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Synthesis, Characterization, and Electronic Properties of Porphyrins Conjugated with N-Heterocyclic Carbene (NHC)–Gold(I) Complexes

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Supporting Information



ABSTRACT: Porphyrins fused to peripheral N-heterocyclic carbenes (NHC) across two neighboring $\beta_i\beta_j$ -pyrrolic positions were used for the synthesis of different mono- and bis-carbenic gold(I) complexes. These studies also revealed how it is possible to modulate the reactivity of the peripheral NHC by deprotonating the inner NH groups of the fused free base porphyrin core. All complexes were fully characterized and displayed high stability, allowing the formation of mono-carbenic and also stable homoleptic and heteroleptic bis-carbenic Au(I) complexes. Optical and electrochemical properties of bis-carbenic Au(I) revealed no or weak electronic communication between the porphyrins, which behave as two independent groups.

INTRODUCTION

N-heterocyclic carbenes (NHCs) have evolved as one of the most important class of ligands in the field of organometallic chemistry, exhibiting broad applications in catalysis,¹ biomedicine,^{2,3} and materials science.^{4,5} Most NHCs are built upon five-membered imidazoles or benzimidazoles and can be easily generated by deprotonating the corresponding azolium salts. These NHCs are considered as highly versatile ligands because their steric and electronic properties can be quite easily modulated according to the nature of their substituents. While their steric properties can be varied according to the size, the shape, and the rigidity of the substituents on the carbene ligand,⁶ the variation of their electronic properties can be achieved by grafting chemical functions onto the backbone with the desired electron-donating or -accepting characters.⁷ For NHCs with identical or at least very similar steric features, the tuning of their electronic properties is of crucial importance for catalytic applications.¹ With regard to facile modulation of the electronic and catalytic properties of their metal complexes, some original NHCs with stimuli-responsive functional groups (redox,⁸ pH,⁹ or light¹⁰) may be used to allow reversible and controlled switching of their electronic properties.

In recent years, hybrid compounds containing NHC ligands attached to porphyrin derivatives have been developed.¹¹⁻¹⁷ Reported porphyrin-NHC systems differ in the position of the NHC (Chart 1). By taking advantage of the flexibility of the "N-confused porphyrins" (NCP, where the positions of one







pyrrolic NH and one β -CH are switched), Furuta and coworkers reported an NHC embedded in a NCP framework (Chart 1, A).¹¹ This unique structure was serendipitously obtained from the reaction of an inner-methylated NCP with Re₂(CO)₁₀ and represents a rare example of an NHC located in the inner core of a macrocycle.¹⁸

More examples of porphyrins with NHCs linked at their periphery are known in the literature. Wang and co-workers used tetraimidazolium salts as NHC precursors, and imidazoliums were separated from the meso positions by $-(C_6H_5)O(CH_2)_3$ - spacers (Chart 1, B).¹² Recently, Ruppert and co-workers avoided the use of spacers by introducing azoles directly onto meso positions.¹³ The alkylation of these compounds afforded porphyrins with meso azolium units, which could further be deprotonated to obtain the corresponding NHC ligands and their metal complexes (Chart 1, C). In our group, we have synthesized porphyrins fused to imidazole and imidazolium units across two neighboring $\beta_{\beta}\beta_{\beta}$ -pyrrolic positions.¹⁴ The deprotonation of the imidazolium ring affords the corresponding NHC (Chart 1, D). It is worth noting that we showed that the electronic properties of peripheral NHC ligands fused to free-base porphyrins can be dramatically altered upon protonation of the inner nitrogen atoms of the porphyrin core.¹⁵ So far, we have reported the synthesis of NHC-Rh(I)^{15,16} and NHC-Pd(II)¹⁷ complexes. Here, we extend our investigations to the synthesis of several Au(I) complexes and also highlight (i) how the porphyrin backbone is able to modulate the coordination properties of the peripheral NHC ligand and (ii) the impact of the peripheral Au(I) complex on the photophysical properties of the porphyrins.

RESULTS AND DISCUSSION

Synthesis and Characterization. Free base porphyrins Fb-I and Fb-BF₄ and their corresponding nickel(II) complexes Ni- I and Ni-BF₄ were used as starting materials (Scheme 1).^{14a} These species are porphyrins fused to imidazolium salts across two neighboring β -pyrrolic positions. Single crystals of Fb- I were obtained by slow diffusion of *n*-pentane in a solution of Fb-I in CH₂Cl₂. An X-ray diffraction analysis unambiguously established its structure (Figure 1). Notably, the porphyrin core

Scheme 1. Synthesis of [NiAuCl] and [FbAuCl] Complexes





Figure 1. ORTEP views of the molecular structure of the imidazolium salt **Fb-I** with atomic displacement parameters at the 50% probability level: (left) front view; (right) side view, *meso* aryl groups omitted for clarity. Hydrogen atoms, except that involved in hydrogen bonding, are omitted for clarity.

is found to be ruffled even in the absence of an inner nickel(II) ion. The imidazolium ring and its fused pyrrole are close to coplanarity with an angle of 10.3° between the two mean planes calculated for each ring. It is also noticeable that the iodide is hydrogen bonded to the C(2)–H of the imidazolium ring with $d_{\rm H-I} = 2.84$ Å.

The synthesis of [(NHC)AuCl] complexes was achieved following different procedures. First, the well-known preliminary formation of NHC-silver complexes was performed with Ag₂O followed by transmetalation reactions with [AuCl-(THT)] (THT = tetrahydrothiophene). This synthesis strategy allowed the synthesis of [NiAuCl] in 50% yield (Scheme 1, procedure A). The formation of the peripheral [AuCl] complex was confirmed by ¹H NMR spectroscopy because the signal arising from the imidazolium proton at δ 11.07 ppm disappeared due to the formation of the C(2)-Au bond. Moreover, the signal of the carbene C(2) could be clearly observed at δ 182.3 ppm in its ¹³C{¹H} NMR spectrum and is in good agreement with data reported in the literature for [(NHC)AuCl] complexes.³ However, the same synthetic approach proved to be unsuccessful in obtaining the desired complex [FbAuCl]. We presume that the silver ion could be trapped by the free base porphyrin core, thus preventing the formation of the NHC-Ag bond.¹⁹ Indeed, alternative silverfree synthetic procedures were then sought. Recently, Nolan, Gimeno, and their co-workers reported improved one-step procedures to obtain [(NHC)AuCl] complexes.²⁰ They consist of in situ formation of the NHCs by deprotonating the corresponding azolium salts with a weak base such as K_2CO_3 in the presence of [AuCl(SMe₂)]. We performed this reaction with Fb-I as the NHC precursor and obtained a mixture of [FbAuI] (major compound) and [FbAuCl] (minor compound) complexes according to mass spectrometry. Then, Fb-BF4 was used as an NHC precursor to prevent the formation of [FbAuI]. In this case, K₂CO₃ was not strong enough to deprotonate the imidazolium ring, because Fb-BF₄ could be recovered. Knowing that, we used KOtBu as a stronger base (Scheme 1, procedure B), and by reacting Fb-BF₄ with 1.1 equiv of KOtBu and [AuCl(THT)] in THF at 35 °C, the corresponding complex [FbAuCl] was obtained in a moderate yield of 38%. All spectroscopic data are in agreement with the proposed structure for [FbAuCl]. A broad signal at δ -2.95 ppm corresponding to the two inner NHs of the free base porphyrin was observed in its ¹H NMR spectrum. The signal of the carbene was also observed at δ 182.0 ppm in its ${}^{13}C{}^{1}H$ NMR spectrum. By use of the same synthetic strategy, the complex [**NiAuCl**] was obtained in 34% yield. Although the yields obtained in both cases by procedure B were rather low, the formation of undesired side products was not observed and the remaining starting materials **Fb-BF**₄ and **Ni-BF**₄ could be recovered after purification by column chromatography.

