Synthesis of A New Class of n-Dopable and Photoluminescent Conjugated Polymers Having Phenazine Units in the Main Chain

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Received July 24, 2000
Revised Manuscript Received October 11, 2000

Introduction. Phenazine and its derivatives have been widely studied from many aspects such as pharmaceuticals, agrochemicals, pigments, and dyes.[1] Although their high electron-accepting and luminescent properties are deemed promising for the production of novel n-dopable polymers, phenazine-based conjugated polymers have attracted less attention so far. Thus, it is of great interest to synthesize processable conjugated polymers having phenazine units in the main chain and to explore potentially novel applications based on their optical, electrical,[2] and magnetic properties.[3]

Many types of conjugated polymers have been synthesized to date,[4] and dihalides were mainly used for their synthesis through polycondensation. Starting from dihaloarenes, conjugated polymers are readily attainable by the transition-metal catalyzed couplings such as nickel(0)-promoted Yamamoto coupling,[5] palladium-catalyzed Suzuki coupling,[6] Heck reaction,[7] and Stille coupling.[8] However, dihalophenazines have not been regarded as a π-conjugative building unit; this is probably because its anthracene-like rigid structure reduces the polymer processability. Indeed, to our knowledge, there has been only one report concerning the synthesis of phenazine-based conjugated polymer from dihalophenazine where poly(phenazine-2,7-diyl) with a number-average molecular weight (M_n) of 1652 was synthesized by the Yamamoto coupling of 2,7-dibromophenazine.[9] This polymer was soluble in DMF but insoluble in common organic solvents like toluene, chloroform, and tetrahydrofuran (THF). It seems to be effective for the synthesis of the processable phenazine-based conjugated polymers to employ dihalophenazines with long alkyl chains. Although several synthetic methods for substituted phenazines have been demonstrated,[1,10,11] complicated multistep reactions are further required for preparation of substituted dihalophenazines.

In the present communication, we report on a simple preparative method for a tetraalkyl-substituted dihalophenazine from a readily prepared dialkyl-substituted dihalobenzene and the synthesis of novel phenazine-containing polymers therefrom.

Results and Discussion. The oxidation of anilines with manganese dioxide (MnO_2) generally leads to azobenzenes in high yields.[12] However, ortho-substituents on anilines prevent the formation of azobenzenes, resulting in substituted phenazines.[11] For example, phenazine-1,6-dicarboxylic acid was prepared from anthranilic acid in the presence of MnO_2 in 16% yield.[11a] On the basis of this result, we performed the MnO_2-promoted oxidation of 2,5-dihexyl-4-iodoaniline, which is readily available from 1,4-dihexyl-2,5-diiodobenzene, to give 1,4,6,9-tetrahexyl-2,7-diiodophenazine (**1**) (Scheme 1).

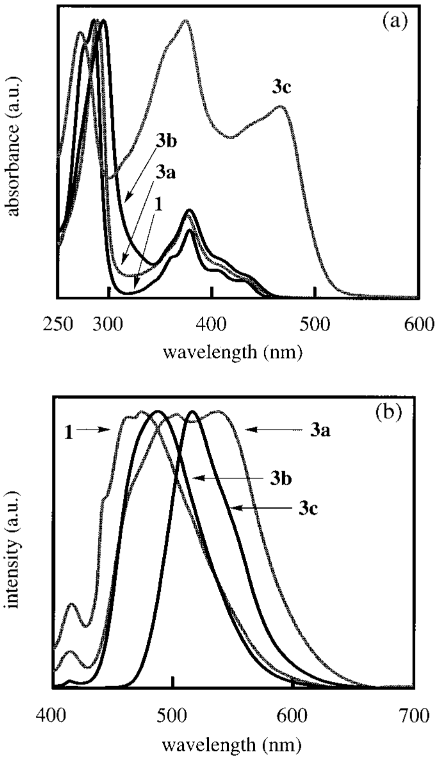
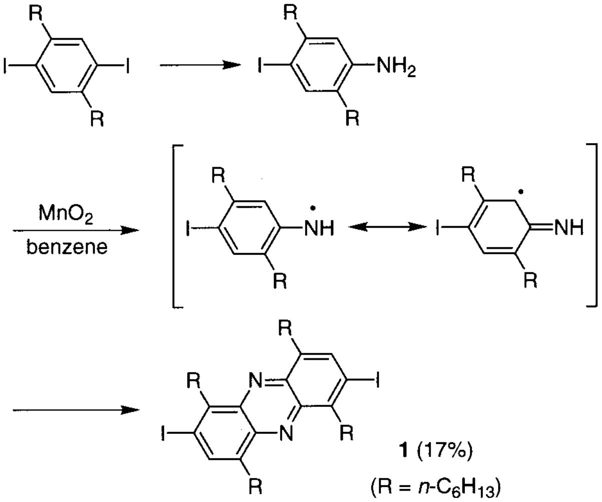


Figure 1. (a) UV/vis absorption spectra (in $CHCl_3$) and (b) the photoluminescence spectra (in $CHCl_3$, excited at 370 nm) of **1** and **3a**−**c**.

