Synthesis of Diazepine-fused Porphyrinoids and Annulated Porphyrin Arrays

Aoife A. Ryan[a], Fanny Pouyatos[a], Aurelie Stallivieri[a], Teodor Silviu Balaban[b], and Mathias O. Senge[a,c]

[a] School of Chemistry, SFI Tetrapyrrole Laboratory, Trinity Biomedical Sciences Institute, 152 – 160 Pearse Street, Trinity College Dublin, Dublin 2, Ireland
[b] Aix Marseille Université, CNRS, UMR iSm2 7313, F-13397 Marseille, France
[c] Medicinal Chemistry, Institute of Molecular Medicine, Trinity Centre for Health Sciences, Trinity College Dublin, St James's Hospital, Dublin 8, Ireland

Reprint requests to Prof. Dr. M. O. Senge. Fax: #353-1-896-8537. E-mail: sengem@tcd.ie

Z. Naturforsch. **2014**, *69b*, 889 – 898 / DOI: 10.5560/ZNB.2014-4100
Received May 15, 2014

Porphyrins with exocyclic rings allow for significant modulation of the photochemical properties of the macrocycle *via* modulation of the aromatic system through electronic and conformational effects. Here we sought to generate such porphyrinoids *via* a stepwise strategy involving two cycloaddition steps, the first improving the synthesis of a relatively unstable dehydropurpurin intermediate which ring opens to form a key 1,5-diketone species. A library of a new class of porphyrinoids, namely diazepine-fused porphyrinoids was synthesized *via* condensation methods from these 1,5-diketone precursors in yields of 8 – 49 %. Cycloaddition methodologies were also applied to bisporphyrins, and their reactivities were investigated.

Key words: Porphyrinoids, Cycloaddition, Diazepine, 1,5-Diketones

Introduction

Tetrapyrroles with exocyclic rings have great biological significance, and there are numerous synthetic derivatives of such [1 – 3]. Depending on the exocyclic ring size a perturbation of the macrocycle is often observed, and these distorted porphyrinoids have interesting photophysical properties and exhibit bathochromic shifts in their absorption profiles [4]. The development of such compounds is attractive for the purpose of applying to areas such as two-photon photodynamic therapy (2PA-PDT), whereby an enhancement of absorption is desirable for the targeting of deeper cancers and in the development of self-assembling solar cells, which have the capacity to mimic biological light-harvesting systems [5]. Our aim was to synthesize novel porphyrinoids incorporating heterocyclic exocyclic rings, namely diazepine derivatives and investigate their photophysical properties, with the overall objective of applying them to PDT, or, *via* supramolecular constructs, in solar cells.

Numerous investigations into various cycloaddition reactions on monomeric porphyrins, generating perturbed macrocycles with enhanced photophysical properties have been executed [6 – 8]. These include various strategies such as Grubbs metathesis, 1,3-dipolar cycloadditions, and intramolecular oxidative coupling, to name but a few. We decided to adopt the attractive [3 + 2] annulation strategy developed by Osuka and co-workers [9] involving a palladium-catalyzed C–C bond forming reaction *via* carbopalladation of a bromo-porphyrin with internal alkynes [10, 11]. The resulting product is a 7,8-dehydropurpurin bearing a fused cyclopentadiene ring (Fig. 1) which causes a significant distortion of the porphyrin macrocycle, which, upon ring opening of zinc(II) derivatives, forms a 1,5-diketone porphyrin (Fig. 1). Diketones readily undergo intramolecular cyclization reactions with various nucleophiles to form heteroaromatic compounds such as pyrylium salts, pyridines and diazepines, and this reactivity will be exploited. For example, the reaction of 1,5-diketones with various

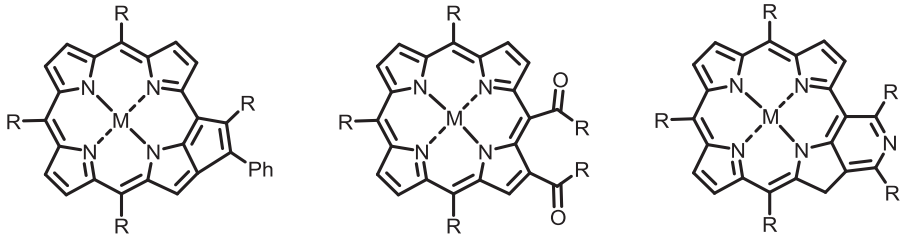


Fig. 1. General formulas for 7,8-dehydropurpurin, 1,5-diketone porphyrin and oxopyridochlorin.

amino derivatives is widely known, with the resulting generation of nitrogen containing heterocycles [12]. Osuka and co-workers utilized this methodology to generate a novel pyridine-fused porphyrinoid, namely an oxopyridochlorin (Fig. 1) which like the dehyropurpurins, exhibit a substantial red-shift of bands in the near-IR region due to enhanced conjugation and distortion of the macrocycle. Here we report a similar strategy with the goal of generating diazepine porphyrinoids.

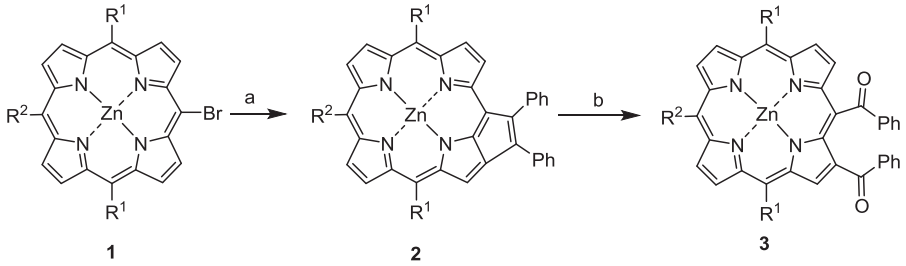
Results and Discussion

As we described previously, the initial strategy which we undertook involved the proposed synthesis of a triply fused dimeric dehydropurpurin [13]. Although [3 + 2] annulation occurred, the predominant product isolated was a 1,5-diketone porphyrin due to the instability of zinc(II) 7,8-dehydropurpurins. In order to further exploit the utility of these materials, we synthesized a library of dehydropurpurins **2a**–**e** using the [3 + 2] annulation strategy. Using bromoporphyrins **1a**–**e**, a Pd(0)-catalyzed reaction of a double bond on the bromoporphyrin with the internal alkyne diphenylacetylene, porphyrins **2a**–**e** were generated in good to excellent yields of up to 85 % yields (Scheme 1).

The zinc dehydropurpurins are unstable in dilute solution, and on exposure to air and light, the cyclopentadiene ring opens, to give 1,5-diketones **3a**–**e** in almost quantitative yields. This is not seen with nickel(II) or palladium(II) porphyrins and is thus presumed to occur from singlet oxygen generation. As shown in Scheme 2, a plausible mechanism for the ring opening includes a light-initiated [2 + 2] cycloaddition of singlet oxygen with the external double bond to give a dioxetane intermediate. This then decomposes to yield the diketone product [14].

