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**EDGE ARTICLE**

# Engineering conjugation in *para*-phenylene-bridged porphyrin tapes†

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We report the synthesis of 7 new *para*-phenylene-bridged zinc porphyrin dimers, five of which were characterized by single-crystal X-ray analysis. A variety of links were tested for holding the *para*-phenylene bridges in π-conjugation with the porphyrins, and the natures of these restraining links strongly influence the properties of the porphyrin dimers. The keto-linked dimer exhibits a long-lived singlet excited state and strong fluorescence at 960 nm (1.7% quantum yield) in contrast to most previously reported conjugated porphyrin tapes, which are essentially non-emissive. Replacement of the cross-conjugated keto links by directly conjugated C–C bonds eradicates the fluorescence and shifts the absorption maximum to 1077 nm. On the other hand, replacement of the keto links with non-conjugated $CPh_2$ links confers fluorescence at 736 nm (10% quantum yield) and results in remarkably similar one- and two-photon absorption behavior to that of *meso–meso* ethynylene-bridged porphyrin dimers (peak two-photon cross section: 7,300 GM at 878 nm). Cross-conjugated keto links do more than just hold the *para*-phenylene bridge coplanar with the porphyrins; they reduce the HOMO–LUMO gap, although to a lesser extent than direct π-conjugated links. Planarized *para*-phenylene-bridged porphyrin dimers provide insights into the relationship between previously investigated classes of conjugated porphyrin oligomers, and they open up possibilities for the synthesis of new types of near-IR two-photon absorbing dyes.

## Introduction

Conjugated porphyrin oligomers exhibit unusual optical and electronic behavior, such as strong two-photon absorption,[1] nonlinear refraction,[2] fast intramolecular charge transport[3] and bright luminescence in the near-infrared (NIR).[4] These properties point to potential applications in two-photon excited photodynamic therapy,[5] molecular electronics[6] and NIR electroluminescent displays.[7] The two most widely studied families of porphyrin oligomers are edge-fused planarized oligomers or "tapes"[8,9] and alkyne-bridged strands,[10–13] represented by the general dimer structures **1** and **2**, respectively, in Fig. 1. The *β,meso,β*-fused

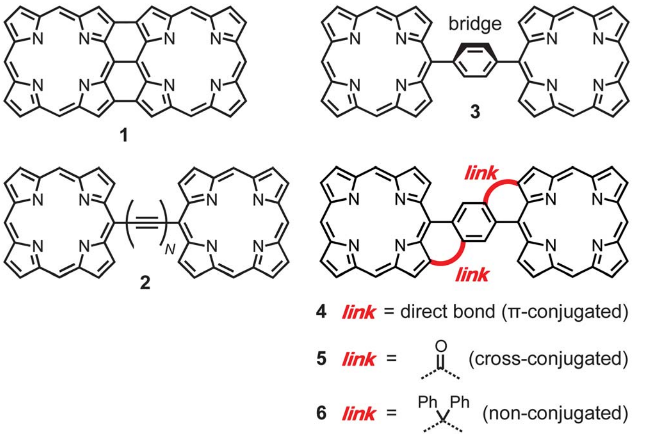

**Fig. 1** General classes of porphyrin dimers: **1**: edge-fused tapes, **2**: alkyne-bridged, **3**: *para*-phenylene-bridged and **4–6**: *para*-phenylene tapes. (Solubilizing sidechains and coordinated metals are omitted for clarity; the structures of **4–6** are specified in more detail in Scheme 1.)

