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## Palladium-catalyzed alkyne polyannulation of diphenols and unactivated internal diynes: a new synthetic route to functional heterocyclic polymers†

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A new polymerization route for the preparation of functional heterocyclic polymers was developed from diphenol derivatives and unactivated internal diynes. The alkyne polyannulations of 4,4'-sulfonyldiphenol and 4,4'-( $\alpha,\omega$ -alkylenedioxy)bis(diphenylacetylene)s or 1,2-bis[4-(2-phenylethynyl)phenyl]-1,2-diphenylethene were catalyzed by Pd<sub>2</sub>(dba)<sub>3</sub> in the presence of bathophenanthroline, silver acetate and copper(II) acetate monohydrate in 1,4-dioxane at 130 °C, affording polymers with benzofuran moieties in satisfactory yields and high molecular weights (*M<sub>w</sub>* up to 34 000). All the polymers were thermally stable, losing merely 5% of their weight at high temperatures of up to 376 °C. They showed a good film-forming ability and their thin solid films showed high refractive indices (RI = 1.900–1.611) in a wide wavelength region of 400–1000 nm. The polymer carrying tetraphenylethene units in the backbone was photosensitive and could be utilized to generate a fluorescent pattern by the photolithography process.

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### Introduction

Developing new methodologies for the synthesis and preparation of novel polymeric materials is an important research topic in polymer science.<sup>1–5</sup> Among all the plausible strategies, new polymerization reactions based on triple-bond building blocks have attracted much interest from our research group.<sup>6–10</sup> For many years, we have been working on the construction of functional macromolecules from alkynes by means of metathesis polymerization, polycoupling, polycyclotrimerization and click polymerization. Most of these polymerization tools were developed from organic reactions of small molecules. It is much more difficult to convert an organic reaction into a useful polymerization technique because several important issues have to be addressed, including the monomer availability, the catalytic efficiency, the interference between functional groups, the polymerization optimization,

the structural selectivity, the control of molecular weights and the solubility and processability of the resulting polymers.

From the aspect of reaction mode, the polymerization reactions developed by our group can be roughly classified as direct-addition and ring formation. Polycyclotrimerization and alkyne–azide click polymerization are two outstanding examples among the various ring formation strategies. Polycyclotrimerization was first employed for the construction of pure hydrocarbon polymers with stable benzene rings.<sup>11–14</sup> Afterwards, nitrogen-rich polytriazines were also obtained under simple and mild conditions by polycyclotrimerization of dinitriles to enrich the scope of this useful polymerization technique.<sup>15</sup> Meanwhile, the click polymerization derived from copper-catalyzed alkyne–azide cycloaddition reaction gave regio-regular polytriazoles and it was later developed to perform under metal-free conditions by using activated alkyne monomers.<sup>16–19</sup> However, another useful strategy to achieve ring formation which is less reported is the annulation process. Annulation refers to a chemical reaction in which a new (fused) ring is formed in an aromatic compound by its reaction with another molecule. Several pioneer projects have been reported by our group in recent years for the synthesis of new functional polymers by the so-called polyannulation. For example, we successfully developed rhodium-catalyzed oxidative polycoupling of arylboronic acids and internal diynes to polymers with highly substituted naphthalene rings.<sup>20</sup> Soon after that, another rhodium-catalyzed atom-economical synthesis of poly(pyrazolyl-naphthalene)s from phenylpyrazole and internal diynes was also reported by the same researchers.<sup>21</sup>

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In these studies, two triple bonds from two diyne monomers merged with the phenyl ring of arylboronic acid or phenylpyrazole to give a polymer with a naphthalene skeleton so as to realize the same result as polycyclotrimerization through annulation polymerization.

Many different kinds of oxygen- or nitrogen-bearing heterocycles can be obtained by annulation, and when they are constructed from benzene rings, such a reaction is called benzannulation. Benzofuran is a privileged structure found in natural products and bio-active compounds, and the methodology for its access thus has attracted much attention.<sup>22–30</sup> Transition metal-catalyzed oxidative annulation of phenols with alkynes offers a platform for the atom-economical formation of benzofuran in a straightforward way. Among them, the palladium-catalyzed annulation between phenol derivatives and unactivated internal alkynes reported by Sahoo and co-workers provided a promising pathway to highly substituted benzofuran (Scheme 1).<sup>31</sup> Starting from common phenol derivatives and simple internal alkynes without any activated functional groups, this reaction gave benzofuran motifs in high yield in the presence of a palladium(0) catalyst and a ligand with a base and oxidant. Through a series of optimized experiments, tris(dibenzylideneacetone)dipalladium [Pd<sub>2</sub>(dba)<sub>3</sub>] and bathophenanthroline were found to be an effective catalyst and ligand, respectively, for this reaction. On the other hand, silver acetate (AgOAc) and copper(II) acetate monohydrate

[Cu(OAc)<sub>2</sub>·H<sub>2</sub>O] were the commonly used base and oxidant, respectively, to assist the catalytic cycle.

Herein, for the extension of our research and the purpose of exploring new polymerization methods, we tried to develop the abovementioned reaction into a novel polymerization. In this work, we present the polymerization of diphenol derivative **1** and unactivated internal diynes **2a–d** and the properties of the resulting polymers **P1/2a–d** (Scheme 2). The monomers are either commercially available or easily synthesized.

## Results and discussion

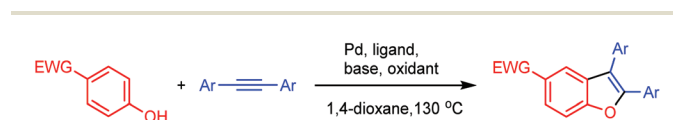
### Monomer synthesis

To examine whether the annulation reaction is a useful tool for synthesizing polymers, we prepared a series of diynes with different molecular structures, and examined whether they can be polymerized. While 4,4'-sulfonyldiphenol (monomer **1**) was commercially available, the diyne monomers **2a–2c** with different numbers of methylene spacers (4, 6 and 8 for **2a**, **2b** and **2c**, respectively) were obtained according to the literature methods.<sup>20</sup> On the other hand, the tetraphenylethene (TPE)-containing monomer (**2d**) was prepared by a two-step synthetic route which consisted of the Sonogashira coupling reaction of phenylacetylene and 4-bromobenzophenone followed by the McMurry homo-coupling of the obtained product. All the monomers were characterized by standard spectroscopic methods and gave satisfactory analysis data corresponding to their structures.

