

Supplementary Materials

Tailoring Carbene-Metal-Amides for Thermally Activated Delayed Fluorescence: A Computationally Guided Study on the Effect of Cyclic (Alkyl)(amino)carbenes

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Computational Results

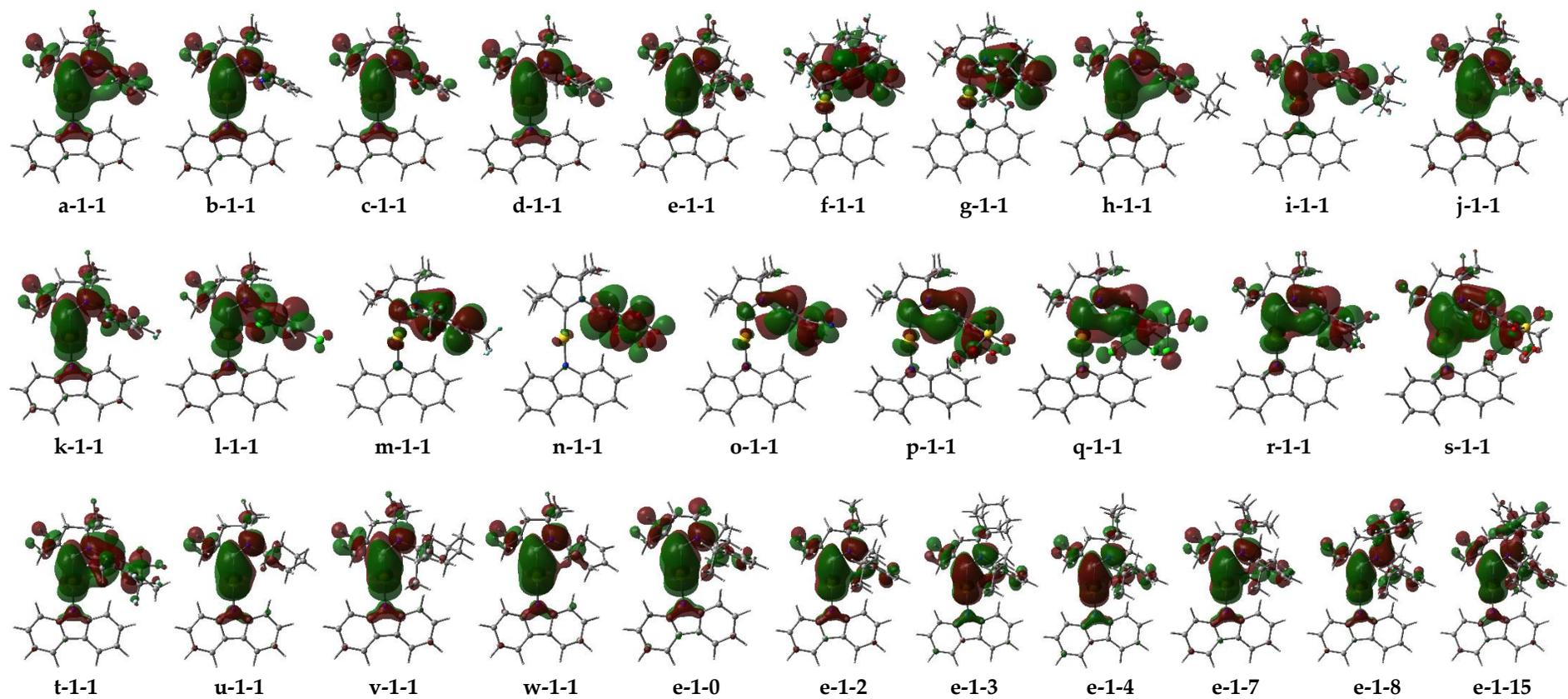


Figure S1. LUMO orbitals of complexes modified at positions 1 and 3

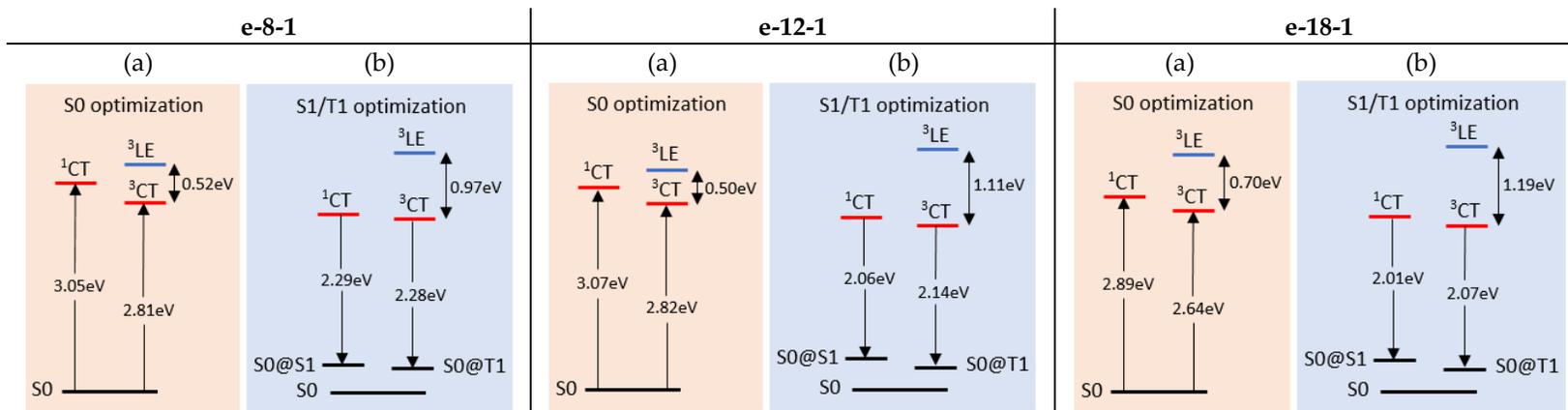


Figure S2. Schematic energy of **e-8-1**, **e-12-1**, and **e-18-1** complexes: (a) vertical excitation energies indicated by the upward arrows; (b) energy levels at optimized S1 and T1 geometries with fluorescence (left) and phosphorescence (right) indicated by the downward arrows.

Table S1. Calculated parameters for complexes modified at position **1**

	%Au in HOMO	%Au in LUMO	Overlap integral	Vertical excitations						Dipole moments (D)		Bond dissociation energy			
				¹ CT - S1 E (eV)	³ CT - T1 E (eV)	³ LE		ΔE_{ST} (eV)	Oscillator strength	S0	S1@S0	Au-N bond		Au-C bond	
						E (eV)	Character					kJ/mol	eV	kJ/mol	eV
a-1-1	2.9	13.9	0.36	3.03	2.73	3.34	T2 (³ LE(A))	0.30	0.2073	11.7	-2.5	367.4	3.81	385.9	4.00
b-1-1	2.8	15.2	0.38	2.96	2.64	3.36	T2 (³ LE(A))	0.32	0.2061	9.6	-3.6	366.6	3.80	391.4	4.06
c-1-1	3.0	13.9	0.35	3.22	2.93	3.33	T2 (³ LE(A))	0.29	0.1900	10.7	-4.8	372.8	3.86	398.2	4.13
d-1-1	3.1	14.4	0.35	3.26	2.98	3.32	T2 (³ LE(A))	0.28	0.1791	10.2	-4.3	373.8	3.87	403.4	4.18
e-1-1	2.8	12.9	0.36	3.11	2.80	3.35	T2 (³ LE(A))	0.31	0.2005	10.8	-2.7	376.7	3.90	401.3	4.16
f-1-1	2.5	1.9	0.23	2.78	2.54	3.31	T6 (mixed ³ CT and ³ LE(A))	0.24	0.1331	9.0	-7.6	357.4	3.70	374.2	3.88
