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Graphitic Nanostructures

Fullerene–Ionic-Liquid Conjugates: A New Class of Hybrid Materials with Unprecedented Properties

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Abstract: A modular approach has been followed for the synthesis of a series of fullerene–ionic-liquid (IL) hybrids in which the number of IL moieties (two or twelve), anion, and cation have been varied. The combination of C_{60} and IL give rise to new unique properties in the conjugates such as solubility in water, which was higher than 800 $mg\,mL^{-1}$ in several cases. In addition, one of the C_{60}–IL hybrids has been employed for the immobilization of palladium nanoparticles through ion exchange followed by reduction with sodium borohydride. Surprisingly, during the reduction several carbon nanostructures were formed that comprised nano-onions and nanocages with few-layer graphene sidewalls, which have been characterized by means of thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy/energy-dispersive X-ray analysis (SEM-EDAX), and high-resolution transmission electron microscopy (HRTEM). Finally, the material thus obtained was successfully applied as catalyst in Suzuki and Mizoroki–Heck reactions in a concentration of just 0.2 mol%. In the former process it was recyclable for five runs with no loss in activity.

Introduction

In recent decades a great deal of interest has been devoted to the study and application of ionic liquids (ILs).[1] The huge potential of these neoteric solvents relies on the fact that their physical and chemical properties can be finely tuned by the selection of anions and cations. In such a way, ILs can be also tailored to exhibit a specific function, thereby leading to task-specific ionic liquids (TSILs).[2] Nowadays ILs find promising applications in several fields such as synthesis and catalysis,[1a,3] biotechnology,[4] separation science,[5] energy storage,[6] electrochemistry, and sensing,[7] among others. Recently, ILs have begun to find applications in combination with carbon nanoforms not only as reaction media for their functionalization,[8] but also for preparing so-called bucky gels.[9] In the latter, the specific interactions between ILs and nanocarbons afford to the hybrids unique properties as well as improved dispersibility in various media that can be employed in electrochemical and energy-storage devices or as supports for catalysis.[10] In addition, several examples in which the surface of carbon nanoforms (CNFs)—namely, single- and multiwalled nanotubes, nanohorns, and graphene—has been covalently modified with ionic-liquid moieties have been reported.[11] Despite the large number of examples for CNF–IL hybrids, just one report deals with the synthesis of a series of fulleropyrrolidine–imidazolium salts and the study of their solubility profiles.[12] It is likely that fullerene–IL hybrids will constitute a new class of materials that could find applications in several fields. In this regard, fullerene–IL mixtures have been successfully employed as glucose sensors[13] or in the preparation of stationary phases for gas chromatography.[14] Analogously, zwitterionic multicharged fullerene derivatives have been used for gene delivery[15] or in medicinal chemistry.[16] However, multilayered cross-linked supported ionic-liquid phases (mlc-SILP) proved to be excellent supports for the immobilization of palladium as catalyst in C–C bond formation.[17]

With this in mind, herein we report the synthesis and characterization of a series of fullerene–ionic-liquid hybrids in which the number of IL moieties, anions, and cations have been varied. Finally, one of these hybrids has been used for the immobilization of palladium nanoparticles and used as a catalyst for C–C coupling reactions.

Results and Discussion

Firstly, malonates **1a–c**[18] were prepared by starting from malonyl chloride and the properly substituted propanol. Hence, the fullerene derivatives endowed with two moieties of IL **3a** and **3b** were obtained through Bingel cyclopropanation[19] reaction followed by nucleophilic substitution with 1-butylimidazole in quantitative yields (Scheme 1). Next, the

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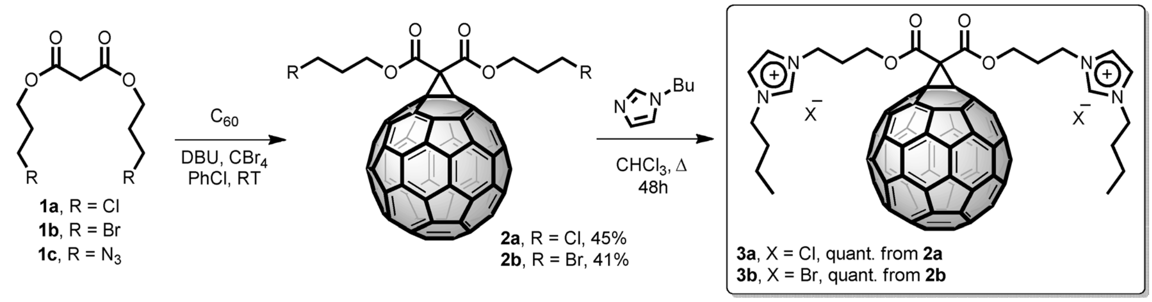
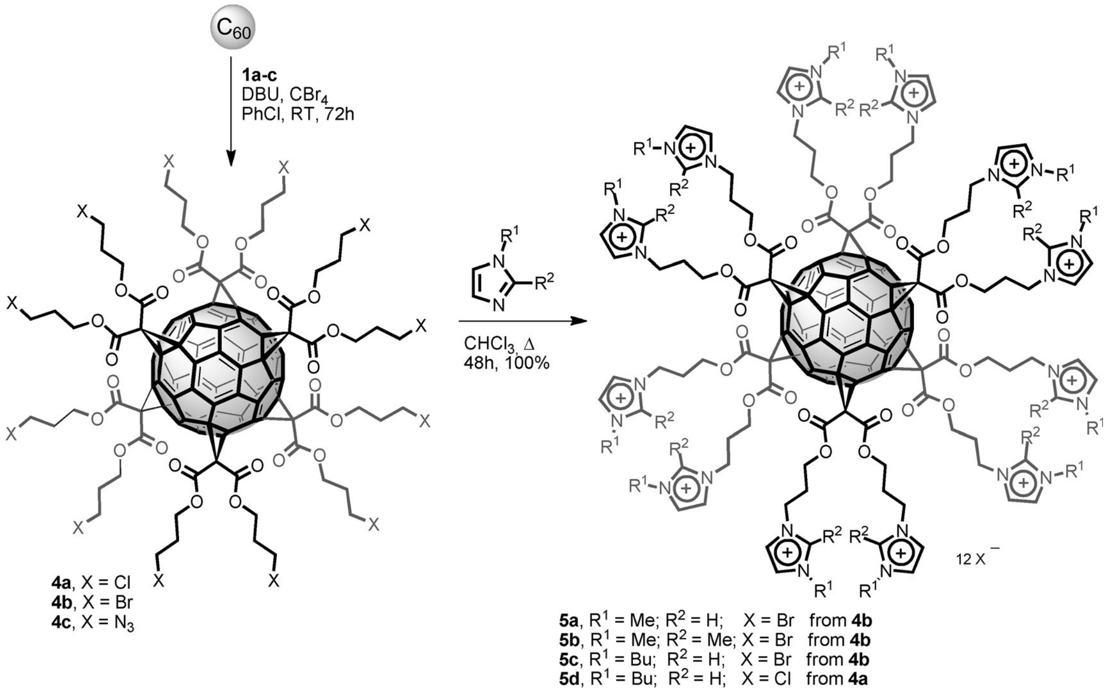


Scheme 1. Synthesis of C_{60}–IL **3a** and **3b** (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).

