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Novel potential phenanthroline/diaryldiazadiene bridging ligands

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crystallographic data, electrochemical and spectroelectrochemical data. See
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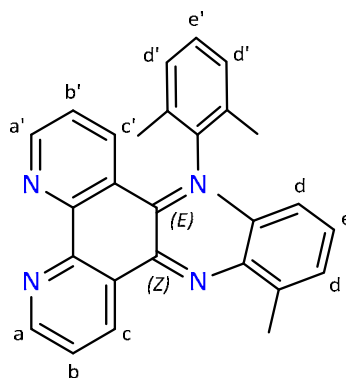
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General materials and procedures

Technical grade solvents were purchased from VWR/Prolabo and redistilled under reduced pressure at 40°C. Acetonitrile for spectroscopic measurements was purchased in spectroscopic grade from Roth. Dry and degassed Methanol and Dichloromethane for inert reactions were purified from the HPLC grade solvents from VWR/Prolabo with a solvent purification system SPS 800 from MBraun. All chemicals were purchased from Sigma Aldrich, ABCR, Acros Organics, Alfa Aesar or VWR/Prolabo and used as purchased ($\geq 95\%$). Inert reactions were performed under an Argon 4.6 atmosphere by means of standard Schlenk techniques. 1,10-Phenanthroline-5,6-dione and the Iridium dimer $[(ppy)Ir]_2(\mu-Cl)_2$ (ppy = 2-phenylpyridine) were synthesized following literature procedures.^{1,2} Size exclusion chromatography was carried out with Sephadex LH-20 as stationary phase (particle size 25-100 μm), purchased from Pharmacia Fine Chemicals AB, Uppsala, Sweden. 1H -NMR spectra were recorded at ambient temperature, unless otherwise stated, with a Bruker 400 MHz spectrometer and Bruker 500 MHz spectrometer. All spectra were referenced to the corresponding solvent residual signal, i.e. 1.940 ppm for Acetonitrile, 7.260 for Chloroform, 5.320 for Dichloromethane and 4.870 for Methanol. LC mass analysis was performed on a Finnigan MAT, SSQ-7000 spectrometer, ESI mass analysis was performed on a Shimadzu LC-MS 2020 equipped with an electrospray ionisation source and a SPD-20A UV/vis detector. X-ray crystallography was performed on a SuperNova (Dual Source) diffractometer, equipped with an ATLAS detector, from Agilent Technologies. The structures were refined by full-matrix least squares techniques against F_o^2 (SHELXL 2013).³ The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.

Synthesis of (phen(N-o-Xyl)₂), L1

Under inert conditions 1.85 mL 2,6-Dimethylaniline (15 mmol) and 6.22 mL Triethylamine (45 mmol) were dissolved in 50 mL dry Toluene and the solution was heated up to 90 °C. Within 10 min 1.6 mL TiCl₄ (15 mmol) were added *via* a syringe and subsequently a suspension of 1.05 g 1,10-Phenanthroline-5,6-dione (5 mmol) in 15 mL Toluene was added. The dark slurry was heated to reflux for 30 min and filtered hot. The solvent was removed from the crude filtrate under reduced pressure at 40°C and the residue purified through silica column chromatography (eluent: Toluene/Methanol (9:1)). The solvent was removed under reduced pressure at 40°C from the oily product fraction and the residue was again subjected to silica column chromatography in order to remove remaining aniline. (eluent: Cyclohexane/Ethylacetate (9:1)). After removal of the solvent, the product was received as crystalline red solid. (0.3 g, 0.7 mmol, 14%). Single crystals were grown by slow evaporation of the solvent from a solution in ethyl acetate.

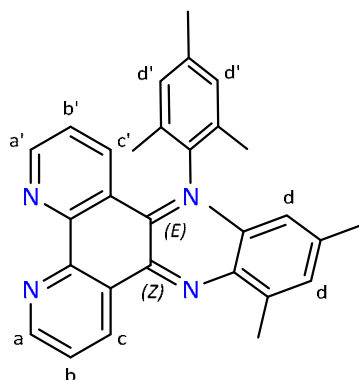
Crystal data for phen(N-o-Xyl)₂: C₂₈H₂₄N₄, M_r = 416.51 g mol⁻¹, red fragment, crystal size 0.2071 x 0.1818 x 0.1202 mm³, monoclinic, space group *P* 2₁/c, a = 15.6277(2) Å, b = 7.31640(10) Å, c = 20.3483(3) Å, β = 102.6660(10)°, V = 2269.98(5) Å³, T = 180.00(14) K, Z = 4, ρ_{calcd.} = 1.219 Mg/m³, μ (Mo-Kα) = 0.073 cm⁻¹, F(000) = 880, altogether 10877 reflections up to h(-17/19), k(-8/8), l(-25/17) measured in the range of 3.459° ≤ θ ≤ 26.251°, completeness θ_{max} = 99.7%, 4445 independent reflections, R_{int} = 0.0184, 3905 reflections with Fo > 4 σ(Fo), 293 parameters, 0 restraints, R1_{obs} = 0.0371, wR2_{obs} = 0.0998, R1_{all} = 0.0431, wR2_{all} = 0.1037, GOOF = 1.044, largest difference peak and hole: 0.288/-0.171 e/Å⁻³. CCDC 1048465 contains 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.

