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Osmium ester-hinged chlorin dimers

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Dedicated to Prof. Jonathan L. Sessler on the occasion of his 65th birthday

ABSTRACT: A bis(dihydroxychlorin) osmate ester is formed as a side product in the osmylation of *meso*-tetraphenylporphyrin. The product can also be formed in good yield along well-known reaction pathways of osmate esters by treatment of the monomeric chlorin diol osmate ester bispyridine complex with acid. The dimer was spectroscopically characterized. The free base dimer can be metalated with zinc(II). The bis([dihydroxychlorinato]zinc) osmate ester dimer was spectroscopically and structurally characterized, showing its clamshell architecture with a 42° angle between the mean planes of the two metallochlorin chromophores and a 9.11 Å zinc-to-zinc separation. Upon reaction with dimethylaminopyridine (DMAP), the clamshell structure pivots around the osmium center and arranges the two chromophores, each zinc center coordinated to DMAP, in maximum separation from each other, as shown by structural analysis. Preliminary ^{1}H NMR titration data are presented that show the bis-zinc clamshell structure to form a 1:1 supramolecular complex with diethylenetriamine (DETA), expressing a three-point recognition motive: the terminal amine functionalities coordinate to the zinc ions in each half-shell, thus bridging both chromophores, and the central amine functionality was deduced to be H-bond to the osmium oxo group pointing toward the inside of the host. The UV-vis spectroscopic response upon DETA binding shows greater complexity in the interaction at higher ligand:host ratios, suggesting multiple binding modes. A similarly complex binding situation is also observed for the interactions of the chlorin osmate ester monomer with DETA.

KEYWORDS: *meso*-tetraarylchlorin, chlorin dimer, osmate ester, clamshell dimer architecture, host-guest chemistry.

INTRODUCTION

The study of synthetic chlorins (dihydroporphyrins) as functional, spectroscopic, or structural models for nature's premiere light-harvesting pigment chlorophyll has become one of the central aspects in the contemporary porphyrinoid chemistry [1–3]. Chlorins can be isolated from natural resources and modified but their isolation is non-trivial [4, 5]; the extracted compounds also tend to be chemically sensitive [6, 7]. Thus, chlorin total syntheses or the conversion of synthetic porphyrins to chlorins are frequently pursued paths to access synthetic chlorins [2, 8–10]. Since a wide range of *meso*-tetraarylporphyrins is readily available [11], their conversion to chlorins is particularly popular [2, 8–10].

The OsO_4-mediated dihydroxylation of *meso*-tetraarylporphyrins **1^{Ar}M** is one reaction to accomplish this conversion [12–14]. This reaction sequence generates, via the intermediate osmate ester **2^{Ar}M**, chemically robust chlorin diols **3^{Ar}M** in their free base or metal ion-complexed form, in generally good yields (Scheme 1) [12–14]. The osmylation of double bonds, in general, is a well-known reaction [15, 16]. The regio- and stereochemical preferences for a second dihydroxylation [14, 17, 18]

[◊] SPP full member in good standing.

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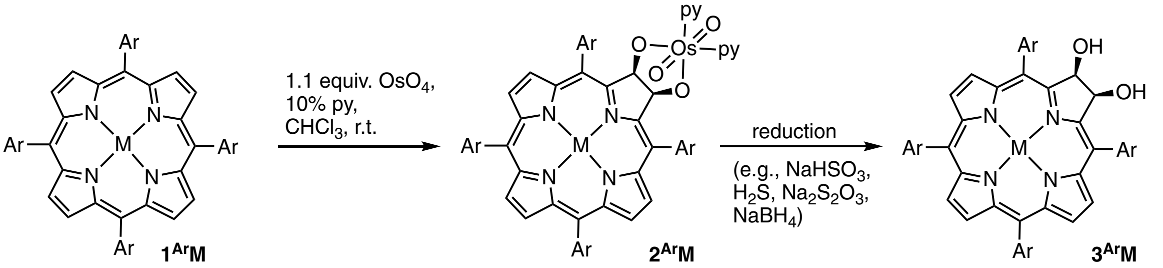


Scheme 1. Literature-known osmium tetroxide-mediated dihydroxylation of *meso*-tetraarylporphyrins $\mathbf{1^{Ar}M}$ to generate *meso*-tetraarylchlorin diols $\mathbf{3^{Ar}M}$ via osmate esters $\mathbf{2^{Ar}M}$ [12].

or the influence of the *meso*-aryl groups on the rate of the osmylation of porphyrins have also been studied [19].

Covalent dimeric (metallo)porphyrins (porphyrin dyads) have been prepared to, inter alia, study the electronic coupling between the chromophores, to construct light-harvesting arrays [20, 21], photosensitizers [22], molecular recognition systems taking advantage of the dimeric recognition motif [23–25], switches, nanoreactors [26], viscosity sensors [27], or to activate small molecules [28]. The two porphyrins can be linked by a single flexible linker located at essentially all positions of the molecule [29] – including metal-metal links between metalloporphyrin [30, 31] – or the porphyrins can be rigidly linked in a plane at multiple positions [32] or to form porphyrin-based cages [33]. Select covalently linked porphyrin dimers possess preorganized cavities to recognize guests via noncovalent interactions, whereby rich chemistry was explored by Borhan and co-workers, Rath and co-workers, and others, using either chiral hosts or achiral hosts showing supramolecular chirogenesis, and their interaction with chiral and achiral guest molecules.[34–41] Dyads involving hydroporphyrins have also been studied [42].

We report here the fortuitous discovery and rational synthesis of non-chiral osmate ester-linked dimers of the free base and zinc complexes of dihydroxychlorin, and their spectroscopic and structural characterization. The reaction of the clamshell architectures with amines and pyridines revealed their reactivity and conformational malleability arising from possible pivoting of the dimer around the osmium atom. Molecular recognition experiments revealed the zinc complex of the clamshell dimer to be a three-point host for diethylene triamine (DETA). Even though we also provide evidence for the sensitivity of the hinge toward reduction, these flexible osmate ester hinges are a simple and novel fashion to arrange two chlorins or metallochlorins into an intriguing clamshell architecture that is set up for molecular recognition events.

