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Synthesis and Light-Harvesting Potential of Cyanovinyl β-Substituted Porphyrins and Dyads

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Abstract
Knoevenagel condensation has been utilized as an alternative way to synthesize a series of β-vinyl-substituted porphyrins and porphyrin dyads with good to excellent yields. The condensation of β-formyl porphyrins and phenylacetonitriles allows control of the substitution pattern and metal centres in the porphyrin dyads, allowing the use of metallated synthons. While the optical and electronic properties of the resulting porphyrin dyes are perturbed by the presence of the cyano substituent, this does not significantly affect their use. For example, Raman spectroscopy, in agreement with density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations, show porphyrin electronic transitions with delocalization of frontier molecular orbital electron density onto the β substituent. A comparison of the photovoltaic performance of a carboxylated cyanostyryl condensation product and the unsubstituted analogue in dye-sensitized solar cells (DSSCs) was made. Although the devices showed similar efficiency, the device containing the cyano-substituted dye showed an extended incident photon-to-current conversion efficiency (IPCE) due to a slight red-shift in absorption and an increase in photovoltage as a result of a longer electron lifetime. This minimal change in light-harvesting performance highlights the potential of this Knoevenagel synthetic methodology for producing light-harvesting porphyrin dyes.

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Abstract: Knoevenagel condensation has been utilized as an alternative way to synthesize a series of β-vinyl substituted porphyrins and porphyrin dyads with good to excellent yields. The condensation of β-formyl porphyrins and phenylacetonitriles allows control of the substitution pattern and metal centres in the porphyrin dyads, allowing the use of metallated synthons. While the optical and electronic properties of the resulting porphyrin dyes are perturbed by the presence of the cyano substituent, this does not significantly affect their use. For example, Raman spectroscopy, in agreement with DFT and TD-DFT calculations, show typical porphyrin electronic transitions with delocalisation of frontier molecular orbital electron density onto the β-substituent. A comparison of the photovoltaic performance of a carboxylated cyanostyryl condensation product and the unsubstituted analogue in dye sensitised solar cells was made. Although the devices showed similar efficiency, the device containing the cyano-substituted dye showed an extended IPCE due to a slight red shift in absorption and an increase in photovoltage as a result of a longer electron lifetime. This minimal change in light harvesting performance highlights the potential of this Knoevenagel synthetic methodology for producing light harvesting porphyrin dyes.

Introduction

Over recent years, synthetic porphyrins have proved to be outstanding light harvesting materials whether as part of antenna systems, on surfaces or for solar cells.[1] One of the key challenges in using them as light harvesting materials is to extend the porphyrin energy absorption of readily prepared synthetic porphyrins across the visible spectrum as much as possible. As has been well documented, the electronic properties of porphyrins can be altered by chemical functionalisation and the attachment of a conjugated system has the ability to extend the porphyrin energy absorption.[2] For example, the β-pyrrolic modification and extension of the porphyrin π-system significantly broadens and red shifts the light absorption.[3] In particular, electron withdrawing substituents have the ability to move electronic absorption toward the red.[4] and, as a result of the improved light harvesting, increase the performance of dye sensitised solar cells (DSSCs).[5] A variety of chemistries have been used to extend the conjugation of either single porphyrins or multiporphyrin arrays. Suzuki, Heck and Wittig reactions have all been used to extend porphyrin conjugation through the β-pyrrolic position by introduction of a vinyl group.[6] The first two processes have poor selectivity toward mono-substituted porphyrins as mono-borylation and bromination of the porphyrin core is low yielding and results in difficult purification.[6a, 7] Those problems can be overcome by the use of Wittig chemistry.[8]

With the ready availability of either the β-pyrrolic porphyrin aldehydes or methylphosphonium salts, we and others have used Wittig chemistry to produce a variety of vinyl linked functionalised porphyrins and porphyrin arrays.[8, 9] The reactions are moderate to high yielding and tolerant of a variety of functionalities and metals. Nonetheless, challenges with this type of synthesis remain including the production of E, Z isomeric mixtures, the problematic isolation of the desired products from unwanted side products such as methylporphyrins, and the sometimes difficult formation of unsymmetrical or multimetalated porphyrin arrays.[8] New synthetic methodology is needed to address these challenges, particularly in the latter case. To this end, Knoevenagel chemistry appears as an interesting alternative. Analogous to the Wittig chemistry, β-formylporphyrins could provide the building blocks for the formation of both conjugated single porphyrins by initial reaction with phenylacetonitriles as well as porphyrin dyads through subsequent reactions with the initially formed porphyrinacyanotrienes (Route b, Scheme 1). Conversely, a single condensation of the appropriate phenylacetonitrile could provide a symmetrical dyad (Route a, Scheme 1). Larger arrays could also be fabricated using the appropriately substituted phenylacetonitriles.

Therefore, in this study we demonstrate the simple synthesis of a series of modified porphyrins by Knoevenagel condensation between β-pyrrolic formylporphyrins and a series of phenylacetonitriles. Symmetrical and unsymmetrical porphyrin dyads have also been synthesised. Electrochemistry and Raman spectroscopy show the effects of the electron withdrawing phenylacetonitrile. We also demonstrate that this facile synthesis can provide a porphyrin modified with a carboxylic acid that can be successfully used as a light harvesting dye in a DSSC.
Results and Discussion

Synthesis of Vinyl β-Substituted Porphyrins

Porphyrin β-pyrrolic aldehydes 1 and 2 react with phenylacetonitriles 3 and 4 at room temperature using 1,8-diazabiclo[3.3.2]octane (DBU) as a base to form porphyrin derivatives 9, 12 and 13 in 84%, 93% and 80% yield, respectively (Scheme 2). The electron rich phenylacetonitriles 5 and 6 failed to react under these conditions. Heating of porphyrin aldehydes 1 and 2 with 5 and DBU by microwave irradiation provided 7 and 10 in 37% yield. The presence of the strong electron donating methoxy group in 6 suppressed the reaction such that a stronger base, potassium tert-butoxide (KOTBu), had to be used. Under those conditions (stronger base and microwave irradiation), products 8 and 11 were then obtained in 59% and 57% yield, respectively. Zinc insertion into the vinyl porphyrins was performed according to standard techniques and gave Zn7-Zn13 in quantitative yields.\(^\text{[10]}\)

The reactivity of the phenylacetonitriles is strongly influenced by the substitution pattern of the benzene ring. While electron deficient phenylacetonitriles, which facilitate carbonanion formation, react under mild conditions, electron-donating substituents tend to suppress the process requiring harsher conditions such as higher temperature or and use of stronger base. However, the microwave conditions also produced uncharacterised baseline material, which resulted in generally lower yields. The substituents on the porphyrin aldehydes had little impact on the outcome of the reactions.

