Communication

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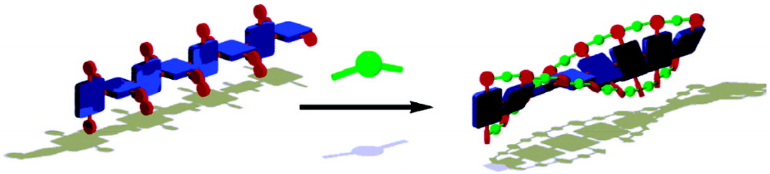
J. Am. Chem. Soc., **2005**, 127 (2), 534-535• DOI: 10.1021/ja043428x • Publication Date (Web): 23 December 2004



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Helicity Induction and Two-Photon Absorbance Enhancement in Zinc(II) Meso−Meso Linked Porphyrin Oligomers via Intermolecular Hydrogen Bonding Interactions

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In nature, helical biopolymers such as DNA or α-helix of polypeptides play important roles in providing highly developed information that is crucial to living systems. Extensive efforts thus have been directed toward helicity induction in synthetic polymers for exploration of novel properties and functions that are difficult to attain without helicity.[1−3] Porphyrin, known as a stable pigment with large absorbance and tunable electrochemical and optical properties, is a promising molecular backbone to form such helical polymers, although there are only a few reports on helical porphyrin arrays.[4]

Here we report a new strategy of helicity induction in meso-meso linked porphyrin oligomers by clipping *meso*-aryl substituents with hydrogen bonding between carboxyl groups and a cyclic urea guest. Meso-meso linked porphyrin arrays are an intriguing structural motif, since they can be coupled to extremely long arrays and the electronic interaction between neighboring porphyrins is only modest due to averaged perpendicular conformation[5] but can be enhanced by a decrease in the dihedral angle.[6] Meso-meso linked porphyrin oligomers **Z*n*$_H$ (*n*** $= 2, 3, 4,$ and 8**)** were synthesized via Ag(I)-promoted coupling of a porphyrin monomer **Z1$_{Me}$** followed by hydrolysis of the ester groups (Chart 1 and Supporting Information [SI]). **Z*n*$_H$** were soluble in toluene or chloroform containing 10% THF, in which their ^{1}H NMR and absorption spectra showed no proof of aggregation. When the guest molecule **G** was added to a solution of **Z*n*$_H$** in toluene/THF (9:1), absorption spectral changes characteristic of the dihedral angle decrease were observed (SI).[6] This is contrast to the case of **Z*n*$_{Me}$** that showed no spectral change with **G.** The typical absorption spectral changes for **Z8$_H$** are shown in Figure 1. Upon addition of **G**, split Soret bands of **Z8$_H$** at 419 and 508 nm and Q-band at 587 nm decreased and new bands at 532, 610, and 675 nm , respectively, increased. The appearance of a low-energy band at 675 nm indicates the lowering of S$_1$-state through enhanced electronic interaction. Along with these changes, the fluorescence spectra exhibit systematic changes such as red shifts and increased fluorescence quantum yields (Φ_F) (Table 1 and SI). Curiously, complexation with **G** led to roughly doubled Φ_F.

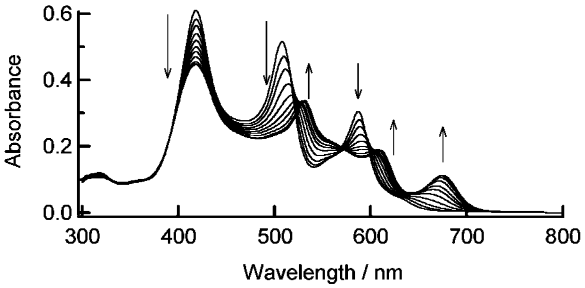


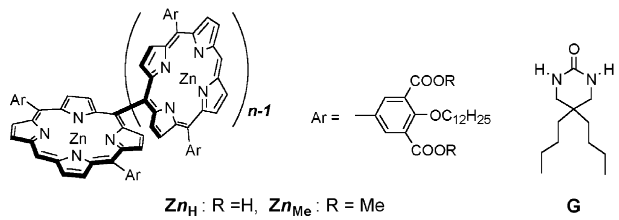
Figure 1. Absorption spectral changes of **Z8$_H$** upon addition of **G** in toluene/THF (9:1). [**Z8$_H$**] $= 1.0 \times 10^{-6}$ M, $0 <$ [**G**] $< 1.0 \times 10^{-3}$ M.

