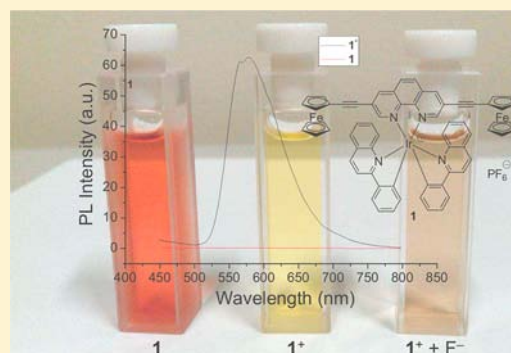


A Bis(ferrocenyl)phenanthroline Iridium(III) Complex as a Lab-on-a-Molecule for Cyanide and Fluoride in Aqueous Solution

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Supporting Information

ABSTRACT: The bis(ferrocenyl)phenanthroline iridium(III) complex **1** is synthesized and elaborated as a lab-on-a-molecule for the competitive and quantitative determination of cyanide and fluoride in aqueous solution. **1** exhibits a strong OFF–ON photoluminescence (PL) response upon addition of cyanide with a good selectivity over other anions. The mechanism involves nucleophilic displacement of the phenanthroline ligand, which quenches PL, to furnish a strongly photoluminescent dicyano iridium complex. In contrast, in the electrochemiluminescence (ECL) channel, cyanide undergoes oxidation and a different selectivity is observed. The strong ferrocenium–fluoride interaction is exploited for the first time in ECL to selectively monitor fluoride by a >60-fold enhancement. In both PL and ECL channels, anion selectivity is further challenged by competitive assays in the presence of other anions. Quantitative determination of CN[−] and F[−] is achieved in both channels.



INTRODUCTION

The development of molecular recognition and sensing of anions is currently a vibrant research activity.¹ While there is a sizable amount of work devoted to pattern analysis, principal component, and neural network analysis,² we have recently emphasized the usefulness of the lab-on-a-molecule strategy. A lab-on-a-molecule is a molecular probe that allows detection and quantification of not just one analyte, but two or more in competitive assays.³ In principle, there are two distinct approaches to lab-on-a-molecule probes: (1) use of several binding sites, one for each analyte, and (2) use of various channels for interrogation, ideally one channel per analyte. From a synthetic and atom-economic point of view, multi-channel sensing using a single receptor unit⁴—so far mostly not working in competitive assays—seems to be more attractive than using single-channel interrogation with several receptors at the probe.⁵ Photoluminescence (PL) and electrochemiluminescence (ECL)⁶ are a powerful combination for two-channel detection, in particular since PL allows for real-time and spatially resolved imaging,⁷ while ECL⁶ nicely adds spatially resolved electrochemical techniques.

Cyanide is a highly toxic anion that is widely present in industrial waste, making its detection and quantification in aqueous solution a matter of environmental concern. While a variety of CN[−] probes are known,^{3d,8} their use in aqueous solution is still limited,⁹ simply because the widely used CN[−]⋯H⁺ hydrogen-bonding motif¹⁰ fails in water. On the other hand, considerable progress has been made in the detection of fluoride,¹¹ which plays a vital role in physiological processes. Most protocols for fluoride sensing follow hydrogen

bonding,¹² nucleophilic attack onto boron^{5c,13} or silicon,¹⁴ and ion-pairing interactions,¹⁵ while a few use anion- π interactions.¹⁶

Herein, we not only present a novel dual-channel lab-on-a-molecule probe for CN[−] and F[−]^{14b} using PL and ECL but also present a new concept to detect fluoride by ECL. Although **1** (see Scheme 1) is equipped with a phosphorescent iridium(III) core,¹⁷ its luminescence was anticipated to be strongly quenched by intramolecular electron transfer due to the presence of electron-rich ferrocenyl units. In advance, we hypothesized that the bis(ferrocenyl)phenanthroline ligand at iridium could possibly be displaced by the more strongly binding cyanide. As a result, its reaction with **1** would deliver the known, highly luminescent iridium complex **3**, similar to cases reported in previous publications.^{3d,18} In contrast, under oxidative conditions in ECL, cyanide should not survive due to its oxidation to (CN)₂, allowing fluoride to associate with the oxidized ferrocenium unit.

