Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Irreversible Visual Sensing of Humidity Using a Cholesteric Liquid Crystal

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General:

liquid crystal host E7 was purchased from Merck as a mixture of 4-cyano-4'-n-aryl- and 4'-n-alkylbiphenyl. (R)-(+)-1,1'-Bi(2-naphthol) (material purity 99%, optical purity 99.76% by HPLC) (**1**) was purchased from Alfa Aesar. Dry Triethylamine (TEA), Tetrachlorosilane (TCS) and tetrahydrofuran (THF) were obtained from commercial sources. THF was dried by passage over activated alumina column.[1] Bis-[binaphthylen-(2.2')-dioxy]-silan (**2**) was synthesized according to literature procedure using THF as solvent.[2]

A Varian Mercury instrument operating at 400 MHz spectra was used to record ^{1}H NMR. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane (TMS) as internal standard. UV-Vis transmission spectra were recorded on an Avantes UV-Vis spectrometer with an Avalight-Hal light source and Avaspec-2048 scanner. Optical microscopic analyses were performed with a Leica DM6000D equipped with a digital camera (Leica DFC 420C, Leica Microsystems Ltd.).

Preparation of CLC monitor films and exposure to humidity:

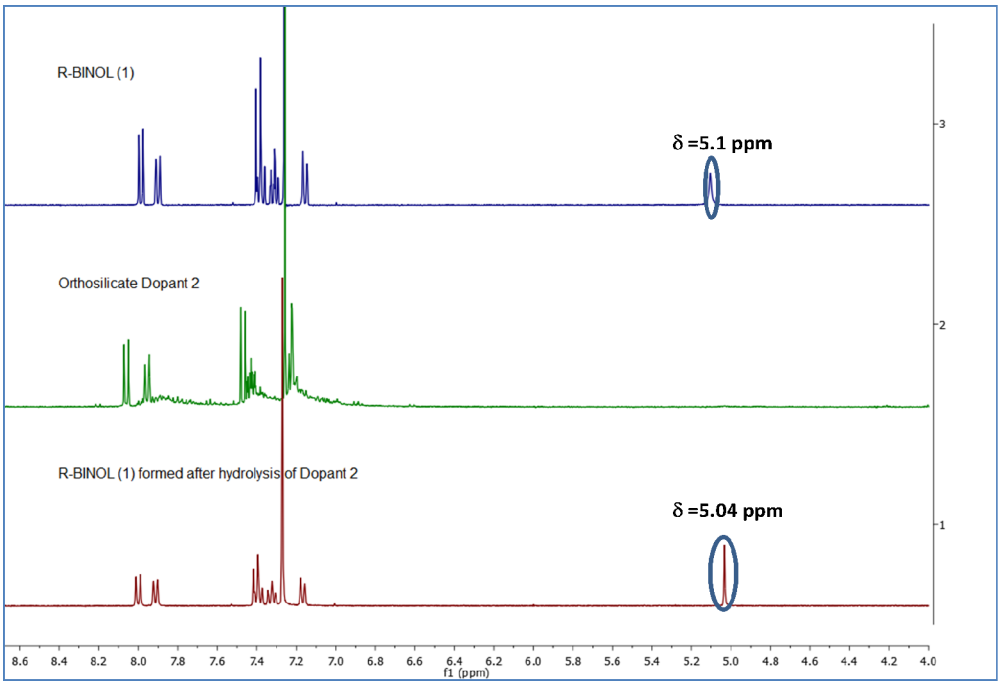
All CLC samples were prepared inside a glove box in a dry nitrogen atmosphere by dissolving chiral dopant **2** in E7 above its clearing point. Sensors were fabricated by coating thin films using wire-bar (RK Print Coat Instruments Ltd., 6 μm and 12 μm) on a uniaxially rubbed triacetylcellulose (TAC, LOFO High Tech Film GmbH) foil. Rubbing was performed with a velvet cloth to induce uniform planar or splay alignment of the liquid crystal molecules. Different relative humidities (RHs) were created by passing dry nitrogen through water and mixing this humid nitrogen with dry nitrogen in various

ratios. The RH of the final gas mixture was measured by using a humidity indicator from Vaisala. CLC films were held inside a chamber (volume ~50 mL), which could be charged with nitrogen of the required RH. Transmission spectra were measured using Avasoft (for AvaSpec-USB2, version 7.3) software.

