Supplementary Material (ESI) for Chemical Communications

Supporting Info
A Bright Tetranuclear Iridium (III) Complex

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General Considerations.

The solvents (puriss grade) and commercially available starting materials were used as received. UV-vis spectra were recorded in a 1 cm path length quartz cell on a Cary 5 spectrophotometer. Emission spectra were recorded on a Spex Fluorolog 112 using a 90° optical geometry. The emitted light was detected with a Hamamatsu R2658 photomultiplier operated in single photon-counting mode. The emission spectra were photometrically corrected using a NBS calibrated 200 W tungsten lamp as reference source. The emission lifetimes were measured from fresh solutions, which were degassed by Ar bubbling for 30 min. Pulsed excitation at 400 nm was provided by a Q switched, frequency tripled, Nd:YAG laser pumping an optical parametric oscillator (OPO). The pulse duration was 5 ns, and the repetition rate was 30 Hz. The emission was filtered through a 420 nm cutoff filter and a grating monochromator before being detected by a fast photomultiplier. The quantum yields were determined using the following equation:

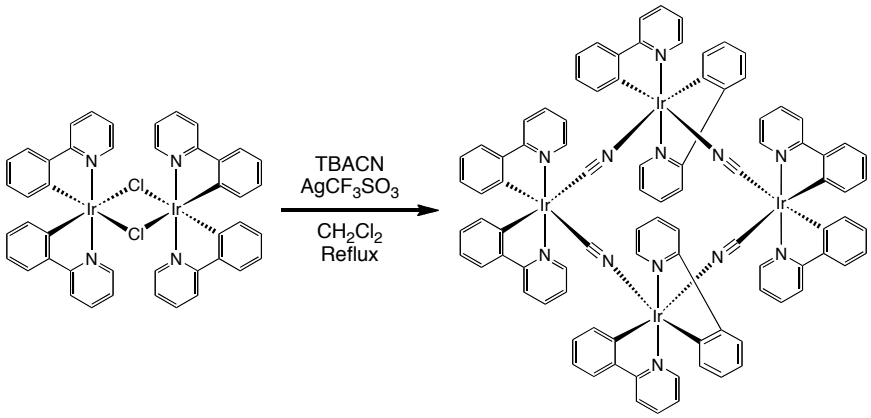
$$_X = \ _rK_{opt}\frac{(D/A_{exc})_X}{(D/A_{exc})_r}$$

Where the subscript *X* denotes the substance whose quantum yield is determined and r is the reference substance quininesulfate (3×10^{-5} M in 1 N H_2SO_4), whose luminescence quantum yield is assumed to be 0.545; K_{opt} is the optical factor referring to the higher refractive index of acetonitrile ($n_D = 1.3415$) compared to the water solution ($n_D = 1.333$); *D* is the integrated area under the emission spectrum; A_{exc} is the absorbance at the exciting wavelength. A secondary standard using recrystallized

$Ru(bpy)_3PF_6$ solution was also employed to verify the yields. Electrochemical data were obtained by cyclic and differential pulse voltammetry (CV and DPV) using a PC-controlled AutoLab system (PGSTAT-10, Eco Chimie). The electrochemical cell was assembled and measured in an Ar-filled glove-box: glassy carbon disk working electrode (Metrohm), Pt-plate auxiliary electrode and Pt-wire quasi reference electrode were mounted in a single-compartment-cell configuration.
Cyclic voltammogram were carried out for a solution obtained by dissolving about 1 mg complex in 3 ml of acetonitrile (anhydrous, 99.9%) containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. After the measurements, ferrocene was added as internal reference for calibration of the other redox couple potentials versus the value relative to the ferrocenium/ferrocene couple. The ATR-FTIR spectra for all the samples were measured using a Digilab 7000 FTIR spectrometer. The FTIR data reported here was taken with the "Golden Gate" diamond anvil ATR accessory (Graseby-Specac) using typically 64 scans at a resolution of 2 cm^{-1}. No ATR correction has been applied to the data. Single crystal suitable for X-ray analysis has been obtained by carefully layering a solution of **EB91** in acetonitrile with hexane. The data collection for X-ray crystal structure was measured at low temperature using Mo K_α radiation and a Bruker APEX II CCD, having kappa geometry. The data were reduced by means of EvalCCD[1] and then corrected for absorption.[2] The solution and refinement were performed by SHELX.[3] The structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. The relatively high electron density peak and hole were very close to the metal centre (0.96 and 0.90 Å, respectively). This was essentially due to the impossibility to clearly measure the faces of the crystal which prevented us to apply the analytical type of absorption correction. NMR spectra were measured with AV-400 spectrometers, and the reported chemical shifts were referenced to TMS. DOSY NMR was measured on a 600.1 MHz DRX spectrometer equipped with a cryoprobe and a gradient.

1) A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220-229.
2) R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33-38.
3) *SHELX*, G. M. Sheldrick**,** *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.

Synthesis of EB91.



In a 250 mL two-necked round bottom flask equipped with a condenser were placed $[Ir(ppy)_2Cl]_2$ (426 mg, 0.40 mmol), tetrabutyl ammonium cyanide (220 mg, 0.82 mmol), and silver(I) trifluoromethane sulfonate (300 mg, 1.17 mmol) in dichloromethane (200 mL). The reaction mixture was refluxed overnight under argon. The reaction mixture was filtered on a short silica gel pad and the volatiles evaporated. The crude was further purified by silica gel chromatography column using dichloromethane as eluent. The main yellow band was collected, the volume of solvent reduced under vacuum, and hexane was added to precipitate the complex. The precipitate was filtered of on fritted glass, washed with hexane and dried to yield **EB91** as a yellow solid (312 mg, 0.15 mmol, yield 74 % based on $[Ir(ppy)_2Cl]_2$).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.09-8.97 (m, 8H); 7.89-7.75 (m, 16H); 7.52-7.43 (m, 8H); 6.83-6.62 (m, 16H); 6.58 (m, 4H); 6.52 (m, 4H); 6.06 (m, 4H); 5.98 (m, 4H).

TOF MS ES: ½$[M]^+$ *m/z*: calc. 1054.1946 found: 1054.1054; $[Ir(ppy)_2(CN)_2H]^+$ *m/z*: calc. 554.1082 found: 554.1077

Elemental analysis: $C_{92}H_{64}Ir_4N_{12}.2\ H_2O$ (**EB91**.2 H_2O) calc.: C, 51.58; H, 3.20; N, 7.85; found: C, 51.58; H, 3.18 ; N, 7.72.

