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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 Placeholder*

**ABSTRACT:** Porphyrins fused to peripheral *N*-heterocyclic carbenes (NHC) across two neighboring  $\beta,\beta$ -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 ones.

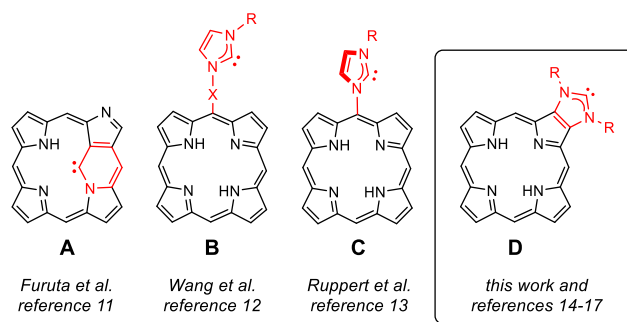
## INTRODUCTION

*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,<sup>1</sup> biomedicine<sup>2,3</sup> and materials science.<sup>4,5</sup> 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,<sup>6</sup> the variation of their electronic properties can be achieved by grafting chemical functions onto the backbone with the desired electron-donating or -accepting characters.<sup>7</sup> For NHCs with identical or at least very similar steric features, the tuning of their electronic properties is of crucial importance for catalytic applications.<sup>1</sup> With regard to facile modulation of the electronic and catalytic properties of their metal complexes, some original NHCs with stimuli-responsive functional groups (redox,<sup>8</sup> pH<sup>9</sup> or light<sup>10</sup>) 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.<sup>11-17</sup> Reported porphyrin–NHC systems differ from 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  $\beta$ -CH are switched), Furuta and coworkers

reported an NHC embedded in a NCP framework (Chart 1, A).<sup>11</sup> This unique structure was serendipitously obtained from the reaction of an inner-methylated NCP with  $\text{Re}_2(\text{CO})_{10}$ , and represents a rare example of NHC located in the inner core of a macrocycle.<sup>18</sup>

**Chart 1. Porphyrin-NHC systems recently reported in the literature.**

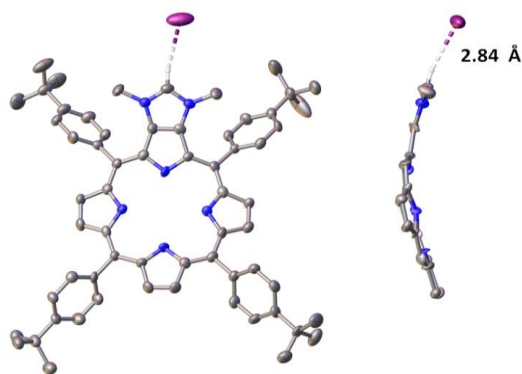


More examples of porphyrins with NHCs linked at their periphery are known in the literature. Wang and coworkers used tetraimidazolium salts as NHC precursors, and imidazoliums are separated from the *meso* positions by  $-(\text{C}_6\text{H}_5)\text{O}(\text{CH}_2)_3-$  spacers (Chart 1, B).<sup>12</sup> Recently, Ruppert and coworkers avoided the use of spacers by introducing azoles directly onto *meso* positions.<sup>13</sup> The alkylation of these compounds afforded porphyrins with *meso* azolium units, which

can 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  $\beta,\beta$ -pyrrolic positions.<sup>14</sup> The deprotonation of the imidazolium ring affords the corresponding NHC (Chart 1, D). Noteworthy, 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.<sup>15</sup> So far, we reported the synthesis of NHC-Rh(I)<sup>15,16</sup> and NHC-Pd(II)<sup>17</sup> 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-BF<sub>4</sub>** and their corresponding nickel(II) complexes **Ni-I** and **Ni-BF<sub>4</sub>** were used as starting materials (Scheme 1).<sup>14a</sup> These species are porphyrins fused to imidazolium salts across two neighboring  $\beta$ -pyrrolic positions. Single crystals of **Fb-I** were obtained by slow diffusion of *n*-pentane in a solution of **Fb-I** in CH<sub>2</sub>Cl<sub>2</sub>. The X-ray diffraction analysis unambiguously establishes its structure (Figure 1). Notably, the porphyrin core is found to be ruffled even in absence of 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  $d_{H-I} = 2.84$  Å.

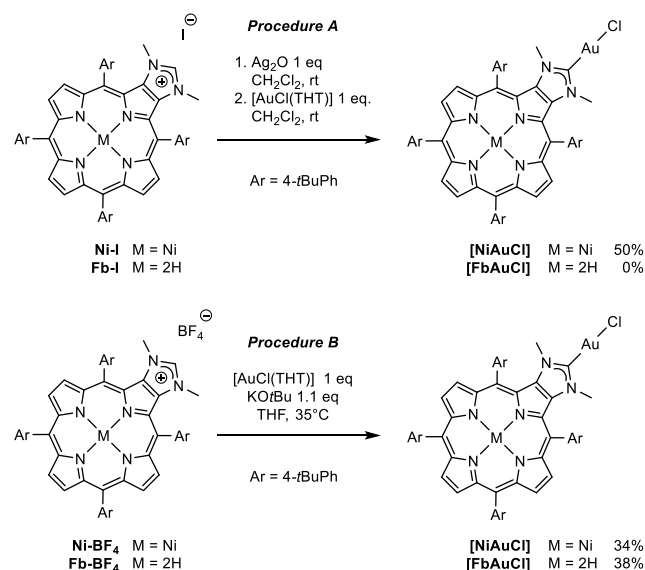


**Figure 1.** ORTEP-views of the molecular structure of the imidazolium salt **Fb-I** with atomic displacement parameters at the 50% probability level. Hydrogen atoms, except the one involved in hydrogen bonding, are omitted for clarity. Left: front view. Right: side view, *meso* aryl groups omitted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

The synthesis of [(NHC)AuCl] complexes was achieved following different procedures. First, the well-known preliminary formation of NHC-silver complexes was performed with Ag<sub>2</sub>O 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 <sup>1</sup>H NMR spectroscopy because the signal arising from the imidazolium proton at  $\delta = 11.07$  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  $\delta = 182.3$  ppm in its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum and is in good agreement with data reported in the literature for [(NHC)AuCl] complexes.<sup>3</sup> However, the same synthetic approach proved to be unsuccessful to obtain the desired complex **[FbAuCl]**. We presume that silver ion could be trapped by the free base porphyrin core, thus preventing the formation of the NHC-Ag bond.<sup>19</sup> Indeed, alternative *silver-free* synthetic procedures were then sought. Recently, Nolan, Gimeno and their co-workers reported improved one-step procedures to obtain [(NHC)AuCl] complexes.<sup>20</sup> They consist in the *in situ* formation of the NHCs by deprotonating the corresponding azolium salts with a weak base such as K<sub>2</sub>CO<sub>3</sub> in the presence of [AuCl(SMe<sub>2</sub>)]. We performed this reaction with **Fb-I** as NHC precursor and obtained a mixture of **[FbAuI]** (major compound) and **[FbAuCl]** (minor compound) complexes according to mass spectrometry. Then, **Fb-BF<sub>4</sub>** was used as NHC precursor to prevent the formation of **[FbAuI]**. In this case, K<sub>2</sub>CO<sub>3</sub> was not strong enough to deprotonate the imidazolium ring because **Fb-BF<sub>4</sub>** could be recovered. Knowing that, we used KO<sup>*t*</sup>Bu as stronger base (Scheme 1, Procedure B) and by reacting **Fb-BF<sub>4</sub>** with 1.1 equivalent of KO<sup>*t*</sup>Bu 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  $\delta = -2.95$  ppm corresponding to the two inner NH of the free base porphyrin was observed in its <sup>1</sup>H NMR spectrum. The signal of the carbene was also observed at  $\delta = 182.0$  ppm in its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. By using the same synthetic strategy, the complex **[NiAuCl]** was obtained in 34% yield. Although the yields obtained in both cases were rather low following Procedure B, the formation of undesired side products was not observed and the remaining starting materials **Fb-BF<sub>4</sub>** and **Ni-BF<sub>4</sub>** could be recovered after purification by column chromatography.

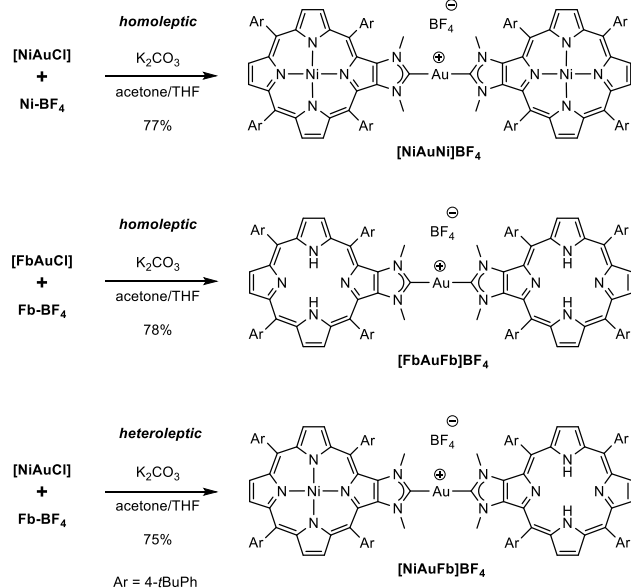
### Scheme 1. Synthesis of **[NiAuCl]** and **[FbAuCl]** complexes.