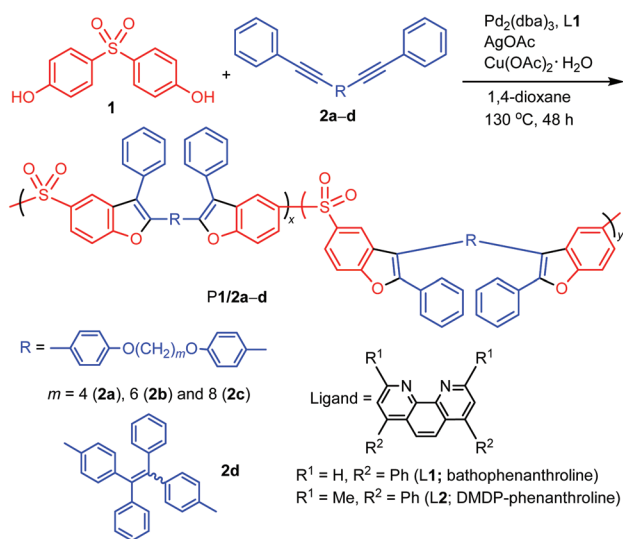
### Polymerization

Several parameters such as the catalyst, solvent, monomer concentration and reaction time need to be taken into consideration for optimizing a polymerization system. Thus, we first studied the effect of a ligand on the polymerization using **1** and **2b** as monomers.

According to the annulation mechanism, we fixed the concentration of the ligand to that of Pd<sub>2</sub>(dba)<sub>3</sub> as 2 : 1. The catalytic effect of two phenanthroline-based ligands with a subtle difference in the R<sup>1</sup> group (H for L1 and Me for L2) was examined. Interestingly, completely different results were obtained. In the presence of L1, a polymer was obtained in a moderate yield of 65% with an M<sub>w</sub> value of 34 000 (Table 1 no. 1). However, only a trace amount of oligomer was obtained when



**Scheme 1** Formation of benzofuran through palladium-catalyzed oxidative annulation of phenol and unactivated internal alkyne.



**Scheme 2** Palladium-catalyzed oxidative polyannulation of 4,4'-sulfonyldiphenol **1** and internal diynes **2a–d**.

**Table 1** Effect of ligand on the polymerization<sup>a</sup>

| No. | Ligand | Yield (%) | M <sub>w</sub> <sup>b</sup> | M <sub>w</sub> /M <sub>n</sub> <sup>b</sup> |
|-----|--------|-----------|-----------------------------|---|
| 1   | L1     | 65        | 34 000                      | 3.9   |
| 2   | L2     | 7         | 3300                        | 1.4   |

<sup>a</sup> Carried out in 1,4-dioxane under nitrogen in the presence of Pd<sub>2</sub>(dba)<sub>3</sub>, ligand, AgOAc, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O at 130 °C for 48 h. [1] = [2b] = 0.10 M, [Pd<sub>2</sub>(dba)<sub>3</sub>] = 10% [2b], [ligand] = 2[Pd<sub>2</sub>(dba)<sub>3</sub>], [Ag] = [Cu] = 4[2b]. <sup>b</sup> Determined by GPC in THF on the basis of a linear polystyrene calibration.

**Table 2** Effect of catalyst loading on the polymerization<sup>a</sup>

| No.            | [Pd] <sup>b</sup><br>(% equiv.) | Yield<br>(%) | <i>M<sub>w</sub></i> <sup>c</sup> | <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>c</sup> |
|----------------|---------------------------------|--------------|-----------------------------------|--|
| 1              | 20                              | 82           | 18 100                            | 2.6  |
| 2              | 15                              | 53           | 27 400                            | 2.6  |
| 3 <sup>d</sup> | 10                              | 65           | 34 000                            | 3.9  |
| 4              | 5                               | 45           | 5900                              | 2.2  |

<sup>a</sup> Carried out in 1,4-dioxane under nitrogen in the presence of different concentrations of Pd<sub>2</sub>(dba)<sub>3</sub>, L1, AgOAc, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O at 130 °C for 48 h. [1] = [2b] = 0.10 M, [L1] = 2[Pd<sub>2</sub>(dba)<sub>3</sub>], [Ag] = [Cu] = 4[2b]. <sup>b</sup> Equivalent to [2b]. <sup>c</sup> Determined by GPC in THF on the basis of a linear polystyrene calibration. <sup>d</sup> Data taken from Table 1, no. 1.

the ligand was changed to L2. Such a contrasting result suggested that the steric bulkiness of the ligand is a key factor for determining its coordination ability and hence its catalytic capability.

Transition metals were usually required to initiate the annulation reactions, especially those involving unactivated internal alkynes due to their comparatively low reactivity. In this work, Pd<sub>2</sub>(dba)<sub>3</sub> was employed as the catalyst. Because the Pd(0) metal centre was stabilized by the dba ligand, the presence of bathophenanthroline was needed to generate the real catalytic species. Generally speaking, increasing the catalyst concentration results in a higher isolated yield but leads to a lower molecular weight. Our trials on investigating the effect of the Pd<sub>2</sub>(dba)<sub>3</sub> concentration on the polymerization were basically in agreement with this statement (Table 2). Compared with the results obtained at different Pd concentrations (20, 15, 10 and 5% of [2b]), it was found that the polymerization conducted at 20% catalyst concentration generated a polymer with a satisfactory molecular weight in a high yield. Although higher molecular weight polymers were furnished at lower catalyst concentrations (15% and 10%), the isolated yield became lower. Poorer results were obtained when the catalyst concentration was further decreased to 5%. Considering the balance between the yield and molecular weight, we fixed the concentration of [Pd<sub>2</sub>(dba)<sub>3</sub>] to 10% for later investigations.

