

# Electronically Divergent Triscyclometalated Iridium(III) 2-(1-naphthyl)pyridine Complexes and Their Application in Three-Component Methoxytrifluoromethylation of Styrene

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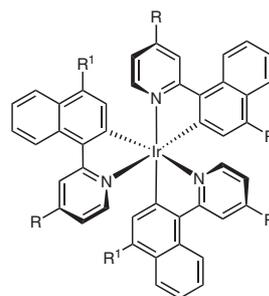
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- C1 R = H, R<sup>1</sup> = H
- C2 R = OCH<sub>3</sub>, R<sup>1</sup> = H
- C3 R = CF<sub>3</sub>, R<sup>1</sup> = H
- C4 R = CH<sub>3</sub>, R<sup>1</sup> = H
- C5 R = CH<sub>3</sub>, R<sup>1</sup> = CH<sub>3</sub>
- C6 R = H, R<sup>1</sup> = CH<sub>3</sub>

- ✓ Synthesis
- ✓ Photophysical properties
- ✓ Electrochemistry
- ✓ Photoredox catalysis

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**Abstract** A systematic study of the photophysical and electrochemical properties of triscyclometalated homoleptic iridium(III) complexes based on 2-(1-naphthyl)pyridine (npy) ligands is presented. A systematic investigation of ligand substitution patterns showed an influence on the lifetime of the excited state, with slight changes in the absorption and emission spectral features. Specifically, the emission lifetime of a complex of an npy ligand substituted with a strongly electron-withdrawing trifluoromethyl group was longer than that of the corresponding complex with the electronically nonperturbed ligand (3.7  $\mu$ s versus 1.5  $\mu$ s). Electronically complementary ligands and complexes with orthogonal configurations showed slightly shorter excited state lifetimes compared with unsubstituted npy (1.4–3.0  $\mu$ s). All complexes displayed reversible or quasireversible redox-couple processes, with the complex of the trifluoromethylated ligand showing the highest ground-state oxidation potential  $E_{1/2}^{\text{ox}}$  [Ir(III)/Ir(IV) = 0.95 V vs. SCE in CH<sub>2</sub>Cl<sub>2</sub>]. This study showed that these complexes can be used as efficient photoredox catalysts, as demonstrated by their application in a regioselective methoxytrifluoromethylation in which the npy complexes showed equal or better performance compared with the archetypical photoredox catalyst tris[2-phenylpyridinato]iridium(III).

**Key words** photoredox catalysis, iridium catalysis, oxytrifluoromethylation, styrene, naphthylpyridines, ligands

In recent years, the luminescent properties of triscyclometalated Ir(III) complexes have been utilized in the development of light-emitting diodes,<sup>2,3</sup> dye-sensitized solar cells,<sup>4</sup> biological labels, and therapeutics<sup>5–7</sup>, as well as in sensor technology<sup>8,9</sup> and the emerging field of photoredox



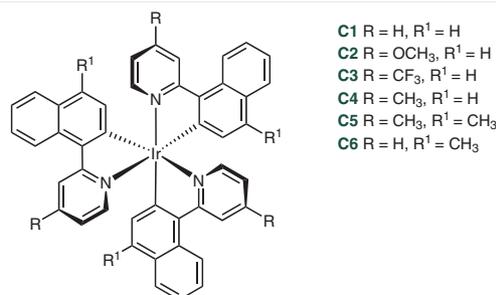
**Carl-Johan Wallentin** initiated his academic career 2004 as a PhD student at Lund University (Sweden) under the directions of Prof. Kenneth Wärnmark. The main efforts during his time as a PhD student focused on various aspects of supramolecular chemistry, with particular emphasis on hydrogen bonding and its utilization in the construction of discrete molecular aggregates. In 2011 he joined the research group of Prof. Corey Stephenson, at that time at Boston University (USA), to explore the upcoming field of photoredox catalysis. Thereafter, he joined the Department of Chemistry and Molecular Biology at Gothenburg University to establish his own group active within the fields of method development and sustainable chemistry. Most recently his efforts have been focusing on the engagement of carboxylic acids in alkene difunctionalization, initiated by visible-light mediated generation of transient acyl radical intermediates.

