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### Homo- and Heteronuclear *meso,meso-(E)*-Ethene-1,2-diyl-Linked Diporphyrins: Preparation, X-ray Crystal Structure, Electronic Absorption and Emission Spectra and Density Functional Theory Calculations

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Abstract: Homo- and heteronuclear meso, meso-(E)-ethene-1, 2-diyl-linked diporphyrins have been prepared by the Suzuki coupling of porphyrinylboronates and iodovinylporphyrins. Combinations comprising 5,10,15-triphenylporphyrin (TriPP) on both ends of the ethene-1,2-diyl bridge  $M_2 10 (M_2 = H_2/$ Ni, Ni<sub>2</sub>, Ni/Zn, H<sub>4</sub>, H<sub>2</sub>Zn, Zn<sub>2</sub>) and 5,15-bis(3,5-di-tert-butylphenyl)porphyrinato-nickel(II) on one end and H<sub>2</sub>, Ni, and ZnTriPP on the other  $(M_211)$ , enable the first studies of this class of compounds possessing intrinsic polarity. The compounds were characterized by electronic absorption and steady state emission spectra, <sup>1</sup>H NMR spectra, and for the Ni<sub>2</sub> bis(TriPP)

#### Introduction

The spectacular arrays of porphyrinoid macrocycles found in natural light-harvesting systems and the arrangements of pigments in photosynthetic reaction centres have inspired the creation and investigation of a myriad of synthetic multiporphyrin constructs.<sup>[1]</sup> Numerous kinds of covalently attached linkers have been employed in order to control the degree of ground and/or excited state communication between the macrocycles. This work generally divides into i) studies that are concerned with understanding and mimicking the energy transduction mechanisms and photoinduced

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complex **Ni**<sub>2</sub>**10**, single crystal X-ray structure determination. The crystal structure shows ruffled distortions of the porphyrin rings, typical of Ni<sup>II</sup> porphyrins, and the (E)-C<sub>2</sub>H<sub>2</sub> bridge makes a dihedral angle of 50° with the mean planes of the macrocycles. The result is a stepped parallel arrangement of the porphyrin rings. The dihedral angles in the solid state reflect the interplay of steric and electronic effects of the bridge on interporphyrin com-

**Keywords:** conjugation • density functional calculations • electronic spectra • porphyrinoids • Suzuki coupling munication. The emission spectra in particular, suggest energy transfer across the bridge is fast in conformations in which the bridge is nearly coplanar with the rings. Comparisons of the fluorescence behaviour of H<sub>4</sub>10 and H<sub>2</sub>Ni10 show strong quenching of the free base fluorescence when the complex is excited at the lower energy component of the Soret band, a feature associated in the literature with more planar conformations. TDDFT calculations on the gas-phase optimized geometry of Ni<sub>2</sub>10 reproduce the features of the experimental electronic absorption spectrum within 0.1 eV.

charge separation of the photosynthetic apparatus,<sup>[1a-f]</sup> and ii) studies aimed at creating new arrays of porphyrinoids to address fundamental questions relating to extended aromatic systems.<sup>[1g-l]</sup> In the former category, covalently-linked oligoporphyrins with strong and controllable excited state electronic communication are most suitable.<sup>[2]</sup> In contrast, the latter work is often aimed at inducing strong ground state electronic communication, by connections using conjugating or fused linkers, basically to generate fully delocalised supermolecules. Examples of this type include the planar triply linked porphyrin tapes of Osuka and co-workers,<sup>[3]</sup> and the popular alkyne-linked dyads and higher arrays.<sup>[4]</sup> Recently, there has been intense interest in the use of strongly conjugated, extended arrays of porphyrins in the burgeoning field of organic materials for non-linear optics.<sup>[4d,1,m,5]</sup> It is therefore of considerable importance to understand the properties of the simplest bridges, in order to optimise the construction of such synthetic oligoporphyrins.

Over the past decade, 5,15-diaryl- and 5,10,15-triarylporphyrin starting materials<sup>[6]</sup> have become readily available, and have been used almost exclusively in recent studies of this type. Their convenient reactivity, versatility in substitution in the aryl groups, and applicability in palladium catalysed coupling reactions have enabled synthesis and charac-



Scheme 1. Generic structures of meso, meso, β-(E)-ethenediyl- and azo-linked diporphyrins.

terization of very large multiporphyrin arrays.<sup>[3a]</sup> Of the various potentially conjugating bridges that have been studied, one that has been rather neglected in recent years is the simple two-carbon ethene-1,2-diyl fragment. More than ten years ago, there was a flurry of activity on this linker in octaalkylporphyrin and particularly octaethylporphyrin (OEP) dyads (A, Scheme 1). Ponomarev and collaborators discovered a novel synthesis from the corresponding ethane-1,2divl dyads,<sup>[7]</sup> while Smith's group introduced the McMurry coupling as a means of generating the linking double bond.<sup>[8]</sup> Higuchi et al. have prepared extended systems with three or four porphyrins involving both ethenediyl and butadivnediyl linkers.<sup>[9]</sup> The electronic absorption and emission spectra and the electrochemistry of the OEP dyads suggested the presence of multiple conformations with differing absorption and emission characteristics.<sup>[10]</sup> In the solid state, the favoured conformation has the alkene approximately orthogonal to the two porphyrin rings, which themselves are related in a staircase manner, more or less parallel.<sup>[8,11]</sup> Clearly, the flanking ethyl substituents contribute strongly to the steric inhibition of full conjugation between the porphyrins through the ethene orbitals. The (E)-ethenediyl OEP dyads exhibit an unusual, extremely broad, low energy absorption band, as well as a characteristic band in the 500 nm region.<sup>[7,10]</sup> It appears from the spectral studies that these particular features are due to the more conjugated, nearplanar conformations.

The aforementioned diaryl- and triarylporphyrins afford an opportunity to study this conformational problem and the properties of this short linker in the absence of the bulky ethyl substituents in the 3- and 7-positions adjacent to the *meso* bridge. The synthesis of a (*Z*)-ethenediyl-linked diphenylporphyrin dyad by a Stille coupling was reported in a patent in 1994,<sup>[12]</sup> but remarkably, until recently, there were no reports of examples of (*E*)-ethenediyl-linked dyads of this type (**B**, Scheme 1). An extended version, namely an all-*trans* octatetraenediyl-linked dyad, was reported by Odobel's group.<sup>[13]</sup> In 2005, Anderson and co-workers reported

### the synthesis, optical properties and voltammetry of the dizinc complex of (E)-1,2-bis[10,20-

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bis(3,5-di-tert-butylphenyl)porphyrin-5-yl]ethene and the Xray crystal structure of the dizinc complex of (E)-1,2bis[10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin-5-yl]ethene.[14] We prepared small amounts of the dinickel(II) complex of the former ligand by the McMurry route in 1998,<sup>[15]</sup> but did not pursue this project again until recently. Our aim in the present work was to develop a method that would make the free bases accessible, not just metal complexes, and

specific combinations of the entities attached to the ethene linker, that is, homo- or heterodiporphyrin, homo- or heterodimetallic, without relying on unselective metallations and difficult separations. Odobel and co-workers reported the only other example of a heterodimetallic "short-bridge" conjugated diporphyrin in 2009, namely a Zn<sup>II</sup>/Au<sup>III</sup> bis(triarylporphyrin) linked by an ethyne bridge. This compound displayed remarkable non-linear optical properties as well as very instructive electrochemical data.<sup>[16]</sup>

As we reported, the Heck-type alkenation of meso-vinylporphyrins with meso-haloporphyrins failed to produce any of the target meso, meso-ethenediyl-linked dyads, but instead led to generally low yields of a new family of meso,β-ethenediyl-linked dyads (C, Scheme 1) via a novel meso-to-ß Pd migration process.<sup>[17]</sup> Herein we report our successful generation of a series of dyads of the desired meso, meso-linked type, this time using the Suzuki coupling of meso-2-iodovinylporphyrins<sup>[18]</sup> and *meso*-porphyrinylboronates. The members of the series are compared in terms of their visible absorption and (in suitable cases) steady state fluorescence spectra, and the X-ray crystal structure of the dinickel(II) complex is also reported. The properties of the ethenediyllinked dyads are also compared with those of the analogous azo-linked triphenylporphyrin dyads that we reported in 2007 (D, Scheme 1).<sup>[19]</sup> We recently prepared other azoporphyrins, including a tetraporphyrin linked by alternating azo and butadiyndiyl bridges.<sup>[20]</sup> Furthermore, we report density functional theory calculations of geometries, orbitals and excited states, and compare these with the experimental results. The hypothesis that was advanced for the OEP ethenedivl-linked dyads, namely the existence of a population comprising both strongly and weakly conjugated conformers, is well supported by our results, although a broad, low-energy absorption band is notably absent from the spectra of the present series.

Synthesis: A general synthesis of ethenediyl-linked diporphyrins by the Suzuki coupling could potentially be achieved by two routes, shown retrosynthetically in Scheme 2, namely i) a porphyrinylvinylboron reagent with a haloporphyrin or ii) a porphyrinylboron reagent with a halovinylporphyrin. We briefly examined the former route but were unable to prepare the desired boron reagents satisfactorily and therefore turned to the second. As in our previous work on the Heck coupling, we used two porphyrin building blocks, namely 5,10,15-triphenylporphyrin (H2TriPP) and 5,15-bis(3,5-di-tert-butylphenyl)porphyrin (H<sub>2</sub>DAP). Using the established method for the formation of meso-pinacolboronato porphyrins,<sup>[21]</sup> the bromoporphyrins  $H_21$ , Ni1 and Zn1 were converted using a ten-fold excess of pinacolborane and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] as catalyst to the three required Suzuki nucleophiles H<sub>2</sub>2, Ni2 and Zn2 in yields of 72, 74 and 77%, respectively (Scheme 3). Nickel complexes of boronatoporphyrins have only been reported recently.<sup>[22]</sup> The corresponding debrominated porphyrins H<sub>2</sub>3, Ni3 and Zn3 were the only other products isolated. The only other point to note is the wide variation in the time to consume the bromo starting materials, which was one hour for Zn, 12 h for the free base, and 18 h for the nickel complex.



