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Supporting Information

Homoconjugation enhances the photophysical and electrochemical properties of a new 3D intramolecular charge transfer iptycene displaying deep blue emission

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Synthetic Details

General Experimental

All reactants and reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. Column chromatography was carried out using silica gel 60, 40−60 μm mesh (Fluorochem) and Aluminium oxide 90 active neutral 0.063−0.200 mm (70−230 mesh ASTM, Merck). Analytical thin-layer chromatography was performed on precoated aluminum silica gel 60 F254 plates (Merck), which were approximately 2 cm × 6 cm in size, and visualized using ultraviolet light (254/365 nm).

NMR spectra were recorded on Jeol ECS 400 MHz and Jeol ECZ 500 MHz spectrometers. Chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) using TMS or the residual solvent as an internal reference. NMR spectra were processed using MestReNova. Multiplicities are reported as singlet (s), doublet (d), triplet (t), and multiplet (m). Melting points were determined in open-ended capillaries using a Stuart Scientific SMP10 melting point apparatus at a ramping rate of 1 °C/min. They are recorded to the nearest 1 °C and are uncorrected. Atmospheric solids analysis probe (ASAP) mass spectra were recorded on a Waters LCT Premier XE spectrometer. The sample was introduced as a solid, applied directly to a glass probe tip. Matrix-assisted laser desorption time-of-flight (MALDI–TOF) mass spectra were recorded on a Bruker Daltonik Autoflex II spectrometer running in positive ion reflectron mode. MALDI–TOF samples were prepared in dichloromethane with trans-2-[3-(4-tert-butylphenyl)-2-methyl2-propenylidene]malononitrile (DCTB) as the matrix. Elemental analyses were obtained on an Exeter Analytical CE440 Elemental analyser.

Thermogravimetric analyses were performed using a TA SDT Q600 instrument. Two alumina crucibles with a small amount of sample (5−10 mg) and an as close to equal (±0.01 mg) amount of alumina reference powder were used for the analysis. Temperature was increased at a rate of 5 °C/min from 25 °C to 700 °C. Data obtained was analysed using TA Instruments Universal Analysis 2000 (Version 4.5A, Build 4.5.0.5) software.

Cyclic voltammetry was recorded using a Princeton Applied Research VersaSTAT 3. A glassy carbon disk, Pt wire, and Ag/Ag^+ ($AgNO_3$ in acetonitrile) were used as the working, counter, and reference electrodes, respectively. Measurements were corrected to the ferrocene/ferrocenium redox couple as an internal standard. 1,2-Dichlorobenzene was used as the solvent with an analyte molarity of *ca.* 10^{-5} M in the presence of 10^{-1} M (n-Bu_4N)(PF_6) as a supporting electrolyte. Solutions were degassed with Ar and experiments run under a blanket of Ar.

UV−vis absorbance was measured using a UV-1800 UV−vis spectrophotometer (Shimadzu) and UVProbe version 2.33 software. Emission spectra were recorded on an SPEX Fluoromax luminescence spectrometer using dM300 version 3.12 software.

The zeonex films of **1** and **2** were prepared by combining toluene solutions of the compound (1 mg/ mL) and zeonex (100 mg/ mL) in a 1:1 v/v ratio. These mixtures were then dropcast onto quartz substrates to produce the *ca*. 1 wt% zeonex films.

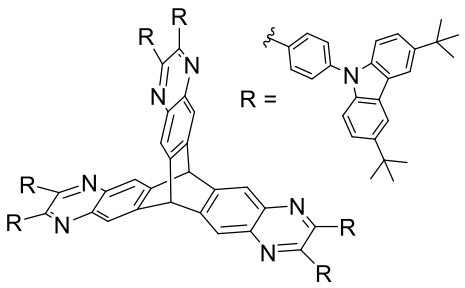
These films were used to measure the prompt spectra at room temperature and phosphorescence spectra, at 80 K, of the compounds. These spectra were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using a high-energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA). Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics)

having sub-nanosecond resolution.[1] The low temperature measurement was collected using a JANIS Research Inc. VNF-100 cryostat.

The time-correlated single photon counting (TCSPC) was performed on toluene solutions of **1** and **2** at 20 μM concentration. The TCSPC system used was a Horiba Delta Flex with excitation provided by a nanoLED-350 with peak excitation at 357 nm. The lifetime was measured at detection wavelength 450 nm. The instrument response function (IRF) was measured using a scattering solution in an identical cuvette at detection wavelength 357 nm. The TCSPC decays were then fitted incorporating IRF reconvolution using the FluorTools DecayFit software.[2]

Synthetic Methods

Compound **1**



A two-neck flask fitted with a condenser was placed under a N_2 atmosphere. Hexaamine hexachloride **4** (17 mg, 0.03 mmol) and diketone **3** (69 mg, 0.09 mmol, 3.0 eq.) were added to the flask followed by acetic acid (20 mL). The mixture was thoroughly degassed by bubbling with N_2 for 30 min and then refluxed overnight. Water (25 mL) was added and the mixture was extracted with dichloromethane. The combined organic portions were washed with sodium bicarbonate, dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The residue was purified by column chromatography on neutral alumina (dichloromethane/hexane 1:1 v/v). After evaporation of the column solvent the resulting solid was sonicated in methanol and then isolated via filtration to obtain **1** as a yellow crystalline solid (34 mg, 45%). mp. > 300 °C

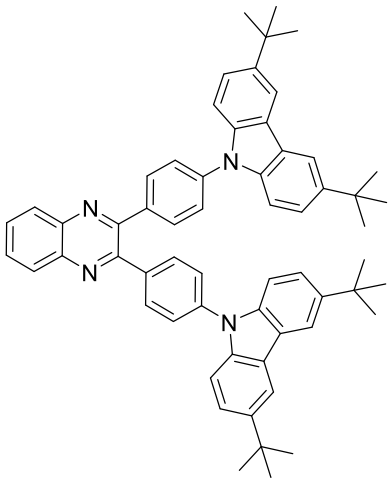
^{1}H NMR (400 MHz, Chloroform-*d*, ppm) δ = 8.47 (s, 6H), 8.15 (d, *J* = 1.7 Hz, 12H), 7.85 (d, *J* = 8.5 Hz, 12H), 7.66 (d, *J* = 8.5 Hz, 12H), 7.48 (dt, *J* = 18.1, 5.2 Hz, 24H), 6.30 (s, 2H), 1.47 (s, 108H).

^{13}C NMR (126 MHz, Chloroform-*d*, ppm) δ = 152.7, 144.4, 143.4, 140.8, 139.3, 139.0, 137.1, 131.6, 126.4, 124.2, 124.0, 123.8, 116.5, 109.4, 53.6, 34.9, 32.2.

MS (MALDI–TOF): m/z 2529.3 [M^+].

Elemental analysis: Calculated for $C_{182}H_{176}N_{12}$: C, 86.35; H, 7.01; N, 6.64. Found C, 85.83; H, 6.93; N, 6.65.

Compound **2**



A two-neck flask fitted with a condenser was placed under a N_2 atmosphere. Diamine **5** (5 mg, 0.05 mmol) and diketone **3** (35 mg, 0.05 mmol, 1.0 eq.) were added to the flask followed by acetic acid (5 mL). The mixture was thoroughly degassed by bubbling with N_2 for 30 min and then refluxed overnight. Water (10 mL) was added and a precipitate formed, which was isolated by filtration and washed with water and cold methanol to obtain **1** as a pale yellow/white solid (31 mg, 66%). mp. > 300 °C

^{1}H NMR (400 MHz, Chloroform-*d*, ppm) δ = 8.29 (dd, J = 6.3, 3.4 Hz, 2H), 8.15 (d, J = 1.7 Hz, 4H), 7.92 – 7.83 (m, 6H), 7.67 (d, J = 8.4 Hz, 4H), 7.48 (dt, J = 18.1, 5.2 Hz, 8H), 1.47 (s, 36H).

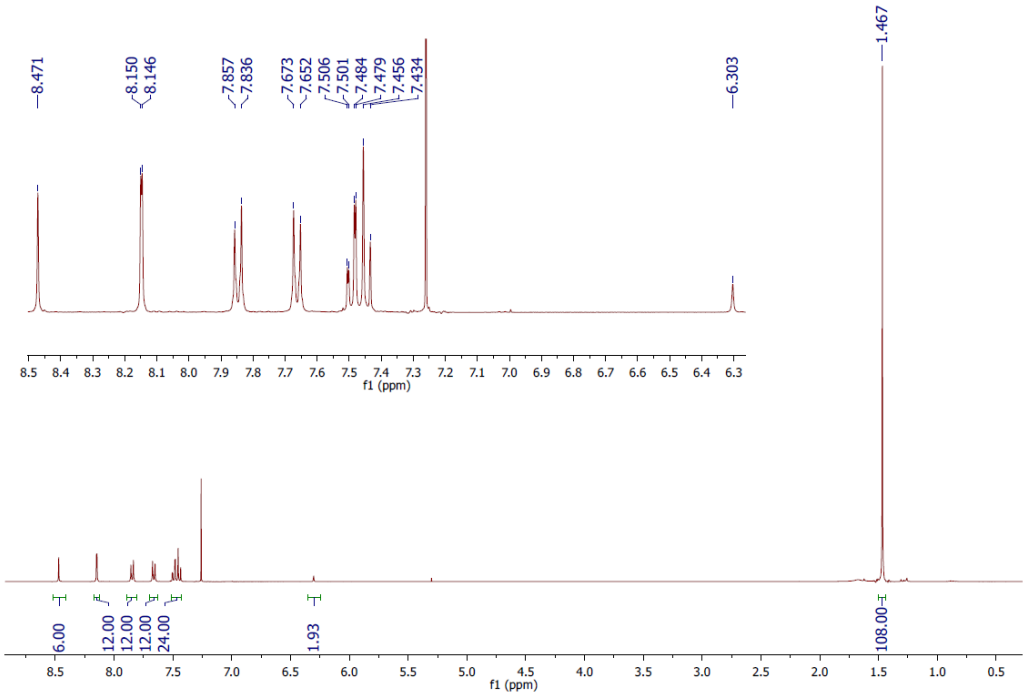
^{13}C NMR (126 MHz, Chloroform-*d*, ppm) δ = 152.8, 143.4, 141.5, 139.3, 139.0, 137.3, 131.6, 130.6, 129.4, 126.5, 124.0, 123.8, 116.5, 109.4, 34.9, 32.2.

