

Cyclobuteno[60]fullerenes as efficient n-type organic semiconductors

Silvia Reboredo,^{[a],[†]} Rosa M. Girón,^{[a],[†]} Salvatore Filippone,^[a] Tsubasa Mikie,^[b] Tsuneaki Sakurai,^[b] Shu Seki,^[b] Nazario Martín,^{[a],[c] [*]}

This work is dedicated to the memory of Harold W. Kroto

Abstract: Cyclobuteno[3,4:1,2][60]fullerenes have been prepared in a straightforward manner by a simple reaction between [60]fullerene and readily available allenoates or alkynoates as organic reagents under basic and mild conditions. The chemical structure of the new modified fullerenes has been determined by standard spectroscopic techniques and confirmed by X-Ray diffraction analysis. Some of these new fullerene derivatives exhibit a remarkable intrinsic electron mobility – determined by using flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements – which surpasses that of the well-known PCBM, thus behaving as promising n-type organic semiconductors.

Introduction

Over the last three decades, chemists have been dealing with the functionalization of fullerenes in order to synthesize derivatives showing a wide variety of specific properties with applications in fields such as bio-medicine, molecular electronics, photovoltaics or materials science.^[1] Among the many synthetic approaches developed for the chemical modification of fullerenes, cycloaddition reactions have proven their versatility and efficiency.^[2] In this regard, three, five and six-member carbocycles and heterocycles, as well as larger cycles have been deeply explored.^[3] Particularly, in our research group we have carried out the synthesis of a wide variety of pyrrolinofullerenes and pyrrolidinofullerenes as well as carbocyclic cyclopentene derivatives in their chiral version by using metal and organic asymmetric catalysis.^[4] However, the formation of cyclobutenes fused on the fullerene sphere is considerably less-known in the literature.^[5] Only a few examples describe the synthesis of these singular cycloadducts. On the one hand, alkynes have been used in phosphine catalyzed processes.^[5a] On the other hand, thermal

conditions are able to trigger a cycloaddition process by using allenamides or *in situ* generated ketenes.^[5b-c] It must be taken into account that the resultant structure is dependent on the employed method or substrate, being the obtained cycloadduct a cyclobutane with an exocyclic double bond^[5a,c] or a cyclobutene.^[5b,d-e]

In this paper, we describe a new and straightforward procedure for the preparation of cyclobuteno[3,4:1,2][60]fullerenes by a simple reaction between readily available allenoates or alkynoates with [60]fullerene under basic and mild experimental conditions. Furthermore, these compounds whose structure has been unambiguously determined by X-ray diffraction, show a remarkable intrinsic electronic mobility, thus behaving as efficient n-type organic semiconductors.

Results and Discussion

In order to address the synthesis of cyclobutenofullerenes, we firstly decided to evaluate the readily available alkynoate **1a** as a possible substrate for the formation of the fullerene cycloadduct. In sharp contrast to the cyclopentene derivatives formed under phosphine catalysis,^[4c] **1a** behaves differently when reacting with a base. We started our research by using 1 equivalent of NaH for 18 hours, with the idea that a base could be enough for triggering the synthesis of the desired cyclobutene adduct. However, while the formation of a new cycloadduct was observed by HPLC, the conversion only reached a 7%. We then turned our attention to a series of bases; NaOH, Et₃N or DABCO among others. None of the evaluated bases gave rise to any cycloadduct. Assuming that the solubility of the bases in toluene as the selected reaction solvent could play a key role in the formation of the cycle, we evaluated tetrabutylammonium hydroxide (TBAOH), a quaternary amine that has a remarkably higher solubility in organic solvents when compared with traditional bases. Surprisingly, not only the reaction selectively took place, but also in a high conversion, 58% measured by HPLC. Once the spectroscopic techniques (¹H NMR, ¹³C NMR, UV-Vis, HRMS) allowed the fully characterization of the product, we corroborated that a cyclobutene ring was obtained as the reaction product (Scheme 1). This new cycloadduct resulted to be quite stable and no special storage conditions were needed.

