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Synthesis and ligand binding properties of triptycene-linked porphyrin arrays

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ABSTRACT

Multiporphyrin arrays are a complex class of molecules with numerous potential applications in energy transfer, photomedicine, and light harvesting. We have developed a facile/versatile route to a class of triptycene-linked porphyrin arrays via both Suzuki and Sonogashira cross-coupling methods, which makes use of the rigid three-pronged orientation of triptycene to construct trimeric porphyrin arrays linked either in the *meso* or β-position with various linker groups. In order to understand the properties of these potential antenna systems and probe their potential applications, the coordination behavior of zinc(II) derivatives with mono- and bidentate N-donor ligands was investigated. Depending on ligand concentration, both one- and two-point binding was observed with a bidentate ligand. Also/in addition, different cavity sizes, obtained by the use of different linker groups, resulted in differences in the binding properties of each trimeric system.

1. Introduction

Synthetic multiporphyrin arrays can mimic naturally occurring tetrapyrrolic aggregates that are involved in photosynthesis, light harvesting and electron transfer. In nature, the rates of these processes are optimized by organizing the active components at ideal distances and orientations, which is achieved by the use of multiple, non-covalent interactions.[1–4] Synthetically this can be achieved using multiple covalent and/or coordination bonds, which serve to dramatically increase the association constants between components and ensure a well-defined geometry for the resulting complex.[5–7]

Triptycene and its derivatives possess rigid three-dimensional frameworks[8–10] and thus have potential applications in host/guest complexes, molecular inclusion compounds and coordination compounds with unusual geometries.[11–14] The 120° orientation provided by this framework constitutes a useful linker group for multichromophore assemblies.[15] Consequently, we became interested in using a triptycene unit as a scaffold for the construction of porphyrin arrays with applications in host/guest chemistry. Triptycene was earlier used by us for the preparation of triptycene/quinones for electron transfer studies.[16]

Three types of *meso* linked triptycenylporphyrin arrays and a β-linked system were prepared with varying cavity sizes and selected examples were easily metalated with zinc(II). Zinc(II) porphyrins have a simple coordination chemistry and typically form 1:1 complexes with N-donor ligands.[17] Thus, we also performed initial investigations into the host/guest chemistry of the zinc(II) triptycenylporphyrin arrays.

2. Results and discussion

2.1. Syntheses

Triptycene-linked porphyrin trimers were chosen as suitable candidates for multidentate host/guest chemistry and were first synthesized using Pd-catalyzed coupling reactions.[8] We anticipated that variation of the porphyrin center-to-center distances would allow an investigation of the coordination properties of the rigid trimers. The synthetic route started by preparation of an appropriately functionalized triptycene derivative.

Commercially available triptycene **1** was reacted with nitric acid under reflux according to a procedure by Zhang et al.[1] A mixture of 2,6,14- and 2,7,14-trinitrotriptycene was obtained, from which the former was isolated in 85% yield via column chromatography on silica gel with dichloromethane/*n*-hexane (1:1) as eluent. Reduction of the nitro residues to amino functions yielded 2,6,14-triaminotriptycene in quantitative yield. 2,6,14-Triiodotriptycene **2**

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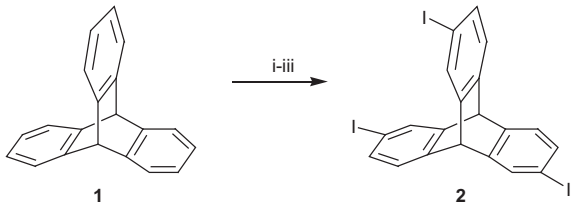
was obtained from a Sandmeyer reaction using hydrochloric acid, sodium nitrite, and potassium iodide (Scheme 1).[11]

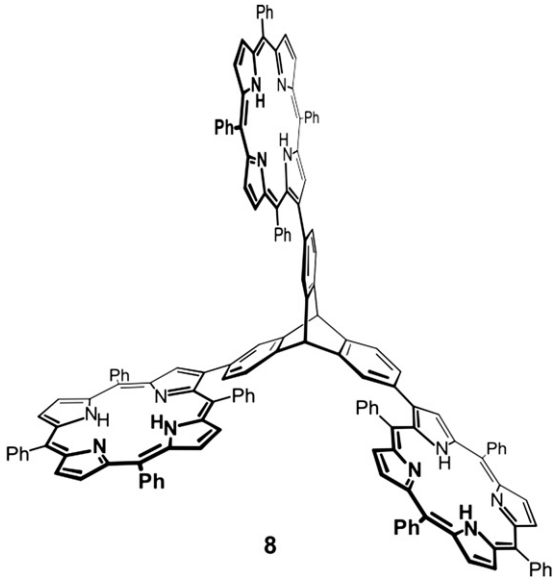


Scheme 1. Synthesis of 2,6,14-triiodotriptycene from triptycene. (i) HNO_3 (ii) Pd/C, $NaBH_4$ (iii)HCl, $NaNO_2$, KI.

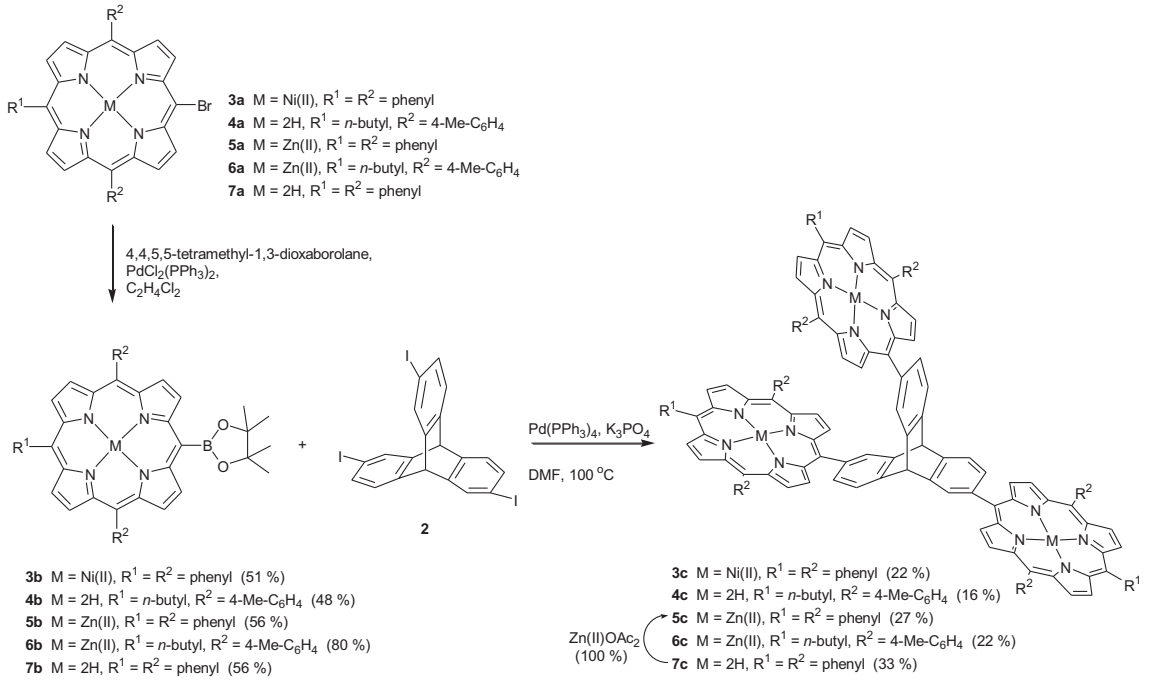
Introduction of a boronate or ethyne functionality onto the *meso* position of a porphyrin would allow subsequent Suzuki–Miyaura or Sonogashira coupling reactions of these derivatives. The halogen-bearing moiety **2** would thus be coupled to the respective porphyrins yielding triptycene-linked porphyrin trimers. Several different porphyrin monomers were synthesized bearing a boronic ester, an ethyne, and a phenylethyne functionality, respectively.

2.1.1. Suzuki reaction. Porphyrins modified at the *meso* positions were obtained via condensation of pyrrole or a pyrrolic derivative with various aldehydes. A_2-type porphyrins with two unsubstituted *meso* positions available for further functionalization, were synthesized from the respective dipyrromethane precursor following a procedure developed by Lee and Lindsey.[12] A nucleophilic substitution reaction[13] yielded trisubstituted A_2B-type porphyrins. Subsequent bromination of the porphyrins with *N*-bromosuccinimide (NBS) then yielded the porphyrin precursors **3a** to **6a**. *meso*-Boronylation was performed according to a procedure by Therien et al. (Scheme 2).[14] For example, the reaction of **5a** and **6a** with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane proceeded as expected in 12 h. Debromination of the starting material was a competing reaction. Thus, a 10-fold excess of pinacolborane was used to ensure a high yield of the boronate porphyrins **5b** (56%) and **6b** (80%).

