Mesomorphic phenanthroline derivatives: novel architectures based on hydrogen bonding†

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Strong hydrogen bonding has been observed in mesomorphic phenanthroline compounds engineered from diacylaminobenzene platforms: a columnar organization is found in the free ligands (n = 12 or 16) whereas a smectic arrangement is evidenced in a palladium complex (n = 16).

Phenanthroline (phen) and its derivatives are powerful *architectons* for various purposes such as complexation properties,[1,2] biological activity[3] and more recently as lyotropic or thermotropic liquid-crystalline materials.[4,5] While we succeeded in producing metallomesogens by wrapping non-mesomorphic bipyridine-based frameworks around copper(I) cations,[6] we found this strategy inappropriate for phen scaffoldings. It is surmised that the lack of internal flexibility around the phen/imine core provides thermally unstable complexes which are prejudicial to the engineering of thermotropic mesomorphic molecules. From a general point of view, mesomorphic derivatized-phen cores are scarce[5] but very interesting in order to obtain flat systems with extended conjugated orbitals due to the planar conformation. It was hoped that π–π stacking of the rigid cores would favour the emergence of mesophases, a situation found in certain liquid-crystalline materials but more rarely in metallomesogens.[7] Another way to favour mesophases is to functionalize the molecules with amide groups, auspicious for stabilization of the supramolecular network *via* hydrogen bonding.[8,9] It is worthwhile noting that liquid-crystalline ferrocene derivatives represent rare examples of H-bonded metallomesogens.[10]

Putting together these two ideas, we here describe new phen ligands bearing a 1,3-diacylaminobenzene core which offers a suitable route for the inclusion of transition metals. Ligands L^n were prepared from 1^n, itself prepared by a multistep procedure from 3,5-dinitro-*p*-toluic acid,[11] and 2-hydroxy-9-methyl-1,10-phenanthroline[12] by an esterification reaction using EDC·HCl and dimethylaminopyridine (Scheme 1). Final com-

pounds and intermediates were purified by careful chromatography on silica followed by double recrystallization in adequate solvents providing analytically pure samples. On the basis of spectroscopic evidence, the molecular structures of the final ligand and intermediates were unequivocally authenticated.‡

The thermotropic liquid crystalline behaviour of $1'^{16}$ and L^n (n = 8, 12, 16) was investigated by an interplay of differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. The optical textures observed for the $1'^{16}$ and ligands L^{12}, L^{16} upon cooling from the isotropic melt clearly showed the existence of a columnar phase (Col) as indicated by the appearance of a texture exhibiting birefringent domains and homeotropic zones. L^8 revealed to be non-mesomorphic over the tested temperature range.

The DSC thermograms registered upon heating and subsequent cooling, showed the presence of peaks characteristic of first order phase transitions. The melting into the mesophase or the isotropic liquid involves significant enthalpy changes, whereas the reverse transitions for the ligands induced by cooling takes place with a strong hysteresis of about 15 to 35 °C while the gap is only 5 °C for the precursor $1'^{16}$. The high melting enthalpies found for L^{12} and L^{16} are due to the destruction of strong interaction forces at the clearing transition. The transition temperatures as well as the enthalpies for all compounds are gathered in Scheme 2.

The columnar hexagonal mesophase was characterized by X-ray patterns§ containing two sharp reflections in a ratio $1:1/\sqrt{3}$ in the small angle region, and two diffuse reflections in the wide angle region at *ca* 4.6 and 3.5 Å corresponding respectively to lateral distances between molten alkyl chains and to the classical π–π stacking distance between aromatic rings. It is assumed that two molecules of L^n form a disk which then pile-up one on top of the other to form the column. Based on preliminary X-ray data of a single crystal for a model compound a drawing representing the hydrogen bonded structures is given in Scheme 3.[13]

