JOURNAL OF
Materials
CHEMISTRY

Chiral linear isocyanide palladium(II) and gold(I) complexes as ferroelectric liquid crystals

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Received 19th April 1999, Accepted 15th June 1999

Creation of helical SmC* and Ch mesophases has been achieved by means of metal ion complexation by chiral isocyanide ligands, which have already proven their ability to induce high optical activity in helical synthetic polymers. Thus, from unstable isocyanide compounds with a mesogenic core derived from phenyl benzoate, five stable complexes have been prepared. Four palladium(II) complexes have been obtained with different chiral tails and, in one case, with a three-ring mesogenic core. Their corresponding SmC* phases have been studied in terms of their ferroelectric properties. High P_s values have been found for complexes derived from (*S*)-octan-2-ol: 93 nC cm^{-2} for $I_2Pd(C_8{*})_2$ and 59 nC cm^{-2} for $I_2Pd(COOPhC_8{*})_2$. A gold(I) complex with (*R*)-2-octyl as the chiral tail is presented as the first SmC* gold(I) complex whose ferroelectric behaviour has been studied. Indeed, the complex has been used as a chiral dopant in a binary mixture, the P_s value of which has been estimated.

Introduction

Isocyanides have proven to be useful and versatile components in a variety of interesting and stable materials, such as organometallic liquid crystals[1] and helical polymers,[2] despite their limited commercial availability and low thermal stability. Their linear shapes and strong binding properties make isocyanides excellent ligands for the formation of metal ion complexes with mesomorphic properties. In this context, the works reported by the groups of Takahashi,[3] Espinet[4] and Mayr[5] have proven the potential of these ligands for the preparation of liquid crystals, as metal ion [M = Pd(II), Pt(II), Au(I) and Au(III)] complexes of achiral isocyanides have displayed nematic, smectic and discotic mesophases.

One of our current research interests is focussed on the study of chemical systems with helical organisation, such as that present in synthetic polymers which have a helical arrangement of the monomeric units, particularly poly(isocyanides),[6] and that in chiral mesophases, *e.g.* cholesteric and tilted smectics, in which the mesogenic molecules are arranged in a helical manner. The possibility of preparing a single family of chemical structures which would display both these two types of helicity prompted us to synthesise[7] a number of monomers in which the isocyanide group is separated from a stereogenic centre by a promesogenic core (Fig. 1). We were able to relate the helicity present in the polymer backbones with that induced in cholesteric and smectic C phases by the precursors to the monomeric isocyanides.[7,8]

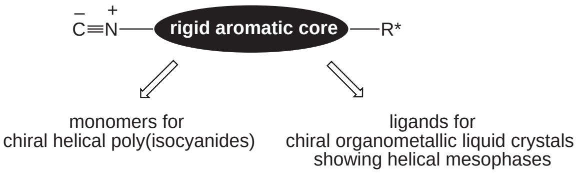

Fig. 1 Schematic representation of the structure of the isocyanide compounds which have been used as monomers for helical polymers and as ligands for organometallic complexes.

With a family of enantiomerically pure isocyanide monomers in hand, which had served in the polymerisations,[7] we realised that these ligands were additionally suitable for coordination to metal ions such as Pd(II) and Au(I). The interest in the use of these isocyanides as ligands stems from the lack of information about chiral organometallic complexes with a linear structure reported in the literature to date. Although various ferroelectric calamitic metallomesogens have been reported,[9] most of them are dimeric complexes consisting of two chiral ligands laterally linked by a metal atom and linear chiral complexes are rare.[10] However, isocyanides are ligands which provide stable organometallic complexes with a typical rod-like shape. To the best of our knowledge, chiral isocyanide-based metal complexes have not yet been described and therefore their capability of presenting a ferroelectric chiral smectic C phase (SmC*) is also unknown.

For these reasons, we planned the synthesis of a family of organometallic complexes with chiral isocyanide ligands (Fig. 2) and the study of their mesomorphic properties. Five palladium complexes and a gold complex have been prepared in order to test this type of chiral ligand as a promoter of helical mesophases by means of metal ion complexation, as isocyanides have already demonstrated high chiral induction in helical synthetic polymers.[7]

All the complexes prepared show liquid crystalline behaviour, which has been optically and thermally characterised. Four different types of ligand have been used for the palladium(II) complexes in order to study the influence of the position and nature of the stereogenic centre on the induction of chiral mesomorphic properties upon metal ion complexation, as well as on the ferroelectric behaviour of the resulting organometallic complexes. The spontaneous polarisation, as a ferroelectric property, has been measured in those complexes showing a SmC* mesophase or in binary mixtures (metal complex–SmC matrix) when the complex does not show the SmC* phase.

