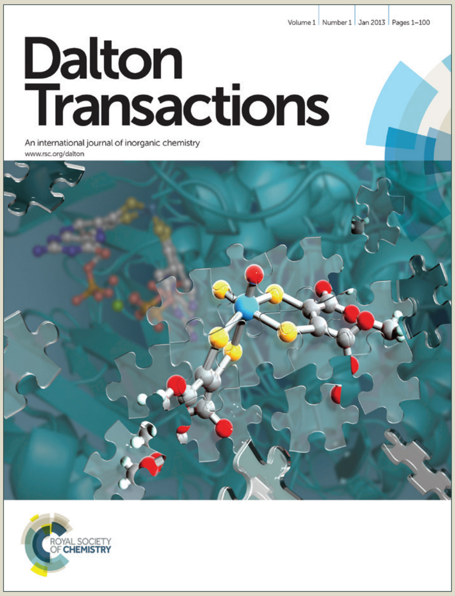
Dalton Transactions

Accepted Manuscript


Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

www.rsc.org/dalton

Journal Name

RSCPublishing

COMMUNICATION

Tuneable Dynamics of a Scandium Nitride Cluster Inside an I_h-C_{80} Cage

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yongqiang Feng,[a] Taishan Wang,*[,a] Junfeng Xiang,[a] Lihua Gan,[b] Bo Wu,[a] Li Jiang[a] and Chunru Wang*[,a]

The internal clusters in metallofullerenes usually exhibit certain motion that is potentially usable in molecular gyroscopes and nano-machines. Based on ^{45}Sc NMR, the motion of the scandium nitride cluster within the C_{80} cage was investigated via varying the temperature and modifying the cage, and changing the cluster size.

In the last few decades, molecular machines[1-7] such as molecular rotors,[2] molecular motors,[3] molecular shuttles,[4] molecular wheelbarrows,[5] molecular elevators,[6] and molecular gyroscopes,[7] etc. have attracted extensive attentions. For these molecule-based engineered systems, the main challenge is how to finely tune the dynamical motion for these nano-architectures.

Endohedral metallofullerenes (EMF) with clusters encapsulated inside the fullerene cages are ideal candidates for molecular machines because of their motional internal moieties.[8-14] For example, a low energy Raman spectroscopy study of $Sc_2C_2@C_{84}$ revealed temperature-dependent quantized rotational states of the internal Sc_2C_2 cluster.[12] A temperature-dependent ^{14}N NMR study on $M_3N@I_h$-C_{80} (M = Sc, Y, Lu) disclosed an increasing rotation barrier of the endohedral $(M_3N)^{6+}$ cluster with the extended size of M_3N.[13] In addition, it was found that the exohedral addend on $Sc_3C_2@C_{80}$ dramatically hindered the free rotation of Sc_3C_2 cluster.[14]

For better understanding the dynamics of encapsulated cluster in metallofullerenes, it is necessary to select a prototype of metallofullerene molecule and make a systematic study on the moving behaviour of its internal species. Herein, $Sc_3N@I_h$-C_{80} was chosen and NMR spectrometry was taken as the main probe tool to investigate its internal dynamics, considering its vrious physical and chemical properties and high yield.[15] Through manipulating the temperature, modifying fullerene cage, and changing the cluster size, it was revealed that the dynamical movement of the internal cluster of $Sc_3N@I_h$-C_{80} is indeed tuneable.

The ^{13}C NMR spectrum of $Sc_3N@I_h$-C_{80} showed two signals at 136.37 and 143.60 ppm with an intensity ratio of 1:3 at room temperature, suggesting the I_h-symmetry of C_{80} cage.[15a] Obviously, the $Sc_3N@I_h$-C_{80} should have a rapidly rotating Sc_3N cluster inside the fullerene cage, if not, the Sc_3N cluster would broke the symmetry of I_h-C_{80} and lead to more than two NMR lines. Moreover, the ^{45}Sc NMR spectrum of $Sc_3N@I_h$-C_{80} under room temperature showed a single peak at 190 ppm, which suggests three equivalent scandium nuclei and also confirms the free rotation of the internal Sc_3N cluster.