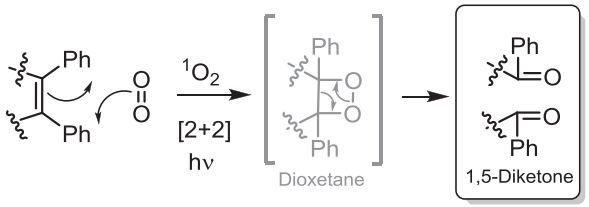
The reactivity of these 1,5-diketones was further investigated as they are widely known to undergo various cyclization reactions to give 5-, 6- and 7-membered ring products, depending on the reagents and conditions used [15 – 17]. We decided to use hydrazine as a substrate to develop a novel diazepine-fused porphyrin, and to explore the reactivity of the porphyrin 1,5-diketones generated and the effect that the fused diazepine moiety would have on the macrocycle. Condensation of 1,5-diketones **3a**–**e** [9] with hydrazine hydrate yielded the desired diazepine products **4a**–**d** in yields of up to 49 % (Scheme 3). Numerous conditions were explored; with the optimum yield obtained employing a microwave unit as the heat source. Although the synthesis gave moderate yields, the reaction was not as successful in terms of yields as that for the pyridinium-porphyrinoid. The condensation mechanism begins with the protonation of the carbonyl oxygen under acidic conditions and subsequent nucleophilic attack of hydrazine at the electrophilic carbon. A series of proton transfer and elimination of water yields a hydrazone intermediate. Another attack by the hydrazine moiety, this time intramolecularly, closes the ring. Subsequent proton transfer and loss of water yields the 1,2-diazepine porphyrin. Attack by the other nitrogen would generate a 6-membered annulated ring (such as a *N*-amino-pyridinium salt), which due to loss of global aromaticity, however, was not formed. These are novel fused porphyrinoid systems, although the macrocycle here is not perturbed as observed for the [3 + 2] adduct and pyridinium derivative. Attempts to generate pyrylium salt derivatives *via* a similar strategy [18 – 20] were largely unsuccessful.

The UV/Vis absorption spectra of porphyrins **2a**, **3a** and **4a** are shown in Fig. 2. Due to the perturbation of the macrocycle in **2a** a split in the Soret band is observed. On returning to aromaticity in **3a**, a typical por-



Entry	R^1	R^2	2	3	Yield (%)
1	4-Methylphenyl	H	**2a**[a]	**3a**[b]	72
2	4-Methylphenyl	Phenyl	**2b**[a]	**3b**[b]	52
3	Phenyl	Phenyl	**2c**[a]	**3c**[b]	85
4	3-Methoxyphenyl	H	**2d**[a]	**3d**[b]	80
5	3-Methoxyphenyl	3-Methoxyphenyl	**2e**[a]	**3e**[b]	39
6	3-Methoxyphenyl	Phenyl	**2f**[a]	**3f**[b]	76

Scheme 1. Synthesis of porphyrin-3,5-bisketones. [a] Diphenylacetylene (1.5 eq.), $Pd_2(dba)_3$ (5 %), (o-Tol)$_3$P (0.2 eq.), toluene, *N*,*N*-dicyclohexylmethylamine (5 eq.), 120 °C, 24 h; [b] $CHCl_3$, air, light, 24 h.

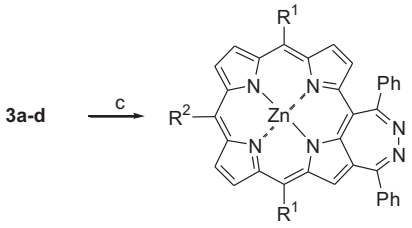


Scheme 2. Ring opening mechanism.

phyrin absorption is seen. The diazepine adducts are characterized by broad Soret bands and also a slight bathochromic shift compared to their 1,5-diketone precursors.

Fig. 3 shows a comparison of the NMR spectra of bromoporphyrin **1f**, dehydropurpurin **2f**, 1,5-diketone porphyrin **3f**, and the diazepine-fused porphyrin **4b**. On generation of **2f** from bromoporphyrin **1f**, there was a substantial increase in shielding of β-signals from between 8.8 and 9.8 ppm to 7.2 to 8.2 ppm. Also, with **1f** there are four β-proton signals, with six signals for the β-protons in **2f**, due to the distortion of the macrocycle. This is most evident for the β-protons closest to the cyclopentadiene ring which occur as two singlets. The methoxy CH_3 signal for **1f** occurs as a 6H singlet but with **2f**, two 3H singlets are observed due to the asymmetry of the macrocycle. Some impurities are present in the spectrum of **2f**, as here the ring opening was promoted to generate diketone **3f**. The spectrum for **3f** returns to that for a porphyrin with the β-signals resonating in the region of 8.6 – 9.1 ppm. The ketone functional groups were also confirmed *via* ^{13}C NMR analysis with low-field resonances of 194.5 and 199.3 ppm for the carbonyl carbons attached to the β and *meso* carbons, respectively. The diazepine-fused porphyrin **4b** exhibits a slight difference in chemical shifts for the β-protons, typical of fused moieties, with the two closest to the fused ring occurring as singlets with the highest field strength in the β-region. The structure was confirmed by HRMS, with a parent ion of $m/z = 864.2222$ (calculated for $[C_{54}H_{36}N_6O_2Zn]$: 864.2191), and also the loss of signals at 194 and 198 ppm in ^{13}C NMR analysis for the carbonyl carbons.

In parallel to cycloaddition reactions of monomers and the generation of diazepine-porphyrinoids, we sought to apply the [3 + 2] annulation methodology to bromo bisporphyrins. Taking the directly linked porphyrin dimer **5**, we were able to execute a double cycloaddition to form **6** (which is a mixture of rotamers)



Entry	R^1	R^2	4	Yield (%)
1	4-Methylphenyl	H	**4a**	8
2	3-Methoxyphenyl	Phenyl	**4b**	49[a]
3	3-Methoxyphenyl	H	**4c**	n/d[b]
4	3-Methoxyphenyl	3-Methoxyphenyl	**4d**	12

Scheme 3. Synthesis of diazepine derivatives. *Reagents and conditions:* c) Hydrazine hydrate (10 eq.), EtOH-acetic acid, reflux or MW. [a] MW conditions, [b] not isolated due to difficulties with purification. HRMS (MALDI): m/z calculated for $[C_{48}H_{33}N_6O_2Zn]$: 789.1956, found 789.1948.

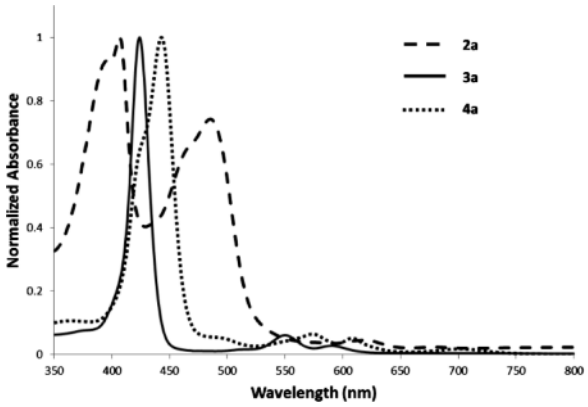


Fig. 2. Normalized absorption spectra of **2a**, **3a** and **4a** in CH_2Cl_2.

