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

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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 $18\pi$ 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

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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 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

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(n) octaethylporphyrin (OEP) 1 that was functionalised from the corresponding meso-formyl Ni(n) OEP was dehydrobrominated with sodium hydride in refluxing 1,2-dimethoxyethane (DME) to afford meso-ethyl derivative 2. Dimerisation of 2 was induced by oxidation with Cu(OAc)2 in pyridine yielding 1,3-butadiyne-bridged Ni(n) 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-ethylphenyl Ni(n) porphyrin 5 using a mixture of tetrakis(triphenylphosphine) Pd(0), chloroacetone and copper(i) iodide.30 This Ni(n) 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(n) 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(triheptylsilylethynyl)porphyrin 7, was employed for oligomerisation. A stepwise approach was used to synthesise oligomers 8N (N = 2–6), which consisted of (i) protodesilylation with TBAF and (ii) Glaser–Hay coupling with CuCl–TMEDA in CH2Cl2 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/CH2Cl2 were red-shifted and intensified with increasing chain-length, reaching out to around 900 nm in the case of the hexamer 86. A similar reaction was employed to prepare various 1,3-butadiyne-bridged porphyrins.34,35

![Fig. 1](#) Types of conjugated porphyrin wires.
Sterically unhindered porphyrins tend to organise themselves in a π-stacked cofacial manner. 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. Addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) to afforded a 2 : 2 complex, (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, (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, (BiPy)$_2$, did not exhibit an enhanced two-photon absorption (TPA) cross section ($\sigma_{\text{TPA}}/N = 3300$ GM) compared with (BiPy)$_2$ ($\sigma_{\text{TPA}}/N = 3750$ GM), the octamer (BiPy)$_8$ exhibited dramatically enhanced TPA values ($\sigma_{\text{TPA}}/N = 6100$) compared with (BiPy)$_8$ ($\sigma_{\text{TPA}}/N = 4600$). This result demonstrated that the TPA enhancement is more effective in the case of double stranded porphyrin arrays (Scheme 4).

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 consisting of a butadiyne linked porphyrin dimer along with its crystal structure. Porphyrin monomer (Zn$_2$) was stirred with phenanthroline macrocycle (Cu(I) iodide, iodine and potassium carbonate in a 1 : 1 mixture of toluene and THF for 5 days at 60 °C (Scheme 5). Rotaxane 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. β-Selective direct borylation of porphyrins has been used for the synthesis of novel functionalised porphyrins and porphyrin-based...
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(s) acetate and pyridine in THF (Scheme 6). 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 563 and 606 nm. The fluorescence quantum yield was considerably reduced (ΦF < 0.01) probably due to structural distortion.

Very recently, preferential formation of cyclic trimers, 17M, has been realised by using a PdCl2(PPh3)2/CuI catalytic system instead of copper catalysis. 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 stereoechemical 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. In their approach, transition metal mediated reactions were proved to be very useful in constructing multicromophoric assemblies and peripherally fabricated porphyrins. 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(PPh3)4 and copper(i) iodide with diethylamine in THF. Later, copper-free Pd-catalysed coupling reaction using Pd3(dba)3 and AsPPh3 with triethylamine in THF was found to be an alternative, which afforded D–A–D–A–D type pentamer 27 in moderate yields. The longest acetylene bridged porphyrin chain was a heptamer, which revealed unusually long hole polaron delocalisation length up to 75 nm. 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.
and at 802 nm for 22. Moreover, 26 displayed a remarkably red-shifted absorption band ($\lambda_{\text{max}} = 883$ 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, $\lambda_{\text{max}} = 843$ 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.$^{51}$

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
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).\textsuperscript{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.\textsuperscript{35} Recently, direct meso-alkynylation of $\beta,\beta$-dipyridylporphyrin 43 with various alkynyllithium reagents has been achieved, in which the adjacent dipyrindyl groups assist the nucleophilic addition through dual coordination to the lithium reagents.\textsuperscript{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.

