Dynamic Combinatorial Chemistry

DOI: 10.1002/ange.200600430

Electric-Field Modulation of Component Exchange in Constitutional Dynamic Liquid Crystals**

*Nicolas Giuseppone and Jean-Marie Lehn**

Dynamic combinatorial chemistry (DCC) forms the covalent domain of constitutional dynamic chemistry (CDC)[1,2] which covers reversible constitutional reorganization on both the molecular (covalent) and supramolecular (noncovalent) levels. It gives access to all possible combinations of the available components, which are connected through reversible covalent bonds. It thus generates constitutional dynamic libraries (CDLs) that, at thermodynamic equilibrium, display all the constituents or leave some of them virtual, depending on the conditions.[1a] Such systems can be driven either by internal organization (self-recognition) or by external interaction (species binding). As a result, the equilibrium may shift to the over-expression of selected products through an adaptative process. To date, the discrimination between the constituents of dynamic libraries has centered on the utilization of target recognition as a driving force, in particular as a result of applications in drug discovery.[3] In the course of our

---

[*] Dr. N. Giuseppone, Prof. Dr. J.-M. Lehn
Institut de Science et d'Ingénierie Supramoléculaires
8 Allée Gaspard-Monge, BP 70028, 67083 Strasbourg (France)
Fax: (+33) 390-245-140
E-mail: lehn@isis.u-strasbg.fr

[**] We thank Dr. Jean-Louis Schmitt for checking the experimental results. We are grateful to Dr. Daniel Guillon, Dr. Jacques Malthête, and Dr. Jacques Prost for their constructive remarks on the manuscript.

investigations toward the design of adaptative chemical systems that respond to a wide array of environmental parameters, we have become interested in the potential offered by the possibility to drive constituent reorganization and amplification/selection by component exchange, by external physical (temperature,[4a] phase transition[5]), or chemical (protons,[4] metal ions[4b,c,6]) triggers. Changes in the composition of the members of a constitutional dynamic library (CDL) represent an adaptation of the dynamic system in response to the perturbation. Such effects are of special interest in terms of developing dynamic materials that respond to environmental effectors.[7,8]

To extend the range of physical external triggers for inducing selection processes, we have explored the possibility of using an electric field to influence the thermodynamic equilibrium in a mixture of constitutionally interrelated compounds. To this end, the development of dynamic liquid crystals (LCs) appeared particularly well-suited for three main reasons: 1) the wide use of LCs as materials, in particular for display technology;[9] 2) the potential existence of various LC phases—such as nematic, smectic, etc.—depending on the constitution of the mixtures and molecular structure of the components;[10] and 3) the well-known behavior of LCs to become macroscopically oriented and stabilized in either electric[11] or magnetic fields.[12]

We herein describe the perturbations imposed by an electric field on mixtures of imines and amines containing an LC-type imine with a negative dielectric anisotropy, namely MBBA (**1**) or EBBA (**5**, Scheme 1). Two distinct phenomena have been observed that are linked to the transitions between isotropic and nematic phases. The first one consists of the expulsion from the LC, upon application of an electric field, of compounds that do not participate in the formation of a nematic phase; the second is based on a direct effect of the electric field on the thermodynamic equilibria in a CDL by the coupling of the field to the LC-forming entity and its subsequent stabilization/amplification.

The effect of constitutional modifications by component exchange on the isotropic/nematic phase transition temperatures ($T_{\mathrm{I/N}}$) of MBBA (**1**) was investigated by following UV/Vis spectroscopic changes upon introduction of various amounts of several additives (Figure 1).[13]

The value of $T_{\mathrm{I/N}}$ decreased linearly as a function of the amount of additive and the slopes of the lines fall into two sets. In one set are the additives which cannot lead to a new imine by constitutional reorganization (triethylamine, cyclopentanol, *N*,*N*-dimethylaniline) and where the addition of 15 mol% of compound results in a decrease in the $T_{\mathrm{I/N}}$ value to close to room temperature. The second set contains the additives which can react with MBBA (**1**) by transimination reactions[14] (cyclopentylamine, aniline, 2,4-dimethoxybenzylamine) with formation of new imines, and where the addition of only 3 mol% of compound is enough to give a $T_{\mathrm{I/N}}$ value close to room temperature. This differential behavior suggested that it was the generation of recombinant imines that led to marked changes in the value of $T_{\mathrm{I/N}}$.