Cationic bis-carbenic [(NHC)Au(NHC)]<sup>+</sup> complexes were then obtained by reacting the aforementioned [(NHC)AuCl] complexes with a second equivalent of NHC generated *in situ*

(Scheme 2). **Ni-BF<sub>4</sub>** and **Fb-BF<sub>4</sub>** were used as NHC precursors and deprotonated *in situ* by K<sub>2</sub>CO<sub>3</sub> in acetone.<sup>21</sup> The homoleptic complexes **[NiAuNi]BF<sub>4</sub>** and **[FbAuFb]BF<sub>4</sub>** were obtained following this procedure in 77 and 78%, 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]<sup>+</sup>** and **[FbAuFb]<sup>+</sup>** were observed at *m/z* = 2121.7 and 2010.0, respectively (Figures S17 and S25). The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of these complexes showed the expected signals. For examples, the <sup>13</sup>C{<sup>1</sup>H} NMR signals of the carbenes are observed at 193.9 and 194.5 ppm respectively for **[NiAuNi]BF<sub>4</sub>** and **[FbAuFb]BF<sub>4</sub>** (Figures S16 and S23). Presence of BF<sub>4</sub><sup>-</sup> anions was confirmed by <sup>19</sup>F NMR spectroscopy (Figures S15 and S24). 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 to determine their ratios.<sup>15,16</sup> 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]BF<sub>4</sub>** confirming that one Au cation is coordinated by two NHC ligands.

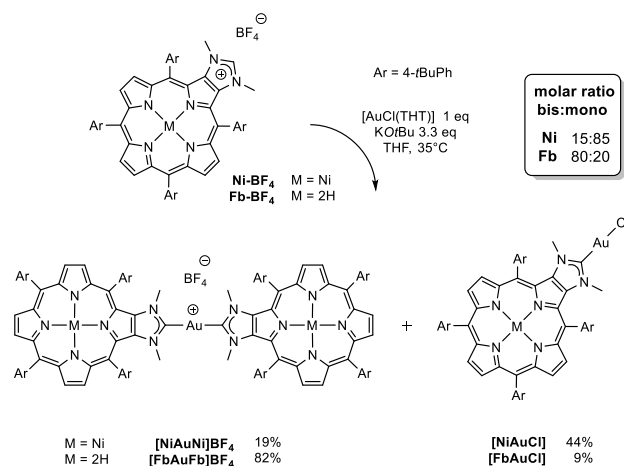
### Scheme 2. Synthesis of **[NiAuNi]BF<sub>4</sub>**, **[FbAuFb]BF<sub>4</sub>** and **[NiAuFb]BF<sub>4</sub>** complexes.



Although the synthesis of heteroleptic bis-carbenic Au complexes remains relatively scarce, some examples can be found in the literature.<sup>22-24</sup> Notably, Nolan and co-workers reported the use of Au hydroxide complexes [(NHC)Au(OH)] as precursors to obtain heteroleptic cationic complexes [(NHC<sup>a</sup>)Au(NHC<sup>b</sup>)<sup>+</sup>] by protonolysis with the appropriate imidazolium salts.<sup>22</sup> Recently, Cazin and coworkers reported a straightforward route permitting the formation of heteroleptic [(NHC<sup>a</sup>)Au(NHC<sup>b</sup>)<sup>+</sup>] complexes under microwave irradiation with imidazolium salts, [(NHC)AuCl] complexes and NaOH as reagents.<sup>23</sup> In the present study, we used the same conditions to synthesize homoleptic and heteroleptic complexes. The heteroleptic complex **[NiAuFb]BF<sub>4</sub>** was obtained in 75%

yield by reacting the complex **[NiAuCl]** with one equivalent of imidazolium salt **Fb-BF<sub>4</sub>** in the presence of potassium carbonate in acetone (Scheme 2). Spectroscopic data are in accordance with the proposed structure for **[NiAuFb]BF<sub>4</sub>**. Two sets of signals corresponding respectively to the Ni and free base porphyrins was observed in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, including the two signals of the carbenes at  $\delta$  = 194.7 and 194.2 ppm in its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Figure S33). The molecular peak corresponding to the cationic species **[NiAuFb]<sup>+</sup>** was observed at *m/z* = 2065.9 by Maldi-Tof mass spectrometry (Figure S34). EDX analyses of **[NiAuFb]BF<sub>4</sub>** showed a chemical composition of Ni/Au/Cl in a *ca.* 1:1:0 ratio consistent with the proposed structure.

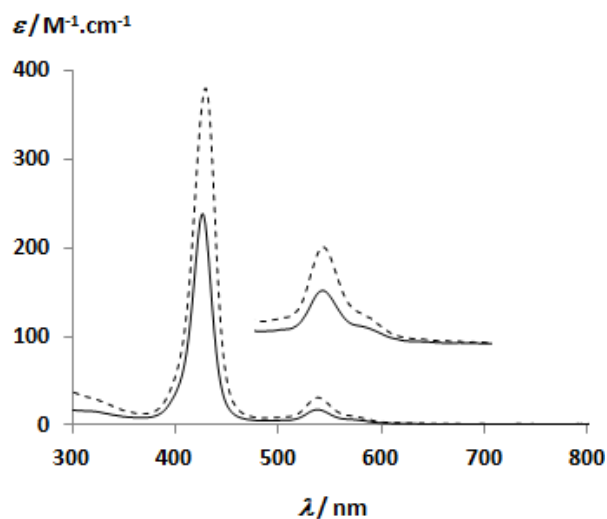
### Scheme 3. Reactivity of **Fb-BF<sub>4</sub>** and **Ni-BF<sub>4</sub>** towards 1 eq of **[AuCl(THT)]** with 3.3 eq of **KOtBu**.



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 eq of **KOtBu** as base (Scheme 1, procedure B). In these conditions, the color of the reaction mixture remained purple indicating that the inner NH's of the porphyrin free base were not deprotonated. However, the reaction mixture turned green when using 3.3 equivalents 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]BF<sub>4</sub>** and mono-carbenic **[FbAuCl]** complexes were obtained in 82% and 9% yields, respectively (molar ratio bis/mono ~ 80:20, Scheme 3). Surprisingly, the bis-carbenic complex **[FbAuFb]BF<sub>4</sub>** was obtained as the major compound despite the use of 1 eq of **[AuCl(THT)]**. Presumably, the generated anionic NHC *in situ* exerts a higher *trans*-effect able to weaken the Au-Cl bond in the intermediate mono-carbenic complex, and thus, promoting the formation of the corresponding bis-carbenic complex. In order to verify this hypothesis, the same reaction with **Ni-BF<sub>4</sub>** and 3.3 eq 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. Based on the same procedure, the bis-carbenic **[NiAuNi]BF<sub>4</sub>** and mono-carbenic **[NiAuCl]** complexes were obtained in 19 and 44% yields, respectively (molar ratio

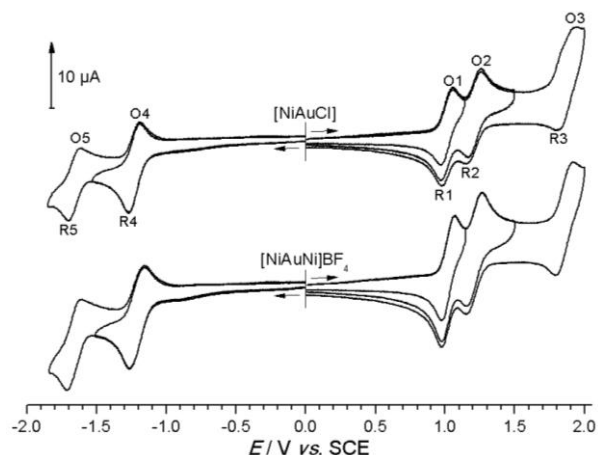
bis/mono ~ 15:85, Scheme 3). The increase in quantity of base improved the yield of **[NiAuCl]** compared to the experiment with 1.1 eq of KO<sup>t</sup>Bu (Scheme 1, procedure B, yield of 34%). However, the high yield formation of the bis-carbenic **[NiAuNi]BF<sub>4</sub>** complex did not occur.

**Electronic and Photophysical Properties.** The electronic interactions between the porphyrin moieties may be estimated from their electronic spectra and their electrochemical proper-



**Figure 2.** UV-visible spectra of **[NiAuCl]** (full line) and **[NiAuNi]BF<sub>4</sub>** (dashed line) in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.

ties.<sup>25</sup> As it can be seen in Figure 2 and Figure S36-S38, the UV-visible spectra of the homoleptic complexes correspond to the superimposition of the spectra of the two corresponding monomers. This, and because there is also no substantial shifting or splitting of the absorption bands going from the monomeric **[MAuCl]** to the dimeric species **[MAuM]BF<sub>4</sub>** (M = Ni or Fb), the electronic communication between the two chromophores within dimeric species is minimal or inexistent (Figure 2 and Figure S36-S38).



