Title: Calix[4]arene-carbazole-containing polymers: Synthesis and properties

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Abstract: New highly fluorescent calix[4]arene-containing phenylene-alt-ethynylene-3,6- and 2,7-carbazolylene polymers (CALIX-PPE-CBZs) have been synthesized for the first time and their photophysical properties evaluated. Both polymers were obtained in good isolated yields (70-84%), having M-w ranging from 7660-26,700 g mol(-1). It was found that the diethynyl substitution (3,6- or 2,7-) pattern on the carbazole monomers markedly influences the degree of polymerization. The amorphous yellow polymers are freely soluble in several nonprotic organic solvents and have excellent film forming abilities. TG/DSC analysis evidences similar thermal behaviors for both polymers despite their quite different molecular weight distributions and main-chain connectivities (T-g, in the range 83-95 degrees C and decomposition onsets around 270 degrees C).The different conjugation lengths attained by the two polymers dictates much of their photophysical properties. Thus, whereas the fully conjugated CAUX-PPE-2,7-CBZ has its emission maximum at 430 nm (E-g = 2.84 eV; Phi(F) = 0.62, CHCl3), the 3,6-linked counterpart (CALIX-PPE-3,6-CBZ) fluoresces at 403 nm with a significant lower quantum yield (E-g = 3.06 eV; Phi(F) = 0.31, CHCl3). The optical properties of both polymers are predominantly governed by the intrachain electronic properties of the conjugated backbones owing to the presence of calix[4]arenes along the polymer chain which disfavor significant interchain interactions, either in fluid- or solid-state.

Author Keywords: Calixarene; Carbazole; Arylene Ethynylene; Polymer; Fluorescence

KeyWords Plus: Containing Conjugated; Optical-Properties; Sensors; Films; Chemosensors; Switches; State

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