DOI: 10.1002/anie.201105031

Magnetochiral Effects in Amphiphilic Porphyrin J-Aggregates**

*Josep M. Ribó**

chirality · circular dichroism · J-aggregates · porphyrinoids · self-assembly

Natural optical activity (NOA)[1] is the phenomenon originates from the differential interaction of a chiral compound with enantiomorphous electromagnetic radiation. NOA can be easily detected in the absence of linear optical polarizations, but in the presence of linear optical anisotropies,[2] its optical determination requires specialized methods (e.g. determination of all 16 elements of the optical Mueller matrix); in the case of samples with strong physical anisotropies or depolarizing characteristics, NOA cannot be measured by optical methods. NOA in transmission experiments is detected by the measurement of circular dichroism (CD) and circular birefringence (ORD), but it can also be detected in emission and scattering (Rayleigh and Raman) phenomena. Magnetic optical activity (MOA; Faraday effect)[1] is the optical activity generated by interaction of linearly polarized electromagnetic radiation with matter (achiral or chiral) in the presence of a magnetic field (magnetic circular dichroism (MCD) and magnetic circular birefringence (MORD)). NOA and MOA where first detected experimentally in the first half of the 19th century by Aragó and Faraday. Notice that NOA is related to chirality of matter but not MOA, which from the point of matter is only the consequence of the presence of electronic energy levels.

In 1984,[1] Wagniere had predicted that chiral compounds in a magnetic field would show differences in the transmission (emission and scattering) of depolarized electromagnetic radiation when a magnetic field is applied parallel or antiparallel to the beam propagation. This observation was called magnetochiral effect (MChE) by Barron and experimentally was first detected by Rikken and Raupach in 1997.[3] Experimental reports on MChE are rare and difficult to detect mainly because it is a weak effect (second order); compared with the Faraday effect (MOA) for the same magnetic field, it is 10^{-3}–10^{-2} less intense. Generally MChE has been detected in absorption and emission experiments, that is, at an electronic transition, and therefore is called magnetochiral dichroism (MChD; see Figure 1). Notice that despite being the correct name, it may anyway be confusing because the difference in absorbance is obtained from the comparison between parallel and antiparallel experiments using depolarized electromagnetic radiation and not by the direct evaluation of a specific optical circular polarization property. Experiments on magnetochiral birefringence (MChB), that is, at non-absorbing energies, have been also reported, but here the experimental difficulties are still more dominant than those for the dichroic measurements.

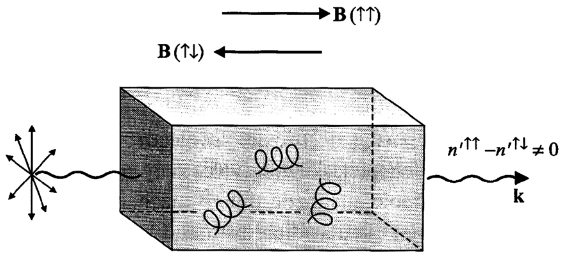

Figure 1. Magnetochiral dichroism experiment. With permission from ref. [1a].

The MChE is of high theoretical importance. Notice that it is a phenomenon originated by matter chirality in its interaction with electromagnetic radiation, that is, it is analogous to NOA, which also is a property of chiral matter. It has been proposed in astrophysical prebiotic scenarios (depolarized radiation and huge magnetic fields) as a source for the enantioselective destruction of racemic mixtures.[4] However, MChE implies associate phenomena that are of potential interest in advanced chiral materials,[1b,5] magnetoresistance anisotropies in macro- and nanosized chiral conductors,[5a] magnetohydrodynamic phenomena[5b] and the electric reading/writing of magnetic states in chiral ferromagnetic materials.[5c]

Ishii and co-workers have reported on MChD in J-aggregates of diprotonated *meso*-tetrakis(4-sulfonatophenyl)-porphyrin (H_4TPPS_4).[6] The interesting aspect of this report is not only the addition of a new chiral compound to the short list of experimental reports on MChD, but also the type of species involved.

MChD in spite of being rarely reported has been detected in diamagnetic, paramagnetic, and ferromagnetic materials.

