Supporting Information

White Light Phosphorescence Emission from a Single Molecule: Application to OLED

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Synthesis of [(1-methyl-2-phenyl-imidazole)2IrCl]2 complex



1-methyl-2-phenyl-imidazole (0.45 g, 2.84 mmol) and $IrCl_3.3H_2O$ (0.5 g, 1.41 mmol) were refluxed overnight in a 3:1 mixture of methoxyethanol/H₂O (100 ml). After being cooled to room temperature, water (30ml) was added and the precipitate was filtered, washed with water and Et₂O to afford 0.55 g (68 %) of the desired dimer as a yellowish

powder. Because of the low solubility of this compound, its ¹H-NMR was recorded in DMSO-d⁶ as its $(C^N)_2$ Ir(Cl)(DMSO) derivative.

¹H NMR (*d6*-dmso, 400 MHz): δ 7.76 (m, 1H); 7.52-7.44 (m, 3H); 7.31 (m, 2H); 6.81-6.64 (m, 4H); 6.32 (d, 1H, J=7.4Hz); 5.93 (d, 1H, J=7.4Hz); 4.11 (s, 3H); 4.08 (s, 3H).

Synthesis of [(1-methyl-2-phenyl-imidazole)2Ir(acac)] complex (N966)

271 mg (0.25 mmol) of the chloro-bridged dimer were dissolved in 50 ml of dichloromethane under inert atmosphere. Separately, 100 mg (1.00 mmol) of acetylacetone were mixed in 1 ml of ethanol with 400 mg (0.5 mmol) of tetrabutylammonium hydroxide [(C_4H_9)_4NOH·30 H_2O]. The so obtained solutions were mixed and heated at reflux during 4 hours. After cooling down to room temperature, the solution was filtered on cellite, and evaporated to dryness to give a viscous oil which precipitate upon addition of methanol (30 mL). The suspension was kept in the fridge for 2 hours, filtered off and washed with cold methanol (30 mL) and hexane (100 ml). The yellow solid was recrystallized three times by dissolving in a minimum amount of a methanol/dichloromethane mixture (10/90, v:v) and crystallizing with hexane in the fridge. The suspension was filtered off, washed with hexane and dried to afford N966 as a yellow solid (207 mg, 66 %), which was characterized by ¹H-NMR in CDCl₃, TOF MS ES, elemental analysis and X-ray crystal structure.

¹H NMR (CDCl₃, 400 MHz, δ ppm): δ 7.35 (dd, 2H, J=7.6, 0.8Hz); 6.99 (d, 2H, J=1.6Hz); 6.88 (d, 2H, J=1.6Hz); 6.71 (dt, 2H, J=7.6, 1.2Hz); 6.61 (dt, 2H, J=7.6, 1.2Hz);

6.39 (dd, 2H, J=7.6, 0.8Hz); 5.15 (s, 1H of acetyl acetonate -CH); 4.09 (s, 6H of imidazole -CH₃); 1.77 (s, 6H of acetyl acetonate)

 $C_{25}H_{25}IrN_4O_2.1/4\ C_6H_{14}\ (627.68):\ calcd.\ C\ 50.74\ H\ 4.58\ N\ 8.93;\ found\ C\ 50.87\ H\ 4.78\ N$

8.98

TOF MS ES+, solution in MeCN, *m/z*: 506.8947 ([M-acac]⁺, calcd.: 507.1161); 547.9647

([M-acac+MeCN]⁺, calcd.: 548.1426).



Figure S1. Crystal structure of N966.

Table S1. Crystal data and structure refinement for N966.

Identification code	n966	
Empirical formula	C26 H27 Cl2 Ir N4 O2	
Formula weight	690.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5352(5) Å	$\alpha = 105.916(6)^{\circ}.$
	b = 9.6023(6) Å	β= 90.915(6)°.
	c = 15.1243(12) Å	$\gamma = 93.309(5)^{\circ}$.
Volume	1328.75(15) Å ³	

Ζ	2
Density (calculated)	1.726 Mg/m ³
Absorption coefficient	5.255 mm ⁻¹
F(000)	676
Crystal size	0.41 x 0.39 x 0.34 mm ³
Theta range for data collection	3.47 to 27.50°.
Index ranges	-12<=h<=12, -12<=k<=12, -19<=l<=19
Reflections collected	29244
Independent reflections	6046 [R(int) = 0.0323]
Completeness to theta = 27.50°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.5399
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6046 / 0 / 317
Goodness-of-fit on F ²	1.141
Final R indices [I>2sigma(I)]	R1 = 0.0178, $wR2 = 0.0371$
R indices (all data)	R1 = 0.0213, $wR2 = 0.0387$
Extinction coefficient	0.00233(15)
Largest diff. peak and hole	0.707 and -0.628 e.Å ⁻³



Figure S2. ¹H-NMR spectrum of the N966 complex measured in CDCl₃ at 298°C, which was found to be consistent with the proposed structure; the abscissa stands for δ in ppm and zoom in the aromatic region of the spectra.



Figure S3. Surface plot of the time resolved emission decay of N966 in degassed CH_2Cl_2 solution



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Figure S4. Emission decay at various wavelength (red dots) and exponential fit (black line)



Figure S5. Excitation spectra of dichloromethane solution of N966 followed at 470 nm (blue), 570 nm (red) and 670 nm (green). Normalized to the emission intensity at the probed wavelength.



