

Photonic NO₂ Gas Sensing with Binaphthyl-Based Dopants

Matthias Spengler, Lukas Pschyklenk, Jochen Niemeyer, Peter Kaul, and Michael Giese*

Dedicated in memory of Professor Carsten Schmuck (1968–2019)

A series of reactive binaphthyl-diimine-based dopants is prepared and investigated with respect to their potential for the chiral induction of structural coloration in nematic liquid crystal mixture E7 and the selective photonic sensing of nitrogen dioxide (NO₂). Studies of the helical twisting power (HTP) in 4-cyano-4'-pentylbiphenyl (5CB) reveal HTP values as high as 375 μm^{-1} and the tremendous impact of structural compatibility and changes of the dihedral binaphthyl angle on the efficiency of the chiral transfer. Detailed investigation of the sensing capabilities of the systems reveals an extraordinarily high selectivity for NO₂ and a response to concentrations as low as 100 ppm. The systems show a direct response to the analyte gas leading to a concentration-dependent shift of the reflectance wavelength of up to several hundred nanometers. Incorporation of copper ions remarkably improves the sensor's properties in terms of sensitivity and selectivity, enabling the tailored tweaking of the system's properties.

their best performance. Phthalocyanine as one of the few liquid crystalline examples has been shown to be suitable for the detection of NO₂ gas already decades ago. In this respect, its semiconducting sensing potential has been extensively investigated.^[4] Although phthalocyanines and their metal complexes (Cu²⁺ and Zn²⁺) can react to low gas concentrations, some examples also cross-respond to other gases or vapors like ammonia or require temperatures above 100 °C to exhibit their full potential.

A common downside of all mentioned approaches alike is that the detection itself requires specialized and elaborate equipment to detect changes in the current, resistance, or UV–vis absorption. The reliable

operation of such devices is inevitably linked to the presence of an electrical energy source that makes an independent operation difficult. Examples of simple techniques for in situ detection that can be easily interpreted are sparse. A simple approach for the direct interpretation of a signal is the observation of a change of the structural coloration of a sample due to an external stimulus. In this respect, liquid crystals (LCs) are well suited due to their flexibility in terms of handling and property tweaking. Often described as the fourth state of matter, these materials combine the molecular order of a crystal with the flow properties of a liquid.^[5] By addition of a chiral additive (dopant) to an LC host, the inherent chirality of the dopant can be transferred onto the superstructure of the host molecules. In case of a nematic LC host system, where all molecules are oriented along one director *N* (Scheme 1), the reorientation occurs in a sense that this director changes direction perpendicular to the molecular axis in a regular fashion leading to the formation of a helical superstructure. The formed chiral nematic or cholesteric liquid crystal (CLC) exhibits completely different photonic properties compared to its nematic parent system. According to Equation (1), the helical structure leads to a selective reflection of circularly polarized light with a wavelength equivalent to the length of the helical pitch (*P*), the average refractive index of the material (*n*_{Avg}), and the angle of incidence (Θ) of the incident light beam (Scheme 1)

$$\lambda_{\text{max}} = n_{\text{Avg}} \cdot P \cdot \sin \theta \quad (1)$$

The ability of a chiral component to induce chirality in a nematic host system can be rationalized by the molar helical twisting power (HTP), β_{M} , which is given by Equation (2)

$$\beta_{\text{M}} = \frac{1}{P \times ee \times \omega} \quad (2)$$

1. Introduction

In the past decade, environmental gas monitoring has attracted significant attention. Especially in urban areas, the concentrations of noxious and climate active gases often exceed critical values. Besides carbon monoxide (CO) and hydrogen sulfide (H₂S), nitric oxide (NO) and nitrogen dioxide (NO₂) are two of the most toxic gases that are harmful for both the environment and biological systems.^[1] The reliable detection of these gases, however, specifically in low concentrations at room temperature is difficult and has been a challenge for scientists. Recent advances in this field are based on semiconducting metal oxides^[2] or metal oxide containing composite materials^[3] that show high sensitivity at low parts per million and parts per billion values, but often cross-respond to other gases (e.g., ammonia or NO) or require elevated temperatures to exhibit

M. Spengler, Dr. J. Niemeyer, Prof. M. Giese
Organic Chemistry and CENIDE
University of Duisburg Essen
Universitätsstraße 7, 45141 Essen, Germany
E-mail: michael.giese@uni-due.de

