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Synthesis and Mesomorphic Properties of Novel Dibenz[*a*,*c*]anthracenedicarboximides

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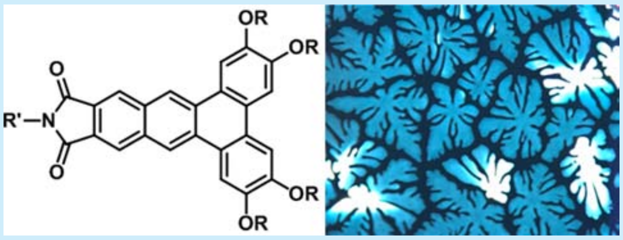
Supporting Information

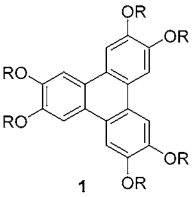
ABSTRACT: The synthesis and characterization of a novel series of dibenz[*a*,*c*]anthracenedicarboximides is reported. Incorporating electron-withdrawing imides bearing flexible alkyl chains allowed for the production of materials that self-assemble into hexagonal columnar mesophases featuring broad temperature ranges. Furthermore, longer *N*-alkyl chains or branched *N*-alkyl chains broaden the mesophase temperature range by lowering the melting transition without greatly influencing the clearing point.



Discotic liquid crystals have garnered significant attention in recent years due to their potential applications in light emitting diodes, field effect transistors, and photovoltaics.[1−3] Typically, a discotic mesogen consists of a rigid aromatic core surrounded by peripheral side chains.[4,5] When these compounds self-assemble in the columnar mesophase, there is effective $\pi-\pi$ orbital overlap between molecules within the columns, which facilitates charge transport. Because of the potential utility of discotic liquid crystals in organic semiconductors, there is considerable motivation for the preparation of discotic liquid crystalline materials that exhibit their mesophase over a broad temperature range.

Hexaalkoxytriphenylenes (**1**) are some of the most extensively studied discotic mesogens, exhibiting narrow columnar temperature ranges above room temperature.[6−8] Dibenz[*a*,*c*]anthracene derivatives, which have an extended aromatic core as compared to triphenylenes, have recently been shown to exhibit columnar mesophases with appropriate substituents on the core (**2** and **3**).[9,10] However, the mesophase temperature range in these dibenzanthracenes is remarkably sensitive to the nature of the substituents attached, with electron-withdrawing substituents such as cyano groups promoting a stable mesophase characterized by a high transition temperature from liquid crystal to isotropic liquid.[10,11] Several other studies on discotic liquid crystals also highlight the importance of electron-withdrawing groups in promoting stable mesophases.[12−16]

Based on this, our group recently prepared a series of cyano-substituted tetraalkoxydibenzanthacenes (**3**).[11] Unfortunately, while this series did display a columnar phase, the melting transition temperatures were also quite high; presumably because the electron-withdrawing groups also stabilize the crystalline phase.[11] Therefore, a potential strategy for the design of dibenzanthracene derivatives that exhibit columnar phases over broad temperature ranges is to incorporate electron-withdrawing groups that promote a high clearing point, but that allow the incorporation of flexible chains in order to lower the melting transition. By maintaining a high clearing point and lowering the melting point, the mesophase temperature range will be broadened.



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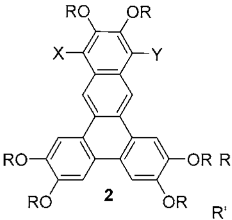

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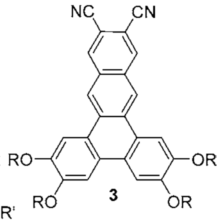

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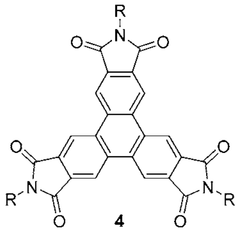

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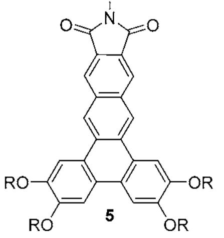

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Imides, especially perylene bisimides, are widely used as electron-deficient materials. Perylene bisimides and their derivatives exhibit n-type semiconducting properties with potential applications in light emitting diodes, photochromic materials, and molecular wires.[17−21] Furthermore, imides fused with conjugated systems such as perylene, anthracene, and naphthalene have found uses as imide dyes for fluorescent imaging and dye-sensistized solar cells.[22,23] This class of compounds is particularly advantageous for these types of applications due to their high photochemical stability, ease of synthetic modification, and their charge transmission abil-

