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Novel triphenylenoimidazole discotic liquid crystals

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ABSTRACT

A novel discotic core was constructed by fusing imidazole unit with well-known triphenylene discotic core. Two new imidazole fused unsymmetrically substituted triphenylene derivatives were prepared and characterized. While the molecular structures of the new compounds were verified by ¹H NMR, UV, MS and elemental analysis, their liquid crystalline properties were determined by polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction studies. These triphenylenoimidazole derivatives were found to exhibit hexagonal columnar mesomorphism over a wide temperature range. © 2011 Elsevier Ltd. All rights reserved.

One of the largest and most important classes of molecules that exhibit columnar liquid crystal phases is represented by triphenylene derivatives. Triphenylenes are, to date, the most widely explored materials out of all discotic mesogens since the triphenylene core is easily accessible through recognized synthetic routes and is excellent at granting mesomorphic properties.¹ Research over the past decade has demonstrated the potential of these and other related discotic materials as active components in organic semiconductor devices such as LEDs, solar cells, field effect transistors, etc.² Hexasubstituted triphenylene derivatives are the most broadly examined discotic materials because they have a strong tendency to form columnar mesophases, which are of interest in one-dimensional energy and electron transport properties. Structure-property relationships of triphenylene-based discotic mesomorphic materials have been well explored because of their considerable technological importance.³

Molecular shape is one of the most imperative factors which determines the self-assembly of molecules into mesomorphic phases. Expansion of triphenylene ring is expected to lead significant changes not only in mesomorphic properties but also in electronic properties. Such supramolecular macro discotics are anticipated to be mesomorphic over broad temperature ranges⁴ and exhibit high charge carrier mobilities⁵ in their columnar phases. Thus efforts have been made to enlarge the triphenylene core to generate phenanthrophenazine,⁶ hexabenzotriphenylene,⁷ triphenylenophthalocyanine,⁸ etc., derivatives. On the other hand, imidazole-based materials have a great prospective in the fields of biological and materials sciences.^{9–15} Imidazole moiety is also

personalized for hydrogen bond formation which has played an important role in the creation of supramolecular mesomorphic aggregates.¹⁶ There have been reports of design and construction of supramolecular mesomorphic assembly on the basis of imidazole moiety.¹⁷ Strong intermolecular hydrogen bonding resulted in formation of supramolecular bilayers of smectogens by the assembly of linear imidazole-containing Schiff's bases.¹⁸ Kadkin et al. reported smectic mesomorphism in imidazole-based biforked amphiphiles.¹⁹ The structure of smectic phase had bilayered structure with a continuous network of hydrogen bonds. Imidazole has also been used as ligand for complexation with metal to achieve metallomesogens.^{18,20}

However, most of the liquid crystalline materials based on imidazole skeleton come from the category of ionic liquids; the mesomorphic materials based on molecular imidazole derivatives have been less investigated. Imidazole based bis(imidazole)-annulated discotic terphenyl derivatives have been reported by Pisula et al.²¹ Columnar order with helical stacking of disks within the column was observed in these compounds. The isotropization temperature was lowered on increasing the bulkiness of peripheral alkyl chain. Very recently, the effect of extension of electron deficient π -conjugated perylene core has been investigated in perylene diester benzimidazole derivatives. Wicklein et al. prepared a series of compounds in which one side of perylene ring had diester and the anhydride ring of the second side was fused with benz-imidazole unit.²² Extension of π -conjugation due to fusion with benzimidazole was confirmed by a red shift in absorption spectra as compared to perylene bisimide. Imidazole group has been connected via a single bond to tetraalkoxymonomethoxy triphenylene by Kimura et al.²³ In its pure form this compound was non-liquid crystalline, while a mixture of this triphenylene-imidazole





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compound with benzene-1,3,5-tricarboxylic acid in 1:3 molar ratio displayed mesomorphism over a broad thermal range. On the basis of lattice constant values and the approximate diameter of single molecule, it was assumed that each disk of the column was constructed from arrangement of three molecules, connected to central benzene-1,3,5-tricarboxylic acid via hydrogen bonding. Also long range intracolumnar order was verified by the presence of a sharp peak in wide angel region.