Suzuki cross-coupling reaction[16] yielded the respective triporphyrin triptycene derivatives **3**–**6c**. Slightly better yields were obtained for coupling of the free-base porphyrin **7b** as compared to the conversion of **5b** due to difficulties in purification of the zinc(II) tricoupled products. The free-base trimer **7c** could be metalated in situ with zinc(II) acetate to give the zinc(II) trimer **5c** in quantitative yield.



The methodology established above was also applicable to the preparation of triptycene-porphyrin trimers with the porphyrins joined to the linker unit/triptycene backbone in a β-position. Porphyrin dimers and trimers with *meso*-β and β–β linkage[17,18] have been intensely studied in recent years, especially due to their rewarding stereochemical features and unique structural chemistry[18]

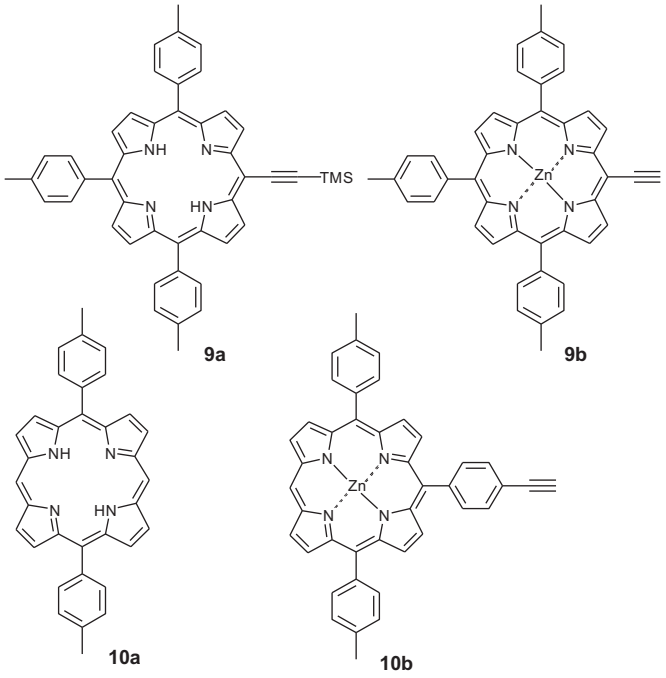


Scheme 2. Synthesis of triptycene-linked porphyrin trimers via Suzuki–Miyaura cross-coupling reaction with 2,6,14-triiodotriptycene and boronylporphyrins.

Next, the boronate porphyrins were reacted with 2,6,14-triiodotriptycene **2** using the conditions described by Chng et al. for the preparation of a dibenzofurane-linked porphyrin dimer:[15] The or their fundamental use in electron transfer.[17b] Using a procedure similar to the one applied to *meso* functionalized porphyrins β-linked porphyrin triptycene systems were accessible as well,

albeit in lower yield due to the increased sterical hindrance at the coupling position. For example, 2-([1′,3′,2′]-dioxaborolan-2′-yl)-5,10,15,20-tetraphenylporphyrin (structure not shown)[18a,b] was reacted with **2** in the presence of $Ba(OH)_2$ and $Pd(PPh_3)_4$ giving the triptycene derivative **8** in 10% yield.

2.1.2. Sonogashira reaction. Precursors of the Sonogashira coupling reaction[19] required an ethyne moiety to react with the triiodotriptycene. The porphyrin monomer **9a** was synthesized by a mixed condensation reaction[20] of pyrrole with two different aldehydes. Here, 3-(trimethylsilyl)propiolaldehyde served as the reactive aldehyde, whereas, *p*-tolylaldehyde was chosen because of its availability and enhanced solubility of *p*-tolyl-substituted porphyrin as compared to the respective phenyl derivatives, thus aiding chromatography. Following a procedure by Seo et al.,[21] pyrrole, *p*-tolylaldehyde, and 3-(trimethylsilyl)propiolaldehyde were condensed in a 4:2.1:2 ratio to yield **9a**. Deprotection of the ethyne group with tetrabutylammonium fluoride (TBAF) then gave the ethynyl-substituted porphyrin **9b**.



For preparation of a porphyrin with a phenylethyne functionality we initially attempted a mixed condensation procedure previously reported by Fazio et al.[22] However, for our target system isolation of the products turned out to be difficult due to the similar polarities of the components of the mixtures. Thus, the 4-ethynylphenyl residue was introduced into 5,15-ditolylporphyrin **10a**[23] by a nucleophilic substitution reaction.[13] 1-Bromo-4-ethynylbenzene was reacted with *n*-butyllithium under inert conditions, to yield the desired organolithium reagent. Addition of 5,15-ditolylporphyrin **10a** in THF yielded the desired free-base product in 69% yield. Subsequent treatment with zinc(II) acetate gave the zinc(II) porphyrin monomer **10b**.[24]

Sonogashira coupling reactions have commonly been used for the synthesis of porphyrin multicomponent systems.[25] The palladium coupling conditions are reasonably attractive as they are performed in neutral to basic conditions, where demetalation does not occur. However, using copper as a co-catalyst, and under specific conditions, transmetalation can occur with the zinc(II)porphyrin. In agreement with Farina Krishnan who reported an improved rate of the Stille reaction upon addition of triphenylarsine,[26a] Lindsey et al. successfully outlined the conditions for a copper-free Sonogashira reaction involving triphenylarsine and tris(dibenzylideneacetone) dipalladium (0).[26b] Thus, under mild, non-acidic, non-metalating conditions, the zinc(II) porphyrins **9b** and **10b** were coupled with 2,6,14-triiodotriptycene to yield the desired ethynyl- and phenylethynyl-linked porphyrin trimers **9c** (28%) and **10c** (36%) (Scheme 3).

2.2. Host/guest properties

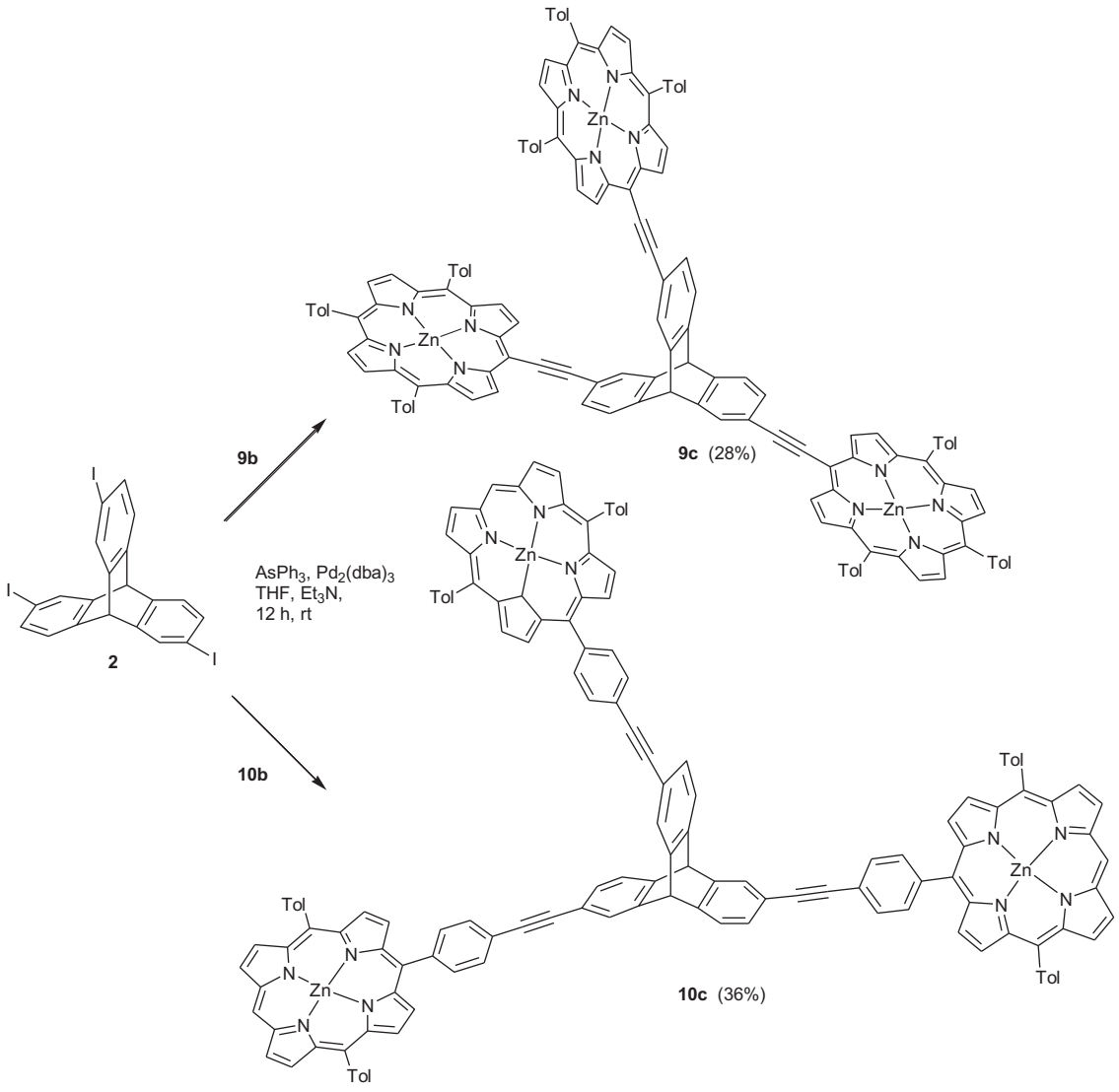
In order to understand the behavior of the trimer complexes **5c**, **9c**, and **10c** upon ligand coordination, investigations by UV/vis spectroscopy were first carried out to determine how the bidentate ligand, 4,4′-bipyridine (bipy) coordinated to a monomeric metalloporphyrin (5,10,15,20-tetramesityl-porphyrinato)zinc(II). UV/vis spectroscopy has been used to elucidate the stoichiometry of binding, binding constants, and a limited amount of structural information. Previous studies showed that upon coordination of an N-donor ligand to a zinc(II) porphyrin, a bathochromic shift of about 10 nm occurred in the Soret region/the Soret band is red-shifted by about 10 nm indicating a 1:1 binding stoichiometry.[27,28] In addition, ^{1}H NMR spectroscopy had shown that at millimolar concentrations a 2:1 porphyrin/ligand sandwich complex was formed upon addition of 0.5 equiv of a bidentate ligand.[29] The 2:1 complex then opens up to give the 1:1 open complex in the presence of excess ligand.

