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One-dimensional porphyrin H-aggregates induced by solvent polarity

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ABSTRACT

A series of new porphyrin derivatives possessing the side arms of alkyl-substituted thiophene oligomer were synthesized. The effects of solvent polarity on the formation of supramolecular assembly have been studied by UV–vis absorption, fluorescence emission, and TEM measurement. The linear-shape porphyrin derivatives bearing two thiophene pentamers at *meso*-position showed the significant spectral changes in both blue-shift and band broadening of Soret bands which indicate the formation of a relatively larger porphyrin H-aggregate that occurred in nonpolar solvent such as *n*-hexane.

Supramolecular assemblies of π-conjugated systems are of increasing interest in recent years due to its potential applications for optoelectronic and photovoltaic devices.[1] Recently, much efforts have been made on porphyrin assembly which is one of the promising candidates for light-driven energy transduction systems, mimicking photophysical processes of photosynthetic organisms.[2–6] Two-dimensional character of porphyrin molecule with 22 π-electrons enables strong π–π interaction,[7] facilitating the formation of one-dimensional nanostructures such as J- and H-aggregates via side-by-side and face-to-face stacking, respectively. Recent reports clearly show that self-assembly via strong π–π stacking is a useful method to form one-dimensional supramolecular systems, consisting of hexabenzocoronene,[8] perylenediimide derivative,[9] and regioregular polythiophenes.[10] To date, a variety of supramolecular aggregates of porphyrins have been studied by employing the auxiliary intermolecular forces or functionality, reinforcing the usual π–π interactions, which are H-bonding gelators,[11,12] metal–ligand coordination,[13] LB film,[14] surfactant,[15] bicyclic guanidine,[16] and (L)-prolinium moiety.[17] However, there are few one-dimensional porphyrin H-aggregates in organic solvents using purely π–π interactions.

Porphyrin H-aggregates have potential advantages for unidirectional transport of excitation energy and electric charge along the axis of molecular stacking, which play crucial roles in electronic devices such as organic solar cell and field-effect transistor.

Herein, we report on the solvent-induced porphyrin H-aggregates where porphyrin derivatives possess the side arms of alkyl-substituted thiophene oligomer. In this synthetic strategy, thiophene oligomers play an important role in enhancing π–π interactions to form porphyrin supramolecular aggregates.

Porphyrin derivatives **9**, **10**, and **11** were prepared by using a fundamental building block **5,** which was synthesized from the coupling of hexanoyl chloride to 2,2′:6′,2″-terthiophene (**1**) to afford 5-hexanoyl-2,2′:5′,2″-terthiophene (**2**), followed by reduction by $LiAlH_4/AlCl_3$ to afford 5-hexyl-5″-2,2′:5′,2″-terthiophene (**3**). Compound **3** is converted into 5-hexyl-tributylstannyl-2,2′:5′,2″-terthiophene (**4**), and 5″-hexyl-2,2′:5′,2″-terthiophene-5-carboxaldehyde (**5**) using $BuLi/Bu_3SnCl$ and $POCl_3$/DMF, respectively (Scheme 1). Compound **8** was synthesized by condensation of 5-bromo-2,2′-bithiophene-5′-carboxaldehyde together with *meso*-pentyldipyrrolmethane (**7**). Finally, conventional synthetic processes of porphyrin have been performed to afford **9** and **10** via acid-catalyzed condensation and oxidation reactions.[18] Stille-type palladium(0)-catalyzed reaction[19] was carried out to give **11** by coupling of **4** with porphyrin derivative **8**. The porphyrin derivatives and other molecules were purified by recycling preparative size-exclusion chromatography and were fully characterized by means of ^{1}H NMR and UV–vis spectroscopy, together with MALDI-TOF-MS.[20]

To investigate the effect of solvent polarity on absorption spectral characteristic, 10 μl of high concentrated $CHCl_3$ solution of **11** is added to 5 ml of $CHCl_3$, toluene, and *n*-hexane, respectively,[21] where the concentration of each solution is adjusted to 3×10^{-6} M. The UV–vis spectrum of **11** in $CHCl_3$ showed an intense Soret band with an absorption maximum at 431.5 nm, together with relatively weak Q-band around 560.5 and 615.0 nm (Fig. 1). We found that a stable colloidal dispersion of **11** could be obtained upon decreasing polarity of solvent, from $CHCl_3$ (λ_{Soret} = 431.5 nm, full width at half-maximum (FWHM) = 1916 cm^{-1}) to *n*-hexane