¹H-NMR (CD₂Cl₂, 400 MHz): δ [ppm] = 8.97 (dd, 1 H, ³J_{H,H} = 5 Hz, ⁴J_{H,H} = 2 Hz, Ha), 8.77 (dd, 1 H, ³J_{H,H} = 5 Hz, ⁴J_{H,H} = 2 Hz, Ha'), 8.68 (dd, 1 H, ³J_{H,H} = 8 Hz, ⁴J_{H,H} = 2 Hz, Hc), 7.56 (dd, 1 H, ³J_{H,H} = 5 Hz, ³J_{H,H} = 8 Hz, Hb), 7.07 (dd, 1 H, ³J_{H,H} = 8 Hz, ⁴J_{H,H} = 2 Hz, Hc'), 7.01 (d, 2 H, ³J_{H,H} = 7 Hz, Hd/d'), 6.97 (dd, 1 H, ³J_{H,H} = 5 Hz, ³J_{H,H} = 8 Hz, Hb'), 6.87 (m, 4 H, Hd/d' + 2 He/e'), 2.03 (s, 6 H, o-CH₃(E)/CH₃(Z)), 1.38 (s, 6 H, o-CH₃(E)/CH₃(Z)).

¹³C{¹H}-NMR (CD₂Cl₂, 100.6 MHz): δ [ppm] = 157.32, 155.36, 153.69, 153.04, 151.88, 151.31, 149.24, 147.22, 135.24, 134.93, 130.96, 128.68, 128.08, 126.06, 125.54, 125.22, 124.62, 124.31, 123.52, 123.34, 18.62, 17.53.

Mass spectrometry (CI): m/z: 401 ([M-CH₄]⁺), **417 ([M]⁺)**, 445 ([M+Et]⁺)

UV/Vis (MeCN, 10⁻⁶ M): ε [M⁻¹ cm⁻¹] (λ_{max} [nm]): 80 (405).

Synthesis of phen(N-Mes)₂, L2

Under inert conditions 2.1 mL 2,4,6-Trimethylaniline (15 mmol) and 6.22 mL Triethylamine (45 mmol) were dissolved in 50 mL dry Toluene and the solution was heated up to 90 °C. Within 10 min 1.6 mL TiCl₄ (15 mmol) were added *via* a syringe and subsequently a suspension of 1.05 g 1,10-Phenanthroline-5,6-dione (5 mmol) in 15 mL Toluene was added. The dark slurry was heated to reflux for 30 min and filtered hot. The solvent was removed from the crude filtrate under reduced pressure at 40°C and the residue purified through silica column chromatography (eluent: Toluol/Methanol (9:1)). The solvent was removed under reduced pressure at 40°C from the oily product fraction and the residue was again subjected to silica column chromatography in order to remove remaining aniline. (eluent: Cyclohexan/Ethylacetat (9:1)). After removal of the solvent, the product was received as crystalline red solid. (0.2 g, 0.5 mmol, 10%). Single crystals were grown by slow evaporation of the solvent from a solution in ethyl acetate.

Crystal data for phen(N-Mes)₂: C₃₀H₂₈N₄, M_r = 444.56 g mol⁻¹, red prism, crystal size 0.1946 x 0.1303 x 0.0707 mm³, triclinic, space group *P*-1, *a* = 9.4981(5) Å, *b* = 10.2782(5) Å, *c* = 13.8108(8) Å, α = 92.571(4)°, β = 109.723(5)°, γ = 107.893(5)°, V = 1191.05(12) Å³, T = 180(2) K, Z = 2, ρ_{calcd.} = 1.240 Mg/m³, μ (Cu-Kα) = 0.572 cm⁻¹, F(000) = 472, altogether 10930 reflections up to h(-11/11), k(-11/12), l(-17/16) measured in the range of 7.637° ≤ θ ≤ 73.506°, completeness θ_{max} = 99.5 %, 4642 independent reflections, R_{int} = 0.0175, 3843 reflections with Fo > 4 σ(Fo), 313 parameters, 0 restraints, R_{1obs} = 0.0385, wR_{2obs} = 0.1009, R_{1all} = 0.0471, wR_{2all} = 0.1073, GOOF = 1.035, largest difference peak and hole: 0.421/-0.180 e/Å⁻³. CCDC 1048466 contains 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.

¹H-NMR (CD₂Cl₂, 400 MHz): δ [ppm] = 8.96 (dd, 1 H, ³J_{H,H} = 5 Hz, ⁴J_{H,H} = 2 Hz, H_a), 8.76 (dd, 1 H, ³J_{H,H} = 5 Hz, ⁴J_{H,H} = 2 Hz, H_{a'}), 8.65 (dd, 1 H, ³J_{H,H} = 8 Hz, ⁴J_{H,H} = 2 Hz, H_c), 7.55 (dd, 1 H, ³J_{H,H} = 5 Hz, ³J_{H,H} = 8 Hz, H_b), 7.11 (dd, 1 H, ³J_{H,H} = 8 Hz, ⁴J_{H,H} = 2 Hz, H_{c'}), 6.98 (dd, 1 H, ³J_{H,H} = 5 Hz, ³J_{H,H} = 8 Hz, H_{b'}), 6.83 (s, 2 H, H_{d/d'}), 6.68 (s, 2 H, H_{d/d'}), 2.26 (s, 3 H, *p*-CH₃(E)/CH₃(Z)), 2.18 (s, 3 H, *p*-CH₃(E)/CH₃(Z)), 1.98 (s, 6 H, *o*-CH₃(E)/CH₃(Z)), 1.34 (s, 6 H, *o*-CH₃(E)/CH₃(Z)).

