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Synthesis of π-Conjugated Polymers Containing Benzodipyrrole Moieties in the Main Chain through Cleavage of C−H Bonds in 1,4-Bis(acetylamino)benzene

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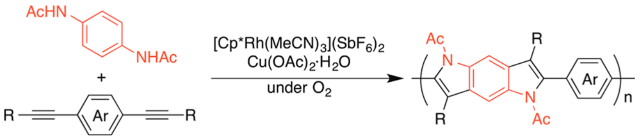
Supporting Information



ABSTRACT: Rhodium-catalyzed copolymerization between 1,4-bis(acetylamino)benzene and diynes through C−H bond cleavage afforded π-conjugated polymers containing benzodipyrrole moieties. The polymers with substituted benzene units exhibited nearly the same absorption peaks and HOMO levels. Fluorenone and benzothiadiazole moieties can be also introduced as electron-acceptor units to the main chain by polymerization in *tert*-amyl alcohol and tetrahydropyran as mixed solvent, leading to absorption at longer wavelength.

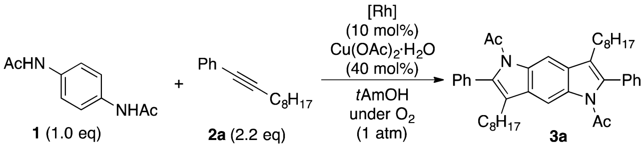
π-Conjugated polymers showed attractive absorption, luminescence, and semiconducting properties, which can be applied to organic photovoltaic cells, light-emitting diodes, or field-effect transistors.[1] To tune their power conversion of efficiency, color or mobility from the synthetic point of view, many π-conjugated polymers with various (hetero)arylene moieties in the main chains were proposed and synthesized.[2] Among them, *N*-hetero arenes are useful to modify the frontier orbital energies correlated to the optical and electronic properties.[3] While aromatics containing amide or imine moieties lower the LUMO levels and tend to accept electrons, pyrrole-type aromatics elevate the HOMO levels and elevate hole affinity.

One of the most conventional methods to prepare soluble π-conjugated polymers is transition metal-catalyzed cross-coupling polymerization through cleavage of carbon−halogen (C−X) bond and carbon−metal bond.[4] This approach bases on successive formation of a single bond between two aromatic units. Although the cross-coupling polymerization usually achieved high molecular weight and reliable regioselectivity, preparation of the halogenated, and metalated monomers sometimes required many synthetic steps to introduce functional groups at desired positions and generate a lot of byproducts and impurities. In recent years, transition metal-catalyzed direct C−H arylations have been applied to polymerization to reduce the cost and waste.[5] In direct C−H arylation polymerization through C−H and C−X cleavage, monomers with acidic protons or directing groups gave soluble π-conjugated polymers in good yield and regioselectivity. Moreover, some results supported that purity or performance of polymers by C−H direct arylation was better than those by conventional cross-coupling method.[6]

Nowadays, transition metal-catalyzed C−H activation followed by alkyne insertion is useful method for synthesis of fused aromatic rings.[7] Fagnou and co-workers developed facile synthesis of indoles by rhodium-catalyzed C−H bond cleavage of acetanilide and alkyne insertion.[8] The reaction proceeded under mild condition and gave indoles in good yield and high regioselectivity. Herein, we applied the C−H functionalization leading to indoles to synthesis of π-conjugated polymers containing *N*-heteroarenes in the main chain. The synthetic efficiency of the polymerization described here is highlighted by simultaneous formation of *N*-heterocycles with extension of the main chain and also by no need to prepare halogenated monomers or organometal monomers.

Before the synthesis of the polymers, annulation between 1,4-bis(acetylamino)benzene and 2.2 equiv of 1-decynylbenzene in *tert*-amyl alcohol (*t*AmOH) was optimized (Table 1). According to Fagnou's work,[8] rhodium complexes with Cp* ligand were investigated. The catalytic amounts of $[Cp^*RhCl_2]_2$ and $AgSbF_6$ in the presence of $Cu(OAc)_2$ as an oxidant under air afforded a benzodipyrrole in the moderate isolated yield

Table 1. Oxidative Annulation of 1 with 2a



entry	[Rh]	T (°C)	t (h)	yield[e] (%)
1[a,b,c]	$[Cp^*RhCl_2]_2$[d]	120	3	56 (57[f])
2	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	60	16	22
3	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	90	16	80 (72[f])

[a] Under air. [b] 2.1 equiv of $Cu(OAc)_2{\cdot}H_2O$ was used. [c] $AgSbF_6$ (10 mol %) was added. [d] 5 mol % of $[Cp^*RhCl_2]_2$. [e] NMR yield. [f] Isolated yield.

