

# Dalton Transactions

Accepted Manuscript



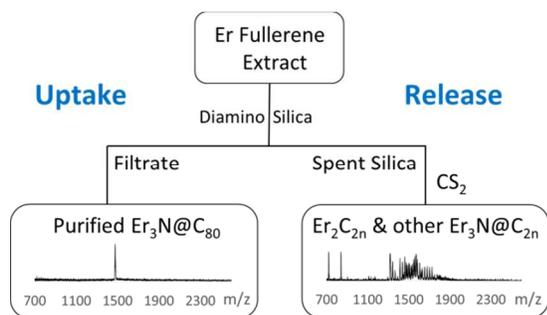
This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Isolation and separation strategy that manipulates uptake and release of rare-earth metallofullerenes immobilized on reactive silica to provide enriched samples.



## ARTICLE

# Fractionation of Rare-Earth Metallofullerenes via Reversible Uptake and Release from Reactive Silica

Cite this: DOI: 10.1039/x0xx00000x

Steven Stevenson,\* Khristina A. Rottinger, and Jessica S. Field

Received 00th January xxxx,  
Accepted 00th January xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Minimal research exists for non-chromatographic separations of rare-earth metallofullerenes containing di-metallic ( $M_2$ ), di-metallic carbide ( $M_2C_2$ ), and tri-metallic nitride ( $M_3N$ ) clusters trapped inside fullerene cages. Herein, we demonstrate a non-HPLC method, (i.e., SAFA, Stir and Filter Approach) for purifying  $Er_3N@I_h-C_{80}$ , a rare-earth, metallic nitride clusterfullerene. We describe a strategic method that chemically releases rare-earth metallofullerenes (e.g.,  $M_2@C_{2n}$ ,  $M_3N@C_{2n}$ ) trapped by aminosilica during SAFA. Recovery of metallofullerenes from spent silica represents a “green approach” because the spent silica and its useful, immobilized rare-earth metallofullerenes would have been discarded as waste material. We observe selectivity during metallofullerene uptake to aminosilica and also during its release from spent silica via addition of  $CS_2$ . We describe a procedure to obtain samples enriched in  $M_2$  and  $M_3N$  endohedrals.  $M_2C_{2n}$  fractions from our SAFA release process contain a wide range of higher metallofullerenes (e.g.,  $Gd_2C_{90}$  -  $Gd_2C_{140}$  or  $Er_2C_{76}$  -  $Er_2C_{122}$ ). It is facile to obtain samples enriched in  $M_3N@C_{82}$  -  $M_3N@C_{92}$ . Note that unreacted  $M_3N@C_{80}$  remains in the filtrate. The strategy for handling rare-earth metallofullerenes with different degrees of reactivity toward aminosilica is also discussed.

## 1. Introduction

Since the early 1990s, the first isolated metallofullerenes<sup>1-4</sup> were fractionated by HPLC, which is still the most common method for their purification. Non-HPLC approaches for endohedral separations take advantage of differences between metallofullerenes and empty-cage fullerenes, which lack an electron transfer from the cluster to the cage surface due to the absence of an encapsulated metal(s). Features of empty-cages and metallofullerenes that can be manipulated include differences in their physical properties,<sup>5, 6</sup> chemical reactivity,<sup>7-16</sup> and electrochemical/redox<sup>17-23</sup> behaviour.

Little literature exists for non-chromatographic separations of endohedral metallofullerenes possessing larger fullerene cages.<sup>24-26</sup> Even less research is available for non-HPLC approaches toward rare-earth metallofullerenes with multi-atom clusters. In this work, we are specifically interested in rare-earth, di-metallic ( $M_2C_{2n}$ ) and metallic nitride ( $M_3N@C_{2n}$ ) endohedrals. Motivation for metallofullerene research is due to emerging applications from entrapped clusters containing rare-earth metals (e.g., Lu, Er, Gd).<sup>27-36</sup> A number of recent reviews discuss  $M_2$  and  $M_3N$  clusters in carbon cages beyond  $C_{80}$ .<sup>37-41</sup>

The incorporation of reactive functional groups onto silica to bind reactive fullerenes is the basis for the SAFA<sup>9, 10</sup> (Stir and Filter Approach) method of purifying endohedrals. The primary advantage of the SAFA technique is the ease of

isolating the most inert fullerene species in a given solution. For example, large quantities of  $Sc_3N@I_h-C_{80}$  were isolated using the SAFA method of adding aminosilica to an extract in solution. SAFA<sup>9, 10</sup> is entirely non-chromatographic and scalable, which are features suitable for industry. Enthusiasm for the SAFA method has been, to date, mitigated by a key concern that we address in this work. Can fullerenes and metallofullerenes that bind to aminosilica during the SAFA process be released and recovered? If yes, would there be selectivity in their chemical release to permit fractions containing different endohedrals as dominant species? Ideally, it is desirable to have an array of fractions, with each sample containing a dominant metallofullerene or metallofullerene type.

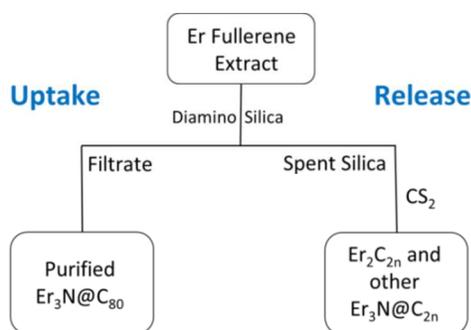
Since the discovery of SAFA,<sup>9</sup> we have recently investigated solvent selection and the effect of moisture on the extent of fullerene uptake to aminosilica.<sup>42</sup> Those findings indicated that aminosilica used in SAFA experiments should be sufficiently vacuum-dried at the proper temperature to ensure complete uptake of fullerene contaminants.<sup>42</sup>

This contribution now addresses the question of reversibility of metallofullerene uptake and how to release the endohedrals after binding to aminosilica, which previously was discarded as spent silica waste material. This research indicates selectivity of metallofullerene uptake during the SAFA process, which can be monitored to stop the reaction at strategic times (i.e., ceasing

the reaction when selected contaminants have been removed from solution by binding to aminosilica). Hence, the SAFA process can be “tuned” toward obtaining a sample enriched in a particular endohedral. We also describe a “green” chemical recovery that uses CS<sub>2</sub> reactivity toward spent aminosilica to release the useful, immobilized metallofullerenes and fullerenes and return them to solution in lieu of discarding the spent silica as waste material. Results for these SAFA release experiments indicate selectivity of metallofullerene release during this recovery process.

