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Pyrrolidino [60] and [70]Fullerene Homo and Heterodimers as electron acceptors for OPV.

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Sule Erten-Ela, [ac] Carmen Villegas, [a] Juan Luis Delgado, [bd*] Nazario Martín [ab*]

New [60] and [70]fullerene homo- and heterodimers absorbing in the visible region have been synthesized and fully characterized. In order to increase the solubility and processability of the new fullerene dimers, different alkyl chains have been used which has allowed determining the influence of the solubilizing alkyl groups, on the photovoltaic performance. Atomic Force Microscopy experiments carried out on blends of these dimers and P3HT evidenced formation of large aggregates which significantly influence the photovoltaic efficiency.

Introduction

The design and development of new organic materials suitable to prepare new and efficient organic photovoltaic devices is currently a very active area of research.[1] The understanding of the elementary processes within Organic Photovoltaics (OPV) has been improved thanks to basic research studies dealing with fundamental aspects such as light harvesting improvement,[2] suitable Donor-Acceptor (D-A) band gap alignment[3] and nanomorphology control.[4] Concerning the D-A scheme, a huge variety of low band gap polymers, or small molecules, have been employed as electron donors.[5] On the other hand, considering the electron acceptor component, PCBM has been by far the most employed derivative, and only recently other fullerene derivatives[6] have been tested for OPV.[7] In order to improve our knowledge on the influence of the acceptor moiety on the photovoltaic performance, in the recent years we have been engaged in the preparation of a variety of new fullerene-based electron acceptors.[8]

Recently, some of us have described the preparation of a new family of soluble [60]- and [70]-fullerene homo and heterodimers linked through 2-pyrazolino-pirrolidino bridges (Figure 1, **1**-**3**).[9] Bulk heterojunction PV devices of **1**-**3** with poly (3-hexylthiophene) (P3HT), showed power conversion efficiencies (PCE) of about 1%. Despite this initial low PCE data, we have decided to continue our exploration on these molecules in order to clarify whether this kind of fullerene dimers are eventually suitable candidates or not to prepare efficient solar cells.

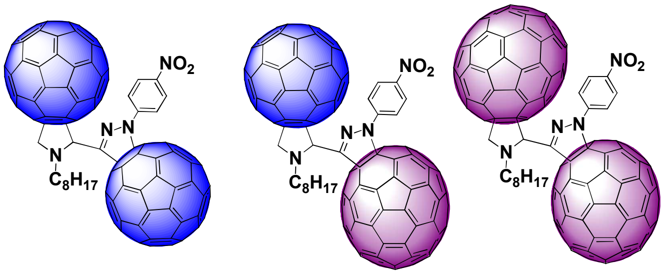

Figure 1. [60] and [70]fullerene homodimers (**1**, **3**) and the [60]/[70]heterodimer (**2**), linked through 2-pyrazolino-pyrrolidino bridges.

To this end, here we present the synthesis, optical and electrochemical properties of a new series of [60] and [70]fullerene homodimers (**4a**-**c**, **5a**-**c**) and the [60]/[70]heterodimer (**6**),[10] linked through pyrrolidino-*p*-phenyl-pyrrolidino (PPhP) bridges.

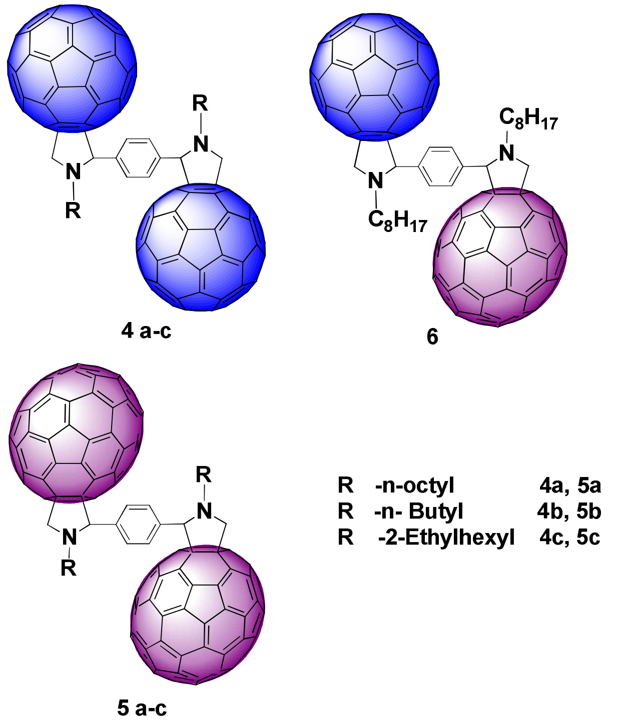

Figure 2. New fullerene-based compounds linked through pyrrolidino-*p*-phenyl-pyrrolidino (PPhP) bridges. [60] and [70]fullerene homodimers (**4a-c**, **5a-c**) and the [60]/[70]heterodimer (**6**).

