Macromolecules **2000,** *33,* 5455−5459

Synthesis, Characterization, and Fluorescence of Copolymers of *N*-Alkylcarbazole and *trans*-Stilbene Obtained by an Oxidative-Coupling Reaction

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Received December 27, 1999; Revised Manuscript Received May 2, 2000

ABSTRACT: A novel kind of conjugated polymer was prepared by an oxidative-coupling polymerization of *N*-alkylcarbazole and *trans*-stilbene. The structure of the copolymers was characterized by elemental analysis, ^{1}H NMR, UV−vis, and FTIR spectra. The copolymers have good solubility in common organic solvents and are thermally stable. Fluorescence spectra showed that these polymers are blue-light-emitting materials.

Introduction

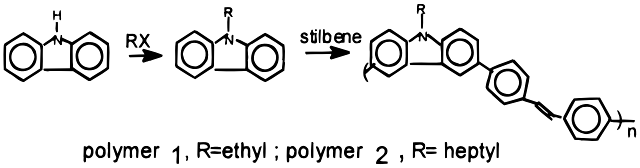
Poly(phenylenevinylene) (PPV) and its derivatives have attracted wide interest due to the applications as active components for a light-emitting diode (LED).[1] PPVs and phenylenevinylene copolymers are the most thoroughly studied light-emitting polymers for LED so far. However, the syntheses and processes are difficult, even tedious, tasks. Hence, various synthetic methods such as the Wittig reaction,[2] Heck reaction,[3] and Wessling reaction[4] were developed to prepare phenylenevinylene polymers and copolymers. But there are some drawbacks that need to be improved, such as complicated synthetic routes, low yield, gel generation, luminescence quenching defects in the individual reaction, and material. Therefore, efforts to improve the synthetic method are necessary and still going on in many laboratories. The Scholl reaction, or oxidative-coupling reaction, was improved to prepare soluble polyphenylenes by Mitsuru et al.[5] Li et al. have prepared polyphenylenes in chloroform and shown that polyphenylenes are blue- to green-light-emitting materials.[6] But their study was limited to the redox potential of aromatic molecules and steric effects; only few polymers were prepared by their method.

In the present work we propose a copolymerization to overcome this limitation and expand the synthetic scope and present a novel, facile synthetic method to prepare analogues of phenylenevinylene copolymers, which contain conjugated aromatic rings and double carbon−carbon bonds in the main chain. The synthesis was conducted simply by the oxidative-coupling polymerization of *N*-alkylcarbazole and stilbene, without introducing reactive groups to the monomers. Both monomers are well-known fluorescent molecules, while the former is widely utilized as a charge-transporting agent in photoconductive materials. Therefore, we can expect that the new polymers will have good luminescence and conducting properties. The synthetic route is shown in Scheme 1. The synthesis, characterization, solubility, stability, absorption, and fluorescence spectra were investigated.

Experimental Section

Materials. *N*-Alkylcarbazole was synthesized according to the literature method.[7] Commercially available solvents were purified according to standard procedures. $FeCl_3$ was treated by refluxing in $SOCl_2$ for 2 h, and then $SOCl_2$ was removed by distillation.

Scheme 1



polymer 1, R=ethyl ; polymer 2 , R= heptyl

Preparation of the Copolymers. Polymers were synthesized in similar manners. Therefore, the preparation procedure of polymer **2** is described as a representative example as follows. In a two-neck flask equipped with gas inlet, electromagnetic stirrer, and funnel, 2.93 g (18 mmol) of $FeCl_3$ and 50 mL of chloroform were stirred while 0.40 g (1.5 mmol) of *N*-heptylcarbazole and 0.54 g (3 mmol) of stilbene were added under an argon atmosphere. The reaction was continued overnight at room temperature. Then $FeCl_3$ was filtered off. The filtrate was poured into methanol. The precipitated product was collected by filtration, washed by methanol for several times, and dried in an oven at 60 °C. The weight of recovered polymer was 0.57 g, yield 60%. Elemental analysis (%): N, 1.17; C, 92.77; H, 6.06.

