Synthesis of modified fullerenes for oxygen reduction reactions†

Rosa Maria Girón, Juan Marco-Martínez, Sebastiano Bellani, Alberto Insuasty, Hansel Comas Rojas, Gabriele Tullii, Maria Rosa Antognazza, Salvatore Filippone and Nazario Martin

The oxygen reduction reaction (ORR) is a key process common in several energy converting systems or electro-chemical technologies such as fuel cells, metal–air batteries, oxygen sensors, etc., which is based on the use of expensive and scarcely available platinum metal. In the search for carbon-based catalysts for ORRs, two different classes of new fullerene hybrids and metal-free fullerene derivatives endowed with suitable active sites have been prepared by highly selective metal- and organo-catalyzed synthetic methodologies. Along with their classical behavior as electron acceptors in polymer-based photo-electrochemical cells, the new fullerene derivatives are able to efficiently catalyze ORRs by using no metals or very low amounts of metals. Remarkably, the activity of metal-free fullerenes has proved to be as high as that observed for metallofullerenes bearing noble metals, and up to ten-fold higher than that of PCBM.

1 Introduction

The oxygen reduction reaction (ORR) is a key process in different energy converting systems or electrochemical technologies (fuel cells, metal air batteries, oxygen sensors, etc.). In these fields the replacement of the traditional platinum based catalysts with non-precious metals or metal-free electrocatalysts is currently a hot scientific challenge. Particularly, the use of carbon nanomaterials such as nitrogen-doped carbon nanotubes or graphene, represents an interesting and novel approach.

In this context, among the different allotropic forms of carbon, fullerenes combine unique chemical, optical, electronic and photophysical properties with a defined molecular structure. Indeed, their good electron accepting and transport capability led to their extended use as suitable n-type materials, widely employed in organic electronics and photovoltaic devices, including the most recent perovskite solar cells.

Thus, bulk heterojunction (BHJ) organic photovoltaic cells (OPVs) are a notable application, which consist of p-type conjugated polymers (e.g. poly(3-hexylthiophene-2,5-diyl), P3HT) and n-type fullerene derivatives, [6,6]phenyl-C61-butyric acid methyl ester (PCBM) being the most widely used. In a typical BHJ approach, a bi-continuous network is created, which allows the promotion of exciton dissociation processes and the achievement of a high power conversion efficiency. The next frontier in the use of acceptor/donor BHJs, based on PCBM, is the realization of photo-electrochemical cells, able to work in contact with aqueous and/or non-aqueous electrolytes upon visible light illumination. One notable example is the realization of efficient photocathodes for hydrogen production by photo-electrochemical water splitting. Recently, some of us have reported a high sensitivity, photo-electrochemical oxygen sensor based on an organic BHJ formed using a low band gap polymer (APFO-3) and PCBM, revealing photo-activity towards the ORR. In the proposed scheme, polymer excitation by visible light leads to the efficient generation of bounded charged species (excitons), which are promptly dissociated into free charges (polarons) by a highly efficient electron transfer process to the fullerene-based acceptor domain. We have recently reported that this process, typical of solid-state photovoltaic cells, occurs in the hybrid system with fully functionalized APFO-3 and PCBM, revealing photo-activity towards the ORR. The ORR, therefore, can be efficiently catalyzed by metal-free fullerenes, as we report here.
interface with the aqueous solution, thus giving rise to photo-electrochemical reactions and, in particular, to the ORR (Fig. 1).

Here, we report the synthesis of new fullerene derivatives, suitably functionalized with catalytically active sites towards the ORR. This allows us to exploit a doubled fullerene functionality, by employing them both as electron acceptors in P3HT-based BHJ, and as redox active sites, thus avoiding the use of expensive noble metals.

Two main approaches have been undertaken in parallel: (i) the synthesis of new fullerene hybrid derivatives endowed with noble metals active in redox processes, such as Ir, Rh or Pt; (ii) the synthesis of metal-free fullerene catalysts, based on the presence of active C–H bonds. To this aim, both metal- and organo-catalytic methodologies have been employed, to obtain fullerene derivatives with tailored electronic and photocatalytic properties characterized by high regio- and stereo-selectivity.

Photoelectrochemical devices for the ORR based on BHJ P3HT:fullerene thin films have been finally realized, confirming an enhanced photocatalytic property of the novel compounds, when compared with the extensively used PCBM, taken as the reference fullerene.

