

Emission Color Trajectory and White Electroluminescence Through Supramolecular Control of Energy Transfer and Exciplex Formation in Binary Blends of Conjugated Polyrotaxanes

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This article is dedicated to the memory of Gianluca Latini, colleague and friend

White electroluminescence and fine-tuning of the emission color from binary blends of a blue-emitting polymer and a green/yellow-emitting threaded molecular wire consisting of a conjugated polymer supramolecularly encapsulated by functionalized cyclodextrins are demonstrated. Encapsulation controls the minimum intermolecular distance on the nanoscale, resulting in suppressed energy-transfer between the blend constituents and reduced formation of interchain charge-transfer complexes. The use of a green-emitting polyrotaxane significantly improves the electrical properties with respect to blends of a blue electroluminescent polyrotaxane and leads to a significant reduction in the turn-on voltage required for achieving white electroluminescence ($V_{\rm ON}=3$ V), with only 20% by weight of the encapsulated material.

1. Introduction

Conjugated polymers are attracting considerable attention because of their tunable electrical and optical properties that make them potential active materials for light-emitting diodes (LEDs),^[1] field-effect transistors,^[2] photovoltaic diodes (PVDs)^[3] and all-organic lasers.^[4,5] In the last few years, supramolecular

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encapsulation of conjugated molecules has been demonstrated as a successful strategy to suppress intermolecular interactions resulting in reduced photoluminescence (PL) quenching by aggregates and impurities, as well as controlled energy-transfer (ET) and exciton migration processes.[6-11] Semiconducting supramolecular assemblies have been obtained by threading conjugated moieties into cyclodextrin macrocycles (CDs) and their subsequent polymerization so as to obtain semiconducting polyrotaxanes.[12-15] As a result of the effective encapsulation provided by the CDs, polyrotaxanes have been successfully incorporated into light-emitting diodes,[16–18]

broadband optical amplifiers,^[19] and all-organic lasers,^[20] and have been shown to be a remarkable class of model compounds to investigate the influence of intermolecular interactions on the photophysics of conjugated semiconductors.^[21–24] In a recent study, we have demonstrated that blends of a blue-emitting rotaxane and a green-emitting copolymer emit white electroluminescence (EL) as a result of controlled ET between the blend constituents,^[25] similarly to what was observed in non-resonant polymer blends.^[26] The same rotaxinated blends also showed "ultrabroad" optical amplification (>850 meV bandwidth) and two-color amplified spontaneous emission resulting from suppressed interchain polaron formation in the threaded assembly^[27] and hindered ET to the lower energy gap polymer.^[25,28]

The use of an encapsulated blue-emitter is not ideal in such a system, since charge injection into the blue-emitter is generally more difficult than in a green-emitter, and the presence of the cyclodextrins further raises the EL turn-on voltage ($\approx 10~\rm V$). Furthermore, because of preferential charge percolation through the unthreaded, and therefore more conductive polymer, a substantial excess of polyrotaxane (about 80% by weight (bw)) was required to achieve white EL, [25] thus raising the potential cost of such blends. A possible strategy to circumvent these difficulties is the use of a "complementary" rotaxinated blend where the encapsulated compound is a green-emitting polyrotaxane and the blue-emitter is instead a commercial unthreaded polymer.

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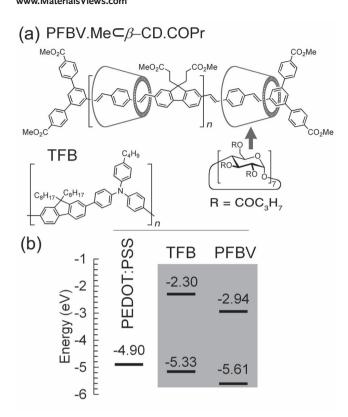


Figure 1. a) Chemical structures of PFBV.Me \subset β -CD.COPr and TFB. The structure of the reference polymer (PFBV) is similar to that reported for the polyrotaxane but without the cyclodextrins (presented here as conical sheaths). PFBV consists of a non-threaded polyfluorene-alt-bivinylphenylene core with octyl chains functionalized fluorene units and terminated by phenyl groups. The chemical structure of PFBV and the energy-minimized molecular structures of PFBV and PFBV.Me \subset β -CD. COPr are reported in Figure S1 (Supporting Information). b) Energy diagram showing the position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels for the isolated materials with no applied field and the work function of PEDOT:PSS.

Here, we report the optical and EL properties of a binary blend of the blue-emitting polyfluorene copolymer, poly(9,9-dioctylfluorene-alt-N-(4-butylphenyl)-diphenylamine) (TFB), and a green-emitting fluorene-divinyl phenylene alternate copolymer encapsulated in functionalized β -cyclodextrins (PFBV.Me $\subset \beta$ -CD.COPr, **Figure 1**), in which most of the 21 hydroxyl groups on each cyclodextrin unit have been converted to butanoate esters to reduce the hydrophilic character of the supramolecular assembly, and thus ensure solubility in organic solvents.