g-1-1	2.7	2.3	0.20	2.67	2.53	3.34	T5 (³ LE(A))	0.14	0.0699	10.4	-6.6	370.0	3.83	374.4	3.88
h-1-1	2.9	14.5	0.35	3.07	2.79	3.33	T2 (³ LE(A))	0.28	0.1820	11.4	-2.7	371.4	3.85	390.9	4.05
i-1-1	2.8	10.0	0.33	2.91	2.61	3.38	T3 (mixed ³ CT and ³ LE(A))	0.30	0.2037	12.2	-3.9	364.1	3.77	378.7	3.92
j-1-1	2.9	13.9	0.37	3.05	2.74	3.34	T2 (³ LE(A))	0.31	0.2033	11.3	-2.6	371.9	3.85	395.3	4.10
k-1-1	2.7	12.3	0.36	2.99	2.67	3.35	T2 (³ LE(A))	0.32	0.2146	11.2	-2.6	364.5	3.78	379.7	3.94
l-1-1	2.7	7.9	0.32	2.96	2.65	3.36	T4 (³ LE(A))	0.31	0.1910	11.1	-2.9	367.0	3.80	384.5	3.99
m-1-1	2.7	2.2	0.21	2.48	2.35	3.36	T6 (³ LE(A))	0.13	0.0661	10.9	-8.9	364.8	3.78	380.0	3.94
n-1-1	2.8	1.0	0.14	1.73	1.68	3.36	T6 (mixed ³ CT and ³ LE(A))	0.05	0.0219	12.6	-14.3	355.6	3.69	369.3	3.83
o-1-1	2.7	2.3	0.19	2.27	2.17	3.38	T6 (³ LE(A))	0.10	0.0483	12.7	-13.1	355.2	3.68	368.5	3.82
p-1-1	3.4	4.5	0.23	2.89	2.75	3.11	T2 (mixed ³ CT and ³ LE(A))	0.14	0.0645	9.4	-13.4	390.4	4.05	412.5	4.28
q-1-1	3.1	5.8	0.26	2.81	2.59	3.22	T3 (mixed ³ CT and ³ LE(A))	0.22	0.1008	11.0	-6.6	373.9	3.87	390.9	4.05
r-1-1	2.8	8.0	0.31	2.76	2.49	3.38	T5 (³ LE(A))	0.27	0.1539	11.8	-5.8	361.4	3.75	375.5	3.89
s-1-1	3.4	7.7	0.29	3.11	2.89	3.26	T2 (mixed ³ CT and ³ LE(A))	0.22	0.1095	8.8	-9.5	398.0	4.12	419.9	4.35
t-1-1	2.8	9.3	0.34	2.88	2.57	3.36	T3 (³ LE(A))	0.31	0.1916	11.3	-4.0	366.1	3.79	385.6	4.00
u-1-1	3.0	16.1	0.35	3.17	2.89	3.34	T2 (³ LE(A))	0.28	0.1916	11.8	-2.9	362.9	3.76	386.6	4.01
v-1-1	3.0	14.0	0.35	3.21	2.92	3.34	T2 (³ LE(A))	0.29	0.1991	11.4	-3.0	361.1	3.74	387.3	4.01
w-1-1	3.0	16.1	0.35	3.13	2.86	3.34	T2 (³ LE(A))	0.27	0.1841	11.6	-2.9	362.6	3.76	387.0	4.01