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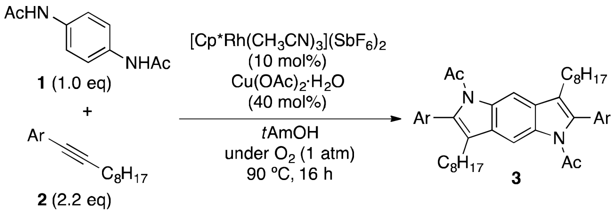
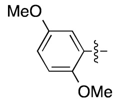
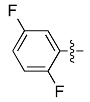
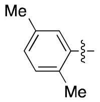
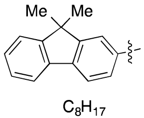
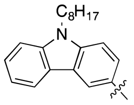
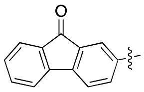
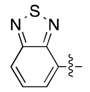
(entry 1, 55%). The cationic complex, $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ showed low efficiency at 60 °C (entry 2, 22% NMR yield) with molecular oxygen and 40 mol % Cu(II) salt. High reaction temperature, however, improved the isolated yield (entry 3, 72%).

Various arenes with the 1-decynyl groups were examined in the optimized reaction condition (Table 2). 2,5-Dimethoxyphenyl (entry 1, 62%) and 2,5-difluorophenyl (entry 2, 62%) decynes were tolerated in this annulation. In contrast, 2,5-dimethyl substitution decreased the yield (entry 3, 8%), probably due to steric hindrance by the methyl groups. Some fused arenes were also investigated. Relatively electron-rich 2-fluorenyl- and 3-carbazolyl-substituted alkynes gave the desired benzodipyrroles in the moderate yield (entries 4–6). Electron-deficient 2-fluorenonyl and 4-benzothiadiazolyl groups were also tolerated (entry 7).

Table 2. Oxidative Annulation of 1 with Various Alkynes

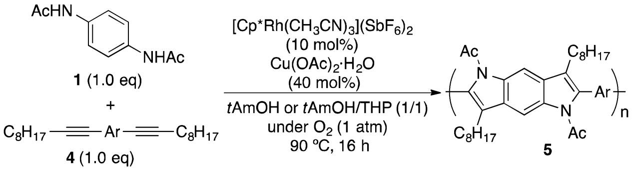


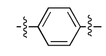
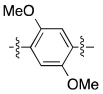
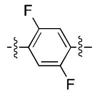
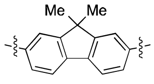
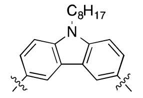
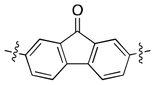
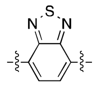
entry	Ar	product	Yield (%)^a
1		3b	62
2		3c	62
3		3d	8
4		3e	63
5		3f	64
6		3g	80
7		3h	76

^{a}Isolated yield.

With the optimized reaction conditions in hand, we explored copolymerization of 1,4-bis(acetylamino)benzene and internal diynes (Table 3) in *t*AmOH. Employing 1,4-bis(1-decynyl)-benzene as a comonomer afforded a polymer in 54% isolated yield and the number-average molecular weight (M_n) was 5500 estimated by size-exclusion chromatography (SEC) based on polystyrene standard (entry 1). Substitution by methoxy groups on the benzene ring of the diyne increased the yield and M_n (entry 2). Other comonomers investigated in Table 1, however, gave high amounts of insolubilities and low yields of soluble polymers (entries 3–7).

Table 3. Polymerization by Rhodium-Catalyzed Oxidative Annulation



en-try	Ar	poly-mer	yield (%)^a	M_n^{d}	M_w/M_n^{d}
1		5a	54^b 57^c	5500^b 5300^c	1.6^b 1.7^c
2		5b	66^b 46^c	15700^b 18300^c	2.8^b 2.4^c
3		5c	39^b 54^c	11000^b 7200^c	2.6^b 1.7^c
4		5e	16^b 47^c	8800^b 14900^c	10.9^b 2.9^c
5		5f	29^b 29^c	6400^b 5600^c	2.5^b 2.2^c
6^d		5g	8^b 54^c	19400^b 18200^c	4.6^b 3.1^c
7		5h	25^b 39^c	16600^b 10000^c	3.7^b 2.6^c

^{a}Isolated yield after reprecipitation. ^{b}*t*AmOH (10 mL/mmol **1**) was used as solvent. ^{c}*t*AmOH (10 mL/mmol **1**) and tetrahydropyran (THP, 10 mL/mmol **1**) were used as solvent. ^{d}Estimated by size-exclusion chromatography (SEC) based on polystyrene standard in THF. Reaction time was 1 h.

To improve the yield, screening of solvents revealed that *t*AmOH/tetrahydropyran (THP) could be applied to polymerization of a wide range of comonomers. Comonomers containing phenyl or 2,5-dimethoxyphenyl groups afforded nearly the same yields and molecular weights as those polymerized in *t*AmOH (entries 1 and 2). Polymerization using diynes with 2,5-difluorophenyl (entry 3), fluorenyl (entry 4), or fluorenonyl (entry 5) group proceeded well. Although the benzothiadiazole moiety in the diyne monomer tended to reduce the amount of the obtained polymer, *t*AmOH/THP solvent system improved the yield (entry 6). In polymerization with the carbazole-containig monomer, the yield and molecular weight were unchanged.