Infra-Read (neat film): 2133 cm^{-1} (bridging cyanide)

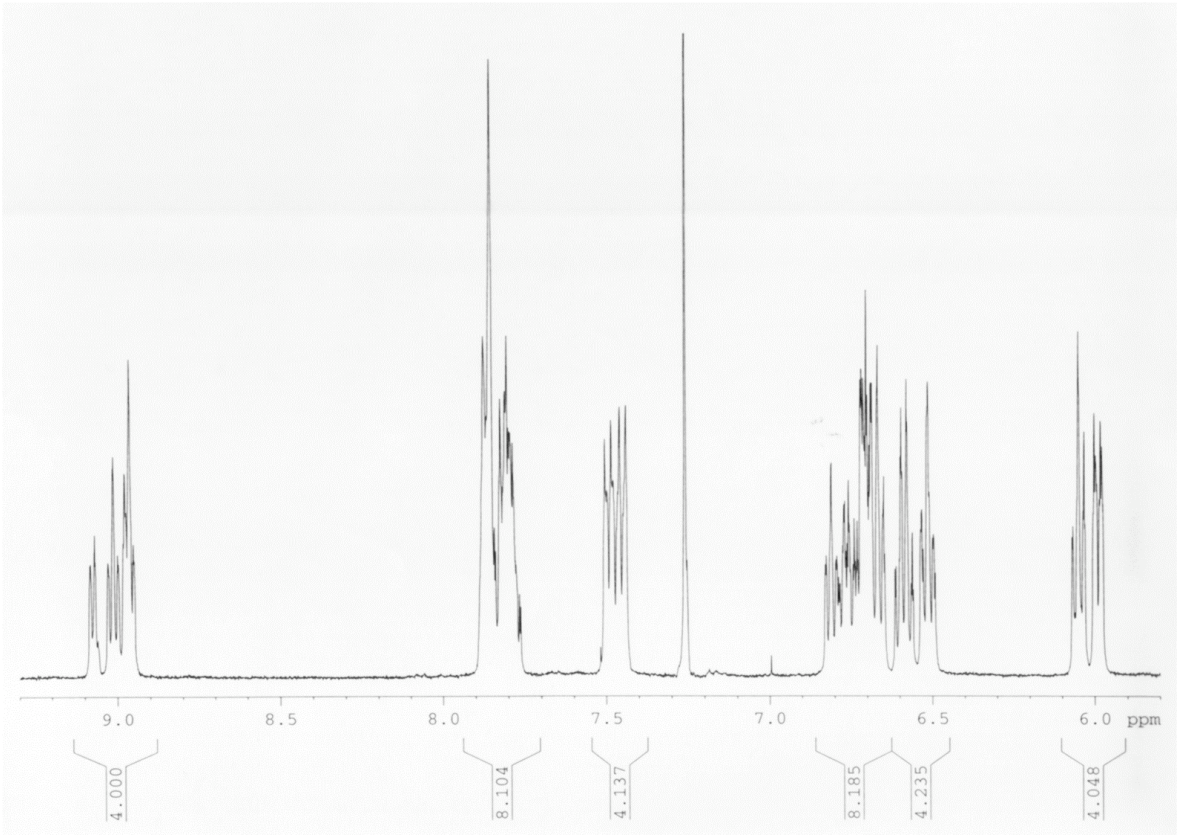


Figure S1. Aromatic part of ^{1}H NMR in $CDCl_3$ of **EB91**.

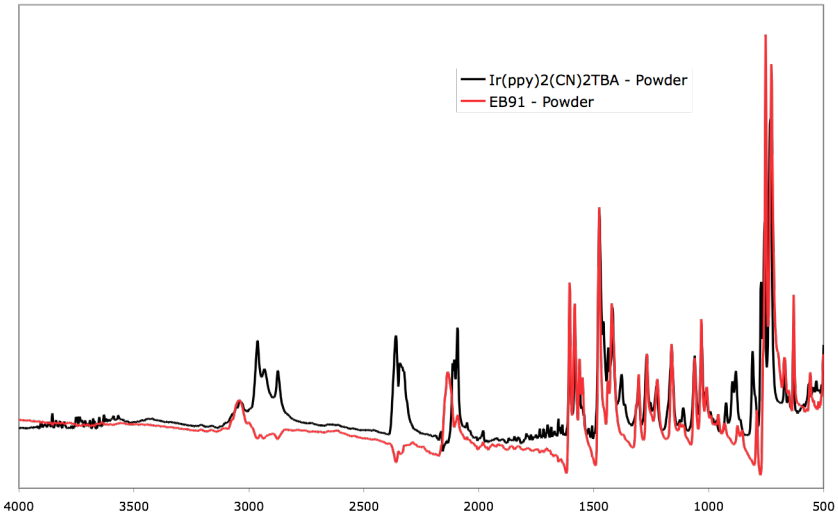


Figure S2. FT-IR spectra of **EB91** and $Ir(ppy)_2(CN)_2TBA$ as powder

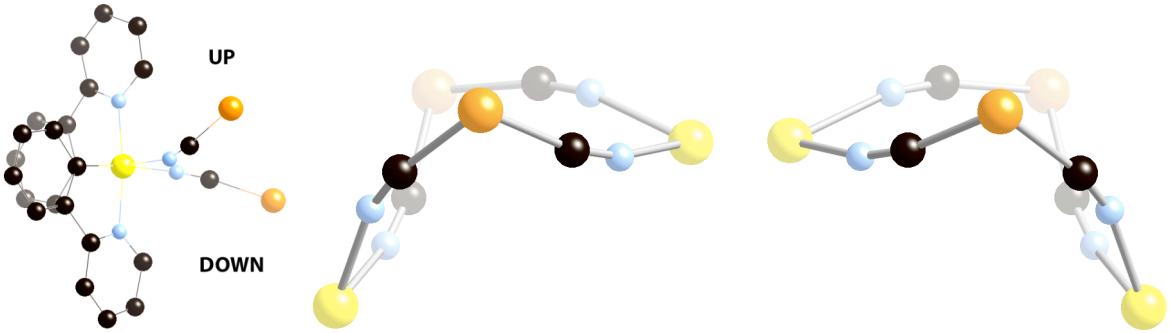


Figure S3. Left shows the linear Ir-NC-Ir pointing UP and DOWN. Right shows the $[IrCN]_4$ unit for the [-Λ-Δ-Λ-Δ] and for the [-Δ-Λ-Δ-Λ] being the non-superimposable mirror image. Yellow atoms are Ir_N-type iridium centres, orange atoms are Ir_C-type iridium centres.