2 Results and discussion

2.1. Synthesis of metallo- and organo-fullerenes catalysts

Over the last few years, fullerene chemistry has been widening its synthetic tools, in the search for more sophisticated structures, for a better control on the stereochemistry of the fullerene derivatives and for a control on the regio- and site-selectivity when higher fullerenes or endohedral fullerenes are used. Following this trend, on one hand, we have directed our attention to the achievement of new selective catalytic methodologies aimed at the preparation of both metallofullerenes and regioisomeric fullerene hydrides. On the other hand, we have modified both metal- and organo-catalysed methodologies, previously described by us, for the introduction of a suitable functionality on the fullerene cage to become catalytically active towards the ORR.

2.1.1. Pyrrolino-metallo-fullerenes. With the aim of preparing stable metallo-fullerene hybrids, we first directed our attention onto iridium(III) complexes due to their wide use in hydrogenation processes and for their ability to form stable and easily isolable complexes. Thus, the design of the iridium-fullerene complexes was based on the preparation of pyrrolino[60]fullerene ligands endowed with a carboxylic group to bind iridium(III) as well as other active metals efficiently. To this purpose, we carried out the 1,3-dipolar cycloaddition reaction of azlactone 1 with [60]fullerene by using a racemic silver BINAP catalyst, followed by the addition of the iridium dimer [Cp*IrCl2]2, (see Scheme 1). A unique compound, 2Ir, was obtained in “one-pot” and in good yield (ca. 40%) as a result of two sequential processes where two chiral centers are formed: in the first step, a pyrrolino[3,4:1,2][60]fullerene carboxylic acid is formed with a stereoogenic center in the C-5 of the pyrrole ring. In the second process, iridium(III) is covalently linked diastereoselectively to the [60]fullerene derivative through the formation of two new bonds, one with the nitrogen of the pyrrole ring and the other one with the oxygen of the carboxylate group. The presence of the metal is confirmed by the IR spectrum of the isolated solid, since the ν(CO) of the starting pyrroline shifts from 1700 cm⁻¹ to 1660 cm⁻¹ in the final product, which is in agreement with the previously observed behaviour of fullereneiminocarboxylate as (N,O)-chelating monocarboxylic ligands.²³ It is worth noting that, despite iridium(III), with its typical pseudo-tetrahedral geometry, being able to adopt two possible configurations and, therefore, afford a diastereomeric mixture, the overall process occurs diastereoselectively, in sharp contrast to other related examples.²⁴

Indeed, this behaviour was observed by ¹H-NMR (see the ESIF) and its structure could be confirmed by X-ray diffraction analysis of a monocystal obtained by slow evaporation of 2Ir in CS₂/hexane.²⁴

As is shown in Fig. 2, the iridium atom adopts a pseudo-octahedral geometry where the Cp* group occupies a face of the octahedron, 1.775 Å being the distance between the metal and the ring centroid. Two other octahedral positions involve the C–N and Ir–O bonds of 2.103(4) Å and 2.095(4) Å length, respectively. Finally, the determined Ir–Cl bond distance resulted to be 2.393(2) Å.

Scheme 1 Diastereomeric synthesis of iridium (2Ir) and rhodium (2Rh) pyrrolino[3,4:1,2][60]fullerene.
very low amount of molecular oxygen. species easily undergo dehydrogenation in the presence of even
cycloaddition of the same azlactone (or fulleranes) have been deeply studied. species for hydrogen storage and, therefore, fullerene hydrides
double bonds have been envisaged as very useful molecular
fullerene
phosphino ethane (dppe) catalysed Lu’s [3 + 2] cycloaddition
formed by the use of the organocatalytic methodology. To this
aim, we extended the scope of our previously reported phos-
double addition on [60]fullerene where a C60
maintain a high catalytic activity. Thus, we designed a regiose-
linked to the carbon cage could replace precious metals but still
wondered if the presence of highly active hydrogen directly
linked to the carbon cage could replace precious metals but still
maintain a high catalytic activity. Thus, we designed a regiose-
selective double addition on [60]fullerene where a C60–H bond is formed by the use of the organocatalytic methodology. To this
aim, we extended the scope of our previously reported phos-
phine catalyzed cycloaddition of allenoates/alkynoates to [60]
Chart 1 into three main types: fullerenes without catalytic sites,
but with higher-lying LUMO levels compared to PCBM, as mere acceptor components (DPM-12 and bisDPM-12, in grey colour, top panel); hybrid fullerenes with metallic catalytic sites (2Ir, 2Rh and 6 compounds, in red) and catalytic, metal-free fullerenes (4a, 4b and 4c compounds, in green).

