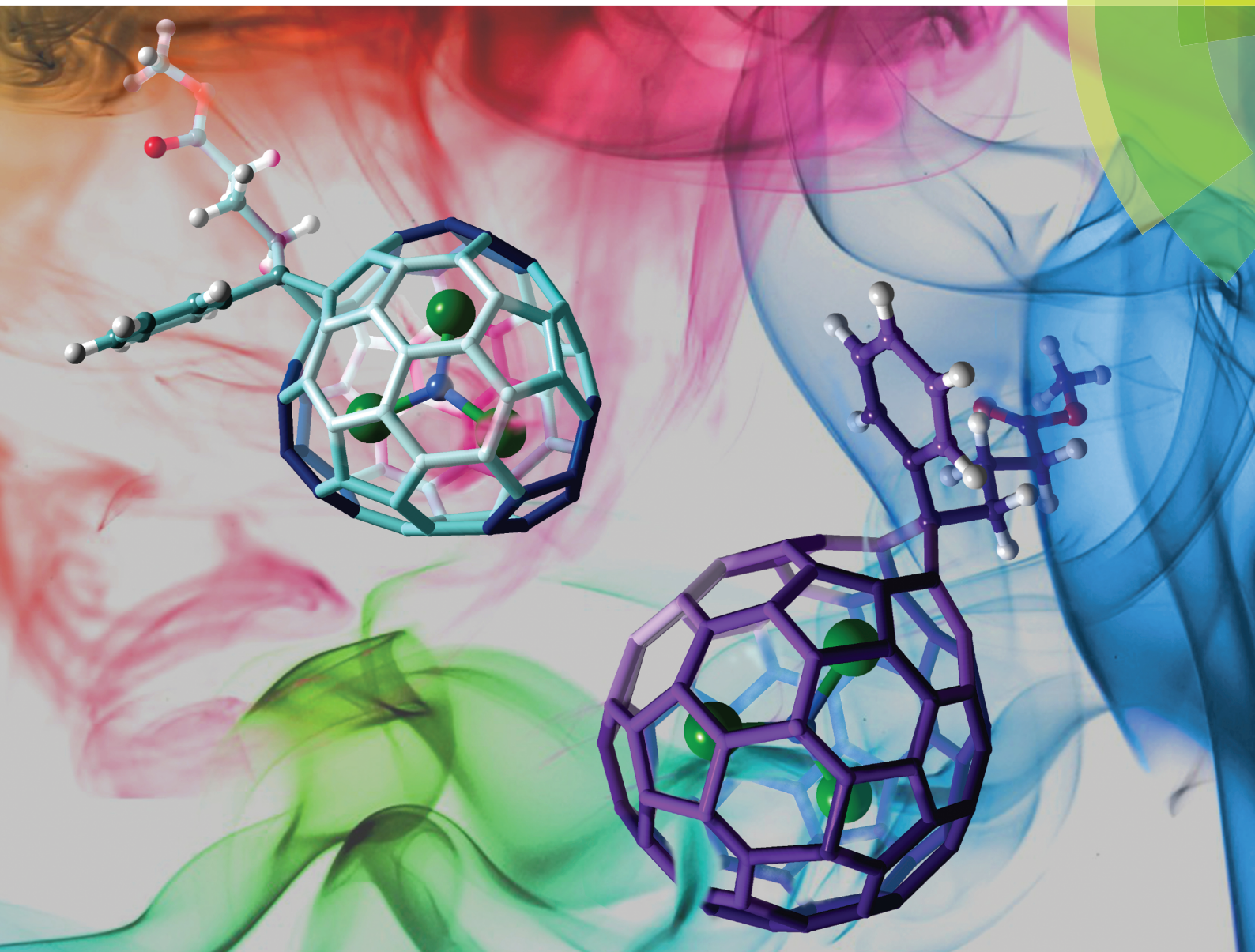


ChemComm

Chemical Communications

www.rsc.org/chemcomm



ISSN 1359-7345



COMMUNICATION

Marilyn M. Olmstead, Alan L. Balch, Josep M. Poblet, Luis Echegoyen *et al.*
Reactivity differences of $\text{Sc}_3\text{N}@C_{2n}$ ($2n = 68$ and 80). Synthesis of the
first methanofullerene derivatives of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$

