



Synthesis, electrochemistry and photophysical properties of phenylenevinylene fullerodendrimers

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Abstract—The synthesis, spectroscopic characterization, electrochemistry and photophysical measurements of new phenylenevinylene fullerodendrimers are described. Cyclic and Osteryoung square wave voltammetry studies indicate that prepared fullerodendrimers show improved electron affinity over the parent C₆₀. Photophysical investigations reveal a strong interaction between the dendrimers and C₆₀. © 2001 Elsevier Science Ltd. All rights reserved.

During the last decade, an explosion of research on organic semiconducting materials with application in photovoltaic devices has occurred.^{1,2} Oligoarylenes, which are building blocks for new organic materials, have been extensively studied.³ Moreover, dendrimers with π -conjugated systems in their branching shell give high fluorescence efficiency,⁴ although these compounds are remarkably rare.⁵ Such dendrimers can be used for the construction of light-harvesting antennae when functionalized with a suitable acceptor at the focal point.⁶ C₆₀ is an interesting building block, and currently there is a growing interest in fullerene-functionalized dendrimers (fullerodendrimers).^{7–9} As fullerenes display strong electron-accepting properties in their ground and excited states,^{10,11} they are interesting candidates for inter- and intramolecular electron-transfer reactions,^{10,12–14} and conjugated polymer/C₆₀ blends have been used as novel materials for photovoltaic cells.^{15–18} In this context, and as part of some of our research on electroactive fullerene derivatives^{19–21} we present here the synthesis, electrochemical and spectroscopic properties of phenylenevinylene fullerodendrimers **3a–b** (Scheme 1).

The synthetic procedure used for the preparation of the pyrazolino[60]fullerene dendrimers **3a–b** is based on the

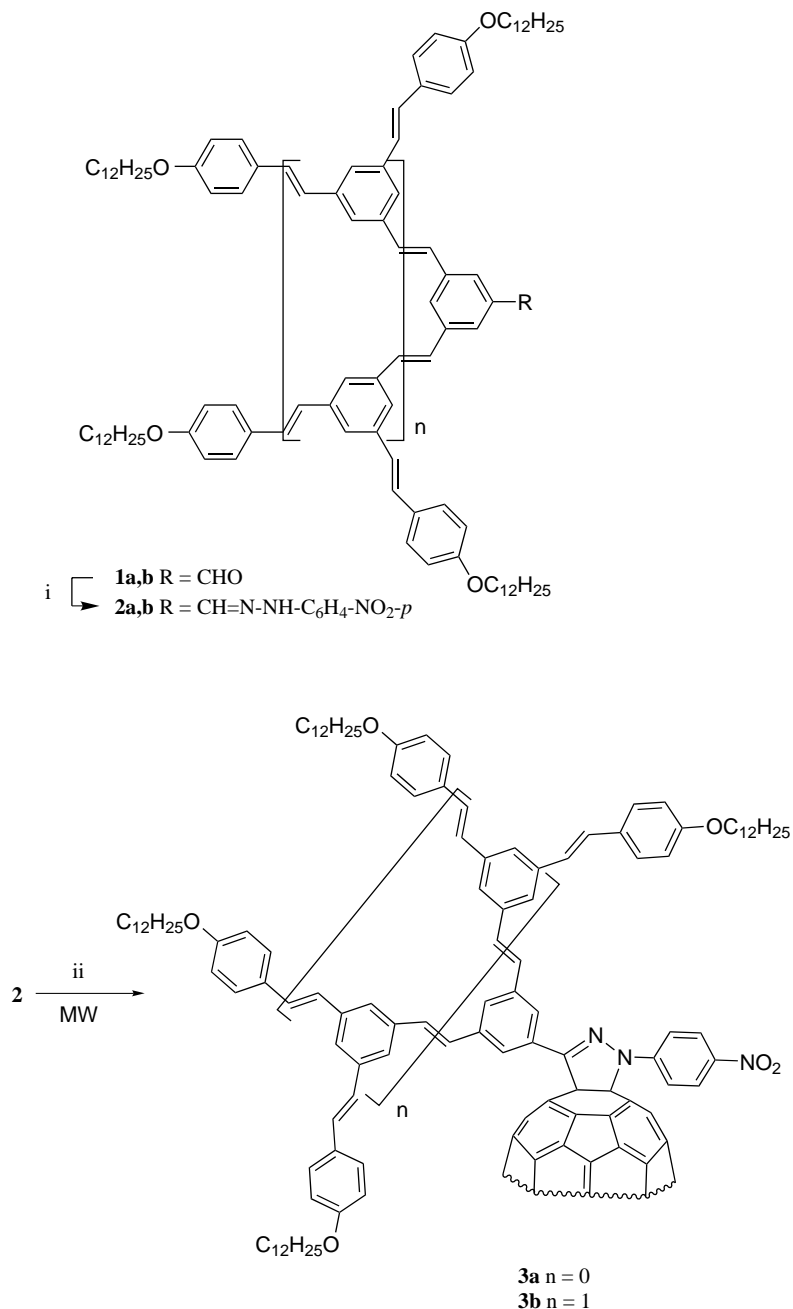
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cycloaddition of nitrilimines to C₆₀.²² Aldehydes **1a–b**[†] were synthesized according to a previously reported methodology,²³ and long chains have been incorporated in order to increase the solubility. Hydrazones **2a–b**[†] were obtained from aldehydes **1a–b** by standard methods and were reacted with NCS to afford the corresponding nitrilimine intermediate, which was reacted in situ with C₆₀ under microwave irradiation²⁴ giving compounds **3a–b**[‡] in good yields (**3a**: 31%, **3b**: 34%) after purification by column chromatography (SiO₂, toluene/hexane: 1/1).

