Surface Chemistry

DOI: 10.1002/anie.200603599

Self-Assembled Monolayers of a Multifunctional Organic Radical**

Núria Crivillers, Marta Mas-Torrent, Sandrine Perruchas, Nans Roques, José Vidal-Gancedo, Jaume Veciana, Concepció Rovira,* Lourdes Basabe-Desmonts, Bart Jan Ravoo, Mercedes Crego-Calama,* and David N. Reinhoudt

The ultimate goal of molecular bottom-up approaches is to employ functional building blocks to construct nanometer-scale devices that address specific applications.[1] Furthermore, immobilization of functional molecules on suitable surfaces is also often required for implementation of a practical device. One powerful and versatile strategy for the modification of surfaces at the molecular level is by the preparation of self-assembled monolayers (SAMs).[2] Although most attention has focused on SAMs of thiols on gold,[3] the use of glass, quartz, or silicon (namely, SiO_2) substrates offers clear advantages for preparing SAMs since these systems exhibit superior stability, are compatible with established silicon technologies, and allow the use of optical techniques as read-out mechanisms.[4] Molecules with a variety of functionalities have previously been anchored on SiO_2 surfaces for the fabrication of chemical sensors,[5] the immobilization of biomolecules,[6] the coordination of metals,[7] the preparation of surfaces with nonlinear optical properties,[8] and the manipulation of the surface wettability.[9] The preparation of SAMs of organic radicals is very appealing since these systems would provide magnetic functionality to the surfaces. However, there appear to be extremely few examples of SAMs based on organic radicals in the literature[10] and, to our knowledge, organic radicals have not been previously anchored on to SiO_2 substrates.

Here, we describe the functionalization of silicon oxide based surfaces with polychorotriphenylmethyl (PTM) radicals.[11] These stable radicals are colored and also exhibit fluorescence in the red region of the spectra. More interestingly, PTM radicals are electroactive and can be easily and reversibly reduced (or oxidized) to their anionic (or cationic) species.[12,13] The oxidized and reduced states show different absorption spectra than the radical and are also nonmagnetic and nonfluorescent. Therefore, the preparation of SAMs functionalized with PTM radicals (PTM SAMs) on solid substrates results in multifunctional surfaces with electrochemical, optical, and magnetic activities. Here we also demonstrate that these SAMs can be used as chemical redox switches with optical (absorption and fluorescence) and magnetic responses.

The strategy employed to fabricate the PTM SAMs on a SiO_2 surface is depicted in Figure 1. The substrate was functionalized with a monolayer of silane molecules with a terminal chemical group that acts as a recognition site. Subsequently, two different PTM radical derivatives are immobilized on the substrate either by covalent or non-covalent interactions.

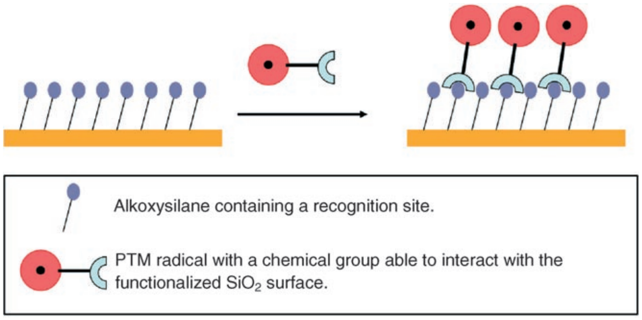


Figure 1. Schematic drawing of the strategy employed to prepare PTM SAMs.

In our first approach, we prepared a SAM of *N*-[3-(trimethoxysilyl)propyl]etylenediamine (**S1**) on SiO_2 surfaces following the procedure previously described.[14] The substrates functionalized with the amino-terminated monolayer were immersed in a solution of the tetradecachloro-4-(chlorocarbonyl)triphenylmethyl radical (PTM-COCl)[15] (see Experimental Section) to give the PTM radical SAM **S2** as a result of the formation of a covalent amide bond (Scheme 1a). Water contact angles for **S1** are in accordance with the values reported in the literature[16] (advancing contact angle $(\theta_{adv}) = (52.0 \pm 0.3)^\circ$ and receding contact angle $(\theta_{rec}) = (45.5 \pm 0.2)^\circ$). The increase in the contact angle values of **S2** $(\theta_{adv} = (88.8 \pm 0.3)^\circ$ and $\theta_{rec} = (45 \pm 4)^\circ)$

