ABSTRACT: A liquid-crystal (LC)-based sensor for detecting nitrite in aqueous solutions was developed using a diazotization reaction as the sensing mechanism. First, tetradecyl 4-aminobenzoate (14CBA) was synthesized and doped into a nematic LC, i.e., 4-cyano-4′-pentylbiphenyl (5CB). When the LC mixture was cast on a glass substrate and then immersed into an aqueous solution without nitrite, the orientation of LC was planar and the LC image was bright. In the presence of nitrite, it reacted with alkylanilines to give corresponding diazonium ions with a positive charge, which aligned at the LC/aqueous interface to cause homeotropic orientation of LC. As a result, a bright-to-dark transition of the LC image was observed. The limit of detection (LOD) of this system for nitrite is 25 μM with high selectivity. In addition, this system can work in environmental water samples such as tap water and pond water. Finally, we demonstrated that the optical signals of LC can be measured and recorded using a built-in digital camera of a smartphone, suggesting the portability of this system for on-site applications.

INTRODUCTION

Nitrite (NO$_2^-$), one of the nitrogen species in the nitrogen cycle, commonly exists in vegetables when nitrogen-based fertilizers are used in agriculture. In addition, nitrite has also been widely used in the food industry as food preservatives. There is no direct evidence to show that nitrite could cause direct harm to the human body; however, it can react with secondary amines to form carcinogenic nitrosamines. On the other hand, nitrite can oxidize Fe$^{2+}$ to Fe$^{3+}$ in hemoglobin, which inhibits the ability of hemoglobin to carry oxygen. Consuming too much nitrite could cause deformities or even direct harm to the human body; however, it can react with secondary amines to form carcinogenic nitrosamines. On the other hand, nitrite can oxidize Fe$^{2+}$ to Fe$^{3+}$ in hemoglobin, which inhibits the ability of hemoglobin to carry oxygen. Therefore, constantly monitoring the concentration level of nitrite in environmental waters is very important and therefore convenient methods that are suitable for routine analysis and on-site applications.25

Precise measurement of ion-selective electrodes relies on regular calibrations of the system to avoid signal drifting and washing of the electrodes to protect them from contamination.23,24 Nevertheless, precise measurement of ion-selective electrodes relies on regular calibrations of the system to avoid signal drifting and washing of the electrodes to protect them from contamination.23,24

Liquid-crystal (LC)-based sensors are the chemical sensors that apply liquid-crystal molecules as the signal reporter. Due to the birefringent property of LCs, LC-based sensors show colorful signals that can be readily interpreted by users without using expensive and bulky instrumentation under ambient light. Therefore, they have been considered as simple and convenient methods that are suitable for routine analysis and on-site applications.25–28

Basically, the detection mechanism of LC-based sensors usually involves a chemical reaction, which uses the target analyte as a reactant. The occurrence of this reaction could lead to reorientation of the LC, such that the texture and/or the color of the optical images of LC are changed as a result. Based on this concept, LC-based sensors have been used for detecting various types of analytes, including macromolecules (e.g., proteins, proteases, virus, and oligonucleotides),29–32 small molecules (e.g., organophosphates, amines, and glucoses),33–35 and cations (e.g.,
protons and metal ions.\textsuperscript{36,37} Nevertheless, the development of the detection mechanism of LC-based sensors for detecting anions is still in its infancy. Specifically, the detection mechanism of LC-based sensors for detecting nitrite has never been explored before.

Among the chemical reactions applied to develop the sensing mechanism for nitrite detection, the Griess reaction, which involves the diazotization reaction followed by azo dye formation, is well-known for the distinct color change after the reagents react with nitrite under acidic conditions.\textsuperscript{38} Therefore, the results can be readily visualized by general users or be recorded by a photometer or a spectrometer. On the other hand, diazotization, which involves only the first step of the Griess reaction, was also used to develop the sensing mechanism for nitrite detection for its high feasibility. Diazotization converts conjugated amines to diazonium compounds in the presence of nitrite, which significantly changes the electron distribution of the \(\pi\)-conjugated system. Therefore, it is often integrated with spectrofluorometric measurements for nitrite detection at low concentration levels. For example, Lu et al. reported an assay for nitrite detection with a limit of detection (LOD) of 18 nM using folic acid, which bears a primary amine group, as the fluorescent probe.\textsuperscript{39} In addition, Li et al. developed an amine-functionalized borondipyrromethene (BODIPY) molecule as the fluorescent probe to detect nitrite with an LOD of 0.65 nM.\textsuperscript{40} To the best of our knowledge, however, the diazotization reaction has never been applied before to develop the mechanism for nitrite detection using LC-based sensors.