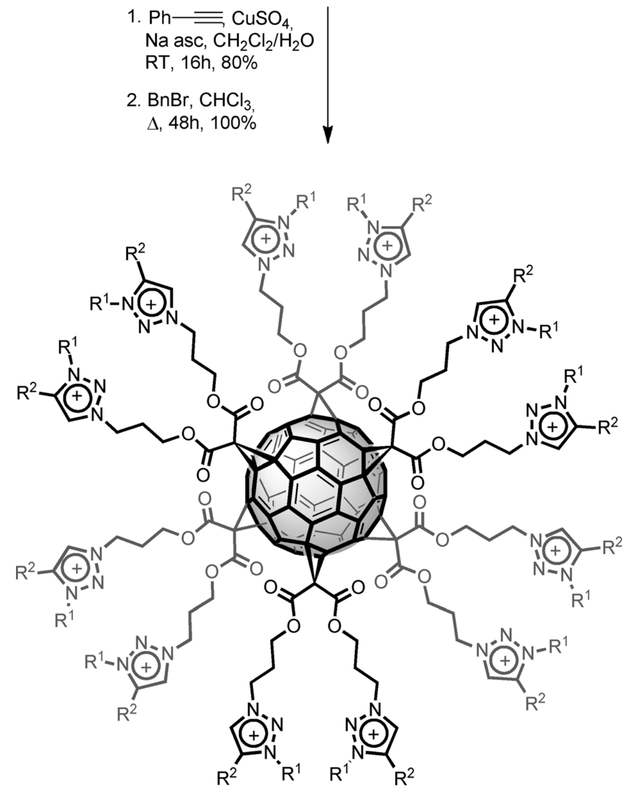


Scheme 2. Synthesis of C_{60}–IL conjugates **5a–d**.

syntheses of C_{60}–IL conjugates that bear twelve ionic-liquid moieties arranged in an octahedral addition pattern were carried out by following the protocol of Sun et al.[20] In this way it has been possible to access highly symmetric hexakis-adducts **4a–c** with satisfactory yields (Scheme 2). Then the octahedral intermediate **4b** was in turn treated with 1-methylimidazole, 1,2-dimethylimidazole, and 1-butylimidazole, and **4a** with 1-butylimidazole in chloroform heated to reflux to afford the hexakis C_{60}–IL hybrids **5a–d** in quantitative yields. Recently, the synthesis of several fullerene hexakis-adducts through the copper(I)-catalyzed alkyne–azide cycloaddition (CuAAC) "click" reaction[21] has been reported that employed a C_{60} dodecakis–alkyne[15c,22] or the dodecakis–azido derivative **4c**.[18a,23] Hence, a different strategy to obtain access to C_{60}–IL conjugate with a different cation has been designed.

In fact, by taking inspiration from the seminal work of Nierengarten and co-workers, derivative **4c** could be employed to build, through the CuAAC approach, a known dodecakis–triazole hybrid.[18a] This could then be easily transformed into the corresponding triazolium salt **6** with benzyl bromide in 80% yield over two steps (Scheme 3). All the fullerene–IL hybrids were thoroughly characterized and their spectroscopic data are in agreement with the proposed structures. Mono-adduct precursors **2a** and **2b**[18b] showed in the ^{13}C NMR spectra 15 sp^2 signals typical of C_{2v} fullerene derivatives[24] along with the signals at $\delta = 71$ and 52 ppm that belong to the two sp^3-carbon atoms of C_{60} and the methanofullerene bridgehead, respectively (see Figure S1 in the Supporting Information). The NMR spectra of hybrid derivatives **3a** and **3b** were more complicated, probably owing to strong intermolecular interactions (Figures S2 and S3 in the Supporting Information). However, the hexakis-adduct has simpler ^{1}H and ^{13}C NMR spectra (see Figures S4 and S5 in the Supporting Information). In the proton spectra of **4a** and **4b** the multiplicity of the three methylenic groups is clearly visible even if the signals are slightly broadened, whereas in the carbon spectra the octahedral substitution pattern of the C_{60} gives rise to two sp^2 signals at $\delta = 146$ and 141 ppm along with an sp^3 signal at $\delta = 69$ ppm. Interestingly, in the ^{1}H NMR spectra of 1-substituted imidazolium C_{60}-ILs **5a**, **5c**, and **5d**, the proton at the C2

4c



6, R^1 =Bn, R^2 = Ph

Scheme 3. Synthesis of C$_{60}$–IL conjugates **6**.

position of the imidazolium ring disappears after exchange with the deuterated solvent (compare Figure 1 and Figure S8 with Figure S9 in the Supporting Information). The ^{1}H NMR spectrum of **5c** shows the presence of all the expected signals with their corresponding integrals, thus indicating the good outcome of the reaction (Figure 1).

The ^{1}H NMR spectrum of the triazolium adduct **6** presents all the signals including ten aromatic protons in the $\delta = 7.0$–8.0 ppm region plus the triazole proton at $\delta = 9.6$ ppm, whereas in its ^{13}C NMR spectra (see Figure S10 in the Supporting Information) the peaks of the benzyl moiety appear in the $\delta = 127$–132 ppm region along with those of the parent triazole.[18a]

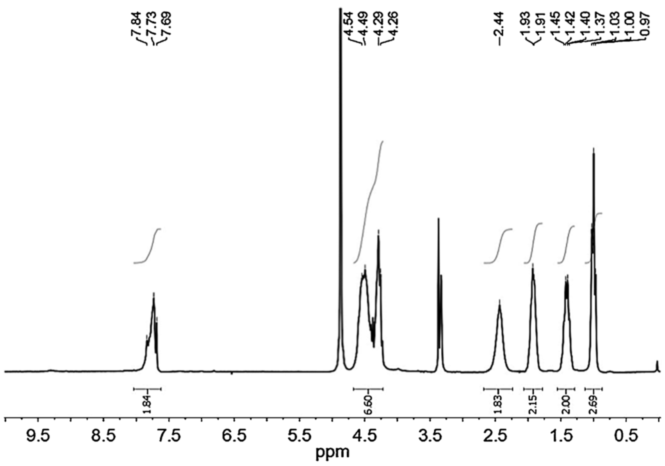


Figure 1. ^{1}H NMR spectrum of **5c**.

Unfortunately, owing to their highly charged nature, we were unable to get good high-resolution (HR) ESI spectra of the imidazolium-based fullerene–IL hybrids. However, the HR-ESI spectrum of **6** clearly showed the presence of multicharged species with 3, 5, and 6 positive charges (see Figure S11 in the Supporting Information).

The presence of the IL moieties on the fullerene cage affords to these hybrids an excellent solubility in polar solvents such as methanol and water. Although several examples of water-soluble fullerene mono-adducts[25] and polymers[26] have been described so far, only a few water-soluble octahedral hexakis-adducts have been reported.[27] This is particularly important given that these easily accessible multicharged molecules might find applications in gene delivery.[15a,b,16c,28]

The UV/Vis spectra of **5a–d** recorded in water are reported in Figure 2 (those of all the C$_{60}$–IL systems in methanol are reported in Figure S12 of the Supporting Information). The spectra show no aggregation in water with three transitions at about 240, 275, and 335 nm. Most interestingly, **5a–d** display an outstanding solubility in water at room temperature and pH 7 higher than 800 mg mL^{-1} (0.19–0.21 mol L^{-1}) to form solutions that were stable for months; this is probably the highest value of solubility for fullerene derivatives reported so far.[25,26,29] The same concentration could be achieved by dissolving hybrid **6** in methanol.

