

Supplementary Information

(24 Pages including the cover page)

**A Trinuclear Bright Red Luminophore Containing
Cyclometallated Ir(III) Motifs**

Vadapalli Chandrasekhar,* S. M. Wahidur Rahaman, Tanima Hajra, Dipak Das, Tapas

Ghatak, Shahnawaz R. Rather, Pratik Sen,* and Jitendra K. Bera*

Department of Chemistry, Indian Institute of Technology Kanpur,

Kanpur 208016, India.

Phone: +91-512-259 7336. Fax: +91-512-259 7436.

* E-mail: jbera@iitk.ac.in

Contents

Materials and methods.	S-3
X-ray Data Collection and Refinement.	S-4
Theoretical Study.	S-5
Syntheses.	S-5
Table S1. Crystallographic Data and Refinement Parameters for compounds 1 and 2 .	S-7
Table S2. Selected Bond Distances (Å) and bond Angles (°) for 1 .	S-8
Table S3. Selected Bond Distances (Å) and bond Angles (°) for 2 .	S-9
Figure S1. NMR spectrum of 1 .	S-10
Figure S2. NMR spectrum of 2 .	S-10
Figure S3. Cyclic voltammograms for 1 .	S-11
Figure S4. Cyclic voltammograms for 2 .	S-12
Figure S5. DFT optimized structure of 1 .	S-13
Figure S6. DFT optimized structure of 2 .	S-13
Figure S7. Contour diagrams of 1 .	S-14
Figure S8. Contour diagrams of 2 .	S-15
Figure S9. DFT optimized structure of $\{L^1.2H\}^{2+}$.	S-16
Figure S10. DFT optimized structure of $\{L^2.H\}^+$.	S-16
Figure S11. Ground and the triplet state energy difference of $\{L^1.2H\}^{2+}$.and $\{L^2.H\}^+$	S-17
Table S4. DFT optimized coordinates for 1 .	S-18
Table S5. DFT optimized coordinates for 2 .	S-23

Materials and methods

All manipulations were carried out under an inert atmosphere with the use of standard Schlenk-line techniques. Glassware were dried prior to use. Solvents were dried by conventional methods, distilled over nitrogen and deoxygenated prior to use. $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Arora Matthey, India. Triflic acid, silver carbonate, and 2-phenyl pyridine were synthesized according to the literature procedure. Reaction of the sodium salt of 1,2,4-triazolide with 2-chloro-5,7-dimethyl-1,8-naphthyridine provided L^1 . L^2 was prepared by the Friedlander condensation of 2-aminonicotinaldehyde with the corresponding acyl derivatives. Elemental analyses were carried out by using a Thermo quest CE instrument model EA/110 CHNS-O elemental analyzer. Infrared spectra were recorded in the range $4000\text{-}400\text{ cm}^{-1}$ on a Vertex 70 Bruker Spectrophotometer on KBR pallets. ^1H NMR spectra were obtained on a JEOL-JNM LAMDA 500 model. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. ESI-MS analyses were performed on a Waters Micromass Quattro Micro triple quadrupole mass spectrometer. UV-Visible spectra were recorded using a Jasco V-670 UV/Vis absorption spectrophotometer. Cyclic voltammetric studies were performed on a BAS Epsilon electrochemical workstation in acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF_6) as the supporting electrolyte. The working electrode was a BAS Pt disk electrode, the reference electrode was Ag/AgCl and the auxiliary electrode was a Pt wire. The ferrocene/ferrocenium couple occurs at $E_{1/2} = +0.51$ (70) V versus Ag/AgCl under the same experimental conditions. The potentials are reported in volts (V); the ΔE ($E_{p,a} - E_{p,c}$) values are in millivolts (mV) at a scan rate 100 mVs^{-1} . Emission spectra were recorded using a Fluorolog FL3-21 (Horiba Jobin Yvon) spectrofluorometer equipped with a xenon flash lamp and also using a PTI QuantaMaster Model QM-4 scanning spectrofluorometer equipped with a 75-watt xenon

lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector for both visible and NIR regions. Emission quantum yields were determined by comparison with the emission of a solution of quinine sulfate ($\Phi = 0.545$) in 1N of H_2SO_4 , employed as a standard.¹⁵ The excitation wavelength used was 350 nm. The quantum yields were then calculated using the expression, $\Phi_S = \Phi_R (A_S/A_R) (n_S^2/n_R^2)$. Here, the subscripts S and R denote sample and reference respectively, Φ is the fluorescence quantum yield, A is the integrated area under the corrected fluorescence spectra, n is the refractive index of the solvent.

X-ray Data Collection and Refinement: Single-crystal X-ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. All the data were collected at 100(2) K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,³ and the data were corrected for absorption using the SADABS program.⁴ The structures were solved and refined with the SHELX suite of programs.⁵ All hydrogen atoms were included in the final stages of the refinement and were refined with a typical riding model. Structure solution and refinement details for compounds **1** and **2** are provided in the supporting information. All non-hydrogen atoms were refined with anisotropic thermal parameters. All non-hydrogen atoms of compound **1** except C34, C28, C53 and N14 were refined with anisotropic thermal parameters. Anisotropic treatment of these four atoms resulted non-positive definite displacement tensors and were therefore subjected to isotropic refinement. The “SQUEEZE” option in PLATON program⁶ was used to remove a disordered solvent molecule from the overall intensity data of compound **1** and **2**. Pertinent crystallographic data are summarized in Table S1. ORTEP-32⁷ was used to produce the diagrams (40% probability thermal ellipsoids). CCDC – 820921 (**1**) and 820922 (**2**) contain the supplementary

crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Theoretical Study. Calculations were performed using density functional theory (DFT) with Becke's three parameter hybrid exchange functional⁸ and the Lee-Yang-Parr correlation functional (B3LYP). Geometry optimized structures were characterized fully via analytical frequency calculations as minima on the potential energy surface. The double- ζ basis set of Hay and Wadt (LanL2DZ) with a small core (1s2s2p3s3p3d4s4p4d) effective core potential (ECP)¹⁰ was used for the Ir. The ligand atoms H, C and N atoms were described using the 6-31G(d,p) basis sets was employed. Vertical excited state calculations of low lying singlet and triplet electronic states were performed within the TD-DFT domain using B3LYP functional and 6-31G(d,p) basis set. All calculations were performed with the Gaussian 03 (G03)¹¹ suite of programs. Gaussview 3.0 was used for generating the orbital plots.