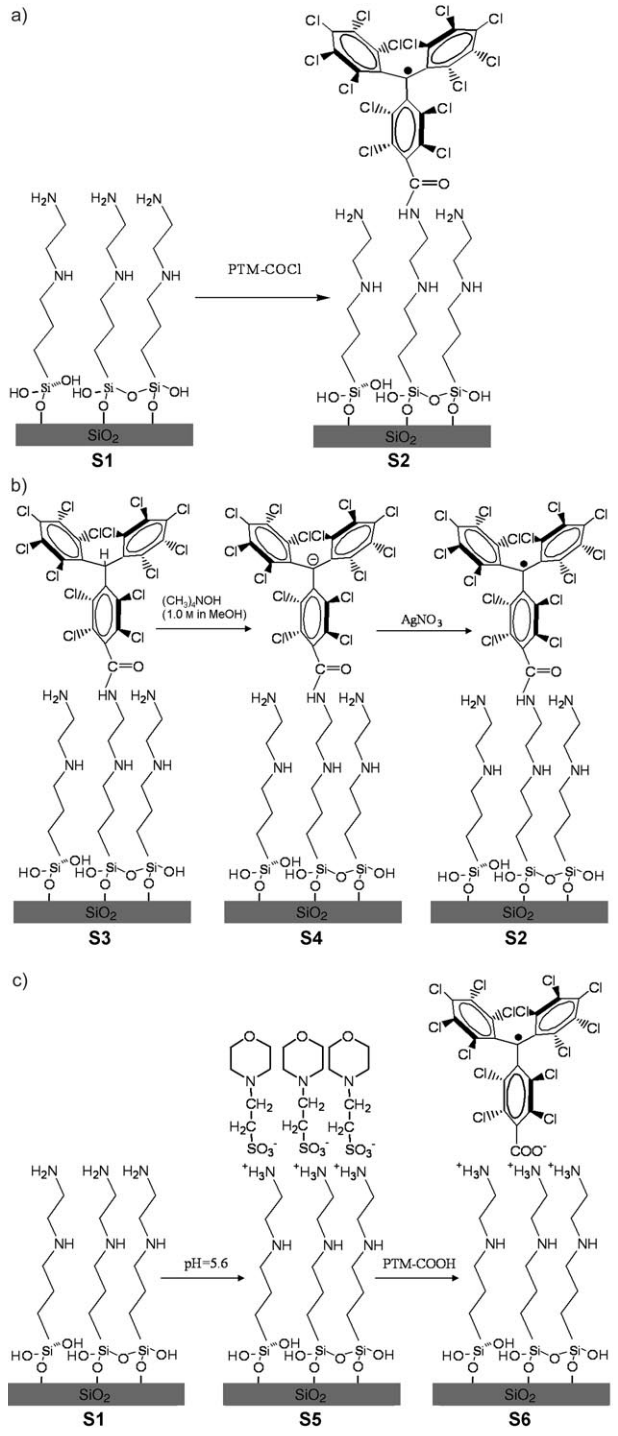
---

[*] N. Crivillers, Dr. M. Mas-Torrent, Dr. S. Perruchas, Dr. N. Roques, Dr. J. Vidal-Gancedo, Prof. J. Veciana, Prof. C. Rovira
Institut de Ciència de Materials de Barcelona (CSIC)
Campus de la UAB
08193 Bellaterra (Spain)
Fax: (+34) 935-805-729
E-mail: cun@icmab.es

Dr. L. Basabe-Desmonts, Dr. B. J. Ravoo, Dr. M. Crego-Calama, Prof. D. N. Reinhoudt
Laboratory of Supramolecular Chemistry and Technology MESA$^+$
Institute for Nanotechnology
University of Twente
P.O. Box 217, 7500 AE Enschede (The Netherlands)
Fax: (+31) 534-894-645
E-mail: smct@tnw.utwente.nl

[**] This work is part of the European Science Foundation EUROCORES (Programmes SONS-FUN-SMARTS I and II) and was also supported by funds from the DGI, Spain (project EMOCIONa, CTQ2006-06333/BQU), and the EC Sixth Framework Programme MAGMANet NoE (Contract no. 515767-2). N.C. thanks the Ministerio de Ciencia y Tecnología for a PhD fellowship.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Chemical transformations of SAMs (see text for details).

