Il-Chun Kwon, Young Kook Koh, Jun-Hyeak Choi, and Hong-Seok Kim*

Department of Industrial Chemistry, Kyungpook National University,
Taegu 702-701, Korea
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Thiazole-containing polyether podands were prepared from the reactions of hydroxymethylthiazole derivatives with di-*p*-tosylates of corresponding tri, tetra, pentaethylene glycols in the presence of potassium hydride.

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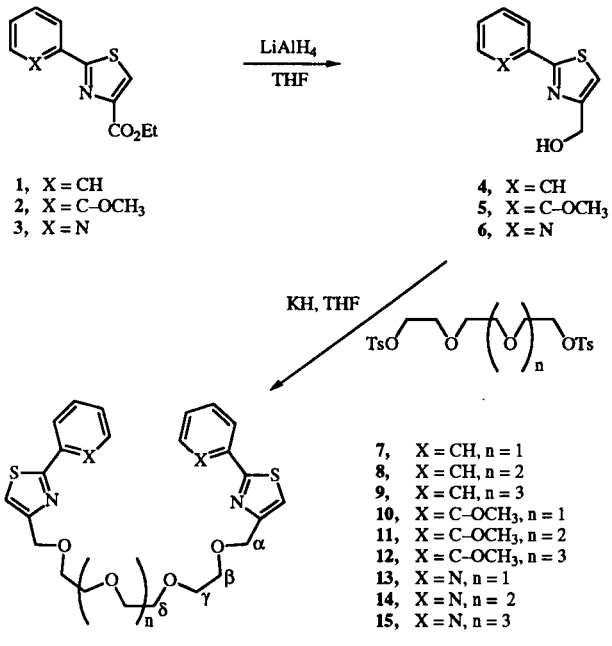
The macrocyclic compounds containing heterocycle have been the subject of much interest in the field of host-guest chemistry during the past fifteen years because of their different complexation properties from normal macrocyclic compounds according to the specific coordination property of heteroatom. Although many macrocyclic compounds containing heterocycles, such as pyridine, bipyridine, triazole, and thiophene have been synthesized and studied [1], the thiazole ring as a subunit of a macrocyclic compound has been known only in a few cases [2]. We now report that synthesis of polyether podands which contain thiazoles.

Scheme 1



1, X = CH
2, X = C–OCH_3
3, X = N

4, X = CH
5, X = C–OCH_3
6, X = N

7, X = CH, n = 1
8, X = CH, n = 2
9, X = CH, n = 3
10, X = C–OCH_3, n = 1
11, X = C–OCH_3, n = 2
12, X = C–OCH_3, n = 3
13, X = N, n = 1
14, X = N, n = 2
15, X = N, n = 3

The thiazole-containing polyether podands **7-15** were prepared as shown in Scheme 1. The starting material, 2-aryl-4-carbethoxythiazoles **1-3**, were readily obtained from the reactions of the corresponding thioamides with ethyl diazopyruvate in the presence of boron trifluoride in dimethoxyethane in good yields [3,4]. The reasons we choose compounds **1-3** as precursors of polyethers **7-15** are that when the polyethers **7-15** form complexes with some metals, **1** could be the fundamental type to observe the π-π stacking effect and **2** and **3** not only π-π stacking ability but also electron donating to the metal because those have methoxy and nitrogen in the *ortho* position. The transformation of the carbethoxy group of compounds **1-3** into hydroxymethyl group of compounds **4-6** was carried out in 98-74% yields by reduction with lithium aluminum hydride at -40°. The polyethers **7-15** were synthesized in 51-13% yields by treatment of compounds **4-6** with the di-*p*-tosylates of the corresponding tri, tetra, and pentaethylene glycols in the presence of potassium hydride (Table 1). The formation of all polyethers have been confirmed by ^1H, ^{13}C nmr, ir, mass, and high resolution mass spectral data.

Table 1
Synthesis of Thiazole Containing Polyethers

Compound	X	n	Yield(%) [a]
7	CH	1	42
8	CH	2	13
9	CH	3	51
10	C-OCH_3	1	26
11	C-OCH_3	2	28
12	C-OCH_3	3	27
13	N	1	47
14	N	2	31
15	N	3	16

[a] Isolated yields.

