

Palladium(II) metallomesogens of crown ether derivatized imines, and their sodium adducts

Javier Arias, Manuel Bardají, Pablo Espinet *

Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain

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Abstract

A series of imines HL_n (**1**) (*n* stands for the alkoxy chain length: 4, 6, 8, 10, and 12) has been synthesized by condensation of 4-aminobenzo-15-crown-5 and *p*-alkoxybenzaldehyde. Orthopalladation afforded the dinuclear derivatives [Pd(μ-OAc)L_n]₂ (**2**) which, by substitution reactions, led to dinuclear and mononuclear derivatives [Pd(μ-Cl)L_n]₂ (**3**) and [Pd(β-diket)L_n] (**4**) (β-diket = H₂₅C₁₂OH₄C₆-C(O)-CH-C(O)-C₆H₄OC₁₂H₂₅). The imine ligands and the acetato bridged complexes are non-mesogenic whilst the chloro-bridged and the diketonato complexes are enantiotropic liquid crystals. They display smectic A mesophases. Complexation with sodium perchlorate afforded the corresponding derivatives [(O₂ClO₂)NaCrown] (Crown = crown derivatives **1–4** for *n* = 4). None of the sodium adducts is mesogenic. The acetato bridged complexes consist of a mixture of *syn* and *anti* isomers and a dramatic increase in the *syn:anti* ratio is produced upon complexation of NaClO₄ (*syn:anti* = 4:96 for complexes **2** versus 54:46 for the corresponding [(O₂ClO₂)NaCrown**2**]). The crown ether derivatives extract sodium picrate from aqueous solutions and the presence of the palladium centers improves clearly the extraction, [Pd(μ-Cl)L_n]₂ being the best and the fastest extractor. A model for the extraction and transport process in these complexes is proposed.

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1. Introduction

The ability of crown ethers to complex cations [1] has been exploited to produce sensors of cations, to extract cations, for ionic transport in membranes, or to prepare stationary phases in chromatography [2].

The formation of mesogenic organic materials from functionalized macrocyclic ligands is a subject of current interest. Examples have been reported using crown ethers, which afford, often by their symmetric functionalization with promesogenic fragments, calamitic, columnar or plasmidic mesophases [3]. Further complexation with alkali salts produces a variety of results: (a) changes in the mesophase type [3b,3e,3f,3g,3h,3i], as in cases when typically

calamitic liquid crystals self-organize into columnar mesophases; (b) an increase [3j] or a decrease [3a,3b,3g,3h] of mesophase stability, the latter leading in the extreme to disappearance of the mesogenic behavior.

Very little work has been reported on the synthesis of metallomesogens containing transition metals and crown ethers. Often the crowns have some oxygen atoms substituted by better coordinating nitrogen or sulfur atoms [4]. The central crown cavity is occupied by the metal, which sometimes induces the mesogenic behavior as found in poliazacrown cobalt [4a], diazapolyether crown copper [4c], luminescent diazacrown lanthanide [4g], or in polythioether crown palladium derivatives [4e,4f]. Therefore, the crown is already blocked and it is not possible to further complex an alkali salt. However, in related phthalocyanine metallomesogens containing uncomplexed crown ethers, the addition of alkali cations induces changes in the structure and the transport properties [3d,5].

* Corresponding author.

E-mail address: espinet@qi.uva.es (P. Espinet).

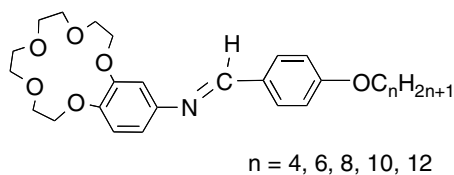


Fig. 1. Imines used in this work.

Dinuclear and mononuclear orthopalladated compounds are one of the most widely studied class of metallomesogens because of their stability and the structural versatility of the system [6]. Our group has reported a variety of cyclopalladated complexes and studied the structure-mesogenic activity relationship, including the first cholesteric metallomesogens [7], as well as complexes displaying ferroelectricity [8], non-linear optics [9] or lyotropism [10].

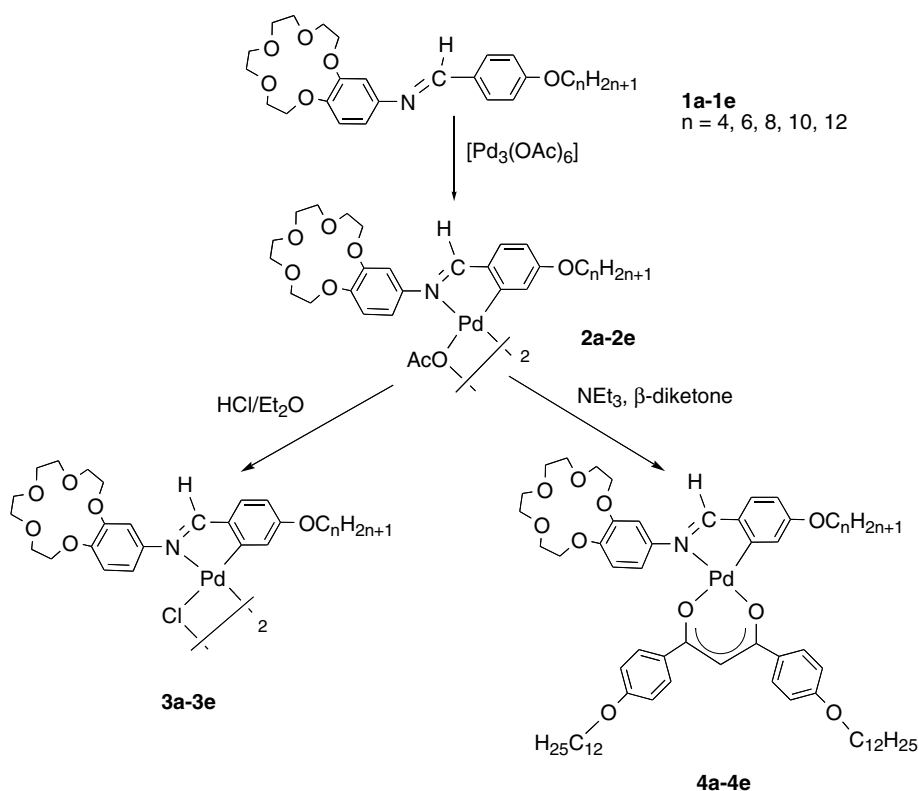
The combination of different coordinating entities, such as a crown ether, an imine and an alkoxy chain, into a unique ligand could give rise to interesting systems capable of selective recognition processes and additional properties. In this paper, we report the synthesis and characterization of Schiff bases functionalized with alkoxy chains of different length and with crown ethers (Fig. 1), and their orthopalladated complexes. Some of these compounds behave as thermotropic liquid crystals. Adducts of these compounds with sodium perchlorate were prepared, which showed no mesogenic behavior. The extraction properties of sodium of these compounds are also reported.

