(B) (2%), HOMO(B)->L+2(B) (4%)
42	294.9898	0	H-14(B)->LUMO(B) (91%)	H-15(B)->LUMO(B) (6%)
43	293.1346	0.0485	H-12(A)->LUMO(A) (16%), H-1(A)->L+2(A) (10%), H-13(B)->LUMO(B) (26%), H-12(B)->L+1(B) (19%)	H-7(A)->LUMO(A) (5%), H-6(A)->LUMO(A) (2%), HOMO(A)->L+1(A) (3%), H-7(B)->L+1(B) (6%)

44	291.9817	0.076	H-1(A)->L+2(A) (23%), H-13(B)->LUMO(B) (39%)	H-12(A)->LUMO(A) (6%), H-7(A)->LUMO(A) (2%), HOMO(A)->L+1(A) (6%), HOMO(A)->L+6(A) (2%), H-12(B)->L+1(B) (6%), H-7(B)->L+1(B) (2%)
45	285.4017	0.0077	HOMO(A)->L+4(A) (40%), HOMO(B)->L+4(B) (46%)	H-1(A)->L+1(A) (3%), H-1(A)->L+3(A) (4%)
46	285.382	0.0011	HOMO(A)->L+3(A) (41%), HOMO(B)->L+5(B) (51%)	H-1(A)->L+4(A) (2%)
47	283.4702	0.2482	H-1(A)->L+1(A) (43%), HOMO(B)->L+2(B) (19%)	H-8(A)->LUMO(A) (8%), HOMO(A)->L+4(A) (3%), H-8(B)->L+1(B) (8%), H-6(B)->LUMO(B) (2%), HOMO(B)->L+4(B) (3%), HOMO(B)->L+7(B) (6%)
48	280.6787	0.0004	H-11(B)->L+1(B) (67%)	H-16(A)->LUMO(A) (2%), H-13(A)->LUMO(A) (8%), H-15(B)->L+1(B) (8%), H-10(B)->L+1(B) (2%)
49	278.8041	0.0192	H-12(A)->LUMO(A) (16%), H-1(A)->L+2(A) (33%), H-12(B)->L+1(B) (18%), HOMO(B)->L+3(B) (13%)	H-7(A)->LUMO(A) (2%), H-7(B)->L+1(B) (3%), HOMO(B)->L+10(B) (2%)
50	272.8706	0.0004	H-5(A)->L+4(A) (13%), H-4(A)->L+3(A) (13%), H-4(B)->L+5(B) (14%), H-3(B)->L+4(B) (10%)	H-3(A)->L+1(A) (5%), H-2(A)->L+2(A) (5%), HOMO(A)->L+7(A) (2%), H-15(B)->LUMO(B) (8%), H-11(B)->L+1(B) (3%), H-5(B)->L+4(B) (3%), H-2(B)->L+2(B) (6%), H-1(B)->L+3(B) (5%), HOMO(B)->L+7(B) (3%)

Optimisations with the BHLYP35 functional

Table S9: *MO energies and % MO contributions from key groups for* ***[trans-1]***$^-$ *optimised with BHLYP35 functional. 'Ditholene core' refers to the C, S and H atoms included on the chelate ring. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

Orbital No.		Energy (eV)	Ditholene core	'Rest of ligand'	Au
118	L+5	3.1	0	98	2
117	L+4	2.55	2	97	1
116	L+3	2.52	1	97	1
115	L+2	2.24	23	77	0
114	L+1	2.22	25	74	1
113	LUMO	0.35	76	3	21
112	HOMO	-2.49	90	7	3
111	H-1	-3.11	83	12	5
110	H-2	-4.09	82	11	7
109	H-3	-4.24	85	13	2
108	H-4	-4.34	91	1	7
107	H-5	-4.72	83	4	13

Table S10: *MO energies and % MO contributions from key groups for* ***[cis-1]***$^-$ *optimised with BHLYP35 functional. 'Ditholene core' refers to the C, S and H atoms included on the chelate ring. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

Orbital No.		Energy (eV)	Ditholene core	'Rest of ligand'	Au
118	L+5	3.1	1	98	1
117	L+4	2.54	2	97	1
116	L+3	2.53	2	98	0
115	L+2	2.27	24	76	0
114	L+1	2.2	24	75	1
113	LUMO	0.36	76	3	21
112	HOMO	-2.48	91	7	3
111	H-1	-3.11	83	12	5
110	H-2	-4.11	85	7	7
109	H-3	-4.22	82	17	1
108	H-4	-4.33	89	3	9
107	H-5	-4.71	81	6	12