demonstrates the higher hydrophobicity of the surface as a result of the anchoring of the hydrophobic PTM units, although the large hysteresis value ($\theta_{adv}-\theta_{rec}$) points to molecular disorder of the terminated PTM units. Ellipsometry reveals an increase in the layer thickness from (0.8 ± 0.1) nm to (1.3 ± 0.1) nm after formation of **S2**. The length of a PTM moiety with the amide linkage is estimated to be around 1.1 nm. The discrepancy between the observed layer thickness and the size of the PTM radical could be accounted for by the facts that: 1) PTM molecules are tilted with respect to the surface, and/or 2) the surface coverage of PTM is not 100%. Indeed, from the Cl/N ratio of (1.59 ± 0.04):1 found by X-ray photoelectron spectroscopy (XPS) of **S2**, we can estimate that there is approximately one PTM molecule anchored for every 4.4 amino-terminated molecules and, therefore the surface coverage is around 70%.[17] We also performed the optical characterization of **S2** to corroborate the chemical nature of the monolayer. The UV/Vis spectra of **S2** recorded in air exhibited an absorption band at 382 nm, which is assigned to the radical character of the triphenylmethyl unit (Figure 2a).[18] The fluorescence spectra of **S2** (λ_{exc} = 370 nm) revealed a maximum emission band at 690 nm (Figure 2b), typical of a PTM radical.[19] Finally, the electron paramagnetic resonance (EPR) spectrum was recorded to demonstrate the radical character of **S2**. The EPR spectrum shows a signal at g = 2.0024, with a linewidth of 5.2 Gauss, which is very close to that observed for other PTM radicals,[18] thus confirming that **S2** contains immobilized organic radical units (Figure 3).

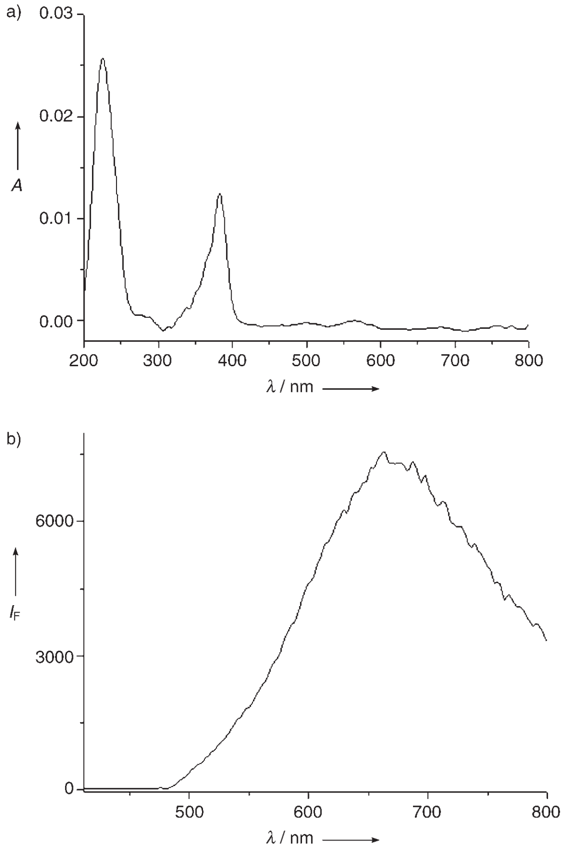


Figure 2. Absorbance (a) and fluorescence (λ_{ex} = 370 nm; b) spectra of **S2** on quartz in air.

In addition, the organic radical monolayer **S2** was also generated in situ as shown in Scheme 1b. Substrates functionalized with **S1** were immersed in a solution of the αH-tetradecachloro-4-(chlorocarbonyl)triphenylmethane (αH-PTM-COCl)[20]—the nonmagnetic counterpart of PTM-COCl—leading to the formation of **S3**. This SAM was also

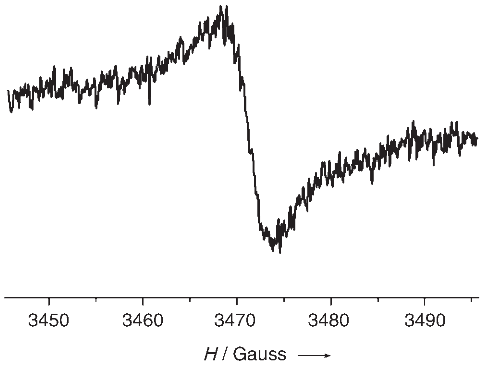


Figure 3. EPR spectrum of **S2** on glass at 300 K.