**Figure 3.** Cyclic voltammograms of **[NiAuCl]** (top) and **[NiAuNi]BF<sub>4</sub>** (bottom) in CH<sub>2</sub>Cl<sub>2</sub> 0.1 M TBAPF<sub>6</sub> ( $C = 5 \times 10^{-4}$  M,  $v = 0.1$  V s<sup>-1</sup>, working electrode: glassy carbon  $\phi = 3$  mm).

**Table 1.** Redox potentials of **[FbAuCl]**, **[NiAuCl]**, **[FbAuFb]BF<sub>4</sub>**, **[NiAuNi]BF<sub>4</sub>** and **[NiAuFb]BF<sub>4</sub>**<sup>a</sup>

Compounds	1 <sup>st</sup> ox. $E_{1/2}$ ( $\Delta E_p$ )	2 <sup>nd</sup> ox. $E_{1/2}$ ( $\Delta E_p$ )	3 <sup>rd</sup> ox. $E_{1/2}$ ( $\Delta E_p$ )	1 <sup>st</sup> red. $E_{1/2}$ ( $\Delta E_p$ )	2 <sup>nd</sup> red. $E_{1/2}$ ( $\Delta E_p$ )	3 <sup>rd</sup> red. $E_{1/2}$ ( $\Delta E_p$ )	HOMO-LUMO gap <sup>b</sup>
<b>[FbAuCl]</b>	0.925 (80)	1.13 (70)		-1.18 (80)	-1.410 (70)		2.105
<b>[NiAuCl]</b>	1.015 (80)	1.215 (90)	1.94/1.81 <sup>c</sup>	-1.23 (80)	-1.660 (85)		2.240
<b>[FbAuFb]BF<sub>4</sub></b>	0.945 (80)	1.14 (90)		-1.15 (105)	-1.395 (80)		2.094
<b>[NiAuNi]BF<sub>4</sub></b>	1.025 (90)	1.21 (110)	1.855 (125)	-1.21 (105)	-1.665 (100)		2.234
<b>[NiAuFb]BF<sub>4</sub></b>	1.06/0.915 <sup>c</sup>	1.26/1.11 <sup>c</sup>	1.855 (110)	-1.11/-1.255 <sup>c</sup>	-1.400 (80)	-1.660 (135)	≈ 2.11

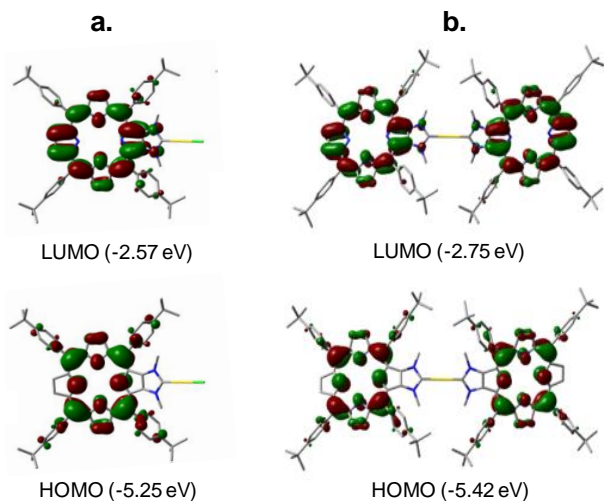
<sup>a</sup> ox.: oxidation; red.: reduction; unless otherwise noted, redox potentials correspond to  $E_{1/2} = (E_{pa} + E_{pc})/2$  and are given in V vs. SCE. Values in parentheses correspond to  $\Delta E_p = |E_{pa} - E_{pc}|$  and are given in mV. <sup>b</sup> Experimental HOMO-LUMO gap =  $E_{1/2}(1^{st}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

This absence of electronic communication is also confirmed by electrochemical analyses. The cyclic voltammograms (CVs) measured in CH<sub>2</sub>Cl<sub>2</sub> 0.1 M TBAPF<sub>6</sub> for all species are presented in Figure S43 (all the potential values written in the manuscript or in the Supporting Information are referenced vs. the saturated KCl calomel electrode, SCE). CVs of **[NiAuCl]** and **[NiAuNi]BF<sub>4</sub>** are represented in Figure 3. Table 1 gathers the redox potentials extracted from the CVs. **[FbAuCl]** cyclic voltammogram exhibits two reversible mono-electronic porphyrin ring centered oxidations at  $E_{1/2} = 0.925$  and 1.130 V, leading to the cation radical (H<sub>2</sub>P<sup>•+</sup>) and dication (H<sub>2</sub>P<sup>2+</sup>), respectively, and two reversible mono-electronic porphyrin ring centered reductions at  $E_{1/2} = -1.180$  and  $-1.410$  V,

leading to the anion radical (H<sub>2</sub>P<sup>•-</sup>) and dianion (H<sub>2</sub>P<sup>2-</sup>), respectively, as expected for free base porphyrins.<sup>26</sup> Thus, the carbene-Au-Cl moiety is not electroactive in the  $-2.0 \rightarrow 2.2$  V potential range. A similar behavior is observed for **[NiAuCl]** with both oxidation processes (Ni(II)P → Ni(II)P<sup>•+</sup> → Ni(II)P<sup>2+</sup>) occurring at  $E_{1/2} = 1.015$  and 1.215 V and both reductions (Ni(II)P → Ni(II)P<sup>•-</sup> → Ni(II)P<sup>2-</sup>) noted at  $E_{1/2} = -1.230$  and  $-1.660$  V. However, for this Ni(II) complex, a third pseudo-reversible 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.<sup>27</sup> This peak also reveals a shoulder at ~1.84 V. This unexpected additional redox system is absent from the **[NiAuNi]BF<sub>4</sub>**'s CV. 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  $[\text{NiAuNi}]\text{BF}_4$  and  $[\text{FbAuFb}]\text{BF}_4$  are practically identical to their respective monomers, as exemplified in Figure 3 for  $[\text{NiAuCl}]$  and  $[\text{NiAuNi}]\text{BF}_4$ . The maximum difference is only  $\pm 30$  mV when comparing 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-Au-carbene fragment.

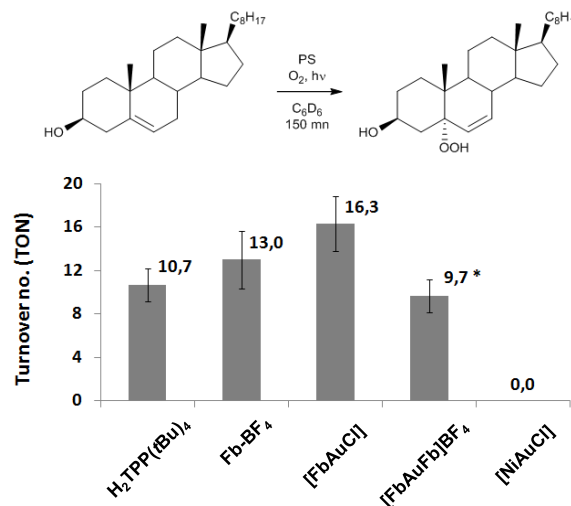
This feature is also observed in the CV of the heteroleptic dimer  $[\text{NiAuFb}]\text{BF}_4$  since it exactly corresponds to the superimposition of the CVs of  $[\text{NiAuCl}]$  and  $[\text{FbAuCl}]$  complexes (Figure S43). Thus, five oxidations are observed though the first four oxidations appear 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) 1-electron oxidation of the free base porphyrin moiety ( $\text{H}_2\text{P} \rightarrow \text{H}_2\text{P}^+$ ), (ii) 1-electron oxidation of the nickel(II) porphyrin moiety ( $\text{Ni(II)P} \rightarrow \text{Ni(II)P}^+$ ), (iii) 1-electron oxidation of the free base porphyrin ( $\text{H}_2\text{P}^+ \rightarrow \text{H}_2\text{P}^{2+}$ ), (iv) 1-electron oxidation of the nickel(II) porphyrin ( $\text{Ni(II)P}^+ \rightarrow \text{Ni(II)P}^{2+}$ ), (v) 1-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 appears in the following order: (i) first reduction corresponding to the 1-electron reduction of the free base porphyrin moiety ( $\text{H}_2\text{P} \rightarrow \text{H}_2\text{P}^-$ ), (ii) first 1-electron reduction of the nickel(II)porphyrin ( $\text{NiP} \rightarrow \text{NiP}^-$ ), (iii) second 1-electron reduction of free base porphyrin ( $\text{H}_2\text{P}^- \rightarrow \text{H}_2\text{P}^{2-}$ ), (iv) second 1-electron reduction of the nickel(II) porphyrin ( $\text{NiP}^- \rightarrow \text{NiP}^{2-}$ ). In conclusion, the level of electronic communication in the homoleptic and heteroleptic dimers is essentially inexistent.