catalysis.<sup>2,10–13</sup> The ground- and excited-state physicochemical properties (i.e. redox-, absorption- and emission characteristics) of these complexes can be fine-tuned through careful ligand design.<sup>14–16</sup> Modifications of the ligands can affect the energy of the low-lying emissive triplet excited states such as the <sup>3</sup>MLCT and <sup>3</sup> $\pi$ - $\pi$  (3LC) states<sup>17</sup> by influencing the HOMO–LUMO energy gap. The effects of such modifications are usually difficult to predict, but electron-withdrawing groups have been reported to decrease the energy of the HOMO by increasing  $\pi$ -backdonation.<sup>18</sup> Conversely, electron-donating groups have the opposite effect. Inductive and mesomeric effects can also give rise to different behaviors and, thus, fluoro and trifluoromethyl substituents have been reported to influence the HOMO–LUMO energy gaps in different ways.<sup>9</sup> Ir(III) metal centers have a strong spin–orbit coupling, which results in a rapid inter-system crossing, producing a long-lived lower-energy triplet state<sup>17</sup> that shows enhanced redox abilities compared with the ground state. Notably, Ir(III) complexes have increased ligand-field-stabilization energies compared with their Ru(II) counterparts, providing them with broader and more-precise redox-tuning opportunities.<sup>15</sup>

Lately, there has been a growing demand for Ir(III) complex sensitizers that can efficiently utilize solar or artificial low-energy light sources. Intensive efforts have been devoted to identifying and developing complexes that have strong absorption bands in the visible region of the electromagnetic spectrum.<sup>19</sup> To this end, homoleptic tris-C,N iridium complexes have been widely investigated, and these efforts have primarily focused on the prototypical 2-phenylpyridine (ppy) ligand.<sup>16</sup> Although more-conjugated 2-(1-naphthyl)pyridine (npy) ligands show promising properties,<sup>20</sup> they remain underexplored.

An especially prominent utilization of visible light is in photoredox catalysis, an emerging tool for organic transformations.<sup>21,22</sup> Typically, these transformations are triggered by excitation of a photoredox-active catalyst that subsequently mediates single-electron-transfer (SET)-based processes. Photoredox catalysts have various inherent limitations stemming from their short lifetimes and the restricted redox windows defined by their corresponding excited states. Consequently, to realize the potential of photoredox catalysis fully, new catalysts addressing these shortcomings need to be developed.

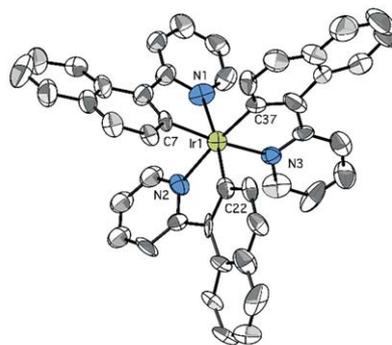
Here, we report the synthesis and the complete characterization of a new family of triscyclometalated Ir(III) complexes, Ir(npy)<sub>3</sub>, in which 2(1-naphthyl)pyridine ligand is substituted by electron-donating methyl or methoxy groups (Figure 1; **C2**, **C4–6**) or with an electron-withdraw-



**Figure 1** Chemical structures of the Ir(III) complexes **C1–6**

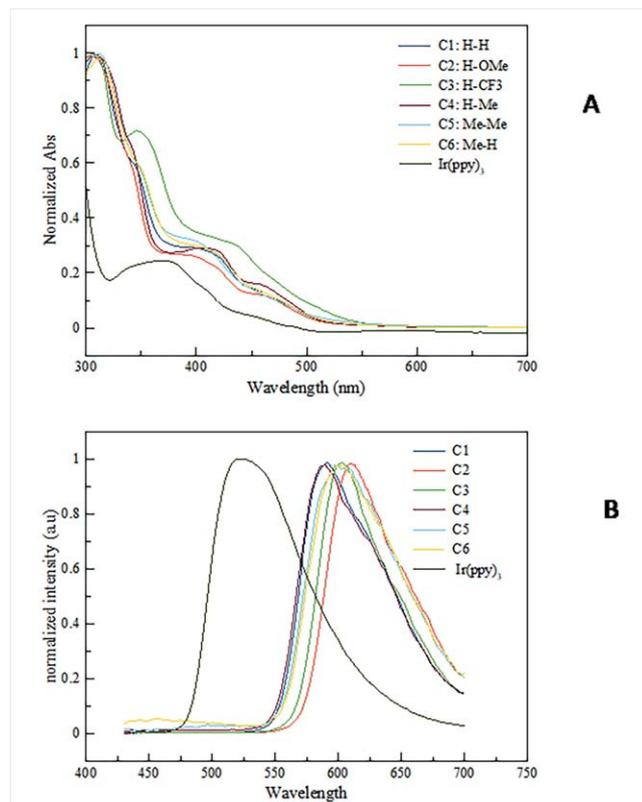
ing trifluoromethyl group (**C3**), together with the application of these complexes in the methoxytrifluoromethylation of styrene.