Cationic bis-carbenic $[(NHC)Au(NHC)]^+$ complexes were then obtained by reacting the aforementioned [(NHC)AuCl]complexes with another 1 equiv of NHC generated in situ (Scheme 2). Ni-BF₄ and Fb-BF₄ were used as NHC precursors

Scheme 2. Synthesis of [NiAuNi]BF₄, [FbAuFb]BF₄, and [NiAuFb]BF₄ Complexes



and deprotonated in situ by K_2CO_3 in acetone.²¹ The homoleptic complexes [NiAuNi]BF4 and [FbAuFb]BF4 were obtained following this procedure in 77 and 78% yields, respectively. MALDI-TOF mass spectrometry provided evidence for the formation of these homoleptic bis(NHC)-Au complexes. The molecular peaks corresponding to the cationic species $[NiAuNi]^+$ and $[FbAuFb]^+$ were observed at m/z2121.7 and 2010.0, respectively (Figures S17 and S25 in the Supporting Information). The ¹H and ¹³C{¹H} NMR spectra of these complexes showed the expected signals. For examples, the ${}^{13}C{}^{1}H$ NMR signals of the carbones were observed at 193.9 and 194.5 ppm, respectively, for $[NiAuNi]BF_4$ and [FbAuFb]BF₄ (Figures S16 and S23 in the Supporting Information). The presence of BF_4^- anions was confirmed by ¹⁹F NMR spectroscopy (Figures S15 and S24 in the Supporting Information). Energy-dispersive X-ray (EDX) spectroscopy was also used to characterize these complexes, which allows elemental analyses of materials with two or more transition metals and/or halides and determination of their ratios.^{15,16} Indeed, the EDX analysis of [NiAuCl] showed a chemical composition of Ni/Au/Cl in a ca. 1/1/1 ratio, in accordance with the proposed structure. Conversely, a chemical composition of Ni/Au/Cl in a ca. 2/1/0 ratio was observed for [NiAuNi]BF₄, confirming that one Au cation is coordinated by two NHC ligands.

Although the synthesis of heteroleptic bis-carbenic Au complexes remains relatively scarce, some examples can be

found in the literature.²²⁻²⁴ Notably, Nolan and co-workers reported the use of Au hydroxide complexes [(NHC)Au(OH)] as precursors to obtain heteroleptic cationic complexes $[(NHC^{a})Au(NHC^{b})]^{+}$ by protonolysis with the appropriate imidazolium salts.²² Recently, Cazin and co-workers reported a straightforward route permitting the formation of heteroleptic [(NHC^a)Au(NHC^b)]⁺ complexes under microwave irradiation with imidazolium salts, [(NHC)AuCl] complexes, and NaOH as reagents.²³ In the present study, we used the same conditions to synthesize homoleptic and heteroleptic complexes. The heteroleptic complex [NiAuFb]BF₄ was obtained in 75% yield by reacting the complex [NiAuCl] with 1 equiv of imidazolium salt Fb-BF₄ in the presence of potassium carbonate in acetone (Scheme 2). Spectroscopic data are in accordance with the proposed structure for [NiAuFb]BF4. Two sets of signals corresponding respectively to the Ni and free base porphyrins were observed in the ¹H and ¹³C{¹H} NMR spectra, including the two signals of the carbenes at δ 194.7 and 194.2 ppm in its ¹³C{¹H} NMR spectrum (Figure S33 in the Supporting Information). The molecular peak corresponding to the cationic species [NiAuFb]⁺ was observed at m/z = 2065.9 by MALDI-TOF mass spectrometry (Figure S34 in the Supporting Information). EDX analyses of [NiAuFb]BF₄ showed a chemical composition of Ni/Au/Cl in a ca. 1/1/0 ratio consistent with the proposed structure.

In the course of these studies, we observed a strong modulation of the coordination properties of the peripheral NHC ligand upon deprotonating the inner NH. Complex [FbAuCl] was obtained in a moderate yield of 38% when using 1.1 equiv of KOtBu as base (Scheme 1, procedure B). Under these conditions, the color of the reaction mixture remained purple, indicating that the inner NHs of the porphyrin free base were not deprotonated. However, the reaction mixture turned green when using 3.3 equiv of KOtBu as the deprotonation of the inner NH of the porphyrin takes place, followed by the formation of the NHC. The appearance of negative charges in the inner core of the porphyrin has dramatic effects on the reactivity of the peripheral NHC. Indeed, bis-carbenic [FbAuFb]BF₄ and monocarbenic [FbAuCl] complexes were obtained in 82% and 9% yields, respectively (molar ratio bis/ mono $\sim 80/20$, Scheme 3). Surprisingly, the bis-carbenic complex [FbAuFb]BF4 was obtained as the major compound despite the use of 1 equiv of [AuCl(THT)]. Presumably, the

Scheme 3. Reactivity of $Fb-BF_4$ and $Ni-BF_4$ toward 1 equiv of [AuCl(THT)] with 3.3 equiv of KOtBu



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generated anionic NHC in situ exerts a higher trans effect able to weaken the Au–Cl bond in the intermediate monocarbenic complex, thus promoting the formation of the corresponding bis-carbenic complex. In order to verify this hypothesis, the same reaction with Ni-BF₄ and 3.3 equiv of KOtBu as reagents was performed. The Ni(II) acts as a *protecting group* preventing the appearance of negative charges in the inner core of the porphyrin. On the basis of the same procedure, the bis-carbenic [NiAuNi]BF₄ and mono-carbenic [NiAuCl] complexes were obtained in 19 and 44% yields, respectively (molar ratio bis/ mono ~15/85, Scheme 3). The increase in quantity of base improved the yield of [NiAuCl] in comparison to the experiment with 1.1 equiv of KOtBu (Scheme 1, procedure B, yield of 34%). However, the high-yield formation of the biscarbenic [NiAuNi]BF₄ complex did not occur.

