Giant Faraday Rotation in Mesogenic Organic Molecules

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S *Supporting Information*

ABSTRACT: Faraday rotation, the rotation of the polarization of light due to a magnetic field in the direction of propagation of the light, is used in applications ranging from quantum memory to the detection of biomagnetic fields. For these applications large Faraday rotation is necessary, but absorption of light is detrimental. In search of these properties, we have characterized the Verdet constant of a so far unexplored class of mesogenic organic molecules. We report their spectra and provide an interpretation. A Verdet constant of almost 2.5×10^5 deg T^{-1} m^{-1} is found around 520 nm. This Verdet constant is 3 orders of magnitude larger than the largest known for organic molecules in a region without spectral features. We attribute this enormous Faraday rotation to resonant enhancement by a triplet excitation that does not appear in the linear absorption spectrum and to near-resonant enhancement by low-energy singlet excitations. Furthermore we are able to switch the Faraday rotation by changing the liquid crystal phase of the compound. These results demonstrate a new class of Faraday rotating materials with great potential to replace current materials and improve existing applications. The inherent flexibility in the synthesis of this class of molecules opens a new field of research in Faraday rotation.

KEYWORDS: *Faraday rotation, liquid crystal, Verdet constant, TD-DFT calculations*
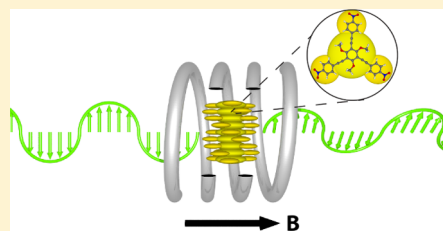
■ INTRODUCTION

Faraday rotation is the rotation of the plane of polarization of light due to magnetically induced circular birefringence.[1] Discovered almost 2 centuries ago, it is now used in a wide range of applications. Faraday rotation is important for optical isolators,[2] magnetic field sensors,[3] current sensors,[4] displacement sensors,[5] integrated communication optics,[6] detection of biomagnetic fields,[7] quantum memory,[8] and many others. It can be described by

$$\theta = VBL \qquad (1)$$

where θ is the polarization rotation, V is the Verdet constant, B is the magnetic field parallel to the propagation of light, and L is the length of propagation through the magnetic field.

The Verdet constant is a wavelength dependent material parameter. Typical Verdet constants of materials currently in use, such as iron oxide films[9] or substituted iron garnet films,[10] can reach millions of degrees per tesla per meter in the visible frequency region. However, these paramagnetic materials suffer from the drawback of magnetic saturation in magnetic fields smaller than 1 T [11] and a large temperature dependence.[12] Organic, diamagnetic materials in contrast saturate at far larger magnetic fields and additionally are relatively insensitive to

temperature changes, which is beneficial for sensing applications. An additional advantage of organic materials over inorganic garnets for Faraday rotation is their processability and flexibility.[13] Unfortunately, diamagnetic organic molecules have relatively small Verdet constants in regions far from resonance. Typical Verdet constants are on the order of hundreds of degrees per tesla per meter in the visible wavelength region, displaying a continuous decline toward longer wavelengths.[14−18] Only for the larger polythiophenes in specific conditions have larger Verdet constants been reported, on the order of 10^4 deg T^{-1} m^{-1}.[19] However, these large Verdet constants currently lack a conclusive explanation.

In search of large Verdet constants without an associated absorption, we have characterized the Verdet constant of an unexplored class of organic molecules. A band in Faraday rotation is found around 520 nm with a Verdet constant of almost 2.5×10^5 deg T^{-1} m^{-1}, 3 orders of magnitude larger than the largest known for an organic molecule in a region without spectral features. We attribute this giant Faraday

rotation to resonant enhancement by weakly absorbing triplet states[20−23] that are calculated to be present in this region, as well as near-resonant enhancement due to strongly absorbing singlet states at a wavelength not much shorter than the wavelength window around 520 nm. The lack of a corresponding strong absorption around 520 nm is a great advantage for applications.

We are also able to switch the Faraday rotation by changing the particular phase of the compound. The feature in Faraday rotation is present in the crystalline state under 60 °C but disappears entirely in the isotropic liquid above 130 °C.

These results demonstrate a new class of Faraday rotating materials with great potential to replace current materials and improve existing applications. The inherent flexibility in the synthesis of this class of molecules opens a new field of materials for Faraday rotation.

