Alignment of Phthalocyanine molecular aggregates by magnetic fields


*Research Institute for Materials, High Field Magnet Laboratory, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, Netherlands
Department of Organic Chemistry, NSR Center, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, Netherlands

Abstract

We have studied the magnetic-field-induced alignment of Crown ether-substituted Phthalocyanine molecules dissolved in chloroform. Varying the concentration and the temperature of the solution, the molecular clustering and medium-long-range ordering of molecules in solution have been studied. High magnetic fields, up to 20 T, are used to induce a macroscopic degree of order, which is probed by “in situ” polarized optical spectra and magnetic-induced dichroism. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molecular aggregates; Phthalocyanines; Magnetic field; Magnetic-field-induced alignment

1. Introduction

Macromolecules and their aggregates are interesting objects, both from fundamental research point of view and future device applications [1,2]. Their utility ranges from the possibility to create 1D electron wires and ionic channels [3,4], to electro-optical properties, useful for photographic and dye industry [5].

In all these fields, it is important to control matter at a molecular level. Among other methods, the use of high magnetic fields is considered in this respect.

Magnetic field-induced alignment of molecules in solution is a universal effect, originating from the fact that virtually any molecule features anisotropic magnetic susceptibility [6,7]. The present work makes use of this effect to study self-assembling molecular solutions and shows as well that high magnetic fields can induce macroscopic order.

2. Crown ether-substituted Phthalocyanines

Crown ether-substituted Phthalocyanine molecules (PCS) the subject of the presented work, are discotic molecules of about 60 Å diameter and about 4 Å thick [8]. The delocalization of their molecular orbitals over the entire core, combined with their large size, results in a permanent high electric dipole. When the molecules are dissolved in chloroform, large intermolecular Van der Waals forces are generated which induce self-assembly of the molecules in long 1D aggregates. Depending on the concentration (typically in the range 0.1–10 mg/ml), aggregates are formed of 10 000 individual molecules, which can be of the order of 1 μm in length.
As schematically shown in Fig. 1, the PCS stacks are formed from molecules assembled in a non-staggered geometry. This arrangement allows the ether rings to form hollow tubes throughout the aggregate, ideal ionic channels. The overlapping orbitals of the central ions permit electronic transfer along the PCS column, forming a real 1D quantum wire. (For a better visualization the molecule is sketched at the top and bottom of the stack.) The configuration is mechanically and electrically protected by the decoxy chains, which act as an isolating mantle [8].

3. Magnetic field-induced molecular alignment

In a magnetic field a molecule acquires an extra energy of \( E = \chi B^2 \), where \( B \) is the magnetic field induction and \( \chi \) is the molecular diamagnetic susceptibility. For almost all molecules, the susceptibility \( \chi \) exhibits anisotropy, \( \Delta \chi = \chi_\parallel - \chi_\perp \), where the indices “||” and “⊥” denote the magnetic susceptibilities parallel and perpendicular to the molecular axes. In terms of energy, this anisotropy would give rise to orientation dependent energy. In a magnetic field, the molecules try to align their molecular axes with respect to the magnetic field direction in such a way that the magnetic energy is minimized. This energy gain is to be compared with the thermal energy \( kT \) and typical numbers show that for individual molecules \( \Delta E \ll kT \) and only a very small degree of alignment can be induced. However, for sufficiently large molecular aggregates, the energy gain may become comparable with \( kT \), thus allowing an important degree of orientation to be achieved [7].

4. Experimental details, results and interpretation

PCS (polycrystalline) powder is dissolved in chloroform using ultrasonic mixing, until no solid component is visible in a 1000 × optical microscope. Placed in a precision optical cuvette (5 mm optical path), the sample is mounted in a temperature-controlled chamber (± 0.02°C stability), in the bore of a resistive “Bitter” magnet. The geometry of the setup is such that the probing light beam is perpendicular to the applied magnetic field.

