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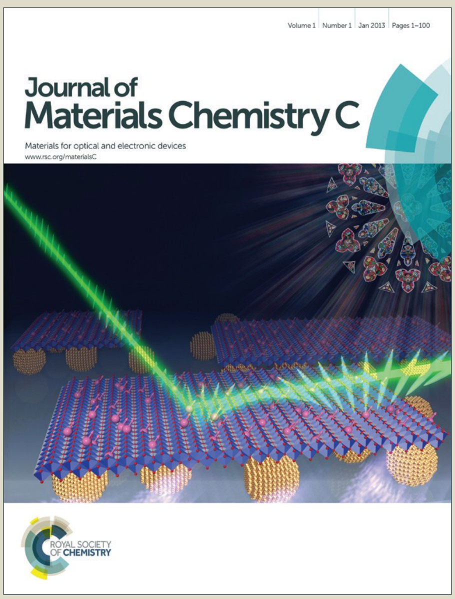

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ARTICLE

Liquid crystalline and charge transport properties of novel non-peripherally octasubstituted perfluoroalkylated phthalocyanines

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Two new perfluoroalkylated phthalocyanine derivatives were synthesised and characterised in order to investigate the effects of the fluorophobic/fluorophilic interactions on their mesophase and electronic properties. Both compounds exhibit columnar mesomorphism and the thermal stability of columnar phase is enhanced by over 20°C as the number of fluorinated carbon increases, probably due to the nano-segregation between the fluorinated and hydrocarbon moieties in the chains. Also a strong tendency to spontaneous homeotropic alignment was observed. Time-of Flight (TOF) measurements were carried out to reveal the mobility characteristics and the ambipolar mobility was measured in the order of 10^{-1}-10^{-2} $cm^2\ V^{-1}s^{-1}$ for the mesophases.

Introduction

Liquid crystalline materials are currently an interesting group of organic semiconductors which possess some distinctive properties based on their strong self-organizing nature such as spontaneous molecular alignment, high solubility in common organic solvents as well as high carrier mobility comparable to amorphous silicon.[1,2] In particular, discotic liquid crystal (DLC's) are attractive materials for organic photovoltaics[1b] because of their tendency towards homeotropically-aligned self-assembly in the columnar mesophase where each column of stacking molecules forms a one-dimensional charge transport path accompanied with insulating parts as their peripheral surroundings. For photovoltaic devices, discotic mesogens should also possess an extended π-conjugation system as its core to gain the better light harvesting. Hence, the phthalocyanine (Pc) family is an interesting and popular candidate for a wide range of DLC semiconductor devices.[4] More specifically, the octaalkyl-substituted Pc is a well-known mesogen that exhibits columnar mesomorphism[5c] and together with other derivatives of this mesogenic Pc they have been extensively studied as organic semiconductors[6] especially on its application to thin film devices such as transistors[7] and solar cells[8].

On the other hand, supramolecular systems of DLCs are also promising to the future materials in organic electronics.[9] In particular perfluoroalkylated liquid crystalline materials are also of interest due to the specific characteristics of the fluorine atom such as low polarisability and strong electronegativity.[10] The former is the origin of smaller van der Waals forces leading to phase separation against the hydrocarbon entity (fluorophobic and fluorophilic interaction) and the latter generates a strong electric dipole along the chemical bond which induces an electron-withdrawing effect into aromatic systems. In liquid crystalline studies, one can see interesting behaviour in the mesomorphism as an effect caused by the introduction of perfluoroalkyl groups to mesogenic derivatives. Addition of fluorinated alkyl groups have shown to increase the chemical and oxidative stability, the melting point and wetherability of the materials.[10] The fluorophobic/fluorophilic interactions that occur within the alkyl and fluoroalkyl chains of the molecule leads to an increased rigidity in the liquid crystal systems which in the case of calamitic mesogens, will enhance the thermal stability of the mesophase and in some cases facilitate the formation of smectic phases,[11] whilst in discotic mesogens such as triphenylenes it has been observed to strongly induce spontaneous homeotropic alignment in the hexagonal columnar (Col_h) phase[12] together with the remarkable modification of mesophase stability.[13] These interactions are thus interesting for the purpose of exploiting them to fine-tune the functionality of other mesogenic systems by control of nano-structures.

Recently, it was found that the non-peripheral type of phthalocyanine LC semiconductors present high drift mobility of charge carrier (~ 10^{-1} cm^2 V^{-1} s^{-1}) in their columnar mesophases together with an ambipolar character.[14] Especially, the hexyl homologue exhibits the high drift mobility over 1 cm^2 V^{-1} s^{-1} in the polycrystalline film.[15] These facts indicate that a steric hindrance for molecular stacks due to the non-peripheral alkyl chains does not negatively affect its charge transport property and a charge transport in the lateral direction to the stacking axis is a possible reason.[16] A wide range of Pc derivatives containing various functional groups have been studied so far, as its chemical structure can be easily modified to fine-tune their mesogenic and electronic properties. Nevertheless, no study on the mesomorphism and electronic properties of perfluoroalkylated phthalocyanines has been carried out, although the effects of direct fluorination of phthalocyanine ring on the electronic properties have been reported to show that strong n-type of semiconducting nature is induced.[17] Perfluoroakyl chains at the periphery of phthalocyanine ring is expected to make its columnar structure stable and thus, the lateral molecular fluctuation could be depressed leading to higher efficiency of charge transport.

In this work, two perfluoroalkylated phthalocyanines were designed and synthesised to study their mesomorphic and charge-transport properties in comparison to the alkylated Pc homologue with the purpose to clarify the effects of fluorination of the non-peripheral chains. All derivatives were designed to contain seven-carbon atoms in a chain for a comparison of mesomorphism excluding the chain length effect.

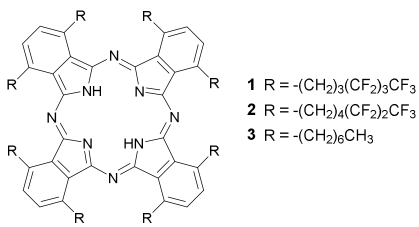


Fig. 1 Structure of the two perfluoroalkylated Pc derivatives and the parent non-fluorinated Pc.

Compounds **1** & **2** contain four and three fluorinated carbons respectively, attached via propylene (C3) chains at the non-peripheral sites of phthalocyanine ring to create a fluorine-rich region at the periphery of the macrocycle, encompassing an aliphatic region and an aromatic system at the core as well as avoiding the n-type nature of the phthalocyanine ring. It is expected that these regions will experience significant nano-segregation due to the fluorophobic/philic interactions and will induce an increased ordering within the columnar arrays (Fig 2).