■ EXPERIMENTAL SECTION

TTB (1,3,5-tris[(4-nitrophenyl)ethynyl]-2,4,6-tris(n-decyloxy)-benzene), TTB* (1,3,5-tris[[(S)-3,7-dimethyloctyloxy]-2,4,6-tris[(4-nitrophenyl)ethynyl]benzene), and BTB* (1,3-bis[[(S)-3,7-dimethyloctyloxy)]-5-fluoro-2,4,6-tris[(4-nitrophenyl)ethynyl]benzene) were synthesized as described by Hennrich et al.[24,25] Thin film samples were created by heating a small amount of material to 120 °C and allowing this material to spread between two glass plates through capillary action. The resulting transparent samples were of sufficient optical quality for Faraday rotation measurements.

Spectral Faraday rotation measurements were performed using a 150 W xenon lamp followed by a monochromator. After being linearly polarized, the beam passes through a photoelastic modulator (Hinds I/FS50) at 45°, operating at 50 kHz. Subsequently this beam passes through the sample in a dc magnet, where Faraday rotation occurs. Finally the light passes through an analyzer placed at 90° with respect to the first polarizer. The beam then hits a photomultiplier tube, and the resulting signal is analyzed by a lock-in amplifier (SR830) at a detection frequency of 100 kHz. This signal can be correlated to the optical rotation and is measured for a discrete set of magnetic field strengths, with the Verdet constant determined from the slope of these values. We also measured Faraday rotation with a 632.8 nm helium−neon laser and an alternating current magnetic field at 857 Hz as described by Valev et al.[26]

To assist the interpretation of the experimental findings, we performed density functional theory (DFT) computations with the Turbomole package (version 5.7 [27,28]). Taking into account the rather large size of the molecules studied experimentally, the aliphatic tails were replaced by methyl groups to reduce the computational cost. As demonstrated by a comparison between the experimental Faraday rotation spectra of TTB and TTB*, the hydrocarbon chains appear to influence the location of particular bands in the spectrum, but they do not change their general characteristics (vide infra). Accordingly the hydrocarbon chains are unlikely responsible for the characteristic main features observed for the Faraday rotation. Geometry optimizations employed the BP functional[29−31] with a standard Turbomole triple-ζ polarized (TZVP) Gaussian-type basis set.[32] Calculations of the excitation spectra were performed using time-dependent DFT (TD-DFT) with the B3LYP functional[33−35] and the TZVP basis set. As pointed out by Peach et al., TD-DFT calculations may significantly underestimate triplet excitation energies because of an underlying triplet instability of the ground state.[36] In a Hartree−Fock (HF) calculation, the singlet ground state of the TTB model system is indeed confirmed to have a triplet instability. Peach et al. found that the use of the Tamm−Dancoff approximation (TDA)[37,38] eliminates much of the problem and provides more accurate triplet excitations. A comparison of the full TD-DFT and TD-DFT/TDA results for our samples shows the expected behavior, namely, a sizable blue shift of the triplet excitations, in particular, when the TDA is applied. The effect is more pronounced with a hybrid functional with a larger

fraction of exact exchange (e.g., BHLYP vs B3LYP; see Figure 2 (vide infra) and the Supporting Information).

■ RESULTS AND DISCUSSION

In the experimental Faraday rotation spectrum of TTB a peak with a Verdet constant of almost 2.5×10^5 deg T^{-1} m^{-1} is seen centered around 520 nm (Figure 1). The feature resembles an
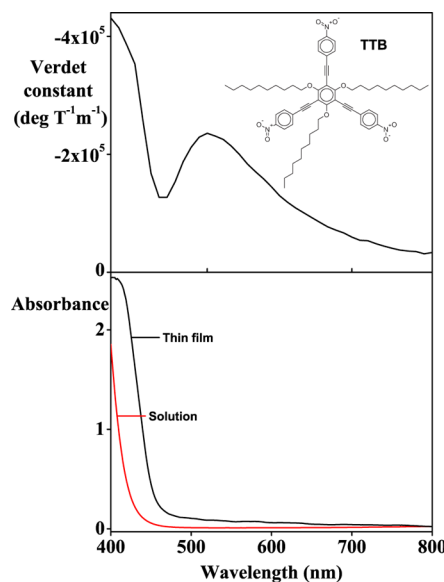

Figure 1. In the experimental Faraday rotation spectrum of a 1.8 μm film of TTB (top) a peak is seen at at 520 nm, associated with an anomalous dispersion feature attributed to a triplet excited state near this wavelength. The transition to the triplet excited state is not visible in the absorption spectrum in thin film (bottom, black) or solution (bottom, red) because it is formally spin-forbidden.

