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New electropolymerizable Ir(III) complexes with β -ketoiminate ancillary ligands

A. Ionescu,^{[a],[b]} R. Caligiuri,^[a] N. Godbert,^{[a],[b]*} A. Candreva,^[a] M. La Deda,^{[a],[b]} E. Furia,^[c] M. Ghedini,^{[a],[b]} and I. Aiello^{[a],[b]*}

Abstract: A series of electropolymerizable cyclometallated Ir(III) complexes were synthesized and their electrochemical and triphenylamino photophysical properties studied. The introduced by using electropolymerizable fragment was triphenylamino-2-phenylpyridine and, respectively, triphenylaminobenzothiazole as cyclometalated ligands. The coordination sphere was completed by two differently substituted new β -ketoiminate ligands deriving from the condensation of acetylacetone or hexafluoroacetylecetone with p-bromoaniline. The influence of the -CH₃/-CF₃ substitution to the electrochemical and photophysical properties was investigated. Both complexes with CH3 substituted β-ketoiminate were emissive in solution and in solid state. Highly stable films were electrodeposited onto ITO coated glass substrates. Their emission was quenched by electron trapping within the polymeric network as proven by electrochemical studies. The -CF₃ substitution of the β -ketoiminate leads instead to the quenching of the emission and inhibits electropolymerization.

Introduction

(CS), Italy,

Due to their specific features induced by the presence of metal centers and, on the other hand, the processability of organic polymers, metallopolymers based on transition metal complexes represent key functional materials in optoelectronics (electrochromics or energy converting devices).

The controlled deposition of homogeneous metallopolymeric thin films of transition metal complexes on different substrates represents a crucial issue in the device application. In this context, electropolymerization features some advantages over other film deposition techniques (e.g.: drop casting,² spincasting,³ layer-by-layer assembly,⁴ electrostatic binding of polyelectrolyte films⁵). Through electropolymerization process,

Dr. A. Ionescu, R. Caligiuri, Dr. N. Godbert, Dr. A Candreva, Prof. M. [a] La Deda, Prof. M. Ghedini, Prof. I. Aiello MAT-INLAB (Laboratorio di Materiali Molecolari Inorganici) and LASCAMM - CR INSTM, Unità INSTM della Calabria, Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, 87036 Arcavacata di Rende (CS), Italy. E-mail: iolinda.aiello@unical.it, nicolas.godbert@unical.it

Dr. A. Ionescu, Dr. N. Godbert, Prof. M. La Deda, Prof. M. Ghedini, [b] Prof. I. Aiello CNR NANOTEC-Istituto di Nanotecnologia U.O.S. Cosenza, 87036

Arcavacata di Rende (CS), Italy Dr. E. Furia [c] Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, Cubo 12/D, 87036 Arcavacata di Rende

the polymer formation and its deposition occur simultaneously, avoiding limitations such as scarce solubility of polymeric networks and leading to controllable film composition, thickness and surface coverages.6

The electrodeposition of metallopolymeric thin films of organometallic complexes (Ru, Os, Fe, Ir, Ni),6,7 on conducting substrates has been achieved by using various electropolymerizable groups such as thiophene,^{8,9} pyrrole,10 aromatic amines,¹¹⁻¹⁴ and triphenylamine.¹⁵⁻¹⁸

In this context, a series of electropolymerizable cyclometallated square planar Pd(II) and Pt(II) complexes incorporating an electropolymerizable triphenylamine-substituted Schiff base H(O^N) as ancillary ligand (Fig. 1), was recently reported.^{19,20} Remarkably, the use of this Schiff base allowed the electrodeposition of highly stable and homogeneous photoconductive and electrochromic Pd(II) and Pt(II) metallopolymers. For triphenylamine containing compounds, the electropolymerization process is promoted in the case of monosubstitution of the TPA fragment only when an electron withdrawing group is employed. Upon oxidation, the TPA fragment is oxidized and a single electron from the nitrogen atom is removed, affording a delocalized radical cation TPA⁺•. Afterwards, dimerization occurs to produce the corresponding tetraphenylbenzidine (TPB) which further electropolymerizes.²¹ TPB is more readily oxidized than TPA, and upon cycling, chain extension leads to a branched polymeric network.22,23





Figure 1. Molecular structure of electropolymerized Pt(II)/Pd(II) complexes.19,20

In the field of transition metal-based optoelectronic devices, Ir(III) luminescent organometallic complexes represent a peculiar emerging class.²⁴⁻²⁹ The high sensitivity of Ir(III)

complexes to electric stimuli (due to their charge-transfer excited states) makes them suitable for the application in optical data recording and security protection, which require time-resolved luminescence technique.³⁰ Up to date, very few examples of Ir(III) organometallic luminescent electrochromic complexes were synthesized and only one quasi-solid device was realized.³¹ For this reason, in a previous recent work, we attempted to incorporate our designed electropolymerizable triphenylamine substituted Schiff base $H(O^N)^{tpa}$ ancillary ligand into Ir(III) complexes (Fig. 2).³² Unfortunately, the resulting $(C^N)_2 Ir(O^N)^{tpa}$ complexes did not display any luminescent properties, but high quality thin films were obtained through electropolymerization process.³²

Following this itinerary, we decided to replace the $H(O^{N})^{tpa}$ Schiff base ancillary ligand with a ligand prompter to induce high luminescence in the resulting complexes. To this regard, differently substituted β -ketoiminates have recently been successfully introduced as ancillary ligands, leading to highly luminescent Ir(III) complexes.^{33,34,35}



Figure 2. Molecular structure of electropolymerized Ir(III) complex [(bz-TPA)Ir(O^N)].³²

Furthermore, up to 10 fold enhancement of photoluminescence has been observed in a rigid PMMA matrix for complexes containing strongly π -donor β -ketoiminates.³⁶

We present herein a series of novel electropolymerizable cyclometallated Ir(III) complexes of general formula [(C^N)₂Ir(O^N)], wherein H(C^N) are triphenylamino-2-phenylpyridine (H(ppy-TPA)) or triphenylamino-benzothiazole (H(bz-TPA)) while H(O^N) are the substituted β -ketoiminate shown in Scheme 1.

