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Abstract

Molecular self-assembly is considered as a promising way to control the manufacture of new materials and their integration into hybrid devices with novel properties. In this work we have synthesized a fulleropyrrolidine bearing a phenylacetylene moiety via the Prato reaction. The characterization of the fulleropyrrolidine by nuclear magnetic resonance and optical spectroscopy is reported, and its self-assembly by crystallization study has been investigated according to the used solvents. If the solvent that effectively solubilizes fullerene derivative is tetrahydrofurane, the nano-square plates with 1–3 μm in length and 50–100 nm in thickness are formed, while if the solvent is toluene, 5 μm diameter 'nano-flowers' are obtained.

Keywords: fullerene, fulleropyrrolidine, self-assembly, nano-square plate, nano-flower
Classification numbers: 4.00, 4.03

1. Introduction

During the last fifteen years, fullerene-based supramolecular assemblies have been extensively investigated. C_{60} is a highly hydrophobic molecule with a perfect icosahedral symmetry. It also possesses exceptional photophysical properties and low reorganization energy [1]. All these properties make fullerene an ideal candidate for a large number of applications such as solar cells [2, 3], organic light-emitting diode (OLED) [4], organic field-effect transistor (OFET) [5, 6]. The high performance of these optoelectronic devices is often conditioned by supramolecular organized structures of fullerene-based materials. So it is the key to mastering the aspects of supramolecular organization in organic optoelectronic devices.

The first example of fullerene-based supramolecular assemblies was the complexation of C_{60} with molecular building blocks that favor the formation of inclusion complexes [7]. Later, by using classical covalent functionalization to make more sophisticated C_{60} structures, the size, order, and complexity of the supramolecular assemblies continuously increased. This method has led to, for example, fullerene-based micelles, vesicles, and aggregates [8–18], polymers [19–25], and liquid crystals [26–35], as well as the organization of fullerene on electrode or nanoparticle surfaces [36–38].

In this paper we explore the self-assembling properties of a fulleropyrrolidine functionalized with a phenylacetylene moiety via the Prato reaction. The characterization of this compound by nuclear magnetic resonance (NMR), optical spectroscopy, x-ray diffraction as well as microscopy allowed identifying the interactions that lead to self-assembly properties.

2. Experimental

2.1. Material

C_{60} (99.9%) was purchased from MER Corporation. Chemicals were purchased from Aldrich and were used as-received. Solvents were purchased form Aldrich or VWR and
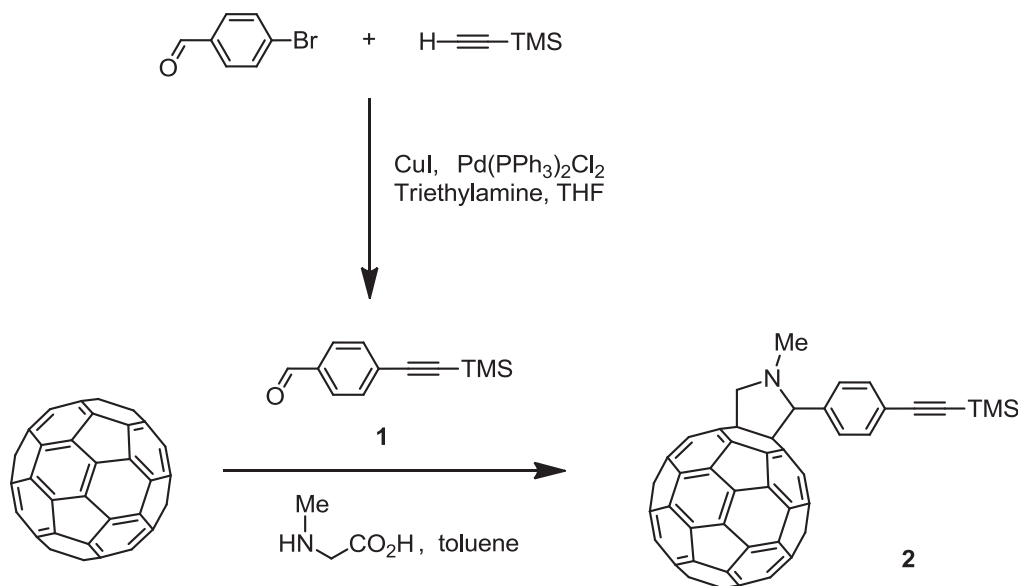
Scheme 1. Reagents and conditions of synthesis of fulleropyrrolidine.

were used as-received. For synthesis, CH_2Cl_2 (CaH_2, N_2), toluene (K/benzophenone, N_2), tetrahydrofuran (THF) (K/benzophenone, N_2) were distilled before use.