## 2. Results and Discussion

There were several objectives of this research. A key goal was to demonstrate the SAFA approach can be used as a non-chromatographic method to isolate a rare-earth metallic nitride clusterfullerene (i.e., Er<sub>3</sub>N@C<sub>80</sub>). We also sought to demonstrate that selectivity can be achieved during both fullerene uptake and subsequent release from spent silica. Figure 1 summarizes our separation strategy for fractionating Er endohedrals.

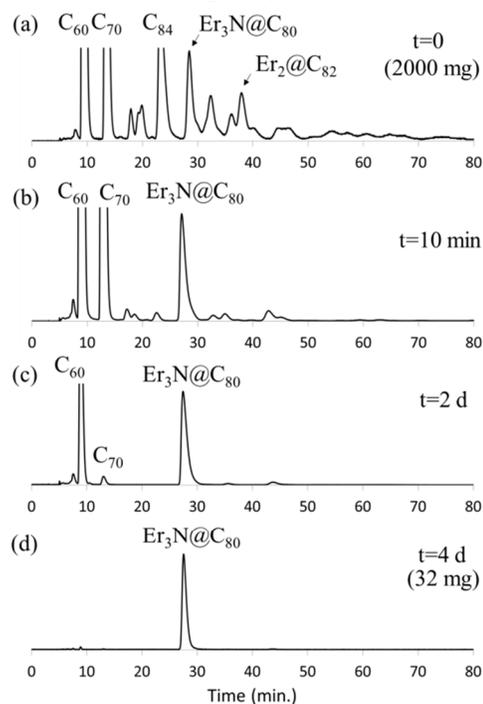


**Figure 1. Overview of the separation strategy for purifying Er<sub>3</sub>N@I<sub>h</sub>-C<sub>80</sub> with the SAFA process and for procuring enriched fractions of Er<sub>2</sub>@C<sub>2n</sub> and Er<sub>3</sub>N@C<sub>2n</sub> higher metallofullerenes using CS<sub>2</sub> release chemistry.**

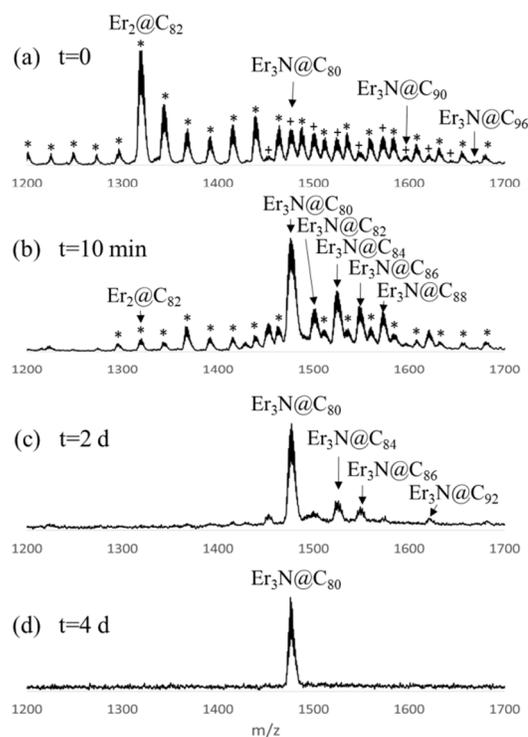
**Er-based metallofullerenes (Uptake):** To demonstrate the SAFA uptake of fullerenes onto reactive silica, 2.0 grams of Er metallofullerene extract is dissolved, and to this stirring solution is added 250 g of dried, diaminosilica gel. The preparation of aminosilica<sup>9</sup> and the importance of using vacuum-dried aminosilica in SAFA uptake experiments are reported elsewhere.<sup>42</sup> Aliquots from the reaction mixture at various times are analysed to provide insight into which metallofullerenes remain in solution (i.e., unreacted) versus which metallofullerenes have reacted and become immobilized onto the solid support (i.e., diaminosilica gel). Loss of HPLC peak area indicates binding (i.e., uptake) onto the reactive silica.

We monitor the progress of the reaction by HPLC (Figure 2) and MALDI mass spectrometry (Figure 3). Comparison of the extract (t = 0 min.) with an aliquot of the reaction mixture at 10 minutes (Figures 2b, 3b) reveals significant uptake of higher empty-cage fullerenes (e.g., C<sub>84</sub>) and classical Er metallofullerenes (e.g., Er<sub>2</sub>@C<sub>82</sub>). After two days of SAFA reaction, there are predominantly two fullerenes (C<sub>60</sub>, Er<sub>3</sub>N@C<sub>80</sub>) remaining in solution, with only traces of higher M<sub>3</sub>N clusterfullerenes (M<sub>3</sub>N@C<sub>2n</sub>) and a small amount of C<sub>70</sub> (Figure 2c). Upon stirring for 4 days, the only species

remaining in solution is the most inert species, Er<sub>3</sub>N@C<sub>80</sub> (Figures 2d, 3d). After solvent removal via rotary evaporation, it should be noted that numerous, small crystals or Er<sub>3</sub>N@C<sub>80</sub> (32 mg) were formed during this process.



**Figure 2. HPLC chromatograms showing selectivity of uptake and indicating unreacted fullerenes and metallofullerenes remaining in solution (a) before addition of diaminosilica to 2 g of Er extract solution, (b) after 10 min, (c) 2d and (d) 4d of reaction time.**



**Figure 3. MALDI mass spectra showing selectivity of uptake and unreacted fullerenes and metallofullerenes remaining in solution**

(a) before addition of diaminosilica to 2 g of Er extract solution, (b) after 10 min, (c) 2d and (d) 4d of reaction time. [\* denotes dimetallofullerenes (e.g.,  $\text{Er}_2\text{C}_{2n}$ ) of differing cage sizes].