Solubility Measurement. A 50−100 mg sample of polymer was accurately weighed and then stirred for 1 h or was treated in an ultrasonator for 10 min in a tube with 2−5 mL of solvent at room temperature. Insoluble polymer was separated by centrifugation, dried in an oven, and then weighed. The solubility was calculated by the formula

$$S = (w_0 - w_i)/10L$$

where S is the solubility in units of g/100 mL, w_0 and w_i are the weight (in milligrams) of the started polymer and the insoluble polymer, respectively, and L is volume of the solvent in milliliters.

Instrumentation and Measurement. UV−vis absorption spectra were measured on a SCHIMADZU UV-160A spectroscopy. IR spectra were recorded on a NICOLET 170SX FT-IR spectrometer. ^{1}H NMR was performed on a MERCURY-VX300 spectroscopy. Fluorescence spectra were measured with a fluorescence spectrophotometer RF-5301PC. Quantum yield was measured using Rhodamine B as a standard. Thermal analyses were conducted on SCHIMADZU DT-40 instrument. Wide-angle X-ray diffraction (WAXD) was measured on a RIGAKU Dmax-rA instrument, with a rotating anode X-ray generator (wavelength 0.154 059 8 nm).

10.1021/ma992162p CCC: $19.00

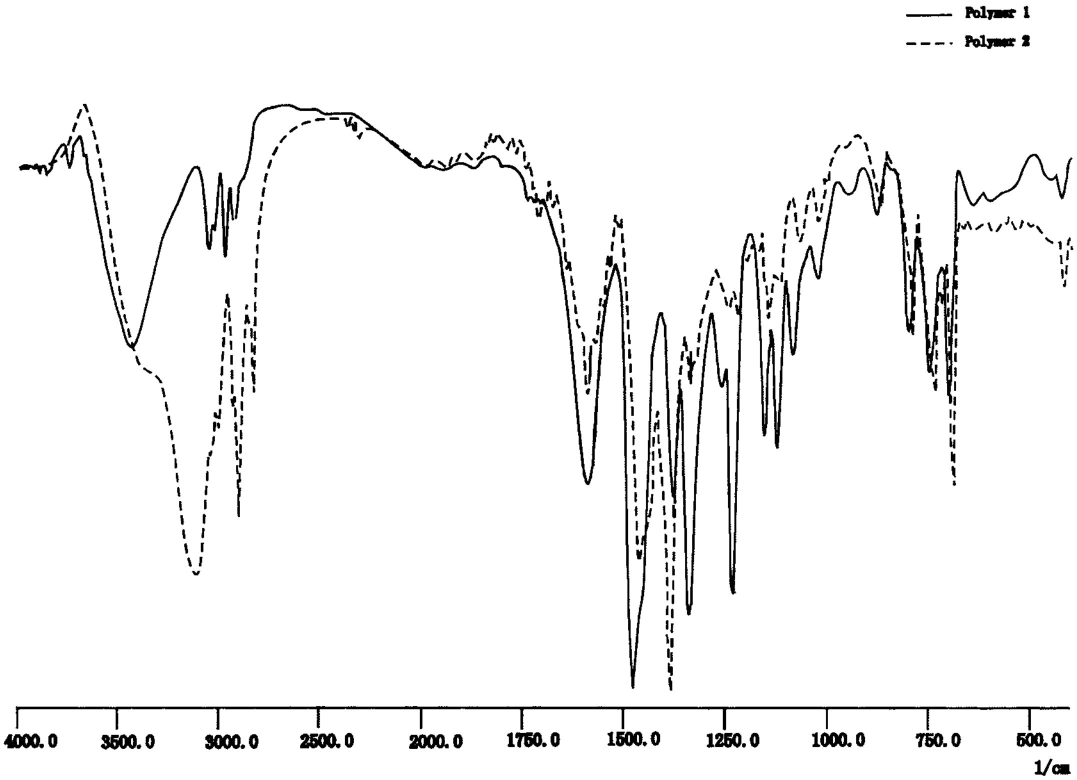


Figure 1. FT-IR spectra of the copolymers on KBR pellets.

