Journal of
Materials Chemistry A

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Towards room-temperature ionic liquid crystals†

Alexandra Alvarez Fernandez, Laurens T. de Haan and Paul H. J. Kouwer*

Cite this: *J. Mater. Chem. A*, 2013, 1, 354

Received 30th August 2012
Accepted 4th October 2012

DOI: 10.1039/c2ta00133k

www.rsc.org/MaterialsA

Ionic liquid crystals (ILCs) with displaying birefringence have great potential in various (bio)sensor schemes. So far, their high transition temperatures prevent their application. We demonstrate in a novel series of ILCs, based on archetypical mesogens, how to reduce clearing temperatures and we explain our results qualitatively.

Since the middle 1980's the expanding class of ionic liquid crystals (ILCs) has been described from many different perspectives: a merge between ionic liquids (ILs) and liquid crystals (LCs), ionic salts displaying a LC phase, or ion conductive anisotropic materials.[1] The versatility in the definition of these materials is reflected in the wide range of applications, ranging from typical IL applications that benefit from anisotropy[2] to characteristic LC applications that require charged species.[3] For instance, the bio-compatibilisation of classical LCs with their characteristic electro-optical switching properties opens up a new avenue of applications in biomedical areas.[3a]

Recent experiments in enzyme catalysis using ILs as solvent showed that materials built from *N*-alkylpyridinium and *N*-alkylimidazolium can successfully host or even accelerate reactions.[4] Analogously, in the design of novel (potentially biocompatible) ILCs, the 1,3-substituted imidazolium salts have been introduced as a promising core in many studies. Different strategies, targeted to understand self-organization and binding interactions[5–7] that induce and stabilize ILC mesophases, have been reported. The common approach is the modification of the side chains[5] (changing the number, length and branching pattern), and the introduction of, for instance, vinyl, hydroxyl, and amide groups.[6] Although their thermal properties are promising, the low birefringence of these materials disqualifies them for most optical applications. The approach towards high birefringent ILCs has already been published: the synthesis of a core where an imidazolium group was coupled to an electron-rich biphenyl group.[7] However, strong ionic and π–π interactions associated with an ionic rigid core yield materials of high clearing temperatures and corresponding high viscosities in particular at room temperature. Previous studies using this design principle have addressed various structure–property relationships with a focus on transition temperatures, but have failed to make the final step towards application requirements. In this study, we have combined several "classical" strategies to give truly room temperature applicable materials while maintaining a high birefringence. The strategies originate from the field of liquid crystals and ionic liquids.

Three molecular parameters were studied, all inspired by results from either classical LCs or ILs. The first is the introduction of a *cis* fatty acid tail as a flexible chain to the core. The bent-shaped tail hinders their close packing, already reducing transition temperatures as observed in liquid crystalline and non-liquid crystalline materials.[8] In order to study the thermal behaviour induced by the lateral kink, reference compounds **2f** and **3f** (containing an octadecyl tail) were synthesised and respectively compared with oleyl analogues **2b** and **3b**. A second, commonly applied strategy to reduce clearing temperatures in LCs is the introduction of (small) lateral substituents to the core. By placing the substituents on the 2-position of the imidazolium group, we anticipated to influence the size and conformation of the cores as well as their inter and intramolecular interactions. The experience from ILs was used to demonstrate the potential of the third parameter selected, the anion, to optimise the properties of materials, including the reduction of the transition temperatures. The studied materials are summarised in Fig. 1.

