Supporting Information

Modulating the luminescence of an iridium(III) complex incorporating a di(2-picolyl)anilino-appended bipyridine ligand with Zn^{2+} cations

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Experimental

General Procedure.

All manipulations were performed using Schlenk techniques under an Ar atmosphere, but the workups were carried out in air. All solvents were dried and purified by standard procedures. All starting materials were used as received. Ir complexes of 4-Me-ppy (4-methyl-2-phenylpyridine) were prepared following the literature procedure.[1] NMR spectra were recorded on Bruker DPX-200, AV 300 or AV 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are given versus $SiMe_4$ and were determined by reference to residual ^{1}H and ^{13}C solvent signals. Attribution of carbon atoms was based on HMBC, HMQC and COSY experiments. UV/vis absorption spectra were recorded using a UVIKON 9413 spectrophotometer, and emission spectra were measured on a PTI C 60 fluorescence spectrophotometer. High resolution mass spectra (HRMS) were performed on a MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. Elemental analyses were performed by the Service central d'analyse du CNRS at Vernaison.

Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube. The spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Phosphorescence lifetimes were measured by multichannel scaling following excitation with a µs-pulsed xenon lamp. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator. The fluorescence lifetime of the ligand was determined by time-correlated single-photon counting following excitation at 374.0 nm with an EPL-375 pulsed diode laser, using the same detector. Spectra at 77 K were obtained with the sample loaded in a quartz tube inside a quartz-walled Dewar flask filled with liquid nitrogen.

Caution! Perchlorate salts are potentially explosive and should be handled with care.

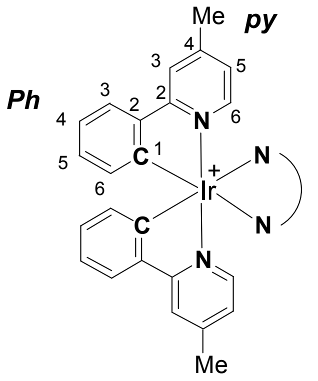
Preparation of bis(di(2-picolyl)aminostyryl)-2,2'-bipyridine, L1. To a THF solution (30 mL) of aldehyde **2**[2] (200 mg, 0.66 mmol) and 4,4'-bis(diethylphosphonomethyl)-2,2'-bipyridine (0.14 g, 0.30 mmol) was added ^{t}BuOK (0.14g, 1.2 mmol). The reaction mixture was stirred for 4 h. The reaction mixture was filtered and evaporated to dryness. Crystallization of the residue in a CH_2Cl_2-pentane mixture afforded **L1** as a yellow powder (0.2 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): 8.64 (d, 4H, ^3J = 4.8 Hz, H_6-Py*), 8.61 (d, 2H, ^3J = 5.1 Hz, H_6-bpy), 8.47 (d, 2H, H_3-bpy), 7.67 (td, 4H, ^3J = 7.7 Hz, ^4J = 1.8 Hz, H_4-py*), 7.41 (d, 4H, ^3J = 8.9 Hz, C_6H_4), 7.37 (d, 2H, ^3J = 16.2 Hz, =CH), 7.34 (dd, 2H, ^3J = 5.2 Hz, ^4J = 1.6 Hz, H_5-bpy), 7.28 (d, 4H, ^3J = 7.7 Hz, H_3-py*), 7.22 (dd, 4H, ^3J = 4.9 Hz, H_5-py*), 6.91 (d, 2H, ^3J = 16.2 Hz, =CH), 6.75 (d, 4H, ^3J = 8.9 Hz, C_6H_4), 4.90 (s, 8H, CH_2). Elemental analysis $C_{50}H_{43}N_8$.0.5 CH_2Cl_2 Calculated C, 75.97, H, 5.55, N, 14.03. Found C, 75.18, H, 5.41, N, 13.88. HRMS *m/z* calcd. for $C_{50}H_{43}N_8$: 755.36107, found: 755.3612.

Note: Compound **L1** is not soluble in CH_3CN. This prevents us to study its behavior in the presence of metal cations.