Solvent is an external parameter which exerts a great influence on the polymerization. Many intrinsic characters of the solvents influence the reaction process. In a polymerization reaction, good dissolving ability of the monomers and the corresponding polymers is one of the vital parameters to consider for the selection of a solvent. In this case, it may be difficult to find a suitable solvent for diphenol monomer 1 because of its relatively high polarity, while the lesser polar monomer 2b with a quite long alkyl chain can be readily dissolved in many solvents. We selected several solvents of different natures with high boiling temperatures for our investigation. Among all the tested organic solvents, 1,4-dioxane seemed to be the most suitable one for the polymerization. Such results were consistent with those for the small molecule reaction (Table 3 no. 1). Polymers with a higher molecular weight were produced in *o*-xylene but the obtained amount was low (Table 3 no. 2). This might be attributed to the poor

**Table 3** Solvent effect on the polymerization<sup>a</sup>

| No.            | Solvent          | Yield (%) | <i>M<sub>w</sub></i> <sup>b</sup> | <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>b</sup> |
|----------------|------------------|-----------|-----------------------------------|--|
| 1 <sup>c</sup> | 1,4-Dioxane      | 65        | 34 000                            | 3.9  |
| 2              | <i>o</i> -Xylene | 33        | 19 600                            | 3.4  |
| 3              | DMF              | 39        | 4900                              | 1.8  |
| 4              | 1-Pentanol       | 10        | 2100                              | 1.2  |
| 5 <sup>d</sup> | Toluene          | Trace     |                                   |  |

<sup>a</sup> Carried out in different solvents under nitrogen in the presence of Pd<sub>2</sub>(dba)<sub>3</sub>, L1, AgOAc, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O at 130 °C for 48 h. [1] = [2b] = 0.10 M, [Pd<sub>2</sub>(dba)<sub>3</sub>] = 10% [2b], [L1] = 2[Pd<sub>2</sub>(dba)<sub>3</sub>], [Ag] = [Cu] = 4[2b]. <sup>b</sup> Determined by GPC in THF on the basis of a linear polystyrene calibration. <sup>c</sup> Data taken from Table 1, no. 1. <sup>d</sup> Reaction conducted with a condenser.

solubility of monomer 1 in the solvent. However, the incorporation of the benzofuran moiety and the alkyl chain in the polymer structure promoted the solubility and thus facilitated the further growth of the polymer chain and hence its molecular weight. In contrast, no polymer was generated in toluene, which might be imputed to the reaction temperature despite the solubility issue. Other non-protic polar solvent, like *N,N*-dimethylformamide (DMF), and protic solvent, like 1-pentanol were not suitable for this polymerization and polymers with low molecular weights were produced in poor yields in these solvents.

We then investigated the influence of the monomer concentration on the polymerization. Generally, increasing the monomer concentration will lead to more efficient intermolecular collision between reacting monomers, thus giving a better polymerization result. While keeping the molar ratio of 1/2b at 1/1 unchanged, the molecular weight of the obtained polymer was gradually enhanced from 10 300 to 39 200 when the monomer concentration was increased from 0.05 M to 0.20 M (Table 4). The isolated yield, however, decreased gradually, possibly due to the increase in the viscosity of the reaction mixture upon thickening of the monomer concentration. Furthermore, gelation occurred at a monomer concentration of 0.50 M. The formation of a gel may provide an explanation for the decrease in polymer yield as mentioned above. Thus, from both the economical point of view and satisfactory reaction results, we chose 0.10 M as the suitable monomer concentration for this polymerization.

**Table 4** Effect of monomer concentration on the polymerization<sup>a</sup>

| No.            | [1] (M) | [2b] (M) | Yield (%) | <i>M<sub>w</sub></i> <sup>b</sup> | <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>b</sup> |
|----------------|---------|----------|-----------|-----------------------------------|--|
| 1              | 0.50    | 0.50     | Gel       |                                   |  |
| 2              | 0.20    | 0.20     | 59        | 39 200                            | 4.4  |
| 3 <sup>c</sup> | 0.10    | 0.10     | 65        | 34 000                            | 3.9  |
| 4              | 0.05    | 0.05     | 71        | 10 300                            | 3.4  |

<sup>a</sup> Carried out in 1,4-dioxane under nitrogen in the presence of Pd<sub>2</sub>(dba)<sub>3</sub>, L1, AgOAc, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O at 130 °C for 48 h. [Pd<sub>2</sub>(dba)<sub>3</sub>] = 10% [2b], [L1] = 2[Pd<sub>2</sub>(dba)<sub>3</sub>], [Ag] = [Cu] = 4[2b]. <sup>b</sup> Determined by GPC in THF on the basis of a linear polystyrene calibration. <sup>c</sup> Data taken from Table 1, no. 1.

**Table 5** Time course of the polymerization<sup>a</sup>

| No.            | Time (h) | Yield (%) | $M_w^b$ | $M_w/M_n^b$ |
|----------------|----------|-----------|---------|-------------|
| 1              | 6        | 34        | 7900    | 1.6         |
| 2              | 12       | 41        | 15 400  | 2.2         |
| 3              | 24       | 46        | 17 900  | 3.0         |
| 4 <sup>c</sup> | 48       | 65        | 34 000  | 3.9         |
| 5              | 60       | 58        | 31 000  | 2.9         |

<sup>a</sup> Carried out in 1,4-dioxane under nitrogen in the presence of  $\text{Pd}_2(\text{dba})_3$ , L1, AgOAc,  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  at 130 °C.  $[\mathbf{1}] = [\mathbf{2b}] = 0.10 \text{ M}$ ,  $[\text{Pd}_2(\text{dba})_3] = 10\% [\mathbf{2b}]$ ,  $[\text{L1}] = 2[\text{Pd}_2(\text{dba})_3]$ ,  $[\text{Ag}] = [\text{Cu}] = 4[\mathbf{2b}]$ .

<sup>b</sup> Determined by GPC in THF on the basis of a linear polystyrene calibration. <sup>c</sup> Data taken from Table 1, no. 1.

We then monitored the time course of the polymerization by calculating the isolated yield and GPC analysis. As shown in Table 5, prolonging the reaction time from 6 h to 48 h significantly enhanced the  $M_w$  value by nearly 4-fold from 7900 to 34 000. The effect of the reaction time on the isolated yield was not obvious. However, further extension of the reaction time from 48 h to 60 h even caused a slight decrease in both the molecular weight and isolated yield. Therefore, the polymerization was generally terminated after 48 h.

After a systematic study on the polymerization conditions, we applied the optimized conditions to polymerize other unactivated internal diyne monomers, *i.e.* **2a**, **2c** and **2d** (Table 6). All the polymerization reactions proceeded smoothly to give polymers in satisfactory to high yields and high molecular weights ( $M_w$  from 13 000 to 34 000). All the polymers possessed good solubility in common organic solvents like dichloromethane, tetrahydrofuran (THF) and chloroform except for P1/**2a**, possibly due to its short alkyl chain length which made it have a low solvating ability. Such a problem can be readily solved by incorporation of long alkyl chains or twisted moieties into the polymer structure such as in P1/**2c** and P1/**2d**.

