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Porphyrinoids

Sunlight-Driven Formation and Dissociation of a Dynamic Mixed-Valence Thallium(III)/Thallium(I) Porphyrin Complex**

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Abstract: *Inspired by a Newton's cradle device and interested in the development of redox-controllable bimetallic molecular switches, a mixed-valence thallium(III)/thallium(I) bis-strap porphyrin complex, with* $\mathrm{Tl^{III}}$ *bound out of the plane of the N core and* $\mathrm{Tl^{I}}$ *hung to a strap on the opposite side, was formed by the addition of TlOAc to the free base and exposure to indirect sunlight. In this process, oxygen photosensitization by the porphyrin allows the oxidation of* $\mathrm{Tl^{I}}$ *to* $\mathrm{Tl^{III}}$*. The bimetallic complex is dynamic as the metals exchange their positions symmetrically to the porphyrin plane with* $\mathrm{Tl^{III}}$ *funneling through the macrocycle. Further exposure of the complex to direct sunlight leads to thallium dissociation and to total recovery of the free base. Hence, the porphyrin plays a key role at all stages of the cycle of the complex: It hosts two metal ions, and by absorbing light, it allows the formation and dissociation of* $\mathrm{Tl^{III}}$*. These results constitute the basis for the further design of innovative light-driven bimetallic molecular devices.*

Metal-ion-based molecular switches are particularly attractive for the design of molecular devices whose properties depend on the oxidation state of the metal.[1] As observed in catenane or rotaxane structures, motion of interlocked subunits can be achieved under redox control owing to a reorganization in the coordination sphere of the oxidized or reduced metal center.[2] Other systems, albeit much less developed, include a translocation of a metal ion between two different coordination sites.[3] Considering bimetallic complexes, there are very few molecular switches that integrate a double translocation of two metal ions in their functioning,[4] and a redox control of such a process is even rarer.[4b] In the course of our research on the supramolecular coordination chemistry of porphyrins, we have recently observed unique dynamic features associated with a specific class of bimetallic porphyrin complexes, which incorporate a metal ion bound out of the plane (OOP) of the N core and a second one hung to a strap above the N core on the opposite side, in the so-called hanging-atop coordination mode (HAT).[5] Thus far, two types of double translocation processes have been characterized, which correspond to an equilibrium between two degenerate forms of the complex, as exemplified in Figure 1 with lead(II)-based metalloporphyrins. Of particular interest is the motion of the metal ions triggered by an allosteric effector (e.g., $\mathrm{AcO^{-}}$) promoting the HAT coordination mode.[5b,d] Furthermore, switching between the two types of motions as depicted in Figure 1 can be readily achieved by a dynamic constitutional evolution of the system triggered by a chemical effector.[5e] These recent findings define a new class of molecular devices, whose working principles resemble that of a Newton's cradle device. Aiming at expanding our toolbox towards the redox control of such double translocation processes, we turned our attention to the complexation of thallium and describe herein an unprece-

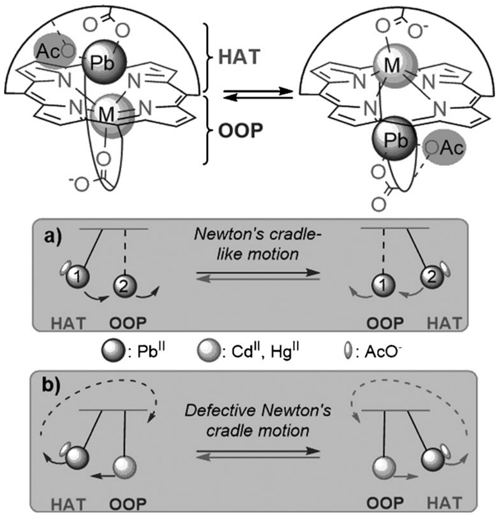

Figure 1. Recent examples of double translocation processes with $\mathrm{Pb^{II}}$ bimetallic complexes of a bis-strap porphyrin ligand bearing overhanging carboxylic acid groups. a) Coupled and compartmentalized intramolecular migrations of $\mathrm{Pb^{II}}$ ions resembling the motion of spheres in a Newton's cradle device (upper strap to N core up coupled with N core down to bottom strap).[5b] b) Intramolecular migration of $\mathrm{Hg^{II}}$ or $\mathrm{Cd^{II}}$ ions through the N core coupled to the intermolecular migration of $\mathrm{Pb^{II}}$ ions from one to the other strap ("defective" Newton's cradle motion, N core up to N core down coupled with bottom strap to upper strap).[5e]