175 YEARS



Cite this: *Chem. Commun.*, 2016, 52, 64

Received 4th September 2015,
Accepted 29th September 2015

DOI: 10.1039/c5cc07416a

www.rsc.org/chemcomm

Reactivity differences of $\text{Sc}_3\text{N}@C_{2n}$ ($2n = 68$ and 80). Synthesis of the first methanofullerene derivatives of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ †

Maira R. Cerón,‡^a Marta Izquierdo,‡^a Núria Alegret,^b Juan A. Valdez,^a
Antonio Rodríguez-Fortea,^b Marilyn M. Olmstead,*^c Alan L. Balch,*^c
Josep M. Poblet*^b and Luis Echegoyen*^a

Using a purification method introduced earlier based on redox properties it was possible to isolate $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ and $\text{Sc}_3\text{N}@D_{3h}\text{-C}_{78}$ and a mixture of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ and $\text{Sc}_3\text{N}@D_3\text{-C}_{68}$. Taking advantage of their chemical reactivity differences, $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ was isolated from $\text{Sc}_3\text{N}@D_3\text{-C}_{68}$ followed by further functionalization, giving rise to five new methano-derivatives of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$.

In 1999 Stevenson *et al.* reported the third most abundant fullerene that can be prepared in an arc reactor, $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$.¹ The discovery of the trimetallic nitride endohedral fullerene (TNT) family includes the non-IPR $\text{Sc}_3\text{N}@D_3\text{-C}_{68}$,² the IPR $\text{Sc}_3\text{N}@D_{3h}\text{-C}_{78}$,³ and the $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ isomer,^{4,5} all containing the same encapsulated triscandium nitride cluster inside.

It is convenient that four different and interesting compounds are obtained in a single arcing experiment but their efficient separation presents many challenges. Several methods to isolate endohedral fullerenes have been reported,^{10–14} but none of them result in the efficient purification of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$. Taking advantage of the differences in the oxidation/reduction potentials of the members of the $\text{Sc}_3\text{N}@C_{2n}$ ($n = 34, 39, 40$) family, we recently reported a selective chemical oxidation method that allows the isolation of pure $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ and $\text{Sc}_3\text{N}@C_{78}$, leaving a mixture of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ and $\text{Sc}_3\text{N}@C_{68}$.¹⁵

Exohedral functionalization of endohedral fullerenes is essential to improve their solubilities and to explore their properties and potential applications.^{16–20} There are very few examples of derivatives of $\text{Sc}_3\text{N}@C_{68}$ ^{21,22} and $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$,^{4,5,23–26} partly because of their low synthetic yields and also due to the very large number of derivative isomers that can be obtained, which

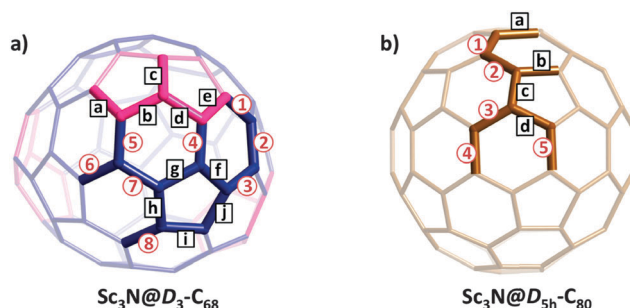


Fig. 1 Optimized structures for (a) $\text{Sc}_3\text{N}@D_3\text{-C}_{68}$ and (b) $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ (Sc_3N cluster is omitted for clarity). The (a) 18 and (b) 9 different types of bonds are labeled; [6,6]-junctions identified with numbers, [5,6] and [5,5]-junctions with letters. In the text and in Table 1, these bonds are labeled with the “b-” prefix to avoid confusion with the product isomers (1–8).

makes their purification and characterization very difficult. For example, the D_3 symmetric non-IPR $\text{Sc}_3\text{N}@C_{68}$ possesses 18 different types of bonds (Fig. 1), so an unsymmetric addend could yield 35 possible regioisomers.^{7,9} In the case of the D_{5h} symmetric $\text{Sc}_3\text{N}@C_{80}$, which has higher symmetry, there are nine different types of bonds and 15 possible regioisomer derivatives (Fig. 1).^{4,5}

There is only one example of an organic solar cell based on an endohedral fullerene acceptor (PCBH- $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$).²⁷ The main advantage of the endohedral fullerenes in photovoltaic applications results from their higher reduction potentials when compared to C_{60} and C_{70} (LUMO level),²⁸ that results in higher open circuit voltages (V_{oc}) and thus to higher power conversion efficiencies.

