Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2011, 21, 5916

Luminescent columnar liquid crystals generated by self-assembly of 1,3,4oxadiazole derivatives[†]

André A. Vieira, ** Hugo Gallardo, * Joaquín Barberá, * Pilar Romero, * José Luis Serrano* and Teresa Sierra **

Received 29th December 2010, Accepted 22nd February 2011 DOI: 10.1039/c0jm04570e

Five new V-shaped acids derived from 1,3,4-oxadiazole are described. These compounds were used to prepare supramolecular complexes *via* hydrogen bonding interactions with 2,4-diamino-6-dodecylamino-1,3,5-triazine in a 3 : 1 ratio. The formation of the complexes was evidenced by infrared and NMR techniques. All the complexes were studied by polarizing optical microscopy, differential scanning calorimetry and small-angle X-ray diffraction. Rectangular and hexagonal columnar mesophases were observed for the complexes at room temperature, without signs of crystallization. Circular dichroism studies demonstrated that, in the liquid crystalline state, these materials show supramolecular optical activity. It is proposed that this phenomenon arises due to a helical columnar organization. Furthermore, the complexes display strong blue light emission in solution, with good photoluminescence quantum yields, and in the mesophase. These materials could therefore be promising candidates for optoelectronic applications.

Introduction

Since the discovery of mesomorphism promoted by hydrogen bonding in organic compounds by Bennett and Jones¹ in 1939, many liquid crystals (LCs) based on self-organized H-bonded systems have been studied.² The great interest in this research area is stimulated by several examples in nature that are capable of forming highly organized structures.3 Among self-organized LC systems based on H-bonding interactions are the columnar organizations.⁴ Columnar liquid crystals exhibit a molecular organization that allows the transport of energy or charge.⁵ These materials have applications such as semiconductors, photoconductors, organic light emitting diodes (OLED) and photovoltaic cells.⁶ Moreover, columnar mesophases are an interesting starting point for the achievement of helical architectures that allow the expression of supramolecular chirality.7 The reproduction8 and control9 of these helical architectures have been the subject of recent works because this can endow a material with unique properties.¹⁰ Within this context, helical organization has been studied to evaluate the impact of light emission from columnar liquid crystals, especially for metallomesogens.11 The possibility of obtaining polarized light emission through supramolecular structures appears to be a major challenge in this field.12

5916 | J. Mater. Chem., 2011, 21, 5916–5922

The 1,3,4-oxadiazole heterocycle is well known in the literature for exhibiting high photoluminescence and electron-accepting properties as well as for its high thermal and hydrolytic stability and resistance to oxidative degradation.¹³ The introduction of a 1,3,4-oxadiazole ring into an aromatic core may also lead to fluorescence properties in the molecule, generate a significant lateral dipole moment and also give a bent rigid core.

We describe here the synthesis and characterization of a novel series of asymmetric V-shaped acids derived from 1,3,4-oxadiazole. A mixture of the 2,4-diamino-6-dodecylamino-1,3,5triazine and the oxadiazole acids in a 1 : 3 ratio gives rise to supramolecular complexes through H-bonds. These complexes have an H-bonded core designed to generate mesomorphism, fluorescence and helical superstructures.

Synthesis

The melamine derivative 2,4-diamino-6-dodecylamino-1,3,5triazine (**M**) was prepared by the reaction of dodecylamine with 2,4-diamino-6-chloro-1,3,5-triazine using sodium hydrogen carbonate as a base.¹⁴ The V-shaped acids **X12E12**, **X**(*S*)10*E12, **X**(*R*)10*E12, **X**(*S*)10*E(*S*)10* and **X12E**(*S*)10* were prepared according to the synthetic pathway outlined in Schemes 1 and 2.

The synthetic route for the acids begins with the 4-alkoxybenzonitriles 1, which were used to obtain the respective tetrazole heterocycles 2 by Huisgen 1,3-dipolar cycloaddition using sodium azide and ammonium chloride in DMF.¹⁵ The tetrazole compounds 2 were reacted with freshly prepared methyl 4-(chlorocarbonyl)benzoate in pyridine to afford the 2,5-disubstituted-1,3,4-oxadiazoles¹⁶ 4 in good yields (68–93%). We also tested a different methodology to obtain the 1,3,4-oxadiazole

^aDepartamento de Química, INCT-Catálise, Universidade Federal de Santa Catarina—UFSC, 88040-900 Florianópolis-SC, Brazil. E-mail: hugo@qmc.ufsc.br; Tel: +55 48 37219544

^bInstituto de Ciencia de Materiales de Aragón, Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza—CSIC, 50009 Zaragoza, Spain. *E-mail: tsierra@unizar.es; Fax: +34 976 762286; Tel: +34 976 762278* † Electronic supplementary information (ESI) available. See DOI: 10.1039/c0jm04570e



Scheme 1 Synthetic route for the intermediate acids 5.



