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Synthesis and characterization of amino-functional, blue light-emitting copolymers and their composites with CdTe nanocrystals

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1. Introduction

A series of wide bandgaps, blue light-emitting copolymers, like poly(para-phenylene)s (PPP)s [1], poly(carbazole)s (PC)s [2], or poly (fluorene)s (PF)s [3–5], have been described over the last decades. PFs are of special importance as light-emitting materials often used in polymer light-emitting diodes (PLED)s [6-8]. PF is in particular of significance due to its high quantum yield [3,7,8], and rather large bandgap. Therefore, PF-based copolymers with emission colors over the entire visible range were synthesized by introducing comonomers revealing a lower bandgap [7-11]. C9-alkylated PFs are well-known to undergo oxidation upon heating, in turn leading to color instability and green electroluminescence [12–15]. In order to avoid this undesired effect, copolymerization with functional and bulky moieties that keep the bandgap wide and to some extent suppress the disturbing keto-defect emission [16-18] of the PFs, is demanded respectively. Furthermore, functional polymers comprised of functional monomers that can be connected to other functional, or light-emitting species such as nanoparticles or semiconductor nanocrystals (NCs) [19], are of increasing impact in modern light-emitting technology [20].

ABSTRACT

Random side-chain functionalized copolymers were synthesized, utilizing a facile Yamamoto protocol by applying 2,7-dibromo-9,9-*bis*(6-bromohexyl)-9*H*-fluorene, (*E*)-1,2-*bis*(4-bromophenyl)ethene, 2,7-dibromo-9,9-dioctyl-9*H*-fluorene as comonomers. The precursor copolymers were post-functionalized utilizing di-*n*-propylamine and the resulting target copolymers were fully characterized. The optical classification parameters have been determined in solutions and in thin films as well. The copolymers revealed blue light emission, wide optical bandgaps Eg_{opt} of at least 2.84 eV and remarkable quantum yields up to 0.78 in chloroform solutions. The amino-functional copolymers allowed tying semiconductor CdTe nanocrystals.

In order to design and synthesize poly(arylene)s, to which PFs belong to, several C–C coupling reactions are available to date. Important is the oxidative coupling [21], but also the reductive coupling, represented by the straightforward Yamamoto coupling [7,20,22]. Likewise, palladium-interceded cross-coupling reactions like the Suzuki polycondensation [23] are useful to achieve PFs. For the functionalization of the conjugated copolymer backbones, the emphasis is on transformation reactions like the substitution of bromo-functional side-chains [24,25]. In order to introduce functional groups like amino-functionalities [26], post-functionalization has proven to be very efficient [25].

In this work, we introduce the synthesis and characterization of two novel amino-functionalized fluorene-based copolymers by a post-treatment of bromo-side chain functionalized precursors. The latter were designed with 2,7-dibromo-9,9-*bis*(6-bromohexyl)-9H-fluorene, (*E*)-1,2-*bis*(4-bromophenyl)ethene and 2,7-dibromo-9,9-dioctyl-9H-fluorene as building blocks following a simple Yamamoto protocol. The resulting random copolymers were post-functionalized in order to tether di-*n*-propylamine groups at the side-chains of the conjugated copolymer backbone. The final products revealed blue light emission with an emission maximum at 434 nm and high relative quantum yields up to 0.78 when compared to the reference fluorophore PF, revealing a quantum yield of 0.45 [27]. Due to the amino-functionalities, the random copolymers might function to tie to a variety of nanoparticles





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[28,29]. Here, we show the interconnection of the functional copolymers with CdTe semiconductor NCs indicated by enhanced deactivation of the amino-functional copolymers emission upon the addition of the CdTe NCs.

2. Experimental part

Materials and instrumentation as well as the synthesis and experimental details of the involved monomers, polymers, nanocrystals and composites are described in the Electronic Supplementary Material (ESM).