Scheme 1



We found that when excited at 370 nm in chloroform, **1** shows luminescence with peak maxima located at 461 and 473 nm and a shoulder at 415 nm (Figure 1b). Using **1** as a monomer, we synthesized three types of conjugated polymers (**3a**−**c**) having phenazine units in the main chain in order to tune the luminescent properties of the phenazine-based polymers. Our approaches to the phenazine-containing conjugated polymers involve the palladium-catalyzed dehalogenative coupling of **1** using bis(pinacolato)diboron (**2a**) as a condensation reagent[13] for homopolymer **3a**, the Suzuki coupling of **1** with 1,3-propanediol diester of 1,4-phenylenediboronic acid (**2b**) for the poly(*p*-phenylene) (PPP)-based polymer, **3b**, and

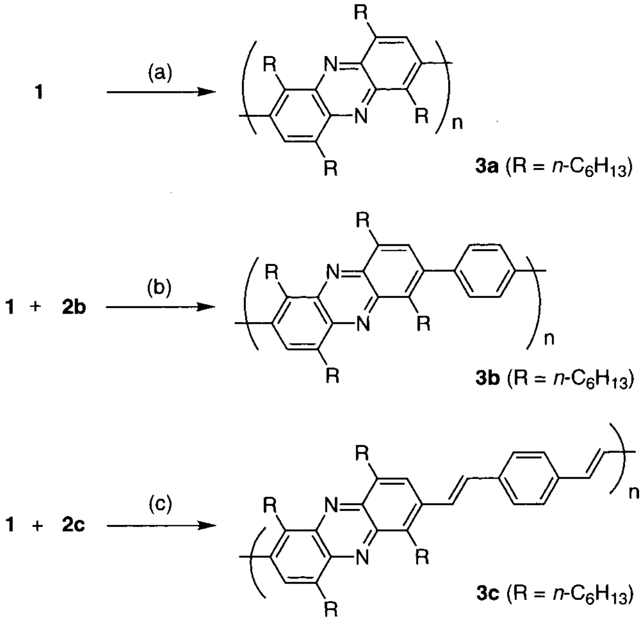
10.1021/ma001282q CCC: $19.00

Table 1. Properties of Polymers Having Phenazine Units in the Main Chain[a]

polymer	M_n[b]	M_w[b]	T_0 (°C)[c]	E_{pc} (V)[d]	E_{pa} (V)[d]	λ_{max} (nm)[e]	λ_{emi} (nm)[f]
3a	3170	7100	376	−0.91, −1.30	−1.15, −1.60	288, 376	414, 503, 537
3b	2970	3760	382	−0.95, −1.32	−1.13, −1.56	294, 378	416, 487
3c	2010	4260	297	−0.94, −1.28, −1.58	−1.20, −1.59	272, 374, 466	516

[a] The part extracted with hot toluene. [b] Estimated by GPC (THF, PSt). [c] The onset temperature of weight loss; heating rate = 10 °C/min, in air. [d] The cathodic peak potential (E_{pc}) and the anodic peak potential (E_{pa}) vs Ag/Ag$^+$ electrode of CH_2Cl_2 solution (20 mL) containing n-Bu_4NBF_4 (0.1 M) and **3** (1 mg). [e] In $CHCl_3$. [f] The peak wavelength of emission in $CHCl_3$ excited at 370 nm.

Scheme 2



(a) $PdCl_2$(dppf), **2a**, NaOH, DMAc, 120 °C, 24 h.
(b) $Pd(PPh_3)_4$, K_2CO_3, DMAc, H_2O, 120 °C, 24 h.
(c) $Pd(OAc)_2$, Bu_4NCl, LiCl, K_2CO_3, DMAc, 120 °C, 24 h.

the Heck reaction of **1** with 1,4-divinylbenzene (**2c**) for the poly(p-phenylenevinylene)- (PPV-) based polymer, **3c** (Scheme 2). Properties of **3** are summarized in Table 1.