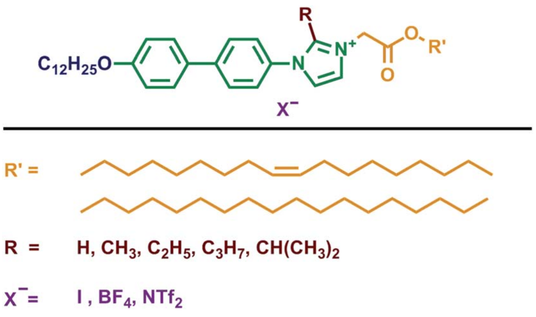
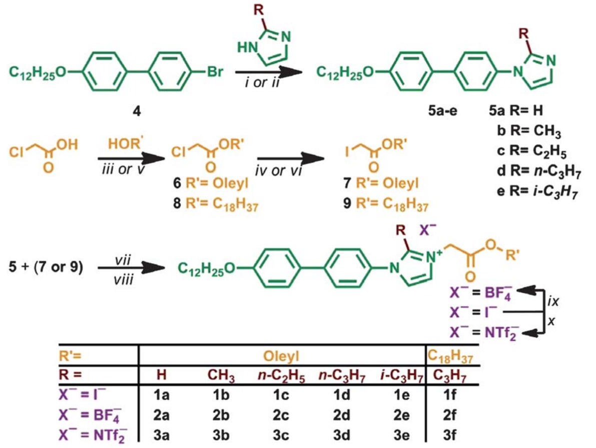


Fig. 1 General structure of the investigated ILCs, changing the lateral substituent **R**, the side chain **R′** and the counter ion **X**.

Radboud University Nijmegen, Institute for Materials and Molecules, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands. E-mail: p.kouwer@science.ru.nl

† Electronic supplementary information (ESI) available: Synthetic procedures and characterisation as well as details of the modeling procedures. See DOI: 10.1039/c2ta00133k



R'=	Oleyl					$C_{18}H_{37}$
R =	H	CH_3	n-C_2H_5	n-C_3H_7	i-C_3H_7	C_3H_7
$X^- = I^-$	1a	1b	1c	1d	1e	1f
$X^- = BF_4^-$	2a	2b	2c	2d	2e	2f
$X^- = NTf_2^-$	3a	3b	3c	3d	3e	3f

Scheme 1 Synthesis of ILCs **1–3**. Key: (i) (R = H, CH_3, C_2H_5) K_2CO_3, CuI, *N*,*N*-dimethylglycine, DMSO, 48–72 h at 110 °C; (ii) (R = n-C_3H_7, i-C_3H_7) Cs_2CO_3, Cu_2O, 4,7-dimethoxy-1,10-phenanthroline, NMP, 5 days reflux; (iii or v) NaI, acetone, rt; (iv or vi) PTSA, toluene, 24 h, reflux (vii or viii) toluene, 80 °C, 24 h; (ix) $NaBF_4$ (aq.) multiple washes; and (x) $AgNTf_2$, methanol.

Compounds **1–3** were synthesised in ten steps starting from the substituted biphenyl[7] **4** (see Scheme 1); the details are described in the ESI.† The Ullmann coupling (step i), the key-step in the protocol, was carried out using different ligands for the copper catalyst depending on the lateral substituent R. The oleyl‡ and octadecyl tails were functionalised with chloroacetic acid and, after being converted to the corresponding iodide, used to alkylate the imidazole group, yielding **1**. Ion exchange of **1** with $NaBF_4$ or $AgNTf_2$ gave the target compounds **2** and **3**.

The mesophase behaviour of **2** and **3** was investigated using optical polarized microscopy (OPM) and differential scanning calorimetry (DSC).§ OPM analysis showed the formation of smectic A (SmA) phases (Fig. 2) for all the samples between crystalline (Cr) and isotropic (Iso) phases. An example of the texture and two DSC traces are shown in Fig. 2.

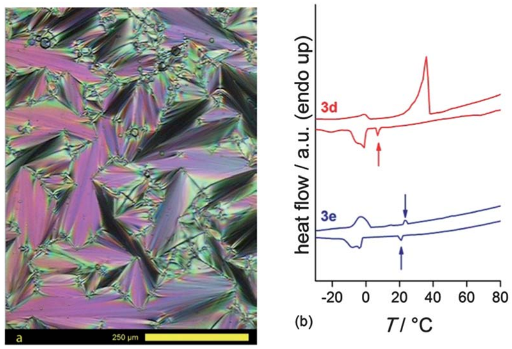


Fig. 2 Polarised optical microscopy image of (a) **2a** at T = 176 °C (SmA) and (b) DSC traces of monotropic ILC **3d** and room temperature ILC **3e**. The arrows indicate SmA-I transitions. Note that most materials we characterised display an enantiotropic SmA phase that appears in DSC in both the heating and the cooling run. Compound **3e** is monotropic, only exhibiting the SmA phase on cooling as a result of supercooling the Cr phase.

