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Cu-catalysed oxidative C–H/C–H coupling polymerisation of benzodiimidazoles: an efficient approach to regioregular polybenzodiimidazoles for blue-emitting materials†

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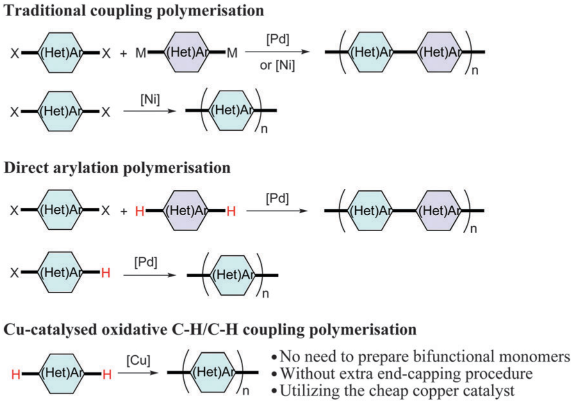
The Cu-catalysed oxidative C–H/C–H coupling reaction of azoles has been used for the first time to develop polymerisation, which provides an efficient method for the preparation of polybenzodiimidazoles. These polymers exhibit high molecular weights, regioregularity, blue-emitting performance and thermal stability.

π-Conjugated polymers have been widely applied in organic optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), organic field-effect transistors (OFETs) and optical sensors.[1] The conventional coupling approaches to π-conjugated polymers, involving transition-metal-catalysed C–X/C–M and C–X/C–X coupling reactions such as Yamamoto,[2] Suzuki[3] and Stille coupling,[4] usually suffer from limitations including tedious synthetic steps to prepare bifunctional aryl halides and/or organometallic monomers, a stoichiometric amount of toxic byproducts, an extra end-capping procedure for removal of terminal halogens or organometallic functional groups, and poor stabilities of some organometallic reagents. Recently, the direct C–H arylation polymerisation *via* the dehydrohalogenative cross-coupling reaction of (hetero)arenes with aryl halides has become widely recognized as an atom- and step-economic method to construct π-conjugated polymers.[5] However, this method still requires the prior preparation of aryl halides as monomers and the end-capping reaction of the halide terminus. Moreover, five-membered heterocyclic halides such as haloimidazoles are often seen as difficult coupling partners.[6] Undoubtedly, the direct oxidative C–H/C–H coupling polymerisation of nonpreactivated (hetero)arenes would be one of the most ideal approaches to π-conjugated polymers, which would eliminate the extra steps associated with the preparation of bifunctional monomers and end-capping reactions. But so far, the transition-metal-catalysed oxidative C–H/C–H coupling polymerisation of azoles still remains unprecedented. Herein, we wish to explore a facile and efficient synthetic strategy to build up π-conjugated polybenzodiimidazoles (PBDI) through Cu-catalysed oxidative C–H/C–H coupling of benzobisimidazoles (Scheme 1).



Scheme 1 Various coupling polymerisations. (Het)Ar = aryl or heteroaryl.

Polybenzimidazoles (PBIs), polybenzodiimidazoles (PBDIs) and their derivatives have been considered as promising materials for the fabrication of optoelectronic devices and proton-exchange membranes.[7,8] Normally, the synthesis of PBDI is implemented by a polycondensation of 1,2,4,5-tetraaminobenzene tetrahydrochloride with oxalic acid.[7c] However, this polycondensation involves drawbacks such as the air sensitivity of substrates and high reaction temperature (180–200 °C). Especially, there is no effective way to control the regioselectivity of polymerisation and, thus, inevitably involving formation of various regiorandom isomers (Scheme 2). Therefore, the development of a highly efficient coupling polymerisation to access regioregular polybenzodiimidazoles, especially starting from relatively stable substrates, is urgently required.

Although Pd-catalysed systems are highly efficient for the C–H activation of azoles,[9] the issues involving the probably ring-opened isomerization of azoles in Pd-systems and removal of the trace Pd from products encourage us to develop a Cu-based catalyst system for the preparation of PBDI.[10] Our recent efforts in direct oxidative C–H/C–H cross-coupling reactions between two different

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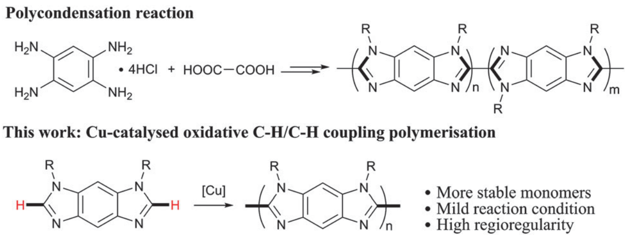
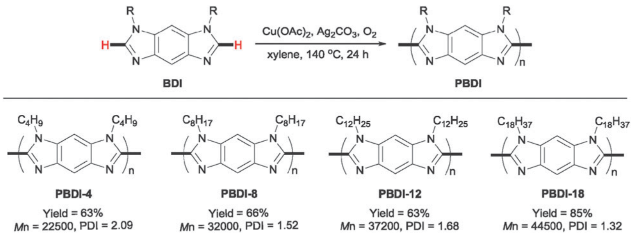


Scheme 2 The polycondensation route and the oxidative C–H/C–H coupling approach to PBDIs.