In past studies regarding LC-based sensors using an LC/aqueous interface as the sensing platform, amphiphilic molecules with a long alkyl chain were generally applied to align at the LC/aqueous interface to cause the homeotropic orientation of LC in the bulk LC layer.\textsuperscript{41–45} Based on this phenomenon, it is anticipated that when amphiphilic molecules with a long alkyl chain are formed in LC-based sensors with a planar orientation of LC, the orientation of LC will change and the corresponding optical image of LC will change as well. In this work, we developed an LC-based sensor for nitrite detection using alkylanilines as the probes. We investigated how the LC images changed when the diazoization reaction occurred in the LC-based sensors with an LC/aqueous interface. In addition, the structural effect of the alkylanilines on the kinetics of the diazoization reaction was studied, and their effects on the performance of the LC-based sensors were discussed. Currently, a smartphone integrated with a digital camera has been considered as a powerful mobile method for imaging optical signals of chemical sensors and biosensors.\textsuperscript{46,47} Therefore, we fabricated a portable device to load LC-based sensors and recorded the LC images using the digital camera of a smartphone. The performances of the LC-based sensors and other portable methods for nitrite detection were compared as well.

\section*{RESULTS AND DISCUSSION}

\textbf{Diazotization of Alkylanilines.} To examine whether alkylanilines can be applied as the probe for nitrite detection, we mixed 4-decylaniline (10CA) and sodium nitrite in an acidic aqueous solution. The product of this reaction was isolated and identified using \(^1\)H NMR and mass spectra (Figures S1 and S2). Our data showed that a triazene product, (E)-1,3-bis(4-decylphenyl)triaz-1-ene (1), was formed. In this reaction, the diazotization of 4-decylaniline yielded the corresponding diazonium as the intermediate. Because diazonium is not stable, it readily further reacted with unreacted 4-decylaniline to give 1 (Scheme 1). Therefore, the resulting triazene product identified the presence of diazonium in this process. Figure 1 shows the UV–vis spectra of 4-decylaniline and 1. Both molecules exhibited absorption bands localized at \(\sim 240\) and \(\sim 295\) nm attributed to the localized \(\pi-\pi^*\) transition of arylamine. In addition, 1 exhibited an additional absorption band localized at 360 nm attributed to the delocalized \(\pi-\pi^*\) transition of aryltriazene. Based on these results, we believed that 4-decylaniline was able to react with nitrite to form decyl diazonium as an amphiphilic product such that it could be applied as the probe for nitrite detection in LC-based sensors.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure1}
\caption{UV–vis spectra of (a) 4-decylaniline and (b) (E)-1,3-bis(4-decylphenyl)triaz-1-ene.}
\end{figure}

\textbf{Effect of Alkylanilines in LC on the Optical Images of LC.} To develop the detection mechanism of LC-based sensors using alkylanilines as the probes, we have to study how the alkylanilines, when doped in the LCs, affect the optical images of LC in aqueous solutions. Therefore, we doped 1.0, 1.6, and 2.0% decylaniline into the LC, i.e., 4-cyano-4′-pentylibiphenyl (SCB), and then filled the LC mixtures into a copper grid on a dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (DMOAP)-coated slide. After that, the whole system was immersed in deionized water containing 10 mM HCl. Figure 2a–c shows that the LC images were bright when 1.0 and 1.6% decylaniline were doped into the LC, while they were dark when 2.0% decylaniline was doped into the LC. The reason for the bright/dark transition of the LC images could be explained as follows. Decylaniline is a weak base. The \(pK_a\) of...
the conjugated acid of aniline is 4.53. Under acidic conditions, its amine group is protonated to form anilinium ions such that it bears a positive charge on one side and a hydrophobic alkyl chain on the other side. When decylaniline was doped in the LC and immersed in acidic solutions, it protonated and aligned at the LC/aqueous interface due to its amphiphilicity. When the concentration of protonated decylaniline exceeded a critical value, the orientation of LC turned from planar to homeotropic. As a result, a bright-to-dark transition of LC images was observed, as illustrated in Figure 2d,e.