On going from carbethoxy derivatives **1**, **2**, and **3** to the hydroxymethyl derivatives **4**, **5**, and **6**, the chemical shift of the thiazole proton was affected considerably: an upfield shift of about 0.9 ppm was observed (pairs **1/4**, **2/5**, **3/6**). In the case of **4** and **5**, the coupling between methylene protons and the hydroxy proton was not observed but in **6**, the coupling between methylene protons and the hydroxy proton was observed with a 5.8 Hz coupling constant. In the ir spectrum, the OH absorption band was observed at 3249-3311 cm^{-1} as a strong band. The mass spectrum of **4** showed the molecular ion at 191 (100% relative abundance). On going from **4-6** to the polyethers **7-15**, there were no remarkable variations in the aromatic region in the

^1H and ^{13}C nmr spectra. The signals of the protons and carbons of the methylene units are shown to have the following order: $\delta_\alpha > \delta_\beta > \delta_\gamma > \delta_\delta$ because of the anisotropic effect of the thiazole ring. The mass spectrum of **7** showed the molecular ion at 496 (9% relative abundance) and its fragmentation is in accordance with the assigned structure.

Thus, the present procedure provides a series of polyethers which contain a thiazole ring. Studies on electrochemical applications of the polyethers are now in progress.

EXPERIMENTAL

General procedures are as described elsewhere [4]. All reactions were carried out under an atmosphere of argon. Solvents were dried and purified according to the known methods [5]. 2-Phenyl-4-carbethoxythiazole (**1**), 2-(2'-methoxyphenyl)-4-carbethoxythiazole (**2**), and 2-(2'-pyridyl)-4-carbethoxythiazole (**3**) were prepared following a reported procedure [4].

General Procedure for the Synthesis of 2-Substituted-4-hydroxymethylthiazoles **4-6**.

To a suspension of lithium aluminum hydride (76 mg, 2 mmoles) in THF (10 ml) was added 2-substituted-4-carbethoxythiazoles **1-3** (2 mmoles) at -78°. After the mixture was stirred at -78° for 2 hours, the mixture was warmed to the room temperature and then ethyl acetate and water were added to the mixture. The mixture was washed with 5% hydrochloric acid solution and then extracted with ethyl acetate. The organic layer was washed with water and brine, dried over anhydrous sodium sulfate and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate:hexane 2:1) to give the corresponding 2-substituted-4-hydroxymethylthiazole.

2-Phenyl-4-hydroxymethylthiazole (**4**).

This compound was obtained as a colorless powder (ether-hexane) in 94% yield, mp 68-69°; ir (potassium bromide): 3268, 3109, 3082, 2936, 2913, 2849, 1524, 1460, 1433, 1242, 1110, 1138, 1030, 1003, 970, 789, 758, 685, 611 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.90 (m, 2H, H-2', 6' of Ph), 7.40 (m, 3H, H-3', 4', 5' of Ph), 7.14 (s, 1H, H-5), 4.80 (s, 2H, CH_2OH), 2.94 (bs, 1H, O*H*); ^{13}C nmr (deuteriochloroform): δ 168.8 (C-2), 157.5 (C-4), 133.6 (C-1' of Ph), 130.1 (C-4' of Ph), 128.9 (C-2', 6' of Ph), 126.6 (C-3', 5' of Ph), 114.4 (C-5), 61.1 (*C*H_2OH); ms: m/z 191 (M^+, 100), 190 (68), 162 (59), 104 (34); R_f 0.68 (ethyl acetate).

Anal. Calcd. for $C_{10}H_9NOS$: C, 62.81; H. 4.75; N, 7.33. Found: C, 62.51; H, 4.84; N, 7.00.

2-(2'-Methoxyphenyl)-4-hydroxymethylthiazole (**5**).

