Calixarene Hosts Synthesized from Green Chemicals of Vanillin and Syringaldehyde: Fluorescence Probes for Pb^{2+}

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Natural chemicals, vanillin and syringaldehyde were successfully condensed with resorcinol affording two different calixarenes. The ability of these calixarenes obtained from vanillin (V-host) and syringaldehyde (S-host) as the hosts for heavy metal ions (Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+}) was investigated by fluorescence studies. The results show that the fluorescence of the calixarenes was effectively quenched by adding Pb^{2+}, particularly for S-host. The result of Stern-Volmer analysis shows a nonlinear relationship with the Pb^{2+} concentration. The quenching was saturated in the Pb^{2+} range 0.20–1.0 M, indicating the multiassociation of Pb^{2+} with the host. The quenching constant (Ksv) was estimated from the linear region in the range 0.25–2 μM of Pb^{2+} to be 1.2×10^6 M^{-1} for the S-host and 0.22×10^6 M^{-1} for the V-host. Moreover, Benesi-Hildebrand analysis obtained the formation constant (K) to Pb^{2+} and the host, for 1.9×10^5 M^{-1} and 1.2×10^6 M^{-1} at the V- and S-host, respectively. These results indicate that Pb^{2+} was effectively included by the S-host.

Introduction

Chemosensors have attracted much attention in various fields of safety, medical engineering, and industrial processes. In particular, water pollution from industrial discharge is a severe problem all over the world. Because the increasing accumulation of Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} in the environment is a great concern (James and Ramamoorthy, 1984), technological advances in heavy metal diagnosis are required for the development of alternative techniques.

A chemosensor provides information about the quantity of a sample chemical species or class of chemical species. Most of the alternative chemosensing techniques were proposed in the early 1960s, for example, solid electrolyte-type sensor (1961), ion electrode sensor (1961), biosensor basic concept (1962), oxide semiconductor-type gas sensor (1962), and fluorometry (1966) (Seiama, 1988; Murray, 1989).

The fluorescence phenomenon was first described by Brewster in 1838. Because of its high sensitivity and selectivity, fluorescence spectroscopy has been widely used, for example, epifluorescence microscopy and video intensification microscopy. Combined with a fluorescence probe, fluorescent labeled molecules have been developed (Kasten, 1993). Until now, fluorescence chemosensors based on small molecules, including macrocyclic compounds linking fluorophores (Nolan and Lippard, 2008; Jiao *et al.*, 2010), organic-inorganic hybrid fluorescent materials (Ma *et al.*, 2013), polymer-based fluorescence chemosensors (Wang *et al.*, 2013; Lim *et al.*, 2014), nanoparticle luminescent chemosensors (Achatz *et al.*, 2010; Bonacchi *et al.*, 2010) and fluorescence-based sensor arrays (Paolesse *et al.*, 2010), have been reported.

Host-guest processes have been widely investigated because of their numerous applications such as selective separators for chemicals (Caira *et al.*, 2006). Calixarene is a cyclic molecule and is one of the famous hosts for organic molecules and heavy-metal guests (Izatt *et al.*, 1983; Izatt *et al.*, 1985; Yusof *et al.*, 2014) Therefore, calixarene has received much attention in analytical chemistry and is widely used in extraction (Sap *et al.*, 2012), ion recognition (Arora *et al.*, 2007) and ion-selective electrodes (Lu *et al.*, 2002). Generally, this macrocyclic compound can be synthesized from phenols and formyl chemicals in one-step under acid-catalyzed, base-induced or neutral conditions (Gutsche, 1989). Calix[n]arenes, where n stands for the number of aryl groups in the macrocycle with $n = 4$–20 have been synthesized (Gutsche, 1998). In particular, calix[4]resorcinarenes were synthesized from resorcinol and formyl chemicals by acid-catalyzed condensation (Aoyama *et al.*, 1988). Furthermore, several studies have described the effectiveness of calix[4]resorcinarene as a metal-ion extraction agent (van der Veen *et al*, 2001; Ghaedi *et al.*, 2009). The condensation of aromatic aldehydes affords the corresponding cyclic calixarenes. Phenolic hydroxyl groups of the aromatic rings inside the macrocycle cavity act as the hosting functionally and incorporate the guest (Yusof *et al.*, 2013).

