

Received 00th January  
20xx,

## Fully Ir(III) tetrazolate soft salts: the road to white-emitting ion pairs

 Valentina Fiorini,<sup>a\*</sup> Andrea D'Ignazio,<sup>a</sup> Karen D. M. Magee,<sup>b</sup> Mark I. Ogden,<sup>b</sup> Massimiliano Massi<sup>b\*</sup> and Stefano Stagni<sup>a\*</sup>

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

**The first examples of anionic Ir(III) bis-tetrazolate complexes and their combination with a cationic Ir(III) tetrazole derivative forming “fully tetrazolate” Ir(III) based soft salts as O<sub>2</sub>-sensitive white emitters are described herein.**

Ir(III)-based ionic transition-metal complexes (Ir-iTMC) occupy a prominent position in the scenery of phosphorescent molecules to be used in solid state lighting, luminescent chemosensing and for bioimaging applications.<sup>1</sup> This is a direct consequence of their belonging to the family of Ir(III) cyclometalated complexes, a class of compounds that displays a combination of outstanding photo- and electroluminescent performance, together with the ease of emission colour tunability via modification of the ligand environment. In this context, even though the family of Ir-iTMC is largely dominated by cationic species with the general formula [Ir(N<sup>^</sup>C)<sub>2</sub>(L<sup>^</sup>L)]<sup>+</sup>, where the neutral ligand (L<sup>^</sup>L) is often represented by aromatic diimines (N<sup>^</sup>N),<sup>1,2</sup> negatively charged Ir(III) cyclometalated complexes have also attracted increasing attention in light of their favourable properties. More specifically, the studies dealing with this class of brightly phosphorescent complexes, which is centred around the archetypal [Ir(ppy)<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> and its fluorinated analogue [Ir(F<sub>2</sub>ppy)<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup>,<sup>3</sup> have led to interesting results on the use of their alkali metal salts as emissive materials for light-emitting electrochemical cells (LEECs),<sup>4</sup> the construction of Ir(III)-Ln(III) arrays,<sup>5</sup> and, in combination with other cationic Ir(III) complexes, the formation of the so called “Ir-based soft salts”<sup>6</sup> where further colour tuning of the emission can be achieved

with the combination or modulation of energy transfer processes between the ionic components. Aiming to provide a new set Ir(III) based soft salts, in which an initial element of novelty is represented by the choice of a an anionic counterpart different than the traditionally employed Ir(III) cyanometalates, we wanted to extend the family of Ir(III) tetrazolate complexes<sup>7</sup> with the preparation of the first examples of their negatively charged analogues. To achieve this aim, we have modified the [Ir(ppy)<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> or [Ir(F<sub>2</sub>ppy)<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> core structure by replacing the cyanide groups with bulkier 5-aryl tetrazolato derivatives. The newly obtained species were found to range from sky-blue to aqua emitters. Furthermore, aiming to prepare soft salts formed by exclusively Ir(III) tetrazolate ions, the anionic species were coupled with the methylated form of a previously reported red emitter, [IrTPYZ-Me]<sup>+</sup>.<sup>7a</sup> The results presented highlight the formation of soft salts whose emission is highly dependent on the oxygen content, suggesting a potential for the luminescence-sensing response to the presence of dissolved O<sub>2</sub>, and a unique example of white-emitting Ir(III) based soft salts.

The preparation of the anionic complexes has been accomplished through a slightly modified procedure by Nazeeruddin (Scheme 1),<sup>3</sup> where the chloride bridged Ir(III) dimer was reacted with an excess of 5-aryl tetrazole and base. The targeted anionic complexes were confirmed by NMR

<sup>a</sup> Department of Industrial Chemistry “Toso Montanari”, University of Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy. E-mail: [stefano.stagni@unibo.it](mailto:stefano.stagni@unibo.it), [valentina.fiorini5@unibo.it](mailto:valentina.fiorini5@unibo.it)

<sup>b</sup> Nanochemistry Research Institute, Department of Chemistry, Curtin University, GPO Box U 1987, Perth, Australia 6845. E-mail: [m.massi@curtin.edu.au](mailto:m.massi@curtin.edu.au)

