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ARTICLE TYPE

Interfacial Mass Transfer by Controlled Multilayer Disassembly

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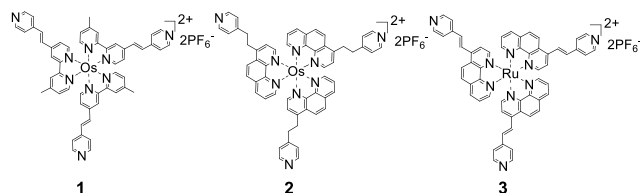
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We demonstrated the one-pot disassembly of self-propagating molecular assemblies (SPMAs) by ligand exchange and the subsequent covalent binding of the molecular components to other surfaces. These functionalized surfaces are suitable for regenerating the SPMAs.

Electron and mass-transfer phenomena are of great significance in biological processes. Whereas electron-transfer has been studied in detail in many artificial systems,¹ mass-transfer between interfaces is relatively rare.² This is somewhat surprising given the fact that mass-transfer between membranes is essential for life. Moreover, interfacial mass-transfer could lead to thin film self-replication on solid surfaces as demonstrated by Kiedrowski.³ A seminal example of mass-transfer between interfaces is Rebek's three-phase test, which is a polymer-based method to detect intermediates in various reactions.⁴ In this report, we demonstrate a specially designed system to transfer metal complexes between interfaces mediated by liquid media. The structural features and properties of a redox-active monolayer can be "copied" to another surface by the disassembly of a metal-organic network.

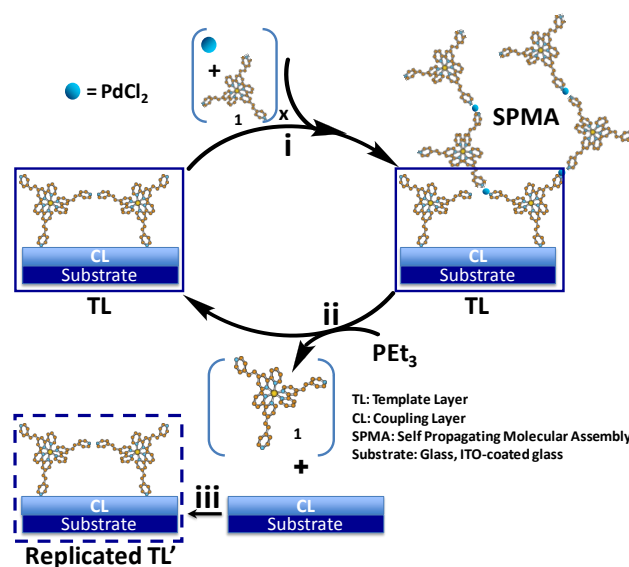
We have recently reported the formation of self-propagating molecular assemblies (SPMAs) on SiO_x and on Indium-Tin-Oxide (ITO)-coated glass.^{5,6} These assemblies are coordination-based networks of osmium (1, 2), ruthenium (3), or cobalt polypyridyl complexes cross-linked via a palladium or platinum salt (Scheme 1 and 2).



Scheme 1. Chemical structures of the polypyridyl complexes (1-3).^{5,7}

The formation of the SPMAs used in this study involves three steps: (a) hydrophilic substrate surfaces are functionalized with a benzyl-chloride terminated coupling layer (CL)⁸ using siloxane chemistry, (b) the CLs are reacted from solution at elevated

temperatures with polypyridyl complex (1) affording template layers (TLs) consisting of covalently bound pyridinium salts of complex 1 that can bind metal salts, and (c) the iterative exposure of these TLs to solutions of a polypyridyl complex (1-3) with multiple metal-binding sites and PdCl₂(PhCN)₂ (Scheme S1, Scheme 2, step i).



Scheme 2. Schematic presentation of the mass-transfer process between molecular interfaces. (i) SPMA formation by alternating depositions of a Pd salt and a polypyridyl complex (1-3) on a template layer (TL); x = number of deposition steps.^{5,7} (ii) Disassembly of the SPMA with PET₃ (triethylphosphine) to regenerate the TL with subsequent release of the complexes in solution. (iii) Reaction of the complexes (1-3) released to the solution with covalently bound chlorobenzyl-terminated coupling layers (CLs) to afford replicated TL's, which can be used to generate SPMAs.