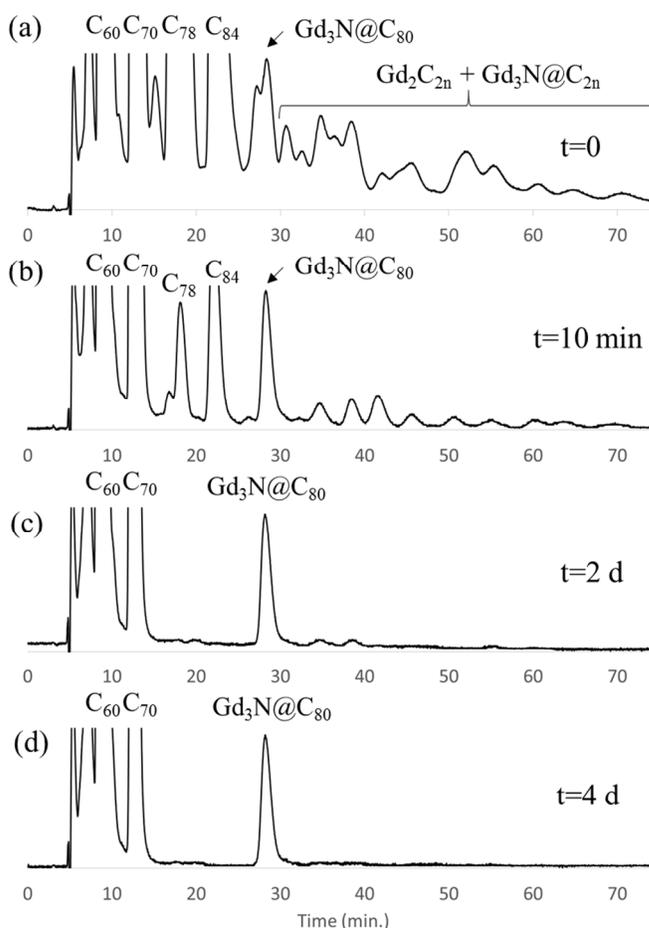
**Gd-based metallofullerenes (Uptake):** Our preliminary SAFA experiments with dried, diaminosilica added to a solution of Gd metallofullerene extract resulted in excessive uptake and loss of  $\text{Gd}_3\text{N}@C_{80}$  to the reactive silica. Therefore, due to the slightly higher reactivity of  $\text{Gd}_3\text{N}@C_{80}$  relative to  $\text{Er}_3\text{N}@C_{80}$ , it is necessary to use the milder aminosilica in lieu of the more reactive diaminosilica. Shown in supplemental information is the modified scheme for SAFA uptake experiments with Gd metallofullerene extract.

For Gd experiments, 500 mg of Gd metallofullerene extract is dissolved in 750 mL of xylenes. The HPLC analysis of this starting material is shown in Figure 4a. Note the much lower yield of  $\text{Gd}_3\text{N}@C_{80}$  relative to  $C_{60}$ ,  $C_{70}$ ,  $C_{78}$ , and  $C_{84}$ , whose peaks are off-scale and confirm the low abundance of  $\text{Gd}_3\text{N}@C_{80}$  in the extract. HPLC analysis of fullerenes remaining in solution after 10 minutes (Figure 4b) indicates that a significant loss of peak area and extensive immobilization has occurred for contaminant, higher empty-cage fullerenes (e.g.,  $C_{78}$ ,  $C_{84}$ ) and higher Gd-based metallofullerenes (i.e.,  $\text{Gd}_2\text{C}_{2n}$  and  $\text{Gd}_3\text{N}@C_{2n}$  species beyond  $C_{80}$ ).

HPLC analysis of the reaction mixture after two days (Figure 4c) demonstrates three primary, fullerene species ( $C_{60}$ ,  $C_{70}$ , and  $\text{Gd}_3\text{N}@C_{80}$ ) remaining in solution (i.e., not bound to aminosilica), with only a trace of other Gd metallofullerenes still unreacted. After four days (Figure 4d), about 80% of the  $\text{Gd}_3\text{N}@C_{80}$  remains in solution. To avoid further uptake of  $\text{Gd}_3\text{N}@C_{80}$  onto the silica, the reaction is stopped by filtering the sample.

**Overview of reversible uptake and release process:** Historically, a key concern of the SAFA method is if fullerenes and metallofullerenes that were bound to the spent silica during the SAFA process could be released and recovered. In a separate work, we demonstrated that addition of  $\text{CS}_2$  to spent silica containing Sc metallofullerenes resulted in samples containing released Sc-based endohedrals, such as  $\text{Sc}_3\text{N}@C_{78}$ ,  $\text{Sc}_4\text{O}_2@C_{80}$ , and  $\text{Sc}_3\text{N}@C_{80}$ .<sup>12</sup> The reaction of  $\text{CS}_2$  with primary and secondary aliphatic amines is well-known.<sup>43,44</sup>

We hypothesized that this  $\text{CS}_2$ /amine reaction may help to release immobilized fullerenes and metallofullerenes trapped by the aminosilica. Although current studies are underway to determine the release mechanism, the findings of this paper demonstrate clearly that  $\text{CS}_2$  addition to spent aminosilica successfully releases both fullerenes and metallofullerenes. It is noteworthy that all release experiments described herein are performed at room temperature. The chemical release of fullerenes and metallofullerenes via  $\text{CS}_2$  under ambient conditions is preferred to anxiety about the stability of metallofullerenes and fullerenes bonded to amines and exposed to higher temperatures.<sup>45,46</sup>



**Figure 4.** HPLC chromatograms showing selectivity of uptake and indicating unreacted fullerenes and metallofullerenes remaining in solution (a) before addition of diaminosilica to 0.5 g of Gd extract solution, (b) after 10 min, (c) 2d and (d) 4d of reaction time.

