Chem Soc Rev

REVIEW ARTICLE

Conjugated porphyrin arrays: synthesis, properties and applications for functional materials

Takayuki Tanaka and Atsuhiro Osuka*

Cite this: DOI: 10.1039/c3cs60443h

Received 2nd December 2013

DOI: 10.1039/c3cs60443h

www.rsc.org/csr

Conjugated porphyrin arrays that possess delocalised electronic networks have, for the most part, been assembled by using alkene or alkyne type bridging units or by directly connecting individual porphyrin chromophores with multiple bonds to form fused porphyrin arrays. Throughout the last two decades, such conjugated porphyrin arrays have been actively explored due to their attractive electronic, optical and electrochemical properties. This review aims to cover the multitude of synthetic methodologies that have been developed for the construction of conjugated porphyrin arrays as well as to summarise their structure–property relationships and use in various applications such as near infrared (NIR) dyes, non-linear optical materials and electron-conducting molecular wires.

1. Introduction

Porphyrin, a square planar 18π aromatic macrocycle consisting of four pyrroles and four methine carbons, is arguably the most significant pigment to be found in nature. Owing to numerous advantageous properties such as structural robustness, attractive absorption and emission properties, strong aromaticity and rich metal coordination chemistry, porphyrin has been successfully utilized across a wide range of research disciplines. In addition to these attributes, it has been increasingly recognised that the porphyrin electronic system is susceptible to conjugative perturbation at the periphery, hence allowing rational electronic fine-tuning that affords systems displaying drastically altered optical and electronic properties. Along this line, a variety of conjugated porphyrin arrays have been constructed over the last two decades. In this review, the emphasis has been placed upon the progress in the chemistry of conjugated porphyrin arrays, with particular attention being focused on systems that exhibit attractive electronic, optical, electrochemical and magnetic properties, thus allowing them

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan. E-mail: osuka@kuchem.kyoto-u.ac.jp; Fax: +81 757533970; Tel: +81 757534007

Takayuki Tanaka

Takayuki Tanaka was born in 1984 in Osaka, Japan. He received his BSc (2007), MSc (2009), and PhD (2012) degrees from Kyoto University. He was selected as a JSPS Research Fellow for Young Scientists in 2009 and a JSPS Postdoctoral Fellow for Research Abroad in 2012. In 2013, he came back to Kyoto University, where he has been working as an Assistant Professor.

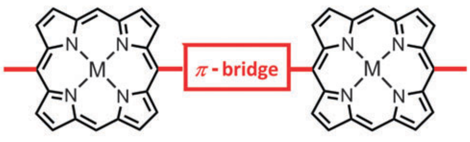
Atsuhiro Osuka

Atsuhiro Osuka received a PhD from Kyoto University in 1982. In 1979, he started his academic carrier 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, subporphyrins, and Möbius aromatic and antiaromatic molecules.

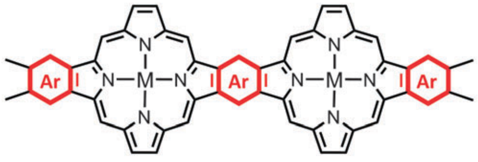
to be considered as promising candidates for future applications such as NIR dyes, photovoltaic dyes, nonlinear optical materials and nano-electronic devices.[1–15]

In the early years of artificial photosynthetic model studies, 1,3- and 1,4-phenylene linkers were widely employed to connect several porphyrins together to form porphyrin arrays or to attach donors or acceptors to porphyrins to form donor–acceptor molecules.[16,17] These porphyrin model compounds were rather conformationally restricted, especially when octaethyl-substituted porphyrin (OEP)-type peripherally alkylated porphyrins were employed.[18–21] Such structural features are favourable for the detailed analysis of the structure–reactivity relationship of intramolecular excitation energy transfer and electron transfer, but result in weak inter-porphyrin interactions due to rather orthogonal arrangements of the phenylene linkers toward the porphyrin plane. In contrast, unsaturated groups such as alkenes and alkynes can often adopt a co-planar arrangement with the porphyrin plane and thus are suitable functionalities for enlarging the conjugative network of porphyrins. The chemistry of these conjugated porphyrins will be reviewed in Section 2. As a different approach, fused porphyrin arrays have been extensively explored, in which two porphyrins are connected with multiple covalent bonds either directly or through an aromatic linker. The chemistry of these fused porphyrin arrays will be presented in Section 3, as well as some discussion related to their applications. The chemistry of other conjugated porphyrinoids is also discussed in Section 4, which includes β–β directly linked corrole oligomers, hybrid tapes encompassing hexaphyrin and porphyrin subunits and subporphyrin dimers (Fig. 1).

While *meso–meso* linked porphyrin oligomers have been extensively studied following the first reported example in 1997,[22] they serve only as photonic wires by transferring excitation energy as opposed to conducting electrons due to the nearly orthogonal geometry between the neighbouring porphyrin chromophores.[23] Therefore, we will not enter into the chemistry of *meso–meso* linked porphyrin arrays in detail in this review, which was reviewed elsewhere.[24] Cyclic conjugative porphyrin arrays also fall outside the scope of this review, since they were also reviewed elsewhere.[25,26]



singly-linked porphyrin oligomer



fused porphyrin oligomer

triply-linked porphyrin oligomer

Fig. 1 Types of conjugated porphyrin wires.

2. Porphyrin arrays bridged by conjugative linkers

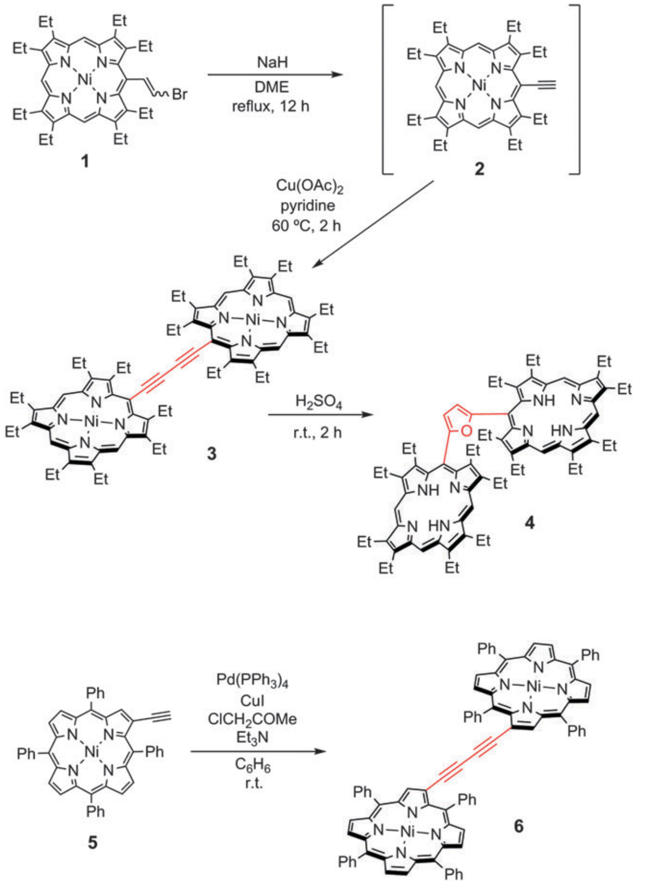
Porphyrin arrays bridged by conjugative linkers have been accessed mainly *via* transition metal catalysed reactions. The extent of electronic perturbations in these oligomers depends on the type of spacer, steric configuration and orbital coefficient at the bridging position.

2.1 Butadiyne-bridged porphyrin oligomers

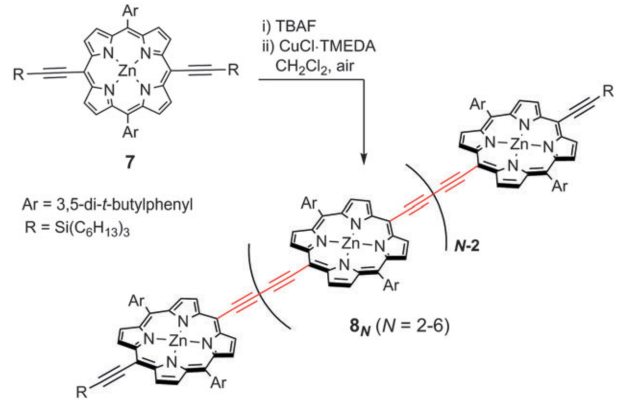
A conjugated porphyrin dimer bridged by a 1,3-butadiyne linker was first reported by Arnold and Johnson in 1978,[27] although the optical and electrochemical properties were reinvestigated later in the 1990s.[28]

meso-Bromovinyl Ni(II) octaethylporphyrin (OEP) **1** that was functionalised from the corresponding *meso*-formyl Ni(II) OEP was dehydrobrominated with sodium hydride in refluxing 1,2-dimethoxyethane (DME) to afford *meso*-ethynyl derivative **2**. Dimerisation of **2** was induced by oxidation with $Cu(OAc)_2$ in pyridine yielding 1,3-butadiyne-bridged Ni(II) OEP **3** (Scheme 1).[27] The absorption spectrum of **3** was markedly altered, indicating considerable interaction between the two porphyrin macrocycles. Later, a range of metal complexes of **3** were examined, and furan-bridged porphyrin dimer **4** was prepared by simple treatment of **3** with sulfuric acid.[29] Gosper and Ali carried out oxidative coupling of *meso*-tetraphenyl-2-ethynyl Ni(II) porphyrin **5** using a mixture of tetrakis(triphenylphosphine) Pd(0), chloroacetone and copper(I) iodide.[30] This Ni(II) TPP porphyrin series showed that a β-to-β type connection induced smaller electronic perturbation compared with the standard *meso*-to-*meso* connection.

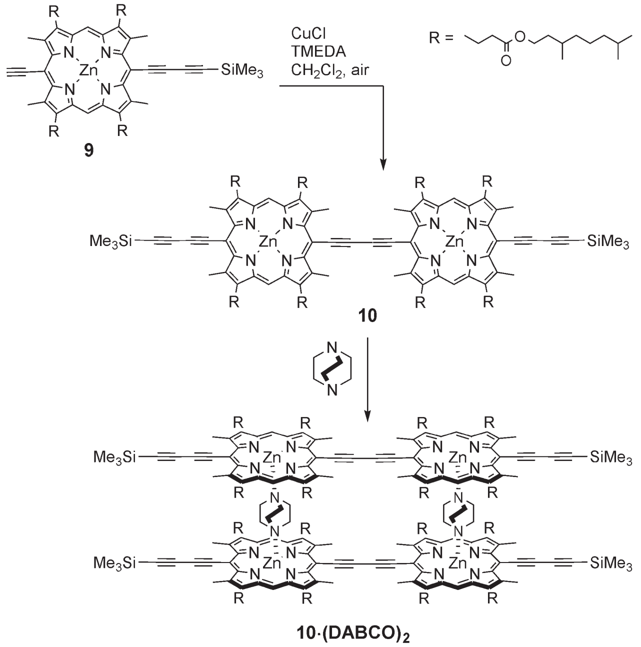
Anderson *et al.* extended the same synthetic strategy by synthesising 1,3-butadiyne-bridged Zn(II) octaalkylporphyrin polymers, which exhibited absorption bands with maxima at around 900 nm.[31,32] Later, a more soluble substrate, 5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-bis(trihexylsilylethynyl)porphyrin **7**, was employed for oligomerisation. A stepwise approach was used to synthesise oligomers $\mathbf{8}_N$ (N = 2–6), which consisted of (i) protodesilylation with TBAF and (ii) Glaser–Hay coupling with CuCl·TMEDA in CH_2Cl_2 under aerobic conditions (Scheme 2).[33] The oligomers were separated by chromatography over a silica gel column. As expected, the absorption Q-bands measured in 1% pyridine/CH_2Cl_2 were red-shifted and intensified with increasing chain-length, reaching out to around 900 nm in the case of the hexamer $\mathbf{8}_6$. A similar reaction was employed to prepare various 1,3-butadiyne-bridged porphyrins.[34,35]



Scheme 1 Synthesis of butadiyne-bridged diporphyrins *via* the oxidative coupling.



Scheme 2 Synthesis of butadiyne-bridged porphyrin oligomers.

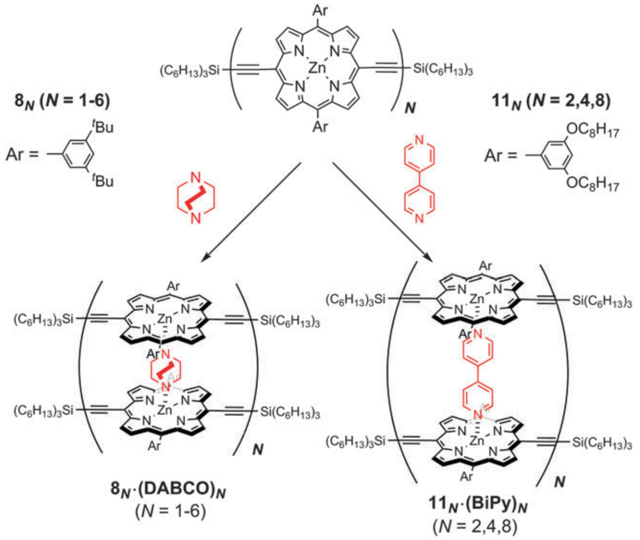


Scheme 3 A 1,3-butadiyne-bridged porphyrin ladder.

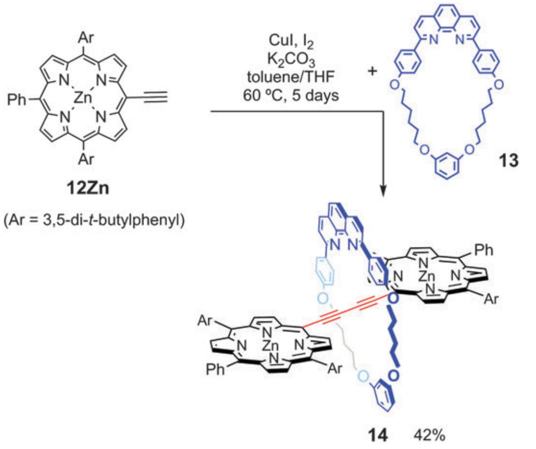
Sterically unhindered porphyrins tend to organise themselves in a π-stacked cofacial manner.[36,37] Cooperative stacking of 1,3-butadiyne-linked porphyrins was demonstrated in the presence of a bidentate ligand which coordinates with the central metal ion of the porphyrins and organises them into a double stranded ladder formation.[32,38] Addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) to **10** afforded a 2 : 2 complex, $\mathbf{10\cdot(DABCO)_2}$ (Scheme 3). ^{1}H NMR titrations confirmed the formation of a highly symmetric structure by exhibiting an upfield shifted, sharp singlet of the DABCO protons at −4.60 ppm brought on by the porphyrin ring current effect. In the UV/Vis absorption spectrum, $\mathbf{10\cdot(DABCO)_2}$ exhibited Soret bands at 428 nm and 495 nm and an intensified Q band at around 720 nm, consistent with the expected co-facial arrangement. The ladder formation was also realised with 1,3-butadiyne-bridged porphyrin oligomers, which showed positive cooperative self-assembly (*i.e.* all-or-nothing assembly) and fairly increased planarity and conjugation, resulting in a reduction in the HOMO–LUMO band gaps. In addition, this feature strongly affects their non-linear optical properties. While a double stranded diporphyrin bound to a bipyridyl ligand, $\mathbf{112\cdot(BiPy)_2}$, did not exhibit an enhanced two-photon absorption (TPA) cross section (σ_2^m/N = 3300 GM) compared with $\mathbf{11_2}$ (σ_2^m/N = 3750 GM), the octamer $\mathbf{11_8\cdot(BiPy)_8}$ exhibited dramatically enhanced TPA values (σ_2^m/N = 6100) compared with $\mathbf{11_8}$ (σ_2^m/N = 4600).[38–40] This result demonstrated that the TPA enhancement is more effective in the case of double stranded porphyrin arrays (Scheme 4). Q5

An active metal-templated direct coupling has been employed to synthesise rotaxanes containing conjugated porphyrins. Anderson *et al.* reported facile formation of a [2]rotaxane **14** consisting of a butadiyne linked porphyrin dimer along with its crystal structure.[41] Porphyrin monomer **12Zn** was stirred with phenanthroline macrocycle **13**, copper(I) iodide, iodine and potassium carbonate in a 1 : 1 mixture of toluene and THF for 5 days at 60 °C (Scheme 5). Rotaxane **14** was isolated in 42% yield, together with a non-interlocked porphyrin dimer (30% yield). A similar strategy has been applied to the synthesis of a series of dumbbell-type rotaxanes containing polyynes that span the porphyrin units in a manner analogous to an axle.[42]

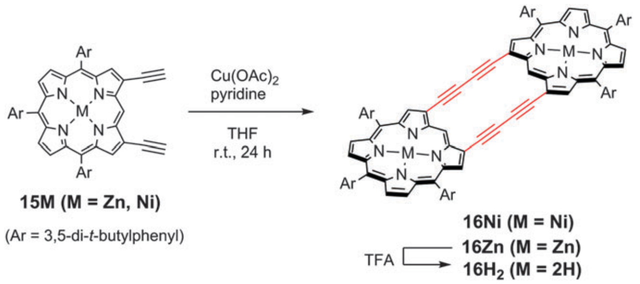
β-Selective direct borylation of porphyrins has been used for the synthesis of novel functionalised porphyrins and porphyrin-based



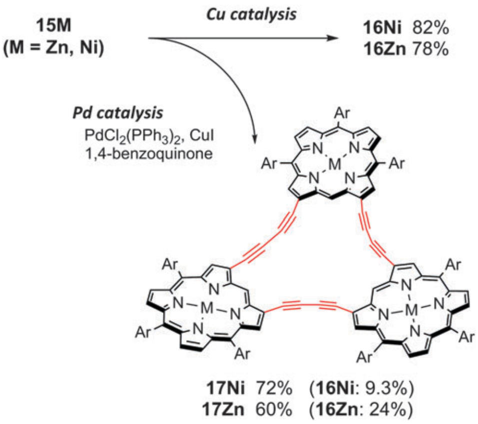
Scheme 4 DABCO- and 4,4′-bipyridyl-coordinated porphyrin ladders.



Scheme 5 Synthesis of a butadiyne-bridged porphyrin rotaxane.



Scheme 6 Synthesis of β,β-butadiyne-bridged diporphyrins.



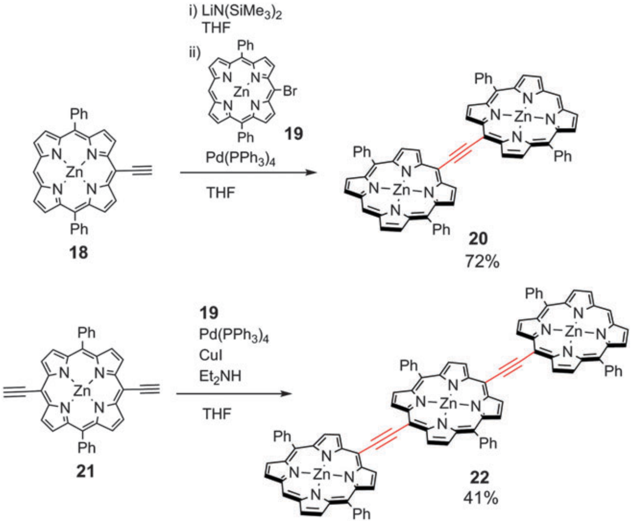
Scheme 7 Preferential synthesis of cyclic porphyrin trimers.

architectures.[43,44] Shinokubo *et al.* synthesised doubly β,β 1,3-butadiyne-linked porphyrin dimer **16M** from 3,7-diethynylated porphyrins **15M** with the aid of copper(II) acetate and pyridine in THF (Scheme 6).[45] The doubly bridged structure adopted a robust and forced planar conformation, which led to a high degree of conjugation. For example, **16Zn** displayed a split Soret band at 441 and 501 nm, and Q bands at 580, 605 and 645 nm, both of which were red-shifted from those of **15Zn** (a split Soret band at 431, 452 and 479 nm, and Q-bands at 563 and 606 nm). The fluorescence quantum yield was considerably reduced ($\Phi_F < 0.01$) probably due to structural distortion.

Very recently, preferential formation of cyclic trimers, **17M**, has been realised by using a $PdCl_2(PPh_3)_2$/CuI catalytic system instead of copper catalysis.[46] Under palladium catalysed conditions, **16Ni** and **17Ni** were formed in 9.3 and 72% yields, respectively. A similar result was obtained for Zn complexes, 24% and 60% for **16Zn** and **17Zn**, respectively, while copper catalysed reactions only provided dimers, **16Ni** in 82% and **17Zn** in 78% (Scheme 7). The differing outcomes provided by the two catalytic systems can be accounted for in terms of stereochemical requirements of intermediates in the key reductive elimination step.