To start with, we measured (polarized) optical spectra in the 200–860 nm range, using a single grating spectrometer-diode array.

In the upper panel of Fig. 2 the transmission spectrum of a 0.7 mg/ml solution at 20°C is presented, for \( B = 0 \). The spectrum shows two broad transmission windows in the green and near-infrared (NIR) region. Within the green window, the spectral shape is due to single molecules, while in the NIR part it is attributed to the molecular ag-
gregates. The shape of the unpolarized transmission spectra is not changing in fields up to 20 T, showing that the magnetic field does not induce any changes in the morphology of the molecules or aggregates. The lower panel in Fig. 2 shows the difference of the transmission at 15 and 0 T. The transmission spectrum for the parallel to magnetic field polarization (dashed line), decreases in the green part and increases in the NIR region.

In contrast, the transmission spectrum in the perpendicular to magnetic field polarization shows the opposite behavior. This suggests that the molecular aggregates align with respect to the magnetic field such that the molecular plane is parallel to the applied field, so in the || to B polarization the transmission in green decreases while in the ⊥ to B polarization it increases. Recalling that the NIR part of the spectra is attributed to the molecular aggregates, a rise in the NIR transmission for a || to B polarization and a decrease in the ⊥ to B polarization, are consistent with the molecular aggregates aligned with their long axes perpendicular to B.

We emphasize that the aligned aggregates still have a rotational degree of freedom, as long as they keep their axes in a plane perpendicular to the magnetic field. In fact this is why the effect is larger in the || polarization, the ⊥ to B polarization “sees” the effect averaged over the rotational degree of freedom.

In order to quantify better the degree of magnetically induced alignment, we measured the polarized optical absorption for a fixed wavelength, 543.5 nm, employing a polarization modulation technique. Fig. 3 shows the change of optical transmission as a function of the applied field for || and ⊥ to field polarization. The results are consistent with the spectrometric data recorded in the same spectral region, but the sensitivity is two orders of magnitude higher.

The transmission data are converted into dichroic ratio data, defined as the ratio between the absorption coefficient in the parallel polarization and in the perpendicular polarization.

The dichroic ratio directly relates the transmission–absorption data to the degree of induced orientation [9]. Fig. 4 presents the magnetic field-induced dichroic ratio for three different concentrations. The inset presents the zero-field dependence of the transmission on the concentration of the solution.

Fig. 3. Optical transmission versus applied magnetic field, taken at 543.5 nm. The solid line represents the evolution in the ⊥ polarization, while the || polarization is represented by the dashed line.

Fig. 4. Magnetic-field-induced dichroic ratio for three concentrations. The inset presents the zero-field dependence of the transmission on the concentration of the solution.
size is concentration dependent, in the sense that higher concentrations favor longer aggregates.

In order to analyze these data quantitatively, the molecular diamagnetic anisotropy and the molecular dichroic ratio must be known and this is not the case. Therefore, at this stage, we can only present a qualitative interpretation. (The precise value of the diamagnetic anisotropy of an individual molecule would permit a highly accurate determination of the number of molecules forming the aggregates and the dichroic ratio of a single PCS would give access to the exact order parameter.)

The quasi-saturation of the curve for the 1 mg/ml solution suggests that the order parameter lies somewhere in the 0.7–0.8 range. Preliminary results, not presented, suggest that higher concentrations allow better alignment.

We have found that the curves cannot be fitted with a simple theoretical model of non-interacting rod-like aggregates, described by the diamagnetic anisotropy found from low fields. The deviations from the model are larger for higher concentrations. This result shows that interaction between aggregates is important, especially at high concentrations, when they become very long and Osanger theory applies.

5. Conclusions

We have studied the orientation behavior of PCS solutions in magnetic fields. We have shown that a high degree of alignment can be obtained. The work also shows that a magnetic field can be used to determine the diamagnetic anisotropy and to probe the inter-molecular and inter-aggregates interactions.

References