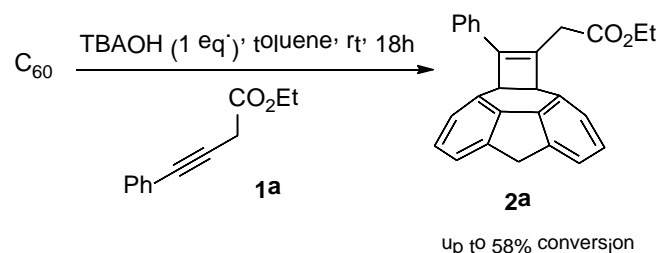
[a] Dr. S. Reboredo,^[†] R. M. Girón,^[†] Dr. S. Filippone, Prof. Dr. N. Martín
Departamento de Química Orgánica I, Facultad de Químicas
Universidad Complutense de Madrid
Av. Complutense S/N 28040 Madrid. Spain.
nazmar@ucm.es

[b] T. Mikie, Dr. T. Sakurai, Prof. Dr. S. Seki
Department of Molecular Engineering,
Kyoto University, Nishikyo-ku, 615-8510 Kyoto.

[c] Prof. Dr. N. Martín
IMDEA–Nanoscience, C/ Faraday, 9,
Campus de Cantoblanco, 28049 Madrid. Spain

[†] These authors contributed equally to the work.

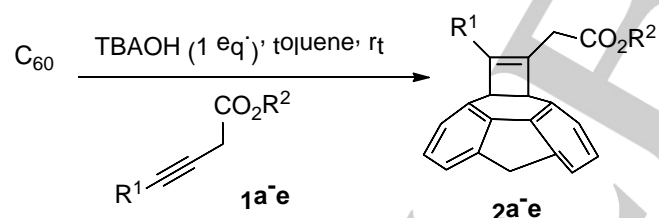
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Scheme 1. Synthesis of cyclobuteno[3,4:1,2][60]fullerene **2a** at rt.

Other different experimental conditions, including the modification of the equivalent ratio as well as the base, did not afford the corresponding adduct (see SI). It is noteworthy to mention the results derived from the increasing of the temperature up to 50°C. We could observe that in just three hours of reaction, the conversion reached a similar value to that obtained from 18 hours of reaction at room temperature (58 vs. 55% for 18 and 3 h, respectively). Even more remarkable is the result derived from the observation of the base storage conditions. We figured out that a freshly opened base was able to afford the desired cycloadduct in the same time but at rt, indicating that the storage of the base is a critical issue for obtaining the best results.

With the optimized conditions in hands, we explored the scope of the reaction with a series of alkynoates (Scheme 2, Table 1). Thus, different aromatic groups were satisfactorily tested and even the ethoxycarbonyl group was successfully modified into a *tert*-butoxy one.



Scheme 2. Scope of the formal [2+2] cycloaddition of alkynoates **1a-e** with [60]fullerene.

Table 1. Formal [2+2] cycloaddition of alkynoates **1a-e** with [60]fullerene.^[a]

Entry	Alkynoate	R ¹ , R ²	Product	Conversion ^[b]
1	1a	Ph, Et	2a	57
2	1b	<i>p</i> ClC ₆ H ₄ , Et	2b	52
3	1c	<i>p</i> BrC ₆ H ₄ , <i>t</i> Bu	2c	34
4	1d	3,4-Cl ₂ C ₆ H ₃ , <i>t</i> Bu	2d	41

5	1e	<i>t</i> Bu-C ₆ H ₄ , <i>t</i> Bu	2e	31
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[a] A mixture of 0.01 mmol [60]fullerene, TBAOH (1 eq.) and the alkynoate **1a-e** (2 eq.) in 3 mL of toluene is stirred at room temperature for 3 h. [b] Conversion has been determined by HPLC analysis.

Gratifyingly, one of the derivatives (**2d**) made possible the unambiguous determination of the chemical structure of the compound, thanks to the X-ray diffraction analysis. The slow evaporation of a mixture of Et₂O/toluene allowed us the successful formation of a suitable high quality single crystal (black and shiny crystals) (Figure 1). As expected, the X-ray analysis reveals the formation of a (6,6) fused cyclobutene ring with a C=C bond length of 1.345 Å.

