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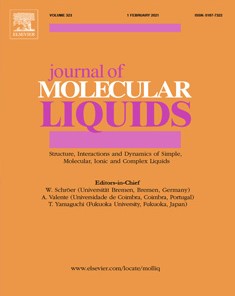
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Photochromic spiropyran-based liquid crystals



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We present a new type of light responsive self-assembling structures based on a spiropyran photoswitch- able unit. The spiropyran central part was modified by functional groups, which enabled the connection of two structurally different elongating parts. Two series of compounds were prepared with reversed ori- entation of the ester as a linkage group in the molecular core. The properties of the target materials were studied by differential scanning calorimetry and polarized light optical microscopy, which confirmed the presence of a nematic phase for most of the materials. In case of a trifluromethyl-substituted compound, a sequence of nematic – smectic A – smectic C phase was detected and confirmed by X-ray diffraction analysis. The photochromic properties of compounds were studied in solution as well as in mesophases. In the condensed state, UV light-induced switching from the spiropyran form to the merocyanine dye led to isothermal transition from the liquid crystalline phase to the isotropic liquid.

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1. Introduction

Photochromic molecular switches are hot topics in soft matter science. They are based on the light-induced rearrangement of chemical species between two (meta)stable states. Such systems have already found diverse applications as sensors, displays, colour filters, photochromic lenses, data storage components, smart materials for biological membranes, biochemical information transmission and drug delivery systems. In this respect especially azo dyes, diarylethenes, fulgides and spiropyrans have been a sub- ject of considerable interest as they can serve as molecular switches.[1]

Recently, various photochromic liquid crystals based on azo photosensitive moiety were studied [2–5] and effective influence of the illumination on mesomorphic properties was found. In this contribution, we introduce another type of a photochromic moiety for designing liquid crystalline materials, and we present new mesogenic compounds based on spiropyran unit. Upon illumina- tion of a spiropyran derivative with UV light, the usually colourless form opens the pyran ring and transforms into an intensively

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coloured merocyanine form, which undergoes a ring closure to the spiropyran form by illumination with visible light, heating or pH change. [6–8]

Liquid crystalline materials have been utilized to demonstrate the possibility to control the supramolecular organization and properties of a switch and the spiropyran unit has been incorpo- rated into the molecular structure. From the structural point point of view, the common spiropyran systems possess an indole/ben- zopyran junction, which results in a perpendicular arrangement of both units. Such arangement disturbs the general requirements for the design of liquid crystalline molecules. Thus, a prolonging mesogenic unit is attached to the spiropyran moiety to induce liq- uid crystalline properties of materials. For this purpose, a biphenyl [9–11] and phenyl benzoate units [12–16] were utilized previ- ously. Spiropyran-based liquid crystals have also become the photo-active part of polymers [17–23] and have been used for dop- ing of a variety of materials such as gels, oligomers, polymers, cap- sules, etc., for various applications. [23–28]

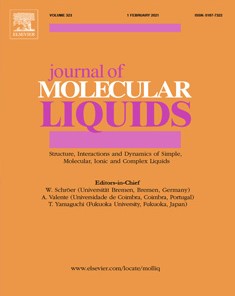
In this contribution we report synthesis of liquid crystals with a molecular core created from spiropyran connected to an alkoxy (benzoyloxy)phenyl unit. The spiropyran is substituted in the pyr- anyl part with various terminal substituents (H, Br, CF3, CN, NO2). In the indole part, which is connecting spiropyran and the meso- genic part, there is an ester linkage. Both the mesomorphic and photochromic properties were studied for two series I and II, which differ in orientation of the ester group (Fig. 1).

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Helical phases assembled from achiral molecules: Twist-bend nematic and helical filamentary B4 phases formed by mesogenic dimers



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a b s t r a c t

The synthesis and characterisation of an homologous series of bent odd-membered mesogenic dimers, the 40 -(6-{4-[(E)-{[4-(alkylthio)phenyl]imino}-methyl]phenoxy}hexyl)[1,10 -biphenyl]-4-carbonitriles (CB6O.Sm) is reported. This general class of materials, despite being achiral, has a strong tendency to form helical structures, and here, for the first time we report three such chiral phases in a single homologous series. Specifically, the heliconical twist-bend nematic (NTB) phase for short terminal thioalkyl chains, and

its smectic equivalent - the twist-bend smectic C (SmCTB) phase for longer chains. All the dimers showed

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Liquid crystals

the helical filament B4

phase, which is typically seen for rigid bent-core mesogens, but has only rarely

Nematic phase Helical nanofilament B4 phase

been reported for flexible dimeric molecules. In addition, on increasing chain length, smectic behaviour

emerges including the smectic A and the smectic CTB phases. We also show that these materials have the potential for their morphology to be controlled through surface interactions. The presence of the little- studied thio-linkage in the terminal chain, and the wide range of properties present in this single group of homologues, with promise of broad applicability in optics, photonics, as well as fundamental signifi- cance as a case study to achieve a better understanding of chirality and symmetry breaking in liquid crys- tals, ensures the importance of this new series of mesogens.

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1. Introduction

How chirality originates in the absence of a chiral inductor is amongst the most important and topical of scientific questions, cutting across all disciplines, and having clear fundamental and technological relevance (see for example [1]). In this context, liquid crystals provide a wonderful test-bed for studying spontaneous mirror symmetry breaking in fluids [2]. Indeed, the first example of spontaneous mirror symmetry breaking in a fluid with no spatial ordering was the twist-bend nematic, NTB, phase [3–6]. In a con- ventional nematic phase, the molecules all tend to align in the same direction, known as the director, whereas their centers of mass are randomly distributed. In the NTB phase, the director forms a helix and is tilted with respect to the helical axis (a heliconical structure); the pitch length of the helix is very short, typically rv10 nm. i.e. just a few molecular lengths. The formation of chirality is spontaneous and so equal numbers of left- and right-handed helices are expected and overall, the system is racemic. This degen-

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eracy may be removed by the introduction of intrinsic molecular chirality, leading to the NTB\* phase [7]. The vast majority of mate- rials that show the NTB phase may be described as odd-membered dimers, in which two mesogenic units are attached by a flexible spacer containing an odd number of atoms, and such molecules have a bent molecular shape [8–11], however this phase has also been observed for rigid bent-core mesogens [12] as well as for oli- gomers including both, linear and bent-core segments [13]. Recently it was shown that odd-membered dimers not only exhibit the NTB phase but also show twist-bend smectic phases [14–17]. In these fascinating heliconical lamellar phases consisting of achiral molecules up to four levels of structural chirality were observed: layer chirality, helicity of a basic repeating unit, a mesoscopic helix and helical filaments. Another phase with a spontaneously chiral structure built of achiral molecules is the helical nanofilament phase (HNF, B4), most commonly observed for rigid bent core mesogens [18,19] and only rarely for bent dimers [20].

In our search for new examples of chiral systems made of achi- ral building blocks, here we report the synthesis and characteriza- tion of non-symmetric dimeric mesogens consisting of a cyanobiphenyl core, an odd-membered spacer and a benzylidene

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Research Article

Light-Driven Fabrication of a Chiral Photonic Lattice of the Helical

Nanoﬁlament Liquid Crystal Phase

[Wongi Park,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Wongi%2BPark%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf)# [Jongmin Lee,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Jongmin%2BLee%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf)# [Moon Jong Han,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Moon%2BJong%2BHan%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Joanna Wolska,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Joanna%2BWolska%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Damian Pociecha,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Damian%2BPociecha%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Ewa Gorecka,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Ewa%2BGorecka%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Min-Kyo Seo,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Min-Kyo%2BSeo%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Yun-Seok Choi,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Yun-Seok%2BChoi%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf)\* [and Dong Ki Yoon](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Dong%2BKi%2BYoon%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf)\*

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ABSTRACT: A photonic lattice is an eﬃcient platform for optically exploring quantum phenomena. However, its fabrication requires high costs and complex procedures when conventional materials, such as silicon or metals, are used. Here, we demonstrate a simple and cost-

eﬀective fabrication method for a reconﬁgurable chiral photonic lattice of the helical nanoﬁlament (HNF) liquid crystal (LC) phase and diﬀraction grating showing wavelength-dependent diﬀraction with a

rotated polarization state. Furthermore, the UV-exposed areas of the HNF ﬁlm having chiral characteristics act as optical building blocks that induce resonant intensity modulation in the reﬂectance and

transmittance modes and the optical rotation of the linear polarization. Our photonic lattice of the HNF can be an eﬃcient platform for a

chirality-embedded photonic lattice at a low cost.

KEYWORDS: photonic lattice, photonic crystal, chiral liquid crystals, optical rotation, diﬀraction grating

■ INTRODUCTION

A crystalline material with periodically aligned atomic

structures has an electronic band structure that shows the energy−momentum distribution of electrons, which is closely

photonic lattice is still challenging. Recently, a bottom-up fabrication method to fabricate photonic lattices with chiral characteristics has been studied based on soft materials, such as block copolymers, colloidal particles, and liquid crystal (LC)

40−42

related to the photonic band structure for colors found in nature, as demonstrated in jewel beetles1 and morpho

butterﬂies.2 Photonic band structures have been extensively

studied by engineering photonic lattices with periodic optical

elements.3 In addition, photonic lattices have been studied as

diﬀraction gratings,4−8 coupled waveguide arrays,9−11 photonic

materials.

In several soft materials, directed self-assembly using the chiral LC phase is an easy and cost-eﬀective way to realize reconﬁgurable chiral optical structures because LC materials

are reversibly structured in the nano- and microscales by

various external stimuli, such as surface treatment, applied

topological structures,12−17 and photonic crystal ﬁbers.18,19

electric ﬁeld, and geometrical conﬁnement.

43−46

Chiral LC

According to the optical analogy based on the similarity of the paraxial equation and the time-dependent Schrödinger equation, photonic lattices can mimic quantum phenom- ena,20−23 such as exciton−polariton condensation24 and electron dynamics in a crystalline structure.25−27 A recent

study has shown that a chirality-embedded photonic lattice

structures can precisely modulate the polarization, reﬂectance,

and transmittance of light when it passes through the chiral

structure by adjusting the molecular structures to have the appropriate optical rotation (OR) and eﬀective birefringence.