The ligands for complexes **C1–6** were synthesized by Suzuki–Miyaura cross-coupling of the appropriate 2-bromopyridine and a small excess (1.1 equiv) of the corresponding commercially available naphthylboronic acid.<sup>23</sup> The ligands were isolated in excellent yields (>90%). The desired homoleptic triscyclometalated complexes **C1–6** were then synthesized in one step by a slightly modified version of the reported procedure,<sup>9</sup> which provided the complexes in moderate yields (39–50%).<sup>24</sup> In general, complexes **C1–6** are air-stable up to 300 °C and show good solubility in both polar and nonpolar solvents. The complexes were characterized by means of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, HRMS, elemental analysis and, in the case of complex **C1**, x-ray diffraction (Figure 2).<sup>25</sup> The <sup>1</sup>H NMR spectra of **C1–6** exhibited well-resolved peaks consistent with the facial configuration. The x-ray analysis of complex **C1** confirmed its structural assignment, including the facial configuration. Thus, complex **C1** is C<sub>3</sub>-symmetric with a pseudooctahedral geometry.



**Figure 2** Molecular structure of complex **C1** at the 50 % probability level.<sup>25</sup> Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles: Ir–N1 = 2.088(12), Ir–N2 = 2.135(11), Ir–N3 = 2.128(11), Ir–C7 = 2.035(12), Ir–C22 = 2.002(17), Ir–C37 = 2.038(13), N1–Ir–N2 = 96.7(5)°, N1–Ir–N3 = 95.8(5)°, N2–Ir–N3 = 99.0(4)°.

The UV-vis absorption [Figure 3(A)] and photoluminescence (PL) spectra [Figure 3(B)] for complexes **C1–6** were measured as solutions in  $\text{CH}_2\text{Cl}_2$  at room temperature (Table 1). All the complexes exhibited similar spectral features; this is fully consistent with the structural similarities of the ligands. All complexes exhibited intense UV absorption bands below 350 nm that were assigned to the spin-allowed ligand-centered  $^1\pi-\pi^*$  transition. This agrees with the absorption features observed for the free ligands, which did not show any distinctive absorptions at longer wavelengths. Absorption bands observed in the 350–400 nm range were ascribed to a typical spin-allowed metal-to-ligand charge-transfer transition ( $^1\text{MLCT}$ ), in which an electron is promoted from a metal d orbital to the vacant  $\pi^*$  orbital on one of the ligands. The absorption observed above 400 nm with minimal molar extinction coefficients ( $10\text{--}100\text{ M}^{-1}\cdot\text{cm}^{-1}$ ) could be attributed to both spin-orbit-coupling-enhanced  $^3\pi-\pi^*$  and  $^3\text{MLCT}$  transitions.<sup>26</sup> Complex **C3** exhibits a red shift in its absorption band despite the expected stabilization of the HOMO. This is opposite to previous observations.<sup>27</sup> The MLCT transitions can be viewed as photoinduced charge separations in which the metal center is oxidized and the ligand is reduced. Typically, these excited species show enhanced redox potentials compared with their ground states, a property that can be utilized in photoredox-catalyzed transformations.<sup>26,28</sup>



**Figure 3** (A) UV-VIS Absorption and (B) photoluminescence spectra of **C1–6** in  $\text{CH}_2\text{Cl}_2$  at room temperature

The complexes exhibited strong orange-red photoluminescence (588–610 nm) upon excitation at 400 nm [Figure 3(B)]. The broad and structureless features of the emission bands indicate MLCT transitions. The complexes were red-shifted in comparison with the corresponding free ligands. Complexes **C2**, **C3**, **C5**, and **C6** were red-shifted, and complex **C4** was blue-shifted compared with the parent complex **C1**. The bathochromic shifts of the complexes relative to **C1** were 19 nm for **C2**, 8 nm for **C3**, 8 nm for **C5** and 7 nm for **C6**. The hypsochromic shift of **C4** relatively to the parent **C1** was 3 nm. All complexes were substantially red-shifted compared with  $\text{Ir}(\text{ppy})_3$ , as expected for a more extended  $\pi$ -system,<sup>15</sup> and the substituent effects in **C1–6** are much smaller and are difficult to rationalize.