In these new compounds we have introduced some structural variations, namely the presence of different alkyl chains and different fullerene units (C_{60} and/or C_{70}), with the final goal of studying their potential influence on the PV properties. Furthermore, the covalent connectivity of the two fullerene units through pyrrolidine rings in **4-6** significantly modifies the reducion potentials, when compared with the previously reported dimers (**1-3**) endowed with a 2-pyrazoline ring, thus improving the open circuit voltage parameter. Consequently, the new fullerene homo and heterodimers exhibit a variety of significant features which make them appealing systems (**4a-c**, **5a-c**, **6**) to prepare organic solar cells.

Experimental Section

General procedure for the synthesis of Fullerene Dimers

To a solution of of 0.69 mmol of C_{60} (for **4a-c**) or C_{70} (for **5a-c**) in chlorobenzene, was added terephtalaldehyde (0.11 mmol) and the corresponding alpha-aminoacid (0.58 mmol). The solution was refluxed for 6 h. Then the solvent was evaporated, and the solid was purified by column chromatography on SEC (Bio-Rad Bio-Beads S-XI) using CS_2 as eluent. The product obtained was twice centrifuged in pentane and methanol to afford a brown solid as pure dimer in each case (dimers are obtained as a mixture of isomers due to the multiple reactive bonds).

This procedure was used to synthesize compounds **4a**, **4b**, **4c**, **5a**, **5b** and **5c**. The alpha-aminoacid used in each case is: *N*-octylglycine for **4a** and **5a**, N- butylglycine for **4b** and **5b** and *N*-(2-ethylhexylglycine) for **4c** and **5c**.

4a:Yield: 48 %
^{1}H-NMR (CS_2:$CDCl_3$, 300 MHz) δ 8.07-7.62 (m, 4H), 5.11 (d, J=9 Hz, 2H), 5.07 (s, 2H), 4.12 (d, J=9 Hz, 2H), 3.27 (m, 2H), 2.61 (m, 2H), 1.39 (m, 24H), 0.97 (m, 6H). UV-Vis (Toluene) λ (ε): 311 (60100), 329 (58700), 433 (7700). FTIR (KBr) v : 2917, 2847, 2777, 523 cm^{-1}. HRMS (MALDI $^+$): m/z calculated for $C_{146}H_{44}N_2$: 1825.3583 [M], found: 1826.3835 [M+1]. HPLC analysis (toluene 1 ml/min, 25° C, 320 nm), peak at 11.02 min.

5a: Yield: 40 %
UV-Vis (Toluene) λ (ε): 400 (34100), 462 (26700), 540 (14100). FTIR (KBr) v : 2913, 2847, 2788, 838 cm^{-1}. HRMS (MALDI$^-$): m/z calculated for $C_{166}H_{44}N_2$: 2065.3538 [M], found: 2065.3569 [M]. HPLC analysis (toluene 1 ml/min, 25° C, 400 nm), broad peak at 20.40 min.

4b: Yield: 53 %
^{1}H-NMR (CS_2:$CDCl_3$, 300 MHz) δ 8.02-7.69 (m, 4H), 5.12 (d, J=9 Hz, 2H), 5.10 (s, 2H), 4.14 (d, J=9 Hz, 2H), 3.31 (m, 2H), 2.62 (m, 2H), 1.29 (m, 8H), 1.25 (m, 6H). UV-Vis (Toluene) λ (ε): 311 (58400), 327 (57300), 433 (7400). FTIR (KBr) v : 2921, 2852, 2792, 526 cm^{-1}. HRMS (MALDI$^+$): m/z calculated for $C_{138}H_{28}N_2$: 1713.2331 [M], found: 1714.2117 [M+1]. HPLC analysis (toluene 1 ml/min, 25° C, 320 nm), peaks at 12.63 and 13.23 min.

5b: Yield: 49 %
UV-Vis (Toluene) λ (ε): 400 (37200), 464 (28900), 539 (15600). FTIR (KBr) v : 2919, 2856, 2783, 836 cm^{-1}. HRMS (MALDI$^+$): m/z calculated for $C_{158}H_{28}N_2$: 1953.2331 [M], found: 1954.2497 [M+1]. HPLC analysis (toluene 1 ml/min, 25° C, 400 nm), broad peak at 25.32 min.

