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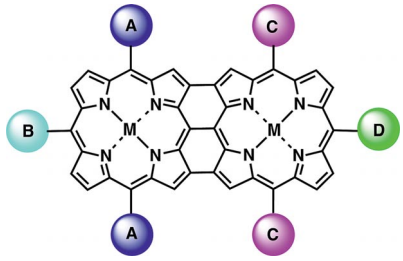
Porphyrinoids

A library of symmetric and unsymmetric singly linked and triply fused porphyrin dimers are synthesized in moderate to very good yields. A variety of functional groups are tolerated. Numerous synthetic strategies, incorporating oxidative radical coupling and organolithium and palladium-catalyzed coupling methods, are utilized.



Keywords: Porphyrinoids / Organolithium reagents / C–C coupling / Cycloaddition / Fused-ring systems

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Synthesis and Functionalization of Triply Fused Porphyrin Dimers

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Keywords: Porphyrinoids / Organolithium reagents / C–C coupling / Cycloaddition / Fused-ring systems

Current applications of porphyrins in medicine and optics, such as photodynamic therapy or nonlinear absorption, increasingly require the use of far-red absorbing dyes. Modification of the porphyrin structure to accommodate these conditions can be achieved by extending the conjugation of the porphyrin π system, which causes a bathochromic shift in the absorption spectrum. Thus, conjugated porphyrin oligomers have found widespread use. However, past synthetic strategies have mainly targeted symmetric porphyrin dimers, trimers, and oligomers which limit the practical use of such chromophores. To further extend the absorption profile, a series of symmetric and unsymmetric dimeric and oligomeric porphyrin β–β, *meso–meso*, β′–β′ triply fused systems were synthesized by oxidative coupling methods. This required an analysis and optimization of the various synthetic strategies. These arrays exhibit a dramatic bathochromic shift into the near-infrared region and many display absorption at wavelengths greater than 1050 nm. Additionally, post-fusing chemical transformations, namely, organolithium, cycloaddition, and transition-metal-catalyzed reactions, at the *meso* and β positions enable the fine-tuning of such arrays to enhance the bathochromic shift and their potential optical applications.

Introduction

Long-wavelength absorption of porphyrins is desired for a wide range of applications[1] and there are many means to achieve such a characteristic. These include the synthesis of porphyrin arrays connected by conjugated linkers,[2] the construction of perturbed porphyrinoid macrocycles through various cycloaddition reactions,[3] and the construction of fused or directly linked porphyrin arrays.[4] The latter is favorable as triply linked porphyrin arrays result in the extension of the absorption profile into the near-IR region. Pioneering methods developed by Sugiura et al.[5] and Osuka and co-workers[6] can be adopted for the generation of so-called triply fused porphyrin dimers and higher arrays.[4a,7] A λ_{max} value greater than 1050 nm may be achieved for these covalently linked multiporphyrin arrays and they can act as multichromophoric model systems for the study of electron transfer in light-harvesting systems. Although the Osuka group, amongst others,[4b,8] have extensively researched this area, their work primarily deals with symmetric arrays and photophysical studies of such porphyrins.[9] Only limited research has been performed on so-called unsymmetric fused dimers[10] and post-modifications of fused arrays.[11] We envisaged the development of new symmetric fused dimers and unsymmetric arrays and their application to research fields such as nonlinear optics (NLO),[12] organic light-emitting diodes (OLEDs),[13] and two-photon absorption photodynamic therapy (2PA-PDT).[14] The introduction of various substituents to the porphyrin periphery[15] and subsequent post-fusing modifications enables the arrays to be fine-tuned for PDT by the introduction of water-solubilizing groups[14a,16] and NLO by the introduction of donor/acceptor groups to generate push–pull systems.[17] Thus, synthetic strategies for the development of such arrays will be described. Following the synthesis by Susumu et al. in 1996 of *meso–meso* directly linked porphyrins by a condensation reaction,[18] there have been substantial developments in the synthesis of such arrays. These include total synthesis,[19] Ulmann coupling,[20] oxidative fusing of free-*meso* porphyrins with oxidants such as silver salts ($AgPF_6$),[5,21] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and $Sc(OTf)_3$,[22] and hypervalent iodine [bis(trifluoroacetoxy)iodobenzene (PIFA)],[23] along with electrochemical oxidation[24] and recently a method involving the use of a manganese(IV)–oxo porphyrin as a catalyst in a two-electron oxidation process.[25] A method developed by us[26] involves the oxidative dimerization of porphyrin anions, and a stepwise synthetic strategy involving the activation of the porphyrin and subsequent Suzuki coupling has been developed.[27] These *meso–meso* directly linked porphyrin dimers are vital precursors for the synthesis of triply fused bisporphyrins and, thus, can be used or optimized to synthesize such arrays, depending on the substitution pattern on the periphery required (symmetric or

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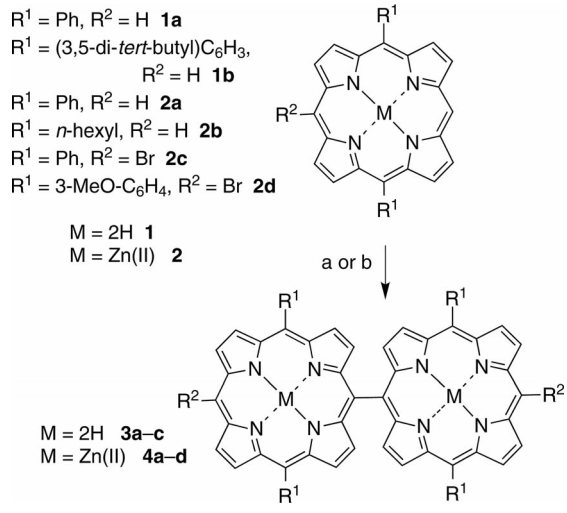
unsymmetric). Similar to singly linked bisporphyrins, various synthetic strategies[7] have been developed for the generation of triply fused porphyrins since their first synthesis by electrochemical oxidation by Osuka and co-workers.[6] One-electron chemical oxidation[28] of monomeric zinc(II) porphyrins with free *meso* positions is the most attractive route for the synthesis of symmetric triply fused porphyrin dimers, and a variety of oxidants can be utilized. The most efficient are $Sc(OTf)_3$/DDQ and hypervalent iodine (PIFA), although other oxidants such as gold derivatives can be used and give similar yields.[29] We primarily focused on the synthesis of new symmetric triply fused bisporphyrins and higher arrays by the above strategies and also the synthesis of unsymmetric fused dimers by similar principles. To fine-tune oligomeric porphyrins, post-fusing functionalizations can be executed. These derivatizations enable fused dimers to be more attractive candidates for practical applications. Within our group, the focus is on PDT, NLO, and OLEDs and, with these in mind, synthetic modifications of the peripheries of fused porphyrin dimers were undertaken. These included activation reactions such as brominations and nitrations, which would enable, for example, the attachment of sugars for PDT by Click chemistry[16b] or push–pull substituents for NLO.[30] Also, functionalization by cycloaddition and organolithium reactions could be beneficial for the enhancement of the bathochromic shift of the array. Most previous post-modifications of fused arrays have dealt with the pre-installation of activating substituents, whereas we wanted to investigate the direct functionalizations of these arrays and synthetic strategies to enable such.

Results and Discussion

Previously, we described the generation of directly linked symmetric dimers in excellent yields by using organolithium reagents, which can be used to introduce aryl and alky *meso* substituents to the porphyrin periphery[31] and for the synthesis of free-base *meso–meso* directly linked bisporphyrins in good yields by radical dimerization.[26b,32]

From the 5,15-disubstituted porphyrins **1a**[33] and **1b**,[18] the free-base dimers **3a**,[26a] **3b**,[26a] and **3c** were obtained in good yields of 59–74% (Table 1). The zinc(II) derivatives of **3a**[21c] and **3c**[8c] have previously been synthesized in similar yields by DDQ and PIFA oxidation methods, but from trisubstituted precursors. Additionally, hypervalent iodine reagents such as PIFA can be applied for the synthesis of directly linked porphyrin arrays. PIFA contains a highly electrophilic iodine center, which can promote diverse coupling reactions,[34] including the synthesis of directly *meso–meso* linked bisporphyrins in excellent yields.[23b] Interestingly, high yields were obtained with electronegative substituents such as trifluoroalkyl groups and, thus, bromo-substituted monomers were chosen as starting materials, which enabled the generation of activated bisporphyrins. Likewise, 5,15-disubstituted porphyrins were employed for the synthesis of bisporphyrins with two free *meso* positions, with the same objective in mind, as post-fusing modifications at these positions could be implemented. By using 0.8 equiv. of PIFA to avoid formation of the triply fused dimers, the bromo-substituted symmetric dimers **4c**[5]and **4d** were synthesized in good-to-excellent yields of 58 and 86% from **2c**[2a] and **2d**, respectively (Table 1). The reaction mechanism involves the oxidative generation of a porphyrin cation radical, which dimerizes to form the bisporphyrin product. Drawing attention to the 3-methoxy substituent in **4d**, we generated materials with this group owing to our interest in Foscan® derivatives,[35] for which it is a useful precursor. The synthesis of dimers **4a** and **4b** with free *meso* positions in acceptable yields from **2a**[2a] and **2b**[36] was unsuccessful. The desired dimers were only synthesized in very low yields and were identified by mass spectrometry and UV/Vis analysis of the reaction mixtures.

Table 1. Synthesis of directly linked bisporphyrins by PIFA oxidation and organolithium reactions.



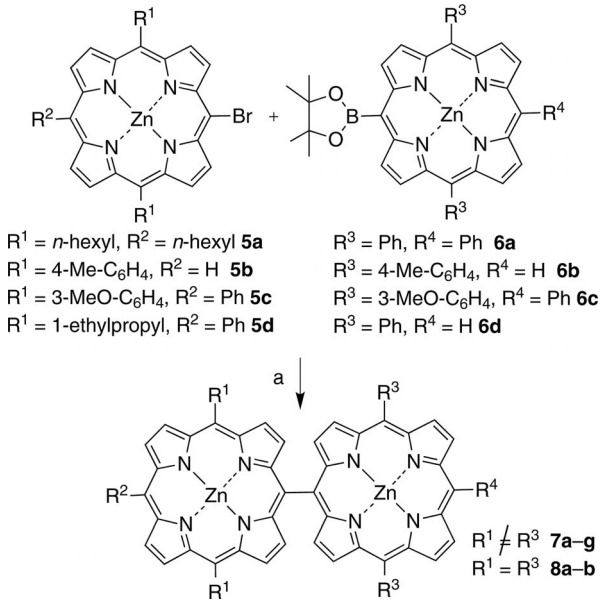
Entry	R^1	R^2	Product	Yield [%]
1	Ph	Ph	**3a**[a]	68
2	Ph	*n*-butyl	**3b**[a]	59
3	Ar	Ph	**3c**[a]	74
4	*n*-hexyl	H	**4a**[b]	n.d.[c]
5	Ph	H	**4b**[b]	n.d.
6	Ph	Br	**4c**[b]	58
7	3-MeO-C_6H_4	Br	**4d**[b]	86

[a] Reagents and conditions: i) R^2Li, –78 to 0 °C, tetrahydrofuran (THF), 1 h. ii) DDQ, 1 h. [b] Reagents and conditions: i) PIFA, CH_2Cl_2, –78 °C. ii) room temp., 0.75 h. iii) $NaBH_4$, MeOH. [c] n.d. = not determined.