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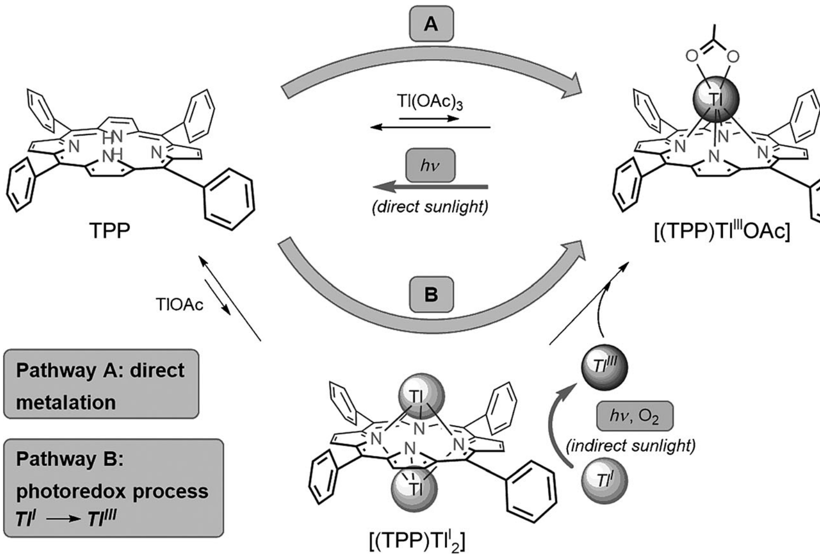
dented photoredox process for the formation and dissociation of a dynamic mixed-valence Tl$^{\mathrm{III}}$/Tl$^{\mathrm{I}}$ porphyrin complex.

