

Self-organization of a new fluororous porphyrin and C₆₀ films on indium-tin-oxide electrode†

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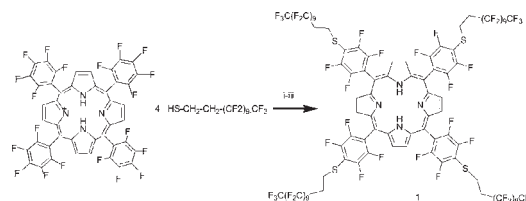
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The highly fluorinated alkyl moieties of a new porphyrin drive the self-organization of thin films with C₆₀ on ITO electrodes.

The supramolecular self-organization of porphyrin derivatives on conductive surfaces has been widely investigated^{1–7} because they are promising building blocks for the fabrication of photoactive materials. There are numerous studies on the spontaneous interactions between the pi system of the porphyrin macrocycle and the curved surface of a fullerene.^{8–10} The porphyrin–fullerene complexes are appealing as materials for solar-energy conversion and energy storage because they can form long-lived charge separated states. The large spherical shape and polarizability of C₆₀ make it an excellent π -acceptor molecule.¹¹ Moreover, because of the small reorganization energy involved in electron transfer reactions (ET), the charge transfer complex formed between C₆₀ and a porphyrin can be remarkably stable.¹² The oxidation and reduction potentials as well as the photophysical properties of porphyrins can be dictated by a variety of means such as metal coordination and exocyclic groups. While the porphyrin macrocycle is a good electron donor/acceptor, it is remarkably robust to oxidative damage, *e.g.* as films on surfaces.¹³ However, most of the exocyclic groups used to self-assemble and/or self-organize porphyrins can be oxidized, thus causing disassembly or reorganization of porphyrinic materials. Thus in applications wherein the nano-architecture of the chromophores is essential for the function of the materials, oxidation of the peripheral functional groups poses a limitation to their usefulness as a photoactive material. This latter consideration then limits the use of many porphyrinoid systems in photonic materials under ambient conditions.

Herein the facile synthesis of a new highly fluorinated porphyrin that forms robust self-organized thin films with fullerene C₆₀ on indium-tin-oxide coated glass is presented. The C–F bond imparts stability to the exocyclic groups, and the small polarizability of fluorine atoms confers a low surface energy to materials¹⁴



Scheme 1 Reagents and conditions: (i) ethyl acetate–DMF (2 : 1 v/v); (ii) DEA; (iii) nitrogen, room temperature, 5 min, 97% yield.

composed of this porphyrin. 5,10,15,20-Tetrakis[4-(1'*H*,1'*H*,2'-*H*,2'*H*-perfluorododecyl)-2,3,5,6-tetrafluorophenyl]porphyrin (TPPF₁₀₀) **1** is readily synthesized by reacting 5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrin (TPPF₂₀) and 1*H*,1*H*,2*H*,2*H*-perfluorododecane-1-thiol (Scheme 1). The high yield and purity minimize the need for column chromatography. Compound **1** was crystallized from acetone in the form of purple hexagonal plates, in the triclinic crystal system, space group *P* $\bar{1}$ (Fig. 1).[†] This molecule has internal crystallographic symmetry. One half of the molecule is related to the other half by inversion symmetry. The strong intermolecular forces between the fluorinated alkanes appended to the porphyrin mediate the formation of a densely packed material as seen in the packing diagram. Similar dispersion interactions allow formation of robust thin films on surfaces¹⁵ (see below). Note the preference for the extended conformation of the fluororous alkane moieties, and that the 0.52 nm spacing between porphyrins indicates pi–pi interactions

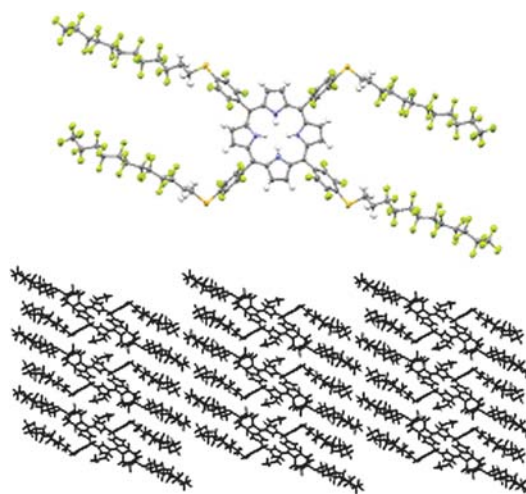


Fig. 1 Ellipsoid model of TPPF₁₀₀ **1** (above) and its packing diagram (below), 50% probability level.

