Novel one-pot synthesis of 5-alkenyl-15-alkynylporphyrins and their derivatisation to a butadiyne-linked benzoporphyrin dimer†

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5-Alkenyl-15-alkynylporphyrins have been obtained unexpectedly by [2 + 2] acid-catalyzed condensation of dipyrrylmethane and TMS propynal in addition to 5,15-dialkynylporphyrin, and the unsymmetrical porphyrin can be converted to a butadiyne-linked dimer by selective desilylation of the alkynyl TMS.

Highly conjugated porphyrins and metalloporphyrins have attracted strong attention in connection with unusual electro-optical and non-linear optical properties such as two-photon absorption.[1–3] Alkynyl substituents are the most effective way of making conjugated connections to the *meso* positions of porphyrins and 5,15-dialkynylporphyrins are useful building blocks for making highly conjugated porphyrin oligomers.[4–7] Additionally, tetrabenzoporphyrins (TBPs) and related π-expanded complexes show intriguing optical properties in the near-IR region and are very attractive for applications such as non-linear optical materials, optical memories, and opto-electronic materials.[8] Considering these properties, π-expanded oligomers of TBPs connected by alkynyl substituents at the *meso* positions might be promising highly conjugated materials. However, to our knowledge, such materials have rarely been reported because of the low solubility of TBPs in common organic solvents.[9] Recently we[10] and others[11] have reported soluble precursors of TBPs which, after purification, could easily be converted to TBPs. Using our method, we have tried to prepare 5,15-dialkynyl-TBP **4a** from bicyclo[2.2.2]octadiene (BCOD) ring-fused 5,15-dialkynylporphyrin **1a** *via* the retro-Diels–Alder reaction (Fig. 1).[10] During the synthesis of **1a** by [2 + 2] acid-catalyzed condensation of a dipyrrylmethane, an unsymmetrical 5-alkenyl-15-alkynylporphyrin **2a** was obtained unexpectedly in addition to the targeted porphyrin **1a**. As far as we know, a few 5-alkenyl-15-alkynylporphyrins, which have been prepared by a partial nucleophilic addition to dialkynylporphyrin[4a] or a long multistep synthesis,[12] have been reported so far. With the [2 + 2] acid-catalyzed synthesis using substituted propynal, only 5,15-dialkynyl porphyrin has been reported.[4a,b,d,8d] This 5-alkenyl-15-alkynylporphyrin **2a** is a very attractive building block, especially for the synthesis of butadiyne-linked porphyrin oligomers and dimers, since selective cleavage of the trimethylsilyl (TMS) group on either the vinyl or alkynyl end is possible by exploiting the different reactivities of the two TMS groups.[13] We also report here the preparation of a butadiyne-linked TBP dimer by selective cleavage of the TMS group at the alkynyl end of porphyrin **2a**.

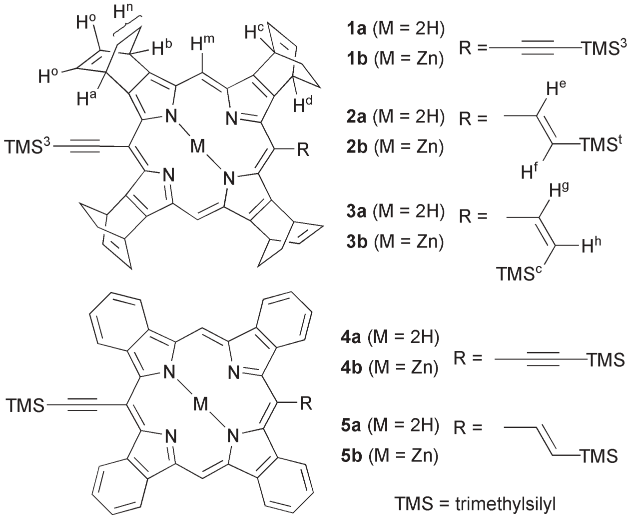
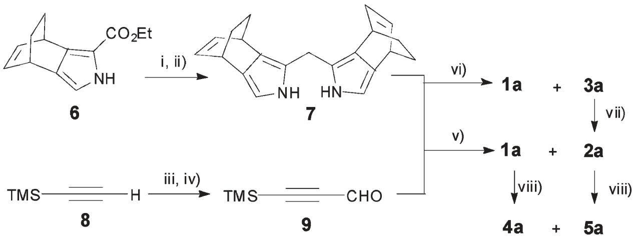


Fig. 1 Porphyrin monomers **1–5**.

