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Upconversion injection in rubrene/perylene-diimide-heterostructure electroluminescent diodes

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The authors implement and demonstrate in this letter a scheme that permits to drive electroluminescence with an extremely low turn-on voltage. The device behaves like compound semiconductors, in which the electroluminescence turn-on voltage is about the same as the open circuit voltage for the photovoltaic effect. However, the electroluminescence turn-on voltage is about half of the band gap of the emitting material that cannot be explained using current models of charge injection in organic semiconductors. The authors hereby propose explanation through an Auger-type two-step injection mechanism. © 2007 American Institute of Physics.

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Apart from their ease of fabrication and suitability to large area applications, there are many unexplored fields related to the peculiar physics of conjugated materials. Of particular interest in that context is the recent discovery of the exceptionally low-threshold injection characteristics of rubrene crystals. We implement here a resonant scheme that permits to drive electroluminescence (EL) with an extremely low turn-on voltage. The heterostructure device behaves like compound semiconductors, in which the EL turn-on voltage is about the same as the open circuit voltage for the photovoltaic effect. Surprisingly, however, this places the EL turn-on voltage at about half of the rubrene band gap (2.2 eV). The physical interpretation can be found into the so-called Auger mechanism that we could implement in our molecular heterojunction diode.

5,6,11,12-tetraphenylnaphtacene, commonly known as rubrene [Aldrich, sublimed grade, see inset of Fig. 1(a)], was used as a hole-transporting material, while N,N’-ditricetylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI) (Aldrich, purum grade) was used as an electron transporting material. Both rubrene and PTCDI are widely studied semiconductors with among the highest field-effect mobility for holes and electrons, respectively. Moreover, rubrene is also currently used as a yellow dopant for achieving efficient light emitting diodes and efficient photovoltaic (PV) cells. We have made heterojunction devices with 60 nm thick rubrene and 20 nm thick PTCDI layers sandwiched between transparent indium tin oxide (ITO) (15 Ω/□, Merck) and 50 nm thick aluminum electrodes. A 40 nm thick poly (3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) at the ITO/rubrene interface and an 8 nm thick bathocuprine (BCP) at the PTCDI/metal interface were used as injection layers. For reference, rubrene-only devices were also made with 20 nm Ca/40 nm Ag metal cathodes. For comparison of the EL characteristics also, PTCDI could be replaced by fullerene C₆₀ or C₇₀. All PEDOT coated substrates were transferred inside an argon evaporation plant with <0.1 ppm oxygen and moisture levels. All organic materials were grown at a constant deposition rate of 0.05 nm/s. All depositions were performed under a base pressure lower than 10⁻⁷ mbar. Device current-luminance-voltage (J-L-V) and current density–voltage (J-V) characteristics of the devices were recorded both in the dark.

FIG. 1. (a) Current (J)-luminance (L)-voltage (V) characteristics of ITO/PEDOT/rubrene/BCP/Ca devices with EL turn-on at 2.2 V. Inset shows the chemical structure of rubrene. (b) Current (J)-voltage (V) characteristics of ITO/PEDOT/rubrene 60 nm/PTCDI 20 nm/BCP 8 nm/Al 50 nm devices with EL turn-on at 0.9 V. Inset shows the same data in semilog scale.

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and under white-light illuminations using a Keithely 236 source measurement unit. Illumination was performed using an AM1.5 solar simulator (Steuerang Solar constant 575). EL measurements were carried in ambient conditions on samples transferred without encapsulation at Thomson Multimedia Research Labs in Rennes. PEDOT:PSS and BCP layers that were used as passive buffer layers for stable and reproducible device structure could be omitted from the device structure without affecting the results presented in the present letter.