Scheme 2. Retrosynthesis of *meso.meso-*ethenediyl-linked diporphyrin by the Suzuki coupling.



Scheme 3. Preparation of the porphyrinylboronates.

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Scheme 4. Preparation of iodovinyl nickel(II) porphyrins by the Takai reaction.[23]

In the former case, although required product was the formed in >70% yield, several unidentified impurities could not be removed without severe losses in recrystallisation. However, such samples were subsequently used successfully in the Suzuki coupling. For Ni7, the undesired Z isomer was also formed, but likewise could not be removed efficiently. We have previously shown that the Takai reaction was not effective for zinc porphyrins, although it

was satisfactory for the preparation of iodovinyl NiOEP,<sup>[23]</sup> and the use of the chromium reagent precludes this method for free bases. We therefore turned to our method for the iodovinylporphyrins via the corresponding free base bromovinyl species, which employs novel organopalladium derivatives in situ (Scheme 5).[18]

We had previously prepared the meso-vinyl free base H<sub>2</sub>8 by the Stille route for our Heck couplings,<sup>[17]</sup> and terminal bromination using pyridinium tribromide in THF solution at room temperature gave  $H_29$  in high yield. This reagent was used many years ago to prepare a mixture of (E)- and (Z)-2-bromovinyl NiOEP.<sup>[24]</sup> The bromine was exchanged with iodine to yield H<sub>2</sub>7 using our one-pot palladation-iodination procedure reported elsewhere.<sup>[18]</sup> Metallation with Ni<sup>II</sup> and  $Zn^{II}$  proceeded smoothly to give Ni7 and Zn7.<sup>[18]</sup> This route to Ni7 is a slight improvement on the Takai version

The electrophilic partners for the proposed Suzuki reactions, the meso-2-halovinylporphyrins, were prepared by two routes, as shown in Schemes 4 and 5. The Takai iodoalkenation<sup>[23]</sup> of the *meso* aldehydes Ni4 and Ni5 using iodoform and chromium(II) chloride was used to prepare nickel meso-2-iodovinylporphyrins Ni6 and Ni7 (Scheme 4).





Scheme 5. Preparation of iodovinylporphyrins by in situ palladation/iodination.<sup>[18]</sup>

above,<sup>[23]</sup> in that the undesired Z isomer is avoided, and the overall yield is comparable. With the required set of triphenylporphyrin Suzuki partners assembled, and the diarylporphyrin Ni<sup>II</sup> complex **Ni6** available, we then embarked on the formation of the desired dyads, as shown in Scheme 6.

Our initial conditions were adapted from those used by Osuka and co-workers in their synthesis of *meso,meso* directly linked dyads,<sup>[25]</sup> namely [Pd(PPh<sub>3</sub>)<sub>4</sub>] as catalyst, cesium carbonate as base, and DMF/toluene as solvent. Cross-coupling between **Ni7** and **Ni2** was attempted at room temperature but after four days no dyad formation was evident, and the two starting materials were slowly decompos-

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ing. By conducting the reaction at 80°C, a moderate yield (45%) of desired dyad Ni<sub>2</sub>10 was isolated after two days. The decomposition reactions of the two starting materials were likewise enhanced, and the deborylation product Ni3 was also isolated. Changing the catalyst to  $[Pd(dppe)_2]$  (dppe=1,2-bis-(diphenylphosphino)ethane) or  $[Pd(dppp)_2]$  (dppp=1,3-bis(diphenylphosphino)propane) in both cases slightly improved the yield of Ni<sub>2</sub>10. Crystals suitable for X-ray single crystal analysis were obtained from dichloromethane/methanol, and the structure is reported below.

The latter catalyst was then used to couple Ni7 with  $H_22$ and Zn2, with isolated yields of  $H_2Ni10$  and NiZn10 of 30 and 26%, respectively. The order of yields found here for the boronates, namely Ni>H<sub>2</sub>>Zn, is the same as in our Heck alkenation reactions with bromoporphyrins.<sup>[17]</sup> To expand the suite of dyads to the hetero*porphyrin* type, coupling of boronates 2 with the iodovinyIDAP nickel complex Ni6 was also performed under the same conditions, yielding dyads  $H_2Ni11$  (34%), Ni<sub>2</sub>11 (45%) and NiZn11 (28%), respectively.

When using the successful catalyst  $[Pd(dppp)_2]$ , a major side reaction was observed, namely the homocoupling of the



Scheme 6. Preparation of the ethenediyl-linked porphyrin dimers by the Suzuki coupling.

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boronates  $H_22$  and Zn2, to give the meso, meso directly linked dyads H<sub>4</sub>12 and Zn<sub>2</sub>12 (Scheme 6). These dyads were unambiguously identified by the unique upfield shifts of the porphyrin  $\beta$ -protons in their NMR spectra, analogous to the known examples of Osuka.<sup>[26]</sup> This coupling was not observed for the Ni analogue. Osuka and co-workers recently reported a convenient method for making  $\beta$ , $\beta$ -directly linked porphyrin dimers through the homocoupling of  $\beta$ borolanylporphyrins using Pd(OAc)<sub>2</sub>/dppp under aerobic conditions.<sup>[27]</sup> The mechanism of such an aerobic oxidative coupling of arylboronic acids has been defined by Adamo et al.<sup>[28]</sup> Thus the formation of some homocoupled product is not unexpected under prolonged heating at 80°C. Just why the Ni complex should be immune is not clear at present, but our results were reproducible. The series of TriPP dyads was completed by coupling the appropriate iodovinyl and boronate partners, leading to H<sub>4</sub>10, H<sub>2</sub>Zn10 and Zn<sub>2</sub>10, in isolated yields of 49, 29, and 10%, respectively. In these cases, however, reactions at 80°C gave little or no target dyads, but reactions at 40 °C proved to be successful. Fortunately, in all cases in which the crude products contained both the ethenediyl and directly linked dyads, the two were separable by normal flash chromatography. The order of reactivity of the porphyrin boronates is apparently  $H_2 \approx Zn \gg$ Ni; the free base and zinc derivatives are capable of reacting close to room temperature while the nickel species requires higher temperatures. Once palladium has inserted into the iodovinylporphyrin, the reactivity of the organopalladium(II) intermediate apparently lies in the order  $Ni\!\gg\!H_2\!>$ Zn; the nickel derivative is stable enough (or perhaps also reactive enough) to participate well in the coupling with Ni2 whereas the free base and zinc derivatives are less effective. We did not identify any breakdown products of the iodovinyl partners, although numerous minor side products were observed.

It is interesting to compare the Suzuki coupling with other techniques used to prepare meso, meso-(E)-ethenediyllinked diporphyrins. The present method gave us access to a range of homo- and heterodinuclear dyads, as demonstrated by the use of two different porphyrins and three kinds of central substitution. As the boronate can be attached to porphyrins irrespective of the presence or absence of a central divalent metal, it may be more versatile than the CuI/CsF promoted Stille coupling used by Anderson.<sup>[14]</sup> On the other hand, the latter method gave significantly higher yields in the cases of homodinuclear dizinc systems. In any case, the concept of Suzuki coupling to form meso, meso-(E)-ethenediyl-linked homo- and heterodinuclear dyads was proved, and sufficient material was obtained to enable us to compare the electronic spectra among the members of the series.

X-ray crystal structure of the dinickel complex  $Ni_210$ : The porphyrin dimer  $Ni_210$  has crystallographic inversion symmetry (Figure 1; ORTEP depiction with all non-hydrogen atoms labelled is shown in Figure S1, Supporting Information). The porphyrin rings display considerable distortion



Figure 1. a)  $Ni_2$  porphyrin dimer **Ni**<sub>2</sub>**10**, viewed perpendicular to the mean planes of the porphyrin rings. b) "Side" view of the molecule illustrating the extent to which the individual porphyrin rings are distorted from planarity. The out-of-plane twist across the ethylene bridge is also evident. The combination of these two factors leads to the loss of co-planarity of the porphyrin rings, which, while parallel, are separated by 3.5 Å.

from planarity. Maximum deviation from the mean plane of the porphyrin ( $C_{20}N_4Ni$ ) occurs for *meso* carbon atoms C5 (0.703 Å), C10 (0.666 Å), C15 (0.586 Å) and C20 (0.561 Å). The displacement of these atoms from the mean plane of the ring occurs such that C5 and C15 project on one side of the mean plane of the porphyrin while C10 and C15 project on the other. This distortion is referred to in the literature as "ruffled"<sup>[29]</sup> and has been observed by us<sup>[19,30]</sup> and others<sup>[8,11]</sup> in a range of Ni porphyrins and porphyrin dimers.

The dihedral angle between the mean plane of the C–C= C–C ethenediyl bridge and the mean planes of the porphyrin rings is 50°. A similar out-of-plane twist is observed in Anderson's Zn<sub>2</sub> dimer (45°)<sup>[14]</sup> and is due to the close proximity of the ethenediyl CH group (C21) to the nearby  $\beta$ -CH group (C3') of the porphyrin, with the twist alleviating some intramolecular steric interference. As noted by Anderson and co-workers, the only other reported structures of (*E*)ethene-1,2-diyl diporphyrins are those derived from NiOEP, for which a chloroform solvate (dihedral angle 74°) and a toluene solvate (89°) are known.<sup>[8,11]</sup> By contrast, the analogous azo-linked Ni<sub>2</sub> porphyrin dimer, which does not contain H atoms on the bridge, displays considerably less outof-plane twist (37°).<sup>[19,30]</sup> Presumably, this is due to reduced intramolecular steric strain.

