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Complex formation of light and heavy lanthanides with DGA and DOODA, and its application to mutual separation in DGA-DOODA extraction system

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Abstract

We studied the stepwise formation constants (β) of water-soluble diglycolamide (DGA) and dioxaoctanediamide (DOODA) for the mutual separation of Ln in a solvent extraction system. TODGA (*N,N,N',N'*-tetraoctyl-diglycolamide) and DOODA(C8) (*N*,*N*,*N*',*N*'-tetraoctyl-dioxaoctanediamide) exhibit opposite behaviors in extracting both light and heavy Ln through Ln-patterns. Metal complexes of two- and three-folding with water-soluble DOODA and DGA, respectively, were found, and each β value was calculated using distribution ratios. Taking β, their distribution ratio, D, and separation factor, SF, values into consideration, the suitable separation conditions (aqueous phase: 30 mM DOODA(C2) in 1 M HNO_3; organic phase: 0.1 M TODGA in *n*-dodecane) of multistage

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extraction (10 × 10 extraction using aqueous and organic phases, including one sample solution) were determined. In this study, La, Pr, and Nd were mainly present in the aqueous phase, whereas Sm–Dy existed in the organic phase. Although these two groups can be easily separated into two phases, the resolution, *Rs,* values provide for little mutual separation between La–Nd and Sm–Dy under the present conditions.

Keywords

TODGA, DOODA, Ln, Solvent extraction, Mutual separation

Introduction

High-level radioactive waste (HLW) generated in the nuclear fuel cycle contains various useful elements, such as platinum group metals and lanthanides (Ln), and a hydrometallurgical method has been developed to recover these metals in this field [1-5]. Radioactivity in HLW mostly arises due to Ln such as Sm-151 (half-life: 90 y), Eu-152 (15.537 y), and Eu-154 (8.593 y). Therefore, the separation of light Ln from heavy Ln will result in short storage times to diminish their radioactivity; this will require viable disposal methods. The recovery of Ln from HLW and industrial waste is important, since Ln are essential components in the production and development of cutting-edge products such as magnets, high-temperature superconductors, and laser devices [6-8].

With a growing demand for Ln in the recent decades, their market value has also seen an increase owing to highly uneven distributions [9]. Consequently, the recycling of Ln from urban mines has become an important subject. Furthermore, all Ln possess the same stable oxidation state (+3) and have similar ionic radii [10], making it difficult to obtain Ln ions individually. Therefore, the development of efficient mutual separation and purification techniques is crucial. Methods for the mutual separation of Ln are generally used in chromatography, where solvent extraction is one of the most powerful tools to recover Ln for industrial use. Various extractants including organophosphorous compounds and β-diketones have been developed [11-16].

Diglycolamide (DGA) is a neutral tridentate ligand that contains two amidic groups and one ether oxygen atom; this oxygen atom may coordinate with metal ions. Thus, DGA was introduced as a strong extractant of Ln and actinides from HNO_3, and its properties and extraction capacity have been widely investigated [17-19]. The length of the alkyl groups attached to the amidic nitrogen of DGA compounds affects their hydrophilicity and lipophilicity. Although bulky substituents may show steric hindrance, DGA with long alkyl chains show high solubility in hydrocarbons, such as *n*-dodecane. *N*,*N*,*N*',*N*'-tetraoctyldiglycolamide (TODGA) (**Figure 1**) is a member of the DGA family and is a well-known extractant for Ln. On the other hand, *N*,*N*,*N*',*N*'-tetramethyldiglycolamide (TMDGA) and *N*,*N*,*N*',*N*'-tetraethyldiglycolamide (TEDGA) are highly soluble in water; thus, they may be utilized as masking agents for Ln. Dioxaoctanediamide (DOODA), shown in Figure 1, is a tetradentate ligand with two ether oxygen atoms introduced into the carbon chain connected to diamide groups [20], which allows for the extraction of Ln from HNO_3. Narita et al. found that Ln are more extractable in DGA than in DOODA [21] because of the larger central frame of DGA. DOODA-like DGA changes its hydrophilicity depending on the length of the alkyl chains. Thus, *N*,*N*,*N*',*N*'-tetraethyldioxaoctanediamide (DOODA(C2)), which contain ethyl groups, may be used as the masking agent while using *N*,*N*,*N*',*N*'-tetraoctyldioxaoctanediamide (DOODA(C8)), which has octyl groups, as the extractant of Ln.

