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Cooperative Motion

Cooperative Molecular Motion within a Self-Assembled Liquid-Crystalline Molecular Wire: The Case of a TEG-Substituted Perylenediimide Disc[**]

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In the emerging area of molecular electronics, molecular wires have become one of the central goals of research.[1,2] Discotic liquid crystals (LCs), consisting of rigid aromatic cores and disordered peripheral alkyl or alkoxy substituents, are promising materials as they self-organize into columnar supramolecular structures owing to interactions between the aromatic cores and nanophase separation.[3] The LC phase simplifies processing and allows self-healing of the assembly.[4] Large aryl cores, such as hexa-*peri*-hexabenzocoronenes (HBCs) have high charge-carrier mobilities that are due to a large π–π overlap.[5] In recent years, self-organization of liquid-crystalline perylenetetracarboxdiimides (PDIs) have gained attention because of the opportunities presented by the combination of their LC, photophysical, semiconducting, and photoconducting properties.[6–11] The supramolecular organization can be improved by generating helical structures through appropriate side groups by attaching the discs to a helical backbone, or by the structure of the core itself.[12] In particular, perylene derivatives can be prepared in different shapes, from disc-like to elongated quaterrylenes, to tune their electronic properties.[4b] The elongated rylenes can form helical columns with different pitch, resulting from different rotation angles α between adjacent PDIs.[4b,13] The packing is particularly interesting for $\alpha = 90°$, as a stable column can be envisaged if the correlation between adjacent units is strong. The question then arises as to whether this correlation persists in the LC phase, in which discotics undergo rapid axial rotation around the column axis on the microsecond time scale. In contrast to symmetric discs, where this axial motion occurs between symmetry-related sites, the rotation of the PDIs in the helical columns can not occur as a simple local process; it requires cooperative motions within the column to preserve the correlation between adjacent moieties, as demonstrated in dipole functionalized HBCs with helical superstructure.[14] Axial motions of limited amplitude, however, can be envisaged as local processes even in the solid. All these types of motions will influence the processability and self-healing capabilities of the molecular assembly.

Advances in solid state NMR[15–17] now allow us to study the structure and dynamics of such systems by ^{13}C NMR in its natural abundance. Both ^{13}C–^{1}H dipole–dipole couplings (DDCs), which probe the motional behavior using the C–H bond direction lying in the molecular plane, and ^{13}C chemical-shift anisotropy (CSA), in which the unique axis for aromatics is perpendicular to the molecular plane, are exploited.[15] This gives unprecedented information on the local packing and the geometry of rotational motions, because the dynamics are probed by two directions perpendicular to each other,[18] thus avoiding ambiguities in data interpretation (see the Supporting Information).

Along these lines, we investigated the structure and dynamics of a triethyleneglycol (TEG)-substituted PDI. In contrast to its alkyl-substituted analogue,[13] which is a solid up to 403 K, TEG-PDI has, along with the solid phase, a LC phase with a temperature range of about 50–60 K. Thus, the side groups have pronounced effects on the phase behavior and the dynamics of the system. Combining NMR with X-ray scattering, we then tackled the following questions: 1) What is the stacking angle α between adjacent PDI molecules in the column; 2) do restricted rotational fluctuations around the column axis occur, and if so, in which phase and with what amplitude; and 3) is complete cooperative axial motion possible in the LC phase?

The thermotropic properties of TEG-PDI (for synthesis and characterization, see the Supporting Information) were investigated by differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), and polarized optical microscopy (POM). On cooling from the LC phase, a glass transition is observed at 214 K by DSC. On heating, recrystallization occurs at around 293 K. Two endothermic peaks are observed at 338 K and 393 K, thus defining the discotic LC phase (see the Supporting Information). The WAXS pattern observed for a TEG-PDI fiber at 373 K in the LC phase (Figure 1a) is characteristic for discotic packing. The PDI building blocks assemble into columns arranged in a hexagonal unit cell with a lattice parameter of 2.23 nm, as derived from the equatorial reflections. The meridional reflections in the wide-angle region give a π stacking distance