**Er-based metallofullerenes (Release):** Results below demonstrate selectivity during the release process. HPLC and MALDI analyses of fractionated samples indicate the presence of different dominant Er endohedrals or different types of endohedrals (i.e.,  $\text{Er}_2\text{C}_{2n}$  versus  $\text{Er}_3\text{N}@C_{2n}$ ). Differences in kinetic release exist as a function of time and added  $\text{CS}_2$  eluent. Furthermore, this uptake and release method represents a new approach for obtaining enriched species of metals and metal clusters in higher fullerene cages ( $C_{90}$ - $C_{140}$ )

A typical SAFA release experiment entails washing the spent diaminosilica with  $\text{CS}_2$ . Two key variables are the volume of added  $\text{CS}_2$ , and the time between  $\text{CS}_2$  washes of the spent silica (Table 1). The release process begins when the spent silica from the SAFA experiment is immediately washed with carbon disulfide after the SAFA filtration (See Experimental).

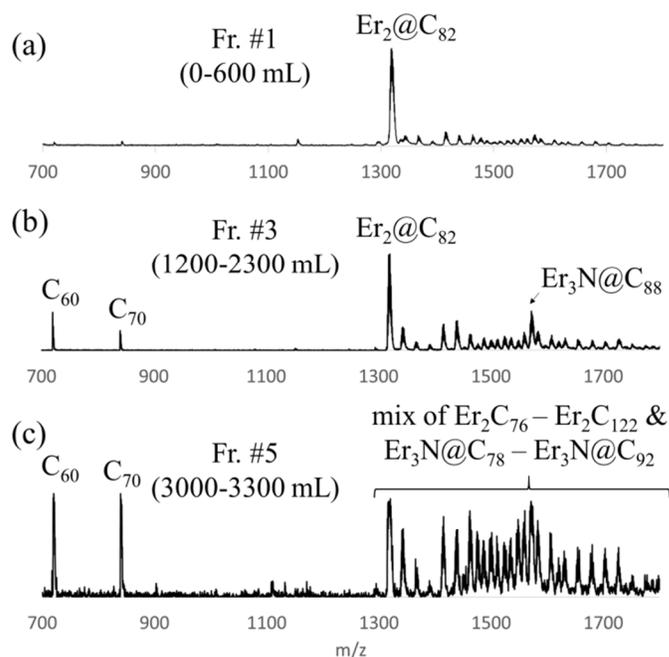
**Table 1. Summary of key experimental parameters (i.e., volume of CS<sub>2</sub> eluent, time between washes of spent silica, and amount of recovered fullerenes after CS<sub>2</sub> SAFA release chemistry).**

Er Release Experiments	Cumulative Volume of CS <sub>2</sub> Added (mL)	Time Between CS <sub>2</sub> Washes of Spent Silica	mg
Fr. #1	0-600	Upon SAFA completion (t=0)	8
Fr. #2	600-1500	5 min	12
Fr. #3	1500-2300	3 days	1200
Fr. #4	2300-3000	7 days	105
Fr. #5	3000-3300	3 weeks	15
<b>Gd Release Experiments</b>			
Fr. #1	0-550	Upon SAFA completion (t=0)	7
Fr. #2	550-800	5 min	2
Fr. #3	800-1000	3 days	30
Fr. #4	1000-1200	3 days	10
Fr. #5	1200-1400	4 days	5

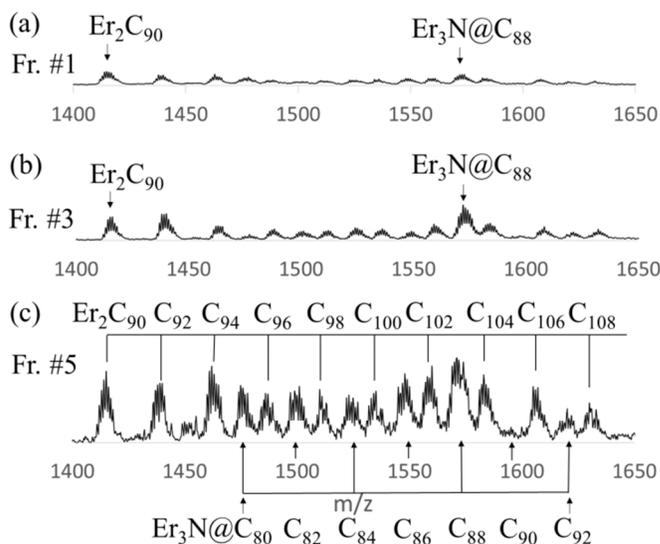
Fraction 1 contains the first 600 mL of collected eluent. MALDI (Figures 5a, 6a) and HPLC (Figure 7a) analyses of the eluent collected in Fraction 1 show a sample highly enriched in Er<sub>2</sub>@C<sub>82</sub> and with minimal C<sub>60</sub> and C<sub>70</sub> present. After sitting for 3 days, the spent silica was washed again with CS<sub>2</sub>. An aliquot of the collected 800 mL of eluent in Fraction 3 was analysed by MALDI (Figures 5b, 6b) and HPLC (Figure 7b). Results from Fraction 3 indicate significant quantities of recovered C<sub>60</sub> and C<sub>70</sub>, additional Er<sub>2</sub>@C<sub>82</sub>, but now Er<sub>3</sub>N@C<sub>88</sub> emerges as the dominant M<sub>3</sub>N endohedral.

Additional cycles of CS<sub>2</sub> and more time between washes result in Fraction 5, whose MALDI (Figures 5c, 6c) and HPLC (Figure 7c) show an enriched fraction containing higher di-metallic (Er<sub>2</sub>C<sub>2n</sub>) and metallic nitride (Er<sub>3</sub>N@C<sub>2n</sub>) endohedrals. The wide range of Er<sub>2</sub>@C<sub>76</sub> through Er<sub>2</sub>@C<sub>122</sub> and Er<sub>3</sub>N@C<sub>78</sub> through Er<sub>3</sub>N@C<sub>92</sub> indicate a successful technique to obtain a highly enriched sample of metal clusters trapped within larger fullerene cages. The findings from Fractions 1, 3, and 5 demonstrate fractionated metallofullerene samples that are enriched in different endohedrals as their dominant species.