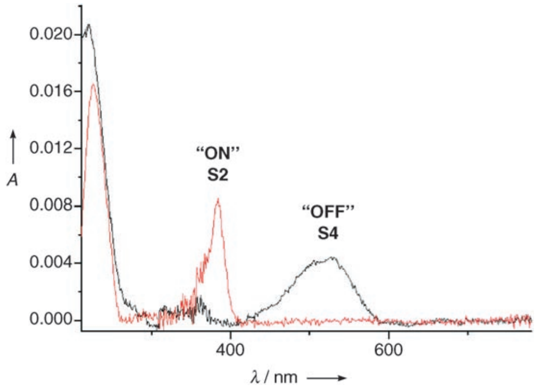


Figure 4. Absorbance spectra of the PTM anion SAM (**S4**, OFF state, black line) before and after oxidation to the PTM radical SAM (**S2**, ON state, red line).

characterized by contact angle, XPS, ellipsometry, and UV/Vis spectroscopy, and similar results were obtained as for **S2**. Reaction of monolayer **S3** with a base and subsequent oxidation resulted in the formation of first the SAM of the PTM anion derivative **S4**, and then the PTM radical SAM **S2**. The optical spectra (absorbance and fluorescence) of this SAM corroborated the success of the reactions and, thus, the formation of the organic radical on the surface (see the Supporting Information). Similar experiments demonstrate the reversibility of the redox process. Figure 4 shows the UV/Vis spectrum corresponding to the reduction–oxidation process of electroactive PTM SAMs. Upon reduction to the PTM anion, the characteristic PTM radical absorption band at 384 nm disappears, whilst a band centered at 525 nm is observed. This system behaves thus as a bistable chemical switch since it is possible to interconvert the SAM between two states which exhibit different properties: an OFF state associated with the PTM anion SAM (nonfluorescent and diamagnetic) and an ON state corresponding to the PTM radical SAM (fluorescent and paramagnetic).

The second strategy employed involved the preparation of PTM radical SAMs solely by interlayer electrostatic interactions.[21] For this purpose we protonated the amino group of **S1** by rinsing the sample with 4-morpholineethanesulfonic acid monohydrate buffer (pH 5.6)[22] to give **S5** and, subsequently, the substrate was immersed in a solution of 4-carboxytetradecachlorotriphenylmethyl radical (PTM-COOH) to give SAM **S6**. This two-step reaction is summarized in Scheme 1c. The contact angle and XPS characterization of **S6** was in agreement with the previous results and confirmed the formation of the monolayer. Additionally, the UV/Vis and fluorescence ($\lambda_{exc} = 370$ nm) spectra of **S6** showed the characteristic PTM absorption peak at 388 nm and an emission band with a maximum centered at 672 nm, respectively (see the Supporting Information).

More interesting with respect to potential device applications is the possibility to locally address the PTM molecules on the surface to fabricate multifunctional patterned surfaces. The technique used to achieve the patterned surfaces was microcontact printing,[23] which involves the inking of an

