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Synthesis and Multistimuli-responsive Behavior of Octaethylporphyrin–Dihexylbithiophene–Dimethylaniline Triads Connected with Diacetylene Linkages

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Octaethylporphyrin–dihexylbithiophene–dimethylaniline triads were synthesized. The triads showed color change from green to yellow upon addition of trifluoroacetic acid. VT-NMR and UV–vis measurements revealed acid- and heat-driven multistimuli-response behaviors. In comparison with pyridine-connected analogs, a porphyrin–bithiophene diad moiety connected with diacetylene linkage expands the difference in basicity between dimethylaniline and pyridine.

Stimuli-responsive molecules are important because they can convert nonvisible information, such as chemical stimuli, to easily usable forms like color change. In particular, multistimuli-responsive molecules, receiving two or more kinds of stimuli, are of interest in the field of smart materials.[1] For recent examples, molecular logic gates,[2] displaying devices,[3] organogelators,[4] and responsive micelles[5] have been studied. Recently we reported acid- and heat-driven spectral changes of octaethylporphyrin–dihexylbithiophene–pyridine triads **1a** and **1b**[6] shown in Figure 1 during the course of our study of long one-dimensional extended π-conjugated systems connected with diacetylene linkages.[7]

To investigate the effect of electronic structure of the proton acceptor moiety on the stimuli-response behavior, an *N*,*N*-dimethylaminophenyl group was chosen as another proton acceptor moiety. Conjugate acids of nonsubstituted pyridine and *N*,*N*-dimethylaniline show almost the same pK_a values (5.2 and 5.1 in water, respectively), indicating their basicities are not so different. However, pyridine and aniline show a distinct difference between their electronic structures around the lone pair of the nitrogen atom. In the pyridine-connected triads **1**, the lone pair of the pyridine nitrogen is orthogonal to the orbitals of the π-conjugated system. In the triads **2** bearing an *N*,*N*-dimethylaminophenyl group instead of the pyridyl group in **1**, that of the aniline nitrogen is anticipated to overlap with the orbitals of the π-conjugated system (Figure 1) and the effective conjugation between them would influence their stimuli-response behaviors. Here we report synthesis, acid- and heat-driven spectral changes, and interesting effects of π-conjugated systems on the stimuli-response behaviors of octaethylporphyrin–dihexylbithiophene–dimethylaniline triads **2**.

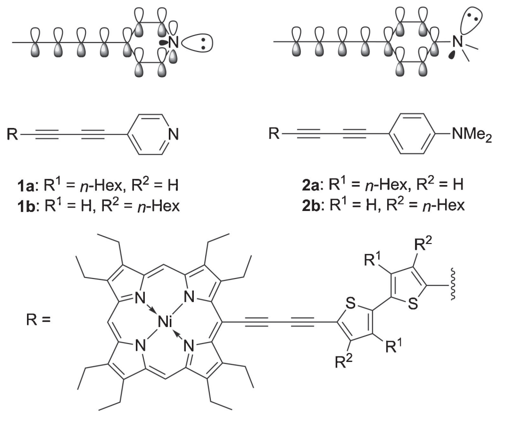
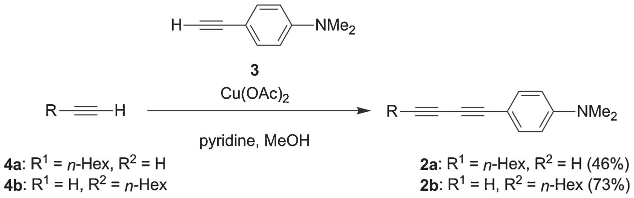


Figure 1. Frameworks of orbital orientations of a lone pair of the nitrogen atom and π-conjugated system of pyridine-connected triads **1a** and **1b** and aniline-connected ones **2a** and **2b**.