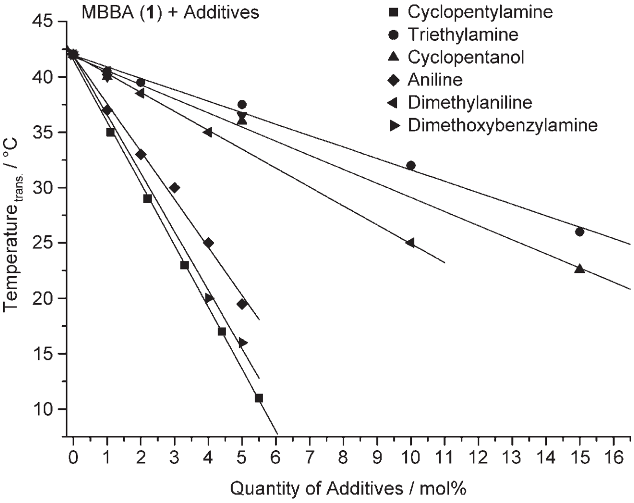
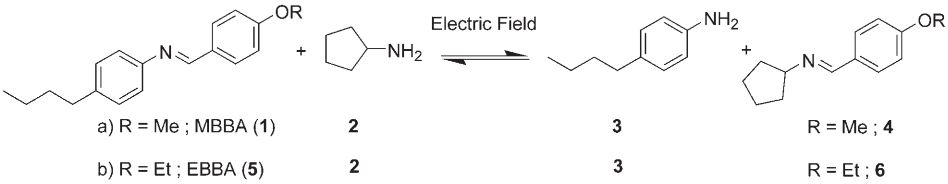


Figure 1. Representation of the evolution of the phase-transition temperature ($T_{\mathrm{N/I}}$) of MBBA (**1**) as a function of increasing amounts of various additives. Phase-transition temperatures were determined by using variable temperature UV/Vis spectroscopy as the average of the transitions recorded in the heating/cooling cycles of 10 μm thickness films ($\lambda = 400$ nm and $V_{\Delta T} = 1$ °C/min). NMR spectroscopic observation was used to ensure that equilibrium was reached.

We then investigated whether an electric field would influence the equilibria involving compounds **1**, **2**, **3**, and **4** as well as **5**, **2**, **3**, and **6**, respectively, where the imines **1** and **5** are LCs, but **4** and **6** are not (Scheme 1) and should result in changes in the $T_{\mathrm{I/N}}$ value.



Scheme 1. Component exchange between MBBA (**1**) or EBBA (**5**) and cyclopentylamine (**2**) leading to a constitutional dynamic equilibrium with 4-butylaniline (**3**) and imines **4** or **6**, respectively, modulated by an applied electric field.

The experiments were performed on thin films of 21-(±5%) μm thickness between transparent indium tin oxide (ITO) plates so that sufficiently high voltages could be applied to the systems. Under these conditions, the maximum voltage applied was $3.5\times10^{4}\,\mathrm{V\,cm^{-1}}(\pm0.15\times10^{4}\,\mathrm{V\,cm^{-1}})$ which enabled a high resistivity ($R \geq 6\times10^{7}\,\Omega\,\mathrm{cm^{-1}}$) to be maintained and to avoid fast degradation of the compounds as well as heating-induced phenomena arising from the electric current.[15] The phase transition could be observed both with the naked eye (as a consequence of the opacity of the nematic phase under a high electric field in the dynamic scattering mode, DSM)[16] and by using a polarized light microscope (Figure 2A).