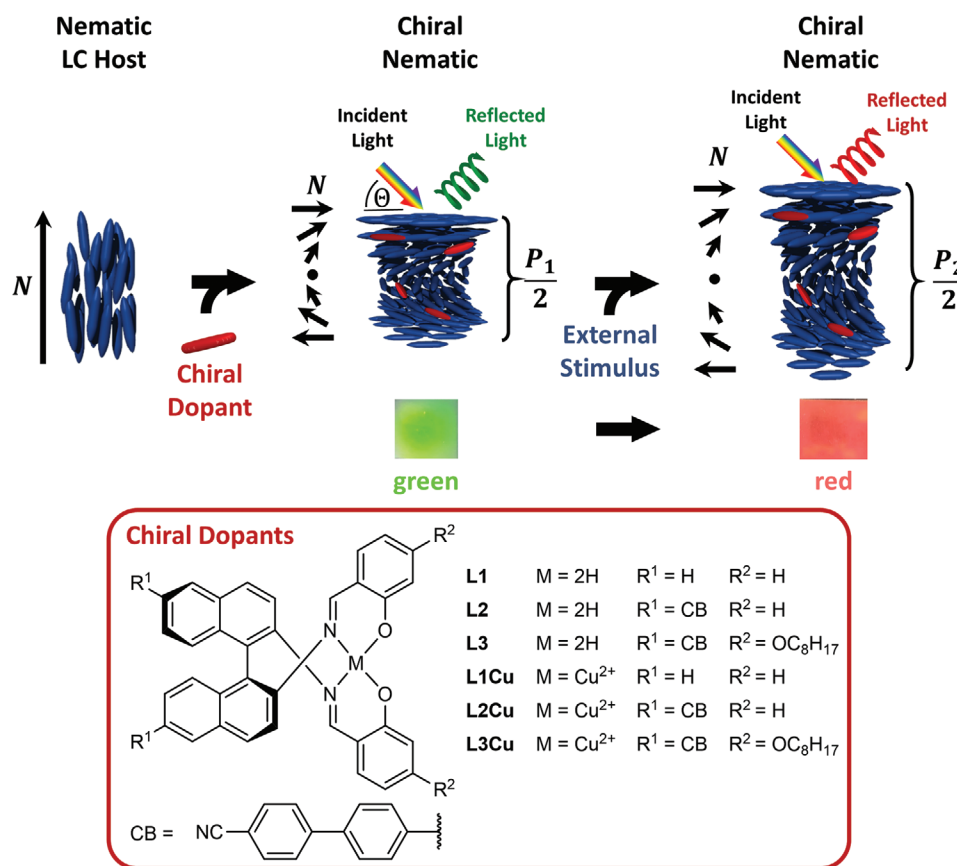
L. Pschyklenk, Prof. P. Kaul
Institute of Safety and Security Research
University of Applied Sciences Bonn-Rhein-Sieg
53359 Rheinbach, Germany



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Scheme 1. Schematic concept for the design of photonic chemosensors by induction of structural coloration.

with P being the helical pitch, ee being the enantiomeric excess of the solute,^[6] The magnitude of the HTP is inherently given by the dopant's molecular structure and strongly depends on the used LC host system and the temperature.

By changing the structure of the dopant due to an external stimulus (e.g., temperature, light, exposure to an analyte), the intrinsic chirality and thus the HTP are affected. A reduction of the chiral transfer leads to an elongation of the helical pitch and a red shift of the reflected light and vice versa.^[7]

CLCs are excellent candidates for sensing applications as they can be easily applied to the surface of a substrate and are independent of electrical energy sources. Recently, Li and co-workers reported on a photoresponsive chiral binaphthyl switch that was used as dopant in nematic 4-cyano-4'-pentylbiphenyl (5CB) to induce and tweak structural coloration across the visible light spectrum depending on irradiation wavelength and temperature.^[8] Due to its intrinsically locked axial chirality, binaphthyl derivatives are especially suitable for the chiral induction in LC host systems.^[9] In this case, the HTP is directly dependent on the dihedral angle between the two naphthalene planes that can be easily altered by straining the molecule.^[10]