4c: Yield: 37 %
^{1}H-NMR (CS_2:$CDCl_3$, 300 MHz) δ 8.10-7.59 (m, 4H), 5.10 (d, J=9 Hz, 2H), 5.06 (s, 2H), 4.06 (d, J=9 Hz, 2H), 3.05 (m, 2H), 2.53 (m, 2H), 1.42 (m, 14H), 1.06 (m, 12H). UV-Vis (Toluene) λ (ε): 312 (58700), 331 (55600), 434 (7700). FTIR (KBr) v : 2919, 2855, 2775, 524 cm^{-1}. HRMS (MALDI$^+$): m/z calculated for $C_{146}H_{44}N_2$: 1825.3583 [M], found: 1826.3532 [M+1]. HPLC analysis (toluene 1 ml/min, 25° C, 400 nm), peaks at 10.32 and 10.99 min.

5c: Yield: 47 %
UV-Vis (Toluene) λ (ε): 401 (33000), 464 (25600), 538 (14000). FTIR (KBr) v : 2917, 2851, 2775, 845 cm^{-1}. HRMS (MALDI$^+$): m/z calculated for $C_{166}H_{44}N_2$: 2065.3583 [M], found: 2066.3680 [M+1]. HPLC analysis (toluene 1 ml/min, 25° C, 400 nm), peaks at 19.74 and 21.36 min.

Results and Discussion

Synthesis and Characterization

The preparation of [60]fullerene homodimers (**4a-c)** has been carried out in a single step, by refluxing a solution of pristine C_{60}, terephthalaldehyde and the corresponding alpha aminoacid in chlorobenzene, following Prato´s methodology.[11] [70]Fullerene homodimers (**5a**-**c**) were prepared using pristine C_{70}, following the same protocol. [60]/[70]Heterodimer (**6**) was prepared by reaction of [60]fullerene aldehyde (**7**)[12] with C_{70} in the presence of *N*-octylglycine. The purification of these dimers was carried out by column chromatography on SEC (Bio-Rad Bio-Beads S-XI) using CS_2 as eluent. Then, the obtained product was twice centrifuged in pentane and methanol to afford a brown solid as pure dimer in each case.

All the dimers were obtained in good yields (37-59 %) and their structure and purity were confirmed by spectroscopic and analytical techniques, namely NMR, HPLC and HR-MS. For instance, in the ^{1}H-NMR experiment of compound **4a** (Figure 3, left) all the diagnostic signals, including the pyrrolidine α protons, are observed. Moreover, high resolution mass spectrometry experiments confirmed the formation and high degree of purity of **4a** (Figure 3, right: $[M+H]^+$ = 1826.3835 (calcd. $C_{146}H_{44}N_2$: 1825.3583)). As expected, these dimers were obtained as mixtures of stereoisomers due to the presence of two stereogenic centers, which were observed by HPLC.[13]

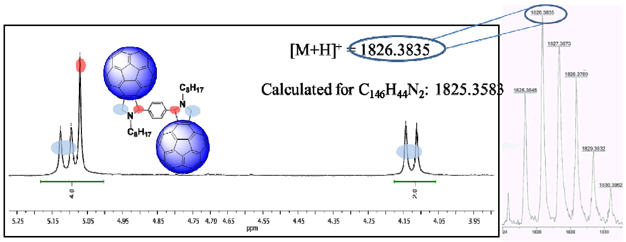

Figure 3. ^{1}H-NMR (CS_2:$CDCl_3$, left) and zoom of HR-MS (right) of **4a**.

Optical properties

The optical absorption spectra of compounds **4a**-**c**, **5a**-**c, 6** were recorded in toluene solution at 25ºC (Figure 4). Compound **4a** displays a typical [60]fullerene monoadduct derivative absorption pattern, showing weak absorption in the visible region at 311, 329 and 433 nm. For the [70]fullerene homodimer **5a**, representative absorption features of [70]fullerenes are seen at 400, 462 and 540 nm. In the case of heterodimer **6**, characteristic bands for both, [60]fullerene precursor **7** (313, 333, 434 nm) and [70]-fullerene (396, 467, 537 nm), are observed being a superimposition of two components.

As it can be seen in Figure 4, there is a clear improvement on the light harvesting properties when the number of [70]fullerene units increases, due to the lesser degree of symmetry of this derivative.[6a] Moreover, these compounds display high extinction coefficients values due to the presence of various fullerene units. Therefore in the case of [70]fullerene homodimer **5a** we observe a broad absorption spectrum, covering a region from 300 to 700 nm.

The aforementioned results reveal, as expected, the better absorption in the visible range of those molecules bearing more than one C_{60} unit, and more significantly, when one or two [70]fullerene units are present in the dumbbell.