2.2. Photocatalytic activity of fullerene derivatives toward the ORR in photoelectrochemical devices

The new fullerene derivatives were finally tested as photo-elec-
trocatalysts in polymer-based devices for the photo-electro-
chemical ORR, and the overall electrochemical performances
were compared to those of devices employing PCBM as a stan-
dard reference material. The compounds used are classified in

Fig. 2 X-ray diffraction of a crystal of 2Ir obtained by slow evaporation
in CS2/hexane.

which is slightly shorter than that of other related pyrrolidino-
carboxylate iridium Cp* complexes.23b The distance between the
two fullerene sp3 carbon atoms is 1.590(8) Å, which is in the
typical range for a fullerene monoadduct.

X-ray analysis confirms the presence of a single diastereomer
(with both enantiomers) with the chlorine atom in a trans
position to the methyl group of the iridium cycle (see also ESI†).

Analogously, a rhodium pyrroline[60]fullerene hybrid 2Rh
was prepared in 38% yield, by using [Cp*RhCl2]2 after the
cycloaddition of the same azlactone 1 (Scheme 1).

Chart 1 Fullerene derivatives used as acceptors/catalysts in photo-
electrochemical devices.

2.1.2. Organocatalytic synthesis of the metal-free fullerene
catalyst. Fullerenes with their 30 (for C60) or more strained C=C
double bonds have been envisaged as very useful molecular
species for hydrogen storage and, therefore, fullerene hydrides
(or fullerenes) have been deeply studied.25,26 Furthermore, these
species easily undergo dehydrogenation in the presence of even
very low amount of molecular oxygen.27 In this regard, we
wondered if the presence of highly active hydrogen directly
linked to the carbon cage could replace precious metals but still
maintain a high catalytic activity. Thus, we designed a regiose-
selective double addition on [60]fullerene where a C60–H bond is formed by the use of the organocatalytic methodology. To this
aim, we extended the scope of our previously reported phos-
phine catalyzed cycloaddition of allenoates/alkynoates to [60]
fullerene.21a,b to 5-hydroxy-3-alkynoates (Scheme 2).

Thus, after alkynoate/allenoate isomerization, 1,2-diphenyl-
phosphino ethane (dppe) catalysed Lu’s [3 + 2] cycloaddition29

of 3a, b afforded the corresponding cyclopentenoate[60]fuller-
enes. These products are not isolated since they underwent an
easy regioselective addition of the hydroxyl group to the cis-1
double bond of C60 giving rise to bisadducts 4a, b endowed with a C60–H bond in 48% and 34% yields, respectively. Eventually,
the corresponding acid 4c was obtained after acidic removal of the tert-butyl ester.

Scheme 2 cis-1 regioselective fullerene bifunctionalization affording
fullerene hydrides.

BHJ thin films (~140 nm), based on rr-P3HT as a photoactive
donor component, were deposited by spin coating on top of
FTO-covered glass substrates. In some cases, a second thin film
fullerene layer was deposited on top of the photoactive
component, in order to directly expose the catalytic sites to the
electrolyte. Photo-catalytic activity towards oxygen reduction
was assessed in sodium phosphate buffer (PBS) at pH 7.4 and
a controlled dissolved oxygen (DO) concentration (5.8 mg L−1).
All the details about material absorbance spectra, device fabri-
cation processing, experimental set up and measurement
conditions are reported in the ESI section.†

Fig. 3 reports Linear Scan Voltammetry (LSV) recorded in the
dark and upon illumination (1 sun) in devices based on

all organic catalysts
fullerene acceptors without any catalytic site (PCBM, DPM-12 and bisDPM-12).

As demonstrated in a previous work, the recorded current signal can be unambiguously attributed to photo-activated electrochemical reactions occurring at the hybrid organic/electrolyte interface and in particular to the ORR (see also Fig. S2 in the ESI section†). Moreover, dark current values (dashed lines) are negligible in all cases.

