

An Electroactive Dynamically Polydisperse Supramolecular Dendrimer

Gustavo Fernández,[†] Emilio M. Pérez,[†] Luis Sánchez,[†] and Nazario Martín^{*,†,||}*Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain, and IMDEA-nanociencia, E-28049 Madrid, Spain*

Received November 21, 2007; E-mail: nazmar@quim.ucm.es

Dendrimers are attractive molecular constructs for the development of nanotechnology because of their well-defined globular nanometric structure.¹ Indeed, they have already found applications in fields as diverse as biotechnology,² catalysis,³ and optoelectronics.⁴ One of the most active areas of research in dendrimer chemistry is the study of their supramolecular properties, be it the investigation of covalent dendrimers as hosts or the construction of dendrimeric structures through noncovalent interactions.⁵ With regards to the latter, monodisperse supramolecular dendrimers based on hydrogen-bonding^{5c,d} and metal–ligand^{5e} interactions have already been described.

We wish to report on a dynamically polydisperse supramolecular dendrimer based on the self-assembly of a branched redox-amphoteric monomer through π – π and van der Waals interactions.

We recently described a receptor for [60]fullerene based on the concave–convex complementarity between the curved aromatic surface of the electron donor 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole (exTTF) and the convex exterior of fullerene.⁶ Our receptor formed complexes with C₆₀ with binding constants higher than 10³ M^{−1}. The combination of supramolecular and electronic reciprocity between host and guest in this system spurred us to exploit it in the construction of self-organized electroactive materials. We have already reported the formation of a donor–acceptor linear supramolecular polymer,⁷ and from that standpoint we set out to investigate the construction of redox-amphoteric dendritic architectures through weak noncovalent interactions. To that end, we designed monomer **1**, in which two units of our fullerene receptor are covalently linked to a PC₆₁BA derivative (see Supporting Information (SI)). We expected this bifurcated molecule to self-assemble to form treelike supramolecules, as shown in Scheme 1.

Monomer **1** was synthesized in five steps and 38% overall yield from exTTF methyl alcohol, TBDMS protected 5-hydroxyisophthalic acid, and PC₆₁BA and fully characterized by ¹H and ¹³C NMR, MALDI-TOF, UV–vis, and FTIR (see SI).

¹H NMR experiments performed on **1** (CDCl₃, 300 MHz, 298 K) show progressive broadening and slight shielding of all signals as concentration increases (1.2–20 mM), which indicates the formation of aggregates of **1**. Likewise, the pattern of the shifts observed in variable temperature (VT) ¹H NMR (318–228 K, 6 mM, CDCl₃, 300 MHz) experiments points to an increase in concentration of self-assembled multimers of **1** upon cooling.⁷ Significantly, the signals corresponding to the hydrogen atoms located between the ester groups of the isophthalate esters, which initially appear isochronous, resolve into two sets of signals that can easily be identified as H* and H^Δ by their integral values. While H^Δ remains largely unaffected by association, H* are shifted upfield, which indicates intermolecular binding of the fullerene fragments within the receptor cavity (see Figure 1a).⁸

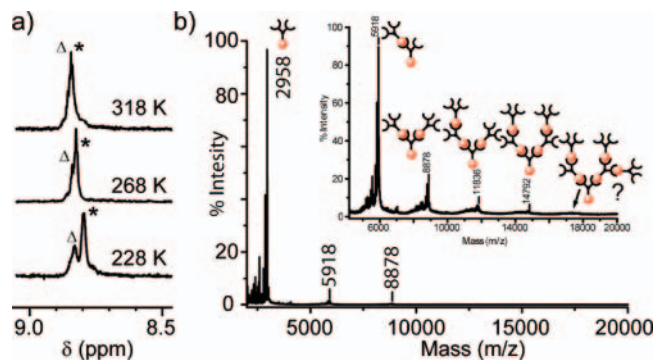
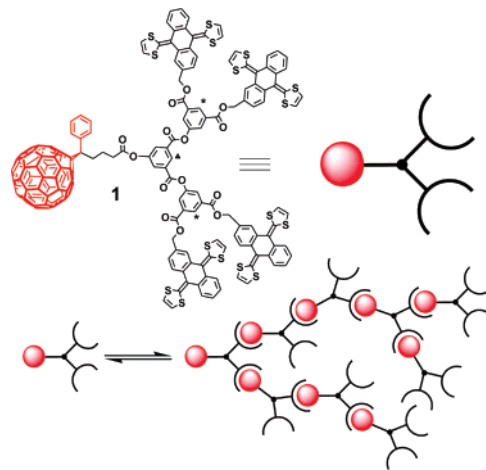