The mean ( $C_{20}N_4Ni$ ) planes of the porphyrin rings are exactly parallel (as must be the case given the  $C_i$  point symmetry of the molecule in the structure). The mean planes are

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not co-planar but are displaced by 3.5 Å. The displacement of the mean planes of the porphyrin rings is a consequence of the out-of-plane twist of the ethylene bridge and the ruffled structure of the porphyrin. The degree of separation in this structure is relatively large but reasonable for a Ni<sub>2</sub> dimer. By comparison, the separation of the mean planes of the porphyrin rings in the Ni<sub>2</sub> azo-linked analogue is slightly less at 3.2 Å due to the reduced out-of-plane twist of the bridge and much less in the Zn<sub>2</sub> ethenediyl-linked dimer (distance between planes 1.5 Å)<sup>[14]</sup> due to the lower degree of porphyrin "ruffle" in that molecule.

Electronic absorption spectra: In order to detect "interporphyrin electronic interaction", the easiest and most obvious tool is the visible absorption spectrum. Of course, there are many subtleties that fall under this umbrella term, and other techniques such as fluorescence lifetimes, voltammetry, spectroelectrochemistry and molecular orbital calculations are all applicable. The discussion can centre on ground state or excited state interactions, and can be treated by several approaches. In this work, we have examined our suite of dimers by the basic techniques of absorption and steady state emission spectroscopy. Our goals here are empirical comparisons among the dyads that we now have at our disposal. The relevant features of the UV-visible spectra of the *meso,meso* (10 and 11) and previously reported<sup>[17]</sup> *meso*, $\beta$  (13) ethenediyl-linked dyads are collected in Table 1.

The first comparison to be made is between alkenyl monoporphyrins and the dyads, for which we have both *meso*, *meso* and *meso*, $\beta$  examples. To set the scene for this discussion, the electronic absorption spectra for a typical ethenyl monomer (*meso*-phenylethenylNiTriPP),<sup>[17]</sup> a *meso*,*meso* (Ni<sub>2</sub>10) and a *meso*, $\beta$  (Ni<sub>2</sub>13)<sup>[17]</sup> ethenediyl-linked porphyrin dyad are shown in Figure 2.The absorption spectra of the *meso*, $\beta$  ethenediyl-linked dyads H<sub>2</sub>Ni13–NiZn13 exhibit a shoulder, B<sub>1</sub>, on the red edge of a broadened Soret band, B, as well as an intensified and red-shifted HOMO–LUMO (Q) transition. We have concluded that porphyrins linked by a *meso*, $\beta$  ethenediyl bridge are weakly conjugated, as

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Figure 2. Electronic absorption spectra of model monomer *meso*-phenylethenylNiTriPP (-----), and dimers *meso*,*meso'*-Ni<sub>2</sub>10 (—) and *meso*, $\beta$ -Ni<sub>2</sub>13<sup>[16]</sup> (-----) (in CH<sub>2</sub>Cl<sub>2</sub>).

a result of the smaller coefficients of the interacting orbitals on the  $\beta$  carbons.<sup>[17]</sup> The Soret bands of *meso*, $\beta$  dyads are similar to those of the sterically-congested OEP ethenediyllinked dyads and triads.<sup>[7,9-10]</sup> However, unlike the OEP series, the *meso*, $\beta$  dyads do not possess a weak, very broad transition in the near-infrared between 800 and 1100 nm. The absence of this band may suggest the associated transition is due to physical properties in octaethylporphyrins that are not present in meso-arylporphyrins. However, while the  $B_1$  shoulder to the Soret band for the *meso*,  $\beta$  dyads is generally less red-shifted than the corresponding shoulder in the OEP species, the HOMO-LUMO transition for the former is considerably more red-shifted. Therefore, the presence of a similar broad, structureless transition beyond 1100 nm is possible. This is outside the range of our instrument and until studies are performed using longer wavelengths, no de-

Table 1. Selected features of the UV-visible absorption and steady state fluorescence spectra of ethenediyl-linked porphyrin dyads (in CH<sub>2</sub>Cl<sub>2</sub>).

Dyad	B [nm]	$B [cm^{-1}]$	$B_1$ [nm]	$B_1  [{ m cm}^{-1}]$	$\Delta(B-B_1)$ [cm <sup>-1</sup> ]	Q [nm]	$\lambda_{em}$ [nm]	$arPsi_{ m f}{}^{[ m a]}$
(meso,meso)								
H <sub>2</sub> Ni10	419	23865	469	21 320	2545	677	649, 710	0.005
Ni <sub>2</sub> 10	410	24390	471	21 230	3160	632	n.m. <sup>[b]</sup>	n.m.
NiZn10	415	24095	468	21 370	2725	626	626, 658sh	0.005
H <sub>4</sub> 10	421	23755	468	21 370	2385	680	657, 720	0.030
H <sub>2</sub> Zn10 <sup>[c]</sup>	417	23980	468	21 370	2610	673	597, 664, 723	$0.025^{[d]}$
$Zn_210^{[d]}$	424	23 585	469	21 320	2265	633	620 sh, 657, 760	0.018
H <sub>2</sub> Ni11	423	23640	466	21 460	2180	675	659, 720	0.003
Ni <sub>2</sub> 11	415	24095	466	21 460	2635	625	n.m. <sup>[b]</sup>	n.m.
NiZn11	423	23640	465	21 505	2135	625	617, 660	0.001
$(meso,\beta)$								
H <sub>2</sub> Ni13	425	23530	448	22320	1210	673	656, 716	0.002
Ni <sub>2</sub> 13	422	23695	458	21 835	1860	619	n.m. <sup>[b]</sup>	n.m.
NiZn13	425	23 530	447	22370	1160	620	ca. 670	$< 0.001^{[d]}$

[a] Calculated by comparison with H<sub>2</sub>TPP ( $\Phi_{\rm f}$ =0.11). [b] Fluorescence of dinickel dyads not measured. [c] Shoulder at 23255 cm<sup>-1</sup> (log  $\varepsilon$  5.17). [d] By comparison with ZnTPP ( $\Phi_{\rm f}$ =0.033). [e] Shoulder at 23255 cm<sup>-1</sup> (log  $\varepsilon$  5.33).

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finitive conclusion can be drawn about this band being an intrinsic property of OEPs or being a consequence of a particular conformation of an ethenediyl-linked dyad.

As exemplified in Figure 2, and similar to Anderson's ethenediyl-linked dyad,<sup>[14]</sup> the dyads **10** (and **11**, not shown) possess considerably red-shifted and intensified Q bands as well as a clear splitting of the Soret band due to the stronger interaction between porphyrins linked in the meso-position by an ethenediyl bridge. The HOMO-LUMO transition for the meso, meso linked dyads is red-shifted compared with porphyrin monomers with extended conjugation and the meso, b ethenediyl-linked dyads. The combination of the diaryl- with the triarylporphyrin results apparently in a smaller degree of inter-porphyrin interaction than in the meso,meso linked dyads, as Ni<sub>2</sub>10 experiences a greater splitting and red-shift than Ni<sub>2</sub>11 (Table 1). The NMR spectrum suggests that the two porphyrins in the dyad Ni<sub>2</sub>11 are very similar electronically, as a single NMR peak is observed for the two intrinsically inequivalent ethenediyl protons. It seems likely therefore that the porphyrin/alkene/porphyrin dihedral angles in Ni<sub>2</sub>11 and Ni<sub>2</sub>10 will be similar. Therefore, the electronic spectra appear to be very sensitive to quite subtle differences in the porphyrin and/or dyad symmetries.

Also of note in Table 1 are the differences between Ni<sub>2</sub>10, H<sub>4</sub>10 and Zn<sub>2</sub>10. The extent of splitting in the Soret band follows the trend Ni > 2H > Zn. This splitting is conceivably related to the dihedral angles between the planes of the porphyrins or perhaps, more importantly, between the planes of the alkene and each porphyrin. The conjugation between the two chromophores of a homo-metal dyad may be inferred as increasing in the order Zn < 2H < Ni. In other conjugated dyads studied by our group, such as the butadiyne-linked OEP series, several measurements supported the same order.<sup>[4a-c]</sup> However, in a way this can be deceptive, as another significant point is the well-documented non-planarity of Ni porphyrins versus the free base and zinc complexes, as seen in the X-ray crystal structure discussed above. This argument can be reduced in simple terms to: "conjugation between aromatic systems is reduced when the systems are most aromatic", that is, strongly aromatic systems prefer to remain "insulated". Proton chemical shifts of peripheral protons of Ni porphyrins always lie upfield of those of free base and Zn porphyrins, supporting the proposition that the former are "less aromatic". So this putative "electronic" effect of Ni may be due really to the small size of the Ni<sup>II</sup> ion and the out-of-plane distortion of the rings.

Once the heterobimetallic dyads are considered, there are several factors that may conflict in influencing porphyrin– porphyrin interaction. To illustrate the degree of difference among these examples, Figure 3 shows the spectra of the series  $H_410$ ,  $H_2Ni10$ , and  $H_2Zn10$ . Considering the complete bis(triphenylporphyrin) dyad series 10, the extent of splitting in the Soret band decreases in the order Ni–Ni > Ni–Zn > 2H–Zn  $\approx 2H$ –Ni > 2H–2H > Zn–Zn. Central substituents of different electronegativity should create a donor–acceptor ("push–pull") situation, resulting in a contraction of the HOMO–LUMO gap and perhaps allowing greater interac-



Figure 3. Electronic absorption spectra of  $H_410$  (-----),  $H_2Ni10$  (-----) and  $H_2Zn10$  (-----) (in CH<sub>2</sub>Cl<sub>2</sub>).

tion. However, the effects of the central substituents upon macrocycle planarity and the porphyrin-alkene-porphyrin dihedral angles will affect the degree of conjugation, which may result in unpredictable trends. Further discussion of the details of this order is not justified, until other data such as electrode potentials and more crystal structures are published.