Ponomarev et al. discovered a novel synthesis of 48(E) from the corresponding ethene-bridged Ni(II) OEP 47,\textsuperscript{57,58} which was prepared via acid-catalysed dimerisation of meso-hydroxymethylporphyrin 46.\textsuperscript{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).\textsuperscript{60} The face-to-face structure 48(Z) as well as its Cu(II) complex was revealed by X-ray diffraction analysis.\textsuperscript{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).\textsuperscript{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
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 \(b\)-substituted ethyl groups.\(^{63}\)

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 \(b\)-formylated Cu(II)TPP\(^{53}\), to afford \(b-b\) 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\(_3\)/C\(_1\) in 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 \(b\)-monoarylated \(meso\)-formyl porphyrin\(^{57b}\), which was prepared by \(b\)-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 \(b\)-substituents.

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(tributylstanny)ethene, Pd(Ph\(_3\))\(_4\), CuI and CsF in DME (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 \(meso-b\) ethene-bridged porphyrin dyads\(^{63M}\) (Scheme 17).\(^{69}\) The mechanism for this unusual \(meso\) to \(b\) rearrangement may involve cyclopalladation onto the \(b\)-C–H followed by migratory reductive elimination.

Later, porphyrin boronates\(^{64M1}\) and iodovinylporphyrins\(^{65M2}\) 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\(^{67M1M2}\) or\(^{68M1}\) in moderate yields (Scheme 18).\(^{70}\)
2.4 Other examples

Extension of \( \pi \)-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).\(^{65}\)

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 butene-bridge (82) and some meso-to-\( \beta \) 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)
and hexadecaocatayne-bridged diporphyrins were synthesised by oxidative coupling of meso-oligonylporphyrins 86a, which were prepared by repeated desilylation and subsequent trimethylsilylthelynylation of 85 (Scheme 24). 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 hexadecaocatayne bridge. The hexadecaocatayne bridge in 90 is the longest conjugative linker between two porphyrins, to the best of our knowledge.

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. This was also the case in anthracene-bridged porphyrin dimer 92 reported by Anderson et al. 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).

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 (BDT) linked array 93, diethynyl(dimethyl[1,2,5]thiadiazolo[3,4-g]quinoxaline) (TDQ)-linked array 94, diethynyl-BBDT-linked array 95 and pentacenene-linked array 96. The absorption spectra of these proquinonoidal arrays displayed significant red-shifts in their absorption wavelengths compared to the corresponding arrays with shorter conjugative linkers.
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 ($\lambda_{\text{max}} = 1006$ nm), highlighting the unusually large quinonoidal resonance contribution to the low-lying electronically excited singlet states of these species systems.

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 ($\lambda_{\text{max}} = 1080$ nm), while a less bathochromic shift was observed for 100 ($\lambda_{\text{max}} = 780$ 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; $\lambda_{\text{max}} = 1243$ nm, $\varepsilon = 170 000$ M$^{-1}$ cm$^{-1}$) (Scheme 27).86,87 The para-nitro substituent of 102b shifted the absorption to longer wavelength ($\lambda_{\text{max}} = 1348$ nm; $\varepsilon = 120 000$ M$^{-1}$ cm$^{-1}$) whereas the para-methoxy substituent of 102c shifted the absorption profile in the opposite direction ($\lambda_{\text{max}} = 1176$ nm; $\varepsilon = 110 000$ 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

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**Scheme 25** Synthesis of 92.

**Scheme 26** Synthesis of quinonoidal porphyrin dimers.

**Scheme 27** Synthesis of porphyrin carbocations.

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

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(u) 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 Cmeso–Nazo = Nazo–Cmeso 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 redshifted 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 200693 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 28 Synthesis of extended porphyrin carbocations.](image)

![Fig. 6 Asymmetric porphyrin carbocations.](image)

![Scheme 29 Synthesis of an imino-conjugated diporphyrin.](image)

![Scheme 30 Synthesis of azo-conjugated diporphyrins.](image)
dimer 126. In this substitution type reaction, the thioether in 125 also acted as a leaving group in an S\(\text{N}\)Ar 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 \(\pi\)-system and the metal d-orbitals.