Results and Discussion

Synthesis

H(O^N) ligands. $H(O^N)^1$ and $H(O^N)^2$ were obtained by condensation of acetylacetone (or its hexafluorinated analogous) with 4-bromoaniline through a microwave assisted procedure modifying the classical synthetic pathway (Scheme 1).³⁷ The choice of these two differently substituted β -ketoiminate ligands

was directed by the desire to evaluate the influence of the electronegative effect of the fluorine substitution onto the luminescent and\or electrochemical properties.

The obtained β -ketoiminate were characterized by IR, ¹H-NMR GC-MS. spectroscopies and Moreover, potentiometric measurements of their acidic constants K_a were performed showing their coordination potential as monoanionic chelating ligands and their relative stability towards hydrolysis in basic conditions. The protonation constants of H(O^N)¹ and H(O^N)² were calculated from the data acquired by carrying out two titrations for each ligand. The experimental data reported in Table 1 were processed by numerical procedures (Experimental).38

Table 1. numerical m	H(O^N) ^{1,2} ethods	log	K _a values	in	0.16	М	NaCl	and	at	60°C	by
β -ketoimina	nes						pKa ±	: 3σ			

p-ketoiminanes	pra ± 50
H(O^N) ¹	8.98 ± 0.03
H(O^N) ²	3.7 ± 0.2

H(**C**^{**N**}) **ligands.** Considering the synthetic procedures of both **H**(**C**^{**N**}) **ligands. H**(**bz-TPA**) was prepared as previously reported³⁷ whereas the synthetic procedure of **H**(**ppy-TPA**) was modified with respect to the literature.³⁹ The structure of both ligands was confirmed by spectroscopic analyses (Experimental). (**C**^{**N**})**Pt**(**O**^{**N**}) **complexes.** The cyclometallated chloro-bridge intermediates, **[**(**C**^{**N**})**2Ir**(*μ*-**CI**)**]**₂, were obtained by a microwave assisted reaction.⁴⁰ The synthesis of complexes **1-4** (Scheme 1) was achieved through a bridge splitting process, reacting the binuclear intermediate **[**(**ppy-TPA**)**2Ir**(*μ*-**CI**)**]**₂ with the corresponding *β*-ketoiminate ligand **H**(**ON**)^{1,2} in basic conditions.

Complexes 1-4 were fully characterized by IR, ¹H-NMR and MS spectroscopies. In particular, the structure of the expected products was confirmed by their ¹H-NMR spectra. Indeed, the coordination of the β -ketoiminate ligand occurred was confirmed from the disappearance of the signal of the *-NH* proton of the ancillary ligand and from the splitting of the aromatic signals of the cyclometallated ligands owe to the loss in symmetry induced by the (**O^N**) ligand coordination to the metal centre.

Electrochemical studies, Density Functional Theory calculations and electropolymerization

Complexes 1-4 were solubilized in ca. 3 ml of freshly distilled and degassed (Ar) dichloromethane solution, reaching the final 1·10⁻⁶ concentration of ca. Μ. То this solution. tetrabutylammonium hexafluorophosphate (0.1 M) was added as supporting electrolyte. The typical voltammetry cell was composed as follows: a Pt disk as working electrode, a Pt wire as counter-electrode and an Ag wire used as pseudo-reference electrode. Potentials applied varied from -1.3 V to 1.5 V, at a standard scan rate of 100 mV s⁻¹. Potential data and estimated energy levels (HOMO) were given with respect to the ferrocene/ferrocinium (Fc/Fc⁺) redox couple used as internal reference (-4.8 eV for the HOMO energy level⁴¹ and -0.45 V vs. SCE⁴² for the oxidation potential of the Fc/Fc⁺ redox couple).

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Scheme 1. Synthesis pathway of $[(C^N)_2 [r(O^N)^n]$ complexes, 1-4, reagents and conditions: *i*) $H(O^N)^1$: acetylacetone, 4-bromoaniline, 300 W, 140°C, 90 min; $H(O^N)^2$: Hexafluoroacetylacetone, 4-bromoaniline, p-toluensulfonic acid (10%), 600 W, 140°C, 30 min; *ii*) H(ppy-TPA): 2-EtOCH₂CH₂OH/H₂O, 250 W, 110°C, 1 h; H(bz-TPA): 2-EtOCH₂CH₂OH/H₂O, 250 W, 200°C, 4 h; *iii*) NaOH, EtOH, N₂, 65°C, 2 h; *iv*) EtOH, N₂, 65°C, 48 h

Fc was indeed added in equimolar quantity with respect to the analysed complex. The solution electrochemical data for complexes **1-4** obtained by cyclic voltammetry are collected in Table 2.

Table 2. Electrochemical data E_{ox}¹ EP^[d] E_{ox}² E_{ox}³ номо номо LUMO (V)^[a] (V)^[a] (V)^[a] (eV)^[b] (eV)[c] (eV)[c] +0.21 +0.56 +0.67 1 YES -5.01 -4.65 -1.31 (IR) (QR) (QR) +0.36 +0.50 -5.16 2 -4.84 -1.73 NO (R) (R) +0.26 +0.53 0.64 3 -5.06 4.79 -1.56 YES (IR) (QR) (QR) +0.45 +0.59 4 -5.25 -4.96 -1.76 NO (R (R)

 E_{ox}^{n} , n=1,2,3, is referred to the oxidation waves observed at growing potential. ^[a]Potentials were given versus ferrocene/ferrocinium (Fc/Fc⁺). ^[b]estimated from the first oxidation potential (using -4.8 eV per Fc/Fc⁺). ^[c]Calculated at the B3LYP/LANL2DZ(6-31G(d)) level of theory. (IR): irreversible wave, (QR): quasi-reversible wave, (R): reversible wave. ^[d]EP=electropolymerization.