This compound was obtained as a colorless powder (dichloromethane-hexane) in 98% yield, mp 88-89°; ir (potassium bromide): 3311, 3265, 3184, 3141, 3087, 2925, 2840, 2805, 1598, 1501, 1466, 1432, 1297, 1258, 1119, 1030, 806, 752 cm^{-1}; ^1H nmr (deuteriochloroform): δ 8.42 (dd, J = 8.3, 1.7 Hz, 1H, H-6' of Ph), 7.42 (td, J = 7.9, 1.5 Hz, 1H, H-4' of Ph), 7.38 (s, 1H, H-5), 7.08 (m, 2H, H-3', 5' of Ph), 4.93 (bs, 1H, O*H*), 4.80 (s, 2H, CH_2OH), 4.03 (s, 3H, OCH_3); ^{13}C nmr (deuteriochloroform): δ 161.4 (C-2), 155.5 (C-2' of Ph), 154.5 (C-4), 130.4 (C-6' of Ph), 127.4 (C-4' of Ph), 120.4 (C-5' of Ph), 120.1 (C-1' of Ph), 114.7 (C-5), 110.8 (C-3' of Ph), 59.2 (*C*H_2OH), 54.8 (O*C*H_3); ms: m/z 221 (M^+, 100), 220 (42), 190 (30), 132 (26), 107 (29); R_f 0.71 (ethyl acetate).

Anal. Calcd. for $C_{11}H_{11}NO_2S$: C, 59.71; H, 5.01; N, 6.33. Found: C, 59.54; H, 5.28; N, 6.27.

2-(2'-Pyridyl)-4-hydroxymethylthiazole (**6**).

This compound was obtained as a colorless powder (dichloromethane-hexane) in 74% yield, mp 99-100°; ir (potassium bromide): 3249, 3075, 2921, 2859, 1586, 1493, 1435, 1362, 1273, 1158, 1038, 1011, 810, 783, 741, 614 cm^{-1}; ^1H nmr (deuteriochloroform): δ 8.57 (d, J = 4.3 Hz, 1H, H-6' of Py), 8.13 (d, J = 7.8 Hz, 1H, H-3' of Py), 7.74 (td, J = 7.8, 1.8 Hz, 1H, H-4' of Py), 7.27 (m, 1H, H-5' of Py), 7.26 (H-5), 4.81 (d, J = 5.8 Hz, 2H, CH_2OH), 2.73 (t, J = 5.8 Hz, O*H*); ^{13}C nmr (deuteriochloroform): δ 169.6 (C-2), 157.7 (C-2' of Py), 151.3 (C-4), 149.5 (C-6' of Py), 137.0 (C-4' of Py), 124.5 (C-3' of Py), 119.7 (C-5' of Py), 117.0 (C-5), 61.2 (*C*H_2OH); ms: m/z 192 (M^+, 53), 191 (100), 175 (6), 162 (24), 105 (38), 78 (35); R_f 0.58 (ethyl acetate).

Anal. Calcd. for $C_9H_8N_2OS$: C, 56.23; H, 4.19; N, 14.57. Found: C, 56.47; H, 4.36; N, 14.71.

General Procedure for the Synthesis of Thiazole-containing Polyethers **7-15**.

To a stirred mixture of potassium hydride (40 mg, 1 mmole), 2-substituted-4-hydroxymethylthiazoles **4-6** (1 mmole) and THF (5 ml) was added a solution of triethylene glycol di-*p*-tosylate (229 mg, 0.5 mmole) in THF (10 ml) dropwise at 80° and the mixture was refluxed until the tlc (silica gel, 100% ethyl acetate) indicated the absence of starting material. The mixture was cooled to room temperature and was poured into water and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over anhydrous sodium sulfate and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate:hexane 3:1) to give the thiazole containing polyethers.

1,10-Bis[2'-phenyl-4'-methylthiazole]triethylene Glycol (**7**).

