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Spontaneous Tl(I)-to-Tl(III) Oxidation in Dynamic Heterobimetallic Hg(II)/Tl(I) Porphyrin Complexes†

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Strapped heterobimetallic Hg(II)/Tl(I) porphyrin complexes, with both metal ions bridged by the N-core in a dynamic way, undergo spontaneous Tl(I)-to-Tl(III) oxidation leading to a mono-Tl(III) complex and a mixed valence Tl(I)/Tl(III) bimetallic complex. It provides a new opportunity to tune metal ion translocations in bimetallic porphyrin systems.

Molecular switches based on the translocation of one or several metal ions between different compartments are attractive because they offer the possibility of redox control relying on a change of the oxidation state(s) of the metal(s).[1,2] Such metal complexes, in particular those involving the translocation of several ions,[3] are not so widespread and the engineering of new ligands is still needed for both fundamental purposes and practical applications, *e.g.* in the fields of sensing systems, logic gates and devices.

In the supramolecular coordination chemistry of porphyrins,[4] translocation of a metal ion from the N-core to an appended binding site has not been considered as a component of the toolbox, until our group unravelled this possibility with the so called overhanging carboxylic acid porphyrins (*e.g.* **1** and **2**, Figure 1a).[5] Since, we have been studying the dynamics of bimetallic species especially with the period 6 post-transition elements.[6] In particular, some complexes undergo an inherent exchange of the metals relative to the porphyrin plane (double translocation processes), either in a purely intraligand fashion (compartmentalized motion resembling a Newton's cradle device, case of homobimetallic complexes),[6c,e] or in combined intra- and intermolecular pathways (non-compartmentalized motion, case of heterobimetallic complexes such as **2$_{Hg}$·PbOAc**[7] in Figure 1b top).[6f] If highly toxic, mercury and thallium merit particular attention for non applied purposes due to an intriguing coordination chemistry as shown herein.

Recently, a dynamic mixed valence bimetallic thallium complex, with Tl(I) selectively bound to the strap (hanging atop, HAT) and Tl(III) selectively bound to the N-core (out-of-plane, OOP), and whose formation is light driven through a Tl(I)-to-Tl(III) photooxidation process, has been scrutinized (**2$_{Tl(III)}$·Tl(I)** in Figure 1b bottom).[8] The formation of heterobimetallic complexes incorporating thallium was the next step towards the achievement of a redox control of double translocation processes with such porphyrins. Herein, we report on the formation, dynamics and unique reactivity of Hg(II)/Tl(I) bimetallic porphyrin complexes with ligands **1** and **2**.
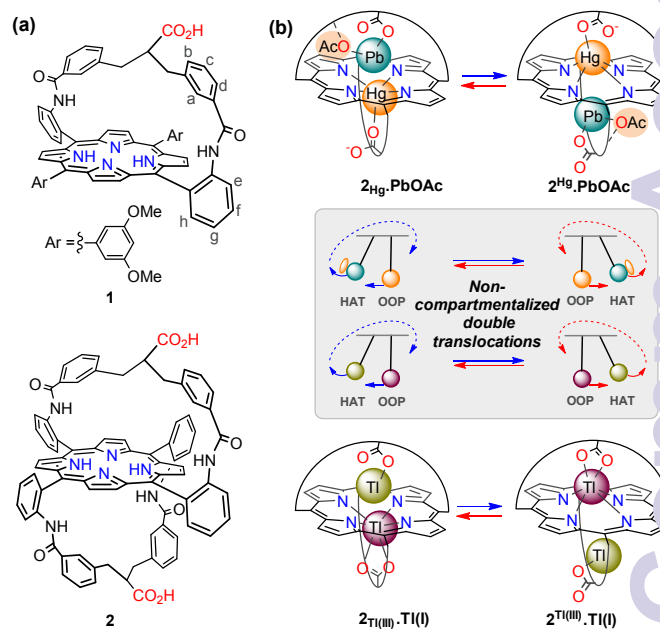
Fig. 1 (a) Structure of porphyrins **1** and **2**. (b) Dynamic behavior of heterobimetallic complexes **2$_{Hg}$·PbOAc** and **2$_{Tl(III)}$·Tl(I)** involving double translocation processes.