2.1. Synthesis of the monomers

2,7-Dibromo-9,9-*bis*(6-bromohexyl)-9*H*-fluorene (**3**) was synthesized by a base-mediated alkylation using a phase transfer catalyst (PTC) [24]. 6,6-(2,7-Dibromo-9*H*-fluorene-9,9-diyl)*bis*(*N*,*N*-dipropylhexan-1-amine)(**4**) was obtained by a substitution reaction in high yield (91%) [30], while (*E*)-1,2-*bis*(4-bromophenyl)ethene (**5**) was synthesized using 4-bromobenzaldehyde as starting material in the presence of TiCl₄[31] according to a McMurry reaction, yielding 48% of the *E*-isomer after recrystallization from ethyl acetate (Scheme 1). Subsequently, a series of side-chain functionalized copolymers were synthesized and post-functionalized (Scheme 2).

2.2. Synthesis of the copolymers – general procedure

The polymerizations were performed according to a facile Ni(0)mediated Yamamoto C–C-coupling protocol [32] using 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (**2**), 2,7-dibromo-9,9-*bis*(6-bromohexyl)-9*H*fluorene (**3**) and (*E*)-1,2-*bis*(4-bromophenyl)ethene (**5**) as building blocks. The nickel(0)-catalyzed polycondensations were conducted in



Scheme 1. The synthetic route for monomers 3, 4, and 5. NMR labels at compounds 3 and 4.



Scheme 2. Synthesis of functional copolymers 6a, 7a and 6b, 7b.

THF (**6a**, **7a**) by means of Ni(COD)₂ and 2,2'-bipyridine as the organometallic counterpart (Scheme 2).

3. Results and discussion

A series of random copolymers **6a**, **7a** and **Pref** (Scheme 2) were obtained by varying the proportions of the building blocks. For copolymer **6a** the molar feed ratio of dioctyl-fluorene moiety **2** to *bis*(6-bromohexyl)-fluorene **3** to (*E*)-stilbene derivative **5** was 40:10:50% and for copolymer **7a** the ratio of the comonomers **2:3:5** was 35:15:50%, correspondingly. A reference copolymer **Pref** comprised of dioctyl-fluorene **2** and (*E*)-stilbene derivative **5** in a feed ratio of 50:50% was additionally prepared.

In order to remove impurities and to obtain unimodal molecular weight distributions, the copolymers **6a**, **7a** and **Pref** were exhaustively purified in a Soxhlet-apparatus by using ethanol as extraction medium. After purification, the functional copolymers were obtained as yellow solids in yields of about 30% [33] and were easily soluble in solvents of

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Fig. 1. ¹H NMR spectra of bromo-functionalized compound **3** and amino-functionalized derivative **4**. All spectra were recorded in CDCl₃.

medium polarity like toluene, chloroform or dichloromethane. Moderate yields are expected in systems with complicated backbone composition and side-chain functionalities, which enhance the solubility and the losses upon purification via extraction and/or several times of precipitation [33,34]. The post-functionalization was conducted in a THF/DMF 1:1 mixture at 85 °C reaction temperature by addition of di-*n*-propylamine at 0 °C and precipitation of the polymers using acetone.

Fig. 1 shows the ¹H NMR spectra recorded in deuterated chloroform (CDCl₃) monitoring the transformation of compound **3** into its amino-functionalized counterpart 4. As shown in Fig. 1, the shifts of the resonances of the C6 protons (for NMR labels of 3 and 4 see Scheme 1), allow the observation of the applied synthetic steps. For compound 3, the triplet resonance at 3.29 ppm, which is assigned to the protons of the C6 carbon atom and its perfect integration indicate the step-wise conversion of 2,7-dibromofluorene (1) into compound 3. The five high-field shifted resonances observable at 0.56–1.95 ppm represent the remaining protons of the aliphatic –CH₂–groups of the functionalized hexyl side-chains. As expected, integration of the intensity indicates the presence of two protons in each of the $-CH_2$ - groups, accordingly. In case of monomer 4, the attachment of the di-n-propylamine moiety shifted the respective C6 proton resonances to higher field values $(3.29 \rightarrow 2.91 \text{ ppm}, \text{Fig. 1})$. These resonances are in parts overlapping with the C7 protons of the di-*n*-propylamine group (Fig. 1). The ¹H NMR spectra of copolymers 6a, 7a are indicative for polymer spectra due to the observed resonance broadening and the resonances at 3.31 ppm are therefore given evidence for the incorporation of 2,7-dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (3) in each of the copolymers' backbone.