A typical synthetic route for porphyrins **1a–5a** is shown in Scheme 1. An acid-catalyzed condensation of α-free dipyrrylmethane **7**, which was prepared from pyrrole **6**[10a] in two steps, and TMS-propynal (**9**), which was prepared from TMS-propyne (**8**) in two steps, was performed in methanol using *p*-toluenesulfonic acid at 0 °C, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[4a] The two types of porphyrins, **1a** and **2a**,



Scheme 1 Synthesis of porphyrins, **1a–5a**. *Reagents and conditions*: (i) methylal, acetic acid, H_2SO_4, CH_2Cl_2, rt, 1 h, quant.; (ii) NaOH, ethylene glycol, 175 °C, 3 h, 92%; (iii) *n*-BuLi, THF, −78 °C, 30 min, then $ClCO_2Me$, rt, 2.5 h, 87%; (iv) DIBAL, −78 °C, 15 min, then MeOH, 2 h, rt, 78%; (v) *p*-TsOH, MeOH, 0 °C, 3 h, then DDQ, rt, 30 min, **1a**: 30%, **2a**: 10%; (vi) in the dark otherwise in same condition with step (v); **1a**: 33%, **3a**: 19%; (vii) *hv*, 84%; (viii) 200 °C, 10 min, quant.

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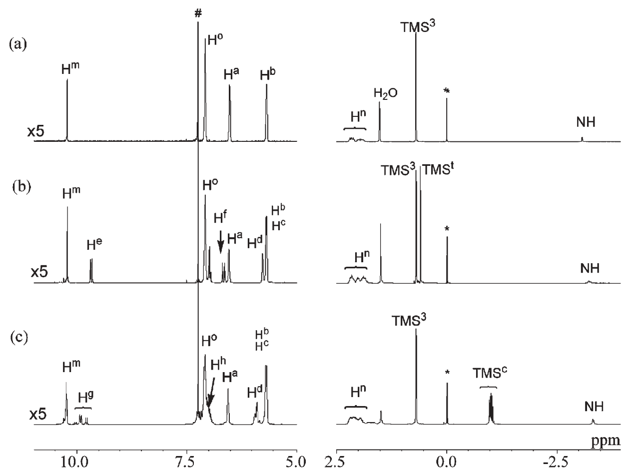


Fig. 2 ^{1}H NMR spectra of porphyrin (a) **1a**, (b) **2a** and (c) **3a** in $CDCl_3$.

were obtained with R_f values of 0.75 and 0.49, respectively, on silica-gel TLC using $CHCl_3$ as the eluent. Purification by silica-gel column chromatography gave the expected 5,15-dialkynylporphyrin **1a** as the first green band in 30% isolated yield and the unexpected porphyrin **2a** as the second red band in 10% yield. The second porphyrin was identified by TOF MS and by ^{1}H and ^{13}C NMR measurements. The TOF MS spectrum of this fraction showed a peak at m/z = 817 (M^+ + 1), which lay two mass units higher than porphyrin **1a** (m/z = 815 (M^+ + 1)). The ^{1}H NMR spectrum of **2a** is shown in Fig. 2 with that of porphyrin **1a** for comparison. Because of the stereoisomers of the BCOD groups, the vinyl hydrogen atoms (H^e and H^f) of porphyrins **2a** showed two pairs of hydrogen peaks at 9.68 and 6.66; and at 9.67 and 6.67 ppm, respectively, with coupling constants of 19 Hz, typical for *trans* vicinal coupling of olefinic hydrogen atoms. Although the hydrogen peak at the methyne position of **1a** (H^a) appeared at 6.53 ppm, those peaks of **2a** appeared at 6.56 (H^a) and 5.78 (H^d) ppm because of the different anisotropic effects of alkene *versus* alkyne groups. The peaks of the other methyne hydrogens, $H^b$and H^c, were almost the same for **1a** and **2a**. The peaks of TMS hydrogens were split into two signals at 0.69 and 0.60 ppm for **2a**.