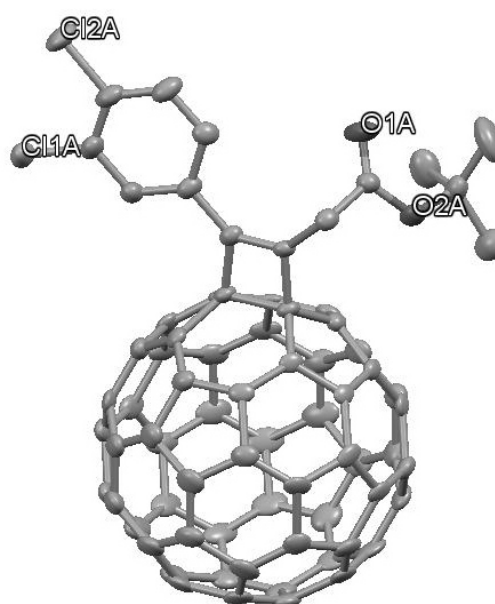
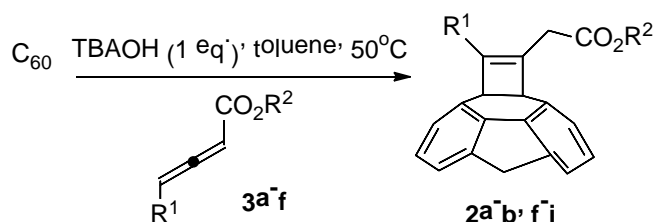


Figure 1. X-ray diffraction analysis of a single crystal of **2d** showing the (6,6) fused cyclobutene ring.

On the other hand, since alkynoates are known to behave in some cases similarly to allenoates,^[6] we decided to evaluate the same reaction under the same experimental conditions but using allenoates instead of alkynoates. However, with these substrates the reaction proceeded slower than in the case of the alkynoates, so we decided to increase the reaction temperature up to 50°C, reaching in this manner conversion values similar to those derived from the use of alkynoates (Scheme 3, Table 2).

Starting with the allenoate **3a**, it has been demonstrated that the reaction works under the aforementioned optimized conditions, thus allowing the formation of the same cycloadduct in a similar conversion value (55 vs 40%). As it can be seen in table 2, the reaction tolerates a series of allenoates with alkyl or aromatic chains or even modifications in the ethoxycarbonyl group.



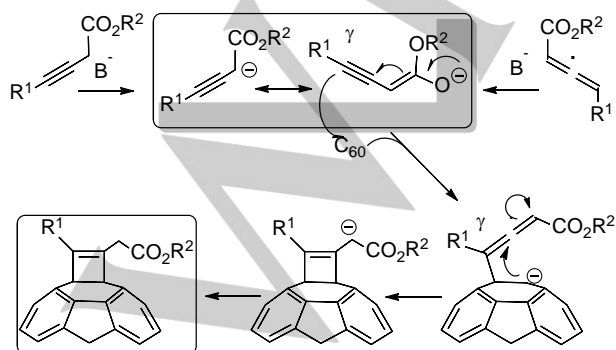
Scheme 3. Scope of the formal [2+2] cycloaddition of allenates **3a-f** with [60]fullerene to form cyclobuteno[3,4:1,2][60]fullerene derivatives (**2a-b, f-i**).

Table 2. Formal [2+2] cycloaddition of allenates **3a-f** with [60]fullerene.^[a]

Entry	Allenoate	R ¹ , R ²	Product	Conversion ^[b]
1	3a	Ph, Et	2a	44
2	3b	<i>p</i> -ClC ₆ H ₄ , Et	2b	22
3	3c	Me, Et	2f	18
4	3d	Et, Et	2g	23
5	3e	Bn, Et	2h	33
6	3f	Ph, Bn	2i	52

[a] A mixture of 0.01 mmol [60]fullerene, TBAOH (1 eq.) and the allenolate **3a-f** (2 eq.) in 3 mL of toluene is stirred at 50°C for 3 h. [b] Conversion has been determined by HPLC analysis.

The scarce literature related to the synthesis of these fullerene cycloadducts encourage us to postulate a plausible mechanism as it is displayed in Scheme 4. Similarly to that reported in literature,^[7] both alkynoates and allenates afford alkynylenolate intermediates after deprotonation in the presence of a strong enough base. While alkynylenolate anions displayed different α and γ regioselectivity depending on the experimental conditions and on the electrophiles used,^[7] all the alkynylenolates used led to a γ regioselective nucleophilic addition to C₆₀ double bond. Furthermore, in sharp contrast to the analogous Michael acceptors,^[7c] the formed fullerene anion, instead of being protonated, it gives rise to the cyclobutene ring closing. Finally, the reaction product is obtained after quenching and protonation of the formed anion in α position with respect to the ester group.