A DGA extractant is well known to have a selectivity for heavy Ln, while DOODA has a preferable extraction for light Ln. Both reagents may be used in the aqueous and organic phases of a certain extraction system simultaneously, where one acts as the extractant and the other as the masking agent. Although this method may enlarge the separation factors (SF) and is useful for recovering Ln individually, very few approaches to the mutual separation of Ln are used currently [22,23].

Batchwise multistage extraction is classically called the Craig extraction method [24,25]. Recently, this method was widely reported by our group [26,27]. Although the batchwise multistage extraction method lacks the flow of aqueous and organic phases, it is advantageous since the experiment can be performed by one person with a small amount of sample solution and without the need of a special device such as a mixer settler. To achieve a high efficiency of the mutual separation of Ln, multistage extraction is essential. Throughout multistage extractions, the yield and removal ratios were obtained and the suitable distribution ratio (*D*) and SF values could be determined.

In this study, both DOODA and DGA reagents were used in an extraction system to obtain a high SF of Ln. Following the stability constants of DGA or DOODA and determining the suitable conditions, 14 Ln underwent batchwise multistage extraction to obtain the extraction curves. Considering the recovery and selectivity of Ln, this method is discussed in terms of its applications.

Experimental

Chemical reagents

An aqueous solution of Ln^{3+} was obtained from a 1000 ppm standard solution (FUJIFILM Wako Pure Chemical Corporation, for atomic absorption standards). HNO_3 (Kanto Chemical Co., Inc., guaranteed grade) and *n*-dodecane (FUJIFILM Wako Pure Chemical Corporation, guaranteed grade) were used without further purification. Over 98% pure TMDGA, TEDGA, TODGA, DOODA(C2), and DOODA(C8) (Figure 1) were sourced from FUJIFILM Wako Pure Chemical Corporation. Ultrapure water (18.2 MΩ·cm) obtained from a Milli-Q (Advantage A10, 5 Millipore Corp.) was used throughout this study.

Solvent extraction

Aqueous (0-500 mM DOODA(C2)/1 M HNO_3, 0-200 mM TMDGA/5 M HNO_3, and 0-200 mM TEDGA/5 M HNO_3) and organic (0.1 M TODGA and 0.5 M DOODA(C8)/*n*-dodecane) solutions were equilibrated through shaking (SIC-320LW, AS ONE) (2000 rpm, 1-20 min, 25 °C) and centrifugation (Himac CT40, HITACHI) (2000 rpm, 2 min, 25 °C). Subsequently, the equilibrated aqueous solutions were used to prepare Ln^{3+} (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) containing solutions. These resulting solutions were then mixed with the prepared organic solutions in a 1:1 volume ratio, to be shaken and centrifuged in a plastic tube (3 mL). After phase separation, the concentrations of Ln^{3+} in the aqueous phases were determined using ICP–AES (SPS3100, Seiko Instruments Inc.) and ICP–MS (SPQ 9000, Seiko-EG&G). The separated organic phases were decomposed using a mixture of HNO_3 and $HClO_4$. The residues were dissolved in diluted HNO_3 and the Ln^{3+} concentrations were determined. The distribution ratio, D, is then determined using the Ln^{3+} concentration in the aqueous, $[Ln^{3+}]_{aq}$, and organic phases, $[Ln^{3+}]_o$, as seen in equation (1) below:

$$D = \frac{[Ln^{3+}]_o}{[Ln^{3+}]_{aq}} \tag{1}$$

Calculation of apparent stability constant values

An apparent stepwise formation constant, β, is taken from the coordination of the masking agent with Ln^{3+} in the aqueous phases. To determine β, theoretical equations are derived as follows, using TODGA extraction with a masking agent, DOODA, as a representative extraction system. First, the reaction in the aqueous phase that produces a $Ln(DOODA)_m$ metal complex is expressed in equation (2). The stepwise formation constant for this reaction, β_m, can then be expressed as equation (3). Given that the organic phase has $Ln(TODGA)_n$ as its chemical species, the distribution ratio, D, can be expressed as equation (4). This can then be transformed into equation (6) by utilizing the distribution ratio without the masking agent, D_0, as defined in equation (5). Taking the logarithm of equation (6), we finally obtain equation (7). This equation allows for the calculation of β from the distribution ratios D and D_0 using the least squares method.