\(^{1}H\) NMR spectroscopy provides evidence for a change in electronics of the modified porphyrins. The \(^{1}H\) NMR spectra of the CN styryl porphyrins 7-13 all show similar chemical shifts characteristic of these types of molecules, with the key difference being the influence of the cyano group both electronically and through space on its neighbouring protons.\(^\text{[10]}\) Thus, compared to the previously reported styryl-substituted porphyrins, the introduction of the cyano group results in a downfield shift of the β-pyrylic proton H\(_2\). For example, comparison of methoxy derivative 8 and the non-cyano substituted derivative shows a shift of β-pyrylic proton H\(_2\) from 9.05 ppm to 9.48 ppm.\(^\text{[11]}\) Clearly, the neighbouring cyano group deshields this proton with the remaining β-pyrylic protons uninfluenced. The \(^{1}H\) NMR spectrum of 8 also contains a singe pyrrolic NH peak and a simplified aromatic region.

During condensation with non-symmetrical CH acids, two possible isomers E and Z can be formed. However, in the case of these CN styryl compounds, only one isomer is formed in contrast
to previously studied Wittig reactions.[11] The NOESY NMR technique was necessary to determine the configuration of the synthesised isomer. The NOESY spectrum showed coupling between $H_{\text{vinyl}}$ and $H_{\text{cis}}$, which is indicative of the $Z$ isomer. The $E$ isomer does not have this spatial orientation, as $H_{\text{vinyl}}$ is not in the proximity of $H_{\text{cis}}$ (Figure 1).

**Synthesis of Porphyrin Dyads**

As indicated in Scheme 1, porphyrin dyads can be made either using a single step (Route A) or two steps (Route B). The attempt to synthesize a symmetrical porphyrin dyad by reacting 2 equivalents of 2-formylporphyrin 14 with 1 equivalent of 1,4-phenylenediacetonitrile 15 with DBU in chloroform gave dyad 16 in a very low yield (12%) (Scheme 3). This synthesis was repeated using various conditions, however a difficult to separate mixture of unreacted aldehyde 14, a mono-adduct and dyad 16 was obtained in all cases. Yields were not improved by microwave irradiation or by increasing the equivalents of porphyrin aldehyde 14 to 1,4-phenylenediacetonitrile 15 (4:1 and 10:1).

![Scheme 3](image)


Consequently, a two-step approach that could also provide a synthetic route to non-symmetrical porphyrin dyads containing different porphyrins or different metal centres was investigated.[19] Mono adducts of a series of porphyrins were initially prepared in the first step by reaction of formylporphyrins 1, 2, 17 with 1,4-phenylenediacetonitrile 15 (Scheme 4). Microwave irradiation was required to maximise the reaction products. Best results were observed by reacting the 2-formylporphyrin with 10 equivalents of 1,4-phenylenediacetonitrile 15 and a large excess DBU in 1,2-dichloroethane. The reactions were heated at 100 °C at 250 W for 30 min in a microwave reactor. Porphyrins 18-20 were obtained in moderate to good yields after purification. Conventional reflux, or the use of a stronger base such as KOtBu, did not drive the reaction to completion, with formylporphyrin starting material consistently observed.

The successful syntheses of cyano compounds 18-20 provided precursors for the preparation of a series of asymmetric and variably metallated porphyrin dyads. The 4-ethylphenylstyrilporphyrin derivative 20 was reacted with 2.5 equivalent of tetraxylylporphyrin aldehyde 2 using microwave irradiation (250 W, 120 deg, 30 min) with complete consumption of 20 and a resulting isolated yield of the asymmetric dyad 21 of 80% (Scheme 4). The excess of aldehyde was necessary to drive the reaction to completion. Attempts to reduce the amount of aldehyde and simultaneously increasing the reaction time were unsuccessful due to apparent increased decomposition. The full conversion of the starting material 20 was essential, as the post-reaction purification of the mixture of 20 and dyad 21 proved to be problematic.

![Scheme 4](image)

Scheme 4. Synthesis of porphyrin dyads. Reaction conditions: (i) DBU, 1,2-dichloroethane, microwave. (ii) NaOMe, 1,2-dichloroethane, microwave. (iii) FeCl$_3$, acetonitrile, reflux, followed by exposure to O$_2$. (iv) Zn(OAc)$_2$, CH$_2$Cl$_2$, MeOH, RT.

The structure of dyad 21 was readily confirmed using NMR spectroscopy and mass spectrometry. Two sets of NH proton signals are evident in the 1H NMR spectrum along with two distinct singlets due to the β-pyrrolic protons adjacent to the vinyl substituents on each porphyrin.

During synthesis of dyad 22 from styrylporphyrin 20 and aldehyde Zn2, two products were obtained. Upon purification, an inseparable mixture of the free base-zinc (Ⅰ) and free base-free base dyad was obtained. Control experiments under the same microwave conditions used in the Knoevenagel synthesis with zinc 5,10,15,20-tetraphenylporphyrin (ZnTPP) in DCE, DCE and...
DBU, and DCE and H₂O showed that the zinc was only retained in the porphyrin core when using DCE. Therefore, it appears that water in a reaction mixture is able to remove zinc under these conditions; given the hydroscopic nature of DBU, it is not surprising that zinc was removed from dyad 22. Replacement of DBU with sodium methoxide consequently allowed the synthesis of 22 without demetallation, with the dyad being formed in 70% yield after 60 min (Scheme 4).

The spectral characteristics of dyad 22 were very similar to that of the free base dyad 21 albeit with the absence of one pyrrolic proton signal due to the insertion of zinc and one vinyl singlet apparent at 7.80 ppm.

Synthesis of the free base-Fe (III) porphyrin dyad 23 was achieved by reaction of Fe18 and formyl porphyrin 2 with DBU as base under microwave conditions with a shortened reaction time in a moderate yield (45%). Zinc insertion was achieved according to standard conditions to produce Zn21 and Zn23.[10]

The UV-visible and mass spectral data were consistent with the formation of the dyads.