The primary structures of the obtained polymers were confirmed by ^{1}H and ^{13}C NMR spectra after reprecipitation (see Supporting Information). Their signals were similar to those of the corresponding low-molecular-weight compounds (**3a–3g**). Particularly, the peaks assignable to benzylic and acetyl protons were appeared nearly 2.7 and 2.1 ppm,

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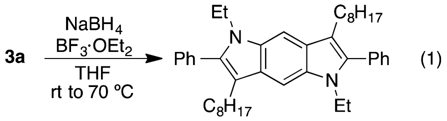
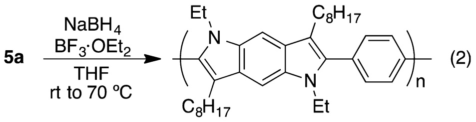
respectively. Several minor peaks were also observed around major peaks, probably corresponding to terminal groups or regioisomers. The peak area indicated that the amounts of minor structures reached around 10% of the major structures.

Although the *N*-acetyl group was important to efficient polymerization, their electron-withdrawing nature may weaken the electron-donating ability of benzodipyrrole units. Scope of reducing condition using the model compound **3a** revealed that combination of boron trifluoride diethyl etherate and sodium borohydride converted acetyl groups of **3a** to ethyl groups almost quantitatively (eq 1). Then, the reduction was applied to the polymer **5a**. After addition of methanol and aqueous NaOH to the reaction mixture, ^{1}H NMR spectra of the resulting precipitate indicated complete disappearance of the acetyl group at 2.09 ppm and presence of some impurities like borate esters at 3.41 ppm. The impurities were successfully removed by washing with aqueous NaOH and additional reprecipitation. The purification process reduced the lower molecular weight component together with the impurities, leading to low yield (38%) and higher estimated molecular weight than **5a**.



6a (90%)



7a (38%, M_n = 8,100)

Properties of the obtained compounds were investigated by UV−vis absorption and cyclic voltammetry. The absorption maximum of **5a** was observed at a slightly longer wavelength (356 nm) than that of **3a** (345 nm). Moreover, introducing methoxy (**5b**) or trifluoromethyl (**5c**) groups on the phenyl ring kept the wavelength of the absorption maxima. The little shift suggested that the substituent on the benzodipyrrole sterically prevented extending the conjugation length. The polymers with fluorenone (**5g**) or benzothiadiazole (**5h**) moieties as acceptor units showed absorption peaks at 442 and 453 nm, respectively. Furthermore, the UV−vis spectrum of contains shoulder around 400 nm (Figures S1−S3, see Supporting Information), leading to the narrow optical energy gap.

HOMO energy levels were determined by cyclic voltammograms. All compounds shown in Table 4 possess nearly the same HOMO energy levels, indicating that the benzodipyrrole moiety dominated the HOMO levels. As expected, the polymer with *N*-ethyl group (**7a**) elevated HOMO energy level as compared with that with *N*-acetyl group (**5a**). Reduction waves of **5g** and **5h** can be observed. The calculated LUMO levels from voltammograms of **5g** and **5h** were −3.45 and −3.32 eV, respectively. These values were virtually consistent with onsets of the UV−vis absorption band so that the bands were attributed to HOMO−LUMO transitions.

In summary, annulation between amides and alkynes through rhodium-catalyzed C−H bond cleavage was applied to polymerization. 1,4-Bis(acetylamino)benzene and various diynes were appropreate for comonomers to afford the π-conjugated polymers containing benzodipyrrole moieties in the main chains. Cyclyc voltammetry and UV−vis absorption spectra revealed that the benzodipyrrole unit worked as electron-donor. Investigation of other *N*-directing groups and catalysts for high molecular weight is currently underway in our group.

Table 4. Optical and Electronic Properties

compound	λ_{abs}[a] (nm)	λ_{em}[b] (nm)	E_{HOMO}[c] (eV)	E_g^{opt}[d] (eV)
3a	345	428	−5.72	3.32
5a	356	438	−5.77	3.10
5b	355	441	−5.70	3.12
5c	347	446	−5.92	3.10
5e	368	435	−5.68	2.99
5f	345	468	−5.60	3.20
5g	442	n.d.	−5.76	2.38
5h	453	589	−5.83	2.32
6a	371	419	−5.11	3.08
7a	344	461	_5.10	2.86

[a] Absorption maximum at the longest wavelength of dichloromethane solution. [b] Emission maximum at the longest wavelength of dichloromethane solution. [c] $E_{\mathrm{HOMO}} = -(E_{\mathrm{ox}}^{\mathrm{onset}} + 5.1)$ and the oxidation potential was determined vs the Fc/Fc+ couple. [d] Energy corresponding to the onset of the absorption spectrum.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, UV−vis spectra, and NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00343.

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Notes

The authors declare no competing financial interest.

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