Table S11: *MO energies and % MO contributions from key groups for trans-**2** optimised with the BHLYP35 functional. 'Ditholene core' refers to the C, S and H atoms included on the chelate ring. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

Orbital No.		Energy (eV)	Ditholene core	'Rest of ligand'	Au		Energy (eV)	Ditholene core	'Rest of ligand'	Au
117	L+4 (α)	0.09	3	94	3	L+5 (β)	0.11	3	95	2
116	L+3 (α)	-0.16	2	96	1	L+4 (β)	-0.13	2	96	2
115	L+2 (α)	-0.5	38	62	1	L+3 (β)	-0.39	33	66	1
114	L+1 (α)	-0.93	46	53	1	L+2 (β)	-0.65	36	63	1
113	LUMO (α)	-3.27	76	3	22	L+1 (β)	-3.19	76	3	22
112	HOMO (α)	-6.10	84	13	3	LUMO (β)	-4.10	90	7	3
111	H-1 (α)	-6.71	65	32	3	HOMO (β)	-5.87	77	16	7
110	H-2 (α)	-7.46	27	70	3	H-1 (β)	-7.3	30	67	3
109	H-3 (α)	-7.77	37	60	3	H-2 (β)	-7.5	34	64	3
108	H-4 (α)	-7.89	3	96	0	H-3 (β)	-7.87	6	94	1

Table S12: *MO energies and % MO contributions from key groups for cis-**2** optimised with the BHLYP35 functional. 'Ditholene core' refers to the C, S and H atoms included on the chelate ring. 'Rest of ligand' includes any other atoms that are not part of the chelate.*

Orbital No.		Energy (eV)	Ditholene core	'Rest of ligand'	Au		Energy (eV)	Ditholene core	'Rest of ligand'	Au
117	L+4 (α)	-0.03	2	96	2	L+5 (β)	-0.01	2	96	2
116	L+3 (α)	-0.04	3	95	2	L+4 (β)	-0.02	3	95	2
115	L+2 (α)	-0.66	41	59	0	L+3 (β)	-0.46	34	66	0
114	L+1 (α)	-0.75	42	57	1	L+2 (β)	-0.58	36	63	1
113	LUMO (α)	-3.27	76	3	22	L+1 (β)	-3.19	76	3	22
112	HOMO (α)	-6.16	85	12	2	LUMO (β)	-4.12	90	7	3
111	H-1 (α)	-6.67	65	32	4	HOMO (β)	-5.85	77	16	7
110	H-2 (α)	-7.53	21	77	2	H-1 (β)	-7.34	26	73	1
109	H-3 (α)	-7.72	41	55	4	H-2 (β)	-7.46	38	58	4
108	H-4 (α)	-7.99	8	90	1	H-3 (β)	-7.96	24	73	3

