

Fused porphyrinoids as promising near-infrared absorbing dyes

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Various aromatic segments have been fused onto the porphyrin periphery to create porphyrinoids that have expanded π -conjugated networks and thus exhibit red-shifted absorption spectra. Fused coplanar porphyrin oligomers, represented by *meso-meso*, β - β , β - β triply linked porphyrin arrays (porphyrin tapes), are endowed with more red-shifted absorption spectra and better nonlinear optical properties. These fused porphyrinoids have emerged as promising near-infrared (NIR) absorbing dyes, pointing to future applications such as conducting wire, NIR emitter, photovoltaics, and nonlinear optical materials. Developments of the fused porphyrinoid chemistry are reviewed in this feature article with focus on the synthesis, the relationships between their absorption spectra and molecular structures, and the applications in materials science.

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I Introduction

Porphyrin is a square planar macrocycle consisting of four pyrroles and four methine carbons, along which an 18π -electronic conjugated network can be delineated. Porphyrin is thus one of the typical aromatic molecules, as indicated by its strong diatropic ring current. Porphyrin displays high absorbance in the visible region owing to a Soret band around 400 nm and Q-bands around 500–600 nm. Natural photosynthetic pigments such as chlorophylls and bacteriochlorophylls are also 18π aromatic macrocycles, absorbing light in more red regions up to around 660 and 770 nm, respectively. These pigments have been extensively studied in order to understand their roles in

photosynthesis. With these backgrounds, both natural and artificial porphyrinic pigments have been extensively examined in diverse fields including artificial photosynthesis, oxidation catalysts, oxygen-reducing catalysts, molecular recognition, and materials science.¹

Recent studies revealed that the electronic properties of porphyrins were quite flexible and strongly perturbed by conjugative peripheral modifications. Among such modifications, the peripheral fusion reactions are quite effective for electronic perturbations and hence the reactions realise large red-shift of the absorption spectra; the Q-bands are indeed shifted to the NIR region in some cases. Not only the absorption spectra but also the nonlinear optical properties for fused porphyrinoids are largely perturbed. Typically, the two-photon absorption (TPA) cross-sections are distinctly enhanced. Naturally, the recent demand for NIR dyes has driven the synthetic chemistry of fused porphyrinoids at a remarkable rate, pointing potential

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applications in NIR electroluminescence displays, nonlinear optical materials, photodynamic therapy, and molecular electronics.^{2–11} In this feature article, the developments of fused porphyrinoids are reviewed with focus on the synthesis, the relationships between their absorption spectra and molecular structures, and the applications in materials science. From a structural viewpoint, fused porphyrins are classified into (a) β,β fusion type, (b) *meso*-Ar, β fusion type, (c) *meso*, β fusion type, and (d) β ,*meso*, β fusion type (Fig. 1). Although the fusion type largely influences the electronic perturbation in the fused porphyrins, the entity and number of fused aromatic segments and the central metal in the porphyrin cavity are also important.

II Porphyrins fused to aromatic hydrocarbons and heterocycles

Fusing an aromatic hydrocarbon or aromatic heterocycle directly onto the porphyrin periphery is an effective means to expand the π -conjugated electronic network of porphyrins. Fusion reaction provides covalent connection between the porphyrin and the aromatic segment and, at the same time, forces a coplanar conformation of the porphyrin and fused aromatic segment, which assures the increased electronic interactions better than those in singly linked precursors.

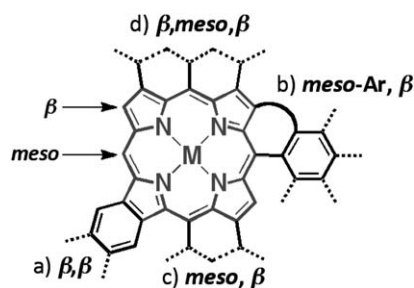


Fig. 1 Fusion types of porphyrin.



Atsuhiko Osuka received a PhD from Kyoto University in 1982. In 1979, he started his academic career at Ehime University as an Assistant Professor. In 1984, he came back to Kyoto University, where he has been a Professor since 1996. His research interests cover many aspects of synthetic approaches toward novel porphyrin-related compounds with intriguing structures, properties, and functions, which were

recognized with the Chemical Society of Japan Award in 2010. Representative molecules explored in his laboratory include artificial photosynthetic reaction center models, *meso*-*meso*-linked porphyrin arrays, porphyrin tapes, expanded porphyrins, sub-porphyrins, and Möbius aromatic and antiaromatic molecules.

(i) β,β Arene-fused porphyrins

A simple example of β,β arene-fused porphyrins is tetrabenzoporphyrin **1**, in which four benzene rings are directly fused onto all the β -positions.^{12,13} While there are so many examples of β,β arene-fused porphyrins covering mono-fused, di-fused, tri-fused, and tetra-fused ones, only tetraarene-fused examples are taken up in this review due to the limited space. Thus, β,β arene-fused porphyrins synthesised by Diels–Alder reaction and 1,3-dipolar cycloadditions⁶ are not taken up here. Tetrabenzoporphyrin **1** was first prepared in *ca.* 30% yield by zinc ion templated condensation of isoindolinone-3-acetic acid at 350 °C (Fig. 2).^{12,14}

A more convenient synthetic route has been developed by using arene-annulated pyrroles prepared by Barton–Zard

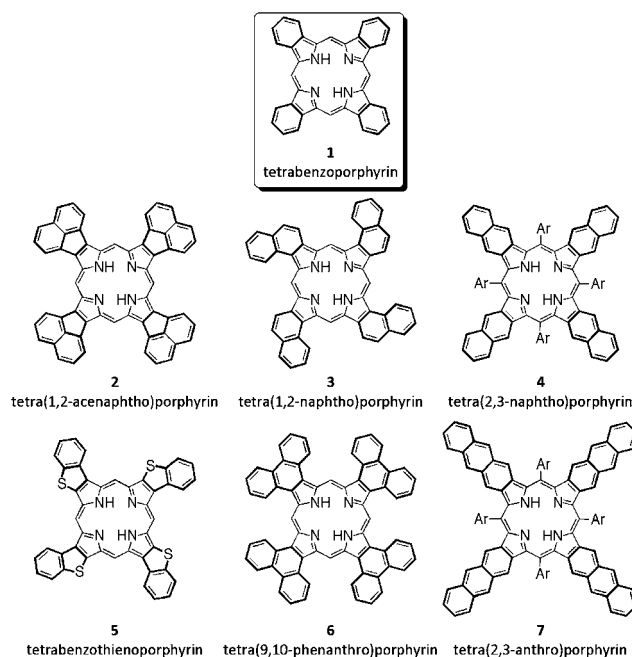
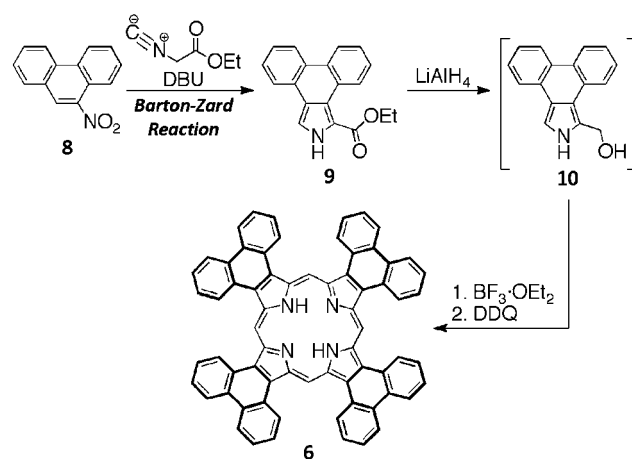
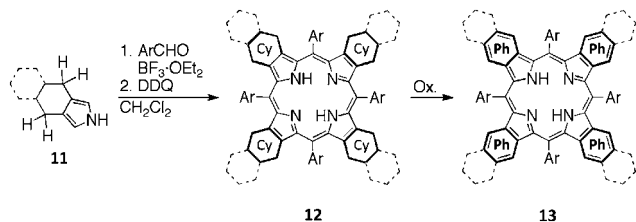


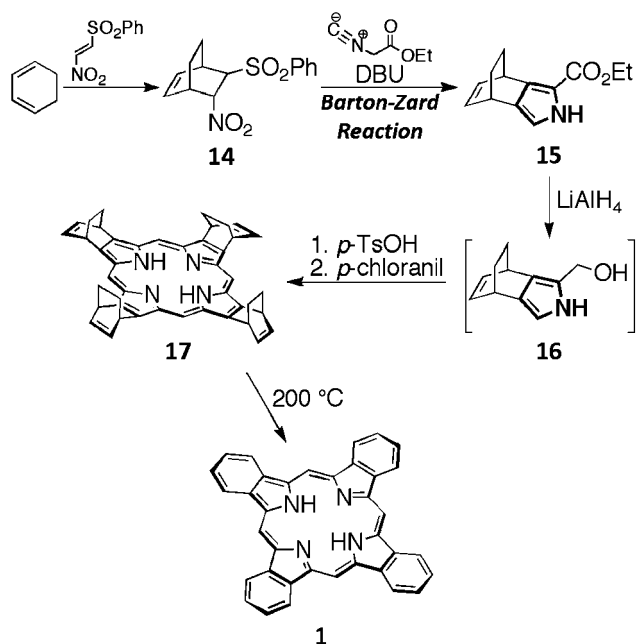
Fig. 2 β,β Arene-fused porphyrins.



Scheme 1 Synthesis of 9,10-phenanthrene-fused porphyrin **6**.



Scheme 2 Synthesis of β,β arene-fused porphyrins via the oxidative aromatization strategy.



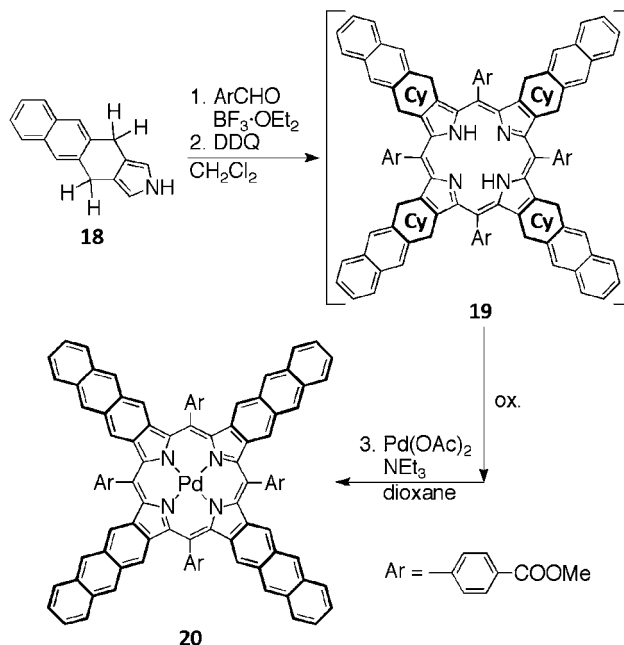
Scheme 3 Synthesis of tetrabenzoporphyrin **1** via the retro-Diels-Alder strategy.

reactions of nitroaromatic compounds with isocynoacetates.¹⁵ This chemistry has been mainly developed by Lash *et al.*^{16,17} and Ono *et al.*^{18,19} independently. As a typical example, synthesis of tetraphenanthroporphyrin **6** is shown in Scheme 1. Barton-Zard reaction of 9-nitrophenanthrene **8** with ethyl isocynoacetate gave phenanthropyrrole **9** in 78% yield. The ester group of **9** was reduced with LiAlH_4 to corresponding alcohol **10**, which was in turn tetramerised with $\text{BF}_3 \cdot \text{OEt}_2$ in CH_2Cl_2 followed by the oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to provide **6** in 13% yield.²⁰

Oxidative aromatization routes to these tetrabenzoporphyrins and tetranaphthoporphyrins were developed by Vinogradov *et al.* (Scheme 2).^{21–25} Pyrroles **11** carrying a fused cyclohexane ring were prepared by Barton-Zard reaction and subsequent decarboethoxylation, and then pyrroles were condensed to give porphyrins **12**, which were oxidatively aromatized to fused porphyrins **13**. The phosphorescence quantum yields of these $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$ complexes were reported to reach as high as 20–50%. Taking advantage of these phosphorescence properties, these complexes were proposed to serve as a tunable phosphorescent NIR oxygen indicator.²⁶

Ono *et al.* developed a smart retro-Diels-Alder strategy, in which β,β arene-fused porphyrins were produced by retro-Diels-Alder reactions of soluble bicyclo[2.2.2]octadiene-fused precursors.^{27,28} Synthesis of tetrabenzoporphyrin **1** is shown in Scheme 3. Barton-Zard reaction of β -nitro sulfone **14** with ethyl isocynoacetate gave ethyl 4,7-dihydro-4,7-ethano-2*H*-isindole-1-carboxylate **15**, which was reduced by LiAlH_4 to the corresponding alcohol **16**. The alcohol **16** was condensed with *p*-TsOH and subsequently oxidized to porphyrin **17** in ca. 30% yield. Upon heating at 200 °C, **17** was converted to **1** in 100% yield. Remarkably, the retro-Diels-Alder reactions proceeded quantitatively. While tetrabenzoporphyrin **1** is an extended planar molecule and is only poorly soluble in common organic solvents, its precursor **17** is quite soluble in many organic solvents and can be strictly purified (>99.9%) through silica-gel chromatography. In addition, **17** formed a homogeneous spin-coat film, which was converted to a film of **1** by simple heating at 210 °C through the retro-Diels-Alder reaction. Organic field-effect transistor (OFET) performance of this film recorded: mobility $\mu = 0.017 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, threshold voltage $V_{\text{th}} = -0.3 \text{ V}$ and $I_{\text{ON}}/I_{\text{OFF}} = 1 \times 10^5$.^{28–30} This intriguing chemistry was recently used for the organic photovoltaic device based on a solution-processable three-layer p-i-n structure that displayed 5.2% power-conversion efficiency (PCE).²⁹

Tetranaphthoporphyrins **4**^{25,30,31} and tetraanthroporphyrins **7**^{32,33} were also prepared by the retro-Diels-Alder strategy, which showed the Q-bands around 773 nm and 800 nm, respectively. While **4** is relatively stable in solution under air, **7** is rather unstable, probably due to facile oxidative degradation. Nevertheless, the $\text{Pd}(\text{II})$ complex **20**, which was prepared by the oxidative aromatization method (Scheme 4), was used for up-conversion on the basis of energetically conjoined triplet-triplet annihilation. Namely, the excitation at $\lambda = 790 \text{ nm}$ (full-width at

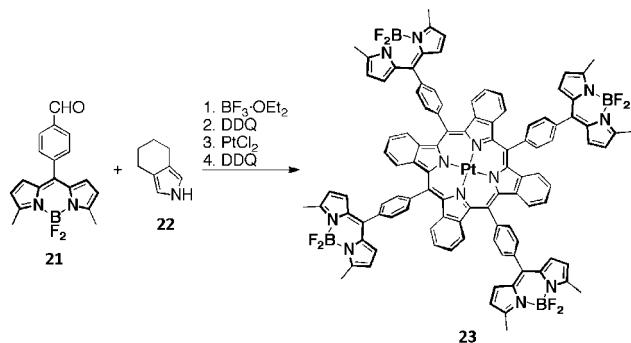


Scheme 4 Synthesis of tetraanthroporphyrin $\text{Pd}(\text{II})$ complex **20**.