As shown in Fig. 3, complexes with the same ancillary ligand (Scheme 1) presented analogous cyclic voltammograms, which are irreversible for 1 and 3 and reversible in the case of 2 and 4. The slight positive shift of the oxiation potential of complexes 2 and 4, with respect to their corresponding analogous 1 and 3 respectively can be reasonably attributed to the fluorination of the β -ketoiminate backbone. For all complexes 1-4 (Fig. 4), the successive observed oxidation waves are typical in features of the triphenylamine fragment embedded onto the cyclometalled ligands.³² While in the case of complexes 2 and 4, two consecutive fully reversible oneelectron oxidation waves are observed that can be ascribed to the oxidation of TPA to TPA⁺• and then TPA²⁺, for the complexes 1 and 3 the situation is different. Indeed, the oxidation process of 1 and 3 becomes irreversible due to the formation of TPB that occurs by dimerization of the radical cation TPA⁺•.

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Figure 3. Cyclic voltammograms of complexes 1-4 in dichloromethane at a 100 mV s⁻¹ scan rate



Figure 4. Comparison of the experimental and computed HOMO energy levels for complexes 1-4

For complexes 1 and 3, upon repetitive oxidation scans, a significant and constant increase in current can be observed. Such behaviour is typical of the electropolymerization of electron-withdrawing substituted triphenylamino fragment³² and the corresponding repetitive cyclic voltammograms for complex **1** and **3** are reported in Fig. 5.

The electropolymerization process was carried out both onto the Pt working electrode as well as on ITO covered glass by application of 50 successive oxidation scans at a 100 mV s⁻¹. Both the washed modified Pt electrode and the covered ITO substrate were immersed in a freshly distilled electrolytic dichloromethane solution and a cyclic voltammogram was recorded in order to prove the film stability. The two scans were carried out in a range of redox that varied to -1.5 V to 1.5 V. The presence of a complete reversible oxidation process, characterized by two consecutive oxidation waves, was indicative of the effective electropolymerization deposition of thin films and their electrochemical stability. However, complex 3 exhibits the phenomenon of electron trapping, as shown in Fig. 6a, as previously reported for β ketoiminate cyclometallated Ir(III) complexes.³⁵

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This process occurs when generated charges are trapped into the polymeric network during reduction and afterwards released upon oxidation leading to the appearance of a sharp intense peak. This characteristic phenomenon has also been previously described for electropolymerized organometallic complexes.43,44 Noteworthy, this charge trapping is rather persistent. Indeed, the film of 3 was reduced at -1.5V and the potential was subsequently returned to 0V. The film was exposed to air for 30 minutes. The recorded cyclovoltammogram was indeed still showing the sharp, although less intense, peak corresponding to this electron trapping.



Figure 5. Electropolymerization of complexes 1 (a) and 3 (b) on ITO covered glass substrates in dichloromethane (50 scans at 100 mV s⁻¹).

To provide a quantum chemical insight into all the synthesized complexes, the Density Functional Theory (DFT) method was employed to investigate their ground-state electronic structures and orbital configurations. DFT calculations have been performed following the standard B3LYP/LANL2DZ(6-31G(d)) level of theory used for Ir(III) complexes.⁴⁵⁻⁴⁷ Computed HOMO energy levels show a very good agreement with the experimental data (Table 2 and Fig. 7) confirming the oxidation of the triphenylammine fragment.

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Figure 6. Two reduction scans after electropolymerization of complex 1 (a) and 3 (b) on ITO substrate.



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Figure 7. Contour plots of the frontier orbitals of complexes 1-4 in the ground state.

Photochemical studies

The photophysical properties of the complexes **1-4** were investigated at room temperature in chloroform solution at the concentrations of $1.15 \cdot 10^{-5}$ M for **1**, $0.84 \cdot 10^{-5}$ M for **2**, $1.45 \cdot 10^{-5}$ M for **3** and $0.95 \cdot 10^{-5}$ M for **4**, and the obtained data are reported in Table 3.

In Fig. 8 are shown the absorption spectra of all complexes. By comparing the spectral features of the complexes bearing the -CH₃ substituents (*i.e.* 1 and 3) with those of their ligands (reported in Fig. S1 in ESI), it is possible to assign the bands in the 250-330 nm range to $LC(\pi-\pi^*)$ transitions localized on the cyclometallated ligand, the shoulder at 350 or 380 nm (in 1 and 3, respectively) to an excitation mostly localized on the β-ketoiminate ligand, while bands in the 380-430 nm range are attributed to MLCT-LC mixed transitions involving the metal and the cyclometallated ligand, and, finally, the 457 nm band of 1 and the 478 nm band of 3 are originated from an MLCT excitation towards the cyclometallated ligand, redshifted in 3 due to the presence of the extended aromatic structure of the benzothiazole fragment. Absorption spectra of the complexes 2 and 4 show the same transitions observed in 1 and 3, but the -CF₃ substituents prompt an electron attractive effect on the metal and, consequently, onto the cyclometallated ligand. This effect induces an energy increase of the transitions involving the metal and the cyclometallated ligand, and the corresponding bands are blue-shifted with respect to the analogous transitions

observed in 1 and 3, resulting in some case outside of the examined spectral range and, in other case, merged with vicinal bands. In particular, the blue-shift of the low-energy band (corresponding to the HOMO/LUMO excitation) of 2 and 4 compared with 1 and 3, is a direct consequence of lowering of the HOMO energy, as reported in Table 2. The differences that the $-CF_3$ substituents exert on the examined complexes are more evident by comparing the emission properties of 1 and 3 with those of 2 and 4. While the first couple is luminescent, the second one is non-emissive (Table 3).