2.2. Synthesis of fulleropyrrolidine

The Prato reaction [39] is an example of cycloaddition [3 + 2] from the azomethine ylides which are highly reactive 1,3 dipoles. The ylide is generated *in situ* after decarboxylation of iminium salts obtained by condensation of amino acids and aldehydes. These ylides react with the C_{60} to form fulleropyrolidines. The synthesis of fulleropyrrolidine 2 is described in scheme 1; it is obtained by condensation of 4-(2-trimethylsilylethynyl)benzaldehyde 1 [40] and *N*-methylglycine onto C_{60}.

4-(2-trimethylsilylethynyl)benzaldehyde 1 was synthesized by Sonosashira coupling of 4-bromobenzaldehyde and trimethylsilylacetylene: To a stirred mixture of 4-bromobenzaldehyde (9.25 g, 50.0 mmol), CuI (380 mg, 2.0 mmol), and $Pd(PPh_3)_2Cl_2$ (700 mg, 1.0 mmol) in 50 mL of THF was added triethylamine (10.1 g, 75.0 mmol). A solution of trimethylsilylacetylene (5.15 g, 52.5 mmol) in 10 mL of THF was then added over one hour. The solvent was evaporated, and the residue was treated with pentane. The filtration through Celite and evaporation of the solvent yielded compound 1.

Fulleropyrrolidine 2: C_{60} (50 mg, 0.069 mmol) was dissolved in dry toluene 50 mL and then 4-(2-trimethylsilylethynyl)benzaldehyde (14 mg, 0.069 mmol) and *N*-methylglycine (62 mg, 0.693 mmol) were added. The mixture was stirred overnight at reflux, and then evaporated to dryness. The purification of the residue by column chromatography (eluent toluene) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH) gave pure 2 as a brown powder.

2.3. Techniques

Absorption spectra were recorded in quartz cuvettes on a Perkin–Elmer Lambda 900 UV-Vis-NIR spectrophotometer. ^{1}H NMR spectra were recorded with a Bruker ac-300 (300 MHz) spectrometer with solvent used as internal reference; MS (MALDI-TOF) spectra were recorded with a PerseptiveBiosystems Voyager DE-STR spectrometer. Scanning electron microscopy (SEM) measurements were performed using a Hitachi S4500 microscope. Molecular modeling was performed using the HyperChem software in conjunction with the MM+ method.

3. Results and discussion

3.1. UV-visible absorption spectra

The UV-visible absorption spectra of fulleropyrrolidine 2 in toluene shows two-band characteristics: a narrow and intense peak at 430 nm and a broad band around 700 nm, as shown in figure 1. These peaks are characteristic of fulleropyrrolidine monoadducts [39].

3.2. ^{1}H NMR spectra

Due to the low solubility of compound 2 in CDCl$_3$, the signal-to-noise ratio of the NMR spectrum is not very good, but can be observed in the region between 4–5 ppm three protons belonging to the pyrrolidine (enlarged view of ^{1}H NMR spectra shown in 4–5 ppm) (figure 2). We note that the four aromatic protons resonate at 7.50 and 7.73 ppm. The signals of these protons should be doublets any time; because of the presence of the fullerene, they appear as a broad signal. The protons of NCH_3 resonate at 2.76 ppm and the protons of Si$(CH_3)_3$ at 0.2 ppm.
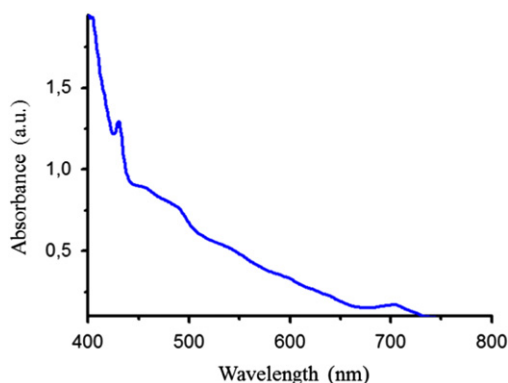
Figure 1. UV–visible spectra of fulleropyrrolidine 2 in toluene.

