Organometallic, Nonclassical Surfactant with Gemini Design Comprising $\pi$-Conjugated Constituents Ready for Modification

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Supporting Information

ABSTRACT: Surfactants are functional molecules comprising a water-compatible head group and a hydrophobic tail. One of their features is the formation of self-assembled structures in contact with water, for instance, micelles, vesicles, or lyotropic liquid crystals. One way to increase the functionality of surfactants is to implement moieties containing transition-metal species. Ferrocene-based surfactants represent an excellent example because of the distinguished redox features. In most existing ferrocene-based amphiphiles, an alkyl chain is classically used as the hydrophobic tail. We report the synthesis and properties of 1-tris(isopropyl)silyl-ethynyl-1′-trimethylammoniummethylferrocene (FcNMe3TIPS). In FcNMe3TIPS, ferrocene is part of the head group (Gemini design) but is also attached to a (protected) $\pi$-conjugated ethynyl group. Although this architecture differs from that of classical amphiphiles and those of other ferrocene-based amphiphiles, the compound shows marked surfactant properties comparable to those of lipids, exhibiting a very low critical aggregation concentration in water (cac = 0.03 mM). It forms classical micelles only in a very narrow concentration range, which then convert into monolayer vesicles. Unlike classical surfactants, aggregates already form at a very low concentration, far beneath that required for the formation of a monolayer at the air–water interface. At even higher concentration, FcNMe3TIPS forms lyotropic liquid crystals, not only in contact with water, but also in a variety of organic solvents. As an additional intriguing feature, FcNMe3TIPS is amenable to a range of further modification reactions. The TIPS group is easily cleaved, and the resulting ethynyl function can be used to construct heterometallic platinum-ferrocene conjugates with cis-trans-(Pt(PEt3)2X (X = Cl, I) complex entities, leading to a heterometallic surfactant. We also found that the benzylic $\alpha$-position of FcNMe3TIPS is rather reactive and that the attached ammonium group can be exchanged by other substituents (e.g., $\equiv$CN), which offers additional opportunities for further functionalization. Although FcNMe3TIPS is reversibly oxidized in voltammetric and UV–vis spectroelectrochemical experiments, the high reactivity at the $\alpha$-position is also responsible for the instability of the corresponding ferrocenium ion, leading to a polymerization reaction.

INTRODUCTION

Surfactants are highly important, functional molecules comprising a water-compatible head group and a hydrophobic tail. They are produced by the chemical industry on a mass scale ($\approx 1.6 \times 10^7$ t/year) and used in detergents, as emulsification agents, or for phase-transfer catalysis. Their main property is that they reduce the interfacial energy (note that the term “surfactant” represents an abbreviation for “surface-active agent”). One of their most important features is the formation of concentration-dependent, self-assembled structures in contact with water, ranging from micelles or vesicles to lyotropic liquid crystals (LLCs) and inverse phases at higher concentrations. The classical design of a surfactant molecule comprises a water-soluble head group attached to a hydrophobic alkyl tail. The properties and behavior of surfactants strongly depend on the relative proportions of the hydrophilic and oleophilic parts. Concepts like the packing parameter $P$ or the hydrophilic lipophilic balance (HLB) have been developed to describe the influence of such molecular variations.1–5 For instance, a surfactant equipped with two alkyl chains often has lipid-like character. Compounds with two head groups at the opposite sides of a long hydrophobic chain are called bolaform surfactants.6 An alternative structure is the so-called gemini architecture with the two heads separated by a relatively short spacer.7 Because of their special properties, several researchers became interested in asymmetric gemini surfactants.6–8

