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Two-dimensional self-organization of rectangular OPE amphiphiles into microcrystalline lamellae†

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Nanographite-like lamellae are obtained by the self-assembly of rectangular OPE amphiphiles peripherally decorated with polar and paraffinic chains.

The self-assembly of biomolecules, bio-inspired compounds or synthetic building blocks to form complex supramolecular structures is being utilized for the fabrication of optoelectronic devices or for biomedical purposes.[1,2] Monodisperse amphiphilic π-systems self-organize into a variety of structures due to their highly reproducible and dynamic self-assembly.[3] The final morphology and the function exerted by the aggregated species are conditioned by the hydrophilic/hydrophobic ratio and also by subtle changes in external factors like concentration and/or polarity of the solvent.[3] In this regard, most of these objects self-assemble into one-[4,5] or three-dimensional architectures.[6,7] Nonetheless, fewer examples have been reported on the anisotropic aggregation of amphiphiles to form two-dimensional (2D) structures despite their potential applicability to develop nanocargos for drug delivery,[2] or highly organized active layers in organic electronics.[8] Many of the reported 2D networks have been prepared from peptidic building blocks,[9] whilst those obtained from synthetic starting materials have been studied to a lesser extent.[10]

Herein, we report on the spontaneous assembly of rectangular amphiphilic oligo(phenylene ethynylenes) (OPEs) into nanographite-like microcrystalline 2D networks guided by a delicate synergy of π–π stacking, solvophobic and van der Waals interactions. Amphiphiles **1** and **2** are based in the 1,2,4,5-tetrakis(2-phenylethynyl)benzene aromatic backbone and are peripherally substituted with two aliphatic decyloxy and two polar oligoether chains of different length (Fig. 1). Compounds **1** and **2** were readily obtained starting from previously reported 1,2-dibromo-4,5-diiodobenzene.[11] The different chemoselectivity of bromine and iodine atoms under Sonogashira–Hagihara conditions has allowed the modulated peripheral substitution with aliphatic and polar chains (see Scheme S1†).[12] Compounds **1** and **2** have been fully characterized by a number of spectroscopic techniques (see ESI†). The two sharp IR bands corresponding to CH_2 stretching vibrations that appear at 2920 (ν_{anti}) and 2852 (ν_{sym}) cm^{-1} (Fig. S1†) are diagnostic of interdigitation of the alkyl chains and can be considered a first indication of the formation of organized structures from amphiphiles **1** and **2**.[1b,4b]

The aggregation features of compound **1** in solution have been studied by concentration-dependent UV-Vis experiments in polar 2-propanol (2-PrOH) and apolar methylcyclohexane (MCH) (Fig. S2†). For polar 2-PrOH, the application of the indefinite or isodesmic model to the molar extinction coefficient[13] gave a binding constant (K_a) value of 3×10^5 M^{-1}. π–π stacking aromatic interactions together with a remarkable solvophobic contribution from the apolar aromatic moiety and the decyl chains account for this high K_a value.[13b] The more favourable solvent–solute interactions and, consequently, reduced solvophobic contribution results in a smaller K_a value of 8.7×10^3 M^{-1} when MCH is utilized. The small size of the ethyleneoxide chains in **2** compared to **1** reduces the K_a value in polar 2-PrOH ($K_a = 1.5 \times 10^5$ M^{-1}) and increases it in apolar MCH ($K_a = 5.7 \times 10^5$ M^{-1}), the trend being similar to that observed for amphiphile **1** (Fig. S2†).

Dynamic light scattering measurements complement the study of the self-assembly of **1** in water solution ($\sim 10^{-5}$ M). The CONTIN analysis of the correlation functions shows three different contributions centered at hydrodynamic radii (R_H) of ~300 nm, ~890 nm and at values higher than ~1 μm (Fig. S3a†), in good agreement with referable systems.[10a] The diffusion coefficient value has been accurately calculated as 0.276×10^{-8} cm^2 s^{-1} for the contribution centered at ~890 nm, which represents ~85% of the population, by

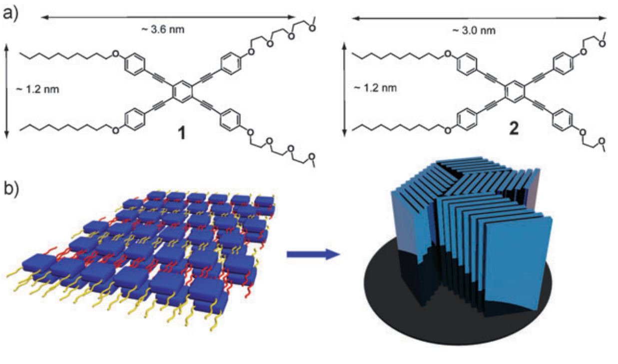

Fig. 1 (a) Chemical structure and molecular dimensions of **1** and **2**. (b) Illustration of the anisotropic 2D self-assembly of **1** and **2** to form microcrystalline lamellae.