The motion rate of endohedral cluster can be revealed by the temperature-dependant NMR technique. Fu et al. studied the Sc_3N dynamics at temperatures from 303 to 393 K by ^{14}N and ^{45}Sc NMR study of $Sc_3N@I_h$-C_{80} in 1,2-dichlorobenzen (ODCB) solution, and an activation energy (E_a) of 75 meV for the Sc_3N cluster was revealed.[13] At the same time, the $Y_3N@I_h$-C_{80} was disclosed to have a E_a of 122 meV for the Y_3N cluster from 268 to 388 K in ODCB solution.[13] In addition, NMR studies from 293 to 413 K on $Sc_2C_2@C_s(6)$-C_{82}[16] and $Sc_2C_2@C_{2v}$-C_{80}[17] by Akasaka et al. indicated that the fixed Sc_2C_2 under room temperature can be activated to rotate after heating up to 373 K. Notably, these studies are based on NMR technique under high temperatures.

However, NMR study at low temperature is more important as the low temperature will decelerate the endohedral motion and help to find out the infection point of its dynamics. Therefore, in this work, the ^{45}Sc NMR spectroscopy for $Sc_3N@C_{80}$ was firstly performed under low temperature in CS_2 solution.

As shown in Figure 1, along with the temperature decreasing from 293 to 213 K, the signal in the ^{45}Sc NMR spectra of $Sc_3N@C_{80}$ exhibited a remarkable broadening with the line width increasing from 30 (273 K) to 257 ppm (233 K) due to the deceleration of the motional endohedral Sc_3N cluster. Such motional narrowing behaviour was also observed in solid ^{45}Sc NMR experiment.[11] However, Figure 1b showed that the NMR line-width is not changed if the temperature is further decreased to 213 K, indicating the Sc_3N cluster has been confined.

Popov et al. has reported that the scandium atoms of $Sc_3N@C_{80}$ could rotate rapidly along an energy minima belt with several lowest energy configurations.[18] It was the same case herein that from 293 to 233 K the three equivalent scandium atoms circulate along this belt in a robust manner, and these rotations slow gradually when temperature decreases, disclosing that this kind of circulation is closely related to the temperature. At or below 233 K, such free motion becomes to be confined in some energy minima points. The changeless ^{45}Sc NMR line-width shows much near energy between these minima points.

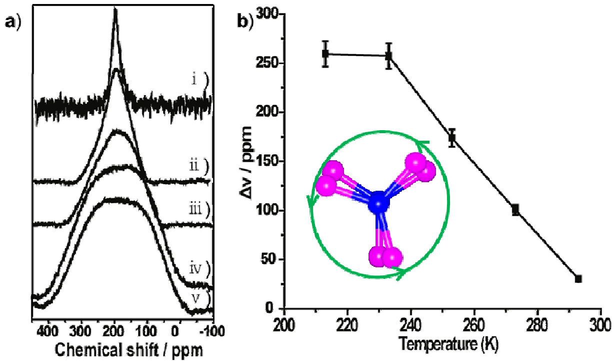


Figure 1. (a) ^{45}Sc NMR spectra (CS_2/d_8-THF, 145 MHz) of $Sc_3N@I_h$-C_{80} at varied temperatures, (i) 293K, (ii) 273K, (iii) 253K, (iv) 233K, (v) 213K. (b) Line-widths Δv of the ^{45}Sc NMR signals for $Sc_3N@I_h$-C_{80} as a function of temperature. (inset: the schematic motion mode of Sc_3N cluster, Sc in purple and N in blue)

