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Journal Name

ARTICLE

Donor–Acceptor Copolymers Containing Phthalazinone–Thiophene Structure Synthesized by Low-cost Copper-catalyzed Ullmann Polymerization

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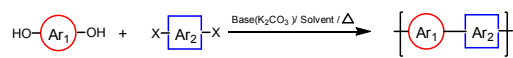
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Herein, we present a low-cost copper-catalyzed Ullmann polycondensation of phthalazinone based monomer which containing both OH and NH group provides an access to polyarylether and conjugated polymers. The synthesis of polymers was accomplished by a combination of low activity varies thiophene and carbazole monomers. Particularly, it was shown that a stronger base (Cs₂CO₃>K₂CO₃) efficiently polymerized the low activity thiophene monomer with the phthalazinone based monomer, obtained number-average molecular weight high up to 17.9 kDa (PDI=2.43). Also the result of reaction process monitoring revealed the Ullmann polymerization in this paper was in favour of the radical mechanisms. The reaction activity of di-halogened monomers was found to be a crucial factor for achieving a high molecular weight polymer. Thus, the number-average molecular weight of donor–acceptor copolymers containing phthalazinone–thiophene structure were 2.2–9.6 kDa. The new copolymer structures were confirmed by ¹H-NMR, FT-IR and GPC. Their thermal properties, density functional theory (DFT), optical properties, electrochemical properties and X-ray diffraction (XRD) were investigated in details. The results showed thiophene unit was beneficial to the π–π interaction between the polymer chains compared with carbazol and phthalazinone units.

1. INTRODUCTION

There has been a great deal of recent effort centred on metal-catalysed C–N and C–O coupling reactions of NH and OH groups with inactivated halides as well as these methods to improve the metal-catalysed Ullmann polycondensation.^{1–3} As we know, polyarylethers are usually synthesized by nucleophilic substitutions in solution. As one of the monomers for polymerization, the aryl halides generally have an active leaving group, such as a –F or a –Cl.⁴ But for Ullmann polycondensation, these reactions generally require the use of aryl bromides or iodides.⁵ The mechanism of Ullmann condensation is different from the traditional nucleophilic substitution (see Scheme 1). In this reaction system, the order of ease of halide replacement is I > Br > Cl >> F, which is the reverse of the order of the activated halide for nucleophilic displacement polycondensation reactions.⁶ This means under this circumstance, aryl bromides or aryl iodides have the higher reaction activity than aryl chloride and aryl fluorides. So

Classical Nucleophilic Aromatic Polymerization:

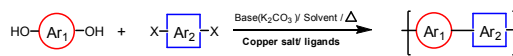


Ar₁: The electron donating groups are favourable

X: F > Cl >> Br > I

Ar₂: The electron withdrawing groups are favourable

Copper-catalyzed Ullmann Polymerization:



Ar₁: The electron donating groups are favourable

X: I > Br >> Cl > F

Ar₂: The electron withdrawing groups are favourable

Scheme 1 Comparison between Classical Nucleophilic Aromatic Polymerization and Copper-catalyzed Ullmann Polymerization

the relatively inexpensive (compared to aryl fluoride) aryl bromides or aryl iodides can be chosen as the monomers in the synthesis of polyarylether via Ullmann condensation reaction, which not only expands the variety of polyarylethers, but also enriches the way to synthesise polyarylethers. Compared with Pd-catalyst C–C/C–N/C–O coupling reactions (such as Negishi, Suzuki–Miyaura, Kumada, Stille and Hiyama polycondensation), copper-catalyst indeed seems to show a number of advantages over Pd-catalyst. Besides the cost of metal (by 10⁵ cheaper than Pd-catalyst), copper catalysts

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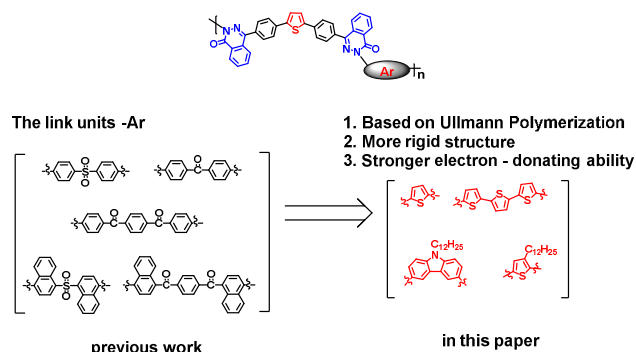
Electronic Supplementary Information (ESI) available: [detailed experimental synthesis procedures, NMR (calculated M_n) and GPC spectra of monomers and polymers, HPLC–MS spectra of polymerized products, DSC and CV curves of polymers]. See DOI: 10.1039/x0xx00000x

mostly employ much cheaper ligands. Specifically palladium needs expensive phosphines, copper satisfy itself with much more trivial N/O ligands, and many ligands are common analytical or general purpose reagents (such as the ligand used in this article: quinoline). Moreover the appealing fact is that low-cost copper-catalyst methods do not exactly follow their Pd-catalyst counterparts. For instance, copper-catalyzed Ullmann reaction has its own applications, where it is superior to Pd-catalyst, e.g. in better tolerance to some functional groups and more flexible chemoselectivity (eg. C-N, C-O cross-coupling).⁷ After all, Ullmann condensation reaction is one of the well-known reactions for aryl-oxygen and aryl-nitrogen bond formation, which have shown the rapid development of good commercial prospects and great market potential.⁸

In a series of papers and patents, small molecular C-N/C-O coupling reactions of NH/OH groups with unactivated halides have been developed (both Cu and Pd catalysed).^{2, 8-14} Also, there are several reports about polyarylether formation via Ullmann polycondensation of various biphenols with dibromides in the presence of copper-catalyst system. The molecular weight is high up to 5.53 kDa (M_w).^{15, 16} In 2008, our group introduced an alternative copper catalyst system. A new class of high molecular weight poly-(phthalazinone ether)s, the molecular weight high up to 25.4 kDa (M_n), have been successfully synthesized *via* the Ullmann polycondensation of 1,2-dihydro-4-(4-hydroxy-phenyl)-1-(2H)-phthalazinone (A1 in Scheme 3) and unactivated aromatic dibromides catalyzed by the use of potassium carbonate as the base in the presence of a catalytic amount of a copper (I) complex with quinoline as ligand.⁵

From the polymer chemistry viewpoint, based on the fact that the NH group in A1 behaves like a phenolic OH group, A1 is a type of a bisphenol monomer, which can react with activated dihalo compounds to produce high molecular weight polymers. In previous work, our research group studies showed that polymerization containing A1 monomer could be achieved with a series of aryl dibromides via Ullmann C-N and C-O condensation reaction.⁵ In this paper, we adopted thiophene unit to displace aryl-dibromides which has a weaker activity and a novel di-NH monomer (A2) which has a weaker nucleophilicity than common OH group to explore the process of Ullmann condensation reaction and expand it to a wider variety of functional groups. The process of Ullmann polymerization was monitored and confirmed by FT-IR and ¹H-NMR. Also, the mechanism of polymerization was investigated.