Scheme 2 Synthesis of the final acids 8 (XE).

intermediate, which used benzyl 4-(2*H*-tetrazol-5-yl)benzoate and 4-alkoxybenzoyl chloride, but the yields were very poor (1–3%). The carbonyl group in the 4-position with respect to the tetrazole ring probably inhibits the progress of this reaction. The acid intermediates **5** were obtained in quantitative yield by simple hydrolysis of the ester function of compounds **4** with potassium hydroxide in ethanol/water. Compounds **7** were obtained by esterification of phenol¹⁷ **6** with the respective acid **5** using N,N'-dicyclohexylcarbodiimide (DCC) and (N,N-dimethylamino)pyridinium 4-toluenesulfonate (DPTS) in dichloromethane (Scheme 2).

The desired final acids **8** (**XE**) were obtained in good yields (75–95%) by deprotection of the triisopropylsilyl intermediate with tetra-*n*-butylammonium fluoride in dichloromethane (see ESI†). The structures and purities of the **XE** compounds were verified by ¹H and ¹³C NMR, elemental analysis, and MALDI-TOF (see ESI†).

Results and discussion

Having synthesized and characterized the final acids (**XE**) and the melamine (**M**), the complexes **M-XE** were prepared (Scheme 3). The complexes were prepared by dissolving both compounds in dichloromethane, mixing them in the ratio 1 mole of melamine to 3 moles of acid **XE** and allowing the solvent to evaporate by stirring the solution at room temperature.



Scheme 3 General preparation of the complexes M-XE from 3 eq. of the acids (XE) and 1 eq. of the triazine (M).

The formation of the complexes **M-XE** was studied by IR and NMR spectroscopy (see ESI[†]). The IR spectra of the acids **XE** differed from those of the complexes **M-XE**, especially in the regions corresponding to carbonyl, –COOH and N–H groups, which are responsible for the interactions between molecules. An effective shift of the carbonyl group stretching band from 1744 to 1735 cm⁻¹ was observed after formation of the complex **M-X12E12**.

The ¹H NMR spectra clearly show the formation of complexes, assuming that there is a rapid equilibrium between the complex and its components.^{8a} Large displacements were also observed for the five NH groups of the melamine complexes as these are responsible for the hydrogen bonds. The downfield shifts of the five N–H hydrogens of melamine (**M**) are shown in Fig. 1.

The proton of the amino group with the dodecyl chain is shifted from 5.20 to 6.84 ppm on complexation. The four protons of the primary amino groups of the melamine are shifted downfield, from 5.32 to 6.48 ppm, and a broad peak is observed at 5–7 ppm after interaction with the acid M-X(S)10*E(S)10* in CDCl₃. Likewise, the protons of the *N*-methylene group of the melamine alkyl chain and the hydrogens of the central aromatic



Fig. 1 ¹H NMR spectrum of the acid $X(S)10*E(S)10^*$, complex M- $X(S)10*E(S)10^*$ and melamine (M) in CDCl₃ solution at 25 °C. Signals due to protons belonging to the amino groups of M are shifted upon formation of the complex.

ring of the acid **X**(*S*)**10*****E**(*S*)**10*** are shifted with respect to those in the non-complexed melamine and acid, respectively.