The lifetimes of the luminescent triplet states of the complexes in degassed solutions of  $\text{CH}_2\text{Cl}_2$ , prepared by multiple freeze-pump-thaw cycles, are summarized in Table 1. The substituents influenced the excited state lifetimes despite the small changes in the absorption and emission spectra. Specifically, the emission lifetime of **C3**, substituted with a strongly electron-withdrawing  $\text{CF}_3$  group was the longest ( $\tau = 3.7\ \mu\text{s}$ ), followed by the electron-rich complex **C1** ( $\tau = 3.0\ \mu\text{s}$ ), whereas the remaining complexes substituted with methyl groups had slightly shorter lifetimes ( $\tau = 1.4\text{--}2.6\ \mu\text{s}$ ). Typically, the electron-donating or -withdrawing properties of the substituent affects the C,N-ligand by either decreasing or increasing the electron density in the ring system where the substituent is attached.<sup>29</sup> The long lifetime of **C3** is in agreement with a HOMO stabilization, but it must be noted that this is not in accord with the observed absorption and emission spectra of **C3**; furthermore, **C2** which contains an electron-donating group, also has a relatively long lifetime.<sup>30</sup> In the context of photoredox catalysis, the excited state of the complex should persist for long enough to permit the reaction to take place. Essentially, a longer lifetime increases the probability that the catalyst will productively interact with substrates while in its excited state.

**Table 1** Photophysical and Electrochemical Data for Complexes **C1–6**

Complex	Emission		Electrochemistry (V)	
	$\lambda_{\text{max}}$	$\tau$ ( $\mu\text{s}$ )	$E_{1/2}$	$E_{\text{III}^*/\text{IV}}^{\text{31}}$
$\text{Ir}(\text{ppy})_3^{\text{a}}$	519	1.5	0.77	–1.73
<b>C1</b>	591	1.5	0.73	–1.36
<b>C2</b>	610	3.0	0.66	–1.37
<b>C3</b>	603	3.7	0.95	–1.11
<b>C4</b>	588	2.6	0.64	–1.47
<b>C5</b>	603	1.4	0.62	–1.44
<b>C6</b>	602	2.6	0.64	–1.42

<sup>a</sup> Approximated excited-state redox potential.<sup>32</sup>

Principally, in photoredox catalysis, the ground- and the excited-state redox potentials of a photocatalyst are used in SET-mediated transformations.<sup>22,28</sup> Consequently, the electrochemical properties of the iridium complexes were probed by cyclic voltammetry to establish the ground-state redox potentials in degassed solutions of 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte in  $\text{CH}_2\text{Cl}_2$  at a scan rate of 0.1 V/s. All complexes exhibited reversible or, possibly, quasireversible oxidation waves [Figure 4(A)] during anodic scanning,  $\delta E_p = 100\text{--}140$  mV, which can be attributed to the metal-centered Ir(III)/Ir(IV) redox couple (Table 1).<sup>18</sup> Reversibility of redox processes for complexes used as a photocatalyst is vital for reaction efficiency.<sup>28</sup> The observed oxidation potentials followed the expected trend that the electron-deficient complex **C3** exhibited the highest ground state  $E_{1/2}^{\text{ox}}$  [Ir(III)/Ir(IV) = 0.95 V versus SCE in  $\text{CH}_2\text{Cl}_2$ ], whereas lower values of  $E_{1/2}$  were observed for the neutral and electron-rich complexes (0.62–0.73 V).

In their excited state, these complexes can act as energy donors, electron acceptors, or electron donors. For any given reaction, the process that dominates is usually determined by both thermodynamic and kinetic factors associated with the reaction. Consequently, reductive initiation of photoredox processes is typically more efficiently mediated by catalysts that are strong reductants in their excited states. It is not possible to determine these experimentally, but they can be approximated by using the energy associated with their emission (Table 1).<sup>33</sup> The excited-state reduction potentials for complexes **C1–6** were all estimated to fall in the range  $-1.11$  to  $-1.47$  V, which is distinctly higher than the value for  $\text{Ir}(\text{ppy})_3$  [ $E_{\text{red}}^*[\text{Ir}(\text{III})/\text{Ir}(\text{IV})] = -1.73$  V]. This difference can be explained by the comparably higher-energy emission of  $\text{Ir}(\text{ppy})_3$  (519 nm versus 588–610 nm).