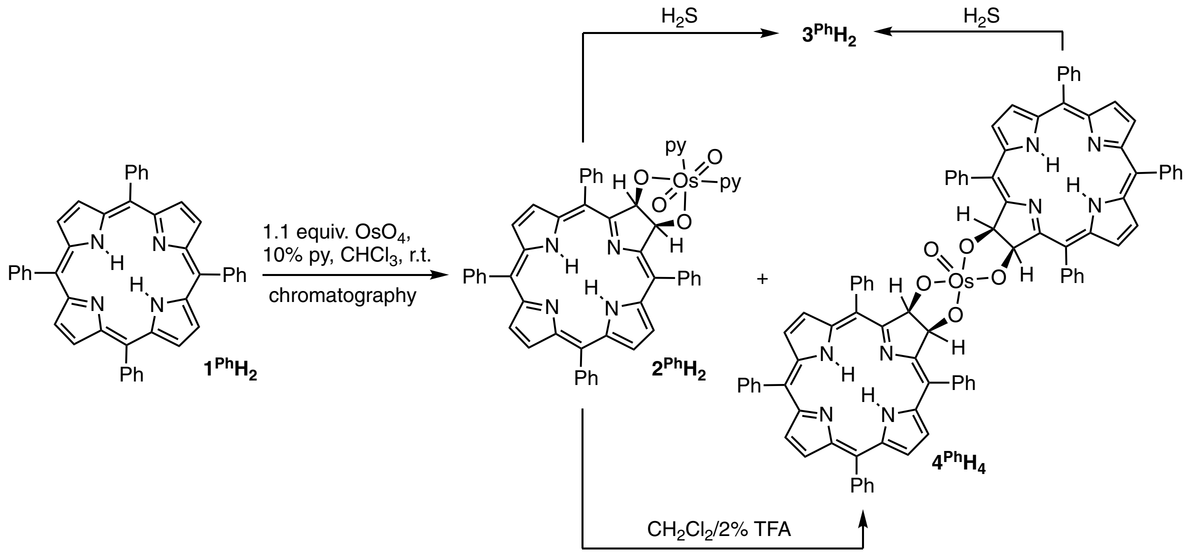
RESULTS AND DISCUSSION

Synthesis

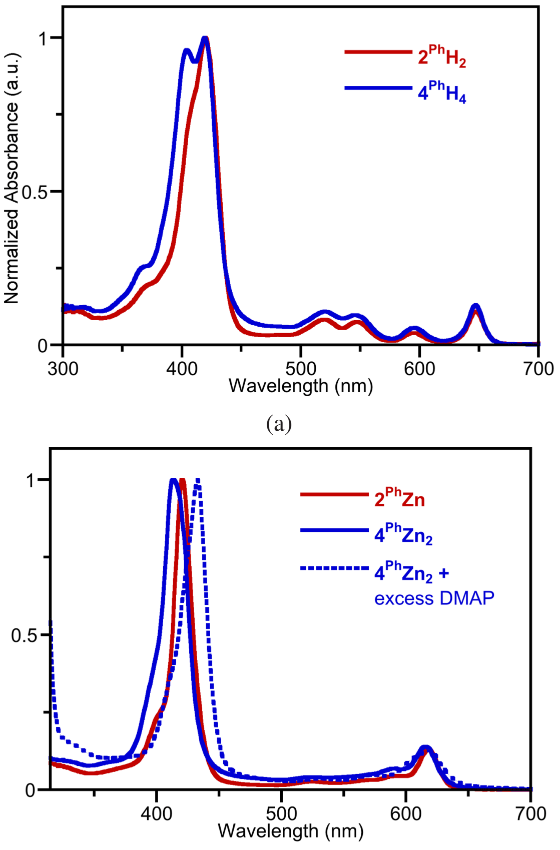
Synthesis and spectroscopic characterization of clamshell chlorin dimers $4^{Ph}H_4$ and $4^{Ph}Zn_2$. When we performed the osmium tetroxide-mediated dihydroxylation of *meso*-tetraphenylporphyrin $\mathbf{1^{Ph}H_2}$ ($\mathbf{1^{Ar}M}$ with Ar = Ph and M = 2H) along the standard procedure – osmylation and quenching of the crude intermediate osmate ester with H_2S before chromatographic separation, the expected dihydroxychlorin $\mathbf{3^{Ph}H_2}$ was isolated as the main and only chlorin-type chromophore (Scheme 2) (other products are the two bacteriochlorin isomers, a variable but small fraction of tetraphenylporpholactone [43,44], and considerable quantities of unreacted porphyrin $\mathbf{1^{Ph}H_2}$) [12,18]. However, when we removed all solvents from a crude osmylation reaction mixture of $\mathbf{1^{Ph}H_2}$ and then separated the osmate ester $\mathbf{2^{Ph}H_2}$ from the starting material (and some bacteriochlorin osmate esters [14]) using silica gel flash column chromatography, we observed a small (< 3 %) fraction of a significantly less polar compound, $\mathbf{4^{Ph}H_4}$, eluting before the main product $\mathbf{2^{Ph}H_2}$ (Scheme 2).

Compound $\mathbf{4^{Ph}H_4}$ possesses, except for a split Soret band, nearly the same chlorin-type UV-vis spectrum (and fluorescence emission spectrum, see ESI) as osmate ester $\mathbf{2^{Ph}H_2}$ (Fig. 1a), which itself has an optical range very similar to that of the corresponding diol chlorin $\mathbf{3^{Ph}H_2}$ [12]. The ^{1}H NMR spectrum of $\mathbf{4^{Ph}H_4}$ showed all the diagnostic peaks for the dihydroxy chlorin osmate ester (such as the pyrroline singlet at 7.42 ppm), but with no indication for the presence of any coordinated pyridines, like those present in osmate ester $\mathbf{2^{Ph}H_2}$ (Fig. 2). However, its FT-IR spectrum shows signals below 350 cm^{-1}, assigned to Os=O vibrations [45, 46] (see ESI). When treated with H_2S, both $\mathbf{2^{Ph}H_2}$ and $\mathbf{4^{Ph}H_4}$ produced identical chlorin diol $\mathbf{3^{Ph}H_2}$ (Scheme 2), providing further experimental evidence of their close structural relationship.

Unlike osmate ester $\mathbf{2^{Ph}H_2}$ or any other hydroporphyrin osmate ester investigated by us [14,18], compound $\mathbf{4^{Ph}H_4}$ proved to be tractable by ESI mass spectrometry; it showed a mass spectrum with a matching isotope pattern for $C_{88}H_{61}N_8O_5Os^+$ at m/z = 1501 amu for M+H$^+$, i.e., the mono-protonated dimer of a chlorin diol and one osmate ester (see ESI). The presence of the diprotonated species M+2H$^+$ (at m/z = 715 amu with the correspondingly 0.5 amu-spaced isotope pattern) lent support for the company of a dimeric chlorin structure, with each



Scheme 2. Literature-known osmium tetroxide-mediated dihydroxylation of *meso*-tetraarylporphyrins $\mathbf{1^{Ar}M}$ to generate *meso*-tetraarylchlorin diols $\mathbf{3^{Ar}M}$ via osmate esters $\mathbf{2^{Ar}M}$ [12].



(a)

(b)

Fig. 1. UV-vis spectra (CH_2Cl_2) of (a) the free base and, (b), the zinc(II) complexes of the chlorins indicated.

half being susceptible to protonation. The split Soret band feature in the UV-vis spectrum of $\mathbf{4^{Ph}H_4}$ is indicative of some minor coupling between the chromophores, similar to that observed for other chlorin dimers from our laboratories [47–49], providing additional support for the dimer structure of chlorin $\mathbf{4^{Ph}H_4}$. The NMR-spectroscopic findings are also commensurate with this interpretation.

Later experiments showed that the treatment of free base chlorin osmate ester $\mathbf{2^{Ph}H_2}$ monomer with acid (2% TFA) rapidly converted it to the corresponding free base dimer $\mathbf{4^{Ph}H_4}$ in 67% yield (at a 50 mg scale of $\mathbf{2^{Ph}H_2}$) (Scheme 2). Since this reaction is susceptible to modest scale-ups, this route allows for the facile preparation of the dimer in up to 100 mg batches in two steps from *meso*-tetraphenylporphyrin $\mathbf{1^{Ph}H_2}$.

Osmate ester dimers of the form $OsO\{(OR)_2\}_2$, such as $\mathbf{4^{Ph}H_4}$, have been known since the earliest days of the study of the reaction of double bonds with OsO_4 (in the presence of base) [15,16]. The inter-conversion of various osmium(VI) ester intermediates in these reactions has also been well-studied [50]. As the conversion of dimer $OsO\{(OR)_2\}_2$ in the presence of pyridines to form the monomer $[OsO_2(OR)_2(py)_2]$ is known [15, 16, 51], the reverse reaction in the presence of acid is not surprising. However, we are not aware of the utilization of this reaction to generate a porphyrinic dimer.