2.2 Ethyne-bridged porphyrin oligomers

Acetylene linkers attached directly at the *meso* position allow for significant modulation of the optical and electronic properties of multiporphyrin arrays. Therien *et al.* have developed a number of ethyne-bridged porphyrin arrays since their first report in 1994.[47] In their approach, transition metal mediated reactions were proved to be very useful in constructing multichromophoric assemblies and peripherally fabricated porphyrins.[43,44,47] With *meso*-ethynylated porphyrin synthons **18** and **21** in hand, ethyne-bridged Zn(II) porphyrin dimer **20** and trimer **22** were prepared *via* Sonogashira coupling (Scheme 8). Porphyrin pentamer **26** was also synthesised by using $Pd(PPh_3)_4$ and copper(I) iodide with diethylamine in THF.[48] Later, copper-free Pd-catalysed coupling reaction using $Pd_2(dba)_3$ and $AsPPh_3$ with triethylamine in THF was found to be an alternative, which afforded D–A–D ("D" and "A" represent donor and acceptor, respectively; see Fig. 2) type trimer **25** and D–A–D–A–D type pentamer **27** in moderate yields.[49] The longest acetylene bridged porphyrin chain was a heptamer, which revealed unusually long hole polaron delocalisation length up to 75 nm.[50] The absorption spectra of **20** and **22** exhibited distinctly split, broad Soret bands in the range of 400–520 nm and the lowest energy bands were observed at 683 nm for **20**



Scheme 8 Synthesis of ethyne-bridged porphyrin arrays.

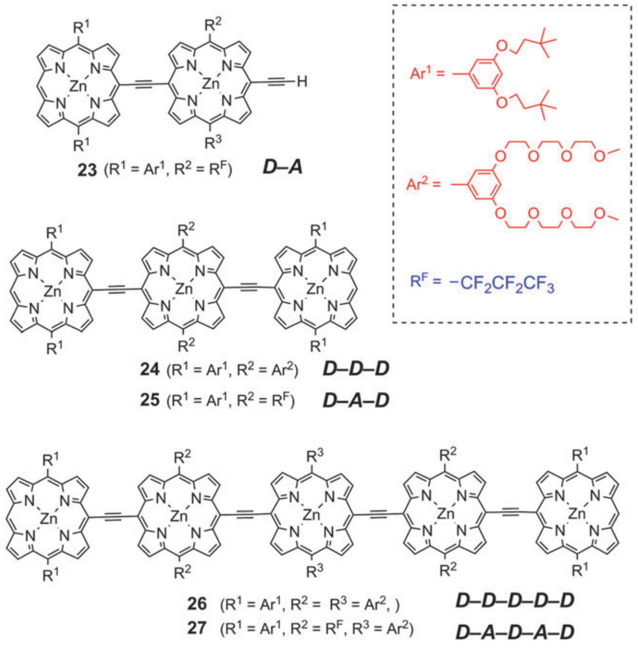
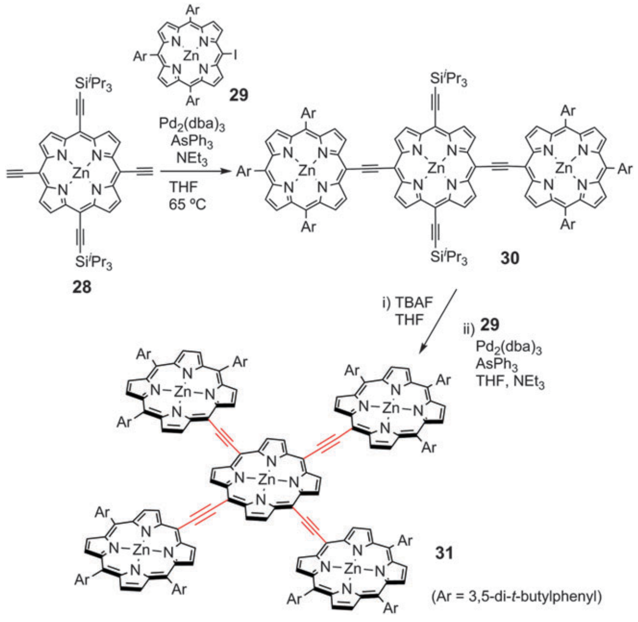


Fig. 2 Donor–acceptor-appended ethyne-bridged porphyrins.

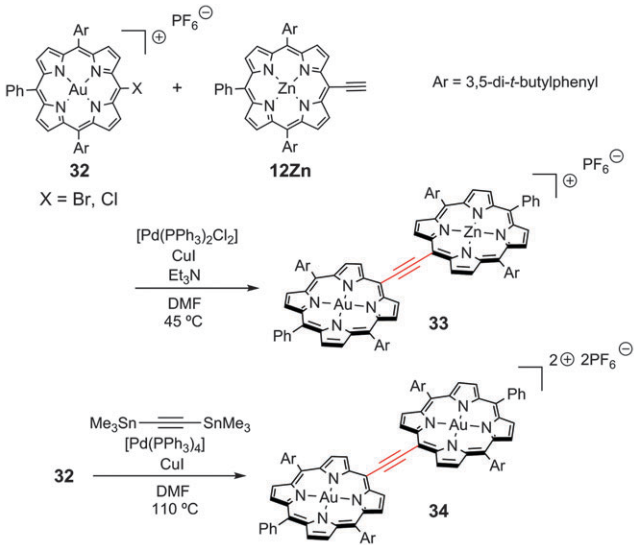
and at 802 nm for **22**. Moreover, **26** displayed a remarkably red-shifted absorption band ($\lambda_{\max}$ = 883 nm) with an extinction coefficient exceeding 225 000 M^{-1} cm^{-1}. In D–A type arrays, broader Soret bands were observed, along with slightly blue-shifted Q-like bands and emission profiles in comparison to the analogous electron-rich arrays (for **27**, $\lambda_{\max}$ = 843 nm). More importantly, it was found that the magnitude of electrochemical and optical properties could be modulated independently in the ethyne-bridged conjugated porphyrin arrays through this alternating electron-donor/acceptor structural motif. Singlet and triplet excited state dynamics and hole polaron delocalisation length of a series of ethyne-bridged porphyrin chains have been investigated in more detail.[51]



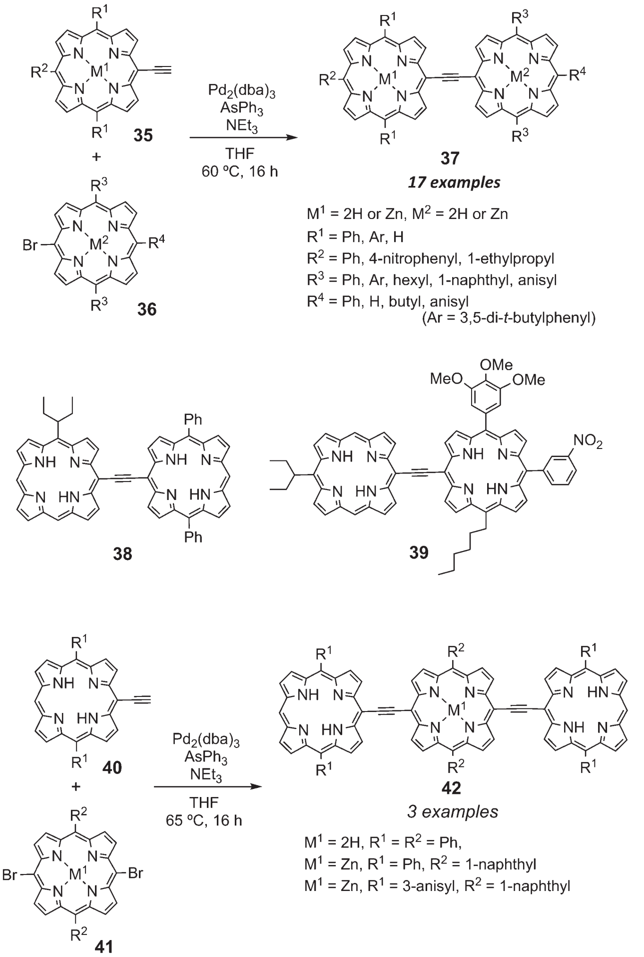
Scheme 9 Synthesis of ethyne-bridged multiporphyrins.

Yeh *et al.* accomplished the synthesis of ethyne-bridged multiporphyrin arrays and examined their spectroscopic and electrochemical properties.[52] Sonogashira coupling of triisopropylsilyl protected Zn(II) porphyrin **28** with iodoporphyrin **29** under copper-free conditions afforded porphyrin trimer **30**, which was further modified to provide the cruciform-shaped pentameric Zn(II) porphyrin array **31** *via* a similar methodology (Scheme 9).

Zn(II) porphyrin–Au(III) porphyrin dyad **33** connected through an ethyne linker was reported along with Au(III) porphyrin homodimer **34** (Scheme 10).[53] Large electronic coupling between the two porphyrins in **33** was revealed by redox potential shifts and an intense charge transfer band at 739 nm, while **34** exhibited a usual red-shifted Q-band at



Scheme 10 Synthesis of Au(III) porphyrin arrays.



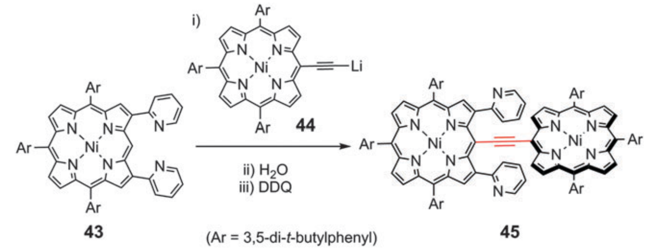
Scheme 11 Synthesis of various ethyne-bridged porphyrins.

624 nm. The heterodimer **33** exhibited a large first molecular hyperpolarisability coefficient ($\beta = 2100 \times 10^{-30}$ esu at $\lambda = 1064$ nm).

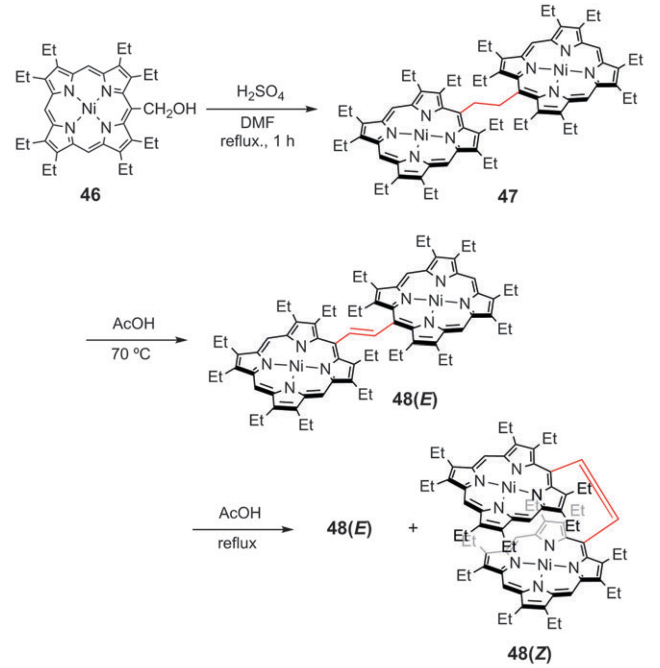
Various symmetric and unsymmetric *meso*-to-*meso* ethyne-bridged porphyrin arrays were synthesised by copper-free Sonogashira reactions (Scheme 11).[54] Porphyrin dimers bearing naked *meso* positions such as **38** and **39** were also prepared. To introduce alkyl or aryl substituents on free *meso* positions, organolithium reagents have been shown to be convenient. Along this line, useful porphyrin building blocks such as **35, 36, 40** and **41** were prepared and used for the synthesis of porphyrin arrays **37** and **42.**[55] Recently, direct *meso*-alkynylation of β,β-dipyridylporphyrin **43** with various alkynyllithium reagents has been achieved, in which the adjacent dipyridyl groups assist the nucleophilic addition through dual coordination to the lithium reagents.[56] This method enabled the synthesis of *meso*-ethyne-bridged Ni(II) diporphyrin **45** in 60% yield through the addition of lithiated *meso*-ethynyl Ni(II) porphyrin **44** to **43** (Scheme 12).

2.3 Ethene-bridged porphyrin oligomers

Ethene-bridged porphyrin oligomers have remained relatively unexplored, probably due to complications associated with inherent *cis*/*trans* isomerism.



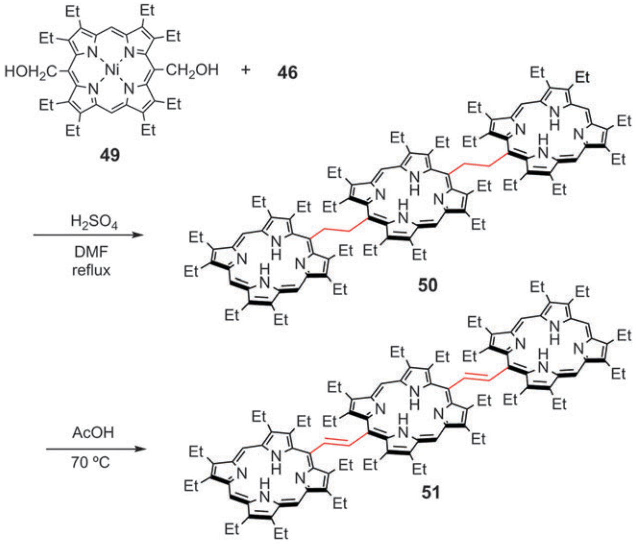
Scheme 12 Synthesis of an ethyne-bridged diporphyrin *via* direct *meso*-alkynylation.



Scheme 13 Synthesis of ethene-bridged diporphyrins *via* ethane-bridged diporphyrin.

Ponomarev *et al.* discovered a novel synthesis of **48(*E*)** from the corresponding ethane-bridged Ni(II) OEP **47**,[57,58] which was prepared *via* acid-catalysed dimerisation of *meso*-hydroxymethyl-porphyrin **46.**[59] Heating of **47** in acetic acid at 60–70 °C for 20 min gave **48(*E*)** predominantly in 85% yield, and further heating in refluxing acetic acid led to the formation of a 1:2 mixture of **48(*E*)** and **48(*Z*).** These isomers were easily separated by column chromatography on silica gel into two pure isomers (Scheme 13).[60] The face-to-face structure **48(*Z*)** as well as its Cu(II) complex was revealed by X-ray diffraction analysis.[61,62] The two porphyrin planes were arranged in a cofacial manner with a mean separation distance of 3.36 Å, which may play an important role in stabilising the structure. Higuchi *et al.* extended this strategy to ethene-bridged trimer **51** and tetramer **52** (Scheme 14 and Fig. 3).[63]

The UV/Vis absorption spectrum of **48(*E*)** exhibited a slightly broadened and red-shifted Soret band at 414 nm and the lowest energy Q-band at 566 nm, while **48(*Z*)** exhibited a blue-shifted Soret band at 393 nm and a red-shifted Q-band at 568 nm, consistent with its face-to-face structure. Compared with



Scheme 14 Synthesis of an ethene-bridged porphyrin trimer.

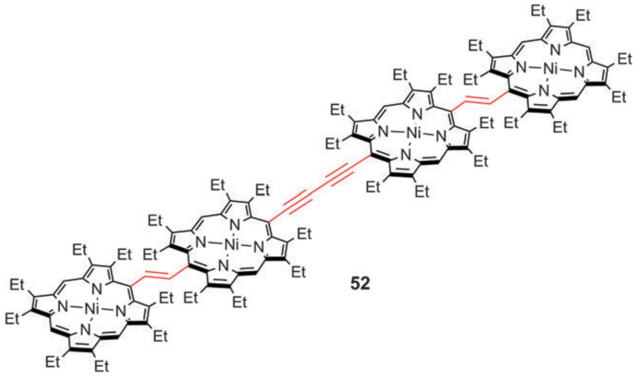
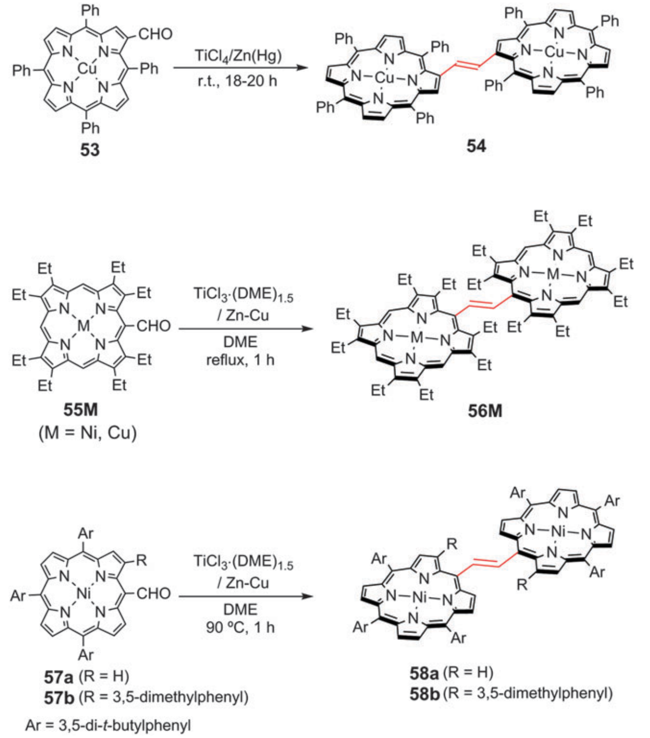


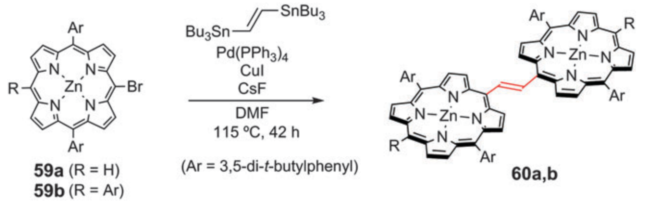
Fig. 3 A conjugated porphyrin tetramer bridged by ethene and butadiyne.

ethyne-bridged diporphyrins, the electronic conjugation in **48(*E*)** appears weak, which is ascribed to a nonplanar but almost parallel configuration as confirmed by X-ray crystal structures.[61,62] The ethene linker tilts at 70–90° relative to the porphyrin plane due to the steric clash between the ethene bridges and the β-substituted ethyl groups.

The McMurry coupling reaction is a useful synthetic tool that can be used to form a carbon–carbon double bond from a formylated porphyrin substrate. Zhilina *et al.* reported the first reductive dimerisation reaction of a β-formylated Cu(II) TPP **53**, to afford β–β ethene-bridged dimer **54.**[64] Smith *et al.* modified this protocol by using an active titanium reagent prepared by refluxing 9.9 equiv. of $TiCl_3{\cdot}(DME)_{1.6}$ and 37.5 equiv. of Zn–Cu couple for 2 h in dry DME.[65,66] Ethene-bridged OEPs **56M** were synthesised from formylated OEPs **55M** in good yields (Scheme 15). Recently, Osuka *et al.* employed this method to β-monoarylated *meso*-formyl porphyrin **57b**, which was prepared by β-selective direct arylation of *meso*-formylporphyrin **57a**, giving *meso*–*meso* ethene-bridged Ni(II) porphyrin dimer **58b.**[67] The two porphyrins in **58b** were twisted with modest dihedral angles (43–49°) between porphyrin and vinylene due to the neighbouring β-substituents.

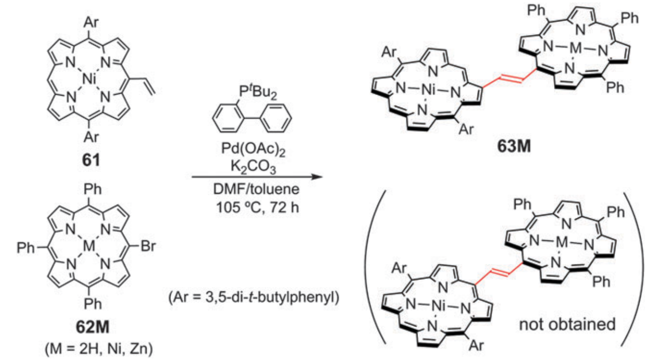


Scheme 15 Synthesis of ethene-bridged diporphyrins *via* McMurry coupling.

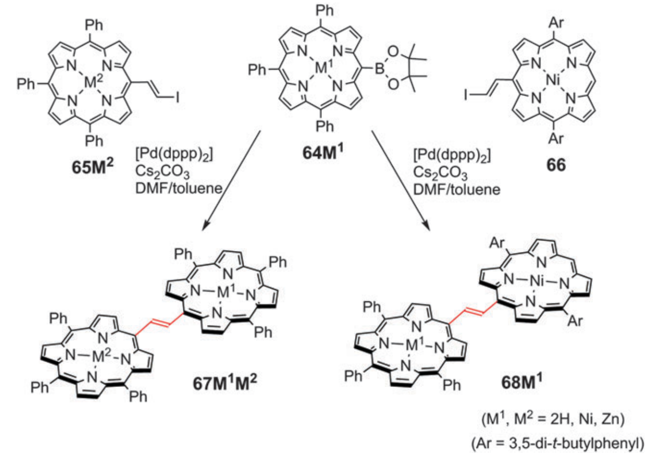


Scheme 16 Synthesis of ethene-bridged diporphyrins *via* Stille coupling.

Transition metal-catalysed reactions again play a key role in the facile formation of ethene-bridged porphyrins. *trans*-Ethene-bridged Zn(II) porphyrin dimers **60a,b** were synthesised by Stille coupling of *meso*-bromo Zn(II) porphyrin **59a,b** using bis(tributylstannyl)ethene, $Pd(PPh_3)_4$, CuI and CsF in DMF (Scheme 16).[68] *meso*-Vinylporphyrins are useful synthetic precursors for Heck-type reactions. Thus, Heck reaction of **61** and **62M** has been examined under classical conditions, which, rather surprisingly, provided only *meso*-β ethene-bridged porphyrin dyads **63M** (Scheme 17).[69] The mechanism for this unusual *meso* to β rearrangement may involve cyclopalladation onto the β-C–H followed by migratory reductive elimination. Later, porphyrin boronates **64M^1** and iodovinylporphyrins **65M^2** or **66** were subjected to Suzuki-coupling conditions in the hope of avoiding such undesired rearrangements. These reactions indeed provided the desired *meso* to *meso* ethene-bridged porphyrin dyads **67M^{1}M^2** or **68M^1** in moderate yields (Scheme 18).[70]



Scheme 17 Synthesis of ethene-bridged diporphyrins *via* Heck reaction.