The formation of Hg(II)/Tl(I) bimetallic species was investigated by NMR and UV-vis absorption spectroscopies, in 9:1 CDCl$_3$/CD$_3$OD or CHCl$_3$/CH$_3$OH solutions and in the presence of

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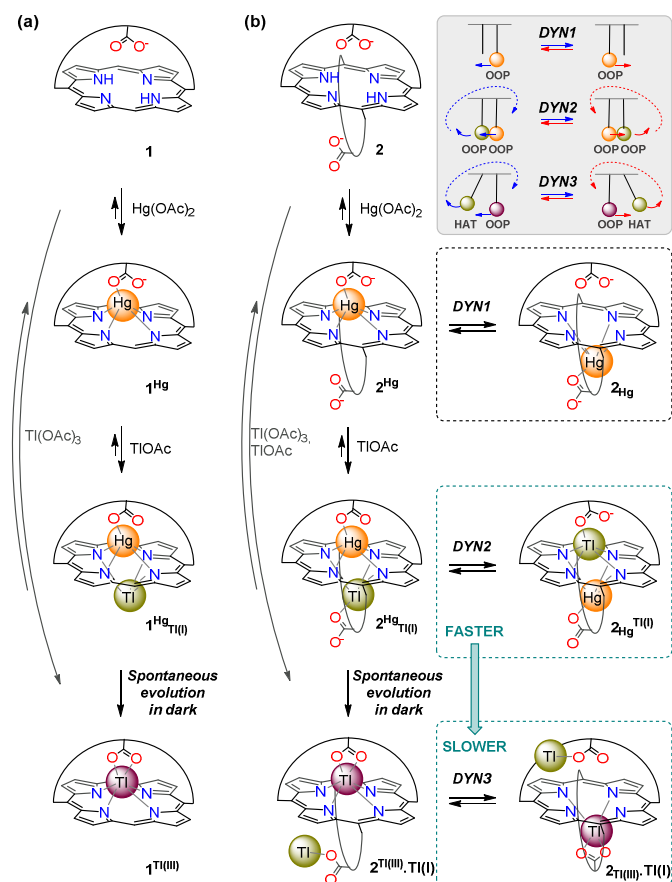 *E-mail : stephane.legac@univ-rennes1.fr; bernard.boitrel@univ-rennes1.fr*
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diisopropylethylamine (DIPEA, 10 equiv.). The addition of 1 equiv. of Hg(OAc)$_2$ to **1** or **2** led to the formation of the monometallic complexes **1**^{Hg} or **2**^{Hg} as the major species

Scheme 1 Complexation behavior of porphyrins **1** (a) and **2** (b) towards Hg(II) and Tl(I), and the dynamics and reactivity of the corresponding complexes.

Fig. 2 Formation and spontaneous evolution of **1**^{Hg}$_{Tl(I)}$ monitored by ^{1}H and ^{205}Tl NMR spectroscopy (CDCl$_3$/CD$_3$OD 9:1, 10 equiv. of DIPEA). **1**^{Hg}$_{Tl(I)}$ was formed by the successive additions of Hg(OAc)$_2$ (a-b) and TlOAc (b-e), and was then allowed to stand in dark up to three days (d-g). S = solvent.

(Scheme 1, Figure 2b and SI). The C_2-symmetric NMR pattern of the latter complex is due to a fast translocation process of the NMR time scale, the mercury ion oscillating through the N-core between the two equivalent out-of-plane positions with apical binding of one of the two overhanging carbonyl groups ("*DYN1*", Scheme 1b).[6b] In both cases, the further addition of 1 equiv. of TlOAc led instantaneously and quasi-quantitatively to a new species of unchanged symmetry (Figure 2c, SI), without observation of homo-complexes of Tl(I). The binding of Tl(I) to **1**^{Hg} and **2**^{Hg} occurs in a fast exchange regime at 298 K, and almost no evolution of the NMR spectra was observed with an excess of TlOAc. These data suggest high association constants ($k_a > 10^5$ M^{-1}), that are hardly compatible with Tl(I) bound selectively to a carboxylate of a strap (HAT coordination mode, as in **2**$^{Tl(III)}$.**Tl(I)**). Indeed, a k_a lower than 10^2 M^{-1} was calculated for the HAT binding of Tl(I) to the Tl(III) complex of **2**.[8] By UV-vis absorption spectroscopy, the addition of TlOAc to **1**^{Hg} and **2**^{Hg} led to new Soret bands at respectively 461 and 464 nm, which are intermediate between those of related homobimetallic species of Hg(II) (~447 nm)[6b] and Tl(I) (~488 nm)[8] with both their metal ions OOP-bound to the N-core. These data strongly suggest that the two metal ions interact with the N-core, the porphyrin behaving as a bridging ligand, which corresponds to the structures of **1**^{Hg}$_{Tl(I)}$ and **2**^{Hg}$_{Tl(I)}$ in Scheme 1. In complex **1**^{Hg}$_{Tl(I)}$, Tl(I) is OOP-bound opposite to the strapped side of the porphyrin, while Hg(II) is OOP-bound with the carboxylate group as intramolecular counterion. The second carboxylate of **2**^{Hg}$_{Tl(I)}$ presumably interacts with Tl(I) via its carbonyl group (π-ligand).[9] Its C_2-symmetric NMR pattern at 298 K (SI) arises from a fast equilibrium on the NMR time scale between two degenerate states, *i.e.* **2**^{Hg}$_{Tl(I)}$ and **2**$_{Hg}$$^{Tl(I)}$, with an intraligand pathway for Hg(II) funneling through the N-core, and an intermolecular exchange of Tl(I) ("*DYN2*", Scheme 1b).[6f,8] The formation of **1**^{Hg}$_{Tl(I)}$ and **2**^{Hg}$_{Tl(I)}$ was also monitored by ^{205}Tl NMR spectroscopy, revealing the high lability of the Tl(I) ion (Figure 2c-e, SI). Indeed, whereas a broad signal was observed at 1 equiv. of TlOAc (bound Tl(I), 1114 ppm), no signal could be detected with a second equivalent (coalescence phenomenon) and a broad highfield shifted signal