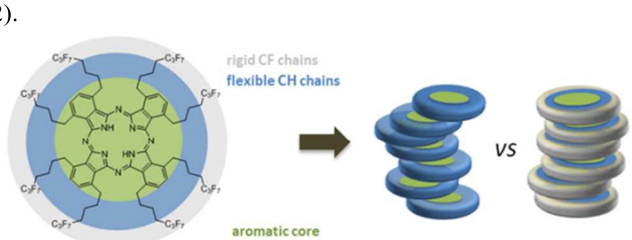


Fig. 2 Schematic representation of the desired self- assembly due to fluorophilic/fluorophobic interactions (nano-segregation). Fluorophilic nature of fluorinated alkyl chains could make the molecular fluctuations in columns less to stabilise the thermal stability with enhancing molecular orders in comparison to the case of hydrocarbon alkyl chains.

Results and discussion,

Mesomorphic Properties

Phase transitions of three compounds **1**, **2** and **3** were detected by differential scanning calorimetry (DSC) at a rate of 1°C/min as shown in fig 3. Whilst **2** exhibits enantiotropic phase transitions for two mesophases, only monotropic behaviour is seen for **1**. In both cases, the clearing temperatures are over

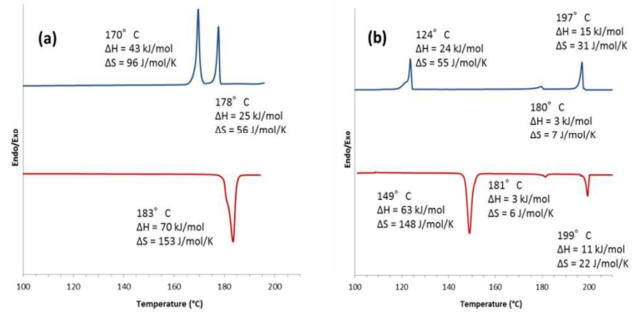


Fig. 3 DSC thermograms of compound **1** (a) and **2** (b) at both heating (red) and cooling (blue) at 1°C/min.

180°C. Considering that **3** has its clearing point at 163°C, it indicates that the introduction of perfluoroalkyl chains to the periphery of the phthalocyanine leads to stabilisation of the mesophase. As the number of fluorinated alkyl groups decreases from four (**1**) to three (**2**), the clearing point is enhanced by *c.a.* 18°C. Though the introduction of a perfluorinated methylene once to the periphery enhances the thermal stability of the columnar mesophase, subsequent addition leads to the lowering of the clearing point. Similar behaviour has also in part been observed in the case of hexabenzocoronenes in which their thermal properties are strongly dependent on the combination of hydrocarbons and fluorinated chains.[13a]

The enhancement of the columnar mesophase by introduction of perfluoroalkyl groups in the periphery has also been observed in the case of alkoxytriphenylenes in which one sees the increased thermal stability of the Col_h mesophase as the number of perfluorinated carbons increases. Other changes, such as the decrease in the enthalpy and entropy values of the clearing point are also observed for **2** in regards to **3**, indicating

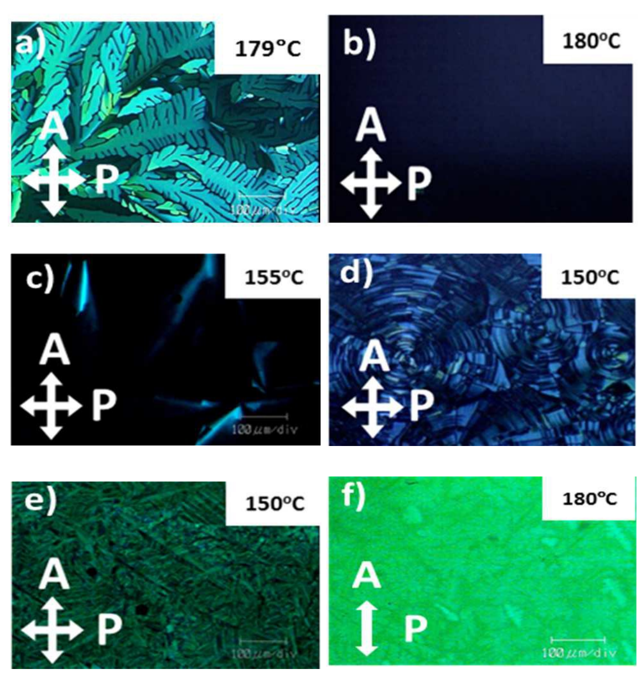


Fig. 4 POM images under cross-polarised conditions of **1** (a), **2** (b) and **3** (c). **2** and **3** show homeotropic regions at the Col_h phase which are lost upon cooling to the Col_r phase for **2** (d) and **3** (e). The dentritic growth of domains can be seen under non-polarised light for **2** (f).

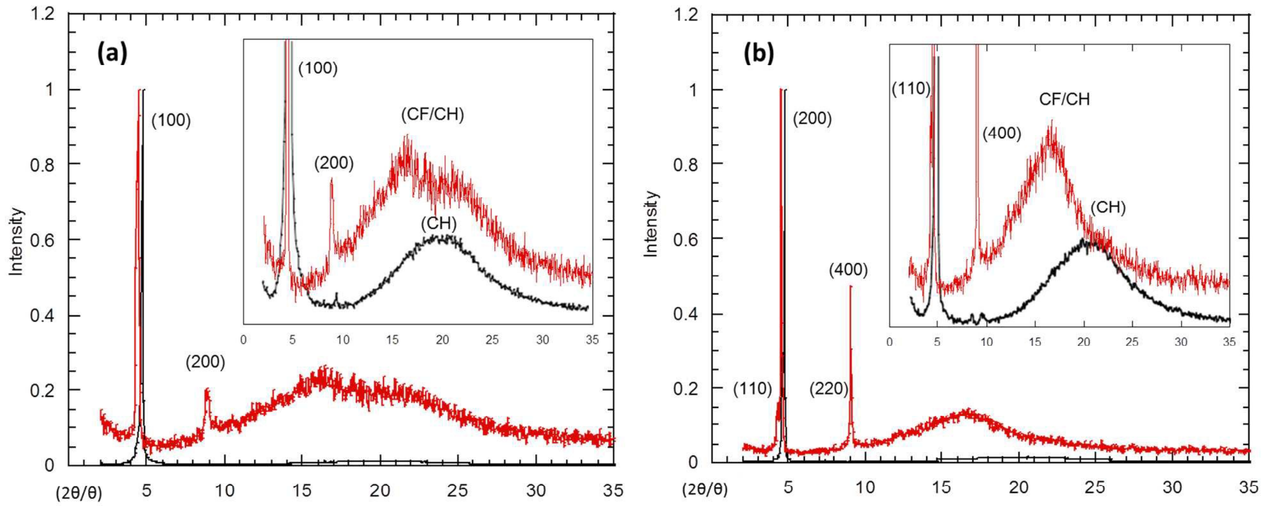


Fig. 5 X-Ray diffraction patterns observed from an aligned film (parallel to beam) of compounds **2** (red) and **3** (black) in both columnar mesophases, (a) Col_h at 190 and 155 °C, respectively, and (b) Col_r at 150 and 140 °C, respectively)

low Van der Waals interactions around the terminal perfluoroalkyl groups. For the melting point, a simple increase is observed with increasing number of fluorinated methylene units.