More recently, the portfolio of surfactants was successfully expanded by introducing additional properties such as pH-, CO2-, photo-, magneto-, or thermoresponsive features.9 Excellent reviews on this topic are available from Eastoe et al. in 2013 or Landfester et al. in 2017.10,11 A particularly powerful approach in the literature is the generation of hybrid surfactants containing an inorganic, transition-metal-containing building block.12 One of the most valuable features of such moieties is their rich redox chemistry. The reversible change of
Among redox-active building blocks, ferrocene (Fc) has proven to be of eminent importance. Ferrocene is a unique organometallic compound and the prototypical metallocene in modern chemistry. It is famous for its efficient methods of synthesis and derivatization, its completely reversible redox properties, and its oxidation state-dependent water solubility. Therefore, ferrocene has been widely used in materials science, in particular in polymer chemistry. Amphiphilic copolymers are well known and feature mostly a poly-(vinylferrocene) or a poly(ferrocenylsilane) backbone and water solubility-mediating groups. The latter are either incorporated into the backbone or attached to the numerous side chains. Various new synthetic procedures have been developed during the recent years, for instance, by Manners et al. or Wurm et al., who provided expanded libraries of polymer-like ferrocene-based amphiphiles with high potential for future applications, for example, in separation methods or for reducing the overall surfactant waste during industrial processes. A good overview over ferrocene-based surfactants was provided by Abbot et al. The field of ferrocene-modified amphiphiles was pioneered by Saji in the late 1980s and several related surfactants have been published since then. Most of these involve monosubstituted ferrocene derivatives. Because pristine ferrocene is insoluble in water, it is often positioned at the end of the hydrophobic tail. The approach presented by Saji is unique because it solved the latter problem by positioning Fc next to a long alkyl chain in (Fc-CH2)(CH3)2N+(C12H25). The authors reported the redox properties and some preliminary characterization of its colloidal properties, including the formation and redox-triggered disassembly in micelles in water.

The systems described above can be developed further by considering the following arguments. Many applications involving surfactants would greatly benefit from charge carrier (electron or hole) transport through the interface, and new perspectives such as micellar batteries, micellar electrocatalysts, or liquid-crystalline semiconductors would open up for such systems. Classical surfactants are useless for such purposes, not only because their heads are not redox-active but also because their tails are electrically insulating as well. Ferrocenyl-based head groups represent a promising entry point to charge-transporting surfactants if an additional \( \pi \)-conjugated side chain can be introduced into the molecule instead of an alkyl chain. However, in a design analogous to the surfactant by Saji, delocalization of charge carriers would be impeded because the ammonium group interrupts the conjugation between the ferrocene and an N-bonded \( \pi \)-conjugated side chain. Therefore, we aim at ferrocene-based surfactants where a \( \pi \)-conjugated substituent is directly attached to a cyclopentadienide ring at the ferrocene nucleus, leading to a \( \pi \)-conjugation over the entire molecule. We here present \( \text{FcNMe}_3\text{TIPS} \) (see Scheme 1) as a first successful realization of this concept. As a further advantage, \( \text{FcNMe}_3\text{TIPS} \) can be modified in several different ways. Thus, it represents a potential building block for the construction of more complex amphiphilic structures. We describe the synthesis and characterization of \( \text{FcNMe}_3\text{TIPS} \) and report on its properties as a surfactant and its redox behavior. Finally, we report first results on exploring possible means for modifying its basic structure.

### RESULTS AND DISCUSSION

**Molecular Synthesis and Characterization.** \( \text{FcNMe}_3\text{TIPS} \) was prepared in five steps starting from ferrocene (Scheme 1). 1,1′-Dibromoferrocene (2) was obtained as reported by Long and co-workers. It was then converted to 1-bromo-1′-idoferrocene (3) according to the procedure of Ilyashenko and co-workers. Standard Sonogashira reaction conditions were used to selectively react 1-bromo-1′-idoferrocene to the 1′-trisopropylsilylwheny (TIPS) substituted derivative (4). Subsequent conversion to 1-trisopropylsilylwhene-1′-diethylammonomethylferrocene (5) was performed according to a known procedure published by Widhalm et al. using \( n \)-BuLi and Eschenmoser's salt \( \text{Me}_3\text{N}+\text{CH}_2\text{I}^- \) under Mannich-like conditions. Quaternization with methyl iodide in MeOH yielded \( \text{FcNMe}_3\text{TIPS} \) (6).

Successful synthesis of \( \text{FcNMe}_3\text{TIPS} \) was proven by a combination of analytical methods. A section of its electrospray ionization mass spectrum (ESIMS) is shown in Figure 1 (for the full spectrum, see Figure S1 of the Supporting Information). The observed signal at 438.2 g/mol and its isotope pattern are in perfect agreement with the calculated mass of \( \text{FcNMe}_3\text{TIPS} \).
pattern for the M⁺ peak C₁₅H₈₀FeNSI⁺. The presence of the triple bond is confirmed by the characteristic stretching vibration ν_C≡C at 2147 cm⁻¹ in the IR spectrum, in the typical region for internal alkynes.43

Solution UV−vis absorption spectra show an intense absorption band at λ_max = 230 nm and a weaker band in the vis region at 400–500 nm (λ_max = 443 nm). The latter is characteristic for the highest occupied molecular orbital−lowest unoccupied molecular orbital transition of ferrocene derivatives and is responsible for their typical orange coloration (see Figure 2a).44 The density functional theory (DFT)-calculated frontier MOs of FcNMe₃TIPS are shown in Figure S2 of the Supporting Information.

