# Practical synthesis of an amphiphilic, non-ionic poly(*para*-phenyleneethynylene) derivative with a remarkable quantum yield in water†

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**Aggregation of poly(*para*-phenyleneethynylene)s is efficiently suppressed by introduction of branched oligoethyleneglycol side chains rendering the polymer backbone, which is readily obtained using an $A_2 + BB'$ polycondensation protocol, soluble and highly emissive in aqueous environments.**

The detection of biologically relevant analytes can be achieved in high sensitivity using sensory materials based on conjugated organic polymers.[1] *In situ* sensing methods operating under ambient conditions necessitate the synthesis of water-soluble, emissive or (semi)conducting polymers that has proven to be challenging due to the high tendency of conjugated hydrophobic backbones to aggregate in aqueous environments, thereby rendering the materials insoluble and leading to detrimental emission quenching. Several strategies have been developed to introduce water-solubility and overcome aggregation, for instance in poly(*para*-phenyleneethynylene)s (P*p*PE)[2] including the use of ionic[3] and polyhydroxylated[4] substituents as well as site isolation utilizing branched[5] and linear[6] polymer side chains. Here, we present a practical synthetic route to a non-ionic, non-protic, amphiphilic P*p*PE derivative, which displays both respectable solubility and an exceptionally high fluorescence quantum yield in water.

Recently, we have reported on an *in situ* deprotection–coupling Sonogashira–Hagihara polycondensation protocol for the synthesis of lengthy and defect-free amphiphilic poly(*meta*-phenyleneethynylene)s.[7,8] The aim of the present work was to extend our newly developed $A_2 + BB'$ polycondensation method[9] to the synthesis of amphiphilic, site isolated P*p*PEs from readily available monomer building blocks. In order to efficiently suppress aggregation arising from ionic substituents and their associated counter-ions or from hydrogen-bonding protic residues, two branched oligoethyleneglycol (OEG) side chains[10,11] were introduced at every repeat unit. The polar, non-ionic and non-protic side chains should render the backbone soluble in a variety of media including water and provide a chemically inert scaffold.

Monomer synthesis was accomplished by alkylation of 2,5-diiodohydroquinone **1**[12] with branched OEG tosylate **2**[10] (Scheme 1).† Applying our $A_2 + BB'$ polycondensation protocol,[7] involved stoichiometric reaction of diiodide **3** ($A_2$ monomer) with trimethylsilylacetylene **4** (TMSA, $BB'$ monomer) in the presence of 5 mol% freshly prepared $Pd(PPh_3)_4$ catalyst, 10 mol% CuI cocatalyst, 6 equiv. of diazabicyclo[5.4.0]undec-7-ene (DBU), and 10 equiv. of water in acetonitrile at room temperature for 3 d. The commercial availability of TMSA and the rapid synthetic access to monomer **3** render this synthesis of polymer **5** highly practical. Polymer **5** was obtained in 83% isolated yield after single precipitation into diethyl ether and extraction to remove residual inorganic impurities. GPC analysis[13] of polymer **5** indicated reasonable degrees of polymerization (DP $\approx$ 30) and polydispersities (PDI $\approx$ 2.0) typical for polycondensation processes. $^1$H-NMR showed successful incorporation of the monomer repeat units into polymer **5** with no discernible end-groups, while in $^{13}$C-NMR no diacetylene defects could be detected.[7] Polymer **5** displayed good solubility in a wide range of different solvents, most importantly in water (0.7 mg mL$^{-1}$).

UV–vis spectra of polymer **5** in various organic solvents exhibit typical absorption maxima $\lambda_{max}$ = 437–441 nm (Fig. 1, Table 1) suggesting that the full effective conjugation length has been reached.[8] In water however, a considerable hypsochromic shift ($\lambda_{max}$ = 427 nm) was observed, similar to the reported case of an ionic P*p*PE.[3d] Since the data suggest a negligible polarity effect of the medium, water seems to cause certain structural reorganization and/or induce some degree of aggregation, both potentially distinguishable by emission spectroscopy. Corrected and normalized fluorescence spectra of polymer **5** in the same solvents were qualitatively similar yet showed distinctly different photoluminescence efficiencies (Fig. 1). Calibration using quinine sulfate as reference standard[14,]† yielded the corresponding quantum yields (Table 1) that do not scale with solvent polarity. Interestingly, chloroform being a good solvent for both polar side chains and non-polar core leads to less intense emission than acetonitrile which preferentially solvates the polar corona. Increasing solvent polarity from acetonitrile *via* methanol to water caused a decrease in photoluminescence efficiency.

