Chemical Papers 68 (2) 239–245 (2014)
DOI: 10.2478/s11696-013-0437-2

ORIGINAL PAPER

Synthesis of a disulfide functionalized diacetylenic derivative of carbazole as building-block of polymerizable self-assembled monolayers

[a,b]**Sushilkumar A. Jadhav***, [b]**Massimo Maccagno**

[a]*Department of Applied Science and Technology, Polytechnic University of Turin, 10129 Turin, Italy*

[b]*Department of Chemistry and Industrial Chemistry, University of Genoa, 16146 Genoa, Italy*

Received 21 March 2013; Revised 6 May 2013; Accepted 10 May 2013

A new symmetrical disulfide containing a diacetylenic unit and bearing a fluorescent carbazolyl end-group forming polymerizable self-assembled monolayers on metallic nanostructures has been synthesized. Suitable modifications of the synthetic steps involved in the synthesis of such derivatives were made in order to assure better synthetic pathway. Conversion of the tosylated derivative into the final symmetrical disulfide is carried out using sodium hydrosulfide (NaSH).

Keywords: symmetrical disulfide, diacetylene, sodium hydrosulfide

Introduction

Organosulfur compounds, because of their capability to get chemisorbed on metallic surfaces, especially on gold ones, are well-known building-blocks for the construction of self-assembled monolayers (SAMs) (Ulman, 1991; Jadhav, 2012a, 2012b; Miyano & Maeda, 1986; Wenzel & Atkinson, 1989; Mino et al., 1991, 1992; Charyach et al., 1993; Batchelder et al., 1994; Kim et al., 1995). The surface modification by SAMs allows tailoring the interfacial properties of the nanostructures both in two (chip) and three (nanoparticles) dimensional surfaces. Both thiols and disulfides are frequently utilized building-blocks for the construction of monolayers or for the surface modification of gold surfaces; hence, synthesis of these compounds and their derivatives has drawn increased attention in recent years (Joly et al., 2010; Operamolla et al., 2007; Kota et al., 2012; Jadhav, 2012b; Zhao et al., 2012). Incorporation of polymerizable diacetylene groups in such compounds provides them with the possibility of being polymerized forming polymers with highly conjugated backbones (polydiacetylenes). The resulting assemblies not only possess the conducting conjugated polydiacetylene chains but they also strengthen the scaffold of the organosulfur compounds around nanostructures such as the nanoparticles. Polymerizable monolayers of polydiacetylenes have shown their potential applications in molecular electronics (Okawa et al., 2011, 2012). Conducting properties and higher-performance are the main features of polydiacetlenes fabricated in monolayers on different substrates such as semiconducting materials which may prove to be alternatives to conventional silicon-based devices (Mandal et al., 2011). The photo-polymerization scheme in monolayers of these compounds is shown in Fig. 1.

Synthesis and physical and optical characterization of a particular class of polydiacetylenes have been previously reported (Alloisio et al., 2007), namely the poly(carbazolyldiacetylenes) (PCDAs) of the general formula: R—$(CH_2)_m$—C≡C—C≡C—$(CH_2)_n$—S—S—$(CH_2)_n$—C≡C—C≡C—$(CH_2)_m$—R, where R is the electron–donor end-group. We have also recently reported the synthesis of thiols and their symmetrical disulfides containing fluorescent end-groups, such as the carbazole and benzotriazole groups as building-blocks of monolayer formations (Jadhav, 2012b). The presence of fluorescent groups makes

*Corresponding author, e-mail: sushilkumar.jadhav@polito.it