The phase behaviour of **2**, ILCs with the BF_4^- anion, is summarized in Fig. 3. In general, the clearing temperatures are lower than expected for molecules containing such a rigid core.[7] This result is attributed to our first design approach: the kink in the terminal chain induced by the *cis* fatty acid tail. By comparing compounds **2b** and **2f** a reduction of around 50 degrees in the clearing temperature can be related to the kink in the side chain. The effect of the lateral substituent R on the mesomorphic behaviour is evident: a decrease of the clearing temperatures was observed by increasing the length of R. In conventional mesogens based on phenyl esters, this trend has been experimentally observed and explained in terms of steric factors where the lateral substituent effectively changes the length-to-breath ratio of the mesogens and, as a result, changes the stability of the mesophase.[9]

The same tendency is observed for **2**. In molecules with such strongly interacting moieties, however, taking only steric factors into account may lead to a significant oversimplification. In the planar conformation, with the imidazolium and the adjacent phenyl group in the same plane, attractive π–π interactions will play a prominent role. We anticipated that the bulky R will also prevent the formation of the planar conformation and in this way contribute as well to the decrease of the transition temperatures.

The most straightforward approach to quantify these intermolecular interactions is to calculate the rotational energy barriers[10] between the imidazolium and phenyl groups of our mesogens, see Fig. 4.

Simple modelling studies clearly show an increase in the rotational energy barrier when the size of the lateral substituent R is increased. For R = H, the energetic penalty of the flat conformation is relatively small, which allows for intermolecular ion-dipole and π–π interactions. Unexpectedly, a significant barrier was already found for the sterically undemanding methyl group. The bulky isopropyl group gives the largest

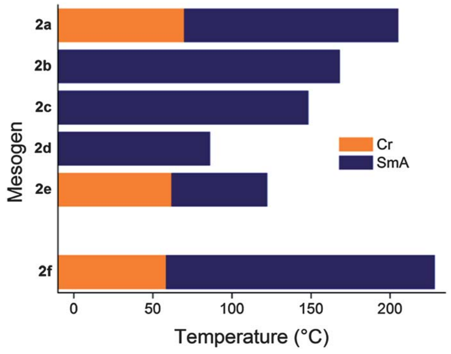


Fig. 3 Mesomorphic properties of series **2**: ILCs with BF_4^- as a counter ion, different lateral substituents R = H, CH_3, C_2H_5, n-C_3H_7 and i-C_3H_7 and a reference compound **2f** containing R' = $C_{18}H_{37}$ as a side chain. The crystal phase of **2b–d** is supercooled as a result of the slow crystallisation process. These materials, instead, show a glass transition at room temperature. Such a behaviour was observed before.[7]

---

‡ The oleyl alcohol used was of technical grade and consisted of approximately 15% *trans* and 85% *cis* double bonds. This ratio was carried over to subsequent products.

§ In our experience, the thermal results of ILCs with the iodide counter ions (**1**) provided unreliable data as a result of decomposition.

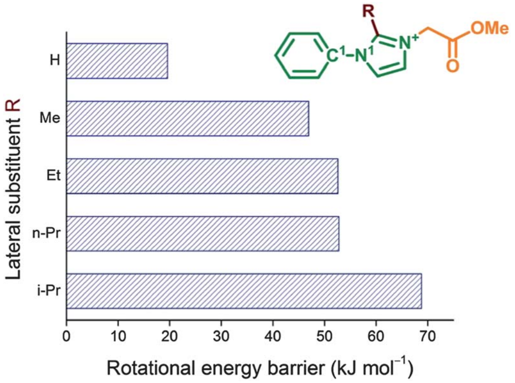


Fig. 4 Calculated energy barriers (HF 13G*) of the C^1–N^1 bond rotation for different lateral substituents R incorporated in the imidazolium molecule displayed right.

barrier. The reduction in conformations combined with the classical steric effects described by Weissflog[9] explains the large impact of the lateral substituents on the clearing temperature. Evaluation of **2d** and **2e** allows us to compare the two effects directly: in **2d** we expect a stronger contribution from the classical steric effects and *vice versa*. Experimentally, a much lower clearing temperature is observed for **2d**, indicating that the length of the *n*-propyl group is the dominating factor.

