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Giant Micelles of Organoplatinum(II) Gemini Amphiphiles

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Abstract

Organoplatinum(II) gemini amphiphiles with two different chain lengths are synthesized and characterized. Self-assembly at the air-water interface is investigated as a function of chain length and reduction in surface area by using Langmuir-trough techniques. The Langmuir-trough experiments lead to a conjecture that surface aggregates may be the adsorbing units. Atomic force microscopy on the transferred Langmuir-Schaefer films reveals spontaneous formation of wormlike micellar aggregates. A shear-induced transition and alignment are proposed for the observed effects.

Introduction

A gemini amphiphile is an equivalent of two single-chain amphiphiles that are connected by a spacer, in the vicinity of the headgroups. It is generally composed of two identical sets of a hydrophilic headgroup and a hydrophobic tail. The headgroups can be cationic, anionic, zwitterionic, or nonionic in nature, whereas the spacer further defines the amphiphile's properties through variations in its size, shape, rigidity, and polarity. The gemini amphiphiles are significant due to their unique solution and interfacial properties, in particular, their low critical micelle concentrations.¹⁻⁸ They are also known to self-aggregate into giant micellar structures, bringing about remarkable rheological properties.^{6,9,10}

Amphiphiles self-assemble into micelles of diverse morphologies, such as toroids, spheres, cylinders and branching networks. Some of the tunable factors known to influence the structure of an aggregate are the packing constraints imposed by the molecular geometry;^{11,12} solution conditions, such as concentration and ionic strength;^{13,14} temperature;¹⁵⁻¹⁸ substrate hydrophobicity;^{19,20} and applied shear.²¹⁻²⁴ Cylindrical micelles that are elongated and flexible are generally termed as “wormlike, or threadlike, or giant micelles”.¹⁰ The solutions of wormlike micelles exhibit characteristic viscoelastic and flow

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Supporting Information: The ¹H, ¹³C, and ³¹P NMR of compounds **3-5**, ESI-MS of **5a** and **5b**, crystallographic reports on compounds **4a** and **4b**, and the coordinates of B3LYP/Lanl2DZ optimized geometries of **5a** and **5b** are included in the Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

birefringence properties.^{25,26} The wormlike and branched micelles have found several applications,¹⁰ such as drag-reducing agents,^{25,27} fracture fluids,^{25,27} polymerization templates,²⁸ and in consumer products.²⁷

Micelles that are formed by functionalized amphiphiles that contain one or more transition metal atoms in its headgroup are known as metallomicelles. The incorporation of a transition metal in metalloaggregates helps in devising applications, on the basis of its geometric, redox, magnetic, and catalytic properties. The headgroup size, charge, and structure can be easily modified to suit a particular function.²⁹⁻³⁵ In addition, derivatization of the rigid, transition metal-containing compounds with long hydrophobic chains enhances their processability as soft materials.^{31,36} Further, the integral position of the metal ions in the headgroup enables localization of its properties at the interfaces; namely, air-water, oil-water, or solid-air interfaces. The utility of such interfacial organization is presently realized in several catalytic reactions.³⁷⁻⁴²

A hybrid material, such as an organometallic gemini, could combine both the qualities of a dimeric amphiphile and that of a built-in transition metal. However, despite the potential it poses, instances of organometallic gemini in the literature are rare,⁴³ particularly in the case of amphiphilic platinum complexes. Although studies⁴⁴⁻⁵⁰ on single- and twin-tailed monomeric Pt amphiphiles exist, until now, reports on organoplatinum geminis are absent.

A homologous series of organoplatinum gemini amphiphiles with differing alkoxy chain lengths are synthesized (denoted with $(C_nO)_2PHEN$ notation, where the chain lengths are $n = 6, 12$; Figure 1). The structural amphiphilicity arises from its hydrophobic alkoxy chains and weakly coordinated Pt- ONO_2 hydrophilic headgroups. The angularity of the rigid phenanthrene spacer imposes a reduced intramolecular separation between the divalent polar Pt centers. In addition, the strong bonding between the platinum atom and the phenanthrene spacer bearing the hydrophobic chains does away with the requirement of adding auxiliary, anionic lipophiles to confer the amphiphilic balance.⁵¹ Further, the adjacent positioning of the two alkoxy chains on the phenanthrene backbone reduces the conformational degrees of freedom available to them. The specific features, such as the polar nature of the Pt headgroups, the angularity of the phenanthrene spacer, and differing lengths of hydrophobic chains, are expected to play a considerable role in determining the disposition of interfacial structures.

Although the general lack of adequate work on the interfacial properties of platinum amphiphiles⁴⁸⁻⁵⁰ is a contributing factor leading to the present study, the primary motivation arose from the need to understand the interfacial self-assembly of organoplatinum gemini amphiphiles. The molecular assembling strategy of Langmuir-trough techniques is employed to study their self-organization at the two-dimensional environment of the air-water interface by limiting the available molecular area. This method facilitates precise control of molecular orientation, phase behavior, thickness, and homogeneous deposition of a thin film on a solid substrate.^{52,53} The Langmuir isotherms for $(C_nO)_2PHEN$ nitrates ($n = 6, 12$), reveal an unusual interfacial behavior, unlike conventional amphiphiles, and suggest a possible aggregation of the organoplatinum amphiphiles at the air-water interface.

The Langmuir layers are deposited on a hydrophobic substrate, and the film morphology is investigated by atomic force microscopy (AFM). This surface-imaging technique not only offers direct visualization of the molecular structures with a subnanometer resolution but also minimizes deformation of the soft matter by way of imaging in intermittent contact mode. Further, its in situ imaging capability permits study of transferred Langmuir-Schaefer (LS) films under conditions analogous to those existing at the air-water interface. The

imaging of the transferred films confirms that the two organoplatinum amphiphiles self-aggregate into wormlike metallomicelles at the air-water interface. Reasonable arguments founded on the experimental results are proposed for the observed phenomena, and where possible, comparisons have been made with expectations and other related systems.

Results and Discussion

We have selected 3,6-dibromophenanthrene-9,10-quinone **1** as the skeleton for a new 60° building block because it presents an ideal substrate for introduction of alkyl chains into the phenanthrene backbone and subsequent platinum insertion. The 9,10-dihexyloxy-, and 9,10-didodecyloxyphenanthrene derivatives (**3a** and **3b**) of dibrominated compound **2** are prepared as per the established procedure⁵⁷ by employing a two-phase system and a phase transfer catalyst in yields of 56 and 59%, respectively. The appearances of a triplet signal at δ 4.16-4.17 ppm integrating for four protons in the ¹H spectrum of **3a** and **3b** suggests that the O-alkylation has taken place.

The metal functionalization of the dialkoxylated compounds **3a** and **3b** by a double oxidative addition⁵⁸ of tetrakis(triethylphosphine)platinum(0) provides the insertion products **4a** and **4b**. The underlying factors for the choice of Pt(II) metal centers and the strongly binding triethylphosphine ligands, are *d*⁸ metal ion square planar geometry, directionality of the coordination bonds, and inherent stability of the final complex. Next, the bromine atoms of compounds **4a** and **4b** are exchanged for the more labile and ionic nitrate anions by metathesis with AgNO₃, yielding compounds **5a** and **5b**. The weakly bound unidentate nitrate anion augments the hydrophilic nature of the headgroups and, thus, promotes its anchoring to polar interfaces. Further, the nitrate ligands of Pt(II) complexes are relatively very labile and are known to undergo rapid hydrolysis or aquation in aqueous solutions.⁵⁹⁻⁶³ Similarly, the aquation of the neutral dinitrato Pt(II) complexes **5** at the air-water interface would result in charged Pt(II) geminis with terminal aquo groups (Figure 2). The net charge on the cationic geminis^{64,65} would then depend on whether they are mono-aquated or diaquated.

Compounds **3-5** are white solids at room temperature. They are soluble in most organic solvents but are insoluble in water due to their high hydrophobicity-to-hydrophilicity ratio. The position of the polar Pt atoms, hemmed between two hydrophobic triethylphosphine groups, and the rigidity of the aromatic ring does little to enhance solubility of compounds **4** and **5**. The melting points of compounds **3a** and **3b** increase with increasing chain length. This trait is reversed after the insertion of the Pt atoms, with the dihexyloxy compounds **4a** and **5a** showing the highest melting points. On cooling, the materials **5a** and **5b** do not crystallize but become a glassy mass.