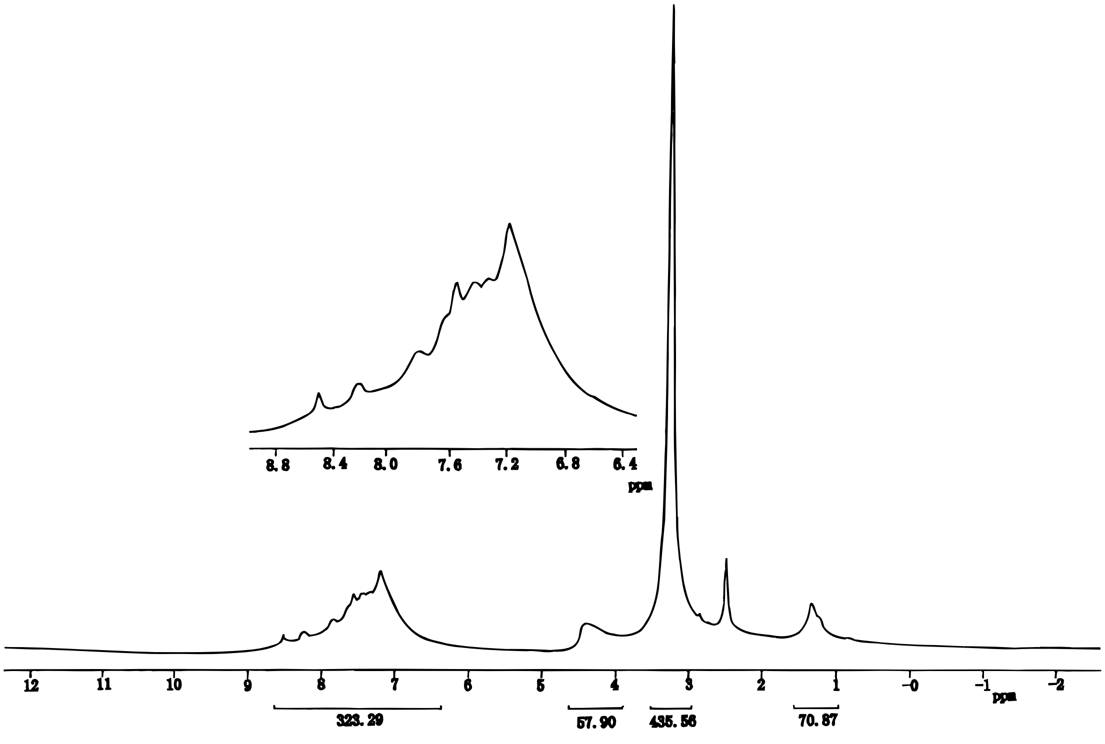


Figure 2. ^{1}H NMR spectrum of copolymer **1** in DMSO.

Results and Discussion

The copolymerization results showed that the two monomers, *N*-alkylcarbazole and stilbene, are a good comonomer pair. The former could not self-polymerize, while the latter yielded only a poor homopolymer. However, the copolymerization of the two monomers generally got yields of about 50%. The inherent viscosity measured at 30 °C in acetone ranged from 0.2 to 0.6 dL g^{-1}. The inherent viscosity of polymer **1** and polymer **2** discussed in this paper is 0.33 and 0.54 dL g^{-1}, respectively.

The copolymers were characterized by ^{1}H NMR, FT-IR, and elemental analyses. In the copolymerization of copolymer **2**, although the feed ratio of *N*-alkylcarbazole to stilbene was changed from 1:2 to 2:1, the elemental composition of the copolymers was slightly changed. This proved further that the monomers have a strong tendency to copolymerize.

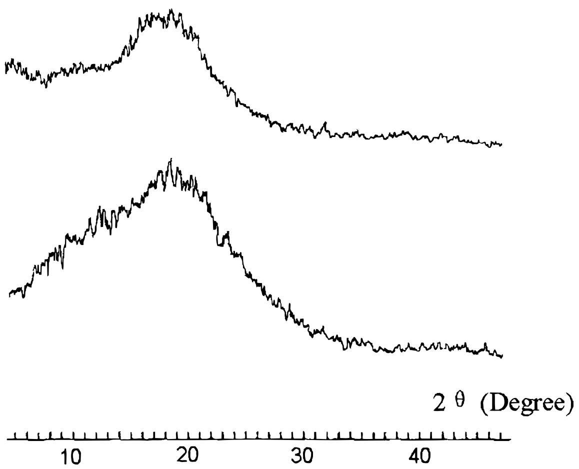


Figure 3. Wide-angle X-ray diffraction curves of the copolymers.