2. Results and Discussion

The synthesis of this new polyrotaxane was achieved using established Suzuki coupling, methylation and acylation methodologies [29,30] and is presented in the Supporting Information, together with the energy minimized structures of PFBV and PFBV.Mec β -CD.COPr, showing that functionalized CDs build

a supramolecular shell around the conjugated core with a diameter of about 2.2 nm. Continuous-wave (cw) and time-resolved PL measurements show an almost complete suppression of ET from TFB to the polyrotaxane, with a 9-fold reduction of ET efficiency, $\eta_{\rm ET}$, with respect to the "unthreaded blend" (from $\eta_{\rm ET}$ = 0.9 to $\eta_{\rm ET}$ = 0.1). As a result of suppressed ET and formation of interchain species in the rotaxinated blend, we obtain a remarkable trajectory of the PL color in the CIE coordinates space, by tuning the relative weight of the blue and green-emitting polymers. In contrast, a drastic switch from blue to green emission is observed upon addition of unthreaded PFBV to TFB, in agreement with several other studies on resonant blends of green and blue-emitting polymers.[31-33] White EL is obtained at a blending ratio of only 20% bw of the rotaxinated material (CIE coordinates for EL, x = 0.26, y = 0.33). The EL turn-on voltage of LEDs incorporating the rotaxinated blend is dramatically reduced with respect to the previously reported, complementary white-emitting rotaxinated blends, namely from V_{ON} = 10 V in that case to $V_{\rm ON}$ = 3.5 V for the blends reported here, [25] thus demonstrating the effectiveness of the applied strategy and boosting the applicative potential of rotaxinated blends for white emission.

2.1. Optical Absorption and Photoluminescence

Before discussing in detail the optical properties of the blended films, we describe the photophysics of the individual blend components, especially the green-emitting PFBV polymer and corresponding polyrotaxane that were synthesized for this study. We start our analysis from the optical absorption and cw PL spectra of dilute xylene solutions (repeat unit concentration = 10^{-5} M) of PFBV and PFBV.Me $\subset \beta$ -CD.COPr (Figure 2a). Both systems show a first absorption band at about 3.2 eV and a structured PL spectrum with peaks at 2.64 eV and 2.46 eV, most likely of vibronic origin. The absorption spectrum of a spin-cast film of PFBV.Me $\subset \beta$ -CD.COPr is narrower than that of PFBV (Figure 2b), suggesting increased conformational order in the "threaded" film, as a result of both higher rigidity of the polyrotaxanes compared to unthreaded PFBV,[29,34] and reduced interactions between the threaded chains.[16,35] Similarly, the PL spectrum of the rotaxane shows the typical shape observed for isolated molecules in solution and lacks the broad featureless component at lower energies ($E \approx 2.12 \text{ eV}$) of PFBV. Such broad low-energy band dominates the PL of the spin-cast film of PFBV, due to increased intermolecular interactions between unthreaded chains in the solid state (Figure 2b).[16,23] We still observe, in the PL spectra of the polyrotaxane films, some of the structure of the diluted solutions, therefore confirming the ability of CDs to reduce interchain interactions also in the solid state. [16,23,35] The optical absorption and PL spectrum of a pure TFB film is shown in Figure 2b.

Looking now at the binary blends of threaded and unthreaded PFBV at increasing TFB fraction (excited at 3.3 eV, at the maximum of absorption of both TFB and PFBV, Figure 2b), we note a significant difference between the emission of the conventional and of the rotaxinated blends. The PL spectra of rotaxinated blends present a distinct spectral component at 2.9 eV, due to the radiative recombination of TFB excitons, whose

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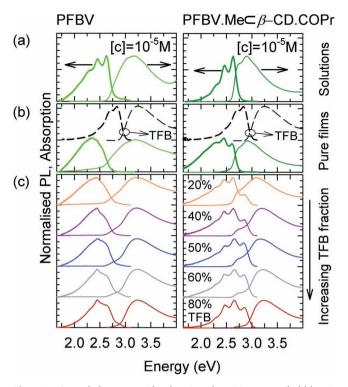


Figure 2. Optical absorption (thin lines) and cw PL spectra (bold lines) of a) diluted xylene solutions (top panel, concentration of the conjugated portion [c] = 10^{-5} M) and of b) pure films of PFBV (left panels) and rotaxinated PFBV.Mec β -CD (right panels) and c) their binary TFB blends at increasing TFB fractions. In (b), the spectra for pure TFB films are reported as dashed lines. All spectra were measured at room temperature and with excitation at 3.3 eV.

relative intensity scales with increasing TFB content. As a result, the emission color can be tuned from the green to the blue, crossing the white region at 20% bw TFB content (CIE coordinates, x = 0.24, y = 0.32). TFB emission is instead completely absent in the PL spectra of unthreaded blends at TFB fractions lower than 60% and becomes only slightly detectable at higher TFB contents. This is because of an efficient ET channel to PFBV that quenches the TFB emission. The presence of residual TFB emission for TFB fractions >60% is consistent with the likely occurrence of partial local demixing between the blend constituents.^[18,36,37] The spectral overlap of the first absorption band of PFBV and PFBV. Me⊂β-CD.COPr with the PL spectrum of TFB (Figure 2b), which is crucial to the efficiency (and rate) of ET (see Equation 1 and 2 in the Supporting Information), is similar for both threaded and unthreaded polymers.