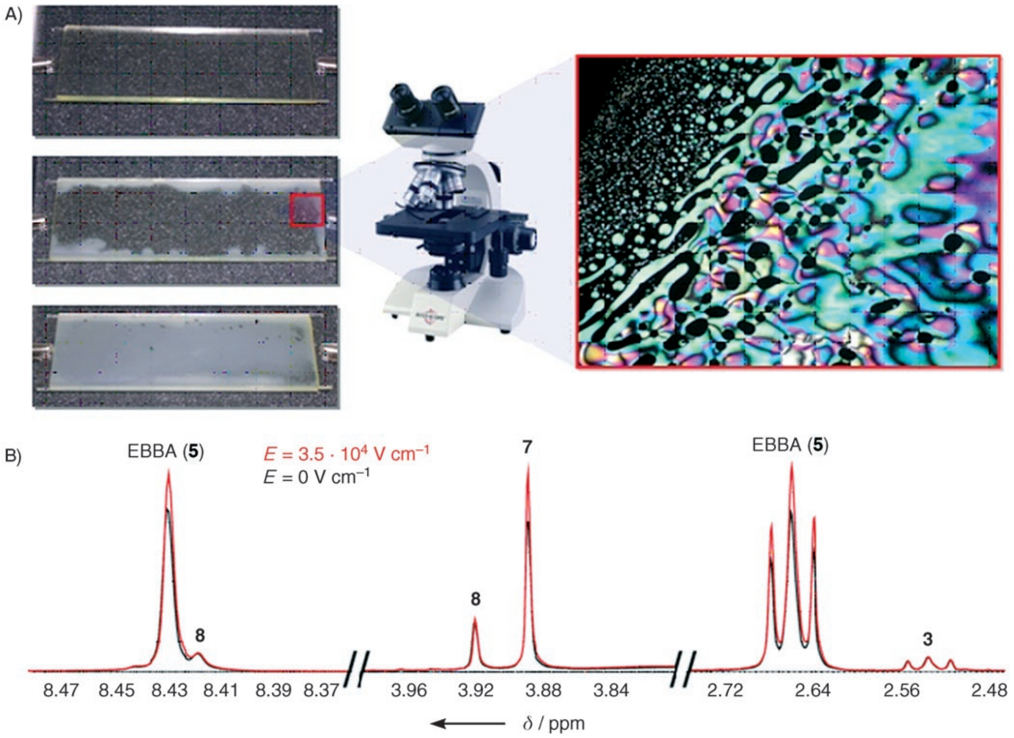


Figure 2. A) Left: Typical appearance of the ITO plates (7.25×2.5 cm) as a function of time in an experiment using MBBA (**1**) in the presence of additives and under the influence of an electric field (when the applied voltage is superior to the minimum necessary for observing the changes through the dynamic scattering mode[16]): top: liquid mixture; middle: coexistence between liquid and nematic phases; bottom: nematic phase over the entire ITO plate. Right: Microscopy observation, using a polarized light microscope in transmission mode (×40), which shows the expansion of the nematic phase into the liquid one under the influence of an electric field ($E=0$ V at the instant of the snapshot). B) Partial 400 MHz ^{1}H NMR spectra showing the changes in chemical composition induced by the application of an electric field ($E=3.5\times10^4$ V cm^{-1} (±5%)) at 24 °C for 2 h on the equilibrium described in Scheme 2 (red spectrum), compared to the control experiment without field (black line).

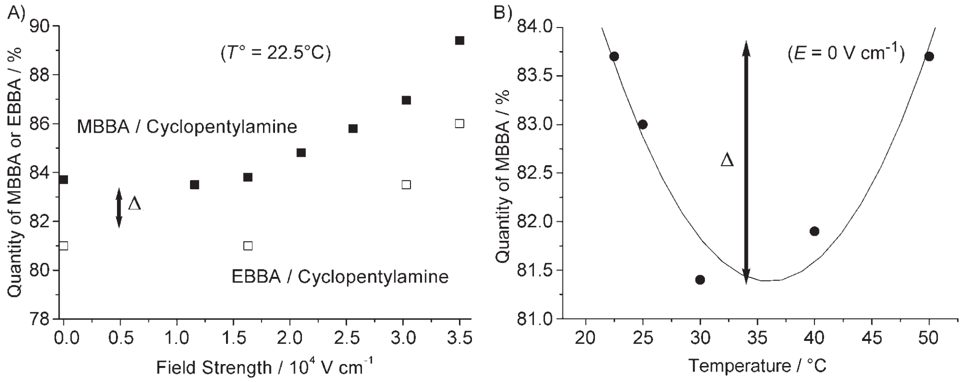


Figure 3. A) Effect of the strength of the electric field, at 22.5 °C after 24 h, on the equilibria described in Scheme 1 for an initial molar ratio of MBBA:cyclopentylamine of 1:0.2 ± 1.1 % (■) and for an initial molar ratio of EBBA:cyclopentylamine of 1:0.25 ± 1.1 % (□)). B) Effect of the temperature, after 24 h, on the equilibrium of the reaction described in Scheme 1 with MBBA (initial molar ratio of MBBA:**2** 1:0.2). Δ shows the scale change for comparing the effect of electric field (A) and temperature (B) on the equilibrium.

