

Supporting Information for:

Highly luminescent bis-cyclometalated Iridium(III) ethylenediamine complex: synthesis and correlation between the solid state polymorphism and the photophysical properties

Anna Maria Talarico,^a Iolinda Aiello,^a Anna Bellusci,^a Alessandra Crispini,^b Mauro Ghedini,^a Nicolas Godbert,^a Teresa Pugliese^a and Elisabeta Szerb^a

^aAnna Maria Talarico, Iolinda Aiello, Anna Bellusci, Mauro Ghedini, Nicolas Godbert, Teresa Pugliese, Elisabeta I. Szerb

Centro di Eccellenza CEMIF.CAL, LASCAMM CR-INSTM Unità INSTM della Calabria and Laboratorio Regionale Licryl, CNR-INFM, Dipartimento di Chimica, Università della Calabria, 87030 Arcavacata di Rende (CS, Italy. Fax: 39 0984 492066; Tel: 39 0984 492064);

E-mail: m.ghedini@unical.it

^bAlessandra Crispini

Centro di Eccellenza CEMIF.CAL-LASCAMM, CR-INSTM Unità della Calabria, Dipartimento di Chimica, Dipartimento di Scienze Farmaceutiche, Università della Calabria, Edificio Polifunzionale, Italy

E-mail: a.crispini@unical.it

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1. Reagents, general procedures, and spectroscopy data.

Materials and measurements: Iridium(III) chloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$), 2-phenylpyridine (ppy), ethylenediamine (eda) and potassium perchlorate (KClO_4), were purchased from Aldrich and used as received. $(\text{ppy})_2\text{Ir}(\mu\text{-Cl})(\text{ppy})_2$ precursor was prepared according to literature procedures.^{S1} Also the solvents were used as received from commercial sources without further purification. ^1H NMR spectra were acquired on a Bruker Advance DRX-300 spectrometer in $(\text{CD}_3)_2\text{CO}$ solution, with TMS as internal standard. Infrared spectra were recorded with a Spectrum One FT-IR Perkin-Elmer spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer by the Microanalytical Laboratory at University of Calabria. Conductivity measurements were performed in acetone, with an InoLab Cond Level 1-720 conductometer equipped with a LR 325/001 immersion cell.

References to Supplementary Information

S1 M. Nonoyama *Bull. Soc. Chem. Jpn.* **1974**, *47*, 767.

Thermal Analyses: Thermogravimetry (TGA) measurements were performed on a Perkin-Elmer TGA1 Thermogravimetric Analyser, and differential scanning calorimetry (DSC) measurements on a Perkin-Elmer Pyris1 Differential Scanning Calorimeter. The TGA and DSC traces were obtained on heating the samples at $10^\circ\text{C}/\text{min}$ from 25 to 350°C for TGA, respectively from 25 to 250°C for DSC experiments.

X-ray Crystallography.

Suitable crystals for the X-ray analysis for polymorphs **1a** and **1b** were obtained by layering water in acetone solutions at room and low (4°C) temperature, respectively. The intensity data were collected at room temperature on a Bruker-Nonius X8 Apex CCD area detector single crystal diffractometers both equipped with graphite monochromator and $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were processed through the *SAINT*^{S2} reduction and *SADABS*^{S3} absorption software. The structures were solved by direct methods through the *SHELXTL-NT*^{S4} structure determination package and refined by full-matrix least-squares based on F^2 . Generally, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as idealized atoms riding on the respective carbon atoms with C-H bond lengths appropriate to the carbon atom hybridization. In the case of **1a**, the oxygen atoms of the perchlorate anion are disordered in two sets A and B with group

occupancy of about 0.6 and 0.4 and therefore introduced in the refinement isotropically. The acetone molecule is highly disordered, with the C=O sitting on a three-fold symmetry axes and the methyl groups occupying three sites. C and O atoms are introduced in the refinement isotropically. SQUEEZE^{S5} routine implemented as the 'SQUEEZE option' in the program PLATON in WinGX system,^{S6} has been used to treat the solvent accessible voids in the structure due to solvent disorder.

