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# A Novel Amphiphilic Re$^{I}$ Complex with Bis(fullerene)-Substituted Bipyridine Ligands: Synthesis, Electrochemistry, and Langmuir Film

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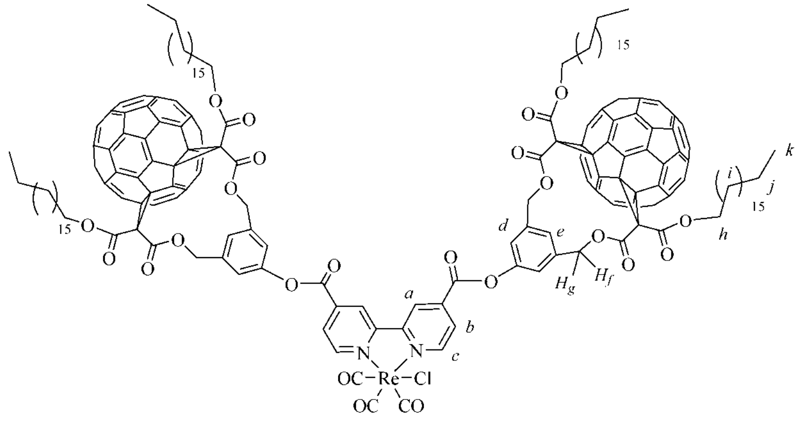
An amphiphilic fullerene ($C_{60}$) derivative with a (bipyridine)-tricarbonylrhenium(I) chloride polar head group has been prepared. Electrochemical studies indicate that some ground state electronic interactions between the fullerene subunit and the metal complexed moiety are present in Re$^{I}$ complex **1**. The Langmuir film of this compound has been characterized by its surface pressure versus molecular area isotherm and Brewster angle microscopy (BAM) observations.

## Introduction

The fullerene ($C_{60}$) is an attractive functional group for a large number of multicomponent molecular architectures with photoinduced electron transfer processes[1] because of its electro- and photophysical properties. Fullerene is especially attractive because it can efficiently induce a rapid charge separation accompanied by a slow charge recombination.[2] Various donors such as porphyrin,[1f,3] TTFs,[4] ferrocene,[5] pyrene,[6] carbazol,[7] oligothiophenes,[8] *N*,*N'*-dialkylaniline,[9] carotenoid,[10] and phthalocyanine[11] have mainly been attached to fullerene ($C_{60}$) to investigate energy- and electron-transfer interactions. Recently, further efforts have been made to produce long-lived and high-energy intramolecular charge separated states, which can be exploited for practical applications such as solar energy conversion.[12] Among these, hybrid systems combining the fullerene with coordination compounds of metal ions such as Ru$^{II}$,[13] Re$^{I}$,[13e] and Cu$^{I}$[1g,14] are interesting because the long-lived metal-to-ligand charge transfer (MLCT) excited state of such complexes has a marked reducing character and is capable of initiating photoinduced electron transfer to the fullerene subunit. In fact, the photoelectrochemical (PEC) devices prepared from fullerene-substituted tris(2,2'-bipyridine)ruthenium(II) derivatives have shown the possibility for a controlled fabrication of the molecular level devices with high energy conversion efficiencies.[15]



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However, only one multicomponent system of such an array with a Re$^{I}$ complex[13e] has been reported to date. In this hybrid system, one fullerene and Re$^{I}$ complex are connected by a long, flexible alkyl linker and have mutual inter-