Notably, the use of DPM-12 and bisDPM-12 fullerene bisadducts allows the increase of the Onset Potential (OP, defined here as the voltage at which the photocurrent density amounts at 100 nA cm$^{-2}$) up to 0.15 V vs. Ag/AgCl and 0.35 V vs. Ag/AgCl, respectively, with respect to the reference PCBM, 0.12 V vs. Ag/AgCl. Correspondingly, at a fixed voltage the photocurrent density increases: at $-0.15$ V vs. Ag/AgCl, for instance, it amounts to $-2.4 \mu$A cm$^{-2}$, $-5.2 \mu$A cm$^{-2}$, and $-8.2 \mu$A cm$^{-2}$ for PCBM, DPM-12 and bisDPM-12, respectively. An analogous behavior has also been reported in organic solar cells, where an increase of the open circuit voltage in the case of DPM-12 and bisDPM-12 was reported, when compared to PCBM. The enhanced performances are possibly attributed to the broader density of states and to the higher-lying LUMO level of the fullerene bisadducts, able to facilitate the electron transfer processes occurring at the organic/electrolyte interfaces.

Iridium, rhodium and platinum are known to be efficient catalysts for the ORR. Hybrid catalysts, 2Ir, 2Rh and 6, are thus expected to provide catalytic properties typical of the embedded metal component, but with a consistently reduced need for precious metals, and with the advantage of a more localized interaction. In this case photo-electrodes were realized by covering the reference P3HT:PCBM BHJ layer with an over-layer of pristine electron acceptor, in order to maximize the localization at the electrolyte interface of the catalytic sites present within the functionalized fullerene derivatives (P3HT:PCBM/hybrid catalyst configuration).

The adopted strategy resulted to be successful. All tested hybrid catalysts show photocurrent density values larger by more than one order of magnitude with respect to reference PCBM, and comparable dark current values (Fig. 4). Photocurrent generation is clearly related to the presence of dissolved oxygen, and its origin can be safely attributed to the occurrence of the ORR (see ESI, Fig. S4† panels a and b). OPs are also considerably increased, shifting from 0.12 V vs. Ag/AgCl for PCBM up to 0.3 V vs. Ag/AgCl for 2Ir and 2Rh and to 0.35 V vs. Ag/AgCl for 6. The reported data allow us to conclude that electrons can be easily transferred towards metallic catalytic centres which, in turn are highly efficient in reducing the overpotential needed to foster the ORR. In other words, the use of hybrid fullerenes endowed with catalytic centres increases both the electron transfer rate (observed as a net photocurrent density increase) and the driving force for electrochemical reactions (observed as an OP increase).

On the other hand, following the recent trend of using carbon based materials as the catalyst for the ORR, we planned the preparation of a molecular organocatalyst by replacement of the metallic atoms from the fullerene derivatives, with a fullerene hydride as the active site. The choice of using catalysts such as 4a-c relies on the reported hydrogen transfer from the fullerene hydrides, namely C$_{60}$H$_{2}$, to dioxygen and on the easy deprotonation of fullerene hydrides leading to very stable fullerene anions.

In order to evaluate the importance of the hydrogen fullerene bond, devices based on analogous cyclopentenoate functionalization but lacking the C$_{60}$–H bond (5a, b) were also prepared.

Fig. 5 summarizes the results of the characterization of photo-electrochemical cells based on 4a, 4b, 4c, 5a and 5b components as hybrid electron acceptor/catalyst components, as compared to the reference device based on PCBM.

We notice that 4a leads to higher catalytic activity, with a more than 5-fold increase in photocurrent density at $-0.15$ V vs. Ag/AgCl with respect to PCBM, and a higher OP value (0.3 V vs. Ag/AgCl). Conversely, 5a and 5b, despite presenting a similar
measurements under O2-saturated conditions on the occurrence of the ORR (see ESI, Fig. S4, panel c respectively. Once more, photocurrent generation is related to di

lization, in the case of photocurrent reached stable values a

recorded at the \( \text{Ag/AgCl} \). OPs are 0.28 V in both cases which are lower with respect to the precious metal hybrid samples. As a \( \text{AgCl} \) vs. \( \text{Ag/AgCl} \) anodic oxidation of \( \text{H}_2\text{O}_2 \) (Scheme 3). Thus, an easier oxygen reduction takes place to form the hydroperoxyl radical, through a hydrogen atom transfer (HAT) or by a proton coupled electron transfer (PCET), driven by the formation of the highly stable fullerene anions \( 4^− \).

