Title: Solid-state sensory properties of CALIX-poly(phenylene ethynylene)s toward nitroaromatic explosives

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Source: Sensors and Actuators B-Chemical

Volume: 161 **Issue:** 1 **Pages:** 702-713 **DOI:** 10.1016/j.snb.2011.11.017 **Published:** Jan 3 2012

Document Type: Article

Language: English

Abstract: This study is primarily focused in establishing the solid-state sensory abilities of several luminescent polymeric calix[4]arene-based materials toward selected nitroaromatic compounds (NACs), creating the foundations for their future application as high performance materials for detection of high explosives. The phenylene ethynylene-type polymers possessing bis-calix[4]arene scaffolds in their core were designed to take advantage of the known recognition abilities of calixarene compounds toward neutral guests, particularly in solid-state, therefore providing enhanced sensitivity and selectivity in the sensing of a given analyte. It was found that all the calix[4]arene-poly(para-phenylene ethynylene)s here reported displayed high sensitivities toward the detection of nitrobenzene, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene (TNT). Particularly effective and significant was the response of the films (25-60 nm of thickness) upon exposure to TNT vapor (10 ppb): over 50% of fluorescence quenching was achieved in only 10 s. In contrast, a model polymer lacking the calixarene units showed only reduced quenching activity for the same set of analytes, clearly highlighting the relevance of the macrocyclics in promoting the signaling of the transduction event. The films exhibited high photostability (less than 0.5% loss of fluorescence intensity up to 15 min of continuous irradiation) and the fluorescence quenching sensitivity could be fully recovered after exposure of the quenched films to saturated vapors of hydrazine (the initial fluorescence intensities were usually recovered within 2-5 min of exposure to hydrazine).

Author Keywords: Calixarenes; Conjugated Polymers; Phenylene Ethynylene; Fluorescence; Solid-State Sensors; Explosives

KeyWords Plus: Fluorescent Conjugated Polymers; Chemical Sensors; TNT Chemosensors; Films; Photoluminescence; Trinitrotoluene; Copolymer; Design

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Funding:

Funding Agency	Grant Number
Fundação para a Ciência e a Tecnologia/MCTES (Portugal)	PTDC/QUI/66663/2006

Publisher: Elsevier Science SA

Publisher Address: PO Box 564, 1001 Lausanne, Switzerland

ISSN: 0925-4005

Citation: Costa A I, Pinto H D, Ferreira L F V, Prata J V. Solid-state sensory properties of CALIX-poly(phenylene ethynylene)s toward nitroaromatic explosives. Sensors and Actuators B-Chemical. 2012; 1 (161): 702-713.