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Engineered Silica Surfaces with an Assembled C_{60} Fullerene Monolayer

Antonino Gulino,[*,†] Sebastiano Bazzano,[‡] Guglielmo G. Condorelli,[†] Salvatore Giuffrida,[†]
Placido Mineo,[‡] Cristina Satriano,[†] Emilio Scamporrino,[†] Giorgio Ventimiglia,[†]
Daniele Vitalini,[‡] and Ignazio Fragalà[*,†]

Dipartimento di Scienze Chimiche, Università di Catania and INSTM UdR of Catania, and Istituto di Chimica e Tecnologia dei Polimeri—CNR Catania, Viale Andrea Doria 6, 95125 Catania, Italy

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A covalently assembled monolayer of 61-(*p*-hydroxyphenylmethano)fullerene [C_{60}] molecules has been synthesized. Both static and dynamic contact angle measurements show that the hydrophobic character increases upon the fullerene linkage. Atomic force microscopy lithography shows that the depth of the monolayer is about 19 Å. UV−vis spectra are well-tuned with the presence of the fullerene on the silica surfaces. The surface atomic composition, investigated by angle-resolved X-ray photoelectron spectra, shows a monotonic increase of the carbon signal upon decreasing the photoelectron takeoff angles, thus confirming the upper layer nature of this signal. Room-temperature photoluminescence spectra, under controlled atmosphere, show that the oxygen presence influences considerably the luminescence quantum yield.

Introduction

Engineering of inorganic surfaces by covalent/noncovalent bonding of organic guest molecules represents an interesting approach to the synthesis of hybrid inorganic/organic nanomaterials.[1] Syntheses based on self-assembly of appropriate molecules on inorganic substrates represent one of the most powerful approaches to obtain materials showing molecular properties.[2]

Fullerenes[3,4] have attracted much attention for optical,[5] electronic[5c,6−8] third-order nonlinear optical,[9] photovoltaic,[10−15] artificial photosynthesis,[16,17] and solar cell[18] applications. Moreover, fullerene thin films have also attracted a great deal of interest as humidity[19] and oxygen sensors,[20−23] and for further analytical[24] applications.

Great efforts have been devoted to obtaining solid-state nanocomposite materials allowing the inclusion of fullerenes, and some works concerning functionalized fullerene molecules bounded to different substrates have already been

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[*] Corresponding author: Antonino Gulino. E-mail address: agulino@dipchi.unict.it. Fax: +39-095-580138.

[†] Università di Catania and INSTM UdR of Catania.

[‡] Istituto di Chimica e Tecnologia dei Polimeri—CNR Catania.

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reported.[5b,10,11,14−22,25−41] Nevertheless, only a few of them deal with covalently assembled fullerene monolayer on functionalized silica substrates, useful for optical applications.[15,35,38−39]

The formation of ordered molecular layers of fullerene on solid substrates is important for optimizing the unique properties of the resulting material.[6,29,31,34] Therefore, there was enough motivation for us to embark on the synthesis and characterization of 61-(*p*-hydroxyphenylmethano)-fullerene [C_{60}] covalently assembled monolayer (F-AM) on silica substrates. Moreover, the presence of only one hydroxyl group on the fullerene derivative allowed its covalent linkage to the substrate.

Many papers deal with photoluminescence measurements of fullerene films.[5a,16,21,26,42] Nevertheless, to the best of our knowledge, our results represent the first ever report on the luminescence of only a fullerene monolayer.

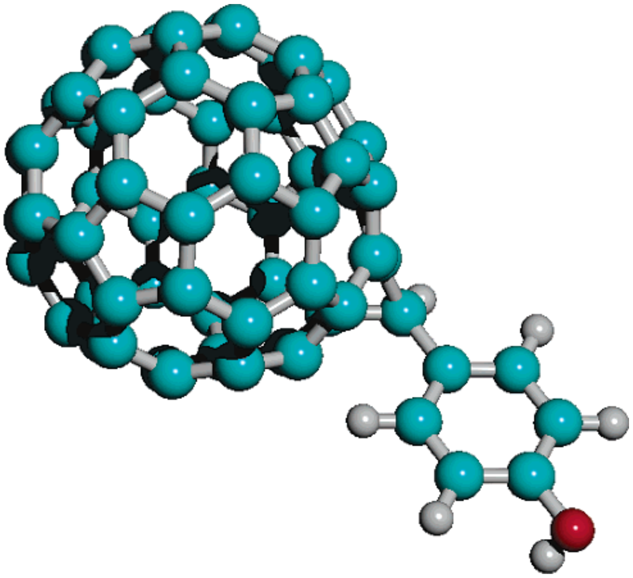

Figure 1. Schematic drawing of the fullerene molecule.