3.3. Self-assembly and SEM photographs

We started by investigating the self-assembly properties of fulleropyrrolidine 2. The sample was dissolved in THF at a concentration of 1 mM, 500 μl of this solution was filled into NMR tube and acetonitrile (AcCN) was slowly added to the top of the tube. This tube was capped and the solution was left two days to allow the slow diffusion of AcCN in THF. After two days at room temperature, the formation of precipitate is observed. The suspension was then homogenized and a drop was deposited on a silicon substrate to be imaged by SEM (scheme 2). Figure 3 shows a typical example of the images obtained: nano-square plates with 1–3 micrometers in length and 50–100 nm in thickness.

Nakanishi has extensively studied the different architectural aspects of fullerene self-assembly as a function of the solvents. They showed that very simple molecules can give rise to a wide variety of assemblies according to the solvents used [12]. The difference of organization results from the balance between the 'good' and 'bad' solvents for fullerene in the mixture. Therefore, we decided to explore the difference between two 'good' solvents of the fulleropyrrolidine 2. We solubilized compound 2 in toluene and then AcCN was added. After seven days, the suspension was imaged by SEM, figure 4 shows the type of assemblies obtained: 'nano-flowers' with about 5 microns in diameter. It is worth mentioning that toluene is a good solvent for both unfunctionalized fullerene and for compound 2 while THF is able to solubilize only the fulleropyrrolidine derivative. The different interactions of the toluene and THF with the fullerene part of 2 are certainly responsible for the difference of supramolecular organization.

3.4. X-ray diffraction and discussion on the formation of precipitate

To understand the organization of molecules in the nano-plates and in the nano-flowers, the precipitates were studied by x-ray diffraction. The diffraction pattern of 2 in the nano-plates (figure 5(a)) shows three reflections, $d_1 = 21.675$ Å; $d_2 = 10.77$ Å and $d_3 = 7.085$ Å. These reflections, with a spacing ratio 1:2:3, indicate a long-range lamellar organization of the C_{60} moieties with an average lamellar periodicity of
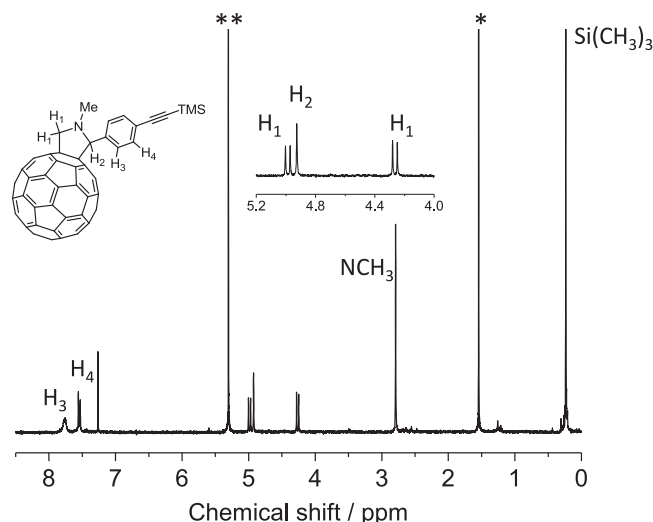

Figure 2. ^{1}H NMR Spectra of fulleropyrrolidine 2 in CDCl$_3$ (** CDCl$_3$, * H$_2$O) ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.72$ (br, 2H; arom. H), 7.51 (d, J = 8.7 Hz, 2H; arom. H), 4.94 (d, J = 9.3 Hz, 1H; H pyrrolidine), 4.89 (s, 1H; H pyrrolidine), 4.23 (d, J = 9.6 Hz, 1H; H pyrrolidine), 2.76 (s, 3H; NCH$_3$), 0.20 ppm (s, 9H; SiMe$_3$); FTIR (KBr): $\tilde{v} = 2948, 2779, 2155, 1500, 1462, 1427, 1331, 1246, 1216, 1122, 1103, 864, 842, 758, 704, 582, 552, 526$ cm^{-1}; UV/Vis (toluene): $\lambda_{max} = 328, 432, 703$ nm; MS (MALDI-TOF): m/z calculated for $C_{74}H_{19}NSi$: 949.13 [M-H]$^+$; found: 948.13.
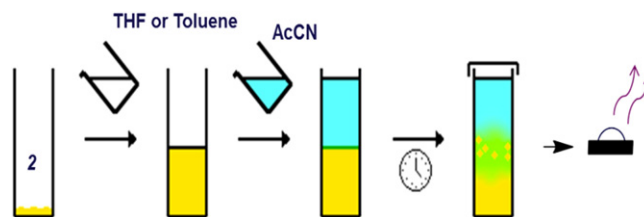

Scheme 2. Crystallization study of fulleropyrrolidine 2.