Electronic and Photophysical Properties. The electronic interactions between the porphyrin moieties may be estimated from their electronic spectra and their electrochemical properties.²⁵ The UV–visible spectra of the homoleptic complexes correspond to the superimposition of the spectra of the two corresponding monomers (Figure 2 and



Figure 2. UV-visible spectra of [NiAuCl] (solid line) and $[NiAuNi]BF_4$ (dashed line) in CH_2Cl_2 at 298 K.

Figures S36–S38 in the Supporting Information). This fact and the finding that there is also no substantial shifting or splitting of the absorption bands on going from the monomeric [MAuCl] to the dimeric species [MAuM]BF₄ (M = Ni, Fb) show that the electronic communication between the two chromophores within dimeric species is minimal or non-existent.

This absence of electronic communication is also confirmed by electrochemical analyses. The cyclic voltammograms (CVs) measured in CH₂Cl₂/0.1 M TBAPF₆ for all species are presented in Figure S43 in the Supporting Information (all potential values given in the text or in the Supporting Information are referenced vs the saturated KCl calomel electrode, SCE). CVs of [NiAuCl] and [NiAuNi]BF₄ are represented in Figure 3. Table 1 gathers the redox potentials extracted from the CVs. The cyclic voltammogram of [FbAuCl] exhibits two reversible monoelectronic porphyrin ring centered oxidations at $E_{1/2} = 0.925$ and 1.130 V, leading to the cation radical (H₂P^{•+}) and dication (H₂P²⁺), respectively, and two reversible monoelectronic porphyrin ring centered



Figure 3. Cyclic voltammograms of [NiAuCl] (top) and [NiAuNi]-BF₄ (bottom) in CH₂Cl₂ 0.1 M TBAPF₆ ($C = 5 \times 10^{-4}$ M, $\nu = 0.1$ V s⁻¹, working electrode glassy carbon, i.d. 3 mm).

reductions at $E_{1/2} = -1.180$ and -1.410 V, leading to the anion radical $(H_2P^{\bullet-})$ and dianion (H_2P^{2-}) , respectively, as expected for free base porphyrins.²⁶ Thus, the carbene-Au-Cl moiety is not electroactive in the -2.0 to +2.2 V potential range. A similar behavior is observed for [NiAuCl], with both oxidation processes (Ni(II)P \rightarrow Ni(II)P⁺ \rightarrow Ni(II)P²⁺) occurring at $E_{1/2}$ = 1.015 and 1.215 V and both reductions (Ni(II)P \rightarrow $Ni(II)P^{\bullet-} \rightarrow Ni(II)P^{2-}$ noted at $E_{1/2} = -1.230$ and -1.660 V. However, for this Ni(II) complex, a third pseudoreversible oxidation is observed at $E_{1/2}$ = 1.875 V (peak O3, top of Figure 3). This latter wave has previously been assigned to the Ni(II)/Ni(III) redox couple.²⁷ This peak also reveals a shoulder at ~1.84 V. This unexpected additional redox system is absent from the CV of $[NiAuNi]BF_4$. This redox system likely arises from an unknown product which is generated by a chemical reaction subsequent to the electron transfer. The CVs of the homoleptic complexes [NiAuNi]BF₄ and [FbAuFb]BF₄ are practically identical with those of their respective monomers, as exemplified in Figure 3 for [NiAuCl] and [NiAuNi]BF₄. The maximum difference is only ± 30 mV in comparison to their redox potentials (Table 1). This similarity supports that each porphyrin unit in the dimer does not interact, or only very weakly, with the other porphyrin through the carbene-Aucarbene fragment.

This feature is also observed in the CV of the heteroleptic dimer [NiAuFb]BF₄, since it exactly corresponds to the superimposition of the CVs of complexes [NiAuCl] and [FbAuCl] (Figure S43 in the Supporting Information). Thus, five oxidations are observed though the first four oxidations and appear as two merged systems and consequently only two oxidation peaks are reliably addressable. According to the potential values of the monomers and the expected lack of electronic communication for this heteroleptic dimer, these five oxidations appear to successively correspond to (i) oneelectron oxidation of the free base porphyrin moiety $(H_2P \rightarrow$ $H_2P^{\bullet+}$), (ii) one-electron oxidation of the nickel(II) porphyrin moiety $(Ni(II)P \rightarrow Ni(II)P^{\bullet+})$, (iii) one-electron oxidation of the free base porphyrin $(H_2P^{\bullet+} \rightarrow H_2P^{2+})$, (iv) one-electron oxidation of the nickel(II) porphyrin ($\tilde{Ni}(II)P^{\bullet+} \rightarrow Ni(II)P^{2+}$), and (v) one-electron oxidation of the nickel(II) metal into Ni(III). In the negative potential region, four reductions can be identified, though the first two reductions are merged. Expectedly, these reductions appear in the following order:

$E_{1/2} (\Delta E_{\rm p})$							
compound	1st oxidn	2nd oxidn	3rd oxidn	1st redn	2nd redn	3rd redn	HOMO–LUMO gap ^b
[FbAuCl]	0.925 (80)	1.13 (70)		-1.18 (80)	-1.410 (70)		2.105
[NiAuCl]	1.015 (80)	1.215 (90)	1.94/1.81 ^c	-1.23 (80)	-1.660 (85)		2.240
[FbAuFb]BF4	0.945 (80)	1.14 (90)		-1.15 (105)	-1.395 (80)		2.094
[NiAuNi]BF ₄	1.025 (90)	1.21 (110)	1.855 (125)	-1.21 (105)	-1.665 (100)		2.234
[NiAuFb]BF4	1.06/0.915 ^c	1.26/1.11 ^c	1.855 (110)	$-1.11/-1.255^{c}$	-1.400 (80)	-1.660 (135)	~2.11

^{*a*}Abbreviations: oxidn, oxidation; redn, reduction. Unless otherwise noted, redox potentials correspond to $E_{1/2} = (E_{pa} + E_{pc})/2$ and are given in V vs SCE. Values in parentheses correspond to $\Delta E_p = |E_{pa} - E_{pc}|$ and are given in mV. ^{*b*}Experimental HOMO–LUMO gap = $E_{1/2}(1$ st oxidn) – $E_{1/2}(1$ st redn). ^{*c*} E_{pa}/E_{pc} values are given since these redox systems corresponds to the superimposition of two merging systems.