anomalous dispersion pattern of a refractive property such as the dipole polarizability around an electronic resonance, with a peak followed by a trough when going from longer to shorter wavelengths, superimposed onto a normal dispersion created by intense absorptions at higher energy (wavelengths shorter than 500 nm). In addition, strong Faraday rotation is observed below 450 nm due to resonant enhancement by absorption at these wavelengths. In the absorption spectrum on the other hand, only one band is observed with a center wavelength shorter than 400 nm, with no peaks past 500 nm.[24]

It is necessary to verify first that the observed feature is indeed caused by Faraday rotation. Faraday rotation is linear as a function of the applied magnetic field (eq 1). The optical rotation measured in a dc magnetic field is also linear as a function of the magnetic field ($R^2 > 0.99$), with no saturation being visible until at least 1 T. Despite this, it is not possible to exclude the magnetic alignment of crystallites as a source of optical rotation. To support Faraday rotation as the source of the observed magnetic field dependent optical rotation, we also performed Faraday rotation measurements in an alternating current magnetic field. In these measurements, the same Faraday rotation was observed. The high modulation frequency of the magnetic field allows us to exclude a magnetic alignment as the cause of the observed magnetic field dependent optical rotation. We can conclude that the feature in the observed optical activity is indeed Faraday rotation.

The Verdet constant is a molecular property that is defined by three perturbations:[39−41] two frequency-dependent electric

fields and a static magnetic field. Resonant enhancement may occur via strongly or weakly electric-dipole-allowed transition, and potentially also via magnetic-dipole-allowed but electric-dipole-forbidden transitions. A corresponding band is not visible in the linear absorption spectrum of the molecule, indicating the lack of any significant electric-dipole-allowed transition. This excludes the possibility of resonant enhancement by an intermolecular charge-transfer excitation induced by aggregation. Nonetheless, formally electric-dipole-forbidden transitions with weak intensity such as singlet−triplet transitions can also resonantly enhance Faraday rotation.[20−23] Computations and careful experiments on related 3-fold symmetrical molecules indicate the presence of triplet states close to these energies.[42]

We calculated the electronic states of TTB for the propeller geometry adopted in crystals[43] (Figure 2). Triplet excitations
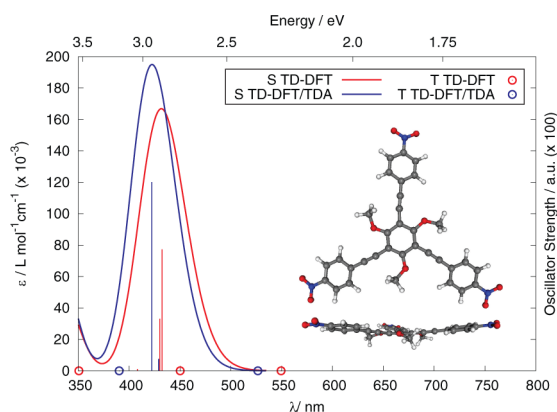

Figure 2. TD-DFT B3LYP/TZVP calculations on the optimized model TTB geometry reveal a triplet excitation at 527 nm, corresponding to the region where the Faraday rotation is observed. S/T stands for singlet/triplet excitation energies calculations.

with a large spin-free component of the transition dipole are present around 527 nm (see Supporting Information), corresponding to the region where the Faraday rotation is observed. While this excitation is formally spin-forbidden, and as such not visible in the absorption spectrum, it may resonantly enhance the Faraday rotation. No electric-dipole-forbidden but magnetic-dipole-allowed singlet transition was calculated at wavelengths longer than 450 nm, which would therefore exclude a mechanism via resonance with electric-dipole or magnetically allowed singlet transition in the wavelength window of interest.

To shed more light on the hypothesis of a resonant enhancement by a weakly absorbing triplet state, we examined two structurally related molecules. TTB* has a blue-shifted and narrower feature in Faraday rotation (Figure 3) than TTB (Figure 1). The bulkiness of the branched alkyl chains impedes a close packing of molecular units but guarantees for a fixed propeller confirmation on the molecular level and a helical twist in the resulting bulk aggregates. This is reflected in a blue-shifted triplet state and the corresponding feature in Faraday rotation.[44] TTB* forms a chiral nematic discotic phase between 66 and 99 °C as a consequence of the homochiral nature of the three alkoxy chains. For BTB*, no separate feature in the Faraday rotation spectrum was detected (Figure 3). The calculations performed for a model of BTB* (see Supporting Information) reveal, however, the presence of triplet excitations around 510 nm. Taking into account the spectral blue shift
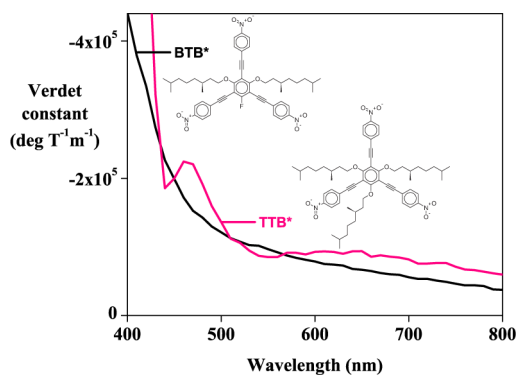