---

[*] Prof. Dr. J. M. Ribó
Department of Organic Chemistry, Institute of Cosmos Science (IEEC-UB), University of Barcelona
c. Martí i Franquès 1, 08028 Barcelona, Catalonia (Spain)
E-mail: jmribo@ub.edu

[**] The author acknowledges the support of the Spanish Ministry of Science (MEC) AYA2009-13920-C02-01-02 and of the COST Action CM07030: Systems Chemistry.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Owing to the low strength of the effect, the previous experimental reports mostly discuss measurements made on pure materials or relatively highly concentrated solutions of compounds with electronic levels implying d or even f orbitals (e.g. chiral octahedral metal complexes), which provide a significant molecular magnetic dipole. In this respect molecular ferromagnets give a more intense MChD than diamagnetic compounds, therefore a new approach has been the preparation of chiral materials with ferromagnetic transition; below the Curie temperature, the internal magnetic field of the molecular magnet originates an intense MChE.[5] The J-aggregates of H_4TPPS_4 reported in ref. [6] are diamagnetic and in contrast to previous reports on MChD, the measured samples are J-aggregate suspensions in water obtained by self-assembly of the monomeric diprotonated porphyrin at concentrations in the mM range. However, the diamagnetic diprotonated porphyrin has an electronic analogy with the octahedral complexes of metals, in which MChD has been previously detected; the degenerate pairs of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the diprotonated porphyrin ring are cyclic π conjugated (planar tricoordinated C and N atoms) but because of the cyclic structure, these molecular orbitals show a d-like topology. The MChD in ref. [6] is detected at the characteristic (Lorentz-shaped) strong red-shifted band (monomer approximately 435 nm, J-aggregate approximately 490 nm) of the J-aggregates, which corresponds to a Fermi exciton; we can reasonably assume that in addition to necessarily being chiral (intrinsic chirality) it will show a d-like topology that leads to a significant magnetic dipole moment. Notice that the chiral J-aggregate gives a bisignate CD band at approximately 490 nm, as signature of the degenerate pair of HOMO and LUMO levels of the diprotonated porphyrin, and that the MChD signal is monosignate.[6] This observation is consistent with previous reports, in which the shapes of the observed MChD signals were bisignate for a monosignate CD, that is, the MChD signals show a shape reminiscent of the first derivate of the corresponding CD trace.[5]

The MChE is a phenomenon that arises from matter chirality and in this respect the J-aggregates of amphiphilic porphyrins show an interesting and surprising behavior. The formation of these J-aggregates occurs through hierarchical self-assembling and auto-organization processes, which are sensitive to several, even unexpected, experimental factors.[7] In this structure formation, bifurcation points appear and lead to spontaneous mirror symmetry breaking and therefore the chiral sign of the outcome can be selected by very weak chiral inductions[8] (in ref. [6], the chiral sign is selected by induction with the enantiomers of tartaric acid). The chiral sign selection may be exerted, at least in one member of the homologous family of H_4TPPS_4 (H_4TPPS_3), by the macroscopic chiral hydrodynamic forces of simple vortex stirring applied during the formation of the J-aggregates;[9] the experiment is reproduced for the first time (see the Supporting Information of ref. [6]) by another group than that of the original report[9]. In the case of H_4TPPS_4, spontaneous CD arise, in less or higher intensity depending on applied procedures (probably because of the formation of different enantiomeric excesses of chiral J-aggregates). Furthermore, when H_4TPPS_4 J-aggregates are obtained as long ribbon-like particles (≥ 150 nm length) they show a reversible CD during vortex stirring, the sign of which depends on the direction of stirring[10] and is independent of the permanent CD signal of nonstirred solutions. This chirality arises from the folding/bending of the elastic thin particles under the torque of the flow shear gradients originated by stirring.[11] This observation suggests that H_4TPPS_4 J-aggregates with a more intense CD signal and probably more intense MChCD would be obtained if the preparation method were optimized and also if the transient chirality obtained by stirring could be locked, for example, by rigidization of the solution in a sol to gel transition or by spin coating of the solutions.

Several porphyrinoids give aggregates showing spontaneous mirror symmetry breaking that leads to chiral bias by induction with chiral dopants or by a few chiral substituents (e.g. [12]) by the sergeant–soldier effect.[13] Therefore, they are candidates for testing MChE and the electro-magnetic properties derived from this effect.