Table S2. Calculated parameters for complexes modified at position 2

	%Au in HOMO	%Au in LUMO	Overlap integral	Vertical excitations						Dipole moments (D)		Bond dissociation energy			
				¹ CT - S1 E (eV)	³ CT - T1 E (eV)	³ LE		ΔE_{ST} (eV)	Oscillator strength	S0	S1@S0	Au-N bond		Au-C bond	
						E (eV)	Character					kJ/mol	eV	kJ/mol	eV
j-1-1	2.9	13.9	0.37	3.05	2.74	3.34	T2 (³ LE(A))	0.31	0.2033	11.3	-2.6	371.9	3.85	395.3	4.10
j-2-1	2.9	11.9	0.36	3.11	2.81	3.33	T2 (³ LE(A))	0.30	0.1976	11.2	-2.8	372.1	3.86	397.4	4.12
j-3-1	3.0	12.4	0.36	3.02	2.71	3.33	T2 (³ LE(A))	0.31	0.1922	10.8	-2.8	370.9	3.84	389.8	4.04
j-4-1	2.9	13.7	0.37	3.06	2.76	3.33	T2 (³ LE(A))	0.30	0.2015	11.3	-2.6	372.8	3.86	396.8	4.11
j-5-1	2.9	13.5	0.37	3.04	2.73	3.34	T2 (³ LE(A))	0.31	0.2058	11.2	-2.8	372.3	3.86	395.8	4.10
j-6-1	3.0	12.8	0.36	3.11	2.81	3.33	T2 (³ LE(A))	0.30	0.1935	11.0	-2.8	373.7	3.87	401.1	4.16
f-1-1	2.5	1.9	0.23	2.78	2.54	3.31	T6 (mixed ³ CT and ³ LE(A))	0.24	0.1331	9.0	-7.6	357.4	3.70	374.2	3.88
f-2-1	2.6	2.8	0.23	2.78	2.60	3.36	T5 (mixed ³ CT and ³ LE(A))	0.18	0.1030	9.1	-6.3	370.2	3.84	389.0	4.03
f-3-1	2.7	3.7	0.27	2.68	2.47	3.35	T5 (mixed ³ CT and ³ LE(A))	0.21	0.1228	8.7	-6.1	362.7	3.76	370.5	3.84
f-4-1	2.6	1.7	0.22	2.79	2.57	3.31	T5 (mixed ³ CT and ³ LE(A))	0.22	0.1288	8.9	-7.7	358.2	3.71	376.0	3.90
f-5-1	2.5	1.8	0.22	2.77	2.54	3.30	T6 (mixed ³ CT and ³ LE(A))	0.23	0.1330	8.8	-7.8	357.5	3.71	376.0	3.90
f-6-1	3.0	3.6	0.25	2.80	2.60	3.33	T3 (mixed ³ CT and ³ LE(A))	0.20	0.1160	8.8	-5.8	371.5	3.85	396.9	4.11
m-1-1	2.7	2.2	0.21	2.48	2.35	3.36	T6 (³ LE(A))	0.13	0.0661	10.9	-8.9	364.8	3.78	380.0	3.94
m-2-1	2.7	2.0	0.20	2.50	2.38	3.36	T6 (³ LE(A))	0.12	0.0596	10.8	-9.2	365.5	3.79	382.6	3.97
m-3-1	2.8	2.4	0.22	2.51	2.36	3.35	T6 (³ A)	0.15	0.0742	10.7	-8.8	366.4	3.80	377.2	3.91
m-4-1	2.7	2.1	0.20	2.49	2.36	3.36	T6 (³ LE(A))	0.13	0.0648	11.0	-9.2	365.7	3.79	382.1	3.96
m-5-1	2.7	2.2	0.21	2.49	2.35	3.36	T6 (³ LE(A))	0.14	0.0666	10.9	-9.0	364.9	3.78	380.7	3.95
m-6-1	2.8	2.0	0.19	2.51	2.38	3.36	T6 (³ LE(A))	0.13	0.0512	10.6	-9.2	366.6	3.80	389.6	4.04
e-1-1	2.8	12.9	0.36	3.11	2.80	3.35	T2 (³ LE(A))	0.31	0.2005	10.8	-2.7	376.7	3.90	401.3	4.16
e-2-1	2.8	10.8	0.35	3.17	2.88	3.35	T2 (³ LE(A))	0.29	0.1952	10.7	-3.0	375.5	3.89	403.2	4.18
e-3-1	3.0	11.4	0.36	3.07	2.77	3.34	T2 (³ LE(A))	0.30	0.1927	10.5	-2.9	376.5	3.90	394.9	4.09
e-4-1	2.8	12.7	0.36	3.12	2.82	3.35	T2 (³ LE(A))	0.30	0.1994	10.8	-2.8	377.3	3.91	403.1	4.18
e-5-1	2.8	12.6	0.36	3.10	2.79	3.35	T2 (³ LE(A))	0.31	0.2029	10.7	-2.9	376.5	3.90	401.8	4.16
e-7-1	3.0	11.9	0.36	3.06	2.76	3.34	T2 (³ LE(A))	0.30	0.1920	10.6	-2.9	372.5	3.86	395.8	4.10
e-8-1	3.0	8.6	0.32	3.05	2.81	3.33	T2 (³ LE(A))	0.24	0.1516	9.7	-4.7	376.6	3.90	397.2	4.12

e-9-1	2.7	10.4	0.36	3.08	2.81	3.33	T2 (³ LE(A))	0.27	0.1726	10.7	-3.1	381.5	3.95	398.8	4.13
e-10-1	2.7	10.4	0.36	3.05	2.74	3.35	T2 (³ LE(A))	0.31	0.2068	10.7	-3.1	371.3	3.85	395.2	4.10
e-11-1	3.0	7.6	0.32	3.15	2.89	3.32	T2 (³ LE(A))	0.26	0.1713	11.0	-3.7	369.8	3.83	386.7	4.01
e-12-1	2.9	5.4	0.28	3.07	2.82	3.32	T2 (³ LE(A))	0.25	0.1659	10.8	-5.0	370.3	3.84	384.9	3.99
e-13-1	3.1	8.4	0.32	3.15	2.90	3.33	T2 (³ LE(A))	0.25	0.1669	10.7	-4.0	374.5	3.88	390.1	4.04
e-14-1	2.6	9.9	0.37	2.92	2.59	3.37	T3 (³ LE(A))	0.33	0.2199	10.1	-5.6	368.0	3.81	385.9	4.00
e-15-1	3.0	6.7	0.32	3.01	2.75	3.33	T2 (³ LE(A))	0.26	0.1672	10.4	-4.4	373.1	3.87	390.9	4.05
e-16-1	3.2	3.9	0.28	3.08	2.88	3.32	T2 (³ LE(A))	0.20	0.1233	10.3	-5.0	377.2	3.91	376.1	3.90
e-17-1	3.9	8.4	0.28	3.36	3.14	3.31	T2 (³ LE(A))	0.22	0.1212	11.1	-4.1	387.4	4.01	417.0	4.32
e-18-1	2.9	5.1	0.30	2.89	2.64	3.34	T2 (³ LE(A))	0.25	0.1567	10.2	-5.6	371.7	3.85	374.8	3.88
e-19-1	2.9	1.8	0.21	2.58	2.44	3.33	T4 (mixed ³ CT and ³ LE(A))	0.14	0.0696	10.0	-9.4	374.3	3.88	365.3	3.79
e-20-1	2.9	4.9	0.31	2.64	2.38	3.30	T4 (mixed ³ CT and ³ LE(A))	0.26	0.1514	10.7	-8.0	363.9	3.77	372.6	3.86