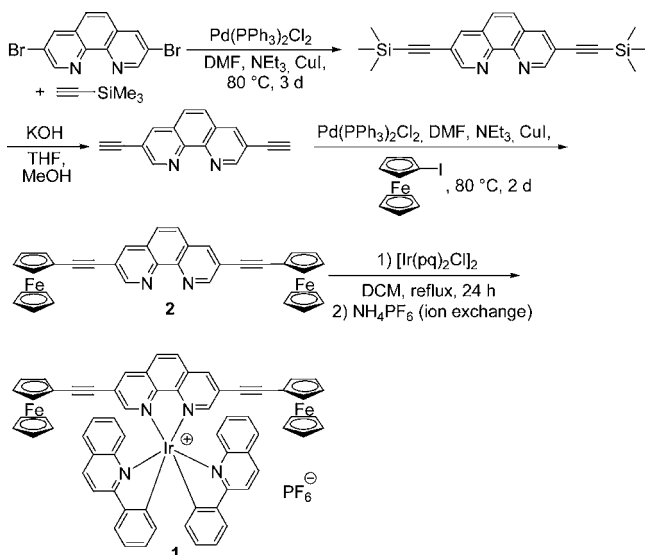
RESULTS AND DISCUSSION

Following analogous procedures,¹⁹ the new complex **1** was prepared from **2**²⁰ and tetrakis(2-phenylquinoline-C²,N')(μ -dichloro)diiridium ([Ir(pq)₂Cl]₂) and characterized by ¹H and ¹³C NMR and elemental analysis (Supporting Information). Complexes **3** and **4** (Chart 1) were prepared as reported earlier.^{18,21} All of the PL and ECL studies were conducted in

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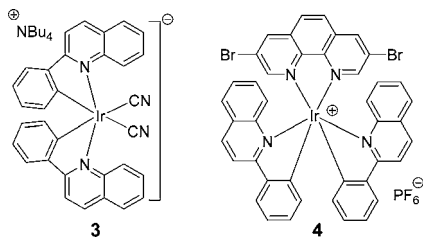
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Scheme 1. Synthesis of Probe 1



MeCN/aqueous buffer (90/10) (v/v, **1** (10 μ M) in 0.1 M Tris-ClO₄, pH 7.24).

Chart 1. Iridium Complexes 3 and 4, Used for Comparison



As expected from its ferrocene residues, **1** proves to be basically nonluminescent ($\Phi_{\text{PL}} = 0.0029$, $\lambda_{\text{exc}} 330$ nm) due to PET (photoinduced electron transfer) quenching of the excited iridium(III) phenylquinoline unit by the electron-rich ferrocene residues. Upon addition of 200 equiv of CN⁻, however, a strong PL increase by a factor of 130 at $\lambda_{\text{em}} 580$ nm was detected (Figure 1a and Figure S1 (Supporting Information)). In contrast, other anions, such as F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, PF₆⁻, ClO₄⁻, and H₂PO₄⁻, did not show any dramatic changes, even in large excess amounts (200 equiv) as depicted in Figure 1a.

As conceived by design,¹⁸ the emission increase in the PL channel was expected to arise from CN⁻ attack onto the iridium center of **1**, leading to a displacement of ligand **2** to produce **3**. When complex **4** as reference was reacted with cyanide, indeed the same emission ($\lambda_{\text{em}} 580$ nm) was seen in PL (Figure S3, Supporting Information). Finally, **3** was independently synthesized in DCM from [Ir(pq)₂Cl]₂¹⁸ with *n*-Bu₄NCN. It displays the same PL as that seen in the probe reaction (Figure 2a). The ¹H NMR spectrum recorded after addition of CN⁻ to **1** in CD₂Cl₂ shows a new set of peaks that is unambiguously assigned to free **2** (Figure S4, Supporting Information). In comparison, there is no detectable change of the NMR spectrum of **1** after addition of F⁻. In summary, **1** operates as an irreversible chemodosimeter for CN⁻ and requires a defined reaction time for quantification.