Detection of Nitrite Using LC-Based Sensors. Next, we investigated whether the diazotization reaction between nitrite and decylaniline could be applied to develop the LC-based sensor system for nitrite detection. Here, we selected the LC doped with 1.6% decylaniline, whose LC image is bright, as the sensing layer. In this situation, some of the decylaniline was protonated to align at the LC/aqueous interface, while others were dispersed in the LCs (Scheme 2, left). Decylaniline could react with nitrite to yield corresponding diazonium ions, which could align at the LC/aqueous interface to cause homeotropic orientation of LC (Scheme 2, right) such that a bright-to-dark transition of the LC images was observed, as illustrated in Figure 2d,e.

Detection of Nitrite Using LC-Based Sensors. Next, we investigated whether the diazotization reaction between nitrite and decylaniline could be applied to develop the LC-based sensor system for nitrite detection. Here, we selected the LC doped with 1.6% decylaniline, whose LC image is bright, as the sensing layer. In this situation, some of the decylaniline was protonated to align at the LC/aqueous interface, while others were dispersed in the LCs (Scheme 2, left). Decylaniline could react with nitrite to yield corresponding diazonium ions, which could align at the LC/aqueous interface to cause homeotropic orientation of LC (Scheme 2, right) such that a bright-to-dark transition of the LC images is expected. To investigate this mechanism, we immersed the LC-based sensor into the solutions containing 1 mM NO$_2^-$ and 10 mM HCl. The final pH value of the solutions was 2, which assured the reactivity of the diazotization reaction. The result in Figure 3a shows that the LC image was dark in the presence of NO$_2^-$. In contrast, when we immersed the LC sensor into the solution containing 10 mM HCl only, the LC image was bright (Figure 3b). This phenomenon suggests that the presence of nitrite leads to a bright-to-dark transition of the LC images. In addition, we carried out two control experiments. One of them applied the LC without doping decylaniline, while the other used the solution without HCl. Both results showed bright LC images (Figure 3c,d), which suggest that the diazotization reaction could not occur in this system in the absence of decylaniline or HCl. These results demonstrated that the proposed mechanism using the diazotization reaction could be applied for nitrite detection in LC-based sensors.

Kinetic Study on the Diazotization of Different Alkylanilines. The kinetic information of the chemical reactions involved in a sensor system should relate to its sensing mechanism, which is very important for the optimization of its performance. For this reason, we investigated the effect of the molecular structure of alkylanilines on the kinetics of the diazotization reaction. We monitored the absorbance of the reaction mixture at 360 nm as a function of reaction time using 4-decylaniline (10CA), 4-(decyloxy)aniline (10COA), and decyl 4-aminobenzoate (10CBA) in equal concentrations as the reactants for diazotization. Figure 4 shows a significant increment of the absorbance upon the addition of nitrite within 20 min. After 60 min, only a slight increment was observed. This result suggests that the diazotization of alkylanilines reached equilibrium after 60 min. The increments of the absorbance for the reaction of...
10CA, 10COA, and 10CBA were 0.058, 0.030, and 0.098, respectively, suggesting that the reaction rate of the diazotization for different alkylanilines follows the order 10CBA > 10CA > 10COA. In addition, the isolated yields of the triazine products for the diazotization reaction using 10CA, 10COA, and 10CBA as reactants were 79, 64, and 84%, respectively. Both results implied that 10CBA is a better reactant in the diazotization reaction of alkylanilines because of the higher reaction rate and isolated yield. Such a phenomenon can be attributed to the electron-withdrawing group of 10CBA, i.e., the carbonyl group, which stabilized the corresponding diazonium intermediate and increased the rate and the yield of reaction. To optimize the performance of the LC-based sensors, we selected 10CBA as the probe for NO₂⁻ detection in the following experiments.