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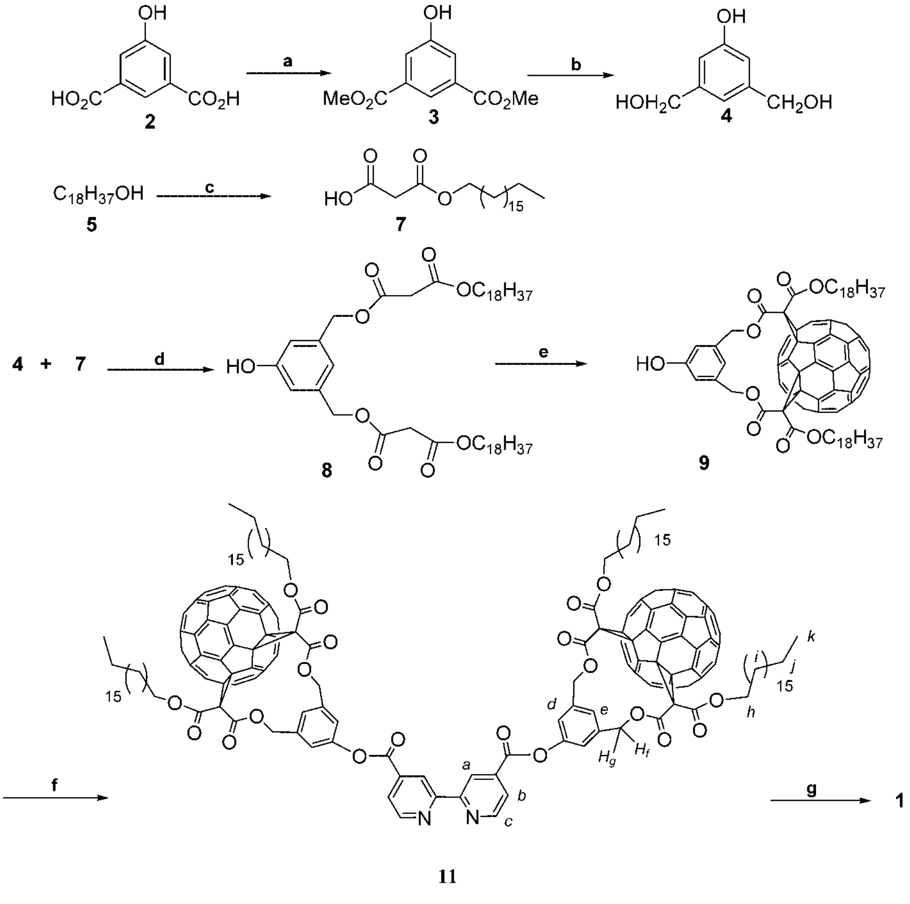
actions through spatial arrangement of the two components. Also, no $Re^I$ complex with more than one fullerene substituent has been reported until now, to the best of our knowledge. On the other hand, studies on Langmuir and Langmuir–Blodgett films from amphiphilic fullerene derivatives have already been reported by Diederich, Nierengarten and others.[16] However, only a limited number of the Langmuir films from fullerene–metal conjugates, such as monofullerene–ruthenium(II) coordination compound has been reported so far.[13g] In line with these aspects, we report herein the first synthesis of $Re^I$ coordination compound **1** that possesses a bis(fullerene)-substituted bipyridine ligand, which has short and relatively rigid linkages between fullerene and the $Re^I$ complex. Furthermore, we also report its electrochemical properties and Langmuir films.