Selectivity for cyanide over other anions is further challenged in a competitive assay, which is carried out by reacting **1** with 200 equiv of cyanide in the presence of 200 equiv of other

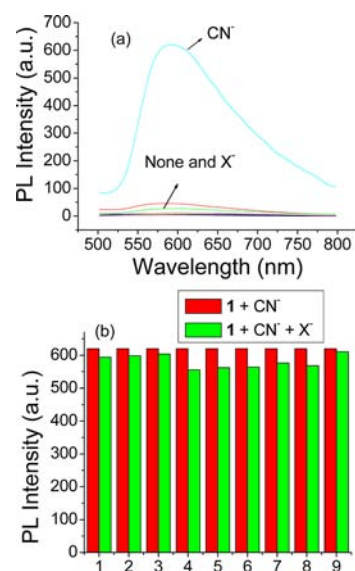


Figure 1. PL response ($\lambda_{\text{exc}} 330$ nm) of **1** (10 μ M) upon addition of (a) 200 equiv of various anions X⁻ and (b) 200 equiv of X⁻ and 200 equiv of CN⁻ at $\lambda_{\text{em}} 580$ nm (X⁻ = F⁻ (1), Cl⁻ (2), Br⁻ (3), I⁻ (4), H₂PO₄⁻ (5), HSO₄⁻ (6), BF₄⁻ (7), AcO⁻ (8), PF₆⁻ (9)) after 120 \pm 1 min of reaction in 0.1 M Tris-ClO₄/MeCN (10/90 v/v, pH 7.24).

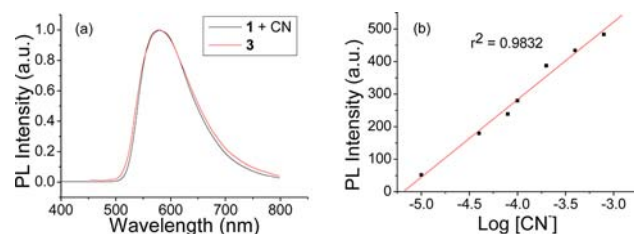


Figure 2. (a) Normalized PL responses from **1** after addition of CN⁻ and (b) linear relationship between PL intensity at $\lambda_{\text{em}} 580$ nm and log [CN⁻]. PL data ($\lambda_{\text{exc}} 330$ nm) were obtained after 180 \pm 1 min of reaction in 0.1 M Tris-ClO₄/MeCN (10/90, v/v, pH 7.24). Absorbance changes at the excitation wavelength ($\epsilon_{330 \text{ nm}} = 56000$ M⁻¹ cm⁻¹ for **1**) are minor during the titration (within 5%).

anions. No interference is seen (Figure 1b). To allow for quantification even at lower concentrations, a reaction time of 180 \pm 1 min was chosen. A good linear relationship between PL intensity and log [CN⁻] was found, furnishing an easy and reliable way to quantify cyanide in aqueous solution (Figure 2b). In summary, **1** is a selective chemodosimeter for cyanide in the PL channel with a detection limit of 10 μ M in aqueous solution.

In oxidative ECL, with TPrA (tri-*n*-propylamine)⁶ serving as coreactant, the ECL response of **1** is extremely low (Figure 3a), while reference **4** is strongly luminescent (Figure S5). According to differential pulse voltammetry (DPV), **1** shows oxidation waves at 0.70 and 1.46 V (vs FeCp*₂) in MeCN representing Fc⁰/Fc¹ and Ir^{III}/Ir^{IV} redox transitions, respectively. Most likely, ECL production of excited *Ir^{III} (eqs 1–3a) by electron transfer from the strongly reducing TPrA[•] radical to Ir^{IV} is greatly diminished in the presence of the ferrocenium unit that serves as the better electron sink (eq 3b).

Upon addition of fluoride to **1**, a distinct emission enhancement (more than 60-fold) is displayed in ECL, while addition of all other anions does not entail any significant change of the ECL intensity (Figure 3a).

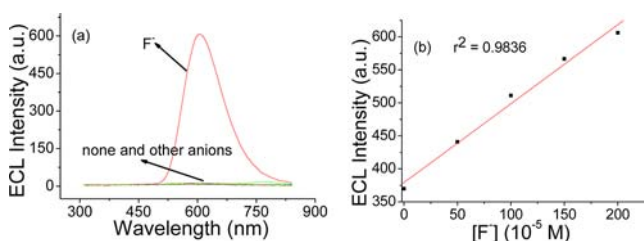
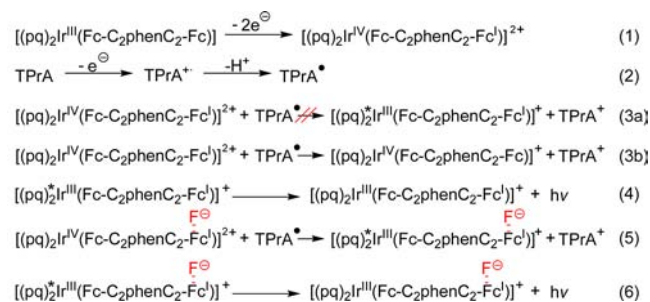


