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One-Pot Synthesis and Redox Properties of Conjugation-Extended 4,4′-Bipyridines and Related Compounds. New Ligands Consisting of a Heterocyclic Three-Ring Assembly

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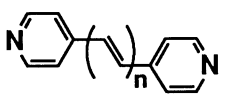
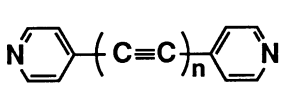
Dipyridyl-substituted heterocycles such as 2,5-di(4-pyridyl)thiophene **3**, 2,5-di(4-pyridyl)furan **4**, 2,5-di(4-pyridyl)thieno[3,2-*b*]thiophene **7**, 1,4-di(4-pyridyl)benzene **6**, 2,5-di(2-pyridyl)thiophene **8**, and 2,5-di(3-pyridyl)thiophene **9** have been efficiently synthesized by a simple one-pot procedure through the palladium-mediated cross-coupling reaction between (trimethylstannyl)pyridines and dibromo-substituted heteroaromatics. The spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, UV) as well as their reduction potentials of these compounds have been determined to evaluate the utility potentials to chelating ligands for metal complexes or to synthetic precursors of viologen-type bipyridinium salts. The conjugation interaction throughout the three rings appears to be more significant in **3** and **4** than in **6**. The formation of stable redical anions and dianions of **3** and **4** has been proved by cyclic voltammetry.

4,4′-Bipyridine is a valuable heterocycle as a synthetic precursor of viologens, the most prototypical and important redox reagents used widely for the basic studies on electrochemical[1] and photoelectrochemical[2] process, for electrochromic materials,[3] and for the electron transfer mediators in the conversion of photoenergy into chemical energy.[4] In addition, the conjugation-extended analogues of 4,4′-bipyridine, such as **1**[5] and **2**[6] involving a central ethenylene and ethynylene chain, respectively, have recently attracted current interest as the ligands of ruthenium complexes, in which an intramolecular long-distance electron transfer[7] is observed in their mixed-valence state,[6b,8] and as the synthetic precursors of conjugation-extended viologens which are the promising candidates for the functional elements of molecular electronic devices.[8a,9]

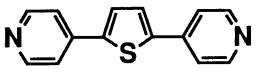
The hitherto unknown **3** and **4** belong to another type of conjugation-extended analogues of 4,4′-bipyridine, whose two terminal pyridine rings are connected via a central five-membered heterocycle. The central heterocycle may act as a weak electron-donating chromophore towards the terminal pyridine or pyridinium moieties of their corresponding metal complexes or their quaternary salts, so that the intramolecular conjugative interaction among the three rings should be enhanced and consequently, the molecules can exist in a more rigidly coplanar conformation than **1** since there is no significant nonbonded atom interaction forcing the molecule to twist around the intercyclic bonds.[10] Good molecular coplanarity and an enhanced conjugative interaction between the terminal redox active centers have been proved to be very important factors for long distance electron transfer[6b] and for stabilizing the corresponding radical ions in multistage redox systems.[10,11]



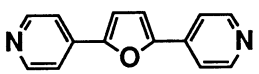
1 (n = 1, 2, or 3)



2 (n = 1 or 2)



3

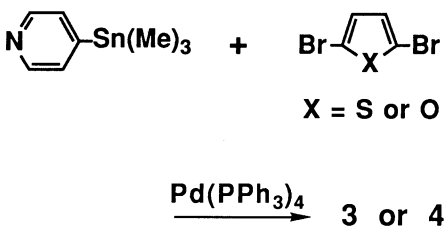


4

In this paper we wish to report a convenient one-pot synthesis of some new di(4-pyridyl)heterocycles and related compounds as well as their spectroscopic and electrochemical properties, proving their coplanar conformation with significant conjugation throughout the three rings.

