



HAL
open science

Iridium(iii) dipyridylamine complexes: synthesis, characterization and catalytic activities in photoredox reactions

Elodie Sauvageot, Ronan Marion, Fabien Sguerra, Adèle Grimault, Richard Daniellou, Matthieu Hamel, Sylvain Gaillard, Jean-Luc Renaud

► **To cite this version:**

Elodie Sauvageot, Ronan Marion, Fabien Sguerra, Adèle Grimault, Richard Daniellou, et al.. Iridium(iii) dipyridylamine complexes: synthesis, characterization and catalytic activities in photoredox reactions. *Organic Chemistry Frontiers*, 2014, 1 (6), pp.639-644. 10.1039/c4qo00059e . cea-01825703

HAL Id: cea-01825703

<https://cea.hal.science/cea-01825703v1>

Submitted on 24 Aug 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Iridium(III) dipyridylamine complexes: synthesis, characterization and catalytic activities in photoredox reactions

Elodie Sauvageot,^{ab} Ronan Marion,^{ab} Fabien Sguerra,^c Adèle Grimault,^{ab} Richard Daniellou,^{de} Matthieu Hamel,^c Sylvain Gaillard^{*ab} and Jean-Luc Renaud^{*ab}

* Corresponding authors

a Normandie University, University of Caen Basse Normandie, Laboratoire de Chimie Moléculaire et Thioorganique, 14050 Caen, France
E-mail: sylvain.gaillard@ensicaen.fr, jean-luc.renaud@ensicaen.fr

^b CNRS, UMR 6507, 14050 Caen, France

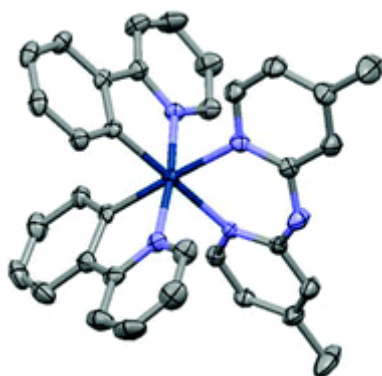
^c CEA, LIST, Laboratoire Capteurs et Architectures Électroniques, F-91191 Gif-sur-Yvette Cedex, France

^d University of Orléans, Institut de Chimie Organique et Analytique, 45067 Orléans, France

^e CNRS, UMR 7311, 45067 Orléans, France

Abstract

Two new series of cyclometalated iridium(III) complexes bearing a dipyridylamine as the N[^]N ligand have been prepared and fully characterized. After investigation of their photophysical properties, their catalytic activities have been evaluated in a model photoredox reaction and compared with the commercially available [Ir(ppy)₂(dtbbpy)][PF₆] complex.



Introduction

Nitrogen ligands are able to bind strongly to transition metal atoms and can stabilize both very low and high oxidation states [1–6]. Among these nitrogen ligands, dipyridylamines (dpa) occupy a unique place in coordination chemistry because they are able to form six-membered chelates upon metal binding. They have found applications in transition metal-catalyzed polymerization, allylic oxidation, transesterification and magnetism and photomagnetism [7]. Despite these interesting examples, the chemistry of 2,2'-dipyridylamines has mainly been limited to the study of their coordination behavior. Since several years, we have developed a research program devoted to the synthesis [8], the coordination [9], and the reactivity of metal complexes coordinated to dipyridylamine derivatives. This interest was directed by their easy functionalization and the possibility to have an anchoring site with the bridged nitrogen atom. These two reasons may give access to a broad range of applications such as supported

catalysis [10], ion detection [11] or Organic Light Emitting Diodes [12]. Here, we present the synthesis and the full characterization of a series of neutral and cationic heteroleptic iridium(III) complexes bearing both C^N ligands and a dipyridylamine motif as the N^N ligand. An evaluation of their catalytic activities in a model photoredox reaction is also reported in order to demonstrate the potentiality of developing supported photoredox catalysis.

Results and discussion

In order to have an orthogonal and homogeneous series of octahedral cationic and neutral iridium(III) complexes, 2-phenylpyridine (ppy), 2-*p*-tolylpyridine (4-Me-ppy), 2-(2,4-difluorophenyl)pyridine (2,4-F-ppy), benzoquinoline (bzq), *N*-phenylpyrazole (ppz) and 2-phenylisoquinoline (piq) were first selected as C^N cyclometalating ligands (**1–6**, Fig. 1). The corresponding iridium(III) dimer complexes were obtained in good to high yields (73 to 99% isolated yields) using a known procedure [13].