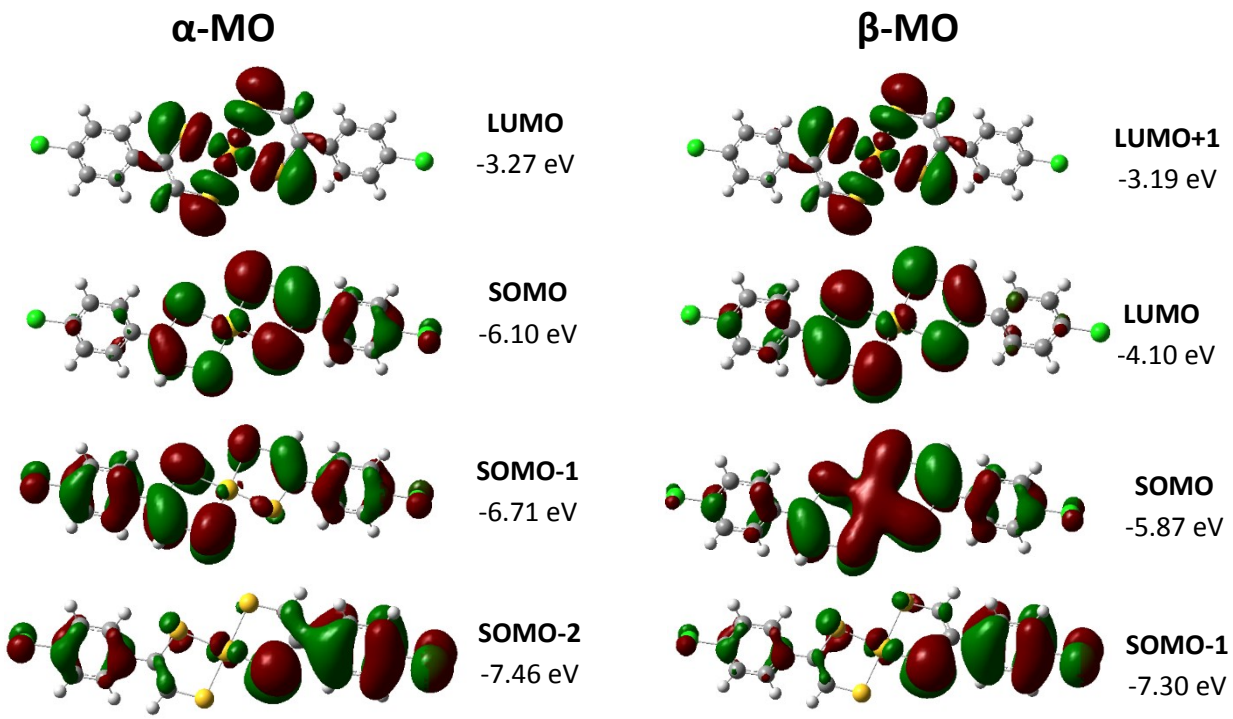

Figure S10: *Frontier molecular orbitals of trans-**2** (BHLYP35 functional, isocontour set at 0.02000).*

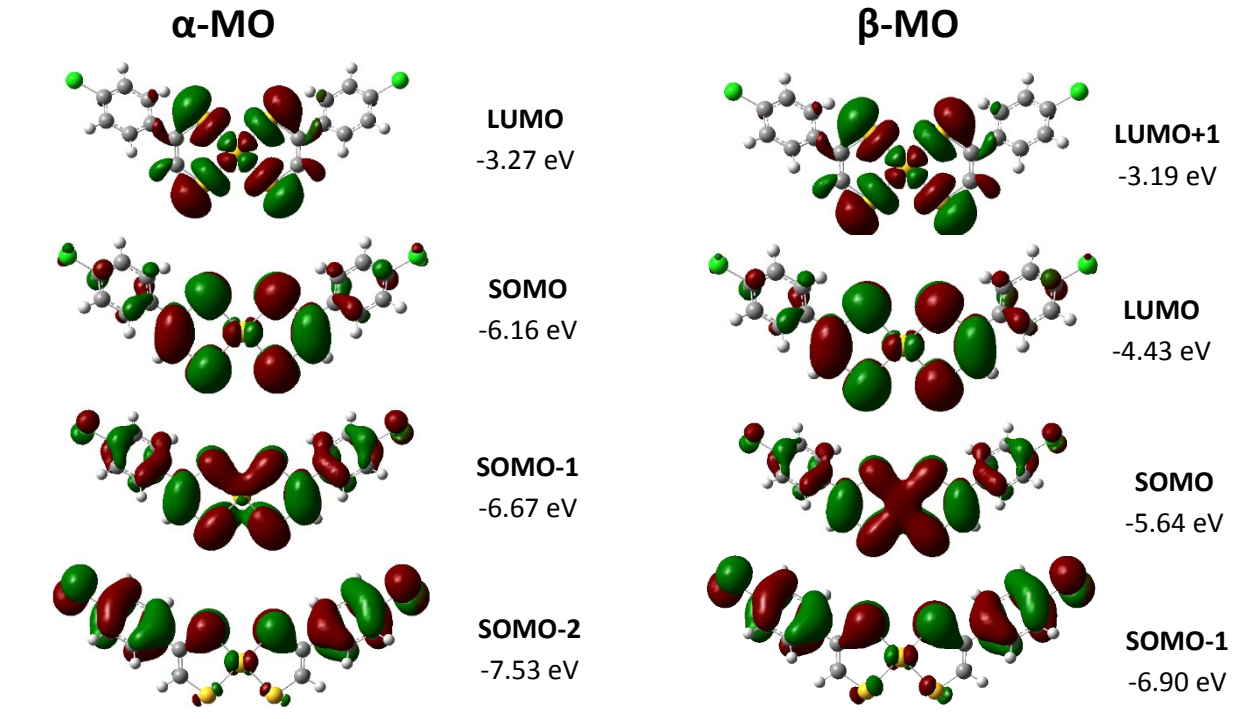

Figure S11: *Frontier molecular orbitals of cis-**2** (B3LYP functional, isocontour set at 0.02000).*