On the other hand, from the polymer structure-property relationship viewpoint, the link units along donor-acceptor polymer backbone is expected to be significantly influenced the backbone twists, the bond length alternation, the electronic communication between the donor unit and acceptor unit, the morphology of polymer thin films, etc. All these factors can affect the optical absorption and emission properties (both in solution and film state), the LUMO and HOMO levels, the π - π stacking of polymer thin films, etc.¹⁷⁻¹⁹ Because of A2 monomer contains phthalazinone-thiophene structure (donor-acceptor units). The obtained polymers, copolymerized with weak conjugated groups such as ketone



Scheme 2 Chemical Structures of Donor-Acceptor Copolymers and the Linker Units.

/di-ketone/sulfone groups, show remarkable photoelectric properties in our previous report.²⁰ Thus considering their distinct properties, we would like to introduce more rigid structure with stronger electron-donating ability into the polymer backbone. Herein the combination of the A2 monomer and four different donor units (varies thiophene and carbazole unit) *via* Ullmann polymerization, shown in scheme 2, provides a unique platform to study the effects of link units along donor-acceptor copolymer backbones on the structure-property correlation. Therefore, the thermal properties, optical properties, electrochemical properties, quantum chemical calculations studies²¹ and physical properties of the resulting conjugated polymers were investigated in details. Furthermore, fused di-NH monomer and low cost copper-catalyzed Ullmann polymerization can be used for synthesized conjugated polymers.

2. EXPERIMENTAL SECTIONS

2.1 Characterization

¹H-NMR (400 Hz) and ¹³C-NMR (100Hz) spectra were obtained with a Bruker spectrometer at an operating temperature of 25 °C using CDCl₃, trifluoroacetic acid-d (TFA-d), d₆-DMSO or 1,1,2,2-tetrachloroethane-d₂ (C₂Cl₄D₂) as solvents. HPLC-MS analyses were carried out on a HP1100LC/MSD instrument. Gel permeation chromatography (GPC) analysis was performed on a HP 1090 HPLC instrument equipped with 5 μ m Phenogel columns (linear, 4 \times 500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. And the values were calibrated versus polystyrene standard. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analyses were using a Micromass GC-TOF CA 156 MALDI-TOF/MS. Infrared measurements were performed on a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer. UV-visible absorption was measured with a PerkinElmer Lambda 35 UV-vis spectrometer. Fluorescence spectra were using a Hitachi F-4500 spectrofluorometer with a xenon lamp and 1.0 cm quartz cells. Thermogravimetric analysis (TGA) of the polymers was performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in a nitrogen atmosphere at a heating rate of 20 °C/min from 25 to

800 °C. Decomposition temperature (T_d) in nitrogen was taken as the temperature of 5% weight loss. Char yield (Cy) was calculated as the percentage of solid residue after heating from 25 to 800 °C in flowing nitrogen. The glass transition temperature (T_g) was obtained with a Mettler DSC822 differential scanning calorimetry (DSC) in flowing nitrogen at a heating rate of 10 °C/min from 25 to 300 or 350 °C. The T_g value was taken at the inflection point. Cyclic voltammetric experiments were carried out on an electrochemistry workstation with a BAS100W voltammetric analyzer. A three-electrode setup was performed in a dichloromethane containing 0.1M tetrabutylammonium hexafluoroborate as the supporting electrolyte, used employing platinum working and counter electrodes and an Ag/Ag⁺ reference electrode (containing 0.01M silver nitrate in dichloromethane). Potentials were recorded relative to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple which occurs at a value of +0.12 V under these conditions. Each sample for CV was prepared by drop-coating the polymer solutions in NMP onto Pt wires. LUMO and HOMO energies were calculated from the onset of the first peak assuming a formal potential of Fc/Fc⁺ of -4.80 eV relative to vacuum level (scan rate 50 mV/s). The optical band gap was calculated from measured at the onset of absorption. Quantum yield measurements of the polymers, dissolved in organic solvent, were performed using quinine sulfate (quantum yield = 0.546, excited at 346 nm, in 0.1 N H₂SO₄) as standards.²² DFT calculations were performed using the Gaussian 09W program at the B3LYP level with a 6-31G(d,p) basis set.²¹

2.2 Materials

Unless otherwise indicated, starting materials were obtained from Aldrich or Alfa Aesar and were used without further purification. Solvent were obtained from Shanghai Energy Chemical. Quinoline was purified by distillation under vacuum. Commercial cuprous chloride was dissolved in concentrated hydrogen chloride and the resulting solution was filtered through an acid funnel to remove the insoluble substance. The liquid obtained was then diluted by pure water then to collect the white precipitate. The white solid was washed by methanol and ether, respectively, and then kept in a desiccator. CuCl/quinolone catalyst was prepared as the literature reported.⁵ The monomer A1 was purchased commercially from Dalian Polymer New Material Co. Ltd. and used without any further treatment. The compounds A2 were prepared according to literature procedures.²⁰ The detailed experimental procedures for synthesis of the monomers D2, D3 and D4 were showed in Supporting Information (SI).