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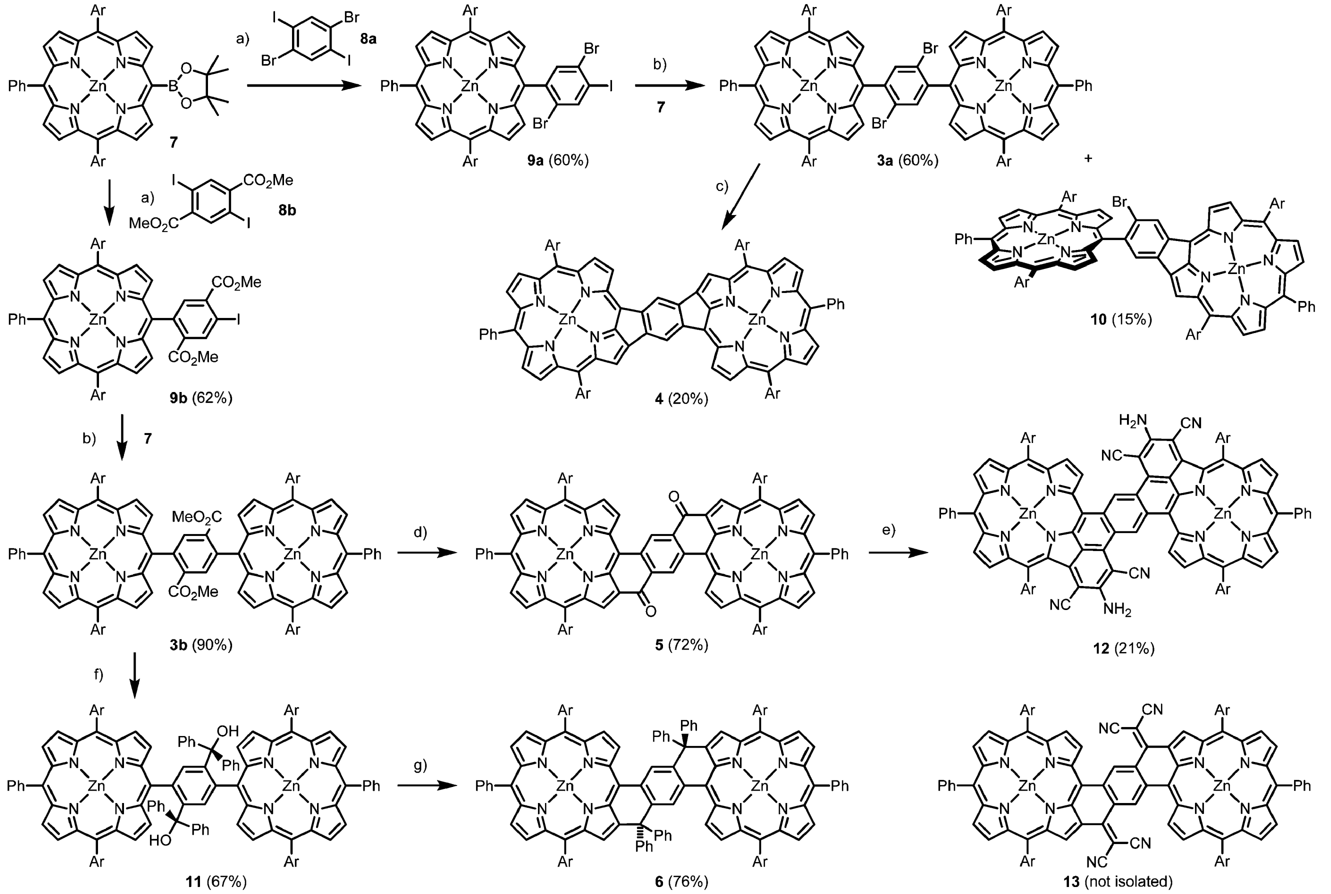


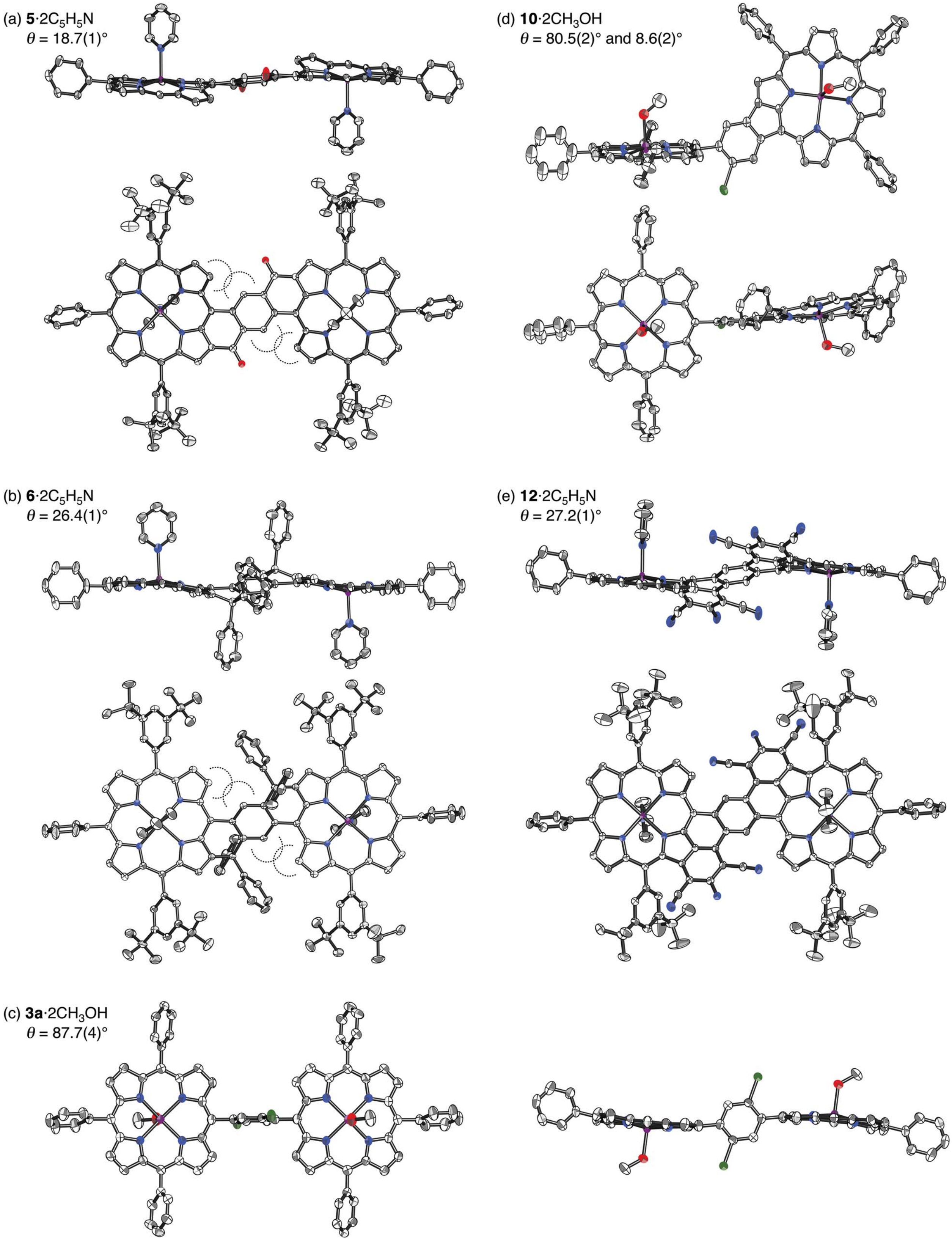
**Scheme 1** The synthesis of porphyrin dimers **4–6**. Ar = 3,5-di(*tert*-butyl)phenyl. a) $Pd(PPh_3)_4$, $Cs_2CO_3$, PhMe/DMF (1 : 1), **8a/b** (10 eq.), 90 °C; b) **7** (1.5 eq.), $Pd(PPh_3)_4$, $Cs_2CO_3$, PhMe/DMF (1 : 1), 90 °C; c) $Pd(PPh_3)_4$, $K_3PO_4$, DMF, 155 °C; d) $BBr_3$, $CH_2Cl_2$, 20 °C, then $Zn(OAc)_2$; e) $CH_2(CN)_2$ (1000 eq.), $TiCl_4$, $CH_2Cl_2$; f) PhLi (100 eq.), THF, −78 °C, then $Zn(OAc)_2$; g) $BF_3{\cdot}OEt_2$, $CH_2Cl_2$, then $Zn(OAc)_2$.