Methanol-insoluble polymers were obtained in good yields, and about 40% of them were extracted with toluene to yield **3a**−**c**. They were soluble in chloroform and THF as well as in toluene. Thus, the polymer solubility in common organic solvents was considerably improved by the introduction of four hexyl pendant groups onto the phenazine ring. Although M_n of the THF-soluble parts of **3** were not satisfactorily high ($M_n < 4 \times 10^3$), we observed that polymers with M_n up to 1×10^4 were soluble in THF according to the GPC traces of **3**. Therefore, the unextractable toluene-insoluble parts seem to have M_n values higher than 1×10^4.

The toluene-extracted polymers (**3a**−**c**) gave fluorescent yellow solutions in toluene, chloroform, and THF. Tough free-standing films were readily obtained by casting these solutions. The polymers showed good thermal stability, the temperatures of the 5% weight loss in air were observed at 393, 417, and 319 °C for **3a**, **3b**, and **3c**, respectively.

We found that **3a**−**c** readily underwent n-doping in dichloromethane solutions, resulting from the high electron affinity of the phenazine unit.[2] The electrochemical reductions of **3** reversibly occurred at around −0.9 and −1.3 V (vs Ag/Ag$^+$), which correspond to the cathodic peak potentials (E_{pc}) of **1** at −0.87 and −1.29 V (vs Ag/Ag$^+$), respectively. The PPV-based polymer, **3c**, showed an additional reduction peak at −1.58 V probably due to the reduction of the olefinic unit.

The UV/vis absorption spectra of **3a** and **3b** in chloroform were similar to that of **1**. On the other hand, **3c** showed a very wide absorption band whose cutoff was located at 590 nm (Figure 1a). This suggests that the π-electrons in the phenazine ring of **3c** delocalize along the main chain via the olefinic bonds to extend the degree of main chain conjugation. In contrast, the main chains of **3a** and **3b** are more twisted due to the attached alkyl side chains, which reduces the conjugation length of the main chain. When excited at 370 nm in chloroform, **3a**−**c** emitted green to yellow light in solution. Polymer **3a** showed a very wide emission range over 400−650 nm (Figure 1b). The quantum yields for **3a**−**c** were 2, 2, and 30%, respectively.

In conclusion, we have demonstrated a convenient preparative method of tetraalkyl-substituted diiodophenazine (**1**) by the oxidation of the corresponding aniline with MnO_2. Three novel conjugated polymers having phenazine units in the main chain (**3a**−**c**) were successfully synthesized from **1** using palladium-catalyzed coupling methods. Polymers **3a**−**c** showed moderate solubility in common organic solvents, were thermally stable in air, and readily underwent n-doping in dichloromethane solution. Moreover, **3a**−**c** in the excited states exhibited intense emissions in wide ranges, which would allow them to be considered as a new class of organic light-emitting diodes for large-area light sources and flexible color displays with low power consumption.

Experimental Section. General Data. The measurements of cyclic voltammetry were carried out in a dichloromethane solution of 0.1 M tetrabutylammonium tetrafluoroborate with a three-electrode system composed of Ag/Ag$^+$ electrode, Pt reference electrode, and Pt wire counter electrode. $PdCl_2$(dppf),[14] **2b**,[15] and **2c**[16] were synthesized according to the literature. $Pd(OAc)_2$ and **2a** were purchased from Wako Pure Chemicals Industries, and Aldrich Chemical Co., respectively.

1,4,6,9-Tetrahexyl-2,7-diiodophenazine (1). A mixture of benzene (350 mL), 2,5-dihexyl-4-iodoaniline[17] (26 g, 67 mmol), and MnO_2 (180 g, 2.1 mol) was stirred at room temperature for 22 h and then at 60 °C for 24 h. After filtration of the mixture, the filtrate was concentrated and then subjected to SiO_2-column chromatography (eluent, hexane). The resulting yellow solid was further purified by recrystallization from ethanol to give 4.5 g (17%) of **1** as a yellow powder. Mp: 138−139 °C. ^1H NMR ($CDCl_3$): δ 0.82−1.05 (m, 12H), 1.25−1.93 (m, 32H), 3.21 (t, 4H), 3.48 (t, 4H), 7.95 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.72, 22.78, 29.73, 29.84, 29.96, 30.95, 31.19, 31.83, 36.60, 102.55, 138.83, 140.26, 140.88, 141.23, 143.81. IR (KBr): 2955, 2921, 2851, 1588, 1466, 1458, 1393, 1318, 1113, 1061, 883, 812, 722, 675, 534, 418 cm^{-1}. Anal. Calcd for $C_{36}H_{54}N_2I_2$: C, 56.25; H, 7.08; N, 3.64; I, 33.02. Found: C, 56.33; H, 6.93; N, 3.74; I, 32.95.