Results and Discussion

Although so far there have appeared several papers dealing with palladium-catalyzed cross-coupling reactions to connect heterocyclic rings,[12] the direct synthesis of three-ring assemblies consisting of two terminal 4-pyridyl groups has never been reported. Our synthetic method is based on the palladium-mediated cross-coupling reaction between (trimethylstannyl)pyridines[13] and dibromo-substituted heteroaromatics. Thus 2,5-dibromothiophene or 2,5-dibromofuran was treated with 2.2—2.4 equiv of 4-(trimethylstannyl)pyridine in the presence of about 0.1 equiv of tetrakis(triphenylphosphine)palladium, Pd[PPh$_3$]$_4$,[14] in dry toluene at refluxing temperature under argon



Scheme 1.

atmosphere as shown in Scheme 1. After a usual workup the reaction mixture was purified on gel permeation chromatography (GPC) giving **3** or **4** in 55—50% yield.

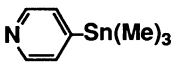
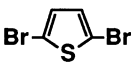
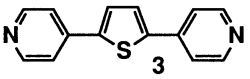
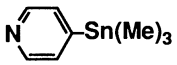
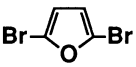
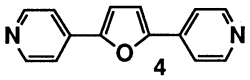
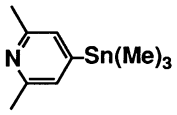
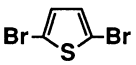
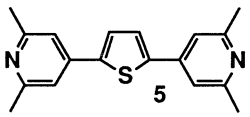
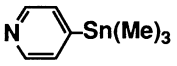
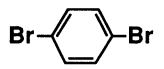
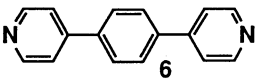
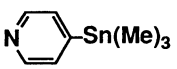
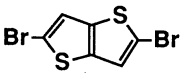
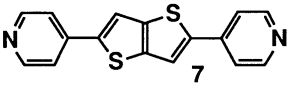
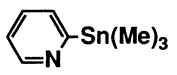
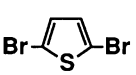
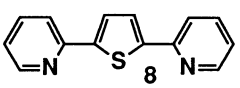
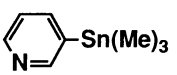
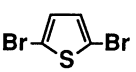
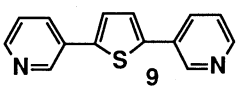
This type of reaction appears to be applicable widely for the general preparation of a variety of heteroaromatic and aromatic ring assemblies having two terminal pyridyl groups. The synthetic results are summarized in Table 1.

The lower yield observed in Entry 5 can be attributed to the poor solubility of compound **7** which has to be purified by sublimation under vacuum. 2,5-Di(2-pyridyl)thiophene **8**[15] and 2,5-di(3-pyridyl)thiophene **9**,[16] previously obtained only in poor overall yields (3.4—5.4%) through multi-step reactions, could be prepared by the present one-pot procedure in higher yield as shown in Entries 6 and 7. When 2,5-diiodothiophene was used instead of the dibromothiophene in Entry 1, compound **3** was produced in less than 10% yield. The reaction was also carried out in DME, but the yield of the product **5** (Entry 3) dropped to 8.7%. $PdCl_2[PPh_3]_2$ catalyst[17] appears to be ineffective since only a trace amount of **5** was obtained when it is submitted in Entry 3. In most examples the reaction was stopped in 4—4.5 h since the yield was not improved by elongation of the reaction time. The (trimethylstannyl)pyridines, readily accessible from the reaction of the corresponding halopyridines with (trimethylstannyl)sodium,[13a] should be prepared and distilled freshly prior to use.

The spectroscopic data and reduction potentials of the dipyridyl-substituted heterocycles and 1,4-di(4-pyridyl)benzene were summarized in Table 2.