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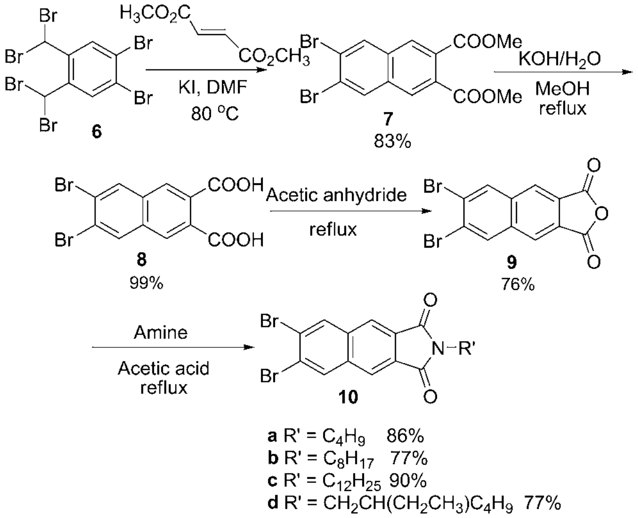
ity.[24−26] Furthermore, *N*-substitution allows the introduction of flexible side chains without compromising the electron-withdrawing ability of the imide group.

Despite their uses as electron-deficient materials, there are few examples of imides as discotic liquid crystalline materials. For example, there are examples of mesogenic perylene bisimides,[27−29] and Wu and co-workers recently reported a series of triphenylene carboximides (**4**) and demonstrated that, depending on the *N*-alkyl chain, some of the series displayed columnar mesophases over broad temperature ranges.[30] These studies suggest that the incorporation of imides onto the dibenzanthracene core may be a promising strategy for producing materials with mesophases over broad temperature ranges.

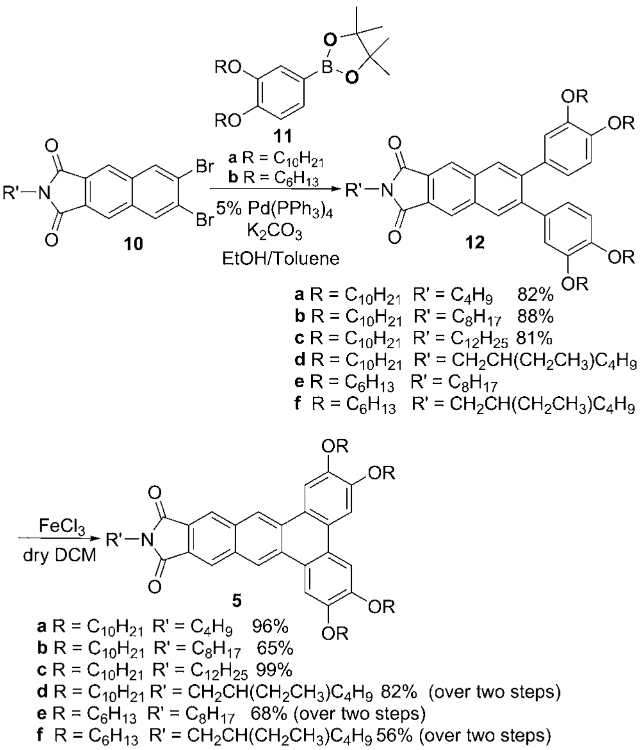
Herein we report the synthesis and mesophase characterization of a series of novel *N*-substituted dibenzanthracenedicarboximides (**5**). We anticipate that these compounds, substituted with alkoxy chains on one end of the molecule and alkyl-substituted, electron-deficient imides on the other, will produce materials with broad mesophase ranges by lowering the melting transition and maintaining a high clearing point.

Scheme 1. Synthesis of 10



Our synthesis began with the preparation of 6,7-dibromo-2-alkyl-benzo[*f*]isoindole-1,3-diones (**10a−d**) (Scheme 1). First, compound **6**,[31] which was prepared via a benzylic bromination from 1,2-dibromo-*o*-xylene, was reacted with dimethyl fumarate in the presence of KI to yield naphthalene **7** in a 31% yield. Compound **7** was subsequently hydrolyzed to the corresponding dicarboxylic acid (**8**) using a procedure adapted from Osawa and co-workers[32] in quantitative yields. The 6,7-dibromo-2,3-naphthalenedicarboxylic acid (**8**) was then converted to the corresponding anhydride (**9**) using a procedure adapted from Baathulaa and co-workers[33] in good yield. The desired benzoisoindole-1,3-diones (**10a−d**) were prepared by heating anhydride **9** at reflux with the appropriate amine, which furnished the desired products in yields of 77−90%.