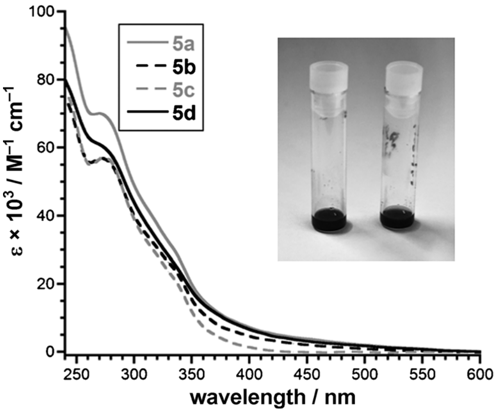
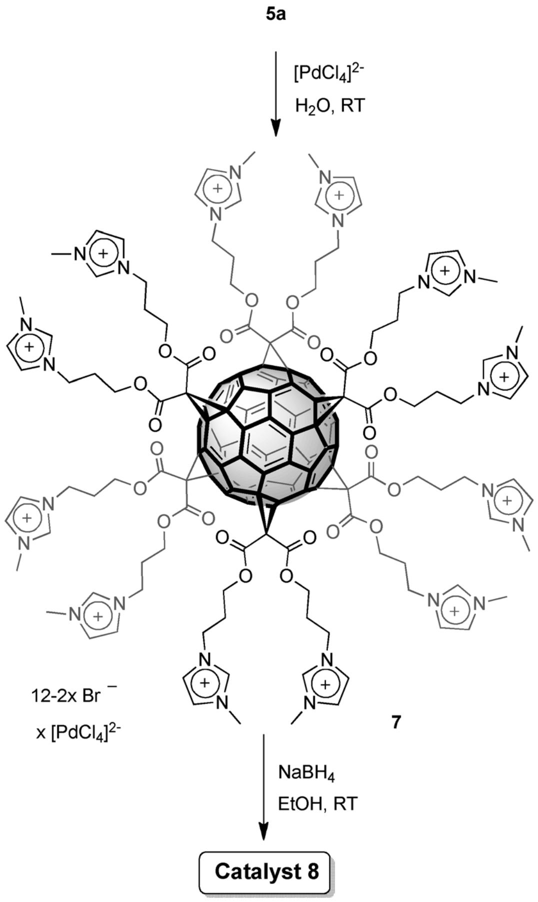


Figure 2. UV/Vis spectra of C$_{60}$–IL conjugates **5a–d** in water. The inset shows a picture of 100 mg mL^{-1} water solutions of **5c** (left) and **5d** (right).

With the hybrid C$_{60}$–IL systems in hand, we next explored their possible practical application as supports for catalysts. In this regard, we chose to immobilize palladium nanoparticles to prepare a new catalyst for C–C coupling reactions by using our systems as a kind of supported ionic-liquid-like phase (SILLP)[30] on the fullerene sphere. The synthesis of the catalytic material was accomplished in two steps, as reported in Scheme 4. First, we immobilized tetrachloropalladate ions (10 wt %) onto C$_{60}$–IL **5a** through anion metathesis, hence the supported PdCl$_4^{2-}$ species was reduced with NaBH$_4$ in etha-



Scheme 4. Synthesis of catalyst **8**.

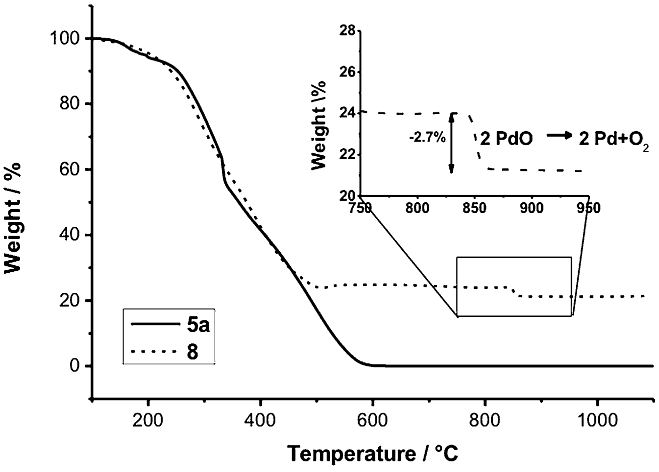


Figure 3. TGA of **5a** and **8** under oxygen flow.

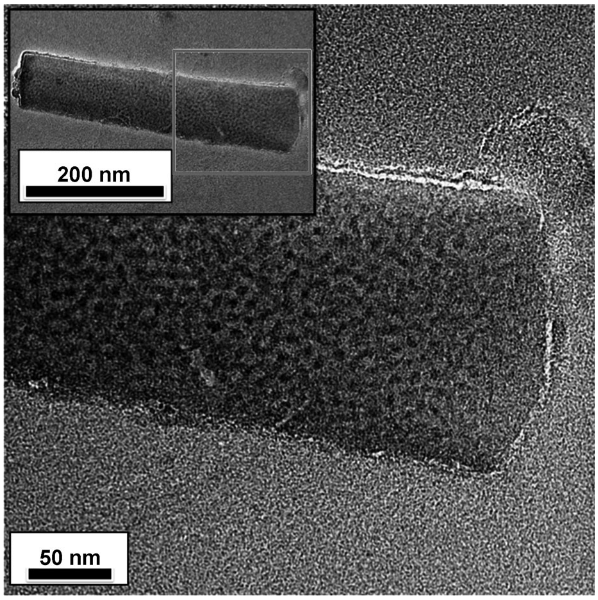


Figure 4. HRTEM pictures of **7**.

nol.[31] The purification of material **8** from inorganic salts was achieved by means of dialysis using a membrane with a cutoff of 1000 Da to afford a finely dispersed insoluble black powder.

Catalyst **8** was characterized by means of several analytical and spectroscopic techniques. Thermogravimetric analysis (TGA) was performed under oxygen flow from 100 to 1000 °C with a heating rate of 10 °C min^{-1} to determine the total amount of Pd species present in the sample and the degradation temperature range (Figure 3).

As expected, the TGA trace of **5a** shows a continuous weight loss in the 140–590 °C range, the temperature at which the combustion was completed and no residue was detected. Conversely, TGA of **8** presents a weight loss with the same slope as **5a** up to approximately 500 °C, after which no additional loss was observed up to 840 °C. Hence, a new small weight loss of 2.7% can be accounted for by the quantitative transformation of PdO to Pd since the former species is not stable over 800 °C.[32] By this last weight loss the Pd content in sample **8** was calculated to result in a loading of 18% as metallic Pd.

The morphologic characterization of hybrids **7** and **8** was carried out by means of high-resolution transmission electron microscopy (HRTEM). The analysis of TEM images helps to shed light on the organization of the hybrids, and in particular it can provide useful information about the presence and dimension of palladium nanoparticles. Interestingly, **7** shows both organized and amorphous nano-objects in which ionic-liquid-like speckled domains are discernable (Figure 4 and Figure S13 in the Supporting Information).[33] Small-sized palladium-rich aggregates are clearly visible and uniformly distributed with a mean diameter of 1.4 ± 0.5 nm (see Figure S13 in the Supporting Information). It is likely that the repulsive action of the positive charge of imidazolium groups prevents their agglomeration into larger domains.[34] Nevertheless, TEM analysis of **7** also displayed the presence of a few larger Pd aggregates (Figure S14 in the Supporting Information). However, the TEM analysis of **8** was very surprising owing to the presence of a number of organized carbon nanostructures with large graphitic domains (see Figure S15 in the Supporting Information) as well as to several carbon nano-onions with diameters in the 20–30 nm range (Figure 5 and Figure S15 in the Supporting Information).