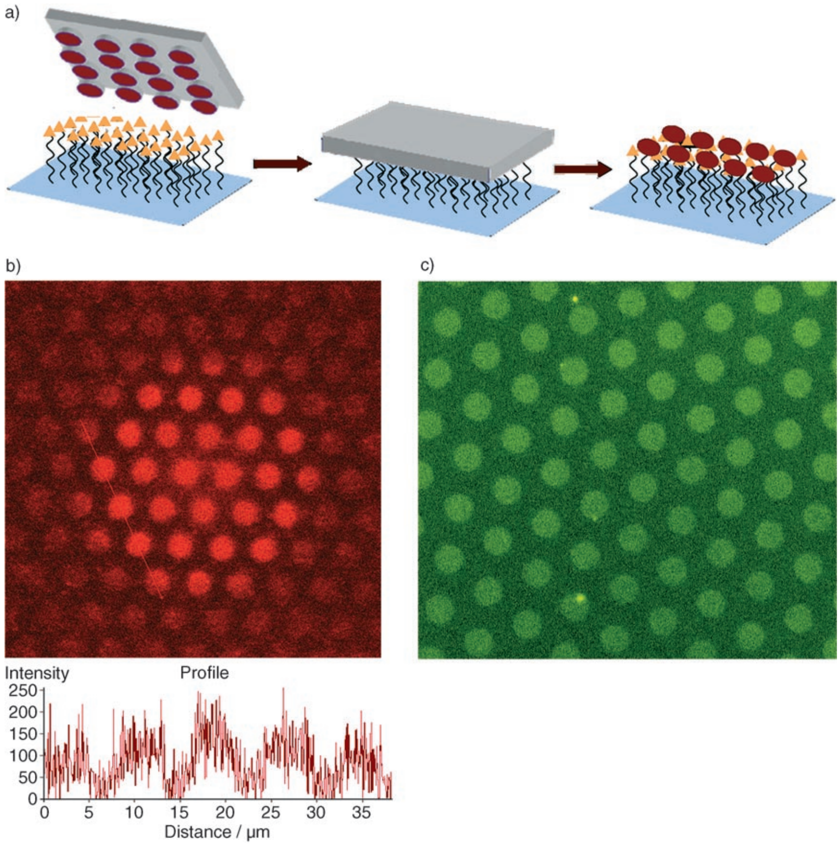


Figure 5. a) Schematic representation of the microcontact printing of a functionalized PTM radical on an adhesive SAM. b) Confocal microscopy image of patterned **S2** on glass ($\lambda_{exc} = 488$ nm). The diameter of the fluorescent dots is 5 µm. c) Fluorescence microscopy image of **S6** on glass ($\lambda_{exc} = 340–370$ nm); the diameter of the fluorescent dots is 10 µm.

elastomeric stamp with suitable molecules. When the stamp is placed into contact with a substrate the ink molecules are transferred from the stamp to the substrate in the regions of contact (Figure 5a). We used a stamp of poly(dimethylsiloxane) (PDMS) with dots of diameter 5 or 10 μm which was inked with a solution of PTM-COCl in DMSO, and brought into contact with **S1**. The resulting patterned **S2** SAM could be visualized by laser scanning confocal microscopy as a consequence of the fluorescent nature of the PTM molecules (Figure 5b). Following the same methodology, we printed PTM-COOH on the protonated SAM **S5** to obtain patterned **S6**, which is formed by electrostatic interactions. The pattern obtained was visualized by fluorescence microscopy (Figure 5c). It is evident from Figure 5b,c that the hexagonal pattern symmetry of the stamp is faithfully replicated as a fluorescent array of PTM radicals on the substrate.

In summary, SAMs of an organic PTM radical have been prepared on SiO$_2$ surfaces by making use of either covalent or noncovalent interactions. As a consequence of the fully reversible redox process, these multifunctional radical SAMs behave as chemical switches that combine electronic absorption, fluorescence emission, and magnetic outputs. Furthermore, the fabrication of surface patterns of these radical molecules has been achieved. The chemical flexibility and versatility of these molecules demonstrates the potential of preparing self-assembled multifunctional molecular devices on surfaces.

Experimental Section

Synthesis: Tetradecachloro-4-(chlorocarbonyl)triphenylmethyl radical, αH-tetradecachloro-4-(chlorocarbonyl)triphenylmethane and 4-carboxytetradecachlorotriphenylmethyl radical were synthesized as previously reported.[15,20,24]

Monolayer preparation: Formation of the PTM monolayer **S2** and **S3** was achieved by immersing the amino-terminated monolayer **S1** in a solution (0.1 mM) of the corresponding PTM derivative in CH$_2$Cl$_2$ (freshly distilled) and triethylamine (100 μL) for 15 h under N$_2$ and in the absence of light. The substrate was then removed from the solution and rinsed with CH$_2$Cl$_2$, ethanol, and CH$_2$Cl$_2$, to remove any physisorbed material, and dried under a nitrogen stream. The formation of the PTM anion monolayer **S4** was achieved by immersing **S3** in a 2 mM solution of tetrabutylamonium hydroxide (1.0 M solution in MeOH) in freshly distilled THF for approximately 15 h under N$_2$. The substrate was removed from the solution and sequentially rinsed with THF, EtOH, and CH$_2$Cl$_2$ and dried in an N$_2$ stream. Next, **S4** was submerged in an oxidant solution of 0.1 mM AgNO$_3$ in an anhydrous mixture of CH$_2$Cl$_2$/MeCN (5:1) for 3 h. The reaction was carried out under N$_2$ and in absence of light. The substrate was then rinsed with CH$_2$Cl$_2$, EtOH, and CH$_2$Cl$_2$ and dried in an N$_2$ stream to obtain **S2**. Monolayer **S6** was prepared by rinsing **S1** with 4-morpholineethanesulfonic acid monohydrate buffer solution (pH 5.6) and washed with water before being immersed in a solution of 0.1 mM PTM-COOH in dry CH$_2$Cl$_2$ for 1 h. The substrate was washed with CH$_2$Cl$_2$ and dried in an air stream.