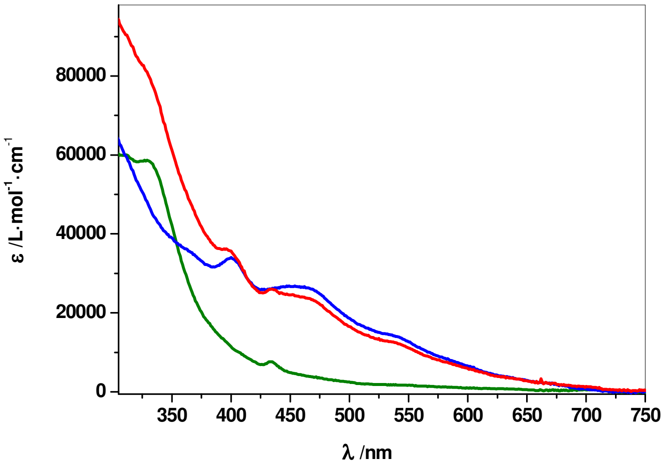

Figure 4. Absorption spectra of **4a** (green), **5a** (blue), and **6** (red) recorded in toluene at 25ºC.

Electrochemistry

The electrochemical properties of compounds **4a**-**c**, **5a**-**c, 6** have been studied at room temperature by means of cyclic voltammetry (CV). Compounds **4a-c** display the typical redox behaviour of a [60]fullerene derivative, with quasireversible reduction waves at -0.87, -1.28, -1.81 and -2.26 V (**4a**, Figure 5). [70]Fullerene homodimer **5a-c** showed a similar behaviour**,** with quasireversible reduction processes at -0.86, -1.27, -1.68 and -2.10 V (**5a**, Figure 5). In the cyclic voltammogram of heterodimer **6** the characteristic reduction waves for both, [60]fullerene and [70]fullerene are observed, being a superimposition of two components (Figure 5).

Table 1. Reduction Potentials (CV) of **4a**-**c**, **5a**-**c**, **6**, C_{60} and C_{70}. V *vs* Ag/AgNO$_3$; GCE as the working electrode; 0.1 M Bu_4NPF_6; *o*-DCB/MeCN (4:1); scan rate 100 mV/s.

Entry	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}
4a	-0.87	-1.28	-1.81	-2.26
5a	-0.86	-1.27	-1.68	-2.10
4b	-0.86	-1.27	-1.80	-2.26
5b	-0.86	-1.27	-1.67	-2.12
4c	-0.86	-1.28	-1.82	-2.28
5c	-0.86	-1.28	-1.69	-2.11
6	-0.86	-1.28	-1.69/-1.82	-2.12/-2.27
C_{60}	-0.76	-1.16	-1.62	-2.09
C_{70}	-0.75	-1.15	-1.57	-1.97

Compounds **4a**-**c**, **5a**-**c** and **6** show reduction potentials shifted to more negative values compared to those of parent [60]fullerene and [70]fullerene, as a consequence of the saturation of a double bond on the fullerene sphere, which raises the LUMO energy level.**[14]** Raising the LUMO energy of the fullerene material will produce a larger difference between the HOMO of P3HT and LUMO of fullerene derivative and, therefore, is expected to obtain better values of V_{oc}.

It is important to note, however, that the length and nature of the alkyl chains do not influence the first and second reduction potential values. However, some differences were observed in the third and fourth reduction potentials. These results are in agreement with that expected for the redox properties in these dumbbells since the most significant differences should influence on the blending and morphology with the donor counterpart.

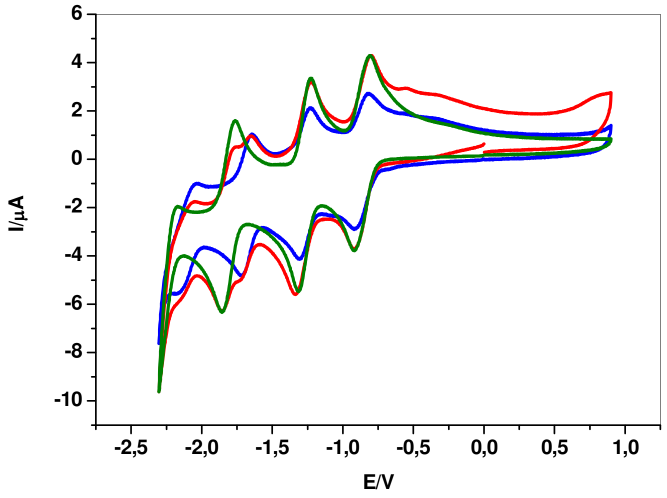

Figure 5. Cyclic voltammograms of **4a** (green), **5a** (blue), and **6** (red). V vs Ag/AgNO$_3$; GCE as the working electrode; 0.1 M Bu$_4$NPF$_6$; *o*-DCB/MeCN (4:1); scan rate 100 mV/s.