In present investigation, we have looked over unsymmetrical examples of imidazole-fused-triphenylene derivatives for the effect of extension of discotic core on the mesomorphic behavior. Here, we report the extension of triphenylene ring with a nitrogen containing heterocycle, that is, imidazole. We adopted this approach to increase π -electron conjugation as well as to reduce overall symmetry of triphenylene ring. We discuss the synthesis, characterization and mesomorphism of novel triphenvlene-imidazole-fused mesogens. The number of peripheral alkyl chains around triphenylene has been varied between 5 and 6. All the newly synthesized compounds were characterized using spectral techniques and elemental analysis. The mesophase behavior of both compounds was investigated by polarizing optical microscopy and differential scanning calorimetry. The mesophase structure of these compounds was established with the help of X-ray diffractometry.

The synthesis of triphenylenoimidazole derivatives **5** is outlined in Scheme 1. Monohydroxytriphenylene **3** was prepared starting from catechol as reported previously.²⁴ Oxidation of the 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene **3** with ceric ammonium nitrate resulted in the formation of *o*-quinone derivatives, that is, 3,6,7,10,11-pentakis(hexyloxy)triphenylene-1,2-diones **4**.²⁵ Coupling of this *o*-quinone with ammonia and aldehyde in presence of acetic acid under reflux condition produces the desired triphenylenoimidazoles **5**.²⁶ Appearance of a new red shifted peak at 371 nm in UV clearly indicates the extension of triphenylene core. The chemical structure and purity of the newly synthesized materials were confirmed by spectral and elemental analysis.²⁶

The thermal behavior of both the compounds was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The transition temperature and associated enthalpy data obtained from the heating and cooling cycles of DSC or POM are collected in Table 1. The peak temperatures are given in °C and the numbers in parentheses indicate the transition enthalpy (ΔH) in kcal mol⁻¹. Compound **5a** was found to be liquid crystalline from 110 to 154 °C on heating. On slow cooling from the isotropic liquid, the microscopic preparation revealed a texture which is typical of that of a hexagonal columnar mesophase with large monodomains (Fig. 1a). On cooling, the crystallization was confirmed by the slow appearance of small needle like domains into the liquid crystal texture. It is notable that this transformation occurred at a much lower temperature than the crystal-to-mesophase transformation determined on heating. The microscopic results were in agreement with the DSC results. Two endothermic peaks were observed during the first heating from -30 to 160 °C (Fig. 2). The peak at 118.9 °C corresponds to the melting of the crystalline phase into the mesophase, followed by a small one at 147.3 °C. associated to the clearing temperature. On first cooling two exothermic peaks were seen, the first one at 143 °C corresponds to isotropic-to-columnar transition and the second one at 30.6 °C. Further heating and cooling scans of the sample gave almost similar thermal behavior. On the other hand, compound **5b** exhibits fan-like optical texture (Fig. 1b) of a hexagonal columnar mesophase upon cooling from the isotropic liquid (146 °C). No sign of crystallization could be detected on cooling up to room temperature; however, the material became very viscous at lower temperature. Probably it vitrifies at certain temperature. Upon heating, the material is shearable at about 116 °C and the DSC shows a glass-like transition at 108.4 °C. On cooling, one exothermic peak was detected at 140.9 °C corresponding to isotropic-to-columnar phase transition. No other transition (such as crystallization or glass transition) was seen down to $-30 \,^{\circ}$ C. It may be noted that the melting as well as isotropization temperature of these compounds is much higher as compared to that reported for hexahexyloxytriphenylene (HAT6).²⁷ This behavior can be explained in terms of increased ratio of rigid-to-flexible portions in the mesogen due to extension of triphenvlene ring into triphenvlene-imidazole ring without increasing the number or length of peripheral alkyl chains. The possibility of intermolecular H-bonded dimer formation, which can also enhance the melting



Scheme 1. Synthesis of triphenylenoimidazole mesogens. Reagents: (i) VOCl₃, CH₂Cl₂; (ii) catechol boron bromide, CH₂Cl₂; (iii) CAN, CH₃CN (iv) R'CHO, CH₃COONH₄, CH₃COOH, reflux.

