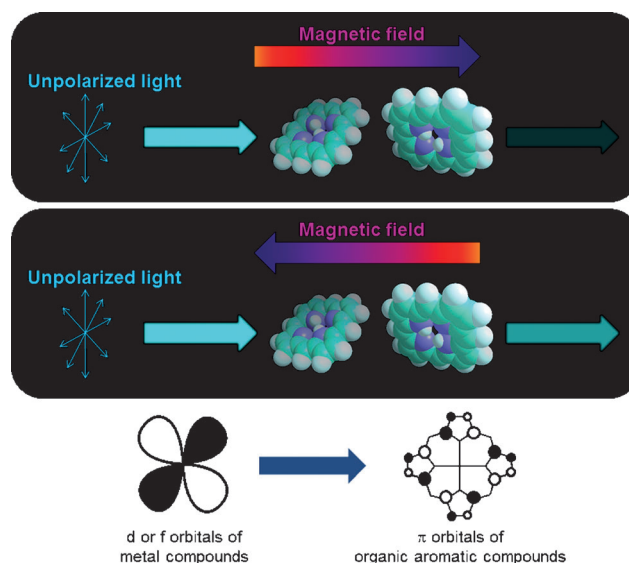


# Magneto-Chiral Dichroism of Organic Compounds\*\*

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The homochirality of life—the biased distribution of L-amino acids and D-sugars—is still unsolved.<sup>[1]</sup> Rikken and Raupach reported that magneto-chiral dichroism (MChD, that is, the dependence of the absorbance of a chiral molecule on the direction of a magnetic field to which it is exposed) could result in asymmetric photochemical reactions,<sup>[2]</sup> since the MChD of two enantiomers is opposite in nature. Therefore, MChD became a plausible candidate for explaining the homochirality of life, in addition to the Earth's rotational motion (the Coriolis force)<sup>[1,3,4]</sup> and circularly polarized light-induced asymmetric photochemical reactions.<sup>[1,5]</sup> The presence of MChD of compounds which have both strong circular dichroism (CD) and magnetic circular dichroism (MCD) effects has been theoretically predicted.<sup>[6,7]</sup> After this prediction and the first observation of MChD in the  $5D_0 \rightarrow 7F_{1,2}$  luminescent transition of a europium(III) complex,<sup>[8]</sup> observations of MChD in several metal compounds have been reported.<sup>[9–12]</sup> However, the MChD of organic compounds that are correlated well with living beings has not been reported, which weakened the relationship between MChD and the homochirality of life. This existence of metal compounds showing MChD mainly originates from the fact that MCD, one of the important origins, is intensified by the d (or f) orbital-based degeneracy and angular momentum on the metals. Herein, we report the first observation of MChD in organic compounds using chiral J-aggregates of water-soluble porphyrins. To acquire intense MCD signals in organic compounds, the large orbital angular momentum of aromatic  $\pi$ -conjugated system was employed.<sup>[13]</sup> Moreover, a very intense CD signal was obtained by the exciton chirality of the twisted configuration between porphyrin constituents,<sup>[14,15]</sup> which can provide the MChD of organic compounds (Figure 1).

Figure 2 a–c shows the UV/Vis, CD, and MCD spectra of the protonated form of *meso*-tetrakis(4-sulfonatophenyl)porphyrine ( $H_4TPPS_4$ , Figure 3 a) and the chiral J-aggregates of  $H_4TPPS_4$  (Figure 3 b). These aggregates were prepared by adding chiral tartaric acid, which induces Coulomb interactions between the positively charged pyrrole protons and the



**Figure 1.** MChD of organic compounds. The absorption coefficient of a chiral molecule is different for an unpolarized light beam when an externally applied magnetic field is parallel and antiparallel to the propagation direction. In the case of porphyrins, the cyclic perimeter model,  $C_{16}H_{16}^{2-}$   $\pi$  system, is appropriate for explaining an orbital angular momentum (quantum number =  $M_L$ ), in which an  $M_L = 0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6, \pm 7$ , and 8 sequence is observed in the molecular orbitals.<sup>[13]</sup> Here, the  $M_L$  values are  $\pm 4$  and  $\pm 5$  for the degenerate highest occupied and lowest unoccupied molecular orbitals (HOMOs and LUMOs), respectively. Although the symmetry of porphyrins is lower than that of  $C_{16}H_{16}^{2-}$ , the same basic nodal pattern sequence can still clearly be observed in the porphyrins, which can explain the intense MCD signals. Thus, the present MChD is intensified by the orbital angular momentum of aromatic  $\pi$ -conjugated system, which is different from the previous MChD based on the orbital angular momentum of metal compounds (d orbital:  $M_L = 0, \pm 1, \pm 2$ , f orbital:  $M_L = 0, \pm 1, \pm 2, \pm 3$ ).