MS (ASAP^{+}): m/z = 837.5 [M-H^{+}]

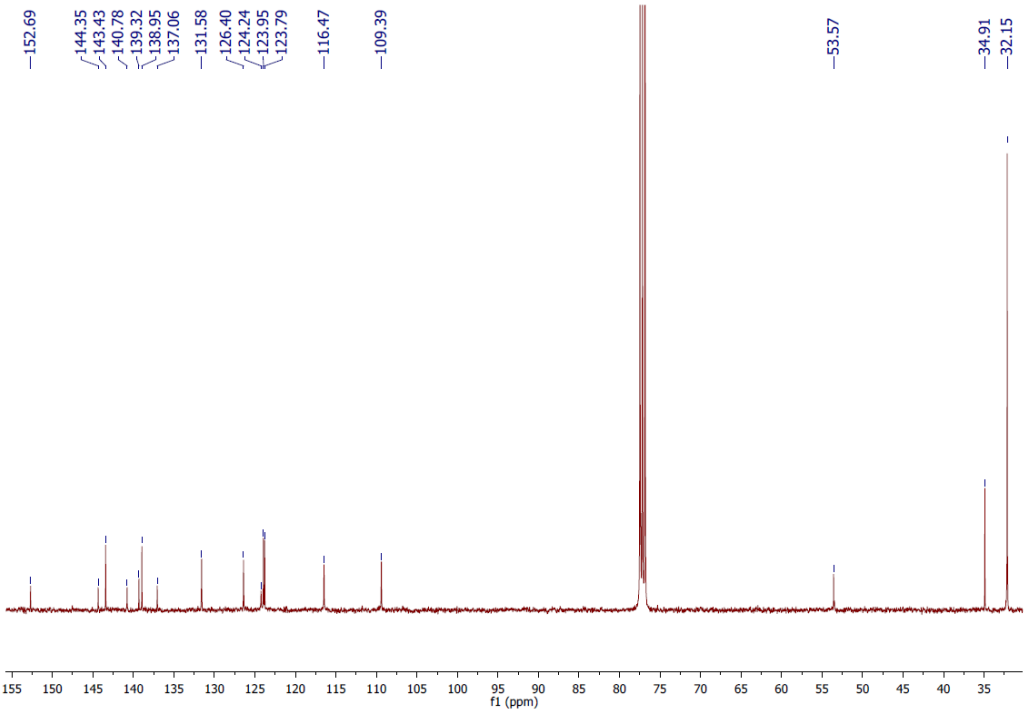
HRMS (ASAP+) m/z [M + H]$^{+}$ = calcd for $C_{60}H_{61}N_4$, found 837.4891

Elemental analysis: Calculated for $C_{60}H_{60}N_4$: C, 86.08; H, 7.22; N, 6.69. Found C, 85.61; H, 7.11; N, 6.91.

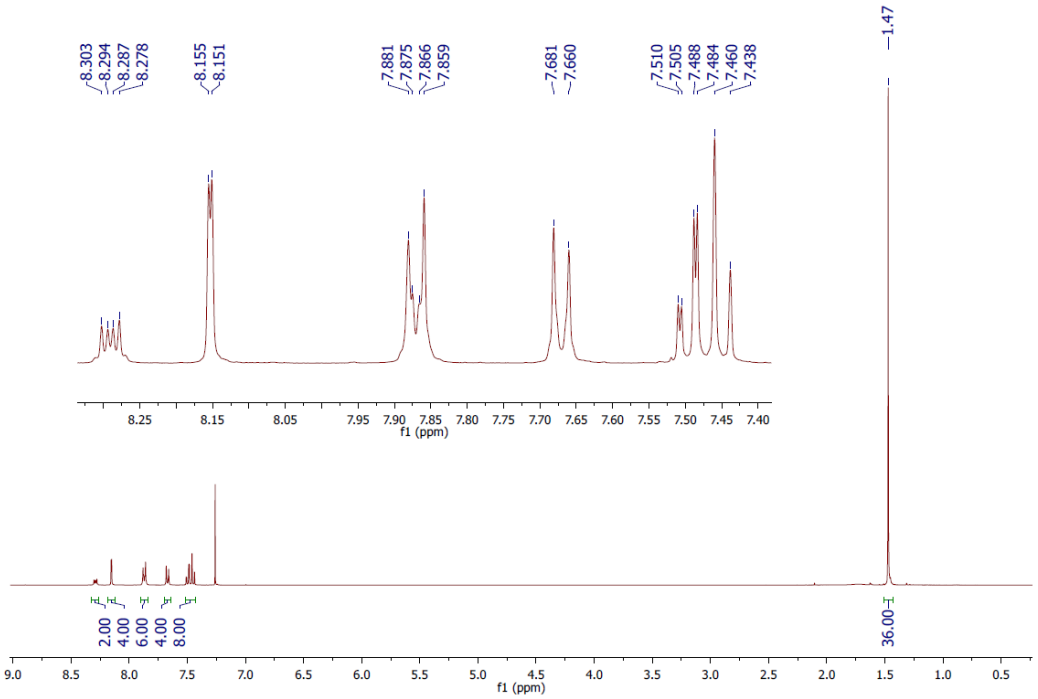
Copies of NMR spectra



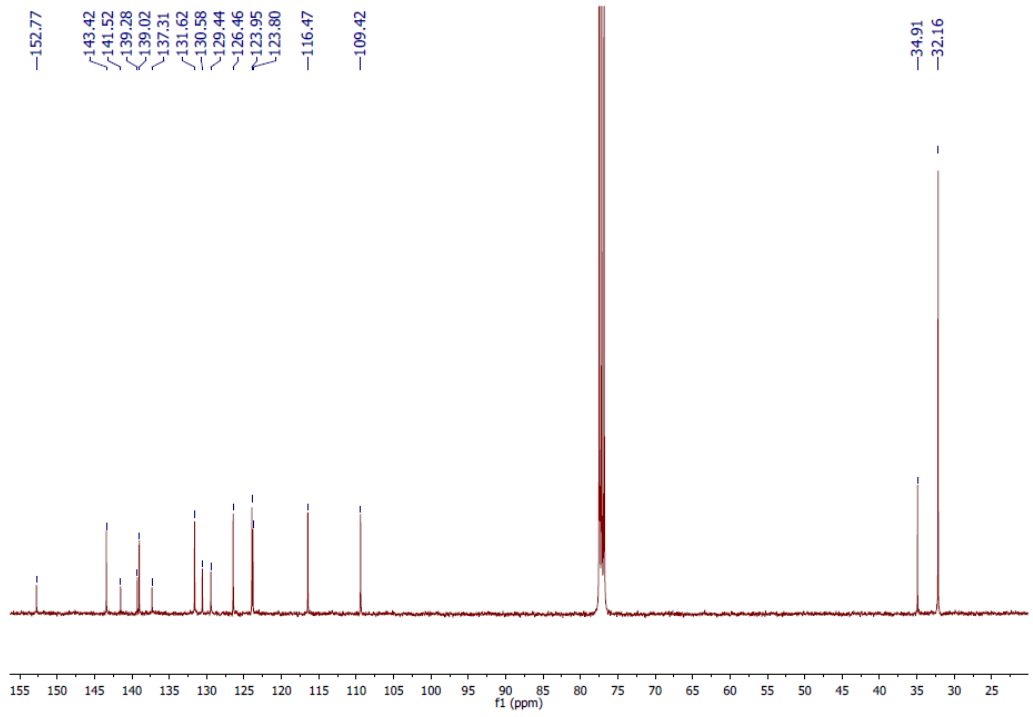
*Spectrum S1: Compound **1** ^{1}H NMR spectrum.*