$$[Ln^{3+}(NO_3^-)_3]_{aq} + m[(DOODA)]_{aq} \rightleftarrows [Ln^{3+}(DOODA)_m(NO_3^-)_3]_{aq} \tag{2}$$

$$\beta_m = \frac{[Ln^{3+}(DOODA)_m(NO_3^-)_3]_{aq}}{[Ln^{3+}(NO_3^-)_3]_{aq}[DOODA]_{aq}^m} \tag{3}$$

$$D = \frac{[\mathrm{Ln}^{3+}(\mathrm{TODGA})_n(\mathrm{NO_3}^-)_3]_\mathrm{o}}{[\mathrm{Ln}^{3+}(\mathrm{NO_3}^-)_l]_\mathrm{aq} + [\mathrm{Ln}^{3+}(\mathrm{DOODA})(\mathrm{NO_3}^-)_3]_\mathrm{aq} + \ldots + [\mathrm{Ln}^{3+}(\mathrm{DOODA})_m(\mathrm{NO_3}^-)_3]_\mathrm{aq}} \tag{4}$$

$$D_0 = \frac{[\mathrm{Ln}^{3+}(\mathrm{TODGA})_n(\mathrm{NO_3}^-)_3]_\mathrm{o}}{[\mathrm{Ln}^{3+}(\mathrm{NO_3}^-)_3]_\mathrm{aq}} \tag{5}$$

$$D = \frac{D_0}{1 + \beta_1[\mathrm{DOODA}]_\mathrm{aq} + \ldots + \beta_m[\mathrm{DOODA}]_\mathrm{aq}^m} \tag{6}$$

$$\log D = \log D_0 - \log(1 + \beta_1[(\mathrm{DOODA})]_\mathrm{aq} + \ldots + \beta_m[\mathrm{DOODA}]_\mathrm{aq}^m) \tag{7}$$

Theoretical calculation of Ln^{3+} concentration in each stage, after multistage extraction

Using the D values for each metal, the Ln^{3+} concentrations in the organic and aqueous phases were calculated using the ratios $D/(1 + D)$ and $1/(1 + D)$, respectively. This calculation was repeated at each extraction stage. Considering the multistage extraction model, the Ln^{3+} concentrations in the aqueous phase at the sth stage ($[\mathrm{Ln}^{3+}]_{\mathrm{aq},\,s}$) and those in the organic phase at the tth stage ($[\mathrm{Ln}^{3+}]_{\mathrm{o},\,t}$) can be expressed as follows [28]:

$$[\mathrm{Ln}^{3+}]_{\mathrm{aq},s} = [\mathrm{Ln}^{3+}]_\mathrm{initial} \times A^M \times \sum_{j=s-n+1}^{s} \{H(M,j) \times \mathrm{O}^{j-1}\} \tag{8}$$

$$[\mathrm{Ln}^{3+}]_{\mathrm{o},t} = [\mathrm{Ln}^{3+}]_\mathrm{initial} \times A^{t-1} \times \sum_{i=N-n+1}^{N} \{H(i,t) \times \mathrm{O}^{i}\} \tag{9}$$

$$H(i,j) = \begin{cases} H(i,j-1) + H(i-1,j) & (i \neq 1, j \neq 1, i, j \in N) \\ H(i,1) = H(1,j) = 1 & (i, j \in N) \\ 0 & (i, j \leq 0) \end{cases} \tag{10}$$

where *N* is the total number of stages in the aqueous phase, *n* is the stage number in the aqueous phase when Ln^{3+} is initially detected ($[Ln^{3+}] = [Ln^{3+}]_{initial}$), and *M* is the total number of stages in the organic phase. These theoretical equations were used to calculate the metal concentrations in the aqueous and organic phases for all extraction stages.

