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Self-Assembly of a Triangle-Shaped, Hexaplatinum-Incorporated, Supramolecular Amphiphile in Solution and at Interfaces

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Abstract

The self-assembly and characterization of a novel supramolecular amphiphile built from a new 60° amphiphilic precursor that incorporates hydrophilic platinum(II) metals and hydrophobic dioctadecyloxy chains is reported. The amphiphilic macrocycle and its precursor compound have been characterized by multinuclear NMR spectroscopy, ESI-MS, and other standard techniques. The coacervate morphology of the amphiphile at the liquid–liquid interface has been studied by using confocal optical microscopy and in situ Raman spectroscopy. The self-assembly of the amphiphilic macrocycle at the air–water interface has been investigated through Langmuir-trough techniques. The study indicates the possible formation of surface micelle-like aggregates. The disparity between the experimental molecular areas and those derived from molecular models support the idea of aggregation. AFM images of the surface aggregates show the formation of a flat topology with arbitrary ridgelike patterns. Reasonable molecular-packing arrangements are proposed to explain the molecular organization within the observed structures.

Keywords

aggregates; metallacycles; self-assembly supramolecular amphiphiles; surface micelles

Introduction

The abiological self-assembly through strong, directional, transition-metal–ligand dative bonds allows for the rapid and ready formation of discrete entities with well-defined shapes

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Dedicated to Professor Yitzhak Apeloig on the occasion of his 65th birthday

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200900595>. The IR, ^1H , and ^{13}C NMR spectra of compounds **2**, **3**, **4**, and **6**; ^{31}P NMR spectra of **3**, **4**, **6**, and an illustration of the upfield shift in the ^{31}P signal; ESI-MS of **4** and **6**; optimized geometries of **4** and **6** (coordinates); hysteresis isotherms of **6**; Raman and UV/Vis spectra of **4** and **6**; emission spectrum of **6**; video of confocal z slices; and color versions of Figures 7, 9, and 11 are included therein.

and sizes in essentially quantitative yields.[1] The successful outcome of the coordination motif requires the mixing of appropriate ratios of the rigid complementary building blocks with predefined angles and symmetry. The structural and functional characteristics of the self-assembled metal–organic scaffolds arise from the inherent functionality of the constituent subunits. However, a great number of the self-assembled supramolecular polygons and polyhedra are aesthetic structures, exhibiting little functionality.[2] To adapt the decorative structures into entities with specific applications, metal–organic assemblies are now being constructed with functional groups such as crown ethers,[3a–d] dendrimers,[3e] carboranes,[3f] ferrocenyl units,[3g] and others.[3h–k]

It is well known that amphiphilic molecules self-assemble in solution to form micellar aggregates. However, micelles are also capable of existing at interfaces. The idea of surface micelles in insoluble monolayers has long been predicted.[4a] Utilization of surface-imaging techniques such as atomic force microscopy (AFM) has only recently led to the direct observation of surface micelles that are adsorbed onto solid surfaces from equilibrated solutions. For example, Mann et al.[4b–d] and Ducker et al.[4e,f] employed AFM to reveal the surface micelles on hydrophobic surfaces. Conversely, experimental reports on surface micelles of Langmuir layers are scarce. Eisenberg et al. published the transmission electron micrographs of surface micelles obtained from Langmuir–Blodgett films of a diblock polymer.[5a] AFM studies on stearic acid Langmuir–Blodgett films by Chi et al. revealed micrograins (0.03–0.05 μm) and macrograins ($>2 \mu\text{m}$).[5b] Kato et al. found that there are monodisperse two-dimensional micelles in the spread monolayers of fluorinated long-chain acids by using AFM.[5c] Krafft et al. have reported surface micelles obtained from Langmuir monolayers of a nonpolar semifluorinated amphiphile.[5d] Honglai et al. studied the surface micelles and elaborate interconnected ridges derived from Langmuir films of a cationic dimeric (gemini) surfactant by using AFM.[5e]

Organometallic amphiphiles combine the qualities of a standard amphiphile with the qualities of a built-in transition metal. The amphiphilic balance is achieved either by complexation with ligands that contain hydrocarbon-rich moieties, or by supplying anionic lipophilic additives.[6a,b] The incorporation of a transition metal assists in devising applications based on the geometry, polarizability, redox behavior, magnetism, and catalytic properties of the metal ion.[6c] Extending this concept, the metal-containing building blocks or the complementary ligand donors employed in the coordination-driven self-assembly can be suitably functionalized to provide the amphiphilic metal–organic scaffolds. The preassembled metallacycles might, in turn, self-organize at the air–water interface to form Langmuir layers or self-associate in solutions to form micellar aggregates. There are few reports on the synthesis, aggregation behavior, and applications of amphiphilic metallacycles. Evaporation of an amphiphilic porphyrin from acetone yields globular mesoscopic aggregates.[7a] Ru^{II} -based metallosurfactants in doped mesoporous silicates form surface aggregates at the air–water interface,[7b] whereas wormlike aggregates were found in aqueous solutions.[7c] A ruthenium-based amphiphilic macrocycle with four voluminous hydrophobic groups has been reported to form inverted aggregates in apolar solvents.[7d] Self-assembly of alkoxy-bridged Re^{I} -based molecular rectangles containing long-chain alkoxy groups show an on–off phenomenon of emission enhancement in the presence of water, presumably owing to self-aggregation of the macrocycles.[7e] Facially amphiphilic cholate bundles, which are self-assembled by using Pd^{2+} ions, are now being evaluated for synthetic ion channels and pores.[7f,g] The effectiveness of using metal–organic scaffolds for reversible ligand gating was confirmed with ion-transport experiments in fluorogenic vesicles.[7h] A shape-persistent coordination square, synthesized from the self-assembly of a stoichiometric mixture of palladium-containing amphiphiles and bipyridine, was found to be a viable prospect as a selectivity filter in ion channels.[7i] Recently, functionalized supramolecular rectangles were

synthesized from a series of 180° donors possessing long hydrophobic and hydrophilic pendants, but their self-association behavior at interfaces were not explored.[7h]

Despite the surplus of platinum complexes and platinum–organic scaffolds, amphiphilic platinum complexes and platinum-containing amphiphilic supramolecules are rare. Only limited information is available on their interfacial behavior, and even those that are reported do not include any direct evidence on interfacial structures. Thin-film transfer conditions including molecule–substrate relationships must be assessed for these amphiphilic metallacycles to enable the selection of a suitable substrate. It is clear that in addition to the synthetic efforts, systematic studies on the interfacial behavior of the platinum amphiphiles and platinum-containing macrocycles must be carried out.