2.3 Syntheses of polymers

General procedure for polymerization. A 50 mL, three-necked round-bottomed flask equipped with a Dean-Stark trap, condenser, inert gas inlet, magnetic stirrer, was charged with

bisphenol monomer (1 mmol), Cesium Carbonate (1 mmol), sulfolane (3 mL) and toluene (6 mL). The mixture was heated to 145 °C (oil bath) under an N₂ atmosphere and maintained at this temperature for 4 h to remove water produced during the reaction. After complete dehydration, the reaction temperature was increased to 190-195 °C (oil bath) and the toluene was distilled. The slurry in the flask was cooled to 80 °C and dihalo monomer (1 mmol) was carefully added. The Cu (I) Cl/quinoline catalyst (0.2/0.4 mmol) was injected into the reaction mixture. The reaction mixture was then heated to 190-195 °C. The resulting mixture was maintained at this temperature for 17 h, after which time, the color of reaction solution became dark red, indicating that the cesium salt of bisphenol monomer had almost gone into solution. Then the solution was poured into the water in the presence of some dilute HCl. The crude polymer was washed six times with hot distilled water to remove inorganic salts. The dried polymer was purified by dissolving in hot NMP, being filtered through a 0.45 mm Teflon micro filter before pouring into ethanol, and subsequently washed six times with hot deionized water. The polymers were purified by Soxhlet extraction with ethanol and acetone sequentially. The purified polymer was dried at 120 °C under vacuum for 24 h. The products were obtained.

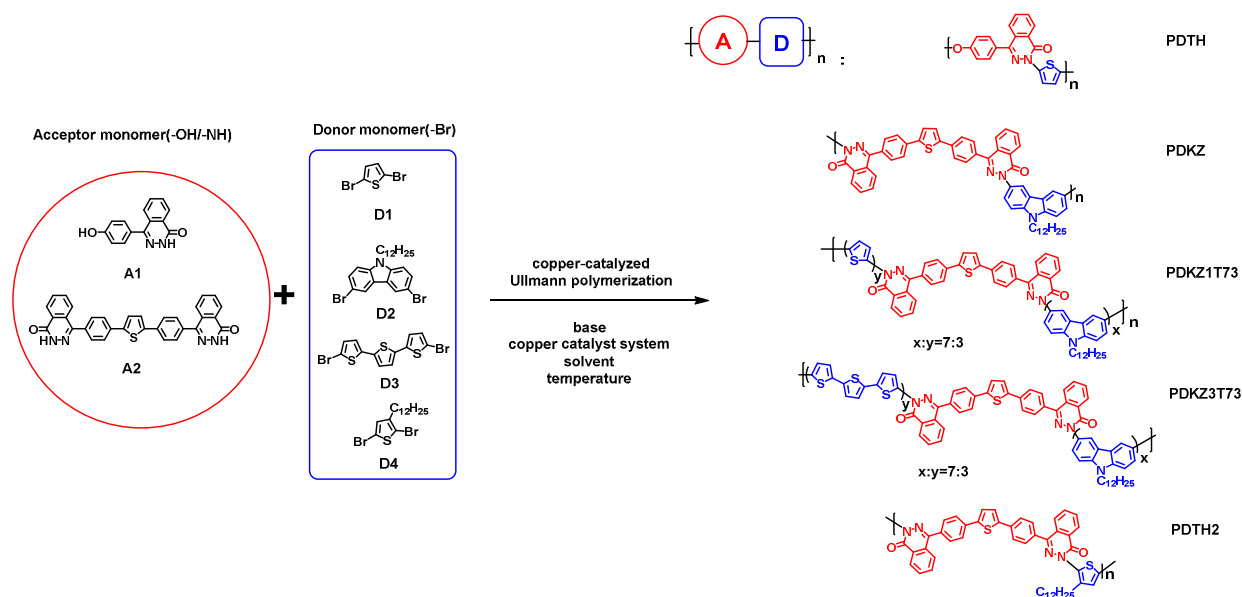
Polymer PDTH. Yellow solid, Yield: 14 %. ¹H-NMR (400 MHz, CDCl₃) δ 8.62 (s, 1H), 7.81 (d, J = 128.4 Hz, 7H), 7.13 (s, 2H). GPC: M_n =17.9 kDa, PDI=2.43(details in SI, Figure S17). Anal. calcd for C₁₈H₁₀N₂O₂S: C, 67.91; H, 3.17; N, 8.80. Found: C, 66.72; H, 4.33; N, 8.83.

Polymer PDKZ. Yellow solid, Yield: 43 %. ¹H-NMR (400 MHz, C₂Cl₄D₂) δ 8.52 (s, 1H), 8.30 (d, J = 33.2 Hz, 1H), 8.04 – 7.52 (m, 8H), 7.41 (d, J = 36.8 Hz, 2H), 4.27 (d, J = 28.1 Hz, 1H), 1.80 (s, 1H), 1.15 (s, 9H), 0.77 (s, 2H). GPC: M_n =5.3 kDa, PDI=2.34; Molecular weight calculated by NMR: M_n =5.9 kDa (details in SI, Figure S12). Anal. calcd for C₅₆H₄₉N₅O₂S: C, 78.57; H, 5.77; N, 8.18. Found: C, 78.24; H, 5.94; N, 8.78.

Polymer PDKZ1T73. Black solid, Yield: 53 %. ¹H-NMR (400 MHz, C₂Cl₄D₂) δ 8.52 (s, 1H), 8.30 (d, J = 32.3 Hz, 1H), 7.84 – 7.31 (m, 10H), 4.26 (d, J = 27.5 Hz, 1H), 1.79 (s, 1H), 1.20 (d, J = 41.7 Hz, 8H), 0.77 (s, 1H). GPC: M_n =2.3kDa, PDI=1.72(chloroform-soluble fraction); Molecular weight calculated by NMR: M_n =6.5 kDa (details in SI). Anal. calcd for C₅₀H_{40.3}N_{4.7}O₂S_{1.3}: C, 76.93; H, 5.20; N, 8.43. Found: C, 76.96; H, 5.58; N, 8.01.

Polymer PDKZ3T73. Black solid, Yield: 81 %. ¹H-NMR (400 MHz, C₂Cl₄D₂) δ 8.52 (s, 1H), 8.35 (s, 1H), 8.16 – 7.08 (m, 9H), 7.04 (s, 1H), 4.27 (d, J = 28.4 Hz, 1H), 1.84 (s, 1H), 1.15 (s, 7H), 0.78 (s, 1H). GPC: M_n =2.2 kDa, PDI=1.74(chloroform-soluble fraction); Molecular weight calculated by NMR: M_n =9.6 kDa (details in SI). Anal. calcd for C_{52.4}H_{41.5}N_{4.7}O₂S_{1.9}: C, 75.83; H, 5.04; N, 7.93; Found: C, 75.21; H, 5.06; N, 8.52.