The physicochemical properties of the SPMAs increase exponentially with the number of deposition steps.^{5,7} The exponential growth results from the storage of an excess of palladium salt inside these films. During immersion of the SPMAs in a solution of a polypyridyl complex, the excess of palladium aids the coordination of polypyridyl complexes beyond

a single molecular layer. Consequently, more palladium can be stored upon increasing the thickness of the SPMA, which again leads to a larger increase in the thickness in the next deposition step. The electron density and roughness remains nearly constant upon film growth. Linear growth can be achieved by reducing the amount of palladium.

In a typical disassembly and mass transfer experiment, presented in Scheme 2, several ITO ($0.7 \text{ cm} \times 5 \text{ cm} \times 0.7 \text{ mm}$) and glass substrates ($1 \text{ cm} \times 2 \text{ cm} \times 0.1 \text{ cm}$) functionalized with a SPMA, consisting of 11 depositions of $\text{PdCl}_2(\text{PhCN})_2$ and complex **1**, and ITO substrates functionalized with a CL were placed in a Teflon sample holder. The distance between the surface planes was fixed at 0.25 cm to 2 cm, which is several orders of magnitude larger than the thickness of the molecular interfaces used (SPMA: 16 nm; CL: 0.8 nm). Then, the set-up was transferred into a glass pressure vessel and immersed in a dry acetonitrile/toluene (1:1, v/v) solution containing an excess of triethylphosphine (PET_3 ; 0.1 M). Then the vessel was sealed and heated for 72 h at 90°C under an inert atmosphere. Subsequently, the vessel was allowed to attain room temperature and the substrates were thoroughly washed with acetonitrile, acetone, and ethanol. UV/vis spectroscopy of the light brown solution indicated the presence of complex **1** (Figure S1).

The thin films (TLs and SPMA) were analyzed by optical (UV/vis) spectroscopy (Figure 1A,B), cyclic voltammetry (CV; Figure 1C,D), and X-ray photoelectron spectroscopy (XPS). These measurements indicate the complete disassembly of the **1**-based SPMA and the formation of new TLs by interfacial mass-transfer of complex **1** and the subsequent reaction of **1** with the CL-functionalized substrates (Scheme 2, steps ii and iii). The UV/vis spectra of the TLs are similar and exhibit the characteristic singlet and triplet metal-to-ligand charge-transfer (MLCT) bands at $\lambda = 500 \text{ nm}$ and $\lambda = 700 \text{ nm}$ of complex **1**. The absorption intensities are similar to TLs obtained independently by the reaction of complex **1** with a CL (Figure 1A). Cyclic voltammograms of these **1**-based TLs on ITO substrates showed a reversible redox process, characteristic of an $\text{Os}^{2+/3+}$ couple (Figure 1C). Whereas there is some variation in the wave shapes, the half-wave potential values are in the expected range of $0.93 \pm 0.1 \text{ V}$ (Table S1). The peak current is directly proportional to the scan rate within the range of 0.1 and 1 Vs^{-1} , indicating a surface-confined process that is not limited by diffusion (Figure 1D). The estimated surface coverage, Γ , ranges from 1.2×10^{-10} to $1.4 \times 10^{-10} \text{ mol/cm}^2$ (Table S1), indicating the presence of a dense structure.⁷ XPS analysis revealed the presence of a pyridinium salt by quaternization of one pyridyl moiety of complex **1**.^{5, 7, 9} The pyridinium and pyridyl N 1s signals were observed in a 1:8 ratio at 400 and 401.5 eV, respectively. No palladium was observed. The good agreement among the UV/vis, electrochemical, and XPS data for all TLs confirms that it remains bound to the substrate surface after the disassembly of the SPMA and that the newly generated TLs have essentially the same structure as the TL used to build-up the SPMA. To confirm the structural similarity and to evaluate the function of the TLs, we regenerated the **1**-based SPMA on the TLs that were obtained after the disassembly process. In parallel, we also built this

