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Synthesis of azobenzene substituted tripod-shaped bi(*p*-phenylene)s. Adsorption on gold and CdS quantum-dots surfaces

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Dedicated to the memory of Professor Inta Muzikante

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ABSTRACT

We report here the synthesis of several tripod-shaped oligo(*p*-phenylene)s with legs composed of two phenylene units. Each leg is end-capped with a thioacetate group for adhesion to metallic surfaces. An azobenzene chromophore group is present on the functional arm of the tripod. The key step in the synthesis is the Pd-catalyzed Suzuki cross-coupling reaction of the silicon derivative core molecule with substituted phenyl moieties and azobenzene derivatives. Gold surfaces prepared by thermal evaporation and CdS quantum-dots surfaces were covered by the tripod-shaped molecules. Modified surfaces were characterized by atomic force microscopy (AFM), fluorescence, and Kelvin Probe analyses.

1. Introduction

Azobenzenes are versatile molecules that have received great attention in fundamental and applied research. The strong electronic absorption band that present these chromophores can be tuned by ring substitution from ultraviolet to red and visible region, allowing chemical fine-tuning of color, and because of this they have been used as dyes and colorants. With appropriate electron-donor/acceptor ring substitution, the π-electron delocalization of the aromatic structure can yield high optical nonlinearity, and azo chromophores have been extensively studied for nonlinear optical applications as well.[1,2] Azobenzene photoswitches are also valuable tools to influence protein activity.[3,4] For this purpose, they have been attached to the protein by covalent bonds[5] or by affinity interactions.[6] The photomechanic properties can be readily induced by reversible *cis*↔*trans* photoisomerization of the azo bond, and the geometric changes that result can be incorporated into polymers and other materials.[7] Molecules containing the azobenzene functionality are good candidates for converting light into mechanical work through *cis*↔*trans* isomerization, that is, controlled by ultraviolet (UV) and visible light.[8,9]

The ability of azo-containing molecules to self-assemble into monomolecular layers (self-assembled monolayers, SAMs) provides an additional nanometer-scale mechanical system, combining the advantages of single-molecule properties with the coherence and template capabilities of macroscopic structures. These films enable such applications as sensors, and molecular-level mechanical manipulators.[8] However, due to the packing into a self-assembled film, steric interactions constraints on the *cis*↔*trans* switching.[10,11] This fact does not exist in the isolated molecule or bulk disordered films, thus some slight disorder in the film can be an enabling condition for the isomerization.[12] Moreover, molecular packing also governs the

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excitonic coupling between chromophores, which can strongly influence the conversion efficiency.[13]

The most common method to generate a disorder in the functional group distribution on monolayer surfaces prepared by self-assembly and also to decrease their average density of monodentate adsorbates is by co-deposition of the active molecule with an inert analog adsorbate. However, it is not possible to avoid non-randomized mixing on the nanoscale that prevents controlling the spacing between the functional surface groups.[14,15]

To generate ordered SAMs with a high control on the orientation of the functional moieties, several shape-persistent and self-standing molecules have been developed, including: *i*) 'molecular caltrops' with four phenylacetylene legs extending from either a tetrahedral silicon core,[16,17] or from an adamantane core,[18–20] *ii*) conically shaped dendron adsorbates with a functional group at the core,[21,22] and *iii*) tripod-shaped oligo(*p*-phenylene)s joined together by a single silicon atom,[23,24] to be used for the functionalization of different surfaces.

In this paper we report, the synthesis of tripod-shaped anchors functionalized by azobenzene chromophores. Adsorption of these molecules on gold surfaces was also carried out. Due to the thioacetate functional group on the tripod legs, fluorescent nanoparticles, such as CdS quantum-dots (CdS QDs) were capped by the synthesized tripods, obtaining also a suitable platform of solubilization of this dendron system in aqueous media. Characterization of the generated surfaces was carried out by AFM, fluorescence, and Kelvin Probe (KP) measurements. We propose these adsorbates to control the orientation and spacing of the azo moieties in the organic thin films in order to improve the optical properties of the azobenzene derivatives.