Solar Cell Performance.

Bulk heterojunction solar cells were fabricated in a FTO/PEDOT:PSS/ P3HT: [60] or [70]fullerene homodimers or the [60]/[70]heterodimer/Al device configuration. PEDOT:PSS was spin coated at 1500 rpm onto FTO coated glass substrate. Blends of P3HT: Fullerene based material (1:2 ratio) in chlorobenzene was spin coated onto PEDOT:PSS layer. Finally, the last process consisted on the thermal evaporation of metal contact in the glove box. [15] Thus a layer of 70 nm Al metal contact was thermally evaporated through shadow mask. Figure 6 shows a schematic illustration of organic bulk heterojunction photovoltaic devices showing all its components.

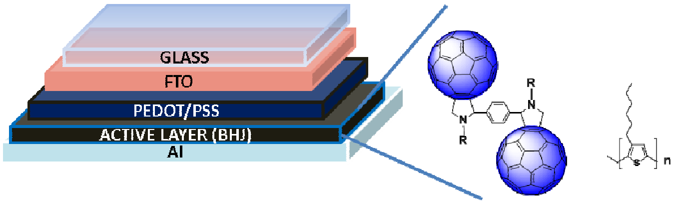

Figure 6. Schematic Illustration of Bulk Heterojunction Organic Photovoltaic Devices prepared with [60] and [70]fullerene homodimers (**4a-c, 5a-c**), [60]/[70]heterodimer (**6**) and P3HT.

The current-voltage (J-V) characteristics were measured for the above described devices under AM1.5G solar illumination conditions. The J-V measurements, and hence the PCE determination were performed with a solar simulator. Figure S13, Figure S14 and Table 2 shows the J-V features as well as the performances of bulk heterojuction organic solar cell devices. [60] and [70]fullerene homodimers (**4a,b** and **5a-b**) endowed with octyl and butyl linear hydrocarbon chains showed low values of short circuit current (J_{SC}), and fill factor (FF) leading to poor power conversion efficiencies. [60] and [70]Fullerene homodimers endowed with a branched 2-ethylhexyl chain (**4c** and **5c)**, showed the best performances. Thus the device prepared with **4c** displayed a short circuit current (J_{sc}) of 3.95 mA/cm^2, an open circuit voltage of 600 mV, a fill factor of 0.30 and an overall power conversion efficiency of 0.72. From the data collected in Figure S13 and Figure S14 , we can conclude that only compound **4c** (PCE= 0.72) displays a photovoltaic performance comparable to those obtained with our previously described [60]- and [70]-fullerene homo and heterodimers linked through 2-pyrazolino-pirrolidino bridges,[8d] thus showing a lower photovoltaic performance of the blends of the new dimers (**4**-**6**) with P3HT. In an attempt to improve the PCE of these devices, we have prepared blends of **5c** and P3HT processed in cholorobenzene and moreover we have performed a process of thermal annealing to the blend. The photovoltaic study of this blend reveals a slightly better PCE of 0.33 %. (Figure S20)

Table 2. Photovoltaic Performance Results of Organic Bulk Heterojunction Photovoltaic Devices

	J_{sc} (mAcm^{-2})	V_{oc} (mV)	FF	η (%)
4c	3.95	600	0.30	0.72
5c	3.01	250	0.33	0.25
6	2.54	275	0.32	0.21
4a	0.66	450	0.34	0.10
4b	0.57	450	0.30	0.08
5a	0.45	140	0.25	0.02
5b	0.12	360	0.33	0.01

In order to gain a better understanding on its nanomorphology composition, atomic force microscopy images of blends of P3HT: [60] or [70]fullerene homodimers or the [60]/[70]heterodimer were obtained.[13] To this end, blend mixtures of P3HT:Dimer were spin coated on top of PEDOT:PSS layer. The surface morphology and roughness of each P3HT: Dimer blend were analyzed. The studied active layers showed root-mean-square (rms) roughness values between 4.91 nm and 39 nm, which would explain the above mentioned low performance of the prepared solar cells. Consequently, devices prepared with fullerenes endowed with 2-ethylhexyl branched chains (**4c** and **5c)** displayed smoother morphology exhibiting rms= 7.5 nm for **4c** and 4.91 nm for **5c**. The devices prepared with **4a**, **4b**, **5a** and **5b**, display a significantly less homogeneous distribution, thus showing the presence of larger donor and acceptor domains, which contribute unefficiently to promote charge transport and PV performance (Figure 8).

