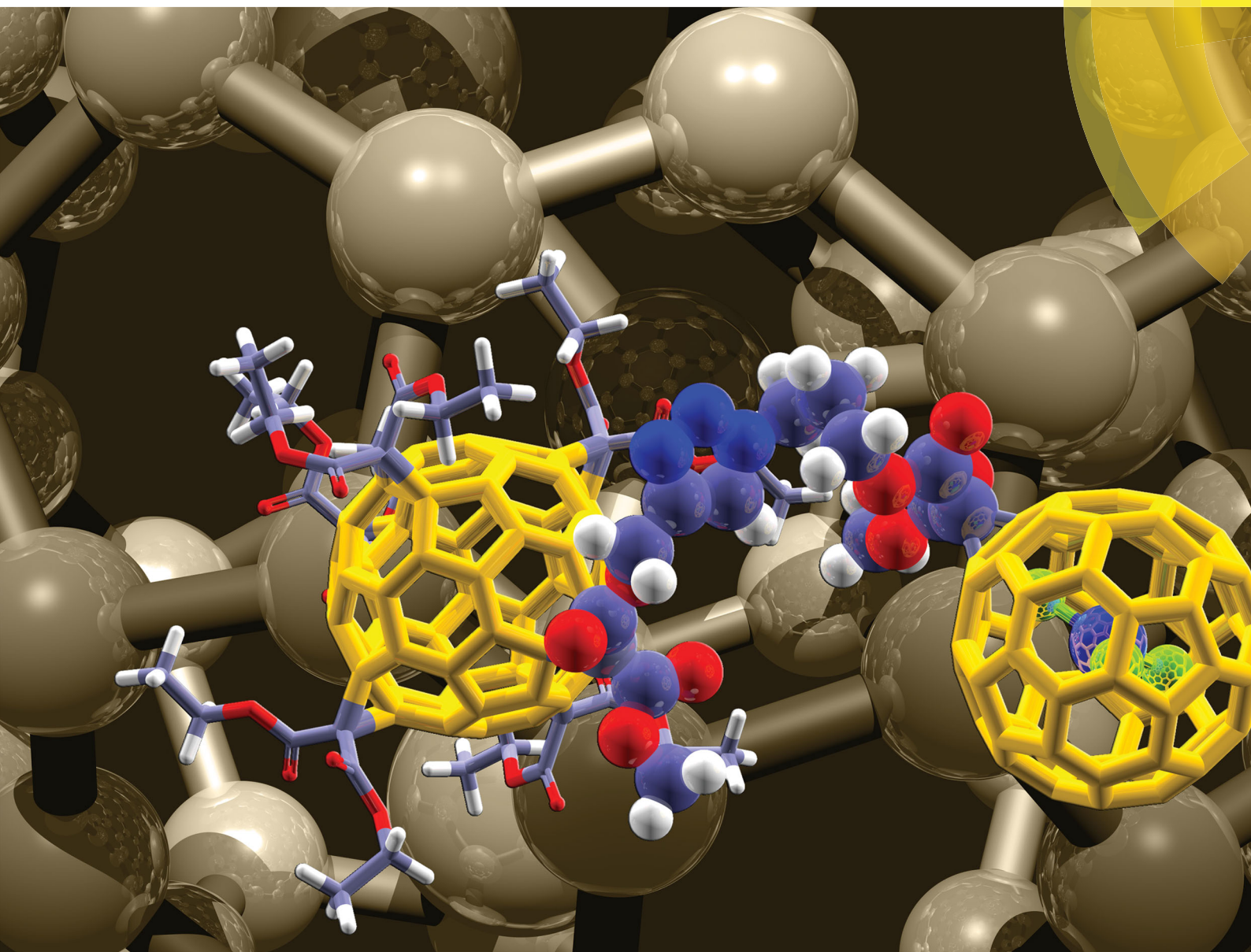


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## COMMUNICATION

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The first molecular dumbbell consisting of an endohedral  $\text{Sc}_3\text{N}@C_{80}$  and an empty  $\text{C}_{60}$ -fullerene building block