![Image](https://example.com/image)

**Figure 2.** (a) Photographic image of a dilute solution of FcNMe₃TIPS in water indicating the surface-active properties (foam formation). (b) Geometry-optimized molecular structure of FcNMe₃TIPS (see also the Supporting Information Figure S3b) and electrostatic potential surface. (c) Concentration-dependent surface tension measurements. The gray dashed lines indicate the interval for which dynamic light scattering (DLS) measurements were performed. (d) Schematic illustration of the arrangement of molecules of FcNMe₃TIPS at the air−water interface according to its overall structure (including its rigid alkylene functionality) and the calculated average area (A_m = 43 Å²) occupied per molecule at the interface (blue, water; gray circles, air/foam at the interface).

**Surfactant Properties of FcNMe₃TIPS.** FcNMe₃TIPS is slightly soluble in water (0.5 mg/mL) as defined by the United States Pharmacopeia and soluble in nonpolar solvents such as dichloromethane (DCM) (60 mg/mL), which is a first indication for amphiphilic properties. In water, the surfactant exhibits a significant foaming capability (see Figure 2a), a characteristic feature of surfactants. The calculation of the electrostatic potential surface of FcNMe₃TIPS (Figure 2b) confirms a surfactant-like architecture and shows that all molecular parts except for the ammonium head group are nonpolar. Concentration-dependent surface tension (γ) measurements in water were performed next (Figure 2c).

It was found that γ remains constant until a concentration of c = 0.007 mM is reached and then decreases. Saturation of the air−water interface is observed at c = 0.79 mM with a minimal surface tension γ_min = 28.5 mN/m. This value is lower than those of other ferrocene-based amphiphiles in the literature (γ_min = 35–55 mN/m) which indicates a very effective stabilization of the interface and a close packing of the surfactant molecules. The surface tension curve can be treated as a Gibbs isotherm, and the surface excess (Γ = 3.90 μmol/m²) and the average area occupied per molecule at the water−air interface (A_m = 43 Å²) were calculated. A_m fits perfectly the distance between the trimethylammonium head group and the ferrocene at the water−air interface as determined from the calculated, geometry-optimized structure (Figure 2d; see also the Supporting Information Figure S3b). Classical surfactants start to form micelles only when the interface is covered by a surfactant monolayer. We checked the occurrence of aggregates in solution by dynamic light scattering (DLS) recorded for different concentrations ranging from c = 0.014 to 0.88 mM (Figure 3). Even at low concentrations, aggregates could be detected with a hydrodynamic diameter D_H (~5 nm), which is in the range expected for micelles (approx. twice the molecular length of the surfactant). However, the aggregate size increases almost linearly with surfactant concentration (Figure 3b). Such behavior cannot anymore be explained by the presence of micellar aggregates.

Transmission electron microscopy (TEM) was performed next (Figure 4a). In agreement with the DLS data, one notes objects in a size range 100–200 nm separated by a thin membrane. The thickness of the membrane is ~3 nm, which matches with a double-layer structure composed of molecules of FcNMe₃TIPS, and these findings can be supported by small-angle X-ray scattering (SAXS), powder X-ray diffraction, and other TEM micrographs displayed in Figure S3a of the Supporting Information.