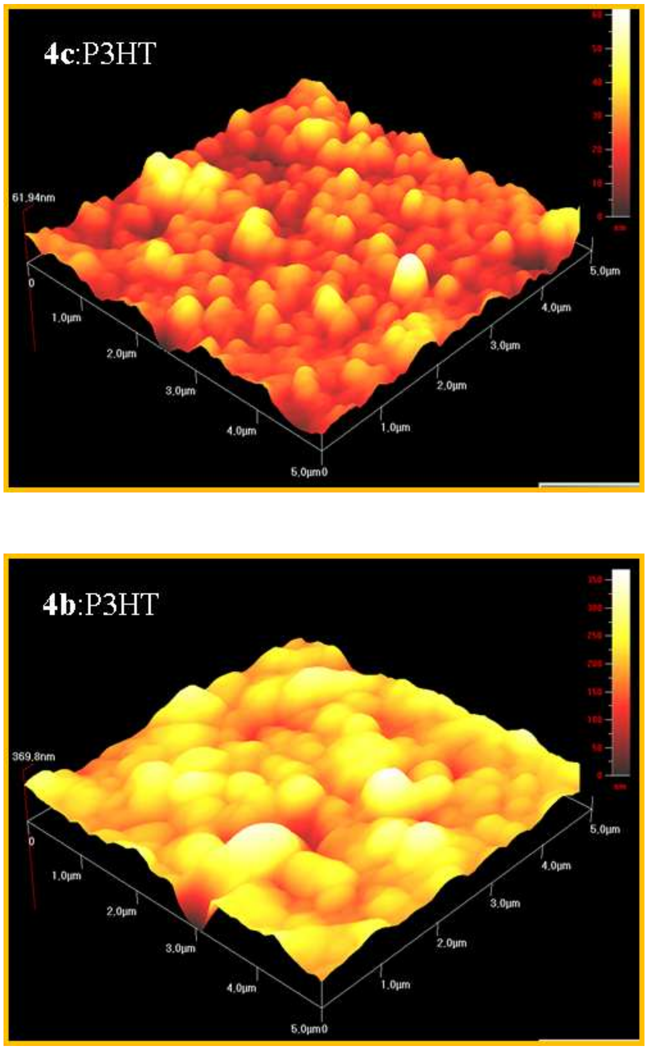

Figure 8. Atomic Force Microscopy images of blends of **4c**:P3HT and **4b**:P3HT.

Conclusions

A new series of homo and heterodimers (**4-6**) involving [60] and [70] fullerenes covalently connected through a pyrrolidino-p-phenyl-pyrrolidino bridge and bearing different solubilizing alkyl chains has been synthesized and fully characterized. The CV data of the new dimers reveal a priori better performances than previous dimers (**1-3**) and therefore, they have been used in the preparation of PV devices with P3HT as donor polymer. In contrast to the expectations, the performances of the PV cells were relatively low, which has been accounted for the roughness morphology found in their surface in the AFM meassurements. Furthermore, the longer separation induced by the presence of the phenyl moieties in between the two fullerene units should negatively influence the interaction between the acceptors, thus favouring the charge recombination processes.

The experimental findings reported in this work reveal the importance of the design in the fullerene derivatives synthesized in the search for efficient PV devices. In our case we have proved that the distance between fullerene units in dumbbell type dimers as well as the different nature of the alkyl chains have a strong impact on the morphology and, therefore, on the device performance.

Acknowledgements

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Notes and references

[a] Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040, Madrid (Spain). *nazmar@ucm.es*

[b] IMDEA-Nanociencia, C/ Faraday 9, Ciudad Universitaria de Cantoblanco, 28049, Madrid (Spain). *juanluis.delgado@imdea.org*

[c] Ege University, Solar Energy Institute, 35100 Bornova, Izmir, Turkey.

[d] New address: POLYMAT, University of the Basque Country UPV/EHU
Avenida de Tolosa 72, 20018 Donostia-San Sebastian (Spain) and Ikerbasque, Basque Foundation for Science, 48011 Bilbao (Spain)
E-mail: *juanluis.delgado@polymat.eu*

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[1] (a) G. Dennler, M. C. Scharber and C. J. Brabec, *Adv. Mater.* 2009, **21**, 1323; (b) B. Kippelen and J.-J. Brédas, *Energy Environ. Sci.* 2009, **2**, 251; (c) B. C. Thompson and J. M. J. Fréchet, *Angew. Chem. Int. Ed.* 2008, **47**, 58; (d) S. Gunes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev*. 2007, **107**, 1324; (e) J. L. Delgado, P.-A. Bouit, S. Filippone, M. A. Herranz and N. Martín, *Chem. Commun*. 2010, **46**, 4853; (f) A. Mishra, P. Bäuerle, *Angew. Chem. Int. Ed*. 2012, **51**, 2020.