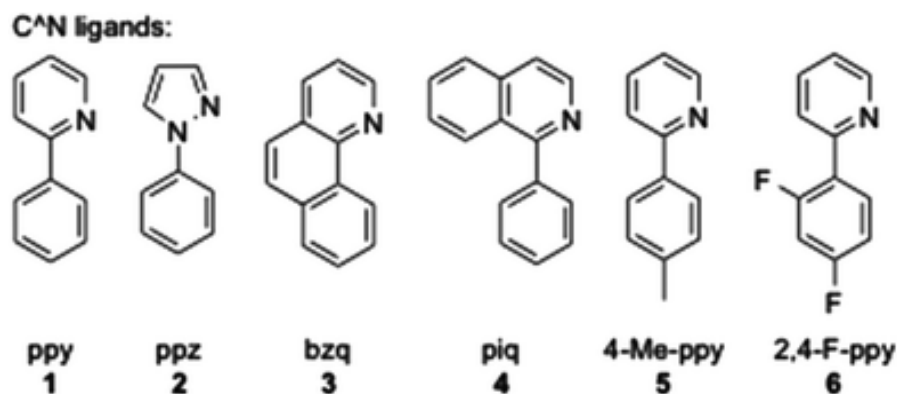


Fig. 1 Cyclometalated ligands used in this study.

Addition of various dipyridylamine derivatives [14] (N^N ligands **a–f**, Fig. 2) to the mentioned iridium dimers followed by anion metathesis led to a library of cationic iridium complexes with yields ranging from 65 to 97% [15]. It is noteworthy that the formation of the expected complexes between iridium(III) dimers and 6-Me-Hdpa was not observed. We assume that this non-coordination came from steric repulsions between the methyl substituent on the pyridine rings and the C^N ligands, already coordinated to the iridium centre.

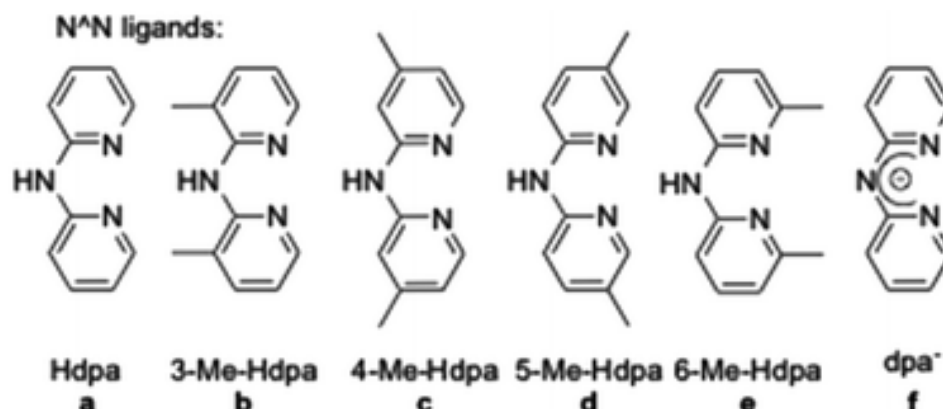
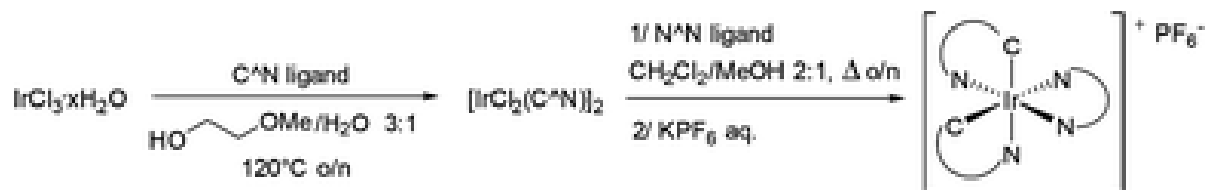


Fig. 2 Dipyridylamine ligands used in this study.

Finally, as summarized in Table 1, a series of 18 complexes was obtained in overall yields ranging from 39 to 80% (Scheme 1).



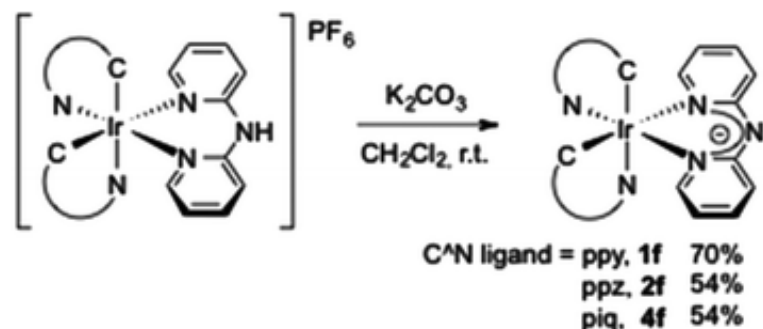
Scheme 1 Synthesis of cationic Ir(III) complexes.