(i) first reduction corresponding to the one-electron reduction of the free base porphyrin moiety $(H_2P \rightarrow H_2P^{\bullet-})$, (ii) first one-electron reduction of the nickel(II)porphyrin (NiP \rightarrow NiP^{•-}), (iii) second one-electron reduction of free base porphyrin $(H_2P^{\bullet-} \rightarrow H_2P^{2-})$, and (iv) second one-electron reduction of the nickel(II) porphyrin (NiP^{•-} \rightarrow NiP²⁻). In conclusion, the level of electronic communication in the homoleptic and heteroleptic dimers is essentially nonexistent.

To explain these electronic properties, computational studies were performed. The geometries of [**FbAuCl**] and [**FbAuFb**]⁺ were first optimized by DFT (B3LYP; Figure 4). As expected,



Figure 4. Representation of the frontier molecular orbitals and corresponding energies for gold complexes: (a) [FbAuCl] and (b) $[FbAuFb]^+$.

the HOMO and LUMO exhibit the π -systems of the porphyrin. Clearly, no atomic contribution of the carbene and gold units has been computed for both complexes. This lack of contribution unambiguously explains the absence of electronic communication across the bridge in the dimer, as concluded by UV-visible spectroscopy and the CVs.17b,25 Consequently, there is no frontier MO coupling between the two porphyrins, thus corroborating the fact that the two porphyrins behave as two disconnected chromophores within the dimeric species. The fluorescence bands for both chromophores [FbAuCl] (Figures S39 and S40 in the Supporting Information) and [FbAuFb]BF₄ (Figures S41 and S42 in the Supporting Information) exhibit two peaks, the 0-0 component of which overlaps strongly with that of the absorption. The excitation spectra superimpose well with the absorption bands, indicating that the species which emits is the same as that which absorbs. Thus, the nature of the

emitting state is again the typical π -excited state. Again, the fluorescence peaks are essentially the same between the two species, thus corroborating the absence of electronic communication in the excited state as well.

Au(I) complexes with NHC ligands are considered as promising new metal-based anticancer drugs.^{2,3} Porphyrins are also efficient photosensitizers (PS) for photodynamic therapy (PDT).²⁸ Indeed, such porphyrin-NHC-Au(I) conjugates may be interesting for dual therapy by combining the cytotoxic effect of Au(I) in the dark with an additional photodynamic effect of the porphyrin upon irradiation. To study the influence of the peripheral Au(I) complex on the ability of the porphyrin core to generate singlet oxygen $({}^{1}O_{2})$ under illumination, the photo-oxidation of a biological molecule such as cholesterol, which can be easily monitored by ¹H NMR spectroscopy, was performed (Figure 5 and Figure S44 in the Supporting Information).²⁹ The free base 5,10,15,20-meso-tetrakis(4-tertbutylphenyl)porphyrin (i.e., the porphyrin core of Fb-BF₄ without the peripheral imidazolium ring), labeled H₂TPP- $(tBu)_4$ in Figure 5, was also tested for comparison. Interestingly, both the imidazolium salt Fb-BF4 and the gold



Figure 5. Photochemical oxidation of cholesterol. Experimental conditions: in C_6D_6 (500 μ L) with cholesterol/PS = 200, cholesterol (5.2 × 10⁻² M) and PS (2.6 × 10⁻⁴ M), 2h 30 min of irradiation (500 W halogen lamp, with filter λ >510 nm). Irradiation experiments were reproduced three times. TON = turnover number, i.e. moles of oxidized cholesterol/mol of PS after 2h 30 min, estimated by ¹H NMR spectroscopy (see Figure S44 in the Supporting Information). The asterisk (*) indicates that this PS was only partially soluble in C_6D_6 : its effective concentration in the course of the experiment was lower, explaining the lower TON.

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complex [FbAuCl] are able to photo-oxidize cholesterol. The complex [FbAuCl] is a better PS in comparison to the nonfunctionalized porphyrin $H_2TPP(tBu)_4$. (average TON 16.3 vs 10.7). This additional phototodynamic effect may be attributed to the "heavy atom" effect of Au(I) at the periphery of the porphyrin, promoting the intercrossing system $S_1 \rightarrow T_1$ and causing the subsequent formation of ${}^{1}O_{2}$ to occur.³⁰ This is consistent with the decrease in fluorescence quantum yields $(\Phi_{\rm F} = 0.22 \text{ and } 0.038)$ and lifetimes $(\tau_{\rm F}(298 \text{ K}) = 5.85 \pm 0.1 \text{ ns})$ $(\lambda_{em} 672 \text{ nm})$ and $4.08 \pm 0.1 \text{ ns} (\lambda_{em} 679 \text{ nm}))$ when going from Fb-I^{17b} to [FbAuCl] (Table S1 in the Supporting Information). The homoleptic complex [FbAuFb]BF₄ generates ${}^{1}O_{2}$ as well, but this cationic species is poorly soluble in C_6D_6 , explaining its lower activity. As expected, the Ni(II) complexes are photochemically inert. All compounds appeared stable under irradiation because their UV-visible spectra remained similar during irradiation, indicating that no decomposition of the porphyrin core occurred.

CONCLUSION

Porphyrins fused to imidazolium salts were successfully used as NHC precursors to synthesize mono- and bis-carbenic Au(I) complexes following different synthetic procedures. The synthesis of bis-carbenic complexes is readily straightforward by using monocarbenic complexes as starting materials. The [NiAuFb]BF₄ complex that now joins the family of rare examples of heteroleptic bis-carbenic complexes was prepared. These complexes are very stable and are easily purified by SiO₂ column chromatography before recrystallization. Interestingly, we showed for the NHC fused to the free base porphyrin that its reactivity toward Au(I) could be modulated simply by deprotonating the inner NH of the porphyrin with a base. Indeed, the formation of the monocarbenic complex **[FbAuCl]** was observed with the porphyrin in its free base state (i.e., with two NH groups in the porphyrin core), whereas the biscarbenic complex [FbAuFb]BF4 was preferentially obtained when deprotonating the inner NH groups of the porphyrin with KOtBu. For bis-carbenic complexes where the two porphyrins are linked together by one Au(I) cation, there is no electronic communication between the porphyrins through the assembling metal, as demonstrated by UV-visible spectroscopy and electrochemical studies. According to DFT calculations, this absence of coupling can be attributed to the lack of atomic contribution of the carbene ligand and the Au(I) cation in the frontier MOs. Finally, the ability of Fb-BF4 and the corresponding gold complex [FbAuCl] to generate ¹O₂ was demonstrated through the photo-oxidation of cholesterol. The use of such compounds combining a metallodrug and a photosensitizer for chemo-photodynamic dual therapy is clearly appealing and should be developed in the future.