[2] (a) L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li, and J. Hou, *Angew. Chem. Int. Ed.* 2011, **50**, 9697; (b) J. A. Mikroyannidis, A. N. Kabanakis, S. S. Sharma and G. D. Sharma, *Adv. Funct. Mater.* 2011, **21**, 746.

[3] (a) C. J. Brabec, A. Cravino, D.Meissner, N. S. Sariciftci, T.Fromherz, M. T. Rispens, L. Sanchez and J.C. Hummelen, *Adv. Funct. Mater.* 2001, **11**, 374; (b) A. Sánchez-Díaz, M. Izquierdo, S. Filippone, N. Martin, E. Palomares, *Adv. Funct. Mater.* 2010, **16**, 2695.

[4] (a) S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, *Appl. Phys. Lett.* 2001*,* **78***,* 841; (b) C.-L. Wang, W.-B. Zhang, H.-J. Sun, R. M. V. Horn, R. R. Kulkarni, C.-C. Tsai, C.-S. Hsu, B. Lotz, X. Gong, and S. Z. D. Cheng, *Adv. Energy Mater*, 2012, **2**, 1375; (c) S. Shoaee, M. P. Eng, E. Espildora, J. L. Delgado, B. Campo, N. Martín, D.

Vanderzande and J. R. Durrant, *Energy Environ. Sci*., 2010, **3**, 971. (d) A. J. Moulé and K. Meerholz, *Adv. Mater*., 2008, **20**, 240. (e) P.-A. Bouit, D. Rauh, S. Neugebauer, J. L. Delgado, E. Di Piazza, S. Rigaut, O. Maury, C. Andraud, V. Dyakonov, N. Martín, *Org. Lett.* 2009, **11**, 4806.

[5] (a) C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia, and S. P. Willia Adv. Mater., 2010, 22, 3839; (b) Bright Walker, Chunki Kim, and Thuc-Quyen Nguyen, *Chem. Mater*, 2011, **23**, 470.

[6] For some recent books: (a) D. M. Guldi and N. Martín Eds., *Fullerenes: From Synthesis to Optoelectronic Properties*, Kluver Academic Publishers, Dordrecht, The Netherlands, 2002; (b) A. Hirsch, *The Chemistry of Fullerenes*, Wiley-VCH, Weinheim, Germany, 2005; (c) F. Langa and J.-F. Nierengarten Eds., *Fullerenes. Principles and Applications*, RSC, Cambridge, United Kingdom, 2007. For a recent review: E. Espíldora, J. L. Delgado, N. Martín, *Isr. J. Chem.*, 2014, **54**, 429.

[7] (a) P. A. Troshin, H. Hoppe, A. S. Peregudov, M. Egginger, S. Shokhovets, G. Gobsch, N. S. Sariciftci, V. F. Razumov, *ChemSusChem*, 2011, **4**, 119; (b) C.-Z. Li, H.-L. Yipab , A. K.-Y. Jen, *J. Mater. Chem.*, 2012, **22**, 4161.

[8] (a) I. Riedel, E. von Hauff, J. Parisi, N. Martín, F. Giacalone, and V. Dyakonov, *Adv. Funct. Mater.* 2005, **15**, 1979; (b) G. García-Belmonte, P. P. Boix, J. Bisquert, M. lenes, H. J. Bolink, A. La Rosa, S. Filippone, N. Martín., *J. Phys. Chem. Lett.* 2010, **1**, 2566; (c) H. J. Bolink, E. Coronado, A. Forment-Aliaga, M. Lenes, A. La Rosa, S. Filippone and N. Martín, *J. Mater. Chem.* 2011, **21**, 1382; (d) X. Wang, E. Perzon, J. L. Delgado, P. de la Cruz, F. Zhang, F. Langa, M. Andersson, and O. Inganäs, *Appl. Phys. Lett.* 2004, ***85***, 5081; (e) E. Perzon, X. Wang, F. Zhang, W. Mammo, J. L. Delgado, P. de la Cruz, O. Inganas, F. Langa and M. R. Andersson, *Synth. Met.*, 2005, **154**, 53. (f) S. Shoaee, T.M. Clarke, M.P. Eng, C. Huang, S. Barlow, E. Espíldora, J.L. Delgado, B. Campo, S.R. Marder, M. Heeney, I. McCulloch, N. Martín, D. Vanderzande, J.R. Durrant, *J. Photon. Energy*, 2012, **14**, 021001. (g) P.-A. Bouit, F. Spänig, G. Kuzmanich, E. Krokos, C. Oelsner, M. A. Garcia-Garibay, J. L. Delgado, N. Martin, D. M. Guldi, *Chem.-Eur. J.* 2010, **16**, 9638. (h) C. Villegas, E. Krokos, P.-A. Bouit, J. L. Delgado, D. M. Guldi, N. Martin, *Energy Environ. Sci.*, 2011, **4**, 679. (i) C. Villegas, J. L. Delgado, P.-A. Bouit, B. Grimm, W. Seitz, N. Martin, D. M. Guldi, *Chem. Sci.* 2011, **2**, 1677.