Finally, we further functionalized 5a and 5b compounds by directly linking the active hydrogen to the carbon cage, as in the case of the more efficient 4a compound, obtaining 4b and 4c, respectively. Once more, photocurrent generation is related to the occurrence of the ORR (see ESI, Fig. S4, panel c†). Additional measurements under \( \text{O}_2 \)-saturated conditions on 4b and 4c are shown in the ESI (Fig. S5†). These data have been compared with those based on PCBM. Importantly, the recorded photocurrent densities for 4b and 4c show values comparable to the ones obtained for the hybrid catalysts P3HT:PCBM/2Ir and P3HT:PCBM/2Rh, in the order of \( -20 \mu \text{A cm}^{-2} \) at \(-0.15 \text{ V vs. Ag/AgCl} \). OPs are 0.28 V in both cases which are lower with respect to the ones of precious metal hybrid samples (0.3 V vs. \text{Ag/AgCl}) for PCBM/2Ir and 0.35 V vs. \text{Ag/AgCl} for PCBM/2Rh and PCBM/6) suggesting the need for further improvement. Conversely, metal-free fullerene samples showed higher durability with respect to the precious metal hybrid samples. As a figure of merit, the photocurrents recorded at \(-0.2 \text{ V vs. Ag/AgCl} \) for consecutive Cyclic Voltammetry (CV) cycles have been taken (see ESI, Fig. S6†). At the fourth cycle a decrease of the photocurrent of 12.9%, 21.2% and 45.4%, with respect to the value recorded at the first cycle, is observed for the case of PCBM, 4c and 6, respectively. Interestingly, while for PCBM and 4c the photocurrent reached stable values after a few cycles of stabilization, in the case of 6 a progressive decrease is observed. This could be due to different ORR mechanisms for the hybrid catalyst when compared to the other cases. As a matter of fact, for the Pt electrode, two-electron reduction of oxygen to \( \text{H}_2\text{O}_2 \) occurs parallel to the four-electron reduction to \( \text{H}_2\text{O} \) (see ESI, Scheme S1†). Consequently, a decrease of the cell voltage could arise because of the lower reversible redox potential of \( \text{H}_2\text{O}_2 \).

Regarding the catalytic activity of the metal-free fullerene derivatives 4a–c, a plausible mechanism to account for the photocurrent increase and observed stability is based on the initial transfer of the photo-generated electron (PET) from the polymer to catalysts 4a–c affording the corresponding fullerene radical anion (Scheme 3). Thus, an easier oxygen reduction takes place to form the hydroperoxyl radical, through a hydrogen atom transfer (HAT) or by a proton coupled electron transfer (PCET), driven by the formation of the highly stable fullerene anions \( 4^− \).

The aforementioned results show the remarkable activity of fullerene-based multiple metal-free catalysts in ORR, with efficiencies comparable to those obtained from metal-containing hybrid catalysts.

3 Conclusions

In summary, we have reported the highly selective catalytic synthesis of two series of fullerene-based molecular catalysts for the ORR. Iridium and rhodium pyrrolinofullerene complexes were prepared with complete diastereoselectivity (d.e. > 99%) and the structure of the iridium–fullerene complex was confirmed by X-ray analysis. On the other hand, metal-free fullerene catalysts, endowed with a highly active \( \text{C}_{60}-\text{H} \) bond, have been obtained by a regioselective \( \text{cis}-1 \) addition to the \( \text{C}_{60} \) cage. The electrocatalytic activity versus the oxygen reduction reactions has been tested in bulk heterojunction photo-electrochemical cells, affording current values up to ten fold higher than those of widely used PCBM. Remarkably, metal-free fullerene derivatives proved to give photocurrents comparable to those of related hybrids, thanks to the highly active \( \text{C}_{60}-\text{H} \) bond on the fullerene cage. Having demonstrated that the approach is highly promising, future efforts will focus on...
further improvement of the overall performances of photo-electrochemical cells.

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Notes and references

1 (a) B. C. H. Steele and A. Heinzel, Nature, 2001, 414, 345–352; (b) F. Cheng and J. Chen, Chem. Soc. Rev., 2012, 41, 2172–2192.