Fig. 9 shows that the emission profiles of 1 and 3 are identical, but the spectrum of the benzothiazolate complex is bathochromically shifted. Both emissions derive from the ³MLCT state decay, but in the case of **1** this state involves the triphenylamine centre, while in the case of 3 it involves the benzothiazole ring. The presence of the benzothiazole rings is responsible for the increased lifetime and the emission quantum yield values of 1 with respect to 3, while the two compounds show an almost identical Stokes' shift (3190 cm⁻¹ and 3620 cm⁻¹, respectively), owe to the comparable rigidity of the molecular structure of the two complexes. Nevertheless, the recorded lifetime and emission quantum yield values (reported in Table 3) are low compared to most Ir(III) complexes⁴⁸, both in presence and in absence of dioxygen. The low oxygen photosensitization efficiency, and the presence of a bi-exponential emission intensity decay strongly suggest the presence of a twisted intramolecular transfer (TICT) process^{49,50}, involving the charge triphenylamine group, which ultimately induces a nonradiative deactivation of the excited state.

The introduction of the trifluoromethyl substituents in **2** and **4** quenches luminescence: the energy increase of the MLCT states, due the electron attracting effect of the fluorine atoms, implies a matching of LC with metal-centred (MC) states, which opens non-radiative deactivating paths.

All complexes 1-4 were deposited on ITO/glass substrate by drop casting from chloroform solution, and their absorption and emission spectra were recorded (see Fig. S2 and S3 in ESI). By comparing these results with those obtained from solution, no difference was evidenced in the glass transparent spectral window. Similarly, to the solution, 1 and 3 are emissive with a maximum at 535 and 578 nm, while 2 and 4 do not emit.

Complexes **1** and **3** have been electropolymerized, and the obtained films on ITO/glass substrate have been studied; absorption spectra (Fig. 10) recorded on the ITO transparent window (from 300 nm onwards) show a unique large band at 395 nm for **1**, and a shoulder for **3**. The electropolymerized complexes do not emit. Actually, the bands attributed to the



LC and MLCT transitions involving the TPA fragment result perturbed, being the electropolymerization involving the cyclometallating ligand; these modifications perturb the emissive state, and consequently these samples are not emissive.







Figure 9. Emission spectra of complex 1 and 3 in chloroform solution at room temperature



Figure 10. Absorption spectra of thin films of complexes 1 and 3 deposited on ITO/glass substrate

Table 3. Photophysical data in chloroform solution at room temperature									
	Absorption, $\lambda/nm~(\epsilon~/M^{\text{-1}}~cm^{\text{-1}})$	Emission,	Air equilibr	ated sample	Deaerated	Deaerated samples			
		λ/nm	EQY	Lifetime, $\tau/\nu\sigma$ (α /%)	EQY	Lifetime, $\tau/\nu\sigma$ (α /%)			
1	256(85220), 300*, 321(68695), 350*, 384(60100), 401(57390), 457(10430)	535, 571, 620*	0.07%	4.2 (49.7); 42.0 (50.3)	0.25%	3.5 (43.2); 132.0 (56.8)			
2	275(302630), 365*, 397(35885), 442(14355)								
3	269(13100), 305*, 380*, 415(8960), 425(8965), 478(3016)	578, 624, 670*	2.1%	4.2 (4.5); 149.0 (95.5)	7.0%	3.5 (3.5); 378.0 (96.5)			
4	268(61070), 304(32460), 380*,419(48170), 463(28270)								
EQY	: Emission Quantum Yield; *: shoulder								

Conclusions

A series of cyclometallated Ir(III) complexes with β ketoiminate ancillary ligands of the type [(C^N)₂lr(O^N)] (1-4) were synthesized and their electrochemical and photophysical properties comprehensively studied. Two differently substituted β -ketoiminate ligands were used. The CH₃/CF₃ substitution resulted non-innocent with respect to either the electrochemical and photophysical properties of the synthesized complexes 1-4. Indeed, only complexes 1 and 3, embedded with the CH_3 substituted β -ketoiminate ligand do electropolymerize, while for complexes 2 and 4, probably owe to the too intense electron-withdrawing effect of the fluorine atoms, the polymerization does not occur. Although the fluorine substitution of the β -ketoiminate ligands, lowers the HOMO levels of complexes 2 and 4, as evidenced by the electrochemical and spectroscopic investigations, this effect being probably responsible of their inertness towards electropolymerization. Triphenylammine fragment can indeed be electropolymerized when a withdrawing group is graft on its backbone in order to localise in specific position the radical generated during oxidation thus allowing the formation of TPB. Since the introduction of the fluorine atoms on the ancillary ligand increase the withdrawing effect exert onto the TPA fragment with respect to the methyl substituents, but prevent the electropolymerization process to occur, the present work demonstrates that the withdrawing effect must be kept mild in order to promote the electropolymerization of TPA.

The introduction of fluorine atoms also has a dramatic effect onto the luminescent properties of the complexes. While complexes 1 and 3 bearing the methyl substituents are luminescent, complexes 2 and 4 (-CF₃ derivatives)

are not. Unfortunately, even if the ITO electrodeposited films of 1 and 3 are stable, they do not display any luminescent properties. While the MCLT-LC mixed transitions maybe be perturbed by the of the electropolymerization TPA fragment, the observation for the electropolymerized thin film of 3 of an electron trapping effect also contribute to the observed quenching of emission. To bypass such a drawback, a possible way to promote luminescence in such Ir(III) electrodeposited thin films may be to introduce the TPA fragment onto the (O^N) fragment, and the presence of a bromine atom onto the β -ketoiminate ligand could represent the prefect site for such functionalization.