Some reports have shown spatially amplitude-modulated photonic lattices using chiral LCs, in which amplitude

could simulate more complex phenomena caused by its twisted

diﬀraction gratings have been demonstrated.

47,48

In particular,

structure, such as magnetic-ﬁeld-applied quantum systems28,29

and pseudospin states in optical graphene.30,31

Most photonic lattices employ complex and expensive top-

down fabrication techniques to adjust photonic band structures. Thus, several alternative methods, such as femto- second laser32−35 or continuous-wave writing36,37 and multi- beam interference lithography,38,39 have been introduced to fabricate photonic lattices to overcome the drawbacks of conventional approaches. However, despite the necessity of exploring chiral quantum systems, implementing chirality in a

cholesteric LCs (CLCs) and blue-phase LCs (BPLCs) have

been introduced to generate self-assembled periodic helical structures depending on the helical twisting power and

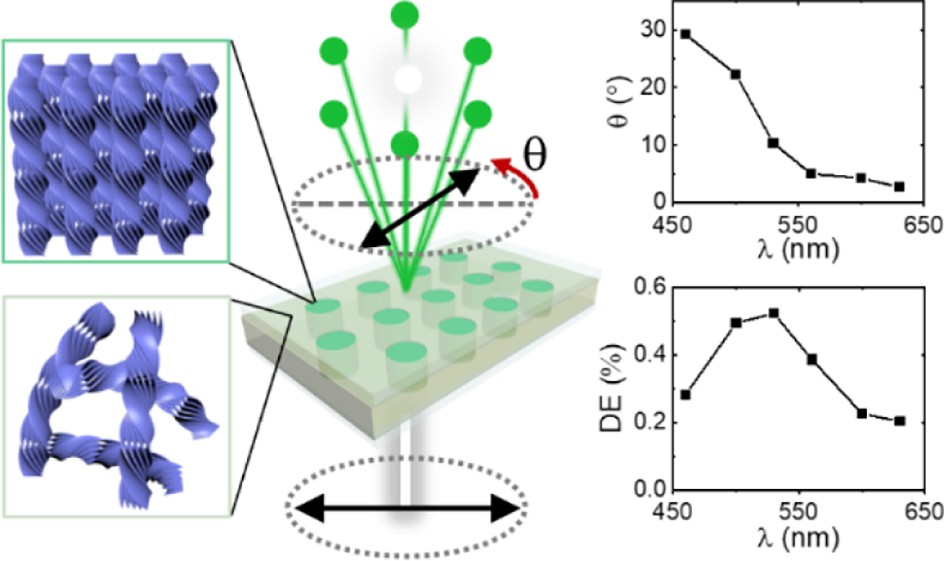


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Soft Matter



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Chiral columns forming a lattice with a giant unit cell†

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Mesogenic materials, quinoxaline derivatives with semi-flexible cores, are reported to form a new type of 3D columnar phase with a large crystallographic unit cell and Fddd lattice below the columnar hexagonal phase. The 3D columnar structure is a result of frustration imposed by the arrangement of helical columns of opposite chiralities into a triangular lattice. The studied materials exhibit fluorescence properties that could be easily tuned by modification of the molecular structure; for compounds with the extended p electron conjugated systems the fluorescence is quenched. For molecules with a flexible structure the fluorescence quantum yield reaches 25%. On the other hand, compounds with a more rigid mesogenic core, for which the fluorescence is suppressed, show eﬀective photogeneration of charge carriers. For some materials bi-polar hole and electron transport was observed.

Introduction

In recent years, columnar liquid crystalline phases that are usually formed by flat and rigid molecules having at least a few side alkyl chains, have attracted great interest from both scientific and industrial points of view. They have been tested for applications in various areas, such as optical device construction1 and in solar cells.2–5 An advantage of organic materials for such applications, as opposed to their inorganic counterparts, is that they are soft and relatively easy to align, and are therefore susceptible to external manipulation. In

electronic applications often high and anisotropic charge car- rier mobility is required; in a columnar structure this condition is easily fulfilled as each column provides a 1D path for charge transport through its central part made of mesogenic cores, while the alkyl chains isolate those inner ‘‘wires’’.6,7 Many types of molecules with an extended system of aromatic rings in the mesogenic core have been tested for the design of optoelec- tronic devices, such as OLEDs (organic light-emitting diodes),8–10 OFETs (organic field-effect transistors)11–13 and other photovoltaic applications;14–16 however the performance of such materials is still problematic. The requirements, e.g. good charge transport and strong fluorescence for OLEDs are often contradictory. They could be met by designing molecules with some conformational freedom; molecular flexibility may promote fluorescence by preventing the formation of

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H-aggregates,17,18 while p–p interactions confined to certain molecular fragments may enhance charge transfer. Quinoxa- line derivatives are perfect candidates for such materials; from an organic synthesis point of view they are easy to modify, and if properly functionalized they are able to generate a columnar packing.19–21 Quinoxaline derivatives with a lath-like shape may be stacked with a random orientation leading to columns with the overall circular cross-section, but might be also arranged into helical stacks. The helical arrangement of molecules along the columns is relatively often observed in columnar phases

formed by molecules or molecular assemblies of non-perfectly circular geometry.22,23 Such molecules twist with respect to each other in order to assure better packing of terminal chains. The packing of helical columns can be locally homochiral24,25 but in general columns of opposite chirality can be randomly mixed in the crystal lattice (racemic mixture) or form mesoscale domains (conglomerate).26–28 Objects of opposite handedness can be also arranged into regular periodic lattice; such a racemic structure is sometimes referred to as ‘antichiral’.29

The regular racemic structure cannot be realized if the columns are arranged in a hexagonal lattice; in this case the frustration should lead to some modification of the structure, since an ideal triangular grid cannot be decorated evenly with two types of objects – the left and right handed helices.30 Arrangement of the helical columns into a frustrated hexagonal structure (with the Fddd lattice) has been recently studied and discussed in relation to other systems built from achiral molecules.31

Here we report systematic studies of the relation between the rigidity of the molecular structure and the phase behavior of quinoxaline based mesogenic molecules. Apart from the

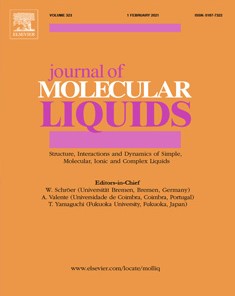
columnar hexagonal phase, in two of the studied compounds

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Self-assembling discotic materials with low symmetry for organic photovoltaics



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a b s t r a c t

Three new discotic liquid crystalline (DLC) penta(phenylethynyl)benzene derivatives (HSC0X, X = 1–3) in nonchiral, homogeneously chiral, and racemic conformations were used as smart dopants between poly

[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl][s-fluoro-2-[2–ethylhexyl]carbonyl]

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thirno[3,4–b]thiophene- diyl]](PTB7) and [6,6]-phenyl-C71-butyric acid methyl ester (PC71

BM) which

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Discotic materials

Liquid crystals Self-organization Organic photovoltaics Solar cells

can achieve one-dimensional (1D) charge transportation for organic solar cells (OSCs). All HSC0X exhibits

columnar rectangular phase stability over a reasonably broad temperature and is characterized by pow- der X-ray analysis and polarized optical microscopy (POM). The thermal imaging revealed the best homo- geneity of heat distribution for devices PTB7:PC71BM:HSC0X ternary active layer with resistance value

26.4–53.5 X. The resulting power conversion efficiency (PCE) values were strongly dependent on the

molecular conformation and specific amount of the dopants in an active layer. A narrow band gap at

1.01 eV was found for the nonchiral discotic material (HSC01) as well as a low-lying highest occupied molecular orbital (HOMO) energy level of rv -5.34 eV and the best PCE of 3.02%.

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1. Introduction

Organic bulk heterojunction (BHJ) solar cells have drawn signif- icant attention over recent decades due to their light weight, low cost, flexibility and solution-processed solar energy-harvesting technology, etc. In recent years, considerable progress in the novel material design and the study of mechanisms between different components, as well as the optimized device structure, has led to an efficient increase in the power conversion efficiency (PCE) of organic solar cells (OSCs). The PCE of polymer solar cells (PSCs) is increasing rapidly, and a value of over 16% has been achieved [1].

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However, the bathch-to-bathch reproducibility of polymers still potentially limits their application on the industrial scale. In com- parison with polymer donors, small-molecule donors show the advantages of well-defined molecular weight, easy purification and small batch-to-batch variations. Furthermore, to enhance well-ordered crystallization, obtaining higher purity and crystal orientations enables fabrication of OSCs with high charge mobility and low energy losses. Despite all these advantages, small- molecule organic solar cells (SM-OSCs) still do not show the same level of device performance as PSCs. The greatest challenge is to control the interpenetrating networks in SM-OSCs because ineffi- cient charge transport pathways would cause uncontrolled exciton recombination, decreased charge carrier mobility and unbalanced charge-transport ability [2–5]. Benzodithiophene (BDT) units have been successfully incorporated into small-molecule donors, and the highest PCEs of 11.50% and 13.63% have been attained for nonfullerene-based binary and ternary blends, respectively [6–7]. Wel et al. reported a dithieno[2,3-d:20 ,30 -d’]benzo[1,2-b:4,5-b’]dit hiophene (DTBDT)-based small-molecule donor. Owing to the

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Controlling spontaneous chirality in achiral materials: liquid crystal oligomers and the heliconical twist-bend nematic phase†

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Liquid crystal oligomers, namely dimers, trimers and tetramers, consisting of cyanobiphenyl and benzylideneaniline-based meso- genic units connected by either linear or bent alkoxy or alkyl spacers are reported. These materials, although built from achiral molecules, show the spontaneously chiral heliconical twist-bend nematic (NTB) phase. We report the relationships between the shape of the oligomer, and the NTB phase stability, the temperature dependence of the helical pitch length and tilt angle, birefringence, and elastic constants.

