Liquid Crystals

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Manipulating Liquid-Crystal Properties Using a pH Activated Hydrazone Switch **

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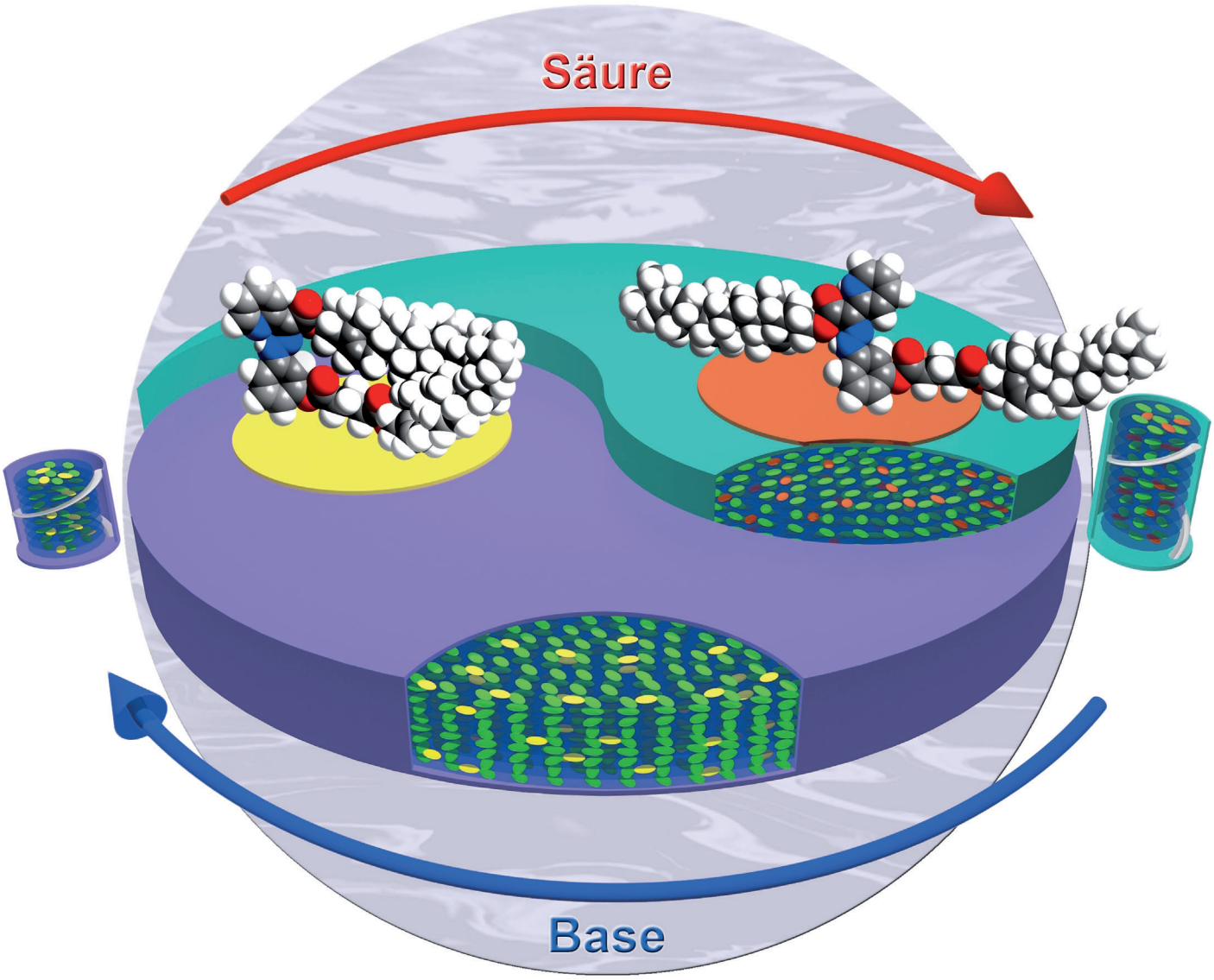
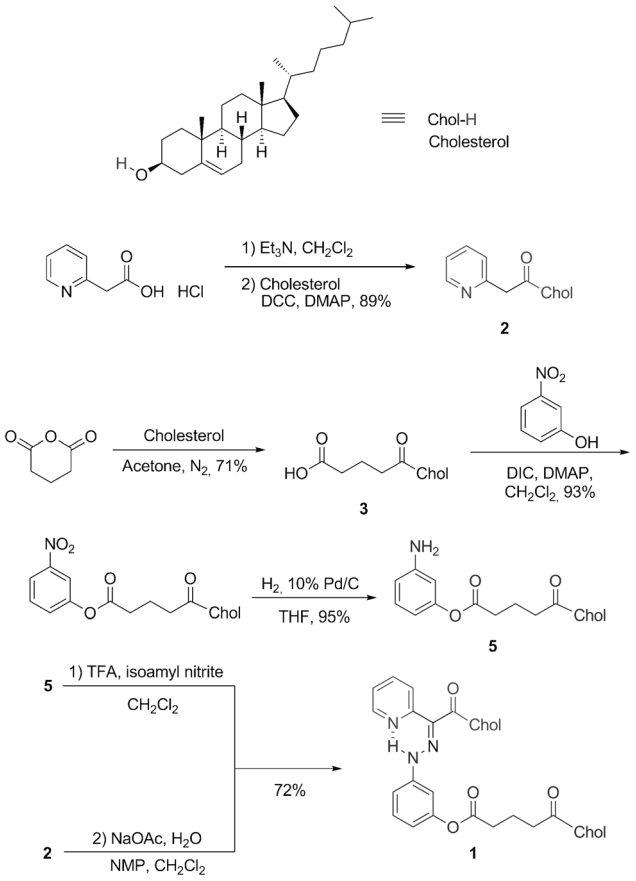
Dedicated to Professor Mordecai Rabinovitz on the occasion of his 80th birthday



