Electronic Supplementary Information (ESI) †

NIR-Emissive Iridium(III) Corrole Complexes as Efficient Singlet Oxygen Sensitizers

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Table S1 Crystallographic data

Compound codes	**1**	**2**
molecular formula	$C_{52}H_{37}Ir_1N_8O_3$, H_2O	$C_{62}H_{43}Ir_1N_{10}O_3$, CH_2Cl_2
Fw	1032.15	1253.19
Radiation	MoKα	MoKα
crystal symmetry	Monoclinic	Monoclinic
space group	P 21/c	P 21/n
a(Å)	9.727(7)	17.082(5)
b(Å)	21.984(17)	16.003(5)
c(Å)	20.425(14)	22.903(6)
α(deg)	90.00	90.00
β(deg)	100.929(4)	107.572(5)
γ(deg)	90.00	90.00
V(Å^3)	4288.3(5)	5969.0(3)
Z	4	4
μ (mm^{-1})	3.172	2.379
T(K)	100	100
D_{calcd} (g cm^{-3})	1.599	1.395
2θ range (deg)	2.74 to 50.88	4.36 to 51.00
e data (R_{int})	7874 (0.1101)	11059 (0.0805)
R1 ($I>2\sigma(I)$)	0.0608	0.0557
WR2 (all data)	0.1377	0.1387
GOF	1.099	1.010
Largest diff. peak and hole(e·Å-3)	2.761 and -2.096	1.336 and -1.178

Table S2 H-bond parameters for **1**

D—H···A	**Symmetry of A**	d_{D-H} **(Å)**	$d_{H\cdots A}$ **(Å)**	$d_{D\cdots A}$ **(Å)**	**∠D—H...A (Å)**
O1w—H1w···N6	-1+x,1/2-y,1/2+z	0.83	2.24	2.992(11)	150
O1w—H2w···N5	1+x,y,z	0.82	2.30	2.951(11)	136

Where D is donor, A is acceptor

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H...N interactions, [2.57 Å] ,(b) C-H...C interactions, [2.95 Å] and (c) parallel displaced π-π stacking interactions [4.34 Å]. The entries in square brackets are the distances.

Fig. S12 X-ray single crystal structure analysis of 10-(2,4,5-trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-iridium(III)*bis*-4,4'-bipyridine, **2**, showing C-H...N interactions, [2.80 Å]. The entry in square brackets is the distance.

Fig. S13 ORTEP diagram of **1**. Ellipsoids are drawn at 50% probability.

Fig. S14 ORTEP diagram of **2**. Ellipsoids are drawn at 50% probability.

Fig. S15 Normalized phosphorescence spectra (right) of **1** (black line), **2** (red line) and**3** (green line) in MeOH/DCM 1:1 (v/v) rigid matrix at 77 K. λ_{exc} = 600 nm.

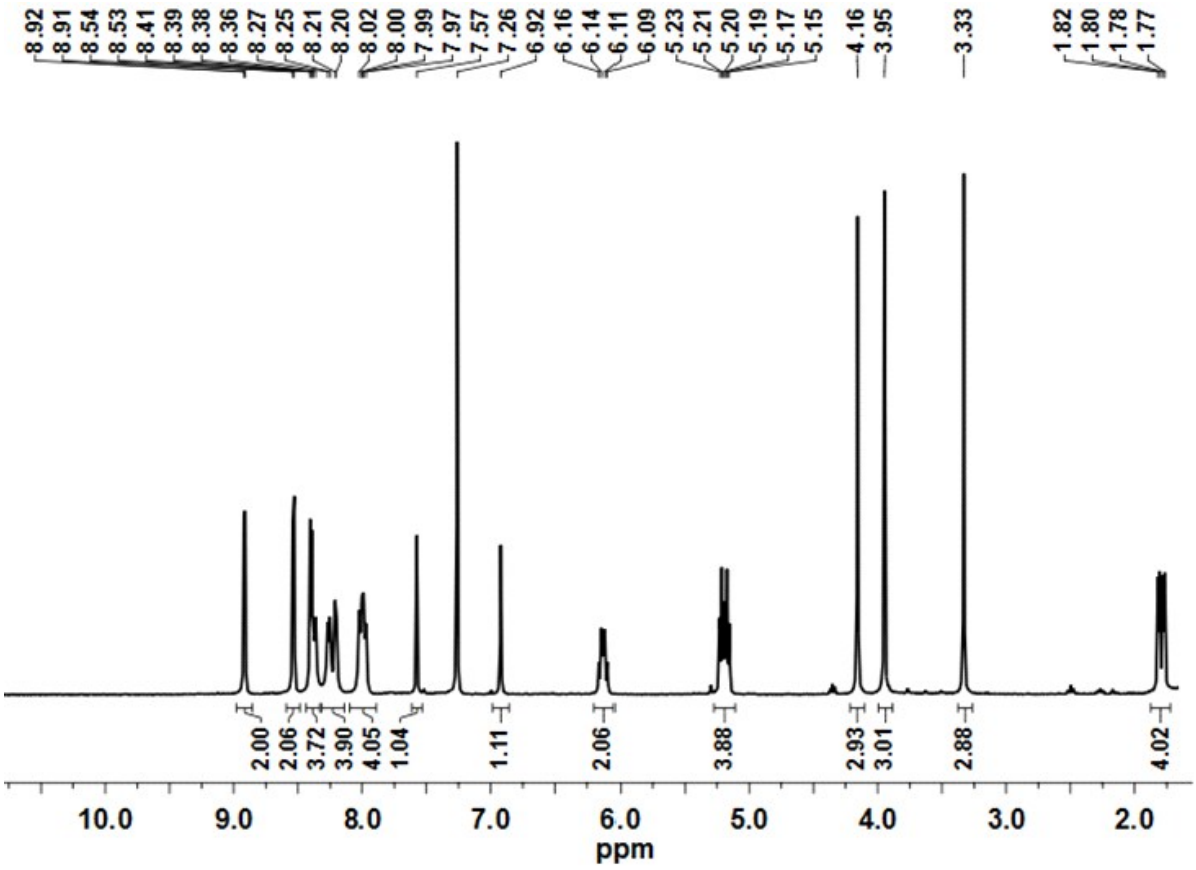


Fig. S1 ^{1}H NMR spectrum of 10-(2,4,5-Trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-iridium(III)*bis*-pyridine, **1**, in $CDCl_3$.

