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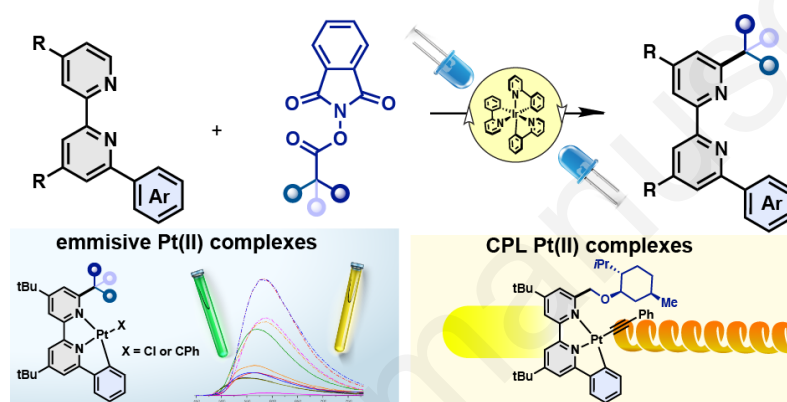
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# Access to functionalized luminescent Pt(II) complexes by photoredox-catalyzed Minisci alkylation of 6-aryl-2,2'-bipyridines

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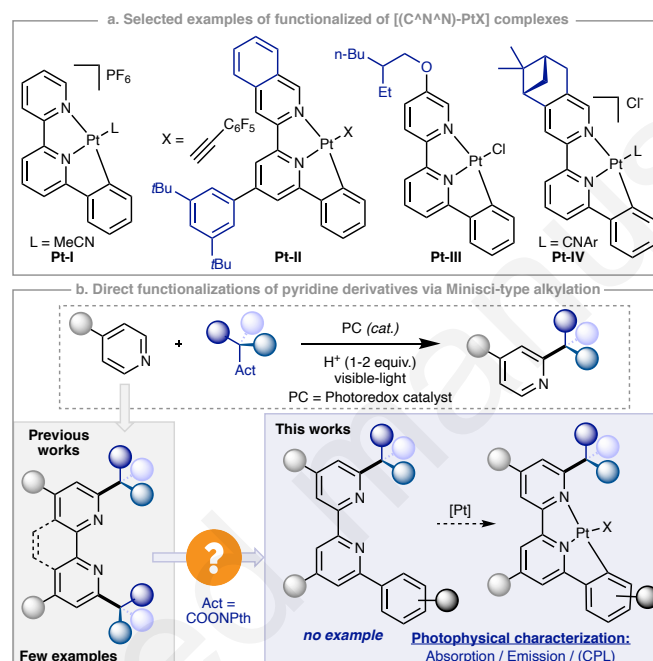
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Photoredox-mediated C–H bond alkylation of 6-aryl-2,2'-bipyridines with *N*-(acyloxy)phthalimides is reported. The reaction exhibits an excellent functional group tolerance, including chiral aliphatic groups. The influence of the incorporated C6'-alkyl group on the photophysical properties of the corresponding (N<sup>^</sup>N<sup>^</sup>C) cyclometalated Pt(II) complexes is described, including chiroptical properties.

Since the pioneering work by Constable, Tocher, and others in the 90s, Pt(II) complexes featuring 6-(phenyl)-2,2'-bipyridine (Phbpy) as cyclometalated ligands (Fig. 1a, **Pt-I**)<sup>1</sup> have become a privileged organometallic in material sciences owing to their remarkable luminescent properties.<sup>2</sup> Considerable efforts were devoted to improve, tune the luminescence properties or combine with other optical features by designing new functionalized Phbpy proligands. For instance, Che *et al.* reported the **Pt-II** complex bearing 3,5-ditertbutylphenyl on the central pyridine ring and isoquinoline which displayed almost quantitative photoluminescence quantum yield and is a competitive photoredox catalyst, dopant in OLEDs or two-photon-excited cellular bioimaging (Fig. 1a).<sup>3</sup> The introduction of an ether aliphatic side chain on a pyridine ring limits

