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Cofacial Porphyrin Dimers Assembled From N-Heterocyclic Carbene-Metal Bonds

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A porphyrin bearing four imidazolium rings on the *meso* positions was used as N-heterocyclic carbene (NHC) precursor for the synthesis of porphyrin dimers with face-to-face orientations. Porphyrins are connected through the formation of eight M-C$_{NHC}$ bonds, with M = Ag^I or Au^I.

Designing porphyrin-based functional molecular systems able to mimic natural systems is of great interest for future applications.[1] For this purpose, it is most of the time necessary to design three-dimensional multiporphyrinic systems where the chromophores are well organized.[2] In this respect, cofacial porphyrin dimers are particularly interesting since they can be used for different applications like host-guest chemistry[3] and catalysis.[4] They were also used as model compounds to investigate photoinduced energy and/or electron transfer processes between donors and acceptors with well-defined distances and orientations.[5] Cofacial porphyrin dimers were mainly obtained upon the formation of covalent,[6] hydrogen[7] or coordination bonds.[3,8] Coordination driven self-assembly between metal ions and ligands is a powerful approach to obtain multiporphyrinic architectures.[2,9] For example, two Zn^{II} porphyrins can be assembled face-to-face by axial coordination of bridging ligands like 1,4-diazabicyclo[2.2.2]octane (DABCO), pyrazine or 4,4'-bipyridine. This "*template effect*" proved to be efficient to bring the macrocycles in close proximity and then, to link them together through the formation of covalent bonds.[10]

The use of peripheral metal ions playing the role of assembling units between two cofacial porphyrins is also an appealing synthetic strategy because the inner metal ions and the empty space between the two porphyrins can be used for different applications.[3-5] Cofacial porphyrin dimers obtained upon formation of coordination bonds are Werner-type coordination compounds built upon formation of M–N and/or M–O bonds.[2,3,8] To our knowledge, excepting the cofacial porphyrin dimer [Fe^{II}(TPP)]$_2$C (TPP = tetraphenylporphyrin) with a carbide bridge between two iron atoms reported by Mansuy and coworkers,[11] there is no other cofacial porphyrin dimer built only upon formation of M–C bonds. During the last decade, *N*-Heterocyclic carbenes (NHC) have attracted considerable attention to obtain discrete metallo-supramolecular architectures.[12] NHC can form robust M-C$_{NHC}$ bonds with most transition metals, but notable exceptions are Ag^I–C$_{NHC}$ bonds, which are enough labile to lead to the formation of Ag^I and free NHC. This reversibility is advantageous for two reasons: the dynamic process allows self-correction leading to the formation of the thermodynamic products,[13,14] and it is possible to easily transmetalate the NHC ligands from Ag^I to other transition metal ions, such as Au^I, to "*freeze*" the system.[15] Taking advantage of these properties, we describe here the synthesis and characterization of cofacial porphyrin dimers built upon formation of eight M-C$_{NHC}$ bonds with M = Ag^I and Au^I (Fig. 1).

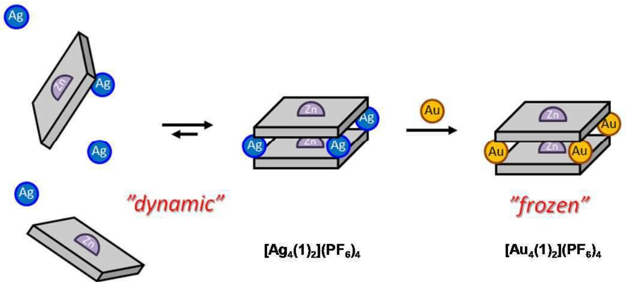

Fig. 1 Synthetic strategy adopted to obtain cofacial porphyrin dimers assembled from N-heterocyclic carbene-metal bonds **[Ag$_4$(1)$_2$](PF$_6$)$_4$** and **[Au$_4$(1)$_2$](PF$_6$)$_4$**.