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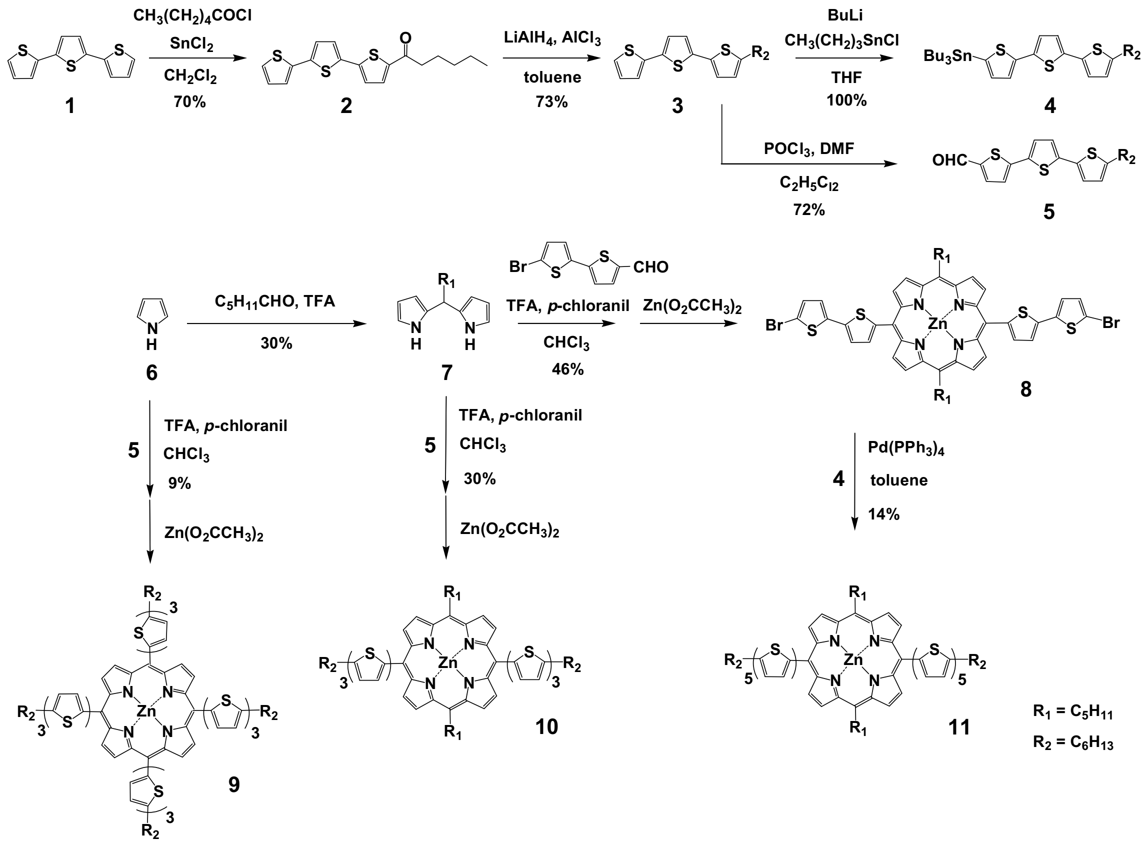

Scheme 1. Synthetic routes for porphyrin derivatives **9**, **10**, and **11**.

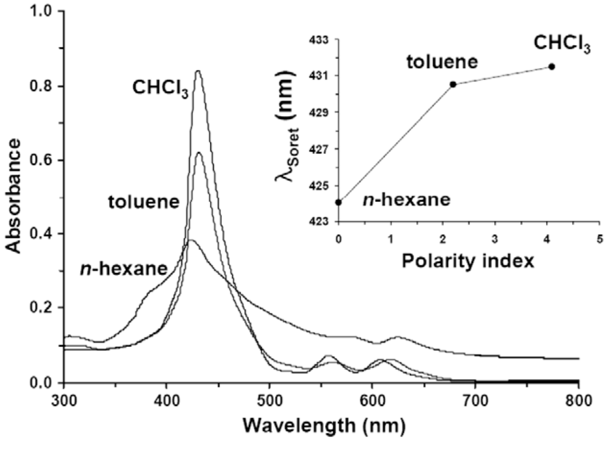

Figure 1. UV–vis spectra of **11** (3.0×10^{-6} M) in $CHCl_3$, toluene, and *n*-hexane. Inset shows blue-shift of Soret absorption peaks in each solvent.

