Systematic Synthesis of Porphyrin Dimers Linked by Conjugated Oligoacetylene Bridges

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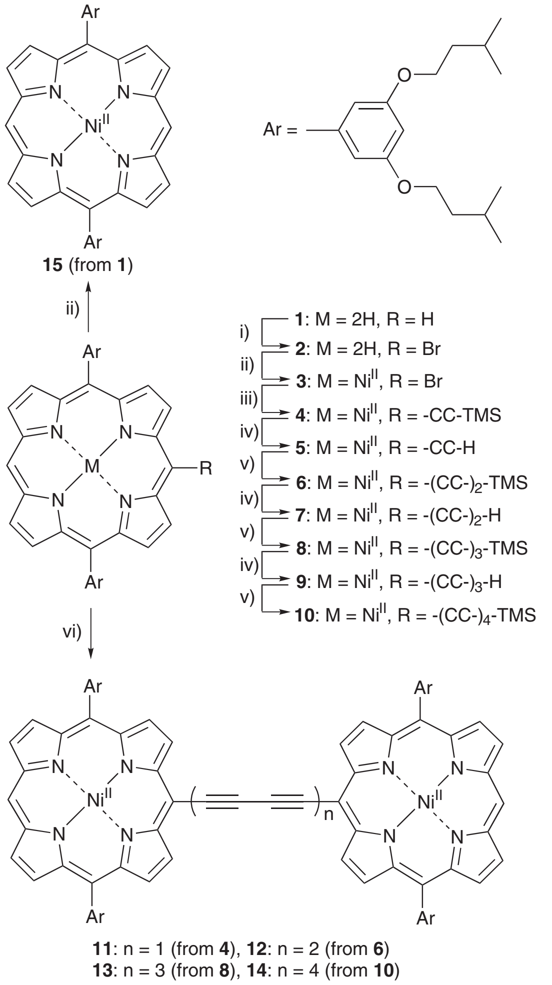
A series of α,ω-bis(*meso*-porphyrinyl)oligoacetylenes were systematically prepared. The exciton interaction between the porphyrins gradually decreased with increasing number of acetylenes, whereas the interaction between the porphyrin and the oligoacetylene unit appeared.

Classic α,ω-bis(aryl)oligoacetylenes (BAOAs) have been the focus as important component molecules for interdisciplinary advanced material chemistry.[1,2] Contemporary studies of this class of materials were started after the pioneering work of Nakagawa and co-workers from 1964 to 1973.[3] They comprehensively investigated a variety of BAOAs capped with the following aromatic hydrocarbons, e.g., phenyl, naphthyl, anthryl, phenanthryl, chrysenyl, fluorenyl, biphenyl-4-yl, and pyrenyl. Accompanying the development of such materials in which the terminal groups are replaced by functional π-systems, research interest has shifted ***from*** the established research objective of elucidating the electronic interaction between the terminal groups through the oligoacetylene unit (OAU),[3] ***via*** their excited state chemistries involving intramolecular photoinduced electron and/or energy transfer between the terminal groups through the OAU,[1] ***to*** the single-molecule-based nano science of transporting electrons through the OAU.[2] The BAOAs capped with metalloporphyrins at the *meso*-position with a large atomic coefficient, which were prepared for the first time by Arnold and co-workers in 1978,[4b] should be interesting,[4,5] because the molecules are sufficiently large to enable detection by scanning tunneling microscopy as individual molecules,[6] in addition to the well-known multiple functions associated with their expanded π-electronic systems.[7] In this work, we systematically prepared and spectroscopically characterized α,ω-bis(porphyrinyl)oligoacetylenes, **11**-**14**.



Scheme 1. Reagent and conditions: (i) 1.0 equiv. NBS, dry $CHCl_3$, 0 °C; (ii) excess $Ni(CH_3CO_2)_2{\cdot}4H_2O$, $(CH_2Cl)_2$, reflux; (iii) 3 equiv. TMS-C≡C-H, CuI, $Pd^0(PPh_3)_4$, dry $NHEt_2$; (iv) $^nBu_4NF$, CH_2Cl_2; (v) 30 equiv. TMS-C≡C-H, CuCl, dry air, dry TMEDA-CH_2Cl_2; (vi) $Cu(CH_3CO_2)_2{\cdot}H_2O$, dry pyridine, 60 °C.

The synthetic route for **11**-**14** is shown in Scheme 1. Retro synthetic consideration made us adopt the oxidative coupling reaction of oligoethynylporphyrins (**4**, **6**, **8**, and **10**, vide infra) as the final step, thereby producing the desired compounds **11**-**14**. An important key intermediate, **4**, having the substituents to increase solubility,[8] was prepared according to a general method.[4a] Extension of the OAU was performed by the mixed coupling reaction of **5**, derived from **4**, and 30 equiv. of trimethylsilylacetylene. Although the desired diyne derivative **6** was the main product of this reaction, unseparable by-product contaminated it. Continuous introduction of dry air to the reaction mixture solved this problem to give **6** along with trace of **11** and the expected 1,4-bis(trimethylsiliy)-1,3-butadyne. This reaction condition is applicable to the further extension of the OAU, affording **8** from **7** (70% yield) and providing **10** from **9** (50%). Considering the instabilities of unprotected acetylenes such as **7** and **9**, the homo-coupling reaction was performed using silyl-protected porphyrins,[4c] **4**, **6**, **8**, and **10**, affording **11**-**14**, respectively, as deeply colored stable solids under ambient conditions.