**Electrochemical Analysis**

Electrochemical analysis of the single cyano styrylporphyrins Zn7 - Zn9 showed (Table 1 and Figure 2), as expected, the presence of four reversible processes: two oxidations and two reductions.[12]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn7</td>
<td>0.33</td>
<td>-1.65</td>
</tr>
<tr>
<td>Zn8</td>
<td>0.31</td>
<td>-1.68</td>
</tr>
<tr>
<td>Zn9</td>
<td>0.33</td>
<td>-1.58</td>
</tr>
<tr>
<td>Zn24</td>
<td>0.29</td>
<td>-1.79</td>
</tr>
</tbody>
</table>

Comparison of one of these cyano substituted porphyrins Zn7 to the analogous cyano-free styrylporphyrin Zn24 (Table 1 and Figure 2a) shows that there is little difference in oxidation potentials, with the major effect of the nitrite group being on the reduction potentials; the introduction of the electron withdrawing group shifts electron density from the porphyrin core, resulting in positive shifts of the reduction potentials by 140-150 mV.[11]

The reduction potentials of the cyanostyrylporphyrins are also affected by the substituents on the benzene ring (Table 1). With reference to Zn7 (Ph derivative), the electron withdrawing ester group on Zn9 shifts both reduction potentials more positively by 70-80 mV. The introduction of the electron donating methoxy group on Zn8 has less of an effect, and shifts the reduction potentials by 30 mV toward negative values (Figure 2b).

Therefore, the introduction of the electron withdrawing cyano group has a significant effect on the reduction potentials of the porphyrin ring, with the aromatic group substituents less influential on the porphyrin electronics.

**UV-visible Spectroscopy**

The ultraviolet-visible (UV-vis) spectra of the cyano styryl-appended porphyrins and dyads are similar to those previously reported for this type of phenylene-linked porphyrin. As reported by Burrell et al. for the analogous symmetrical free base phenylene-linked dyads,[13] the dyad spectra observed are linear combinations of their constituent porphyrin monomers albeit with a strong shoulder present on the low-energy side of the Soret band at ~ 490 nm that leads to a broadening of the Soret band, as can be seen in Figure S1 for Zn free base dyad 22. This shoulder and the related band broadening has been attributed to the beginning of a split Soret band as a result of limited electronic coupling between the two porphyrins of the dyad; dyads with strong coupling such as those with acetylene or butadiyne bridges have two Soret bands due to splitting.[14]

In contrast, the Q bands are largely unaffected. Analogous to the single tetraarylporphyrins (TAPs) and zinc TAP starting materials, the free base dyads show four Q bands and the metallated compounds only two as a result of the porphyrin D2h (TAPs) and D4h (zinc TAP) symmetries.[15]

**Raman Spectroscopy and DFT Calculations**

Of interest here is the role and degree to which the CN group affects the styryl substituent and the CN and OCH₃ aryl functionalization electronically tune the β-aryl substituent and the porphyrin core. Species Zn10, Zn11 and Zn13 offer such comparisons and allow for some comparison with the literature in order to determine the effect of CN substitution on the styryl functionality.[11] All compounds exhibit similar spectra with strong Raman bands between 1500 and 1580 cm⁻¹ (Figures S2 and 3).

A number of small spectral variances are observed between compounds, most of which occur in this high energy region. The
strong coupling of typical porphyrin vibrations (ν(Cb–Cb), ν(Pyr. half-ring) and ν(Pyr. breathing)) to β-substituent vibrations indicate an intimately connected electronic system is present. Bands at 1579, 1566, 1524 and 1500 cm\(^{-1}\) for Zn13 (Figure 3), for example, show vibrational contribution from the β-substituent and yield the largest shifts and changes in intensity. This indicates a successful electronic tuning of the auxiliary β-substituent dependent on the electron withdrawing nature of the functional group (CN>H>OMe). The band at 1383 cm\(^{-1}\), known as the \(\nu_4\) band, which is often used as a spectroscopic marker for the metalloporphyrin core size, shows little change between compounds, but is blue-shifted when compared to unsubstituted ZnTPP (1356 cm\(^{-1}\)).\(^{[16]}\) The steric torsion induced by β-substitution is known to cause deformation of the porphyrin structure (ruffled, saddled, domed or waved) and can be monitored through shifts of the \(\nu_4\) band.\(^{[16]}\) Such spectral variations indicate both electronic and geometric tuning by the β-substituted unit. Analogous spectra for Zn10 and Zn11 can be found in Figure S2.

Deformation of these bonds is supportive for variation of the ν (Pyr. half-ring) based \(\nu_4\) band observed in experimental FT-Raman data. These variations are predicted to be no more than 2.5 pm, which represents small disparities.

Distortion of the porphyrin core is well documented to cause a breakdown of the Gouterman four orbital model, consequential for the physical and optical properties.\(^{[18]}\) Figure S5 details frontier molecular orbitals for the compounds of interest and ZnTPP with the energetics of these orbitals summarised in Figure 4. Typical \(a_{1u}, a_{2u}\) and \(e_g\) (HOMO-1, HOMO, LUMO and LUMO+1) orbitals are observed for ZnTPP. For Zn10, Zn11 and Zn13 orbitals HOMO-1, HOMO and LUMO+1 remain mostly unperturbed while HOMO-2, LUMO and LUMO+2 exhibit electron density on the β-substituent, especially so for HOMO-2. With β-substitution, a splitting of the \(e_g\) set occurs, narrowing the band gap, while \(a_{1u}\) and \(a_{2u}\) become more energetically disparate.

To investigate structural deformation, density functional theory (DFT) analysis was carried. FT-Raman data was used as a verification method for DFT ground state geometries by comparing experimental and calculated Raman spectra to generate a mean absolute deviation (MAD).\(^{[17]}\) MADs for the three compounds investigated are sufficiently small (<6 cm\(^{-1}\)) which indicates an effective model of the structure has been achieved. Tabulated Raman peaks can be found in Table S1 with DFT assisted assignments.

Optimised ground state geometries for Zn10, Zn11 and Zn13 exhibit saddling distortions with pyrrole-pyrrole angles of ~13° and are shown in Figure S3. A slight increase in saddling is noted for the phenyl derivative Zn10. Such distortion results in a predicted mean N-Zn bond-length of 2.072 Å for all compounds, compared to a ZnTPP mean of 2.066 Å. These results are consistent with a blue-shifted \(\nu_4\) band.

Bond length variation (Figure S4) from ZnTPP is observed mostly within the β-substituent pyrrole ring; with elongations of bond 2 and 3 and a shortening of bond 4 (atoms 2-3, 3-4 and 4-5 respectively). Similar patterns are observed for all three compounds, indicating a likeness of the bonding network.