*Spectrum S2: Compound **1** ^{13}C spectrum.*



*Spectrum S3: Compound **2** ^{1}H NMR spectrum.*



*Spectrum S4: Compound **2** ^{13}C NMR spectrum.*

Thermal Gravimetric Analysis

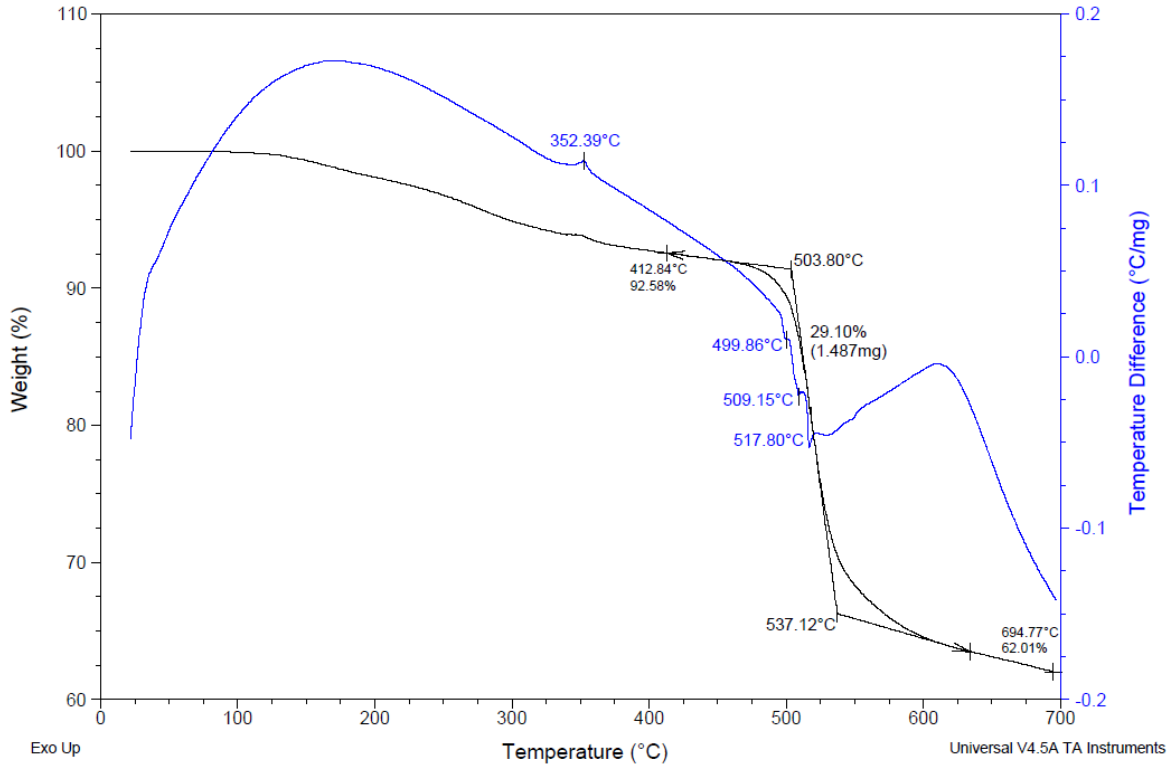


*Figure S1:Thermal gravimetric analysis (black line) of compound **1**.*

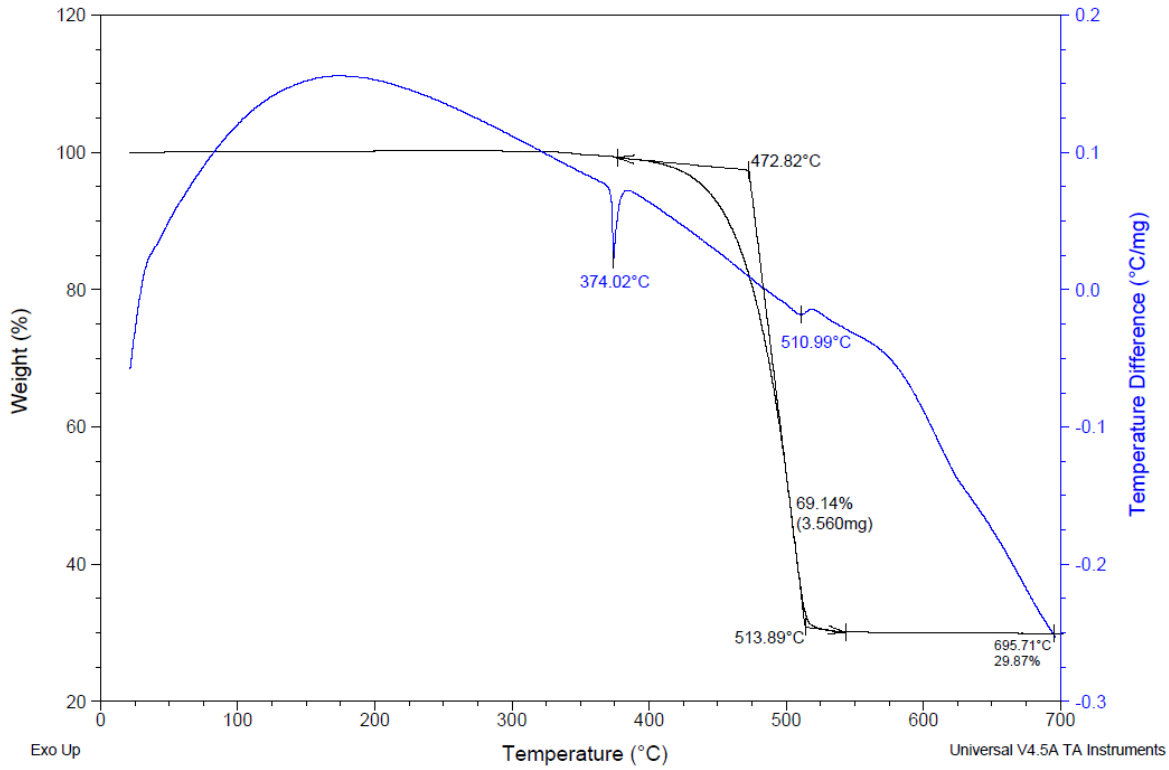


*Figure S2: Thermal gravimetric analysis (black line) compound **2.***

Emission spectra

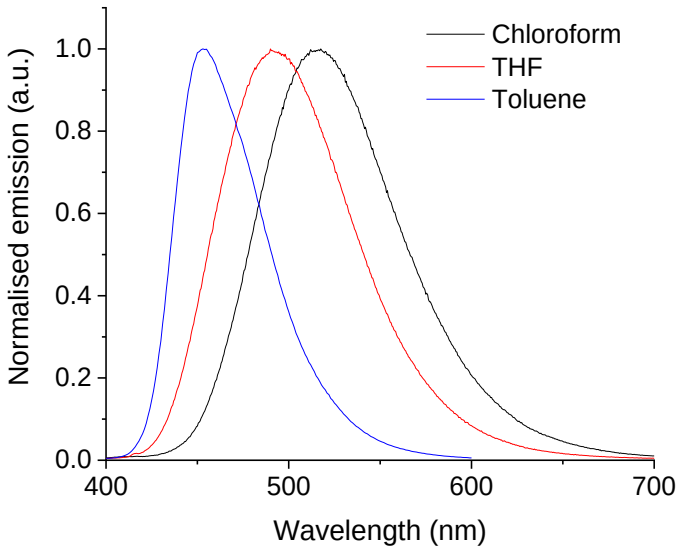


*Figure S3: Emission spectra for compound **1** recorded in different polarity solvents to highlight positive solvatachromism (λ_{exc} = 370 nm).*

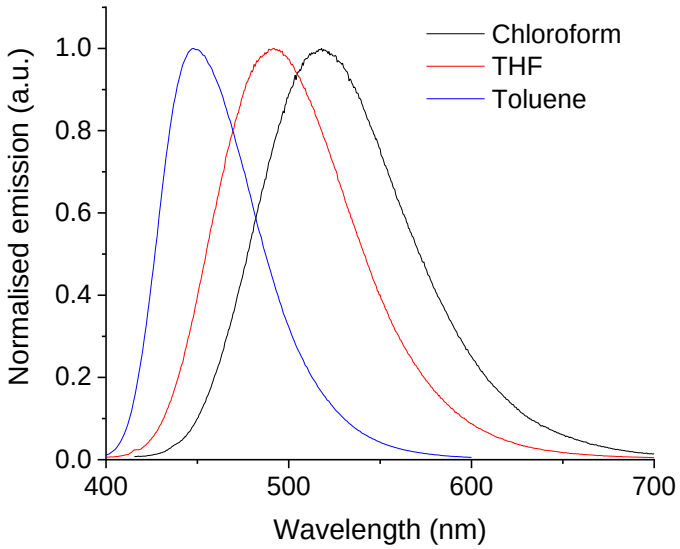


*Figure S4: Emission spectra for compound **2*** recorded in different polarity solvents to highlight positive solvatachromism (λ_{exc} = 370 nm).

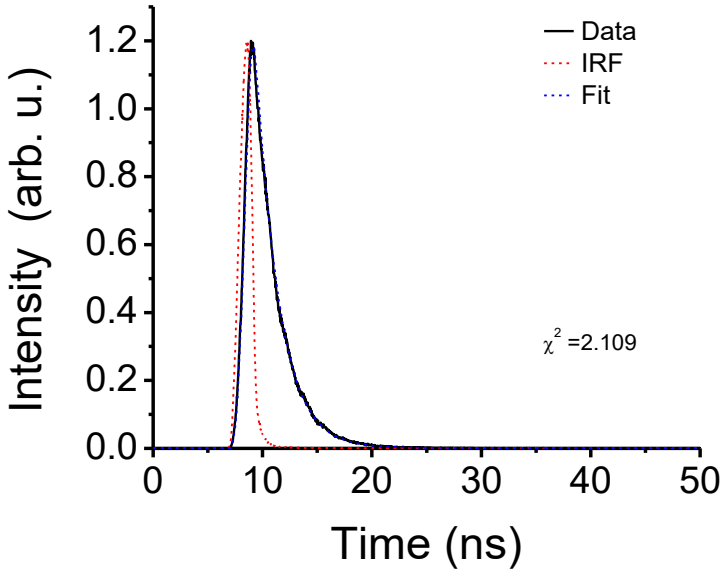


*Figure S5: The data, IRF and fit of the fluorescence lifetime of compound **1** in a 20 µM solution. The detection wavelength was 450 nm and the lifetime was measured to be 2.01 ± 0.05 ns.*

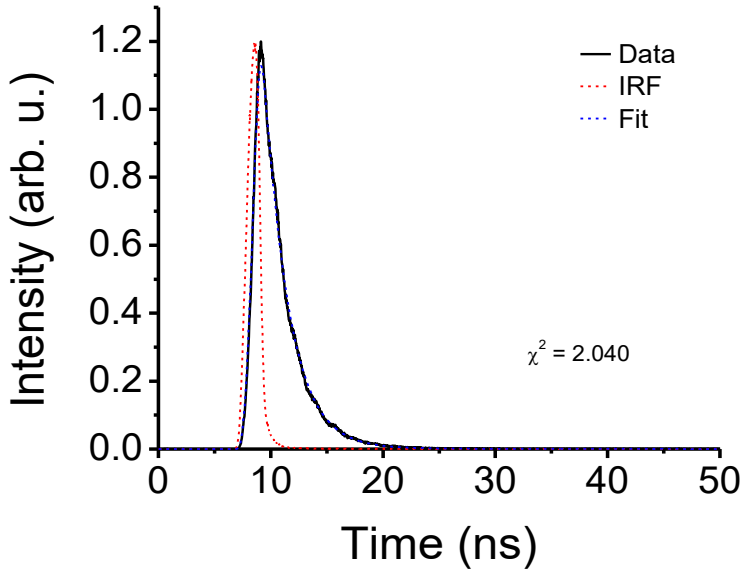


*Figure S6: The data, IRF and fit of the fluorescence lifetime of compound **2** in a 20 µM toluene solution. The detection wavelength was 450 nm and the lifetime was measured to be 2.11 ± 0.05 ns.*

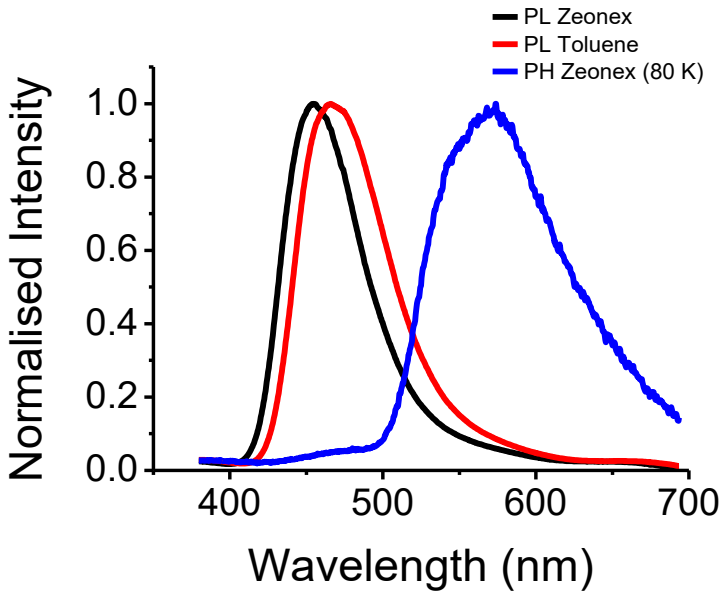


*Figure S7: The prompt PL and phosphorescence (PH) of a 1 wt% zeonex film of compound **1**. The PL is immediately after the pulse (0 ns) and at room temperature and the PH spectra is at a delay of 40 ms at 80 K. The energy gap between them is 0.49 eV. The prompt PL of the compound in a 20 μM toluene solution is shown for comparison. The slight shift is due to the increased polarity of toluene compared to zeonex.*

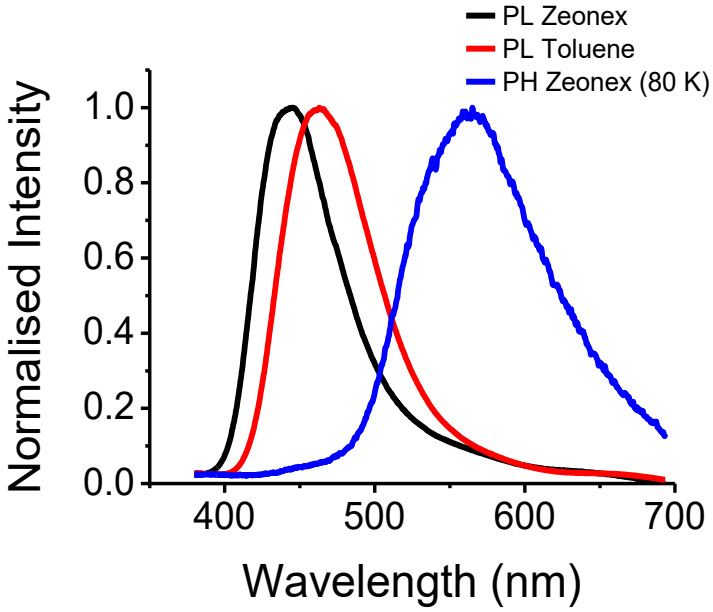


Figure S8: The prompt PL and phosphorescence (PH) of a 1 wt% zeonex film of compound **2**. The PL is immediately after the pulse (0 ns) and at room temperature and the PH spectra is at a delay of 40 ms at 80 K. The energy gap between them is 0.54 eV. The prompt PL of the compound in a 20 μM toluene solution is shown for comparison. The slight shift is due to the increased polarity of toluene compared to zeonex.