Here we report the separation of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ from $\text{Sc}_3\text{N}@C_{68}$ based on their chemical reactivity differences.^{10,29,30} Exohedral functionalization of $\text{Sc}_3\text{N}@C_{68}$ was performed using a cyclopropanation reaction with the *p*-toluenesulfonyl tosyl hydrazone of phenyl butyric acid methyl ester to yield the corresponding PCBM-type derivatives. We also present for the first time the synthesis and characterization of five PCBM methano-derivatives of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ (including the X-ray diffraction structure of one of the isomers) and two PCBM methano-derivatives of $\text{Sc}_3\text{N}@C_{68}$.

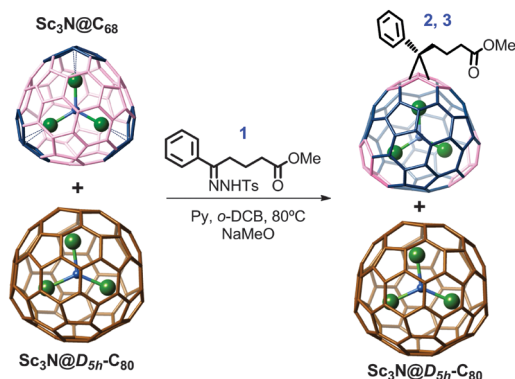
^a Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, USA. E-mail: echegoyen@utep.edu; Tel: +1 915-747-7573

^b Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Tarragona 43007, Spain. E-mail: josepmaria.poblet@urv.cat; Tel: +34 977559569

^c Department of Chemistry, University of California at Davis, Davis, CA 95616, USA. E-mail: mmolmstead@ucdavis.edu, albalch@ucdavis.edu; Tel: +1 530-752-0941

† Electronic supplementary information (ESI) available. CCDC 1421222. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc07416a
‡ M.R.C. and M.I. contributed equally.





Scheme 1 Synthesis of PCBM analogues of $\text{Sc}_3\text{N@C}_{68}$.

Separation of $\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$: a sample containing a mixture of $\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$ and $\text{Sc}_3\text{N@C}_{68}$ was obtained as described previously, by the selective oxidative/reductive removal of $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ and $\text{Sc}_3\text{N@C}_{78}$.¹⁵ $\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$ was then isolated from $\text{Sc}_3\text{N@C}_{68}$ by using a chemical reaction with the *p*-toluenesulfonyl tosyl hydrazone of phenyl butyric acid methyl ester (Compound 1, Scheme 1).^{31,32} This reaction afforded new endohedral derivatives of $\text{Sc}_3\text{N@C}_{68}$ and also provided a convenient separation method to purify $\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$.

The use of very accurate quantities of the reagents was crucial to successfully remove the $\text{Sc}_3\text{N@C}_{68}$ and isolate pure $\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$. Once the isomeric compounds 2 and 3 in Scheme 1 (PCBM- $\text{Sc}_3\text{N@C}_{68}$) are formed, the pristine endohedral fullerene ($\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$) can be easily separated from the reaction crude using regular silica gel column chromatography (Fig. S2, ESI[†]). To ensure the complete removal of $\text{Sc}_3\text{N@C}_{68}$, the reaction was followed by HPLC, taking an aliquot of the reaction crude and injecting it into the HPLC using a 5-PBB column. The optimized procedure employed 11.2 equivalents of tosyl hydrazone 1 per equivalent of $\text{Sc}_3\text{N@C}_{68}$ while heating during 1 hour at 95 °C. Using these conditions we recovered mainly multiple adducts of $\text{Sc}_3\text{N@C}_{68}$ as detected by MALDI-TOF (Fig. S3, ESI[†]) and a small fraction of monoadducts of PCBM- $\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$ (Fig. S3 and S4, ESI[†]).