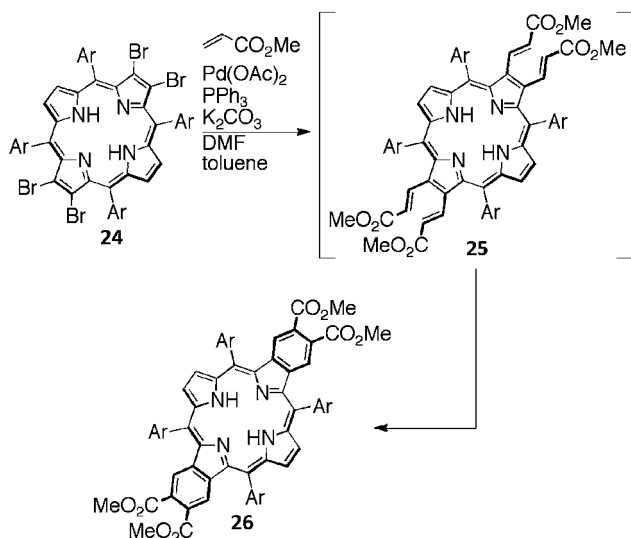
half maximum; fwhm ~ 23 nm) of a solution of **20** and rubrene (emitter) resulted in the fluorescence at 570 nm (fwhm ~ 65 nm).³³

BODIPY-appended benzoporphyrin platinum complex **23** was prepared by the oxidative aromatisation method (Scheme 5) and was shown to exhibit efficient NIR phosphorescence ($\lambda_{\text{em}} = 772$ nm, $\Phi_{\text{p}} = 0.26$) from a long-lived equilibrated state, $^3(\text{BODIPY})^*\text{-Por} \rightleftharpoons \text{BODIPY-}^3(\text{Por})^*$, that was formed *via* complex intramolecular excitation energy transfer reactions.³⁴

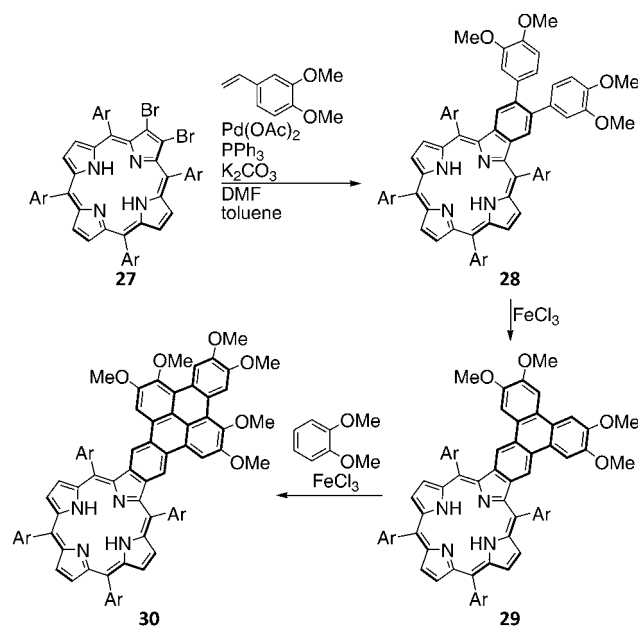
A new synthetic method of benzoporphyrins was reported, in which 2,3,12,13-tetrabromoporphyrin **24** reacted with an excess amount of methyl acrylate in the presence of the *in situ* generated Pd(0) catalyst at 128 °C for three days under a strictly inert atmosphere to produce *opp*-dibenzoporphyrin **26** ($\lambda_{\text{max}} = 611$ nm in CH_2Cl_2) probably *via* intermediate **25** (Scheme 6).³⁵ Interestingly, the oxidative aromatisation proceeded in one-pot. This approach was extended to the synthesis of triphenylene-fused porphyrin **29** ($\lambda_{\text{max}} = 587$ nm in CH_2Cl_2) and dibenzo[*fg,op*]tetracene-fused porphyrin **30** ($\lambda_{\text{max}} = 613$ nm in CH_2Cl_2) (Scheme 7).³⁶ *opp*-Dibenzoporphyrins have been examined as a pigment in a dye-sensitised solar cell, recording the device performance in the range of 1.54–3.14%.³⁷



Scheme 5 Synthesis of BODIPY-appended benzoporphyrin Pt(II) complex **23**.



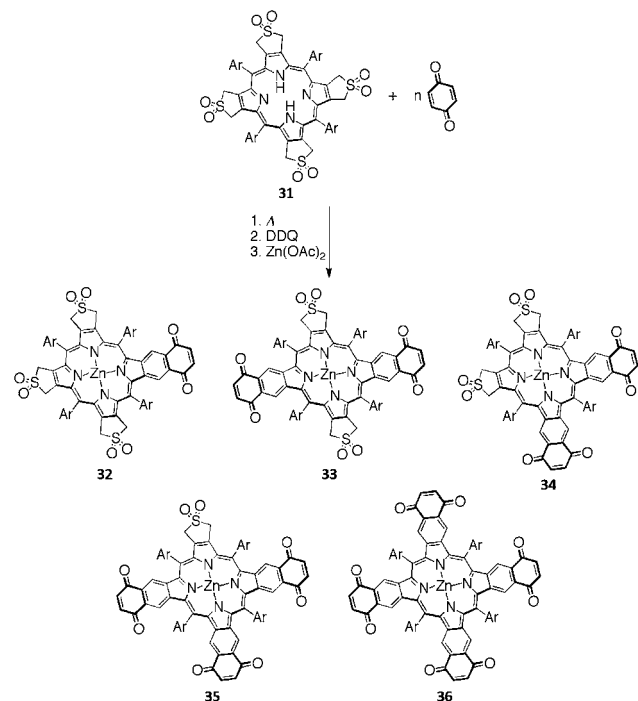
Scheme 6 Synthetic approach to β,β' -fused porphyrin *via* Heck-type coupling.



Scheme 7 Synthesis of triphenylene-fused porphyrin **29** and dibenzo[*fg,op*]tetracene-fused porphyrin **30**.

Naphthoquinone-fused porphyrins **32–36** were prepared by Kräutler *et al.* through the thermal reaction of a β,β' -tetrasulfonoporphyrin with 1,4-benzoquinone (Scheme 8). These fused porphyrins were called “black porphyrins” since they absorb light in the visible range with substantial absorbance.³⁸

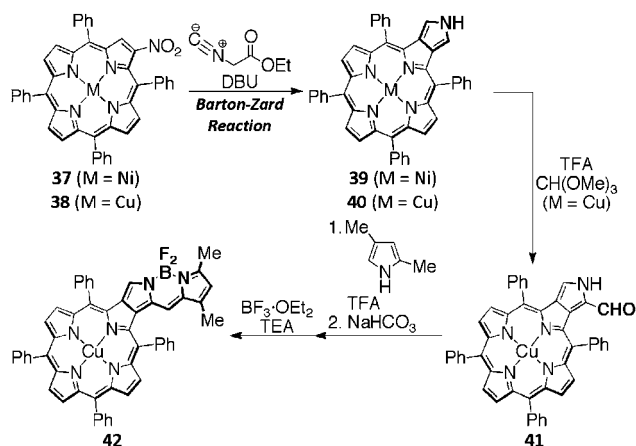
Barton–Zard reaction was applied to 2-nitro-tetraphenyl Ni(II) porphyrin **37**. Namely, the reaction of **37** with ethyl isocynoacetate in a 10 : 1 mixture of THF–isopropyl alcohol using



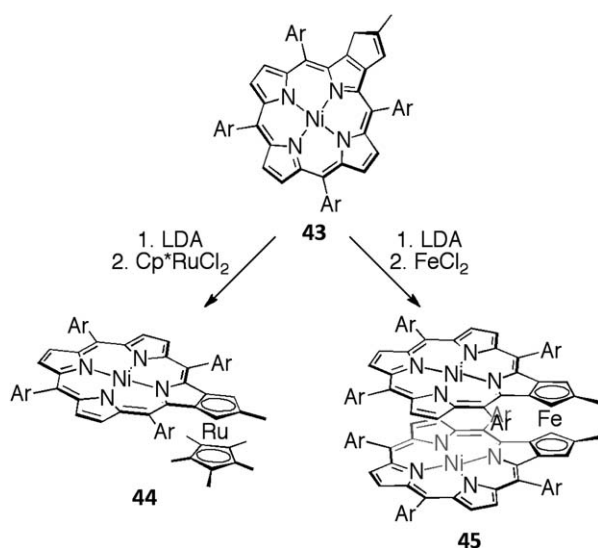
Scheme 8 Synthesis of “black porphyrins”.

DBU as a base afforded fused pyrroloporphyrin **39** ($\lambda_{\text{max}} = 604$ nm in CH_2Cl_2) in 40% yield.³⁹ Similar Barton–Zard reaction of **38** gave fused pyrroloporphyrin Cu(II) complex **40**, which was regioselectively formylated at the α -position of the pyrrole with $\text{CH}(\text{OMe})_3$ and TFA to give formylated product **41**. Condensation of **41** with 2,4-dimethylpyrrole followed by treatment with $\text{BF}_3 \cdot \text{OEt}_2$ and TEA gave BODIPY-fused Cu(II) porphyrin **42** ($\lambda_{\text{max}} = 675$ nm in CH_2Cl_2) (Scheme 9).⁴⁰

Although there have been many reports on metallocene-appended porphyrins at *meso*-position, directly metallocene-fused porphyrins still remain quite rare. In 2001, Smith and co-workers reported β, β' -ruthenocene-fused porphyrin **44** and ferrocenoporphyrin dimer **45** from cyclopentadiene-fused porphyrin **43** as a key precursor. **43** was prepared from *in situ* generated Pd(0) catalysed [3 + 2] cycloaddition of **37** with 2-[(trimethylsilyl)methyl]-2-propen-1-yl acetate followed by thermal elimination of nitrous acid and acid-catalysed double bond migration (Scheme 10).⁴¹



Scheme 9 Synthesis of pyrroloporphyrin **39** and **40**, and BODIPY-fused porphyrin **42**.



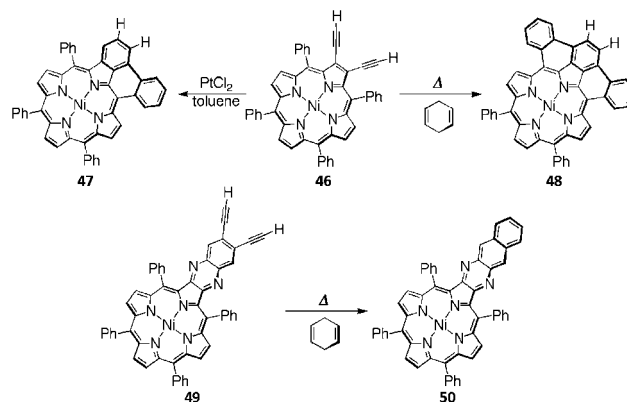
Scheme 10 Synthesis of metallocene-fused porphyrins.

Bergman cyclisation of β, β' -diethynylporphyrin **46** was reported by Smith *et al.* in 2001.⁴² Under these conditions (5% 1,4-cyclohexadiene in chlorobenzene at 190 °C), an unexpected tandem radical cyclisation with the adjacent *meso*-phenyl groups proceeded, giving picenoporphyrin **48** in 89% yield ($\lambda_{\text{max}} = 629$ nm in CH_2Cl_2). Extension of this strategy to porphyrinic enediyne **49** afforded **50** ($\lambda_{\text{max}} = 660$ nm in CH_2Cl_2) in 92% yield.⁴³ Although harsh conditions were necessary in the initial cases, Zaleski *et al.* reported that the addition of DDQ as a hydrogen atom acceptor accelerated the Bergman cyclisation under the milder conditions (stirring for 30 min at room-temperature).⁴⁴ The dependence of the cyclisation on the alkyne terminal group as well as the photo-induced cyclisation was carefully studied.^{45,46} Later, the same group reported that the heating of **46** in the presence of PtCl_2 in toluene at 85–90 °C gave a different fused product **47** ($\lambda_{\text{max}} = 610$ nm in CH_2Cl_2) in 35–48% yield (Scheme 11).^{47,48}

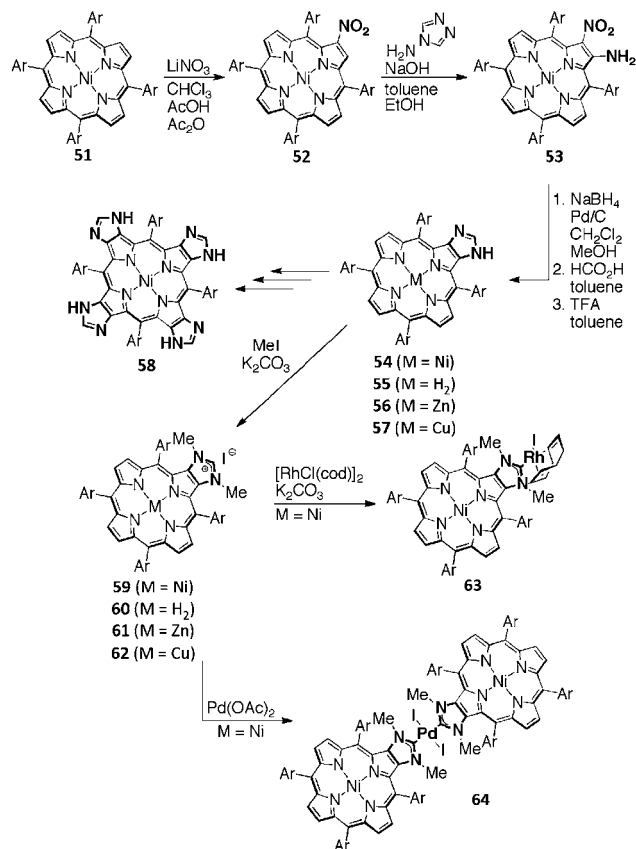
Richeter *et al.* attempted the synthesis of *N*-heterocyclic carbene (NHC)-fused porphyrins by following the reaction route shown in Scheme 12. Tetrakis(4-*tert*-butylphenyl) Ni(II) porphyrin **51** was nitrated with LiNO_3 in a mixture of acetic acid and acetic anhydride to afford **52**, which was reacted with 4-amino-4*H*-1,2,4-triazole to give **53**. Subsequent reduction of **53** with NaBH_4 and Pd/C followed by condensation with $\text{HC}(\text{OMe})_3$ furnished imidazole-fused Ni(II) porphyrin **54**, which was converted to the corresponding free base **55**, Zn(II) porphyrin **56** and Cu(II) porphyrin **57**, and then to imidazolium salts **59**, **60**, **61** and **62**, respectively. These salts were used for the construction of externally metalated complexes such as Rh(I) complex **63** and Pd(II) bridged dimer **64**.^{49–51} These molecules may find applications as a tunable reaction catalyst. They also reported more fusion of imidazole groups onto the peripheral β -positions, and finally succeeded in the full fusion of four imidazole rings to give **58**, which is expected as a key precursor of square grid polymeric network materials.⁵²

(ii) *meso, \beta* Arene-fused porphyrins

As in earlier examples, *meso*-(formylvinyl) Ni(II) porphyrin **65** was treated with strong acids such as concentrated sulfuric acid to afford Ni(II) benzochlorin **67** ($\lambda_{\text{max}} = 677$ nm in CHCl_3) in



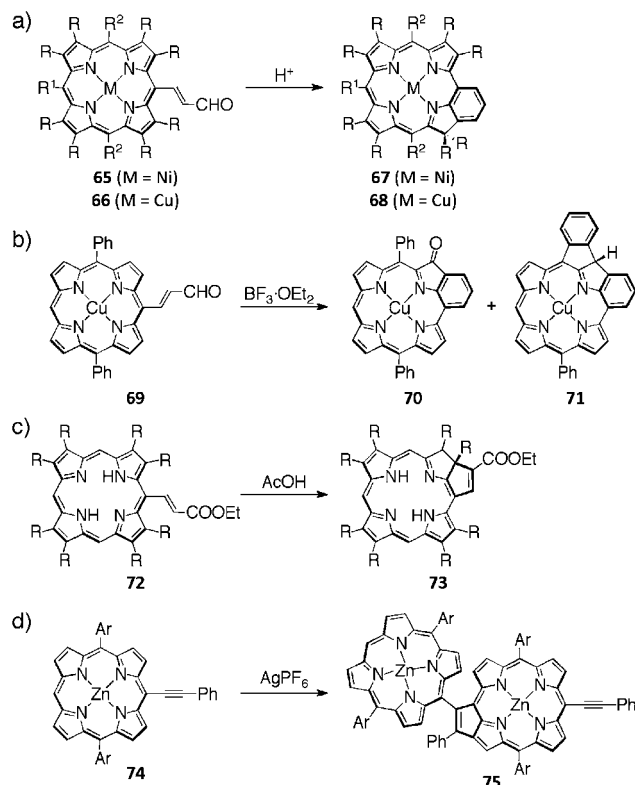
Scheme 11 Bergman-type cyclisation of enediyne porphyrins.