This surfactant has a tendency for the formation of vesicular structures. The vesicles appear to be broken up caused by the high-vacuum conditions in electron microscopy. Area-selected energy-dispersive X-ray spectroscopy (EDX) confirms the presence of Fe (from FeC) and Si (from the TIPS end group) and the signals for iodine originating from the I⁻ counterion (see Scheme 1). According to the theory of Israelachvili, surfactants with a packing parameter in the range 0.5−1 are prone to form vesicles instead of micelles.1 Therefore, an independent method for the determination of the cac was required. To these ends, FcNMe₃TIPS was dissolved in water at different concentrations. The aqueous phase was then layered with n-hexane containing the lipophilic dye azobenzene (see also Figure S4 of the Supporting Information). The optical absorbance of the dye in the oil phase was determined at λ = 316 and 228 nm by UV−vis spectroscopy. At low concentration of the surfactant, the concentration of the dye remains constant (Figure S5). Starting at an FcNMe₃TIPS concentration of ~0.01 mM, some azobenzene moves into the aqueous phase, and, as a result, the measured absorbance in the oil phase decreases. The
concentration of 0.01 mM is identical to that for which we have observed the occurrence of micelles (Figure 3b). Therefore, it can be concluded that azobenzene-loaded micelles are present in water. Surprisingly, a minimum is reached at \( c = 0.03 \) mM, and on increasing the concentration further, the absorption increases again to the original value. In agreement with DLS and TEM (Figures 3 and 4), we explain this behavior by the transition from a micellar state to the vesicular state. Because the inner cavity of the vesicles is also filled with water, azobenzene cannot enter the water phase anymore. This means that the cac (\( \approx \) the concentration at which the first aggregates form in solution) is very low (at \( \approx 0.01 \) mM) and that the shape transition commences at a concentration of \( \approx 0.03 \) mM. Classic surfactants like cetyltrimethylammonium bromide and sodium dodecyl sulfate have a significantly higher cac value of 0.92–1 and 6–8 mM, respectively, while the cac of ferrocene-based amphiphiles as they were, for instance, explored by Saji and co-workers is usually in the range of 0.1–2 mM. In contrast, lipids have typically much lower cac’s in the nM region. The cac of FcNMe₃TIPS is thus in between those of lipids and classic surfactants.

Thus, the formation of aggregates commences even before a monolayer is formed at the air–water interface. This unusual behavior can be explained by the peculiar structure of FcNMe₃TIPS. The rigid alkyne functionality reduces the flexibility of the overall amphiphile and the possibilities of how the amphiphiles can arrange at the water–air interface. According to Figure 2d, a close packing of molecules of FcNMe₃TIPS leads to an energetic destabilization of the Gibbs monolayer. Notably, the close proximity of the positive charges at the trimethylammonium head groups results in strong Coulombic repulsion. Therefore, the formation of aggregates with a certain degree of curvature (micelles, vesicles) and an increased distance between the positive charges might be energetically favored, thereby decreasing the prevalent charge repulsion, instead of forming a closely packed Gibbs monolayer. Such behavior has rarely been described in the

Figure 3. (a) Aggregate size distribution curves determined from DLS measurements in aqueous solution of FcNMe₃TIPS at \( c = 0.014 \) mM (black), 0.22 mM (red), and 0.88 mM (blue). (b) Correlation of the hydrodynamic diameter \( D_H \) with surfactant concentration.

Figure 4. (a) TEM of aggregates formed by FcNMe₃TIPS in water (\( c = 0.8 \) mM). (b) Energy-dispersive X-ray spectroscopy (EDX) data; Cu signals from the TEM grid.

Figure 5. Alternative determination of the cac. Absorption of azobenzene in the cyclohexane phase at different concentrations of the surfactant in the aqueous phase.
literature but was reported for conical ionic fullerene amphiphiles following the image charge theory by Nitta and co-workers.\textsuperscript{51,56,57} Our arguments are also supported by comparison to similar structures as our surfactant, but with alkyl chains.\textsuperscript{29} Those compounds have a higher average surface tension ($\gamma_{\text{min}} = 35-55$ mN/m), and the overall surface activity is reduced. This can be explained by the higher space required by the flexible alkyl chains at the air-water interface.

A surfactant is expected to form lyotropic liquid crystals (LLCs) at higher concentration. We therefore also examined the phases of FcNMe\textsubscript{3}TIPS formed at high concentration levels in different solvents (water, acetonitrile, a mixture of acetonitrile and isopropanol as well as in apolar solvents like dichloromethane). There are only few reports on LLCs with ferrocene-based amphiphiles.\textsuperscript{58,59} Because many LLC phases are optically anisotropic, polarized optical microscopy (POLMIC) is a convenient method to observe LLCs. POLMIC images show that FcNMe\textsubscript{3}TIPS forms LLC phases not only in polar solvents but also in nonpolar solvents (see Figure 6a and the Supporting Information Figure S5). Maltese-cross patterns (columnar droplets), giant mosaicalike LLCs, and fanlike textures were observed in polar and apolar solvents, indicating the presence of LLCs in the circular/lamellar and the smectic phase, respectively.\textsuperscript{60-62} Small-angle X-ray scattering (SAXS) reveals a signal at a scattering vector $q = 2.21$ nm$^{-1}$ corresponding to a lattice plane spacing of $d = 2.84$ nm. The distance of 2.84 nm equals twice the length of the ferrocene amphiphile as estimated from the geometry-optimized, calculated structure and indicates an end-to-end orientation of the triisopropylsilyl ethynyl lipophilic tails.