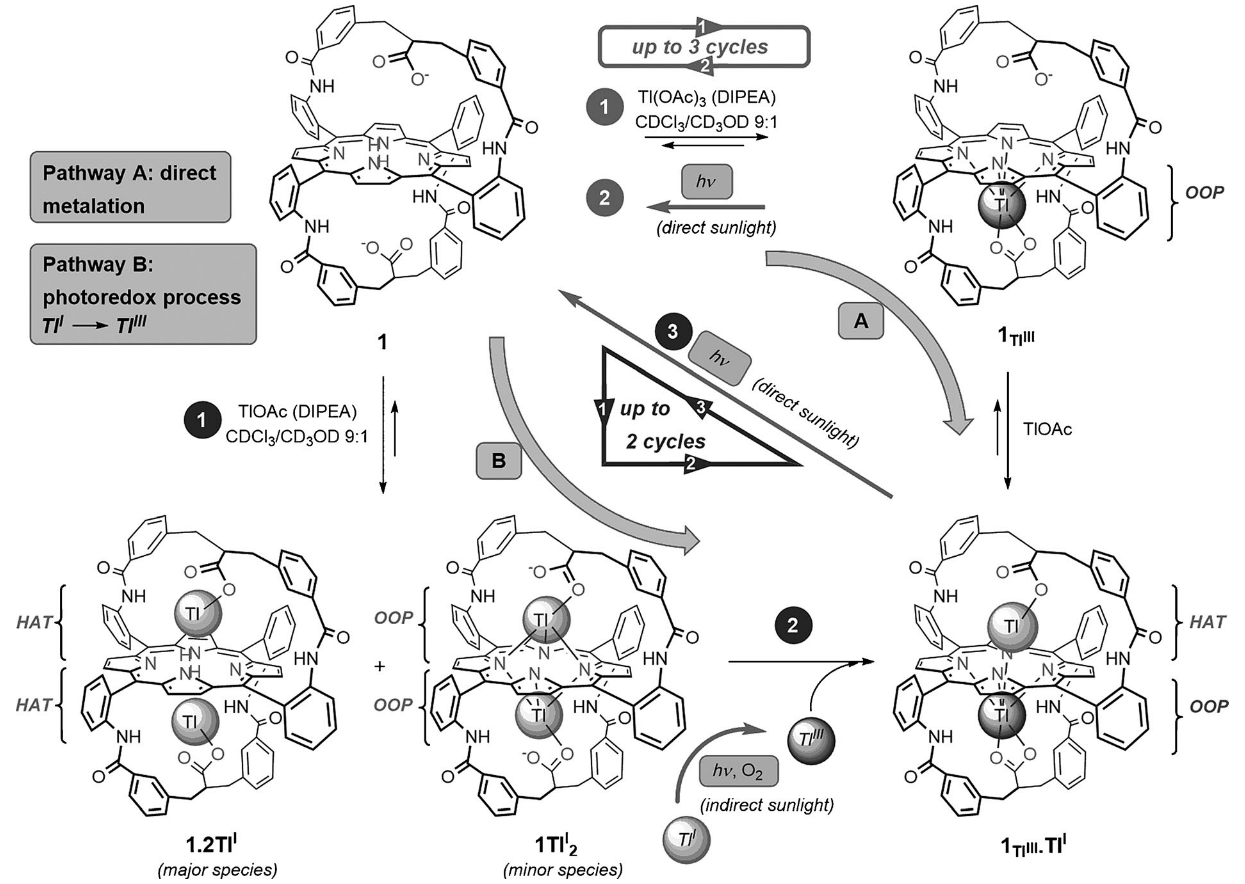
In light of previous work reporting very different chemical and spectroscopic properties for thallium(III) versus thallium(I) porphyrin complexes, a preliminary NMR spectroscopic study was conducted with tetraphenylporphyrin (TPP) and the Tl$^{\mathrm{III}}$ and Tl$^{\mathrm{I}}$ acetate salts. In a CDCl$_3$/CD$_3$OD solution (9:1), the addition of five equivalents of Tl(OAc)$_3$ or TlOAc to TPP led to the mononuclear Tl$^{\mathrm{III}}$ complex [(TPP)Tl$^{\mathrm{III}}$OAc] and to the dinuclear Tl$^{\mathrm{I}}$ complex [(TPP)Tl$^{\mathrm{I}}_2$], respectively, which were both formed as minor products (Scheme 1; see also the Supporting Information). The latter bimetallic complex was stable in the dark, but we observed the slow formation of [(TPP)Tl$^{\mathrm{III}}$OAc] upon leaving the NMR tube under ambient light in the laboratory (Scheme 1, pathway B; these conditions are defined as indirect sunlight). Typically, approximately 90 % conversion was achieved upon exposure to indirect sunlight for about 36 hours. To the best of our knowledge, such a process is unprecedented, the few photochemical studies of bis-Tl$^{\mathrm{I}}$ porphyrins pointing to a photo-induced degradation of the ligand.[6] Photo-oxidation of Tl$^{\mathrm{I}}$ salts has been scarcely reported; it was always studied in aqueous solution and without any photosensitizer, and its mechanism is not fully understood.[7] Most likely, photo-excitation of the Tl$^{\mathrm{I}}$ salts by UV irradiation is a primary step that subsequently leads to oxygen activation, and reactive oxygen species then oxidize the metal ion following the general equation: $\mathrm{Tl^{I}} + 2\,\mathrm{H^{+}} + \mathrm{O_2} \rightarrow \mathrm{Tl^{III}} + 2\,\mathrm{H_2O_2}$.[7a] In the present case of [(TPP)Tl$^{\mathrm{I}}_2$], the oxygen dependence of the photo-oxidation process has been demonstrated (see the Supporting Information), supporting a mechanism involving singlet oxygen formed by porphyrin photosensitization.[8,9] TlOAc was not photo-oxidized in the absence of porphyrin under these experimental conditions, whereas [(TPP)Zn] was able to promote the photo-oxidation of Tl$^{\mathrm{I}}$ to Tl$^{\mathrm{III}}$, giving evidence that Tl$^{\mathrm{I}}$ complexation to the macrocycle is not a prerequisite for this process (see the Supporting Information). Furthermore, we also observed that [(TPP)Tl$^{\mathrm{III}}$OAc], which is stable in the dark, could be efficiently demetalated (> 90 %) upon exposure to direct sunlight for approximately 16 hours, independent of the presence of oxygen, leading very cleanly to the free base TPP as the only product (Scheme 1; see also the Supporting Information). Although more detailed studies are still needed, these two processes, photo-induced formation and photo-dissociation of a Tl$^{\mathrm{III}}$ porphyrin complex, are very attractive as they only require sunlight—and oxygen for the former process—and can be controlled by simply changing the light exposure of the sample.



Scheme 1. Complexation properties of TPP towards TlOAc and Tl(OAc)$_3$ and photoredox behavior of the resulting complexes. Experimental conditions: 298 K, CDCl$_3$/CD$_3$OD (9:1), DIPEA (10 equiv). DIPEA = *N*,*N*-diisopropylethylamine.