Preparation of 1. The chloride-bridged dimer [Ir(*C^N*-4-Me-ppy)$_2$(µ-Cl)]$_2$ (100 mg, 0.09 mmol), the bipyridine derivative **L1** (140 mg, 0.19 mmol), and $AgPF_6$ (60 mg 0.24 mmol) were mixed in dichloromethane (10 mL). The reaction mixture was stirred under Ar for 2 h. The solution was then concentrated to dryness and the product was extracted with CH_2Cl_2 (3 x 5 mL). Crystallization from a CH_2Cl_2/diethyl ether mixture gave an orange-red powder (186 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): 8.68 (s, 2H, H_3-bpy), 8.61 (d, 4H, H_6-Py*, ^3J = 4.4 Hz), 7.70 (s, 2H, H_6-bpy), 7.65 (m, 2H, H_3-Ph, 4H, H_3-Py*, 2H, H_3-Py), 7.48 (d, 4H, C_6H_4, ^3J = 8.9 Hz), 7.44 (d, 2H, H_6-Py, ^3J = 6.0 Hz), 7.41 (d, 2H, =CH^8, ^3J = 16.2 Hz), 7.27 (m, 2H, H_5-bpy), 7.25 (d, 4H, H_4-Py*, ^3J = 7.9 Hz), 7.20 (dd, 4H, H_5-Py*, ^3J = 6.8 Hz), 7.11 (d, 2H, =CH^7, ^3J = 16.2 Hz), 7.01 (td, 2H, H_4-Ph, ^3J = 7.5 Hz, ^4J = 1.0 Hz), 6.90 (td, 2H, H_5-Ph, ^3J = 7.5 Hz, ^4J = 1.2 Hz), 6.84 (dd, 2H, H_5-Py, ^3J = 6.0 Hz, ^4J = 1.4 Hz), 6.69 (d, 4H, C_6H_4, ^3J =

8.8 Hz), 6.34 (dd, 2H, H_6-Ph, ^3J = 7.5Hz, ^4J = 0.8 Hz), 4.86 (s, 8H, CH_2), 2.49 (s, 6H, CH_3). $^{13}C[^1H]$ NMR (75 MHz, $CDCl_3$): 167.23 (C_2-py), 158.13 (C_2-py*), 156.05 (C_2-bpy), 151.67 (C_1-Ph), 149.74 (C_6-py*), 149.53 (C_4-py), 149.38 (C_9), 149.13 (C_4-bpy), 149.05 (C_6-bpy), 147.90 (C_6-py), 143.64 (C_2-Ph), 137.19 (C_8), 136.89 (C_4-py*), 131.84 (C_6-Ph), 130.32 (C_5-Ph), 129.65 (C_{10}), 124.90 (C_{12}), 124.36 (C_3-Ph), 124.26 (C_5-py), 122.44 (C_5-bpy), 122.17 (C_5-py*,C_3-bpy), 122.08 (C_4-Ph), 120.80 (C_3-py*), 120.06 (C_3-py), 119.70 (C_7), 112.54 (C_{11}), 56.98 (CH_2), 21.29 (CH_3). Elemental analysis $C_{74}H_{62}F_6N_{10}IrP$-0.5 CH_2Cl_2 Calculated C, 60.83, H, 4.32, N, 9.52. Found C, 60.20, H, 4.36, N, 9.18. HRMS *m/z* calcd. for $C_{74}H_{62}N_{10}Ir$: 1283.47883, found: 1283.4793.

Numbering



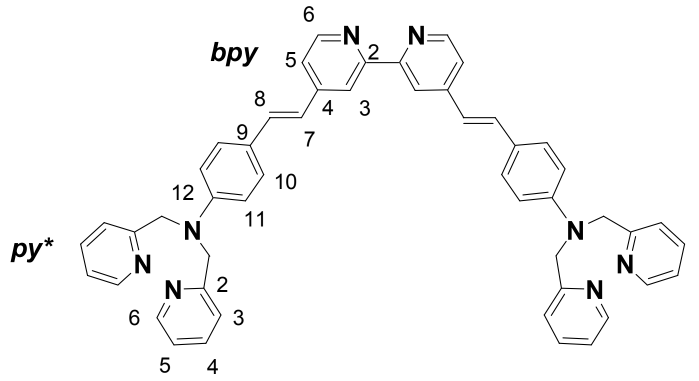


Table S1. Absorption and emission data for **1** and **L1**

Compound	Absorption λ_{max} / nm (ε / $dm^3\ mol^{-1}\ cm^{-1}$)^a	Emission λ_{max} / nm	Emission lifetime τ
L1	246sh (26700), 270sh (28700), 280 (29100), 334sh (16800), 385 (30900)	480 $^{(a)}$ 450 $^{(b)}$	< 1 ns $^{(a)}$ 1.7 ns $^{(b)}$
1	263 (31100), 387 (19900), 449 (27500)	638, 703, 775 $^{(c)}$	67 μs $^{(c)}$

$^{(a)}$ At 298 K in CH_2Cl_2. $^{(b)}$ At 77 K in ether/isopentane/ethanol (2:2:1, v/v). $^{(c)}$ At 77 K in ethanol/methanol (4:1, v/v).