The addition of incremental amounts of bipy to (5,10,15,20-tetramesitylporphyrinato)zinc(II) (ϵ=756,600 M^{-1} cm^{-1}) in dichloromethane resulted in a Soret band shift from 420 to 428 nm ($\Delta\lambda$=8 nm) with one distinct isosbestic point at 424 nm, clearly indicating an equilibrium between two defined species (Fig. 1).[30] The titration data were analysed using the non-linear regression analysis program Specfit™, which analyses the entire series of spectra simultaneously.[31] The best/optimum data fit was obtained for/when applying a 1:1 binding model and resulted in a binding constant of log $K_{1:1}$=4.4±0.004, which was expected for the formation of an open complex.[27,28]

UV/vis experiments were carried out on trimers **5c**, **9c**, and **10c** with mono- and bidentate ligands to determine the coordination properties of these rigid porphyrin arrays. Bidentate ligands are capable of displaying multiple binding interactions with these porphyrin trimers (Fig. 2). Previous UV/vis and ^{1}H NMR investigations on porphyrin systems have revealed that dimeric bridging ligand complexes preferentially adapt the bridged structure at low concentrations of ligand, in spite of the fact that the *endo* side is considerably more accessible than the *exo* side.[28,32] Using/In ^{1}H NMR spectroscopy, this phenomenon was reflected in/resulted in a high-field resonance at δ=−5 ppm for the CH_2 protons of a 1,4-diazabicyclo[2.2.2]octane ligand (DABCO) tightly bound to two zinc(II) porphyrins, which was completely absent when monodentate ligands were used.[27,28,33] Monomeric and dimeric binding have also been differentiated using UV/vis spectroscopy. Formation of a 1:1 dimer/ligand sandwich complex was accompanied by a 5 nm red-shift, compared to a 10 nm red-shift in the 1:2 open system, which was observed with the addition of excess ligand.[27] Also, association constants determined from UV/vis titrations for the formation of dimeric sandwich complexes are much greater than those for the corresponding monodentate binding motifs.[34]

Therefore, a bidentate ligand such as bipy, is capable of forming a 1:1 trimer/ligand sandwich complex (Fig. 2a), a 1:2 complex, displaying both sandwich and open complexation (Fig. 2b), and a 1:3 trimer ligand complex, where all ligands are bound in an open complex (Fig. 2c).

*2.2.1. Directly linked porphyrin trimer **5c**.* The absorption spectrum of the directly linked trimer **5c** (ϵ=816,000 M^{-1} cm^{-1}) exhibited a λ_{max} at 424 nm with a shoulder at 417 nm. This was indicative of a slight electronic interaction between the porphyrin components.[35] Upon titration of **5c** with bipy in dichloromethane, two new



Scheme 3. Sonogashira coupling reaction of 2,6,14-triiodotriptycene with ethynyl functionalized porphyrins.

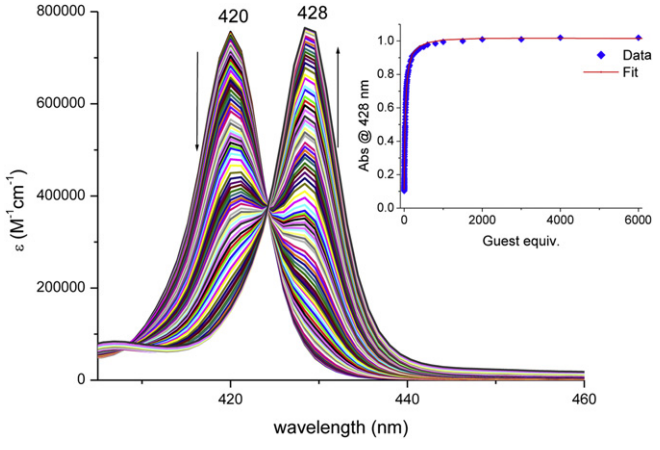


Fig. 1. Changes in the absorption spectra (Soret band spectral region) of (5,10,15,20-tetramesitylporphyrinato)zinc(II) (1.34×10^{-6} M) recorded in dichloromethane, upon addition of bipy. Inset: the changes at 428 nm with a 1:1 fit (0–6000 equiv).

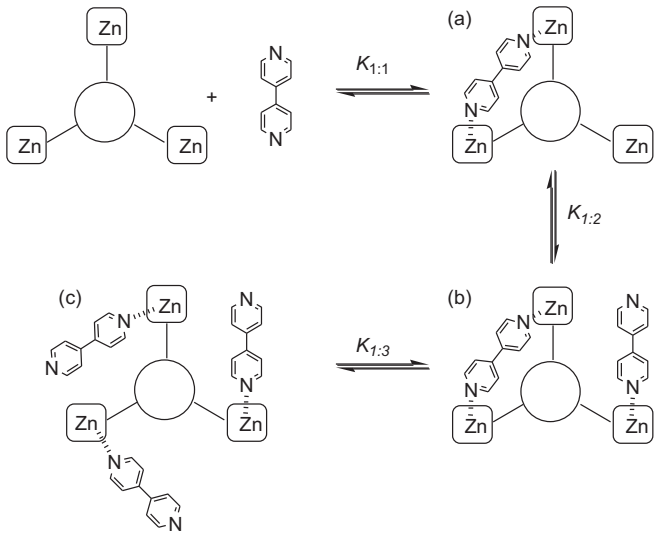


Fig. 2. Schematic representation of the species in the equilibria of binding bipy to a trisporphyrin.

transitions formed at 430 ($\Delta\lambda$=6 nm) and 433 nm ($\Delta\lambda$=9 nm), with isosbestic points at 427 and 428 nm, respectively (Fig. 3). Titration with pyridine resulted in a 9 nm bathochromic shift (Table 1), thus confirming that the final species in the **5c**/bipy solution was the 1:3 open complex.