Scheme 4. Plausible mechanism for the formation of cyclobuteno[3,4:1,2][60]fullerene derivatives.

In the search for possible applications of these readily available and stable fullerene derivatives, we went one step further with the synthesis of two more cyclobutenes with a slightly different modification in the chemical structure that could resemble that of the well-known methanofullerene Phenyl-C61-Butyric-Acid-Methyl-Ester ([60]PCBM). [60]PCBM has been extensively investigated and used as a highly efficient n-type organic semiconductor^[10] with a variety of applications, for instance, in nanoscience^[11] and photovoltaic devices.^[12]

The design of two new allenates containing a phenyl group as well as a methoxycarbonyl group could give rise to new cycloadducts having exactly the same number of atoms and identical functional groups, in addition to the cyclobutene double bond which resembles the cyclopropane ring in PCBM (Figure 2). It is well-known that pristine cyclopropane undergoes the typical reactivity of an olefin. This is due to the bent bonds, in which the electron density does not lie along the direct lines connecting the carbon atoms.^[13] Thus, the bonding orbitals show a comparatively high-lying energy for a saturated hydrocarbon forming bonds with a considerable π character.^[14] These new cycloadducts were synthesized in 48% and 31% conversion values, respectively, for **2j** and **2k**.

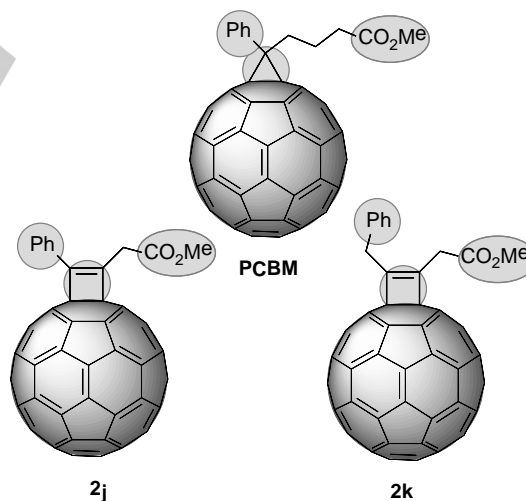
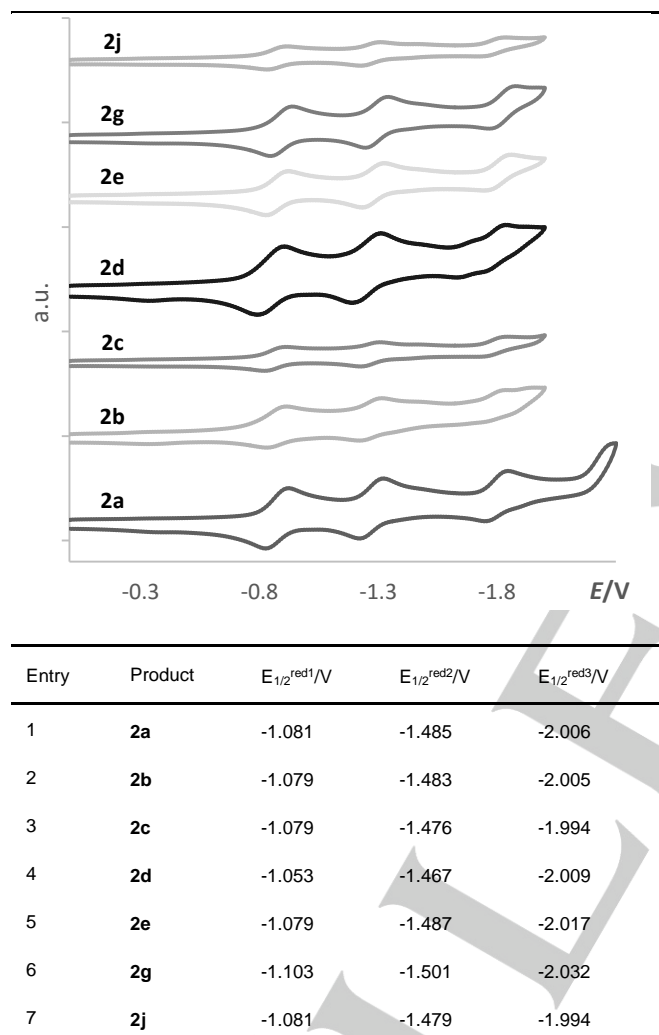


Figure 2. Cyclobutene adducts (**2j** and **2k**) as PCBM analogues.