Scheme 12 Synthesis of imidazole-fused porphyrins and their NHC-type peripheral metal complexes.

moderate yield through the intramolecular Friedel–Crafts acylation and 1,2-alkyl rearrangement (Scheme 13a).^{53–56} Later, the corresponding Cu(II) complexes **66** were found to be cyclised upon treatment with Lewis acids such as $\text{BF}_3 \cdot \text{OEt}_2$ or SnCl_4 , and the resulting Cu(II) benzochlorins **68** were demetalated to the benzochlorin free bases.⁵⁷ When similar conditions were applied for 5,15-diphenyl Cu(II) porphyrin **69**, an oxobenzochlorin product **70** ($\lambda_{\text{max}} = 730 \text{ nm}$ in CHCl_3) and a doubly cyclised product **71** were obtained (Scheme 13b).⁵⁸ Different from the above examples, the acid treatment of *meso*-acrylate bearing porphyrins **72** provided purpurin products **73** that had a fused five-membered ring across the *meso*- and β -positions (Scheme 13c).^{59–63} An interesting example is that treatment of *meso*-(phenylethynyl) Zn(II) porphyrin **74** with AgPF_6 in CHCl_3 gave a porphyrin–dicyclopentadiene-fused porphyrin (dehydropurpurin) dyad **75** ($\lambda_{\text{max}} = 645 \text{ nm}$ in THF) in 34% yield (Scheme 13d).⁶⁴ These benzochlorins and purpurins are interesting in photodynamic therapy, since they possess significant photosensitising efficiency.⁶⁵ The tumour uptake was controlled by judicious choice of the peripheral substituents.

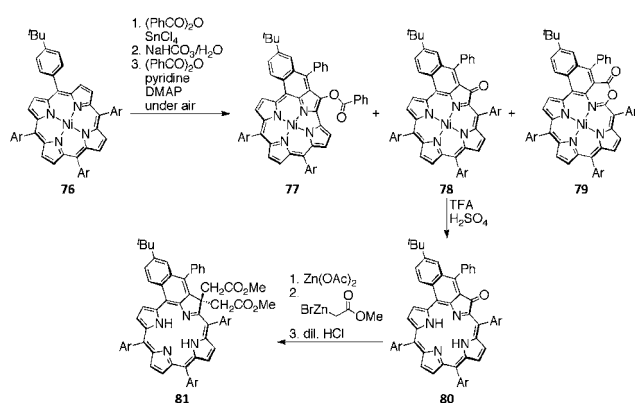
Intramolecular Friedel–Crafts acylation was used to create oxonaphthoporphyrins by Callot *et al.*^{3,66,67} Interestingly, Friedel–Crafts acylation of Ni(II) TPP **76** with aryl anhydrides followed by aerobic oxidation in the presence of pyridine, 4-dimethylaminopyridine, and excess anhydride produced ring-contracted naphthocorrole **77** ($\lambda_{\text{max}} = 760 \text{ nm}$ in CH_2Cl_2) in



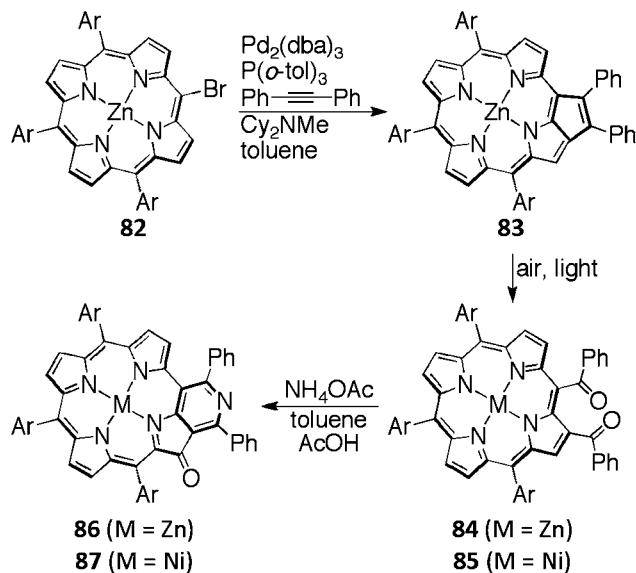
Scheme 13 Examples of fusion reaction between *meso*- and β positions.

addition to oxonaphthoporphyrin **78** and naphthoporpholactone **79**.^{68,69} They also investigated the effective conversion of **78** to naphthochlorin **81** by the Reformatsky reaction (Scheme 14).⁷⁰

Dehydropurpurins such as **83** were formed by Pd(0)-catalysed [3 + 2] annulation of bromoporphyrins **82** with internal alkynes.⁷¹ The peripherally introduced carbon–carbon double bond of **83** was quantitatively cleaved by exposure to air under room light, giving 3,5-dibenzoylporphyrin **84**. Treating **84** with NH_4OAc furnished a pyridine-fused porphyrinoid, oxypyridochlorin **85**. Compound **86** showed unique absorption bands



Scheme 14 Intramolecular Friedel–Crafts acylation of Ni(II) TPP with aryl anhydrides.

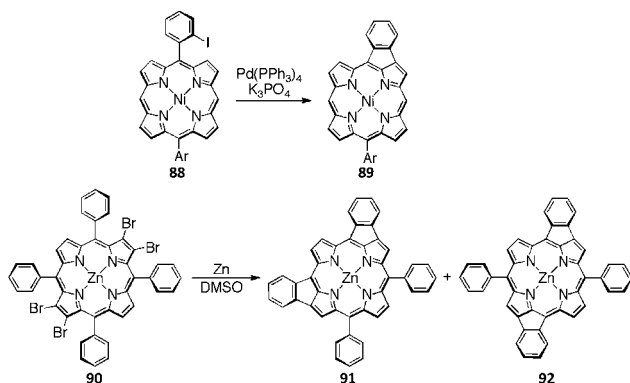


Scheme 15 Pd(0)-catalysed [3 + 2]-type annulation of **82** with internal alkyne and synthesis of oxopyridochlorin **86** and **87**.

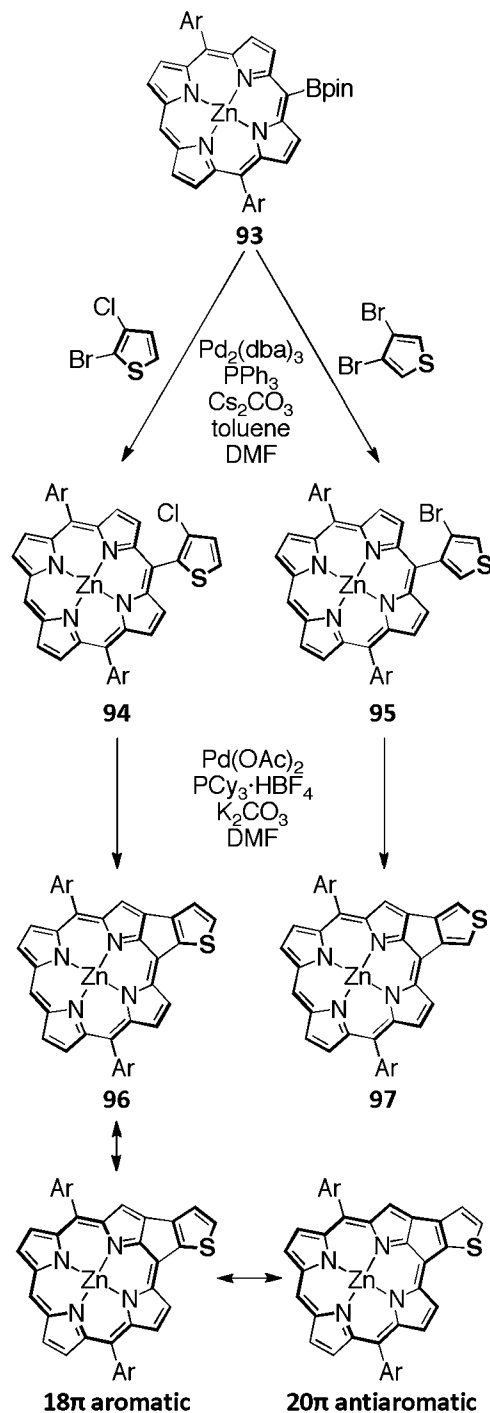
reaching into the NIR region in their neutral state ($\lambda_{\text{max}} = 767 \text{ nm}$ in CH_2Cl_2), which was perturbed by protonation (with TFA; $\lambda_{\text{max}} \sim 900 \text{ nm}$ in CH_2Cl_2) (Scheme 15).⁷²

Boyle *et al.* found that refluxing 5-(2-iodophenyl)-15-(4-methoxycarbonylphenyl)porphyrin Ni(II) complex **88** in the presence of $\text{Pd}(\text{PPh}_3)_4$ (10 mol%) and K_3PO_4 (10 equiv.) resulted in the formation of fused porphyrin **89**, possibly through an intramolecular C–H activation step (Scheme 16).^{73,74} A similar fusion reaction was also reported for an organozinc species. When 2,3,12,13-tetrabromoporphyrin **90** was heated in the presence of 50 equiv. of zinc in DMSO at 85°C , doubly fused products **91** and **92** were formed in moderate yields as an inseparable mixture.⁷⁵

Recently, thienoporphyrins **96** and **97** were prepared by Suzuki–Miyaura coupling and subsequent intramolecular Heck reactions. Comparison of the magnetic, optical, and electrochemical properties indicated that **96** has a larger antiaromatic contribution than **97** (Scheme 17).⁷⁶



Scheme 16 Examples of metal-mediated fusion reaction.



Scheme 17 Thiophene-fused porphyrins **96** and **97**.

Pyrene-fused porphyrin **98** ($\lambda_{\text{max}} = 724 \text{ nm}$ in CHCl_3) was prepared by the oxidation of *meso*-(1-pyrenyl)porphyrin Ni(II) complex with $\text{PhI}(\text{OTf})_2$ and $\text{BF}_3\cdot\text{OEt}_2$ in 65% yield (Fig. 3).⁷⁷ The corresponding Zn(II) complex was prepared by the combined use of DDQ and $\text{Sc}(\text{OTf})_3$. Naphthalene-fused porphyrins have been reported by several groups. In 2005, Cammidge *et al.* found the Pd-catalysed intramolecular ring-closure reaction of *meso*-(8-triflate-1-naphthyl)porphyrin to give naphthalene-fused porphyrin **99**.⁷⁸ *meso*-(1-Naphthyl)porphyrin

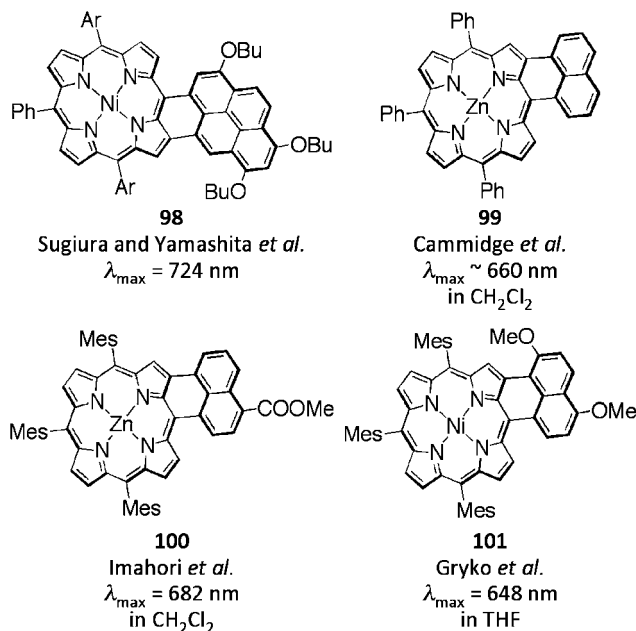


Fig. 3 Naphthalene- and pyrene-fused porphyrins.

derivatives **100** and **101** were prepared in 16% and 83% yields, respectively by the oxidative fusion reaction. $\text{Fe}(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ was recommended for chlorination-free oxidative fusion reaction.^{79,80} These results indicate the importance of the electron-donating groups of the *meso*-naphthyl group in the oxidative fusion reaction. These fused porphyrins exhibit the Q-bands at 648–682 nm.

Recently Wu *et al.* reported *N*-annulated-perylene-fused Zn(II) porphyrins **102** and **103** by the oxidative cyclisation with DDQ and $\text{Sc}(\text{OTf})_3$,⁸¹ and perylene monoimide-fused Ni(II) porphyrins **104** and **105** by the oxidation with FeCl_3 in nitromethane.⁸² The unexpected formation of **105** was ascribed to the high reactivity of the β -position in Ni(II) porphyrin. The fused porphyrins **102**

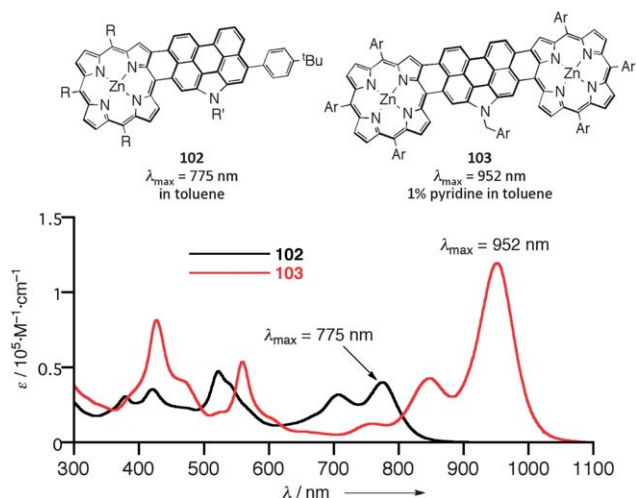


Fig. 4 UV/Vis/NIR absorption spectra of *N*-annulated perylene-fused porphyrins **102** and **103**.

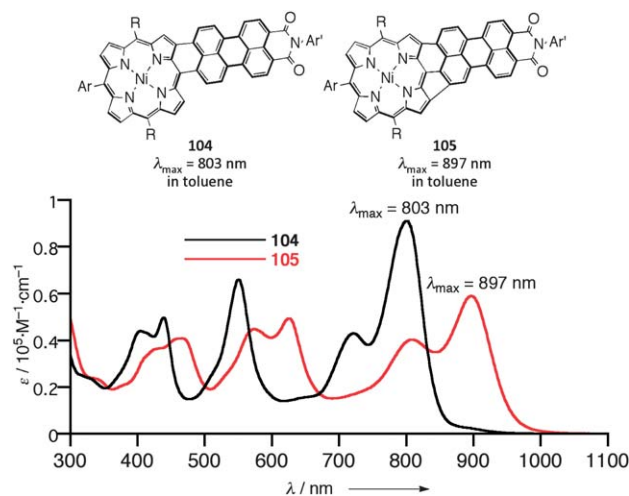
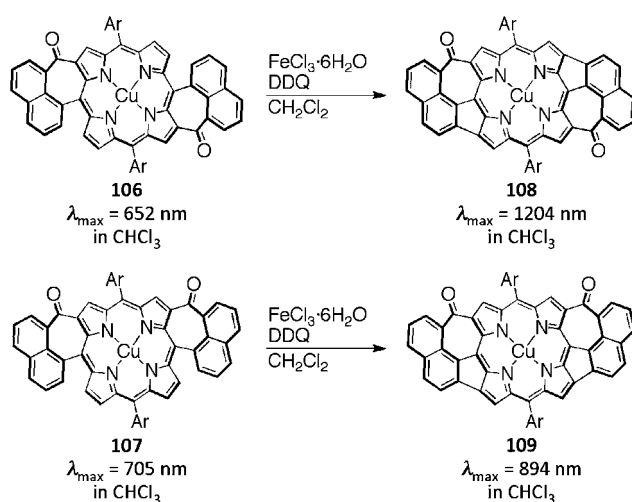


Fig. 5 UV/Vis/NIR absorption spectra of perylene monoimide-fused porphyrins **104** and **105**.

and **104** show red-shifted Q-bands in the NIR region at 775 and 803 nm (Fig. 4 and 5), respectively. The lowest Q-band of the triply linked porphyrin **105** is more red-shifted to 897 nm, and the dimer **103** displays an even more red-shifted Q-band at 952 nm.