**Limit of Detection for Nitrite.** Next, we investigated the limit of detection (LOD) of the system for detecting NO₂⁻ by varying the concentration of NO₂⁻ in the repeated experiments. The doping concentration of 10CBA in SCB was 3.3%, which was determined by the highest concentration of 10CBA that could lead to a bright LC image in the absence of NO₂⁻. This value was larger than that of decylaniline, i.e., 1.6%, suggesting that the pKₐ of the conjugated acid of 10CBA is smaller than that of aniline, and it can be attributed to the additional carbonyl group of 10CBA, which stabilizes deprotonated 10CBA. As a result, more 10CBA was required in this system to cause the optical transition of the LC images. Figure 5a shows that when 10CBA was doped into LC, the optical image of LC was dark when the concentration of NO₂⁻ was 100 μM, and it was partially dark when the concentration of NO₂⁻ was higher than 100 μM. In contrast, the optical images of LC were bright when the concentration of NO₂⁻ was lower than 50 μM. Based on the bright-to-dark transition of the LC image, the LOD for NO₂⁻ was determined to be 100 μM when 10CBA was used as the probe. To study the effect of alkyl chain length on alkylanilines, we synthesized dodecylanilinobenzoate (12CBA) and tetradecyanilinobenzoate (14CBA) and applied them as probes in this system. Figure 5a,b shows that the LODs for NO₂⁻ were 50 and 25 μM, respectively, when 12CBA and 14CBA were used as the probes in this system. These results suggested that a lower LOD was achieved when the alkyl chain on the probe was longer. Previous studies have reported that the amphiphilic molecules with a longer alkyl chain exhibited a stronger anchoring ability in the system using an LC/aqueous interface as the sensing platform and therefore a dark LC image was obtained at a lower concentration of amphiphilic molecules. This phenomenon rationalizes the lowest LOD using 14CBA as the probe because fewer diazonium products were required to cause the bright-to-dark transition of the LC image. Because the LOD of this system was different when 10CBA, 12CBA, and 14CBA were used as the probe, semiquantitative analysis of the NO₂⁻ concentration was performed by arranging three LC-based sensors using different probes in an array format. As shown in Figure S3a, all three LC-based sensors showed a dark LC image when the NO₂⁻ concentration was 100 μM, while the LC of the 10CBA-doped sensor turned bright when the NO₂⁻ concentration was 50 μM (Figure S3b). At the same time, all three LC-based sensors showed a bright LC image when the NO₂⁻ concentration was 10 μM (Figure S3c). Therefore, we can determine the concentration level of NO₂⁻ in aqueous solutions through the number of bright LC-based sensors shown in the array.

**Selectivity of LC-Based Sensors for NO₂⁻ Detection.** The selectivity of the LC-based sensors for NO₂⁻ detection was investigated using the solutions containing other ions for repeated experiments. These ions include some anions, i.e., NO₃⁻, Br⁻, CH₃COO⁻, CO₂⁻, and PO₄²⁻, and some cations, i.e., Mg²⁺, Ca²⁺, Zn²⁺, and Fe³⁺, that could be potential interferences in environmental waters. The results in Figure S4 show that the LC image was dark only in the solution containing NO₂⁻, while the LC images were bright in the solutions containing other anions and cations, suggesting the good selectivity of this system for NO₂⁻ detection. Furthermore, we investigated the interference effect by spiking the above-mentioned ions into the solutions containing NO₂⁻. The results in Figure S5 show that all LC images were dark in the solutions containing NO₂⁻ spiked with equal concentrations of NO₃⁻, CH₃COO⁻, CO₂⁻, PO₄²⁻, Mg²⁺, Ca²⁺, Zn²⁺, and Fe³⁺ and all of the above-mentioned ions, which means that the detection of NO₂⁻ using the LC-based sensor was not affected by other anions or cations coexisting in the solution.

