Click-chemistry as an efficient synthetic tool for the preparation of novel conjugated polymers†

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The Cu(I)-catalysed 1,3-dipolar "click" cycloaddition is utilised as an efficient reaction for the preparation of novel fluorene-based conjugated polymers.

Conjugated polymers[1] have been extensively explored in the past decades triggered by their potential application in various opto-electronic devices, including light-emitting diodes, organic lasers, thin-film transistors and nonlinear optical devices.[2] The photophysical and conductive properties of these types of polymers depend on the molecular structure as well as the morphology of the material in the solid state.[3] Although several synthetic routes to prepare conjugated polymers have been explored,[4] alternative synthetic routes that lead to conjugated polymers with new molecular structures in a straightforward and practical manner might lead to new functional materials that can be used to construct devices. To obtain polymers of sufficient length and purity these synthetic procedures should be highly effective and selective. Sharpless and co-workers recently introduced click-chemistry as a new way of categorising organic reactions that are modular in nature, highly efficient, mild and selective, and require only simple reaction and work-up procedures.[5] From the list of click reactions, we were especially interested in the Cu(I)-catalysed 1,3-dipolar "click" cycloaddition between azides and alkynes, since the resulting 1,4-disubstituted 1,2,3-triazoles can be part of conjugated polymers and are highly stable units.[6] Besides various applications in life-sciences,[7] this 1,3-dipolar cycloaddition has recently be explored as an efficient synthetic tool for various targets including dendrimers and dendronized polymers,[8] hyperbranched polymers,[9] and chromophores[10] but so far it has not been applied for the synthesis of conjugated polymers. In this communication we show that the 1,3-dipolar cycloaddition is an excellent reaction for the preparation of novel triazole-linked conjugated polymers.

We were interested in conjugated polymers based on fluorene because they are attractive for display applications owing to their pure blue and efficient electroluminescence.[11] We therefore prepared 2,7 di-azido-fluorene monomers with C6 (**1a**) and C12 (**1b**) tails at the 9-position to improve both the solubility and stability of the polymers. 2,5-Diethynylpyridine **2**, 1,4-diethynyl benzene **3**, and 2,7-diethynyl-9,9-dihexyl-fluorene **6** were prepared and used as co-monomers for the click-polymerisation reactions.

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† Electronic supplementary information (ESI) available: experimental procedures for the synthesis of **1–6** and **P1–P6**. See http://dx.doi.org/10.1039/b507776a
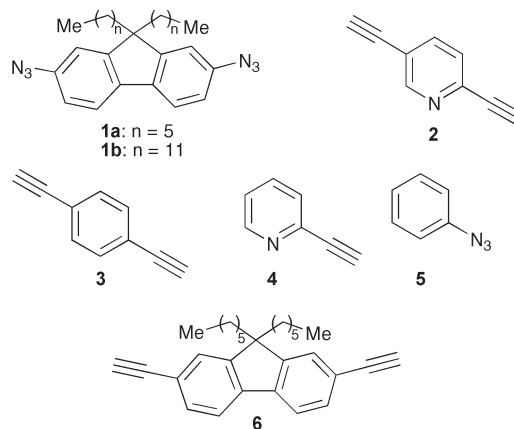
The mono-functionalised building blocks **4** and **5** were prepared and used for the termination of the polymerisation reaction. All monomers **1–6** were synthesised as described in the literature or *via* straightforward procedures (see supporting information).

In a first approach to form conjugated polymers *via* click-chemistry we mixed fluorene building block **1a**, containing two hexyl substituents at the *9* position of the fluorene unit, with building block **2** in a degassed THF/MeCN solution. The reaction was started by the addition of Cu(II)/Cu(0) and tris-benzyltriazoylamine as a ligand.[12] A reaction took place as was evident from the formation of a precipitate, however, the isolated material (**P0**) was insufficiently soluble for detailed characterisation.