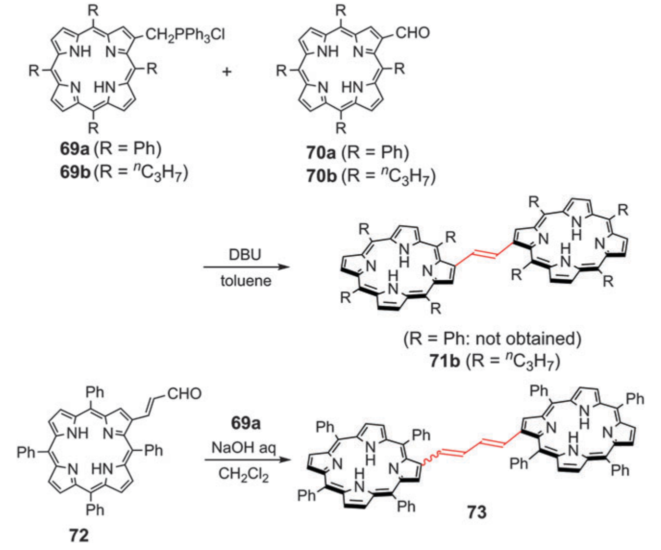
Scheme 18 Synthesis of ethene-bridged diporphyrins *via* Suzuki coupling.

2.4 Other examples

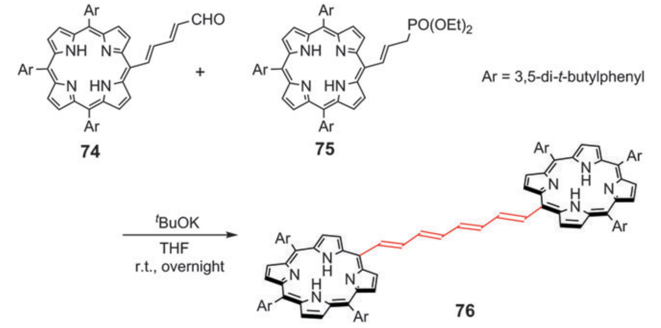
Extension of π-conjugative bridges, namely, elongation of polyene or polyyne bridges, is a promising strategy for realising large electronic perturbations.

Officer *et al.* succeeded in preparing porphyrin phosphonium chloride **69a** in gram quantities, which was reacted with porphyrinylacrolein **72** to give 1,3-butadiene-bridged porphyrin dimer **73** in good yield (Scheme 19).[71–73] Although the reaction of **69a** with formylated TPP **70a** failed to provide the desired ethene-bridged dimer, the same reaction of tetraalkylporphyrin **70b** with porphyrin phosphonium salt **69b** has recently been accomplished, giving ethene-bridged porphyrin dimer **71b** in 65% yield.[74] This success has been ascribed to less steric congestion at the *meso* position of **70b**.

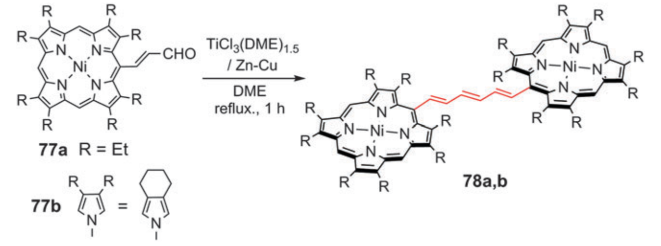
Odobel *et al.* performed a Wittig–Horner–Emmons reaction using porphyrinyl pentadienal **74** and porphyrinyl phosphonate **75** by using potassium *tert*-butoxide as a base in THF to obtain octa-1,3,5,7-tetraene-bridged porphyrin dimer **76** in 68% yield (Scheme 20).[75] 1,3,5-Hexatriene-bridged dimers **78a,b** were prepared by Smith *et al.* through McMurry coupling of **77a,b**, respectively (Scheme 21).[65]



Scheme 19 Synthesis of conjugated diporphyrins *via* Wittig reaction.



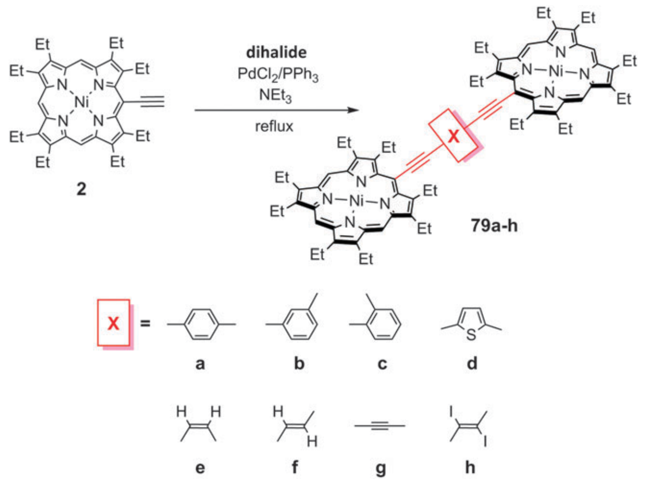
Scheme 20 Synthesis of diporphyrin **76** *via* Wittig–Horner–Emmons reaction.



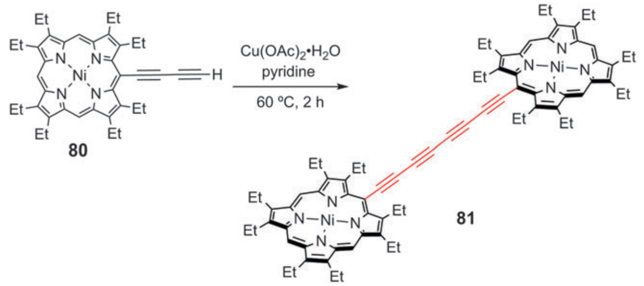
Scheme 21 Synthesis of diporphyrins **78a,b** *via* McMurry coupling.

Starting from *meso*-ethynyl Ni(II) OEP **2** as the primary building block, a series of dimers bridged by conjugative linkers including diethynylbenzenes (**79a–c**), 2,5-diethynylthiophene (**79d**), hexenediyne (**79e,f,h**), and hexatriyne (**79g**) were prepared by palladium-catalysed coupling reactions with dihalogenated molecules (Scheme 22).[76] Oxidative coupling of **80** provided octa-1,3,5,7-tetrayne-bridged dimer **81** (Scheme 23). In addition, dimers with a butenyne-bridge (**82**) and some *meso*-to-β dimers such as **83** and **84** were also synthesized (Fig. 4).[77] Synthesis of a similar diethynylethene-bridged porphyrin dimer and trimer was reported by Diederich *et al.*[78]

Sugiura *et al.* prepared a series of polyyne-bridged porphyrin dimers. Butadiyne- (**87**), octatetrayne- (**88**), dodecahexayne- (**89**)



Scheme 22 Synthesis of various conjugated diporphyrins.



Scheme 23 Synthesis of diporphyrin **81** *via* Glaser–Hay coupling.

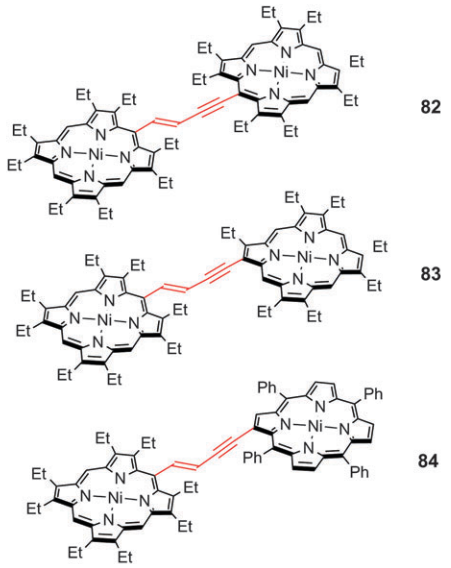
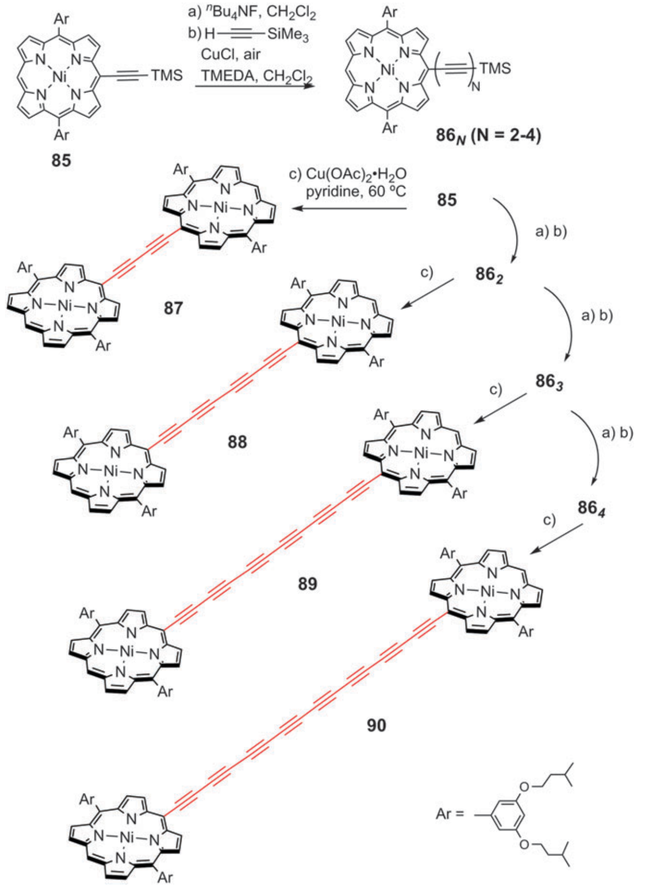


Fig. 4 Butenyne-bridged diporphyrins.

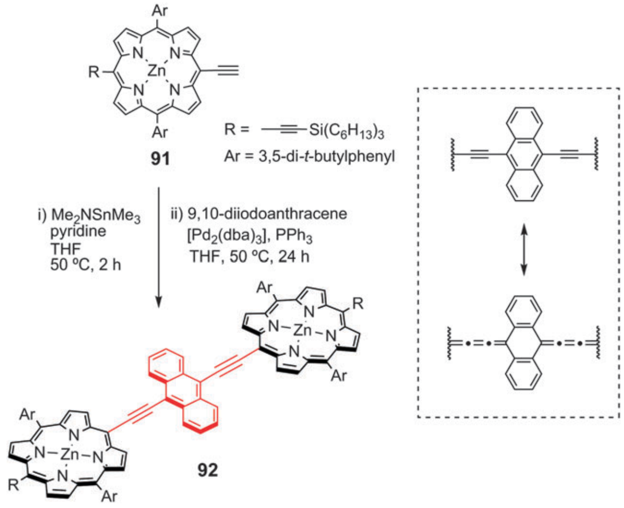
and hexadecaoctayne- (**90**) bridged diporphyrins were synthesised by oxidative coupling of *meso*-oligoynylporphyrins **86_n**, which were prepared by repeated desilylation and subsequent trimethylsilylethynylation of **85** (Scheme 24).[79] Exciton coupling interactions are observed between the terminal porphyrins in dimers **87** and **88**, while the exciton interaction between the two porphyrins is negligible in dimer **90**, which instead displays the electronic interaction between the porphyrin and hexadecaoctayne bridge. The hexadecaoctayne bridge in **90** is the longest conjugative linker between two porphyrins, to the best of our knowledge.



Scheme 24 Synthesis of polyyne-bridged diporphyrins.

Incorporation of 9,10-anthrylene units in conjugated polymers decreases the band-gap by reducing the energy difference between the aromatic and quinonoidal resonance structures.[80] This was also the case in anthracene-bridged porphyrin dimer **92** reported by Anderson *et al.*[81,82] Diporphyrin **92** was synthesised by stannylation of **91** followed by Stille coupling reaction with 9,10-diiodoanthracene (Scheme 25). The absorption and emission spectra of **92** were red-shifted in comparison to the corresponding ethynylphenylethynyl-bridged analog by 20 nm and 71 nm, respectively, indicating strong porphyrin–porphyrin interaction (Fig. 5). Q6

Benzo[1,2-*c*:4,5-*c*′]bis([1,2,5]thiadiazole) (BBTD) is known to induce substantial quinonoidal character in a conjugated backbone when conjugated with a suitable π-system. Therien *et al.* reported a series of proquinonoidal porphyrin arrays including diethynylbenzo[*c*][1,2,5]thiadiazole (BTD) linked array **93**, diethynyl(dimethyl-[1,2,5]thiadiazolo[3,4-*g*]quinoxaline) (TDQ)-linked array **94**, diethynyl-BBTD-linked array **95** and pentacene-linked array **96**.[83] The absorption spectra of these proquinonoidal arrays displayed significant red-shifts in their



Scheme 25 Synthesis of **92**.

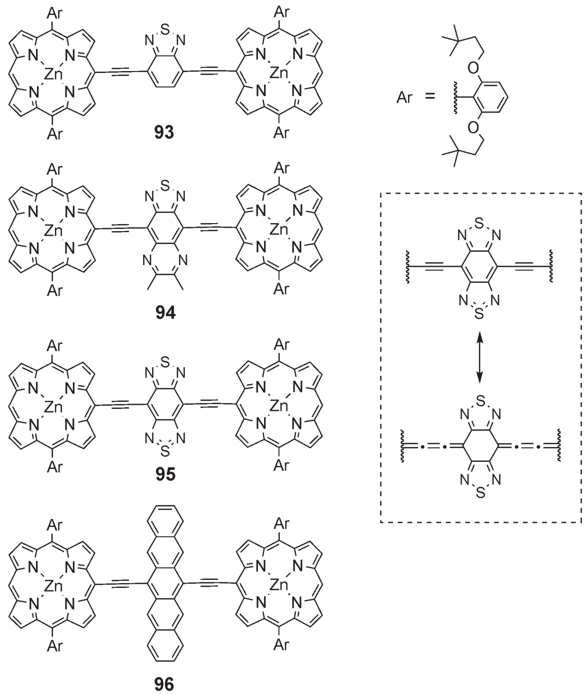
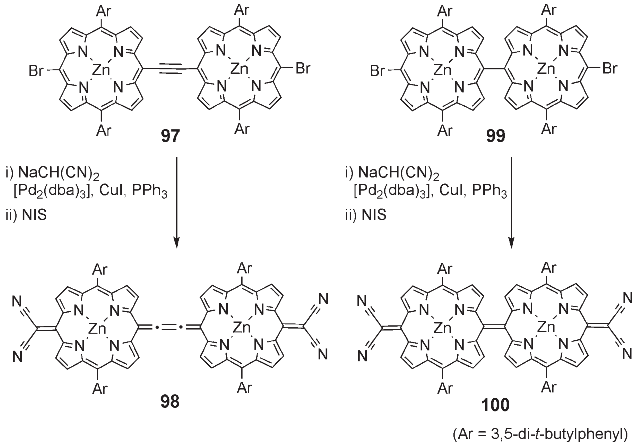


Fig. 5 BTD-, TDQ-, BBTD- and pentacene-incorporated diporphyrins.

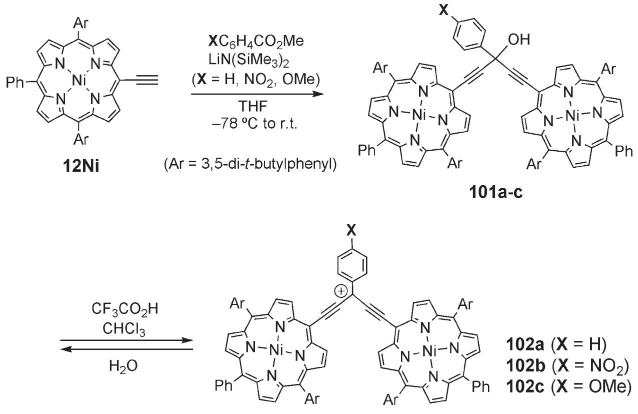
Q-bands, which were consistent with electrochemically determined reduced HOMO–LUMO band gaps. Among them, **95** exhibited the smallest HOMO–LUMO band gap (1.11 eV) and the lowest energy band (λ_{max} = 1006 nm), highlighting the unusually large quinonoidal resonance contribution to the low-lying electronically excited singlet states of these species systems.



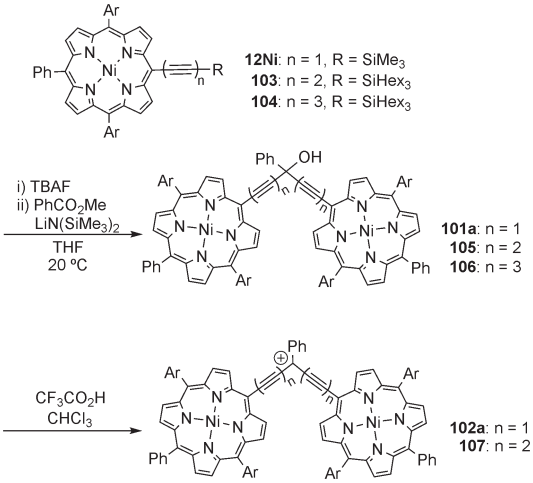
Scheme 26 Synthesis of quinonoidal porphyrin dimers.

Dibromoporphyrin dimers **97** and **99** were transformed to fully quinonoidal porphyrin dimers **98** and **100**, respectively, by palladium/copper catalysed nucleophilic substitution with the malononitrile anion followed by oxidation with *N*-iodosuccinimide (NIS) (Scheme 26).[84] The absorption spectrum of **98** was shifted into the NIR region (λ_{max} = 1080 nm), while a less bathochromic shift was observed for **100** (λ_{max} = 780 nm), probably due to its non-planar geometry in the ground state.

Porphyrin carbocations, or so-called ''porphocyanines'', have recently been developed by Anderson *et al.* It is well known that carbocations tend to be more electronically delocalised than neutral conjugated hydrocarbons, giving rise to NIR absorption profiles and large negative third-order nonlinearity.[85–87] The carbocation **102a–c** were generated from porphyrin dimer alcohol precursors **101a–c** upon treatment with TFA, as revealed by dramatic changes in the UV/Vis/NIR spectrum (for **102a**; λ_{max} = 1243 nm, ε = 170 000 M^{-1} cm^{-1}) (Scheme 27).[86,87] The *para*-nitro substituent of **102b** shifted the absorption to longer wavelength (λ_{max} = 1348 nm; ε = 120 000 M^{-1} cm^{-1}) whereas the *para*-methoxy substituent of **102c** shifted the absorption profile in the opposite direction (λ_{max} = 1176 nm; ε = 110 000 M^{-1} cm^{-1}), showing the ability to control the degree of delocalisation of porphyrins. Extending the conjugation lengths in these porphyrin carbocations resulted in a further shift of absorptions (Scheme 28).[88] Thus, carbocation **107** was generated from **105** in a similar manner, while alcohol **106** was rather unstable and could not be handled as a long-lived carbocation. The symmetry of the π-system has a



Scheme 27 Synthesis of porphyrin carbocations.



Scheme 28 Synthesis of extended porphyrin carbocations.

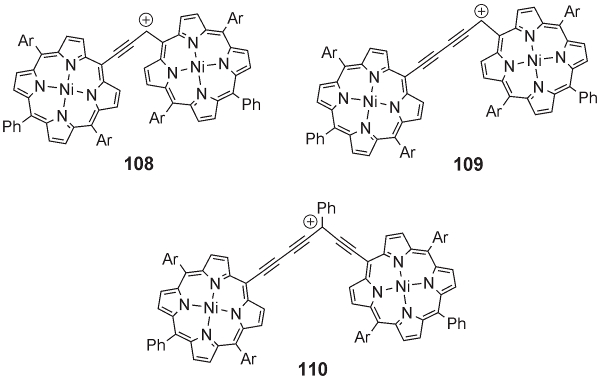


Fig. 6 Asymmetric porphyrin carbocations.

strong effect on the position, intensity and width of the absorption bands as observed in unsymmetrical carbocations **108**, **109** and **110** (Fig. 6).

Redox switching between quinone and hydroquinone in the central bridging section was tested to modulate the electronic properties of porphyrin dimer **111M** by Yeh *et al.* (Fig. 7).[89] Optical and electrochemical studies indicated that the electronic coupling is almost disrupted in quinone-incorporated porphyrin dimer **111M** because of its cross-conjugation network, but is enhanced in the hydroquinone-incorporated dimer.

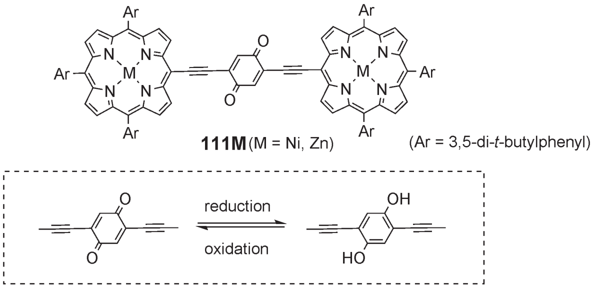


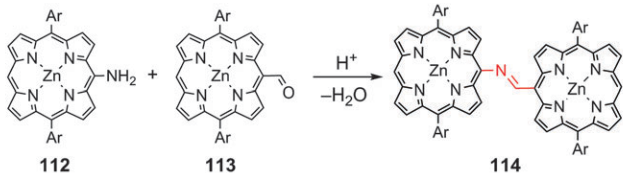
Fig. 7 Quinone-bridged diporphyrins.