Figure S6. Normalized emission spectra of N966 at various concentration in CH_2Cl_2 : from top to bottom: 10^{-3} M, 10^{-4} M, 10^{-5} M, 10^{-6} M, 10^{-7} M.



Figure S7. 77 K emission spectra of N966 in dichloromethane glass



Figure S8. Fit of the room temperature N966 emission spectra in dichloromethane using Gaussians.

Computational Section:

The geometries of the investigated complexes were optimized under C_2 symmetry constraints using the BP86 exchange-correlation function,^{1,2} together with a TZP (DZP) basis set for Ir (N, C, H), including scalar-relativistic corrections as implemented in the ADF program.³ The calculated optimized structural parameters for the ground and excited states of the investigated complexes are reported in Table S2 and compared with X-ray data for N966 and for the [Ir(ppy)₂acac] complex.

The agreement between ground state calculated structural data and available experimental parameters is good, and minor differences are computed between the N966 and $[Ir(ppy)_2acac]$ complexes. For N966, the main variations calculated going from the S₀ to T₁/T₂ structures are related to a ca. 0.02 Å shortening of the C-C distances, and a slight increase (decrease) of the Ir-O distances in T₁(T₂), suggesting an overall rather rigid metal coordination sphere.

At the optimized geometries we performed ground and excited state DFT/TDDFT calculations at the B3LYP/LANL2DZ level of theory^{4,5} in CH₂Cl₂ solution by means of the PCM solvation model,⁶ as implemented in the Gaussian 03 program package.⁷ The non-equilibrium⁸ implementation of the PCM algorithm was used for TDDFT calculations. Both singlet-singlet and singlet-triplet TDDFT excitations have been computed. We report in manuscript Figure 2 the results of single point calculations performed at the S₀ optimized geometries, together with plots of selected unoccupied molecular orbitals.

The absorption spectrum (Figure S9) has been simulated by calculating the lowest 50 singlet-singlet transitions at the S_0 geometry.

<N-Ir-O

94.5

92.6

ported.							
	[Ir(ppy) ₂ acac]			N966			
Parameter	Exp.	S ₀	T ₁	Exp.	S ₀	T ₁	T ₂
Ir-N	2.010	2.038	2.051	2.033	2.032	2.032	2.035
Ir-C	2.003	1.993	1.970	2.010	2.001	1.979	1.996
Ir-O	2.146	2.171	2.169	2.160	2.169	2.183	2.154
C-C		1.449	1.436	1.456	1.444	1.417	1.418
<n-ir-n< td=""><td>176.3</td><td>174.0</td><td>176.3</td><td>172.0</td><td>172.2</td><td>174.8</td><td>174.5</td></n-ir-n<>	176.3	174.0	176.3	172.0	172.2	174.8	174.5
<0-Ir-0	90.0	89.1	85.5	88.2	88.2	85.6	87.7
<n-ir-c< td=""><td>81.7</td><td>80.7</td><td>81.6</td><td>80.1</td><td>80.1</td><td>81.1</td><td>80.7</td></n-ir-c<>	81.7	80.7	81.6	80.1	80.1	81.1	80.7

93.6

96.3

97.0

94.8

95.4

Table S1: Comparison between calculated geometrical structures and available experimental data for the $[Ir(ppy)_2acac]$ and N966 complexes. Average X-ray data are reported.



Figure S9: Simulated absorption spectrum of N966 in CH_2Cl_2 solution. The absorption profile has been obtained by a Gaussian convolution with σ =0.2 eV. Vertical lines correspond to unbroadened oscillator strengths. The inset show the detail in the 300-550 nm range.

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Device Preparation and Characterization.

Poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) was purchased from HC-Starck and solvents used were obtained from Aldrich. Indium tin oxide (ITO)coated glass plates (15 Ω) were patterned using conventional photolithography (obtained from Naranjosubstrates, www.naranjosubstrates.com). The substrates were extensively cleaned using sonification in subsequently water-soap, water, and 2-propanol baths. After drying, the substrates were placed in a UV-ozone cleaner (Jelight 42-220) for 20 minutes. A simple light emitting diode is fabricated utilizing N966, which is blended with the large bandgap host molecule 4,4',4"-tri(N-carbazolyl)triphenylamine (TCTA) at a ratio of TCTA:N966=6:4 and spincoated from a chlorobenzene solution on an indium tin oxide (ITO) coated patterned substrate, resulting in 50 nm thick films. Prior to the deposition of the emitting layer a 100 nm layer of PEDOT:PSS was deposited to increase the device preparation yield. To confine the excitons to the emissive layer and to prevent the loss of holes by recombination at the cathode a 20 nm layer of 1,3,5-tris(2-Nphenylbenzimidazolyl) benzene (TPBI) is thermally evaporated. Finally a barium cathode protected by an 80 nm silver layer, were thermally evaporated using a shadow mask under a vacuum (< 1×10^{-6} mbar) using an Edwards Auto500 evaporator integrated into an inert atmosphere glovebox.

Current density and luminance versus voltage were measured using a Keithley 2400 source meter and a photodiode coupled to a Keithley 6485 pico-amperometer using a Minolta LS100 to calibrate the photocurrent. External quantum efficiencies (EQE) were determined using an integrated sphere coupled to an UDT instruments S370 Optometer. An Avantes luminance spectrometer was used to measure the EL spectrum. Lifetime data were obtained by applying a constant voltage over the device and monitoring the current flow and simultaneously the current generated by a Si-photodiode (Hamamatsu S1336-8BK) calibrated using a Minolta LS100 luminance meter.



Figure S10. I-V-L curve of the device