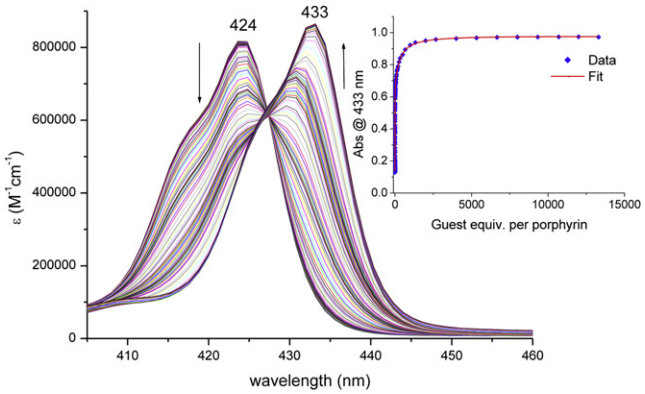


Fig. 3. The changes in the absorption spectra (Soret region) of the directly linked trimer **5c** (8×10^{-7} M) upon addition of bipy, recorded in dichloromethane. Inset: the changes at 433 nm fit to a five-component system.

Table 1
The absorption maxima and binding constants for the complexation between **5c** and mono- and bidentate ligands

	λ_{max} (nm)	Log $K_{1:1}$	Log $K_{1:2}$	Log $K_{1:3}$
5c	424, 548, 587			
5c+bipy	433, 563, 602	5.3±0.03	5.4±0.03	3.3±0.02
5c+pyr	433, 563, 602	4.8±0.18	4.1±0.22	3.4±0.23

The changes in the spectra with increasing concentrations of bipy were best described by a five-component system (host, guest, 1:1 host/guest, 1:2 host/guest and 1:3 host/guest) after fitting by Specfit™, the fit of which is shown as an inset in Fig. 3. The 6 nm red-shift relative to the absorption of the uncomplexed trimer was attributed to the 1:2 trimer/ligand complex (Fig. 2b) since it seemed unlikely that the zinc(II) metal would remain four-coordinate in the presence of excess bipy. The binding constants for this fit are shown in Table 1.

The binding constants for the 1:1 and 1:2 species were of similar magnitude and indicated the formation of the more stable sandwich complexes. The species distribution plot for the five-component system (Fig. 4) revealed a simultaneous formation of the 1:1 and 1:2 trimer/ligand species at low concentrations of bipy.

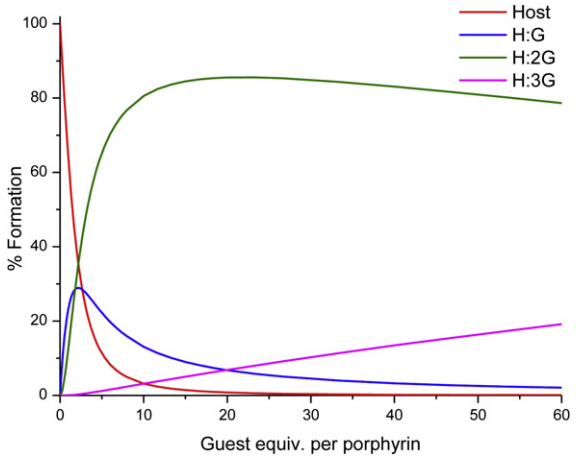


Fig. 4. The species distribution plot of the directly linked trimer **5c** (8×10^{-7} M) upon the addition of bipy recorded in dichloromethane 0–60 equiv.

*2.2.2. Ethyne-linked porphyrin trimer **9c**.* The spectra for compound **9c** (ϵ=996,400 M^{-1} cm^{-1}) exhibited a λ_{max} at 443 nm. Upon titration with bipy, a new transition at 449 nm developed and an isosbestic point at 444 nm was identified (Fig. 5). Upon the formation of a 1:1 complex, the monomer exhibited an 8 nm red-shift. In the case of dimeric ligands, the formation of a 1:1 open complex was accompanied by a 10 nm red-shift, whereas the formation of a sandwich complex resulted in a 5 nm red-shift.[28,29,32a,b,d] However, titration with pyridine resulted in an overall bathochromic shift of 6 nm (Table 2).

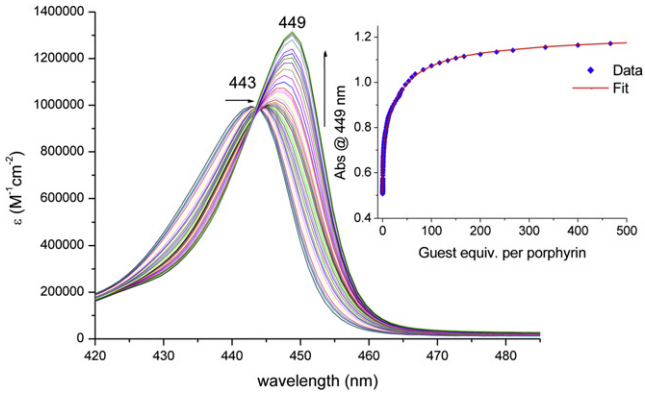


Fig. 5. UV/vis titration (Soret region) of the ethyne-linked trimer **9c** (9.2×10^{-7} M) with bipy recorded in dichloromethane (0–70,000 equiv). Inset: The changes at 449 nm with a 1:2 trimer/ligand fit (0–500 equiv).

Table 2
The absorption maxima and binding constants for the complexation between **5c** and mono- and bidentate ligands

	λ_{max} (nm)	Log $K_{1:1}$	Log $K_{1:2}$	Log $K_{1:3}$
8c	443, 567, 614			
8c+bipy	449, 582, 635	6.18±0.01	5.14±0.09	3.79±0.09
8c+pyr	449, 581, 636	4.62±0.10	3.95±0.17	3.43±0.14

The binding constants for the formation of the 1:1 and 1:2 **9c**/bipy complexes were considerably higher than for the formation of the **9c**/pyr complexes, and indicated the formation of sandwich-type complexes with the bidentate ligand. The changes in the spectra were therefore attributed to a five-component system (host, guest and 1:1, 1:2 and 1:3 host/guest complexes). The binding isotherm is shown as an inset in Fig. 5.

The species distribution diagram in Fig. 6 obtained from the fit showed that the 1:1 complex reached 62% formation at only 1 equiv

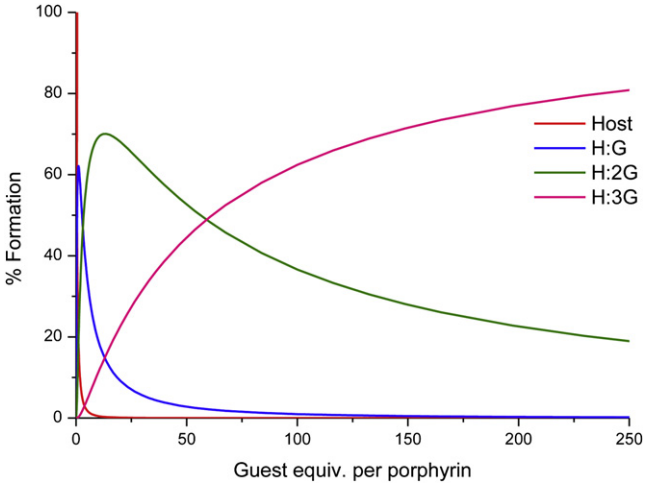


Fig. 6. The species distribution diagram of the ethyne-linked trimer **9c** (9.22×10^{-7} M) upon the addition of bipy (0–500 equiv) recorded in dichloromethane.

of ligand per porphyrin. The 1:2 complex became the main species in solution after the addition of 3 equiv of ligand, whereas the 1:3 species was predominant in solution after the addition of almost 60 equiv of bidentate ligand.

*2.2.3. Phenylethynyl-linked trimer **10c**.* In the case of the phenylethynyl-linked porphyrin trimer **10c** (ϵ=958,100 M^{-1} cm^{-1}), the addition of bipy resulted in a decrease in the absorption at 415 nm while a new band appeared at 422 nm, with an isosbestic point at 419 nm (Fig. 7). With the addition of further equivalents of bipy,

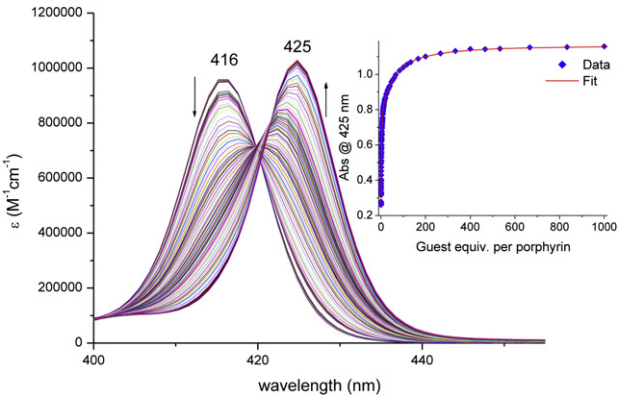


Fig. 7. UV/vis titration spectra (Soret region) of the phenylethynyl-linked trimer **10c** (1.13×10^{-6} M) with bipy recorded in dichloromethane (from 0 to 5000 equiv). Inset: The binding isotherm with 1:3 trimer/ligand fit, which was determined using Specfit™, at 425 nm (0–1000 equiv).[36]

a second isosbestic point was identified at 421 nm ($\Delta\lambda$=6 nm), and a final absorption with a λ_{max} at 425 ($\Delta\lambda$=10 nm) resulted. This was comparable to UV/vis investigations carried out with pyridine, where a new absorption at 425 nm ($\Delta\lambda$=10 nm) was observed with a single isosbestic point at 420 nm. This confirmed the final species in the trimer/bipy solution to be the 1:3 open complex. Using Specfit™ the changes in the absorption spectra upon titration with bipy were assigned to a five-component system (host; guest; and 1:1; 1:2 and 1:3 trimer/ligand complexes). The binding isotherm is shown as an inset in Fig. 7.