Figure 3. ECL emission of **1** (10 μM) (a) in the presence of 200 equiv of each anion $X^- = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{H}_2\text{PO}_4^-, \text{HSO}_4^-, \text{BF}_4^-, \text{AcO}^-, \text{PF}_6^-$ and (b) at λ_{em} 605 nm with respect to $[\text{F}^-]$. All samples were measured within 2 min after mixing in 0.1 M *n*-Bu₄NPF₆ Conditions: Tris-ClO₄ buffer (MeCN/water 90/10, v/v, pH 7.24) using a sweep range of 0.5–1.8 V at a scan rate $\nu = 100 \text{ mV s}^{-1}$, 50 mM TPrA as coreactant.



Because F^- does not react with **1** in its ground state, its detection by ECL must be different from the CN^- sensing protocol in PL that is based on ligand displacement. We have thus undertaken a series of mechanistic investigations to elucidate the most plausible scenario of operation.

A mechanistically relevant finding is that **1** after oxidation at one ferrocene unit, i.e. 1^+ , becomes photoluminescent, showing a typical iridium emission at λ_{em} 584 nm (eq 4; Figure S6 (Supporting Information)). Hence, in the presence of one ferrocenium unit in 1^+ , intramolecular electron transfer quenching of *Ir^{III} is no longer effective. The lack of any significant ECL emission with $\text{Cl}^-, \text{Br}^-, \text{I}^-, \text{H}_2\text{PO}_4^-, \text{HSO}_4^-, \text{BF}_4^-, \text{AcO}^-$, and PF_6^- , however, indicates that *1^+ is only produced in the presence of F^- . Why?

Notably, addition of F^- does not influence the PL wavelength or significantly the PL intensity of *1^+ (Figure S7 (Supporting Information)). This finding clearly excludes the notion that F^- displaces ligand **2** under oxidative conditions. Thus, the huge ECL intensity increase in the presence of F^- must have a more intricate background.

To check for any involvement of an iridium–fluoride interaction during sensing, we investigated the ECL of **4** in the presence of F^- : the ECL intensity slightly decreases (Figure S5 (Supporting Information)), in contrast to the finding in the ECL sensing using **1**. This finding clearly excludes any iridium–fluoride interaction in the sensing mechanism.

To shed further light on the mechanism of fluoride detection, we turned our attention to $\text{F}^- \cdots \text{Fc}^+$ ion–ion pairing in solution that is well established by electrochemical methods (Figure S9 (Supporting Information)).²² In the absence of fluoride, a symmetric redox wave of Fc^0/Fc^+ appears (Figure 4), suggesting that the ferrocene unit of **1** exhibits full electrochemical reversibility, as corroborated equally in cyclic voltammetry (Figure S10 (Supporting Information)). Upon addition of F^- , the oxidation waves of **1** at the Fc^0/Fc^+ and $\text{Ir}^{\text{III}}/$

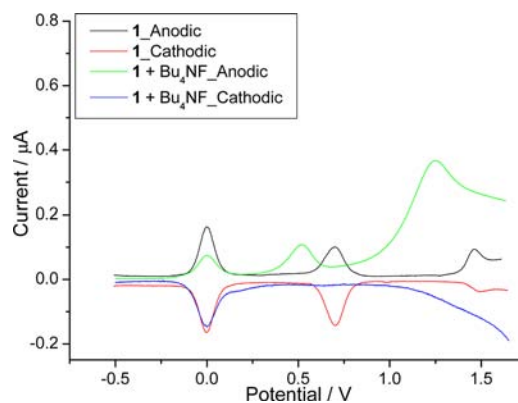


Figure 4. DPV of **1** (1 mM) in the presence of 200 equiv of *n*-Bu₄NF·3H₂O in MeCN vs DMFc at a scan rate of 100 mV s^{-1} .