oligomer tapes (homologs of **1**), pioneered by Osuka and coworkers exhibit the lowest conductance attenuation $\beta$-factors[14] and the smallest HOMO–LUMO gaps reported for any neutral molecular $\pi$-system; for example the dodecamer has an absorption maximum at 2580 nm.[9,15] These tapes exhibit extremely rapid $S_1$–$S_0$ non-radiative decay, resulting in minuscule fluorescence quantum yields,[16–18] which limits the utility of their remarkable absorption. In contrast, butadiyne-bridged porphyrin oligomers exhibit weaker electronic coupling, slower $S_1$–$S_0$ internal conversion and substantial fluorescence quantum yields.[4] *Para*-phenylene-bridged oligomers (represented by **3** in Fig. 1) show only very weak electronic coupling because the $\pi$-orbitals of the bridge are almost orthogonal to those of the porphyrin units due to steric interactions.[19] Here we present an investigation of a series of planarized *para*-phenylene-bridged tape-like porphyrin dimers, **4–6**, in which covalent links keep the bridge in conjugation with both porphyrin units (Fig. 1). The nature of the link used to enforce planarity strongly influences the photophysical behavior of the porphyrin dimer. When the link is a direct bond, as in **4**, the absorption extends far into the NIR and the dimer is essentially non-fluorescent, as for **1**. In contrast, when the link is non-conjugated, as in **6**, the dimer is strongly fluorescent; its linear-absorption and two-photon absorption spectra closely resemble those of an alkyne-bridged dimer, **2**. The cross-conjugated system, **5**, exhibits intermediate behavior with surprisingly strong NIR fluorescence.

## Results and discussion

### Synthesis

Porphyrin dimers **4–6** were synthesized as summarized in Scheme 1. Suzuki coupling of porphyrin boronic ester **7**[20,21] with a *para*-diiodo benzene, **8a** or **8b**, gave the phenylene-bridged porphyrin dimers **3a** and **3b**. Conversion of dibromo dimer **3a** to the indene-fused tape **4** was achieved in 20% yield by intramolecular Heck coupling, using reaction conditions developed by Boyle and coworkers.[22,23] Some intramolecular Heck coupling also occurred as a side-reaction during Suzuki coupling in the synthesis of **3a**, giving the partially fused dimer **10** as a minor byproduct. Planarization of dimer **3b** to give keto-linked tape **5** was achieved in 72% yield by double intramolecular Friedel–Crafts acylation using boron tribromide, under conditions similar to those of Ruppert, Callot and coworkers.[24] Conversion of **3b** to **5** shifts the infrared C=O stretch frequency from 1720 cm$^{-1}$ to 1647 cm$^{-1}$, reflecting conjugation of the carbonyl to both the porphyrin and the phenylene bridge. The bis-ester dimer **3b** was converted into **6** using the same approach that Müllen and coworkers applied in the synthesis of ladder-type oligomers.[25] Bis-ester **3b** was treated with excess phenyl lithium, to form bis-alcohol **11**, then intramolecular Friedel–Crafts alkylation was achieved with boron trifluoride, to give dimer **6** in 51% yield over two steps.