Steady state fluorescence: The fluorescence properties of trans-stilbenes (1,2-diarylethenes) have been studied extensively and the trends noted in their emission spectra serve as a useful basis for comparison with the bis(porphyrinyl)ethenes.<sup>[31]</sup> Partial conjugation between simple aryl groups across an ethenediyl bridge results in an increase in fluorescence intensity and Stokes shift relative to biphenyls. Modification of electron distribution due to the presence of either donor or acceptor substituents alone results in redshifts and lower quantum yields. However, conjugative interaction between such unlike substituents in the same molecule increases the intensity. Steric inhibition of inter-aryl conjugation causes larger Stokes shifts, but can markedly decrease quantum yields. With these points in mind, we have recorded the steady state emission of all those new dyads in which at least one of the macrocycles is a free base or Zn<sup>II</sup> complex, initially using the wavelength of the highest-energy component of the Soret band for excitation. The data are included in Table 1. Ni<sup>II</sup> porphyrins are usually non-emissive, due to spin-orbit quenching by the d<sup>8</sup> metal ion. Mononuclear free base and Zn<sup>II</sup> porphyrins without heavy atom substituents usually emit fluorescence with quantum yields between 0.03 and 0.15 and Stokes shifts  $<1000 \text{ cm}^{-1}$ . The steady state fluorescence properties of the series of mononuclear alkenyl-substituted free base porphyrins and their zinc complexes that we prepared by Heck coupling have been recorded and their features fit into this typical pattern.<sup>[31]</sup> Thus

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the more unusual data in Table 1 represent the influence of dinuclearity and the ethenediyl bridge.

In Figure 4, the emission spectra of the series  $H_410$ ,  $H_2Zn10$ , and  $Zn_210$  are shown, together with those of H<sub>2</sub>Ni10. There have been very few studies of the fluorescence spectra of analogous dyads containing Ni<sup>II</sup> porphyrins, and as far as we know, the saturated ethane-1,2-diyl bridge is the only type that has been investigated.<sup>[32]</sup> Not surprisingly, all the ethenediyl-linked dyads have lower quantum yields than their mononuclear analogues. The Ni<sup>II</sup>-containing dyads have very low quantum yields, indeed less than 1%, as expected. As the concentrations of all the dyads were maintained at about  $10^{-7}$  M, most likely this quenching is not intermolecular. Such a dramatic intramolecular quenching provides strong evidence of energy transfer across the bridge, complementing the data on ground state interactions from the absorption spectra, although as the emission properties of no other Ni-containing dyads have been studied, we cannot actually attribute the quenching specifically to the ethenediyl linker per se. The emission spectra of H<sub>4</sub>10, H<sub>2</sub>Zn10, and Zn<sub>2</sub>10 show remarkable redshifts of the main fluorescence band when the dyad contains only free base or Zn porphyrins. For comparison, the dizinc dyad studied by Anderson and co-workers gave a quantum yield of 4.1% and a fluorescence maximum at 765 nm (in benzene + 1% pyridine).<sup>[14]</sup> In aromatic dyads,<sup>[33]</sup> including porphyrin dvads,<sup>[34]</sup> linked by an alkene-containing bridge, a large Stokes shift has been observed, which was attributed to a change in conformation of the dyad as a result of the electronic excitation.

Comparing the fluorescence spectra of  $H_410$ ,  $H_2Zn10$ , and  $Zn_210$  in Figure 4, it is clear that the emission of the heteronuclear dyad exhibits features of both its homonuclear analogues, but the elements associated with the free base appear to dominate. The spectrum of  $H_2Ni10$  is also a strongly attenuated version of  $H_410$ . In heterobimetallic porphyrin oligomers linked by diarylethynediyl units, Lindsey and coworkers attributed the resulting features to energy transfer



Figure 4. Steady state fluorescence spectra of  $H_410$  (----),  $H_2Zn10$  (-----),  $Zn_210$  (-----), excited at the maximum of the highest energy component of the respective Soret envelopes.

from the more electron-rich macrocycle to the more electron-deficient one.<sup>[35]</sup> However, without the detailed information afforded by transient absorption spectra and excited state lifetimes, we cannot speculate more about the relative contributions of through-space and through-bridge mechanisms for this transfer. Because all of our examples of *meso*, $\beta$  linked dyads contain nickel, discerning a difference between *meso*, $\beta$  and *meso,meso* linkages is difficult due to the inherently weak fluorescence.

One striking observation from Figure 4 and the data in Table 1 is that the emission envelopes are not mirror images of the absorption spectra. The fluorescence component at highest energy has an anti-Stokes shift from the  $S_1 \rightarrow S_0$  absorption band. Therefore, it is likely that excitation is accompanied by changes in geometry.<sup>[36]</sup> Considering the "normal" Stokes shifts observed in alkenyl-substituted monomers, the behaviour of the dyads may be attributed to the existence of a distribution of conformations that are more or less conjugated. Accordingly, a change in geometry after excitation can lead to the apparent anti-Stokes shifts, or the emission envelope is simply the superposition of the components derived from the various ground state geometries, as expected for any molecule with several conformations that individually have rather different absorption/emission properties. To investigate this aspect further, we measured both the emission spectra of H<sub>4</sub>10, H<sub>2</sub>Zn10, Zn<sub>2</sub>10, and H<sub>2</sub>Ni10 at different excitation wavelengths, and the excitation spectra contributing to particular maxima in the emission spectra. To illustrate the results, the data for  $Zn_210$ ,  $H_410$  and H<sub>2</sub>Ni10 are displayed in Figures 5, 6 and 7, respectively.



Figure 5. Steady state fluorescence spectra of  $\mathbb{Zn}_2 10$  excited at different wavelengths: 420 nm (----), 472 nm (----) and 523 nm (-----), and excitation spectra monitored at the 621 nm emission band (-----) at the 657 nm emission band (-----) and at the 760 nm emission band (----).

For  $Zn_210$ , the major emission band peaking at 760 nm arises from excitation at both major components of the Soret envelope, namely at 420 and 472 nm, but the shorter wavelength fluorescence band at 657 nm arises selectively by excitation at the higher energy Soret component. The excitation spectra likewise show that the emission band at 657 nm results from a conformation that has the characteristics of a monoporphyrin, that is, a Soret band with just the

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Figure 6. Steady state fluorescence spectra of  $H_410$  excited at different wavelengths: 419 nm (—), 468 nm (----) and 520 nm (----), and excitation spectra monitored at the 657 nm emission band (—) and at the 720 nm emission band (----).



Figure 7. Steady state fluorescence spectra of  $H_2Ni10$  excited at different wavelengths: 416 nm (----), 469 nm (-----) and 521 nm (-----), and excitation spectra monitored at 649 nm emission band (----) and at 710 nm emission band (----).

higher energy component. The emission band at 760 nm, however, results also from the red-shifted Soret component, suggesting the lower energy fluorescence band results from a more planar, more conjugated conformation. Turning to  $H_410$  (Figure 6), the same number of emission bands is observed at each excitation frequency, but the relative intensities among these differ, with excitation at the 468 nm Soret component selectively enhancing the long wavelength emission band at 720 nm. Thus the conclusions from both are similar.

The dyad  $H_2Ni10$  exhibits unique emission and excitation spectra in comparison with the other three (Figure 7). The emission intensity from excitation at 469 nm, is much less than those from excitation at either 416 or 521 nm. The excitation spectra confirm that the residual fluorescence of  $H_2Ni10$  is largely due to absorption at these wavelengths. Although the relative intensities between the Soret and Q bands in the excitation spectra are distorted from those of ground state absorption spectra, they resemble the absorption profile of a monoporphyrin. This striking result is clear evidence that the nickel moiety quenches the excited state of the dyad most efficiently when the two porphyrins are conjugated across the ethenediyl bridge, that is, from conformations that possess the signature 469 nm band.

Density functional theory calculations of geometries: The calculation of electronic structures and the application of density-functional theory to the time-dependent domain have been studied for conjugated porphyrin dyads, especially those containing alkynyl bridges.<sup>[4c, 37]</sup> Sundström and coworkers have used semi-empirical equilibrium geometry calculations to investigate the possibility of different conformations of ethenediyl-linked octaethylporphyrin dimers contributing differently to their electronic spectra.<sup>[10a]</sup> Johnson et al. also calculated van der Waals forces for β-ethenediyllinked chlorins to determine similar properties,<sup>[38]</sup> but there has been little theoretical investigation into the electronic structure and nature of the singlet excited states of ethenediyl-linked porphyrin dyads. The calculations reported in this section extend the theoretical investigation on ethenediyl-linked dyads. Emphasis will be placed upon the physical properties of these dyads that can be explained qualitatively by the modelling results.

All geometry, electronic structure and time-dependent calculations were performed as restricted closed-shell calculations using the DFT model with B3LYP exchange-correlation functionals and a 6-31G basis set. Although the 6-31G(d) basis set is much more desirable as it allows a better account of the bonding interaction between atoms, the phenomenal increase in the number of degrees of freedom resulting from this basis set for a porphyrin dyad, which contains a very large number of atoms, makes the calculation extremely difficult.<sup>[1g]</sup> As discussed above, the absorption and emission spectra of ethenediyl-linked porphyrin dyads are explainable by hypothesising different conformations of the dyads, in equilibrium, in solution; each conformation has a different degree of conjugation and so gives rise to slightly different absorption and emission spectra that overlap with the spectra of other conformations.

To investigate the suite of possible conformations, equilibrium geometry calculations were performed on the di-nickel triphenylporphyrin dyad, **Ni**<sub>2</sub>**10**, from four different initial geometries. The first starting geometry was generated from a calculation at the semi-empirical level using the PM3 method.<sup>[39]</sup> This geometry was then manipulated by rotation of the two porphyrins about their bond with the alkene. The rotations consisted of placing both porphyrins in plane with the alkene (0°, 0°), one porphyrin in plane and one orthogonal to the alkene (90°, 90°) to generate the second,

third and fourth starting geometries respectively. The results of the DFT equilibrium geometry calculations on these starting geometries are listed in Table 2, in terms of the angle between the mean planes of the porphyrins,  $\alpha$ , and the angles between the mean plane of each porphyrin and the plane of the alkene,  $\beta$  and  $\gamma$ .