2.5 Porphyrin oligomers bridged by heteroatom containing linkers

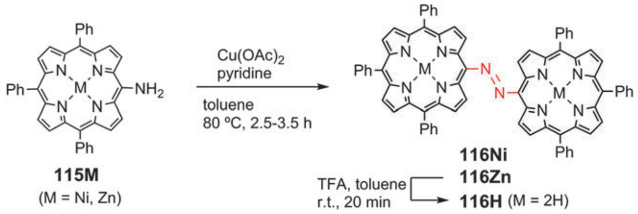
In 2002, Anderson *et al.* reported imino- and azo-bridged porphyrin dimers and evaluated the electronic coupling between the porphyrins.[90] Imino-bridged porphyrin dimer **114** was prepared from *meso*-amino Zn(II) porphyrin **112** and *meso*-formyl Zn(II) porphyrin **113** (Scheme 29). Later, Arnold *et al.* successfully synthesised azo-bridged porphyrin dimer **116M** by copper(II) mediated oxidative coupling of *meso*-amino porphyrins **115M** (Scheme 30).[91,92] X-ray diffraction analysis of **116Ni** revealed that the dihedral angle between the C_{meso}–N_{azo} = N_{azo}–C_{meso} mean plane and porphyrin mean planes was 37°, being significantly smaller than that observed in ethene-bridged porphyrin dimers such as **60b** (89°).[68] Consequently, the Q-band in the absorption spectrum was red-shifted to 841 nm for **116Zn.** These results clearly indicate the strong conjugative nature of an azo-linker. Photoisomerisation of **116M** to (*Z*)-isomers was not observed.

Bisporphyrinylamines are an interesting platform to evaluate the conjugative electronic coupling *via* the lone-pair electrons of the bridging nitrogen atom. These molecules were prepared by Arnold *et al.* in 2006[93] and later by Ruppert *et al.* in 2011.[94] The Buchwald–Hartwig aromatic aminations of halo-porphyrins (**62Ni, 119** and **123**) with *meso*-aminoporphyrin **117** or β-aminoporphyrin **121** gave dimers **120, 122** and **124** (Schemes 31 and 32). These diporphyrins exhibited broader Soret-bands and red-shifted Q-like bands. In addition, chemical oxidation of **120** by $AgSbCl_6$ afforded the ammonium radical cation that displayed strong absorption at 1120 nm, indicating strong cation delocalisation over two porphyrins. This trend was stronger in *meso–meso* linked dimer **120** than in *meso*-β linked dimer **122** or β–β linked dimer **124**.

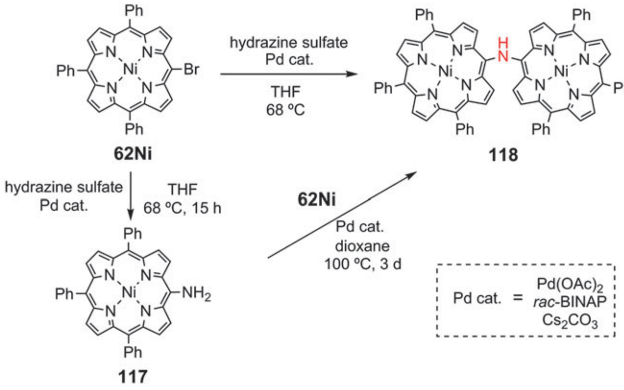
Very recently, Senge *et al.* reported sulfur-bridged diporphyrin **126** (Scheme 33).[95] In this reaction, the isooctyl-3-mercaptopropionate group in **125** was easily deprotected in the presence of a strong base to generate a porphyrin thiolate, which attacked another molecule of **125** to afford porphyrin



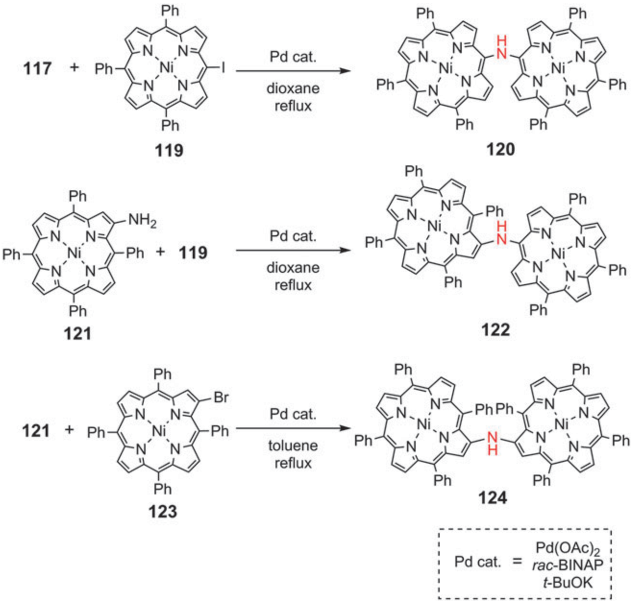
Scheme 29 Synthesis of an imino-conjugated diporphyrin.



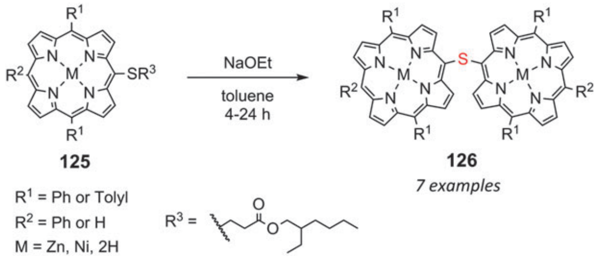
Scheme 30 Synthesis of azo-conjugated diporphyrins.



Scheme 31 Synthesis of an amino-bridged diporphyrin.



Scheme 32 Synthesis of various amino-bridged diporphyrins.

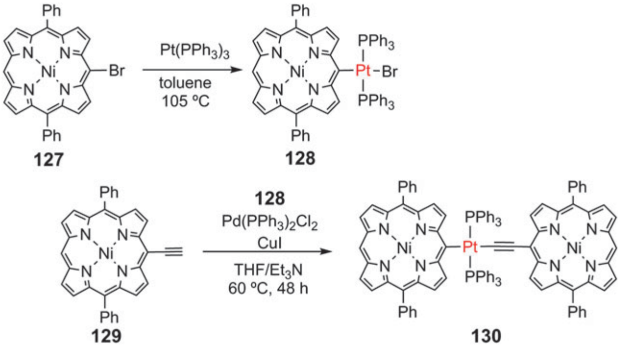


Scheme 33 Synthesis of sulfur-bridged diporphyrins.

dimer **126**. In this substitution type reaction, the thioether in **125** also acted as a leaving group in an S_NAr type substitution reaction.

2.6 Porphyrin oligomers linked by transition metals

A supramolecular approach offers an opportunity for the controlled synthesis of well-defined multi-porphyrin arrays. Porphyrin oligomers assembled through metal-coordination have been actively developed in the last decade. These compounds provide valuable information on electronic communication between the porphyrin π-system and the metal d-orbitals.

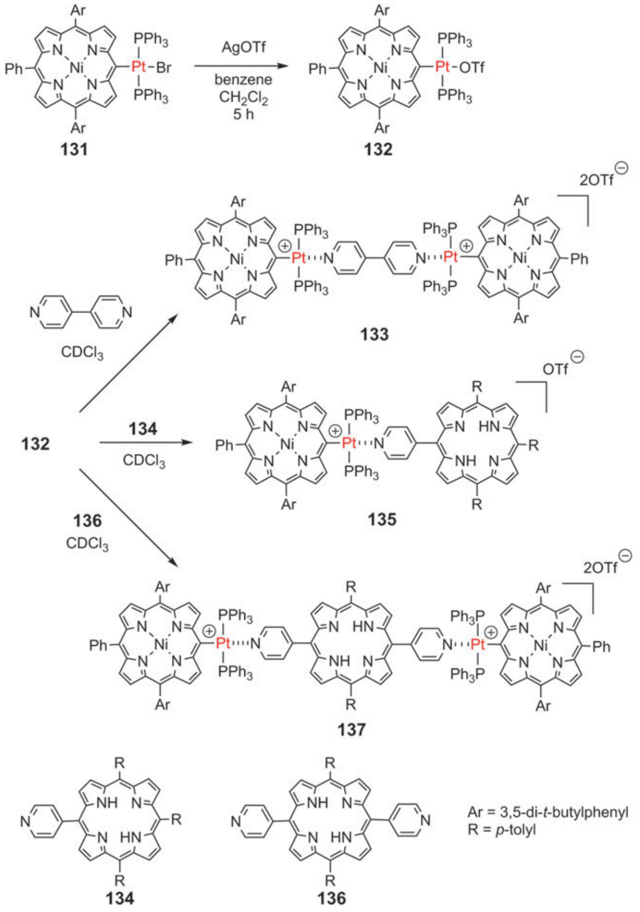


Scheme 34 Synthesis of a Pt(II)-ethynyl-bridged diporphyrin.

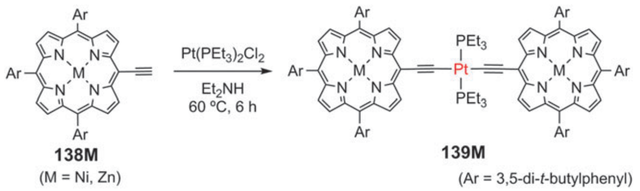
Arnold *et al.* investigated the structures and fundamental properties of *meso*-η^1-metalloporphyrins.[96] *meso*-Platinioporphyrin **128** was prepared by oxidative addition of Pt(0) generated *in situ* from the reaction of $Pt(dba)_2$ and PPh_3 to the C–Br bond of *meso*-bromoporphyrin **127**. With this peripherally functionalised metalloporphyrin in hand, alkynylplatinum-bridged diporphyrin **130** was prepared in 38% yield as the first example of transition metal-bridged porphyrin arrays with two carbon–metal bonds (Scheme 34).[97] Coordination by 4,4′-bipyridyl ligands or by *meso*-pyridylporphyrin onto platinum at the *meso*-position of porphyrin led to self-assembled porphyrin arrays up to five porphyrin units in size.[98] These arrays can be assembled from a more soluble precursor, *meso*-(triflatoplatinio)porphyrin **132**, which was prepared by the treatment of *meso*-(bromoplatinio)porphyrin **131** with silver triflate in benzene. From **132**, bipyridyl coordinated dimer **133** and pyridylporphyrin coordinated dimer **135** and trimer **137** were prepared in high yields (Scheme 35). By following a similar procedure, platinum-diacetylene-bridged porphyrin dimers **139M** were synthesised (Scheme 36).[99] While the Zn(II) complex **139Zn** showed small interporphyrin electronic coupling *via* the platinum–diacetylene linker, the corresponding Ni(II) complex **139Ni** exhibited NIR absorption in the cationic and dicationic forms, suggesting a certain d_{xz}–π orbital interaction (Scheme 37). Q7

Ruppert and Callot have developed a unique assembling method of porphyrin arrays by using an enaminoketone's external coordination sites. External coordination of **140M^1** with Ni(II), Pd(II) and Cu(II) ions allowed the formation of coplanar dimers **141M^{1}M^2**, which showed red-shifted absorption spectra relative to the monomers, indicating stronger conjugation through the connecting metal that is positioned between the two porphyrins.[100,101] Accordingly, these dimers showed split reversible oxidation peaks. A stepwise metalation enabled the preparation of palladium-coordinated Ni(II) porphyrin dimer **142** and trimer **143**.[102]

A fused N-heterocyclic ligand can also serve as an external ligand for metal ion coordination. A porphyrin bearing a fused-imidazolium salt moiety, **144**, was treated with $Pd(OAc)_2$ in refluxing toluene to afford palladium bridged fused imidazolium porphyrin dimer **145** (Scheme 38). The structure was fully characterised by X-ray diffraction analysis.[103]

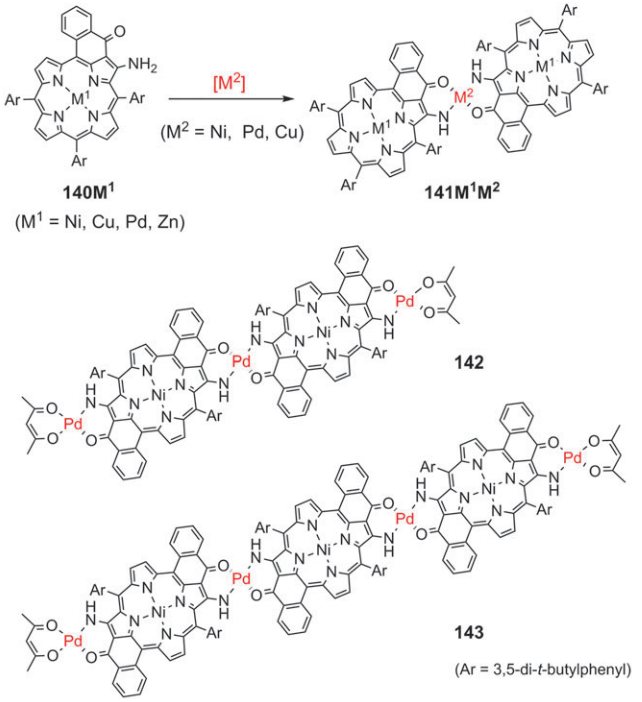


Scheme 35 Synthesis of various Pt(II)-coordinated porphyrin arrays.

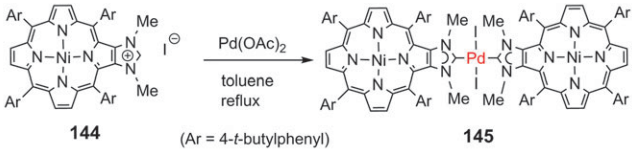


Scheme 36 Synthesis of a Pt(II)-diethynyl-bridged diporphyrin.

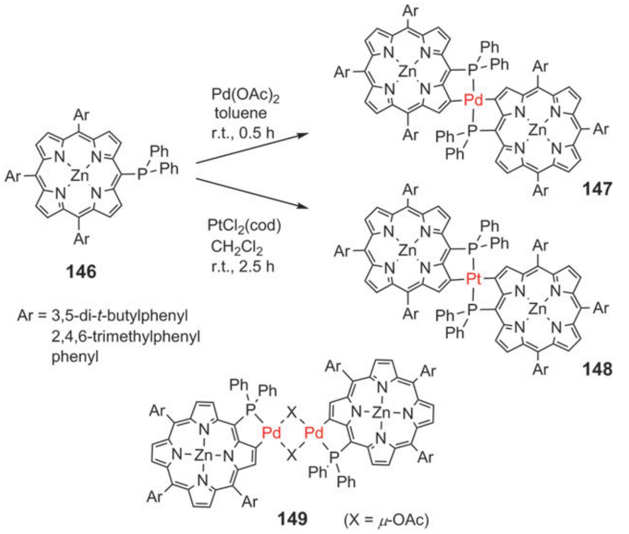
Q8 Matano *et al.* reported the first examples of peripherally β-η^1-palladio- and platinioporphyrins **147** and **148**, which were formed by regioselective metalation of *meso*-phosphanylporphyrins **146** *via* β-C–H bond activation (Scheme 39).[104,105] The Pd(II) bis-μ-acetate bridged dimer **149** was also formed in low yield during the complexation of **146** with 0.5 equiv. of $Pd(OAc)_2$. These coplanar porphyrin dimers linked by peripherally fused phosphametallacycles exhibited perturbed optical and electrochemical properties, presumably due to pπ–dπ orbital interaction, a hypothesis supported by theoretical studies. Thus, it is noteworthy that a peripheral carbon–metal–carbon linkage has a significant impact on electronic communication between two porphyrins.



Scheme 37 Synthesis of metalated enaminoketone porphyrin assemblies.

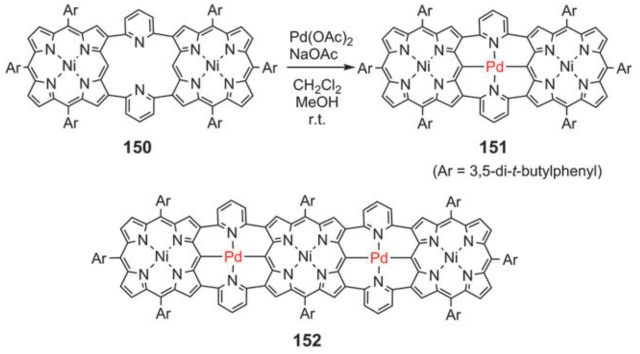


Scheme 38 Synthesis of a Pd(II)-bridged fused imidazolium diporphyrin.



Scheme 39 Synthesis of β-η^1-palladio- and platinioporphyrins.

Treatment of β–β′ dipyridyl-bridged diporphyrin **150** with $Pd(OAc)_2$ in the presence of sodium acetate in CH_2Cl_2/MeOH resulted in facile metalation that afforded Pd(II) complex **151** in 85% yield (Scheme 40).[106] Pd(II)-bridged trimer **152** was prepared similarly. These complexes display remarkably bent structures as revealed by X-ray diffraction analyses and large two-photon absorption cross-section values, 15 700 GM for **151** and 24 000 GM for **152**.



Scheme 40 Synthesis of pyridyl-coordinated Pd(II)-bridged porphyrins.

3. Fused porphyrin oligomers

Connecting two porphyrins by multiple covalent bonds can enhance the electronic interaction among the constituent porphyrin units due to a forced coplanar structure. These "fused porphyrin oligomers" have attracted considerable attention because of their remarkable photophysical properties such as extensively red-shifted absorptions, very short excited-state lifetimes and large nonlinear optical properties.[107–110] These arrays also have potential use as conducting molecular wires by virtue of their conjugated electronic characteristics.

Recently, single-molecule conductance measurements of porphyrin molecular wires have been demonstrated by an STM break-junction technique as shown in Fig. 8. In such a system, the molecular conductance, σ_M, generally decreases exponentially with molecular length, R, as quantified by the attenuation factor, β, which is a useful measure of the ability to mediate long-range charge transportation. The β value of butadiyne-bridged porphyrin wires **153**$_N$ with terminal thioacetate anchors was revealed to be 0.04, which is much lower than those of typical organic molecules (0.1–0.6).[111] Three types of pyridine-terminated porphyrin arrays, butadiyne-bridged arrays **154**$_N$, *meso–meso* directly linked arrays **155**$_N$ and *meso–meso*, β–β, β–β triply linked arrays **156**$_N$, were prepared to compare the β values (Fig. 9). The molecular conductance measurements have revealed an exceptionally weak attenuation nature of fused arrays **156**$_N$ ($\beta = 0.02$) compared with butadiyne-bridged arrays **154**$_N$ (β = 0.04) and *meso–meso* linked arrays **155**$_N$ ($\beta = 0.11$).[112] A short time later, ethyne-bridged porphyrin wires **157**$_N$ bearing terminal thiophenol anchor groups were also synthesised, with β values measured to be 0.03.[113]

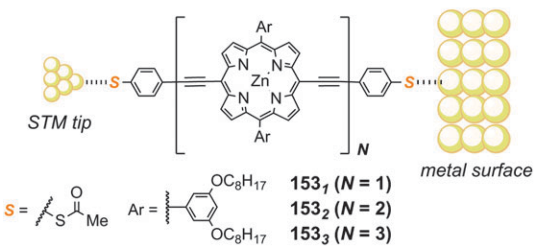


Fig. 8 Schematic description of STM break junction-based single molecule conductance measurements for the 1,3-butadiyne-bridged porphyrin oligomers.

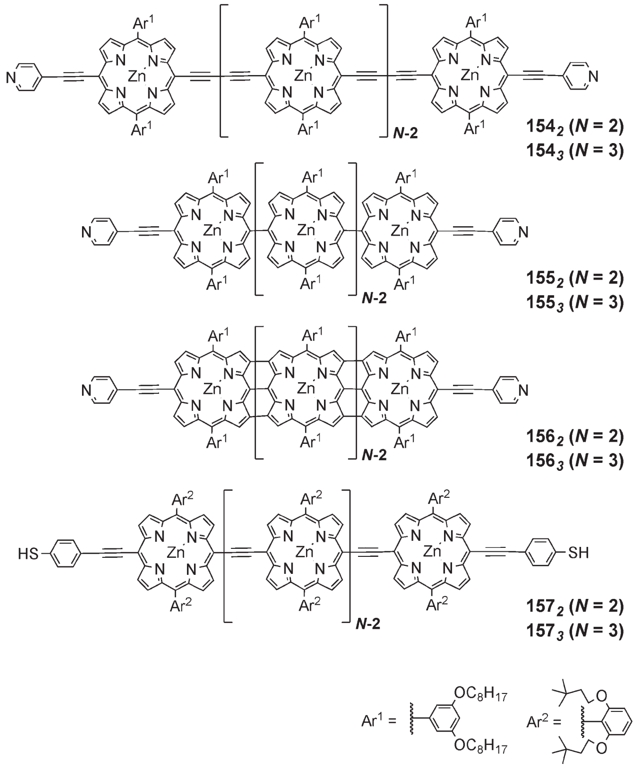
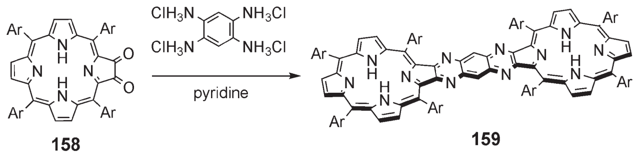


Fig. 9 Pyridine- or thiophenol-terminated porphyrin oligomers for the conductance measurements.