Insertion of zinc(II) into free base $\mathbf{4^{Ph}H_4}$ was, as expected for a regular chlorin, facile using standard conditions [52], generating $\mathbf{4^{Ph}Zn_2}$ (Scheme 3). Again, the NMRs and UV-vis spectra of the zinc chlorin dimer $\mathbf{4^{Ph}Zn_2}$ are very similar to those of the corresponding zinc chlorin monomer $\mathbf{2^{Ph}Zn}$ (or other chlorin diol derivatives) (Fig. 1b; see also ESI). Its composition, as determined by ESI+ HRMS, is indicated to be $C_{88}H_{56}N_8O_5OsZn^+$ (at *m/z* = 1626 amu for M^+, as well as the corresponding half-weight peak for dicationic M^{2+}, at *m/z* = 813 amu) (see ESI for details).

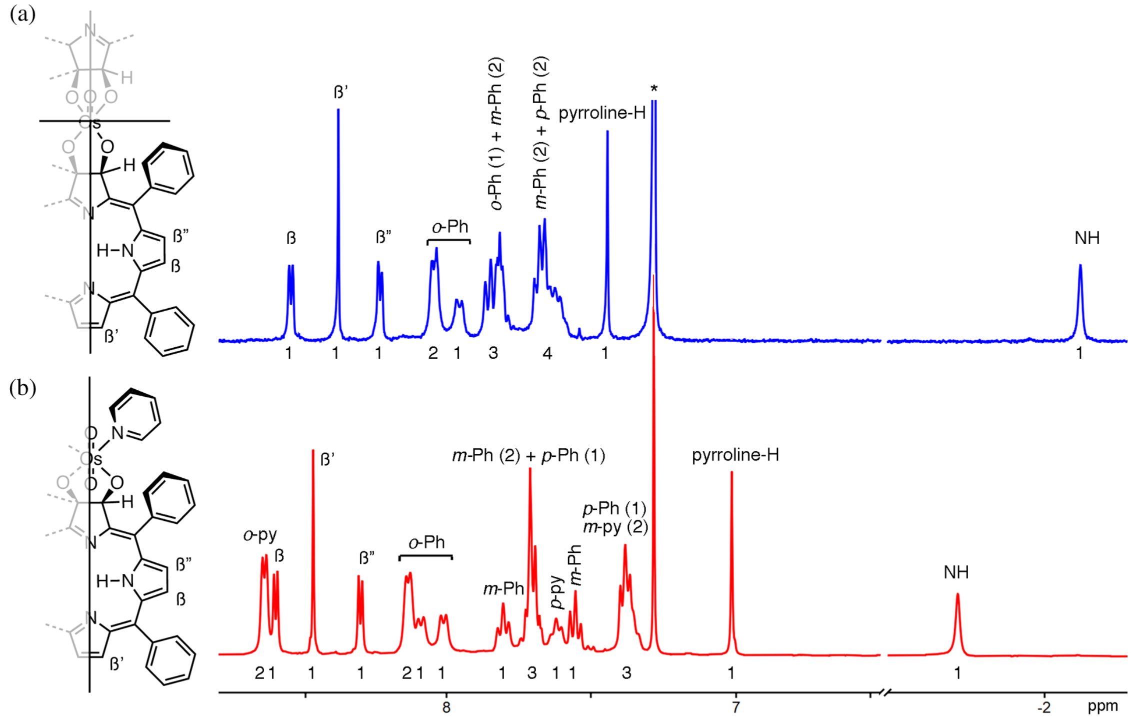
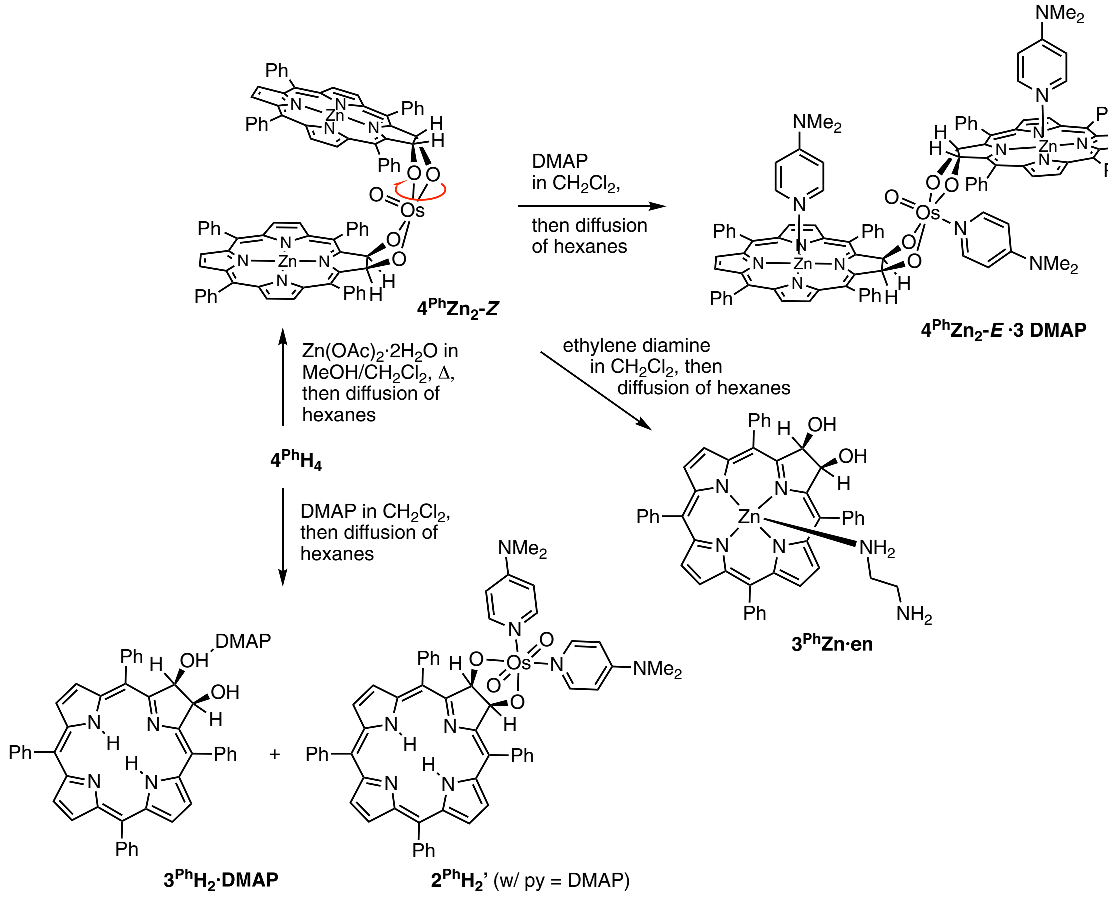


Fig. 2. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 21°C) of (a) porphyrin osmate ester dimer **$4^{Ph}H_4$** and (b) porphyrin osmate ester monomer dipyridine adduct **$2^{Ph}H_2$**. All assignments backs by NOe spectra and preparation of the monomeric osmate ester with pyridine d_5 [43].



Scheme 3. Schematic representation of the reactions investigated of clamshell chlorin complex **$4^{Ph}Zn_2$** with amines and pyridines.