Table 1

Phase transition temperatures (peak, $^{\circ}$ C) and associated enthalpy changes (kcal mol⁻¹, in parentheses) of triphenylenoimidazole compounds (see Scheme 1 for chemical structures)

Compound		First heating scan	First cooling scan
5a	DSC	Cr 118.9 (15.86) Col _h 147.3 (0.34) I	I 143.0 (0.34) Col _h 30.6 (9.32) Cr
	POM	Cr 110 Col _h 154 I	I 151 Col _h 51 Cr
5b	DSC	g 108.4 (0.17) Col _h I	l 140.9 (0.18) Col _h
	POM	g 116 Col _h 146 I	l 137 Col _h



Figure 1. Optical photomicrograph (a) of **5a** at 138 °C (upper photograph, crossed polarizers, magnification $\times 200$) and (b) of **5b** at 130 °C on cooling from the isotropic liquid (lower photograph, crossed polarizers, magnification $\times 500$).

point, was ruled out as the IR spectrum of **5a** does not display any H-bonded N-H absorption. Probably, the steric hindrance of the long aliphatic peripheral chains around the core prevents the molecule to form H-bonded dimer. The compound **5a** crystallizes at lower temperature, whereas **5b** remains mesomorphic up to room temperature. This indicates that attachment of additional flexible hexyl chain to imidazole-fused triphenylene discotic suppresses crystallization and favors liquid crystallinity.

In order to reveal the mesophase structure and hence the supramolecular organization of these compounds, X-ray diffraction experiments were carried out using unoriented samples. X-ray diffraction patterns for compounds were recorded in the columnar phase around 10 °C below the clearing temperature while cooling from the isotropic phase. The X-ray diffraction patterns of the mesophase exhibited by samples are supportive of a discotic hexagonal columnar arrangement. The X-ray diffraction pattern of compound **5a** and its one-dimensional intensity versus theta (θ) graph derived from the pattern are shown in the Figure 3. In the



Figure 2. DSC thermogram of 5a on heating and cooling cycles (scan rate 10 $^\circ C\mbox{ min}^{-1}).$

small angle region, two peaks were observed, one very strong and second weak peak. Taken in the ascending order of diffraction angle, the *d*-spacings of the first reflection (lowest angle and highest intensity) to the second one is in the ratio of $1:1/\sqrt{3}$. These values correspond to those expected from a two-dimensional hexagonal lattice. In the wide angle region there is one broad peak at θ \sim 10°. This broad peak with a *d*-spacing of \sim 4.7 Å was due to the liquid like packing of the aliphatic chains. The intercolumnar distances, *a*, calculated by using the relation $a = d_{10}/(\cos 30^\circ)$, where d_{10} is the spacing corresponding to the strongest peak in the small angle region, was found to be 20.45 Å. All the features fit into the well-known model for the Col_b phase in which the disc-like core of the molecules stack one on top of the other to form columns surrounded by alkyl chains and these columns in turn arrange themselves in a two-dimensional hexagonal lattice. Figure 4 represents X-ray diffraction pattern and one-dimensional intensity versus theta (θ) graph of compound **5a** at various temperatures while heating, as may be seen from the figure that the pattern of the compound has numerous sharp peaks in low and wide angle at 100 °C. This indicates that the material is in crystalline phase at this temperature. Whereas at higher temperatures (125, 140 °C) the material exhibited liquid crystalline behavior. This behavior is in accordance with DSC and POM results.

Compound **5b** shows similar XRD behavior. The intercolumnar distance for **5b** was found to be 21.33 Å. It is evident that as number of alkyl chains increases the diameter of the cylindrical columns formed by the discotic molecules also increases (Table 2). The intercolumnar distance of hexahexyloxytriphenylene (**H6TP**) was found, as expected, in between of **5a** and **5b**.

In conclusion, the molecular architecture obtained by fusing imidazole with triphenylene may be considered as a new discotic core whose full potential has yet to be realized in discotic field. The synthesis, characterization and mesomorphic behavior of



Figure 3. X-ray diffraction pattern and intensity versus θ profile of 5a at 130 °C.



Figure 4. Intensity versus θ profile of 5a at 100, 125 and 140 °C while heating.