PCBM- $\text{Sc}_3\text{N@D}_3\text{-C}_{68}$: to characterize the PCBM- $\text{Sc}_3\text{N@C}_{68}$ monoadducts the reaction was repeated with fewer equivalents of 1 to yield two main monoadduct isomers (2 and 3, Fig. 2). The two isomers were purified by HPLC and characterized by

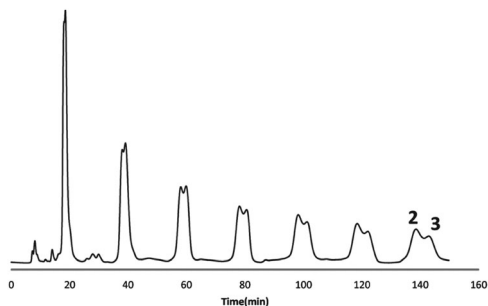
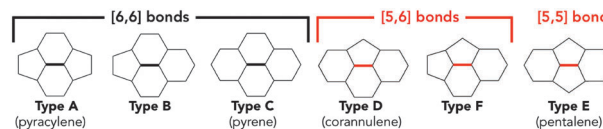


Fig. 2 Recycling HPLC profile of the two isomers of PCBM- $\text{Sc}_3\text{N@C}_{68}$. Conditions: Bucky-clutcher column ($\varphi = 250 \text{ mm} \times 10 \text{ ID}$); toluene; flow rate: 2 mL min^{-1} ; λ : 320 nm at room temperature.



Scheme 2 Different possible bonds on a fullerene.

$^1\text{H-NMR}$, mass spectrometry and UV-vis spectroscopy (Fig. S5–S11, ESI[†]). Although the D_3 symmetry of $\text{Sc}_3\text{N@C}_{68}$ can result in 35 possible regioisomers, we only observed two, which suggests a highly regioselective formation pathway, possibly directed by the encapsulated cluster inside.^{33,34}

$\text{Sc}_3\text{N@D}_3\text{-C}_{68}$ possesses eight different types of [6,6]-bonds, nine different types of [5,6]-bonds and one type of [5,5]-bond (Fig. 1a, Scheme 2). Due to the lack of symmetry of the addend used, with the spectroscopic evidences at hand, we cannot discard any of the 35 possible regioisomers for $\text{Sc}_3\text{N@D}_3\text{-C}_{68}$.

Cyclopropanation reactions using hydrazones typically occur under thermodynamic control. Dorn and co-workers as well as Poblet and co-workers predicted that the main product under thermodynamic control for a Bingel reaction on $\text{Sc}_3\text{N@D}_3\text{-C}_{68}$, is the “open” [6,6]-adduct on bond b-2 (Fig. 1a).^{21,34} All attempts to grow single crystals of these PCBM derivatives for structural assignment were unsuccessful; therefore DFT calculations were performed to determine the preferred addition sites. An adduct on bond b-2 has been also confirmed to be the lowest-energy product at 0 K as well as the most abundant isomer up to 353 K (80 °C) (see Table 1 and Fig. 1a, a full list of all the computed monoadducts can be found in the ESI[†]). Thus, if the reaction were to take place under thermodynamic control (*vide infra*), addition to bond b-2 would be the preferred product. The second preferred isomer would be on either bond b-a or bond b-b. Comparable results were observed by Akasaka and co-workers for a Diels–Alder reaction, where it was predicted by

Table 1 Relative energies for the lowest-energy PCBM monoadducts for $\text{Sc}_3\text{N@D}_3\text{-C}_{68}$ and $\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$ including solvent effects (*o*-dichlorobenzene)^a

Reacting bond ^b	Bond type	E_{rel} (kcal mol ⁻¹)
$\text{Sc}_3\text{N@D}_3\text{-C}_{68}$		
b-2*	[6,6] – Pyrene	0.0
b-a	[5,6] – Corannulene	4.2
b-b	[5,6] – Type F	4.5
b-e	[5,6] – Corannulene	6.8
b-3	[6,6] – Type B	8.4
$\text{Sc}_3\text{N@D}_{5h}\text{-C}_{80}$		
b-4*	[6,6] – Pyrene	0.0
b-c	[5,6] – Corannulene	7.6
b-b	[5,6] – Corannulene	8.1
b-a	[5,6] – Corannulene	8.6
b-1*	[6,6] – Type B	8.7
b-3	[6,6] – Type B	10.7
b-2	[6,6] – Type B	11.2
b-d	[5,6] – Corannulene	11.6
b-5*	[6,6] – Pyracylene	22.1