In order to reproduce the trend observed in Fig. 3 and to drive our ILCs towards lower clearing temperatures, the counter ion was exchanged. We selected the triflimide (NTf_2^-) anion because of its excellent behaviour in well-known and already commercialised ILs,[11] and in ILCs[12] (low viscosity, low melting temperatures). The results of series **3** are summarized in Fig. 5.

Upon ion exchange from BF_4^- to NTf_2^-, a decrease of roughly one hundred degrees in the clearing temperature of the material was observed, yielding truly room temperature processable materials. In line with the results of ILs,[13] we noticed the high fluidity of these materials in comparison with **2** during the microscopy experiment. Fig. 5 clearly highlights the role of the Coulombic interactions as a key method to drastically manipulate the transition temperatures of ILCs. The same trend related to the nature of the substituent R for compounds **3d** and **3e** was reproduced. It supports our previous conclusion that the length of the lateral substituents is the dominating factor. Until now, the high effectiveness of NTf_2^- remains a matter of speculation.

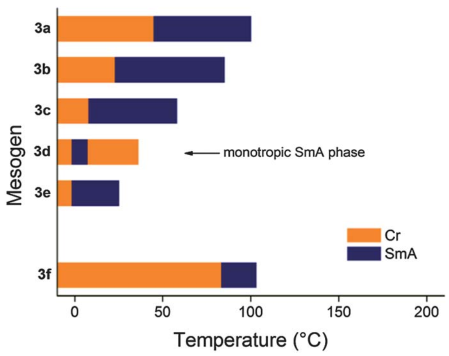


Fig. 5 Mesomorphic properties of series **3**: ILCs with NTf_2^- as a counter ion with different lateral substituents R = H, CH_3, C_2H_5, n-C_3H_7 and i-C_3H_7 and a reference compound **3f** containing R′ = $C_{18}H_{37}$, as a side chain. Mesogen **3d** exhibits a monotropic SmA phase, which only shows up in the cooling run.

Two effects can easily be regarded: the high electronegativity of the fluorine atoms redistributes the negative charge over the entire anion; and the anion is much larger than many of the other (spherical) anions. Currently, we are investigating the role of the counter ion in more detail, separating the effects of its size, shape and charge distribution.

Conclusions

The availability of room temperature anisotropic ionic materials with potential optical applications is restricted by the rigidity of the core combined with its strong electrostatic interactions. We have presented a number of design principles to reduce clearing temperatures, aimed at hindering molecular packing in the system: (a) introducing a kink in the terminal chain; (b) attaching lateral substituents; and (c) making use of different counter ions. Experimentally, the sum of these three strategies led to a reduction of nearly two hundred degrees in the clearing temperatures, yielding highly birefringent room temperature ILCs. We are now studying the application of these novel materials as anisotropic biocompatible solvents.

Acknowledgements

Paul Schlebos is acknowledged for the molecular modelling studies and the EU ITN 2007-215851 “Hierarchy” for financial support.

Notes and references

1 (*a*) K. V. Axenov and S. Laschat, *Materials*, 2011, **4**, 206–259; (*b*) K. Binnemans, *Chem. Rev.*, 2005, **105**, 4148–4204.

2 (*a*) N. Yamanaka, R. Kawano, W. Kubo, T. Kitamura, Y. Wada, M. Watanabe and S. Yanagida, *Chem. Commun.*, 2005, 740–742; (*b*) D. J. Abdallah, A. Robertson, H.-F. Hsu and R. G. Weiss, *J. Am. Chem. Soc.*, 2000, **122**, 3053–3062.