Arnold \textit{et al.} investigated the structures and fundamental properties of \textit{meso}-\(\eta^1\)-metalloporphyrins.96 \textit{meso}-Platinioporphyrin 128 was prepared by oxidative addition of Pt(0) generated \textit{in situ} from the reaction of Pt(dbach)\(_2\) and PPh\(_3\) to the C–Br bond of \textit{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 \textit{meso}-pyridylporphyrin onto platinum at the \textit{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, \textit{meso}-triflatoplatinio)porphyrin 132, which was prepared by the treatment of \textit{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-diacylene-bridged porphyrin dimers 139M were synthesised (Scheme 36).99 While the Zn(II) complex 139Zn showed small interporphyrin electronic coupling via the platinum–diacylene linker, the corresponding Ni(II) complex 139Ni exhibited NIR absorption in the cationic and dicationic forms, suggesting a certain d\(_{xz}\)–p\(_x\) orbital interaction (Scheme 37).

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, 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
Matano et al. reported the first examples of peripherally \( \beta-\eta^1 \)-palladio- and platinioporphyrins 147 and 148, which were formed by regioselective metalation of \( \textit{meso} \)-phosphanylporphyrins 146 via \( \beta-C-H \) bond activation (Scheme 39).\(^{104,105}\) The Pd(\( \eta^1 \)) bis-\( \mu \)-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 \( \pi \)-\( \pi \)-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.

Treatment of \( \beta-\beta' \) dipyridyl-bridged diporphyrin 150 with Pd(OAc)\(_2\) in the presence of sodium acetate in CH\(_2\)Cl\(_2\)/MeOH resulted in facile metalation that afforded Pd(\( \eta^1 \)) complex 151 in 85% yield (Scheme 40).\(^{106}\) Pd(\( \eta^1 \))-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.
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, $\sigma_M$, generally decreases exponentially with molecular length, $R$, as quantified by the attenuation factor, $\beta$, which is a useful measure of the ability to mediate long-range charge transportation. The $\beta$ 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 $\beta$ 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 $154_N$ ($\beta = 0.04$) 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 $\beta$ values measured to be 0.03.113

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 pyrazinoquinoloxaline-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 $165$ was intensified and red-shifted by 22 nm compared with that of $164$.119,120 Several metal complexes of the fused porphyrinoids were also synthesised.
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(n) 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}.123

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 dipyrrrole 168 with tripyrrane carbaldehyde 169 followed by DDQ oxidation and Zn(n) 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 172M^M 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
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(i) metalation and oxidation, afforded anthraquinone-bridged porphyrin dimer **182** (Scheme 45). Thermal reaction of **182** with an 80-fold excess of C\textsubscript{60} in 1,2-dichlorobenzene at 140 °C furnished hexafullereno-porphyrin **183** in about 80% yield after size-exclusion chromatography.\textsuperscript{127}

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

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

### 3.2 meso-β Fused porphyrin oligomers

Synthesis of N-annulated perylene-fused diporphyrin **193** was reported by Wu et al.\textsuperscript{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(O\textsubscript{3})\textsubscript{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).
Recently, Anderson et al. reported the synthesis of several fused porphyrin dimers from 1,4-phenylene-bridged diporphyrins.\textsuperscript{135} Fused benzene-bridged diporphyrin \textsuperscript{195}, prepared by Pd-catalysed intramolecular β-arylation of dibromide \textsuperscript{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 \textsuperscript{196}, prepared by Friedel–Crafts acylation of diester \textsuperscript{194b}, exhibited a split Soret-like band and intense Q-like bands at around 900 nm. Diporphyrin \textsuperscript{194b} carrying two ester groups at the bridging benzene was converted to \textsuperscript{198} upon treatment with PhLi followed by intramolecular Friedel–Crafts alkylation. This diporphyrin \textsuperscript{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 \textsuperscript{196} was reacted with a large excess of malononitrile to give further fused diporphyrin \textsuperscript{197}. Very recently, Wu et al. have reported para-quinodimethane-fused porphyrin dimer \textsuperscript{200} from the reaction of dialdehyde \textsuperscript{199a} with mesitylmagnesium bromide followed by intramolecular Friedel–Crafts alkylation (Scheme 50).\textsuperscript{136} Dimer \textsuperscript{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”).\textsuperscript{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 \textsuperscript{202M} were thus obtained from singly meso-β linked diporphyrins \textsuperscript{201M} and meso–meso, β-β, β-β triply linked diporphyrins \textsuperscript{204M} were obtained from singly meso–meso linked diporphyrin \textsuperscript{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 \textsuperscript{205Ni}, were obtained, depending on the central metal of the porphyrin. Meanwhile, a combination of DDQ and Sc(OTf)\textsubscript{3} proved to be quite an effective and clean oxidation method to accomplish the fusion reaction by which \textsuperscript{204M} were obtained.
without any side-products. 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. The physical properties of fused porphyrin arrays are particularly noteworthy. 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.