$d = 21.5$ Å. Other reflections, typically (hkl) with h, k or l indices simultaneously non-zero, reflect three-dimensional extension of the supramolecular nanostructure. In the same way, the diffraction pattern of the nano-flowers shows three reflections, $d_1 = 24.4$ Å, $d_2 = 12.18$ Å and $d_3 = 8.16$ Å (figure 5(b)). These three reflections show once again the lamellar organization of the fulleropyrrolidine in the nanostructures.

By molecular modeling, we estimated that the length of a molecule of 2 is 17.7 Å (figure 6(a)). The interlamellar distance of about 21.5 Å and 24.4 Å in the nano-plates and the nano-flowers, respectively, do not correspond to either the length of a molecule or the length of an interdigitated bilayer of 2 (26.4 Å—figure 6(b)). It is therefore inferred that the molecules are inclined about 35° in the layers of the nano-plates and 22° within the layers of the nano-flowers (cosα = $d/26,4$) (figure 6(c)).

'Nano-flowers' assemblies have been obtained by Nakanishi *et al* by slow cooling of a solution of fulleropyrrolidine containing long alkyl chains in 1,4-dioxane at 60 °C to 5 °C [41]. They explained the formation of these
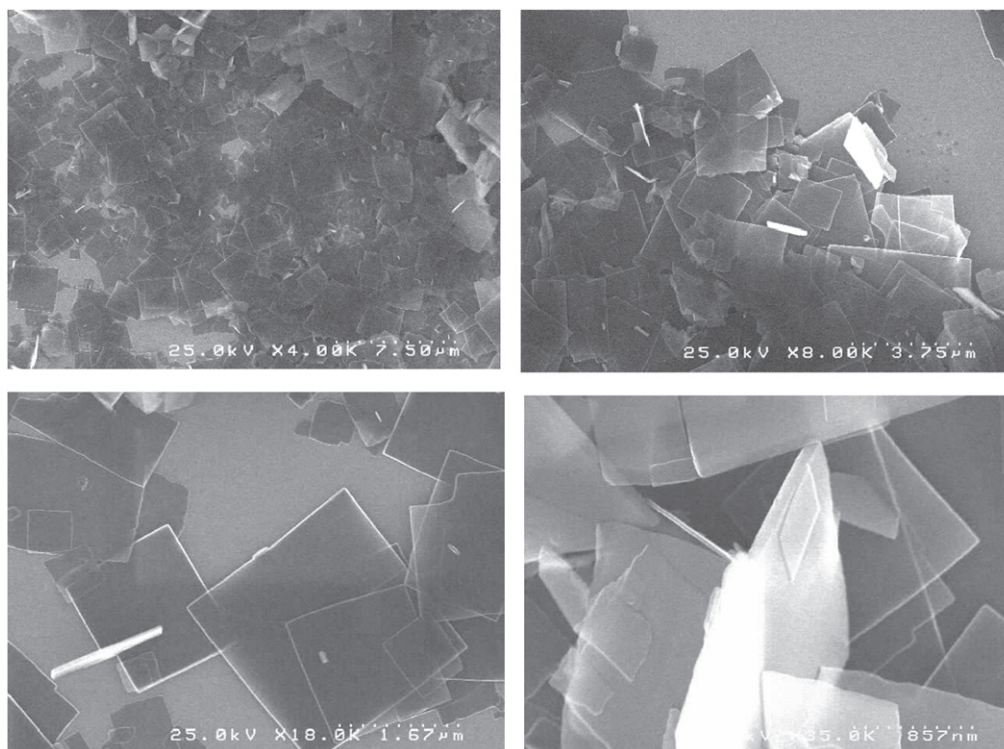
Figure 3. SEM images of nano-plates obtained by self-assembly of fulleropyrrolidine 2 in the mixture of THF/AcCN.
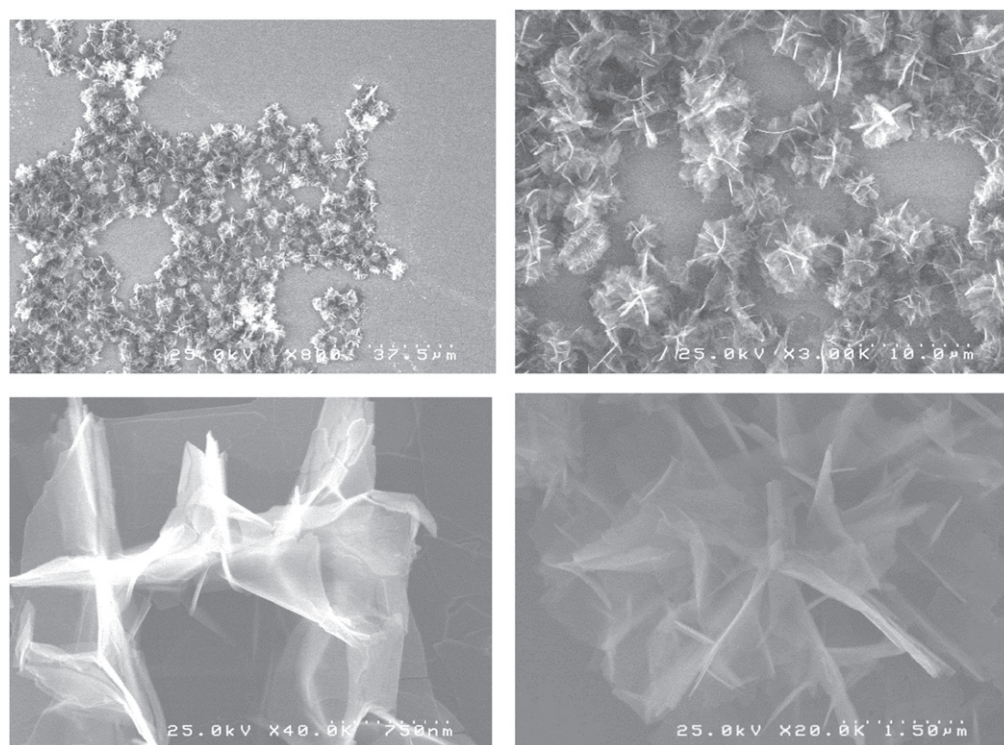