**Detection of NO₂⁻ in Real Water Samples.** To explore the feasibility of this system for practical applications, we performed the experiments using two real water samples, i.e., tap water and pond water. From the bright and dark images of LC shown in Figure 6a, it can be seen that the LOD of this system for NO₂⁻ in tap water is 25 μM. This value is the same as that in deionized water. It is also comparable to the maximum contaminant level of NO₂⁻ in drinking water, i.e., 1 ppm (21.7 μM) set by the United States Environmental Protection Agency (U.S. EPA) or 3 ppm (65.2 μM) set by...
the World Health Organization (WHO).\textsuperscript{49} Therefore, the LC-based sensor developed in this work is suitable for screening the safety level of NO$_2^-$ in drinking water. On the other hand, we noticed that the LOD of this system for NO$_2^-$ in pond water is 100 µM (Figure 6b). This value is higher than that in deionized water and tap water. Nevertheless, it is comparable to the safety level of NO$_2^-$ in aquaculture, i.e., 5 ppm (109 µM).\textsuperscript{50} Overall, our results demonstrated that the LC-based sensors are capable of detecting NO$_2^-$ in environmental water samples.

**Determination of the Signal of the LC-Based Sensors Using a Smartphone.** The above-mentioned LC images were taken using a polarized optical microscope (POM), which is bulky and expensive, thereby limiting the applications of LC-based sensors. In addition, observing the LC images through the naked eye is subjective to personal deviation, which may affect the precision and accuracy of the sensor system. In a recent study, it has been reported that the determination of optical signals of LC-based sensors can be accomplished using a threedimensional (3D)-printed device integrated with a smartphone.\textsuperscript{51} Herein, we investigated whether this approach can be used to record the signals of LC-based sensors for nitrite detection. The schematic illustration and the real image of the device are shown in Figure 7a,b. A 3D-printed device was used to accommodate an LC-based sensor, and then this device was loaded on a magnifier with a clip binder. Next, the system was clipped onto the lens of the digital camera and placed onto a light-emitting diode (LED) light source, as shown in Figure 7c. In such a circumstance, the optical signals of this system were measured in a closed system and the distance between the sample and the light source was fixed such that the interference from ambient light could be eliminated. We loaded this device with different concentrations of NO$_2^-$ in tap water. Figure 7d–h shows that the LOD for NO$_2^-$ is 25 µM. This value is the same as that determined by the LC images captured by POM, suggesting that our observation device could be used to collect the optical signals of LC-based sensors. Nevertheless, we noted that when the NO$_2^-$ concentration was close to the LOD, i.e., 25 µM, the LC image was only partially dark, which makes it ambiguous for the user to determine whether the LC image is bright or dark. To avoid this ambiguity, we measured the average grayscale values of the LC images, and these values are indicated below the LC images in Figure 7d–h. The results showed that the average grayscale values of the LC images for 500, 100, 50, 25, and 0 µM of NO$_2^-$ were 29.2 ± 6.2, 40.6 ± 3.4, 42.3 ± 3.9, 56.2 ± 6.9, and 79.8 ± 4.2, respectively. The plot of the grayscale of the LC images versus the concentration of NO$_2^-$ is shown in Figure 7i. It is obvious that the grayscale value of the LC images decreased significantly when the concentration of NO$_2^-$ increased from 0 to 25 µM. The standard deviation of the average grayscale values for 0 and 25 µM did not overlap. Based on these results, we can determine that the concentration of NO$_2^-$ in tap water was lower than 25 µM when the grayscale value of the LC image was smaller than 63.1 (the largest deviation of the average grayscale values). The results of this method were highly repeatable. In 10 repeated experiments for 500, 100, and 50 µM NO$_2^-$, all of the grayscale values of the LC image were smaller than 63.1. These results also demonstrated that the LC signals of this system can be simply measured and recorded by a portable approach, which is very important for on-site and point-of-care applications. In addition, we found that this system exhibited good stability and reproducibility. Whether the experiments were performed after the LC-based sensors were stored in a dark place at room temperature for 1 month or the experiments were performed by two different individuals in our group, the LOD values of the sensors for NO$_2^-$ detection were the same.