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(1006 ppm) appeared at 4 equiv. of TlOAc (average of free/bound Tl(I) [δ_{TlOAc} = 978 ppm]).

All attempts to obtain X-ray structures of $\mathbf{1^{Hg}_{Tl(I)}}$ and $\mathbf{2^{Hg}_{Tl(I)}}$ failed. Instead, single crystals of the monometallic complex $\mathbf{1^{Tl(III)}}$ (Scheme 1a) were obtained from slow evaporation of a solution of $\mathbf{1^{Hg}_{Tl(I)}}$, and this was done in dark conditions (Figure 3). Its structure is very similar to that of the previously described monometallic Tl(III) complex of $\mathbf{2}$,[8] with the metal ion located on the strapped side 0.781 Å out of the 24-atom porphyrin mean plane (24MP) and with the carboxylate group as intramolecular counterion.
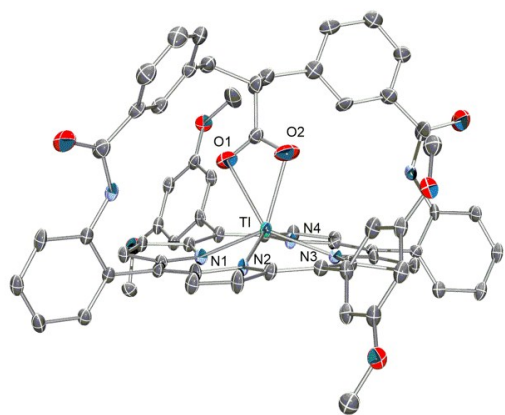
Fig. 3 X-ray structure of $\mathbf{1^{Tl(III)}}$ (Ortep view at 30 % probability, H atoms omitted for clarity). Selected distances (Å): O1-Tl 2.447, O2-Tl 2.342, N1-Tl 2.240, N2-Tl 2.208, N3-Tl 2.227, N4-Tl 2.193, Tl-24MP 0.781.

This unexpected spontaneous Tl(I)-to-Tl(III) oxidation in dark conditions was further investigated by NMR spectroscopy. The complexes $\mathbf{1^{Hg}_{Tl(I)}}$ and $\mathbf{2^{Hg}_{Tl(I)}}$, prepared from the addition of 1 equiv. of Hg(II) and 5 equiv. of Tl(I), slowly evolved in solution at room temperature and in dark to give respectively $\mathbf{1^{Tl(III)}}$ and $\mathbf{2^{Tl(III)}.Tl(I)}$ (Scheme 1). Indeed, both their ^{1}H and ^{205}Tl NMR spectra upon evolution were identical to those of $\mathbf{1^{Tl(III)}}$ and $\mathbf{2^{Tl(III)}.Tl(I)}$[8] obtained by addition of the corresponding metal salts (Figure 2d-g and SI). Interestingly, the sequence $\mathbf{2^{Hg}}$ -> $\mathbf{2^{Hg}_{Tl(I)}}$ -> $\mathbf{2^{Tl(III)}.Tl(I)}$ allows to shift across three types of dynamics involving translocation of metal ions ("*DYN1*" -> "*DYN2*" -> "*DYN3*", Scheme 1b). Qualitatively, from comparison of the low temperature ^{1}H NMR spectra of $\mathbf{2^{Hg}_{Tl(I)}}$ and $\mathbf{2^{Tl(III)}.Tl(I)}$, it appears that the dynamics "*DYN2*" of the former is faster than "*DYN3*" of the latter (SI). Indeed, $\mathbf{2^{Hg}_{Tl(I)}}$ retains a C_2-symmetric pattern down to 233 K, whereas a dissymmetric one is observed at 263 K for $\mathbf{2^{Tl(III)}.Tl(I)}$. This is in accordance with a O-Hg interaction weaker than a O-Tl one in the intermediate monometallic complexes upon dissociation of Tl(I) (carbonyl as π-ligand *vs* COO$^-$ as counterion).