The spontaneous formation of chirality in a system composed of achiral molecules is of fundamental and technological importance in both the physical and biological sciences, and as such hugely topical.1 Spontaneous mirror symmetry breaking has been observed in various liquid crystalline phases,2 the first fluid to exhibit this phenomenon in the absence of positional order was the twist-bend nematic phase (NTB).3–5 More recently, spontaneous chirality has also been confirmed in an isotropic liquid.6 In the NTB phase the molecules more or less point along the same direction known as the director, and the director forms a helix and is tilted with respect to the helical axis; statistically equal numbers of the degenerate left and right-handed helices form. The pitch length is remarkably short, just a few nanometres.5 The molecular structural prerequisite for the observation of the NTB phase is an overall bent shape, and the overwhelming majority of twist-bend nematogens are odd-membered liquid crystal dimers.7



A dimer consists of two mesogenic units attached via a flexible

molecules are achiral. An absolutely central question in our understanding of these chiral structures assembled from achiral molecules is how to control the chirality with a view to designing new materials with tailored properties such as pitch length and its temperature dependence. It has been shown that the pitch length and its temperature dependence for NTB phases exhibited by dimers and trimers are very different.10

Very few reports of higher oligomers that form the NTB phase have appeared.7,11–20 Here we report the first extensive and systematic study of oligomers with identical mesogenic units in

order to better understand how the tendency to exhibit sponta- neous chirality depends on molecular structure. The structures and acronyms of the oligomers are shown in Fig. 1 and Fig. S1 (ESI†). In describing these structures, and in order to highlight the essential role played by molecular shape, we use general designations, in which B refers to a linkage with an odd number of atoms which imposes a bent arrangement of neigh- bouring units, and L to a linkage with an even number of atoms which gives a linear arrangement of neighbouring units (Fig. S2, ESI†). The phase transition temperatures, together with associated entropy changes are given in Table S1 (ESI†) and shown in Fig. S3 (ESI†). The relative stabilities of the NTB phases for the dimer (CB6OCB), trimer (CB6O.O6CB), and tetramer (CB6O.6O.O6CB), all having the same hexyloxy flexible spacers (B), are compared in Fig. 1 in terms of a scaled transition temperature, and it was found that this increases monotonically with increasing number of mesogenic units in

TB

spacer, normally an alkyl chain. The degeneracy of the helices

the oligomer. The absolute NTB–N (TN

N) and N-Iso (TNI)

may be lifted if the molecules are chiral and the chiral NTB phase is seen.3 More recently, twist-bend smectic phases have also been reported for achiral odd-membered dimers8,9 and these exhibit multiple levels of chirality even though their constituent

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1cc07012f

transition temperatures also increase passing from the dimer to trimer to tetramer (Fig. S3, ESI†), by around 30 K and 10 K, respectively. Previous studies have focussed on the evolution of liquid crystal behaviour from a conventional low molar mass mesogen containing a single mesogenic unit to the corres- ponding dimer and trimer, and revealed a much smaller increase in TNI on passing from the dimer to trimer than from

the monomer to dimer.21,22 The data reported here indicate that

this trend continues on passing from the trimer to tetramer, and suggests that the mesogenic units in the oligomeric species

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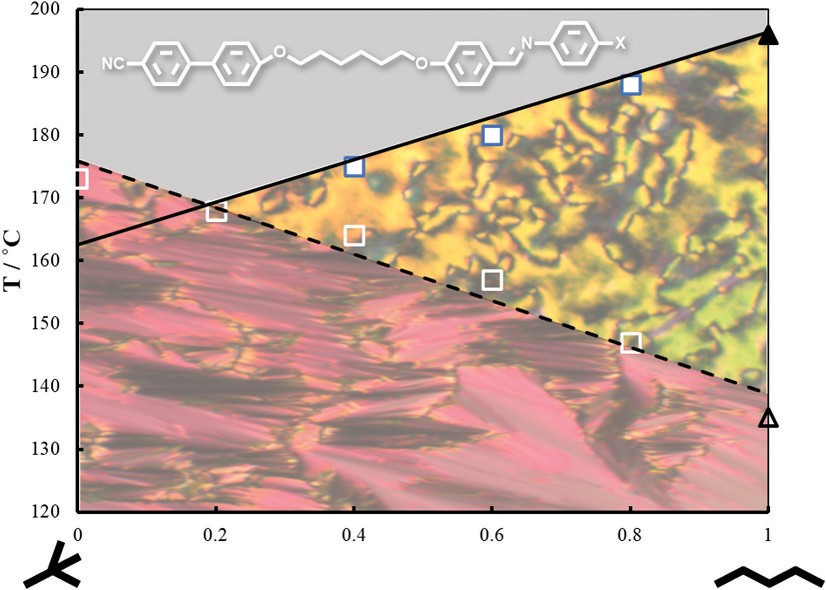
Remarkable stabilisation of the intercalated smectic phases of nonsymmetric dimers by *tert*-butyl groups

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**ABSTRACT**

The synthesis and characterisation of two groups of nonsymmetric dimers, the 1-(4-cyanobiphenyl-

4‘−yloxy)-ω-(4-butyl, 4-(1-methylpropyl) or 4-*t*-butylanilinebenzylidene-4’−oxy)alkanes, and the

1-(4-cyanobiphenyl-4‘−yl)-ω-(4-butyl, 4-(1-methylpropyl) or 4-*t*-butylanilinebenzylidene-4’−oxy) alkanes, are reported. The length and parity of the flexible spacer is varied. The *tert-*butyl homo- logues show higher melting points than the corresponding *sec*-butyl or *n*-butyl substituted dimers,

suggesting that chain branching improves packing efficiency within the crystalline structure. The branched chain homologues have a stronger tendency to exhibit smectic phases than the *n*-butyl-

substituted dimers, and for longer spacers are exclusively smectic. A comparison of the nematic- isotropic transition temperatures (*T*NI) for dimers containing the different terminal chains is possible for one set of materials, and reveals a large reduction in *T*NI on passing from the *n*-butyl to *sec-*butyl-substituted, but a much smaller decrease on changing *sec*-butyl for *tert*-butyl. A different trend is observed for the smectic A-isotropic transition temperatures for which the *tert*- butyl substituted dimers show a higher value than the corresponding *sec*-butyl homologue, and only marginally lower than that of the *n*-butyl-substituted dimer. This surprising behaviour is interpreted in terms of the ability of the *tert*-butyl group to pack more efficiently into the intercalated smectic A phase as the spacer length increases.

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**Keywords** Intercalation; branched chain; smectic phases; twist- bend

**Introduction**

Liquid crystalline dimers consist of molecules con- taining two mesogenic units linked *via* a flexible spacer, most commonly an alkyl chain [1,2]. In recent years, there has been a dramatic resurgence of interest in this class of materials arising first from the observation of the twist-bend nematic phase for dimers containing an odd-membered spacer (see, e.g. [3–25]), and even more recently from the discovery

of the twist-bend smectic phases [26–28]. Prior to this, liquid crystal dimers had been the focus of considerable research interest following the discovery of the intercalated smectic phases for nonsymmetric dimers, in which the two mesogenic units differ in structure [29–31]. The intercalated smectic phases were first observed for members of the 1-(4-cyano- biphenyl-4’−yloxy)-ω-(4-alkylanilinebenzylidene-4’- oxy)alkanes [29].

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Tuneable helices of plasmonic nanoparticles using liquid crystal templates: molecular dynamics investigation of an unusual odd–even effect in liquid crystalline dimers†

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Liquid crystalline (LC) dimers formed helical nanofilaments depending on the parity of the alkyl linker, revealing an unusual odd–even effect. Molecular dynamics simulations were used to investigate the observed tendency. Elongation of the linker translates to an increase of the pitch of the helices, which allows achieving tuneable helical assemblies of Au nanoparticles doped to the LC matrix. The impact of the tuneable pitch of helices on the chiral optical properties of composites was investi- gated with full-wave simulations based on the T-matrix method.

Thin films of gold nanoparticles (NPs) exhibiting plasmonic circular dichroism (PCD)1 are foreseen to revolutionise photonic technolo- gies of the 21st century.2 Unfortunately, the availability of thin film materials exhibiting PCD properties is highly limited. A common way to fabricate materials exhibiting chiral structures (and thus properties) is the use of organic molecules that can act as small building blocks organising into 3D mesoscopic objects. When doped with gold NPs, these objects can serve as templates for their organisation, thereby inducing PCD properties. Although research exploiting this powerful approach is dynamically progressing for aqueous dispersions, translating these achievements to the realm of thin films is challenging. The foremost limiting step is the precise control over the helical morphology of the templates in the form of thin film, which requires further progress in materials chemistry and molecular components design. One of the most perspective types of

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materials, which can spontaneously form chiral structures, also in thin films, are liquid crystals.3 Chiral LCs exhibit strong chiro-optical properties and can be utilised as matrices to prepare composites in which a helical arrangement of gold NPs leads to enhanced PCD responses.4 Interestingly, helical structures of LC phases may also be formed by achiral molecules, e.g. bent-core or bent dimeric mole- cules, limiting the requirement to introduce chirality at the mole- cular level, which complicates organic synthesis.5 Such achiral molecules were recently shown to assemble into twist-bend nematic phase,6,7 its lamellar analogue twist-bend smectic C phase,8,9 and helical nanofilament (HNF) phases or dark conglomerate phases.10

The HNF phase is particularly attractive for fabricating composites with gold NPs for photonic applications. Such composites can benefit from the synergy of the LC matrix soft character of the LC matrix and the strong optical properties of gold NPs.11

One of the challenges of designing chiral LC matrices built from achiral dimer-type mesogens is that minute changes in their molecular architecture might translate to drastic modifications of the phase sequence. For instance, a crucial parameter determin- ing chiral phase formation is the length/parity of the linker unit in dimeric molecules. Typically, helical structures are formed by dimers with an odd number of atoms in the linker. Interestingly, in one of our recent works, we showed a mesogen that disobeys this general rule. We have reported the formation of helical nanofilaments by a dimeric compound with an even-numbered alkyl internal spacer and hydroquinone p-oleyloxybenzoate (HOB) arms.11 Upon cooling from an isotropic melt, LC dimer formed an HNF phase, which could host gold NPs.11

Here, we investigated whether other members of the homologues series, referred to as HOB-n-HOB where n denotes the number of carbon atoms in the linkage, can also form twisted layered struc- tures. Through the use of X-ray diﬀraction (XRD), polarised light microscopy (POM), and transmission electron microscopy (TEM), we determined phase sequences of the novel compounds, while mole- cular dynamic simulations were utilised to provide insights into the observed results. We also confirmed that even members of the family could be successfully used as matrices to prepare helical

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Soft Matter



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New patterns of twist-bend liquid crystal phase behaviour: the synthesis and characterisation of the 1-(4-cyanobiphenyl-40-yl)-10-(4-alkylaniline- benzylidene-40-oxy)decanes (CB10O·m)†

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The synthesis and characterisation of the 1-(4-cyanobiphenyl-40 -yl)-10-(4-alkylanilinebenzylidene-40 - oxy)decanes (CB10O·m) are reported. This series shows a rich liquid crystal polymorphism including twist-bend nematic and smectic phases. All the homologues reported exhibit an enantiotropic conventional nematic phase. For the homologues with m r 10, the local packing in the nematic phases and the layer spacing in the smectic phases indicates an intercalated arrangement of the molecules. An intercalated smectic CA phase is observed if m/11 E 0.5. Either side of this condition, the twist-bend nematic phase is observed, a novel pattern of behaviour for a series on increasing a terminal chain length. For longer chain lengths, m = 12, 14, 16 and 18, two twist-bend smectic C (SmCTB) phases are observed, and the packing of the molecules is now of a bilayer-type. The higher temperature variant is termed SmCTB-SH in which SH (single helix) refers to the presence of a short, distorted clock-type helix. In the lower temperature SmCTB-DH phase, an additional longer helix is superimposed on the short one,

and DH denotes double helix.