Experimental Details

Aldrich grade reagents and solvents, packed under nitrogen, were used throughout all present syntheses.

The 61-(*p*-hydroxyphenylmethano)fullerene [C_{60}] (Figure 1) was synthesized, purified, and characterized as already reported.[43] The fullerene sodium salt was obtained by reaction of a fullerene methanol solution with sodium *tert*-butoxide and the obtained *tert*-butylic alcohol was removed by vacuum during the reaction.

Fused silica (quartz) substrates were cleaned by immersion in "piranha" solution (70:30 concentrated H_2SO_4:30% H_2O_2, (v/v)) at 80 °C for 1 h and then left to cool to room temperature.[2a,h] Subsequently, substrates were repeatedly rinsed with double distilled water and immersed in a 5:1:1 H_2O:30% H_2O_2:28% NH_3 (v/v/v) mixture at room temperature for 40 min.[2a,h] Then, they were washed with double distilled water and dried under vacuum immediately before coupling agent deposition. All the successive sample manipulations were performed in a glovebox under N_2 atmosphere.

In particular, freshly cleaned substrates were immersed, at room temperature for 30 min, in a 1:100 (v/v) *n*-heptane solution of the chemisorptive siloxane, trichloro[4-(chloromethyl)phenyl]silane, 4-$ClCH_2C_6H_4SiCl_3$, to afford a monolayer of the coupling agent (CA).[2a,h] Then, they were washed with copious amounts of pentane, sonicated in acetone for 1 min to remove any physisorbed CA, immersed in a 5×10^{-3} M tetrahydrofuran (THF) solution of the fullerene sodium salt, and heated to 65 °C under stirring for 48 h.

Finally, the substrates were cooled to room temperature and then repeatedly washed with THF to remove any residual physisorbed fullerene sodium salt. The obtained fullerene monolayer is strongly adherent to the quartz substrate (F-AM system) and does not dissolve in THF, dimethylformamide (DMF), heptane, pentane, or acetone.

UV−visible (UV−vis) measurements were performed using an UV−vis-1601 Shimadzu spectrophotometer.

Both static and dynamic contact angle (ϑ) measurements were performed at room temperature in air with a Kernco goniometer. On the sample surface 2 μL water drops were applied, and measurements of ϑ were made on both sides of the two-dimensional projection of the droplet. Five different measurements were performed on different surface portions of every substrate in order

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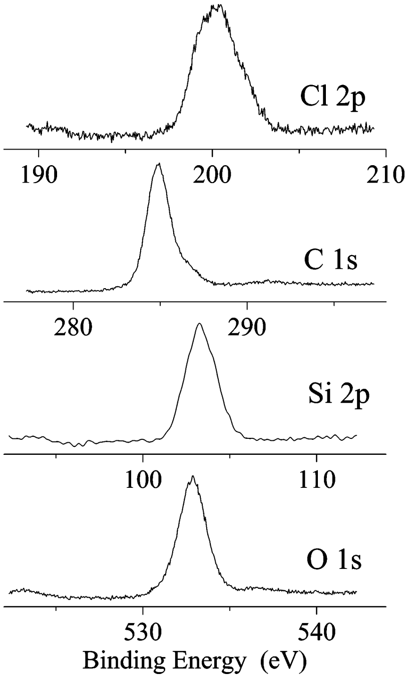


Figure 2. Al Kα excited XPS of silica substrates after the coupling agent deposition, step ii, in the C 1s, Cl 2p, Si 2p, and O 1s energy regions. Structures due to satellite radiation have been subtracted from the spectra.

to have statistically reliable results. Both advancing and receding procedures were executed.