2. Results and discussion

2.1. Syntheses and structural characterization

The imines **1** were readily prepared by condensation of the corresponding *p*-alkoxybenzaldehydes ($n = 4, 6, 8, 10,$ and 12) and amino crown derivatives. Treatment of the imines with the stoichiometric amount of palladium acetate afforded the dinuclear cyclopalladated derivatives **2**. The reaction of **2** with HCl in diethyl ether, or with a β -diketone in the presence of triethylamine, lead to dinuclear chloro-bridged derivatives **3** or mononuclear diketonato derivatives **4**, respectively (Scheme 1).

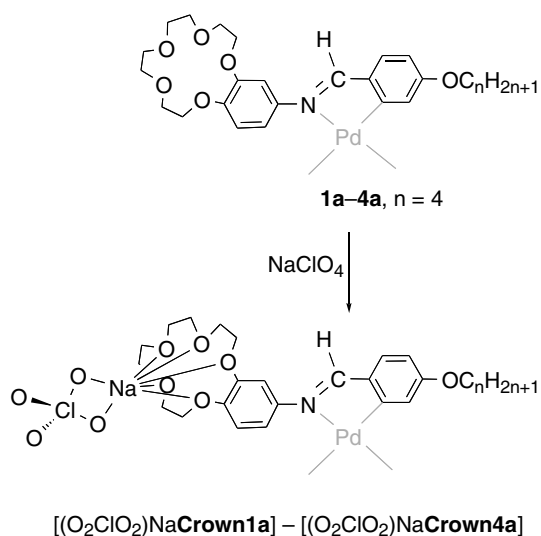
These compounds are white **1**, orange **2**, or yellow **3–4** solids at room temperature. They were characterized by IR and NMR spectroscopy, as well as by elemental analysis. The IR spectra of the free imines show a stretching band at 1607 cm^{-1} , assigned to $\nu(\text{C}=\text{N})$, which is shifted to lower wavenumbers, compared to the free imines, by *ca.* 20 cm^{-1} for derivatives **2**, *ca.* 30 cm^{-1} for **3**, and *ca.* 5 cm^{-1} for **4** [11]. The IR spectra of compounds **3** show the presence of $\nu(\text{Pd}-\text{Cl})$ bands (247 cm^{-1}) [12]. The acetato-bridged complexes **2** are a mixture of *syn* and *anti* isomers relative to the imine arrangement in each half of the molecule [7,13], in a 4:96 ratio as shown by ^1H NMR, whilst chloro-bridged derivatives **3** are the pure *anti* isomer. The largest difference in chemical shift, compared to the free imines, is observed for the iminic proton (8.39 for **1**, 7.45 for **2**, 7.81 for **3**, and 8.04 ppm for **4**) and then for



Scheme 1.

the aromatic protons, whilst the crown ether methylene hydrogen atoms and the alkyl chains are only very slightly shifted. The assignments given in Section 4 were assessed by COSY and NOESY experiments.

Complexation of compounds **1a–4a** (for chain length $n = 4$) with NaClO_4 was achieved by addition of sodium perchlorate in a ratio 15-crown ether:sodium = 1:1 (Scheme 2). Sodium was chosen as the alkaline cation



Scheme 2.

because it has the best radius to fit the 15-crown ether moiety [14]. The evidences supporting the formulation of the complexes as containing perchlorate covalently bonded to sodium are discussed later.

These sodium-containing complexes are pale yellow (for **1a**) or yellow solids at room temperature. They were characterized by IR and NMR spectroscopy, as well as elemental analysis. The elemental analyses were consistent with the a Pd:Na = 1:1 ratio, but this is not very significant as the method of preparation (evaporation to dryness) should produce this result also for a 1:1 mixture. More significant, the complexes are soluble in CDCl_3 , where NaClO_4 is insoluble, and a main change in the NMR spectra is observed (Fig. 2): the methylene crown ether resonances split due to the loss of symmetry upon sodium coordination (compare the signals in the range 3.0–4.5 ppm for the pairs a/b and c/d in Fig. 2). Some small shifts of the aromatic protons are also observed.

Additional major changes are observed in the ^1H NMR spectrum of derivative $[(\text{O}_2\text{ClO}_2)\text{NaCrown2a}]$ (spectrum d) compared to **2a** (spectrum c): two different sets of resonances, in molar ratio close to 1:1, are seen. The signals for the methyl groups of the acetato bridges and those of the imine resonances reveal that this apparent splitting corresponds in fact to a dramatic increase of the *syn:anti* ratio in the complexes $[(\text{O}_2\text{ClO}_2)\text{NaCrown2a}]$ (*syn:anti* = 54:46) as compared to their orthopalladated precursors **2a** (*syn:anti* = 4:96). When the solid $[(\text{O}_2\text{ClO}_2)\text{NaCrown2a}]$ is

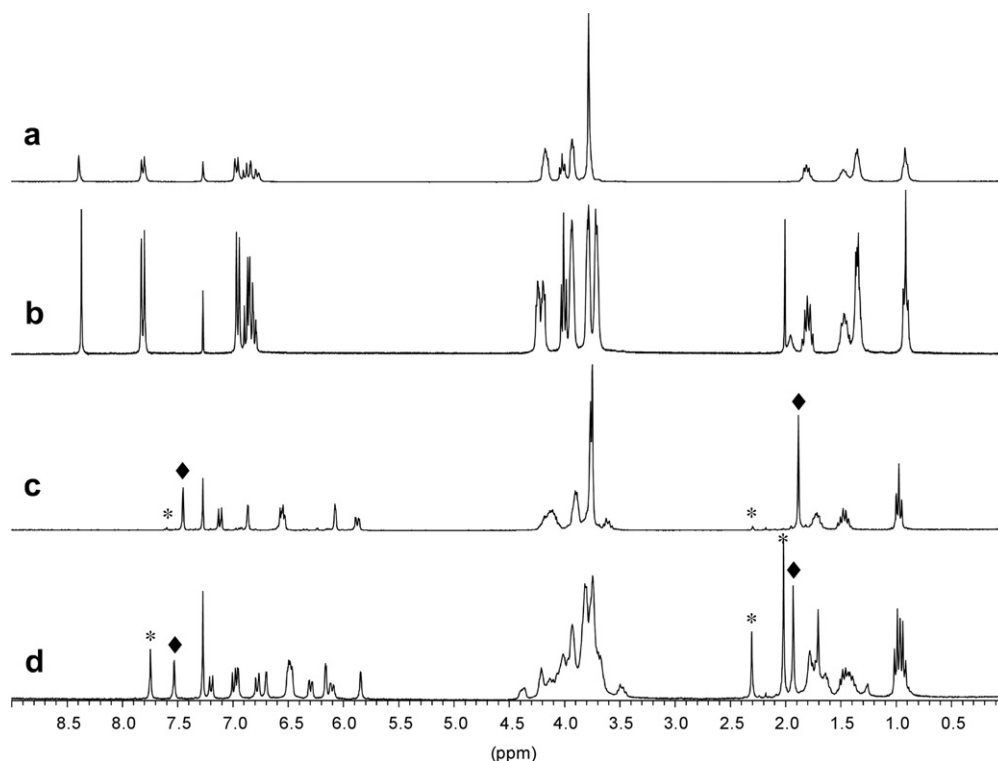


Fig. 2. ^1H NMR spectra in CDCl_3 of the following derivatives: (a) **1a**, (b) $[(\text{O}_2\text{ClO}_2)\text{NaCrown1a}]$, (c) **2a**, and (d) $[(\text{O}_2\text{ClO}_2)\text{NaCrown2a}]$. The presence of signals of the *syn* (*) and *anti* (♦) isomers is highlighted for their corresponding imine and acetate hydrogen atoms (note that in the *syn* isomer the two acetato groups are non-equivalent by symmetry).