EXPERIMENTAL SECTION

Materials. The syntheses of imidazolium salts Ni-I, Ni-BF₄, Fb-I, and Fb-BF₄ are described in ref 14a. Reactions were performed under argon using oven-dried glassware and Schlenk techniques. The gold complex [AuCl(THT)] was prepared by the procedure described in ref 31. Acetone (CHROMASOLV, for HPLC, \geq 99.9%) was purchased from Sigma-Aldrich. Dry THF and CH₂Cl₂ were obtained by a PureSolve MD5 solvent purifications system from Innovative Technology. Preparative purifications were performed by silica gel flash column chromatography (Merck 40–60 μ M). Solvents used as eluents are technical grade. ¹H, ¹⁹F, and ¹³C{¹H} spectra were recorded on a Bruker 300 or 400 MHz spectrometer, and all NOESY experiments were recorded on the 400 MHz spectrometer. ¹H and ¹³C{¹H} NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the solvent as an internal standard. ¹⁹F NMR spectra were calibrated to CFCl₃ on the basis of this external reference standard. Abbreviations used for ¹H NMR spectra are as follows: s, singlet; d, doublet. UV/vis absorption spectra were recorded in CH₂Cl₂ with a JASCO V-760 UV–visible–NIR spectrophotometer in 10 mm quartz cells (Hellma). High-resolution mass spectra (HRMS) were recorded on ESI-TOF Q instruments in positive mode or on a MALDI-TOF spectrometer in positive mode using dithranol as a matrix and PEG as the internal reference. Elemental analyses were performed using an Elementar Vario Micro Cube instrument.

Synthesis of [NiAuCl]. Procedure A. A solution of the porphyrin Ni-I (100 mg, 9.2×10^{-5} mol) was prepared in CH₂Cl₂ (10 mL). Then, Ag₂O (21 mg, 9.2×10^{-5} mol, 1 equiv) was added and the reaction mixture was vigorously stirred at room temperature, under an argon atmosphere protected from light. After 6 h, [AuCl(THT)] (30 mg, 9.2×10^{-5} mol, 1 equiv) was added and the mixture was stirred for an additional 12 h under the same conditions. The reaction was monitored by TLC analysis. When the reaction was complete, the solvent was evaporated and the title compound was purified by column chromatography (SiO₂; eluent CH₂Cl₂/*n*-hexane 7/3). Crystallization from CH₂Cl₂/MeOH afforded [NiAuCl] as red needles in 50% yield (55 mg).

Procedure B. A solution of the porphyrin Ni-BF4 (40 mg, 3.8 \times 10^{-5} mol, 1 equiv) and [AuCl(THT)] (12.2 mg, 3.8×10^{-5} mol, 1 equiv) was prepared in dry THF (6 mL). Then, KOtBu (5.1 mg, $4.6 \times$ 10^{-5} mol, 1.1 equiv) was added and the reaction mixture was stirred at room temperature under an argon atmosphere. After 20 h, the solvent was evaporated and the title compound was purified by column chromatography (SiO₂; eluent from CH₂Cl₂ to CH₂Cl₂/MeOH 95/ 5). Crystallization from CH2Cl2/MeOH afforded [NiAuCl] as red needles in 34% yield (15 mg). The starting material Ni-BF4 was recovered partially after column chromatography (10 mg). ¹H NMR (300 MHz, CDCl₃): δ 8.71 (s, 2H, H_{pyrr}), 8.67 (s, 4H, H_{pyrr}), 8.08 (d, 4H, H_{Ar ortho}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.97 (d, 4H, H_{Ar ortho}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.97 (d, 4H, H_{Ar ortho}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.78 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.72 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.73 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.74 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, H_{Ar meta}, ${}^{3}J_{H-H} = 8.3 \text{ Hz}$), 7.75 (d, 4H, Hz), 3.15 (s, 6H, H_{NMe}), 1.56 (s, 18H, H_{tBu}), 1.55 (s, 18H, H_{tBu}) ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 182.3 (C_{carbene}), 152.9, 151.2, 144.7, 144.1, 143.6, 140.2, 137.8, 137.1, 135.3, 134.1, 132.8, 132.5, 132.4, 126.9, 125.2, 124.3, 120.8, 116.1, 37.9 (C_{NMe}), 35.2, 35.1, 31.8 (C_{tBu}), 32.7 (C_{tBu}) ppm. UV/vis (CH₂Cl₂): λ_{max} (log ε) 426 (5.41), 537 (3.76), 573 (4.26 L mol⁻¹ cm⁻¹) nm. HR-MS (MALDI-TOF): m/z calcd for C₆₃H₆₄AuClN₆Ni [M]⁺ 1194.3900, found 1194.3892. Anal. Calcd for C₆₃H₆₄N₆NiAuCl·H₂O [1214.37 g/mol]: C, 62.31; H, 5.48; N, 6.92. Found: C, 62.16; H, 4.97; N, 7.02.

Synthesis of [FbAuCl]. *Procedure A.* This procedure was similar to procedure A described for the synthesis of [NiAuCl]. The target compound could not be obtained following this procedure.

Procedure B. A solution of the porphyrin $Fb-BF_4$ (35 mg, 3.5 \times 10^{-5} mol, 1 equiv) and [AuCl(THT)] (11.2 mg, 3.5×10^{-5} mol, 1 equiv) was prepared in dry THF (10 mL). Then, KOtBu (4.3 mg, 3.9 \times 10⁻⁵ mol, 1.1 equiv) was added and the reaction mixture was stirred at room temperature under an argon atmosphere. After 20 h, the solvent was evaporated and the title compound was purified by column chromatography (SiO₂; eluent from CH₂Cl₂ to CH₂Cl₂/ MeOH 95/5). Crystallization from CH₂Cl₂/MeOH afforded [FbAuCl] as a purple powder in 38% yield (15 mg). The starting material Fb-BF4 was recovered partially after column chromatography (5 mg). ¹H NMR (400 MHz, CD_2Cl_2): δ 8.94 (d, 2H, H_{pyrr} , ³ J_{H-H} = $= 8.3 \text{ Hz}), 2.71 \text{ (s, 6H, } H_{\text{NMe}}), 1.65 \text{ (s, 18H, } H_{\text{(Bu)}}), 1.48 \text{ (s, 18H, } H_{\text{(Bu)}}), -2.95 \text{ (broad s, 2H, } H_{\text{NH}}) \text{ ppm.} \quad {}^{13}\text{C}{}^{1}\text{H} \text{ NMR} \text{ (100.6 MHz)}, 100.6 \text{ MHz}, 100.6 \text$ CD₂Cl₂): δ 182.0 (C_{carbene}), 156.2, 153.0, 151.7, 142.5, 139.5, 139.5, 139.3, 139.0, 139.0, 136.8, 135.6, 134.9, 129.0, 129.0, 125.5, 124.6, 121.8, 117.9, 37.5 ($C_{\rm NMe}$), 35.4, 35.3, 31.9 ($C_{\rm fBu}$), 31.8 ($C_{\rm fBu}$) ppm. UV/vis (CH_2Cl_2) : $\lambda_{max} (\log \varepsilon) 429 (5.60), 527 (4.25), 566 (4.09), 599 (3.79), 661 (3.75 L mol⁻¹ cm⁻¹) nm. HR-MS (MALDI-TOF):$ *m*/z calcd for C₆₃H₆₇AuClN₆ [M + H]⁺ 1139.4781, found 1139.4768. Anal.