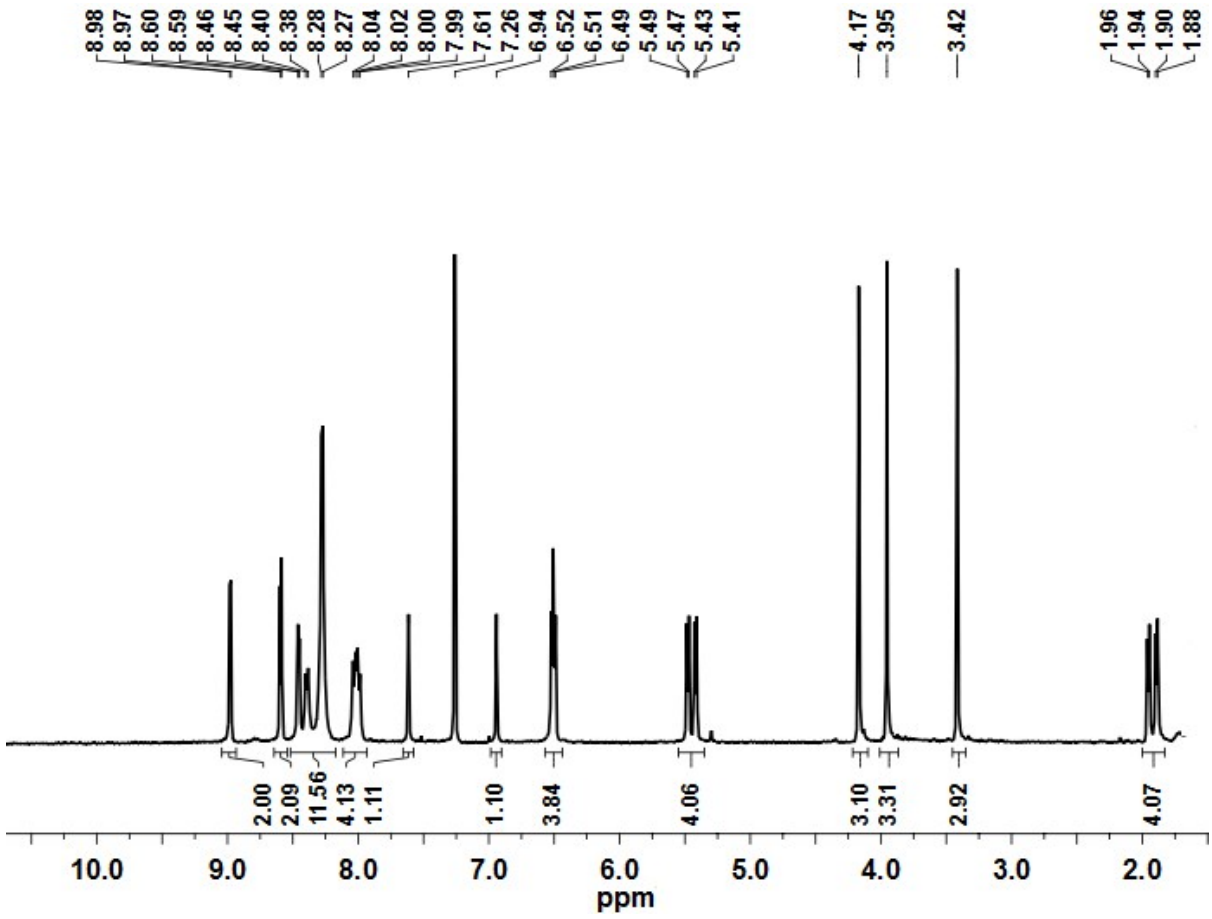


Fig. S2 ^{1}H NMR spectrum of 10-(2,4,5-Trimethoxyphenyl)-5,15-bis(4-cyanophenyl) corrolato-iridium(III)*bis*-4,4'-bipyridine, **2** in $CDCl_3$.

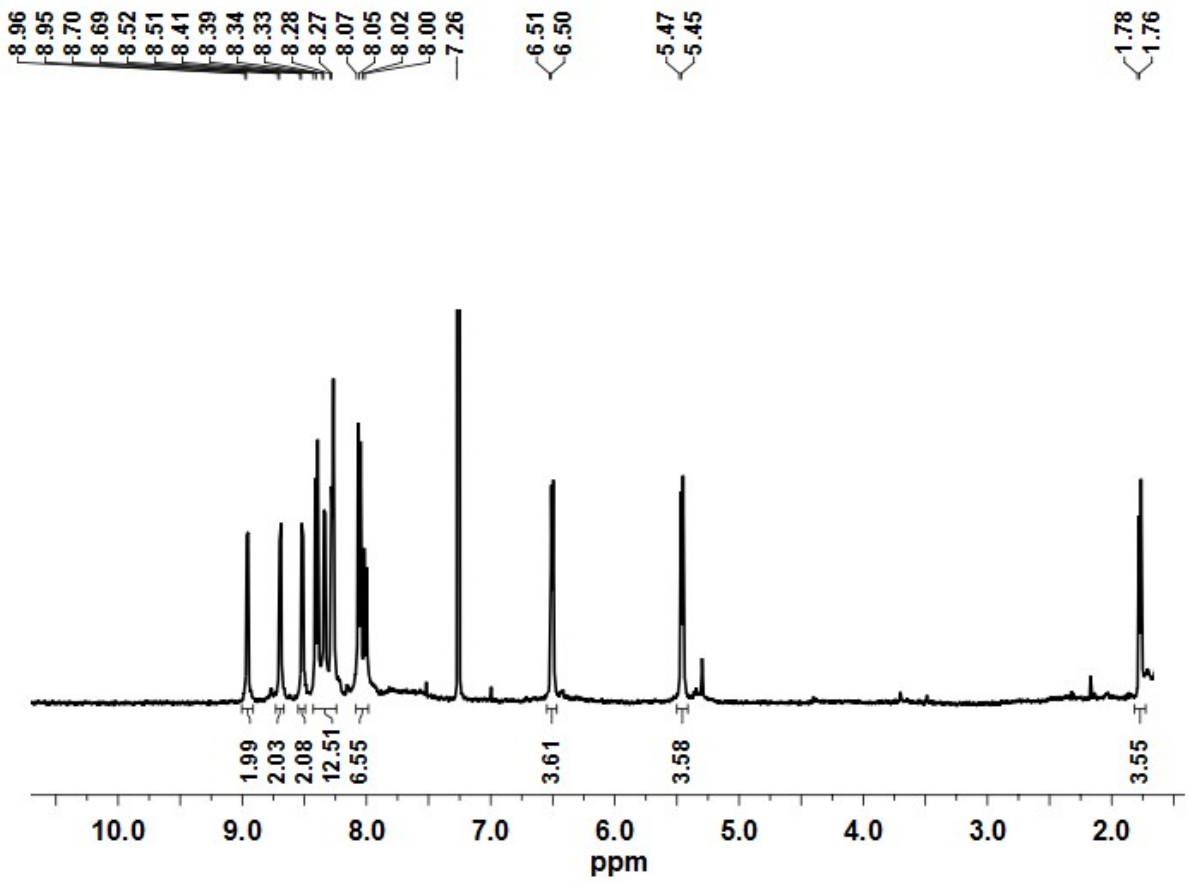


Fig. S3 ^{1}H NMR spectrum of 5,10,15-Tris(4-cyanophenyl)corrolato-iridium(III)*bis*-4,4'-bipyridine, **3** in $CDCl_3$.