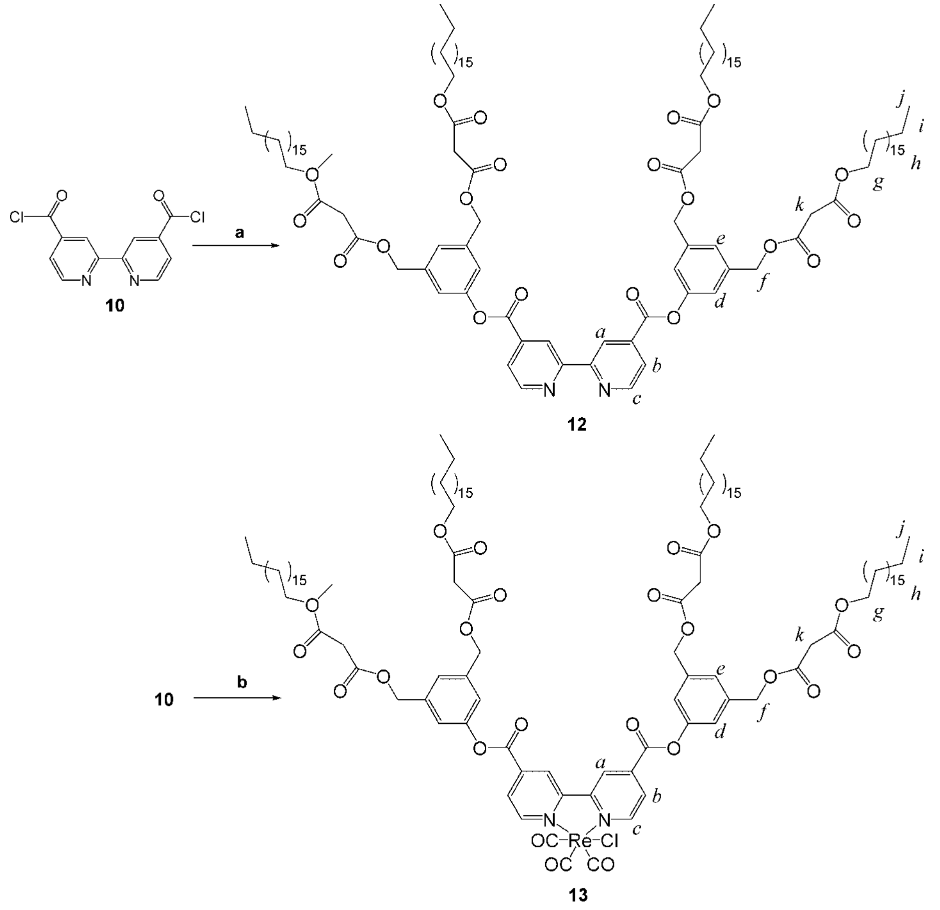
## Results and Discussion

The synthetic route leading to the bis(fullerene)-substituted 2,2′-bipyridine ligand used for the preparation of rhenium(I) complex **1** is depicted in Scheme 1. Commercially available 5-hydroxyisophthalic acid (**2**) was esterified to give diester **3** (93% yield), and subsequent reduction of **3** with LAH produced 3,5-bis(hydroxymethyl)phenol (**4**) in a yield of 85%. Octadecanol (**5**) reacted with meldrum's acid (**6**) to afford malonic acid monooctadecyl ester (**7**) in 89% yield. Esterification of **4** with monoester **7** of malonic acid in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) yielded bis(malonate) **8** (73% yield). The functionalization of $C_{60}$ was based on the highly regioselective Diederich reaction,[17] which led to macrocyclic bis adducts of $C_{60}$ through macrocyclization of the carbon sphere with the bis(malonate) derivatives in a double Bingel addition.[18] Treatment of $C_{60}$ with **8**, iodine, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded mono adduct **9**[11b] in 28% yield. The reaction of mono adduct **9** with 2,2′-bipyridine-4,4′-dicarbonyl dichloride (**10**)[19] which was prepared by oxidation of 4,4′-dimethyl-2,2′-bipyridine with $K_2Cr_2O_7$ and subsequent conversion of the diacid to diacyl dichloride **10**, went smoothly in the presence of triethylamine to produce bis adduct **11**[20] in 83% yield. Finally, fullerene-functionalized ligand **11** reacted with pentacarbonylrhenium(I) chloride in toluene to afford complex **1**[20] in 92% yield.

To compare the electrochemical and photochemical properties of ligand **11** and its $Re^I$ complex **1**, model compounds **12**[20] and **13**[20] that lack fullerene moieties were synthesized in an analogous method (Scheme 2).