The binding constants obtained for this fit are shown in Table 3. The binding constant for the formation of the 1:1 complex was greater than the latter two, indicating the formation of the more stable sandwich complex. The 6 nm red-shift was attributed to the formation of a 1:2 trimer/ligand complex, whereas the overall red-shift of 10 nm relative to the original trimer absorption was consistent with the formation of the 1:3 open complex.

Table 3
The absorption maxima and binding constants for the complexation between **10c** and mono- and bidentate ligands

	λ_{max} (nm)	Log $K_{1:1}$	Log $K_{1:2}$	Log $K_{1:3}$
10c	415, 542, 578			
10c bipy	425, 557, 595	5.1±0.01	3.7±0.07	3.9±0.07
10c pyr	425, 556, 596	3.5±0.08	3.3±0.17	3.5±0.09

The speciation diagram in Fig. 8 depicted 69% formation of the 1:1 ligand/trimer complex at 11 equiv of bipy per porphyrin. The 1:2 and 1:3 trimer/ligand species were formed simultaneously, with the former reaching its maximum concentration at 53 equiv of guest. Both species had similar binding constants and were consistent with external complexation.[34]

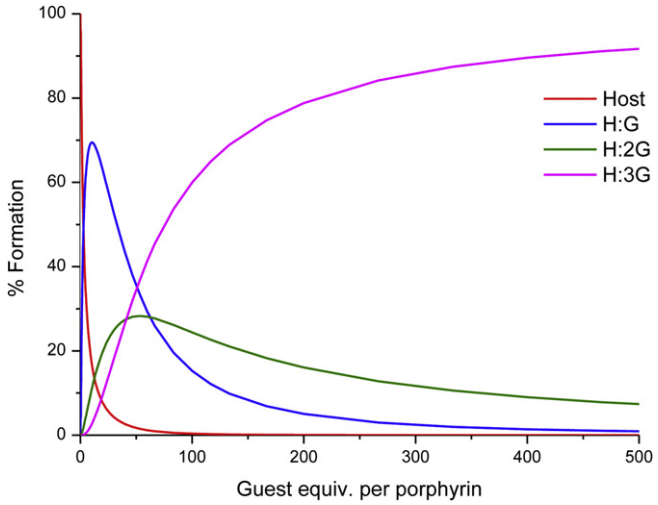


Fig. 8. The species distribution plot of the phenylethynyl-linked trimer **10c** (1.13×10^{-6} M) upon addition of bipy recorded in dichloromethane.

3. Conclusions

2,6,14-Trisubstiuted triptycenylporphyrins were synthesized in yields up to 36% both via Suzuki and Sonogashira coupling reactions. The porphyrin precursors were prepared by nucleophilic addition reactions of A_2-type porphyrins or mixed condensation reactions and linked to the triptycene core either through the *meso* or β position. The systems investigated provide a proof of concept for the construction of larger porphyrin arrays based on/with a rigid triptycene core.

Preliminary studies were performed to investigate the host/guest properties of the triptycene-linked porphyrin trimers. Complexation experiments with the trimers and bidentate 4,4′-bipyridine were performed and binding constants were determined using Specfit™. Pyridine, a monondentate ligand, was used for a comparative study. In each array, the binding constants for the formation of the 1:1 complex were greater by an order of magnitude with 4,4′-bipyridine compared with pyridine. This was consistent with intramolecular sandwich-type complexation. Larger binding constants were also obtained for the formation of the 1:2 trimer/ligand complexes of **9c** and **10c** with bipy, whereas **5c**, displayed a comparable value for both bipy and pyr.

An intermediate species was detected for compounds **5c** and **9c** and was 6 nm red-shifted from the uncoordinated porphyrin array. This was assigned to the 1:2 trimer/ligand complex, which displayed both sandwich and open binding interactions. At higher concentration of bipy, overall red-shifts of 9/10 nm was observed. These shifts were comparable to results obtained with pyridine and were consistent with the formation of a 1:3 trimer/ligand open complex. Compound **8c** displayed different behavior: an intermediate species, with a clear set of isosbestic points could not be detected and a red-shift of 6 nm was observed in the presence of excess ligand. A comparison with pyridine confirmed that the final species was in fact the 1:3 open complex.

The types of trimers presented herein have not been investigated previously. They are not fully symmetric and, consequently, both sandwich and open complexation were observed simultaneously in titrations with bipy. Previous investigations on the coordination chemistry of multiporphyrin arrays focused either on fully symmetric systems, whereby sandwich and/or open complexes were observed sequentially,[28,29,32a,37] or on dendrimer-type systems where the intermediate complexes could not be decisively classified.[38]

4. Experimental

4.1. General information

^{1}H NMR spectra were recorded on a Bruker DPX 400 (400 MHz for ^{1}H NMR and 100.6 for ^{13}C NMR). Chemical shifts are reported in (ppm) referenced to tetramethylsilane set at 0.00 ppm. HRMS spectra were measured on Micromass/Waters Corp. USA liquid chromatography timer-of-flight spectrometer equipped with ES source. Low resolution mass spectra were recorded on Micromass/Waters Corp. USA Quattro micro_LC–MS>MS. UV/vis measurements were performed on a Perkin–Elmer, Lambda 1050 spectrophotometer or a Perkin–Elmer, Lambda 25 spectrophotometer. Melting points were acquired on a Stuart SMP10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60F$_{254}$ (Merck) precoated aluminum sheets. Flash chromatography was carried out using Fluka Silica Gel 60 (230–400 mesh). Anhydrous THF distilled over sodium/benzophenone was used. All commercial chemicals were supplied by Aldrich and used without purification. UV/vis titrations were performed with a Perkin–Elmer, Lambda 1050 spectrophotometer or with a Perkin Elmer, Lambda 25 spectrophotometer. Solutions of porphyrins were prepared in spectrophotometric grade dichloromethane (Aldrich). Analytical data for compounds **2**,[1] **4a**,[40] **5a**,[41] **7a**[39] **9a**,[21] **9b**,[21] **10a**,[23] and **10b**[24] agree with those reported in the literature and related compounds.[40]

4.2. Syntheses

*4.2.1. [5-Bromo-15-(n-butyl)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) (**6a**).* Porphyrin **3a** was metalated using Zn(OAc) according to a procedure by Tomizaki et al.[41] to yield a purple solid: (204.5 mg, 93%): mp >300 °C; R_f=0.31 (SiO_2, dichloromethane/*n*-hexane, 1:2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.15 (t, ^3J=7.3 Hz, $CH_2CH_2CH_2CH_3$), 1.84 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.49 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.77 (s, 6H, tolyl–CH_3), 4.82 (t, ^3J=8.0 Hz, $CH_2CH_2CH_2CH_3$), 7.60 (d, ^3J=7.6 Hz, Ar–H), 8.05 (d, ^3J=7.8 Hz, Ar–H), 8.94 (m, 4H, H_β), 9.41 (d, ^3J=4.7 Hz, 2H, H_β), 9.65 ppm (d,^3J=4.7 Hz, 2H, H_β); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ=14.2, 21.6, 23.7, 35.4, 41.1, 103.5, 121.1, 122.2, 127.3, 129.0, 132.4, 132.5, 133.1, 134.4, 137.2, 139.6, 149.6, 149.6, 150.0, 150.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=423 (5.6), 554 (4.5), 592 nm (4.3); HRMS (ES^+) [$C_{38}H_{31}N_4BrZn$] calcd for [M+H] 686.1024, found 686.1013.