In a recent study, we disentangled the physical mechanism underlying the reduced ET in blends of threaded and unthreaded polymers, also with the assistance of surface

analysis techniques such as confocal AFM, fluorescence lifetime imaging microscopy and μ-Raman scattering.^[25] Possible causes of reduced ET in "threaded blends" are a different nanoscale texture between films of threaded and unthreaded polymers that yields phase-separated domains rich in the polyrotaxane, where exciton migration to the interfaces is hindered by the supramolecular encapsulation, [23,31,38] and, more importantly, the exclusion of a significant volume of space by the CDs from the close proximity to the conjugated core that reduces the transfer rate for either a Förster or Dexter mechanism. For Förster transfer this should have a significant effect even if the cyclodextrin size is smaller than the Förster radius.[39] Similarly, we can attempt a semi-quantitative analysis of the transfer process, while still aware of the limits intrinsic to the Förster model, such as a purely Coulombic interaction between isolated donor-acceptor transition point-dipoles and not 3D distributions of large chromophores.^[10,39] We obtain similar Förster transfer radii of 4.0 nm (PFBV:TFB) and 4.5 nm (PFBV.Me $\subset\beta$ -CD. COPr:TFB) which are both larger than the CDs radius, thus suggesting a scenario similar to the one reported previously (see Supporting Equation 1 and 2 for the complete expression of Förster radius).

2.2. Time-Resolved Photoluminescence

Further insight into the photophysics of these systems is provided by the analysis of the PL temporal decay. **Figure 3**a shows the decay for pure films of both PFBV and PFBV.Me $\subset \beta$ -CD. COPr in the 0–800 ps time domain, with excitation at 3.4 eV and collection at either 2.67 eV (for the rotaxane) or at 2.54 eV (for the unthreaded analogue), i.e., at approximately the respective peaks of emission of intrachain excitons. The decays of

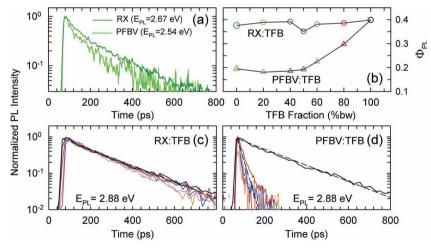


Figure 3. a) Pure films: Time decay of PL intensity for pure films (thickness ≈ 150 nm) of PFBV and PFBV.Me⊂β-CD.COPr (indicated as RX for space reasons) on Spectrosil substrates excited at 3.4 eV at room temperature. b) PL quantum efficiency (Φ_{PL}) of thin films of pure polymer films and binary blends at increasing TFB content (Rx:TFB, circles; PFBV:TFB, triangles). c,d) Blends and pure TFB films: PL decay curve at 2.88 eV for a pure TFB film (solid black line, τ = 200 ± 10 ps) and binary TFB blends with c) PFBV.Me⊂β-CD.COPr (τ = 180 ± 10 ps) and d) PFBV (τ = 20 ± 5 ps). The color scheme is the same as for the corresponding PL quantum efficiency in (b) and PL spectrum in Figure 2. Single-exponential fits of the decay curves are reported as dashed lines.

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PFBV are slightly non-exponential due to structural disorder in

the solid state and exciton migration to interchain and defects

states. $^{[23,35]}$ This effect is present also for the PFBV.Me $\subset \beta$ -CD.

COPr (indicated as RX in legend for space reasons) possibly as

threaded and unthreaded blends. Figure 4a,b show the contour plots of time-resolved PL emission for TFB:PFBV and TFB: PFBV.Me⊂β-CD.COPr blends, respectively. The normalized PL spectra at different delay times (namely, t = 0, 3, 15 ns from the

