Title: Substituted p-phenylene ethynylene trimers as fluorescent sensors for nitroaromatic explosives

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Abstract: New sensory materials based on p-phenylene ethynylene trimers integrating calix[4]arene receptors (CALIX-PET) and tert-butylphenol (TBP-PET) moieties have been synthesized and their sensitivity and selectivity for the detection of nitroaromatic compounds (NACs) such as nitrobenzene (NB), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT) and picric acid (PA) investigated in fluid phase and solid-state. It was found that both fluorophores displayed high sensitivities toward NACs detection in solution as evaluated by the Stern-Volmer formalism. For all the tested explosives, the ratio of fluorescence intensities (F-0/F) is a linear function of the quencher concentration only after appropriate correction of fluorescence quenching data for inner-filter effects. The quenching efficiencies for CALIX-PET and TBP-PET follow the order PA >> TNT > DNT > NB, which correlate well with the quenchers electron affinities as evaluated from their LUMOs energies thereby suggesting a photoinduced electron transfer as the dominant mechanism of fluorescence quenching. The selectivity of these sensors was checked against exemplar interferents possessing differentiated electronic properties (benzoic acid, 2,4-dichlorophenol and benzoquinone) and reduced quenching activity was detected. The quenching efficiencies and response times of the two fluorophores in the solid-state toward NB, 2,4-DNT and TNT vapors were evaluated through steady-state fluorescence quenching experiments with the materials dispersed in polymeric matrices or as neat films. The most significant fluorescence quenching responses were achieved for drop-casted films of TBP-PET upon exposure to nitroaromatics.

Author Keywords: Calixarenes; Fluorescence; Sensors; p-Phenylene ethynylene Trimer; Explosives

KeyWords Plus: Polymer-Films; Conjugated Polymers; Chemical Sensors; TNT Chemosensors

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