Random copolymers **6b**, **7b** were obtained after a substitution reaction replacing the C6-bromo-atoms in the side-chains of **6a**, **7a** using di-*n*-propylamine in THF. For copolymers **6b**, **7b** an analogue signal for the nitrogen-neighbored C6 protons is not as pronounced as for **6a**, **7a**, however, the success of the post-functionalization was

additionally proven by detection of nitrogen utilizing elemental analysis. A nitrogen content of 8.3% and 9% was detected for polymers **6b** and **7b**, respectively. However, the determined values remained slightly below theoretical values of the initial monomer feed ratio of 10% and 15% used for the preparation of precursor copolymers **6a** and **7a**, correspondingly. The successful post-functionalization was furthermore confirmed by the detection of the vibrational bands at 2050 cm⁻¹ and 2348 cm⁻¹ in the infrared spectra, assigned to the C–NH⁺ stretching vibration.

Gel permeation chromatography analysis of all copolymers resulted in unimodal molecular weight distributions. The number average molecular weight, (M_n) of **Pref** is about 12000 g \times mol⁻¹ with a polydispersity index (PDI) of 2.20, while for the precursor copolymers **6a** and **7a** it is in the order of 18000 g \times mol⁻¹ with PDI values of 2.49 and 2.75, accordingly. The purification of the aminofunctional copolymers **6b** and **7b** by precipitation into acetone lead to about by half reduced M_n values with corresponding PDI values of 2.28 and 1.90. This finding is most likely due to an increased solubility of the higher molecular weight fractions in polar solvents like acetone [29]. Nonetheless, acetone seems to be the optimal medium for amino-functionalized copolymers. Compared to more polar solvents like methanol the yields of the amino-functional copolymers **6b** and **7b** were drastically reduced even below 10% (side-chain solubility). The same holds true for less polar solvents than acetone (backbone solubility).

The optical properties of copolymers **6a,b, 7a,b** and **Pref** were additionally determined. Table 1 illustrates the optical properties in solution and film of the synthesized copolymers, which all exhibit blue light emission. The absorption and emission spectra of the precursor **6a, b** and post-functionalized copolymers **7a, b** were illustrated in Fig. S1 in the supporting information file.

The amino-functional copolymers 6b and 7b possessed remarkable quantum yields in the range of 0.77 and 0.78, correspondingly. These quantum yields are increased by a significant factor of 1.28 and 1.42 compared to the bromo-functional precursor copolymers 6a and 7a, accordingly. Moreover, the copolymers revealed wide bandgaps of 2.84 eV in solution while in the films the optical bandgaps were slightly reduced to 2.70 eV (Table 1). Therefore, the functional copolymers might suit to host lower bandgap compounds such as semiconductor NCs. Consequently, solid-state measurements of the optical properties of copolymers and NC-polymer systems were conducted. In Fig. 2a, the relative emission intensities of bare polymers and the NC-polymer films are depicted. These fluorescence measurements, using an excitation wavelength of 410 nm, showed that all polymers efficiently emit blue light. Upon addition of the NCs, a reduction of the polymers fluorescence signal occurred. The sequence of the quenching effect (QE) assigned to the polymer backbone band follows the order $QE_{Pref} < QE_{6b} < QE_{7b}$. In particular, the signal assigned to the nanocomposite comprised of Pref is quenched by a factor of 8.4 compared to the bare polymer, while the intensities of

Table 1			
Optical properties of the copolymers 6a , b	, 7a , b and Pref in	CHCl ₃ solutions a	and in thin films.