The molecular composition of the system described in Scheme 1 at equilibrium was obtained from the ^{1}H NMR spectra of the solutions of complete mixtures in $CDCl_3$ set between the ITO plates, and by superimposition of the NMR spectra of the pure compounds. Under neat conditions, the rate of the transimination reaction was slow enough ($V_0=1.84\,\mathrm{M\,h^{-1}}$, $t_{1/2}=64$ min; for a **1**:**2** ratio of 1:0.64 and for $T=22.7$ °C) to allow accurate measurements by NMR spectroscopy.[17] A static electric field was applied to the two dynamic mixtures illustrated in Scheme 1 and the evolution of the equilibrium amounts (namely, expression) of MBBA (**1**) and EBBA (**5**) was followed as a function of field strength (Figure 3).

The data showed a nonlinear displacement of the equilibrium, which shifts towards the generation of MBBA and EBBA, respectively, as the field strength increases. That this change (about 6 %) was not a result of a variation in temperature is indicated by the fact that heating the ITO plates (even by tens of degrees) led to a much smaller displacement of the equilibrium (about 2 %) than that observed with the electric field.[15,18] Several other mixtures involving aniline, benzylamine, isopentylamine, and allylamine, and even libraries containing all these amines together led to similar observations. In all these cases an accelerated loss of the volatile amines by evaporation occurred (Figure 3 A), which led to irreversible systems. To confirm these findings, we studied a nondynamic system consisting of a mixture of MBBA (**1**) and cyclopentanol in which component exchange does not occur; a similar enhanced loss of cyclopentanol by evaporation under the influence of the electric field was observed.[19] The behavior of the present systems may be related to some electrohydrodynamic effects in the DSM that result from the coupling of the LC molecules (of negative dielectric anisotropy) to the electric field, and that lead to an extrusion (and subsequent evaporation) of the foreign (volatile) substances not involved in the LC molecules.[20] It could also present interesting applications, for example, for the controlled release of molecules or for the design of sensors.

The next step was to design a fully reversible system to examine the direct influence of the electric field on the equilibrium itself. A proof of principle was finally obtained using EBBA (**5**) and (the nonvolatile) 2-methoxyaniline (**7**; b.p. 225 °C) in the process described in Scheme 2, which led through transimination to an equilibrating reaction with **3** and the non-LC imine **8**.

The ^{1}H NMR spectra of mixtures of EBBA (**5**) and **7**, chosen so as to correspond to a $T_{I/N}$ value close to room temperature (molar ratio **5**:**7** = 79.3:20.7 ± 1.2 %) were determined in the absence and in the presence of an applied electric field ($E = 3.5 \times 10^4$ V cm^{-1}(±5 %)) after 2 h equilibration at 24 °C (Figure 2 B). The relative variation of the percentage of 4-butylaniline (**3**) with respect to the initial molar ratio of **5**:**3** (93:7) for various strengths of the electric field is shown in Figure 4, together with kinetic data for reaching equilibrium in the presence of the electric field and after switching it off.

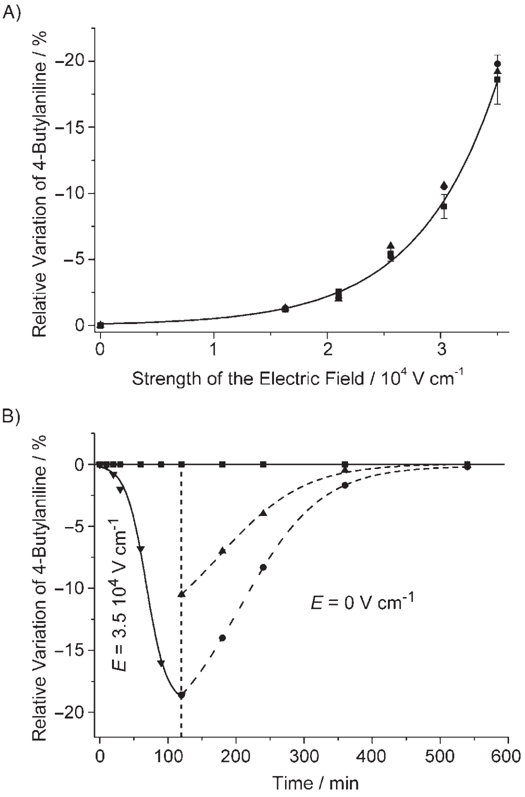
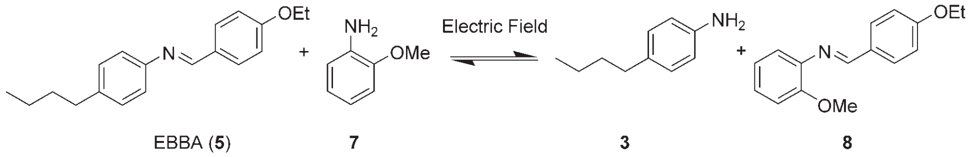