Synthesis

[{Ir(ppy)₂]₃(L¹)₂](OTf)₃ (1**).** A mixture containing [(ppy)₂Ir(μ -Cl)]₂ (100 mg, 0.09 mmol) and AgOTf (50 mg, 0.20 mmol) in 20 mL of acetone was refluxed under N₂ for 2 hours. The yellow slurry was allowed to cool and AgCl was removed by filtration. The filtrate was evaporated to dryness under reduced pressure to get yellow oil. The oily mass was redissolved in 20 mL of 1,2-dichloroethane (DCE) followed by the addition of L¹ (30 mg, 0.13 mmol). This solution was heated under reflux for 12 h under a N₂ atmosphere. Subsequently, the volume of the bright yellow colored solution was reduced to ~2 mL and diethyl ether was added to induce precipitation and solid precipitate was filtered, washed with diethyl ether (5 mL, 3 times) and dried in vacuum. This compound was identified as **1**. Crystals suitable for X-ray data collection were obtained by layering hexane onto the dichloroethane solution of **1**. Yield: 126 mg (85%).

Anal. Calc. for $C_{93}H_{70}F_9Ir_3N_{16}O_9S_3$: C, 46.55; H, 2.94; N, 9.34%. Found: C, 46.54; H, 2.70; N, 9.24%. 1H NMR ($CDCl_3$, 500 MHz, δ): 9.37 (s, 1H), 9.12 (d, $J = 5.4$, 1H), 9.05 (d, $J = 5.4$, 3H), 9.01 (s, 1H), 8.67 (d, $J = 3.8$, 1H), 8.66 (d, $J = 3.8$, 1H), 8.34 (d, $J = 3.8$, 2H), 8.30 (s, 1H), 8.15 (s, 1H), 8.10 (d, $J = 8.8$, 2H), 8.07–7.97 (m, 10H), 7.92 (dt, $J = 7.5$, $J = 1.6$, 2H), 7.70 (d, $J = 8.1$, 2H), 7.64 (dd, $J = 7.6$, $J = 1.2$, 4H), 7.44–7.41 (m, 4H), 7.37–7.34 (m, 3H), 7.26 (t, $J = 6.7$, 1H), 7.00 (dt, $J = 7.5$, $J = 1.2$, 1H), 6.94–6.86 (m, 6H), 6.78 (dt, $J = 7.6$, $J = 1.1$, 1H), 6.72 (dt, $J = 7.7$, $J = 1.2$, 5H), 6.23 (d, $J = 7.7$, 1H), 6.16 (d, $J = 6.9$, 1H), 6.02 (d, $J = 7.7$, 3H), 2.69 (s, 3H), 2.68 (s, 3H), 2.67 (s, 3H), 2.64 (s, 3H). IR (KBr pellet, ν cm^{-1}): 3097(br), 2922(w), 2851(w), 1740(m), 1480(s), 1269(vs), 1160(m), 1030(s), 758(s), 637(s). ESI-MS: m/z 726.19. $[Ir(ppy)_2(L^1)]^+$, m/z 767.23 $[Ir(ppy)_2(L^1)(CH_3CN)]^+$.

$[Ir(ppy)_2(L^2)](OTf)$ (2). The reaction of $[(ppy)_2Ir(\mu-Cl)]_2$ (90 mg, 0.08 mmol), AgOTf (45 mg, 0.18 mmol) and L^2 (10 mg, 0.05 mmol) was carried out following a procedure similar to that described for the synthesis of **1**. Yield: 125 mg (87%). Anal. Calc. for $C_{35}H_{24}F_3IrN_6O_3S_1$: C, 49.00; H, 2.82; N, 9.80%. Found: C, 48.11; H, 2.75; N, 9.71%. 1H NMR ($CDCl_3$, 500 MHz, δ): 9.89 (s, 1H), 8.76 (s, 2H), 8.67 (d, $J = 3.1$, 1H), 8.38 (dd, $J = 8.3$, $J = 1.8$, 1H), 8.18 (dd, $J = 4.1$, $J = 1.9$, 1H), 8.04 (d, $J = 8.3$, 1H), 7.96 (dd, $J = 2.9$, $J = 1.3$, 1H), 7.88 (d, $J = 8.3$, 1H), 7.82–7.78 (m, 2H), 7.71–7.67 (m, 2H), 7.65 (dd, $J = 7.6$, $J = 1.6$, 1H), 7.51–7.48 (m, 2H), 7.05 (dt, $J = 7.6$, $J = 1.3$, 1H), 6.92–6.84 (m, 5H), 6.17–6.14 (m, 2H). IR (KBr pellet, ν cm^{-1}): 3061(br), 2922(w), 2851(w), 1604(s), 1476(s), 1260(vs), 1165(m), 1030(s), 758(s), 637(s). ESI-MS: m/z 709.17 $[Ir(ppy)_2(L^2)]^+$.

Table S1. Crystallographic Data and Pertinent Refinement Parameters for Compounds **1** and **2**.

	1 • (CH₂)₂Cl₂	2
Empirical formula	C ₉₇ H ₇₈ Cl ₄ F ₉ Ir ₃ N ₁₆ O ₉ S ₃	C ₃₅ H ₂₄ F ₃ IrN ₆ O ₃ S
Formula Weight	2597.33	857.86
Crystal System	Triclinic	Monoclinic
Space Group	P-1	P21/n
a (Å)	13.6930(18)	8.6494(8)
b (Å)	16.735(2)	31.080(3)
c (Å)	26.001(3)	12.1964(11)
α (deg)	88.665(2)	90.00
β (deg)	86.297(2)	94.251(2)
γ (deg)	85.269(2)	90.00
V (Å ³)	5924.4(13)	3269.7(5)
Z	2	4
ρ _{calcd} (g cm ⁻³)	1.456	1.743
μ (mm ⁻¹)	3.573	4.211
F(000)	2544	1680
Reflections		
Collected	41017	29144
Independent	20009	8093
Observed [I > 2σ (I)]	13483	6113
No. of variables	1094	438
GOF	1.052	1.021
R _{int}		
Final R indices	R1 = 0.0780	R1 = 0.0424
[I > 2σ(I)] _a	wR2 = 0.2076	wR2 = 0.0966
R indices (all data) ^a	R1 = 0.1061	R1 = 0.0662
	wR2 = 0.2224	wR2 = 0.1127

^aR₁ = Σ ||F_o| - |F_c||/Σ|F_o| with F_o² > 2σ(F_o²). wR₂ = [Σw(|F_o² - |F_c²||²/Σ|F_o²|²)]^{1/2}

Table S2. Selected Bond Distances (Å) and Bond Angles (°) of **1**.