Polymer PDTH2. Black solid, Yield: 11 %. ¹H-NMR (400 MHz, C₂Cl₄D₂) δ 8.52 (s, 1H), 7.84 – 7.30 (m, 5H), 2.40 (d, J = 51.2 Hz, 1H), 1.13 (dd, J = 164.8, 140.9 Hz, 8H). GPC: M_n =2.7 kDa, PDI=1.44(chloroform-soluble fraction); Molecular weight calculated by NMR: M_n =2.2 kDa (details in SI). Anal. calcd for C₄₈H₄₈N₄O₂S₂: C, 74.19; H, 6.23; N, 7.21. Found: C, 73.47; H, 4.79; N, 9.37.



Scheme 3 The synthetic route of polymers

RESULTS AND DISCUSSION

Preparation and characterization of copolymers by Ullmann polycondensation

Firstly, we select CuCl/quinoline(CQ) catalyst system and K_2CO_3 as base to polymerize A1 with D1. This system has been previously applied to the successful polymerization of 1,2-dihydro-4-(4-hydroxy-phenyl)-1-(2H)-phthalazinone (A1) and unactivated aromatic dibromides for a class of high molecular weight poly(phthalazinone ether)s.⁵ But this is the first time that it has been tested for the preparation of the lower unactivated thiophene dibromides (strong donor unit). After the polymerization conducted at 195 °C for 24h, we found that the obtained products were granuliform and mainly oligomers (HPLC-MS in Figure S23). Then aiming for getting higher molecular weight polymer, the same polymerization was attempted in a stronger base like Cs_2CO_3 . Thorough investigations, the reaction solution became more viscous with time, and the obtained products were thin strips after poured into water. The molecular weight of polymer was 17.9 kDa (PDI=2.43). The concurrently products during polymerization period were monitored by Fourier transform infrared (FT-IR). The comparison of FT-IR data of the seven samples shows the progress of the condensation reaction (Figure 1). There is no special functional group in thiophene units, at the same time, the characteristic absorption peak of C-S-C at 600- 800 cm^{-1} is in the fingerprint region, whose intensity is too weak to

identify. While the absorption bands of C=C in thiophene appear at 1610- 1640 cm^{-1} , which is covered by the lactam C=O in phthalazinone and the C=C in benzene ring. On this account, analysis the functional groups in thiophene from FTIR is not reliable to track the progress of polymerization. However, the stretching vibration of C-O would change when the hydrogen atom of C-O-H in A1 was substituted by thiophene. In this case, characteristic stretching band of A1 appears at 1050 cm^{-1} (C-O-H). The intensity decreases with the increase of reaction time, moving to the lower wavenumber and disappearing when the reaction time up to 15h with no changing at all. This indicates that most of the OH group in DHPZ have been completed and polymerization reaction has come to the end. In summary, it further verified that the Ullmann polymerization reaction had occurred and also confirmed that ordinarily Ullmann polymerization reaction requires a long reaction time.¹

Moreover, mechanisms involving copper catalysis are not better understood than those of palladium catalysis. The radical mechanisms and the oxidative addition-reductive elimination are still under debate.^{2, 6} During our polymerization of PDTH, one of polymer purification processes was Soxhlet extracted with ethanol for 24 h. As showed Figure S24, de-halogenated by-products were detected by HPLC-MS in ethanol both in entry 1 and 2. As van Koten reported that a radical mechanism would easily explain the formation of de-halogenated products, which are often observed as side-product during reactions.²³ A plausible radical mechanism is figured out in Scheme 4. We believe the Ullmann polymerization in this paper is in favour of the radical mechanisms.²⁴

Table 1 Characteristics of polymers formed by copper-catalyzed Ullmann polymerization

Entry	Polymer	base	Copper catalyst/ligand ^a	Temperature (°C)	M_n (kDa)	PDI	Additional information	Yield ^e
1	PDTH	K ₂ CO ₃	CQ	195	--	--	oligomer	--
2	PDTH	CS ₂ CO ₃	CQ	195	17.9 ^b	2.43	--	14%
3	PKZ	CS ₂ CO ₃	CQ	220	--	--	side chain decomposition	--
4	PKZ	CS ₂ CO ₃	CQ	195	5.3(5.9) ^c	2.34	--	43%
5	PKZ	CS ₂ CO ₃	CPD	195	1.8 ^d (2.2)	1.55	--	--
6	PKZ1T73	CS ₂ CO ₃	CQ	210	--	--	side chain decomposition	--
7	PKZ1T73	CS ₂ CO ₃	CQ	195	2.3 ^d (6.5)	1.72	feed ratios(D2:D1): 8.0:2.0 ^c	53%
8	PKZ3T73	CS ₂ CO ₃	CQ	195	2.2 ^d (9.6)	1.74	feed ratios(D2:D3): 7.6:2.4 ^c	81%
9	PDTH2	CS ₂ CO ₃	CQ	195	2.7 ^d (2.2)	1.44	--	11%

^a CQ stands for CuCl/quinoline, CPD stands for CuI/1, 10-Phenanthroline monohydrate/2, 2-dipyridyl.

^b Determined by GPC in CHCl₃ at 40 °C on the basis of a polystyrene calibration, details showed in Figure S17-S22.

^c The M_n (in parentheses)and feed ratios are determined by ¹H-NMR, details showed in Figure S7-S16.

^d Chloroform-soluble fraction.

^e Isolated after precipitation and purification.

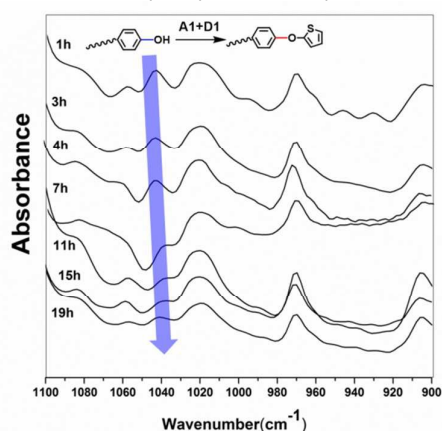


Figure 1 The spectra of Fourier transform IR profile of the Ullmann polycondensation (Amplification of the FT-IR profile in 900-1100 cm⁻¹. The full scale spectra are shown in SI).