aggregation of the **Pt-III** complex (Fig. 1a).<sup>4</sup> The synthesis of a Phbpy bearing a chiral substituent, such as pinene-fused pyridine, allowed preparing the **Pt-IV** complex which gives rise to polarized luminescence, appealing for applications in photonic devices, such as LED, optical amplifiers, and optical information (Fig. 1a).<sup>5</sup> The access to tailorable luminescence properties Pt complexes for application in materials sciences is predicated on synthesizing novel functionalized ligands. The development of last-stage modification of Arbpy ligands *via* regioselective C–H bond functionalization could enable the fast preparation of on-demand functionalized  $[(C^{\wedge}N^{\wedge}N)-Pt]^+$  complexes.



**Figure 1.** Examples of  $[(C^{\wedge}N^{\wedge}N)-PtX]$  and our strategy to functionalize  $C^{\wedge}N^{\wedge}N$  pro-ligands

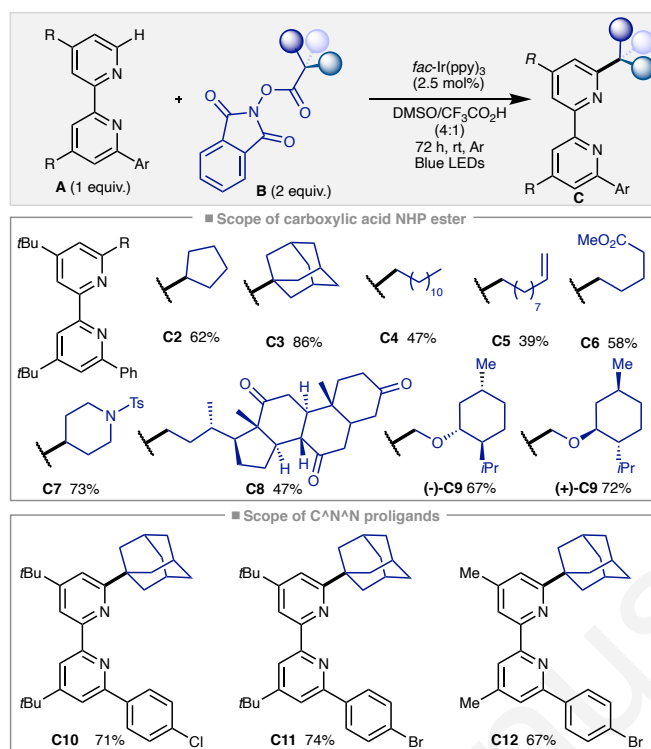
Photoredox-catalyzed Minisci-type alkylation is an ideal method to functionalize *para*-substituted pyridines at the C2-position (Fig. 2b).<sup>6</sup> Although a few examples of direct alkylation of bipyridines were reported (Fig. 1b, grey box),<sup>7</sup> surprisingly, these protocols were never applied to Arbpy. In fact, their functionalizations in the presence of organometallics remains challenging owing to the possible cyclometalated ligand scrambling which can switch off the catalyst activity. Herein, we report our efforts in Minisci-type alkylation reaction of Arbpy for the synthesis of functionalized  $C^{\wedge}N^{\wedge}N$  proligands including some holding chiral substituents. The alkyl substituent's effects on luminescent properties of corresponding  $[(C^{\wedge}N^{\wedge}N)-Pt]^+$  complexes including chiroptical features were also investigated (Fig. 2a, blue box).