Owing to the inevitable formation of oligomerized products, dimers **4a** and **4b** were not isolated and this method was not feasible for the synthesis of bisporphyrins with unsubstituted *meso* positions. Notably, this PIFA oxidation method can also be used for the synthesis of triply fused β–β, *meso–meso*, β′–β′ linked bisporphyrins, by using an excess of PIFA oxidant.[8c] Moreover, for most cases in the literature, bromo-substituted directly linked dimers were synthesized by stepwise strategies[37] or by using other oxidants such as $AgPF_6$ and I_2.[5]

To overcome the challenge of synthesizing directly linked porphyrin dimers with free *meso* positions, a stepwise approach, which culminates in a Suzuki–Miyaura coupling between a bromoporphyrin and borylated porphyrin to give singly linked bisporphyrins, is necessary.[38] This strategy was adopted to synthesize unsymmetric hexasubstituted dimers and dimers with free *meso* positions, which would enable "post-fusing" modifications. The Suzuki coupling of bromoporphyrins **5a**–**d** with borylated porphyrins **6a**–**d**[39] produced the desired dimers **7a**–**f** in yields of 43–66% (Table 2). Although the yields for these Suzuki couplings were good, they were hindered by the competing homocoupling of the borylated porphyrins **6a** and **6b** to generate dimers **8a**[5] and **8b** as side-products in yields of 18 and 22%, respectively. Such directly linked dimers were used in subsequent fusing reactions to form triply linked dimers and also, in the cases of free-*meso* dimers **7c**–**d**, in functionalization reactions.

Table 2. Synthesis of directly linked porphyrin dimers by Suzuki coupling.

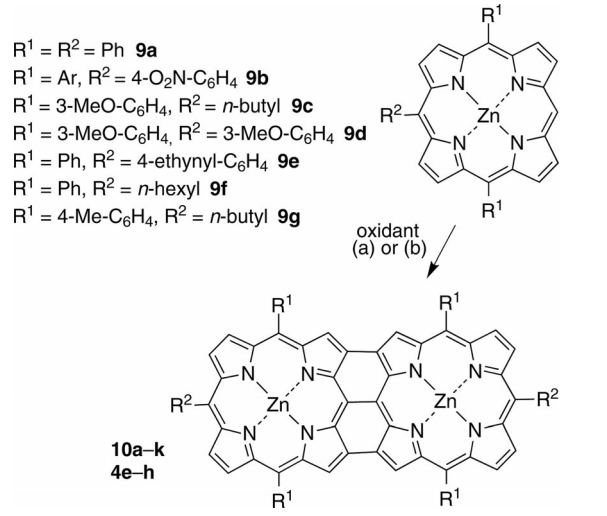


Entry	R^1	R^2	R^3	R^4	Product[a]	Yield [%]
1	*n*-hexyl	*n*-hexyl	Ph	H	**7a**	52
2	Ph	Ph	4-Me-C_6H_4	H	**7b**	76
3	3-MeO-C_6H_4	Ph	3-MeO-C_6H_4	H	**7c**	56
4	1-ethylpropyl	Ph	4-Me-C_6H_4	H	**7d**	63
5	3-MeO-C_6H_4	Ph	4-Me-C_6H_4	H	**7e**	61
6	Ph	Ph	3-MeO-C_6H_4	Ph	**7f**	69
7	Ph	Ph	Ph	Ph	**8a**	18
8	4-Me-C_6H_4	H	4-Me-C_6H_4	H	**8b**	20

[a] Reagents and conditions: $Pd(PPh_3)_4$ (0.1–0.2 equiv.), Cs_2CO_3 (2.1 equiv.), toluene/*N*,*N*-dimethylformamide (3:1 v/v), 80 °C, 18–24 h.

We aspired to synthesize a variety of A_3 and A_2B symmetric bisporphyrins with a range of substituents, some of which would permit follow-up chemistry to be performed. The central metal ion is of great importance to the oxidative process and, thus, zinc porphyrins were employed for the synthesis, as they have a lower first oxidation potential and, therefore, are more easily oxidized than their Ni or Pd counterparts.[40] Similarly to that for singly linked arrays, the reaction mechanism involves oxidative double ring closure via a porphyrin cation radical,[7,41] which undergoes radical cation coupling. Electron-withdrawing substituents on the porphyrin periphery can affect the yields for oxidative fusing,[29] although it was shown recently that an electron-deficient porphyrin tape can be synthesized in good yields.[42] In spite of this, a series of symmetric dimers were synthesized and their yields were compared in relation to their substituents (Table 3). Comparable yields were obtained with both DDQ/$Sc(OTf)_3$ and PIFA oxidants. The new triply fused bisporphyrins **10b**–**k** were prepared from 5,10,15-trisubstituted zinc(II)porphyrin precursors **9a**–**g**[5,15,32,43] in moderate-to-excellent yields of 42–73% by following the Osuka oxidation method, and this strategy can be applied for the synthesis of other fused arrays. For some oxidations with DDQ/$Sc(OTf)_3$, two products were observed: the desired triply fused dimer and the directly linked bisporphyrins **4e**–**g** as side-products, and the yields of dimers **10c**, **10f**,[32] and **10g** were thereby affected. Through optimization of the conditions by increasing the reaction temperature and increasing the reaction duration, the for-

Table 3. Synthesis of triply fused symmetric dimers.



Entry	R^1	R^2	Product	Yield [%]
1	Ph	Ph	**10a**[a]	67[8c]
2	Ar[c]	4-O_2N-C_6H_4	**10b**[a]	56
3	3-MeO-C_6H_4	*n*-butyl	**10c**, **4e**[a]	60, 23
4	3-MeO-C_6H_4	3-MeO-C_6H_4	**10d**[a]	73
5	Ph	4-ethynyl-C_6H_4	**10e**[a]	67
6	Ph	*n*-hexyl	**10f**, **4f**[a]	42, 30[32]
7	4-Me-C_6H_4	*n*-butyl	**10g**, **4 g**[a]	58, 29
8	Ph	H	**10h**[b]	n.d.[d]
9	*n*-hexyl	H	**10i**[b]	n.d.
10	Ph	Br	**10j**,[a,b] **4h**	n.d.
11	3-MeO-C_6H_4	Br	**10k**[a,b]	15

[a] Reagents and conditions: DDQ (5 equiv.), $Sc(OTf)_3$ (5 equiv.), toluene, 50 °C, 3 h. [b] i) PIFA (2.5 equiv.), CH_2Cl_2, –78 °C to room temp., 3 h. ii) $NaBH_4$ (10 equiv.), MeOH, 0.5 h. [c] Ar = 3,5-di-*tert*-butyl-C_6H_3. [d] n.d.: not determined.

mation of these side-products was minimized. For the dimers **10h** and **10i** with free *meso* positions and the bromo dimers **10j** and **10k**, both the DDQ and PIFA method were employed. Unfortunately, owing to the inherent polymerizations of monomers **2a** and **2b**, dimers **10h** and **10i** were not isolated, although their formation was indicated by their near-IR absorption profiles.

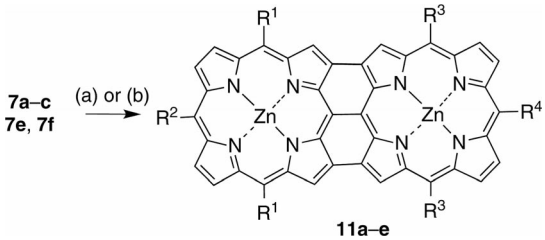
As with their singly linked bisporphyrin counterparts, this strategy is not attractive for the synthesis of free-*meso* dimers. For **10k**, the best results were acquired with PIFA as oxidant, although the yields were much lower than those for the alkyl and aryl-substituted dimers **10a**–**g**. Previous syntheses of fused bromo dimers with these oxidants also gave poor results, and Anderson and co-workers reporting only 9% yield for the synthesis of (3,5-di-*tert*-butyl)phenyl derivative of **10j** with DDQ.[44] This is because the electron-withdrawing nature of the bromo substituent raises the oxidation potential of the porphyrin and, thereby, reduces the yields of such arrays. With DDQ, the singly directly linked derivative of **10j** (**4h**)[21c] was isolated in 10% yield, but the desired triply fused dimer was not obtained.

By adopting a synthetic strategy similar to that for the symmetric arrays, directly linked unsymmetric bisporphyrins were fused oxidatively by using DDQ/$Sc(OTf)_3$ or PIFA (Table 4). With dimers **7a**–**c**, **7e**, and **7f**, attempts to synthesize triply fused porphyrins had mixed results. For the free-*meso* arrays, dimers **11b**–**d** were not detected. Although all crude samples exhibited typical triply fused near-infrared absorption profiles, the desired dimers were not detected by mass spectrometry, and purification was not possible. Again, there is preferential fusing at this "free-*meso*" side of the directly linked bisporphyrin, which results in a mixture of dimeric and tetrameric products. Owing to the poor solubility of these arrays, their isolation could not be achieved by chromatographic methods. Trace quantities of *n*-hexyl-substituted dimer **11a** were detected, but full characterization was not achievable owing to the low yields obtained. With the milder PIFA oxidant, oligomerization was not minimized, and similar results were observed for dimers **11c**–**d**. For the hexasubstituted dimer **11e**, this problem was not encountered and it was obtained in a good yield of 56% following the oxidation of **7f** with DDQ/$Sc(OTf)_3$; this indicates that the method can be applied to unsymmetric directly linked dimers.

All triply fused bisporphyrins exhibited characteristic ^{1}H NMR spectra, and the signals shifted drastically to higher fields upon fusing, owing to a decrease in aromaticity with respect to their starting materials. As these arrays have extensive π-electron systems delocalized through the entire molecule, a profound effect on the ring current of the array is observed.[45] With these bisporphyrins, the inner β protons resonate as singlets at $\delta \approx 7.0$ ppm. This characteristic singlet was observed for all symmetric fused dimers **10a**–**10k** and the unsymmetric dimer **11e**. The resolution of peaks was dependent on the solubility of the array in $CDCl_3$. In some cases, the use of [D_5]pyridine in $CDCl_3$ minimized aggregation and enabled the generation of sharper and more distinguished peaks in ^{1}H NMR spectra. However, in spite of this, broad signals were still observed for the majority of fused arrays, possibly indicative of conformational equilibria in solution.

