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ARTICLE TYPE

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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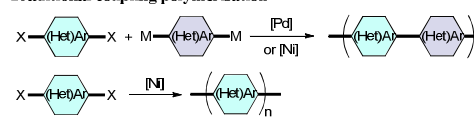
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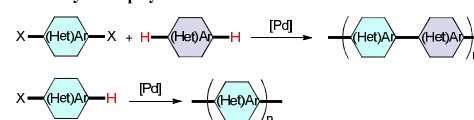
The Cu-catalysed oxidative C–H/C–H coupling reaction of azoles has been used for the first time to develop polymerisation, which provides an efficient method for the preparation of polybenzodiimidazoles. These polymers exhibit high molecular weights, regioregularity, blue-emitting performance and thermal 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 Suzuki³ 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).

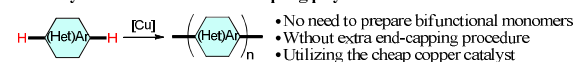
Traditional coupling polymerisation



Direct arylation polymerisation



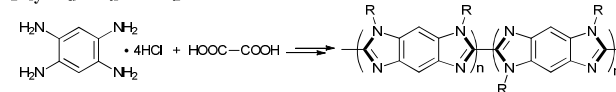
Cu-catalysed oxidative C–H/C–H coupling polymerisation



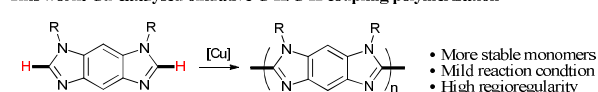
Scheme 1 Various coupling polymerisations. (Het)Ar = aryl or heteroaryl.

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,

Polycondensation reaction



This work: Cu-catalysed oxidative C–H/C–H coupling polymerisation

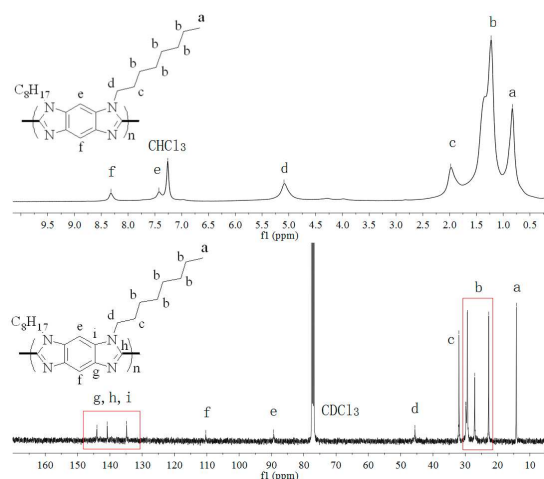


Scheme 2 Polycondensation route and oxidative C–H/C–H coupling approach to PBDIs.

the development of a highly efficient coupling polymerisation to access regioregular polybenzodiiimidazoles, 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 azoles have demonstrated 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'*]diiimidazole (**BDI-8**) in the presence of Cu(OAc)₂. Delightedly, the Cu-catalysed coupling polymerisation is apt to occur under the condition using Ag₂CO₃ and O₂ 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). Moreover, reducing the amount of Ag₂CO₃ to 0.5 equivalent led to a higher *M*_n of 32000 (PDI of 1.52) with a yield of 66% (Table S1, entry 3). But the further reducing the loading of Ag₂CO₃ afforded a decreased yield and *M*_n (Table S1, entry 4). Upon increasing the amount of Cu(OAc)₂ to one equivalent and without using Ag₂CO₃, only oligomeric products were obtained (Table S1, entries 5 and 6). Trace water might retard the catalytic activity of the copper and as a result, employing Cu(OAc)₂·H₂O as the catalyst resulted in a significant reduction of *M*_n (Table S1, entry 7). Among the solvents screened, xylene proved to be a more efficient solvent (Table S1, entries 3 and 8-11). The further prolonging reaction time had no obvious effect on *M*_n and yield of **PBDI-8** (Table S1, entry 12).

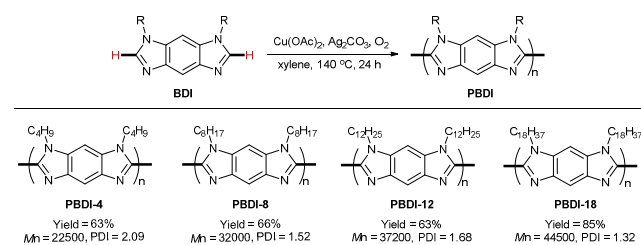
The structure of **PBDI-8** was identified by ¹H and ¹³C-NMR spectra. The ¹H-¹H NOESY and ¹³C-¹H COSY were also investigated to determine the assignment of the NMR chemical shifts (Fig. S4, ESI†). As shown in Fig. 1, all the signals could be assigned to protons and carbons in the repeating unit, and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



40 **Fig. 1** ¹H- and ¹³C-NMR spectra of **PBDI-8** in CDCl₃.