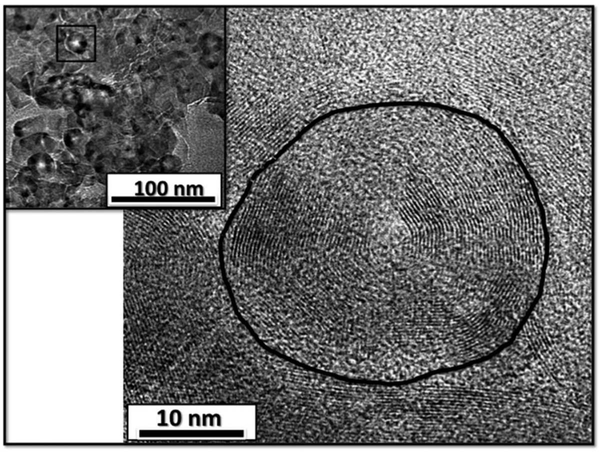


Figure 5. HRTEM pictures of **8**.

In all cases, the interplane distance estimated after noise reduction and calculating the intensity profile was 0.345 nm. This value, slightly higher than that of d_{002} value of graphite (0.335 nm), clearly indicates a local structure similar to turbostratic graphite ($d_{002} = 0.344$ nm).[35]

In accordance with the XRD data (see below), the palladium nanoparticles are highly dispersed throughout the sample and large aggregates were not detected by TEM. Nevertheless, the presence of these kinds of carbon nanoforms in the sample raise the question about how these nanostructures were formed. Per the data, carbon nano-onions can be prepared through different methods such as electron irradiation,[36] ion implantation,[37] plasma-enhanced chemical vapor deposition,[38] high-temperature annealing[39] or plasma spraying of nanodiamonds,[40] chemical vapor deposition using a transition-metal catalyst,[41] counter-flow diffusion flames,[42] and underwater arc discharge,[43] the latter being the preferred one to produce bulk amounts. However, all the above techniques usually require high doses of energy, whereas in our case the reduction of Pd^{II} to Pd^0, which seems to be the step in which the nanocarbons are formed, is carried out at room temperature. To shed light on this process, we carried out a blank experiment by treating C_{60}–IL **5a** with $NaBH_4$ in ethanol, but this reaction only resulted in the hydrolysis of the hybrid, thus giving rise to the formation of 3-(3-hydroxypropyl)-1-methylimidazolium bromide (see the ^1H NMR spectra in Figure S16 of the Supporting Information), in accord with other reported Bingel adducts in the presence of hydride ions/alcohol.[19b,44] This latter result justifies the higher Pd content (18 wt%) with respect to the anticipated one (10 wt%). Unfortunately, SEM analyses carried out on **8** (Figure S17 in the Supporting Information) did not help to add conclusive data. On the basis of these findings, an explanation for the formation of the experimentally observed carbon nanostructures cannot be proposed, and more in-depth studies, which are out of the scope of the present work, will be carried out in due course to completely reveal the mechanism of formation of such nanocarbons.

The X-ray diffraction (XRD) data of **8** is shown in Figure S18 in the Supporting Information. A very broad peak at approximately 40° 2θ owing to metallic Pd (PDF no. 180870) is observed. Metallic Pd particles smaller than 2 nm were found by applying the Scherrer equation that evaluates the full width at half-maximum (FWHM) of the reflection line at approximately 40° 2θ. Such a result is in good agreement with the particle size estimated by TEM analysis. The broad peak at approximately 20° 2θ is attributed to a poor ordering of graphene sheets.[45] In fact, reduced graphite oxide or reduced graphene oxide might exhibit a peak in the range between 20 and 25° owing to restacking. In that case, no graphitic stacking is achieved owing to lattice mismatch, structural defects, or the presence of residual functional groups.[46] X-ray photoelectron spectroscopy (XPS) analysis was used to analyze the outer part of the materials. Figure 6 shows the survey spectra of samples **7** and **8**. The comparison of the two spectra proved that dialysis purification of the final product was successful in eliminating the Na, Br, and Cl present in precursor **7**, as confirmed by semiquantitative scanning electron microscopy/energy-dispersive X-ray analysis (SEM-EDAX) analysis (Figure S17 in the Supporting Information). The final product **8** shows, along with carbon, the presence of O, N, and Pd.

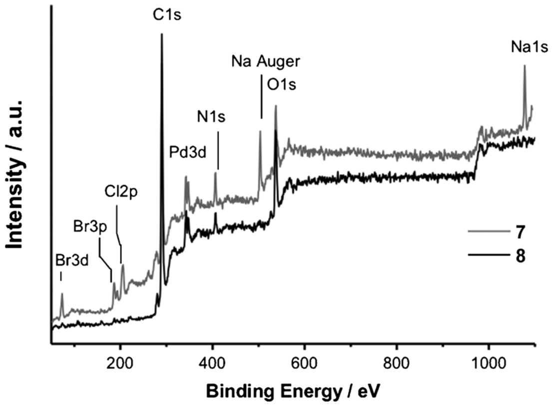


Figure 6. XPS survey spectra of **7** and **8**.

The results obtained by the analysis of the region of C1s, O1s N1s, and Pd3d are summarized in Table 1. The C1s peak shows for both samples three components at 284.4, 286.3, and 288.3 eV owing to sp^2 graphitic carbon, to the sp^3 C–C bond and C–O, and to the C=O bond, respectively.[47] The main difference in the carbon region between samples of **7** and **8** is that, after reducing treatment in $NaBH_4$, the increase in the graphitic component with respect to the others occurs, as evidenced by Figure 7a and Table 1. Oxygen and nitrogen regions show binding energy values of 532 and 401 eV, respectively

Table 1. XPS binding energies [eV] and atomic ratios of elements constituting samples **7** and **8**. The relative percentages are given in parentheses.

	C1s	$Pd3d_{5/2}$	Pd/C	O/C	N/C
7	284.6 (67), 286.3 (30), 288.3 (3)	337.1	0.018	0.13	0.07
8	284.6 (85), 286.2 (13), 288.5 (2)	335.6 (35), 337.3 (65)	0.016	0.14	0.04

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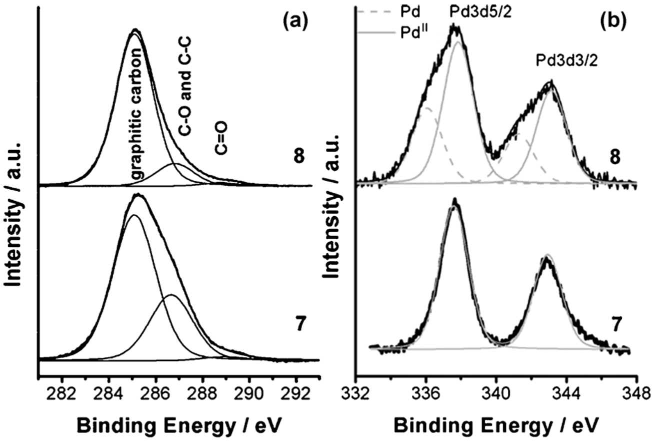


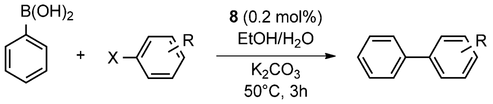
Figure 7. High-resolution XPS of a) C1s and b) Pd3d of **7** and **8**.