Titration NMR experiments in CD₂Cl₂ showed that all NH proton signals, as well as the methylene hydrogen atoms of the alkyl chain of the melamine **M** and the hydrogens of the central aromatic ring of the acid **X12E(S)10***, were displaced upon increasing the proportion of acid while keeping the melamine concentration constant (see Fig. S8 and S9 in the ESI†). These experiments allow the estimation of the binding constant (488 \pm 27 M⁻¹ in CD₂Cl₂ at 25 °C) for the complexation of the melamine derivative and the acids. This value was calculated by nonlinear curve fitting of the chemical shifts. These titration experiments also demonstrated that these complexes have a 1 : 1 stoichiometry in solution, as previously described in similar systems.⁹⁶ The stoichiometry, however, becomes 3 : 1 in the bulk material when the molar amount of the acid is three times that of the melamine, as also demonstrated previously.^{8a,9a}

Previous studies showed that DOSY experiments can also help to determine whether hydrogen bonding interactions are established between the melamine derivative M and carboxylic acids. This technique allows the diffusion coefficients to be correlated with the molecular composition by observing the chemical shifts. Self-diffusion of chemical species in a solvent depends on its molecular size and hydrodynamic volume. According to this principle, the association can promote changes in the molecular diffusion coefficient itself and this can be used to detect the presence of a complex formed by hydrogen bonds in solution.¹⁸ DOSY experiments were performed in CD₂Cl₂ for the pure acid X12E(S)10* and pure melamine (M) as well as the complex M-X12E(S)10* (see ESI[†]). The signals corresponding to protons within the complex M-X12E(S)10* have the same diffusion coefficient (5.9 \times 10⁻¹⁰ \pm 0.03 m² s⁻¹). This value corresponds to the apparent diffusion coefficient of the complex because there is rapid exchange between the complex and the components on the NMR time scale. More importantly, this coefficient measured for the complex is much smaller than that of the melamine (12.6 \times $10^{-10} \pm 0.03 \text{ m}^2 \text{ s}^{-1}$) and this can be accounted for by the fact that the melamine and the acid X12E(S)10* diffuse within the same supramolecular species in solution. In the case of weak interaction between melamine M and acid, the diffusion coefficients of both components would have remained unchanged in the DOSY spectrum of the mixture.

Thermal properties

The acids **XE** do not exhibit mesomorphism and have melting points in the range 141–165 °C (see ESI†). Investigation of the thermal stability of these new V-shaped acids by thermogravimetric analysis (TGA) indicated that they have good stability with decomposition under nitrogen at temperatures above 272 °C.

The thermal behavior of the final complexes **M-XE** was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Transition temperatures and enthalpy values are given in Table 1.

All of the complexes showed liquid crystalline behavior over broad temperature ranges, which is indicative of the strength of hydrogen bonding between acid and melamine, in agreement with previous results.^{8,9} The textures observed by polarizing optical microscopy, on cooling from the isotropic liquid, are consistent with the presence of columnar mesomorphism. A microphotograph of the natural texture at 25 °C observed for the complex **M-X12E12** is shown in Fig. 2 and this phase was further characterized as Col_r. This type of texture was common to all complexes except for **M-X(S)10*E(S)10***, which showed no birefringence between crossed polarizers but a change in fluidity on cooling to the temperature indicated by DSC (see Table 1). The measured enthalpies associated with the corresponding transitions to the isotropic state had high values, a finding consistent with those reported for previous complexes of this type, which were described as Col_r .^{8a} The only exception was complex **M-X(S)10*E(S)10***, which gave a smaller enthalpy value that is more consistent with the transition from Col_h to I, as described for previously reported chiral complexes.^{9b}

Moreover, all of the complexes show glass transitions in their DSC thermograms (see ESI[†]) and these correspond to the transition between a glassy state and the mesophase in the heating process. Accordingly, these complexes retain the organization of the mesophase in a glassy state, and this is stable at room temperature without crystallization. This fact provides added value to these materials since they have columnar order frozen at room temperature and this would help processing, such as the formation of thin films for the evaluation of properties (optical activity and luminescence). The complex M-X12E(S)10* is the only one that shows some tendency to crystallize. Indeed, during the heating process, the mesophase undergoes a cold transition. This was interpreted as a partial crystallization on heating at the same time as the transition from the mesophase to the isotropic state. This is accounted for by the broad peak observed in the DSC heating scan (see ESI[†]), corresponding to the transition to the isotropic liquid, that has a higher enthalpy than the corresponding peak in the cooling scan.

With respect to clearing temperatures and mesophase ranges, it is important to note the broad mesophase ranges shown by these complexes. In addition, all of them display moderate clearing temperatures, which enables easy processing for the evaluation of properties and avoids the high temperatures at which the melamine can decompose. Depending on the peripheral tails, reasonable dependence between the clearing temperature and the presence of branches in the tail (*i.e.* citronellyl derivatives) is observed. Accordingly, the complexes bearing the chiral tail, M-X(S)10*E12, M-X(R)10*E12, M-X12E(S)10* and M-X(S)10*E(S)10*, have lower clearing temperatures than the achiral complex, M-X12E12, with the greatest difference observed for the complex with all six chiral tails.