Introduction



Heliconical liquid crystal phases formed by achiral molecules constitute the newest class of liquid crystal phases and have attracted considerable global research interest. The simplest of these phases is the twist-bend nematic (NTB) phase, first identified some ten years ago for the odd-membered liquid crystal dimer CB7CB1–3 and a decade after a prediction was made by Dozov that bent molecules should exhibit both twist- bend nematic and smectic phases.4 In the NTB phase, the director forms a helix and is tilted with respect to the helical axis, and this was the first example of spontaneous chiral symmetry breaking in a fluid with no positional order. The spontaneous formation of chirality ensures that equal numbers of left- and right-handed helices are formed, but if the consti- tuent molecules are chiral, this degeneracy is removed and the chiral NTB phase is obtained.5 More recently, heliconical twist-bend

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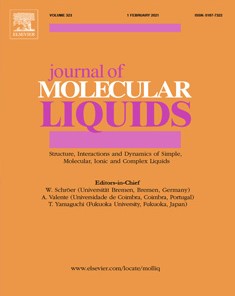
smectic C (SmCTB) phases have also been discovered for liquid crystal dimers6,7 and in bent-core mesogens.8,9 It appears that a range of variants of this phase, similar to the SmC\* subphases observed for chiral molecules, are possible.10

The key structural requirement for the observation of the NTB phase is a bent molecular structure and this is most often realised using odd-membered liquid crystal dimers. These consist of molecules containing two mesogenic groups con- nected by a spacer having an odd number of atoms (see, for example, ref. 11–29) although other structures such as higher oligomers,30–36 semi-rigid bent core liquid crystals,37,38 and hydrogen-bonded systems39–43 are also known to support the formation of the NTB phase. The search for the twist-bend smectic phases has also been focussed on bent mesogenic dimers, but in order to drive smectic phase formation, the molecular design must also incorporate molecular inhomo- geneity. This was achieved using non-symmetric liquid crystal dimers having different mesogenic units.44 It is known that if the mesogenic units in such structures are selected in order to exhibit a specific, favourable interaction then depending on the ratio of the length of the flexible spacers and terminal chains, a range of smectic phases may be observed including intercalated and interdigitated variants.45–48 Using this design strategy, examples of the SmCTB phase have been found for members of the CBnO·m series, see Fig. 1, with n = 6 and m = 10–12, 14,

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Intrinsically chiral ferronematic liquid crystals: An inversion of the helical twist sense at the chiral nematic – Chiral ferronematic phase transition



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Strongly dipolar mesogenic compounds with a chiral center located in a lateral alkyl chain were synthe- sized, and shown to form the ferroelectric nematic phase. The presence of molecular chirality induced a helical structure in both the N\* and NF\* phases, but with opposite helix sense in the two phases. The relaxation frequency of the polar fluctuations is only weakly affected by helical structure, it was found to be slightly lower for the chiral NF\* phase than for its achiral, non-branched counterpart with the same lateral chain length.

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1. Introduction

The recent discovery of the ferroelectric nematic or ferrone- matic, NF, phase [1–7] is of profound fundamental and technolog- ical importance, and heralds a new field of scientific endeavour in condensed matter, complementing the extensively studied solid ferroelectrics. Previously, polar order in soft matter had been observed only in phases with some degree of positional order, smectic [8–10] and columnar phases [11] or in lyotropic nematics made of polymers [12]. In the conventional nematic, N, phase the long axes of the rod-like molecules are more or less aligned in the same direction, along the director, and their centres of mass are randomly distributed. The director is denoted by the unit vec- tor n having inversion symmetry such that n = - n, and hence, the phase is non-polar. Chiral systems show the chiral nematic phase, N\*, in which the molecular chirality causes the director to form a helix. The sense of the helix is pre-determined by the sense of molecular chirality and molecular conformation [13]. At the molec- ular level the N and N\* phases are indistinguishable. The NF phase was predicted over a century ago, in which the molecular dipole moments align in the same direction, i.e. n – - n, giving a ferrolec- tric fluid [14]. Polar order in liquids is an absolutely fundamental issue not only in chemistry and physics but may also have far

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reaching implications in biological sciences. It is widely believed that chirality holds the key to an understanding of the origins of life and liquid crystals are ideal systems to study chirality, its ori- gins and chirality propagation. Some forty years ago, it was pre- dicted that the ferroelectric nematic phase, in order to reduce electrostatic energy, will twist giving a polar N\* phase with n – - n [15], the spontaneous chirality being controlled through steric and electrostatic interactions between achiral molecules. Such a mechanism may have fundamental implications for the ori- gins of chirality. This spontaneous chirality has not been observed in the very small number of ferronematogens studied to date, but does pose the fascinating question, how will an intrinsically chiral ferronematogen behave? So far the only chiral system reported comprises an achiral ferronematogen doped with a chiral additives [16–18], and although such systems have much merit, the inter- pretation of their behaviour at a molecular level, both experimen- tally and theoretically, is made significantly more complex by their bicomponent nature. To better understand how intrinsic molecular chirality affects the formation of the NF phase, here for the first time we report the synthesis and characterization of intrinsically chiral ferroelectric nematogens, and compare their properties to those of structurally similar achiral materials. These compounds are based on the prototype ferroelectric nematogen, RM-734 [4], here referred to as I-1, and their structures and transitional prop- erties are shown in Table 1. The chiral center has been introduced into a laterally attached alkyl chain at the third atom away from

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Article

Tunable Intermolecular Charge Transfer in Ionic Liquid Crystalline

Derivatives of the [*closo*-B10H10]2− Anion

[Litwin Jacob,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Litwin%2BJacob%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Edyta Rzeszotarska,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Edyta%2BRzeszotarska%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Maria Koyioni,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Maria%2BKoyioni%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Rafał Jakubowski,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Rafa%C5%82%2BJakubowski%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Damian Pociecha,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Damian%2BPociecha%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Anna Pietrzak,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Anna%2BPietrzak%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [and Piotr Kaszynski](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Piotr%2BKaszyn%CC%81ski%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf)\*

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ABSTRACT: A new paradigm of ionic liquid crystals exhibiting low-energy charge transfer bands is demonstrated. Thus, four series of ion pairs of 1,10-disubstituted derivatives of the [*closo*-B10H10]2− anion and substituted pyridinium cations were prepared and their thermal and photophysical properties were investigated. All pyridinium ion pairs form a smectic A (SmA) phase with clearing temperatures above 200 °C and intermolecular charge transfer (CT) band in the solid and fluid states and in CH2Cl2 solutions. The CT band maximum is in the range of 320−510 nm and its position correlates with the difference in frontier molecular orbital (FMO) energies of the ions (highest occupied molecular orbital

(HOMO) of the anions and the lowest unoccupied molecular orbital (LUMO) of the cations), which, in turn, correlate well with the substituent *σ*p parameters. Experimental results are augmented with extensive density functional theory (DFT) calculations and X- ray diffraction (XRD) analyses.

■ INTRODUCTION

Organic compounds exhibiting intermolecular charge transfer

(CT) phenomena1−3 constitute an important class of materials

Functional ionic liquid crystals27 (ILCs) are of increasing importance for contemporary technologies mainly in the context of ion transport in electrolytes, dye-sensitized solar

28−30

investigated in the context of organic solar cells, photo-

cells, and electrochromic materials.

Typically, the focus is

detectors, two-photon absorbers, and nonlinear optical systems.4−9 One attractive approach to such materials involves self-organizing behavior of two-component liquid crystals (LCs), in which one constituent acts as an electron donor and the other as an electron acceptor.10,11 Such materials offer advantages over other CT binary systems by more facile and reproducible preparation, predictable molecular organization, and modular approach. For these reasons, binary donor− acceptor (D−A) discotic LCs,12−14 forming alternating

on one of the ions possessing the property of interest (*e.g*.,

photophysical or redox activity), while the counterion is a spectator necessary for the charge balance. Consequently, materials in which both ions are active are rare and those exhibiting intermolecular CT are essentially neglected.31 We report here the first, to our knowledge, ionic liquid crystals with tunable intermolecular CT bands based on the [*closo*- B10H10]2− anion.

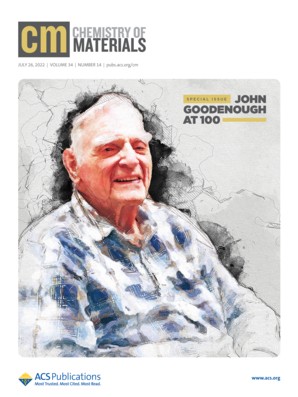
The [*closo*-B10H10]2− anion32 (Figure 1) is a three- dimensional (3-D) sigma aromatic system33 with the *D*

columns, have been investigated as organic semiconductors, relatively efficient anisotropic charge conductors,15,16 and laser addressable dichroics.17 These materials typically involve electron-rich *π* systems, such as derivatives of tripheny- lene,13,18,19 hexabenzocoronene,12,15 and truxene,20 and electron acceptors, for example, trinitrofluorenone,14,16,18,21,22 naphthalenediimide,23 perylenediimide,12,15 mellitictrii- mide,19,24 and tetracyanoquinodimethane (TCNQ).25 It has been demonstrated that the energy of the CT interactions in alternating D−A discotic LCs can be adjusted using a series of electron donors and acceptors.24,26 While most effort in self- organizing materials exhibiting low-energy CT behavior has been dedicated to discotic LCs, other types of such LCs, *e.g*. calamitic and ionic, received little to no attention.

