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Synthesis of Novel Porphyrin Arrays Directly-linked through the *Meso*-carbons

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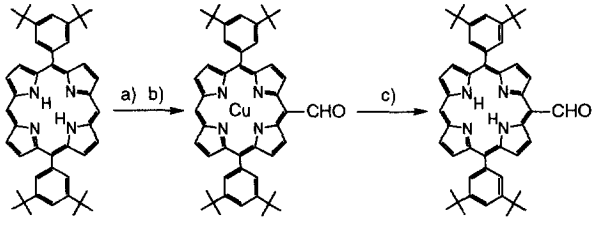
Abstract : Novel dimeric and trimeric arrays of free-base porphyrins directly-linked through their *meso*-carbons without any spacer were synthesized and characterized. The significant spectral change occurred in the absorption spectra of these arrays compared with that of the reference monomer, indicating strong electronic interactions in spite of the orthogonal geometry between the adjacent porphyrins.

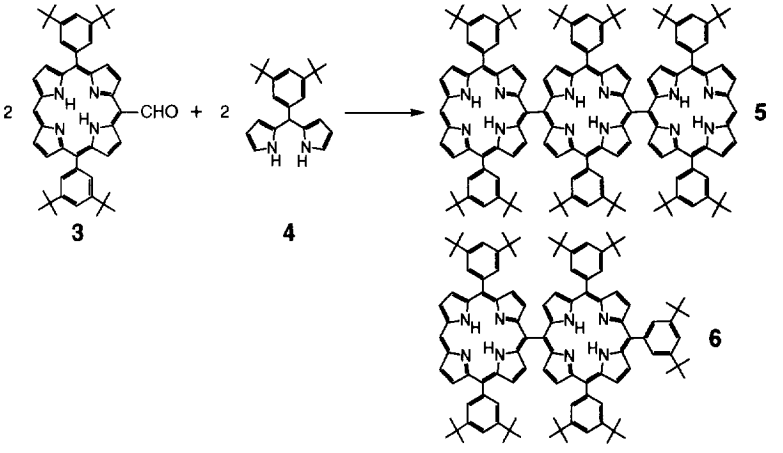
Multichromophoric systems based on porphyrins have considerably attracted wide attention related to an elucidation of electron and energy transfers in the natural photosynthetic systems.[1] In recent years, applications of the molecular systems have been extended to the area of supramolecular photonics.[2] Especially, a great number of porphyrin arrays have been synthesized by various bridgings between porphyrin rings and their photophysical processes were investigated.[3-9] Among them, the porphyrin arrays with diphenylethyne spacers reported by Lindsey et al.[7] are excellent functional models for the light-harvesting complex of the bacterial system. For the design of the porphyrin array, electronic interaction between the porphyrin rings has essential importance. A series of ethynyl-bridged porphyrin arrays synthesized by Therien et al.[8] exhibited interesting absorptive and emissive properties based on the strong electronic interaction between the porphyrin rings, and it is expected that the porphyrin arrays will be used for efficient energy and electron transfer systems. In order to obtain the porphyrin array in which the π-electron systems are strongly interacted, direct linking of the porphyrin rings is considered to be one of the best methods. With this in mind, we synthesized the novel porphyrin arrays in which the porphyrin rings are directly-linked through their *meso*-carbons without any spacer.

The synthetic route to the porphyrin trimer is shown in Scheme 1 and 2. Metalation of 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin **1**[10] with copper acetate monohydrate followed by Vilsmeier formylation gave copper *meso*-formylporphyrin **2**. Subsequently, demetalation of **2** with 10% H_2SO_4 / trifluoroacetic acid (TFA) led to free-base *meso*-formylporphyrin **3**. *Meso*-(3,5-di-*tert*-butylphenyl)dipyrrylmethane **4** was obtained by acid-catalyzed



1 **2** **3**

Scheme 1. Reagents and conditions: a) $Cu(OAc)_2 \cdot H_2O$, CH_3OH-$CHCl_3$, reflux, 2.5h. b) (i) $POCl_3$, DMF, 1,2-dichloroethane, ca. 60°C, 2h; (ii) aq. NaOAc, ca. 60°C, 2h. c) 10% H_2SO_4 / TFA, r.t., 5min.