The extension of conjugation in triply fused porphyrin arrays results in a significant bathochromic shift in the absorption profile; the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is reduced, which causes a sizeable shift into the near-infrared region.[46] There were significant differences between the profile of the fused dimer **10g** and those of its directly linked dimeric counterpart **4g** and monomer **9g** (Figure 1). Monomer **9g** exhibited a characteristic metalated-porphyrin absorption profile with a λ_{max} of 590 nm. Directly linked dimer **4g** exhibited a splitting of the Soret band owing to excitonic coupling between the porphyrin units and had a λ_{max} of 566 nm. However, with triply fused dimer **10g**, a substantial shift was observed. There was a broad splitting of the Soret band (at 414 and 576 nm), again because of excitonic coupling between the porphyrin

Table 4. Synthesis of triply fused unsymmetric dimers.[a,b]



Entry	R^1	R^2	R^3	R^4	Product	Yield [%]
1	*n*-hexyl	*n*-hexyl	Ph	H	**11a**	<5
2	Ph	Ph	4-Me-C_6H_4	H	**11b**	n.d.[c]
3	3-MeO-C_6H_4	Ph	3-MeO-C_6H_4	H	**11c**	n.d.
4	3-MeO-C_6H_4	Ph	4-Me-C_6H_4	H	**11d**	n.d.
5	Ph	Ph	3-MeO-C_6H_4	Ph	**11e**[a]	52

[a] Reagents and conditions: DDQ (1–5 equiv.), $Sc(OTf)_3$ (1–5 equiv.), toluene, 50 °C, 3 h. [b] Reagents and conditions: i) PIFA (1–2.5 equiv.), CH_2Cl_2, –78 °C to room temp., 3 h. ii) $NaBH_4$ (10 equiv.), MeOH, 0.5 h. [c] n.d.: not detected.

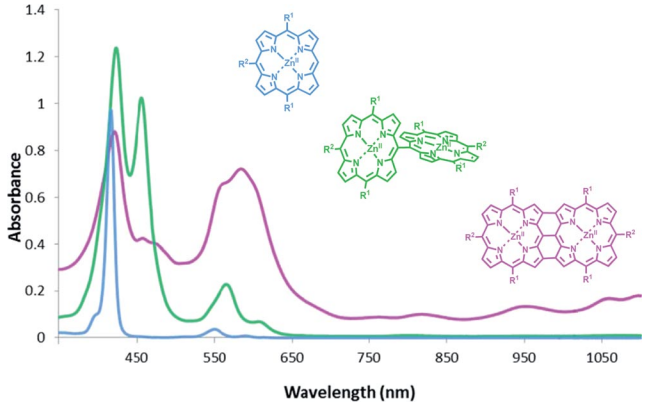


Figure 1. UV/Vis/NIR absorption spectra of monomer **9g** (blue), direct dimer **4g** (green), and fused dimer **10g** (pink) in tetrahydrofuran (R^1 = 4-Me-C_6H_4, R^2 = *n*-butyl).

units, and the λ_{max} was well into the near-IR region at 1092 nm. Additionally, strong visible-region absorbances were observed at 803 and 945 nm. A similar absorption profile was observed for dimers **10a**–**k**, and such characteristic spectra provide a useful analytical tool for the formation of the fused array. These absorption patterns were also observed for the crude mixtures of free-*meso* dimers **10h**–**i** and their higher oligomers and demonstrated that fusing had occurred.

An interesting effect was seen when a coordinating solvent was employed for the UV/Vis/NIR analysis of fused dimers. There have been many studies of solvent effects on the absorption profiles of monomeric porphyrins. The spectral shifts are generally attributed to displacement of the metal ion, which distorts the macrocycle, or from a charge transfer to the macrocycle from the coordinating solvent, which increases the HOMO energy level and, thereby, reduces the energy gap.[47] As noted by Osuka and coworkers,[36] the absorption is redshifted on addition of a coordinating solvent. With dimers **10a** and **10d**, a significant bathochromic shift of their profiles in CH_2Cl_2 was observed when 2% triethylamine (TEA) was added (Figure 2). With dimer **10a**, there was a redshift of 38 nm from 1067 to 1105 nm, and with dimer **10d**, this effect was less pronounced and a shift of 13 nm was observed.

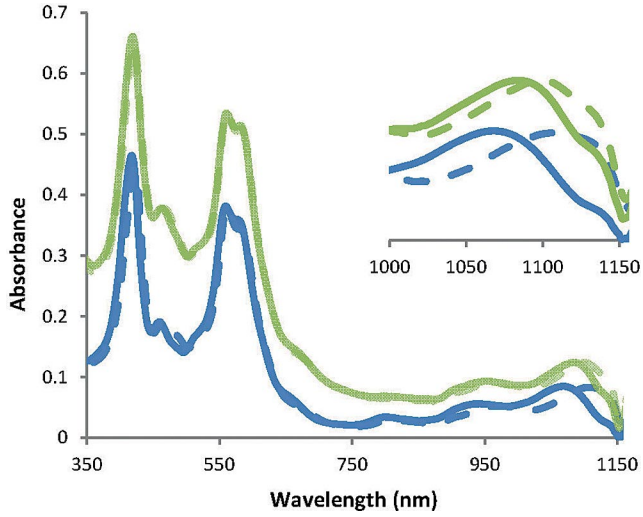
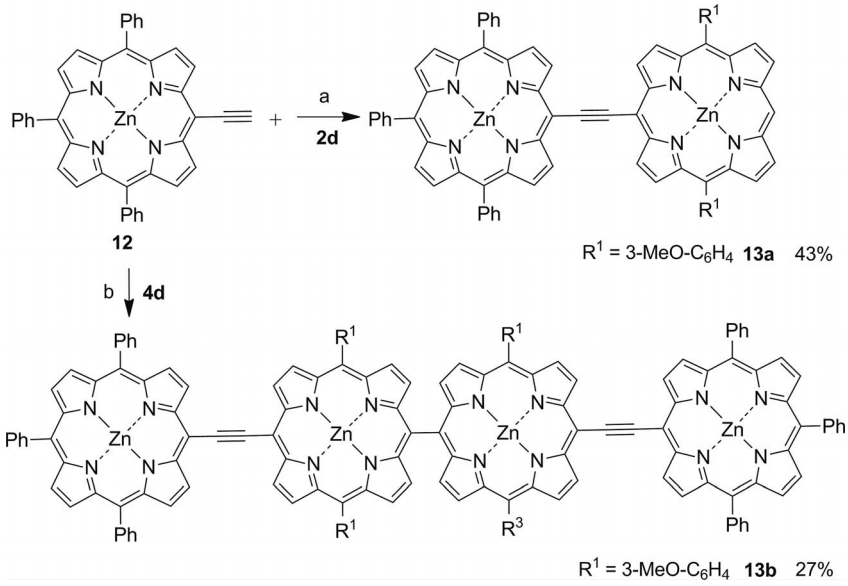


Figure 2. UV/Vis/NIR spectra of dimers **10a** (blue) and **10d** (green) in (a) CH_2Cl_2 (solid line) and (b) CH_2Cl_2 with 2% TEA (dashed line).

For the development of a new tetrameric porphyrin incorporating a fused moiety and a conjugated linker, two strategies were investigated. It was hoped that an alkynyl linker would enhance the optical properties of the array owing to the increase in π conjugation. The first strategy involved the synthesis of alkynyl-linked dimer **13a** in a yield of 43% by the copper-free Sonogashira coupling[48] of monobromo porphyrin **2d** with alkynyl porphyrin **12** (Scheme 1).[49] This yield was moderate because of separation difficulties; the desired dimer streaked during column chromatography and some product was lost through contamination and co-elution with other fractions. Although copper-free Sonogashira conditions were used, the Glaser homocoupled dimer was also detected in trace quantities (<5%) and was most likely formed by a palladium-catalyzed homocoupling.[48b] This alkynyl dimer contains one free *meso* position, whereby oxidative fusing can be performed to generate the fused tetramer. The second strategy involved the copper-free Sonogashira coupling[48b] of directly linked bromo bisporphyrin **4d** with alkynyl porphyrin **12** to give the desired tetramer **13b** in 27% yield (Scheme 1). The yield of **13b** was low owing to difficulties in separation and the formation of other oligomeric, namely trimeric and dimeric, derivatives of **13b** as side-products. Subsequent



Scheme 1. Synthesis of alkynyl dimer **13a** and tetramer **13b** by copper-free Sonogashira coupling. Reagents and conditions: (a) **12** (1 equiv.), **2d** (1 equiv.), $Pd_2(dba)_3$ (0.1 equiv.), $AsPh_3$ (2.1 equiv.), THF/TEA (3:1 v/v), 67 °C, 22 h. (b) **12** (2 equiv.), **4d** (1 equiv.), $Pd_2(dba)_3$ (0.15 equiv.), $AsPh_3$ (2.1 equiv.), THF/TEA (3:1 v/v), 67 °C, 48 h.

oxidation of dimer **13a** and tetramer **13b** to give the triply fused tetramer was executed by using both the DDQ/$Sc(OTf)_3$ and the PIFA methods. After many attempts, the desired tetramer was obtained from both strategies and with both oxidation methods in moderate yields, the highest of which was obtained with PIFA oxidation of dimer **13a**. Here, there was less steric hindrance than with **13b** and oxidative fusing occurred at the free-*meso* side. Furthermore, the dimer is more soluble in CH_2Cl_2 than tetramer **13b** and this affected the yield. Its formation was confirmed by HRMS (calculated for $C_{148}H_{88}N_{16}O_4Zn_4$ $[M + 2H]^+$ 2408.4340; found 2408.4282) and UV/Vis analysis. The ^1H NMR spectra were difficult to assign because of overshadowing solvent peaks, although oxidative fusing of the central porphyrin units was evident as there were significant shift of the signals to higher fields. The characteristic singlet at δ = 6.9 ppm is attributed to the inner β protons of the central porphyrin units. This is substantially shifted from the resonances of the starting materials **13a** and **13b**, for which the β protons are observed at δ = 9–10.5 ppm. This is the first example of an alkynyl-linked array incorporating a triply fused bisporphyrin moiety, and it exhibited unusual photophysical characteristics. There was a considerable change in absorption, and the profiles of the products from the synthetic strategies (the oxidative fusing of tetramer **13b** and dimer **13a**) were identical. The absorption profile of the fused tetramer is significantly different to those of **13a** and **13b** (Figure 3).

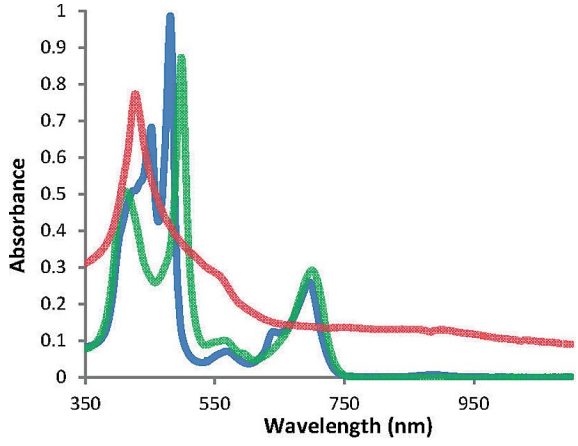


Figure 3. UV/Vis/NIR spectra of dimer **13a** (blue), tetramer **13b** (green), and fused tetramer (red) in ethyl acetate.