¹³C{¹H}-NMR (CD₂Cl₂, 100.6 MHz): δ [ppm] = 157.71, 155.51, 153.55, 152.87, 147.03, 146.77, 144.74, 135.25, 134.84, 133.78, 132.57, 131.15, 129.33, 128.71, 126.25, 125.46, 125.03, 124.46, 123.46, 20.89, 18.54, 17.37.

Mass spectrometry (CI): *m/z*: 429 ([M-CH₄]⁺), **445 ([M]⁺)**, 473 ([M+Et]⁺)

UV/Vis (MeCN, 10⁻⁶ M): ε [M⁻¹ cm⁻¹] (λ_{max} [nm]): 120 (425).

Synthesis of $\{(\text{ppy})_2\text{Ir}[\text{phen}(\text{N-o-Xyl})_2]\}(\text{PF}_6)_2$, Ir-L1

Under inert conditions, a solution of 50 mg of phen(N-o-Xyl)₂ (0.12 mmol) and 64.3 mg $\{(\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2\}$ (0.06 mmol) was heated and stirred at 60°C for 24 hours. Dichloromethane was removed under inert conditions and an aqueous solution of ammonium hexafluoridophosphate (98 mg / 10 mL water) was added to precipitate the corresponding complex salt. The precipitate was filtrated and washed with diethylether. The dried solid was subjected to size exclusion chromatography in an azeotropic mixture of chloroform/acetone/methanol. The solvent was removed from the product fraction and the residue dissolved in methanol. The product was complex was precipitated upon addition of an aqueous solution of hexafluoridophosphate and the precipitate filtered, washed with diethylether, and the remaining solid dried *in vacuo*. Yield: 80 mg (63.3 %) of a brown powder. Single crystals were grown by slow vapour diffusion of diethyl ether into a solution of the complex in acetonitrile.

Crystal data for $\{(\text{ppy})_2\text{Ir}[\text{phen}(\text{N-o-Xyl})_2]\}(\text{PF}_6)\cdot\text{MeCN}$: C₅₂H₄₃F₆IrN₇P, M_r = 1103.10 g mol⁻¹, brown column, crystal size 0.104 x 0.0633 x 0.041 mm³, triclinic, space group *P*-1, *a* = 8.9794(4) Å, *b* = 16.0111(6) Å, *c* = 17.5265(8) Å, α = 113.881(4)°, β = 92.391(4)°, γ = 101.791(3)°, *V* = 2233.54(18) Å³, *T* = 150.1(4) K, *Z* = 2, $\rho_{\text{calcd.}}$ = 1.640 Mg/m³, μ (Cu-K α) = 6.732 cm⁻¹, *F*(000) = 1100, altogether 19581 reflections up to *h*(-11/11), *k*(-17/19), *l*(-21/21) measured in the range of 7.456° ≤ θ ≤ 74.484°, completeness Θ_{max} = 99.4 %, 9011 independent reflections, *R*_{int} = 0.0865, 7805 reflections with *F*_o > 4 σ (*F*_o), 605 parameters, 0 restraints, *R*_{1_{obs}} = 0.0509, *wR*_{2_{obs}} = 0.1344, *R*_{1_{all}} = 0.0624, *wR*_{2_{all}} = 0.1412, *GOOF* = 1.155, largest difference peak and hole: 2.069/-2.258 e/Å⁻³. CCDC 1048467 contains 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.

Mass spectrometry (HR-ESI): 917.294 ([M-PF₆]⁺)

UV/Vis (MeCN, 10⁻⁶ M): ϵ [M⁻¹ cm⁻¹] (λ [nm]): 150 (500).

Reaction of Ir-L1 with Tetrakis(acetonitrile)copper(I) hexafluoridophosphate

1. Under an argon atmosphere, a solution of Ir-L1 (5 mg, 4.7 μmol) in dichloromethane (1 mL) was stirred at room temperature. Excess solid tetrakis(acetonitrile)copper(I) hexafluoridophosphate (10 mg, 26.8 μmol) was added. An immediate darkening of the solution was observed and the mixture was allowed to react for 24 hours. The solvent was removed and the residue taken up with 0.6 mL deuterated chloroform and filtered through glass wool. The residual solution was investigated *via* ¹H-NMR spectroscopy (see Figure S10).

Under an argon atmosphere Ir-L1 (5 mg, 4.7 μmol) was dissolved in deuterated chloroform. After an ¹H-NMR spectrum had been recorded, solid excess of tetrakis(acetonitrile)copper(I) hexafluoridophosphate (10 mg, 26.8 μmol) was added and a second spectrum was recorded after ten minutes. The solution was then stirred in the NMR tube for 24 hours before another spectrum was recorded. (for all spectra see Figure S11).