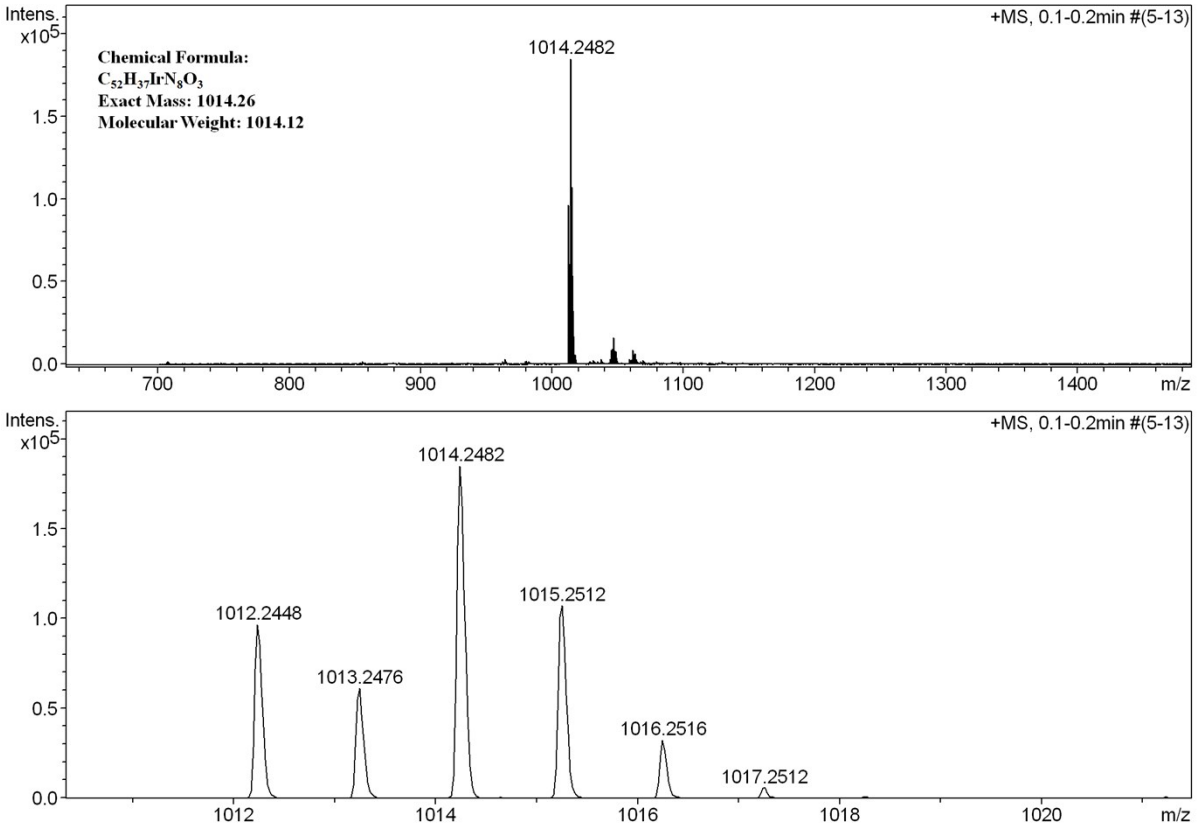


Fig. S4 ESI-MS spectrum of 10-(2,4,5-Trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-iridium(III)*bis*-pyridine, **1** in CH_3CN shows the measured spectrum with isotopic distribution pattern.

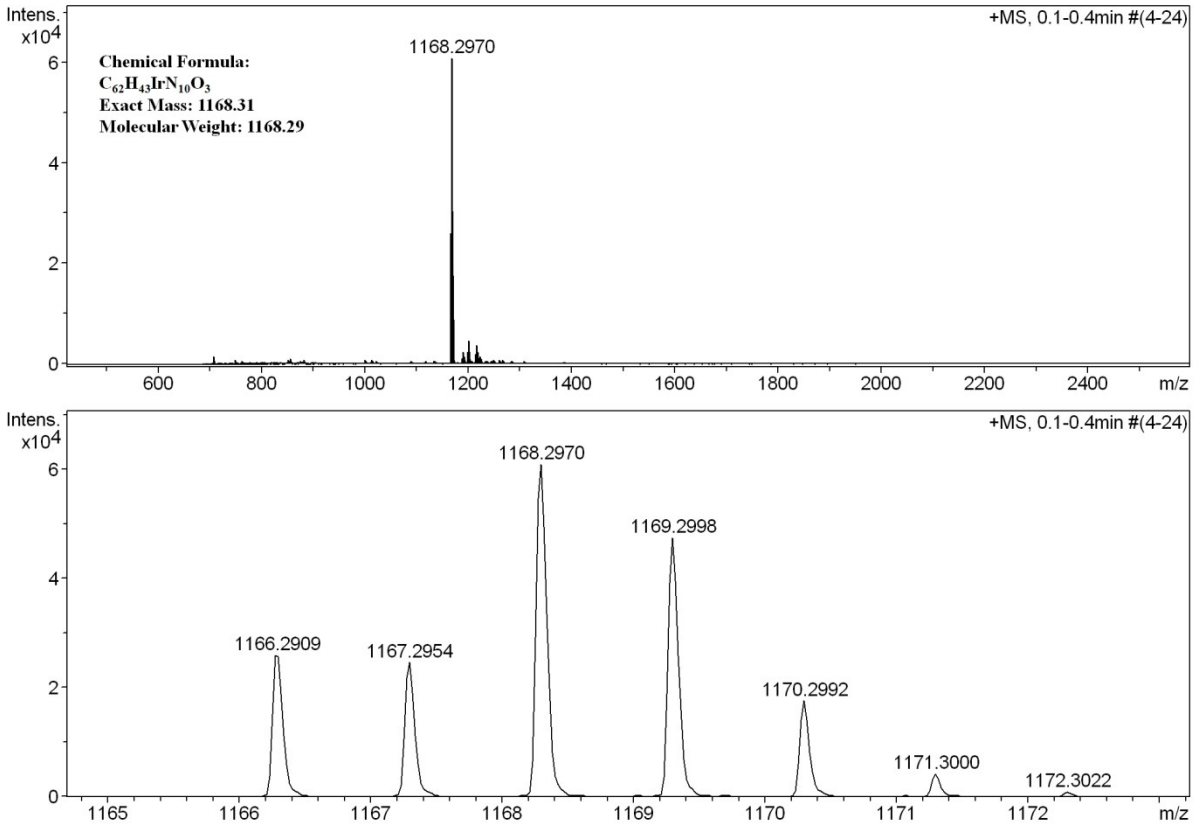


Fig. S5 ESI-MS spectrum of 10-(2,4,5-Trimethoxyphenyl)-5,15-bis(4-cyanophenyl) corrolato-iridium(III)*bis*-4,4'-bipyridine, **2** in CH_3CN shows the measured spectrum with isotopic distribution pattern.