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Electronic Supplementary Information (ESI) available: experimental details, synthetic procedures and characterization (^{1}H/^{13}C, 2D (COSY, NOESY, HSQC, HMBC, DOSY) NMR, UV-Vis spectra, MS spectra, hydrodynamic radii calculation. See DOI: 10.1039/x0xx00000x

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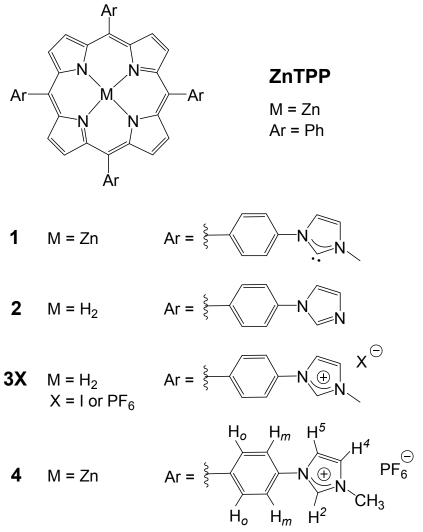
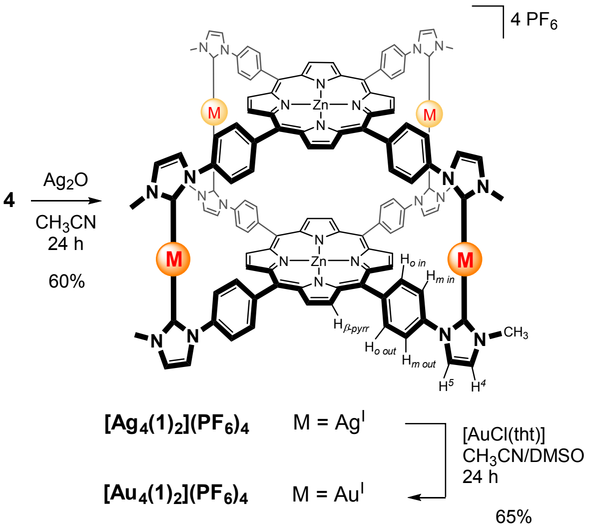


Chart 1 Structures of porphyrins **1-4** and **ZnTPP**.



Scheme 1 Synthesis of cofacial porphyrin dimers **$[M_4(1)_2](PF_6)_4$** (M = Ag^I or Au^I).

For this purpose, we first synthesized a Zn^{II} porphyrin *meso*-functionnalized with four imidazolium salts as precursor of the porphyrin with four NHC ligands **1** depicted in Chart 1. It was obtained in a four step procedure starting from 4-(1*H*-imidazol-1-yl)benzaldehyde (see ESI).[16] The free-base *meso* 5,10,15,20-tetrakis(4'-imidazolyl-phenyl)porphyrin **2** (Chart 1) was prepared.[17] Then, methylation of the four peripheral imidazole groups with CH_3I afforded the cationic porphyrin **3I** in 80% yield (Chart 1).[18] The ^1H NMR spectrum of porphyrin **3I** clearly showed the fourfold symmetry of the compound and the deshielded signal of the four imidazolium protons H^2 at δ = 10.11 ppm (DMSO-d_6, see ESI). Then, anion metathesis reaction with KPF_6 afforded the corresponding porphyrin **$3PF_6$** in 96% yield (Chart 1). Finally, the metalation of **$3PF_6$** with Zn^{II} gave porphyrin **4** in 90% yield. The expected signals of the hexafluorophosphate anions of porphyrin **4** were observed by ^{31}P and ^{19}F NMR spectroscopy, while the metalation of the porphyrin core with Zn^{II} was confirmed by ^1H NMR, UV-vis absorption spectroscopy and mass spectrometry (see ESI).

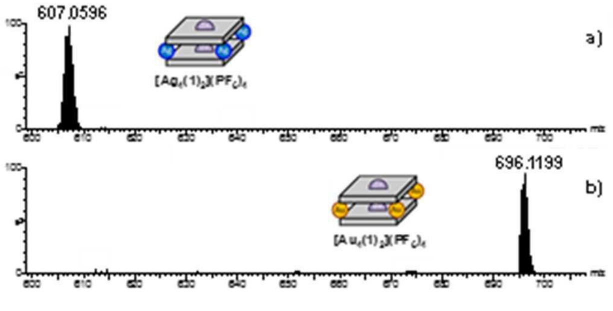


Fig. 2 High resolution ESI-MS spectra of cofacial porphyrin dimers **$[Ag_4(1)_2](PF_6)_4$** (a) and **$[Au_4(1)_2](PF_6)_4$** (b).