(iii) β ,*meso*, β Arene-fused porphyrins

As a pioneering work, Scott *et al.* reported bis(naphthoazulen-8-one)-fused Cu(II) porphyrins as the first well characterised examples of triply linked systems in 2004 (Scheme 18). They synthesised these molecules from a porphodimethane bearing spiro-acenaphthenone moieties. The metalporphodimethane underwent photo-induced oxidative rearrangement in the presence of DDQ to form *cis*- and *trans* doubly linked porphyrins **106** and **107**, which show the Q-bands at 652 and 705 nm. These porphyrins were further oxidised with a combination of FeCl_3 /DDQ to give *meso*, β , β triply fused porphyrins, **108** and



Scheme 18 Naphthoazulenone-fused porphyrins.

109, respectively. Interestingly, while **109** shows a rather sharp and intense band at 894 nm, largely red-shifted and broad bands are observed in the NIR region for **108** ($\lambda_{\text{max}} = 1204$ nm). These results reveal the importance of an additional direct linkage for the further red-shifts of the Q-band. The observed more red-shifts for the *trans*-isomers can be ascribed to the larger transition dipole moments that reflect the molecular symmetry.⁸³

Anthracene-fused porphyrin **112** was tested by Anderson *et al.* for a panchromatic dye for dye-sensitised solar cells by using both titanium dioxide and tin oxide as the electron-transport materials.⁸⁴ They used porphyrins **110** and **111** as reference molecules (Fig. 6). While a solar cell incorporating **112** was shown to exhibit photocurrent collection at the wavelength up to 1100 nm, the device efficiency was low ($\eta < 0.1\%$). The low conversion efficiency was accounted for in terms of inefficient electron injection into the oxide.

Recently porphyrins attached to BODIPY through three direct C–C bonds, **113** and **114** have been synthesised by Wu *et al.* in a stepwise route (Fig. 7).⁸⁵ The effective π -conjugation of these molecules can be confirmed from the bathochromic shift

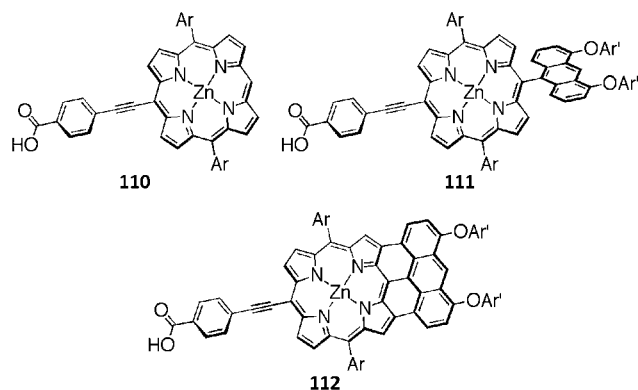


Fig. 6 Anthracene-fused porphyrin **112** for dye-sensitised solar cells and reference compounds **110** and **111**.

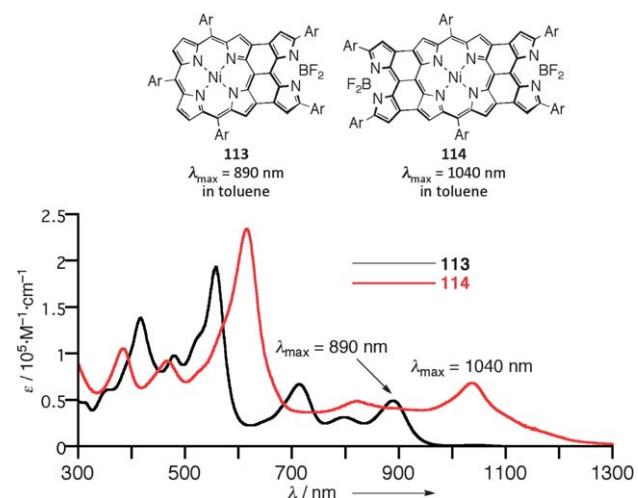


Fig. 7 UV/Vis/NIR absorption spectra of BODIPY-fused porphyrins **113** and **114**.

of absorption spectra ($\lambda_{\text{max}} = 890$ nm for **113** and 1040 nm for **114**). These values are larger than the corresponding azulene-fused porphyrins ($\lambda_{\text{max}} = 1014$ nm for **116**) and anthracene-fused porphyrins ($\lambda_{\text{max}} = 855$ nm for **118** and 973 nm for **119**), which illuminates the intrinsic potential of a BODIPY moiety in the bathochromic shift of absorptions.

(iv) Porphyrins fused to four aromatic segments

Given the D_{4h} symmetric square molecular shape of porphyrin, it may be possible to fuse four aromatic segments at all the four peripheries of porphyrin. However, such examples have been rather limited to date, due mainly to synthetic difficulty. Osuka *et al.* reported azulene-fused porphyrins, **115**, **116** and **117** in 2006 (Fig. 8).⁸⁶ These azulene-fused porphyrins show relatively broad absorption spectra in the NIR region ($\lambda_{\text{max}} = 855$ nm for **115**, 1014 nm for **116**, and 1136 nm for **117**). Anderson *et al.* reported anthracene-fused porphyrins, **118**, **119**, and **120**.^{87–89} As compared with the azulene-fused porphyrins, anthracene-fused porphyrins show sharper and more intense Q-bands ($\lambda_{\text{max}} = 855$ nm for **118**, 973 nm for **119**, and 1417 nm for **120**) (Fig. 9). Nearly planar structures of the quadruply fused porphyrins **117** and **120** have been revealed by X-ray single-crystal diffraction

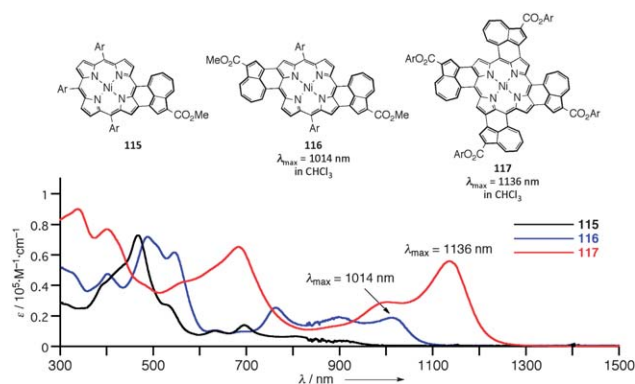


Fig. 8 UV/Vis/NIR absorption spectra of azulene-fused porphyrins **115**, **116**, and **117**.

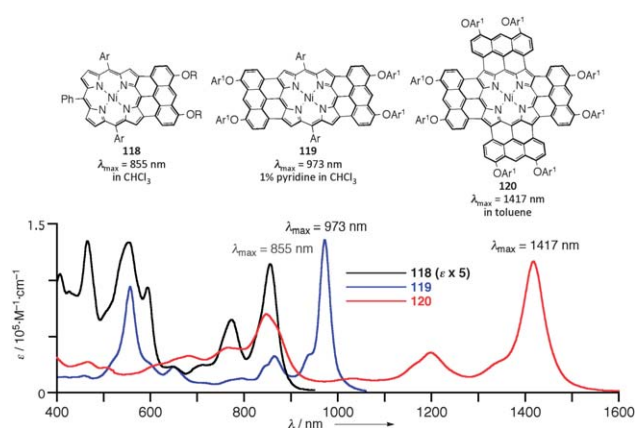


Fig. 9 UV/Vis/NIR absorption spectra of anthracene-fused porphyrins **118**, **119**, and **120**.

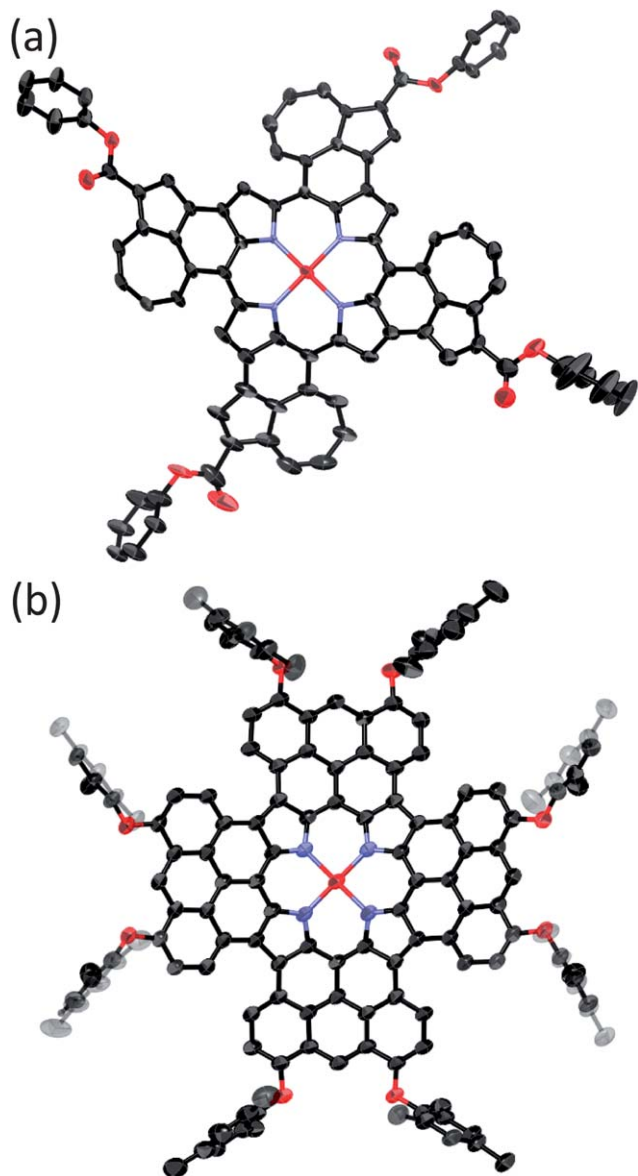


Fig. 10 X-ray crystal structures of (a) azulene-fused porphyrin **117** and (b) anthracene-fused porphyrin **120**.

analysis (Fig. 10). Here it is noteworthy that the synthesis of these tetraaromatics-fused porphyrins needs to overcome the intrinsic solubility problem of large planar fused products. Hence, large solubilising groups are implemented at the ester part in the case of **111** and **117**, and the 1,8-di(mesityloxy) anthracen-19-yl substituent was employed in the synthesis of **119** and **120** because of its aggregation-preventing steric hindrance and favorable reactivity in the oxidative fusion reaction.

(v) Thermal fusion of porphyrins with unactivated polycyclic aromatic hydrocarbons (PAHs)

Very recently, Thompson *et al.* developed the thermal C–H activation fusion process for porphyrins bearing unactivated *meso*-PAH groups.⁹⁰ Many PAHs such as naphthalene,

pyrene, coronene, and perylene were fused to porphyrins under these conditions. Importantly, this method was applied for Zn(II) and Mg(II) porphyrins that are usually not tolerated under Scholl conditions due to facile demetalation. Although fused products were isolated merely as a mixture of inseparable regioisomers, such a facile and strong fusion protocol would be a quite useful alternative in materials science.

III Fused porphyrin oligomers

Considerable attention has been focused on the exploration of extensively π -conjugated porphyrin oligomers.^{91–97} One of the reliable synthetic strategies is to bridge porphyrins with conjugative linkers such as ethene,⁹⁸ ethyne^{99,100} and butadiyne.^{101,102} Conjugated porphyrin oligomers prepared in this manner exhibit strongly perturbed optical and electronic properties and usually induce red-shifted absorption bands close to the NIR region. A different promising and straightforward method for the effective π -conjugation is to connect two porphyrins with multiple covalent bonds by which the overall structure is forced to be coplanar. Syntheses of large fused porphyrinoids often meet difficulties such as poor solubility and serious aggregation by π – π stacking, and facile oxidative degradation due to raised HOMO levels. Despite these difficulties, the range of fused porphyrin oligomers has been expanded in recent years.

(i) β – β Fused porphyrin oligomers

Porphyrin wire, defined as a one-dimensionally conjugated porphyrin oligomer with rigid and planar molecular shape, has been explored as an ideal molecular motif where the π -electrons can be fully delocalised over the entire molecule, thus allowing effective electronic connection between the two terminals bridged by porphyrin wires. Efforts have been devoted to synthesise β – β fused porphyrin oligomers. Representative examples are listed in Fig. 11. Crossley *et al.* reported doubly β – β pyrazinoquinoxaline-bridged porphyrin dimer **122** in 1987,^{103–107} and extended their strategy to the corresponding trimer and tetramer **123**,^{105,106} a L-shaped trimer,¹⁰⁶ and a switchable porphyrin dimer.¹⁰⁷ Smith *et al.* used **40** for the synthesis of **124**,^{111,112} and further extended their strategy to fused pentameric array **125**.¹¹³ Fused-benzene-bridged porphyrin dimer **121** was first synthesised by Kobayashi *et al.*, and later by Ono *et al.*^{108–110} The retro-Diels–Alder route developed by Ono *et al.* allowed a very facile and elegant access to this fused diporphyrin. Namely, the fused-benzene-bridged Zn(II) porphyrin dimer **130** ($\lambda_{\text{max}} = 636$ nm, CHCl₃ containing 1% pyridine) was effectively prepared by the retro-Diels–Alder reaction of the corresponding bicyclo[2.2.2]octadiene bridged porphyrin dimer **129** (Scheme 19).^{111,114} A coplanar fused-anthraquinone-bridged porphyrin dimer **127**¹¹⁵ ($\lambda_{\text{max}} = 663$ nm) was also prepared by the retro-Diels–Alder strategy. In this case, upon heating at 270–350 °C, the oxidative demethylation occurred concurrently. Uno and Ono *et al.* extended their retro-Diels–Alder strategy to