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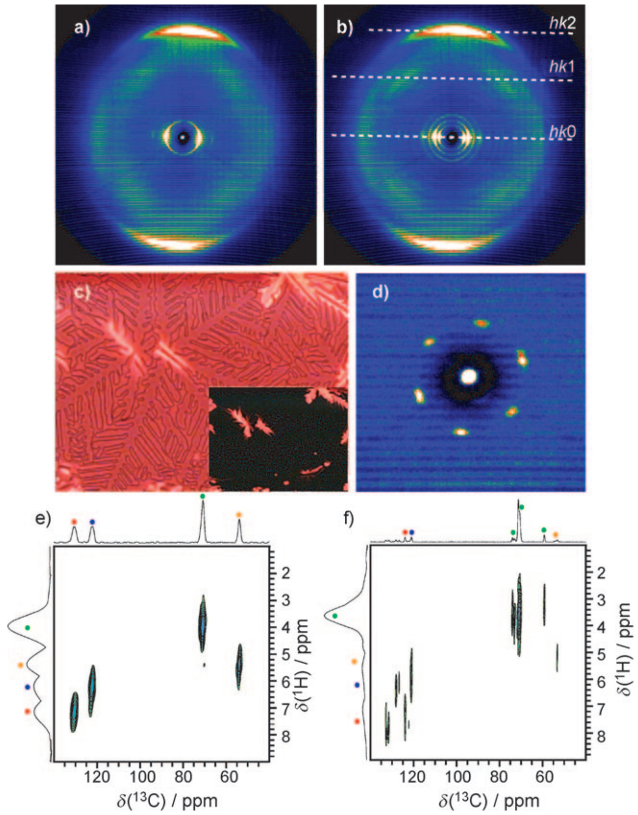

Figure 1. 2D WAXS patterns of TEG-PDI obtained at a) 373 K and b) 303 K. c) Optical microscopy image of a homeotropically aligned film inserted between cross-polarizers at 313 K. d) 2D WAXS diffraction pattern of the homeotropically aligned TEG-PDI recorded in transmission mode at 303 K. The 2D ^{13}C{^{1}H} REPT-HSQC NMR correlation spectra in (e) and (f) are also recorded at 373 and 303 K, respectively.

of 0.34 nm. The additional weak and diffuse off-meridional reflections correspond to a *d*-spacing of 0.70 nm, indicating correlations of adjacent TEG-PDI molecules stacked perpendicular to each other, as also found in other discotic systems.[19] On cooling back to 303 K, these scattering features become more pronounced (Figure 1 b), which is characteristic of an improved ordering. The discotic character of TEG-PDI is confirmed with POM when the sample is cooled down by 1 K min^{-1} from the isotropic phase. Figure 1 c shows typical dendritic textures formed during solidification, which appear black between cross-polarizers, indicating a homeotropic alignment.[20] In contrast to analogous systems,[4b] in this case the columns "stand" on the surface, as verified by the WAXS hexagonal pattern of the reflections (Figure 1 d). The two-dimensional ^{13}C{^{1}H} heteronuclear correlation NMR spectra (Figure 1 e,f) of TEG-PDI was recorded at the same temperatures as the WAXS patterns; in the frozen state at 303 K, TEG-PDI has six different signals from aromatic C−H groups can be observed; these signals average to only two sites in the LC state.

Apart from the different packing in the frozen and LC states of TEG-PDI, the line narrowing observed for the different proton sites and the difference in δ_{iso} values for the carbon sites suggest that the molecular dynamics in these two states are quite different. To address this difference, site-specific ^{13}C{^{1}H} heteronuclear dipolar sideband NMR patterns were recorded for both phases using REPT-HDOR and REREDOR techniques[21] (Figure 2 b,c).

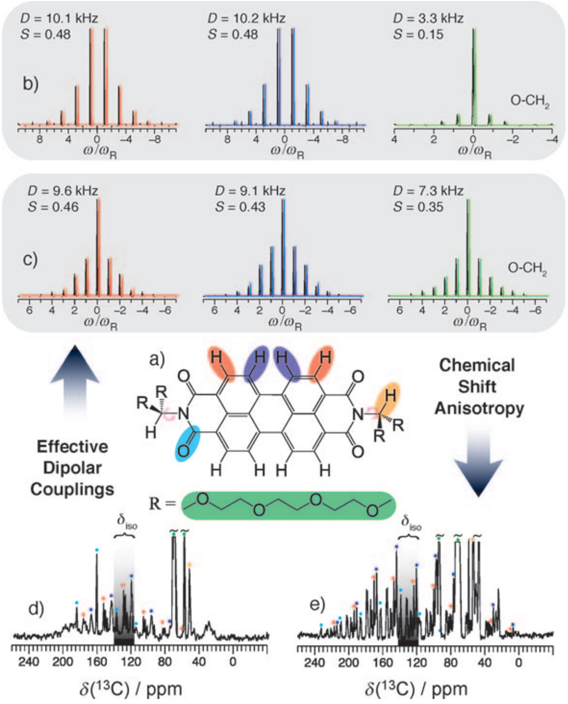

Figure 2. a) Molecular structure of the TEG-PDI sample investigated. The color labeling is used throughout this work. Site-specific ^{13}C{^{1}H} heteronuclear dipolar recoupling experiments recorded for the b) LC and c) frozen state of TEG-PDI, using REPT-HDOR and REREDOR techniques.[21] The frequency dependence of the sideband patterns, given in multiples of the rotational frequency ω_R, is used to determine the dipolar coupling constants *D* and the dynamic order parameter *S*. d,e) ^{13}C CSA spinning sideband patterns for the different ^{13}C environments of TEG-PDI in its d) LC and e) frozen states.