The study of the self-assembly of an amphiphilic triangular supramolecule in solution and its aggregation behavior at interfaces is an effort in this direction. The preformed triangular supramolecule is a novel amphiphile that could be considered as a charged triangular core embedded in liquid paraffin. It represents an intriguing structural deviation from the conventional head-to-tail amphiphiles. The bipyridine and phenanthrene aromatic segments are noncovalently linked to form a stable triangular core, in which the six positively charged hydrophilic platinum atoms reside at the corners, providing the macroamphiphile with a net charge of +6. The six hydrophobic alkoxy chains are located on the phenanthrene periphery, and thus possess the conformational freedom to bend around the rigid framework to minimize its solvophobic interactions in water. The incorporation of hydrophobic functionalities in the platinum(II) acceptors is a novel approach that has not yet been utilized. It involves a multi-mediated, multi-interaction strategy in which the noncovalent forces, including the stronger metal–ligand dative bonds and one or more of the weaker intermolecular interactions, such as the hydrophobic force, are employed in the self-assembly of the mesostructures. Although the amphiphilic triangular macrocycle possess distinct distribution of the hydrophobic and hydrophilic groups, it is difficult to predict how this unusual amphiphile will aggregate. The rules that govern conventional amphiphiles are not applicable here. Further, the hydrophobic force has no directional constraints, a factor that leads to poor molecular organization with high degrees of conformational freedom, thereby posing an additional complexity. It is anticipated that the aggregation behavior might also be dependent on the tethers on which the units are assembled, because the freedom of intermolecular approach of one amphiphile to another is somewhat constrained by their presence. To better understand and correlate the aggregation properties of the hexacationic triangular amphiphile to its molecular structure, it is essential to investigate the self-organization of the molecules at interfaces and in solution.

Results and Discussion

Synthesis and characterization

The angular unit 3,6-dibromo-phenanthrene-9,10-quinone[8a–c] **1** functions as an ideal substrate to build the necessary functionalities, namely, dialkoxy chains and divalent Pt headgroups at the two opposing ends to give a collective 60° directionality to the entire motif.

The 9,10-dioctadecyloxyphenanthrene derivatives (**2**, **3** and **4**) of dibrominated compound **1** are prepared as outlined in Scheme 1. The procedure was adapted from earlier reports.[9a,b] The platinum(II) insertion product **3** was obtained by a double oxidative addition of tris (triethylphosphine)platinum(0)[8d] to compound **2**. The bromine atoms are exchanged for the more labile and ionic nitrate anions by metathesis with silver nitrate to yield compound **4**. The weakly bound unidentate nitrate anion supplements the hydrophilic nature of the headgroups by promoting its anchoring to polar interfaces.

Compounds **2–4** are white solids at room temperature. Functionalizing with long hydrocarbons enhanced the solubility of the inorganic complexes **2–4** in nonpolar solvents such as pentane and *n*-hexanes. Compounds **2–4** have been characterized by elemental analysis, IR, ^1H , ^{13}C { ^1H }, and ^{31}P { ^1H } NMR spectroscopy. The appearance of a triplet signal at $\delta=4.16\text{--}4.17$ ppm, in which the integration indicates four protons in the ^1H NMR spectrum of the dialkoxylated compound **2** indicates that the O-alkylation was successful. Four equivalent phosphorus atoms in the molecules **3** and **4** give rise to a sharp singlet in the ^{31}P { ^1H } NMR spectrum, with concomitant ^{195}Pt satellites. The ^1H NMR spectrum of derivatives **3** and **4** shows multiplicity for peaks corresponding to the hydrogen atoms of methylene ($-\text{PCH}_2-$, 1.02 ppm) and methyl ($-\text{PCH}_2\text{CH}_3$, 1.5 ppm) groups. The aromatic proton signal at 8.4 ppm is accompanied by doublets centered about the major peak due to additional three-bond ($^3J_{\text{H-Pt}}$) spin-spin coupling to platinum (^{195}Pt ; $I=1/2$; 33.8% natural abundance) of 60–73 Hz for precursors **3** and **4**. The structure of **4** is supported by ESI-MS. In the ESI-MS of nitrate **4**, a signal is observed that corresponds to the singly charged species of $[\mathbf{4}-\text{NO}_3]^+$ (m/z 1636.5), the isotope pattern of which reveals a spacing of $\Delta m=1$ amu.

The slow recrystallization of compound **3** from a hot solution of ethanol yields stable lamellar rodlike crystals of uniform size and thickness, whereas those grown in a mixture of ethanol/water (10:1) assemble into more flat nonuniform plates of larger dimensions (Figure 1). Scanning electron microscopy (SEM, Figure 2) and polarized optical microscopy (Figure 1d) of the flat platelike crystals reveal a layered morphology. The facets and edges of the crystal would make it an interesting prospect for catalysis on crystal surfaces.[10] In general, the influence of a solvent on the structure of the crystalline material originates either from its favorable interactions with the solute on specific faces or through preferential adsorption at specific faces that will inhibit growth of that face relative to other unaffected areas.[11] In the present case, the replacement of some of the ethanol molecules with water may increase the surface area of some faces at the expense of others, leading to the formation of the observed flat platelike morphology. The space-group determination through X-ray analysis of the crystals was unsuccessful. However, a partial structural refinement indicated the interdigitation of the octadecyloxy chains from two adjacent molecules and the segregation of the hydrophobic chains (see Figure S9 in the Supporting Information).

Self-assembly in solution

The amphiphilic charged triangular macrocycle **6** was prepared by using the coordination-driven self-assembly process. The rigid 180° 4,4'-bipyridyl donor **5** and 60° platinum acceptor **4** reacted in stoichiometric ratios to yield the supramolecular amphiphile (Scheme 2).

A colorless solution of the linear linker **5** in $[\text{D}_6]\text{acetone}/\text{D}_2\text{O}$ (10%) was slowly added to a colorless solution of the nitrate precursor **4** and in $[\text{D}_6]\text{acetone}/\text{D}_2\text{O}$ (10%) to produce a yellow solution, which upon evaporation of the solvent yielded the thermodynamically favored macrocyclic product **6**.