PL spectra of diluted solutions of the pure polymers for direct comparison of the spectral features. The PL decay curves at

a result of residual intermolecular interactions despite the CD excitation pulse) are shown in Figure 4c,d together with the cw macrocycles,[16,22,29] or of complex energy transfer processes, favored by both closer proximity and/or more significant distortions of the backbones. Such residual interactions appear to be 2.3 eV are reported in Figure 4e. retained more significantly in the solid state for organic-solvent We note a striking difference between the conventional and soluble rotaxanes^[29] compared to water-soluble ones, but we the rotaxinated blends, the latter showing a pronounced blue PL note that even for the latter the presence of significant interaccomponent (≈2.8 eV) at early times due to TFB emission. This tions is demonstrated by the higher PL efficiency of blends with emission is weaker and faster in the PFBV:TFB case, as a result increasing concentrations of poly-ethylene oxide (PEO).[40] As of efficient ET from TFB to PFBV as was discussed above. The expected, the PL kinetics of PFBV is faster than for the polyroeffect is particularly evident in the time-resolved PL spectra in taxane, [23,25] with an effective decay time $\tau_{\rm F} = 63 \pm 5$ ps (defined Figure 4c,d where the TFB contribution to the PL spectrum of as the time at which the PL intensity is reduced by 1/e) with the unthreaded blend is strongly suppressed even at t = 0 ns (solid purple curve in Figure 4c).[43] respect to the threaded system ($\tau_E = 115 \pm 5$ ps), in agreement with the PL quantum efficiencies, $\Phi_{\rm PL}$, which are about 0.38 \pm Most importantly, in both cases, the fast initial PL is fol-0.04 for PFBV.Me $\subset \beta$ -CD.COPr and 0.18 \pm 0.02 for PFBV. The

lowed by a long-lived emission centered at approximately 2.3 eV. This spectral feature can be explained by considering the nature of our blends, especially with regard to the energy offset between the frontier orbitals of the blend components. As shown in Figure 1b, both the LUMO and HOMO levels of PFBV lie at lower energy with respect to TFB, which corresponds to a type II heterojunction.^[3,44] The band-edge offsets are approximately 0.5 eV for the HOMO levels and ≈0.95 eV for the LUMO levels, which are comparable or larger than the typical exciton binding energy of polymer systems (≈0.5 eV).[44] This displacement of the frontier levels has been widely observed to lead to the formation of exciplex states at the polymer interface.[3,44,45] Exciplexes in polymer blends with similar band-edge offset as the systems under study have been investigated thoroughly both experimentally and theoretically. Particularly representative examples are PFB:F8BT (in which PFB stands for poly(9,9'-dioctylfluorene-alt-bis-N, N'-(4-butylphenyl)-bis-N, N'-phenyl-1,4-phenylenediamine), and F8BT stands for poly(9,9-dioctylfluorene-alt-benzothiadiazole)), $^{[2,3,5,38,46-48]}$ TFB:F8BT, $^{[2,3,5,46,47]}$ and F8:PFB (in which F8 stands for poly(di-octylfluorene).[1]

overall Φ_{PL} of pure films and blends, as measured in cw using Interestingly, exciplex emission is observed also for the

rotaxinated blend despite the interchain distance of ≈1.1 nm sterically imposed by CD macrocycles (Supporting Information Figure S1). The observation of residual exciplex emission from the rotaxinated blend is most likely a result of the partial encapsulation of the polymer backbone in PFBV.Me⊂β-CD.COPr, which was 1.3 cyclodextrins per repeating unit (the maximum threading ratio achievable being 2.3). [22] In a semi-quantitative picture, we can estimate the relative weight of the exciplex contribution to the total emission by using the relative intensity at t = 0 ns of the slow portion of the decay traces (Figure 4e). Biexponentials fits of the decay curves of both unthreaded and rotaxinated blends yield a fast component due to intrachain emission and partial interchain aggregation of ≈800 ps, and a slow decay with lifetime of ≈10 ns. As expected, given the partial suppression of π - π interactions in rotaxinated systems, the exciplex contribution is a factor of three lower for the TFB:PFBV.Me⊂β-CD.COPr blend than for the TFB:PFBV system. Such control of exciplex formation in rotaxinated blends provides an additional degree of freedom for tuning the

an integrating sphere, are reported in Figure 3b. Time-resolved measurements also allow us to quantify the energy transfer efficiency upon blending (Figure 3c,d). We find that the PL decays of TFB (energy-donor) in the absence and presence of energy acceptors (Figure 3c,d) follow a singleexponential kinetics with a lifetime for the pure TFB film, τ_D = 200 ± 10 ps (where D denotes the fact that we are monitoring the donor emission). The lifetime of TFB in the rotaxinated blends (Figure 3c) is essentially the same as for the pure TFB, once the relevant uncertainties are taken into account (τ_{DA} = 180 ± 10 ps, where A indicates the presence of the energyacceptor in the blend). In contrast, the reduction is dramatic in the "unthreaded blends", for which the TFB lifetime decreases by a factor of ten ($\tau_{DA} = 20 \pm 5$ ps, Figure 3d). A weak reduction of the PL quenching is observed for the PFBV blends at TFB contents above 60% bw, in agreement with the observation of the TFB emission band in the PL spectra ($\tau_{DA} = 36 \pm 5$ ps, τ_{DA} = 50 ± 5 ps for TFB fraction of 60 and 80% bw respectively). In the simple approximation that blending does not introduce any additional decay pathway other than ET, the ET efficiency, η_{ET} , can be directly measured by comparing the PL lifetime of the energy-donor species (TFB) in the presence (τ_{DA}) and in the absence (τ_D) of energy acceptors according to $\eta_{ET} = 1$ – $\tau_{\rm DA}/\tau_{\rm D}$. [39] We obtain $\eta_{\rm ET}=0.10\pm0.01$ for the PFBV.Me $\subset\beta$ -CD. COPr:TFB blend at any TFB fraction, whereas $\eta_{ET} = 0.90 \pm 0.3$ for the unthreaded blend (in the case of TFB fraction <60% bw, the ET efficiency decreases to $\eta_{\rm ET} = 0.82 \pm 0.15$ and $\eta_{\rm ET} = 0.65 \pm 0.05$ 0.09 for TFB fraction of 60% and 80% bw).