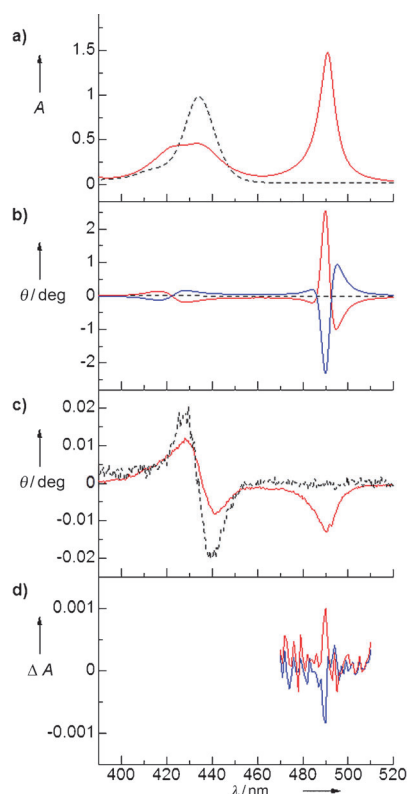
negatively charged sulfonato groups.<sup>[16]</sup> This formation of the J-aggregates shifts the Soret band ( $\pi \rightarrow \pi^*$ ) to the red-side (491 nm) considerably, owing to the exciton interaction between the  $H_4TPPS_4$  constituents. For both the enantiomers of the chiral J-aggregates of  $H_4TPPS_4$ , very intense, reproducible CD signals were acquired by the addition of chiral tartaric acid and subsequent addition of sulfuric acid (Figure 2).<sup>[16,17]</sup> Positive/negative and negative/positive CD spectral patterns are induced in the J-band region by the addition of L- and D-tartaric acids, respectively. This finding shows the enantioselective formation of the chiral J-aggregates of  $H_4TPPS_4$ . According to the method reported by Ribó et al., the chiral J-aggregates of  $H_4TPPS_3$  (Figure S2 in the Supporting Information) were also prepared by concentrating the acidic solution with a rotary evaporator.<sup>[3,16]</sup> The chiral J-aggregates of  $H_4TPPS_3$  could be enantioselectively prepared by changing the rotation directions of the rotary evaporator

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[\*\*] This work was supported by the Global COE Program for Chemistry Innovation.

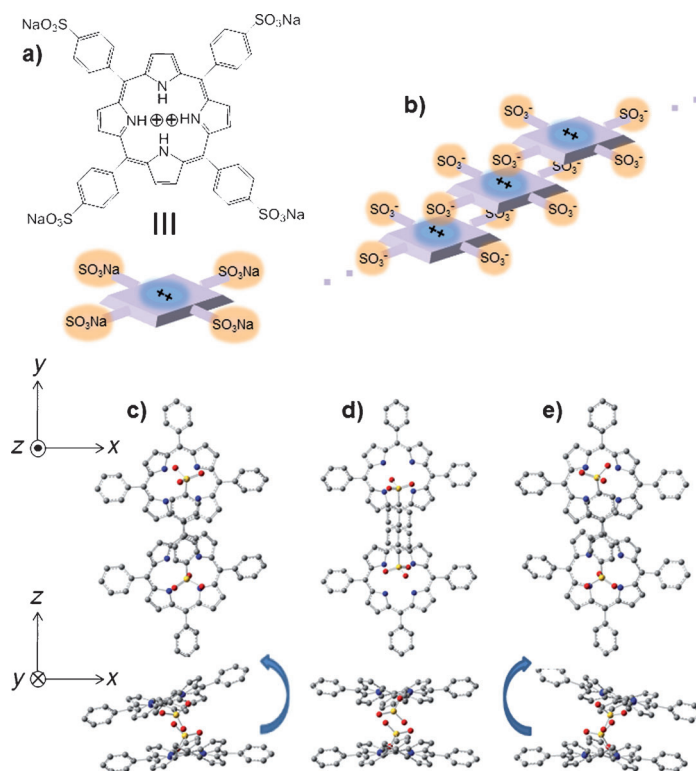
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201101809>.