The ^{31}P { ^1H } NMR spectrum of the amphiphilic macrocycle **6** in $[\text{D}_6]\text{acetone}/\text{D}_2\text{O}$ (10%) shows a sharp singlet at $\delta=14.54$ ppm together with accompanying ^{195}Pt satellites. This suggests the formation of a single macrocyclic species. This self-assembly reaction also successfully proceeded in CD_2Cl_2 , as proven by the appearance of a sharp singlet at 13.49 ppm for the macrocycle **6**. This phosphorous signal is shifted upfield relative to its position in the ^{31}P NMR spectrum of precursor **4**.

The differences in the $^1J_{\text{Pt-P}}$ values of precursor **4** and supramolecular triangle **6** as well as the shift of the proton signals in the ^1H NMR spectrum are in agreement with Pt–N coordination. Two sets of doublets are observed for both α - and β -pyridine protons of the amphiphilic triangle

(Figure 3). The nonequivalent resonances for the inner and outer pyridine protons may arise because of a possible hindered rotation about the Pt–N bond.[12]

Evidence for the triangular macrocyclic structure was obtained by using ESI-MS spectrometry. The ionization technique allowed the intact triangular macrocycle, minus several nitrate counterions, to be observed. The amphiphilic supramolecular triangle **6** gave $[\mathbf{6}-2\text{NO}_3]^{2+}$, $[\mathbf{6}-3\text{NO}_3]^{3+}$, and $[\mathbf{6}-4\text{NO}_3]^{4+}$ peaks, with m/z ratios of 2722.0, 1794.0, and 1330.0, respectively. The isotopically resolved charged states correlate well with their theoretical distributions (Figure 4).

The geometry optimization of 60° gemini amphiphile **4** and triangular macrocycle **6** (with the alkoxy tails removed for computational simplicity) were carried out by using the Gaussian 03 [13a] program at the B3LYP (Becke's exchange and Lee, Yang, and Parr's correlation functionals) level[13b,c] by using the Lanl2DZ (Los Alamos pseudopotential and double- ζ basis set) basis set,[13d] to obtain the structural parameters required for analyzing the interfacial self-assembly.

Self-assembly of a preformed amphiphilic macrocycle at liquid–liquid interfaces

A dispersion of self-assembled hexacationic amphiphiles **6** was prepared from a chloroform/water (100:4000 μL) immiscible solvent mixture by mechanical stirring. Laser scanning confocal optical microscopy on the molecular superstructures in the dispersions reveal coacervate[14] phases (Figure 5 a and b) with a porous (spongelike) morphology. The dimensions of the self-assembled superstructures are too large ($> 1 \mu\text{m}$) to be considered as a micelle ($< 10 \text{ nm}$) or a microemulsion (50–200 nm). Further, the mesophases in the present system are essentially irreversible, showing no equilibrium dissociation of the particles into monomers. Hence, we prefer to refer to these molecular superstructures that separate from water as coacervates. The confocal microscopic technique permits the collection of optical slices of a coacervate by changing the plane of focus (different z positions) and by only allowing the light from the plane of focus to reach the detector. The z slices reveal that the pores are not only present on the surface, but that they also permeate throughout the entire mesostructure (see the movie as part of the Supporting Information). These pores/channels may be likened to the mono- or bicontinuous channels that are found in analogous soft materials such as sponges (L_3 phase) and bicontinuous interfacially jammed emulsion gels (bijels).[15] Our knowledge of the internal organization and the formation mechanism of these superstructures are currently limited. However, we believe that the pores may have been derived from the interconnected water-filled voids generated from coalescence of growing particles during agglutination. In addition, the irreversible association may be due to multiple hydrophobic associations that involve the six hydrophobic alkoxy tails as well as effective screening of the hexacationic surface charges of the supramolecular amphiphile by the nitrate counterions (i.e., removal of the electrostatic barrier to particle aggregation).

The coacervates have been further characterized by in situ Raman spectroscopy. Figure 5 c shows the Raman scattering spectrum of an optically trapped globular aggregate in solution. The collection of Raman scattering peaks indicate the structure of the amphiphilic triangular molecule **6**. Although it is difficult to assign each peak with confidence, Raman scattering peak assignments can be proposed based on the Raman spectra of the precursor molecule and literature references of relevant compounds. The most prominent peak at 1614 cm^{-1} is most likely due to a ring stretch from the bipyridine molecule,[16a] although a significantly less intense peak at a slightly lower wavelength (1607 cm^{-1}) was also present in the precursor nitrate **4**, which likely corresponds to a benzene ring stretch.[16b] The peak at 1587 cm^{-1} is also probably due to a benzene ring stretch mode from the precursor molecule **4**. [16a] The peaks at 1295 cm^{-1} , 1425 cm^{-1} , and $\sim 2914 \text{ cm}^{-1}$ occur in regions that contain well-known CH vibrations found in hydrocarbon chains.[16c,d] These peaks correspond to CH_2 twisting,

CH₂ bending and CH stretching modes, respectively, although the peak at 1294 cm⁻¹ is also a prominent signal of the bipyridine group that corresponds to the inter-ring stretch. It is possible that the signal at 1033 cm⁻¹ corresponds to a nitrate stretch because the nitrate precursor molecule **4** contained a peak in this region and the literature reports a nitrate stretch at ~1046 cm⁻¹.^[16e] It is not clear what the peak at 1326 cm⁻¹ represents. Raman scattering of the amphiphilic triangular sample **6** in the dry state showed a nearly identical spectral pattern, indicating that no significant decomposition of the sample occurs during sonication or stirring in solution.

Self-assembly of a preformed amphiphilic macrocycle at the air–water interface

The surface-pressure (Π) and surface-potential (mV) isotherms are presented in Figure 6. A jump from zero surface pressure is observed near 825 Å² molecule⁻¹ as the molecules compete for space at the air–water interface. A corresponding sharp increase in surface potential (from 700 to 850 mV) may be attributed to the change in the structure of the generated ionic double layer and sudden reorientation of the surface dipoles. The double-layer forces arise from the hexacationic surface charges (insoluble ion) adsorbed at the air–water interface (Langmuir layer) and free nitrate counter ions (soluble) that are retained in the surface phase adjacent to the phase boundary by electrostatic attraction of the boundary charges.^[17] In addition, the molecular crowding may force the alkoxy tails into more orthogonal orientations with respect to the air–water interface, thus leading to a greater contribution of their terminal methyl group dipoles to the measured surface potential. At 30 mN m⁻¹ (550 Å² molecule⁻¹), the film becomes more compressible as indicated by the sharp decrease in the slope of the surface-pressure and surface-potential isotherms, which suggests molecular restructuring to maximize packing efficiency. Further compression possibly leads to additional improvement in packing, as suggested by a second decrease in the slope of the surface pressure isotherm near 350 Å² molecule⁻¹. The surface potential levels off near 1020 mV as the monolayer achieves its maximum packing efficiency, and film collapse is observed at 45 mN m⁻¹ without any further increase in surface potential.