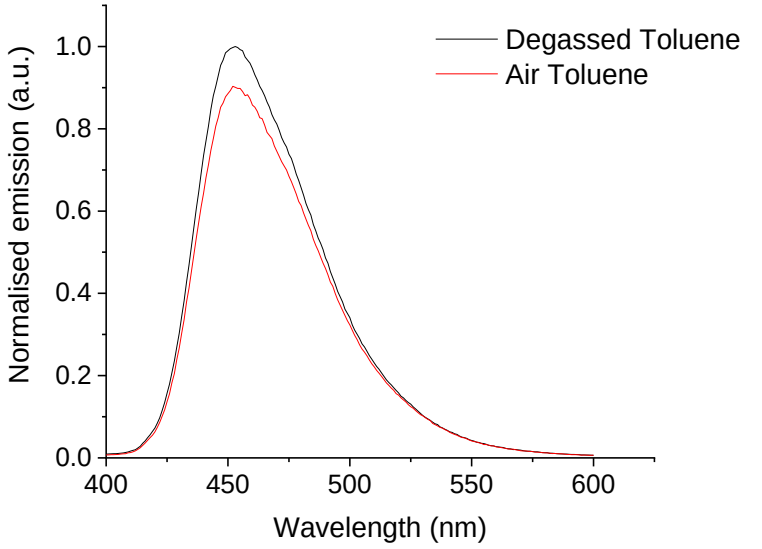


*Figure S9: Compound **1** air and degassed emission toluene (λ_{exc} = 370 nm).*

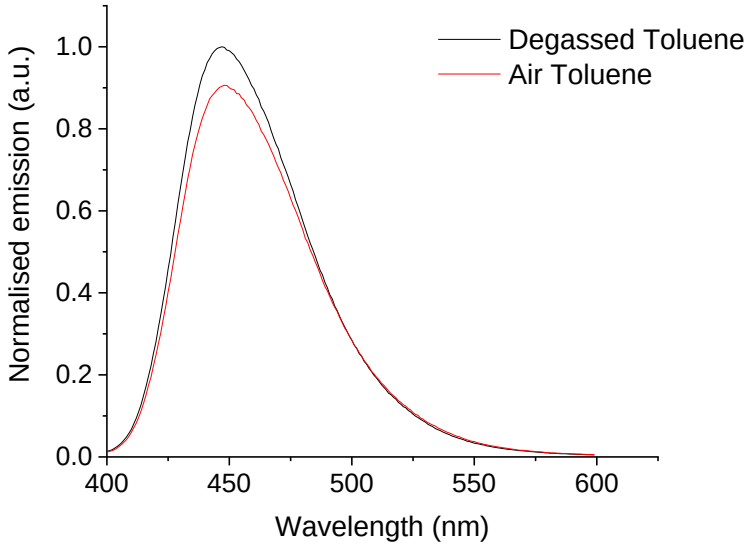


*Figure S10: Compound **2** air and degassed emission toluene (λ_{exc} =370 nm).*

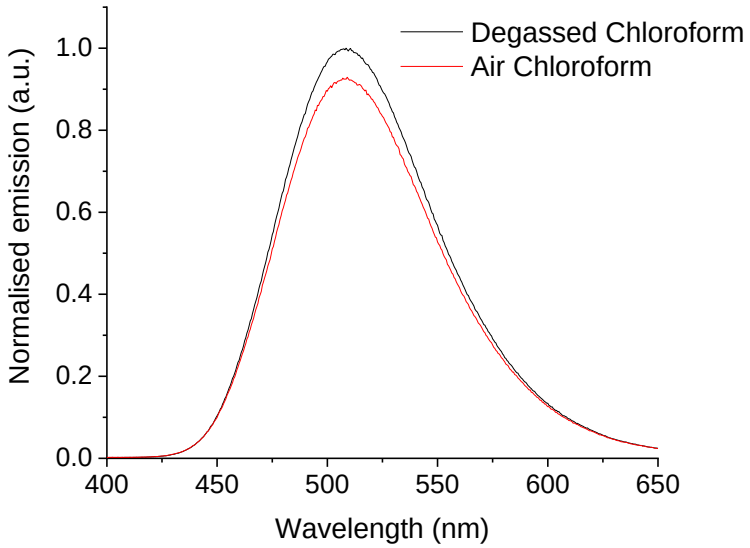


*Figure S11: Compound **1** air and degassed emission chloroform (λ_{exc} = 380 nm).*

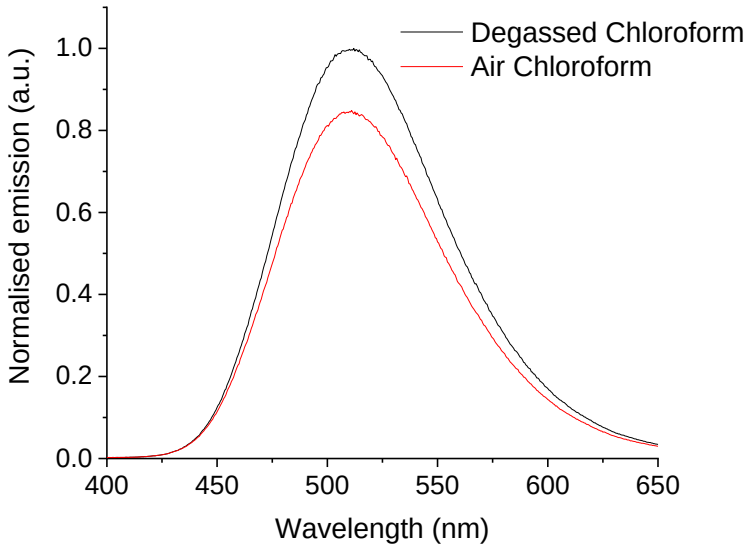


*Figure S12: Compound **2** air and degassed emission chloroform (λ_{exc} = 380 nm).*

Computational Studies

All calculations were carried out with the Gaussian 09 package.[3] Optimised S_0 geometries were determined using B3LYP[4,5] with the 6–31G* basis set.[6,7] Compound **1** failed to converge during the geometry optimisation. Therefore, once the total energy was stable for twenty guesses it was determined via a single point calculation. All S_0 geometries were true minima based on no imaginary frequencies found. Electronic structure and TD-DFT calculations were also carried out on the optimised geometries at TD–B3LYP/6–31G* and TDA–PBE0/def2-SVP.[8,9] The MO diagrams were generated with the aid of Gabedit[10]. TD-DFT data were formatted with the GaussSum[11] package. TD-DFT qualitatively predicts the three main bands observed in the experimental absorption spectrum of compound **2**, although the energy is underestimated. On this basis TD-DFT was considered adequate to simulate the ICT band of compound **1**. Further transitions were not calculated for **1** as it was deemed too computationally intensive. Total energy for **1** = −7698.74563114 hartree. Total energy for **2** = −2541.63839631 hartree.

Table S1: Cartesian coordinates for the optimised geometry of **1**.

Atom	Symbol	X	Y	Z
1	C	5.364788	-2.99212	-0.63536
2	C	3.330242	-1.90262	-0.6617
3	C	3.285055	-1.94296	0.76402
4	C	5.24581	-3.16011	0.799202
5	H	2.332645	-1.26582	-2.46979
6	C	2.276152	-1.28001	-1.38516
7	C	2.203027	-1.33107	1.454572
8	C	1.203883	-0.72694	0.734176
9	C	1.237815	-0.70615	-0.69608
10	H	2.194033	-1.37237	2.539931
11	C	6.561161	-3.39023	-1.42712
12	C	7.868857	-3.17817	-0.96222
13	C	6.391686	-3.91279	-2.71922
14	C	8.969896	-3.49927	-1.75025
15	H	8.031632	-2.75915	0.025259
16	C	7.487338	-4.2334	-3.51372
17	H	5.385521	-4.04571	-3.10276
18	C	8.789371	-4.03409	-3.03338
19	H	9.974898	-3.34634	-1.37067
20	H	7.341259	-4.62126	-4.5167
21	C	6.171799	-3.98345	1.622841
22	C	6.50894	-3.55704	2.917474
23	C	6.659752	-5.22463	1.183661
24	C	7.336513	-4.32171	3.732475
25	H	6.121683	-2.60822	3.273818
26	C	7.461227	-6.01012	2.005825
27	H	6.388476	-5.59624	0.201091
28	C	7.819	-5.55995	3.284395
29	H	7.624218	-3.95909	4.713965

