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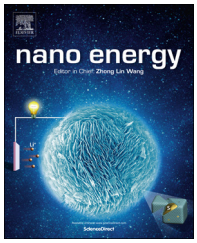

RAPID COMMUNICATION

New bioinspired hole injection/transport materials for highly efficient solution-processed phosphorescent organic light-emitting diodes

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Abstract
A new concept to supramolecular assembly of existed functional polymers, capable of forming network-like organizational clusters through multiple hydrogen-bonding interactions has been exploited. In this paper, a new adenine-based poly(triphenylamine-carbazole) (PTC-A) has been prepared which exhibits a high self-complementary ability in solution and solid states owing to the formation of adenine–adenine (A–A) pairs by induced *hierarchical self-assembly*. Comparing with uracil-substituted PTC sample (PTC-U), PTC-A presents a much higher thermal stability,

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Supramolecular assembly

electrochemical stability and solvent-resistance ability due to the formation of the more stable physically cross-linking structure. When the PTC-A is utilized as a hole injection/transport layer in a trilayer OLED device, a remarkable improvement in performance relative to the control PTC and PTC-U under similar experimental conditions has been achieved. Further comparison with a control device using a conventional PEDOT:PSS, the efficiency of the solution-processed phosphorescent PLED device with PTC-A is significantly higher than those of PTC-U and PEDOT:PSS-based devices. Thus, PTC-A represents the next-generation hole injection/transport material for high efficiency LED device and low-cost fabrication process.

Introduction

Organic and polymer light-emitting diodes (LEDs) have drawn considerable attention from industrial and scientific communities because of their high resolution, low power consumption and fast response times [1,2]. More recently, researchers have witnessed significant progress regarding to brightness, multi- or full-color emission, and durability and thermal stability of LEDs [3,4]. Indeed, the balance of charge injection and transport from each electrode is an important factor with regard to improve the efficiency of LEDs. Studies on organic materials possessing high hole-injection and conductivity were mainly focused on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) because of its planar structure which leads to high electron delocalization along the chain, and its relatively high conductivity (10^{-3}–10^{-5} S/cm) and good transparency affecting carrier injection and device performance directly [5–7]. However, PEDOT:PSS is fabricated from water dispersion and water is relatively more destructive than oxygen for organic and polymer LEDs [8]. Therefore, PEDOT:PSS is not very stable in the LEDs architecture [9]. Efforts to develop novel hole injection materials (HTMs) containing neither ion nor hydrophilic functionality and possessing properties similar or superior to PEDOT:PSS have been actively pursued. Therefore, covalently cross-linked HTMs leading to the formation of solvent-resistant hole-injection layers have been employed in order to replace PEDOT:PSS, including thermally [10–13], photochemically [14–17] and electrochemically [18–21] cross-linked materials. However, additional processes are required for creating the crosslinked structures. Highly complementary noncovalent bonds (e.g., hydrogen bonds, electrostatic interactions or chain entanglements) leading to physically cross-linked structure may act as well as the covalently cross-linked materials without additional processes. Our previous studies reported that the hydrogen bonding interactions of nucleobase-functionalized polymers resulted in highly cross-linked structures through biocomplementary hydrogen bonding with substantially increased glass transition temperature [22–25]. We speculated that introducing nucleobase units into the side-chain HTMs may induce their physically crosslinked behavior considerably. The charge transfer through supramolecular interactions is also expected to be improved through the donor-acceptor conjugate from the complex of supramolecular architectures [26,27].

Recently, we have confirmed that DNA-mimetic π-conjugated polymer PTC-U has high thermal stability, non-corrosion, excellent hole injection/transport abilities in solid state owing to the uracil induced physically cross-linking [28]. However, the association constant of PTC-U is not strong enough to achieve a sufficient crosslink density to exhibit a high electrochemical stability. In this study, a new DNA-mimetic π-conjugated polymer containing pendant adenine group has been successfully synthesized. The DNA base adenine molecules are known to assemble spontaneously through the hydrogen-bondings, and form the characteristic two-dimensional ordering structure [29–31]. Thus, adenines can rearrange themselves to form a more stable complex in multiple directions as compare to uracil [29a], indicating that a more stable physically cross-linking structure can be formed by PTC-A (Fig. 1a). In comparison with PTC-U, the morphology of the adenine-conjugating polymer assembly significantly improves its cross-link density and electrochemical properties. This PTC-A possesses excellent hole injection/transport and electron-blocking properties which shows satisfactory solubility only in polar solvents and thus makes it a promising candidate for hole injection /transport layer (HITL) in the fabrication of high-efficiency organic or multilayer polymer light-emitting devices. In addition to the observed extraordinarily high hole-injection/transporting capacity, other characteristics and performances are extremely rare in previous studies. We achieved a luminous efficiency of 8.0 cd/A and a maximum brightness of 47,226 cd/m^2 from the Alq3-based trilayer device using PTC-A as HITL. Most importantly, solution-processed OLED device using iridium-based triplet emitting layers and physically cross-linked PTC-A films as a HITL achieved a maximum brightness levels as high as 36,066 cd/m^2, external quantum efficiency and luminance efficiency of 9.46% and 35.6 cd/A, respectively, which is much higher than those of PTC-U and PEDOT:PSS-based devices. We believe that the PCT-A will open up many exciting opportunities in the fields of OLED and PLED owing to its ability to manipulate the hole injection/transport, charge balance, and high-efficiency performance.

Material and methods

PTC-A and PTC-U were prepared by “cross-coupling polymerization” of nucleobase-functionalized monomer in the presence of $Pd(PPh_3)_4$ as catalyst system. The general materials and instrumentation used in this work are described in more detail in Supplementary information.

Results and discussion

Nucleobase-functionalized polymers used in this study are based on noncrystalline and π-conjugation PTCs functionalized