Structural characterization of the mesophase

For all complexes, X-ray experiments were carried out at 25 °C with the samples slowly cooled from the isotropic liquid so that the mesophase could develop completely. The reflections obtained for the complexes **M-XE** are consistent with rectangular (Col_r) and hexagonal columnar (Col_h) mesophases.

The achiral complex M-X12E12 and the chiral complexes M-X(S)10*E12, M-X(R)10*E12, and M-X12E(S)10* displayed a rectangular columnar mesomorphic order (Col_r). The X-ray patterns of complex M-XE, whose mesophase was proposed to be rectangular columnar (Col_r) by POM, are shown in the ESI[†].

Table 1 Th	nermal properties	and lattice parameters	of the complexes M-XE
------------	-------------------	------------------------	-----------------------

Complexes	Parameters lattice/Å	Phase	Temp./°C	$\Delta H/kJ mol^{-1}$	Phase ^c	Temp. ^b /°C	Phase
M-X12E12	a = 81.6 Å b = 77.0 Å	Ι	111.6	16.7	Col_{r}	70.0	g
M-X(S)10*E12	b = 77.6 Å a = 77.6 Å b = 79.2 Å	Ι	100.3	14.2	Col_r	60.8	g
M-X(<i>R</i>)10*E12	b = 79.2 Å a = 77.0 Å b = 77.8 Å	Ι	100.9	13.2	Col_{r}	63.1	g
M-X(S)10*E(S)10*	b = 77.6 A a = 48.1 Å b = 3.4 Å	Ι	78.0	6.2	Col_h	64.4	g
M-X12E(S)10*	$\begin{array}{c} n = 3.4 \text{ A} \\ a = 77.0 \text{ Å} \\ b = 77.8 \text{ Å} \end{array}$	Ι	97.1	11.6	Col_{r}	73.4	g

^{*a*} All X-ray diffraction experiments were carried out at room temperature. ^{*b*} Transition temperatures were determined by DSC on cooling at 10 °C min⁻¹. ^{*c*} Crystallization was not observed until -20 °C. I = isotropic liquid, Col_h = hexagonal columnar mesophase, and Col_r = rectangular columnar mesophase. g = glassy state that maintains the mesophase organization.



Fig. 2 A polarized optical microphotograph of M-X12E12, texture at 25 °C.

The lattice parameters a and b of the rectangular arrangement were calculated from the diffraction maxima observed in the SAXS pattern.

In general, the parameters of the rectangular mesophase depend on the size of the tails in the V-shaped acid but, as the alkyl chains used are similar for all the complexes M-XE, large differences were not observed between these parameters. Thus, M-X12E12 showed the biggest *a* and *b* parameters (a = 81.6 Å; b = 77.0 Å), while the complexes M-X(S)10*E12, M-X(R)10*E12, and M-X12E(S)10* presented parameters around 77 Å for *a* and *b*.

In contrast, at 25 °C the complex M-X(S)10*E(S)10*, with six chiral chains, gave X-ray patterns that are unambiguously characteristic of hexagonal columnar mesomorphic order (Col_b). This is revealed by the presence of a set of four low-angle sharp maxima with a reciprocal spacing ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$. These four maxima can be assigned to the (100), (110), (200) and (210) reflections of a two-dimensional hexagonal lattice. This arrangement is probably the result of the presence of six branched chains in the final complex, which reduces the interaction between the aromatic cores and leads to the formation of a hexagonal phase.⁸ A lattice parameter a = 48.1 Å was calculated from the diffraction pattern. Furthermore, two diffuse maxima in the wide-angle X-ray scattering (WAXS) region were observed. The inner maximum corresponds to the aliphatic chains and this is usually observed in liquid-crystalline materials. The outer maximum is related to the average stacking parameter (h), which was deduced to be 3.4 Å. With the values of the stacking parameter (h) it was possible to determine the number of complexes per unit cell (Z). Considering a density close to 1 g cm $^{-3}$, the average value for these tetrameric complexes, the *Z* value for the complex **M-X(***S***)10*E(***S***)10*, is 1. This value is reasonable compared to those generally observed for hexagonal mesomorphism.¹⁹ The wide- and small-angle X-ray scattering (SAXS) patterns of the Col_h mesophase for this complex are shown in Fig. 3. A value Z = 4 is deduced for the Col_r mesophase exhibited by the remaining complexes. This is reasonable considering the large values obtained for the rectangular lattice constants compared to the hexagonal lattice constant and it is also consistent with our previous results found for similar systems.^{8a}**