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Deformation of these bonds is supportive for variation of the ν (Pyr. half-ring) based \(\nu_4\) band observed in experimental FT-Raman data. These variations are predicted to be no more than 2.5 pm, which represents small disparities.
Resonance Raman provides a method of identifying active chromophoric regions within molecules as a result of region specific vibrational enhancement that occurs coincident with ground → excited state distortions. Spectra were collected across the Soret band region (emission precludes measurement in the Q band region) to investigate the origins of optical transitions for dyes Zn13 (Figure 5), Zn10 and Zn11 (Figure S6). Strong porphyrin bands are present as expected, while the presence of bands at 1079, 1182 and 1240 also demonstrate the involvement of the β substituent at excitations of 406 and 413 nm. This pattern of enhancement is considerably changed from electronically separated porphyrins with β-substituents as seen by Earles et al. and indicates an effective communication between these units similar to that observed by Walsh et al.

For Zn13, and Zn11 there are slight differences in the 1500-1620 cm\(^{-1}\) pattern of band enhancement as the excitation wavelength is tuned to the B band; especially present at excitations of 406 and 413 nm. This result is consistent with TD-DFT calculations, which predict two transitions that involve different MOs but are generally similar in nature. Modes 1507 and 1589 cm\(^{-1}\) evolve beside the ground state bands 1500 and 1579 cm\(^{-1}\) indicating these bands are not equivalent. The origin of these bands is thought to be strongly β-substituent coupled vibrations that are minimally polarisable, however are resonantly enhanced due to β-substituent contribution to the B band. Phenyl derivative Zn10, which has no para substituent, shows only one pattern of band enhancement is present, indicative of a homogeneous transition in the Soret region.

Interestingly, in all resonance Raman data, the nitride band (2215 cm\(^{-1}\)) is weak, when compared to a direct porphyrin β-bound nitride group studied by van der Salm et al. Hence, the contribution from the styryl nitride group to the absorption properties is less. Vibrations associated with the appended phenyl group and ethene linker indicate that the β-substituent is electronically connected to the transitions, consistent with the TD-DFT analysis (Table S2).

In comparison to analogs lacking cyano-substitution at the styryl region, core size marker band v4 (1360 cm\(^{-1}\)) is red-shifted in these species (1380 cm\(^{-1}\)), while v2 remains unchanged at 1550 cm\(^{-1}\). This indicates that despite a non-participation of the styryl CN unit for absorption; some structural effect is present from this region, likely in the form of electronic withdrawal. In support of this proposition, Zn13, Zn10 and Zn11 appear to lack the typical ~1620 cm\(^{-1}\) band associated with the C=C vibrational mode. DFT calculations indicate this band shifts to lower wavenumber and likely is obscured by band structure at 1590 cm\(^{-1}\). The effect of CN substituents on \(\nu(C=\text{C}_{\text{styryl}})\) modes has been investigated in terthiophene systems and reflect a vibrational redshift of this band, similar to results presented here.

Dye Sensitised Solar Cell Performance

For the study of the influence of the cyano group on the light harvesting characteristics of the porphyrin, a new cyano-substituted styril-appended porphyrin carboxylic acid Zn25 was prepared from the ester Zn12 and compared in the dye sensitised solar cell (DSSC) to the analogous cyano-free porphyrin acid Zn26 (Figure 6) whose light harvesting characteristics have been well studied. DSSCs were fabricated in a standard glass configuration with a 12 μm TiO\(_2\) layer, platinized counter electrode and iodine electrolyte as described in the experimental section.

The sensitisation of TiO\(_2\) was performed in tetrahydrofuran (THF) solution and the UV/Vis spectra of Zn25 and Zn26 in THF and adsorbed on TiO\(_2\) are shown in Figure 7. In the solution spectrum of Zn25, the Soret band at 428 nm has a significant shoulder 446 nm (Figure 7a), which indicates formation of aggregates. Both the TiO\(_2\) spectra (Figure 7b) show a significant broadening of the Soret band, again indicative of both H and J aggregates on the semiconductor surface with the cyanoporphyrin Zn25 showing a slightly more broadened Soret band.

<table>
<thead>
<tr>
<th>Dye</th>
<th>(V_{oc}) [mV]</th>
<th>(J_{sc}) [mA/cm(^2)]</th>
<th>FF</th>
<th>(\eta) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn25</td>
<td>630</td>
<td>7.05</td>
<td>0.70</td>
<td>3.11</td>
</tr>
<tr>
<td>Zn26</td>
<td>606</td>
<td>7.12</td>
<td>0.71</td>
<td>3.07</td>
</tr>
</tbody>
</table>

*The data is obtained from an average of 3 devices.

A summary of the photovoltaic results obtained from the DSSCs with Zn25 and Zn26 on 12 μm TiO\(_2\) films is presented in Table 2. The photovoltage observed for the DSSC sensitised with Zn25 is higher than that of Zn26 although the observed photocurrent for the Zn25 device is slightly lower. With equivalent FFs, the final photovoltaic efficiencies are almost identical (3.1 %).
Figure 8 shows the incident photon-to-current conversion efficiencies (IPCEs) of both porphyrin-sensitized solar cells. While Zn26 has a larger IPCE across the entire absorption spectrum, Zn25 has a broader light harvesting range, although this is not sufficient to provide the same amount of current, corresponding to an observed higher \( J_{oc} \) for Zn26. In addition, as shown in Table 1 for other cyanostyrylporphyrins, the first reduction potential of a cyanostyrylporphyrin is significantly more positive than the analogous non-cyano styrylporphyrin (140 mV for Zn7 vs Zn24).

Thus, the LUMO of cyanostyrylporphyrin Zn25 would be expected to be lower than that of the non-cyano porphyrin Zn26, resulting in a smaller driving force and potentially less current.

Devices containing Zn25 and Zn26 were further investigated by electrochemical impedance spectroscopy performed at \( V_{oc} \) conditions and 1 sun light exposure. Nyquist and Bode plots are shown in Figure S7.

To gain a better insight into electron recombination (\( V_{oc} \)) in the investigated cells, the electron lifetimes were estimated from the Bode plots. The calculated values of electron lifetimes for Zn25 and Zn26 were 3.2 and 2.5 ms, respectively (see SI). The longer electron lifetime for Zn25 corresponds to the higher \( V_{oc} \) observed for these devices.