Controlling the bulk properties of functional materials is one of the main objectives of the field of molecular switches and machines.[1] Despite the continuous effort towards this goal,[2] very few systems have been developed to date that can propagate structural changes on dimensional scales beyond their own sizes, that is, from microscopic to mesoscopic and macroscopic levels.[3–5] Liquid crystals[6] (LCs) are prime targets for such studies, because the control of their self-assembled supramolecular structures can lead to adaptive functional materials that can be used as actuators, micromechanical systems, active smart surfaces, sensors, and responsive reflectors, among others.[7] The modulation of the properties of LCs by using molecular switches is usually accomplished photochemically,[3] and there are very few examples of the use of other stimuli for this purpose.[8] The use of chemical input in controlling the supramolecular assembly of LCs is very scarce in general. Abbott et al. have pioneered this field and demonstrated[9] how the chemical modulation of hydrogen bonds or electrostatic interactions can be used in highly sensitive sensing applications. Our interest in developing a complementary approach that relies on controllable molecularly defined transitions[10] (as opposed to bulk effects)[11] in manipulating the long-range order of supramolecular LC assemblies, has led us to the use of our chemically activated hydrazone-based switches[12] for such an application. Herein, we report how the pH-induced rotary motion in these systems can be utilized in propagating changes beyond the molecular scale. To achieve this goal we synthesized a hydrazone switch functionalized with cholesterol, a well-studied chiral mesogen, and doped it in a commercially available LC, nematic phase 5 (NP5).[13] This approach allowed us to control the photophysical properties of the LC by using acid and base inputs. To our knowledge, this is the first example of the use of a chemically activated molecular switch in the modulation of the long-range organization and properties of LCs.

The cholesterol-modified hydrazone switch **1** was synthesized from commercially available starting materials in five steps with an overall 40% yield (Scheme 1). The rotor moiety **2** was obtained from the DCC coupling between 2-pyridin-2-ylacetic acid hydrogen chloride and cholesterol, whereas the stator moiety **5** was obtained from the esterification of **3** with 3-nitrophenol and subsequent reduction with hydrogen in the presence of 10% Pd/C. Finally, the coupling between **2** and **5** yielded **1**, which was characterized using NMR spectroscopy (Figures S16 and S17 in the Supporting Information) and high-resolution ESI mass spectrometry.