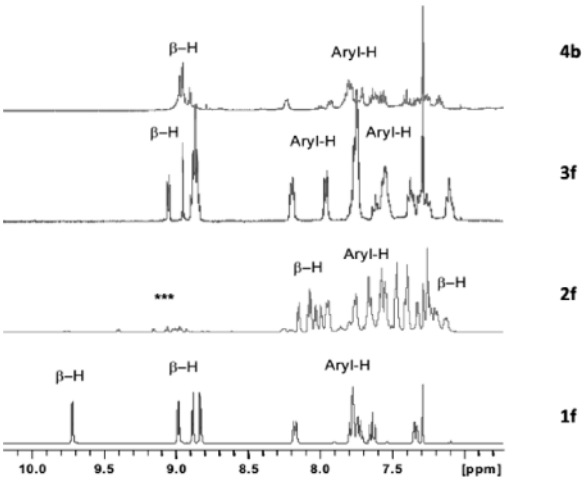
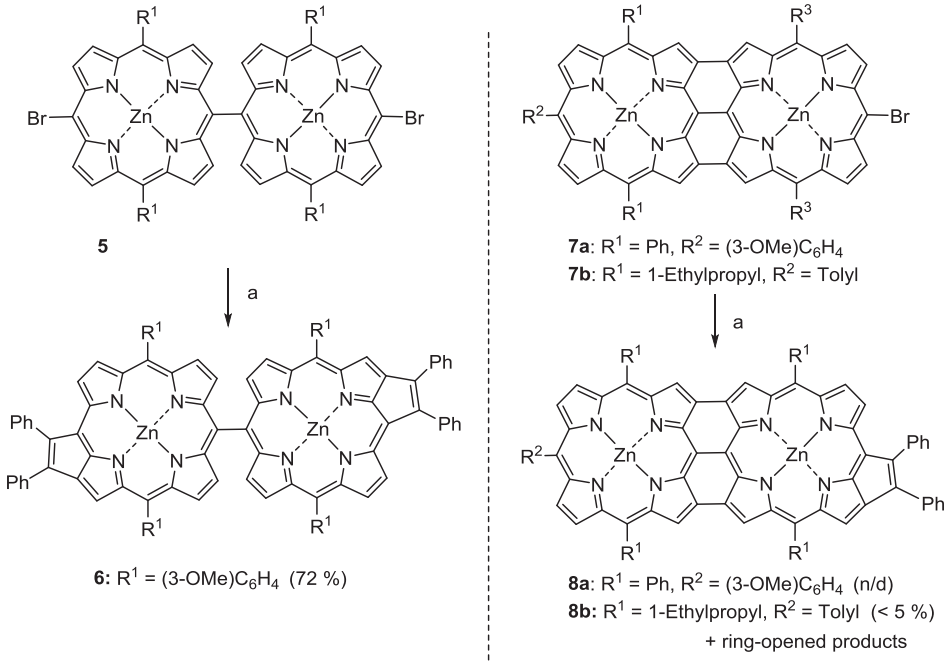


Fig. 3. ^{1}H NMR (400 MHz) spectra of **1f**, **2f**, **3f**, and **4b** in $CDCl_3$ (*** impurities, compound not isolated before ring opening).

in excellent yield of 72 %. This bis-dehydropurpurin has an interesting UV spectrum, although due to inevitable ring opening on oxidation to generate triply fused systems, these compounds were not used in further syntheses. Additionally, the methodology was applied to the triply fused bromo dimers **7a** and **7b** (Scheme 4). Employing the bromo-dimer **7a** [3 + 2] annulation reactions were attempted, but without success. The main fraction isolated was unreacted starting material, with no detection of the annulated dimer **8a**. This may be attributed to the insolubility of the starting material, but further investigations are needed. Trying to overcome the solubility issue, dimer **7b** was used, with alkyl and tolyl substituents. The reactivity was enhanced but the desired product **8b** was obtained only in a yield of less than 5 %, and it co-eluted with debrominated starting material. Also observed was the ring-opened derivative of **8b**, which may have formed during purification when exposed to the air or due to the presence of trace oxidants in the starting material. The products formed were only characterized by HRMS



Scheme 4. Synthesis of directly linked bis-dehydropurpurins **6a** and fused derivatives **8a** and **8b**. *Reagents and conditions*: diphenylacetylene (1.5 – 3 eq.), $Pd_2(dba)_3$ (5 %), (*o*-Tol)$_3$P (0.2 eq.), toluene, *N*,*N*-dicyclohexylmethylamine (5 – 10 eq.), 120 °C, 24 h.

with the ring-opened dimer showing a parent ion peak at $m/z = 1342.3580$ (calculated for $[C_{84}H_{62}N_8O_2Zn_2]$: 1342.3579).

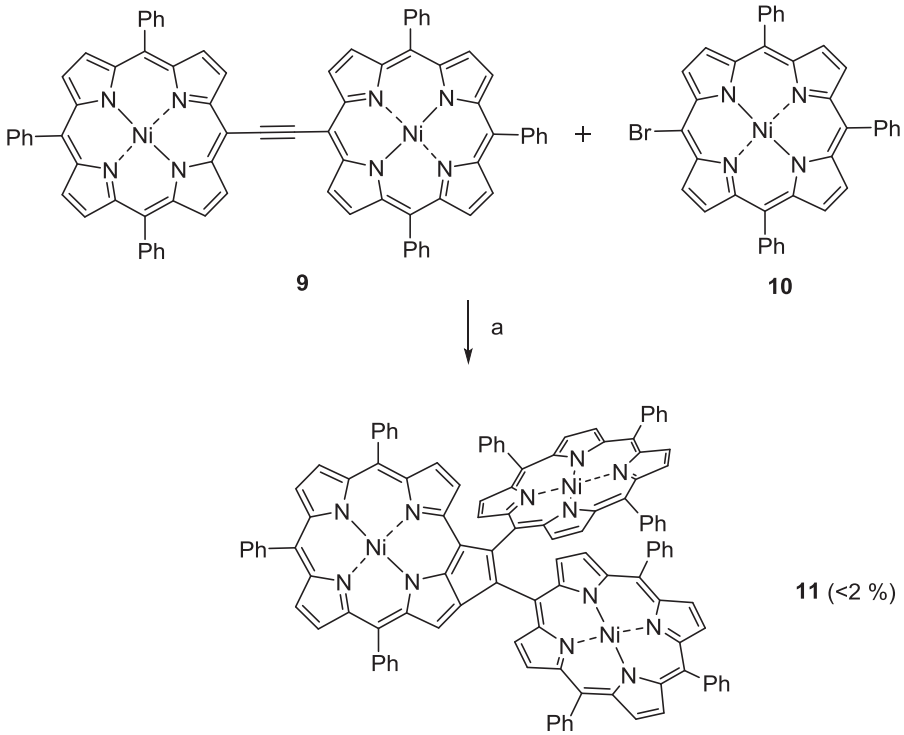
Additionally, using the alkynyl-linked dimer **9** as the internal alkyne source, the [3 + 2] methodology with bromo-porphyrin **10** was employed to generate the dehydropurpurin trimer **11**. Although multiple attempts were carried out, **11** could only be isolated in a yield of 2 % and only be identified *via* HRMS (Scheme 5). Here, lengthening the linker, for example to a diphenylacetylene, between the porphyrin units may help to improve the reaction as the steric hindrance in the cycloaddition would be minimized.