washed with water, NaClO_4 is extracted and the starting material is recovered, as observed by the ^1H NMR spectrum of the solid residue (*syn* and *anti* isomers again show a 4:96 molar ratio). Similarly, when a CDCl_3 solution of $[(\text{O}_2\text{ClO}_2)\text{NaCrown2a}]$ is shaken with water, NaClO_4 is extracted into the water layer and the CDCl_3 solution reverts to **2a** in *syn:anti* ratio = 4:96. The existence of a *syn/anti* exchange (slow for the monodimensional experiment, hence the separated observation of the two isomers) was verified for $[(\text{O}_2\text{ClO}_2)\text{NaCrown2a}]$ by an EXSY NMR experiment which confirmed that the eight resonances (imine and acetate) of the *anti* isomers exchange with the corresponding nine resonances of the *syn* isomer. The very different *syn:anti* ratio observed for the complexes with and without sodium perchlorate must be due to marked changes in polarity of the two isomers upon sodium complexation, these leading to a relative increase of stability of the *syn* complex.

The IR spectrum of $[(\text{O}_2\text{ClO}_2)\text{NaCrown2a}]$ shows several absorptions in the vicinity of 1100 cm^{-1} , corresponding to the perchlorate group anion with the typical splitting associated to covalently bonded perchlorate (C_{2v} symmetry), both in the solid state and in chloroform solution (Fig. 3; the spectrum of a gold complex containing ionic perchlorate is given for comparison). The same is observed for the rest of the complexes containing sodium perchlorate. This, along with the solubility of the complexes in CDCl_3 (NaClO_4 is insoluble in this solvent) suggests a tight association of the perchlorate anions to the cationic complex, including covalent interactions of the oxygen atoms of the perchlorate to the sodium cation. Coordination of the sodium atom by perchlorate finds support in some X-ray structures reported in the literature [15], where two oxygen atoms of the perchlorate are involved in covalent bonding to sodium. Thus two oxygen atoms of the perchlorate group together with the oxygen atoms of the crown ether would complete the coordination of sodium,

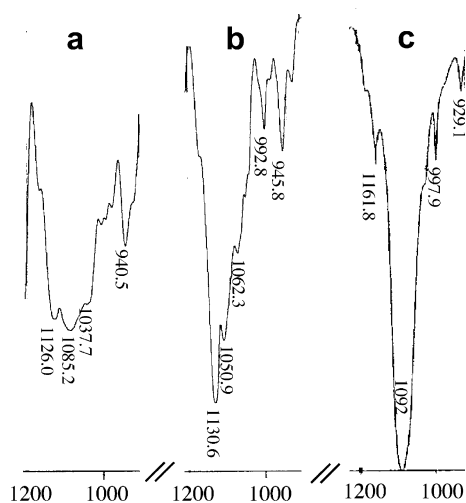


Fig. 3. (a) $[\text{NaCrown2a}]\text{ClO}_4$ in Nujol mull; (b) $[\text{NaCrown2a}]\text{ClO}_4$ in CHCl_3 solution; (c) $[\text{Au}(\mu\text{-Pr}_2\text{PCH}_2\text{PPh}_2)_2](\text{ClO}_4)_2$ in Nujol mull.

and the complexes are better represented as $[(\text{O}_2\text{ClO}_2)\text{NaCrown2a}]$. The same applies to the rest of $[(\text{O}_2\text{ClO}_2)\text{NaCrown}]$ compounds.

2.2. Mesogenic behavior

Optical, thermal and thermodynamic data of derivatives prepared, studied using polarized light optical microscopy and differential scanning calorimetry, are collected in Tables 1–4 and compared in Fig. 4. The SmA mesophases were identified in optical microscopy by their typical oily streaks and homeotropic textures or by their fan-shaped textures (Fig. 5).

All the imine ligands are non-mesogenic (Table 1), although the related imines containing an alkoxy chain in *para* position instead of the crown ether moiety are mesogenic [16]. The change in alkoxy chain length modifies the melting points only up to 18°C . Thus, the crown ether turns out to be the dominant structural motif influencing the thermal behavior of the imine, leading to an unfavorable length to width aspect ratio, while the alkoxy chain produces only a small influence. Orthometallation to give dinuclear complexes **2** causes an increase of the melting points, and non-mesogenic behavior (Table 2). This is typically observed for many acetate bridged palladium derivatives due to their open book (or roof) geometry, which is unfavorable towards mesogenic behavior.

The chloro bridged dinuclear complexes, having a favorable planar structure and stronger intermolecular interactions [6], are enantiotropic liquid crystals (Table 3).

Table 1
Optical, thermal and thermodynamic data for the imine ligands **1a–1e** HL_n

Derivative	<i>n</i>	Transition ^a	$T/^\circ\text{C}^b$	$\Delta H/\text{kJ mol}^{-1}$
1a	4	C–C' ^c	81.2	15.17
		C'–I	109.6	31.23
1b	6	C–I	98.5	31.29
1c	8	C–C' ^c	60.2	11.18
		C'–I	91.6	26.85
1d	10	C–I	105.0	30.15
1e	12	C–C' ^c	45.3	8.29
		C'–I	101.0	38.52

^a C, C' = crystal, I = isotropic liquid.

^b Data for the first heating scan.

^c Only observed by DSC.

Table 2
Optical, thermal and thermodynamic data for the complexes **2a–2e** $[\text{Pd}(\mu\text{-OAc})\text{L}_n]_2$

Derivative	<i>n</i>	Transition ^a	$T/^\circ\text{C}^b$	$\Delta H/\text{kJ mol}^{-1}$
2a	4	C–I	211.3	66.54
2b	6	C–I	177.16	49.46
2c	8	C–I	118.5 ^c	–
2d	10	C–I	133.6 ^c	–
2e	12	C–I	180 ^c	–

^a C, C' = crystal, I = isotropic liquid.

^b Data for the first heating scan.

^c Transition with decomposition.

Table 3
Optical, thermal and thermodynamic data for the complexes **3a–3e** [Pd(μ -Cl) L_n]₂

Derivative	<i>n</i>	Transition ^a	T/°C ^b	ΔH /kJ mol ⁻¹
3a	4	C–S _A ^c	220	–
		S _A –I	223.2	53.26 ^d
		I–S _A	115.2	–5.4
3b	6	C–S _A	206.45	44.06
		S _A –I	214.79	6.07
		I–S _A	174.24	–1.33
3c	8	C–S _A	205.1	45.37
		S _A –I	222.4	6.31
		I–S _A ^c	190	–
3d	10	C–S _A	177.3	35.87
		S _A –I	234.8	8.44
		I–S _A	228.5	–0.71
3e	12	C–S _A	169.9	34.19
		S _A –I	231.6	10.36
		I–S _A	220.5	–1.69

^a C, C' = crystal, S_A = smectic A, I = isotropic liquid.