Interestingly, the ^{13}C NMR resonances of the pyridyl carbons (the averaged chemical shift of C-2,3,5,6) of **3** (135.15 ppm) and **4** (134.1 ppm) appear at higher field by 3.9 and 4.95 ppm, respectively, than that (139.05 ppm) of **6**. In addition, the longest wavelength absorption maxima in the electronic spectra of **3** and **4** are shifted bathochromically by 52 and 62 nm, respectively, from that of **6**. Therefore the conjugation interaction throughout the three rings should be more significant in **3** and **4** than in **6**. The formation of stable radical anions and dianiones, and the maintenance of a coplanar conformation for the whole molecule through the redox

Table 1. Pd-Catalyzed Cross-Coupling Reaction of (Trimethylstannyl)pyridines with Heteroaromatic Dibromides or with *p*-Bromobenzene[a]

Entry	Stannylpyridine	Dibromide	Product	Yield[b]/%
1			 **3**	55
2			 **4**	50
3			 **5**	30
4			 **6**	50
5			 **7**	24
6			 **8**	64
7			 **9**	64

a) All the reactions were carried out in refluxing toluene using 2.2—2.4 mol equiv of the stannylpyridine in the presence of 0.1 mol equiv of $Pd(PPh_3)_4$. b) Isolated yield based on the dibromide.

Table 2. Spectroscopic Data and Redox Potentials of Conjugation-Extended Bipyridyl Compounds **3**—**9**

Compd	IR[a]	^{1}H NMR[b]	^{13}C NMR[c]		UV λ_{max}[d]	E_1^{red}	E_2^{red}	ΔE^{red}
	cm^{-1}	ppm	ppm		nm (log ε)	V vs. SCE[f]		
		8.64 (PyH-2,6)	150.6 (PyC-2,6)	142.6 (ThC-2,5)	216 (3.59)			
3	1589	7.50 (PyH-3,5)	140.7 (PyC-4)	126.5 (ThC-3,4)	233 (3.97)	−1.72	−1.98	0.26
		7.52 (ThH-3,4)	119.7 (PyC-3,5)		330 (4.48)			
		8.64 (PyH-2,6)	152.2 (PyC-4)	136.6 (ThC-2,5)	226 (4.27)			
4	1606	7.57 (PyH-3,5)	150.4 (PyC-2,6)	110.8 (ThC-3,4)	325 (4.60)	−1.99	−2.19	0.28
	1577	6.98 (FrH-3,4)	117.8 (PyC-3,5)		340 (4.50)			
		7.18 (PyH-3,5)	158.6 (PyC-2,6)	142.7 (ThC-2,5)	220 (3.85)			
5	1604	7.46 (ThH-3,4)	141.4 (PyC-4)	126.0 (ThC-3,4)	239 (3.96)	−1.88	−2.05	0.17
	1560	2.57 (Me)	116.4 (PyC-3,5)		330 (4.49)			
		8.69 (PyH-2,6)	150.4 (PyC-2,6)	138.7 (PhC-1,4)				
6	1589	7.54 (PyH-3,5)	147.3 (Py-4)	121.4 (PhC-2,3,5,6)	278 (4.51)	−1.98[h]	−2.14[g]	0.16[g]
		7.76 (PhH-2,3,5,6)	127.7 (PyC-3,5)					
		8.55 (PyH-2,6)			210 (4.40)			
7	1589	7.71 (PyH-3,5)	—	—	353 (4.74)	−1.75[g]	−1.89[g]	0.14[g]
		8.00 (TThH-3,5)						
		8.59 (PyH-6)	152.4 (PyC-2)	118.9 (PyC-3)				
		7.67 (PyH-3)	149.6 (PyC-6)	145.0 (ThC-2,5)	254 (3.56)			
8[e]	1581	7.69 (PyH-4)	136.6 (PyC-4)	125.6 (ThC-3,4)	341 (4.51)	−1.95	−2.13	0.18
	1554	7.16 (PyH-5)	122.1 (PyC-5)					
		7.63 (ThH-3,4)						
		8.91 (PyH-2)	148.8 (PyC-6)	123.6 (PyC-5)				
		8.54 (PyH-6)	146.8 (PyC-2)	140.9 (ThC-2,5)	324 (4.21)			
9[e]	1564	7.89 (PyH-4)	132.7 (PyC-4)	125.3 (ThC-3,4)		−2.01[g]	−2.29[g]	0.28[g]
	1537	7.33 (PyH-5)						
		7.38 (ThH-3,4)						