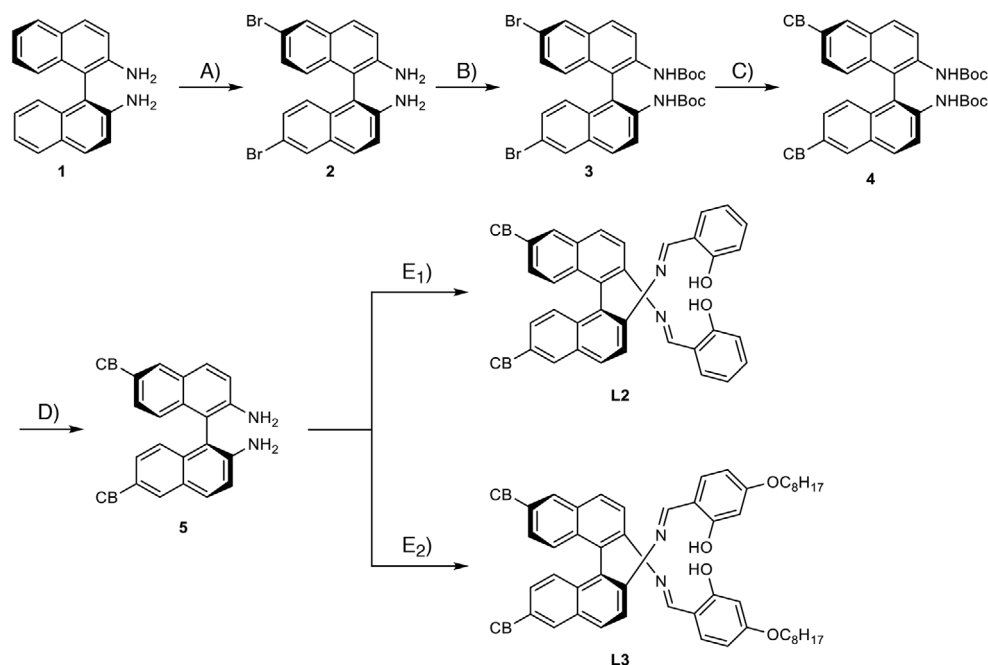
In the present proof-of-principle study, we evaluate the application potential of different tetradentate binaphthyl-diamine (BINAM) Schiff bases L1–L3 and their copper complexes (Scheme 1) as dopants in commercially available nematic liquid crystal mixtures. The systems are investigated with respect to their potential for the photonic sensing of environmentally

hazardous NO₂. Additional experiments using NO, CO, and H₂S give a detailed idea of the selectivity of the sensor systems. As copper(II) complexes are well known to interact with NO₂, these complexes are thought to be suitable reactive additives for selective sensing devices.^[11] By doping nematic LC host E7 (Figure S1, Supporting Information) with a chiral binaphthyl-diimine (BINIM) dopant, structural color can be induced. The interaction of NO₂ gas with the reactive copper(II) complex is thought to cause a structural change of the BINIM, affecting its inherent chirality and inducing a shift of the reflectance peak maximum that can be followed in situ by the naked eye and reflectance measurements. Modulation of the dopant's structure allows to compare the sensor's performance in terms of sensitivity and selectivity and to derive design principles for the optimization of future photonic sensor systems.

2. Results and Discussion

2.1. Synthesis of Chiral Schiff Base Dopants

Tetradentate Schiff base L1 and its copper complex L1Cu were synthesized according to a procedure reported in the literature starting from (*S*)-2,2'-binaphthyl diamine (1).^[12] The synthetic procedures of dopants L2 and L3 are shown in **Scheme 2**. Starting from compound 1, bromination using *N*-bromosuccinimide (NBS) in dioxane at room temperature gave intermediate 2, followed by Boc-protection with sodium hexamethyldisilazide



Scheme 2. Synthetic route for the synthesis of ligands L2 and L3: A) NBS, 1,4-dioxan, 5 h, room temperature, 43%; B) NaHMDS, Boc_2O , THF, 4 h, room temperature, 61%; C) NaHCO_3 , $\text{Pd}(\text{TPP})_4$, CB-BPin, THF/ H_2O (4:1), 97%; D) CF_3COOH , DCM, 2 h, room temperature, 89%; E₁) salicylaldehyde, DCM/EtOH, reflux, 75%; E₂) 4-octyloxysalicylaldehyde, DCM/EtOH, reflux, 88%.

(NaHMDS) and di-*tert*-butyl dicarbonate (Boc_2O) in dry THF.^[13] Protected amine **3** was subsequently coupled with 4-cyanobiphenyl-4'-boronic acid pinacol ester (CB-BPin), which was synthesized according to a literature-known procedure in a Suzuki type reaction to give **4**.^[14] Deprotection using trifluoroacetic acid in DCM and final imine formation with salicylaldehyde or 4-octyloxysalicylaldehyde in a DCM/EtOH mixture yielded ligands L2 and L3 after precipitation from MeOH. Formation of the copper complexes L1Cu–L3Cu was achieved by refluxing the respective ligand with an equimolar amount of copper acetate monohydrate in a mixture of DCM and EtOH and subsequent precipitation from MeOH to remove the excess of acetic acid.^[15]