We next examined the complexation properties of C_2-symmetric bis-strap porphyrin **1** towards Tl$^{\mathrm{I}}$ and Tl$^{\mathrm{III}}$ acetate salts by ^{1}H and ^{205}Tl NMR spectroscopy (Scheme 2). In a CDCl$_3$/CD$_3$OD (9:1) solution, the monometallic Tl$^{\mathrm{III}}$ complex $\mathbf{1}_{\mathbf{Tl^{III}}}$ was readily obtained by addition of a slight excess of Tl(OAc)$_3$ to **1**, and no other species were detected with a higher amount of the metal salt (see the Supporting Information).[10] The β-pyrrolic protons exhibit a ^{4}J coupling constant of approximately 60 Hz with the ^{205}Tl isotope, giving rise to a dense set of eight signals (dd) in the 8.5–9.5 ppm region. ^{205}Tl-decoupled ^{1}H NMR spectra were recorded to allow for the assignment of these signals (see the Supporting Information). The dissymmetric ^{1}H NMR pattern indicates that Tl$^{\mathrm{III}}$ is located on one side of the macrocycle, which was confirmed by an X-ray structure (Figure 2 a). One of the carboxylic acids behaves as an intramolecular counterion (Tl–O1: 2.328 Å, Tl–O2: 2.368 Å), and pulls the metal 0.914 Å away from the 24-atom porphyrin mean plane (24MP, out-of-plane coordination). In solution, an intraligand exchange of Tl$^{\mathrm{III}}$ between the two sides of the macrocycle occurs by funneling through the N core (Scheme 3 a).[11] Indeed, a ROESY 2D NMR experiment shows exchange correlations between protons of opposite straps (see the Supporting Information). Similarly to [(TPP)Tl$^{\mathrm{III}}$OAc], $\mathbf{1}_{\mathbf{Tl^{III}}}$ was stable in the dark and tolerated well the ambient light of the laboratory. However, exposure to direct sunlight led to photo-demetalation and to the total recovery of free base **1**, which was not affected by this process (Scheme 2, top; Figure 3 a–c). Therefore, three metalation/photo-demetalation cycles were achieved in a single NMR tube (light-gray loop in Scheme 2; Figure 3 a–g).

The further addition of TlOAc to a solution of $\mathbf{1}_{\mathbf{Tl^{III}}}$ (Scheme 2, pathway A) led to a clear modification of the ^{1}H NMR spectrum consistent with the complexation of Tl$^{\mathrm{I}}$ in a fast exchange regime ($K_a \approx 80\,\mathrm{M}^{-1}$; see the Supporting Information). In the absence of base, the new species retains a dissymmetric ^{1}H NMR pattern, whereas a broad NMR



Scheme 2. Complexation properties of bis-strap porphyrin **1** towards TlOAc and $Tl(OAc)_3$ and photoredox behavior of the resulting complexes.

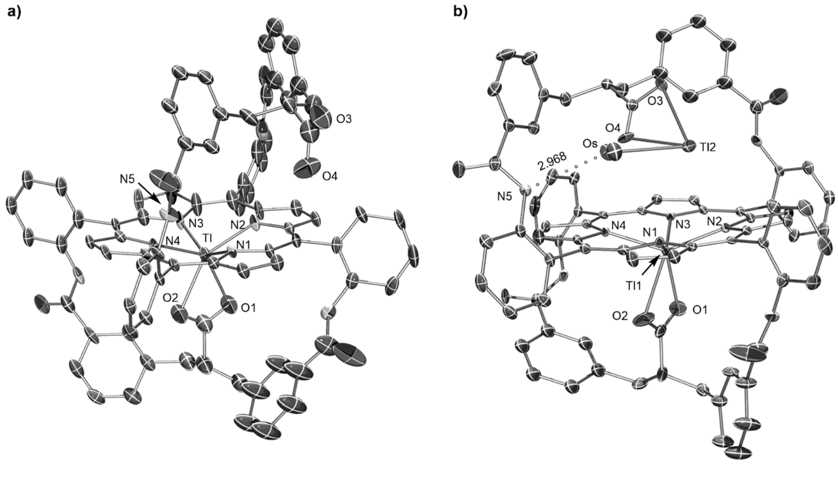
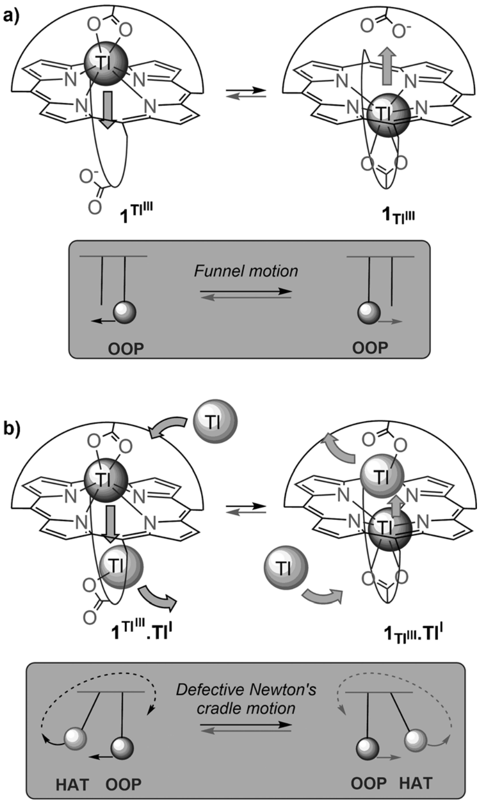