Figure 4. A) Effect of the strength of the electric field, at 24 °C for 2 h on the equilibrium described in Scheme 2 (molar ratio of EBBA:**7** 79.3:20.7 ± 1.2 %); each reaction was repeated three times and the error bars represent values between ± 10 %. B) Kinetics of the variation of the equilibrium between ITO plates under a field $E = 3.5 \times 10^4$ V cm^{-1} (± 5 %; ▲; solid line curve); kinetics of equilibration after stopping the electric field and dissolution ($C = 3.84$ M in CDCl$_3$; ●, dashed line curve); and kinetics of equilibration after stopping the electric field and dissolution, for an initial applied field of $E = 3.03 \times 10^4$ V cm^{-1} (± 5 %; ▲, dashed line curve). The values are given using the relative variation in the percentage of amine **3** (experiments with and without field (■; solid line curve)), and corrected for the dilution effect.



Scheme 2. Transimination reaction between EBBA (**5**) and 2-methoxyaniline (**7**) leading to an equilibrium with 4-butylaniline (**3**) and imine **8**, modulated by the presence of an electric field.

The spectra in Figure 2 B show an increase in the amount of **5** and **7** at equilibrium under the applied electric field, and a concomitant decrease of **3** and **8**. The increase in **7** is of particular importance: as it is nonvolatile relative to cyclopentylamine (**2**), loss by evaporation cannot here be the driving force for the evolution of the system, thus the changes observed may be ascribed to the direct effect of the electric field on the equilibrium. Moreover, there is an exponential correlation between the strength of the field and the equilibrium displacement (Figure 4 A). Furthermore, the field-induced perturbation was fully reversible, as shown in Figure 4 B by the evolution of the system as a function of time under applied electric field, compared to the control experiment, and after the field had been shut off. Whereas the equilibrium was attained in about 2 h in the presence of the field, after switching it off, the initial position of the equilibrium was restored after about 6 h in a CDCl$_3$ solution at 24 °C. The reversibility between the ITO plates at 24 °C was a very slow process in the absence of DSM (more than several days), while heating the plates without field at 45 °C for 4 h led to the return of the equilibrium to its initial position. Thus, a faster interconversion over several cycles would require acting on both parameters: electric field and temperature.

Finally, we investigated whether, in the absence of an applied field, a temperature-induced phase transition would by itself have an effect on the constitutional equilibrium (Figure 5).

The changes in composition remained very minor compared to those observed under an applied electric field, with relative variations in the fraction of 4-butylaniline of less than 3 % both inside a single phase and at the phase transitions.

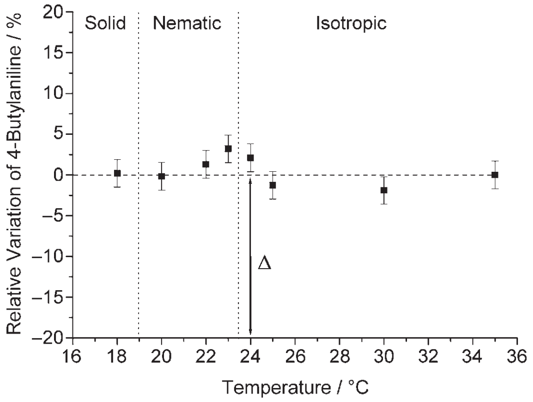


Figure 5. Effect of the temperature, after two hours, on the equilibrium described in Scheme 2 (molar ratio of EBBA:**6** 79.3:20.7 ± 1.2 %) and under slight mechanical stirring; the error bars represent values between ± 2.5 %, which is close to the accuracy of the ^{1}H NMR method. The Δ symbol shows on the same scale the change of the equilibrium in presence of an electric field ($E = 3.5 \times 10^4$ V cm^{-1} (± 5 %), after two hours, Figure 4).