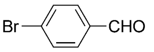
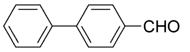
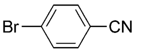
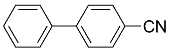
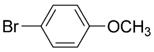
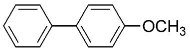
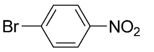
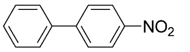
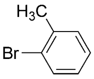
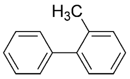
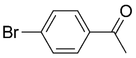
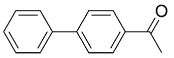
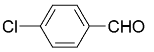
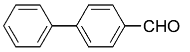
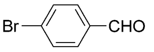
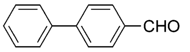
(see Figure 6), typical of C–O and aromatic nitrogenated species. However, the Pd3d spectra, shown in Figure 7b, are characterized by the typical two spin–orbit components, $Pd3d_{5/2}$ and $Pd3d_{3/2}$, separated by approximately 5.4 eV. The spectrum relative to **7** is typical of Pd^{II} with a binding energy centered at 337.1 eV. The spectrum of **8** exhibits two doublets attributed to two different chemical species: Pd^0 and Pd^{II}, respectively.[48] The relative amount of the two components indicated a degree of reduction of 35 % after treatment with $NaBH_4$. It is worth noting that XPS is a surface-sensitive technique; this means that the surface signal weight is much more than the bulk, and this phenomenon is particularly important in the case of very small nanoparticles like the ones that have been found in this sample. For that reason, the real degree of reduction could probably be higher than 35 %.

Material **8**, which contained highly dispersed Pd nanoparticles, thus constitutes a good candidate for a catalyst in Pd-mediated cross-coupling reactions given that metal nanoparticles are known to be more active than their particulate metal counterparts in catalytic reactions.[49] Moreover, since metal nanoparticles are thermodynamically unstable, the synergistic effect of coordination, steric, and electrostatic interactions can be exploited in the present approach, thereby preventing nanoparticle coalescence and percolation.[34b] In this regard, **8** was used as catalyst in the Suzuki reaction between phenylboronic acid and a set of aryl bromides in ethanol/water at 50 °C in the presence of K_2CO_3 as base. All the reactions were carried out for three hours using the catalyst in a 0.2 mol % loading (Table 2). Conversions were often quantitative with isolate yields that ranged from 68 to 99 %. The catalyst was shown to be inactive toward aryl chlorides, given that 4-chlorobenzaldehyde gave no reaction under the common reaction conditions (Table 2, entry 7).

In addition, the recyclability of the catalyst was checked for the reaction between 4-bromobenzaldehyde and phenylboronic acid (0.2 mol %, 3 h). After easy recovery of **8** by centrifugation, it was used for five consecutive runs to give rise to complete conversion and yield, thus showing no loss in catalytic activity. Moreover, by lowering the catalyst loading to just 0.02 mol %, the biphenyl-4-carboxaldehyde was formed quantitatively with a turnover number (TON) of 5000 (Table 2, entry 8). All the above results make this catalyst a good candidate for further tests under continuous-flow conditions.[17b]

Table 2. Suzuki–Miyaura reactions catalyzed by **8**.[a]



Entry	Substrate	Product	Conv. [%]	Yield [%]
1			>99	99
2			>99	99
3			88	87
4			>99	99
5			87	68
6			>99	99
7[b]			–[c]	–[c]
8[d]			>99	99

[a] Reaction conditions: Phenylboronic acid (1.1 mmol), aryl halide (1 mmol), K_2CO_3 (1.2 mmol), EtOH (1.2 mL), H_2O (1.2 mL), catalyst (0.2 mol %, 1 mg), reaction time 3 h. [b] Reaction time: 19 h. [c] No reaction. [d] Reaction conditions: Phenylboronic acid (1.1 mmol), aryl halide (1 mmol), K_2CO_3 (1.2 mmol), EtOH (0.6 mL), H_2O (0.6 mL), catalyst (0.02 mol %).

These promising results prompted us to explore the catalytic activity of material **8** in another Pd-promoted C–C coupling process such as the Mizoroki–Heck reaction (Table 3). Reaction between a set of four aryliodides and methyl acrylate in DMF/water at 90 °C in the presence of triethylamine (TEA) as base gave the corresponding alkenes in high yields and excellent selectivity, with the expected *trans* isomer as the only product, once again by employing just 0.2 mol % of catalyst **8**.

Conclusion

Two different strategies have been reported that allow easy access to several C_{60}–IL conjugates in which the anion, cation, and side chain have been varied. For this class of new hybrid materials, the combination of C_{60} and IL gives rise to outstanding solubility profiles in classically non-C_{60}-friendly solvents such as water and methanol in which imidazolium-based hexakis-adducts show solubilities higher than 800 mg mL^{-1}. This unprecedented solubility can be exploited in several key fields such as medicinal chemistry for gene delivery, photodynamic cancer therapy, and DNA photocleavage, but also in materials chemistry, catalysis, analytical, and coordination chemistry, among others. With this in mind, one of the C_{60}–IL hybrids has

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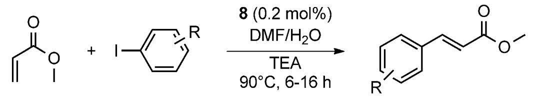
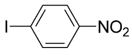
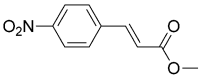
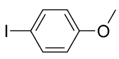
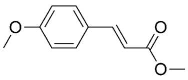
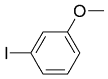
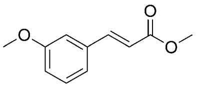
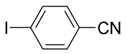
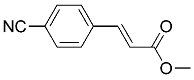
Table 3. Mizoroki–Heck reactions catalyzed by **8**.[a]



Entry	Substrate	Product	Conv. [%]	Yield [%]
1[b]			>99	99
2[c]			>99	99
3[c]			>99	89
4[b]			99	99

[a] Reaction conditions: Methyl acrylate (1.5 mmol), aryliodide (1 mmol), triethanolamine (TEA; 2 mmol), DMF (4 mL), H_2O (1 mL), catalyst (0.2 mol%, 1 mg). [b] Reaction time: 6 h. [c] Reaction time: 16 h.

been used for the immobilization of palladium nanoparticles through ion exchange with $PdCl_4^{2-}$ followed by reduction with sodium borohydride. Surprisingly, during the reduction, several carbon nanostructures were formed that comprised nano-onions and nanocages that displayed few-layer graphene sidewalls, which were characterized by means of TGA, XPS, XRD, SEM-EDAX, and HRTEM. More in-depth studies have to be carried out to completely reveal the mechanism of formation of such carbon nanostructures, including the effect of other metals as well as other reduction protocols on the resulting nanoforms. Finally, the nanomaterial thus obtained was successfully applied as a recyclable catalyst in Suzuki and Mizoroki–Heck reactions in just 0.2 mol% loading. In the former process, the catalyst was recycled for five consecutive runs with no loss in catalytic activity.

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Keywords: C–C coupling · fullerenes · hybrid materials · ionic liquids · nanostructures

[1] a) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789; *Angew. Chem.* **2000**, *112*, 3926–3945; b) J. S. Wilkes, *Green Chem.* **2002**, *4*, 73–80; c) R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792–793; d) C. Chiappe, D. Pieraccini, *J. Phys. Org. Chem.* **2005**, *18*, 275–297; e) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123–150.

[2] a) J. H. Davis Jr., *Chem. Lett.* **2004**, *33*, 1072–1077; b) S. G. Lee, *Chem. Commun.* **2006**, 1049–1063; c) R. Giernoth, *Angew. Chem. Int. Ed.* **2010**, *49*, 2834–2839; *Angew. Chem.* **2010**, *122*, 2896–2901; d) P. S. Wheatley, P. K. Allan, S. J. Teat, S. E. Ashbrook, R. E. Morris, *Chem. Sci.* **2010**, *1*, 483–487.