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between the chromophores. The interactions between some of the fluoroalkanes in the crystal are strong enough to force two of the opposing aryl groups to adopt a 60° dihedral angle relative to the porphyrin, whereas for the parent TPPF₂₀ these are at 90° because of steric interactions between the pyrrole βH and the ortho F groups.

UV-visible spectroscopy of the interaction between **1**§ and fullerene C₆₀ was first studied in solution at the greatest concentrations allowed by the solubility of the compounds; however, the electronic spectrum of the complex is the sum of the spectra of the individual chromophores, which is consistent with previous reports.¹⁶ Nonetheless, the interaction between the two chromophores in the solid state can be substantially greater.⁸ The interactions and electronic communication between the chromophores in the solid state such as thin films are readily observable by fluorescence spectroscopy and microscopy. Therefore we have developed a means for forming a co-deposited film of **1** and C₆₀ on indium-tin-oxide (ITO) by immersing the electrode in a solution containing both (6 × 10⁻⁵ M each) at room temperature. CCl₄ is a good solvent in which both the chromophores are soluble together at concentrations up to ca. 10⁻⁴ M. Deposition from half this concentration results in similar films.

The pale orange 6 × 10⁻⁵ M solution of **1** in CCl₄ was prepared just prior to use. The solution of C₆₀ was prepared by sonication in CCl₄ (1 mg/4 mL) for 3 h to yield a pale purple solution that was filtered. All concentrations were determined using the extinction coefficients.¹⁷ The 1 : 1 mole ratio solution of **1** and C₆₀ was prepared by mixing the two solutions in the proper ratio and the final concentration of each was determined. The thin films samples were prepared on a slide of ITO coated glass that had been ozone cleaned, rinsed with ethyl alcohol and thoroughly washed with nanopure water. After drying, the slide was immersed vertically into the solution of **1** and C₆₀ for 60 min, dried vertically in air, and then rinsed with nanopure water. The ITO coated slide was imaged by atomic force microscopy (AFM) before and after immersion.

In addition to intermolecular interactions, solvent, concentration, evaporation rate, surface properties, and mode of deposition combine to dictate the morphology of self-organizing systems on surfaces.^{18,19} In this case the fluorinated alkanes drive the formation of the thin films with C₆₀, since similar films are not observed using an analogue with hydrocarbon chains and the same deposition conditions, *vide infra*. In order to assure the same amount of **1** is deposited in all the experiments, UV-visible spectra were recorded after each immersion. The Soret band of **1** on ITO is weakly red-shifted to 422 nm. The fluorescence of **1** is strongly quenched in the presence of C₆₀ in the self-organized thin film on the substrate (Fig. 2). These data can be interpreted as photoinduced electron transfer from the porphyrin to the fullerene, as observed previously for por-C₆₀ systems.^{10,11,20}

In order to characterize the morphology and the thickness of the films, AFM studies of the films on the substrates were conducted. As expected, AFM experiments reveal that the overall morphologies of the films of **1** alone and the film from dipping in the **1**-C₆₀ mixture are significantly different. The morphology of the material deposited on ITO (rms roughness of 0.5 nm) from immersion in a 6 × 10⁻⁵ M solution of **1** in CCl₄ appears as irregular flat domains of different horizontal and vertical sizes. Similar immersions in C₆₀ yield sporadic aggregates. Conversely, immersion in a solution containing both components results in