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). From meso-free Ni(II) porphyrin 209, a mixture of doubly fused oligomers 210N (N = 2–5) was obtained (Scheme 54). Sugiura et al. reported the synthesis of similar meso-β doubly linked oligomers by the use

Scheme 51 Synthesis of directly fused diporphyrins via BAHA oxidation.

Scheme 52 Synthesis of a triply fused porphyrin dodecamer via DDQ-Sc(OTf)3 oxidation.

Scheme 53 Synthesis of directly fused diporphyrins via DDQ-Sc(OTf)3 oxidation.
of TeCl₄. When meso-brominated Ni(II) porphyrins 211 were subjected to AuCl₃ 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, β–β triply linked diporphyrins (Scheme 55). 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(BF₄)₂ to afford doubly fused diporphyrins 215M (Scheme 56). 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).

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, C₆₀-binding hosts with unique positive heterotrophic cooperativity and metal surface patterning. Peripherally modified porphyrin tapes have also been prepared.

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). 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.
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\(^2\) were invented to suppress strong \(\pi-\pi\) stacking (Fig. 15).\(^{143,160}\) Hybrid porphyrin tapes, which bear electron-withdrawing \(C_6F_5\) groups as \(meso\)-substituents (Fig. 16), were developed to increase chemical stability against oxidation by lowering HOMO levels.\(^{161,162}\) Donor–acceptor hybrid porphyrin tape dimer\(^2\) and trimer\(^2\) have also been prepared (Fig. 16). Compared with all-donor-type porphyrin tape dimer\(^2\) and trimer\(^2\), these tapes displayed positively shifted oxidation and reduction potentials in their cyclic voltammograms, indicating increased stability against oxidative degradation. Triply linked quinonoidal porphyrin tape was synthesised from (Scheme 58).\(^{163}\) While has a non-planar, butterfly-like structure in the solid-state, the planar structure of allows effective \(\pi\)-delocalisation, exhibiting an intense NIR band at 958 nm.

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 18\(\pi\) 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 \(\text{Co(OAc)}_2\) and triphenylphosphine or \(\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}\),\(^{165-167}\) their precise and regioselective syntheses have been recently achieved.\(^{167-169}\) Upon heating with \(p\)-chloranil, corrole underwent regioselective oxidative coupling reaction at the \(3,3\)’-position to give dimer and trimer (Scheme 59). From 236, subsequent oxidation with \(p\)-fluoranil afforded tetramer 238 and hexamer 239. The crystal structures of the Co(II)–pyridine complexes of 237 and 238 were successfully determined.

Direct borylation of 233 gave borylated corrole, which served as a useful precursor to produce a variety of substituted corroles on the basis of Pd-catalysed coupling reactions. Singly linked corrole dimer was thus obtained in 82% yield.
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). 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 corrole dimers. Zheng et al. succeeded in preparing meso–meso linked porphyrin–corrole hybrids 246 and their Co(II)–PPh₃ complexes 246Co(PPh₃)₂ by BF₃·OEt₂-catalysed condensation of meso-formylporphyrin 245 with dipyromethanes followed by DDQ oxidation (Scheme 62).

### 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. Among these, meso-hexakis(pentafluorophenyl)-substituted hexaphyrin 234 is the most studied molecule due to its 26 aromatic network, rectangular shape, sharp Soret band and relatively long-lived S₁-state (125 ps).

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 dipyromethane 247 (Scheme 63). 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 NaBH₄ quantitatively to afford the corresponding 28 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. Such an aromaticity-switching behaviour in triply linked porphyrin arrays is quite rare and so further

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**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.
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 C3-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 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 (ΦF = 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.

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.

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Notes and references

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