^a Due to the non-symmetric addend, two different regioisomers are possible at each bond, with energy differences always within 1 kcal mol⁻¹ (see ESI[†]). For those bonds that contain a symmetry element (denoted with an asterisk) only one possible regioisomer exists. ^b Bonds are labelled without the prefix b- in Fig. 2.



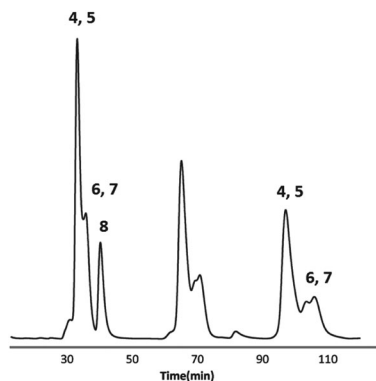


Fig. 3 Recycling HPLC profile of the five isomers of PCBM- $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$. Conditions: Bucky-clatcher column ($\phi = 250 \text{ mm} \times 10 \text{ ID}$); toluene; flow rate: 2 mL min^{-1} ; λ : 320 nm at room temperature.

DFT that bonds adjacent to the pentalene unit are chemically more reactive.

PCBM- $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$: the same PCBM reaction was performed using pure $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ and compared to that reported for the $I_h\text{-C}_{80}$ isomer. While $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ yields only one PCBM derivative isomer, we observed five isomers for $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$, out of the 15 distinct possibilities (4, 5, 6, 7 and 8).³⁵ The five isomers were purified by HPLC (Fig. 3) and characterized by NMR spectroscopy, mass spectrometry and UV-vis spectroscopy (Fig. S12–S25). Cyclic voltammetry (CV) was recorded for isomers 4, 6, 7 and 8 and the crystal structure was obtained for isomer 7.

$\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ possesses five different [6,6]-bonds and four different [5,6]-bonds (Fig. 1b, Scheme 2). Based on the available spectroscopic data it is not possible to discard any of the 15 possible regioisomers for $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$.

Unfortunately, we cannot compare our results with the monoadduct of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ synthesized *via* a 1,3-dipolar cycloaddition^{25,26} or to those calculated for the Diels–Alder additions,^{36–38} because it has been shown that for endohedral fullerenes different reaction types yield different regioisomers. For example, 1,3-dipolar cycloadditions on $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ result in addition to [5,6]-bonds as the thermodynamic product,^{39,40} while cyclopropanation reactions typically results in additions to [6,6]-bonds,¹⁷ with only one exception reported.⁴¹ For this reason we computed the lowest-energy regioisomers using DFT. The results collected in Table 1 show that bond b-4 leads to the thermodynamically preferred monoadduct, followed by bond b-c at $7.6 \text{ kcal mol}^{-1}$. Adducts on bonds b-b, -a and -1 are between 8 and 9 kcal mol^{-1} higher in energy; the remaining adducts are at more than 10 kcal mol^{-1} . Predicted molar fractions up to 400 K show that bond b-4 leads to the most abundant adduct (see ESI†). These results are in full agreement with the X-ray structural determination of compound 7, *vide infra*. Therefore, we might infer that this type of addition is likely to take place under thermodynamic control. If this were the case, adducts on bonds b-c and -b could be the other observed isomers in the HPLC chromatogram (compounds 4, 5, 6 and 8; Fig. 1b and 3). However, we cannot completely discard adducts on bonds b-a and -1, which are very close in