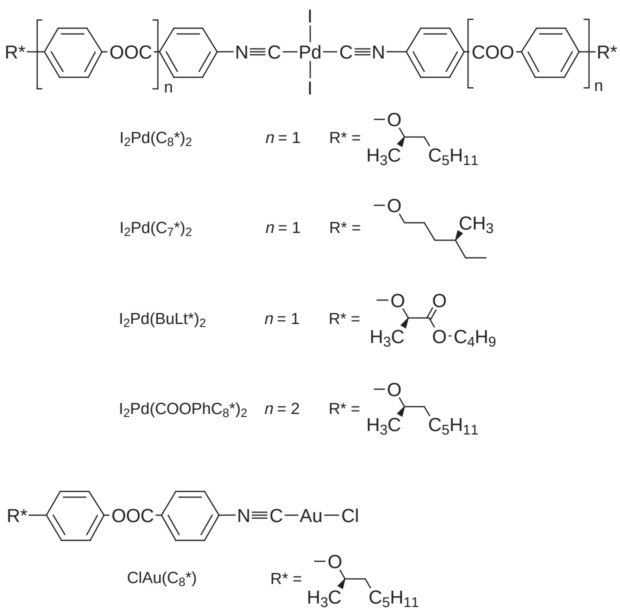

Fig. 2 Chemical structure of all the complexes prepared. The corresponding ligand is named by means of a symbol representing the chiral moiety linked to the basic mesogenic core, *i.e.* phenyl benzoate.

Experimental

Methods and materials

Bis(benzonitrile)palladium(II) dichloride was obtained commercially from Aldrich Chemical Co. [AuCl(tht)] (tht = tetrahydrothiophene) was prepared according to the literature method.[11] The isocyanides were prepared according to methods described previously.[7]

Microanalysis was performed with a Perkin-Elmer 240 B microanalyzer. ^{1}H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer in deuteriochloroform solutions. The textures of the mesophases were studied through an optical microscope (Nikon) with crossed polarizers, which was connected to a Mettler FP82 hot stage and a Mettler central processor. Measurements of the transition temperatures were made using a TA2910 differential calorimeter with a heating or cooling rate of 10 °C min^{-1}. The apparatus was calibrated with indium (156.6 °C, 28.44 J g^{-1}) and tin (232.1 °C, 60.5 J g^{-1}).

The spontaneous polarization and the response time were obtained simultaneously using the triangular wave form method.[12] In the experimental set-up the triangular wave voltage was supplied by a HP3245A Function Generator. The current–voltage cycles were recorded by a digital acquisition system, tech ADC488/16A. All the equipment was interfaced to a microcomputer. Cells used for measurement of the pure compunds were composed of two gold–brass electrodes of 12 μm diameter. Mixtures were measured in cells coated with polyimide using indium tin oxide (ITO) electrodes.

Ferroelectric measurements. Values of the spontaneous polarization (P_s) were determined by integrating the displacement current peak which appears, due to the reversal of the P_s, in response to an applied triangular voltage.[13] The maximum amplitude, frequency and cell thickness were 400 V_{pp}, 30 Hz and 100 μm, respectively, for the complex $I_2Pd(C_8*)_2$, 280 V_{pp}, 30 Hz and 100 μm, respectively, for the complex $I_2Pd(COOPhC_8*)_2$, and 25 V_{pp}, 50 Hz and 5 μm, respectively, for the mixtures.

Binary mixtures of the complexes with the achiral host were prepared by dissolving the appropriate amounts of each component in freshly distilled methylene chloride, and shaking at room temperature to allow evaporation of the solvent. This operation was repeated twice.