(a) **5**·$2C_5H_5N$
$\theta$ = 18.7(1)°

(b) **6**·$2C_5H_5N$
$\theta$ = 26.4(1)°

(c) **3a**·$2CH_3OH$
$\theta$ = 87.7(4)°

(d) **10**·$2CH_3OH$
$\theta$ = 80.5(2)° and 8.6(2)°

(e) **12**·$2C_5H_5N$
$\theta$ = 27.2(1)°

**Fig. 2** Orthogonal views of crystallographic structures of zinc porphyrin dimers (a) **5**·$2C_5H_5N$, (b) **6**·$2C_5H_5N$, (c) **3a**·$2CH_3OH$, (d) **10**·$2CH_3OH$ and (e) **12**·$2C_5H_5N$.¶ Thermal ellipsoids at 50% level; H atoms omitted for clarity; side aryl groups not shown in top views; *t*-Bu groups omitted in (c) and (d). Dashed curves indicate steric interactions. $\theta$ is the dihedral angle between the mean planes of the porphyrin and the central phenylene unit.

The keto-linked tape **5** is a promising intermediate for the synthesis of porphyrin dimers with a wide range of other bridges, both using classical Knoevenagel condensations and also by forming *para*-quinodimethane indeno[1,2-*b*]fluorene bridges.[26] As a first step towards exploring the chemistry of this diketone, we tested its reaction with malononitrile, expecting to form **13**, but the only compound isolated from this reaction was the condensation product of four equivalents of malononitrile, **12** (identified by X-ray analysis†, see below). We have not yet thoroughly explored the properties of this unexpected product.

## X-ray crystal structures

Single-crystal X-ray structure determinations were carried out on compounds **3a**, **5**, **6**, **10** and **12** (Fig. 2).¶ Values of the dihedral angle, $\theta$, between the 24-atom mean plane of the porphyrin and the 6-atom mean plane of the central *para*-phenylene are listed in Fig. 2. As expected, the central phenylene is nearly coplanar with both porphyrin units in dimers **5**, **6** and **12** ($\theta$ = 18–27°), whereas it is almost orthogonal in **3a** and **10** ($\theta$ = 88 and 80°). The $\pi$-systems of **4**, **5** and **6** are slightly twisted due to the steric clashes between the CH of the phenylene bridge and the adjacent pyrrole units. The structure of dimer **6** (Fig. 2b) shows that the phenyl substituents on the bridge adopt *pseudo* axial and equatorial positions, leaving the whole $\pi$-system essentially planar. The geometries of the *meso*,$\beta$-fused indene and benzocyclohexenone units of **10** and **5** are similar to those reported in analogous porphyrin monomers.[23a,24,27–29]

## Absorption, electrochemistry and nonlinear optics

The UV-visible-NIR absorption spectra of porphyrin dimers **4–6** show that they are strongly $\pi$-conjugated (Fig. 3). The longest wavelength absorption Q band of dimer **4** ($\lambda_{max}$ 1077 nm) is