a) νC=N in KBr disk. b) in $CDCl_3$ at 200 MHz. c) in $CDCl_3$ at 50.4 MHz. d) in MeCN. e) The physical and spectroscopic data have never been reported so far. The melting points are in consistent with the literatures; see Refs. 15 and 16. f) Obtained by the cyclic voltammetry: 1.0 mmol dm^{-3} in MeCN with 0.1 mol dm^{-3} Et_4NClO_4 (scan rate: 50 mV s^{-1}, reference electrode: SCE). g) The peak potential and ΔE_p of the irreversible wave.

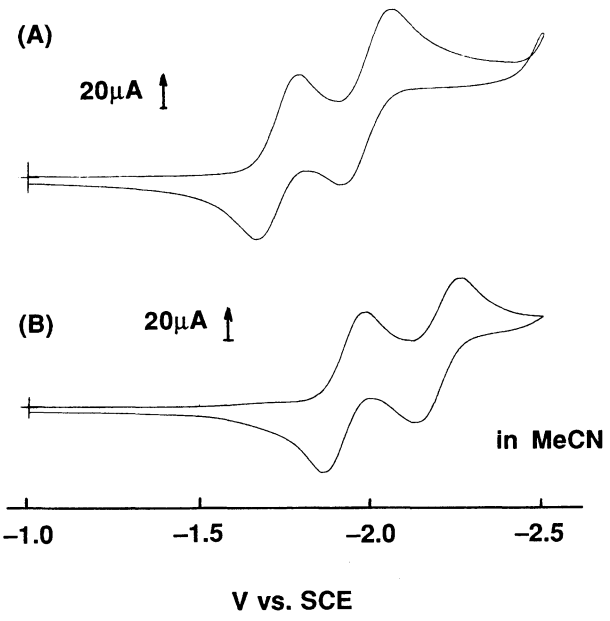


Fig. 1. Cyclic voltammograms of **3** (A) and **4** (B), 1 mM in MeCN/0.1 M Et_4NClO_4 at room temperature (scan rate: 50 mV s^{-1}; reference electrode: SCE).

process are revealed particularly in **3** and **4**, since both of their reduction waves in the cyclic voltammograms are reversible as shown in Fig. 1, whereas those of **6** are irreversible.

The ΔE^{red} values, a measure to estimate the thermodynamic stability of the anion radical, are larger in **3** and **4** than in **6**. These data lead to an important finding that the heterocycle-insertion into 4,4′-bipyridine brings about no significant weakening effect on the conjugative interaction among the three rings, whereas the benzene-insertion weakens the interaction.

The bis(pentaammine-ruthenium(II)) complex of **3** has been obtained as hexafluorophosphate salt. Further efforts are being continued to prepare the mixed-valence ruthenium(II)–ruthenium(III) complex and to investigate its intervalence transitions. New conjugation-extended 4,4′-bipyridines **3** and **4** are expected to have a high utility potential to the chelating ligands in the transition metal chemistry and to the precursors of individual molecules for electronic devices.

Experimental

Melting points (uncorrected) were determined with a

Yanagimoto MP-J3 melting point apparatus. The IR and electronic spectra (UV) were measured by using a Horiba FT-300 and a Hitachi U-3210 spectrophotometer, respectively; The NMR spectra were measured in $CDCl_3$ with a Varian XL-200 or a Bruker AM-600 spectrometer using TMS as an internal standard. The assignments of all signals were made by employing a first-order analysis with the aid of a two-dimensional carbon–proton shift correlation technique. The mass spectra were taken on a JEOL-JMS-HX-110 mass spectrometer. The cyclic voltammograms were taken on a Yanagimoto P-1100 polarographic analyzer. The GPC was carried out on a Japan Analytical Industry LC-908 apparatus using J28-9E22 column.