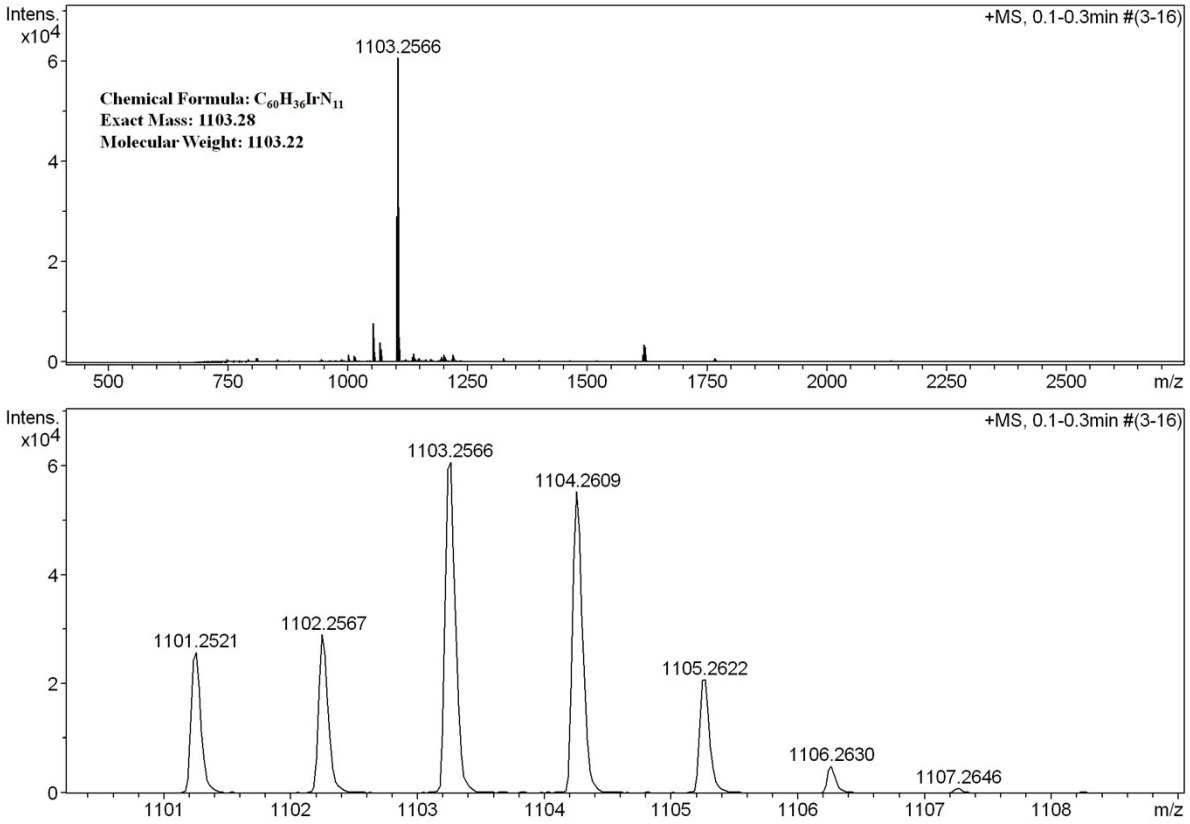


Fig. S6 ESI-MS spectrum of 5,10,15-Tris(4-cyanophenyl)corrolato-iridium(III)*bis*-4,4'-bipyridine, **3** in CH_3CN shows the measured spectrum with isotopic distribution pattern.

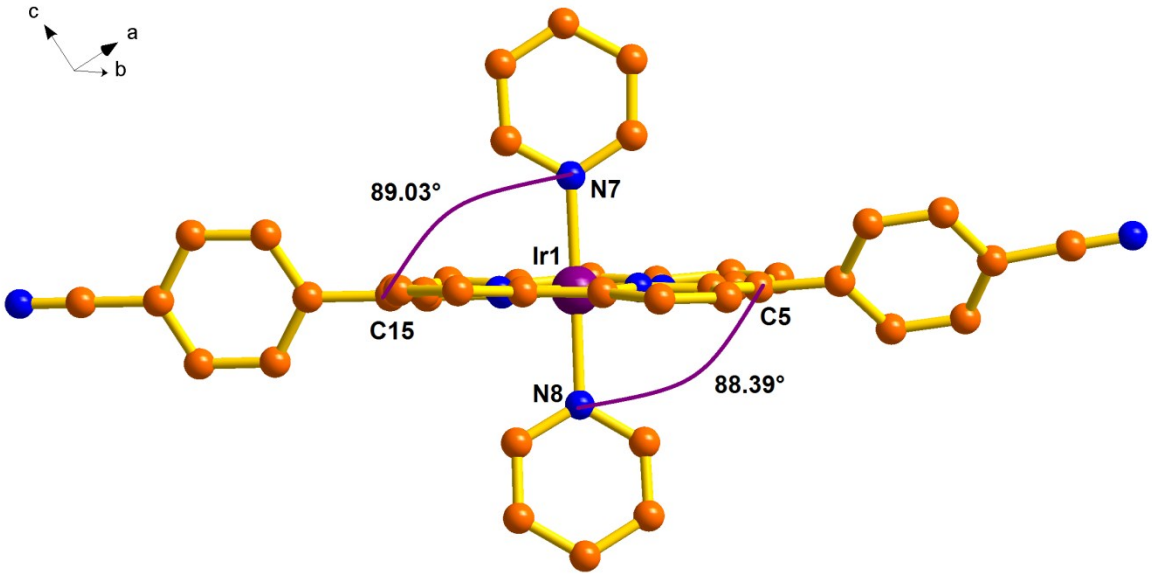


Fig. S7 Single-crystal X-ray structure of 10-(2,4,5-Trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-iridium(III)*bis*-pyridine, **1** showing the perpendicular orientation of the axial pyridine ligands w.r.t the *meso*-substituents.