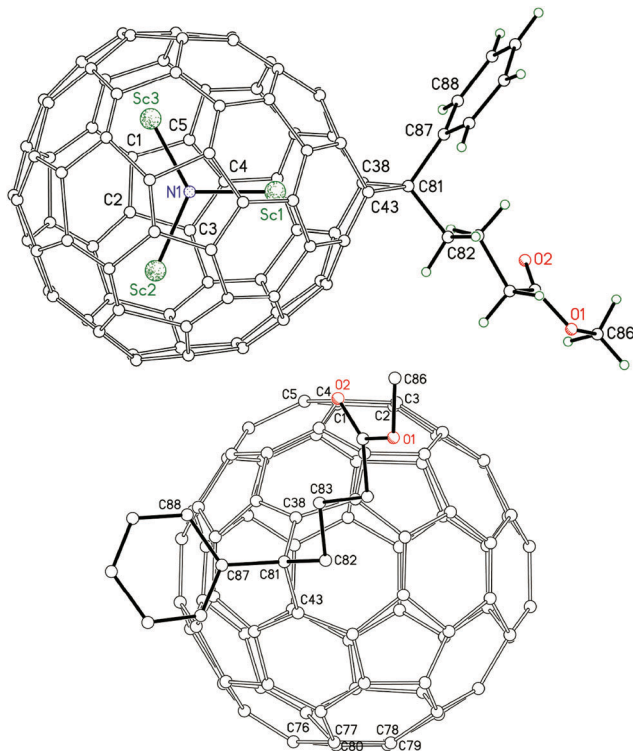


Fig. 4 Two views of the molecular structure of 7. The top view looks down former five-fold axis of the cage and on to the plane of the Sc_3N unit, while the bottom view is oriented with the former five-fold axis of the cage aligned vertically and omits the Sc_3N unit for clarity.

energy to adducts on bonds b-c and -b. A detailed study of the reaction paths, is beyond the scope of this work.

Crystallographic results: black, single crystals of 7- CS_2 were grown from a solution in CS_2 , CDCl_3 and hexanes by slow diffusion. The structure of the compound is shown in Fig. 4. As the top drawing shows, the internal Sc_3N group, which is ordered, is oriented so that one of the scandium ions is located near the site of addition. The lower drawing, which omits the Sc_3N group for clarity, shows the position of addition along the band of hexagons at the middle of the $D_{5h}\text{-C}_{80}$ cage. Adduct formation has resulted in the rupture of the bond that formerly connected C38 and C43 in the cage. The non-bonded C38...C43 distance in 7 is $2.20(2) \text{ \AA}$, whereas in pristine $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ the corresponding bonded C–C distance is 1.462 \AA , which is the longest such distance in the cage.²⁵

The redox properties were studied for isomers 4, 6, 7 and 8 of PCBM- $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ using CV, with a scan rate of 100 mV s^{-1} in *o*-DCB solutions and 0.05 M of *n*- Bu_4NPF_6 as supporting electrolyte. The CV results are summarized in Table S1, see ESI.† The cyclic voltammograms of isomers 4, 6, 7 and 8 showed three or four irreversible reduction waves, all cathodically shifted compared to those reported for the corresponding pristine fullerene $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$.²⁶ These results are in agreement with previous reports of cathodic shifts upon double bond removal by chemical functionalization.^{35,41} Isomers 4, 6, 7 and 8 also showed two or four reversible oxidation waves cathodically shifted compared to those of the corresponding pristine fullerene (Fig. S14, S19, S22 and S25, see ESI†).^{35,41}



The CV results showed that PCBM methano-derivatives of the $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ possess higher reduction potentials when compared to PC_{61}BM and PC_{71}BM (LUMO level),³¹ thus higher open circuit voltages (V_{oc}) could be expected when used in organic photovoltaic solar cells. The CV of isomers **7** and **8** exhibited very similar reduction potentials to those reported for $\text{PCBH-Lu}_3\text{N}@I_h\text{-C}_{80}$,²⁷ thus if all other factors remain constant, similar open circuit voltages could be expected.

In conclusion, we report for the first time a convenient separation method of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ from $\text{Sc}_3\text{N}@C_{68}$ based on chemical reactivity differences, and the exohedral functionalization of the two members of the $\text{Sc}_3\text{N}@C_{2n}$ ($n = 34$ and 40) family, to yield the corresponding PCBM analogues. We also synthesized and characterized the first methano-derivatives of $\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$ and the X-ray diffraction structure of one of the isomers. Using $\text{Sc}_3\text{N}@C_{68}$ and the PCBM-diazo precursor we predict preferential addition on the b-2 bond, the same regioisomer reported for the 1,3-dipolar cycloaddition and the Bingel reaction.

