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Molecular Architecture of Calixarenes and Their Self-Assembled Mono- and Multi-layers for Nonlinear Optical (NLO) Applications

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Abstract

The synthesis and characterization of supermolecular chromophore—calix[4]stilbazole were described. The calix[4]arene-based, chromophore forms densely packed, highly ordered monolayers on silica surfaces. Ultra-high second order nonlinearities were observed in these systems, and spectroscopic second harmonic generation was used to characterize the frequency dispersion of the second order susceptibilities.

Keywords: Self-assembly using surface chemistry, Self-organization in macromolecules, Non-linear optical methods, All-optical modulator, Organic/inorganic interfaces, and lasers.

1. Introduction

The design and synthesis of artificial supermolecular architectures on surfaces represent an important aspect of molecular self-assembly and highly ordered mesoscale structures with desired chemical functionalities and physical properties. Several approaches such as the Langmuir-Blodgett technique and liquid crystals have been reported to generate molecular-based materials with organized polar structures [1-2]. However, the orientation in these materials is maintained by weak bonding or steric hindrance, which lose the polar alignment over time. The synthetic strategy here (Fig. 1) is to fix dipole orientation by structural interlocking of NLO chromophores into a cone conformation, and then to utilize them to build polar self-assembled monolayers. In this paper, we discuss the molecular design of calixarene-based, NLO molecular "pyramids", their monolayer self-assemblies on oxide surfaces, and spectroscopic second order NLO properties.

Figure 1. A schematic illustration of a self-assembled monolayer consisting of robust calixarene pyramids on silica surfaces.

Organic NLO chromophores are typically π -conjugated molecules with a D- π -A structure, where D and A are electron donor and acceptor, respectively, and π is a π -conjugated segment or sensitizer. This structural feature has been widely used to attain large values of the molecular second-order nonlinear susceptibility, β [3]. By tethering these linear molecular units together through methylene bridges, a calixarene-based NLO chromophoric pyramid is derived. To achieve optimum molecular β , the orientation of each D- π -A unit should be fixed in nearly the same direction. Therefore, our approach involves the synthesis of a calix[4]arene with a frozen "cone" conformation by substitution at the lower rim with large functional groups. With a molecular building block having rigid structure and fixed dipole orientation, it is expected that these self-assembled monolayers (SAMs) will have higher alignment, better thermal and structural stability than SAMs using single chromophoric unit. The structure of our calixarene SAMs is summarized in Figure 1.

2. Results and Discussion

The synthesis of target chromophores starts with conformation freezing of the desired cone-structure of commercially available *p-t*-butyl-calix[4]arene by introducing ethoxyethyl groups on the phenolic OH groups. The subsequent nitration reaction replaces the *t*-butyl groups with nitro groups which were then reduced with hydrazine in the presence of Raney Ni. The desired chromophore was obtained by coupling the *p*-aminocalixarene with 4-pyridyl-carboxaldehyde in the presence of acetic acid. The final product was analyzed with matrix-assisted laser desorption/ionization mass spectrometry, ^1H NMR, and IR spectroscopy [4]. The mass spectrometry yields the correct parent ion and NMR indicates a cone conformation with a strong proton-proton coupling, $J = 12$ Hz, on the bridging methylene groups.

The formation of self-assembled monolayers is based on the method reported earlier [5]. Substrates were treated with coupling surfactants such as *p*-chloromethyl-phenyl-trichlorosilane, followed by a quaternization reaction to achieve four-point-attachment to the surfaces. The four-point-attachment was monitored by the complete disappearance of the pyridyl mode at 1597 cm^{-1} in the surface FTIR and the appearance of the pyridinium mode at 1638 cm^{-1} . This result shows that covalent bonds (C-N) are formed between the coupling layer and the calixarene chromophore layer. The electronic absorption spectra also confirm the quaternization, exhibiting a characteristic charge transfer band at 380 nm that is 30 nm read-shifted in comparison with solution spectra.

In order to study the NLO properties and molecular orientation on surfaces, spectroscopic second harmonic generation (SHG) was measured on the monolayers of calixarene. These measurements were performed using a modelocked Ti:sapphire laser in either femtosecond (150 fs autocorrelation width) or picosecond (2 ps width) mode with 100 MHz repetition rate, for fundamental wavelengths between 890 nm and 750 nm. Results using picosecond pulses to generate *p*-polarized SHG from *p*-polarized fundamental are shown in Figure 2 for a fundamental wavelength of 890 nm. An average molecular orientation of $\psi \sim 35 \pm 5^\circ$ was deduced by modeling the angular dependent SHG response ($n_{\text{film}} = 1.7$); an absolute magnitude of $d_{33} \sim 80\text{ pm/V}$ for monolayers of calixarene was deduced by calibrating to reference Y-cut quartz [5]. The solid lines in Figure 2 are best theoretical fits, modulated by an interference term, which was caused by the interference from the calixarene monolayers on both the front and the back of the substrate. Complete destructive (or constructive) interference was achieved across the entire pulse spectrum indicating good uniformity in these thin films. For the 1 mm fused silica samples considered here, effects of pulse walkoff due to mismatched group velocities of the fundamental and SH pulses can be neglected.

Figure 2. SHG signal vs. incident angle for *p*-polarized SHG from *p*-polarized (solid circles) fundamental at a wavelength of 890 nm and 2 ps pulsewidth, and best theoretical fit (solid line).

Figure 3 shows the measured values of d_{33} versus fundamental wavelength for monolayer films of calixarene together with the linear absorption spectrum αd taken from the same sample. Here, α and d are the linear absorption coefficient and film thickness, respectively. The nonlinear

optical spectrum closely resembles the linear optical absorption spectrum, which is fairly featureless. The wavelength dependence (fundamental $\lambda = 890\text{--}750\text{ nm}$; harmonic $\lambda = 445\text{--}375\text{ nm}$) indicates a gradual increase of d_{33} as the fundamental moves to shorter wavelength, consistent with normal refractive index dispersion in this spectral region approaching the charge transfer resonance at 390 nm. From Figure 3, the charge transfer resonance is fairly broad; the measured value for d_{33} at the longest wavelength (60 pm/V at 890 nm) is still somewhat resonantly enhanced. We find a value of $d_{33} \sim 110\text{ pm/V}$ at $\lambda = 775\text{ nm}$, indicating a nearly twofold two-photon-resonant enhancement at the peak of the charge transfer band.

Figure 3. Second-order nonlinear susceptibility d_{33} (solid squares) vs. fundamental wavelength (top and right axes) or second harmonic wavelength (bottom and right axes) along with the linear absorption spectrum αd (solid line) vs. wavelength (bottom and left axes) for a self-assembled monolayer of calix[4]stilbazole. The lowest two-photon resonance is at 390 nm corresponding to 780 nm in d_{33} dispersion.

3. Conclusion

To summarize, we have made a significant step forward in construction of supramolecular architecture by demonstrating the formation of self-assembled monolayers with pyramid-like molecular building blocks. Structural interlocking via the bridging methylene groups among the D- π -A units yields films with extremely large second-order nonlinearities ($d_{33} \sim 60\text{ pm/V}$; $\lambda = 890\text{ nm}$), and robust molecular dipole alignment.

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