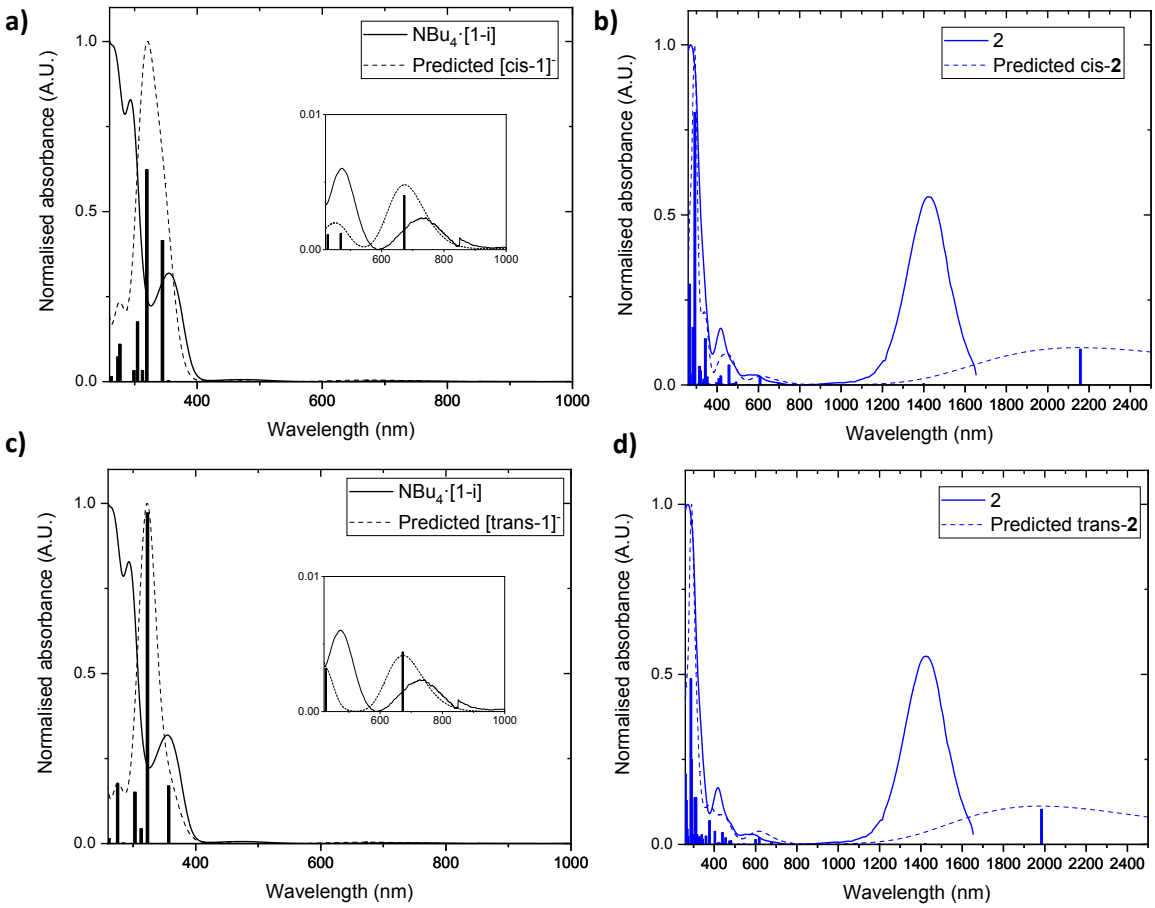

Figure S12: *Simulated and experimental UV/Vis/NIR spectra of a)* ***NBu$_4$·[1-i]*** *and* ***[cis-1]$^-$*** *, b)* ***2*** *and* ***cis-2****, c)* ***NBu$_4$·[1-i]*** *and* ***[trans-1]$^-$*** *and a)* ***2*** *and* ***trans-2*** *based on TD-DFT calculations using the BHLYP35 functional. The predicted spectrum is shown in dashed lines, and the experimental spectra in solid lines.*