Bond Distances			
Ir1–C11	1.969(12)	Ir2–C46	1.993(14)
Ir1–C12	2.029(13)	Ir2–C35	2.019(12)
Ir1–N1	2.038(10)	Ir2–N9	2.032(9)
Ir1–N2	2.059(9)	Ir2–N8	2.046(11)
Ir1–N5	2.130(10)	Ir2–N7	2.160(9)
Ir1–N4	2.242(10)	Ir2–N10	2.174(10)
Ir3–C80	2.014(13)	Ir3–C69	2.021(15)
Ir3–N16	2.064(12)	Ir3–N15	2.089(14)
Ir3–N11	2.151(10)	Ir3–N13	2.211(11)
Bond Angles			
C11–Ir1–C12	88.5(5)	C46–Ir2–N7	177.0(5)
C11–Ir1–N1	94.9(5)	C35–Ir2–N7	89.9(4)
C12–Ir1–N1	80.5(5)	N9–Ir2–N7	95.9(4)
C11–Ir1–N2	80.3(4)	N8–Ir2–N7	88.2(4)
C12–Ir1–N2	93.6(5)	C46–Ir2–N10	88.9(4)
N1–Ir1–N2	172.5(4)	C35–Ir2–N10	177.1(4)
C11–Ir1–N5	91.5(4)	N9–Ir2–N10	84.0(4)
C12–Ir1–N5	176.4(5)	N8–Ir2–N10	98.0(4)
N1–Ir1–N5	103.1(4)	N7–Ir2–N10	92.8(4)
N2–Ir1–N5	82.9(4)	C80–Ir3–C69	89.7(5)
C11–Ir1–N4	165.4(4)	N11–Ir3–N13	74.2(4)
C12–Ir1–N4	106.1(4)	N15–Ir3–N13	85.2(5)
N1–Ir1–N4	88.2(4)	N16–Ir3–N13	97.6(4)
N2–Ir1–N4	97.8(4)	C69–Ir3–N13	102.3(5)
N5–Ir1–N4	73.9(4)	C80–Ir3–N13	167.8(5)
C46–Ir2–C35	88.4(5)	N15–Ir3–N11	99.8(5)
C46–Ir2–N9	81.8(5)	N16–Ir3–N11	87.0(4)
C35–Ir2–N9	96.7(5)	C69–Ir3–N11	176.0(5)
C46–Ir2–N8	94.0(5)	C80–Ir3–N11	93.7(5)
C35–Ir2–N8	81.1(5)	C69–Ir3–N16	91.4(6)
N9–Ir2–N8	175.3(4)	C80–Ir3–N15	98.9(5)
C80–Ir3–N16	79.7(5)	N16–Ir3–N15	173.1(5)
C69–Ir3–N15	81.9(7)		

Table S3. Selected Bond Distances (Å) and Bond Angles (°) of **2**.

Bond Distances			
Ir1–C11	2.012(6)	Ir1–N4	2.205(4)
Ir1–C12	2.014(5)	Ir1–N5	2.133(4)
Ir1–N2	2.049(5)	Ir1–N1	2.042(4)
Bond Angles			
C11–Ir1–C12	85.3(2)	C11–Ir1–N1	81.2(2)
N2–Ir1–N4	89.36(17)	N5–Ir1–N4	75.76(16)
C12–Ir1–N4	104.95(19)	N1–Ir1–N4	96.66(17)
N2–Ir1–N5	99.28(18)	C11–Ir1–N4	169.70(19)
C12–Ir1–N5	179.3(2)	N1–Ir1–N5	86.26(17)
C11–Ir1–N5	94.02(19)	N1–Ir1–N2	172.70(18)
C12–Ir1–N2	80.6(2)	C11–Ir1–N2	93.6(2)
C12–Ir1–N1	93.8(2)		

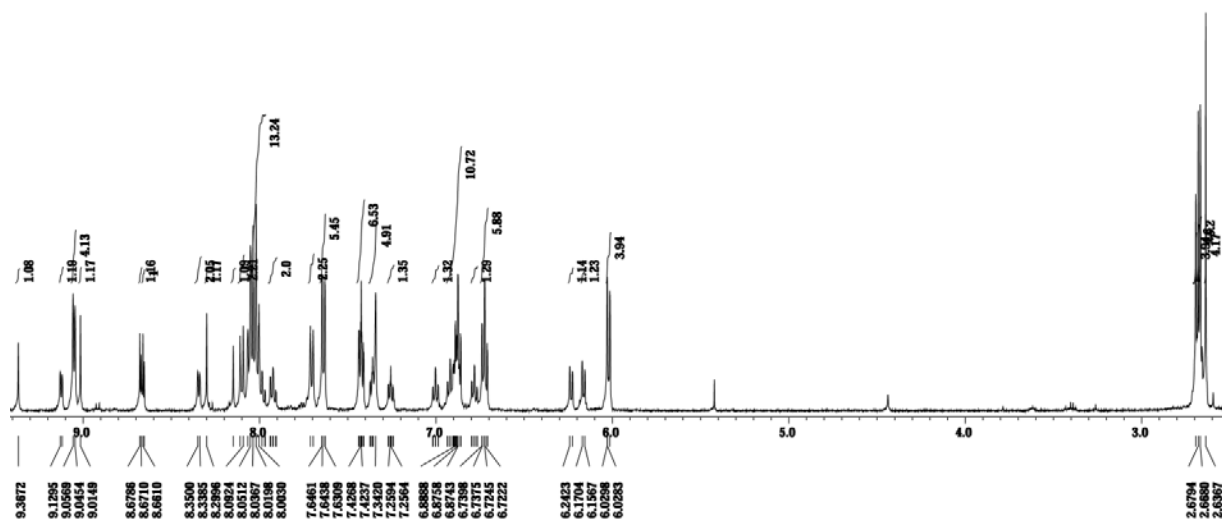


Figure S1. ^1H NMR spectrum of 1.