Generally, the line width is proportional to correlation time (τ), which can be defined as[13]:

$$\tau = \tau_0 \exp(E_a/kT) \qquad (1)$$

where E_a is the rotational barrier energy and T is the temperature. Based on the NMR data shown in Figure 1a and Equation (1), the active energy E_a was estimated to be 122 meV. The larger E_a value in this work compared to the previous reported (~75 meV in ODCB)[9i,13] may be due to the higher barrier for the Sc_3N cluster rotation at lower temperatures. That is to say, at lower temperatures the Sc_3N cluster has smaller motion inertia, and it needs more energy to move to another site. On the other hand, the varied motion of the entire $Sc_3N@C_{80}$ in the two different solvents (CS_2 and ODCB) maybe another possible reason for the different activation energies. In Table 1, experimental E_a for endohedral clusters in several metallofullerenes are listed. Also, the solvents and NMR temperature ranges are included.

Table 1. Experimental activation energies (E_a) for endohedral clusters in several metallofullerenes.

metallofullerenes	E_a/meV	solvent	T/K	NMR
$Sc_3N@I_h$-C_{80}[a]	122	CS_2	213~293	^{45}Sc
$Sc_3N@I_h$-C_{80}[13]	75	ODCB	303~393	^{45}Sc
$Y_3N@I_h$-C_{80}[13]	122	ODCB	268~388	^{14}N
$CeSc_2N@C_{80}$[25]	79	ODCB	313~383	^{45}Sc
$Sc_2C_2@C_s(6)$-C_{82}[16]	642	ODCB	293~413	^{45}Sc
$Sc_2C_2@C_{2v}$-C_{80}[17]	653	ODCB	293~413	^{45}Sc

[a] data in this work

Interestingly, in $Sc_2C_2@C_s(6)$-C_{82} the E_a for Sc_2C_2 cluster rotating inside the C_{82} cage is as large as 642 meV,[16] which was deduced from the ^{45}Sc NMR analysis where the two scandium nuclei became equivalent until 373 K; however, in $Sc_2C_2@C_{2v}$-C_{80} the E_a was even higher up to 653 meV[17]. When it comes to $Sc_3N@I_h$-C_{80}, the internal Sc_3N cluster with three equivalent Sc atoms rotates rapidly inside the I_h-C_{80} cage even at 253 K. These results imply that the cage structure can greatly influence the motion of the internal cluster. In addition, it also can be found that the $Sc_3N@C_{80}$ is a good object to investigate the rotation property for potential application in nano-machine.

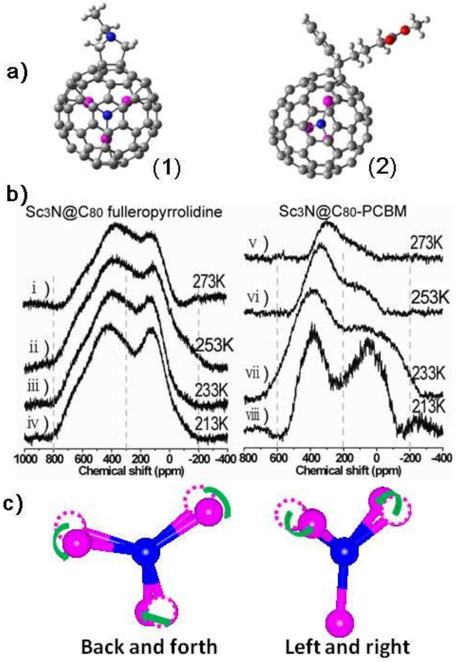


Figure 2. a) Optimized structures of $Sc_3N@C_{80}$ fulleropyrrolidine (**1**) and $Sc_3N@C_{80}$-PCBM (**2**). (C: gray, Sc: purple, N: blue, O: red, H: white). b) ^{45}Sc NMR spectra (CS_2/d_8-THF, 145 MHz) of $Sc_3N@I_h$-C_{80} derivatives at varied temperatures. (i) 273K, (ii) 253K, (iii) 233K, (iv) 213K of (**1**); (v) 273K, (vi) 253K, (vii) 233K, (viii) 213K of (**2**). (c) Two possible oscillating modes of Sc_3N cluster.