Compounds **3-5** are characterized by elemental analysis, ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy. Four equivalent phosphorus atoms in each of the molecules **4a** and **4b** give rise to a sharp singlet in the ³¹P{¹H} spectrum at 13.31 and 13.10 ppm, respectively, with concomitant ¹⁹⁵Pt satellites. The ¹H NMR spectrum of derivatives **4a** and **4b** shows multiplicity for peaks corresponding to the hydrogens of methylene (-PCH₂-, 1.02 ppm) and methyl (-PCH₂CH₃, 1.5 ppm) groups, which are in close proximity to the phosphorus atom. The multiplicity arises not only from the coupling between the methylene and methyl protons but also from additional coupling with the phosphorus nuclei. The aromatic proton signal at 8.4 ppm is accompanied by doublets centered about the major peak due to additional three-bond (³J_{H-Pt}) spin-spin coupling to platinum (¹⁹⁵Pt; *I* = 1/2; 33.8% natural abundance) of 63-73 Hz.

The final structures are well supported by mass spectrometry using electron spray ionization (ESI-MS). In the ESI-MS of **5a** and **5b**, signals are observed that correspond to the singly charged species of [(**5a**-NO₃)⁺](*m/z* 1300.9), and [(**5b**-NO₃)⁺](*m/z* 1469.0), whose isotope pattern reveals a spacing of $\Delta m = 1$ amu.

The geometry optimizations of gemini amphiphiles **5a** and **5b** are carried out using the Gaussian03 package⁶⁶ at the B3LYP (Becke's exchange and Lee, Yang, and Parr's correlation functionals) level^{67,68} using the Lanl2DZ (Los Alamos pseudopotential and double- ζ basis set) basis set,⁶⁹ to obtain the structural parameters required for analyzing the interfacial assembly. The choice of B3LYP functional for amphiphiles **5a** and **5b** is 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 that of the Pt atom,^{70,71} because of the limited availability of high-quality atomic orbital basis sets (see Supporting Information for optimization results).

Solid State Organization

Single crystals of the soft materials **4a** and **4b** are obtained by layer diffusion of methanol into a dichloromethane/chloroform solution. The crystal structure shows that each Pt atom is coordinated by two P atoms from triethylphosphine groups, the C_{sp2} atom of the phenanthrene ring and a Br atom, in a square-planar environment (Figure 3). The bulky phosphine groups are trans-coordinated due to sterics. The coordination planes of both platinum atoms lie orthogonal to the plane of the phenanthrene core.

A molecular-level feature of these molecules is the relative anti-disposition of the alkoxy chains, as they originate from the periphery of the phenanthrene ring. In the case of compound **4b**, the dodecyloxy chains realign their direction of chain propagation to achieve a parallel orientation, after the initial anti-disposition (Figure 3). One of the dodecyloxy chains assumes an extended trans zigzag conformation, whereas the other chain adopts a folded conformation near the phenanthrene ring, followed by a trans zigzag conformation along its chain length and gauche conformation toward the chain end. Furthermore, the chains are uniformly tilted by 65°, relative to the plane of the phenanthrene ring, in order to achieve minimum free volume by balancing the molecular cross sections of the hydrophobic chain with that of the larger aromatic molecular segment. The tilt direction of the intercalating dodecyloxy chains changes its sign from one layer to the next (Figure 4b). This kind of alternating tilt to the layer normal is typically seen in the anticlinic phases of smectic liquid crystals (which possess orientational as well as positional order). The orientational order in an anticlinic phase is generally attributed to the bent molecular architecture,⁷² and in the present case, the angular shape of our phenanthrene spacer might be the cause of tilting in the layers. Further, the phenanthrene ring preferentially packs into layers by aligning parallel to the adjacent rigid segments. The upside-down (head-to-tail) packing of the complexes provides stability by reducing the charge density on a given crystallographic plane (Figure 4a). The tilted tails gather together to form a thick hydrophobic layer and help fashion a herringbone type of arrangement. The segregated packing of polar coordination sites and nonpolar dodecyloxy chains is reflective of the amphiphilic nature of compound **4b**. Analogous segregation effects are observed in amphiphilic complexes of group 10d metals previously reported in the literature.⁴⁴⁻⁴⁷ In contrast, both the hexyloxy chains of compound **4a** show a significant conformational disorder and represent a poor segregating system. This indicates that the efficient packing of the hydrophobic chains depends on their respective lengths.

The shortest Pt ... Pt intramolecular distance (7.85 Å) within the molecule and Pt ... Pt intermolecular (15.6 Å) distance between adjacent molecules indicates the absence of metal-metal interaction (Pt ... Pt > 4 Å). It also demonstrates the role of the angular spacer in

forcing the intramolecular Pt headgroups to be closer than the Pt atoms in two neighboring molecules. The plane separations ($>12 \text{ \AA}$) between the adjacent phenanthrene rings are long enough to exclude π - π interactions, as well. The coordination planes containing the bulky triethylphosphine groups are orthogonal to the plane of the phenanthrene ring, which sterically hinders interplanar stacking and metal-metal interactions, a trait also observed in a related, but nonamphiphilic, organoplatinum complex.⁷³

Surface Pressure-Area Isotherms

Millimolar solutions of the organoplatinum gemini amphiphiles **5a** and **5b** in chloroform are spread on a pure water surface, symmetrically compressed by movable barriers, and the resulting force imparted by the films is measured as surface pressure (Π)-area (A) isotherms, at 25°C (Figure 5).

The Π - A isotherms reveal an initial rise of surface pressure on compression (region I), followed by a slowly rising plateau with an upward slope (region II) and terminating with a relatively steep ascent for molecular areas smaller than $35 \text{ \AA}^2$ (region III). Although the isotherms share the same contour, their interfacial characteristics, such as the extrapolated area at $\Pi=0$ (minimum area per molecule) and phase transitions, differ with chain length.

The “take-off” areas corresponding to the onset of surface pressure show a maximum for the short-chain amphiphile **5a** ($\sim 189 \text{ \AA}^2$, $n=6$) and a minimum for the longer-chain amphiphile **5b** ($167 \text{ \AA}^2$, $n=12$). Further, for a given Π in region I, the molecular area is larger for the short-chain amphiphile. It indicates that the short-chain amphiphile occupies a larger molecular area and exhibits loose molecular packing. Since the structures of the two geminis differ only in length of the chains and not in the nature of the spacer or the headgroups, the decrease in packing density with decrease in chain length may be explained by the weaker chain-chain attractive forces in the short-chained amphiphile that less effectively offset the electrostatic repulsion among the cationic headgroups.⁵³ The magnitude of such electrostatic repulsions is determined by ion-specific interactions,⁷⁴ such as ion hydration, extent of counterion pairing (effective charge on hydrophilic group), and nonuniform charge distributions⁶ arising out of dissimilar intermolecular and intramolecular Pt ... Pt atom distances.

The phase transitions, observed as inflection points A and B, move to higher surface pressure with an increase in alkoxy chain length ($\Pi = 30, 35 \text{ mN m}^{-1}$ for $n = 6, 12$, respectively). This transition is pronounced for the smaller chain length, as the relatively stretched out molecules become more compact. In region III, both materials reach higher compressibilities capable of withstanding surface pressures up to 50 mN m^{-1} without a noticeable collapse.

The molecular areas of $(\text{C}_n\text{O})_2\text{PHEN}$ nitrates ($n = 6, 12$) are calculated by extrapolating the linear regions I and III of the Π - A isotherms to zero surface pressure. The experimental molecular areas at region I for $n = 6, 12$ are found to be ~ 168 and $148 \text{ \AA}^2$, respectively. They show the expected decrease with the increase in alkoxy chain length due to close packing of the longer chains.⁷⁵ The two probable orientations of the amphiphiles **5a** and **5b** during the initial rise are the “face-on” structure, in which the phenanthrene core lies parallel to the water interface, with the alkoxy tails extending into air, and the “edge-on” conformation, in which the phenanthrene core is normal to the interface, with the two hydrophilic Pt cations preferentially immersed in water. Although the occurrence of face-on conformational structures at the air-water interface have been previously indicated in amphiphilic group 10d metal complexes,⁴⁸⁻⁵⁰ their occurrence in the thin films of amphiphiles **5a** and **5b** are unlikely. In the face-on conformation, the majority of the hydrophobic segments of the

molecules will be forced to come in contact with the hydrophilic surface. Hence, this conformation is energetically unfavorable.