Scheme 1. Synthesis of ligand **11** and complex **1**: a) MeOH, $H_2SO_4$, reflux, 24 h, 93%; b) $LiAlH_4$, THF, reflux, 48 h, 85%; c) Meldrum's acid (**6**), 110–120 °C, 2 h, 89%; d) DCC, DMAP, HOBT, THF, room temp., 12 h, 73%; e) $C_{60}$, $I_2$, DBU, room temp., 24 h, 28%; f) **10**, $Et_3N$, $CHCl_3$, room temp., 12 h, 83%; g) $Re(CO)_5Cl$, toluene, 80 °C, 12 h, 92%;.



Scheme 2. Synthesis of model compounds **12** and **13**: a) **8**, $Et_3N$, $CHCl_3$, room temp., 12 h, 29%; b) $Re(CO)_5Cl$, EtOH, reflux, 12 h, 86%.

The structure and purity of the new compounds were confirmed by $^1H$ NMR and IR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis.[20] The $^1H$ NMR spectra of **11** and **1** show the characteristic features of the 1,3-phenylenebis(methylene)-tethered fullerene *cis*-2 bis adduct substituent.[11b,13g] In **11** and **1**, a set of AB quartets are clearly observed for the benzylic $CH_2$ groups ($H_f$ and $H_g$) and an $AX_2$ system is revealed for the aromatic protons ($H_d$ and $H_e$) of the 1,3,5-trisubstituted bridging phenyl ring. The spectra are also characterized by three sets of aromatic signals in a typical pattern for a 4,4′-disubstituted 2,2′-bipyridine ($H_a$, $H_b$, and $H_c$). Thus, the $^1H$-NMR spectrum of complex **1** is consistent with the proposed structure. Detailed assignments of the peaks in **11** and **1** are given and compared with model compounds **12** and **13**.[20]

The structure of **1** was also confirmed by mass spectrometry. The MALDI-TOF MS of **1** is characterized by a singly charged peak at $m/z = 3574.81$, which can be assigned to **1** after loss of one chlorine atom.

The electrochemical properties of rhenium(I) complex **1** and ligand **11** were investigated and compared with those of model compounds **12** and **13** by cyclic voltammetry (CV) together with differential pulse voltammetry (DPV) in tetrahydrofuran (THF) with tetrabutylammonium tetrafluoroborate ($TBABF_4$) as a supporting electrolyte (Table 1). In the negative potential region, complex **1** shows nine reduction processes. As shown by comparison with corresponding ligand **11**, which lacks rhenium moiety, complex **1** showed five waves (–0.21, –0.69, –1.29, –1.62, and –2.11 V), which correspond to $C_{60}$-centered reductions. These reduction waves are regularly spaced around 500 mV. The first three fullerene-centered reduction waves of triad compound **1** are shifted about 30 mV more cathodically with respect to those (–0.19, –0.66, and –1.25 V) of the corresponding fullerene model compound, ligand **11**. This indicates that the LUMO energy levels of the ground state of the fullerene moiety are elevated by $Re^I$ complexation. However, Armaroli et al.[13e] reported that the first two fullerene-centered reductions of a $C_{60}$–$Re^I$ dyad showed opposite shifts. They suggested that this observation could be a consequence of a small electronic interaction due to spatial proximity for the two chromophores (more facile fullerene reduction) in $C_{60}$–$Re^I$. The triad of the present work seems to have adopted an extended conformation through rigid linkers between fullerene and the $Re^I$ complex, which prevents spatial interactions among the chromophores. So, our electrochemical results suggest that the electron donation from $Re^I$ to fullerene chromophores mainly occurs through the bonds. We have to mention that Armaroli et al.[13e] used a fullerene model compound without a bipyridine ligand, which does not provide a background for the representation of only a difference in $Re^I$. Thus, it is difficult to directly compare their results with the results of the present work. Therefore, the present work only provides more convincing results to explain the electron donating effects of $Re^I$. The additional waves at –1.00 and –1.48 V that originated from the bipyridine–malonate domain also shifted negatively compared with those of ligand **11** (–0.98, –1.43 V). This indicates that the complexation of rhenium to the bipyridine ligand can influence this negative shift. However, the corresponding waves of model compound **13** (–0.97, –1.47 V) showed a relatively large positive shift by the complexation of rhenium of corresponding ligand **12** (–1.22, –1.57 V). The redox processes of ligand **11** were found to have also shifted positively from those of ligand **12**. These results indicate that the electron-withdrawing $C_{60}$ group strongly affects the characteristics of ligand **11**. In model compounds **12** and **13** there are oxidation processes at the redox potentials of 0.81 V ($\Delta E_p$ = 100 mV) and 0.77 V ($\Delta E_p$ = 110 mV), respectively (not shown in Table 1). This may be caused by a redox reaction of the aromatic ester group. Interestingly, the negative potential shift of compound **13** shows that the oxidation of this group is easier, probably because of an electron donating function of rhenium. On the other hand, the additional waves $E_2$ and $E_8$ in Table 1 seem to originate from the metal center because only the compounds with rhenium metal show these waves.