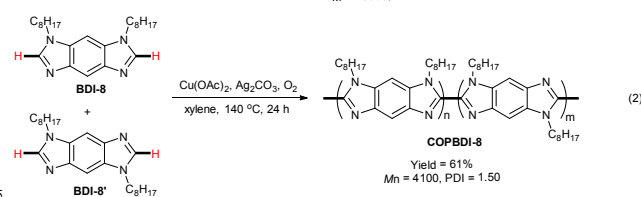
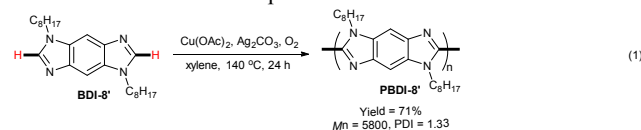
Utilizing the optimized reaction condition of polymerisation, dibutyl, didodecyl and dioctadecyl substituted PBDIs were

prepared (Scheme 3). All polymers were characterized and identified by GPC, ¹H and ¹³C-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.



50 **Scheme 3** Cu-catalysed oxidative C–H/C–H coupling polymerisations of various alkyl substituted BDIs. Reaction conditions: **BDI** (0.25 mmol), Cu(OAc)₂ (20 mol%), Ag₂CO₃ (0.5 equiv), and xylene (1.0 mL) under O₂ (1 atm) at 140 °C for 24 h; The products were obtained by reprecipitation from CHCl₃/MeOH after Soxhlet extraction; *M*_n and PDI were estimated by GPC on polystyrene standards.

The regioisomeric **PBDI-8'** was prepared through the polymerisation of 1,5-dioctyl-1*H*,7*H*-benzo[1,2-*d*:4,5-*d'*]diiimidazole (**BDI-8'**) under the optimized reaction condition [Eq. (1)]. The regiorandom copolymer **COPBDI-8** was also obtained through the copolymerisation of **BDI-8** and **BDI-8'** using the same reaction condition [Eq. (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 repeat units.



65 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 CHCl₃ 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 CHCl₃ solution. The film of polymers **PBDI-8**, **PBDI-8'**, **PBDI-12** and **PBDI-18** show significantly red-shifted emissions than that 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 applications as blue-emitting materials. 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.

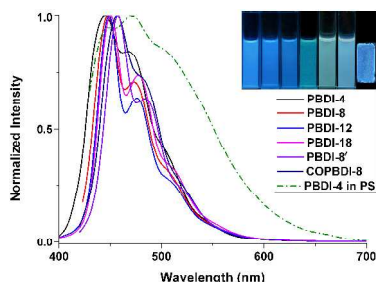


Fig. 2 Fluorescence spectra of polymers in CHCl_3 . Insert: Fluorescence images under UV light (365 nm). From left to right: **PBDI-4**, **PBDI-8**, **PBDI-12**, **PBDI-18**, **PBDI-8'**, and **COPBDI-8** in CHCl_3 and **PBDI-4** in PS film (1 wt%).

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.

Table 1 Photophysical and thermal properties of polymers

Polymer	In CHCl_3 solution			In PS film		T_d °C ^c
	λ_{abs} nm	λ_{em} nm	Φ_F^a	λ_{em} nm ^b		
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.

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

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Notes and references

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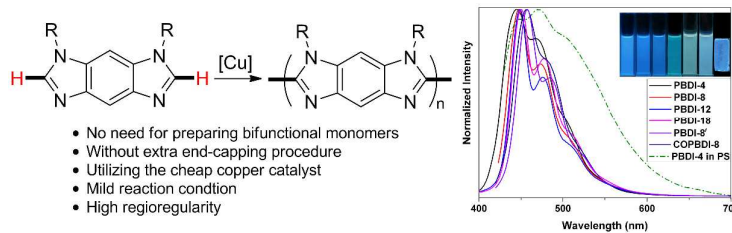
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c000000x

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Graphic Abstract

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an efficient approach to regioregular polybenzodiiimidazoles for blue-emitting
materials**

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