($\lambda_{Soret} = 424.0$ nm, FWHM = 6817 cm^{-1}) via toluene ($\lambda_{Soret} =$ 430.5 nm, FWHM = 2051 cm^{-1}), where the Soret band in *n*-hexane was significantly both blue-shifted ($\Delta\lambda_{Soret} = 7.5$ nm) and broadened (ΔFWHM = 4766 cm^{-1}) relative to that of $CHCl_3$ (inset in Fig. 1). The Q-bands in the visible region for **11** were red-shifted to 575.5 and 620.5 nm in *n*-hexane. The *n*-hexane solution of **10** ($\lambda_{Soret} = 427.0$ nm, FWHM = 1781 cm^{-1}) also showed similar blue-shift ($\Delta\lambda_{Soret} = 7.0$ nm) as large as **11** but was hardly broadened (ΔFWHM = 37 cm^{-1}), compared to a $CHCl_3$ solution ($\lambda_{Soret} =$ 434.0 nm, FWHM = 1744 cm^{-1}) (S4). On the other hand, the Soret band of the *n*-hexane solution of **9** ($\lambda_{Soret} = 444.5$ nm, FWHM = 2610 cm^{-1}) was not only slightly blue-shifted ($\Delta\lambda_{Soret} = 3$ nm) but was also slightly broadened (ΔFWHM = 421 cm^{-1}) compared to a $CHCl_3$ solution ($\lambda_{Soret} = 447.5$ nm, FWHM = 2189 cm^{-1}) (S4). According to exciton theory,[22] these observations, including blue-shift and band broadening of Soret band, indicate a characteristic of the formation of H-aggregates of porphyrin derivatives **9**, **10,** and **11**. A blue-shift of Soret band is consistent with a parallel stacking of the porphyrin molecules denoted as H-aggregate, due to excitonic coupling of the electronic transitions in the porphyrin π-systems,[23] whereas the red-shift is a sign of J-aggregation formation.[24] To be highlighted, significant spectral changes of both λ_{Soret} and FWHM for **11** indicate that the formation of a relatively larger H-aggregate occurred in nonpolar solvent such as *n*-hexane than **9** and **10**.

For a further insight into the solvent-induced H-aggregation of **11**, Soret absorption bands were monitored at different $CHCl_3$/*n*-hexane ratios, where when the content of *n*-hexane increased from 0% to 80%, the blue-shift gradually increased (431.5 nm for 0%, 430.5 nm for 20%, 429.5 nm for 40%, 427.5 nm for 60%, and 427 nm for 80%), and when it reached 100% (424 nm) a dramatic increase was observed (inset A in Fig. 2). A similar trend of broadening of Soret band was also observed, for which FWHM increase with the content of *n*-hexane to be 2211 cm^{-1} for 0%, 2304 cm^{-1} for 20%, 2374 cm^{-1} for 40%, 2501 cm^{-1} for 60%, 3038 cm^{-1} for 80%, and 6817 cm^{-1} for 100% (inset B in Fig. 2).

Upon excitation at $\lambda = 400.0$ nm in $CHCl_3$, fluorescence of **11** showed the emission at 634 nm predominantly from the zinc porphyrin (Fig. 3A). However, the *n*-hexane solution showed a rather weak and blue-shifted emission at 609 nm by porphyrin, where the relatively large emissions at 506 and 537 nm were newly produced which may be attributed to the excitation wavelength scattered by hundreds of rod-like architecture of H-aggregates. It is noted that the emission at 506 and 537 nm does not result from