2.2. Determination of HTP Values

The aim of this study is to evaluate the application potential of the tetradentate binaphthyl Schiff base dopants for the selective detection of NO_2 gas. By doping a nematic LC host system, structural coloration can be induced. The direct interaction of the analyte with the dopant molecule induces a change of the dopant's intrinsic chirality and helical twisting power and thus a change of the structural coloration. For a reliable induction of structural coloration in a LC host system, the used dopants need to exhibit high HTPs and at the same time pose high molecular compatibility with the host molecules. A high compatibility defines how well the host molecules adopt the helical sense of the dopant and transfer it onto the whole LC system. The determination of the HTP values of chiral dopants L1–L3 and their respective copper complexes L1Cu–L3Cu was performed using the Grandjean-Cano wedge cell method (Figure S2, Supporting Information).^[16]

As the HTP of a given dopant strongly depends on the used LC host system and the measuring temperature, we used 4-cyano-4'-pentylbiphenyl (5CB) (Figure S1, Supporting Information) as it is a commonly used system for the determination of HTP values and enables the uniform measurement at room temperature to provide reliable and comparable results.^[17] The results of the HTP measurements are summarized in **Table 1** (see also Figures S3 and S4, Supporting Information) revealing a remarkable increase of the HTP values by tenfold from $29 \mu\text{m}^{-1}$ for L1 to $318 \mu\text{m}^{-1}$ for L3. One aspect that explains the high HTPs is the improved compatibility of guest and host conferred by the CB substituents in 6,6'-positions which leads to a changed alignment of the host molecules with respect to the dopant molecules. Different mechanisms for the induction of chirality in nematic liquid crystals have been described in the past where the molecules either align along the binaphthyl axis (Figure S5A, Supporting Information) or along the CB substituent (Figure S5B, Supporting Information).^[18] Mori et al. proposed another mechanism where the LC molecules orient parallel to the binaphthyl planes explaining the change of the HTP depending on the binaphthyl angle.^[19] It is commonly recognized that the dihedral angle Θ of the binaphthyl subunit plays a key role in the efficiency of the chiral transfer and the induction of the cholesteric pitch.^[18b,20] While both *cisoid* ($\Theta < 90^\circ$) and *transoid* ($\Theta > 90^\circ$) conformations are known to exhibit high HTPs, the values of unsubstituted binaphthyls with a quasi-orthogonal conformation ($\Theta \approx 90^\circ$) are usually significantly lower. This suggests a change of the dihedral angle away from the quasi-orthogonal conformation to angles closer to 0° or 180° due to the functionalization in 2,2'- and 6,6'-positions. Interestingly, the formation of the copper complexes increased the HTPs even further compared to the free ligands, indicating

Table 1. Summary of HTPs of ligands and copper complexes in 5CB.

X	HTP (β_M) [μm^{-1}]	
	LX	LXCu
1	29 ± 0.5^a	32 ± 0.2
2	199 ± 3	230 ± 3
3	318 ± 8	375 ± 6

^a) Determined by measuring a sample with $\omega = 0.5$ mol%.

the formation of a geometrically locked cisoid conformation yielding a stronger chiral transfer (see also Table 1).^[21] This suggests a positive sign of the HTP of the free BINIM (right-handed helix) and a negative sign (left-handed helix) for the copper complexes. With values of 230 and 375 μm^{-1} , the copper complexes of L2 and L3 exhibited extraordinarily high helical twisting powers well exceeding previously reported values of metal complex dopants in different nematic host systems.^[22]

2.3. Tuning of the Photonic Properties

Having determined the HTP values of the chiral dopants, we next tried to induce structural coloration. However, trials to induce structural color in 5CB failed, because the clearing point temperature was significantly reduced, or the LC properties were quenched completely due to the presence of the chiral dopants. Therefore, a detailed study of the effects of different dopant concentrations on the structural color in 5CB was not possible. In this respect, E7 was employed as nematic LC substitute for 5CB, as it is a eutectic mixture of different cyanobiphenyl derivatives with a clearing point at ≈ 60 °C (Figure S1, Supporting Information).^[23] Due to the structural similarity of the two host systems, strong deviations from the results are not expected. For the induction of structural coloration, we doped the nematic LC with different dopant concentrations between 0.6 and 1.6 mol%. Of the used dopants, only L2, L3, and L3Cu