Evidence for intermolecular amide hydrogen bonding was deduced from FT-IR measurements especially by taking into account the N–H and C=O stretching vibrations and N–H
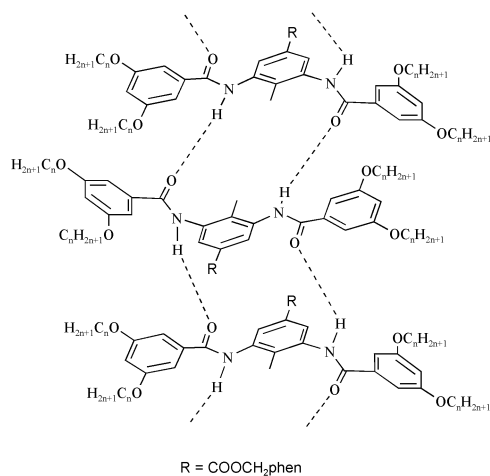
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† Electronic supplementary information (ESI) available: FT-IR spectra of compounds L^{12} and $1'^{16}$ and X-ray diffraction pattern of the palladium complex of L^{16}. See http://www.rsc.org/suppdata/cc/b1/b110239g/
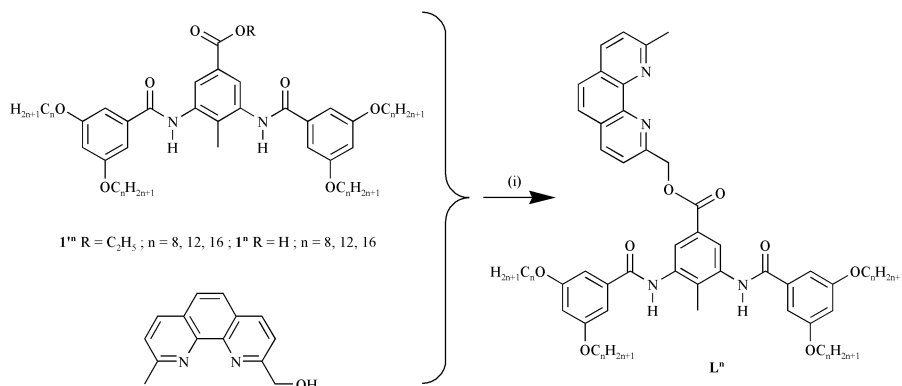
Scheme 1 (i) CH$_2$Cl$_2$, DMAP (1 equiv.), EDC·HCl (2 equiv.), 15 h, 73% for L^8, 76% for L^{12} and 75% for L^{16}.
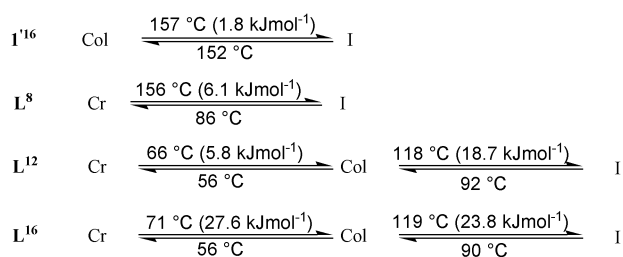
R = COOCH₂phen

Scheme 3

bending vibration. Variable-temperature spectra have been performed with KBr pellets in the various physical states and in chloroform solutions at rt. Spectra of **L12** and **L16** are similar and characterized during the heating cycle by a broadening and a weakening of N–H stretching vibrations with shifts from 3229 cm^{-1} in the crystalline phase to 3290 cm^{-1} in the isotropic phase. In contrast the chloroform solutions (9.3×10^{-3} M^{-1}) afford single bands at 3426 ($\nu_{NH,st}$), 1700 (ν_{COO}), 1677 ($\nu_{C=C}$), and 1525 ($\nu_{NH,ben}$) cm^{-1}. Strong NH–hydrogen bonding is clearly evidenced by comparing the NH stretching vibration in the mesomorphic state *versus* the solution ($\Delta\nu_{NH,st}$ = 200 cm^{-1}). The evolution of C=O stretching and N–H bending vibrations during heating of **L12** from 40 to 180 °C is provided in Fig. S1.† In the crystalline phase the C=O stretching vibration is characterized by a single band at 1645 cm^{-1} and after melting in the mesomorphic phase a shoulder clearly appears at 1655 cm^{-1} with a simultaneous decrease of the original band. In the isotropic phase (over 120 °C) we still observe a splitting of the band with a concomitant shift to 1657 and 1673 cm^{-1}. These values are in agreement with previous studies on mesogenic hydrogen bonded amide aggregates.[14] As expected, no global weakening or shift of the C=C and COO bands are observed during the heating process. It is worthwhile to note that similar studies performed with the **1′16** precursor revealed the absence of any significant perturbations of the characteristic stretching and bending vibrations (see Fig. S2†).