† Electronic Supplementary Information (ESI) available: [NMR (<sup>1</sup>H, <sup>13</sup>C) and ESI-MS spectra of all the Ir(III) based species. UV-vis absorption, emission spectra recorded at r.t., 77K and neat solid r.t.; 1931 C.I.E plots for Ir(III) soft salts]. See DOI: 10.1039/x0xx00000x

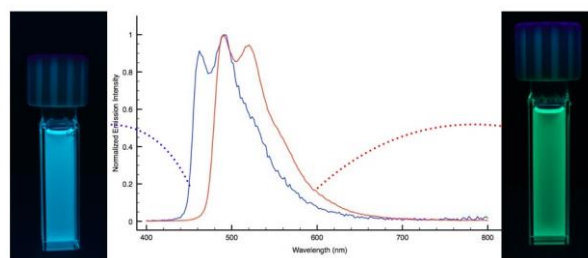
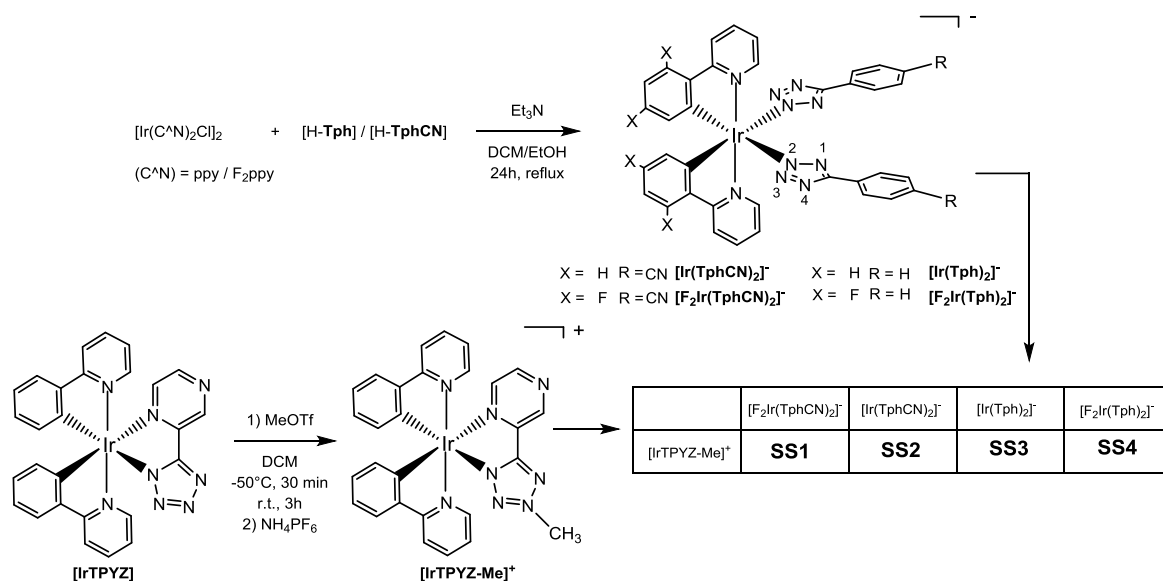


Figure 1: Normalized emission profiles of [F<sub>2</sub>Ir(TphCN)<sub>2</sub>]<sup>-</sup> (left, blue trace) and [Ir(TphCN)<sub>2</sub>]<sup>-</sup> (right, red trace) CH<sub>2</sub>Cl<sub>2</sub>, r.t. .



Scheme 1: Synthetic procedure for Ir(III) anionic and cationic complexes; acronyms used for complexes and soft salts.

spectroscopy (ESI<sup>+</sup> Fig. S1-S8) and ESI-Mass spectrometry (ESI<sup>+</sup> Fig. S15-S18). In particular, the NMR characterisation provided results consistent with the formation of species having the expected C<sub>2</sub> symmetry. Resonances at *ca.* 163 ppm in the <sup>13</sup>C-NMR spectra suggest that the tetrazolate ligands are exclusively coordinated via the N-2 atoms.<sup>7a</sup>

The cationic complex  $[\text{IrTPYZ-Me}]^+$  was obtained by the reaction of the neutral Ir(III) tetrazolate precursors with one equivalent of methyl triflate (Scheme 1).<sup>7</sup> The methylation regioselectively occurred at the N-3 position of the coordinated tetrazolate ring, as suggested by the presence of

one single tetrazole carbon (Ct) resonance at *ca.* 166 ppm (ESI<sup>+</sup> Fig. S9, S10), which is shifted downfield with respect to that of the neutral precursor.