Scheme 2. Reagents and conditions: (i) BF_3·Et_2O, $CHCl_3$, r.t.; (ii) chloranil, r.t.

condensation of 3,5-di-*tert*-butylbenzaldehyde with excess pyrrole in the absence of solvent according to the reported procedure.[11] The porphyrin trimer **5** was synthesized by acid-catalyzed [2+2]-condensation between **3** and **4** followed by oxidation with chloranil. The obtained trimer **5** was characterized by UV-vis, ^{1}H NMR and FAB mass spectra.[12] The yield of this porphyrin trimer **5** was low (0.5% yield) because of the steric hinderance at the *meso*-position of the porphyrin ring. In the present reaction condition, *meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin and unexpected porphyrin dimer **6** (4% yield) were also obtained.[13] This result suggests that the pyrrylcarbinyl cation was formed from dipyrrylmethane[14] and reacted with *meso*-formylporphyrin.

The absorption spectra of the dimer **6** and the trimer **5** in CH_2Cl_2 are shown in Figure 1. It is apparent that the direct linkage at the *meso*-carbons of the porphyrin rings perturbed the spectra of the porphyrin arrays. At the Soret bands of both **6** and **5**, two intense absorption peaks are observed. The lower energy absorption peak of the

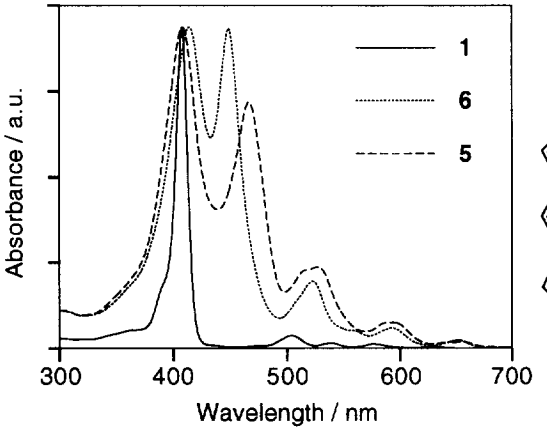


Figure 1. Absorption spectra recorded in CH_2Cl_2 for monomer **1**, dimer **6**, and trimer **5**. The absorbance is normalized at the maximum intensity.

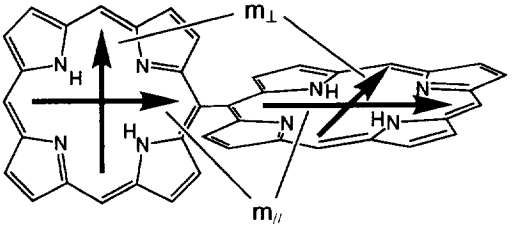


Figure 2. Transition dipole moments for the present porphyrin arrays.

Soret region of the trimer **5** are at longer wavelength as compared with the corresponding absorption peak of the dimer **6**, whereas the higher energy absorption peaks are not so shifted and at nearly the same wavelength as the Soret peak of the monomer **1**. Such absorption splittings and shifts in the Soret regions can be explained by Kasha's molecular exciton model.[15,16] The lower energy absorption peaks of these arrays originate from the coupling of the transition dipole moments along a line joining the porphyrin centers ($m_{//}$). On the other hand, the transition dipole moments perpendicular to a line joining the porphyrin centers ($m_{\perp}$) don't contribute to the blue shift of the higher energy absorption peaks as compared with the Soret peak of the monomer, indicating that the adjacent porphyrin rings have an orthogonal geometry as shown in Figure 2. The Q bands of **6** and **5** are significantly red-shifted as compared with those of the monomer **1**. The fluorescence maxima of **6** (λ_{max} = 661, 724 nm) and **5** (λ_{max} = 666, 727 nm) are also red-shifted from those of the monomer **1** (λ_{max} = 638, 700 nm) as shown in Figure 3. The red shifts of the transitions to the S_1 states in these arrays imply significant electronic interactions between the porphyrin rings.[17]