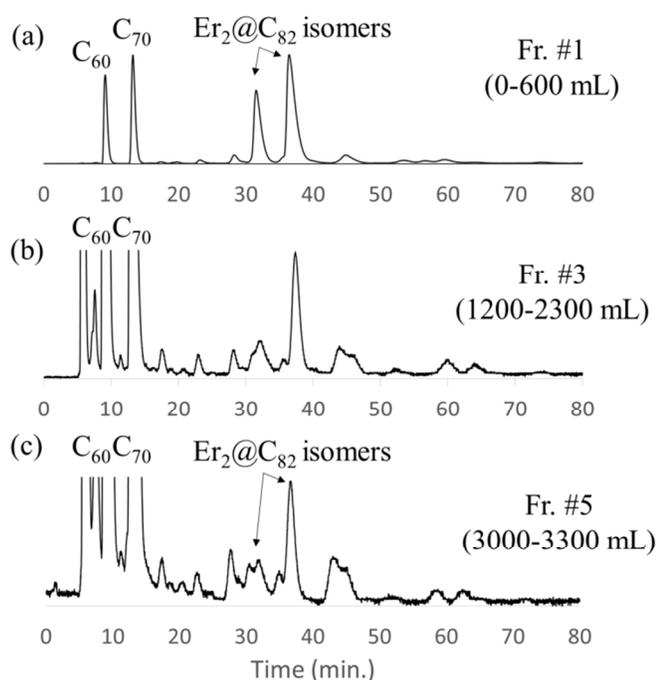
From 2000 mg of Er metallofullerene extract, 32 mg of crystalline, purified Er<sub>3</sub>N@I<sub>h</sub>-C<sub>80</sub> is obtained. Subtracting the amount of purified material, there is mathematically 1968 mg of fullerene and metallofullerenes immobilized onto the diaminosilica and available for recovery. Results from Table 1 indicate a total recovery of 1340 mg. This amount corresponds to a recovery of nearly 70%. It should also be noted that the 1200 mg of fullerenes and metallofullerenes obtained in Fraction 3 alone represents roughly 90% of the total fullerene and metallofullerene material recovered in all five Er release fractions.



**Figure 5. MALDI mass spectra showing selectivity of release and fractionation of different types of Er metallofullerenes for samples obtained upon addition of (a) 0-600 mL, (b) 1200-2300 mL, and (c) 3000-3300 mL of CS<sub>2</sub> eluent. See Table 1 for time intervals between CS<sub>2</sub> washes of spent diaminosilica.**



**Figure 6. Expansion of MALDI mass spectra showing selectivity of release and fractionation of different types of Er metallofullerenes for samples obtained upon addition of (a) 0-600 mL, (b) 1200-2300 mL, and (c) 3000-3300 mL of CS<sub>2</sub> eluent.**



**Figure 7.** HPLC analysis showing selectivity of release and fractionation of different types of Er metallofullerenes for samples obtained upon addition of (a) 0-600 mL, (b) 1200-2300 mL, and (c) 3000-3300 mL of CS<sub>2</sub> eluent.

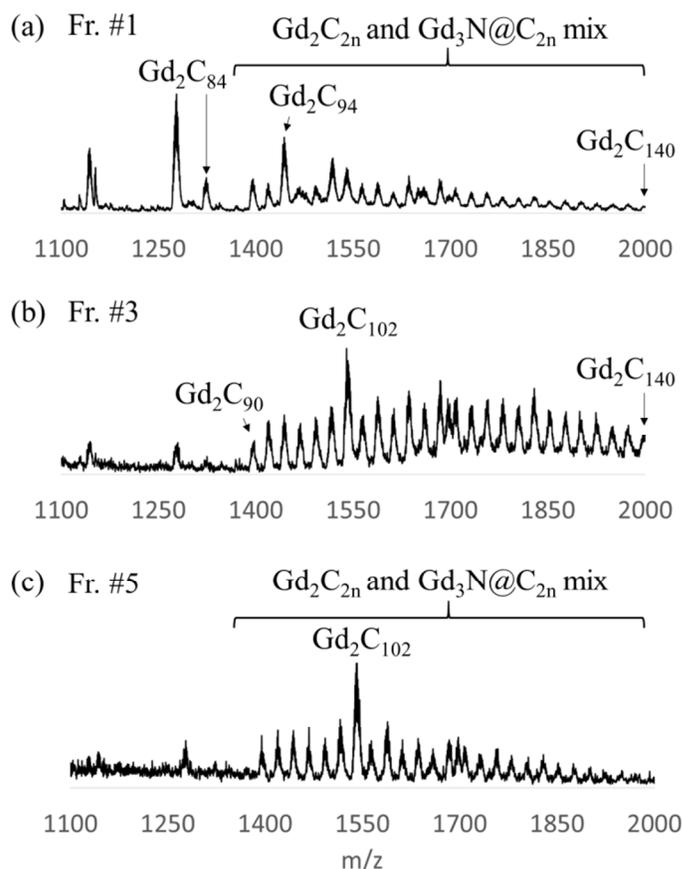
#### Gd-based metallofullerenes (Release):

We designed Gd release experiments to determine if similar CS<sub>2</sub> washes of Gd spent silica would result in the recovery of Gd-based metallofullerenes. Table 1 represents a summary of the volume of CS<sub>2</sub> eluent and time between washes of the Gd spent silica. Fraction 1 is obtained by washing the spent silica immediately with CS<sub>2</sub> after completion of the SAFA filtration. Analysis of Fraction 1 indicates a wide range of Gd<sub>2</sub>C<sub>2n</sub> species, from Gd<sub>2</sub>C<sub>84</sub> through Gd<sub>2</sub>C<sub>140</sub> (Figure 8a). The MALDI data suggests the dominant species in this fraction is Gd<sub>2</sub>C<sub>94</sub>. Dominant in Fraction 1, Gd<sub>2</sub>C<sub>94</sub> may actually be the carbide species, Gd<sub>2</sub>C<sub>2</sub>@C<sub>92</sub>, which was recently characterized and confirmed by X-ray crystallography.<sup>47</sup>

After letting the spent silica sit for three days, another CS<sub>2</sub> wash is performed and provides Fraction 3. Analysis of this fraction (Figure 8b) indicates Gd<sub>2</sub>C<sub>102</sub> is now the dominant species. The range of Gd metallofullerenes has shifted to the larger Gd<sub>2</sub>C<sub>90</sub> through Gd<sub>2</sub>C<sub>140</sub> endohedrals. Repetitive cycles of waiting and washing results in a sample corresponding to Fraction 5 (Table 1 and Figure 8c). The MALDI data reveals that Gd<sub>2</sub>C<sub>102</sub> is still the dominant species, but with Gd<sub>2</sub>C<sub>102</sub> having a more pronounced abundance relative to other Gd<sub>2</sub>C<sub>2n</sub> species.