Angle-resolved X-ray photoelectron spectra (XPS) were made at different off-take angles (45, 30, 15, and 5°) with a PHI 5600 Multi Technique System (base pressure of the main chamber, 2×10^{-10} Torr). Resolution, corrections for satellite contributions, procedures to account for steady-state charging effect, and background removal have been described elsewhere.[44]

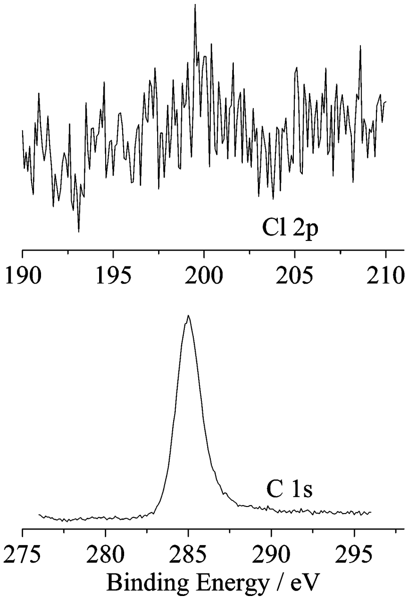
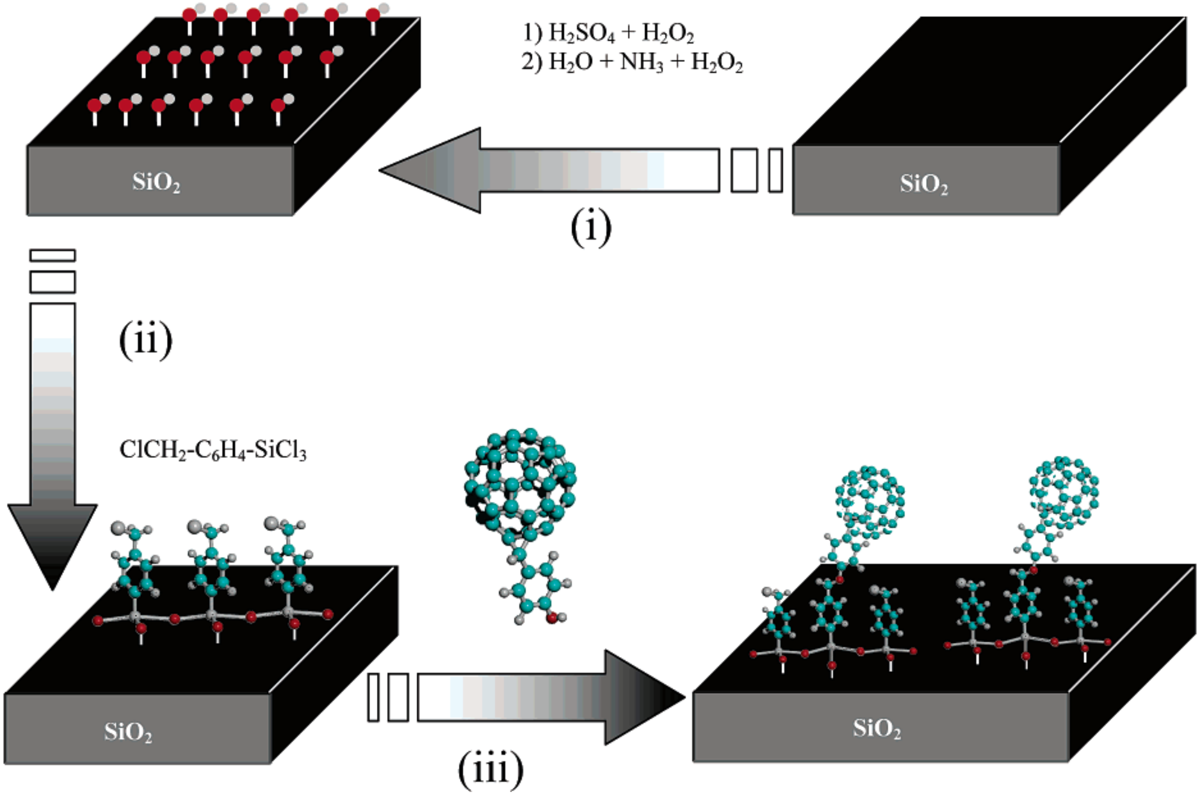


Figure 3. Al Kα excited XPS of F-AMs in the C 1s and Cl 2p energy regions. Structures due to satellite radiation have been subtracted from the spectra.

Atomic force microscopy (AFM) measurements were performed with a Solver P47 NTD-MDT instrument in semicontact mode (resonance frequency, 150 Hz).

Room-temperature photoluminescence (PL) spectra were obtained with a SPEX Fluorolog 111 instrument equipped with a xenon lamp (450 W), operating in the 200−800 nm range. The F-AM was fixed into a fluorescence cuvette and photoexcited with a 400 nm line beam. The emission was recorded at 90° with respect to the exciting line beam. Controlled atmosphere measurements were performed, allowing the appropriate gas to bubble 30 min in the cuvette sealed with a closely fitting suba-seal rubber lid.