Chemical modification can change the molecular symmetry, which in turn will influence the internal dynamic behaviour.[19] Two chemically-modified $Sc_3N@C_{80}$, denoted as $Sc_3N@C_{80}$ fulleropyrrolidine[15b] (**1**) and $Sc_3N@C_{80}$-PCBM[15c] (**2**), were synthesized and investigated by ^{45}Sc NMR spectroscopy. These two derivatives have different structures as shown in Figure 2a. The $Sc_3N@C_{80}$ fulleropyrrolidine has addend on [5,6] site with closed fullerene cage, whereas the $Sc_3N@C_{80}$-PCBM is 6,6-open phenyl-C_{81}-butyric acid methyl ester metallofulleroid. So it is interesting to study the corresponding dynamic behaviours of their internal Sc_3N cluster. As shown in Figure 2b, ^{45}Sc NMR spectra of $Sc_3N@C_{80}$ fulleropyrrolidine and $Sc_3N@C_{80}$-PCBM exhibit distinctive patterns, which are all different from that of the pristine $Sc_3N@C_{80}$. For $Sc_3N@C_{80}$ fulleropyrrolidine, two distinctive ^{45}Sc NMR signals (-30~800 ppm) were observed at 273 K, whereas for $Sc_3N@C_{80}$-PCBM under the same temperature, a broad ^{45}Sc NMR signal (-50~450ppm) was observed.

Obviously, the molecular symmetry of $Sc_3N@C_{80}$ lowers after chemical modifications, leading to non-identical scandium atoms in both of the $Sc_3N@C_{80}$ fulleropyrrolidine and $Sc_3N@C_{80}$-PCBM derivatives, so very broad ^{45}Sc resonant peaks were observed in their ^{45}Sc NMR spectra. Moreover, these two different ^{45}Sc NMR patterns disclosed that the closed-cage modification in fulleropyrrolidine at [5,6] site hinders the Sc_3N cluster rotation more seriously than the open-cage structure of $Sc_3N@C_{80}$-PCBM. Consequently, these two endohedral dynamics give rise to different line width in ^{45}Sc NMR. It was suggested that the perturbation of the fullerene π-system and the inner electronic distributions could lead to tremendous influence on the cluster dynamics.[19] These two addition patterns result in different aromaticity of the fullerene cages and inhomogeneous electron population on the internal Sc nuclei. Similar results were also found in the cases of $Sc_3N@C_{80}$-$(CH_2)_2$NTrt (Trt = trityl) isomers, where the X-ray crystallography of [6,6]-$Sc_3N@I_h$-$C_{80}(CH_2)_2$NTrt shows totally 15 sites, whereas the [5,6] isomer shows only two sets of different Sc_3N positions.[15e]

The ^{45}Sc NMR of $Sc_3N@C_{80}$ fulleropyrrolidine and $Sc_3N@C_{80}$-PCBM were then studied at low temperatures. For these two derivatives, two-line NMR patterns with a intensity ratio of 1:2 were showing more and more apparently when decreasing temperature (see Figure 2b), indicating that the motional processes for two of the three scandium atoms were dramatically different with the third one. In $Sc_3N@C_{80}$-PCBM, another ^{45}Sc NMR signal can be observed at 253 K. Different from the circulation of the Sc_3N cluster in pristine $Sc_3N@C_{80}$ (inset of Figure 1b), the motional modes in modified $Sc_3N@C_{80}$ become oscillations as schematically illustrated in Figure 2c, which is in agreement with the disorder pattern portrayed in the single crystal result.[15c] The temperature-dependent NMR results reveal that these oscillations are also closely related to the temperature.