Entry	Complex	Yield ^a (%)
1	[Ir(ppy) ₂ (Hdpa)][PF ₆] 1a	70
2	[Ir(ppy) ₂ (3-Me-Hdpa)][PF ₆] 1b	80
3	[Ir(ppy) ₂ (4-Me-Hdpa)][PF ₆] 1c	77
4	[Ir(ppy) ₂ (5-Me-Hdpa)][PF ₆] 1d	77
5	[Ir(ppz) ₂ (Hdpa)][PF ₆] 2a	67
6	[Ir(ppz) ₂ (3-Me-Hdpa)][PF ₆] 2b	71
7	[Ir(ppz) ₂ (4-Me-Hdpa)][PF ₆] 2c	79
8	[Ir(ppz) ₂ (5-Me-Hdpa)][PF ₆] 2d	79
9	[Ir(bzq) ₂ (Hdpa)][PF ₆] 3a	39
10	[Ir(bzq) ₂ (3-Me-Hdpa)][PF ₆] 3b	42
11	[Ir(bzq) ₂ (4-Me-Hdpa)][PF ₆] 3c	50
12	[Ir(bzq) ₂ (5-Me-Hdpa)][PF ₆] 3d	44
13	[Ir(piq) ₂ (Hdpa)][PF ₆] 4a	61
14	[Ir(piq) ₂ (3-Me-Hdpa)][PF ₆] 4b	73
15	[Ir(piq) ₂ (4-Me-Hdpa)][PF ₆] 4c	60
16	[Ir(piq) ₂ (5-Me-Hdpa)][PF ₆] 4d	67
17	[Ir(4-Me-ppy) ₂ (Hdpa)][PF ₆] 5a	77
18	[Ir(2,4-F-ppy) ₂ (Hdpa)][PF ₆] 6a	53

^a Overall yields for the two steps, starting from IrCl₃·xH₂O.

Table 1 Synthesis of dipyridylamine iridium(III) complexes

Taking advantage of the acidic proton on the bridged nitrogen atom, we thought to prepare a series of neutral iridium complexes. The deprotonation was easily achieved in the presence of K₂CO₃ in dichloromethane at room temperature [16] and yielded the corresponding “aza-acac” type ligands coordinated to the iridium(III) centre (54–70%). It is noteworthy that a complex mixture was observed by NMR analysis from [Ir(bzq)₂(Hdpa)][PF₆] **3a**, and we were not able to isolate any complex (Scheme 2).



Scheme 2 Synthesis of neutral iridium complexes bearing anionic dpaa.

To unambiguously establish the atom connectivity in the $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})][\text{PF}_6]$ complexes, single crystals for X-ray diffraction (XRD) were grown by slow gas diffusion of pentane into a saturated dichloromethane or chloroform solution of $[\text{Ir}(\text{ppy})(4\text{-Me-Hdpa})][\text{PF}_6]$ complex **1c**. Ball and stick representations of crystallized complexes $[\text{Ir}(\text{ppy})(4\text{-Me-Hdpa})][\text{PF}_6]$ **1c** are presented in Fig. 3. These X-ray diffraction analyses confirmed the expected 6-membered ring chelate. It is worth mentioning that dipyridylamine ligands did not have a planar geometry due to the pyramidal nitrogen atom between the two pyridine rings.

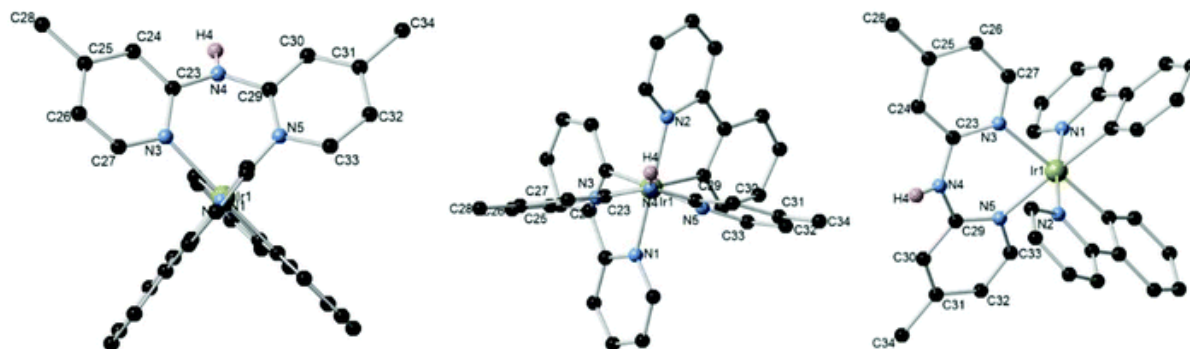


Fig. 3 Different views of the ball and stick representation of $[\text{Ir}(\text{ppy})_2(4\text{-Me-Hdpa})][\text{PF}_6]$ **1c**. Some hydrogen atoms and counter anions were omitted for clarity. Selected bonds (Å) and angles ($^\circ$): Ir1–N3 2.159(2), Ir1–N5 2.164(2), N3–Ir1–N5 86.21(9), C23–N4–C29 131.3(2).

With these complexes in hand, their absorption properties were measured between 230 and 600 nm. In a general trend, the absorption spectra, recorded in CHCl_3 , show that the wavelength depends exclusively on the $\text{C}^{\wedge}\text{N}$ ligands. For all complexes, the maximum of absorption, which can be assigned to a $\pi\text{-}\pi^*$ ligand-centred (LC) transition, was found between 238 and 277 nm (Table 2). The complexes bearing $\text{C}^{\wedge}\text{N}$ ligands such as ppz (**2a–d**), bzq (**3a–d**), piq (**4a–d**) and 2,4-F-ppy (**6a**) presented a maximum of absorption which can be ascribed to a second $\pi\text{-}\pi^*$ ligand-centered transition, in a region between 292 and 323 nm (Table 2). It is noteworthy that concerning the complexes bearing bzq (**3a–d**) and ppy (**1a–d**), a third local maximum of absorption was found at 425 nm. This weak and broad band corresponds to a $d\pi\text{-}\pi^*$ metal-to-ligand charge transfer ($^1\text{MLCT}$) absorption, as also observed with other iridium complexes [18]. More interestingly, for further applications in photoredox chemistry, the iridium complexes bearing a “piq” ligand exhibited this third local maximum at 440 nm and a more intense absorbance (Fig. 4). Then, if the position of the methyl substituent is considered, $[\text{Ir}(\text{piq})_2(3\text{-Me-Hdpa})][\text{PF}_6]$ **4b** showed a slightly lower absorbance than the Hdpa, 4-Me-Hdpa and 5-Me-Hdpa analogous complexes (**4a**, **4c–d**, respectively, Fig. 4).