While the UV-vis spectra of Zn25 and Zn26 on TiO\(_2\) (Figure 7b) suggested that a comparable amount of dye was absorbed, a dye uptake measurement from the TiO\(_2\) sensitized photoanodes was carried out. However, as shown in Figure S8, aggregation of the resulting tetrabutylammonium salt of Zn25 prevented accurate quantification of the dye uptake. Nonetheless, as has been shown, the photocurrent of the two dyes is similar supporting the presence of the same amount of dye on the TiO\(_2\) surface.

**Conclusions**

Knoevenagel chemistry has been utilised to provide a series of functionalised porphyrins and porphyrin dyads with moderate to excellent yields. We have established by NMR analysis that the products were present as only the \( Z \) isomer. Porphyrin dyads were also prepared by Knoevenagel chemistry, with porphyrin geometry and metalation state being controlled in the step-by-step synthesis.

Electrochemical analysis shows the incorporation of the electron withdrawing cyano group into the porphyrin side chains is able to shift electron density off the porphyrin core in relation to their Wittig-linked counterparts. Electrochemical analysis also indicated that the aromatic substituent on the side chain benzene ring is able to affect reduction of the porphyrin, although the cyano group remains the dominant influence.

Raman data, in concert with DFT and TD-DFT calculations, shows little difference in structure between Zn10, Zn11 and Zn13. Spectroscopy indicates that the Soret band electronic transitions resemble normal porphyrin transitions, simply with some delocalisation of frontier molecular orbital electron density onto the \( \beta \) substituent.

The effect on light harvesting and electron injection by the cyano substitution was also examined by fabricating DSSCs. The introduction of the side chain cyano group into a light harvesting porphyrin dye Zn25 shows slightly higher photovoltage but lower photocurrent when compared to the cyano-free analog Zn26. The IPCE spectrum demonstrated broader light harvesting by Zn25 (red shift about 25 nm) but less current measured. This is rationalised on the basis of lower driving force as a result of the electron withdrawing character of the cyano group depleting the electron density of the \( \pi \) conjugated system of the porphyrin and lowering the HOMO.

Impedance spectroscopy supported the higher \( V_{oc} \) for Zn25 sensitized devices through longer electron lifetimes. The higher resistance of the dye/TiO\(_2\)/electrolyte interface for Zn25 is likely a consequence of less efficient electron injection. Nonetheless, the effect of the cyano functionality on the dye performance was minimal, demonstrating the value of this simpler and more efficient Knoevenagel method for the production of these types of conjugated dyes.

**Experimental Section**
Materials: All reagents, solvents and compounds 3, 4, 5, 6 and 15 were obtained from commercial sources and used without further purification. Aldehydes 1, 2 and 14 were synthesized via Vilsmeier formylation as described previously.[34] The synthesis of Zn25 and Zn26 were performed according to literature procedures.[11, 24] Flash chromatography used silica, 40-60μm with the indicated solvents.

Spectroscopy: Electronic absorption spectra were obtained using a Shimadzu UV-1800 spectrophotometer.

Proton (H) nuclear magnetic resonance (NMR) spectra were obtained at 400 MHz using a Bruker Ultrashield 400 plus spectrometer. 1H NMR data is expressed in ppm, with all peaks shifted in reference to tetramethylsilane as the internal standard.

Electrochemistry: Electrochemical experiments were performed in a three-electrode cell with a glassy carbon working electrode, a platinum mesh as the counter electrode, and Ag/AgCl (leakless) as the reference electrode. All potentials are reported against the apparent formal potential of the ferrocene/ferrocenium couple. The cyclic voltammograms (CVs) of compounds were obtained at 1 mM in degassed CH2Cl2 with 100 mM tetraethylammonium perchlorate present. Cyclic voltammetry (CV) measurements were performed using a CH Instruments 760 electrochemical analyzer (CH instrument, CHI650D). All electrochemical experiments were performed at room temperature (23 ± 2 °C) in air.

Raman Spectroscopy: FT-Raman spectra were recorded on solid-state KBr disks using a Bruker MultiRAM instrument with 1064 nm excitation wavelength and a liquid nitrogen cooled D418T Germanium detector controlled by OPUS v7.2 software. Spectral resolution was 4 cm−1, power used was 15 mW and typically 256 scans were co-added. Resonance Raman spectra were recorded with the excitation beam focussed onto the sample with an oblique-angle backscattering geometry. The scattered photons were collected with a plano-convex lens and focussed onto the entrance slit of an Acton Research SpectraPro500i spectrometer with an aperture-matched lens. Laser radiation was rejected before the slit using long-pass filters (Semrock Inc.). The beam was horizontally dispersed with a 1200 grooves mm−1 grating onto a liquid-nitrogen cooled Spec10:100B CCD, which was controlled using WinSpec/32 software (Roper Scientific) and calibrated with a 1.1 v/v toluene/acetonitrile mixture. Wavelengths 350.7, 406.7 and 413.1 nm were provided by an Innova I-302 krypton ion laser (Coherent Inc.), 448 nm was provided by a diode laser (CrystaLaser), and 457.9 and 488.0 nm were provided by an Innova Sabre argon ion laser (Coherent Inc.).

Calculations: Gaussian09 was used to optimise structures with the same parameters. The mean absolute deviation (MAD) between experimental and simulated non-relativistic electronic spectra was used to validate the calculations.

DSSC Fabrication: Two investigated porphyrins were tested in a standard, glass configuration dye-sensitized solar cells with iodine/iodide electrolyte. TiO2 photoanodes were prepared on fluorine-doped tin oxide (FTO) substrates (Hartford Glass, R∞ ≤ 7 Ω sq−1) using a screen printing technique with commercially available paste. A blocking layer and TiO2 layer were employed. The thickness of the TiO2 layer was 12 μm (one layer screen printed 43T mesh transparent Dysosol paste (DSL 18NR-T) and one layer coating Dysol paste WER2-0).

The active areas of films were 0.16 cm2 (4 x 4 mm). Films were sintered stepwise using a programmable hotplate with a maximum temperature of 500°C. TiO2 films at 110°C were immersed into 0.2 mM solution of Zn25 or Zn26 in tetrahydrofuran (THF) for 2 h. Sandwich-type DSSCs were assembled using a 25 μm Hymlan sealant and thermally platini zed counter electrode on FTO (Hartford Glass, R∞ ≤ 7 Ω sq−1). The electrolyte solution, composed of 0.6 M DMPII, 0.5 M 4-tert-butylypyridine, 0.1 M LiI and 0.05 M I2 in a solvent mixture of 85:15 acetonitrile/water, was injected into the inter-electrode spacing through a hole in the counter electrode, which was subsequently sealed.