Scheme 1. The synthetic route for the hydrazone switch **1**. DCC = 1,3-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine, DIC = diisopropylcarbodiimide, NMP = *N*-methylpyrrolidone.

The ^{1}H NMR spectrum of **1** in CD_2Cl_2 (Figure 1a) shows a characteristic hydrazone N-H signal at $\delta = 14.72$ ppm, indicating that it primarily adopts the *E* configuration in solution. Based on integration, the *E* to *Z* (minor N-H signal at $\delta = 11.95$ ppm) isomer ratio is 91:9. The addition of trifluoroacetic acid (TFA, 3 equiv) to **1** in CD_2Cl_2 results in its complete protonation (Figure 1b), which is accompanied by a darkening of the solution from light yellow to light brown. The upfield shift of the hydrazone N-H signal (from $\delta = 14.72$ to 13.25 ppm) indicates that the N-H group is now H-bonded to the ester oxygen, i.e., (*Z*)-**1-H**$^+$ is formed. This conclusion is corroborated by the downfield shift of the pyridyl and phenyl ring protons, which indicate the former has been protonated. As for the cholesterol unit, the most prominent shift upon protonation occurs for the proton closest to the pyridyl ring, i.e., proton 9, which shifts from $\delta =$ 4.82 to 4.93 ppm. Upon passing the (*Z*)-**1-H**$^+$ solution through a short plug of potassium carbonate (K_2CO_3), the color immediately reverts to light yellow indicating its deprotonation. We were able to capture a snapshot of this process, and observe the metastable (*Z*)-**1** isomer as it equilibrates back to

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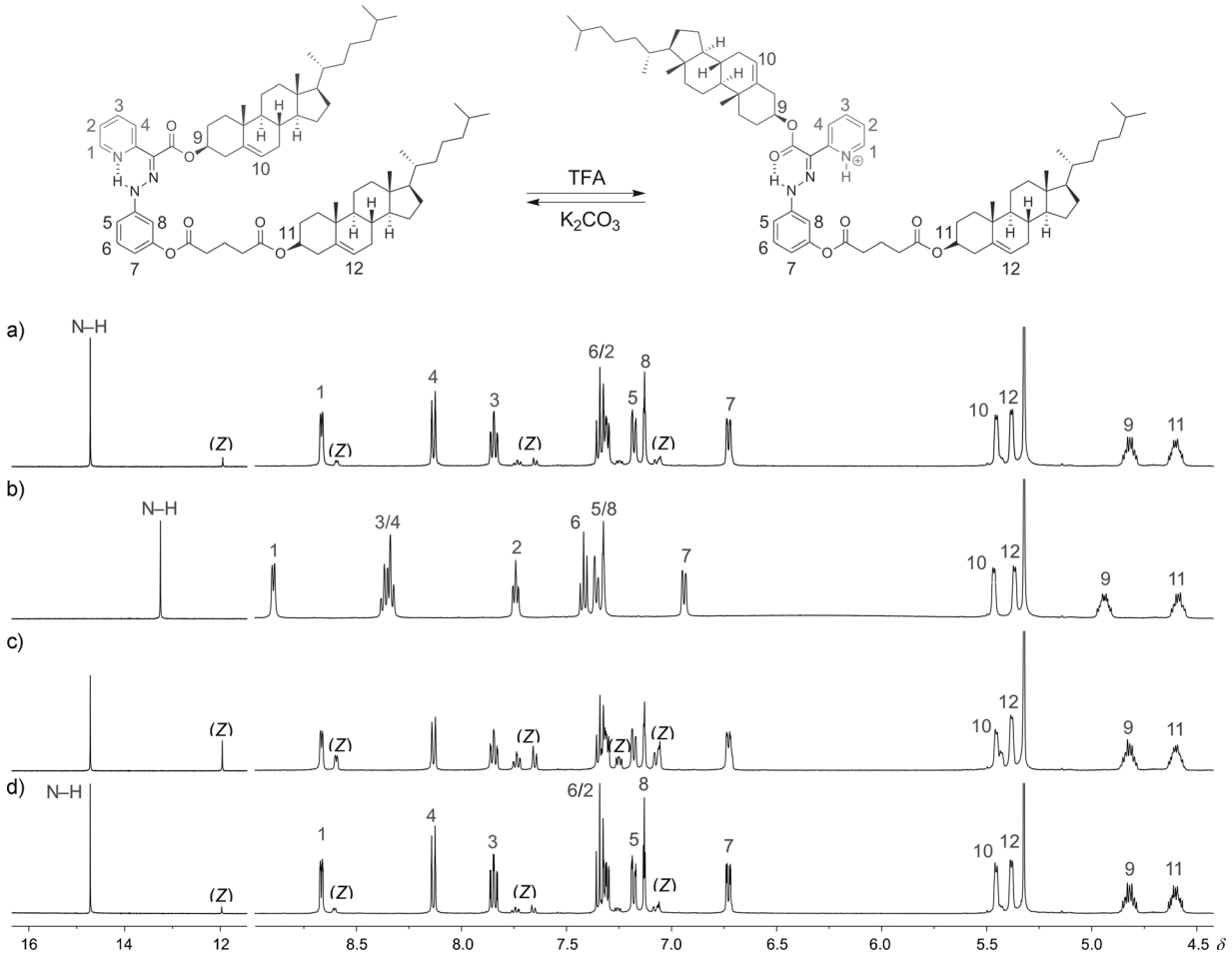