Triads **2a** and **2b** were synthesized by the Eglinton coupling[8] of 4-ethynyl-*N*,*N*-dimethylaniline (**3**) with porphyrin-connected terminal alkynes **4a** and **4b**,[7c] respectively (Scheme 1). Structures of **2a** and **2b** were confirmed by ^{1}H NMR, IR, and MS spectra.[9,10]

In the UV–vis spectra, compounds **2a** and **2b** showed characteristic absorptions of porphyrin derivative (Figure 2). The wavelengths of absorption maxima attributed to the Q and Soret bands of **2a** were 590 and 448 nm, respectively. That attributed to the Q band of **2b** was 596 nm, and the Soret band of **2b** showed maxima at 479 and 449 nm. The red shift of absorption maxima of **2b** in comparison with those of **2a** indicates that **2b** has more extended π-conjugated system than **2a** due to the higher planarity of bithiophene moiety connected in a tail-to-tail manner than that in a head-to-head manner. The presence of splitting of the Soret band of **2b** also shows high magnitude of interaction among the π-conjugated systems in **2b** through the bithiophene moiety.[7a]



Scheme 1. Synthesis of triads **2a** and **2b**. The substituent R denotes the same substituent shown in Figure 1.

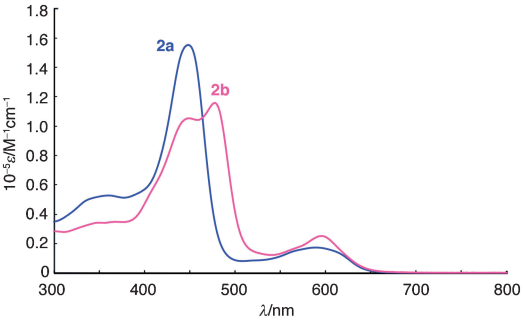


Figure 2. UV–vis spectra of **2a** and **2b** in $CHCl_3$.

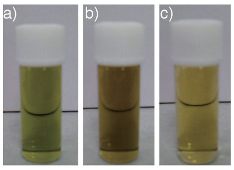


Figure 3. Photographs of **2a** in $CHCl_3$ with (a) no TFA, (b) low TFA concentration, and (c) high TFA concentration.

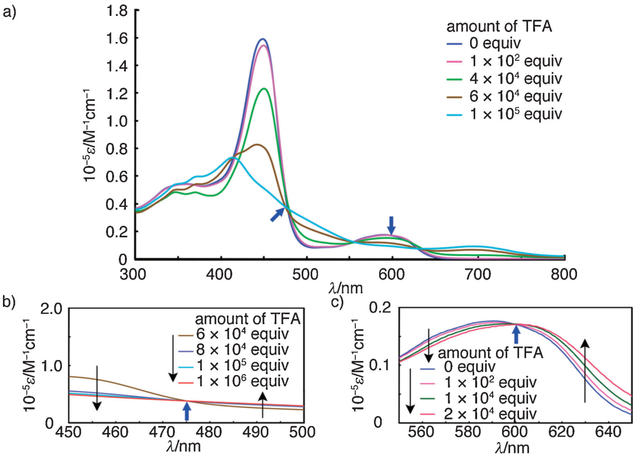


Figure 4. Change of UV–vis spectra of **2a** in $CHCl_3$ by addition of TFA. Isosbestic points are denoted by blue block arrows.