The orthogonal positioning of the bulky triethylphosphine groups distributed evenly on either side of the phenanthrene ring restricts the molecular spacing in the medial plane to be no smaller than the total bond length of $\sim 12 \text{ \AA}$ [$\text{P}(\text{Et}_3)\text{-Pt-P}(\text{Et}_3)$]. It diminishes not only the possibility of π - π stacking interactions but also that of a closely packed monolayer based on an edge-on conformation. Consequently, the balance between attractive hydrophobic forces, repulsive electrostatic interactions, and steric effects will determine the arrangement of the amphiphiles at the air-water interface.

The possibilities of a face-on orientation and that of a close-packed monolayer via an edge-on conformation are also eliminated on the basis of experimental molecular areas, and the argument for surface aggregates as adsorbing units is put forward as follows: The molecular-area estimates obtained from Gaussian66 molecular models give an area per molecule of $\sim 241 \text{ \AA}^2$ ($13.4 \text{ \AA} \times 18 \text{ \AA}$) in addition to the typical molecular area occupied by the two untilted alkoxy tails ($\sim 40 \text{ \AA}^2$) for a face-on conformation and a molecular area of $\sim 216 \text{ \AA}^2$ ($12 \text{ \AA} \times 18 \text{ \AA}$) for an edge-on conformation. The experimental molecular areas obtained by extrapolation are expected to be lower than the theoretical values (the latter does not account for the packing efficiency of the molecules), but the limiting molecular areas at region I are too small for a molecule to adopt either a face-on or an edge-on conformation at the interface. This is suggestive of molecular aggregation at the interface rather than a simple molecular reorientation. Similarly, the very low limiting molecular areas (~ 60 and $78 \text{ \AA}^2$ for $n = 6, 12$, respectively) at the high-density region III rules out unequivocally the presence of a monomolecular surface film. Such low values of surface area per molecule for gemini amphiphiles at the air-water interface have been previously observed in several cases, and aggregate formation has been proposed as a probable cause.⁷⁵⁻⁷⁹ The smaller area per monomer calculated by extrapolating the initial rise in the isotherm is indicative of early formation of aggregates.

Isotherm experiments reveal a small hysteresis on limited compression and expansion but show a large hysteresis upon decompression from higher pressures (Figure 6). The occurrence of such metastable monolayers has been reported in an amphiphilic Pt complex⁴⁹ and more commonly in macromolecules.^{80,81} The apparent lack of reversibility in the charged monolayers indicates dissimilarity in the association/disassociation processes during compression and decompression, respectively. Such an irreversible molecular organization also favors the existence of nonmonomolecular structures at the interface.

Micellization Studies

To better understand the unusual interfacial behavior and to detect the existence of aggregates at the air-water interface, the morphology of LS films is examined as a function of lateral surface pressure by using AFM on a hydrophobic substrate, such as octadecyltrichlorosilane (OTS)-derivatized silicon wafer. The LS films are maintained in hydrated conditions without removing them from the subphase water at any point of time during sample preparation as well as imaging to avoid any morphological change due to drying.

A dense population of wormlike micelles is observed for both the geminis **5a** and **5b** on the OTS/Si (111) substrate (Figures 7 and 8, respectively). The contour lengths of wormlike micelles extend to several hundred nanometers. The heights of the cylindrical aggregates show a monotonic increase with the chain length. Further, an increase in the chain length also increases the micelle packing density and aggregation numbers, as is evident from the attendant increase in the apparent widths of the cylindrical aggregates.

The tighter packing of the worm micelles precludes our efforts to elicit additional information with certainty on the structural scale lengths, such as the persistence length or the cross-sectional radius of the wormlike micelles. There is also no clear indication for the existence of branching. The wormlike micelles are known to exist in cationic geminis^{1,82,83} and in cationic monomeric amphiphiles,⁸⁴ as well. A cryo-TEM study also reported the direct observation of wormlike shear-induced structures (SIS) in a gemini surfactant.²¹ Analogous studies⁸⁵⁻⁸⁷ in block copolymers shows that a spherical micellar phase transforms into a cylindrical phase under a strong external flow field.

Under the given aqueous conditions existing at the air-water interface and during imaging in fluid, the 12 triethyl groups, equally distributed on the phosphorus atoms near the polar head groups in each gemini amphiphile, would constitute the outer corona of any conceivable aggregate organization, where the tails form the core (Figure 9).⁸⁸ Several of the triethyl segments near the headgroups are constrained to sample the surrounding water molecules. However, the energy penalty associated with this arrangement is comparatively less than in a reverse wormlike micelle, where the tails forming the outer corona would make contact with the hydrophilic environment. Further, the hydrophilic sequestration of the charged hydrated headgroups within the reverse micellar core would result in highly unfavorable electrostatic interactions. In contrast, the arrangement of the headgroups near the curved surface of the wormlike micelle lessens the electrostatic repulsions between the polar headgroups and promotes favorable headgroup interactions (hydration) with the contiguous water molecules. The triethyl groups, albeit feeble, are expected to reciprocate the attractive hydrophobic interactions of the substrate. The octadecyltrichlorosilane (OTS)-derivatized silicon surface serves as an ideal candidate since it offers a featureless surface and is strongly hydrophobic to make up for the weak hydrophobicity of the triethyl groups. The AFM images reveal that the stronger hydrophobic interactions of the substrate do provide a tighter hold on the interfacial structures in a time scale that allows imaging of the true interfacial morphology.

Another salient feature of the wormlike metallomicelles of $(C_nO)_2PHEN$ nitrates ($n=6, 12$) is the strong anisotropy, owing to their alignment in the flow. Similar alignments have been reported in SIS involving cylindrical micelles⁸⁹ and in monolayers of a diblock-copolymer,⁹⁰ wherein the cylinders align parallel to the shearing direction. Monte Carlo simulations⁹¹ on the thin films of confined cylindrical micelles, under steady shear, suggest a two-step mechanism governing their alignment: First, the micelles aligned perpendicular to the shear break up, and then they are realigned in the shear direction. An earlier study in threadlike polyionic micellar system shows that even small flow rates give rise to highly ordered, near-surface, hexagonally aligned phases in the flow direction from an initially entangled micellar state.^{92,93} The inflection point and the succeeding plateau in the Langmuir isotherms could correspond to a progressive orientation and continued elongation of the disconnected micellar segments, that is, isotropic (disordered) to anisotropic (orientational order) phase change. Similar shear-induced phase transitions have been reported in wormlike micelles.⁹⁴⁻⁹⁸ In one such study, the isotropic-to-nematic phase transition in worm micelles shows up as a kink in the shear stress behavior.⁹⁷

Molecular dynamics simulations⁹⁹ of gemini amphiphiles with hydrophobic spacers also indicate that monomers aggregate into spherical micelles that, upon repeated collisions among themselves, fuse into equilibrium wormlike micelles. In addition, sphere-to-wormlike micelle transitions have been explained on the basis of a decrease in surface area per amphiphile as a result of reduction in surface charge either by counterion binding or by association with additives.¹³ Such transitions are also observed as a function of concentration change in a gemini surfactant⁹ and as a function of ionic strength in ionic polymeric amphiphiles.¹⁴ Chemical trapping studies¹⁰⁰ in gemini amphiphiles demonstrate

that ion pairing and concomitant interfacial dehydration driven by the hydrophobic effect allow tighter packing of cationic amphiphiles, enabling sphere-to-rod transitions.

On the basis of suggestions in the literature, we presume that the aggregates existing at the air-water interface, before applied shear, are essentially spherical, although there is a possibility of a certain number of individual molecules existing in a free state. Further, it is unlikely that molecules would spontaneously self-assemble into cylindrical micelles of reduced curvature at low surface pressures without initially self-assembling into a spherical structure, since smaller (spherical) micelles are favored both by entropy and a higher curvature than that of cylinders or bilayers. The spherical aggregates upon application of shear and consequent reduction in the surface area undergo adhesive intermicellar collisions before self-assembling into energetically stable, wormlike micelles. The wormlike micelle morphology is thus a resultant of both shear-induced alignment and growth.