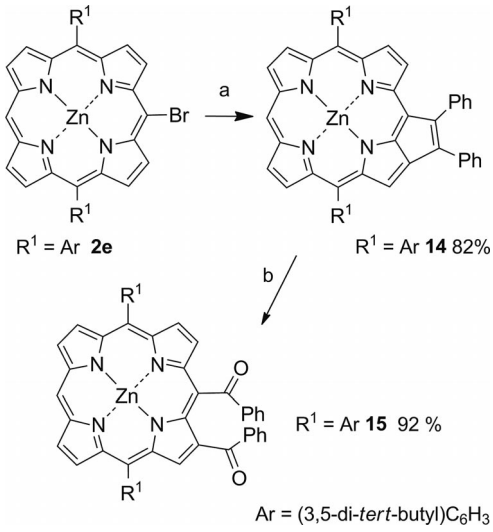
The Soret bands of oligomers **13a**–**b** are split, similar to those of the alkynyl-linked dimers, and the maximum absorption wavelengths are 696 and 700 nm for the dimer and tetramer, respectively. Upon fusing, a completely different profile was observed, specifically, a panchromatic spectrum with few distinguishable peaks. This could be attributed to aggregation effects of the fused tetramer, but it is clear there is absorbance in the near-IR region. Despite the indistinguishable peaks, the presence of a triply fused porphyrin moiety was confirmed by the shift in absorption.

To further functionalize the β positions of the dimers, a chlorin formation with organolithium reagents was investigated. Although high yielding for the introduction of *meso* substituents, the introduction of β substituents by organolithium methods can be quite challenging and low yielding and can result in the formation of chlorins, bacteriochlorins, and porphodimethenes, depending on the reaction conditions and substrates.[50] By comparison with 5,10,15,20-tetraphenylporphyrin (TPP), it was anticipated that the introduction an *n*-butyl group at the β position of fused symmetric dimer **10a** would generate a fused porphyrin–chlorin hybrid. By using our previously developed method, whereby TPP was monobutylated at the β position in 17% yield, the fused dimer **10a** was butylated under standard organolithium conditions.[23] Butylation was confirmed by HRMS (calculated for $C_{80}H_{50}N_8Zn_2$ $[M - 2H]^+$ 1250.2741; found 1252.2770), and the other main component was unreacted starting material **10a**, separation from which was not possible. The classic reduction of the porphyrin periphery to generate a chlorin species was also attempted with **10a**. The diimide reduction of monomeric porphyrins to their respective chlorins and bacteriochlorins, developed by Whitlock et al.,[51] is widely known. Preliminary studies indicated that the reduction of **10a** occurred efficiently, although isolation of the porphyrin–chlorin hybrid was not possible because of its instability.

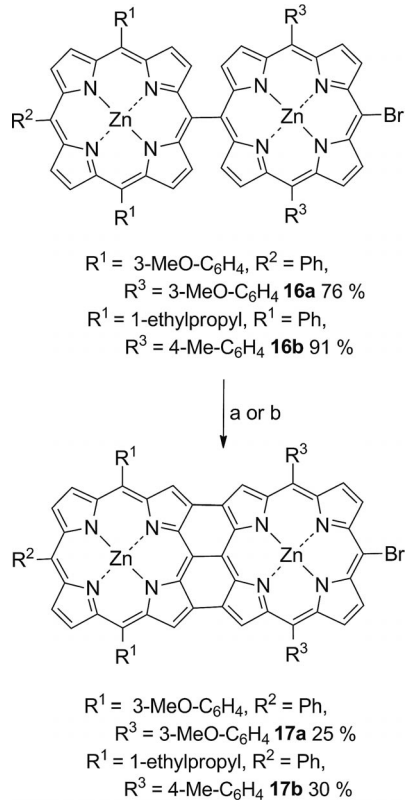
Cycloaddition reactions of monomeric porphyrins generate perturbed macrocycles with enhanced photophysical properties.[3a,52] To investigate the reactivity of the fused dimers, we decided to adopt the [3+2] annulation strategy developed by Osuka and co-workers.[3b] This involves a palladium-catalyzed C–C bond forming reaction by carbopalladation of a bromoporphyrin with internal alkynes.[53] The product is a 7,8-dehydropurpurin that incorporates a fused cyclopentadiene ring, which causes significant distortion of the porphyrin macrocycle.

Tetrapyrroles with exocyclic five-membered rings have biological significance, but in spite of this their synthetic derivatives are not very common.[54] These species with perturbation of the macrocycle have interesting photophysical properties and exhibit a bathochromic shift in their absorption profiles.[55] We sought to apply this chemistry to dimeric porphyrins and to develop a new "fused-on-fused" system, which we hoped would further enhance the properties of the triply fused array.[56] The initial strategy involved the synthesis of a dehydropurpurin macrocycle with a free *meso* position and subsequent fusing under standard oxidative conditions, which we anticipated would yield the desired triply fused dimeric dehydropurpurin. To test the reaction conditions, the [3+2] annulation was performed with bromoporphyrin **2e**[57] and diphenylacetylene to form dehydropurpurin **14** in an excellent yield of 82%. Attempts to triply fuse **14**[3b] by employing standard oxidative conditions with DDQ/$Sc(OTf)_3$ were ineffective, and the main product isolated was the ring-opened adduct **15**[3b] (Scheme 2). Unfortunately, as discovered by Osuka and coworkers, the zinc dehydropurpurins are unstable in solution and on exposure to air and light. The cyclopentadiene ring opens to furnish 1,5-diketone **15**, presumably from singlet oxygen generation. The outer C–C double bond in the

cyclopentadiene ring presumably undergoes a [2+2] cycloaddition with singlet oxygen generated in situ and forms a dioxetane intermediate, which decomposes to form the diketone product[58] and, hence, does not survive these strong oxidative conditions.



Scheme 2. Synthesis of dehydropurpurin **14** and 1,5-diketone **15**. Reagents and conditions: (a) diphenylacetylene, $Pd_2(dba)_3$, $(o\text{-Tol})_3P$, toluene, *N*,*N*-dicyclohexylamine, 120 °C, 24 h. (b) DDQ, $Sc(OTf)_3$, toluene, room temp., 3 h.



Scheme 3. Oxidative fusing of bromo dimers **16a** and **16b** to give fused dimers **17a** and **17b**. Reagents and conditions: (a): i) PIFA (2.5 equiv.), CH_2Cl_2, –78 °C to room temp., 3 h. ii) $NaBH_4$ (10 equiv.), MeOH, 0.5 h. (b) DDQ, $Sc(OTf)_3$, toluene, 50 °C, 3 h.

Related studies on [3+2] cycloadditions require triply fused bromo dimers. For this, the directly linked dimers **7c** and **7d** were brominated at their free *meso* position by using standard bromination conditions of *N*-bromosuccinimide (NBS) and chloroform to yield dimers **16a** and **16b** in excellent yields of 76 and 91%, respectively (Scheme 3). These bromoporphyrins were oxidized with PIFA or DDQ/$Sc(OTf)_3$ to form the triply fused dimers **17a** and **17b** in approximate yields of 25–30%. Preliminary results for the [3+2] cycloaddition reaction of these dimers indicate the formation of the desired cyclo adducts in low yields, although further investigations are necessary.

Conclusions

A library of symmetric directly singly and triply linked dimers were synthesized in moderate-to-good yields by oxidative fusing and tolerate a wide range of functionalities on the porphyrin periphery. In most cases, attempts to triply fuse monomers and dimers with one or two free *meso* positions were unsuccessful owing to the inevitable formation of oligomerized products. Although there was limited success with alkyl-substituted dimers, this route is not viable as the yields were low. A series of unsymmetric directly linked dimers were synthesized in good yields by a stepwise strategy. However, the oxidative double ring closing of free-*meso* dimers was unsuccessful. As a result, a change in strategy was needed for post-functionalization of triply fused arrays. All triply linked dimers isolated exhibited a substantial bathochromic shift in their absorption profile into the near-infrared region, which makes these arrays potential candidates for optical applications such as PDT and NLO. There are considerable possibilities for the development of a library of unsymmetrically fused dimers, the properties of which could be fine-tuned for optical applications. The fused tetramer synthesized is the first example of a fused array incorporating alkynyl-linked porphyrins, and other linkages could also be explored. Numerous strategies towards the functionalization of porphyrin arrays were investigated. The reactivity of directly linked dimers reflects that of monomeric porphyrins, and brominations and cycloadditions were achievable in high yields. For fused arrays, the reactivity is somewhat diminished owing to the poor solubility of the arrays. However, these investigations showed that fused dimers can be functionalized directly through organolithium reactions and indirectly through palladium-catalyzed coupling reactions with pre-installed activators such as bromine. Such post-fusing modifications demonstrate the ability to fine-tune the arrays for optical applications, as the bathochromic shift can be enhanced, and, although further investigations are necessary, preliminary studies are promising. Further research into the diimide reduction reaction is necessary, and this would provide a straightforward route to chlorin-fused dimers. With more solubilizing substituents, the reactivity of the bromo dimers should improve. It could also be possible to generate fused dimers with free *meso* positions by debromination

methods, and the reactivity of such could be probed by using organolithium methods.

Experimental Section

General Procedure for the Oxidative Coupling of 5,10,15-Trisubstituted Porphyrins with DDQ/Sc(OTf)$_3$: A 100 mL Schlenk tube was charged with metalloporphyrin (1 equiv.) dissolved in dry toluene. The solution was degassed by three freeze–pump–thaw cycles. DDQ (5 equiv.) and Sc(OTf)$_3$ (5 equiv.) were added, and the reaction was heated to 50 °C under argon for 3–18 h. THF was added and the reaction was stirred at room temperature for a further 1 h. The reaction mixture was then passed through a short plug of alumina or silica gel with CH_2Cl_2 and then THF as eluents. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel to yield the desired triply fused dimer.

Bis[5,15-Bis(3,5-di-*tert*-butylphenyl)-20-(4-nitrophenyl)porphyrin-13,15,17-triylato]zinc(II) (10b): Compound **10 b** was synthesized according to the general procedure above from [5,15-bis(3,5-di-*tert*-butylphenyl)-10-(4-nitrophenyl)porphyrinatozinc(II)] (**9b**, 20 mg, 0.023 mmol), DDQ (26 mg, 0.115 mmol), and Sc(OTf)$_3$ (57 mg, 0.115 mmol) in dry toluene (20 mL) heated at 50 °C for 3 h. THF (5 mL) was added, and the reaction mixture was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alumina with CH_2Cl_2 and then CH_2Cl_2/THF (1:1, v/v) as eluent to give an intense purple fraction. The solvents were removed, and the residue was filtered through a second plug of alumina with CH_2Cl_2 as eluent. The solvents were removed in vacuo and **10b** was isolated as a dark solid (13 mg, 0.007 mmol, 64%), m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (s, 72 H, *tert*-butyl-*H*), 7.37 (s, 4 H, H_β), 7.61 (d, $^3J_{H,H}$ = 4.5 Hz, 4 H, H_β), 7.67 (m, 12 H, Ar-*H*), 7.75 (d, $^3J_{H,H}$ = 4.6 Hz, 4 H, H_β), 8.00 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, C_6H_4-*H*), 8.48 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, C_6H_4-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 30.8, 106.2, 107.5, 120.9, 122.2, 124.2, 127.7, 128.1, 130.1, 131.9, 133.4, 135.9, 139.5, 147.3, 147.8, 151.6, 153.5, 153.9, 154.1 ppm. UV/Vis (THF): λ_{max} (logε) = 423 (5.12), 566 (5.17), 886 (4.00), 967 (4.33), 1110 (4.63) nm. HRMS (MALDI): calcd. for $C_{108}H_{104}N_{10}O_4Zn_2$ [M]$^+$ 1732.6825; found 1732.6816.