Functionalised Porphyrin Monomers

7 In a 10-mL microwave reaction vial, a solution of 2-formyl-5,10,15,20-tetraphenylporphyrin 1 (30 mg, 47 μmol), phenylacetoacetone 5 (30 mg, 0.27 mmol), DBU (0.7 mL) in 1,2-dichloroethane (1.0 mL). The reaction was heated at 110 °C, power 250 W for 50 min under microwave irradiation. The cooled solution was then purified by flash chromatography (silica, CH3Cl2) and crystallisation from CH2Cl2/MeOH, to give the desired product 7 (13 mg, 37%) as a purple-brown solid. 1H-NMR (400 MHz, CDCl3): δ 9.49 (s, 1H, Hβpyrrole), 8.94 (d, 1H, J= 5.0 Hz, H3pyrrole), 8.87 (d, 1H, J= 5.0 Hz, H3pyrrole), 8.32-8.27 (m, 2H, Hαpyrrole), 8.24-8.17 (m, 6H, Hαpyrrole), 7.84-7.66 (m, 12H, Hαpyrrole), 7.61 (d, 1H, J= 1.2 Hz, Hαpyrrole), 7.40-7.35 (m, 5H, Hαpyrrole), -2.59 (br s, 2H, NH).

8 A solution of 2-formyl-5,10,15,20-tetraphenylporphyrin 1 (60 mg, 93 μmol), 4-methoxyphenylacetonitrile 6 (82 mg, 0.56 mmol), KOtBu (100 mg) in DMF (2.1 mL) was heated to 100 °C, 250 W for 20 min in a microwave reactor. The cooled reaction was then purified by flash chromatography (silica, CH3Cl2) and crystallisation from CH2Cl2/MeOH, to give the desired product 8 (41 mg, 57%) as a purple-brown solid. 1H-NMR (400 MHz, CDCl3): δ 9.45 (s, 1H, Hβpyrrole), 9.83 (d, 1H, J=5.0 Hz, 7Hpyrrole), 8.86 (d, 1H, J=5.0 Hz, H3pyrrole), 8.82-8.76 (m, 3H, H2pyrrole), 8.71 (d, 1H, J=5.0 Hz, Hαpyrrole), 8.31-8.28 (m, 2H, Hαpyrrole), 8.23-8.15 (m, 6H, Hαpyrrole), 7.82-7.67 (m, 12H, Hαpyrrole), 7.45 (s, 1H, Hαpyrrole), 7.29 (d, 2H, J=9.0, Hαpyrrole), 6.90 (d, 2H, J=9.0, Hαpyrrole), 3.88 (s, 3H, H3methoxy), -2.59 (br s, 2H, NH). UV-vis(CH3Cl2)max(log ε) 428 (5.26), 523 (4.22), 758 (3.57) nm. HRMS, m/z: calcd for MH+(C33H32N2O): 742.2971, found: 742.3005.

9 A solution of 2-formyl-5,10,15,20-tetraphenylporphyrin 1 (30 mg, 47 μmol) and methyl 4-(cyanoethyl)benzolate 4 (49 mg, 0.28 mmol) in CH2Cl2 (8 mL) was stirred at room temperature under argon. Excess DBU (0.5 mL) was added and stirred for 30 min. The reaction mixture was directly purified by flash chromatography (silica, CH3Cl2) and concentrated in vacuo. Crystalisation in CH2Cl2/MeOH gave the desired product 9 (33 mg, 84%) as a purple solid. 1H-NMR (400 MHz, CDCl3): δ 9.51 (s, 1H, Hβpyrrole), 8.95 (d, 1H, J=5.0 Hz, H3pyrrole), 8.88 (d, 1H, J=5.0 Hz, Hβpyrrole), 8.82 (d, 1H, J=5.0 Hz, H3pyrrole), 8.78 (d, 1H, J=5.0 Hz, Hβpyrrole), 8.71 (d, 1H, J=5.0 Hz, H3pyrrole), 8.62 (d, 1H, J=5.0 Hz, Hβpyrrole), 8.23-8.15 (m, 6H, Hαpyrrole), 7.82-7.67 (m, 12H, Hαpyrrole), 7.45 (s, 1H, Hαpyrrole), 7.29 (d, 2H, J=9.0, Hαpyrrole), 6.90 (d, 2H, J=9.0, Hαpyrrole), 3.88 (s, 3H, H3methoxy), -2.59 (br s, 2H, NH). UV-vis(CH3Cl2)max(log ε) 429 (4.97), 524 (3.96), 566 (3.60), 601 (3.50), 658 (3.26) nm. HRMS, m/z: calcd for MH+(C35H34N2O): 772.3076, found: 772.3094.

FULL PAPER
A solution of 2-formyl-5,10,15,20-tetrakis(3,5-dimethylphenyl)porphyrin 2 (76 mg, 0.100 mmol) and methyl 4-(cycano methylen)benzoate 3 (46 mg, 0.300 mmol) in CH₂Cl₂ (15 mL) was stirred at room temperature under argon. Excess DBU (1.6 mL) was added and stirred for 60 min. The reaction mixture was directly purified by flash chromatography (silica, CH₂Cl₂) and concentrated in vacuo. Crystallisation in CH₂Cl₂/MeOH gave the desired product 13 (70 mg, 80%) as a purple solid. 1H-NMR (400 MHz, CDCl₃): δ 9.55 (d, 1H, Δ= 1.0 Hz, H₈-pyrrole), 9.01 (d, 1H, Δ= 4.7 Hz, H₈-pyrrole), 8.86 (d, 1H, Δ= 4.7 Hz, H₈-pyrrole), 8.80 (d, 1H, Δ= 4.7 Hz, H₈-pyrrole), 8.78 (d, 1H, Δ= 4.7 Hz, H₈-pyrrole), 8.10-8.05 (m, 2H, H₉₂₀), 7.95-7.92 (m, 2H, H₈ₓₓ), 7.85-7.80 (m, 6H, H₈ₓₓ), 7.74 (d, 1H, Δ= 1.0 Hz, H₇ₓₓ), 7.53-7.48 (m, 2H, H₈₂₀), 7.45-7.39 (m, 3H, H₈ₓₓ), 7.28-7.27 (m, 1H, H₈ₓₓ), 2.65 (s, 6H, H₈ₓₓ), 2.61 (s, 6H, H₈ₓₓ), 2.60 (s, 6H, H₈ₓₓ), 2.47 (s, 6H, H₈ₓₓ), 2.59 (br s, 2H, NH). UV-vis (CH₂Cl₂) λₓₓₜₜ (log ε) 432 (5.47), 527 (4.54), 570 (4.15), 603 (4.11), 664 (3.99) nm. HRMS, m/z: calcd for M⁺ (C₃₀H₂₆N₄O₂): 878.4097, found: 878.4057.

