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

Lydia Sosa-Vargas, Fabien Nekelson, Daiju Okuda, Minokazu Takahashi, Yukimasa Matsuda, Quang-Duy Dao, Yoshida Hiroyuki, Akihiko Fujii, Masanori Ozaki, & Yo Shimizu

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$^{3}$ 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$^{5}$ 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 wettability of the materials.$^{10}$ The fluorophobic/fluorophilic interactions that occur within the alkyl and fluorooalkyl 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 ($\sim 10^{-1}$ 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 the non-peripheral type of perfluoroalkylated phthalocyanines was carried out, which is the object of this study.
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. Perfluoroalkyl 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,

Mesomorph 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 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 hexabenzo coronenes in which their thermal properties are strongly dependent on the combination of hydrocarbons and fluorinated chains. 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 Colh 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. 3 DSC thermograms of compound 1 (a) and 2 (b) at both heating (red) and cooling (blue) at 1°C/min.

Fig. 4 POM images under cross-polarised conditions of 1 (a), 2 (b) and 3 (c). 2 and 3 show homeotropic regions at the Colh phase which are lost upon cooling to the Col phase for 2 (d) and 3 (e). The dentritic growth of domains can be seen under non-polarised light for 2 (f).
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, 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 (Colh) 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 (Colr) 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 Colr of p2gg symmetry in 2 we were also able to detect the presence of a

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

<table>
<thead>
<tr>
<th>compound</th>
<th>phase transition</th>
<th>T(°C)</th>
<th>ΔH (kJmol⁻¹)</th>
<th>ΔS (Jmol⁻¹K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cryst→Iso</td>
<td>183</td>
<td>70</td>
<td>153</td>
</tr>
<tr>
<td>(mesophase→Iso)</td>
<td>180</td>
<td>25</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cryst→Colr</td>
<td>149</td>
<td>63</td>
<td>148</td>
</tr>
<tr>
<td>Cryst→Colh</td>
<td>181</td>
<td>3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Cryst→Colh</td>
<td>199</td>
<td>11</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cryst→Colr</td>
<td>114</td>
<td>48</td>
<td>119</td>
</tr>
<tr>
<td>Cryst→Colh</td>
<td>146</td>
<td>1</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Cryst→Colh</td>
<td>162</td>
<td>13</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

Col 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 (21.7 Å to 22.3 Å for the Colh 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 phthalocyanine mesogens can be detected in this case. 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. Fig. 7 shows typical transient photocurrent decay curves of hole and electron transport obtained at 186 °C (Colh) and 168°C (Colr) 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 octaalkylphthalocyanines. 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. 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, 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 Colh and Colr 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.
peripherally attached alkyl phthalocyanines series, the hexyl predicted on the symmetry of phthalocyanine ring. 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. In fact, for hexaalkoxytriphenylene analogues, the observed hole mobility is hardly affected by the introduction of perfluorinated alkyl chains.

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, respectively. 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), 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 rotation angle along the molecular axis normal to the plane is sensitive for transfer integral in a face-to-face dimer of phthalocyanine where 45° periodicity of electronic splitting energy oscillation is predicted on the symmetry of phthalocyanine ring. 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 cm² V⁻¹ s⁻¹ for crystal and pseudo-Colh mesophase, respectively even though it does not show high intracolumnar ordering in the mesophase. The crystalline structure 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. On the other hand, analysis of the mesophase by molecular dynamics (MD) simulation shows the presence of a dynamic molecular motions in the Colh phase analogous to the “de Vries” smectic phase which is seen in calamitic mesogens. 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 phthalocyanine (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 Colh phase. However, XRD analysis shows that no highly-ordered phase is present and the Colh is of a disordered nature. In the case of the Colh 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-colmnan 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.

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. 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.
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). $\nu_{\max}$ (KBr/cm$^{-1}$) 3346 (OH), 2958, 2886 (CH$_2$), 1225, 1119 (CF$_3$), 1069 (CF$_2$); $\delta_{ii}$ (500MHz, CDCl$_3$) 3.71-3.66 (m, 2H, J 2H, 6, CH$_2$-OH), 2.15-2.05 (m, 2H, F-C$_2$-CH$_2$), 1.75-1.62 (m, 4H, CH$_3$-CH$_2$OH) 1.50 (s, 3H, H-OH); $\delta_{e}$ (471MHz, CFC$_1$/CDCl$_3$) -81.1 (m, 3F, CF$_3$), -116.0 (m, 2F$_i$, CF$_2$-CF$_2$F), -128.3 (m, 2F, CF$_2$-CH$_3$).