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.93 (dd, 2H), 7.90 (d, 2H), 7.74 (d, 2H), 7.63 (m, 4H), 7.53 (dd, 2H), 7.22/7.17 (dt/m, 4H, mixed with the solvent residual signal), 7.08 (t, 2H), 7.03 (m, 4H), 6.92 (dt, 2H), 6.80 (dt, 2H), 6.16 (dd, 2H), 2.40 (s, 6H), 1.97 (s, 6H).

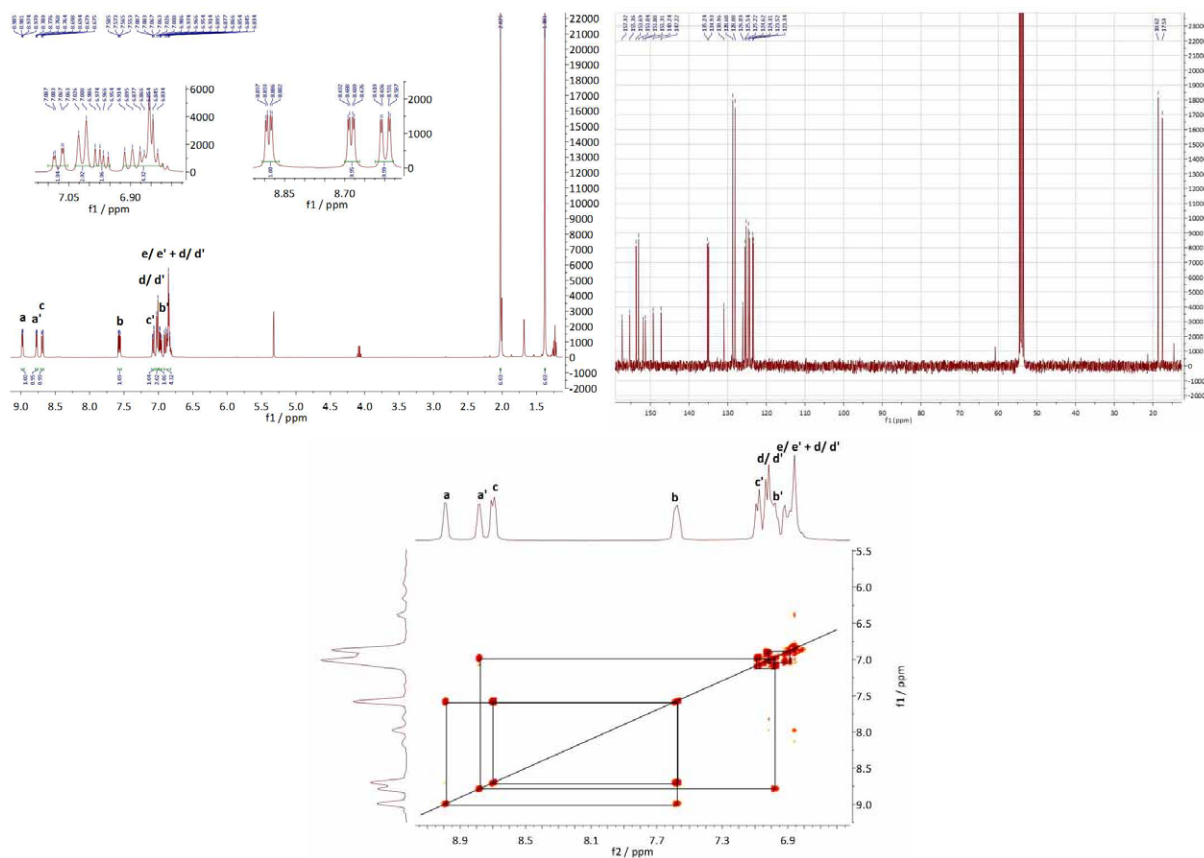


Figure S1: NMR spectra of L1 in CD₂Cl₂; top left: ¹H-NMR spectrum; top right: ¹³C{¹H}-NMR spectrum; bottom: H,H-COSY spectrum of the aromatic region.