Table 1. Fluorescence Quantum Yield[a] (Φ_F) of **Z*n*$_H$** and **Z*n*$_H$-G**

	$\Phi_F(\lambda_{max}/nm)$		$\Phi_F(\lambda_{max}/nm)$
Z2$_H$	0.029 (664)	**Z2$_H$-G**	0.045 (655)
Z3$_H$	0.040 (645)	**Z3$_H$-G**	0.063 (670)
Z4$_H$	0.048 (650)	**Z4$_H$-G**	0.087 (683)
Z8$_H$	0.062 (653)	**Z8$_H$-G**	0.111 (698)

[a] In toluene/THF (9:1). Number in parentheses indicates a peak position.

Chart 1. Structures of **Z*n*$_H$**, **Z*n*$_{Me}$**, and **G**



The addition of **G** to **Z*n*$_H$** also caused low-frequency shifts of ca. 20 cm^{-1} for carbonyl stretching, indicating the hydrogen bonding between the carboxylic groups and **G**. ^{1}H NMR titration studies indicated downfield shifts of the β-pyrrolic protons and the *meso*-aryl protons, which are consistent with decreases both in the dihedral angles between neighboring porphyrins and the tilting angles of the *meso*-aryl groups (SI).[6] The stoichiometries of the **Z*n*$_H$-G** complexes were respectively determined to be 1:2, 1:4, and 1:6 for **Z2$_H$**, **Z3$_H$**, and **Z4$_H$** from the Job's plot analysis, hence indicating full complexation (SI).

Complementary hydrogen-bonding interactions of the carboxylic acid groups of **Z*n*$_H$** with **G** lead to a helical conformation. The energy-minimized structure of **Z2$_H$-G** was calculated by the DFT method at the B3LYP/6-31G** level to have a dihedral angle of 72° between porphyrins and a tilting angle of 58° of the *meso*-aryl groups, and hydrogen-bonding distances of $\underline{N}$H- - -$\underline{O}$ (2.9 Å) and $\underline{O}$H- - -$\underline{O}$ (2.6 Å). These results lead to **Z8$_H$-G** structure shown in Figure 2, in which the significant tilting of the *meso*-aryl group requires hydrogen-bonding networks along the array to keep each porphyrin ring held in a regular one-handed helical arrangement.

These porphyrin arrays are applicable for chirality amplification, since hydrogen-bonding interactions are dynamic in nature and local chiral structural information can be transmitted along the whole

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10.1021/ja043428x CCC: $30.25 © 2005 American Chemical Society

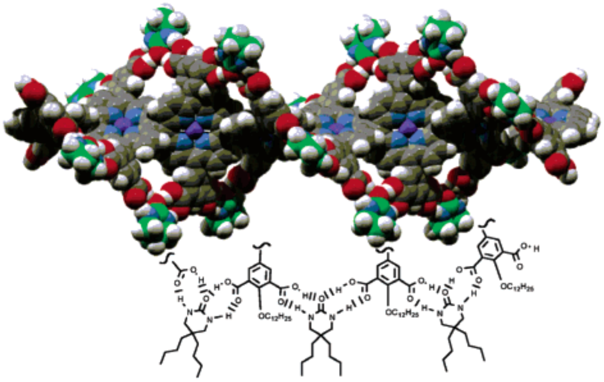

Figure 2. Energy minimized structure of $\mathbf{Z8_H}$-$\mathbf{G}$. Alkyl and alkoxy chains of $\mathbf{Z8_H}$ and **G** are omitted for clarity. Carbon atoms of **G** are shown as green. Expected hydrogen bonding network is also shown.

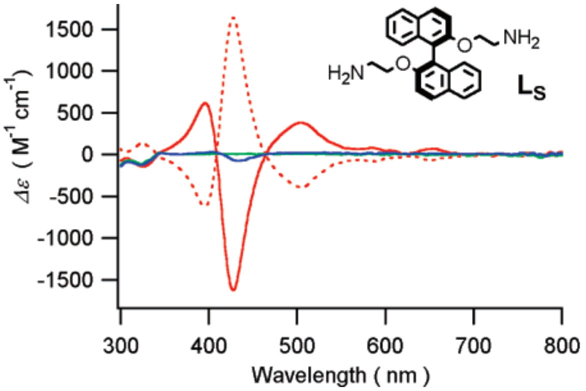

Figure 3. CD spectra of $\mathbf{Z8_H}$-$\mathbf{G}$ (red), $\mathbf{Z8_H}$ (blue), and $\mathbf{Z8_{Me}}$ (green) in the presence of $\mathbf{L_S}$ (solid line) or $\mathbf{L_R}$ (broken line). [**L**] = 1.4 × 10^{-5} M, [$\mathbf{Z8_H}$] and [$\mathbf{Z8_{Me}}$] = 0.9 μM.