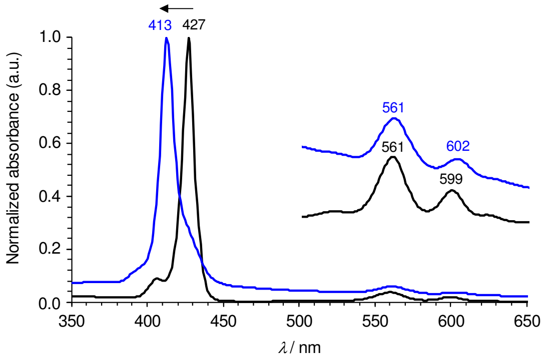


Fig. 3 UV-Vis absorption spectra of **ZnTPP** (black) and **$[Ag_4(1)_2](PF_6)_4$** (blue) in DMSO (normalized absorbance of the Soret absorption band at A = 1.0).

Porphyrin **4** with four *meso* imidazolium groups was used as NHC precursor for the preparation of cofacial porphyrin dimers **$[M_4(1)_2](PF_6)_4$** (M = Ag^I or Au^I, Scheme 1). The reaction of porphyrin **4** with four equivalents of Ag_2O in CH_3CN for 24 hours in the dark afforded **$[Ag_4(1)_2](PF_6)_4$** in a good yield of 60%. All spectroscopic data are in agreement with the dimeric structure proposed for **$[Ag_4(1)_2](PF_6)_4$**. Satisfyingly, ESI-TOF mass spectrometry (positive mode, Figure 2a) features the molecular peak at *m/z* = 607.0596 Da with an isotopically resolved profile in good agreement with the calculated distribution for the tetracationic species **$[Ag_4(1)_2]^{4+}$** (calcd *m/z* = 607.0595 Da). An optical hallmark of a cofacial porphyrin dimer is the presence of blue-shifted Soret absorption band relative to the one of a reference monomeric porphyrin (H aggregate).[6-8] Here, **ZnTPP** was taken as reference compound (Chart 1). The dimer **$[Ag_4(1)_2](PF_6)_4$** exhibits a split Soret absorption band with a maximum at λ = 413 nm and a shoulder at $\lambda \sim$ 424 nm (Fig 3). Compared to **ZnTPP**, the Soret absorption band is blue shifted by 14 nm. This large blueshift indicates the existence of excitonic coupling between the porphyrins and a short interchromophoric distance of 3–4 Å.[19]

Formation of cofacial porphyrin dimer **$[Ag_4(1)_2](PF_6)_4$** was also confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in DMSO-

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d_6 (Fig. 4). The signal of the imidazolium protons of porphyrin **4** at δ = 10.07 ppm disappeared upon formation of the eight Ag^I–NHC bonds of **$[Ag_4(1)_2](PF_6)_4$**. The signal of the C_{NHC} bound to Ag^I was observed as a broad signal at $\delta \sim$ 179.9 ppm (DMSO-d_6) by $^{13}C\{^1H\}$ NMR spectroscopy (see ESI). This chemical shift is consistent with those of C_{NHC} reported in the literature for homoleptic $[Ag(NHC)_2]^+$ complexes.[12-15] In the ^1H NMR spectrum of monomeric porphyrin **4**, the signals of the *ortho* and *meta* protons of the *meso* aryl groups were observed as two doublets at δ = 8.47 and 8.21 ppm (Fig. 4a) because there are only two different kinds of protons (H_o and H_m, see Chart 1). In the ^1H NMR spectrum of **$[Ag_4(1)_2](PF_6)_4$**, four well separated signals were observed for the *ortho* and *meta* protons at δ = 8.30, 8.20, 7.80 and 7.72 ppm. Diffusion-ordered spectroscopy (DOSY) ^1H NMR showed that all these aromatic signals belong to the same molecular species presenting a diffusion coefficient value of 8.84×10^{-11} m^2 s^{-1} in DMSO-d_6 at 298K (see ESI). It suggests that rotation of *meso* aryl groups is restricted within **$[Ag_4(1)_2](PF_6)_4$** (Fig. 4b). Indeed, different chemical environments are experienced by the *meso* aryl protons, namely $H_{o\ in}$, $H_{m\ in}$, $H_{o\ out}$ and $H_{m\ out}$ (Scheme 1 and Fig. 3b; attribution of the signals is based on 2D COSY and ROESY NMR experiments, see ESI). The protons of one porphyrin oriented inside the cofacial porphyrin dimer ($H_{o\ in}$ and $H_{m\ in}$) have upfield chemical shifts because of the shielding effect of the second porphyrin. This shielding effect is weaker for protons oriented outside the cofacial porphyrin dimer ($H_{o\ out}$ and $H_{m\ out}$). It is noteworthy that the singlet of the β-pyrrolic protons ($H_{\beta\text{-}pyrr}$) is shifted upfield by $\Delta\delta$ = 0.52 ppm due to the shielding effect of the neighboring porphyrins within **$[Ag_4(1)_2](PF_6)_4$**. As expected, the diffusion coefficient value of the cofacial porphyrin dimers **$[Ag_4(1)_2](PF_6)_4$** is lower than that of monomeric species **4** (10.80×10^{-11} m^2 s^{-1}).

