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Virtually pure near-infrared electroluminescence from exciplexes at polyfluorene/hexaazatrinaphthylene interfaces

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Electronic processes at the heterojunction between chemically different organic semiconductors are of special significance for devices such as light-emitting diodes (LEDs) and photovoltaic diodes. Here, we report the formation of an exciplex state at the heterojunction of an electron-transporting material, a functionalized hexaazatrinaphthylene, and a hole-transporting material, poly(9,9-dioctylfluorene-*alt*-N-(4-butylphenyl)diphenylamine) (TFB). The energetics of the exciplex state leads to a spectral shift of ~ 1 eV between the exciton and the exciplex peak energies (at 2.58 eV and 1.58 eV, respectively). LEDs incorporating such bulk heterojunctions display complete quenching of the exciton luminescence, and a nearly pure near-infrared electroluminescence arising from the exciplex (at ~ 1.52 eV) with $>98\%$ of the emission at wavelengths above 700 nm at any operational voltage. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.

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The electronic processes at organic semiconductor heterojunctions exploited in organic light-emitting diodes (LEDs) and photovoltaic cells are of crucial importance for the operation of such devices, and have therefore been widely discussed in the literature.^{1–3} In particular, excited states with charge-transfer character localized at the heterojunction, traditionally termed exciplexes, have been exploited in white LEDs,⁴ and exciplex/charge-transfer excitons energetics has been correlated specifically with the open-circuit-voltage in bulk heterojunction (BHJ) photovoltaic cells,⁵ and more generally with the device performance.⁶ The nature of the exciplex state has also been extensively investigated for type-II heterojunctions incorporating a variety of polyfluorenes, and the tendency to form such exciplexes proposed as a general property of these systems.^{7,8} Another conjugated semiconductor system that has been shown to support exciplexes⁹ is the combination of 5,6,11,12,17,18-hexaazatrinaphthylene (HATNA) with poly(9,9'-dioctylfluorene-*alt*-N-(4-butylphenyl)-diphenylamine) (TFB). HATNA derivatives are promising electron-transport materials that have shown mobilities of up to $0.9 \text{ cm}^2/\text{V s}$ depending on substituents.¹⁰ Recently, some of us have reported a successful strategy to twist the otherwise planar structure of HATNA by introducing bulky silyl groups in confronting positions and to influence their properties by means of such distortions.¹¹ Distorted polycyclic aromatic hydrocarbons^{12–17} have emerged as promising materials for OLED

applications^{18–22} since the twisted conformation substantially reduces intermolecular π - π interactions, leading to enhanced solubility and to a reduction of aggregation-induced quenching in the solid state.

Here, we focus our attention on one of such twisted derivatives of HATNA, that carries six (triisopropylsilyl)-acetylenyl substituents (HATNA*, Fig. 1(a)).¹¹ The presence of rigid acetylenes with such large triisopropylsilyl (TIPS) groups in confronting positions forces the aromatic core to deviate from planarity and to adopt a symmetrical propeller-like structure.

Interestingly, we find that HATNA* forms an exciplex at the interface with TFB (see Fig. 1(b) for the energy levels), which emits with a broad unstructured spectrum peaking at 1.58 eV, i.e., with a spectral red-shift of about 1 eV with respect to the exciton emission energy. In view of the burgeoning interest in near-infrared (NIR) materials and devices^{23–29} along with the interesting optoelectronic properties of HATNA*, we tested the HATNA*-TFB system in LEDs and found a nearly pure NIR electroluminescence (EL) arising from the exciplex with $>98\%$ of the emission at wavelengths above 700 nm.