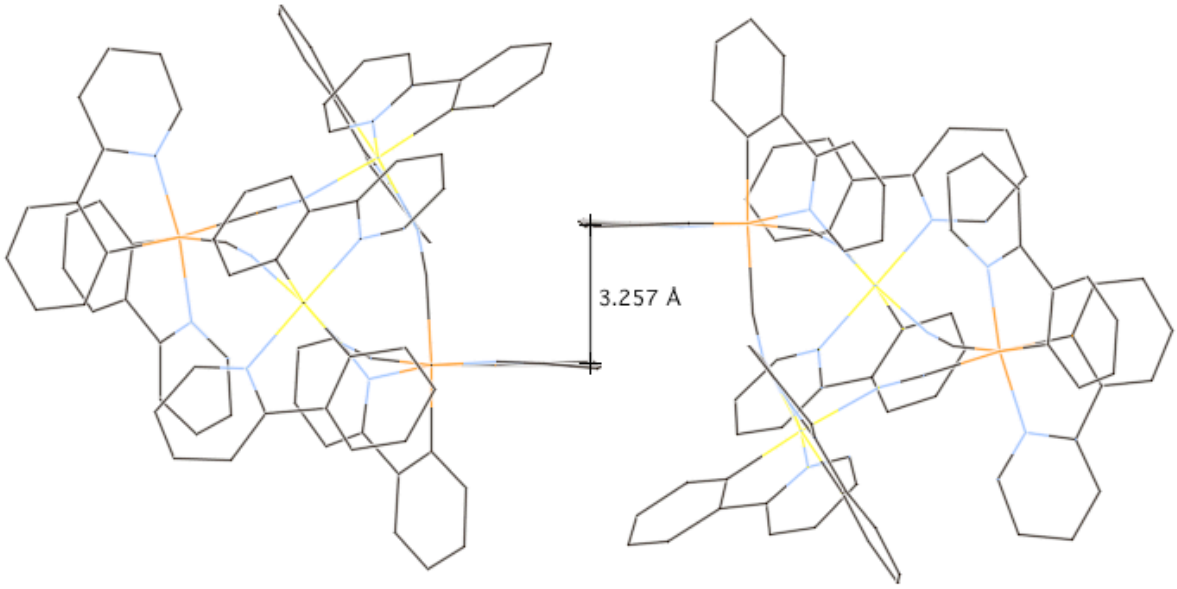


Figure S4. Interaction between the [-Δ-Λ-Δ-Λ] and the [-Λ-Δ-Λ-Δ] complexes in the crystal.

DOSY NMR

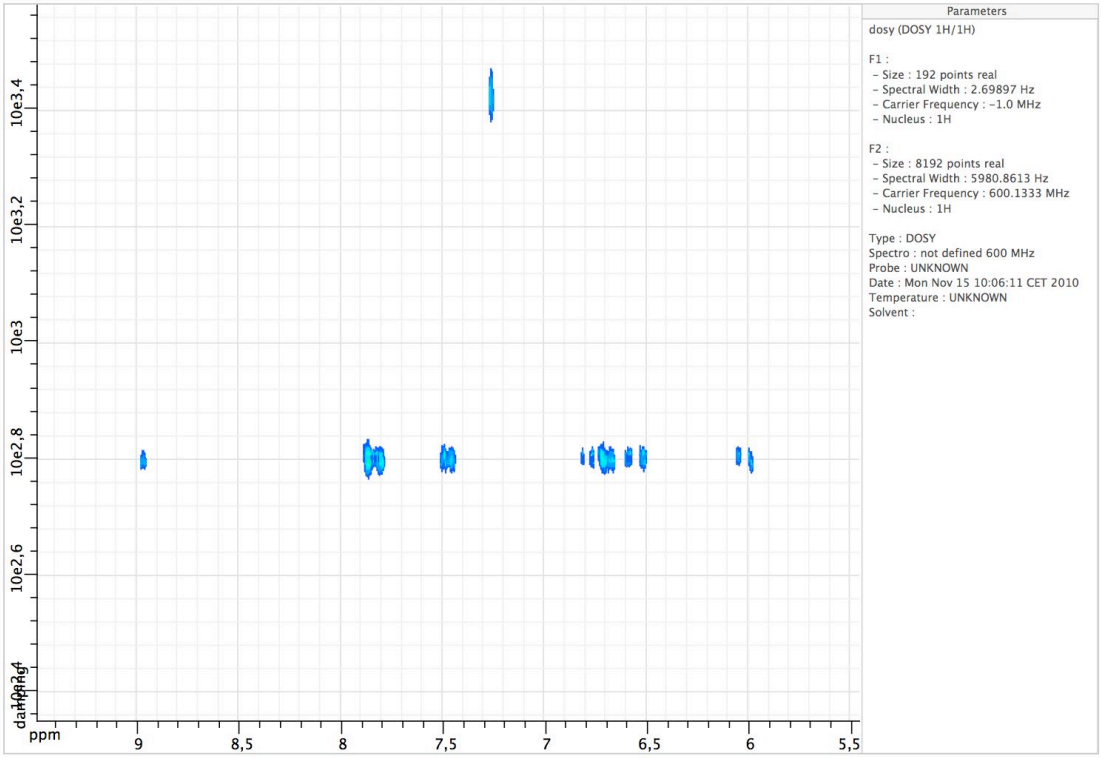


Figure S5. DOSY NMR experiment for **EB91** (600 MHz, $CDCl_3$, 300 K). R_H = 6.63 Å.