In conclusion, diazepine-fused porphyrinoids were synthesized in moderate yields from 1,5-diketone precursors. These materials display bathochromic shifts in their absorption profiles. Additionally, the [3 + 2] annulation methodology was applied to singly and triply linked porphyrin dimers. Future work will involve the synthesis of other fused hetero-aromatic moieties at the porphyrin periphery *via* similar principles and larger nitrogen heterocyclic derivatives, and also their incorporation into oligomeric porphyrins.

Experimental

General methods

All commercial chemicals used were of analytical grade and were supplied by Sigma Aldrich, Frontier Scientific, Inc. and Tokyo Chemical Industry (TCI) and used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 and Agilent 400 (400 MHz for ^{1}H NMR; 100.6 MHz for ^{13}C NMR) and/or Bruker AV 600 instrument (600 MHz for ^{1}H NMR; 150.9 MHz for ^{13}C NMR). Chemical shifts are reported in ppm and locked on residual solvent peaks. The assignment of signals was confirmed by 2D spectra (COSY, HSQC) except for those porphyrins with low solubility. UV/Vis absorption measurements were performed with a Shimadzu MultiSpec-1501 instrument. Microwave reactions were carried out in a CEM Discover 600 W microwave reactor. HRMS spectra were measured on MaldiQ-Tof Premier Micromass and Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometers equipped with an electrospray ionization source (ESI). Melting points were acquired on a Stuart SMP-10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 (fluorescence in-



Scheme 5. Synthesis of porphyrin trimer **11**. *Reagents and conditions:* a) **9** (1.5 eq.), **10** (1 eq.) $Pd_2(dba)_3$ (0.2 eq.), $(o\text{-Tol})_3P$ (0.2 eq.), toluene, *N*,*N*-dicyclohexylmethylamine (5 – 10 eq.), 120 °C, 24 h.

dicator F_{254}; Merck) pre-coated aluminum sheets. Flash chromatography was carried out using Fluka Silica Gel 60 (230 – 400 mesh).

Porphyrins **1a**–**f** [13, 21], **9** and **10** [13] were synthesized according to previously reported methods [22].

*[3,5-Dibenzoyl-10,20-bis(4-methylphenyl)porphyrinato]-zinc(II) (**3a**)*

Porphyrin **1a** (200 mg, 0.32 mmol), diphenylacetylene (84 mg, 0.48 mmol) and $(o\text{-Tol})_3P$ (19 mg, 0.06 mmol) were dried under a pressure of 10^{-2} mbar in a 25 mL Schlenk tube before being used. Toluene (5 mL) was added under argon. The mixture was then subjected to three freeze-pump-thaw cycles to degas the solution. The reaction was protected from light for the next steps. $Pd_2(dba)_3$ (15 mg, 0.02 mmol) and *N*,*N*-dicyclohexylmethylamine (0.35 mL, 1.65 mmol) were added to the mixture which was then heated at 110 °C for 24 h. Upon reaction completion, the solvent was removed under reduced pressure. The product was filtered through silica using CH_2Cl_2 as eluent and the solvent removed to obtain the ring-closed compound **2a**. The product was then dissolved in CH_2Cl_2 (16 L) and exposed to light for 72 h to obtain the ring-opened compound **3a**. Yield: 176 mg (0.23 mmol, 72 %). M. p. > 300 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (s, 3H, tolyl-CH_3), 2.74 (s, 3H, tolyl-CH_3), 7.11 – 7.13 (m, 2H, Ph-*H*), 7.37 (t, J = 8.0 Hz, 2H, Ph-*H*), 7.50 – 7.54 (m, 6H, C_6H_4/Ph-*H*), 7.59 (d, J = 7.6 Hz, 2H, C_6H_4 – *H*), 7.83 – 7.85 (m, 2H, Ph-*H*), 8.08 (d, J = 7.6 Hz, 4H, C_6H_4-*H*), 8.91 – 8.96 (m, 3H, H_β), 9.09 – 9.11 (m, 2H, H_β), 9.38 – 9.40 (m, 2H, H_β), 10.27 ppm (s, 1H, H_{meso}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.8, 107.6, 121.0, 122.6, 127.3, 127.8, 128.7, 130.2, 131.9, 132.3, 132.9, 134.3, 135.3, 137.3, 138.0, 139.1, 141.2, 144.8, 138.4, 150.1, 150.6, 151.1, 151.8, 194.2, 198.7 ppm. – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 424 (5.14), 550 (3.92), 590 nm (3.78). – HRMS (MALDI): m/z = 760.1807 (calcd. 760.1817 for [$C_{48}H_{32}N_4O_2Zn$]).

*[3,5-Dibenzoyl-10,20-bis(4-methylphenyl)-15-phenyl-porphyrinato]zinc(II) (**3b**)*

Porphyrin **1b** (200 mg, 0.28 mmol), diphenylacetylene (76 mg, 0.43 mmol) and $(o\text{-Tol})_3P$ (17 mg, 0.06 mmol) were dried under a pressure of 10^{-2} mbar before being used. Toluene (5 mL) was added under argon. The mixture was

then subjected to three freeze-pump-thaw cycles. $Pd_2(dba)_3$ (13 mg, 0.01 mmol) and *N*,*N*-dicyclohexylmethylamine (0.29 mL, 1.40 mmol) were added to the mixture which was then heated at 110 °C for 24 h. Upon reaction completion, the solvents were removed *in vacuo*. The residue was filtered through a short plug of silica gel using CH_2Cl_2 as eluent, and the solvent was removed *in vacuo* to obtain the ring-closed compound **2b**. This was then dissolved in CH_2Cl_2 (14 L) and exposed to light for 72 h to obtain the ring-opened compound **3b**. Yield: 124 mg (0.15 mmol, 52 %). M. p. > 300 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.63$ (s, 3H, tolyl-CH_3), 2.70 (s, 3H, tolyl-CH_3), 7.08 (t, $J = 7.8$ Hz, 2H, Ph-*H*), 7.25 (d, $J = 7.3$ Hz, 1H, Ph-*H*), 7.36 (t, $J = 7.8$ Hz, 2H, Ph-*H*), 7.46 (d, $J = 7.8$ Hz, 2H, $C_6H_4 - H$), 7.51 – 7.58 (m, 6H, Ph-*H*), 7.73 – 7.76 (m, 4H, C_6H_4/Ph-*H*), 7.94 (d, $J = 7.8$ Hz, 2H, $C_6H_4 - H$) 8.04 (m, 4H, C_6H_4/Ph-*H*), 8.16 – 8.20 (m, 2H, H_β), 8.83 – 8.86 (m, 3H, H_β), 8.92 (s, 1H, H_β), 9.04 ppm (d, $J = 4.6$ Hz, 2H, H_β). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 29.7$, 116.5, 121.2, 122.8, 123.0, 126.4, 127.2, 127.4, 127.6, 128.0, 128.2, 128.9, 129.8, 130.5, 130.9, 131.5, 131.6, 132.0, 132.1, 132.5, 132.6, 132.9, 134.5, 137.0, 137.2, 138.5, 139.7, 139.9, 141.6, 143.0, 143.3, 145.8, 146.0, 150.2, 150.5, 150.6, 151.3, 151.8, 194.8, 199.4 ppm. – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 429 (5.38), 556 (4.09), 597 nm (3.78). – HRMS (MALDI): $m/z = 836.2161$ (calcd. 836.2130 for $[C_{54}H_{36}N_4O_2Zn]$).