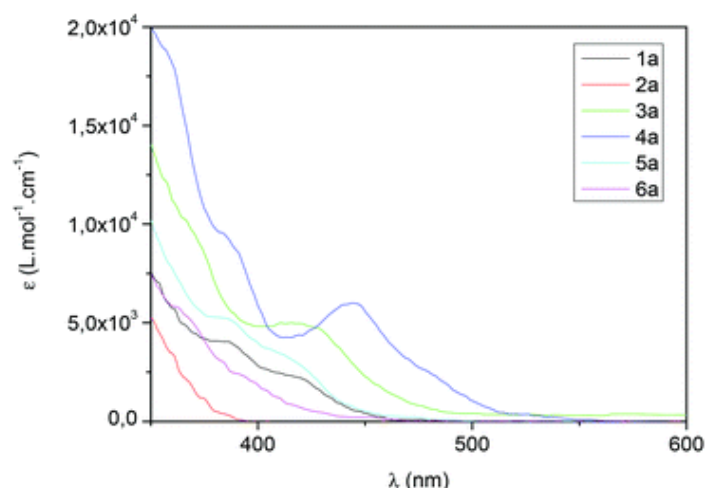


Fig. 4 Absorption spectra of $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{Hdpa})][\text{PF}_6]$ complexes.

Entry	Complex	λ/nm ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$)	Emission max (nm)
1	[Ir(ppy) ₂ (Hdpa)][PF ₆] 1a	277 (3.60)	486, 516
2	[Ir(ppy) ₂ (3-Me-Hdpa)][PF ₆] 1b	277 (4.11)	489, 517
3	[Ir(ppy) ₂ (4-Me-Hdpa)][PF ₆] 1c	276 (4.02)	489, 515
4	[Ir(ppy) ₂ (5-Me-Hdpa)][PF ₆] 1d	277 (4.11)	489, 516
5	[Ir(ppy) ₂ (dpa)] 1f	277 (3.97), 398 (1.00)	517
6	[Ir(ppz) ₂ (Hdpa)][PF ₆] 2a	254 (4.35), 315 (1.77) sh	395, 419, 439
7	[Ir(ppz) ₂ (3-Me-Hdpa)][PF ₆] 2b	252 (3.83), 315 (1.64) sh	395, 417, 441
8	[Ir(ppz) ₂ (4-Me-Hdpa)][PF ₆] 2c	254 (4.36), 310 (1.85) sh	398, 419, 447
9	[Ir(ppz) ₂ (5-Me-Hdpa)][PF ₆] 2d	255 (3.87), 322 (1.57)	396, 447
10	[Ir(ppz) ₂ (dpa)] 2f	253 (3.45), 316 (1.45) sh	427
11	[Ir(bzq) ₂ (Hdpa)][PF ₆] 3a	248 (6.04), 323 (2.37), 410 (0.50)	519, 547
12	[Ir(bzq) ₂ (3-Me-Hdpa)][PF ₆] 3b	242 (5.70), 411 (0.46)	523, 548
13	[Ir(bzq) ₂ (4-Me-Hdpa)][PF ₆] 3c	260 (6.73), 315 (3.21), 410 (0.53)	523, 553
14	[Ir(bzq) ₂ (5-Me-Hdpa)][PF ₆] 3d	259 (6.31), 322 (2.75), 411 (0.51)	521, 546
15	[Ir(piq) ₂ (Hdpa)][PF ₆] 4a	239 (5.49), 292 (4.23), 444 (0.60)	610, 639
16	[Ir(piq) ₂ (3-Me-Hdpa)][PF ₆] 4b	238 (5.51), 293 (4.25), 445 (0.53)	609, 640
17	[Ir(piq) ₂ (4-Me-Hdpa)][PF ₆] 4c	239 (5.11), 293 (3.76), 445 (0.53)	609, 635
18	[Ir(piq) ₂ (5-Me-Hdpa)][PF ₆] 4d	239 (5.40), 292 (4.06), 446 (0.58)	604, 637
19	[Ir(piq) ₂ (dpa)] 4f	238 (3.96), 293 (2.92)	628
20	[Ir(4-Me-ppy) ₂ (Hdpa)][PF ₆] 5a	262 (5.31)	482, 515
21	[Ir(2,4-F-ppy) ₂ (Hdpa)][PF ₆] 6a	254 (5.21), 305 (2.52)	457, 487