3.1 β,β-Fused porphyrin oligomers

Pioneering work by Crossley *et al.* involving a 2 : 1 condensation of porphyrin-2,3-dione **158** with 1,2,4,5-tetraaminobenzene tetrahydrochloride successfully gave rise to pyrazinoquinoxaline-fused diporphyrin **159**. This reaction methodology was extended to the synthesis of trimeric array **160** and tetrameric array **161**, with the molecular length of the latter reaching 65 Å (Scheme 41 and Fig. 10).[114–116] L-shaped trimer **162** was also prepared *via* the same strategy.[117] A porphyrin-2,3-dione skeleton can be capped by 1,2-diaminobenzene in a stepwise manner, giving extended fused diporphyrin **163**.[118] The absorption spectrum of **163** displayed a split Soret-band at 440 and 508 nm along with an extensively red-shifted Q-band at 735 nm. The same strategy was employed for the synthesis of quinone-bridged fused diporphyrin **164** by condensing **158** with 2,3,5,6-tetraamino-1,4-benzoquinone (Scheme 42). As expected, the bridging quinone unit of **164** can be switched to the corresponding hydroquinone form in **165** following reduction with $NaBH_4$. The Soret-band of **165** was intensified and red-shifted by 22 nm compared with that of **164**.[119,120] Several metal complexes of the fused porphyrinoids



Scheme 41 Synthesis of pyrazinoquinoxaline-fused diporphyrin **159**.

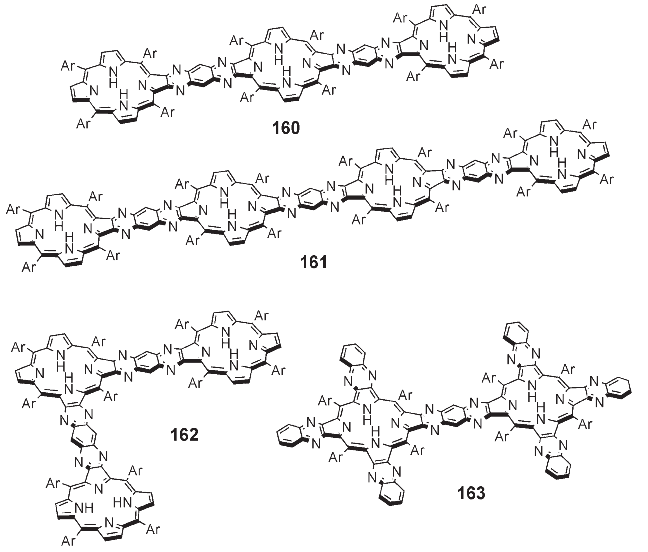
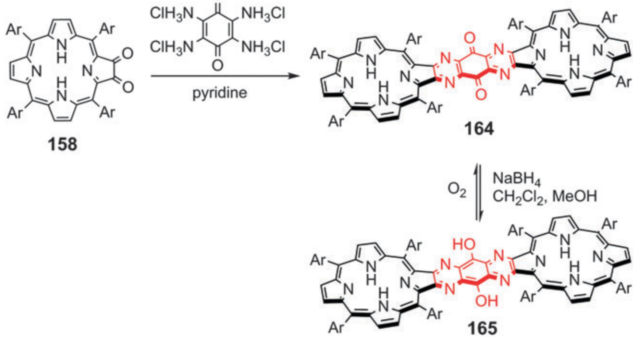


Fig. 10 Pyrazinoquinoxaline-fused porphyrin arrays.



Scheme 42 Synthesis of a pyrazinoquinone-fused diporphyrin.

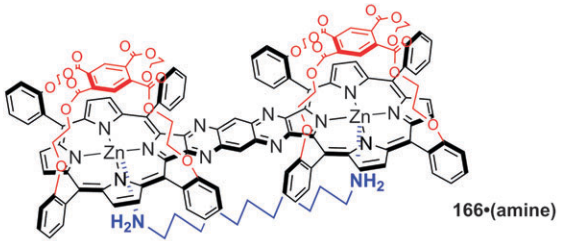


Fig. 11 Fused porphyrin 'molecular ruler'.

were similarly prepared.[121] Among them, dizinc(II) *syn*-capped pyrazinoquinoxalino-fused-diporphyrin **166** was developed as 'a molecular ruler', which can form a strong intramolecular 1 : 1 complex (**166·(amine)**) with 1,12-diaminododecane whose molecular length (16.4 Å) is optimal to span the two Zn(II) binding sites (15.3 Å) (Fig. 11). The UV/Vis and NMR binding studies unambiguously demonstrated this recognition behavior with a binding constant of about 7.2×10^7 M^{-1}.[122]

Benzene-fused diporphyrin **167** was prepared by Kobayashi *et al.* by mixed acid-catalysed condensation of pyromellitic dipotassium diimide and potassium *t*-butyl phthalimide in a low yield (Fig. 12).[123] Later, similar benzene-fused diporphyrins **171M** were synthesised from bicyclo[2.2.2]octadiene-fused diporphyrin **170Zn**, which was prepared by [3+1] condensation of dipyrrole **168** with tripyrrane carbaldehyde **169** followed by DDQ oxidation and Zn(II) insertion (Scheme 43).[124] Notably, **171M** were fairly insoluble in common organic solvents due to the rigid planar structure and serious aggregation, while the precursors **170M** were highly soluble. Thus, this thermal retro-Diels–Alder reaction provides a promising means to prepare planar fused benzene motifs in a highly pure form. Benzene-fused porphyrin pentamer cruciform **172M¹M²** was also prepared successfully (Fig. 13).[125] Anthraquinone-fused diporphyrins **178** were similarly prepared from *syn*- or *anti*-shaped precursors **174Zn** or **176Zn**, respectively (Scheme 44).[126] Interestingly, extrusion of

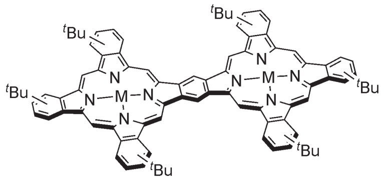
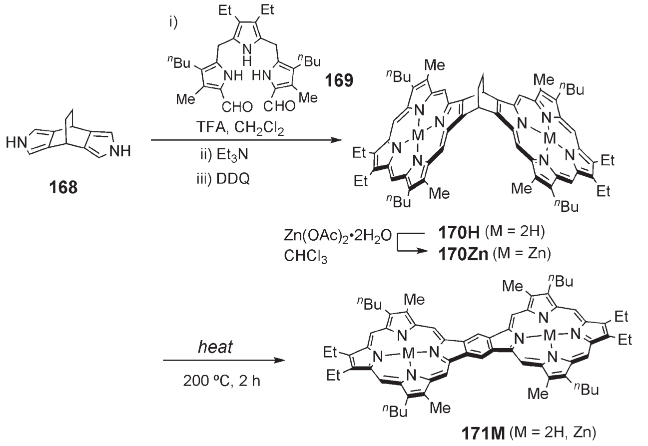


Fig. 12 Benzene-fused diporphyrins.



Scheme 43 Synthesis of benzene-fused diporphyrins *via* thermal retro-Diels–Alder reaction.

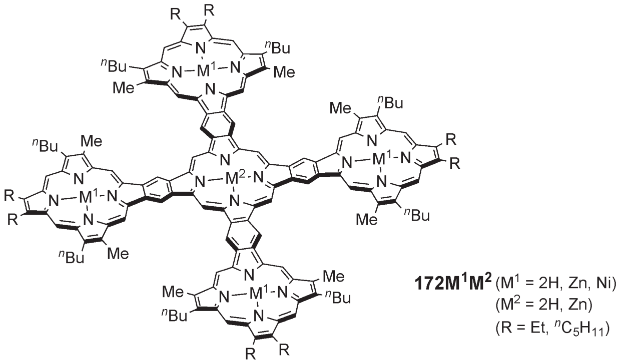
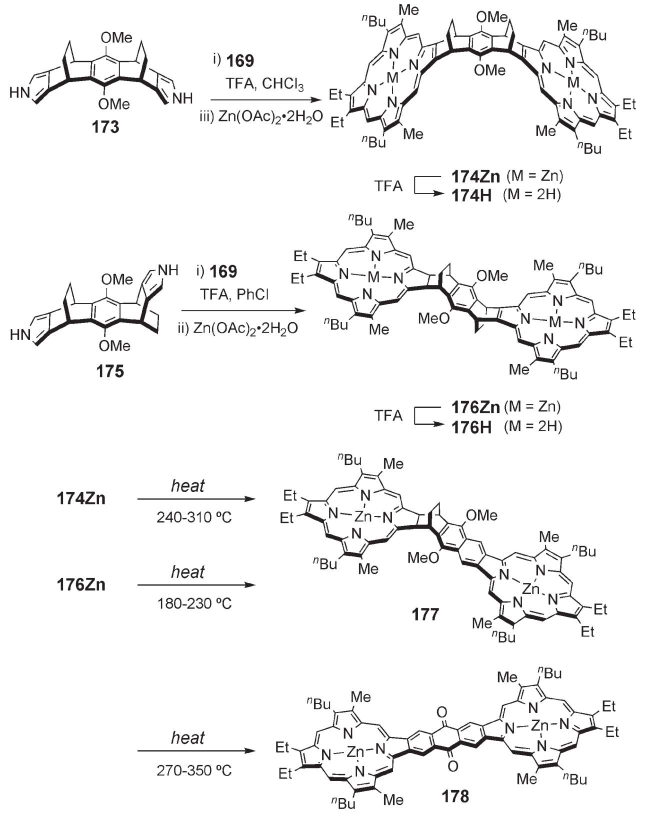
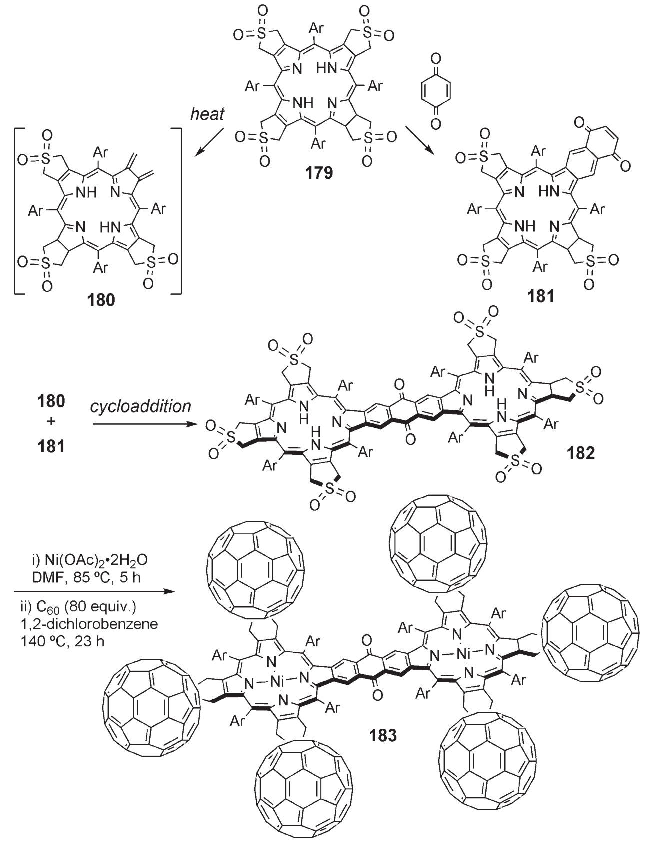


Fig. 13 Benzene-fused porphyrin pentamers.



Scheme 44 Synthesis of an anthraquinone-fused diporphyrin *via* thermal retro-Diels–Alder reaction.



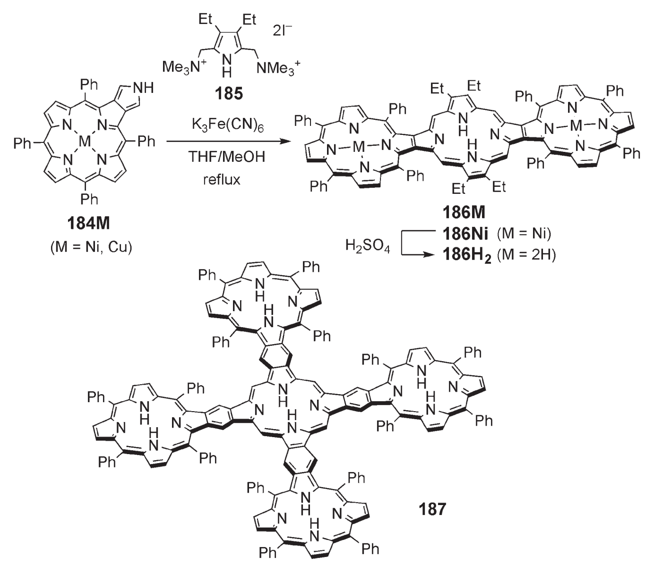
Scheme 45 Synthesis of a fullerene-appended anthraquinone-fused diporphyrin.

one ethylene molecule from **174Zn** proceeded at 240–310 °C to give intermediate **177** but the same reaction of **176Zn** occurred at lower temperature, 180–230 °C. Unique hexameric porphyrin assembly **174Zn** observed in the solid-state structure would be one reason for its quite different thermal behavior.

[4+2] Cycloaddition of dienophilic quinono-porphyrin **181** and porphyrin-β,β-diene **180**, both of which were provided from tetra-sulfoleno-porphyrin **179** followed by Ni(II) metalation and oxidation, afforded anthraquinone-bridged porphyrin dimer **182** (Scheme 45). Thermal reaction of **182** with an 80-fold excess of C_{60} in 1,2-dichlorobenzene at 140 °C furnished hexafullereno-porphyrin **183** in about 80% yield after size-exclusion chromatography.[127]

Smith *et al.* developed an efficient synthetic route to directly fused diporphyrin **186M** and related arrays using pyrroloporphyrin subunit **184M** (Scheme 46).[128,129] They extended this strategy to the synthesis of two-dimensionally extending cruciform pentaporphyrin array **187** (Scheme 47).[130]

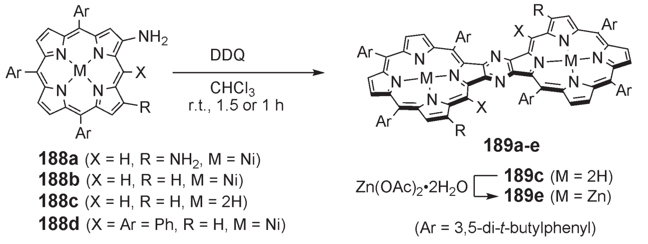
Recently, Shinokubo *et al.* have demonstrated the oxidative fusion of β-aminoporphyrin **188a–d** to afford pyrazine-fused diporphyrins **189a–e.**[131] This straightforward dimerisation protocol is a promising methodology for connecting π-conjugated molecules to construct rigid π-systems.



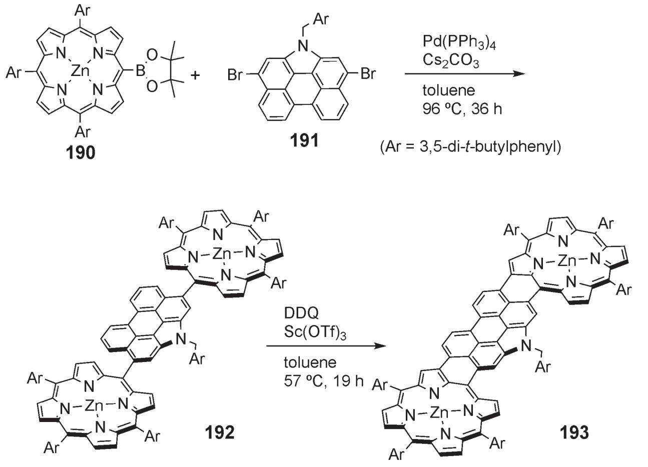
Scheme 46 Synthesis of β,β-fused porphyrin trimers and a benzene-fused porphyrin cruciform.

3.2 *meso*-β Fused porphyrin oligomers

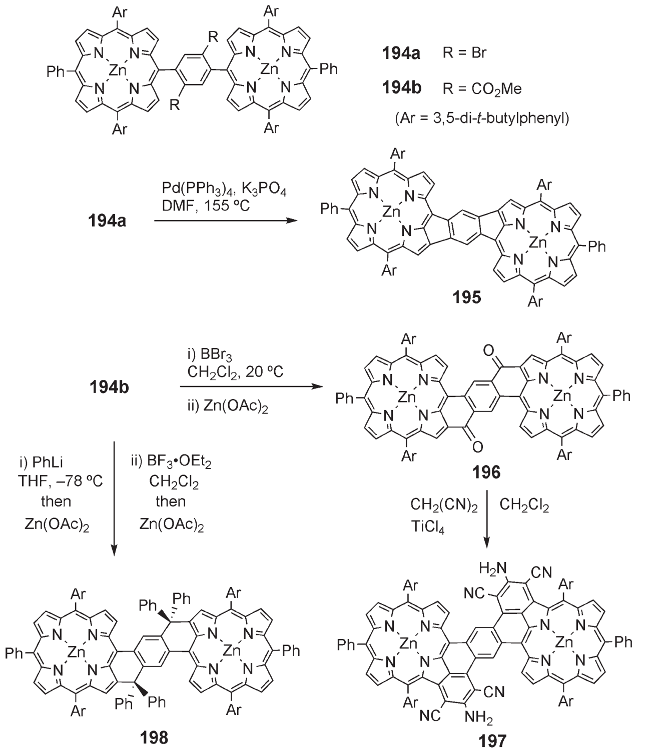
Synthesis of *N*-annulated perylene-fused diporphyrin **193** was reported by Wu *et al.*[132–134] Singly linked precursor **192** was prepared by Suzuki-coupling of dibrominated *N*-annulated perylene **191** with porphyrin boronate **190.** Subsequent oxidative fusion with DDQ and $Sc(OTf)_3$ furnished **193** in 74% yield (Scheme 48). Diporphyrin **193** exhibited a strong NIR absorption band at 952 nm and NIR photoluminescence with a quantum yield of 0.056 (Scheme 49).



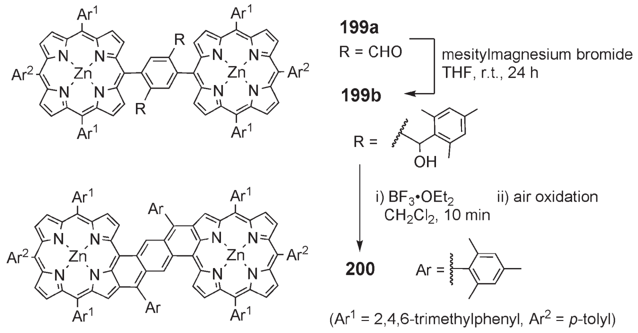
Scheme 47 Synthesis of pyrazine-fused diporphyrins *via* oxidative fusion reaction.



Scheme 48 Synthesis of a perylene-fused diporphyrin.



Scheme 49 Synthesis of various *meso*, β-fused diporphyrins.



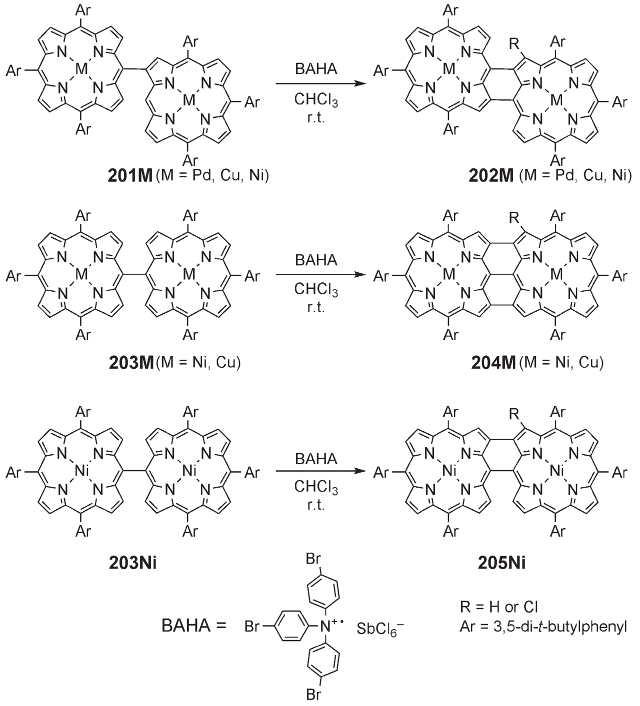
Scheme 50 Synthesis of a *para*-quinodimethane-fused diporphyrin.

Recently, Anderson *et al.* reported the synthesis of several fused porphyrin dimers from 1,4-phenylene-bridged diporphyrins.[135] Fused benzene-bridged diporphyrin **195**, prepared by Pd-catalysed intramolecular β-arylation of dibromide **194a**, exhibited a strongly perturbed absorption spectrum consisting of a split Soret-like band and red-shifted but weak Q-bands up to 1077 nm. Diporphyrin **196**, prepared by Friedel–Crafts acylation of diester **194b**, exhibited a split Soret-like band and intense Q-like bands at around 900 nm. Diporphyrin **194b** carrying two ester groups at the bridging benzene was converted to **198** upon treatment with PhLi followed by intramolecular Friedel–Crafts alkylation. This diporphyrin **198** displayed an intense Q-like absorption at 717 nm and relatively stronger fluorescence at 736 nm with a quantum yield of 0.10. Diketo dimer **196** was reacted with a large excess of malononitrile to give further fused diporphyrin **197**.