3 (*a*) S. J. Woltman, G. D. Jay and G. P. Crawford, *Nat. Mater.*, 2007, **6**, 929–938; (*b*) T. Kato, *Science*, 2002, **295**, 2414–2418; (*c*) J. C. Shah, Y. Sadhale and D. M. Chilukuri, *Adv. Drug Delivery Rev.*, 2001, **47**, 229–250; (*d*) X. Y. Lu, V. Nguyen, M. J. Zhou, X. H. Zeng, J. Z. Jin, B. J. Elliott and D. L. Gin, *Adv. Mater.*, 2006, **18**, 3294–3298; (*e*) M. J. Zhou, P. R. Nemade, X. Y. Lu, X. H. Zeng, E. S. Hatakeyama, R. D. Noble and D. L. Gin, *J. Am. Chem. Soc.*, 2007, **129**, 9574–9575.

4 (*a*) F. van Rantwijk and R. A. Sheldon, *Chem. Rev.*, 2007, **107**, 2757–2785; (*b*) P. Lozano, T. De Diego, D. Carrie, M. Vaultier and J. L. Iborra, *J. Mol. Catal. B: Enzym.*, 2003, **21**, 9–13.

5 (*a*) C. K. Lee, H. W. Huang and I. J. B. Lin, *Chem. Commun.*, 2000, 1911–1912; (*b*) D. Ster, U. Baumeister, J. L. Chao, C. Tschierske and G. Israel, *J. Mater. Chem.*, 2007, **17**, 3393–3400.

6 (*a*) S.-C. Luo, S. Sun, A. R. Deorukhkar, J.-T. Lu, A. Bhattacharyya and I. J. B. Lin, *J. Mater. Chem.*, 2011, **21**, 1866–1873; (*b*) J. Y. Z. Chiou, J. N. Chen, J. S. Lei and I. J. B. Lin, *J. Mater. Chem.*, 2006, **16**, 2972–2979; (*c*) K.-M. Lee, Y.-T. Lee and I. J. B. Lin, *J. Mater. Chem.*, 2003, **13**, 1079–1084.

7 P. H. J. Kouwer and T. M. Swager, *J. Am. Chem. Soc.*, 2007, **129**, 14042–14052.

8 (*a*) D. J. Dyer and D. M. Walba, *Chem. Mater.*, 1994, **6**, 1096–1098; (*b*) S. M. Kelly, *Liq. Cryst.*, 1993, **14**, 675–698.

9 W. Weisflogg, Laterally Substituted and Swallow-Tailed Liquid Crystals, in *Handbook of Liquid Crystals – Low Molecular Weight Liquid Crystals II*, ed. J. G. D. Demus, G. W. Gray, H.-W. Spiess and V. Vill, Weinheim, 1998, vol. 2, ch. XI.

10 (*a*) S. Laschat, *Beilstein J. Org. Chem.*, 2012, **8**, 118–119; (*b*) M. Butschies, S. Sauer, E. Kessler, H. U. Siehl, B. Claasen, P. Fischer, W. Frey and S. Laschat, *ChemPhysChem*, 2010, **11**, 3752–3765.

11 (*a*) C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki and J. F. Brennecke, *J. Chem. Eng. Data*, 2004, **49**, 954–964; (*b*) C. Austen Angell, Y. Ansari and Z. Zhao, *Faraday Discuss.*, 2012, **154**, 9–27.

12 (*a*) M. Trilla, R. Pleixats, T. Parella, C. Blanc, P. Dieudonne, Y. Guari and M. W. C. Man, *Langmuir*, 2008, **24**, 259–265; (*b*) K. Goossens, P. Nockemann, K. Driesen, B. Goderis, C. Gorller-Walrand, K. Van Heeke, L. Van Meervelt, E. Pouzet, K. Binnemans and T. Cardinaels, *Chem. Mater.*, 2008, **20**, 157–168.

13 A. Noda, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2001, **105**, 4603–4610.