**Comparison of the Portable Methods for NO$_2^-$ Detection.** Finally, we compared LC-based sensors with other portable methods for NO$_2^-$ detection, which are currently adopted in the field of environmental or food analysis. These methods include spectroscopic methods, i.e., UV−vis,\textsuperscript{52} chemiluminescence,\textsuperscript{53} fluorescence,\textsuperscript{54} and electrochemical methods.\textsuperscript{55} The performance characters of these methods are listed in Table 1. The detection time of these methods ranges from 0.5 to 20 min, while that of the LC-based sensor is 30 min. In terms of the LODs, the LOD of spectroscopic methods ranges from 0.13 µM to 1 nM, while the LOD of the electrochemical method is 10 µM. Although the LC-based sensors exhibited higher LOD (25 µM), spectroscopic and electrochemical methods require electrical instrumentation as the detectors, such as a photometer, luminosity meter, and spectrometer. In contrast, the signals of the LC-based sensors can be observed through the human naked eye or be recorded by the built-in digital camera of a smartphone. Regarding the applicable sample types, most of them are applicable to water samples; however, the methods applying specific chemical reactions, i.e., chemiluminescence,
were applicable to more complex samples such as urine. Overall, the LC-based sensors for NO$_2^-$ detection can be performed without sample pretreatment procedures, as well as using electronic instrumentation as the signal detector, which waives the cost of the signal detector of a sensor system. It also allows the LC signals to be processed using image recognition software that could be readily transmitted for data analysis. Moreover, the LOD of the LC-based sensors for NO$_2^-$ detection is acceptable for screening the safety level of NO$_2^-$ in drinking water and pond water. In contrast to spectroscopic and electrochemical methods, LC-based sensors should be a simpler and alternative method for on-site NO$_2^-$ detection.

**CONCLUSIONS**

In conclusion, we applied the diazotization reaction to develop LC-based sensors for NO$_2^-$ detection. The detection mechanism is based on the specific reaction between NO$_2^-$ and alkylanilines to yield the corresponding diazonium at the LC/aqueous interface, which changes the orientation of LC and results in a bright-to-dark transition of the optical signals of LC. Kinetic investigation showed that the alkylaniline bearing an electron-withdrawing group, i.e., a carbonyl group, exhibited the highest reaction rate and isolated yield.

**EXPERIMENTAL SECTION**

**Materials and Instruments.** Decylaniline (10C) was purchased from Alfa Aesar. Sodium nitrite (NaNO$_2$), sodium bromide (NaBr), sodium bromate (NaBrO$_3$), magnesium chloride (MgCl$_2$), calcium chloride (CaCl$_2$), iron(III) chloride (FeCl$_3$), and zinc(II) chloride (ZnCl$_2$) were purchased from Sigma-Aldrich. Potassium carbonate (K$_2$CO$_3$) was purchased from J.T. Baker. Potassium phosphate tribasic (K$_3$PO$_4$) was obtained from a Milli-Q system (Millipore). Real water samples, i.e., tap water and pond water, were collected in the campus of Tamkang University. A Bruker AC-300 FT-NMR spectrometer was used to record the NMR spectra.

**Synthesis of Dodecyl 4-Aminobenzoate (12CBA).** The mixture of 4-aminobenzoic acid (1.00 g, 7.35 mmol), bromododecane (1.82 g, 7.3 mmol), and KHCO$_3$ (1.46 g, 14.6 mmol) was allowed to react in 15 mL of dimethylformamide (DMF) at 100 °C overnight. After cooling, plenty of water was added into the reaction mixture to quench the reaction. The precipitate in the solution was filtered and dried to give 12CBA as a white solid. $^1$H NMR (300 MHz, CDCl$_3$): δ 7.85 (d, 2H, J = 8.6), 6.64 (d, 2H, J = 8.7), 4.25 (t, 2H), 4.03 (br, 2H), 1.25–1.75 (m, 20H), 0.87 (t, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$): δ 166.74, 150.69, 131.52, 120.13, 113.74, 111.25, 64.51, 31.88, 29.61, 29.31, 28.80, 26.05, 25.72, 22.65, 14.08, 5.67. Electron ionization mass spectrometry (EI-MS) (m/z): 305 [M$^+$]; high-resolution mass spectrometry (HRMS) (m/z): calc for C$_{19}$H$_{31}$NO$_2$: 305.2355; found: 305.2356.