30	H	7.798404	-6.98475	1.66856
31	N	4.243805	-2.6011	1.461572
32	N	4.39516	-2.41343	-1.32802
33	C	9.884875	-6.9105	3.741122
34	C	8.401278	-6.69407	5.447714
35	C	10.59002	-6.82279	2.542131
36	C	10.42168	-7.6183	4.843929
37	C	7.30048	-6.41716	6.256457
38	C	9.472928	-7.48263	5.93278
39	C	11.82309	-7.47021	2.455176
40	H	10.20399	-6.26448	1.695797
41	C	11.65825	-8.25527	4.724633
42	C	7.29883	-6.9173	7.559163
43	H	6.459052	-5.83793	5.891112
44	C	9.440848	-7.96804	7.24135
45	C	12.3817	-8.19832	3.525924
46	H	12.36084	-7.39762	1.51682
47	H	12.05781	-8.79503	5.579158
48	C	8.3553	-7.69076	8.082884
49	H	6.438336	-6.69398	8.179396
50	H	10.27032	-8.57172	7.600055
51	C	10.99496	-3.52575	-4.12162
52	C	10.12574	-5.59366	-4.477
53	C	11.22937	-2.20134	-3.75635
54	C	11.91125	-4.21932	-4.94925
55	C	9.363442	-6.76039	-4.4692
56	C	11.35762	-5.5411	-5.17375
57	C	12.39994	-1.59153	-4.20906
58	H	10.52437	-1.64801	-3.1449
59	C	13.07357	-3.58061	-5.38537
60	C	9.8375	-7.86102	-5.18406
61	H	8.42945	-6.82411	-3.92082
62	C	11.80404	-6.65985	-5.87957
63	C	13.3439	-2.25519	-5.01988
64	H	12.57264	-0.56201	-3.91707
65	H	13.76787	-4.12511	-6.01987
66	C	11.05058	-7.84106	-5.90298
67	H	9.235032	-8.76209	-5.17284
68	H	12.75107	-6.60516	-6.40991
69	N	9.907911	-4.36521	-3.83577
70	N	8.654286	-6.34713	4.111979
71	C	13.74203	-8.91582	3.420028
72	C	13.54868	-10.4299	3.673251
73	C	14.39194	-8.74435	2.033613
74	C	14.71438	-8.34162	4.477807
75	H	13.12702	-10.6262	4.664688

76	H	12.87143	-10.8674	2.930805
77	H	14.50958	-10.9557	3.609419
78	H	14.58932	-7.69146	1.802049
79	H	15.35184	-9.27263	2.008648
80	H	13.7665	-9.15917	1.234929
81	H	15.68631	-8.84743	4.420263
82	H	14.87845	-7.2699	4.317421
83	H	14.33186	-8.47107	5.495745
84	C	8.348241	-8.23562	9.524952
85	C	7.078734	-7.83382	10.30004
86	C	8.420682	-9.78094	9.495553
87	C	9.572076	-7.68201	10.29292
88	H	6.979869	-6.74566	10.3861
89	H	6.170392	-8.22407	9.82693
90	H	7.122307	-8.24216	11.31615
91	H	9.32735	-10.137	8.995067
92	H	8.42312	-10.1845	10.51584
93	H	7.55967	-10.2029	8.964679
94	H	9.586612	-8.06645	11.32045
95	H	10.5155	-7.96922	9.816756
96	H	9.542365	-6.58737	10.3395
97	C	11.56544	-9.05971	-6.6944
98	C	10.60919	-10.2647	-6.60806
99	C	11.72117	-8.67939	-8.18609
100	C	12.93903	-9.49892	-6.1336
101	H	10.47981	-10.6108	-5.5762
102	H	9.619847	-10.0312	-7.01783
103	H	11.01673	-11.1011	-7.18724
104	H	12.42546	-7.85221	-8.32389
105	H	12.09417	-9.53458	-8.76344
106	H	10.75986	-8.37304	-8.61424
107	H	13.32333	-10.3618	-6.69174
108	H	13.68309	-8.69857	-6.2049
109	H	12.85748	-9.78485	-5.07869
110	C	14.63742	-1.576	-5.51186
111	C	15.86418	-2.3664	-4.99767
112	C	14.65562	-1.55507	-7.05891
113	C	14.76525	-0.12316	-5.0151
114	H	15.88423	-2.38844	-3.90205
115	H	15.85807	-3.40284	-5.35129
116	H	16.79455	-1.90072	-5.34605
117	H	13.80081	-0.99337	-7.45262
118	H	15.5739	-1.07949	-7.42549
119	H	14.61298	-2.56482	-7.4806
120	H	15.6984	0.313474	-5.38879
121	H	13.94134	0.504994	-5.37262

122	H	14.78966	-0.06627	-3.92085
123	C	0.032158	0.00892	-1.30381
124	H	0.058428	0.02548	-2.39547
125	C	-0.03054	-0.03054	1.304614
126	H	-0.05678	-0.04704	2.396287
127	C	0.019539	1.409428	-0.69334
128	C	0.033298	2.59684	-1.38045
129	C	-0.01619	1.387798	0.736845
130	C	0.011502	3.81967	-0.65498
131	H	0.047102	2.640693	-2.46566
132	C	-0.02744	2.553818	1.459721
133	C	-0.00257	3.79811	0.771805
134	N	-0.04228	4.998643	-1.32278
135	H	-0.04102	2.564631	2.545765
136	N	0.055132	4.956142	1.475055
137	C	-0.05785	6.126602	-0.62829
138	C	0.07452	6.104586	0.814794
139	C	-0.26799	7.363394	-1.4301
140	C	0.286098	7.315969	1.652323
141	C	-1.12624	8.391184	-1.0078
142	C	0.335619	7.478286	-2.69251
143	C	-0.31699	7.394636	2.917908
144	C	1.14214	8.356811	1.258161
145	C	-1.35523	9.506739	-1.80752
146	H	-1.62111	8.32255	-0.0447
147	C	0.109485	8.589017	-3.49842
148	H	0.971167	6.672499	-3.04452
149	C	-0.10695	8.491628	3.74638
150	H	-0.96525	6.58652	3.240266
151	C	1.382842	9.441453	2.095384
152	H	1.649334	8.307496	0.300333
153	C	-0.73585	9.618136	-3.06014
154	H	-2.00715	10.30163	-1.46019
155	H	0.570007	8.656664	-4.47877
156	C	0.749381	9.526431	3.343138
157	H	-0.61415	8.55953	4.70333
158	H	2.077493	10.21882	1.794553
159	N	-0.96424	10.7536	-3.87444
160	N	0.974428	10.64137	4.184851
161	C	-2.21722	11.27795	-4.22552
162	C	0.024222	11.55467	-4.46518
163	C	0.870766	11.98968	3.809818
164	C	1.331121	10.59257	5.540922
165	C	-3.49957	10.82136	-3.92618
166	C	-2.02978	12.41768	-5.04495
167	C	1.413356	11.47522	-4.38528

168	C	-0.59819	12.59634	-5.19544
169	C	0.507225	12.55958	2.590964
170	C	1.160318	12.80587	4.93022
171	C	1.595513	9.498725	6.363187
172	C	1.457107	11.91381	6.034851
173	C	-4.58657	11.53208	-4.43642
174	H	-3.65959	9.934597	-3.32195
175	C	-3.13857	13.10682	-5.5397
176	C	2.167412	12.43461	-5.0621
177	H	1.904939	10.69739	-3.81045
178	C	0.184845	13.54059	-5.86203
179	C	0.460979	13.95148	2.503208
180	H	0.258955	11.94831	1.729727
181	C	1.104879	14.19562	4.809602
182	C	1.962052	9.744358	7.687041
183	H	1.529922	8.481137	5.992728
184	C	1.825775	12.1257	7.364559
185	C	-4.43966	12.6807	-5.24138
186	H	-5.57906	11.16887	-4.19563
187	H	-2.97961	13.97993	-6.16701
188	C	1.583768	13.47615	-5.81265
189	H	3.24682	12.36135	-4.99474
190	H	-0.30642	14.33413	-6.41887
191	C	0.759097	14.7967	3.591992
192	H	0.17993	14.38322	1.54949
193	H	1.330053	14.80948	5.677715
194	C	2.080798	11.0449	8.219123
195	H	2.163332	8.886048	8.31777
196	H	1.918339	13.14507	7.729853
197	C	-5.64594	13.46291	-5.79778
198	C	2.423962	14.52951	-6.56176
199	C	0.711273	16.33388	3.485547
200	C	2.481552	11.30795	9.684289
201	C	-5.59776	14.92159	-5.28395
202	C	-5.59386	13.46469	-7.34419
203	C	-6.99327	12.85139	-5.36806
204	C	3.938586	14.30217	-6.39431
205	C	2.096441	14.47274	-8.07291
206	C	2.089966	15.9398	-6.01991
207	C	2.104891	16.91859	3.817344
208	C	0.316933	16.81451	2.075853
209	C	-0.32744	16.89056	4.488197
210	C	2.720327	10.00569	10.47234
211	C	3.787878	12.13625	9.723589
212	C	1.355664	12.0966	10.39455
213	H	-5.64469	14.95265	-4.18936

214	H	-4.67897	15.43159	-5.5922
215	H	-6.44587	15.49561	-5.67766
216	H	-5.63514	12.4428	-7.73819
217	H	-6.4436	14.02333	-7.75608
218	H	-4.67654	13.92963	-7.72049
219	H	-7.81628	13.44257	-5.78543
220	H	-7.10955	11.82344	-5.73003
221	H	-7.11062	12.84635	-4.27836
222	H	4.247309	14.36318	-5.34446
223	H	4.251397	13.32809	-6.78749
224	H	4.49019	15.0725	-6.94511
225	H	1.036916	14.66982	-8.26743
226	H	2.681072	15.22218	-8.62095
227	H	2.333296	13.48634	-8.48785
228	H	2.676089	16.70245	-6.54773
229	H	1.030753	16.18578	-6.14954
230	H	2.320485	16.0129	-4.95091
231	H	2.429482	16.64909	4.827966
232	H	2.861232	16.54965	3.115143
233	H	2.086696	18.01379	3.753916
234	H	-0.68076	16.46352	1.788502
235	H	0.30048	17.91004	2.051097
236	H	1.030503	16.47818	1.31503
237	H	-0.36871	17.9854	4.429756
238	H	-1.32838	16.5002	4.271558
239	H	-0.08168	16.62167	5.52097
240	H	1.820696	9.380858	10.51099
241	H	3.532958	9.410111	10.04089
242	H	2.999748	10.24531	11.50463
243	H	3.674405	13.10049	9.217014
244	H	4.083567	12.33765	10.76078
245	H	4.607482	11.59754	9.234464
246	H	1.628137	12.29942	11.43784
247	H	1.162968	13.05851	9.90781
248	H	0.418352	11.52852	10.39193
249	C	-1.2367	-0.7259	0.675591
250	C	-2.27485	-1.32033	1.347219
251	C	-1.20303	-0.70322	-0.75464
252	C	-3.32916	-1.92055	0.605479
253	H	-2.33085	-1.33951	2.431789
254	C	-2.20291	-1.2844	-1.49279
255	C	-3.28486	-1.91683	-0.82081
256	N	-4.39323	-2.45231	1.256454
257	H	-2.19435	-1.29255	-2.57891
258	N	-4.24421	-2.55306	-1.53765
259	C	-5.36302	-3.01017	0.547117