When all stages from the condensation reaction to the purification on silica-gel column chromatography were performed in the dark, only *cis*-type porphyrin **3a** (R_f = 0.39) was obtained in 19% yield besides porphyrin **1a** (33%). Porphyrin **3a** could be converted to the *trans* form by photoirradiation, which was monitored by NMR. A solution of **3a** in $CDCl_3$ in a NMR tube was irradiated with the light (λ_{ex} = 420 nm) under an argon atmosphere. After an irradiation for 12 h, the ratio of *trans* **2a** to *cis* **3a** was increased to 0.84 (see ESI, Fig. S1†). This result suggested that for the [2 + 2] porphyrin synthesis using BCOD ring-fused dipyrrylmethane and TMS-propynal, dialkynylporphyrin **1a** and *cis*-type porphyrin **3a** were formed at first, after which the *cis* porphyrin was converted to *trans* by room light. The ^{1}H NMR spectra of **3a** is shown in Fig. 2(c). For porphyrin **3a**, four types of hydrogen peaks were observed for H^g at 10.04, 9.92, 9.91 and 9.79 ppm with coupling constants of 15 Hz, typical for *cis* vicinal coupling.‡ Interestingly, the alkynyl and vinyl TMS hydrogen peaks of **3a** were observed at 0.64 ppm as a singlet and at −1.06 to −0.94 ppm as multiple singlets, respectively, while both TMS hydrogens of **2a** were observed as singlets at 0.69 and 0.60 ppm. This result indicated that the TMS moiety at the end of the *cis*-alkenyl group was located above the porphyrin ring and their ring currents influenced its chemical shift.

The UV-vis absorption spectra of BCOD porphyrins **1a**, **2a** and **3a** are shown in Fig. 3. Porphyrins **2a** and **3a** showed similar spectra and their Soret bands (peaks at 417 nm) were blue-shifted by 5 nm compared to that of porphyrin **1a** (422 nm), which indicated that **1a** was more conjugated than porphyrins **2a** and **3a**. When porphyrins **1a** and **2a** were heated to 200 °C under vacuum, benzoporphyrins **4a** and **5a** were obtained quantitatively (Scheme 1). Their UV-vis absorption spectra are shown in Fig. 3(a). The sharp Soret bands of **4a** and **5a** were observed at 460 nm (shoulder at 449 nm) and 450 nm (shoulder at 441 nm), respectively, which were red-shifted by more than 30 nm compared to those of the corresponding precursor BCOD porphyrins. The absorbance of Q bands of porphyrin **4a** and **5a** were stronger than those of BCOD porphyrins and reached to 710 and 689 nm, respectively. In THF containing 5% pyridine, porphyrins **4a** and **5a** showed Soret peaks at 459 and 448 nm, respectively, and Q bands reached to 710 and 690 nm, respectively (see ESI,† Fig. S2). The reported spectrum of free-base TBP without any substituents at *meso* positions has shown the Soret peak at 427 nm and a longer Q band peak at 662 nm in THF containing 5% pyridine.[8d,14] These results suggested that π-expansion by alkenyl and alkynyl substituents also caused a red shift of more than 20 nm.

In order to investigate the generality of the unsymmetrical reaction described above, various dipyrrylmethanes and alkynylaldehydes were reacted under conditions similar to the preparation of porphyrins **1a** and **2a**. When triisopropylsilyl-(TIPS)propynal was used instead of TMS propynal, 5-alkenyl-15-alkynylporphyin was obtained in 10% yield in addition to 5,15-dialkynylporphyrin in 14% yield (ESI,† Table S1). However,

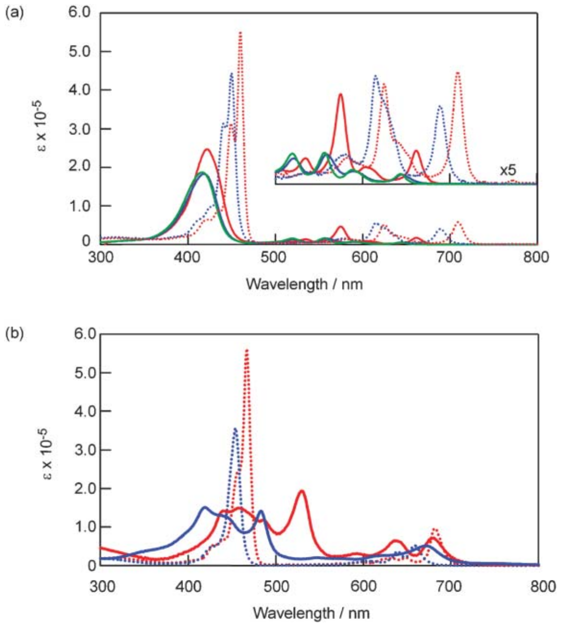
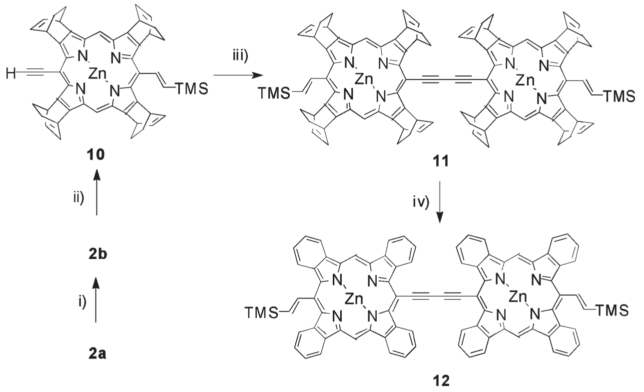