The PL decay of both energy acceptors (PFBV and PFBV. Me \subset β-CD.COPr) is progressively slower at increasing TFB fraction as a result of a matrix effect by TFB that reduces the interactions between the PFBV moieties (see Supporting Information Figure S2a,b). [25,41] Such an effect is stronger for PFBV, due to better miscibility of an unthreaded polymer with TFB with respect to a polyrotaxane^[25] and in agreement with the smaller phase-separation observed in films of the unthreaded blends as shown in Figure 5.[42]

A further interesting aspect of PFBV blends with TFB is the presence of a long-lived PL emission, which is observed for both

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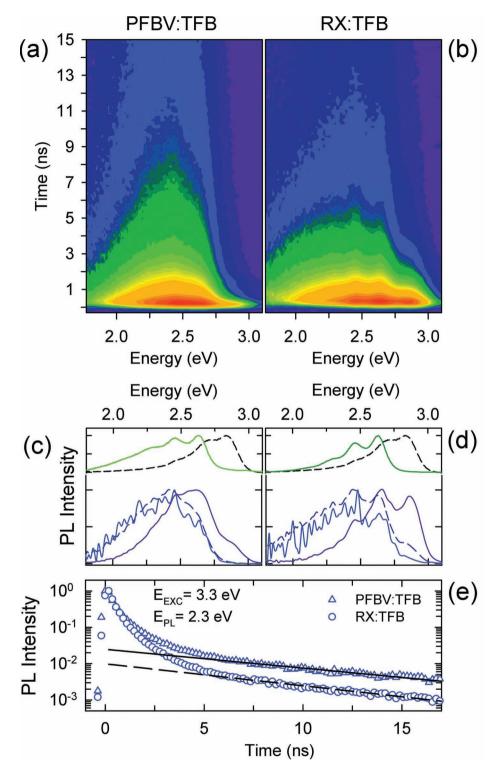


Figure 4. Contour plot of the PL time decay as a function of the emission energy for spin-cast films of a) PFBV:TFB and b) PFBV:Me=χ-CD.COPr:TFB 1:1 blends. c) Top: Steady-state PL spectra of diluted solutions of TFB (dashed black line) and PFBV (solid green line). Bottom: PL spectra at increasing time after excitation (t = 0 ns, purple curve; t = 3 ns, dashed dark blue curve; t = 15 ns, blue curve) for a $\overline{1}.1$ TFB:PFBV blend. d) Top: Steady-state PL spectra of diluted solutions of TFB (dashed black line) and PFBV.Mecβ-CD.COPr (solid dark green line). Bottom: PL spectra at increasing time after excitation (t = 0 ns, purple curve; t = 3 ns, dashed dark blue curve; t = 15 ns, blue curve) for a 1:1 TFB: PFBV.Me $\subset \beta$ -CD.COPr blend. e) PL decay curves at 2.3 eV for a PFBV.Me⊂β-CD.COPr:TFB blend (open circles) and a PFBV:TFB blend (open triangles). The long decay component of the bi-exponential fit to the experimental data is shown as a dashed line for the PFBV:TFB blend and as a solid line for the rotaxinated blend. All measurements were excited at 3.3 eV and performed at room temperature.

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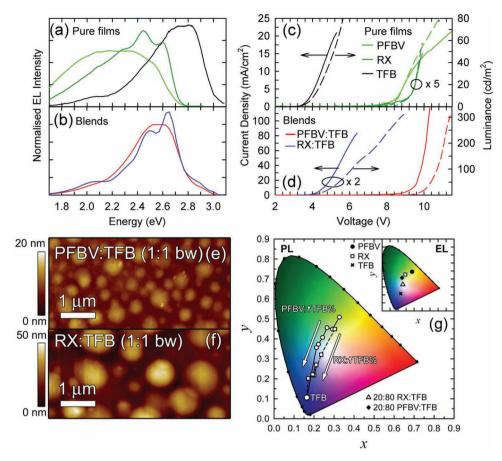


Figure 5. Area-normalized EL spectra of ITO/PEDOT/polymer/Ca/Al devices incorporating active layers of a) pure PFBV, PFBV.Me $\subset \beta$ -CD.COPr and TFB and b) their binary TFB blends (80% bw TFB fraction). c,d) J-V-L of the very same LEDs as in (a,b) (the color code in (a) is the same as in (c) (as for (b,d)). Tapping mode AFM images of as-prepared films of e) 1:1 PFBV:TFB and of f) PFBV:Me $\subset \beta$ -CD.COPr:TFB on glass substrates. g) CIE chromaticity diagram of the PL spectra shown in Figure 1 for pure and blended films (increasing TFB content is indicated by arrows for: 0, 20, 40, 50, 60, 80, 100% TFB fractions). Inset: CIE diagram and color coordinates for the EL spectra of the same devices as in (a,b).

emission color and can be exploited to achieve white luminescence and electroluminescence.