4*d*

molecular symmetry, a large highest occupied molecular

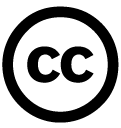
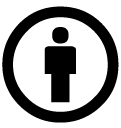
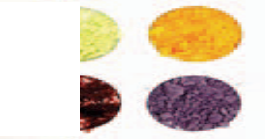
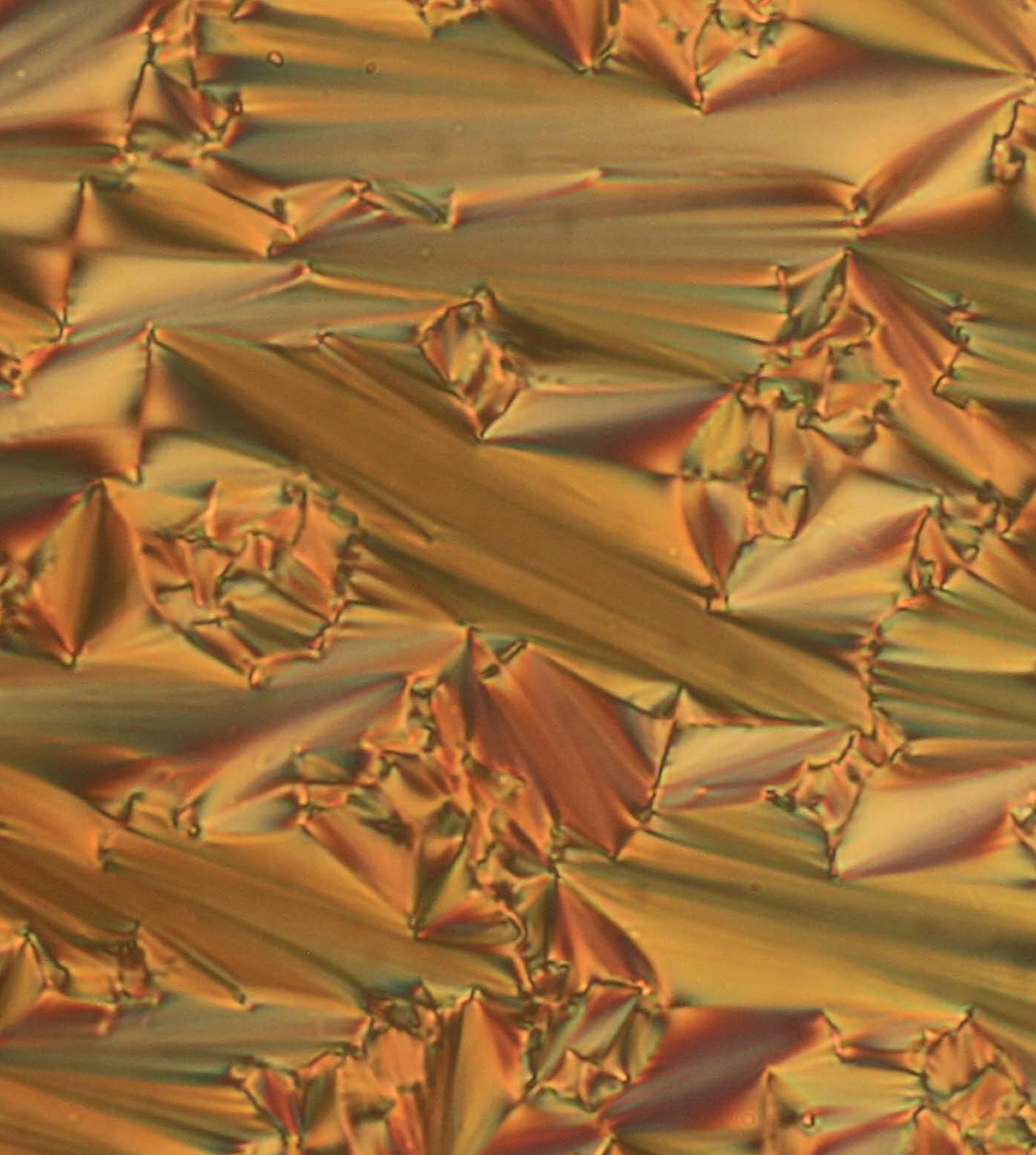
orbital−lowest unoccupied molecular orbital (HOMO− LUMO) gap rendering practical transparency above 200 nm, and a high-lying doubly degenerate HOMO.34 The orbital symmetry allows for efficient electronic interactions between the anion and *π* substituents,35 and intense intramolecular cluster-to-*π* substituent CT bands have been observed in some



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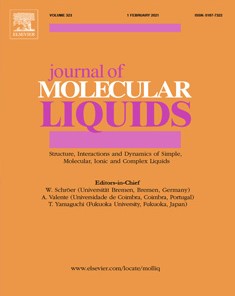
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Introducing the azocinnamic acid scaffold into bent-core liquid crystal design: A structure–property relationship study



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a b s t r a c t

A series of bent-core liquid crystals possessing the azocinnamoyl unit in both elongating side arms was synthesized. The chain length was kept fixed for each molecule (C12H25), whereas the substituents at the central and outer rings were varied. The LC phases were assigned by polarizing optical microscopy, dif- ferential scanning calorimetry and X-ray diffraction. The investigated compounds are suitably diverse to reveal some aspects of the relationship between molecular structure and the mesomorphic properties. Namely, non-substituted parent compound is crystalline only and the methyl group in position 2 or the chlorine atom in position 4 of the central ring suppresses LC phase formation. Introduction of the strong electron-withdrawing nitro group between the side arms on the central ring leads to a B7 phase. Compounds possessing a bromine atom or two chlorine atoms in the neighbourhood of the ester groups form LC phases typical for rod-like molecules, namely a nematic – smectic phase sequence. The results are compared with those reported for the azobenzoyl analogues.

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1. Introduction

For development of new liquid crystalline (LC) materials with potential for innovative applications, it is essential to select appro- priate building blocks and to arrange them in suitable structural geometries. In this way, complex systems can be produced with control over the assembly processes and material properties. Namely, building blocks can be functionalized to enable respon- siveness, electron-conductivity or certain biologically relevant functions. Thus, research of possibilities to modulate LC properties through synthetic design of building blocks is still progressing [1–

3].

The first investigation of relatively simple cinnamoyl-based LCs, methyl and ethyl 4-(4-alkyloxyphenylazo)cinnamates, was reported by Vorländer in 1937 [4] and since then this unit has been applied to LC materials as thermotropic [5–7] and polymeric sys- tems [8–10]. In comparison to benzoyl analogues, the ethylene group between the phenyl ring and the carboxylate group in those

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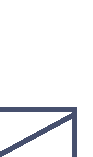
derived from cinnamic acid enhances the longitudinal polarisabil- ity and extends the molecular length.

Regarding thermotropic systems, the bent-core LCs incorporat- ing the cinnamoyl unit are less considered than rod-like ones. The lack of investigation probably masks the inherent interest in these compounds as evidenced by studies describing full characteriza- tion of LC features of both symmetric and non-symmetric bent- core LCs with the cinnamoyl unit. A variety of LC phases (B1, B3 and B6) has been reported in the homologous series derived from molecules based on unsubstituted or methyl-substituted resorci- nol bis(cinnamoylalxoxybenzoates) [11]. Introduction of 4- chlororesorcinol as the central ring has led to compounds which exhibit a nematic phase at low temperatures and a SmC phase appearing as a monotropic phase [12]. 2-Methylresorcinol and 5- chlororesorcinol have been esterified with 4-(4-n-hexadecyloxy phenoxycarbonyl)cinnamic acid to give the compounds, which exhibit two enantiotropic LC phases [13]. The high-temperature phase of the former compound can be defined as a ColF and the low-temperature phase is a racemic SmCsPA phase. In the case of latter, on cooling from the isotropic liquid textures typical for SmCP phases can be observed, while the low-temperature phase

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*Review*

**Liquid Crystal Dimers and Smectic Phases from the Intercalated to the Twist-Bend**

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**Abstract:** In this review we consider the relationships between molecular structure and the tendency of liquid crystal dimers to exhibit smectic phases, and show how our application of these led to the recent discovery of the twist-bend, heliconical smectic phases. Liquid crystal dimers consist of molecules containing two mesogenic groups linked through a flexible spacer, and even- and odd-membered dimers differ in terms of their average molecular shapes. The former tend to be linear whereas the latter are bent, and this difference in shape drives very different smectic behaviour. For symmetric dimers, in which the two mesogenic groups are identical, smectic phase formation may be understood in terms of a microphase separation into distinct sublayers consisting of terminal chains, mesogenic units and spacers, and monolayer smectic phases are observed. By contrast, intercalated smectic phases were discovered for nonsymmetric dimers in which the two mesogenic units differ. In these phases, the ratio of the layer spacing to the molecular length is typically around

0.5 indicating that unlike segments of the molecules overlap. The formation of intercalated phases is driven by a favourable interaction between the different liquid crystal groups. If an odd-membered dimer possesses sufficient molecular curvature, then the twist-bend nematic phase may be seen in which spontaneous chirality is observed for a system consisting of achiral molecules. Combining the empirical relationships developed for smectogenic dimers, and more recently for twist-bend nematogenic dimers, we show how dimers were designed to show the new twist-bend, heliconical smectic phases. These have been designated SmCTB phases in which the director is tilted with respect

to the layer plane, and the tilt direction describes a helix on passing between layers. We describe

three variants of the SmCTB phase, and in each the origin of the symmetry breaking is attributed to the anomalously low-bend elastic constant arising from the bent molecular structures.

