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A polystyrene bearing perylene diimide pendants with enhanced solid state emission for white hybrid light-emitting diodes

Erika Kozma, Wojciech Mróz, Francesco Galeotti*

CNR-Istituto per lo Studio delle Macromolecole, Via Bassini 15, 20133 Milano, Italy

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ABSTRACT

We report the preparation of a luminescent linear polystyrene decorated with randomly distributed pendants of perylene diimide, where the quenching processes due to aggregation states, typical of perylene diimides, are efficiently suppressed. Compared to a blend with the same polystyrene/dye ratio, the copolymer shows a nearly four-fold increase in quantum efficiency. Stable white emitting devices are straightforwardly prepared by the combination of this red emitting copolymer, a suitable organic green emitter, and an inorganic commercial blue light source. The selected organic dyes have appropriate photophysical characteristics for converting the blue source into a white light emission and exhibit good film forming properties even in the blend. The control of the film thickness of the blended organic dyes along with their relative concentration allows a fine tuning of the color emission. The optimized hybrid white LED displays white emission with chromaticity coordinates of $x = 0.31$, $y = 0.34$, a color rendering index of 83 and an efficiency of 28 lm/W.

1. Introduction

Light-emitting diodes (LEDs) are becoming increasingly popular as valid alternative to conventional light sources due to their compact structure, low energy consumption, and long lifetime. LEDs based on group-III nitride crystals have been developing rapidly and are used in many different applications [1,2]. While the efficiency of this class of LEDs in the blue wavelengths is quite high, it normally decreases rapidly when the wavelength increases above 450 nm [3,4]. This is a challenge that must be addressed in order to support a wider usage of LEDs in ambient lighting, where the generation of white emission requires all color contributions. On the other hand, the emergent organic LED technology (OLED) has proven of being suitable for display applications but, until now, organic electroluminescence stability is still limited for continuous lighting purposes [5–7]. In addition, the development of purely organic white-light emitting materials with high outputs still remains a relatively less explored area. One alternative approach to obtain the white light is based on a hybrid organic–inorganic system in which the electroluminescence from group-III nitrides provides the blue component and serves as the pump for exciting the green and red photoluminescence (PL) of organic substances [8,9].

However, despite their high emission efficiency in solution, many organic materials are non-luminescent in the solid state, because of the PL quenching caused by intermolecular interaction occurring in the condensed phase. This phenomenon is detrimental especially for red-light emitters, because their molecular structure, usually comprising π-extended polycyclic aromatic hydrocarbons, is particularly susceptible to aggregate by π–π stacking [10–12]. This is the case of perylene diimide (PDI), an important class of pigments widely employed in fibers and automotive industry. Besides their industrial importance as pigments, PDIs also combine a strong absorption in the visible region with almost unity fluorescence quantum yields (QY) in diluted solution and high photochemical stability. They are typically characterized by strong π–π interactions, depending on the chemical structure, which consistently decrease both their solubility and their solid state PL efficiency [13]. While the tendency of PDI for crystallinity or close packing is widely exploited as *n*-channel materials for organic field effect transistors [14,15], in order to extend the use of PDIs in other optoelectronic applications such as organic photovoltaics [16], LCD color filters [17], fluorescent sensors [18] and solar concentrators [19], researchers have explored different procedures for limiting or preventing PDI aggregation. These include dispersion in a transparent matrix [20], functionalization with bulky substituents

* Corresponding author.
E-mail address: f.galeotti@ismac.cnr.it (F. Galeotti).

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[21–24], "grafting-to" immobilization [25] and copolymerization [26].

We have recently reported on the copolymerization of an oligofluorene-based dye with styrene through a nitroxide-mediated radical polymerization (NMRP) approach, leading to a fine tuning of the photophysical behavior and suitable processability for realizing an efficient OLED [27,28]. Here, we report on the synthesis by NMRP of a copolymer comprising a polystyrene (PS) backbone and randomly distributed PDI pendants. Then, we show the successful application of the resulting material as red emitter in a white hybrid organic–inorganic LED (WHLED), taking advantage from the highly enhanced solubility and solid state PL efficiency of the copolymer with respect to the pure dye. As a blue light source we employ a GaN commercial LED (450 nm centered emission); as a green emitter we use a fluorene-thieno-pyrrolo-dione (*TPD-FLU*) alternated copolymer which absorption/emission features fit very well with our purpose. This hybrid system generates stable white light with CIE chromaticity coordinates (0.31, 0.34) and efficiency of 28 lm/W.