We looked at both blends and pure materials, starting our investigations with preparation of thin films (~ 90 nm thick) of HATNA* by spin-coating (at 1.8 krpm for 120 s) a 2.5 wt. % toluene solution on a spectro-sil substrate and, following the same procedure, of a thin film of TFB (American Dye Source) from a 2 wt. % *p*-xylene solution. To investigate the photophysics of the HATNA*-TFB heterojunction, we also prepared blends (1:1 weight ratio in toluene) thin films

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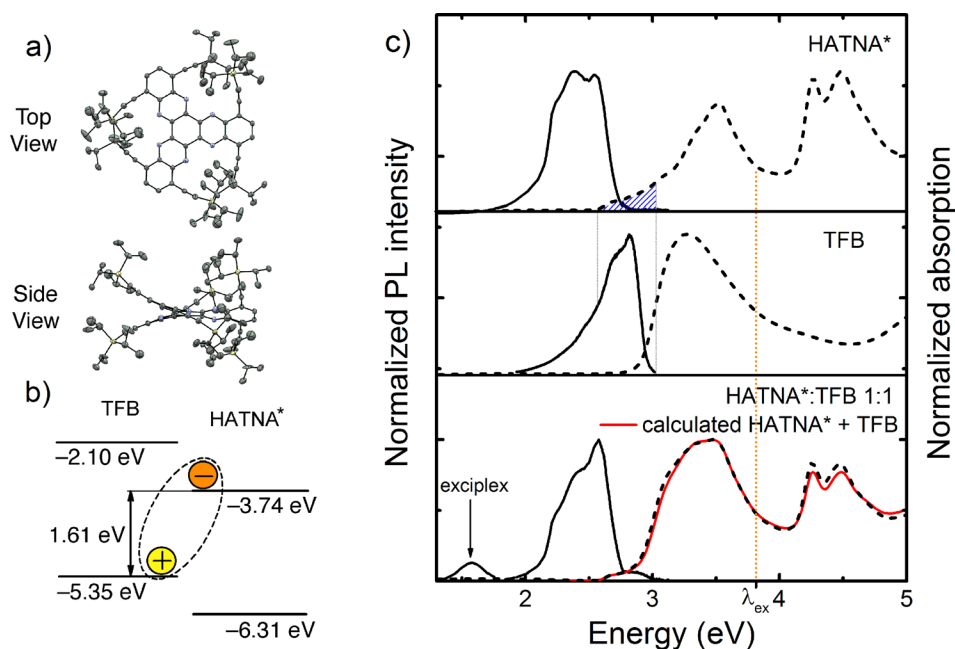


FIG. 1. (a) Top and side views of the crystal structure of HATNA*. (b) Energy levels of the HATNA* (HOMO = -6.31 ± 0.10 eV, LUMO = -3.74 ± 0.10 eV) and TFB (HOMO = -5.35 ± 0.11 eV, LUMO = -2.11 ± 0.20 eV) estimated by cyclic voltammetry and optical absorption. The exciplex formation and binding energy is also schematically shown. (c) Absorption (dashed line) and emission (solid lines) spectra of thin films of TFB, HATNA*, and HATNA*:TFB 1:1 weight ratio normalized to the maximum value. The linear combination of the TFB and the HATNA* spectra (red solid line) is superimposed to the blend absorption spectrum. The PL is excited with a 3.8 eV (325 nm) He-Cd laser. The spectral overlap between the TFB emission and the HATNA* absorption is highlighted in blue.