2 Z. Chen, D. Higgins, A. Yu, L. Zhang and J. Zhang, Energy Environ. Sci., 2011, 4, 3167–3192.

3 (a) L. Dai, Y. Xue, L. Qu, H.-J. Choi and J.-B. Baek, Chem. Rev., 2015, 115, 4823–4892; (b) D.-W. Wang and D. Su, Energy Environ. Sci., 2014, 7, 576–591.

4 K. Gong, F. Du, Z. Xia, M. Durstock and L. Dai, Science, 2009, 323, 760–764.

5 (a) D. Higgins, P. Zamani, A. Yu and Z. Chen, Energy Environ. Sci., 2016, 9, 357–390; (b) J. Guan, X. Chen, T. Wei, F. Liu, S. Wang, Q. Yang, Y. Lu and S. Yang, J. Mater. Chem. A, 2015, 3, 4139–4146.

6 A. Hirsch and M. Brettreich, Fullerene: Chemistry and Reactions, Wiley VCH, Weinheim, Germany, 2005.

7 L. W. Tutt and A. Kost, Nature, 1992, 356, 225–226.

8 L. Echegoyen and L. E. Echegoyen, Acc. Chem. Res., 1998, 31, 593–601.

9 D. M. Guldi and M. Prato, Acc. Chem. Res., 2000, 33, 695–703.

10 J. E. Anthony, A. Facchetti, M. Heeney, S. R. Marder and X. Zhan, Adv. Mater., 2010, 22, 3876–3892.

11 (a) J. L. Delgado, P.-A. Bouit, S. Filippone, M. A. Herranz and N. Martin, Chem. Commun., 2010, 46, 4853–4865; (b) B. C. Thompson and J. M. J. Fréchet, Angew. Chem., Int. Ed., 2008, 47, 58–77.

12 (a) A. Abrusci, S. D. Stranks, P. Docolmo, H.-L. Yip, A. K. Y. Jen and H. J. Snaith, Nano Lett., 2013, 13, 3124–3128; (b) P.-W. Liang, C.-C. Chueh, S. T. Williams and A. K. Y. Jen, Adv. Energy Mater., 2015, 5, 1402321–1402328.

13 (a) F. Fumagalli, S. Bellani, M. Schreier, S. Leonardi, H. C. Rojas, A. Ghadirzadeh, G. Tallui, A. Savoini, G. Marra, L. Meda, M. Gratzel, G. Lanzani, M. T. Mayer, M. R. Antognazza and F. Di Fonzo, J. Mater. Chem. A, 2016, 4, 2178–2187; (b) T. Bourgeteau, D. Tondelier, B. Ge, R. Brisse, R. Cornut, V. Artero and B. Jouselme, ACS Appl. Mater. Interfaces, 2015, 7, 16395–16403; (c) M. Haro, C. Solis, G. Molina, L. Otero, J. Bisquert, S. Gimenez and A. Guerrero, J. Phys. Chem. C, 2015, 119, 6488–6494; (d) G. M. Suppes, P. J. Fortin and S. Holdcroft, J. Electrochem. Soc., 2015, 162, H551–H556; (e) M. P. Gustafson, N. Clark, B. Winther-Jensen and D. R. MacFarlane, Electrochim. Acta, 2014, 140, 309–313.

14 H. Comas Rojas, S. Bellani, F. Fumagalli, G. Tallui, S. Leonardi, M. T. Mayer, M. Schreier, M. Grätzl, G. Lanzani, F. Di Fonzo and M. R. Antognazza, Energy Environ. Sci., 2016, DOI: 10.1039/c6ee01655c.

15 S. Bellani, A. Ghadirzadeh, L. Meda, A. Savoini, A. Tacca, G. Marra, R. Meira, J. Morgado, F. Di Fonzo and M. R. Antognazza, Adv. Funct. Mater., 2015, 25, 4531–4538.

16 A. Guerrero, M. Haro, S. Bellani, M. R. Antognazza, L. Meda, S. Gimenez and J. Bisquert, Energy Environ. Sci., 2014, 7, 3666–3673.