*[3,5-Dibenzoyl-10,15,20-triphenylporphyrinato]zinc(II) (**3c**)*

Zinc bromoporphyrin **1c** (202 mg, 0.30 mmol) and diphenylacetylene (79 mg, 0.44 mmol) were added to a 25 mL Schlenk flask and were dried under a pressure of 10^{-2} mbar for 20 min. Anhydrous toluene (10 mL) and (*o*-Tol)$_3$P (18 mg, 0.06 mmol) were added, and the solution was degassed by three freeze-pump-thaw cycles. $Pd_2(dba)_3$ (14 mg, 0.02 mmol), and *N*,*N*-dicyclohexylmethylamine (0.32 mL, 0.15 mmol) were added, and the flask was sealed and the mixture stirred at 120 °C for 24 h in the dark. The solvent was evaporated under reduced pressure, and the crude reaction mixture was purified by column chromatography in the dark using *n*-hexane-ethyl acetate = 20 : 1 (v/v). The solvents were removed *in vacuo*, to yield the desired product as the second fraction **2c** (brown spot). $R_f = 0.22$ (*n*-hexane-ethyl acetate = 9 : 1, v/v). – UV/Vis (CH_2Cl_2): $\lambda_{max} = 401$, 413, 490, 624, 684 nm. – HRMS (MALDI): $m/z = 776.1896$ (calcd. 776.1918 for $[C_{52}H_{32}N_4Zn]$). Crude **2c** was dissolved in $CHCl_3$ (4 – 5 L) and was allowed to stir exposed to ambient light and air for 48 h. The solvent was removed *in vacuo*, and **3c** was isolated as a green powder (204 mg, 0.25 mmol, 85 %). M. p. > 300 °C. – $R_f = 0.33$ (*n*-hexane-ethyl acetate = 9 : 1, v/v). – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.20$ (t, $J = 7.8$ Hz, 2H, Ph-*H*), 7.41 (m, 3H, Ph-*H*), 7.57 (t, $J = 7.5$ Hz, 1H, Ph-*H*), 7.72 – 7.78 (m, 9H, Ph-$H_)$, 7.95 (d, $J = 7.6$ Hz, 2H, Ph-*H*), 8.20 (d, $J = 6.2$ Hz, 4H, Ph-*H*), 8.24 (d, $J = 6.2$ Hz, 2H; Ph-*H*), 8.88 (d, $J = 4.8$ Hz, 1H; H_β), 8.94 – 8.98 (m, 5H; H_β), 9.01 ppm (d, $J = 4.8$ Hz, 1H, H_β). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 121.8$, 123.1, 123.3, 126.6, 126.7, 127.7, 127.8, 128.1, 130.5, 131.6, 131.8, 132.4, 132.5, 132.6, 132.9, 133.0, 134.4, 134.4, 134.4, 135.6, 138.2, 141.8, 142.1, 142.2, 142.9, 149.0, 150.6, 150.8, 151.8, 194.4 (C=O), 198.8 ppm (C=O). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 429 (5.02), 555 (3.77), 596 nm (3.46). – HRMS (MALDI): $m/z = 808.1826$ (calcd. 808.1817 for $[C_{52}H_{32}N_4O_2Zn]$).

*[3,5-Dibenzoyl-10,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) (**3d**)*

Bromoporphyrin **1d** (25 mg, 0.04 mmol), diphenylacetylene (10 mg, 0.06 mmol) and (*o*-Tol) $_3$P (3 mg, 0.01 mmol) were added to a 25 mL Schlenk tube and dried under a pressure of 10^{-2} mbar for 20 min. Toluene (3 mL) was added, and the solution was degassed *via* three freeze-pump-thaw cycles. $Pd_2(dba)_3$ (2 mg, 0.002 mmol) and *N*,*N*-dicyclohexylmethylamine (37 mg, 0.17 mmol) were added, and the reaction mixture was heated to 110 °C and stirred at this temperature for 19 h, shielded from ambient light. The reaction mixture was filtered through a short plug of silica using CH_2Cl_2 as eluent. Solvents were removed to yield a crude dark-orange solid containing **2d** as confirmed by UV/Vis and HRMS analysis: UV/Vis (CH_2Cl_2): λ_{max} = 414, 537, and 571 nm. – HRMS (MALDI): $m/z = 760.1853$ (calcd. 760.1817 for $[C_{48}H_{32}N_4O_2Zn]$). Porphyrin **2d** (25 mg) was dissolved in $CHCl_3$ (3 L) and stirred open to the air at room temperature, for 20 h. The transformation was monitored *via* UV/Vis analysis and upon completion, solvents were removed *in vacuo*, and the residue was purified *via* a short column of silica (CH_2Cl_2-hexane, 4 : 1, v/v). Solvents were removed to yield porphyrin **3c** (24 mg, 0.03 mmol, 80 %). M. p. > 300 °C. – $R_f = 0.37$ (*n*-hexane-EtOAc = 3 : 1, v/v). – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.91$ (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 7.04 – 7.08 (t, $J = 15.2$ Hz, 2H, $C_6H_4 - H$), 7.24 – 7.27 (t, $J = 13.5$ Hz, 2H, $C_6H_4 - H$), 7.33 (m, 4H, Ph-*H*), 7.49 (m, 1H, $C_6H_4 - H$), 7.59 (m, 1H, Ph-*H*), 7.63 (m, 2H, $C_6H_4 - H$), 7.74 (m, 4H, Ph-*H*), 7.79 (m, 2H, Ph-*H*), 8.91 (m, 3H, H_β), 9.09 (m, 2H, H_β), 9.38 (m, 2H, H_β), 10.28 ppm (s, 1H, H_{meso}). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.4$, 55.5, 108.0,113.5, 120.5, 122.3, 127.4, 127.6, 127.7, 128.0, 130.4, 131.6, 132.2, 132.4, 132.7, 132.8, 135.5, 138.0, 141.1, 142.8, 143.3, 143.6, 144.2, 144.9, 148.8, 150.3, 150.4, 151.0, 151.8, 157.8, 157.9, 194.4 (C=O), 198.9 ppm (C=O). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 415 (5.47), 479 (4.15)

543 nm (4.15). – HRMS (MALDI): $m/z = 792.1732$ (calcd. 792.1715 for $[C_{48}H_{32}N_4O_4Zn]$).