We have carried out the electrochemical study of the new prepared compounds **2a-e**, **2g** and **2j**. The electrochemical behavior results to be similar to other fullerene monoadducts with three quasireversible waves between 0 and -2 V. A first reduction wave is observed at around -1.080 V for all the compounds featuring an electron rich aromatic ring linked directly to the

cyclobutene moiety (**2a,e,j**, table 3 entries 1,5,7). While the monosubstitution on the aromatic group with a chlorine or a bromine atom (**2b,c**) does not affect the first half-wave reduction potential (entries 2,3), the reduction peaks of **2d**, endowed with two chlorine atoms is cathodically shifted by 30 mV at -1.053 V (entry 4). On the other hand, the substitution of the cyclobutene moiety with an ethyl group give rise to an anodic shift up -1.103 V (**2g**, entry 6).

Table 3. Cyclic voltammetry of compounds **2a-e**, **2g** and **2j**.^[a]



[a] Potential in Volts vs ferrocene/ferrocenium measured with cyclic voltammetry in *o*-DCB/MeCN (4:1) containing Bu₄N⁺PF₆⁻ (0.1M) as a supporting electrolyte. Glassy carbon, platinum wire, and Ag/Ag⁺ electrodes were used as working, counter, and reference electrodes, respectively; scan rate: 0.1V/s.

In order to determine the potential charge carrier transport property of the new cyclobutene-containing cycloadducts, we have carried out a comparative study with PCBM by using flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements.^[15] Interestingly, these results revealed that the cyclobutene derivatives **2a**, **2j-k** showed an electron mobility significantly larger than that observed for PCBM (See Table 4).

The kinetic traces of the photoconductivity transients for the best candidates (**2j-k**) are given in Figure 3 together with that of the reference pristine PCBM. The identical and gradual rise in the transients was observed in **2j** and PCBM, suggesting a significant contribution from triplet-triplet annihilation processes to produce free charge carriers in these compounds.^[16] It is noteworthy that an intense and rapid rise in the conductivity signals were clearly observed for **2j** and **2k** associated with a prompt decay ($k > 10^7 \text{ s}^{-1}$, competitive to the time constant of the present set of apparatus with the microwave cavity with a quality factor $Q = 2500$). The photo-dissociation processes of free charge carriers are rather different fashion through singlet excited states in **2j** and **2k** than in PCBM, and recombined with the counter charge carriers in the system within 200 ns after an excitation. This is also supported by the relatively lower photo-carrier generation yield summarized in Table 3 by the photocurrent accumulation up to ms time scale. The estimated value of electron mobility (μ) for **2j** was three fold higher than the value of PCBM and two than that for **2a** and **2k**. Compound **2g** bearing two ethyl groups in the cyclobutene moiety exhibited only a slight increase in the electron mobility, which confirms the importance of the phenyl group as substituent in these compounds. Besides the potential high electron-conducting nature of the new fullerene compounds with characteristic photo-carrier generation processes, they are excellent candidates as new n-type materials for application in the fabrication of PV devices since the new fullerene derivatives **2a**, **2j** and **2k** are thermally stable compounds as revealed by their thermogravimetric analyses (TGA).

Table 4. Intrinsic mobility of charge carriers in **2a**, **2g**, **2j-k** and PCBM observed by FP-TRMC measurements.

Entry	Compound	$\phi \Sigma \mu / 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$\phi^{[a]} / 10^{-4}$	$\mu^{[b]} / \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
1	2a	2.3	3.5	0.066
2	2g	1.3	2.8	0.044
3	2j	3.3	3.5	0.095
4	2k	2.1	2.9	0.072
5	PCBM	1.9	6.0	0.035

[a] Determined by photocurrent measurements for the compounds casted onto an interdigitated comb-type Au electrode with poly(dioctylfluorene) (PDOF) standard (See SI, Figure S3). [b] Estimated as electron mobility in the compounds.