[†] The compounds were fully characterized by IR, NMR spectroscopy and mass spectrometry.

[‡] **3a**: yield: 31% (49% based on unreacted C₆₀). ¹H NMR (CDCl₃) δ 0.89 (t, 6H, $J=6.5$ Hz, CH₃), 1.27 (broad s, 36H), 1.76–1.83 (m, 4H, 2 \times CH₂), 3.98 (t, 4H, $J=6.5$ Hz, 2 \times OCH₂), 6.90 (d, 4H, $J=8.4$ Hz, Ar), 7.45 (d, 4H, $J=8.4$ Hz, Ar), 7.12 (B of ABq, 2H, $J=16.5$ Hz, 2 \times CH=), 7.03 (B of ABq, 2H, $J=16.5$ Hz, 2 \times CH=), 7.71 (s, 1H, Ar), 8.20 (s, 2H, Ar), 8.29 (d, 2H, $J=9.5$ Hz, Ar), 8.36 (d, 2H, $J=9.8$ Hz, Ar). ¹³C NMR (CDCl₃) δ 159.4, 149.9, 147.8, 147.4, 147.1, 146.6, 146.5, 146.3, 146.1, 145.8, 145.6, 145.5, 144.7, 144.6, 144.3, 143.4, 143.2, 142.7, 142.5, 142.3, 142.2 (two signals), 140.6, 139.6, 139.0, 137.3, 136.4, 132.2, 130.0, 129.5, 128.1, 125.6, 119.6, 114.9, 68.3, 32.1, 29.8 (2C), 29.6, 29.5, 29.4, 26.2, 22.9, 14.3. FT-IR (KBr) ν /cm⁻¹ 2846.4, 1580.1, 1507.1, 1454.1, 1321.5, 1169.0, 1109.3, 837.5, 738.1, 525.9. MALDI-TOF, m/e 1532.2. **3b**: yield: 33% (69% based on unreacted C₆₀). ¹H NMR (CDCl₃) δ 0.90 (broad s, 12H), 1.29 (broad s, 72H), 1.65–1.85 (broad m, 8H), 3.83–3.94 (broad m, 8H), 6.74–7.40 (broad m, 37H, Ar), 8.15–8.26 (broad m, 4H, Ar). FT-IR (KBr) ν /cm⁻¹ 2849.0, 1578.7, 1505.0, 1465.3, 1329.2, 1238.4, 1170.4, 1108.0, 835.8, 745.1, 523.9. MALDI-TOF, m/e 2310.3.



Scheme 1. Reagents and conditions: (i) *p*-NO₂-C₆H₄-NH-NH₂, EtOH, AcOH, reflux; (ii) NCS, pyridine, CHCl₃, then C₆₀, Et₃N, toluene.

The electrochemical properties of compounds **2a–b** and **3a–b** were studied by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) at room temperature in *o*-dichlorobenzene/acetonitrile (4:1) as solvent and using tetrabutylammonium perchlorate as the supporting electrolyte. On the oxidation side, the CV of hydrazones **2a–b** showed two irreversible peaks (0.79 and 1.13 V for **2a** and 0.74 and 1.15 V for **2b**, the latter probably corresponding to more than one electron), which remained unaltered in cycloadducts **3a–b**. Much more interesting was the reduction side: as depicted in Fig. 1 and Table 1, pyrazolino[60]fullerenes **3a–b** showed five waves, four of them quasi-reversible

corresponding to the [60]fullerene cage (but the last one can probably be attributed to the overlapping of two signals, one due to the C₆₀ cage and the other to the organic addend) and another one, irreversible, which should correspond to the organic addend. Interestingly, although most of the C₆₀ derivatives present reduction potentials shifted to more negative values,²⁵ **3a–b** show an anodic shift up to 70 mV relative to the parent C₆₀.