iii) 1-(4-toluenesulfonyloxy)-5, 5, 6, 7, 7-heptafluoroheptane. 1H, 1H, 2H, 2H, 3H, 3H, 4H, 4H-heptafluorohept-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 dropwise 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. $\nu_{\max}$ (KBr/cm$^{-1}$) 3013 (Ar-H), 2965, 2934 (CH$_2$), 1600, 1497 (C=C Ar), 1226, 1178 (CF$_3$), 1120, 1099 (CF$_2$); $\delta_{ii}$ (500MHz, CDCl$_3$) 7.78 (d, 2H, Ar-H), 7.35 (d, 2H, Ar'-H), 4.06 (t, 2H, J 6, CH$_2$-OH), 2.45 (s, 3H, CH$_3$), 2.10-1.87 (m, 2H, CH$_2$-CH$_2$F$_3$), 1.80-1.58 (dm, 4H, CH$_2$-CH$_2$OH); 6F (471MHz, CFC$_1$/CDCl$_3$) -80.5 (t, 3F, J 9, CF$_3$), -115.3 (m, 2F$_i$, CF$_2$-CH$_3$), -127.7 (m, 2F, CF$_2$-CF$_2$CH$_3$).

1-(4-toluenesulfonyloxy)-4, 4, 5, 5, 6, 6, 7, 7-heptafluoroheptane. Following the procedure above 4, 4, 5, 5, 6, 6, 7, 7-nonafafluorohept-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. $\nu_{\max}$ (KBr/cm$^{-1}$) 1599 (C=C Ar), 1233 (SO$_2$), 1177 (CF$_3$-CF$_2$); 6H (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$_2$-CH$_3$O), 2.46 (s, 3H, CH$_3$), 2.12-1.89 (m, 2H, CH$_2$-CH$_2$F$_3$), 1.96-1.62 (dm, 2H, CH$_2$-CH$_3$H$_2$).

iv) 1-iodo-5, 5, 6, 6, 7, 7-heptafluoroheptane. Sodium iodide (6.7 g, 44 mmol) was dissolved together with 1-(4-toluenesulfonyloxy)-5, 5, 6, 6, 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 thiosulphate (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). $\nu_{\max}$ (KBr/cm$^{-1}$) 2957, 2886 (CH$_2$), 1224, 1174 (CF$_3$), 1115, 1063.
mixture of hexane/dichloromethane to give the
under reduced pressure. The organics were extracted
with twice
stirred for 16 hours. An aqueous solution of hydrochloric acid
under reduced pressure after filtration. The crude product was
aqueous solution of hydrochloric acid (50 mL, 10%), sodium
warmed to room temperature over a period of ca. one hour and
the organozinc reagent (70 mL, ≈0.2 M in tetrahydro furan, 14
and lithium chloride (0.6 g, 14 mmol) were added to the slurry
Bis(trifluoromethanesulfonyloxy)phthalonitrile (2.1 g, 5 mmol)
over two hours in order for the remaining zinc dust
to settle
tetrahydrofuran (40.0 mL) was added dropwise via addition
added and the heating/cooling cycle repeated once again. Once
the mixture is at room temperature, a solution of 1-iodo-5, 6, 6, 7, 7-heptafluoroheptan-6-ol (0.2 mL, 2 mmol) was
heated to reflux. Trimethyl silyl chloride (0.3 mL, 2 mmol) was
then added to a solution of 4, 4, 5, 5, 6, 6, 7, 7, 7-nonanfluoroheptan-1-ol (10.0 g, 23 mmol) in anhydrous acetone (120 mL).
After
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-nonanfluoroheptan-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).

5, 6, 6, 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, 6, 6, 7, 7-heptafluoroheptan-6-ol (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 to use. Conversion is assumed as ca. ≥90%.

4, 5, 6, 6, 7, 7, 7-nonanfluoroheptyl-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 trimethyl silyl chloride (0.3 mL, 2 mmol) were added to the zinc dust slurry. 1-Iodo-5, 6, 6, 7, 7-heptafluoroheptan-6-ol (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), 6-bis(5, 5, 6, 6, 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, 2.6 M in hexane) was added to give a dark red slurry. 3, 6-Bis(trifluoromethanesulfonyl oxy)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
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\( \varepsilon = 722 \text{ nm (5.0)} \); elemental analysis calcd. for C_{x}\text{H}_{y}\text{N}_{z}\text{F}_{w} (\%): 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 (\( \lambda = 337\) 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**

2. Division of Electrical, Electronic and Information Engineering, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan.
3. Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seto, Otsu, Shiga 520-2194, Japan.

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 (\( c2\text{mm to p2gg} \)) occurring in 2 and the nodal patterns observed of the HOMO/LUMO MO’s in the non-fluorinated Pc.


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.

Enhancement of Col mesophase thermal stability
High carrier mobility in ambipolar nature
Strong tendency of homeotropic alignment