In dichloromethane solutions at room temperature, all the anionic Ir(III) complexes show quite typical absorption profiles, with the spectral region up to 300 nm dominated by intense ligand centred (<sup>1</sup>LC)  $\pi$ - $\pi^*$  transitions involving both the cyclometalating and the ancillary tetrazolate ligands. Weaker and broader spin allowed (<sup>1</sup>MLCT) and spin forbidden (<sup>3</sup>MLCT) bands are found at longer wavelength (300 to 380 nm) (ESI<sup>+</sup> Fig. S20, S24, S28, S32). The spectra do not significantly change

CH <sub>2</sub> Cl <sub>2</sub> as solvent	Absorption	Emission 298 K				Emission 77K		
	$\lambda_{\text{abs}}(\text{nm}); (10^{-4}\epsilon)(\text{M}^{-1}\text{cm}^{-1})$	$\lambda_{\text{em}}(\text{nm})$	$\tau_{\text{air}}(\mu\text{s})$	$\tau_{\text{Ar}}(\mu\text{s})$	$\phi_{\text{air}}(\%)$	$\phi_{\text{Ar}}(\%)$	$\lambda_{\text{em}}(\text{nm})$	$\tau(\mu\text{s})$
$[\text{Ir}(\text{Tph})_2]^-$	255(4.8), 346(0.44), 387(0.20)	484, 514	0.12	1.27	5.5	60.6	480, 510	4.09
$[\text{F}_2\text{Ir}(\text{Tph})_2]^-$	254(5.9), 308(1.2), 370(0.22)	462, 490	0.16	1.99	5.9	49.0	458, 490	3.23
$[\text{Ir}(\text{TphCN})_2]^-$	260(7.3), 295(3.1) 393 (0.2)	490, 520	0.11	0.80	3.4	24.9	480, 516, 556	4.03
$[\text{F}_2\text{Ir}(\text{TphCN})_2]^-$	260(4.0), 377(0.24), 318(1.1)	462, 492	0.17	1.35	3.3	22.0	460, 490, 522	3.25
$[\text{IrTPYZ-Me}]^+$	265(6.8), 327(1.7), 377(1.1)	686	0.09	0.095	2.7	3.6	582	4.50
<b>SS1</b> $[\text{F}_2\text{Ir}(\text{TphCN})_2]^-$ $[\text{IrTPYZ-Me}]^+$	261(4.93), 314(1.50), 377(0.39)	460, 490, 680	0.16, 0.15, 0.09	1.19, 1.11, 0.11	2.8	7.0	454, 484, 574	3.8, 3.9, 4.6
<b>SS2</b> $[\text{Ir}(\text{TphCN})_2]^-$ $[\text{IrTPYZ-Me}]^+$	263(7.09), 343(1.18), 385(0.69)	486, 518, 664	0.10, 0.10, 0.11	0.66, 0.65, 0.14	3.1	14.8	480, 574	1.07, 2.45
<b>SS3</b> $[\text{Ir}(\text{Tph})_2]^-$ $[\text{IrTPYZ-Me}]^+$	262(5.19), 320(1.49), 381(0.63)	486, 518, 680	0.12, 0.12, 0.09	1.46, 1.44, 0.11	3.6	12.3	480, 510, 574	3.13, 3.27, 3.16
<b>SS4</b> $[\text{F}_2\text{Ir}(\text{Tph})_2]^-$ $[\text{IrTPYZ-Me}]^+$	255(3.60), 317(0.95), 377(0.43)	462, 490, 680	0.19, 0.20, 0.09	1.28, 1.22, 0.10	3.0	16.9	454, 488, 578	2.28, 2.80, 3.07

Table 1: Photophysical properties of Ir(III) anionic and cationic complexes and soft salts.