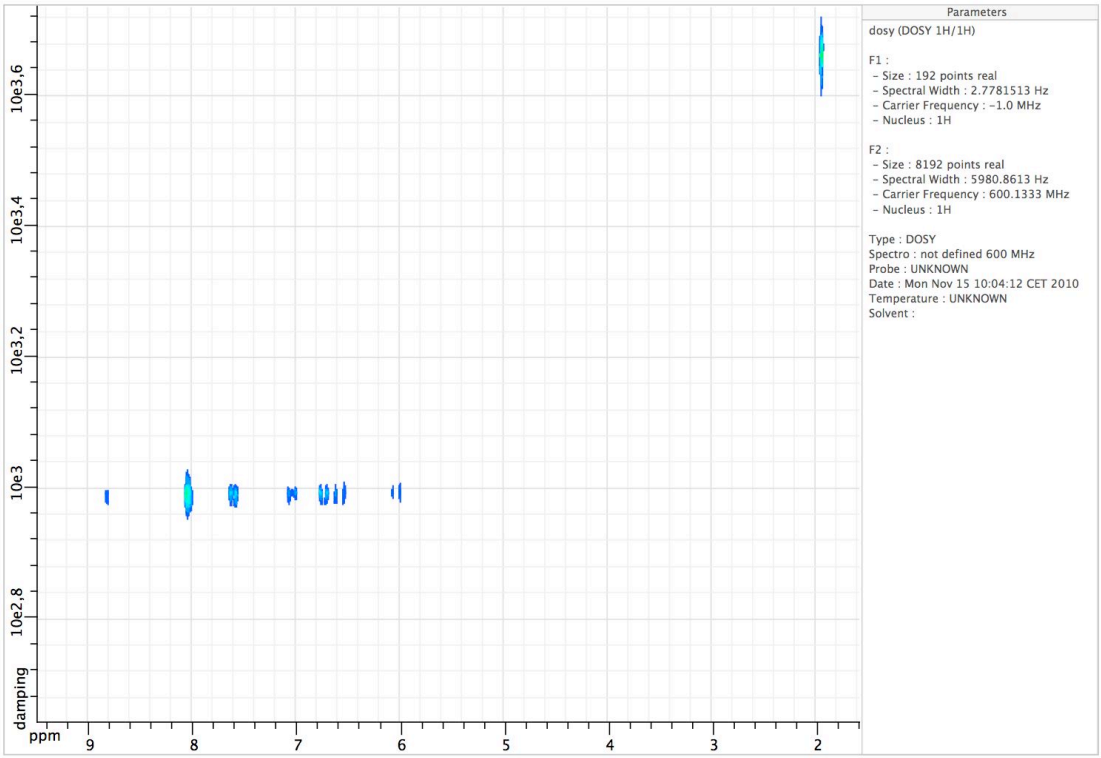


Figure S6. DOSY NMR experiment for **EB91** (600 MHz, CD_3CN, 300 K). R_H = 6.74 Å.

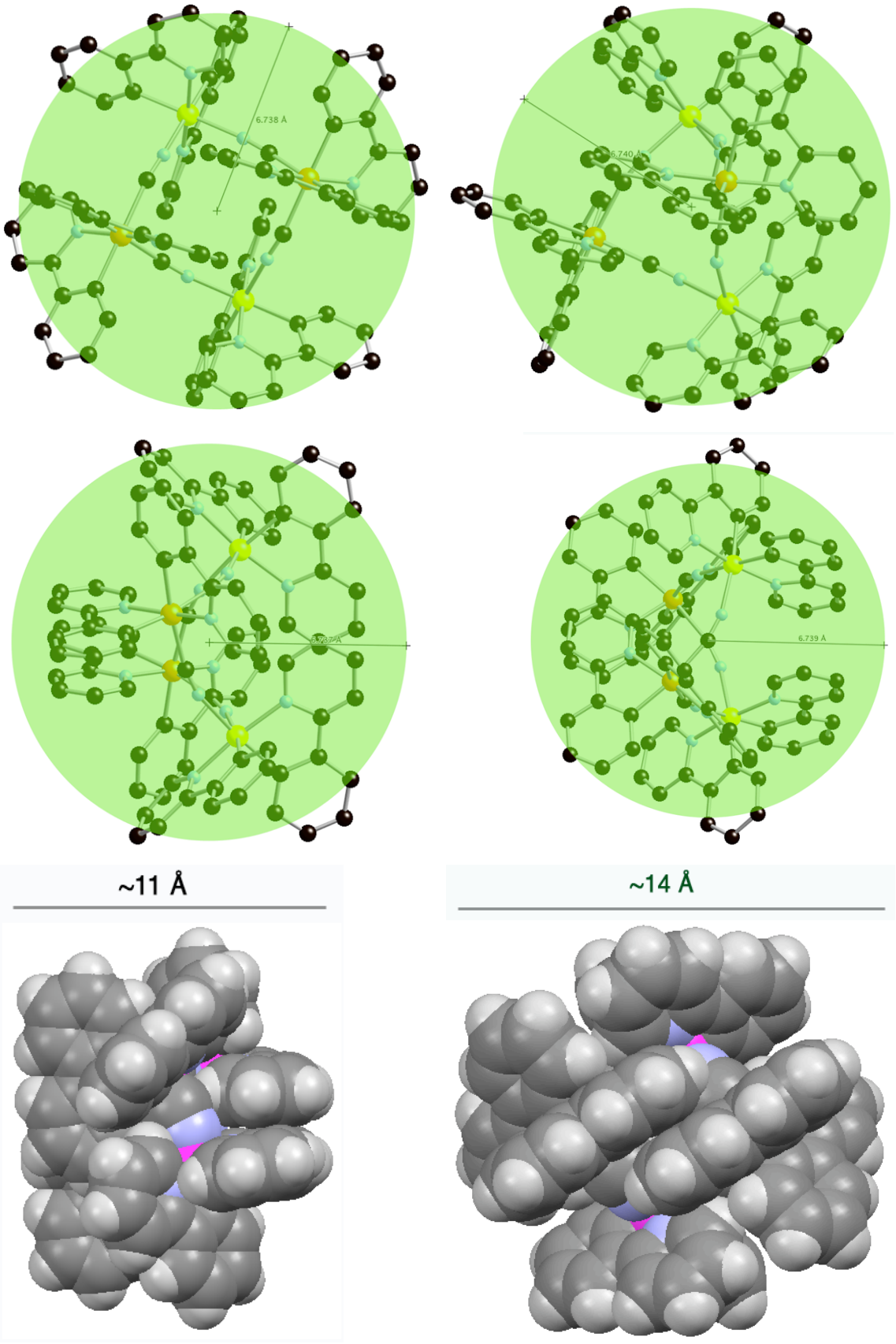


Figure S7. Top: different view of **EB91** superposed with a circle of r ~ 6.74 Å. Bottom: space filling views of **EB91**.