Addition of trifluoroacetic acid (TFA) to a chloroform solution of **2a** and **2b** gave color change. The solution color of **2a** and **2b** turned from green to yellow with increasing amount of TFA (Figure 3). In the UV–vis spectra of **2a** (3.4 µM) in $CHCl_3$, slight red shift of absorption occurred upon addition of TFA until the amount of acid reached 2×10^4 equiv (Figure 4). In the region of this amount of acid, an isosbestic point was found at 600 nm. Upon addition of more acid the spectra was drastically changed. In the region from 6×10^4 to 1×10^6 equiv of acid, initial Soret and Q bands decreased and new absorptions appeared at 700 and 500 nm. Another isosbestic point appeared at 475 nm during this change. These changes suggest that at least two equilibria exist in the reaction of **2a** with TFA. In the ^{1}H NMR spectra of **2a** (1.8 mM) in tetrachloroethane-d_2, two different changes were observed by addition of TFA-*d* (Figure 5). One change was downfield shift of signals at 6.6 and 7.4 ppm assigned to aromatic protons of the dimethylaminophenyl moiety, which was completed upon addition of 10 equiv of TFA-*d*. The other change was broadening of the signals at 9.4 ppm assigned to the *meso*-protons of the porphyrin moiety, which showed more sluggish change than the former. The former indicates protonation of the dimethylamino group, and the latter is thought to be caused by interaction between porphyrin moiety and the acid (Scheme 2).[12] Addition of triethylamine to the mixture of **2a** and trifluoroacetic acid gave recovery of the initial peaks of **2a** in the UV–vis and ^{1}H NMR spectra. **2b** showed similar behavior to **2a** in the ^{1}H NMR and UV–vis spectra (Figures S3[9] and S4[9]).[13]

To investigate the effect of electronic structure of the proton acceptor moiety on the basicity, protonation behaviors of **2a** and **2b** were compared by ^{1}H NMR with pyridine-connected analogs

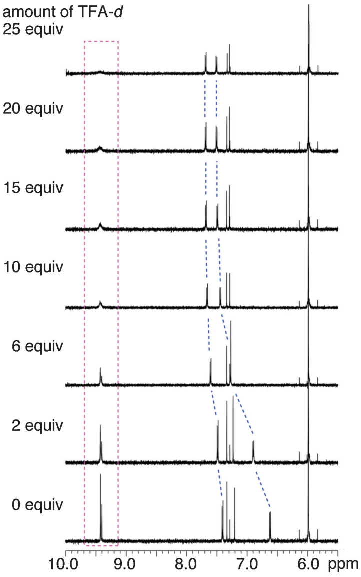
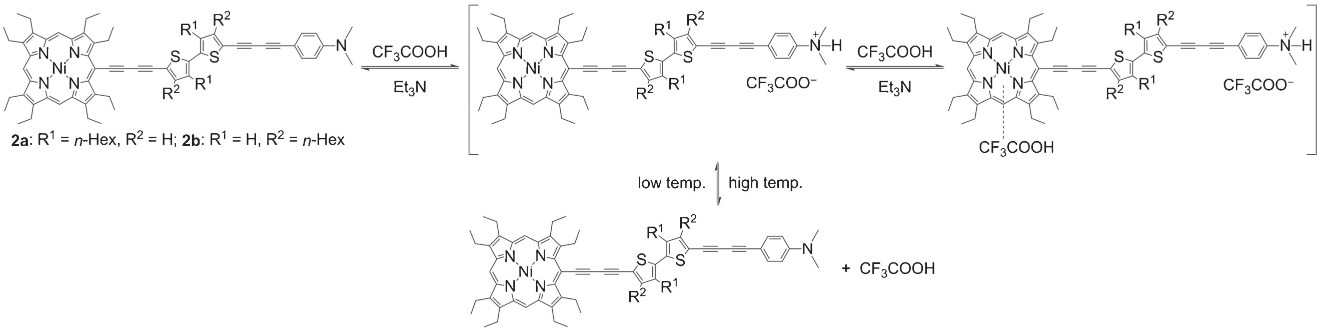


Figure 5. Change of ^{1}H NMR spectra of **2a** in $C_2D_2Cl_4$ by addition of TFA-*d* (300 MHz).[11]

1a and **1b**. Both **2a** and **2b** required 10 equiv of TFA to complete the protonation of the aniline moiety, observed in ^{1}H NMR as the first-step change, while 1.1 and 1.2 equiv of TFA were necessary for **1a** and **1b**,[6b] respectively, under the same condition. Interestingly, these results suggest that the gap of basicity between dimethylaminophenyl and pyridyl groups is expanded and made observable by substitution with a long extended π-conjugated system. The π-conjugated system is believed to reduce basicity of the lone pair of the aniline nitrogen of **2** by effective conjugation.