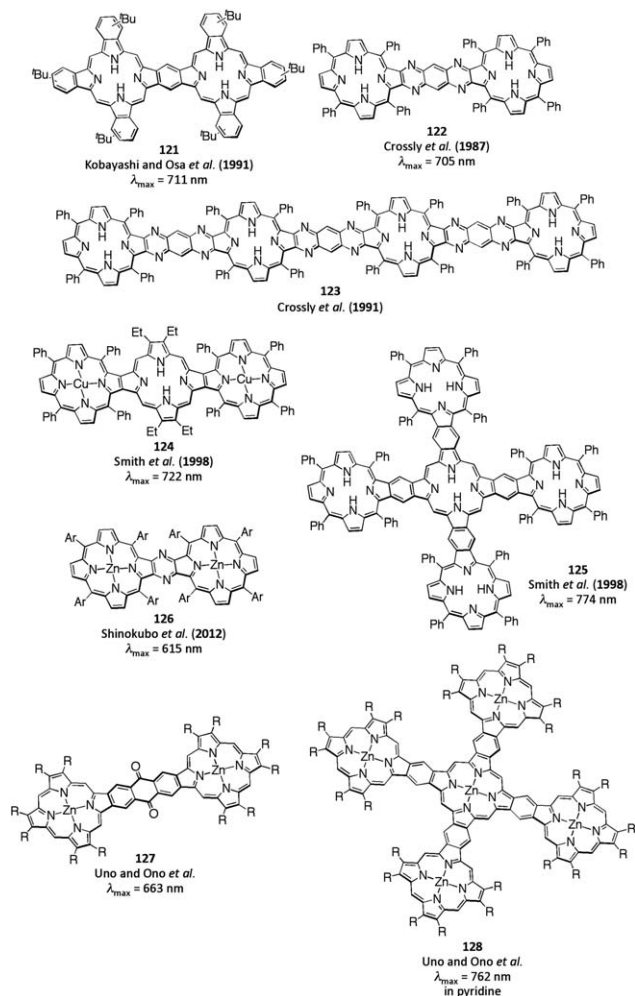
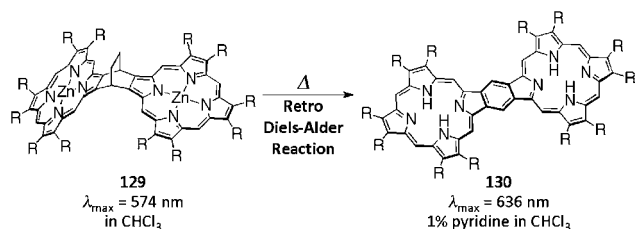
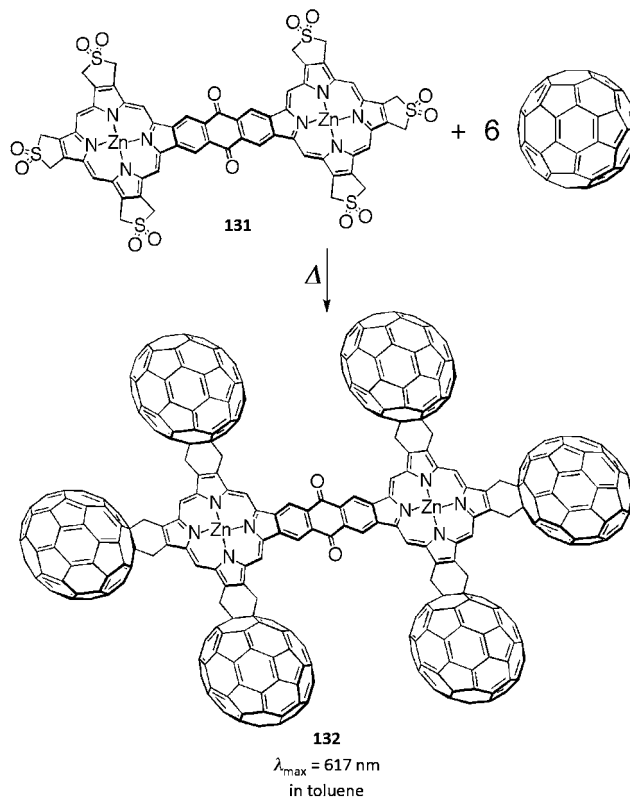


Fig. 11 Fused porphyrin oligomers.



Scheme 19 Synthesis of diporphyrin fused to a benzene unit via the retro-Diels-Alder strategy.

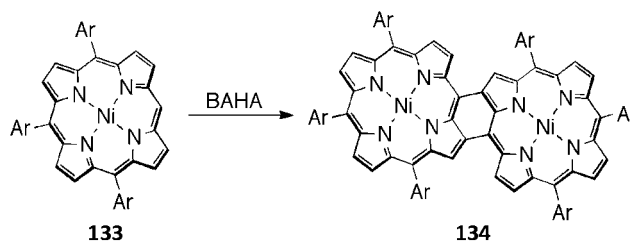
fused-benzene-bridged cruciform Zn(II) porphyrin pentamers **128** ($\lambda_{\text{max}} = 762 \text{ nm}$ in pyridine).¹¹⁰ Fused anthraquinone-bridged porphyrin dimer **131**, prepared by a subsequent Diels-Alder reaction, was subsequently converted to a hexafullenodiporphyrin **132** upon the cycloaddition reaction with C_{60} (Scheme 20).¹¹⁶ Very recently, Shinokubo *et al.* reported the synthesis of pyrazine-fused porphyrin dimer **126** by DDQ oxidation of β -aminoporphyrin.¹¹⁷ The synthesised dimer exhibits red-shifted Q-like bands reaching the NIR region, which may be appealing for materials science.



Scheme 20 Synthesis of a fullerene-appended diporphyrin bridged by fused anthraquinone.

(ii) *meso-meso*, β - β , β - β Triply linked porphyrin arrays (porphyrin tapes)

Osuka *et al.* have explored *meso-meso*, β - β , β - β triply linked porphyrin arrays (porphyrin tapes) by the oxidative doubly fusion reactions of singly *meso-meso* linked porphyrin arrays.^{10,11,117–121} These studies on the directly fused porphyrin arrays were initiated by a serendipitous finding that the oxidation of 5,10,15-triaryl Ni(II) porphyrins **133** with tris(4-bromophenyl)ammonium hexachloroantimonate (BAHA) gave *meso*- β doubly fused porphyrin dimer **134** ($\lambda_{\text{max}} = 756 \text{ nm}$ in CHCl_3) (Scheme 21).¹²² The oxidative fusion reaction of *meso-meso* linked porphyrin oligomers was first accomplished by using BAHA as an oxidant.¹²³ While porphyrin tapes were obtained in good yields, the concurrent peripheral chlorination at the porphyrin periphery was problematic. The use of hexafluorobenzene as a solvent led to significant suppression of the peripheral chlorination.¹²⁴ Later, a combination of DDQ with

Scheme 21 Synthesis of *meso*- β fused diporphyrins **134**.

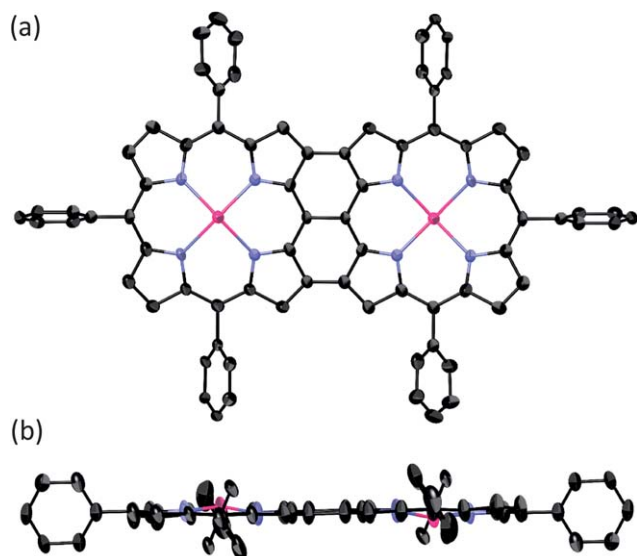


Fig. 12 X-ray crystal structure of a completely fused diporphyrin **136_2**.¹²⁶

$\text{Sc}(\text{OTf})_3$ was found to be a quite effective reagent to cause the clean oxidative fusion to afford triply linked porphyrin oligomers.¹²⁵ Fig. 12 shows the X-ray crystal structure of triply fused diporphyrin **136_2**.¹²⁶ The two $\text{Zn}(\text{II})$ porphyrin units are completely coplanar with a mean-plane deviation value of 0.051 Å.

The linear porphyrin tapes **136_n** were synthesised and characterised up to dodecamer **136_12** in the first report,¹²⁵ and later were extended to 24-mer with the help of bulky *meso*-substituents.¹²⁷ The absorption red-shift in a series of triply fused porphyrin tape is remarkable, reaching deeply into the IR region (Fig. 13). These spectra have been interpreted in terms of the effective π -conjugation along the longer molecular axis.

Two-dimensionally extended porphyrin oligomers such as L-shaped trimer **137**, T-shaped tetramer **139**, and even square-shaped tetramer (porphyrin sheet) **138** were prepared (Fig. 14).^{128,129} The porphyrin sheet **138** holds the central cyclo-octatetraene (COT) core that is forced to be planar. Probably because of this structure, **138** exhibits a strong paratropic ring current.¹²⁹ Dimeric porphyrin tapes were prepared by other

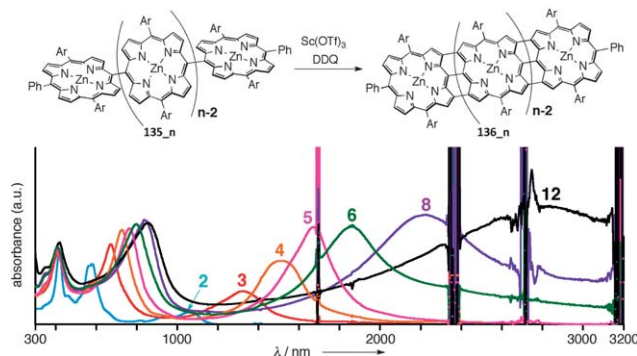


Fig. 13 UV/Vis/IR absorption spectra of porphyrin tapes **136_n**.

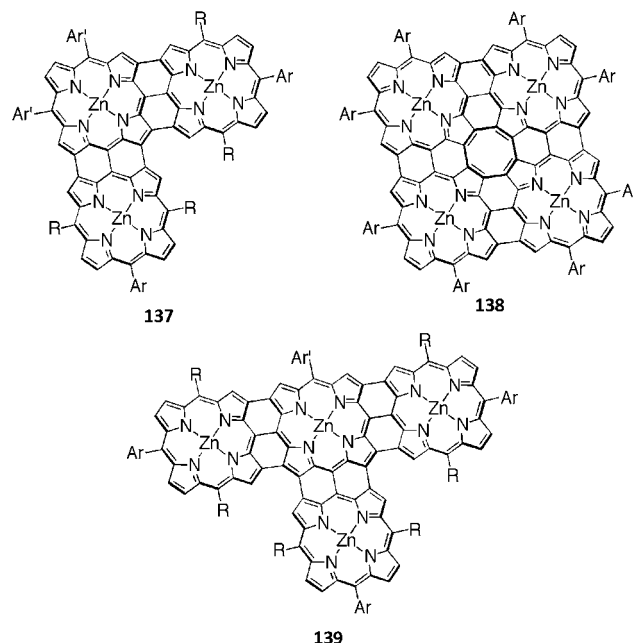


Fig. 14 Two-dimensionally extended porphyrin tapes.

methods.^{130–132} Dimeric porphyrin tapes fused with pyrene units were prepared by the oxidation with FeCl_3 .¹³³

The conductance of porphyrin tapes **142** was compared with those of 1,3-butadiyne-bridged porphyrin oligomers **140** and *meso-meso* singly linked porphyrin oligomers **141** (Fig. 15). All the porphyrin oligomers were attached to the end 4-pyridylethyne groups for better connection to gold.

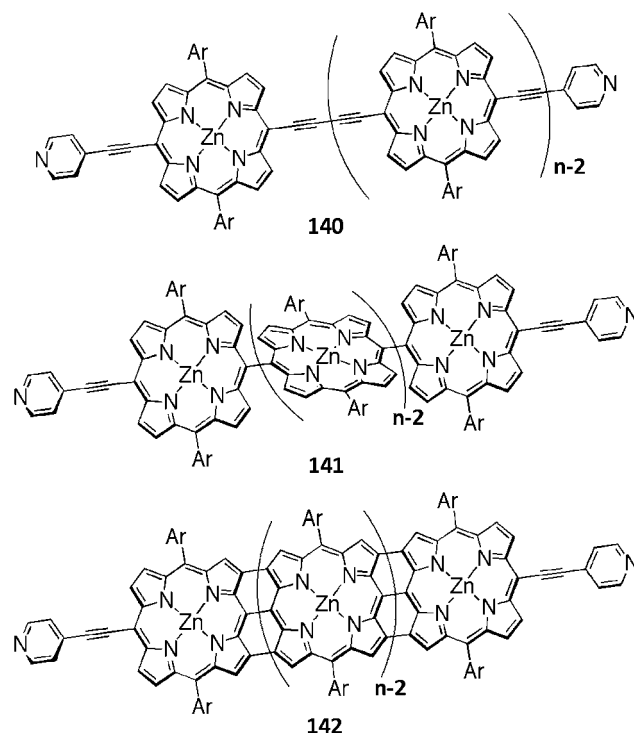


Fig. 15 Linear porphyrin oligomers for the conductance measurement.

The conductance was measured by a scanning tunneling microscope (STM) with a gold tip and a gold substrate, and Au|oligoporphyrin|Au electric junction. The attenuation decay factors were determined to be $0.042 \pm 0.005 \text{ \AA}^{-1}$ for **140**, $0.11 \pm 0.01 \text{ \AA}^{-1}$ for **141** and $0.019 \pm 0.01 \text{ \AA}^{-1}$ for **142**.¹³⁴ The porphyrin tape **142** was most conducting but only better than the array **140** (Fig. 15).

The oxidation of 5,10,15-triaryl Ni(II) porphyrin **133** with BAHA led to the production of *meso*- β doubly linked diporphyrin **134** in 53% yield.¹²² A similar oxidation of 5,15-diaryl Ni(II) porphyrin **143** with DDQ and $\text{Sc}(\text{OTf})_3$ gave further coupled *meso*, β doubly linked porphyrin oligomers **145**_{*n*} in addition to *meso*, β singly linked dimer **144** (Scheme 22).¹³⁵ The lowest energy Q-bands become increasingly intensified and red-shifted upon elongation of the array as following; dimer (741 nm), trimer (892 nm), tetramer (996 nm) and pentamer (1075 nm). These tapes exhibit large TPA values.¹³⁶ A similar *meso*, β doubly linked fused diporphyrin was obtained from the oxidation of **143** with TeCl_4 .¹³⁷

Despite the attractive optical properties of the porphyrin tapes, their poor solubility and facile oxidative degradation hampered further studies on longer arrays. The former arose from the flat molecular shape that induces strong π - π stacking and the latter originated from high-lying HOMOs. Facially encumbered porphyrin tapes have been invented to increase both the chemical stability and solubility by suppressing π - π stacking and protecting against the attack of oxidising agents.^{138,139} Porphyrin tapes **148**_{*n*} bearing two different aryl groups, a 2,4,6-tris(3,5-di-*tert*-butylphenoxy)phenyl group (protecting) and a 3,5-dioctyloxyphenyl group (solubility), were prepared up to 24-mer (Scheme 23). Importantly, detailed studies on these arrays led to an estimate of the effective conjugation length (ECL) to be $n = 14$ –16.¹²⁷

Recently electron-deficient porphyrin tapes have been developed to improve the chemical stability by lowering the

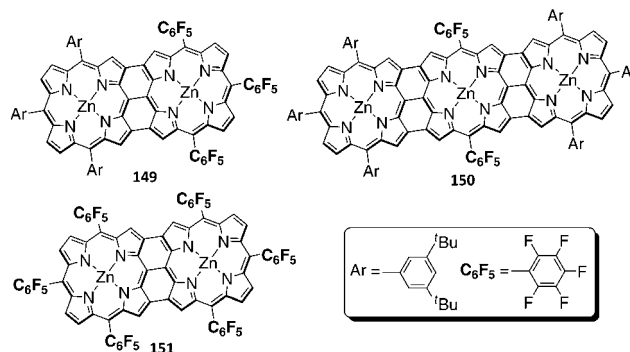
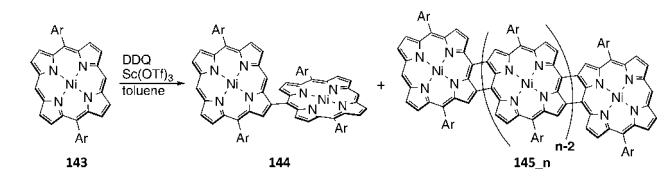
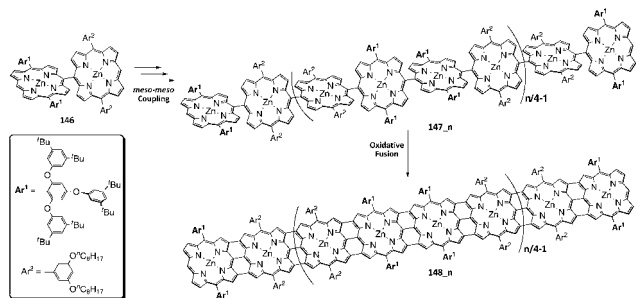


Fig. 16 Electron-deficient porphyrin tapes **149**, **150**, and **151**.