A test reaction showed that the polymer formed after a click reaction between **1b**, a fluorene based monomer bearing two dodecyl substituents, and **2** shows good solubility in THF. The polymer formation (room temperature) was monitored in time starting from the monomers **1b** and **2**. After six hours the polymerisation reaction was already progressed significantly as was evident from SEC analysis (**P1**, Table 1). Interestingly, we observed three separate peaks with molecular weights of 2.6×10^3, 3.9×10^3, 7.9×10^3 corresponding to 4, 6 and 12 repeating units, respectively. In addition, some polymers with higher molecular weight could be detected. After 24 hours polymer **P2** was obtained and still some of these oligomers were visible. At this time over 90% of the material **P2** consisted of polymers with molecular weight of 31×10^3 (46 repeating units). After 170 h (**P3**) SEC analysis only revealed polymers with an average molecular weight of 48×10^3 (73 repeating units). The fact that the reaction still proceeds after such a long reaction time shows that the Cu(I)-catalysed 1,3-dipolar "click" cycloaddition is very robust

Table 1 Polymerisation reactions performed under various conditions and the polymer characteristics

| Polymer (building blocks used)	Reaction time	Reaction Temperature	$M_w{}^a$ (10^3)			PDI			$\Phi_F{}^{cde}$ (%)		λ_{Abs} (10^{-2})	$\lambda_{Abs\ Max}$ (nm)^c	$\lambda_{Em}{}^c$	
P1 (1b + 2)	6 h	25 °C	2.6	3.9	7.9	1.01	1.01	1.13						
P2 (1b + 2)	24 h	25 °C	31			2.31			23		9.13	340	360	379
P3 (1b + 2)	170 h	25 °C	48			1,93			23		9.07	340	360	379
P4 (1b + 2)	65 h	−10 °C	59			2.86			53		8.98	340	364	382
P5 (1b + 3)	170 h	25 °C	396	60^b		1.23	3.14		55		8.72	340	359	377
P6 (1b + 6)	170 h	25 °C	13			1.61			42^f		8.61	361	373	391

^{a} Molecular weight determined by SEC in THF, based on polystyrene standards ^{b} SEC in CH$_2$Cl$_2$ ^{c} In THF ^{d} Reference, anthracene in EtOH ^{e} Excitation at 340 nm ^{f} Excitation at 357 nm

and therefore ultimately suited for this type of polymerisation reactions.

All subsequent polymerisation reactions were performed starting from **1b** and various other monomers leading to polymers **P4–P6**. The polymerisation reactions were performed in THF/MeCN mixtures (9:1), and initiated by the addition of the copper catalyst. The polymerisation reactions were stopped at both ends of the growing chain by the addition of an excess of stopper **5** and, after 2 hours, stopper **4**. This procedure should result in polymers with well-defined and unreactive end-groups. Copper was removed from the reaction mixture *via* an extensive extraction procedure using N,N,-diethylcarbamodithioic acid as copper salt scavenger. Polymers were isolated and purified by precipitation procedures using methanol en dichloromethane to remove the side-product resulting from the reaction between stopper compounds **4** and **5**. Polymers were analysed with analytical SEC, NMR, UV-vis and fluorescence spectroscopy. The ^{1}H NMR spectra of the polymers showed the presence of the expected repeating unit in the proper molar ratio. ^{1}H NMR spectroscopy as well as SEC analysis indicated that after the washing procedure no starting material or side-product as a result of coupling between **4** and **5** was left in the samples. ^{13}C NMR spectroscopy of **P6** revealed that the click reaction was highly selective since signals due to homo-coupled acetylene were not observed.