Experimental Section

Materials and methods

All commercially available chemicals were purchased from Sigma Aldrich or Alfa Aesar and were used without further purification. Microwave assisted syntheses were carried out using a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC). IR spectra (KBr pellets) were recorded on a Spectrum One Perkin-Elmer FT-IR spectrometer. ¹H-NMR spectra were recorded on a Brucker WH-300 spectrometer in deuterated solvents with TMS as internal standard. ¹H-NMR spectra of all newly synthesized ligands and complexes are reported in SI. Melting points were determined with a Leica DMLP polarising microscope equipped with a Leica DFC280 camera and a CalCTec (Italy) heating stage. Mass spectra were obtained using an AB Sciex API 2000 mass spectrometer equipped with a turbo ion spray ionization source in the positive mode [ion spray voltage (IS) 5500 V; curtain gas 20 psi, temperature 300 °C, ion source gas (1) 30 psi, ion source gas (2) 40 psi, declustering and focusing potentials 50 and 400 V, respectively] through direct infusion (5 μ L min⁻¹) of a solution containing the appropriate compound dissolved in chloroformmethanol (20 µg mL⁻¹). Elemental analyses were performed with a PerkinElmer 2400 analyzer CHNS/O.

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Potentiometric analysis

The cell arrangement was analogous to the one described by Forsling⁵¹ and the reference electrode was prepared according to Brown⁵ . Alkaline glass electrode was the same used in a previous work $^{\rm 53}\!;$ it attained a constant potential within few minutes after the addition of the reagents and remained unchanged for several hours to within \pm 0.1 mV. The titrations were carried out as described in a previous paper⁵⁴. The electromotive force values were recorded with a precision of $\pm 10^{-5}$ V by an OPA 111 low-noise precision DIFET operational amplifier. A slow stream of nitrogen gas was passed through the gas inlet tube into the test solutions stirred during titrations after the passage through four bottles (a-d) containing: a) 1 M NaOH, b) 1 M H2SO4, c) twice distilled water, and d) 0.16 M NaCl. The cell assembly was retained in a thermostat kept at $(60.0 \pm 0.1)^{\circ}$ C. The sodium chloride, hydrochloric acid stock solutions and sodium hydroxide titrant solutions were prepared and standardized as described previously⁵⁵. All solutions were prepared with twice distilled water.

The acidic constants, K_a , of $H(O^N)^1$ and $H(O^N)^2$, were evaluated, at 60°C and in 0.16 M NaCl, by numerical treatment of potentiometric data.⁵³ The adoption of the constant ionic medium method has been necessary in order to minimize activity coefficient variation in spite of the change of the reagent concentrations. In this way, it has been possible to replace activities with concentrations in the calculations and to minimize the liquid junction potential due to the hydrogen ion concentration. The hydrogen ion concentration was varied in order to determine acidic constant of ligands, taking into account that protonation takes place at different acidities⁵⁶. All the measurements were performed as potentiometric titrations with an alkaline glass electrode, GE, with cell (G)

Reference Electrode / Test Solution / GE

(G).

Test solution had the general composition: $C_L \ M \ H(O^N)^{1,2}$, $C_A \ M \ HCl$, $C_B \ M \ NaOH$, $(0.16 - C_A - C_B) \ M \ Na^+$, where C_L were varied between $(1^{\cdot}10^{\cdot3} \ and \ 4^{\cdot}10^{\cdot3}) \ M$. The electromotive force of cell (G) can be written, in mV, at the temperatures of 60°C as eq. (1):

 $E = E^{\circ} + 66.10 \log [H^{+}] + E_{j}$

where E° was constant in each series of measurements and E_j was the liquid junction potential which was a linear function of $[H^+]$, $E_j =$ $j[H^+]^{57}$. In each run E° values, constant to within 0.1 mV, were calculated from measurements in solutions of $(2 \cdot 10^{-3} \ge [H^+] \ge 1 \cdot 10^{-4})$ M in the absence of $H(O^{\Lambda}N)^{1,2}$. $[H^+]$ was decreased stepwise by coulometric generation of OH^- ions with the circuit (C)

- Pt / Test Solution / Auxiliary Electrode + (C) In the test solution of a given volume V dm³, $C_B = (\mu F 10^{-6} / V)$ mol dm⁻³ where μF stands for the micro–faradays passed through the cell, according to the assumption that at the cathode the only reactions that occur are H⁺ + e⁻ $\rightarrow \frac{1}{2}$ H₂ and H₂O + e⁻ $\rightarrow \frac{1}{2}$ H₂ + OH⁻.

After the introduction of a known amount of the ligands, solved in a known excess of C_B M NaOH, the acidification was achieved, in the pH range from 12 to 2, by adding H⁺ standardized solutions, according to the equilibria reported in eqs. (2) and (3): $I(O_{AN})^{1}\Gamma + H^{+} \rightarrow H(O_{AN})^{1}$ (2)

	(2)
$[(O^{\Lambda}N)^2]^- + H^+ \rightleftharpoons H(O^{\Lambda}N)^2$	(3)
The primery C C C and [11 ⁺] date form	the bacic of the tr

The primary C_L , C_A , C_B and $[H^+]$ data form the basis of the treatment to obtain the equilibrium constants

Electrochemistry and electropolymerization

All potentials were measured using an Autolab Potentiostat/Galvanostat. Cyclic voltammetry experiments were performed in a 3 mL cell of dry, freshly distilled, and degassed (Ar) dichloromethane solution using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte, a Pt disk

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working electrode, a Pt wire counter-electrode and an Ag wire as pseudoreference electrode. Voltammograms were registered at a 100 mV/s scan rate from a ca. 10⁻³ M complex solution. Redox potentials are given with respect to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple used as internal reference. Estimation of HOMO energy values -4.8 eV for Fc/Fc⁺²⁹. were performed considering Electropolymerization was carried out by cyclic voltammetry, performed with an Autolab Potentiostat/Galvanostat controlled by the Nova 1.1 software. A conventional three-electrode cell was employed. with a Pt wire as counter-electrode, an Ag wire as pseudoreference electrode and a 2 mm wide ITO stripe on glass as working electrode. Tetrabutylammonium hexafluorophosphate (0.1M) was used as supporting electrolyte and experiments were performed in a dry, freshly distilled and degassed (Ar) dichloromethane solution. The electropolymerization process was achieved by continuously cycling the applied potential around the oxidation potential of the studied complex at a constant scan rate.