Synthesis of palladium(II) complexes

General procedure. To a solution of 101 mg (0.26 mmol) of bis(benzonitrile)palladium(II) dichloride in 2.5 ml of dry acetone, an excess of KI was added (175 mg, 1.05 mmol). The mixture was allowed to react for 2 h in order to achieve substitution of chlorine by iodine in the complex. After this time, the isocyanide ligand (0.56 mmol) in 2.5 ml of dry acetone was added dropwise. The resulting solution was stirred for 6 h at room temperature and the solvent removed by rotary evaporation. The crude product thereby obtained was dissolved in methylene chloride, washed three times with water and dried over $MgSO_4$. Once the solvent was removed the resulting oil was dissolved in the minimum amount of methylene chloride and the complex was precipitated by adding the necessary amount of hexane.

$I_2Pd(C_8*)_2$. Yield: 60%. ^{1}H NMR: δ 0.86 (m, 3H), 1.28–1.73 (m, 13H), 4.3 (q, J = 6.0, 1H), 6.9 (d, J = 9.1, 2H), 7.1 (d, J = 9.1, 2H), 7.7 (d, J = 8.6, 2H), 8.3 (d, J = 8.6 Hz, 2H). Elemental analysis (calculated values in parentheses): C, 49.19 (49.71); H, 4.22 (4.74); N, 2.52 (2.64)%.

$I_2Pd(C_7*)_2$. Yield: 58%. ^{1}H NMR: δ 0.9 (m, 6H), 1.16 (m, 2H), 1.3 (m, 3H), 1.50 (m, 2H), 3.95 (t, J = 6.8, 2H), 6.9 (d, J = 9.1, 2H), 7.1 (d, J = 9.1, 2H), 7.7 (d, J = 8.8, 2H), 8.3 (d, J = 8.8 Hz, 2H). Elemental analysis (calculated values in parentheses): C, 48.05 (48.77); H, 4.15 (4.45); N, 2.44 (2.71)%.

$I_2Pd(BuLt*)_2$. Yield: 55%. ^{1}H NMR: δ 0.87 (t, J = 7.3, 3H), 1.3 (m, J = 7.3, 2H), 1.60 (t, J = 7.3, 2H), 1.62 (d, J = 6.7, 3H), 4.15 (m, 2H), 4.7 (q, J = 6.7, 1H), 6.9 (d, J = 9.1, 2H), 7.1 (d, J = 9.1, 2H), 7.7 (d, J = 8.8, 2H), 8.3 (d, J = 8.8 Hz, 2H). Elemental analysis (calculated values in parentheses): C, 45.59 (46.07); H, 3.57 (3.87); N, 2.57 (2.56)%.

$I_2Pd(COOPhC_8*)_2$. Yield: 63%. ^{1}H NMR: δ 0.85 (t, J = 6.7, 3H), 1.27–1.73 (m, 13H), 4.3 (q, J = 6.0, 1H), 7.0 (d, J = 9.1, 2H), 7.2 (d, J = 9.1, 2H), 7.3 (d, J = 8.7 Hz, 2H), 7.7 (d, J = 8.7, 2H), 8.2 (d, J = 8.8, 2H), 8.4 (d, J = 8.5 Hz, 2H). Elemental analysis (calculated values in parentheses): C, 53.31 (53.45); H, 4.17 (4.21); N, 2.25 (2.20)%.

Synthesis of the gold(I) complex [$ClAu(C_8*)$]

A solution of ligand C_8* (73.9 mg, 0.20 mmol) in dry methylene chloride (10 ml) was added dropwise to a solution of [AuCl(tht)] (61.0 mg, 0.20 mmol) in dry methylene chloride (5 ml). The reaction mixture was stirred for 15 min, concentrated under vacuum and methanol added to precipitate the gold complex, which was filtered off and purified by crystallisation from methylene chloride and methanol. Yield: 66%. ^{1}H NMR: δ 0.87 (m, 3H), 1.27–1.72 (m, 13H), 4.3 (q, J = 6.0, 1H), 6.9 (d, J = 9.0, 2H), 7.1 (d, J = 9.0, 2H), 7.7 (d, J = 8.4, 2H), 8.3 (d, J = 8.4 Hz, 2H). Elemental analysis (calculated values in parentheses): C, 42.88 (43.20); H, 3.98 (3.63); N, 2.27 (2.40)%.

Mesomorphic properties

As was noted in the previous section, all the chiral isocyanide ligands prepared are non-mesogenic liquid materials which are unstable in air. However, this characteristic did not prohibit the isolation of chemically stable palladium(II) and gold(I) complexes, all of which exhibited mesomorphic behaviour across a wide range of temperatures. Thermal and thermodynamic data for the five complexes are gathered in Table 1.

