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Optical Properties of Benzotriazole-Based Conjugated Polyelectrolytes

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Abstract: A series of conjugated polyelectrolytes (CPEs) based on an electron-deficient polybenzotriazole backbone and different pendant ionic functionalized side chains were synthesized directly from the corresponding ionic monomers. Of particular interest was to use the different chemical structures to understand how the optical features are influenced by the ionic side chains. The combination of optical absorption and light scattering reveals that the formation of emissive aggregates is favoured in low dielectric constant solvents, in particular for the structures containing cationic (tetraalkylammonium and pyridinium) functionalities. A lower tendency to aggregate is found for CPEs with anionic sulfonate groups. The aggregated species absorb at longer wavelengths and exhibit higher emission quantum yields, relative to better solvated chains. This information allows one to better predict properties, especially for less-studied systems with electron-deficient conjugated backbones.

Conjugated polyelectrolytes (CPEs) are defined by a chemical structure containing a π -conjugated backbone with pendant ionic functionalities.^[1] The π -conjugated backbone provides CPEs with the same type of electronic delocalization found in neutral conjugated polymers, while the pendant charged side chain end groups enable processability from environmentally-friendly, highly polar solvents, such as water and methanol. This feature allows one to fabricate multilayer electronic devices in combination with neutral polymers, which are typically soluble in less polar solvents. CPEs have thus found useful applications in a variety of organic electronic devices, including solar cells,^[2] field-effect transistors,^[3] light-emitting diodes,^[4] and thermoelectric generators.^[5]

Conjugated polymers consisting of electron-deficient heterocyclic units, such as perylene bisimides, diketopyrrolopyrrole,^[7] benzothiadiazole,^[8] and benzotriazole, have received special attention within the context of *n*-type charge transport in organic electronic devices.^[10] CPEs with electron-deficient backbones remain, however, relatively rare.^[11] Understanding the optical properties of electron-deficient CPEs is a necessary basic knowledge that should enable subsequent rational implementation in various technologies. Optical behaviour is anticipated to be dependent on the chain aggregates in media of different polarity,^[12] which is difficult to predict based only on the consideration of molecular structures.

Herein, we report the synthesis of CPEs with electron-deficient benzotriazole (BTz) repeat units by using Pd-catalyzed Yamamoto polymerization^[13] of monomers with ionic side chains. The benzotriazole-based conjugated backbone is of particular interest^[14] because polymers with BTz repeat units comprise a class of thermostable,^[15] *n*-type semiconductors with relatively strong electron affinity.^[16] Dynamic light scattering (DLS), optical absorption spectroscopy, and photoluminescence (PL) spectroscopy were used to probe how aggregation in different media modulate the optical properties of these materials.

There are only a few examples for the preparation of CPEs with electron-deficient conjugated backbone.^[11] CPE synthesis most commonly involves conversion of neutral functional groups (i.e. alkylhalides) in non-ionic conjugated polymers to ionic functional groups. Pd-catalysis^[7] has been frequently used in the preparations for precursor homopolymers with electron-rich monomers and D π A polymers consisting of alternating electron-rich and electron-deficient units.^[18] This type of synthetic approach is less effective in the preparation of homopolymers containing only electron-poor structural units.^[9] Additionally, quantitative conversion of neutral functional groups on the precursor polymer chain into ionic units provides the additional challenge to find the right solvent, since the characteristics of the macromolecules change from soluble in non-polar solvents to miscible in high dielectric media.

Scheme 1. Synthesis of PBTz-Br, PBTz-PyrBr and PBTz-TMABr containing the same benzotriazole conjugated backbone, but with 6-bromohexyl, pyridinium, and tetraalkylammonium side chains, respectively (COD = 1,5-cyclooctadiene, 2,2'-bpy = 2,2'-bipyridyl, Ni(COD)₂ = bis(1,5-cyclooctadiene)nickel(0))

The chemical structures and synthesis of three polymers, PBTz-Br, PBTz-PyrBr and PBTz-TMABr are outlined in Scheme 1. These polymers contain the same benzotriazole conjugated

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Supporting information for this article is given via a link at the end of the document.