Assignment of the mesophases was achieved by polarised optical microscopy (POM) and X-Ray diffraction (XRD) analysis for the non-aligned samples. The optical textures observed for the mesophase of **1** indicates it is not an optically uniaxial phase due to the absence of homeotropic dark domains under crossed polarising condition (Fig. 4a). On the other hand, the textures of the higher temperature mesophase in both **2** and **3** show a predominant dark image (Fig. 4b and 4c) indicating an optical uniaxial phase with strong homeotropic alignment character. For the lower temperature phase, such dark image is not seen resulting in a columnar mesophase with an inclination of molecular planes against the stacking axis of the molecules (Figs. 4d and 4e). As in the case of perfluorinated hexa(alkyloxy)triphenylenes,[12] a strong tendency for homeotropic alignment was also observed in **2** with the spontaneous formation of large dendritic-like homeotropic domains (Fig. 4f). The homeotropic regions observed for **2** are markedly larger in comparison to **3** as no birefringent areas could be seen over a large region.

Temperature dependent X-Ray diffraction measurements were carried out for **2** and **3** as shown in fig. 5. For the high temperature mesophases (Fig. 5a) a typical set of diffraction peaks for the hexagonal columnar (Col_h) mesophase was detected (see the analysed data in Table S1) and this result is fully supported by POM results. For the lower temperature measurement, typical diffraction patterns were also observed to identify it as a rectangular columnar (Col_r) mesophase. However, the symmetry of the rectangular lattice is modified by the introduction of perfluoroalkyl groups from *c2mm* in **3** to *p2gg* in **2**. As the number of molecules in the lattice remains unchanged, the essential change of molecular packing is derived from the difference in peripheral chains and consequently the presence of fluorinated methylene chains affects the direction of molecular inclination against the columnar axis (from a parallel to a herringbone arrangement).. as shown in fig. 6. Prior to the stabilisation of the Col_r of *p2gg* symmetry in **2** we were also able to detect the presence of a

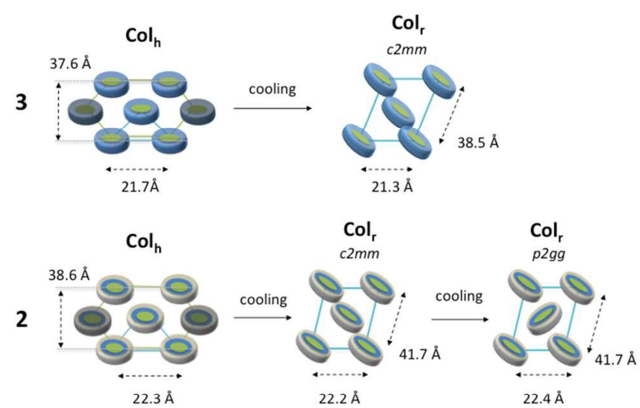


Fig. 6 Lattice changes upon the incorporation of fluorinated groups at the periphery of phthalocyanine.

Table 1. Phase transition parameters of both perfluoroalkylated derivatives (**1**, **2**) and the parent phthalocyanine (**3**) detected by DSC

compound	phase transition	T(°C)	ΔH ($kJmol^{-1}$)	ΔS ($Jmol^{-1}K^{-1}$)
1	Cryst→Iso	183	70	153
	(mesophase→Iso)	180	25	56
2	Cryst→Col_r	149	63	148
	Col_r→Col_h	181	3	6
	Col_h →Iso	199	11	22
3	Cryst→Col_r	114	48	119
	Col_r→Col_h	146	1	3
	Col_h →Iso	162	13	30

( ): monotropic phase transition, Cryst: crystal, Iso: isotropic liquid, Col_r: rectangular columnar mesophase, Col_h: columnar hexagonal mesophase.