SPMA on the replicated TL's. The nearly identical UV/vis spectra (Figure 1A spectra a'-c') and the similar SPMA growth behavior obtained after the deposition of 11 depositions of $\text{PdCl}_2(\text{PhCN})_2$ and complex **1** confirm the efficient interfacial transfer of complex **1** (Figure 1B), and the structural and functional similarities of the original TLs and replicated TL's. These results are not obvious because the overall process also involves the release of the palladium salt and a reactive phosphine that also might have reacted with the CLs.¹⁰ Reaction of PET_3 with the CLs under the same conditions as the mass-transfer experiments resulted in the formation of some surface-bound phosphonium salt (10% by XPS). Apparently, sufficient benzyl chloride moieties remain for complexes **1-3** to bind to the CLs.

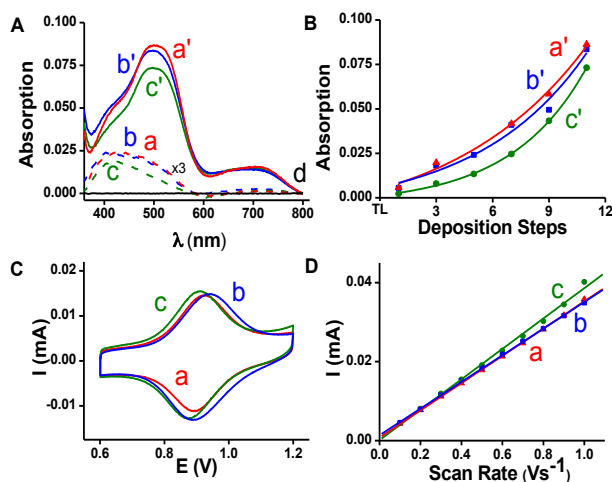


Figure 1. Optical (UV/vis) spectroscopy (A, B) and cyclic voltammetry (CV) (C, D) data. **A.** Absorption spectra of (a) TL used for the built-up of a **1**-based SPMA, (b) TL generated after disassembly of the **1**-based SPMA with PET_3 , (c) replicated TL'. (a-c; enlarged 3x for clarity), and (a'-c') are the **1**-based SPMA on ITO-coated glass substrates functionalized with (a') TL formed by reacting a CL with complex **1**, (b') TL after disassembly of the **1**-based SPMA with PET_3 , (c') replicated TL'. (d) baseline. **B.** Exponential correlation between the intensities of the MLCT bands ($\lambda \approx 500 \text{ nm}$) and the number of complex **1** deposition steps for the SPMA (a'-c') built on the three TLs (a-c). **C.** Cyclic voltammograms of TLs (a-c). The scan rate is 400 mVs^{-1} . **D.** Plot of peak currents as a function of the scan rate of the TLs (a-c), with $R^2 > 0.98$ for the linear fits (see ESI for experimental details).

We further demonstrated selective transfer of one type of pyridyl complex to ITO substrates functionalized with CLs by the one-pot disassembly of **2**- and **3**-based SPMA on glass substrates with PET_3 (Scheme 1; Figure S2). Different metals (**2**: osmium, and **3**: ruthenium) were used to accurately determine the composition of the replicated TL's by electrochemistry and XPS. Although the structures of these complexes are similar, we tuned the reactivity of the terminal pyridine groups by using C-C (**2**) vs C=C (**3**) moieties.⁵ These experiments were carried out under the same conditions used for the disassembly of the **1**-based SPMA and the formation of the replicated **1**-based TL' (Scheme 2).