Very recently, Wu *et al.* have reported *para*-quinodimethane-fused porphyrin dimer **200** from the reaction of dialdehyde **199a** with mesitylmagnesium bromide followed by intramolecular Friedel–Crafts alkylation (Scheme 50).[136] Dimer **200**, which can be regarded as a porphyrin analogue of zethrenes, showed a Q-like absorption band at 955 nm, indicating effective π-conjugation over the fused linkage.

3.3 Directly fused porphyrin oligomers

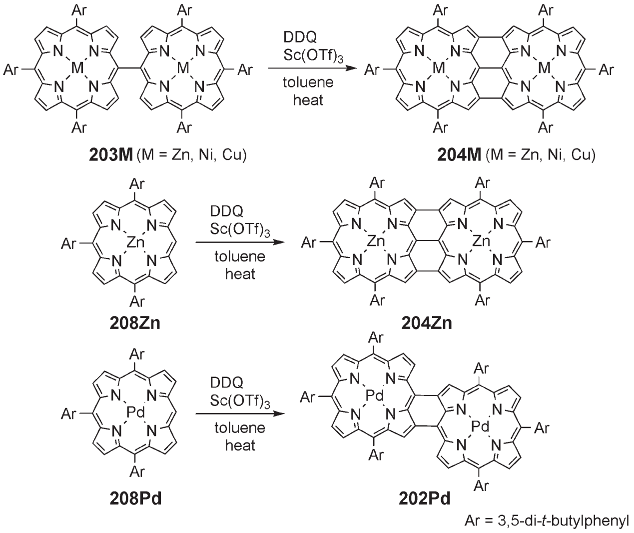
Osuka *et al.* have explored a variety of directly fused porphyrin oligomers including *meso*-β, *meso*-β doubly fused porphyrin arrays, *meso*–*meso*, β–β doubly fused porphyrin arrays and *meso*–*meso*, β–β, β–β triply fused porphyrin arrays (so-called "porphyrin tapes").[137–139] Initially, tris(4-bromophenyl)aminium hexachloroantimonate (BAHA) was used to accomplish oxidative fusion reactions of porphyrins. *meso*-β, *meso*-β Doubly linked diporphyrins **202M** were thus obtained from singly *meso*-β linked diporphyrins **201M** and *meso*–*meso*, β–β, β–β triply linked diporphyrins **204M** were obtained from singly *meso*–*meso* linked diporphyrin **203M** (Scheme 51). Although fused porphyrins were obtained in good yields, the concurrent peripheral chlorination at the porphyrin periphery was problematic. In addition, partly fused diporphyrins, *i.e.* *meso*–*meso*, β–β doubly fused diporphyrins **205Ni**, were obtained, depending on the central metal of the porphyrin. Meanwhile, a combination of DDQ and $Sc(OTf)_3$ proved to be quite an effective and clean oxidation method to accomplish the fusion reaction by which **204M** were obtained



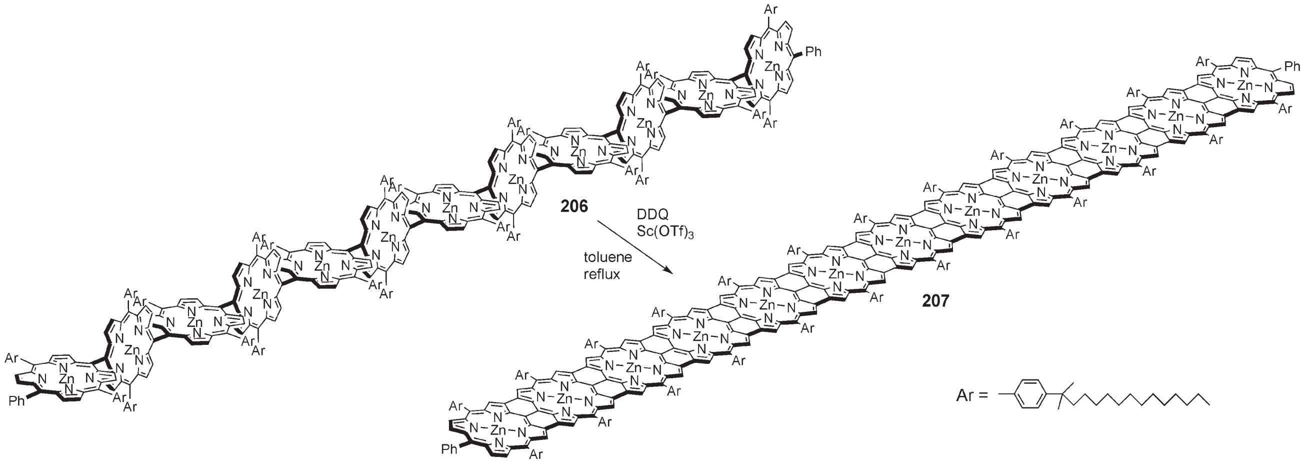
Scheme 51 Synthesis of directly fused diporphyrins *via* BAHA oxidation.

without any side-products.[140–142] Surprisingly, even *meso–meso* linked porphyrin dodecamer **206** was completely fused to triply linked dodecamer **207** (Scheme 52), and later, with the aid of bulkier substituents to suppress undesired aggregation, the triply fused porphyrin 24mer was synthesised as the longest reported porphyrin tape to date in moderate yield.[143] The physical properties of fused porphyrin arrays are particularly noteworthy.[107,108] For *meso*-β, *meso*-β doubly fused diporphyrin **202M**, the Soret-like bands were split and the Q-like bands were intensified and red-shifted to 750–830 nm, indicating extensive conjugation over the diporphyrin π-electronic system. As the number of porphyrin units increased, the Q-like bands increasingly intensified and red-shifted deeply into the NIR region (1075 nm for a pentamer). The Q-like bands of triply linked dimer **204M** reached 850–1050 nm, depending upon the central metal, and those of further oligomers were exceedingly red-shifted deeper into the IR region. Further studies have demonstrated that this absorption red-shift seems to reach the saturation point at about 2800 nm, corresponding to the length of porphyrin tape 14mer and to the effective conjugation length (ECL) of *ca.* 12 nm.[143]

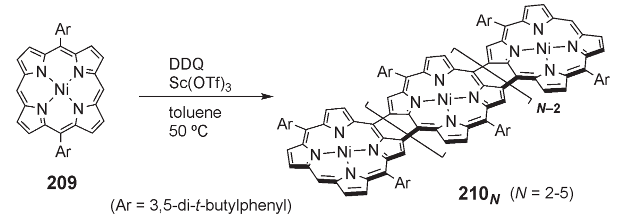
The above mentioned fused porphyrin arrays can be synthesised directly from porphyrin monomers. While DDQ-Sc(OTf)$_3$ oxidation reaction of *meso*-free Zn(II) porphyrin **208Zn** afforded the triply linked product **204Zn**, the same reaction of *meso*-free Pd(II) porphyrin **208Pd** gave *meso*-β doubly linked product **202Pd** in a good yield (Scheme 53).[144,145] From *meso*-free Ni(II) porphyrin **209**, a mixture of doubly fused oligomers **210$_N$** (N = 2–5) was obtained (Scheme 54).[146] Sugiura *et al.* reported the synthesis of similar *meso*-β doubly linked oligomers by the use



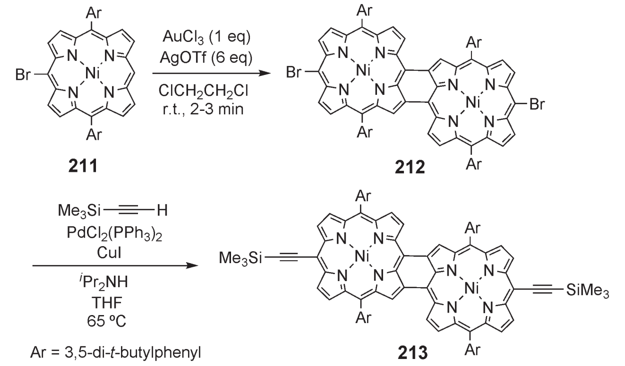
Scheme 53 Synthesis of directly fused diporphyrins *via* DDQ-Sc(OTf)$_3$ oxidation.



Scheme 52 Synthesis of a triply fused porphyrin dodecamer *via* DDQ-Sc(OTf)$_3$ oxidation.



Scheme 54 Synthesis of *meso*-β, *meso*-β doubly linked porphyrin oligomers.



Scheme 55 Synthesis of *meso*-β, *meso*-β doubly linked diporphyrins *via* $AuCl_3$-AgOTf oxidation.

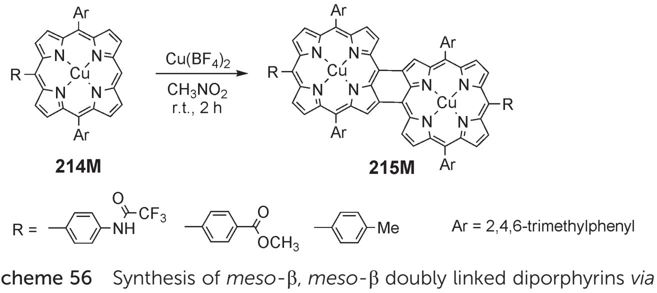
of $TeCl_4$.[147] When *meso*-brominated Ni(II) porphyrins **211** were subjected to $AuCl_3$ and AgOTf in 1,2-dichloroethane, *meso*-β doubly linked diporphyrins **212** were formed rapidly (2–3 min) in 73–82% yields without noticeable formation of *meso–meso*, β–β, β–β triply linked diporphyrins (Scheme 55).[148] Notably, the bromide functionality was tolerant under oxidation conditions, and hence was used to prepare *meso*-ethynylated dimer **213**. Recently, Gust *et al.* developed a clean oxidant $Cu(BF_4)_2$ to afford doubly fused diporphyrins **215M** (Scheme 56).[149]

meso-β Doubly linked Zn(II) porphyrin *anti*-trimer **217** and *syn*-trimer **219** were separately synthesised by DDQ-Sc(OTf)$_3$ oxidation of the corresponding *meso*-β singly linked porphyrin precursors **216** and **218**, respectively (Scheme 57).[150] Reflecting their differing molecular shapes, the absorption and fluorescence spectra as well as TPA characters were distinctly different.

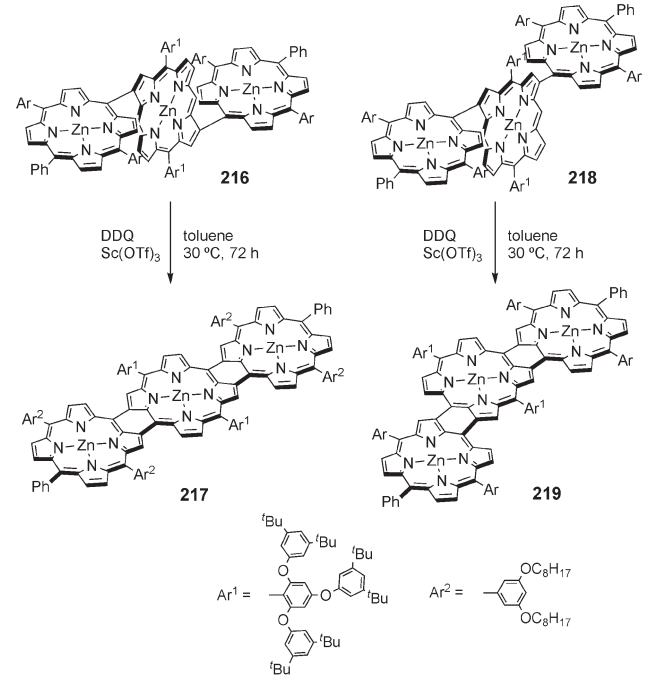
3.4 Applications of porphyrin tapes

Various functionalised porphyrin tapes have been exploited in various applications such as multi-charge storage systems,[151] electron-transporting amphiphilic columnar liquid crystals,[152] C_{60}-binding hosts with unique positive heterotrophic cooperativity[153] and metal surface patterning.[154] Peripherally modified porphyrin tapes have also been prepared.[155–157]

Two-dimensionally extended porphyrin tapes, such as L-shaped trimer **220**, T-shaped tetramer **221** and square-shaped tetramer **222M** (porphyrin sheet), have been developed in order to study structure–property relationships (Fig. 14).[158,159] TPA values of **220** and **221** were smaller than those of the linear trimer and tetramer, indicating that the unidirectional change in the molecular polarisability arising from π-electron delocalisation is a key factor for the enhancement of nonlinear optical properties. Porphyrin sheet **222Zn** exhibits only a broad Soret band and weak Q-like bands, and shows a paratropic ring current above the central cyclooctatetraene (COT) unit. These data have been interpreted in terms of the antiaromatic character arising from the planar COT core.[159]



Scheme 56 Synthesis of *meso*-β, *meso*-β doubly linked diporphyrins *via* $Cu(BF_4)_2$ oxidation.



Scheme 57 Synthesis of *syn*- and *anti*-doubly linked porphyrin trimers.

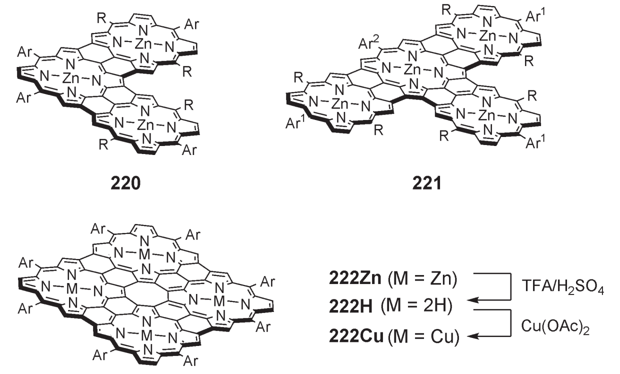


Fig. 14 Two-dimensionally extended porphyrin tapes.

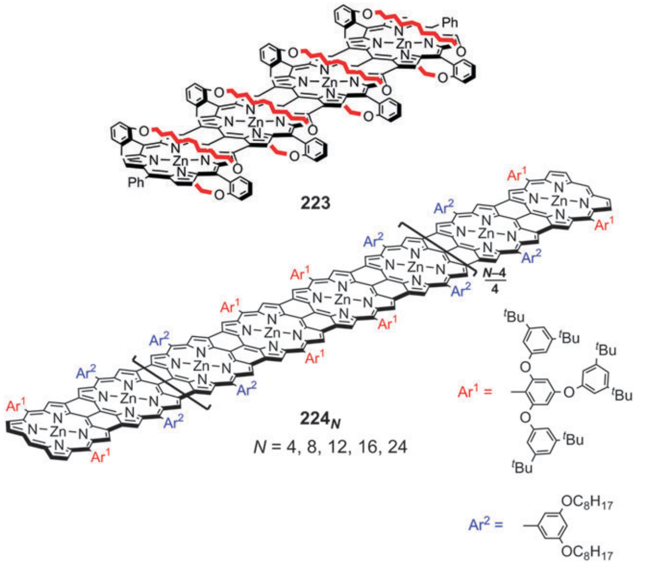
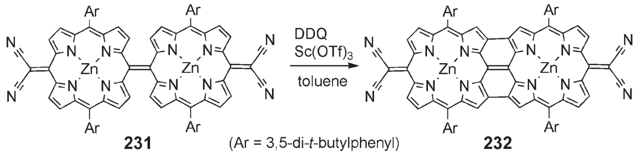


Fig. 15 Sterically encumbered porphyrin tapes.



Scheme 58 Synthesis of a triply linked quinonoidal diporphyrin.

Despite these attractive properties, the poor solubility and facile oxidative degradation of porphyrin tapes are problematic. Facially encumbered porphyrin tapes such as strapped porphyrin tapes **223** and porphyrin tapes bearing bulky *meso*-substituents (**224_N**) were invented to suppress strong π–π stacking (Fig. 15).[143,160] Hybrid porphyrin tapes, which bear electron-withdrawing C_6F_5 groups as *meso*-substituents, were developed to increase chemical stability against oxidation by lowering HOMO levels.[161,162] Donor–acceptor hybrid porphyrin tape dimer **227** and trimer **229Zn**, heterometal complex **229Ni** and electron-deficient porphyrin tape **228** have also been prepared (Fig. 16). Compared with all-donor-type porphyrin tape dimer **225** and trimer **226**, these tapes displayed positively shifted oxidation and reduction potentials in their cyclic voltammograms, indicating increased stability against oxidative degradation. Triply linked quinonoidal porphyrin tape **232** was synthesised from **231** (Scheme 58).[163] While **231** has a non-planar, butterfly-like structure in the solid-state, the planar structure of **232** allows effective π-delocalisation, exhibiting an intense NIR band at 958 nm.

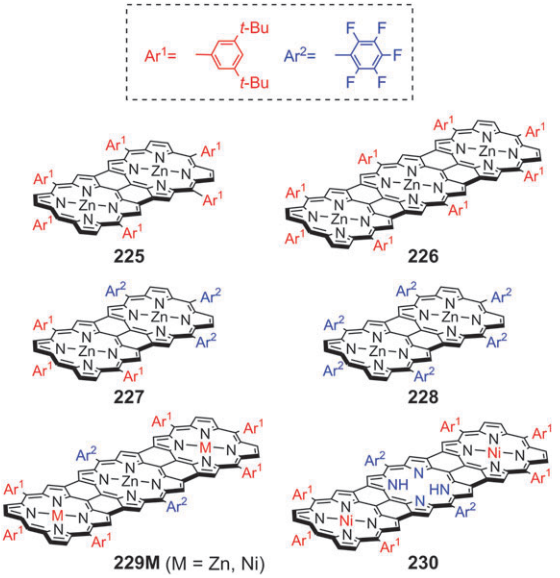


Fig. 16 Hybrid porphyrin tapes.

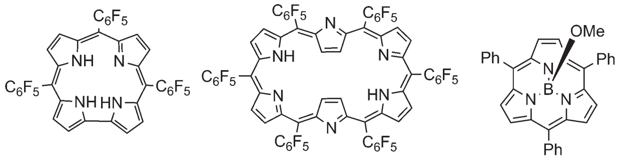
4. Oligomers consisting of porphyrin-related compounds and hybrid arrays

Recently, ring-contracted and ring-expanded porphyrins have emerged as novel porphyrin-related chromophores because of their intriguing physical properties, well-defined aromatic or antiaromatic nature and unique metal coordination abilities. Despite the limited synthetic scope, reports concerning oligomers of these new porphyrin variants are steadily growing (Fig. 17).

4.1 Corrole oligomers

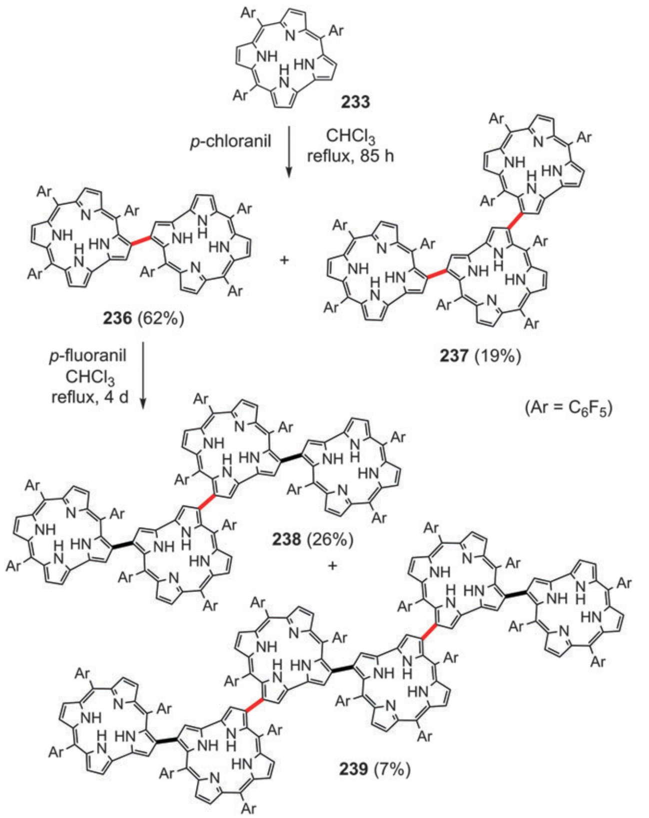
Corroles are 18π aromatic 'ring-contracted' porphyrinoids that contain a direct pyrrole–pyrrole linkage. Their unique metal-coordination chemistry has been studied, especially as ligands for oxidation catalysis.[164] Although spontaneous formation of corrole dimers had been recognized during the metalation with $Co(OAc)_2$ and triphenylphosphine or $Cu(OAc)_2{\cdot}H_2O$,[165–167] their precise and regioselective syntheses have been recently achieved. Osuka *et al.* performed facile oxidative coupling of 5,10,15-tris(pentafluorophenyl)corrole **233**.[168] Upon heating with *p*-chloranil, corrole **233** underwent regioselective oxidative coupling reaction at the 3,3′-position to give dimer **236** and trimer **237** (Scheme 59). From **236**, subsequent oxidation with *p*-fluoranil afforded tetramer **238** and hexamer **239**. The crystal structures of the Co(III)–pyridine complexes of **237** and **238** were successfully determined.

