Synthesis and characterizations of C-3-Nitrophenylcalix[4]resorcinarene as a potential chemosensor for La(III) ions

K T A Priyangga¹, Y S Kurniawan¹ and L Yuliati¹,²,*¹
¹ Ma Chung Research Center for Photosynthetic Pigments, Universitas Ma Chung, Villa Puncak Tidar N-01, Malang 65151, East Java, Indonesia
² Department of Chemistry, Faculty of Science and Technology, Universitas Ma Chung, Villa Puncak Tidar N-01, Malang 65151, East Java, Indonesia
* E-mail: leny.yuliati@machung.ac.id

Abstract. C-3-nitrophenylcalix[4]resorcinarene (calix-3NO₂) is a macrocyclic compound with phenolic and nitrobenzene moieties and thus, promising to make a stable complex with a certain metal ion. Due to their high economic value for advanced materials, the detection of rare earth metals such as La(III) ions gains significant attention. In this work, we employed the calix-3NO₂ to establish a simple detection technique for La(III) ions using an ultraviolet (UV) spectrophotometer. The calix-3NO₂ was obtained in 40% yield through a condensation reaction between resorcinol and 3-nitrobenzaldehyde in acidic condition. It was confirmed that the calix-3NO₂ was able to detect La(III) ions in water:methanol media (4:1 v/v) by giving a significant additional peak at 268 nm due to charge transfer between ligand and metal ions. Furthermore, the calix-3NO₂ had selectively bound to La(III) ions compared with other metal ions such as Al(III), Ba(II), Ca(II), Cu(II), Mg(II), Mn(II), Ni(II), Zn(II), K(I), and Na(I). These findings are important in the design of an organic probe used for sensitive detection of La(III) ions using a simple UV spectroscopic technique.

1. Introduction
Due to its outstanding physicochemical properties, rare earth metals are considered as critical materials which are used in various applications, such as green and advanced technologies [1–3]. Lanthanum (La) is considered as one of the most important rare earth metals, which is widely used as a catalyst and energy-storage material [4]. In contrast to the important usage of La, the La ions are only found at the range of 10–300 mg kg⁻¹ concentration in its mineral ore [1]. It was also reported that a trace amount of La ions (La(III)) is often present in the electronic wastes [5]. Considering those significant applications of La in our daily appliances, the recovery of La(III) ions from several sources has been evaluated over the past several years [4–6]. In the recovery purposes, it is necessary to ensure the presence of the La(III) ions in electronic waste. Therefore, the development of sensitive material to detect La(III) ions is critical prior to this recovery process.

Modified graphite materials were reported to be able to detect La(III) ions electrochemically [7]. Even though the successful detection of La(III) ions using the electrochemical method was achieved, it was not established using a UV-Vis spectrophotometer as it gave no significant signal response at 200–900 nm [7]. On the other hand, a spectroscopic method for the detection of metal ions has gained significant interests due to its simplicity and low-cost. It is known that an optical signal can be generated...
after a suitable complexation phenomenon between organic compounds and certain metal ions [8]. Detection of La(III) ions using a fluorescent spectroscopic method has been successfully achieved using organic compounds, i.e. polynedate pyridyl-based quinoxaline derivative as the ligand [9]. In our previous works, we reported a sensitive detection of Fe(III) and Cu(II) ions using UV-Vis spectroscopic technique [10,11]. To the best of our knowledge, sensitive detection of La(III) ions using organic complexation agents by employing UV-Vis spectroscopic technique has not been developed yet.

As great organic complexation agents, calixarenes are supramolecular guest compounds that are easily synthesized through a one-step reaction from the phenolic compound and aldehydes derivatives [12]. The calixarenes-based compounds are well-known for complexation with certain metal ions [13-15]. As examples, calix[4]arene derivatives have been reported for their outstanding discrimination ability for metal ions complexation [12]. Similar to calix[4]arene framework, calix[4]resorcinarene framework was reported to be a suitable organic ligand for metal cations [16].

In this present work, we successfully synthesized one calix[4]resorcinarene derivative, which was C-3-nitrophenylcalix[4]resorcinarene (calix-3NO₂) from a condensation reaction between resorcinol and 3-nitrobenzaldehyde. The structure of the calix-3NO₂ is illustrated in figure 1. The sensing capability of the calix-3NO₂ was then evaluated against La(III), Al(III), Ba(II), Ca(II), Cu(II), Mg(II), Mn(II), Ni(II), Zn(II), K(I), and Na(I) metal ions using the UV spectroscopy.

Figure 1. Chemical structure of C-3-nitrophenylcalix[4]resorcinarene.