[3] a) J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508–3576; b) R. Sheldon, *Chem. Commun.* **2001**, 2399–2407.

[4] a) P. Domínguez de María, Z. Maugeri, *Curr. Opin. Chem. Biol.* **2011**, *15*, 220–225; b) S. N. Riduan, Y. Zhang, *Chem. Soc. Rev.* **2013**, *42*, 9055–9070.

[5] a) M. D. Joshi, J. L. Anderson, *RSC Adv.* **2012**, *2*, 5470–5484; b) V. Pino, A. M. Afonso, *Anal. Chim. Acta* **2012**, *714*, 20–37; c) C. F. Poole, S. K. Poole, *J. Sep. Sci.* **2011**, *34*, 888–900.

[6] a) D. R. MacFarlane, N. Tachikawa, M. Forsyth, J. M. Pringle, P. C. Howlett, G. D. Elliott, J. H. Davis, M. Watanabe, P. Simon, C. A. Angell, *Energy Environ. Sci.* **2014**, *7*, 232–250; b) B. Scrosati, J. Hassoun, Y.-K. Sun, *Energy Environ. Sci.* **2011**, *4*, 3287–3295.

[7] a) K. Fujita, K. Murata, M. Masuda, N. Nakamura, H. Ohno, *RSC Adv.* **2012**, *2*, 4018–4030; b) M. J. A. Shiddiky, A. A. J. Torriero, *Biosens. Bioelectron.* **2011**, *26*, 1775–1787.

[8] E. Vázquez, F. Giacalone, M. Prato, *Chem. Soc. Rev.* **2014**, *43*, 58–69.

[9] a) T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii, T. Aida, *Science* **2003**, *300*, 2072–2074; b) J. Lee, T. Aida, *Chem. Commun.* **2011**, *47*, 6757–6762; c) T. Fukushima, T. Aida, *Chem. Eur. J.* **2007**, *13*, 5048–5058.

[10] M. Tunckol, J. Durand, P. Serp, *Carbon* **2012**, *50*, 4303–4334.

[11] a) N. Karousis, T. Ichihashi, S. Chen, H. Shinohara, M. Yudasaka, S. Iijima, N. Tagmatarchis, *J. Mater. Chem.* **2010**, *20*, 2959–2964; b) M. J. Park, J. K. Lee, B. S. Lee, Y.-W. Lee, I. S. Choi, S.-g. Lee, *Chem. Mater.* **2006**, *18*, 1546–1551; c) Y. Zhang, Y. Shen, D. Han, Z. Wang, J. Song, F. Li, L. Niu, *Biosens. Bioelectron.* **2007**, *23*, 438–443; d) B. Yu, F. Zhou, G. Liu, Y. Liang, W. T. S. Huck, W. Liu, *Chem. Commun.* **2006**, 2356–2358; e) B. Wang, X. Wang, W. Lou, J. Hao, *J. Phys. Chem. C* **2010**, *114*, 8749–8754; f) Y. Zhang, Y. Shen, J. Yuan, D. Han, Z. Wang, Q. Zhang, L. Niu, *Angew. Chem. Int. Ed.* **2006**, *45*, 5867–5870; *Angew. Chem.* **2006**, *118*, 5999–6002; g) L. Rodríguez-Pérez, E. Teuma, A. Falqui, M. Gómez, P. Serp, *Chem. Commun.* **2008**, 4201–4203; h) S. Guo, S. Dong, E. Wang, *Adv. Mater.* **2010**, *22*, 1269–1272; i) H. Yang, C. Shan, F. Li, D. Han, Q. Zhang, L. Niu, *Chem. Commun.* **2009**, 3880–3882; j) N. Karousis, S. P. Economopoulos, E. Sarantopoulou, N. Tagmatarchis, *Carbon* **2010**, *48*, 854–860; k) A. P. Saxena, M. Deepa, A. G. Joshi, S. Bhandari, A. K. Srivastava, *ACS Appl. Mater. Interfaces* **2011**, *3*, 1115–1126; l) P. Bhunia, E. Hwang, M. Min, J. Lee, S. Seo, S. Some, H. Lee, *Chem. Commun.* **2012**, *48*, 913–915; m) L. Rodríguez-Pérez, R. García, M. Á. Herranz, N. Martín, *Chem. Eur. J.* **2014**, *20*, 7278–7286.

[12] T. Itoh, M. Mishiro, K. Matsumoto, S. Hayase, M. Kawatsura, M. Morimoto, *Tetrahedron* **2008**, *64*, 1823–1828.

[13] W. Zhilei, L. Zaijun, S. Xiulan, F. Yinjun, L. Junkang, *Biosens. Bioelectron.* **2010**, *25*, 1434–1438.

[14] a) C. D. Tran, S. Challa, *Analyst* **2008**, *133*, 455–464; b) A. Speltini, D. Merli, A. Profumo, *Anal. Chim. Acta* **2013**, *783*, 1–16.

[15] a) R. Maeda-Mamiya, E. Noiri, H. Isobe, W. Nakanishi, K. Okamoto, K. Doi, T. Sugaya, T. Izumi, T. Homma, E. Nakamura, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 5339–5344; b) C. Klumpp, L. Lacerda, O. Chaloin, T. D. Ros, K. Kostarelos, M. Prato, A. Bianco, *Chem. Commun.* **2007**, 3762–3764; c) D. Sigwalt, M. Holler, J. Iehl, J.-F. Nierengarten, M. Nothisen, E. Morin, J.-S. Remy, *Chem. Commun.* **2011**, *47*, 4640–4642.

[16] a) T. Da Ros, M. Prato, *Chem. Commun.* **1999**, 663–669; b) N. Tagmatarchis, H. Shinohara, *Mini-Rev. Med. Chem.* **2001**, *1*, 339–348; c) R. Bakry, R. M. Vallant, M. Najam-ul-Haq, M. Rainer, Z. Szabo, C. W. Huck, G. K. Bonn, *Int. J. Nanomed.* **2007**, *2*, 639–649.

[17] a) C. Aprile, F. Giacalone, P. Agrigento, L. F. Liotta, J. A. Martens, P. P. Pescarmona, M. Gruttadauria, *ChemSusChem* **2011**, *4*, 1830–1837; b) C. Pavia, E. Ballerini, L. A. Bivona, F. Giacalone, C. Aprile, L. Vaccaro, M. Gruttadauria, *Adv. Synth. Catal.* **2013**, *355*, 2007–2018; c) C. Pavia, F. Giacalone, L. A. Bivona, A. M. P. Salvo, C. Petrucci, G. Strappaveccia, L. Vaccaro, C. Aprile, M. Gruttadauria, *J. Mol. Catal. A* **2014**, *387*, 57–62.

[18] a) J. Iehl, R. Pereira De Freitas, B. Delavaux-Nicot, J. F. Nierengarten, *Chem. Commun.* **2008**, 2450–2452; b) M. Rae, F. Perez-Balderas, C. Baleizão, A. Fedorov, J. A. S. Cavaleiro, A. C. Tomé, M. N. Berberan-Santos, *J. Phys. Chem. B* **2006**, *110*, 12809–12814.