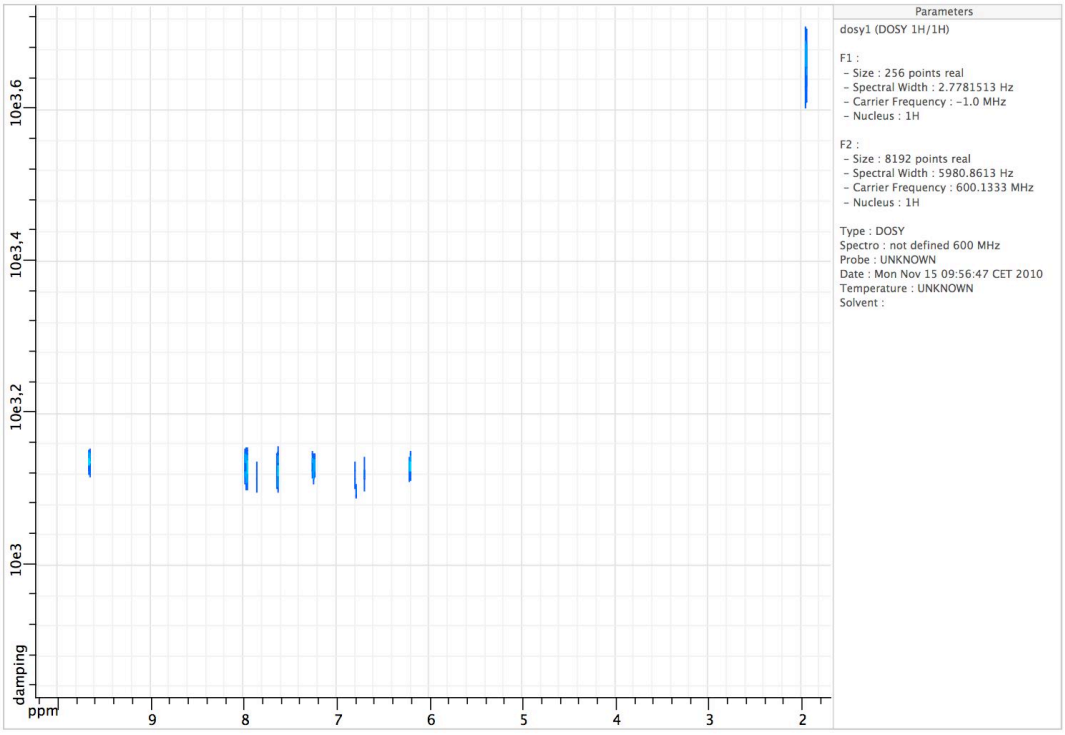


Figure S8. DOSY NMR experiment for $[Ir(ppy)_2(CN)_2Na]$ (600 MHz, CD_3CN, 300 K). R_H = 4.79 Å.

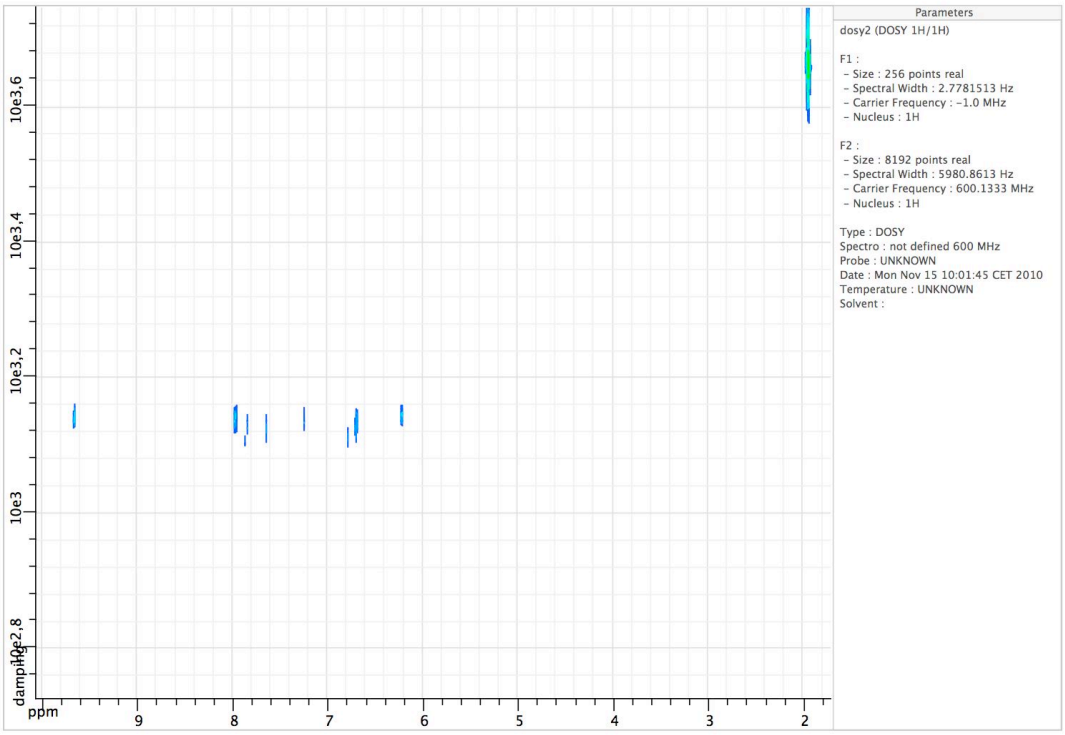


Figure S9. DOSY NMR experiment for $[Ir(ppy)_2(CN)_2Na]$, 4x concentration, (600 MHz, CD_3CN, 300 K). R_H = 4.70 Å.