backbone, but differ with respect to the side chains: 6-bromohexyl (PBTz-Br), pyridinium (PBTz-PyrBr), and tetraalkylammonium side chains (PBTz-TMABr). Monomer 1 for PBTz-Br was synthesized from the commercially available dibromobenzothiadiazole in three steps, including reduction (NaBH_4 in EtOH), annulation (NaNO_2 in $\text{CH}_3\text{CO}_2\text{H}$),^[6] and alkylation ($\text{BrC}_6\text{H}_{12}\text{Br}$, $t\text{-BuOK}$, MeOH). However, Yamamoto polymerization of 1 provided PBTz-Br, which precipitated out of solution as the reaction proceeded. PBTz-Br exhibits low molecular weight ($M_n = 7.2$ kDa, $\bar{D} = 2.0$) as indicated by gel permeation chromatography (GPC) in CHCl_3 using a calibration versus polystyrene standards. In addition, PBTz-Br has insufficient solubility in common organic solvents to carry out subsequent chemical functionalization of the side chains.

To circumvent the complications encountered with PBTz-Br, compound 1 was instead converted to the ionic monomers 2 and 3 in nearly quantitative yield by treating 1 with pyridine and trimethylamine, respectively.^[18,19,20] Ni-catalyzed Yamamoto polymerizations of 2 and 3 independently provide two cationic CPEs with different pendant ionic functionalities in good yields (PBTz-PyrBr: 88% and PBTz-TMABr: 92%). After polymerization, the products were precipitated in CHCl_3 , filtered, washed with CHCl_3 , acetone, and hexanes by Soxhlet extraction, followed by further purification via dialysis in water for one week. The molecular weight cut off of the dialysis membrane was 3 - 5 kDa. The number average molecular weight (M_n) and dispersity ($\bar{D}$) were characterized by GPC in water versus poly(ethyleneglycol) standards. The GPC studies provided unexpectedly large M_n values (PBTz-PyrBr: $M_n = 112$ kDa, $\bar{D} = 3.2$; PBTz-TMABr: $M_n = 157$ kDa, $\bar{D} = 1.5$). The higher molecular weight of PBTz-TMABr, would appear to be due to a stronger tendency of polymer chains to aggregate, compared to PBTz-PyrBr chains, a feature that is subsequently discussed within the context of light scattering experiments.^[21]

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive spectroscopic technique used to determine the elemental compositions of materials. The XPS spectra of PBTz-Br, PBTz-PyrBr and PBTz-TMABr showing N 1s region are provided in the Supporting Information. The peak fitting curves match well with the chemical structures. Specifically, the spectrum of PBTz-Br shows two peaks at 401.4 eV and 403.0 eV with an integrated ratio of 2:1, consistent with the two chemically distinct nitrogen atoms in the benzothiadiazole unit. Both PBTz-PyrBr and PBTz-TMABr exhibit an extra peak at higher binding energy, corresponding to the nitrogen atoms on the pendant pyridium and tetraalkylammonium functional groups, respectively. The ratios of the three different nitrogen atoms are 2:1:1 for the two CPEs, which are in good agreement with the expected stoichiometry.

Solution absorption spectra of PBTz-PyrBr and PBTz-TMABr in three different solvents (H_2O , $\text{H}_2\text{O}:\text{MeOH}$, and MeOH) are provided in Figure 1. The three polymers exhibit a band in the wavelength range characteristic of polymers containing a π -conjugated backbone.^[9,22] In the same solvent, the absorption maxima (λ_{max}) of PBTz-TMABr consistently appear at longer wavelengths relative to those of PBTz-PyrBr.

CPEs reported in the literature typically exhibit a red-shift in absorption with increasing solvent polarity. In contrast, the λ_{max} of both PBTz-PyrBr and PBTz-TMABr blue shift as the solvent polarity is increased (polarity: $\text{H}_2\text{O} > \text{MeOH}$). These changes lead to an obvious darkening of the solutions with decreasing solvent polarity (see Supporting Information). Such negative

solvatochromic effects suggest a more pronounced tendency to form aggregates of CPE chains in solvents of lower polarity.^[24]

Figure 1. The UV/Vis absorption of PBTz-PyrBr and PBTz-TMABr solutions in various polar solvents with the fixed concentration of 0.0167 mg/mL.