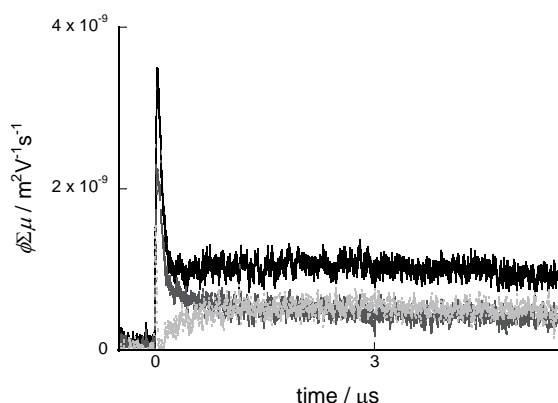


Figure 3. Conductivity transient in FP-TRMC observed for pristine **2j** (black-solid), **2k** (grey-dashed), and PCBM (reference, ash-dotted) upon excitation at 355 nm, 4.6×10^{15} photons cm^{-2} .

Conclusions

In summary, we have carried out the synthesis of new fullerene derivatives endowed with a less-explored fused cyclobutene ring by using allenates or their *in situ* precursor alkynoates as readily available starting materials and a simple organic base under mild conditions. Furthermore, a plausible mechanism for the formation of the cyclobuteno[3,4:1,2][60]fullerenes has been provided (Scheme 4). Although the chemical structure of the new cycloadducts has been thoroughly established by spectroscopic techniques, it could be unambiguously confirmed by X-ray diffraction analysis.

Interestingly, the new family of compounds resemble to the well-known fullerene derivative PCBM, which has been extensively used as n-type material in bulk heterojunction solar cells as the main reference compound for photovoltaic devices involving fullerenes. The new cyclobuteno[3,4:1,2][60]fullerenes have the same functional groups and the presence of a double bond in the cyclobutene moiety resembling the cyclopropane ring in PCBM. FP-TRMC measurements revealed that the new compounds exhibit higher electron mobility than PCBM, thus, confirming their interest as appealing n-type organic semiconductors.

Experimental Section

General procedure for the formal [2+2] cycloaddition of alkynoates

1a-e/allenates 3a-h with [60]fullerene: In an ordinary vial a suspension of [60]fullerene (1 eq.) and $\text{Bu}_4\text{NOH} \cdot 30\text{H}_2\text{O}$ (1 eq.) in 3.0 mL of toluene is prepared and stirred at room temperature. Then, the corresponding alkynoate **1a-e**/allenate **3a-h** (2 eq.) is added and the mixture is stirred for 3h at rt (for the alkynoates) or 50°C (for the allenates). Finally, the solvent is evaporated under vacuum and dark residue is then purified by silica-gel column chromatography using CS_2 as eluent (for recovering unreacted [60]fullerene). Then, mixtures of solvents (indicated in each case) are used affording the desired cyclobuteno[4,5:1,2][60]fullerene derivatives **2a-k**.

Acknowledgements

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Keywords: [60]fullerene • alkynoate • allenate • cyclobutene • electron mobility

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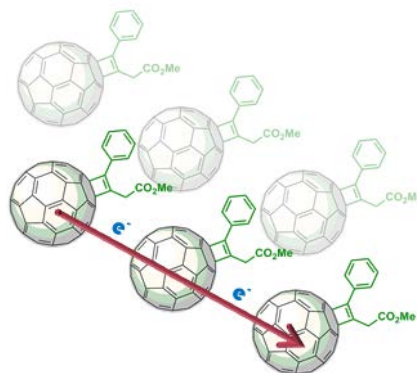
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Layout 1:

FULL PAPER

Cyclobutene[60]fullerene are already available!

A new synthetic approach based on alkynoates and/or allenoates leads to a new family of fullerene derivatives exhibiting remarkable semiconducting behaviour.



*S. Reboredo, R. M. Girón, S. Filippone, T. Mikie, T. Sakurai, S. Seki, N. Martín**

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Cyclobuteno[60]fullerenes as efficient n-type organic semiconductors

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