Further studies would be necessary to determine whether the MALDI dominant Gd<sub>2</sub>C<sub>102</sub> in Fractions 3 and 5 would be Gd<sub>2</sub>@C<sub>102</sub> or the carbide, Gd<sub>2</sub>C<sub>2</sub>@C<sub>100</sub>. HPLC fraction collection for this species may now be easier to isolate due to its higher abundance in Fraction 5 relative to other Gd endohedral contaminants. A multistage HPLC separation for

isolating Gd<sub>2</sub>C<sub>102</sub> is previously reported.<sup>47</sup> A combination of this new approach to obtain an enriched Gd<sub>2</sub>C<sub>102</sub> sample via its release from spent silica (Fraction 5, Figure 8c), followed by HPLC fraction collection for a final purification step may be a useful and alternative method.



**Figure 8.** MALDI mass spectra showing selectivity of release and fractionation of different types of Gd metallofullerenes for samples obtained upon addition of (a) 0-550 mL, (b) 800-1000 mL, and (c) 1200-1400 mL of CS<sub>2</sub> eluent. See Table 1 for time intervals between CS<sub>2</sub> washes of spent diaminosilica.

In comparison to Er release experiments (70% recovery), the amount of recovered Gd endohedrals and fullerenes was much lower. Subtracting 100 mg of SAFA filtrate from the 500 mg of Gd fullerene extract suggests that 400 mg of fullerenes and metallofullerenes were immobilized by the aminosilica during SAFA uptake. Based on a total of 54 mg of released material (Table 1), only 14% of the immobilized Gd metallofullerenes and fullerenes were recoverable.

This lower percent recovery may be related to our observed higher reactivity of Gd versus Er endohedrals. Hence, the binding of the more reactive Gd metallofullerene may be too strong to overcome with our CS<sub>2</sub> release method at ambient conditions. Another possibility for the lower recovery yield of Gd species may be the type of reactive silica used in the Gd SAFA (monoamino silica, i.e., primary amine) versus Er SAFA (diamino silica, i.e., mixture of primary and secondary amines), for which the latter may permit a more facile release of fullerene and metallofullerenes with CS<sub>2</sub>.

### 3. Experimental

#### SAFA, Fullerene Uptake (Stir and Filter Approach)

Er metallofullerene extract (2000 mg) is dissolved in 1800 mL of xylenes and stirred in a 5L round bottom flask. To this solution is added 250 g of vacuum oven, dried diaminosilica at 60 °C for 8 h. The dried, diamino silica gel is removed from the vacuum oven at room temperature and added immediately to the stirring extract solution to minimize re-absorption of water from humidity in the lab. Aliquots are removed from the reaction mixture at arbitrary times to monitor the uptake of contaminant fullerenes and metallofullerenes. These syringe filtered aliquots are then characterized by HPLC and MALDI mass spectrometry.

Gd metallofullerene extract (500 mg) is dissolved in 750 mL of xylenes and stirred in a 2L round bottom flask. To this solution is added 30 g of vacuum oven dried aminosilica at 60 °C for 8 h. The aminosilica is removed from the vacuum oven at room temperature and immediately added to the stirring, extract solution. Aliquots are removed from the reaction mixture at arbitrary times to monitor the uptake of contaminant fullerenes and metallofullerenes. These syringe filtered aliquots are submitted for HPLC and MALDI mass spectral analysis.

**Fullerene Release from Aminosilica:** Upon conclusion of the SAFA experiment, the slurry is filtered via vacuum filtration and washed with fresh xylenes until no further colour is observed in the drops eluting from the Buchner funnel. Immediately, carbon disulfide is added onto this spent silica, and the volume of the eluent collected is monitored. During the reaction of CS<sub>2</sub> and spent aminosilica, fullerenes and metallofullerenes are released, dissolved in CS<sub>2</sub> and collected in fractions as a function of the volume of eluent.

For Gd release experiments, Fractions 1 and 2 are obtained immediately (i.e., after the SAFA filtrate is obtained). The spent silica is allowed to sit and dry in the hood for 3 days, with more CS<sub>2</sub> added to the spent silica to release more fullerene and metallofullerenes Fraction 3. After another 3 days, the addition of more CS<sub>2</sub> is repeated to yield Fraction 4. Fraction 5 is obtained upon waiting an additional 4 days before adding more CS<sub>2</sub> to elute additional fullerenes. It should be noted that by the 5<sup>th</sup> fraction, only traces of additional material are recovered, and the point of diminishing returns is eventually reached.

For Er release experiments, Fractions 1 and 2 are obtained by immediately washing the spent aminosilica after the SAFA reaction slurry is filtered. The time intervals between CS<sub>2</sub> washes of the remaining spent silica are 3 days, 7 days, and 3 weeks for Fractions 3, 4, and 5 respectively.

**HPLC Analysis:** Aliquots were analysed by injection into a 4.6 x 250 mm PYE column (SES Research, Nacalai Tesque). Other chromatographic conditions include a mobile phase flow rate of 0.61 mL/min toluene, 360 nm UV detection, and 50-500 µL injection volumes.

**MALDI Analysis:** Mass spectral analyses of aliquots are performed on a Bruker Microflex LT mass spectrometer. Samples are deposited from a CS<sub>2</sub> solution onto a stainless steel plate without using a matrix. The analysis is performed in the positive-ion mode.