Calcd for $C_{63}H_{66}N_6AuCl\cdot CH_2Cl_2$ [1222.42 g/mol]: C, 62.77; H, 5.60; N, 6.86. Found: C, 62.24; H, 5.28; N, 6.88.

Synthesis of [NiAuNi]BF₄. From [NiAuCl] as Starting Material. A solution of the porphyrin Ni-BF₄ (100 mg, 9.5×10^{-5} mol, 1 equiv) and [NiAuCl] (125 mg, 1.0×10^{-4} mol, 1.1 equiv) was prepared in an acetone/THF (85/15 v/v) mixture (35 mL). Then, K₂CO₃ (17 mg, 1.2×10^{-4} mol, 1.3 equiv) was added and the reaction mixture was vigorously stirred at room temperature under an argon atmosphere. After 15 h, the solvent was evaporated and the target compound was purified by column chromatography (SiO₂; eluent from CH₂Cl₂ to CH₂Cl₂/MeOH 95/5). Crystallization from CH₂Cl₂/*n*-pentane afforded [NiAuNi]BF₄ as red needles in 77% yield (161 mg).

From [AuCl(THT)] as Starting Material. A solution of the porphyrin Ni-BF₄ (35 mg, 3.3×10^{-5} mol, 1 equiv) and [AuCl(THT)] (5.3 mg, 1.7×10^{-5} mol, 0.5 equiv) was prepared in dry THF (3 mL). Then, KOtBu (12.2 mg, 1.1×10^{-4} mol, 3.3 equiv) was added and the reaction mixture was stirred at room temperature under an argon atmosphere. After 1.5 h, the solvent was evaporated and the target compound was purified by column chromatography (SiO₂; eluent from CH₂Cl₂ to CH₂Cl₂/MeOH 95/5). Crystallization from CH₂Cl₂/n-pentane afforded [NiAuNi]BF₄ as red needles in 48% yield (17 mg). ¹H NMR (400 MHz, CDCl₃): δ 8.72 (s, 4H, H_{pyrr}), 8.69 (d, 4H, H_{pytr} , ${}^{3}J_{H-H} = 5.0 \text{ Hz}$), 8.67 (d, 4H, H_{pytr} , ${}^{3}J_{H-H} = 5.0 \text{ Hz}$), 8.11 (d, 8H, $H_{Ar ortho}$, ${}^{3}J_{H-H} = 8.0 \text{ Hz}$), 7.94 (d, 8H, $H_{Ar ortho}$, ${}^{3}J_{H-H} = 8.4 \text{ Hz}$), 7.84 (d, 8H, $H_{Ar metor}$, ${}^{3}J_{H-H} = 8.0 \text{ Hz}$), 7.72 (d, 8H, $H_{Ar metor}$, ${}^{3}J_{H-H} = 8.4 \text{ Hz}$), 3.20 (s, 12H, H_{NMe}), 1.55 (s, 36H, H_{fBu}), 1.54 (s, 36H, H_{cBu}), 1.54 (s, 36H, H_{cBu}), 1.55 (s, 26C) H_{tBu} ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 193.9 (C_{carbene}), 153.7, 153.2, 151.4, 144.5, 143.9, 140.9, 137.7, 137.7, 136.8, 135.2, 134.0, 133.3, 133.0, 132.8, 125.7, 125.5, 124.4, 121.2, 115.9, 37.0 (C_{NMe}) , 35.2, 35.0, 31.7 (C_{tBu}) , 31.7 (C_{tBu}) ppm. ¹⁹F NMR (282.2 MHz, CDCl₃): δ –154.16 (s, ¹⁰BF₄), –154.22 (s, ¹¹BF₄) ppm. UV/vis $(CH_2Cl_2): \lambda_{max} (\log \varepsilon) 429 (5.61), 538 (4.52), 571 (4.01 L mol⁻¹)$ cm⁻¹) nm. HR-MS (ESI): m/z calcd for $C_{126}H_{128}N_{12}AuNi_2$ [M – BF₄]⁺ 2121.8752, found 2121.8805. Anal. Calcd for N, 7.32. Found: C, 66.35; H, 5.66; N, 7.49.

Synthesis of [FbAuFb]BF₄. From [FbAuCl] as Starting Material. A solution of the porphyrin Fb-BF₄ (100 mg, 1.0×10^{-4} mol, 1 equiv) and [FbAuCl] (126 mg, 1.1×10^{-4} mol, 1.1 equiv) was prepared in an acetone/THF (85/15 v/v) mixture (35 mL). Then, K₂CO₃ (18 mg, 1.2×10^{-4} mol, 1.3 equiv) was added and the reaction mixture was vigorously stirred at room temperature under an argon atmosphere. After 15 h, the solvent was evaporated and the target compound was purified by column chromatography (SiO₂; eluent from CH₂Cl₂/*n*-hexane afforded [FbAuFb]BF₄ as a purple powder in 78% yield (163 mg).