Table 2 Photophysical properties of dipyriddyamine iridium(iii) complexes

The emission spectra have also been recorded and weak emission was found between 388 and 416 nm for the iridium complexes bearing the ppz ligand (**2a–d**). More intense emissions in the visible area and wavelengths ranging from 457 to 639 nm were observed for the other C^N ligands. More precisely, complexes having a “ppy” type ligand have an emission in the blue region. For example, the emission wavelengths are in the blue region (457–487 nm) for the “2,4-F-ppy” ligand (**6a**), in the blue-green region (482–517 nm) for “ppy” (**1a–d**) and “4-Me-ppy” ligands (**5a**), in the green region (516–553 nm) for “bzq” ligands (**3a–d**), and finally in the red-orange domain for the “piq” ligand (**4a–d**, Table 2). All these emissions may be due to metal-to-ligand charge transfer (³MLCT). Moreover, for complexes **1a–d**, **2a–c**, **3a–d**, **4a–db**, **5a** and **6a**, a second maximum is also observed and is due to the vibronic transition.

The redox behaviour of these iridium complexes in acetonitrile was characterized by cyclic voltammetry (see ESI for all the CVs). Due to the presence of a NH function in the N[^]N ligand, an irreversible oxidation of the nitrogen atom was observed around 1.25 V_{SCE}. Such oxidation corresponds to previously described results for ruthenium Hdpa complexes [17]. We assume that this irreversible oxidation might be due to water traces in our solution. As depicted in Table 3 (see ESI), redox processes are reversible for complexes **1a–f**, **2a–f** and **4a–d** but not for complexes **3a–d** and **6a**. The oxidation wave (between +1.19 V and +1.30 V) corresponds to the metal centred Ir^{III/IV} process whereas the reduction wave (between –1.30 V and –1.79 V) is assigned to the ligand-based (H)dpa^{0/–} process [18]. With complexes **3**, in cyclic voltammetry, the oxidation wave was not reversible (see ESI).

Complex	$E_{1/2}$ (M ⁺ /M [*]) (V)	$E_{1/2}$ (M [*] /M [–]) (V)	$E_{1/2}$ (M ⁺ /M) (V)	$E_{1/2}$ (M/M [–]) (V)	λ max em (nm)	Emission energy (eV)
[Ir(ppy) ₂ (Hdpa)][PF ₆] 1a	–1.32	1.25	1.23	–1.30	486	2.55
[Ir(ppy) ₂ (3-Me-Hdpa)][PF ₆] 1b	–1.32	1.13	1.21	–1.40	489	2.53
[Ir(ppy) ₂ (4-Me-Hdpa)][PF ₆] 1c	–1.34	1.08	1.19	–1.45	489	2.53
[Ir(ppy) ₂ (5-Me-Hdpa)][PF ₆] 1d	–1.33	1.06	1.20	–1.47	489	2.53
Ir(ppy) ₂ (dpa) 1f	–1.18	1.05	1.22	–1.34	517	2.39
[Ir(ppz) ₂ (Hdpa)][PF ₆] 2a	–1.83	1.77	1.28	–1.34	399	3.11
[Ir(ppz) ₂ (3-Me-Hdpa)][PF ₆] 2b	–1.80	1.55	1.21	–1.46	411	3.01
[Ir(ppz) ₂ (4-Me-Hdpa)][PF ₆] 2c	–1.81	1.53	1.25	–1.53	405	3.06
[Ir(ppz) ₂ (5-Me-Hdpa)][PF ₆] 2d	–1.95	1.79	1.24	–1.40	388	3.19
Ir(ppz) ₂ (dpa) 2f	–1.60	1.58	1.30	–1.32	427	2.90
[Ir(bzq) ₂ (Hdpa)][PF ₆] 3a		0.81		–1.60	515	2.41
[Ir(bzq) ₂ (3-Me-Hdpa)][PF ₆] 3b		0.86		–1.54	516	2.40
[Ir(bzq) ₂ (4-Me-Hdpa)][PF ₆] 3c		0.64		–1.62	549	2.26
[Ir(bzq) ₂ (5-Me-Hdpa)][PF ₆] 3d		0.59		–1.79	521	2.38
[Ir(piq) ₂ (Hdpa)][PF ₆] 4a	–0.83	0.50	1.20	–1.53	610	2.03
[Ir(piq) ₂ (3-Me-Hdpa)][PF ₆] 4b	–0.85	0.43	1.19	–1.61	609	2.04
[Ir(piq) ₂ (4-Me-Hdpa)][PF ₆] 4c	–0.84	0.48	1.19	–1.55	609	2.03
[Ir(piq) ₂ (5-Me-Hdpa)][PF ₆] 4d	–0.88	0.60	1.17	–1.45	604	2.05
[Ir(4-Me-ppy) ₂ (Hdpa)][PF ₆] 5a	–1.42	1.10	1.15	–1.47	482	2.57
[Ir(2,4-F-ppy) ₂ (Hdpa)][PF ₆] 6a		1.39		–1.32	457	2.71
[Ir(ppy) ₂ (dtbbpy)][PF ₆]	–0.96	0.66	1.21	–1.51	581	2.14 ^a
[Ir(2,4-F-ppy) ₂ (dtbbpy)][PF ₆]	–0.92	0.97	1.49	–1.44		2.41 ^a

a From ref. 18b.