posed high enough HTPs and at the same time, an adequate solubility in the LC host to induce noticeable structural coloration. However, the intensity of the structural color of E7 doped with 1.0 and 1.2 mol% of L2 was significantly lower compared to L3 and L3Cu (Figures S6 and S7, Supporting Information). On the other hand, no significant and visible structural coloration could be observed for dopants L1, L1Cu, and L2Cu as they started to precipitate from the LC mixture at concentrations below 1.0 mol%. This shows that besides the HTP, structural similarity (i.e., similar polarity) of dopant and LC host is another crucial variable that needs to be addressed for the successful induction of structural color. This effect becomes even more essential for dopants with lower HTPs as higher concentrations are needed to induce a helical pitch of similar length. Based on these results, the compatibility of the dopants increases with advancing functionalization in the order $L1 < L2 < L3$ and decreases upon formation of the copper complexes due to higher polarity of the molecule (e.g., $L1 > L1\text{Cu}$, $L2 > L2\text{Cu}$, and $L3 > L3\text{Cu}$). Therefore, the following discussion focuses on systems containing L3 and L3Cu as representative examples. **Figure 1A** shows some representative images of the strong structural coloration of E7 doped with L3 and L3Cu revealing the significant blue shift of the reflected color for higher dopant concentrations. Interestingly, observing the samples under circularly polarizing filters exposes an opposite orientation of the cholesteric arrangement. In fact, L3 induces a helical orientation selectively reflecting left circularly polarized light (L-CPL), whereas the copper complex induces an arrangement selectively reflecting R-CPL. Deußen et al. thoroughly investigated the induction of chirality of 6,6'-disubstituted binaphthol derivatives.^[21a] They not only found a significant correlation of the HTPs with the molecular length of the dopant according to a the longer, the better principle, they also confirmed the induction of an opposing chirality of open-chain (transoid) and closed-bridge (cisoid) binaphthyl dopants. This indicates the presence of two different conformations of ligand and metal complex (Figure 1D,E). While the ligand is predominantly present in an S-transoid conformation inducing the formation of a

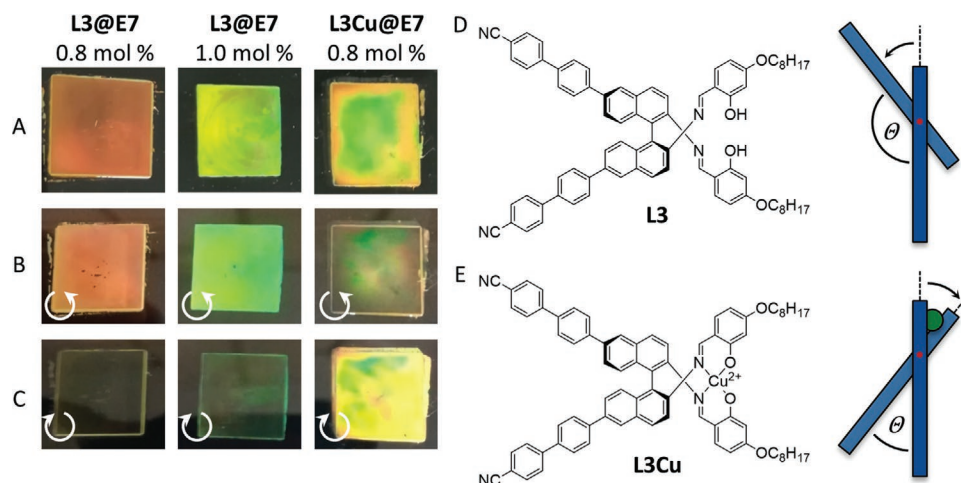


Figure 1. Photographs of the structural coloration of cholesteric LC E7 doped with different concentrations of L3 and L3Cu under A) normal light, B) left circularly polarized light, and C) right circularly polarized light. D) Molecular structure and proposed model of the S-transoid conformation of L3 (left-handed helicity) and locked S-cisoid conformation of L3Cu (right-handed helicity).