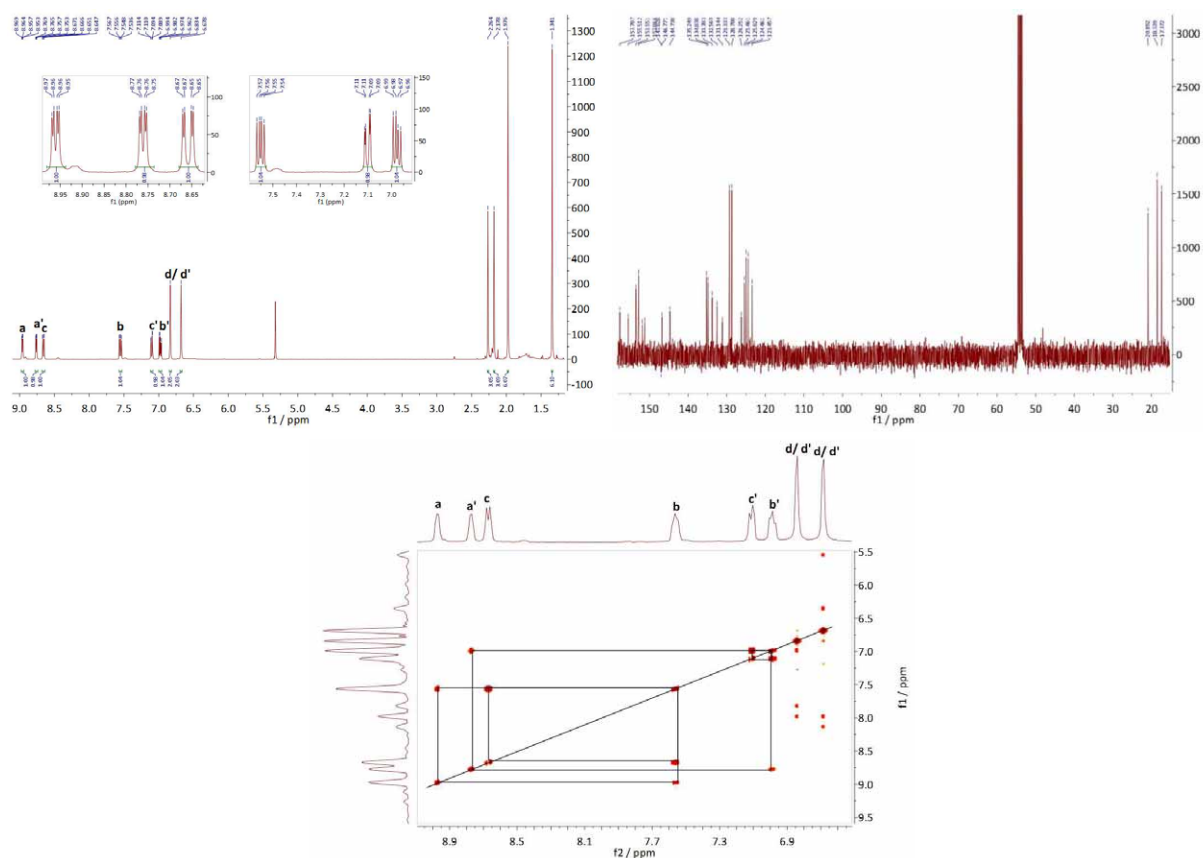


Figure S2: NMR spectra of L2 in CD₂Cl₂; top left: ¹H-NMR spectrum; top right: ¹³C[¹H]-NMR spectrum; bottom: H,H-COSY spectrum of the aromatic region.

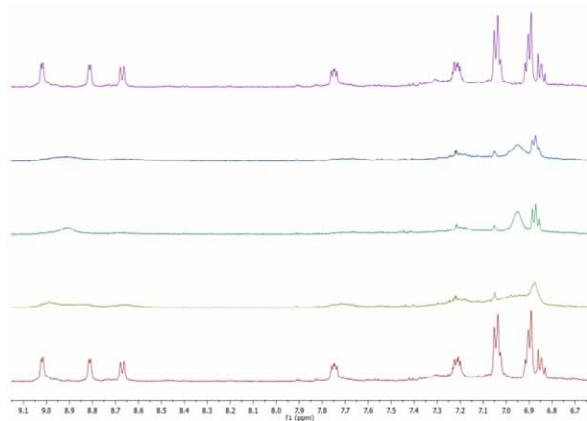


Figure S3: Aromatic region of the temperature dependent ¹H-NMR spectra of L1 in DMSO-d₆ at 300 K, 350 K, 375 K, 350 K, and 375 K, subsequently.

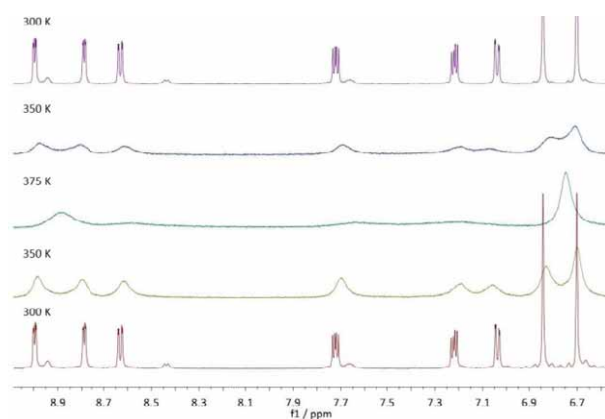


Figure S4: Aromatic region of the temperature dependant $^1\text{H-NMR}$ spectra of **L2** in DMSO-d_6 at 300 K, 350 K, 375 K, 350 K, and 300 K, subsequently.

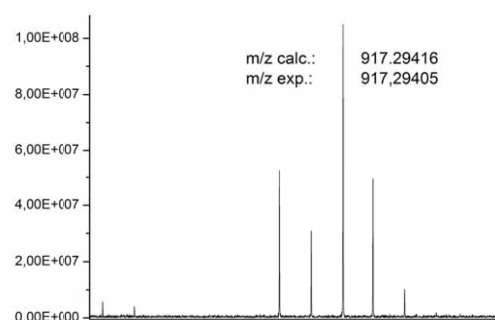


Figure S5: HR-ESI mass spectrum of **Ir-L1** with characteristic isotopic pattern.