DFT calculations

Full geometry optimizations of all Ir(III) complexes in their singlet ground state were performed through DFT calculations using the B3LYP functional^{58,59} and the mixed "Double- ζ " quality basis sets, the relativistic effective core potential (ECP) and basis set LANL2DZ⁶⁰ was used to treat the heavy metal Ir(III) atom, whilst the basis set 6-31G(d)⁴⁷ was employed for the remaining atoms. The relativistic effective core potential (ECP)^{62,63} on the Ir atom replaced the inner core electrons leaving the outer core [(5s)2(5p)6] electrons and the (5d6) valence electrons of the Ir(III) metal center. No symmetry constraints were applied during the geometry optimizations, which were carried out with the Gaussian 09 package⁶⁴. This calculation level has widely been used throughout the literature for the computational modellisation of both neutral or ionic Ir(III) complexes⁴⁷.

Photochemistry

(1).

Spectrofluorimetric grade solvents were used for the photophysical investigations in solution, at room temperature. A Perkin Elmer Lambda 900 spectrophotometer was employed to obtain the absorption spectra. Steady-state emission spectra were recorded on a HORIBA Jobin-Yvon Fluorolog-3 FL3-211 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation and single-grating emission monochromators (2.1 nm/mm dispersion; 1200 grooves/mm), and a Hamamatsu R928 photomultiplier tube or a TBX-04-D singlephoton-counting detector or a InGaAs liquid nitrogen-cooled solidstate detector. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Time-resolved measurements were performed using the time-correlated singlephoton counting (TCSPC) option on the Fluorolog 3. Laser Nanoled at 379 nm fwhm 750 ps with repetition rate at 1 MHz, 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 dispersion; 1200 grooves/mm) and collected with a TBX-04-D single-photon-counting detector. The photons collected at the detector are 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. Emission quantum yields were determined using the optically dilute method⁶⁵ on aerated solutions which absorbance at excitation wavelengths was < 0.1; Ru(bipy)₃Cl₂ (bipy = 2,2'-bipyridine) in water was used as

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standard ($\Phi = 0.028$)⁶⁶. The experimental uncertainty on the molar extinction coefficients is 5%, while on the emission quantum yields is 10%. The examined compounds

are fairly stable in solution, as demonstrated by the constancy of their absorption spectra over a week.

Synthesis

Synthesis of H(O^N)^{1,2} ligands

H(O^N)¹. Acetylacetone (559 mg, 5.60 mmol) and 4-bromoaniline (480 mg, 2.80 mmol) were introduced without solvent into a vial and irradiated with microwaves (300 W, 140°C) for 90 min. The crude product, recovered with methanol and chloroform, was purified by column chromatography over alumina gel using petroleum ether\ethyl ether (v\v:1\1) as eluent. White solid; yield 41 %; m.p. 58°C. ¹H-NMR (CDCl₃, 300 MHz, TMS) δ = 12.43 (s, 1H, -NH), 7.45 (d, J_{H-H}=8.7 Hz, 2H), 6.98 (d, J_{H-H}=8.6 Hz, 2H), 5.21 (s, 1H), 2.10 (s, 3H), 1.98 (s, 3H). FT-IR (KBr) v (cm⁻¹) = 1611, 1565, 1484, 1278, 1192, 752. GC-MS: *m*/z 255 [(M+2)⁺, 45], 253 (M⁺, 50), 240 (54), 238 (61), 212 (14), 210 (13), 159 (83), 131 (100), 84 (24), 76 (21). E.A. calculated (%) for C₁₁H₁₂BrNO: C, 51.99; H, 4.76; N, 5.51; found: C, 52.03; H, 4.86; N, 5.82.

H(O^N)². Hexafluoroacetylacetone (499 mg, 2.4 mmol) and 4bromoaniline (412 mg, 2.4 mmol) were introduced without solvent into a vial. Afterwards, *p*-toluenesulfonic acid (10%) was introduced as catalyst. The mixture was irradiated using microwaves (600 W, 140 °C) for 30 min. The crude product was recovered with methanol and chloroform and purified by column chromatography over silica gel with petroleum ether\ethyl acetate (v\v:9.5\0.5) as eluent. Yellow solid; yield 49 %; m.p. 80 °C. ¹H-NMR (CDCl₃, 300 MHz, TMS) δ = 11.76 (s, 1H, -NH), 7.55 (d, J_{H-H}=8.4 Hz, 2H), 7.13 (d, J_{H-H}=8.1 Hz, 2H), 6.05 (s, 1H). FT-IR (KBr) v (cm⁻¹) = 1642, 1596, 1574, 1141, 1012, 799. GC-MS: *m*/z 363 [(M+2)⁺, 93], 361 (M⁺, 100), 294 (88), 292 (93), 213 (50), 185 (44), 165 (36), 76 (38). E.A. calculated (%) for C₁₁H₆BrF₆NO: C, 36.49; H, 1.67; N, 3.87; found: C, 36.11; H, 1.98; N, 3.59.