**Table 6** Polymerization of **1** with different diyne monomers **2a–d** under the optimized conditions<sup>a</sup>

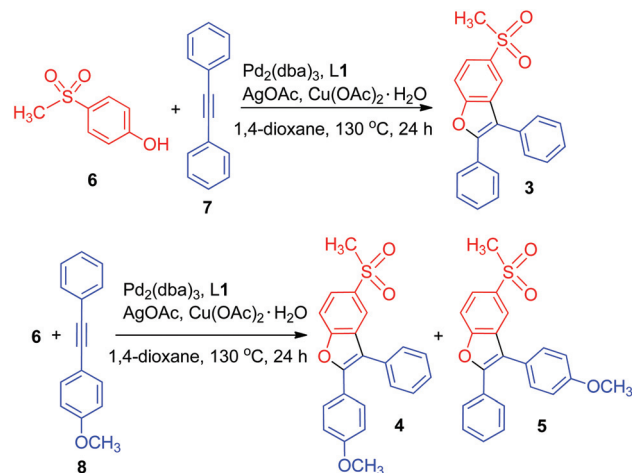
| No.            | Polymer       | Yield (%) | $M_w^b$ | $M_w/M_n^b$ | $S^d$ |
|----------------|---------------|-----------|---------|-------------|-------|
| 1              | P1/ <b>2a</b> | 82        | 19 200  | 3.6         | Δ     |
| 2 <sup>c</sup> | P1/ <b>2b</b> | 65        | 34 000  | 3.9         | √     |
| 3              | P1/ <b>2c</b> | 62        | 23 100  | 3.2         | √     |
| 4              | P1/ <b>2d</b> | 34        | 13 000  | 1.8         | √     |

<sup>a</sup> Carried out in 1,4-dioxane under nitrogen in the presence of  $\text{Pd}_2(\text{dba})_3$ , L1, AgOAc,  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  at 130 °C for 48 h.  $[\mathbf{1}] = [\mathbf{2b}] = 0.10 \text{ M}$ ,  $[\text{Pd}_2(\text{dba})_3] = 10\% [\mathbf{2b}]$ ,  $[\text{L1}] = 2[\text{Pd}_2(\text{dba})_3]$ ,  $[\text{Ag}] = [\text{Cu}] = 4[\mathbf{2b}]$ .

<sup>b</sup> Determined by GPC in THF on the basis of a linear polystyrene calibration. <sup>c</sup> Data taken from Table 1, no. 1. <sup>d</sup> Solubility (*S*) tested in commonly used organic solvents such as THF and chloroform; √ = completely soluble, Δ = partially soluble.

### Model reaction

The annulation reaction of 4-methylsulfonylphenol (**6**) and a symmetric unactivated internal alkyne **7** was intensively

**Scheme 3** Synthetic routes to model compound **3** and a mixture of **4** and **5**.

studied to serve as the model reaction (Scheme 3). In the presence of  $\text{Pd}_2(\text{dba})_3$ , L1, AgOAc and  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  in 1,4-dioxane at 130 °C for 24 h under nitrogen, a model compound **3** was obtained at a yield of 51%. Moreover, in order to check the regio-selectivity of this annulation reaction, we further examined the model reaction of **6** with an unsymmetric unactivated internal alkyne **8** with the purpose of simulating the chemical environment of monomers **2a–c** (Scheme 3).

### Structure characterization

**Model compounds.** The chemical structure of **3** was confirmed by NMR, IR and high resolution mass spectroscopy techniques with satisfactory results. For example, the phenyl protons *ortho* to the sulfonyl group of **6** resonated at  $\delta$  7.65, which shifted to  $\delta$  8.12 and  $\delta$  7.93 after the annulation (Fig. 1C). Similarly, the resonance of the phenyl carbons *para* to the sulfonyl group of **6** shifted from  $\delta$  161.1 to  $\delta$  156.3 after the reaction due to the formation of a benzofuran ring in **3** (Fig. 2C). After column purification, single crystals of **3** were obtained from its dichloromethane/hexane solution and their structure was characterized crystallographically (Fig. 3A). Interestingly, neither the pale yellow powder of **3** showed solid-state emission nor its nanoaggregates in a THF/ $\text{H}_2\text{O}$  mixture exhibited the aggregation-induced-emission effect. However, its microcrystallites emitted blue light, demonstrating a phenomenon of crystallization-induced-emission (Fig. 3C).

Under the same conditions used for preparing **3**, a mixture of **4** and **5** was generated from **6** and **8**. Due to their similar physical properties, it was difficult to separate them by using column chromatography. The attempt to grow single crystals from this mixture also failed probably due to their poor molecular packing stemming from their more irregular structures. However, different methoxy proton resonances (labeled as *p* and *p'* for **4** and **5** in Fig. 1D, respectively) and absorptions of the phenyl protons (labeled as *q* and *q'* for **4** and **5**, respectively) adjacent to the methoxy group were observed in their



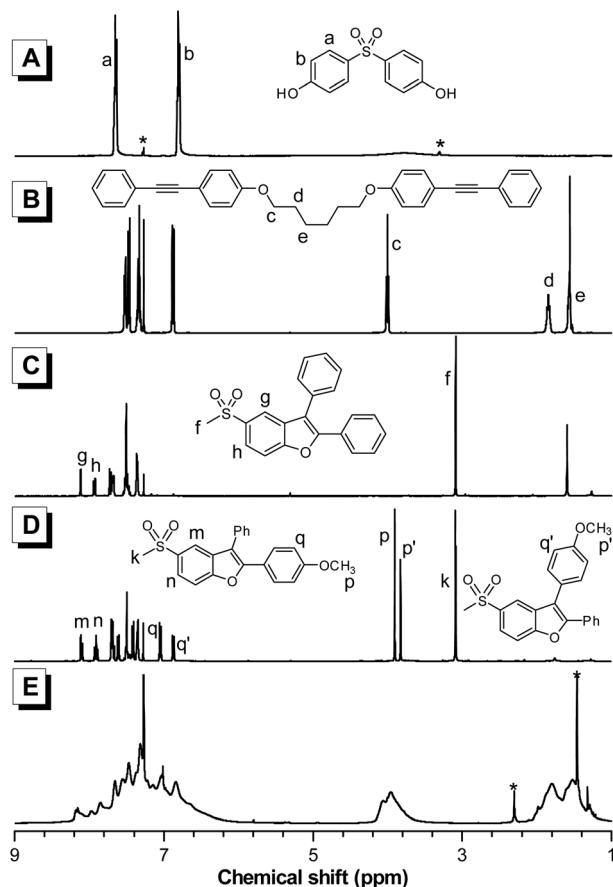


Fig. 1  $^1\text{H}$  NMR spectra of (A) **1**, (B) **2b**, (C) **3**, (D) a mixture of **4** and **5** and (E) **P1/2b** in chloroform- $d$ . The solvent peaks were marked with asterisks. A few drops of methanol- $d_3$  were added in (A) to assist the dissolution of **1**.