Conclusion

The directed self-assembly of the organoplatinum gemini amphiphiles at the air-water interface by the Langmuir method suggests a substantial self-aggregation of the amphiphiles. The investigation of interfacial morphology vindicates the aggregation theory by revealing the presence of giant wormlike metallomicelles. These SIS, unlike worm micelles of certain amphiphiles, do not require extraneous electrolytes for their growth and are observed only when the Langmuir layers are submitted to steady shear. A strong alignment of the worm micelles in the direction of flow is also observed. A shear-induced phase transition is proposed for the extended plateau in the Langmuir isotherms. To the best of our knowledge, this represents the first direct observation of strongly aligned worm micelles at the air-water interface for organometallic amphiphiles.

The formation of giant micelles at the air-water interface indicates the conditions that enable the creation of comparable micelle structures in aqueous solution are also relevant at interfaces. The investigation into the interfacial morphologies of the organoplatinum gemini amphiphiles gains significance, since vital properties of flowing systems, such as drag and lubrication, are evidently interfacial phenomena. The organoplatinum metallomicelles also could offer routes to stimuli-responsive anisotropic materials and help in the understanding of charged biopolymer organizations in nature.

Experimental Section

Langmuir-Trough Measurements

Langmuir-Schaefer (LS) films are prepared on a commercial Langmuir trough (36×7.5 cm, KSV) housed in a dust-free cabinet. Deionized, double-distilled (DDI) water is used as a subphase. The experimental conditions, such as subphase temperature (25°C), compression speed (2 mm min^{-1}), spreading solution volume ($18\text{ }\mu\text{L}$), concentration (1 mM), subphase volume ($\sim 270\text{ mL}$), and monolayer aging time ($30\text{--}45\text{ min}$), are kept unchanged for the sake of reproducibility and comparison. A low compression speed is required to achieve compression under equilibrium conditions. The Teflon trough and Delrin barriers are thoroughly cleaned with chloroform (HPLC) and absolute ethanol and rinsed with DDI water prior to usage. The surface pressure is measured by a platinum Wilhelmy plate attached to an electrobalance (resolution= $4\text{ }\mu\text{Nm}^{-1}$) while being held parallel to the symmetrically moving barriers to avoid the preferential flow of monolayer observed in cases of unilateral compression. The Wilhelmy plate is cleaned with chloroform and absolute ethanol and then flamed until red-hot in the outer regions of the Bunsen flame. The plate wettability after flaming is qualitatively checked by dipping it in DDI water. Prior to monolayer spreading, the interface is aspirated clean until the surface pressure change is

<0.1 mN/m upon reducing the interfacial area from 240 to 30 cm² in two successive blank runs. Adequate care is undertaken while applying minute droplets of the solution on different parts of the water surface to enable consistent formation of well-spread films. All experiments were repeated at least twice with freshly prepared stock solutions.

Silanization

The procedure for preparing self-assembled monolayers (SAM) of OTS on Si wafers is adapted from an earlier report,¹⁰¹ with certain modifications in substrate, reaction, and processing conditions. Substrates ($\sim 10 \times 5$ mm²) are cut from a polished N⁺-type Si(111) wafer (MEMC Electronic Materials Sdn Bhd., Malaysia). Anhydrous octadecyltrichlorosilane (CH₃-(CH₂)₁₇-SiCl₃, OTS) was purchased from Sigma-Aldrich, Inc. DDI water (~ 18 M Ω), HPLC grades of hexane and chloroform, and spectral grades of acetone and toluene are used for the substrate preparation and postdeposition cleaning.

After removing the organic residues by sonication in acetone for 20-30 min, the native surface oxides on the substrates are removed by immersing in dilute hydrofluoric acid (HF/DDI H₂O = 1:36 by volume) for less than 1 min before rinsing thoroughly in DDI water. The substrates are reoxidized and hydroxylated in 120 mL of stirring acidic piranha solution (36 mL H₂O₂/84 mL H₂SO₄) for 15-20 min, followed by rinsing with DDI water. They are dried under ultra high pure (UHP) nitrogen flow and kept in an oven at 100 °C for 5-10 min to ensure complete removal of water.

The silicon substrates are placed in a millimolar (mM) solution of OTS dissolved in hexane and stirred for ~ 18 -20 h under anhydrous glovebox conditions. Later, while still in the glovebox, they are transferred into a bottle containing chloroform, and the solvent is vigorously stirred for 30 min. Subsequently, the modified substrates are transferred to a lidded bottle containing fresh chloroform before removing it from the glovebox. They are sonicated three times for 15-20 min, each in CHCl₃ and in toluene, to remove the physisorbed OTS clusters. The functionalized substrates are dried under UHP nitrogen flow and stored in covered dishes.

The static contact angles of DDI water on the chemisorbed surfaces are measured using a goniometer (CAM 100, KSV Instruments Ltd.) in a sessile drop configuration. The contact angles are found to be in the range of 108°-110° for OTS/Si(111) substrates, indicating successful hydrophobization of the surfaces. The AFM images of the SAM reveal a uniform, featureless surface devoid of clusters and a surface roughness of <0.5 nm.

LS Film Transfer

Chemically modified OTS/silicon (111) surfaces are used as hydrophobic substrates for the LS film transfer. The LS films at different surface areas are transferred to the hydrophobic substrates via 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 are gently immersed through the well of the trough, carefully flipping it over to keep the transferred surface facing up and then placing it in a Petri dish. The remnants of the LS film and the subphase water are removed without affecting the immersed sample in the Petri dish. Further, the subphase water in the Petri dish is partially replaced with fresh DDI water without exposing the sample to air. It is then lidded and taken for in situ imaging.

Intermittent Contact AFM Imaging

The substrates with transferred LS layers are imaged by a Picoscan instrument operating in intermittent contact (tapping) mode using a multipurpose small scanner with a 8.5 μ m (x) $\times$ 9.0 μ m (y) $\times$ 0.9 μ m (z) scan range. The measurements are performed on the samples in

water at room temperature ($\sim 22^\circ\text{C}$) and not more than 5–10 h after the LS film transfer. The Al-coated silicon probes (MikroMasch) have weak force constants of 0.12 and 0.35 N m^{-1} and are used in intermittent contact mode to prevent surface deformation and damage. While imaging, samples are maintained in as-transferred (hydrated) conditions without removing them from the subphase water to avoid any morphological change due to drying. Typically, scans are made on at least three distinct locations in each sample, and for a given set of conditions, at least two independently prepared samples are imaged. The scan size and angles are varied to check for drift. The recorded two-dimensional images are processed using Image Metrology software for noise reduction. After imaging, the films are gradually dried in a desiccator and saved for further analysis.

Ellipsometry

The average layer thickness of the dried LS films on octadecyl-derivatized Si (111) wafers is obtained by measuring the ellipsometric angles Ψ and Δ in air. The measurements are performed with a J. A. Woollam Co., Inc. ellipsometer, model XLS-100, and controlled by Wvase32 software (version 3.632). The light sources used are D_2 (deuterium) and QTH (quartz tungsten halogen) lamps. The experiments are performed at an angle of incidence of $\Phi = 75^\circ$. The values are expected to be lower than those determined by atomic force measurements as a result of averaging out the lateral inhomogeneities in measured areas ($\sim 1 \text{ mm}^2$).

General Methods

All reagents were purchased and used without further purification. 3,6-Dibromo-9,10-phenanthrenequinone was prepared according to literature procedures.^{52–54} All NMR spectra were recorded on Varian Unity 300 or XL-300 spectrometers. The ^1H 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 is not used, relative to the residual protons of deuterated acetone ($\delta_{\text{H}} = 2.05$ ppm). The $^{13}\text{C}\{^1\text{H}\}$ chemical shifts are reported relative to solvent signals. The $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 ($\delta_{\text{P}} = 0.00$ ppm). 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.