Mass spectroscopic studies clearly support the structure of **11**-**14**.[9] The ^{1}H-NMR chemical shifts of each β-proton of the dimers are similar among **11**-**14**, and also similar to those of the corresponding protons of monomers, **4**, **6**, **8**, and **10**. This phenomenon indicates that the magnetic deshielding effect of one porphyrin on the β-proton of the other porphyrin is negligible when the two porphyrins are separated by more than one butadiyne unit, ca. 6.8 Å. Nakagawa and co-workers pointed out that the intensity of the IR-forbidden C≡C stretching mode increased with an increase in the number of acetylenes in their BAOAs.[3] A similar tendency was also observed in our system. The highest wave number of the vibration was observed in **12** ($2186\,cm^{-1}$), and this wave number became lower with an increase in the number of acetylenes, e.g., $2093\,cm^{-1}$ for **14**.

The electronic absorption spectra of the monomers having OAUs (**4**, **6**, **8**, and **10**) and the dimers (**11**-**14**) in $CHCl_3$ are shown in Figures 1a and 1b, respectively, along with that of reference compound **15**. First of all, it should be emphasized that vibration mode, which are typically observed in the absorption spectra of Nakagawa et al.'s BAOAs,[3] do not exist in the spectra of our monomers and dimers. The shapes of the absorption spectra of the monomers resemble that of **15**; however, the extension of the OAU causes a red shift of the Soret bands.[4c] For **8** and **10**, the Soret bands show weak splitting due to the excitonic coupling between the porphyrin and the OAU. In contrast, the absorption spectra of the dimers are markedly different from those of the monomers. In the dimers, the absorption spectra consist of three bands, Q(0,0)-band-like *Band-I* around $17000\,cm^{-1}$ (ca. 590 nm), Q(1,0)-band-like *Band-II* at $18000\,cm^{-1}$ (ca. 560 nm), and Soret-band-like *Band-III* at $22000\,cm^{-1}$ (ca. 450 nm). *Band-III* in the absorption spectrum of butadiyne-inserted **11** was excitonically split into two bands with $1380\,cm^{-1}$ width (Δ), as was observed for a structurally similar dimer.[4] The excitonic coupling of **12** and **13** resembles that of **11**, however, the width decreases to 1000 and $870\,cm^{-1}$, respectively. These Δ values decrease linearly with increasing length of the acetylene linkage. The split disappeared in the absorption spectrum of **14**. The full-width at half maximum of the broadened absorption spectrum of **14** is $3500\,cm^{-1}$.

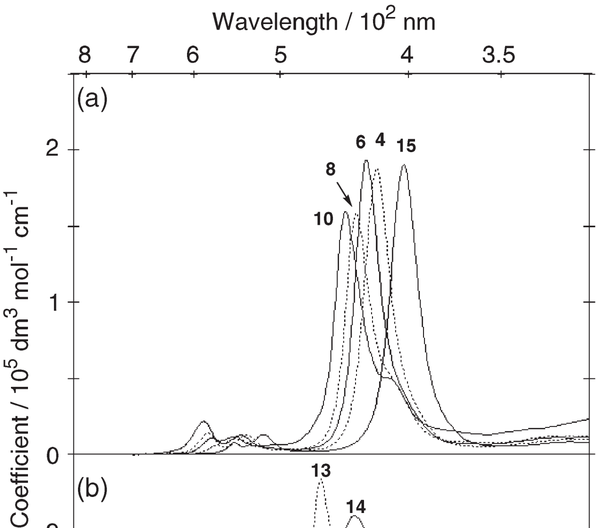


Figure 1. Absorption spectra of (a) **10** (bold solid line), **8** (bold dotted line), **6** (thin solid line), **4** (bold dotted line), and **15** (thin solid line), (b) **14** (bold solid line), **13** (bold dotted line), **12** (thin solid line), and **11** (bold dotted line) in $CHCl_3$.

With the absorption character of the monomers in mind, we make the following conclusions for the absorption spectra of the dimers. For short OAU-bridged dimers such as **12** and **13**, the main exciton interactions occur between the porphyrins.[4] For the longest OAU-bridged dimer in our series (**14**), the interaction between the excitons associated with the porphyrins is negligible. The absorption of the hexadecaoctayne part may be sufficiently stabilized to interact with the porphyrin's excitons. This interaction broadens the Soret band of **14**. The split Soret bands of **8** and **10** support this explanation. The intermediate-length OAU-bridged dimer **13** exhibits both interactions, the coupling between the two porphyrins and the coupling between the porphyrin and the dodecahexayne part.

We have systematically prepared and revealed the electronic absorption spectra of oligoalkynyl-bridged porphyrin dimers along with monomers having OAUs. We are currently working on the detailed assignment of the absorption spectra, the photoexcited state chemistry, as well as the potential use of these molecules in single-molecule-based nano science.

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9 Selected spectroscopic data are as follows. **11**: IR (KBr) 2135 ($\nu_{C\equiv C}$) cm^{-1}. **12**: IR (KBr) 2186 ($\nu_{C\equiv C}$) cm^{-1}. **13**: IR (KBr) 2144 ($\nu_{C\equiv C}$) cm^{-1}. **14**: ^{1}H-NMR ($CDCl_3$) $\delta = 9.70$ (s, 2H), 9.37 (d, $J = 4.9$ Hz, 4 H), 9.00 (d, $J = 4.6$ Hz, 4 H), 8.92 (d, $J = 4.9$ Hz, 4 H), 8.87 (d, $J = 4.6$ Hz, 4 H), 7.15 (d, $J = 2.2$ Hz, 8 H), 6.84 (t, $J = 2.2$ Hz, 4 H), 4.11 (t, $J = 6.5$ Hz, 16 H), 1.87 (m, 24 H), 0.98 (d, $J = 6.5$ Hz, 48 H) ppm; MALDI-TOF MS m/z 1915 calcd for $C_{120}H_{118}N_8Ni_2O_8$, m/z 1918; IR (KBr) 2093 ($\nu_{C\equiv C}$) cm^{-1}.

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