On the other hand, natural chemicals such as vanillin with an aldehyde group are obtained from plants. As mentioned previously, environmental protection and environmental cleanup are needed for sustainable development. Therefore, herein, we used natural chemicals as the raw materials for the synthesis of calixarenes with regard to green chemistry. Vanillin (4-hydroxy-3-methoxybenzalde-

hyde) has an aldehyde group, a hydroxyl group, and a methoxy group. This chemical is the primary extract of vanilla bean. Syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde), which can be obtained from spruce and maple trees (Creighton *et al.*, 1941), has an aldehyde group similar to that of vanillin as well as two methoxy groups.

In this study, the green chemicals vanillin and syringaldehyde were used to synthesize new calixarene hosts, and they were evaluated as new fluorophore calixarene hosts or chemical probes for heavy metal ions.

1. Experimental

1.1 Reagents

All the reagents were used as received without further purification. Vanillin was purchased from Sigma-Aldrich Corp. Syringaldehyde, *p*-hydroxybenzaldehyde, and resorcinol were purchased from Tokyo Chemical Industry Co., Ltd. Methanol, ethanol, hydrochloric acid, $Pb(NO_3)_2$, $NiSO_4 \cdot 6H_2O$, $CdSO_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$ were purchased from Nacalai Tesque Inc.

1.2 Synthesis of Calixarenes

Both the calixarenes were synthesized by the condensation reactions shown in **Figure 1**. The reference calixarene was synthesized from *p*-hydroxybenzaldehyde without a methoxy group. Briefly, the vanillin, syringaldehyde, or *p*-hydroxybenzaldehyde (0.125 mol) was reacted with resorcinol (0.125 mol) and 12 M HCl (25 mL) in an ethanol solution (150 mL) at 70°C under nitrogen atmosphere. The reaction mixture was stirred for 12 h, affording in a pink color precipitate. Then, each precipitate was washed several times with hot water and purified by washing twice with methanol and twice with ethanol. The yields of the vanillin calixarene (V-host; 2,18,14,20-tetra(3-hydroxy-4-methoxybenzyl)calix[4]resorcinarene-4,6,10,12, 16,18,22,24-octol), syringaldehyde calixarene (S-host; 2,18,14,20-tetra(3-hydroxy-2,4-dimethoxybenzyl)calix[4]-resorcinarene-4,6,10,12,16,18,22,24-octol) and *p*-hydroxy benzaldehyde calixarene (PH-host; 2,18,14,20-tetra(*p*-hydroxybenzyl)calix[4]resorcinarene-4,6,10,12,16,18,22,24-octol) were approximately 32%, 28%, and 37%, respectively. The chemical structures of V-, S-, and PH-hosts were elucidated using ^{1}H-NMR spectra in deuterated dimethyl sulfoxide (DMSO) and FTIR spectra as follows: ^{1}H-NMR (500 MHz, DMSO) [V-host]: δ 8.31–7.90 (12H, CH, m), 6.40–6.31 (8H, CH, m), 6.15 (12H, OH, s), 5.42 (4H, CH, s), 3.45 (12H, OCH$_3$, s). [S-host]: δ 8.43–7.64 (8H, CH, m), 6.43–6.19 (8H, CH, m), 5.95 (12H, OH, s), 5.44 (4H, CH, s), 3.40 (24H, OCH$_3$, s). [PH-host]: δ 8.83–8.35 (16H, CH, m), 6.60–5.90 (8H, CH, m), 5.41 (4H, CH, s). FTIR (KBr pellet, cm^{-1}): V-host [cm^{-1}]: 3425 (-OH), 3020 (C-H, aromatic), 1618 (C-C, aromatic), 1276 (C-O-C), 1076 (C-O-C). S-host [cm^{-1}]: 3396 (-OH), 2935 (C-H, aromatic), 1616 (C-C), 1220 (C-O-C), 1080 (C-O-C). PH-host [cm^{-1}]: 3385 (-OH), 3014 (C-H, aromatic), 1602 (C-C). In the ^{1}H-NMR spectra of the calixarenes, the peak at δ 5.42 ppm originat-
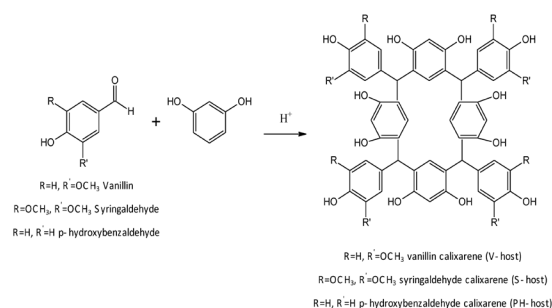