Preparation of 2,5-Di(4-pyridyl)thiophene (3). To a solution of 2,5-dibromothiophene (1.08 g, 4.46 mmol) in dry toluene (44 ml) were added 4-stannylpyridine[13a] (2.60 g, 10.75 mmol) and then tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$)[14] (1.03 g, 0.89 mmol) under argon atmosphere. The resulting mixture was heated under reflux for 5 h. After being cooled to room temperature, the reaction mixture was quenched with 1.0 mol dm^{-3} of aqueous ammonia and extracted with chloroform. The combined extracts were washed with brine and dried over Na_2SO_4. Solvent evaporation and chromatography of the residue on silica gel by eluting with acetone provided the crude product (944 mg) which was dissolved in THF and rechromatographed on GPC. The product was further chromatographed on silica gel with acetone elution to remove a trace of contaminant (a stabilizer for THF), and finally recrystallized from acetone to give pure **3** (587 mg, 55% yield): Colorless needles; mp 170—172 °C; MS (DEI) *m/z* (rel intensity) 240 (M^++2, 5), 239 (M^++1, 17), 238 (M^+, 100); IR (KBr) ν_{max} 3059, 3034, 1589, 1410, 1286, 1215, 987, 816, and 681 cm^{-1}; ^1H NMR, ^{13}C NMR, and UV: See Table 2. Found: C, 70.33; H, 4.48; N, 11.87; S, 13.67%. Calcd for $C_{14}H_{10}N_2S$: C, 70.56; H, 4.23; N, 11.76; S, 13.46%.

Preparation of 2,5-Di(4-pyridyl)furan (4). A similar procedure to that described above was carried out using 2,5-dibromofuran (1.36 g, 6.01 mmol), dry toluene (54 ml), 4-stannylpyridine (3.20 g, 13.23 mmol), and $Pd(PPh_3)_4$ (1.39 g, 1.20 mmol) to give **4** (659 mg, 50% yield): Colorless needles; mp 176—177 °C (from acetonitrile); MS (DEI) *m/z* (rel intensity) 224 (M^++2, 1), 223 (M^++1, 22), 222(M^+, 100); IR (KBr) ν_{max} 3140, 1606, 1577, 1415, 1215, 1030, 985, 827, 789, 696, and 673 cm^{-1}; ^1H NMR, ^{13}C NMR, and UV: See Table 2. Found: C, 75.62; H, 4.58; N, 12.61%. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.61%.

Preparation of 2,5-Bis(2,6-dimethyl-4-pyridyl)thiophene (5). A similar procedure to that described above was followed with 2,5-dibromothiophene (1.0 g, 4.13 mmol), dry toluene (40 ml), 2,6-dimethyl-4-stannylpyridine[13a] (2.57 g, 9.51 mmol), and $Pd(PPh_3)_4$ (573 mg, 0.50 mmol) to give **5** (370 mg, 30% yield): Colorless needles; mp 152—154 °C (from acetonitrile); IR (KBr) ν_{max} 3050, 2985, 1604, 1560, 1448, 1423, 1221, 1032, 849, and 810 cm^{-1}, ^1H NMR, ^{13}C NMR, and UV: See Table 2. Found: C, 73.46; H, 6.20; N, 10.92; S, 9.54%. Calcd for $C_{18}H_{18}N_2S$: C, 73.43; H, 6.16, N, 10.89; S, 9.52%.

Preparation of 1,4-Di(4-pyridyl)benzene (6). A similar procedure to that described above was followed with 1,4-dibromobenzene (1.15 g, 4.89 mmol), dry toluene (44 ml), 4-stannylpyridine (2.60 g, 10.75 mmol), and $Pd(PPh_3)_4$ (1.13 g, 1.00 mmol) to give **6** (566 mg, 50% yield): Colorless needles; mp 202—204 °C (from acetonitrile); IR (KBr) ν_{max} 3089, 3053, 1589, 1549, 1479, 1417, 1398, 1225, 1039, 991, 798, and 702 cm^{-1}; ^1H NMR, ^{13}C NMR, and UV: See Table 2. Found: C, 82.56; H, 5.28; N, 12.22%. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06%.