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

To explain these electronic properties, computational studies were performed. The geometries of  $[\text{FbAuCl}]$  and  $[\text{FbAuFb}]^+$  were first optimized by DFT (B3LYP; Figure 4). As expected, the HOMO and LUMO exhibit the  $\pi$ -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 CV's.<sup>17b,25</sup> 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  $[\text{FbAuCl}]$  (Figures S39 and S40) and  $[\text{FbAuFb}]\text{BF}_4$  (Figures S41 and S42) exhibit two peaks which the 0-0 component overlaps strongly with that of the absorption. The excitation spectra superimpose well with the absorption bands indicating that the species that emits is the same that absorbs. So the nature of the emitting state is again the typical  $\pi$ -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.



**Figure 5.** Photochemical oxidation of cholesterol. Experimental conditions: in  $\text{C}_6\text{D}_6$  (500  $\mu\text{L}$ ) with cholesterol/PS = 200, cholesterol ( $5.2 \times 10^{-2}$  M) and PS ( $2.6 \times 10^{-4}$  M), 2h30 of irradiation (500 W halogen lamp, with filter  $\lambda > 510$  nm). Irradiation experiments were reproduced 3 times. TON = turnover number, *i.e.* moles of oxidized cholesterol / moles of PS after 2h30, estimated by  $^1\text{H}$  NMR spectroscopy, see Figure S44. \* = this PS was only partially soluble in  $\text{C}_6\text{D}_6$ : its effective concentration in the course of the experiment was lower explaining the lower TON.

Au(I) complexes with NHC ligands are considered as promising new metal-based anticancer drugs.<sup>2,3</sup> Porphyrins are also efficient photosensitizers (PS) for photodynamic therapy (PDT).<sup>28</sup> 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 ( $^1\text{O}_2$ ) under illumination, the photo-oxidation of a biological molecule such as cholesterol which can be easily monitored by  $^1\text{H}$  NMR spectroscopy, was performed (Figure 5 and Figure S44).<sup>29</sup> The free base 5,10,15,20-*meso*-tetra(4-*tert*-butylphenyl)porphyrin (*i.e.* the porphyrin core of  $\text{Fb-BF}_4$  without the peripheral imidazolium ring) labeled  $\text{H}_2\text{TPP}(t\text{Bu})_4$  in Figure 5, was also tested for

comparison. Interestingly, both imidazolium salt **Fb-BF<sub>4</sub>** and gold complex **[FbAuCl]** are able to photo-oxidize cholesterol. The complex **[FbAuCl]** is a better PS compared to the non-functionalized porphyrin **H<sub>2</sub>TPP(*t*Bu)<sub>4</sub>**. (average TON = 16.3 vs 10.7). This additional photodynamic effect may be attributed to the “heavy atom” effect of Au(I) at the periphery of the porphyrin promoting the inter-crossing system  $S_1 \rightarrow T_1$  and the subsequent formation of  $^1O_2$  to occur.<sup>30</sup> This is consistent with the decrease in fluorescence quantum yields ( $\Phi_F = 0.22$  and 0.038) and lifetimes ( $\tau_F$  (298 K) =  $5.85 \pm 0.1$  ns [ $\lambda_{em} = 672$  nm] and  $4.08 \pm 0.1$  ns [ $\lambda_{em} = 679$  nm]) when going from **Fb-I**<sup>7b</sup> to **[FbAuCl]** (Table S1). The homoleptic complex **[FbAuFb]BF<sub>4</sub>** generates  $^1O_2$  as well, but this cationic species is poorly soluble in C<sub>6</sub>D<sub>6</sub> 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 mono-carbenic complexes as starting materials. The **[NiAuFb]BF<sub>4</sub>** complex that now joins the family of rare examples of heteroleptic bis-carbenic complexes was prepared. These complexes are very stable and easily purified by SiO<sub>2</sub> column chromatography before recrystallization. Interestingly, we showed for the NHC fused to the free base porphyrin that its reactivity towards Au(I) could be modulated simply by deprotonating the inner NH of the porphyrin with a base. Indeed, the formation of the mono-carbenic complex **[FbAuCl]** was observed with the porphyrin in its free base state (*i.e.* with two NH groups in the porphyrin core), whereas the bis-carbenic complex **[FbAuFb]BF<sub>4</sub>** was preferentially obtained when deprotonating the inner NH groups of the porphyrin with KO*t*Bu. 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-BF<sub>4</sub>** and the corresponding gold **[FbAuCl]** complex to generate  $^1O_2$  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-BF<sub>4</sub>**, **Fb-I** and **Fb-BF<sub>4</sub>** are described in reference 14a. Reactions were performed under argon using oven-dried glassware and Schlenk techniques. Gold complex **[AuCl(THT)]** was prepared with the procedure described in reference 31. Acetone (CHROMASOLV®, for HPLC,  $\geq 99.9\%$ ) was purchased from Sigma-Aldrich®. Dry THF and CH<sub>2</sub>Cl<sub>2</sub> were obtained by a solvent purification system PureSolve MD5 from Innovative Technology. Preparative purifications were performed by silica gel flash column chromatography (Merck® 40-60  $\mu$ m). Solvents used

as eluents are technical grade.  $^1H$ ,  $^{19}F$  and  $^{13}C\{^1H\}$  spectra were recorded on a Bruker 300 or 400 MHz spectrometer and all NOESY experiments were recorded on the 400 MHz spectrometer.  $^1H$ ,  $^{13}C\{^1H\}$  NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the solvent as an internal standard.  $^{19}F$  NMR spectra were calibrated to CFCl<sub>3</sub> on the basis of this external reference standard. Abbreviations used for  $^1H$  NMR spectra are as follow: s singlet, d doublet. UV/Vis absorption spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> with a JASCO V-760 UV-Visible/NIR Spectrophotometer in quartz cells of 10 mm (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 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,  $9.2 \times 10^{-5}$  mol) was prepared in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Then, Ag<sub>2</sub>O (21 mg,  $9.2 \times 10^{-5}$  mol, 1 eq.) was added and the reaction mixture was vigorously stirred at room temperature, under argon atmosphere and protected from light. After 6 hours, [AuCl(THT)] (30 mg,  $9.2 \times 10^{-5}$  mol, 1 eq.) was added and the mixture was stirred for additional 12 hours in the same conditions. The reaction was monitored by TLC analysis. When finished, the solvent was evaporated and the *title compound* was purified by column chromatography (SiO<sub>2</sub>; eluent CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 7:3). Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH afforded **[NiAuCl]** as red needles in 50% yield (55 mg). **Procedure B.** A solution of the the porphyrin **Ni-BF<sub>4</sub>** (40 mg,  $3.8 \times 10^{-5}$  mol, 1 eq.) and [AuCl(THT)] (12.2 mg,  $3.8 \times 10^{-5}$  mol, 1 eq.) was prepared in dry THF (6 mL). Then, KO*t*Bu (5.1 mg,  $4.6 \times 10^{-5}$  mol, 1.1 eq.) was added and the reaction mixture was stirred at room temperature and under argon atmosphere. After 20 hours, the solvent was evaporated and the *title compound* was purified by column chromatography (SiO<sub>2</sub>; eluent from CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5). Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH afforded **[NiAuCl]** as red needles in 34% yield (15 mg). Starting material **Ni-BF<sub>4</sub>** was recovered partially after column chromatography (10 mg).  $^1H$  NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.71 (s, 2H, H<sub>pyrr</sub>), 8.67 (s, 4H, H<sub>pyrr</sub>), 8.08 (d, 4H, H<sub>Ar ortho</sub>,  $^3J_{H-H} = 8.3$  Hz), 7.97 (d, 4H, H<sub>Ar ortho</sub>,  $^3J_{H-H} = 8.3$  Hz), 7.78 (d, 4H, H<sub>Ar meta</sub>,  $^3J_{H-H} = 8.3$  Hz), 7.72 (d, 4H, H<sub>Ar meta</sub>,  $^3J_{H-H} = 8.3$  Hz), 3.15 (s, 6H, H<sub>NMe</sub>), 1.56 (s, 18H, H<sub>Bu</sub>), 1.55 (s, 18H, H<sub>Bu</sub>) ppm.  $^{13}C\{^1H\}$  NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  182.3 (C<sub>carbene</sub>), 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<sub>NMe</sub>), 35.2, 35.1, 31.8 (C<sub>Bu</sub>), 32.7 (C<sub>Bu</sub>) ppm. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\epsilon$ ) = 426 (5.41), 537 (3.76), 573 (4.26 L.mol<sup>-1</sup>.cm<sup>-1</sup>) nm. HR-MS (MALDI-TOF): *m/z* calcd for C<sub>63</sub>H<sub>64</sub>AuClN<sub>6</sub>Ni [M]<sup>+</sup> 1194.3900, found 1194.3892. Anal. Calcd. for C<sub>63</sub>H<sub>64</sub>N<sub>6</sub>NiAuCl. H<sub>2</sub>O [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.** 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<sub>4</sub>** (35 mg,  $3.5 \times 10^{-5}$  mol, 1 eq.) and [AuCl(THT)] (11.2 mg,  $3.5 \times 10^{-5}$  mol, 1 eq.) was prepared in dry THF (10 mL). Then, KO*t*Bu (4.3 mg,  $3.9 \times 10^{-5}$  mol, 1.1 eq.) was added and the reaction mixture was stirred at room temperature and under argon atmosphere. After 20 hours, the solvent was evaporated and the *title compound* was purified by column chromatography (SiO<sub>2</sub>; eluent from CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5). Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH afforded **[FbAuCl]** as a purple powder in 38% yield (15 mg). Starting material **Fb-BF<sub>4</sub>** was recovered partially after column chromatography (5 mg).  $^1H$  NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.94 (d, 2H, H<sub>pyrr</sub>,  $^3J_{H-H} = 5.0$  Hz), 8.86 (d, 2H, H<sub>pyrr</sub>,  $^3J_{H-H} = 5.0$  Hz), 8.80 (s, 2H, H<sub>pyrr</sub>), 8.25 (d, 4H, H<sub>Ar ortho</sub>,  $^3J_{H-H} = 8.3$  Hz), 8.00 (d, 4H, H<sub>Ar ortho</sub>,  $^3J_{H-H} = 8.3$  Hz), 7.87 (d, 4H, H<sub>Ar meta</sub>,  $^3J_{H-H} = 8.3$  Hz), 7.60 (d, 4H, H<sub>Ar meta</sub>,  $^3J_{H-H} = 8.3$  Hz), 2.71 (s, 6H, H<sub>NMe</sub>), 1.65 (s, 18H, H<sub>Bu</sub>), 1.48 (s, 18H, H<sub>Bu</sub>), -2.95 (bs, 2H, H<sub>NH</sub>) ppm.  $^{13}C\{^1H\}$  NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  182.0 (C<sub>carbene</sub>), 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<sub>NMe</sub>), 35.4, 35.3, 31.9 (C<sub>Bu</sub>), 31.8 (C<sub>Bu</sub>) ppm.

UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 429 (5.60), 527 (4.25), 566 (4.09), 599 (3.79), 661 (3.75 L.mol<sup>-1</sup>.cm<sup>-1</sup>) nm. HR-MS (MALDI-TOF):  $m/z$  calcd for C<sub>63</sub>H<sub>67</sub>AuClN<sub>6</sub> [M+H]<sup>+</sup> 1139.4781, found 1139.4768. Anal. Calcd. for C<sub>63</sub>H<sub>66</sub>N<sub>6</sub>AuCl.CH<sub>2</sub>Cl<sub>2</sub> [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]BF<sub>4</sub>. From [NiAuCl] as starting material.** A solution of the porphyrin Ni-BF<sub>4</sub> (100 mg, 9.5×10<sup>-5</sup> mol, 1 eq.) and [NiAuCl] (125 mg, 1.0×10<sup>-4</sup> mol, 1.1 eq.) was prepared in an acetone/THF (85:15 v/v) mixture (35 mL). Then, K<sub>2</sub>CO<sub>3</sub> (17 mg, 1.2×10<sup>-4</sup> mol, 1.3 eq.) was added and the reaction mixture was vigorously stirred at room temperature under argon atmosphere. After 15 hours, the solvent was evaporated and the target compound was purified by column chromatography (SiO<sub>2</sub>; eluent: from CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5). Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane afforded [NiAuNi]BF<sub>4</sub> as red needles in 77% yield (161 mg). **From [AuCl(THT)] as starting material.** A solution of the porphyrin Ni-BF<sub>4</sub> (35 mg, 3.3×10<sup>-5</sup> mol, 1 eq.) and [AuCl(THT)] (5.3 mg, 1.7×10<sup>-5</sup> mol, 0.5 eq.) was prepared in dry THF (3 mL). Then, KO<sup>t</sup>Bu (12.2 mg, 1.1×10<sup>-4</sup> mol, 3.3 eq.) was added and the reaction mixture was stirred at room temperature and under argon atmosphere. After 1.5 hours, the solvent was evaporated and the target compound was purified by column chromatography (SiO<sub>2</sub>; eluent: from CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5). Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane afforded [NiAuNi]BF<sub>4</sub> as red needles in 48% yield (17 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.72 (s, 4H, H<sub>pyrr</sub>), 8.69 (d, 4H, H<sub>pyrr</sub>, <sup>3</sup>J<sub>H-H</sub> = 5.0 Hz), 8.67 (d, 4H, H<sub>pyrr</sub>, <sup>3</sup>J<sub>H-H</sub> = 5.0 Hz), 8.11 (d, 8H, H<sub>Ar ortho</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz), 7.94 (d, 8H, H<sub>Ar ortho</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz), 7.84 (d, 8H, H<sub>Ar meta</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz), 7.72 (d, 8H, H<sub>Ar meta</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz), 3.20 (s, 12H, H<sub>NMe</sub>), 1.55 (s, 36H, H<sub>tBu</sub>), 1.54 (s, 36H, H<sub>tBu</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  193.9 (C<sub>carbene</sub>), 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<sub>NMe</sub>), 35.2, 35.0, 31.7 (C<sub>tBu</sub>), 31.7 (C<sub>tBu</sub>) ppm. <sup>19</sup>F NMR (282.2 MHz, CDCl<sub>3</sub>):  $\delta$  -154.16 (s, <sup>10</sup>BF<sub>4</sub>), -154.22 (s, <sup>11</sup>BF<sub>4</sub>) ppm. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 429 (5.61), 538 (4.52), 571 (4.01 L.mol<sup>-1</sup>.cm<sup>-1</sup>) nm. HR-MS (ESI):  $m/z$  calcd for C<sub>126</sub>H<sub>128</sub>N<sub>12</sub>AuNi<sub>2</sub> [M-BF<sub>4</sub>]<sup>+</sup> 2121.8752, found 2121.8805. Anal. Calcd. for C<sub>126</sub>H<sub>128</sub>N<sub>12</sub>AuNi<sub>2</sub>BF<sub>4</sub>.CH<sub>2</sub>Cl<sub>2</sub> [2296.58 g/mol]: C, 66.42; H, 5.71; N, 7.32. Found: C, 66.35; H, 5.66; N, 7.49.

**Synthesis of [FbAuFb]BF<sub>4</sub>. From [FbAuCl] as starting material.** A solution of the porphyrin Fb-BF<sub>4</sub> (100 mg, 1.0×10<sup>-4</sup> mol, 1 eq.) and [FbAuCl] (126 mg, 1.1×10<sup>-4</sup> mol, 1.1 eq.) was prepared in an acetone/THF (85:15 v/v) mixture (35 mL). Then, K<sub>2</sub>CO<sub>3</sub> (18 mg, 1.2×10<sup>-4</sup> mol, 1.3 eq.) was added and the reaction mixture was vigorously stirred at room temperature under argon atmosphere. After 15 hours, the solvent was evaporated and the target compound was purified by column chromatography (SiO<sub>2</sub>; eluent: from CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5). Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane afforded [FbAuFb]BF<sub>4</sub> as a purple powder in 78% yield (163 mg). **From [AuCl(THT)] as starting material.** A solution of the porphyrin Fb-BF<sub>4</sub> (35 mg, 3.5×10<sup>-5</sup> mol, 1 eq.) and [AuCl(THT)] (5.6 mg, 1.8×10<sup>-5</sup> mol, 0.5 eq.) was prepared in dry THF (3 mL). Then, KO<sup>t</sup>Bu (13.0 mg, 1.2×10<sup>-4</sup> mol, 3.3 eq.) was added and the reaction mixture was stirred at room temperature and under argon atmosphere. After 1.5 hours, the solvent was evaporated and the target compound was purified by column chromatography (SiO<sub>2</sub>; eluent: from CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5). Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane afforded [FbAuFb]BF<sub>4</sub> as a purple powder in 48% yield (17 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.02 (d, 4H, H<sub>pyrr</sub>, <sup>3</sup>J<sub>H-H</sub> = 5.0 Hz), 8.95 (d, 4H, H<sub>pyrr</sub>, <sup>3</sup>J<sub>H-H</sub> = 5.0 Hz), 8.75 (s, 4H, H<sub>pyrr</sub>), 8.45 (d, 8H, H<sub>Ar ortho</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz), 8.19 (d, 8H, H<sub>Ar ortho</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz), 7.95 (d, 8H, H<sub>Ar meta</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz), 7.85 (d, 8H, H<sub>Ar meta</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz), 3.21 (s, 12H, H<sub>NMe</sub>), 1.63 (s, 36H, H<sub>tBu</sub>), 1.62 (s, 36H, H<sub>tBu</sub>), -2.90 (bs, 4H, H<sub>NH</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  194.5 (C<sub>carbene</sub>), 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<sub>NMe</sub>), 35.6, 35.4, 32.0 (C<sub>tBu</sub>), 32.0 (C<sub>tBu</sub>) ppm. <sup>19</sup>F NMR (282.2 MHz, CDCl<sub>3</sub>):  $\delta$  -153.33 (s, <sup>10</sup>BF<sub>4</sub>), -153.58 (s, <sup>11</sup>BF<sub>4</sub>) ppm. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log