Figure 2. Crystal structures of $\mathbf{1}_{\mathrm{Tl^{III}}}$ (a) and $\mathbf{1}_{\mathrm{Tl^{III}}}\cdot\mathrm{Tl^{I}}$ (b). Ellipsoids set at 20% and 30% probability, respectively; H atoms and solvents of crystallization were removed for clarity. Selected distances [Å] for $\mathbf{1}_{\mathrm{Tl^{III}}}$: Tl–N1 2.226, Tl–N2 2.262, Tl–N3 2.190, Tl–N4 2.215, Tl–O1 2.328, Tl–O2 2.368, Tl–24MP 0.914; for $\mathbf{1}_{\mathrm{Tl^{III}}}\cdot\mathrm{Tl^{I}}$: Tl1–N1 2.240, Tl1–N2 2.219, Tl1–N3 2.235, Tl1–N4 2.204, Tl1–O1 2.267, Tl1–O2 2.588, Tl1–24MP 0.826, Tl1–Tl2 4.072, Tl2–24MP 2.973, Tl2–O3 2.679, Tl2–O4 2.719, Tl2–Os 2.897, Tl2–O3 (inter) 2.762.

signature characteristic of a C_2-symmetric compound with ${}^{4}J(\mathrm{H}_{\beta\mathrm{pyr}}\text{–}\mathrm{Tl^{III}})$ coupling constants of approximately 63 Hz was observed in the presence of DIPEA (Figure 4 f, see also the Supporting Information). An X-ray structure of this species revealed the formation of a mixed-valence $\mathrm{Tl^{III}}/\mathrm{Tl^{I}}$ complex, namely $\mathbf{1}_{\mathrm{Tl^{III}}}\cdot\mathbf{Tl^{I}}$, owing to the binding of $\mathrm{Tl^{I}}$ to the free COO^- group of $\mathbf{1}_{\mathrm{Tl^{III}}}$ (Figure 2 b). $\mathrm{Tl^{I}}$ was found at 2.973 Å above the 24 MP with no interaction with the N core (shortest $\mathrm{Tl^{I}}$–N2 distance: 3.373 Å) and with a $\mathrm{Tl^{III}}$–$\mathrm{Tl^{I}}$ distance of 4.072 Å. Its coordination sphere involves five oxygen atoms: The O3 and O4 atoms of the overhanging carboxylate ion, the Os atom of a weakly bound methanol, which also forms a hydrogen bond with an amide group of the strap (dashed line), and the O3 atom of a second complex (intermolecular coordination), which leads to a dimeric assembly (see the Supporting Information). This radiocrystallographic structure represents the first example of a hanging-atop monovalent metal ion. Mixed-valence bimetallic complexes with the two metal ions located on opposite sides of a porphyrin system have not been reported thus far and are of particular interest for the design of bimetallic devices under redox control. A 2D NMR ROESY experiment of $\mathbf{1}_{\mathrm{Tl^{III}}}\cdot\mathbf{Tl^{I}}$ also shows exchange correlations between protons of the two straps (see the Supporting Information), indicating that the metal ions exchange their



Scheme 3. Dynamic behavior of $\mathbf{1}_{\mathrm{Tl^{III}}}$ (a) and $\mathbf{1}_{\mathrm{Tl^{III}}}\cdot\mathrm{Tl^{I}}$ (b).