Table 1. Electrochemical properties of **1**, **11**, **12**, and **13**.[a]

| Compound | Reduction<br>$E_1$ | $E_2$ | $E_3$ | $E_4$ | $E_5$ | $E_6$ | $E_7$ | $E_8$ | $E_9$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | –<br>0.21<br>(175) | –<br>0.51<br>(i) | –<br>0.69<br>(102) | –<br>1.00<br>(138) | –<br>1.29<br>(106) | –<br>1.48<br>(118) | –<br>1.62<br>(61) | –<br>1.80<br>(98) | –<br>2.11<br>(146) |
| **11** | –<br>0.19<br>(93) | | –<br>0.66<br>(96) | –<br>0.98<br>(96) | –<br>1.25<br>(111) | –<br>1.43<br>(98) | –<br>1.75<br>(125) | | –<br>2.27<br>(114) |
| **12** | | | | –<br>1.22<br>(200) | | –<br>1.57<br>(100) | | | |
| **13** | | –<br>0.49<br>(100) | | –<br>0.97<br>(110) | | –<br>1.47<br>(100) | | –<br>1.90<br>(120) | |

[a] Cyclic voltammetric measurements: glassy carbon disk working electrode (3 mm in diameter), Pt wire counter electrode, and silver wire pseudoreference electrode ($Ag/Ag^+$) were used. The electrolyte contained degassed THF, 0.1 M $Bu_4NBF_4$ and $3 \times 10^{-4}$ M synthesized compounds. The scan rate was 100 mV/s. Values for $E_{1/2}$ (in V) as $(E_{pa} + E_{pc})/2$ and $\Delta E_p$ (in mV) are given in parentheses. DPV technique was also used to confirm redox potentials, and the results were in good agreement with CV technique within the first decimal point. (i) denotes irreversible. The experiments were performed at ambient temperature and pressure.

The UV/Vis spectrum of **1** in a $CHCl_3$ solution shows the characteristic absorption features of the fullerene units as well as the diagnostic MLCT band of the 2,2′-bipyridine rhenium(I) complex at 380 nm. Interestingly, preliminary luminescence measurements of **1** in $CHCl_3$ solution ($\lambda_{exc}$ = 292 and 380 nm) show strong quenching of the emission by introducing the fullerene moieties in **1**, which indicates the occurrence of intramolecular photoinduced processes. Detailed photophysical studies are currently under investigation and will be reported in due time.