HOMO level. Employing a 3,5-di-*tert*-butylphenyl-substituted porphyrin as a donor-type (D) and a pentafluorophenyl-substituted porphyrin as an acceptor type (A), hybrid D-A dimer **149** and D-A-D trimer **150** as well as A-A dimer **151** were prepared (Fig. 16).^{140,141} Owing to their better solubility in common organic solvents, the crystal structures of **150** and **151** were obtained (Fig. 17). As expected, the cyclic voltammetry experiments revealed positively shifted oxidation and reduction potentials for these electron-deficient porphyrin tapes; e.g. the first oxidation potentials (E_{ox1} : potentials vs. ferrocene/ferrocenium ion couple) of 0.22 V for **149**, 0.41 V for **151** and -0.03 V for **136_2**, respectively, which clearly illustrated increased stability against oxidative degradation. Interestingly, the TPA cross-section values measured by a wavelength-scanning open-aperture Z-scan method were increased in hybrid tapes **149** and



Scheme 22 Synthesis of *meso*- β fused porphyrin oligomers.



Scheme 23 Synthesis of **148**_{*n*}.

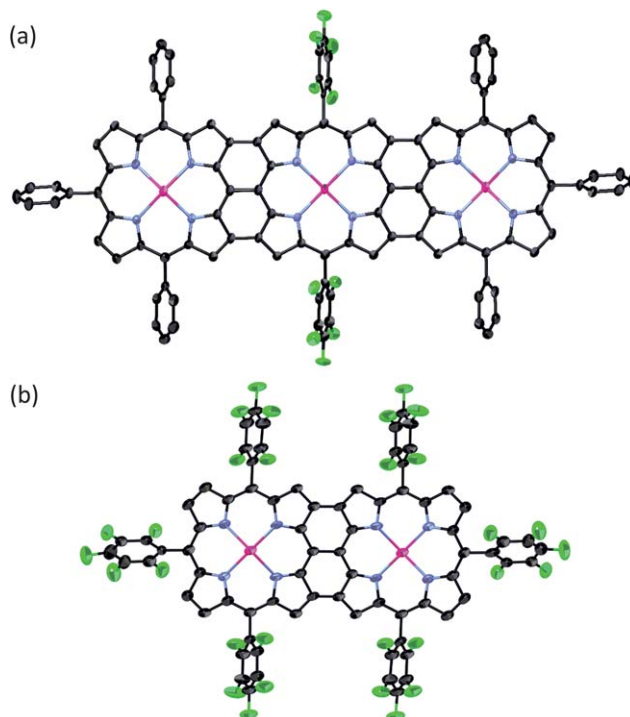


Fig. 17 X-ray crystal structures of electron-deficient porphyrin tapes (a) **150** and (b) **151**.

150 to be 2200 and 27 000 GM respectively, probably as a consequence of the donor–acceptor electronic properties.

In the last decade, various applications of porphyrin tapes have been reported by a several groups. Host **152**, which consists of two porphyrin tapes arranged in a face-to-face fashion with a certain separation so as to accommodate guest molecules, was designed and prepared. Upon complexation with 4,4'-bipyridine, the host **152** displayed a strong negative cooperativity in the second guest binding, suggesting the notable electronic communication of the triply linked Zn(II) porphyrin dimer.¹⁴² In sharp contrast, the same host molecule showed strong positive heterotropic cooperativity for guest binding of 4,4'-bipyridine and C₆₀.¹⁴³ Triply linked Cu(II) porphyrin dimer **154** bearing hydrophilic and hydrophobic tails was reported to form a room-temperature columnar liquid crystal (LC), which showed upon photoirradiation at 355 nm a maximum transient conductivity of $2.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁴⁴ In a similar approach, Cu(II) complexes of triply linked porphyrin dimers bearing dodecyl chains and semifluoroalkyl chains and only semifluoroalkyl chains were prepared. These complexes behave similarly in solution but display different semiconducting behaviors in LC states.¹⁴⁵ By elongating the porphyrin tapes, ultralow-bandgap columnar LC semiconductors with wide LC mesophase temperature and high-absorption temperature were developed. LC made from a pentameric porphyrin tape showed high charge carrier mobility ($2.4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).¹⁴⁶

Multi-charge storage capabilities of porphyrin tapes have been revealed by Diederich *et al.* Typically, C₆₀–Zn(II) porphyrin tape conjugate **153** displayed nine reversible redox processes involving a total of fifteen electrons.^{147,148} Porphyrin tape **155** was used for construction of addressable patterned surfaces on a Ag(100) substrate with deposition with C₆₀ (Fig. 18).¹⁴⁹

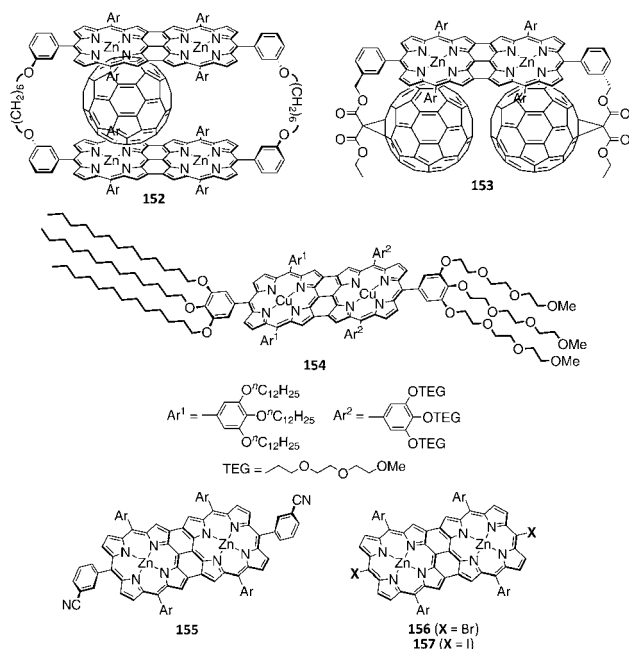


Fig. 18 Various derivatives of the porphyrin tape.

The singlet excited state of the porphyrin tapes is usually very short-lived,^{147,150} but halogenated porphyrin tapes **156** and **157** underwent very fast intersystem crossing to their triplet excited states, whose lifetimes were relatively long. These properties are suitable as photoactive materials in reverse saturable absorption in the NIR region.¹⁵¹

(iii) Fused hexaphyrins

In recent years, expanded porphyrins have emerged as a promising class of functional chromophores that have larger and more flexible conjugated electronic systems as compared with porphyrins.^{152–159} 5,10,15,20,25,30-Hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1)¹⁶⁰ is a benchmark expanded porphyrin with regard to its strong 26 π aromaticity and flat rectangular molecular shape. Its shorter molecular side is similar in length to that of porphyrins.^{161,162} Taking advantage of this structurally matching feature, novel π -extended hexaphyrins have been envisioned by peripheral fusion reactions. Actually, *meso-meso*, β - β , β - β triply linked porphyrin–hexaphyrin hybrid **158** was synthesised by Osuka *et al.* in 2011.¹⁶³ The hexaphyrin unit was formed by acid-catalysed cross-condensation of *meso*-porphyrinyl dipyrromethane and 5-pentafluorophenyldipyrromethane with pentafluorobenzaldehyde, followed by DDQ/Sc(OTf)₃ oxidation. The hybrid tape **158** exhibited split Soret-like bands at 532, 566 and 752 nm and red-shifted Q-like band at 1333 nm, indicating effective conjugation over both the porphyrin and hexaphyrin segments. The tape **158** was reduced with NaBH₄ to give

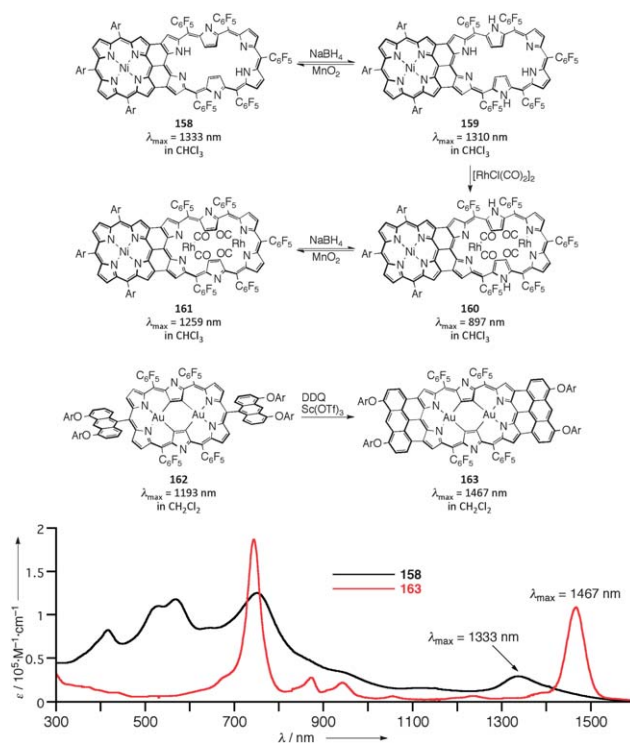


Fig. 19 Fused porphyrin–hexaphyrins **158–161**, and anthracene-appended hexaphyrins **162–163**, and UV/Vis/NIR absorption spectra of fused hexaphyrins **158** and **163**.

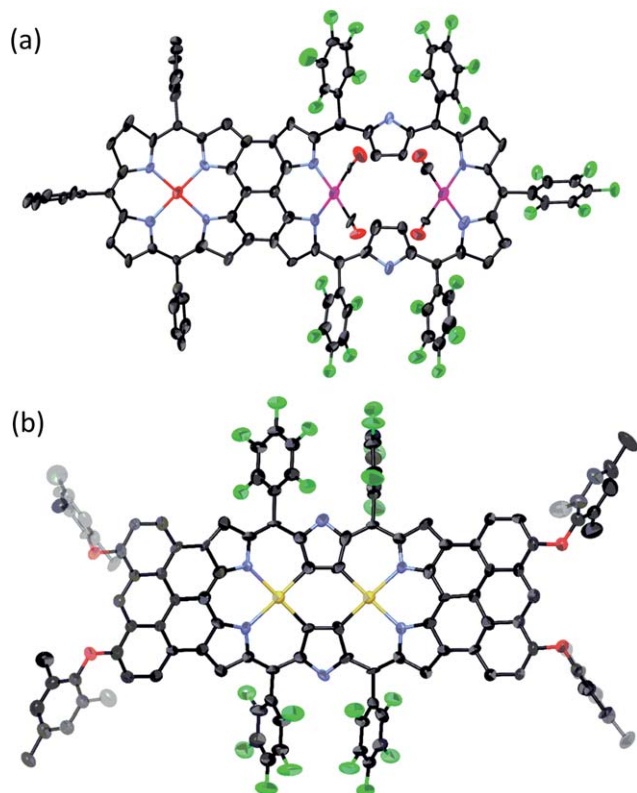


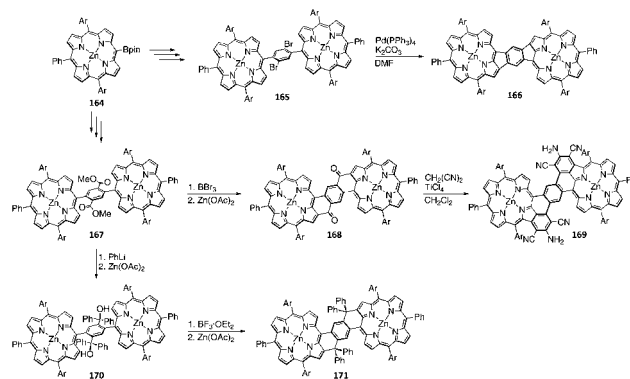
Fig. 20 X-ray crystal structure of fused hexaphyrins: (a) **161** and (b) **163**.

corresponding 28π congener **159** (Fig. 19). Interestingly, the reduced tape **159** showed solvent-polarity-dependent antiaromaticity. The antiaromatic character became much stronger in its bis-Rh(i) complex **160** owing to the restricted conformation in the hexaphyrin segment by Rh(i) coordination.¹⁶⁴ The structure of **161** was elucidated by X-ray diffraction analysis (Fig. 20).

Very recently doubly anthracene-fused hexaphyrin **163** was synthesised (Fig. 19).¹⁶⁵ The oxidative fusion reaction of bis(mesityloxy)anthracene-bearing hexaphyrin bis-Au(III) complex **162** proceeded successfully upon treatment with DDQ and Sc(OTf)₃. The single-crystal X-ray analysis displayed an elongated, rectangular, almost planar structure of **163** (Fig. 20). In the UV/Vis/NIR absorption spectrum, two sharp and intense bands were observed mainly at 743 and 1467 nm (Fig. 19). The most red-shifted band was remarkably sharp and intensified ($\epsilon = 108500 \text{ M}^{-1} \text{ cm}^{-1}$, fwhm = 223 cm^{-1}). These absorption characteristics originate from the effective conjugation along the long molecular axis that enables permissible HOMO–LUMO transition.

IV Other fused porphyrins

Anderson *et al.* examined the optical properties of various 1,4-phenylene-bridged porphyrin dimers (Scheme 24 and Fig. 21).¹⁶⁶ Dimer **166** was prepared from Pd-catalysed cyclisation of **165**, and dimer **168** was prepared from intramolecular Friedel–Crafts acylation of **167** and was transformed to fused



Scheme 24 Synthesis of *p*-phenylene-bridged porphyrin tapes **166**, **168**, **169**, and **171**.

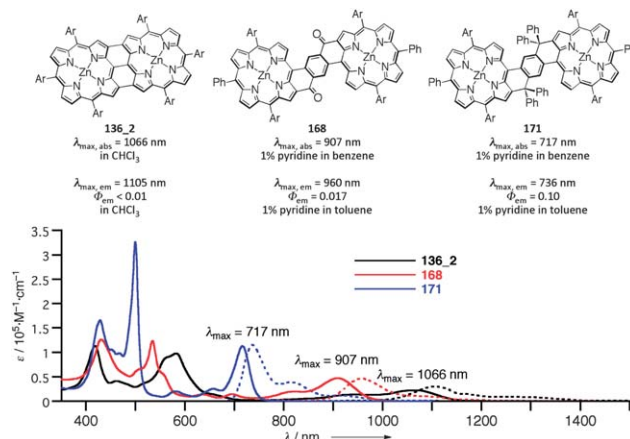


Fig. 21 UV/Vis/NIR absorption spectra (solid) and emission (dashed) of *p*-phenylene-linked diporphyrins **168** and **171**, and porphyrin tape **136_2**.

dimer **169** by the condensation with malononitrile. Dimer **167** was converted to dimer **170** by Grignard addition reaction and was further converted to dimer **171**. Among these, **166** shows the most red-shifted absorption band at 1077 nm in toluene containing 1% pyridine, and **168** and **171** show the lowest energy Q-bands at 907 and 717 nm, respectively. While **168** and **171** display fluorescence ($\lambda_{\text{em}} = 960 \text{ nm}$, $\Phi_{\text{em}} = 0.017$ for **168** and $\lambda_{\text{em}} = 736 \text{ nm}$, $\Phi_{\text{em}} = 0.10$ for **171**), **166** is non-fluorescent. It is noteworthy that the fluorescence quantum yields of **168** and **171** are remarkably high in the NIR region. Femtosecond transient absorption spectroscopy has revealed a very rapid decay of the S₁-state of **166**. TPA values as determined by two-photon excited fluorescence in CCl₄/pyridine are 2100 GM at 1200 nm for **168** and 7300 GM at 878 nm for **171**.