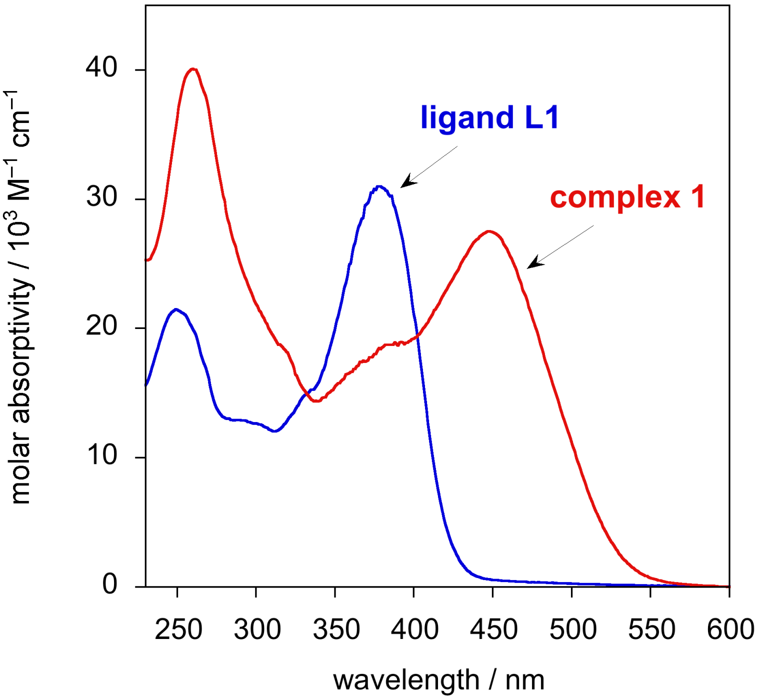


Figure S1. Absorption spectra of **1** and **L1** in CH_2Cl_2 at 298 K.

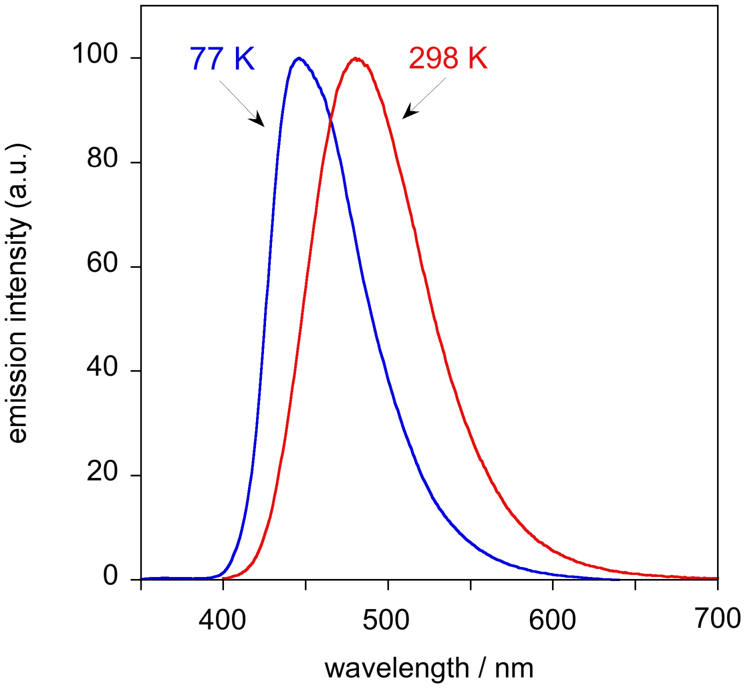


Figure S2. Emission spectra of **L1** in CH_2Cl_2 at 298 K (red line) and in ether/isopentane/ethanol (2:2:1, v/v) at 77 K (blue line) (λ_{ex} = 380 nm).