Dynamic light scattering (DLS) was used to estimate the particle size through analysis of the hydrodynamic radii (R_{hyd}) of PBTz-PyrBr and PBTz-TMABr in the same solvent systems used for absorption measurements.^[25] Both PBTz-PyrBr and PBTz-TMABr show two different peaks in the autocorrelation function, which correspond to two R_{hyd} values for each material. These values are provided in Table 1. Each polymer exhibits R_{hyd} on the order of nanometers and several hundred nanometers (see Supporting Information). This bimodal distribution suggests the presence of both small and large sized aggregates in solution. For bimodal distributions, it is necessary to examine both R_{hyd} and the peak percent by mass. This latter factor describes the relative proportion of the two components based on mass and thereby allows comparisons of similar samples to be made between multimodal distributions.

A comparison of the larger aggregates allows us to observe trends with changes in solvent polarity. As the solvent polarity decreases, for both PBTz-PyrBr and PBTz-TMABr, the peak percent by mass of the larger aggregates increases. This is consistent with the observation that the absorption maxima redshift as the solvent polarity decreases. PBTz-TMABr consistently exhibits larger R_{hyd} with higher peak percent by mass in various solvents than PBTz-PyrBr. This fact is consistent with both the GPC analysis and the absorption measurements. Since these CPEs are highly soluble in water, aggregation is likely mediated by the electrostatic pairing of the ionic functionalities in lower dielectric media.

Table 1. The average hydrodynamic Radii, the percentage peak by mass and fluorescence quantum yield (Φ) of PBTz-PyrBr and PBTz-TMABr in various solvents.

Solvents	Average hydrodynamic Radii (nm)		Fluorescence quantum yield Φ	
	PBTz-PyrBr	PBTz-TMABr	PBTz-PyrBr	PBTz-TMABr
H ₂ O	285 (24%) ^[a]	369 (74%) ^[a]	11%	16%
H ₂ O:MeOH (1:1)	370 (68%) ^[a]	409 (78%) ^[a]	16%	25%
MeOH	345 (76%) ^[a]	380 (88%) ^[a]	53%	61%

[a] Percentage of the larger aggregate.

Fluorescence spectroscopy can provide an additional handle for understanding polymer chain aggregation. Interchain aggregation between conjugated polymer chains is known to occur as a function of solvent, resulting in decreased fluorescence intensity due to self-quenching.^[23,26,27] The solution fluorescence spectra of PBTz-PyrBr and PBTz-TMABr (see Supporting Information) show the opposite trend. The emission maxima (λ_{em}) of the two CPEs are located at similar values in H₂O (583 nm (PBTz-PyrBr), 585 nm (PBTz-TMABr)) and 1:1 H₂O:MeOH (560 nm (PBTz-PyrBr), 575 nm (PBTz-TMABr)), but a redshift in λ_{em} , with an increase of emission intensity at λ_{em} , and better definition of the vibronic features are observed in MeOH.

Scheme 2. Synthesis of PBTz-Na with anionic, sulfonated side chains.

Changes in fluorescence can be quantified by determining the fluorescence quantum yields (Φ). Rhodamine 101 salt in MeOH was chosen as the reference.^[28] The resulting values of Φ are provided in Table 1, and the hydrodynamic radii are provided in the Supporting Information. PBTz-PyrBr and PBTz-TMABr solutions show more intense fluorescence as the polarity of solvent decreases. Specifically, the calculated Φ values of PBTz-PyrBr and PBTz-TMABr increase from 11% and 16% in water to 53% and 61% in MeOH, respectively. These results,

combined with the absorption and DLS data, indicate increased emission upon aggregation.^[29] Such aggregate-induced emission characteristics^[30] have the potential to include these CPEs in the array of materials used in aggregation induced emission enhancement technologies.^[31]

Figure 2. UV/Vis absorption, fluorescence quantum yield (Φ) and PL intensity of PBTz-Na in H₂O.