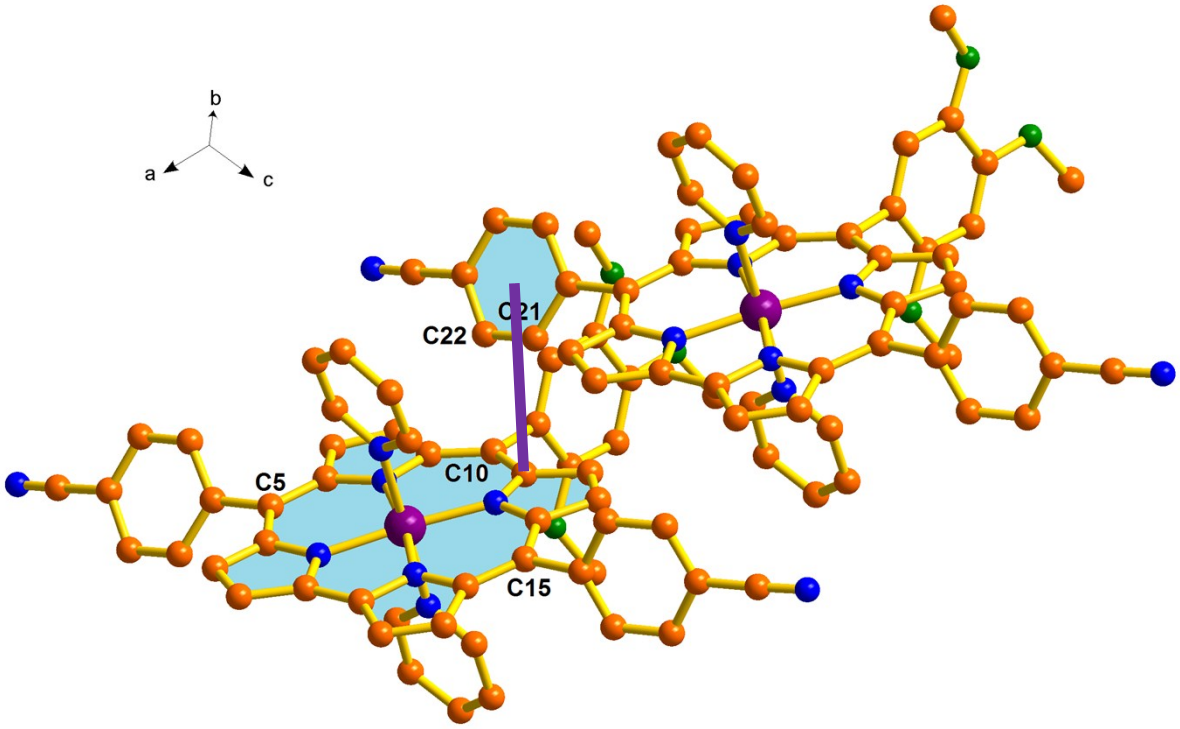


Fig. S8 X-ray single crystal structure analysis of 10-(2,4,5-trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-iridium(III)*bis*-pyridine, **1**, showing edge-to-face π-π stacking interactions [4.48 Å]. The entry in square brackets is the distance.

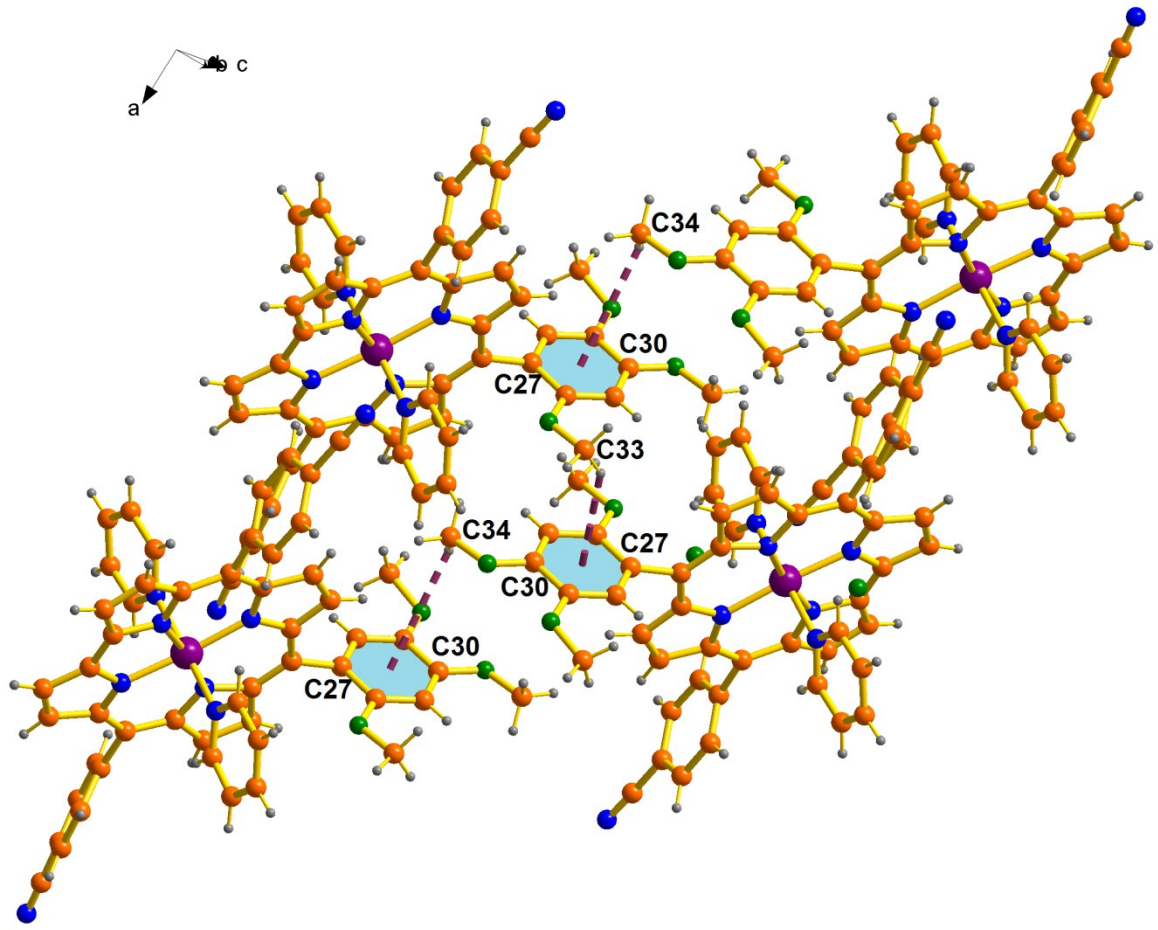


Fig. S9 X-ray single crystal structure analysis of 10-(2,4,5-trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-iridium(III)*bis*-pyridine, **1**, showing C-H...π interactions, [2.98-3.62Å] . The entry in square brackets is the distance.