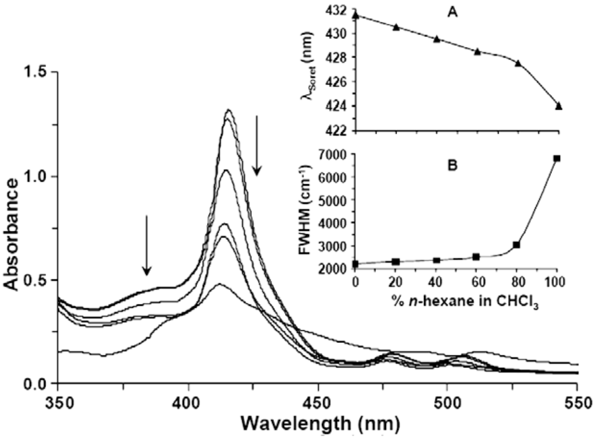

Figure 2. UV–vis spectra of **11** (7.5×10^{-6} M) in a mixture of $CHCl_3$/*n*-hexane. Inset A and B show changes of Soret absorption peaks and FWHM, respectively, upon the content of *n*-hexane in the solvent mixtures.

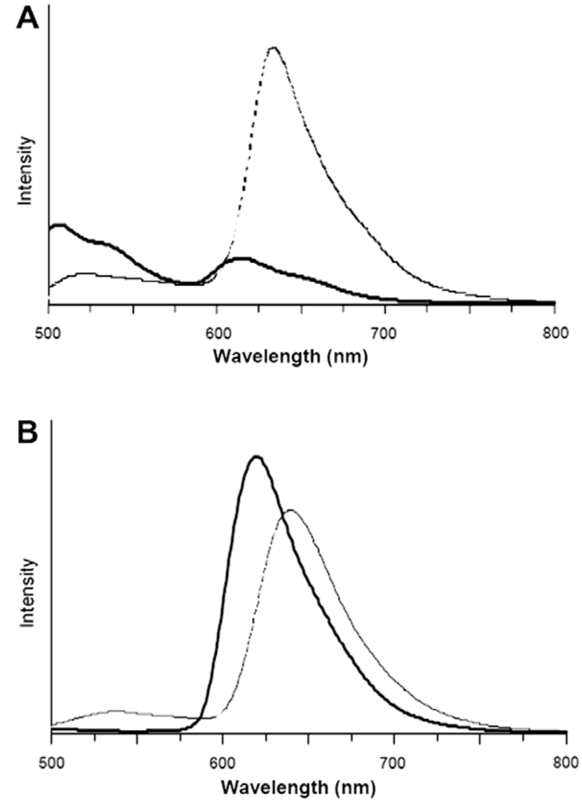

Figure 3. Fluorescence spectra of **10** (B) and **11** (A) (3.0×10^{-6} M) in $CHCl_3$ (broken line) and *n*-hexane (solid line), upon excitation at Soret absorption peak.

side arms of oligothiophene because a $CHCl_3$ solution shows no fluorescence emission at same wavelengths (Fig. 3B). In sharp contrast, **10** emitted mainly red color of fluorescence both in $CHCl_3$ (λ = 634 nm) and *n*-hexane (λ = 620 nm) without emission at shorter wavelength, indicating the formation of smaller H-aggregates than that of **11**.

From these results, it was revealed that the formation of supramolecular H-aggregates depends on the morphology of porphyrin derivatives for **9** (star-type) and **11** (linear-type), and on the length of oligothiophene units, attached to a *meso*-position of zinc porphyrin, for **10** (thiophene trimer) and **11** (thiophene pentamer). In nonpolar solvent such as *n*-hexane, which is a good solvent for alkyl side chains and a poor solvent for oligothiophene-appended porphyrin molecules, conformational transition of **11** undergo from random phase in polar solvent to a more ordered H-aggregate in order to decrease the unfavorable interaction between the solvent and aromatic main moiety.