Synthesis of H(ppy-TPA) ligand

2-bromoaniline (365 mg, 2.31 mmol) and N,N-diphenylphenyl boronic acid (1 g, 3.46 mmol) were solubilized in 30 ml of ethanol In this mixture, 10 ml of an aqueous solution of K₂CO₃ (638 mg, 4.62 mmol) and then $Pd(OAc)_2$ (1.5 mol%, 8 mg) were introduced. This was stirred for 10 minutes at 80°C. Afterwards, the crude product was extracted with ethyl acetate after the introduction of 60 ml of brine. The desired product was purified by column chromatography over silica with petroleum ether\ ethyl acetate as eluent (v\v:9\1). The product was further purified through ricristallisation with dichloromethane\petroleum ether. White solid; yield 61 %; m.p. 177 °C. ¹H-NMR (CDCl₃, 300 MHz, TMS) δ = 8.65 (d, 1H), 7.86 (d, 2H), 7.75 - 7.65 (m, 2H), 7.30 - 7.25 (m, 4H), 7.20 - 7.12 (m, 7H), 7.05 (t, 2H). FT-IR (KBr) v (cm⁻¹) = 1584, 1489, 1480, 1465, 1433, 782, 753, 725, 691. E.A. calculated (%) for C23H18N2: C, 85.68; H, 5.63; N, 8.69; found: C, 85.89; H, 5.34; N, 8.50.

Synthesis of [(C^N)2lr(µ-Cl)]2

[(ppy-TPA)₂**Ir**(μ -**CI)]. H(ppy-TPA)** (300 mg, 0.93 mmol) was solubilized in 15 ml of degassed 2-ethoxyethanol. In this solution was added the Ir(III) salt, IrCl₃· 3H₂O, (164 mg, 0.46 mmol) suspended into 5 ml of degassed H₂O. The reaction mixture was irradiated with microwaves (250 W, 110°C) for 1 h. Afterwards, a little quantity of

H₂O was added to promote precipitation of product that was filtered off and washed with water and methanol. Brown solid; yield 60 %; m.p. >250°C. ¹H-NMR (CDCl₃, 300 MHz, TMS) δ = 8.89 (d, J_{H:H}=5.64 Hz, 1H), 7.43 (d, 1H), 7.24 (t, 2H), 7.09 (t, 4H), 6.94-6.85 (m, 6H), 6.45 (dd, J₁=2.1 Hz, J₂=0.1 Hz, 1H), 6.21 (t, J₁₂=J₂₁= 5.9 Hz, 1H), 5.48 (d, J_{H:H}=2.16 Hz, 1H). FT-IR (KBr) v (cm⁻¹) = 1573, 1487, 1463, 1272, 751, 696. E.A. calculated (%) C₉₂H₆₈Cl₂Ir₂N₈: C, 63.47; H, 3.94; N, 6.44; found: C, 63.68; H, 3.85; N, 6.37.

[(bz-TPA)₂Ir(μ-CI)]. H(bz-TPA) (215 mg, 0.57 mmol) was solubilized in 15 ml of degassed 2-ethoxyethanol and then the Ir(III) salt, IrCl₃· 3H₂O, (100 mg, 0.28 mmol) was added suspended in 5 ml of degassed H₂O. The mixture was irradiated with microwaves (250 W, 200°C) for 4 hours. Afterwards, a little quantity of water was added to promote the precipitation of the desired product that was filtered off and then washed with water, ethanol and diethyl ether. Orange solid; yield 70 %; m.p. >250°C. ¹H-NMR (CDCl₃, 300 MHz, TMS) δ = 8.58 (d, 1H), 7.30 - 7.27 (m, 1H), 7.01 (d, 1H), 6.95 - 6.90 (m, 5H), 6.82 - 6.77 (m, 2H), 6.74 - 6.67 (m, 5H), 6.45 (d, 1H), 5.45 (s, 1H); The recorded ¹H-NMR spectrum is in agreement to what reported in literature.³² FT-IR (KBr) v (cm⁻¹) = 1572, 1491, 1430, 751, 696. E.A. calculated (%) for C₁₀₀H₆₆Cl₂Ir₂N₈S₄: C, 61.11; H, 3.49; N, 5.70; found: C, 61.23; H, 3.27; N, 5.51.

Synthesis of [(C^N)₂Ir(O^N)ⁿ] complexes, 1-4

 $H(O^N)^n$ was solubilized in 10 ml of a degassed solution of NaOH in EtOH (10 mg\ml) and the mixture was stirred at 65°C for 2 hours. After, [(C^N)₂Ir(μ -CI)] was added to the solution that was stirred for 48 hours in the same conditions of reaction. The solid obtained was filtered off and washed with water and ethanol. The crude product was purified by column chromatography.

[(ppy-TPA)₂**Ir(O^N)**¹], 1. The reaction was conducted using **H(O^N)**¹ (70 mg, 2.59 · 10⁻⁴ mol) and **[(ppy-TPA)**₂**Ir(μ-CI)]**₂ (150 mg, 8.62 · 10⁻⁵ mol). The product was purified over alumina gel using dichloromethane as eluent. Yellow solid; yield 41 %; m.p. 150°C; ¹H-NMR (CDCI₃, 300 MHz, TMS) δ = 8.68 (d, J_{H+H} = 5.28 Hz, 1H), 8.51 (d, J_{H+H} = 5.49 Hz, 1H), 7.41 – 7.29 (m, 4H), 7.23 – 7.04 (m, 9H), 6.95 – 6.81 (m, 14H), 6.72 (dd, J₁= 2.31 Hz, J₂= 8.25 Hz, 1H), 6.48 (dd, J₁= 2.31 Hz, J₂= 8.23 Hz, 1H), 6.36 – 6.28 (two overlapping dd, 2H), 5.82 (d, 2H), 5.41 (d, 2H), 5.14 (dd, J₁= 2.52 Hz, J₂= 8.35 Hz, 1H), 4.85 (s, 1H), 1.82 (s, 3H), 1.56 (s, 3H); FT-IR (KBr) v (cm⁻¹) = 1572, 1479, 1274, 751, 696; MS (ESI+, direct infusion) m/z = 1087.7 (100% [(ppy-TPA)₂Ir(O^N)¹+H]⁺). E.A. calculated (%) for C₅₇H₄₅BrIrN₅O: C, 62.92; H, 4.17; N, 6.44; found: C, 62.83; H, 4.09; N, 6.49.