^b Data for the first heating and cooling scans.

^c Only observed by polarized optical microscopy.

^d Combined enthalpies.

Table 4
Optical, thermal and thermodynamic data for the complexes **4a–4e** [Pd(β -diket) L_n]

Derivative	<i>n</i>	Transition ^a	T/°C ^b	ΔH /kJ mol ⁻¹
4a	4	C–C'/ ^c	66.2	2.57
		C–S _A	86	55.42
		S _A –I	122.6	5.56
		I–S _A	121.2	–5.6
4b	6	C–S _A	75.8	41.8 ^d
		S _A –I	113.5	3.15
		I–S _A	111.4	–4.42
4c	8	C–S _A	85.6	64.01
		S _A –I	132.8	5.84
		I–S _A	131.3	–6.24
4d	10	C–S _A	59.8	38.38
		S _A –I	126.9	5.38
		I–S _A	124.3	–4.97
4e	12	C–S _A	70	75.19
		S _A –I	135	6.06
		I–S _A	133.3	–5.99

^a C, C' = crystal, S_A = smectic A, I = isotropic liquid.

^b Data for the first heating and cooling scans.

^c Only observed by DSC.

^d Combined enthalpies.

Clearing points are in the short range 210–235 °C. As the mesophase is cooled down, the material became very viscous, and crystallization is not observed because of supercooling of the SmA phase (no T_g was observed). The ranges of mesophase broaden with alkoxy chain length from 3 °C ($n = 4$) to 62 °C ($n = 12$). When this behavior is compared to the reported for the related complexes containing imines with an alkoxy chain instead of the crown ether fragment (therefore typical H-shaped palladium derivatives), the

same SmA mesophases are found. However, the crown ether derivatives show higher melting points and shorter liquid crystal ranges, as is to be expected from decreasing the alkoxy chain/palladium ratio from 2 to 1 and adding the flexible crown ether moiety [16]. The thermal stability of the mesophase of complexes **3a–3e** is low, probably due to the high clearing point temperature. Moreover, decomposition is important after three heating-cooling cycles.

Typical strategies to improve the mesogenic properties are to reduce the molecular symmetry and to increase the number of chains. Both are expected to reduce the melting points. In effect, the mononuclear β -diketonato complexes **4**, with a planar geometry and three alkoxy chains, show a dramatic decrease of the melting points. Their melting points are in the short range 60–86 °C (about 100–134 °C lower than the corresponding complexes **3**) and their clearing points in the short range 114–135 °C (about 90–108 °C lower than the corresponding complexes **3**). This means a considerable broadening in mesophase range (from 37 °C for $n = 4$ to 67 °C for $n = 10$), more marked for short alkoxy chains (Table 4). The mesophase is very viscous and again supercooling of the SmA phase rather than crystallization was observed (even down at –30 °C; no T_g was observed). The lowering in transition temperatures has a positive effect on the thermal stability of the compounds in their SmA phase, and after 10 cycles there was no noticeable decomposition. The corresponding derivatives containing imines with an alkoxy chain instead of the crown ether fragment (typical K-shaped palladium complexes) also display SmA phases but additionally show SmC and N phases [10].

We have also studied the mesogenic behavior of the adducts [(O₂ClO₂)NaCrown] (Crown = crown derivatives **1a–4a**). The thermal data are collected in Table 5. As expected, complexation of the crown ether moiety with sodium ion changed the thermal behavior. As stated in the introduction complexation of alkaline cations with organic liquid crystals usually leads to more complicated mesophases depending on the cation and the counter ion, although a decrease of the mesophase stability or loss of the mesophase has also been reported. In our case, however, none of the complexes is mesogenic, and they melt with decomposition. The imine adduct [(O₂ClO₂)NaCrown**1a**] shows a higher melting point than **1a**, while the rest of [(O₂ClO₂)NaCrown] complexes, derived from **2a–4a**, display lower melting temperatures (with decomposition) than their precursor complexes. We also studied more in more detail the variation of the mesogenic properties of [Pd(μ -Cl) L_{12}]₂ and [Pd(β -diket) L_{12}] (with the longest chain, lower melting points and larger SmA ranges than for $n = 4$) with other sodium salts with different anions (see Sections 4 and 4.3). Melting points (always with decomposition) were higher than for the precursors, as found for other crown ether based mesogens [3f,3j,3l] and the liquid crystal properties were lost. In no case we found mesogenic behavior. The unfavorable aspect ratio of the structures of the Na-

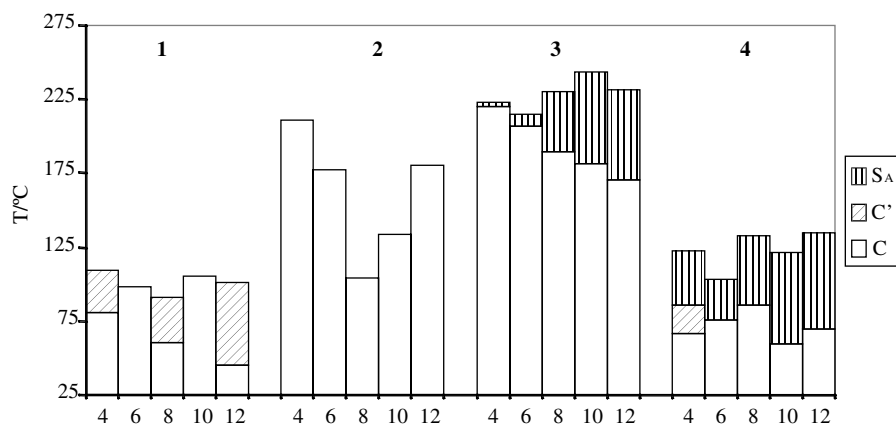


Fig. 4. Thermal behavior of compounds **1** HL_n, **2** [Pd(μ-OAc)L_n]₂, **3** [Pd(μ-Cl)L_n]₂, and **4** [Pd(β-diket)L_n] (on heating; *n* = 4, 6, 8, 10, and 12).

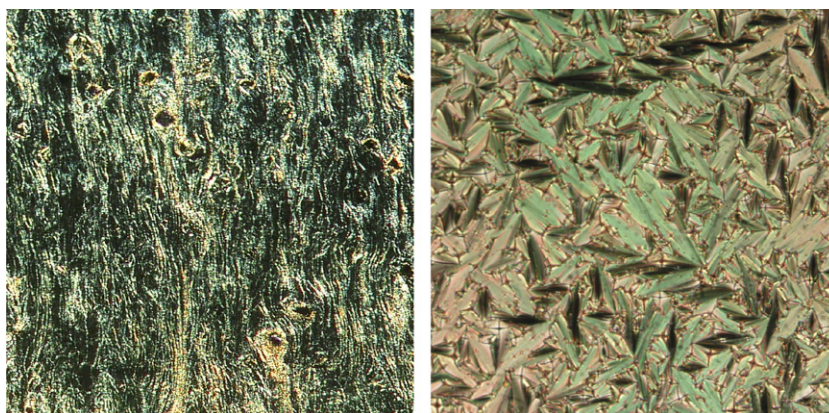


Fig. 5. Typical polarized optical microscopic textures (100×). Left: **3d**, obtained on heating from the solid at 200 °C. The picture shows oily streaks and homeotropic zones. Right: **4e**, obtained on cooling from isotropic liquid at 131 °C.