*[3,5-Dibenzoyl-10,15,20-tris(3-methoxyphenyl)-porphyrinato]zinc(II) (**3e**)*

Porphyrin **1e** (200 mg, 0.26 mmol), diphenylacetylene (69 mg, 0.39 mmol) and (*o*-Tol)$_3$P (16 mg, 0.05 mmol) were dried under high vacuum for 1 h. Dry toluene (15 mL) was added under argon. The solution was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was shielded from light. $Pd_2(dba)_3$ (12 mg, 0.01 mmol) and *N*,*N*-dicyclohexylmethylamine (0.28 mL, 1.30 mmol) were added to the Schlenk tube, and the reaction mixture was heated at 110 °C for 24 h. The solvent was removed *in vacuo*, and the residue was filtered through silica gel using a mixture of CH_2Cl_2-hexane (2 : 1, v/v). The solvents were removed to obtain the ring-closed product **2e**. The product was then dissolved in of CH_2Cl_2 (18 L) and exposed to light for at 24 h. The ring opening reaction was followed by UV/Vis analysis, and upon completion, the solvent was removed under reduced pressure. A short column chromatography was then performed using a mixture of CH_2Cl_2-hexane. Yield: 91 mg (0.10 mmol, 39 %). M. p. > 300 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.91$ (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 7.14 (t, $J = 7.6$ Hz, 2H, $C_6H_4 - H$), 7.23 (m, 1H, $C_6H_4 - H$), 7.32 – 7.37 (m, 5H, Ph-*H*), 7.52 – 7.70 (m, 8H, C_6H_4/Ph-*H*), 7.76 – 7.83 (m, 6H, C_6H_4-*H*/Ph-*H*), 8.87 – 9.00 ppm (m, 7H, H_β) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.4$, 55.5, 55.5, 113.5, 113.7, 120.4, 121.4, 122.8, 122.9, 127.4, 127.5, 127.6, 127.7, 128.0, 130.4, 131.5, 131.7, 132.4, 132.5, 132.9, 133.0, 135.6, 138.1, 141.5, 142.8, 143.4, 143.6, 143.7, 145.5, 146.0, 148.9, 150.4, 150.5, 150.7, 150.9, 151.7, 157.7, 157.9, 194.3, 198.8 ppm. – UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 428 (5.36), 554 (4.14), 594 nm (3.82). – HRMS (MALDI): $m/z = 898.2118$ (calcd. 898.2134 for $[C_{55}H_{38}N_4O_5Zn]$).

*[3,5-Dibenzoyl-10,20-bis(3-methoxyphenyl)-15-phenyl-porphyrinato]zinc(II) (**3f**)*

Bromoporphyrin **1f** (70 mg, 0.09 mmol), diphenylacetylene (25 mg, 0.14 mmol) and (*o*-Tol)$_3$P (6 mg, 0.02 mmol) were charged to a 10 mL Schlenk tube and dried under high vacuum for 20 min. Toluene (3 mL) was added, and the solution was degassed *via* three freeze-pump-thaw cycles. $Pd_2(dba)_3$ (4 mg, 0.01 mmol) and *N*,*N*-dicyclohexylmethylamine (85 mg, 0.47 mmol) were added, and the reaction was heated to 120 °C and stirred at this temperature for 24 h, shielded from ambient light. The reaction mixture was filtered through a short plug of silica using CH_2Cl_2 as eluent. The solvent was removed to yield a dark-orange solid **2f** as confirmed by UV/Vis and HRMS analysis: UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 416 (5.33), 489 (5.18), 619 (4.02) nm; HRMS (MALDI) $m/z = 836.2136$ (calcd. 836.2130 for $[C_{54}H_{36}N_4O_2Zn]$). A solution of crude **2f** (65 mg) in $CHCl_3$ (3 L) was stirred, open to the air at room temperature, for 20 h. The transformation was monitored *via* UV/Vis analysis until the purpurin had changed to porphyrin **3f**. Upon completion, solvents were removed *in vacuo*, and the residue was purified *via* a short column of silica (CH_2Cl_2-hexane, 4 : 1, v/v) to give two fractions, the second of which contained **3f**. The solvents were removed to yield porphyrin **3f** (62 mg, 0.07 mmol, 76 %). M. p. > 300 °C. – $R_f = 0.32$ (*n*-hexane-EtOAc = 3 : 1, v/v). – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.97$ (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 7.10 (m, 2H, $C_6H_4 - H$), 7.25 (m, 1H, $C_6H_4 - H$), 7.37 (m, 2H, Ph-*H*), 7.56 (m, 4H, $C_6H_4 - H$), 7.63 (m, 2H, Ph-*H*), 7.75 (m, 7H, Ph-*H*), 7.97 (d, $J = 7.9$ Hz, 2H, Ph-*H*), 8.20 (d, $J = 8.0$ Hz, 2H, Ph-*H*), 8.87 (m, 5H, H_β), 8.96 (d, $J = 4.7$ Hz, 1H, H_β), 9.08 ppm (d, $J = 4.7$ Hz, 1H, H_β). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.4$, 55.5, 113.1, 113.2, 120.6, 120.9, 122.5, 122.9, 123.1, 123.4, 126.4, 127.1, 127.2, 127.5, 127.6, 127.8, 128.0, 130.5, 131.5, 131.7, 132.0, 132.1, 132.6, 132.7, 132.8, 134.4, 135.2, 135.5, 135.7, 135.9, 141.8, 142.9, 143.3, 143.9, 144.2, 145.7, 145.8, 148.9, 149.1, 149.3, 150.2, 150.4, 150.6, 151.0, 151.5, 157.7, 157.8, 194.8, 199.3 ppm. – UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 428 (5.22), 553 (4.07), 596 nm (3.64). – HRMS (MALDI): $m/z = 868.1988$ (calcd. 868.2028 for $[C_{54}H_{36}N_4O_4Zn]$).

*[7,8-(6,9-Diphenyl)diazepine-10,20-bis(4-methylphenyl)-porphyrinato]zinc(II) (**4a**)*

Porphyrin **3a** (50 mg, 0.07 mmol) and hydrazine hydrate (24 %, 0.3 mL, excess) were refluxed in acetic acid (6 mL) and toluene (6 mL) for 24 h. The mixture was cooled before being washed using CH_2Cl_2 and water. The organic layer was dried with sodium sulfate, and after filtration the solvent was removed *in vacuo*. The residue was then purified by silica gel column chromatography using CH_2Cl_2-EtOAc (10 : 1, v/v) as eluent. The targeted compound **4a** was the third fraction. Yield: 4 mg (0.005 mmol, 8 %). M. p. > 300 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.64$ (s, 6H, $C_6H_4 - H$), 7.40 – 7.49 (m, 6H, aryl-*H*), 7.53 – 7.56 (m, 4H, aryl-*H*), 7.75 – 7.83 (m, 4H, tolyl-*H*), 7.99 – 8.02 (m, 2H, tolyl-*H*), 8.09 – 8.13 (m, 2H, tolyl-*H*), 8.45 – 8.46 (m, 2H, H_β), 8.94 (m, 3H, H_β), 9.28 – 9.31 (m, 2H, H_β), 9.88 ppm (s, 1H, H_{meso}). – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 29.5$, 100.2, 117.8, 121.9, 127.2, 127.5, 127.7, 129.7, 130.8, 131.1, 131.5, 131.7, 131.9, 132.2, 132.3, 132.6, 132.7, 132.8, 132.9, 133.1, 133.5, 133.7, 134.2, 134.3, 134.4, 146.1, 152.2, 152.6, 154.6, 155.5, 158.5, 162.5, 167.6 ppm. – UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 443 (4.98), 574 (3.79), 608 nm (3.69). – HRMS (MALDI): $m/z = 757.2066$ (calcd. 757.2058 for $[C_{48}H_{32}N_6Zn]$).