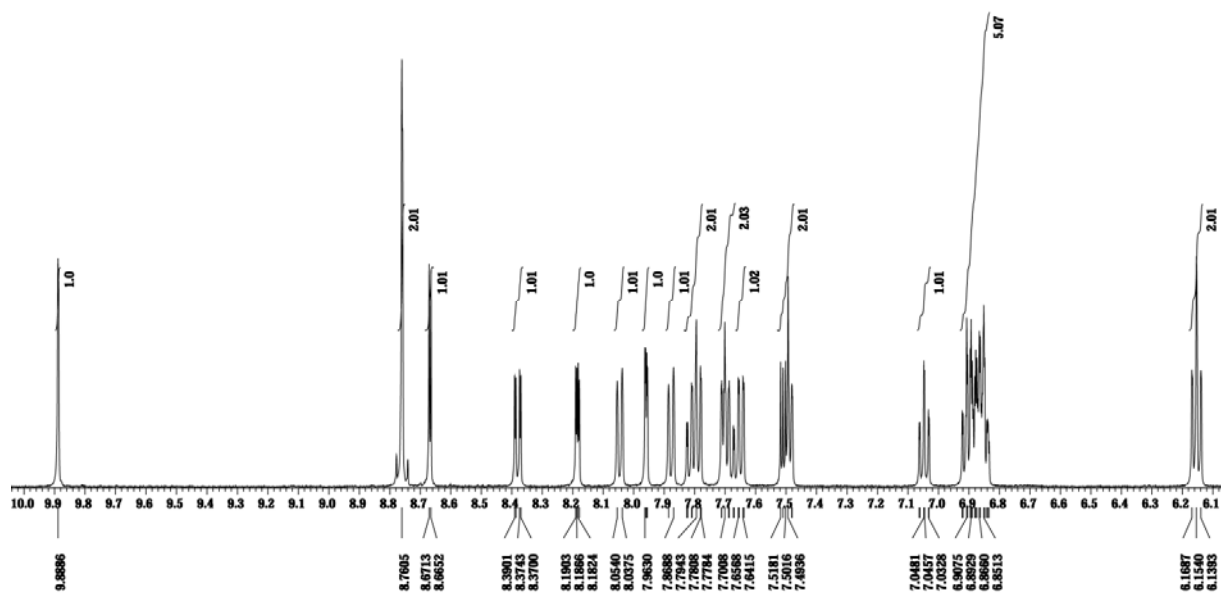
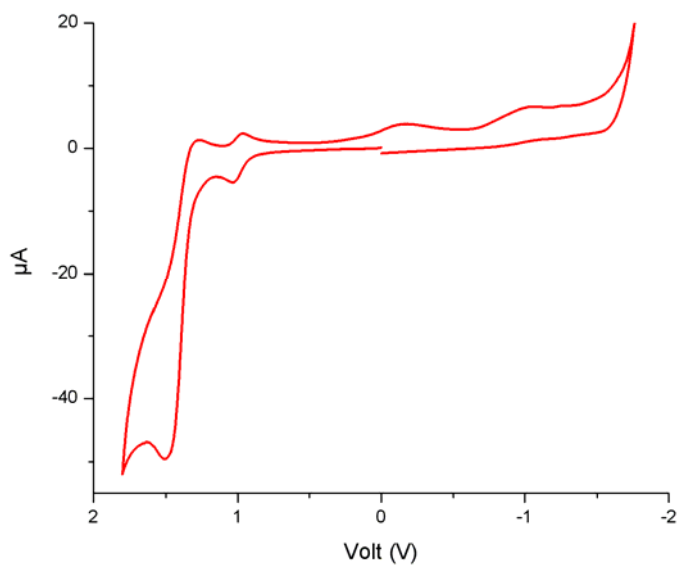
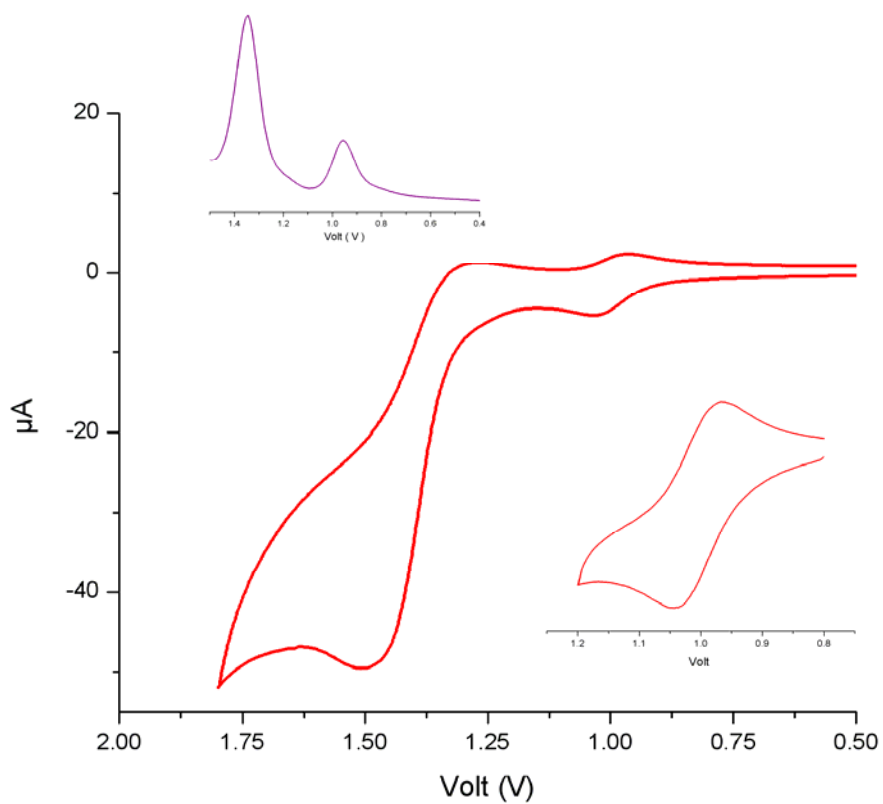


Figure S2. ^1H NMR spectrum of 2.

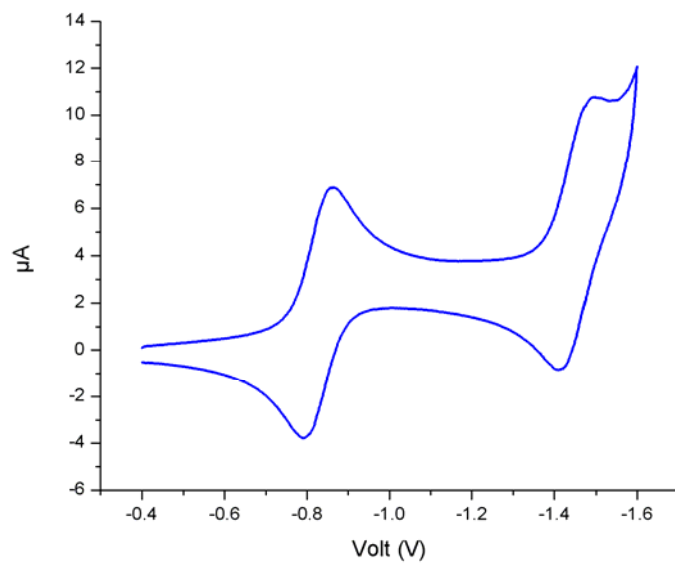


(a)

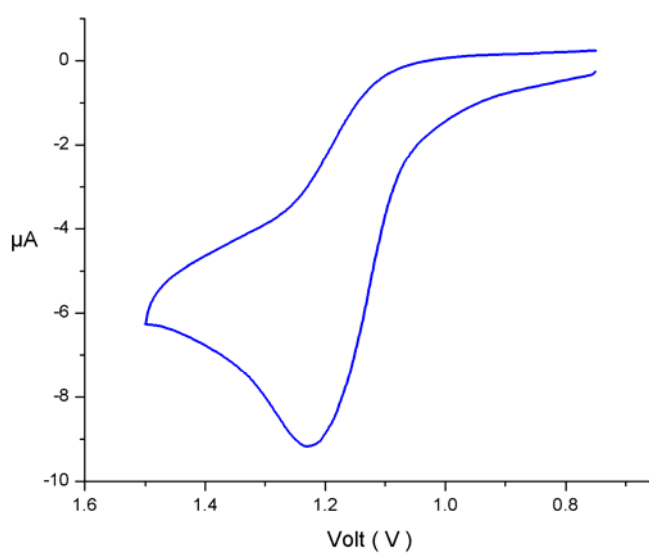


(b)

Figure S3. Cyclic voltammograms for **1** showing (a) the complete cycle, (b) the oxidation [Inset: the DPV diagram (top) and the expanded region of the first oxidation (bottom)] at a scan rate of 100 mV/s with 0.1 M [Bu₄N][PF₆] as supporting electrolyte



(a)



(b)

Figure S4. Cyclic voltammograms for **2** showing (a) the reduction and (b) the oxidation processes at a scan rate of 100 mV/s with 0.1 M [Bu₄N][PF₆] as supporting electrolyte.