Scheme 3 Cu-catalysed oxidative C–H/C–H coupling polymerisation of various alkyl substituted BDIs. Reaction conditions: **BDI** (0.25 mmol), $Cu(OAc)_2$ (20 mol%), Ag_2CO_3 (0.5 equiv.), and xylene (1.0 mL) under O_2 (1 atm) at 140 °C for 24 h; the products were obtained by reprecipitation from $CHCl_3$–MeOH after Soxhlet extraction; M_n and PDI were estimated by GPC on polystyrene standards.

azoles have demonstrated that the Cu-based catalyst system is a great substitute for Pd-catalysed systems.[9b,11] Therefore, the initial investigation started with the coupling polymerisation of 1,7-dioctyl-1*H*,7*H*-benzo[1,2-*d*:4,5-*d*]diimidazole (**BDI-8**) in the presence of $Cu(OAc)_2$. Delightedly, the Cu-catalysed coupling polymerisation is apt to occur under the conditions using Ag_2CO_3 and O_2 as oxidants, affording the polymer **PBDI-8** with a moderate number-average molecular weight (M_n = 8100) in 63% yield (soluble fraction in chloroform) (Table S1, entry 1, ESI†). Moreover, reducing the amount of Ag_2CO_3 to 0.5 equivalent led to a higher M_n of 32 000 (PDI of 1.52) with a yield of 66% (Table S1, entry 3, ESI†). But further reducing the loading of Ag_2CO_3 afforded a decreased yield and M_n (Table S1, entry 4, ESI†). Upon increasing the amount of $Cu(OAc)_2$ to one equivalent and without using Ag_2CO_3, only oligomeric products were obtained (Table S1, entries 5 and 6, ESI†). Trace water might retard the catalytic activity of copper and as a result, employing $Cu(OAc)_2{\cdot}H_2O$ as the catalyst resulted in a significant reduction of M_n (Table S1, entry 7, ESI†). Among the solvents screened, xylene proved to be a more efficient solvent (Table S1, entries 3 and 8–11, ESI†). Further prolonging reaction time had no obvious effect on M_n and yield of **PBDI-8** (Table S1, entry 12, ESI†).

The structure of **PBDI-8** was identified by ^1H and ^{13}C-NMR spectroscopy. The ^1H–^1H NOESY and ^{13}C–^1H COSY were also investigated to determine the assignment of the NMR chemical shifts (Fig. S4, ESI†). As shown in Fig. 1, all the signals could be assigned to protons and carbons in the repeating unit, and no signal of the terminal units was observed, which suggested a high molecular weight and regioregularity of the polymer.

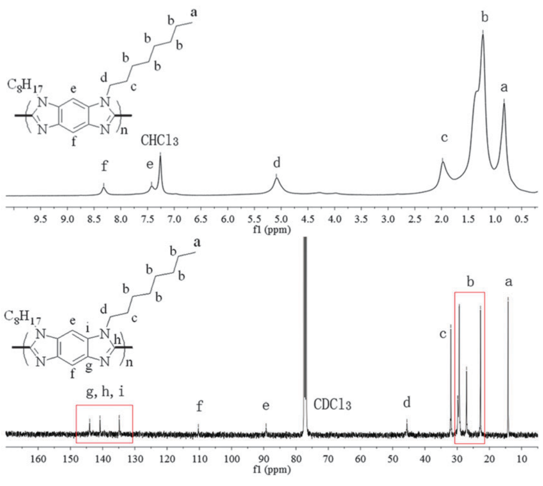
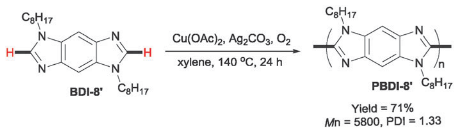


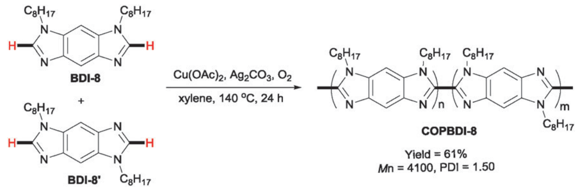
Fig. 1 ^1H- and ^{13}C-NMR spectra of **PBDI-8** in $CDCl_3$.

Utilizing the optimized reaction conditions of polymerisation, dibutyl, didodecyl and dioctadecyl substituted PBDIs were prepared (Scheme 3). All polymers were characterized and identified by GPC, ^1H and ^{13}C-NMR spectroscopies. It was found that the M_n of polymers increased with the increase of alkyl chain lengths. The polymer **PBDI-18** exhibits the most narrow molecular weight distribution (PDI = 1.32) as compared with the other polymers.