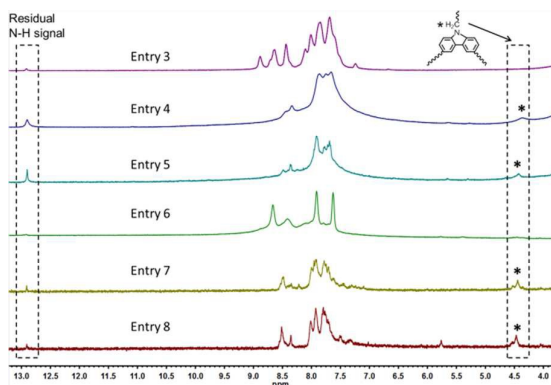
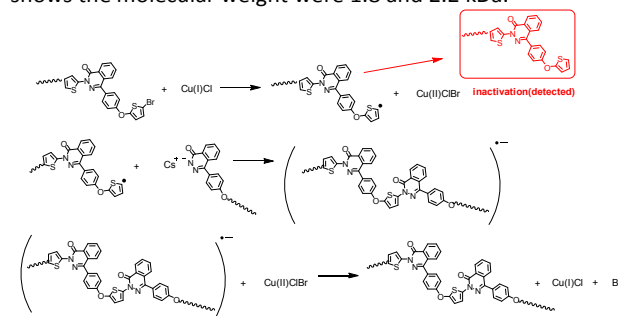


Figure 2 The ¹H-NMR spectra of polymers synthesised under different conditions.

Similar to A1 monomer, A2 monomer containing di-NH reaction sites could polymerize with di-halogen monomer by Ullmann polymerization, to give molecular weight polymers with M_n ranging from 2.2 to 9.6 kDa (Table 1). When similar polymerizations were performed at 195 °C for 24h using CS₂CO₃ as base, the molecular weights of resultant PDKZ was 5.9 kDa (Entry 4), possibly due to the combination effects of lower NH activity reaction sites and more rigid structure of polymer backbones. In order to obtain high molecular weight polymers, we performed the polymerizations at higher temperature 220 °C (Entry 3), the side chain decomposition reactions occurred (determined by ¹H-NMR, Figure 2). Interestingly, the carbazole monomer seems to be unstable during the CQ catalyst Ullmann polymerization system at 220 °C. In Hay's previous report, a number of other catalysts were screened and it was found that Venkataraman's air stable homogeneous copper catalyst Cu(PPh₃)₃Br was less effective for the formation of polymers derived from A1 with unactivated aromatic dibromides.⁵ Herein, the common used CuI/1, 10-Phenanthroline monohydrate/2, 2-dipyridyl (CPD) catalyst system was conducted, the GPC and ¹H-NMR results shows the molecular weight were 1.8 and 2.2 kDa.



Scheme 4 Putative Mechanism of Ullmann polycondensation (favour in radical mechanism as van Koten reported)

Copolymerization of D2 and D1, D2 and D3 in sulfolane at 195 °C with CQ, Cs₂CO₃ as the catalyst yielded the desired polymers, as illustrated in Table 1. The comonomers feed ratios are 7:3 and the corresponding polymers are named as PDKZ1T73 and PDKZ3T73, respectively. These two polymers are insoluble at room temperature in most organic solvent such chloroform (even at 40 °C), DMAc and chlorobenzene. The molecular weight of PDKZ1T73 and PDKZ3T73 are inaccurate, determined by GPC using chloroform at 40 °C. Also, determining the *M_n* from ¹H-NMR by unreacted NH signal (Figure 2) is inherently problematic as a result of the polymer not only containing one NH and one –Br end-capped polymer chains, making the estimation imprecise. Regardless, the *M_n* values of PDKZ1T73 and PDKZ3T73 are 6.5 and 9.6 kDa. Also, rising the reaction temperature from 195 to 210 °C led to the side chain decomposition of carbazole unit (Entry 6). In addition, for the monomer with long alkythio groups such as dodecylthiophene, we can only get the low molecular weight polymer (PDTH2, *M_n*=2.2 kDa). We speculate the long alkyl chain decreased the reactivity of D4 in Ullmann reactions and steric hindrance effect might play a role that dodecyl group ortho to dibromine thiophene can dramatically reduce the yield.

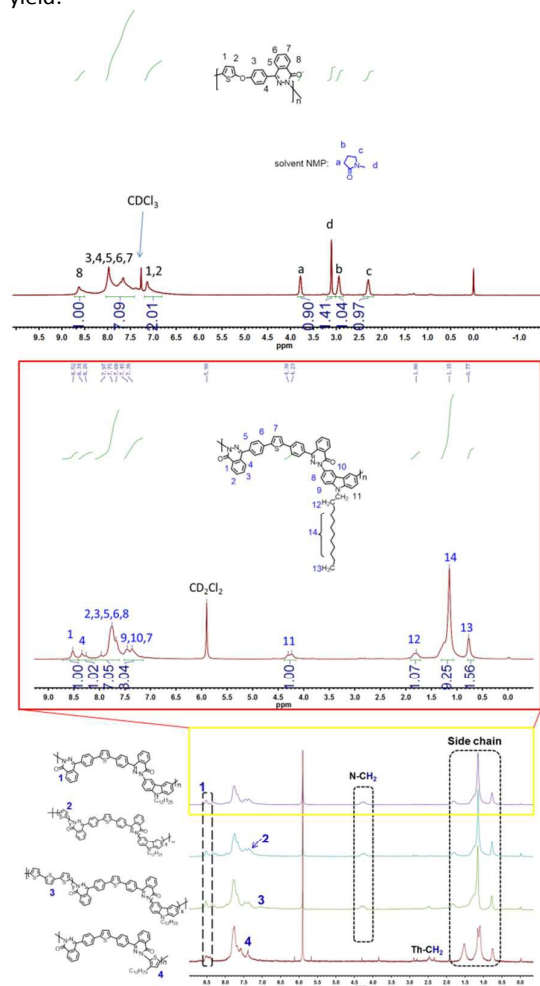


Figure 3 The ¹H-NMR spectra of polymers (PDTH in CDCl₃, PDKZ, PDKZ1T73, PDKZ3T73 and PDTH2 in 1, 1, 2, 2-tetrachloroethane-d₂)