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a linear fit to a plot of the inverse of time versus the square of the scattering vector (Fig. S3b†).

Unlike our previously reported rectangular OPE decorated with four peripheral TEG chains, which form vesicles or toroids from polar solutions,[6b] the anisotropic self-organization of **1** onto surfaces forms microcrystalline lamellar superstructures that can be visualized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. A number of thick stratified sheets, distributed on large areas of the surface, have been observed when a $\sim 10^{-5}$ M solution of **1** in water is utilized (Fig. S4a and S5†). The amphiphilicity of **1** also allows the formation of overlapped polyhedral lamellae, thinner than those observed for water, by using a solution of **1** in apolar MCH at $\sim 10^{-4}$ M (Fig. S4b and S6†).

The different thicknesses of the 2D sheets observed in both water and MCH could be justified by considering the higher fraction of *n*-mer aggregates (α_n)[6b,13] (Fig. S4c†) and average amphiphile number per stack (N)[6b,13] (inset in Fig. S4c†) calculated for polar 2-PrOH in comparison with MCH. The lower α_n and N values determined for **1** in MCH could also be related to the appearance of the sheets at the edge of the deposited droplet onto the surface. In these regions, the dewetting process that increases the local concentration in these areas results in an enhanced self-assembly process of compound **1**.[14] The dewetting process has been confirmed by confocal fluorescence microscopy (Fig. S7a†). Light irradiation of a droplet of a $\sim 10^{-4}$ M solution of **1** in MCH deposited onto a glass plate generates rapid evaporation of the solvent that gives rise to concentric circular regions with a high population of fluorescent objects. An expanded view of these objects demonstrates the formation of overlapping sheets (Fig. S7b†).

The strong tendency of compound **1** to form 2D supramolecular structures has been confirmed by TEM imaging either from cryo-ultramicrotomed films or from $\sim 10^{-5}$ M aqueous solution. TEM images of microtomed films of untreated **1** embedded into an epoxy resin show dark fringes of different thicknesses. Several of these fringe regions are constituted of thin 2D lamellae of around 10 nm thickness (Fig. S8†). Further evidence of the anisotropic 2D aggregation of **1** into sheets has been extracted from TEM micrographs obtained from $\sim 10^{-5}$ M aqueous solutions of **1**. These images show flat and stratified lamellae with a high degree of crystallinity (Fig. 2 and Fig. S9†). In fact, the electron diffraction pattern shows concentric and dotted rings at 2.1, 1.2, 1.0, 0.8, 0.7 and 0.6 nm (Fig. S10†). Unexpectedly, the TEM image in Fig. 2a also presents areas identified as Moiré fringes that result from overlapping and rotated 2D crystalline layers formed upon self-organization of **1** in aqueous solution (Fig. 2a). Despite the fact that Moiré patterns have been observed for physisorbed atoms or organic molecules by scanning tunneling microscopy,[15a] and for block copolymer assemblies[15b] and single wall carbon nanotubes[15c] by TEM, to the best of our knowledge, this is the first time that this phenomenon has been observed for supramolecular structures formed by aggregation of a discrete amphiphile and it is an unambiguous indication of the extremely high organization levels reached by these 2D sheets. Amphiphile **2** also forms layered architectures, although its low solubility in aqueous solutions requires the use of a THF–H_2O (1 : 1) mixture as solvent to obtain TEM images. Again, these TEM images reveal the presence of stratified sheets (Fig. S11†).

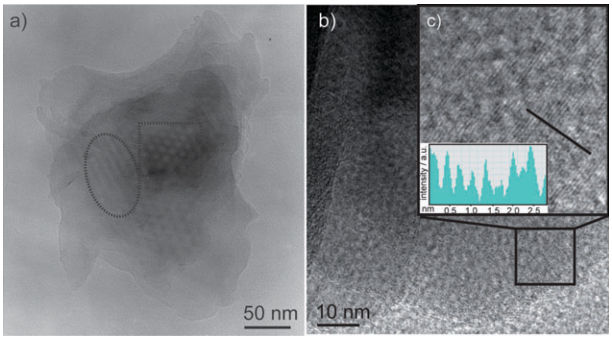

Fig. 2 TEM images showing the 2D sheets formed from **1**. (a) Sheets deposited from $\sim 10^{-5}$ M aqueous solution onto carbon-coated copper grids. (b) HR-TEM images showing several overlapping lamellae. (c) HR-TEM of the expanded region of image (b). The inset in (c) depicts the density profile of the lattice highlighted with the black line.