This compound was obtained as a colorless oil in 42% yield; ir (neat): 3102, 3065, 2868, 1522, 1462, 1439, 1290, 1240, 1140, 1101, 1034, 1001, 936, 766, 691 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.92 (m, 4H, H-2', 6' of Ph), 7.40 (m, 6H, H-3', 4', 5' of Ph), 7.25 (s, 2H, H-5), 4.75 (s, 4H, thiazole-CH_2), 3.77 (m, 4H, thiazole-CH_2OCH_2), 3.73 (m, 4H, thiazole-$CH_2OCH_2CH_2$), 3.69 (s, 4H, thiazole-$CH_2OCH_2CH_2OCH_2$); ^{13}C nmr (deuteriochloroform): δ 168.2 (C-2), 155.2 (C-4), 133.7 (C-1' of Ph), 129.9 (C-3', 5' of Ph), 128.8 (C-4' of Ph), 126.6 (C-2', 6' of Ph), 115.5 (C-5), 70.7 (thiazole-*C*H_2), 70.7 (thiazole-CH_2OCH_2), 70.2 (thiazole-$CH_2OCH_2CH_2$), 69.3 (thiazole-$CH_2OCH_2CH_2OCH_2$); ms: m/z 496 (M^+, 9), 363 (3), 323 (5), 322 (5), 307 (9), 190 (100), 175 (100); high resolution ms: m/z 496.1512 (M^+, $C_{26}H_{28}N_2O_4S_2$ requires 496.1491) ; R_f 0.51 (ethyl acetate).

1,13-Bis[2'-phenyl-4'-methylthiazole]tetraethylene Glycol (**8**).

This compound was obtained as a colorless oil in 13% yield, ir (neat): 3102, 3062, 2866, 1522, 1460, 1438, 1350, 1237, 1141, 1101, 1003, 935, 766, 691; ^1H nmr (deuteriochloroform): δ 7.93 (m, 4H, H-2', 6' of Ph), 7.40-7.44 (m, 6H, H-3', 4', 5' of Ph), 7.26

(s, 2H, H-5), 4.75 (s, 4H, thiazole-CH_2), 3.77 (m, 4H, thiazole-CH_2OCH_2), 3.72 (m, 4H, thiazole-$CH_2OCH_2CH_2$), 3.70-3.66 (m, 8H, thiazole-$CH_2OCH_2CH_2OCH_2CH_2$); ^{13}C nmr (deuteriochloroform): δ 168.3 (C-2), 155.1 (C-4), 133.6 (C-1' of Ph), 130.0 (C-3', 5' of Ph), 128.9 (C-4' of Ph), 126.6 (C-2', 6' of Ph), 115.7 (C-5), 70.7 (thiazole-CH_2), 70.6 (thiazole-$CH_2OCH_2CH_2$), 70.1 (thiazole-$CH_2OCH_2CH_2OCH_2$), 69.3 (thiazole-$CH_2OCH_2CH_2OCH_2CH_2$); ms: m/z 542 (M+2, 5), 541 (M+1, 4), 540 (M^+, 1), 190 (100), 174 (87), 104 (30), 71 (62); high resolution ms: m/z 540.1783 (M^+, $C_{28}H_{32}O_5N_2S_2$ requires 540.1753); R_f 0.42 (ethyl acetate).

1,16-Bis[2'-phenyl-4'-methylthiazole]pentaethylene Glycol (**9**).

This compound was obtained as a colorless oil in 51% yield; ir (neat): 3099, 3061, 2866, 1521, 1461, 1440, 1353, 1291, 1241, 1140, 1099, 1036, 1001, 939, 858, 767, 692 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.93 (m, 4H, H-2', 6' of Ph), 7.40-7.44 (m, 6H, H-3', 4', 5' of Ph), 7.27 (s, 2H, H-5), 4.75 (s, 4H, thiazole-CH_2), 3.77 (m, 4H, thiazole-CH_2OCH_2), 3.72 (m, 4H, thiazole-$CH_2OCH_2CH_2$), 3.68 (m, 8H, thiazole-$CH_2OCH_2CH_2OCH_2CH_2$), 3.66 (m, 4H, thiazole-$CH_2OCH_2CH_2OCH_2CH_2OCH_2$); ^{13}C nmr (deuteriochloroform): δ 168.3 (C-2), 155.0 (C-4), 133.6 (C-1' of Ph), 130.0 (C-3', 5' of Ph), 128.9 (C-4' of Ph), 126.6 (C-2', 6' of Ph), 115.7 (C-5), 70.7 (thiazole-CH_2), 70.6 (thiazole-$CH_2OCH_2CH_2OCH_2$), 70.1 (thiazole-$CH_2OCH_2CH_2OCH_2CH_2$), 69.3 (thiazole-$CH_2OCH_2CH_2OCH_2CH_2OCH_2$); ms: m/z 586 (M+1, 10), 585 (M+, 6), 410 (4), 218 (7), 190 (100), 174 (83), 104 (24); high resolution ms: m/z 584.1984 (M^+, $C_{30}H_{36}O_6N_2S_2$ requires 584.2015); R_f 0.30 (ethyl acetate).