Scheme 1



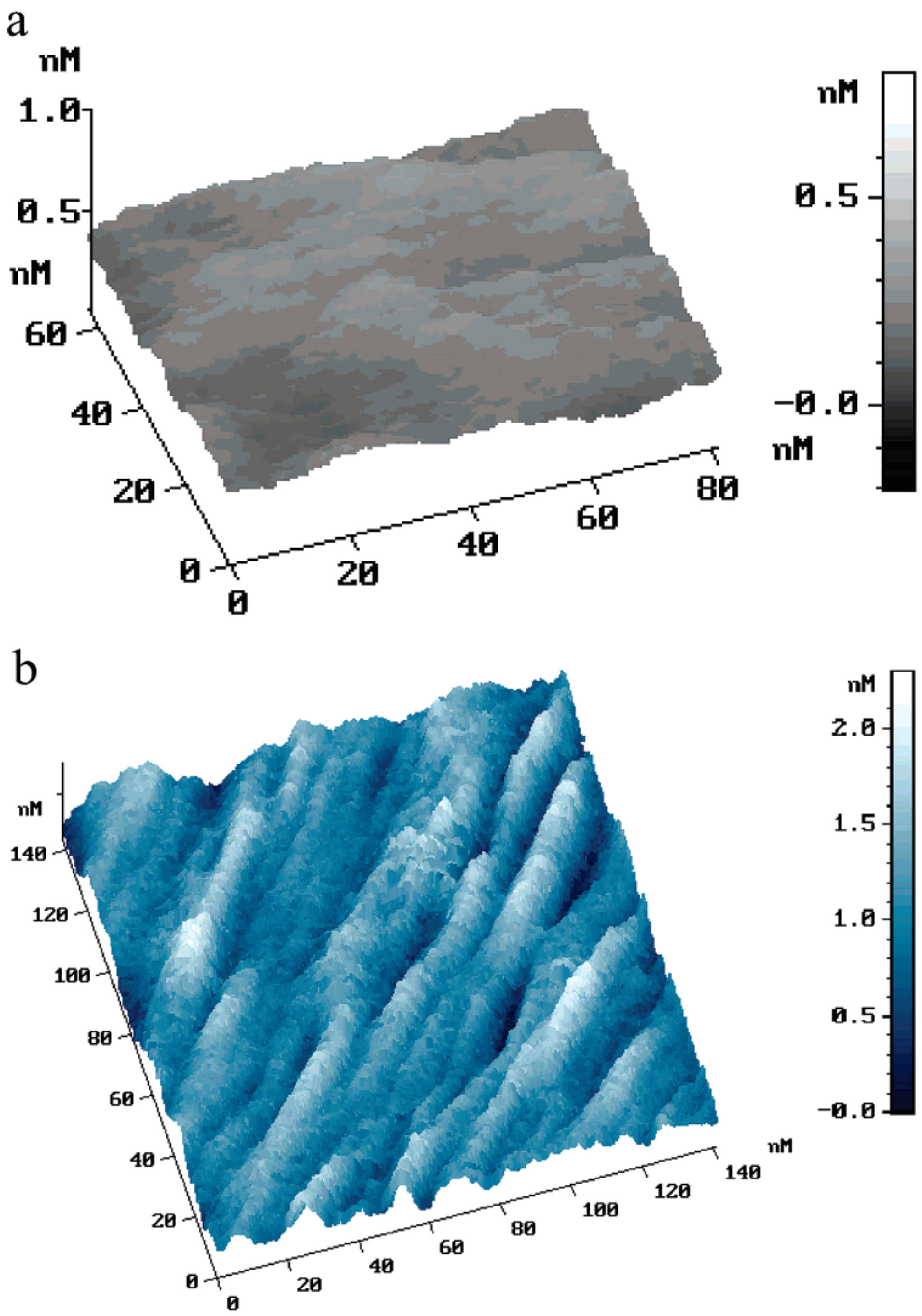


Figure 4. Typical AFM images of the (a) uncoupled starting substrates after the cleaning procedure and (b) representative F-AM.

Results and Discussion

Three successive steps have been expedient for the synthesis of the F-AM (Scheme 1):

(i) Silica surfaces were first cleaned and hydroxylated; (ii) then, under rigorously inert atmosphere, they were treated with the chemisorptive siloxane to afford a monolayer of the coupling agent; (iii) finally, the fullerene was covalently linked to the silylated substrates.