The mesophases were identified according to their optical textures. The SmC* phase showed in all cases the typical broken fan-shaped and schlieren textures. The broken fan-shaped texture shows dechiralization lines indicating the

Table 1 Transition temperatures (°C) and transition enthalpies (kJ mol^{-1}; in parentheses) of the palladium(II) and gold(I) isocyanide complexes

Compound	Phase Transition						
$I_2Pd(C_8^*)_2$	C	133.7 (55.1)	(SmC*	109.5 (1.2)	Ch	127.3) (0.5)	I
$I_2Pd(COOPhC_8^*)_2$	C	155.3 (26.7)	SmC*			288	decomp.
$I_2Pd(C_7^*)_2$	C	176.4 (32.4)	SmC*	188.9 (1.4)	Ch	246.7 (1.6)	I
$I_2Pd(BuLt^*)_2$	C	100.9 (51.9)			(Ch	92.7) (0.3)	I
$ClAu(C_8^*)$	C	152.0 (13.0)	SmC*	185	SmA	285	decomp.

presence of a helical structure within the SmC* phase (Fig. 3). The cholesteric phases appeared as oily streaks when cooling from the isotropic liquid. The SmA phase of the gold complex showed typical fan-shaped and homeotropic textures, the latter after mechanical stress.

An overall view of the results reveals that, like their achiral analogues, a large increase in the mesogenic character of the isocyanide ligands occurs upon their complexation. However, the presence of methyl-branching in the terminal tails prevents stabilisation of the mesomorphic state to the same extent as occurs in the achiral complexes, due to steric hindrance. Obviously, this negative effect is less important as the methyl-branching is located further away from the rigid core. Nevertheless, it is worthwhile emphasising that non-mesomorphic isocyanide ligands with chiral tails of a different nature induce chirality in the form of chiral mesophases with a helical structure. Moreover, and according to our expectations, four of the five complexes prepared exhibit the potentially ferroelectric SmC* phase, which has allowed us to evaluate the properties of these linear complexes as ferroelectric materials.

The dimeric palladium(II) complexes show SmC* and cholesteric phases stable within the whole temperature ranges of the phases, except for $I_2Pd(COOPhC_8^*)_2$ which only presents an SmC* phase across a wide temperature range. This complex undergoes decomposition during the transition to the isotropic liquid at 288 °C. The increased size of the polarizable part of the molecule, *via* the incorporation of a third aromatic ring into the mesogenic core, accounts for the prevalence of smectic over nematic behaviour in this complex because of the associated increase in intermolecular interactions. This effect has also been observed in the monomeric gold(I) complex, but for a different reason. A monomeric structure with a strong dipole associated with a terminal group such as Cl–Au–CN favours the formation of an achiral SmA phase over the SmC* phase, thus indicating the existence of strong intermolecular interactions in the mesophase which must be also responsible for the decomposition observed when reaching the clearing point (285 °C).

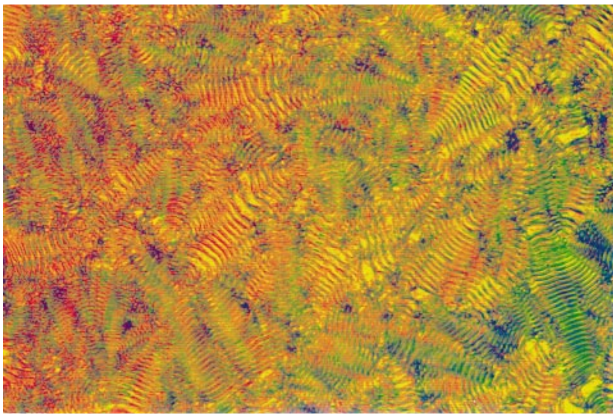

Fig. 3 Photomicrograph of $I_2Pd(C_7^*)_2$ in its chiral smectic C phase. The broken fan-shaped texture presents dechiralization lines which are characteristic of the helical structure of the SmC* phase.