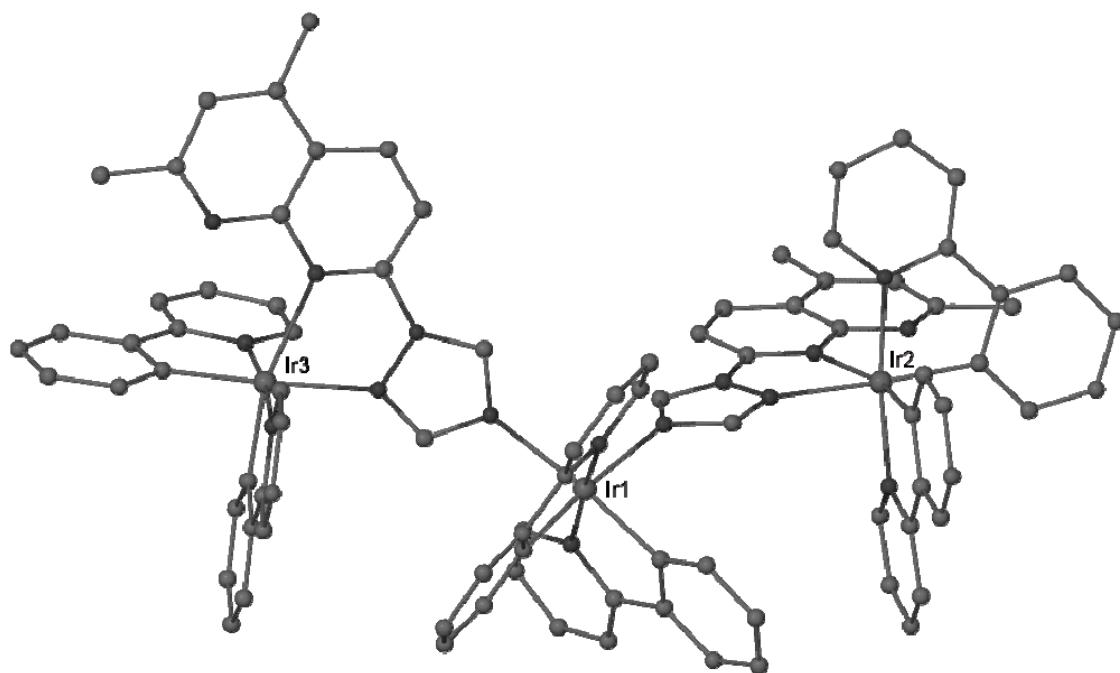


Figure S5. DFT optimized structure of [1].

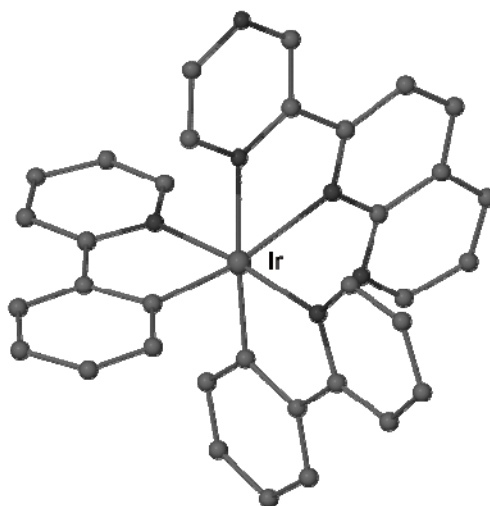


Figure S6. DFT optimized structure of [2].

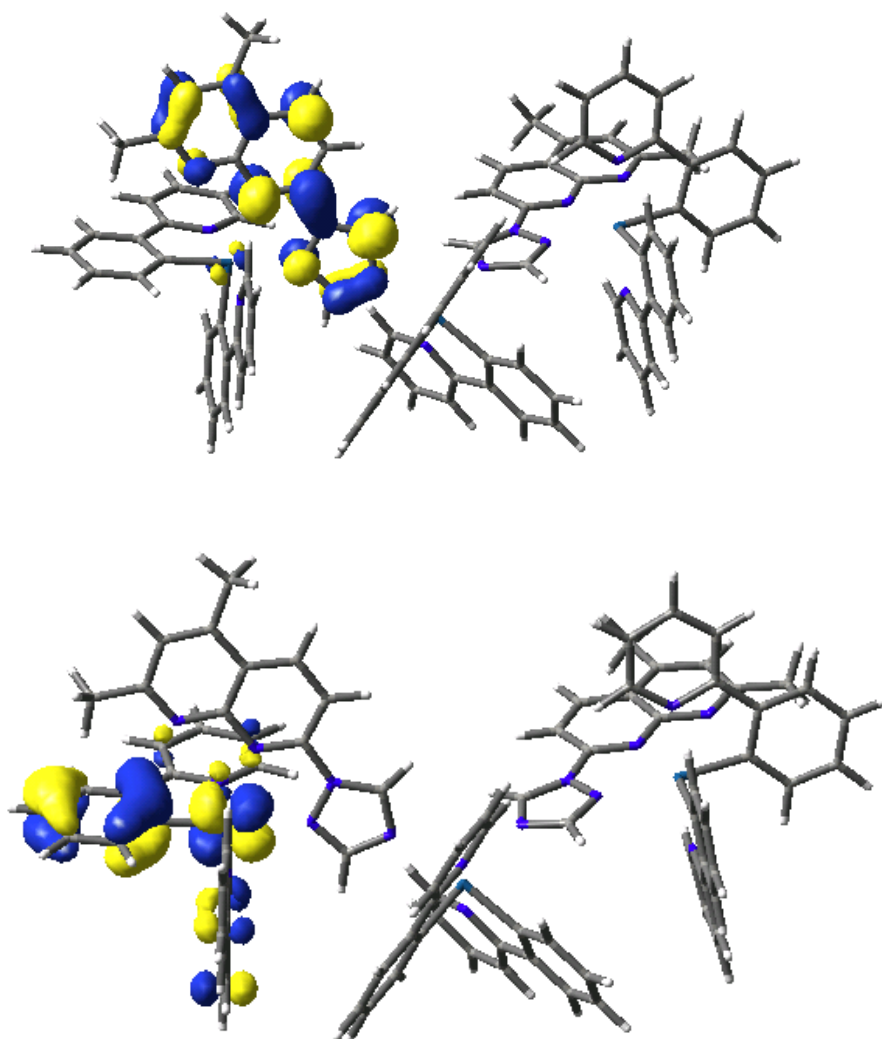


Figure S7. Contour surfaces of HOMO (bottom) and LUMO (top) computed for the DFT optimized structure of **1**.