References to Supplementary Information

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- S2 *SAINT*, Version 6.45 Copyright (c) 2003, Bruker Analytical X-ray Systems Inc.
S3 G.M. Sheldrick, *SADABS*. Version 2.10, Bruker AXS Inc., Madison, WI, USA, 2003
S4 *SHELXTL-NT*, Version 5.1 Copyright (c) 1999, Bruker Analytical X-ray Systems Inc.
S5 P. v.d. Sluis and A. L. Spek, *Acta Crystallogr., Sect A* **1990**, 46, 194-201.
S6 L.J. Farrugia, *J. Appl. Cryst.*, **1999**, 32, 837

Photophysics: Spectrofluorimetric grade acetone and acetonitrile (Acros Organics) were used for the photophysical investigations in solution, at room temperature. Spectrofluorimetric grade acetonitrile (Acros Organics) was used for 77 K measurements. Absorption spectra were recorded with an UV-Vis Perkin-Elmer Lambda 900 spectrophotometer. The experimental uncertainty on the band maximum for absorption spectra is 2 nm.

Steady-state emission spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube.

Emission quantum yields of sample in solution were determined using the optically dilute method on deaerated solutions whose absorbance at excitation wavelengths was <0.1; Ru(bpy)₃Cl₂ (bpy = 2,2'-bipyridine) in H₂O was used as standard ($\phi = 0.028$).^{S7,S8} The experimental uncertainty on the emission quantum yields is 10%.

The emission quantum yields of solid samples were obtained by means of a 102 mm diameter integrating sphere coated with Spectralon[®] and mounted in the optical path of the spectrofluorimeter using, as excitation source, a 450 W Xenon lamp coupled with a double-grating monochromator for selecting wavelengths. The experimental uncertainty on the emission quantum yields is 5%.

Time-resolved measurements were performed using the time-correlated single-photon counting (TCSPC) option on the Fluorolog 3. NanoLED at 370 nm, fwhm < 200 ps, was used to excite the sample. Excitation sources were mounted directly on the sample chamber at 90° to a single-grating emission monochromator (2.1 nm mm⁻¹ dispersion; 1200 grooves mm⁻¹) and collected with a TBX-04-D single-photon-counting detector. The photons collected at the detector were correlated by a time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected using an IBH

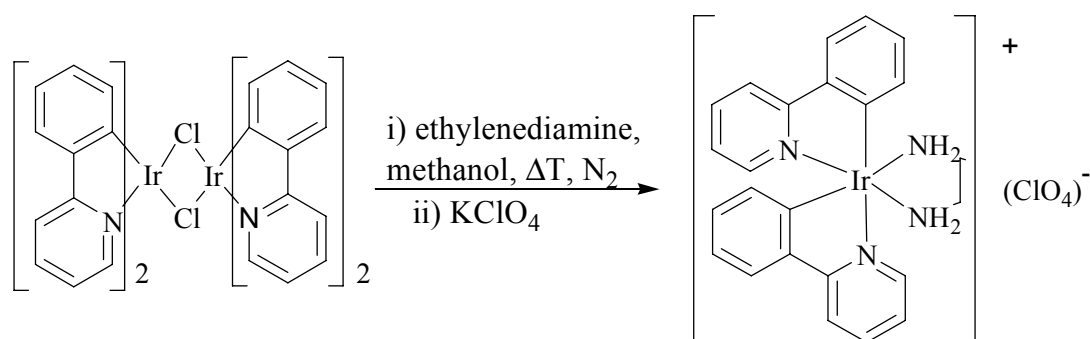
Data Station Hub photon counting module and data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). Goodness of fit was assessed by minimizing the reduced Chi squared function (χ^2) and visual inspection of the weighted residuals.

References to Supplementary Information

S7 J. N. Demas, G. A. Crosby *J. Phys. Chem.* **1971**, *75*, 991.

S8 K. Nakamaru, *Bull. Soc. Chem. Jpn.* **1982**, *5*, 2697.