The endohedral dynamics of $Sc_3N@C_{80}$ were further studied by changing the cluster size gradually. Figure 3a showed the molecule structures of $Sc_{3-x}Y_xN@I_h$-C_{80} (x = 0-3), where scandium atoms were changed to yttrium one by one. ^{13}C and ^{45}Sc NMR spectroscopy were performed to investigate the size effect on the dynamic behavior of internal species.

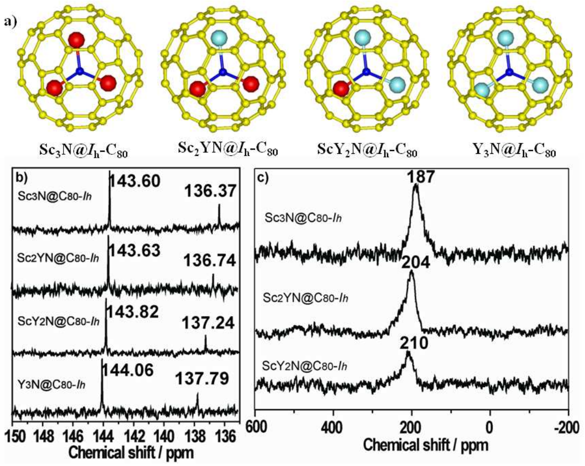


Figure 3. (a) Schematic molecule structures of $Sc_3N@I_h$-C_{80}, $Sc_2YN@I_h$-C_{80}, $ScY_2N@I_h$-C_{80} and $Y_3N@I_h$-C_{80}. (C: yellow, Sc: red, Y: light blue, N: dark blue). (b) ^{13}C NMR spectra (d_4-ODCB, 150 MHz) of $Sc_{3-x}Y_xN@I_h$-C_{80} (x = 0-3). (c) ^{45}Sc NMR spectra (d_4-ODCB, 145 MHz) of $Sc_{3-x}Y_xN@I_h$-C_{80} (x = 0-2).

The 150 MHz ^{13}C NMR spectra of $Sc_{3-x}Y_xN@I_h$-C_{80} (x = 0-3) were measured at room temperature as shown in Figure 3b, in which all showed two signals with chemical shift in an intensity ratio of 1:3, suggesting free rotation movements of the internal species in these metallofullerenes. However, along with the size of internal species increasing from $Sc_3N@C_{80}$ to $Y_3N@C_{80}$, the ^{13}C NMR lines upshift perceptibly, which can be ascribed to the pyramidalizition of carbon atoms as quantified by the π-orbital axis vector (POAV) as well as the changed aromaticity of carbon cage.[20,21] Furthermore, the NMR line width increases from $Sc_3N@C_{80}$ to $Y_3N@C_{80}$ (see Table 2), corresponding to a shorter ^{13}C relaxation process caused by slower motion of endohedral cluster inside I_h-C_{80} cage.[9i,22] Dunch et al. have investigated the role of the internal cluster on the relaxation of the fullerene cage carbons, which revealed that the relaxation rate of $Y_3N@C_{80}$ is slightly larger than that of $Sc_3N@C_{80}$ due to the internal cluster size effect.[22b] Also the ^{13}C relaxation process could be influenced by a scalar coupling between ^{13}C and ^{39}Y as reported previously.[22]

Table 2. ^{13}C NMR line width Δv (Hz) of $Sc_{3-x}Y_xN@I_h$-C_{80} (x = 0-3).