Figure 1. ^{1}H NMR spectra (CD_2Cl_2, 500 MHz, 0.01 M, 298 K) of a) **1** (*E* and *Z* isomers); b) (*Z*)-**1**-H^+ obtained after adding TFA (3 equiv) to **1**; c) a mixture of unequilibrated *E* and *Z* isomers of **1** obtained immediately after passing **1** through a plug of K_2CO_3; and d) **1** after equilibration.

(*E*)-**1** (Figure 1c). The original isomer ratio (Figure 1d) is reached within a few minutes, thereby completing an entire switching cycle. From the evidence described above it is clear that **1**, which is the largest hydrazone switch made so far, is still able to undergo a complete and reversible acid/base-induced *E*/*Z* isomerization.[12]

To better understand the structural changes that **1** undergoes upon switching, DFT calculations (B3LYP-D3/6-31G*)[14] were carried out using a dichloromethane solvent model. A detailed search of conformational and configurational space yielded minimum energy structures for neutral **1** and its protonated analogue (*Z*)-**1**-H^+ (Figure 2). Compound **1** adopts a conformation in which the cholesterol units are oriented in a *syn* fashion. This structural preference may be the result of dispersive interactions between the hydrocarbon chains, resulting in an overall attractive interaction relative to a conformation in which the cholesterol units are oriented *anti* to each other. Protonation effects a dramatic change in structural preference, with the cholesterol units in (*Z*)-**1**-H^+ being oriented *anti* to each other (Figure 2). This change in the conformation of the cholesterol units upon isomerization from **1** to (*Z*)-**1**-H^+ leads to a 10.4% calculated increase in the solvent-accessible surface area.

After establishing the switching cycle of **1** in solution, and having a better appreciation of the associated structural changes, we doped it (5 wt%) in NP5, which is an achiral nematic liquid crystal. As a control, we also doped NP5 with **2** (the rotor moiety of **1**), which can be protonated without inducing a molecular motion. The differential scanning calorimetry (DSC) measurement of NP5 reveals that it exists in nematic phase between −6°C and 72°C (Figure S1 in the Supporting Information). Doping NP5 with **1** or **2** (Figures S2 and S3 in the Supporting Information), results only in slight shifts in the phase transition temperatures (−7 to 71°C and −7 to 70°C, respectively). These data indicate that doped NP5 retains its LC properties. The polarized optical microscope (POM) image of NP5 on an untreated glass slide with a cover slip under cross-polarized view shows a typical Schlieren texture (Figure 3a). **1**/NP5 and **2**/NP5 display the characteristic oily-streak textures of a cholesteric (chiral nematic) phase (Figure 3b and c, respectively). These results indicate that doping the achiral nematic NP5 compound with chiral mesogens **1** and **2** induces the formation of cholesteric liquid crystal organization.