The molecular footprint (the area occupied by the molecule at the air–water interface) has been theoretically estimated by using the molecular dimensions derived from the two limiting structures (Figure 7). The stretched model (Figure 7 a), in which the tails are fully extended, should give the maximum molecular area (7.24×7.24=52.42 nm²). The bent conformer (Figure 7b), which excludes the length of the tail from consideration, would give the minimum molecular area (3.41×3.41=11.63 nm²). However, these calculated areas do not account for the packing efficiency of the molecules. Alternatively, the experimental molecular areas are obtained by extrapolating the linear regions I and III to zero surface pressure (for instance, region I in Figure 6: limiting molecular area, A₀=7.60 nm²). The theoretical molecular areas of the stretched conformer (52.42 nm²) and the bent conformer (11.63 nm²) reveal that they are considerably larger than the experimental molecular areas (for example, A₀=7.6 nm²). The limiting molecular areas are too small for the molecules to adopt a monomolecular layer. This suggests that molecular aggregation is occurring at the air–water interface, hence, the formation of a nonmonomolecular film is presumed. A nonmonomolecular film, rather than a simple molecular reorientation, would offer a better explanation for the isotherms. The aggregation claim is also supported by a large hysteresis observed during compression–expansion experiments (see Figure S10 in the Supporting Information), which indicate an irreversible molecular organization.

At lower surface pressures, the Brewster angle microscope (BAM) image (Figure 8 a) reveals an isotropic film with no observable features that are within the resolution limits (~20 μm) and the experimental setup of the BAM. The bright-white specks observed in the lower-left region of an image taken at 40 mN m⁻¹ (Figure 8 b) shows the early appearance of collapse lines. The

final collapse of the film results in the formation of ridges and cracks (Figure 8 c), which is consistent with the formation of multilayer domains. The apparent lack of contrast at lower surface pressures suggests that the molecular-restructuring events, proven by sharp changes in the slope of the isotherms, do not correspond to the formation of discrete (isotropic) ordered phases.

Reflectivity spectra[18] of the monolayer at the air–water interface were collected at surface pressures of 0, 4, 12, and 30 mN m⁻¹ (Figure 9). The films were unstable at higher surface pressures, as indicated by a steady decrease in the surface pressure while the spectra were collected. The compound exhibits several distinct peaks that increase in intensity and shift by 1–2 nm to longer wavelengths as the films are compressed from 0 to 30 mN m⁻¹. The reflectivity spectrum grows in intensity upon compression, but does not exhibit any dramatic shifting of peaks as might be expected for nucleation of discrete phases upon compression. This result is consistent with the increase in molecular packing density in the plane of the air–water interface, as supported by the Π versus A isotherm and BAM images (Figures 6 and 8, respectively).

The Langmuir layers at the air–water interface were transferred by the LS method to an alkyl–silane-modified silicon wafer, and the morphology was imaged under fluid conditions. It revealed flat discontinuous structures with irregular ridgelike patterns that exhibited minimal long-range order (Figure 10). The absence of an ordered phase is in agreement with the results obtained from BAM images and the reflectivity spectrum. The height of the structures is mostly confined to 5.0–6.5 nm, whereas the width of the structures shows a wide range from 30–400 nm. The heights are evaluated from the AFM image by finding the average difference between the crests and troughs in the line profile.

It is necessary to correlate molecular structure with the observed morphology to extract additional information about the internal organization of the aggregates. Having discounted the existence of a monomolecular layer through limiting molecular area (derived from the Π versus A isotherm) and hysteresis experiments, a nonmonomolecular arrangement may offer a better fit to the height data. For example, when two bent triangular assemblies are laid on top of one another, the maximum height of the stacked structure corresponds to approximately 6.3 nm. The hydrocarbon chains of the two triangular assemblies may further disorder to achieve a uniform packing density and consequently, attain smaller heights. The estimated height agrees with the height range (5.0–6.5 nm) obtained from AFM line-profile measurements. The two amphiphilic molecules can essentially stack in four different modes, namely, core–tail | tail–core, core–tail | core–tail, tail–core | tail–core, and tail–core | core–tail. Under the given aqueous conditions existing at the air–water interface and during the imaging process carried out solution, the last two stacking modes would have their hydrophobic tail ends exposed to polar water molecules, thereby making them energetically less favorable. This only leaves the first two arrangements, in which the charged core has a favorable interaction with the neighboring water molecules. Out of these two arrangements, the core–tail | tail–core arrangement (Figure 11 d) is expected to be energetically more stable, because sequestration of the hydrophobic alkoxy tails results in favorable van der Waals interactions and also ensures maximum charge separation between two triangular cores. This packing arrangement (Figure 11 c) is also supported by the hydrocarbon-droplet assumption model,[19] which predicts sequestration of hydrophobic tails in the center and placement of charged groups near the polar interface. Also, the variations in aggregate width may be explained by accommodating as many double units (Figure 11 d) as are required to arrive at the different widths. This direct study of the aggregate morphology by AFM confirms surface aggregation at the air–water interface and verifies the Π versus A isotherm results.

Conclusion

The synthesis and characterization of a novel triangular supramolecular amphiphile, based on a new 60° amphiphilic phenanthrene corner unit that incorporates platinum(II) acceptors and octadecyloxy groups is reported. The amphiphilic triangular assembly is self-assembled in near-quantitative yields despite the presence of long alkoxy chains in the platinum acceptors. The amphiphilic precursor and the amphiphilic triangular supramolecule are characterized by multinuclear NMR spectroscopy and ESI-MS. The amphiphilic supramolecule represents an important addition to the growing class of functionalized metallocsupramolecules.

The aggregation of the amphiphilic metallacycle at the liquid–liquid interface lead to a coacervate phase with a porous structure. The Langmuir isotherm of the triangular assembly indicates the presence of nonmonomolecular films and the formation of surface micelle-like structures. By using two limiting models, the molecular-area calculations are shown to support the aggregation behavior. The fluid AFM studies on the amphiphilic triangle show the formation of aggregates with flat morphology and random ridgelike patterns. The salient features of the shape-persistent triangular macrocycle, such as the central void and the outer lipid shell, might make this charged amphiphile a potential candidate for use as a selectivity filter in ion channels. Appropriate modifications to the hydrophilic interiors, hydrophobic shells, and lengthening the linear donor ligands might allow these molecules to function like unimolecular inverse micelles with an adaptable nanocavity.