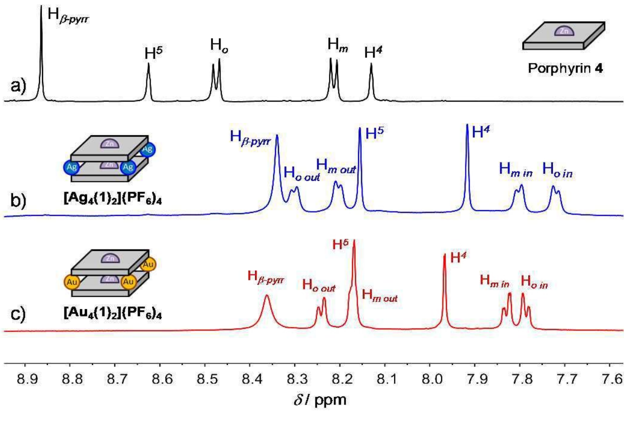

Fig. 4 Stacked partial ^1H NMR (600 MHz, 25°C, DMSO-d_6) spectra of porphyrin **4** (a), cofacial porphyrin dimers **$[Ag_4(1)_2](PF_6)_4$** (b) and **$[Au_4(1)_2](PF_6)_4$** (c).

Knowing that Ag^I–NHC complexes are used as carbene transfer agents, we considered substituting Ag^I ions in **$[Ag_4(1)_2](PF_6)_4$** for Au^I ions. The reaction of **$[Ag_4(1)_2](PF_6)_4$** with 4 equivalents of [AuCl(tht)] (tht = tetrahydrothiophene) in a CH_3CN/DMSO 9:1 mixture for 24 hours at room temperature afforded the corresponding cofacial porphyrin dimer **$[Au_4(1)_2](PF_6)_4$** in 65% yield. ESI-TOF mass spectrometry (positive mode) featured the expected molecular mass peak at *m/z* = 696.1199 Da (Fig. 2b) with an isotopically resolved profile, which fits perfectly with the calculated theoretical distribution of the tetracationic species **$[Au_4(1)_2]^{4+}$** (calcd *m/z* = 696.1213 Da). The substitution of all four Ag^I by Au^I ions was also confirmed by $^{13}C\{^1H\}$ NMR spectroscopy because only one sharp signal corresponding to the eight C_{NHC} was observed at δ = 181.7 ppm (DMSO-d_6), in the range of chemical shifts of C_{NHC} reported in the literature for homoleptic $[Au^I(NHC)_2]^+$ complexes (Fig. 5a).[12-15] The transmetalation reaction maintains the face-to-face orientation between the two porphyrins, because the UV-visible spectrum of **$[Au_4(1)_2](PF_6)_4$** is very similar to the one of **$[Ag_4(1)_2](PF_6)_4$** and exhibits a blue shifted Soret absorption band with a maximum at λ = 413 nm (Fig. 5b). Moreover, the ^1H NMR spectrum of **$[Au_4(1)_2](PF_6)_4$** (Fig. 4c) is also very similar to the one of **$[Ag_4(1)_2](PF_6)_4$** (Fig. 4b). The β-pyrrolic protons of **$[Au_4(1)_2](PF_6)_4$** at δ = 8.36 ppm confirmed that the two porphyrins are still in close proximity and four signals are observed for *meso* aryl protons $H_{o\ in}$, $H_{m\ in}$, $H_{o\ out}$ and $H_{m\ out}$. The diffusion coefficient value of 8.60×10^{-11} m^2 s^{-1} estimated by DOSY ^1H NMR spectroscopy in DMSO-d_6 for **$[Au_4(1)_2](PF_6)_4$** is close to the one found for**$[Ag_4(1)_2](PF_6)_4$**. It confirms that these two cofacial porphyrin dimers have similar hydrodynamic radii in solution (11.2 and 11.6 Å, respectively for **$[Ag_4(1)_2](PF_6)_4$** and **$[Au_4(1)_2](PF_6)_4$**), whereas the hydrodynamic radius of monomeric porphyrin **4** calculated with the Stokes-Einstein relationship is smaller (9.2 Å, see ESI).[20]