Table S3. Calculated parameters for complexes modified at position **3**

	%Au in HOMO	%Au in LUMO	Overlap integral	Vertical excitations						Dipole moments (D)		Bond dissociation energy			
				¹ CT - S1 E (eV)	³ CT - T1 E (eV)	³ LE		ΔE_{ST} (eV)	Oscillator strength	S0	S1@S0	Au-N bond		Au-C bond	
						E (eV)	Character					kJ/mol	eV	kJ/mol	eV
e-1-0	2.8	13.5	0.37	3.03	2.71	3.35	T2 (³ LE(A))	0.32	0.1994	10.6	-2.6	369.4	3.83	392.1	4.06
e-1-1	2.8	12.9	0.36	3.11	2.80	3.35	T2 (³ LE(A))	0.31	0.2005	10.8	-2.7	376.7	3.90	401.3	4.16
e-1-2	2.8	12.9	0.36	3.11	2.80	3.35	T2 (³ LE(A))	0.31	0.2037	11.0	-2.7	374.8	3.88	402.8	4.18
e-1-3	2.7	12.0	0.36	3.08	2.77	3.34	T2 (³ LE(A))	0.31	0.2176	11.5	-2.6	372.9	3.87	393.7	4.08
e-1-4	2.8	13.0	0.36	3.12	2.82	3.35	T2 (³ LE(A))	0.30	0.2078	11.3	-2.5	377.3	3.91	402.7	4.17
e-1-7	2.8	12.3	0.36	3.06	2.75	3.35	T2 (³ LE(A))	0.31	0.2176	11.2	-2.6	372.9	3.86	395.1	4.09
e-1-8	2.8	10.2	0.34	3.08	2.80	3.35	T2 (³ LE(A))	0.28	0.2182	11.5	-3.7	375.0	3.89	393.2	4.08
e-1-15	2.7	10.5	0.35	2.98	2.68	3.35	T2 (³ LE(A))	0.30	0.2218	11.3	-3.2	371.9	3.85	386.7	4.01

X-Ray Crystallography

Crystals suitable for X-ray diffraction study were obtained by slow layer diffusion of hexanes/petroleum ether into dichloromethane solution for **e-2-1** at room temperature. Crystals were mounted in oil on glass fiber and fixed on the diffractometer in a cold nitrogen stream. Data were collected using XtaLAB AFC11 (RINC): quarter-chi single diffractometer at 100 K. Data were processed using the CrystAlisPro-CCD and –RED software. Multi-scan absorption correction was applied for all crystals. For the final refinement, the contribution of severely disordered CH₂Cl₂ molecules in the crystals **e-2-1** was accounted for by applying a solvent void mask calculated using BYPASS, implemented through Olex2. Structures were solved by direct method/intrinsic phasing and refined by the full-matrix least-squares against F² in an anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms with C-H = 0.95–1.00 Å, and U_{iso} = 1.2–1.5 U_{eq} (parent atom). All calculations were performed using the SHELXL software and Olex2 graphical user interface.

e-2-1, CCDC number 2259783, C₃₅H₄₇AuN₂ (*M* = 676.67 g/mol): monoclinic, space group P2₁/c (no. 14), *a* = 9.71163(5) Å, *b* = 18.40218(10) Å, *c* = 17.11055(10) Å, β = 95.3962(5)°, *V* = 3044.36(3) Å³, *Z* = 4, *T* = 100.00(10) K, μ(Cu Kα) = 9.241 mm⁻¹, *D*_{calc} = 1.476 g/cm³, 20350 reflections measured (7.072° ≤ 2Θ ≤ 151.65°), 6090 unique (*R*_{int} = 0.0181, *R*_{sigma} = 0.0150) which were used in all calculations. The final *R*₁ was 0.0207 (*I* > 2σ(*I*)) and *wR*₂ was 0.0564 (all data).