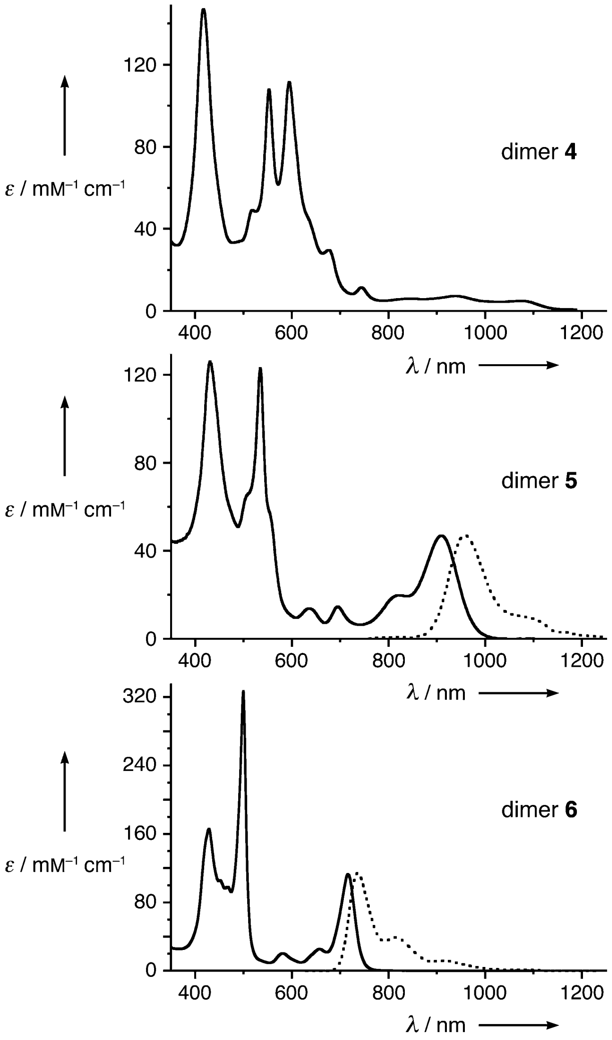


**Fig. 3** UV-vis–NIR spectra of porphyrin dimers **4**, **5** and **6**. The dotted lines show fluorescence spectra for **5** and **6** (excited at 430 nm, arbitrary vertical scale; absorption spectra in benzene with 1% pyridine; fluorescence spectra in toluene with 1% pyridine).

**Table 1** Redox potentials and HOMO–LUMO gaps[a]

| Compound | $E_{red}^2$ | $E_{red}^1$ | $E_{ox}^1$ | $E_{ox}^2$ | $E_g$/eV | $E_g^{opt}$/eV |
|---|---|---|---|---|---|---|
| **4** | −1.55 | −1.41 | 0.01 | 0.19 | 1.42 | 1.15 |
| **5** | −1.25 | −1.09 | 0.32 | 0.46 | 1.41 | 1.33 |
| **6** | −1.80 | −1.73 | 0.10 | 0.31 | 1.83 | 1.71 |
| **3a** |  | −1.87 | 0.41 |  | 2.28 | 2.25 |
| **3b** |  | −1.83 | 0.34 |  | 2.17 | 2.25 |

[a] Redox potentials measured in $CH_2Cl_2$ with 0.1 M $Bu_4NPF_6$; potentials in volts relative to internal Fc/Fc$^+$ at $E$ = 0. Electrochemical gap: $E_g = E_{ox}^1 - E_{red}^1$. Optical gap $E_g^{opt}$ estimated from the midpoint of the Q-band fluorescence and absorption for **5** and **6**, or from the longest wavelength absorption maximum for **4**, **3a** and **3b**.

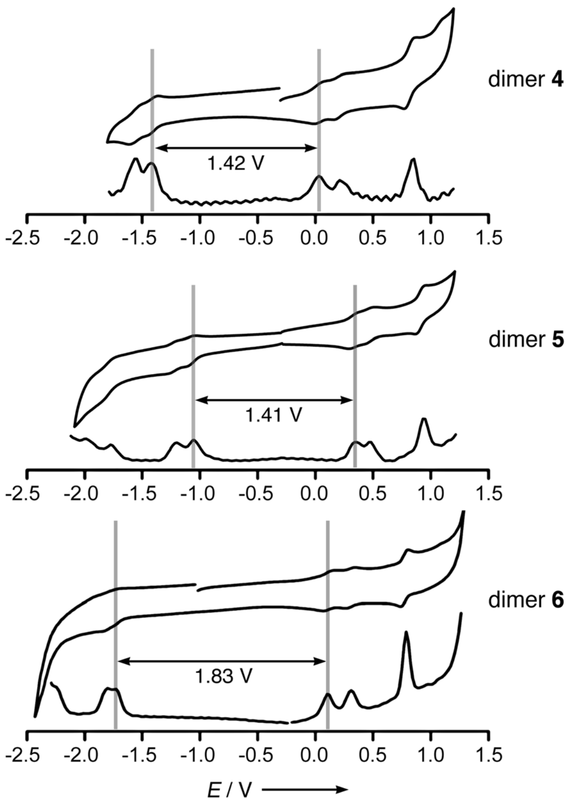


**Fig. 4** Cyclic and square-wave voltammograms for porphyrin dimers **4**, **5** and **6** in $CH_2Cl_2$ with 0.1 M $Bu_4NPF_6$ (potentials relative to internal ferrocene/ferrocinium at $E$ = 0). Grey vertical lines indicate $E_{red}^1$ and $E_{ox}^1$.

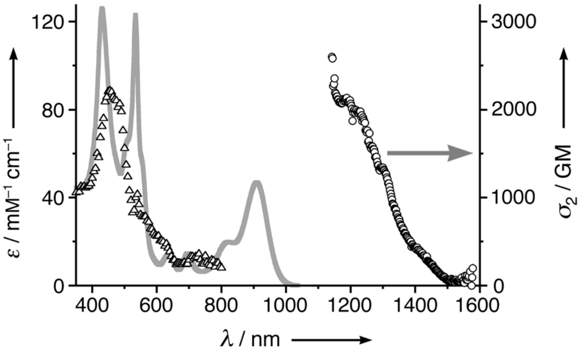
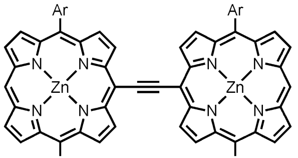