array through the hydrogen-bonding interaction. Among many chiral diamines examined, we found that 2,2′-bis-(2-aminoethoxy)-1,1′-binaphthyl ($\mathbf{L_R}$ or $\mathbf{L}_S$, Figure 3) was most effective for this purpose. When $\mathbf{L_S}$ or $\mathbf{L_R}$ was added to a solution of $\mathbf{Z}\boldsymbol{n}_\mathbf{H}$-$\mathbf{G}$, the CD spectrum of the resulting solution displayed strong Cotton effects. The opposite Cotton effects were obtained for the diamine of opposite chirality. The intensity of Cotton effects in $\mathbf{Z}\boldsymbol{n}_\mathbf{H}$-$\mathbf{G}$ complex was much larger than $\mathbf{Z}\boldsymbol{n}_\mathbf{H}$ alone or $\mathbf{Z}\boldsymbol{n}_\mathbf{Me}$, indicating the importance of preorganized helical structures for large Cotton effects. The Cotton effect in terms of $g_{\mathrm{abs}} = \Delta\epsilon/\epsilon$ in the presence of $\mathbf{L_S}$ became larger for longer arrays; $g_{\mathrm{abs}} = -1.0 \times 10^{-3}$, -2.2×10^{-3}, -2.4×10^{-3}, and -3.1×10^{-3} for $\mathbf{Z2_H}$-$\mathbf{G}$, $\mathbf{Z3_H}$-$\mathbf{G}$, $\mathbf{Z4_H}$-$\mathbf{G}$, and $\mathbf{Z8_H}$-$\mathbf{G}$, respectively. Interestingly, the highest Cotton effect was observed at ca. [$\mathbf{L_S}$] = 1.5 × 10^{-5} M for $\mathbf{Z8_H}$-$\mathbf{G}$, where the number of $\mathbf{L_S}$ coordinated with the zinc(II) atom of $\mathbf{Z8_H}$-$\mathbf{G}$ has been estimated to be one or less on the basis of the association constant (4.1 × 10^3 M^{-1}) of $\mathbf{L_S}$ with $\mathbf{Z2_{Me}}$. These results suggest that not full but partial or minimum coordination of $\mathbf{L_S}$ can induce one-handed helical porphyrin arrays. Another interesting observation is a chirality memory effect. Upon addition of an equivalent amount of $\mathbf{L_R}$ to a solution of $\mathbf{Z8_H}$-$\mathbf{G}$ and $\mathbf{L_S}$, the Cotton effect around 320 nm due to the binaphthyl moiety was exactly canceled out, but the Cotton effect at 429 nm due to the porphyrin array, although the Δε value was decreased from 1600 $\mathrm{M^{-1}cm^{-1}}$ to ca. 1100 $\mathrm{M^{-1}cm^{-1}}$, was still observed, and its intensity remained upon further addition of $\mathbf{L_R}$ or $\mathbf{L_S}$ (SI). These results suggested substantial stability of a chiral conformation of the helical porphyrin array once formed. Such a chirality memory effect was not observed for shorter arrays $\mathbf{Z3_H}$-$\mathbf{G}$ and $\mathbf{Z4_H}$-$\mathbf{G}$, probably due to insufficient kinetic stability of the helix.

Finally, we examined the two-photon absorption (TPA) properties of these helical arrays. Organic molecules with large TPA values have attracted considerable attention due to their potential applications including 3-D optical memory and fabrication, photodynamic therapy, and optical limiting.[7] The TPA spectra were measured by an open-aperture *Z*-scan method with wavelength-tunable 120-fs pulses. While the TPA cross section $\delta^{(2)}$ values were small (ca. 10^2 GM or less) at 800 nm for $\mathbf{Z}\boldsymbol{n}_\mathbf{Me}$ and $\mathbf{Z}\boldsymbol{n}_\mathbf{H}$ without **G**, those of the helical array were found to be much larger; 4500, 9600, 11800, and 12800 GM for $\mathbf{Z2_H}$-$\mathbf{G}$, $\mathbf{Z3_H}$-$\mathbf{G}$, $\mathbf{Z4_H}$-$\mathbf{G}$, and $\mathbf{Z8_H}$-$\mathbf{G}$, respectively (SI). The enhanced TPA values can be ascribed to increased electronic interactions between porphyrins in the helical structures. These TPA values are comparable to those of *meso*-alkynyl-conjugated porphyrin arrays.[8]

In summary, nonhelical meso−meso linked porphyrin arrays can be made helical by host−guest hydrogen-bonding interactions, as evinced by the absorption and fluorescence spectra that are distinctly altered from those of nonhelical arrays. In addition, the helical arrays exhibit the chirality amplification and memory and enhanced TPA values.

Supporting Information Available: Experimental details for syntheses and characterizations of $\mathbf{Z}\boldsymbol{n}_\mathbf{Me}$, $\mathbf{Z}\boldsymbol{n}_\mathbf{H}$, and **L**; UV-vis, CD, and ^{1}H NMR titration experiments and Job's plots, and TPA spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA043428X