Circular dichroism

The possibility of forming chiral helical architectures in columnar liquid crystals has already been mentioned.⁷ Taking into account the propeller-like conformation proposed for this type of complex,^{8a} we carried out circular dichroism (CD) measurements in the mesophase for the chiral complexes M-X(S)10*E12, M-X(R)10*E12, M-X(S)10*E(S)10* and M-X12E(S)10* (Fig. 4). The objective was to determine whether the chirality of the chiral tails is transmitted to the supramolecular organization of the mesophase and whether this can be related with a helical disposition of the complexes along the column.



Fig. 3 X-Ray diffraction pattern of complex M-X(S)10*E(S)10*. (a) WAXS diagram and (b) SAXS diagram.



Fig. 4 CD spectra recorded on thin films (25 °C) of complexes (a) M-X(S)10*E12 (solid line), M-X(R)10*E12 (dashed line) and respective (b) absorbance spectra, (c) M-X(S)10*E(S)10* and (d) M-X12E(S)10*. For the absorbance spectra of (c) and (d) see ESI†.

The CD measurements were performed on films prepared on untreated quartz slides, heated until the isotropic phase and slowly cooled to room temperature. All of the spectra are averages of several CD spectra recorded at different film positions relative to the light beam. Indeed, the origin of these CD peaks in the mesophase of all **M-XE** chiral complexes was authenticated by recording the spectra at six different orientations obtained by rotating (in-plane) the sample cells by 60°. The spectra obtained were almost identical for all sample orientations (see ESI†). This rules out the possible linear dichroism effects due to macroscopic orientation.²⁰ The complex **M-X12E12** was CD silent because of the absence of chirality in its chemical structure.

All the CD spectra show signals that are accounted for by a helical disposition of at least two chromophores²¹ in the mesophase, and this is consistent with the proposed helical stacking. Analysis of the CD spectra measured for all the chiral complexes showed that they differ in shape, and this can be related to the presence of two types of chromophores, *i.e.* 2,5-diphenyl-1,3,4oxadiazole and phenyl benzoate (λ_{max} 323 and 274 nm, respectively), randomly stacked along the column and with the different positions of the chiral tails. The optical activity of all complexes was maintained with time.

The relationship between the appearance of CD bands and the formation of chiral superstructures, the sign of which is addressed by the configuration of the stereogenic centers in the tails, is clearly confirmed by the CD spectra of the pair of enantiomers M-X(R)10*E12 and M-X(S)10*E12. Both spectra show opposite signs and this arises from an inversion of the configuration of the chiral center from the M-X(S)10*E12 complex to M-X(R)10*E12 (Fig. 4a). In addition, both spectra present a profile that can be interpreted as two overlapped exciton coupling signals corresponding to the absorption bands of both types of chromophores (as mentioned above).

Photophysical properties

The photophysical properties of the complexes M-XE were investigated in dilute dichloromethane solutions and in thin

films, at room temperature. The UV-vis absorption and fluorescence spectroscopy data for solutions and thin films are summarized in Table 2.

As shown in Fig. 5, all materials showed similar absorption patterns with intense absorption bands with maxima at 264 nm and 318 nm.

The absorption band at 318 nm is assigned to the π - π^* transition and this is characteristic of the 1.3.4-oxadiazole heterocycle due to the high molar absorption coefficients measured ($\varepsilon \approx 10\,000 \text{ mol}^{-1} \text{ cm}^{-1}$). All of these compounds displayed strong blue emission in solution (λ_{FL} 370–540 nm), with intense emission maxima at 423 nm and 429 nm. It is important to note that the absorption and emission spectra in solution are not significantly different to those of the carboxylic acid derivatives alone or the supramolecular complexes M-XE. This observation indicates that the intermolecular interaction between the carboxylic acid and the melamine molecules does not affect the electronic structure of the chromophores. The complexes showed good photoluminescence quantum yields ($\phi_{\rm FL} = 0.65-0.70$) in dichloromethane solution in comparison to the standard quinine sulfate. There were small changes in the absorbance and fluorescence spectra of the films of complexes M-XE compared with the solution spectra.