**Functionalization of FcNMe\textsubscript{3}TIPS and Redox Properties.** As it was mentioned before, the new surfactant FcNMe\textsubscript{3}TIPS has the potential advantage that it can be modified further such as to endow it with even superior levels of functionality. The most attractive position for such modification is obviously the TIPS-protected ethynyl end group. The TIPS group is easily cleaved from (5) using tetrabutylammonium fluoride (Scheme 2). The resulting H-terminated alkyne (7) is now amenable to a wide range of further functionalizations. For proof of concept, the square-planar platinum fragment trans-Pt(PEt\textsubscript{3})\textsubscript{2}Cl was attached to (7) to give the neutral complex (8). The latter was converted to the heterobimetallic surfactant (9) by subsequent quaternization of the amine function with concomitant substitution of the chloro by an iodo ligand at the platinum ion. The success of these reactions was unambiguously proven.
by NMR spectroscopy (see the Experimental Section and Figure S6 of the Supporting Information). Two-dimensional (2D) NMR spectroscopic investigations confirmed the purity of complexes (8) and (9). In particular, Pt satellites for the ethynl-carbon atoms of (9) were observed in its $^{13}$C NMR spectrum. The triplet at $-4823$ ppm ($J_{PP} = 2337$ Hz) in the $^{195}$Pt NMR spectrum indicates the formation of a trans-Pt(PET$_3$)$_2$I(−C≡CR) fragment, while the $^{31}$P NMR spectrum accordingly shows a singlet at 8.57 ppm with Pt satellites with an identical $J_{PP} = 2337$ Hz.

According to the report of Lindsay et al.$^{42}$ it should also be possible to exchange the ammonium group in α-position to the ferrocene ring by nucleophiles. We adapted the procedure according to Scheme 3 and obtained the corresponding nitrile compound (10). The $^1$H NMR spectrum shown in Figure S7 proves the upfield shift of the resonance signal for the methylene protons in α-position upon substitution of the trimethylammonium group by the nucleophile cyanide and underlines the successful synthesis of FcCNTIPS (10). Compound (10) itself can be further functionalized to the respective carboxamides, the carboxylic acid, or to amines.

An important feature of ferrocene-based amphiphiles is their reversible one-electron oxidation to the corresponding ferrocenium species (Fc$^+$. In the case of FcNMe$_3$TIPS, the charge of the surfactant increases from +1 to +2. More importantly, the formerly neutral ferrocene nucleus changes to a cationic ferrocenium and hence may become a part of the hydrophilic head as opposed to the oleophilic part of the molecule (c. f. Figure 2b). Both effects should cause a major change of the packing parameter $P$. We first investigated the redox properties of the iodide salt of the cationic FcNMe$_3$TIPS surfactant by cyclic voltammetry (CV). As shown in Figure S8 in the Supporting Information, CVs recorded in dichloromethane (DCM) show three consecutive redox waves. Comparison with tetrabutylammonium iodide indicates that the first two processes at $E = -165$ and 88 mV are due to the $I^−/I^−$ redox couple$^{65,66}$ and that the most anodic wave at a half-wave potential $E_{1/2} = 332$ mV is assignable to the Fc/Fc$^+$ redox couple. To avoid this interference, the iodide counterions were replaced by nitrate using an ion-exchange resin, and the corresponding nitrate salt was used further on in the electrochemical investigations. The latter showed only the reversible Fc/Fc$^+$ couple at an $E_{1/2}$ of 332 mV (see Figure 7a) in organic solvents. In water as the solvent, oxidized FcNMe$_3$TIPS is obviously immobilized at the electrode surface as revealed by the typical, sharp and nondifusive anodic adsorption peak. The presence of a normal diffusion-controlled reverse peak on the cathodic scan suggests that oxidized FcNMe$_3$TIPS is chemically (at least partially) stable on the short CV time scale.