*4.2.2. [5-(4′,4′,5′,5′-Tetramethyl-{1′,3′,2′}dioxaborolan-2′-yl)-10,15,20-triphenylporphyrinato]nickel(II) (**3b**).* The bromoporphyrin **3a** (1 equiv) was placed in a Schlenk tube and dried under vacuum. Dry 1,2-dichloroethane (20 ml) and dry triethylamine (13 equiv) were added under argon. The solution was degassed via three freeze-pump-thaw cycles, before the vessel was purged with argon. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (10 equiv) and dichlorobis(triphenylphosphine)palladium(II) (0.03 equiv) were then added, and the Schlenk tube was sealed and stirred at 90 °C overnight. The reaction was quenched carefully with a saturated KCl solution, washed with water, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel dichloromethane/*n*-hexane (1:2, v/v, *h*=31 cm, *ø*=6 cm) and gave the pure product as second fraction as purple crystals after recrystallization from dichloromethane/methanol, yield: 201.5 mg (0.28 mmol, 51%): mp=230 °C; R_f=0.53 (dichloromethane/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.72 ppm (s. 12H, CH_3), 7.71 (m, 9H, Ar–*H*), 8.02 (m, 6H, Ar–*H*), 8.70 (d, 2H, ^3J=4.9 Hz, H_β), 8.74 (d, 2H, ^3J=4.9 Hz, H_β), 8.86 (d, 2H, ^3J=5.1 Hz, H_β), 9.79 ppm (d, 2H, ^3J=5.1 Hz, H_β); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=24.73, 84.39, 118.25, 126.38, 127.23, 127.29, 131.12, 131.86, 132.61, 133.18, 133.26, 133.54, 140.33, 140.44, 141.25, 141.45, 142.48, 146.44 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=413 (5.27), 528 (4.21), 569 nm (3.78); HRMS (ES^+) [$C_{44}H_{35}BN_4NiO_2$]: calcd for [M+H] 721.2285, found 721.2272.

*4.2.3. 5-Butyl-15-(4′,4′,5′,5′-tetramethyl-[1′,3′,2′]dioxaborolan-2′-yl)-10,20-bis(4-methylphenyl)porphyrin (**4b**).* Prepared by reaction of 5-bromo-15-butyl-10,20-ditolylporphyrin **4a** following the procedure in Section 4.2.2. The crude product was purified by column chromatography on silica gel dichloromethane/*n*-hexane (1:2, v/v) and gave the pure product as second fraction as purple crystals after recrystallization from dichloromethane/methanol (207.3 mg, 0.308 mmol) in 48% yield: mp=260 °C; R_f=0.37 (dichloromethane/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.14 (t, ^3J=7.4 Hz, 3H, CH_2CH_3), 1.84 (s, 14H, CH_3+CH_2CH_3), 2.55 (m, 2H, $CH_2CH_2CH_2$), 2.76 (s, 6H, tolyl–CH_3), 5.04 (t, ^3J=7.9 Hz, 2H, $CH_2CH_2CH_2CH_3$), 7.59 (d, ^3J=7.8 Hz, 4H, Ar$_H$), 8.10 (d, ^3J=7.8 Hz, 4H, Ar$_H$), 8.92 (d, ^3J=4.8 Hz, 2H, H_β), 8.95 (d, ^3J=4.8 Hz, 2H, H_β), 9.49 (d, ^3J=4.8 Hz, 2H, H_β), 9.82 ppm (d, ^3J=4.8 Hz, 2H, H_β); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=14.24, 21.58, 23.71, 25.33, 35.28, 40.94, 85.06, 119.58, 122.50, 127.29, 134.45, 137.24, 139.67 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)= 417 (5.35), 517 (4.22), 549 (3.79), 589 (3.77), 644 nm (3.53); HRMS (ES^+) [$C_{44}H_{45}BN_4O_2$]: calcd for [M+H] 673.3714, found 673.3685.

*4.2.4. [5-(4′,4′,5′,5′-Tetramethyl-{1′,3′,2′}dioxaborolan-2′-yl)-10,15,20-triphenylporphyrinato]zinc(II) (**5b**).* Produced from bromoporphyrin **5a** following the procedure in Section 4.2.2. The crude product was purified by column chromatography on silica gel dichloromethane/*n*-hexane (1:2, v/v, *h*=24 cm, *ø*=3 cm) and gave the pure product as second fraction as purple crystals after recrystallization from dichloromethane/methanol, yield: (241.1 mg, 56%): mp=148 °C; R_f=0.17 (dichloromethane/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.83 (s, 12H, CH_3), 7.72 (m, 9H, Ar$_H$), 8.17 (m, 6H, Ar$_H$), 8.83 (d, ^3J=4.7 Hz, 2H, H_β) 8.85 (d, ^3J=4.9 Hz, 2H, H_β), 8.99 (d, ^3J=4.7 Hz, 2H, H_β), 9.83 (d, ^3J=4.7 Hz, 2H, H_β) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=25.02, 84.91, 120.64, 122.30, 126.20, 127.13, 127.19, 131.24, 131.85, 132.56, 132.69, 134.02, 134.17, 142.44, 142.55, 149.02, 149.69, 150.09, 154.10 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=417 (5.13), 546 (4.27), 581 nm (3.57); HRMS (ES^+) [$C_{44}H_{35}BN_4O_2Zn$] calcd for [M+H] 727.2223, found 727.2206.

*4.2.5. [5-Butyl-15-(4′,4′,5′,5′-tetramethyl-[1′,3′,2′]dioxaborolan-2′-yl)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) (**6b**).* The reaction followed the procedure given in Section 4.2.2. However, prior to purification metalation with zinc(II) acetate was performed on the crude product. Filtration through a frit using silica gel and dichloromethane/*n*-hexane (1/1, v/v) eluted the debrominated porphyrin side product. Changing the eluent to dichloromethane yielded the title compound **6b** as a purple solid (390.4 mg, 80% for two steps): mp >300 °C; R_f=0.51 (dichloromethane/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.17 (t, ^3J=7.4 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.90 (m, 14H, CH_3, $CH_2CH_2CH_2CH_3$), 2.54 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.79 (s, 6H, tolyl–CH_3), 4.92 (m, 2H, $CH_2CH_2CH_2CH_3$), 7.62 (d, ^3J=7.2 Hz, 4H, Ar–*H*), 8.13 (d, ^3J=7.3 Hz, 4H, Ar–*H*), 9.05 (m, 4H, H_β), 9.50 (m, 2H, H_β), 9.91 ppm (m, 2H, H_β); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ=14.2, 21.5, 23.8, 25.3, 35.6, 41.2, 85.1, 120.4, 123.2, 127.7, 128.9, 131.8, 132.9, 134.4, 137.0, 140.1, 149.2, 149.7, 150.0, 154.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=419 (5.7), 548 (4.5), 585 nm (4.1); HRMS(ES^+) [$C_{44}H_{43}N_4O_2Zn$] calcd for [M+H] 734.2771, found 734.2749.

*4.2.6. 5-(4′,4′,5′,5′-Tetramethyl-[1′,3′,2′]dioxaborolan-2′-yl)-10,15,20-triphenylporphyrin (**7b**).* 5-Bromo-10,15,20-triphenylporphyrin **7a** (400 mg, 0.65 mmol), triethylamine (1.17 mL, 8.42 mmol), borolane (0.94 mL, 6.48 mmol), and dichlorobis(triphenylphosphine)palladium(II) (13.6 mg, 0.02 mmol) were reacted according to 4.2.2. Column chromatography using dichloromethane as eluent

yielded a purple solid (241.1 mg, 56%): mp >300 °C; R_f=0.2 (SiO_2, dichloromethane/*n*-hexane 1:2, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ=−2.75 (s, 2H, N*H*), 1.87 (s, 12H, CH_3), 7.78 (m, 9H, Ar−*H*), 8.24 (m, 6H, Ar−*H*), 8.85 (dd, ^3J=4.4, 14.2 Hz, 4H, H_β), 9.00 (d, ^3J=4.6 Hz, 2H, H_β), 9.89 ppm (d, ^3J=4.6 Hz, 2H, H_β); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ=23.3, 85.2, 120.0, 121.8, 126.6, 127.7, 134.5, 142.0, 142.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=417 (5.4), 514 (4.3), 546 (4.0), 588 (4.0), 649 nm (3.9); HRMS(ES$^+$) [$C_{44}H_{38}N_4$] calcd for [M+H] 665.3088, found 665.3109.