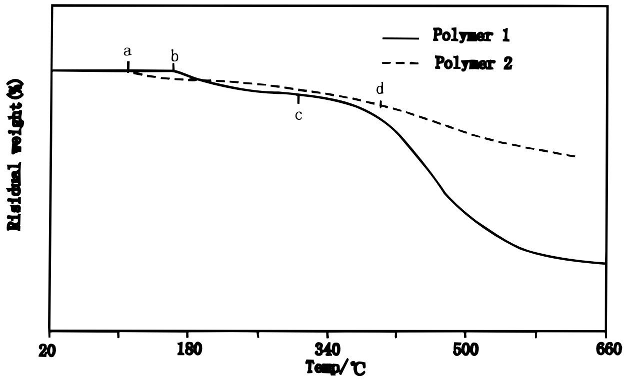


Figure 4. Thermogravimetric analysis of the copolymers: (a) 108 °C; (b) 159 °C; (c) 303 °C, 4.5%; and (d) 396 °C, 7.7%.

Table 1. Solubility of the Copolymers (g/100 mL)

	toluene	alcohol	chloroform	acetone	DMF
polymer **1**	0.78	0.34	2.23	1.97	2.70
polymer **2**	1.13	0.16	3.70	1.60	4.37

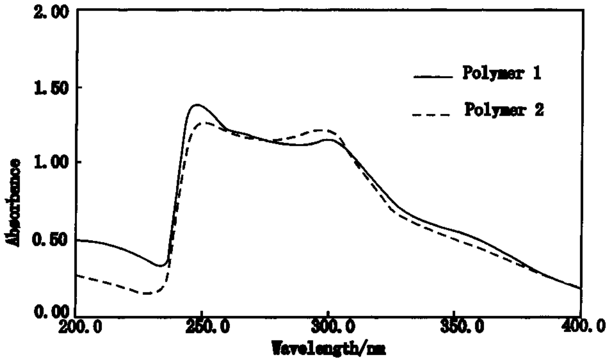


Figure 5. UV–vis spectra of the copolymers in chloroform solution.

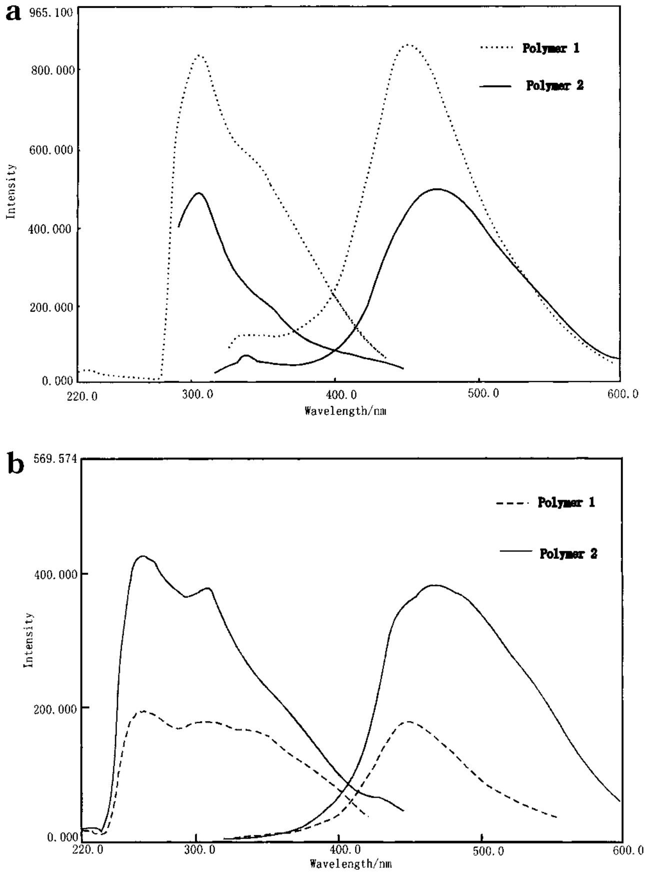


Figure 6. Fluorescence and excitation spectra of the copolymers in toluene (6.1 excited at 305 nm) and chloroform (6.2 excited at 308 nm).

