Synthesis and Characterization of Fluorene Based π-Conjugated Oligomers and Polymers for Optoelectronic and Sensory Applications

Abstract

The development of highly luminescent fluorene based main-chain organic/organometallic oligomers and polymers has attracted much attention due to their smart application in many areas of materials science such as organic light emitting diodes (OLEDs), solar cells, chemosensors, and field-effect transistors (FETs). Fascinated by the current research trend, a series of fluorenyl-alkynyl based rod-shaped oligomers with alkynyl termini and their corresponding Au(I)/Pt(II) containing main-chain organometallic oligomers and polymers have been synthesized and characterized by various spectroscopic tools. Judicious incorporation of different donor and acceptor aromatic moieties such as phenyl, naphthalene, anthracene, benzotriazole, benzothiadiazole through alkynyl spacers in between two fluorenyl-alkynyl units allowed fine tuning of the optical and electronic properties. The binuclear Au(I)-alkynyl σ-complexes and Pt(II) containing metallopolymers exhibit phosphorescence at 77 K due to heavy atom effect, inducing efficient intersystem crossing leading to triplet emission, as manifested by the life time values in the range of millisecond. These phosphorescent organometallic wires are attractive building blocks for application in OLEDs and other optoelectronic devices. Highly emissive fluorene and thiophene based π-conjugated copolymers even in solid state, have also been synthesized and their electroluminescence properties have been explored following the device configuration ITO/PEDOT:PSS(50 nm)/P1-P2(80 nm)/BCP(40 nm)/Al(100 nm). Both the polymers exhibit electroluminescence in the cyan range with the maxima (λ_{max}) at 469 and 481 nm with low onset voltage of 4 V. Furthermore, fluorene and perylene diimide *n*-type copolymers have been successfully designed and developed as non-fullerene acceptors for *all polymer* solar cells to develop efficient, low cost and lightweight photovoltaic devices. All the polymers display wide absorption band ranging from 250 to 650 nm, and the optical band gaps determined from the absorption band edges are found to be 1.76-1.84 eV. The favorable energy levels make the synthesized *n*-type π-conjugated polymers as potential candidates to explore as non-fullerene acceptor in *all polymer* solar cells. Finally, 1,2,3-triazole functionalized polyfluorene π-conjugated emissive polymers have been explored for trace detection of nitroaromatics (NACs) both in solution and solid state. The reversible fluorescent probes exhibit

nanomolar detection of picric acid in contact mode by naked eye, demonstrating its practical utility as quick and inexpensive way detection of trace NACs.

Keywords: Fluorenyl-alkynyl, metal-acetylide, Organometallic σ-complex, Gold(I) and platinum(II), Oligomers and polymers, Photophysical properties, Solvatochromism, Triplet state emission, Optoelectronic device, Organic light emitting diodes, Perylene diimide, *n*-Type semiconducting polymer, Non-fullerene acceptor, *All polymer* solar cell, Fluorescent probe, *Molecular wire* effect, Nitroaromatics detection, Selectivity and sensitivity, Trace detection, Repeatability.