Preparation of 2,5-Di(4-pyridyl)thieno[3,2-*b*]thiophene (7). A mixture of 2,5-dibromothieno[3,2-*b*]thiophene (600 mg, 2.01 mmol), 4-stannylpyridine (1.17 g, 4.83 mmol), $Pd(PPh_3)_4$ (671 mg, 0.58 mmol), and dry toluene (24 ml) was heated under reflux for 5 h. The reaction mixture was worked up as described for the preparation of **3** and the crude product was first chromatographed on silica gel by eluting with a 1 : 1 mixture of $CHCl_3$–acetone and then sublimed at 220 °C/0.1—0.5 mmHg (1 mmHg=133.322 Pa). Pure **7** (141 mg, 24% yield) was isolated after recrystallization from toluene: Pale yellow needles; mp 316—318 °C (decomp); MS (EI) *m/z* (rel intensity) 296 (M^++2, 13), 295 (M^++1, 27), 294 (M^+, 100); IR (KBr) ν_{max} 3089, 3045, 3012, 1589, 1543, 1504, 1466, 1410, 1356, 1321, 1219, 1180, 995, 804, and 692 cm^{-1}; ^1H NMR, ^{13}C NMR, and UV: See Table 2. Found: C, 64.83; H, 3.63; N, 9.29; S, 21.02%. Calcd for $C_{16}H_{10}N_2S_2$: C, 65.27; H, 3.42; N, 9.52; S, 21.78%.

Preparation of 2,5-Di(2-pyridyl)thiophene (8). A similar procedure to that described for the preparation of **3** was followed using 2,5-dibromothiophene (1.05 g, 4.34 mmol), dry toluene (40 ml), 2-stannylpyridine[13a] (2.50 g, 10.34 mmol), and $Pd(PPh_3)_4$ (1.20 g, 1.04 mmol) to give **8** (656 mg, 64% yield): Colorless needles; mp 164—166 °C (from acetonitrile); MS (EI) *m/z* (rel intensity) 240 (M^++2, 7), 239 (M^++1, 21), 238 (M^+, 100); IR (KBr) ν_{max} 3062, 2999, 1581, 1554, 1458, 1427, 1296, 1153, 1088, 989, 957, 889, 820, 775, 742, and 708 cm^{-1}; ^1H NMR, ^{13}C NMR, and UV: See Table 2. Found: C, 70.59; H, 4.39; N, 11.69; S, 13.22%. Calcd for $C_{14}H_{10}N_2S$: C, 70.56; H, 4.23; N, 11.76; S, 13.46%.

Preparation of 2,5-Di(3-pyridyl)thiophene (9). A similar procedure to that described for the preparation of **3** was followed with 2,5-dibromothiophene (1.05 g, 4.34 mmol), dry toluene (40 ml), 3-stannylpyridine[13a] (2.50 g, 10.34 mmol), and $Pd(PPh_3)_4$ (1.20 g, 1.04 mmol) to give **9** (656 mg, 64% yield): Pale yellow plates; mp 103—106 °C (from acetonitrile); MS (EI) *m/z* (rel intensity) 240 (M^++2, 5), 239 (M^++1, 17), 238 (M^+, 100); IR (KBr) ν_{max} 3039, 3023, 2981, 1564, 1537, 1475, 1454, 1406, 1317, 1279, 1240, 1184, 1122, 1090, 1041, 1021, 968, 939, 795, and 700 cm^{-1}; ^1H NMR, ^{13}C NMR, and UV: See Table 2. Found C, 70.76; H, 4.53; N, 11.79; S, 13.74%. Calcd for $C_{14}H_{10}N_2S$: C, 70.56; H, 4.23; N, 11.76; S, 13.46%.

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