Bis[5-Butyl-10,20-bis(3-methoxyphenyl)porphyrin-13,15,17-triylato]-zinc(II) (10c):[59] Compound **10c** was synthesized from **9c** (20 mg, 0.031 mmol), DDQ (35 mg, 0.156 mmol), and Sc(OTf)$_3$ (77 mg, 0.156 mmol) in dry toluene (20 mL) heated at 50 °C for 3 h, according to the general procedure above. THF (6 mL) was added, and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alumina with CH_2Cl_2 as eluent to give side-product **4e** and with CH_2Cl_2/THF (1:1, v/v) as eluent to give a fraction containing dimer **10c**. The solvents were removed in vacuo, and the residue was subjected to column chromatography with CH_2Cl_2 as eluent to give two fractions, the first of which was side-product **4e**, and the second was the desired dimer **10c**. The solvents were removed, and **10c** was isolated as a dark solid (14 mg, 0.011 mmol, 70%), m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/[D$_5$]pyridine, 10:1): δ = 0.82 (m, 6 H, CH_3), 1.46 (m, 4 H, CH_2), 1.95 (m, 4 H, CH_2), 3.78 (s, 12 H, OCH_3), 5.17 (m, 4 H, CH_2), 6.99 (m, 6 H, H_β/C_6H_4-*H*), 7.14 (m, 8 H, C_6H_4-*H*), 7.32 (m, 4 H, C_6H_4-*H*), 7.53 (m, 8 H, H_β), 8.15 (m, 2 H, C_6H_4-*H*) ppm. UV/Vis (THF): λ_{max} (logε) = 422 (5.20), 459 (4.89), 559 (4.95), 949 (4.14), 1092 (4.41), 1094 (4.41) nm. HRMS (MALDI): calcd. for $C_{76}H_{58}N_8O_4Zn_2$ [M]$^+$ 1274.3164; found 1274.3123.

Bis[5,10,20-bis(4-methoxyphenyl)porphyrin-13,15,17-triylato]zinc-(II) (10d): Compound **10d** was synthesized according to the general procedure above from **9d** (40 mg, 0.058 mmol), DDQ (66 mg, 0.289 mmol), and Sc(OTf)$_3$ (142 mg, 0.289 mmol) in dry toluene (40 mL) heated at 50 °C for 4.5 h. THF (8 mL) was added, and the mixture was stirred for a further 0.8 h at room temperature. The reaction mixture was filtered through a short plug of silica gel with CH_2Cl_2 as eluent to give one fraction, which was discarded as no fused product was detected by UV/Vis/NIR analysis. With CH_2Cl_2/THF (1:1, v/v) as eluent, a second (main) fraction containing **10d** was isolated. The solvents were removed in vacuo and **10d** was isolated as a dark purple solid (33 mg, 0.024 mmol, 83%), m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/[D$_5$]pyridine, 10:1): δ = 3.88 (s, 12 H, OCH_3), 3.94 (s, 6 H, OCH_3), 7.01 (s, 4 H, H_β), 7.02 (d, $^3J_{H,H}$ = 8.3 Hz, 6 H, C_6H_4-*H*), 7.09 (dd, $^3J_{H,H}$ = 8.3, 2.4 Hz, 4 H, C_6H_4-*H*), 7.27 (m, 2 H, C_6H_4-*H*), 7.29 (m, 2 H, C_6H_4-*H*), 7.40 (t, $^3J_{H,H}$ = 7.8 Hz, 6 H, C_6H_4-*H*), 7.51 (d, $^3J_{H,H}$ = 4.6 Hz, 4 H, H_β), 7.56 (d, $^3J_{H,H}$ = 4.6 Hz, 4 H, H_β), 7.63 (d, $^3J_{H,H}$ = 8.3 Hz, 4 H, C_6H_4-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$/[D$_5$]pyridine, 10:1): δ = 55.4, 112.3, 112.9, 118.8, 124.1, 124.8, 126.1, 126.5, 127.3, 130.3, 130.7, 133.8, 134.2, 135.9, 142.9, 152.8, 153.1, 154.4, 157.8, 158.9 ppm. UV/Vis (EtOAc): λ_{max} (logε) = 420 (4.91), 471 (4.52), 562 (4.86), 584 (4.82), 820 (4.62), 952 (4.00), 1092 (4.23) nm. HRMS (MALDI): calcd. for $C_{82}H_{54}N_8O_6Zn_2$ [M]$^+$ 1374.2749; found 1374.2723.

Bis[5-(4-ethynylphenyl)-10,20-diphenylporphyrin-13,15,17-triylato]-zinc(II) (10e): Bisporphyrin **10e** was synthesized by following the general procedure above from **9e** (60 mg, 0.109 mmol), DDQ (113 mg, 0.498 mmol), and Sc(OTf)$_3$ (245 mg, 0.498 mmol) in dry toluene (60 mL) heated at 50 °C for 3.5 h. THF (15 mL) was added, and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alumina with CH_2Cl_2/THF (1:1, v/v) as eluent. The solvents were removed, and **10e** was isolated as a dark solid (48 mg, 0.040 mmol, 79%), m.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$/[D$_5$]pyridine, 10:1): δ = 3.22 (s, 2 H, C≡C*H*), 6.98 (s, 4 H, H_β), 7.50 (m, 20 H, Ph-*H*), 7.66 (d, $^3J_{H,H}$ = 8.0 Hz, 8 H, H_β), 7.71 (m, 8 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$/[D$_5$]pyridine, 10:1): δ = 77.7, 83.7, 126.4, 126.5, 127.0, 130.6, 132.9, 135.9, 139.4 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 421 (5.01), 563 (4.85), 586 (4.85), 671 (4.83), 968 (4.01), 1096 (4.27) nm. HRMS (MALDI): calcd. for $C_{80}H_{42}N_8Zn_2$ [M]$^+$ 1242.2115; found 1242.2145.

Bis[5-butyl-10,20-bis(4-methylphenyl)porphyrin-13,15,17-triylato]-zinc(II) (10g): Compound **10g** was synthesized according to the general procedure above from **9g** (30 mg, 0.049 mmol), DDQ (56 mg, 0.246 mmol), and Sc(OTf)$_3$ (121 mg, 0.246 mmol) in dry toluene (30 mL) heated at 50 °C for 3.5 h. THF (7 mL) was added, and the reaction was stirred for a further 0.5 h at room temperature. The reaction mixture was filtered through a short plug of alumina with CH_2Cl_2 as eluent to give side-product **4g** and with THF as eluent to give a second fraction containing dimer **10g**. The solvents were removed in vacuo, and the residue was subjected to column chromatography (silica gel, CH_2Cl_2/*n*-hexane, 9:1 + 1% TEA) to give **10g** as the main fraction. The solvents were removed, and **10g** was isolated as a dark purple solid (16 mg, 0.013 mmol, 54%), m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/[D$_5$]pyridine, 10:1): δ = 0.97 (t, $^3J_{H,H}$ = 7.8 Hz, 6 H, CH_3), 1.47 (m, 4 H, CH_2), 2.04 (m, 4 H, CH_2), 2.57 (s, 12 H, tolyl-CH_3), 3.89 (m, 4 H, CH_2), 7.01 (s, 4 H, H_β), 7.32 (d, $^3J_{H,H}$ = 7.2 Hz, 8 H, C_6H_4-*H*), 7.59 (m, 4 H, C_6H_4-*H*), 7.59 (m, 4 H, H_β), 8.21 (d, $^3J_{H,H}$ = 4.3 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$/ [D$_5$]pyridine, 10:1): δ = 14.0, 20.9, 22.7, 35.0, 40.7, 117.5, 122.3, 126.8, 127.5, 135.7, 139.9, 148.4, 154.9 ppm. UV/Vis (THF): λ_{max} (logε) = 414 (4.99), 443 (4.70), 576

(4.89), 945 (4.16), 1092 (4.22) nm. HRMS (MALDI): calcd. for $C_{76}H_{58}N_8Zn_2$ $[M]^+$ 1210.3367; found 1210.3375.

Bis[5-bromo-10,20-bis(3-methoxyphenyl)porphyrin-13,15,17-triylato]zinc(II) (10k):[59] Compound **10k** was synthesized from [5-bromo-10,20-(3-methoxyphenyl)porphyrinato]zinc(II) **2d** (60 mg, 0.091 mmol) dissolved in dry CH_2Cl_2 (60 mL) in a 100 mL Schlenk tube. The solution was degassed and cooled to –78 °C. PIFA (32 mg, 0.075 mmol) was added at –78 °C, and the reaction mixture was warmed to room temp. and then stirred at this temperature for 2 h. $NaBH_4$ (12 mg, 0.305 mmol) in MeOH (5 mL) was added, and the reaction was stirred for a further 45 min. The reaction mixture was added to H_2O (100 mL), and the organic layer was extracted with CH_2Cl_2/THF (1:1, v/v). The organic layer was washed with $NaHCO_3$ (2× 50 mL) and H_2O (30 mL) and then dried with Na_2SO_4, which was then removed by filtration. The solvents were removed in vacuo, and the dark residue was redissolved and filtered through a short plug of silica with $CHCl_3$/THF (1:1, v/v) as eluent to give a green fraction. The solvents were removed in vacuo, and the residue was recrystallized from CH_2Cl_2/*n*-hexane to give a dark purple solid (3 mg, 0.002 mmol, 14%), m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 12 H, OCH_3), 7.04 (s, 4 H, H_β), 7.16 (m, 4 H, C_6H_4-*H*), 7.70 (m, 6 H, C_6H_4-*H*), 7.73 (m, 10 H, C_6H_4-*H*/H_β), 8.45 (m, 2 H, H_β), 8.61 (m, 2 H, H_β) ppm. UV/Vis (CH_2Cl_2/THF, 1:1, v/v): λ_{max} (logε) = 425 (5.01), 459 (4.66), 566 (4.68), 871 (3.98), 1110 (4.17) nm. HRMS (MALDI): calcd. for $C_{68}H_{40}Br_2N_8O_4Zn_2$ $[M]^+$ 1318.0122; found 1318.0150.