The acid/base switching of **1**/NP5 was studied on untreated glass slides with cover slips and in 90° twisted aligned cells (Figures S5 and S9 in the Supporting Informa-

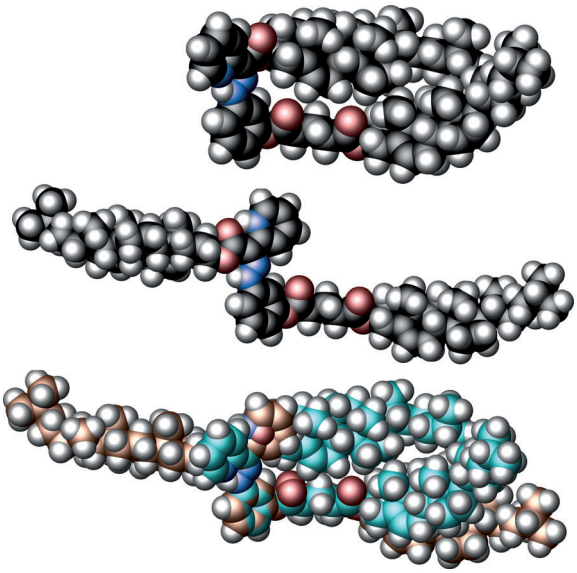

Figure 2. DFT (B3LYP-D3/6-31G*) calculated structures for **1** (top) and (*Z*)-**1**-H^+ (center), and a partial superposition of the two (bottom). At the bottom, **1** is shown in cyan and (*Z*)-**1**-H^+ is shown in brown.

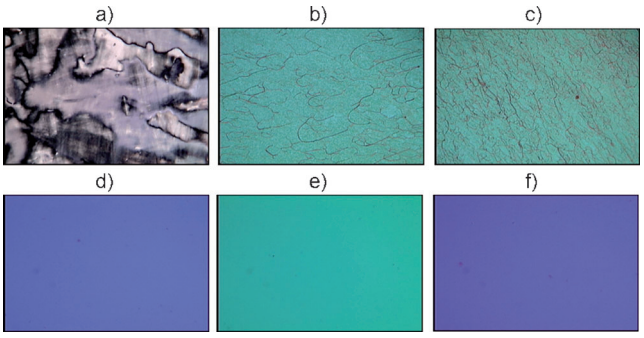

Figure 3. Cross-polarized views of a) NP5, b) **1**/NP5, and c) **2**/NP5, on untreated glass slides with cover slips; d) **1**/NP5, e) **1**/NP5 after exposure to TFA, and f) **1**/NP5 after exposure to TFA, followed by Et_3N, in 90° twisted aligned cells. NP5 was doped with 5 wt% of **1** in the relevant samples.

tion). Initially (Figure 3d), a purple-colored image was observed under cross-polarized view. Adding TFA to the doped LC rapidly changes the reflected color from purple to green, indicating that the helical pitch in **1**/NP5 has changed. We attribute this effect to the surface-area change that accompanies the switching of the dopant from **1** to (*Z*)-**1**-H^+. Subsequent addition of triethylamine to the mixture reverts the color back to the initial purple state, indicating that (*Z*)-**1**-H^+ was deprotonated and subsequently isomerized back to **1**, thus completing a switching cycle.[15] To test our hypothesis that the change in the geometry of **1** upon isomerization is responsible for the modulation of the self-assembly of NP5, we conducted two control experiments. First, we exposed NP5 to TFA followed by Et_3N, which yielded no discernible changes as observed by POM (Figures S4 and S7 in the Supporting Information). We then treated **2**/NP5 with TFA followed by Et_3N, and yet again no appreciable changes were observed by POM (Figures S6 and S9 in the Supporting Information). These control experiments demonstrate that the addition of acid or protonation of the pyridyl group by itself cannot explain the change in color observed upon switching **1**/NP5. More importantly, they show that the isomerization of the hydrazone backbone in **1** is a prerequisite for modulating the long-range supramolecular assembly of the LC. Once the acid-induced rotary motion is transmitted to NP5, it is propagated and amplified, leading to the observed change in readout color.