Table 3 Redox properties and excited state redox properties of iridium complexes

As the excited state for the iridium complexes is mainly a triplet state, the potential in the excited state can be approximated to the optic gap (energy gap) and then can be calculated from the emission wavelength (Table 3). This energy gap gives also access to the corresponding half potential $E_{1/2}$ (M⁺/M^{*}) and $E_{1/2}$ (M^{*}/M[–]).

Taking advantage of the photophysical properties of these dipyridylamine iridium complexes, we anticipated that our new iridium complexes could also have interesting photoredox catalytic activities. Photoredox chemistry is a flourishing research area and photoinduced redox processes using visible light offer a great variety of catalytic transformations useful in organic synthesis [19]. As a model reaction we chose the aza-Henry reactions between *N*-phenyl tetrahydroisoquinoline, which will be *in situ* oxidized to the corresponding iminium, and nitromethane [20]. This reaction is formally an α -alkylation of amines *via* a CH-functionalization. Catalytic activities of all our complexes will be compared with the commercially available $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]$ (dtbbpy = 4,4'-di-*tert*-butylbipyridine) [18a].

No conversion was detected in the absence of light and low conversions were observed in the absence of catalysts as already reported by Stephenson et al [20]. After a rapid screening of the reaction conditions with the commercially available complex (see ESI for a picture of the irradiation system used in this work), we found that a 0.25 M solution of *N*-phenyl tetrahydroisoquinoline (0.5 mmol) in nitromethane, in the presence of 1 mol% of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]$, under air and blue LED irradiation led to the best results and provided the alkylated product with a complete conversion within 11 h (Scheme 3). We have also highlighted practical problems encountered during the scale up. Indeed, the conversion decreased proportionately to the increase of the starting material quantities, namely conversion was twice as low starting from 1 mmol of *N*-phenyl tetrahydroisoquinoline **7**. We assume that, in batch reactions, the power of the LEDs is crucial to allow efficient processing and to retain catalytic activities more LED strips have to be used.



Scheme 3 Iridium(iii)-catalysed CH-functionalization of **7**.

We evaluated the photoredox activities of all our complexes under the mentioned optimized reaction conditions and followed the conversion rate by GC analysis (see ESI for the conversion of all complexes). First, we noted that, whatever the dipyridylamine derivatives used, these N^N ligands have a marginal impact on the reactivity, and thus slight variations of the conversion were observed (see ESI). The essential feature for the redox activity is the nature of the C^N ligand (**1–6**, Fig. 1). Low conversions (5 to 13%) were obtained with complexes **2** having a “ppz” type ligand. Such activity is in good agreement with their photophysical properties. Good to excellent catalytic activities were achieved with the other C^N ligand families, the “piq” ligand **4** providing the best results. As described in Fig. 5, $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]$ has a higher TOF than our dipyridyl-iridium complexes and the reaction is complete within 9 h. However, full conversion can be achieved with $[\text{Ir}(\text{piq})_2(\text{Hdpa})][\text{PF}_6]$ **4a** within 11 h.

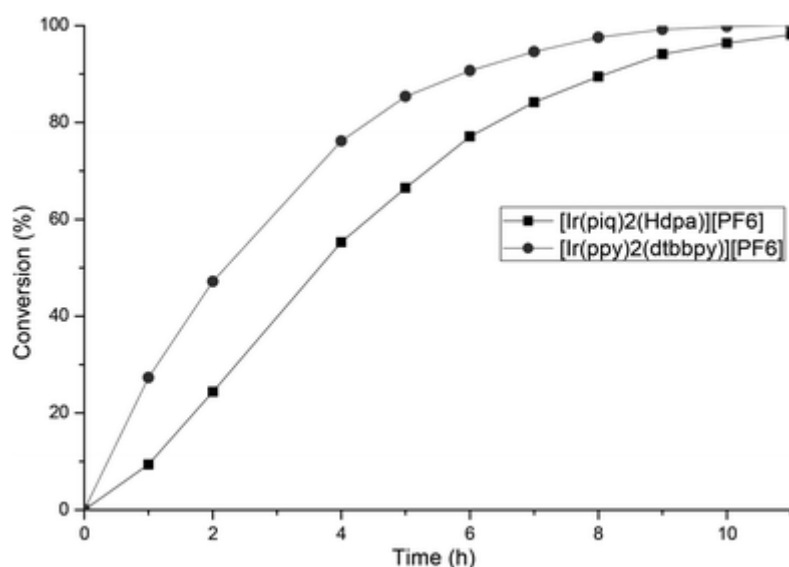


Fig. 5 Conversion of **7** into **8** followed by GC.

Finally, results of the aza-Henry reaction with seven more active complexes and [Ir(ppy)₂(dtbbpy)][PF₆] are summarized in Table 4 and it is validated that these iridium complexes are active in photoredox chemistry. The amines were isolated in moderate to high yields (49–79%). Thus, under these reaction conditions, the alkylated *N*-phenyl tetrahydroisoquinoline was isolated in 79% yield in the presence of [Ir(ppy)₂(dtbbpy)][PF₆] and in 69% yield in the presence of [Ir(piq)₂(Hdpa)][PF₆].