Optical absorption and emission were also measured in thin films of all these complexes. Good quality films were obtained by casting the corresponding dichloromethane solution onto a quartz plate (Fig. 6). There were no significant changes in the fluorescence and absorption spectra of films of the complexes M-XE compared with the solution. Spectra were recorded on as-prepared cast films and films heated and slowly cooled down to room temperature. The absorption and fluorescence spectra of the films are shown in Fig. 6 (spectra normalized for ease of comparison). The two types of absorption spectra were similar. In contrast, a red-shift of the emission maximum was observed on heating-cooling the sample (Table 2). The origin of the band shift observed in the excitation and emission spectra of the films is known to originate from the cooperative effects of energy transfer existing in the solid state.²² We consider here that there is greater organization in the mesophase (after slow heatingcooling) than in the as-prepared film.

The results are in agreement with preliminary X-ray observations, which showed that the samples did not show significant diffraction maxima unless they were heated in the capillary to the clearing point and then allowed to cool down to room temperature. These observations could be related with the degree of order achieved in the glassy state depending on the cooling rate. The slowly cooled sample has a higher chance of developing a more organized mesophase, which on further cooling freezes below the $T_{\rm g}$.

In any case, the results demonstrate that this class of complex **M-XE** is capable of maintaining the intrinsic fluorescence from the 1,3,4-oxadiazole in solution to the glassy solid. The optical band gaps (E_g) of these compounds were determined by their corresponding absorption in thin films, using a method reported in the literature.²³ The optical band gap for these compounds (E_g) is around 3.15 eV.

Table 2	Optical	properties	of the	complexes	M-XE
---------	---------	------------	--------	-----------	------

Compound	Abs. λ_{max}/nm		Fl. λ_{max}/nm			
	Sol. ^a	Film^b	Sol. ^a	Film^b	$\phi_{\mathrm{FL}}{}^c$	E_g^{d}/eV
M-X12E12	318	314	423	421	0.67	3.15
M-X(S)10*E12	318	314	423	421	0.67	3.15
M-X(R)10*E12	318	314	429	421	0.65	3.15
M-X(S)10*E(S)10*	318	314	429	421	0.70	3.15
M-X12E(S)10*	318	314	423	421	0.67	3.15

^{*a*} CH₂Cl₂ solution (10⁻⁵ mol L⁻¹). ^{*b*} Measurements in mesophase. ^{*c*} Fluorescence quantum yield relative to quinine sulfate ($\phi_{FL} = 0.546$) in CH₂Cl₂. ^{*d*} Optical band gap determined from absorption spectra of the films.



Fig. 5 Absorbance (dashed line) and emission (solid line) normalized spectra of the complexes M-XE in solution in CH_2Cl_2 .



Fig. 6 Normalized absorbance (solid line) and emission (dashed line) spectra of the complex **M-X12E12** in the as-prepared film (black) and in the film heated and slowly cooled down to rt (red).

Conclusions

In summary, fluorescent V-shaped acid derivatives of heterocyclic 1,3,4-oxadiazoles were synthesized with different alkyl chains. These acids **XE** were used to form supramolecular complexes through hydrogen bonding with three acid molecules around the 2,4-diamino-6-dodecylamino-1,3,5-triazine (M). The formation of the complexes was characterized by IR, NMR and DOSY. None of the V-shaped acids presented mesomorphism; on the other hand, all of the complexes M-XE exhibited liquid crystalline profiles. The thermal properties were studied by POM, DSC and the mesophases were characterized by wide- and small-angle X-ray scattering. These materials showed a tendency to rectangular columnar mesomorphism, but a hexagonal columnar phase was also obtained in one case. All of the mesophases showed freezing below the glass transition and crystallization did not occur. The complexes M-X(S)10*E12, M-X(R)10*E12, M-X(S)10*E(S)10* and M-X12E(S)10*prepared from chiral acids derived from citronellyl-transfer the chirality to the supramolecular structures, as evidenced by the appearance of CD signals, which is consistent with the formation of helical architectures for these materials. Furthermore, all of the complexes display strong photoluminescence in solution, solid phase and mesophase with good quantum yields. Thus, the complexes were characterized as highly organized, strongly luminescent systems with potential interest for electrooptical applications.