The position of the stereogenic centre relative to the rigid core can affect the mesomorphic properties of a compound. This is clearly illustrated by the behaviour of the complexes $I_2Pd(C_8^*)_2$ and $I_2Pd(C_7^*)_2$. Obviously, a methyl branch in the chiral tail far away from the mesogenic core does not affect the intermolecular interactions between metal containing mesogenic cores, which are already strong. Hence, $I_2Pd(C_7^*)_2$ shows the highest melting point and a mesomorphic interval much wider compared to the homologous $I_2Pd(C_8^*)_2$ and $I_2Pd(BuLt^*)_2$ complexes.

The environment of the stereogenic centre in the chiral tails has been modified by preparing the phenyl benzoate monomers with tails derived from (*S*)-octan-2-ol and (*S*)-butyl lactate. A –COO– group in the stereogenic centre dramatically affects the mesomorphic properties: the complex $I_2Pd(BuLt^*)_2$ shows relatively low transition temperatures and solely nematic behaviour, disfavouring a layered arrangement, unlike its analogue $I_2Pd(C_8^*)_2$.

Ferroelectric properties

All the complexes showing the SmC* phase were studied as ferroelectric liquid crystals. Given the high temperatures of some of the mesophases and especially because of the decomposition of $I_2Pd(COOPhC_8^*)_2$ and $ClAu(C_8^*)$, the spontaneous polarisation of the materials was evaluated in cells consisting of two gold–brass electrodes. The compound was sandwiched between the electrodes, not necessarily above the clearing temperature, allowing the preparation of 100 µm thick cells.

The behaviour of each SmC* complex turned out to be very different depending on the molecular structure. When a chiral tail such as (*R*)-2-octyl is responsible for the chiral nature of the molecule and hence of the mesophase, high P_s values are obtained. The palladium complexes $I_2Pd(C_8^*)_2$ and $I_2Pd(COOPhC_8^*)_2$ gave rise to maximum P_s values of 93 and 59 nC cm^{-2} respectively. Fig. 4 displays the plot of P_s *versus* temperature for the complex $I_2Pd(C_8^*)_2$. The shape of the plot corresponds to a first order transition between the cholesteric phase and the ferroelectric smectic C. Indeed, P_s values increase abruptly just below the Ch–SmC* transition and reach high levels (*ca.* 80 nC cm^{-2}), thereafter the P_s values slowly rise to 93 nC cm^{-2} on cooling within the mesophase interval until crystallisation (at 81 °C).

In order to avoid decomposition of $I_2Pd(COOPhC_8^*)_2$ on heating up to the clearing temperature, the cell for this complex was prepared at 170 °C and the spontaneous polarisation studied on cooling from this point. At this temperature the P_s

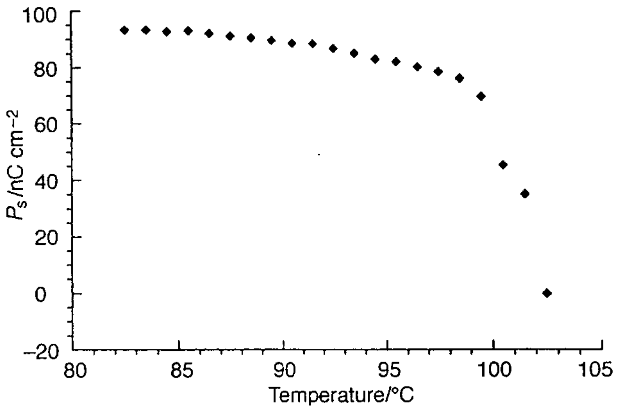

Fig. 4 Plot of spontaneous polarisation *versus* temperature for $I_2Pd(C_8^*)_2$.

value did not differ greatly from the maximum value reached before crystallisation. The maximum P_s value obtained was 59 nC cm^{-2}, lower than that of complex $I_2Pd(C_8^*)_2$. Two factors may be responsible for this lower value. Firstly, the additional –COO– group incorporates a longitudinal dipole[14] which should make smaller the dipole component perpendicular to the long molecular axis, and hence parallel to the polar axis of the phase. Secondly, the incorporation of a third aromatic ring with its corresponding –COO– linkage to the isocyanide ligand causes a large increase in the molecular length. This simple factor could explain the lower P_s value by means of a decrease in dipolar density within the mesophase.