Table 5
Optical and thermal data for the derivatives [(O₂ClO₂)NaCrown]
(Crown = Crown1a–Crown4a)

Derivative	Transition ^a	T/°C
[(O ₂ ClO ₂)NaCrown1a]	C–I	130 ^{b,c}
[(O ₂ ClO ₂)NaCrown2a]	C–I	170 ^b
[(O ₂ ClO ₂)NaCrown3a]	C–I	198 ^b
[(O ₂ ClO ₂)NaCrown4a]	C–I	80 ^{b,c}

^a C = crystal, I = isotropic liquid.

^b Transition with decomposition. Only observed by polarized optical microscopy.

^c Mixture of isotropic liquid and solid.

complexed molecules, discussed above, accounts for the loss of liquid crystal behavior upon sodium complexation.

2.3. Experiments of cation extraction

It is known that crown-ether compounds can extract alkaline salts into organic solvents and transport them through “membranes” built with organic solvent separators. The complexes reported here also show these properties. Quantitative measurements were carried out only on their extraction efficiency, comparing the complexes with

the free ligand, all with the same alkoxy chain *n* = 12 (Table 6; see also Section 4). Sodium picrate was used in order to have colored solutions in water, so that the salt concentration can be easily estimated using visible spectroscopy. For all the cases, the presence of palladium improved dramatically the extraction efficiency, especially for the chloro-bridged derivative which is the best and the fastest extractor. The results in terms of extraction efficiency are as follows: [Pd(μ-Cl)L₁₂]₂ > [Pd(μ-OAc)L₁₂]₂ > [Pd(β-diket)L₁₂] ≫ HL₁₂. The time to reach the extraction maxima follows the sequence: [Pd(μ-OAc)L₁₂]₂ > HL₁₂ = [Pd(β-diket)L₁₂] ≫ [Pd(μ-Cl)L₁₂]₂.

Table 6
Efficiency as extractor of derivatives **1e–4e** (*n* = 12)

Extractor	% Extracted ^a	t/min ^b
HL ₁₂	7	40
[Pd(μ-OAc)L ₁₂] ₂	76	73
[Pd(μ-Cl)L ₁₂] ₂	86	12
[Pd(β-diket)L ₁₂]	33	40

^a Calculated as follows: (A₀ – A)/A₀ × 100; A₀ = starting absorbance; A = final absorbance.

^b Time to reach the equilibrium (no more sodium is extracted).

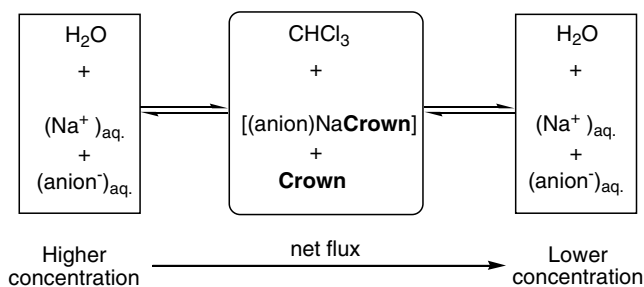


Fig. 6. Transport induced by complexation of sodium perchlorate or picrate with crown-ether compounds.

Picrate is known to behave structurally, in crown ether complexes, in a way quite similar to perchlorate. In effect [(picrate)NaCrown] complexes show in the solid state, the sodium atom coordinated with the crown ether, the alkoxy oxygen of picrate and one oxygen of one *ortho*-NO₂ group. It is obvious then that the extraction behavior of Na(picrate) and NaClO₄ must be the same: Both salts are incorporated to CHCl₃ solutions of the crown-containing compounds (whether organic or orthopalladated) in the form of the covalent species [(anion)NaCrown] (anion = picrate, ClO₄).

As we have discussed before for the compounds with NaClO₄, washing with water removes the sodium salt from the corresponding crown ether complex. Hence the transport phenomenon can be easily understood as consisting in the extraction of the sodium salt from a more concentrated water solution, in the form of the corresponding covalent complex, and its liberation to the less concentrated water solution (Fig. 6). The observation of covalently bonded perchlorate in the solutions in chloroform of the complexes reported here strongly supports this model.

3. Conclusions

Imines derived from 4-aminobenzo-15-crown-5 do not behave as liquid crystals, but their orthopalladated complexes induce mesogenic properties for compounds with planar geometry. Therefore, the substitution of alkoxy chains by a crown ether moiety in the aniline ring of the imine ligand does not preclude the formation of SmA mesophases, although in a more limited temperatures range. The addition of sodium perchlorate gives the corresponding adducts, none of which behaves as liquid crystal. In fact the addition of a sodium salt to a solid mesogen precludes the appearance of the mesophase upon melting. The major spectroscopic changes observed in the adducts is the increase of the *syn* isomer for the acetato bridged adduct, and the observation of covalently bonded perchlorate in the compounds. This observation supports that covalent structures are formed in solution which are responsible for the solubilization of sodium salts in chloroform in the form [(anion)NaCrown]. The extraction properties of the crown ether compound are not only maintained but improved by orthopalladation of the crown-functionalized imine.

4. Experimental

4.1. General procedures

IR spectra were recorded on a FT 1720X Perkin–Elmer spectrophotometer (4000–400 cm⁻¹) using KBr pellets, or a Perkin–Elmer 883 spectrophotometer (4000–200 cm⁻¹) using Nujol mulls between polyethylene sheets. ¹H NMR spectra were recorded on Bruker AC-300 or ARX-300 instruments in CDCl₃ solutions (if no other solvent is stated); chemical shifts are quoted relative to SiMe₄ (external, ¹H). The EXSY experiment was carried out with a standard phase sensitive NOESY pulse sequence. Elemental analyses were performed with a Perkin–Elmer 2400 micro-analyzer. The textures of the mesophases were studied with a Leica DMRB microscope, equipped with a Mettler FP-82HT hot stage (heating rate of 10 K min⁻¹) and a temperature controller Mettler FP-90. Transition temperatures and enthalpies were measured by differential scanning calorimetry, with a Perkin–Elmer DSC-7, using aluminium crucibles. The apparatus was calibrated with indium (156.6 °C, 28.45 J g⁻¹) as standard. UV–Vis absorption spectra were recorded at 298 K on a Shimadzu UV-1603.

4.2. Syntheses

The reactions were carried out in the air atmosphere unless otherwise stated. 4-aminobenzo-15-crown-5 (Aldrich) was used as received and literature methods were used to prepare *p*-alkyloxybenzaldehyde [17], [Pd₃(OAc)₂] [18], β-diketone [19]. Only example procedures and IR and NMR data for *n* = 8 are described here, as the syntheses and the IR and NMR data were similar for the rest of the compounds. Yields and analytical data are given for all the compounds.