In order to span the entire emission intensity range, the solvent was systematically varied from acetonitrile to water (Fig. 2). Fluorescence emission was found to decrease with increasing amount of water in a non-linear fashion (inset Fig. 2). It is important to note that the shape of the fluorescence band did not change considerably,† indicating almost negligible aggregation that would have causes a broad, red-shifted, excimer-like emission. This finding is furthermore supported by UV–vis absorption measurements on annealed films that did not show any sign of aggregation, such as narrower and bathochromically shifted absorption bands.[8,]† Therefore, the observed solvent effects are most likely due to different solvation of the amphiphilic polymer, causing structural reorganization of the backbone chromophores in polar/aqueous environments.

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† Electronic supplementary information (ESI) available: synthesis and characterization details. See http://www.rsc.org/suppdata/cc/b4/b413616k/

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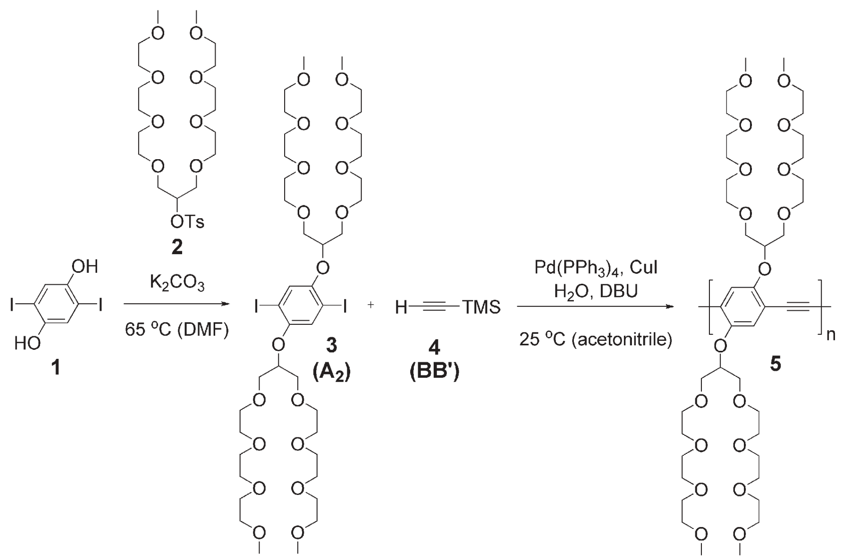

**Scheme 1** Synthesis of water-soluble P*p*PE derivative **5** from readily available monomers **3** and **4** *via* an $A_2 + BB'$ polycondensation route.

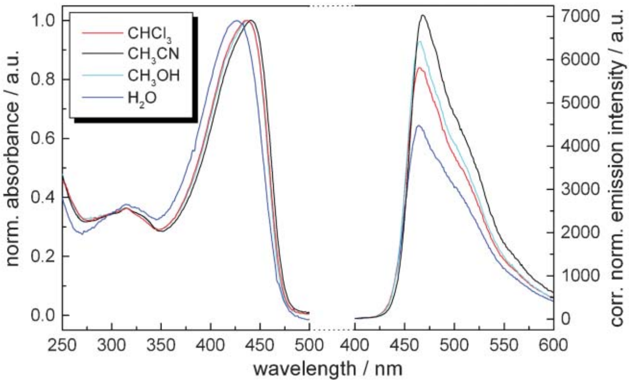

**Fig. 1** UV–vis absorption and fluorescence emission spectra of polymer **5** in various solvents (25 °C). Absorption spectra are scaled to the same optical density, while emission spectra are corrected and normalized.