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**An unprecedented hybrid dumbbell consisting of a metallofullerene and an empty fullerene was afforded via simple click reaction of suitable precursor derivatives of  $\text{Sc}_3\text{N@C}_{80}$  and a  $\text{C}_{60}$  hexakisadduct.**

Dumbbell shaped fullerenes represent an interesting class of compounds. Their molecular architectures have been attracting great attention due to their distinct chemical/physical properties.<sup>1</sup> To date, various series of such dimers based on the introduction of different types of fullerenes (e.g.  $\text{C}_{60}$ ,  $\text{C}_{70}$ , heterofullerenes, endofullerenes) as well as various linkers serving as bridges have been reported (see Fig. 1).<sup>2–11</sup> One striking characteristic of dimeric fullerene dumbbells is their tunable properties by the possibility of modifying the chemical nature of fullerene building blocks or the chemical linkage between them. So far however, only either empty fullerenes, heterofullerenes ( $\text{C}_{59}\text{N}$ ) or the non-metallic endohedral fullerenes such as  $\text{He@C}_{60}$ ,  $\text{H}_2\text{@C}_{60}$  and  $\text{N@C}_{60}$ <sup>2</sup> have been employed where the corresponding molecular architectures containing endohedral clusterfullerenes are elusive. Among these examples and due to their unique high spin behavior, dimers based on  $\text{N@C}_{60}$  promise feasibility for quantum computer applications.<sup>2</sup> However, the incorporation of endohedral clusterfullerenes, especially metal nitride cluster fullerenes (NCFs), is still lacking. In these endofullerene derivatives the encapsulated cluster comprising of both metal and non-metal ions gives rise to an electron transfer between the endohedral guest and the carbon cage. This feature which is absent in empty fullerenes or  $\text{N@C}_{60}$  makes the synthesis of dumbbells an interesting task since the properties of both kinds of fullerenes can be combined in one molecule. The only cases of dimeric endohedral metallofullerenes were reported to take place in the solid state after crystallization.<sup>12–14</sup>

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† Electronic supplementary information (ESI) available: Experimental section, <sup>1</sup>H and <sup>13</sup>C NMR spectra, UV-vis-NIR spectrum and the MALDI-TOF mass spectrum. See DOI: 10.1039/c7cc03012f

‡ These authors contributed equally to this work.

# The first molecular dumbbell consisting of an endohedral $\text{Sc}_3\text{N@C}_{80}$ and an empty $\text{C}_{60}$ -fullerene building block†

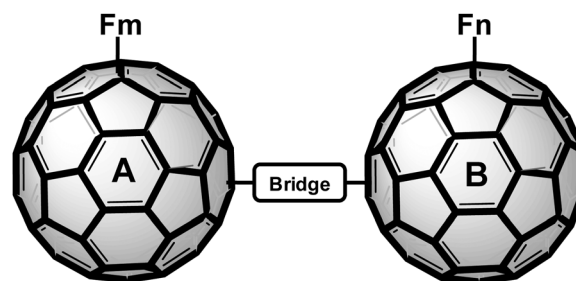
Tao Wei,‡ M. Eugenia Pérez-Ojeda  ‡ and Andreas Hirsch  \*