Fig. 1 Chemical structures of vanillin calixarene (V-host), syringaldehyde calixarene (S-host) and *p*-hydroxybenzaldehyde calixarene (PH-host)

ing from the ring current effect indicated the formation of the calixarene ring. Moreover, the peak of aldehyde in the range 9–10 ppm was absent, indicating that resorcinol and each aldehyde reacted and cyclized to afford the corresponding calixarenes. Moreover, the peak of aromatic aldehyde did not appear in the FTIR spectra of V-, S-, and PH-hosts. Furthermore, the hosts were characterized by mass spectroscopy (MS). The molecular weights of V-, S-, and PH-hosts, calix[4]resorcinarenes, were 976 g/mol, 1096 g/mol, and 856 g/mol, respectively. The MS data (reflection mode, positive ion) were obtained using autoflexIII smartbeam (Bruker, U.S.A.). When NaI was used for ionization, the molecular weight of Na (=23) was added to the calculated molecular weight, resulting in the molecular weights of V-, S-, and PH-hosts as 999.244, 1119.576, and 879.384, respectively. The MS data confirmed that V-, S-, and PH-hosts were calix[4]resorcinarenes, not other calix[n]resorcinarenes. These calixarenes were soluble in organic solvents such as acetone, ethanol, methanol, butanol, *n*-hexanol, THF, DMF, and DMSO.

1.3 Fluorescence and absorption spectra in the presence of heavy metal ions

The calixarenes, V-, S-, and PH-hosts, were dissolved in ethanol, and 1.0×10^{-5} M calixarene-ethanol solutions were prepared. The fluorescence spectra of V-, S-, and PH-hosts were measured without and with various metal ions such as Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} in the range from 2.5×10^{-7} M to 1.0 M. The excitation was carried out at 280 nm in each case.

To measure their UV-visible absorption spectra, various heavy metal ions Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} in the concentration range from 2.5×10^{-7} M to 1.0 M were added into a 1.0×10^{-5} M calixarene-ethanol solution.

2. Results and Discussion

2.1 Fluorescence quenching

The calixarene moiety shows a slight fluorescence. Therefore, it is difficult to measure their fluorescence. If the host-guest complexation of these calixarenes results in fluorescence, they can be used as fluorometric sensors. Because calixarene has a phenyl group in the chemical structure, fluorescence is expected because of π–π* transition. **Figure 2**
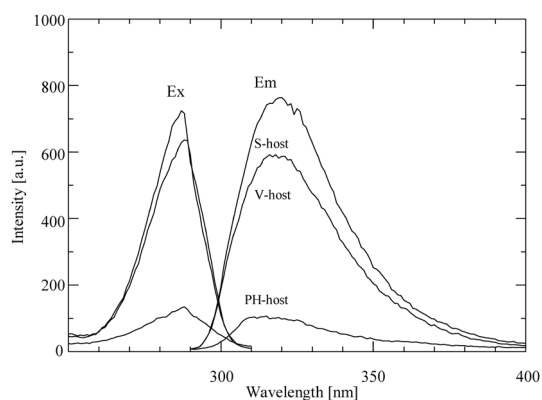
Fig. 2 Fluorescence and excitation spectra of V-, S- and PH-hosts at 1.0×10^{-5} M