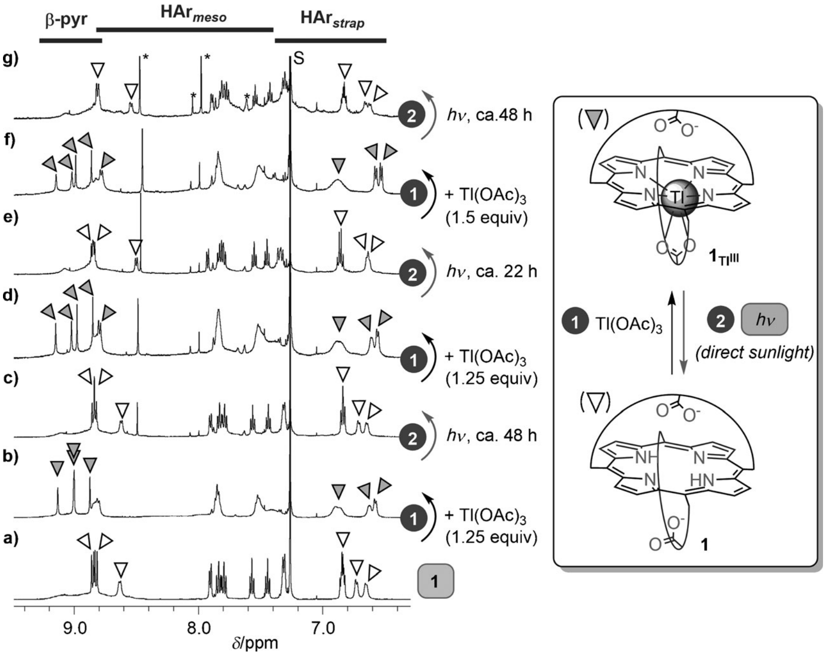


Figure 3. ^{1}H NMR study confirming the sunlight-driven formation and dissociation of $\mathbf{1}_{\mathrm{Tl^{III}}}$. Conditions: $CDCl_3/CD_3OD$ (9:1), 298 K, DIPEA (10 equiv). Three cycles were performed in a single NMR tube (a–c, c–e, e–g). S = solvent, * = impurity.

positions relative to the porphyrin plane (Scheme 3b). This equilibrium between the two degenerate forms of the complex corresponds to a double translocation combining an intramolecular motion for $\mathrm{Tl^{III}}$ (funneling through the N core as in $\mathbf{1}_{\mathrm{Tl^{III}}}$) with an intermolecular pathway for $\mathrm{Tl^{I}}$ exchanging between the two overhanging carboxylate groups, similarly to that previously reported for $\mathrm{Pb^{II}}$ based heterobimetallic complexes (see Figure 1b; "defective" Newton's cradle motion).[5e] The photoredox behavior of $\mathbf{1}_{\mathrm{Tl^{III}}}\cdot\mathbf{Tl^{I}}$ is similar to that of $\mathbf{1}_{\mathrm{Tl^{III}}}$, that is, it is characterized by its stability in the dark and a clean photodissociation of the $\mathrm{Tl^{III}}$ ion upon exposure to direct sunlight, leading to an average spectrum of **1** and $\mathbf{1{\cdot}2\,Tl^{I}}$ (see below) with the relative amount of **1** increasing with the time of light exposure (diagonal in Scheme 2; see also the Supporting Information).

The complexation properties of the free base **1** towards TlOAc were then investigated in the same $CDCl_3/CD_3OD$ solution. In the presence of DIPEA, a mixture of two species was obtained with an excess of five equivalents of TlOAc (Figure 4a; see also the Supporting Information). At 298 K, the major species displayed an ill-defined spectrum whereas a well resolved signature characteristic of a C_2-symmetric compound was observed for the minor one. A similar titration experiment by UV/Vis spectroscopy indicates that the major species presents a Soret band slightly red-shifted compared to that of **1** (430 vs. 421 nm), whereas that of the C_2-symmetric species is observed at 488 nm (see the Supporting Information). These data are in agreement with a mixture of two bimetallic complexes, namely $\mathbf{1{\cdot}2\,Tl^{I}}$ and $\mathbf{1\,Tl^{I}_2}$, for which the two $\mathrm{Tl^{I}}$ ions are bound in a fast exchange regime to the strap (HAT) and in a slow exchange regime to the N core (OOP), presumably with the participation of the carbonyl group of the overhanging carboxylate groups, respectively (Scheme 2, bottom).[6b] This mixture of bis-$\mathrm{Tl^{I}}$ complexes did not show any evolution when kept in the dark nor when exposed to indirect sunlight in a deoxygenated solution. However, under ambient atmosphere, both ^{1}H and ^{205}Tl NMR monitoring revealed the gradual appearance of the mixed-valence complex $\mathbf{1}_{\mathrm{Tl^{III}}}\cdot\mathbf{Tl^{I}}$ upon exposure of the NMR tube to indirect sunlight (Figure 4b–e; Scheme 2, pathway B), with approximately 60% conversion after about 35 hours of light exposure (Figure 5c,f). More detailed experiments that are still in progress in our laboratory tend to show that the binding of $\mathrm{Tl^{I}}$ to the strap or to the N core has little influence on the global process, that is, the $\mathrm{Tl^{I}}$ to $\mathrm{Tl^{III}}$ photo-oxidation and the insertion of the latter ion into the N core. Although it is difficult to estimate the proportion of $\mathrm{Tl^{III}}$ that binds to the porphyrin N core, its insertion might be hindered by the HAT $\mathrm{Tl^{I}}$ complexation, as it is supposed to proceed by a deconvolution mechanism involving the overhanging carboxylic acid.