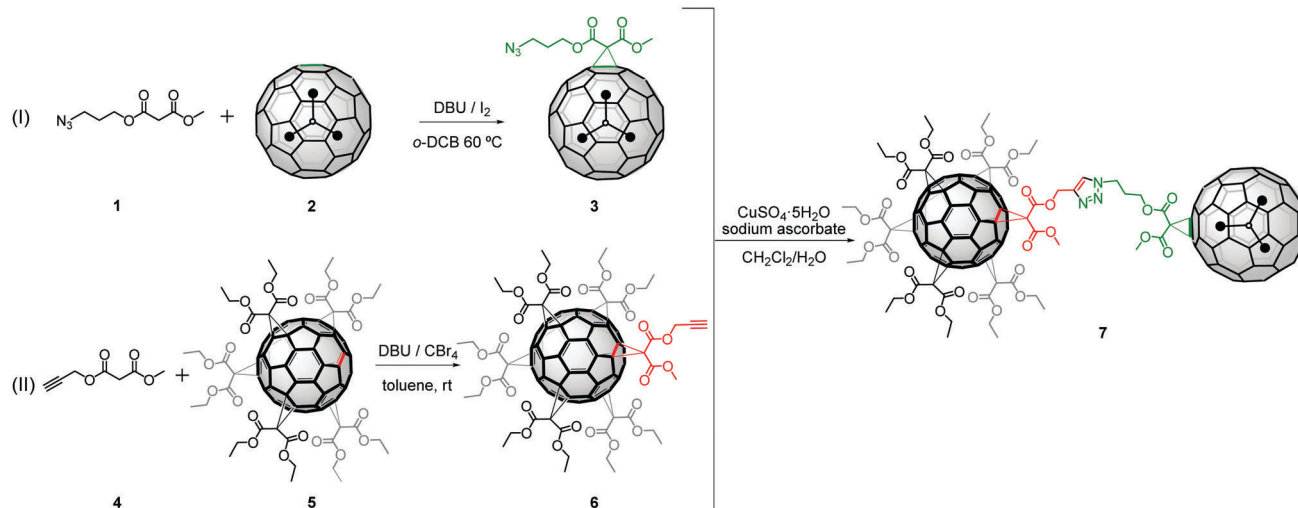
Fig. 1 Previously reported types of dumbbell shaped fullerene dimers: (A, B) = ( $\text{C}_{60}$ ,  $\text{C}_{60}$ ), ( $\text{C}_{60}$ ,  $\text{C}_{70}$ ), ( $\text{C}_{70}$ ,  $\text{C}_{70}$ ), ( $\text{C}_{59}\text{N}$ ,  $\text{C}_{59}\text{N}$ ), ( $\text{C}_{59}\text{N}$ ,  $\text{C}_{60}$ ), ( $\text{C}_{69}\text{N}$ ,  $\text{C}_{69}\text{N}$ ), ( $\text{N@C}_{60}$ ,  $\text{N@C}_{60}$ ), ( $\text{N@C}_{60}$ ,  $\text{C}_{60}$ ), ( $\text{He@C}_{60}$ ,  $\text{C}_{60}$ ), ( $\text{H}_2\text{@C}_{60}$ ,  $\text{H}_2\text{@C}_{60}$ ), and ( $m$ ,  $n$ ) = 0–5, F denotes the functionalized group.

Our group has previously demonstrated the versatility of [5:0] pentakisadducts of  $\text{C}_{60}$  with  $\text{C}_{2v}$  symmetry as useful building blocks for the synthesis of large and highly functional architectures involving an octahedral [5:1] addition pattern.<sup>15</sup> For the targeted synthesis of the first dumbbell consisting of an endohedral and an empty fullerene we decided to prepare a [5:1]-adduct of  $\text{C}_{60}$  equipped with 10 chains which will facilitate the solubility of the dumbbell (aliphatic ones in this case) and one terminal alkyne group. This should serve as an anchor unit for the “click” coupling with a monoadduct of the endohedral clusterfullerene- $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$  containing the complementary azide functionality in its periphery.

$\text{Sc}_3\text{N@I}_h\text{-C}_{80}$  was chosen as an endohedral fullerene building block since it is easily available in rather high yields.<sup>16</sup> On the other hand, its high cage symmetry bearing two available reaction positions allows the formation of only two possible regioisomeric monoadducts. Altogether the synthesis of the targeted fullerene dumbbell consists of three steps: (1) the synthesis of an azido-malonate monoadduct of  $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ ; (2) the selective synthesis of a [5:1] hexakisadduct of  $\text{C}_{60}$  provided with an alkyne and (3) the covalent connection of these subunits *via* “click” reaction.

In the first step, we aimed to synthesize an azidomalonate monoadduct of  $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$  using Bingel–Hirsch reaction conditions (Scheme 1 (I) and for further details see S2.1, ESI†).





Scheme 1 Schematic synthesis route of dumbbell-7.

The subsequent purification afforded a pure major product (denoted as **3**) which was confirmed by matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometry analysis showing an ionic peak at  $m/z = 1308$  (Fig. S6, ESI†).