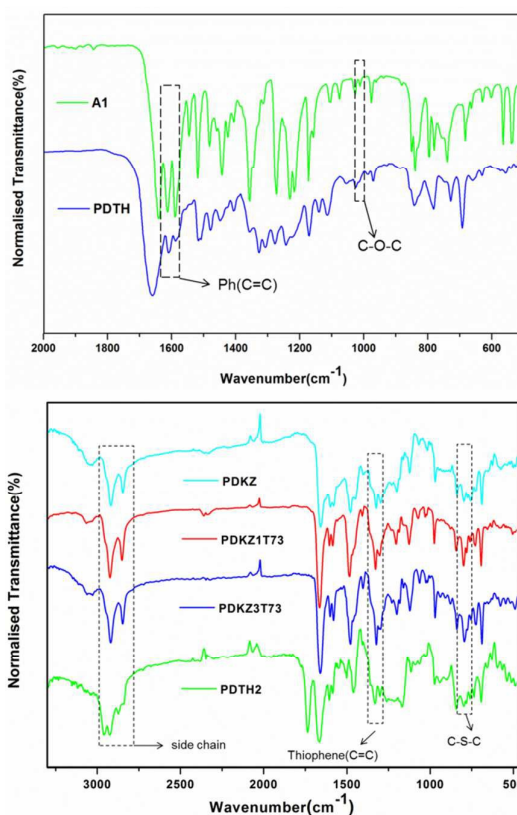


Figure 4 The FT-IR spectra of copolymers

Five of the new polymers have been characterized by ¹H-NMR and FT-IR. The ¹H-NMR spectra of these polymers are shown in Figure 3. The spectroscopic proton assignments are well in agreement with the proposed structures. And the ¹H NMR integral values of polymers are consistent with the number of their protons. Comparing with the FT-IR spectrum of A1 (Figure 4), disappearance of absorption at 1050 cm⁻¹ (C-O-H) indicates the complete connection of O-H and C-Br groups. Characteristic stretching bands of benzene groups appeared at 1600 cm⁻¹, whose intensity decreased from A1 to PDTH. This phenomenon was due to the electron-rich thiophene groups linked to oxygen atoms in A1, which enhanced the electron-donating of oxygen atom; thereby offset the electron-withdrawing of lactam. In the FT-IR spectrum of four polymers containing A2 monomer, the characteristic signal of aliphatic side chains appears at 2800 to 3000 cm⁻¹. The signal at 803 cm⁻¹ is contributed by the C-S-C in the thiophene unit. And the signal assigned to C=C in thiophene rings appears at 1330 cm⁻¹. These characteristic bands were correlated sufficiently well with the expected structure of the target polymers.

Thermal properties

The thermal stability of five polymers was measured by thermogravimetric analysis (TGA). These polymers showed sufficiently high 5% weight-loss temperature (Td) in the range 382 °C - 408 °C and a char yield at 800 °C in the range 61%-76% (Figure 5). According to the differential scanning calorimetry (DSC) analysis, four polymers containing A2 monomer (PDKZ, PDKZ1T73, PDKZ3T73 and PDTH2) does not

show obvious melting point or glass transition temperature below 300 °C. While PDTH exhibits a glass transition temperature at 260 °C, result from containing ether bond in the polymer backbone. (Figure S25)

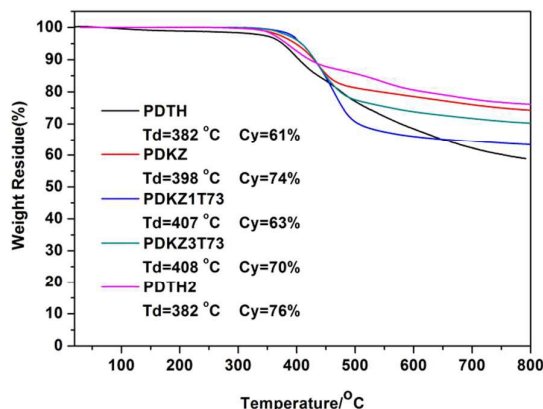


Figure 5 The TGA curves of copolymers

Theoretical Calculations

Quantum-chemical calculations by the density functional theory (DFT) at the B3LYP/6-31(d, p) level using the Gaussian 09 program were employed to investigate the structure of these polymers. For computational simplification, the dodecyl group was instead by hexyl group, and the polymer backbones were changed into two repeating units. The optimized molecular geometries of the model compounds, the dihedral angles and their calculated frontier orbitals are depicted in Figure 6. Also, the calculated HOMO and LUMO values are figured out in Table 3.

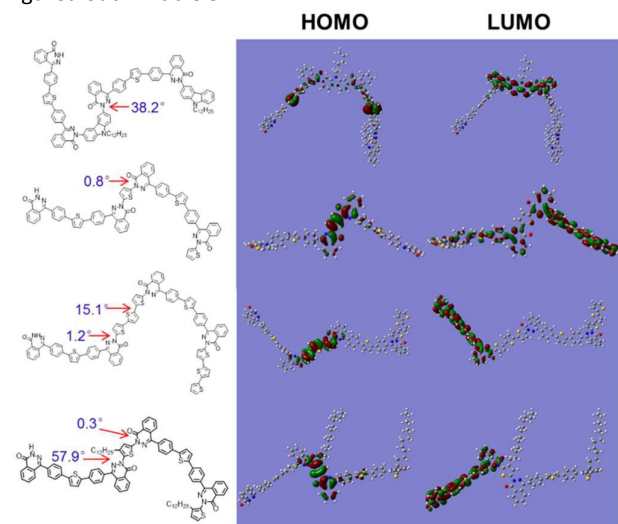


Figure 6 The optimized geometries Frontier molecular orbital distribution of polymers calculated using DFT with a 6-31g** basis set. HOMO and LUMO levels are shown, respectively.

In all four conjugated D-A polymers, the HOMOs are distributed evenly across most of the electron-rich units (thiophene and carbazole rings), and the LUMOs are more

concentrated on the electron-poor phthalazinone unit. That's all in agreements with reported observations on other D-A systems; demonstrated phthalazinone is an effective acceptor unit which can be applied into optoelectronics research field. Since the steric effect has unnegligible influence on the electronic and optical properties of these polymers, theoretically examination the steric relationship of the donor units with phthalazinone unit were conducted. As illustrated in Figure 6, the dihedral angles between the donor units and phthalazinone unit can be varies from 0.8° to 58.9°, when the N atom linked with different donor units. Also, these could lead to different intermolecular interaction and packing in the solid state. The influence on optical properties and electrochemical properties in more details would be discussed as follows.