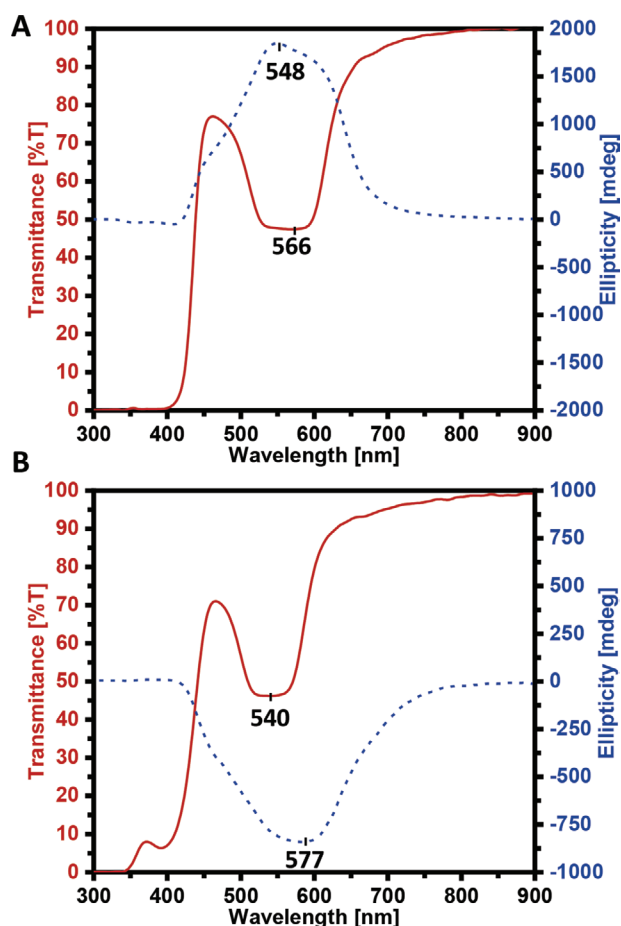


Figure 2. UV-vis (solid line) and CD spectra (dashed line) of E7 doped with A) 1.0 mol% L3 and B) 0.8 mol% L3Cu reveal the opposing helical arrangement with a positive and a negative ellipticity.

left-handed helix (D), the copper ion locks the conformation in an *S*-cisoid conformation supporting the induction of a right-handed helix (E).^[24]

To confirm and quantify these observations, we performed reflectance, UV-vis, and circular dichroism (CD) measurements of E7 doped with 1.0 mol% L3 and 0.8 mol% L3Cu in thin LC films. Although, the homogeneity of the structural coloration was better in L3@E7, both samples showed similar reflectance peak maxima of 598 and 573 nm, respectively (Figure S6F,H, Supporting Information). These findings could be confirmed by UV-vis and CD measurements of the samples (Figure 2) where both revealed similar maxima and proved the opposing helical arrangement with a positive CD signal for L3@E7 (A) and a negative signal for L3Cu@E7 (B). It has to be noted that the maxima found here are slightly shifted with respect to one another due to different experimental setups and the use of a quartz glass substrate.

2.4. Gas Sensing Experiments

The focus of this study was to evaluate the application potential of the chiral copper complex as reactive dopant for the

selective photonic sensing of NO₂ gas. The direct interaction of the analyte molecules with the copper complex will change the chiral structure of the dopant and thereby the HTP of the system yielding a shift of the structural coloration of the CLC. In a previous study, we investigated the optical CO₂ gas-sensing capabilities of encapsulated chiral nematic liquid crystals.^[25] In the present study, we used the same experimental setup for our gas sensing experiments of BINIM-doped E7. The setup allows a continuous recording of reflection spectra while a defined analyte gas concentration is injected into the chamber (see Figure S8, Supporting Information). The sample was spin coated onto a uniaxially rubbed polyvinyl alcohol (PVA)-coated microscope cover slip and placed in the measuring chamber. Before exposing the sample to the analyte gas, the chamber was flushed with synthetic air for several minutes. The response of the system was followed by measuring the shift of the reflectance peak maximum ($\Delta\lambda_{\text{max}}$) as a function of time (min). All experiments were performed under dry conditions using N₂ gas or synthetic air to prevent a response of the systems due to hydrolysis of the imine. To ensure comparability in terms of sensitivity and selectivity, we investigated two samples of E7 doped with 1.0 mol% L3 and L3Cu, respectively, as these dopants exhibited the most uniform structural coloration on the PVA substrate with reflected wavelengths of 613 and 485 nm (Figure S9, Supporting Information).

2.4.1. Sensitivity of the Sensor Systems

Starting with an initial concentration of 1000 ppm NO₂ in N₂, against our expectations, both samples showed a significant and extraordinarily fast response to the analyte gas. Within a few seconds, the reflectance maxima red-shifted for several hundred nanometers. In case of L3Cu@E7, the shift by far exceeded the detection limit of 900 nm of the used reflection probe making a reliable evaluation of the data impossible. Therefore, additional experiments using lower analyte concentrations between 100 and 500 ppm were performed to further elucidate the underlying processes (see Figure 3; Figure S10, Supporting Information). As the performed measurements showed a concentration dependent linear behavior of the reflectance peak shift upon exposure to NO₂, the response rates (nm min⁻¹) were determined from the slope of the linear fit (see Table S1, Supporting Information). Figure 3 displays the response plots (change of the reflectance maximum as a function of time) for experiments using 100 ppm (A) and 400 ppm (B) NO₂ for L3Cu@E7 as representative examples. The results clearly reveal two different processes taking place upon exposure to the analyte gas. At a concentration of 100 ppm, the reflectance maximum slowly and irreversibly shifts to longer wavelengths (see Figure 3A). In contrast, exposure to NO₂ with a concentration of 400 ppm yields a significantly stronger bathochromic shift of 330 nm during the first detection cycle, which shows reversibility with some hysteresis (≈ 70 nm). The change of the initial blue structural coloration of the sample (C) to a red color upon exposure to NO₂ (D) that subsequently reverses to a green color upon purging with synthetic air (E) can be followed by the naked eye.