Materials

3,6-Dibromo-9,10-bis(hexyloxy)phenanthrene (3a)—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) is stirred at room temperature for 5 min. Then 1-bromohexane (7.13 g, 43.2 mmol) followed by KOH (12.0 g, 214 mmol) in H_2O (60 mL) is added. After stirring for 2 days, the reaction mixture is diluted with H_2O (200 mL) before extracting with EtOAc (4×100 mL). The combined extracts are washed with H_2O (1 H 200 mL) and brine (1 H 150 mL), dried over MgSO_4 , and evaporated to dryness. To the oily residue is then added MeOH (100 mL), and the colorless crude product is precipitated out. After filtration and drying, further purification is achieved by column chromatography (SiO_2 , n -hexane/ $\text{CH}_2\text{Cl}_2 = 10:1$). Yield: 2.47 g (4.61 mmol, 56%); colorless product. m.p.: $56\text{--}58^\circ\text{C}$. ^1H NMR (CD_2Cl_2 , 300 MHz): $\delta_{\text{H}} = 0.93$ (t, 6H, $J_{\text{HH}} = 7.1$ Hz, CH_3), 1.32–1.43 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.50–1.60 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.88 (q, 4H, $J_{\text{HH}} = 7.1$ Hz, OCH_2CH_2), 4.17 (t, 4H, $J_{\text{HH}} = 6.7$ Hz, OCH_2), 7.71 (dd, 2H, $J_{\text{HH}} = 8.9$, 1.9 Hz, Ar-H), 8.10 (d, 2H, $J_{\text{HH}} = 8.8$ Hz, Ar-H), 8.66 (d, 2H, $J_{\text{HH}} = 1.9$ Hz, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125.7 MHz): $\delta_{\text{C}} = 14.4$, 23.2, 26.4, 30.9, 32.3, 74.2, 120.7, 124.8, 125.9,

129.3, 129.4, 130.9, 143.7. C-H-N calcd. for $C_{26}H_{32}O_2Br_2$: C 58.22%, H 6.01%. Found: C 58.24%, H 6.06%.

3,6-Dibromo-9,10-bis(dodecyloxy)phenanthrene (3b)—Prepared analogous to **3a**, using 1-bromododecane (10.8 g, 43.2 mmol). Yield: 3.39 g (4.80 mmol, 59%); colorless product. m.p.: 70–72 °C. 1H NMR (CD_2Cl_2 , 300 MHz): δ_H = 0.89 (t, 6H, J_{HH} = 6.7 Hz, CH_3), 1.28–1.41 (m, 32H, CH_2), 1.50–1.59 (m, 4H, $OCH_2CH_2CH_2$), 1.88 (q, 4H, J_{HH} = 7.1 Hz, OCH_2CH_2), 4.17 (t, 4H, J_{HH} = 6.7 Hz, OCH_2), 7.71 (dd, 2H, J_{HH} = 8.8, 1.8 Hz, Ar-*H*), 8.10 (d, 2H, J_{HH} = 8.8 Hz, Ar-*H*), 8.66 (d, 2H, J_{HH} = 1.9 Hz, Ar-*H*). ^{13}C NMR (1H) (CD_2Cl_2 , 125.7 MHz): δ_C = 14.5, 23.3, 26.8, 30.0, 30.1, 30.2, 30.3, 30.4, 31.0, 32.5, 74.3, 120.7, 124.8, 125.9, 129.4, 129.5, 130.9, 143.8. C-H-N calcd. for $(C_{38}H_{56}O_2Br_2)$: C 64.77%, H 8.01%. Found: C 64.79%, H 8.10%.

3,6-Bis[trans-Pt(PEt_3) $_2$ Br]-9,10-bis(hexyloxy)phenanthrene (4a)—Under nitrogen, a solution of 3,6-dibromo-9,10-bis(hexyloxy)phenanthrene **3a** (488 mg, 0.91 mmol in dry and degassed toluene (30 mL)) is syringed into a solution of freshly prepared $[Pt(PEt_3)_3]$ (2.00 g, 3.64 mmol in dry and degassed toluene (30 mL)) and stirred at 105 °C for 3 days. After evaporation to dryness, the residue is washed with MeOH (3 H 15 mL), followed by recrystallization from CH_2Cl_2 /MeOH. Yield: 977 mg (0.70 mmol, 77%); colorless product. m.p.: 224–226 °C. 1H NMR (CD_2Cl_2 , 300 MHz): δ_H = 0.94 (t, 6H, J_{HH} = 7.1 Hz, CH_3), 1.02–1.12 (m, 36H, PCH_2CH_3), 1.36–1.45 (m, 8H, $CH_2CH_2CH_3$), 1.54–1.72 (m, 28H, PCH_2CH_3 and $OCH_2CH_2CH_2$), 1.90 (q, 4H, J_{HH} = 7.1 Hz, OCH_2CH_2), 4.19 (t, 4H, J_{HH} = 6.6 Hz, OCH_2), 7.49 (d, 2H, J_{HH} = 8.4 Hz, J_{HPt} = 62.7 Hz, Ar-*H*), 7.72 (d, 2H, J_{HH} = 8.3 Hz, Ar-*H*), 8.48 (s, 2H, J_{HPt} = 72.8 Hz, Ar-*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 125.7 MHz): δ_C = 8.1, 14.3, 14.4, 14.6, 14.8, 23.3, 26.6, 31.2, 32.4, 73.7, 121.0, 125.4, 128.9, 129.8, 136.9, 138.1, 141.9. $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 121.4 MHz): δ_P = 13.31 (s, J_{PPt} = 2765 Hz). C-H-N calcd. for $(C_{50}H_{92}Pt_2P_4Br_2O_2)$: C 42.92%, H 6.63%. Found: C 43.12%, H 6.82%.

3,6-Bis[trans-Pt(PEt_3) $_2$ Br]-9,10-bis(dodecyloxy)phenanthrene (4b)—Prepared analogous to **4a** using 3,6-dibromo-9,10-bis(dodecyloxy)phenanthrene **3b** (621 mg, 0.88 mmol). Yield: 785 mg (0.50 mmol, 57%); colorless product. m.p.: 106–108 °C. 1H NMR (CD_2Cl_2 , 300 MHz): δ_H = 0.88 (t, 6H, J_{HH} = 6.7 Hz, CH_3), 1.02–1.12 (m, 36H, PCH_2CH_3), 1.28–1.44 (m, 32H, CH_2), 1.55–1.72 (m, 28H, PCH_2CH_3 and $OCH_2CH_2CH_2$), 1.90 (q, 4H, J_{HH} = 7.1 Hz, OCH_2CH_2), 4.14 (t, 4H, J_{HH} = 6.6 Hz, OCH_2), 7.56 (d, 2H, J_{HH} = 8.4 Hz, J_{HPt} = 62.8 Hz, Ar-*H*), 7.71 (d, 2H, J_{HH} = 8.3 Hz, Ar-*H*), 8.48 (s, 2H, J_{HPt} = 72.4 Hz, Ar-*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 125.7 MHz): δ_C = 8.1, 14.3, 14.5, 14.6, 14.8, 23.3, 26.9, 30.0, 30.2, 30.3, 30.4, 31.2, 32.5, 73.7, 121.0, 125.4, 128.9, 129.8, 136.9, 138.1, 141.9. $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 121.4 MHz): δ_P = 13.10 (s, J_{PPt} = 2765 Hz). C-H-N calcd. for $(C_{62}H_{116}Pt_2P_4Br_2O_2)$: C 47.51%, H 7.46%. Found: C 47.81%, H 7.57%.