The complex with a chiral tail derived from (*S*)-4-methylhexan-1-ol, $I_2Pd(C_7^*)_2$, did not show a measurable current peak in its response to a triangular alternating electric field. The distant location of the stereogenic centre (which favours lateral interactions, as deduced from the high melting and transition temperatures) prevents an effective coupling of molecular dipoles along the polar axis of the ferroelectric phase giving rise to P_s values below the error limit of the experimental setup.

The cholesteric (*S*)-butyl lactate derivative, $I_2Pd(BuLt^*)_2$, was used as dopant in a mixture[15] in order to estimate its potential ferroelectric properties. The mixture was studied in 5 μm cells. Only an estimated value of 5 nC cm^{-2}, by extrapolation, can be given, which merely confirms its ferroelectric behaviour. This low P_s value was rather unexpected and the reason behind this could lie with the difficulty of finding a suitable SmC host. The host was chosen because of its structural similarity to the organic ligand, as was done previously in a study of chiral bis(salicylideneaniline) complexes with satisfactory results.[9c] Experiments with other SmC hosts gave rise to either non-miscible mixtures or non-measurable P_s values

The evaluation of $ClAu(C_8^*)$ as the first gold(I) complex showing a ferroelectric SmC* phase ran into difficulties on account of the conductivity inherent to the complex (in spite of several re-precipitations) which made impossible the evaluation of the P_s value. As for $I_2Pd(BuLt^*)_2$, a binary mixture was prepared so that an estimation of the ferroelectric behaviour of the gold(I) complex could be carried out. Thus, a material was obtained which aligned uniformly in a 5 μm cell but which still gave rise to a very small P_s value (P_s 5 nC cm^{-2} max.) due to the above mentioned effect of the SmC host, and also the difficulty of correctly integrating the current peak because of the conductivity inherent in the gold complex (Fig. 5).

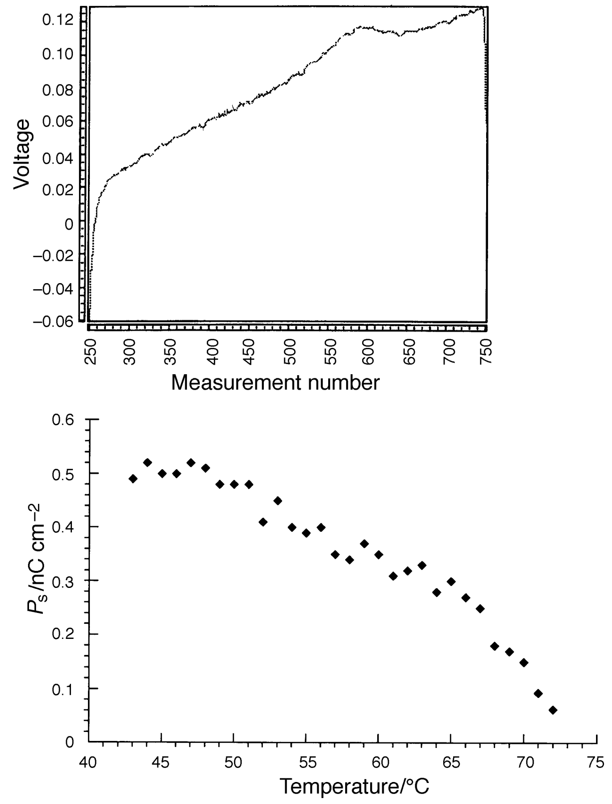

Fig. 5 (Top) Displacement current peak as recorded on an oscilloscope for the binary mixture of $ClAu(C_8^*)$ at 45 °C (triangular wave, 25 V_{pp} and 50 Hz amplitude and frequency, respectively). (Bottom) Plot of spontaneous polarisation *versus* temperature for $ClAu(C_8^*)$.

Conclusions

Chiral isocyanide compounds, which had already shown induction of helical conformations in synthetic polymers, have been used for the preparation of stable palladium(II) and gold(I) complexes which show mostly helical mesophases on melting. The SmC* phases have been unequivocally identified and hence the first linear ferroelectric metallomesogens have been described and studied. The palladium(II) complexes derived from (*S*)-octan-2-ol gave rise to high P_s values of 93 and 59 nC cm^{-2}. Moreover, the first gold(I) complex showing ferroelectric behaviour has been described, the P_s value of which, although rather small, has been evaluated in a binary mixture.

Acknowledgements

This work was supported by a project from Fundación Ramón Areces.

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Paper 9/03084K