2.3. Electroluminescence

To test this hypothesis, we fabricated and tested LEDs with indium-tin oxide (ITO) anodes[49] coated with poly(ethylene dioxythiophene):poly(styrene sulfonic acid), PEDOT:PSS,[50] and Ca-Al cathodes (ITO/PEDOT:PSS/active layer/Ca/Al), and incorporating active layers of both pure materials and relative blends, for which we report the EL spectra in Figure 5a,b. In contrast to the optically excited luminescence, the EL spectra of both the threaded and the unthreaded blends display strong signs of emission from interchain states, as typically observed for type II polymer heterojunctions. [44,46] The fact that EL and PL spectra are different in both single materials and in blends reflects the energy selective nature of the charge transport process. In EL, the electronic levels of electroluminescent molecules play the dominant role, controlling the formation and recombination of excitons, so that the contribution of the blend components to the EL spectrum is different compared to what observed upon photo-excitation. Furthermore, in type II systems, holes (electrons) are transported preferentially in the component with the highest (lowest) HOMO (LUMO) level. As a result, excitons are formed primarily at the polymer/polymer interface where the probability for exciplex formation is the highest. The EL spectrum of PFBV.Me⊂β-CD.COPr is blueshifted (average EL energy = 2.42 eV) with respect to PFBV, which instead shows a featureless band at about 2.2 eV. As a result of controlled ET and exciplex formation in the "threaded blend" (2:8 PFBV.Me⊂β-CD.COPr:TFB bw), the EL spectrum is structured and with a more pronounced blue component than the PFBV:TFB system, that results in an overall "cold" white light, corresponding to CIE color coordinates, x = 0.26, y = 0.33. Figure 5c,d report the current density-voltage-luminance characteristics of the LEDs in Figure 5a,b. Importantly, the turn-on voltage for white EL is only 3.5 V, which is a factor of 3 lower than for the white-emitting LEDs incorporating blends of a blue-emitting polyrotaxane. [25] The EL external quantum efficiency is essentially comparable to those with the complementary blends, i.e. here we obtain a maximum EQE = 0.1% for LEDs incorporating the rotaxane and its TFB blend (vs. 0.15% in ref. [25]), and EQE = 0.02% for the PFBV blend (vs. 0.01% in www.afm-iournal.de

the complementary blend with the blue-emitting rotaxane).^[25] A detailed analysis of the EL response is reported in the Supporting Information together with the current density dependence of the EQE (Supporting Information Figure S3). We note that these devices were not optimized in terms of layer thickness and electrodes work function, and that significant improvements might therefore still be expected by optimizing the electron-hole balance, e.g., by facilitating injection of the minority carriers.[19,51] Further improvements are expected by

using polyrotaxanes threaded with cyclodextrins functionalized

As a result of hindered ET and suppressed interchain interactions, we obtain a trajectory of the CIE color coordinates for the PL of the rotaxinated blends that span from blue to the green and cross the white color region at about 20% bw of PFBV.Me $\subset \beta$ -CD.COPr (Figure 5g). The EL CIE coordinates for the investigated polymers and blends are reported in the inset of Figure 5g.

3. Conclusions

with charge transport groups.