**Fig. 5** Nonlinear absorption spectra of porphyrin dimer **5**: Triplet excited state absorption ($T_1$–$T_n$, triangles) and two-photon absorption ($\sigma_2$, circles), together with the linear absorption ($S_0$–$S_n$, grey). The $T_1$–$T_n$ spectrum was recorded in benzene with 1% pyridine, whereas the $\sigma_2$ was recorded in $CCl_4$ with 1% pyridine.[31]

almost as red-shifted as that of a zinc *β*,*meso*,*β*-fused dimer **1** ($\lambda_{max}$ 1185 nm).[16,17] We were unable to detect any luminescence from dimer **4**, whereas dimers **5** and **6** exhibit significant fluorescence, mirroring the Q absorption band (**5**: $\lambda_{max,\ abs}$ 907 nm; $\lambda_{max,\ em}$ 960 nm; $\Phi_{em} = 0.017$. **6**: $\lambda_{max,\ abs}$ 717 nm; $\lambda_{max,\ em}$ 736 nm; $\Phi_{em} = 0.10$).[30]

The small HOMO–LUMO gaps implied by the absorption and fluorescence spectra of **4–6** are confirmed by their redox potentials (Table 1 and Fig. 4). Surprisingly, dimers **4** and **5** have essentially the same electrochemical HOMO–LUMO gap, despite the more red-shifted absorption and smaller optical gap of **4**. As expected, the keto-linked dimer **5** is easier to reduce and harder to oxidize than **4** or **6**. In contrast to the planarized dimers **4–6**, the unplanarized dimers **3a** and **3b** show electrochemical gaps similar to those of porphyrin monomers, without resolvable splitting between the successive first and second oxidation and reduction processes.

Femtosecond pump–probe absorption spectroscopy and nanosecond laser flash photolysis experiments were carried out to gain insights into the photophysics of compounds **4–6**. Dimer **4** gave a transient absorption spectrum with extremely fast biexponential decay ($\tau = 1.7 \pm 0.8$ ps and $12.9 \pm 4.9$ ps), with no evidence for long-lived excited states. Thus, the lack of fluorescence from this dimer can be attributed to ultrafast $S_1$–$S_0$ relaxation, as in *β*,*meso*,*β*-fused dimers of type **1**. In contrast, the keto-linked dimer **5** showed much slower decay of a singlet state ($\tau = 0.25 \pm 0.06$ ns) and a triplet state ($\tau = 27 \pm 2$ μs in the absence of $O_2$). The triplet yield was found to be $\Phi_T = 0.049 \pm 0.001$. Although $S_1$–$S_0$ internal conversion is slower in **5** than in **4**, it is still the main relaxation channel competing with fluorescence ($\Phi_{IC} = 0.934$; $k_{IC} = 3.7 \times 10^9\ s^{-1}$). The $T_1$–$T_n$ absorption spectrum (Fig. 5) and $S_1$–$S_n$ absorption spectrum (Supporting Information†) of **5** both show peaks in similar regions to the $S_0$–$S_n$ linear absorption spectrum. The two-photon absorption cross-section of **5** (measured by two-photon excited fluorescence in $CCl_4$/pyridine;[31] Fig. 5) reaches $\sigma_2 = 2100$ GM at 1200 nm, indicating the presence of a two-photon allowed transition enhanced by resonance with the Q band. Few other chromophores exhibit such strong two-photon absorption in this region of the NIR.[32–34] Transient absorption experiments on dimer **6** (in benzene containing 1% pyridine) showed decay of a singlet state ($\tau = 1.40 \pm 0.27$ ns) and a triplet state ($\tau = 219 \pm 34$ μs in the absence of $O_2$). This singlet lifetime agrees well with the value from time-resolved fluorescence decay measurements (1.53 ns in toluene containing 1% pyridine). The two-photon absorption spectrum of **6** (measured by two-photon excited fluorescence) shows that it exhibits remarkably strong two-photon absorption: $\sigma_2 = 7{,}300$ GM at 878 nm. Both the linear absorption spectrum and the two-photon absorption spectrum of **6** are very similar to those of the alkyne-bridged dimer **2a** (Fig. 6).[1b,c,12,35]



**2a**

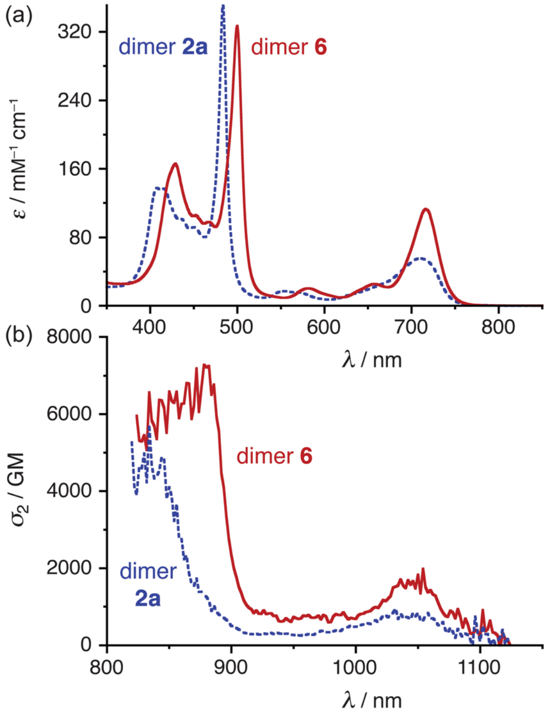


**Fig. 6** (a) A comparison of the linear absorption spectra of zinc porphyrin dimers **6** and **2a** (in benzene with 1% pyridine). (b) A comparison of the two-photon absorption spectra of **6** and **2a** (in $CH_2Cl_2$ with 1% pyridine).