260	C	-5.24533	-3.13305	-0.89218
261	C	-6.55787	-3.43418	1.327751
262	C	-6.17175	-3.93035	-1.74058
263	C	-7.86671	-3.21038	0.871564
264	C	-6.38553	-3.99588	2.602919
265	C	-6.5127	-3.46183	-3.01957
266	C	-6.65676	-5.18621	-1.34167
267	C	-8.96594	-3.55828	1.65073
268	H	-8.03185	-2.76115	-0.10213
269	C	-7.47933	-4.3433	3.388607
270	H	-5.37854	-4.1384	2.980785
271	C	-7.34177	-4.2	-3.85716
272	H	-6.12761	-2.50119	-3.3453
273	C	-7.45962	-5.94499	-2.18724
274	H	-6.38225	-5.58997	-0.37279
275	C	-8.78249	-4.13235	2.916379
276	H	-9.97179	-3.39584	1.2774
277	H	-7.3309	-4.7615	4.378965
278	C	-7.82186	-5.45287	-3.44898
279	H	-7.6326	-3.80533	-4.82528
280	H	-7.79471	-6.9307	-1.88157
281	N	-9.89907	-4.49106	3.709584
282	N	-8.65947	-6.21266	-4.29946
283	C	-10.9884	-3.66405	4.021827
284	C	-10.1123	-5.73902	4.313697
285	C	-9.88913	-6.7876	-3.94369
286	C	-8.41173	-6.51337	-5.64729
287	C	-11.2275	-2.32994	3.697047
288	C	-11.9014	-4.38508	4.829365
289	C	-9.34643	-6.90263	4.270035
290	C	-11.3435	-5.7113	5.013196
291	C	-10.5898	-6.74059	-2.7398
292	C	-10.4306	-7.45664	-5.06823
293	C	-7.31386	-6.209	-6.45006
294	C	-9.48571	-7.28411	-6.1553
295	C	-12.3993	-1.73779	4.169392
296	H	-10.525	-1.75606	3.101797
297	C	-13.0651	-3.76348	5.286039
298	C	-9.8162	-8.0257	4.952068
299	H	-8.41302	-6.947	3.718783
300	C	-11.7855	-6.85207	5.68573
301	C	-11.8232	-7.38945	-2.67068
302	H	-10.2002	-6.21198	-1.87618
303	C	-11.6673	-8.09624	-4.96635
304	C	-7.31749	-6.66356	-7.76935
305	H	-6.47087	-5.64293	-6.06804

306	C	-9.45887	-7.72386	-7.48005
307	C	-13.3401	-2.42854	4.960994
308	H	-12.5756	-0.70049	3.908787
309	H	-13.7569	-4.32906	5.904636
310	C	-11.0284	-8.03113	5.672642
311	H	-9.21112	-8.92425	4.913036
312	H	-12.732	-6.81625	6.218651
313	C	-12.3865	-8.07981	-3.7638
314	H	-12.3575	-7.34855	-1.72848
315	H	-12.0705	-8.60598	-5.83741
316	C	-8.37634	-7.41793	-8.3156
317	H	-6.45945	-6.41871	-8.3848
318	H	-10.2902	-8.31408	-7.85641
319	C	-14.6353	-1.76867	5.474452
320	C	-11.5385	-9.27463	6.427602
321	C	-13.7474	-8.79878	-3.67771
322	C	-8.37524	-7.91175	-9.77595
323	C	-15.86	-2.54781	4.938546
324	C	-14.6516	-1.79355	7.021448
325	C	-14.7688	-0.30227	5.020933
326	C	-10.5794	-10.4739	6.302642
327	C	-11.692	-8.94016	7.930475
328	C	-12.9123	-9.70011	5.85666
329	C	-13.5576	-10.3033	-3.98488
330	C	-14.3914	-8.67536	-2.28347
331	C	-14.7233	-8.18629	-4.71051
332	C	-7.10883	-7.48298	-10.5417
333	C	-8.44794	-9.45713	-9.80047
334	C	-9.60206	-7.3311	-10.5188
335	H	-15.881	-2.5381	3.842758
336	H	-15.8502	-3.59407	5.261883
337	H	-16.7915	-2.0955	5.301098
338	H	-13.7983	-1.24068	7.430549
339	H	-15.571	-1.33225	7.403031
340	H	-14.6049	-2.81517	7.413093
341	H	-15.7032	0.119833	5.408051
342	H	-13.9468	0.318019	5.396164
343	H	-14.7944	-0.21319	3.928845
344	H	-10.4504	-10.7873	5.260318
345	H	-9.59016	-10.2509	6.7184
346	H	-10.9842	-11.329	6.855882
347	H	-12.3976	-8.11892	8.094713
348	H	-12.0622	-9.81326	8.48224
349	H	-10.7305	-8.64507	8.365908
350	H	-13.2932	-10.5804	6.389255
351	H	-13.658	-8.90413	5.953851

352	H	-12.8324	-9.95376	4.793398
353	H	-13.1407	-10.4654	-4.98448
354	H	-12.8778	-10.7676	-3.26125
355	H	-14.5191	-10.8296	-3.93523
356	H	-14.5867	-7.63104	-2.01435
357	H	-15.3518	-9.20325	-2.27308
358	H	-13.7631	-9.11854	-1.50244
359	H	-15.696	-8.6919	-4.66608
360	H	-14.8844	-7.12048	-4.51222
361	H	-14.3457	-8.28105	-5.7341
362	H	-7.01002	-6.39247	-10.5895
363	H	-6.19857	-7.88986	-10.0866
364	H	-7.15689	-7.85504	-11.5714
365	H	-9.3531	-9.83024	-9.30988
366	H	-8.45361	-9.82481	-10.8342
367	H	-7.58543	-9.89747	-9.28726
368	H	-9.62102	-7.67884	-11.5593
369	H	-10.5436	-7.63475	-10.0491
370	H	-9.57214	-6.23551	-10.5267

Table S2: Cartesian coordinates for the optimised geometry of **2**.

Atom	Symbol	X	Y	Z
1	C	0.079716	4.761334	-0.35945
2	C	-0.25213	7.038388	-0.52617
3	C	-1.61525	6.873596	-0.14069
4	C	-1.3393	4.583272	-0.10885
5	H	1.290013	8.438268	-1.07798
6	C	0.24989	8.339534	-0.78294
7	C	-2.4418	8.015803	0.011488
8	C	-1.92695	9.269844	-0.23324
9	C	-0.57654	9.432091	-0.63799
10	H	-3.47494	7.864643	0.308824
11	H	-2.5585	10.14685	-0.12166
12	H	-0.1942	10.43089	-0.82937
13	C	1.077273	3.656358	-0.31448
14	C	1.040645	2.660357	0.674255
15	C	2.142835	3.647725	-1.2284
16	C	2.02081	1.674389	0.734123
17	H	0.239115	2.652111	1.405501
18	C	3.127081	2.666191	-1.17385
19	H	2.200903	4.435079	-1.97267
20	C	3.071375	1.665446	-0.19366
21	H	1.970888	0.900682	1.4934
22	H	3.953578	2.679672	-1.87711
23	C	-2.0105	3.25682	-0.04172

24	C	-3.04495	3.051247	0.884958
25	C	-1.70039	2.217642	-0.93321
26	C	-3.71909	1.836559	0.950426
27	H	-3.30597	3.854923	1.565628
28	C	-2.39433	1.012484	-0.89703
29	H	-0.92868	2.359669	-1.68258
30	C	-3.40107	0.804126	0.05616
31	H	-4.48535	1.676273	1.701893
32	H	-2.17173	0.233348	-1.61857
33	N	-2.13466	5.630305	0.035497
34	N	0.575537	5.963222	-0.60223
35	C	-3.49191	-1.70261	0.150453
36	C	-5.47962	-0.60255	0.147525
37	C	-2.14664	-2.06636	0.176669
38	C	-4.50686	-2.68823	0.211758
39	C	-6.50375	0.341042	0.088425
40	C	-5.77599	-1.98603	0.207562
41	C	-1.83335	-3.42476	0.240035
42	H	-1.35665	-1.32315	0.154979
43	C	-4.16032	-4.03905	0.274634
44	C	-7.8219	-0.11594	0.116854
45	H	-6.29368	1.402708	0.013582
46	C	-7.10548	-2.41097	0.23425
47	C	-2.81628	-4.43497	0.284778
48	H	-0.78383	-3.69558	0.256245
49	H	-4.94991	-4.78452	0.319955
50	C	-8.1556	-1.48394	0.19552
51	H	-8.61022	0.626979	0.073199
52	H	-7.31695	-3.47599	0.281613
53	C	4.806538	0.291045	0.993425
54	C	4.471409	-0.15466	-1.20779
55	C	4.802942	0.823092	2.281626
56	C	5.689733	-0.76117	0.648881
57	C	4.012361	-0.20726	-2.52261
58	C	5.473366	-1.04819	-0.7564
59	C	5.675116	0.274023	3.222291
60	H	4.150435	1.646216	2.553411
61	C	6.550116	-1.28848	1.613669
62	C	4.582097	-1.14793	-3.38143
63	H	3.229907	0.455659	-2.8768
64	C	6.023289	-1.97776	-1.64103
65	C	6.556511	-0.78484	2.921185
66	H	5.662657	0.693933	4.221484
67	H	7.223029	-2.09548	1.336146
68	C	5.591591	-2.04382	-2.97248
69	H	4.21882	-1.17804	-4.4023

70	H	6.79127	-2.65753	-1.28154
71	N	4.066567	0.659083	-0.13972
72	N	-4.08728	-0.4322	0.112242
73	C	-2.46324	-5.93416	0.348827
74	C	-3.06224	-6.65886	-0.88004
75	C	-0.94255	-6.18141	0.353028
76	C	-3.05111	-6.54964	1.64113
77	H	-4.15174	-6.55623	-0.9219
78	H	-2.65365	-6.2515	-1.81191
79	H	-2.82915	-7.73047	-0.84558
80	H	-0.45561	-5.71948	1.219422
81	H	-0.74372	-7.25817	0.399162
82	H	-0.4635	-5.79655	-0.55449
83	H	-2.81757	-7.62013	1.697005
84	H	-2.63424	-6.06339	2.530522
85	H	-4.14031	-6.4442	1.684085
86	C	-9.61467	-1.97995	0.234569
87	C	-10.631	-0.82322	0.186981
88	C	-9.88269	-2.90085	-0.9795
89	C	-9.85593	-2.77409	1.540435
90	H	-10.5156	-0.14298	1.038586
91	H	-10.5395	-0.23713	-0.73456
92	H	-11.6497	-1.22575	0.221827
93	H	-9.21963	-3.77246	-0.98499
94	H	-10.9161	-3.26905	-0.96107
95	H	-9.7306	-2.36102	-1.92112
96	H	-10.8887	-3.14243	1.580697
97	H	-9.1906	-3.64022	1.619226
98	H	-9.68553	-2.14224	2.419666
99	C	6.218331	-3.07886	-3.92762
100	C	5.619838	-3.00994	-5.34562
101	C	7.740713	-2.82569	-4.03822
102	C	5.977358	-4.50463	-3.37688
103	H	4.543133	-3.21468	-5.34467
104	H	5.781872	-2.03092	-5.81093
105	H	6.097547	-3.76151	-5.98438
106	H	8.238142	-2.90107	-3.06539
107	H	8.204504	-3.56083	-4.70779
108	H	7.943284	-1.82561	-4.43843
109	H	6.423901	-5.25369	-4.04266
110	H	6.4185	-4.63801	-2.3834
111	H	4.905192	-4.71694	-3.29609
112	C	7.51367	-1.39016	3.967187
113	C	7.202621	-2.89575	4.142045
114	C	8.975943	-1.22337	3.489376
115	C	7.384205	-0.71393	5.34564