Fig. 3 UV-vis absorption spectra of (a) porphyrins **1a** (red solid line), **2a** (blue solid line), **3a** (green solid line), **4a** (red dotted line) and **5a** (blue dotted line) in CH_2Cl_2 and (b) zinc porphyrin monomers **4b** (red dotted line) and **5b** (blue dotted line), and dimers **11** (red solid line) and **12** (blue solid line) in DMF.

with phenylpropynal under the same experimental conditions, an analogous unsymmetrical porphyrin was not obtained, but only the corresponding 5,15-dialkynylporphyrin in 3% isolated yield (ESI,† Table S1).§ Furthermore, when β-unsubstituted dipyrrylmethane or all-β-ethyldipyrrylmethane was used instead of BCOD ring-fused dipyrrylmethane, the corresponding 5,15-dialkynylporphyrins were obtained in 3 and 34% yields, respectively, without formation of unsymmetrical porphyrins, consistent with previous reports (ESI,† Table S1).[4a,b,d,8d] These results suggested that the combination of BCOD ring-fused dipyrrylmethane and trialkylsilylpropynal was critical for the one-pot synthesis of 5-alkenyl-15-alkynyl unsymmetrical porphyrins. The mechanism of the partial hydrogenation of alkynes are not clear and is under investigation with a speculation as follows; a protonation of the alkynyl carbon at α position of TMS was followed by a 1,2-hydride transfer from the methyne position of a porphodimethene intermediate to the β-carbon of TMS.

Selective cleavage of the TMS group of the unsymmetrical porphyrin **2b** gave the porphyrin **10** and Glaser–Hay coupling of **10** gave porphyrin dimer **11** in 33% yield (Scheme 2).[4b] It was possible to convert dimer **11** quantitatively to benzoporphyrin dimer **12** by heating it to 200 °C under vacuum. Since Zn complexes of TBP monomers and dimers were poorly soluble in common organic solvents, such as CH_2Cl_2 and THF, their absorption spectra were measured in DMF (7×10^{-7} M) as shown in Fig. 3(b). The absorption spectrum of dimer **11** showed broadening and splitting of the Soret band, as has been reported for butadiyne-linked porphyrin dimers in CH_2Cl_2.[2,4b] This splitting has been explained by the simple point-dipole exciton coupling theory developed by Kasha.[4b,15] The TBP dimer **12** showed a more blue-shifted Soret band at 530 nm and relatively strong Q bands at 636 and 680 nm.



Scheme 2 Synthesis of porphyrin dimers, **11** and **12**. *Reagents and conditions*: (i) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3$, 75 °C, 2 h, 85%; (ii) K_2CO_3, THF, 70 °C, 5 h, 99%; (iii) CuCl, TMEDA, O_2, CH_2Cl_2, rt, 20 min, 33%; (iv) 200 °C, 10 min, quant.

In conclusion, we have found a novel one-pot synthesis of 5-alkenyl-15-alkynylporphyrin **2**, and have succeeded in preparing the TBP dimer in moderate yield by selective desilylation of porphyrin **2b**. The further development of these unsymmetrical porphyrins to the higher oligomers by selective cleavage of the TMS or TIPS group is under investigation.

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Notes and references

‡ The coupling constants for the other vinyl proton, H^h, could not be estimated accurately, because of overlapping signals.

§ The same experimental condition for TMS propynal was performed but not optimized for phenylpropynal. This would be the reason for the low yield.

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