*[7,8-(6,9-Diphenyl)diazepine-5-phenyl-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) (**4b**)*

Porphyrin **3f** (20 mg, 0.02 mmol), hydrazine hydrate (0.1 mL) mmol, acetic acid (1 mL), and toluene (1 mL) were placed in a 5 mL flask, and the mixture was irradiated with the microwave source at 110 °C for 7 min. After completion, the reaction mixture was allowed to cool and diluted with CH_2Cl_2. The solution was washed with H_2O (2×10 mL), extracted with CH_2Cl_2, dried over Na_2SO_4 and filtered. Solvents were removed to leave a green solid which was redissolved in CH_2Cl_2 and filtered through a short plug of silica. The solvents were removed *in vacuo* to leave a green solid of **4b** (10 mg, 0.01 mmol, 49 %). M. p. > 300 °C. – $R_f = 0.27$ (CH_2Cl_2-EtOAc 10 : 1, v/v). – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.93$ (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 7.16 – 7.18 (d, $J = 15.7$ Hz, 2H, $C_6H_4 - H$), 7.24 – 7.27 (dd, $J = 11.0$ Hz, 2H, $C_6H_4 - H$), 7.35 (m, 2H, $C_6H_4 - H$), 7.38 – 7.42 (t, $J = 15.5$ Hz, 2H, $C_6H_4 - H$), 7.55 – 7.58 (t, $J = 13.7$ Hz, 2H, $C_6H_4 - H$), 7.63 (m, 2H, Ph-*H*), 7.75 (m, 2H, Ph-*H*), 7.82 (m, 5H, Ph-*H*), 7.93 – 7.94 (d, $J = 8.0$ Hz, 2H, Ph-*H*), 8.23 (m, 2H, Ph-*H*), 8.90 – 8.91 (d, $J = 4.8$ Hz, 2H, H_β), 8.96 ppm (m, 5H, H_β). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 55.5, 113.5, 113.7, 120.4, 122.8, 123.2, 126.7, 127.4, 127.5, 127.8, 128.1, 129.3, 130.5, 130.9, 132.4, 132.5, 132.9, 134.3, 135.6, 138.2, 141.7, 142.3, 142.9, 143.4, 143.5, 145.6, 146.0, 149.0, 150.4, 150.6, 150.8, 150.9, 151.6, 157.8, 157.9 ppm. – UV/Vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$) = 428 (5.01), 555 (3.95), 703 nm (3.80). – HRMS (MALDI): $m/z = 864.2222$ (calcd. 864.2191 for $[C_{54}H_{36}N_6O_2Zn]$).

*[7,8-(6,9-Diphenyl)diazepine-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) (**4c**)*

Porphyrin **3d** (56 mg, 0.07 mmol) and hydrazine dihydrochloride (70 mg, 0.71 mmol) were refluxed in EtOH (15 mL) for 24 h. The mixture was cooled before being diluted with CH_2Cl_2. The solution was washed with H_2O (2 $\times$ 10 mL) and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure, and the residue was purified using silica gel column chromatography CH_2Cl_2-EtOAc (10 : 1, v/v). The product could not be isolated in pure enough form for characterization. HRMS (MALDI): m/z = 789.1948 (calcd. 789.1956 for $[C_{48}H_{33}N_6O_2Zn]$).

*[7,8-(6,9-Diphenyl)diazepine-10,15,20-tris(3-methoxyphenyl)porphyrinato]zinc(II) (**4d**)*

Porphyrin **3e** (52 mg, 0.06 mmol) and hydrazine hydrate (24 %, 0.12 mL, 0.60 mmol) were refluxed in acetic acid (7 mL) and toluene (7 mL) for 24 h. The mixture was cooled before being washed using CH_2Cl_2 and water. The organic layer was dried over Na_2SO_4, and after filtration the solvent was removed *in vacuo*. The product was purified using silica column chromatography CH_2Cl_2-EtOAc (10 : 1, v/v). The targeted compound **4d** was isolated as the third fraction. Yield: 6 mg (0.01 mmol, 12 %). M. p. > 300 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.96$ (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 7.19 – 7.21 (m, 3H, $C_6H_4 - H$), 7.33 – 7.38 (m, 3H, C_6H_4/Ph-*H*), 7.49 (app br.s, 3H, $C_6H_4 - H$), 7.56 – 7.67 (m, 6H, C_6H_4/Ph-*H*), 7.73 – 7.80 (m, 8H, C_6H_4/Ph-*H*), 8.78 (s, 1H, H_β), 8.86 – 8.92 (m, 3H, H_β), 8.94 (s, 1H, H_β), 9.00 – 9.02 ppm (m, 2H, H_β). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 55.4, 55.4, 105.7, 113.0, 113.2, 113.3, 113.6, 113.9, 120.3, 120.4, 120.7, 121.1, 121.2, 121.5, 121.6, 122.7, 126.6, 127.0, 127.1, 127.2, 127.4, 127.6, 127.7, 128.1, 128.7, 128.9, 130.7, 131.5, 132.4, 132.4, 132.5, 132.6, 134.0, 135.3, 140.9, 143.5, 143.7, 143.9, 147.2, 147.7, 149.8, 150.4, 150.8, 151.0, 151.5, 157.5, 157.6, 157.7, 167.6, 171.9 ppm. – UV/Vis (CH_2Cl_2): λ_{max} = 429, 494, 555, 597, 705 nm. – HRMS (MALDI): $m/z = 894.2290$ (calcd. 894.2297 for $[C_{55}H_{48}N_6O_3Zn]$).

