



Synthesis, photophysical and electrochemical properties of π -conjugated pyrene based down-shifting molecules with fluorinated aryl groups

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ABSTRACT

Pyrene molecule, with excellent photophysical properties (strong absorption cross section, excellent emission properties and a long-excited state lifetime), excellent thermal and photochemical stability, has been widely used as a building block for the synthesis of pyrene-based fluorophores for optoelectronic applications. In this work, we report the synthesis of two series of pyrene- π -A compounds, series I (3–6) and II (10–13), in which nitro, cyano, cyanoacrylonitrile and cyanoacrylic acid as electron acceptor groups are connected to the pyrene core via aryl or fluoroaryl π -conjugating bridges. The incorporation of fluorine atom on the π -extension bridge cause a slightly red-shift at emission wavelength (λ_{em}) in solution and polymethylmethacrylate (PMMA) films and increase the Stokes shift due to greater stabilization of molecular orbitals in the excited state, especially for series I. Solvatochromic measurements and theoretical computational studies suggest a higher intramolecular charge transfer in the excited state for series II when compared to series I due to their stronger electron acceptor moieties. All pyrene derivatives are stable and exhibited initial mass loss at temperature above 200 °C. The good photophysical and thermal properties of the synthesized pyrene derivatives, associated with high molar absorption coefficients in the UV spectrum and good fluorescence emission in the range of 430–480 nm (series I) and 505–567 nm (series II) in PMMA films, make them possible candidates for organic light-emitting diode (OLED) and luminescent down-shifting (LDS) layers for stable perovskite solar cells, respectively.

1. Introduction

Perovskite solar cells (PSCs), with efficiency records increasing surprisingly fast since 2009 [1] have become one of the main focus of research in photovoltaics (PV), however problems associated with the stability of these devices are hindering their market application [2].

UV degradation is one of the most severe issues, chiefly caused by TiO₂'s photogenerated electrons that decompose the perovskite absorber material, coupled with the additional intrinsic degradation of this material under UV exposure [3]. One way to overcome this issue can be achieved by the use of Luminescent Down Shift layers (LDS) positioned on top of the photovoltaic cell which benefits from the exploitation of the energy of otherwise lost photons, while still protecting the absorber material from the harmful UV radiation. An LDS layer is typically a polymer sheet with luminescent molecules embedded in it, which can convert the short-wavelength photons into long-wavelength photons by the process of photon absorption and emission [4].

Over the years, many luminescent materials, such as quantum dots

[5,6], rare-earth ion complexes [7,8] and organic dyes [9–13] have been investigated for LDS applications, with emphasis on its effect in external quantum efficiency (EQE) of PV cells. In particular, organic dyes have been highlighted due to their high absorption coefficient, good Luminescent Quantum Yield (LQY), large Stokes shift, and good solubility in polymeric matrix [14,15].

Very few studies have been focused on the effects of LDS in the stability and photoconversion efficiency of perovskite solar cells and so far the luminescent materials used were a Yttrium vanadate:Europium nano-phosphor material [16], ZnSe quantum dots [17], a photocurable fluoropolymers [18] and the well-known Kremer fluorescent blue dye [19].

Pyrene is a widely studied polycyclic aromatic hydrocarbon (PAH) due to its unique photophysical properties such as strong absorption cross section, excellent emission properties, long excited state lifetime and excellent thermal and photochemical stability [20]. Due to these favourable characteristics, pyrene has been used as a building block for the synthesis of aggregation-induced emission luminogens (AIEgens)

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