Ir^{IV} redox transitions display 190 and 220 mV cathodic shifts, respectively (Figure 4 and Figure S10 (Supporting Information)), along with a full loss of the Fc^1/Fc^0 reduction wave. Such behavior points to surface adsorption,²² while the increased current at $E > 0.7 \text{ V}$ may be attributed to the large amounts of *n*-Bu₄NF·3H₂O (see Figure S11 (Supporting Information)). In summary, the firm $\text{F}^- \cdots$ ferrocenium interaction, possibly accompanied by adsorption as suggested by the irreversible CV wave,²² prevents electron uptake under reducing conditions on the time scale of the electrochemical experiment.

The various findings strongly suggest the following mechanism for fluoride detection using **1** in the ECL channel: in the absence of fluoride, 1^{2+} (1^{2+} contains Fc^1 and Ir^{IV} units) is reduced by TPrA^\bullet at the ferrocenium unit, generating a nonluminescent species (eq 3b and Figure 5c). In the presence

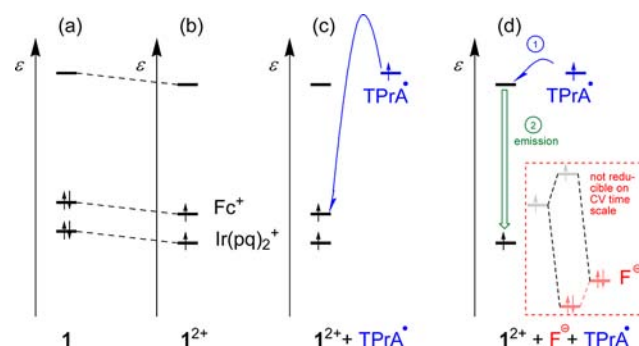


Figure 5. Pictorial representations of the orbital energies and electronic configuration in **1** (a) and 1^{2+} (b) and during electron injection of TPrA^\bullet into 1^{2+} (c) and into 1^{2+} after complexation to fluoride (d).

of F^- , the strong $\text{F}^- \cdots$ ferrocenium interaction prevents reduction at the ferrocenium unit of 1^{2+} on the time scale of the ECL experiment, thus channeling electron transfer from the TPrA^\bullet radical to the LUMO of the oxidized iridium unit (eq 5 and Figure 5d) rather than to the $\text{F}^- \cdots$ ferrocenium unit. The thus formed $\text{*1}^{2+} \cdots \text{F}^-$ is luminescent due to its *Ir^{III} excited state (eq 6¹⁷) and the lack of intramolecular electron transfer quenching. The mechanism suggests that out of all investigated anions only F^- coordinates to the ferrocenium unit. As judged by the redox potential of **1** in presence of other anions, this is indeed the case (Figure 6).

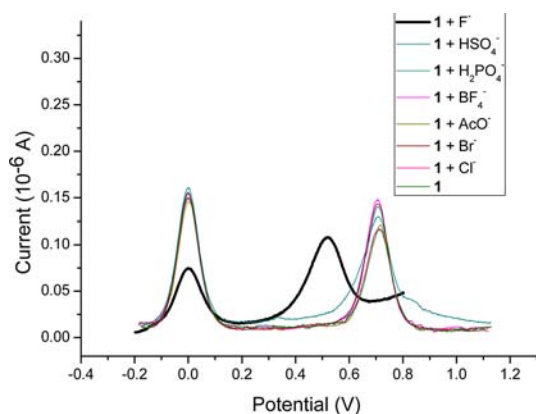


Figure 6. DPV of **1** (1 mM) in the presence of 200 equiv of various anions (in 0.1 M *n*-Bu₄NPF₆ in MeCN; scan rate 0.1 V s⁻¹; DMFc as reference). Iodide and cyanide are not shown because they are oxidized themselves under mild anodic conditions.

To evaluate the selectivity for fluoride in competitive assays, experiments were performed by measuring the ECL of **1** in presence of 200 equiv of fluoride and of 200 equiv of other anions (Figure S12 (Supporting Information)). Cyanide does not interfere much, because under ECL conditions (a) reaction of **1** with CN⁻ is slow, (b) **3** is basically nonluminescent (Figure S13 (Supporting Information)), and (c) CN⁻ is oxidized.^{3d} Some interference is detected with iodide, however, as the latter is easily oxidized itself. A good relationship between ECL intensity and the concentration of F⁻ allows for an easy quantitative analysis (Figure 3b).