Table 2. Angles between the mean planes of the porphyrins ( $\alpha$ ) and between each porphyrin and the plane of the alkene ( $\beta$  and  $\gamma$ ) of the minimized structures from various starting geometries of the dyad **Ni<sub>2</sub>10**.

Ni <sub>2</sub> 10 Starting geometry	α [°]	$\beta$ [°]	γ [°]
PM3 optimised	89.94	44.34	46.10
0°, 0°	68.75	40.05	47.51
0°, 90°	81.14	40.58	40.56
90°, 90°	72.03	36.01	36.02

The equilibrium geometry calculations on all four starting geometries produce slightly different conformations, which differ as much as 10° with respect to the plane of the porphyrins and the plane of the alkene, and 21° in the angle between the planes of the porphyrins. The convergence criterion for the root-mean-square displacement in the elements of the density matrix was set to be less than 0.0012 on two successive self-consistent field iterations, which was the default setting for the software. Geometry calculations performed previously on ethenediyl-linked OEPs found two conformations from two different starting geometries; one conformation held both porphyrins completely orthogonal to the alkene ("P-type"), while the two macrocycles were almost in plane with the alkene in the second conformation ("U-type").<sup>[10a]</sup> While our molecular mechanics (MM) calculations produce different conformations from those found in previous work, this work complements the results found by Sundström and co-workers<sup>[10a]</sup> and supports the plausibility of different conformers with similar energies contributing to the absorption and emission spectra of ethenediyl-linked dyads.

Density functional theory calculations of molecular orbitals of Ni<sub>2</sub>10: Discussions of the electronic structures of conjugated porphyrin dyads are often concentrated on the eight frontier orbitals that are derived from interactions of the four "Gouterman orbitals" of each porphyrin across the  $\pi$ conjugating bridge.<sup>[4a-e, 37d]</sup> For these dyads, the labels of each frontier orbital are assigned on the basis of the molecule lying in the xy plane with the x axis along the 15,5,5',15' positions of the porphyrins (the porphyrins being substituted in the 5,5' positions by the alkene). As most conformations of the dyads used for electronic structure calculations possess only  $C_1$  symmetry, no symmetry labels can be assigned to the frontier orbitals. Instead, each orbital has been labelled x or y depending on its origin. The orbitals labelled x are ultimately derived from the  $a_{2u}$  and  $e_{gx}$  orbitals of a  $D_{4h}$  metalloporphyrin, while the orbitals labelled y are derived from the  $a_{1u}$  and  $e_{gy}$  orbitals. These orbitals for the "parallel" conformation of Ni<sub>2</sub>10 are shown in Figure 8.



Figure 8. Eight frontier molecular orbitals calculated by DFT for Ni<sub>2</sub>10.

Both the HOMO-1 and LUMO display in-phase orbital interactions that span the carbons on the alkene and the adjacent *meso* carbons, while the HOMO and LUMO + 3 display out-of-phase orbital interactions in this region. All of the x orbitals show substantial electron density on the alkene, which shows the integral role of this bridge, in these particular conformations, in the electronic structure of the dyad. For *meso,meso* linked dyads, the y orbitals possess nodes at the *meso*-carbons, so as a result these non-interacting orbitals do not possess coefficients on the alkene. In comparison to the four orbitals of the Gouterman model, the x ( $a_{2u}$ -derived) orbitals are elevated in respect to y ( $a_{1u}$ -derived) orbitals, which is expected due to the overlap of

the alkene  $\pi$ -orbitals with the porphyrin orbitals. Interestingly, the results of electronic structural calculations on the ethynediyl-linked dyads by Therien and co-workers placed the out-of-phase *x* orbital, but not the in-phase orbital, above the *y* orbitals,<sup>[37b]</sup> whereas calculations of the butadiynediyl-linked dyad by Wilson and Arnold gave comparable results to those for the ethenediyl-linked dyad **Ni**<sub>2</sub>**10**.<sup>[4c]</sup> The more recent calculations of Ohira and Brédas for alkynebridged diporphyrins at the 6-31G\*\* level placed the two *y* levels as HOMO-3 and HOMO-2, and the two *y*\* levels as LUMO +2 and LUMO +3,<sup>[37d]</sup> so slightly different theoretical methods do not agree on the exact placement of the porphyrin-localised pairs with respect to the *x*, *x*\* sets.

Kyrychenko and Albinsson have used the orbital splitting in the lowest excited singlet state as a measure of the excitonic coupling within arylethylenediyl-linked porphyrin dimers.<sup>[40]</sup> The relationship is such that the greater the splitting between the excited states, the greater the excitonic coupling. As the orbitals in the excited-state that represent interaction between the porphyrins will be involved in excitonic coupling, the difference in energies between the  $x_1^*$ and  $x_2^*$  states should be a qualitative measure of the splitting in the lowest excited singlet state for the ethenediyllinked porphyrin dyads. This splitting is represented graphically in Figure 9. In our earlier DFT studies, we were uniquely able to address this gap in a dyad by considering the reduced and oxidised states of the butadiyndiyl dyads.<sup>[4c]</sup> The spectrum of the monoanion has one electron in the orbital labelled  $x_1^*$ , thus allowing a transition  $x_1^* \to x_2^*$ , which can be observed in the electronic spectrum (under spectroelectrochemical conditions at low temperature).<sup>[4b,41]</sup>



Figure 9. Calculated eight-orbital manifold showing the splitting in the lowest excited singlet state.

Time-dependent density functional theory calculations for ethenediyl-linked porphyrin dyad Ni<sub>2</sub>10: Calculations for the lowest 100 excited states of ethenediyl-linked porphyrin dyad Ni<sub>2</sub>10 in the gas phase were carried out in the time-dependent domain. For this di-nickel dyad, excited state calculations were performed for two conformations, the minimized structure resulting from the PM3 minimization, and that resulting from the (0,90°) starting geometry (see above). The large number of excited states was generated in order to calculate a theoretical absorption spectrum for each dyad so as to add support to the orbital and MM calculations performed already. The TD calculations were also performed to see if an excited state would be predicted in the near-infrared or infrared as was observed for the ethenediyl-linked OEP dimers.

While these calculations produced an extensive amount of data, Table 3 shows a selection of the excited states which yield an oscillator strength,  $f_{,\geq} 0.01$ , for optical transitions of wavelength  $\geq$  385 nm for the conformation of Ni<sub>2</sub>10 that was optimised semi-empirically. The full list of excited states for Ni<sub>2</sub>10 is available in the Supporting Information. Table 3 reveals that the first excited state has contributions from three  $y \rightarrow y^*$  transitions and the classical  $x_2 \rightarrow x_1^*$  HOMO– LUMO transition. Beyond the first excited state, the number of transitions leading to each excitation becomes too large to relate simply to the orbitals, but it is evident that each excited state with an oscillator strength >0.01 is largely comprised of transitions involving the eight frontier orbitals. The remainder of the transitions results mostly from lower-lying orbitals to either the frontier or slightly higher anti-bonding orbitals.

The first Soret band in the experimental data (410 nm) corresponds to the 33rd excited state, and the second Soret band (471 nm) with the 22nd excited state, according to their large oscillator strengths. Interestingly, while these excited states over-estimate the energies of these transitions (396 and 468 nm, respectively), the difference between the predicted and real energies is only of the order of 0.1 eV. For the HOMO–LUMO transition, the difference between the predicted and real data is less than 0.01 eV. A comparison between the experimental absorption data and excited state transition energies for Ni<sub>2</sub>10 are shown in Figure 10. The general absorption profile of the dyad is clearly evident in the time-dependent data. Interestingly, of the 100 excited states, the majority of the absorption spectrum may be characterised largely by about 10 of these states.

For Ni<sub>2</sub>10, Figure 10 shows that the two conformations used for the excited state calculations produce the same transitions but these differ slightly in energy and oscillator strength. Interestingly, in comparing the two conformations, the more planar dyad (optimised from the 0, 90° starting geometry) has a more red-shifted HOMO-LUMO transition, but slightly blue-shifted Soret bands. For the more planar geometry, the red-shifted Soret band also possesses larger oscillator strength relative to its blue-shifted Soret partner whereas the less planar dyad has a higher oscillator strength for its blue-shifted Soret band. This comparison shows qualitatively that different conformations are accentuated in different parts of the absorption profile, with the more planar dyad having a more prominent role in the red-shifted Soret band, and the less planar dyad having a more prominent role in the blue-shifted Soret band. This hypothesis is supported nicely by the excitation spectra shown in Figures 5-7, as the first fluorescence band arises from conformations of the dyad where there is less conjugation. In the absorption spectra of ethenediyl-linked OEP dyads, a weak, structureless band was observed between 800 and 1100 nm.<sup>[7c,10a]</sup> It was speculated above that while this band was not observed in the visible-near-IR region for the dyads in this study, it may still exist but lies beyond the spectral region which was

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Table 3. TDDFT calculated excitation energies, one-electron transitions and oscillator strengths for selected optical transitions of Ni<sub>2</sub>10 in the gas phase ( $\lambda \ge 385$  nm,  $f \ge 0.05$ , % contribution  $\ge 10$  %).