Figure 1. (a) Partial VT NMR (CDCl₃, 300 MHz) spectra of **1**, showing the splitting of H* and H^Δ; (b) MALDI-TOF (ditanol) mass spectrum of **1**, showing the formation of oligomers up to the hexamer in the gas phase.

Scheme 1. Chemical Structure of **1** and Cartoon Representation of Its Self-Assembly to Form Supramolecular Dendrimers



MALDI-TOF mass spectra of **1** utilizing ditranol as matrix provided conclusive data supporting the formation of oligomers in the gas phase. As shown in Figure 1b, peaks at m/z = 2958 (monomer), 5918 (dimer), 8878 (trimer), 11836 (tetramer), and 14792 (pentamer) are clearly distinguishable, and a broad lump between m/z = 17700 and 18000 corresponding to the hexamer is also noticeable.

The electronic absorption spectrum of **1** shows the appearance of a charge-transfer band centered at λ = 487 nm (see SI), a phenomenon that we had already observed in the UV–vis spectra of the parent exTTF-based receptor upon complexation of C₆₀.⁶ Cyclic voltammograms of **1** (THF, Ag/AgNO₃ as reference electrode, glassy carbon as working electrode, Bu₄NClO₄ as supporting electrolyte, scan rate 100 mV s^{−1}, 298 K) at different concentrations also support this image. On growing concentration, all redox processes become more energetic and irreversible, in analogy to what was observed for the formation of linear polymers composed of a structurally related monomer.⁷

[†] Universidad Complutense.^{||} IMDEA-nanociencia.

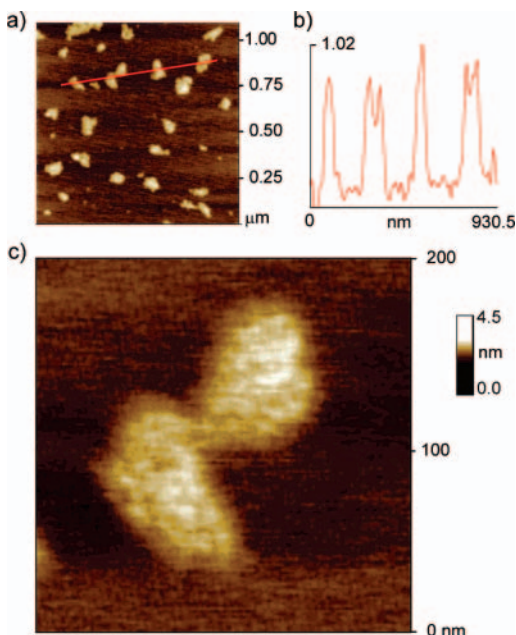


Figure 2. AFM images (tapping mode, air, 298 K) of a drop-cast of a chloroform solution of **1** ($1.0 \mu\text{M}$) on mica: (a) $1.10 \times 1.10 \mu\text{m}$; (b) profile of the structures along the red line depicted in panel a; (c) $200 \text{ nm} \times 200 \text{ nm}$.