As a pioneering work, Anderson *et al.* reported the synthesis of 5,15-dialkylideneporphyrin **172** as a hybrid of porphyrin and TCNQ. The absorption spectrum of **172** exhibits two bands of similar intensity, distinctly different from those of normal porphyrins.¹⁶⁷ Cumulenic dimer **173** and quinonoidal dimer **174** were also prepared.¹⁶⁸ The coplanar conformation of **173** was revealed by X-ray analysis. While **173** shows the absorption spectrum containing a strong, broad band at 1080 nm, the

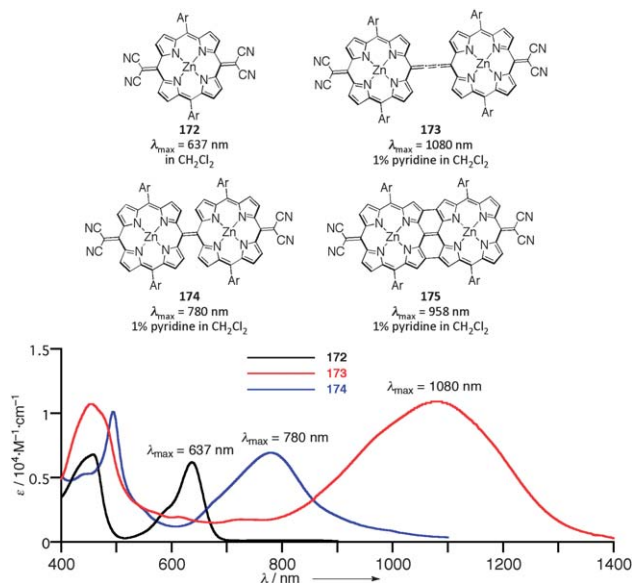


Fig. 22 UV/Vis/NIR absorption spectra of quinonoidal porphyrins.

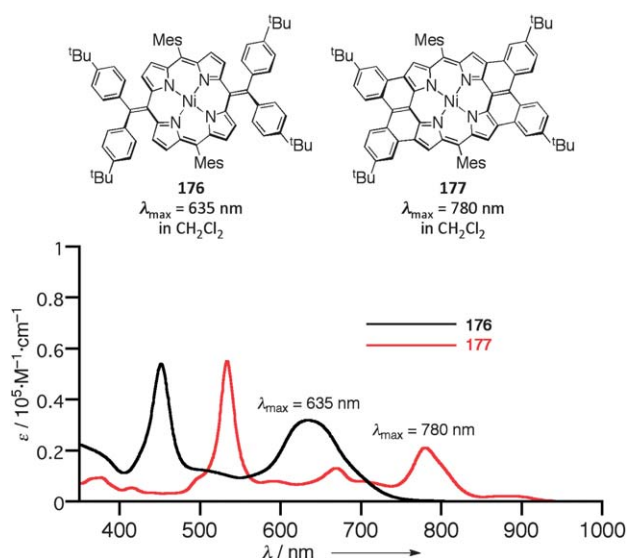


Fig. 23 UV/Vis/NIR absorption spectra of quinoidal porphyrins.

absorption spectrum of **174** is less bathochromically shifted. Not confirmed by X-ray crystallography, this has been ascribed to an expected non-planar conformation of **174**. Triply linked dimer **175** was also prepared, which shows a peak at 958 nm (Fig. 22).¹⁶⁹

Very recently, Wu *et al.* synthesised non-fused and fused quinonoidal porphyrins **176** and **177** through Corey–Fuchs reaction of 5,15-dioxo-porphodimethene with CBr_4 and PPh_3 and subsequent Suzuki–Miyaura coupling to give **176**. The final oxidative ring-closure of **176** with DDQ and methanesulfonic acid gave **177**. Both the Soret and Q-bands are more red-shifted in **177**, and TPA values as determined by a wavelength-scanning open-aperture Z-scan method are 450 GM for **176** and 510 GM for **177** at 1200 nm (Fig. 23).¹⁷⁰

V Conclusions

In the last decade, the chemistry of fused porphyrinoids has witnessed remarkable progress. Various aromatic groups including polycyclic aromatic hydrocarbons, heteroaromatic molecules, and porphyrins themselves are fused on the periphery of porphyrins in various manners. The fusion reactions cause structural constraints to force the coplanar conformations of the fused segments and porphyrins, hence giving rise to large perturbation of the optical and electronic properties of porphyrins. It has been increasingly recognised that porphyrins are, simply from the synthetic viewpoint, an interesting and promising platform to test various chemical transformations, particularly transition-metal-catalysed reactions.^{171–174} Fused porphyrinoids thus synthesised display significantly altered optical and electronic properties, which are rather difficult to see in other non-porphyrinic substrates. In addition to pure academic interest, increasing attention has been paid to these fused porphyrinoids because of the recent demands in practical applications such as OFETs, photovoltaic solar cells, long-wavelength penetrating photodynamic therapy, and so on. Despite the promise of the fused porphyrinoids, there are only a limited number of the oxidative fusion reactions such as FeCl_3 oxidation and co-use of DDQ and $\text{Sc}(\text{OTf})_3$. New efficient fusion reactions under milder conditions are highly desirable in future developments.

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References

- 1 *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific Publishing, Singapore, 2010, vol. 1–25.
- 2 M. G. H. Vicente, L. Jaquinod and K. M. Smith, *Chem. Commun.*, 1999, 1771.
- 3 S. Fox and R. W. Boyle, *Tetrahedron*, 2006, **62**, 10039.
- 4 N. Aratani, D. Kim and A. Osuka, *Chem.-Asian J.*, 2009, **4**, 1172.
- 5 N. Ono, H. Yamada and T. Okujima, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific, Singapore, 2010, vol. 2, ch. 7, p. 1.
- 6 J. A. S. Cavaleiro, A. C. Tome and M. G. P. M. S. Neves, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific, Singapore, 2010, vol. 2, ch. 9, p. 193.
- 7 A. V. Cheprakov, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific, Singapore, 2011, vol. 13, ch. 58, p. 1.
- 8 C. Jiao and J. Wu, *Synlett*, 2012, **23**, 171.

- 9 J. P. Lewtak and D. T. Gryko, *Chem. Commun.*, 2012, **48**, 10069.
- 10 A. M. V. M. Pereira, S. Richeter, C. Jeandon, J.-P. Gisselbrecht, J. Wytko and R. Ruppert, *J. Porphyrins Phthalocyanines*, 2012, **16**, 464.
- 11 V. V. Roznyatovsky, C.-H. Lee and J. L. Sessler, *Chem. Soc. Rev.*, 2013, **42**, 1921–1933.
- 12 L. Edwards, M. Gouterman and C. B. Rose, *J. Am. Chem. Soc.*, 1976, **98**, 7638.
- 13 R. B. Koehorst, J. F. Kleibeuker, T. J. Schaafsma, D. A. de Bie, B. Geurtsen, R. N. Henrie and H. C. van der Plas, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1005.
- 14 R. P. Linstead and T. F. Weiss, *J. Chem. Soc.*, 1950, 2975.
- 15 T. D. Lash, in *The Porphyrin Handbook*, ed. K. Kadish, K. M. Smith and R. Guilard, Academic Press, New York, 1999, vol. 2, ch. 10, p. 125.
- 16 T. D. Lash and J. J. Catarello, *Tetrahedron*, 1993, **49**, 4159.
- 17 T. D. Lash and B. H. Novak, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 683.
- 18 N. Ono, H. Hironaga, S. Simizu, K. Ono, K. Kuwano and T. Ogawa, *J. Chem. Soc., Chem. Commun.*, 1994, 1019.
- 19 N. Ono, H. Hironaga, K. Ono, S. Kaneko, T. Murashima, T. Ueda, C. Tsukamura and T. Ogawa, *J. Chem. Soc., Perkin Trans. 1*, 1996, 417.
- 20 B. H. Novak and T. D. Lash, *J. Org. Chem.*, 1998, **63**, 3998.
- 21 O. S. Finikova, A. V. Cheprakov, I. P. Beleskaya and S. A. Vinogradov, *Chem. Commun.*, 2001, 261.
- 22 O. S. Finikova, A. V. Cheprakov, P. J. Carroll and S. A. Vinogradov, *J. Org. Chem.*, 2003, **68**, 7517.
- 23 O. S. Finikova, A. V. Cheprakov, I. P. Beletskaya, P. J. Carroll and S. A. Vinogradov, *J. Org. Chem.*, 2004, **69**, 522.
- 24 O. S. Finikova, S. E. Aleshchenkov, R. P. Briñas, A. V. Cheprakov, P. J. Carroll and S. A. Vinogradov, *J. Org. Chem.*, 2005, **70**, 4617.
- 25 O. S. Finikova, A. V. Cheprakov and S. A. Vinogradov, *J. Org. Chem.*, 2005, **70**, 9562.
- 26 F. Niedermair, S. M. Borisov, G. Zenkl, O. T. Hofmann, H. Weber, R. Saf and I. Klimant, *Inorg. Chem.*, 2010, **49**, 9333.
- 27 S. Ito, T. Murashima, H. Uno and N. Ono, *Chem. Commun.*, 1998, 1661.
- 28 H. Yamada, T. Okujima and N. Ono, *Chem. Commun.*, 2008, 2957.
- 29 Y. Matsuo, Y. Sato, T. Niinomi, I. Soga, H. Tanaka and E. Nakamura, *J. Am. Chem. Soc.*, 2009, **131**, 16048.
- 30 M. Rein and M. Hanack, *Chem. Ber.*, 1988, **121**, 1601.
- 31 S. Ito, N. Ochi, H. Uno, T. Murashima and N. Ono, *Chem. Commun.*, 2000, 893.
- 32 H. Yamada, D. Kuzuhara, T. Takahashi, Y. Shimizu, K. Uota, T. Okujima, H. Uno and N. Ono, *Org. Lett.*, 2008, **10**, 2947.
- 33 V. Yakutkin, S. Aleshchenkov, S. Chernov, T. Miteva, G. Nelles, A. Cheprakov and S. Balushev, *Chem.-Eur. J.*, 2008, **14**, 9846.
- 34 M. T. Whited, P. I. Djurovich, S. T. Roberts, A. C. Durrell, C. W. Schlenker, S. E. Bradforth and M. E. Thompson, *J. Am. Chem. Soc.*, 2011, **133**, 88.
- 35 R. Deshpande, L. Jiang, G. Schmidt, J. Rakovan, X. Wang, K. Wheeler and H. Wang, *Org. Lett.*, 2009, **11**, 4251.
- 36 L. Jinag, J. T. Engle, L. Sirk, C. S. Hartley, C. J. Ziegler and H. Wang, *Org. Lett.*, 2011, **13**, 3020.
- 37 R. Deshpande, B. Wang, L. Dai, L. Jiang, C. S. Hartley, S. Zou, H. Wang and L. Kerr, *Chem.-Asian J.*, 2012, **7**, 2662.
- 38 S. Banala, T. Rühl, K. Wurst and B. Kräutler, *Angew. Chem., Int. Ed.*, 2009, **48**, 599.
- 39 J. Jaquinod, C. Gros, M. M. Olmstead, M. Antolovich and K. M. Smith, *Chem. Commun.*, 1996, 1475.
- 40 K. Tan, L. Jaquinod, R. Paolesse, S. Nardis, C. D. Natale, A. D. Carlo, L. Prodi, M. Montalti, N. Zaccheroni and K. M. Smith, *Tetrahedron*, 2004, **60**, 1099.
- 41 H. J. H. Wang, L. Jaquinod, D. J. Nurco, M. G. H. Vicente and K. M. Smith, *Chem. Commun.*, 2001, 2646.
- 42 H. Aihara, L. Jaquinod, D. J. Nurco and K. M. Smith, *Angew. Chem., Int. Ed.*, 2001, **40**, 3439.
- 43 J. D. Spence, E. D. Cline, D. M. LLagostera and P. S. O'Toole, *Chem. Commun.*, 2004, 180.
- 44 M. Nath, J. C. Huffman and J. M. Zaleski, *Chem. Commun.*, 2003, 858.
- 45 M. Nath, J. C. Huffman and J. M. Zaleski, *J. Am. Chem. Soc.*, 2003, **125**, 11484.
- 46 M. Nath, M. Pink and J. M. Zaleski, *J. Am. Chem. Soc.*, 2005, **127**, 478.
- 47 M. Nath, M. Pink and J. M. Zaleski, *J. Organomet. Chem.*, 2011, **696**, 4152.
- 48 L. J. K. Boerner, S. Mazumder, M. Pink, M.-H. Baik and J. M. Zaleski, *Chem.-Eur. J.*, 2011, **17**, 14539.
- 49 S. Richeter, A. H. Aïssa, C. Taffin, A. van der Lee and D. Leclercq, *Chem. Commun.*, 2007, 2148.
- 50 J.-F. Lefebvre, D. Leclercq, J.-P. Gisselbrecht and S. Richeter, *Eur. J. Org. Chem.*, 2010, 1912.
- 51 J.-F. Lefebvre, M. Lo, D. Leclercq and S. Richeter, *Chem. Commun.*, 2011, **47**, 2976.
- 52 M. Lo, J.-F. Lefebvre, D. Leclercq, A. van der Lee and S. Richeter, *Org. Lett.*, 2011, **13**, 3110.
- 53 D. P. Arnold, R. G. Holmes, A. W. Johnson, A. R. P. Smith and G. A. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1660.
- 54 M. G. H. Vicente, I. N. Rezzano and K. M. Smith, *Tetrahedron Lett.*, 1990, **31**, 1365.
- 55 M. G. H. Vicente and K. M. Smith, *J. Org. Chem.*, 1991, **56**, 4407.
- 56 A. R. Morgan and S. Gupta, *Tetrahedron Lett.*, 1994, **35**, 5347.
- 57 A. Osuka, Y. Ikawa and K. Maruyama, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 3322.
- 58 R. W. Boyle and D. Dolphin, *Chem. Commun.*, 1994, 2463.
- 59 A. R. Morgan, A. Rampersaud, G. M. Garbo, R. W. Keck and S. H. Selman, *J. Med. Chem.*, 1989, **32**, 904.
- 60 A. R. Morgan and N. C. Tertel, *J. Org. Chem.*, 1986, **51**, 1347.
- 61 M. J. Gunter and B. C. Robinson, *Tetrahedron Lett.*, 1990, **31**, 285.
- 62 B. C. Robinson, *Tetrahedron*, 2000, **56**, 6005.
- 63 M. J. Gunter, B. C. Robinson, J. M. Gulbis and E. R. T. Tiekink, *Tetrahedron*, 1991, **47**, 7853.