Additionally, both  $^1\text{H}$  and  $^{13}\text{C}$  NMR were performed to unambiguously elucidate its structure. The  $^1\text{H}$  NMR spectrum of **3** exhibits one set of signals featuring one quartet, one singlet and two triplets centered at 4.59, 4.11, 3.50 and 2.09 ppm, respectively (Fig. S7, ESI†). The singlet at 3.50 ppm corresponds to the methoxy group and the other three resonances can be attributed to protons of the three remaining methylene groups. A potential [5,6]-adduct would give rise to two sets of non-equivalent protons as a result of different chemical environments stemming from the 5,6-ring junction, whereas the more symmetrical [6,6]-adduct gives only one set of proton signals. The fact that just one symmetrical [6,6]-adduct was formed is in good agreement with previous studies on  $\text{M}_3\text{N}@I_h\text{-C}_{80}$  adducts synthesized *via* Bingel-Hirsch reactions.<sup>17</sup> The  $^{13}\text{C}$  NMR spectrum of **3** shows 5 signals in the range of 20–60 ppm and two additional signals around 163 ppm for the attached group, besides, another 80 resonances distributed in the 85–155 ppm region were observed for the carbon cage, consistent with  $C_1$  symmetry (Fig. S8, ESI†). The  $C_1$  symmetry caused by addition of an asymmetric functionalized moiety is in line with the previously reported  $\text{Sc}_3\text{N}@C_{80}\text{-PCBM}$ , in which the  $C_1$  symmetry was clearly confirmed by both  $^{13}\text{C}$  NMR and X-ray crystallographic studies.<sup>18</sup>

In the second step, the [5 : 1] hexakisadduct of  $\text{C}_{60}$  (denoted as **6**) was readily synthesized by Bingel-Hirsch reactions (Scheme 1 (II)) and for further details see S2.2, ESI†. Finally, in order to construct the target dumbbell, a copper-catalyzed Huisgen 1,3-dipolar cycloaddition between azides and alkynes “click” reaction was conducted by using **3** and 1.5-fold of **6** under modified Sharpless conditions at room temperature with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.3 equiv.) and sodium ascorbate (0.9 equiv.) in a  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  biphasic system, under a nitrogen atmosphere for 96 h (Scheme 1). Upon such a mild and long reaction treatment the assumed 1,2,3-triazole-linked dumbbell comprising of **3**

and **6** was formed. Surprisingly, despite the presence of a Cu(I) catalyst, the clicked product afforded was not the expected sole 1,4-adduct but an isomeric mixture in a 3 : 1 ratio of 1,4 and a 1,5-adducts which would have been likely under thermal conditions. This interesting observation is indicative of some not yet well understood effects of copper on the  $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$  properties, charge transfer or redox activity.<sup>19</sup> On account of a very similar polarity of these two isomers, their complete separation is quite challenging. Fortunately, a partial pure major isomer (denoted as **7**) was successfully isolated on a silica-gel chromatographic column thanks to the good solubility provided by the linkage to the hexakisadduct of  $\text{C}_{60}$ . The yield of the major isomer of dumbbell-7, was roughly estimated to be 45% regardless of its small quantity that could not be isolated from the mixture of isomers.

The purified product enables characterization to confirm its molecular structure as well as its electronic properties. Given that mass spectrometry can provide the most intuitive information about the composition of the molecule, it was immediately applied to **7**. As shown in Fig. 2, the MALDI-TOF mass spectrum of dumbbell-7 exhibited an evident ionic peak at  $m/z = 2972$  corresponding to the clicked products of **3** and **6**. The chemical identification of dumbbell-7 was further achieved by comparing the isotopic distribution analysis of the experimental measured result with the calculated one since a good agreement is observed. Consequently, for the first time, an unprecedented dumbbell based on endohedral clusterfullerenes was successfully achieved *via* chemical modification.