Experimental Section

General Methods

All reagents were purchased and used without further purification. 3,6-Dibromo-9,10-phenanthrenequinone[8a–c] **1** and tris(triethylphosphine)platinum(0)[8d] were prepared according to literature procedures. All NMR spectra were recorded on Varian Unity 300 or XL-300 spectrometers. The ^1H NMR chemical shifts are reported relative to the residual protons of deuterated dichloromethane ($\delta_{\text{H}}=5.32$ ppm), deuterated chloroform ($\delta_{\text{H}}=7.21$ ppm), or when CD_2Cl_2 or CDCl_3 was not used, relative to the residual protons of deuterated acetone ($\delta_{\text{H}}=2.05$ ppm). The $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts are reported relative to the solvent signals. The $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 ($\delta_{\text{P}}=0.00$ ppm). IR (KBr) spectra were recorded from 400 to 4000 cm^{-1} on a Bruker Tensor 37 Spectrometer. UV/Vis spectra were recorded on an Agilent 8453 UV/Vis spectroscopy system by using an open top UV/Vis quartz cell (10 mm, 3.0 mL). Fluorescence emission spectra were recorded with a SPEX Fluorolog-2 fluorimeter using an excitation wavelength of 360 nm (acquisition parameters: 25°C, integration: 1 s; number of scans=1; increment by 1 nm; slit width=2.5 nm). Melting points (open capillary, uncorrected) were measured on a Mel-Temp instrument. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. The mass spectra were obtained on a Micromass Quattro II spectrometer under electrospray ionization conditions.

Compound 2

A mixture of 3,6-dibromo-9,10-phenanthrenequinone (3.00 g, 8.20 mmol), Bu_4NBr (3.00 g, 9.30 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (14.4 g, 82.8 mmol) in H_2O (60 mL) and THF (60 mL) was stirred at room temperature for 5 min. Then, 1-bromooctadecane (14.4 g, 214 mmol) was added followed by potassium hydroxide (12.0 g, 214 mmol) in H_2O (60 mL). After stirring for 2 days, the reaction mixture was diluted with H_2O (200 mL) before the white suspension was filtered through a sintered funnel. The white residue was washed with H_2O (1×200 mL), dried over MgSO_4 , and evaporated to dryness. The product was recrystallized from hot *n*-hexane. Further purification was achieved in two successive columns (SiO_2 , CHCl_3) to give a fluffy white

product. Yield: 5.85 g (6.70 mmol, 82%); m.p. 78–80°C; ^1H NMR (300 MHz, CDCl_3): $\delta_{\text{H}}=0.88$ (t, $J_{\text{HH}}=6.7$ Hz, 6H; CH_3), 1.18–1.39 (m, 56H; CH_2), 1.48–1.58 (m, 4H; CH_2), 1.89 (p, $J_{\text{HH}}=7.1$ Hz, 4H; OCH_2CH_2), 4.16 (t, $J_{\text{HH}}=6.7$ Hz, 4H; OCH_2), 7.70 (dd, $J_{\text{HH}}=8.8$ Hz, 2H; Ar-*H*), 8.08 (d, $J_{\text{HH}}=8.7$ Hz, 2H; Ar-*H*), 8.64 ppm (d, $J_{\text{HH}}=1.9$ Hz, 2H; Ar-*H*); ^{13}C NMR (^{1}H) (125.7 MHz, CDCl_3): $\delta_{\text{C}}=14.1, 22.7, 26.2, 29.4, 29.5, 29.7, 30.4, 31.9, 73.7, 120.3, 124.2, 125.4, 128.7, 128.8, 130.4, 143.1$ ppm; IR(KBr): $\nu=2953, 2915, 2849, 1591, 1472, 1346, 1310, 1122, 812, 718$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{50}\text{H}_{80}\text{O}_2\text{Br}_2$: C 68.79, H 9.24; found: C 69.05, H 9.30.

Compound 3

A solution of **2** (791 mg, 0.91 mmol) in dry and degassed toluene (30 mL) was syringed into a solution of freshly prepared $[\text{Pt}(\text{PEt}_3)_3]$ (2.00 g, 3.64 mmol) in dry and degassed toluene (30 mL) under a nitrogen atmosphere and stirred at 105°C for 3 days. After evaporation to dryness, the black residue was washed with methanol (3×15 mL), then recrystallized from MeOH and eluted through two successive columns by using CH_2Cl_2 /hexane (1:1). An oily yellow residue was obtained after concentrating the fractions. The residue was stirred in methanol to precipitate a pure-white product. Yield: 1.15 g (0.66 mmol, 73%); m.p. 94–96°C; ^1H NMR (300 MHz, CDCl_3): $\delta_{\text{H}}=0.87$ (t, $J_{\text{HH}}=6.6$ Hz, 6H; CH_3), 1.01–1.12 (m, 36H; PCH_2CH_3), 1.20–1.46 (m, 56H; CH_2), 1.53–1.76 (m, 28H; PCH_2CH_3 and CH_2), 1.90 (q, $J_{\text{HH}}=7.1$ Hz, 4H; OCH_2CH_2), 4.14 (t, $J_{\text{HH}}=6.6$ Hz, 4H; OCH_2), 7.58 (d, $J_{\text{HH}}=8.3$ Hz, $J_{\text{HPt}}=61.0$ Hz, 2H; Ar-*H*), 7.71 (d, $J_{\text{HH}}=8.3$ Hz, 2H; Ar-*H*), 8.48 ppm (s, $J_{\text{HPt}}=72.6$ Hz, 2H; Ar-*H*); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CD_2Cl_2): $\delta_{\text{C}}=8.0, 8.1, 14.3, 14.4, 14.6, 14.8, 23.3, 26.9, 29.9, 30.3, 31.2, 32.5, 73.7, 121.0, 125.4, 128.9, 129.8, 136.9, 138.1, 142.0$ ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2): $\delta_{\text{P}}=12.90$ ppm (s, $J_{\text{PPt}}=2765$ Hz); IR(KBr): $\nu=2961, 2920, 2851, 1085, 1036, 766, 733$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{74}\text{H}_{140}\text{Pt}_2\text{P}_4\text{Br}_2\text{O}_2$: C 51.20, H 8.13; found: C 51.14, H 8.11.