[9] (a) J. L. Delgado, F. Oswald, F. Cardinali, F. Langa, N. Martín, *J. Org. Chem.* 2008, **73**, 3184; (b) J. L. Delgado, S. Filippone, A. Martín-Domenech, M. Altable, E. Maroto, F. Langa, N. Martín and R. Martínez-Alvarez, *J. Am. Soc. Mass Spectrom.*, 2011, **22**, 557; (c) J. L. Delgado, F. Cardinali, E. Espíldora, M. R. Torres, F. Langa, and N. Martín, *Org. Lett.* 2008, **10**, 3705. (d) J. L. Delgado, E. Espíldora, M. Liedtke, A. Sperlich, D. Rauh, A. Baumann, C. Deibel, V. Dyakonov, N. Martín, *Chem.-Eur. J.* 2009, **15**, 13474. (e) A. Sperlich, M. Liedtke, J. Kern, H. Kraus, C. Deibel, S. Filippone, J. L. Delgado, N. Martín, V. Dyakonov, *Phys. Status Solidi RRL* 2011, **3**, 128. (f) J. L. Delgado, S. Osuna, P.-A. Bouit, R. Martínez-Alvarez, E. Espíldora, M. Solá and N. Martín, *J. Org. Chem.* 2009, **74**, 8174.

[10] Compound **6** has been recently described: Oleg G. Poluektov, J. Niklas, K. L. Mardis, S. Beaupré, M. Leclerc, C. Villegas, S. Erten-Ela, J. L. Delgado, N. Martín, A. Sperlich, V. Dyakonov, *Adv. Energy Mat.,* 2014, **4**, 1301517.

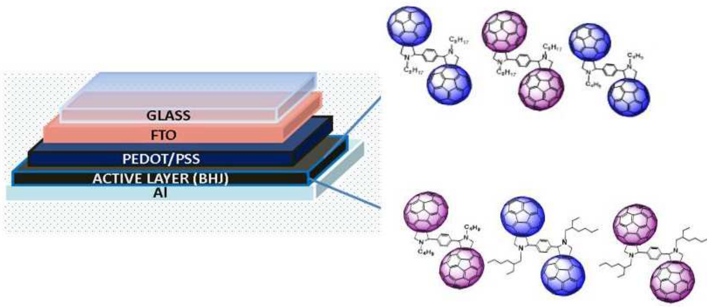
[11] a) M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc*. 1993, **115**, 9798; b) M. Prato, M. Maggini, *Acc. Chem. Res*., 1998, **31**, 519; c) N. Tagmatarchis, M. Prato, *Synlett*, 2003, 768.

[12] Y. Rio, D. Sanchez-Garcia, W. Seitz, T. Torres, J. L. Sessler, and D.M. Guldi, *Chem-Eur. J.* 2009, **15**, 3956.

[13] See Electronic Supplementary Information (ESI)

[14] a) N. Martín, L. Sanchez, B. Illescas, and I. Perez, *Chem. Rev.* 1998, **98**, 2527; b) L. Echegoyen, and L.E. Echegoyen, *Acc. Chem. Res*. 1998, **31**, 593; (c) J. L. Delgado, N. Martín, P. de la Cruz and F. Langa. *Chem. Soc. Rev*., 2011, **40**, 5232.

[15] FTO glasses are cut into square plates (2.5 x 2.5 cm). Fluorine-doped tin oxide (FTO) is patterned by etching with an acid mixture of HCl and Zinc dust. All FTO glasses are cleaned with acetone and isopropyl alcohol for 20 minutes in ultrasonic bath then, Helmanex soap and finally cleaned distilled water several times, afterwards all glasses are dried by N_2 purging.



New homo and heterodimers involving [60] and [70] fullerenes have been synthesized and used to prepare organic solar cells.