116	H	6.173832	-3.04515	4.489266
117	H	7.319564	-3.44707	3.203057
118	H	7.87973	-3.34503	4.879271
119	H	9.228412	-0.16408	3.365643
120	H	9.670279	-1.65601	4.220511
121	H	9.150906	-1.72108	2.529677
122	H	8.080807	-1.18013	6.05165
123	H	7.62579	0.354156	5.301246
124	H	6.374923	-0.81993	5.759656

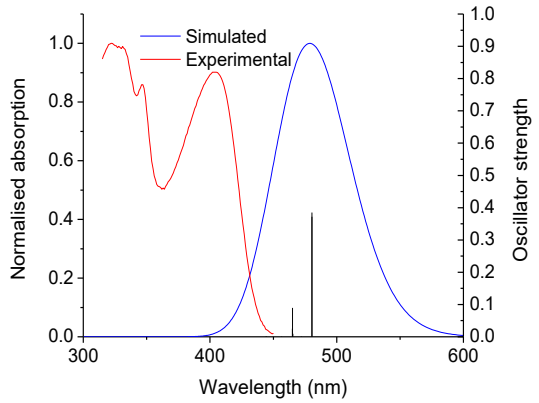


*Figure S13: Simulated and experimental (toluene) absorption spectra for compound **1** with calculated oscillator strengths.*

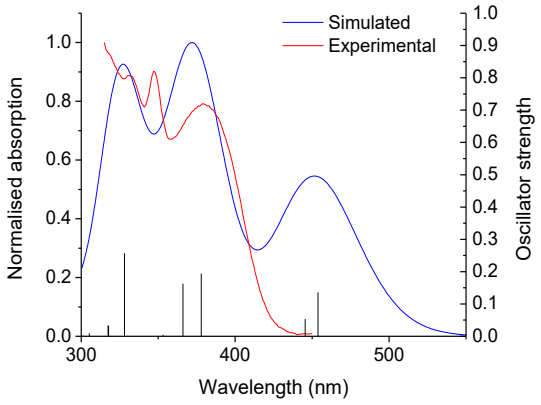


*Figure S14: Simulated and experimental (toluene) absorption spectra for compound **2** with calculated oscillator strengths.*

*Table S3: Transitions to the first 10 singlet and first 10 triplet states calculated for the optimised ground state geometry of **1** at TD-B3LYP/6-31G*. ΔE_{st} = 0.14 eV.*

No.	Transition	Energy (cm^{-1})	Wavelength (nm)	*f*	Orbital contribution
1	$S_0 \rightarrow T_1$	19657	509	0	H-2→LUMO (17%), H-1→L+1 (16%), HOMO→LUMO (46%)
2	$S_0 \rightarrow T_2$	19660	509	0	H-2→L+1 (16%), H-1→LUMO (17%), HOMO→L+1 (46%)
3	$S_0 \rightarrow T_3$	19832	504	0	H-2→LUMO (38%), H-1→L+1 (38%)
4	$S_0 \rightarrow T_4$	20146	496	0	H-15→LUMO (11%), H-4→L+1 (11%), H-3→LUMO (28%)
5	$S_0 \rightarrow T_5$	20153	496	0	H-15→L+1 (11%), H-5→L+1 (15%), H-4→LUMO (12%), H-3→L+1 (22%)
6	$S_0 \rightarrow T_6$	20293	493	0	H-5→LUMO (26%), H-4→L+1 (27%)
7	$S_0 \rightarrow S_1$	20812	481	0.3718	H-2→LUMO (18%), H-1→L+1 (18%), HOMO→LUMO (55%)
8	$S_0 \rightarrow S_2$	20814	480	0.3848	H-2→L+1 (17%), H-1→LUMO (18%), HOMO→L+1 (55%)
9	$S_0 \rightarrow S_3$	21180	472	0.0012	H-2→LUMO (47%), H-1→L+1 (46%)
10	$S_0 \rightarrow S_4$	21487	465	0.0093	H-5→LUMO (12%), H-4→L+1 (25%), H-3→LUMO (44%), H-3→L+1 (12%)
11	$S_0 \rightarrow S_5$	21497	465	0.0895	H-5→LUMO (34%), H-4→L+1 (44%)
12	$S_0 \rightarrow S_6$	21508	465	0.0253	H-5→LUMO (19%), H-5→L+1 (23%), H-4→LUMO (17%), H-3→L+1 (27%)
13	$S_0 \rightarrow T_7$	21872	457	0	H-2→LUMO (27%), H-1→L+1 (28%), HOMO→LUMO (37%)
14	$S_0 \rightarrow T_8$	21874	457	0	H-2→L+1 (26%), H-1→LUMO (29%), HOMO→L+1 (36%)
15	$S_0 \rightarrow S_7$	21908	456	0.0005	H-2→LUMO (28%), H-1→L+1 (29%), HOMO→LUMO (38%)
16	$S_0 \rightarrow S_8$	21910	456	0.0006	H-2→L+1 (27%), H-1→LUMO (31%), HOMO→L+1 (38%)
17	$S_0 \rightarrow T_9$	21977	455	0	H-2→L+1 (50%), H-1→LUMO (46%)
18	$S_0 \rightarrow T_{10}$	21979	455	0	H-2→L+1 (52%), H-1→LUMO (45%)
19	$S_0 \rightarrow T_{11}$	22241	450	0	H-15→L+1 (10%), H-5→L+1 (13%), H-4→LUMO (13%)
20	$S_0 \rightarrow S_9$	22524	444	0.0001	H-4→LUMO (36%), H-3→LUMO (18%), H-3→L+1 (35%)

*Table S4: Transitions to the first 10 singlet and first 10 triplet states calculated for the optimised ground state geometry of **2** at TD-B3LYP/6-31G*. ΔE_{st} = 0.21 eV.*

No.	Transition	Energy (cm^{-1})	Wavelength (nm)	*f*	Orbital contribution
1	$S_0 \rightarrow T_1$	20319	492	0	H-5→LUMO (28%), H-1→LUMO (19%), HOMO→LUMO (30%)
2	$S_0 \rightarrow T_2$	20469	489	0	H-5→LUMO (11%), H-1→LUMO (17%), HOMO→LUMO (52%)
3	$S_0 \rightarrow S_1$	22037	454.	0.1359	HOMO→LUMO (99%)
4	$S_0 \rightarrow S_2$	22450	445	0.0536	H-1→LUMO (98%)
5	$S_0 \rightarrow T_3$	22684	441	0	H-5→LUMO (34%), H-1→LUMO (49%)
6	$S_0 \rightarrow T_4$	24317	411	0	H-8→LUMO (34%), H-1→LUMO (13%), HOMO→L+1 (34%)
7	$S_0 \rightarrow T_5$	24731	404	0	H-8→LUMO (46%), HOMO→L+1 (30%)
8	$S_0 \rightarrow T_6$	25360	394	0	H-2→L+3 (60%), HOMO→L+9 (10%)
9	$S_0 \rightarrow T_7$	25410	394	0	H-3→L+2 (63%), H-1→L+8 (11%)
10	$S_0 \rightarrow T_8$	25530	392	0	H-1→L+1 (66%)
11	$S_0 \rightarrow T_9$	25942	385	0	H-4→LUMO (67%), HOMO→LUMO (11%)
12	$S_0 \rightarrow T_{10}$	26214	381	0	H-1→L+2 (22%), H-1→L+3 (18%), HOMO→L+2 (12%), HOMO→L+3 (38%)
13	$S_0 \rightarrow T_{11}$	26322	380	0	H-1→L+1 (10%), H-1→L+2 (29%), HOMO→L+2 (15%), HOMO→L+3 (20%)
14	$S_0 \rightarrow S_3$	26459	378	0.194	HOMO→L+1 (97%)
15	$S_0 \rightarrow S_4$	26567	376	0.0004	H-2→LUMO (99%)
16	$S_0 \rightarrow T_{12}$	26607	376	0	H-2→LUMO (92%)
17	$S_0 \rightarrow T_{13}$	26732	374	0	H-3→LUMO (95%)
18	$S_0 \rightarrow T_{14}$	26738	374	0	H-3→LUMO (99%)
19	$S_0 \rightarrow S_4$	27318	366	0.1627	H-1→L+1 (97%)
20	$S_0 \rightarrow S_5$	28308	353	0.0044	H-8→LUMO (70%), H-5→LUMO (26%)

*Table S5: Transitions to the first 10 singlet and first 10 triplet states calculated for the optimised ground state geometry of **1** at TDA-PBE0/def2-SVP. ΔE_{st} = 0.18 eV.*

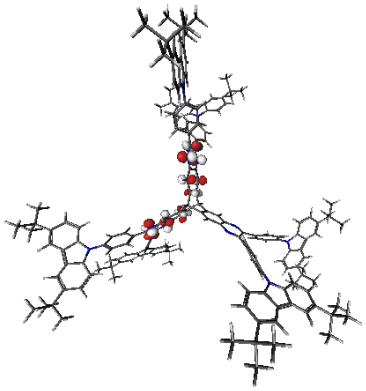
No.	Transition	Energy (cm^{-1})	Wavelength (nm)	*f*	Major contribs
1	$S_0 \rightarrow T_1$	21121	473	0	H-2→LUMO (15%), H-1→L+1 (14%), HOMO→LUMO (41%)
2	$S_0 \rightarrow T_2$	21124	473	0	H-2→L+1 (14%), H-1→LUMO (14%), HOMO→L+1 (42%)
3	$S_0 \rightarrow T_3$	21333	469	0	H-2→LUMO (34%), H-1→L+1 (35%)
4	$S_0 \rightarrow T_4$	21983	455	0	H-15→LUMO (11%), H-4→L+1 (11%), H-3→LUMO (29%)
5	$S_0 \rightarrow T_5$	21989	455	0	H-15→L+1 (11%), H-5→L+1 (15%), H-4→LUMO (12%), H-3→L+1 (21%)
6	$S_0 \rightarrow T_6$	22109	452	0	H-5→LUMO (26%), H-4→L+1 (26%)
7	$S_0 \rightarrow S_1$	22598	443	0.4803	H-2→LUMO (19%), H-1→L+1 (19%), HOMO→LUMO (52%)
8	$S_0 \rightarrow S_2$	22600	442	0.4983	H-2→L+1 (18%), H-1→LUMO (19%), HOMO→L+1 (52%)
9	$S_0 \rightarrow S_3$	23053	434	0.0021	H-2→LUMO (46%), H-1→L+1 (45%)
10	$S_0 \rightarrow S_4$	23359	428	0.0139	H-4→L+1 (23%), H-3→LUMO (46%), H-3→L+1 (11%)
11	$S_0 \rightarrow S_5$	23369	428	0.1281	H-5→LUMO (34%), H-4→L+1 (47%)
12	$S_0 \rightarrow S_6$	23386	428	0.0277	H-5→LUMO (19%), H-5→L+1 (22%), H-4→LUMO (17%), H-3→L+1 (27%)
13	$S_0 \rightarrow T_7$	23718	422	0	H-15→L+1 (13%)