Acknowledgements

We thank the following institutions for financial support: CNPq, FAPESC, and INCT-Catalise, MICINN projects MAT2009-14636-C03-01 and CTQ2009-09030, FEDER funding and Gobierno de Aragón.

Notes and references

- 1 G. M. Bennett and B. Jones, J. Chem. Soc., 1939, 420-425.
- 2 (a) T. Kato, T. Yasuda, Y. Kamikawa and M. Yoshio, Chem. Commun., 2009, 729–739; (b) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel and M. Tosoni, Angew. Chem., Int. Ed., 2007, 46, 4832–4887.
- 3 (a) G. N. Ramachandran and G. Karkha, Nature, 1954, 174, 269–270;
 (b) J. D. Watson and F. Crick, Nature, 1953, 171, 737–738; (c)
 A. Klug, Angew. Chem., Int. Ed., 1983, 22, 565–582.
- 4 (a) U. Beginn, Prog. Polym. Sci., 2003, 28, 1049–1105; (b) S. Jin,
 Y. Ma, S. C. Zimmerman and S. D. Zheng, Chem. Mater., 2004,
 16, 2975–2977; (c) A. R. A. Palmans, J. A. J. M. Vekemans,
 R. A. Hikmet, H. Fischer and E. W. Meijer, Adv. Mater., 1998, 10,
 873–876; (d) I. Paraschiv, K. De Lange, M. Giesbers, B. Van
 Lagen, F. C. Grozema, R. D. Abellon, L. D. A. Siebbeles,
 E. J. R. Sudholter, H. Zuilhof and A. T. M. Marcelis, J. Mater.
 Chem., 2008, 18, 5475–5481.

- 5 (a) M. O'Neill and S. M. Kelly, Adv. Mater., 2003, 15, 1135-1146; (b) J. W. Goodby, V. Gortz, S. J. Cowling, G. Mackenzie, P. Martin, D. Plusquellec, T. Benvegnu, P. Boullanger, D. Lafont, Y. Queneau, S. Chambert and J. Fitremann, Chem. Soc. Rev., 2007, 36, 1971-2032; (c) S. Kumar, Chem. Soc. Rev., 2006, 35, 83-109; (d) R. Cristiano, H. Gallardo, A. J. Bortoluzzi, I. H. Bechtold, C. E. M. Campos and R. L. Longo, Chem. Commun., 2008, 5134-5136.
- 6 (a) S. Sergeyev, W. Pisula and Y. H. Geerts, Chem. Soc. Rev., 2007, 36, 1902–1929; (b) Y. Shirota and H. Kageyama, Chem. Rev., 2007, 107, 953-1010; (c) M. Sawamura, K. Kawai, Y. Matusuo, K. Kanie and T. Kato, Nature, 2002, 419, 702-705; (d) I. Seguy, P. Jolinat, P. Destruel and R. Mamy, J. Appl. Phys., 2001, 89, 5442-5448; (e) A. M. Van de Craats, N. Stutzmann, M. M. Nielsen and M. Watson, Adv. Mater., 2003, 15, 495-499; (f) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel and M. Tosoni, Angew. Chem., Int. Ed., 2007, 46, 4832-4887.
- 7 F. Vera, J. L. Serrano and T. Sierra, Chem. Soc. Rev., 2009, 38, 781-796.
- 8 (a) J. Barberá, L. Puig, P. Romero, J. L. Serrano and T. Sierra, J. Am. Chem. Soc., 2006, 128, 4487-4492; (b) J. Barberá, L. Puig, P. Romero, J. L. Serrano and T. Sierra, Chem. Mater., 2005, 17, 3763-3771; (c) E. Beltrán, E. Cavero, J. Barberá, J. L. Serrano, A. Elduque and R. Giménez, Chem.-Eur. J., 2009, 15, 9017-9023.
- 9 (a) F. Vera, R. M. Tejedor, P. Romero, J. Barberá, M. B. Ros, J. L. Serrano and T. Sierra, Angew. Chem., Int. Ed., 2007, 46, 1873-1877; (b) F. Vera, P. Romero, J. Barberá, M. B. Ros, J. L. Serrano and T. Sierra, Angew. Chem., Int. Ed., 2010, 49, 1-6; (c) R. M. Tejedor, L. Oriol, J. L. Serrano and T. Sierra, J. Mater. Chem., 2008, 18, 2899-2908.
- 10 S. Chandrasekar, Handbook of Liquid Crystals, Wiley-VCH, Weinheim, 1998, vol. 2B.
- 11 (a) D. Pucci, G. Barberio, A. Bellusci, A. Crispini, B. Donnio, L. Giorgini, M. Ghedini, M. La Deda and E. I. Szerb, Chem.-Eur. J., 2006, 12, 6738; (b) K. Binnemans, J. Mater. Chem., 2009, 19, 448-453.
- 12 (a) D. B. Amabilino and J. Veciana, Top. Curr. Chem., 2006, 265, 253-302; (b) M. Grell and D. C. Bradley, Adv. Mater., 1999, 11, 895-905.
- 13 (a) J. Bettenhausen, M. Greczmiel, M. Jandke and P. Strohriegl, Synth. Met., 1997, 91, 223-228; (b) J. A. Mikroyannidis,