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[19] a) C. Bingel, *Chem. Ber.* **1993**, *126*, 1957 – 1959; b) I. Lamparth, A. Hirsch, *J. Chem. Soc. Chem. Commun.* **1994**, 1727 – 1728; c) A. Hirsch, I. Lamparth, H. R. Karfunkel, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 437 – 438; *Angew. Chem.* **1994**, *106*, 453 – 455; d) J.-F. Nierengarten, V. Gramlich, F. Cardullo, F. Diederich, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2101 – 2103; *Angew. Chem.* **1996**, *108*, 2242 – 2244.

[20] a) H. Li, S. A. Haque, A. Kitaygorodskiy, M. J. Meziani, M. Torres-Castillo, Y.-P. Sun, *Org. Lett.* **2006**, *8*, 5641 – 5643; b) H. Li, A. Kitaygorodskiy, R. A. Carino, Y.-P. Sun, *Org. Lett.* **2005**, *7*, 859 – 861.

[21] a) J. F. Nierengarten, *Pure Appl. Chem.* **2012**, *84*, 1027 – 1037; b) M. Sánchez-Navarro, A. Muñoz, B. M. Illescas, J. Rojo, N. Martín, *Chem. Eur. J.* **2011**, *17*, 766 – 769.

[22] a) J. Luczkowiak, A. Muñoz, M. Sánchez-Navarro, R. Ribeiro-Viana, A. Ginieis, B. M. Illescas, N. Martín, R. Delgado, J. Rojo, *Biomacromolecules* **2013**, *14*, 431 – 437; b) P. Compain, C. Decroocq, J. Iehl, M. Holler, D. Hazelard, T. M. Barragán, C. O. Mellet, J. F. Nierengarten, *Angew. Chem. Int. Ed.* **2010**, *49*, 5753 – 5756; *Angew. Chem.* **2010**, *122*, 5889 – 5892; c) J. F. Nierengarten, J. Iehl, V. Oerthel, M. Holler, B. M. Illescas, A. Muñoz, N. Martín, J. Rojo, M. Sánchez-Navarro, S. Cecioni, S. Vidal, K. Buffet, M. Durka, S. P. Vincent, *Chem. Commun.* **2010**, *46*, 3860 – 3862; d) J. Lehl, J. F. Nierengarten, *Chem. Eur. J.* **2009**, *15*, 7306 – 7309; e) R. Rísquez-Cuadro, J. M. García Fernández, J. F. Nierengarten, C. Ortiz Mellet, *Chem. Eur. J.* **2013**, *19*, 16791 – 16803.

[23] a) J. Iehl, J. F. Nierengarten, *Chem. Commun.* **2010**, *46*, 4160 – 4162; b) S. Cecioni, V. Oerthel, J. Iehl, M. Holler, D. Goyard, J. P. Praly, A. Imberty, J. F. Nierengarten, S. Vidal, *Chem. Eur. J.* **2011**, *17*, 3252 – 3261.

[24] X. Camps, A. Hirsch, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1595 – 1596.

[25] a) M. Brettreich, A. Hirsch, *Tetrahedron Lett.* **1998**, *39*, 2731 – 2734; b) S. Filippone, F. Heimann, A. Rassat, *Chem. Commun.* **2002**, 1508 – 1509; c) K. Kokubo, K. Matsubayashi, H. Tategaki, H. Takada, T. Oshima, *ACS Nano* **2008**, *2*, 327 – 333; d) A. B. Kornev, E. A. Khakina, S. I. Troyanov, A. A. Kushch, A. Peregudov, A. Vasilchenko, D. G. Deryabin, V. M. Martynenko, P. A. Troshin, *Chem. Commun.* **2012**, *48*, 5461 – 5463; e) A. M. López, F. Scarel, N. R. Carrero, E. Vázquez, A. Mateo-Alonso, T. D. Ros, M. Prato, *Org. Lett.* **2012**, *14*, 4450 – 4453; f) A. B. Kornev, A. S. Peregudov, V. M. Martynenko, G. V. Guseva, T. E. Sashenkova, A. Y. Rybkin, I. I. Faingold, D. V. Mishchenko, R. A. Kotelnikova, N. P. Konovalova, J. Balzarini, P. A. Troshin, *Mendeleev Commun.* **2013**, *23*, 323 – 325.

[26] a) F. Giacalone, N. Martín, *Adv. Mater.* **2010**, *22*, 4220 – 4248; b) Z. Yao, K. C. Tam, *Macromol. Rapid Commun.* **2011**, *32*, 1863 – 1885.

[27] a) M. Brettreich, S. Burghardt, C. Böttcher, T. Bayerl, S. Bayerl, A. Hirsch, *Angew. Chem. Int. Ed.* **2000**, *39*, 1845 – 1848; *Angew. Chem.* **2000**, *112*, 1915 – 1918; b) M. Braun, U. Hartnagel, E. Ravanelli, B. Schade, C. Böttcher, O. Vostrowsky, A. Hirsch, *Eur. J. Org. Chem.* **2004**, 1983 – 2001; c) N. Chronakis, U. Hartnagel, M. Braun, A. Hirsch, *Chem. Commun.* **2007**, 607 – 609; d) P. Witte, F. Hörmann, A. Hirsch, *Chem. Eur. J.* **2009**, *15*, 7423 – 7433; e) F. Hörmann, A. Hirsch, *Chem. Eur. J.* **2013**, *19*, 3188 – 3197.

[28] a) E. Nakamura, H. Isobe, *Acc. Chem. Res.* **2003**, *36*, 807 – 815; b) H. Isobe, W. Nakanishi, N. Tomita, S. Jinno, H. Okayama, E. Nakamura, *Chem. Asian J.* **2006**, *1*, 167 – 175; c) B. Sitharaman, T. Y. Zakharian, A. Saraf, P. M. J. Ashcroft, S. Pan, Q. P. Pham, A. G. Mikos, L. J. Wilson, D. A. Engler, *Mol. Pharm.* **2008**, *5*, 567 – 578.

[29] C. F. Richardson, D. I. Schuster, S. R. Wilson, *Org. Lett.* **2000**, *2*, 1011 – 1014.

[30] a) A. Riisager, R. Fehrmann, S. Flicker, R. van Hal, M. Haumann, P. Wasserscheid, *Angew. Chem. Int. Ed.* **2005**, *44*, 815 – 819; *Angew. Chem.* **2005**, *117*, 826 – 830; b) C. P. Mehnert, *Chem. Eur. J.* **2005**, *11*, 50 – 56.

[31] a) S. Kidambi, M. L. Bruening, *Chem. Mater.* **2005**, *17*, 301 – 307; b) Y. M. A. Yamada, Y. Uozumi, *Tetrahedron* **2007**, *63*, 8492 – 8498; c) J. Zhang, L. Meng, D. Zhao, Z. Fei, Q. Lu, P. J. Dyson, *Langmuir* **2008**, *24*, 2699 – 2704; d) F. Durap, Ö. Metin, M. Aydemir, S. Özkar, *Appl. Organomet. Chem.* **2009**, *23*, 498 – 503.

[32] S. Eriksson, M. Boutonnet, S. Järås, *Appl. Catal. A* **2006**, *312*, 95 – 101.

[33] a) S. Chen, K. Kobayashi, R. Kitaura, Y. Miyata, H. Shinohara, *ACS Nano* **2011**, *5*, 4902 – 4908; b) S. Chen, S. Zhang, X. Liu, J. Wang, J. Wang, K. Dong, J. Sun, B. Xu, *Phys. Chem. Chem. Phys.* **2014**, *16*, 5893 – 5906.

[34] a) D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *J. Am. Chem. Soc.* **2004**, *126*, 15876 – 15882; b) L. Li, J. Wang, T. Wu, R. Wang, *Chem. Eur. J.* **2012**, *18*, 7842 – 7851.