In summary, we have synthesized and characterized the first example of green-emitting organic-soluble conjugated polyrotaxane whose binary blend with a blue-emitting polymer exploits tunable photoluminescence color and white EL as a result of controlled ET and exciplex formation between the polymeric species by supramolecular encapsulation. Three main factors contribute to the improved performances of rotaxinated blends with respect to conventional "unthreaded" blends, namely i) the supramolecular encapsulation in polyrotaxanes that prevents ET by hindering close molecular contact both between adjacent PFBV moieties and between PFBV and TFB, thus resulting in higher PL quantum yields and blue emission due to TFB excitons, ii) reduced chromophore density in the polyrotaxane, and iii) increased phase-separation in the TFB:polyrotaxane blends. Most importantly, the use of a green-emitting encapsulated polymer circumvents the difficulties encountered with a binary blend of a blue electroluminescent polyrotaxane, and leads to drastically lowered turn-on voltage of white EL, that we achieve with only 20% bw of encapsulated moieties in the binary blend.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] R.-Q. Png, P.-J. Chia, J.-C. Tang, B. Liu, S. Sivaramakrishnan, M. Zhou, S.-H. Khong, H. S. O. Chan, J. H. Burroughes, L.-L. Chua, R. H. Friend, P. K. H. Ho, Nat. Mater. 2010, 9, 152.
- [2] R. Capelli, S. Toffanin, G. Generali, H. Usta, A. Facchetti, M. Muccini, Nat. Mater. 2010, 9, 496.
- [3] L.-M. Chen, Z. Hong, G. Li, Y. Yang, Adv. Mater. 2009, 21, 1434.
- [4] J. Clark, G. Lanzani, Nat. Photonics 2010, 4, 438.
- [5] B. K. Yap, R. Xia, M. Campoy-Quiles, P. N. Stavrinou, D. D. C. Bradley, Nat. Mater. 2008, 7, 376.
- [6] G. Calzaferri, S. Huber, H. Maas, C. Minkowski, Angew. Chem. Int. Ed. 2003, 32, 3732.
- [7] M. J. Frampton, T. D. W. Claridge, G. Latini, S. Brovelli, F. Cacialli, H. L. Anderson, Chem. Commun. 2008, 24, 2797.
- [8] C. Botta, G. Patrinoiu, P. Picouet, S. Yunus, J.-E. Communal, F. Cordella, F. Quochi, A. Mura, G. Bongiovanni, M. Pasini, S. Destri, G. Di Silvestro, Adv. Mater. 2004, 16, 1716.
- [9] P. Sozzani, A. Comotti, S. Bracco, R. Simonutti, Angew. Chem. Int. Ed. 2004, 43, 2792.
- [10] L. Poulsen, M. Jazdzyk, J. E. Communal, J. C. Sancho-Garcia, A. Mura, G. Bongiovanni, D. Beljonne, J. Cornil, M. Hanack, H. J. Egelhaaf, J. Gierschner, J. Am. Chem. Soc. 2007, 129, 8585.
- [11] Y. Ouchi, K. Sugiyasu, S. Ogi, A. Sato, M. Takeuchi, Chem. Asian J. **2012**, 7, 75.
- [12] F. Cacialli, Philos. Trans.: Math., Phys., Eng. Sci. 2000, 358, 173.
- [13] M. J. Frampton, H. L. Anderson, Angew. Chem. Int. Ed. 2007, 46, 1028.
- [14] J. Terao, S. Tsuda, Y. Tanaka, K. Okoshi, T. Fujihara, Y. Tsuji, N. Kambe, J. Am. Chem. Soc. 2009, 131, 16004.
- [15] J. Terao, Y. Tanaka, S. Tsuda, N. Kambe, M. Taniguchi, T. Kawai, A. Saeki, S. Seki, J. Am. Chem. Soc. 2009, 131, 18046.
- [16] F. Cacialli, J. S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samorì, J. P. Rabe, M. J. O'Connell, P. N. Taylor, H. L. Anderson, Nat. Mater. 2002, 1, 160.
- [17] A. Petrozza, S. Brovelli, J. J. Michels, H. L. Anderson, R. H. Friend, C. Silva, F. Cacialli, Adv. Mater. 2008, 20, 3218.
- [18] F. E. Oddy, S. Brovelli, M. T. Stone, E. J. F. Klotz, F. Cacialli, H. L. Anderson, J. Mater. Chem. 2009, 19, 2846.
- [19] G. Latini, G. Winroth, S. Brovelli, S. O. McDonnell, H. L. Anderson, J. M. Mativetsky, P. Samorì, F. Cacialli, J. Appl. Phys. 2010, 107,
- [20] M. M. Mróz, S. Perissinotto, T. Virgili, G. Gigli, M. Salerno, M. J. Frampton, H. L. Anderson, G. Lanzani, Appl. Phys. Lett. 2009, 95, 031108.
- [21] S. Brovelli, F. Cacialli, Small 2010, 6, 2796.
- [22] S. Brovelli, G. Latini, M. J. Frampton, S. O. McDonnel, F. E. Oddy, O. J. Fenwick, H. L. Anderson, F. Cacialli, Nano Lett. 2008, 8, 4546.
- [23] M. H. Chang, M. J. Frampton, H. L. Anderson, L. M. Herz, Appl. Phys. Lett. 2006, 89, 232110.
- [24] F. Di Stasio, P. Korniychuk, S. Brovelli, P. Uznanski, S. O. McDonnell, G. Winroth, H. L. Anderson, A. Tracz, F. Cacialli, Adv. Mater. 2011, 23, 1804.
- [25] S. Brovelli, F. Meinardi, G. Winroth, O. Fenwick, G. Sforazzini, M. J. Frampton, L. Zalewski, J. A. Levitt, F. Marinello, P. Schiavuta, K. Suhling, H. L. Anderson, F. Cacialli, Adv. Funct. Mater. 2010, 20,
- [26] S. Brovelli, H. Guan, G. Winroth, O. Fenwick, F. Di Stasio, R. Daik, W. J. Feast, F. Meinardi, F. Cacialli, Appl. Phys. Lett. 2010, 96.
- [27] S. Brovelli, T. Virgili, M. M. Mroz, G. Sforazzini, A. Paleari, H. L. Anderson, G. Lanzani, F. Cacialli, Adv. Mater. 2010, 22, 3690.
- [28] M. M. Mróz, T. Virgili, S. O. M. Donnell, M. J. Frampton, H. L. Anderson, G. Lanzani, Phys. Rev. B 2009, 80, 045111.
- [29] M. J. Frampton, G. Sforazzini, S. Brovelli, G. Latini, E. Townsend, C. C. Williams, A. Charas, L. Zalewski, N. S. Kaka, M. Sirish,