More detailed investigations of the oxidation process using UV−vis spectroelectrochemistry (SEC, 0.1 M NBu$_4$PF$_6$ in DCM) revealed a more complex behavior on longer time scales. When employing a rather high overpotential to ensure rapid oxidation, the vis band of the neutral compound at $\lambda_{max} = 443$ nm decreased upon oxidation and two new bands with similar or higher intensity at $\lambda_{max} = 585$ and 782 nm develop (Figure 4d). Both are typical of ferrocenium species.$^{65,66}$ Rapid rereduction at likewise high overpotential reproduced the spectrum of the neutral compound almost quantitatively (see Figure 5a). When, however, the electrolysis was conducted at a slower rate and with a gradual, stepwise increase of the applied potential, no ferrocenium formation was observed.

Figure 7. CV of the nitrate salt of FcNMe$_3$TIPS in DCM/0.1 M NBu$_4$PF$_6$ (a) and in water (b). Repetitive scans of the Fc/Fc$^+$ wave in the presence of “magic blue” (c), and changes in the UV−vis spectra on electrochemical oxidation of FcNMe$_3$TIPS (d).

Rather, a filming of the working electrode was encountered (see Figure S9b). Chemical oxidation of the nitrate salt of FcNMe$_3$TIPS in a CV cell (0.1 M NBu$_4$PF$_6$ in DCM) using tris(4-bromophenyl)aminiunium hexachloridantoantimonate (magic blue) as the oxidizing agent$^{67,68}$ (0.5 or 1 eq., respectively) likewise suggests rapid degradation and polymerization, leading to the deposition of an insulating film on to the electrode surface on repeated scanning (see Figure 7c). In water as the solvent, oxidized FcNMe$_3$TIPS degrades at an even faster rate. Thus, oxidizing FcNMe$_3$TIPS with dropwise addition of an aqueous solution of cerium ammonium nitrate led to an instantaneous, greenish-blue coloration and then to a rapid discoloration to pale orange with the concomitant formation of a yellow-orange, insoluble precipitate (see Figure S9c of the Supporting Information for UV−vis data).

Scheme 4 offers a possible explanation for these observations. Oxidation to the ferrocenium ion is expected to increase the electrophilicity of the methylene carbon, which links the ferrocene and the adjacent trimethylammonium head group. The latter is now even more readily attacked by external nucleophiles to release NMe$_3$ or may attack a nearby, unoxidized molecule of FcNMe$_3$TIPS, most likely at the more electron-rich TIPS−C≡C-substituted Cp ring (note that ferrocenes are by a factor of ca. $10^6$ more reactive toward electrophiles than benzene). The resulting methylene-bridged diferrocenium cation with one oxidized and one reduced ferrocene unit might then undergo homogeneous charge-transfer with yet another molecule of FcNMe$_3$TIPS, thereby triggering an electrocatalytic process, or follow reactions such as the substitution of the ammonium head group. We note here again that nucleophilic substitution of the NMe$_3$ leaving group of trimethylammoniummethylene-substituted ferrocenes is a standard procedure for preparing Fc−CH$_2$Nu derivatives (Nu = OH, OR, CN, SR, etc.).$^{35,41,42}$ Thus, substitution at the trimethylammonium head group offers another way to further modify the surfactant properties of FcNMe$_3$TIPS, and work along these lines is presently being pursued in our laboratories.
required for the formation of a full monolayer at the air–water interface, leading to a very low value of the minimum surface tension \( (\gamma_{\text{min}} = 28.5 \text{ mN/m}) \). In agreement with its packing parameter, it has a high tendency for the formation of vesicles instead of micelles. The critical aggregation concentration was determined by two independent methods. It could be confirmed that aggregates are already present in solution at significantly lower concentrations as required for the formation of a full monolayer at the air–water interface. This behavior also differs from that of classical surfactants.

As an additional advantage, FcNMe₃TIPS can be modified in various different ways. We demonstrated that the protective TIPS group is easily cleaved to yield complex 7 with an unprotected ethynyl functionality (see Scheme 2). Complex 7 was then used to prepare the heterobimetallic Fe–Pt complexes (8) and (9), where the ethynyl linker connects the ferrocenyl group to a trans-configured Pt(P(PEt₃)₂)Cl or Pt(P(PEt₃)₂)I entity. The latter could endow them also with the ferrocenyl group to a trans-configured Pt(P(PEt₃)₂)Cl or Pt(P(PEt₃)₂)I entity. The latter could endow them also with the ferrocenyl group to a trans-configured Pt(P(PEt₃)₂)Cl or Pt(P(PEt₃)₂)I entity.