in the case of the cationic complex  $[\text{IrTPYZ-Me}]^+$  (ESI<sup>†</sup> Fig. S38). The only difference is represented by a slight hypsochromic shift that was displayed by the MLCT bands. On the contrary, anionic and cationic complexes displayed completely different photoluminescence properties from each other. Indeed, all the anionic Ir(III) complexes display wavelength-independent and intense sky-blue ( $\lambda = 460, 490 \text{ nm}$ , figure 1, blue trace and ESI<sup>†</sup> Fig. S25, S33) or aqua emission ( $\lambda = 490, 520 \text{ nm}$ , figure 1, red trace and ESI<sup>†</sup> Fig. S21, S29) originating from excited states of triplet character, an assignment supported by the oxygen sensitivity of the quantum yield ( $\phi$ ) lifetimes ( $\tau$ ) values (Table 1). The emission profiles appear strongly structured, which is representative for the interplay of  $^3\text{LC}/^3\text{MLCT}$  type emissive excited states. The likely prevalent contribution of the  $^3\text{LC}$  states over the  $^3\text{MLCT}$  ones is suggested by the rather small rigidochromic blue shift that was encountered at 77K (ESI<sup>†</sup> Fig. S21, S25, S29, S33).

The addition of a methyl group to the coordinated tetrazolate ring of the neutral precursor  $[\text{IrTPYZ}]$  (Scheme 1) resulted in the formation of the corresponding deep-red emitting ( $\lambda = 686 \text{ nm}$ ) cationic derivative. The  $[\text{IrTPYZ-Me}]^+$  complex displayed broad and structureless emission profile, again originating from excited states of triplet multiplicity. The MLCT character of emissive excited states was made evident in consideration of the pronounced rigidochromic blue shift at 77K (ESI<sup>†</sup> Fig. S39).

All anionic complexes were chosen to be incorporated in ion pairs along with the cationic species  $[\text{IrTPYZ-Me}]^+$  (Scheme 1). According to the method reported by Thompson and co-workers,<sup>6b</sup> the new Ir(III)-based soft salts were prepared by dissolving equimolar amounts of the anionic and cationic Ir(III) complexes in  $\text{H}_2\text{O}$  at room temperature (Scheme 1). The subsequent extraction with dichloromethane gave rise to crude products whose  $^1\text{H-NMR}$  analysis confirmed the presence of two distinct patterns of signals in 1/1 ratio. The isolation of the soft salt was further confirmed by the lack of triethylammonium peaks in the  $^1\text{H-NMR}$  spectra (ESI<sup>†</sup> Fig. S11-S14).

Upon excitation at 370 nm of their air-equilibrated dichloromethane diluted ( $10^{-5} \text{ M}$ ) solutions, the soft salts SS1-SS4 display emission profiles that effectively exhibit the contributions coming from both the anionic and cationic counterparts (ESI<sup>†</sup> Fig. S44, S50, S57, S62), with excited state lifetimes similar to those determined for the corresponding

mononuclear complexes in the same experimental conditions (Table 1), suggesting that energy transfer and/or electron transfer processes have a minor role in determining the emission behaviour of the ion pairs.

This feature led to the emission of an orange colour from the SS2 and SS3 ion pair while, relative to the ion pair denoted as SS1 and SS4, the blue contribution stemming from  $[\text{F}_2\text{Ir}(\text{TphCN})_2]^-$  or  $[\text{F}_2\text{Ir}(\text{Tph})_2]^-$  respectively and the red one originating from the  $[\text{IrTPYZ-Me}]^+$  component did coexist in the appropriate balance to give an almost pure white light (1931 CIE coordinates  $X = 0.3288$ ;  $Y = 0.3284$  for SS1. (See ESI<sup>†</sup> Tab. S5 for 1931 CIE of SS4). This picture changed dramatically upon passing to deoxygenated solutions, which all displayed the predominant emission of the anionic complexes. The occurrence of such similar trend can be traced back to the different rates of enhancement of the emission intensities that are displayed by the single mononuclear complexes and points again to how the anion and cation that constitute the soft salts basically behave as photophysically independent entities, with a likely minor role played by energy and/or electron transfer processes, the intervention of which is probably limited by the presence of the bulky 5-aryl tetrazolates in the structures of the anionic complexes. In conclusion, it appears how the new anionic Ir(III) tetrazolate complexes can be coupled to new Ir(III) cationic tetrazole derivatives to form “fully tetrazolate” soft salts in which it is possible to achieve a properly additive synthesis of the emission colours. Based on this behaviour, an almost pure white light emission (1931 CIE coordinates  $X=0.3288$ ;  $Y=0.3284$  for SS1,  $X=0.3080$ ;  $Y=0.3298$  for SS4) can be obtained upon the appropriate choice of the ionic components. In all cases, the emission colour is sensitive to the presence of dissolved dioxygen, a peculiarity that might entail the use of these new ion pairs as ratiometric  $\text{O}_2$  luminescence sensors. Studies are in progress in our laboratories in order to achieve the emission of white light also from  $\text{O}_2$  free solutions, a feature that might favour the use of these systems in the fabrication of light emitting devices.

