



Self-assembled monolayers of fluorene- and nitrofluorene-terminated thiols on polycrystalline gold electrode: Electrochemical and optical properties

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ABSTRACT

In this paper, two new thiols, [4-(9H-fluoren-9-ylmethyl)-phenyl]-methanethiol (**6a**) and [4-(2-nitro-9H-fluoren-9-ylmethyl)-phenyl]-methanethiol (**6b**), were synthesized, and self-assembled monolayers (SAMs) of these thiols were formed on gold electrodes. The structure and surface properties of molecular films were investigated by contact angle measurements and attenuated total reflectance infrared spectroscopy (ATR-FTIR). The blocking behavior of Au-**6a** and Au-**6b** SAMs was examined with cyclic voltammetry in the presence of redox probes such as $K_3Fe(CN)_6$, $Ru(NH_3)_6Cl_3$ and ferrocene. Electrochemical measurements revealed that the voltammetric behavior of the redox probes was dependent on the nature of the probe molecules, the electrolytic solution composition and the monolayer structure. The optical properties of the SAMs were studied by steady-state and time-resolved fluorescence spectroscopy. It was obtained that the fluorescence emission bands of Au-**6a** and Au-**6b** monolayers were red-shifted and broadened compared to those of free thiols in solution as well as significant reduction at their emission intensities. The fluorescence decay profiles of **6a** and **6b** monolayers were described by a monoexponential function. In order to determine the possible deactivation mechanism between the metal support and photoexcited molecules, spectroelectrochemical steady-state fluorescence and lifetime measurements on the Au-fluorophore electrodes were also performed as a function of the applied potential. These results indicate that the fluorescence quenching occurs via an energy transfer mechanism from the excited molecules to the gold substrate.

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1. Introduction

In recent years, self-assembled monolayers (SAMs) of surface-active organic molecules on various substrates have attracted considerable attention due to their potential applications in important technological fields such as molecular electronics [1,2], optical switches [3], chemical sensors [4], and corrosion inhibitors [5]. There are many more possible systems to prepare such organized assemblies like silanes on silicon surfaces [6], fatty acids on metal oxides [7,8], and thiols [9–11] or disulfides [12,13] on noble metals. Among them, long-chain alkanethiols on gold have proven to be excellent model systems to form monolayers with controllable thickness and desirable function. These stable monolayers can be easily composed by soaking an Au substrate in the solution of a suitable alkanethiol without the requirement of expensive equipment. Both experimental and theoretical studies have demonstrated that the propulsive force in their formation process is the chemical bond formation between the substrate and sulfur atoms, and the hydrophobic interactions between the alkyl chains [14,15].

The surface properties of thiol monolayers for various purposes can be easily tailored by changing the chemical nature of the terminal groups attached to the other end of alkyl chains [16–18]. In this sense, the modification of the metal surface with photoactive molecules positioned at the outside of SAM is of fundamental importance in development of artificial optoelectronic devices. It is well known that, under ambient conditions, the photophysical and photochemical properties of probe molecules transferred onto a solid substrate are affected by many factors such as rigid environment, molecular orientation, and surface irregularities [19]. Furthermore, the excited states of the fluorophores in SAM can be quenched by the metal support either via energy transfer or electron transfer processes, and their emission intensity is, thus, partially decreased [20]. Therefore, the length and chemical structure of the molecular bridge separating the terminal fluorophore from the metal surface is a major factor for quantum yields of photoactive group [21,22]. The photophysical (or photochemical) behavior and quenching process of the excited state observed upon irradiation of the SAMs which contain the photoactive groups such as fluorene [23–25], stilbene [26], anthracene [27] and coumarin [28] as a terminal group at the end of a long alkyl spacer have been investigated in previous studies. However, no report has so far been published on the photosensitiveness of the thiol

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SAMs formed from a short aromatic linker and a terminal fluorophore group. In this study, we report the first synthesis and photo-physical properties of fluorene- and nitrofluorene-terminated thiols with a benzene linker.

When compared to those of linear thiols, aromatic thiols can form more densely packed and well-ordered films as a result of π - π stacking interactions [29]. Additionally, monolayers containing aromatic rings display a high electrical conductivity due to the easy delocalization of electrons in the ring while the saturated hydrocarbon chains act as effective insulating layers [30]. Thus, the electrons are transported through these layers by the tunneling mechanism. This behavior can be emerged as a significant disadvantage for us because, with increasing tunneling rate, the lifetimes of the excited molecules bound to the metal can be decreased via electron transfer process. To avoid this problem, we purposely added a methylene unit in between the benzene and the fluorene rings. Furthermore, a second methylene unit was also inserted to increase the degree of order in between the aryl and sulfur head group [31].

The radiative deactivation of the resultant molecular fluorophores (**6a** and **6b** in Scheme 1) on gold was investigated by steady-state fluorescence emission spectroscopy, and their fluorescence lifetimes were measured with time-resolved fluorescence spectroscopy. Cyclic voltammetry experiments were used to examine the relationship between the packing quality and the electron transfer behavior of the films in the presence of electroactive redox probes. Additionally, spectroelectrochemical experiments were performed as a combination of electrochemistry and emission spectroscopy. These measurements provided quite useful information to better understand the effect of the short benzene ring in the absence and presence of electron acceptor nitro substituent on the mechanism of molecular dynamics following photoexcitation. The molecular structure and surface properties of these films were also characterized using horizontal attenuated total reflectance infrared (HATR-FTIR) spectroscopy and contact angle measurements, respectively.