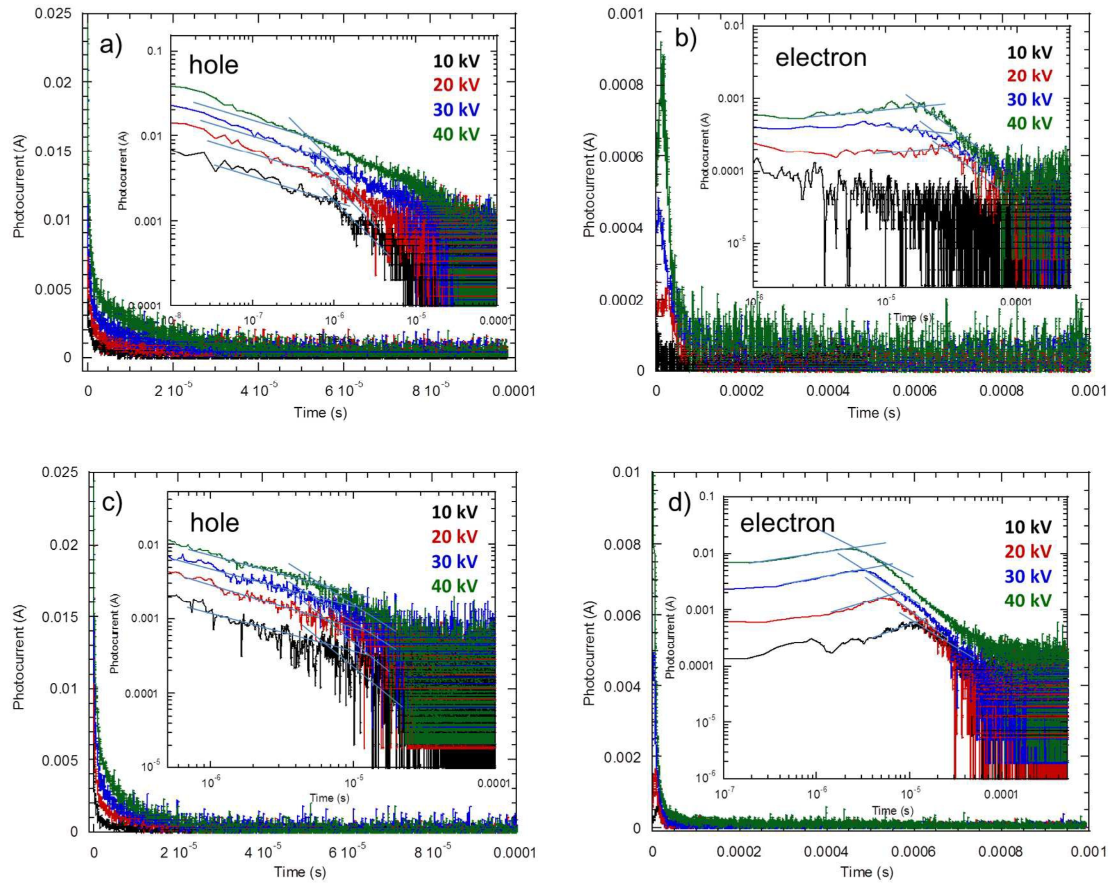


Fig. 7 Typical photocurrent decay curves of both hole and electron for **2** under the variation of applied electric field. The insets show the double logarithmic plots of the photocurrent. (a) and (b) for the Col_h phase (186°C) and (c) and (d) for the Col_r mesophase (168°C).

Col_r lattice of *c2mm* symmetry over a 10°C range. Whilst evidence of this transition could not be observed on the DSC thermograms, XRD and POM analyses (fig. S2) attest to the existence of this rearrangement. An increase in the lattice size (21.7Å to 22.3 Å for the Col_h phase) was also detected upon the addition of the perfluoroalkyl groups, probably due to the relatively rigid character and the large diameter of the perfluorinated chains that could lead to the less interdigitation of chains within the columnar arrays in addition to the fluorophobic/fluorophilic interactions in the periphery. In the mid-region of the spectra, a broad halo at ca. 5.4 Å derived from the disordered perfluoroalkyl parts can also be seen overlapping with the halo from the aliphatic chains at ca. 4.5 Å. This suggests that there is a significant fluorophilic effect amongst the fluoroalkylated regions in the columnar structure. However, no peak that corresponds to the molecular stacking periodicity observed for the peripheral-type phtalocyanine mesogens can be detected in this case.[18] The phase transition properties of **1**, **2** and **3** are summarised in Table 1.

Charge Transport Properties

The evaluation of the charge transport properties of **2** and **3** were carried out by Time of Flight (TOF) experiments.[19]

Fig. 7 shows typical transient photocurrent decay curves of hole and electron transport obtained at 186 °C (Col_h) and 168°C (Col_r) for **2**. The molecular alignment of the measured area of the cell was determined as fully homeotropic by evidence of optical texture (dark image) observed under crossed polarising conditions. The transient photocurrent decay curves obtained tend to show more dispersive than in **3**. The decay curves of electron are the better in shape than those of hole and this is common in the non-peripheral type of octaalkyl-phthalocyanines.[14, 15] Interestingly, in this fluorinated alkyl derivative **2**, the hole mobility is higher than electron one, though the hydrocarbon chain derivatives **3** shows the opposite property. The mobility was found to be mostly independent of the applied field following the behaviour of typical liquid crystalline semiconductors.[20]The temperature dependence of the carrier mobility for **2** and **3** is shown in Fig. 8 where temperature-independent nature is roughly seen for both hole and electron. Essentially the same behaviour can be seen for both two compounds. This indicates that the dynamic motions of the molecules within a columnar structure provide a narrow distribution of state density at high temperature appropriate for electronic hopping[21,22], even though the disordering of molecules disrupts the periodical structures necessary for efficient charge hopping. The resultant mobilities of hole and electron are in the order of 10^{-1} and 10^{-2} cm^2 V^{-1} s^{-1}, respectively in both Col_h and Col_r mesophases. Though **3** exhibits hole and electron mobilities in the order of 10^{-1} cm^2 V^{-1} s^{-1} in both mesophases, the introduction of perfluorinated alkyl groups results in decrease of electron mobility by two orders of magnitude with no change of mobility order for hole.

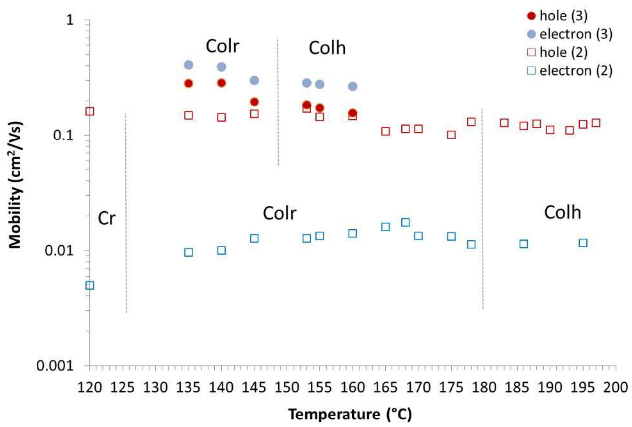


Fig. 8 Temperature dependence of the hole and electron mobility of perfluoroalkylated **2** and non-fluorinated **3** phthalocyanine derivatives at 10kVcm^{-1} of applied bias.

It has been previously reported that the replacement of terminal methyl groups with trifluoromethyl ones in the case of hexaalkoxytriphenylene mesogens produces an enhancement of the molecular dynamics of the columnar mesophase. This has been demonstrated by NMR spin-lattice relaxation studies, which also show a more ordered system is induced within the columnar axis by reducing the lateral fluctuations of the discotic assembly.[23] In fact, for hexaalkoxytriphenylene analogues, the observed hole mobility is hardly affected by the introduction of perfluorinated alkyl chains.[24]