When the same system was studied at higher temperatures, the liquid to nematic phase transition was observed up to 55 °C, when the mixture starts losing its electric resistance.[21]

It is known that applying an electric field to genuine liquid crystals with either positive[11,15b] or negative[22] dielectric anisotropy leads only to a small change in the $T_{I/N}$ values (typically ≤ 1 K for an applied field of 2×10^5 V cm^{-1}). The marked change in the $T_{I/N}$ values observed here must result from a specific property of the present system, namely its constitutional variation under application of an electric field. Furthermore, when the mixture described in Scheme 2 was studied under a field of 3.5×10^4 V cm^{-1} (± 5 %) for 2 h at a **5**:**7** ratio of 69.5:30.5 (± 1.3 %), which does not allow a phase transition from liquid to nematic at 24 °C, a comparable change occurred in the composition at equilibrium (18 % for the relative variation of **3**). This observation indicates the coupling of EBBA (**5**) to the electric field even in the liquid paranematic phase, as a result of the electric field induced formation of cybotactic groups—small sets of locally organized molecules.

In conclusion, we have shown that the interaction between an electric field and LC molecules having a negative dielectric anisotropy can lead to two different phenomena: 1) a purification of the system by extrusion of the molecules that do not couple to the electric field, probably through electrohydrodynamic processes; and 2) a direct action of the electric field on a constitutional dynamic equilibrium involving LC molecules formed from components connected through reversible imine-type bonds.[23] The amplified constituent is that which couples the strongest to the electric field (the liquid crystal), and this amplification can consequently result in a phase transition from liquid to nematic. The processes described here broaden the scope of CDC by demonstrating the influence of a particularly interesting environmental parameter, the electric field, and illustrate the adaptation of the dynamic mixtures to a physical effector through the formation of the "fittest" constituent, that presenting the strongest coupling to the field.[24] This approach may in principle be applied 1) to more complex mixtures, in particular containing several different dynamic LC molecules, 2) to systems involving different reversible covalent processes, as well as 3) to supramolecular LCs or LC polymers.[8] The phenomena discovered could also be of potential interest for practical applications in various areas, such as the fine-tuning of a given material or controlled release processes.

Experimental Section

General aspects: All reagents were purchased at the highest commercial quality and used without further purification except for EBBA (**5**) which was recrystallized by slow cooling from a hot saturated solution in heptane, and for 2-methoxyaniline (**7**) which was distilled two times, immediately prior to use. The phase-transition temperatures (42.5 °C for MBBA and 78.5 °C for EBBA) agreed with those reported in the literature. ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. To avoid the catalysis of the transimination reaction, traces of acid in the deuterated chloroform were removed by flash chromatography through neutral alumina immediately prior to use. The ITO plates were purchased from Aldrich (70–100 ohm; ref: 576352) and the electric field was applied with a TTi EX752M multimode PSU generator. The resistivity of the thin films was measured with a Keithley 6517A instrument. The temperature of the samples was regulated by placing the ITO plates on a thermostated surface, controlled by a Polystat cc2 Huber system, and checked at the surface of the glass slides using a thermocouple (Bead Probe Keithley 6517-TP).

General procedure for cross-over experiments and determinations of thermodynamic and kinetic data: In a typical protocol the compounds to exchange were mixed in a closed vial. The mixture was heated up to 60 °C for 5 min, then cooled down to room temperature, and left for 2 h at that temperature. Then, 38 μL (± 5 %) of the neat mixture was placed between two ITO plates by using a microsyringe, and the glass plates were gently pressed to get a thin film (21 μm, ± 5 %) over the entire surface (18.1 cm^2; see Figure 2 A). The plates were thermostated, and then connected to the cathode and the anode of the generator; electric fields between 0 and 75 V were applied (for an applied field of 75 V, the experimental errors will lead to a value of 3.5×10^4 V cm^{-1} ($\pm 0.15 \times 10^4$ V cm^{-1}). After a given time, the electric field was shut off, and the whole mixture contained between the two plates was dissolved in $CDCl_3$ (2 mL), immediately prior to ^{1}H NMR measurements (within 5 minutes). The ^{1}H NMR spectra were recorded until stabilization of the equilibria for both the experiment with the field as well as the thermostated control experiment (without field but with the same initial mixture). The values for the changes in sample composition were obtained from comparison of the spectra for the two corresponding experiments after the same time of equilibration in solution.