From these patterns, it can be deduced that the effective ^{13}C–^{1}H dipolar couplings, and thus the dynamical order parameters, for the carbon atoms of the perylene core are reduced by a factor of about two, to $S = 0.46$–0.48 in both phases (see the Supporting Information). Therefore, substantial motion of the perylene cores is present in both phases. The TEG side chains are quite mobile and flexible in both phases, with $S = 0.35$ in the frozen state and $S = 0.15$ in the LC state, which is close to the transition to an isotropic liquid. The seemingly minor difference between the local dynamics of the perylene core in the two different thermotropic phases probed by the ^{13}C–^{1}H DDC sideband patterns is intriguing, and suggests that the information on the dynamics obtained in this way is incomplete. Additional information about the core dynamics can be obtained by an interaction that is sensitive to packing and has its unique axis perpendicular to the molecular plane, rather than in the plane as for the ^{13}C–^{1}H bond. Fortunately, the ^{13}C CSA tensors of the perylene core fulfill these conditions.[18] Figure 2 d,e show slow-spinning ^{13}C MAS NMR spectra for TEG-PDI, and indicate significant changes in the ^{13}C CSA spinning sideband envelopes for the different carbon sites, when going from the frozen (Figure 2e) to the LC phase (Figure 2d). Moreover, the low number of spinning sidebands and the intensity shift towards the isotropic resonances observed in the LC state also indicate significant averaging because of increased molecular dynamics.

To understand the different averaging of ^{13}C–^{1}H DDC sidebands and ^{13}C CSA patterns, we then considered how the anisotropic ^{13}C CSA and ^{13}C–^{1}H dipolar coupling tensors are influenced by axial motion of the core. Figure 3a shows the two types of spectra in the rigid case. It is natural to assume that in the frozen state, the axial motion of the core is restricted in amplitude. We modeled this case by considering rapid angular fluctuations that are described by a Gaussian distribution of rotational angles with variance σ. The corresponding motionally averaged CSA lineshapes and DDC sideband spectra are readily calculated.[22] With $\sigma < \pm 40°$, the asymmetry of the ^{13}C CSA tensor $\eta_{CS} = (\delta_{xx} - \delta_{yy})/(\delta_{zz} - \delta_{iso})$ is only slightly reduced, whereas the magnitude for the CSA is maintained ($\delta_{CS} = \delta_{zz} - \delta_{iso}$). On the other hand, the dipolar coupling tensor changes from an axially symmetric tensor ($\eta_D = 0$) in the static case to a non-axial tensor ($\eta_D = 0.46$) accompanied by a reduction of the absolute magnitude for the dipolar coupling by a factor of 1.47 (see the Supporting Information, Figure S2 for details). For a complete axial rotation (Figure 3c), both the ^{13}C CSA and ^{13}C–^{1}H dipolar coupling tensors become axially symmetric. However, the magnitudes of the two interactions are very different: the δ_{zz} element of the CSA is for example unchanged, whereas the absolute value for the dipolar coupling is reduced by a factor of two (dynamic order parameter $S = 0.5$). The ^{13}C–^{1}H DDC sideband patterns, however, can hardly be distinguished from those for a restricted motion, whereas the ^{13}C CSA lineshape changes significantly because of the developing axial symmetry of the tensor. The spectra in Figure 2 are then consistent with a scenario in which restricted angular fluctuations of the TEG-PDI molecules dominate in the frozen state. These fluctuations occur in the molecular plane with angles up to ±40°, but also include minor out-of-plane excursions, reducing the dynamic order parameters to $S = 0.43$–0.46. In the LC state of TEG-PDI, the molecules rotate fully, or equivalently by 90° jumps, which leads to the same averaging of the NMR interactions. The averaging of the carbonyl ^{13}C CSA tensor also supports this scenario. Quantum chemical calculations[13] show that the unique axis of the carbonyl groups are all oriented in the molecular plane. Upon fast axial rotation, an averaged, axially symmetric tensor results with a significantly reduced magnitude and change of sign for δ_{CS}. Exactly this behavior is observed in the ^{13}C spinning sideband patterns in Figure 2d,e (in the region 80 to 240 ppm).