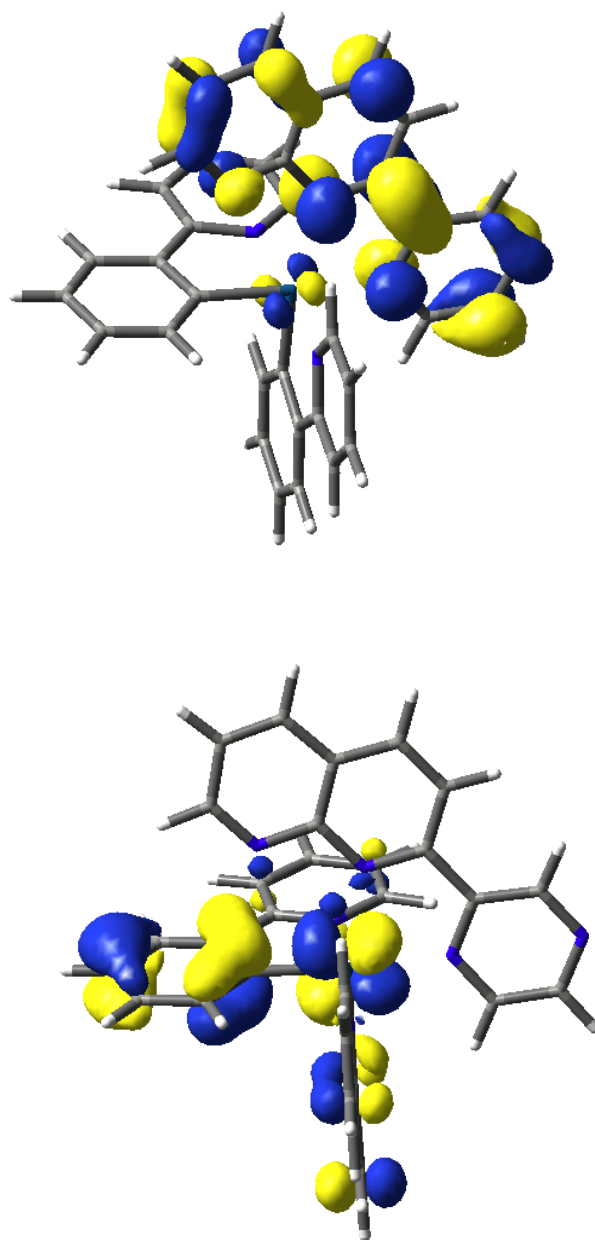


Figure S8. Contour surfaces of HOMO (bottom) and LUMO (top) computed for the DFT optimized structure of **2**.

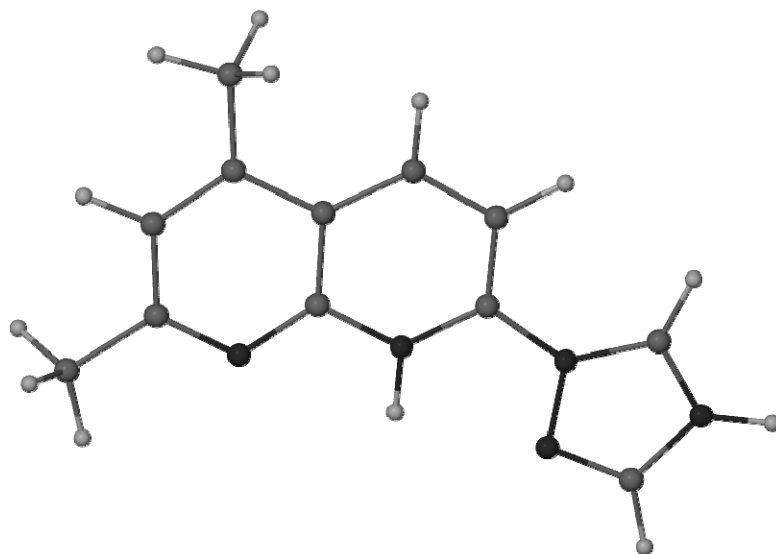


Figure S9. DFT optimized structure of $\{L^1.2H\}^{2+}$.

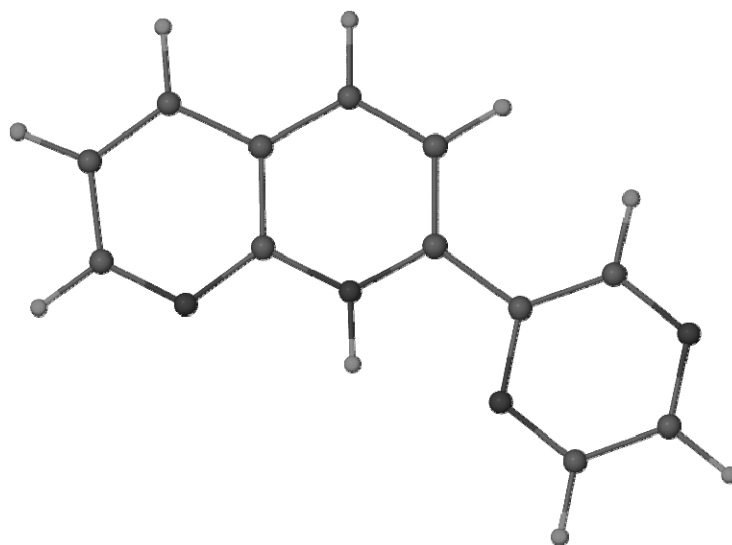


Figure S10. DFT optimized structure of $\{L^2.H\}^+$.