Electronic absorption of thin films

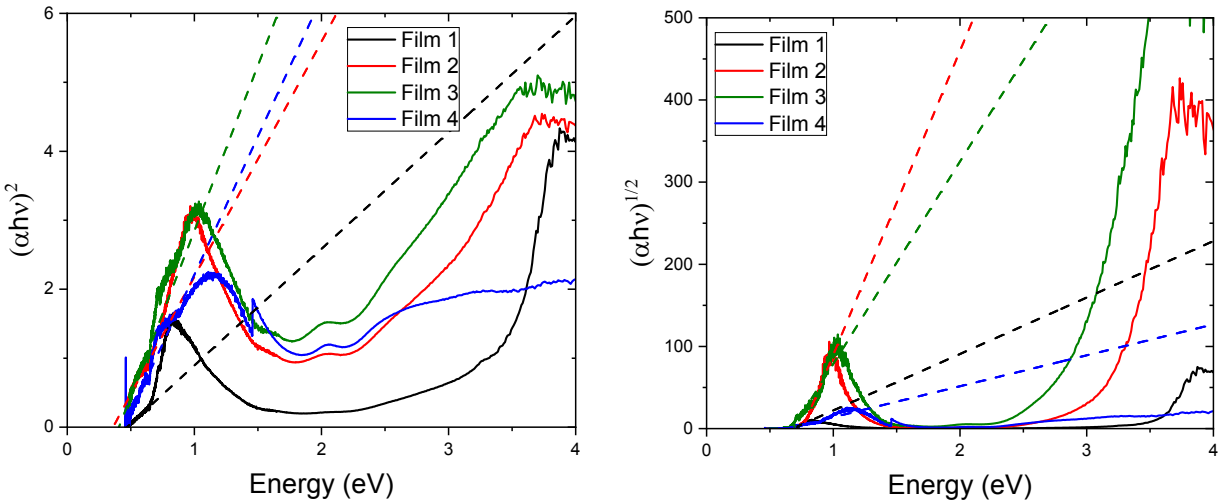

Figure S13: *Tauc plots for Films 1-4 for LEFT: a direct transition, RIGHT: an indirect transition.*

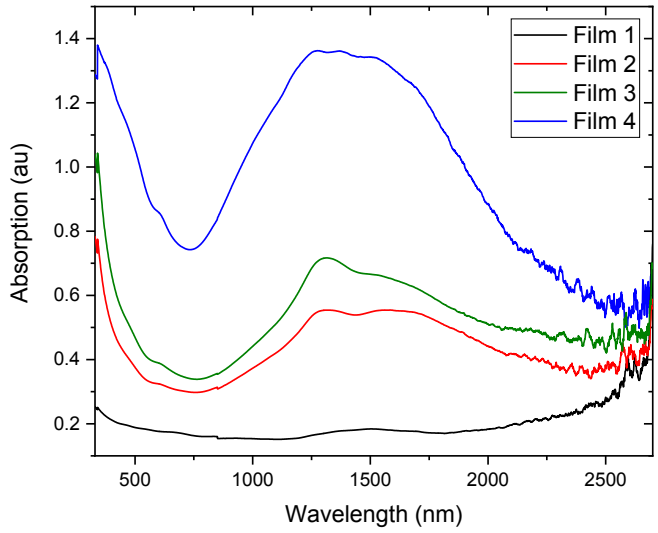

Figure S14: *Electronic absorption spectra of Films 1-4 measured by transmission absorption spectroscopy.*