with the same solution concentrations and spin-speed (HATNA*:TFB). The steady-state photoluminescence (PL) spectra were recorded after exciting at 325 nm with a continuous wave (CW) He-Cd laser by means of an ANDOR-Shamrock spectrograph coupled with an ANDOR-Newton charge-coupled device (CCD) unit. Time-resolved PL measurements were carried out with a time-correlated single photon counting (TCSPC) spectrometer previously reported.³⁰ The LEDs were fabricated by spin-coating (4 krpm for 60 s and 5 krpm for 10 s) a 2.8 wt. % of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)³¹ (PEDOT:PSS, Sigma Aldrich) water dispersion to a thickness of ~ 80 nm over an ITO-coated glass pre-treated with oxygen plasma.^{32,33} The substrates were then baked at 150 °C for 10 min in a nitrogen atmosphere to remove residual water. The active layer, HATNA*:TFB 1:1, was deposited by spin-coating (1.8 krpm for 120 s) a 2.5 wt. % toluene solution so as to obtain a thickness of ~ 90 nm. Ca/Al electrodes (30 nm/150 nm, respectively) were thermally evaporated under vacuum ($\sim 10^{-6}$ mbars) on top of the active layer. The LUMO level for HATNA* was estimated by electrochemical measurements carried out on a Princeton Applied Research Parstat 2273 in a 3-electrode single compartment cell with Pt disc working electrode ($\varnothing = 0.5$ mm), a platinum wire counter electrode ($\varnothing = 0.5$ mm), and a silver wire pseudoreference electrode in a 0.1M $n\text{Bu}_4\text{PF}_6/\text{CH}_2\text{Cl}_2$ solution at room temperature. The LUMO levels were estimated from the E_{ONSET} of the first reduction wave according to $E_{\text{LUMO}} = -4.8 - e (E_{\text{ONSET}} - E_{1/2}^{\text{Fc}})$, where $E_{1/2}^{\text{Fc}}$ was measured *in situ* (eV) by adding ferrocene (Fc) to the cell as internal reference after the measurements.³⁴ The optical gap for HATNA* was estimated from the onset wavelength (λ_{ONSET}) of the absorption spectra carried out on a Perkin-Elmer Lambda 950 spectrometer in solution. The current-voltage-luminance characteristics were measured with a Keithley 2004 source-meter and a calibrated Si photodiode coupled to a Keithley 2000 multimeter. EL spectra were taken with the same ANDOR spectrometer described above.

We report the absorption and emission spectra of HATNA*, TFB, and of the blend in Fig. 1(c). We find that the absorption of the blend can essentially be reproduced by the superposition of the absorption spectra of the single components with little or no evidence of additional bands due to ground-state interactions between HATNA* and TFB.

The PL from HATNA* neat films (top panel of Fig. 1(c)) is clearly structured with vibronic peaks at 2.58, 2.38, and 2.18 eV ($\Delta E = 0.20$ eV), and, interestingly, a 0–1 transition slightly more intense than the 0–0 one ($\text{PL}_{0-0}/\text{PL}_{0-1} \approx 0.99$). The latter suggests emission from weakly bound excimers or aggregates³⁵ whose presence is also corroborated by the TCSPC data discussed below. Emission from TFB, which we report in the middle panel of Fig. 1(c), is consistent with previous literature, confirms the slightly higher value of the energy gap of TFB compared to HATNA* (emission peak at 2.82 eV), and do not show any sign of aggregation in the form of a weaker 0–1 transition compared to the 0–0 one. Finally, we report the PL spectrum of the 1:1 blend in the bottom panel of the same figure (Fig. 1(c)). Remarkably, this displays a featureless emission band centred at 1.58 eV ($\lambda_{\text{max}} = 785$ nm) in addition to the emission of pure HATNA* (2.0–2.8 eV) and a vestigial TFB emission. We note that the HATNA* emission in the blend is characterized by a much stronger 0–0 transition ($\text{PL}_{0-0}/\text{PL}_{0-1} \approx 1.06$) than in the pure HATNA* thin film, consistently with the expected suppression of aggregation as a result of embedding HATNA* in TFB.^{36,37} Emission from TFB is nearly completely suppressed, as expected, as a result of efficient energy transfer from TFB to HATNA* (note that although HATNA*'s absorption spectrum is not very strong at low energies, this does extend so as to provide a significant overlap with emission from TFB, see Fig. 1(c)).

We assign the emission at 1.58 eV to an exciplex state formed between the HATNA* and TFB and confirm via TCSPC (Fig. 2) that luminescence from such a state is indeed much longer-lived (~ 15 ns) than from the pure compounds (3 ns or less though non mono-exponential). More

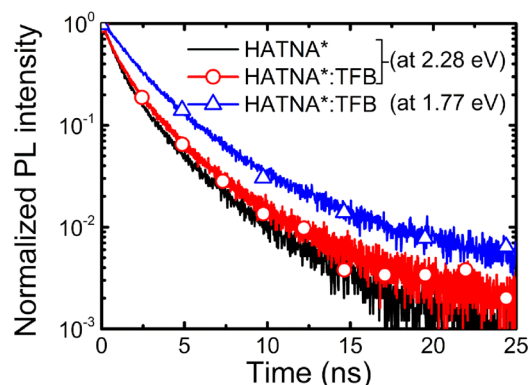


FIG. 2. Photoluminescence temporal decays of thin films of HATNA* (black curve) and HATNA*:TFB blend (red curve with empty circles) taken at 2.28 eV (545 nm) and HATNA*:TFB blend (blue curve with empty triangles) taken at 1.77 eV (700 nm).