L.E. thanks the NSF for generous support of this work under the grant (CHE-1408865) and to the NSF-PREM program (DMR-1205302). The Robert A. Welch Foundation is also gratefully acknowledged for an endowed chair to L.E. (AH-0033). A.L.B. and M.M.O. thank the U. S. NSF (CHE-1305125), and the Advanced Light Source, Beamline 11.3.1, Lawrence Berkeley Laboratory, for support. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract no. DE-AC02-05CH11231. J.M.P thanks MINECO (CTQ2014-52774-P) and the Generalitat of Catalonia (2014SGR-199 and XRQTC) for support.

Notes and references

- 1 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, **402**, 898.
- 2 S. Stevenson, P. W. Fowler, T. Heine, J. C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible and H. C. Dorn, *Nature*, 2000, **408**, 427–428.
- 3 J. M. Campanera, C. Bo, M. M. Olmstead, A. L. Balch and J. M. Poblet, *J. Phys. Chem. A*, 2002, **106**, 12356–12364.
- 4 J. C. Duchamp, A. Demortier, K. R. Fletcher, D. Dorn, E. B. Iezzi, T. Glass and H. C. Dorn, *Chem. Phys. Lett.*, 2003, **375**, 655–659.
- 5 M. Krause and L. Dunsch, *ChemPhysChem*, 2004, **5**, 1445–1449.
- 6 K. Kobayashi, Y. Sano and S. Nagase, *J. Comput. Chem.*, 2001, **22**, 1353–1358.
- 7 M. M. Olmstead, H. M. Lee, J. C. Duchamp, S. Stevenson, D. Marciu, H. C. Dorn and A. L. Balch, *Angew. Chem., Int. Ed.*, 2003, **42**, 900–903.
- 8 M. M. Olmstead, A. de Bettencourt-Dias, J. C. Duchamp, S. Stevenson, D. Marciu, H. C. Dorn and A. L. Balch, *Angew. Chem., Int. Ed.*, 2001, **40**, 1223–1225.
- 9 S. S. Park, D. Liu and F. Hagelberg, *J. Phys. Chem. A*, 2005, **109**, 8865–8873.
- 10 Z. Ge, J. C. Duchamp, T. Cai, H. W. Gibson and H. C. Dorn, *J. Am. Chem. Soc.*, 2005, **127**, 16292–16298.
- 11 C. D. Angeli, T. Cai, J. C. Duchamp, J. E. Reid, E. S. Singer, H. W. Gibson and H. C. Dorn, *Chem. Mater.*, 2008, **20**, 4993–4997.
- 12 S. Stevenson, K. Harich, H. Yu, R. R. Stephen, D. Heaps, C. Coumbe and J. P. Phillips, *J. Am. Chem. Soc.*, 2006, **128**, 8829–8835.
- 13 B. Elliott, L. Yu and L. Echegoyen, *J. Am. Chem. Soc.*, 2005, **127**, 10885–10888.
- 14 S. Stevenson, M. A. Mackey, J. E. Pickens, M. A. Stuart, B. S. Confait and J. P. Phillips, *Inorg. Chem.*, 2009, **48**, 11685–11690.
- 15 M. R. Cerón, F.-F. Li and L. Echegoyen, *Chem. – Eur. J.*, 2013, **19**, 7410–7415.
- 16 T. Akasaka and S. Nagase, *Endofullerenes: A New Family of Carbon Clusters*, Dev. Fullerene Sci., Kluwer Academic Publishers, vol. 3, 2002.
- 17 M. Chen, X. Lu, M. R. Cerón, M. Izquierdo and L. Echegoyen, in *Endohedral Metallofullerenes: Basic and Applications*, ed. X. Lu, L. Echegoyen, A. L. Balch, S. Nagase and T. Akasaka, CRC Press, 2014, ch. 6, pp. 173–210.