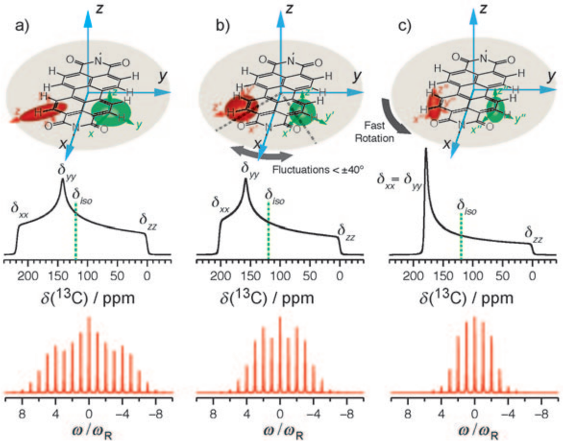

Figure 3. Motional averaging of the anisotropic ^{13}C–^{1}H dipolar coupling and ^{13}C chemical shift tensors associated with the aromatic carbons for the inner core of PDI. In the static case (a), the unique component of the ^{13}C CSA tensor is perpendicular to the molecular plane,[14] whereas the unique component of the dipolar coupling tensor is along the C–H bond in the molecular plane. b) Angular fluctuations and c) fast rotation around the *z* axis perpendicular to the molecular plane.

Combining the results of X-ray scattering and advanced solid-state NMR techniques, we now obtain a detailed picture of both the structure and dynamics of the PDI cores in the columns of these materials:

1) Whereas in the alkyl-substituted analogue, the angle between adjacent perylene moieties is circa 35°,[13] X-ray analysis shows that for the system with TEG side chains, the elongated perylene units are perpendicular to each other (Figure 4). On cooling from the discotic LC phase, a frozen state is reached in which a pronounced change in the intracolumnar packing is obvious from NMR spectroscopy, but the overall organization is similar to the LC phase as evident from the X-ray patterns. At least six different carbon environments are distinguished in the frozen state owing to the packing, although the molecule in solution exhibits only two sites.
2) This structural change has pronounced effects on the dynamics of the system. Whereas the core is rigid in the

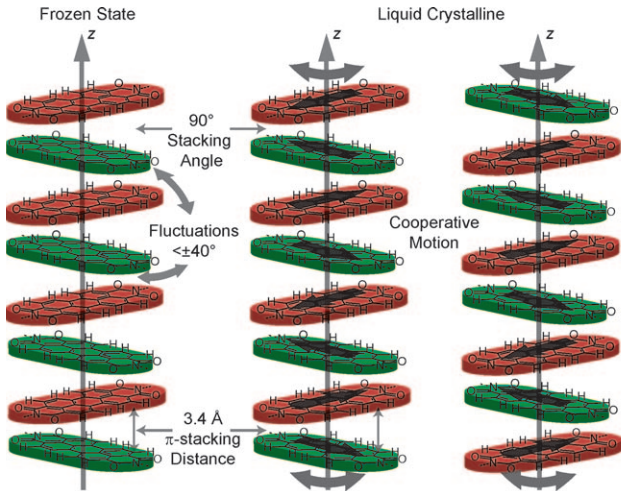

Figure 4. Axial motion for TEG-PDI in its two thermotropic phases. In the frozen state, in-plane local fluctuations of the cores occur independently. In the LC phase, a cooperative motion along the stacking axis rotates the molecules by 90° in a spiral fashion. The persistence length of the cooperative motion is unknown.

solid phase of an PDI analogue with alkyl substitution,[13] substantial axial fluctuations of about ±40° in amplitude are observed in TEG-PDI. This motion leads to a drastic change of the ^{13}C–^{1}H DDCs, but details of the motional amplitude cannot faithfully be determined from the DDC sideband patterns alone. The fact that the axial motion is be restricted in amplitude is readily deduced from the ^{13}C NMR sideband patterns, which are governed by the large ^{13}C CSAs with their orientation along the column axis.

3) Remarkably, only two aromatic carbon sites are observed in the LC phase. Full axial rotation of the elongated PDI units around the column axis is detected in both the DDC and the CSA sideband patterns. This motion also averages the differences in chemical shifts resulting from the packing in the solid phase. The DDC sideband patterns indicate, however, that the planes of the perylene moieties remain parallel to each other in the column ($S_p = 2\,S_{DDC} \approx 0.95$). This behavior is reminiscent of the discotics formed from triphenylene derivatives, which also form LC phases over rather narrow temperature ranges, yet have a high degree of order in the columns.[3]

The simplest motional process that is consistent with all the observations involves cooperative rotation of the PDI molecules by 90° around the column axis (Figure 4). Thus, whereas the restricted angular fluctuations in the solid phase can be considered as local processes, the increased dynamics in the LC phase must be highly cooperative in nature, and indeed they show that the correlation between adjacent perylene units is maintained during the axial rotation. Such cooperative dynamic modes are of course particularly important in processing columnar discotic systems to align on surfaces.[19]

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