Titration experiments

The stoichiometry were estimated by a nonlinear least-squares fitting using the absorbance versus the concentration of the metal ions.[3] The complexation constants were determined by global analysis of the evolution of all absorption spectra by using Specfit Global analysis system V3.0 for 32-bit Windows system.[4]

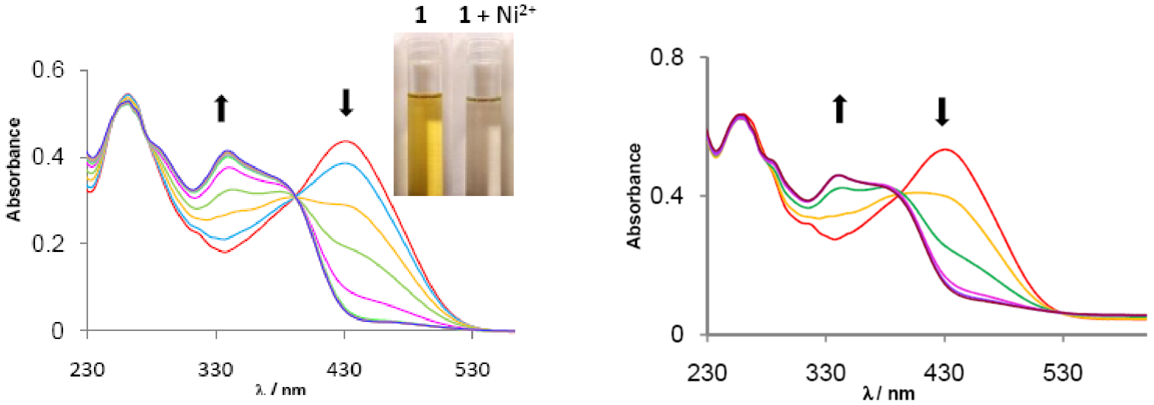


Figure S3. Absorption spectral changes of **1** (conc = 2 × 10^{-5} M) in CH_3CN upon addition of $Ni(ClO_4)_2$ (left) and $Cd(ClO_4)_2$ (right).

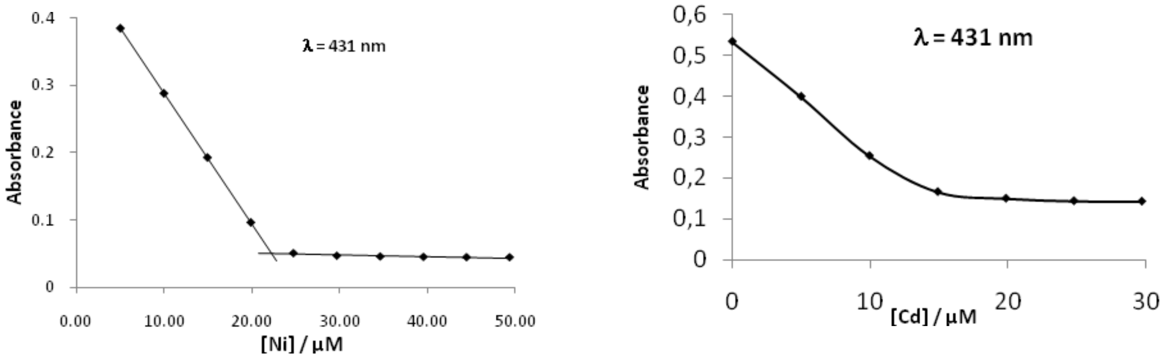


Figure S4. A plot of absorbance against [Ni^{2+}] monitored at 431 nm (*left*) and [Cd^{2+}] monitored at 431 nm (*right*).