The reaction is sufficiently fast to proceed at lower temperatures. Click-polymerisation at −10 °C at slightly more dilute conditions gave polymers of high molecular weight (59×10^3) after 65 h, with a slightly larger polydispersity (**P4**). Interestingly, the reaction mixture had a more transparent appearance at this low temperature. We also performed click-polymerisations with monomers **1b** and **3**, to give a bimodal distribution of polymers with average molecular weights of 60×10^3 and 396×10^3, respectively (**P5**). The difference in polymerisation behaviour between **2** and **3** is not understood yet, but the presence of the pyridyl-triazole unit in the polymer **P4** is likely the origin of the difference. The click-polymerisation of building blocks **1** and **6** resulted in medium-sized polymers (**P6**, molecular weight 13×10^3, 14 repeating units, Scheme 2) based on two fluorene moieties per repeating unit. In the GPC trace we also observed peaks of smaller oligomers. In this case it is likely that the difference in polymerisation behaviour is due to a difference in reactivity of the monomers.

We also studied the photophysical properties of the polymers. The absorption spectra are essentially a superposition of that of the monomers used, indicating that there is no ground state interaction between the different moieties of the polymer. The photoluminescence spectra show that the emission is dominated by
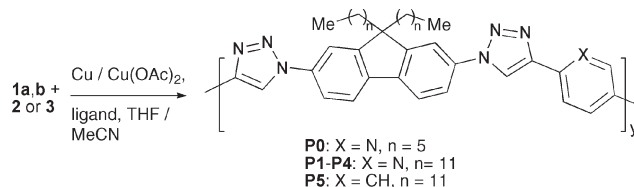
Scheme 1 Copper(I)-catalysed 1,3-dipolar cycloadditions between building blocks **1** and **2** or **3** forming fluorene-based triazole-linked conjugated polymers.
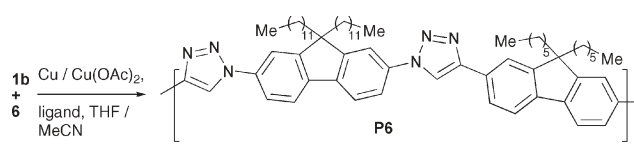
Scheme 2 Cu(I)-catalysed 1,3-dipolar cycloadditions between building blocks **1b** and **6** resulting in a polymer with two fluorene units per repeating unit.

the fluorene unit as the characteristic bands around 360 and 380 nm are observed for all polymers. The quantum yields observed in solution (THF) are high. **P2**, **P3** give identical quantum yields, indicating that the polymer length (between 31×10^3 and 48×10^3) does not influence the fluorescent properties of the material in solution. Interestingly, the effect of polymerisation temperature has a large impact on the quantum yield of the polymer obtained. **P4**, produced at −10 °C has a quantum yield that is roughly twice as high (53% compared to 23%). This remarkable result is probably a consequence of the absence of side-reactions at this low temperature. The polymers **P5** and **P6** also show higher quantum yields then that of **P2**, but a direct comparison is not appropriate since different building blocks have been used.

Both the UV-vis and fluorescence spectra indicate that in the present polymers there is poor electronic communication between the fluorene units. Preliminary cyclovoltametric measurements on a model compound consisting of two pyridyl-triazole units bridged by a fluorene unit (the product between **1a** and **4**) indeed showed only one two-electron reduction at −1.86 V also pointing at a poor communication. Interestingly, no oxidation was observed, suggesting that the present materials might be useful as conductive materials.

In conclusion, we have shown that the Cu(I)-catalysed 1,3-dipolar "click" cycloaddition between azides and alkynes, is a new and promising tool for the synthesis of conjugated polymers. The novel polymers obtained, linked *via* 1,4-disubstituted 1,2,3-triazole

units, have interesting luminescent properties that will be studied in detail in due time. Polymers of type **P1–P4** are of special interest since bipyridine type ligands are incorporated in the polymer, enabling the preparation of transition metal complexes of this material. In addition, the broad applicability of the click reaction[5–9] makes these new polymers nice candidates to prepare novel biohybride materials. Currently, the potential of these metallo-conjugated polymers for the construction of phosphorescent emitting materials as well as novel nano-sized catalytic objects is investigated in our laboratories.

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