Table 2

Intercolumnar distances (Å) of **5** derived from their diffraction patterns

Compound	d-Spacing (Å)	Intercolumnar distance (Å)
5a	17.71	20.45
5b	18.47	21.33
H6TP ^{27a}	18.34	21.17

two novel triphenylenoimidazole derivatives are presented here. One derivative **5a** is having five peripheral hexyloxy chains around the discotic core, while the other one **5b** contains one additional peripheral hexyl chain at the periphery. Liquid crystalline behavior of these two imidazole fused triphenylene derivatives was confirmed by polarizing optical microscopy and differential scanning calorimetry. They exhibit columnar mesophase over a wide range of temperature. Hexagonal columnar structure of the mesophase of these compounds was confirmed by X-ray diffraction studies

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- 26. Ammonium ceric nitrate (405 mg, 0.739 mmol) was added to a stirred solution of monohydroxytriphenylene 3 (500 mg, 0.671 mmol) in acetonitrile at room temperature. The reaction mixture was stirred at room temperature for about 3 min. The product was separated from the solvent by normal filtration. The residue was purified by column chromatography over silica gel (eluant: 10% ethyl acetate in hexane) to yield 4 as a dark blue colored solid (332.8 mg, 65.33%). A stirred mixture of 4 (332.8 mg, 0.438 mmol), formaldehyde (0.0711 ml, 37 wt %), glacial acetic acid (2 ml) and ammonium acetate (701.7 mg, 9.1 mmol) was refluxed for 4.5 h. After cooling the reaction mixture was diluted with water. Concentrated aqueous ammonia solution (sp. gr 0.91, 25-28 wt %) was added to neutralize the solution up to pH 7. A brown precipitate was formed. It was filtered, washed with distilled water. The residue was extracted with a mixture of chloroform and distilled water. The organic extract was dried over anhydrous sodium sulfate, concentrated and the product was purified by repeated column chromatography over silica gel (eluant: 5% ethyl acetate in hexane). Solvent was then removed in rotary evaporator. The residue left was now dissolved in dichloromethane and the resulting solution was added to cold methanol to afford 5a as gray color solid (90 mg, 27%). Similarly, 5b was obtained by reacting 4 with heptanal in 28% yield. Selected data for compound 4: ¹H NMR (400 MHz, CDCl₃): δ 8.96 (s, 1H),

7.67 (d, 2H), 7.43 (s, 1H), 7.06 (s, 1H), 4.21 (m, 10H), 1.93 (m, 10H), 1.3–1.6 (m, 30H), 0.93 (m, 15H). UV-vis (CHCl₃): λ_{max} 271, 339, 383, 561 nm. Compound **5a**: ¹H NMR (400 MHz, CDCl₃): δ 8.78 (s, 1H), 8.31 (s, 1H), 7.8–8.0 (m, 5H), 4.49 (t, *J* = 6.6, 2H), 4.32 (t, *J* = 6.6, 2H), 4.26 (m, 6H), 1.96 (m, 10H), 1.2–1.7 (m, 30H), 0.94 (m, 15H). ¹³C NMR (100 MHz, CDCl₃): δ 15.08, 149.9, 149.3, 149.0, 148.7, 129.6, 128.5, 123.3, 123.1, 121.5, 110.1, 108.3, 107.1, 106.9, 101.9, 69.8, 69.6, 69.2, 31.7, 29.4, 25.9, 22.7, 14.0. UV-vis (CHCl₃): λ_{max} 282, 353, 371 nm. IR (KBr): 3120, 2955, 2931, 2920, 2854, 1614, 1584, 1518, 1504, 1425, 1385, 1265, 1174, 925, 839 cm⁻¹. Elemental Anal. Calcd for C₄₉H₇₂N₂O₅: C, 76.52; H, 9.44; N, 3.64. Found: C, 76.63; H, 9.64; N, 3.69. HRMS (Methanol+Chloroform, *m*/z):

769.55 (M)⁺, 770.55 (M+H)⁺, 771.56 (M+2H)⁺, 647.41, 643.38, 615.36, 409.19, 361.12, 306.19, 305.19, 187.13, 131.06. Compound **5b**: ¹H NMR (400 MHz, CDCl₃): *δ* 8.79 (s, 1H), 7.8–7.9 (m, 5H), 4.46 (t, *J* = 6.8, 2H), 4.32 (t, *J* = 6.7, 2H), 4.26 (m, 6H), 3.13 (t, *J* = 7.8, 2H), 1.96 (m, 10H), 1.2–1.7 (m, 38H), 0.94 (m, 18H). UV–vis (CHCl₃): *λ*_{max} 283, 351, 369 nm. Elemental Anal. Calcd for $C_{55}H_{84}N_2O_5$: C, 77.42; H, 9.92; N, 3.28. Found: C, 77.03; H, 10.17; N, 3.06.

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