The modification of the substrate surfaces, after every reaction step, was monitored by water contact angle (ϑ) measurements. Starting uncoupled silica substrates showed a ϑ value in the 9−13° range. After cleaning (step i), the ϑ value decreased to 5°, due to the hydroxylated silica surfaces.[2a,h] The static contact angle changed from 5 to 79° after treatment with the CA (step ii). This hydrophobic change is due to the presence of densely packed benzyl chloride surface functionalities.[2a,h] Finally, after step iii, ϑ showed a further increase of the hydrophobic character falling to 82° (maximum dynamic advancing angle = 87° and minimum dynamic receding angle = 50°), upon the fullerene linkage.[40]

Figure 2 shows XP spectra of silica substrates after the CA deposition (step ii in Scheme 1). The C 1s peak and unresolved Cl 2p doublet are at 284.9 and 200.3 eV binding energies (BE), respectively. Their intensities, making the due allowance for the relevant atomic sensitivity factors, exactly match the theoretical C/Cl atomic concentration ratio (7:1), C being 49.4% and Cl being 7.2%. This result confirms a complete cross-linking of the siloxane moieties on the silica surfaces. Moreover, the C 1s peak shows a shoulder at higher BE = 286.3 eV whose intensity is about one-sixth with respect that of the main peak. This observation is nicely tuned with the theoretical C benzylic/aromatic functionalities ratio (1:6). Both Si 2p at 103.3 eV and O 1s at 533.0 eV peaks show symmetric shapes, thus precluding any further speculation.

Figure 3 shows XP spectra of F-AMs. The C 1s peak and weak unresolved Cl 2p doublet are at 285.0 and 199.5 eV BEs, respectively.[45] Both carbon and chlorine atomic concentrations show a monotonic increase on decreasing of the photoelectron takeoff angles, with respectively C being 24.0% and Cl being 0.08% at 45°, 30.5% and 0.10% at 30°, 50.0% and 0.13% at 15°, and 64.2% and 0.28% at 5°, thus confirming the upper layer nature of these signals.

The surface structures of both untreated quartz substrate and F-AM were obtained by the AFM technique. Figure 4a shows typical AFM images of the amorphous surface of starting substrates after the cleaning procedure (step i). The obtained peak-to-peak $R_{\max}$ value is 3.86 Å with a 0.48 Å roughness. Figure 4b shows a representative F-AM surface. It is clear that the surface morphology is totally different and new densely packed, elongated features are superimposed to the original substrate.[32,38] In this case, the obtained peak-to-peak $R_{\max} = 24.84$ Å with a 4.42 Å roughness. Molecular mechanics force field calculations (MM+ method), performed on the fullerene covalently bonded to the siloxane assembly, give an assembly length of 19.8 Å.[15] Therefore, the measured averaged cross-section 18.84 Å of the fullerene−siloxane monolayer corresponds to the size of the fullerene−siloxane assembly. To further investigate the thickness of the F-AM, atomic force lithography using the AFM tip was performed. Thus, grafted molecules were removed along a straight line by rastering the surface with the AFM tip under a suitable constant force. The depth of the scratch obtained is about 19 Å that corresponds to the length of the fullerene−siloxane assembly (Scheme 1). The fullerene in the siloxane−fullerene system can rotate around different bonds, thus allowing adjacent fullerene molecules to aggregate together. Furthermore, many already reported studies deal with the aggregation and clustering behavior of [60]fullerene molecules.[46] All these observations help to rationalize the AFM surface structure of the F-AM shown in Figure 4b, which is due to the geometrical possibility and strong propensity of neighboring fullerene molecules to aggregate together. Additional AFM measurements on a silica substrate with a submonolayer of fullerene still show a similar surface structure with the presence of large and elongated aggregates and areas with no aggregates.

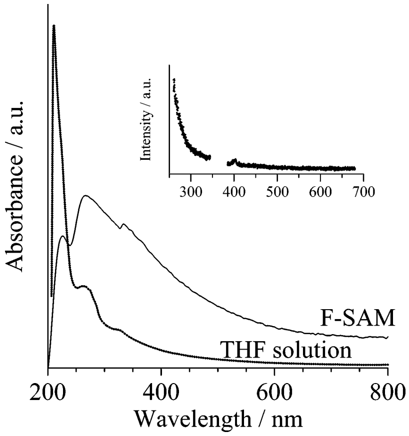


Figure 5. UV−vis spectra of the F-AM (solid line) and fullerene (THF) 5×10^{-6} M solution (dotted line). Excitation spectrum monitored at 730 nm (inset): the harmonic band at 365 has been omitted.