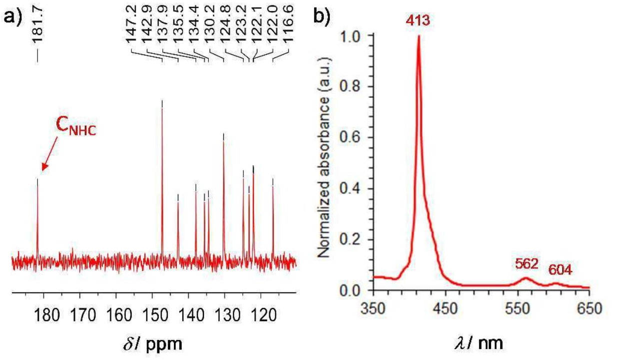

Fig. 5 a) Aromatic region of the $^{13}C\{^1H\}$ NMR spectrum (600 MHz, 25°C, DMSO-d_6) of **$[Au_4(1)_2](PF_6)_4$**; b) UV-Vis absorption spectrum of **$[Au_4(1)_2](PF_6)_4$** in DMSO (normalized absorbance of the Soret absorption band at A = 1.0).

Finally, relative stability of the two systems in the presence of a coordinating anion such as iodide was investigated. The two dimers **$[Ag_4(1)_2](PF_6)_4$** and **$[Au_4(1)_2](PF_6)_4$** were treated with lithium iodide in DMSO and the spectral evolution was monitored by UV-vis absorption spectroscopy. The dimer **$[Ag_4(1)_2](PF_6)_4$** is not stable in the presence of lithium iodide, as indicated by the important decrease of the Soret absorption band at λ = 413 nm concomitant with the apparition of a new absorption band at λ = 430 nm. This is due to the formation of the monomeric cationic species zinc(II) *meso* 5,10,15,20-

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tetrakis(4'-*N*-methylimidazolyl-phenyl)porphyrin, as it was also confirmed by ^{1}H NMR spectroscopy (see ESI). On the contrary, **$[Au_4(1)_2](PF_6)_4$** is stable and did not decompose upon addition of lithium iodide (see ESI). This is in good agreement with the higher stability of the Au-C_{NHC} bonds over the lability of Ag-C_{NHC}.bonds.

To conclude, we have synthesized and characterized cofacial porphyrin dimers assembled for the first time from eight M-C_{NHC} bonds with M = Ag^I or Au^I. The reversibility of the Ag^I-C_{NHC} bonds allows the two porphyrins to self-assemble with a face-to-face orientation to obtain **$[Ag_4(1)_2](PF_6)_4$**, which can then be easily converted into the robust analog **$[Au_4(1)_2](PF_6)_4$** through a transmetalation reaction. Changing the nature of the assembling metal ions and the nature of the spacers between NHCs and *meso* positions are also interesting in view of obtaining different cofacial dimers. Therefore, a fine tuning of the "*through space*" electronic interactions between the porphyrins may be expected by varying the interchromophoric distances. This work is currently under progress in our group.

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Conflicts of interest

There are no conflicts to declare.

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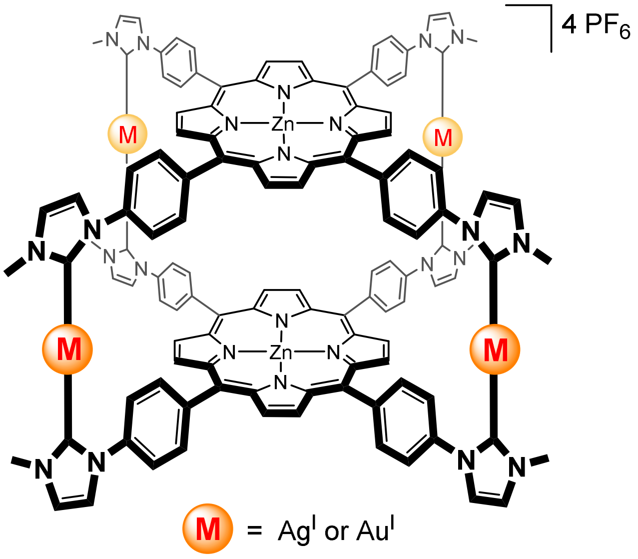

Cofacial porphyrin dimers assembled from eight metal-carbene bonds were synthesized by using porphyrins with four imidazolium groups as precusors.