From [AuCl(THT)] as Starting Material. A solution of the porphyrin \mathbf{Fb} - \mathbf{BF}_4 (35 mg, 3.5 \times 10⁻⁵ mol, 1 equiv) and [AuCl(THT)] (5.6 mg, 1.8×10^{-5} mol, 0.5 equiv) was prepared in dry THF (3 mL). Then, KOtBu (13.0 mg, 1.2×10^{-4} mol, 3.3 equiv) was added and the reaction mixture was stirred at room temperature under an argon atmosphere. After 1.5 h, the solvent was evaporated and the target compound was purified by column chromatography (SiO₂; eluent from CH₂Cl₂ to CH₂Cl₂/MeOH 95/5). Crystallization from CH_2Cl_2/n -hexane afforded [FbAuFb]BF₄ as a purple powder in 48% yield (17 mg). ¹H NMR (400 MHz, CD₂Cl₂): δ 9.02 (d, 4H, $\begin{array}{l} \text{H}_{\text{pyrr}}, \, ^{3}_{\text{H}-\text{H}} = 5.0 \text{ Hz}), \, 8.95 \text{ (d, 4H, }_{\text{H}_{\text{pyrr}}}, \, ^{3}_{\text{H}-\text{H}} = 5.0 \text{ Hz}), \, 8.95 \text{ (d, 4H, }_{\text{H}_{\text{pyrr}}}, \, ^{3}_{\text{H}-\text{H}} = 5.0 \text{ Hz}), \, 8.75 \text{ (s, 4H, }_{\text{H}_{\text{pyrr}}}), \, 8.45 \text{ (d, 8H, }_{\text{Ar orthov}}, \, ^{3}_{\text{J}_{\text{H}-\text{H}}} = 8.0 \text{ Hz}), \, 8.19 \text{ (d, 8H, }_{\text{H}_{\text{Ar orthov}}}, \, ^{3}_{\text{J}_{\text{H}-\text{H}}} = 8.0 \text{ Hz}), \, 7.85 \text{ (d, 8H, }_{\text{H}_{\text{Ar orthov}}}, \, ^{3}_{\text{J}_{\text{H}-\text{H}}} = 8.0 \text{ Hz}), \, 7.85 \text{ (d, 8H, }_{\text{H}_{\text{Ar orthov}}}, \, ^{3}_{\text{J}_{\text{H}-\text{H}}} = 8.0 \text{ Hz}), \, 7.85 \text{ (d, 8H, }_{\text{H}_{\text{H}_{\text{orthov}}}, \, ^{3}_{\text{J}_{\text{H}-\text{H}}} = 8.0 \text{ Hz}), \, 7.85 \text{ (d, 8H, }_{\text{H}_{\text{H}_{\text{metav}}}, \, ^{3}_{\text{J}_{\text{H}-\text{H}}} = 8.0 \text{ Hz}), \, 7.85 \text{ (d, 8H, }_{\text{H}_{\text{H}_{\text{H}_{\text{H}}}}), \, 1.63 \text{ (s, 36H, }_{\text{H}_{\text{fBu}}}), \, 1.62 \text{ (s, 36H, }_{\text{H}_{\text{fBu}}}), \, -2.90 \text{ (broad s, 4H, }_{\text{H}_{\text{NH}}}), \, \text{ppm.}^{-13}\text{C}^{\{1\text{H}\}} \text{ NMR} \end{array}$ (100.6 MHz, CD_2Cl_2): δ 194.5 ($C_{carbene}$), 156.5, 153.2, 151.8, 143.6, 139.8, 139.7, 139.1, 138.9, 137.2 (2C), 135.5, 135.0, 129.2 (2C), 125.8, 124.6, 122.1, 118.0, 37.7 (C_{NMe}), 35.6, 35.4, 32.0 (C_{fBu}), 32.0 (C_{fBu}), ppm. ¹⁹F NMR (282.2 MHz, CDCl₃): δ –153.33 (s, ¹⁰BF₄), –153.58 (s, ¹¹BF₄) ppm. UV/vis (CH₂Cl₂): λ_{max} (log ε) 433 (5.86), 528 (4.53), 567 (4.39), 601 (4.24), 663 nm (4.15 L mol⁻¹ cm⁻¹) nm. HR-MS (ESI): m/z calcd for $C_{126}H_{132}N_{12}Au \ [M - BF_4]^+$ 2010.0358, found 2010.0419. Anal. Calcd for C126H132N12AuBF4·3CH2Cl2 [2353.08 g/ mol]: C, 65.85; H, 5.91; N, 7.14. Found: C, 65.47; H, 5.74; N, 7.40.

Synthesis of [NiAuFb]BF4. A solution of the porphyrin Fb-BF4 $(70 \text{ mg}, 7.0 \times 10^{-5} \text{ mol}, 1 \text{ equiv})$ and [NiAuCl] (100 mg, 8.5×10^{-5} mol, 1.2 equiv) was prepared in an acetone/THF (85/15 v/v) mixture (35 mL). Then, K_2CO_3 (12 mg, 8.5×10^{-5} mol, 1.2 equiv) was added and the reaction mixture was vigorously stirred at room temperature under an argon atmosphere. After 24 h, the solvent was evaporated and the target compound was purified by column chromatography (SiO₂; eluent from CH₂Cl₂ to CH₂Cl₂/MeOH 95/5). Crystallization from CH_2Cl_2/n -hexane afforded [NiAuFb]BF₄ as a purple powder in 75% yield (114 mg). ¹H NMR (400 MHz, CD₂Cl₂): δ 9.01 (d, 2H, $H_{pyrr,}{}^{3}J_{H-H} = 5.0 \text{ Hz}$, 8.95 (d, 2H, $H_{pyrr,}{}^{3}J_{H-H} = 5.0 \text{ Hz}$), 8.75 (s, 2H, $H_{pyrr,}$), 8.72 (s, 2H, H_{pyrr}), 8.71 (s, 4H, H_{pyrr}), 8.43 (d, 4H, H_{Ar} orthor ${}^{3}J_{H-H}^{II} = 8.2 \text{ Hz}$, 8.18 (d, 4H, H_{Ar ortho}, ${}^{3}J_{H-H}^{II} = 8.1 \text{ Hz}$), 8.12 (d, 4H, $\begin{array}{l} H_{Ar \ orthov} \ ^{3}J_{H-H} = 8.3 \ Hz), \ 7.95 \ (d, \ 4H, \ H_{Ar \ orthov} \ ^{3}J_{H-H} = 8.3 \ Hz), \ 7.93 \ (d, \ 4H, \ H_{Ar \ metav} \ ^{3}J_{H-H} = 8.2 \ Hz), \ 7.84 \ (d, \ 4H, \ H_{Ar \ metav} \ ^{3}J_{H-H} = 8.1 \ Hz), \ 7.82 \ (d, \ 4H, \ H_{Ar \ metav} \ ^{3}J_{H-H} = 8.3 \ Hz), \ 7.75 \ (d, \ 4H) \ 7.75 \$ Hz), 3.19 (s, 6H, H_{NMe}), 3.18 (s, 6H, H_{NMe}), 1.62 (s, 18H, H_{fBu}), 1.60 (s, 18H, H_{fBu}), 1.56 (s, 18H, H_{fBu}), 1.55 (s, 18H, H_{fBu}), -2.91 (broad s, 2H, H_{NH}) ppm. ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ 194.7 (C_{carbene}), 194.2 (C_{carbene}), 156.4, 153.3, 153.2, 151.8, 151.7, 145.1, 144.5, 143.9, 143.5, 141.1(2C), 139.8, 139.7, 139.0, 138.9, 138.4, 137.4, 137.2, 135.7, 135.5, 135.0, 134.4, 133.2, 132.8, 132.8, 129.2, 129.2, 127.2, 125.8, 125.7, 124.8, 124.6, 122.0, 121.3, 118.0, 116.5, 37.8 $\begin{array}{l} (C_{\rm NMe}), \ 37.7 \ (C_{\rm NMe}), \ 35.6, \ 35.5, \ 35.4, \ 35.3, \ 32.0 \ (C_{tBu}), \ 32.0 \ (C_{tBu}), \ 31.9 \ (C_{tBu}), \ 31.9 \ (C_{tBu}), \ 31.9 \ (C_{tBu}), \ 91.6 \ (C_{tBu}), \ 31.9 \ (C_{tBu}), \ 31.9$ 432 (5.77), 534 (4.49), 566 (4.20), 600 (3.83), 660 (3.66 L mol⁻¹ cm $^{-1}$ nm. HR-MS (ESI): m/z calcd for $\rm C_{126}H_{130}N_{12}AuNi$ [M -BF₄]⁺ 2065.9555, found 2065.9645. Anal. Calcd for 5.87; N, 7.36. Found: C, 66.91; H, 5.71; N, 7.37.