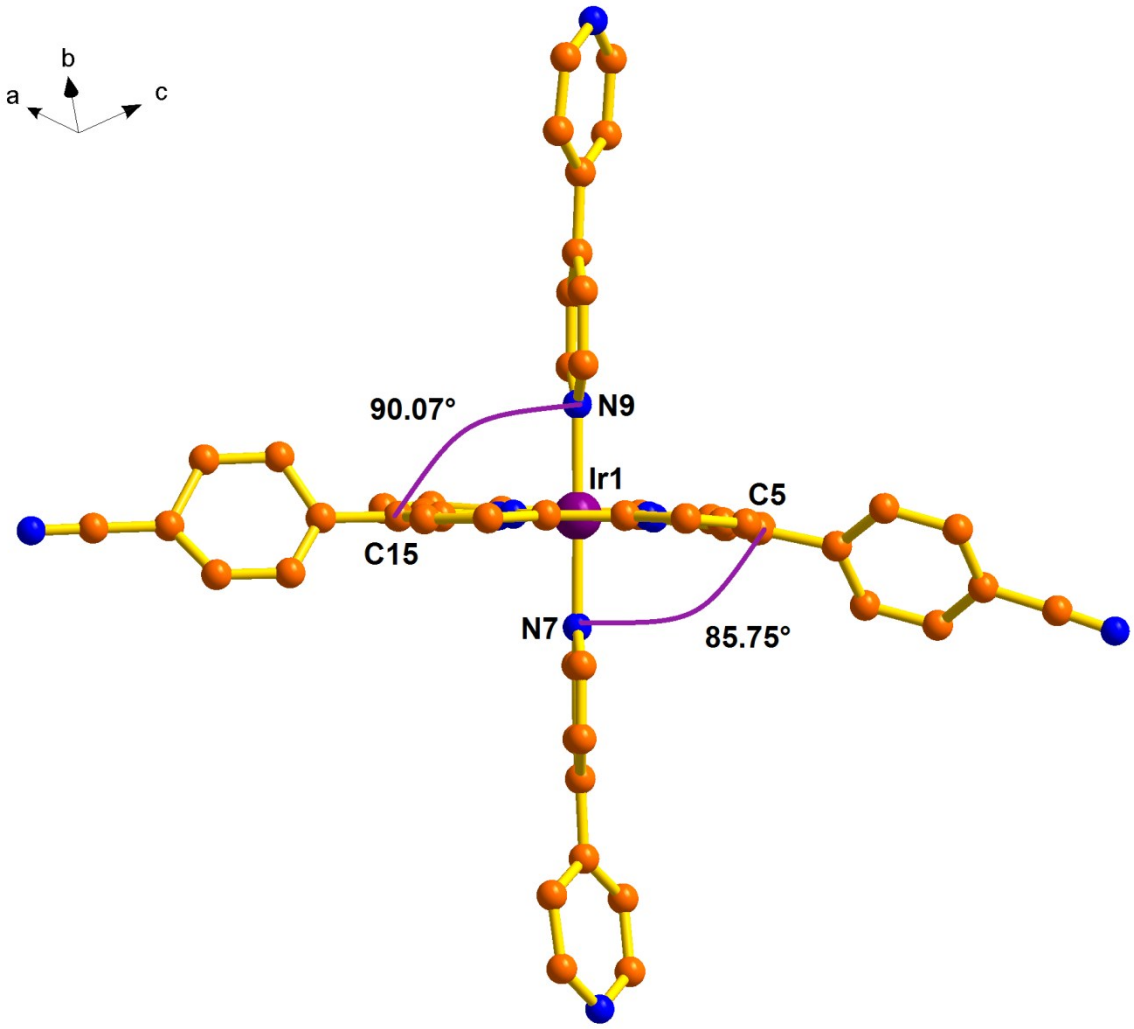


Fig. S10 Single-crystal X-ray structure of 10-(2,4,5-Trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-iridium(III)*bis*-4,4'-bipyridine, **2** showing the perpendicular orientation of the axial 4,4'-bipyridyl ligands w.r.t the *meso*-substituents.

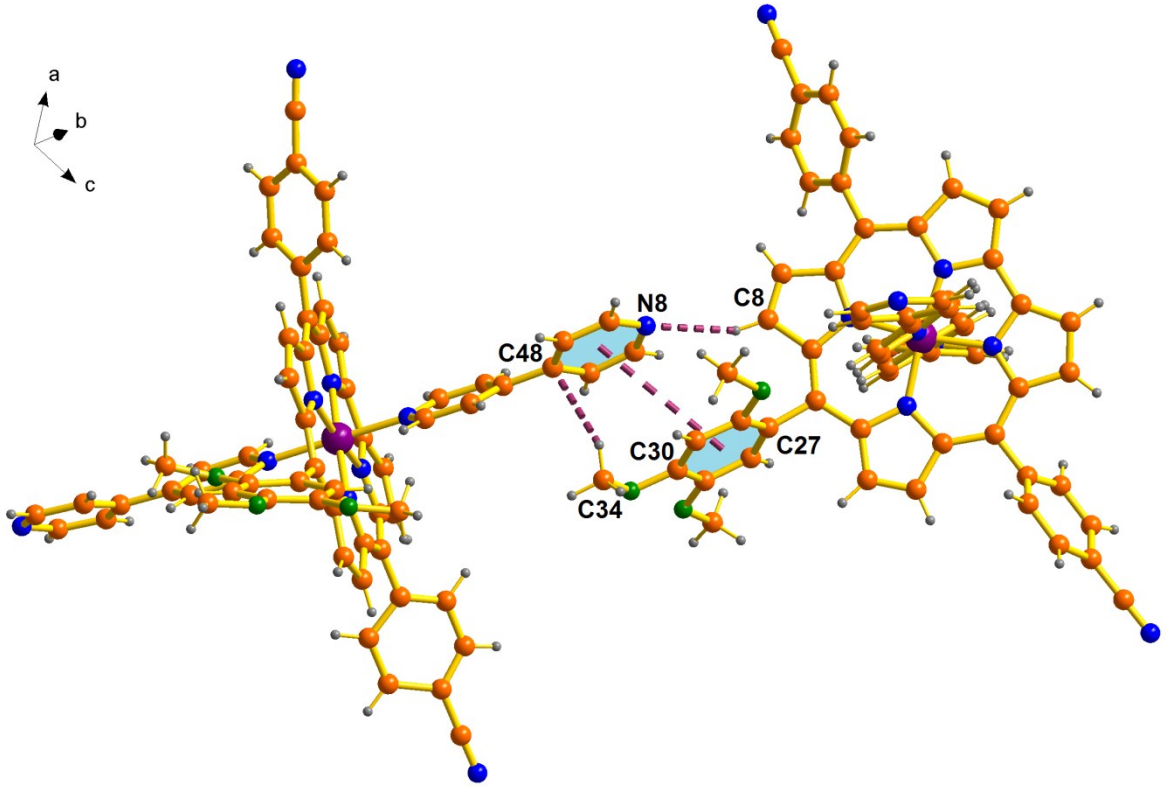


Fig. S11 X-ray single crystal structure analysis of 10-(2,4,5-trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-iridium(III)*bis*-4,4'-bipyridine, **2**, showing (a) C-H...N interactions, [2.57 Å] ,(b) C-H...C interactions, [2.95 Å] and (c) parallel displaced π-π stacking interactions [4.34 Å]. The entries in square brackets are the distances.