*4.2.7. 2,6,14-[Tris(5,10,15-triphenylporphyrin-20-ylato)nickel(II)] triptycene (**7c**).* The borolanylporphyrin **3b** (1 equiv), 2,6,14-triiodotriptycene **2** (0.3 equiv), potassium phosphate (4 equiv) and tetrakis(triphenylphosphine)palladium(0) (0.1 equiv) were placed in a Schlenk tube and dissolved in anhydrous DMF under argon. The mixture was heated at 100 °C for 12 h. The solvent was removed and the residue was redissolved in dichloromethane and washed with aqueous sodium hydrogen carbonate solution. The crude product was purified by dry-loaded column chromatography on silica gel, dichloromethane/*n*-hexane (1:2, v/v, *h*=53 cm, *ø*=3 cm) and gave the pure product as second fraction as orange crystals after recrystallization from dichloromethane/methanol (20.6 mg, 0.01 mmol, 22%). Alternatively, this compound was prepared by Suzuki coupling of the free-base porphyrin **7b** directly followed in situ by metalation with zinc(II)acetate and standard work up: mp >310 °C; R_f=0.47 (dichloromethane/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.96 ppm (s, 1H, C*H*), 6.10 (s, 1H, C*H*), 7.71 (m, 30H, Ar$_H$), 8.05 (m, 21H, Ar$_H$), 8.18 (s, 1H, Ar$_H$), 8.25 (s, 1H, Ar$_H$), 8.33 (s, 1H, Ar$_H$), 8.78 (m, 16H, H_β), 8.92 ppm (m, 8H, H_β); ^{13}C NMR (150.9 MHz): δ=53.97, 54.01, 118.83, 118.84, 118.87, 118.91, 118.96, 122.43, 126.69, 126.71, 127.56, 129.43, 131.16, 132.02, 132.06, 132.29, 132.36. 132.42, 133.57, 138.02, 140.80 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=418 (5.54), 528 nm(5.06); HRMS (LD$^+$) [$C_{134}H_{80}N_{12}Ni_3$] calcd 2030.4689, found 2030.4669.

*4.2.8. 2,6,14-Tris[5-n-butyl-10,15-bis(4-methylphenyl)porphyrin-20-yl]triptycene (**4c**).* Produced from the borolanylporphyrin **4b** following procedure given in 4.2.7. The crude product was purified by column chromatography on silica gel dichloromethane/*n*-hexane (1:1, v/v, *h*=31 cm, *ø*=3 cm) and gave the pure product as the sixth fraction as purple crystals after recrystallization from dichloromethane/methanol (8.9 mg, 0.005 mmol, 16%): mp=237 °C; R_f=0.13 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C, TMS): δ=−2.64 ppm (s, 2H, N*H*), -2.61 (s, 2H, N*H*), −2.57 (s, 2H, N*H*), 1.16 (t, 12H, ^3J=7.3 Hz, CH_3), 1.85 (m, 6H, CH_2CH$_3$), 2.57 (m, 6H, CH$_2$CH_2CH$_2$), 2.77 (m, 18H, C$_6$H$_5$−CH_3), 5.06 (m, 6H, CH_2CH$_2$CH$_2$CH$_3$), 6.13 (s, 1H, C*H*), 6.26 (s, 1H, C*H*), 7.61 (m, 12H, Ar$_H$), 8.14 (m, 18H, Ar$_H$), 8.48 (s, 1H, Ar$_H$), 8.53 (s, 1H, Ar$_H$), 8.60 (s, 1H, Ar$_H$), 8.91 (m, 5H, H_β), 8.99 (m, 13H, H_β), 9.51 ppm (m, 6H, H_β); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ=13.97, 14.06, 21.41, 22.54, 23.51, 29.21, 29.56, 31.79, 35.11, 40.75, 54.17, 119.25, 119.46, 116.53, 120.29, 122.34, 127.19, 128.69, 130.47, 130.75, 132.04, 134.33, 137.05, 137.08, 137.15, 139.30, 139.43, 144.11, 144.87 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=422 (5.40), 446 (5.01), 518 (4.44), 554 (4.25), 593 (4.04), 649 nm (4.05); HRMS (ES$^+$) [$C_{134}H_{110}N_{12}$]: calcd for [M+2H] 1888.9133, found 1888.9158.

*4.2.9. 2,6,14-[Tris(5,10,15-triphenylporphyrin-20-ylato)zinc(II)]triptycene (**5c**).* [5-(4′,4′,5′,5′-Tetramethyl-[1′,3′,2]-dioxaborolan-2′-yl)-10,15,20-triphenylporphyrin]zinc **5b** (200 mg, 0.27 mmol), 2,6,14-triiodotriptycene **2** (52.1 mg, 0.08 mmol), potassium phosphate (233.3 mg, 1.10 mmol), and tetrakis(triphenylphosphine)palladium(0) (31.6 mg, 0.03 mmol) were reacted as described for Section 4.2.7. Column chromatography on silica gel using dichloromethane/*n*-hexane (1:1, v/v) as eluent yielded the title compound (44.4 mg, 27%): mp >310 °C; R_f=0.09 (dichloromethane/*n*-hexane, 2:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ=6.16 (s, 1H, C*H*), 6.31 (s, 1H, C*H*), 7.82 (m, 27H, Ar−H), 8.01 (d, ^3J=7.1 Hz, 1H, Ar−H), 8.13 (d, ^3J=7.3 Hz, 1H, Ar−H), 8.17 (m, 1H, Ar−H), 8.30 (m, 20H, Ar−H), 8.52 (s, 1H, Ar−H), 8.61 (s, 1H, Ar−H), 8.70 (s, 1H, Ar−H), 8.99−9.11 (m, 18H, β*H*), 9.22 ppm (m, 6H, β*H*); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ=56.2, 120.7, 122.4, 126.6, 127.5, 130.6, 132.0, 132.1, 132.4, 134.5 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=424 (5.9), 548 (4.6), 587 nm (4.0); HRMS (MALDI LD$^+$) [$C_{134}H_{80}N_{12}Zn_3$+H]: calcd 2048.4503, found 2048.4529.

*4.2.10. 2,6,14-[Tris(5-n-butyl-10,20-bis(4-methylphenyl)porphyrin-15-ylato)zinc(II)]triptycene (**6c**).* [5-*n*-Butyl-15-(4′,4′,5′,5′-tetramethyl-[1′,3′,2′]dioxa-borolan-2′-yl)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) **6a** (200 mg, 0.27 mmol), 2,6,14-triiodotriptycene **2** (51.5 mg, 0.08 mmol), and potassium phosphate (230.7 mg, 1.10 mmol) were added to a 100 mL Schlenk flask and dried under vacuum. The vacuum was released to allow the addition of dry dimethylformamide (25 mL). The mixture was degassed via three freeze-pump-thaw cycles before the vessel was purged with argon and tetrakis(triphenylphosphine)palladium(0) (31.4 mg, 0.03 mmol) was added. The Schlenk flask was sealed and heated to 100 °C overnight (TLC control; dichloromethane/*n*-hexane 1:1, v/v). Then, the solvent was removed and the residue was redissolved in dichloromethane and washed with aqueous sodium hydrogen carbonate. The crude porphyrin mixture was dried in vacuo and subjected to purification via column chromatography on silica gel using dichloromethane/*n*-hexane (2:1, v/v) as eluent ti yield the title compound (22 mg, 22%); mp >300 °C; R_f=0.41 (SiO_2, dichloromethane/*n*-hexane 1:2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.18 (t, ^3J=7.3 Hz, 9H, CH$_2$CH$_2$CH$_2$CH_3), 1.90 (m, 6H CH$_2$CH$_2$CH_2CH$_3$), 2.60 (m, 6H, CH$_2$CH_2CH$_2$CH$_3$), 2.77 (s, 6H, tolyl−CH_3), 2.79 (s, 12H, tolyl−CH_3), 5.04 (m, 6H, CH_2CH$_2$CH$_2$CH$_3$), 6.10 (s, 1H, Ar$_H$), 6.26 (s, 1H, Ar$_H$), 7.62 (m, 12H, Ar$_H$), 7.97 (d, ^3J=7.3 Hz, 1H, Ar$_H$), 8.14 (m, 18H, Ar$_H$), 8.54 (s, 1H, Ar$_H$), 8.63 (s, 1H, Ar$_H$), 9.07 (m, 18H, H_β), 9.58 ppm (m, 6H, H_β); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ=13.9, 21.4, 23.6, 35.4, 41.0, 46.2, 54.3, 120.5, 122.2, 127.2, 128.6, 130.4, 130.7, 131.7, 132.1, 132.3, 134.2, 136.9, 139.9, 149.9, 150.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=424 (6.0), 552 (4.8), 593 nm (4.6); HRMS (MALDI LD$^+$) [$C_{134}H_{104}N_{12}Zn_3$]: calcd for [M+H] 2072.6381, found 2072.6462.