Direct borylation of **233** gave borylated corrole **240**, which served as a useful precursor to produce a variety of substituted corroles on the basis of Pd-catalysed coupling reactions. 2,2′-Singly linked corrole dimer **241** was thus obtained in 82%

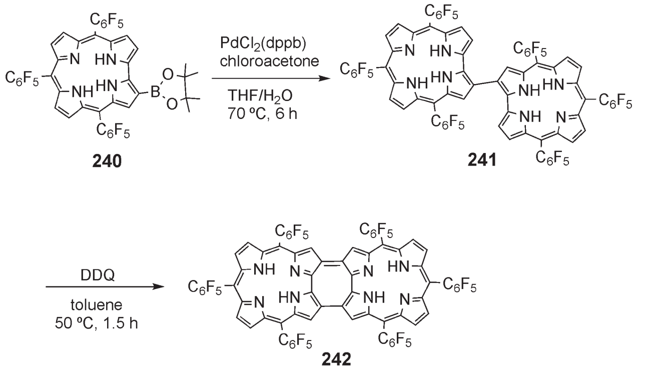


corrole
(233)
hexaphyrin
(234)
subporphyrin
(235)

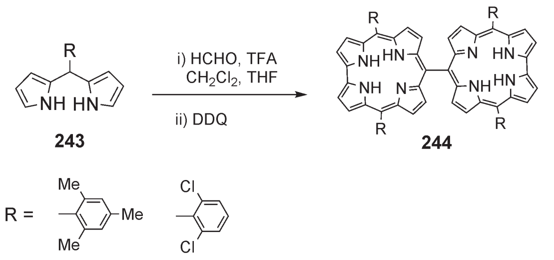
Fig. 17 Corrole, hexaphyrin and subporphyrin.



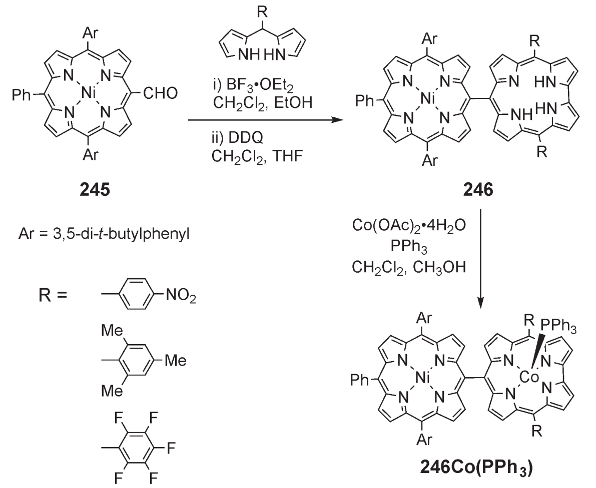
Scheme 59 Synthesis of 3,3′-linked corrole oligomers.



Scheme 60 Synthesis of a doubly linked corrole dimer.



Scheme 61 Synthesis of *meso–meso* linked corrole dimers.



Scheme 62 Synthesis of a *meso–meso* linked porphyrin-corrole dyad.

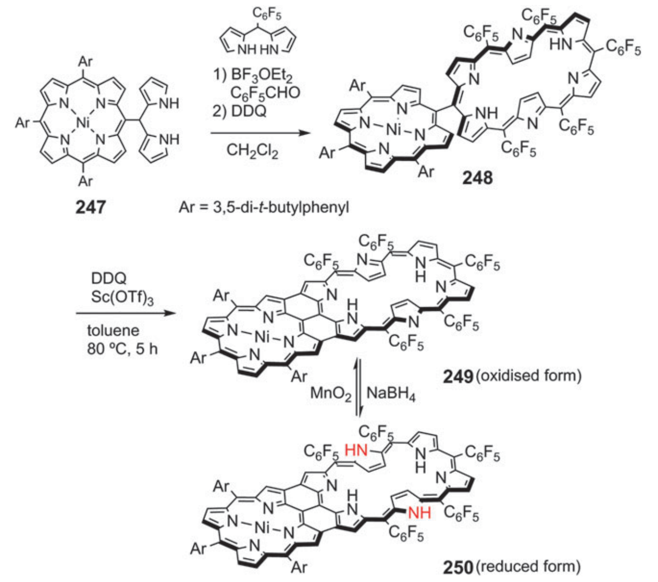
yield.[169] Further oxidation of **241** with DDQ in toluene provided 2,18-doubly linked corrole dimer **242**, as an air- and moisture-stable solid in moderate yield (Scheme 60).[170] Surprisingly, corrole dimer **242** has been characterized as a singlet biradical as indicated by a broad absorption band in the NIR region, the ESR spectrum (g = 2.0053) and temperature-dependent magnetic susceptibility experiments. DFT calculations estimated the singlet biradical character of **242** to be approximately 87%.

Acid-catalysed condensation reactions can directly produce oligomers without using coupling strategies. Gryko *et al.* synthesised *meso–meso* linked corroles **244** from simple dipyrromethane **243** and formaldehyde (Scheme 61).[171] Zheng *et al.* succeeded in preparing *meso–meso* linked porphyrin–corrole hybrids **246** and their Co(III)–PPh$_3$ complexes **246Co(PPh$_3$)** by BF$_3$·OEt$_2$-catalysed condensation of *meso*-formylporphyrin **245** with dipyrromethanes followed by DDQ oxidation (Scheme 62).[172]

4.2 Porphyrin–hexaphyrin hybrid arrays

Expanded porphyrins have recently emerged as a promising class of functional molecules owing to their intriguing redox exchange behaviour, imine–amine interconversion and versatile metal coordination ability.[173–182] Among these, *meso*-hexakis(pentafluorophenyl)-substituted hexaphyrin **234** is the most studied molecule due to its 26π aromatic network, rectangular shape, sharp Soret band and relatively long-lived S$_1$-state (125 ps).[173,174,183]

In 2011, Osuka *et al.* reported *meso–meso*, β–β, β–β triply linked porphyrin–hexaphyrin hybrid tape **249** which was synthesised by DDQ-Sc(OTf)$_3$ oxidation of *meso–meso* linked porphyrin–hexaphyrin **248**, which was in turn formed from *meso*-porphyrinyl dipyrromethane **247** (Scheme 63).[184] Hybrid tape **249** exhibited a split Soret-like band at 532, 566 and 752 nm and a red-shifted Q-like band at 1333 nm, indicating effective conjugation over both the porphyrin and hexaphyrin segments. Hybrid tape **249** can be reduced with NaBH$_4$ quantitatively to afford the corresponding 28π hexaphyrin **250**, which exhibited weakly antiaromatic nature due to the partly forced-planar [28]hexaphyrin segment. The anti-aromaticity became stronger in its Rh(I) complex because of a more restricted planar conformation.[185] Such an aromaticity-switching behaviour in triply linked porphyrin arrays is quite rare and so further

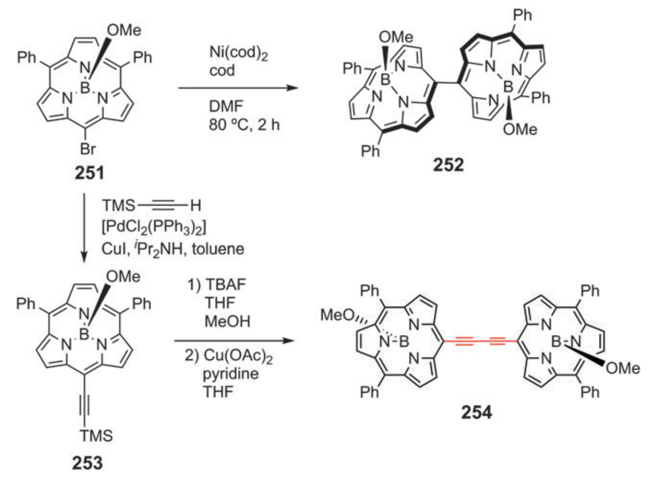


Scheme 63 Synthesis of triply linked porphyrin–hexaphyrin hybrid tapes.

elaborations of this fused expanded porphyrin motif will be promising for the creation of novel functional materials.[186]

4.3 Subporphyrin dimers

Subporphyrins are 14π aromatic 'genuine ring-contracted porphyrins' that consist of three pyrroles regularly arranged by methine carbons.[187–189] This newcomer in the family of porphyrinoids has been attracting increasing attention in light of its C_3-symmetric bowl-shaped structure, bright emission and strong substituent tuning due to facile rotation characteristics of *meso*-aryl substituents. Although the product yield in the first report was quite low, recent synthetic developments have helped to increase the synthetic yields to around 10% or more.[190] *meso–meso* Directly linked subporphyrin dimer **252** and butadiyne-bridged subporphyrin dimer **254** were synthesised from *meso*-bromosubporphyrin **251** *via* Ni(0)-mediated homo-coupling and Cu(II)-mediated oxidative homo-coupling, respectively (Scheme 64).[191,192] Dimer **252** displayed a Soret-like band at 403 nm with a broad shoulder at around 388 nm and broadened Q-band-like bands at 462 and 516 nm, while **254** exhibited a split Soret band and red-shifted Q-like bands up to 600 nm. The fluorescence quantum yields of **252** and **254** were increased to 0.40 and 0.42, respectively, compared with those of *meso*-triphenyl subporphyrin **235** (Φ_F = 0.13). These features reflect the effective conjugative nature of subporphyrin oligomers even in the case of *meso–meso* directly linked dimers because of the smaller rotational barrier of appended *meso*-aryl substituents, which is estimated to be around 14.7 kcal mol^{-1} for **252**.



Scheme 64 Synthesis of *meso–meso* directly linked and butadiyne-bridged subporphyrin dimers.

5. Conclusions

In the last two decades, a wide range of conjugated porphyrin arrays have been explored mainly by two synthetic strategies. One strategy is to bridge porphyrins with a π-linker such as ethyne and ethene, which has been conducted in a controlled manner by classical organic reactions or transition metal-catalysed reactions. The electronic interaction depends upon the nature of the linker, bridging position, and geometric relationship of constituent porphyrins. Another strategy is to fuse porphyrins with multiple direct bonds, which has often been performed using oxidative conditions. Fused porphyrin arrays exhibit perturbed absorption spectra, with observed perturbations intensifying as the number of porphyrin units present in the arrays increases. Among these systems, *meso–meso*, β–β, β–β triply linked porphyrin arrays display remarkable photophysical properties such as extremely red-shifted absorption profiles that reach out into the IR region, large TPA cross-section values and exceptionally reduced charge-transport attenuation factors. The lowest energy Q-band of porphyrin tape 24mer is observed at 2800 nm, which has still, at the time of writing this review, remained the lowest electronic transition recorded for a neutral molecule. In addition, new conjugated arrays of porphyrinoids have been developed, which include directly linked corrole oligomers, hybrid tapes of porphyrin and rectangular hexaphyrins, and subporphyrin dimers. These results strongly highlight the necessity for further exploration of conjugated porphyrinoids. Although current practical and technological limitations confine preparations of these conjugated porphyrin arrays to laboratory scale, we strongly believe that the attractive attributes of the porphyrin arrays show-cased in this review can fuel significant scientific breakthroughs in the near future.

Acknowledgements

The work at was supported by Grant-in-Aid (No. 25220802 (S)) Q12 for Scientific Research from MEXT of Japan.

Notes and references

1 *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, New York, 1999, vol. 1–10.
2 *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, New York, 2003, vol. 11–20.

3 *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific Publishing, Singapore, 2010, vol. 1–25.
4 *Multiporphyrin Arrays Fundamentals and Applications*, ed. D. Kim, Pan Stanford Publishing, 2012.
5 H. L. Anderson, *Chem. Commun.*, 1999, 2323.
6 M. G. H. Vicente, L. Jaquinod and K. M. Smith, *Chem. Commun.*, 1999, 1771.
7 J. R. Reimers, N. S. Hush and M. J. Crossley, *J. Porphyrins Phthalocyanines*, 2002, **6**, 795.
8 N. Aratani and A. Osuka, *Chem. Rec.*, 2003, **3**, 255.
9 S. Fox and R. W. Boyle, *Tetrahedron*, 2006, **62**, 10039.
10 K. S. Kim, J. M. Lim, A. Osuka and D. Kim, *J. Photochem. Photobiol., C*, 2008, **9**, 13.
11 N. Aratani, D. Kim and A. Osuka, *Chem.–Asian J.*, 2009, **4**, 1172.
12 J. P. Lewtak and D. T. Gryko, *Chem. Commun.*, 2012, **48**, 10069.
13 A. M. V. M. Pereiraa, S. Richetera, C. Jeandona, J.-P. Gisselbrechta, J. Wytkoa and R. Ruppert, *J. Porphyrins Phthalocyanines*, 2012, **16**, 464.
14 H. Mori, T. Tanaka and A. Osuka, *J. Mater. Chem. C*, 2013, **1**, 2500.
15 G. de la Torre, G. Bottari, M. Sekita, A. Hausmann, D. M. Guldi and T. Torres, *Chem. Soc. Rev.*, 2013, **42**, 8049.
16 M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435.
17 D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 1993, **26**, 198.
18 A. Osuka and K. Maruyama, *Pure Appl. Chem.*, 1990, **62**, 1511.
19 K. Maruyama, A. Osuka and N. Mataga, *Pure Appl. Chem.*, 1994, **66**, 867.
20 A. Osuka, N. Mataga and T. Okada, *Pure Appl. Chem.*, 1997, **69**, 797.
21 D. Holten, D. F. Bocian and J. S. Lindsey, *Acc. Chem. Res.*, 2002, **35**, 57.
22 A. Osuka and H. Shimidzu, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 135; N. Aratani, A. Osuka, Y. H. Kim, D. H. Jeong and D. Kim, *Angew. Chem., Int. Ed.*, 2000, **39**, 1458.
23 D. Kim and A. Osuka, *Acc. Chem. Res.*, 2004, **37**, 735.
24 N. Aratani and A. Osuka, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 1361; N. Aratani and A. Osuka, *Macromol. Rapid Commun.*, 2001, **22**, 725; N. Aratani, A. Tsuda and A. Osuka, *Synlett*, 2001, 1663.
25 S. Anderson, H. L. Anderson and J. K. M. Sanders, *Acc. Chem. Res.*, 1993, **26**, 469.
26 Y. Nakamura, N. Aratani and A. Osuka, *Chem. Soc. Rev.*, 2007, **36**, 831.
27 D. P. Arnold, A. W. Johnson and M. Mahendran, *J. Chem. Soc., Perkin Trans.*, 1978, **35**, 366.
28 D. P. Arnold and L. J. Nitschinsk, *Tetrahedron*, 1992, **48**, 8781; D. P. Arnold and G. A. Heath, *J. Am. Chem. Soc.*, 1993, **115**, 12197; D. P. Arnold, D. A. James, C. H. L. Kennard and G. Smith, *J. Chem. Soc., Chem. Commun.*, 1994, 2131; D. P. Arnold, R. D. Hartnell, G. A. Heath, L. Newby and R. D. Webster, *Chem. Commun.*, 2002, 754; D. P. Arnold, G. A. Heath and D. A. James, *J. Porphyrins Phthalocyanines*, 1999, **3**, 5.
29 D. P. Arnold, D. E. Lynch, G. Smith and C. H. L. Kennard, *Aust. J. Chem.*, 1993, **46**, 1313.
30 J. J. Gosper and M. Ali, *J. Chem. Soc., Chem. Commun.*, 1994, 1707.
31 H. L. Anderson, S. J. Martin and D. D. C. Bradley, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 655.
32 H. L. Anderson, *Inorg. Chem.*, 1994, **33**, 972.
33 P. N. Taylor, J. Huuskonen, G. Rumbles, R. T. Aplin, E. Williams and H. L. Anderson, *Chem. Commun.*, 1998, 909.
34 M. Balaz, H. A. Collins, E. Dahlstedt and H. L. Anderson, *Org. Biomol. Chem.*, 2009, **7**, 874; M. K. Kuimova, H. A. Collins, M. Balaz, E. Dahlstedt, J. A. Levitt, N. Sergent, K. Suhling, M. Drobizhev, N. S. Makarov, A. Rebane, H. L. Anderson and D. Phillips, *Org. Biomol. Chem.*, 2009, **7**, 889.
35 H. Yamada, K. Kushibe, T. Okujima, H. Uno and N. Ono, *Chem. Commun.*, 2006, 383; H. Yamada, T. Okujima and N. Ono, *Chem. Commun.*, 2008, 2957.
36 C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525.
37 H. L. Anderson and J. K. M. Sanders, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1400.
38 P. N. Taylor and H. L. Anderson, *J. Am. Chem. Soc.*, 1999, **121**, 11538; M. Drobizhev, Y. Stepanenko, A. Rebane, C. J. Wilson, T. E. O. Screen and H. L. Anderson, *J. Am. Chem. Soc.*, 2006, **128**, 12432.
39 M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor and H. L. Anderson, *J. Phys. Chem. B*, 2005, **109**, 7223.
40 T. E. O. Screen, J. R. G. Thorne, R. G. Denning, D. G. Bucknall and H. L. Anderson, *J. Am. Chem. Soc.*, 2002, **124**, 9712; T. E. O. Screen, J. R. G. Thorne, R. G. Denning, D. G. Bucknall and H. L. Anderson, *J. Mater. Chem.*, 2003, **13**, 2796.
41 M. J. Langton, J. D. Matichak, A. L. Thompson and H. L. Anderson, *Chem. Sci.*, 2011, **2**, 1897.
42 L. D. Movsisyan, D. V. Kondratuk, M. Franz, A. L. Thompson, R. R. Tykwinski and H. L. Anderson, *Org. Lett.*, 2012, **14**, 3424.
43 H. Shinokubo and A. Osuka, *Chem. Commun.*, 2009, 1011.
44 H. Yorimitsu and A. Osuka, *Asian J. Org. Chem.*, 2013, **2**, 356.
45 I. Hisaki, S. Hiroto, K. S. Kim, S. B. Noh, D. Kim, H. Shinokubo and A. Osuka, *Angew. Chem., Int. Ed.*, 2007, **46**, 5125.
46 S. Tokuji, H. Yorimitsu and A. Osuka, *Angew. Chem., Int. Ed.*, 2012, **51**, 12357.
47 V. S.-Y. Lin, S. G. DiMagno and M. J. Therien, *Science*, 1994, **264**, 1105.
48 V. S.-Y. Lin and M. J. Therien, *Chem.–Eur. J.*, 1995, **1**, 645; T. V. Duncan, S. P. Wu and M. J. Therien, *J. Am. Chem. Soc.*, 2006, **128**, 10423; T. V. Duncan, P. R. Frail, I. R. Miloradovic and M. J. Therien, *J. Phys. Chem. B*, 2010, **114**, 14696.

49 K. Susumu and M. J. Therien, *J. Am. Chem. Soc.*, 2002, **124**, 8550.

50 K. Susumu, P. R. Frail, P. J. Angiolillo and M. J. Therien, *J. Am. Chem. Soc.*, 2006, **128**, 8380.

51 P. J. Angiolillo, V. S.-Y. Lin, J. M. Vanderkooi and M. J. Therien, *J. Am. Chem. Soc.*, 1995, **117**, 12514; R. Kumble, S. Palese, V. S.-Y. Lin, M. J. Therien and R. M. Hochstrasser, *J. Am. Chem. Soc.*, 1998, **120**, 11489; R. Shediac, M. H. B. Gray, H. T. Uyeda, R. C. Johnson, J. T. Hupp, P. J. Angiolillo and M. J. Therien, *J. Am. Chem. Soc.*, 2000, **122**, 7017; I. V. Rubtsov, K. Susumu, G. I. Rubtsov and M. J. Therien, *J. Am. Chem. Soc.*, 2003, **125**, 2687.

52 T.-H. Huang, Y.-J. Chen, S.-S. Lo, W.-N. Yen, C.-L. Mai, M.-C. Kuo and C.-Y. Yeh, *Dalton Trans.*, 2006, 1015.

53 J. Fortage, A. Scarpaci, L. Viau, Y. Pellegrin, E. Blart, M. Falkenström, L. Hammarström, I. Asselberghs, R. Kellens, W. Libaers, K. Clays, M. P. Eng and F. Odobel, *Chem.–Eur. J.*, 2009, **15**, 9058.

54 A. Ryan, A. Gehrold, R. Perusitti, M. Pintea, M. Fazekas, O. B. Locos, F. Blaikie and M. O. Senge, *Eur. J. Org. Chem.*, 2011, 5817.

55 M. O. Senge, *Acc. Chem. Res.*, 2005, **38**, 733.

56 S. Anabuki, S. Tokuji, N. Aratani and A. Osuka, *Org. Lett.*, 2012, **14**, 2778.

57 G. V. Ponomarev and A. M. Shul'ga, *Khim. Geterotsikl. Soedin.*, 1986, **5**, 278.

58 D. Arnold, A. W. Johnson and M. Winter, *J. Chem. Soc., Perkin Trans.*, 1977, 1643.

59 G. V. Ponomarev and A. M. Shul'ga, *SU Pat.*, 1172922, 1985 (*Chem. Abstr*., 1986, **104**, 168272e).

60 G. V. Ponomarev, V. V. Borovkov, K.-i. Sugiura, Y. Sakata and A. M. Shul'ga, *Tetrahedron Lett.*, 1993, **34**, 2153.

61 M. O. Senge, M. G. H. Vicente, K. R. Gerzevske, T. P. Forsyth and K. M. Smith, *Inorg. Chem.*, 1994, **33**, 5625.

62 R. Kitagawa, Y. Kai, G. V. Ponomarev, K.-i. Sugiura, V. V. Borovkov, T. Kaneda and Y. Sakata, *Chem. Lett.*, 1993, 1071.

63 H. Higuchi, K. Shimizu, J. Ojima, K.-i. Sugiura and Y. Sakata, *Tetrahedron Lett.*, 1995, **36**, 5359; H. Higuchi, K. Shimizu, M. Takeuchi, J. Ojima, K.-i. Sugiura and Y. Sakata, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1923; H. Higuchi, M. Shinbo, M. Usuki, M. Takeuchi, Y. Hasegawa, K. Tani and J. Ojima, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 1887; H. Higuchi, T. Maeda, K. Miyabayashi, M. Miyake and K. Yamamoto, *Tetrahedron Lett.*, 2002, **43**, 3097.