2. Experimental section

2.1. Synthesis of thiol compounds

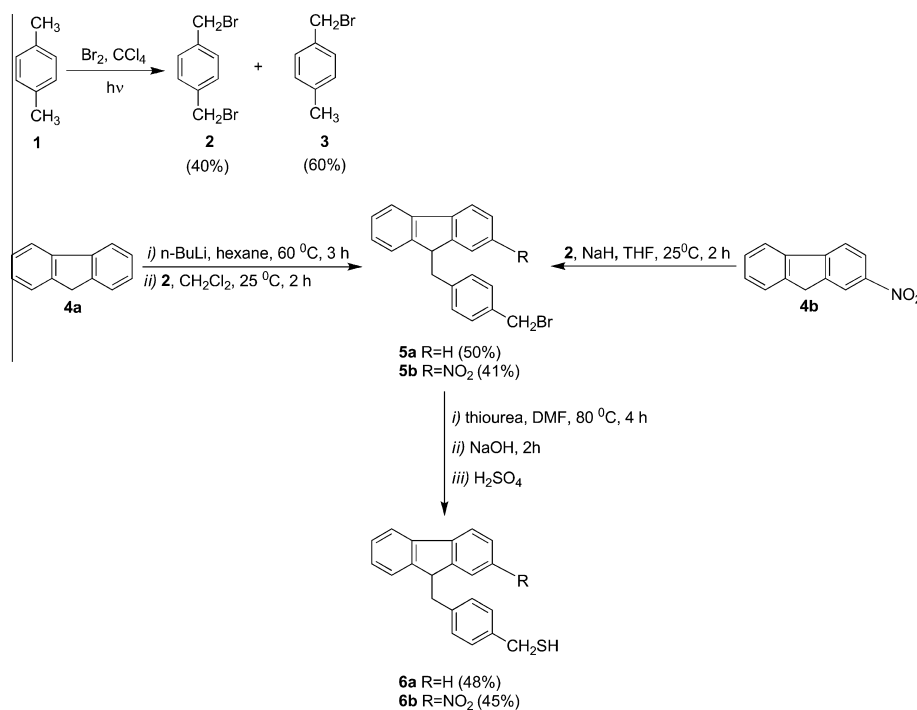
The synthesis of **6a** and **6b** was achieved as outlined in Scheme 1 by our group.

2.1.1. Synthesis of 1,4-Bis(bromomethyl)benzene (**2**)

To a magnetically stirred solution of p-xylene (**1**) (25 g, 0.24 mol) in 75 mL of dry CH_2Cl_2 was added dropwise a solution of bromine (56 g, 0.35 mol) in 5 mL of CH_2Cl_2 . The reaction mixture was irradiated with a 500-W lamp for 5 min at room temperature. The solvent was evaporated. The residue was purified by column chromatography on silica gel eluting with *n*-hexane to yield **2** (17 g, 40%) as a white crystal (mp:141–144 °C, Lit. [32] 142–144 °C). ^1H NMR (400 MHz, CDCl_3) δ 4.48 (s, 4H), 7.37 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 33.1, 129.7, 138.2; FTIR (KBr pellet, cm^{-1}) 3046, 3024, 3008, 2972, 2855, 1923, 1804, 1689, 1508, 1437, 1419, 1297, 1254, 1228, 1198, 1126, 1085, 857, 848.

2.1.2. Synthesis of 9-(4-Bromomethyl-benzyl)-9H-fluorene (**5a**)

To a solution of **4a** (0.79 mg, 4.76 mmol) in 30 mL of dry hexane under nitrogen atmosphere was added *n*-butyl lithium (1.6 M, 6.09 mmol, 3.8 mL). The mixture was heated at 60 °C for 3 h. After allowing to cool to room temperature, it was treated with a solution of **2** (2.76 g, 10.50 mmol) in CH_2Cl_2 (5 mL). The resulting mixture was stirred for 2 h at the same temperature. 50 mL of water was added and organic layer was separated, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatograph on silica gel eluting with CH_2Cl_2 /hexanes (10%) to afford **5a** (0.29 mg, 50%) as a white crystal (mp: 98–102 °C). ^1H NMR (400 MHz, CDCl_3) δ 3.12 (d, 2H, $J = 7.3$ Hz), 4.22 (t, 1H, $J = 7.3$ Hz), 4.52 (2H, s), 7.18–7.38 (m, 10H), 7.75 (d, 2H, $J = 7.3$); ^{13}C NMR (100 MHz, CDCl_3) δ 33.8, 39.9, 48.8, 120.1, 125.0, 126.9, 127.4, 129.2, 130.2, 136.1, 140.4, 141.1, 146.8; FTIR (KBr pellet, cm^{-1}) 3036, 3018, 2946, 2926,



Scheme 1. Synthesis of **6a** and **6b** thiols.

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