As mentioned above, the exposure of $\mathbf{1}_{\mathrm{Tl^{III}}}\cdot\mathbf{Tl^{I}}$ to direct sunlight gives **1**; therefore, two cycles were performed in a single NMR tube (dark-gray triangle in Scheme 2; Figure 5): The addition of TlOAc to **1** led to

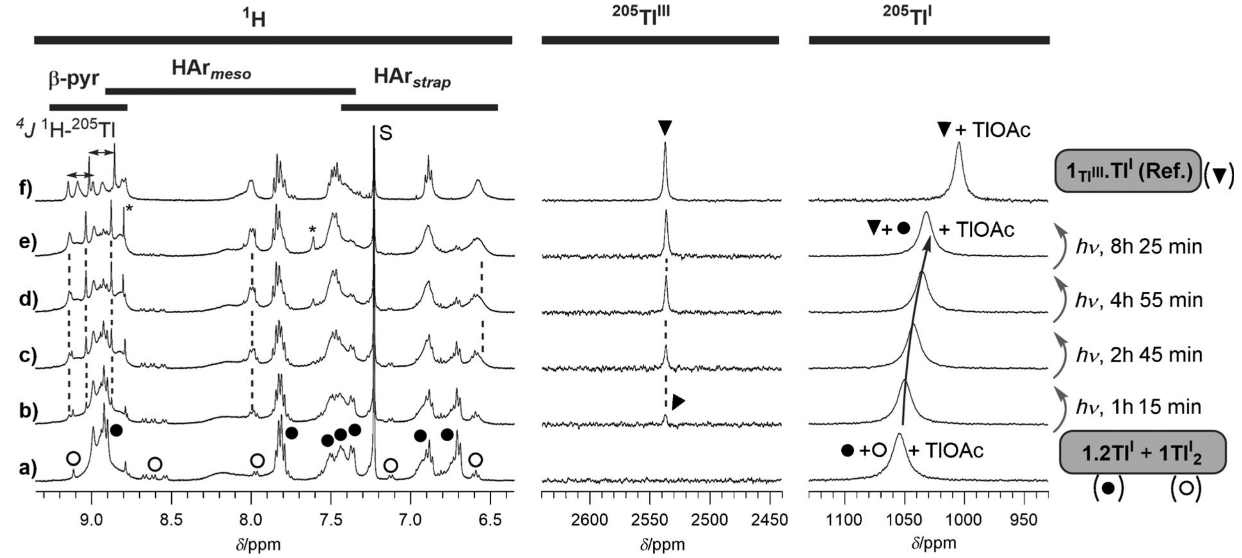


Figure 4. a) ^{1}H (left) and ^{205}Tl (right) NMR spectra of a mixture of **$1{\cdot}2Tl^{I}$** and **$1Tl^{I}_{2}$**, formed by the addition of five equivalents of TlOAc to **1**. Conditions: $CDCl_3/CD_3OD$ (9:1), 298 K, DIPEA (10 equiv). b–e) Evolution of the NMR spectrum upon exposure of the NMR tube to indirect sunlight for approximately 8 hours, showing the gradual apparition of **$1_{Tl^{III}}{\cdot}Tl^{I}$** (Scheme 2, pathway B). f) Reference spectra of a sample of **$1_{Tl^{III}}{\cdot}Tl^{I}$** that was formed by the addition of $Tl(OAc)_3$ (1.25 equiv) and TlOAc (5 equiv) to **1** (Scheme 2, pathway A). S = solvent, * = impurity.