3,6-Bis[trans-Pt(PEt_3) $_2$ (NO $_3$)]-9,10-bis(hexyloxy)phenanthrene (5a)—At room temperature, $AgNO_3$ (146 mg, 0.86 mmol) is added to a stirred solution of **4a** (400 mg, 0.29 mmol) in acetone (50 mL). Continuous stirring for 6 h in the dark results in a heavy creamy precipitate, which is then filtered off. The solvent of the remaining solution is removed under a flow of nitrogen before the residue is redissolved in CH_2Cl_2 (50 mL) and filtered through a glass fiber filter. Afterward, the solvent is removed again under a flow of nitrogen before the product is recrystallized at -21 °C from *n*-hexane. Yield: 260 mg (0.19 mmol, 66%); colorless product. m.p.: 188–190 °C. 1H NMR (CD_2Cl_2 , 300 MHz): δ_H = 0.93 (t, 6H, J_{HH} = 6.9 Hz, CH_3), 1.10–1.21 (m, 36H, PCH_2CH_3), 1.35–1.42 (m, 32H, CH_2), 1.44–1.60 (m, 28H, PCH_2CH_3 and $OCH_2CH_2CH_2$), 1.89 (q, 4H, J_{HH} = 7.1 Hz, OCH_2CH_2), 4.13 (t, 4H, J_{HH} = 6.6 Hz, OCH_2), 7.60 (d, 2H, J_{HH} = 8.4 Hz, J_{HPt} = 58.4 Hz, Ar-*H*), 7.73 (d, 2H, J_{HH} = 8.4 Hz, Ar-*H*), 8.42 (s, 2H, J_{HPt} = 70.9 Hz, Ar-*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 125.7

MHz): $\delta_C = 7.9, 13.1, 13.4, 13.6, 14.4, 23.2, 26.5, 31.1, 32.4, 73.8, 121.2, 124.9, 125.9, 128.6, 129.1, 136.3, 142.0$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.4 MHz): $\delta_P = 19.23$ (s, $J_{\text{PPT}} = 2887$ Hz). ESI-MS: 1300.9 (calcd. for $(\mathbf{5a} - \text{NO}_3)^{2+}$ 1300.5). C-H-N calcd. for $(\text{C}_{50}\text{H}_{92}\text{Pt}_2\text{P}_4\text{O}_8\text{N}_2)$: C 44.05%, H 6.80%, N 2.05%. Found: C 43.90%, H 6.84%, N 2.22%.

3,6-Bis[trans-Pt(PEt₃)₂(NO₃)]-9,10-bis(dodecyloxy)phenanthrene (5b)—Prepared analogous to **5a**, using 3,6-bis[trans-Pt(PEt₃)₂Br]-9,10-bis(dodecyloxy)phenanthrene **4b** (500 mg, 0.32 mmol) and AgNO₃ (163 mg, 0.96 mmol). Yield: 394 mg (0.26 mmol, 81%). m.p.: 100–102 °C. ^1H NMR (CD_2Cl_2 , 300 MHz): $\delta_H = 0.88$ (t, 6H, $J_{\text{HH}} = 6.7$ Hz, CH_3), 1.10–1.20 (m, 36H, PCH_2CH_3), 1.23–1.63 (m, 60H, PCH_2CH_3 and CH_2), 1.90 (q, 4H, $J_{\text{HH}} = 7.1$ Hz, OCH_2CH_2), 4.13 (t, 4H, $J_{\text{HH}} = 6.6$ Hz, OCH_2), 7.60 (d, 2H, $J_{\text{HH}} = 8.5$ Hz, $J_{\text{HPt}} = 59.2$ Hz, Ar-*H*), 7.73 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, Ar-*H*), 8.42 (s, 2H, $J_{\text{HPt}} = 67.8$ Hz, Ar-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125.7 MHz): $\delta_C = 7.9, 13.2, 13.4, 13.6, 14.4, 23.3, 26.9, 29.9, 30.0, 30.2, 30.3, 30.4, 31.2, 32.5, 73.8, 121.3, 124.7, 125.9, 128.6, 129.0, 136.3, 142.1$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.4 MHz): $\delta_P = 19.25$ (s, $J_{\text{PPT}} = 2888$ Hz). ESI-MS: 1469.0 (calcd. for $(\mathbf{5b} - \text{NO}_3)^{2+}$ 1468.7). C-H-N: calcd. for $(\text{C}_{62}\text{H}_{116}\text{Pt}_2\text{P}_4\text{O}_8\text{N}_2)$: C 48.62%, H 7.63%, N 1.83%. Found: C 48.78%, H 7.83%, N 1.91%.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

- (1). Zana, R.; Xia, J. Gemini Surfactants: Synthesis, Interfacial and Solution-Phase Behavior, and Applications. Marcel Dekker; New York: 2004.
- (2). Rosen, MJ. Surfactants and Interfacial Phenomena. 3rd ed.. Wiley; New York: 2004. Chapter 12; p. 415–427.
- (3). Zana R. Adv. Colloid Interface Sci. 2002; 97:205–253. [PubMed: 12027021]
- (4). Menger FM, Keiper JS. Angew. Chem., Int. Ed. 2000; 39:1906–1920.
- (5). In M, Zana R. J. Dispers. Sci. Technol. 2007; 28:143–154.
- (6). Camesano TA, Nagarajan R. Colloids Surf., A. 2000; 167:165–177.
- (7). Pisárík M, Rosen MJ, Polakovičová M, Devínský F, Lacko I. J. Colloid Interface Sci. 2005; 289:560–565. [PubMed: 16112237]
- (8). Wang X, Wang J, Wang Y, Yan H, Li P, Thomas RK. Langmuir. 2004; 20:53–56. [PubMed: 15744999]
- (9). Bernheim-Groswasser A, Zana R, Talmon Y. J. Phys. Chem. B. 2000; 104:4005–4009.
- (10). Zana, R.; Kaler, E. Giant Micelles. CRC Press; Boca Raton, FL: 2007. Surfactant Science Series
- (11). Israelachvili JN, Mitchell DJ, Ninham BW. J. Chem. Soc., Faraday Trans. 2. 1976; 72:1525–1568.
- (12). Israelachvili, JN. Intermolecular and Surface Forces. 2nd ed.. Academic Press; London, San Diego: 1992.
- (13). Lin Z, Cai JJ, Scriven LE, Davis HT. J. Phys. Chem. 1994; 98:5984–5993.
- (14). Zhulina EB, Borisov OV. Macromolecules. 2005; 38:6726–6741.
- (15). Dan N, Safran SA. Adv. Colloid Interface Sci. 2006; 123–126:323–331. [PubMed: 16842728]
- (16). Davies TS, Ketner AM, Raghavan SR. J. Am. Chem. Soc. 2006; 128:6669–6675. [PubMed: 16704268]