Optical Properties

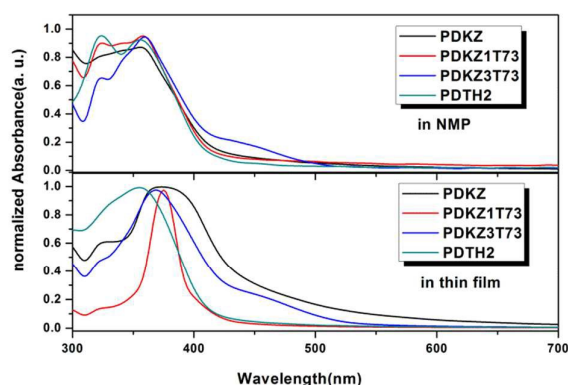


Figure 7 The UV-vis spectra of copolymers in NMP and thin film

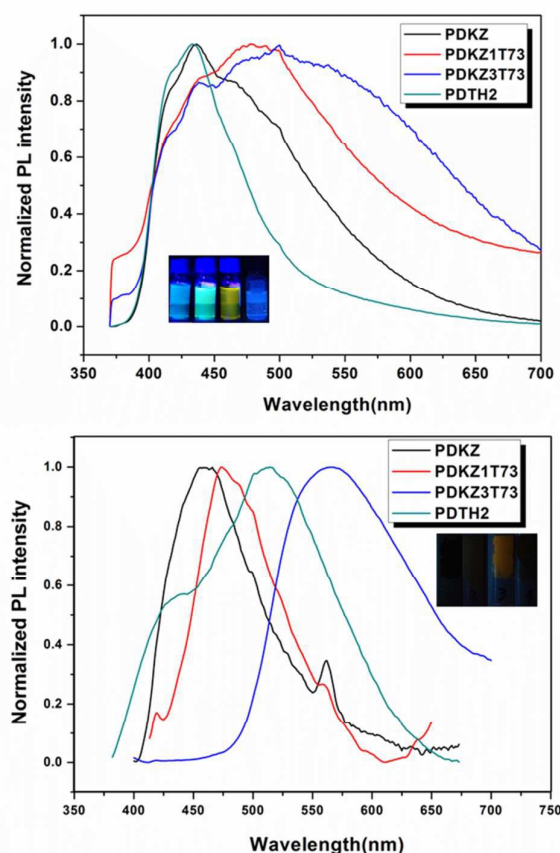
Among five new synthesized polymers, PDKZ, PDKZ1T73, PDKZ3T73 and PDTH2 are conjugated polymers. In the case of PDTH derived from A1, which was used for investigate thoroughly the Ullmann polymerization conditions. Because of ether bond along the PDTH chains, PDTH shows weak conjugated effects and not suitability used for further optical studies, compared with polymers containing A2 monomer (thiophene units as a donor in the core and phthalazinone as an acceptor on both sides of the monomer structure).

The normalized optical absorption spectra of polymers in dilute ($\sim 10^{-6}$ M) NMP solution are shown in Figure 7. The PDKZ, in which only carbazole was incorporated as the donor unit, show a broad absorption band ($\lambda_{\max} = 365$ nm). The PDKZ1T73, PDKZ3T73 and PDTH, in which thiophene was incorporated as the donor unit, displayed two absorption bands: the first one at 330 nm, which is assigned to localized $\pi-\pi^*$ transitions, and the second band at 365 nm, which corresponds to the intermolecular charge transfer (ICT) between D-A charge transfer states. Figure 7 also shows the optical absorption spectra of the polymer thin films. The corresponding optical properties are also summarized in Table 2. The thin film absorption spectrum of four polymers is identical in line shape to the solution spectrum. The absorption maximum (λ_{\max}) varies from 355 nm in PDTH to 376 nm in PDKZ. Absorption spectra of the polymer thin films shows a slight red-shift compared to the polymer in solution, indicating improved intermolecular interactions and long-range order in the solid state.

Table 2 The summarised optical properties of copolymers

Polymers	$\lambda_{\text{abs,sol}}^a$	$\lambda_{\text{abs,fil}}^b$	$\lambda_{\text{em,sol}}^c$	$\lambda_{\text{em,fil}}^d$	Stokes shift	$\lambda_{\text{fs}}(\lambda_{\text{em,fil}} - \lambda_{\text{em,sol}})$	Φ_f^e
PDKZ	356	373	436	465	80	29	0.06
PDKZ1T73	358	375	478	473	120	-5	0.15
PDKZ3T73	360	369	499	564	139	65	0.11
PDTH2	355	355	432	514	77	82	0.26

^aAbsorbtion in NMP. ^bAbsorption maxima of the polymer films coated on a glass slide(1mg/ml NMP at 120 °C) ^cEmission in NMP. ^dEmission maxima of the polymer films. ^eQuantum yield calculated using quinine sulfate as a standard in 0.1 N H₂SO₄.²²

**Figure 8** The PL spectra of copolymers in NMP and thin film

In addition, we measured photoluminescence (PL) spectra of these polymers in solution ($\sim 10^{-6}$ M in NMP) and thin film state upon the excitation at their each absorption maximum (Figure 8). The order of maximum emission wavelength is PDKZ3T73>PDKZ1T73>PDKZ. That shows good correlation with the order of thiophene content in polymer chains. The reason can be explain as follows. First, thiophene shows less space steric hindrance with naphthalene than carbazole(the dihedral angles in Figure 6). Second, thiophene is stronger donor units than carbazole.²⁶ That's could led to stronger D-A effect. Then longer emission wavelength could be achieved.²⁷ Besides, PDTH2 show short emission wavelength. That's result from that the alkyl substituent shows large space steric hindrance with naphthalene and destroys the D-A effect. Eventually, blue fluorescence was observed. The fluorescence quantum yields

of PDKZ, PDKZ1T73, PDKZ3T73 and PDTH2 measured in NMP are 0.06, 0.15, 0.11 and 0.26, respectively. All these polymers show a large Stokes shifts (77- 130 nm), which are typically associated with polymers that have strong ICT characteristics.²⁸ That's well agreement with the low quantum yield due to fluorescence quenching by electron exchange according the Dexter mechanism, which the photo induced ICT process is common phenomenon for polymers.²⁹ In the film state, the emissions of synthesized polymers show different manner with those in NMP. The PDKZ, PDTH2 and PDKZ3T73 were found in longer wavelength region than those in NMP. The red shift emission in the film state could be derived from the enhanced the intermolecular interaction among the neighbouring polymer backbones. The PDKZ1T73 shows similar manner with it in NMP. It seems that short thiophene units copolymerized with naphthalene disordered morphology of polymer which retards the efficient packing of polymer chains in the solid state. Also, the image of fluorescents of polymer thin film is shown in Figure 7 and Figure S28.