Scanning electron microscopy

Film 1

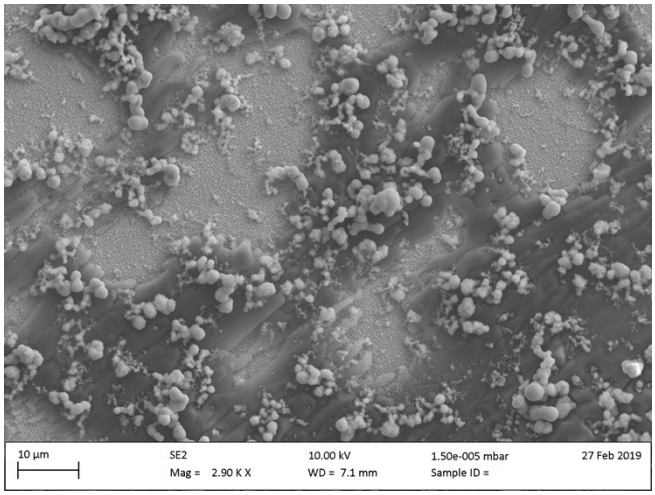

Figure S15: *SEM image of Film 1.*

Film 2

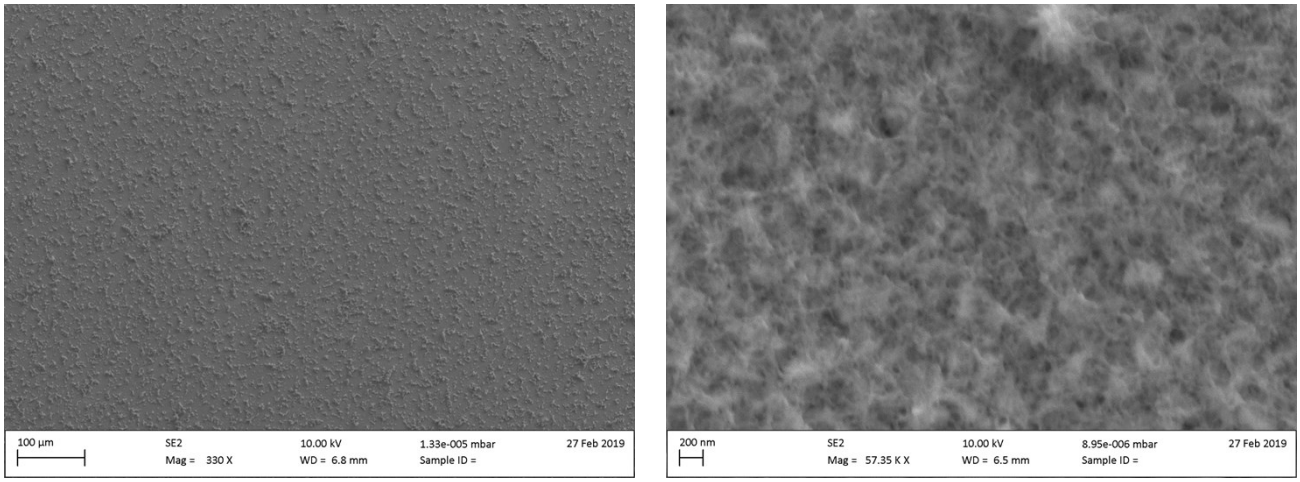

Figure S16: *SEM images of Film 2.*

Film 3

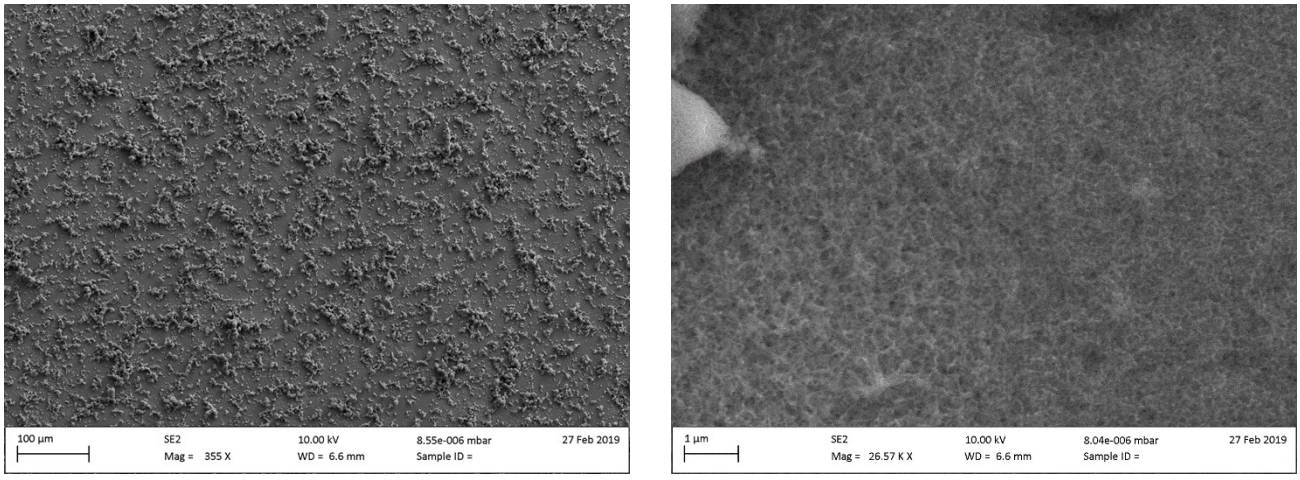

Figure S17: *SEM images of Film 3.*

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