shows the fluorescence and excitation spectra of V-, S-, and PH-hosts. Here, the concentration of each host was fixed at 1.0×10^{-5} M, and the excitation wavelength was 280 nm. V- and S-hosts showed a broad peak in the range 290–400 nm with a high emission intensity at 320 nm. PH-host showed a weaker peak than V- and S-hosts. The excitation spectra of the calixarenes are shown as Ex in the figure. The highest peak was observed at 285 nm in each case when 320 nm wavelength was monitored for the fluorescence maximum of the calixarene.

Figure 3 shows the fluorescence spectra of (I) V-host and (II) S-host in the presence of Pb^{2+} ion in the range from 2.5×10^{-7} M to 1.0 M concentration. Apparently, the fluorescence of the hosts was quenched with Pb^{2+}. The quenching was especially effective in S-host for the Pb^{2+}. Moreover,
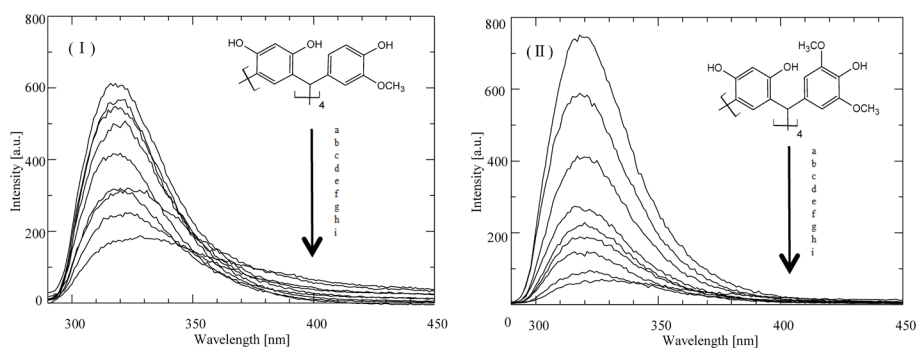

Fig. 3 Fluorescence spectra of (I) V-host and (II) S-host at 1.0×10^{-5} M (a) without Pb^{2+} ion and with (b) 0.25 μM, (c) 0.5 μM, (d) 1 μM, (e) 2 μM, (f) 2 mM, (g) 20 mM, (h) 200 mM, and (i) 1 M Pb^{2+} ion
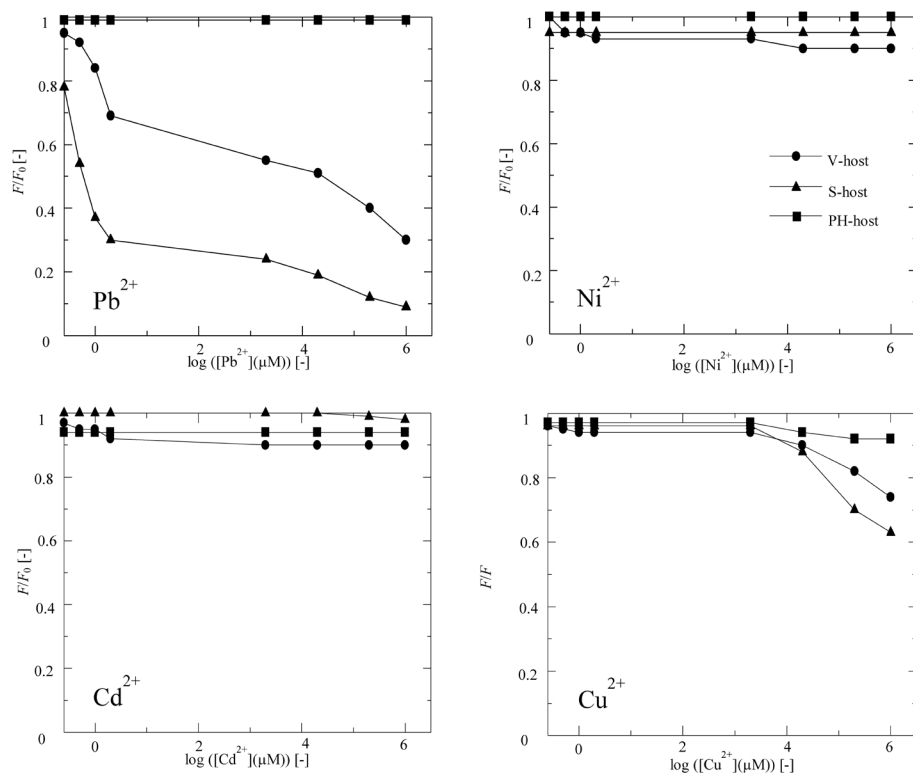