When **L16** was allowed to react with [PdCl₂(CH₃CN)₂] a deep-yellow complex was isolated which after recrystallization in CH₂Cl₂/CH₃CN afforded the analytically pure mononuclear complex [Pd(**L16**)Cl₂] in 76% isolated yield.‡ Preliminary microscopic and X-ray diffraction measurements suggests that this complex is mesomorphic near rt and exhibits a Smectic A mesophase. From X-ray data obtained at 70 °C, a layer thickness of 34.0 ± 0.2 Å was found in good agreement with the length of the complex in its most extended conformation (Fig. S3†).¶This monolayer type of organization is in strong contrast with the columnar arrangement found in the free ligand and might suggest that within the pallado-mesogen the hydrogen bonding is not the driving force. Finally, we also note some decomposition of this Pd-complex during melting in the isotropic phase. In order to reduce the transition temperature we are working on the synthesis of doubly substituted phen ligands. Further experiments will afford a deeper insight into this interesting set of mesomorphic compounds.

Notes and references

1 N. M. Karayannis, A. N. Speca, D. E. Chasan and L. L. Pytlewski, *Coord. Chem. Rev.*, 1976, **20**, 37.
2 R. P. Thummel and C. M. Chamchoumis, *Advances in Nitrogen Heterocycles*, 2000, **4**, 107.
3 A. Mohindru, J. M. Fisher and M. Rabinovitz, *Biochem. Pharm.*, 1983, **32**, 3627.
4 S. Munoz and G. W. Gokel, *J. Am. Chem. Soc.*, 1993, **115**, 4899.
5 S. J. P. Bousquet and D. W. Bruce, *J. Mater. Chem.*, 2001, 1769.
6 A. El-ghayoury, L. Douce, A. Skoulios and R. Ziessel, *Angew. Chem., Int. Ed.*, 1998, **37**, 2205.
7 J. L. Serrano, *Metallomesogens*, VCH, Weinheim, 1996C. Tschierske, *Prog. Polym. Sci.*, 1996, **21**, 775; J. L. Serrano, *Prog. Polym. Sci.*, 1997, **21**, 873; U. Stebani, G. Lattermann, M. Wittenberg and J. H. Wendorff, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1858; C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485; D. Guillon, *Struct. Bonding (Berlin)*, 1999, **95**, 41; B. Donnio and D. W. Bruce, *Struct. Bonding (Berlin)*, 1999, **95**, 193.
8 J. Malthête, A.-M. Levelut and L. Liébert, *Adv. Mater.*, 1992, **4**, 37.
9 T. Kato, Y. Kubota, T. Uryu and S. Ujiie, *Angew. Chem., Int. Ed.*, 1997, **36**, 1617.
10 R. Deschenaux, F. Monnet, E. Serrano, F. Turpin and A.-M. Levelut, *Helv. Chim. Acta*, 1998, **81**, 2072.
11 D. Pucci, M. Weber and J. Malthête, *Liq. Cryst.*, 1996, **21**, 153.
12 G. R. Newkome, K. J. Theriot, V. K. Gupta, F. R. Fronczek and G. R. Baker, *J. Org. Chem.*, 1989, **54**, 1766.
13 M. Cesario and T. Prangé work in progress.
14 T. Kato, T. Kutsuna, K. Hanabusa and M. Ukon, *Adv. Mater.*, 1998, **10**, 606; R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic compounds*, Third edition, Wiley, New York, USA, 1976.