Experimental Details

General Considerations. Unless stated otherwise, all reactions were carried out in air. Solvents were distilled and dried as required. Potassium *tert*-butoxide and carbazole were purchased from FluoroChem. The carbene complex (EtL)AuCl [1] were obtained according to literature procedures. ¹H and ¹³C{¹H} NMR spectra were recorded using a Bruker Avance 500 MHz NMR spectrometer. ¹H NMR spectra were referenced to CD₂Cl₂ at δ 5.32 (¹³C, δ 53.84) ppm. All electrochemical experiments were performed using an Autolab PGSTAT 302N computer-controlled potentiostat. Cyclic voltammetry (CV) was performed using a three-electrode configuration consisting of either a glassy carbon macrodisk working electrode (GCE) (diameter of 3 mm; BASi, Indiana, USA) combined with a Pt wire counter electrode (99.99 %; GoodFellow, Cambridge, UK) and an Ag wire pseudo-reference electrode (99.99 %; GoodFellow, Cambridge, UK). The GCE was polished between experiments using alumina slurry (0.3 μm), rinsed in distilled water and subjected to brief sonication to remove any adhering alumina microparticles. The metal electrodes were then dried in an oven at 100 °C to remove residual traces of water, the GCE was left to air dry and residual traces of water were removed under vacuum. The Ag wire pseudoreference electrodes were calibrated to the ferrocene/ferrocenium couple in THF at the end of each run to allow for any drift in potential, following IUPAC recommendations [2]. All electrochemical measurements were performed at ambient temperatures under an inert Ar atmosphere in THF containing complex under study (0.14 mM) and supporting electrolyte [n-Bu₄N][PF₆] (0.13 mM). Data were recorded with Autolab NOVA software (v. 1.11). Elemental analyses were performed by the University of Manchester. UV-visible absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV/vis spectrometer. Mass spectrometry data was obtained using APCI(ASAP) (Atmospheric Solids Analysis Probe) at the University of Manchester.