We present the synthesis of 1-triisopropylsilyl-1′-trimethylammoniummethylferrocene (FcNMe₃TIPS). FcNMe₃TIPS features a trimethylammonium head group and an oleophilic part constituted by the ferrocene nucleus and the attached TIPS-protected ethynyl functionality at the other cyclopentadienide ring. This unusual architecture sets the title compound apart from other ferrocene-based amphiphiles in the literature. FcNMe₃TIPS has typical features of a surfactant and shows colloidal behavior similar to lipids. It packs very efficiently at the air–water interface, leading to a very low value of the minimum surface tension \( (\gamma_{\text{min}} = 28.5 \text{ mN/m}) \). In agreement with its packing parameter, it has a high tendency for the formation of vesicles instead of micelles. The critical aggregation concentration was determined by two independent methods. It could be confirmed that aggregates are already present in solution at significantly lower concentrations as required for the formation of a full monolayer at the air–water interface. This behavior also differs from that of classical surfactants.

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was added dropwise. After complete addition, the reaction temperature was stirred with gradual warming to room temperature overnight. Aqueous sodium thiosulphate (20% w/v, 300 mL) was added to the reaction vessel, followed by diethyl ether (100 mL), and the organic layer was separated and subsequently washed with aqueous sodium thiosulphate (3 × 100 mL) and dried over MgSO₄. The solvent was removed in vacuo. The product was isolated in 86% yield (10.42 g, 26.66 mmol). The product was contaminated with some minor impurities, which could not be removed via flash column chromatography. ¹H NMR (400 MHz, CDCl₃): δ 4.42 (vt, 3JHH = 1.9 Hz, 2H), 4.38 (vt, 3JHH = 1.9 Hz, 2H), 4.22 (vt, 3JHH = 1.9 Hz, 2H), 4.13 (vt, 3JHH = 1.9 Hz, 2H).

Preparation of 1-Trisopropylsilylthelynyl-1′-bromoferrocene (FcBrTIPS) (4). FcBrI (8.21 g, 21 mmol, 1 equiv), was added, and the reaction mixture was cooled to 0 °C. Then, an excess of MeI (0.5 mL, 8.03 mmol, 2.9 equiv) was added. The reaction mixture was heated to reflux for 5 min, 500 mL of diethyl ether were added, and the resulting shiny orange precipitate was filtered via cannula and washed with diethyl ether until the washings were colorless. The quaternary FcNMMe₂TIPS was obtained as the iodide salt in 93% yield (1.47 g, 2.6 mmol). ¹H NMR (400 MHz, CDCl₃): δ 4.82 (s, 2H, H-11), 4.55–4.53 (m, 4H, H-9, H-7), 4.41 (vt, 2H, JHH = 1.9 Hz, H-8), 4.39 (vt, 2H, JHH = 1.9 Hz, H-6), 3.31 (s, 9H, H-12), 1.10–1.14 (m, 21H, H-1, H-2). ¹³C NMR (101 MHz, CDCl₃): δ 104.67 (s, C-3), 74.06 (s, C-8), 73.36 (s, C-7), 72.48 (s, C-10), 70.79 (s, C-6), 67.50 (s, C-11), 66.92 (s, C-5), 52.86 (s, C-12), 18.95 (s, C-1), 11.40 (s, C-2). ESIMS: M⁺ (C₂₅H₄₀FeNSi) = 438.23, M⁺–NMe₃ (C₂₂H₁₂FeSi⁺) = 379.15. Anal. Calcld for C₂₅H₄₀FeNSi: C, 53.21; H, 6.93; N, 2.73. IR (powder): 2942, 2936, 2147 cm⁻¹.