	$Sc_3N@C_{80}$	$Sc_2YN@C_{80}$	$ScY_2N@C_{80}$	$Y_3N@C_{80}$
136~138 ppm	23.35	25.90	26.05	30.88
143~145 ppm	20.07	25.19	25.42	31.58

Figure 3c showed the ^{45}Sc NMR spectra of $Sc_{3-x}Y_xN@I_h$-C_{80} (x = 0-2), in which the single peak indicates the free motion of internal clusters, and a similar shift to lower magnetic field of the ^{45}Sc NMR signals from $Sc_3N@C_{80}$ to $ScY_2N@C_{80}$ is shown. Popov[23] has reported that Sc_3N cluster in $Sc_3N@C_{80}$ possesses a planar triangle with a Sc-N bond length of 2.033 Å whilst in $Y_3N@C_{80}$ the Y-N bond length of the internal Y_3N cluster is elongated to 2.060 Å and thus the Y_3N cluster is strained inside the I_h-C_{80} cage. As shown in Figure 3c, for $ScY_2N@I_h$-C_{80} with one Sc nucleus, its line-width (95 ppm) is comparable to that of $Sc_3N@I_h$-C_{80} with three Sc nuclei (104 ppm), disclosing slower rotation in $ScY_2N@I_h$-C_{80}. In addition, the line-width of ^{45}Sc NMR spectra for $ScLu_2N@I_h$-C_{80}[24] lies around 120 ppm indicating weakened motion as the internal Lu^{3+} has larger ionic radii (0.90 Å) as well as its heavier nucleus. Similarly, for the ^{45}Sc NMR spectrum of $CeSc_2N@I_h$-C_{80}[25] in ODCB at 298 K, its line-width is about 115 ppm implying weakened motivation of the inner cluster compared to that of $ScY_2N@I_h$-C_{80}.

In conclusion, a tuneable dynamic motion of a scandium nitride cluster inside an icosahedral I_h-C_{80} fullerene cage was achieved by varying the temperature, modifying the fullerene cage, or changing the internal cluster size. Since controlling the molecule dynamics could alter their electronic, optical and magnetic properties, it would be of great potential to design and make logic molecular devices based on the $Sc_3N@C_{80}$ metallofullerene.

This work was supported by the National Basic Research Program (2012CB932901), National Natural Science Foundation of China (61227902, 21203205), NSAF (11179006), and the Key Research Program of the Chinese Academy of Sciences (KGZD-EW-T02). T. Wang also thanks the Youth Innovation Promotion Association of CAS.

Notes and references

[a]*Beijing National Laboratory for Molecular Sciences, Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: wangtais@iccas.ac.cn, crwang@iccas.ac.cn.*
[b]*School of chemistry and chemical engineering Western University, Chongqing 400715, China*

† Electronic Supplementary Information (ESI) available: experimental details, HPLC chromatograms, MALDI-TOF mass spectra, NMR profiles and theoretical calculations. See DOI: 10.1039/c000000x/

1 a) E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem. Int. Ed.*, 2007, **46**, 72-191; b) G. Rapenne, *Org. Biomol. Chem.*, 2005, **3**, 1165-1169; c) S. D. Karlen, C. E. Godinez and M. A. Garcia-Garibay, *Org. Lett.*, 2006, **8**, 3417-3420.

2 a) N. Koumura, R. W. Zijlstra, R. A. van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152-155; b) G. S. Kottas, L. I. Clarke, D. Horinek and J. Michl, *Chem. Rev.*, 2005, **105**, 1281-1376.

3 R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. Bastiaansen, D. J. Broer and B. L. Feringa, *Nature*, 2006, **440**, 163-163.

4 a) J.-P. Collin, C. Dietrich-Buchecker, P. Gaviña, M. C. Jimenez-Molero and J.-P. Sauvage, *Acc. Chem. Res.*, 2001, **34**, 477-487; b) A. M. Brouwer, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia and G. W. Wurpel, *Science*, 2001, **291**, 2124-2128.

5 G. Jimenez-Bueno and G. Rapenne, *Tetrahedron Lett.*, 2003, **44**, 6261-6263.

6 J. D. Badjić, V. Balzani, A. Credi, S. Silvi and J. F. Stoddart, *Science*, 2004, **303**, 1845-1849.

7 a) T.-A. V. Khuong, H. Dang, P. D. Jarowski, E. F. Maverick and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, 2007, **129**, 839-845; b) J. E. Nuñez, A. Natarajan, S. I. Khan and M. A. Garcia-Garibay, *Org. Lett.*, 2007, **9**, 3559-3561.