1,10-Bis[2'-(2'-methoxyphenyl)-4'-methylthiazole]triethylene Glycol (**10**).

This compound was obtained as a colorless oil in 26% yield, ir (neat): 3110, 3064, 3018, 2910, 2867, 1586, 1493, 1470, 1300, 1250, 1023, 972, 752 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 8.37 (dd, J = 7.7, 1.7 Hz, 2H, H-6' of Ph), 7.36 (m, 2H, H-4' of Ph), 7.30 (s, 2H, H-5), 7.06 (t, J = 8.2 Hz, 2H, H-5' of Ph), 6.99 (d, J = 8.2 Hz, 2H, H-3' of Ph), 4.77 (s, 4H, thiazole-CH_2), 3.98 (s, 6H, OCH_3), 3.77 (m, 4H, thiazole-CH_2OCH_2), 3.72 (m, 4H, thiazole-$CH_2OCH_2CH_2$), 3.69 (s, 4H, thiazole-$CH_2OCH_2CH_2OCH_2$); ^{13}C nmr (deuteriochloroform): δ 162.2 (C-2), 156.3 (C-2' of Ph), 153.0 (C-4), 130.4 (C-6' of Ph), 129.5 (C-4' of Ph), 122.4 (C-1' of Ph), 120.9 (C-5), 116.7 (C-5' of Ph), 111.3 (C-3' of Ph), 70.62 (thiazole-CH_2), 70.58 (thiazole-CH_2OCH_2), 70.0 (thiazole-$CH_2OCH_2CH_2$), 69.3 (thiazole-$CH_2OCH_2CH_2OCH_2$), 55.5 (OCH_3); ms: m/z 556 (M^+, 19), 423 (5), 352 (7), 337 (9), 221 (100), 220 (100), 205 (100), 204 (100); high resolution ms: m/z 556.1705 (M^+, $C_{28}H_{32}N_2O_6S_2$ requires 556.1702); R_f 0.62 (ethyl acetate).

1,13-Bis[2'-(2'-methoxyphenyl)-4'-methylthiazole]tetraethylene Glycol (**11**).

This compound was obtained as a colorless oil in 28% yield, ir (neat): 3099, 3006, 2921, 2875, 1590, 1497, 1462, 1354, 1297, 1250, 1107, 1019, 942, 760 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 8.37 (dd, J = 7.9, 1.6 Hz, 2H, H-6' of Ph), 7.35 (m, 2H, H-4' of Ph), 7.30 (s, 2H, H-5), 7.05 (m, 2H, H-5' of Ph), 7.00 (d, J = 8.5 Hz, 2H, H-3' of Ph), 4.76 (s, 4H, thiazole-CH_2), 4.00 (s, 6H, OCH_3), 3.76 (m, 4H, thiazole-CH_2OCH_2), 3.70 (m, 4H, thiazole-$CH_2OCH_2CH_2$), 3.67 (s, 8H, thiazole-$CH_2OCH_2CH_2OCH_2CH_2$); ^{13}C nmr (deuteriochloroform): δ 162.2 (C-2), 156.4 (C-2' of Ph), 153.0 (C-4), 130.4 (C-6' of Ph), 129.5 (C-4' of Ph), 122.4 (C-5' of Ph), 121.0 (C-5), 116.7 (C-1' of Ph), 111.4 (C-3' of Ph), 70.7 (thiazole-CH_2), 70.6 (thiazole-$CH_2OCH_2CH_2$), 70.0 (thiazole-$CH_2OCH_2CH_2OCH_2$), 69.4 (thiazole-$CH_2OCH_2CH_2OCH_2CH_2$), 55.5 (OCH_3); ms: m/z 600 (M^+, 7), 396 (3), 336 (10), 292 (9), 248 (9), 220 (100), 205 (100), 204 (93); high resolution ms: m/z 600.1938 (M^+, $C_{30}H_{36}N_2O_7S_2$ requires 600.1964); R_f 0.36 (ethyl acetate).