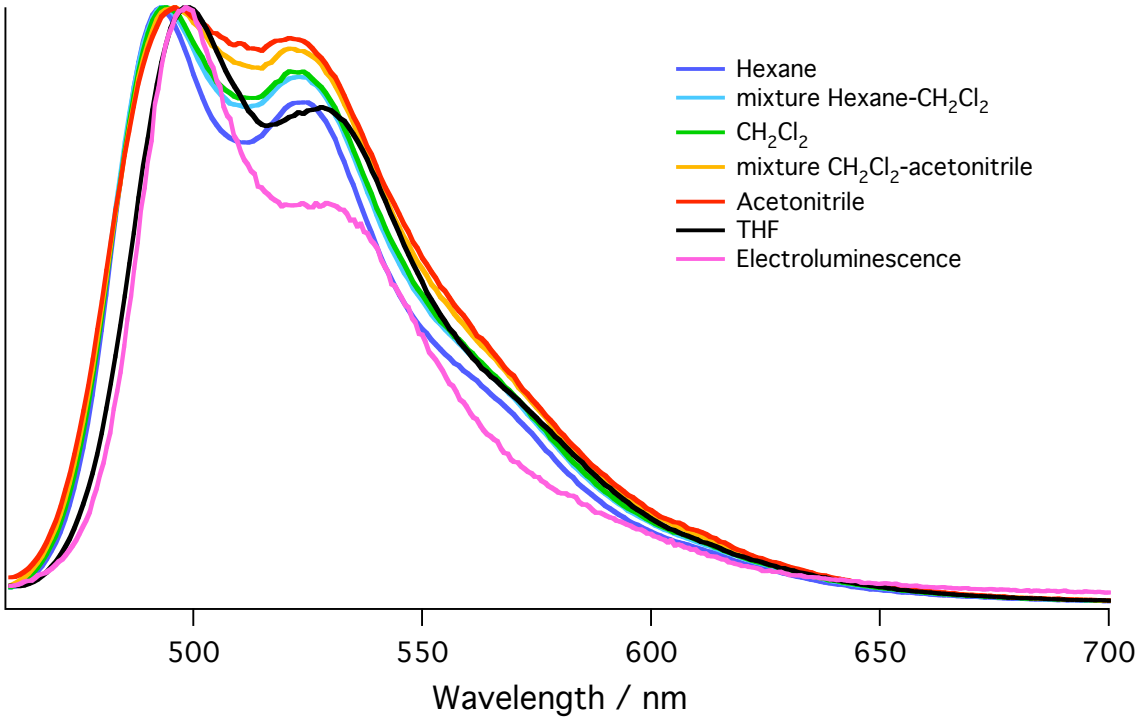


Figure S10. Emission at room-temperature in various solvents.

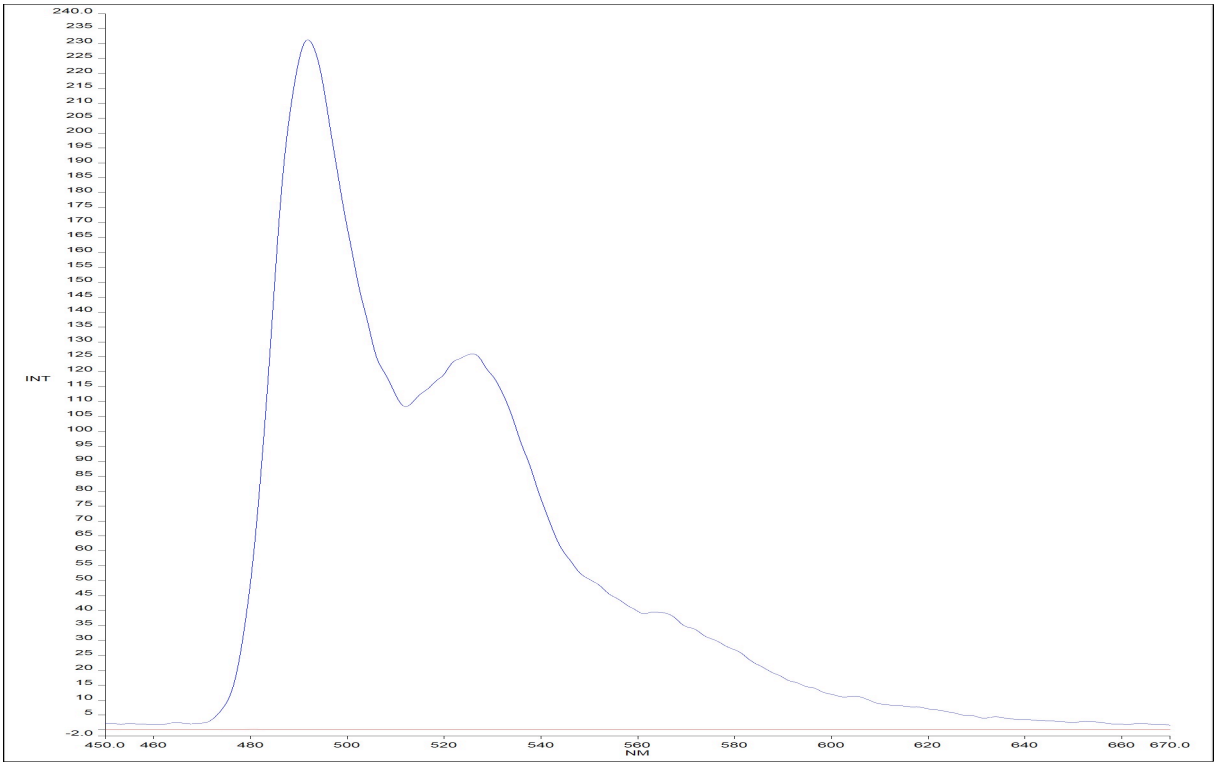


Figure S11. Emission spectrum at 77 K. Excitation at 400 nm.