A single process of charge transport in molecular aggregation is a charge transfer between two molecules and this mechanism is explained by Marcus theory where HOMO-HOMO and LUMO-LUMO interactions are key factors described as transfer integral for hole and electron transports, repectively.[25] The DFT calculation of phthalocyanine is reported to show the spatial distribution of HOMO is larger than LUMO at the edge of phthalocyanine ring (the peripheral sites)[26], and this may provide a possibility of charge hopping from edge to edge of neighbouring phthalocyanine molecules. Thus, this may be able to explain the decrease of electron mobility due to the bulkiness of fluorinated alkane which would be sensitive for the face-to-face interaction of stacking phthalocyanines. J. Tant et al. reported that the rotaion angle along the molecular axis normal to the plane is sensitive for transfer integral in a face-to-face dimer of phthalcyanine where 45° periodicity of electronic splitting energy ocilation is predicted on the symmetry of phthalocyanine ring. [26] However, in the case of non-peripheral tyoe of phthalocyanine liquid crystal, disordering stacking of molecules implies more fluctuations in the lateral direction of columnar axis. Therefore, it is possible to think that a variation of the lateral fluctuation is more effective to the electronic splitting in a stacking dimer than rotational one and the bulky perfluoroalkyl groups are likely to more efficiently prevent molecules from contact except for the edge of phthalocyanine rings. In the non-peripherally attached alkyl phthalocyanines series, the hexyl derivative has shown the best charge transport properties with a drift mobility of 1.5 and 0.1 cm^2 V^{-1} s^{-1} for crystal and *pseudo*-Col$_h$ mesophase, respectively even though it does not show high intracolumnar ordering in the mesophase. The crystalline structure[26] would enable us to state that the high carrier mobility is originated by the two-dimensional charge transport both along the columnar stacks and the lateral contact between the Pc moieties.[16] On the other hand, analysis of the mesophase by molecular dynamics (MD) simulation shows the presence of a dynamic molecular motions in the Col$_h$ phase analogous to the "de Vries" smectic phase which is seen in calamitic mesogens.[27] This phase shows a high degree of molecular contact among columns, which would encourage a two-dimensional transport of carriers and hence help to explain the high mobilities observed for this material. In the case of **2** however, the carrier transport is limited more by the larger volume of perfluoroalkyl chains to a one-dimensional path and the difference of spatial distribution of HOMO and LUMO of phthalocyanine molecule could provide an interpretation for the higher positive carrier mobility and lower electronic one. Therefore, it is indicated that this contrast of ambipolar mobility between non-fluorinated and fluorinated peripheries of Pc ring deeply concerns to the molecular contact at the edge of Pc ring in columnar mesophase for the case of non-peripheral type of Pc LCs.

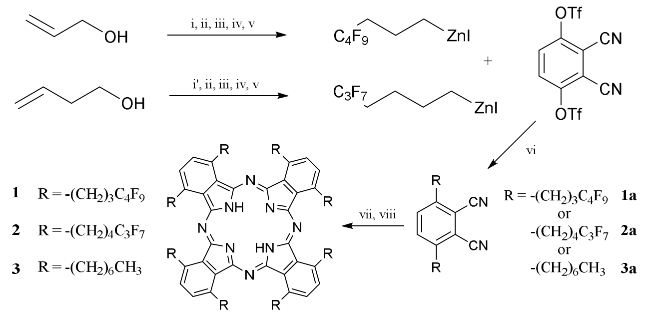
Conclusions

It was expected that the introduction of fluorinated groups on the phthalocyanine mesogen would result in a better ordered system and enhance the charge transport properties in comparison with the alkylated phtalocyanine (**3**). DSC and POM provided evidences for an enhanced and more ordered mesophase in **2** that presents strong tendency of spontaneous homeotropic alignment to substrates in the Col$_h$ phase. However, XRD analysis shows that no highly-ordered phase is present and the Col$_h$ is of a disordered nature. In the case of the Col$_r$ phase, the fluoroalkyl groups induce a stabilisation in the tilt of the columnar stacks observed by the change of geometry from *p2gg* in **3** to *c2mm* in **2**. This ordering depresses both hole and electron transports along the columnar axis and, however, the fluorophilic interaction around the periphery of columns compensates the low intra-columnar electronic interaction with the high inter-colmnar one resulting in the comparable level of hole mobility and the lower electronic mobility in the Col mesophases. Whilst the introduction of perfluoroalkyl groups on the non-peripheral positions of the phthalocyanine was in general terms unfavourable for the electron transport, the introduction of perfluorinated alkyl groups to the periphery of the phthalocyanine molecule is still attractive. Also, as fluorophobic/fluorophilic interactions are intrinsically good for nano-segregation within molecular aggregation to induce ordering, the incorporation of fullerene derivatives containing fluorinated alkyl groups in order to create a miscible system would produce interesting effects when one thinks of the results obtained from previously reported organic thin film solar cell studies facilitated with binary systems with phthalocyanine liquid crystalline semiconductor and n-type semiconductors such as fullerene derivatives.[8]

Experimental

Syntheses of compounds

The perfluoroalkylated phthalocyanines (1 & 2) were synthesised using the procedure described in scheme 1 reported by Cook *et. al.* albeit with some modifications to allow the introduction of the fluoroalkyl moieties.[22] The compounds were isolated and characterised by 1H-NMR, UV-Visible spectroscopy and elemental analysis and their mesophase properties studied by differential scanning calorimetry (DSC), polarised optical microscopy (POM) and X-Ray diffraction analysis.



Scheme 1. i) *n*-C_4F_9I, $P(Ph_3)_4Pd$ in hexane at 5°C,/Ar. **i')** *n*-C_3F_7I, $P(Ph_3)_4Pd$ in hexane at 4°C,/Ar. **ii)** $LiAlH_4$ in diethyl ether at rt. **iii)** TsCl, TEA in dichloromethane at 5°C. **iv)**NaI in acetone (reflux/N_2). **v)** $Br_2(CH_2)_2$, TMSCl, Zn* in tetrahydrofuran (reflux/Ar). **vi)** $[(PPh_3)_2Cl_2]Ni$, PPh_3, n-BuLi, LiCl in tetrahydrofuran at -78°C/Ar. **vii)** Li(s), penta-1-ol (reflux/N_2). **viii)** Glacial acetic acid, rt.

General methods

All solvents used in the reactions are reagent grade unless specified. Inert atmosphere refers in all cases to nitrogen gas, unless otherwise specified. Column chromatography was performed at room temperature using Merck®60 silica-gel, using reagent grade solvents as eluents. Recrystallisation of the phthalocyanine materials was carried out using EL grade methanol and toluene. Grignard reagents were prepared immediately prior to use following conventional protocols. The experimental procedures described in this section are for the metal-free np-octakis (5, 5, 6, 6, 7, 7, 7-heptafluoroheptyl) phthalocyanine. The same protocol was applied to obtain both fluoroalkylated species. On the other hand, the synthetic protocol of the alkylated phthalocyanine is not discussed as the procedure has been widely reported.[28]

i) 1H, 1H, 2H, 2H, 3H, 3H, 4H, 4H-heptafluoro-3-iodophepta-1-ol 3-buten-1-ol (4.8 mL, 66 mmol) was dissolved in hexane (40.5 mL) and cooled to 4°C under an argon atmosphere. To this solution, n-perfluoropropyliodide (8.0 mL, 55 mmol) and tetrakistriphenylphosphine palladium (0) (3.22 g, 2.8 mmol) are added under a stream of argon. Upon addition, the reaction is left warming to room temperature whilst stirring under the argon atmosphere for two hours. The mixture is filtered and the solids washed with diethyl ether. A yellow filtrate is recovered and the solvent evaporated under reduced pressure to give the title compound as an orange oil (18.8 g, 92% yield). ν_{max} (KBr/cm^{-1}) 3349 (OH), 2945, 2890 (CH_2), 1228, 1122 (CF_2), 1052 (CF_3), 737 (CI); δ_H (500MHz, $CDCl_3$) 4.56-4.50 (m, 1H, CHI), 3.90-3.77 (m, 2H, CH_2OH), 3.01-2.82 (m, 2H, F7C3-CH2), 2.07-1.99 (m, 2H, CH_2-CH_2OH); δ_F (471MHz, $CFCl_3/CDCl_3$) -80.8 (m, 3F, CF_3), -114.0 (dq, 2F, *J* 9.4 & 301, CF_2-CF_3), -128.4 (m, 2F, CF_2CH_2).