1,16-Bis[2'-(2'-methoxyphenyl)-4'-methylthiazole]pentaethylene Glycol (**12**).

This compound was obtained as a colorless oil in 27% yield; ir (neat): 3099, 3018, 2933, 2875, 1590, 1497, 1462, 1351, 1293, 1254, 1111, 1019, 945, 760 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 8.37 (dd, J = 7.9, 1.7 Hz, 2H, H-6' of Ph), 7.36 (m, 2H, H-4' of Ph), 7.30 (s, 2H, H-5), 7.07 (m, 2H, H-5' of Ph), 7.00 (d, J = 8.6 Hz, 2H, H-3' of Ph), 4.77 (s, 4H, thiazole-CH_2), 4.00 (s, 6H, OCH_3), 3.76 (m, 4H, thiazole-CH_2OCH_2), 3.70 (m, 4H, thiazole-$CH_2OCH_2CH_2$), 3.65 (s, 12H, thiazole-$CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2$); ^{13}C nmr (deuteriochloroform): 162.3 (C-2), 156.4 (C-2' of Ph), 153.1 (C-4), 130.5 (C-6' of Ph), 128.6 (C-4' of Ph), 122.5 (C-5' of Ph), 121.0 (C-5), 116.7 (C-1' of Ph), 111.4 (C-3' of Ph), 70.7 (thiazole-CH_2), 70.6 (thiazole-$CH_2OCH_2CH_2OCH_2$), 70.1 (thiazole-$CH_2OCH_2CH_2OCH_2CH_2$), 69.5 (thiazole-$CH_2OCH_2CH_2OCH_2CH_2OCH_2$), 55.5 ($OCH_3$); ms: m/z 645 (M+1, 6), 440 (3), 380 (8), 336 (2), 292 (2), 264 (2), 248 (4), 220 (100), 205 (51), 204 (43); high resolution ms: m/z 644.2232 (M^+, $C_{32}H_{40}N_2O_8S_2$ requires 644.2226); R_f 0.36 (ethyl acetate).

1,10-Bis[2'-(2'-pyridyl)-4'-methylthiazole]triethylene Glycol (**13**).

This compound was obtained as a colorless powder (dichloromethane) in 47% yield; mp 85-87°; ir (neat): 3106, 3056, 2994, 2883, 2358, 1582, 1439, 1354, 1138, 1100, 1053, 1019, 787 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 8.60 (m, 2H, H-6' of Py), 8.17 (d, J = 7.8 Hz, 2H, H-3' of Py), 7.77 (td, J = 7.8, 1.8 Hz, 2H, H-4' of Py), 7.38 (s, 2H, H-5), 7.30 (m, 2H, H-5' of Py), 4.76 (s, 4H, thiazole-CH_2), 3.78 (m, 4H, thiazole-CH_2OCH_2), 3.73 (m, 4H, thiazole-$CH_2OCH_2CH_2$), 3.71 (s, 4H, thiazole-$CH_2OCH_2CH_2OCH_2$); ^{13}C nmr (deuteriochloroform): δ 169.0 (C-2), 155.3 (C-4), 151.2 (C-2' of Py), 149.4 (C-6' of Py), 137.1 (C-4' of Py), 124.5 (C-3' of Py), 119.9 (C-5' of Py), 118.5 (C-5), 70.74 (thiazole-CH_2), 70.67 (thiazole-CH_2OCH_2), 70.2 (thiazole-$CH_2OCH_2CH_2$), 69.2 (thiazole-$CH_2OCH_2CH_2OCH_2$); ms: m/z 498 (M^+, 4), 308 (13), 250 (26), 219 (27), 191 (100), 175 (100); high resolution ms: m/z 498.1421 (M^+, $C_{24}H_{26}N_4O_4S_2$ requires 498.1396); R_f 0.33 (ethyl acetate).