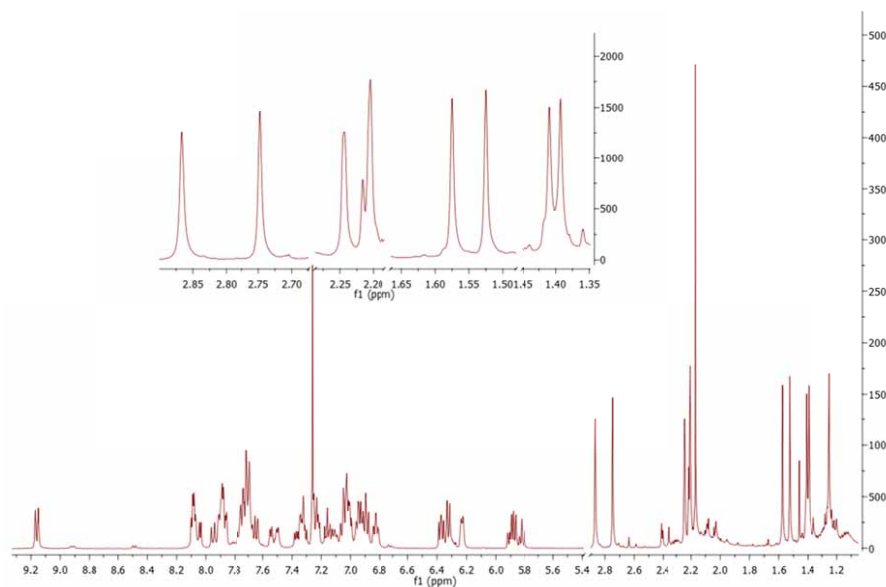


Figure S6: $^1\text{H-NMR}$ spectrum of **Ir-L1**; inlay: the aliphatic region is highlighted, showing eight separable peaks for the methyl groups of the *o*-Xylidene substituents.

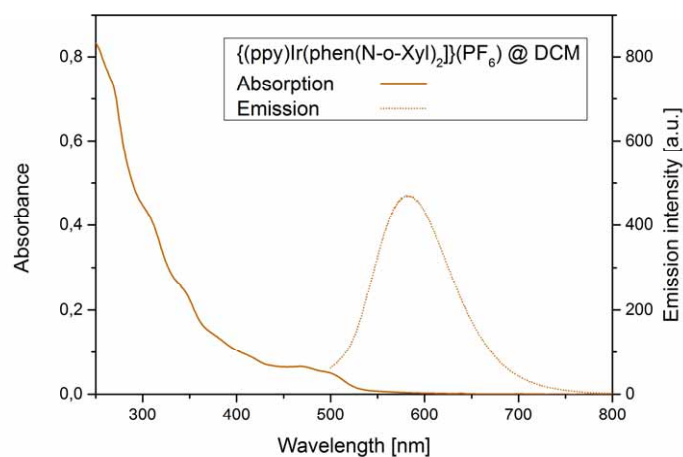


Figure S7: Absorption and emission spectra of Ir-L1 in dichloromethane (10^{-5} M).

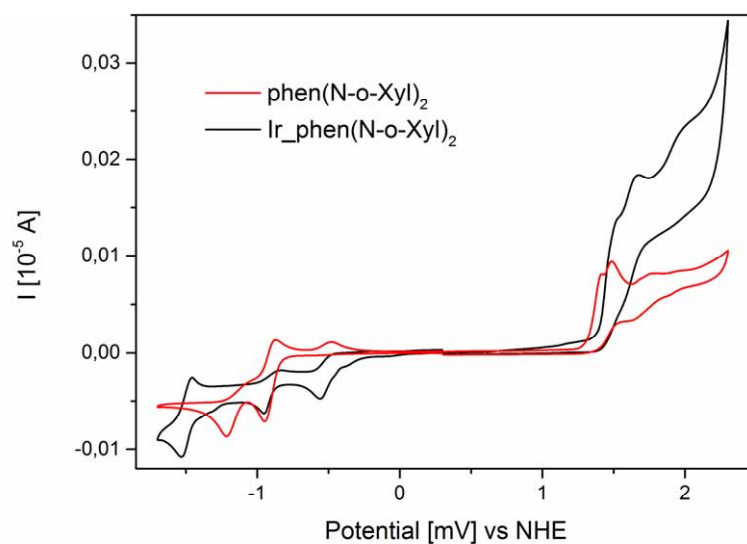


Figure S8: Cyclic voltammogram of L1 and Ir-L1 recorded in 1 mM solutions in deaerated acetonitrile with 0.1 M (*n*Bu₄N)PF₆ as supporting electrolyte, scan rate 50 mV/s, Ferrocene as internal standard (Fc/Fc⁺ vs NHE 0.63 V)