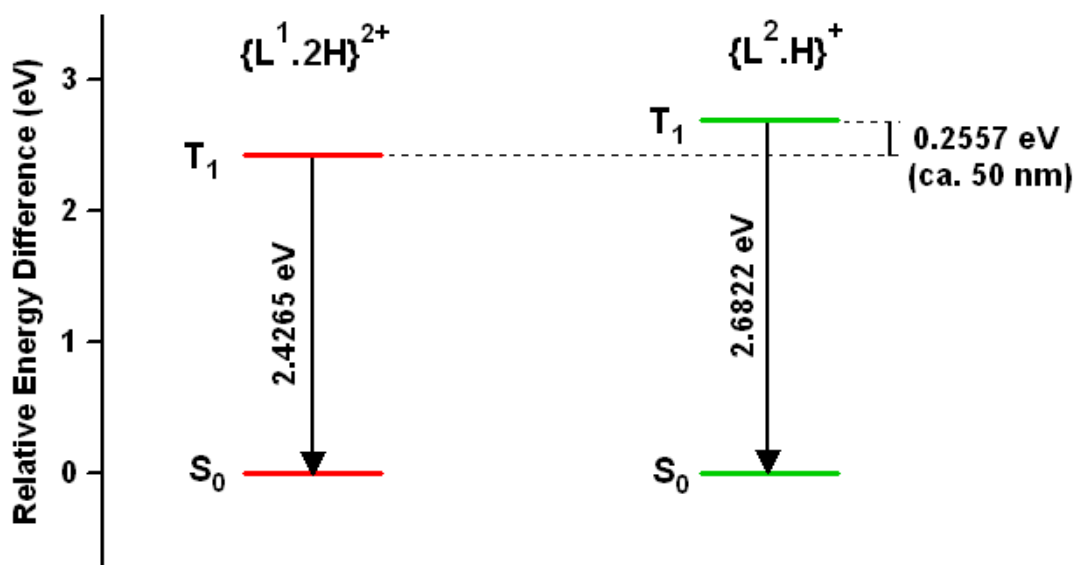


Figure S11. Vertical transition energies of the fully optimized ground state and first triplet state in $\{L^{1.2H}\}^{2+}$ and $\{L^2.H\}^+$. The ground state was optimized with B3LYP/6-31G(d,p) basis and the corresponding single point triplet energy was computed using TD-DFT/B3LYP/6-31g(d,p) basis. The triplet state energy values are plotted relative to the optimized ground state energy, which has been arbitrarily set to zero for both species. The computed energy difference between the ground and the lowest triplet state for compounds $\{L^{1.2H}\}^{2+}$ and $\{L^2.H\}^+$ are 2.4265 and 2.6822 eV respectively. It is observed that the first triplet state in compound $\{L^{1.2H}\}^{2+}$ is stabilized by 0.2557 eV than the lowest triplet state in compound $\{L^2.H\}^+$.

Table S4. DFT optimized coordinates for **1**.

	X	Y	Z
Ir	0.00000	-1.89185	0.00005
Ir	-6.11469	0.46330	-0.40005
Ir	6.11476	0.46321	0.39986
N	-6.02303	2.05202	-1.75256
C	-8.08655	0.80549	-0.66883
C	-3.32163	-5.36478	0.57752
H	-4.04444	-6.15474	0.75319
C	-1.40436	-3.33512	0.10753
N	-0.23578	-2.00526	2.07138
C	-7.29039	3.61768	-3.05172
H	-8.25256	4.00470	-3.36345
N	-5.36502	1.98804	1.29691
C	-4.05840	2.00857	1.51366
C	-7.23942	2.54396	-2.14573
C	-9.16082	0.10590	-0.10578
H	-8.98376	-0.72015	0.57401
C	-1.78617	-3.69423	1.42635
C	-9.71936	2.21150	-1.85558
H	-9.94396	3.02395	-2.53995
C	-8.38815	1.86424	-1.56331
C	-2.73713	-4.70353	1.65239
H	-3.01869	-4.98397	2.66278
C	-2.00636	-4.01735	-0.95691
H	-1.73069	-3.78894	-1.98169
C	-1.12370	-2.95583	2.49904
C	-10.48164	0.45066	-0.40290
H	-11.29618	-0.11251	0.04422
C	-4.89042	2.59699	-2.24244
H	-3.96536	2.14702	-1.90041
C	-4.88994	3.65353	-3.13688
H	-3.95290	4.05512	-3.50527
C	-2.95629	-5.01774	-0.72628
H	-3.40254	-5.53718	-1.56939
C	-6.12295	4.17417	-3.54851
H	-6.16733	5.00073	-4.25051

C	-3.39199	2.91220	2.35977
H	-2.31640	2.88690	2.48250
C	-1.32327	-3.14901	3.87535
H	-2.01527	-3.91144	4.21172
C	0.26094	-1.40395	4.34355
H	0.82482	-0.78322	5.03043
C	0.42613	-1.25301	2.97582
H	1.11365	-0.52061	2.56862
C	-4.15790	3.84678	3.02427
H	-3.67961	4.56312	3.68331
C	-6.14278	2.90742	1.96353
C	-5.55648	3.87079	2.84766
C	-10.76672	1.50689	-1.27579
H	-11.79438	1.76597	-1.50828
N	0.23581	-2.00562	-2.07124
N	-1.77049	-0.36844	0.07242
N	-3.92581	0.21403	-0.10052
C	1.40425	-3.33526	-0.10715
N	-6.44098	-1.17532	0.84000
N	1.77052	-0.36852	-0.07261
N	-3.30511	1.01547	0.81312
N	-7.46610	2.82328	1.73393
N	3.30509	1.01555	-0.81313
C	1.78608	-3.69458	-1.42590
C	1.12369	-2.95631	-2.49872
C	-6.25493	-0.98644	-1.78424
C	-0.42604	-1.25349	-2.97582
H	-1.11350	-0.52096	-2.56876
N	3.92587	0.21390	0.10027
C	-6.59817	-1.10615	2.17763
H	-6.50522	-0.11880	2.61344
C	-6.15023	-0.84612	-3.17407
H	-6.03510	0.13815	-3.61612
C	-6.44016	-2.29215	-1.25831
C	2.00615	-4.01738	0.95742
H	1.73044	-3.78880	1.98215
C	-2.98058	-0.60639	-0.51805
H	-3.17159	-1.39887	-1.22489
C	2.00584	0.64331	-0.90090
H	1.28995	1.09213	-1.57015

C	-6.58078	-2.37259	0.19442
C	1.32328	-3.14973	-3.87500
H	2.01525	-3.91225	-4.21123
C	3.32139	-5.36512	-0.57676
H	4.04417	-6.15515	-0.75229
C	-0.26083	-1.40467	-4.34353
H	-0.82466	-0.78402	-5.03052
N	6.44116	-1.17524	-0.84035
C	2.95602	-5.01788	0.72697
H	3.40217	-5.53723	1.57018
C	-6.38705	-3.24474	-3.48540
H	-6.44719	-4.10550	-4.14342
C	-6.88990	-2.21967	2.95026
H	-7.02180	-2.11550	4.02111
C	2.73699	-4.70398	-1.65175
H	3.01858	-4.98457	-2.66209
C	0.63158	-2.38107	-4.79991
H	0.77974	-2.53986	-5.86330
C	4.05832	2.00883	-1.51348
N	5.36497	1.98816	-1.29692
C	-2.00588	0.64317	0.90096
H	-1.29004	1.09184	1.57035
C	6.25509	-0.98665	1.78389
C	-6.21469	-1.96155	-4.01415
H	-6.14503	-1.82734	-5.09013
C	3.39185	2.91273	-2.35925
H	2.31624	2.88753	-2.48185
C	2.98067	-0.60662	0.51770
H	3.17175	-1.39930	1.22431
C	-6.87042	-3.52897	0.93364
H	-6.99480	-4.47401	0.41921
C	-6.50035	-3.40865	-2.10929
H	-6.64604	-4.40511	-1.70320
C	-7.02783	-3.45600	2.31078
H	-7.27003	-4.34743	2.88083
C	6.44038	-2.29230	1.25783
C	6.58095	-2.37259	-0.19492
C	6.50066	-3.40888	2.10871
H	6.64642	-4.40529	1.70252
N	6.02295	2.05179	1.75254