**Synthesis of Tetradecyl 4-Aminobenzoate (14CBA).** The synthetic procedures of 14CBA were similar to those of 12CBA. 14CBA was a white solid. $^1$H NMR (300 MHz, CDCl$_3$): δ 7.85 (d, 2H, J = 8.7), 6.64 (d, 2H, J = 8.7), 4.25 (t, 2H), 4.03 (br, 2H), 1.25–1.75 (m, 24H), 0.88 (t, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$): δ 166.74, 150.66, 131.53, 120.19, 113.76, 87.94, 64.52, 31.91, 29.65, 29.58, 29.32, 28.82, 26.07, 22.67, 14.10. EI-MS (m/z): 333 [M$^+$]; HRMS (m/z): calc for C$_{21}$H$_{35}$NO$_2$: 333.2368; found: 333.2662.

**Reaction Kinetics Studied Using UV–Vis Spectrometry.** To a cuvette containing 4-decylaniline (10CA), 4-(decyloxy)aniline (10COA), or decyl 4-aminobenzoate (10CBA) in acetonitrile (3 × 10$^{-5}$ M, 0.6 mL), aqueous solutions of NaNO$_2$ (3 × 10$^{-5}$ M, 0.6 mL) and HCl (3 × 10$^{-2}$ M, 0.6 mL) were added. After mixing, the absorbance of this solution at 360 nm was recorded every 5 min using a Thermo Scientific Evolution 60S UV–vis spectrophotometer. The kinetic plots of the reaction were obtained by plotting the absorbance against the reaction time.

**Isolated Yields of Triazene Products for the Diazotization Reaction.** To a solution of acetonitrile (10 mL) containing HCl (10 mM) and NaNO$_2$ (40 mM), different alkylanilines (0.1 mmol) were added, and the mixture was allowed to react at room temperature. After 1 h, the reaction mixture was filtered and dried over vacuum to give the triazene products as white solids. The yields of the reaction were calculated by dividing the weight of the isolated products by the theoretical yield of the products.

**Preparation of DMOAP-Coated Slides.** To prepare clean slides for surface-coating, glass slides (purchased from Fisher Scientific) were immersed in a solution containing 5% Decon-90 as the detergent for 2 h. To remove the residual detergent, the slides were sonicated in deionized water for 15 min and then rinsed thoroughly with deionized water. To coat DMOAP on the surface of slides, cleaned glass slides were immersed in an aqueous solution containing 0.1% (v/v) DMOAP for 10 min. Finally, DMOAP-coated slides were rinsed with deionized water.
water again, dried under a stream of nitrogen, and then heated at 100 °C in a vacuum oven for 15 min.

**Preparation of LC-Based Sensors.** The copper grids (100 mesh, purchased from Ted Pella) were sonicated in methanol, ethanol, and acetonitrile sequentially for 15 min and then heated at 100 °C for at least 12 h to evaporate the residual solvent. The LC-based sensor was prepared by placing a piece of cleaned copper grid on a DMOAP-coated slide (5 mm × 5 mm), and then, 0.2 μL of SCB doped with different alkylamines was dispensed onto the grid. Finally, the whole LC-based sensor was immersed in the aqueous solution containing different ions. After 30 min, the optical images of LC were captured using a polarizing optical microscope (Leica, Germany) and captured with a charge-coupled device (CCD) camera mounted on the microscope. To record the signal of LC-based sensors using a smartphone, the LC images were captured using a built-in digital camera of a smartphone and their grayscale values were analyzed using ImageJ (an open-source image-processing program). Standard deviations of the grayscale values were determined by 10 repeated experiments.

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