2. Results and discussion

2.1. Synthesis

We carried out the synthesis of the tripods **1a** and **1b** (Fig. 1). Each tripod leg is composed of two phenylene units and it is end-capped with a thioacetate group. Their preparation was accomplished by coupling azobenzene and phenyl derivatives to a silicon core, being in both cases the key step of the synthesis the Pd-catalyzed Suzuki cross-coupling reaction (Schemes 1–5). We chose tripodal oligo(*p*-phenylene)s as anisotropic adsorbates because the *p*-phenylene legs are sufficiently rigid to maintain the perpendicular orientation of the functional arm at the focal point of the tripod with respect to the surface.[25,26]

Tour and Cai have described the use of a silicon atom as the core for constructing tripod-shaped structures.[16,23] We already used ethoxy triphenylsilanes for this purpose, however, we found that the ethoxy moiety easily decomposed in presence of water.[24] Due to this fact, we chose as the silicon core the more stable tetraphenyl derivatives **3a** and **3b**. These molecules are unsymmetrically substituted with three iodine atoms for the elongation of the tripod legs, and the less reactive chlorine (**3a**) or bromine (**3b**) atoms that allow the introduction of the active chromophore at the end of the synthesis.

The preparation of **3a** was carried out in two steps. First, the generation of *p*-chlorophenylmagnesium bromide at −78 °C, followed by treatment with tetrachlorosilane to produce a trichlorosilane derivative, and then substitution of the chlorine atoms by etoxy groups to give compound **2a** in 35% yield (Scheme 1). We observed that this compound is more stable that the corresponding chlorosilane derivative. Second, the treatment of **2a** with the monolithium salt of *p*-diiodobenzene afforded **3a** in 71% yield. This synthetic pathway provides **3a** with a 25% overall yield (Scheme 1). Compound **3b** was prepared from *p*-dibromobenzene by following the same reaction sequence (Scheme 1). The smaller overall yield found for **3b** (6%) in comparison to that of **3a**, can be attributed to a higher reactivity of the bromine atom towards the exchange of lithium under the reaction conditions.

Three ends of the supporting legs in **1a** and **1b** are derived from a thioacetate benzyl alcohol group. These groups were introduced in the last part of the synthesis. Thioacetate moiety as the caltrops feet has received recently much attemption since it increases the stability of the thiol group preventing degradation. Moreover, the in situ deprotection of the acetyl protected thiol under alkaline conditions allows the preparation of high quality SAMs, by controlling the used base.[16,27]

To achieve the thioacetate group derivatization, compound **4** was used for the elongation of the tripod legs. This compound has a hydroxyl group that will allow its exchange by a sulfur atom. Compound **4** was prepared by protection of the alcohol group in 3-(hydroxymethyl) phenylboronic acid pinacol ester by treatment with *tert*-butyldimethylsilyl chloride (TBDMSCl) in presence of 4-dimethylaminopyridine (DMAP) (Scheme 2).

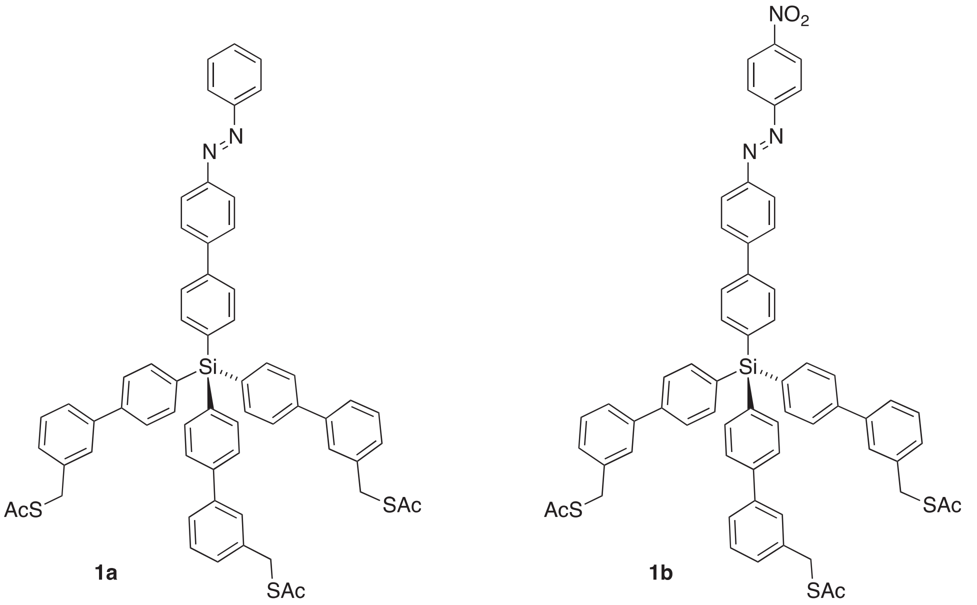

Fig. 1. Oligo-(*p*-phenylene) tripods substituted by azoderivative chromophores.