Electrochemical Properties

Table 3 The electrochemical properties of copolymer thin films

copolymer	Cal(CV and UV-vis)			Cal(Gaussian09)		
	LUMO ^a (eV)	HOMO (eV)	E _g ^b (eV)	LUMO (eV)	HOMO (eV)	E _g (eV)
PDKZ	-3.46	-5.83	2.37	-1.91	-5.23	3.33
PDKZ1T73	-2.56	-5.59	3.03	-2.06	-5.09	3.03
PDKZ3T73	-3.28	-5.75	2.47	-2.15	-4.73	2.58
PDTH2	-2.53	-5.62	3.09	-1.98	-5.23	3.25

^a Thin films measured in CH₃CN with 0.1 M tetrabutylammonium hexafluorophosphate. The calculation details for the E_{LUMO} and E_{HOMO} were shown in Figure S27 ^b Estimated from the onset of the absorption in thin films (E_g^{opt} = 1240/λ_{onset}).

Cyclic voltammetry (CV) was carried out to examine the electrochemical properties and determined the HOMO and LUMO levels of the polymers in thin film state (Table 3, details in Figure S27). Each sample for CV was prepared by drop-coating the polymer solutions in NMP onto working electrode. These four polymers showed reversible p-doping or n-doping processes. The LUMO levels of PDKZ, PDKZ1T73, PDKZ3T73 and PDTH2 are -3.46, -2.56, -3.28 and -2.53 eV. The PDTH2, which has the highest content of 3-dably-thiophen units in the polymer backbones, exhibited the highest LUMO levels. It

should be noted that the HOMO levels of polymer containing thiophene units was higher than that containing carbazole units. That's owed to the stronger donor ability of thiophene than carbazole. It's worth noting that the trends in electrochemical data of polymers, predicted by DFT theory, track closely with the experimentally observed trend. But for PDKZ1T73, its E_g value was bigger than PDKZ. This result is well agreement with the λ_{fs} in table 2. We speculated that as before in Optical Properties part: short thiophene units copolymerized with naphene disordered morphology of polymer than that of carbazole unit which retards the efficient packing of polymer chains in the solid state.

Morphology Characterization of Polymer Thin Film

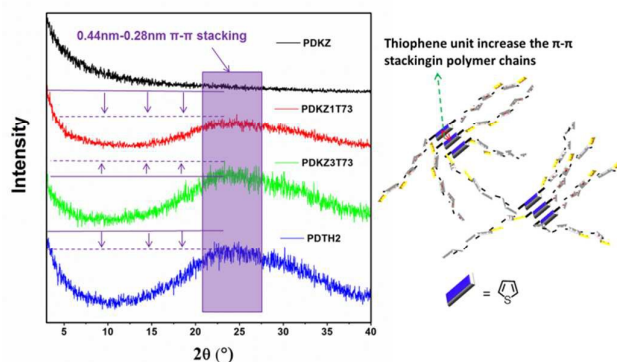


Figure 9 The XRD spectra of the polymer thin films

The morphology of polymer thin films was investigated by X-ray diffraction (XRD) measurement. As shown in Figure 9, no clear lamella diffraction peak can be observed for these polymers thin films, suggesting that there are rarely ordered arrangement in the films of the four polymers toward lamellar direction. In contrast, the features of π - π stacking can be distinguished in polymer containing thiophene unit (PDKZ1T73, PDKZ3T73 and PDTH2). The diffraction peak of these three film appeared at $2\theta = 20.2$ - 31.9° , corresponding to a π - π distance of 2.8- 4.4 Å. The intensity order of π - π stacking reflection signal was PDKZ3T73>PDTH2>PDKZ1T73>PDKZ. That's well agreement with the thiophene content in polymer main chains. It's worth mentioning that PDTH2 shows weaker intensity of π - π stacking reflection signal than PDKZ3T73. This is due to the dodecyl chain induces π - π interaction between the polymer chains. As we known, compact π - π stack is helpful to facilitate the π -electron transport in conjugated polymers.

Conclusions

In summary, for the first time, by using low-cost copper-catalyzed Ullmann C-O/C-N cross-coupling reaction as the polymerization method (Cs_2CO_3 as base) and phthalazinone units containing -OH and -NH as the monomer, sorts of polymers were prepared with satisfying M_n , through low activity dibromo thiophene monomers. The number-average molecular weight of PDTH is high up to 17.9 kDa. Due to the rigid spatial structure of A2 and the steric hindrance of dodecyl group ortho to dibromine thiophene, the M_n of polymers

containing A2 is varies from 2.2 to 9.6 kDa. Thanks to phthalazinone-thiophene structure (donor-acceptor effect) of A2, these conjugated polymers show remarkable photoelectric properties with deep HOMO level (<5.27 eV). By copolymerized with various donor monomers, the maximum emission wavelength of polymer thin films is changed from 465 nm to 564 nm. The XRD results show thiophene unit is more in favour of the π - π stacking in film state than phthalazinone unit. This validated structure-property correlation is a useful strategy to optimize the solid-state packing and further optoelectronic device performance. In conclusion, this work provides an effective method to synthesis polyarylethers and conjugated polymers via low-cost copper-catalyzed Ullmann polymerization.

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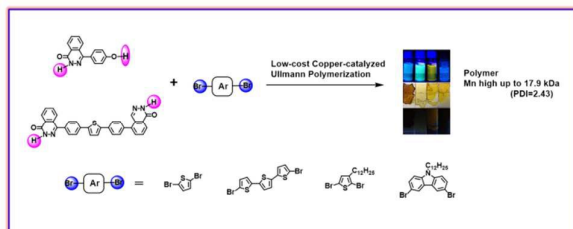
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We present a low-cost copper-catalyzed Ullmann polycondensation of phthalazinone based monomer provides an access to polyarylether and conjugated polymers.