The formation of the dumbbell was further confirmed by the  $^1\text{H}$  NMR spectroscopy study as shown in Fig. S19 (ESI†). In the  $^1\text{H}$  NMR spectrum of dumbbell-7, the four resonances centered at 4.52, 4.12, 3.57 and 2.29 ppm are obviously derived from monomer **3** and the other three resonances centered at 4.34, 3.80, and 1.31 ppm clearly originated from monomer **6**. Interestingly, all these resonances of dumbbell-7 are either low field or high field shifted compared to two monomers, suggesting that linking these two building blocks for the dumbbell formation brings





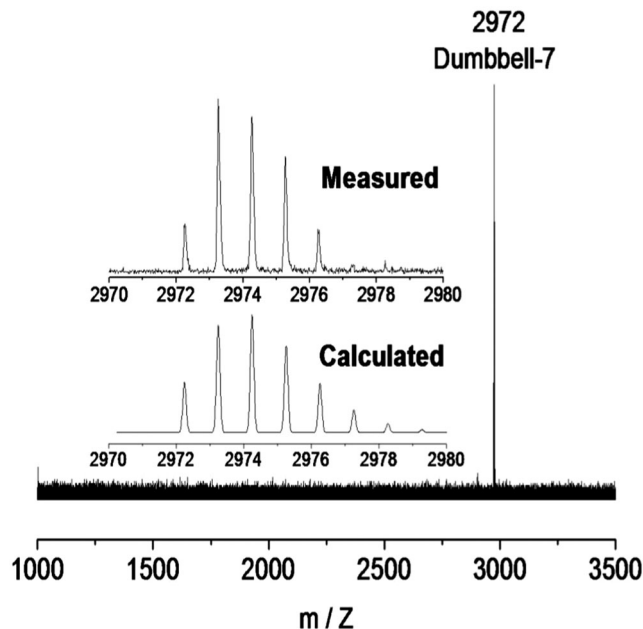


Fig. 2 MALDI-TOF spectrum of dumbbell-7. The inset shows the measured and calculated isotope distributions.

about changes in the chemical environment. Noticeably, a singlet resonance centered at 7.71 ppm corresponding to the proton situated at 1,2,3-triazole as a result of the *click* reaction between the azido group within **3** and the alkynyl group within **6**, clearly states that the formation of the dumbbell has been successfully proceeded. Unfortunately, the limited amount of dumbbell-7 precluded the acquisition of its  $^{13}\text{C}$  NMR spectrum.

The electronic properties of dumbbell-7 were investigated by UV-vis-NIR spectroscopy. The UV-vis-NIR spectrum of dumbbell-7 dissolved in toluene is shown in Fig. 3, which includes also those of monomers **3** and **6** for comparison. Apparently, the overall electronic absorption spectrum of **3** is featureless without sharp absorption peaks and exhibits two broad shoulder peaks at about 440 and 748 nm, which is less rich in characteristics than that of **6**, for which two obvious absorption peaks are observed at 316 and 334 nm together with a broad peak at 385 nm. For dumbbell-7, several characteristic absorption peaks, which are derived from the two building blocks, at 319, 336, 417 and 737 nm, are clearly observed. Specifically, two sharp absorption peaks, at 319 and 336 nm, in the UV region apparently originated from one of the individuals of **6**, whereas the other individual of **3** accounts for the remaining two absorption peaks in the visible region. Besides, the absorption peaks at 319 and 336 nm of dumbbell-7 seem to be red-shifted compared to those of **6**, in contrast, a blue-shift for the other two peaks, at 417 and 737 nm, is detected in comparison with that of **3**. Regardless of the slight red/blue shift, the overall absorption spectrum of dumbbell-7 is quite similar to the superposition spectra of the two monomers, indicating that dumbbell-7 inherits the electronic properties of the two constituents. Therefore this methodology opens up the possibility of combining the electronic properties of two fullerenes with deeply different natures. By a careful selection of

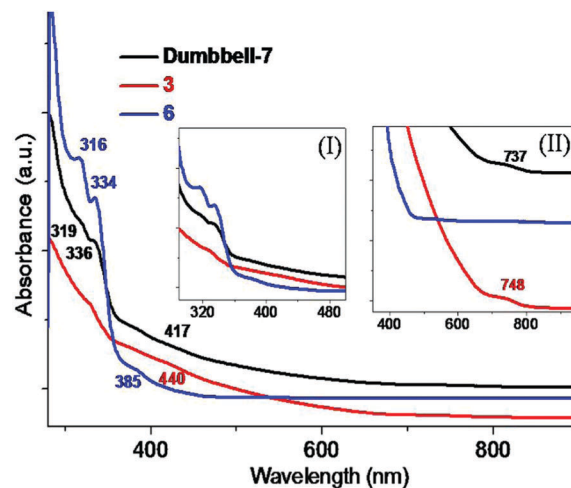


Fig. 3 UV-vis-NIR spectrum of dumbbell-7 dissolved in toluene in comparison with those of **3** and **6**. Insets: Enlarged spectra in 300–500 nm (I) and 350–950 nm (II) regions.