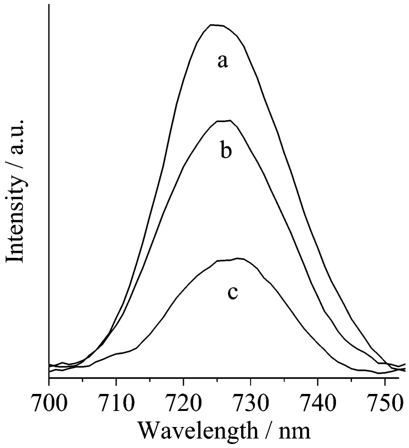


Figure 6. Photoluminescence ($\lambda_{\mathrm{exc}} = 400$ nm) quenching of F-AM: in nitrogen (a); in air (b); in oxygen (c).

UV−vis spectra of the resulting F-AM show high-quality signals, which find counterparts in the fullerene tetrahydrofuran (THF) 5×10^{-6} M solution (Figure 5). The spectrum shows bands at 227, 267, and 333 nm corresponding to those at 210, 266, and 330 nm in THF solution.[5c,10,13,17,19,35,42f,h−j,n] The calculated[47] number of molecules per cm^2 is 1.1×10^{14} corresponding to a fullerene molecule over 90 Å^2. Therefore, it can be deduced that the molecular arrangement of the F-AM corresponds to that which realizes the closest packing possible in the fullerene monolayer plane.

Photoluminescence (PL) at 730 nm was observed when the F-AM was excited at 400 nm.[42d,f−k,m] This result is in agreement with already reported literature data on similar systems. The excitation spectrum (inset of Figure 5), monitored at 730 nm, matches the general trend of the absorption spectrum, which shows an increasing absorbance on going to the UV region, thus confirming the photoluminescent nature of this band.

Figure 6 shows room-temperature PL emission under different controlled conditions. From the results it is evident that the F-AM emission is strongly affected by the environment conditions. In particular, the highest emission of the

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F-AM (Figure 6a) was obtained under a 100% nitrogen atmosphere (achieved by N_2 flux saturation of the sample-containing cuvette).[42i] By contrast, the lowest emission was observed when the F-AM sample was excited in a 100% oxygen atmosphere (Figure 6c).[20−22] These experiments clearly show the dependence of the F-AM PL emission upon the oxygen concentration. In fact, measurements in air gave intermediate PL intensity (Figure 6b).[42i] Experiments changing the exposition atmosphere of the F-AM have shown that the obtained results are highly reproducible, thus confirming the reversibility of the present system.

C_{60} fluorescence has been observed and distinguished from phosphorescence, being the latter in the region above 800 nm.[42h,l,48] On the basis of these already reported data, the present observed PL should be assigned to a fluorescent emission. However, as can be seen in Figure 6, the oxygen presence influences considerably the quantum yield.

Generally, because of short radiative lifetime, the fluorescence emission is not significantly quenched by molecular oxygen. Although our study is not really concerned with kinetic measurements, to explain the remarkable and reversible quenching of fluorescence presently observed, according to an already reported model,[49] we suppose an equilibrium between fullerene, molecular oxygen, and their nonfluorescent adduct:

$$\text{fullerene} + O_2 \leftrightarrow \text{fullerene}\cdot O_2$$

$$\frac{F_0 - F}{F} = \frac{\alpha}{1-\alpha} = K[O_2]$$

where F and F_0 represent fluorescence in the absence and presence of the quencher, respectively, α is the nonfluorescent adduct fraction, and K is the equilibrium constant for the adduct formation.

This evident sensitivity of the fluorescence of present F-AM to the molecular oxygen concentration represents a further interesting property of this system.

Conclusions

In conclusion, a new assembled fullerene monolayer on silica substrates was synthesized and characterized. Both static and dynamic contact angle measurements confirmed the hydrophobic character of the silica surfaces upon the fullerene linkage. Atomic force microscopy and lithography showed the surface structure and the dimension (19 Å) of grafted molecules. UV−visible spectra confirmed the presence of fullerene molecules on the silica surfaces. Oxygen-sensitive photoluminescence spectra have been obtained. To the best of our knowledge, our results represent the very first report on the luminescence of only one fullerene monolayer.

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