Fig. 4 Fluorescent intensity ratio of calixarenes without and with various metal ions in the range from 2.5×10^{-7} M to 1.0 M. Excitation was carried out at 280 nm in each case

the fluorescence intensity obtained without and various metal ions (Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+}) was measured and then the ratio F/F_0 was calculated for each result obtained at different heavy metal concentrations. Here, F_0 and F were the intensities in the absence and presence of the heavy metal ion. **Figure 4** shows the relationship between F/F_0 and heavy metal-ion concentration. Particularly, in the case of Pb^{2+}, the ratio of F/F_0 intensity changed significantly decreasing S-host fluorescence, but other metal ions did not quench well. Particularly, PH-host without a -OCH_3 group showed less quenching. However, when the concentration was in the range from 2×10^{-3} M to 1.0 M, Cu^{2+} ion showed less quenching of the calixarene fluorescence. This indicates that the difference between PH-host and other hosts bearing a -OCH_3 group can be attributed to the chelation effect between the -OCH_3 group and Pb^{2+}.

2.2 Analysis of Pb^{2+} binding to the hosts

Figure 5 shows the Stern-Volmer plots associated with the fluorescence titration of the calixarenes with Pb^{2+} in the range from 2.5×10^{-7} M to 1.0 M. As shown in Eq. (1), the Stern-Volmer equation can be derived from the fluorescence intensities obtained in the absence and presence of a quencher.

$$\frac{F_0}{F} = 1 + k_q\tau_0[Q] = 1 + K_{sv}[Q] \tag{1}$$

In this equation, F_0 and F are the fluorescence intensities in the absence and presence of the quencher, respectively, k_q is the bimolecular quenching constant, τ_0 is the lifetime of the fluorophore in the absence of the quencher, and Q is the concentration of quencher. The Stern-Volmer quenching constant can be expressed as $K_{sv} = k_q\tau_0$ (Joseph, 1999). The variation in the fluorescence intensity with different Pb^{2+} ion concentration showed a nonlinear response. Thus, the quenching was saturated in the range 0.20–1.0 M of Pb^{2+}. In the linear region between the F_0/F and Pb^{2+} concentration, the quenching constant (K_{sv}) was estimated as 1.2×10^6 M^{-1} for S-host and 0.22×10^6 M^{-1} for V-host. Interestingly, the quenching occurred at lower Pb^{2+} concentrations in the range 0.25–2 μM. The saturated quenching behavior in the Stern-Volmer relationship indicated the multiassociation of Pb^{2+} (Samworth *et al.*, 1988; Valeur, 2002; Htun, 2004). To analyze Pb^{2+} binding to the calixarene hosts, the Benesi-Hildebrand method (Imoto and Onogi, 1997; Bhardwaj *et al.*, 2008) was applied using absorption spectroscopy. Here, the absorption spectra of the host were measured in the presence of Pb^{2+}.