Interestingly, the L3-doped system also responded to NO₂ gas, which can be attributed to the interaction of the NO₂

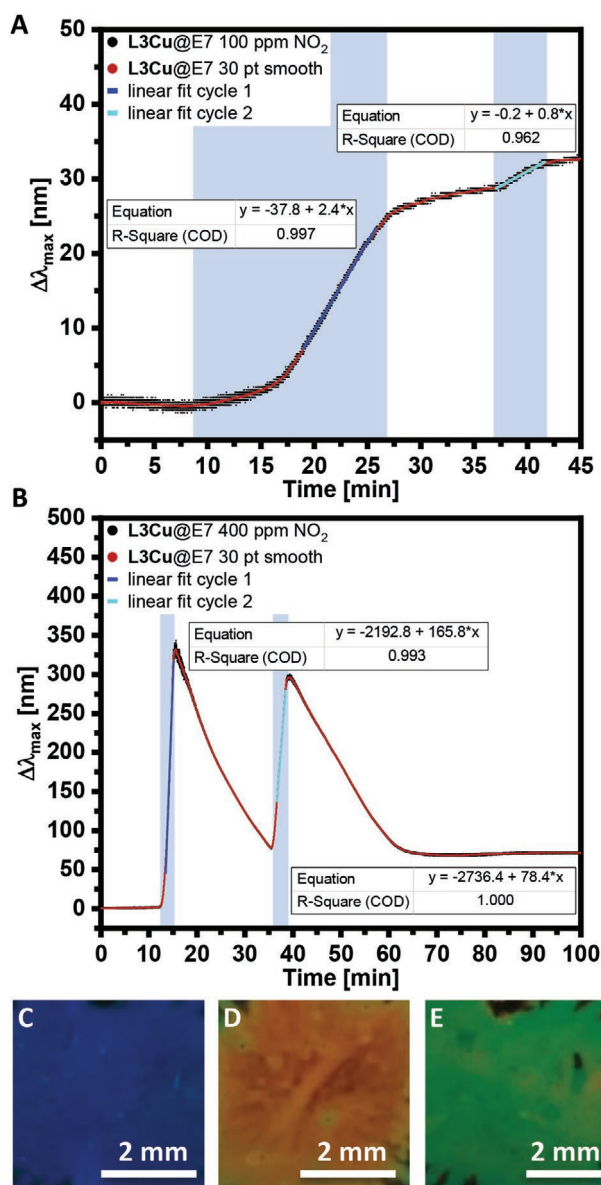


Figure 3. Response plots of 1.0 mol% chiral dopant L3Cu in E7 show the maximum behavior as a function of time upon exposure to NO₂-rich atmosphere (blue regions) and purging with synthetic air (white regions): A) 100 ppm and B) 400 ppm. Real images of a sample C) before and D) after exposure to 500 ppm NO₂ and E) after purging with synthetic air reveal reversible and irreversible changes of the structural coloration.

molecules with the polar HO–N–N–OH cavity of the BINIM dopant which changes the dihedral angle of the binaphthyl unit.^[26] However, the notably weaker response of this system makes it irrelevant for efficient gas sensing at low concentrations (Figures S11A and S12, Supporting Information). We attribute the observed hysteresis of the structural color of the copper system to a strong and partly irreversible coordination of NO₂ to the metal ion at the relatively low temperatures, which induces a change of the HTP value (i.e., dihedral angle) of the dopant. Similar observations have been experimentally

observed for copper phthalocyanine, which showed a strong chemisorption of NO₂ molecules leading to a partly irreversible response at room temperature.^[11b,c,27] These results show that both a reversible and an irreversible interaction of NO₂ with the copper ion takes place. A coordination of NO₂ to the copper ion changes the geometry of the metal complex and thus alters the dihedral angle of the binaphthyl unit that changes the HTP and leads to a change of the structural color of the sample.