4.2.1. Preparation of the imine HL_n I

To an ethanol solution (50 mL) of 4-aminobenzo-15-crown-5 (0.4991 g; 1.71 mmol) were added *p*-octyloxybenzaldehyde (404 μl; 1.71 mmol) and five drops of acetic acid as catalyst. The mixture was refluxed for 4 h, then anhydrous MgSO₄ was added and filtered. The filtrate was evaporated to dryness and the residue was washed with methanol to afford the imine as a white solid. Yield of **1a**: 68%. Anal. Calc. (%): C, 67.70; H, 7.50; N, 3.16. Found: C, 67.53; H, 7.45; N, 3.20%. Yield of **1b**: 85%. Anal. Calc. (%): C, 68.77; H, 7.91; N, 2.97. Found: C, 69.22; H, 7.88; N, 2.97%. Yield of **1c**: 94%. Anal. Calc. (%): C, 69.71; H, 8.27; N, 2.80. Found: C, 69.42; H, 8.02; N, 2.74%. Yield of **1d**: 79%. Anal. Calc. (%): C, 70.55; H, 8.59; N, 2.65. Found: C, 70.35; H, 8.26; N, 2.60%. Yield of **1e**: 88%. Anal. Calc. (%): C, 71.32; H, 8.89; N, 2.52. Found: C, 70.93; H, 8.49; N, 2.60%. ¹H RMN of **1c** HL₈: 0.89 (t, *J*(HH) = 7.0 Hz, 3H, CH₃), 1.29–1.81 (m, 12H, CH₃–(CH₂)₆–), 3.77 (m, 8H, O–CH₂–CH₂–O), 3.92 (m, 4H, Ph–O–CH₂–CH₂–O), 4.01 (t, *J*(HH) = 6.3 Hz, 2H, O–CH₂–(CH₂)_n), 4.17 (m, 4H, Ph–O–CH₂–CH₂–O),

6.77 (dd, $J(\text{HH}) = 8.3$ and 2.2 Hz, 1H, $\text{CH}_{\text{ar}}-\text{N}=\text{C}$), 6.83 (d, $J(\text{HH}) = 2.2$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{N}=\text{C}$), 6.88 (d, $J(\text{HH}) = 8.3$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{N}=\text{C}$), 6.96 (d, $J(\text{HH}) = 8.7$ Hz, 2H, $\text{CH}_{\text{ar}}-\text{C}=\text{N}$), 7.81 (d, $J(\text{HH}) = 8.7$ Hz, 2H, $\text{CH}_{\text{ar}}-\text{C}=\text{N}$), 8.39 (s, 1H, $\text{CH}=\text{N}$); IR (KBr): 1607 ($\nu(\text{C}=\text{N})$), 1245, 1128, 1060 cm^{-1} ($\nu(\text{C}-\text{O}-\text{C})$).

4.2.2. Preparation of $[\text{Pd}(\mu\text{-OAc})\text{L}_n]_2$ **2**

To a suspension of $[\text{Pd}_3(\text{OAc})_6]$ (0.0934 g; 0.139 mmol) in acetic acid (15 mL), was added the stoichiometric amount of imine HL_8 (0.2078 g; 0.416 mmol) and the mixture was stirred at 50°C for 15 h. After that, the suspension was evaporated to dryness, dichloromethane was added and then filtered through a pad of Kiesselegur. Partial evaporation and addition of hexane afforded the compound as an orange solid. Yield of **2a**: 75%. Anal. Calc. (%): C, 53.34; H, 5.80; N, 2.30. Found: C, 53.47; H, 6.10; N, 2.27%. Yield of **2b**: 51%. Anal. Calc. (%): C, 54.76; H, 6.18; N, 2.20. Found: C, 54.00; H, 5.90; N, 2.36%. Yield of **2c**: 84%. Anal. Calc. (%): C, 56.07; H, 6.53; N, 2.11. Found: C, 55.65; H, 6.32; N, 2.01%. Yield of **2d**: 75%. Anal. Calc. (%): C, 57.26; H, 6.84; N, 2.02. Found: C, 57.21; H, 6.91; N, 2.11%. Yield of **2e**: 79%. Anal. Calc. (%): C, 58.37; H, 7.14; N, 1.94. Found: C, 57.81; H, 6.91; N, 1.89%. ^1H RMN of **2c** $[\text{Pd}(\mu\text{-OAc})\text{L}_8]_2$: 0.89 (t, $J(\text{HH}) = 6.0$ Hz, 3H, CH_3), 1.31–1.74 (m, 12H, $\text{CH}_3-(\text{CH}_2)_6-$), 1.88 (s, 3H, CH_3-COO), 3.75 (m, 8H, $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 3.90 (m, 4H, $\text{Ph}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 4.11 (m, 6H, $\text{O}-\text{CH}_2-(\text{CH}_2)_n$ and $\text{Ph}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 5.88 (dd, $J(\text{HH}) = 8.5$ and 2.2 Hz, 1H, $\text{CH}_{\text{ar}}-\text{N}=\text{C}$), 6.07 (d, $J(\text{HH}) = 2.2$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{N}=\text{C}$), 6.56 (d, $J(\text{HH}) = 8.5$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{N}=\text{C}$), 6.55 (dd, $J(\text{HH}) = 8.3$ and 2.2 Hz, 1H, $\text{CH}_{\text{ar}}-\text{C}=\text{N}$), 6.87 (d, $J(\text{HH}) = 2.2$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{C}=\text{N}$), 7.12 (d, $J(\text{HH}) = 8.3$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{C}=\text{N}$), 7.45 (s, 1H, $\text{CH}=\text{N}$), IR (KBr): 1588 ($\nu(\text{C}=\text{N})$), 1573 ($\nu(\text{C}=\text{O})$), 1265, 1224, 1131, 1044 cm^{-1} ($\nu(\text{C}-\text{O}-\text{C})$).

4.2.3. Preparation of $[\text{Pd}(\mu\text{-Cl})\text{L}_n]_2$ **3**

To a dichloromethane (distilled) solution (20 mL) of $[\text{Pd}(\mu\text{-OAc})\text{L}_8]_2$ (0.217 g; 1.7 mmol) under a N_2 atmosphere, was added dropwise the stoichiometric amount of a 2N solution of HCl (3.4 mmol) in ether. After stirring for 2 h, the solution was concentrated to dryness and the residue recrystallized from cold acetone. Yield of **3a**: 53%. Anal. Calc. (%): C, 51.38; H, 5.52; N, 2.40. Found: C, 50.95; H, 5.12; N, 2.36%. Yield of **3b**: 61%. Anal. Calc. (%): C, 52.95; H, 5.92; N, 2.29. Found: C, 52.61; H, 5.72; N, 2.19%. Yield of **3c**: 40%. Anal. Calc. (%): C, 54.38; H, 6.29; N, 2.19. Found: C, 54.38; H, 6.08; N, 2.18%. Yield of **3d**: 69%. Anal. Calc. (%): C, 55.69; H, 6.63; N, 2.10. Found: C, 55.11; H, 6.23; N, 2.23%. Yield of **3e**: 64%. Anal. Calc. (%): C, 56.90; H, 6.95; N, 2.01. Found: C, 56.30; H, 6.58; N, 2.10%. ^1H RMN of **3c** $[\text{Pd}(\mu\text{-Cl})\text{L}_8]_2$: 0.89 (t, $J(\text{HH}) = 7.0$ Hz, 3H, CH_3), 1.29–1.76 (m, 12H, $\text{CH}_3-(\text{CH}_2)_6-$), 3.78 (m, 8H, $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 3.94 (m, 4H, $\text{Ph}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 4.16 (m, 4H, $\text{Ph}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 4.22 (m, 2H, $\text{O}-\text{CH}_2-(\text{CH}_2)_n$), 6.55–7.23 (6H, CH_{ar}),

7.82 (s, 1H, $\text{CH}=\text{N}$), IR (KBr): 1578 ($\nu(\text{C}=\text{N})$), 1270, 1228, 1138, 1055 ($\nu(\text{C}-\text{O}-\text{C})$), 247 cm^{-1} ($\nu(\text{PdCl})$).