**General Zinc Insertion Procedure**

Porphin monomers were converted to zinc (II) porphyrins according to the following general procedure. Cyano-linked porphyrin was dissolved in CH₂Cl₂ and stirred at room temperature. 1.3 equivalents of Zn(OAc)₂·2H₂O in minimal amount of methanol were added and continued to stir for 30 min. MALDI indicated the reaction was complete and flash chromatography (silica, CH₂Cl₂) and concentration in vacuo gave the desired products.

**Zn7**

Porphyrin 7 (12 mg, 17 μmol) was reacted with Zn(OAc)₂·2H₂O. Zn7 was collected as a purple solid (10 mg, 71%). 1H-NMR (400 MHz, CDCl₃): δ 9.59 (s, 1H, H₈-pyrrole), 8.89 (d, 1H, Δ= 5.0 Hz, H₈-pyrrole), 8.84 (d, 1H, Δ= 5.0 Hz, H₈-pyrrole), 8.82-8.78 (m, 3H, H₈₂₀), 7.93 (s, 2H, H₈ₓₓ), 7.95 (s, 2H, H₈ₓₓ), 7.82 (s, 2H, H₈ₓₓ), 7.80 (s, 2H, H₈ₓₓ), 7.48 (s, 1H, H₆ₓₓ), 7.44-7.59 (m, 3H, H₈₂₀), 7.36 (d, 2H, Δ= 9.5 Hz, H₆ₓₓ), 7.27 (s, 6H, H₈ₓₓ), 2.66 (s, 6H, H₈ₓₓ), 2.64 (s, 6H, H₈ₓₓ), 2.61 (br s, 2H, NH), UV-vis (CH₂Cl₂) λₓₓₜₜ (log ε) 432 (5.54), 525 (4.45), 567 (4.19), 603 (4.14), 664 (4.15) nm. HRMS, m/z: calcd for M⁺ (C₂₉H₂₅N₄O₂Zn): 804.2106, found: 804.5668.

**Zn8**

Porphyrin 8 (32 mg, 41 μmol) was reacted with Zn(OAc)₂·2H₂O. Zn8 was collected as a purple solid (28 mg, 82%). 1H-NMR (400 MHz, CDCl₃): δ 9.50 (s, 1H, H₈-pyrrole), 8.89 (d, 1H, Δ= 5.0 Hz, H₈-pyrrole), 8.79-8.73 (m, 3H, H₈₂₀), 8.68-8.65 (m, 3H, H₈₂₀), 2.61 (br s, 2H, NH), 2.72 (s, 6H, H₈ₓₓ), 2.23 (m, 2H, H₈ₓₓ), 2.22 (s, 6H, H₈ₓₓ). UV-vis (CH₂Cl₂) λₓₓₜₜ (log ε) 432 (5.59), 558 (4.56), 598 (4.28) nm. HRMS, m/z: calcd for M⁺ (C₂₉H₂₅N₄O₂Zn): 946.3463, found: 946.3771.

**Zn9**
Zn10

Porphyrin 10 (42 mg, 49 µmol) was reacted with Zn(OAc)$_2$·2H$_2$O.

Zn11

Porphyrin 11 (42 mg, 48 µmol) was reacted with Zn(OAc)$_2$·2H$_2$O.

Zn12

Porphyrin 12 (40 mg, 44 µmol) was reacted with Zn(OAc)$_2$·2H$_2$O.

Zn13

Porphyrin 13 (40 mg, 44 µmol) was reacted with Zn(OAc)$_2$·2H$_2$O.

Zn14

Porphyrin 14 (50 mg, 44 µmol) was reacted with Zn(OAc)$_2$·2H$_2$O.

Zn15

Porphyrin 15 (40 mg, 44 µmol) was reacted with Zn(OAc)$_2$·2H$_2$O.

Zn25

KOH (46 mg, 0.71 mmol) in MeOH (12 mL)/H$_2$O (1.2 mL) was added to a solution of Zn25 (40 mg, 0.041 mmol) in THF (12 mL). The mixture was heated to reflux for 22 h. Once cooled to room temperature, H$_2$O (25 mL) and CH$_2$Cl$_2$ (25 mL) were added followed by 2M H$_2$PO$_4$ (430 µL, 0.86 mmol). The organic layer was extracted and washed with H$_2$O (2 x 40 mL). Reaction was concentrated in vacuo to give the desired product Zn25 (39 mg, 100%) as a purple solid: $^{1}H$-NMR (400 MHz, acetone-$d_{6}$): $\delta$ 9.64 (s, 1H, H$_{pyrrolic}$), 8.97 (d, 1H, $\beta$-aryl), 8.87-8.91 (m, 3H, H$_{pyrrolic}$), 8.79 (d, 1H, $\beta$-aromatic), 7.96 (s, 1H, H$_{aromatic}$), 7.86-7.87 (m, 6H, H$_{pyrrolic}$), 7.62 (d, 2H, $\beta$= 8.0 Hz, H$_{aromatic}$), 7.49-7.44 (m, 3H, H$_{pyrrolic}$), 7.37 (s, 1H, H$_{aromatic}$), 2.61 (s, 6H, H$_{aliphatic}$), 2.61 (s, 6H, H$_{aliphatic}$).

Synthesis of Porphyrin Dyads

General Procedure

A solution of 2-formyl porphyrin (60 mg), 1,4-diazabicyc[2.2.2]octene (DBU) (1.5 mL) and dichloroethane (2.1 mL) was heated for 30 min at 100°C and 250 W in a microwave reactor. The cooled reaction was then purified by column chromatography (silica, CH$_2$Cl$_2$) and crystallised in CH$_2$Cl$_2$/MeOH to give the desired compounds.