$\epsilon$ ) = 433 (5.86), 528 (4.53), 567 (4.39), 601 (4.24), 663 nm (4.15 L.mol<sup>-1</sup>.cm<sup>-1</sup>) nm. HR-MS (ESI):  $m/z$  calcd for C<sub>126</sub>H<sub>132</sub>N<sub>12</sub>Au [M-BF<sub>4</sub>]<sup>+</sup> 2010.0358, found 2010.0419. Anal. Calcd. for C<sub>126</sub>H<sub>132</sub>N<sub>12</sub>AuBF<sub>4</sub>.3CH<sub>2</sub>Cl<sub>2</sub> [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]BF<sub>4</sub>.** A solution of the porphyrin Fb-BF<sub>4</sub> (70 mg, 7.0×10<sup>-5</sup> mol, 1 eq.) and [NiAuCl] (100 mg, 8.5×10<sup>-5</sup> mol, 1.2 eq.) was prepared in an acetone/THF (85:15 v/v) mixture (35 mL). Then, K<sub>2</sub>CO<sub>3</sub> (12 mg, 8.5×10<sup>-5</sup> mol, 1.2 eq.) was added and the reaction mixture was vigorously stirred at room temperature under argon atmosphere. After 24 hours, the solvent was evaporated and the target compound was purified by column chromatography (SiO<sub>2</sub>; eluent: from CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5). Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane afforded [NiAuFb]BF<sub>4</sub> as a purple powder in 75% yield (114 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.01 (d, 2H, H<sub>pyrr</sub>, <sup>3</sup>J<sub>H-H</sub> = 5.0 Hz), 8.95 (d, 2H, H<sub>pyrr</sub>, <sup>3</sup>J<sub>H-H</sub> = 5.0 Hz), 8.75 (s, 2H, H<sub>pyrr</sub>), 8.72 (s, 2H, H<sub>pyrr</sub>), 8.71 (s, 4H, H<sub>pyrr</sub>), 8.43 (d, 4H, H<sub>Ar ortho</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.2 Hz), 8.18 (d, 4H, H<sub>Ar ortho</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.1 Hz), 8.12 (d, 4H, H<sub>Ar ortho</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.3 Hz), 7.95 (d, 4H, H<sub>Ar ortho</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.3 Hz), 7.93 (d, 4H, H<sub>Ar meta</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.2 Hz), 7.84 (d, 4H, H<sub>Ar meta</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.1 Hz), 7.82 (d, 4H, H<sub>Ar meta</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.3 Hz), 7.75 (d, 4H, H<sub>Ar meta</sub>, <sup>3</sup>J<sub>H-H</sub> = 8.3 Hz), 3.19 (s, 6H, H<sub>NMe</sub>), 3.18 (s, 6H, H<sub>NMe</sub>), 1.62 (s, 18H, H<sub>tBu</sub>), 1.60 (s, 18H, H<sub>tBu</sub>), 1.56 (s, 18H, H<sub>tBu</sub>), 1.55 (s, 18H, H<sub>tBu</sub>), -2.91 (bs, 2H, H<sub>NH</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  194.7 (C<sub>carbene</sub>), 194.2 (C<sub>carbene</sub>), 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 (C<sub>NMe</sub>), 37.7(C<sub>NMe</sub>), 35.6, 35.5, 35.4, 35.3, 32.0 (C<sub>tBu</sub>), 32.0 (C<sub>tBu</sub>), 31.9 (C<sub>tBu</sub>), 31.9 (C<sub>tBu</sub>) ppm. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$  -153.52 (s, <sup>10</sup>BF<sub>4</sub>), -153.58 (s, <sup>11</sup>BF<sub>4</sub>) ppm. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 432 (5.77), 534 (4.49), 566 (4.20), 600 (3.83), 660 (3.66 L.mol<sup>-1</sup>.cm<sup>-1</sup>) nm. HR-MS (ESI):  $m/z$  calcd for C<sub>126</sub>H<sub>130</sub>N<sub>12</sub>AuNi [M-BF<sub>4</sub>]<sup>+</sup> 2065.9555, found 2065.9645. Anal. Calcd. for C<sub>126</sub>H<sub>130</sub>N<sub>12</sub>AuNiBF<sub>4</sub>.3/2CH<sub>2</sub>Cl<sub>2</sub> [2280.35 g/mol]: C, 67.10; H, 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 in an atmosphere of dry oxygen-free argon at room temperature (20 ± 2 °C). The supporting electrolyte was a 0.1 mol.L<sup>-1</sup> TBAPF<sub>6</sub> (tetra-*n*-butyl-ammonium hexafluorophosphate)/CH<sub>2</sub>Cl<sub>2</sub> 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 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 ( $\varnothing$  = 3 mm). Before each measurement, the GC electrode was polished with a diamond suspension and rinsed with water. In these conditions, the Fc<sup>+</sup>/Fc redox potential is found to be 0.46 V vs. SCE.

**DFT calculations.** All density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculations were performed with Gaussian 09<sup>32</sup> at the Université de Sherbrooke with the Mammouth supercomputer supported by Le Réseau Québécois De Calculs Hautes Performances. The DFT geometry optimisations as well as TD-DFT calculations<sup>33</sup> 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 solubilising (1,3-ditertbutylphenyl) groups.<sup>34</sup> VDZ (valence double  $\zeta$ ) with SBKJC effective core potential was used for Au atoms.<sup>34</sup> A THF solvent field was applied to all calculations. The calculated absorption spectra, were obtained from GaussSum 2.1.<sup>35</sup>



**Absorption, emission and excitation spectra.** All samples were prepared in CH<sub>2</sub>Cl<sub>2</sub> or 2-MeTHF (2-methyltetrahydrofuran), which was distilled over CaH<sub>2</sub> 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 air-tight 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 a LED laser (excitation at 375 nm. FWHM = 90 ps). The quantum yields,  $\Phi_F$ , were measured using H<sub>2</sub>TPP (tetraphenylporphyrin free base as the standard  $\Phi_F = 0.11$ ).<sup>36</sup>

**X-ray diffraction analysis.** Crystal evaluation and data collection were performed on a Rigaku-Oxford Diffraction Gemini-S diffractometer with sealed-tube Mo- $K\alpha$  radiation using the *CrysAlis Pro* program.<sup>37</sup> This program was also used for the integration of the frames using default parameters, the correction for Lorentz and polarization effects, and for 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 elsewhere<sup>38</sup> using the *Superflip* program<sup>39</sup> and they were refined using full-matrix least-squares procedures as implemented in *CRYSTALS*<sup>40</sup> on all independent reflections with  $I > 2\sigma(I)$ . See the Supporting Information (page S43) to obtain more details about the refinement procedure. Crystal data for **Fb-I** formula: C<sub>64</sub>H<sub>67</sub>Cl<sub>2</sub>N<sub>6</sub>, moiety: C<sub>63</sub>H<sub>65</sub>N<sub>6</sub>,CH<sub>2</sub>Cl<sub>2</sub>I,  $T = 175$  K,  $M_r = 1118.04$  g.mol<sup>-1</sup>, crystal size = 0.25x0.30x0.40 mm<sup>3</sup>, triclinic, space group  $P-1$ ,  $a = 11.3072(10)$  Å,  $b = 15.9169(15)$  Å,  $c = 18.8810(15)$  Å,  $\alpha = 100.574(7)^\circ$ ,  $\beta = 107.045(7)^\circ$ ,  $\gamma = 109.056(8)^\circ$ ,  $V = 2920.6(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.271$  g.cm<sup>-3</sup>,  $\mu = 0.684$  mm<sup>-1</sup>,  $\theta_{\text{max}} = 24.952^\circ$ , experimental resolution = 1.05 Å, 14625 reflections measured, 7484 unique, 5017 with  $I > 2\sigma(I)$ ,  $R_{\text{int}} = 0.065$ ,  $\langle \sigma(I)/I \rangle = 0.1179$ , 652 refined parameters,  $R_1(I > 2\sigma(I)) = 0.1205$ ,  $wR_2(I > 2\sigma(I)) = 0.1343$ ,  $R_1(\text{all data}) = 0.1577$ ,  $wR_2(\text{all data}) = 0.1690$ , GOF = 1.1220,  $\Delta\rho(\text{min/max}) = -1.21/2.37$  e.Å<sup>-3</sup>.

