Defect chemistry of polyfluorenes: identification of the origin of "interface defects" in polyfluorene based light-emitting devices†

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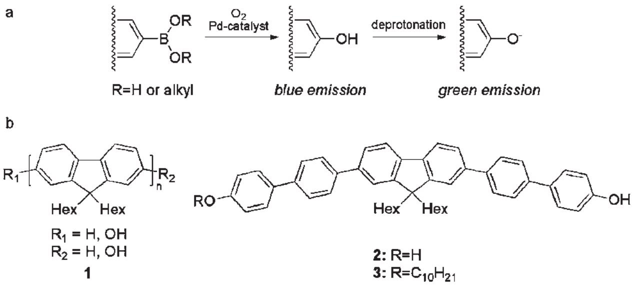
Deprotonation of hydroxy terminated polyfluorenes results in a greenish emission also providing a rational explanation for so called "interface defects" in polymeric light-emitting devices (PLEDs).

Among the wide variety of conjugated polymers suitable for application in polymeric light-emitting devices (PLEDs), polyfluorenes (PFs) have undoubtedly emerged as one of the most promising candidates for realizing blue electroluminescent devices.[1–5] However, investigations on the electroluminescent properties of polyfluorenes identified degradation processes during device operation (accompanied by the occurrence of a green emission band at 2.2 to 2.3 eV) as a critical drawback for practical applications.[6–9] Not surprisingly, numerous research activities focused on this topic controversially discussing aggregates and excimers[10–14] as well as chemical defects (*i.e.*, ketonic defect sites)[8–9,15] as the potential origin of the low-energy emission band. In this context it has been shown that the latter explanation is in accordance with quantum chemical calculations[16] and experimental results from single molecule spectroscopy.[17] Conversely, other features in electroluminescence (EL) spectra (*e.g.* "interface defects") cannot be explained with ketonic defect sites.[18,19]

In literature various synthesis routes for the preparation of polyfluorenes and polyfluorene based materials have been described. Nevertheless, reductive coupling (Yamamoto coupling) and transition-metal mediated cross-coupling reactions (in particular Suzuki cross-coupling reactions) are most frequently applied because of their good yields, the high molecular weights of the obtained polymers and the possibility of preparing strictly alternating copolymers (in case of Suzuki cross-coupling reactions).[20] While the Yamamoto coupling has been subject of several studies on possible side reactions occurring during polymer synthesis in the presence of oxygen (keto defect sites as by-products),[8,9] oxygen also paves the way for other degradation processes, *e.g.*, in palladium catalyzed Suzuki cross-coupling protocols. In the latter case different peroxide species[21] can be formed capable of undergoing protiodeboronation reactions of boronic acids or boronic acid esters resulting in the formation of hydroxy end groups (*cf.* Scheme 1a).[22] Even though this is a well known side reaction, the impact of hydroxy end groups on the photophysical properties of polyfluorenes has hitherto not been studied. In more general terms, the impact of end groups ("end chain defects") on the photophysical properties of conjugated polymers is only rarely considered although the emissive properties of polymers are especially sensitive to minute amounts of contaminants as a result of efficient exciton migration and trapping processes.

Thus, as a prototypical example, in this work we discuss the properties of polyfluorenes containing hydroxy end groups. We observe significant changes in their photophysical properties upon deprotonation. While intense blue photoluminescence (PL) is found for the protonated species, the addition of a strong base results in a (reversible) red-shift of the corresponding absorption and emission spectra in solution and in the solid state resulting in a green emission. This effect of deprotonation, which has similarly been reported for other conjugated systems,[23] also plays a role in polymeric light-emitting devices, where polymers with hydroxy end groups are capable of undergoing deprotonation reactions with, *e.g.*, calcium electrodes. Thus, these deprotonation reactions are a possible explanation for so called "interface defects", which have been reported by Gamerith *et al.* to contribute to the greenish emission colour of polyfluorene based PLEDs.[18,19]



Scheme 1 (a) Protiodeboronation reactions of boronic acids or boronic acid esters result in the formation of hydroxy end groups which can be deprotonated. (b) Polyfluorene with a significant amount of hydroxy end groups (**1**), 9,9-dihexyl-2,7-*bis*(4′-hydroxy-1,1′-biphen-4-yl)fluorene (**2**) and its monoetherified analogue (**3**) as model compounds (*cf.* ref. 4 and 22).