the appropriate parental counterparts, the dumbbell formation might be a very versatile tool to tune the electronic properties as demanded by the applications. It will allow the synthesis of novel fullerene derivatives with attractive properties which may diversify the potential applications of fullerene-based multi-functional molecules.

Besides, in order to elucidate which is the real influence of the endofullerene, dumbbell-7 was further compared to congener dimer-9, which was synthesized by substitution of the azido monoadduct of  $\text{Sc}_3\text{N@C}_{80}$  with the azido monoadduct of  $\text{C}_{60}$  (**8**) (for details see S3, ESI $^\dagger$ ). Under the same experimental conditions, only 1,4-adduct formation was observed which clearly indicates the influence of the endofullerene in the copper catalyzed *click* mechanism as explained above. As expected, the UV-vis-NIR spectrum of dimer-9 bears a resemblance to the overlap of the absorption peaks from the corresponding monomers **8** and **6** (Fig. S20, ESI $^\dagger$ ).

Moreover, noting the existing six charges within **3** as a result of charge transfer from encaged species to the carbon cage, the investigation on the probable charge transfer between these two building blocks is convinced to be quite attractive, and will be carried out in the future.

In summary, we have synthesized and isolated the hitherto unknown dumbbell-7 *via* bonding of the endohedral cluster-fullerene monoadduct **3** with the  $\text{C}_{60}$  hexakisadduct **6**. The structure of synthetic dumbbell-7 was unambiguously characterized by MALDI-TOF mass spectrometry and  $^1\text{H}$  NMR spectroscopy. The electronic structure was carefully studied by UV-vis-NIR spectroscopy and compared to parental building blocks and congener dimer-9, and the peculiar electronic properties achieved by a combination of two different moieties in the dumbbell are unveiled. Our success in the first construction of an endohedral clusterfullerene dumbbell opens up a new perspective in fullerene chemistry.