## ASSOCIATED CONTENT

### Supporting Information

For all compounds: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, UV-visible and mass spectra, cyclic voltammograms. For **[FbAuCl]** and **[FbAuFb]BF<sub>4</sub>**: excitation and emission spectra, photophysical data, crystallographic data of **Fb-I**. 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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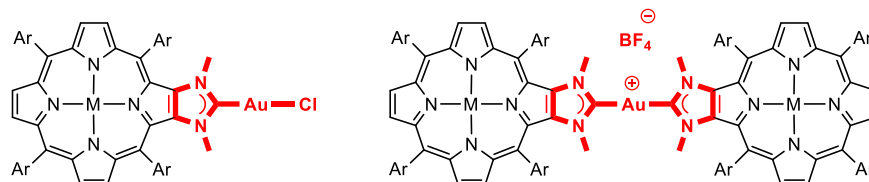
## REFERENCES

- [1] (a) Herrmann, W. A.; Köcher, C. *Angew. Chem. Int. Ed.* **1997**, *36*, 2162-2187. (b) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39-91. (c) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309. (d) Glorius, F. *Top. Organomet. Chem.* **2007**, *21*, 1-20. (e) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed.* **2007**, *46*, 2768-2813. (f) Hahn, F. E.; Jahnke, M. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122-3172. (g) Alcaide, B.; Almendros, P.; Luna, A. *Chem. Rev.* **2009**, *109*, 3817-3858. (h) Díez-González, S.; Marion, N.; Nolan, S. P.; *Chem. Rev.* **2009**, *109*, 3612-3676. (i) Nolan, S. P., Ed. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006. (j) Dröge, T.; Glorius, F. *Angew. Chem. Int. Ed.* **2010**, *49*, 6940-6952. (k) Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev.* **2011**, *40*, 5151-5169.
- [2] (a) Teyssot, M.-L.; Jarrousse, A.-S.; Manin, M.; Chevry, A.; Roche, S.; Norre, F.; Beausoin, C.; Morel, L.; Boyer, D.; Mahiou, R.; Gautier, A. *Dalton Trans.* **2009**, 6897-6902. (b) Oehninger, L.; Rubbiani, R.; Ott, I. *Dalton Trans.* **2013**, *42*, 3269-3284. (c) W. Liu, W.; Gust, R. *Chem. Soc. Rev.* **2013**, *42*, 755-773.
- [3] (a) Ray, S.; Mohan, R.; Singh, J. K.; Samantaray, M. K.; Shaikh, M. M.; Panda, D.; Ghosh, P. *J. Am. Chem. Soc.* **2007**, *129*, 15042-15053. (b) Hickey, J. L.; Ruhayel, R. A.; Barnard, P. J.; Baker, M. V.; Berners-Price, S. J.; Filipovska, A. *J. Am. Chem. Soc.* **2008**, *130*, 12570-12571. (c) Weaver, J.; Gaillard, S.; Toye, C.; MacPherson, S.; Nolan, S. P.; Riches, A. *Chem. Eur. J.* **2011**, *17*, 6620-6624. (d) Rubbiani, R.; Can, S.; Kitanovic, I.; Alborzinia, H.; Stefanopoulou, M.; Kokoschka, M.; Moenchgesang, S.; Sheldrick, W. S.; Woelfl, S.; Ott, I. *J. Med. Chem.* **2011**, *54*, 8646-8657. (e) Liu, W.; Bendorf, K.; Proetto, M.; Abram, U.; Hagenbach, A.; Gust, R. *J. Med. Chem.* **2011**, *54*, 8605-8615. (f) Schuh, E.; Pfluger, C.; Citta, A.; Folda, A.; Rigobello, M. P.; Bindoli, A.; Casini, A.; Mohr, F. *J. Med. Chem.* **2012**, *55*, 5518-5528. (g) Hackenberg, F.; Muller-Bunz, H.; Smith, R.; Streciwilk, W.; Zhu, X.; Tacke, M. *Organometallics* **2013**, *32*, 5551-5560. (h) Sivaram, H.; Tan, J.; Huynh, H. V. *Dalton Trans.* **2013**, *42*, 12421-12428. (i) Bertrand, B.; Stefan, L.; Pirrotta, M.; Monchaud, D.; Bodio, E.; Richard, P.; Le Gendre, P.; Warmerdam, E.; de Jager, M. H.; Groothuis, G. M. M.; Picquet, M.; Casini, A. *Inorg. Chem.* **2014**, *53*, 2296-2303. (j) Messori, L.; Marchetti, L.; Massai, L.; Scaletti, F.; Guerri, A.; Landini, I.; Nobili, S.; Perrone, G.; Mini, E.; Leoni, P.; Pasquali, M.; Gabbiani, C. *Inorg. Chem.* **2014**, *53*, 2396-2403. (k) Bertrand, B.; de Almeida, A.; van der Burgt, E. P. M.; Picquet, M.; Citta, A.; Folda, A.; Rigobello, M. P.; Le Gendre, P.; Bodio, E.; Casini, A. *Eur. J. Inorg. Chem.* **2014**, *27*, 4532-4536. (l) Boselli, L.; Ader, I.; Carraz, M.; Hemmert, C.; Cuvillier, O.; Gornitzka, H. *Eur. J. Med. Chem.* **2014**, *85*, 87-94. (m) Boselli, L.; Carraz, M.; Mazeret, S.; Paloque, L.; Gonzalez, G.; Benoit-Vical, F.; Valentin, A.; Hemmert, C.; Gornitzka, H. *Organometallics* **2015**, *34*, 1046-1055.
- [4] (a) Mercks, L.; Albrecht, M. *Chem. Soc. Rev.* **2010**, *39*, 1903-1912. (b) Visbal, R.; Ospino, I.; López-de-Luzuriaga, J. M.; Laguna, A.; Gimeno, M. C. *J. Am. Chem. Soc.* **2013**, *135*, 4712-4715. (c) Li, K.; Cheng, G.; Ma, C.; Guan, X.; Kwok, W.-M.; Chen, Y.; Lu, W.; Che, C.-M., *Chem. Sci.* **2013**, *4*, 2630-2644. (d) Weidner, T.; Baio, J. E.; Mundstock, A.; Grosse, C.; Karthäuser, S.; Bruhn, C.; Siemeling, U. *Aust. J. Chem.* **2011**, *64*, 1177-1179. (e) Zhukhovitskiy, A. V.; Mavros, M. G.; Voorhis, T. V.; Johnson, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 7418-7421. (f) Crudden, C. M.; Horton, J. H.; Ebralidze, I. I.; Zenkina, O. V.; McLean, A. B.; Drevniok, B.; She, Z.; Kraatz, H.-B.; Mosey, N. J.; Seki, T.; Keske, E. C.; Leake, J. D.; Rousina-Webb, A.; Wu, G. *Nat. Chem.* **2014**, *6*, 409-414.
- [5] (a) Hurst, E. C.; Wilson, K.; Fairlamb, I. J. S.; Chechik, V. *New J. Chem.* **2009**, *33*, 1837-1840. (b) Vignolle, J.; Tilley, T. D. *Chem.*