Batchwise multistage extraction

A schematic diagram of the batchwise 3 × 3 multistage extraction of the organic and aqueous phases is illustrated in **Figure 2**. For the first extraction, an aqueous phase (aq1) containing Ln^{3+} ions was mixed with an organic phase (o1) and shaken. After this, the organic phase (o1) was removed and introduced into the second aqueous phase (aq2) and shaken, while the aqueous phase (aq1) after the first stage was introduced into the second organic phase (o2) and shaken (2nd step). After the second extraction step, the pairs of organic and aqueous phases at the third extraction step were o1-aq3, o2-aq2, and o3-aq1. After three extractions, o1 and aq1 were recovered and sampled for elemental analysis. The extractions at the fourth step involved o2-aq3 and o3-aq2, where o2 and aq2 were sampled. Finally, the fifth step included only o3-aq3 extraction and a sampling of both phases. There were nine extractions for the multistep extraction. The Ln^{3+} concentrations in the aqueous and organic phases after extraction were measured using ICP–AES. Considering the 10 × 10 multistage extraction, this method would require a 19th step and a total of 100 extractions.

Resolution, Rs, value calculations between two metals

Two metals (A and B) were compared at a time. Their peak shapes were characterized, and the peak positions (*t*) and full width at half maximum ($W_{0.5}$) were obtained from the extraction curves. If the peak shape was not clear, *t* and $W_{0.5}$ were calculated assuming a Gaussian distribution. The mutual separation between A and B can be evaluated based on the resolution (*Rs*) values. The *Rs* value is given by the following equation (11), using *t* and $W_{0.5}$ [29,30]. A complete separation is considered when $Rs > 1.5$.

$$Rs = \frac{1.18 \times (t_A - t_B)}{W_{0.5,\,A} + W_{0.5,\,B}} \tag{11}$$

Results and discussion

Ln patterns in DGA-DOODA extraction systems

The relationships between *D* and the atomic numbers of Ln, called Ln patterns, were investigated to determine their extraction behavior in DGA–DOODA extraction systems. It is already established that both extractants have high *D*(Ln) with high HNO_3 concentration owing to ion-pair extraction with a neutral donor. Furthermore, DGA and DOODA selectively extract both heavy and light Ln, respectively [31]. **Figure 3** shows the Ln pattern, where (a) is obtained from a solution of 0.1 M TODGA/*n*-dodecane with varying DOODA(C2) concentrations of 0-100 mM in 1 M HNO_3, (b) is from 0.5 M DOODA(C8)/*n*-dodecane with different TMDGA concentrations of 0-40 mM in 5 M HNO_3, and (c) is from 0.5 M DOODA(C8)/*n*-dodecane with different TEDGA concentrations of 0-30 mM in 5 M HNO_3. Here, two water-soluble DGAs are employed to compare their abilities. 5 M HNO_3 has a strong oxidizing feature, which easily decomposes the dissolved masking agent at high temperatures. Therefore, such solutions should be refrigerated and used immediately.

The Ln pattern in **Figure 3(a)** shows the gradual increase of *D* with the atomic number of Ln, which indicates the preferable extraction of heavy Ln. Furthermore, all *D* values decrease with increasing DOODA(C2) concentrations, where a greater decrease in *D* for light Ln compared to heavy Ln is seen because of the masking effect on DOODA(C2). From the results, the separation factors (SF = *D*(M)/*D*(M’)) were studied. In this work, we focus on the mutual separation of light Ln and the SF values between La and Gd under these conditions, as summarized in **Table 1**. It was found that the SF(Gd/La) values of 100-200 in those with DOODA are higher than those without DOODA (14.2), which suggests a good performance of the mutual separation of light Ln under these conditions.

The Ln patterns in **Figure 3(b)** and **(c)** show a gradual decrease in *D*(Ln) with their atomic numbers. With the addition of water-soluble DGA into the aqueous phase, heavy Ln showed a significant decrease in *D* with their concentrations. These results suggest a strong complexation of heavy Ln by DGA compounds. In this work, we focus on the mutual separation of heavy Ln, and the SF(Gd/Lu) values for these experiments are summarized in **Table 2**. This table indicates that these values in those with DGA (5.5-9 for TMDGA and 18-23 for TEDGA) are higher than those without DGA (0.834). The results suggest that DGA has a strong complexation with heavy Ln, and TEDGA forms more complexes with Ln than with TMDGA. Although TMDGA has a low molecular weight with a short alkyl chain and may exhibit low steric hindrance, its melting point (59 °C) is higher than that of TEDGA (below room temperature) and shows a low complex formation with Ln [32].

