Synthesis of the porphyrin-fused porphyrin, [2]porphyracene

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A novel porphyrin-fused porphyrin is formed by an oligomerization reaction of a (porphyrinato)nickel complex with $TeCl_4$; the isolated compound, [2]porphyracene, was characterized by spectroscopic methods and direct observation using scanning tunnelling microscopy; the excitation energy value of 13460 cm^{-1} (743 nm) is the lowest value reported for porphyrin dimers.

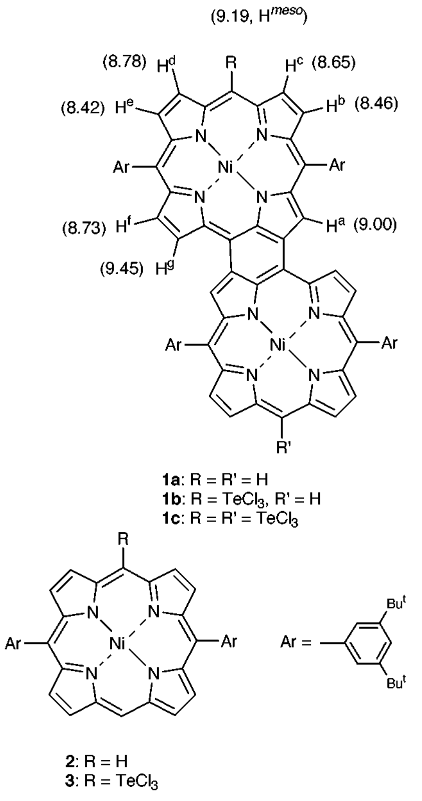
Porphyrins hold a unique position among organic compounds since they have a small HOMO–LUMO gap and can incorporate almost all types of metal ions in the central cavity.[1] Reflecting these characteristics, porphyrins are present not only in various biological systems, but are applied in many advanced materials. Recently much efforts has been focused on the expansion, contraction, isomerization and modification of the porphyrin chromophore to lead to more elaborated functions.[2–7]

In the course of our synthetic study on chalcogen substituted porphyrins for advanced materials,[8] we serendipitously discovered a novel reaction between [5,15-bis(3,5-di-*tert*-butylphenyl)porphyrinato]nickel **2** with tellurium(IV) tetrachloride ($TeCl_4$) to give a highly conjugated porphyrin-fused porphyrin. Here we report the new expanded porphyrin **1a**, denoted [2]porphyracene (porphyrin + acene; the number [2] implies the number of porphyrin nuclei) since this condensation manner is an acene type.

To prepare **3** which has a $TeCl_3$ group at a *meso*-position, the reaction of **2** with 1 equiv. of $TeCl_4$ in dry CH_2Cl_2 at room temperature[9] was carried out. The obtained reaction mixture was analyzed by matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and was found to give a series of peaks from $M^+ = 1483$ up to 6000 with equal mass spacings of *ca.* 744. This indicates clearly, contrary to the initial expectation, the formation of oligomeric products of **2**, from the dimer to the octamer. Separation of the dimer fraction from higher oligomers was successfully achieved using gel permeation liquid chromatography. The dimer fraction was further separated into three components **A**, **B** and **C** having $M^+ = 1483$, 1716 and 1949, respectively, using silica-gel flash chromatography. In a typical reaction, 48.3 mg of **1** and 8.8 mg of $TeCl_4$ gave 15.0 mg of **A**, 1.0 mg of **B**, 0.7 mg of **C**, and 20.0 mg of higher oligomers. The ^1H NMR spectrum of the main product **A** is different from those of porphyrin dimers directly connected at *meso*–*meso* or *meso*-β positions.[6] On the basis of detailed ^1H NMR analysis including truncated driven differential nuclear Overhauser effect measurements and MALDI-TOF mass spectra, the structure of **A** was assigned to be **1a** (Fig. 1) where the two porphyrin rings are fused at β- and *meso*-positions. The structures of **B** and **C** were assigned to be **1b** and **1c**, respectively, in a similar manner.

To confirm the structural assignment, we performed a direct observation of **1a** using scanning tunnelling microscopy (STM) (Fig. 2).† The STM image of **1a** adsorbed on a Cu(100) surface shows four lobes arranged in a parallelogram which are attributable to 3,5-di-*tert*-butylphenyl groups which are STM active substituents.[10] The size of the parallelogram is 13 × 9 Å which is consistent with the molecular size of **1a** estimated by a preliminary molecular geometry calculation [15.5 × 8.8 Å; Fig. 2(c)].

Aromatic protons of **1a** (H^b, H^c, H^d, H^e, H^f and H^{meso}) were upfield shifted by 0.18–0.67 ppm compared with the corre-



1a: R = R' = H
1b: R = $TeCl_3$, R' = H
1c: R = R' = $TeCl_3$

2: R = H
3: R = $TeCl_3$

Fig. 1 Compounds **1**–**3** along with ^1H NMR assignments for **1a**.