We began by reacting 4,4'-di-*tert*-butyl-6-phenyl-2,2'-bipyridine (**A1**) with cyclohexanecarboxylic acid NHP [= *N*-hydroxyphthalimide] ester (**B1**) (Table 1). The optimized conditions [*i.e.*, 2.5 mol% *fac*-Ir(ppy)<sub>3</sub>, DMSO – TFA (4:1) as the solvent mixture and blue light irradiation over 72 h] afford **C1** in 67% yield (entry 1). The alkylation reaction exclusively occurs at the C6'-position. No reaction occurred without catalyst or using another Ir complexes with lower excited state reduction potentials<sup>7c</sup> while a significant lowering in yield was observed with [Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (entries 2-5). TFA, in excess, is required to protonate both bipyridine and NHP ester (entries 6 and 7). As explained by Opatz *et al.*, acid induces the protonation of the pyridine lowering the LUMO's energy facilitating the radical addition.<sup>8</sup> Interestingly, the co-solvent markedly influenced the reactivity profile; indeed, only trace amounts of **C1** were obtained in DMA or CH<sub>3</sub>CN (entry 8 and 9). A lower reaction time gives a 20 % loss of yield (entry 10). Other alkyl radical sources such as carboxylic acids associated with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or oxalate salts displayed no or lower reactivity (entries 11 and 12).

**Table 1.** Optimization of the reaction conditions

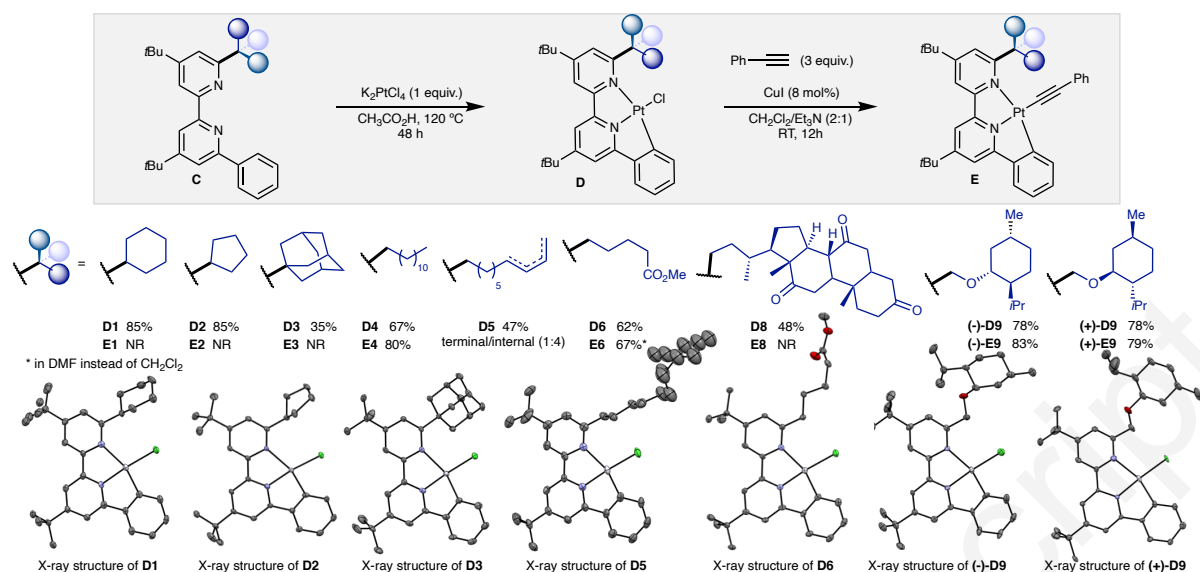
Entry	Deviation from above conditions	Yield in <b>C1</b>
1	—	67%
2	No photocatalyst	0%
3	[Ir(ppy) <sub>2</sub> (dtbbpy)][PF <sub>6</sub> ]	0%
4	[Ir(dF{CF <sub>3</sub> }ppy) <sub>2</sub> (dtbbpy)][PF <sub>6</sub> ]	0%
5	[Ru(bpy) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	40%
6	in DMSO	0%
7	in DMSO/TFA (8:1)	56%
8	in DMA/TFA (4:1)	5%
9	in CH <sub>3</sub> CN/TFA (4:1)	12%
10	48 h	55%
11	Using CyCO <sub>2</sub> H, (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> instead of <b>B1</b>	0%
12	Using CyOCOCO <sub>2</sub> Cs, (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> instead of <b>B1</b>	21%