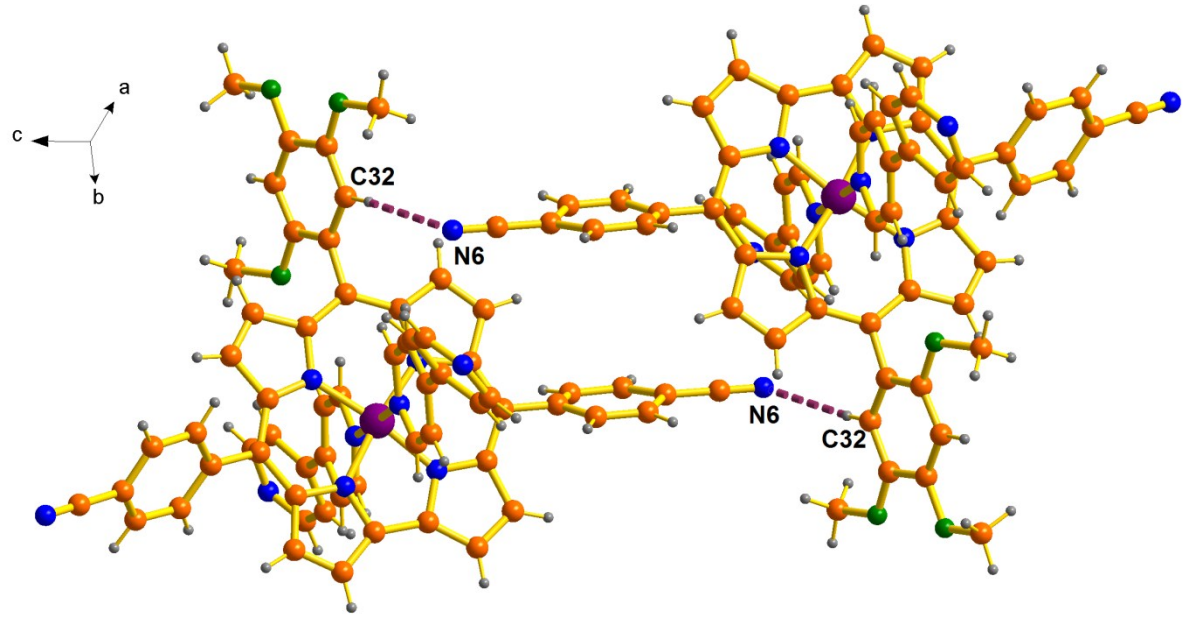


Fig. S12 X-ray single crystal structure analysis of 10-(2,4,5-trimethoxyphenyl)-5,15-bis(4-cyanophenyl)corrolato-iridium(III)*bis*-4,4'-bipyridine, **2**, showing C-H...N interactions, [2.80 Å]. The entry in square brackets is the distance.

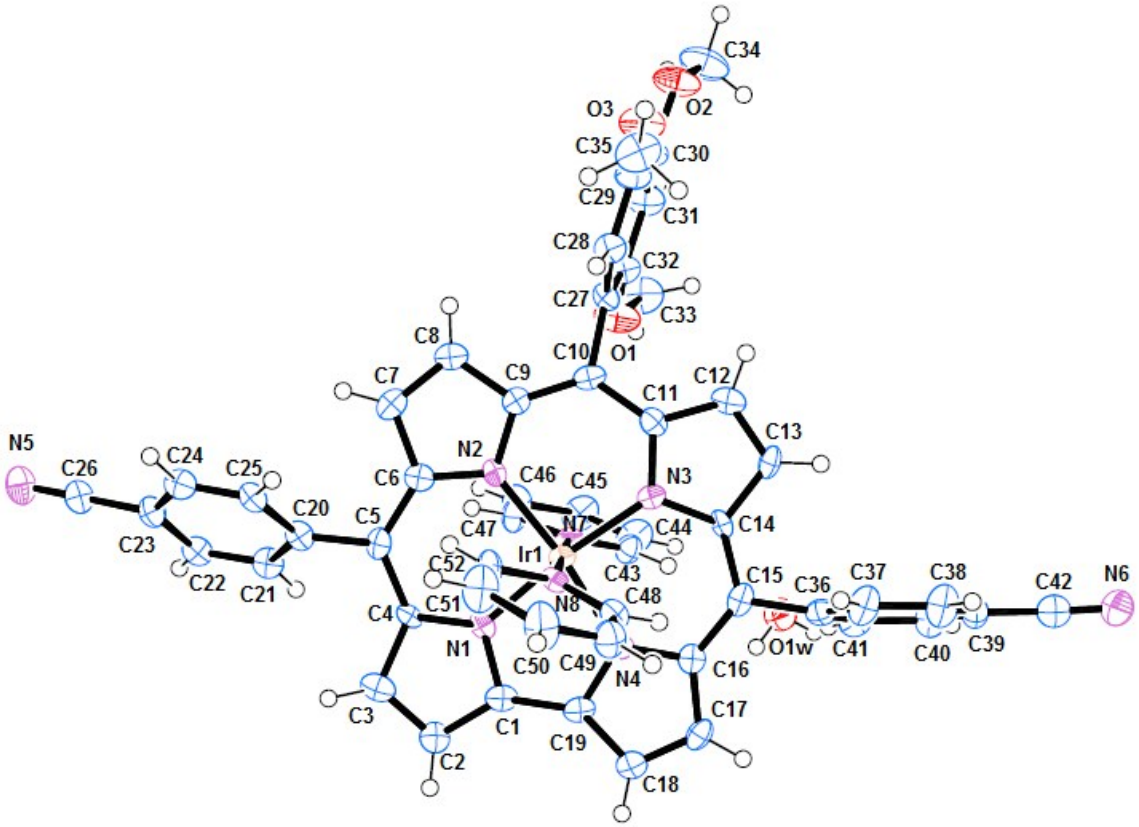


Fig. S13 ORTEP diagram of **1**. Ellipsoids are drawn at 50% probability.