The most directed evidence for the formation of large one-dimensional H-aggregates was given by transmission electron

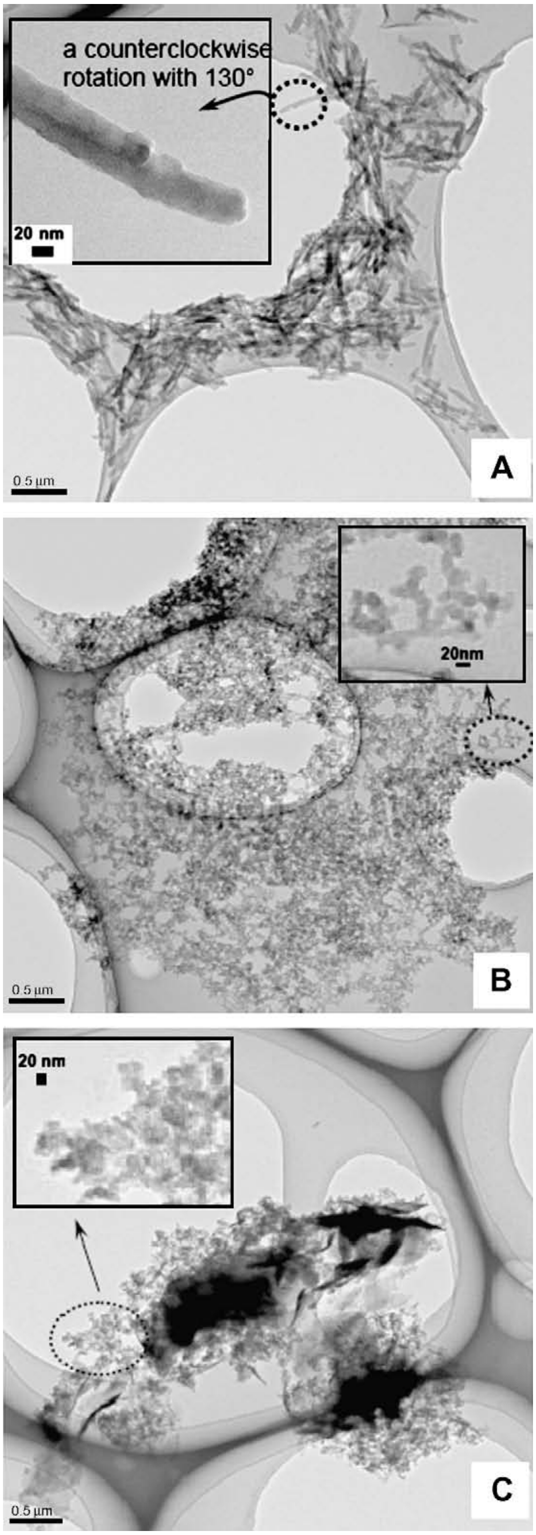

Figure 4. TEM images of **9** (C), **10** (B), and **11** (A), deposited onto the carbon-coated copper grid from *n*-hexane solution containing a small amount (0.02%) of $CHCl_3$.

microscope (TEM). Samples for the TEM experiment were prepared by drop-casting from the *n*-hexane solution (1.0×10^{-7} M) of porphyrin derivatives onto a carbon-coated copper grid. TEM images taken without a staining reagent are shown in Figure 4 for **9**, **10**, and **11**. We clearly find rod-type supramolecular architectures for **11** with 100–500 nm in length and 40–60 nm in diameter in Figure 4A. We suggest that the large dimension of 1D aggregates may result from weakly intercalated porphyrin H-aggregates via van der Waals forces between alkyl chains (Fig. 4A), which is well consistent with a significant absorption spectral change in *n*-hexane. For sharp comparison, the TEM images of **9** and **10** were recorded where spherical particles of 15–30 nm in diameter for **10** were entangled continuously (Fig. 4B). However, it is hard to see a stable ordered assembly structure for **9** (Fig. 4C). From morphology and size of structures in TEM images, significant changes in absorption spectra together with fluorescence emission profiles were reflected in the formation of large H-aggregates of **11** in *n*-hexane.

In summary, porphyrin derivatives bearing thiophene oligomer were newly synthesized and the formation of 1D supramolecular assembly has been studied by means of UV–vis absorption, fluorescence spectroscopy, and TEM measurement. Porphyrin derivative **11**, bearing two pentameric thiophenes at *meso*-position of porphyrin molecule, has been driven to form a relatively large H-aggregate by solvophobic interactions. Such a stable 1D H-aggregate of porphyrins is a promising building block for future nanoscale and for molecular electronic devices such as single-electron transistors.

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Supplementary data

Synthetic methods and characterization data (^{1}H NMR, MALDI-TOF-MS, and UV–vis) for compounds are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.09.140.

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