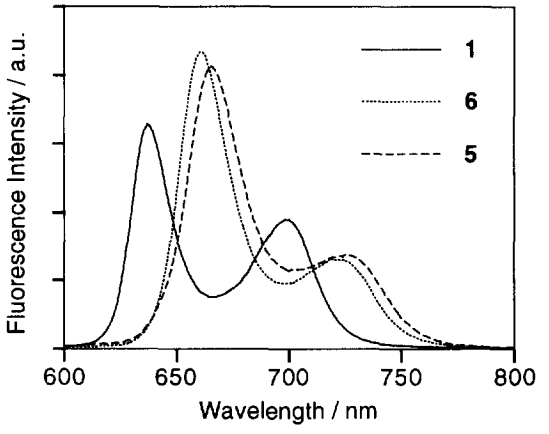


Figure 3. Fluorescence spectra recorded in CH_2Cl_2 for monomer **1**, dimer **6**, and trimer **5**.

The present porphyrin arrays with direct linkage at the *meso*-carbons exhibited strong electronic interactions in spite of the orthogonal geometry between the adjacent porphyrin rings. Various multi-porphyrin systems with the analogous interactions could be synthesized by the similar routes. The investigations of the detailed photophysical properties of these porphyrin arrays are in progress.

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10. Spectral data for monomer **1**: UV-vis (CH_2Cl_2) λ_{max} (rel ε) 408 (1.000), 504 (0.039), 540 (0.016), 577 (0.013), 631 nm (0.005). ^{1}H NMR (400 MHz, $CDCl_3$) δ -3.02 (s, 2H, N-H), 1.58 (s, 36H, *tert*-butyl), 7.84 (t, 2H, *p*-phenyl-H), 8.15 (d, 4H, *o*-phenyl-H), 9.14 (d, 4H, β-H), 9.40 (d, 4H, β-H), 10.32 (s, 2H, *meso*-H). FAB HRMS : *m/z* 686.4334 (M^+), calcd for $C_{48}H_{54}N_4$ 686.4348.
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12. Spectral data for trimer **5**: UV-vis (CH_2Cl_2) λ_{max} (rel ε) 409 (1.000), 467 (0.767), 518 (sh), 527 (0.253), 594 (0.080), 645 (0.019), 656 nm (0.020). ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.30 (s, 4H, N-H), -1.57 (s, 2H, N-H), 1.33 (s, 36H, *tert*-butyl), 1.49 (s, 72H, *tert*-butyl), 7.58 (t, 2H, *p*-phenyl-H), 7.75 (t, 4H, *p*-phenyl-H), 8.04 (d, 4H, *o*-phenyl-H), 8.11 (d, 4H, β-H), 8.13 (d, 8H, *o*-phenyl-H), 8.23 (d, 4H, β-H), 8.62 (d, 4H, β-H), 8.74 (d, 4H, β-H), 9.12 (d, 4H, β-H), 9.45 (d, 4H, β-H), 10.37 (s, 2H, *meso*-H). FAB HRMS : *m/z* 2055.70 (M^+), calcd for $C_{144}H_{158}N_{12}$ 2055.27.
13. Spectral data for dimer **6**: UV-vis (CH_2Cl_2) λ_{max} (rel ε) 415 (1.000), 449 (0.994), 523 (0.208), 557 (sh), 593 (0.063), 652 nm (0.025). ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.35 (s, 2H, N-H), -2.11 (s, 2H, N-H), 1.42 (s, 36H, *tert*-butyl), 1.45 (s, 36H, *tert*-butyl), 1.56 (s, 18H, *tert*-butyl), 7.68 (t, 2H, *p*-phenyl-H), 7.72 (t, 2H, *p*-phenyl-H), 7.82 (t, 1H, *p*-phenyl-H), 8.03 (d, 2H, β-H), 8.06 (d, 4H, *o*-phenyl-H), 8.10 (d, 4H, *o*-phenyl-H), 8.13 (d, 2H, β-H), 8.14 (d, 2H, *o*-phenyl-H), 8.59 (d, 2H, β-H), 8.67 (d, 2H, β-H), 8.92 (d, 2H, β-H), 8.96 (d, 2H, β-H), 9.10 (d, 2H, β-H), 9.43 (d, 2H, β-H), 10.35 (s, 1H, *meso*-H). FAB HRMS : *m/z* 1559.0138 (M^+), calcd for $C_{110}H_{126}N_8$ 1559.0105.
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