precisely, we report in Table I the results obtained when fitting the characteristics of Fig. 2 with a bi-exponential function (for the emission in the 2.0–2.8 eV region) and three-exponential function (for the emission at 1.58 eV). For HATNA* pure films we find time constants of 0.9 and 3.0 ns, respectively, and we assign them to an exciton³⁸ and an excimer/aggregate^{39,40} state, respectively. The relative weight of the excimer/aggregate lifetime decreases in favour of the exciton when HATNA* is blended with TFB, consistently with the observation and interpretation of the higher PL_{0-0}/PL_{0-1} ratio found in the spectra (Fig. 1(c)). The blend shows an additional long-lived component in the fluorescence decay taken at 1.77 eV, with a lifetime of 14.7 ns that we attribute to the exciplex state at the HATNA*:TFB interface.

Remarkably, we observe a significant spectral shift between the 0–0 transition of the exciton (E_{0-0})⁴¹ and the exciplex emissions (E_x), of approximately 1 eV. Note that this value significantly exceeds those reported previously for a slightly different variant of HATNA-TFB (~ 0.45 eV)⁹ and for polyfluorenes heterojunctions (~ 0.15 – 0.35 eV).⁴²

Such a spectral shift (E_{0-0} – E_x) may be due to a substantial difference in either (i) the relative positions of the frontier levels of the materials in agreement with our estimations (Fig. 1(b)), but note the large uncertainties on the energy levels or (ii) the stabilization energy (B) of the exciplex arising from the Coulombic attraction energy at the equilibrium distance and the ground-state repulsion energy,⁴³ as well as from structural relaxation effects. In regard of (i), we note that the TFB levels as measured in our laboratory are slightly different from those reported by Clark and collaborators,⁹

TABLE I. PL lifetimes for TFB, HATNA*, and HATNA*:TFB for the emissions in the visible and near-infrared regions. Relative weight for the lifetimes is also reported.

	λ_{em}		τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	Relative weight ($\tau_1:\tau_2:\tau_3$)
TFB	2.70 eV	460 nm	0.3	1.2		50:50:0
HATNA*	2.28 eV	545 nm	0.9	3.0		47:53:0
HATNA*:TFB	2.28 eV	545 nm	0.9	2.9		54:46:0
HATNA*:TFB	1.77 eV	700 nm	1.6	3.7	14.7	43:45:11

possibly due to differences in suppliers, molecular weights, and other experimental details. Similarly, we expect even more significant differences between the energy levels of HATNA* and HATNA,⁹ owing to functionalization with TIPS-acetylenyl instead of dodecylthioethers. The extended conjugation with six acetylenes and their moderate electron withdrawing nature (in comparison to the electron donating nature of thioethers) raises the absolute value of the HOMO/LUMO levels of HATNA* with respect to the vacuum level (albeit the energy gap is similar, ~ 2.6 eV). Indeed, we note that control of chain microstructure is well known to influence the optical properties of conjugated semiconductors.⁴⁴ Given the large uncertainties generally affecting electrochemical measurement of the frontier levels (typically ± 0.1 eV or so), we are not able to quantify with great accuracy of the relative contribution of such effects to the shift,⁴⁵ but we note that both are of the same sign. This is because a downward shift of the levels reduces E_{0-0} and because the twisted conformation should increase the configurational relaxation energy. We can nevertheless speculate that the coulombic contribution should be similar for HATNA and HATNA*, as both materials are remarkably similar in their chemical make-up (no metallic or heavy atoms), and therefore dielectric properties and “charge-screening” should be similar. A strong correlation between geometry and electronic structure of conjugated polymers is both notorious and well-illustrated by a number of cases, such as in the case of substituted poly(p-phenylene vinylene), PPV, derivatives carrying substitutions in the 2–3 positions.^{46–48}