As shown in **Figure 6**, the absorption spectra of V- and S-hosts had an absorption maxima at 283 nm and 286 nm, respectively. When 2 μM Pb^{2+} was added, the UV band intensity due to the phenyl group at 280 nm increased in the presence of Pb^{2+}. However, in PH-host, less change was observed in the UV-visible spectra with increased concentration. Therefore, the absorption intensities of V- and S-hosts measured at different Pb^{2+} concentrations were analyzed for the Benesi-Hildebrand plots (**Figure 7**). The formation con-
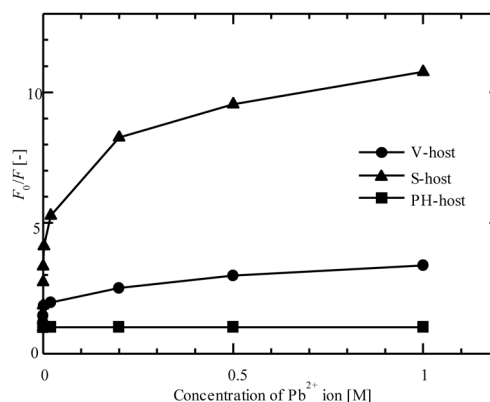

Fig. 5 Stern-Volmer plots associated with the calixarenes and Pb^{2+} ion concentration. F_0 and F are the fluorescence intensities at the maximum emission wavelength. The calixarene concentration was 1.0×10^{-5} M, and the excitation wavelength was 280 nm
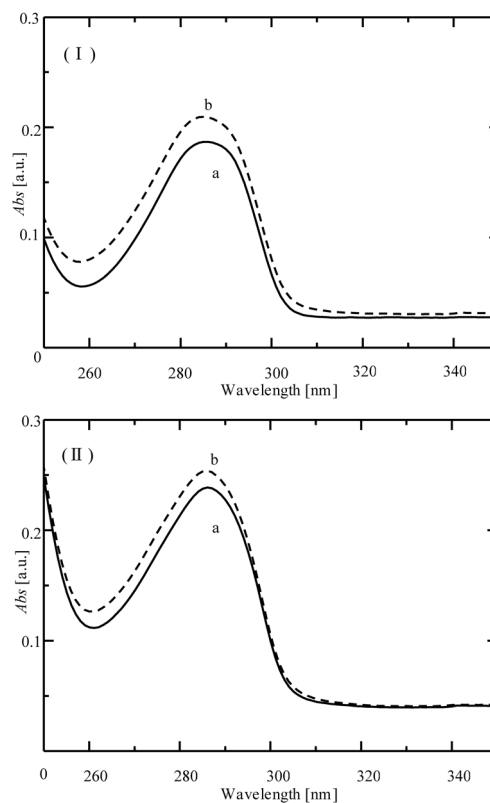

Fig. 6 UV-visible spectra of (I) V-host and (II) S-host at 1.0×10^{-5} M (a) without Pb^{2+} ion and (b) with 2 μM Pb^{2+} ion

stant κ between calixarene and Pb^{2+} was calculated using Eq. (2),

$$\frac{[A]_0 l}{d_A - d_{A0}} = \frac{1}{K_{\varepsilon_c}} \times \frac{1}{[D]_0} + \frac{1}{\varepsilon_c} \tag{2}$$