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A solution of 2-formyl-5,10,15,20-tetrakis(4-methylphenyl)porphyrin 14 (60 mg, 66 µmol) 1,4-diazabicyc[2.2.2]octene (7 mg, 43 µmol) in CH$_2$Cl$_2$ (3 mL) was stirred at room temperature under argon. Excess DBU (0.5 mL) was added and stirred for 4 hrs. The reaction mixture was directly purified by flash chromatography (silica, CH$_2$Cl$_2$/Hexane (7:3) and concentrated in vacuo. Crystallisation in CH$_2$Cl$_2$/MeOH gave the desired product 16 (8 mg, 12%) as a purple solid. $^{1}H$-NMR (400 MHz, ACN-$d_{6}$): $\delta$ 9.56 (s, 2H, H$_{pyrrolic}$), 8.97 (d, 2H, $\beta$= 5.0 Hz, H$_{pyrrolic}$), 8.90 (d, 2H, $\beta$= 5.0 Hz, H$_{pyrrolic}$), 8.87 (d, 2H, $\beta$= 5.0 Hz, H$_{pyrrolic}$), 8.84-8.78 (m, 6H, H$_{pyrrolic}$), 8.23 (d, 4H, $\beta$= 8.0 Hz, H$_{aromatic}$), 8.15-8.07 (m, 12H, H$_{aromatic}$), 7.68-7.64 (m, 6H, H$_{aliphatic}$ and H$_{aromatic}$), 7.60-7.55 (m, 12H, H$_{aromatic}$), 7.46 (s, 2H, H$_{aliphatic}$), 2.71 (s, 12H, H$_{aliphatic}$), 2.60 (s, 6H, H$_{aliphatic}$), 2.55 (br s, 4H, NH). UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log e) 431 (5.49), 527 (4.68), 573.5 (4.31), 601 (4.25), 662 (4.02) nm. HRMS, m/z: calculated for M$^{+}$ (C$_{54}$H$_{50}$N$_{10}$O$_{2}$): 957.3677, found: 957.3673.

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18 was collected as a purple solid (58 mg, 80%). $^{1}H$-NMR (400 MHz, CDCl$_3$): $\delta$ 9.50 (s, 1H, H$_{pyrrolic}$), 8.95 (d, 1H, $\beta$= 5.0 Hz, H$_{pyrrolic}$), 8.88 (d, 1H, $\beta$= 5.0 Hz, H$_{pyrrolic}$), 8.83 (d, 1H, $\beta$= 5.0 Hz, H$_{pyrrolic}$), 8.79 (d, 1H, $\beta$= 5.0 Hz, H$_{pyrrolic}$), 8.77 (d, 1H, $\beta$= 5.0 Hz, H$_{pyrrolic}$), 8.73 (d, 1H, $\beta$= 5.0 Hz, H$_{pyrrolic}$), 8.32-8.28 (m, 2H, H$_{pyrrolic}$), 8.23-8.18 (m, 6H, H$_{aromatic}$), 7.84-7.70 (m, 12H, H$_{aromatic}$), 7.00-6.25 (m, 4H, H$_{aliphatic}$), 3.82 (br s, 2H, NH$_{2}$). UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log e) 431 (5.22), 525 (4.20).
567 (3.82), 602 (3.76), 660 (3.57) nm. HRMS, m/z: calcd for MH+ (C23H16N6O2): 781.3080, found: 781.3079.

**Fe18**

10 mL of acetonitrile was refluxed under argon for 2 hrs to remove any dissolved oxygen. The reaction's temperature was then lowered to 70 °C and iron (II) chloride (190mg, 0.96 mmol) added. A solution of 18 (34mg, 0.044 mmol) in 5 mL of degassed chloroform was then added to the reaction over 5 mi. The reaction was then heated back up to reflux, stirred for 3 hrs and then left exposed to air overnight at room temperature. The reaction was then concentrated in vacuo, redissolved in dichloromethane and washed with 0.1M HCl (3 x 25 mL). The reaction was purified by column chromatography (silica, 100% dichloromethane - 98% dichloromethane: 2% methanol) and filtered through filter paper to give the desired compound Fe18 as a purple/brown solid (22 mg, 58%).

UV-vis (CH2Cl2), λmax (log e) 433 (4.94), 515 (4.06), 668 (3.36) nm. HRMS, m/z: calcd for MH+-Cl (C25H24FeN6): 834.2194, found: 834.2316.

**Zn21**

Porphyridy dye 21 (4 mg, 2.5 µmol) was dissolved in CH3Cl (0.4 mL) and stirred at room temperature. A solution of Zn(OAc)2·2H2O (1.4 mg, 6.3 µmol) in MeOH (0.4 mL) was added and stirred for 30 min. MALDI induced reaction completion and the reaction was then concentrated in vacuo. Crystallisation in CH2Cl2/MeOH gave the desired product Zn21 (4 mg, 100%) as a purple solid. 1H-NMR (400 MHz, CDCl3): δ 9.74 (s, 1H, H-pyrrolic), 8.90 (d, 1H, 3J=5.0 Hz, H-phenyl), 8.80 (d, 1H, 3J=5.0 Hz, H-pyrrolic), 8.82-8.77 (m, 3H, H-pyrrolic), 7.94 (s, 2H, H-βXyl), 7.84-7.60 (m, 6H, H-phenyl), 7.65 (s, 1H, H-phenyl), 7.46-7.35 (m, 7H, H-βXyl + H-phenyl), 7.23 (s, 1H, H-phenyl), 3.84 (2H, H-benzoxyl), 2.65 (6H, H-phenyl), 2.61 (6H, H-βXyl), 2.60 (6H, H-phenyl), 2.48 (2H, H-phenyl), 2.60 (br s, 2H, NH). UV-vis (CH2Cl2), λmax (log e) 435 (4.96), 527 (4.09), 563 (4.07), 604 (4.01) 662 (3.94) nm. HRMS, m/z: calcd for MH+ (C116H92N202Zn): 1752.6089, found: 1752.6138.
(1.4 mg, 4.3 μmol) in MeOH (0.4 mL) was added and stirred for 30 min. MALDI indicated reaction completion and the reaction was concentrated in vacuo. Crystallisation in CH₂Cl₂/MeOH gave the desired product Zn23 (6 mg, 100%) as a purple solid. UV-vis (CH₂Cl₂) 433 (5.06), 526 (4.05), 566 (3.65), 603 (3.58), 662 (3.52) nm. HRMS, m/z: calcld for M⁺ (C₉₀H₇₀ClFeN₁₂Zn): 1667.4584, found: 1667.4596.

Supporting Information (see footnote on the first page of this article): UV-visible spectra, Raman spectra and DFT calculation data, electrochemical impedance data, dye uptake and ¹H-NMR spectra.

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Keywords: porphyrin • porphyrin dyad • Knoevenagel condensation • light harvesting • dye sensitised solar cell


β-Vinyl substituted porphyrins and porphyrin dyads are readily synthesized using Knoevenagel condensations, with the efficacy of this type of porphyrin dye determined in a dye sensitised solar cell.