[35] a) O. Zhou, R. M. Fleming, D. W. Murphy, C. H. Chen, R. C. Haddon, A. P. Ramirez, S. H. Glarum, *Science* **1994**, *263*, 1744 – 1747; b) H. Takuya, S. D. Mildred, K. Yoong Ahm, T. Mauricio, E. Morinobu, in *Dekker Encyclopedia of Nanoscience and Nanotechnology, Second Edition - Six Volume Set (Print Version)*, CRC Press, **2008**, pp. 691 – 706.

[36] a) D. Ugarte, *Nature* **1992**, *359*, 707 – 709; b) F. Banhart, T. Füller, P. Redlich, P. M. Ajayan, *Chem. Phys. Lett.* **1997**, *269*, 349 – 355.

[37] E. Thune, T. Cabioc'h, P. Guérin, M. F. Denanot, M. Jaouen, *Mater. Lett.* **2002**, *54*, 222 – 228.

[38] X. H. Chen, F. M. Deng, J. X. Wang, H. S. Yang, G. T. Wu, X. B. Zhang, J. C. Peng, W. Z. Li, *Chem. Phys. Lett.* **2001**, *336*, 201 – 204.

[39] a) V. L. Kuznetsov, A. L. Chuvilin, Y. V. Butenko, I. Y. Mal'kov, V. M. Titov, *Chem. Phys. Lett.* **1994**, *222*, 343 – 348; b) E. Thune, T. Cabioc'h, M. Jaouen, F. Bodart, *Phys. Rev. B* **2003**, *68*, 115434.

[40] A. V. Gubarevich, J. Kitamura, S. Usuba, H. Yokoi, Y. Kakudate, O. Odawara, *Carbon* **2003**, *41*, 2601 – 2606.

[41] C. He, N. Zhao, X. Du, C. Shi, J. Ding, J. Li, Y. Li, *Scripta Mater.* **2006**, *54*, 689 – 693.

[42] S.-S. Hou, D.-H. Chung, T.-H. Lin, *Carbon* **2009**, *47*, 938 – 947.

[43] a) N. Sano, H. Wang, M. Chhowalla, I. Alexandrou, G. A. J. Amaratunga, *Nature* **2001**, *414*, 506 – 507; b) N. Sano, H. Wang, I. Alexandrou, M. Chhowalla, K. B. K. Teo, G. A. J. Amaratunga, K. Iimura, *J. Appl. Phys.* **2002**, *92*, 2783 – 2788.

[44] a) I. Lamparth, C. Maichle-Mössmer, A. Hirsch, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1607 – 1609; *Angew. Chem.* **1995**, *107*, 1755 – 1757; b) J. Cerar, M. Pompe, M. Guček, J. Cerkovnik, J. Škerjanc, *J. Chromatogr. A* **2007**, *1169*, 86 – 94.

[45] a) Y. Kim, Y. Noh, E. J. Lim, S. Lee, S. M. Choi, W. B. Kim, *J. Mater. Chem. A* **2014**, *2*, 6976 – 6986; b) S. P. Dubey, A. D. Dwivedi, I.-C. Kim, M. Sillanpaa, Y.-N. Kwon, C. Lee, *Chem. Eng. J.* **2014**, *244*, 160 – 167.

[46] a) S. Park, J. An, J. R. Potts, A. Velamakanni, S. Murali, R. S. Ruoff, *Carbon* **2011**, *49*, 3019 – 3023; b) Z. Bo, X. Shuai, S. Mao, H. Yang, J. Qian, J. Chen, J. Yan, K. Cen, *Sci. Rep.* **2014**, *51*, 4.

[47] a) Z. Syrgiannis, V. La Parola, C. Hadad, M. Lucío, E. Vázquez, F. Giacalone, M. Prato, *Angew. Chem. Int. Ed.* **2013**, *52*, 6480 – 6483; *Angew. Chem.* **2013**, *125*, 6608 – 6611; b) K. Flavin, K. Lawrence, J. Bartelmess, M. Tasior, C. Navio, C. Bittencourt, D. F. O'Shea, D. M. Guldi, S. Giordani, *ACS Nano* **2011**, *5*, 1198 – 1206; c) M. Liu, Y. Yang, T. Zhu, Z. Liu, *Carbon* **2005**, *43*, 1470 – 1478; d) A. Jung, R. Graupner, L. Ley, A. Hirsch, *Phys. Status Solidi B* **2006**, *243*, 3217 – 3220.

[48] G. Z. Hu, F. Nitze, X. Jia, T. Sharifi, H. R. Barzegar, E. Gracia-Espino, T. Wagberg, *RSC Adv.* **2014**, *4*, 676 – 682.

[49] a) B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2002**, *124*, 14127 – 14136; b) M. Moreno-Mañas, R. Pleixats, *Acc. Chem. Res.* **2003**, *36*, 638 – 643; c) D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem. Int. Ed.* **2005**, *44*, 7852 – 7872; *Angew. Chem.* **2005**, *117*, 8062 – 8083; d) L. S. Ott, R. G. Finke, *Inorg. Chem.* **2006**, *45*, 8382 – 8393; e) Z. Hou, N. Theyssen, W. Leitner, *Green Chem.* **2007**, *9*, 127 – 132; f) C. Ornelas, L. Salmon, J. Ruiz Aranzaes, D. Astruc, *Chem. Commun.* **2007**, 4946 – 4948; g) Y. Tsuji, T. Fujihara, *Inorg. Chem.* **2007**, *46*, 1895 – 1902; h) J. Durand, E. Teuma, M. Gómez, *Eur. J. Inorg. Chem.* **2008**, 3577 – 3586; i) J. N. Park, A. J. Forman, W. Tang, J. Cheng, Y. S. Hu, H. Lin, E. W. McFarland, *Small* **2008**, *4*, 1694 – 1697; j) J. Dupont, J. D. Scholten, *Chem. Soc. Rev.* **2010**, *39*, 1780 – 1804; k) M. Lamblin, L. Nassar-Hardy, J. C. Hierso, E. Fouquet, F. X. Felpin, *Adv. Synth. Catal.* **2010**, *352*, 33 – 79; l) N. Mejías, R. Pleixats, A. Shafir, M. Medio-Simón, G. Asensio, *Eur. J. Org. Chem.* **2010**, 5090 – 5099; m) A. Corma, H. Garcia, *Chem. Soc. Rev.* **2008**, *37*, 2096 – 2126; n) M. M. Coulter, J. A. Dinglasan, J. B. Goh, S. Nair, D. J. Anderson, V. M. Dong, *Chem. Sci.* **2010**, *1*, 772 – 775.

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FULL PAPER

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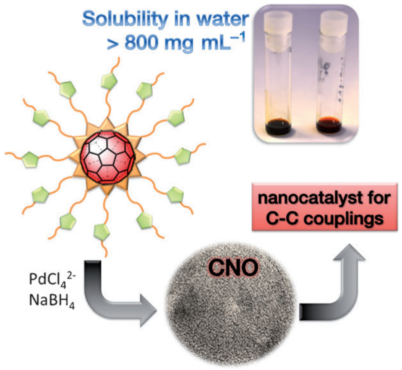

Graphitic Nanostructures

V. Campisciano, V. L. Parola, L. F. Liotta, F. Giacalone, M. Gruttadauria**

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Fullerene–Ionic-Liquid Conjugates: A New Class of Hybrid Materials with Unprecedented Properties

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