The regioisomeric **PBDI-8′** was prepared through the polymerisation of 1,5-dioctyl-1*H*,7*H*-benzo[1,2-*d*:4,5-*d*]diimidazole (**BDI-8′**) under the optimized reaction conditions [eqn (1)]. The regiorandom copolymer **COPBDI-8** was also obtained through the copolymerisation of **BDI-8** and **BDI-8′** using the same reaction conditions [eqn (2)]. Both polymers exhibit small number-average molecular weights as compared with the others. The ^1H-NMR spectrum confirms that **COPBDI-8** consists of two different repeating units.



(1)



(2)

Subsequently, the photophysical properties of these polymers were investigated and the results are summarized in Table 1. The emission spectra and fluorescence images are shown in Fig. 2. The UV-vis spectra of all polymers in $CHCl_3$ give the absorption maxima from 405 to 428 nm (Fig. S1, ESI†). The absorption spectra are gradually red-shifted with the increase of alkyl chain lengths of polymers except for **COPBDI-8**. It is noteworthy that the six polymers exhibit similar emission spectra in the blue-light region with high fluorescence quantum yields in $CHCl_3$ solution. The films of polymers **PBDI-8**, **PBDI-8′**, **PBDI-12** and **PBDI-18** show significantly red-shifted emissions compared

Table 1 Photophysical and thermal properties of polymers

	In $CHCl_3$ solution			In PS film	
Polymer	λ_{abs} (nm)	λ_{em} (nm)	$\Phi_F{}^a$	$\lambda_{em}{}^b$ (nm)	$T_d{}^c$ (°C)
PBDI-4	405	449	0.20	470	352
PBDI-8	411	447	0.28	480, 507, 622	362
PBDI-12	415	448	0.28	521	373
PBDI-18	428	450	0.13	524, 622	404
PBDI-8′	417	458	0.16	522, 622	359
COPBDI-8	406	457	0.21	481, 507	279

[a] Absolute fluorescence quantum yields were measured in $CHCl_3$ at $\sim 10^{-6}$ M with an integrating sphere. [b] Emission maximum in PS film (1 wt%). [c] Detected by TGA analysis and heating rate = 10 °C min^{-1}.

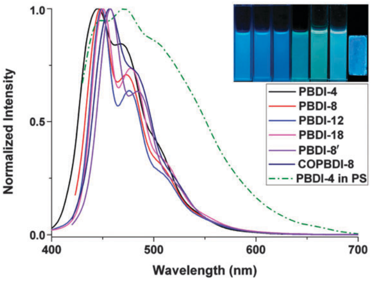


Fig. 2 Fluorescence spectra of polymers in $CHCl_3$. Inset: fluorescence images under UV light (365 nm). From left to right: **PBDI-4**, **PBDI-8**, **PBDI-12**, **PBDI-18**, **PBDI-8′**, and **COPBDI-8** in $CHCl_3$ and **PBDI-4** in PS film (1 wt%).

to those in solution, but the film of **PBDI-4** shows a slightly red-shifted emission, probably because the long-chain alkyls may be conducive to the π–π stacking interaction of the polymer molecules in the solid state. As shown in Fig. 2, under a 365 nm UV lamp, **PBDI-4** emits bright blue fluorescence both in solution and in polystyrene (PS) film, indicating the potentiality for application as a blue-emitting material. Comparing **COPBDI-8** with **PBDI-8** and **PBDI-8′**, **COPBDI-8** in PS film shows a more blue-shifted emission (Fig. S2, ESI†), indicating a less regioregularity and the resulting weaker π–π stacking interaction.

The thermal stabilities of the polymers were evaluated by thermogravimetric analysis (TGA, Table 1, and see Fig. S3, ESI†). Thermal decomposition temperatures (T_d, the temperature at which the compounds lose 5% of their weight) of the five homopolymers **PBDI-4**, **PBDI-8**, **PBDI-8′**, **PBDI-12**, and **PBDI-18** range from 352 °C to 404 °C. However, the copolymer **COPBDI-8** exhibits a lower thermal decomposition temperature, which indicates that the regioregular homopolymers are more thermally stable than the regiorandom copolymer.

In conclusion, we have developed an efficient method to prepare polybenzodiimidazoles *via* Cu-catalysed oxidative C–H/C–H coupling polymerisation of benzodiimidazoles. It is the first time Cu-catalysed oxidative C–H/C–H coupling reaction of azoles has been used to develop polymerisation. The resulting polymers exhibit high molecular weights, regioregularity, blue-emitting performance and good thermal stability. We expect that this efficient strategy would be applied in direct oxidative C–H/C–H coupling polymerisation of other heteroarenes to construct various π-conjugated polymer materials.

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