The EL spectrum of the LEDs incorporating the blend as emissive layer and the device structure are reported Fig. 3(a) and the current and radiance versus voltage characteristics of a similar device are shown in Fig. 3(b). Interestingly, the EL spectrum displays an emission at 1.52 eV ($\lambda_{max} = 816$ nm, EL in the NIR > 98%) arising *uniquely* from the exciplex state, whereas the emissions from the HATNA* and TFB excitons are completely suppressed *at any operational voltages*. This is in line with expectations, owing to the energy-selective nature of the charge transport processes in OS, and the very nature of the exciplex/CT state that in EL has to form from combination of electrons travelling (preferentially) in the HATNA* phase and holes in the TFB phase. Purity of the NIR EL emission provides good evidence of both the existence of percolating phases of either components and of the preferential transport of oppositely signed charge carriers in each of them. Importantly, it also provides excellent confirmation of the good stability of the exciplex at the interface, quantifiable in at least a few “kTs.”

The LEDs show a relatively low turn-on voltage of 2.0 ± 0.3 V (defined as the intercept of the I-V curve with the x-axis in the semi-log plot in the 0–3.5 V range) and a radiance of 0.041 ± 0.003 mW/cm² (measured at 100 mA/cm²). The external quantum efficiency (EQE) for the device is $0.035\% \pm 0.005\%$. Although this might seem low compared to state-of-the-art visible LEDs, it is in fact within expectations, owing to the general increase of the non-radiative rate for decreasing energy gaps (the “energy-gap law”).⁴⁹ EQEs of 0.02%–0.05% have in fact been reported for polymer-based LEDs with emission at 1.48 eV (850 nm) and lower energies.^{50,51} Note that additional reduction of the

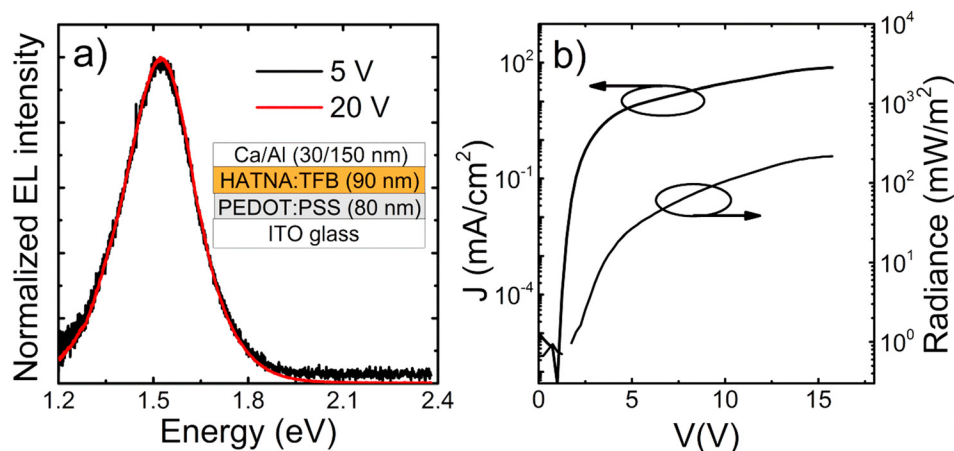


FIG. 3. Electroluminescence spectrum of HATNA*:TFB 1:1 LED taken at 5 V (black curve) and 20 V (red curve) (a) and the current-voltage-luminance characteristics of HATNA*:TFB 1:1 LEDs (b). The LED structure is reported.

efficiency are expected for devices exploiting exciplex emission, owing to the effects of different hyperfine interactions on either side of the heterojunction for the electron and hole participating in the CT state.³

In conclusion, we have demonstrated the formation of an exciplex state at the HATNA*/TFB heterojunction that emits at 1.58 eV with a lifetime of 14 ns. NIR emission is achieved thanks to a large spectral shift of ~ 1 eV between the exciplex and the exciton emissions. We achieved NIR-pure and voltage-independent exciplex EL with $>98\%$ of the emission in the NIR with a EQE of 0.035% in line with best performing polymer-based LEDs with exciton emission in a similar wavelength range.

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