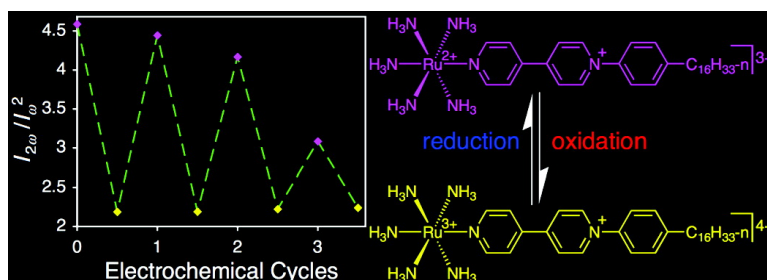## Communication

Redox-Switching of Nonlinear Optical Behavior in Langmuir−Blodgett Thin Films Containing a Ruthenium(II) Ammine Complex

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Redox-Switching of Nonlinear Optical Behavior in Langmuir−Blodgett Thin Films Containing a Ruthenium(II) Ammine Complex

Leïla Boubekeur-Lecaque,[†] Benjamin J. Coe,*,[†] Koen Clays,[‡] Stijn Foerier,[‡] Thierry Verbiest,[‡] and Inge Asselberghs[‡]

School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, U.K. and Department of Chemistry, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

Received December 17, 2007; E-mail: b.coe@manchester.ac.uk

Molecular nonlinear optical (NLO) effects show promise for various applications, e.g., in optical data processing and biological imaging.[1] Within this field, transition metal complexes offer many possibilities for creating multifunctional materials.[2] Recently, methods for modulating molecular NLO responses have attracted attention,[3] e.g., the first report of a reversible redox-switching of the first hyperpolarizability β.[4] Various related solution studies with both quadratic and cubic NLO effects have been described,[5] but corresponding work with organized materials is very scarce. Redox-switching of the second harmonic generation (SHG) from self-assembled monolayers (SAMs) of ferrocenyl (Fc) thiols on gold has been reported.[6] However, these SAMs greatly attenuate the 532 nm SHG from bare gold, and a ca. 5-fold intensity increase was ascribed to oxidation of the Fc electron donors; this counterintuitive claim was supported by ZINDO-derived β values. Later independent studies confirm that oxidizing Fc units *decreases* β,[5b] so the reported switching is likely due to only molecular orientational changes (originally noted as a contributing factor).[6]

In order to progress toward potential applications of redox-switchable NLO phenomena, significant challenges must be overcome, especially for quadratic effects. First, it is necessary to incorporate active chromophores into polar materials, with many molecules required for significant effects. Second, the material must be electrochemically addressable, preferably as a thin film. We have studied dipolar Ru^{II} ammine complexes with metal-to-ligand charge-transfer (MLCT) transitions and very large static β values, β_0.[7] The well-understood optical properties of such chromophores are ideally suited to external control.[4] Noncentrosymmetric arrangements of NLO chromophores can be deposited on various substrates via the Langmuir−Blodgett (LB) technique.[8] Several reports of Ru^{II} complexes showing NLO effects in LB films have appeared.[9] Of special relevance, a small photoinduced modulation of 295 nm SHG from alternating, highly diluted films containing a [Ru^{II}(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridyl) derivative was ascribed to changes in β on MLCT excitation.[9b] However, the ground state complex shows an intense bpy-based absorption near 295 nm, so excitation-induced absorption changes may affect the SHG signal. Sortino, Di Bella, and colleagues reported redox-switching of linear optical absorption in SAMs of {Ru^{II}(NH$_3$)$_5$}$^{2+}$-4,4′-bipyridinium complexes on transparent platinum[10] and also described Langmuir−Schäfer films of such species.[11] SAMs of a [Ru^{II}(bpy)$_3$]$^{2+}$ derivative on indium tin oxide (ITO) show redox-switching of a ligand-based UV absorption.[12]

We have synthesized the new pro-ligand salt [C$_{16}$-PhQ$^+$]PF$_6$ and reacted this with [Ru^{II}(NH$_3$)$_5$(H$_2$O)](PF$_6$)$_2$ to give complex salt **1**, with characterization via ^{1}H NMR spectroscopy and CHN elemental analyses. Hyper-Rayleigh scattering (HRS) and Stark spectroscopy

have shown that *N*-arylpyridinium electron acceptors give especially large β_0 responses,[13] and the hexadecyl chain engenders the amphiphilic properties required for LB deposition. The visible absorption spectrum of **1** in MeCN shows a broad MLCT band at $\lambda_{max} = 624$ nm ($\epsilon = 16\ 100$ M^{-1} cm^{-1}), and cyclic voltammetry gives a reversible Ru$^{III/II}$ wave at $E_{1/2} = 0.50$ V vs Ag−AgCl; these data are very similar to those for the model species **2**.[13] For the latter, respective β_0 values of 220×10^{-30} and 186×10^{-30} esu have been determined from HRS in MeCN at 295 K and from Stark measurements in PrCN at 77 K.[13,14]
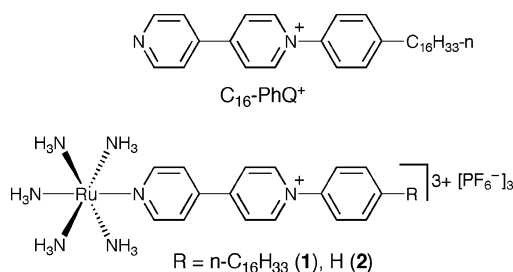
Using a water subphase and a CHCl$_3$ solution of **1** at 295 K gave stable Langmuir monolayers that deposited on both sides of hydrophilic glass by vertical dipping. Analysis of the pressure−area isotherm assuming monomolecular coverage affords an unfeasibly small apparent area of 12 Å^2 molecule^{-1}. This observation, reminiscent of studies with a nickel bis(dithiolene) complex, indicates that the film is not one molecule thick due to aggregation or stacking.[15] However, the Langmuir curve obtained with **1** is perfectly reproducible and independent of concentration, volume of solution, and compression rate. Multilayer LB films were deposited (up to 18 layers); despite uncertainty over the exact nature of the layer at the interface, the deposition behavior is uniform and reproducible with transfer ratios close to unity. The purple coloration of **1** is clearly visible to the naked eye with even one layer, and film formation gives a large blue-shift in the MLCT λ_{max} to 530 nm (0.35 eV higher than that in MeCN), indicative of H-aggregates as observed for example with amphiphilic squaraines.[16] The absorbance at 530 nm increases linearly with the number of layers, consistent with a homogeneous deposition.