1,13-Bis[2'-(2'-pyridyl)-4'-methylthiazole]tetraethylene Glycol (**14**).

This compound was obtained as a colorless oil in 31% yield, ir (neat): 3096, 2867, 1585, 1568, 1521, 1489, 1436, 1353, 1326, 1293, 1272, 1247, 1094, 1013, 946, 891, 860, 789, 742, 618 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 8.60 (d, J = 4.8 Hz, 2H, H-6' of Py), 8.18 (d, J = 7.8 Hz, 2H, H-3' of Py), 7.78 (td, J = 7.8, 1.8 Hz, 2H, H-4' of Py), 7.38 (s, 2H, H-5), 7.30 (m, 2H, H-5' of Py), 4.75 (s, 4H, thiazole-CH_2), 3.78 (m, 4H, thiazole-CH_2OCH_2), 3.71 (m, 4H, thiazole-$CH_2OCH_2CH_2$), 3.68 (s, 8H, thiazole-$CH_2OCH_2CH_2OCH_2CH_2$); ^{13}C nmr (deuteriochloroform): δ 169.1 (C-2), 155.4 (C-4), 151.3 (C-2' of Py), 149.4 (C-6' of Py), 137.0 (C-4' of Py), 124.5 (C-3' of Py), 119.8 (C-5' of Py), 118.4 (C-5), 70.7 (thiazole-CH_2), 70.6 (thiazole-

$CH_2OCH_2CH_2$), 70.1 (thiazole-$CH_2OCH_2CH_2OCH_2$), 69.2 (thiazole-$CH_2OCH_2CH_2OCH_2CH_2$); ms: m/z 543 (M+1, 6), 352 (6), 294 (11), 219 (9), 191 (91), 175 (100), 105 (36); high resolution ms: m/z 542.1637 (M^+, $C_{26}H_{30}N_4O_5S_2$ requires 542.1658); R_f 0.63 (ethyl acetate-methanol, 7:3).

1,16-Bis[2'-(2'-pyridyl)-4'-methylthiazole]pentaethylene Glycol (**15**).

This compound was obtained as a colorless oil in 16% yield, ir (neat): 3094, 3002, 2869, 1585, 1567, 1522, 1489, 1448, 1351, 1270, 1295, 1247, 1143, 1013, 994, 948, 892, 862, 789, 743, 619 cm^{-1}; ^1H nmr (deuteriochloroform): δ 8.60 (d, J = 4.8 Hz, 2H, H-6' of Py), 8.17 (d, J = 7.8 Hz, 2H, H-3' of Py), 7.78 (td, J = 7.8, 1.8 Hz, 2H, H-4' of Py), 7.39 (s, 2H, H-5), 7.31 (m, 2H, H-5' of Py), 4.76 (s, 4H, thiazole-CH_2), 3.78 (m, 4H, thiazole-CH_2OCH_2), 3.72 (m, 4H, thiazole-$CH_2OCH_2CH_2$), 3.67 (s, 12H, thiazole-$CH_2OCH_2CH_2OCH_2CH_2OCH_2$); ^{13}C nmr (deuteriochloroform): δ 169.1 (C-2), 155.4 (C-4), 151.3 (C-2' of Py), 149.5 (C-6' of Py), 137.0 (C-4' of Py), 124.5 (C-3' of Py), 119.8 (C-5' of Py), 118.5 (C-5), 70.7 (thiazole-CH_2), 70.6 (thiazole-$CH_2OCH_2CH_2OCH_2$), 70.1 (thiazole-$CH_2OCH_2CH_2OCH_2CH_2$), 69.2 (thiazole-$CH_2OCH_2CH_2OCH_2CH_2OCH_2$); ms: m/z 587 (M+1, 5), 396 (9), 338 (6), 191 (88), 175 (100), 105 (30); high resolution ms: m/z 586.1899 (M^+, $C_{28}H_{34}N_4O_6S_2$ requires 586.1920); R_f 0.53 (ethyl acetate-methanol, 7:3).

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