We have performed a series of experiments, summarized below, that help to draw a plausible scenario for the oxidation process:

(i) this evolution takes place with similar kinetics in deoxygenated solutions (SI), which rules out the previously described Tl(I)-to-Tl(III) photooxidation process based on oxygen photosensitization.[8] Also, an equimolar amount of

Hg(II) was required to oxidize Tl(I), suggesting that the redox couple Hg(II)/Hg(0) is involved, the process thus following the balanced chemical equation *Tl(I) + Hg(II) -> Tl(III) + Hg(0)*. Although the standard electrode potentials indicate that this reaction should not take place ($E°_{Tl(III)/Tl(I)}$ = 1.25 and $E°_{Hg(II)/Hg}$ = 0.85 V *vs* SHE), standard conditions are clearly not met in the present study where the porphyrin plays a key role. Indeed, Tl(I) and Hg(II) do not react together in the absence of porphyrin (SI).

(ii) the process is considerably boosted by the presence of 4-dimethylaminopyridine (DMAP). With *ca.* 15 equiv. relative to $\mathbf{1^{Hg}_{Tl(I)}}$ or $\mathbf{2^{Hg}_{Tl(I)}}$, Tl(I)-to-Tl(III) oxidation was complete within only 3 hours (SI). Neither the ^{1}H NMR spectra of both complexes were affected by the presence of DMAP, even at low temperature, nor those of the final Tl(III) complexes $\mathbf{1^{Tl(III)}}$ and $\mathbf{2^{Tl(III)}.Tl(I)}$. In addition, catalytic or equimolar amounts of DMAP did not significantly increase the rates. Therefore DMAP likely stabilizes an intermediate species in the oxidation process, the larger the amount of DMAP the higher the rate.

(iii) there is a noticeable influence of the order of introduction of the metal salts. Whereas addition of Tl(I) to $\mathbf{1^{Hg}}$ led exclusively to $\mathbf{1^{Hg}_{Tl(I)}}$, adding Hg(II) to $\mathbf{1.Tl(I)}$ (structure in inset in Figure 4) led to a *ca.* 4:1 initial ratio of $\mathbf{1^{Hg}_{Tl(I)}}$ and $\mathbf{1^{Tl(III)}}$ (SI), suggesting that the process goes faster when Hg(II) is not bound to the porphyrin N-core. Also, the ~1/500 dilution of an NMR tube solution containing exclusively $\mathbf{1^{Hg}_{Tl(I)}}$ revealed, from UV-vis spectroscopy analysis, the spontaneous formation of a significant amount of $\mathbf{1^{Tl(III)}}$ within a few minutes (Soret band at 436 nm, SI). The fast oxidation upon dilution is thought to arise from a partial dissociation of the complex releasing "free" Hg(II) ions.

(iv) working at μM concentrations (UV-vis spectroscopy experiments), the addition of Hg(II) to $\mathbf{1.Tl(I)}$ led to two competing processes (denoted "A" and "B"), that are respectively the formation of $\mathbf{1^{Tl(III)}}$ and $\mathbf{1^{Hg}_{Tl(I)}}$ (Figure 4, Soret bands at 426, 436 and 462 nm). A *ca.* 1.5:1 "frozen ratio" of these two species is reached after 10 min, a point where $\mathbf{1.Tl(I)}$ is fully consumed. This shows that part of Hg(II) is used to oxidize Tl(I), the other part being trapped into the porphyrin and thus not anymore reactive. Interestingly, the "frozen ratio" of $\mathbf{1^{Tl(III)}}$ and $\mathbf{1^{Hg}_{Tl(I)}}$ is amplified to a *ca.* 5:1 value with a 10 times higher amount of TlOAc (200 equiv. *vs* 20 equiv., Figure 4b *vs* a). Considering that a higher amount of TlOAc inhibits the assistance role of the carboxylate of the strap towards the insertion of mercury, these data confirm the reactivity of Hg(II) out of the porphyrin N-core. This last result strongly contrasts with the slow evolution over 2-3 days of $\mathbf{1^{Hg}_{Tl(I)}}$ at mM concentration.