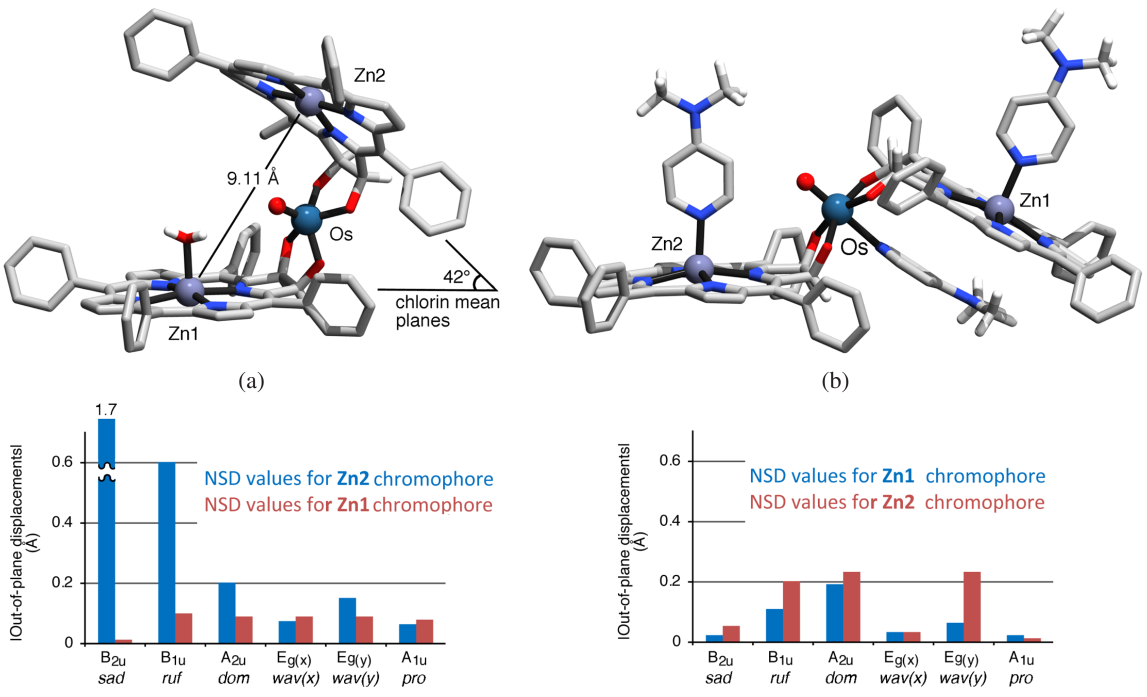


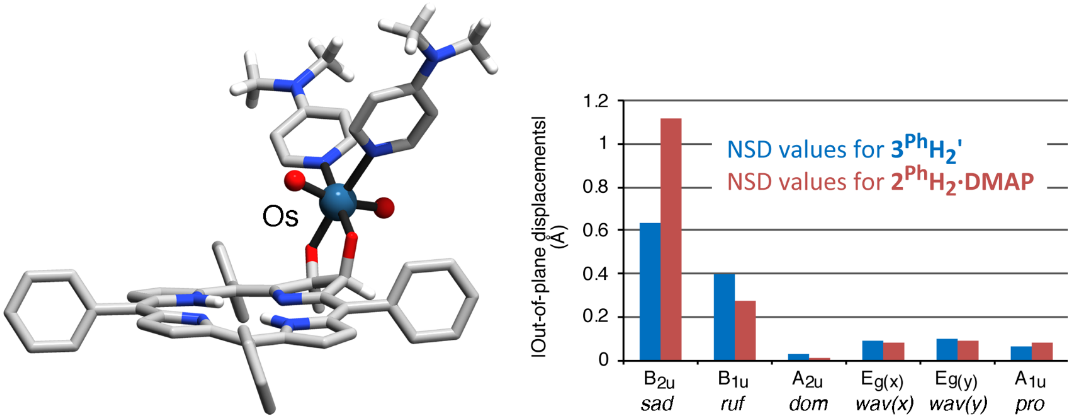
Fig. 3. Stick representation of the X-ray single crystal structures of (a) dimer $\mathbf{4^{Ph}Zn_2}$, as a mono-water adduct, and (b) 'swung-open' dimer $\mathbf{4^{Ph}Zn_2{\cdot}3\ DMAP}$. All H-atoms attached to sp^3-hybridized carbon atoms, as well as all disorder and solvents removed for clarity. (c and d) NSD analysis of the conformations of the chromophores indicated; analysis by the porphyrin NSD online tool [53] based on the method of Shelnutt [54]. For details on the X-ray diffraction and conformational analyses, see ESI.

Single crystal X-ray characterization of clamshell chlorin dimer $\mathbf{4^{Ph}Zn_2}$ and free base chlorin osmate ester $\mathbf{2^{Ph}H_2'}$

A crystal of chlorinato zinc dimer $\mathbf{4^{Ph}Zn_2}$ suitable for single crystal X-ray diffraction analysis could be grown (for experimental details, see ESI). The structure of $\mathbf{4^{Ph}Zn_2}$ confirms the (pseudo)symmetric osmate ester-linked dimer architecture derived from analytical and spectroscopic data (Fig. 3a). As typical for bis-osmate esters [16], the O_5-distorted square pyramidal coordinated Os(VI) center carries an oxo moiety at the axial position (Os=O bond length of 1.651 Å), whereas the *cis*-diol oxygen atoms of each chlorin occupy adjacent positions at the idealized square plane of the pyramid. Interestingly, the two metallochlorin chromophores are facing each other, forming a clamshell structure with a zinc-to-zinc distance of 9.11 Å, and one of the osmium oxo groups points toward the center of the clamshell. In the crystal of $\mathbf{4^{Ph}Zn_2}$, one of the zinc centers is coordinated to water, forming a square pyramidally coordinated metal center, the other zinc remains square planar. Both coordination geometries are standard for zinc porphyrins and chlorins [53]. As a result of the different coordination spheres, the conformational distortion of the chlorinato chromophores, as analyzed using a normal-structural decomposition (NSD) analysis (Fig. 3c) [53, 54], differ quantitatively and qualitatively in their deformation modes. The chromophore containing the square planar zinc is significantly saddled (B_{2u} distortion mode) and somewhat ruffled (B_{1u}), whereas the chromophore containing the square pyramidal zinc ion is overall much less distorted, with only minor ruffling, doming (B_{2u}), and waving ($E_{g(y)}$) modes.

An X-ray diffraction analysis of a crystal of free base $\mathbf{4^{Ph}H_4}$ suggested that it also possesses the same clamshell architecture as the chlorinato zinc dimer $\mathbf{4^{Ph}Zn_2}$. However, its incomplete data set prevented us from discerning any further details or treating the structure as anything more than a suggestion (see ESI).