The size of the supramolecular dendrimers in solution was investigated by dynamic light scattering (DLS). The results show two sets of hydrodynamic radii, each accounting for approximately half of the population (see SI). The first set is a narrow distribution of particle sizes expanding from 5 to 15 nm, which corresponds to structures from the monomer to the trimer. The second one ranges from $\sim 785 \text{ nm}$ to $>1 \mu\text{m}$ and must be due to multimetric associates of the monomer. Similar results were recently reported for dendrimer-based assemblies.^{5d}

A final insight into the size and morphology of the associates of **1** was provided by atomic force microscopy (AFM). Figure 2 shows typical AFM images (tapping mode, air) of supramolecular dendrimers of **1**, obtained by dropcasting a diluted solution of **1** in CHCl_3 ($1.0 \mu\text{M}$) onto freshly exfoliated mica. The images show associates of area up to $0.02 \mu\text{m}^2$ which are remarkably uniform in height ($0.9\text{--}1.1 \text{ nm}$, see Figure 2b). With regards to their shape, a triangular form in which two vertices are rounded off—somewhat reminiscent of a bunch of grapes—is clearly predominant (see Figure 2a,c and SI). In fact, nearly all of the supramolecular dendrimers observed can be considered composites of these. Thus, the size and geometry of the nanoscopic structures observed correspond very well to those expected for branched, planar oligomers of **1**.⁹

In conclusion, we have described the self-assembly of monomer **1** into dynamically polydisperse supramolecular dendrimers, mainly through $\pi\text{--}\pi$ interactions. This represents a conceptually new type of noncovalent organization of electroactive materials, lying at the interface between dendrimers¹⁰ and supramolecular polymers.^{7,11,12} The possibility of exploiting it in the construction of optoelectronic devices is currently under investigation.

Acknowledgment. We are thankful to A. Soubrié (Centro de Microscopía y Citometría, UCM) for AFM imaging, Dr. F. Ortega

(UCM) for DLS experiments, and Dr. M. Alonso (UAM) for the MALDI-TOF spectra. This work has been supported by the MEC of Spain (CTQ2005-02609/BTQ and Consolider-Ingenio 2010-CSD2007-0010, Nanociencia Molecular) and Comunidad de Madrid (P-PPQ-000225-0505). E.M.P. and G.F. are indebted to MEC for a Juan de la Cierva postdoctoral contract and a FPU studentship, respectively.