Apparent stepwise formation constants (β) were obtained for DOODA(C2), TMDGA, and TEDGA.

Using the results in **Figure 3(a)-(c)**, the *D* values are replotted against DOODA(C2) concentration with additional experiments in order to better observe their behavior. The results are shown in **Figure 4**.

Figure 4(a) shows that the results using 0.1 M TODGA/*n*-dodecane and DOODA (C2)/1 M HNO_3 show a decrease in *D* with DOODA(C2) concentration. We calculated the apparent stepwise formation constant (β) for each Ln element using Equation (7), and the results are summarized in **Table 3**. Currently, there is a lack of sufficient information regarding these β values [33-35], especially those comparing light and heavy Ln. **Table 3** shows the β_1 and β_2 values, which suggest that the 1:2 complex of Ln:DOODA is formed in the aqueous phase. Given that DOODA has a tetradentate coordination and the coordination number of Ln ions is generally 9, the complexation of two-folding Ln with DOODA may be present. This result concurs with a previous report on the extraction of actinides and other stable metals [15]. In addition, the β values for light Ln are higher than those for heavy Ln; DOODA shows a rare characteristic to selectively complex with light Ln rather than heavy Ln.

Figure 4(b) and **(c)** show the results using 0.5 M DOODA(C8)/*n*-dodecane and TMDGA or TEDGA/5 M HNO_3 show the decrease of D with DGA concentrations and the apparent stepwise formation constant (β) for each Ln element. **Table 4** shows β_1 to β_3 of both DGA, which suggests that the 1:3 complex of Ln:DGA is formed in the aqueous phase. The tridentate coordination of DGA and the coordination number 9 of Ln ions indicate that a complexation of three-folding Ln with DGA may be present. This result corresponds with that of a previous study [27], although this study shows the results of actinides with no stability constants. The β values for heavy Ln are higher than those for light Ln, which is based on their charge densities. In addition, the β values for TEDGA are higher than those for TMDGA, and the β values support the strong complexation with TEDGA.

Determination of shaking conditions

Before the multistage extractions, shaking conditions were determined. Although all D values should be the same, a short shaking time is convenient because of the multiple stages in the multistage extraction process. To confirm the shaking time, the experiment is followed by 3 × 3 multistage extractions, as described in **Figure 2**, and all D values are obtained and compared with each other. The extractions of the different shaking times, 10 and 15 min, with fixed 2000 rpm were performed using a solution of 0.5 M HNO_3 and 0.1 M TODGA/*n*-dodecane. The average D and 1σ values for 10 and 15 min of shaking are 0.21 ± 0.45 and 0.16 ± 0.013 for La, respectively, and those for Eu are 8.08 ± 3.26 and 5.14 ± 0.33, respectively. From these results, we chose 15 min of shaking for the multi-stage extractions because of the low deviations, and the experimental results are consistent with the calculated values within 10% errors. In a previous study, 10 min of shaking was sufficient to obtain the extraction equilibration [23]. However, in this study, 15 min of shaking was proven to be better for obtaining correlated experimental and calculated results.

Multistage extractions using 10 × 10 stage of aqueous and organic phases

In order to confirm the mutual separation of Ln, multistage extraction was performed with 10 stages of the organic phase (0.1 M TODGA/*n*-dodecane), one stage of aqueous phase containing Ln^{3+} (30 mM DOODA(C2)/1 M HNO_3), and nine stages of aqueous phases as the scrubbing solution (30 mM DOODA(C2)/1 M HNO_3). The D values obtained by the batch extractions using this condition were 0.06, 0.249, 0.374, 2.175, 7.017, 12.32, 8.74, 21.2, 25.7, 33.5, 46.6, 46.8, and 40.7 for La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, respectively. The results of the extraction curves are shown in **Figure 5(a)** and **5(b)** for the aqueous and organic phases, respectively, and the yield of each Ln is shown in **Table 5**. These figures and tables indicate that La, Pr, and Nd are present mostly in the aqueous phase, and Sm and heavier Ln exist in the organic phase, which is due to their D values. The yields of Nd and Sm in the organic phase from Table 5 are 18.7 and 93.7%, respectively, which indicates selective separation even when they are neighboring elements. After the separation, the Ln remaining in the organic phase can be stripped using water. In addition, multistage extractions greater than 10 ×10 can be set up, which will lead to better separation performance.