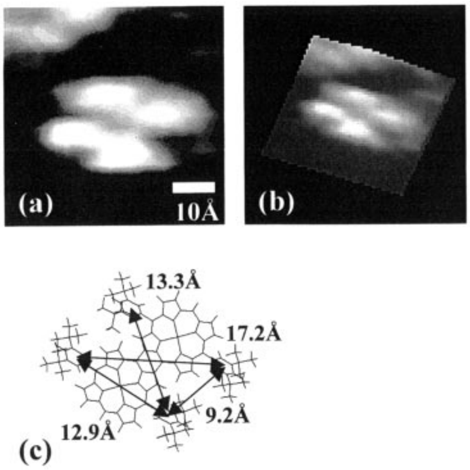


Fig. 2 STM image of **1a**: (a) top view, (b) perspective view, (c) molecular geometry of **1a**. The image shows a four-lobed pattern in a parallelogram arangement. The observed size of the parallelogram is 13 × 9 Å.

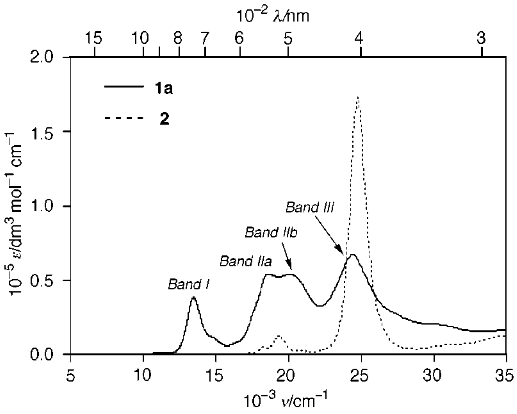
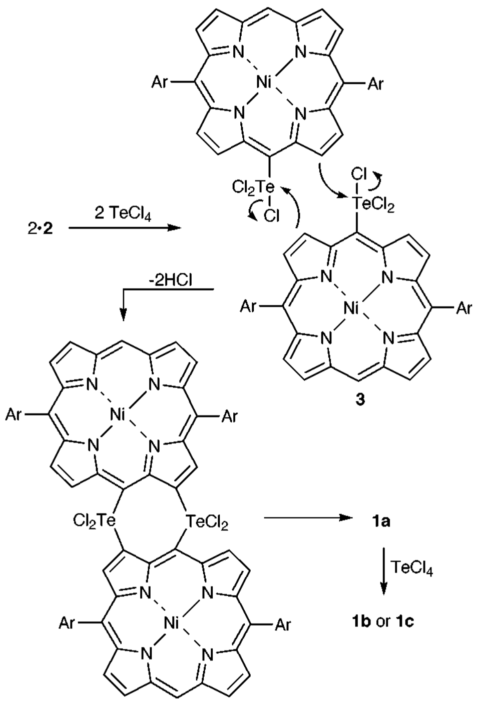


Fig. 3 Absorption spectra of [2]porphyracene **1a** (solid line) and **2** (dotted line) in $CHCl_3$.

sponding protons of **2** indicating the electron donating nature of the fused porphyrin ring. On the other hand, aromatic protons H^a and H^g showed downfield shifts of 0.09 and 0.34 ppm, respectively, owing to the ring current effect of the adjacent macrocycle and the compression effect from the sterically crowded protons.

The electronic spectra of **1a** and **2** are shown in Fig. 3. The spectrum of **1a** is essentially composed of three bands, band I, Q-band-like bands IIa and IIb and Soret-band-like band III. Reflecting the highly conjugated structure, band I appeared at 13460 cm^{-1} (743 nm) *i.e.* at a much longer wavelength than those of a porphyrin dimer connected by an acetylene linkage reported by Therien and coworkers (λ_{max} 14640 cm^{-1}; 683 nm)[2] or fused dimers reported by Crossley and Burn (λ_{max} 14180 cm^{-1}; 705 nm)[4] and by Smith and coworkers (λ_{max} 15340 cm^{-1}; 652 nm).[5] The other absorption bands of **1a**, bands IIa, IIb and III, were at quite similar wavelengths to those of **2**, although the intensity of band III was decreased and those of bands IIa and IIb were increased. These phenomena suggest a lowering of the symmetry and new π-electronic system for [2]porphyracene.

Considering that reported oxidative oligomerization of porphyrins take place at *meso–meso* and/or *meso*-β positions to form a single connection,[6] it is unprecedented that the present edge-fused oligomerization reaction of the nickel porphyrin complex takes place to give a double connection. Since the corresponding free base of **2** did not give oligomeric products, increased reactivity of the nickel porphyrin **2** at its β-positions may be responsible for the reaction.[6e] As shown in Scheme 1, the dimerization reaction of **2** probably takes place through a cyclic intermediate **4**,[11] which has not, so far, been detected. The final detelluration reaction is similar to that of bis(aryl)tellurium dichloride to give aryl coupling products.[9] The isolation of **1b** and **1c** suggests that these are the intermediates of [4]porphyracene and higher oligomers.



Scheme 1 A proposed reaction mechanism for dimerization.

In conclusion, a novel and highly conjugated [2]porphyracene has been isolated. In addition to the expanded π-system of the porphyrin, [2]porphyracene has two central cavities for homo- or hetero-metallation. These characteristics will allow us to use porphyracene for the preparation of advanced materials. We are currently investigating detailed properties of [*n*]porphyracenes including characterization of higher oligomers.

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Notes and references

† The STM image was observed with a home-made ultrahigh vacuum apparatus. An atomically clean single crystal Cu(100) surface was used as the substrate onto which **1a** was sublimed. Details of STM experiments will be published elsewhere.

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