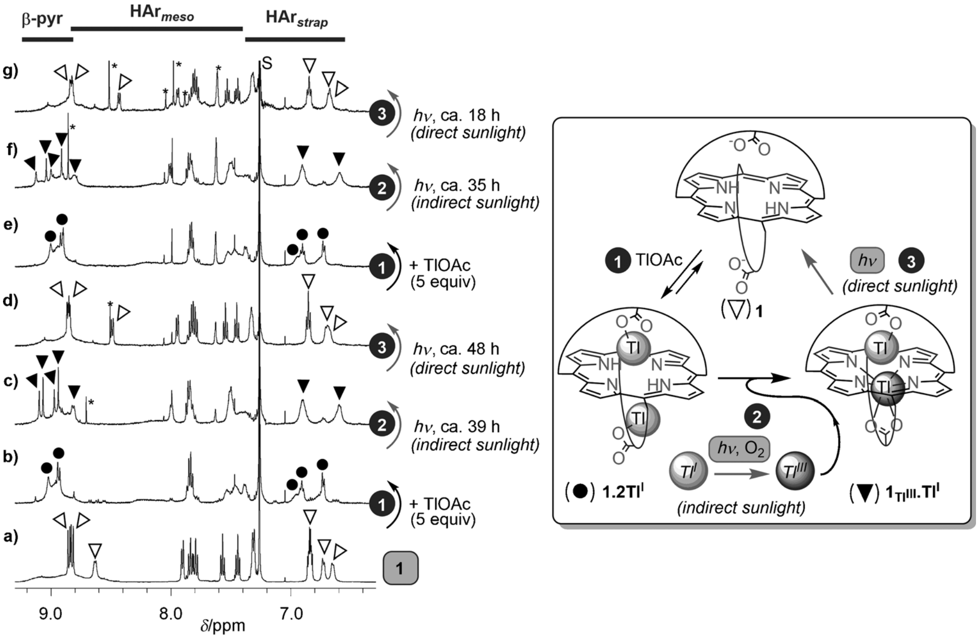


Figure 5. ^{1}H NMR study confirming the sunlight-driven formation and dissociation of **$1_{Tl^{III}}{\cdot}Tl^{I}$**. Conditions: $CDCl_3/CD_3OD$ (9:1), 298 K, DIPEA (10 equiv). Two cycles were carried out in a single NMR tube (a–d, d–g). S = solvent, * = impurity.

a mixture of bis-Tl^{I} complexes, exposure to indirect sunlight afforded **$1_{Tl^{III}}{\cdot}Tl^{I}$**, and subsequent exposure to direct sunlight gave back the free base **1** (Figure 5 a–d); this experiment was repeated twice in the same NMR tube (Figure 5 d–g), highlighting the remarkable properties of our system.

In conclusion, the site-selective binding of the redox-active metal ions Tl^{III} and Tl^{I} to ligand **1**, which meets the geometrical prerequisites of so-called Newton's cradle-like bimetallic devices, opens new perspectives for the supramolecular coordination chemistry of porphyrins. The mixed-valence complex **$1_{Tl^{III}}{\cdot}Tl^{I}$** displays dynamic features relying on metal ion translocations, and both its formation and dissociation are driven by sunlight. In this system, the porphyrin is not only a ditopic host for metal ions, but it also acts as a photosensitizer playing a key role in the oxidation or reduction of the metal ions, hence triggering their incorporation or release. It thus operates at all stages of the cycle of the device (assembling/functioning/disassembling). We are currently investigating the photoredox behavior of related heterobimetallic thallium-based complexes, aiming for light-driven molecular switches[12] based on double translocation processes.

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[9] The presence of $^1O_2$ under these experimental conditions is supported by the fact that 1,3-cyclohexadiene that had been added to the NMR tube was damaged when exposed to the ambient light of the laboratory.

[10] The notation $\mathbf{1_M}$ or $\mathbf{1^M}$ refers to the location of the metal ion that is bound out of the plane of the N core, on one or the other side of the macrocycle. For instance, $\mathbf{1_{Tl^{III}}}$ (with Tl^{III} subscripted) corresponds to an out-of-plane Tl^{III} cation arbitrarily shown as bound to the lower side of the porphyrin ring, as drawn in Scheme 2.

[11] An intermolecular exchange process was ruled out. Indeed, a ^1H NMR spectrum of a 1:1 mixture of **1** and $\mathbf{1_{Tl^{III}}}$ recorded at high temperature revealed well differentiated patterns corresponding to C_2-symmetric compounds for both species; see the Supporting Information for details.

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