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Title: Synthesis, Structure, and Optical Properties of an Alternating Calix[4]arene-Based Meta-Linked Phenylene Ethynylene Copolymer

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Abstract: Novel alternating copolymers comprising biscalix[4]arene-p-phenylene ethynylene and m-phenylene ethynylene units (CALIX-m-PPE) were synthesized using the Sonogashira-Hagihara cross-coupling polymerization. Good isolated yields (60-80%) were achieved for the polymers that show M_n ranging from 1.4×10^4 to 5.1×10^4 g/mol (gel permeation chromatography analysis), depending on specific polymerization conditions. The structural analysis of CALIX-m-PPE was performed by ^1H - ^{13}C , ^{13}C - ^{13}C - ^1H heteronuclear single quantum correlation (HSQC), ^{13}C - ^1H heteronuclear multiple bond correlation (HMBC), correlation spectroscopy (COSY), and nuclear overhauser effect spectroscopy (NOESY) in addition to Fourier transform-Infrared spectroscopy and microanalysis allowing its full characterization. Depending on the reaction setup, variable amounts (16-45%) of diyne units were found in polymers although their photophysical properties are essentially the same. It is demonstrated that CALIX-m-PPE does not form ground-or excited-state interchain interactions owing to the highly crowded environment of the main-chain imparted by both calix[4]arene side units which behave as insulators inhibiting main-chain pi-pi stacking. It was also found that the luminescent properties of CALIX-m-PPE are markedly different from those of an all-p-linked phenylene ethynylene copolymer (CALIX-p-PPE) previously reported. The unexpected appearance of a low-energy emission band at 426 nm, in addition to the locally excited-state emission (365 nm), together with a quite low fluorescence quantum yield ($\Phi = 0.02$) and a double-exponential decay dynamics led to the formulation of an intramolecular exciplex as the new emissive species. (C) 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 5040-5052, 2010

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