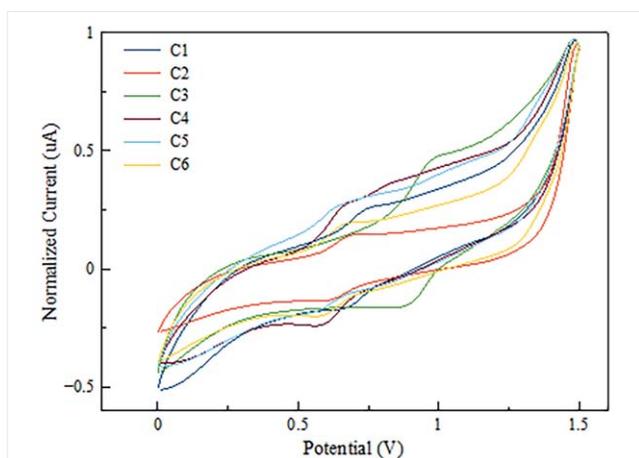


Figure 4 Cyclic voltammograms of complexes **C1–6**

Organofluorine compounds play an integral role in the fields of materials science, pharmaceuticals, and agrochemicals. Notably, the trifluoromethyl moiety alters the lipo-

philicity, binding selectivity, and affinities of biologically active compounds.<sup>34–36</sup> Thus, the development of mild and practical procedures for trifluoromethylation has become a vital research endeavor. Currently, trifluoromethyl group can be introduced by using either nucleophilic or electrophilic reagents. A prominent example belonging to the latter group is Umemoto's reagent, 5-(trifluoromethyl)dibenzo[*b,d*]thiophenium tetrafluoroborate.

Yasu et al.<sup>34</sup> reported that Umemoto's reagent can be used for dual functionalization of styrenes. In their report, the authors suggested that the reaction proceeds through an exergonic single-electron reduction of Umemoto's reagent ( $E_{1/2}^{\text{red}} = -0.37$  V versus SCE in  $\text{CH}_2\text{Cl}_2$ ) by photoexcited  $\text{Ir}^{\text{III}}(\text{ppy})_3$  [ $E_{1/2}^{\text{ox}}[\text{Ir}(\text{III})/\text{Ir}(\text{IV})] = -1.73$  V versus SCE in MeCN] to afford an electrophilic trifluoromethyl radical that adds to styrene. The resulting radical adduct reduces the oxidatively quenched  $\text{Ir}^{\text{IV}}(\text{ppy})_3$ , which turns over the photoredox cycle and yields a benzylic cation that, in turn, is trapped by nucleophilic MeOH. Given that our complexes **C1–6** have relatively low oxidation potentials (Table 1), we reasoned that alkoxytrifluoromethylation of styrenes, as reported by Yasu et al.<sup>34</sup> would be an ideal reaction to test their photoredox catalysis properties.