Langmuir films of compound **1** have been characterized by their surface pressure versus molecular area (π/A) isotherms and Brewster angle microscopy (BAM) observation.[21] Figure 1 shows a surface pressure/area isotherm (π-A isotherm) of compound **1** on a water surface. Under continuous compression, the surface pressure started to increase steeply around 200 Å$^2$/molecule and the Langmuir film collapsed around $\pi_c \approx$ 50 mN/m. The results suggest that compound **1** forms very stable monolayers on the water surface because of the balance between the hydrophobicity of the fullerene surrounded by two long alkyl chains and the hydrophilicity of the bipyridine $Re^I$ complex. Good reversible behavior in the successive compression/expansion cycles (data not shown) is also consistent with the amphiphilic structure of compound **1**, where aggregation of fullerenes is largely prevented by the long alkyl chains. These results are in a good agreement with the previous findings on a related amphiphilic fullerene derivative with ruthenium(II).[13g] The occupied surface area obtained by extrapolation of the steeply rising portion of the π-A isotherm to zero pressure is 166 Å$^2$/molecule, which is very close to the molecular area estimated by molecular modeling of compound **1**. A Brewster angle microscope was used to monitor the structural change of the Langmuir films during compression. The insets of Figure 1 show the BAM images of the Langmuir films at 200, 300, and 500 Å$^2$/molecule. The images clearly show that the domain size (brighter regions in the images) becomes larger as the surface pressure is increased, and a homogeneous monolayer is formed below 200 Å$^2$/molecule.

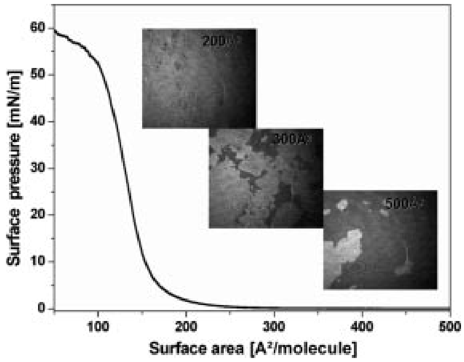


Figure 1. π-A isotherm recorded during compression of the monolayer of compound **1**. The insets are the BAM images of the Langmuir films at 200, 300, and 500 Å$^2$/molecule.

## Conclusions

We have synthesized a new $Re^I$ complex with bis(fullerene)-substituted bipyridine ligands, which is a suitable amphiphilic derivative for the preparation of stable Langmuir films. Electrochemical properties of this compound have also shown that some ground state electronic interactions between the fullerene subunit and the metal complexed moiety are present in this complex. We are currently investigating the physical properties of Langmuir–Blodgett films of this molecule and attempting to apply their behavior in PEC cells for solar energy conversion.

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[20] Selected physical data for **1**, **11**, **12**, and **13**. Compound **1**: M.p. 162 °C. $^{1}$H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta$ = 9.38 (d, 1 H, *c*ArH), 9,02 (s, 1 H, *a*ArH), 8.30 (d, $J$ = 5.1 Hz, 1 H, *b*ArH), 7.68 (s, 1 H, *e*ArH), 7.27 (s, 2 H, *d*ArH), 5.85 (d, $J$ = 12.8 Hz, 2 H, *f*$CH_2$), 5.25 (d, $J$ = 12.8 Hz, 2 H, *g*$CH_2$), 4.35 (t, $J$ = 5.2 Hz, 4 H, *h*$OCH_2$), 1.70 (m, 4 H, *j*$CH_2$), 1.25 (s, 60 H, *i*$CH_2$), 0.85 (t, $J$ = 6.4 Hz, 6 H, *k*$CH_3$) ppm. FTIR (KBr): $\tilde{\nu}$ = 2021, 1924, 1905, 1750 cm$^{-1}$. MALDI-TOF MS: $m/z$ = 3574.81 [M – Cl]$^{+}$, 721 [$C_{60}$ + H]$^{+}$. $C_{235}H_{168}ClN_2O_{23}Re$ (3609.58): calcd. C 78.20, H 4.69; found C 78.32, H 4.64. Compound **11**: M.p. 120 °C. $^{1}$HNMR (200 MHz, $CDCl_3$, 25 °C): $\delta$ = 9.25 (s, 1 H, *c*ArH), 9.00 (d, $J$ = 5.1 Hz, 1 H, *a*ArH), 8.10 (d, $J$ = 5.1x Hz, 1 H, *b*ArH), 7.55 (s, 1 H, *e*ArH), 7.27 (s, 2 H, *d*ArH), 5.85 (d, $J$ = 13.6 Hz, 2 H, *f*$CH_2$), 5.25 (d, $J$ = 13.6 Hz, 2 H, *g*$CH_2$),