For purpose of comparison, we also performed an X-ray diffraction analysis of the monomeric free base chlorin osmate ester $\mathbf{2^{Ph}H_2'}$ (Fig. 4a). The previously reported chlorin (and tetrahydroporphyrin) mono- and bis-osmate ester structures were of the *meso*-tetrakis(pentafluorophenyl)porphyrin series [14]. This diol osmate ester structure is generally as expected [14, 16], with an octahedrally coordinated Os(VI) center, two *trans*-oxo groups (average Os-O distance of 1.749 Å, O-Os-O angle of 162°), the *cis*-diolato moieties, and *cis*-arranged pyridines (in this case, DMAPs) arranged in an idealized square plane. The chlorin chromophore of the osmate ester is only modestly distorted from planarity, with some minor saddling and ruffling distortion modes (Fig. 4b). In contrast, we have shown that in the absence of the 'clamping action' of the osmate ester, the corresponding free base diol chromophore $\mathbf{2^{Ph}H_2}$ (H-bonded



(a) (b)

Fig. 4. (a) Stick representation of the X-ray single crystal structure of free base **$2^{Ph}H_2$'**, with py = DMAP. All H-atoms attached to sp^3-hybridized carbon atoms, as well as all disorder and solvents removed for clarity. (b) NSD analysis of the conformations of the chromophores indicated; analysis by the porphyrin NSD online tool [53] based on the method of Shelnutt [54]. For details on the X-ray diffraction and conformational analyses, see ESI.

to DMAP) is much more distorted from planarity [55], presumably to minimize interactions of the diol moieties arising from the eclipsed arrangement on the pyrroline ring.

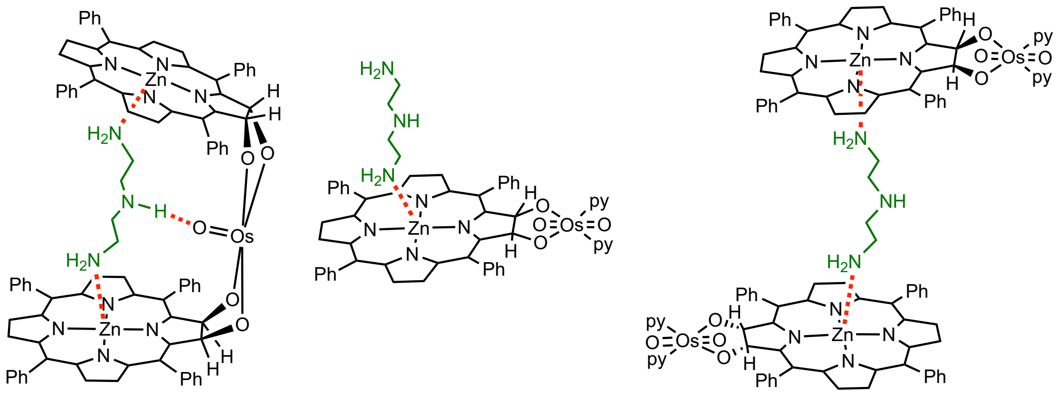
Reactions of chlorin osmate ester dimers $4^{Ph}H_4$ and $4^{Ph}Zn_2$ with pyridines and amines

The chlorin osmate ester monomers are generally robust and can be chromatographed, crystallized and handled using the same techniques (and precautions) used for the corresponding *meso*-arylchlorin diols [14]. Dimers **$4^{Ph}H_4$** and **$4^{Ph}Zn_2$** are similarly robust, but with notable exceptions. Next to the expected susceptibility of osmate ester dimer **$4^{Ph}H_4$** (as well as **$4^{Ph}Zn_2$** and the corresponding monomer **$2^{Ph}M$**) to reduction to the corresponding diols using H_2S (*vide supra*), we also found the dimers to react with ethylenediamine (en) and dimethylaminopyridine (DMAP) in ways not seen for the monomers. In what amounts to a reversal of the formation of **$4^{Ph}H_4$** from monomer **$2^{Ph}H_2$** by treatment with acid, treatment of dimers **$4^{Ph}M_2$** forms the corresponding diols **$3^{Ph}M$** [55] and monomer osmate esters **$2^{Ph}M$** (Scheme 3). However, neither reaction is of any preparative value and was only observed upon exposure of the dimers to en/DMAP over multiple days during attempts to grow X-ray-quality crystals of the dimers. Nonetheless, this reaction represents a potential limitation to using the chlorin osmate ester dimers in molecular recognition experiments with diamines and pyridines (*vide infra*).

One reaction with DMAP was unique to the zinc complex **$4^{Ph}Zn_2$**: Upon allowing a solution of **$4^{Ph}Zn_2$** in $CHCl_3$ and several equivalents of DMAP to sit at ambient temperature while allowing pentane to diffuse into the solution, the tris-DMAP adduct of **$4^{Ph}Zn_2$** crystallized (Fig. 3b). One DMAP axially coordinates each zinc chlorin and the osmate ester is axially coordinated by a DMAP *trans* to the oxo group (N-Os-O angle 177°, Os-O distance expectedly elongated from the non-coordinated structure to 1.69 Å). Importantly, this DMAP coordination led to a pivoting of one of the two chlorin chromophores around the osmium hinge by 180°, effectively changing the chromophore clamshell *cis*-architecture into an *anti*-arrangement of the chromophores. Perceivably, this tris-DMAP adduct is a precursor to the cleavage of the osmate ester using DMAP described above. We have not tested the time frame for this rearrangement, but this reaction constitutes another potential complication (or opportunity) in the use of the clamshell structure as a host for guests with donor atoms.

Clamshell chlorin dimer $4^{Ph}Zn_2$ as host for diethylenetriamine

Multiple studies have shown the suitability of monomeric [56] and dimeric metalloporphyrins as molecular recognition hosts for σ-donor bases, whereby the coordination of diamines to bis-zinc porphyrins is particularly popular [23–25, 34–41]. Likewise, the two zinc centers of dimer **$4^{Ph}Zn_2$** are also potential binding sites for diamines should the two donor atoms be able to span the 9.11Å zinc-to-zinc distance without undue thermodynamic penalty. In contrast to the reported clamshell dimers, however, osmate ester-linked dimer **$4^{Ph}Zn_2$** possesses also a potential third guest recognition site – the osmate oxo group that points toward the center of the clamshell. We envisioned this oxo functionality to be utilized as an H-bond acceptor guest recognition element for an H-bond donor functionality. Raymond and co-workers described the design of multimodal, three-dimensional ligands that were designed to recognize metal-oxo groups (such as UO_2^{2+}, OsO_2^{2+}, or VO^{2+}) through direct ligand donor group interactions and additional hydrogen bonds between the ligands and the oxo



(a) (b) (c)

Fig. 5. Schematic representation of (a) the hypothetical binding models of DETA with clamshell dimer $\mathbf{4^{Ph}Zn_2}$ with additional stereognostic feature, (b) binding models of DETA with chlorinato zinc osmate ester monomer $\mathbf{2^{Ph}Zn}$ forming a square pyramidally coordinated zinc center (and ambiguous stereochemistry because of the binding of the amine on either the side of the osmate ester, or the opposite side) (c) the hypothetical binding of two monomeric chlorinato zinc osmate esters $\mathbf{2^{Ph}Zn}$ to a single DETA. Chlorin chemical structures are simplified for clarity.

groups on the guest, termed stereognostic coordination chemistry [57–60]. The situation in $\mathbf{4^{Ph}Zn_2}$ is inverted as the potential host is offering the osmium(VI) oxo functionality as a recognition site for a guest. Also, all three recognition elements of the host are arranged in a plane.