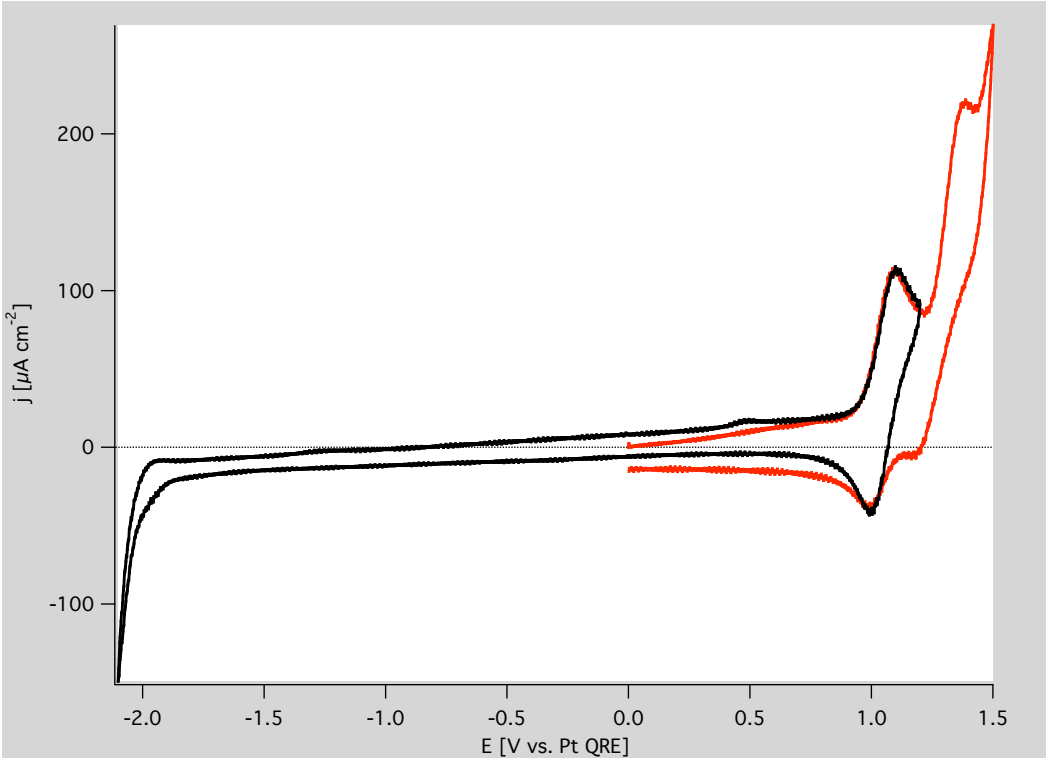


Figure S12. Cyclic voltamogram of **EB91**

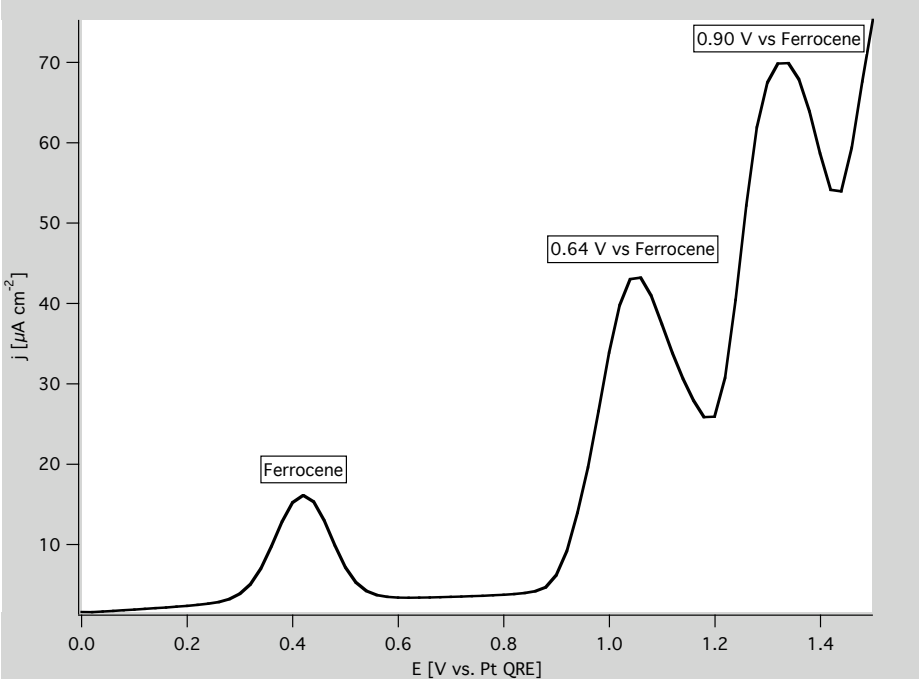


Figure S13. DPV of **EB91**

Device fabrication.

1,3-Bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene (OXD7), 2-(4-Biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and 1,3,5-tris[N-(phenyl)benzimidazole]benzene (TPBI) were purchased from Luminescence Technology Corp. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios CH8000) were purchased from HC Starck while poly(9-vinylcarbazole) (PVK) was purchased from Aldrich. All materials were used as received. The device structure consists of a 120 nm transparent ITO layer as the bottom electrode, supported on a glass substrate. A 60 nm PEDOT:PSS layer and the emissive layer (EML) were spun in sequence on top of ITO, using a Delta6 RC spincoater from Suss Microtec. Then, TPBI (30 nm), Cs_2CO_3 (1 nm) and the aluminum top metal contact (100 nm) were evaporated in sequence in an evaporation chamber at a pressure of 2.0 – 5.0 x 10^{-7} mbar. The ITO surface was treated for 10 min with O_2-plasma cleaner prior to any further processing. The PEDOT layer was annealed at 200 °C for 5 minutes. The emissive layer was spun from a chlorobenzene solution containing 1.5% w/w of total solid. The solutions were stirred for an hour at room temperature, and filtered through a 0.2 μm PTFE filter (Millex, Millipore) prior to spinning. The freshly fabricated OLEDs were characterized optically and electrically under inert atmosphere with a C9920-12 External Quantum Efficiency Measurement System from HAMAMATSU. The emissive layer was PVK:OXD7:**EB91** (68 :29 :3 in weight).

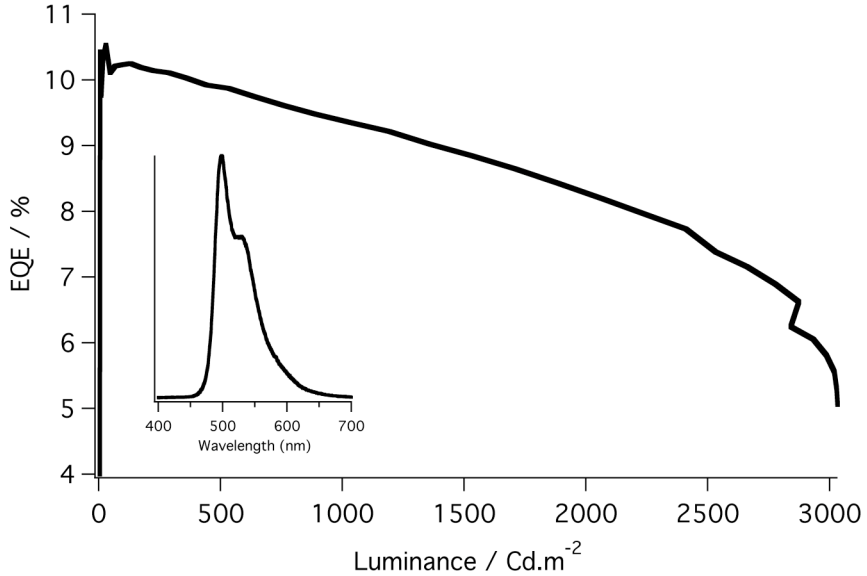


Figure S14. External quantum efficiency versus Luminance. Inset: electroluminescence spectrum, CIE (0.24; 0.60)