Scheme 2. Synthesis of 5



The synthesis of series **5** involved a Suzuki−Miyaura cross-coupling between **10** and dialkoxy phenylboronates (**11**)[34] to afford compounds **12a−g** (Scheme 2). An oxidative ring closing was then performed in dry DCM using 6 equiv of iron(III) chloride for 30 min to afford the desired *N*-alkyl-2,3,6,7-tetrakis(alkyloxy)-11,12-dibenz[*a*,*c*]anthracenedicarboximides (**5a−f**) in yields of 65−99%. In this way, six novel dibenz[*a*,*c*]anthracenedicarboximides with four different alkyl chain lengths (butyl, octyl, dodecyl, and a branched chain) on the nitrogen atom and two different alkoxy chain lengths (hexyloxy and decyloxy) were prepared.

The liquid crystalline properties of compounds **5a−f** were studied by polarized optical microscopy, differential scanning calorimetry (DSC), and variable temperature powder X-ray diffraction (XRD). The results are summarized in Tables 1 and 2.

Table 1. Phase Behaviour of Compounds 5a−f Based on DSC with Scan Rate of 5 °C·min^{-1} on Heating

compd	R′, R	phase transition temperature (°C)
5a	R′ = C_4H_9, R = $C_{10}H_{21}$	Cr 101 Col_h 214 I
5b	R′ = C_8H_{17}, R = $C_{10}H_{21}$	Cr 64 Col_h 222 I
5c	R′ = $C_{12}H_{25}$, R = $C_{10}H_{21}$	Cr 48 Col_h 206 I
5d	R′ = $CH_2CH(C_2H_5)C_4H_9$, R = $C_{10}H_{21}$	Cr 28 Col_h 223 I
5e	R′ = C_8H_{17}, R = C_6H_{13}	Cr 131 Col_h 250 I
5f	R′ = $CH_2CH(C_2H_5)C_4H_9$, R = C_6H_{13}	Cr 87 Col_h 278 I

Table 2. X-Ray Diffraction Data of 5a−f

compd	*d*-spacing (Å)	Miller index (*hkl*)	phase
5a	21.5	100	Col_h (a = 24.8 Å)
5b	22.1	100	Col_h (a = 25.5 Å)
5c	22.7	100	Col_h (a = 26.2 Å)
5d	22.6	100	Col_h (a = 26.1 Å)
5e	19.2	100	Col_h (a = 22.1 Å)
5f	19.0	100	Col_h (a = 21.9 Å)

Polarized optical microscopy on thin films cooled from the isotropic liquid state revealed dendritic textures and homeotropically aligned domains that are typical for a columnar hexagonal phase (Figure 1). Powder XRD diffractograms showed a prominent peak at low angle which is assigned to the (1 0 0) reflection, as well as a broad reflection corresponding to the alkyl halo. The (1 1 0) reflection was not observed for any of these samples; however, combined with the polarized optical microscopy results, the XRD results are consistent with a columnar hexagonal phase.

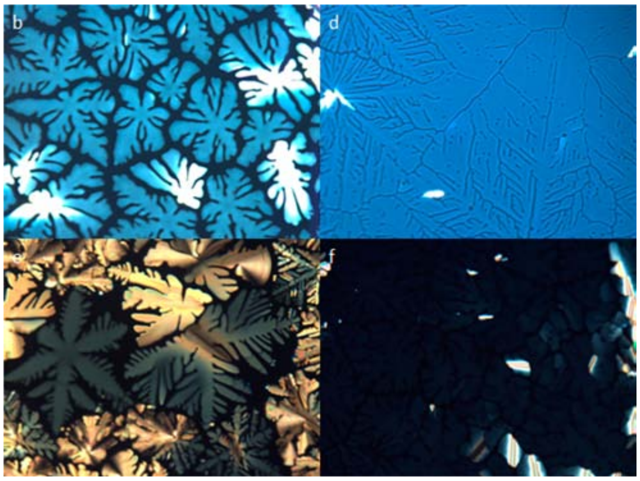


Figure 1. Representative polarized optical micrographs of **5b**, **5d**, **5e**, and **5f** obtained on cooling near the isotropic-columnar mesophase transition temperature. All micrographs were taken at 200× magnification.

Overall, as the chain on the nitrogen atom becomes longer, there is a broadening of the columnar phase primarily by a lowering of the melting transition temperature. This is most easily observed by comparing compounds **5a**–**c**, where the alkoxy chains are held constant and the *N*-alkyl chains are increased from butyl to octyl to dodecyl. While all of these compounds have clearing points between 206 and 222 °C, the melting transition declines steadily as the chain length on the nitrogen is increased from butyl to octyl to dodecyl. Surprisingly, compound **5d**, bearing the branched *N*-alkyl chain, did not show any destabilization of the columnar mesophase as compared to the linear isomer (**5b**), but did display a depression of the melting transition. Consequently, **5d** displayed the broadest columnar mesophase range, primarily by a lowering of the melting transition. This observation suggests that the branched chain disrupts the crystalline state, but does not negatively influence the stability of the mesophase.