### Conclusions

We demonstrate the successful purification of a rare-earth metallic nitride clusterfullerene (Er<sub>3</sub>N@I<sub>h</sub>-C<sub>80</sub>) using SAFA, a non-HPLC method. The high purity of non-chromatographically isolated Er<sub>3</sub>N@I<sub>h</sub>-C<sub>80</sub> is supported by HPLC and MALDI analyses. The ease of obtaining crystalline Er<sub>3</sub>N@I<sub>h</sub>-C<sub>80</sub> is noted. During the SAFA uptake, one can strategically stop the reaction mixture when a desired metallofullerene(s) is still remaining in solution by monitoring its peak area in relation to the loss of HPLC peak area for contaminant fullerenes. We have also developed a novel, chemical method of adding CS<sub>2</sub> to spent aminosilica for fullerene and metallofullerene recovery in good yield. The reversibility of their release from spent silica is sufficiently selective to provide unique fractions, which contain different metallofullerenes or metallofullerene types. This fractionation process permits enriched samples of di-metal and metallic nitride clusters entrapped in higher fullerene cages (e.g., Gd<sub>2</sub>C<sub>90</sub> - Gd<sub>2</sub>C<sub>140</sub> and Er<sub>2</sub>C<sub>76</sub> - Er<sub>2</sub>C<sub>122</sub> for M<sub>2</sub>C<sub>2n</sub> species, and M<sub>3</sub>N@C<sub>78</sub> - M<sub>3</sub>N@C<sub>92</sub> for M<sub>3</sub>N@C<sub>2n</sub> endohedrals). This ambient, chemical release method for releasing bound fullerenes represents a “green process” in terms of recovering precious rare-earth metallofullerenes (M<sub>2</sub>C<sub>2n</sub>, M<sub>3</sub>N@C<sub>2n</sub>) from spent aminosilica, which otherwise would be disposed of as waste material.

### Acknowledgements

The authors thank the National Science Foundation, RUI CHE Grant 1151668.

### Notes and references

\*Corresponding author, stevenss@ipfw.edu, Indiana-Purdue University at Fort Wayne, Department of Chemistry, 2101 E. Coliseum Blvd, Fort Wayne, IN 46805-1499 USA .

**Electronic Supplementary Information (ESI) available:** Overview of the separation strategy for isolating samples containing Gd<sub>3</sub>N@C<sub>80</sub> as the dominant metallofullerene.

1. H. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Ohkohchi, Y. Ando and Y. Saito, *Journal Of Physical Chemistry*, 1993, **97**, 4259-4261.
2. R. Beyers, C. H. Kiang, R. D. Johnson, J. R. Salem, M. S. Devries, C. S. Yannoni, D. S. Bethune, H. C. Dorn, P. Burbank, K. Harich and S. Stevenson, *Nature*, 1994, **370**, 196-199.
3. S. Stevenson, H. C. Dorn, P. Burbank, K. Harich, J. Haynes, C. H. Kiang, J. R. Salem, M. S. Devries, P. H. M. Vanloosdrecht, R. D. Johnson, C. S. Yannoni and D. S. Bethune, *Analytical Chemistry*, 1994, **66**, 2675-2679.
4. S. Stevenson, H. C. Dorn, P. Burbank, K. Harich, Z. Sun, C. H. Kiang, J. R. Salem, M. S. Devries, P. H. M. Vanloosdrecht, R. D. Johnson, C. S. Yannoni and D. S. Bethune, *Analytical Chemistry*, 1994, **66**, 2680-2685.