ii) 1H, 1H, 2H, 2H, 3H, 3H, 4H, 4H-heptafluorohepta-1-ol Diethyl ether (26.0 mL) was added drop-wise via addition funnel to a round-bottom flask containing lithium-aluminium hydride (1.82 g, 48 mmol). A solution of the 1H, 1H, 2H, 2H, 3H, 3H, 4H, 4H-perfluoro-3-iodohepta-1-ol (11.8 g, 32 mmol) in diethyl ether (14.0 mL) were slowly added to the lithium-aluminium hydride slurry. Upon addition the mixture was left stirring for one hour. The reaction was cooled to 0°C and quenched carefully using distilled water (10.0 mL). An aqueous solution of sulphuric acid (6.5 mL, 5% v/v) was added to the reaction mixture and left to stir for two hours. The emulsion obtained was extracted with diethyl ether (100 mL) and washed twice with distilled water (100 mL), brine (100 mL) and dried with magnesium sulphate. The organics were filtered and the solvent removed under reduced pressure to yield the title compound as an orange oil (4.8 g, 60% yield). ν_{max} (KBr/cm^{-1}) 3346 (OH), 2958, 2886 (CH_2), 1225, 1119 (CF_2), 1069 (CF_3); δ_H (500MHz, $CDCl_3$) 3.71-3.66 (t, 2H, J 6, CH_2-OH), 2.15-2.05 (m, 2H, F_7C_3-CH_2), 1.75-1.62 (m, 4H, CH_2-CH_2OH) 1.30 (s, 1H, CH_2OH); δ_F (471MHz, $CFCl_3/CDCl_3$) -81.1 (m, 3F, CF_3), -116.0 (m, 2F, , CF_2-CF_3), -128.3 (m, 2F, CF_2CH_2).

iii) 1-(4-toluenesulfonyloxy)-5, 5, 6, 6, 7, 7, 7-heptafluoroheptane. 1H, 1H, 2H, 2H, 3H, 3H, 4H, 4H-heptafluorohepta-1-ol (4.8 g, 19 mmol) was dissolved in anhydrous dichloromethane (45.0 mL) and triethylamine (7.3 mL, 52 mmol). This mixture was cooled to 4°C and to this, a solution of tosyl chloride (4.8 g, 25 mmol) in dichloromethane (20.0 mL) was added drop-wise via addition funnel over ca. 30 minutes. Upon addition, the reaction was left to warm to room temperature and left stirring for 16 hrs. The organics were extracted with dichloromethane, washed thrice with distilled water (30 mL), brine (50 mL) and dried over magnesium sulphate. The solvent was removed under reduced pressure after filtration and hexane (25 mL) was added to precipitate the triethylamine salt, which was removed via filtration. The filtrate was chromatographed over silica-gel using a 2:1 mixture of hexane/dichloromethane as eluent. The title compound was recovered as the second fraction from the column as a colourless oil (5.9 g, 77% yield) after solvent removal. ν_{max} (KBr/cm^{-1}) 3013 (Ar-H), 2965, 2934 (CH_2), 1600, 1497 (C=C Ar), 1226, 1178 (CF_2), 1120, 1099 (CF_3); δ_H (500MHz, $CDCl_3$) 7.78 (d, 2H, Ar-H), 7.35 (d, 2H, Ar-H'), 4.06 (t, 2H, J 6, CH_2O), 2.45 (s, 3H, CH_3), 2.10-1.87 (m, 2H, $CH_2C_3F_7$), 1.80-1.58 (dm, 4H, CH_2CH_2); δF (471MHz, $CFCl_3/CDCl_3$) -80.5 (t, 3F, *J* 9, CF_3), -115.3 (m, 2F, , CF_2-CH_2), -127.7 (m, 2F, $CF_2CF_2CH_2$).

1-(4-toluenesulfonyloxy)-4, 4, 5, 5, 6, 6, 7, 7, 7-heptafluoroheptane. Following the procedure above 4, 4, 5, 5, 6, 6, 7, 7, 7-nonafluorohepta-1-ol (10.0 mL, 53 mmol) was dissolved in anhydrous dichloromethane together with triethylamine (19.0 mL, 133 mmol) and tosyl chloride (12.6 g, 64 mmol) in dichloromethane (30.0 mL) were added. The product was recovered as a colourless oil (20.8 g, 90% yield) after solvent removal. ν_{max} (KBr/cm^{-1}) 1599 (C=C Ar), 1233 (SO_2), 1177 (CF_2, CF_3); δH (500MHz, $CDCl_3$) 7.80 (d, 2H, *J* 8.5, Ar-H), 7.36 (d, 2H, *J* 8.5 Ar-H'), 4.11 (t, 2H, *J* 6, CH_2O), 2.46 (s, 3H, CH_3), 2.12-1.89 (m, 2H, $CH_2C_3F_7$), 1.96-1.62 (dm, 2H, CH_2CH_2).

iv) 1-iodo-5, 5, 6, 6, 7, 7, 7-heptafluoroheptane. Sodium iodide (6.7 g, 44 mmol) was dissolved together with 1-(4-toluenesulfonyloxy)-5, 5, 6, 6, 7, 7, 7-heptafluoroheptane (5.8 g, 15 mmol) in dry acetone (70.0 mL) and heated to reflux over two hours under a nitrogen atmosphere. Distilled water (20 mL) was added to the reaction mixture and the organics extracted with diethyl ether (100 mL). The organic phase was washed twice with an aqueous solution of sodium thiosulfate (150 mL, 1% v/v), brine (150 mL) and dried over magnesium sulphate. After filtration the solvent was evaporated and the product submitted to vacuum distillation (40°C, 3 mmHg) to give the title compound as a light yellow oil (4.2 g, 73% yield). ν_{max} (KBr/cm^{-1}) 2957, 2886 (CH_2), 1224, 1174 (CF_2), 1115, 1063

(CF_3), 724 (CH_2I); δ_H (500MHz, $CDCl_3$) 3.19 (t, 2H, J 7, CH_2I), 2.14-2.03 (m, 2H, $CH_2C_3F_7$), 1.95-1.89 (m, 2H, CH_2CH_2), 1.78-1.72 (m, 2H, CH_2CH_2); δ_F (471MHz, $CFCl_3/CDCl_3$) -81.1 (m, 3F, CF_3), -115.8 (m, 2F, , CF_2-CH_2), -128.3 (m, 2F, $CF_2CF_2CH_2$).