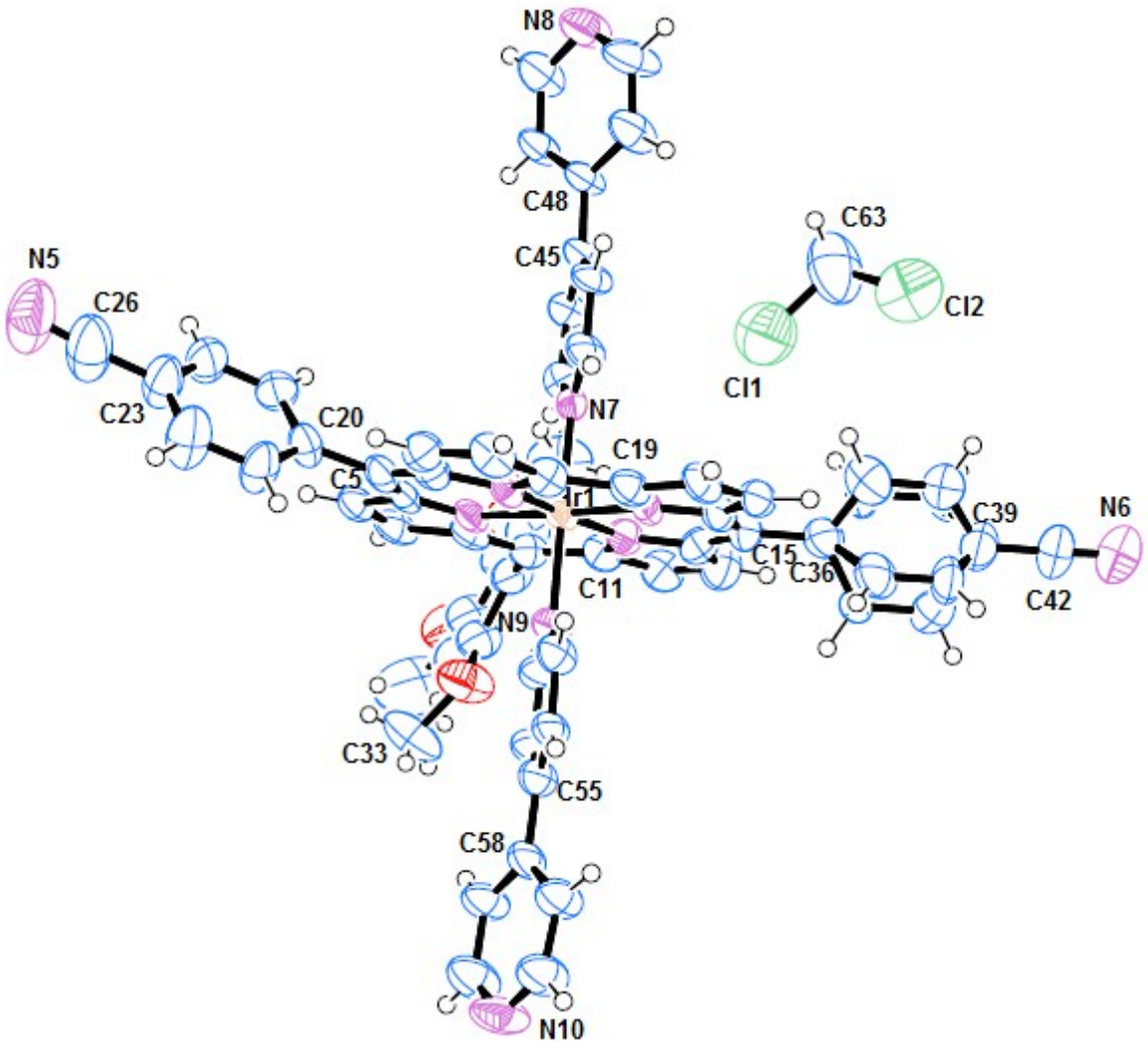
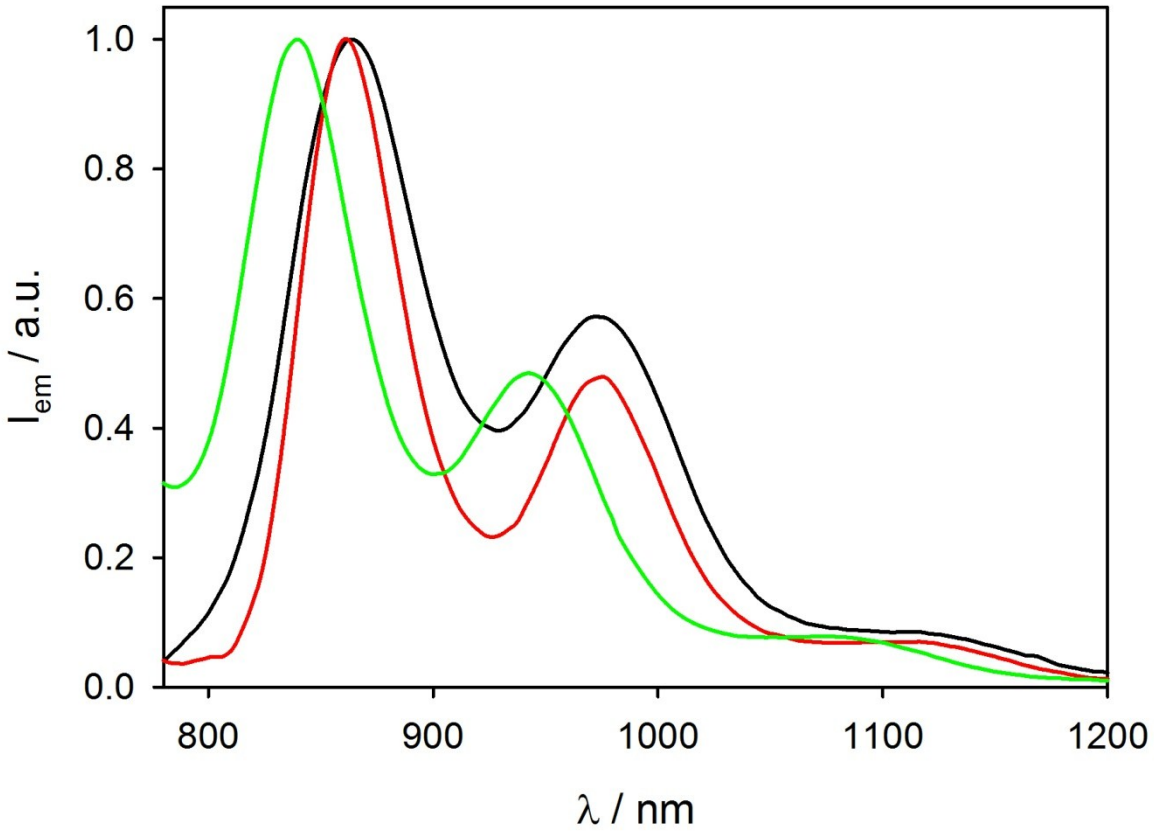


Fig. S14 ORTEP diagram of **2**. Ellipsoids are drawn at 50% probability.



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