With these conditions in hand, we turned our attention to the scope of the reaction (Scheme 1). Firstly, we investigated the reactivity of redox-active esters. The cyclopentyl group was linked to the bipyridine to afford **C2** in a 62% yield. More sterically demanding adamantane-1-carboxylic acid NHP ester also underwent Minisci coupling with **A1** to afford the C6'-alkylated bipyridine **C3** in 86% yield. From tridecanoic acid NHP ester, the C6'-lauryl substituted bipyridine **C4** was isolated in 47% yield. The reaction is not limited to the introduction of unfunctionalized alkyl groups. Undec-10-enoic acid NHP-ester reacted to afford the proligand **C5** in 39% yield; and from 6-methoxy-6-oxohexanoic acid NHP ester **1**, the C6'-alkylated bipyridine **C6** was obtained in 58% yield. Interestingly, alkene and ester groups remain intact, which could afford further post-modifications for immobilization strategies or to introduce biomolecules for designing organometallic probes. The bipyridine **C7** bearing 1-tosylpiperidine was prepared in 73% yield. Densely functionalized dehydrocholic acid NHP ester derived from naturally occurring and bioactive chiral acid feedstocks was also usefully employed providing **C8** in 47%. Both enantiopure (-)- and (+)-menthyloxyacetic acid NHP ester underwent Minisci-alkylation affording the ether-substituted proligands (-)- and (+)-**C9** in good yields, without epimerization. Finally, we investigated the reactivity of 6-aryl-2,2'-bipyridines, which have been easily prepared using our previous conditions.<sup>9</sup> 4,4'-Di-tert-butyl- (or dimethyl)-2,2'-bipyridine substituted by 4-bromophenyl or 4-chlorophenyl at C6 position was alkylated at C6' position using adamantane-1-carboxylic acid NHP ester to give **C10-C12** in 69-74% yields. Interestingly, the C-halo bonds (Cl, Br) remain during the alkylation reaction allowing further post-functionalizations. However, this methodology is limited to 6-aryl-2,2'-bipyridines holding 4,4' substituents to increase the solubility and avoid the formation other regioisomers.



**Scheme 1.** Scope of photoredox-catalyzed C-H bond alkylation of 6-aryl-2,2'-bipyridines

Then, we prepared the corresponding  $[(\text{C}^{\text{N}}\text{N})\text{-PtCl}]$  complexes **D1-D6**, **D8**, (-) and (+)-**D9** via a reported procedure<sup>4</sup> by reaction of the corresponding prolignand with  $\text{K}_2\text{PtCl}_4$  in boiling acetic acid (Scheme 2). The lowest yield was observed with the adamantyl-substituted **C3** prolignand. From **C5**, the complex **D5** was isolated in 47% yield, albeit double-bond isomerization of the olefin part occurred, leading to a complex mixture of regioisomers. Chain walking is often promoted by the Pt(II) complex.<sup>10</sup> In the X-ray structures of **D1**, **D2**, **D5**, **D6**, (-) and (+)-**D9**, the Pt atom resides in a distorted square planar geometry that is comparable to those found for previously reported  $[(\text{C}^{\text{N}}\text{N})\text{-PtCl}]$  derivatives. The structure of **D3** displays a strong pyramidalization of the pyridine ring bearing the adamantyl group. Strong steric repulsions might explain this conformational strain between the chloro ligand and the adamantyl C-H bond (Table S1 for crystal data and selected bond lengths and angles).



**Scheme 2.** Preparation of tridentate cyclometalated platinum(II) complexes containing chloro or  $\sigma$ -alkynyl auxiliaries and their X-ray structures