**Figure 2.** a) UV/Vis, b) CD, c) MCD, and d) MChD spectra of the chiral J-aggregates prepared by addition of L-tartaric acid (red solid line) or D-tartaric acid (blue solid line), as well as the spectra of the  $H_4TPPS_4$  monomer (black broken line). The UV/Vis and MCD spectra of the chiral J-aggregates prepared by adding D-tartaric acid were almost identical to those prepared by adding L-tartaric acid.

(Figure S2 in the Supporting Information),<sup>[3]</sup> and the CD spectral patterns in the chiral J-aggregates are similar between  $H_4TPPS_3$  and  $H_4TPPS_4$ .<sup>[18]</sup> However, the intense, reproducible CD signals were not obtained for the MChD measurements, because it was difficult to control the conditions of the solution by concentrating it using the rotary evaporator. The MCD spectrum of the  $H_4TPPS_4$  monomer shows an intense, dispersion-type signal corresponding to the Soret band, called the Faraday A term.<sup>[13]</sup> This MCD signal reflects the orbital angular momentum due to the large aromatic  $\pi$ -conjugated system of porphyrin in addition to the degeneracy of the Soret band. In the case of the chiral J-aggregates of  $H_4TPPS_4$ , an intense, integral-type MCD signal (Faraday B term) is observed at the J-band (490 nm), which indicates the non-degeneracy of the J-band.<sup>[13]</sup>

Because both the very intense CD signal and the MCD signal are simultaneously observed in the J-band region of the spectra of the chiral J-aggregates of  $H_4TPPS_4$ , MChD signals were evaluated in the J-band region by measuring the difference between the absorbance in directions parallel and antiparallel to the externally applied magnetic field (Figure 2d).<sup>[19]</sup> When preparing the J-aggregates by adding L-tartaric acid, a sharp, positive MChD signal is observed at 490 nm. The MChD signal of the J-aggregates prepared using D-tartaric acid is observed at the same wavelength (490 nm), but the sign is reversed to the negative side. The peak position



**Figure 3.** Molecular structures of a)  $H_4TPPS_4$  and b) the J-aggregates of  $H_4TPPS_4$ , as well as optimum structures of  $H_4TPPS_1$  (the protonated form of 5-(4-sulfonatophenyl)-10,15,20-triphenylporphyrine) dimer calculated by the DFT method [c) left-handed helical, d) parallel, and e) right-handed helical structures].

(490 nm) of the MChD spectra is found to be identical to that of the spectra obtained from the product of the CD and MCD spectra. This finding is consistent with the previous prediction that the MChD intensity qualitatively reflects the intensity of the product of the CD and MCD spectra.<sup>[7,8]</sup> Therefore, we confirm the presence of MChD in organic compounds for the first time.

Although the chiral J-aggregates of porphyrins formed by mechanical rotation have attracted considerable attention in terms of the relationship between chirality and vortex,<sup>[1,3,4,16]</sup> the configurations between porphyrin units were unknown. To obtain information about the configurations, DFT (B3LYP/6-31G\*) calculations were carried out. The very strong CD signal of the chiral J-aggregates is attributed to exciton chirality, which occurs when the chromophores form a twisted configuration. The DFT calculations indicate that the configuration between the porphyrin units can form left-handed helical, planar, and right-handed helical structures as shown in Figure 3.