Compound 4

AgNO_3 (43.1 mg, 0.25 mmol) was added to a stirred solution of **3** (200 mg, 0.12 mmol) in acetone (50 mL) at room temperature. Continuous stirring for 6 h in the dark resulted in a heavy creamy precipitate, which was then filtered off. The solvent of the remaining solution was removed under a flow of nitrogen before the residue was redissolved in CH_2Cl_2 (50 mL) and filtered through a 0.02 μm Whatman syringe filter. Then, the solvent was removed, again under a flow of nitrogen, before the product was recrystallized from *n*-pentane. Yield: 163 mg (0.10 mmol, 83%); m.p. 90–92°C; ^1H NMR (300 MHz, $[\text{D}_6]\text{acetone}$): $\delta_{\text{H}}=0.88$ (t, $J_{\text{HH}}=6.7$ Hz, 6H; CH_3), 1.14–1.24 (m, 36H; PCH_2CH_3), 1.26–1.48 (m, 56H; CH_2), 1.53–1.67 (m, 28H; PCH_2CH_3 and CH_2), 1.95 (q, $J_{\text{HH}}=7.1$ Hz, 4H; OCH_2CH_2), 4.17 (t, $J_{\text{HH}}=6.5$ Hz, 4H; OCH_2), 7.66 (d, $J_{\text{HH}}=8.5$ Hz, $J_{\text{HPt}}=60.0$ Hz, 2H; Ar-*H*), 7.79 (d, $J_{\text{HH}}=8.4$ Hz, 2H; Ar-*H*), 8.54 ppm (s, $J_{\text{HPt}}=69.1$ Hz, 2H; Ar-*H*); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CD_2Cl_2): $\delta_{\text{C}}=7.9, 13.2, 13.4, 13.6, 14.4, 23.3, 26.9, 29.9, 30.2, 30.3, 31.2, 32.5, 73.8, 121.2, 124.9, 125.9, 128.6, 129.1, 136.3, 142.1$ ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2): $\delta_{\text{P}}=19.26$ ppm (s, $J_{\text{PPt}}=2887$ Hz), $^{1\text{P}}\{^1\text{H}\}$ NMR (121.4 MHz, $[\text{D}_6]\text{acetone}$): $\delta_{\text{P}}=20.03$ ppm (s, $J_{\text{PPt}}=2883$ Hz); UV/Vis (1 μm , CHCl_3 , 24°C): 262, 270, 294, 314, 328, 359 and 378 nm; ESI-MS: 1636.5 (calcd for $[\text{4-NO}_3]^+$, 1636.9), 787.5 (calcd for $[\text{4-2NO}_3]^{2+}$, 787.4); IR(KBr): $\nu=2964, 2918, 2849, 1472, 1275, 1088, 1035, 991, 766, 733$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{74}\text{H}_{140}\text{Pt}_2\text{P}_4\text{O}_8\text{N}_2$: C 52.28, H 8.30, N 1.65; found: C 52.32, H 8.27, N 1.64.

Compound 6

In a 2-dram vial, a solution of 4,4'-bipyridine **5** (15 μmol) in $[\text{D}_6]\text{acetone}$ (2 mL) containing D_2O (10% v/v) was added dropwise to a solution of platinum acceptor **4** (1 equiv) in the same solvent mixture (2 mL). The vial was sealed with Teflon tape and the reaction mixture was

stirred and heated in an oil bath at 50°C for 2 days. The yellow solution was then transferred into a NMR tube for analysis. Afterwards, the solvent was removed under a flow of nitrogen. The solid yellow residue was dissolved in CH₂Cl₂ and precipitated out by the addition of diethyl ether. It was then filtered and dried in vacuum to yield a yellow product. M.p. >201°C (decomp.); ¹H NMR (300 MHz, 10% D₂O in [D₆]acetone): δ_H=0.84 (t, *J*_{HH}=6.8 Hz, 18H; CH₃), 1.16–1.68 (m, 288H; PCH₂CH₃ and CH₂), 1.95 (q, *J*_{HH}=7.02 Hz, 12H; OCH₂CH₂), 4.19 (t, *J*_{HH}=5.39 Hz, 12H; OCH₂), 7.77 (d, *J*_{HH}=8.75 Hz, 6H; Ar–H), 7.95 (d, *J*_{HH}=8.34 Hz, 6H; Ar–H), 8.50–8.52 (m, *J*_{HH}=8.0 Hz, 6H; Py–H_β), 8.62–8.63 (m, *J*_{HH}=6.0 Hz, 6H; Py–H_β), 8.75 (s, 6H; Ar–H), 9.21 (d, *J*_{HH}=5.39 Hz, 6H; Py–H_α), 9.39 ppm (d, *J*_{HH}=5.69 Hz, 6H; Py–H_α); ¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ_C=7.52, 12.54, 13.88, 18.20, 22.46, 26.17, 29.14, 29.54, 30.50, 31.70, 58.20, 70.28, 72.97, 73.26, 73.64, 74.99, 78.34, 79.02, 80.36, 81.03, 83.72 ppm; ³¹P{¹H} NMR (121.4 MHz, 10% D₂O in [D₆]acetone): δ_P=14.54 ppm (s, ¹⁹⁵Pt satellites, ¹*J*_{PP}=2678.93 Hz); IR (KBr): ν=2961, 2921, 2852, 1537, 1364, 1036, 765, 732 cm^{−1}; UV/Vis (1 μm, CHCl₃, 24°C): 262, 270, 289, 312, 326, 360 and 378 nm; fluorescence (90.7 μm, CHCl₃): λ_{exc}=360 nm; λ_{emi}=405 nm; ESI-MS: *m/z*: 2722.1 (calcd for [6–2NO₃]²⁺=2721.9), 1794.0 (calcd for [6–3NO₃]³⁺=1794.0), 1330.0 (calcd for [6–4NO₃]⁴⁺=1330.0); elemental analysis calcd (%) for C₂₅₂H₄₄₄N₁₂Pt₆P₁₂O₂₄·1.4CH₂Cl₂: C 53.51, H 7.92, N 2.96; found: C 53.31, H 7.93, N 2.93.

Geometry optimization

Geometry optimization was carried out by using the Gaussian 03 package at the B3LYP (Becke's exchange and Lee, Yang, and Parr's correlation functionals) level using the Lanl2DZ (Los Alamos pseudo-potential and double-ζ basis set) basis set. The choice of B3LYP functional was dictated by the size of the molecules, convergence time, and cost effectiveness. The relativistic Lanl2DZ pseudopotential is the typical basis set used for structural calculations of transition-metal complexes, including those of the Pt atom,[20] because of the limited availability of high-quality atomic orbital basis sets.