Polymer 3a. A solution of *N*,*N*-dimethylacetamide (DMAc) (20 mL) containing **1** (770 mg, 1.0 mmol), **2a** (250 mg, 1.0 mmol), $PdCl_2$(dppf) (22 mg, 0.030 mmol), and NaOH (160 mg, 4.0 mmol) was stirred under nitrogen at 120 °C for 24 h. Then the reaction mixture was poured into 200 mL of methanol. The precipitate was filtered, washed with a water/methanol (1:1) mixture and then with methanol. After drying in a vacuum, the polymer was extracted with toluene in a Soxhlet apparatus for 24 h, and then the resulting extract was concentrated and reprecipitated into 200 mL of methanol to give **3a** as a green-yellow powder in 33% yield (170 mg) (43% of the polymer was extracted with toluene). ^{1}H NMR ($CDCl_3$): δ 0.70−0.99 (CH_3), 1.10−2.16 ($ArCH_2CH_2CH_2CH_2CH_2$), 2.86−3.65 ($ArCH_2$), 7.44−7.67 (Ar*H*). IR (KBr): 2955, 2924, 2872, 2855, 1609, 1528, 1466, 1437, 1401, 1377, 1308, 1177, 1152, 1113, 1059, 901, 723, 536 cm^{-1}. Anal. Calcd for $(C_{36}H_{54}N_2)_n$: C, 83.99; H, 10.57; N, 5.44. Found: C, 82.87; H, 10.54; N, 5.15; I, 0.72.

Polymer 3b. A sealable 10 mL ampule was charged with **1** (230 mg, 0.30 mmol), **2b** (74 mg, 0.30 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), K_2CO_3 (170 mg, 1.2 mmol), DMAc (5.0 mL), water (1.0 mL) and a stirring bar. The mixture was degassed twice by the freeze−pump−thaw procedure, and then the ampule was sealed off with a gas burner under vacuum, followed by stirring at 120 °C for 24 h. After the same workup processes used for **3a** described above, **3b** was obtained as a yellow powder in 37% yield (66 mg) (38% of the polymer was extracted with toluene). ^{1}H NMR ($CDCl_3$): δ 0.88−0.98 (CH_3), 1.10−2.03 ($ArCH_2CH_2CH_2CH_2CH_2$), 3.07−3.50 ($ArCH_2$), 7.30−7.66 (Ar*H*). IR (KBr) 3025, 2957, 2924, 2872, 2855, 1686, 1615, 1534, 1466, 1408, 1377, 1318, 1177, 1105, 1063, 1021, 845, 722 cm^{-1}. Anal. Calcd for $(C_{42}H_{58}N_2)_n$: C, 85.37; H, 9.89; N, 4.74. Found: C, 84.03; H, 9.64; N, 4.18; I, 1.04.

Polymer 3c. A solution of DMAc (8.0 mL) containing **1** (307 mg, 0.40 mmol), **2c** (52 mg, 0.40 mmol), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol), *n*-Bu_4NCl (111 mg, 0.40 mmol), anhydrous LiCl (17 mg, 0.40 mmol), and K_2CO_3 (220 mg, 1.6 mmol) was stirred under nitrogen at 120 °C for 24 h. After the same workup procedure used for **3a** described above, **3c** was obtained as a brown-yellow powder in 36% yield (92 mg) (45% of the polymer was extracted with toluene). ^{1}H NMR ($CDCl_3$): δ 0.78−1.00 (CH_3), 1.03−1.98 ($ArCH_2CH_2CH_2CH_2CH_2$), 3.09−3.73 ($ArCH_2$), 7.10−8.01 (Ar*H* and $CH{=}CH$). IR (KBr): 3025, 2955, 2924, 2855, 1609, 1534, 1509, 1466, 1420, 1399, 1377, 1337, 1136, 1113, 1063, 955, 864, 808, 723 cm^{-1}. Anal. Calcd for $(C_{46}H_{64}N_2)_n$: C, 85.66; H, 10.00; N, 4.34. Found: C, 78.34; H, 9.30; N, 4.27; I, 6.34.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture and Sports, Japan. The authors thank Dr. Masahiro Teraguchi for helpful discussion.

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MA001282Q