To probe the impact of the choice of ionic functionalities, the anionic, sulfonate-terminated CPE, PBTz-Na, was synthesized. The anionic monomer **4** was synthesized in two steps from benzotriazole as shown in Scheme 2.^[18,32] Yamamoto coupling reaction of **4** provided PBTz-Na in 61% yield. Although the backbone of PBTz-Na is identical to those of PBTz-PyrBr and PBTz-TMABr, the number of methylene units that link the ionic groups is shorter by two due to restrictions in synthetic access. Absorption and fluorescence quantum yield measurements of PBTz-Na in H₂O and DMF:H₂O (1:1) solutions are provided in Figure 2 and Figure 3, respectively. Unexpectedly, the anionic-PBTz-Na shows an opposite trend in optical features relative to cationic-CPEs. Specifically, for PBTz-Na one finds that λ_{max} shifts from 449 nm in H₂O to 439 nm in (1:1) DMF:H₂O. DLS results under similar conditions to those carried out with the cationic counterparts, provided in the Supporting Information, indicate a higher contribution to R_{hyd} from larger particles in H₂O (29 %, 98 nm) than in DMF:H₂O (7 %, 103 nm). However, the calculated Φ value of PBTz-Na in H₂O (8%) is lower than solution in DMF:H₂O (1:1) (16%). These results indicate the absence of emissive aggregate in PBTz-Na solutions, or the fluorescence is sufficiently quenched by H₂O.

We found that 1:1 DMF:H₂O (1:1), a less polar solvent mixture than H₂O, can dissolve all the CPEs and can thereby be used to carry out direct comparisons. The resulting absorption spectra and calculated Φ values are provided in Figure 3. Unlike many other CPEs reported in the literature, PBTz-Na, PBTz-PyrBr, and PBTz-TMABr reveal dissimilar optical properties despite containing the same conjugated backbone. The λ_{max} values of the cationic PBTz-PyrBr and PBTz-TMABr are located at longer wavelengths than that of the anionic PBTz-Na. Among these CPEs, CPE-TMABr exhibits the most red-shifted λ_{max} , possibly due to the high degree of aggregation based on DLS results. The larger R_{hyd} of these CPEs in DMF:H₂O (1:1) at [CPE] of 0.0167 mg mL⁻¹ are shown as follows, PBTz-Na, 103 nm; PBTz-PyrBr, 227 nm; and PBTz-TMABr, 145 nm. These

comparative results indicate that the side groups of these CPEs impacts properties beyond solubility in polar media. Molecular aggregations in solvents induced by the cationic side chains seem to be more significant than for the anionic counterpart, although the impact by the shorter tether group in PBTz-Na, which should render the material more soluble in H₂O cannot be extracted from these data.

Figure 3. a) The UV/Vis absorbance spectra, b) fluorescence quantum yield (Φ) and PL intensity of PBTz-Na, PBTz-PyrBr and PBTz-TMABr in DMF:H₂O (1:1) at the same concentration (0.0167 mg mL⁻¹).

In conclusion, we have synthesized three CPEs with poly-benzotriazole conjugated backbones and different side chains via Yamamoto coupling polymerization directly from the ionic

monomers. The optical properties and multi-chain aggregation in this series of polymers were investigated. Different ionic side chains (pyridinium, tetraalkylammonium vs. sulfonate-terminated) impact how the materials aggregate in solutions, as observed in absorption, emission, and DLS measurements. CPEs with tetraalkylammonium side chains exhibit the most red-shifted absorption maxima, the largest aggregate size, and the highest fluorescence quantum yield (up to 61% in MeOH). With the sulfonated species PBTz-Na one finds a low driving force toward aggregation. Correlating the light scattering results and optical properties of these CPEs as a function of solvent reveals that the negative solvatochromic effects observed for the cationic CPEs is due to increased aggregation in lower dielectric media. Our current thinking is that the interchain angles within the backbone may be minimized in the aggregate structures, thereby increasing delocalization and decreasing the band gap.^[33] An alternative explanation arises from consideration that the tighter arrangement of chains in the aggregate could yield interchain delocalization. Another relevant future line of inquiry concerns to what degree anionic functional groups may interact more strongly with an electron deficient backbone, relative to cations. Despite these uncertainties, the study provides insight into the role of structural modification of pendant ionic functionalities on the optoelectronic properties of the CPEs and thereby is relevant within the context of applications in different sensory and device technologies, particularly when considering how to deposit layers from solution.

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Keywords: conjugated polyelectrolytes • aggregate • solvatochromic effect • organic semiconductor emission • polymer

COMMUNICATION

The optical properties of homo-conjugated polyelectrolytes based on benzotriazole backbone were investigated, and the effects from different charged side chains and solvents were discussed.

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Page No. – Page No.

Optical Properties of Benzotriazole-Based Conjugated Polyelectrolytes

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