The photophysical properties of the Pt(II) complexes **D** have been investigated in solution by means of UV-visible absorption and luminescence spectroscopies. The steady-state absorption and luminescence spectra of complexes **D1-6**, **8**, **(-)** and **(+)-D9** are presented in Fig. S1, and the related data are summarized in Table S2. They all display similar absorption spectral features with a set of intense absorption bands in the UV region, from 250 to 370 nm, assigned to ligand centered  $^1(\pi-\pi^*)$  transition ( $^1LC$ ) of the functionalized ( $N^N^C$ ) ligands. Moderately intense absorption bands in the visible part of the spectra, from 380 to 470 nm, are attributed to metal-to-ligand charge transfer  $d(Pt) \rightarrow \pi^*(N^N^C)$  ( $^1MLCT$ ) in accordance with reported congeners.<sup>11</sup> **D3** bearing a bulky adamantyl substituent shows slightly blue-shifted absorption bands from 300 to 470 nm imputed to the distorted square planar structure (Fig. S1, inset). All **D** complexes exhibit room-temperature phosphorescence with broad spectral shape typical of excited state originated from MLCT and LMCT transitions (Fig. S1).<sup>12</sup> The low photoluminescence quantum yields ranging from 1 to 6 % are in line with those previously observed owing to deactivation pathways through the population of the d-d excited states.<sup>12</sup> In contrast, **D3** is luminescent silent certainly due to the strong distortion of the  $N^N^C$  ligand by the bulky adamantyl substituent, that may produces additional vibrational deactivation pathways. Interestingly, the introduction of an alkyl group at the C6'-position of the Arbp<sub>y</sub> ligand does not degrade the standard photophysical properties of chloro Pt(II) complexes, including those containing

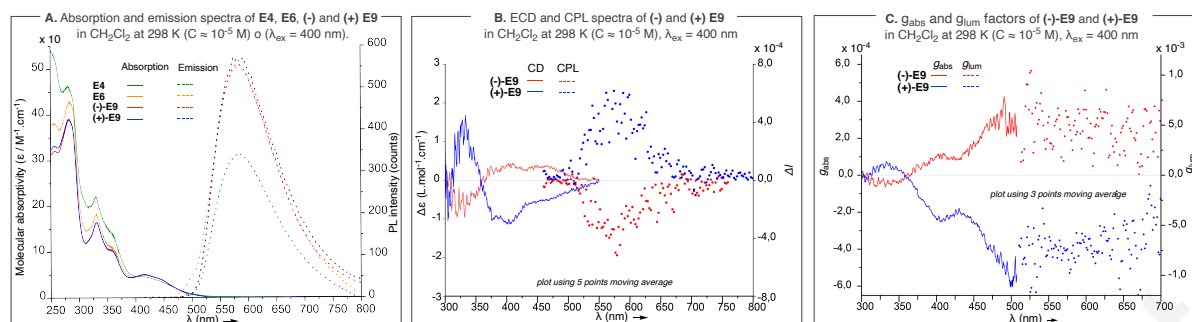
functional groups such as ester or alkene, opening the door to anchor Pt complexes onto surface or link to biomolecules. All **D** complexes were engaged in Sonogashira's conditions with phenylacetylene (Scheme 2). The C6'-alkyl group of the N<sup>^</sup>N<sup>^</sup>C ligand alters the reactivity. The alkynyl complexes **E4**, **E6**, (-) and (+)-**E9** were isolated, in moderate to good yields, while no reactivity was observed with the other complexes, ascribed to hampered insertion by the bulky alkyl groups. The photophysical properties of the **E** complexes were similarly studied (Fig. 2a and Table 2). The electronic absorption spectra of **E4**, **E6**, (-) and (+)-**E9** consist of two groups of electronic transitions, with intense absorption bands below 400 nm, attributed to  $\pi$ - $\pi^*$  transitions, and broad low-energy bands from 400 up to 490 nm, assigned to charge transfer transitions (MLCT and LLCT).<sup>12</sup> Their luminescence intensities have been significantly enhanced compared to their chloro-analogs, with photoluminescence quantum yields of about 15%. The relatively long luminescence lifetimes of half-microsecond are typical of <sup>3</sup>MLCT excited states (Fig. S3, Tables 2 and S3). The chiroptical properties of complexes (-) and (+)-**E9** have been investigated through electronic circular dichroism (ECD) and circularly polarized luminescence (CPL) (Fig. 2b). The chiroptical activities are lower than those observed for Pt(II) complexes in which the chiral unit is fused with the cyclometalated ligands<sup>13</sup> or arise from helicene ligands.<sup>14</sup> The (-)-**E9** ECD spectrum shows a positive band below 350 nm and negative bands tailing up to 550 nm. These signals correspond to intra-ligand (IL) and MLCT-LLCT transitions. There is a relatively high contribution to the rotatory strength of the lowest excited-states (MLCT-LLCT transitions). (+)-**E9** has nearly a mirror-image ECD spectrum with opposite Cotton-effects. The dissymmetry factors  $g_{\text{abs}}$  ( $g_{\text{abs}} = \Delta\epsilon/\epsilon$ ) for (-)-**E9** and (+)-**E9** are of about  $5 \times 10^{-4}$  at 500 nm, region of MLCT-LLCT transitions (Fig. 3c), one order of magnitude lower than other reported chiral (C<sup>^</sup>N<sup>^</sup>N)Pt(II).<sup>13a, 13b, 14</sup>