Excited state	Orbital composi	Orbital composition [%]			Excita	Excitation		
					[eV]	[nm]	$[cm^{-1}]$	strength f
1	HOMO $(x_2)$	$\rightarrow$	LUMO $(x_1^*)$	82	1.97	629	15894	0.84
12	HOMO-2 $(y_2)$	$\rightarrow$	LUMO $(x_1^*)$	34	2.53	490	20399	0.05
	HOMO-1 $(x_1)$	$\rightarrow$	LUMO + 2 $(y_2^*)$	20				
	HOMO $(x_2)$	$\rightarrow$	LUMO + 2 $(y_2^*)$	20				
13	HOMO-5	$\rightarrow$	LUMO $(x_1^*)$	28	2.56	484	20647	0.05
	HOMO-3 $(y_1)$	$\rightarrow$	LUMO $(x_1^*)$	15				
	HOMO-1 $(x_1)$	$\rightarrow$	LUMO + 1 $(y_1^*)$	11				
	HOMO $(x_2)$	$\rightarrow$	LUMO + 1 $(y_1^*)$	11				
22	HOMO-3 $(y_1)$	$\rightarrow$	LUMO + 2 $(y_2^*)$	10	2.69	460	21731	0.60
	HOMO-2 $(y_2)$	$\rightarrow$	LUMO + 1 $(y_1^*)$	13				
	HOMO-1 $(x_l)$	$\rightarrow$	LUMO + 3 $(x_2^*)$	31				
23	HOMO-2 $(y_2)$	$\rightarrow$	LUMO $(x_1^*)$	12	2.75	451	22184	0.05
	HOMO-2 $(y_2)$	$\rightarrow$	LUMO + 3 $(x_2^*)$	34				
	HOMO-1 $(x_1)$	$\rightarrow$	LUMO + 2 $(y_2^*)$	29				
26	HOMO-3 $(y_1)$	$\rightarrow$	LUMO $(x_1^*)$	10	2.78	445	22461	0.09
	HOMO-3 $(y_1)$	$\rightarrow$	LUMO + 3 $(x_2^*)$	26				
	HOMO-1 $(x_1)$	$\rightarrow$	LUMO + 1 $(y_1^*)$	27				
33	HOMO-1 $(x_1)$	$\rightarrow$	LUMO + 3 $(x_2^*)$	40	3.15	393	25430	1.02
	HOMO-3 $(y_1)$	$\rightarrow$	LUMO + 3 $(x_2^*)$	39				
34	HOMO-7	$\rightarrow$	LUMO + 3 $(x_2^*)$	18	3.21	387	25866	0.74
	HOMO-2 $(y_2)$	$\rightarrow$	LUMO + 3 $(x_2^*)$	21				



Figure 10. Experimental absorption spectrum (-) and predicted line spectra from TDDFT calculations of the excited states of the conformations generated by geometry optimizations of Ni<sub>2</sub>10 with two starting geometries (see text).

observed. It is therefore significant then that no such transition was predicted by the TDDFT calculations. As a result, it is suggested that this band results from a dynamic process unique to the OEP ethenediyl-linked dyads that cannot be accounted for in gas-phase calculations of static structures.

In the crystal structures of *meso,meso* ethenediyl-linked OEP dyads reported previously, the dihedral angle between the porphyrin and the alkene is almost  $90^{\circ}$ .<sup>[8,11]</sup> The only example of a *meso,meso* ethenediyl-linked dyad with free  $\beta$ -

positions, the di-zinc triarylporphyrin dyad synthesised by Anderson's group, has a dihedral angle between the porphyrins and the alkene of 45°.<sup>[14]</sup> However, it is notable that all crystal structures of trans-ethenediyllinked porphyrin dyads show both porphyrins twisting in opposite directions with respect to the alkene, resulting in the porphyrin planes being almost parallel with each other.<sup>[8,11,14]</sup> Preliminary calculations of the equilibrium geometry of meso, meso ethenediyl-linked dyad Zn<sub>2</sub>10 predict the twist of the alkene from the plane of the macrocycle remarkably well (42.9°),<sup>[31]</sup> but the two porphyrins are twisted in the same sense from the alkene, resulting in a near-orthogonal disposition of the porphyrin planes. The major difference between the

calculated and crystal conformations may be crystal packing forces, which result in the alignment of the two porphyrins in the Anderson dyad.<sup>[14]</sup> The inter-porphyrin angle is expected, intuitively, to be less relevant to the absorption and emission properties of ethenediyl-linked porphyrin dyads, than the angle between the porphyrins and the alkene.

#### Conclusion

We have prepared a variety of homo- and heterodiporphyrin, and homo- and heterodimetallic porphyrins linked by a meso, meso-(E)-ethene-1,2-diyl bridge, using the Suzuki coupling of porphyrinyl boronates and iodovinyl porphyrins. This complements the Stille-coupling strategy of Anderson and co-workers for homonuclear analogues. Through crystal structure determination, electronic absorption and steady state emission studies, and theoretical geometry and spectral calculations, we have characterized the series thoroughly. The overall conclusions from this study are that the ethenedivl-linked dyads exist in solution in a family of conformations that differ in the extent of conjugation across the bridge, due to differing dihedral angles between the porphyrin and alkene planes. The fluorescence band at highest energy, with a "monoporphyrin" excitation signature, results from less planar conformations, while the lower energy emission components result from conformations with smaller dihedral angles. Anderson and co-workers likewise attributed the large Stokes shift, the broad absorption bands and the low fluorescence quantum yield in their analogue of Zn<sub>2</sub>10 (compared to the ethynediyl-linked dyad), to the effects of populations with different torsional angles.<sup>[14]</sup> Wasie-

lewski and co-workers concluded from temperature- and solvent-dependence studies that two major conformations give rise to the emission of a  $\beta$ , $\beta$  ethenediyl-linked methyl-pyrochlorophyllide *a* dyad, and that the two conformations are related by a "bicycling" rotation of the single bonds between the alkene and the macrocycle.<sup>[36]</sup> Similar experiments would be valuable in the current situation, but are beyond the scope of the current work. Electronic structure calculations show that the *meso,meso* linked dyads have substantial porphyrin interaction across the *x* bonding and anti-bonding orbitals with a high electron density located on the alkene. This highlights the importance of this bridge in the electronic structures of these dyads.

#### **Experimental Section**

General procedure for Suzuki coupling for porphyrin dyads: Iodoethenylporphyrin (0.02 mmol), borolanylporphyrin (0.02 mmol), bis[bis(1,3-(diphenylphosphino)propane]palladium(0) (3.7 mg, 0.004 mmol, 20 mol%), and  $Cs_2CO_3$  (7.8 mg, 0.024 mmol) were added to a Schlenk tube and dried under vacuum. The vacuum was released under argon to allow the addition of dry DMF (0.75 mL), and dry toluene (1.5 mL). The mixture was degassed via three freeze-pump-thaw cycles before the vessel was purged with argon again. The Schlenk flask was sealed and the reaction mixture was allowed to stir for 2 d. The progress of the reactions was monitored by TLC using CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 50:50 for free base porphyrin and CHCl<sub>3</sub>/*n*-hexane (50:50) for metallated porphyrins. After 2 d, TLC showed the complete consumption of borolanylporphyrin, so the mixture was diluted with toluene (10 mL) and washed with water (10 mL x 2). The organic layer was collected, dried and the residue was subjected to column chromatography.

5-[(10,15,20-Triphenyl)porphyrin-5-yl]-[(10,15,20-triphenyl)porphyrin]

(H<sub>4</sub>12) and (E)-1-(10,15,20-triphenylporphyrin-5-yl)-2-[10,15,20-triphenylporphyrinatonickel(II)-5-yl]ethene (H<sub>2</sub>Ni10): Produced from Ni7 (14.9 mg) and  $H_22$  (13.3 mg) by the general method at 80 °C.  $CH_2Cl_2/n$ hexane 30:70 was used as eluent for the column. The first minor band contained an unidentified green compound. The second band contained  $H_{2}\mathbf{3}$  while the third band contained the directly linked dyad  $H_{4}\mathbf{12}.$  The fourth band corresponded to the desired product H<sub>2</sub>Ni10, which was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/methanol (6.9 mg, 30%). H<sub>4</sub>12: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 8.93$  (d,  ${}^{3}J(H,H) = 4.9$  Hz, 4H,  $\beta$ -H), 8.90 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 4H,  $\beta$ -H), 8.59 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 4H,  $\beta$ -H), 8.29 (m, 4H, o-Ph-H), 8.22 (m, 8H, o-Ph-H), 8.08 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 4H, β-H), 7.78 (m, 6H, m, p-Ph-H), 7.67 (m, 12H, m, p-Ph-H), -2.21 ppm (brs, 4 H, N-H); UV/Vis (DCM):  $\lambda_{max}$  (log  $\varepsilon$ ) = 414 (5.42), 450 (5.45), 524 (4.77), 560sh (4.26), 594 (4.32), 652 nm (4.02); HRMS (ESI<sup>+</sup>): m/z: calcd for C<sub>76</sub>H<sub>50</sub>N<sub>8</sub>+H<sup>+</sup>: 1075.4232 [M+H<sup>+</sup>]; found: 1075.4237. **H<sub>2</sub>Ni10**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 9.83$  (d, <sup>3</sup>*J*(H,H) = 4.9 Hz, 2H,  $\beta$ -H, NiTriPP), 9.76 (d,  ${}^{3}J(H,H) = 4.6$  Hz, 2H,  $\beta$ -H, H<sub>2</sub>TriPP), 9.61 (d,  ${}^{3}J(H,H) = 15.3$  Hz, 1H, 1-alkene-H), 9.41 (d,  ${}^{3}J(H,H) = 15.6$  Hz, 1 H, 2-alkene-H), 8.99 (d,  ${}^{3}J(H,H) = 4.6$  Hz, 2 H,  $\beta$ -H, H<sub>2</sub>TriPP), 8.96 (d, 2H,  ${}^{3}J(H,H) = 4.9$  Hz, 2H,  $\beta$ -H, NiTriPP), 8.84 (br s, 4H,  $\beta$ -H, H<sub>2</sub>TriPP), 8.75 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 2H,  $\beta$ -H, NiTriPP), 8.72 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 2H, β-H, NiTriPP), 8.26 (m, 6H, o-Ph-H, H<sub>2</sub>TriPP), 8.06 (m, 6H, o-Ph-H, NiTriPP), 7.79 (m, 9H, m, p-Ph-H, H2TriPP), 7.72 (m, 9H, m, p-Ph-H, NiTriPP), -2.30 ppm (brs, 2H, N-H, H<sub>2</sub>TriPP); UV/Vis (DCM):  $\lambda_{max}$  $(\log \varepsilon) = 419$  (5.26), 469 (5.27), 521 (4.55), 560 (4.48), 606 (4.57), 677 nm (4.46); HRMS (ESI<sup>+</sup>): m/z: calcd for  $C_{78}H_{50}N_8Ni+H^+$ : 1157.3590 [*M*+H<sup>+</sup>]; found: 1157.3570.