- (17). Lof D, Niemec A, Schillen K, Loh W, Olofsson G. *J. Phys. Chem. B.* 2007; 111:5911–5920. [PubMed: 17488116]
- (18). Magid LJ. *J. Phys. Chem. B.* 1998; 102:4064–4074.
- (19). Besteman K, van Eijk K, Vilfan ID, Ziese U, Lemay SG. *Biopolymers.* 2007; 87:141–148. [PubMed: 17626297]
- (20). Grant LM, Ducker WA. *J. Phys. Chem. B.* 1997; 101:5337–5345.
- (21). Oda R, Panizza P, Schmutz M, Lequeux F. *Langmuir.* 1997; 13:6407–6412.
- (22). Mendes E, Narayanan J, Oda R, Kern F, Candau SJ, Manohar C. *J. Phys. Chem. B.* 1997; 101:2256–2258.
- (23). Zheng Y, Lin Z, Zakin JL, Talmon Y, Davis HT, Scriven LE. *J. Phys. Chem. B.* 2000; 104:5263–5271.
- (24). Weber V, Schosseler F. *Langmuir.* 2002; 18:9705–9712.
- (25). Ezrahi S, Tuval E, Aserin A. *Adv. Colloid Interface Sci.* 2006; 128-130:77–102. [PubMed: 17239810]
- (26). Berret J-F, Lerouge S, Decruppe J-P. *Langmuir.* 2002; 18:7279–7286.
- (27). Yang J. *Curr. Opin. Colloids Interface Sci.* 2002; 7:276–281.
- (28). Walker LM, Kuntz DM. *Curr. Opin. Colloid Interface Sci.* 2007; 12:101–105.
- (29). Griffiths PC, Fallis IA, Willock DJ, Paul A, Barrie CL, Griffiths PM, Williams GM, King SM, Heenan RK, Görgl R. *Chem.—Eur. J.* 2004; 10:2022–2028. [PubMed: 15079842]
- (30). Dominguez-Gutierrez D, Surtchev M, Eiser E, Elsevier CJ. *Nano Lett.* 2006; 6:145–147. [PubMed: 16464024]
- (31). Bowers J, Amos KE, Bruce DW, Webster JRP. *Langmuir.* 2005; 21:1346–1353. [PubMed: 15697280]
- (32). Sommerdijk NAJM, Booy KJ, Pistorius AMA, Feiters MC, Nolte RJM, Zwanenburg B. *Langmuir.* 1999; 15:7008–7013.
- (33). Constable EC, Mundwiler S, Meier W, Nardin C. *Chem. Commun.* 1999; 16:1483–1484.
- (34). Garcia P, Marques J, Pereira E, Gameiro P, de Castro B, Salema R. *Chem. Commun.* 2001; 14:1298–1299.
- (35). Cruz-Campa I, Arzola A, Santiago L, Parsons JG, Varela-Ramirez A, Aguilera RJ, Noveron JC. *Chem. Commun.* 2007; 28:2944–2946.
- (36). Chu BW-K, Yam VW-W. *Inorg. Chem.* 2001; 40:3324–3329. [PubMed: 11421675]
- (37). Khan, MN. *Micellar Catalysis.* CRC Press; New York: 2006. Chapter 6; p. 343-370.
- (38). Manabe K, Mori Y, Wakabayashi T, Nagayama S, Kobayashi S. *J. Am. Chem. Soc.* 2000; 122:7202–7207.
- (39). Danks MJ, Jervis HB, Nowotny M, Zhou W, Maschmeyer TA, Bruce DW. *Catal. Lett.* 2002; 82:95–98.
- (40). Qiu LG, Xie AJ, Shen YH. *J. Mol. Catal. Chem.* 2006; 244:58–63.
- (41). Kung HH, Kung MC. *Top. Catal.* 2005; 34:77–83.
- (42). Polyzos A, Hughes AB, Christie JR. *Langmuir.* 2007; 23:1872–1879. and references therein. [PubMed: 17279669]
- (43). Gallardo BS, Abbott NL. *Langmuir.* 1997; 13:203–208.
- (44). Neve F, Crispini A, Campagna S. *Inorg. Chem.* 1997; 36:6150–6156.
- (45). Kato M, Ikemori M. *Acta Crystallogr.* 2003; C59:m25–m26.
- (46). Cocker TM, Bachman RE. *Mol. Cryst. Liq. Cryst.* 2004; 408:1–19.
- (47). Kato M, Okada Y, Shishido Y, Kishi S. *Acta Crystallogr.* 2006; C62:m171–m173.
- (48). Samha H, Martinez T, De Armond MK. *Langmuir.* 1992; 8:2001–2004.
- (49). Wang K, Haga M.-a, Monjushiro H, Akiba M, Sasaki Y. *Inorg. Chem.* 2000; 39:4022–4028. [PubMed: 11198856]
- (50). Kobayashi K, Sato H, Kishi S, Kato M, Ishizaka S, Kitamura N, Yamagishi A. *J. Phys. Chem. B.* 2004; 108:18665–18669.
- (51). Kimizuka N, Oda N, Kunitake T. *Inorg. Chem.* 2000; 39:2684–2689. [PubMed: 11197026]

- (52). Ulman, G. An Introduction to Ultrathin Organic Films. Academic Press; New York: 1991. p. 101-236.
- (53). Gaines, GL, Jr.. Insoluble Monolayers at Liquid-Gas Interfaces. Interscience; New York: 1966. p. 193-199.
- (54). Fox JM, Goldberg NR, Katz TJ. J. Org. Chem. 1998; 63:7456–7462. [PubMed: 11672398]
- (55). Bhatt MV. Tetrahedron. 1964; 20:803–821.
- (56). Schmidt J, Eitel M. J. Prakt. Chem. 1932; 134:167–176.
- (57). Paruch K, Katz TJ, Incarvito C, Lam K-C, Rhatigan B, Rheingold AL. J. Org. Chem. 2000; 65:7902–7608. [PubMed: 11073597]
- (58). Manna J, Kuehl CJ, Whiteford JA, Stang PJ. Organometallics. 1997; 16:1897–1905.
- (59). Addison, CC.; Sutton, D. Progress in Inorganic Chemistry. Cotton, FA., editor. Vol. Vol. 8. Wiley; New York: 1967. p. 195-286.
- (60). Britten JF, Lippert B, Lock CJL, Pilon P. Inorg. Chem. 1982; 21:1936–1941.
- (61). Rochon FD, Melanson R. Inorg. Chem. 1987; 26:989–992.
- (62). Hara K, Taguchi M, Yagasaki A. Polyhedron. 2001; 20:1903–1905.
- (63). Rochon FD, Tessier C. Can. J. Chem. 2002; 80:379–387.
- (64). Borse MS, Devi S. Adv. Colloid Interface Sci. 2006; 123-126:387–399. [PubMed: 16806032]
- (65). Shukla D, Tyagi VK. J. Oleo. Sci. 2006; 55:381–390.
- (66). Frisch, MJ.; Trucks, GW.; Schlegel, HB.; Scuseria, GE.; Robb, MA.; Cheeseman, JR.; Montgomery, JA., Jr.; Vreven, T.; Kudin, KN.; Burant, JC.; Millam, JM.; Iyengar, SS.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, GA.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, JE.; Hratchian, HP.; Cross, JB.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, RE.; Yazyev, O.; Austin, AJ.; Cammi, R.; Pomelli, C.; Ochterski, JW.; Ayala, PY.; Morokuma, K.; Voth, GA.; Salvador, P.; Dannenberg, JJ.; Zakrzewski, VG.; Dapprich, S.; Daniels, AD.; Strain, MC.; Farkas, O.; Malick, DK.; Rabuck, AD.; Raghavachari, K.; Foresman, JB.; Ortiz, JV.; Cui, Q.; Baboul, AG.; Clifford, S.; Cioslowski, J.; Stefanov, BB.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, RL.; Fox, DJ.; Keith, T.; Al-Laham, MA.; Peng, CY.; Nanayakkara, A.; Challacombe, M.; Gill, PMW.; Johnson, B.; Chen, W.; Wong, MW.; Gonzalez, C.; Pople, JA. *Gaussian 03*, revision C. 02. Gaussian, Inc.; Wallingford, CT: 2004.
- (67). Becke AD. J. Chem. Phys. 1993; 98:5648–5652.
- (68). Lee C, Yang W, Parr RG. Phys. Rev. B: Condens, Matter Mater. Phys. 1988; 37:785–789.
- (69). Hay PJ, Wadt WR. J. Chem. Phys. 1985; 82:270–310.
- (70). Ozimiskia WP, Garnuszeka P, Bednareka E, Dobrowolskia J. Cz. Inorg. Chim. Acta. 2007; 360:1902–1914.
- (71). Karhánek D, Kaer P, Kuzma M, Šplíchalová J, ervený L. J. Mol. Model. 2007; 13:1009–1016. [PubMed: 17632740]
- (72). Kunitake T. Angew. Chem., Int. Ed. Engl. 1992; 31:709–726.
- (73). Kryschenko YK, Seidel SR, Muddiman DC, Nepomuceno AI, Stang PJ. J. Am. Chem. Soc. 2003; 125:9647–9652. [PubMed: 12904031]
- (74). Romsted LS. Langmuir. 2007; 23:414–424. [PubMed: 17209589]
- (75). Rosen MJ, Mathias JH, Davenport L. Langmuir. 1999; 15:7340–7346. and references therein.
- (76). Zhao JX, Yang XF, Jiang R, Ma YH, Cao JJ. Colloids Surf., A. 2006; 275:142–147.
- (77). Seredyuk V, Alami E, Nyden M, Holmberg K, Peresyphkin AV, Menger FM. Colloids Surf., A. 2002; 203:245–258.
- (78). Seredyuk V, Alami E, Nyden M, Holmberg K, Peresyphkin AV, Menger FM. Langmuir. 2001; 17:5160–5165.
- (79). Menger FM, Littau CA. J. Am. Chem. Soc. 1993; 115:10083–10090.
- (80). Constantino CJL, Dhanabalan A, Oliveira ON Jr. Rev. Sci. Instrum. 1999; 70:3674–3680. and references therein.