Supporting Information Available: Experimental details and supplementary figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Fréchet, J. M. J.; Tomalia, D. A., Eds. *Dendrimers and Other Dendritic Polymers*; Wiley: New York, 2001. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*; Wiley-VCH: Weinheim, Germany, 2001. (c) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819–3867. (d) Helms, B.; Meijer, E. W. *Science* **2006**, *313*, 929–930.
- (2) (a) Lee, C. C.; MacKay, J. A.; Fréchet, J. M. J.; Szoka, F. C. *Nat. Biotechnol.* **2005**, *23*, 1517–1526. (b) Boas, U.; Heegaard, P. M. H. *Chem. Soc. Rev.* **2004**, *33*, 43–63.
- (3) (a) Van Heerbeek, R.; Kamer, P. C. J.; Van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Rev.* **2002**, *102*, 3717–3756. (b) Twyman, L. J.; King, A. S. H.; Martin, I. K. *Chem. Soc. Rev.* **2002**, *31*, 69–82.
- (4) (a) Yokoyama, S.; Otomo, A.; Nakahama, T.; Okuno, Y.; Mashiko, S. *Top. Curr. Chem.* **2003**, *228*, 205–226. (b) Balzani, V.; Ceroni, P.; Maestri, M.; Saudan, C.; Vicinelli, V. *Top. Curr. Chem.* **2003**, *228*, 159–191. (c) Van der Boom, M. E. *Angew. Chem., Int. Ed.* **2002**, *41*, 3363–3366.
- (5) (a) Fréchet, J. M. J. *Proc. Nat. Acad. Sci.* **2002**, *99*, 4782–4787. (b) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74–91. For recent examples, see: (c) Franz, A.; Bauer, W.; Hirsch, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1564–1567. (d) Hermans, T. M.; Broeren, M. A. C.; Gomopoulos, N.; Smeijers, A. F.; Mezari, B.; Van Leuwen, E. N. M.; Vos, M. R. J.; Magusin, P. C. M. M.; Hilbers, P. A. J.; Van Genderen, M. H. P.; Sommerdijk, N. A. J. M.; Fylas, G.; Meijer, E. W. *J. Am. Chem. Soc.* **2007**, *129*, 15631–15638. (e) Yang, H.-B.; Hawkrige, A. M.; Huang, S. D.; Das, N.; Bunge, S. D.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 2120–2129.
- (6) Pérez, E. M.; Sánchez, L.; Fernández, G.; Martín, N. *J. Am. Chem. Soc.* **2006**, *128*, 7172–7173.
- (7) Fernández, G.; Pérez, E. M.; Sánchez, L.; Martín, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 1094–1097.
- (8) Similar shifts were observed for a related receptor upon complexation of fullerene. See: Pérez, E. M.; Sierra, M.; Sánchez, L.; Torres, M. R.; Viruela, R.; Viruela, P. M.; Ortí, E.; Martín, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 1847–1851.
- (9) The tendency of dendrimers to adopt planar conformations when deposited on surfaces is well documented (see ref 1). In contrast, PC_{61}BM , that is, the methyl ester of PC_{61}BA , forms approximately semispherical aggregates through fullerene–fullerene interactions, and a related compound featuring one receptor only forms linear assemblies (see ref 7).
- (10) For fullerodendrimers, see: (a) Hahn, U.; Maisonhaute, E.; Amatore, C.; Nierengarten, J.-F. *Angew. Chem., Int. Ed.* **2007**, *46*, 951–954. (b) Lenoble, J.; Campidelli, S.; Maringa, N.; Donnio, B.; Guillon, D.; Yevlampieva, N.; Deschenaux, R. *J. Am. Chem. Soc.* **2007**, *129*, 9941–9952. (c) Pérez, L.; García-Martínez, J. C.; Díez-Barra, E.; Atienzar, P.; García, H.; Rodríguez-López, J.; Langa, F. *Chem. Eur. J.* **2006**, *12*, 5149–5157. (d) Burghardt, S.; Hirsch, A.; Schade, B.; Ludwig, K.; Boettcher, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 2976–2979. (e) Jensen, A. W.; Maru, B. S.; Zhang, X.; Mohanty, D. K.; Fahlman, B. D.; Swanson, D. R.; Tomalia, D. A. *Nano Lett.* **2005**, *5*, 1171–1173. (f) Nierengarten, J.-F.; Armaroli, N.; Accorsi, G.; Rio, Y.; Eckert, J.-F. *Chem. Eur. J.* **2003**, *9*, 36–41. (g) Guldí, D. M.; Swartz, A.; Luo, C.; Gómez, R.; Segura, J. L.; Martín, N. *J. Am. Chem. Soc.* **2002**, *124*, 10875–10886.
- (11) For supramolecular polymers with fullerenes, see: (a) Giacalone, F.; Martín, N. *Chem. Rev.* **2006**, *106*, 5136–5190. (b) Haino, T.; Matsumoto, Y.; Fukazawa, Y. *J. Am. Chem. Soc.* **2005**, *127*, 8936–8937. (c) Liu, Y.; Wang, H.; Liang, P.; Zhang, H.-Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 2690–2694. (d) Sánchez, L.; Rispens, M. T.; Hummelen, J. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 838–840.
- (12) In fact, it is easy to visualize **1** alternatively as a dendron, a monomer for a supramolecular polymer, and a fullerodendrimer in itself (see ref 10c,g).

JA710505H