**Keywords:** liquid crystal dimers; intercalated; interdigitated; twist-bend nematic; twist-bend smectic;

chirality; resonant soft X-ray scattering

**1. Overview**

Over the last decade arguably the hottest topic in liquid crystals science has been the twist-bend nematic, NTB, phase following its discovery in 2011 [1], some ten years after its prediction by Dozov [2]. We will return to the NTB phase later, but widely overlooked in Dozov’s seminal work was the prediction of twist-bend smectic phases, and in this review, we trace the discovery of these phases for liquid crystal dimers [3]. Although the aim of this Special Issue is to provide an overview of the state-of-the-art of current UK liquid crystals research, the work we describe would not have been possible without a close collaboration between the Universities of Aberdeen and Warsaw. Indeed, the very essence of liquid crystals research is the need for a multidisciplinary approach, and science should know no borders. In keeping with this Special Issue’s aim, however, we have attempted to focus primarily on the contribution to the overall work made in Aberdeen, but note that this story is fundamentally one of collaboration.

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Soft Matter



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Unmasking the structure of a chiral cubic thermotropic liquid crystal phase by a combination of soft and tender resonant X-ray scattering†

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Nataˇsa Vaupoticˇ \*ad



A resonant X-ray scattering response for two structural models of a chiral cubic phase with a giant unit cell, one composed of a continuous grid and micelles and the other with three continuous grids, is studied theoretically and compared to experimental measurements. For both structural models resonant enhancement of all the symmetry-allowed diﬀraction peaks is predicted, as well as the existance of several symmetry forbidden peaks (pure resonant peaks). Experimental measurements were performed at the carbon and sulphur absorption edge. Only one pure resonant peak was observed, which is predicted by both models. Two low-angle symmetry allowed peaks, not observed in non-resonant scattering, were resonantly enhanced and their intensity angular dependence can distinguish between the two structural models.

Resonant X-ray scattering (RXS) has proven an indispensable tool to determine structures of diﬀerent phases of thermotropic liquid crystals.1,2 Because the intensity of the scattered light depends both on the spatial variation of the electron density as well as the molecular bond orientation, spatial variation of the molecular orientation can be determined from measurements. The method is based on the fact that polarizability of molecules becomes anisotropic if the energy of the incident X-ray beam is close to the absorption edge of a chemical element present in a molecule. Often, sulphur with the absorption edge at the energy



2472 eV, corresponding to the wavelength l = 0.5 nm, is used. Carbon, being the most abundant element in organic mole- cules, seems like a natural choice for the resonant element, but its absorption edge is at very low energy, (283 eV, l = 4.4 nm), thus measurements must be performed in high vacuum for the X-rays not to be absorbed by air. Recently, RXS at the carbon absorption edge (resonant soft X-ray scattering, RSoXS) proved useful to determine the structure in the twist-bend nematic

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[10.1039/d2sm01030e](https://doi.org/10.1039/d2sm01030e)

phase,3–5 its smectic analogues6 and multi-helical smectic phases,7–9 the structure of blue phases4 and the structure of a two-continuous-grid cubic phase with the Ia3% d symmetry (double gyroid phase).10 The continuous-grid cubic phases with extremely large unit cells, of the order of 10 nm, are of special interest, both from the fundamental point of view as well as potential applications.11–13 In the continuous-grid phases molecules arrange into a system of interweaving channels, each being made of linear fragments connected through multi-fold junctions. In the double gyroid phase these junctions are three- fold and planar and the planes of the neighbouring junctions are rotated by some angle. Along one grid, the rotation is clockwise and counter clockwise along the other grid, which makes the whole structure achiral. If channels accommodate elongated molecular cores, the average direction of the long molecular axes also rotates from one junction to the other.

A perplexing and extensively studied is a chiral cubic (CC) phase.14 Upon the first observation,15,16 chirality of the struc- ture was not observed, and the phase was assigned an achiral Im3% m symmetry. Multiple models for its structure were put forward17,18 and their common shortcoming was that they failed to reproduce, even qualitatively, proper intensities of the peaks observed by the X-ray scattering (especially the two most intensive peaks with the Miller indices (123) and (004)). Following the discovery of the optical activity of the CC phase, the topic gained even more interest and there were several attempts to explain the origin of the phase chirality.14,19–21

Validation of two structural models20,21 that were proposed in

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Article

Exploring Photoswitchable Properties of Two Nitro Nickel(II) Complexes with (N,N,O)‑Donor Ligands and Their Copper(II)

Analogues

[Patryk Borowski,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Patryk%2BBorowski%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf)§ [Sylwia E. Kutniewska,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Sylwia%2BE.%2BKutniewska%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf)§ [Radosław Kaminski,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Rados%C5%82aw%2BKamin%CC%81ski%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Adam Krówczynski,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Adam%2BKro%CC%81wczyn%CC%81ski%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Dominik Schaniel,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Dominik%2BSchaniel%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [and Katarzyna N. Jarzembska](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Katarzyna%2BN.%2BJarzembska%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf)\*

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ABSTRACT: Two photoswitchable nickel(II) nitro coordination com- pounds and their copper(II) analogues are reported. In all these systems, the metal center is chelated by (N,N,O)-donor ligands containing either 2- picolylamine or 8-aminoquinoline fragments. The studied compounds were thoroughly investigated using crystallographic and spectroscopic techniques supplemented by computational analysis. They are easy to synthesize and stable, and all compounds undergo the nitro group isomerization reaction.

Nevertheless, there are signiﬁcant diﬀerences between the copper and nickel

systems regarding their structural and switchable properties. According to the

solid-state IR spectroscopy results, 400−660 nm light irradiation of the ground-state (η2-O,O′)-κ-nitrito copper(II) complexes at 10 K induces a rather moderate conversion to a metastable linkage isomer, which is visible only up to approximately 60−80 K. In turn, upon visible light irradiation (ca.

530 nm excitation wavelength), the ground-state nitro isomers of the examined nickel(II) complexes transform into the endo-nitrito forms. It was possible to achieve about 35% conversion for both nickel(II) systems and to determine the resulting crystal structures at 160 K in the case of single crystals after 30−45 min of exposure to LED light (crystals decayed with longer irradiation), and

roughly 95% conversion was achieved for thin-ﬁlm samples as indicated by the IR spectroscopy results. Traces of the endo-nitrito

linkage isomers remained up to 200−220 K, and the isomerization reaction was proven to be fully reversible.

1. INTRODUCTION

Molecular switches triggered by UV−vis light may ﬁnd wide applications in high-capacity storage devices,1 optoelectronics,2 medicine,3 as color-changing materials, etc.4,5 Therefore, the

importance of studies dedicated to the conscious design of new functional photoswitchable systems with the desired properties cannot be overestimated.6−11 Transition-metal complexes in which the metal center is coordinated by molecular fragments that can exist in multiple isomeric forms are among the potential functional materials of this kind.12 Examples of ambidentate ligands known to display solid-state linkage isomerism include NO,13,14 NO2,8,12,15−25 SO2,26−29 SCN,30

31

In view of the above, two new nitro NiII complexes and their CuII analogues, namely 2a ((N,N,O)-(2-methyl-1-phenyl-3-(2'- pikoliloamido)prop-2-en-1-one) nickel(II)/copper(II) nitrite complex) and 2b ((N,N,O)-(2-methyl-1-phenyl-3-(8'- (quinolin)ami-do)methylene)-prop-2-en-1-one) nickel(II)/ copper(II) nitrite complex), were designed and synthesized (Scheme 1). The metal centers in these compounds are chelated by (N,N,O)-donor ligands and the ambidentate nitro moiety.

Their structural and switchable properties in the solid state, including the eﬀects of the metal centers and modiﬁcations of

the aromatic ligand fragments, were thoroughly investigated

and analyzed. It is worth noting that the ﬁrst solid-state

and N2.

Transition-metal complexes containing nick-

el,12,22,24,25 cobalt,32−34 iron,35 ruthenium,13,36 osmium,37 palladium, or platinum19−21,23 centers are the most represen- tative examples of such systems. Light-induced structural changes in crystals can be investigated using photocrystallo- graphic methods.9,38−40 As far as copper complexes are

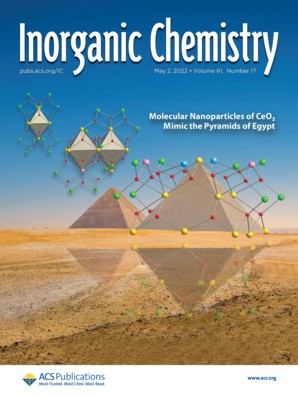
concerned, to date, no multi-temperature X-ray diﬀraction or

photocrystallographic studies of the ONO isomerization

reaction have been reported; however, mixtures of various linkage isomers were observed in the solid state.41,42

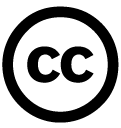
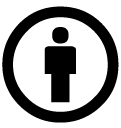
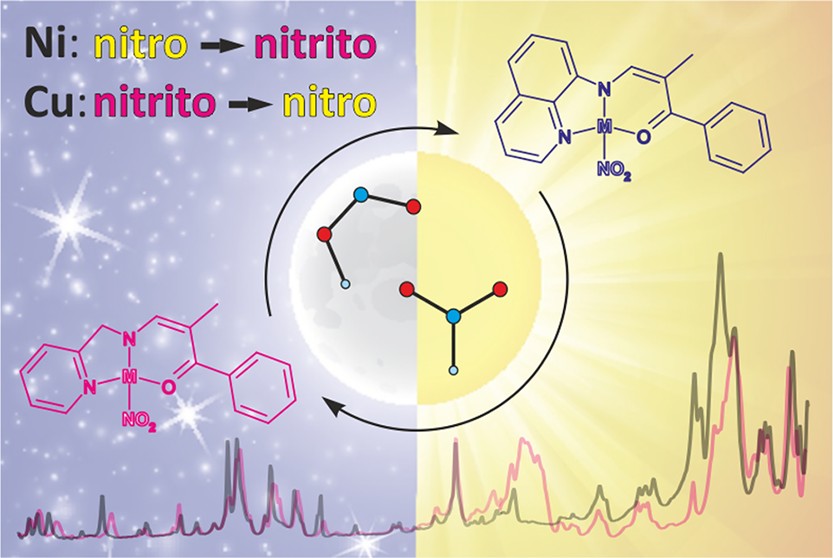
experiments conﬁrming the photoisomerization of the nitro

group in copper systems are reported in this contribution. The



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An optically reversible room-temperature solid-state cobalt(III) photoswitch based on nitro-to-nitrito linkage isomerism†‡

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Adam Kro´wczyn´ski,a Dominik Schaniel b and Katarzyna N. Jarzembska \*a



A simple trinitro cobalt complex [Co(3,30 -diamino-N-methylpro- panediamine)(NO2)3] was proven to be photoswitchable at room tem- perature as the Pca21 polymorph with the maximum nitro-to-nitrito conversion reaching ca. 55%. Solid-state IR, UV-vis and XRD indicate that the transformation can be triggered optically in both ways via

470 nm and 570–660 nm LED light, respectively.