14	$S_0 \rightarrow T_8$	23718	422	0	H-15→LUMO (13%)
15	$S_0 \rightarrow T_9$	23763	421	0	H-23→L+1 (15%), H-22→LUMO (14%)
16	$S_0 \rightarrow T_{10}$	23963	417	0	H-2→LUMO (26%), H-1→L+1 (26%), HOMO→LUMO (37%)
17	$S_0 \rightarrow S_7$	24016	416	0.001	H-2→LUMO (24%), H-1→L+1 (25%), HOMO→LUMO (38%)
18	$S_0 \rightarrow S_8$	24018	416	0.0011	H-2→L+1 (23%), H-1→LUMO (27%), HOMO→L+1 (37%)
19	$S_0 \rightarrow S_9$	24096	415	0	H-2→L+1 (51%), H-1→LUMO (45%)
20	$S_0 \rightarrow S_{10}$	24696	405	0.0001	H-4→LUMO (34%), H-3→LUMO (12%), H-3→L+1 (43%)

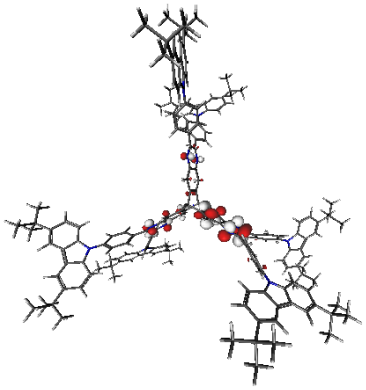
*Table S6: Transitions to the first 10 singlet and first 10 triplet states calculated for the optimised ground state geometry of **2** at TDA-PBE0/def2-SVP. ΔE_{st} = 0.25 eV.*

No.	Transition	Energy (cm-1)	Wavelength (nm)	*f*	Major contribs
1	$S_0 \rightarrow T_1$	21829	458	0	H-4→LUMO (14%), HOMO→LUMO (75%)
2	$S_0 \rightarrow T_2$	22267	449	0	H-5→LUMO (38%), H-1→LUMO (38%)
3	$S_0 \rightarrow T_3$	23761	421	0	H-8→LUMO (39%), H-5→LUMO (25%), H-1→LUMO (26%)
4	$S_0 \rightarrow S_1$	23818	420	0.1885	HOMO→LUMO (98%)
5	$S_0 \rightarrow S_2$	24260	412	0.0739	H-1→LUMO (97%)
6	$S_0 \rightarrow T_4$	25543	392	0	H-8->LUMO (44%), H-5→LUMO (11%), H-1→LUMO (24%)
7	$S_0 \rightarrow T_5$	25890	386	0	H-1→LUMO (10%), HOMO→L+1 (61%)
8	$S_0 \rightarrow T_6$	26618	376	0	H-1→L+1 (22%), H-1→L+2 (30%), HOMO→L+2 (13%), HOMO→L+3 (10%)
9	$S_0 \rightarrow T_7$	26806	373	0	H-1→L+2 (17%), H-1→L+3 (19%), HOMO→L+3 (46%)
10	$S_0 \rightarrow T_8$	27057	370	0	H-4→LUMO (14%), H-1→L+1 (38%), H-1→L+2 (16%)
11	$S_0 \rightarrow T_9$	27262	367	0	H-2→L+3 (67%)
12	$S_0 \rightarrow T_{10}$	27303	366	0	H-3→L+2 (70%)
13	$S_0 \rightarrow S_3$	27854	359	0.2195	HOMO→L+1 (94%)
14	$S_0 \rightarrow S_4$	28595	350	0.0003	H-2→LUMO (98%)
15	$S_0 \rightarrow S_5$	28792	347	0.0155	H-8→LUMO (10%), H-3→LUMO (79%)
16	$S_0 \rightarrow S_6$	28793	347	0.1867	H-1→L+1 (90%)
17	$S_0 \rightarrow S_7$	28900	346	0.0077	H-8→LUMO (61%), H-5→LUMO (19%), H-3→LUMO (15%)
18	$S_0 \rightarrow S_8$	32048	312	0.2909	H-5→L+1 (10%), H-4→LUMO (82%)
19	$S_0 \rightarrow S_9$	32607	307	0.0402	H-1→L+2 (27%), H-1→L+3 (11%), HOMO→L+2 (16%), HOMO→L+3 (36%)
20	$S_0 \rightarrow S_{10}$	32650	306	0.0356	H-1→L+2 (29%), H-1→L+3 (10%), HOMO→L+2 (17%), HOMO→L+3 (32%)

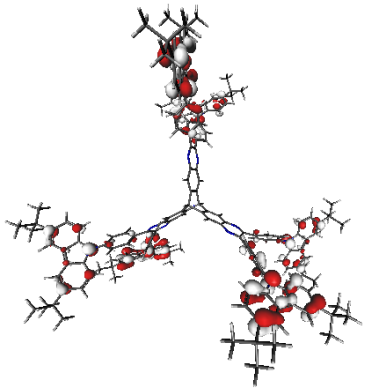
LUMO+1
−2.26 eV



LUMO
−2.26 eV



HOMO
−5.16 eV



HOMO−1
−5.18 eV

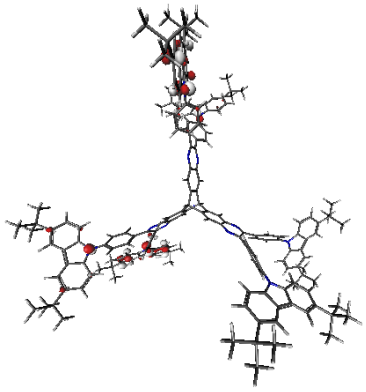
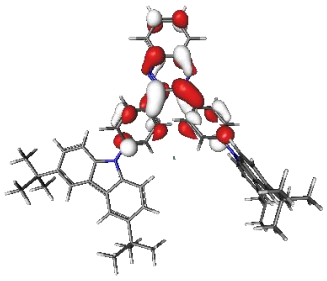
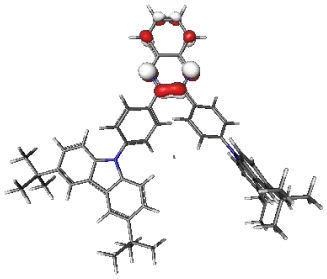


*Figure S15: Compound **1** HOMO and LOMO plots with energies calculated at B3LYP/6−31G*.*

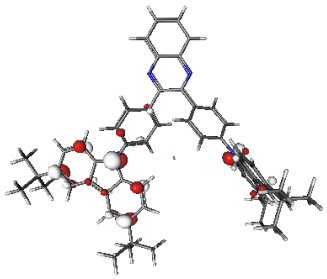
LUMO+1
−1.41 eV



LUMO
−2.06 eV



HOMO
−5.15 eV



HOMO−1
−5.22 eV

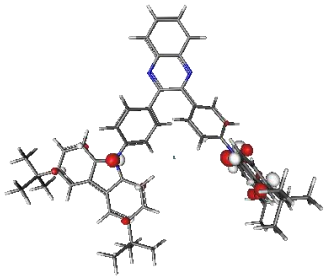


*Figure S16: Compound **2** HOMO and LUMO plots with energies calculated at B3LYP/6−31G*.*

Electrochemistry

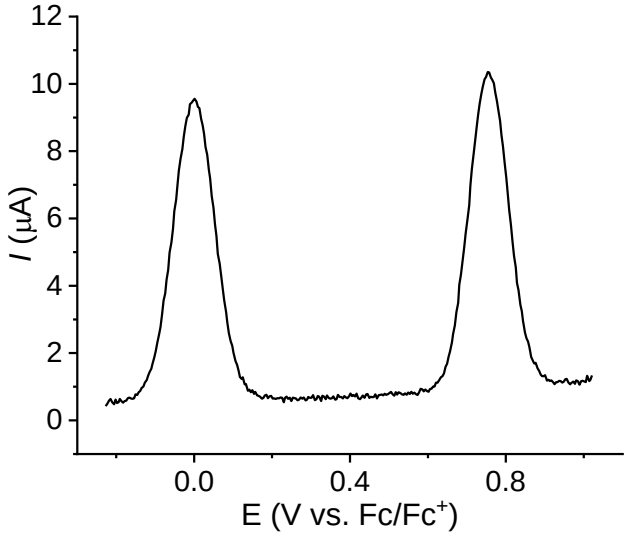


*Figure S17: SWV of a solution containing equimolar quantities of compound **2** and ferrocene as a coulometric standard.*

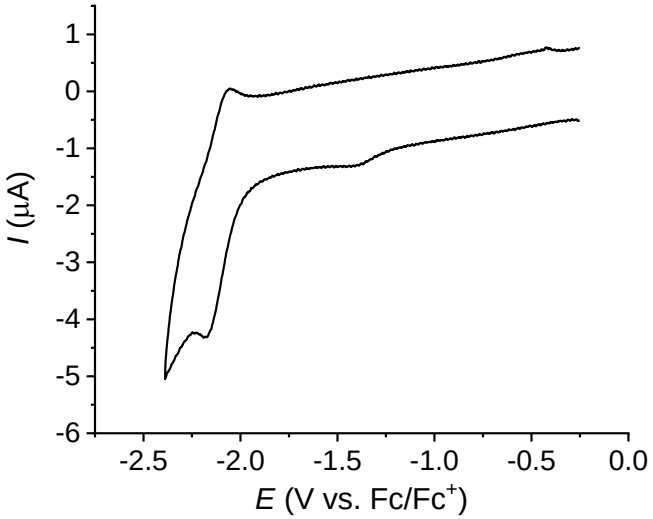


*Figure S18: CV of compound **2** showing a single irreversible reduction.*

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