64 Z. I. Zhilina, Y. V. Ishkov, I. S. Voloshanovskii and A. S. A Andronati, *Dokl. Akad. Nark SSSR*, 1988, **303**, 326.

65 M. G. H. Vicente and K. M. Smith, *J. Org. Chem.*, 1991, **56**, 4407.

66 M. O. Senge, K. R. Gerzevske, M. G. H. Vicente, T. P. Forsyth and K. M. Smith, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 750.

67 S. Tokuji, H. Aware, H. Yorimitsu and A. Osuka, *Chem.–Eur. J.*, 2013, **19**, 64.

68 M. J. Frampton, H. Akdas, A. R. Cowley, J. E. Rogers, J. E. Slagle, P. A. Fleitz, M. Drobizhev, A. Rebane and H. L. Anderson, *Org. Lett.*, 2005, **7**, 5365.

69 O. B. Locos and D. P. Arnold, *Org. Biomol. Chem.*, 2006, **4**, 902.

70 O. Locos, B. Bašić, J. C. McMurtrie, P. Jensen and D. P. Arnold, *Chem.–Eur. J.*, 2012, **18**, 5574.

71 E. E. Bonfantini and D. L. Officer, *Tetrahedron Lett.*, 1993, **34**, 8531.

72 A. K. Burrel and D. L. Officer, *Synlett*, 1998, 1297.

73 D. G. Johnson, W. A. Svec and M. R. Wasielewski, *Isr. J. Chem.*, 1988, **28**, 193.

74 X. Jiang, P. Li, Y. Wang, Q. Shen, J. Tao and W. Shi, *Chin. J. Chem.*, 2012, **30**, 405.

75 E. Blart, F. Suzenet, J.-P. Quintard and F. Odobel, *J. Porphyrins Phthalocyanines*, 2003, **7**, 207.

76 D. P. Arnold and D. A. James, *J. Org. Chem.*, 1997, **62**, 3460; D. P. P. Arnold, G. A. Heath and D. A. James, *New J. Chem.*, 1998, 1377.

77 D. P. Arnold and L. J. Nitschinsk, *Tetrahedron Lett.*, 1993, **34**, 693.

78 J. Wytko, V. Berl, M. McLaughlin, R. R. Tykwinski, M. Schreiber, F. Diederich, C. Boudon, J.-P. Gisselbrecht and M. Gross, *Helv. Chim. Acta*, 1998, **81**, 1964.

79 K. Nakamura, T. Fujimoto, S. Takara, K.-i. Sugiura, H. Miyasaka, T. Ishii, M. Yamashita and Y. Sakata, *Chem. Lett.*, 2003, **32**, 694.

80 R. O. Garay, H. Naarmann and K. Müllen, *Macromolecules*, 1994, **27**, 1922.

81 P. N. Taylor, A. P. Wylie, J. Huuskonen and H. L. Anderson, *Angew. Chem., Int. Ed.*, 1998, **37**, 986.

82 M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor and H. L. Anderson, *J. Am. Chem. Soc.*, 2004, **126**, 15352.

83 K. Susumu, T. V. Duncan and M. J. Therien, *J. Am. Chem. Soc.*, 2005, **127**, 5186.

84 I. M. Blake, L. H. Rees, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2000, **39**, 1818.

85 Y. Xu, L. Jaquinod, A. Wickramasinghe and K. M. Smith, *Tetrahedron Lett.*, 2003, **44**, 7753.

86 K. J. Thorley, J. M. Hales, H. L. Anderson and J. W. Perry, *Angew. Chem., Int. Ed.*, 2008, **47**, 7095.

87 S. Ohira, J. M. Hales, K. J. Thorley, H. L. Anderson, J. W. Perry and J.-L. Brédas, *J. Am. Chem. Soc.*, 2009, **131**, 6099.

88 K. J. Thorley and H. L. Anderson, *Org. Biomol. Chem.*, 2010, **8**, 3472.

89 C.-L. Mai, Y.-L. Huang, G.-H. Lee, S.-M. Peng and C.-Y. Yeh, *Chem.–Eur. J.*, 2008, **14**, 5120.

90 T. E. O. Screen, I. M. Blake, L. H. Rees, W. Clegg, S. J. Borwick and H. L. Anderson, *J. Chem. Soc., Perkin Trans. 1*, 2002, 320.

91 L. J. Esdaile, P. Jensen, J. C. McMurtrie and D. P. Arnold, *Angew. Chem., Int. Ed.*, 2007, **46**, 2090.

92 B. Bašić, J. C. McMurtrie and D. P. Arnold, *Eur. J. Org. Chem.*, 2010, 4381; B. Bašić, J. C. McMurtrie and D. P. Arnold, *J. Porphyrins Phthalocyanines*, 2010, **14**, 481.

93 L. J. Esdaile, M. O. Senge and D. P. Arnold, *Chem. Commun.*, 2006, 4192.

94 A. M. V. M. Pereira, M. G. P. M. S. Neves, J. A. S. Cavaleiro, C. Jeandon, J.-P. Gisselbrecht, S. Choua and R. Ruppert, *Org. Lett.*, 2011, **13**, 4742.

95 A. A. Ryan, S. Plunkett, A. Casey, T. McCabe and M. O. Senge, *Chem. Commun.*, 2014, **50**, 343.

96 D. P. Arnold, Y. Sakata, K.-i. Sugiura and E. I. Worthington, *Chem. Commun.*, 1998, 2331; M. J. Hodgson, P. C. Healy, M. L. Williams and D. P. Arnold, *J. Chem. Soc., Dalton Trans.*, 2002, 4497; D. P. Arnold, P. C. Healy, M. J. Hodgson and M. L. Williams, *J. Organomet. Chem.*, 2000, **607**, 41.

97 R. D. Hartnell, A. J. Edwards and D. P. Arnold, *J. Porphyrins Phthalocyanines*, 2002, **6**, 695.

98 R. D. Hartnell and D. P. Arnold, *Organometallics*, 2004, **23**, 391.

99 Y.-J. Chen, S.-S. Chen, S.-S. Lo, T.-H. Huang, C.-C. Wu, G.-H. Lee, S.-M. Peng and C.-Y. Yeh, *Chem. Commun.*, 2006, 1015.

100 S. Richeter, C. Jeandon, R. Ruppert and H. J. Callot, *Chem. Commun.*, 2001, 91.

101 S. Richeter, C. Jeandon, J.-P. Gisselbrecht, R. Ruppert and H. J. Callot, *J. Am. Chem. Soc.*, 2002, **124**, 6268.

102 S. Richeter, C. Jeandon, R. Ruppert and H. J. Callot, *Chem. Commun.*, 2002, 266.

103 S. Richeter, A. Hadj-Aïssa, C. Taffin, A. van der Lee and D. Leclercq, *Chem. Commun.*, 2007, 2148.

104 Y. Matano, K. Matsumoto, Y. Nakao, H. Uno, S. Sakaki and H. Imahori, *J. Am. Chem. Soc.*, 2008, **130**, 4588.

105 Y. Matano, K. Matsumoto, H. Hayashi, Y. Nakao, T. Kumpulainen, V. Chukharev, N. V. Tkachenko, H. Lemmetyinen, S. Shimizu, N. Kobayashi, D. Sakamaki, A. Ito, K. Tanaka and H. Imahori, *J. Am. Chem. Soc.*, 2012, **134**, 1325.

106 J. Song, N. Aratani, J. H. Heo, D. Kim, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.*, 2010, **132**, 11869.

107 D. Kim and A. Osuka, *J. Phys. Chem. A*, 2003, **107**, 8791; 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; A. Tsuda and A. Osuka, *Adv. Mater.*, 2002, **14**, 75; Y. Matsuzaki, A. Nogami, A. Tsuda, A. Osuka and K. Tanaka, *J. Phys. Chem. A*, 2006, **110**, 4888; P. Kim, T. Ikeda, J. M. Lim, J. Park, M. Lim, N. Aratani, A. Osuka and D. Kim, *Chem. Commun.*, 2011, **47**, 4433.

108 T. K. Ahn, K. S. Kim, D. Y. Kim, S. B. Noh, N. Aratani, C. Ikeda, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2006, **128**, 1700; M.-C. Yoon, S. B. Noh, A. Tsuda, Y. Nakamura, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2007, **129**, 10080.

109 D. Bonifazi, M. Sholl, F. Song, L. Echegoyen, G. Accorsi, N. Armaroli and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, **42**, 4966.

110 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.

111 G. Sedghi, K. Sawada, L. J. Esdaile, M. Hoffmann, H. L. Anderson, D. Bethell, W. Haiss, S. J. Higgins and R. J. Nichols, *J. Am. Chem. Soc.*, 2008, **130**, 8582.

112 G. Sedghi, V. M. García-Suárez, L. J. Esdaile, H. L. Anderson, C. J. Lambert, S. Martin, D. Bethell, S. J. Higgins, M. Elliott, N. Bennett, J. E. Macdonald and R. J. Nichols, *Nat. Nanotechnol.*, 2011, **6**, 517; G. Sedghi, L. J. Esdaile, H. L. Anderson, S. Martin, D. Bethell, S. J. Higgins and R. J. Nichols, *Adv. Mater.*, 2012, **24**, 653.

113 Z. Li, T.-H. Park, J. Rawson, M. J. Therien and E. Borguet, *Nano Lett.*, 2012, **12**, 2722.

114 M. J. Crossley and L. G. King, *J. Chem. Soc., Chem. Commun.*, 1984, 352.

115 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1987, 39.

116 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1991, 1569.

117 M. J. Crossley, L. J. Govenlock and J. K. Prashar, *J. Chem. Soc., Chem. Commun.*, 1995, 2379.

118 T. Khoury and M. J. Crossley, *Chem. Commun.*, 2007, 4851.

119 M. J. Crossley and L. A. Johnston, *Chem. Commun.*, 2002, 1122.

120 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.

121 M. J. Crossley, P. L. Burn, S. J. Langford and J. K. Prashar, *J. Chem. Soc., Chem. Commun.*, 1995, 1921; R. S. Armstrong, G. J. Foran, W. A. Hough, D. M. D'Alessandro, P. A. Lay and M. J. Crossley, *Dalton. Trans.*, 2006, 4805.

122 M. J. Crossley and P. Thordarson, *Angew. Chem., Int. Ed.*, 2002, **41**, 1709.

123 N. Kobayashi, M. Numao, R. Kondo, S. Nakajima and T. Osa, *Inorg. Chem.*, 1991, **30**, 2241.

124 S. Ito, K. Nakamoto, H. Uno, T. Murashima and N. Ono, *Chem. Commun.*, 2001, 2696; H. Uno, K. Nakamoto, K. Kuroki, A. Fujimoto and N. Ono, *Chem.–Eur. J.*, 2007, **13**, 5773; H. Uno, M. Hashimoto and A. Fujimoto, *Heterocycles*, 2009, **77**, 887.

125 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.

126 H. Uno, A. Masumoto and N. Ono, *J. Am. Chem. Soc.*, 2003, **125**, 12082.

127 S. Banala, R. G. Huber, T. Müller, M. Fechtel, K. R. Liedlbc and B. Kräutler, *Chem. Commun.*, 2012, **48**, 4359.

128 L. Jaquinod, O. Siri, R. G. Knoury and K. M. Smith, *Chem. Commun.*, 1998, 1261.

129 R. Paolesse, L. Jaquinod, F. D. Sala, D. J. Nurco, L. Prodi, M. Montalti, C. Di Natale, A. D'Amico, A. Di Carlo, P. Lugli and K. M. Smith, *J. Am. Chem. Soc.*, 2000, **122**, 11295.

130 M. G. H. Vicente, M. T. Cancilla, C. B. Lebrilla and K. M. Smith, *Chem. Commun.*, 1998, 2355.

131 M. Akita, S. Hiroto and H. Shinokubo, *Angew. Chem., Int. Ed.*, 2012, **51**, 2894.

132 C. Jiao, K.-W. Huang, Z. Guan, Q.-H. Xu and J. Wu, *Org. Lett.*, 2010, **12**, 4046.

133 C. Jiao and J. Wu, *Synlett*, 2012, 171.

134 Z. Sun and J. Wu, *Aust. J. Chem.*, 2011, **64**, 519.

135 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.
136 W. Zeng, M. Ishida, S. Lee, Y. M. Sung, Z. Zeng, Y. Ni, C. Chi, D. Kim and J. Wu, *Chem.–Eur. J.*, 2013, **19**, 16814.
137 A. Tsuda, A. Nakano, H. Furuta, H. Yamochi and A. Osuka, *Angew. Chem., Int. Ed.*, 2000, **39**, 558.
138 A. Tsuda, H. Furuta and A. Osuka, *Angew. Chem., Int. Ed.*, 2000, **39**, 2549.
139 A. Tsuda, H. Furuta and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 10304.
140 A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79.
141 T. Ikeue, K. Furukawa, H. Hata, N. Aratani, H. Shinokubo, T. Kato and A. Osuka, *Angew. Chem., Int. Ed.*, 2005, **44**, 6899; S. Hiroto and A. Osuka, *J. Org. Chem.*, 2005, **70**, 4054; Y. Inokuma, N. Ono, H. Uno, D. Y. Kim, S. B. Noh, D. Kim and A. Osuka, *Chem. Commun.*, 2005, 3782; T. Ikeue, N. Aratani and A. Osuka, *Isr. J. Chem.*, 2005, **45**, 293.
142 L.-A. Fendt, H. Fang, M. E. Plonska-Brzezinska, S. Zhang, F. Cheng, C. Braun, L. Echegoyen and F. Diederich, *Eur. J. Org. Chem.*, 2007, 4659; A. A. Ryan and M. O. Senge, *Eur. J. Org. Chem.*, 2013, 3700.
143 T. Ikeda, N. Aratani and A. Osuka, *Chem.–Asian J.*, 2009, **4**, 1248.
144 M. Kamo, A. Tsuda, Y. Nakamura, N. Aratani, K. Furukawa, T. Kato and A. Osuka, *Org. Lett.*, 2003, **5**, 2079.
145 Y. Nakamura, N. Aratani, A. Tsuda, A. Osuka, K. Furukawa and T. Kato, *J. Porphyrins Phthalocyanines*, 2003, **7**, 264.
146 A. Tsuda, Y. Nakamura and A. Osuka, *Chem. Commun.*, 2003, 1096.
147 K. Sugiura, T. Matsumoto, S. Ohkouchi, Y. Naitoh, T. Kawai, Y. Takai, K. Ushiroda and Y. Sakata, *Chem. Commun.*, 1999, 1957.
148 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.
149 B. J. Brennan, J. Arero, P. A. Liddell, T. A. Moore, A. L. Moore and D. Gust, *J. Porphyrins Phthalocyanines*, 2013, **17**, 247; B. J. Brennan, M. J. Kenney, P. A. Liddell, B. R. Cherry, J. Li, A. L. Moore, T. A. Moore and D. Gust, *Chem. Commun.*, 2011, **47**, 10034.
150 T. Ikeda, N. Aratani, S. Easwaramoorthi, D. Kim and A. Osuka, *Org. Lett.*, 2009, **11**, 3080.
151 D. Bonifazi, M. Scholl, F. Y. Song, L. Echegoyen, G. Accorsi, N. Armaroli and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, **42**, 4966; 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.
152 T. Sakurai, K. Shi, H. Sato, K. Tashiro, A. Osuka, A. Saeki, S. Seki, S. Tagawa, S. Sasaki, H. Matsunaga, K. Osaka, M. Tasaka and T. Aida, *J. Am. Chem. Soc.*, 2008, **130**, 13812; 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; S. Tanaka, T. Sakurai, Y. Honsho, S. Seki, K. Kato, M. Takata, A. Osuka and T. Aida, *Chem.–Eur. J.*, 2012, **18**, 10554.
153 H. Sato, K. Tashiro, H. Shinmori, A. Osuka and T. Aida, *Chem. Commun.*, 2005, 2324; H. Sato, K. Tashiro, H. Shinmori, A. Osuka, Y. Murata, K. Komatsu and T. Aida, *J. Am. Chem. Soc.*, 2005, **127**, 13086.
154 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.
155 T. Tanaka, Y. Nakamura and A. Osuka, *Chem.–Eur. J.*, 2008, **14**, 204; T. Tanaka, Y. Nakamura, N. Aratani and A. Osuka, *Tetrahedron Lett.*, 2008, **49**, 3308.
156 N. K. S. Davis, A. L. Thompson and H. L. Anderson, *Org. Lett.*, 2010, **12**, 2124.
157 V. V. Diev, K. Hanson, J. D. Zimmerman, S. R. Forrest and M. E. Thompson, *Angew. Chem., Int. Ed.*, 2010, **49**, 5523.
158 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.
159 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; Y. Nakamura, N. Aratani, K. Furukawa and A. Osuka, *Tetrahedron*, 2008, **64**, 11433.
160 T. Ikeda, J. M. Lintuluoto, N. Aratani, Z. S. Yoon, D. Kim and A. Osuka, *Eur. J. Org. Chem.*, 2006, 3193; T. Ikeda, A. Tsuda, N. Aratani and A. Osuka, *Chem. Lett.*, 2006, **35**, 946.
161 T. Tanaka, B. S. Lee, N. Aratani, M.-C. Yoon, D. Kim and A. Osuka, *Chem.–Eur. J.*, 2011, **17**, 14400.
162 H. Mori, T. Tanaka, B. S. Lee, P. Kim, D. Kim and A. Osuka, *Chem.–Asian J.*, 2012, **7**, 1811.
163 I. M. Blake, A. Krivokapic, M. Katterle and H. L. Anderson, *Chem. Commun.*, 2002, 1662.
164 I. Aviv and Z. Gross, *Chem. Commun.*, 2007, 1987; Z. Gross and H. B. Gray, *Adv. Synth. Catal.*, 2004, **346**, 165.
165 A. Mahammed, I. Giladi, I. Goldberg and Z. Gross, *Chem.–Eur. J.*, 2001, **7**, 4259.
166 I. Luobeznova, L. Simkhovich, I. Goldberg and Z. Gross, *Eur. J. Inorg. Chem.*, 2004, 1724.
167 J. F. B. Barata, A. M. G. Silva, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva and J. A. S. Cavaleiro, *Tetrahedron Lett.*, 2006, **47**, 8171.
168 S. Hirabayashi, M. Omote, N. Aratani and A. Osuka, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 558.
169 S. Hiroto, I. Hisaki, H. Shinokubo and A. Osuka, *Angew. Chem., Int. Ed.*, 2005, **44**, 6763.
170 S. Hiroto, K. Furukawa, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.*, 2006, **128**, 12380; S. Cho, J. M. Lim, S. Hiroto, P. Kim, H. Shinokubo, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 6412.
171 B. Koszarna and D. T. Gryko, *Chem. Commun.*, 2007, 2994.
172 C. Chen, Y.-Z. Zhu, Q.-J. Fan, H.-B. Song and J.-Y. Zheng, *Chem. Lett.*, 2013, **42**, 936.

173 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.

174 J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 7190.

175 J. L. Sessler and D. Seidel, *Angew. Chem., Int. Ed.*, 2003, **42**, 5134.

176 S. Shimizu and A. Osuka, *Eur. J. Inorg. Chem.*, 2006, 1319.

177 T. K. Chandrashekar and S. Venkatraman, *Acc. Chem. Res.*, 2003, **36**, 676.

178 R. Misra and T. K. Chandrashekar, *Acc. Chem. Res.*, 2008, **41**, 265.

179 M. Stępień, N. Sprutta and L. Latos-Grażyński, *Angew. Chem., Int. Ed.*, 2011, **50**, 4288.

180 S. Saito and A. Osuka, *Angew. Chem., Int. Ed.*, 2011, **50**, 4342.

181 A. Osuka and S. Saito, *Chem. Commun.*, 2011, **47**, 4330.

182 T. Higashino and A. Osuka, *Heterocycles*, 2013, **87**, 31.

183 T. K. Ahn, J. H. Kwon, D. Y. Kim, D. W. Cho, D. H. Jeong, S. K. Kim, M. Suzuki, S. Shimizu, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2005, **127**, 12856.

184 T. Tanaka, N. Aratani, J. M. Lim, K. S. Kim, D. Kim and A. Osuka, *Chem. Sci.*, 2011, **2**, 1414.

185 T. Tanaka, N. Aratani and A. Osuka, *Chem.–Asian J.*, 2012, **7**, 889.

186 K. Naoda, H. Mori, N. Aratani, B. S. Lee, D. Kim and A. Osuka, *Angew. Chem., Int. Ed.*, 2012, **51**, 9856.

187 Y. Inokuma and A. Osuka, *Dalton Trans.*, 2008, 2517.

188 T. Torres, *Angew. Chem., Int. Ed.*, 2006, **45**, 2834.

189 A. Osuka, E. Tsurumaki and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 679.

190 Y. Inokuma, J. H. Kwon, T. K. Ahn, M.-C. Yoon, D. Kim and A. Osuka, *Angew. Chem., Int. Ed.*, 2006, **45**, 961.

191 M. Kitano, J. Sung, K. H. Park, H. Yorimitsu, D. Kim and A. Osuka, *Chem.–Eur. J.*, 2013, **19**, 16523.

192 M. Kitano, S.-y. Hayashi, T. Tanaka, H. Yorimitsu, N. Aratani and A. Osuka, *Angew. Chem., Int. Ed.*, 2012, **51**, 5593.