Bis[(5-*n*-butyl)-10,20-bis(3-methoxyphenyl)porphyrin-15-ylato]zinc(II) (4e): Compound **4e** was isolated as a side-product from the synthesis of **10c**. The reaction mixture was filtered through a short plug of alumina with CH_2Cl_2 as eluent to give a fraction containing **4e**. The solvents were removed in vacuo to yield a red-purple solid (4 mg, 0.003 mmol, 19%), m.p. > 300 °C; R_f = 0.53 (CH_2Cl_2/*n*-hexane = 2:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89–0.93 (m, 6 H, CH_3), 1.19 (m, 4 H, CH_2), 1.93 (m, 4 H, CH_2), 3.93 (s, 12 H, OCH_3), 5.19 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, CH_2), 7.25 (d, $^3J_{H,H}$ = 8.6 Hz, 4 H, C_6H_4-*H*), 7.57 (t, $^3J_{H,H}$ = 7.7 Hz, 4 H, C_6H_4-*H*), 7.82 (m, 8 H, C_6H_4-*H*), 8.08 (m, 4 H, H_β), 8.67 (m, 4 H, H_β), 9.12 (d, $^3J_{H,H}$ = 4.8 Hz, 4 H, H_β) 9.71 (d, $^3J_{H,H}$ = 4.8 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0, 22.5, 31.8, 41.0, 55.3, 109.9, 112.6, 119.6, 120.9, 127.9, 128.9, 131.7, 133.5, 142.5, 149.2, 154.9, 157.6 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 424 (5.35), 457 (5.27), 568 (4.59) nm. HRMS (MALDI): calcd. for $C_{76}H_{62}N_8O_4Zn_2$ $[M]^+$ 1278.3477; found 1278.3438.

Bis[(5-*n*-butyl)-10,20-bis(4-methylphenyl)porphyrin-15-ylato]zinc(II) (4g): Compound **4g** was synthesized as a side-product of **10g** and was isolated as the first fraction from filtration through a plug of alumina with CH_2Cl_2 as eluent. The solvents were removed in vacuo to give a red-purple solid **4g** (8 mg, 0.007 mmol, 27%) M.p. > 300 °C; R_f = 0.45 (CH_2Cl_2/*n*-hexane = 3:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (m, 6 H, CH_3), 1.19 (m, 4 H, CH_2), 1.92 (m, 4 H, CH_2), 2.64 (s, 12 H, tolyl-CH_3), 5.17 (t, $^3J_{H,H}$ = 8.2 Hz, 4 H, CH_2), 7.50 (d, $^3J_{H,H}$ = 7.8 Hz, 8 H, C_6H_4-*H*), 8.07 (d, $^3J_{H,H}$ = 4.9 Hz, 4 H, H_β), 8.12 (d, $^3J_{H,H}$ = 7.8 Hz, 8 H, C_6H_4-*H*), 8.65 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, H_β), 9.10 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_β), 9.68 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 21.3, 23.7, 35.6, 41.1, 118.7, 121.2, 122.1, 127.0, 128.8, 131.7, 131.9, 133.4, 134.1, 136.8, 139.7, 149.4, 149.9, 150.1, 154.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 423 (5.54), 456 (5.45), 566 (4.80) nm. HRMS (MALDI): calcd. for $C_{76}H_{62}N_8Zn_2$ $[M]^+$ 1214.3680; found 1214.3663.

[5,10,20-Trihexyl-15-(10′,20′-diphenylporphyrin-5′-yl)-13,15,17-triylato]zinc(II) (11a): Bisporphyrin **11a** was synthesized from directly linked dimer **7a** (20 mg, 0.019 mmol), DDQ (22 mg, 0.096 mmol), and $Sc(OTf)_3$ (47 mg, 0.096 mmol) in dry toluene (20 mL) heated at 50 °C for 3 h. THF (6 mL) was added, and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a short plug of alumina with CH_2Cl_2/THF (1:1, v/v) as eluent. The solvents were removed, and the residue was subjected to column chromatography (CH_2Cl_2/*n*-hexane, 5:1, v/v) to give three fractions, the first of which was unreacted starting material **7a** (3 mg, 14%), the second contained **11a**, and the third contained oligomerized product. The solvents were removed, and **11a** was isolated as a dark solid (3 mg, 0.002 mmol, 15%). UV/Vis (THF): λ_{max} (logε) = 416 (4.97), 578 (4.70), 672 (4.56), 987 (3.87), 1106 (4.09) nm. HRMS (MALDI): calcd. for $C_{70}H_{62}N_8Zn_2$ $[M]^+$ 1142.3680; found 1142.3625.

{5-[5′-Phenyl-10′,20′-bis(3-methoxyphenyl)porphyrin-13′,15′,17′-triylato]-10,15,20-triphenylporphyrinato}zinc(II) (11e): Fused dimer **11e** was synthesized from dimer **7f** (40 mg, 0.032 mmol), DDQ (36 mg, 0.158 mmol), and $Sc(OTf)_3$ (78 mg, 0.158 mmol) in toluene (50 mL). The reaction was heated to 50 °C and stirred at this temperature for 3 h. THF (8 mL) was added, and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was filtered through a plug of alumina with CH_2Cl_2 and then CH_2Cl_2/THF (1:1, v/v) as eluent. The solvents were removed in vacuo to give a dark residue, which was redissolved in CH_2Cl_2 and subjected to column chromatography (*n*-hexane/ethyl acetate, 6:1, v/v) to give two fractions. The first yielded unreacted starting material **7f** (6 mg, 15%), and the second contained the desired fused dimer **11e**. The solvents were removed in vacuo to yield a dark solid (21 mg, 0.017 mmol, 52%), m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/[D_5]pyridine, 20:1): δ = 3.93 (s, 6 H, OCH_3), 7.03 (m, 4 H, H_β), 7.13 (m, 4 H, C_6H_4-*H*), 7.23 (m, 2 H, C_6H_4-*H*), 7.43 (m, 2 H, C_6H_4-*H*), 7.49–7.62 (m, 20 H, Ph-*H*/ H_β), 7.70–7.83 (m, 8 H, Ph-*H*/H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/[D_5]pyridine, 20:1): δ = 55.4, 112.9, 126.5, 126.9, 127.3, 128.8, 130.6, 130.9, 157.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 422 (5.15), 455 (4.11), 556 (4.53), 579 (4.50), 917 (3.66), 1039 (3.90) nm. HRMS (MALDI): calcd. for $C_{78}H_{46}N_8O_2Zn_2$ $[M]^+$ 1254.2327; found 1254.2286.

{5-[(10′,20′-Bis(3-methoxyphenyl)porphyrinato-5-yl)zinc(II)]ethynyl-10,15,20-triphenylporphyrinato}zinc(II) (13a): This procedure was adapted from a method by Lindsey et al.[45] Alkynyl porphyrin **12** (56 mg, 0. 089 mmol), bromoporphyrin **2d** (60 mg, 0.089 mmol), $AsPh_3$ (57 mg, 0.185 mmol), and tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$, 8 mg, 0.008 mmol) were added to a 100 mL Schlenk tube and dried under high vacuum. The flask was purged with argon, and dry THF (12 mL) and TEA (4 mL) were added. The solution was degassed by three freeze–pump–thaw cycles. The flask was sealed, and the reaction mixture was heated to 67 °C. After 22 h, the solvents were removed, and the residue was redissolved in CH_2Cl_2 and filtered through a plug of silica with CH_2Cl_2 as eluent. The solvents were removed, and the residue was subjected to column chromatography (silica, *n*-hexane/ethyl acetate, 4:1, v/v) to give four fractions. The first fraction contained monomer **12** (8 mg, 14%), and fractions two and three contained mixtures of undesired oligomers. The fourth fraction contained the desired dimer **13a**. The solvents were removed in vacuo to give a dark green solid **13a** (46 mg, 0.038 mmol, 43%), m.p. > 300 °C; R_f = 0.35 (*n*-hexane/EtOAc, 3:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$/[D_5]-pyridine, 20:1): δ = 4.07 (s, 6 H, OCH_3), 7.38 (dd, $^3J_{H,H}$ = 7.3, 2.4 Hz, 2 H, C_6H_4-*H*), 7.78 (m, 11 H, Ph/C_6H_4-*H*), 7.89 (m, 2 H, C_6H_4-*H*), 8.23 (m, 6 H, Ph-*H*), 8.30 (m, 2 H, C_6H_4-*H*), 9.01 (d, $^3J_{H,H}$ = 4.6 Hz, 2 H, H_β), 9.04 (d, $^3J_{H,H}$ = 4.4 Hz, 2 H, H_β), 9.11 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, H_β), 9.21 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, H_β),

9.30 (d, $^3J_{H,H}$ = 4.4 Hz, 2 H, H_β), 9.96 (d, $^3J_{H,H}$ = 4.6 Hz, 2 H, H_β), 10.11 (s, 1 H, H_{meso}), 10.46 (d, $^3J_{H,H}$ = 4.6 Hz, 2 H, H_β), 10.49 (d, $^3J_{H,H}$ = 4.6 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/[D_5]pyridine, 20:1): δ = 55.6, 100.7, 107.2, 113.1, 120.1, 120.8, 121.1, 122.0, 122.1, 122.4, 126.3, 126.4, 127.3, 127.4, 128.0, 130.6, 131.5, 131.6, 131.8, 132.0, 132.2, 132.7, 132.8, 133.1, 134.4, 134.5, 134.6, 143.0, 143.2, 143.3, 144.5, 149.6, 149.7, 149.8, 150.0, 150.4, 150.7, 152.6, 153.0 153.5, 157.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 452 (5.06), 481 (5.22), 568 (4.08), 696 (4.64) nm. HRMS (MALDI): calcd. for $C_{74}H_{46}N_8O_2Zn_2$ [M]$^+$ 1206.2327; found 1206.2341.

Bis(5-{[10′,20′-bis(3-methoxyphenyl)porphyrinato-15′-yl]zinc(II)}ethynyl-10,15,20-triphenylporphyrin-15′-ylato)zinc(II) (13b): Alkynyl porphyrin **12** (65 mg, 0.104 mmol), bromoporphyrin dimer **4d** (66 mg, 0.049 mmol), $AsPh_3$ (32 mg, 0.104 mmol), and $Pd_2(dba)_3$ (7 mg, 0.007 mmol) were added to a Schlenk tube and dried under high vacuum. The flask was purged with argon, and dry THF (10 mL) and TEA (1 mL) were added. The solution was degassed by three freeze–pump–thaw cycles. The flask was sealed, and the reaction mixture was heated to 67 °C. After 48 h, the solvents were removed, and the residue was redissolved in CH_2Cl_2 and filtered through a plug of silica with CH_2Cl_2/ethyl acetate (9:1, v/v) as eluent. The solvents were removed, and the residue was subjected to column chromatography (silica, *n*-hexane/ethyl acetate, 6:1, v/v) to give four fractions. The first three fractions contained undesired dimeric and trimeric products, and the fourth fraction contained the desired tetramer **13b**. The solvents were removed in vacuo to give dark green solid **13b** (34 mg, 0.011 mmol, 27%), m.p. > 300 °C; R_f = 0.27 (hexane/ethyl acetate = 3:2, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.93 (m, 12 H, OCH_3), 7.26 (m, 4 H, C_6H_4-*H*), 7.62 (m, 4 H, C_6H_4-*H*), 7.84 (m, 22 H, Ph/C_6H_4-*H*), 8.19 (m, 4 H, H_β) 8.26 (d, $^3J_{H,H}$ = 6.4 Hz, 8 H, C_6H_4-*H*), 8.32 (m, 8 H, Ph-*H*), 8.73 (m, 4 H, H_β), 8.95 (d, $^3J_{H,H}$ = 6.5 Hz, 8 H, H_β), 9.24 (d, $^3J_{H,H}$ = 4.1 Hz, 4 H, H_β), 9.28 (m, 4 H, H_β), 10.55 (d, $^3J_{H,H}$ = 4.3 Hz, 8 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.4, 55.5, 101.0, 102.4, 113.6, 120.3, 122.5, 123.0, 126.7, 126.8, 127.4, 127.6, 127.7, 131.0, 132.1, 132.3, 133.2, 133.4, 134.2, 134.3, 134.5, 142.5, 142.6, 143.6, 150.1, 150.3, 150.4, 150.7, 152.9, 153.0, 155.0, 157.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 411 (5.31), 498 (5.54), 564 (4.61), 700 (5.07) nm. HRMS (MALDI): calcd. for $C_{148}H_{90}N_{16}O_4Zn_4$ [M]$^+$ 2410.4497; found 2410.4441.