Based on simple metric considerations of the cavity size of dimeric molecule $\mathbf{4^{Ph}Zn_2}$ (9.11 Å Zn-to-Zn separation), we identified diethylenetriamine (DETA) or diethanolamine (DEA) as potential suitable guests, hoping to achieve the three-point recognition motive shown in Fig. 5a for DETA. Indeed, ^{1}H NMR titration data presented below support the supposition that this binding model can be achieved. However, the results can only be regarded as preliminary. This is because UV-vis spectroscopic data suggest that the binding equilibria between the tridentate ligand DETA and a potentially conformationally flexible host with multiple potential binding sites, including the osmate esters as H-bond acceptor as well as Lewis acid, is complex and not yet fully understood. As precedent cases of, for example, the binding equilibria between a simpler and more rigid zinc chlorin dimer with a small and rigid diamine was already shown to be extraordinarily complex [23], the complexity of the $\mathbf{4^{Ph}Zn_2}$/DETA system is not unexpected.

An ^{1}H NMR titration of up to 1 equiv. DETA to a $\mathbf{4^{Ph}Zn_2}$ (5.3 mM in $CDCl_3$) shows the two methylene peaks of DETA shifting a remarkable 3.5 to 5 ppm upfield, a clear indication for the formation of a single unique species with a symmetric binding to zinc and being exposed to the strong diatropic ring current of the chlorins. The experimental shifts are comparable to those observed and computed for diamines binding to other clamshell porphyrins [61] (Fig. 6). Merely considering the position of DETA between the two chromophores, a similar upfield shift of the amine proton signals of DETA would have been expected. However, a slight downfield shift of the (average) NH/NH_2 signals is observed. We interpret this as an indication that the central NH group is, as designed, strongly H-bound to the osmate ester oxo group. Such bonding would cause a large high-field shift for the NH signal. The minor observed low-field shift is the average between the π-system-induced high-field and H-bond-induced low-field shift. Concomitantly with the shifts observed for the guest, some dimer host proton peaks near the guest (*o*-Ph and pyrroline-H peaks) also experience minor shifts.

Once a 1:1 host:guest ratio is exceeded, the appearance of multiple free and bound DETA species can be discerned, and the situation becomes rapidly complex (see ESI).

The corresponding titration of monomer $\mathbf{2^{Ph}Zn}$ with DETA also shows some of the methylene shifts associated with the amines binding to the zinc, but at least 5 or 6 peaks for the methylene protons can be discerned, indicating the formation of zinc chlorin binding to DETA at only one end (in the low concentration regime, at least) or as a mixture of primary and secondary amine binding (see ESI). However, it is not clear if the square pyramidal complex formed carries the osmate ester on the same side of the chlorin as the amine (and possibly H-bonds with the osmate ester oxo groups), or the opposite side. With increasing [DETA] (even well under 1 equiv.), many ligand peaks appear, supporting multiple amine binding modes (such as shown in Figs. 5b and 5c), as well as diastereomeric stereochemistries.

In an attempt to gather further support for any of the binding models, we performed UV-vis titrations (in toluene) of micromolar solutions of $\mathbf{2^{Ph}Zn}$ (3.67×10^{-6} M) and $\mathbf{4^{Ph}Zn_2}$ (3.93×10^{-6} M) with DETA (Figs. 7a and 7b).

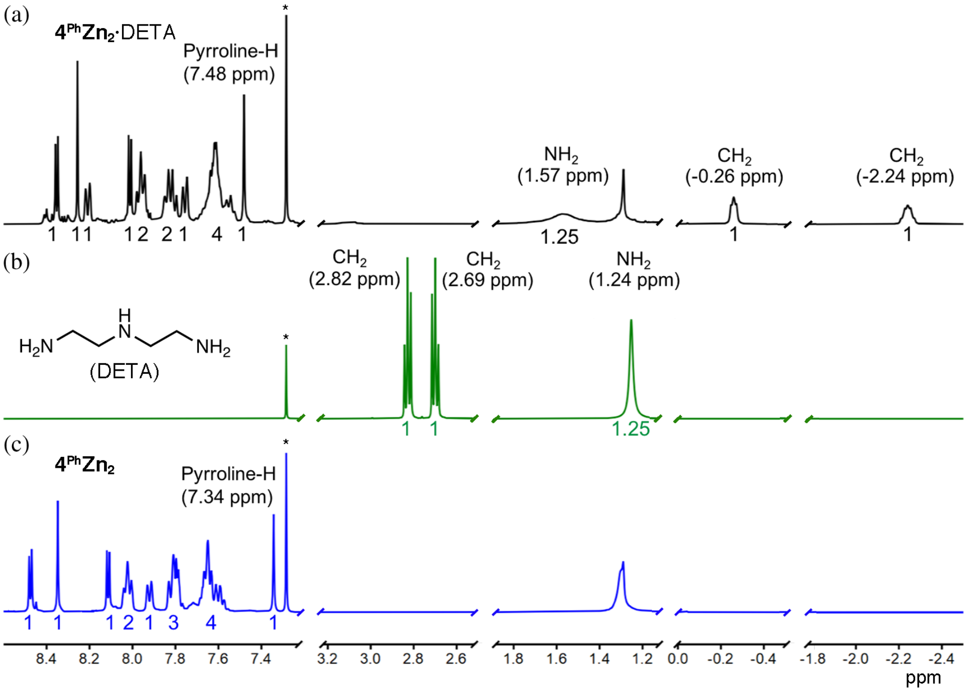
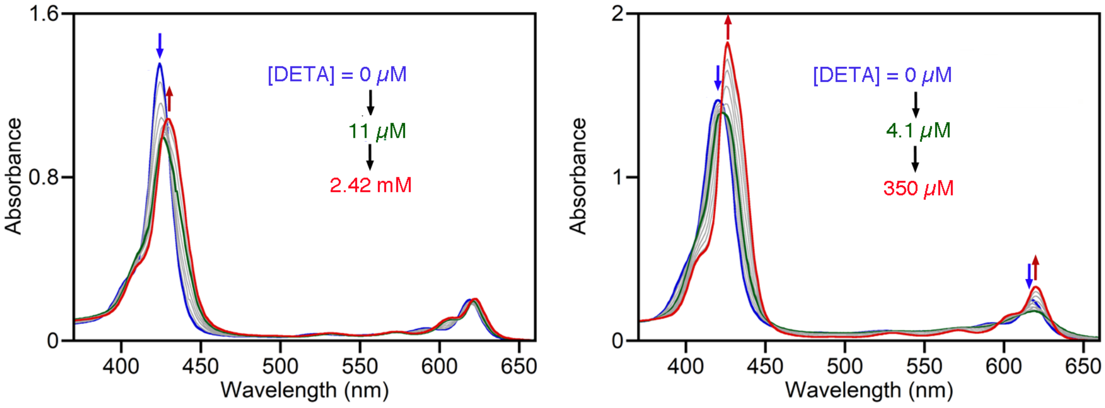


Fig. 6. ^{1}H NMR spectra (CDCl$_3$, 400 MHz, 298 K) of (a) **$4^{Ph}Zn_2$**, (b) diethylene triamine (DETA), and (c) a 1:1 mixture of **$4^{Ph}Zn_2$** and DETA.

In both cases, we found evidence for the presence of two-step processes, both associated with minor redshifts and intensity modulations of the Soret band and each with their set of isosbestic points (see also ESI). The second process required about a 100-fold larger [DETA] than the first step, and remains unexplained. However, the [DETA] required for saturation of the first process is 2.7-fold higher for the monomer **$2^{Ph}Zn$** than for dimer **$4^{Ph}Zn_2$**; in both cases, the binding isotherms of the first steps can be modeled using a 1:1 binding model.