1-iodo-4, 4, 5, 5, 6, 6, 7, 7, 7-nonafluoroheptane. Following the procedure above, sodium iodide (10.51 g, 69 mmol) was added to a solution of 4, 4, 5, 5, 6, 6, 7, 7, 7-nonafluorohepta-1-ol (10.0 g, 23 mmol) in anhydrous acetone (120 mL). After work up and distillation the product was recovered as a colourless oil (7.3 g, 81% yield). ν_{max} (KBr/cm^{-1}) 1221 (CF_3CF_2), 1132 (CH_2I); δ_H (500MHz, $CDCl_3$) 3.26 (t, 2H, J 7, CH_2I), 2.28-2.11 (m, 4H, CH_2 CH_2).

v) 5, 5, 6, 6, 7, 7, 7-heptafluoroheptyl-1-zinc iodide. Activated zinc dust (3.2 g, 48 mmol) was added to anhydrous tetrahydrofuran (30.0 mL) and stirred under an inert atmosphere. To this slurry, 1, 2-dibromoethane (0.2 mL, 2 mmol) was added via syringe and heated to reflux. The mixture was allowed to cool down to room temperature and heated to reflux. Trimethyl silyl chloride (0.3 mL, 2 mmol) was then added and the heating/cooling cycle repeated once again. Once the mixture is at room temperature, a solution of 1-iodo-5, 5, 6, 6, 7, 7, 7-heptafluoroheptane (6.3 g, 16 mmol) in tetrahydrofuran (40.0 mL) was added drop-wise via addition funnel. The reaction mixture is left stirring at 50°C under an inert atmosphere for 16 hours. The zinc reagent is left to stand over two hours in order for the remaining zinc dust to settle prior its use. Conversion is assumed as c.a.≈90%.

4, 4, 5, 5, 6, 6, 7, 7, 7-nonafluoroheptyl-1-zinc iodide. Following the procedure above, activated zinc dust (3.2 g, 48 mmol) in anhydrous tetrahydrofuran (40.0 mL) was stirred under an inert atmosphere. 1, 2-dibromoethane (0.2 mL, 2 mmol) and trimethylsilyl chloride (0.3 mL, 2 mmol) were added to the zinc dust slurry. 1-Iodo-5, 5, 6, 6, 7, 7, 7-heptafluoroheptane (6.0 g, 15 mmol) in tetrahydrofuran (20 mL) was added drop-wise and left to stir at 50°C during 16 hours and then left to settle prior use. Conversion is assumed as ≈90%.

vi)3, 6-bis (5, 5, 6, 6, 7, 7, 7-heptafluoroheptyl) phthalonitrile. Bis(triphenylphosphine)nickel(II)dichloride (0.3 g, 0.5 mmol) was stirred together with triphenylphosphine (0.25 g, 0.95 mmol) under an argon atmosphere in anhydrous tetrahydrofuran (10.0 mL). *n*-Butyllithium (0.4 mL, 2.6M in hexane) was added to give a dark red slurry. 3, 6-Bis(trifluoromethanesulfonyloxy)phthalonitrile (2.1 g, 5 mmol) and lithium chloride (0.6 g, 14 mmol)were added to the slurry under a stream of argon. The reaction is cooled to -78°C and the organozinc reagent (70 mL, ≈0.2 M in tetrahydrofuran, 14 mmol) is added drop-wise via addition funnel. It was then left to warm to room temperature over a period of ca. one hour and stirred for 16 hours. An aqueous solution of hydrochloric acid (10 mL, 10%) was added carefully and the solvent removed under reduced pressure. The organics were extracted with twice with ethyl acetate (100 mL) and subsequently washed with an aqueous solution of hydrochloric acid (50 mL, 10%), sodium hydroxide (50 mL, 5%) and brine (100 mL). The organic layer is dried with magnesium sulphate and the solvent removed under reduced pressure after filtration. The crude product was purified by column chromatography over silica-gel using a 2:1 mixture of hexane/dichloromethane to give the ***title compound*** as a white solid (1.4 g, 50% yield). M. p. 69°C, ν_{max} (KBr/cm^{-1}) 2981, 2956, 2889 (CH_2), 2228 (CN), 1594, 1563 (C=C Ar) 1223, 1115 (CF_2, CF_3); δ_H (500MHz, $CDCl_3$) 7.50 (s, 2H, Ar-H), 2.92 (t, 4H, *J*7.5, $ArCH_2$), 2.17-2.05 (m, 4H, CH_2CF_2), 1.81-1.68 (m, 4H, $ArCH_2CH_2R$); δ_F (471MHz, $CFCl_3/CDCl_3$) -80.6 (t, 3F, *J* 11, CF_3), -115.3 (t, 2F , CF_2-CH_2), -127.9 (s, 2F, CF_2CF_2).

3, 6-bis(4, 4, 5, 5, 6, 6, 7, 7, 7-nonafluoroheptyl)phthalonitrile. Following the procedure above, bis(triphenylphosphine)nickel(II)dichloride (0.3 g, 0.5 mmol) was stirred together with triphenylphosphine (0.25 g, 0.95 mmol) under an argon atmosphere in anhydrous tetrahydrofuran (10.0 mL). *n*-Butyllithium (0.4 mL, 2.6M in hexane) was added to give a dark red slurry. 3, 6-Bis(trifluoromethanesulfonyloxy)phthalonitrile (2.1 g, 5 mmol) and lithium chloride (0.6 g, 14 mmol)were added to the slurry under a stream of argon. The reaction is cooled to -78°C and the organozinc reagent (60 mL, ≈0.2 M in tetrahydrofuran, 14 mmol) is added drop-wise via addition funnel. After work up and purification the ***title compound*** is obtained as a white solid (1.27 g, 42% yield). M.p. 109°C, ν_{max} (KBr/cm^{-1}) 2959 (CH_2), 2230 (CN), 1562 (C=C Ar), 1217, 1132 (CF_2, CF_3); δ_H (500MHz, $CDCl_3$) 7.56 (s, 2H, Ar-H), 3.00 (t, 4H, *J* 8.0, Ar-CH_2), 2.20 (m, 2H, CH_2-CF_2), 2.03 (m, 4H, R-CH_2CH_2).