## Conclusion

Four new planarized *para*-phenylene-bridged porphyrin dimers were synthesized, illustrating the scope for intramolecular Friedel–Crafts acylation, Friedel–Crafts alkylation and Heck coupling as alternatives to the oxidative ring-closures in the synthesis of large planar π-systems.[36] The absorption spectra and electrochemistry of dimers **4–6** show that they are strongly conjugated. The structures of **4** and **5** differ only by two carbonyl groups, yet they have totally different fluorescence behavior; the keto-linked dimer **5** exhibits strong fluorescence at 960 nm, whereas indene-fused dimer **4** is non-emissive. It is interesting to compare the fluorescence behavior of **5** ($\lambda_{em}$ = 960 nm; $\Phi_{em}$ = 1.7%) with that of a perylene-bridged porphyrin tape reported recently by Wu and coworkers ($\lambda_{em}$ = 982 nm; $\Phi_{em}$ = 0.8%).[37]

The fluorescence quantum yield of **5** is low compared with visible fluorescent dyes, but it is comparable to those of the most fluorescent compounds with emission in the 900–1000 nm wavelength range,[38–41] such as the laser dye Styryl-13 ($\lambda_{em}$ = 925 nm; $\Phi_{em}$ = 2%)[39] and ytterbium complexes ($\lambda_{em} \approx$ 985 nm; $\Phi_{em}$ = 0.5–4%).[42] The only compounds with substantially higher photoluminescence efficiencies in this spectral region are semiconductor nanocrystal quantum dots, such as PbS ($\lambda_{em} \approx$ 1000 nm; $\Phi_{em} \approx$ 30%)[43] and CdSe/CdTe/ZnSe ($\lambda_{em} \approx$ 950 nm; $\Phi_{em} \approx$ 50%).[44] The discovery that the keto-linked porphyrin tape **5** exhibits a relatively long-lived singlet excited state and substantial two-photon absorption, together with the rich chemistry of ketones, indicates that this tape is a promising prototype for a new class of NIR dyes with applications in photodetectors or as nonlinear absorbers.

Comparison between the absorption, fluorescence, two-photon absorption and electrochemistry of dimers **5** and **6** shows that the cross-conjugated keto-links in **5** do more than just hold the *para*-phenylene bridge coplanar with the porphyrins. Cross-conjugation through these keto-links must play an important role in reducing the HOMO–LUMO gap, although it is less effective in this role than the direct π-conjugated links in dimer **4**.

The remarkable similarity between the one- and two-photon absorption spectra of dimers **2a** and **6** implies that a planarized *para*-phenylene bridge transmits electronic coupling between the *meso*-positions of two porphyrins very much like an alkyne bridge. This is an important observation because it suggests that hydrophilic analogues of **6** may be suitable dyes for two-photon excited photodynamic therapy.[5] The $CAr_2$-linked phenylene bridge provides a similar electronic coupling to the $C_2$ bridge, but it should confer better stability and solubility, and the axial aryl substituents of the bridge would hinder aggregation.

Recently there has been an explosion of interest in porphyrins fused to polycyclic aromatic systems as panchromatic absorbers.[45–53] The results presented here suggest many approaches to the creation of even larger chromophores. The observation that diketone **5** reacts with malononitrile to form **12**, an unexpected product with a fused polycyclic aromatic bridge between the two porphyrin units, highlights the scope for using **5** as a precursor to other highly delocalized π-systems.

## Acknowledgements

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## Notes and references

¶ Low temperature, single crystal diffraction data were collected on I19(EH1) at the Diamond Light Source (compounds **5**, **6** and **12**), using a Nonius Kappa CCD diffractometer[54] (compound **3a**) and Station 9.8 at the SRS, Daresbury (compound **10**). Data were solved using SIR92[55] or SHELXS-86[56] and refined within the CRYSTALS suite.[57] Inter-plane angles were calculated with PLATON.[58] Full refinement details are given in the Supporting Information†; crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 860947–860952) and can be obtained *via* www.ccdc.cam.ac.uk/data_request/cif.