4.2.4. Preparation of $[\text{Pd}(\beta\text{-diket})\text{L}_n]_4$

To a dichloromethane solution (10 mL, freshly distilled to remove any traces of HCl) of β -diketone (0.0457 g; 7.709 mmol) under a N_2 atmosphere, was added the stoichiometric amount of NEt_3 (7.709 mmol) and stirred for 5 min. Then a dichloromethane (distilled) solution (10 mL) of $[\text{Pd}(\mu\text{-OAc})\text{L}_8]_2$ (0.0512 g; 3.855 mmol) was added and the mixture stirred for 2 h. After filtering through a pad of Kiesselegur, the clear solution was concentrated to dryness and the residue was washed with acetone to give a yellow solid. Yield of **4a**: 40%. Anal. Calc. (%): C, 67.38; H, 8.04; N, 1.23. Found: C, 66.85; H, 7.60; N, 1.60%. Yield of **4b**: 73%. Anal. Calc. (%): C, 67.82; H, 8.19; N, 1.20. Found: C, 67.64; H, 7.83; N, 1.02%. Yield of **4c**: 70%. Anal. Calc. (%): C, 68.24; H, 8.34; N, 1.17. Found: C, 68.11; H, 7.98; N, 1.20%. Yield of **4d**: 51%. Anal. Calc. (%): C, 68.64; H, 8.48; N, 1.14. Found: C, 68.20; H, 8.13; N, 1.33%. Yield of **4e**: 51%. Anal. Calc. (%): C, 69.02; H, 8.61; N, 1.12. Found: C, 68.64; H, 8.18; N, 0.88%. ^1H RMN of **4c** $[\text{Pd}(\beta\text{-diket})\text{L}_8]_4$: 0.89 (t, $J(\text{HH}) = 6.0$ Hz, 9H, CH_3), 1.28–1.82 (m, 52H, $\text{CH}_3-(\text{CH}_2)_6-$ and $\text{CH}_3-(\text{CH}_2)_{10-}$), 3.81 (m, 8H, $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 3.99 (m, 4H, $\text{O}-\text{CH}_2-(\text{CH}_2)_{10}$), 4.03 (m, 4H, $\text{Ph}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 4.16 (t, $J(\text{HH}) = 6.8$ Hz, 2H, $\text{O}-\text{CH}_2-(\text{CH}_2)_6$), 4.22 (m, 4H, $\text{Ph}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 6.64 (s, 1H, $\text{OC}-\text{CH}-\text{CO}$), 6.66 (dd, $J(\text{HH}) = 8.5$ and 2.4 Hz, 1H, $\text{CH}_{\text{ar}}-\text{N}=\text{C}$), 7.34 (d, $J(\text{HH}) = 8.5$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{N}=\text{C}$), 7.36 (d, $J(\text{HH}) = 2.4$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{N}=\text{C}$), 6.93 (d, $J(\text{HH}) = 8.6$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{C}=\text{N}$), 7.02 (dd, $J(\text{HH}) = 8.6$ and 2.4 Hz, 1H, $\text{CH}_{\text{ar}}-\text{C}=\text{N}$), 7.14 (d, $J(\text{HH}) = 2.4$ Hz, 1H, $\text{CH}_{\text{ar}}-\text{C}=\text{N}$), 6.85 (d, $J(\text{HH}) = 8.8$ Hz, 2H, $\text{CH}_{\text{ar}}-\text{C}=\text{O}$), 7.71 (d, $J(\text{HH}) = 8.8$ Hz, 2H, $\text{CH}_{\text{ar}}-\text{C}=\text{O}$), 6.93 (d, $J(\text{HH}) = 8.8$ Hz, 2H, $\text{CH}_{\text{ar}}-\text{C}=\text{O}$), 8.00 (d, $J(\text{HH}) = 8.8$ Hz, 2H, $\text{CH}_{\text{ar}}-\text{C}=\text{O}$), 8.04 (s, 1H, $\text{CH}=\text{N}$); IR (KBr): 1603 ($\nu(\text{C}=\text{N})$), 1590, 1580 ($\nu(\text{C}=\text{O})$), 1257, 1224, 1176, 1134, 1056 cm^{-1} ($\nu(\text{C}-\text{O}-\text{C})$).

4.2.5. General procedure for complexation with NaClO_4

To an acetonitrile solution (for derivative **1a**) or suspension (for complexes **2a–4a**) of the crown ether derivative, was added the stoichiometric amount of NaClO_4 . The resulting clear solution was stirred for 6 h and then concentrated to dryness to give a pale yellow (for $[\text{NaCrown1a}]\text{ClO}_4$) or yellow (for $[\text{NaCrown2a}]\text{ClO}_4$ – $[\text{NaCrown4a}]\text{ClO}_4$) solid. Anal. Calc. (%) for $[\text{NaCrown1a}]\text{ClO}_4 \cdot \text{H}_2\text{O}$: C, 51.42; H, 6.04; N, 2.4. Found: C, 51.8; H, 5.41; N, 2.55%. Anal. Calc. (%) for $[\text{NaCrown2a}]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$: C, 42.82; H, 5.06; N, 1.85. Found: C, 42.64; H, 4.81; N, 2.23%. Anal. Calc. (%) for $[\text{NaCrown3a}]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$: C, 46.02; H, 5.73; N, 1.73. Found: C, 45.52; H, 5.1; N, 1.72%. Anal. Calc. (%) for $[\text{NaCrown4a}]\text{ClO}_4 \cdot \text{H}_2\text{O}$: C, 60.0; H, 7.32; N, 1.09. Found: C, 60.01; H, 7.09; N, 1.13%. ^1H RMN of $[\text{NaCrown1a}]\text{ClO}_4$: 0.99 (t, $J(\text{HH}) = 7.0$ Hz, 3H, CH_3), 1.48–1.93 (m, 4H, CH_3-