The FT-IR spectra of the copolymers in KBr pellets are shown in Figure 1. The spectra exhibit a C–H stretch of unsaturated –C=C– bands at 1600 and 1500 cm^{-1}, a saturated C–H vibration at 1450 and 1350 cm^{-1}, and a N–C stretching at 1230 and 1350 cm^{-1}. The spectra do not show multiple peaks of monosubstituted benzene ring in the region 1700–1920 cm^{-1} but show characteristic absorption of 1,4-disubstitution on a benzene ring at 830 cm $^{-1}$, indicating the para-coupling on the stilbene moieties. A weak but sharp band at 950 cm^{-1}, corresponding to the out-of-plane bending mode of the *trans*-vinylene groups, appeared for the both copolymers. Absorptions at 880 and 800 cm $^{-1}$, characteristic of 1,2,4-trisubstitution on an aromatic ring, are found from each polymer, indicating the coupling took place at position 3 and 6 on the moieties of carbazole.

Figure 2 shows the ^{1}H NMR spectrum of polymer **1** in DMSO obtained from MERCURY-VX 300 NMR spectroscopy. Obviously the signals of the ethyl protons are in the high field while those of the aromatic protons are in the low field of 7–8.5 ppm. Although the signals were broad and overlapping, it is possible to assign the signals by comparing the frequencies with those of monomers and considering orientation rules. Hence, the signals in the region 7–7.6 and 7.6–8.5 ppm are attributed to the moieties of stilbene and carbazole, respectively. The possible structure of polymer **1** is shown in Scheme 1; the ratio of carbazole and stilbene units calculated from the integrated area is near 1:1.

The solubility of the copolymers measured at room temperature is shown in Table 1. The results illustrate that the copolymers had good solubility in many common organic solvents. The longer alkyl side chains led to better solubility in chloroform and toluene, but the short alkyl side chains resulted in good solubility in ethanol and acetone. Therefore, the copolymers are easy to process. Solid films were cast from chloroform and toluene solution, and viscosity was measured in acetone.

The X-ray diffraction experiment showed that the copolymers are amorphous. As shown in Figure 3, the diffuse intensity curves indicate a random structure in

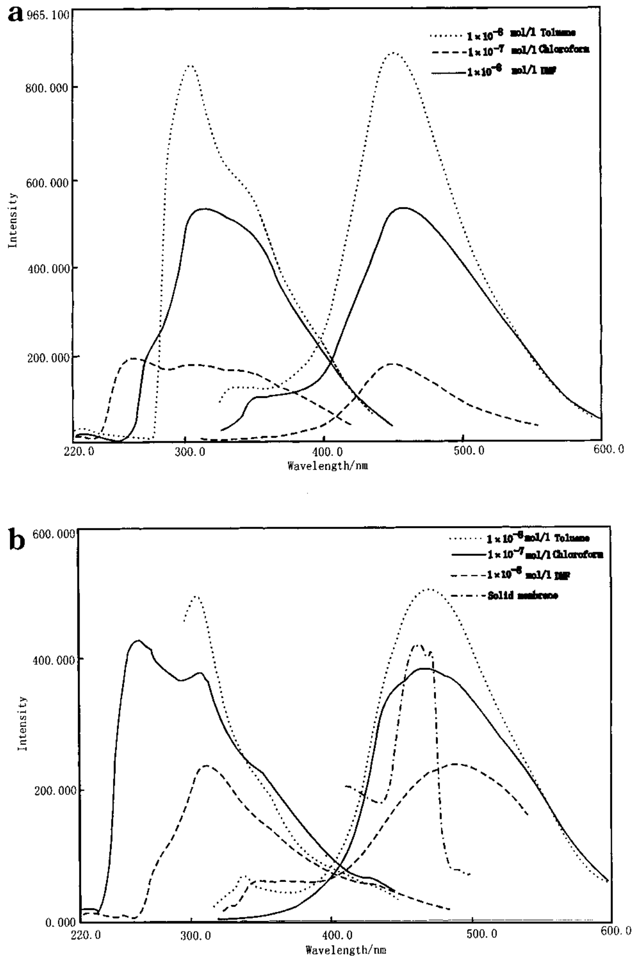


Figure 7. Fluorescence and excitation spectra of copolymer **1** (a) and copolymer **2** (b) in different solvent as well as PL ((b) excited at 280 nm) spectrum of solid film of polymer **2**.