Received: February 1, 2006

Keywords: dynamic combinatorial chemistry · electrochemistry · imines · liquid crystals · phase transitions

---

[1] a) J.-M. Lehn, *Chem. Eur. J.* **1999**, *5*, 2455; b) R. L. Cousins, S. A. Poulsen, J. K. M. Sanders, *Curr. Opin. Chem. Biol.* **2000**, *4*, 270; c) S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem.* **2002**, *114*, 938; *Angew. Chem. Int. Ed.* **2002**, *41*, 898.

[2] a) J.-M. Lehn, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4763; b) J.-M. Lehn, *Science* **2002**, *295*, 2400.

[3] O. Ramström, J.-M. Lehn, *Nat. Rev. Drug Discovery* **2001**, *1*, 26.

[4] a) N. Giuseppone, J.-M. Lehn, *Chem. Eur. J.* **2006**, *12*, 1715; b) N. Giuseppone, J.-M. Lehn, *J. Am. Chem. Soc.* **2004**, *126*, 11448; c) N. Giuseppone, G. Fuks, J.-M. Lehn, *Chem. Eur. J.* **2006**, *12*, 1723.

[5] S. Nampally, J.-M. Lehn, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 5938.

[6] N. Giuseppone, J.-L. Schmitt, J.-M. Lehn, *Angew. Chem.* **2004**, *116*, 5010; *Angew. Chem. Int. Ed.* **2004**, *43*, 4902.

[7] J.-M. Lehn in *Supramolecular Science: Where It Is and Where It Is Going* (Eds.: R. Ungaro, E. Dalcanale), Kluwer, Dordrecht, The Netherlands, **1999**, 287.

[8] J.-M. Lehn, *Polym. Int.* **2002**, *51*, 825, and references therein.

[9] For a recent review on the use of liquid crystals for display technology, see: P. Kirsch, M. Bremer, *Angew. Chem.* **2000**, *112*, 4384; *Angew. Chem. Int. Ed.* **2000**, *39*, 4216.

[10] P.-G. de Gennes, *The Physics of Liquid Crystals* Clarendon, Oxford, **1973**.

[11] a) C.-P. Fan, M. J. Stephen, *Phys. Rev. Lett.* **1970**, *25*, 500; b) I. Lelidis, M. Nobili, G. Durand, *Phys. Rev. E* **1993**, *48*, 3818; c) I. Lelidis, G. Durand, *Phys. Rev. E* **1993**, *48*, 3822; d) I. Lelidis, G. Durand, *Phys. Rev. Lett.* **1994**, *73*, 672; e) I. Lelidis, G. Durand, *Phys. Rev. Lett.* **1996**, *76*, 1868.

[12] a) J. Tang, S. Fraden, *Phys. Rev. Lett.* **1993**, *71*, 3509; b) M. I. Boamfă, K. Viertler, A. Wewerka, F. Stelzer, P. C. M. Christianen, J. C. Maan, *Phys. Rev. E* **2003**, *67*, 050701.

[13] a) To improve the reliability of LC displays, some studies addressed the influence of traces of water in mixtures of imine-type liquid crystals.[13b] The presence of residual water was demonstrated, as well as subsequent changes in the $T_{I/N}$ values of the mixtures; however, the use of mixtures of LCs as dynamic systems, has not been explored; b) H. Sorkin, A. Denny, *RCA Rev.* **1973**, *34*, 308.

[14] The choice of transimination as the exchange reaction is of crucial importance to avoid the presence of water (that would be formed in amine–carbonyl condensations) in the present systems so as to maintain high resistance to the electric current upon application of a high voltage. For catalyzed and noncatalyzed transimination reactions, see: N. Giuseppone, J.-L. Schmitt, E. Schwartz, J.-M. Lehn, *J. Am. Chem. Soc.* **2005**, *127*, 5528, and references therein.