8 a) A. Mateo-Alonso, D. M. Guldi, F. Paolucci and M. Prato, *Angew. Chem. Int. Ed.*, 2007, **46**, 8120-8126; b) T. Huang, J. Zhao, M. Feng, A. A. Popov, S. Yang, L. Dunsch and H. Petek, *Nano Lett.*, 2011, **11**, 5327-5332.

9 a) T. Wang and C. Wang, *Acc. Chem. Res.*, 2014, **47**, 450-458; b) A. A. Popov, S. Yang and L. Dunsch, *Chem. Rev.*, 2013, **113**, 5989; c) X. Lu, T. Akasaka and S. Nagase, *Acc. Chem. Res.*, 2013, **46**, 1627; d) J. Zhang, S. Stevenson and H. C. Dorn, *Acc. Chem. Res.*, 2013, **46**, 1548; e) X. Lu, L. Feng, T. Akasaka and S. Nagase, *Chem. Soc. Rev.*, 2012, **41**, 7723; f) X. Lu, L. Bao, T. Akasaka and S. Nagase, *Chem. Commun.*, 2014, **50**, 14701-14715; g) X. Lu, T. Akasaka and S. Nagase, *Chem. Commun.*, 2011, **47**, 5942; h) M. Yamada, T. Akasaka and S. Nagase, *Acc. Chem. Res.*, 2010, **43**, 92-102; i) J. Zhang and H. C. Dorn, Fuller. Nanotube. Car. N., 2014, **22**, 35-46.

10 T. Akasaka, S. Nagase, K. Kobayashi, M. Wälchli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshino and T. Erata, *Angew. Chem. Int. Ed.*, 1997, **36**, 1643-1645.

11 K. R. Gorny, C. H. Pennington, J. A. Martindale, J. P. Phillips, S. Stevenson, I. Heinmaa and R. Stern. *Condensed Matter*, 2006, arXiv: cond.

12 M. Krause, M. Hulman, H. Kuzmany, O. Dubay, G. Kresse, K. Vietze, G. Seifert, C. Wang and H. Shinohara, *Phys. Rev. Lett.*, 2004, **93**, 137403.

13 W. Fu, X. Wang, H. Azuremendi, J. Zhang and H. C. Dorn, *Chem. Commun.*, 2011, **47**, 3858-3860.

14 T. Wang, J. Wu, W. Xu, J. Xiang, X. Lu, B. Li, L. Jiang, C. Shu and C. Wang, *Angew. Chem. Int. Ed.*, 2010, **49**, 1786-1789.

15 a) S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch and H. C. Dorn, *Nature*, 1999, **401**, 55; b) C. M. Cardona, A. Kitaygorodskiy, A. Ortiz, M. Á. Herranz and L. Echegoyen, *J. Org. Chem.*, 2005, **70**, 5092-5097; c) C. Shu, W. Xu, C. Slebodnick, H. Champion, W. Fu, J. E. Reid, H. Azurmendi, C. Wang, K. Harich and H. C. Dorn, *Org. Lett.*, 2009, **11**, 1753-1756; d) J. R. Pinzón, T. Zuo and L. Echegoyen, *Chem. Eur. J.*, 2010, **16**, 4864-4869; e) T. Cai, C. Slebodnick, L. Xu, K. Harich, T. E. Glass, C. Chancellor, J. C. Fettinger, M. M. Olmstead, A. L. Balch, H. W. Gibson and H. C. Dorn, *J. Am. Chem. Soc.*, 2006, **128**, 6486-6492.

16 a) X. Lu, K. Nakajima, Y. Iiduka, H. Nikawa, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase and T. Akasaka, *J. Am. Chem. Soc.*, 2011, **133**, 19553-19558; b) Y. Miyake, S. Suzuki, Y. Kojima, K. Kikuchi, K. Kobayashi, S. Nagase, M. Kainosho, Y. Achiba, Y. Maniwa and K. Fisher, *J. Phys. Chem.*, 1996, **100**, 9579.

