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First optical resolution of *meso–meso* linked diporphyrin

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Abstract

meso–meso Linked diporphyrin was separated by chiral HPLC in its optically pure and thermally stable forms, indicating a high rotation barrier around the *meso–meso* linkage. Its CD spectrum provided rich information on the absorption characteristics of *meso–meso* linked diporphyrin. © 2000 Elsevier Science Ltd. All rights reserved.

Recently, several groups including us reported the syntheses of directly *meso–meso* linked diporphyrins and oligoporphyrins independently.[1,2] These molecules exhibit unique optical and electrochemical properties arising from their direct *meso–meso* connection. For example, electronic interactions are rather modest in the ground-state probably due to the averaged perpendicular conformation, but are enhanced in the excited state.[3] The split Soret bands of *meso–meso* linked porphyrin arrays can be qualitatively explained by the exciton coupling theory on the basis of averaged perpendicular conformation.[1,3,4] In addition, the expected perpendicular conformation allows a very efficient intramolecular state-to-state excitation energy-transfer reaction in the corresponding hybrid metal complex with a sub-picosecond rate constant in spite of very close spatial proximity.[5] Information on rotational barrier around the *meso–meso* bond is indispensable for understanding these phenomena. A chiral *meso–meso* linked diporphyrin will be very useful in examining the rotational barrier. Here we report the first optical separation of chiral *meso–meso* linked diporphyrin.

When the *meso–meso* linkage has a large rotational barrier, *meso–meso* linked Zn(II) diporphyrin formed from Zn(II) porphyrin bearing different aryl groups at 5- and 15-positions should be chiral (Scheme 1), and the corresponding *meso–meso* linked Zn(II) triporphyrin can be separated into diastereomers, *meso* and *dl*-pair. We employed 5-(3,5-di-*tert*-butylphenyl)-15-(2,6-dimethoxy)phenyl Zn(II) porphyrin **1** as the starting porphyrin monomer and the *meso–meso* coupling was performed by the Ag(I)-promoted oxidation method (1.5 equiv. of $AgPF_6$ in $CHCl_3$ at room temperature, Scheme 2).[1a] Subsequent separation by size exclusion column chromatography gave dimer **2** (30%), trimer **3** (15%) and higher oligomers (14%) along with the

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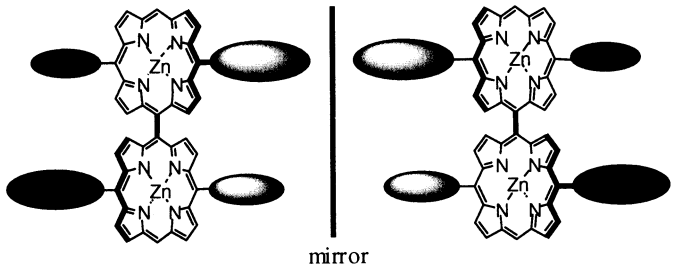
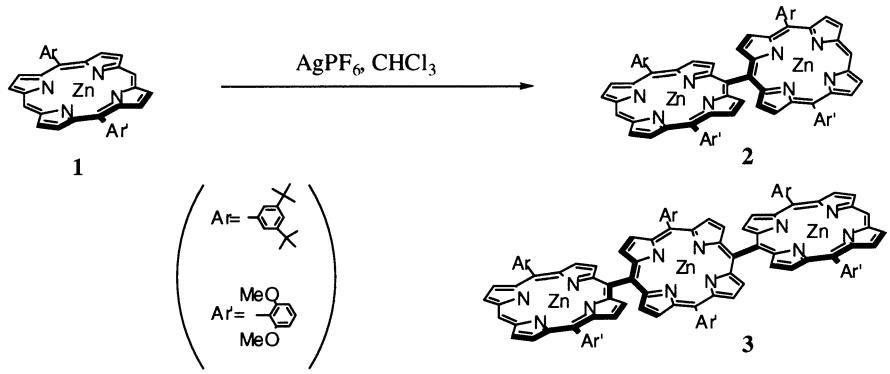
recovery of **1** (40%). All new compounds were fully characterized by 500 MHz ^{1}H NMR, FABMS, UV–vis, and fluorescence measurements.[6]



Scheme 1.



Scheme 2.

The ^{1}H NMR spectrum of **2** showed two signals for the methoxyl groups at 3.44 and 3.46 ppm and two signals for the *tert*-butyl groups at 1.42 and 1.43 ppm at room temperature in DMSO-d_6, indicating that free rotation is prohibited for *meso*-(2,6-dimethoxyphenyl) bond, *meso*-(3,5-di-*tert*-butylphenyl) bond, and *meso–meso* bond. Variable temperature ^{1}H NMR revealed that the signals of the *tert*-butyl groups were coalescenced at about 363 K, but those of the methoxyl groups were not coalescenced even at 423 K. This difference can be ascribed to their different rotational barriers. Observation of the distinct two signals for the methoxyl protons at high temperature requires the high rotational barriers for both *meso*-(2,6-dimethoxyphenyl) bond and *meso–meso* bond, since free rotation of either bond should result in the coalescence. On the other hand, the observed coalescence for the *tert*-butyl protons indicates a free rotation of the 3,5-di-*tert*-butylphenyl group at 363 K.