Preparation of patterned surfaces by microcontact printing: Poly(dimethylsiloxane) (PDMS) stamps were fabricated by pouring a 10:1 (v/v) mixture of Sylgard 184 elastomer and curing agent over a patterned silicon master. The mixture was cured in the oven for 24 h at 60° and then carefully peeled away from the master. To obtain the patterned surface **S2**, the PDMS stamp was inked (2 times, 1 minute each) with a 0.1 mM solution of PTM-COCl in DMSO. The stamp was dried with an air stream and brought into contact with **S1**. After 4 minutes the stamp was carefully removed. The patterned glass surface **S6** was achieved by inking the stamp in a 0.1 mM acetonitrile solution of PTM-COOH for 2 minutes and was then brought into contact with the functionalized glass slide for 1 minute. The samples of **S2** and **S6** were rinsed in THF and acetonitrile, respectively.

Characterization of the SAMs: The water contact angle, XPS, AFM, and ellipsometry characterization was performed on SAMs prepared on silicon oxide. The absorbance and fluorescence spectra were recorded from SAMs on quartz. The EPR spectrum and the optical visualization of the patterned samples were carried out on SAMs prepared on glass slides.

Received: September 3, 2006
Revised: December 14, 2006

Keywords: molecular devices · monolayers · radicals · self-assembly · surface chemistry

---

[1] a) J. V. Barth, G. Constantini, K. Kern, *Nature* **2005**, *437*, 671–679; b) B. D. Gates, Q. Xu, M. Stewart, D. Ryan, G. Willson, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1171–1196.

[2] A. Ulman, *Chem. Rev.* **1996**, *96*, 1533–1554.

[3] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103–1170.

[4] S. Onclin, B. J. Ravoo, D. N. Reinhoudt, *Angew. Chem.* **2005**, *117*, 6438–6462; *Angew. Chem. Int. Ed.* **2005**, *44*, 6282–6304.

[5] a) M. Crego-Calama, D. N. Reinhoudt, *Adv. Mater.* **2001**, *13*, 1171–1174; b) L. Basabe-Desmonts, J. Beld, R. S. Zimmerman, J. Hernando, P. Mela, M. F. García Parajó, N. F. Van Hulst, A. Van den Berg, D. N. Reinhoudt, M. Crego-Calama, *J. Am. Chem. Soc.* **2004**, *126*, 7293–7299; c) E. Brasola, F. Mancin, E. Rampazzo, P. Tecilla, U. Tonellato, *Chem. Commun.* **2003**, 3026–3027.

[6] a) T. P. Sullivan, W. T. S. Huck, *Eur. J. Org. Chem.* **2003**, 17–29; b) D. Barnes-Seeman, S. B. Park, A. N. Koehler, S. L. Schreiber, *Angew. Chem.* **2003**, *115*, 2478–2481; *Angew. Chem. Int. Ed.* **2003**, *42*, 2376–2379.

[7] H. Lee, L. J. Kepley, H. G. Hong, T. E. Mallouk, *J. Am. Chem. Soc.* **1988**, *110*, 618–620.

[8] a) M. E. van der Boom, G. Evmenenko, C. J. Yu, P. Dutta, T. J. Marks, *Langmuir* **2003**, *19*, 10531–10537; b) S. Yitzchaik, T. J. Marks, *Acc. Chem. Res.* **1996**, *29*, 197–202.

[9] a) M. K. Chaudhury, G. M. Whitesides, *Science* **1992**, *255*, 1230; b) C. P. Tripp, R. P. N. Veregin, M. L. Hair, *Langmuir* **1993**, *9*, 3518–3522.