The emission spectra of **2a–b** and **3a–b** exhibit maxima at 458, 489 and 882 nm (**2a**), 433 and 862 nm (**2b**), 424, 694, 707, 965 and 983 nm (**3a**) and 427 and 827 nm (**3b**) in methylene dichloride at room temperature. As

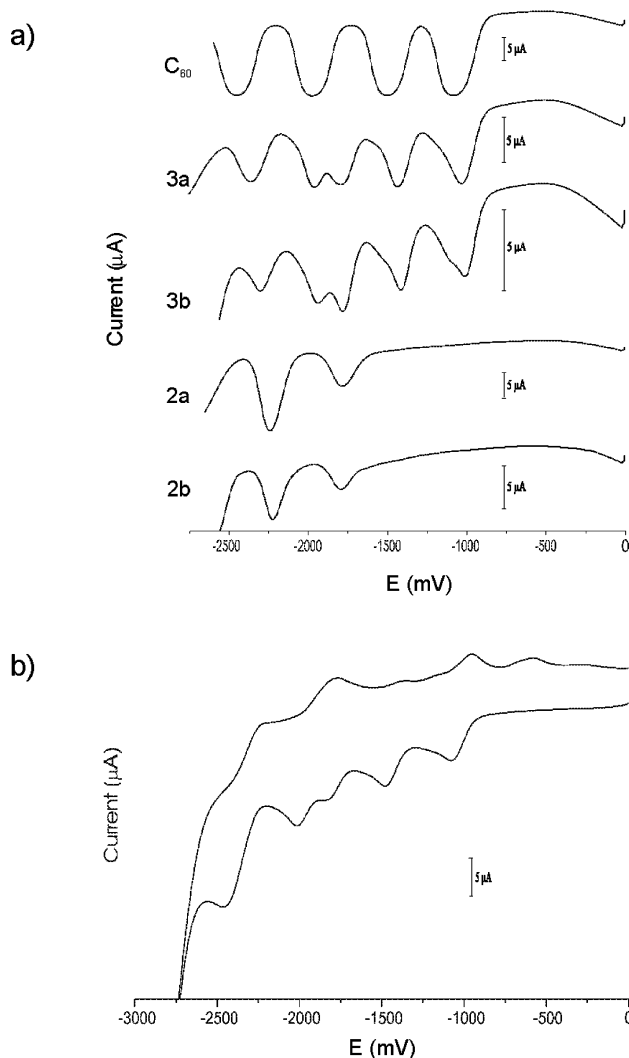


Figure 1. (a) OSWVs of **2a–b**, **3a–b** and C₆₀. (b) CV of **3a**.

Table 1. Electrochemical data (V versus Ag/AgNO₃)^b of the redox processes of compounds **2a–b**, **3a–b** and C₆₀ detected by OSWV in *o*-dichlorobenzene/acetonitrile (4:1) under identical experimental conditions

	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E^5_{red}
C ₆₀	-1.08	-1.50		-1.97	-2.45
3a	-1.03	-1.43	-1.79 ^a	-1.96	-2.36
3b	-1.01	-1.41	-1.78 ^a	-1.94	-2.30
2a			-1.78 ^a		-2.24 ^a
2b			-1.79 ^a		-2.22 ^a

^a Irreversible according to CV.

^b Working electrode: GCE; auxiliary electrode: Pt; 0.1 M TBAP, ODCB:ACN (4:1).

depicted in Fig. 2, the fluorescence is strongly quenched (up to 62% for **3a** and 54% for **3b**) relative to the corresponding hydrazones **2a** and **2b**, respectively, indicating significant interaction between phenylenevinylene moiety single excited state and fullerene ground state. Moreover, different behavior is observed for **3a** and **3b**; while **3a** shows emission at 694, 707 (ascribed to the