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- L. J. Parrott, J. S. Wilson, F. Cacialli, H. L. Anderson, Adv. Funct. Mater. 2008, 18, 3367.
- [30] J. Terao, A. Tang, J. J. Michels, A. Krivokapic, H. L. Anderson, Chem. Commun. 2004, 56.
- [31] A. R. Buckley, M. D. Rahn, J. Hill, J. Cabanillas-Gonzalez, A. M. Fox, D. D. C. Bradley, Chem. Phys. Lett. 2001, 339, 331.
- [32] A. J. Cadby, R. Dean, C. Elliott, R. A. L. Jones, A. M. Fox, D. G. Lidzey, Adv. Mater. 2007, 19, 107.
- [33] E. Moons, J. Phys.: Condens. Matter 2002, 14, 12235.
- [34] J. J. Michels, M. J. O'Connell, P. N. Taylor, J. Wilson, F. Cacialli, H. L. Anderson, *Chem. Eur. J.* **2003**, *9*, 6167.
- [35] M. H. Chang, M. J. Frampton, H. L. Anderson, L. M. Herz, Phys. Rev. Lett. 2007, 98, 027402.
- [36] J. Chappell, D. G. Lidzey, P. C. Jukes, A. M. Higgins, R. L. Thompson, S. O'Connor, I. Grizzi, R. Fletcher, J. O'Brien, M. Geoghegan, R. A. L. Jones, *Nat. Mater.* 2003, 2, 616.
- [37] J. Morgado, E. Moons, R. H. Friend, F. Cacialli, Adv. Mater. 2001, 13, 810.
- [38] A. C. Morteani, R. H. Friend, C. Silva, J. Chem. Phys. 2005, 122, 244906.
- [39] J. R. Lakowicz, Principles of Fluorescence Spectroscopy, Springer, New York 2006.
- [40] J. S. Wilson, M. J. Frampton, J. J. Michels, L. Sardone, G. Marletta, R. H. Friend, P. Samori, H. L. Anderson, F. Cacialli, Adv. Mater. 2005, 17, 2659.

- [41] A. Cadby, R. Dean, R. A. L. Jones, D. G. Lidzey, Adv. Mater. 2006, 18, 2713.
- [42] The AFM images in Figure 5e,f show a smaller phase separation in the spin-cast PFBV:TFB film compared to the rotaxane:TFB film (with the same blending ratio). The roughness of the film of the unthreaded blend (roughness = 2.33 nm) is significantly lower than for the rotaxinated blend (roughness = 12.2 nm) thus suggesting a poor intermixing between the polyrotaxane and TFB blend constituents with respect to PFBV.
- [43] K. Balakrishnan, A. Datar, T. Naddo, J. L. Huang, R. Oitker, M. Yen, J. C. Zhao, L. Zang, J. Am. Chem. Soc. 2006, 128, 7390.
- [44] A. C. Morteani, R. H. Friend, C. Silva, in *Organic Light Emitting Devices*, (Eds: K. Muellen, U. Scherf), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2006, p. 35.
- [45] S. A. Jenekhe, J. A. Osaheni, Science 1994, 265, 765.
- [46] A. C. Morteani, A. S. Dhoot, J. S. Kim, C. Silva, N. C. Greenham, C. Murphy, E. Moons, S. Ciná, J. H. Burroughes, R. H. Friend, Adv. Mater. 2003, 15, 1708.
- [47] J. G. S. Ramon, E. R. Bittner, J. Chem. Phys. 2007, 126, 181101.
- [48] M. Muccini, Nat. Mater. 2006, 5, 605.
- [49] J. S. Kim, F. Cacialli, R. H. Friend, Thin Solid Films 2003, 445, 358.
- [50] T. M. Brown, J. S. Kim, R. H. Friend, F. Cacialli, R. Daik, W. J. Feast, Appl. Phys. Lett. 1999, 75, 1679.
- [51] M. Voigt, J. Chappell, T. Rowson, A. Cadby, M. Geoghegan, R. A. L. Jones, D. G. Lidzey, Org. Electron. 2005, 6, 35.

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