17 H. Kurihara, X. Lu, Y. Iiduka, N. Mizorogi, Z. Slanina, T. Tsuchiya, T. Akasaka and S. Nagase, *J. Am. Chem. Soc.*, 2011, **133**, 2382-2385.

18 A. A. Popov and L. Dunsch, *J. Am. Chem. Soc.*, 2008, **130**, 17726.

19 a) B. Elliott, A. D. Pykhova, J. Rivera, C. M. Cardona, L. Dunsch, A. A. Popov and L. Echegoyen, *J. Phys. Chem. C*, 2013, **117**, 2344; b) M. Yamada, T. Wakahara, T. Nakahodo, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, N. Mizorogi and S. Nagase, *J. Am. Chem. Soc.*, 2006, **128**, 1402; c) A. A. Popov, A. D. Pykhova, I. N. Ioffe, F.-F. Li and L. Echegoyen, *J. Am. Chem. Soc.*, 2014, **136**, 13436.

20 a) T. Suzuki, Q. Li, K. C. Khemani and F. Wudl, *J. Am. Chem. Soc.*, 1992, **114**, 7301-7302; b) A. Pasquarello, M. Schlüter and R. Haddon, *Phys. Rev. A*, 1993, **47**, 1783; c) A. Pasquarello, M. Schlüter and R. Haddon, *Science*, 1992, **257**, 1660.

21 a) S. Yang, M. Kalbac, A. Popov and L. Dunsch, *ChemPhysChem*, 2006, **7**, 1990-1995; b) N. Chen, L.-Z. Fan, K. Tan, Y.-Q. Wu, C.-Y. Shu, X. Lu and C.-R. Wang, *J. Phys. Chem. C*, 2007, **111**, 11823-11828; c) S. Yang, A. A. Popov and L. Dunsch, *Angew. Chem. Int. Ed.*, 2008, **47**, 8196-8200.

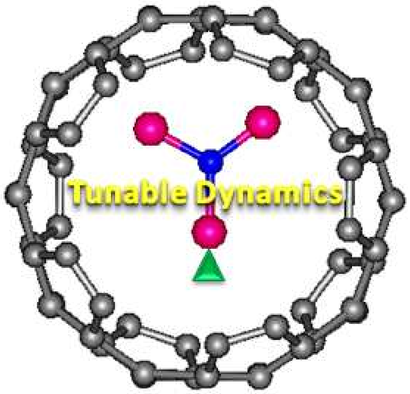
22 a) J. Zhang, T. Fuhrer, W. Fu, J. Ge, D. W. Bearden, J. Dallas, J. Duchamp, K. Walker, H. Champion, H. Azurmendi, K. Harich and H. C. Dorn, *J. Am. Chem. Soc.*, 2012, **134**, 8487; b) S. Klod, L. Zhang and L. Dunsch, *J. Phys. Chem. C*, 2010, **114**, 8264.

23 a) Q. Deng and A. A. Popov, *J. Am. Chem. Soc.*, 2014, **136**, 4257; b) A. A. Popov and L. Dunsch, *J. Am. Chem. Soc.*, 2007, **129**, 11835.

24 S. Yang, A. A. Popov, C. Chen and L. Dunsch, *J. Phys. Chem. C*, 2009, **113**, 7616.

25 X. Wang, T. Zuo, M. M. Olmstead, J. C. Duchamp, T. E. Glass, F. Cromer, A. L. Balch and H. C. Dorn, *J. Am. Chem. Soc.*, 2006, **128**, 8884.

Table of Contents



A tuneable dynamic motion of a Sc_3N cluster inside an I_h-C_{80} fullerene cage was investigated by ^{45}Sc NMR technique.