2. Experimental

2.1. Materials and instruments

10-Nonadecanone was purchased from TCI Europe, 4-aminostyrene from Alpha Aesar. Perylene-3,4,9,10-tetracarboxylic dianhydride, styrene, quinoline, $Zn(OAc)_2$ and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy (TEMPO) were purchased from Aldrich and used as received without further purification. Solvents were dried and/or distilled by the usual methods and typically used under an inert gas atmosphere. N-(10-nonadecyl)-3,4,9,10-tetracarboxylic acid dianhydride (**1**) was obtained according to the literature procedure [29].

The blue LED (Osram, LE RTDUW S2W) was purchased from RS Components.

^{1}H NMR spectra were recorded on a 400 MHz Bruker spectrometer operating at 11.7 T.

FTIR spectra were recorded by a Bruker TENSOR27 spectrophotometer.

The molecular weight distribution was obtained by means of a size exclusion chromatography (SEC) multi-detector system from Waters, in THF solutions using a calibration curve of polystyrene standards.

AFM investigations were performed using an NT-MDT NTEGRA apparatus in tapping mode under ambient conditions.

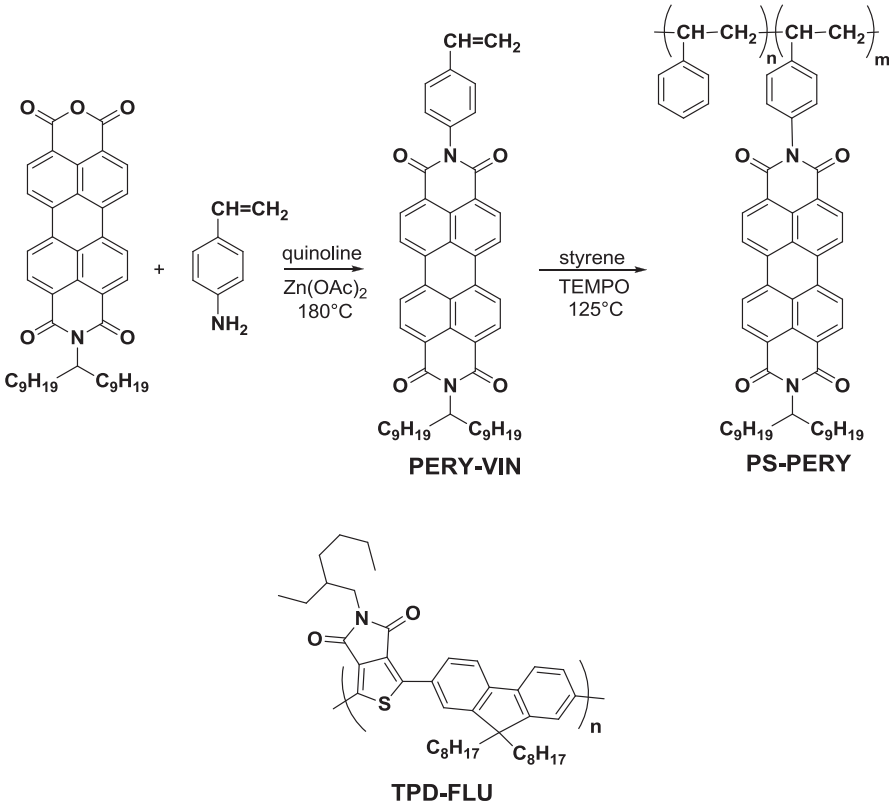
PL and EL spectra were recorded with Spex 270M monochromator in conjunction with liquid nitrogen cooled CCD. The light source for PL was monochromated xenon lamp. Absorption spectra were measured with Perkin Elmer UV/VIS/NIR Lambda 900 spectrometer. QYs were obtained using an integrating sphere. Electrical characterization of the device was performed with a Keithley 2602 source-meter combined with calibrated photodiode with Lambert source assumption.

2.2. Synthesis

Scheme 1 outlines the synthesis of the polystyrene–perylene diimide polymers.

2.2.1. N-Vinyl-N′-(10-nonadecyl)-perylene-3,4,9,10-tetracarboxylic diimide (PERY-VIN)

The condensation reaction of N-(10-nonadecyl)-3,4,9,10-tetracarboxylic acid dianhydride (500 mg, 0.76 mmol) and 4-aminostyrene (108.5 mg, 0.912 mmol) was accomplished by conducting the imidization reaction in the presence of zinc acetate (214 mg, 1.16 mmol) in quinoline (5 mL) at 160 °C for 4 h under nitrogen atmosphere. The resulting N-Vinyl-N′-(10-nonadecyl)-



Scheme 1. Synthetic route for the preparation of perylene diimide labeled polystyrene (PS-PERY, up) and structure of TPD-FLU (down).