{5-[5′-Bromo-10′,20′-bis(3-methoxyphenyl)porphyrin-15′-ylato]-10,20-bis(3-methoxy)-15-phenylporphyrinato}zinc(II) (16a):[60] Bromo bisporphyrin **16a** was produced from dimer **7c** (150 mg, 0.120 mmol) and NBS (32 mg, 0.180 mmol) dissolved in $CHCl_3$ (50 mL) in a 100 mL round-bottomed flask at 0 °C. Pyridine (0.1 mL) was added, and the reaction was stirred at this temperature for 3 h. The solvents were removed in vacuo, and the residue was redissolved in CH_2Cl_2 and filtered through a plug of silica with CH_2Cl_2 as eluent. The solvents were removed in vacuo to give a dark solid **16a** (120 mg, 0.091 mmol, 76%), m.p. > 300 °C; R_f = 0.54 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 6 H, OCH_3), 3.94 (s, 6 H, OCH_3), 7.23 (m, 4 H, C_6H_4-*H*), 7.56 (m, 4 H, C_6H_4-*H*), 7.80 (m, 11 H, Ph/C_6H_4-*H*), 8.03 (m, 4 H, H_β), 8.12 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, Ph-*H*), 8.64 (m, 2 H, H_β), 8.68 (m, 2 H, H_β), 9.04 (q, $^3J_{H,H}$ = 12.1 Hz, 4 H, H_β), 9.08 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, H_β), 9.85 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.3, 120.2, 120.3, 121.6, 122.6, 126.6, 127.2, 127.5, 131.8, 132.8, 133.7, 134.1, 134.5, 143.0, 143.4, 143.9, 144.1, 149.9, 150.2, 150.5, 150.9, 155.3, 157.7 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 418 (5.21), 450 (5.17), 558 (4.55) nm.

{5-[5′-Bromo-10′,20′-bis(4-methylphenyl)porphyrin-15′-ylato]-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato}zinc(II) (16b): Compound **16b** was synthesized from dimer **7d** (30 mg, 0.026 mmol) and NBS (5 mg, 0.026 mmol) dissolved in $CHCl_3$ (40 mL) at 0 °C. Pyridine (0.1 mL) was added, and the reaction mixture was stirred at this temperature for 3 h. The solvents were removed in vacuo, and the residue was redissolved in CH_2Cl_2 and filtered through a plug of silica with CH_2Cl_2 as eluent. The solvents were removed in vacuo to give a purple solid **16b** (29 mg, 0.024 mmol, 91%), m.p. > 300 °C; R_f = 0.48 (CH_2Cl_2/*n*-hexane = 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, $^3J_{H,H}$ = 7.1 Hz, 12 H, CH_3), 2.66 (s, 6 H, tolyl-*H*), 2.80 (m, 8 H, CH_2), 5.05 (m, 1 H, C*H*), 5.16 (m, 1 H, C*H*), 7.51 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, C_6H_4-*H*), 7.83 (m, 3 H, Ph-*H*), 8.08 (m, 4 H, Ph-*H*/H_β), 8.13 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, C_6H_4-*H*), 8.32 (m, 2 H, H_β), 8.66 (d, $^3J_{H,H}$ = 4.6 Hz, 2 H, H_β), 9.04 (m, 2 H, H_β), 9.10 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, H_β), 9.41 (m, 2 H, H_β), 9.77 (m, 2 H, H_β), 9.87–9.88 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 21.5, 22.7, 29.7, 34.8, 50.5, 105.0, 113.5, 121.1, 122.5, 124.9, 126.4, 127.2, 127.4, 130.1, 132.1, 132.8, 133.1, 134.2, 134.3, 137.2, 139.6, 143.5, 143.6, 149.6, 150.3, 151.2, 155.3 ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 414 (5.32), 450 (5.27), 554 (4.54) nm. HRMS (MALDI): calcd. for $C_{70}H_{57}N_8Zn_2Br$ [M]$^+$ 1216.2472; found 1216.2509.

{5-[5′-Bromo-10′,20′-bis(3-methoxyphenyl)porphyrin-13′,15′,17′-yl-ato]-10,20-bis(3-methoxyphenyl)-15-phenylporphyrinato}zinc(II) (17a):[59,60] Compound **17a** was synthesized from bromo dimer **16a** (20 mg, 0.038 mmol) and PIFA (35 mg, 0.094 mmol) dissolved in CH_2Cl_2 (60 mL) in a 250 mL Schlenk tube. The reaction was stirred at room temperature for 3 h. $NaBH_4$ (7 mg, 0.190 mmol) in MeOH (5 mL) was added, and the reaction was stirred for a further 1 h at room temperature. The reaction mixture was poured into H_2O (50 mL) and was then extracted with CH_2Cl_2. The organic layer was washed with $NaHCO_3$ (2× 50 mL) and H_2O (50 mL), dried with Na_2SO_4, and filtered. The solvents were removed to give a dark green residue, which was redissolved in CH_2Cl_2 and filtered through a short plug of alumina. The solvents were removed in vacuo to yield a dark green solid **17a** (22 mg, 0.011 mmol, 44%), m.p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$/[D_5]pyridine, 10:1): δ = 3.86–3.93 (m, 12 H, OCH_3), 6.55 (d, $^3J_{H,H}$ = 4.3 Hz, 2 H, H_β), 6.95 (m, 2 H, aryl-*H*), 7.04 (m, 4 H, C_6H_4-*H*), 7.12 (d, $^3J_{H,H}$ = 4.3 Hz, 2 H, H_β), 7.16 (m, 4 H, C_6H_4-*H*), 7.35 (m, 2 H, aryl-*H*), 7.45 (m, 4 H, aryl-*H*), 7.64 (d, $^3J_{H,H}$ = 4.3 Hz, 2 H, H_β), 7.75 (m, 4 H, C_6H_4-*H*), 8.44 (d, $^3J_{H,H}$ = 4.3 Hz, 2 H, H_β), 9.09–9.11 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_β), 9.68–9.69 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_β) ppm. UV/Vis (THF): λ_{max} (logε) = 423 (5.10), 562 (4.64), 1037 (3.94) nm.

{5-[5′-Bromo-10′,20′-bis(4-methylphenyl)porphyrin-13′,15′,17′-yl-ato]-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato}zinc(II) (17b):[59] Compound **17b** was synthesized from bromo dimer **16b** (20 mg, 0.016 mmol), DDQ (19 mg, 0.082 mmol), and $Sc(OTf)_3$ (40 mg, 0.082 mmol) dissolved in toluene (25 mL) in a 100 mL Schlenk tube. The reaction mixture was heated to 50 °C and stirred at this temperature for 3 h. THF (8 mL) was added, and the reaction mixture was stirred for a further 0.5 h at room temperature. The reaction mixture was filtered through a short plug of alumina with CH_2Cl_2 as eluent to give a fraction that contained starting material **16b** and with CH_2Cl_2/THF (1:1, v/v) as eluent to give fused dimer **17b**. The solvents were removed in vacuo to give a dark green solid **17b** (12 mg, 0.010 mmol, 65%), m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (m, 12 H, CH_3), 2.31 (m, 8 H, CH_2), 2.53 (s, 6 H, tolyl-CH_3), 5.44 (m, 2 H, CH_2), 6.84 (m, 2 H, H_β), 7.16 (m, 2 H, H_β), 7.39–7.87 (m, 21 H, Ph-*H*/H_β) ppm. UV/Vis (THF): λ_{max} (logε) = 422 (5.18), 565 (5.04), 965 (4.32) nm. HRMS (MALDI): calcd. for $C_{70}H_{53}N_8Zn_2Br$ [M]$^+$ 1212.2159; found 1212.2200.

Supporting Information (see footnote on the first page of this article): General methods including experimental procedures, characterization data, and ^{1}H and ^{13}C NMR spectra. The 1D and 2D NMR spectra of compounds **10d**, **10e**, **11e**, and **13a** are provided.