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To study deprotonation effects in polyfluorenes, a polyfluorene homopolymer bearing significant amounts of hydroxy end groups (**1**) was prepared under ambient conditions according to a literature procedure (the successful incorporation of hydroxy end groups was shown *via* NMR and MALDI TOF MS measurements, *cf.* Scheme 1b).[22] Furthermore, 9,9-dihexyl-2,7-*bis*(4′-hydroxy-1,1′-biphen-4-yl)fluorene (**2**) and its monoetherified analogue (**3**) were synthesized following the procedure of Sović *et al.*[4] to investigate deprotonation effects on simplified model compounds (*cf.* Scheme 1b). Photophysical measurements in solution were conducted with these materials either in THF (in case of **1**) or in EtOH (in case of **2** and **3**) using KOH or KO^{t}Bu as a base for deprotonation experiments. Thin films of **1** suitable for PL measurements were obtained *via* spin-coating from diluted THF solutions; films of the corresponding deprotonated species were realized by spin-coating a diluted solution of **1**, polystyrene (as matrix for film-smoothing) and KO^{t}Bu in THF and EtOH.[24]

In solution, all compounds under investigation were found to exhibit photophysical properties strongly affected by the addition of base. The strong blue emission peaks of **1**, **2** and **3** showed drastic decreases in emission intensity upon deprotonation with a simultaneous increase in a new but very weak emission band peaking between 500 and 550 nm (*cf.* Fig. 1 and titration experiments in the ESI†).[25] While for the absorption spectra of **2** and **3** a similar behavior was observed (*i.e.* a red-shift of the absorption maxima after addition of base, *cf.* ESI†), the absorption maximum of **1** remained virtually unchanged after deprotonation indicating absorption properties strongly dominated by the polyfluorene backbone. The above described behavior is strongly reminiscent of the ketonic defect in polyfluorenes, where also the emission properties are much more affected by the degradation process.[9] For the electronic structure of the deprotonated chains, this suggests a situation qualitatively similar to that described by Zojer *et al.* for oxidized polyfluorene with a localized, low-lying, only weakly allowed defect-induced state and a strongly absorbing delocalized state, whose electronic structure is hardly affected by the "defect".[16] It is worth noting that in the herein described experiments upon addition of acid or upon reprotonation from air (presumably caused by carbon dioxide)[26] the parental photophysical properties of **1**, **2** and **3** were entirely recovered. Moreover, it could be shown that the absorption and emission spectra of fully hydrogen terminated polyfluorenes (prepared according to a literature procedure)[22] were neither affected by the addition of base nor by the addition of acid providing further evidence that deprotonation of the investigated materials is responsible for the observed effects.

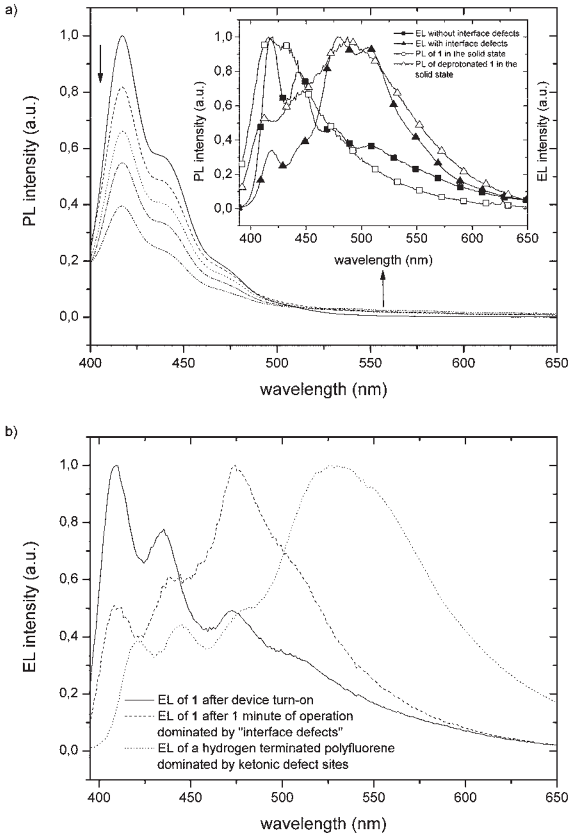

Fig. 1 (a) Titration experiments of **1** show that upon addition of base the blue photoluminescence (PL) decreases with simultaneous increase in a new but very weak red-shifted emission band (the residual blue emission stems from polyfluorenes without hydroxy end groups). In the inset, electroluminescence (EL) spectra of a polyfluorene based PLED without interface defects (filled squares, *cf.* ref. 27), EL spectra of a polyfluorene based PLED with interface defects (filled triangles, *cf.* ref. 27), PL spectra of thin films of **1** before deprotonation (open squares) and PL spectra of thin films of **1** after addition of KO^{t}Bu (open triangles) are shown. The emission maximum of the deprotonated species of **1** is in excellent agreement with so called "interface defects". (b) PLEDs prepared from **1** emit blue light only for a few seconds after device turn-on and give EL spectra totally dominated by the green emission around 500 nm after a maximum time period of 1 min. In contrast, device degradation of hydrogen terminated polyfluorenes (ketonic defect sites) results in a green emission peaking around 550 nm (*cf.* ref. 8 and 27).