$^1\text{H}$  NMR spectrum. From the integral of the peaks ( $p$  and  $p'$ ), the ratio of **4/5** was calculated to be  $\sim 3:2$ , suggesting a poor regio-selectivity of this reaction and also a random alternative sequence of repeating units in the polymers. The characteristic peaks associated with the resonances of the protons of the benzofuran ring were also found with a complicated splitting pattern due to the asymmetric nature of the starting material.

**Polymer.** All the polymers gave satisfactory spectroscopic data corresponding to their molecular structures. The IR and NMR spectra of **P1/2b** are given below as examples.

Fig. 1 shows the  $^1\text{H}$  NMR spectra of **P1/2b** and its corresponding monomers **1** and **2b** as well as the model compound **3** and a mixture of **4** and **5**. As we discussed previously, the two phenyl protons adjacent to the sulfonyl group of **3** resonated at  $\delta$  8.12 and 7.93. These peaks were also observed in the spectrum of the polymer but appeared broader, possibly due to the existence of polymer chains with various lengths or molecular weights. Other characteristic peaks of the model compounds were all reserved and could be readily identified. For example, the methylene protons next to the oxygen atom absorbed at  $\delta$  4.00 in **2b**, which was observed in the spectrum of **P1/2b** at the same position as that in the monomer. The peaks for the alkyl chain absorption were also observed at high field.

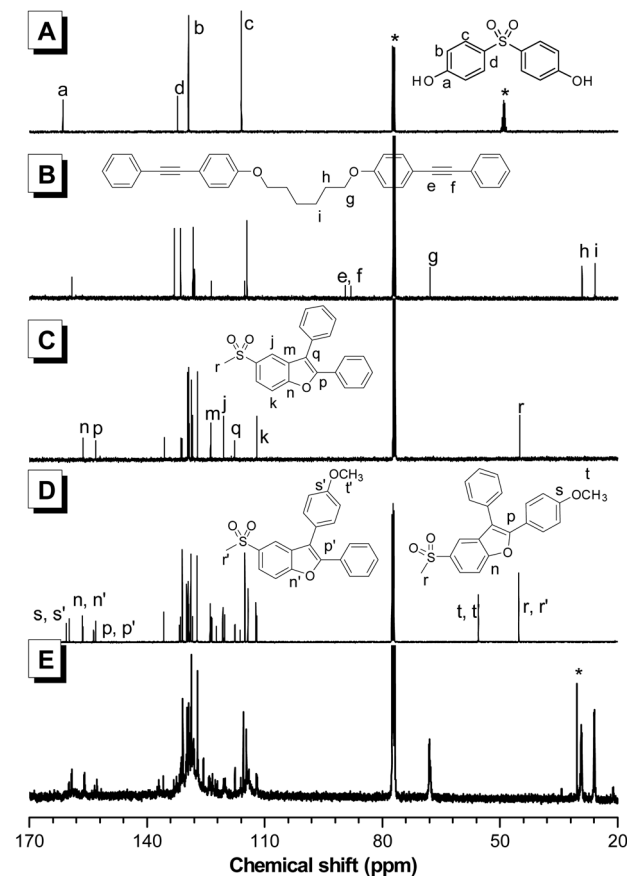


Fig. 2  $^{13}\text{C}$  NMR spectra of (A) **1**, (B) **2b**, (C) **3**, (D) a mixture of **4** and **5** and (E) **P1/2b** in chloroform- $d$ . The solvent peaks were marked with asterisks. A few drops of methanol- $d_3$  were added in (A) to assist the dissolution of **1**.

The  $^{13}\text{C}$  NMR analysis also provides persuasive information on the polymer structure. The characteristic carbon resonances of the benzofuran ring were clearly observed at  $\delta$  159.9, 159.1

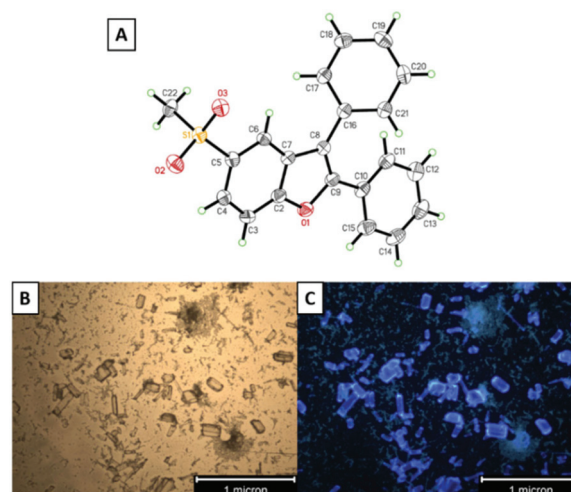


Fig. 3 (A) Crystal structure of model compound **3**, (B) bright-field and (C) fluorescence microscopy images of micro-crystallites of **3**.

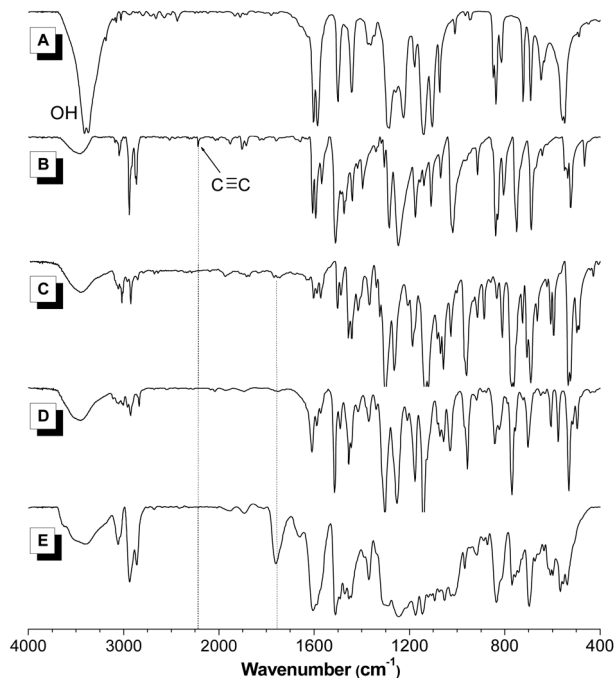


Fig. 4 FT-IR spectra of (A) **1**, (B) **2b**, (C) model compound **3**, (D) a mixture of **4** and **5** and (E) **P1/2b**.

and 155.9 in the  $^{13}\text{C}$  NMR spectrum of **P1/2b**. Moreover, the internal acetylene carbons ( $\text{C}\equiv\text{C}$ ) of **2b** resonated at  $\delta$  89.4 and 88.0 (Fig. 4B), which were not observed in the  $^{13}\text{C}$  NMR spectra of both model compounds and **P1/2b**. The disappearance of these two peaks indicated the complete consumption of diyne functional groups and thus the accomplishment of the polymerization. The absorption peaks for the alkyl chain carbons in **2b** ( $\delta$  68.0, 29.3 and 26.0) were preserved at high field in the polymer spectrum.