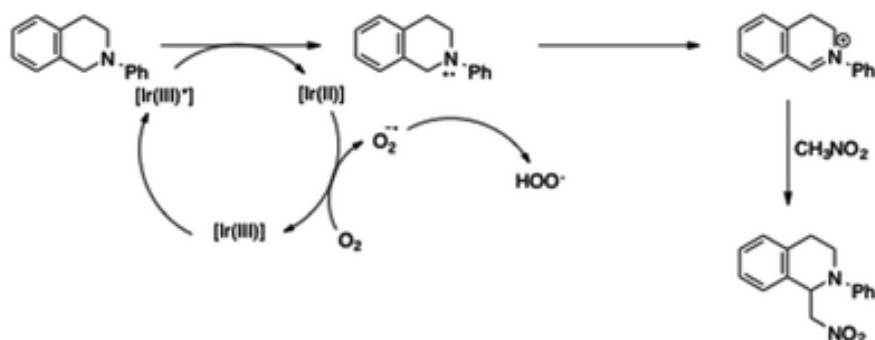
Entry	Complex	Yield ^b (%)
1	[Ir(bzq) ₂ (Hdpa)][PF ₆] 3a	49
2	[Ir(bzq) ₂ (5-Me-Hdpa)][PF ₆] 3d	56
3	[Ir(piq) ₂ (Hdpa)][PF ₆] 4a	69
4	[Ir(piq) ₂ (3-Me-Hdpa)][PF ₆] 4b	62
5	[Ir(piq) ₂ (4-Me-Hdpa)][PF ₆] 4c	60
6	[Ir(piq) ₂ (5-Me-Hdpa)][PF ₆] 4d	57
7	[Ir(piq) ₂ (dpa)] 4f	50
8	[Ir(ppy) ₂ (dtbbpy)][PF ₆]	79

^a General conditions: [Ir] (1 mol%) and **7** (52 mg, 0.25 mmol, 1 equiv.) in 1 mL of CH₃NO₂ at r.t. for 11 h.

^b Isolated yields.

Table 4 Iridium(III)-catalysed CH-functionalization of **7**^a

Stephenson et al. have proposed a catalytic cycle for this transformation (Scheme 4) [20]. Reductive quenching of the excited state of the iridium complex forms the amine radical cation. The powerful reducing iridium(II) complex may then reduce oxygen to the corresponding radical anion. Finally, the iminium ion is produced by hydrogen abstraction from the ammonium radical. Addition of nitromethane to the iminium led to the alkylated amine.



Scheme 4 Mechanism proposed by Stephenson for the iridium(III)-catalysed CH-functionalization of **7**.

Oxidation of the amine (or reduction of the excited iridium complex) is the crucial step in this catalytic cycle. As a consequence, the half potential $E_{1/2}$ (M^*/M) must be lower than $E_{1/2}$ (R_3N^+/R_3N) (for the tetrahydroisoquinoline, $E_{1/2} = 0.93$ V) to enable the overall amine alkylation. Then, the mechanism and the potentials in Table 3 clearly explain the absence of reactivity when iridium complexes **3**, bearing a phenylpyrazole ligand, are used. Conversely, complexes **3d** and **4**, which have a half potential in reduction in the same range as the half potential of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]$, led to similar catalytic activities and afforded the amine with the highest yields. These simple results clearly demonstrate the correlations between the photophysical properties of the iridium complexes and their catalytic activities in photoredox reactions.

Conclusion

In conclusion, two new series of neutral and cationic iridium complexes bearing dipyritylamine derivatives as N[^]N ligands have been synthesized and fully characterized. Almost 20 different complexes have been prepared with generally good yields. Absorption and emission properties of this series of complexes have also been reported and shown that some complexes exhibit absorption in the visible region corresponding to the blue area, depending on the C[^]N ligand. Their evaluation for photoredox reaction has been performed and compared with commercially available $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]$. These new complexes bearing Hdpa motifs presented interesting catalytic activities and may compete with known iridium complexes. Furthermore, these results open now some new perspectives in photoredox organic transformations using supported iridium catalysts. These studies are now ongoing in our laboratories.

Acknowledgements

This work was supported by the “Ministère de la Recherche et des Nouvelles Technologies”, CNRS (Centre National de la Recherche Scientifique). The LABEX SynOrg (ANR-11-LABX-0029) is acknowledged for a PhD grant (E.S.). The authors thank the “Agence Nationale de la Recherche”, within the CSOSG program (ANR-12-SECU-0002), and the “Région Basse-Normandie” for their funding (R.M., F.S. and A.G.).

References

1. R. Guillard and K. M. Kadish, *Chem. Rev.*, 1988, **88**, 1121
2. R. van Asselt, E. Rijnberg and C. J. Elsevier, *Organometallics*, 1994, **13**, 706.
3. P. K. Byers, A. J. Canty, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1986, 1722.