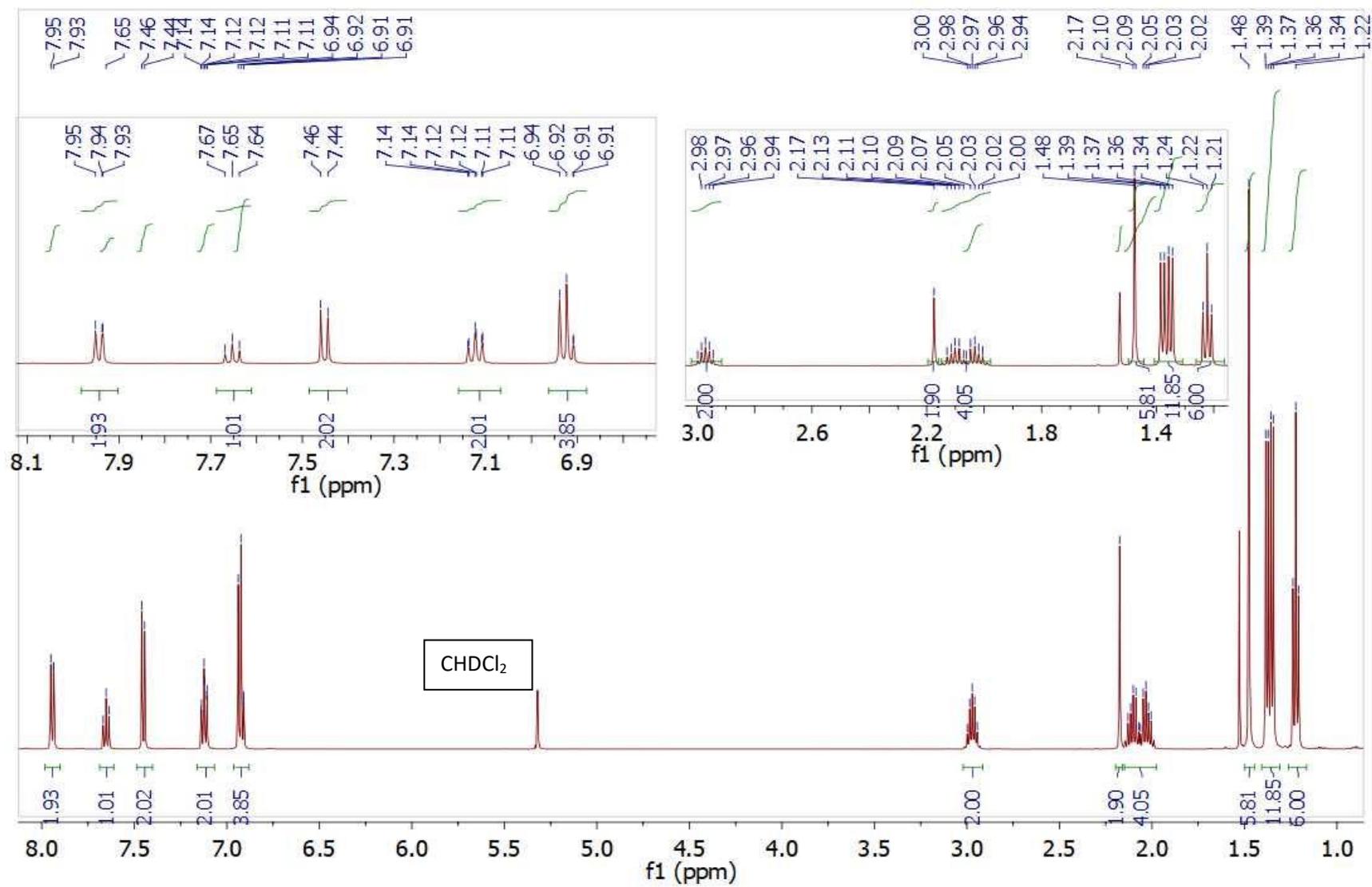


Figure S3. ^1H NMR (500 MHz, CD_2Cl_2) for e-2-1

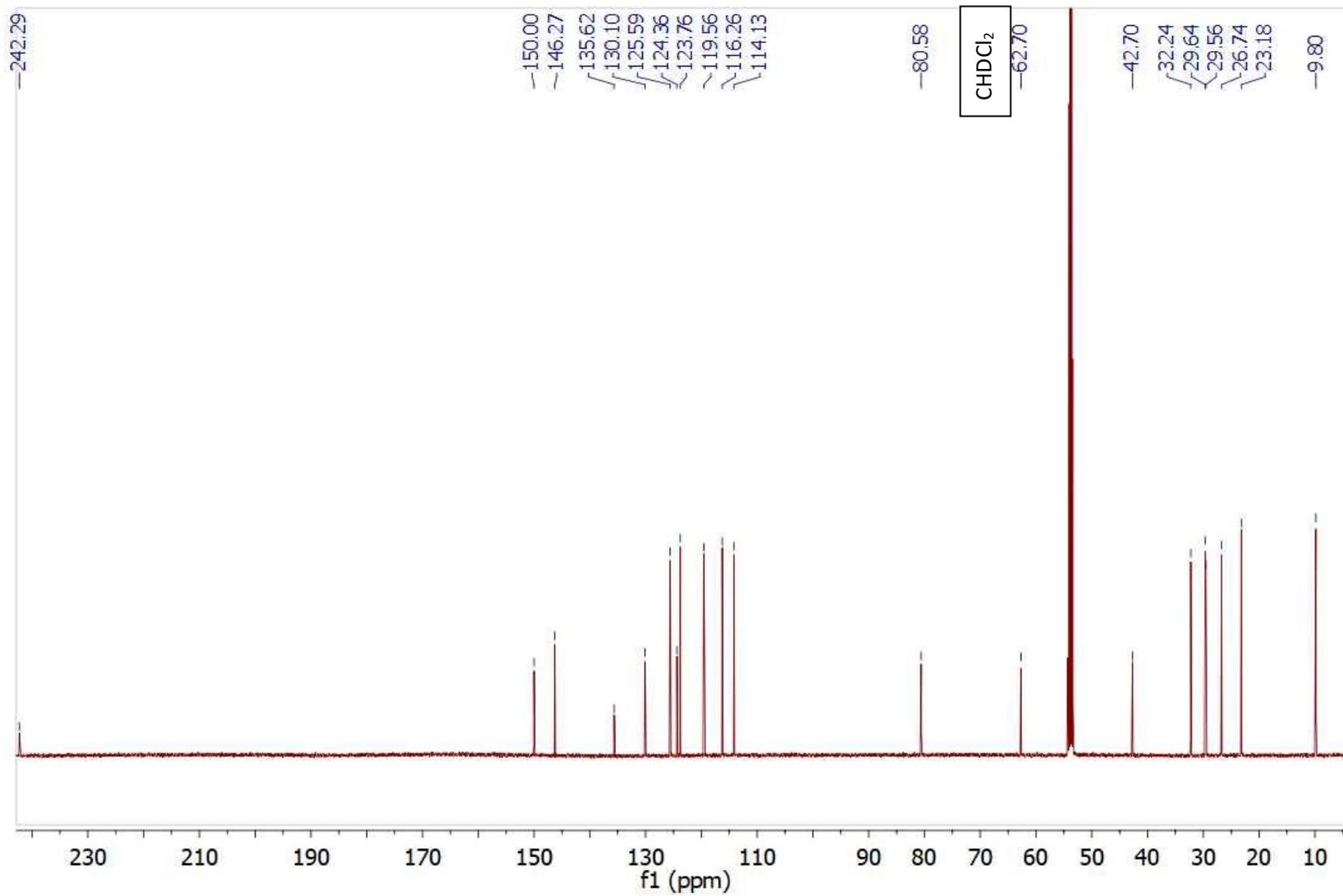


Figure S4. ^{13}C NMR (125 MHz, CD_2Cl_2) for e-2-1

Table S4. UV-vis data for **e-2-1** in various solvents

	λ_{abs} [nm], ($10^3 \epsilon/M^{-1} \text{ cm}^{-1}$)			
	DCM	THF	Toluene	MCH
e-2-1	387 (sh) (4.4)	379 (8.0)	392 (8.2)	408 (8.4)
	367 (11.3)	367 (12.5)	367 (10.1)	365 (7.3)