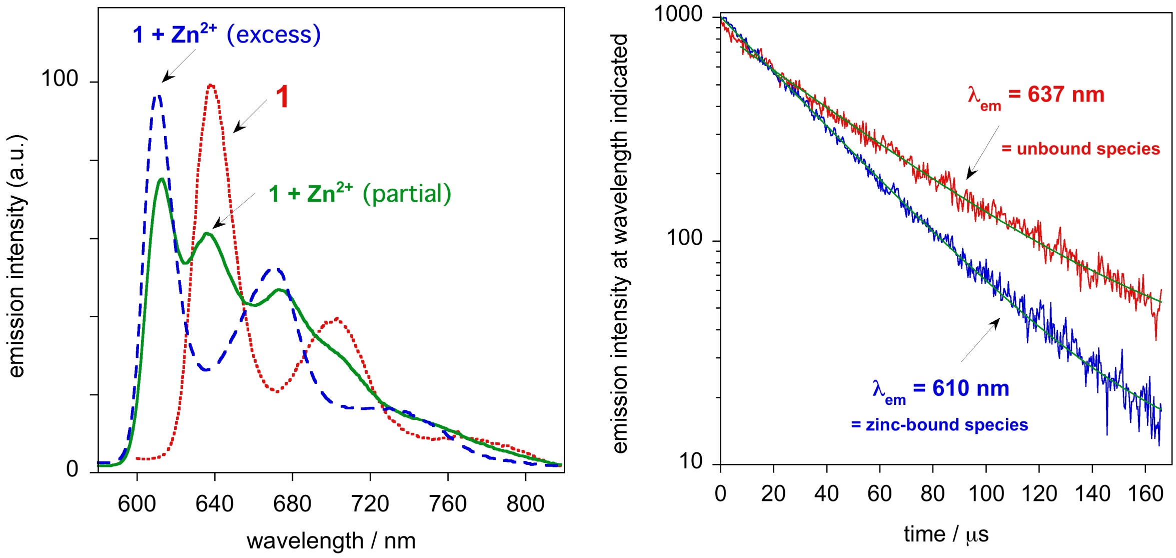


Figure S5. *Left:* Emission spectrum of **1** after the addition of a sub-stoichiometric amount of $Zn(ClO_4)_2$ (greeen solid line); λ_{ex} = 385 nm (isosbestic point), in ethanol/methanol (4:1, v/v) at 77 K. The spectra of **1** in the absence (red dotted line) and in the presence of excess Zn^{2+} (blue dashed line) are also shown.
Right: Corresponding emission decays registered at the wavelengths of the unbound and bound species, and exponential fits.

Crystallographic structure of 1

The crystal structure of **1** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC-718415. These data can be obtained free of charge at www.cccdc.cam.ac.uk/conts/retrieving.html [of from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Single crystals for X-ray diffraction studies were grown by slow diffusion of pentane in a CH_2Cl_2 solution of complex **1** at 20°C. It was extremely difficult to find a suitable sample due to the fact the crystals desolvate very quickly in few seconds. The sample were studied on a CCD Saphire 3 Xcalibur Oxford Diffraction with graphite monochromatized MoK_α radiation. The data collection and refinement parameters are presented Table S2. The structure was solved with SIR-97[5] which reveals the non-hydrogen atoms of the molecules After complete refinement, we found one pentane molecule, two stoechiometric dichloromethane molecules, two half CH_2Cl_2 molecules disordered between two positions and one water molecule. Due to difficulties to manage the disordered CH_2Cl_2 and the water molecule, we have used the Platon Squeeze option. The density max (4.392) is at the place of the deleted water molecule. The whole structure was refined by full-matrix least-square techniques on F^2, with hydrogens refined using the Riding mode (SHELXL-97) with initial isotropic parameters.[6,7]

Table S2. Crystallographic Data and Refinement for Complex **1**

formula	$C_{74}H_{62}F_6N_{10}IrP/(CH_2Cl_2)_2$
Fw	1598.36
Crystal system	Triclinic
Space group	$P\text{-}_1$
a [Å]	12.7790(10)
b [Å]	19.042(2)
C [Å]	19.6530(10)
α[°]	62.541(7)
β[°]	78.889(6)
γ [°]	70.056(7)
V [Å]	3898.0(10)
Z	2
D_{calcd} [g/cm^3]	1.332
F(000)	1612
λ(MoKα) [Å]	0.71069
θ range [°]	2.60-27.00
no.of rfns collected	45285
no. of unique rfns	14986
no. of params	947
goodness of fit on F^2	1.006
final *R*, *R*w	0.0581, 0.1586
$\Delta\rho_{max,min}$ [e. Å^{-3}]	4.449, -3.474

Table S3. Selected bond lengths (Å) and angles (°) for complex **1**

Ir(1)-N(3)	2.136(5)	Ir(1)-C(11)	2.021(6)
Ir(1)-N(7)	2.138(5)	Ir(1)-C(23)	2.014(6)
Ir(1)-N(1)	2.037(5)	C(23)-Ir(1)-N(1)	92.9(2)
Ir(1)-N(2)	2.050(5)	C(23)-Ir(1)-N(2)	80.2(2)
N(1)-Ir(1)-N(7)	98.07(19)	C(23)-Ir(1)-N(3)	173.1(2)
N(1)-Ir(1)-N(3)	90.6(2)	C(23)-Ir(1)-N(7)	97.1(2)
N(3)-Ir(1)-N(7)	76.53(19)	C(11)-Ir(1)-N(1)	80.4(2)
N(2)-Ir(1)-N(7)	89.23(18)	C(11)-Ir(1)-N(2)	93.0(2)
N(2)-Ir(1)-N(3)	96.9(2)	C(11)-Ir-N(3)	175.0(3)
C(11)-Ir(1)-C(23)	89.7(2)	C(11)-Ir(1)-N(7)	173.1(2)

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