To confirm that the response of the sensor system is due to the structural change of the chiral dopants and not caused by the LC host system, we performed a reference experiment (Figure S12B, Supporting Information) using commercially available E8 doped with (*S*)-4-cyano-4'-(2-methylbutyl)biphenyl (CB15, 38.5 mol%, see Figure S1, Supporting Information). In fact, the reference system did not show any response to the analyte gas, proving that the coordination of the NO₂ gas to the ligand system is crucial for photonic sensing.

2.4.2. Selectivity of the Sensor Systems

As L3Cu showed a significant response to NO₂ gas, we wanted to investigate whether the sensor system also cross responds to other toxic and environmentally hazardous analytes. Therefore, we repeated the measurements using NO, CO, and H₂S with concentrations of 500 ppm (Figure S13, Supporting Information). The experiments reveal the remarkable selectivity for NO₂. Measurements with NO show only a slight irreversible shift of a few nanometers proving that the previously observed response of the systems is due to the interaction with NO₂ and not caused by NO impurities (Figure S13A,B, Supporting Information). Also, CO did not induce a shift of the reflectance peak maximum. A noticeable reaction, which allowed a reliable determination of the shift rate, was observed for L3Cu upon exposure to H₂S (Figure 4). After a short equilibration time due to concentration fluctuations inside the measuring chamber, the sample showed a constant red shift of the reflectance maximum with a shift rate of 1.0 nm min⁻¹.

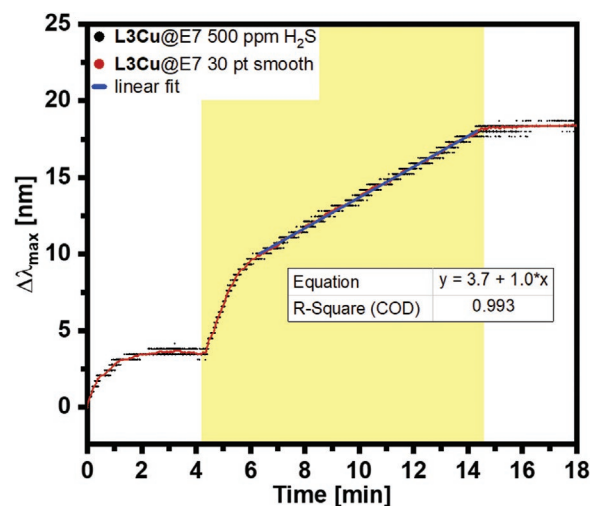


Figure 4. Response plot of E7 doped with L3Cu (1.0 mol%) upon exposure to H₂S with a concentration of 500 ppm.

Like NO₂, H₂S is known to interact with copper ions, making this combination suitable for the selective detection of this toxic analyte.^[1,28] However, in our case, the sensitivity of the sensor system is two orders of magnitude lower compared to NO₂ with the same concentration showing the remarkable selectivity for NO₂. We attribute the observed irreversible shift upon H₂S exposure to a slow metal displacement of the Cu(II) ion by CuS. Sun et al. reported on binaphthol-benzimidazole copper complexes that reacted to different concentrations of H₂S, HS⁻, and S²⁻ in aqueous media and to different concentrations of H₂S in the gas phase by metal displacement of the copper ion and formation of the free benzimidazole ligand causing a permanent shift of the fluorescence signal.^[29]

3. Conclusion

In summary, a series of chiral binaphthyl dopants was synthesized and investigated with respect to their capabilities to induce structural coloration in a LC host and their selective sensing of NO₂ gas. Measurements of the helical twisting powers reveal a remarkable improvement of the efficiency of the chiral transfer with increasing functionalization of the dopants proving the importance of structural and geometrical propagation. With β_M values as high as $\approx 380 \mu\text{m}^{-1}$, the formed copper complexes exhibit some of the highest ever reported HTP values for such materials. The structural modifications not only significantly influence the compatibility with the nematic LC host leading to improved structural colorations across the visible light spectrum using low dopant concentrations but also play a crucial role for the sensing performance of the developed sensor systems. Gas sensing experiments reveal the superior sensitivity and selectivity of the copper complex L3Cu for the reliable, fast, and partly reversible detection of NO₂ gas at concentrations as low as 100 ppm. Reference experiments using alternative environmentally hazardous gases like CO, H₂S, or NO reveal the superior selectivity of the sensor systems. This study paves the way for novel photonic sensing devices for a great variety of analytes. Current follow-up studies focus on the investigation of the sensing performance of a series of related metal complexes in order to develop a photonic sensor array for highly selective and sensitive sensing of hazardous gases.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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