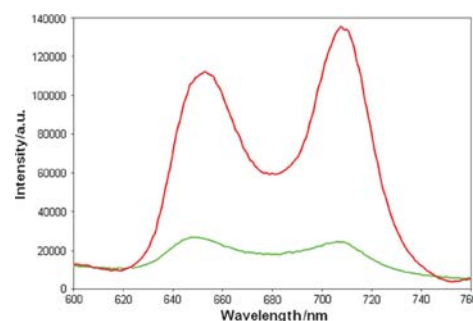


Fig. 2 Fluorescence spectra of film of **1** on ITO (red) and film of **1**-C₆₀ formed by dipping the ITO into a 1 : 1 solution once (green). Spectra are normalized to porphyrin absorption at the 422 nm excitation and baselines are corrected.

thin films with a granular morphology. In order to determine the thickness of the **1**-C₆₀ film, a 4 μm² well was shaved on the surface using a contact mode imaging tip and applying a force equal to 619 nN. The well was then imaged in tapping mode. Three nanoshaving experiments were conducted on each of five films prepared by the same methods, and the average thickness of the films was 7 ± 0.4 nm. Due to the asperities in the substrate and film surfaces (film rms roughness of ca. 1 nm), the averages of each were used, as calculated by the Veeco software.

A second dipping in the 1 : 1 solution yields ca. 12 nm thick films with analogous granular morphologies which is consistent with the ca. double absorbance of the Soret band. A second deposition of only **1** yields more complete films with similar flat topologies. Further dipping of either does not add any materials to the substrate (supporting information).†

AFM in combination with laser scanning confocal microscopy was used to correlate film morphology to photonic activity of the material. For films of **1** only on ITO, the intensity of the fluorescence is inhomogeneously distributed across the ITO surface. Areas with strong fluorescence have corresponding AFM images that show large flat domains, with an average lateral dimension of 1.5 μm, and smaller flat domains, with an average lateral dimension of 33 nm. There is a paucity of any material observed on the substrate when only C₆₀ is in the dipping solution. In contrast, when the ITO is immersed in a 1 : 1 solution of **1**-C₆₀, a thin film is formed (Fig. 3), with characteristic features observed neither for **1** nor for C₆₀ alone. The co-deposition of **1** and C₆₀ results in films with a high coverage and granular texture on ITO surfaces. Consistent with the fluorescence spectra of the films (Fig. 2), the confocal fluorescence microscopy reveals that the porphyrin fluorescence is strongly quenched. Thus both the AFM and fluorescence experiments confirm that the C₆₀ resides close to the porphyrin and that the two components do not separate into domains of each. This observation indicates that the interactions between TPPF₁₀₀ and C₆₀, which are expected to increase significantly as the solvent evaporates, dictate the morphology of the material deposited onto the ITO surface and the photophysical properties are consistent with other solid state porphyrin-C₆₀ constructs.⁸

Larger AFM scans at multiple positions of the co-deposited film indicate the morphology persists over large areas. Samples stored in air and ambient light are stable for more than one month with no observed decomposition of the chromophores indicated by UV-visible spectroscopy. Considering the previous

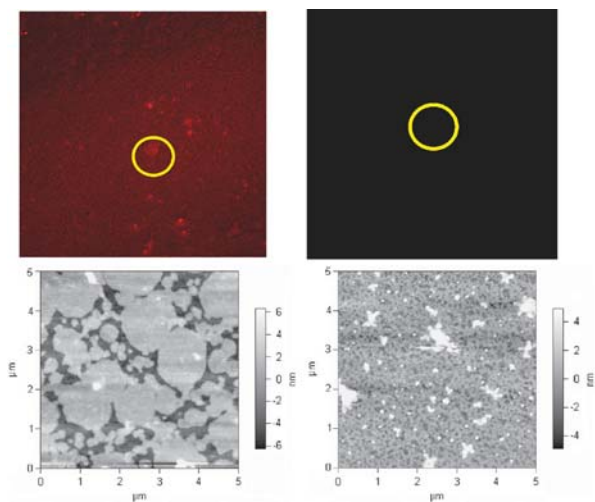


Fig. 3 Combined laser scanning and atomic force microscopy characterization of films. Left: deposition of **1** on ITO results in an incomplete film with observable fluorescence (top left) and corresponding flat features (bottom left). Right: deposition from a 1 : 1 solution of **1** and C₆₀ in CCl₄ results in a high coverage film with no observable fluorescence (top right) and a granular topology (bottom right). Confocal data: all samples excited with a 488 nm laser. Five frames (317.2 × 317.2 μm, 60× objective) were collected and averaged in order to reduce background noise. AFM data: all samples were imaged with a Park 0.1 silicon nitride tip ($k = 0.1 \text{ N m}^{-1}$) in contact mode.