[10] a) M. M. Matsushita, N. Ozaki, T. Sugawara, F. Nakamura, M. Hara, *Chem. Lett.* **2002**, *6*, 596–597; b) Y. Kashiwagi, K. Uchyama, F. Kurashima, J. Anazi, T. Osa, *Anal. Scien.* **1999**, *15*, 907–909.

[11] M. Ballester, J. Riera, J. Castaner, C. Badía, J. M. Monsó, *J. Am. Chem. Soc.* **1971**, *93*, 2215–2225.

[12] C. Sporer, I. Ratera, D. Ruiz-Molina, J. Vidal-Gancedo, K. Wurst, P. Jaitner, C. Rovira, J. Veciana, *J. Phys. Chem. Sol.* **2004**, *65*, 753–758.

[13] a) C. Sporer, I. Ratera, D. Ruiz-Molina, Y. Zhao, J. Vidal-Gancedo, K. Wurst, P. Jaitner, K. Cáliz, A. Persoons, C. Rovira, J. Veciana, *Angew. Chem.* **2004**, *116*, 5378–5381; *Angew. Chem. Int. Ed.* **2004**, *43*, 5266–5268; b) I. Ratera, D. Ruiz-Molina, C. Sporer, S. Marcén, S. Montant, J.-F. Létard, E. Freysz, C. Rovira, J. Veciana, *Polyhedron* **2003**, *22*, 1851–1856; c) I. Ratera, J.-F. Létard, S. Marcén, D. Ruiz-Molina, E. Freysz, C. Rovira, J. Veciana, *Chem. Phys. Lett.* **2002**, *363*, 245–251.

[14] R. Zimmerman, L. Basabe-Desmonts, F. van der Baan, D. N. Reinhoudt, M. Crego-Calama, *J. Mater. Chem.* **2005**, *15*, 2772–2777.

[15] M. Ballester, J. Riera, J. Castañar, C. Rovira, J. Veciana, C. Onrubia, *J. Org. Chem.* **1983**, *48*, 3716–3720.

[16] N. Balachander, C. N. Sukenik, *Langmuir* **1990**, *6*, 1621–1627.

[17] The surface coverage of PTM is estimated by considering the top-view of the PTM radical as an ellipse (1.2×0.7 nm), with an area of $(\pi \times 0.6 \times 0.35) = 0.66\ \text{nm}^2$, and by considering that experimentally the area per alkyl chain at full coverage is in the range 22–25 Å^2; see M. J. Stevens, *Langmuir* **1999**, *15*, 2773–2778.

[18] O. Armet, J. Veciana, C. Rovira, J. Riera, J. Castañer, E. Molins, J. Rius, C. Miravitlles, S. Olivilla, J. Brichfeus, *J. Phys. Chem.* **1987**, *91*, 5608–5616.

[19] a) M. A. Fox, E. Gaillard, Ch. Chen, *J. Am. Chem. Soc.* **1987**, *109*, 7088–7094; b) T. L. Chu, S. I. Weissmann, *J. Chem. Phys.* **1954**, *22*, 21–25.

[20] S. Chopin, J. Cousseau, E. Levillain, C. Rovira, J. Veciana, A. S. D. Sandanayaka, Y. Araki, O. Ito, *J. Mater. Chem.* **2006**, *16*, 112–121.

[21] a) R. Maoz, H. Cohen, J. Sagiv, *Langmuir* **1998**, *14*, 5988–5993; b) M. Wells, D. L. Dermody, H. C. Yang, T. Kim, R. M. Crooks, *Langmuir* **1996**, *12*, 1989–1996; c) F. Corbellini, A. Mulder, A. Sartori, M. J. W. Ludden, A. Casnati, R. Ungaro, J. Huskens, M. Crego-Calama, D. Reinhoudt, *J. Am. Chem. Soc.* **2004**, *126*, 17050–17058.

[22] P. Maury, M. Péter, V. Mahalingam, D. Reinhoudt, J. Huskens, *Adv. Funct. Mater.* **2005**, *15*, 451–457.

[23] a) Y. N. Xia, J. A. Rogers, K. E. Paul, G. M. Whitesides, *Chem. Rev.* **1999**, *99*, 1823–1848; b) A. Kumar, G. M. Whitesides, *Appl. Phys. Lett.* **1993**, *63*, 2002–2004.

[24] M. Ballester, J. Castañer, J. Riera, A. Ibáñez, J. Pujadas, *J. Org. Chem.* **1982**, *47*, 259–264.