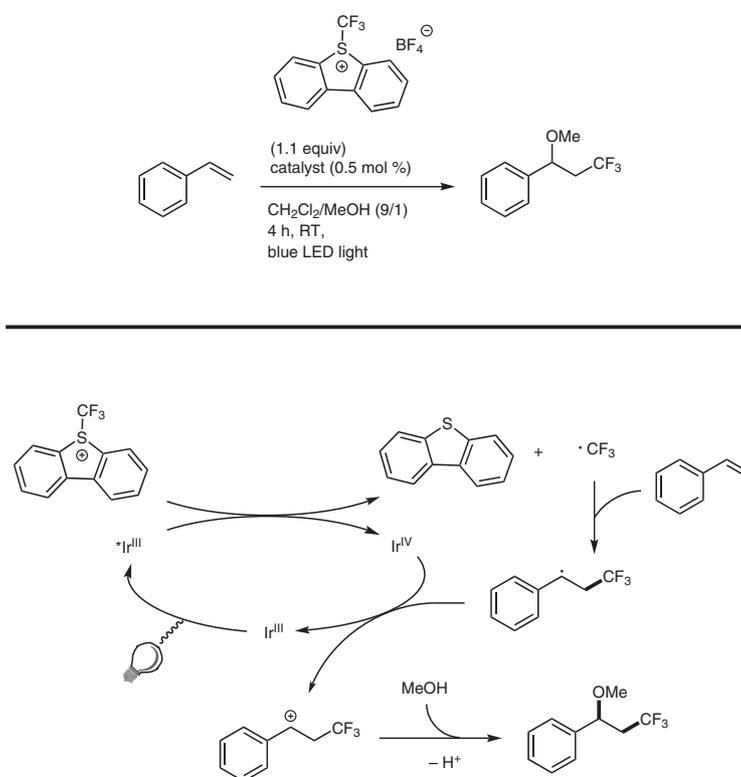
An initial attempt to reproduce the reported procedure with  $\text{Ir}(\text{ppy})_3$  as catalyst gave the product in 87% yield, which is slightly lower than the reported yield of 99% (Table 2, entries 1 and 2).<sup>37</sup> Such discrepancies can be expected, as the reactions typically depend on the efficiency of irradiation and, therefore, the reaction setup.<sup>38</sup> When we used **C1–6** in our experimental setup (see Supplementary Information) under the usual reaction conditions we obtained the corresponding products in yields ranging from 56 to 100%. Complexes **C1**, **C2**, and **C3** gave yields toward the higher end of this range (97–100%), and are therefore more efficient than is  $\text{Ir}(\text{ppy})_3$  in this specific transformation. Complex **C4** provided the product in the same yield as  $\text{Ir}(\text{ppy})_3$  (87%). Complexes **C5** and **C6** gave the product in lower yields of 79 and 56%, respectively. Note that the electronically neutral **C1**, the most-electron-deficient complex **C2**, and the most-electron-rich complex **C3** all provided the product in similar yields. Common to these complexes are the relatively high reduction potentials associated with the catalysts in the turnover event of the catalytic cycle [Ir(IV)/Ir(III) = 0.62–0.95 V]. This indicates that the efficiency of the reaction is coupled to the efficiency of oxidation of the key benzyl radical intermediate. However, the other complexes **C4–6** are all potent reductants in their excited states, and they have both a reasonable reduction potential for the Ir(IV)/Ir(III) couple (0.62–0.64 V) and more than adequate lifetimes of their excited states. Taken together, these characteristics do not differ substantially from those of the better-performing catalysts **C1**, **C2**, and **C3**, as is especially evident in the comparison with **C2**. It is therefore more likely that catalyst deactivation provides a better explanation of the slightly inferior performance of **C4**, **C5**, and **C6**. Deactivation

of the catalyst is often observed in photoredox catalysis, and it stems from the reactions between intermediate high-energy radicals and the ligands of the catalysts.<sup>39</sup> The lower-performing complexes **C4**, **C5**, and **C6** in this work all contain methyl substituents. Hydrogen-atom abstraction from these substituents must be regarded as a very likely side reaction that could initiate deactivation of the catalyst. No byproduct associated with degradation of the catalysts was observed, but this does not rule out radical-based degenerative pathways for these catalysts. As such, in out-performing Ir(ppy)<sub>3</sub> as a catalyst in the methoxytrifluoro-

methylation, complexes **C1**, **C2**, and **C3** provide an addition to the current range of photoredox catalysts, in terms of an accessible redox window in the catalytic cycle.

In conclusion, six 2-(1-naphthyl)pyridine ligands and their corresponding Ir(III) complexes **C1–6** were synthesized, and characterized by means of crystallographic, spectroscopic and electrochemical studies. The systematic modification of the ligands by the introduction of electron-withdrawing or electron-donating groups with varying degrees of substitution and strength on the phenyl or pyridyl ring was shown to permit tuning of the photophysics and electrochemistry of the resulting complexes. The complexes were found to be strongly luminescent (588–610 nm) and

**Table 2** Comparison of Synthesized Complexes **C1–6** with Ir(ppy)<sub>3</sub>



Entry	Catalyst	Conversion of styrene <sup>a,b</sup> (%)	Yield <sup>a,b</sup> (%)
1 <sup>22</sup>	Ir(ppy) <sub>3</sub>	100	99
2	Ir(ppy) <sub>3</sub>	87	87
3	<b>C1</b>	98	97
4	<b>C2</b>	100	100
5	<b>C3</b>	100	100
6	<b>C4</b>	87	87
7	<b>C5</b>	79	79
8	<b>C6</b>	65	56

<sup>a</sup> Average of two experiments.