Figure 3. The feature in Faraday rotation in thin films of TTB* is blue-shifted and narrower than in thin films of TTB (Figure 1) because of the bulkiness of the branched alkyl chains in TTB*. Thin films of BTB*, however, show no separate feature in the Faraday rotation spectrum despite the presence of calculated triplet excitations around 510 nm. The corresponding band is likely hidden in the dispersion because of strongly absorbing singlet states.

observed in the calculation for BTB* compared to TTB (which is expected to be even more pronounced when considering branched hydrocarbon chains in the molecule, based on the discussion above), it seems possible that in this case the feature in the Faraday rotation spectrum assigned to resonance with a triplet state is simply hidden in the resonant enhancement by strongly absorbing states. Consequently, one broad band in Faraday rotation spectrum is observed here.

The liquid crystal nature of the molecule leads us to investigate the effect of temperature on the Faraday rotation spectrum (Figure 4). Under 60 °C TTB is crystalline, and it is columnar hexagonal from 60 to 68.5 °C. It displays a discotic nematic mesophase from 68.5 to 112 °C, from which temperature on it is present as an isotropic liquid.[24] The feature in Faraday rotation is present for the crystalline phase.
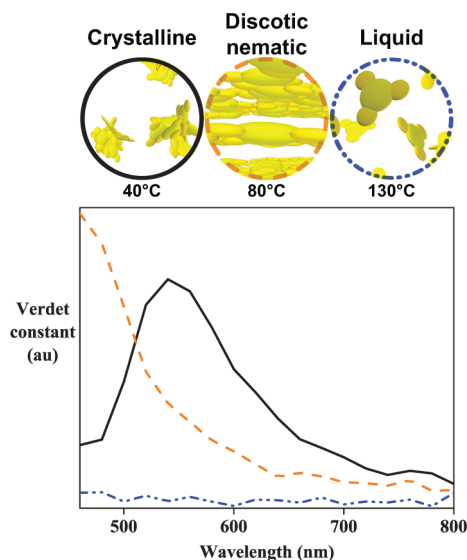

Figure 4. The Faraday rotation spectrum of TTB changes upon heating. The phase change from crystalline (full black) over discotic nematic (striped orange) to an isotropic liquid (dotted blue) is accompanied by a change in conformation and conformational flexibility. Correspondingly, the feature in Faraday rotation is no longer visible in the isotropic liquid phase.

In the discotic nematic phase the feature shifts to the blue, and finally the band in Faraday rotation is no longer visible in the isotropic liquid phase. This shift from crystalline to isotropic liquid is accompanied by a change in conformation and conformational freedom. In the crystalline phase the molecule is present in a fairly rigid, propeller geometry.[45] The disappearance of the Faraday rotation band in the isotropic liquid goes along with the complete loss of this conformational refinement for both TTB and TTB*. Consistent with this, a diluted solution in dichloromethane does not display a band in the Faraday rotation.

CONCLUSION

Materials with high Verdet constants and low absorption in the spectral region of interest are particularly interesting for a wide variety of applications of Faraday rotation. In search of these properties, we have characterized the Verdet constant of an unexplored class of organic molecules. A Verdet constant of almost 2.5×10^5 deg T^{-1} m^{-1} is found with no associated absorption, 3 orders of magnitude larger than the largest known for an organic molecule in a region without spectral features. On the basis of the available data, the enormous Faraday rotation is potentially caused by a combination of intense low-energy singlet excitations close to 520 nm and further resonant enhancement by a triplet excitation that is calculated to be right in the relevant wavelength window. While the transition is formally spin-forbidden, due to some degree of spin−orbit coupling, it may provide a mechanism for enhancing the Faraday rotation. We plan to address the cause of the strong Faraday rotation around 520 nm in more detail in a follow-up study. We are able to switch the Faraday rotation by changing the particular phase of the molecule. These results demonstrate a new class of Faraday rotating materials with great potential to replace current materials and increase the sensitivity in applications. The inherent flexibility in the synthesis, aggregation state, and concentration of this class of molecules opens a new field of research in Faraday rotation.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Calculated spectra and triplet excitations with a large spin-free component of transition dipole for TTB and BTB* model molecules; experimental NMR spectra for BTB* (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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