Langmuir-trough measurements

Custom-built PTFE troughs (18×56 cm²) with single barrier compression were used for the reflectivity, surface potential, and BAM measurements. The troughs were enclosed in dust-free cabinets and maintained at 20°C by using a circulating water bath. The surface pressure was measured by using a filter-paper Wilhelmy plate attached to a force transducer. The surface potential was measured by using a vibrating plate condenser. Compound **6** was prepared as a 1 mM solution in chloroform (Sigma, HPLC grade) and stored at 4°C until use. Surface-pressure and surface-potential isotherms were obtained on double-distilled-water subphases (20°C). Blank compressions followed by surface aspiration were performed to ensure the absence of contaminants at the interface prior to spreading the monolayer. Up to 8 μL of solution was slowly deposited dropwise onto the clean air–water interface by using a 10 μL Hamilton gastight syringe. After aging for 10 min, the films were compressed at 18.5 cm²min^{−1} until film collapse occurred. Reflectivity at normal incidence was differentially measured between the Langmuir-layer covered interface and the layer-free interface behind the compression barrier as previously described.[18] Reflectivity spectra were collected at several film-packing densities by compressing to a target surface pressure then holding the film at constant area to avoid surface perturbations owing to barrier feedback. Film morphology at the air–water interface was visualized by using a mini Brewster angle microscope (NFT, Göttingen). For BAM imaging, the compression was momentarily paused at defined surface pressures (between 0 and 40 mN m^{−1}) to reduce film movement during image capture.

Hysteresis experiments and LS film transfers were carried out on a commercial Langmuir trough (36×7.5 cm, KSV) with a well. Deionized, double-distilled (DDI) water was used as a subphase. The experimental conditions, such as subphase temperature (25°C), compression

speed (5 mm min^{-1}), spreading solution volume ($4 \mu\text{L}$), concentration (1 mM), subphase volume ($\sim 260 \text{ mL}$), and monolayer aging time ($5\text{--}6 \text{ min}$), were unchanged. The Teflon trough and Delrin barriers were thoroughly cleaned with chloroform (HPLC) and absolute ethanol then rinsed with DDI water prior to usage. The surface pressure was measured by a platinum Wilhelmy plate attached to an electrobalance (resolution= $4 \mu\text{Nm}^{-1}$) while being held parallel to the symmetrically moving barriers. The Wilhelmy plate was cleaned with chloroform and absolute ethanol and then flamed in the outer regions of the Bunsen flame until it became red hot. The plate wettability after flaming was qualitatively checked by dipping it in DDI water. Prior to monolayer spreading, the interface was aspirated until the surface pressure change was $<0.1 \text{ mN m}^{-1}$ upon reducing the interfacial area from 240 to 30 cm^2 in two successive blank runs.

Silanization

The procedure for preparing self-assembled monolayers (SAM) of octadecyltrichlorosilane ($\text{CH}_3\text{--}(\text{CH}_2)_{17}\text{--SiCl}_3$, OTS) on Si wafers was followed from earlier reports[9b,c] Substrates ($\sim 10 \times 5 \text{ mm}^2$) were cut from a polished N^+ -type Si(111) wafer (MEMC Electronic Materials, Malaysia). Anhydrous OTS was purchased from Sigma-Aldrich. DDI water ($\sim 18 \text{ M}\Omega$), HPLC grades of hexane and chloroform, and spectral grades of acetone and toluene were used for the substrate preparation and postdeposition cleaning. After removing the organic residues by sonication in acetone for $20\text{--}30 \text{ min}$, the surface oxides on the substrates were removed by immersing in dilute hydrofluoric acid ($\text{HF/DDI H}_2\text{O}=1:36 \text{ v/v}$) for less than a minute, before thoroughly rinsing with DDI water. The substrates were reoxidized and hydroxylated in 120 mL of stirred acidic piranha solution ($\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ $36:84 \text{ mL}$) for $15\text{--}20 \text{ min}$, followed by rinsing with DDI water. They were dried under ultra high pure (UHP) nitrogen flow and kept in an oven at 100°C for $5\text{--}10 \text{ min}$ to ensure the complete removal of water. The silicon substrates were placed in a millimolar (mM) solution of OTS dissolved in hexane, and stirred for approximately $18\text{--}20 \text{ h}$ under anhydrous glove-box conditions. Later, while still in the glove box, they were transferred into a bottle containing chloroform and the solvent was vigorously stirred for 30 min . Subsequently, the modified substrates were transferred to a bottle containing fresh chloroform, which was sealed before removing it from the glove box. They were sonicated three times for $15\text{--}20 \text{ min}$ in both CHCl_3 and toluene to remove the physisorbed OTS clusters. The functionalized substrates were dried under UHP nitrogen flow and stored in covered dishes. The static contact angles of DDI water on the chemisorbed surfaces were measured by using a goniometer (CAM 100, KSV Instruments) in a sessile drop configuration. The contact angles were found to be in the range of $108^\circ\text{--}110^\circ$ for OTS/Si(111) substrates, indicating successful hydrophobization of the surfaces. The AFM images of the SAM revealed a uniform, featureless surface devoid of clusters and a surface roughness of less than 0.5 nm .

LS film transfer

The LS films at different surface areas were transferred onto hydrophobic silanized substrates through the horizontal transfer (Schaefer) method by holding them in contact with the film at the water-air interface for at least 1 min . Next, the substrates were gently immersed through the well of the trough, carefully flipping it over to keep the transferred surface facing upwards and then placing it in a Petri dish. The remnants of the LS film and the subphase water were removed without affecting the immersed sample in the Petri dish. Furthermore, the subphase water in the Petri dish was partially replaced with fresh DDI water without exposing the sample to air. It was then sealed and taken for imaging in fluid solution.