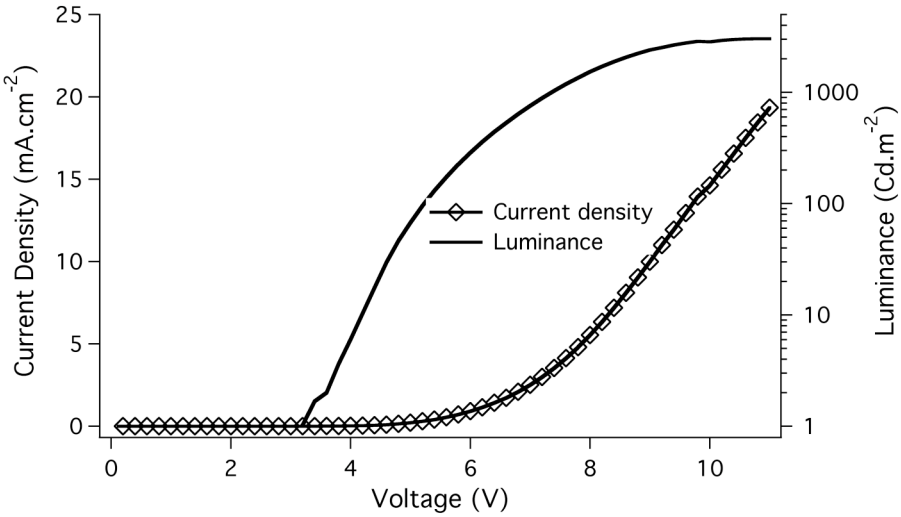


Figure S15. Current density and luminance plotted *vs* voltage

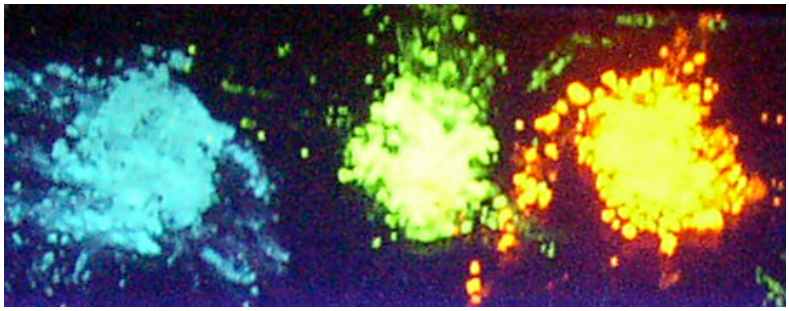


Figure S16. Luminescence under UV light of solid sample of blue, green (**EB91**) and orange tetranuclear complexes.

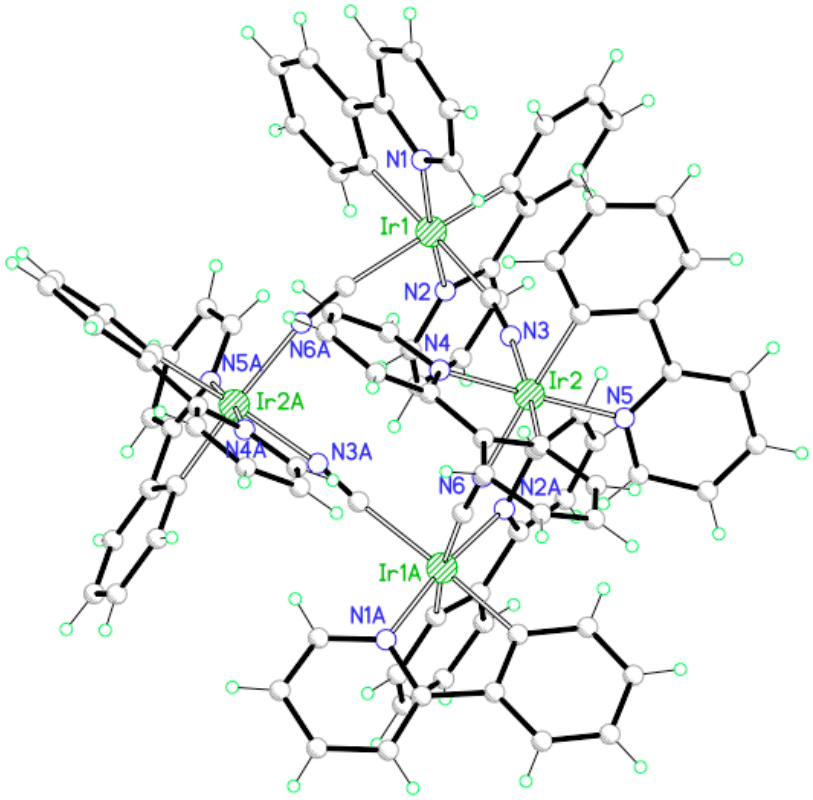


Table S1. Crystal data and structure refinement for eb91.

Identification code	eb91	
Empirical formula	$C_{110}H_{91}Ir_4N_{21}$ (**EB91**.9 CH_3CN)	
Formula weight	2475.84	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 21.007(6) Å	a= 90°.
	b = 21.431(3) Å	b= 114.479(16)°.
	c = 24.366(5) Å	g = 90°.
Volume	9984(4) $Å^3$	
Z	4	
Density (calculated)	1.647 Mg/m^3	
Absorption coefficient	5.374 mm^{-1}	
F(000)	4824	
Crystal size	0.49 x 0.42 x 0.21 mm^3	
Theta range for data collection	3.31 to 25.00°.	
Index ranges	-23<=h<=24, -25<=k<=25, -28<=l<=28	

Reflections collected	50504
Independent reflections	8390 [R(int) = 0.1055]
Completeness to theta = 25.00°	95.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.3694
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8390 / 30 / 622
Goodness-of-fit on F^2	1.107
Final R indices [I>2sigma(I)]	R1 = 0.0980, wR2 = 0.2388
R indices (all data)	R1 = 0.1403, wR2 = 0.2877
Largest diff. peak and hole	6.677 and -4.861 e.Å^{-3}