- 64 A. Nakano, N. Aratani, H. Furuta and A. Osuka, *Chem. Commun.*, 2001, 1920.
- 65 G. Li, A. Graham, E. Potter, Z. D. Grossman, A. Oseroff, T. J. Dougherty and R. K. Pandey, *J. Org. Chem.*, 2001, **66**, 1316.
- 66 H. J. Callot, E. Schaeffer, R. Cromer and F. Metz, *Tetrahedron*, 1990, **46**, 5253.
- 67 S. Richiter, C. Jeandon, N. Kyritsakas, R. Ruppert and H. J. Callot, *J. Org. Chem.*, 2003, **68**, 9200.
- 68 C. Jeandon, R. Ruppert and H. J. Callot, *Chem. Commun.*, 2004, 1090.
- 69 C. Jeandon, R. Ruppert and H. J. Callot, *J. Org. Chem.*, 2006, **71**, 3111.
- 70 J. Fouchet, C. Jeandon, R. Ruppert and H. J. Callot, *Org. Lett.*, 2005, **7**, 5257.
- 71 A. K. Sahoo, S. Mori, H. Shinokubo and A. Osuka, *Angew. Chem., Int. Ed.*, 2006, **45**, 7972.
- 72 S. Tokuji, Y. Takahashi, H. Shinmori, H. Shinokubo and A. Osuka, *Chem. Commun.*, 2009, 1028.
- 73 S. Fox and R. W. Boyle, *Chem. Commun.*, 2004, 1322.
- 74 D.-M. Shen, C. Liu and Q.-Y. Chen, *J. Org. Chem.*, 2006, **71**, 6508.
- 75 D.-M. Shen, C. Liu and Q.-Y. Chen, *Chem. Commun.*, 2005, 4982.
- 76 Y. Mitsushige, S. Yamaguchi, B. S. Lee, Y. M. Sung, S. Kuhri, C. A. Schierl, D. M. Guldi, D. Kim and Y. Matsuo, *J. Am. Chem. Soc.*, 2012, **134**, 16540.
- 77 O. Yamane, K. Sugiura, H. Miyasaka, K. Nakamura, T. Fujimoto, K. Nakamura, T. Kaneda, Y. Sakata and M. Yamashita, *Chem. Lett.*, 2004, **33**, 40.
- 78 A. N. Cammidge, P. J. Scaife, G. Berber and D. L. Hughes, *Org. Lett.*, 2005, **7**, 3413.
- 79 M. Tanaka, S. Hayashi, S. Eu, T. Umeyama, Y. Matano and H. Imahori, *Chem. Commun.*, 2007, 2069.
- 80 J. P. Lewtak, D. Gryko, D. Bao, E. Sebai, O. Vakuliuk, M. Scigaj and D. T. Gryko, *Org. Biomol. Chem.*, 2011, **9**, 8178.
- 81 C. Jiao, K.-W. Huang, Z. Guan, Q.-H. Xu and J. Wu, *Org. Lett.*, 2010, **12**, 4046.
- 82 C. Jiao, K.-W. Huang, C. Chi and J. Wu, *J. Org. Chem.*, 2011, **76**, 661.
- 83 H. S. Gill, M. Harmjanz, J. Santamaría, I. Finger and M. J. Scott, *Angew. Chem., Int. Ed.*, 2004, **43**, 485.
- 84 J. M. Ball, N. K. S. Davis, J. D. Wilkinson, J. Kirkpatrick, J. Teuscher, R. Gunning, H. L. Anderson and H. J. Snaith, *RSC Adv.*, 2012, **2**, 6846.
- 85 C. Jiao, L. Zhu and J. Wu, *Chem.-Eur. J.*, 2011, **17**, 6610.
- 86 K. Kurotobi, K. S. Kim, S. B. Noh, D. Kim and A. Osuka, *Angew. Chem., Int. Ed.*, 2006, **45**, 3944.
- 87 N. K. S. Davis, M. Pawlicki and H. L. Anderson, *Org. Lett.*, 2008, **10**, 3945.
- 88 N. K. S. Davis, A. L. Thompson and H. L. Anderson, *Org. Lett.*, 2010, **12**, 2124.
- 89 N. K. S. Davis, A. L. Thompson and H. L. Anderson, *J. Am. Chem. Soc.*, 2011, **133**, 30.
- 90 V. V. Diev, C. W. Schlenker, K. Hanson, Q. Zhong, J. D. Zimmerman, S. R. Forrest and M. E. Thompson, *J. Org. Chem.*, 2012, **77**, 143.
- 91 V. S.-Y. Lin and M. J. Therien, *Chem.-Eur. J.*, 1995, **1**, 645.
- 92 D. P. Arnold, G. A. Heath and D. A. James, *New J. Chem.*, 1998, **22**, 1377.
- 93 D. P. Arnold, *Synlett*, 2000, 296.
- 94 A. K. Burrell and D. L. Officer, *Synlett*, 1998, 1297.
- 95 D. Holten, D. F. Bocian and J. S. Lindsay, *Acc. Chem. Res.*, 2002, **35**, 57.
- 96 M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor and H. L. Anderson, *J. Am. Chem. Soc.*, 2004, **126**, 15352.
- 97 K. Susumu, P. R. Frail, P. J. Angiolillo and M. J. Therien, *J. Am. Chem. Soc.*, 2006, **128**, 8380.
- 98 O. Locos, B. Bašić, J. C. McMurtrie, P. Jensen and D. P. Arnold, *Chem.-Eur. J.*, 2012, **18**, 5574.
- 99 V. S.-Y. Lin, S. G. DiMaggio and M. J. Therien, *Science*, 1994, **264**, 1105.
- 100 T. V. Duncan, S. P. Wu and M. J. Therien, *J. Am. Chem. Soc.*, 2006, **128**, 10423.
- 101 H. L. Anderson, *Inorg. Chem.*, 1994, **33**, 972.
- 102 P. N. Taylor, J. Huuskonen, G. Rumbles, R. T. Aplin, E. Williams and H. L. Anderson, *Chem. Commun.*, 1998, 909.
- 103 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1987, 39.
- 104 T. Khoury and M. J. Crossley, *Chem. Commun.*, 2007, 4851.
- 105 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1991, 1569.
- 106 M. J. Crossley, L. J. Govenlock and J. K. Prashar, *J. Chem. Soc., Chem. Commun.*, 1995, 2379.
- 107 K. Sendt, L. A. Johnston, W. A. Hough, M. J. Crossley, N. S. Hush and J. R. Reimers, *J. Am. Chem. Soc.*, 2002, **124**, 9299.
- 108 N. Kobayashi, M. Numao, R. Kondo, S. Nakajima and T. Osa, *Inorg. Chem.*, 1991, **30**, 2241.
- 109 S. Ito, K. Nakamoto, H. Uno, T. Murashima and N. Ono, *Chem. Commun.*, 2001, 2696.
- 110 H. Uoyama, K. S. Kim, K. Kuroki, J.-Y. Shin, T. Nagata, T. Okujima, H. Yamada, N. Ono, D. Kim and H. Uno, *Chem.-Eur. J.*, 2010, **16**, 4063.
- 111 L. Jaquinod, O. Siri, R. G. Khoury and K. M. Smith, *Chem. Commun.*, 1998, 1261.
- 112 R. Paolesse, L. Jaquinod, S. Della, D. J. Nurco, L. Prodi, M. Montalti, C. D. Natale, A. D'Amico, A. D. Carlo, P. Lugli and K. M. Smith, *J. Am. Chem. Soc.*, 2000, **122**, 11295.
- 113 M. G. H. Vicente, M. T. Cancilla, C. B. Lebrilla and K. M. Smith, *Chem. Commun.*, 1998, 2355.
- 114 H. Uno, K. Nakamoto, K. Kuroki, A. Fujimoto and N. Ono, *Chem.-Eur. J.*, 2007, **13**, 5773.
- 115 H. Uno, A. Masumoto and N. Ono, *J. Am. Chem. Soc.*, 2003, **125**, 12082.
- 116 S. Banala, R. G. Huber, T. Müller, M. Fechtel, K. R. Liedl and B. Kräutler, *Chem. Commun.*, 2012, **48**, 4359.
- 117 M. Akita, S. Hiroto and H. Shinokubo, *Angew. Chem., Int. Ed.*, 2012, **51**, 2894.
- 118 N. Aratani and A. Osuka, *Macromol. Rapid Commun.*, 2001, **22**, 725.

- 119 N. Aratani and A. Osuka, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 1361.
- 120 N. Aratani, A. Tsuda and A. Osuka, *Synlett*, 2001, 1663.
- 121 D. Kim and A. Osuka, *Acc. Chem. Res.*, 2004, **37**, 735.
- 122 A. Tsuda, A. Nakano, H. Furuta, H. Yamochi and A. Osuka, *Angew. Chem., Int. Ed.*, 2000, **39**, 558.
- 123 A. Tsuda, H. Furuta and A. Osuka, *Angew. Chem., Int. Ed.*, 2000, **39**, 2549.
- 124 A. Tsuda, H. Furuta and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 10304.
- 125 A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79.
- 126 T. Tanaka, Y. Nakamura and A. Osuka, *Chem.-Eur. J.*, 2008, **14**, 204.
- 127 T. Ikeda, N. Aratani and A. Osuka, *Chem.-Asian J.*, 2009, **4**, 1248.
- 128 Y. Nakamura, S. Y. Jang, T. Tanaka, N. Aratani, J. M. Lim, K. S. Kim, D. Kim and A. Osuka, *Chem.-Eur. J.*, 2008, **14**, 8279.
- 129 Y. Nakamura, N. Aratani, H. Shinokubo, A. Takagi, T. Kawai, T. Matsumoto, Z. S. Yoon, D. Y. Kim, T. K. Ahn, D. Kim, A. Muranaka, N. Kobayashi and A. Osuka, *J. Am. Chem. Soc.*, 2006, **128**, 4119.
- 130 M. O. Senge, M. Pintea and A. Ryan, *Z. Naturforsch., B: J. Chem. Sci.*, 2011, **66**, 553.
- 131 B. J. Brennan, M. J. Kenny, P. A. Liddell, B. R. Cherry, J. Li, A. L. Moore, T. A. Moore and D. Gust, *Chem. Commun.*, 2011, **47**, 10034.
- 132 A. K. Sahoo, Y. Nakamura, N. Aratani, K. S. Kim, S. B. Noh, H. Shinokubo, D. Kim and A. Osuka, *Org. Lett.*, 2006, **8**, 4141.
- 133 V. V. Diev, K. Hanson, J. D. Zimmerman, S. R. Forrest and M. E. Thompson, *Angew. Chem., Int. Ed.*, 2010, **49**, 5523.
- 134 G. Sedghi, L. J. Esdaile, H. L. Anderson, S. Martin, D. Bethell, S. J. Higgins and R. J. Nichols, *Adv. Mater.*, 2012, **24**, 653.
- 135 M.-C. Yoon, S. B. Noh, A. Tsuda, Y. Nakamura, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2007, **129**, 10080.
- 136 A. Tsuda, Y. Nakamura and A. Osuka, *Chem. Commun.*, 2003, 1096.
- 137 K. Sugiura, T. Matsumoto, S. Ohkouchi, Y. Naitoh, T. Kawai, Y. Takai, K. Ushiroda and Y. Sakata, *Chem. Commun.*, 1999, 1957.
- 138 T. Ikeda, J. M. Lintuluoto, N. Aratani, Z. S. Yoon, D. Kim and A. Osuka, *Eur. J. Org. Chem.*, 2006, 3193.
- 139 T. Ikeda, A. Tsuda, N. Aratani and A. Osuka, *Chem. Lett.*, 2006, **35**, 946.
- 140 T. Tanaka, B. S. Lee, N. Aratani, M.-C. Yoon, D. Kim and A. Osuka, *Chem.-Eur. J.*, 2011, **17**, 14400.
- 141 H. Mori, T. Tanaka, B. S. Lee, P. Kim, D. Kim and A. Osuka, *Chem.-Asian J.*, 2012, **7**, 1811.
- 142 H. Sato, K. Tashiro, H. Shinmori, A. Osuka and T. Aida, *Chem. Commun.*, 2005, 2324.
- 143 H. Sato, K. Tashiro, H. Shinmori, A. Osuka, Y. Murata, K. Komatsu and T. Aida, *J. Am. Chem. Soc.*, 2005, **127**, 13086.
- 144 T. Sakurai, K. Shi, H. Sato, K. Tashiro, A. Osuka, A. Saeki, S. Seki, S. Tagawa, S. Sasaki, H. Matsunaga, K. Osaka, M. Takata and T. Aida, *J. Am. Chem. Soc.*, 2008, **130**, 13812.
- 145 T. Sakurai, K. Tashiro, Y. Honsho, A. Saeki, S. Seki, A. Osuka, A. Muranaka, M. Uchiyama, J. Kim, S. Ha, K. Kato, M. Takata and T. Aida, *J. Am. Chem. Soc.*, 2011, **133**, 6537.
- 146 S. Tanaka, T. Sakurai, Y. Honsho, S. Seki, K. Kato, M. Takata, A. Osuka and T. Aida, *Chem.-Eur. J.*, 2012, **18**, 10554.
- 147 D. Bonifazi, M. Scholl, F. Song, L. Echegoyen, G. Accorsi, N. Armaroli and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, **42**, 4966.
- 148 D. Bonifazi, G. Accorsi, N. Armaroli, F. Song, A. Palkar, L. Echegoyen, M. Scholl, P. Seiler, B. Jaun and F. Diederich, *Helv. Chim. Acta*, 2005, **88**, 1839.
- 149 D. Bonifazi, H. Spillmann, A. Kiebele, M. de Wild, P. Seiler, F. Cheng, H.-J. Güntherodt, T. Jung and F. Diederich, *Angew. Chem., Int. Ed.*, 2004, **43**, 4759.
- 150 H. S. Cho, D. H. Jeong, S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Tsuda and A. Osuka, *J. Am. Chem. Soc.*, 2002, **124**, 14642.
- 151 K. J. McEwan, P. A. Fleitz, J. E. Rogers, J. E. Slagle, D. G. McLean, H. Akdas, M. Katterle, I. M. Blake and H. L. Anderson, *Adv. Mater.*, 2004, **16**, 1933.
- 152 H. Furuta, H. Maeda and A. Osuka, *Chem. Commun.*, 2002, 1795.
- 153 J. L. Sessler and D. Seidel, *Angew. Chem., Int. Ed.*, 2003, **42**, 5134.
- 154 S. Shimizu and A. Osuka, *Eur. J. Inorg. Chem.*, 2006, 1319.
- 155 T. K. Chandrashekar and S. Venkatraman, *Acc. Chem. Res.*, 2003, **36**, 676.
- 156 R. Misra and T. K. Chandrashekar, *Acc. Chem. Res.*, 2008, **41**, 265.
- 157 M. Stępień, N. Sprutta and L. Latos-Grażyński, *Angew. Chem., Int. Ed.*, 2011, **50**, 4288.
- 158 S. Saito and A. Osuka, *Angew. Chem., Int. Ed.*, 2011, **50**, 4342.
- 159 A. Osuka and S. Saito, *Chem. Commun.*, 2011, **47**, 4330.
- 160 The number in the square-bracketed prefix indicates the number of π electrons in the effective macrocyclic conjugation.
- 161 M. G. P. M. S. Neves, R. M. Martins, A. C. Tomé, A. J. D. Silvestre, A. M. S. Silva, V. Félix, M. G. B. Drew and J. A. S. Cavaleiro, *Chem. Commun.*, 1999, 385.
- 162 J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 7190.
- 163 T. Tanaka, N. Aratani, J. M. Lim, K. S. Kim, D. Kim and A. Osuka, *Chem. Sci.*, 2011, **2**, 1414.
- 164 T. Tanaka, N. Aratani and A. Osuka, *Chem.-Asian J.*, 2012, **7**, 889.
- 165 K. Naoda, H. Mori, N. Aratani, B. S. Lee, D. Kim and A. Osuka, *Angew. Chem., Int. Ed.*, 2012, **51**, 9856.
- 166 M. Pawlicki, M. Morisue, N. K. S. Davis, D. G. McLean, J. E. Haley, E. Beuerman, M. Drobizhev, A. Rebane, A. L. Thompson, S. I. Pascu, G. Accorsi, N. Armaroli and H. L. Anderson, *Chem. Sci.*, 2012, **3**, 1541.
- 167 I. M. Blake, H. L. Anderson, D. Beljonne, J.-L. Brédas and W. Clegg, *J. Am. Chem. Soc.*, 1998, **120**, 10764.
- 168 I. M. Blake, L. H. Rees, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2000, **39**, 1818.

- 169 I. M. Blake, A. Krivokapic, M. Ketterle and H. L. Anderson, *Chem. Commun.*, 2002, 1662.
- 170 W. Zeng, B. S. Lee, Y. M. Sung, K.-W. Huang, Y. Li, D. Kim and J. Wu, *Chem. Commun.*, 2012, **48**, 7684.
- 171 H. Shinokubo and A. Osuka, *Chem. Commun.*, 2009, 1011.
- 172 N. N. Sergeeva, M. O. Senge and A. Ryan, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific, Singapore, 2010, vol. 3, ch. 12, p. 325.
- 173 K. B. Fields, J. V. Ruppel, N. L. Snyder and X. P. Zeng, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific, Singapore, 2010, vol. 3, ch. 13, p. 367.
- 174 H. Yorimitsu and A. Osuka, *Asian J. Org. Chem.*, DOI: 10.1002/ajoc.201200183.