(*E*)-1,2-Bis[10,15,20-triphenylporphyrinatonickel(II)-5-yl]ethene (Ni<sub>2</sub>10): Produced from Ni7 (14.9 mg) and Ni2 (14.7 mg) by the general method at 80 °C. CHCl<sub>3</sub>/*n*-hexane 30:70 was used as the eluent for the column. The first minor band contained an unidentified green compound. The second band contained Ni3 while the third band corresponded to the desired product **Ni**<sub>2</sub>**10**, which was recrystallised from CHCl<sub>3</sub>/methanol (13.5 mg, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$ =9.61 (d, <sup>3</sup>*J*-(H,H)=5.2 Hz, 2H, β-H), 9.01 (s, 2H, alkene-H), 8.88 (d, <sup>3</sup>*J*(H,H)=5.2 Hz, 2H, β-H), 8.69 (d, <sup>3</sup>*J*(H,H)=5.2 Hz, 2H, β-H), 8.67 (d, <sup>3</sup>*J*-(H,H)5.2 Hz, 2H, β-H), 8.01 (m, 12H, *o*-Ph-H), 7.68 ppm (m, 18H, *m*, *p*-Ph-H); UV/Vis (DCM):  $\lambda_{max}$  (log  $\varepsilon$ )=410 (5.32), 471 (5.35), 538 (4.60), 632 nm (4.59); MS (LDI<sup>+</sup>): *m*/*z*: calcd for C<sub>78</sub>H<sub>48</sub>N<sub>8</sub>Ni<sub>2</sub>: 1212.27 [*M*<sup>+</sup>]; found: 1214.49.

 $\label{eq:solution} \begin{array}{l} 5-[(10,15,20\mbox{-}Triphenyl)\mbox{-}porphyrinatozinc(II)\mbox{-}5-yl]\mbox{-}[(10,15,20\mbox{-}triphenyl)\mbox{-}porphyrinatozinc(II)\mbox{-}] \\ porphyrinato-zinc(II)\mbox{-}[(2n_212)\mbox{-}and\mbox{-}(E)\mbox{-}1\mbox{-}[(10,15,20\mbox{-}triphenyl)\mbox{-}porphyrinatozinc(II)\mbox{-}] \\ porphyrinato-zinc(II)\mbox{-}[(2n_212)\mbox{-}and\mbox{-}(E)\mbox{-}1\mbox{-}[(10,15,20\mbox{-}triphenyl)\mbox{-}porphyrinatozinc(II)\mbox{-}1\mbox{-}[(10,15,20\mbox{-}triphenyl)\mbox{-}porphyrinatozinc(II)\mbox{-}1\mbox{-}[(10,15,20\mbox{-}triphenyl)\mbox{-}porphyrinatozinc(II)\mbox{-}1\mbox{-}[(10,15,20\mbox{-}triphenyl)\mbox{-}porphyrinatozinc(II)\mbox{-}1\mbox{-}[(10,15,20\mbox{-}triphenyl)\mbox{-}porphyrinatozinc(II)\mbox{-}1\mbox{$ 

thene (NiZn10): Produced from Ni7 (14.9 mg) and Zn2 (14.8 mg) by the general method at 80 °C. The product was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 40:60. The first minor band comprised a mixture of unidentified porphyrins. The second band contained Zn3 while the third band contained the directly linked dyad Zn<sub>2</sub>12. The fourth band corresponded to the desired product NiZn10, which was recrystallised using CHCl<sub>3</sub> (1% pyridine)/methanol (7.7 mg, 32%). Zn<sub>2</sub>12: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$ =8.91 (d, <sup>3</sup>*J*(H,H)=4.9 Hz, 4H,  $\beta$ -H), 8.89 (d, <sup>3</sup>*J*(H,H)=4.9 Hz, 4H,  $\beta$ -H), 8.49 (d, <sup>3</sup>*J*(H,H)=4.9 Hz, 4H,  $\beta$ -H), 8.26 (m, 4H, o-Ph-H), 8.18 (m, 8H, o-Ph-H), 7.81 (d, <sup>3</sup>*J* 4.9 Hz, 4H,  $\beta$ -H), 7.75 (m, 6 H, *m*, *p*-Ph-H), 7.62 ppm (m, 12 H, *m*, *p*-Ph-H); UV/Vis (DCM):  $\lambda_{max}$  (log  $\varepsilon$ ) = 420 (5.32), 458 (5.29), 564 (4.60), 606 nm (3.81).

**NiZn10**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 9.84 (d, <sup>3</sup>*J* (H,H) = 4.9 Hz, 2H, β-H, NiTriPP), 9.79 (d, <sup>3</sup>*J*(H,H) = 4.6 Hz, 2H, β-H, ZnTriPP), 9.54 (d, <sup>3</sup>*J*(H,H) = 15.2 Hz, 1H, 2-alkene-H), 9.47 (d, <sup>3</sup>*J*(H,H) = 15.2 Hz, 1H, 1-alkene-H), 8.99 (d, <sup>3</sup>*J*(H,H) = 4.6 Hz, 2H, β-H, ZnTriPP), 8.91 (d, <sup>3</sup>*J*(H,H) = 4.9 Hz, 2H, β-H, NiTriPP), 8.83 (br s, 4H, β-H, ZnTriPP), 8.71 (d, <sup>3</sup>*J*(H,H) = 4.9 Hz, 2H, β-H, NiTriPP), 8.69 (d, <sup>3</sup>*J*(H,H) = 4.9 Hz, 2H β-H, NiTriPP), 8.04 (m, 6H, o-Ph-H, NiTriPP), 7.70 ppm (m, 18H, *m*, *p*-Ph-H, ZnTriPP, NiTriPP); UV-Vis (DCM):  $\lambda_{max} (\log \varepsilon) = 415 (5.33), 468 (5.19), 549 (4.18), 626 nm (4.13); MS (ESI<sup>+</sup>):$ *m/z*: calcd for C<sub>78</sub>H<sub>48</sub>N<sub>8</sub>NiZn: 1218.2647 [*M*<sup>+</sup>]; found: 1218.2637.

(*E*)-1,2-Bis(10,15,20-triphenylporphyrin-5-yl)ethene (H<sub>4</sub>10): Produced from H<sub>2</sub>7 (13.8 mg) and H<sub>2</sub>2 (13.3 mg) by the general method at 40 °C. The product was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 30:70. The first minor band contained an unidentified mixture of porphyrins. The second band contained H<sub>2</sub>3 and the third band contained the directly linked dyad H<sub>4</sub>12. The fourth band corresponded to the desired product H<sub>4</sub>10, which was recrystallised using CHCl<sub>3</sub>/methanol (10.8 mg, 49 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 9.96 (s, 2H, alkene-H), 9.93 (d, <sup>3</sup>J(H,H) = 5.2 Hz, 4H, β-H), 9.01 (d, <sup>3</sup>J(H,H) = 4.9 Hz, 4H, β-H), 8.84 (s, 8H, β-H), 8.26 (m, 12H, *o*-Ph-H), 7.78 (m, 18H, *m*, *p*-Ph-H), -2.26 ppm (br s, 4H, N-H); UV/Vis (DCM):  $\lambda_{max}$  (log  $\varepsilon$ ) = 421 (5.21), 468 (4.86), 519 (4.28), 596 (4.27), 680 nm (4.08); HRMS (LSIMS<sup>+</sup>) *m*/z: calcd for C<sub>78</sub>H<sub>53</sub>N<sub>8</sub>+H<sup>+</sup>: 1101.4365 [*M*+H<sup>+</sup>]; found: 1101.4393).

(E)-1-[10,15,20-Triphenylporphyrinatozinc(II)-5-yl]-2-(10,15,20-triphenylporphyrin-5-yl)-ethene (H<sub>2</sub>Zn10): Produced from H<sub>2</sub>7 (13.8 mg) and Zn2 (14.8 mg) by the general method at 40 °C. The product was purified by column chromatography using CH2Cl2/n-hexane 50:50. The first minor band contained an unidentified mixture of porphyrins. The second band contained Zn3 and the third band contained the directly linked dyad Zn<sub>2</sub>12 (9.1 mg). The fourth band corresponded to the desired product H<sub>2</sub>Zn10, which was recrystallised using CHCl<sub>3</sub>(1% pyridine)/methanol (7.2 mg, 31 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 10.08$  (d, <sup>3</sup>J-(H,H) = 4.8 Hz, 2H,  $\beta$ -H, ZnTriPP), 10.03 (d,  ${}^{3}J(H,H) = 15.3$  Hz, 1H, alkene-H), 9.97 (d,  ${}^{3}J$  (H,H) = 15.3 Hz, 1H, alkene-H), 9.97 (d,  ${}^{3}J$ (H,H) = 4.7 Hz, 2H, β-H, H<sub>2</sub>TriPP), 9.14 (d, <sup>3</sup>*J*(H,H)=4.6 Hz, 2H, β-H, ZnTriPP), 9.02 (d, <sup>3</sup>J(H,H)=4.5 Hz, 2H, β-H, H<sub>2</sub>TriPP), 8.96 (s, 4H, β-H, H<sub>2</sub>TriPP), 8.85 (s, 4H, β-H, ZnTriPP), 8.26 (m, 12H, o-Ph-H, H2TriPP, ZnTriPP), 7.78 (m, 18H, p-Ph-H, H<sub>2</sub>TriPP, ZnTriPP), -2.26 ppm (brs, 2H, N-H, H<sub>2</sub>TriPP); UV/Vis (DCM):  $\lambda_{max}$  (log  $\varepsilon$ ) = 417 (5.21), 468 (4.82), 518 (4.16), 560 (4.17), 608 (4.18), 673 nm (3.97); HRMS (ESI+) m/z: calcd for  $C_{78}H_{51}N_8Zn + H^+$ : 1163.3518 [*M*+H<sup>+</sup>]; found: 1163.3528.