Preparation of 1-Ethynyl-1′-dimethylaminomethylferrocene (FcNMe₃TIPS) (5). FcNMMe₂Cl (300 g, 0.71 mmol, 1 equiv) was dissolved in 40 mL of anhydrous THF, and 1.06 mL (1.06 mmol, 1.5 equiv) of a 1 M solution of tetrabutylammonium fluoride in THF was added dropwise. After the reaction mixture was stirred for 2 h, the solvent was removed in vacuo and the product was purified by column chromatography (PE/EA = 100:0 to 75:25%). The product was isolated in quantitative yield (190 mg, 0.71 mmol). ¹H NMR (400 MHz, CDCl₃): δ 4.37 (vt, 3JHH = 1.9 Hz, 2H), 4.18–4.14 (m, 6H), 3.29 (s, 2H), 2.74 (s, 2H), 2.17 (s, 6H).
H-5), 4.27 (vt, 2H, JHH = 1.8 Hz, H-6), 3.11 (s, 9H, H-10), 2.19–2.14 (m, 12H, H-P1), 1.11 (dt, JHH = 8.2 Hz, JHP = 15.8 Hz, 18H, H-P2). 13C NMR (151 MHz, CDCl3): δ 95.33 (s, with satellites, JPC = 31.68 Hz, C-3), 73.44 (s, C-6), 73.33 (s, C-7), 73.33 (s, C-8), 71.85 (s, C-4), 70.00 (s, C-5), 66.42 (s, C-9), 52.10 (s, C-10), 17.20 (t, JPC = 17.7 Hz, with shoulders, C-P1), 8.71 (s, with shoulders, C-P2). 31P NMR (162 MHz, CDCl3): δ 8.57 (s, with satellites, JPP = 2337 Hz). 195Pt NMR (86 MHz, CDCl3): δ -4823.57 (t, JPP = 2337 Hz).

Preparation of FcCNTIPS (10). FcNMe3TIPS (35 mg, 0.062 mmol, 1 equiv) was dissolved in a mixture of acetonitrile/methanol (20:10 mL), and 40.33 mg (0.62 mmol, 100%) was added. The reaction mixture was stirred at reflux for 48 h and then cooled to room temperature. The solvent was removed in vacuo, and the resulting brown solid was washed with water (3 times), and then the solvent was removed in vacuo, resulting in a brown solid. The solvent was removed with MeOH and then the solvent was removed in vacuo, resulting in a brown solid. The solvent was removed with MeOH and 30 mL and dried under reduced pressure. FcCNTIPS was obtained as a brown solid (17.50 mg, 70%). 1H NMR (400 MHz, CDCl3): δ 4.28 (m, 4H), 4.21 (t, JHH = 1.9 Hz, 2H), 4.05 (m, 21H). 13C NMR (151 MHz, CDCl3): δ 83.17 (s, 9H, C-P2), 8.57 (s, with satellites, C-10), 73.30 (s, C-6), 73.32 (s, C-7), 73.28 (s, C-8), 71.80 (s, C-4), 70.01 (s, C-5), 66.43 (s, C-9), 52.10 (s, C-10), 17.20 (t, JPC = 17.7 Hz, with shoulders, C-P1), 8.71 (s, with shoulders, C-P2). 31P NMR (162 MHz, CDCl3): δ 8.57 (s, with satellites, JPP = 2337 Hz). 195Pt NMR (86 MHz, CDCl3): δ -4823.57 (t, JPP = 2337 Hz).

Ion-Exchange Procedure for Electrochemical Investigations (FcNMe3TIPS NO3). First, 500 mg of the iodide salt of FcNMe3TIPS (0.88 mmol) was dissolved in 50 mL of MeOH and flushed through a plug of freshly activated, KNO3-loaded Amberlite IRA-402. This procedure was repeated 10 times, and then the solvent was removed in vacuo, resulting in a yellow solid with white impurities (KNO3). The precipitate was dissolved in dichloromethane and washed twice with 30 mL of distilled water. The organic phase was dried over MgSO4 and the solvent was removed in vacuo. CV measurements confirmed the complete displacement of I− by NO3−.

Characterization. NMR experiments were carried out on a Varian Unity Inova 400, a Bruker Avance III DRX 400, or a Bruker Avance DRX 600 spectrometer. 1H and 13C spectra were referenced to the respective solvent signal, whereas 31P and 195Pt spectra were referenced to external standards (85% H3PO4) and saturated K2[PtCl6] in D2O, respectively. Two-dimensional (2D) NMR experiments were used to assign unequivocal signals. Numbering of the nuclei can be seen in the Supporting Information in the respective NMR data. Spectroscopy and spectroelectrochemical measurements were performed using DFT with the TURBOMOLE program package for ab initio electronic structure calculation using the BP86/def2-TZVP level of theory. TURBOMOLE V7.1 2016, a development of the University Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
DLS, dynamic light scattering
EDX, energy-dispersive X-ray spectroscopy
ESIMS, electrospray ionization mass spectrometry
Fe, Fe', ferrocene, ferroenium
HLB, hydrophilic to lipophilic balance
LLC, lyotropic liquid crystals
P, packing parameter
POLMIC, polarization microscopy
SEC, spectrómicroscopy
TIPS, triisopropylsilyl
TIPS, triisopropylsilylethylene
SAXS, small-angle X-ray scattering

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