C	8.38808	1.86432	1.56318
C	8.08658	0.80554	0.66868
C	5.55634	3.87134	-2.84715
N	7.46605	2.82332	-1.73407
C	6.14270	2.90765	-1.96341
C	4.15773	3.84746	-3.02356
H	3.67939	4.56403	-3.68232
C	6.15042	-0.84647	3.17374
H	6.03526	0.13775	3.61590
C	-9.74191	3.57869	2.09191
H	-9.95106	2.78954	1.37057
H	-10.13377	4.52966	1.71360
H	-10.27748	3.36739	3.02499
C	6.59835	-1.10592	-2.17798
H	6.50543	-0.11851	-2.61366
C	6.38739	-3.24512	3.48483
H	6.44762	-4.10593	4.14277
C	6.87053	-3.52890	-0.93427
H	6.99487	-4.47400	-0.41996
C	6.42866	4.80251	-3.50337
C	-8.26711	3.68328	2.34838
C	7.23929	2.54386	2.14568
C	4.89029	2.59653	2.24256
H	3.96527	2.14643	1.90057
C	6.21497	-1.96198	4.01371
H	6.14534	-1.82789	5.08971
C	7.29016	3.61751	3.05175
H	8.25229	4.00465	3.36345
C	9.71926	2.21172	1.85542
H	9.94378	3.02419	2.53980
C	7.02792	-3.45576	-2.31141
H	7.27007	-4.34714	-2.88157
C	7.77180	4.68719	-3.23435
H	8.47981	5.36417	-3.70271
C	6.89004	-2.21935	-2.95073
H	7.02193	-2.11506	-4.02158
C	4.88971	3.65299	3.13711
H	3.95264	4.05440	3.50561
C	-0.63151	-2.38022	4.80012
H	-0.77967	-2.53883	5.86354

C	6.12267	4.17378	3.54867
H	6.16698	5.00029	4.25075
C	9.16091	0.10606	0.10563
H	8.98392	-0.72001	-0.57415
C	-6.42884	4.80183	3.50404
C	5.89516	5.85168	-4.44207
H	6.70499	6.47048	-4.83170
H	5.18170	6.51396	-3.93926
H	5.38049	5.39955	-5.29736
C	10.48171	0.45095	0.40275
H	11.29630	-0.11214	-0.04437
C	10.76669	1.50722	1.27562
H	11.79432	1.76642	1.50809
C	8.26703	3.68344	-2.34838
C	-7.77194	4.68671	3.23476
H	-8.47997	5.36360	3.70322
C	9.74187	3.57861	-2.09219
H	9.95106	2.78905	-1.37131
H	10.13382	4.52934	-1.71336
H	10.27730	3.36783	-3.02546
C	-5.89540	5.85065	4.44316
H	-5.18195	6.51314	3.94062
H	-5.38074	5.39823	5.29829
H	-6.70526	6.46927	4.83299

Table S5. DFT optimized coordinates for **2**.

	X	Y	Z
N	-1.26969	0.60983	-1.66966
C	-2.25178	-0.53019	0.49683
N	2.61687	-0.77722	-1.41022
N	-0.64229	4.71664	1.69628
N	1.69723	1.01123	-0.26574
C	-2.66822	1.34726	-3.95204
C	0.67489	-0.19352	2.97255
C	-3.18816	-0.19818	-0.51895
C	-4.56018	-0.45164	-0.34950
C	2.80579	0.42589	-0.82687
C	-0.62455	1.14409	-2.72568
C	1.81225	2.23681	0.26360
C	0.48245	4.18205	1.22182
C	4.97062	-0.83923	-1.96623
C	3.04919	2.93173	0.31417
C	-3.33393	0.79009	-2.86919
C	0.79302	-2.17827	1.71416
C	-1.66170	2.58657	1.32889
C	0.57462	2.84586	0.79961
C	-5.02140	-1.03900	0.82290
C	4.17694	2.34786	-0.20579
C	-1.28334	1.52728	-3.88374
C	-4.10974	-1.37525	1.82894
C	-1.71011	3.91397	1.75236
C	1.35457	-2.83483	2.82228
C	3.65786	-1.37691	-1.95422
C	5.17890	0.39144	-1.39222
C	-2.74458	-1.12590	1.66629
C	-2.62275	0.41526	-1.71957
C	4.08169	1.07109	-0.80413
C	1.57036	-2.15183	4.00910
C	1.22200	-0.79928	4.09156
C	0.44751	-4.64052	-1.13126

C	0.50031	-2.78154	0.41999
C	-0.39152	-2.45890	-1.79521
C	-0.13388	-3.79863	-2.08715
C	0.76076	-4.13134	0.12180
N	-0.52401	2.05442	0.85501
H	-3.21863	1.63410	-4.84249
H	0.37722	0.84762	2.98645
H	-5.27123	-0.19327	-1.12868
H	0.44809	1.24627	-2.61911
H	1.33695	4.84865	1.16468
H	5.77949	-1.39424	-2.42879
H	3.10937	3.90870	0.77528
H	-4.40505	0.63364	-2.90853
H	-2.52629	1.93343	1.36683
H	-6.08043	-1.23688	0.95304
H	5.13560	2.85701	-0.16593
H	-0.72284	1.95078	-4.70911
H	-4.46507	-1.83990	2.74467
H	-2.63287	4.33586	2.14107
H	1.61287	-3.88359	2.74250
H	3.46312	-2.34245	-2.41684
H	6.16112	0.85522	-1.38385
H	-2.06244	-1.40724	2.46203
H	2.00055	-2.66398	4.86402
H	1.36493	-0.22724	5.00100
H	0.64150	-5.68326	-1.36166
H	-0.84008	-1.83684	-2.56267
H	-0.39199	-4.19409	-3.06614
H	1.20274	-4.78828	0.86534
Ir	-0.34869	-0.00955	0.08922
N	0.46643	-0.85216	1.81381
C	-0.07112	-1.91296	-0.54505