Intermittent contact AFM imaging

The substrates with transferred LS layers were imaged by a Picoscan instrument operating in intermittent contact (tapping) mode using a multipurpose small scanner with a $8.5 (x) \times 9.0 (y)$

$\times 0.9 \mu\text{m}$ (z) scan range. The measurements were performed on the samples in water, at room temperature ($\sim 22^\circ\text{C}$) not more than 5 h after the LS film transfer. The Al-coated silicon probes (MikroMasch) had weak force constants of 0.12 and 0.35 Nm^{-1} and were used in the intermittent contact mode to prevent surface deformation and damage. During imaging, the samples were maintained in their hydrated conditions without removing them from the subphase water to avoid any morphological change owing to drying. Typically, scans were made on at least three distinct locations in each sample, and for a given set of conditions at least two independently prepared samples were imaged. The scan size and angles were varied to check for drift. The recorded two-dimensional images were processed by using Image Metrology software for noise reduction.

Laser scanning confocal optical microscopy

Confocal images of bicontinuous emulsions were obtained by using an Olympus FV 1000 model IX81 microscope with spectral imaging. Excitation was with a 404 nm laser line, whereas the emission was at 700 nm. The 660 nm long pass filter was used. Images were taken by using an aqueous-60 $\times$ objective.

Images of the rodlike crystals of compound **3** were obtained by using an Olympus FV300 confocal. The transmitted light image was obtained by using the 488 nm laser line. All images were taken by using a 10 $\times$ PLANAPO objective. Some images were taken at either zoom level 1 or 2. The scale bars were as measured by the computer. Snapshots of the side views were obtained by using Volocity (Improvision version 3.7) volume-rendering software.

Crystals were visualized on an Olympus IX70 microscope using polarized light to study the thickness and polarization properties of the sample. A 20 $\times$ PLANAPO LWD objective was used with a Q Imaging color camera for image capture. The scale in these images is not the same as the confocal images.

In situ raman spectroscopy

The beam from a 647.1 nm Kr^+ laser (Innova 90, Coherent) was passed through a band-pass filter (F10-647.1-4, CVI Laser) and a 4 $\times$ beam expander (model 50-25-4 $\times$ -647, Special Optics) mounted on a Nikon TE 300 inverted fluorescence microscope. After passing through another band-pass filter (D647/10, Chroma Tech), the expanded beam was then reflected by a dichroic beam splitter (655DCLP, Chroma Tech) into a 100 $\times$ oil immersion 1.4NA objective (CFL PLAN APO, Nikon Inc.), which focused the laser to a $0.6 \mu\text{m}$ diameter spot in the sample solution. This same objective collected the sample Raman scattering, which was passed through the beam splitter, a high pass filter (E660 LP, Chroma Tech), and a holographic notch filter (Kaiser), after which it was focused onto a monochromator (500IS, Bruker) with a slit width of $50 \mu\text{m}$. A charge-coupled-device (CCD) camera (DV420, Andor) was used to collect the spectra over 3 pixels or $78 \mu\text{m}$ in the vertical dimension. Laser power was approximately 6 mW at the sample and integration times were 30 s. Samples were deposited on top of glass cover slips or inside glass wells attached to the cover slips. Sample particles in solution were optically trapped in the laser focus. Alternatively, the laser focus was used to collect Raman scattering from particles or dry samples adhered to the glass cover slip. Background subtraction and white-light correction were performed by using Matlab (MathWorks) as described earlier for the acquired sample spectra.[21] Baseline fitting was done by using a fourth-order polynomial.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. a) and b) Confocal optical micrographs and c) and d) polarized optical micrographs of Pt-inserted precursor **3** grown in pure ethanol (a and c) and ethanol/water (90:10, b and d). Crystals that lie on their edges appear darker in contrast to those that lie on their faces (scale=100 μm).

Figure 2. SEM image of crystalline platelike aggregates of precursor **3** grown in ethanol/water (90:10). Inset shows the peeled layers at the end of a crystal.

Figure 3. ^1H NMR spectrum (300 MHz, 10% D_2O in $[\text{D}_6]$ acetone) of the aromatic portion of the amphiphilic triangular assembly **6**, which displays the proton signals of both bipyridyl and phenanthrene segments.

Figure 4. ESI-MS of **6** in 10% D₂O in [D₆]acetone. Inset shows the isotopic labeling of the $[6-2\text{NO}_3]^{2+}$ peak.

Figure 5. Laser-scanning confocal optical microscopy. a) Fluorescent image and b) transmitted image of the molecular superstructures of triangular assembly **6**. c) Raman spectrum of an individual, optically trapped **6** coacervate.[14]

Figure 6.

a) Surface potential versus area isotherm and b) surface pressure versus area isotherms of amphiphilic triangular assembly **6** with octadecyloxy chains at an air–water interface (compression speed, $18.5 \text{ \AA}^2 \text{ molecule}^{-1}$; subphase temperature, 20°C). The phase states of the amphiphiles are indicated in the isotherm (I=mobile liquid phase, II=phase transition/ordered phase, and III=rigid solid phase). Break point X marks the beginning of the phase transition, T marks the surface pressure where the Langmuir-Schaefer (LS) films are transferred onto silanized surfaces for AFM study, and C represents the collapse point. The dotted line represents the extrapolated molecular area, A_0 , at $\Pi=0$.

Figure 7. The two limiting Gaussian models illustrating the molecular dimensions of amphiphilic triangular macrocycle **6** in a) fully stretched and b) bent conformations.

Figure 8. Low-resolution ($4 \times 6 \text{ mm}^2$) BAM images of Langmuir layers of amphiphilic supramolecule **6** at various surface pressures: a) <35 and b) 40 mN m^{-1} , and c) collapse pressure, C. Optical interference fringes are artifacts of the imaging technique.

Figure 9. Reflectivity spectrum of the amphiphilic metallacycle **6** at various surface pressures (0 (○), 4 (□), 12 (◇), and 30 mN m⁻¹ (Δ)).

Figure 10.

Fluid AFM of the LS layer of the amphiphilic supramolecule **6** transferred onto silanized silicon wafer at a surface pressure of 34–35 mN m⁻¹. The bottom part shows the line profile of the observed morphology.

Figure 11.

a) A space-filling model of the triangular supramolecular amphiphile **6** in which the alkoxy tails are in a bent conformation, b) a representation of the bent conformer illustrating the triangular core and six folded tails, c) plausible packing arrangement of the bent molecules **6** to account for the observed height in the AFM measurements, and d) the central double unit in Figure 11c possessing a core-tail|tail-core stack.

Scheme 1.

Synthesis of 60° amphiphilic organoplatinum(II) corner unit **4**.

Scheme 2.

Self-assembly of triangular amphiphilic charged macrocycle **6** from amphiphilic 60° phenanthrene corner units **4** and linear bipyridyl donor molecules **5**. The + 6 charge is balanced by the presence of 6×NO₃[−] ions.