The Toso Montanari Foundation and the Australian Research Council (grant number FT1301000033) are gratefully acknowledged for the financial support. The authors also wish to thank Professor Eli Zysman-Colman (University of St. Andrews) for useful discussions.

## Notes and references

- (a) L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura and F. Barigelletti, *Top. Curr. Chem.*, 2007, **281**, 143-203. (b) V. Fernandez-Moreira, F. L. Thorp-Greenwood and M. P. Coogan, *Chem. Commun.*, 2010, **46**, 186-202; (c) Zhang, K. Y.; Lo, K. K.-W. Chemosensing and Diagnostics. In *Coordination and Organometallic Chemistry (Volume 8) of Comprehensive Inorganic Chemistry II*; V. W.-W. Yam Ed.; Elsevier: Amsterdam, 2013, 657 – 732 and references cited therein
- R. D. Costa, E. Orti, H. J. Bolink, F. Monti, G. Accorsi and N. Armaroli, *Angew. Chem. Int. Ed.*, 2012, **51**, 8178-8211.

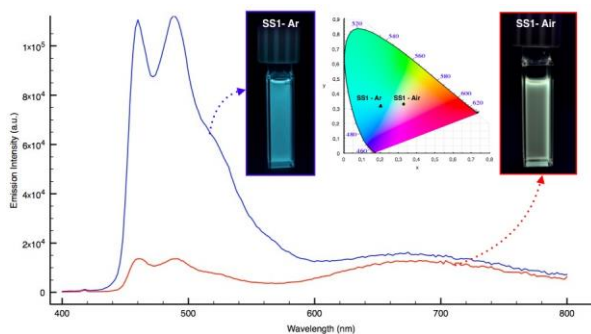


Figure 2: Emission profiles of SS1, air equilibrated (red trace) and deoxygenated solution (blue trace),  $\text{CH}_2\text{Cl}_2$ , r.t. .

- 3 M. K. Nazeeruddin R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppioli and M. Graetzel, *J. Am. Chem. Soc.*, 2003, **125**, 8790-8797.
- 4 H. F. Chen, C. Wu, M. C. Kuo, M. E. Thompson and K. T. Wong, *J. Mater. Chem.*, 2012, **22**, 9556-9561.
- 5 N. M. Ali, V. L. MacLeod, P. Jennison, I. V. Sazanovich, C. A. Hunter, J. A. Weinstein and M. D. Ward, *Dalton Trans.*, 2012, **41**, 2408-2419.
- 6 (a) M. Mauro, K. C. Schuermann, R. Prétôt, A. Hafner, P. Mercandelli, A. Sironi and L. De Cola, *Angew. Chem. Int. Ed.*, 2010, **49**, 1222-1226. (b) C. Wu, H. F. Chen, K. T. Wong and M. E. Thompson, *J. Am. Chem. Soc.*, 2010, **132**, 3133-3139; c) A. Ionescu, E. I. Szerb, Y. J. Yadav, A. M. Talarico, M. Ghedini and N. Godbert, *Dalton Trans.*, 2014, **43**, 784-789; for heterometallic Ir(III)-Ru(II) ion pairs see: d) M. Sandroni and E. Zysman-Colman, *Dalton Trans.*, 2014, **43**, 3676-3680; e) K. N. Swanick, M. Sandroni, Z. Ding and E. Zysman-Colman, *Chemistry – Eur. J.*, 2015, **21**, 7435-7440.
- 7 a) S. Stagni, S. Colella, A. Palazzi, G. Valenti, S. Zacchini, F. Paolucci, M. Marcaccio, R. Q. Albuquerque and L. De Cola, *Inorg. Chem.*, 2008, **47**, 10509-10521; b) M. V. Werrett, S. Muzzioli, P. J. Wright, A. Palazzi, P. Raiteri, S. Zacchini, M. Massi and S. Stagni, *Inorg. Chem.*, 2014, **53**, 229–243.