These structural differences originate from the steric hindrance that arises from the ruffled structure of the protonated form of the monomers, whereas the dimerization is obviously induced by the Coulomb interactions between the positively charged pyrrole protons and the negatively charged sulfonate groups. The optimum structure of the  $H_4TPPS_4$  monomer calculated by the DFT method (B3LYP/6-31G\* Gaussian 03) shows the ruffled structure (Figure S4 in

the Supporting Information), which is consistent with the previous X-ray analyses of  $H_4TPP$ .<sup>[20]</sup> This finding can be reasonably explained by the steric hindrance of four pyrrole protons, which were alternately located above or below the mean plane consisting of four carbon atoms at the *meso* positions, and thus four pyrrole planes ruffle with inclined phenyl rings. The structural characteristics, such as the ruffled pyrrole rings and inclined phenyl rings, are unchanged by the dimerization. Moreover, the helical structure is reproduced well by the DFT calculation even when using larger basis sets (6-311G\*\*). These findings strongly suggest that the ruffled structure of the monomer is unambiguous. Thus, the right-handed (or left-handed) helical structure is preferably formed when the pyrrole protons in the upper porphyrin and lower porphyrin, which interact with the sulfuric acid functional groups in the lower porphyrin and upper porphyrin, respectively, are both located at the right-hand (or left-hand) side, because the Coulomb interactions with the sulfuric acid functional groups are more favorable in the far pyrrole protons from another porphyrin than the near pyrrole protons from another porphyrin owing to the steric hindrance. On the other hand, the planar structure is preferentially generated when the interacting pyrrole protons in the upper porphyrin and the lower porphyrin are located at the right-hand and left-hand sides, respectively. For the chiral tetramer adopting the optimized helical and planar structures, a CD spectrum was calculated by the exciton chirality method, which reproduced well the dispersion-type CD spectral pattern at the J-band (Figure S7 in the Supporting Information). This finding strongly suggests that the chiral J-aggregates contain the helical and planar structures.

We have demonstrated the presence of MChD in organic compounds for the first time. Because the MChD originates from the  $\pi$ -electronic properties of aggregates of conventional organic aromatic compounds (benzene derivatives, polycyclic aromatic hydrocarbons (PAHs), chlorophylls, and so on), such as the orbital angular momentum and the exciton chirality, the MChD of the  $\pi$ - $\pi^*$  transitions not only has significant advantages such as tunable wavelengths and high chemical reactivity that are useful for asymmetric synthetic methods and magneto-optical devices, but it also opens up new possibilities for clarifying the asymmetry in biological systems.<sup>[21–27]</sup>

## Experimental Section

$H_2TPPS_4$  was purchased from Aldrich Co. and purified by using methanol, by which salts were removed.  $H_2TPPS_3$  was prepared according to the reported method.<sup>[28]</sup> The chiral J-aggregates of  $H_4TPPS_4$  were prepared by improving the reported method.<sup>[16]</sup> Aqueous chiral tartaric acid (8.3 M, 375  $\mu$ L, Tokyo Kasei Co.) was added to the aqueous solution (1.88 mL) containing  $H_2TPPS_4$ . After one day, conc. sulfuric acid (10  $\mu$ L, Kanto Chemical Co.) was further added to the solution. After one more day, the sample solution was moved to the cuvette, and then all measurements were carried out within one day to stably accumulate the spectroscopic data.

UV/Vis absorption spectra were measured using a JASCO U-570 spectrometer. CD measurements were performed using a JASCO J-720 spectrodichromometer or JASCO E-250. MCD measurements were performed using JASCO E-250 equipped with a JASCO electro-

magnet (+1.35 or –1.35 T). For MChD measurements, the monochromatic light emitted from a Xe lamp (JASCO PS-X150B) equipped with a monochromator (JASCO CT-25CP) and a mechanical chopper travelling through a sample in the JASCO electromagnet (+1.35 or –1.35 T) was detected by a photomultiplier (Hamamatsu Photonics R928). The photomultiplier signals obtained through a lock-in amplifier (Stanford Research SR830) were recorded point-by-point at 1 nm in the J-band regions (470–510 nm). Here, in order to evaluate only effects of reversing the externally applied magnetic field (**H**), we measured the absorbance in directions parallel to **H** and then the absorbance in directions antiparallel to **H**. Subsequently, we measured the antiparallel absorbance first and then the parallel absorbance. By repeating this procedure 15–25 times, the data was accumulated, and thus, the averaged MChD spectra were evaluated from the difference between the parallel and antiparallel absorption spectra.

Received: March 14, 2011

Revised: May 18, 2011

Published online: July 27, 2011

**Keywords:** chirality · circular dichroism · magneto-chiral dichroism · porphyrinoids · UV/Vis spectroscopy

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