Evidence for the high rotational barrier of the *meso–meso* bond also comes from the fact that the trimer **3** was separated into two diastereomers by silica gel column chromatography with *n*-hexane–AcOEt as eluting solvent. The methoxyl signal region of the first and second eluting trimers appeared at 3.56, 3.59 and 3.61 ppm in a ratio of 1:1:1 and at 3.55, 3.57, 3.60 and 3.62 ppm in a ratio of 2:2:1:1, respectively. Simple consideration of the molecular symmetry leads to a conclusion that the *meso*-isomer has four different methoxyl signals in a ratio of 2:2:1:1, while the *dl*-pair-isomer has three different methoxyl signals in a ratio of 1:1:1. We therefore assigned the first eluting fraction as the *dl*-pair isomer and the slowly eluting fraction as the *meso*-isomer, respectively. Refluxing of *meso*- and *dl*-pair isomers of **3** in $Cl_2CHCHCl_2$ at 420 K for 3 h did

not cause any scrambling, also indicating a rather high rotational barrier for the *meso–meso* bond.

Optical resolution of the racemic dimer **2** was performed by HPLC with a chiral preparative column.[7] The CD spectra[8] of enantiomers of **2** are shown in Fig. 1 (solid line represents CD spectra of the first eluted dimer, and dashed line represents that of the second eluted one). The CD spectral shape is quite similar to the induced CD spectral shape reported for oligosaccharide-complexes of *meso–meso* linked diporphyrin bearing four boronic acid groups.[2f] To the best of our knowledge, this is the first CD spectra of chiral *meso–meso* linked diporphyrin. The absorption spectrum of the *meso–meso* linked diporphyrin (Fig. 1 upper) can be explained in terms of the exciton coupling theory by postulating two degenerate transition dipole moments of B_x and B_y, which are respectively parallel and perpendicular to the long axis of the *meso–meso* coupled diporphyrin.[4] The interaction of two B_x components leads to red-shifted Soret band at 448 nm, while the other dipole–dipole interactions should be cancelled due to the expected orthogonal geometry and thus give rise to unshifted Soret band at 413 nm. The CD spectrum can be interpreted as a superposition of a relatively weak couplet at the red-shifted Soret band and a strong couplet at the unshifted Soret band with opposite signs. The stronger Cotton effect around 413 nm corresponds to the interaction of the transition dipole moments perpendicular to the long molecular axis, since their spatial arrangement is chiral. On the other hand, the weak Cotton effect at the red-shifted Soret band is difficult to explain within framework of the simple two generate dipole moments postulate stated above, since the two B_x components are aligned parallel to each other and thus should be CD silent. One possible explanation might be a bent conformation with respect to the *meso–meso* bond, but this effect should be small. Another more plausible explanation may be a mixing of intramolecular charge-transfer character in the red-shifted Soret transition, which has been also suggested by a recent study on the electro-absorption spectra of *meso–meso* linked porphyrin arrays.[9] This measurement revealed that the change in the dipole moment upon photo-excitation is non-zero at the red-shifted Soret band, suggesting the charge-transfer character for this transition. Calculation of the excited state by INDO/S (WinMOPAC ver. 3.0) indicated that Soret band contains several intramolecular

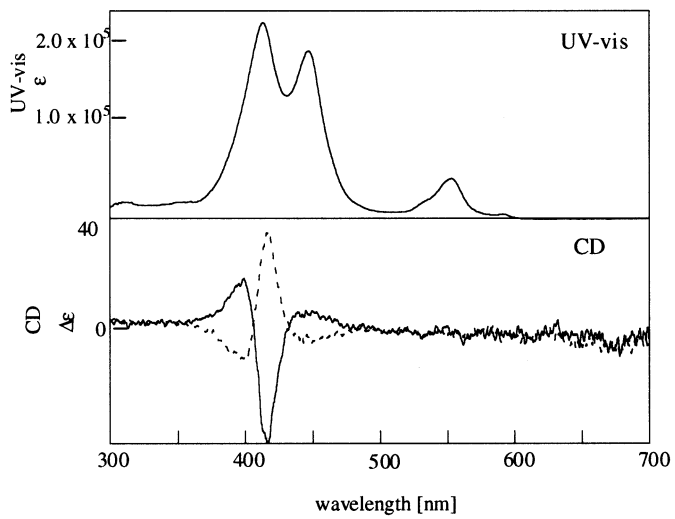


Figure 1. UV–vis and CD spectra of **2** in CH_2Cl_2

transitions over the two porphyrin units with charge-transfer character. This inter-porphyrin charge resonance character, even though it is weak, may be important for the observed weak Cotton effect at the red-shifted Soret band. Finally, the molar ellipticity of **2** ($[\theta]_{413} = 1.3\times10^5$ deg cm^{-1} dm^3 mol^{-1}) is relatively large compared to that of previous covalently linked chiral porphyrin dimers,[10] and should be useful for sensing as demonstrated by Shinkai et al.,[2f] as well as understanding the absorption characteristics of *meso–meso* linked porphyrin arrays.

Acknowledgements

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(t, $J=2$ Hz, 2H, Ar), 7.69 (t, $J=9$ Hz, 2H, Ar), 7.56 (t, $J=2$ Hz, 1H, Ar), 7.52 (t, $J=9$ Hz, 1H, Ar), 7.01 (dd, $J=5$, 9 Hz, 4H, Ar), 6.85 (d, $J=9$ Hz, 2H, Ar), 3.61 (s, 6H, methoxy), 3.59 (s, 6H, methoxy), 3.56 (s, 6H, methoxy), 1.53 (s, 36H, *t*-butyl), 1.52 (s, 36H, *t*-butyl), and 1.50 (s, 36H, *t*-butyl); FAB Mass m/z 2094, calcd for $C_{126}H_{116}N_{12}O_6Zn_3$ m/z 2090.7.

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