Electrochemical Studies. All electrochemical manipulations were performed using Schlenk techniques under an atmosphere of dry oxygen-free argon at room temperature (20 \pm 2 °C). The supporting electrolyte was a 0.1 mol L^{-1} TBAPF₆ (tetra-*n*-butylammonium hexafluorophosphate)/CH2Cl2 solution which was degassed under vacuum before use. Voltammetric analyses were carried out in a conventional three-electrode cell. A double-junction saturated calomel electrode (SCE), with background electrolyte between the two frits, was used as the reference electrode. The auxiliary electrode was a platinum slab in an independent compartment filled with the background electrolyte and separated from the analyzed solution by a sintered-glass disk. For all voltammetric measurements, the working electrode was a glassy-carbon (GC) disk electrode (i.d. 3 mm). Before each measurement, the GC electrode was polished with a diamond suspension and rinsed with water. Under these conditions, the Fc⁺/Fc redox potential was found to be 0.46 V vs SCE.

DFT Calculations. All density functional theory (DFT) and timedependent density functional theory (TD-DFT) calculations were performed with Gaussian 09³² at the Université de Sherbrooke with the Mammouth supercomputer supported by Le Réseau Québécois De Calculs Hautes Performances. The DFT geometry optimizations as well as TD-DFT calculations³³ were carried out using the B3LYP method. A 6-31g* basis set was used for the central chromophores, and a 3-21g* basis set was used for solubilizing 4-*tert*-butylphenyl groups.³⁴ VDZ (valence double ζ) with SBKJC effective core potential was used for Au atoms.³⁴ A THF solvent field was applied to all calculations. The calculated absorption spectra were obtained from GaussSum 2.1.³⁵

Absorption, Emission, and Excitation Spectra. All samples were prepared in CH_2Cl_2 or 2-MeTHF (2-methyltetrahydrofuran), which was distilled over CaH_2 under nitrogen. The absorption spectra of the complexes were recorded at 298 K using a Varian Cary 300 spectrophotometer or a HP-8453 diode array spectrophotometer. The steady-state emission and excitation spectra were measured at 298 K in an airtight 1.0 cm capped quartz cell and a 5.0 mm (i.d.) NMR tube inserted into a liquid nitrogen filled quartz EPR Dewar, respectively. The steady state fluorescence (<820 nm) and the corresponding excitation spectra were acquired on an Edinburgh Instruments FLS980 fluorimeter equipped with single monochromators. The fluorescence

lifetimes were measured on the same instrument using an LED laser (excitation at 375 nm. fwhm 90 ps). The quantum yields, $\Phi_{\rm F}$, were measured using H_2TPP (free base 5,10,15,20-meso-tetraphenylporphyrin as the standard, $\Phi_{\rm F}=0.11).^{36}$

X-ray Diffraction Analysis. Crystal evaluation and data collection were performed on a Rigaku-Oxford Diffraction Gemini-S diffractometer with sealed-tube Mo K α radiation using the CrysAlis Pro program.³⁷ This program was also used for the integration of the frames using default parameters, the correction for Lorentz and polarization effects, and the empirical absorption correction using spherical harmonics using symmetry-equivalent and redundant data. The structure was solved using the ab initio iterative charge-flipping method with parameters described elsewhere³⁸ using the Superflip program³⁹ and was refined using full-matrix least-squares procedures as implemented in CRYSTALS⁴⁰ on all independent reflections with I> $2\sigma(I)$. See page S43 in the Supporting Information to obtain more details about the refinement procedure. Crystal data for Fb-I: formula $C_{64}H_{67}Cl_2IN_6$, moiety $C_{63}H_{65}N_6 \cdot CH_2Cl_2I$, T = 175 K, $M_r = 1118.04$, crystal size $0.25 \times 0.30 \times 0.40 \text{ mm}^3$, triclinic, space group $P\overline{1}$, a = 11.3072(10) Å, b = 15.9169(15) Å, c = 18.8810(15) Å, $\alpha = 16.9169(15)$ $100.574(7)^{\circ}, \beta = 107.045(7)^{\circ}, \gamma = 109.056(8)^{\circ}, V = 2920.6(2) \text{ Å}^3, Z = 109.056(8)^{\circ}, \gamma = 1$ 2, $\rho_{\text{calcd}} = 1.271 \text{ g cm}^{-3}$, $\mu = 0.684 \text{ mm}^{-1}$, $\theta_{\text{max}} = 24.952^{\circ}$, experimental resolution 1.05 Å, 14625 reflections measured, 7484 unique reflections, 5017 reflections with $I > 2\sigma(I)$, $R_{int} = 0.065$, $\langle \sigma(I)/I \rangle = 0.1179$, 652 refined parameters, $R1(I > 2\sigma(I)) = 0.1205$, $wR2(I > 2\sigma(I)) = 0.1343$, R1(all data) = 0.1577, wR2(all data) = 0.1690, GOF = 1.1220, $\Delta \rho(\text{min/max}) = -1.21/2.37 \text{ e} \text{ Å}^{-3}.$

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00966.

¹H and ¹³C{¹H} NMR spectra, UV–visible and mass spectra, and cyclic voltammograms for all compounds, excitation and emission spectra and photophysical data for [**FbAuCl**] and [**FbAuFb**]**BF**₄, and details of the crystallographic structure determination of **Fb-I** (PDF) Crystallographic data of **Fb-I** (CIF) Crystallographic data of **Fb-I** (CIF)

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Notes

The authors declare no competing financial interest.

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