- Commun.* **2009**, 7230-7232. (c) Lara, P.; Rivada-Wheelaghan, O.; Conejero, S.; Poteau, R.; Philippot, K.; Chaudret, B. *Angew. Chem. Int. Ed.* **2011**, *50*, 12080-12084. (d) Ling, X.; Schaeffer, N.; Roland, S.; Pileni, M.-P. *Langmuir* **2013**, *29*, 12647-12656. (e) Richter, C.; Schaepe, K.; Glorius, F.; Ravoo, B. *J. Chem. Commun.* **2014**, *50*, 3204-3207. (f) Lara, P.; Suarez, A.; Collire, V.; Philippot, K.; Chaudret, B. *ChemCatChem* **2014**, *6*, 87-90. (g) Baquero, E. A.; Tricard, S.; Flores, J. C.; de Jesus, E.; Chaudret, B. *Angew. Chem. Int. Ed.* **2014**, *53*, 13220-13224. (h) Crespo, J.; Guari, Y.; Ibarra, A.; Larionova, J.; Lasanta, T.; Laurencin, D.; Lopez-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Richeter, S. *Dalton Trans.* **2014**, *43*, 15713-15718.
- [6] Wuertz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523-1533.
- [7] (a) Droege, T.; Glorius, F. *Angew. Chem. Int. Ed.* **2010**, *49*, 6940-6952. (b) Nelson, D. J.; Nolan, S. P. *Chem. Soc. Rev.* **2013**, *42*, 6723-6753.
- [8] (a) Sanderson, M. D.; Kamplain, J. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2006**, *128*, 16514-16515. (b) Khramov, D. M.; Rosen, E. L.; Lynch, V. M.; Bielawski, C. W. *Angew. Chem. Int. Ed.* **2008**, *47*, 2267-2270. (c) Rosen, E.; Varnado, Jr., C. D.; Tennyson, A. G.; Khramov, D. M.; Kamplain, J. W.; Sung, D. H.; Cresswell, P. T.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2009**, *28*, 6695-6706. (d) Tennyson, A. G.; Ono, R. J.; Hudnall, T. W.; Khramov, D. M.; Er, J. A. V.; Kamplain, J. W.; Lynch, V. M.; Sessler, J. L.; Bielawski, C. W. *Chem. Eur. J.* **2010**, *16*, 304-315. (e) Tennyson, A. G.; Lynch, V. M.; Bielawski, C. W. *J. Am. Chem. Soc.* **2010**, *132*, 9420-9429.
- [9] Biju, A. T.; Hirano, K.; Fröhlich, R.; Glorius, F. *Chem. Asian J.* **2009**, *4*, 1786-1789.
- [10] (a) Neilson, B. M.; Lynch, V. M.; Bielawski, C. W. *Angew. Chem. Int. Ed.* **2011**, *50*, 10322-10326. (b) Neilson, B. M.; Bielawski, C. W. *J. Am. Chem. Soc.* **2012**, *134*, 12693-12699.
- [11] Toganoh, M.; Hihara, T.; Furuta, H. *Inorg. Chem.* **2010**, *49*, 8192-8184.
- [12] Wang, J.-W.; Meng, F.-H.; Zhang, L.-F. *Organometallics* **2009**, *28*, 2334-2337.
- [13] (a) Haumesser, J.; Gisselbrecht, J.-P.; Weiss, J.; Ruppert, R. *Chem. Commun.* **2012**, *48*, 11653-11655. (b) Haumesser, J.; Gisselbrecht, J.-P.; Karmazin-Brelot, L.; Bailly, C.; Weiss, J.; Ruppert, R. *Organometallics* **2014**, *33*, 4923-4930.
- [14] (a) Lefebvre, J.-F.; Leclercq, D.; Gisselbrecht, J.-P.; Richeter, S. *Eur. J. Org. Chem.* **2010**, 1912-1920. (b) Lo, M.; Lefebvre, J.-F.; Leclercq, D.; van der Lee, A.; Richeter, S. *Org. Lett.* **2011**, *13*, 3110-3113.
- [15] Lefebvre, J.-F.; Lo, M.; Leclercq, D.; Richeter, S. *Chem. Commun.* **2011**, *47*, 2976-2978.
- [16] Lefebvre, J.-F.; Lo, M.; Gisselbrecht, J.-P.; Coulembier, O.; Clément, S.; Richeter, S. *Chem. Eur. J.* **2013**, *19*, 15652-15660.
- [17] (a) Richeter, S.; Hadj-Aïssa, A.; Taffin, C.; van der Lee, A.; Leclercq, D. *Chem. Commun.* **2007**, 2148-2150. (b) Abdelhameed, M.; Karsenti, P.-L.; Langlois, A.; Lefebvre, J.-F.; Richeter, S.; Ruppert, R.; Harvey, P. D. *Chem. Eur. J.* **2014**, *20*, 12988-13001.
- [18] For example of tetracarbene ligand with macrocycle topology, see: Hahn, F. E.; Langenhahn, V.; Lügger, T.; Pape, T.; Le Van, D. *Angew. Chem. Int. Ed.* **2005**, *44*, 3759-3763.
- [19] (a) Scheidt, W. R.; Mondal, J. U.; Eigenbrot, C. W.; Adler, A.; Radonovich, L. J.; Hoard, J. L. *Inorg. Chem.* **1986**, *25*, 795-799. (b) Simakova, P.; Gautier, J.; Prochazka, M.; Herve-Aubert, K.; Chourpa, I. *J. Phys. Chem. C* **2014**, *118*, 7690-7697.
- [20] (a) Collado, A.; Gómez-Suárez, A.; Martin, A. R.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2013**, *49*, 5541-5543. (b) Visbal, R.; Laguna, A.; Gimeno, M. C. *Chem. Commun.* **2013**, *49*, 5642-5644.
- [21] (a) Liu, W.; Bendorf, K.; Proetto, M.; Hagenbach, A.; Abram, U.; Gust, R. *J. Med. Chem.* **2012**, *55*, 3713-3724. (b) Guo, S.; Sivaram, H.; Yuan, D.; Huynh, H. V. *Organometallics* **2013**, *32*, 3685-3696. (c) Rodríguez-Castillo, M.; Laurencin, D.; Tielens, F.; van der Lee, A.; Clément, S.; Guari, S.; Richeter, S. *Dalton Trans.* **2014**, *43*, 5978-5982.
- [22] (a) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 2742-2744. (b) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Organometallics* **2010**, *29*, 5402-5408.
- [23] Lazreg, F.; Cordes, D. B.; Slawin, A. M. Z.; Cazin, C. S. J. *Organometallics* **2015**, *34*, 419-425.
- [24] (a) Schick, S.; Pape, T.; Hahn, F. E. *Organometallics* **2014**, *33*, 4035-4041. (b) Jin, H.; Tan, T. T. Y.; Hahn, F. E. *Angew. Chem. Int. Ed.* **2015**, *54*, 13811-13815.
- [25] (a) Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 6168-6179. (b) Abdelhameed, A.; Langlois, A.; Karsenti, P.-L.; Richeter, S.; Ruppert, R.; Harvey, P. D. *Chem. Commun.* **2014**, *50*, 14609-14612.
- [26] (a) Kadish, K. M.; Caemelbecke, E. V.; Royal, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: 2000; Vol. 8, Ch. 55, p 25. (b) Inisan, C.; Saillard, J.-Y.; Guillard, R.; Tabard, A.; Mest, Y. L. *New J. Chem.* **1998**, 823-830.
- [27] Kadish, K. M.; Caemelbecke, E. V.; Royal, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: 2000; Vol. 8, Ch. 55, pp 66-68.
- [28] (a) Dolmans D. E. J. G. J., Fukumura, D., Jain R. K. *Nat Rev Cancer*, **2003**, *3*, 380-387. (b) Juillerat-Jeanneret, L. *Trends Cancer Res.* **2006**, *2*, 71-84. (c) Ethirajan, M.; Chen, Y.; Joshi, P.; Pandey, R. K. *Chem. Soc. Rev.* **2011**, *40*, 340-362.
- [29] Fouchet, J.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Org. Lett.* **2005**, *7*, 5257-5260.
- [30] (a) Mohamed, A. A.; Rawasgdeg-Omary, M. A.; Omary, M. A.; Fackler, J. P. *Dalton Trans.* **2005**, *15*, 2597-2602. (b) Kim, S.; Ohulchanskyy, T. Y.; Bharali, D.; Chen, Y. H.; Pandey, R. K.; Prasad, P. N. *J. Phys. Chem. C* **2009**, *113*, 12641-12644. (c) Obata, M.; Hirohara, S.; Rika Tanaka, R.; Kinoshita, I.; Ohkubo, K.; Fukuzumi, S.; Tanihara, M.; Yano, S. *J. Med. Chem.* **2009**, *52*, 2747-2753. (d) Zhou, L.; Wei, S.; Ge, X.; Zhou, J.; Yu, B.; Shen, J. *J. Phys. Chem. B* **2012**, *116*, 12744-12749. (e) Zhou, L.; Ge, X.; Liu, J.; Zhou, J.; Wei, S.; Li, F.; Shen, J. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 5317-5324.
- [31] Usón, R.; Laguna, A. *Inorg. Synth.* **1982**, *21*, 71-74.
- [32] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P. Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian, Inc.*, Wallingford CT, **2004**.
- [33] (a) Hohenberg, P.; Kohn W. *Phys. Rev.* **1964**, *136*, B864-871. (b) Hohenberg, P.; Kohn W. *J. Phys. Rev.* **1965**, *140*, A1133-1138. (c) Parr, R. G.; Yang, W. *Density-functional theory of atoms and molecules*, Oxford Univ. Press: Oxford, 1989. (d) Salahub, D. R.; Zerner, M. C. *The Challenge of d and f Electrons*, Amer. Chem. Soc. Washington, D.C. 1989. (e) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454-464. (f) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D.R. *J. Chem. Phys.* **1998**, *108*, 4439-4449. (g) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 8218-8224. (h) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789. (i) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200-206. (j) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- [34] (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939-947. (b) Gordon M. S.; Binkley, J. S.; Pople J. A.; Pietro, W. J.; Hehre W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797-2803. (c) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039-5048. (d) Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1986**, *7*, 359-378. (e)

Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1987**, *8*, 861-879. (f)  
Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1987**, *8*, 880-893.  
[35] O'Boyle, N.M.; Tenderholt, A.L.; Langner, K.M. *J. Comp. Chem.* **2008**, *29*, 839-845.  
[36] Nifiatis, F.; Athas, J. C.; Gunaratne, K. D. D.; Gurung, Y.; Monette, K. M.; Shivokevich, P. J. *The Open Spectroscopy Journal* **2011**, *5*, 1-12.

[37] Rigaku Oxford-Diffraction, 2012. CrysAlis PRO. Rigaku Oxford-Diffraction, Yarnton, England.  
[38] van der Lee, A. *J. Appl. Cryst.* **2013**, *46*, 1306-1315.  
[39] Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.*, **2007**, *40*, 786-790.  
[40] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.



M = Ni or 2H      Ar = 4-*t*BuPh