2. Synthesis of complex 1 [(ppy)₂Ir(eda)](ClO₄)



Scheme S1 Synthesis of Iridium(III) complex **1**.

A stirred suspension of $(\text{ppy})_2\text{Ir}(\mu\text{-Cl})(\text{ppy})_2$ (0.150 g, 0.140 mmol) and ethylenediamine (0.017 g, 0.280 mmol) in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (15 mL, 2:1 v/v) was heated to reflux. After 2 hours the resulting yellow solution was cooled to room temperature and 5 equivalents of KClO_4 (0.10 g, 0.70 mmol) dissolved in 5 mL of MeOH were added. The resulting mixture was stirred 4 hours. After evaporating the solvents, the yellow residue was dissolved with 10 mL of acetone and filtered to remove the insoluble white inorganic salts. The pure product was obtained after recrystallisation with $(\text{CH}_3)_2\text{CO}/\text{CH}_2\text{Cl}_2$ as a yellow powder. Yield: 0.157 mg (85%). M.p.: 300°C (dec.). Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{ClIrN}_4\text{O}_4$ (660.14): C, 43.67; H, 3.66; N, 8.49. Found: C, 43.97; H, 3.38; N, 8.28. ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 300 Mz): δ 8.99 (d, $^3J = 5.4$ Hz, 2H), 8.18 (d, $^3J = 7.8$ Hz, 2H), 8.03 (td, $^3J = 7.8$ Hz, $^4J = 1.6$ Hz, 2H), 7.71 (dd, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, 2H), 7.48 (td, $^3J = 6.7$ Hz, $^4J = 1.4$ Hz, 2H), 6.82 (td, $^3J = 7.4$ Hz, $^4J = 1.2$ Hz, 2H), 6.68 (td, $^3J = 7.5$ Hz, $^4J = 1.2$ Hz, 2H), 6.26 (dd, $^3J = 7.8$ Hz, $^4J = 0.8$ Hz, 2H), 4.73 (br s, 2H), 4.10 (br s, 2H), 3.22 (br s, 2H), 3.10 (br s, 2H). IR (KBr, cm^{-1}): 3322 (N-H); 3285 (N-H); 1105 (ClO_4); Λ_{M} ($c = 1.05 \times 10^{-4}$ mol/L in acetone) = 120 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$.

From diffusion of water into an acetone solution of the powder complex **1** at different temperatures, two polymorphic forms have been isolated: the room temperature trigonal phase **1a**, and the low temperature triclinic phase **1b**, respectively.

CAUTION: Though while working with **[(phpy)₂Ir(eda)](ClO₄)** we have not met with any incident, care should be taken in handling since perchlorates are potentially explosive. They should not be prepared and stored in large amounts.

3. Thermal data

The thermal stability of complex **1**, in all three different states (powder **1**, trigonal phase **1a** and low temperature triclinic phase **1b**) was tested both by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

For the powder complex **1** no thermal processes were detected on TGA or DSC scans until 300°C, where decomposition occurs.

For the room temperature trigonal phase **1a**, the desolvation process of the acetone molecule is occurring gradually on a broad range of temperature starting from 100°C until the final decomposition of the complex (310°C), resulting in the DSC trace in an absence of significant transition (figure S1).