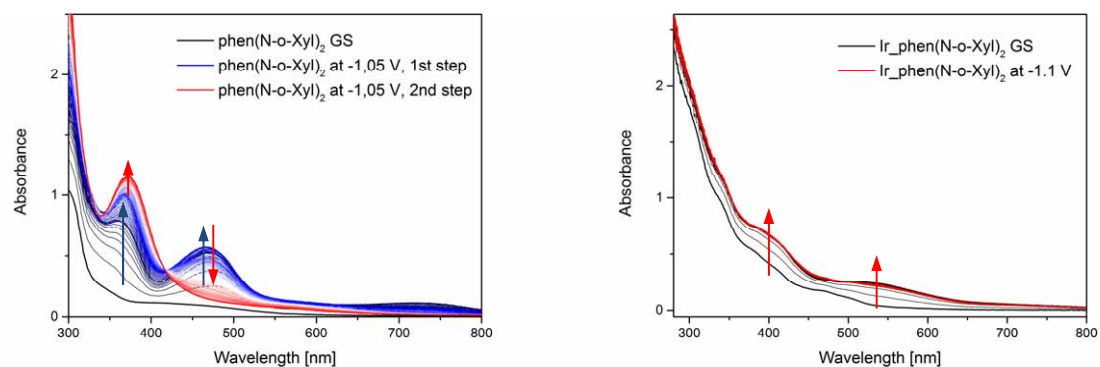


Figure S9: Spectroelectrochemical data for **L1** and **Ir-L1** at -1.05 V recorded in 1 mM solutions in deaerated acetonitrile with 0.1 M $(n\text{Bu}_4\text{N})\text{PF}_6$ as supporting electrolyte; blue arrows indicate the spectral changes during the first process observed, red arrows indicate significant changes observed during a second process; left: reduction of **L1** at -1.05 V vs. NHE; right: reduction of **Ir-L1** at -1.1 V; red arrows indicate spectral changes observed upon reduction.

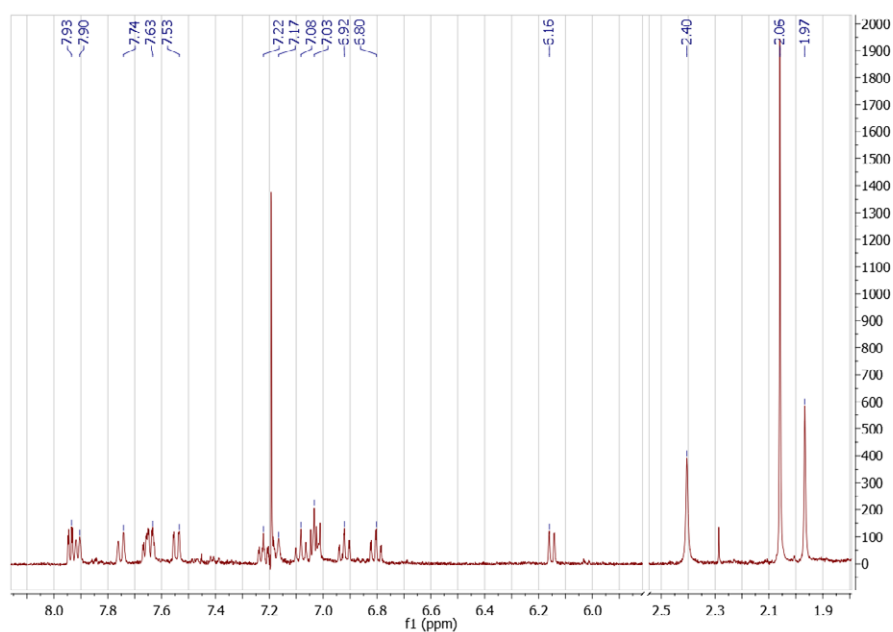


Figure S10: ^1H -NMR spectrum of **Ir-L1** after reaction with excess of tetrakis(acetonitrile)copper(I) hexafluorophosphate in dichloromethane, removal of the solvent, uptake in deuterated chloroform and filtration through glass wool.

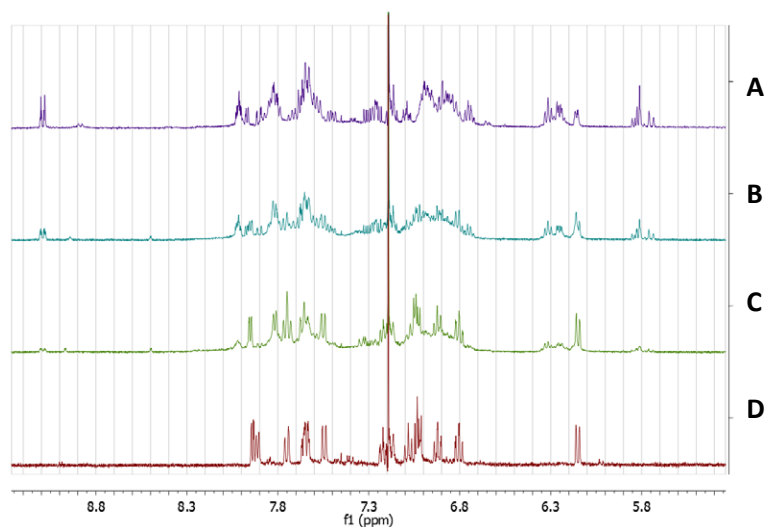


Figure S11: $^1\text{H-NMR}$ spectra (aromatic region) showing the progression of the reaction between **Ir-L1** and tetrakis(acetonitrile)copper(I) hexafluorophosphate in deuterated chloroform; **A** educt spectrum; **B** ten minutes after addition of the copper complex; **C** 24 hours after addition of the copper complex; **D** spectrum of the product obtained after reaction in dichloromethane and filtration in deuterated chloroform (**Figure S7**).