From the investigations on ketonic defect sites and their contribution to the green emission of polyfluorenes and polyfluorene based materials it is well known that chemical defects influence the photophysical properties much more strongly in the solid state than in solution.[8,9,15] Therefore, the effects of deprotonation on the thin film emission characteristics of **1** were also studied, indeed showing that in this experimental setup the green emission band of the deprotonated species is dominant in the corresponding PL spectra. As depicted in Fig. 1, the blue emission band of **1** (open squares) peaking between 400 and 450 nm is decreased upon addition of KO^{t}Bu at the expense of a new emission maximum around 500 nm (open triangles). Again, the effects of deprotonation were entirely reversible upon exposure to acidic vapor (*e.g.* HCl vapor) or reprotonation from air but were not found in polymers bearing no hydroxy end groups (*i.e.* in fully hydrogen terminated polyfluorenes).[22] This reversibility excludes ketonic defect emission as the origin of the observed feature.

When comparing the emission properties of deprotonated **1** (emission maximum around 500 nm) with the "standard" green emission band of polyfluorenes (*e.g.* in PLEDs, emission maximum around 550 nm, *cf.* Fig. 1 and ESI†) significant differences concerning the corresponding emission maxima become evident.[8,27] While the latter green emission band can be readily explained with the occurrence of ketonic defect sites,[8] the changes in the photophysical properties caused by deprotonation are strongly reminiscent of so called "interface defects" (*cf*. Fig. 1).[18] These interface defects, which are frequently observed in standard PLED architectures containing, *e.g*., calcium layers, have been reported to contribute to the overall green emission of polyfluorene based PLEDs (*cf*. ESI), albeit at a shorter wavelength than the "standard" ketonic defects.[18,28] Their chemical origin, however, has hitherto remained unclear. The above presented concept of deprotonation of hydroxy terminated polyfluorenes (*e.g*. by interaction with calcium layers in PLEDs; simplified reaction scheme: $2\ \mathrm{Ar{-}OH} + \mathrm{Ca} \rightarrow 2\ \mathrm{Ar{-}O^-} + \mathrm{Ca^{2+}} + \mathrm{H_2}$), therefore, provides the first rational explanation for that observation. Consequently, it is anticipated to contribute significantly to the further understanding of degradation mechanisms occurring during device operation.

In accordance with the discussed concept, investigations on PLEDs prepared from **1** (ITO/PEDOT:PSS/**1**/Ca/Al) exhibited strong interface defects shortly after device turn-on (*cf*. Fig. 1 and ESI†), whereas analogous devices with fully hydrogen terminated polyfluorenes showed increased device stabilities. PLEDs from **1** were found to be weakly electroluminescent in the blue spectral region for a few seconds, however, after prolonged device operation (for a maximum of 1 min) EL spectra dominated by the green emission around 500 nm were obtained. Conversely, PLEDs from hydrogen terminated polyfluorenes provided blue EL with significantly higher luminance values. In the corresponding PLEDs only standard device degradation associated with the emission from ketonic defect sites was found (*cf*. Fig. 1).

In conclusion, the present work describes the impact of hydroxy end groups on the photophysical properties of polyfluorenes. These end groups, which can inadvertently be formed *via* protiodeboronation reactions in the course of Suzuki polymerisations, are capable of deprotonation in solution, in the solid state and in PLEDs. The resulting green emission band is in excellent agreement with frequently observed interface defects[18] in PLEDs, where, *e.g*., calcium layers can act as a base. Therefore, the concept of deprotonation of hydroxy end groups gives the first rational explanation for interface defects and points out that aside from ketonic defect sites ("on chain defects") also hydroxy end groups ("end chain defects") have to be avoided in order to provide stable polyfluorene based emitter materials.

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26 Because of these reprotonation effects attempts to determine the quantum yields of the deprotonated species were unsuccessful.

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