Single crystal X-ray diffraction data for **3a**: $C_{122}H_{124}Br_2Cl_{12}N_8O_4Zn_2$, $M_r$ = 2482.27, triclinic ($P\bar{1}$), $a$ = 10.3370(20) Å, $b$ = 15.4310(30) Å, $c$ = 19.6110(40) Å, $\alpha$ = 82.820(30)°, $\beta$ = 84.350(30)°, $\gamma$ = 82.950(30)°, $V$ = 3069.2(11) Å$^3$, $Z$ = 1, $\mu$ = 1.356 mm$^{-1}$, $D_c$ = 1.343 Mg m$^{-3}$, $T$ = 100(2) K, 11702 independent reflections [$R_{int}$ = 0.032], $R_1$ = 0.1146, w$R_2$ = 0.1167 [$I > 3\sigma(I)$].

Single crystal X-ray diffraction data for **5₁**: $C_{126}H_{120}N_{10}O_2Zn_2 \cdot 2(C_7H_{16}) \cdot 2(C_5H_5N)$, $M_r$ = 2295.77, triclinic ($P\bar{1}$), $a$ = 11.998(2) Å, $b$ = 14.379(3) Å, $c$ = 19.482(4) Å, $\alpha$ = 82.891(6)°, $\beta$ = 87.456(5)°, $\gamma$ = 76.474(5)°, $V$ = 3242.4(11) Å$^3$, $Z$ = 1, $\mu$ = 0.427 mm$^{-1}$, $D_c$ = 1.176 Mg m$^{-3}$, $T$ = 150(2) K, 21647 independent reflections [$R_{int}$ = 0.109], $R_1$ = 0.0704, w$R_2$ = 0.1272 [$I > 2\sigma(I)$].

Single crystal X-ray diffraction data for **5₂**: $C_{126}H_{120}N_{10}O_2Zn_2 \cdot 1.426(C_7H_{16}) \cdot 1.496(C_7H_8)$, $1.518(C_5H_5N)$, $M_r$ = 2295.77, triclinic ($P\bar{1}$), $a$ = 10.038(11) Å, $b$ = 18.807(18) Å, $c$ = 19.38(2) Å, $\alpha$ = 78.31(4)°, $\beta$ = 84.46(4)°, $\gamma$ = 82.55(4)°, $V$ = 3544(6) Å$^3$, $Z$ = 1, $\mu$ = 0.392 mm$^{-1}$, $D_c$ = 1.096 Mg m$^{-3}$, $T$ = 150(2) K, 15005 independent reflections [$R_{int}$ = 0.049], $R_1$ = 0.1106, w$R_2$ = 0.2531 [$I > 2\sigma(I)$].

Single crystal X-ray diffraction data for **6**: $C_{150}H_{140}N_{10}Zn_2 \cdot 4(C_7H_8) \cdot C_6H_6$, $M_r$ = 2660.26, triclinic ($P\bar{1}$), $a$ = 11.254(3) Å, $b$ = 16.718(4) Å, $c$ = 19.850(4) Å, $\alpha$ = 83.634(6)°, $\beta$ = 79.865(4)°, $\gamma$ = 87.849(7)°, $V$ = 3653.1(14) Å$^3$, $Z$ = 1, $\mu$ = 0.387 mm$^{-1}$, $D_c$ = 1.209 Mg m$^{-3}$, $T$ = 100(2) K, 24243 independent reflections [$R_{int}$ = 0.047], $R_1$ = 0.0769, w$R_2$ = 0.1594 [$I > 2\sigma(I)$].

Single crystal X-ray diffraction data for **10**: $2(C_{116}H_{117}BrN_8O_2Zn_2) \cdot CHCl_3 \cdot 3(CH_4O) \cdot H_2O$, $M_r$ = 2660.26, triclinic ($P\bar{1}$), $a$ = 15.4354(8) Å, $b$ = 16.6155(9) Å, $c$ = 21.9618(12) Å, $\alpha$ = 98.915(1)°, $\beta$ = 98.974(1)°, $\gamma$ = 93.126(1)°, $V$ = 5478.4(5) Å$^3$, $Z$ = 1, $\mu$ = 0.893 mm$^{-1}$, $D_c$ = 1.198 Mg m$^{-3}$, $T$ = 150(2) K, 32269 independent reflections [$R_{int}$ = 0.023], $R_1$ = 0.0915, w$R_2$ = 0.1069 [$I > 3\sigma(I)$].

Single crystal X-ray diffraction data for **12**: $C_{136}H_{122}N_{16}Zn_2 \cdot 4(C_6H_{12}) \cdot 2(C_6H_6)$, $M_r$ = 2660.26, triclinic ($P\bar{1}$), $a$ = 12.428(4) Å, $b$ = 14.323(5) Å, $c$ = 21.854(8) Å, $\alpha$ = 80.953(8)°, $\beta$ = 87.360(11)°, $\gamma$ = 69.226(11)°, $V$ = 3592(2) Å$^3$, $Z$ = 1, $\mu$ = 0.393 mm$^{-1}$, $D_c$ = 1.204 Mg m$^{-3}$, $T$ = 100(2) K, 22887 independent reflections [$R_{int}$ = 0.037], $R_1$ = 0.0796, w$R_2$ = 0.1880 [$I > 2\sigma(I)$].

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