where d_A is absorbance of calixarene with Pb^{2+}, d_{A0} is the absorbance of calixarene, l is the path length, $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor (calixarene) and donor (Pb^{2+}), and ε_c is the molar coefficient of the complex (calixarene-Pb^{2+}). Using the UV-visible spectra
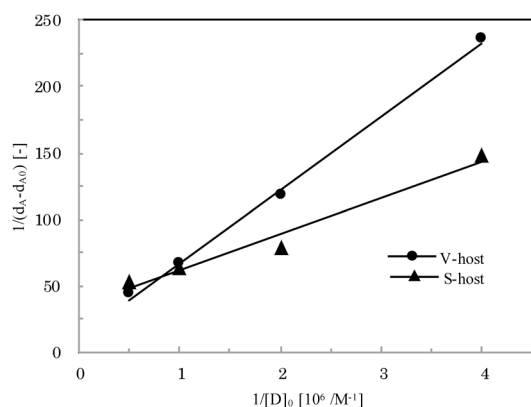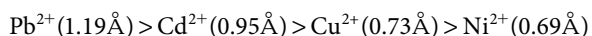
Fig. 7 Benesi–Hildebrand plots of V- and S-host

obtained after the Pb^{2+} addition, $1/(d_A-d_{A0})$ and $1/[D]_0$ were plotted. Here, the slope and intercept of the line were used to evaluate the formation constant κ and molar coefficient ε of the complex, respectively. In V-host, the slope was 6.0×10^{-5}, and the intercept was 11.6. In S-host, the slope was 3.0×10^{-5}, and the intercept was 35.0. The values of κ for Pb^{2+} ion were $1.9\times10^5\,M^{-1}$ and $1.2\times10^6\,M^{-1}$ for V- and S-hosts, respectively. This indicates that Pb^{2+} could be effectively complexed by S-host. In contrast, the change in the absorption spectra in the range 0.25–2 μM confirmed that the quenching was efficient at the lower concentration range. However, a significant spectral change was not observed in these cases in the concentration range. This indicates that the change in the absorption spectra in the range 0.25–2 μM was caused by the interaction of Pb^{2+} with the phenyl ring without and with -OCH_3 groups: the quenching was not due to the Pb^{2+}-calixarene interaction with the -OCH_3 groups. Thus, the quenching occurring in the lower concentration range can be attributed to Pb^{2+} hosting in the calixarene cavity. Then, the multiassociation of Pb^{2+} occurred by interacting with the -OCH_3 phenyl groups of the calixarene.

In addition to a novel ion-exchange mechanism and the chelate effect, the quenching of calixarenes can be explained in terms of the size of the heavy metal ion for the hosts. The size of the heavy metal ions used in this study followed the order:

$$Pb^{2+}(1.19\,\text{Å}) > Cd^{2+}(0.95\,\text{Å}) > Cu^{2+}(0.73\,\text{Å}) > Ni^{2+}(0.69\,\text{Å})$$

A comparison of the metal diameter and host cavity size shows that Pb^{2+} had an ion radius of 1.19 Å (six coordination number), and the capacity of calix[4]resorcinarene was 2.59 Å (Gutsche, 1989). Clearly, a comparison between V- and S-hosts shows that the quenching behavior of Pb^{2+} was caused first by interactions of -OCH_3 groups for the multi-association. Thus, the Pb^{2+} ions could access the phenolic hydroxyl groups and formed host–guest complexes. Notably, Cu^{2+} ions with a smaller ion diameter than Pb^{2+} ions exhibited quenching only in the range 0.20–1.0 M. Because of the smaller ion size of Cu^{2+}, the high concentration might be responsible for the interactions between -OCH_3 groups and Cu^{2+}.

Conclusions

V- and S-hosts were successfully synthesized from natural sources, vanillin and syringaldehyde, and used to study the chemical interactions with Pb^{2+} by fluorometry. The UV absorption intensity of the phenyl ring of the calixarene varied when the concentration of each added heavy metal ion was increased, particularly for Pb^{2+}. The results indicated that the fluorescence behavior showed the multiassociation of Pb^{2+} in the calixarene hosts prepared from plant sources.

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