The IR spectrum of **P1/2b** is shown in Fig. 4 and the spectra of its monomers and model compounds are also given in the same figure for comparison. The large absorption band with two sharp peaks at 3411 and 3372  $\text{cm}^{-1}$  stemmed from the OH stretching vibration of monomer **1** (Fig. 4A). On the other hand, the  $\text{C}\equiv\text{C}$  stretching vibration of **2b** emerged as a small sharp band at 2218  $\text{cm}^{-1}$ . Both these bands disappeared in the spectrum of **P1/2b**. Meanwhile, an absorption band associated with the benzofuran skeleton arose at 1760  $\text{cm}^{-1}$ . This band was also observed in the spectra of the model compounds although with a much lower intensity. Other typical absorption bands in the monomers, like those at 2940, 2864 and 1600  $\text{cm}^{-1}$ , were all reserved in the spectrum of the polymer.

### Thermal stability

The thermal stabilities of all the polymers were evaluated by thermogravimetric analysis (TGA). Among the polymers generated from diyne monomers with different alkyl chain lengths, **P1/2b** showed better thermal stability, losing merely 5% of its weight at temperatures (degradation temperature,  $T_d$ ) above

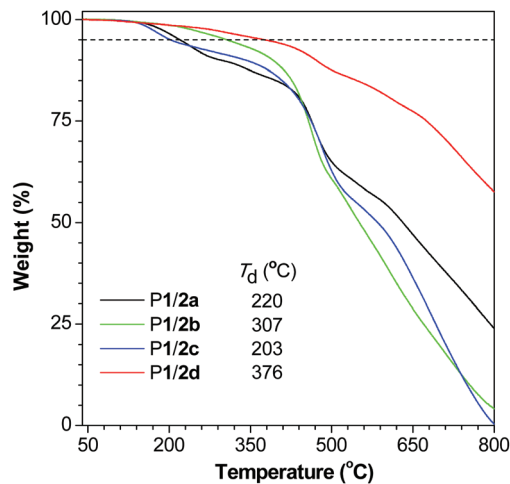


Fig. 5 TGA thermograms of **P1/2** recorded under nitrogen at a heating rate of 10  $^{\circ}\text{C min}^{-1}$ .

300  $^{\circ}\text{C}$  under nitrogen (Fig. 5). The  $T_d$  values of other two polymers (**P1/2a** and **P1/2c**) with a shorter or longer alkyl chain were lower than **P1/2b** but were still above 200  $^{\circ}\text{C}$ . The thermal stability of TPE-containing **P1/2d** was outstanding, showing a high  $T_d$  at 376  $^{\circ}\text{C}$ . More importantly, **P1/2d** retained more than 50% of its original weight when heated to 800  $^{\circ}\text{C}$ . Such a property made it promising as a ceramic material.

### Light refraction

All the polymers showed good film-forming ability. Transparent thin films could be easily prepared by spin-coating their 1,2-dichloroethane solutions on silica substrates. As shown in Fig. 6, the thin films of all the polymers showed high refractive indices (RI or  $n$ ) in a wide wavelength region (400–1000 nm). As summarized in Table 7, the RI values of all the polymers at

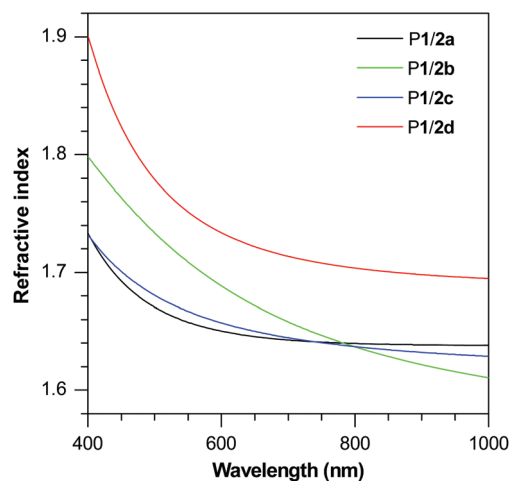


Fig. 6 Wavelength dependence of refractive indices of thin films of **P1/2**.

**Table 7** Refractive indices and chromatic dispersions of P1/2<sup>a</sup>

| Polymer | $n_{632.8}$ | $\nu_D$ | $D$   |
|---------|-------------|---------|-------|
| P1/2a   | 1.6469      | 21.5    | 0.046 |
| P1/2b   | 1.6770      | 9.7     | 0.103 |
| P1/2c   | 1.6522      | 18.3    | 0.055 |
| P1/2d   | 1.7253      | 10.8    | 0.093 |

<sup>a</sup> Abbreviation:  $n$  = refractive index,  $\nu_D$  = Abbé number =  $(n_D - 1)/(n_F - n_C)$ , where  $n_D$ ,  $n_F$  and  $n_C$  are the RI values at wavelengths of 589.2, 486.1 and 656.3 nm, respectively,  $D$  = chromatic dispersion =  $1/\nu_D$ .

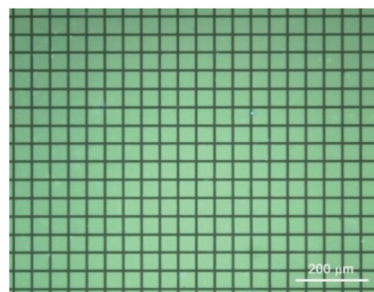
632.8 nm were  $\geq 1.64$ , which were much higher than those of many commercial optical plastics. Among them, the RI value of P1/2d with TPE moieties impressively reached 1.72 due to its relatively high aromatic content. Similar to the result obtained from the TGA analysis, the RI value of P1/2b was 1.67 which was the highest among all the polymers with alkyl chains.