4.40 (t, *J* = 6.2 Hz, 4 H, *h*$OCH_2$), 1.75 (m, 4 H, *j*$CH_2$), 1.25 (s, 60 H, *i*$CH_2$), 0.85 (t, *J* = 6.4 Hz, 6 H, *k*$CH_3$) ppm. FTIR (KBr): $\tilde{\nu}$ = 1750 cm$^{-1}$. MALDI-TOF MS: *m*/*z* = 3304.21 [M$^+$]. $C_{232}H_{168}N_2O_{20}$ (3303.89): calcd. C 84.34, H 5.13; found C 84.41, H 4.98. Compound **12**: M.p. 84 °C. $^1$H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta$ = 9.25 (s, 1 H, *c*ArH), 8.96 (d, *J* = 5.1 Hz, 1 H, *a*ArH), 8.05 (d, *J* = 5.1 Hz, 1 H, *b*ArH), 7.31 (s, 1 H, *e*ArH), 7.27 (s, 2 H, *d*ArH), 5.25 (s, 4 H, *f*$CH_2$), 4.15 (t, *J* = 6.5 Hz, 4 H, *g*$CH_2$), 3.45 (d, *J* = 4.7 Hz, 2 H, *k*$CH_2$), 1.60 (m, 4 H, *i*$CH_2$), 1.25 (s, 60 H, *h*$CH_2$), 0.85 (t, *J* = 6.4 Hz, 6 H, *j*$CH_3$) ppm. FTIR (KBr): $\tilde{\nu}$ = 1738 cm$^{-1}$. $C_{112}H_{176}N_2O_{20}$ (1870.63): calcd. C 71.91, H 9.48; found C 71.88, H 9.43. Compound **13**: M.p.95 °C. $^1$H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta$ = 9.32 (d, *J* = 5.1 Hz, 1 H, *c*ArH), 9.00 (s, 1 H, *a*ArH), 8.27 (d, *J* = 5.1 Hz, 1 H, *b*ArH), 7.36 (s, 1 H, *e*ArH), 7.27 (s, 2 H, *d*ArH), 5.23 (s, 4 H, *f*$CH_2$), 4.12 (t, *J* = 6.5 Hz, 4 H, *g*$CH_2$), 3.45 (d, *J* = 4.7 Hz, 2 H, *k*$CH_2$), 1.60 (m, 4 H, *i*$CH_2$), 1.25 (s, 60 H, *h*$CH_2$), 0.85 (t, *J* = 6.4 Hz, 6 H, *i*$CH_3$) ppm. FTIR (KBr): $\tilde{\nu}$ = 2030, 1910, 1900, 1750 cm$^{-1}$. $C_{115}H_{176}ClN_2O_{23}Re$ (2176.32): calcd. C 63.47, H 8.15; found C 63.50, H 8.18.

[21] An LB trough (KSV 5000, KSV instruments, Finland) was used to form Langmuir monolayers of compound **1** at the water/air interface. A chloroform solution of compound **1** at a concentration of 0.05 mM was spread onto the water surface of the LB trough, and then compressed to a surface pressure of about 60 mN/m. A Brewster angle microscope (BAM, Nanofilm Technology, Germany) equipped with a CCD camera was used to examine the morphology of the Langmuir films.

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