crystallographic data,⁹ one possible molecular arrangement is with C₆₀ sandwiched between porphyrin molecules. Using the crystal data (fullerene diameter of 0.75 nm, and a porphyrin–C₆₀ distance of 0.26 nm) a 7 nm thick film would have *ca.* seven layers. Alternatively the C₆₀ could reside between the fluorinated chains. Since sequential dipping of the substrate in separate solutions of **1** and C₆₀ does not lead to films, there must be some intermolecular interactions and pre-organization in the evaporating solvent during deposition beyond π -stacking.

To understand the role of the fluorocarbon chains, the corresponding porphyrin bearing four hydrocarbon chains of the same length was synthesized (compound **2**, see supporting information).[†] The same co-deposition experiments with **2** and C₆₀ on ITO were conducted, and quite different results were found. Though UV-Vis data indicate the presence of some **2**–C₆₀ material on the surface, AFM experiments demonstrated that thin films are not formed, but only sporadic, amorphous aggregates. To compare the robustness of the two surface deposited films, the slides were sonicated in water and in 50 mM NaCl aqueous solution for 10 min. Remarkably, UV-Vis spectra show that only *ca.* 5% of the **1**–C₆₀ film is removed while nearly 70% of the **2**–C₆₀ film is lost and the presence of the fullerene is barely detectable. This indicates that the increased intermolecular interactions of the fluorocarbon moieties between the porphyrins and with C₆₀ and the surface drive the self-organization of these films.

In conclusion we synthesized a new porphyrin bearing fluorinated alkanes through a facile and efficient procedure. The properties of the fluoroalkane groups allow the porphyrin chromophore to self-organize with C₆₀ via a co-deposition process into thin films. The films are characterized by significant quenching of the porphyrin fluorescence by electron

transfer to the fullerene.²¹ The photoelectrochemical properties of this film will be the subject of further studies.

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Notes and references

[†] Crystallographic data for **1**. C₉₂H₂₆F₁₀₀N₄S₄·4C₂H₆O, $M = 3447.72$, $T = 100 \text{ K}$, triclinic, $P\bar{1}$, $a = 9.3570(19)$, $b = 10.938(2)$, $c = 30.832(6) \text{ \AA}$, $\alpha = 87.69(3)$, $\beta = 88.34(3)$, $\gamma = 77.12(3)^\circ$, $V = 3073.1(11) \text{ \AA}^3$, $Z = 1$, $D_c = 1.863 \text{ g cm}^{-3}$, $\mu = 0.284 \text{ mm}^{-1}$, $F(000) = 1698$, crystal $0.20 \times 0.20 \times 0.08 \text{ mm}^3$, $\theta_{\text{max}} = 27.56$, ranges $-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-39 \leq l \leq 38$, $R_{\text{int}} = 0.086$, $wR_2 = 0.191$, reflections collected = 12247, independent reflections = 6936, parameters = 973.

[‡] The electronic spectrum of **1** in CCl₄ displays a Soret band (417 nm, $\epsilon = 246\,000 \text{ M}^{-1} \text{ cm}^{-1}$) and four Q-bands (509 nm, $\epsilon = 16\,400 \text{ M}^{-1} \text{ cm}^{-1}$; 538 nm, $\epsilon = 1840 \text{ M}^{-1} \text{ cm}^{-1}$; 587 nm, $\epsilon = 4800 \text{ M}^{-1} \text{ cm}^{-1}$; 639 nm, $\epsilon = 229 \text{ M}^{-1} \text{ cm}^{-1}$).

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