	$Abs_{sol}^{a}(lg\epsilon) \text{ [nm]} (L \times mol^{-1} \times cm^{-1})$	Abs _{film} [nm]	Em _{sol} ^{a,b} [nm]	Em _{film} ^b [nm]	Eg _{sol} ^{a,c} [eV]	Eg _{film} ^c [eV]	$\Phi_{sol}{}^{a,d}$
6a	382 (5.86)	400	432/455	451/477	2.88	2.42	0.60
7a	388 (5.80)	397	435/458	451/480	2.85	2.41	0.55
6b	388 (5.39)	397	434/456	451/479	2.84	2.70	0.77
7b	388 (5.37)	398	434/458	449/478	2.84	2.69	0.78
Pref	391 (6.06)	401	434/461	451/477	2.89	2.71	0.59

^a In chloroform solution (10^{-7} mol/L).

^b λ_{exc.} 390 [nm].

^c Calculated from the absorption band edge.

^d Determined according to Demas and Crosby [38] using PF (Φ_{sol} 0.45) [27] as a reference. Note in literature, the Φ values for PF vary over a wide range [28,39] also depending on the structural features of the investigated copolymer [26,27].



Fig. 2. Emission (a) and normalized emission (b) spectra of copolymers **Pref. 6b**, **7b** (1 mg/mL in THF) and their composites with CdTe (λ_{ex} : 410 nm) drop casted from THF and a DMF/THF (1/3) mixture, respectively. Pictures of **7b**, CdTe and their composite (1/1) (in that order left to right) with no and under illumination (λ_{ex} : 366 nm) (c).

the **6b** and **7b** composites were reduced by a magnitude of 12.5 and 24.7, correspondingly, regarding their neat copolymer bands. Additionally, the normalized emission spectra of the investigated nanocomposite films are illustrated in Fig. 2b. The emissions at 610 nm, originating from the CdTe nanocrystals, exposed intensity enhancement (IE) in the order: $IE_{7b+CdTe} > IE_{Pref+CdTe} > IE_{6b+CdTe}$. The improved fluorescence deactivation in the case of 7b may thus have a correlation with the content of the amino-groups in the copolymer side-chain, most likely influencing the surface states of the CdTe NCs [35,36]. The pictures in Fig. 2c show the deactivation of **7b** upon CdTe addition that might most probably occur via collisional quenching, for which bromobenzene is particularly known as an efficient quencher of many fluorophores [37]. Obviously, the NCs stabilizer HS-C₆H₄-Br representing a substituted bromobenzene may act as a photoluminescence quencher by a direct contact with the polymer in solid films. Additional luminescence drop can be provided by remaining *N*,*N*-dimethylformamide used as a solvent for the CdTe NCs, which is also known for its quenching ability. Therefore, this observed luminescence decrease is promising for sensing bromo-containing aromatic compounds. In order to further enhance the luminescence properties of the NCs-polymer composites, a robust chemical binding between the CdTe NCs and the respective polymer molecules under elimination of the bromo-substituent will be performed in the future as well as the employment of different stabilizing molecules in the NCs synthesis. More detailed measurements involving photo-physical and

electro-optical investigations will be carried out in our laboratories taking the observed deactivation process of differently labeled NCs into consideration.

4. Conclusion

We prepared two bromo-functionalized fluorene-based copolymers using a facile Yamamoto protocol, which were further aminofunctionalized. The copolymers were comprised of varying contents of 2,7-dibromo-9,9-bis(6-bromohexyl)-9H-fluorene, (E)-1,2-bis(4bromophenyl)ethene and 2,7-dibromo-9,9-dioctyl-9H-fluorene. The amino-functional copolymers revealed wide bandgaps of 2.84 eV, favorable quantum vields of up to 0.78 in solution and proved themselves to interconnect to the surface of CdTe NCs. The investigation of the deactivation and the intensity enhancement process of the polymer and the CdTe nanocrystal emission illustrated a dependence on the bromo-functions of the NC stabilizing ligands and the nitrogen content of the copolymers. Thus, tethering CdTe NCs on an amino-functional copolymer backbone, leading to an emission intensity enhancement of the NCs emission, might be regarded as a nitrogen-content depending process and the luminescence decrease of the copolymers is promising for sensing bromo-containing aromatic compounds.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.08.068.

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