To determine the separation ability in this work, we calculated Rs values using Equation (11). As shown in **Figure 5**, peaks for Pr and Nd in the aqueous phase and Sm, Eu, and Gd in the organic phase are observed. Therefore, we focused on the separation of these metals with the addition of La or Tb (Dy). First, we summarized the peak positions (t) and the full width at half maximum ($W_{0.5}$) in **Table 6**, and the calculated Rs values are presented in **Table 7**. Generally, a resolution Rs of 1.5 or higher, is the standard for complete separation [23]. The results in **Table 7** do not reach 1.5; therefore, the mutual separation between La–Nd or Sm–Dy is hardly achieved. Multistage extractions greater than 10 × 10 would provide a better resolution of the peaks and the recovery of metals, which may lead to higher Rs values.

In order to perform the mutual separation of heavy Ln, we study the multistage extraction of 10 × 10 for the organic phase (0.5 M DOODA(C8)/*n*-dodecane), a sample solution (10 mM TEDGA + Ln/5 M HNO_3), and 9 scrub solutions (10 mM TEDGA/5 M HNO_3). The

D values obtained by the batch extractions under these conditions were 37.1, 6.8, 8.59, 7.76, 12.7, 6.77, 2.33, 1.29, 0.84, 0.591, 0.469, 0.405, and 0.313 for La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, respectively. The *D*(Dy) and *D*(Ho) values are close to 1, which may lead to the separation of Dy with lighter Ln and Ho (to organic phase) with heavier Ln (to aqueous phase). In addition, TEDGA is preferred over TMDGA in this work because it has a higher complexation than TMDGA (**Table 4**). The results of the extraction curves are shown in **Figure 6(a)** and **(b)** for the aqueous and organic phases, and their recoveries in the aqueous and organic phases are summarized in **Table 8**. As shown in **Figure 6** and **Table 8**, La–Nd is completely extracted into the organic phase, while Er–Lu almost remains in the aqueous phase. We chose the condition of heavy Ln separation with a *D* value of 1 near Dy and Ho; however, the result did not reflect the *D* values obtained in the batch extraction. This discrepancy requires further consideration in the future.

Conclusion

This study focused on the mutual separation of Ln elements by utilizing a synergistic effect from an extractant and masking agent. Furthermore, the stepwise formation constants of Ln ions with DOODA(C2), TMDGA, and TEDGA were calculated using their *D* values. DOODA and DGA show opposite behaviors, where DGA shows complexation with heavy Ln following the charge density, whereas DOODA shows a strong ability to complex with light Ln. Using these features, high SF values can be obtained by two-reagent applications in the different phases of an extraction system. The gradual increase in SF with the concentration of a suitable masking agent was confirmed. Taking a 10 x 10 multistage extraction utilizing 30 mM DOODA (C2)/1 M HNO_3 and 0.1 M TODGA/*n*-dodecane, the recoveries of neighboring elements, Nd and Sm, in the organic phase are 18.7 and 93.7%. Additionally, the light Ln (La, Ce, Pr, and Nd) in HLW can be separated from the middle Ln, such as Sm and Eu, which have long radioactivity. After separation, light Ln can be preserved for a short time and reused when their radioactivity is below the clearance level. In addition, Dy can be separated very easily from Nd magnets using this method. However, more number of experiments are required to obtain suitable conditions, which are needed to satisfy the mutual separation of heavy Ln.

Acknowledgements

We gratefully acknowledge Dr. M. Watanabe of the Research Group for Radiochemistry at JAEA for managing the laboratory and ensuring safety. We also thank Mr. R. Ono of Tokyo Institute of Technology, Y. Tsuchida at Yokohama National University, and T. Matsutani at Chiba University for useful information on this work.

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Supplementary information

This section will not appear in the printed version of your paper but it will contain a link; the webpage containing the electronic supplementary information will appear when one clicks on the hyperlink. Here you can list the details of your research which would be too long for the main text, *e.g.* a larger number of spectra *etc*. Start with 1 for Figure and Table numbers in this section.