Figure 4. SEM images of nano-flowers obtained by self-assembly of fulleropyrrolidine 2 in the mixture of toluene/AcCN.

objects by the successive folding of a very thin film of molecules.

4. Conclusion

We have described herein the synthesis and characterization of fulleropyrrolidine monoadduct bearing a phenyl-trimethylsilylacetylene moiety formed by Prato reaction. The

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K H Le Ho and S Campidelli
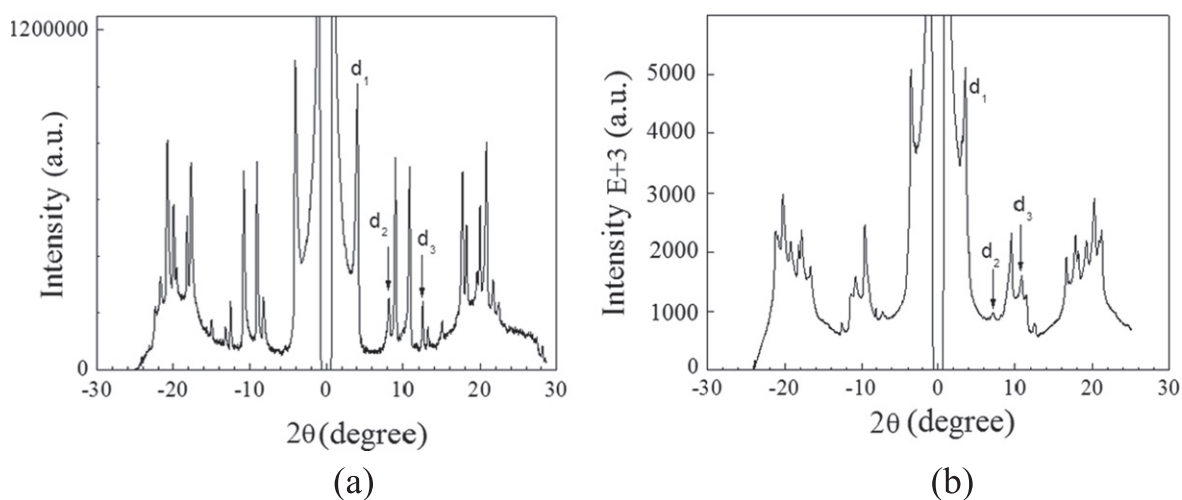
Figure 5. Small-angle x-ray diffractogram of the nano-plates (a) and the nano-flowers (b) formed by fulleropyrrolidine 2.
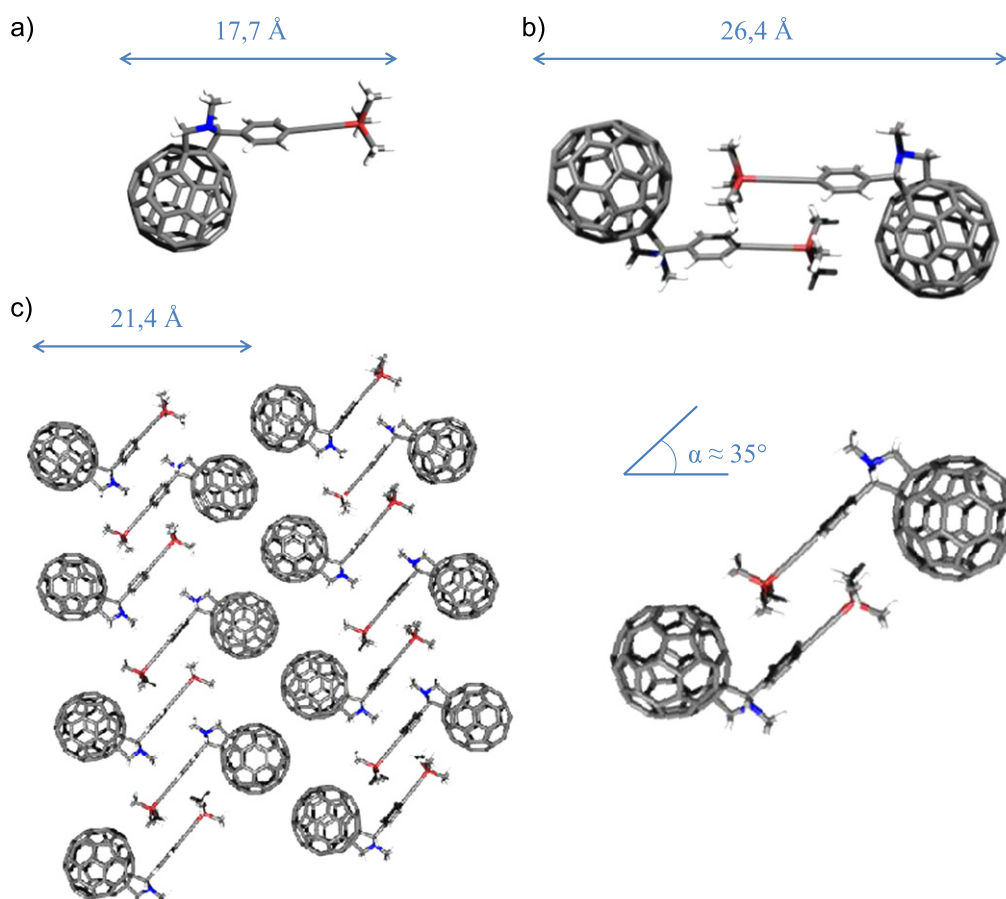
Figure 6. Estimated length of **2** (a) and an interdigitated bilayer of 2 (b); representation of the organization of 2 in the bilayers of nano-plates (c).

self-assembly properties of the fulleropyrrolidine derivative have been investigated. The formation of the nano-plates and 'nano-flowers' seem more dependent on the interactions of the molecules with the solvent than the interactions between molecules themselves. Indeed, the organization is governed by the careful balance between 'good' and 'bad' solvents for the fullerene derivatives.

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K H Le Ho and S Campidelli

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