Comparative (J-L-V) characteristics of rubrene-only and rubrene/PTCDI heterojunction devices are shown in Fig. 1. Rubrene-only devices have an EL threshold at 2.2 eV [Fig. 1(a)]. They deliver a luminance of \( \sim 180 \text{ cd/m}^2 \) at 2.4 V with \((x=0.55, y=0.44)\) CIE color coordinates. Interestingly, rubrene/PTCDI heterojunction devices deliver visible yellow light at a driving voltage as low as 0.9 V. They emit with the same luminance and similar CIE coordinates at 1.4 V, which is \( \sim 1 \text{ V} \) below the single layer diode. The EL turn-on voltage of rubrene/PTCDI devices corresponds to half of the 2.2 eV rubrene band gap. Forward current enters the milliampere regime at drive voltages as low as 1 V \( \text{b} \approx 1 \text{ eV} \) thermal emission from the PTCDI-LUMO to the rubrene-LUMO energy barrier for thermal emission from PTCDI-LUMO to rubrene-LUMO can be ruled out from the following equivalent arguments. First, it should take place more efficiently from the Ca electrode in contact with the single rubrene layer device in Fig. 1(b), photoinduced charge transfer takes place under illumination from the rubrene electron donor to the PTCDI electron acceptor. We get an open circuit voltage \( V_{OC} = 0.9 \text{ V} \), which is approximately the rubrene/PTCDI HOMO-LUMO offset in the flatband regime. In consequence, disorder at the heterojunction cannot be called to interpret the low EL-threshold voltage \( V_{th} \) \( V_{th} \approx V_{OC} \). Thermal emission over the electron barrier from PTCDI-LUMO to rubrene-LUMO can be ruled out from the following equivalent arguments. First, it should take place more efficiently from the Ca electrode in contact with the single rubrene layer device in Fig. 3(b) than from the Al electrode in contact with PTCDI in Fig. 3(a), which is not the case as Fig. 1 shows. Second, the energy barrier for thermal emission from PTCDI-LUMO to rubrene-LUMO is \( F_t \approx 1 \text{ eV} \) and the thermal emission current density can be estimated from the Richardson-Dushman equation, \( J_{th} \approx AT^2 \exp(-F_t/kT) \), where the theoretical value of \( A \) is 123 A cm\(^{-2}\) K\(^{-2}\). One obtains \( J_{th} \approx 50 \text{ pA/cm}^2 \), very far from the \( J \approx 1 \text{ mA/cm}^2 \) measured at \( V=1 \text{ V} \) [Fig. 1(b)]. EL at a relatively lower voltage than the semiconductor band gap has been reported in distributed heterojunction polymer light emitting diodes. It was identified as exciplex formation at the polymer-polymer interface, an energetically favor-
able situation for charge recombination without crossing the junction to the opposite polymer. As shown in Fig. 2(a), identical EL-spectral features for both single and bilayer devices rule out this possibility. In consequence, the half-gap voltage EL threshold observed in Fig. 1(b) bears all the features of an energy upconversion process.

Energy upconversion from charge injection requires the capture of energy by an electron located on an occupied level. A large energy can be produced by recombination of an electronhole pair, a process commonly referred as Auger recombination. In semiconductor heterostructures and quantum dots, Auger recombination is the transfer of energy and momentum released by the recombination of an electron-hole pair to a third particle, i.e., an electron (or hole), giving rise to an energetic electron (or hole).³ Auger recombination in inorganic semiconductors is obtained under the high carrier concentration regime provided by high doping or by high current density injection.¹⁵ Traditionally, conjugated organic materials are low carrier concentration semiconductors and the occurrence of Auger recombination is less likely to occur in organics than in inorganic semiconductors. However, with the particular energy level conjunction that we get at the rubrene/PTCDI interface, where the PCTDI-LUMO is exactly midway between the rubrene HOMO and LUMO levels, a two-step excitation can take place, with the PTCDI-conduction band acting as a stepping stone.

Schematically, we propose the following mechanism. The rather large mobilities of the compounds and large energy barrier at the heterojunction permit accumulation of charges of both signs at the interface under 1 V bias, which energy barrier at the heterojunction permit accumulation of charges of both signs at the interface under 1 V bias, which...