<sup>b</sup> Determined by <sup>1</sup>H NMR with an internal standard.

to exhibit long triplet lifetimes of 1386–3692 ns. In addition, the complexes exhibited reversible or quasireversible oxidation waves with  $E_{1/2}$  ranging from 0.62 to 0.95 V. Highly efficient oxytrifluoromethylation of styrene by using **C1–6** as photoredox catalysts was achieved with up to quantitative yields. Under the reaction conditions used, complexes **C1–4** showed a better or similar performance compared with the archetypical photoredox catalyst Ir(ppy)<sub>3</sub>.

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### Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0037-1611716>.

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- (23) **2-(1-Naphthyl)pyridine (L1); Typical Procedure**  
A Straus flask equipped with a stirrer bar was charged with 2-bromopyridine (1.0 equiv.), 1-naphthylboronic acid (1.1 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (4 mol%), 2 M aq Na<sub>2</sub>CO<sub>3</sub> (2.5 mL/mmol), toluene (3.8 mL/mmol), and ethanol (1.3 mL/mmol). The mixture was degassed by three freeze–pump–thaw cycles and then refluxed under inert conditions overnight. The mixture was cooled to r.t. and extracted with EtOAc (3 × 20 mL). The organic phases were combined, dried (MgSO<sub>4</sub>), and concentrated. The pure ligand was obtained by flash column chromatography [silica gel, EtOAc–hexane (1:4)].  
Compound was isolated as viscous liquid that solidified upon standing. Yield: 1.6 g (99%).  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.81 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1 H), 8.11 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.93 (dt, *J* = 7.2, 1.3 Hz, 2 H), 7.82 (td, *J* = 7.7, 1.8 Hz, 1 H), 7.63–7.54 (m, 3 H), 7.54–7.46 (m, 2 H), 7.33 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 159.27, 149.56, 138.51, 136.44, 133.96, 131.18, 128.93, 128.39, 127.51, 126.52, 125.90, 125.62, 125.33, 125.09, 122.06. HRMS (ESI+): *m/z*: [M + H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>N: 206.0970; found: 206.095.
- (24) **Iridium(III) Complexes C1–6; General Procedure**  
A Straus flask was charged with the ligand **L1–6** (12.0 equiv), Na<sub>2</sub>CO<sub>3</sub> (6.0 equiv), IrCl<sub>3</sub> (1.0 equiv), and deionized H<sub>2</sub>O (60 mL). The mixture was degassed by three freeze–pump–thaw cycles, and the sealed Straus flask was heated at 205 °C for 48 h. The mixture was then cooled and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The extracts were dried (MgSO<sub>4</sub>), filtered through a pad of Celite, and concentrated. The product was isolated by flash chromatography [silica gel, EtOAc–hexane (1:3) (for ligand), then CH<sub>2</sub>Cl<sub>2</sub> (for complexes)].
- (25) CCDC 1875304 contains the supplementary crystallographic data for compound **C1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/getstructures](http://www.ccdc.cam.ac.uk/getstructures).
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- (37) **Oxytrifluoromethylation of Styrene; General Procedure**  
The oxytrifluoromethylation was performed according to the reported procedure; see ref. 33. An oven-dried microwave vial was cooled to r.t. under high vacuum then charged with 5-(trifluoromethyl)dibenzo[*b,d*]thiophenium tetrafluoroborate (42.0 mg, 1.1 equiv), the appropriate catalyst (0.5 mol%), and styrene (10.4 mg, 0.1 mmol), which had been filtered through a pad of basic Al<sub>2</sub>O<sub>3</sub> before addition. The microwave vial was sealed and carefully degassed in by three vacuum–nitrogen cycles. A mixture of MeOH (0.2 mL) and CH<sub>2</sub>Cl<sub>2</sub> (1.8 mL), previously degassed by three freeze–pump–thaw cycles, was added. The resulting mixture was irradiated with a blue LED light strip (7 W) at a distance of 2 cm with stirring for 4 h. The vial was then opened, and the internal standard trimethoxybenzene was added. The reaction mixture with the internal standard was briefly stirred and then transferred to an NMR tube equipped with a sealed D<sub>2</sub>O capillary, which was used for locking and shimming of the spectrometer. The yield was determined by using 128 scans with a relaxation time of 60 s. The reported yield is based on the integration of the most upfield signals ( $\delta = 2.27$  and 2.43 ppm) of the product. The experiments were performed twice, and the conversions and yields are reported as average values.
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