(CH_2)₆), 3.73–3.82 (2m, 8H, O–CH₂–CH₂–O), 3.96 (m, 4H, Ph–O–CH₂–CH₂–O), 4.03 (t, $J(\text{HH}) = 6.3$ Hz, 2H, O–CH₂–(CH₂)₂), 4.20–4.27 (2m, 4H, Ph–O–CH₂–CH₂–O), 6.86 (m, 3H, CH_{ar}–N=C), 6.97 (d, $J(\text{HH}) = 8.7$ Hz, 2H, CH_{ar}–C=N), 7.83 (d, $J(\text{HH}) = 8.7$ Hz, 2H, CH_{ar}–C=N), 8.41 (s, 1H, CH=N); IR (KBr): 1606 cm⁻¹ ($\nu(\text{C}=\text{N})$), 1249, 1121, 1041 cm⁻¹ ($\nu(\text{C}-\text{O}-\text{C})$), 1090, 625 cm⁻¹ ($\nu(\text{ClO}_4^-)$). ¹H RMN of [NaCrown2a]ClO₄: 0.93 (m, CH₃), 1.41–1.77 (m, CH₃–(CH₂)₂–), 3.66–4.35 (m, O–CH₂–CH₂–O, Ph–O–CH₂–CH₂–O, O–CH₂–(CH₂)_n and Ph–O–CH₂–CH₂–O); isomer A: 1.93 (s, 3H, CH₃–COO), 5.84 (d, $J(\text{HH}) = 2.2$ Hz, 1H, CH_{ar}–N=C), 6.48 (dd, $J(\text{HH}) = 8.5$ and 2.2 Hz, 1H, CH_{ar}–N=C), 7.18 (d, $J(\text{HH}) = 8.5$ Hz, 1H, CH_{ar}–N=C), 6.10 (dd, $J(\text{HH}) = 8.5$ and 2.2 Hz, 1H, CH_{ar}–N=C), 6.48 (d, $J(\text{HH}) = 8.5$ Hz, 1H, CH_{ar}–C=N), 6.75 (d, $J(\text{HH}) = 2.2$ Hz, 1H, CH_{ar}–C=N), 7.52 (s, 1H, CH=N); isomer B: 2.02 (s, 1.5H, CH₃–COO), 2.30 (s, 1.5H, CH₃–COO), 6.15 (d, $J(\text{HH}) = 2.2$ Hz, 1H, CH_{ar}–N=C), 6.29 (dd, $J(\text{HH}) = 8.3$ and 2.2 Hz, 1H, CH_{ar}–N=C), 6.97 (d, $J(\text{HH}) = 8.3$ Hz, 1H, CH_{ar}–N=C), 6.48 (dd, $J(\text{HH}) = 8.3$ and 2.2 Hz, 1H, CH_{ar}–C=N), 6.78 (d, $J(\text{HH}) = 8.3$ Hz, 1H, CH_{ar}–C=N), 6.94 (d, $J(\text{HH}) = 2.2$ Hz, 1H, CH_{ar}–C=N), 7.73 (s, 1H, CH=N); IR (KBr): 1588 ($\nu(\text{C}=\text{N})$), 1573 ($\nu(\text{C}=\text{O})$), 1265, 1224, 1131, 1044 cm⁻¹ ($\nu(\text{C}-\text{O}-\text{C})$), 1090, 625 cm⁻¹ ($\nu(\text{ClO}_4^-)$). ¹H RMN (CD₃CN) of [NaCrown3a]ClO₄: 0.96 (t, $J(\text{HH}) = 7.3$ Hz, 3H, CH₃), 1.43–1.80 (m, 4H, CH₃–(CH₂)₂–), 3.70–3.72 (2m, 8H, O–CH₂–CH₂–O), 3.93 (m, 4H, Ph–O–CH₂–CH₂–O), 4.07 (t, $J(\text{HH}) = 6.5$ Hz, 2H, O–CH₂–(CH₂)₂), 4.30 (m, 4H, Ph–O–CH₂–CH₂–O), 6.65 (d, $J(\text{HH}) = 2.0$ Hz, 1H, CH_{ar}–C=N), 6.74 (dd, $J(\text{HH}) = 2.0$ and 8.6 Hz, 1H, CH_{ar}–C=N), 7.00 (dd, $J(\text{HH}) = 2.5$ and 8.6 Hz, 1H, CH_{ar}–N=C), 7.06 (d, $J(\text{HH}) = 2.5$ Hz, 1H, CH_{ar}–N=C), 7.09 (d, $J(\text{HH}) = 8.6$ Hz, 1H, CH_{ar}–N=C), 7.44 (d, $J(\text{HH}) = 8.2$ Hz, CH_{ar}–C=N), 8.03 (s, 1H, CH=N), IR (KBr): 1578 ($\nu(\text{C}=\text{N})$), 1270, 1228, 1138, 1055 ($\nu(\text{C}-\text{O}-\text{C})$), 1090, 625 cm⁻¹ ($\nu(\text{ClO}_4^-)$), 247 cm⁻¹ ($\nu(\text{PdCl})$). ¹H RMN of [NaCrown4a]ClO₄: 0.89 (m, 6H, (CH₂)_n–CH₃), 1.03 (t, $J(\text{HH}) = 7.0$ Hz, 3H, CH₃), 1.27–1.82 (m, 44H, CH₃–(CH₂)_n), 3.74–3.81 (2m, 8H, O–CH₂–CH₂–O), 4.04 (2m, 4H, Ph–O–CH₂–CH₂–O, and O–CH₂–(CH₂)_n), 4.14 (m, 2H, O–CH₂–(CH₂)₂), 4.27 (m, 4H, Ph–O–CH₂–CH₂–O), 6.64 (s, 1H, OC–CH–CO), 6.75–6.85–7.13–7.18–7.30 (5m, 6H, CH_{ar}–C=N–CH_{ar}), 6.93 (d, $J(\text{HH}) = 8.3$ Hz, 2H, CH_{ar}–C=O), 7.77 (d, $J(\text{HH}) = 8.3$ Hz, 2H, CH_{ar}–C=O), 7.02 (d, $J(\text{HH}) = 8.7$ Hz, 2H, CH_{ar}–C=O), 7.95 (d, $J(\text{HH}) = 8.7$ Hz, 2H, CH_{ar}–C=O), 7.89 (s, 1H, CH=N); IR (KBr): 1603 ($\nu(\text{C}=\text{N})$), 1590, 1580 ($\nu(\text{C}=\text{O})$), 1257, 1224, 1176, 1134, 1056 cm⁻¹ ($\nu(\text{C}-\text{O}-\text{C})$), 1090, 625 cm⁻¹ ($\nu(\text{ClO}_4^-)$).

4.3. Mesogenic behavior after addition of a sodium salt

The experiments were carried out in two ways: (a) A stoichiometric amount of solid NaOOCCH₃ was added to the solids **3e** or **4e** and the mixture was finely grounded; (b) a stoichiometric amount of solid

NaCF₃SO₃ was added to an acetone solution of **4e**, concentrated and vacuum dried. In both cases the behavior of the resulting material under heating was studied by optical polarized microscopy.

4.4. Extraction experiments

To a dichloromethane solution (10 mL) of the extracting Pd compound (5×10^{-4} M) was added an aqueous solution of sodium picrate (10 mL, 5×10^{-5} M) prepared in situ by mixing solutions of picric acid and sodium hydroxide. The mixture was vigorously stirred and samples were taken every 5 min to monitor the diminution of sodium picrate concentration in the aqueous phase by UV–Vis spectrophotometry ($\lambda = 356$ nm), until successive determinations showed no variation. This was taken as indication that equilibrium had been reached.

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