To have a better understanding of the origin of the observed photophysical changes, we monitored the modulation in selective reflection of the doped LC as a function of added acid and base. The reflection band of **1**/NP5 is centered at ca. 550 nm, and upon protonation with TFA it shifts bathochromically to 640 nm (Figure 4). Subsequent addition

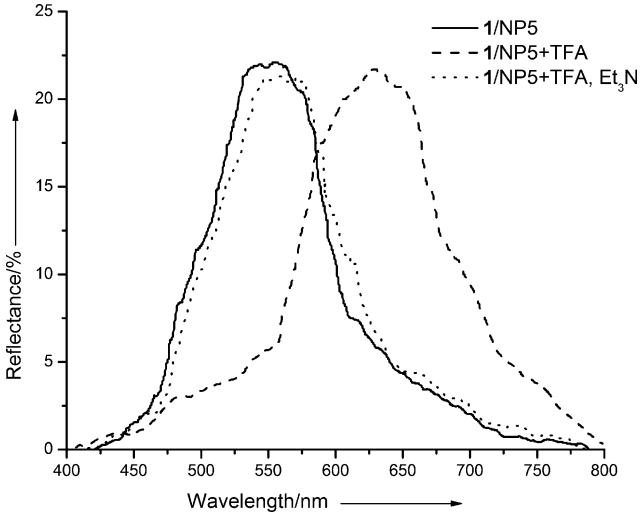

Figure 4. Changes in selective reflection spectra of **1**/NP5 (——) (5 wt% doping) after being treated with acid (-----) followed by base (•••••).

of Et_3N to the system reverts the band to its original position (i.e., 550 nm). In contrast, the reflection band of **2**/NP5 (Figure S10 in the Supporting Information) remains unchanged upon treatment with TFA followed by Et_3N. To verify that the observed changes in selective reflection result from a change in the pitch of the cholesteric LC, we measured the helical twisting power (HTP) of **1** and **2** and their protonated forms in NP5 using Cano's wedge cell method.[16] The HTP of **1** was determined to be 56 μm^{-1} (wt%) and after being treated with TFA, an increase was observed in the distance between the Cano lines, and the value changed to 46 μm^{-1} (wt%). After the addition of Et_3N, the HTP went back to 56 μm^{-1} (wt%), thus completing a switching cycle. However, and similar to the reflection spectra, the HTP of **2** in NP5 did not change, and remained at 58 μm^{-1} (wt%) upon treatment with TFA and Et_3N. Both the selective reflection and HTP measurements support our conclusion that motion at the molecular level is required to effect the observed optical changes in the LC.

In conclusion, we have demonstrated that **1**, a cholesterol-modified hydrazone molecular switch, is a cholesteric meso-

gen that can induce (through doping) the formation of a chiral nematic phase in the achiral LC material NP5. More importantly, we have shown that by doping **1** into NP5 we were able to amplify its motion at the molecular level into an event at the macroscopic level, i.e., the modulation of the color reflected from the LC. This example represents the first use of a chemically activated molecular switch in effecting a response at the microscopic/mesoscopic level in a LC. The advantage of this approach in controlling the photophysical properties of a supramolecular LC is that it relies on controllable molecularly defined transitions, which can be easily tuned. We are currently working on taking advantage of the modularity of the hydrzone-based switch, and the acid/base switching of the LC properties, in designing highly sensitive sensing applications.

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[13] Nematic Phase 5 (NP5) is the commercial name used by Merck Licristal (Merck, Darmstadt) of a eutectic mixture of 1-(4-methoxyphenyl)-2-(4-ethylphenyl)diazene 2-oxide and 1-(4-methoxyphenyl)-2-(4-*n*-butylphenyl)diazene 2-oxide. For details, please see D. J. Margerum, L. J. Miller (Hughes Aircraft Company), EP0056519A2, **1981**.
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[15] This process can be repeated up to three times, after which the accumulation of salts hinders the switching process.
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