17 N. Martin, M. Altabe, S. Filippone and A. Martín-Domenech, Synlett, 2007, 3077.

18 E. E. Maroto, M. Izquierdo, S. Reboredo, J. Marco-Martínez, S. Filippone and N. Martin, Acc. Chem. Res., 2014, 47, 2660–2670.

19 E. E. Maroto, A. de Cózar, S. Filippone, Á. Martín-Domenech, M. Suarez, F. P. Cossio and N. Martin, Angew. Chem., Int. Ed., 2011, 50, 6060–6064.

20 (a) E. E. Maroto, J. Mateos, M. Garcia-Borrás, S. Osuna, S. Filippone, M. À. Herranz, Y. Murata, M. Solà and N. Martin, J. Am. Chem. Soc., 2015, 137, 1190–1197; (b) E. E. Maroto, M. Izquierdo, M. Murata, S. Filippone, K. Komatsu, Y. Murata and N. Martin, Chem. Commun., 2014, 50, 740–742; (c) K. Sawai, Y. Takano, M. Izquierdo, S. Filippone, N. Martin, Z. Slanina, N. Mizorogi, M. Waelchli, T. Tsuchiya, T. Akasaka and S. Nagase, J. Am. Chem. Soc., 2011, 133, 17746–17752.

21 (a) J. Marco-Martínez, S. Reboredo, M. Izquierdo, V. Marcos, J. L. López, S. Filippone and N. Martin, J. Am. Chem. Soc., 2014, 136, 2897–2904; (b) J. Marco-Martínez, V. Marcos, S. Reboredo, S. Filippone and N. Martin, Angew. Chem., Int. Ed., 2013, 52, 5115–5119.

22 (a) S. H. Laurie, in Comprehensive Coordination Chemistry, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, ch. 20.2, p. 739; (b) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 4th edn, 1986, p. 233.

23 (a) W. Bauer, M. Prem, K. Polborn, K. Sünkel, W. Steglich and W. Beck, Eur. J. Inorg. Chem., 1998, 1998, 485–493; (b) D. Carmona, M. Pilar Lamata, F. Viguri, E. San José, A. Mendoza, F. J. Lahoz, P. García-Orduña, R. Atencio and L. A. Oro, J. Organomet. Chem., 2012, 717, 152–163.

24 See the ESI†

25 Fullerenes the Hydrogenated Fullerenes, ed., F. Cataldo and S. Igesias-Groth, Springer Science+Business Media B.V., Dordrecht, 2010.

26 J. Nossal, R. K. Saini, L. B. Alemany, M. Meier and W. E. Billups, Eur. J. Org. Chem., 2001, 4167–4180.

27 G. W. Wang, Y. J. Li, F. B. Li and Y. C. Liu, Lett. Org. Chem., 2005, 2, 595–598.

28 R. M. Giron, S. Reboredo, J. Marco-Martínez, S. Filippone and N. Martin, Faraday Discuss., 2014, 173, 311–322.

29 C. Zhang and X. Lu, J. Org. Chem., 1995, 60, 2906–2908.

30 (a) A. Sánchez-Díaz, M. Izquierdo, S. Filippone, N. Martin and E. Palomares, Adv. Funct. Mater., 2010, 20, 2695–2700;
(b) G. Garcia-Belmonte, P. P. Boix, J. Bisquert, M. Lenes, H. J. Bolink, A. La Rosa, S. Filippone and N. Martin, J. Phys. Chem. Lett., 2010, 1, 2566–2571; (c) Y.-J. Cheng, M.-H. Liao, C.-Y. Chang, W.-S. Kao, C.-E. Wu and C.-S. Hsu, Chem. Mater., 2011, 23, 4056–4062.

31 (a) D. Cao, A. Wieckowski, J. Inukai and N. Alonso-Vante, J. Electrochem. Soc., 2006, 153, A869–A874; (b) Y. Nie, L. Li and Z. Wei, Chem. Soc. Rev., 2015, 44, 2168–2201; (c) J. Qiao, R. Lin, B. Li, J. Ma and J. Liu, Electrochim. Acta, 2010, 55, 8490–8497.

32 (a) J. Qiao, M. Saito, K. Hayamizu and T. Okada, J. Electrochem. Soc., 2006, 153, A967–A974; (b) V. A. Sethuraman, J. W. Weidner, A. T. Haug, M. Pemberton and L. V. Protsailo, Electrochim. Acta, 2009, 54, 5571–5582.