- I. K. Spiliopoulos, T. S. Kasimis, A. P. Kulkarni and S. A. Jenekhe, *Macromolecules*, 2003, **36**, 9295–9302; (c)
- C. S. Wang, G. Y. Jung, Y. L. Hua, C. Pearson, M. R. Bryce, M. C. Petty, A. S. Batsanov, A. E. Goeta and J. A. K. Howard, Chem. Mater., 2001, 13, 1167-1173.
- Y. Cao, X. Chai, S. Chen, Y. Jiang, W. Yang, R. Lu, Y. Ren, 14 M. Blanchard-Desce, T. Li and J. Lehn, Synth. Met., 1995, 71, 1733-1734
- 15 (a) E. Meyer, C. Zucco and H. Gallardo, J. Mater. Chem., 1998, 8, 1351-1354; (b) H. Gallardo, R. Magnago and A. J. Bortoluzzi, Liq. Cryst., 2001, 28, 1343-1352.
- 16 (a) R. Cristiano, A. A. Vieira, F. Ely and H. Gallardo, *Liq. Cryst.*, 2006, **33**, 381–390; (b) R. M. Srivastava, R. A. W. Neves, R. Schneider, A. A. Vieira and H. Gallardo, Liq. Cryst., 2008, 35, 737-742; (c) H. Gallardo, R. Cristiano, A. A. Vieira, R. A. W. Neves and R. M. Srivastava, Synthesis, 2008, 605-609; (d) R. Cristiano, D. M. P. D. Santos, G. Conte and H. Gallardo, Liq. Cryst., 2006, 33, 997-1003.
- 17 See ESI[†] for the preparation of the monophenol 7.
- 18 (a) Y. Cohen, L. Avram and L. Frish, Angew. Chem., Int. Ed., 2005, 44, 520-554; (b) C. S. Johnson, Jr, Prog. Nucl. Magn. Reson. Spectrosc., 1999, 34, 203-256; (c) E. J. Cabrita and S. Berger, Magn. Reson. Chem., 2001, 39, S142-S148.
- 19 (a) J. Barberá, L. Puig, J. L. Serrano and T. Sierra, Chem. Mater., 2004, 16, 3308-3317; (b) L. Álvarez, J. Barberá, L. Puig, P. Romero, J. L. Serrano and T. Sierra, J. Mater. Chem., 2006, 16, 3768-3773.
- 20 G. Gottarelli, S. Lena, S. Masiero, S. Pieraccini and G. P. Spada, Chirality, 2008, 20, 471-485.
- 21 A. Painelli, F. Terenziani, L. Angiolini, T. Benelli and L. Giorgini, Chem.-Eur. J., 2005, 11, 6053-6063.
- 22 (a) J. R. Lackowicz, Principles of Fluorescence Spectroscopy, Kluwer Academic Publishers, New York, 2nd edn, 1999; (b) N. F. Marcelo, A. A. Vieira, R. Cristiano, H. Gallardo and I. H. Bechtold, Synth. Met., 2009, 159, 675-680.
- 23 (a) A. Joshi, M. O. Manasreh, E. A. Davis and B. D. Weaver, Appl. Phys. Lett., 2006, 89, 111907-111910; (b) R. Cristiano, E. Westphal, I. H. Bechtold, A. J. Bortoluzzi and H. Gallardo, Tetrahedron, 2007, 63, 2851-2858.