Meso-substituted porphyrin gives chiral aggregates by self-assembly, because the conformational chirality of the substituents at the *meso* positions is locked in the aggregate. In spite of having been intensively studied by several research groups, this circumstance shows an evident lack of indisputable structural data (stereochemical and electronic). Hence it is not possible to establish reliable relationships between structure and MChE. Therefore, the report of Ishii and coworkers[6] stresses that more efforts are necessary: 1) to study the processes of self-assembly and auto-organization that control the stereochemistry and morphology (size and shape) of the J-aggregate particles and 2) the use of advanced diffraction techniques to infer their structure. To emphasize the lack of reliable structural data, we do not consider it appropriate to present here the usual reasonable structural cartoons representing porphyrin J-aggregates.

Received: July 18, 2011
Revised: September 1, 2011
Published online: November 15, 2011

---

[1] a) L. Barron, *Molecular Light Scattering and Optical Activity*, 2nd ed., Cambridge University Press, Cambridge, **2004**; b) G. H. Wagniere, *On Chirality and the Universal Asymmetry: Reflections on Image and Mirror Image*, VHCA, Wiley-VCH, Zürich, Weinheim, **2007**.
[2] J. Schellman, H. P. Jensen, *Chem. Rev.* **1987**, *87*, 1359–1399.
[3] G. L. J. A. Rikken, E. Raupach, *Nature* **1997**, *390*, 493–494.
[4] G. L. J. A. Rikken, E. Raupach, *Nature* **2000**, *405*, 932–935.
[5] a) V. Krstić, S. Roth, M. Burghard, K. Kern, G. L. J. A. Rikken, *J. Chem. Phys.* **2002**, *117*, 11315; b) V. Krstić, G. Wagniere, G. L. J. A. Rikken, *Chem. Phys. Lett.* **2004**, *390*, 25–28; c) C. Train, R. Gheorghe, V. Krstic, L.-M. Chamoreu, N. Ovanesyan, G. L. J. A. Rikken, M. Gruselle, M. Verdaguer, *Nat. Mater.* **2008**, *7*, 729–734.
[6] Y. Kitagawa, H. Segawa, K. Ishii, *Angew. Chem.* **2011**, *123*, 9299–9302; *Angew. Chem. Int. Ed.* **2011**, *50*, 9133–9136.
[7] A. Sorrenti, Z. El-Hachemi, J. Crusats, J. M. Ribo, *Chem. Commun.* **2011**, *47*, 8551–8553.
[8] a) Z. El-Hachemi, C. Escudero, O. Arteaga, A. Canillas, J. Crusats, G. Mancini, R. Purrello, A. Sorrenti, A. D'Urso, J. M.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Ribo, *Chirality* **2009**, *21*, 408–412; b) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687–5754.

[9] J. M. Ribó, J. Crusats, F. Sagues, J. Claret, R. Rubires, *Science* **2001**, *292*, 2063–2066.

[10] O. Arteaga, A. Canillas, J. Crusats, Z. El-Hachemi, J. Llorens, E. Sacristan, J. M. Ribo, *ChemPhysChem* **2010**, *11*, 3511–3516.

[11] a) Z. El-Hachemi, O. Arteaga, A. Canillas, J. Crusats, J. Llorens, J. M. Ribo, *Chirality* **2011**, *23*, 585–592; b) O. Arteaga, A. Canillas, J. Crusats, Z. El-Hachemi, J. Llorens, A. Sorrenti, J. M. Ribo, *Isr. J. Chem.* **2011**, *11*, 3511–3516.

[12] F. Helmich, M. J. M. Smulders, C. C. Lee, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2011**, *133*, 12238–12246.

[13] M. M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger, J. V. Selinger, *Angew. Chem.* **1999**, *111*, 3328–3345; *Angew. Chem. Int. Ed.* **1999**, *38*, 3138–3154.

ChemistryViews

Education & entertainment

Exciting news

Spot your favorite content

www.ChemistryViews.org

Unique articles

Multi-media

Free & easy access to new magazine

New online service brought to you by

ChemPubSoc Europe

WILEY-VCH

603701008