The calculated value of the overall binding constant K for **$4^{Ph}Zn_2$** ($K = 4.62 \times 10^7$ L M^{-1}) is much larger compared to the corresponding value for monomer **$2^{Ph}Zn$** ($K = 8.72 \times 10^5$ L^3 M^{-1}), suggesting the effective binding in the clamshell dimer. However, while it is tempting to associate the better binding of DETA to **$4^{Ph}Zn_2$** as support for the expectedly stronger 3-point host-guest binding model of DETA within the clamshell (and the binding constant computed to be realistic), the complexity of the interaction of monomer **$2^{Ph}Zn$** with DETA as seen in the NMR titrations question the validity of a simple 1:1 binding model used to derive the comparison binding constants (see ESI).

To complicate matters, the electronic spectral changes after adding diethanolamine (DEA) resemble the changes seen with the addition of DETA to both monomer and



(a) (b)

Fig. 7. UV-vis titration of (a) **$2^{Ph}Zn$** (3.67×10^{-6} M) and (b) **$4^{Ph}Zn_2$** (3.93×10^{-6} M) with diethylenetriamine (DETA) in toluene. Color-coded are the low (blue to green) and high (green to red) [DETA] regimes of the titration.

dimer complexes (see ESI). This suggests that DEA is also a suitable guest molecule but also that offering a mixture of OH-donor and NH acceptor groups cannot be clearly distinguished from the binding of molecules with NH_2-donor and NH acceptor groups, whereas usually alcohol binding to a zinc porphyrin has a different optical signature than amine binding [40, 41, 62].

More in-depth investigations of the binding of DETA, DEA, and related molecules to the osmate-hinged clamshell dimer **$4^{Ph}Zn_2$** are needed for more conclusive statements to be made regarding the binding model and strength. Nonetheless, the data thus far certainly suggest the presence of a novel and intriguing host-guest system. Further studies are underway.

EXPERIMENTAL

Instruments

All ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument in $CDCl_3$ and are referenced to residual solvent peaks. UV-vis and fluorescence spectra (including the host-guest titrations in toluene for better handling of small quantities of solvent) were recorded with Cary 50 and Cary Eclipse spectrophotometers, Varian, Inc., respectively, in CH_2Cl_2. IR spectra were recorded on a Bruker Alpha instrument with a diamond ATR cell. High- and low-resolution mass spectra were provided by the Mass Spectrometry Facility, Department of Chemistry, University of Connecticut.

X-ray diffractometry

All details of the X-ray diffraction analysis of **$4^{Ph}Zn_2$**, **$4^{Ph}Zn_2 \cdot 3$ DMAP**, **$2^{Ph}H_2'$**, with py = DMAP and incomplete single crystal structure of **$4^{Ph}H_4$** as evidence of clam-shall architecture (Fig. S31) are included in the ESI.

Materials

Solvents and reagents were used as received. Aluminum-backed, silica gel 60, 250 µm thickness analytical plates, 20 × 20 cm, glass-backed, silica gel 60, 500 µm thickness preparative TLC plates, and premium grade, 60 Å, 32–63 µm flash column silica gel were used.

(Meso-tetraphenyl-2,3-cis-dihydroxychlorin)osmate ester bispyridine adduct ($2^{Ph}H_2$). Prepared by osmylation of **$1^{Ph}H_2$** (200 mg) as described previously [12], but instead of the reductive workup using H_2S, the crude reaction mixture was reduced to dryness and chromatographed (silica-gradient CH_2Cl_2 to 5% MeOH in CH_2Cl_2), providing the product as a brown, powdery solid in ~35% yield. $R_f = 0.52$ (silica-10% acetone in CH_2Cl_2); MW = 1025.17 g/mol; ^1H NMR (400 MHz, $CDCl_3$, δ): 8.60 (d, J = 5.1 Hz, 4H), 8.57 (d, J = 5.1 Hz, 2H), 8.44 (s, 2H), 8.27 (d, J = 5.0 Hz, 2H), 8.11 (d, J = 5.9 Hz, 4H), 8.06 (d, J = 7.7 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 7.8 Hz, 2H), 7.70 – 7.64 (m, 6H), 7.59 (d, J = 6.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.35 (q, J = 6.0 Hz, 6H), 6.99 (s, 2H), -1.72 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, δ): 162.95, 152.72, 149.89, 142.32, 142.16, 140.97, 139.85, 135.46, 134.16, 133.90, 132.29, 132.12, 127.47, 127.44, 127.05, 126.90, 126.56, 126.17, 124.77, 124.35, 121.98, 114.08, 96.67 ppm; UV-vis (CH_2Cl_2) λ_{max}, (log ε): 419 (5.48), 519 (4.40), 548 (4.36), 595 (4.07), 647 (4.52) nm; Fluorescence (CH_2Cl_2, $\lambda_{excitation}$ = 419 nm) $\lambda_{max\text{-}emission}$ = 647, 716 nm. FT-IR (diamond ATR, neat): 3337 $\nu_{(N\text{-}H)}$, 456 $\nu_{(Os\text{-}N)}$, 294, 268 $\nu_{(Os=O)}$ cm^{-1}. HR-MS (EI, 3-NBA) m/e expected for $C_{58}H_{43}N_6O_9{}^{192}Os$ [$M \cdot 2matrix \cdot H^+$]: 1159.2712, found 1159.2720. As seen in other osmate ester monomers [14], an ESI HR-MS spectrum could not be acquired.

[(meso-Tetraphenyl-2,3-cis-dihydroxychlorinato)-zinc(II)]osmate ester Bispyridine Adduct ($2^{Ph}Zn$). Prepared in 85% yield by metalation of **$2^{Ph}H_2$** using $Zn(OAc)_2 \cdot 2H_2O$ in CH_2Cl_2/CH_3OH as described for the synthesis of **$4^{Ph}Zn_2$**, or in ~40% yield via osmylation of **$2^{Ph}Zn$** using the procedure for **$2^{Ph}H_2$**. The product was isolated as a greenish-purple solid using column chromatography (silica-gradient CH_2Cl_2 to 5% MeOH in CH_2Cl_2). $R_f = 0.46$ (silica-10% acetone in CH_2Cl_2); MW = 1088.53 g/mol; ^1H NMR (400 MHz, $CDCl_3$, δ): 8.63 (s, 4H), 8.48 (d, J = 4.7 Hz, 2H), 8.40 (s, 2H), 8.15 (d, J = 4.6 Hz, 2H), 8.10 – 7.92 (m, 10H), 7.73 – 7.48 (m, 12H), 7.43 (s, 2H), 7.34 (d, J = 7.3 Hz, 2H), 6.87 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, δ): 158.52, 154.30, 147.63, 146.37, 143.30, 143.18, 139.80, 134.19, 133.68, 132.28, 131.67, 128.58, 127.62, 126.96, 126.69, 126.32, 126.18, 125.72, 123.82, 113.55, 96.01 ppm; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε): 420 (5.63), 617 (4.75); Fluorescence (CH_2Cl_2, $\lambda_{excitation}$ = 420 nm) $\lambda_{max\text{-}emission}$ = 621 nm; FT-IR (diamond ATR, neat): 436 $\nu_{(Os\text{-}N)}$, 186, 175 $\nu_{(Os=O)}$ cm^{-1}; HR-MS (EI, 3-NBA) m/e expected for $C_{44}H_{28}N_4O_4{}^{192}Os^{64}Zn$ [M^+]: 932.0991, found 932.0975. As seen in other osmate ester monomers [14], an ESI HR-MS spectrum could not be acquired.