Heat-driven responses of **2a** and **2b** were also different from those of **1a** and **1b**. In the VT-^{1}H NMR spectra of **2a** and **2b** with 25 equiv of TFA-*d* in tetrachloroethane-d_2, elevation of the temperature afforded upfield shifts of the signals assigned to aromatic protons of the dimethylaminophenyl moiety and sharpening of the signals assigned to *meso*-position protons (Figures 6 and S5[9]). Those changes suggest that deprotonation of **2**–TFA complex and regeneration of nonprotonated **2** occur at high temperature (Scheme 2). The UV–vis spectra supported this assumption because reappearance of absorption maxima of nonprotonated **2a** was observed at high temperature despite the presence of excess TFA (Figure 7). In contrast, pyridine derivative **1a** showed only sharpening of the *meso*-proton and no shift of aromatic proton, indicating its TFA complex was stable even at high temperature and no deprotonation occurred.[6] The basicity of **2** is believed to be weak enough to dissociate the TFA complex upon escape of the TFA from the solution phase as a vapor at high temperature.

In conclusion, porphyrin derivatives **2** bearing a long-one-dimensional-extended π-conjugated system and dimethylaminophenyl group as a proton acceptor were synthesized by utilizing transition-metal-catalyzed cross-coupling reactions. Drastic color changes and multistimuli-responsive behavior of **2** in response to both acid and temperature were observed. Through comparison of acid–base reaction behaviors of **2** with those of pyridine-connected analog **1**, the long-one-dimensional-



Scheme 2. Hypothetical states of equlibria of mixture of **2** and TFA.

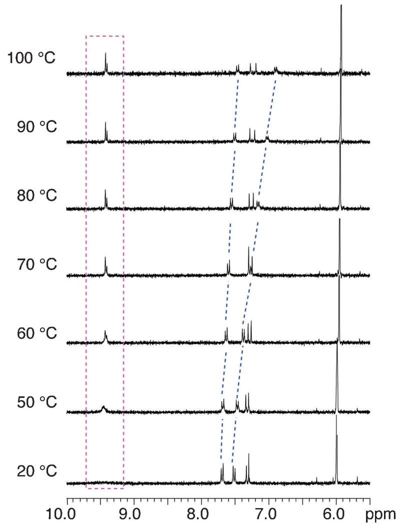


Figure 6. VT-^{1}H NMR spectra of **2a** with 25 equiv of TFA-*d* in $C_2D_2Cl_4$ (300 MHz).[11]

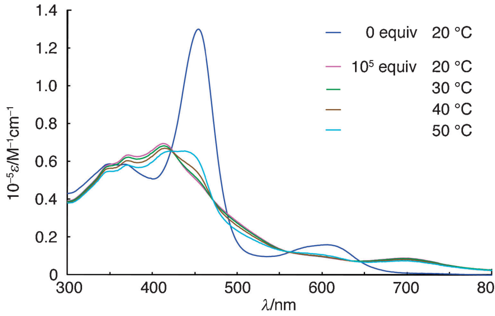


Figure 7. VT-UV–vis spectra of **2a** with and without TFA in $CHCl_3$.

extended π-conjugated system was found to expand and make observable the gap of basicity among proton acceptor moieties. Further tuning of multistimuli-responsive behaviors such as colors and detecting target molecules based on the study of these unique porphyrin derivatives are now underway.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
10 ^{1}H NMR spectra of **2a** and **2b** are shown in Figures S1[9] and S2.[9]
11 A signal observed at 6.0 ppm is attributed to C_2HDCl_4.
12 An unsubstituted octaethylporphyrin nickel(II) complex also shows reversible broadening of a signal assigned to the *meso*-proton in the ^{1}H NMR spectra upon addition of excess TFA.
13 Evaluation of effects of the difference at the bithiophene moiety between **2a** and **2b** on the acid-response behavior is now underway.