4. W. de Graaf, J. Boersma, W. J. J. Smeets, A. L. Spek and G. van Koten, *Organometallics*, 1989, **8**, 2907.
5. J. Canty *Acc. Chem. Res.*, 1992, **25**, 83.
6. D. G. Brown, P. K. Byers and A. J. Canty, *Organometallics*, 1990, **9**, 1231.
7.
 - (a) M. E. Wright, S. A. Svejda, M. J. Jin and M. A. Peterson, *Organometallics*, 1990, **9**, 136.
 - (b) G. Chelucci, S. Chessa and G. Orrù, *J. Mol. Catal. A*, 2004, **220**, 145.
 - (c) J. Gil-Moltó and C. Nájera, *Eur. J. Org. Chem.*, 2005, 4073.
 - (d) H.-L. Kwong, L.-S. Cheng, W.-S. Lee, W.-L. Wong and W.-T. Wing, *Eur. J. Inorg. Chem.*, 2000, 1997.
 - (e) H. S. Scott, T. M. Ross, N. F. Chilton, I. A. Gass, B. Moubaraki, G. Chastanet, N. Paradis, J.-F. Létard, K. R. Vignesh, G. Rajaraman, S. R. Batten and K. S. Murray, *Dalton Trans.*, 2013, **42**, 16494.
8. S. Gaillard, M. K. Elmekdem, C. Fischmeister, C. M. Thomas and J.-L. Renaud, *Tetrahedron Lett.*, 2008, **49**, 3471.
9.
 - (a) Z. Zheng, M. K. Elmekdem, C. Fischmeister, T. Roisnel, C. M. Thomas, J.-F. Carpentier and J.-L. Renaud, *New J. Chem.*, 2008, **32**, 2150.
 - (b) C. Romain, S. Gaillard, M. K. Elmekdem, L. Toupet, C. Fischmeister, C. M. Thomas and J.-L. Renaud, *Organometallics*, 2010, **29**, 1992.
10.
 - (a) F. Sinner, M. R. Buchmeiser, R. Tessadri, M. Mupa, K. Wurst and G. K. Bonn, *J. Am. Chem. Soc.*, 1998, **120**, 2790.
 - (b) R. Kröll, C. Eschbaumer, U. S. Schuber, M. R. Buchmeiser and K. Wurst, *Macromol. Chem. Phys.*, 2001, **202**, 645.
11.
 - (a) J. Ni, K.-J. Wei, Y. Min, Y. Chen, S. Zhan, D. Li and Y. Liu, *Dalton Trans.*, 2012, **41**, 5280.
 - (b) Y. Xie, Y. Ding, C. Wang, J. P. Hill, K. Ariga, W. Zhang and W. Zhu, *Chem. Commun.*, 2012, **48**, 11513.
 - (c) S. Martić, G. Wu and S. Wang, *Inorg. Chem.*, 2008, **47**, 8315.
12.
 - (a) Q.-D. Liu, W.-L. Jia, G. Wu and S. Wang, *Organometallics*, 2003, **22**, 3781.
 - (b) J. Lee, Q.-D. Liu, M. Motala, J. Dane, J. Gao, Y. Kang and S. Wang, *Chem. Mater.*, 2004, **16**, 1869.
 - (c) D.-R. Bai and S. Wang, *Organometallics*, 2006, **25**, 1517.
 - (d) R. Tan, Z.-B. Wang, Y. Li, D. J. Kozera, Z.-H. Lu and D. Song, *Inorg. Chem.*, 2012, **51**, 7039.
13. K. Nonoyama *Bull. Chem. Soc. Jpn.*, 1974, **47**, 467.
14.
 - (a) S. Wagaw and S. L. Buchwald, *J. Org. Chem.*, 1996, **61**, 7240.
 - (b) M.-H. Yang, C.-C. Chou, H.-C. Lee, G.-H. Lee, M.-K. Leung and S.-M. Peng, *Chem. Commun.*, 1997, 2279.
15. Q. Zhao, S. Liu, M. Shi, C. Wang, M. Yu, L. Li, T. Yi and C. Huang, *Inorg. Chem.*, 2006, **45**, 6152.
16. H. Ben Ammar, J. Le Nôtre, M. Salem, M. T. Kaddachi and P. H. Dixneuf, *J. Organomet. Chem.*, 2002, **662**, 63.
17. D. E. Morris, Y. Ohsawa, D. P. Segers, M. K. DeArmond and K. W. Hanck, *Inorg. Chem.*, 1984, **23**, 3010.

18. (a) J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard and G. Malliaras, *J. Am. Chem. Soc.*, 2004, **126**, 2763.
(b) M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal Jr., G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712.
19. For recent reviews, see:
(a) D. M. Schultz and T. P. Yoon, *Science*, 2014, **343**, 985.
(b) C. K. Prier, D. A. Rankic and D. W. C. Mac Millan, *Chem. Rev.*, 2013, **113**, 5322.
(c) M. Reckenthäler and A. G. Griesbeck, *Adv. Synth. Catal.*, 2013, **355**, 2727.
(d) J. Hu, J. Wang, T. H. Nguyen and N. Zheng Beilstein, *J. Org. Chem.*, 2013, **9**, 1977.
20. G. Condie, J. C. González-Gómez and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2010, **132**, 1464