SHG measurements were carried out with the multilayer films of **1** by using a 1064 nm Nd^{3+}:YAG laser with detection at 45° in transmission, and a complete lack of activity confirmed the centrosymmetric Y-type deposition obtained. In order to produce films capable of showing SHG activity, spacer layers of arachidic acid were also deposited on hydrophilic glass to give alternating noncentrosymmetric multilayered structures (Figure 1), corresponding with a Z-type deposition. Up to five bilayers were deposited with good overall stability. These films show MLCT bands at $\lambda_{max} = 530$ nm and SHG signals. A periodic fringe pattern is observed
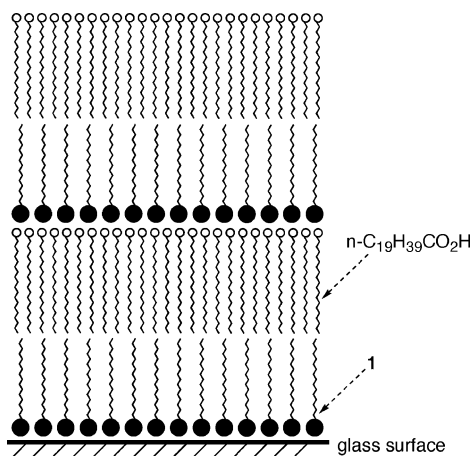
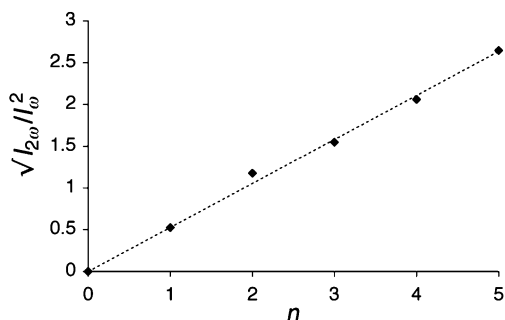**Figure 1.** Simplified representation of a part of the alternating LB films.

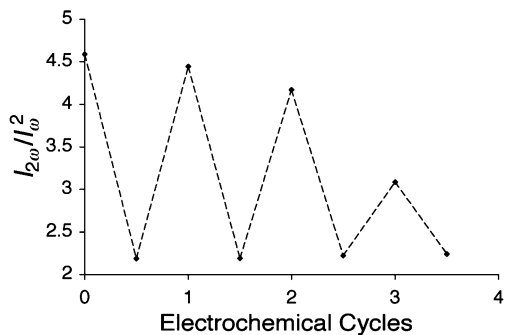**Figure 2.** Square root of the corrected SHG intensity against *n* on glass.

Figure 3. Electrochemical switching of the 532 nm SHG from an alternating LB film containing **1** on ITO-coated glass.

with films deposited on both sides of the substrate, so we examined the evolution of the SHG signal using slides coated on one side only. The effects of laser fluctuations are removed by using the corrected SHG intensity $I_{2\omega}/I_{\omega}^2$ ($I_{2\omega}$ = 532 nm intensity; I_{ω} = 1064 nm intensity). The quadratic dependence of $I_{2\omega}/I_{\omega}^2$ on the number of deposited layers *n* (Figure 2) further confirms the homogeneity of the deposition.

For redox-switching experiments, an alternating three bilayer LB film containing **1** was deposited onto one side of ITO-coated glass integrated into a modified electrochemical cell.[5d] The slide forms the working electrode and was held at 1 V vs Ag for 2 min to oxidize the complex and then at 0 V for 2 min to effect reduction back to the Ru[II] form. Oxidation causes a ca. 50% decrease in the SHG intensity, and the signal is almost completely restored on reduction (Figure 3). This process was repeated, giving an essentially reversible switching over two cycles, but the signal from the Ru[II] form diminishes with further cycling. HRS studies show that the β response of **2** decreases 10−20-fold upon oxidation and the effect is fully reversible over many cycles.[4] The lower apparent

extent of switching with our films probably arises from: (i) reabsorption of SHG by the Ru[II] form; (ii) incomplete oxidation due to the need for charge compensation (BF_4^- ions must migrate from the electrolyte into the film), and insulation by the alkyl chains. The gradual loss of SHG activity for the Ru[II] form may originate from changes in the film structure. LB monolayers of **1** give a much weaker SHG when compared to the alternating multilayers and do not show a convincing redox-switching. However, using more highly active complexes[17] may also allow such an effect to be demonstrated with SAMs.

In summary, we have demonstrated for the first time redox-switching of bulk NLO behavior based on a well-understood molecular-level change. Further studies will use directed synthesis and changes in film thickness, counteranion, etc. to increase the magnitude and durability of the effect.

Supporting Information Available: Complete ref 5c; analytical data and further experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA711170Q