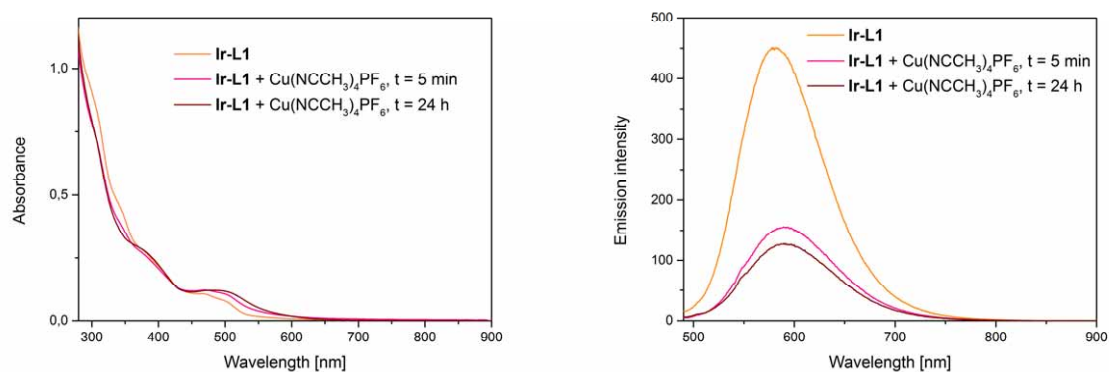


Figure S12: UV/Vis spectra (left) and emission spectra (right) of a solution of **Ir-L1** in dichloromethane before (orange line), 5 minutes after (pink line), and 24 hours after the addition of $\text{Cu}(\text{NCCH}_3)_4\text{PF}_6$ (brown line); a darkening of the solution is characterized by the rise of an absorption band between 450 nm and 650 nm, and significant decrease of emission intensity, indicative for a reaction between the diazadiene and copper(I).⁴

Table S1. Crystal data and structure refinement for **L1**.

Empirical formula	C ₂₈ H ₂₄ N ₄	
Formula weight	416.51	
Temperature	180.00(14) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 15.6277(2) Å	α = 90°.
	b = 7.31640(10) Å	β = 102.6660(10)°.
	c = 20.3483(3) Å	γ = 90°.
Volume	2269.98(5) Å ³	
Z	4	
Density (calculated)	1.219 Mg/m ³	
Absorption coefficient	0.073 mm ⁻¹	
F(000)	880	
Crystal size	0.2071 x 0.1818 x 0.1202 mm ³	
Theta range for data collection	3.459 to 26.251°.	
Index ranges	-17 ≤ h ≤ 19, -8 ≤ k ≤ 8, -25 ≤ l ≤ 17	
Reflections collected	10877	
Independent reflections	4445 [R(int) = 0.0184]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4445 / 0 / 293	
Goodness-of-fit on F ²	1.044	
Final R indices [I > 2σ(I)]	R ₁ = 0.0371, wR ₂ = 0.0998	
R indices (all data)	R ₁ = 0.0431, wR ₂ = 0.1037	
Largest diff. peak and hole	0.288 and -0.171 e.Å ⁻³	

Table S2. Crystal data and structure refinement for **L2**.

Empirical formula	C ₃₀ H ₂₈ N ₄	
Formula weight	444.56	
Temperature	180(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.4981(5) Å	α = 92.571(4)°.
	b = 10.2782(5) Å	β = 109.723(5)°.
	c = 13.8108(8) Å	γ = 107.893(5)°.
Volume	1191.05(12) Å ³	
Z	2	
Density (calculated)	1.240 Mg/m ³	
Absorption coefficient	0.572 mm ⁻¹	
F(000)	472	
Crystal size	0.1946 x 0.1303 x 0.0707 mm ³	
Theta range for data collection	7.637 to 73.506°.	
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 12, -17 ≤ l ≤ 16	
Reflections collected	10930	
Independent reflections	4642 [R(int) = 0.0175]	
Completeness to theta = 67.679°	99.5 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4642 / 0 / 313	
Goodness-of-fit on F ²	1.035	
Final R indices [I > 2σ(I)]	R1 = 0.0385, wR2 = 0.1009	
R indices (all data)	R1 = 0.0471, wR2 = 0.1073	
Largest diff. peak and hole	0.421 and -0.180 e.Å ⁻³	

Table S3. Crystal data and structure refinement for Ir-L1.

Empirical formula	C ₅₂ H ₄₃ F ₆ Ir N ₇ P	
Formula weight	1103.10	
Temperature	150.1(4) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.9794(4) Å	α = 113.881(4)°.
	b = 16.0111(6) Å	β = 92.391(4)°.
	c = 17.5265(8) Å	γ = 101.791(3)°.
Volume	2233.54(18) Å ³	
Z	2	
Density (calculated)	1.640 Mg/m ³	
Absorption coefficient	6.732 mm ⁻¹	
F(000)	1100	
Crystal size	0.104 x 0.0633 x 0.041 mm ³	
Theta range for data collection	7.456 to 74.484°.	
Index ranges	-11 ≤ h ≤ 11, -17 ≤ k ≤ 19, -21 ≤ l ≤ 21	
Reflections collected	19581	
Independent reflections	9011 [R(int) = 0.0865]	
Completeness to theta = 67.679°	99.4 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9011 / 0 / 605	
Goodness-of-fit on F ²	1.155	
Final R indices [I > 2σ(I)]	R1 = 0.0509, wR2 = 0.1344	
R indices (all data)	R1 = 0.0624, wR2 = 0.1412	
Largest diff. peak and hole	2.069 and -2.258 e.Å ⁻³	

Notes and references

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