[15] a) Under these conditions the heating appeared negligible (ca. 1 °C measured at the surface of the ITO plates), in agreement with literature results: b) W. Helfrich, *Phys. Rev. Lett.* **1970**, *24*, 201; c) A. J. Nicastro, P. H. Keys, *Phys. Rev. A* **1981**, *30*, 3156.

[16] G. H. Heilmeier, L. A. Zoanoni, L. A. Barton, *Appl. Phys. Lett.* **1968**, *13*, 46.

[17] The rate of the reaction in a $CDCl_3$ solution ($C = 3.84\,\text{M}$) was found to be $t_{1/2} = 60$ min at 22.5 °C and $t_{1/2} = 30$ min at 30 °C, which is also suitable for NMR measurements.

[18] The change in the direction of the displacement of the equilibrium above 30 °C (Figure 3B, right-hand part of the curve) was found to arise from evaporation of cyclopentylamine. Thus, the effect of heating on the equilibrium is in the opposite direction (left-hand part of the curve, Figure 3B) than that caused by the field before evaporation takes over.

[19] For example, the use of a molar ratio of MBBA:cyclopentanol of 55:45 leads to an evaporation of 7.5 % of the cyclopentanol without field, and of 38.5 % with a field of $3.5 \times 10^4\,\text{V cm}^{-1}$, after 18 h at 23 °C. Moreover, if MBBA is replaced by pentaethylene glycol (with no liquid-crystal properties and similar viscosity), no differential evaporation was observed.

[20] The effect amounts to a sort of purification under high voltage; for electrohydrodynamic effects in the MBBA-type nematic phases, see: D. Jin, H. Kim, S. H. Kim, S. K. Kim, *J. Phys. Chem. B* **1997**, *101*, 10757.

[21] The coexistence between liquid-crystalline and liquid domains is observed between the ITO plates.

[22] S. Dhara, N. V. Madhusudana, *Europhys. Lett.* **2004**, *67*, 411.

[23] For a theoretical study of the effect of an external electric field on bond activation reactions, see: S. Shaik, S. P. de Visser, D. Kumar, *J. Am. Chem. Soc.* **2004**, *126*, 11746.

[24] We thank a referee for comments concerning the origin of the chemical effects observed by application of the electric field. In particular, the "coupling to the field" merely indicates that the observed effects result from the interaction of the electric field with the liquid-crystalline species. Such coupling may involve several factors/mechanisms. The energy necessary to displace the equilibrium as described in Scheme 2 and Figure 4 is calculated to be about $\Delta\Delta G \approx 80\,\text{cal mol}^{-1}$. The electric interaction energy with the system is too weak to explain the observations, even if a contribution from flexoelectricity[10] is taken into account. When the field is applied close to the phase transition, the effect could be in the correct range, but should change on varying the temperature, which appears not to be the case. The heat capacity associated with the isotropic/nematic phase transition is known to be also in the range required to shift the equilibrium,[25] however, the lack of a temperature effect (Figure 5) indicates that it is not a major factor. Finally, electrohydrodynamic instabilities observed in the DSM mode are known to be caused by ionic currents;[26] the contribution of the field heterogeneity related to the motions of ionic particles throughout the sample could be more than enough to displace the equilibrium with the experimentally measured values of the conductivity. Ionic motions and the conceivable accumulation of charges on the electrode surfaces would lead to high local field values, capable of sufficient interaction with the liquid crystal to result in its amplification from the DCL.

[25] R. Chang, F. B. Jones, J. J. Ratto, *Mol. Cryst. Liq. Cryst.* **1976**, *33*, 13 ($\Delta H_{(\text{Nematic–Isotropic})} = 0.10\,\text{kcal mol}^{-1}$; $T = 45.8\,°\text{C}$).

[26] a) E. F. Carr, *Mol. Cryst. Liq. Cryst.* **1969**, *7*, 253; b) W. Helfrich, *J. Chem. Phys.* **1969**, *51*, 4093; c) S. Hirata, T. Tako, *Jpn. J. Appl. Phys. Part 2* **1982**, *21*, L607; d) S. J. Tavener, T. Mullin, G. I. Blake, K. A. Cliffe, *Phys. Rev. E* **2000**, *63*, 011708.