Interestingly, the formed TLs consist of osmium complex **2**. Although our data indicate that both **2**- and **3**-based SPMA

undergo disassembly upon reaction with PEt_3 . The CV of the replicated TL' shows clearly one reversible redox process (Figure 2A). The redox couple at $E_{1/2} = 0.85$ V versus Ag/AgCl is characteristic for the presence of an interface consisting of osmium complexes (**2**) ($\Gamma \approx 2.1 \times 10^{-11}$ mol/cm²). No signal was apparent indicating the presence of ruthenium complex (**3**). Differential pulse voltammetry (DPV) of the reaction solution shows that both complexes are stable under the applied reaction conditions and are available for reacting with the CLs (Figure 2B). The two potential peaks at 0.85 V and 1.46 V vs. Ag/AgCl are characteristic of complexes **2** and **3**, respectively.

Reacting only complex **2** or **3** (0.2 mM) for 72 h at 90 °C with ITO substrates functionalized with CLs immersed in dry toluene/acetonitrile (1:1, v/v) resulted in the formation of the corresponding TLs, as judged by electrochemical analyses (Figure S3). Apparently, the reactivity of complex **3** is sufficiently high to form a TL (in the absence of complex **2**). The CV of the **2**-based TL is nearly identical to the replicated TL' (Figure S3A).

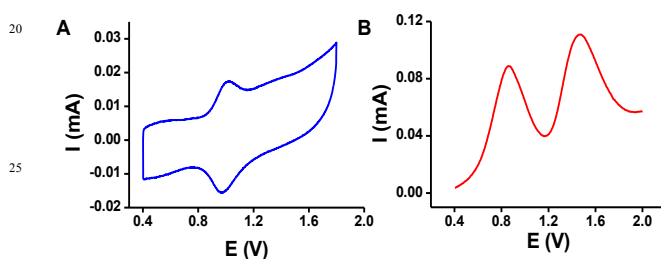


Figure 2. A. Representative cyclic voltammogram (CV) of the replicated **2**-based TL' formed by disassembly of **2**- and **3**-based SPMA with PEt_3 and selective transfer of osmium complex **2** to ITO substrates functionalized with CLs. The scan rate is 400 mVs⁻¹. B. Differential pulse voltammogram (DPV) of the reaction solution after the disassembly of **2**- and **3**-based SPMA with PEt_3 . The following conditions were applied: scan rate: 20 mVs⁻¹, pulse width: 16 ms, pulse amplitude: 50 mV, and pulse period, 200 ms. For both **A** and **B**: electrolyte: 0.1 M TBABF₄/CH₃CN was used at room temperature. Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. The functionalized ITO-coated glass substrates were used as working electrodes.

The selective generation of the **2**-based TL was also indicated by XPS measurements. An interface of 1.5 nm was observed on the ITO substrate having an elemental ratio of N:Os = 10:1, which is in good agreement with the expected ratio (9:1). In addition, no signal indicative of ruthenium complex (**3**) was observed. The pyridinium and pyridyl N 1s signals for the **2**-based TL were observed at 401.9 and 400.2 eV,^{5, 7, 9} respectively, with an elemental ratio N⁺:N = 1:9 (expected 1:8). Apparently, the complexes are covalently bound to the CL with one of the pyridine groups.

In summary, we showed that interfacial transfer of metal complexes can be achieved and triggered using a metal exchange process that occurs between different ligands (i.e., PEt_3 and substituted pyridines) at the boundaries of a solution-solid state interface. This metal-ligand process is likely to be highly complex and involves reversible steps. The transfer and subsequent covalent binding of the polypyridyl complexes takes place from a medium that contains an excess of other reactive

species including PEt_3 and metal salts thereof. Nevertheless, this process is highly selective and can even proceed in a selective manner in the presence of an equimolar amount of another polypyridyl complex. The overall structure and functionality of the replicated templates is identical to the templates used for their formation. To this end, the coupled disassembly-assembly processes¹¹ of metal-organic networks presented here are examples of System Chemistry involving solid interfaces. Such processes might provide fundamental insight into signaling, communication and molecular replication.¹²

Notes and references

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These authors contributed equally.

§ DFT calculations indicate that the electron density of the pyridine moieties of complexes **1** and **3** is nearly identical (Q(pyridine) is 0.00 and 0.01, respectively), whereas these moieties exhibit a higher electron density for complex **2** (Q(pyridine) is -0.05).

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