*Synthesis of dimer **6***

Bromoporphyrin dimer **5** (30 mg, 0.02 mmol), diphenylacetylene (12 mg, 0.07 mmol) and (o-Tol)$_3$P (3 mg, 0.01 mmol) were added to a 25 mL Schlenk tube and dried under high vacuum for 0.25 h. Toluene (3 mL) was added, and the solution was degassed *via* three freeze-pump-thaw cycles. $Pd_2(dba)_3$ (2 mg, 0.002 mmol) and *N*,*N*-dicyclohexylmethylamine (45 mg, 0.23 mmol) were added, and the reaction mixture was heated to 110 °C and stirred at this temperature for 24 h, shielded from ambient light. The reaction mixture was filtered through a short plug of silica using CH_2Cl_2 as eluent. The solvents were removed *in vacuo*, and the residue was subjected to column chromatography (silica, CH_2Cl_2-hexane, 2 : 1, 4 : 1, v/v) to yield one main fraction, orange in color. Solvents were removed to give a dark solid **6** (28 mg, 0.02 mmol, 78 %). M. p. > 300 °C. – $R_f = 0.21$ (CH_2Cl_2-*n*-hexane = 3 : 1, v/v). – ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 3.81$ (s, 6H, OCH_3), 3.85 (s, 6H, OCH_3), 6.93 (s, 1H, H_β), 6.97 (s, 1H, H_β), 7.07 – 7.08 (d, $J = 8.2$ Hz, 2H, $C_6H_4 - H$), 7.12 – 7.13 (d, $J = 8.2$ Hz, 2H, $C_6H_4 - H$), 7.23 – 7.27 (m, 4H, aryl-*H*), 7.38 – 7.41 (m, 24H, aryl-H/H_β), 7.59 – 7.60 (d, $J = 7.2$ Hz, 6H, aryl-*H*), 7.69 – 7.71 (m, 2H, H_β), 7.79 – 7.81 (d, $J = 6.8$ Hz, 4H, aryl-*H*), 7.86 – 7.88 (m, 2H, aryl-*H*), 8.06 – 8.07 ppm (d, $J = 4.8$ Hz, 2H, H_β). – ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.2, 55.3, 113.1, 113.3, 119.1, 119.2, 119.5, 120.0, 123.9, 124.9, 125.5, 126.4, 126.6, 126.9, 127.3, 127.4, 127.5, 127.6, 127.9, 128.1, 128.3, 128.5, 128.7, 128.8, 130.1, 130.4, 134.2, 134.3, 134.5, 135.7, 137.1, 141.2, 142.7, 143.4, 149.7, 150.3, 150.7, 151.5, 152.7, 153.1, 153.8, 154.4, 157.7, 157.9, 163.9 ppm. – UV/Vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$) = 410 (5.46),

513 nm (5.54). – HRMS (MALDI): m/z = 1518.3477 (calcd. 1518.3505 for $[C_{96}H_{62}N_8O_4Zn_2]$).

*Synthesis of trimer **11***

Bromoporphyrin **10** (48 mg, 0.07 mmol) and dimer **9** (129 mg, 0.07 mmol) were added to a 25 mL Schlenk flask and dried under high vacuum. Anhydrous toluene (7 mL) and (*o*-Tol)$_3$P (4.5 mg, 0.01 mmol) were added, and the solution was degassed by three freeze-pump-thaw cycles. $Pd_2(dba)_3$ (4.3 mg, 0.005 mmol,) and *N*,*N*-dicyclohexylmethylamine (0.08 mL, 0.35 mmol) were added to the flask, and the mixture was stirred at 120 °C for 24 h in the dark. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2. This solution was passed through silica gel using *n*-hexane-CH_2Cl_2 = 10 : 1 (v/v) in order to separate a first orange fraction, the green fraction (dimers in excess) and the brown fraction (trimer). Then, the organic solvents were evaporated. To isolate **11**, preparative TLC (silica) was used (*n*-hexane-CH_2Cl_2 = 5 : 1, v/v). Yield (2 mg, < 2%). R_f = 0.31 (*n*-hexane-CH_2Cl_2 = 3 : 1, v/v). – HRMS (MALDI): m/z = 1802.3781 (calcd. 1802.3750 for $[C_{116}H_{68}N_{12}Ni_3]$).

Acknowledgement

This work was supported by grants from Science Foundation Ireland (SFI P.I. 09/IN.1/B2650 and 12/TIDA/B2381).

[1] T. D. Lash, *J. Porphyrins Phthalocyanines* **2001**, *5*, 267.
[2] M. O. Senge, *Chem. Commun.* **2011**, *47*, 1943.
[3] V. V. Roznvatovskiy, C. H. Lee, J. L. Sessler, *Chem Soc. Rev.* **2013**, *42*, 1921.
[4] A. Nakano, N. Aratani, H. Furuta, A. Osuka, *Chem. Commun.* **2001**, 1920.
[5] T. S. Balaban, *Acc. Chem. Res.* **2005**, *38*, 612.
[6] H. Shinokubo, A. Osuka, *Chem. Commun.* **2009**, 1011.
[7] M. Mizumura, H. Shinokubo, A. Osuka, *Angew. Chem. Int. Ed.* **2008**, *47*, 5378.
[8] D.-M. Shen, C. Liu, Q.-Y. Chen, *Chem. Commun.* **2005**, 4982.
[9] A. K. Sahoo, S. Mori, H. Shinokubo, A. Osuka, *Angew. Chem. Int. Ed.* **2006**, *45*, 7972.
[10] R. C. Larock, M. J. Doty, Q. Tian, J. M. Zenner, *J. Org. Chem.* **1997**, *62*, 7536.
[11] G. Wu, A. L. Rheingold, S. J. Geib, R. F. Heck, *Organometallics* **1987**, *6*, 1941.
[12] S. Tokuji, Y. Takahashi, H. Shinmori, H. Shinokubo, A. Osuka, *Chem. Commun.* **2009**, 1028.
[13] A. A. Ryan, M. O. Senge, *Eur. J. Org. Chem.* **2013**, 3700.
[14] N. Hoffmann, *Chem. Rev.* **2008**, *108*, 1052.
[15] V. G. Kharchenko, L. I. Markova, O. V. Fedotova, N. V. Pchelintseva, *Khim. Geterot. Soed.* **2003**, 1283; *Chem. Heterocycl. Comp.* **2003**, *39*, 1121.
[16] C. G. Overberger, J. J. Monagle, *J. Am. Chem. Soc.* **1956**, *78*, 4470.
[17] X. Huang, J. Dou, D. Li, D. Wang, *J. Chil. Chem. Soc.* **2009**, *54*, 20.
[18] J. A. VanAllan, G. A. Reynolds, *J. Org. Chem.* **1968**, *33*, 1102.
[19] T. S. Balaban, A. T. Balaban in *Science of Synthesis; Houben-Weyl Methods of Molecular Transformations*, Vol. 14, Georg Thieme Verlag, Stuttgart, **2003**, chapter 14.1, pp. 11 – 200.
[20] A. T. Balaban, T. S. Balaban in *Science of Synthesis Knowledge Updates*, Vol. 2013/3 (Eds.: E. J. Thomas, A. P. Dobbs), Georg Thieme Verlag, Stuttgart, **2013**, section 14.1.5, pp. 145 – 216.
[21] A. A. Ryan, S. Plunkett, A. Casey, T. McCabe, M. O. Senge, *Chem. Commun.* **2014**, *50*, 353.
[22] M. O. Senge, Y. M. Shaker, M. Pintea, C. Ryppa, S. S. Hatscher, A. Ryan, Y. Sergeeva, *Eur. J. Org. Chem.* **2010**, 237.