- 18 M. N. Chaur, F. Melin, A. L. Ortiz and L. Echegoyen, *Angew. Chem., Int. Ed.*, 2009, **48**, 7514–7538.
- 19 D. M. Rivera-Nazario, J. R. Pinzón, S. Stevenson and L. A. Echegoyen, *J. Phys. Org. Chem.*, 2013, **26**, 194–205.
- 20 M. R. Cerón, F.-F. Li and L. A. Echegoyen, *J. Phys. Org. Chem.*, 2014, **27**, 258–264.
- 21 T. Cai, L. Xu, C. Shu, J. E. Reid, H. W. Gibson and H. C. Dorn, *J. Phys. Chem. C*, 2008, **112**, 19203–19208.
- 22 T. Yang, X. Zhao, S. Nagase and T. Akasaka, *Chem. – Asian J.*, 2014, **9**, 2604–2611.
- 23 N. B. Shustova, A. A. Popov, M. A. Mackey, C. E. Coumbe, J. P. Phillips, S. Stevenson, S. H. Strauss and O. V. Boltalina, *J. Am. Chem. Soc.*, 2007, **129**, 11676–11677.
- 24 S. Yang, C. Chen, M. Jiao, N. B. Tamm, M. A. Lansikh, E. Kemnitz and S. I. Troyanov, *Inorg. Chem.*, 2011, **50**, 3766–3771.
- 25 S. Osuna, A. Rodríguez-Fortea, J. M. Poblet, M. Sola and M. Swart, *Chem. Commun.*, 2012, **48**, 2486–2488.
- 26 T. Cai, L. Xu, M. R. Anderson, Z. Ge, T. Zuo, X. Wang, M. M. Olmstead, A. L. Balch, H. W. Gibson and H. C. Dorn, *J. Am. Chem. Soc.*, 2006, **128**, 8581–8589.
- 27 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, *Nat. Mater.*, 2009, **8**, 208–212.
- 28 C. M. Cardona, B. Elliott and L. Echegoyen, *J. Am. Chem. Soc.*, 2006, **128**, 6480–6485.
- 29 H. Shinohara, *Rep. Prog. Phys.*, 2000, **63**, 843–892.
- 30 L. Dunsch and S. Yang, *Small*, 2007, **3**, 1298–1320.
- 31 J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao and C. L. Wilkins, *J. Org. Chem.*, 1995, **60**, 532–538.
- 32 B. Q. Mercado, M. N. Chaur, L. Echegoyen, J. A. Gharamaleki, M. M. Olmstead and A. L. Balch, *Polyhedron*, 2013, **58**, 129–133.
- 33 A. A. Popov and L. Dunsch, *J. Am. Chem. Soc.*, 2007, **129**, 11835–11849.
- 34 N. Alegret, A. Rodríguez-Fortea and J. M. Poblet, *Chem. – Eur. J.*, 2013, **19**, 5061–5069.
- 35 C. Shu, W. Xu, C. Slebodnick, H. Champion, W. Fu, J. E. Reid, H. Azurmendi, C. Wang, K. Harich, H. C. Dorn and H. W. Gibson, *Org. Lett.*, 2009, **11**, 1753–1756.
- 36 S. Osuna, R. Valencia, A. Rodríguez-Fortea, M. Swart, M. Solà and J. M. Poblet, *Chem. – Eur. J.*, 2012, **18**, 8944–8956.
- 37 S. Osuna, M. Swart, J. M. Campanera, J. M. Poblet and M. Solà, *J. Am. Chem. Soc.*, 2008, **130**, 6206–6214.
- 38 T. Yang, S. Nagase, T. Akasaka, J. M. Poblet, K. N. Houk, M. Ehara and X. Zhao, *J. Am. Chem. Soc.*, 2015, **137**, 6820–6828.
- 39 C. M. Cardona, A. Kitaygorodskiy, A. Ortiz, M. A. Herranz and L. Echegoyen, *J. Org. Chem.*, 2005, **70**, 5092–5097.
- 40 T. Cai, Z. Ge, E. B. Iezzi, T. E. Glass, K. Harich, H. W. Gibson and H. C. Dorn, *Chem. Commun.*, 2005, 3594–3596.
- 41 M. Izquierdo, M. R. Cerón, M. M. Olmstead, A. L. Balch and L. Echegoyen, *Angew. Chem., Int. Ed.*, 2013, **52**, 11826–11830.