### Chromatic dispersion

Chromatic dispersion ( $D$ ) describes the wavelength dependence of the refractive index of a material. Polymers with a small  $D$  value exhibit good chromatic dispersion and are promising for applications as optical materials because a large  $D$  value leads to unfavorable effects such as degradation of image resolution. The Abbé number ( $\nu_D$ ) of a material serves as a measure of the variation or dispersion in its RI value with a wavelength which is defined as  $(n_D - 1)/(n_F - n_C)$ , where  $n_D$ ,  $n_F$  and  $n_C$  are the RI values at wavelengths of Fraunhofer D, F and C spectral lines of 589.2, 486.1 and 656.3 nm, respectively.<sup>20</sup> The  $\nu_D$  values of all the tested polymers fell on the scale of 9.7–21.5 and the corresponding  $D$  values (the reciprocal of  $\nu_D$ ) were around 0.046–0.103. The optical data of refractive indices and the Abbé numbers indicated that most of our polymers had low optical dispersions and hence demonstrated their potential applications as optical materials.

### Photopatterning

Since TPE-containing P1/2d possessed good film-forming ability and was light-emissive in the solid state as verified by the emission spectrum shown in Fig. S1,<sup>†</sup> we thus utilized such properties for the fabrication of a luminescent pattern by the photolithography process (Fig. 7). After the polymer solution in 1,2-dichloroethane was spin-coated on a silicon wafer, the obtained thin film was irradiated by UV light in air for 20 min through a copper photomask. The irradiated parts (dark lines) underwent UV-induced oxidation in air and their emission was thus quenched. On the other hand, the emission of the covered parts (green squares) remained unaffected. Consequently, a two-dimensional fluorescent pattern with sharp edges was fabricated without going through the development process.



**Fig. 7** Two-dimensional fluorescent photopattern generated by UV-induced oxidation of a thin film of P1/2d in air. The photograph was taken under UV light illumination (330–385 nm).

## Conclusions

In this work, a new polymerization route for the preparation of heterocyclic polymers was developed. The alkyne polyannulation of diphenols and internal diynes catalyzed by  $\text{Pd}_2(\text{dba})_3$  in the presence of bathophenanthroline,  $\text{AgOAc}$  and  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  proceeded smoothly in 1,4-dioxane at 130 °C for 48 h, generating polymers with benzofuran rings in satisfactory yields with high molecular weight, good solubility and high thermal stability. High refractive indices were acquired from the thin solid films of the polymers in a wide wavelength region of 400–1000 nm. The TPE-containing polymer could be utilized for the fabrication of a fluorescent pattern.

## Experimental section

### General information

$\text{Pd}_2(\text{dba})_3$  was purchased from Alfa Aesar. Chemicals such as monomer **1**, **L1**,  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ,  $\text{AgOAc}$  and other reagents concerned with monomer synthesis were all purchased from Aldrich and used as received without further purification. THF was distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. Other solvents including 1,4-dioxane, *o*-xylene, DMF, 1-pentanol and toluene were commercially available from Aldrich.

Weight- ( $M_w$ ) and number-average ( $M_n$ ) molecular weights and polydispersities ( $M_w/M_n$ ) of the polymers were estimated by using a Waters Gel Permeation Chromatography (GPC) system equipped with a Waters 515 HPLC pump, a set of Styragel columns (HT3, HT4 and HT6; molecular weight range:  $10^2$  to  $10^7$ ), a column temperature controller, a Waters 486 wavelength-tunable UV-vis detector and a Waters 2414 differential refractometer. The polymers were dissolved in THF ( $\sim 1$  mg  $\text{mL}^{-1}$ ) and filtered through 0.45  $\mu\text{m}$  PTFE syringe-type filters before being injected into the GPC system. THF was used as an eluent at a flow rate of 1.0  $\text{mL min}^{-1}$ . The column temperature was maintained at 40 °C and the working wavelength of the UV-vis detector was set at 254 nm. A set of monodispersed polystyrene standards (from Waters) covering the molecular weight range of  $10^3$  to  $10^7$  were used for the molecular weight

calibration. IR spectra were recorded on a Perkin-Elmer 16 PC FTIR spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker ARX 400 NMR spectrometer using chloroform-*d* as the solvent. High resolution mass spectra (HRMS) were recorded on a GCT Premier CAB 048 mass spectrometer operated in a MALDI-TOF model. Single crystal X-ray diffraction intensity data were recorded at 100 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Processing of the intensity data was carried out through the SAINT and SADABS routines and the structure and refinement were obtained by employing the SHELTL suite of X-ray programs (version 6.10). UV-vis absorption spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer. Thermogravimetric analyses (TGA) were conducted under nitrogen on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10 °C min $^{-1}$ . Refractive indices (RI or *n*) were determined on a J A Woollam Variable Angle Ellipsometry System with a wavelength tunability from 400 to 1000 nm. Photopatterning of the polymer film was conducted on a Spectroline ENF-280C/F UV lamp at a distance of 3 cm as the light source. The incident light intensity was  $\sim 18.5$  mW cm $^{-2}$ . The films for RI measurement and the photopattern were prepared by spin-coating the polymer solution (10 mg of P1/2d in 1 mL of 1,2-dichloroethane) at 1000 rpm for 1 min on a silicon wafer. The polymer film was dried in a vacuum oven at room temperature overnight. The pattern was generated by UV irradiation of the polymer film through a copper photomask for 20 min in air without going through the development process. The photo was taken on an optical microscope (Olympus BX 41) under a UV light source.

### Monomer synthesis

All the diyne monomers, named 4,4'-( $\alpha,\omega$ -alkylenedioxy)bis(diphenylacetylene)s (2a–2c) and 1,2-bis[4-(2-phenylethynyl)phenyl]-1,2-diphenyl-ethene (2d), were synthesized according to the literature methods. All the characterization data were consistent with those reported in the literature.