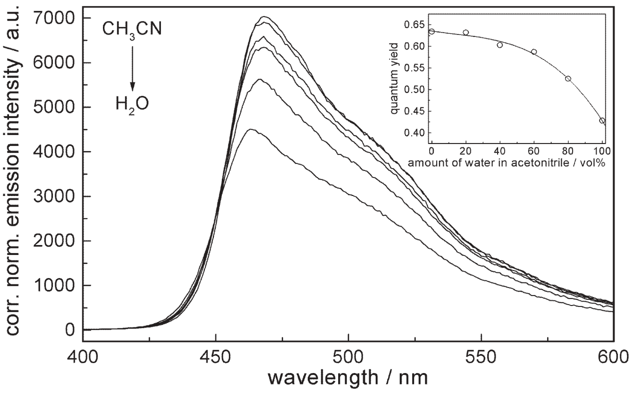

**Fig. 2** Fluorescence emission spectra of polymer **5** in acetonitrile–water solvent mixtures (25 °C). The inset shows the calculated quantum yields as a function of solvent composition (the line obtained from the non-linear least squares fit of the data is included as a guide to the eye).

**Table 1** Absorption and emission characteristics of polymer **5**

| Solvent | $\lambda_{abs}{}^{a}$/nm | $\lambda_{em}{}^{a}$/nm | $\Phi_f{}^{b}$ |
|---|---|---|---|
| Chloroform | 437 | 465 | 0.53 |
| Acetonitrile | 441 | 468 | 0.63 |
| Methanol | 438 | 466 | 0.57 |
| Water | 427 | 464 | 0.43 |

[a] $\lambda_{max}$ of absorption and emission bands, respectively. [b] Using quinine sulfate as reference standard.[14,†]

In general, the quantum yields in solution are high and even in water, which imposes an enormous hydrophobic effect to drive aggregation, remarkably efficient photoluminescence has been observed. In fact, to the best of our knowledge polymer **5** exhibits by far the highest quantum yield in water ($\Phi_f = 0.43$) of any known P*p*PE derivative (ionic P*p*PEs:[3] $\Phi_f = 0.03$–$0.10$; polyhydroxylated P*p*PE:[4] $\Phi_f = 0.07$). This exceptional behavior is attributed to the significant steric demand of the employed side chains that are attached twice per repeat unit and place their branch points in close proximity to the backbone. Thereby, an efficient shielding of the P*p*PE core is achieved as indicated by molecular mechanics calculations.† In related poly(*para*-phenylene)s, these branched OEG side chains were found to efficiently prevent aggregation in the solid state.[10] In addition to the chosen substituents, the observed high quantum yields can be explained by the absence of diacetylene defects due to our method of polymer preparation.[7,3a]

The utility of our $A_2 + BB'$ polycondensation approach[7] arising from its practicality due to rapid monomer availability as well as the quality of the obtained materials has successfully been demonstrated by the synthesis of a chemically inert, water-soluble, and highly emissive P*p*PE derivative, which could potentially be used in ultrasensitive biosensing.[1,15] In this context it is important to note that in aqueous solutions of polymer **5**, variation of several other parameters, such as addition of metal cations ($Li^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Zn^{2+}$) and changing pH (4–11) did not lead to a noticeable change in the qualitative and quantitative absorption and emission characteristics. The approach described should be generally applicable to the design of conjugated polymers both soluble and emissive in aqueous environments.

Ongoing studies in our laboratories include detailed characterization in the solid state to obtain structural insight into the remarkable ability of the branched OEG side chains to efficiently encapsulate and solubilize the hydrophobic P*p*PE backbone in water as well as time-resolved fluorescence studies to deduce conformational and aggregation behavior in aqueous solution. Furthermore, we are currently exploring the alignment of such polymers on templating substrate surfaces.[16]

Note added in proof: after submission of this manuscript, Jiang, Aida, and coworkers reported on a dendronized, polyanionic P*p*PE derivative with an extraordinarily high fluorescence quantum yield of 57% in water.[17]

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