**Table 2.** Absorption and emission data for **E4**, **E6** (-)- and (+)-**E9**.

	$\lambda_{\text{abs}}^{\text{a}}$ / nm ( $\epsilon$ $10^{-3}$ / M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{\text{em}}^{\text{b}}$ / nm ( $\tau/\mu\text{s}$ ; $\Phi^{\text{c}}$
<b>E4</b>	280 (46.0), 329 (21.8), 360 (13.5), 418 (4.4)	584 (0.47; 0.10)
<b>E6</b>	282 (42.5), 331 (18.0), 361 (10.6), 420 (4.3)	584 (0.46; 0.17)
(-)- <b>E9</b>	285 (38.7), 333 (16.1), 363 (9.7), 419 (5.0)	584 (0.52; 0.15)
(+)- <b>E9</b>	285 (38.7), 333 (16.1), 363 (9.7), 419 (5.0)	584 (0.54; 0.15)

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K ( $C \approx 10^{-5}$  M). <sup>b</sup> In degassed CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K ( $C \approx 10^{-5}$  M). <sup>c</sup> With Ru(bpy)<sub>3</sub>Cl<sub>2</sub> as reference





**Figure. 2.** Photophysical data of for platinum alkynyl complexes **E4**, **E6** (-) and (+)-**E9**

Interestingly, the excited states of (-)- and (+)-**E9** also display optical activities, evidenced by the CPL spectra (Fig. 2b). The CPL spectrum of (-)-**E9** appears mirror-image of its enantiomer (+)-**E9**. The maximum emission is around 570 nm, similar to those observed in non-polarized steady-state luminescence. While the CPL anisotropies of (-)- and (+)-**E9** are observable, their dissymmetry factors  $g_{lum}$  ( $g_{lum} = 2\Delta I(\lambda)/I(\lambda)$ ) remained rather low with values of about  $-5 \times 10^{-4}$  and  $5 \times 10^{-4}$  over the whole emission bands, respectively (Fig. 2c).

In summary, a mild and straightforward protocol for the synthesis of diverse 6'-alkyl-6-aryl-2,2'-bipyridines with good to excellent yields and broad functional group tolerance was developed using visible-light-induced C–H bond alkylation using (redox-activated) carboxylic acids as cheap and abundant alkyl radical precursors. Adamantyl aside, modification of bipyridine C6'-position through a methylene connexion does not perturb the electronic levels of luminescent Pt(II) complexes, while allowing anchoring functionalities or modifying the physical properties. This method enables the introduction of chiral group onto bipyridine scaffold, which after coordination led to Pt(II) complexes with CPL emission. Although  $g$  values remain low, it is the first time to observe Pt(II) chiroptic properties thanks to a chiral substituent placed at a remote position of the Pt center and which is not involved in the MLCT or LLCT processes (no modification of absorption/emission properties). This late-stage modification strategy lays a fundamental change in the ligand design for the search of better materials.

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## Conflicts of interest

There are no conflicts to declare.

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