*4.2.11. 2,6,14-Tri[(5-ethynyl-10,15,20-tris(4-methylphenyl)porphyrinato)zinc(II)]triptycene (**8**).* Under a nitrogen atmosphere 2,6,14-triiodotriptycene **2** (40.0 mg, 63.3 μmol, 1 equiv), 2-([1′,3′,2′]-dioxaborolan-2′-yl)-5,10,15,20-tetraphenylporphyrin (281 mg, 380 μmol, 6 equiv), and $Ba(OH)_2 \cdot 8H_2O$ (200 mg, 663 μmol) were dissolved in toluene/H_2O (20 mL/4 mL) und the resulting mixture was degassed by a nitrogen stream for 20 min. $Pd(PPh_3)_4$ (14.6 mg, 12.7 μmol, 20 mol %) was added and the mixture was heated to reflux for 18 h. The crude mixture was filtered through a plug of silica eluting with CH_2Cl_2 and EtOAc. The filtrate was washed with a saturated solution of NH_4Cl and H_2O and the solvent was removed in vacuo. Column chromatography on silica gel (CH_2Cl_2/*n*-hexane, 1:1→3:2→2:1→1:0, v/v) yielded **8** as a purple microcrystalline solid (12.8 mg, 6.12 μmol, 10%): mp >300 °C; R_f=0.26 (CH_2Cl_2/*n*-hexane, 2:1); IR (ATR): ν=3301 (w), 3052 (m), 3021 (m), 2923 (w), 1596 (m), 1574 (w), 1560 (w), 1468 (m), 1439 (s), 1405 (w), 1348 (m), 1261 (w), 1216 (w), 1177 (m), 1155 (w), 1071 (m), 1032 (w), 1001 (m), 986 (m), 964 (s), 929 (w), 878 (w), 842 (w), 828 (w), 796 (s), 723 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ=−2.64 to −2.49 (m, 6H, N*H*), 5.04 (s, 1H, triptycene$_H$), 5.21 (s, 1H, triptycene$_H$), 6.29−6.48 (m, 3H, Ar$_H$), 6.64−6.88 (m, 6H, Ar$_H$), 7.16−7.25 (m, 4H, Ar$_H$), 7.27−7.43 (m, 5H, Ar$_H$), 7.66−7.90 (m, 33H, Ar$_H$), 8.15−8.41 (m, 18H, Ar$_H$), 8.64−8.97 ppm (m, 21H, H_β); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ=53.4, 53.5, 119.6, 119.7, 119.8, 119.9, 120.3, 120.4, 121.6, 122.2, 122.5, 122.8, 122.9, 125.7, 125.8, 126.5, 126.6, 126.7, 127.1, 127.2, 127.7, 127.8, 128.7, 128.8, 130.8, 130.9, 131.9, 132.1, 132.3, 132.4, 132.7, 133.6, 133.8, 134.4, 134.5, 134.6, 135.3, 135.4, 135.5, 136.3, 139.7, 139.8, 139.9, 134.0, 141.8, 141.9, 142.2, 142.3, 142.5, 143.7, 144.9 ppm; UV/vis (CH_2Cl_2): λ_{max}

(log ϵ)=424 (5.44), 519 (4.46), 554 (4.25), 594 (4.08), 650 nm (4.07); HRMS (MALDI LD$^+$) [$C_{152}H_{99}N_{12}$]: calcd for [M+H] 2091.8116, found 2091.8079. HRMS (ESI, positive) $C_{152}H_{99}N_{12}$: calcd for [M+H]$^+$ 2091.8110, found 2091.8085.

*4.2.12. 2,6,14-Tri[(5-ethynyl-10,15,20-tris(4-methylphenyl)porphyrinato)zinc(II)]triptycene (**9c**).* [5-Ethynyl-10,15,20-tris(4-methylphenyl)porphyrinato]zinc(II) **9b** (100 mg, 0.15 mmol) 2,6,14-triiodotriptycene **2** (31.5 mg, 0.05 mmol), and triphenylarsine (91.7 mg, 0.3 mmol) were added to a 100 mL Schlenk flask and dried under vacuum. The vacuum was released to allow for the addition of dry THF (10 mL) and dry triethylamine (5 mL). The mixture was degassed via three freeze-pump-thaw cycles before the vessel was purged with argon and tris(dibenzylideneacetone)dipalladium(0) (27.4 mg, 0.03 mmol) was added. The Schlenk tube was sealed and the reaction mixture stirred overnight at 30 °C. Then, dichloromethane (60 mL) was added, the mixture was washed with water (2×30 mL) and dried over sodium hydrogen carbonate. The solvent was evaporated under reduced pressure and the product purified by column chromatography on silica gel. The crude product was subjected to column chromatography on silica gel using dichloromethane/*n*-hexane (1:1, v/v) as eluent to yield the title compound **5c** (31 mg, 28%): mp >300 °C; R_f=0.61 (SiO_2, dichloromethane/*n*-hexane 3:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ=2.75 (m, 27H, tolyl−CH_3), 5.93 (s, 1H, Ar$_H$), 6.00 (s, 1H, Ar$_H$), 7.59 (m, 24H, Ar$_H$), 7.83 (m, 6H, Ar$_H$), 8.11 (m, 24H, Ar$_H$), 8.29 (s, 1H, Ar$_H$), 8.32 (s, 1H, Ar$_H$), 8.35 (s, 1H, Ar$_H$), 8.91 (m, 12H, H_β), 9.06 (m, 6H, H_β), 9.86 ppm (m, 6H, H_β); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ=21.4 (CH_3), 53.9 (Ar−C), 121.4 (qC), 124.2 (Ar−C), 127.2 (qC), 127.2 (Ar−C), 128.7 (Ar−C), 129.2 (Ar−C), 130.6 (Ar−C), 131.7 (Ar−C), 132.8 (Ar−C), 134.1 (Ar−C), 134.2 (qC), 137.1 (qC), 139.4 (qC), 144.9 (qC), 149.8 ppm (qC); UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=443 (6.0), 527 (4.2), 566 (4.7), 614 nm (4.9); HRMS (MALDI LD$^+$) [$C_{149}H_{98}N_{12}Zn_3$]: calcd for [M+H] 2246.5912, found 2246.5916.

*4.2.13. 2,6,14-Tri[(5,15-bis(4-methylphenyl)-10-(4-phenylethynyl) porphyrinato)zinc(II)]triptycene (**10c**).* [5,15-Bis(4-methylphenyl)-10-phenylethynylporphyrinato]zinc(II) **10b** (100 mg, 0.15 mmol) 2,6,14-triiodotriptycene **2** (32.2 mg, 0.05 mmol), triphenylarsine (93.6 mg, 0.3 mmol), and tris(dibenzylideneacetone)dipalladium(0) (28.0 mg, 0.03 mmol) were reacted according to the procedure given in Section 4.2.12. The crude product was subjected to column chromatography on silica gel using dichloromethane/*n*-hexane (1:1, v/v) as eluent to yield the title compound (39.6 mg, 36%): mp >300 °C; R_f=0.49 (SiO_2, dichloromethane/*n*-hexane 1:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ=2.77 (m, 18H, tolyl−CH_3), 5.66 (s, 1H, Ar$_H$), 5.68 (s, 1H, Ar$_H$), 7.49 (d, ^3J=6.9 Hz, 3H, Ar$_H$), 7.62 (m, 12H, Ar$_H$), 7.74 (m, 3H, Ar$_H$), 7.87 (m, 3H, Ar$_H$), 7.96 (d, ^3J=7.9 Hz, 6H, Ar$_H$), 8.15 (m, 12H, Ar$_H$), 8.24 (d, ^3J=7.9 Hz, 6H, Ar$_H$), 9.04 (m, 12H, H_β), 9.13 (m, 6H, H_β), 9.37 (m, 6H, H_β), 10.20 ppm (m 3H, H_{meso}); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ=21.4, 53.7, 106.0, 124.7, 125.2, 127.2. 128.2, 128.8, 129.6, 130.3, 131.6, 132.0, 132.6, 134.3, 137.0, 143.2 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ϵ)=415 (6.0), 542 (4.6), 581 nm (3.5); HRMS (MALDI LD$^+$) [$C_{146}H_{92}N_{12}Zn_3$]: calcd for [M+H] 2204.5442, found 2204.5479.

4.3. Determination of binding constants

Binding constants were determined by using the non-linear least-squares program SPECFIT/32™, which is a multivariate data analysis program for modeling and fitting experimental data sets (such as chemical kinetics and equilibrium titrations) obtained from multivariate spectrophotometric measurements.

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