### Synthesis of model compounds

**Synthesis of model compound 3.** To a 50 mL Schlenk tube were added 4-methylsulfonylphenol (6, 172 mg, 1 mmol), diphenylacetylene (7, 89 mg, 0.5 mmol), Pd $_2$ (dba) $_3$  (23 mg, 0.025 mmol), bathophenanthroline (L1, 18 mg, 0.05 mmol), AgOAc (167 mg, 1 mmol) and Cu(OAc) $_2$ ·H $_2$ O (199 mg, 1 mmol). After purging with nitrogen 3 times, 4 mL of degassed 1,4-dioxane was injected into the tube by using a hypodermic syringe. The resulting mixture was stirred at 130 °C for 24 h under a nitrogen atmosphere in a sealed Schlenk tube. The reaction mixture was then cooled to room temperature, diluted with dichloromethane, and filtered through cotton. After solvent evaporation under reduced pressure, the crude product was purified by using silica-gel column chromatography using a hexane/ethyl acetate mixture as the eluent to give model compound 3 as a yellow solid (88 mg, 51%). IR (KBr),  $\nu$  (cm $^{-1}$ ): 3059, 3019, 2923, 1768, 1602.  $^1\text{H}$  NMR (CDCl $_3$ , 400 MHz),  $\delta$  (ppm): 8.12 (d, *J* = 1.7 Hz, 1H),

7.93 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.72 (d, 1H), 7.68 (m, 2H), 7.50 (m, 5H), 7.36 (t, *J* = 3.3 Hz, 3H), 3.09 (s, 3H).  $^{13}\text{C}$  NMR (CDCl $_3$ , 100 MHz),  $\delta$  (ppm): 156.3, 153.1, 135.6, 131.3, 131.1, 129.6, 129.5, 129.3, 129.2, 128.6, 128.3, 127.1, 123.8, 120.5, 117.7, 112.0, 103.7, 45.0. HRMS (MALDI-TOF): *m/z* 348.0820 ( $\text{M}^+$ , calcd 348.0820).

**Synthesis of model compounds 4 and 5.** A mixture of compounds 4 and 5 was prepared from 6 (172 mg, 1 mmol), 1-methoxy-4-(phenylethynyl)benzene (8, 104 mg, 0.5 mmol), Pd $_2$ (dba) $_3$  (23 mg, 0.025 mmol), L1 (18 mg, 0.05 mmol), AgOAc (167 mg, 1 mmol) and Cu(OAc) $_2$ ·H $_2$ O (199 mg, 1 mmol) using the same procedure for preparing compound 3 as described above. Yellow solid, yield 62% (117 mg). IR (KBr),  $\nu$  (cm $^{-1}$ ): 3064, 2925, 2839, 1755, 1607.  $^1\text{H}$  NMR (CDCl $_3$ , 400 MHz),  $\delta$  (ppm): 8.09 (d, *J* = 7.7 Hz, 1H), 7.91 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.50 (m, 2H), 7.42 (d, 1H), 7.35 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.91 and 3.84 (s, 3H), 3.08 (s, 3H).  $^{13}\text{C}$  NMR (CDCl $_3$ , 100 MHz),  $\delta$  (ppm): 160.3, 159.5, 156.1, 156.0, 153.3, 152.7, 135.4, 135.4, 131.45, 131.2, 131.2, 130.7, 129.6, 129.6, 129.2, 129.0, 128.6, 128.5, 128.1, 126.9, 123.6, 123.3, 123.2, 122.0, 120.4, 119.9, 117.3, 116.0, 114.7, 114.0, 111.9, 111.8, 55.3, 55.2, 44.9. HRMS (MALDI-TOF): *m/z* 378.0926 ( $\text{M}^+$ , calcd 378.0926).

### Polymerization

All the polymerization reactions were carried out under a nitrogen atmosphere in a sealed Schlenk tube except for Table 3, no. 5 as toluene was used as the solvent. A typical procedure for the polymerization of 1 and 2b is given below as an example.

In a 25 mL Schlenk tube with a three-way stopcock on the sidearm were added 1 (50 mg, 0.2 mmol), 2b (92 mg, 0.2 mmol), Pd $_2$ (dba) $_3$  (18.3 mg, 0.02 mmol), L1 (13.3 mg, mmol), AgOAc (133.5 mg, 0.8 mmol) and Cu(OAc) $_2$ ·H $_2$ O (159.7 mg, 0.8 mmol) under nitrogen. After purging with nitrogen 3 times, 2 mL of degassed 1,4-dioxane was injected into the tube by using a hypodermic syringe. The resulting mixture was stirred at 130 °C for 48 h under a nitrogen atmosphere. The solution was added dropwise into 100 mL of the hexane/chloroform mixture *via* a cotton filter under stirring. The precipitate was collected by centrifugation and dried under vacuum at room temperature to a constant weight. A brown powder of polymer P1/2b was obtained in 65% yield.  $M_w$  34 000;  $M_w/M_n$  3.9. IR (KBr),  $\nu$  (cm $^{-1}$ ): 3060, 2937, 2861, 1761, 1603.  $^1\text{H}$  NMR (CDCl $_3$ , 400 MHz),  $\delta$  (ppm): 8.14–6.83 (aromatic protons), 3.95 (OCH $_2$  protons), 1.81–1.53 (alkyl chain).  $^{13}\text{C}$  NMR (CDCl $_3$ , 100 MHz),  $\delta$  (ppm): 159.9, 159.1, 155.9, 153.4, 152.7, 137.1–112.0, 68.0, 29.3, 26.0.

**P1/2a:** brownish powder; yield 82%.  $M_w$  19 200;  $M_w/M_n$  3.6 (GPC, polystyrene calibration). IR (KBr),  $\nu$  (cm $^{-1}$ ): 3058, 2922, 2872, 1754, 1605.  $^1\text{H}$  NMR (CDCl $_3$ , 400 MHz),  $\delta$  (ppm): 8.13–6.83 (aromatic protons), 4.04 (OCH $_2$  protons), 1.96 (alkyl chain).  $^{13}\text{C}$  NMR (CDCl $_3$ , 100 MHz),  $\delta$  (ppm): 159.1, 155.9, 152.8, 133.4–114.9, 67.6, 26.1.

**P1/2c:** brownish powder; yield 62%.  $M_w$  23 100;  $M_w/M_n$  3.2 (GPC, polystyrene calibration). IR (KBr),  $\nu$  (cm $^{-1}$ ): 3058, 2924, 2853, 1761, 1605.  $^1\text{H}$  NMR (CDCl $_3$ , 400 MHz),  $\delta$  (ppm):



8.16–6.83 (aromatic protons), 4.04–3.93 (OCH<sub>2</sub> protons), 1.76–1.44 (alkyl chain). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  (ppm): 160.0, 159.2, 156.0, 153.4, 152.7, 137.0–112.1, 68.1, 29.4, 26.1.

**P1/2d**: yellow powder; yield 34%. *M<sub>w</sub>* 13 000; *M<sub>w</sub>/M<sub>n</sub>* 1.8 (GPC, polystyrene calibration). IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3054, 3025, 2959, 2857, 1764, 1591. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 8.16–7.11 (aromatic protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  (ppm): 155.9, 152.9, 143.4–112.11, 89.7.

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