- (81). Micic M, Orbulescu J, Radotic K, Jeremic M, Sui G, Zheng Y, Leblanc RM. *Biophys. Chem.* 2002; 99:55–62. [PubMed: 12223239]
- (82). Zana R, Talmon Y. *Nature.* 1993; 362:228–230.
- (83). Danino D, Talmon Y, Zana R. *Langmuir.* 1995; 11:1448–1456.
- (84). Shikata T, Imai S.-i. *Langmuir.* 2000; 16:4840–4845.
- (85). Hamley IW. *J. Phys.: Condens. Matter.* 2001; 13:R643–R671.
- (86). Park C, Simmons S, Fetters LJ, Hsiao B, Yeh F, Thomas EL. *Polymer.* 2000; 41:2971–2977.
- (87). Zvelindovsky AVM, Sevink GJA. *Europhys. Lett.* 2003; 62:370–376.
- (88). May, S.; Ben-Shaul, A. Chapter 2. In: Zana, R.; Kaler, E., editors. *Giant Micelles*. Vol. Vol. 140. CRC Press; Boca Raton, FL: 2007. p. 41-79. *Surfactant Science Series*
- (89). Butler PD, Magid LJ, Hamilton WA, Hayter JB, Hammouda B, Kreke PJ. *J. Phys. Chem.* 1996; 100:442–445.
- (90). Angelescu DE, Waller JH, Adamson DH, Deshpande P, Chou SY, Register RA, Chaikin PM. *Adv. Mater.* 2004; 16:1736–1740.
- (91). Arya G, Panagiotopoulos AZ. *Phys. Rev. E.* 2004; 70:031501.
- (92). Hamilton WA, Butler PD, Magid LJ, Han Z, Slawacki TM. *Phys. Rev. E.* 1999; 60:R1146–R1149.
- (93). Hamilton WA, Butler PD, Baker SM, Smith GS, Hayter JB, Magid LJ, Pynn R. *Phys. Rev. Lett.* 1994; 72:2219–2222. [PubMed: 10055819]
- (94). Berret J-F, Roux DC, Porte G. *J. Phys. II France.* 1994; 4:1261–1279.
- (95). Shikata T, Pearson DS. *Langmuir.* 1994; 10:4027–4030.
- (96). Coppola L, Gianferri R, Nicotera I, Oliviero C, Ranieri GA. *Phys. Chem. Chem. Phys.* 2004; 6:2364–2372.
- (97). Berret J-F, Roux DC, Porte G, Lindner P. *Europhys. Lett.* 1994; 25:521–526.
- (98). Rehage, H. Chapter 9. In: Zana, R., editor. *Dynamics of Surfactant Self-Assemblies: Micelles, Microemulsions, Vesicles, and Lyotropic Phases*. Vol. Vol. 125. CRC Press; Boca Raton, FL: 2005. p. 419-473.
- (99). Karaborni S, Esselink K, Hilbers PAJ, Smit B, Karthaus J, van Os NM, Zana R. *Science.* 1994; 266:254–256. [PubMed: 17771445]
- (100). Geng Y, Romsted LS, Menger F. J. *Am. Chem. Soc.* 2006; 128:492–501. [PubMed: 16402836]
- (101). Wang M, Liechti KM, Wang Q, White JM. *Langmuir.* 2005; 21:1848–1857. [PubMed: 15723481]

Figure 1.
Amphiphilic nature of an organoplatinum gemini amphiphile, (C₆O)₂PHEN.

Scheme 1.
 Synthesis of Gemini Amphiphiles 5a and 5b

Figure 2. Charged states of organoplatinum gemini amphiphile under aqueous conditions (e.g., air-water interface): mono-aquo, $[(C_6O)_2\text{-PHEN}(\text{OH}_2)]\text{NO}_3$, and di-aquo, $[(C_6O)_2\text{PHEN}(\text{OH}_2)_2]2\text{NO}_3$ complexes.

Figure 3.

(a, b) ORTEP representation of molecular structures **4a** and **4b**. Displacement ellipsoids are plotted at the 50% probability level. Hydrogen atoms are omitted for clarity. (c) Ball and stick diagram of compound **4b** showing the anti-disposition of the alkoxy chains (arrow).

Figure 4. Wire-frame models demonstrating the packing structure of complex **4b**: (a) upside-down arrangement of the organoplatinum amphiphiles and (b) alternate tilt arrangement (herringbone-like network).

Figure 5.

Surface pressure-area (II-A) isotherms of $(\text{C}_6\text{O})_2\text{PHEN}$ nitrate **5a** and $(\text{C}_{12}\text{O})_2\text{PHEN}$ nitrate **5b** at the air-water interface at a compression speed of 2 mm min^{-1} and at a subphase temperature of 25°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 points A and B mark the beginning of the phase transition.

Figure 6. $(\text{C}_6\text{O})_2\text{PHEN}$ nitrate **5a**: hysteresis isotherms at different target surface pressures (Π) of (a) 8, (b) 25, and (c) 40 mN m^{-1} . Symmetrical compression and decompression speeds = 2 mm min^{-1} at 25 $^\circ\text{C}$.

Figure 7.

(a) AFM height image of cylindrical micelles of amphiphile $(\text{C}_6\text{O})_2\text{PHEN}$ nitrate **5a**, deposited near the transition break point (A) in the Langmuir isotherm onto OTS/Si (111) substrate and acquired in situ under fluid conditions. The inset in the upper left corner is an image of the flat, featureless surface of untransferred OTS/Si (111) substrate (control; 2000 nm²). Lighter levels in the images correspond to higher height. The bright spots in the images show the drift is negligible. Height data of cylindrical micelles (cross-sectional analysis of high and low points in line profiles) are ~0.9-1.8 nm (by AFM) and 1.5 nm (by ellipsometry). (b) The contours are highlighted in the gray scale conversion of image 7a.

Figure 8.

(a) AFM height image of wormlike aggregates of amphiphile (C₁₂O)₂PHEN nitrate **5b**, deposited near the transition break point (B) in the Langmuir isotherm onto OTS/Si (111) substrate and acquired in situ under fluid conditions. The double-headed arrow indicates the alignment direction. The heights of the micellar aggregates were found to be ~1.6-2.2 nm (by AFM) and 1.9 nm (by ellipsometry). The scan size and angles are varied to check for drift. A z-scale bar is shown at the bottom. (b) The contours are highlighted in the grayscale conversion of image 8a.

Figure 9.

Illustration depicting the cross-sectional packing arrangement in a wormlike micelle of $(C_6O)_2PHEN^{2+}$ existing in aqueous conditions (at the air-water interface and during fluid AFM). The diaquated complex is chosen for illustrative simplicity only. Monoaquated and neutral species may very well exist in these aggregates. The hydrocarbon chains may disorder to attain a uniform packing density within the core, which is almost entirely devoid of water. The model is based on the theory of hydrocarbon droplet assumption (opposing forces model).⁸⁸

Table 1

Crystallographic Data for Compounds 4a and 4b

crystal data	4a	4b
empirical formula	C ₅₀ H ₉₂ Pt ₂ P ₄ Br ₂ O ₂	C ₆₂ H ₁₁₆ Pt ₂ P ₄ Br ₂ O ₂
formula weight	1399.12	1567.44
temperature (°K)	150(1)	150(1)
wavelength (Å)	0.71073	0.71073
crystal system	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
unit cell dimensions (Å, deg)	<i>a</i> = 13.8359(3) <i>b</i> = 13.9322(2) <i>c</i> = 30.3691(5)	<i>a</i> = 17.8653(3) <i>b</i> = 13.8624(2) <i>c</i> = 30.8478(4) β = 105.6140(8)°
volume (Å ³)	5854.08(18)	7353.59(19)
Z	4	4
<i>D</i> _x (Mg m ⁻³)	1.587	1.454
θ	2.89-27.51°	2.37-27.46°
absorption coefficient (mm ⁻¹)	6.282	5.046
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> 1 = 0.0439, <i>wR</i> 2 = 0.0881	<i>R</i> 1 = 0.0540, <i>wR</i> 2 = 0.1164
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0683, <i>wR</i> 2 = 0.0996	<i>R</i> 1 = 0.0873, <i>wR</i> 2 = 0.1316
shape and color	prism, colorless	plate, colorless
crystal size	0.30 × 0.25 × 0.25 mm	0.35 × 0.30 × 0.18 mm

^a $R1 = \Sigma(|F_O| - |F_C|) / \Sigma |F_O|$, $wR2 = [\Sigma(w(F_O^2 - F_C^2)^2) / \Sigma(F_O^2)^2]^{1/2}$.