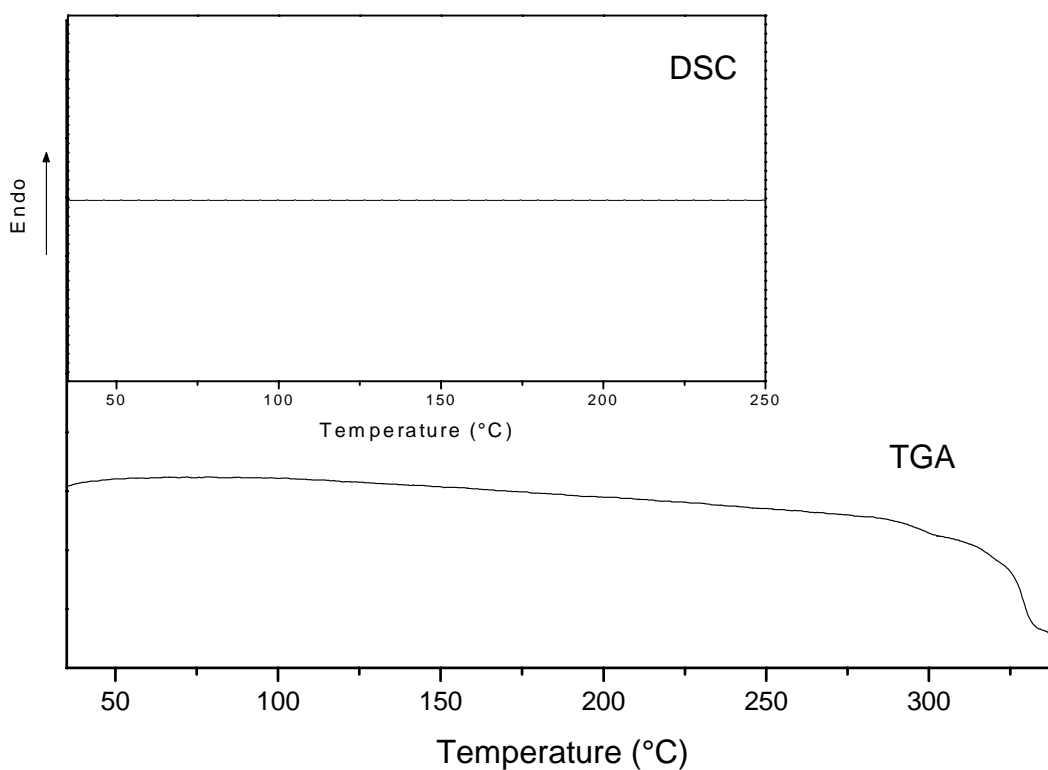


Figure S1. TGA and DSC traces for polymorph **1a**.

The TGA scan of polymorph **1b** reveals a desolvation process of one acetone molecule in a single narrow step (180-200°C), in correspondence with an endotherm peak ($\Delta H = 8.6$ KJ/mol) observed on the DSC trace (Figure S2).

Thermogravimetric data for the polymorph **1b**: experimental mass loss (7.85%) corresponds to one acetone molecule (calcd. 8.08%).