CONCLUSION

In summary, we have established the highly cyanide and fluoride selective lab-on-a-molecule **1** operating in MeCN–water at pH near 7. Complex **1** works as a dual-channel (PL and ECL) light-up probe. While PL detection of cyanide follows a classical ligand displacement mechanism (chemodosimeter), the ECL process is without precedence, thus providing a new strategy for further fluoride probes. It requires two features that are both linked to the oxidized ferrocenium of **1** in the ECL process: (a) a nonluminescent probe that becomes luminescent after oxidation of its ferrocene unit and (b) a strong F⁻–Fc⁺ ion–ion pairing protecting the ferrocenium against reduction by TPrA[•].

EXPERIMENTAL SECTION

Materials. All chemicals and solvents were of reagent grade and were used without further purification. The iridium complex [Ir(pq)₂Cl]₂,^{3d} **3**,^{3d} **4**,^{19,21} and compound **2**²⁰ were synthesized by following reported methods.

Instrumentation. *NMR Spectra.* ¹H and ¹³C NMR spectra were recorded on a Bruker Advance 400 (400 MHz). Chemical shifts are reported in ppm.

Luminescence and UV–Vis Measurements. Using a solution containing the compound (10 μM) in MeCN/Tris-ClO₄ buffer (90/10 v/v), the UV–vis measurements were carried out on a Varian Cary 100 Bio UV–visible spectrophotometer and the luminescence measurements on a Varian Cary Eclipse fluorescence spectrophotometer with excitation and emission slit widths set at 5 nm. The PL quantum yields (Φ_{PL}) were determined using [Ru(bpy)₃]²⁺ (Φ = 0.062 in acetonitrile²³) as a reference.

Electroanalytical Investigations. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using a standard three-electrode setup (1 mm Pt disk working

electrode, Pt auxiliary electrode, and silver wire as reference electrode) connected to a PARSTAT 2273 Advanced Electrochemical System. The measurements were carried out on a 1 mM solution of the compound in acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. All potentials are recorded at a scan rate of 100 mV s⁻¹ and are referenced to decamethylferrocene (DMFc) as internal standard.

Mass Spectroscopy. ESI-MS measurements were recorded on a LCQ Deca Thermo Quest instrument.

Elemental Analysis. Elemental analysis was performed on an elemental analyzer from EuroVector.

ECL Investigations. All ECL measurements were done with solutions using the metal complexes (10 μM) in MeCN/buffer (90/10 v/v), containing additionally TPrA (50 mM) as coreactant and 0.1 M tetra-*n*-butylammonium hexafluorophosphate as electrolyte. A standard three-electrode setup (3.0 mm diameter Pt working electrode, Pt wire auxiliary electrode, and silver wire as reference electrode) connected to a Princeton Applied Research Model 362 potentiostat was used. To generate the ECL reaction, the working electrode was swept from 0.5 to 1.8 V and back to 0.5 V (vs silver wire used as quasi-reference electrode) at a scan rate of 100 mV s⁻¹. The electrode was cleaned after each scan. ECL competition experiments on solutions of **1** (10 μM) were carried out after addition of 200 equiv of fluoride in presence of 200 equiv of each other anion (in Tris-ClO₄ buffer solution; MeCN/buffer 90/10 v/v, pH 7.24). The resulting emission spectra were obtained with a CCD camera at –50 °C (0.500 m imaging triple grating monochromator/spectrograph), which was connected to a Spectrapro 2500i spectrometer (Acton Research Corp.).

Synthesis. 3,8-Bis(2-(trimethylsilyl)ethynyl)-1,10-phenanthroline,²⁴ 3,8-diethynyl-1,10-phenanthroline,²⁴ iodoferrrocene,²⁵ and bis-(2-phenylquinoline-C²;N¹)(3,8-dibromo-1,10-phenanthroline)iridium hexafluorophosphate²⁶ (**4**) from [Ir(pq)₂Cl]₂²⁷ and 3,8-dibromophenanthroline²⁸ were prepared as described in the literature.