vii-viii) Metal-free 1, 4, 8, 11, 15, 18, 22, 25-octakis(5, 5, 6, 6, 7, 7, 7-heptafluoroheptyl)phthalocyanine. 3, 6-Bis(5, 5, 6, 6, 7, 7, 7-heptafluoroheptyl) phthalonitrile (1.1 g, 2 mmol) was dissolved in *n*-pentanol (30.0 mL) and heated to 60°C under an inert atmosphere. Lithium granules (0.003 g, 0.4 mmol) are added to the solution and the mixture is then heated to reflux and stirred for 16 hours. The mixture is cooled to room temperature after which glacial acetic acid (15 mL) is added and the reaction left to stir for 30 minutes. The solvent is removed under reduced pressure and cold acetone (150 mL) is added to precipitate the product, which is then filtered and washed with cold methanol. The crude product is purified by soxhlet extraction using methanol, hexane and recrystallized from hot toluene. The title compound is recovered as fine blue needles (0.15 g, 15% yield). ν_{max} (KBr/cm^{-1}) 2981, 2956, 2889 (CH_2), 2228 (CN), 1594, 1563 (C=C Ar) 1223, 1115 (CF_2, CF_3); M. p. 147, 199°C, δ_H (500MHz, d^8-THF) 7.12 (s, 8H, Ar-H), 3.68 (t, 16H, *J* 7, $ArCH_2$), 1.37-1.28 (m, 32H, $CH_2CH_2CF_2$), 0.99-0.97 (m, 4H, $CH_2CH_2CF_2$), -0.82 (s, 2H, NH); MS (MALDI-TOF) *m/z* (%): isotopic cluster at 2307.30 [M$^+$] (100); UV-Vis (THF) λ_{max}(log ε)= 726 nm (5.3); elemental analysis calcd. for $C_{88}H_{74}N_8F_{56}$ (%): C 45.81, H 3.23, N 4.86, F 46.11; found: C 45.73, H 3.32, N 4.82, F 45.91.

Metal-free 1, 4, 8, 11, 15, 18, 22, 25-octakis(4, 4, 5, 5, 6, 6, 7, 7, 7-nonafluoroheptyl)phthalocyanine. Following the procedure above 3, 6-Bis(4, 4, 5, 5, 6, 6, 7, 7, 7-heptafluoroheptyl) phthalonitrile (0.9 g, 1 mmol) was dissolved in n-pentanol (16.0 mL) and heated to 60°C under an inert atmosphere. Lithium granules (0.002 g, 0.2 mmol) are added to the solution and the mixture is then heated to reflux and stirred for 16 hours. The mixture is cooled to room temperature after which glacial acetic acid (15 mL) is added and the reaction left to stir for 30 minutes. After work up and purification the product was recovered as dark green crystals (0.07 g, 8% yield). M. p. 183°C, δ_H (500MHz, d^8-THF) 8.05 (s, 8H, Ar-H), 4.63 (t, 16H, *J* 7, $ArCH_2$), 2.52-2.37 (m, 32H, CH2CH2CF2),0.13 (s, 2H, NH); MS (MALDI-TOF) *m/z* (%): isotopic cluster at 2595.19 [M$^+$] (100); UV-Vis (THF) λ_{max}(log ε)= 722 nm (5.0); elemental analysis calcd. for $C_{88}H_{58}N_8F_{72}$ (%): C 40.73, H 2.25, N 4.32, F 52.70; found: C 40.85, H 2.32, N 4.37, F 52.77.

Measurements

The phase transition behaviour was characterised by differential scanning calorimetry experiments using a TA Instruments Q200-SP DSC calibrated with indium standards. POM analysis was completed using an Olympus optical polarising microscope with a Mettler Toledo FP82HT hot stage. The X-Ray diffraction analysis was made on a 0.5 x 0.5 mm liquid crystal cell using a Rigaku RINT2000 equipped with a temperature controller to analyse the structure over a temperature range.
The charge transport properties of **2** were carried out by Time of Flight (TOF) experiments. The samples were purified by soxhlet extraction followed by column chromatography after treatment with an acetic acid in order to attain full conversion of the Li derivative of Pc to the metal-free. The samples were washed with EDTA prior to the recrystallisation in spectroscopic grade toluene. The samples were injected by capillary action at the isotropic phase into an asymmetric sandwich-type Al/ITO coated cells of approximately 20μm-thick (as measured by interferometry). The time of flight measurements were carried out on slow cooling from the isotropic to the crystalline phase. Carrier transport was measured using the conventional time of flight set-up and a N_2 laser (λ= 337 nm) as excitation source, whilst recording the photocurrents with an oscilloscope. Temperature variation was obtained with a hot-stage and temperature controller.

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Notes and references

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Electronic Supplementary Information (ESI) available: XRD lattice parameters of compounds **2** and **3**, UV-Visible spectra (**1**,**2**,**3**), detailed POM analysis of **2**, XRD evidence for the symmetry rearrangement (*c2mm* to *p2gg*) occurring in **2** and the nodal patterns observed of the HOMO/LUMO MO's in the non-fluorinated Pc.

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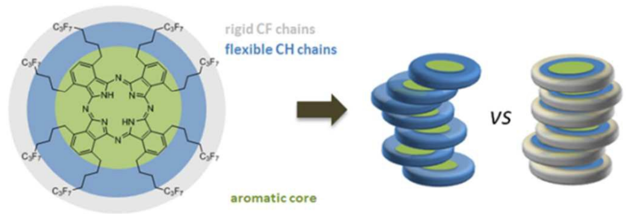
Two new perfluoroalkylated phthalocyanine derivatives were synthesised to investigate the effects of the fluorophobic/fluorophilic interactions on their mesophase and electronic carrier transport properties. Both compounds exhibit columnar mesomorphism and the thermal stability of columnar phase is enhanced by over 20°C as the number of fluorinated carbon increases, probably due to the nano-segregation between the fluorinated and hydrocarbon moieties in the chains. Also a strong tendency to spontaneous homeotropic alignment was observed. Time-of Flight (TOF) measurements reveal the ambipolar mobility was measured in the order of 10^{-1}-10^{-2} $cm^2 V^{-1}s^{-1}$ for the mesophases.



Enhancment of Col mesophase thermal stability

High carrier mobility in ambipolar nature

Strong tendency of homeotropic alignment