 at 40 °C. CHCl<sub>3</sub>/*n*-hexane (30:70) was used as the eluent for the column. The first band contained **Zn3**, the second band corresponded to directly linked dimer **Zn<sub>2</sub>12** and the third band contained the desired product **Zn<sub>2</sub>10**, which was recrystallised using CHCl<sub>3</sub>(1% pyridine)/methanol (2.5 mg, 10%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 10.01$  (d, <sup>3</sup>*J*-(H,H)5.2 Hz, 4H,  $\beta$ -H), 9.97 (s, 2H, alkene-H), 9.01 (d, <sup>3</sup>*J*(H,H)=5.2 Hz, 4H,  $\beta$ -H), 8.85 (d, <sup>3</sup>*J*(H,H)=5.2 Hz, 4H,  $\beta$ -H), 8.83 (d, <sup>3</sup>*J*(H,H)=5.2 Hz, 4H,  $\beta$ -H), 8.824 (m, 8H, *o*-Ph-H), 8.21 (m, 4H, *o*-Ph-H), 7.72 ppm (m, 18H, *m*, *p*-Ph-H); UV/Vis (DCM):  $\lambda_{max}$  (log $\varepsilon$ )=424 (5.35), 469 (5.19), 555 (4.55), 633 nm (4.48); MS (ESI<sup>+</sup>): *m/z*: calcd for C<sub>78</sub>H<sub>48</sub>N<sub>8</sub>Zn<sub>2</sub>: 1226.2585 [*M*<sup>+</sup>]; found: 1224.2461.

(E)-1-[10,20-Bis(3,5-di-tert-butylphenyl)porphyrinatonickel(II)-5-yl]-2-(10,15,20-triphenylporphyrin-5-yl)ethene (H2Ni11): Produced from Ni6 (17.9 mg) and H<sub>2</sub>2 (13.3 mg) by the general method at 80 °C. CH<sub>2</sub>Cl<sub>2</sub>/nhexane 50:50 was used as the eluent for the column. The first minor band contained an unidentified green compound. The second band contained the desired product H<sub>2</sub>Ni11, which was recrystallised using CH<sub>2</sub>Cl<sub>2</sub>/methanol (8.9 mg, 34 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 9.85$ (d, <sup>3</sup>*J*(H,H)=4.9 Hz, 2H, β-H, NiDAP), 9.76 (d, <sup>3</sup>*J*(H,H)=4.9 Hz, 2H β-H, H<sub>2</sub>TriPP), 9.74 (s, 1 H, meso-H, NiDAP), 9.64 (d, <sup>3</sup>J(H,H)=15.2 Hz, 1H, 2-alkene-H), 9.45 (d, <sup>3</sup>*J*(H,H)=15.2 Hz, 1H, 1-alkene-H), 9.11 (d, <sup>3</sup>*J*-(H,H) = 4.9 Hz, 2H  $\beta$ -H, NiDAP), 9.00 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 2H,  $\beta$ -H, NiDAP), 8.96 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 2H,  $\beta$ -H, H<sub>2</sub>TriPP), 8.91 (d,  ${}^{3}J$ -(H,H)=4.9 Hz, 2H, β-H, NiDAP), 8.82 (br s, 4H, β-H, H<sub>2</sub>TriPP), 8.23 (m, 6H, o-Ph-H,  $H_2$ TriPP), 7.93 (d,  ${}^{4}J(H,H) = 1.7$  Hz, 4H, o-Ar-H, NiDAP), 7.76 (m, 11H, m, p-Ph-H, H2TriPP, p-Ar-H, NiDAP), 1.50 (s, 36H, tBu-H, NiDAP), -2.34 ppm (brs, 2H, N-H, H<sub>2</sub>TriPP); UV/Vis (DCM):  $\lambda_{max}$  (log  $\varepsilon$ ) = 423 (5.38), 466 (5.33), 523 (4.56), 562 (4.45), 606 (4.56), 675 nm (4.42); MS (ESI<sup>+</sup>) m/z: calcd for C<sub>88</sub>H<sub>79</sub>N<sub>8</sub>Ni: 1304.5703  $[M^+]$ ; found: 1305.5643. Third and fourth bands were collected, containing  $H_2 3$  and  $H_4 12,$  respectively.

(E)-1-[Bis(3,5-di-tert-butylphenyl)porphyrinatonickel(II)-5-yl]-2-

[10,15,20-triphenylporphyrinatonickel(II)-5-yl]ethene (Ni,11): Produced from Ni6 (17.9 mg) and Ni2 (14.7 mg) by the general method at 80 °C.  $CHCl_3/n$ -hexane (50:50) was used as the eluent for the column. The first minor band contained an unidentified green compound. The second band contained the desired product Ni<sub>2</sub>11, which was recrystallised using CHCl<sub>3</sub>/methanol (12.2 mg, 45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 9.70$  (s, 1 H, meso-H, NiDAP), 9.65 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 2 H, β-H, NiDAP), 9.63 (d, <sup>3</sup>J (H,H) = 4.9 Hz, 2H, β-H, NiTriPP), 9.08 (d, <sup>3</sup>J-(H,H) = 4.9 Hz, 2H,  $\beta$ -H, NiDAP), 9.07 (s, 2H, alkene-H), 8.Ni3 (d, <sup>3</sup>J-(H,H) = 4.9 Hz, 2H,  $\beta$ -H, NiDAP), 8.88 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 2H,  $\beta$ -H, NiDAP), 8.87 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 2H,  $\beta$ -H, NiTriPP), 8.69 (d,  ${}^{3}J(H,H) =$ 4.9 Hz, 2H, β-H, NiTriPP), 8.67 (d, <sup>3</sup>*J*(H,H)=4.9 Hz, 2H, β-H, NiTriPP), 8.01 (m, 6H, o-Ph-H, NiTriPP), 7.90 (d, <sup>4</sup>J(H,H)=1.7 Hz, 4H, o-Ar-H, NiDAP), 7.74 (d, <sup>4</sup>J(H,H)=1.7, 2H, p-Ar-H, NiDAP), 7.68 (m, 9H, m, p-Ph-H, H<sub>2</sub>TriPP), 1.50 ppm (s, 36 H, *t*Bu-H, NiDAP); UV-Vis (DCM):  $\lambda_{max}$  $(\log \varepsilon) = 415$  (5.30), 466 (5.33), 533 (4.59), 625 (4.53) nm; MS (LDI<sup>+</sup>) m/z: calcd for C<sub>88</sub>H<sub>76</sub>N<sub>8</sub>Ni<sub>2</sub>: 1360.5 [*M*<sup>+</sup>]; found: 1361.5.

(E)-1-[10,20-Bis(3,5-di-tert-butylphenyl)porphyrinatonickel(II)-5-yl]-2-[10,15,20-triphenylporphyrinatozinc(II)-5-yl]ethene (NiZn11): Produced from Ni6 (17.9 mg) and Zn2 (14.8 mg) by the general method at 80 °C. The product was purified by column chromatography using CHCl<sub>3</sub>/nhexane (50:50). The first minor band contained an unidentified mixture of porphyrins. The second band contained the desired product NiZn11, which was recrystallised using CHCl<sub>3</sub>(1% pyridine)/methanol (7.7 mg, 28%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 9.87$  (d, <sup>3</sup>J(H,H) = 5.1 Hz, 2H, β-H, NiDAP), 9.80 (d, <sup>3</sup>J(H,H)=4.9 Hz, 2H, β-H, ZnTriPP), 9.70 (s, 1H, meso-H, NiDAP), 9.58 (d,  ${}^{3}J(H,H) = 15.2$  Hz, 1H, 2-alkene-H), 9.51 (d,  ${}^{3}J(H,H) = 15.2$  Hz, 1H, 1-alkene-H), 9.09 (d,  ${}^{3}J(H,H) =$ 4.9 Hz, 2 H,  $\beta$ -H, NiDAP), 8.98 (d,  ${}^{3}J(H,H) = 5.1$  Hz, 2 H,  $\beta$ -H, NiDAP), 8.97 (d,  ${}^{3}J(H,H) = 4.6$  Hz, 2H,  $\beta$ -H, ZnTriPP), 8.89 (d,  ${}^{3}J(H,H) = 4.9$  Hz, 2H, β-H, NiDAP), 8.82 (br s, 4H, β-H, ZnTriPP), 8.21 (m, 6H, o-Ph-H, ZnTriPP), 8.17 (m, 2H, o-Ph-H, ZnTriPP), 7.92 (d, <sup>4</sup>J(H,H)=1.7 Hz, 4H, o-Ar-H, NiDAP), 7.74 (d, <sup>4</sup>J(H,H)=1.7 Hz, 2H, p-Ar-H, NiDAP), 1.48 ppm (s, 36 H, *t*Bu-H, NiDAP); UV/Vis (DCM):  $\lambda_{max}$  (log  $\varepsilon$ ) = 423 (5.31), 465 (5.11), 534 (4.37), 552 (4.40), 625 nm (4.32); MS (ESI<sup>+</sup>): m/z:

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calcd for  $C_{88}H_{75}N_8NiZn$ : 1366.4838 [*M*<sup>+</sup>]; found: 1366.4851. Third and fourth bands were collected, containing **Zn3** and **Zn<sub>2</sub>12**, respectively.

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