High resolution TEM (HR-TEM) images confirm the presence of overlapping lamellae of microcrystalline material (Fig. 2b and Fig. S12†). Many regions show layered columnar structures characterized by periods of sublayers with a common stacking direction and separated by ~ 3.5 Å (Fig. 2c and Fig. S11†). This distance, typical of π–π interactions, resembles that observed for nanographenes,[16] which hold great promise for the fabrication of nanoelectronic and spintronic devices.[17]

To investigate the organization of amphiphiles **1** and **2** within the lamellae, we have studied the bulk-state structure of the aggregates by X-ray diffraction experiments. Both **1** and **2** present a high number of reflections (Fig. 3 and Fig. S13 and Table S1 and S2†), those observed at lower angles being diagnostic of lamellar organization.

A two-dimensional oblique network—with lattice parameters of a = 4.8 nm, b = 2.4 nm and γ = 91.5°, for **1**, and a = 3.8 nm, b = 2.2 nm and γ = 92.3°, for **2**—can be assigned upon indexing the observed reflections. These cell

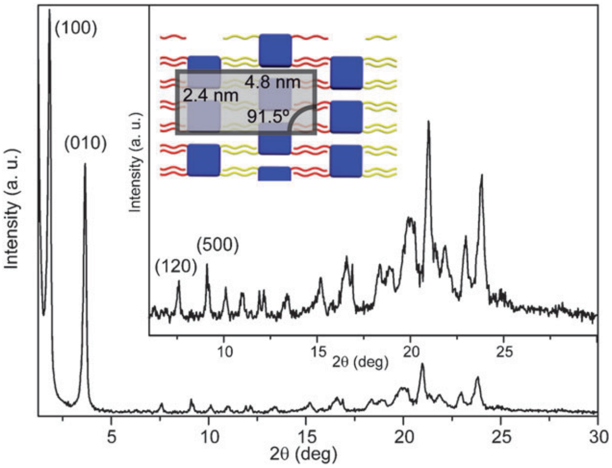

Fig. 3 X-Ray diffraction patterns (298 K) of **1** plotted against the angle 2θ. The inset shows the expanded region of large angles and a schematic illustration of the $p2$ oblique unit cell.

dimensions can accommodate two molecules per unit cell if they have opposing orientations and if there is some interdigitation of the coincident lateral chains (insets in Fig. 3 and Fig. S13†). This organization makes the proposed oblique cell compatible with a *p*2 plane group, although the less symmetric *p*1 plane group cannot be totally ruled out.

For the case of amphiphile **1**, the comparison between the values for the diagonal extracted from the lattice parameters of the *p*2 oblique unit cells (5.45 nm) and that measured from CPK modeling (6.0 nm), suggests some interdigitation of the peripheral chains. Furthermore, the value of 5.45 nm implies a slight coiling of these chains out of the plane. A similar situation can be deduced from the smaller compound **2**. Some of these reflections can also be identified in the electron diffraction pattern extracted from TEM images (Fig. S10†). Finally, both X-ray diffractograms show a clear reflection at a 2θ value of $\sim 23.7^\circ$, which is ascribable to an organized number of lamellae separated by a uniform distance of ~ 3.7 Å and fits well with the typical distance reported for π–π stacking aromatic interactions.[18] Additionally, comparable interplanar distances have been reported for compounds containing the same aromatic backbone.[19] The X-ray diffraction studies reinforce the argument that the self-assembly of amphiphiles **1** and **2** is firstly directed by the interdigitation of their peripheral polar and apolar substituents into lamellae that subsequently grow by means of π–π stacking aromatic interactions to give rise to nanographite-like sheets.

In conclusion, the peripheral decoration of a rigid 1,2,4,5-tetrakis(2-phenylethynyl)benzene moiety with polar TEG and apolar decyl chains results in the anisotropic 2D assembly of these OPE-based amphiphiles to form highly organized microcrystalline lamellae. Unlike many other examples of amphiphilic systems, in which the 2D sheets fold into 3D micelles or vesicles, the tendency of the rod aromatic units and the alkyl chains to crystallize frustrates this folding process. Interestingly, the 2D lamellar organization is observed for both polar and apolar solvents due to the presence of hydrophilic and aliphatic chains. X-Ray diffraction analyses in the bulk-state demonstrate that van der Waals interactions between the peripheral chains give rise to oblique unit cells. The nanosheets thus formed efficiently interact by π–π stacking aromatic interactions and form nanographitic structures that were unambiguously detected by X-ray data and visualized by HR-TEM. The high crystallinity reached by the nanographitic aggregates allows the observation of overlapping sheets that give rise to domains presenting Moiré patterns. The microcrystalline non-covalent 2D sheets formed from the reported amphiphiles could be exploited as the active component in functional supramolecular systems. Work is in progress to evaluate the self-assembling features of these amphiphiles under different experimental conditions and also their photophysical properties.

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