*3,8-Bis(ferrocenylethynyl)-1,10-phenanthroline (2).*²⁹ Iodoferrrocene (1.00 g, 3.20 mmol), [Pd(PPh₃)₂Cl₂] (50.8 mg, 5 mol %), CuI (27.6 mg, 10 mol %), dry DMF (20 mL), triethylamine (20 mL), and 3,8-diethynyl-1,10-phenanthroline (330 mg, 1.45 mmol) were mixed in a sealed tube under a nitrogen atmosphere. The mixture was refluxed to 80 °C for 48 h. Thereafter, DMF was distilled out at reduced pressure, furnishing a dark brown crude residue. The latter was dissolved in DCM (150 mL) and washed twice with aqueous potassium cyanide (1.12 g of KCN in 20 mL of water) and finally with water. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to furnish a dark brown oil. The latter was purified by column chromatography using first hexane and then DCM to furnish **2**²⁹ as a red-brown solid. Yield: 100 mg (0.168 mmol, 12%). ¹H NMR (400 MHz, CD₂Cl₂): δ 4.30 (s, 10H, CpH), 4.34 (m, 4H, 3', 4'-CpH), 4.61 (m, 4H, 2', 5'-CpH), 7.81 (s, 2H, 5-H, 6-H), 8.33 (d, J = 2.1 Hz, 2H, 4-H, 7-H), 9.16 (d, J = 2.1 Hz, 2H, 2-H, 9-H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 64.5, 69.8, 70.5, 72.1, 83.2, 94.0, 120.7, 127.2, 128.5, 137.7, 144.4, 152.4. ESI-MS (C₃₆H₂₅N₂Fe₂)⁺: calcd m/z 597.3, found m/z 597.5.

Bis(2-phenylquinoline-C²;N¹)[3,8-bis(ferrocenylethynyl)-1,10-phenanthroline]iridium Hexafluorophosphate (1). [Ir(pq)₂Cl]₂ (108 mg, 84.7 μmol) and **2** (130 mg, 212 μmol) were dissolved in DCM (20 mL), and the solution was refluxed for 24 h. To the DCM solution was added NH₄PF₆ (100 mg, excess) in methanol (10 mL), and the resulting solution was stirred for 1 h. Purification was done by chromatography on a silica column using 2% methanol in DCM for elution. The solvent was removed on a rotary evaporator to give a red-brown powder. Yield: 39.3 mg (28.8 μmol, 68%). ¹H NMR (400 MHz, CD₂Cl₂): δ 4.30 (m, 10H, Cp H), 4.41 (m, 4H, Cp H), 4.59 (m, 4H, Cp H), 6.65 (dd, 2H, J₁ = 0.8 Hz, J₂ = 7.7 Hz, 3''-H), 6.91 (m, 4H, 4''-H, 5''-H), 7.22 (dd, 2H, J₁ = 1.9 Hz, J₂ = 9.0 Hz, 6''-H), 7.28 (m, 4H, 6'-H, 7'-H), 7.69 (dd, 2H, J₁ = 1.2 Hz, J₂ = 8.1 Hz, 5'-H), 7.81 (s, 2H, 5-H, 6-H), 8.15 (dd, 2H, J₁ = 1.0 Hz, J₂ = 8.0 Hz, 8'-H), 8.28 (m, 4H, 3'-H, 4'-H), 8.39 (d, 2H, J = 1.8 Hz, 4-H, 7-H), 8.49 (d, 2H, J = 1.8 Hz, 2-H, 9-H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 70.6, 70.8, 72.4, 72.5, 81.2, 98.6, 118.0, 123.9, 124.2, 124.5, 127.2, 127.6, 128.1, 128.5, 129.5,

130.6, 131.3, 131.4, 135.2, 139.3, 140.6, 144.9, 146.2, 148.1, 149.9, 150.4, 170.3. ESI-MS ($C_{66}H_{44}Fe_2IrN_4$)⁺: calcd m/z 1197.2, found m/z 1197.5. Anal. Calcd for $C_{66}H_{44}F_6Fe_2IrN_4P_2/3CH_2Cl_2$: C, 57.25; H, 3.27; N, 4.01. Found: C, 57.05; H, 3.53; N, 4.02.

■ ASSOCIATED CONTENT

■ Supporting Information

Text and figures giving spectral characterization data of **1** and **4** and PL, CV, DPV, and ECL data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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