5. C. D. Angeli, T. Cai, J. C. Duchamp, J. E. Reid, E. S. Singer, H. W. Gibson and H. C. Dorn, *Chemistry Of Materials*, 2008, **20**, 4993-4997.
6. Y. S. Grushko, V. S. Kozlov, T. O. Artamonova and M. A. Khodorkovskii, *Fullerenes Nanotubes And Carbon Nanostructures*, 2012, **20**, 351-353.
7. K. Akiyama, T. Hamano, Y. Nakanishi, E. Takeuchi, S. Noda, Z. Y. Wang, S. Kubuki and H. Shinohara, *Journal Of The American Chemical Society*, 2012, **134**, 9762-9767.
8. Z. X. Ge, J. C. Duchamp, T. Cai, H. W. Gibson and H. C. Dorn, *Journal Of The American Chemical Society*, 2005, **127**, 16292-16298.
9. S. Stevenson, K. Harich, H. Yu, R. R. Stephen, D. Heaps, C. Coumbe and J. P. Phillips, *Journal Of The American Chemical Society*, 2006, **128**, 8829-8835.
10. S. Stevenson, M. A. Mackey, C. E. Coumbe, J. P. Phillips, B. Elliott and L. Echegoyen, *Journal Of The American Chemical Society*, 2007, **129**, 6072-+.
11. S. Stevenson, M. A. Mackey, J. E. Pickens, M. A. Stuart, B. S. Confait and J. P. Phillips, *Inorganic Chemistry*, 2009, **48**, 11685-11690.
12. S. Stevenson and K. A. Rottinger, *Inorganic Chemistry*, 2013, **52**, 9606-9612.
13. Z. Y. Wang, Y. Nakanishi, S. Noda, K. Akiyama and H. Shinohara, *Journal of Physical Chemistry C*, 2012, **116**, 25563-25567.
14. A. H. Han, T. Wakahara, Y. Maeda, T. Akasaka, M. Fujitska, O. Ito, K. Yamamoto, M. Kako, K. Kobayashi and S. Nagase, *New Journal Of Chemistry*, 2009, **33**, 497-500.
15. T. Tsuchiya, T. Akasaka and S. Nagase, *Pure And Applied Chemistry*, 2010, **82**, 505-521.
16. T. Kodama, K. Higashi, T. Ichikawa, S. Suzuki, H. Nishikawa, I. Ikemoto, K. Kikuchi and Y. Achiba, *Chemistry Letters*, 2005, **34**, 464-465.
17. M. D. Diener and J. M. Alford, *Nature*, 1998, **393**, 668-671.
18. T. Tsuchiya, T. Wakahara, S. Shirakura, Y. Maeda, T. Akasaka, K. Kobayashi, S. Nagase, T. Kato and K. M. Kadish, *Chemistry Of Materials*, 2004, **16**, 4343-4346.
19. T. Tsuchiya, T. Wakahara, Y. F. Lian, Y. Maeda, T. Akasaka, T. Kato, N. Mizorogi and S. Nagase, *Journal Of Physical Chemistry B*, 2006, **110**, 22517-22520.
20. J. W. Raebiger and R. D. Bolskar, *Journal of Physical Chemistry C*, 2008, **112**, 6605-6612.
21. R. D. Bolskar and J. M. Alford, *Chemical Communications*, 2003, 1292-1293.
22. B. Elliott, L. Yu and L. Echegoyen, *Journal Of The American Chemical Society*, 2005, **127**, 10885-10888.
23. M. R. Ceron, F. F. Li and L. Echegoyen, *Chemistry-A European Journal*, 2013, **19**, 7410-7415.
24. C. M. Beavers, H. X. Jin, H. Yang, Z. M. Wang, X. Q. Wang, H. L. Ge, Z. Y. Liu, B. Q. Mercado, M. M. Olmstead and A. L. Balch, *Journal Of The American Chemical Society*, 2011, **133**, 15338-15341.
25. B. Q. Mercado, A. Jiang, H. Yang, Z. M. Wang, H. X. Jin, Z. Y. Liu, M. M. Olmstead and A. L. Balch, *Angewandte Chemie-International Edition*, 2009, **48**, 9114-9116.
26. H. Yang, H. X. Jin, H. Y. Zhen, Z. M. Wang, Z. Y. Liu, C. M. Beavers, B. Q. Mercado, M. M. Olmstead and A. L. Balch, *Journal Of The American Chemical Society*, 2011, **133**, 6299-6306.
27. L. J. Wilson, D. W. Cagle, T. P. Thrash, S. J. Kennel, S. Mirzadeh, J. M. Alford and G. J. Ehrhardt, *Coordination Chemistry Reviews*, 1999, **192**, 199-207.
28. P. P. Fatouros, F. D. Corwin, Z. J. Chen, W. C. Broaddus, J. L. Tatum, B. Kettenmann, Z. Ge, H. W. Gibson, J. L. Russ, A. P. Leonard, J. C. Duchamp and H. C. Dorn, *Radiology*, 2006, **240**, 756-764.
29. H. C. Dorn and P. P. Fatouros, *Nanoscience and Nanotechnology Letters*, 2010, **2**, 65-72.
30. C. Y. Chen, G. M. Xing, J. X. Wang, Y. L. Zhao, B. Li, J. Tang, G. Jia, T. C. Wang, J. Sun, L. Xing, H. Yuan, Y. X. Gao, H. Meng, Z. Chen, F. Zhao, Z. F. Chai and X. H. Fang, *Nano Letters*, 2005, **5**, 2050-2057.
31. K. Kobayashi, M. Kuwano, K. Sueki, K. Kikuchi, Y. Achiba, H. Nakahara, N. Kananishi, M. Watanabe and K. Tomura, *Journal Of Radioanalytical And Nuclear Chemistry-Articles*, 1995, **192**, 81-89.
32. C. Y. Shu, X. Y. Ma, J. F. Zhang, F. D. Corwin, J. H. Sim, E. Y. Zhang, H. C. Dorn, H. W. Gibson, P. P. Fatouros, C. R. Wang and X. H. Fang, *Bioconjugate Chemistry*, 2008, **19**, 651-655.
33. E. B. Iezzi, J. C. Duchamp, K. R. Fletcher, T. E. Glass and H. C. Dorn, *Nano Letters*, 2002, **2**, 1187-1190.
34. D. M. McCluskey, T. N. Smith, P. K. Madasu, C. E. Coumbe, M. A. Mackey, P. A. Fulmer, J. H. Wynne, S. Stevenson and J. P. Phillips, *Acs Applied Materials & Interfaces*, 2009, **1**, 882-887.
35. R. B. Ross, C. M. Cardona, D. M. Guldi, S. G. Sankaranarayanan, M. O. Reese, N. Kopidakis, J. Peet, B. Walker, G. C. Bazan, E. Van Keuren, B. C. Holloway and M. Drees, *Nature Materials*, 2009, **8**, 208-212.
36. J. R. Pinzon, M. E. Plonska-Brzezinska, C. M. Cardona, A. J. Athans, S. S. Gayathri, D. M. Guldi, M. A. Herranz, N. Martin, T. Torres and L. Echegoyen, *Angewandte Chemie-International Edition*, 2008, **47**, 4173-4176.
37. M. N. Chaur, F. Melin, B. Elliott, A. Kumbhar, A. J. Athans and L. Echegoyen, *Chemistry-A European Journal*, 2008, **14**, 4594-4599.
38. M. N. Chaur, A. J. Athans and L. Echegoyen, *Tetrahedron*, 2008, **64**, 11387-11393.
39. A. A. Popov, S. F. Yang and L. Dunsch, *Chemical Reviews*, 2013, **113**, 5989-6113.
40. X. Lu, L. Feng, T. Akasaka and S. Nagase, *Chemical Society Reviews*, 2012, **41**, 7723-7760.
41. S. F. Yang, *Current Organic Chemistry*, 2012, **16**, 1079-1094.
42. S. Stevenson, C. B. Rose, A. A. Robson, D. T. Heaps and J. P. Buchanan, *Fullerenes Nanotubes And Carbon Nanostructures*, 2013, **in press**, DOI: 10.1080/1536383X.1532013.1798725.
43. F. E. Critchfield and J. J. Johnson, *Analytical Chemistry*, 1956, **28**, 430-436.
44. R. A. Donia, J. A. Shotton, L. O. Bentz and G. E. P. Smith, *J. Org. Chem.*, 1949, **14**, 946-951.
45. E. V. Basiuk, V. A. Basiuk, V. P. Shabel'nikov, V. G. Golovaty, J. O. Flores and J. M. Saniger, *Carbon*, 2003, **41**, 2339-2346.
46. J. Janaki, M. Premila, P. Gopalan, V. S. Sastry and C. S. Sundar, *Thermochimica Acta*, 2000, **356**, 109-116.
47. H. Yang, C. X. Lu, Z. Y. Liu, H. X. Jin, Y. L. Che, M. M. Olmstead and A. L. Balch, *Journal Of The American Chemical Society*, 2008, **130**, 17296-17300.