Similar trends are noticed with the hexyloxy derivatives **5e** and **5f**, with the branched derivative (**5e**) having a lower melting transition temperature and broader columnar phase than the straight 8-carbon chain derivative (**5f**). Surprisingly, however, despite the fact that they have isomeric chains, the clearing points are quite different. In addition, when compared to the corresponding decyloxy derivatives, the hexyloxy derivatives display columnar phases that are shifted to higher overall temperatures.

The trends observed with series **5** demonstrate that the introduction of imide groups onto the aromatic core of the molecule produces materials with broad columnar temperature ranges. This is likely due to the electron-withdrawing imides bearing flexible alkyl chains, allowing for the molecule to maintain its electron-withdrawing character while also having increased flexibility around the aromatic core.

The spectroscopic properties of series **5** were also examined, with compound **5d** used to represent the series. The UV–visible spectra of **5d** in different solvents show absorbance maxima close to 350 nm, as well as some weak absorption bands at longer wavelengths consistent with an intramolecular charge transfer band (Figure 2). The absorbance maxima show slight shifts as a function of solvent. The emission spectra of **5d** (excitation at 340 nm) show more pronounced solvent dependence for their emission maxima as solvent is varied (Figure 3), showing a red shift in emission maxima as solvent polarity is increased. When the emission maxima are plotted against the dielectric constant of each solvent, a correlation is observed with an R^2 value of 0.90 (see Supporting Information (SI)). These results suggest that the polar excited state is stabilized in polar solvents, leading to a red shift in emission.

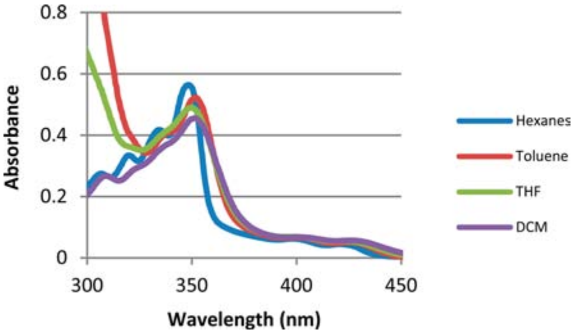


Figure 2. UV-visible spectra of 1 × 10^{-5} M solutions of **5d**.

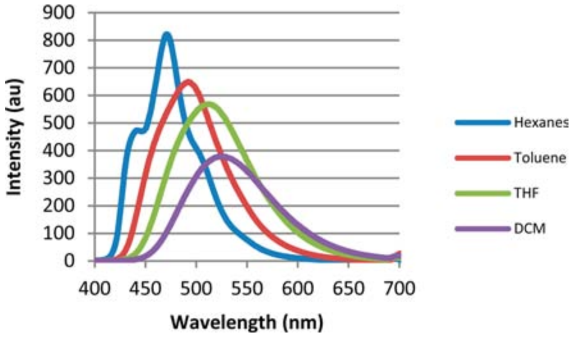


Figure 3. Emission spectra of 2 × 10^{-6} M solutions of **5d** (excitation at 340 nm).

The HOMO and LUMO energy levels were explored both computationally and experimentally. Density functional theory calculations on a truncated model compound (lacking the alkyl chains) gave a HOMO energy of −5.43 eV and a LUMO energy of −2.07 eV, with an estimated band gap of 3.36 eV. Cyclic voltammetry on compound **5d** (see SI) in DCM with Bu_4NPF_6 as the supporting electrolyte showed a quasireversible oxidation peak at 0.65 V vs Fc/Fc^+, from which an estimated HOMO energy of 5.45 eV is obtained. An irreversible reduction peak is also observed at 1.6 V. The LUMO energy was estimated from the HOMO energy and the estimated optical band gap at 2.17 eV. These experiment results are in reasonable agreement with the calculated energy levels. It is also noteworthy that despite the electron-withdrawing imide group, compound **5** does not appear to be an effective electron-accepting material, as suggested by the relatively high LUMO energy. This result can be attributed to the electron-rich aromatic core with four electron-donating alkoxy groups.

In summary, we have reported the modular synthesis of a novel series of *N*-substituted dibenzanthracenedicarboximides. This series displays broad columnar phases with low melting transition temperatures, demonstrating that substituents that combine an electron-withdrawing nature and a flexible alkyl chain can effectively stabilize the columnar phase of these types of compounds. In addition, the modular synthetic approach and relative ease of synthesis make this class of compounds a promising candidate for the design of new discotic materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures and characterization data for all new compounds; DSC traces and powder XRD data for compounds **5a–f**; cyclic voltammetry for compound **5d**. 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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