Photoswitchable solid-state materials may find various important real-life applications, including those in opto(bio)electronics, sen- sors, or in high-capacity storage devices.1–3 Among molecular switches, transition-metal complexes possessing ambidentate ligands4–17 constitute a promising and readily modifiable group of compounds. The industrially desirable photoswitchable materi- als should work under ambient conditions, be stable, relatively cheap, non-toxic, and easy to synthesize in high-yield. In turn, the photo-induced transformation should be selective, efficient, con- trollable, reversible and reproducible.



The nitrite ambidentate ligand has lately caught a lot of scientific attention. It has appeared, however, that as far as the nitro transition-metal coordination compounds are concerned, most of the early reported systems were characterized by rather moderate conversion percentages of the photoinduced linkage isomers (PLIs). The first system of this kind confirmed to undergo full nitro-to-nitrito transformation (M–N(O)2 - M–ONO, M –

metal) was published by Warren et al.18 Since then Raithby and

co-workers have introduced a few more high-conversion photo- switchable transition-metal nitro complexes.19–21 Furthermore,

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† Dedicated to Professor Paul R. Raithby, celebrating his outstanding career in inorganic and organometallic chemistry, on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available: Synthesis, compound characterization, X-ray structural data, supporting spectroscopic plots, cavity volume data, TGA and additional computational details. CCDC 2171480–

2171486. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2cc05134f>

Mochida’s group has recently reported new efficient platinum(II) nitro coordination compounds22,23 and we have presented some nickel(II)-based systems of this kind.24–26 Nevertheless, up to now PLIs have been usually noted and/or generated in crystal structures at relatively low temperatures (below 240 K). There are only a few exceptions, mostly platinum-group compounds, such as the 100%- photoswitching PdII complex with PLIs detected in the solid state up to 260 K under continuous illumination,20 or the PtII nitro complex21 for which PLI was observed at 300 K, though with a rather moderate conversion level (30%). It should be noted that there are also examples of nickel(II) complexes undergoing reversible nitro-to-nitrito conversion at higher temperatures, such as the simple [Ni(C6H4(NH2)2)2(NO2)] complex exhibiting thermally induced switching in the 383–393 K temperature range,27 which is accompanied by a colour change. Also, [Ni(C8H18- N4O2)(NO2)2]-H2O exhibits similar properties, switching reversibly from the nitro to the exo-nitrito form with colour change while heating from 298 to 383 K.28 In both cases the process was confirmed spectroscopically.

When compared to the nitro nickel-based systems, studies regarding photoswitchable behaviour of another non-toxic and relatively cheap 4th-row transition-metal, cobalt,29 are rather scarce. The most thoroughly investigated nitro cobalt complex undergoing the isomerization reaction upon UV-vis light irra- diation is nitropentaaminecobalt(III).30,31 Hence for this study, we have selected [Co(Me-dpt)(NO2)3] (Me-dpt = 3,3 0 -

diamino-N-methylpropanediamine) (Fig. 1),32 which constitu-

tes a cobalt(III) analogue of the previously studied, and proved photoswitchable, nickel(II) complex.33

In [Co(Me-dpt)(NO2)3] the cobalt centre is coordinated by a tridentate amine ligand and three nitro groups (Fig. 1). The system had been previously studied structurally regarding its polymorphism.32 For the purpose of this project the Pca21 form with one molecule in the asymmetric unit was synthesized. Careful analysis of the collected X-ray diﬀraction data on fresh crystals revealed that the examined compound exists as two linkage isomers in the crystal structure, which had not been

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Effect of Diamine Bridge on Reactivity of Tetradentate

ONNO Nickel(II) Complexes

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Two new square planar ONNO nickel(II) complexes C2\_core and C3\_core have been synthesized and characterized by single crystal X-ray diffraction, NMR spectroscopy, thermogravimetry, and DFT calculations. The experimental results revealed the effect of the length of diamine bridge in the ligand on the behavior of the studied complexes in the reaction with *N*- heterocyclic aromatic amines, while DFT calculations provided a basis for the rationalization of this observation. The complex

with propylenediamine bridge (C3\_core) readily reacts with

pyridine and its derivatives to form high-spin (paramagnetic) complexes with octahedral geometry as characterized by X-ray diffraction; electron-donating substituents on the pyridine ring facilitate the coordination of axial ligands. In contrast, the complex with ethylenediamine bridge (C2\_core) does not undergo such a reaction because of the high deformation energy of the core required for the formation of C2\_Py complex.

Introduction

Nickel(II) complexes (d8-configuration) can exist in singlet or triplet spin state. Square planar Ni(II) complexes are diamagnetic, with a singlet ground state (S = 0). However, when their geometry changes to square pyramidal or octahedral (with coordination number of five and six, respectively), these complexes become paramagnetic, with a triplet ground state (S = 1). Such transition between two spin states was denoted Coordination-Induced Spin-State Switching (CISSS). This effect was first discovered for Ni(II) by Herges and co-workers,[1–3] and later was observed for other transition metal complexes, e. g., Fe(II), Fe(III), Mn(II), Mn(III), and Co(II). Spin-state switching phenomena in transition metal complexes is currently an intensively studied area in coordination chemistry, because such systems have a potential for application in memory devices, chemical sensors, and contrast agents for magnetic resonance imaging.[4–8]

A number of Ni(II) complexes, in which the metal center is located in ONNO environment, have been synthesized previously.[9–13] The most common representatives of tetradentate ONNO ligands are found in the salen series, [salen = N,N’-bis (salicylidene)ethylenediamine].[13,14] However, their acacen ana- logues [acacen = N,N’-bis(acetylacetone)ethylenediamine] are

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*Institut de Química Computacional and*

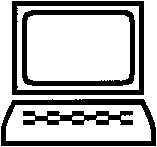
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much less frequently used as ligands in coordination chemistry and the library of their complexes with transition metals is significantly smaller.[9,15,16] The principal examples of such com- pounds are [Co(acacen)L2]+ complexes, which have been studied extensively as potential protein inhibitors (e. g., for selective inhibition of Human α-Thrombin).[17,18] Another prominent repre- sentative of such complexes is Fe(II) spin-crossover complex with the wide thermal hysteresis loop.[19,20]

Square planar nickel(II) complexes can change their coordina- tion sphere by addition of donor ligands, this transformation can be detected by shifts in the UV-Vis spectra.[1,3,13] Propensity of Ni(II) complexes towards formation of octahedral complexes depends on the nature of equatorial ligands and basicity of the axial ligand. The first structurally characterized octahedral nickel (II) complexes with acacen equatorial ligand were reported in

2010.[11] Recrystallization of Ni{N,N-ethylenebis(1,1,1-trifluoroace-

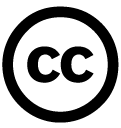
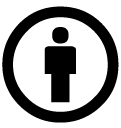
tylacetoneiminato)} [NiL] from pyridine resulted in brown crystals of [NiL(Py)2] characterized by X-ray diffraction. Moreover, the reaction with the bidentate ligand 1,4-diazabicyclo[2.2.2]octane (dabco) led to the formation of one-dimensional coordination polymer, in which dabco axially bridges [NiL] units in a linear fashion. It was noted that no corresponding solid products were formed in the absence of CF3 groups in the equatorial ligand.[11] Thus, the incorporation of highly polar functional group (such as CF3) near coordination sphere of transition metal plays the important role in the formation of octahedral complexes with N- donor ligands. Very recently, a family of planar nickel(II) complexes with four phenazine-based acacen-type ligands has been reported.[9] The complexes demonstrate CISSS behavior with fluorescence detection and can find application as molec- ular sensors. The addition of pyridine to them in the excited state is more favorable than in the ground state. The electron- withdrawing CF3 substituents in the ligand strongly affect the acidity of the nickel center and facilitate coordination of axial ligands, increasing the CISSS sensitivity.



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Letter

Pathway-Dependent Grain Coarsening of Block Copolymer Patterns under Controlled Solvent Evaporation

[Arkadiusz A. Leniart,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Arkadiusz%2BA.%2BLeniart%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Przemyslaw Pula,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Przemyslaw%2BPula%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [Robert W. Style,](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Robert%2BW.%2BStyle%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf) [and Pawel W. Majewski](https://pubs.acs.org/action/doSearch?field1=Contrib&amp;text1=%22Pawel%2BW.%2BMajewski%22&amp;field2=AllField&amp;text2&amp;publication&amp;accessType=allContent&amp;Earliest&amp;ref=pdf)\*

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ABSTRACT: Solvent evaporation annealing (SEA) is a straightforward, single-step casting and annealing method of block copolymers (BCP) processing yielding large-grained morphologies in a very short time. Here, we present a quantitative analysis of BCP grain-

coarsening in thin ﬁlms under controlled evaporation of the solvent. Our study is aimed at understanding time and BCP concentration inﬂuence on the rate of the lateral growth of BCP

grains. By systematically investigating the coarsening kinetics at various BCP concentrations,

we observed a steeply decreasing exponential dependence of the kinetics power-law time exponent on polymer concentration. We used this dependence to formulate a mathematical model of BCP ordering under nonstationary conditions and a 2D, time- and concentration-

dependent coarsening rate diagram, which can be used as an aid in engineering the BCP processing pathway in SEA and also in other directed self-assembly methods that utilize BCP−solvent interactions such as solvent vapor annealing.

olvent-assisted block copolymer (BCP) self-assembly is one of the most attractive methods of processing these materials for fabrication of ordered nanometer-scale patterns.1

S

In particular, high-molecular-weight (MW) systems, due to their very high viscosity, tend to develop long-range order only in the presence of plastifying solvent molecules.2−4 The solvent−BCP interactions are at the core of a popular directed self-assembly method known as solvent vapor annealing

While most quantitative studies on BCP ordering were performed under equilibrium conditions, that is, constant temperature,11,12 there are few reports on BCP grain coarsening kinetics under nonstationary conditions.13−16

Understanding of BCP self-assembly under nonstationary processing conditions, has gained particular importance with the advent of accelerated processing techniques that utilize fast

17,18

(SVA), where an as-cast, disordered BCP ﬁlm is exposed to

thermal ramps, for example, in photothermal

19

or microwave

the vapors of a good solvent. The solvent swells the ﬁlm and

heating

and during solvent swelling and deswelling ramps in

20−23

increases polymer diﬀusivity which induces microphase

SVA experiments.