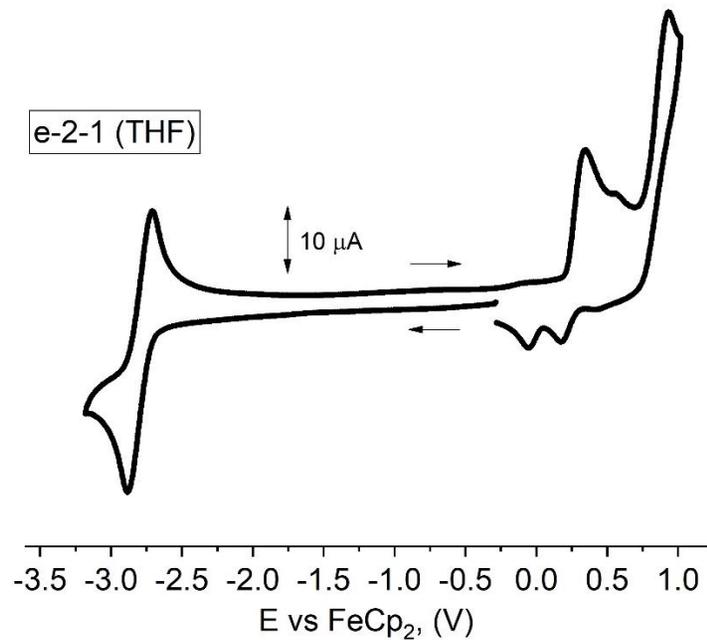


Figure S5. Full range cyclic voltammogram for **e-2-1**. Recorded using a glassy carbon electrode in THF solution (1.4 mM) with $[\text{n-Bu}_4\text{N}]\text{PF}_6$ as supporting electrolyte (0.13 M), scan rate 0.1 V s^{-1} .

Table S5. Formal electrode potentials (peak position E_p for irreversible and $E_{1/2}$ for quasi-reversible processes (*), V , vs. FeCp₂), onset potentials (E , V , vs. FeCp₂), peak-to-peak separation in parentheses for quasi-reversible processes (ΔE_p in mV), E_{HOMO}/E_{LUMO} (eV) and band gap values (ΔE , eV) for the redox changes exhibited.^a

	Reduction		E_{LUMO} (eV)	Oxidation				E_{HOMO} (eV)	ΔE (eV)
	E_{1st}	$E_{onset\ red}$		E_{1st}	$E_{onset\ ox}$	E_{2nd}	E_{3rd}		
e-2-1	-2.79 (176)	-2.72	-2.67	0.15 (397)	0.22	0.37 (384)	0.93	-5.61	2.94

^a In tetrahydrofuran solution, recorded using a glassy carbon electrode, concentration 1.4 mM, supporting electrolyte [ⁿBu₄N][PF₆] (0.13 M), measured at 0.1 Vs⁻¹.

^b In difluorobenzene solution, recorded using a glassy carbon electrode, concentration 1.4 mM, supporting electrolyte [ⁿBu₄N][PF₆] (0.13 M), measured at 0.1 Vs⁻¹. $E_{HOMO} = -(E_{onset\ ox\ Fe/Fc^+} + 5.39)$ eV; $E_{LUMO} = -(E_{onset\ red\ Fe/Fc^+} + 5.39)$ eV [3].

Photophysical Characterization

UV-visible absorption spectra were recorded using a Varian Cary 5000 UV-Vis-NIR spectrometer. Photoluminescence measurements were recorded on an Edinburgh Instruments FLS980 spectrometer with a solids mount attachment where appropriate. Absolute photoluminescence quantum yields were recorded using a Hamamatsu Quantaaurus-QY C11347-11. Quantum yields have been measured in air for solid samples and under nitrogen for solutions. Time resolved luminescence data were collected on a time-correlated single photon counting (TCSPC) Edinburgh Instruments FLS980 spectrometer using F-900 software. A xenon flash lamp and EPL pulsed diode lasers were used as excitation sources. The collected data were analyzed using F-900 software.

References

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