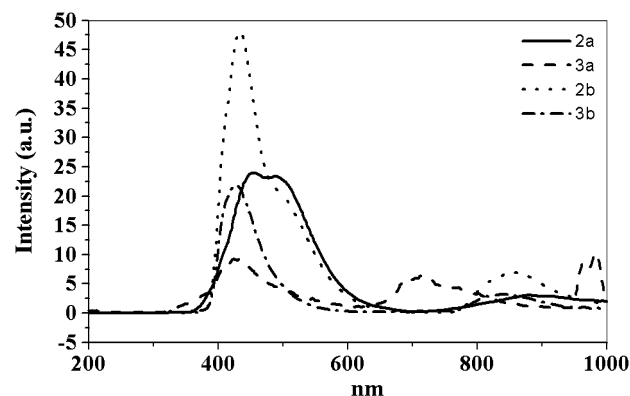


Figure 2. Corrected fluorescence spectra of **2a** (1.52×10^{-5} M, $\lambda_{\text{exc}} = 331.5$ nm), **2b** (6.54×10^{-6} M, $\lambda_{\text{exc}} = 327$ nm), **3a** (6.78×10^{-6} M, $\lambda_{\text{exc}} = 326$ nm), and **3b** (4.89×10^{-6} M, $\lambda_{\text{exc}} = 327$ nm) in CH₂Cl₂ at room temperature. All the spectra are normalized to a constant absorbance.

fullerene cage as a consequence of an energy transfer process), 965 and 983 nm, these bands are absent in **3b**, suggesting that electron transfer might be playing a key role in this case. To be certain that the observed interactions are intramolecular and not intermolecular, the fluorescence emission spectra were taken at different concentrations and were unchanged.

In conclusion, two new phenylenevinylene fullerodendrimers have been synthesized and both show improved electron affinity with respect to the parent C₆₀. Photo-physical studies reveal strong interactions between both moieties and a charge transfer process can be envisaged particularly in **3b** in the excited state, while in **3a** both processes, charge transfer and energy transfer, coexist.

Acknowledgements

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References

- Sariciftci, N. S. *Prog. Quant. Electron.* **1995**, *19*, 131–159.
- Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100–110 and references cited therein.
- Segura, J. L.; Martín, N. *J. Mater. Chem.* **2000**, *10*, 2403–2435.
- Schenning, A. P. H. J.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 4489–4495.
- Meier, H.; Lehmann, M.; Kolb, U. *Chem. Eur. J.* **2000**, *6*, 2462–2469.
- Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701–1710.
- Camps, X.; Schönberger, H.; Hirsch, A. *Chem. Eur. J.* **1997**, *3*, 561–567.
- Diederich, F.; Gómez-López, M. *Chem. Soc. Rev.* **1999**, *28*, 263–277.

9. Nierengarten, J. F. *Chem. Eur. J.* **2000**, *6*, 3667–3670.
10. Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527–2547.
11. Guldi, D. *Chem. Commun.* **2000**, 321–327.
12. Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537–546.
13. Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445–2457.
14. Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695–703.
15. Peeters, E.; van Hal, P. A.; Knol, J.; Brebec, C. J.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. B* **2000**, *104*, 10174–10190.
16. Segura, J. L.; Gómez, R.; Martín, N.; Luo, C.; Guldi, D. M. *Chem. Commun.* **2000**, 701–702.
17. Armaroli, N.; Barigelleti, F.; Ceroni, P.; Eckert, J. F.; Nicoud, J. F.; Nierengarten, J. F. *Chem. Commun.* **2000**, 599–600.
18. Eckert, J. F.; Nicoud, J. F.; Nierengarten, J. F.; Liu, S. G.; Echegoyen, L.; Barigelleti, F.; Armaroli, N.; Ouali, L.; Kraznikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467–7479.
19. de la Cruz, P.; Espíldora, E.; García, J. J.; de la Hoz, A.; Langa, F.; Martín, N.; Sánchez, L. *Tetrahedron Lett.* **1999**, *40*, 4889–4892.
20. de la Cruz, P.; de la Hoz, A.; Langa, F.; Martín, N.; Pérez, M. C.; Sánchez, L. *Eur. J. Org. Chem.* **1999**, 3433–3436.
21. Langa, F.; de la Cruz, P.; Espíldora, E.; González-Cortés, A.; de la Hoz, A.; López-Arza, V. *J. Org. Chem.* **2000**, *65*, 8675–8684.
22. de la Cruz, P.; Díaz-Ortiz, A.; García, J. J.; Gómez-Escalonilla, M. J.; de la Hoz, A.; Langa, F. *Tetrahedron Lett.* **1999**, *40*, 1587–1590.
23. Díez-Barra, E.; García-Martínez, J. C.; Rodríguez-López, J. *Tetrahedron Lett.* **1999**, *40*, 8181–8184.
24. de la Hoz, A.; Díaz-Ortiz, A.; Moreno, A.; Langa, F. *Eur. J. Org. Chem.* **2000**, 3659–3673.
25. Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593–601.