[(ppy-TPA)₂**Ir(O^N)**²], 2. The reaction was conducted using H(O^{AN})² (93 mg, 2.58 \cdot 10⁻⁴ mol) and **[(ppy-TPA)**₂**Ir(μ-CI)]**₂ (150 mg, 8.62 \cdot 10⁻⁵ mol). The product was purified over alumina gel using dichloromethane as eluent. Yellow-orange solid; yield 12 %; m.p. 186 °C; ¹H-NMR (CDCI₃, 300 MHz, TMS) δ = 8.49 (d, J_{H-H} =5.28 Hz, 1H), 8.31 (d, J_{H-H} = 5.49 Hz, 1H), 7.46 – 7.30 (m, 3H), 7.27 – 7.18 (m, 10H), 7.12 (dd, 1H), 6.99 – 6.83 (m, 14H), 6.71 (dd, 1H), 6.50 (dd, 1H), 6.39 – 6.32 (m, 2H), 5.67 (s, 2H), 5.32 (s, 2H), 5.19 (d, 1H); FT-IR (KBr) v (cm⁻¹) = 1574, 1483, 1460, 1277, 1192, 1154, 751, 696; MS (ESI+, direct infusion) *m/z* = 1195.5 (100% [(ppy-TPA)₂Ir(O^AN)²+H]⁺). E.A. calculated (%) for C₅₇H₃₉BrF₆IrN₅O: C, 57.24; H, 3.29; N, 5.85; found: C, 57.29; H, 3.19; N, 5.43.

[(bz-TPA)₂**Ir(O^N)**¹**]**, **3**. The reaction was conducted using H(O^AN)¹ (85 mg, $3.35 \cdot 10^{-4}$ mol) and **[(bz-TPA)**₂**Ir(μ-CI)]**₂ (150 mg, $7.63 \cdot 10^{-5}$ mol). The product was purified over silica gel using dichloromethane as eluent. Red solid; yield 51 %; m.p. 168°C; ¹H-NMR (CDCI₃, 300 MHz, TMS) δ = 8.15-8.10 (m, 2H), 7.67-7.37 (m, 2H), 7.34-7.23 (m, 8H), 7.08-6.94 (m, 12H), 6.91-6.83 (m, 4H), 6.73 (dd, 1H), 6.51-6.41 (m, 3H), 6.36 (dd, 1H), 5.78 (dd, 2H), 5.51 (d, 2H), 5.16 (dd, 1H), 4.87 (s, 1H), 1.76 (s, 3H), 1.59 (s, 3H); FT-IR (KBr) v (cm⁻¹) = 1569, 1430,

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1312, 1283, 1266, 1241, 752, 696; MS (ESI+, direct infusion) m/z = 1201.6 (100% [(bz-TPA)_2Ir(O^N)^1+H]^+). E.A. calculated (%) for C₆₁H₄₅BrIrN₅OS₂: C, 60.99; H, 3.77; N, 2.33; found: C, 60.78; H, 3.57; N, 2.62.

[(bz-TPA)₂**Ir(O^N)**²**]**, **4**. The reaction was conducted using H(O^N)² (83 mg, 2.34 \cdot 10⁻⁴ mol) and **[(bz-TPA)**₂**Ir(μ-C)]**₂ (150 mg, 7.63 \cdot 10⁻⁵ mol). The product was purified over silica gel using petroleum ether/ethyl acetate (v/v:9/1) as eluent. Dark red solid; yield 26 %; m.p. 121 °C; ¹H-NMR (CDCl₃, 300 MHz, TMS) δ = 7.94 (d, J_{H+H} = 7.77 Hz, 1H), 7.84 (d, J_{H+H} = 7.8 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.65 – 7.33 (m, 6H), 7.09 – 7.04 (m, 5H), 7.01 – 6.96 (m, 4H), 6.92 – 6.84 (m, 12H), 6.73 (dd, J₁=8.25 Hz, J₂= 2.31 Hz, 1H), 6.50 – 6.42 (m, 3H), 5.65 (d, 1H), 5.64 (s, 1H), 5.48 (d, J_{H+H} = 2.07 Hz, 1H), 5.22 (dd, 1H); FT-IR (KBr) v (cm⁻¹) = 1572, 1485, 1430, 1191, 1144, 753, 696; MS (ESI+, direct infusion) *m*/*z* = 1307.6 (100% [(bz-TPA)₂Ir(O^N)²+H]⁺). E.A. calculated (%) for C₆₁H₃₉BrF₆IrN₅OS₂: C, 56.00; H, 3.00; N, 5.35; found: C, 55.91; H, 2.89; N, 5.46.

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Entry for the Table of Contents

Layout 1:

FULL PAPER

Thin filn cyclome obtained electron polymer

ns of TPA containing Ir(III)		Author(s), Corresponding Author(s)*
etalated complexes were d by electrodeposition and		Page No. – Page No.
a trapping was observed onto rized films.		Title
	TPA Functionalized Ir(III) Complexes Solution Solid State	
	Spin Coated Thin Film	
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	Electropolymerized Thin Film Electron Trapping	
	+ Emission Quenching	