2. Experimental section

2.1. Materials and apparatus

The material used in this work were 3-nitrobenzaldehyde (C₇H₅NO₂), resorcinol (C₆H₄O₂), hydrochloric acid (HCl) 37% v/v, ethanol (C₂H₅OH), methanol (CH₃OH), lanthanum chloride (LaCl₃), aluminum chloride hexahydrate (AlCl₃·6H₂O), barium chloride (BaCl₂), calcium chloride (CaCl₂), copper(II) chloride dihydrate (CuCl₂·2H₂O), magnesium chloride (MgCl₂), manganese(II) chloride tetrahydrate (MnCl₂·4H₂O), nickel(II) chloride hexahydrate (NiCl₂·6H₂O), zinc chloride (ZnCl₂), potassium chloride (KCl), and sodium chloride (NaCl), which were purchased from Merck in pro analytical grade. The instrumentations used in this work were Fourier transform infrared spectroscopy (FTIR, JASCO 6800), proton and carbon nuclear magnetic resonance spectrometer (¹H- and ¹³C-NMR, JEOL JNM-ECZ500R/S1 500 MHz), and UV spectrophotometer (JASCO V-760).

2.2. Synthesis and characterizations of calix-3NO₂

The synthesis of calix-3NO₂ was conducted using a similar procedure as reported by Yamin et al. (2014) with several modifications [13]. In general, 3-nitrobenzaldehyde (4.53 g, 30 mmol) and resorcinol (3.30 g, 30 mmol) were dissolved and homogenized in absolute ethanol (75 mL) for 30 min. The HCl 37% v/v (3.0 mL) was then added dropwise into the mixture and the mixture was refluxed at 80 °C for 24 h. After the reaction was completed, the mixture was cooled at room temperature and then the mixture was added with cold distilled water (50 mL) to result in the formation of yellow precipitate. The solid product was washed with a mixture of cold ethanol and water until the filtrate was colorless. After drying at 80 °C for 15 h, the calix-3NO₂ product was obtained as a yellow powder.
The product was characterized using FTIR, ¹H-NMR, and ¹³C-NMR spectrometries. The FTIR spectrum was obtained through an attenuated total reflectance (ATR) method, while the NMR spectrum was recorded in deuterated chloroform containing tetramethylsilane as the internal standard in the solvent.

2.3. Evaluation of calix-3NO₂ as a chemosensor agent for La(III) ions

At first, 20 mg L⁻¹ of calix-3NO₂ was prepared as a stock solution by dissolving its solid product in a distilled water:methanol media (4:1 v/v). The chemosensing ability was evaluated by mixing calix-3NO₂ stock solution (1.5 mL) with a single of various metal ions (i.e. La(III), Al(III), Ba(II), Ca(II), Cu(II), Mg(II), Mn(II), Ni(II), Zn(II), K(I), and Na(I)) solution at a concentration of 20 mM in distilled water:methanol (4:1 v/v) media to reach a total volume of 3 mL. Afterward, the UV spectrum of each mixture was measured with a UV spectrophotometer at 200–400 nm. As a comparison purpose, the absorption spectrum of the calix-3NO₂ was recorded without the presence of metal ions.

The sensitivity test of La(III) ions detection was conducted similarly as mentioned above, but with various concentrations of La(III) ions. The stock solution of calix-3NO₂ (1.5 mL) was mixed with La(III) ions solution (1.5 mL) to give final La(III) ions concentration of 1.25, 2.5, 5, 10, and 20 mM in distilled water:methanol (4:1 v/v) media. The UV spectrum of each mixture was recorded at 200–400 nm.

3. Results and discussion

3.1. Synthesis and characterizations of calix-3NO₂

The calix-3NO₂ was synthesized from resorcinol and 3-nitrobenzaldehyde compounds as the starting materials. Under the acidic condition, both starting materials were reacted to form a cyclic structure of calix[4]resorcinarenes as shown in figure 2. The calix-3NO₂ was successfully synthesized in 40% yield. The successful synthesis was indicated by the disappearance of the C–H aldehyde peaks of 3-nitrobenzaldehyde as the starting material at 2817 and 2713 cm⁻¹ and the appearance of C–H methine peak of the C-arylcalix[4]resorcinarenes at 1428 cm⁻¹ as shown in figure 3. The peaks at 1612 and 1519 cm⁻¹ could be assigned to C=C aromatic stretching, while the N–O stretching and bending peaks were observed at 1351 and 830 cm⁻¹, respectively. The absorption peak at 1199 cm⁻¹ corresponded to the C–O stretching, and the O–H stretching peak of calix-3NO₂ was detected as a broad peak at 3372 cm⁻¹.

![Figure 2. Reaction scheme for the synthesis of calix-3NO₂.](image-url)
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Figure 3. FTIR spectra of resorcinol (red line), 3-nitrobenzaldehyde (blue line), and calix-3NO₂ (black line).

Figure 4. (a) ¹H-NMR and (b) ¹³C-NMR spectra of calix-3NO₂.