In the case of SEA, the solvent

separation of polymer chains into distinct domains and their coarsening. A similar swelling and ordering eﬀect is observed when a BCP ﬁlm is immersed in a mixture of marginal and

good solvents of an appropriately selected composition.5

Conveniently, ordered morphologies can be obtained for certain BCP−solvent combinations directly at the casting step

by exploiting the tendency of these materials to microphase

separate in a concentrated solution, above the critical order− disorder solvent concentration (φODT).6−9 This facile approach has been recently advanced by extending the ordering and grain coarsening phase during casting and demonstrated to yield well-ordered BCP morphologies of high-MW poly- (styrene-block-methyl methacrylate) (PS-b-PMMA),4 poly-

evaporation rate eﬀectively deﬁnes the duration of the grain

coarsening phase. We have previously investigated the kinetics

of pattern coarsening in a cylindrical PS-b-P2VP diblock copolymer by analyzing the end-point morphology of dry BCP

thin ﬁlms obtained after a series of solvent evaporation ramps.

Our results indicated the importance of a narrow BCP

concentration window in the immediate vicinity of the φODT that strongly contributes to the accelerated growth of the domains. We were not able, however, to decouple the

coarsening time and BCP concentration eﬀects on grain

coarsening kinetics described with a conventional power-law

model:11,24

(styrene-block-ethylene oxide),10 and poly(styrene-block-2- vinylpyridine) (PS-b-P2VP).7 This single-step solvent evapo-



ration annealing (SEA) approach relies on the rational

selection of a nonvolatile solvent or, more conveniently, a volatile−nonvolatile solvent mixture. The nonvolatile solvent,

by longer retention in the cast wet ﬁlms, extends the BCP

residence time in the swollen state above the critical order−

disorder concentration, φODT, and enables morphology ordering.6,10

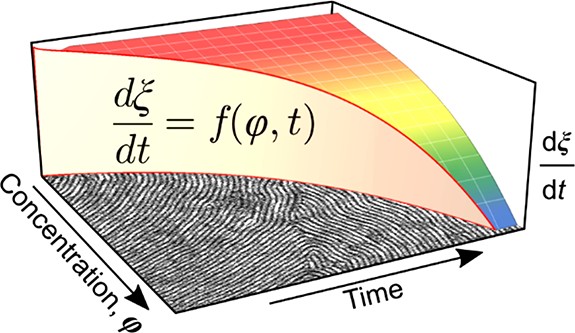
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Soft Matter



REVIEW

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Solvent-assisted self-assembly of block copolymer thin films

Przemyslaw Pula, Arkadiusz Leniart and Pawel W. Majewski \*



Solvent-assisted block copolymer self-assembly is a compelling method for processing and advancing practical applications of these materials due to the exceptional level of the control of BCP morphology and significant acceleration of ordering kinetics. Despite substantial experimental and theoretical eﬀorts devoted to understanding of solvent-assisted BCP film ordering, the development of a universal BCP patterning protocol remains elusive; possibly due to a multitude of factors which dictate the self- assembly scenario. The aim of this review is to aggregate both seminal reports and the latest progress in solvent-assisted directed self-assembly and to provide the reader with theoretical background, including the outline of BCP ordering thermodynamics and kinetics phenomena. We also indicate significant BCP research areas and emerging high-tech applications where solvent-assisted processing might play a dominant role.

Scope of the review and introduction

Block copolymers (BCP) constitute an important class of self- assembling materials consisting of two or more chemically dissimilar polymeric chains called blocks. Progress in BCP science has been documented by numerous reviews focused on their synthesis,1–3 processing,4–10 and their applications.6,11–16 Argu- ably, the greatest advantage of BCP-mediated manufacturing of nanoscale patterns is the low-cost and high-throughput of this approach compared to the conventional methods such as photo- and e-beam lithography. Numerous applications for

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BCP-ordered templates have been proposed, including optical coatings,17,18 metamaterials,19–21 photonic crystals,22,23 plas- monic nanostructures,24,25 and membranes.26,27 These emer- ging applications have propelled research efforts aimed at understanding and harnessing the self-assembly of BCP thin films and led to the development of various directed self- assembly (DSA†) methods. DSA methods are used to accelerate the self-assembly process and to reduce patterns’ defectivity to an application enabling level and, by using directional biases, to orient (align) anisotropic BCP morphologies.4,8,10,28

† Here, we use the DSA term to encompass any method that directs the BCP self- assembly.7,8 More narrowly, it has been used in the context of graphoepitaxial and chemoepitaxial ordering.28–30



Przemyslaw Pula

Przemysław Puła obtained his MSc degree in Nanostructure Engineer- ing in 2019 from the Department of Physics at the University of Warsaw. In the same year, he started his PhD studies under the supervision of Prof. Majewski. His research is focused on self- assembly of block copolymer-low molecular weight compounds blends and their use in fabri- cation of volatile organic com-

pound gas sensors. Arkadiusz Leniart



Arkadiusz Leniart is currently a PhD candidate in Chemistry at the University of Warsaw. He received his M.Sc. degree in Physics in 2017. His research focuses on directed self-assembly of block copolymer thin films and development of photothermal and solvent-assisted annealing methods enabling rapid fabri- cation of ordered nanostructured coatings. Besides his scientific activity, he is also a professional chess player awarded with the Grandmaster title.

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Stabilizing Differential Interfacial Curvatures by Mismatched Molecular Geometries: Toward Polymers with Percolating 1 nm Channels of Gyroid Minimal Surfaces

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ABSTRACT: Soft materials with self-assembled networks possess saddle-shaped interfaces with distributed negative Gaussian curva- tures. The ability to stabilize such a geometry is critically important for various applications but can be challenging due to the possibly “deficient” packing of the building blocks. This nontrivial challenge has been manifested, for example, by the limited availability of cross- linkable bicontinuous cubic (Q) liquid crystals (LCs), which can be utilized to fabricate compelling polymers with networked nano-

channels uniformly sized at ∼1 nm. Here, we devise a facile approach

to stabilizing cross-linkable Q mesophases by leveraging the synergistic self-assembly from pairs of scalably synthesized polymer- izable amphiphiles. Hybridization of the molecular geometries by mixing significantly increases the propensity of the local deviations in

the interfacial curvature specifically required for Q assemblies. “Normal” (type 1) double gyroid LCs possessing 1 nm ionic channels conforming to minimal surfaces can be formulated by simultaneous hydration of the amphiphile mixtures, as opposed to the formation of hexagonal or lamellar mesophases exhibited by the single-amphiphile systems, respectively. Fixation of the bicontinuous network in polymers via radical polymerization has been efficaciously facilitated by the presence of the bifunctional polymerizable groups in one of the employed amphiphiles. High-fidelity lock-in of the ordered continuous

1 nm channels has been unambiguously confirmed by the observation of single-crystal-like diffraction patterns from synchrotron small-angle X-ray scattering and large-area periodicities by transmission electron microscopy. The produced polymeric materials exhibit the required mechanical integrity as well as chemical robustness in a variety of organic solvents that benefit their practical applications for selective transport of ions and molecules.

KEYWORDS: *percolating nanochannels, polymerizable LCs, gyroid, interfacial curvature, minimal surfaces*

olymeric materials comprising 3-D percolating nano- channels (nanopores) have great technological impacts in areas such as precise nanofiltration,1 gas separation,2

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In contrast, self-assembly of amphiphilic molecules6−19 or block copolymers20−26 can give rise to thermodynamically

stable 3-D continuous nanostructures with precisely defined

fuel cells,

and so forth. In these applications, the nanochannels

geometry over long-length scales, as exemplified by bicontin-

serve to selectively shuttle small molecules or ions, therefore requiring the sizes to be well-defined in the regime of ∼1 nm.

Traditional strategies to access 3-D permeable nanochannels in

uous cubic (Q) mesophases. Furthermore, the feature sizes are highly tunable in the range from 1 to ∼100 nm, depending on

the employed amphiphilic building blocks. Particularly,

polymeric materials have utilized the morphologies developed



from spinodal decomposition or bicontinuous microemul- sion.4,5 While the bulk synthesis of polymers consisting of 3-D interconnected nanochannels can be realized by these two approaches, the corresponding structures suffer from the absence of long-range order and large sizes significantly above

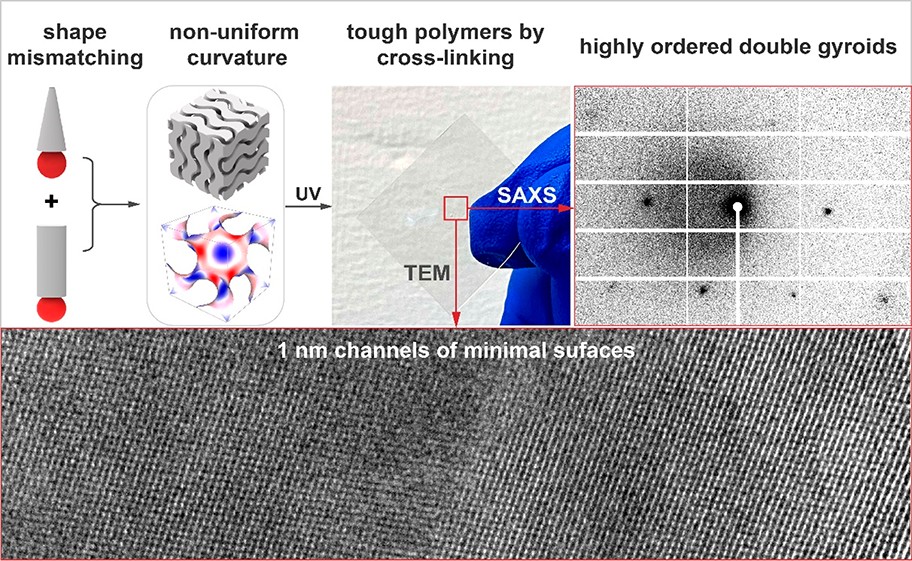
50 nm.

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