Table 2. Quantum Efficiency of the Polymers Relative to Rhodamine B in Solution

	chloroform	toluene	DMF
polymer **1**	0.03	0.68	0.19
polymer **2**	0.03	0.18	0.04

the solid polymer. The copolymers showed good thermal stability (Figure 4) as weight loss was less than 5% on heating to 303 °C for polymer **1** and 8% at 396 °C for polymer **2**.

Figure 5 shows the UV−vis absorption spectra of the copolymers in chloroform. The absorption bands are at 248, 300, and 350 nm for polymer **1** and at 250, 302, and 350 nm for polymer **2**. Obviously, the two copolymers had very similar absorption bands and a slight red shift due to the larger molecular weight of polymer **2**. In the spectra of monomers there only is a band at 300 nm which came from a $\pi-\pi^*$ transition for stilbene and three bands at 240, 270, and 300 nm attributed to the $n-\sigma^*$, $\pi-\pi^*$, and $n-\pi^*$ transition for *N*-heptylcarbazole. Hence, the absorption bands at 350 nm came from the longer conjugated length and lower transition energy in the polymers.

The fluorescence and excitation spectra of the copolymers in solution are shown in Figure 6, which illustrates that polymer **1** exhibits a shorter emitting wavelength. The emission maximum in chloroform and toluene is at 448, 451 nm for polymer **1** and at 467, 470 nm for polymer **2**, respectively. The red shift of the emission wavelength due to larger molecular weight is quite large in solution. Because the copolymers have a fully conjugated rigid backbone, the conjugation length should increase with chain length; it is reasonable to have longer emitting wavelength for polymer **2**.

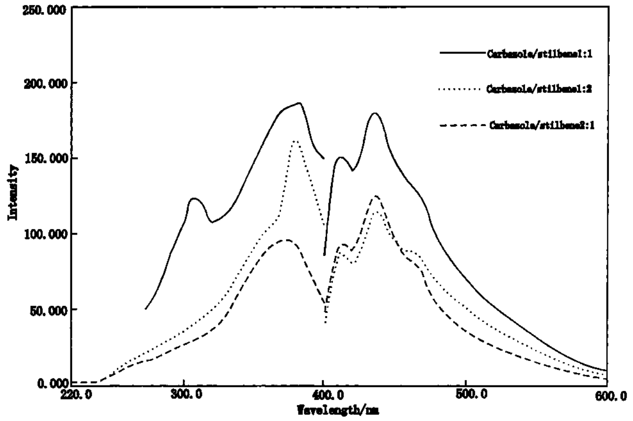


Figure 8. Fluorescence and excitation spectra of copolymer **2** (excited at 285 nm) with different feed ratio.

Figure 7 showed fluorescence and excitation spectra of the copolymers in different solvents. The emission maxima were at 447, 451, and 455 nm for polymer **1** and at 467, 470, and 489 nm for polymer **2** in chloroform, toluene, and DMF, respectively. The polymers had much higher emission intensity in toluene than in chloroform or DMF, since chlorine atoms and carbonyl groups quench fluorescence. For the solid-state film of copolymer **2** spin-coated on SiO_2 glass, the maximum emission wavelength was at 470 nm as showed in Figure 7b. The cutoff emitting wavelength was within 500 nm, indicating a narrow genuine blue emission.

Table 2 lists the quantum yield of the copolymers in different solvents using Rhodamine B as a standard. The photoluminescence (PL) efficiency in chloroform is very poor but quite high in toluene; an unusually high yield was obtained in polymer **1**. This may be due to its short side chain and high rigid backbone.

Figure 8 shows the fluorescence spectra of polymer **2** with different feed ratios in the copolymerization. The maximum emission wavelengths were all at ca. 436 nm, indicating a similar conjugated length and short wavelength emission.

In these copolymers the fluorophores were bonded only on the main chains; the stiff molecular chains reduced both inter- and intramolecular interaction. Therefore, a narrow emission peak is formed. Hence, a genuine blue PL light emission was obtained from both copolymer **1** and copolymer **2**.

Conclusion

A new kind of conjugated polymer was prepared by directly co-coupling of *N*-alkylcarbazole and stilbene. The copolymers had good solubility in common organic solvents and excellent thermal stability. The photoluminescence of the polymers was blue. The long alkyl side chains on the backbone of the polymers improved solubility, and short side chains led to high quantum efficiency.

References and Notes

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