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[1] R. K. Pandey, G. Zheng, in: *The Porphyrin Handbook*, vol. 6 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, pp. 157–230.
[2] a) V. Lin, S. DiMagno, M. Therien, *Science* **1994**, *264*, 1105–1111; b) H. L. Anderson, *Inorg. Chem.* **1994**, *33*, 972–981.
[3] a) D.-M. Shen, C. Liu, Q.-Y. Chen, *Chem. Commun.* **2005**, 4982–4984; b) A. K. Sahoo, S. Mori, H. Shinokubo, A. Osuka, *Angew. Chem.* **2006**, *118*, 8140; *Angew. Chem. Int. Ed.* **2006**, *45*, 7972–7975.
[4] a) A. Tsuda, A. Nakano, H. Furuta, H. Yamochi, A. Osuka, *Angew. Chem.* **2000**, *112*, 572; *Angew. Chem. Int. Ed.* **2000**, *39*, 558–561; b) N. K. S. Davis, A. L. Thompson, H. L. Anderson, *Org. Lett.* **2010**, *12*, 2124–2127.
[5] K.-i. Sugiura, T. Matsumoto, S. Ohkouchi, Y. Naitoh, T. Kawai, Y. Takai, K. Ushiroda, Y. Sakata, *Chem. Commun.* **1999**, 1957–1958.
[6] A. Tsuda, H. Furuta, A. Osuka, *Angew. Chem.* **2000**, *112*, 2649; *Angew. Chem. Int. Ed.* **2000**, *39*, 2549–2552.
[7] A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79–82.
[8] a) K. J. McEwan, P. A. Fleitz, J. E. Rogers, J. E. Slagle, D. G. McLean, H. Akdas, M. Katterle, I. M. Blake, H. L. Anderson, *Adv. Mater.* **2004**, *16*, 1933–1935; b) F. Cheng, S. Zhang, A. Adronov, L. Echegoyen, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 6062–6070; c) Q. Ouyang, Y.-Z. Zhu, C.-H. Zhang, K.-Q. Yan, Y.-C. Li, J.-Y. Zheng, *Org. Lett.* **2009**, *11*, 5266–5269; d) N. K. S. Davis, A. L. Thompson, H. L. Anderson, *J. Am. Chem. Soc.* **2011**, *133*, 30–31; e) V. V. Diev, K. Hanson, J. D. Zimmerman, S. R. Forrest, M. E. Thompson, *Angew. Chem.* **2010**, *122*, 5655; *Angew. Chem. Int. Ed.* **2010**, *49*, 5523–5526; f) V. V. Diev, C. W. Schlenker, K. Hanson, Q. Zhong, J. D. Zimmerman, S. R. Forrest, M. E. Thompson, *J. Org. Chem.* **2011**, *77*, 143–159.
[9] H. S. Cho, D. H. Jeong, S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Tsuda, A. Osuka, *J. Am. Chem. Soc.* **2002**, *124*, 14642–14654.
[10] T. Sakurai, K. Shi, H. Sato, K. Tashiro, A. Osuka, A. Saeki, S. Seki, S. Tagawa, S. Sasaki, H. Masunaga, K. Osaka, M. Takata, T. Aida, *J. Am. Chem. Soc.* **2008**, *130*, 13812–13813.
[11] a) T. Tanaka, Y. Nakamura, A. Osuka, *Chem. Eur. J.* **2008**, *14*, 204–211; b) J. Chen, N. Aratani, H. Shinokubo, A. Osuka, *Chem. Asian J.* **2009**, *4*, 1126–1133.
[12] M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos, E. M. Ni Mhuircheartaigh, *Adv. Mater.* **2007**, *19*, 2737–2774.
[13] a) A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897–1091; b) C. Borek, K. Hanson, P. I. Djurovich, M. E. Thompson, K. Aznavour, R. Bau, Y. Sun, S. R. Forrest, J. Brooks, L. Michalski, J. Brown, *Angew. Chem.* **2007**, *119*, 1127; *Angew. Chem. Int. Ed.* **2007**, *46*, 1109–1112.
[14] a) M. Balaz, H. A. Collins, E. Dahlstedt, H. L. Anderson, *Org. Biomol. Chem.* **2009**, *7*, 874–888; b) K. Ogawa, Y. Kobuke, *Anti-Cancer Agents Med. Chem.* **2008**, *8*, 269–279; c) K. Ogawa, Y. Kobuke, *Org. Biomol. Chem.* **2009**, *7*, 2241–2246.
[15] M. O. Senge, Y. M. Shaker, M. Pintea, C. Ryppa, S. S. Hatscher, A. Ryan, Y. Sergeeva, *Eur. J. Org. Chem.* **2010**, 237–258.
[16] a) V. Sol, V. Chaleix, Y. Champavier, R. Granet, Y. M. Huang, P. Krausz, *Bioorg. Med. Chem.* **2006**, *14*, 7745–7760; b) O. B. Locos, C. C. Heindl, A. Corral, M. O. Senge, E. M. Scanlan, *Eur. J. Org. Chem.* **2010**, 1026–1028.
[17] E. G. A. Notaras, M. Fazekas, J. J. Doyle, W. J. Blau, M. O. Senge, *Chem. Commun.* **2007**, 2166–2168.
[18] K. Susumu, T. Shimidzu, K. Tanaka, H. Segawa, *Tetrahedron Lett.* **1996**, *37*, 8399–8402.
[19] R. T. Holmes, J. J. Lin, R. G. Khoury, C. P. Jones, K. M. Smith, *Chem. Commun.* **1997**, 819–820.
[20] X.-Q. Lu, Y. Guo, Q.-Y. Chen, *Synlett* **2011**, 77–80.
[21] a) A. Osuka, H. Shimidzu, *Angew. Chem.* **1997**, *109*, 93; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 135–137; b) N. Aratani, A. Osuka, Y. H. Kim, D. H. Jeong, D. Kim, *Angew. Chem.* **2000**, *112*, 1517; *Angew. Chem. Int. Ed.* **2000**, *39*, 1458–1462; c) N. Yoshida, H. Shimidzu, A. Osuka, *Chem. Lett.* **1998**, 55–56.
[22] M. Kamo, A. Tsuda, Y. Nakamura, N. Aratani, K. Furukawa, T. Kato, A. Osuka, *Org. Lett.* **2003**, *5*, 2079–2082.
[23] a) L.-M. Jin, J.-J. Yin, L. Chen, C.-C. Guo, Q.-Y. Chen, *Synlett* **2005**, 2893–2898; b) L.-M. Jin, L. Chen, J.-J. Yin, C.-C. Guo, Q.-Y. Chen, *Eur. J. Org. Chem.* **2005**, 3994–4001.
[24] a) T. Ogawa, Y. Nishimoto, N. Ono, N. Yoshida, A. Osukua, *Chem. Commun.* **1998**, 337–338; b) T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono, A. Osuka, *Angew. Chem.* **1999**, *111*, 140; *Angew. Chem. Int. Ed.* **1999**, *38*, 176–179.
[25] A. Takai, B. Habermeyer, S. Fukuzumi, *Chem. Commun.* **2011**, *47*, 6804–6806.
[26] a) M. O. Senge, X. Feng, *Tetrahedron Lett.* **1999**, *40*, 4165–4168; b) M. O. Senge, X. Feng, *J. Chem. Soc. Perkin Trans. 1* **2000**, 3615–3621.
[27] a) N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* **1979**, *20*, 3437–3440; b) N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513–519.
[28] J. H. Fuhrhop, D. Mauzerall, *J. Am. Chem. Soc.* **1969**, *91*, 4174–4181.
[29] A. K. Sahoo, Y. Nakamura, N. Aratani, K. S. Kim, S. B. Noh, H. Shinokubo, D. Kim, A. Osuka, *Org. Lett.* **2006**, *8*, 4141–4144.
[30] M. Fazekas, M. Pintea, M. O. Senge, M. Zawadzka, *Tetrahedron Lett.* **2008**, *49*, 2236–2239.
[31] M. O. Senge, *Acc. Chem. Res.* **2005**, *38*, 733–743.
[32] M. O. Senge, M. Pintea, A. Ryan, *Z. Naturforsch. B* **2011**, *66*, 553–558.
[33] C. Bruckner, J. J. Posakony, C. K. Johnson, R. W. Boyle, B. R. James, D. Dolphin, *J. Porphyrins Phthalocyanines* **1998**, *2*, 455–465.
[34] a) T. Dohi, M. Ito, K. Morimoto, M. Iwata, Y. Kita, *Angew. Chem.* **2008**, *120*, 1321; *Angew. Chem. Int. Ed.* **2008**, *47*, 1301–1304; b) T. Wirth, *Angew. Chem.* **2005**, *117*, 3722; *Angew. Chem. Int. Ed.* **2005**, *44*, 3656–3665.
[35] M. O. Senge, J. C. Brandt, *Photochem. Photobiol.* **2011**, *87*, 1240–1296.
[36] S. Hiroto, A. Osuka, *J. Org. Chem.* **2005**, *70*, 4054–4058.
[37] R. W. Wagner, J. Seth, S. I. Yang, D. Kim, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Org. Chem.* **1998**, *63*, 5042–5049.
[38] N. Aratani, A. Osuka, *Org. Lett.* **2001**, *3*, 4213–4216.
[39] a) A. G. Hyslop, M. A. Kellett, P. M. Iovine, M. J. Therien, *J. Am. Chem. Soc.* **1998**, *120*, 12676–12677; b) E. M. Finnigan, R. Rein, N. Solladié, K. Dahms, D. C. G. Götz, G. Bringmann, M. O. Senge, *Tetrahedron* **2011**, *67*, 1126–1134; c) S. Punidha, N. Agarwal, I. Gupta, M. Ravikanth, *Eur. J. Org. Chem.* **2007**, 1168–1175.
[40] R. H. Felton, H. Linschitz, *J. Am. Chem. Soc.* **1966**, *88*, 1113–1116.
[41] N. Aratani, A. Osuka, *Chem. Rec.* **2003**, *3*, 225–234.
[42] H. Mori, T. Tanaka, N. Aratani, B. S. Lee, P. Kim, D. Kim, A. Osuka, *Chem. Asian J.* **2012**, *7*, 1811–1816.
[43] L. He, Y.-Z. Zhu, J.-Y. Zheng, Y.-F. Ma, Y.-S. Chen, *J. Photochem. Photobiol. A: Chem.* **2010**, *216*, 15–23.
[44] I. M. Blake, A. Krivokapic, M. Katterle, H. L. Anderson, *Chem. Commun.* **2002**, 1662–1663.

[45] J. S. Lindsey, S. Prathapan, T. E. Johnson, R. W. Wagner, *Tetrahedron* **1994**, *50*, 8941–8968.
[46] N. Aratani, A. Osuka, H. S. Cho, D. Kim, *J. Photochem. Photobiol. C: Photochem. Rev.* **2002**, *3*, 25–52.
[47] P. Bhyrappa, P. Bhavana, *Chem. Phys. Lett.* **2001**, *342*, 39–44.
[48] a) K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467–4470; b) R. W. Wagner, T. E. Johnson, F. Li, J. S. Lindsey, *J. Org. Chem.* **1995**, *60*, 5266–5273.
[49] O. B. Locos, K. Dahms, M. O. Senge, *Tetrahedron Lett.* **2009**, *50*, 2566–2569.
[50] a) B. Krattinger, H. J. Callot, *Eur. J. Org. Chem.* **1999**, 1857–1867; b) N. N. Sergeeva, Y. M. Shaker, E. M. Finnigan, T. McCabe, M. O. Senge, *Tetrahedron* **2007**, *63*, 12454–12464.
[51] a) H. W. Whitlock Jr., R. Hanauer, M. Y. Oester, B. K. Bower, *J. Am. Chem. Soc.* **1969**, *91*, 7485–7489; b) M. O. Senge, W. W. Kalisch, S. Runge, *Tetrahedron* **1998**, *54*, 3781–3798.
[52] H. Shinokubo, A. Osuka, *Chem. Commun.* **2009**, 1011–1021.
[53] a) G. Wu, A. L. Rheingold, S. J. Geib, R. F. Heck, *Organometallics* **1987**, *6*, 1941–1946; b) R. C. Larock, M. J. Doty, Q. Tian, J. M. Zenner, *J. Org. Chem.* **1997**, *62*, 7536–7537.
[54] C. Bauder, R. Ocampo, H. J. Callot, *Tetrahedron* **1992**, *48*, 5135–5150.
[55] M. O. Senge, *Chem. Commun.* **2006**, 243–256.
[56] A. Nakano, N. Aratani, H. Furuta, A. Osuka, *Chem. Commun.* **2001**, 1920–1921.
[57] R. Shediac, M. H. B. Gray, H. T. Uyeda, R. C. Johnson, J. T. Hupp, P. J. Angiolillo, M. J. Therien, *J. Am. Chem. Soc.* **2000**, *122*, 7017–7033.
[58] a) A. A. Frimer, *Chem. Rev.* **1979**, *79*, 359–387; b) P. D. Bartlett, A. P. Schaap, *J. Am. Chem. Soc.* **1970**, *92*, 3223–3225; c) S. Mazur, C. S. Foote, *J. Am. Chem. Soc.* **1970**, *92*, 3225–3226.
[59] The attainment of carbon spectra was not as straightforward, and for dimers **10c**, **10k**, **17a**, and **17b** the addition of [D_5]-pyridine had a negative effect on the ^{13}C NMR spectra as this solvent overshadows the spectrum. Therefore, for these dimers, carbon assignments were impossible to achieve.
[60] HRMS was attained but the *m*/*z* value was approximately 0.9 higher than the exact mass. This could be attributed to a solubility issue of the dimer.

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