(v) only one equivalent excess of Hg(OAc)$_2$ inhibits the oxidation of Tl(I). Indeed, a bimetallic Hg(II) complex of $\mathbf{2}$,[6b] formed by the addition of 2 equiv. of Hg(II) and 15 equiv. of DMAP to $\mathbf{2}$, did not show any evolution after 3 hours at RT when in presence of 5 equiv. of TlOAc (SI). In these conditions, the amount of remaining free base $\mathbf{2}$ corresponds to trace, confirming that the oxidation does not occur when Tl(I) cannot bind to the strap of the ligands.

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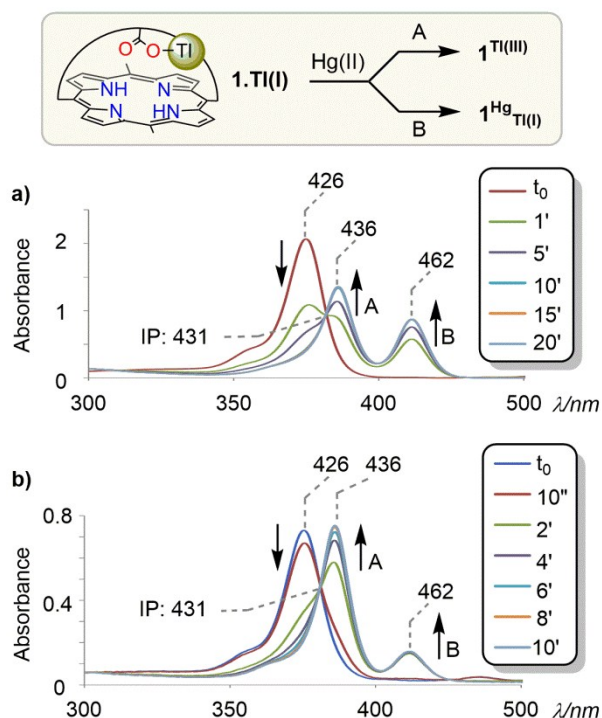
Fig. 4 UV-vis monitoring of the reaction of **1.Tl(I)** with Hg(OAc)$_2$ (1 equiv.) in two sets of initial conditions: with (a) 20 equiv. and (b) 200 equiv. of TlOAc added to **1** (CHCl$_3$/MeOH 9:1, 10 equiv. of DIPEA). IP = isosbestic point.

These data suggest that the oxidation process goes through an intermediate bimetallic hanging-atop porphyrin complex, with both Tl(I) and Hg(II) bound to the strap of the free base ligand as drawn in Scheme 2b (this association may be stabilized by the binding of DMAP to Hg(II)). This proposed association is based on the X-ray structure of a pentanuclear Pb(II) assembly of **1**, showing that a HAT metal ion can be involved in the binding of a second metal (Scheme 2a).[6g] Such a transient hanging-atop Tl(I)-Hg(II) association at the level of the strap may allow electron transfer between the metals *via* an inner sphere mechanism otherwise not possible.
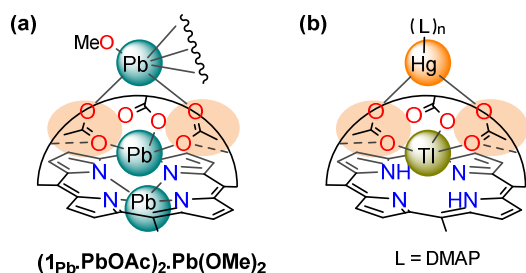
Scheme 2 (a) A pentanuclear Pb(II) based assembly with **1**.[6g] (b) Proposed intermediate in the Tl(I)-to-Tl(III) oxidation process mediated by Hg(II).

In conclusion, bridged Hg(II)/Tl(I) heterobimetallic porphyrin complexes have been readily formed with a high selectivity and display an unprecedented reactivity. They indeed spontaneously undergo a "self-oxidation" process affording mono or bimetallic Tl(III) species. An Hg(II)/Tl(I) association at

the level of a strap of the free porphyrin ligands is thought as a key intermediate in the process. The complex **2^{Hg}$_{Tl(I)}$** is dynamic in solution, as the metals inherently invert their position relative to the porphyrin plane. Such an oxidation process enlarges the toolbox to control the dynamics of porphyrin bimetallic species involving metal ion translocations, and extension of this work to other heterobimetallic complexes is now under study in our laboratories.

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