Measurement of helical twisting power and handedness:

For determination of the pitch using the Grandjean-Cano method,[3] a glass slide was thoroughly cleaned in ethanol, acetone and iso-propanol. The clean glass was spin-coated with polyimide (Optmer AL 1051, JSR, Japan) and allowed to harden in a vacuum oven at 200 ºC and 200 mbar for 2h. The polyimide layer was then planarly rubbed with a velvet cloth to induce parallel alignment of the liquid crystal molecules. A drop of in E7 was casted on the substrate and covered by a pre-coated and planarly rubbed plane-convex lens (R = 516.8 mm from Newport Corporation). The pitch was then determined by measuring the distances between the consecutive Cano lines. The helical twisting power of CLC film with dopant **2** were calculated according to the weight % of the chiral dopants. While determining β according to equations $\lambda = n.p$ and $\beta = (p \bullet ee \bullet c)^{-1}$, the wavelength (λ) was directly determined by transmission spectra and the mean refraction index of E7 host was assumed to be n = 1.6. The handedness of the cholesteric phase was determined using a spectrophotometer (Shimadzu UV 3102-P), measuring transmission of both left and right circular polarized light. From selective transmission of the right polarized light (and reflection of the left handed light) it was concluded that the cholesteric material featured a left handed helix implying that the material has a negative helical twisting power.

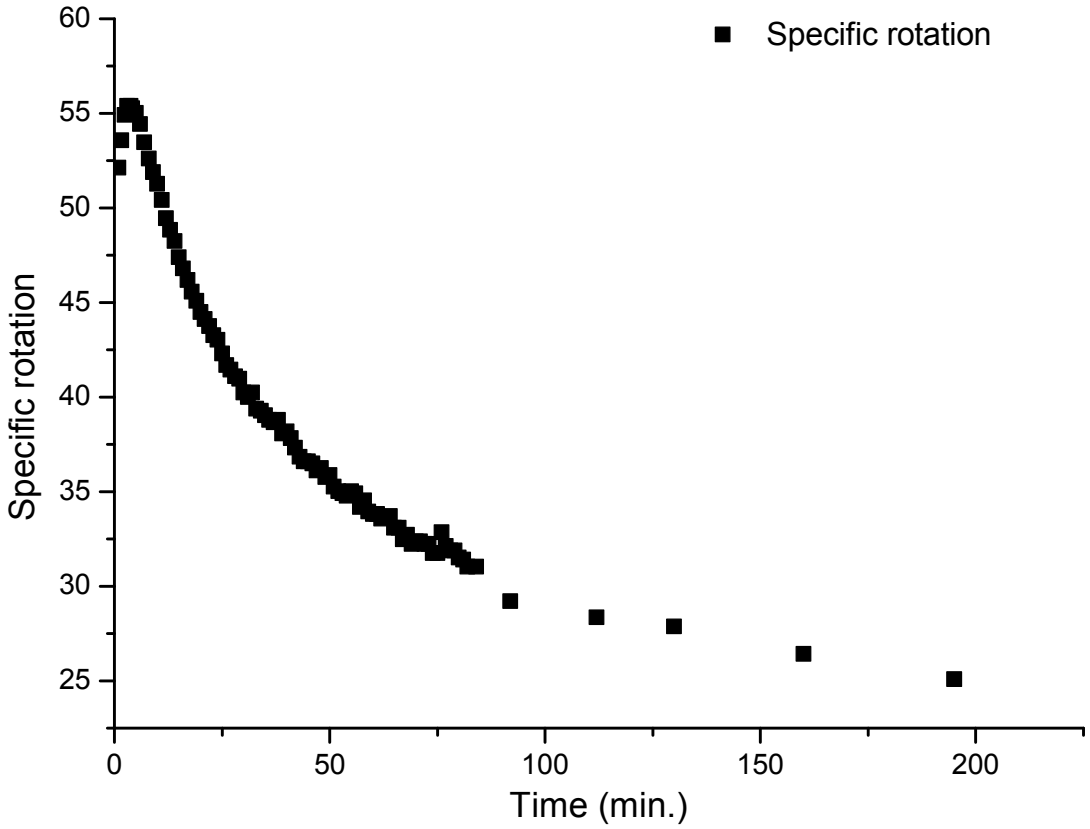
Supporting Figure 1: ^{1}HNMR spectra of dopant **2** (before and after exposure to air) and R–BINOL (**1**) in $CDCl_3$.



Kinetics of hydrolysis of dopant:

33 mg of dopant (2) was dissolved in 3.9 ml THF and instantly the solution was poured in a 1 dm cell. Then the cell was placed in a JASCO digital polarimeter (model no. DIP-370) and the optical rotation of the sample was measured. Then 0.1 ml H_2O were added to the solution and the optical rotation were monitored with time at 27 ^{O}C using a Na D lamp (λ=589 nm). A plot was constructed for specific rotation vs. time. With time initially a sharp increase of specific rotation from +52.12 at 1min. to +55.39 at 3.8 min. was observed then a gradual decrease was noticed to +25.09 at 195 min.

Supporting Figure 2: Plot of specific rotation vs. time for the dopant (2).



References:

1) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, **1996,** *15,* 1518.

2) R. Müller, L. Heinrich, *Chemische Berichte*, **1961**, *94*, 2225.

3) I. Dierking, *Textures of Liquid crystals*, Wiley-VCH, Weinheim, Germany, **2003**.

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