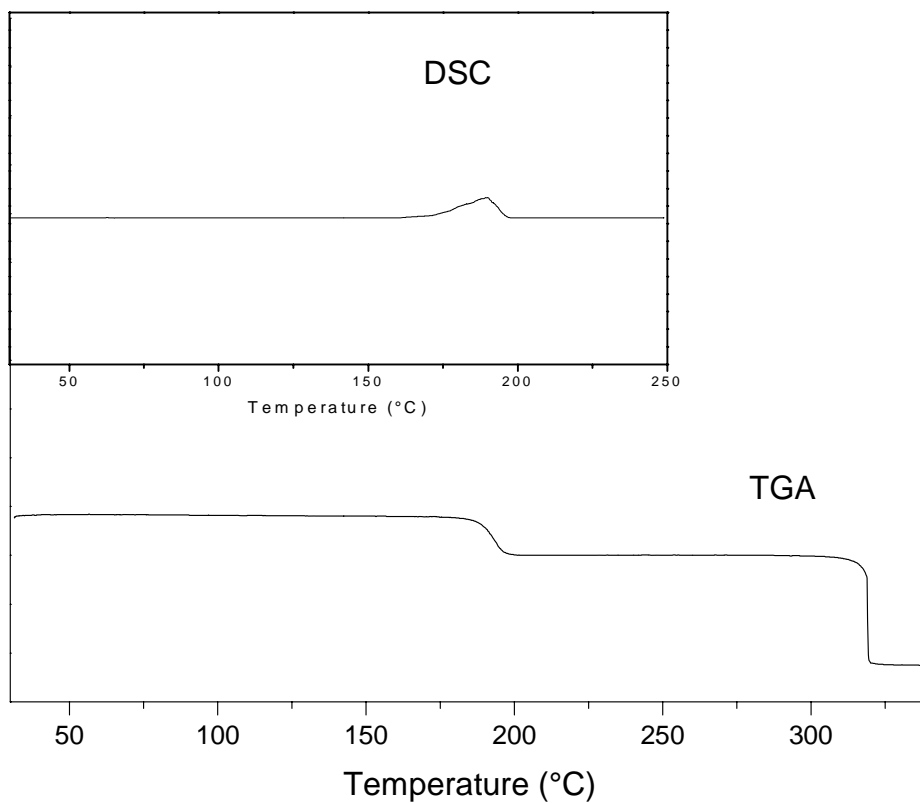


Figure S2. TGA and DSC traces for polymorph **1b**.

The observed differences in the thermal behaviour of **1a** and **1b** can be attributable to a much less specific host – guest interactions found in polymorph **1b** compared with polymorph **1a**.

Table S1. Photophysical properties in solution

	Absorption	Emission at room temperature						Emission at 77 K		
	λ (nm) ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	λ max (nm) ^a	λ max (nm) ^b	ϕ ^b	τ ^b (ns)	ϕ ^c	$10^5 \times k_r$ ^b (s ⁻¹)	$10^5 \times k_{nr}$ ^b (s ⁻¹)	λ max (nm) ^a	eV
1	^a 257 (4); 344 (0.6); 395 (0.4); 429 (0.35); 476 (0.05)	498 (523)	502 (526)	0.68	1600	0.015	4.25	2	496 (528)	2.5

^a data for complex in air equilibrated acetonitrile. ^b data for complex in degassed acetone ^c data for complex in air equilibrated acetone.

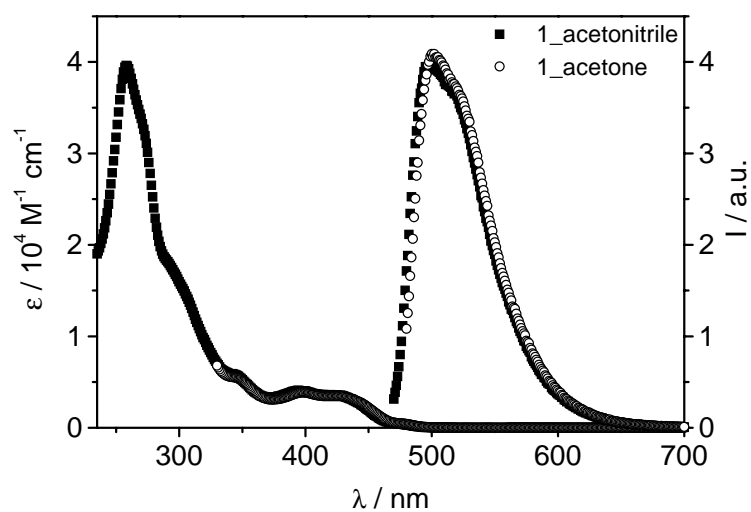


Figure S3. Absorption and emission spectra of the complex in acetone and in acetonitrile solutions

Table S2. Photophysical properties in solid crystalline organizations

Emission			Solid state luminescence lifetimes				
			τ (ns) / Rel. Ampl.				
	λ_{\max} (nm)	ϕ	λ_{\max} 480 nm	λ_{\max} 520 nm	λ_{\max} 570 nm	λ_{\max} 610 nm	λ_{\max} 700 nm
1_ trigonal	518 (557,600)	0.04	50 (13 %)	76 (22%)	140 (32%)	160 (14%)	430 (20%)
			157 (65%)	208 (67%)	380 (36%)	480 (30%)	1200 (51%)
			400 (22%)	795 (11%)	1600 (32%)	1700 (56%)	2700 (29%)
1_ triclinic	502 (524)	0.24	150 (15%)	170 (21%)	250 (31%)	320 (23%)	830 (63 %)
			390 (68%)	425 (66%)	640 (66%)	905 (54 %)	2700 (37%)
			970 (17%)	1120(13%)	1980 (13%)	2500 (23%)	