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## Notes and references

- For recent typical reviews (a) F. Giacalone and N. Matin, *Chem. Rev.*, 2006, **106**, 5136–5190; (b) A. L. Balch and K. Winkler, *Chem. Rev.*, 2016, **116**, 3812–3882.
- B. J. Farrington, M. Jevric, G. A. Rance, A. Ardavan, A. N. Khlobystov, G. A. D. Briggs and K. Porfyrakis, *Angew. Chem., Int. Ed.*, 2012, **124**, 3647–3650.
- K. Komatsu, K. Fujiwara and Y. Murata, *Chem. Commun.*, 2000, 1583–1584.
- G. S. Forman, N. Tagmaatarchis and H. Shinohara, *J. Am. Chem. Soc.*, 2002, **124**, 178–179.
- J. C. Hummelen and F. Wudl, *Science*, 1995, **269**, 1554–1556.
- F. Hauke, M. Á. Herranz, L. Echegoyen, D. Guldi, A. Hirsch and S. Atalick, *Chem. Commun.*, 2004, 600–601.
- B. Nuber and A. Hirsch, *Chem. Commun.*, 1996, 1421–1422.
- F. Hörmann, A. Hirsch, K. Porfyrakis and G. A. D. Briggs, *Eur. J. Org. Chem.*, 2011, 117–121.
- K. Komatsu, G. W. Wang, Y. Murata, T. Tanaka, K. Fujiwara, K. Yamamoto and M. Saunders, *J. Org. Chem.*, 1998, **63**, 9358–9366.
- M. Murata, Y. Murata and K. Komatsu, *J. Am. Chem. Soc.*, 2006, **128**, 8024–8033.
- G. W. Wang, K. Komatsu, Y. Murata and M. Shiro, *Nature*, 1997, **387**, 583–586.
- L. Bao, C. Pan, Z. Slanina, F. Uhlik, T. Akasaka and X. Lu, *Angew. Chem., Int. Ed.*, 2016, **55**, 9234–9238.
- L. Feng, T. Tsuchiya, T. Wakahara, T. Nakahodo, Q. Piao, Y. Maeda, T. Akasaka, T. Kato, K. Yoza, E. Horn, N. Mizorogi and S. Nagase, *J. Am. Chem. Soc.*, 2006, **128**, 5990–5991.
- D. Konarev, L. V. Zorina, S. Khasanov, A. A. Popov, A. Otsuka, H. Yamochi, G. Saito and R. N. Lyubovskaya, *Chem. Commun.*, 2016, **52**, 10763–10766.
- (a) F. Hörmann, W. Donaubaue, F. Hampel and A. Hirsch, *Chem. – Eur. J.*, 2012, **18**, 3329–3337; (b) L. K. Wasserthal, A. Kratzer and A. Hirsch, *Eur. J. Org. Chem.*, 2013, 2355–2361; (c) F. Hörmann and A. Hirsch, *Chem. – Eur. J.*, 2013, **19**, 3188–3197; (d) L. K. Wasserthal, B. Shade, K. Ludwig, C. Böttcher and A. Hirsch, *Chem. – Eur. J.*, 2014, **20**, 5961–5966; (e) X. Yu, W. B. Zhang, K. Yue, X. Li, H. Liu, Y. Xin, C. L. Wang, C. Wesdemiotis and S. Z. D. Cheng, *J. Am. Chem. Soc.*, 2012, **134**, 7780–7787; (f) J. Iehl and J. F. Nierengarten, *Chem. – Eur. J.*, 2009, **15**, 7306–7309; (g) J. Iehl, J. F. Nierengarten, A. Harriman, T. Bura and R. Ziessel, *J. Am. Chem. Soc.*, 2012, **134**, 988–998; (h) P. Fortgang, E. Maisonhaute, C. Amatore, B. Delavaux-Nicot, J. Iehl and J. F. Nierengarten, *Angew. Chem., Int. Ed.*, 2011, **50**, 2364–2367; (i) J. Iehl and J. F. Nierengarten, *Chem. Commun.*, 2010, **46**, 4160–4162.
- 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**, 55–57.
- (a) C. M. Cardona, A. Kitaygorodskiy and L. Echegoyen, *J. Am. Chem. Soc.*, 2005, **127**, 10448–10453; (b) C. Y. Shu, T. Cai, L. S. Xu, T. M. Zuo, J. Reid, K. Harich, H. C. Dorn and H. W. Gibson, *J. Am. Chem. Soc.*, 2007, **129**, 15710–15717; (c) O. Lukyanova, C. M. Cardona, J. Rivera, L. Z. Lugo-Morales, C. J. Chancellor, M. M. Olmstead, A. Rodríguez-Fortea, J. M. Poblet, A. L. Balch and L. Echegoyen, *J. Am. Chem. Soc.*, 2007, **129**, 10423–10430.
- C. Y. Shu, W. Xu, C. Slebodnick, H. Champion, W. J. Fu, J. E. Reid, H. Azurmendi, C. R. Wang, K. Harich, H. C. Dorn and H. W. Gibson, *Org. Lett.*, 2009, **11**, 1753–1756.
- During the course of the reaction it was observed that the typical yellowish color from aqueous phase containing Cu(I) species protected against oxidation in the presence of a huge excess of sodium ascorbate and an inert nitrogen atmosphere turned into blue as an evidence of some oxidative processes which could be tentatively promoted by the endofullerene moiety. Other authors have previously described that the presence of a Cu additive in the electric arc reactor dramatically affects the yield of metallofullerene Sc<sub>3</sub>N@I<sub>h</sub>-C<sub>80</sub>, especially under amounts of Cu and Sc. However they have not yet been able to address the reason for this behaviour. S. Stevenson, M. A. Mackey, M. C. Thompson, H. L. Coumbe, P. K. Madasu, C. E. Coumbe and J. P. Phillips, *Chem. Commun.*, 2007, 4263–4265.