Bis(meso-tetraphenyl)-2,3-cis-dihydroxychlorin) osmate ester $4^{Ph}H_4$. *meso*-Tetraphenyl-2,3-*vic*-dihydroxychlorin osmate ester bispyridine complex **$2^{Ph}H_2$** (36 mg, 3.50 × 10^{-5} mol) was dissolved in CH_2Cl_2 (2 mL). To this solution was added CH_2Cl_2/2% TFA (2 mL), upon which the color of the solution changed from brown-red to green. The solution was stirred for 30 min at ambient temperature. Then acetone (2–3 mL) was added, upon which the color of the solution reverted to a slightly different brown-red. Solid Na_2CO_3 (~5 g) was added and the reaction mixture was filtered. The filtrate was reduced to dryness by rotary evaporation and subjected to column chromatography (silica gel – solvent gradient, from a 3:2 CH_2Cl_2:hexanes mixture to 100% CH_2Cl_2). Recrystallization of the main product by slow solvent exchange from $CHCl_3$ to isopropanol, followed by filtration and air drying, afforded **$4^{Ph}H_4$** in 67% yield (35 mg, 2.35 × 10^{-5} mol) as dark, crystalline material.

R_f = 0.66 (silica-CH_2Cl_2); MW = 1499.73 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.52 (d, *J* = 4.7 Hz, 4H), 8.35 (s, 4H) 8.21 (4, *J* = 5.5 Hz, 4H), 8.02 (d, *J* = 5.4 Hz, 8H), 7.93 (d, *J* = 7.5 Hz, 4H), 7.82 (dd, *J* = 14.7, 5.1 Hz, 12H), 7.68 – 7.58 (m, 16H), 7.42 (s, 4H), -2.15 (s, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, δ): 158.98, 153.23, 141.67, 140.68, 140.59, 135.72, 134.58, 134.00, 133.82, 132.72, 131.88, 127.95, 127.88, 127.65, 127.13, 126.61, 124.80, 122.93, 113.90, 98.65. ppm; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε): 403 (5.05), 419 (5.07), 519 (4.10), 546 (4.05), 596 (3.82), 647 (4.18); Fluorescence (CH_2Cl_2, $\lambda_{excitation}$ = 419 nm) $\lambda_{max\text{-}emission}$ = 649, 714 nm; FT-IR (diamond ATR, neat): 3351 $\nu_{(N\text{-}H)}$, 307 ($\nu_{Os=O}$) cm^{-1}; HRMS (ESI+, 100% CH_3CN, TOF) *m/z*: calc'd for $C_{88}H_{62}N_8O_5{}^{192}Os^{2+}$ $[M+2H]^{2+}$: 751.2229, found 751.2243.

Bis[(meso-tetraphenyl-2,3-cis-dihydroxychlorinato)zinc(II)]osmate ester 4^{Ph}Zn$_2$. Free-base osmate ester chlorin dimer **4^{Ph}H$_4$** (50 mg, 3.33 × 10^{-5} mol) was dissolved in 20 mL of CH_2Cl_2. To this, $Zn(OAc)_2{\cdot}2H_2O$ (73 mg, 3.33 × 10^{-4} mol, 10 equiv) dissolved in CH_3OH (1.5 mL) was added and the reaction mixture was heated to reflux until the reaction was completed (45–50 min; monitored by UV-vis spectroscopy). After completion, the solvent was removed by a rotatory evaporator. The crude reaction mixture was redissolved in CH_2Cl_2 and washed with deionized water to remove the excess zinc salt. The organic layer passed through anhydrous sodium sulfate and reduced to dryness under vacuum. The crude product was purified by column chromatography (silica-CH_2Cl_2/5% acetone) to yield **4^{Ph}Zn$_2$** as a purple solid in 82% yield (45 mg, 2.76 × 10^{-5} mol); MW = 1626.46 g/mol; R_f = 0.58 (silica-CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.47 (d, *J* = 4.7 Hz, 4H), 8.35 (s, 4H), 8.11 (d, *J* = 4.7 Hz, 4H), 8.04 – 7.99 (m, 8H), 7.92 (d, *J* = 7.6 Hz, 4H), 7.84 – 7.77 (m, 12H), 7.68 – 7.58 (m, 16H), 7.34 (s, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 155.28, 154.36, 148.29, 146.71, 142.05, 141.08, 134.50, 133.46, 132.57, 131.77, 129.71, 128.15, 127.64, 127.52, 126.98, 126.56, 125.48, 114.44, 97.65 ppm; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε): 413 (5.62), 588 (4.46), 616 (4.77); Fluorescence (CH_2Cl_2, $\lambda_{excitation}$ = 413 nm) $\lambda_{max\text{-}emission}$ = 617 nm; FT-IR (diamond ATR, neat): 180 cm^{-1} ($\nu_{Os=O}$); HRMS (ESI+, 100% CH_3CN, TOF) *m/z*: calc'd for $C_{88}H_{56}N_8O_5{}^{192}Os^{64}Zn_2$ $[M]^{2+}$: 813.1176, found 813.1097.

CONCLUSIONS

In conclusion, an osmate ester-linked dimer of dihydroxychlorins formed either as a minor side product from the osmylation of the corresponding porphyrin or via acid-induced conversion of a chlorin diol osmate ester monomer. Surprisingly, therefore, more than 25 years after the original development of the OsO_4-mediated dihydroxylation of *meso*-arylporphyrins, new reaction products are being identified to form in this reaction. The dimer can be metallated with zinc(II) using standard protocols. The molecular structure of the bis-chlorinato zinc dimer **4^{Ph}Zn$_2$** is that of a clamshell with a 41° opening angle, a Zn-to-Zn distance of 9.11 Å, and an oxo-functionality of the osmate ester pointing toward the inside of the clamshell. Preliminary experiments toward the use of this intriguing zinc chlorin clamshell architecture with a suitably placed osmium oxo group as an H-bond acceptor in the center of the shell as a potential three-point recognition motive (two zinc Lewis acid centers and one oxo H-bond acceptor site) for DETA were successful, but also pointed at the complexities of the system. Additionally, the osmate ester hinge is conformational flexible. Thus, the reaction of the bis-chlorinato zinc complex **4^{Ph}Zn$_2$** with DMAP resulted in the axial ligation of a DMAP to each zinc center and the inversion of the clamshell by rotation of the two shells by about 180° around the osmate ester hinge. Evidence for the sensitivity of the hinge toward reduction was also gathered. For instance, treatment of the free base dimer **4^{Ph}H$_4$** with ethylene diamine led to the reduction of the osmate ester and the liberation of the monomeric chlorin diol **3^{Ph}H$_2$′**. These reactions are potential limitations in using the dimers for molecular recognition, but the conformational flexibility also presents options to utilize the dimers in ways as yet unknown.

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Supporting information

A reproduction of the experimental data (such as ^{1}H, ^{13}C NMR spectra, FT-IR, MS spectra, and details for the X-ray diffractometry of all novel compounds described is given in the supplementary material. This material is available free of charge *via* the Internet at https://www.worldscientific.com/doi/suppl/10.1142/S1088424623500888

CCDC entries 2237175 (**2^{Ph}H$_2$′**), 2237176 (**4^{Ph}Zn$_2$**), and 2237177 (**4^{Ph}Zn$_2$·3DMAP**) contain the supplementary crystallographic data (.cif) for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk.

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