The successful formation of calix-3NO₂ was also confirmed by NMR spectroscopy, in which spectra are shown in figure 4. The presence of C–H methine group in calix-3NO₂ was confirmed by a singlet peak at 5.22 ppm on the ¹H-NMR spectra and a peak at 103.4 ppm on the ¹³C-NMR spectra. The detailed assignments of the NMR peaks are shown as followed. ¹H-NMR δ (ppm): 4.89+5.22 (s+s, 4H, –CH– methine), 5.61–6.45 (m, 8H, aromatic protons of resorcinol), 6.75–7.94 (m, 16H, aromatic protons of benzaldehyde), 8.81–9.15 (m, 8H, –OH). ¹³C-NMR δ (ppm): 103.4 (–CH– methine), 119.7+119.8+120.3+122.9+129.1+135.3+147.5+149.0+153.5+154.1 (10 C aromatics). The FTIR and NMR spectra of the synthesized calix-3NO₂ were similar to the literature [13], indicating the successful synthesis of calix-3NO₂.

3.2. Evaluation of calix-3NO₂ as a chemosensor agent for La(III) ions
A good chemosensor agent should be able to give the distinguishable and significant response of the desired metal ion over the other metal ions. Therefore, the sensing ability of calix-3NO₂ was investigated for various metal ions, i.e. La(III), Al(III), Ba(II), Ca(II), Cu(II), Mg(II), Mn(II), Ni(II), Zn(II), K(I), and Na(I). These metal ions were selected to represent trivalent, divalent, and monovalent metal ions. The UV spectra of calix-3NO₂ without and with the addition of various single metal ions are shown in figure 5. While the addition of other metal ions only gave a slight spectrum difference as compared to the spectrum of the free ligand, it was confirmed that the addition of La(III) ions led to the increase in the absorbance intensity of the calix-3NO₂ at the UV region. This remarkable increase in the absorption intensity was also followed by a significant hypsochromic shift from 279 to 268 nm, which was only
observed with the addition of La(III) ions. This shifted peak and increased absorption intensity could be generated from the charge-transfer between La(III) ions and the calix-3NO$_2$ ligand in the solution mixture through electrostatic and cation-π interactions [14,15]. In most cases, the absorbance of a calix compound is low since it can exist in various conformations such as cone, flattened partial cone, 1,2-alternate, 1,3-alternate, or a mixture of them. It was reported that the addition of certain metals could lead to a more stable and rigid conformation, which in turn gave a higher absorbance [17]. In this work, a similar phenomenon was observed where the addition of La(III) was shown to increase the absorbance of the calix-3NO$_2$. The formation of the La(III)-calix-3NO$_2$ complex resulted in a higher molar absorptivity due to the better stability and the more rigidity of the complex than the calix-3NO$_2$. Since such significant increased absorption intensity was not observed when another metal ion was added, this result clearly indicated that the calix-3NO$_2$ was selective for La(III) ions detection over the other metal ions, which would be a great benefit for La(III) ions chemosensing application.

![Figure 5](image1.png)

**Figure 5.** Optical spectra of calix-3NO$_2$ (10 mg L$^{-1}$) without and with the addition of each single metal ions solution at 20 mM concentration.

![Figure 6](image2.png)

**Figure 6.** (a) Optical spectra of calix-3NO$_2$ (10 mg L$^{-1}$) without and with the addition of La(III) solution at 1.25–20 mM concentration, and (b) a linear plot of absorbance at 268 nm vs La(III) ion concentration.

Since the calix-3NO$_2$ was only responsive for La(III) ions, the sensitivity for La(III) ions was further evaluated. When the calix-3NO$_2$ solution was mixed with La(III) ions at a various concentration (1.25–20.0 mM), the optical spectrum of the calix-3NO$_2$ was changed as shown in figure 6(a). As expected, the higher concentration of La(III) ions led to the higher absorption peak intensity in the UV region of 230–320 nm. The absorption peak was blue-shifted from 279 nm to 268 nm with the increase of the
La(III) ion concentrations. When the absorbance value at 268 nm was plotted as a function against the La(III) ion concentration as shown in figure 6(b), a linear plot was obtained with the positive linear correlation ($R^2$) value of 0.9735. This result showed that the absorbance signal of calix-La(III) complexes at 268 nm was reliable enough to be used for the quantification of La(III) ion concentration in the range of 1.25–20 mM.

4. Conclusions
A simple and sensitive sensing technique for La(III) ion detection using the calix-3NO$_2$ in water:methanol media (4:1 v/v) was successfully carried out. The absorbance of calix-3NO$_2$ was increased and blue-shifted from 279 to 268 nm by the addition of La(III) ions. This could be observed as the indication of suitable complexation between the calix-3NO$_2$ and La(III) ions through electrostatic and cation-π interactions. In contrast, the addition of the other metal ions (i.e. Al(III), Ba(II), Ca(II), Cu(II), Mg(II), Mn(II), Ni(II), Zn(II), K(I), and Na(I)) did not give a significant difference in the absorbance spectrum of free calix-3NO$_2$, demonstrating that the calix-3NO$_2$ was a potential chemosensor for La(III) ion detection.

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