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Notes

Rapid and Effective Multihalogenations of 2,2',5',2''-Terthiophene with 2-Halo-4,5-dichloropyridazin-3(2*H*)-ones under Ambient Conditions

Eun Jung Kim, Kwang-Ju Jung, In-Hye Lee, Bo Ram Kim, Jeum-Jong Kim,[†] Jong Keun Park,[‡] Sang-Gyeong Lee, and Yong-Jin Yoon[*]

Department of Chemistry & Environmental Biotechnology National Core Research Center, Research Institute of Natural Sciences, Graduate School for Molecular Materials and Nanochemistry, Gyeongsang National University, Jinju, Gyeognam 660-701, Korea. [*]E-mail: yjyoon@gnu.ac.kr
[†]Advanced Solar Technology Research Department, Electronic and Telecommunications Research Institute, Daejeon 305-700, Korea
[‡]Department of Chemistry Education, Gyeongsang National University, Jinju, Gyeongnam 660-701, Korea
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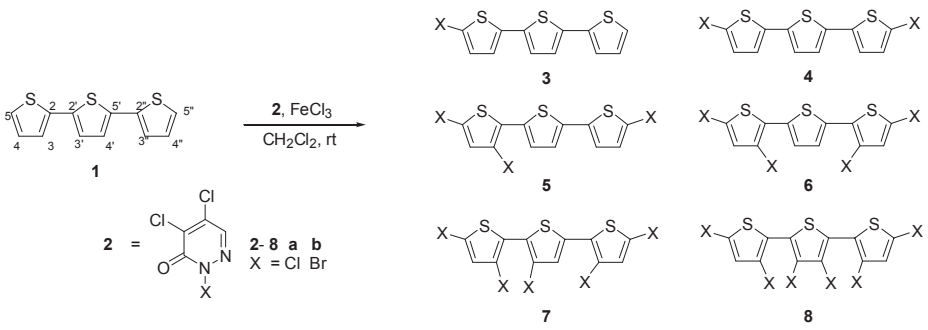
Recently, we demonstrated utility as synthetic auxiliaries of 2-substituted-pyridazin-3(2*H*)-ones due to pyridazin-3(2*H*)-ones are inexpensive, stable and easily prepared heterocycles.[1] 2-Halopyridazin-3(2*H*)-ones were also developed as useful and eco-friendly electrophilic halogenating agents.[1c,1h] Since pyridazin-3(2*H*)-ones have some advantages involving the formation of stable anions[2] and the electron acceptable moiety,[1,2] we explored the application of 2-halopyridazin-3(2*H*)-ones for the halogenation of electron rich compounds as electrophilic halogen sources.

In connection with our research programs for the synthesis of the well-defined macromolecules involving multihaloterthiophenes, we need some multihaloterthiophenes such as tetra- to hexahaloterthiophenes. Although some synthetic methods of haloterthiophenes are reported,[3-9] the direct multihalogenations of terthiophene for preparing tetra- to hexahaloterthiophenes, to the best of our knowledge, has not been reported yet and highlight this still very active research area. Thus, we investigated the direct multihalogenation of terthiophene using 2-halopyridazin-3(2*H*)-ones as electrophilic halogenating agents. Herein, we report the efficient, rapid and direct halogenations of 2,2',5',2''-terthiophene using 2-halopyridazin-3(2*H*)-ones under ambient conditions.

2-Halopyridazin-3(2*H*)-ones **2** were easily prepared according to the literature methods.[1h,10] We first studied the direct halogenations of 2,2',5',2''-terthiophene (**1**) using 2-halo-4,5-dichloropyridazin-3(2*H*)-one **2** under neutral and ambient conditions. Compound **1** (1 equiv.) was treated with **2** (1 equiv.) in methylene chloride at room temperature for 10 minutes to give the corresponding 5-haloterthiophene **3** or 5,5''-dihaloterthiophene **4**. However, terthiophene were not completely converted to haloterthiophenes. According to the literature,[1c,1h,10,11] the reactivity of halogen at N2-position of **2** may enhance by the chelation of **2** with metal halide. Therefore, we screened about six metal halides (1 mol %) such as CuCl, $CuCl_2$, $PdCl_2$, $FeCl_3$ $AlCl_3$, $ZnCl_2$ (Table 1). Iron(III) chloride was showed the best results for the conversion ratio and the regioselectivity (Entries 9 and 10 in Table 1). We also screened about six solvents such as CH_2Cl_2, AcOEt, THF, MeOH, CH_3COCH_3 and *n*-hexane (Table 2). The halogenation in methylene chloride was showed the best results.

From preliminary experiments, we selected the 2,2',5',2''-terthiophene (**1**)/**2**/$FeCl_3$ (1 mol %)/CH_2Cl_2 system as the optimum condition at room temperature. In order to determine the



Scheme 1. Halogenations of 2,2',5',2''-terthiophene (**1**) using 2-halo-4,5-dichloropyridazin-3(2*H*)-ones **2** in the presence of $FeCl_3$ in CH_2Cl_2 at room temperature

Table 1. Screening of metal chlorides for halogenation of 2,2',5',2''-terthiophene (**1**)[a]

Entry	**2**	MCl_n (1 mol %)	Conversion ratio (%)[b]	Product distribution (%)[b]			
				3		**4**	
1	**2a**	-	50	**3a**	80	**4a**	20
2	**2b**	-	74	**3b**	69	**4b**	31
3	**2a**	CuCl	55	**3a**	90	**4a**	10
4	**2b**	CuCl	78	**3b**	68	**4b**	32
5	**2a**	$CuCl_2$	66	**3a**	80	**4a**	20
6	**2b**	$CuCl_2$	70	**3b**	82	**4b**	18
7	**2a**	$PdCl_2$	59	**3a**	93	**4a**	7
8	**2b**	$PdCl_2$	67	**3b**	80	**4b**	20
9	**2a**	$FeCl_3$	74	**3a**	94	**4a**	6
10	**2b**	$FeCl_3$	70	**3b**	87	**4b**	13
11	**2a**	$AlCl_3$	48	**3a**	86	**4a**	14
12	**2b**	$AlCl_3$	50	**3b**	81	**4b**	19
13	**2a**	$ZnCl_2$	75	**3a**	78	**4a**	22
14	**2b**	$ZnCl_2$	71	**3b**	85	**4b**	15

[a]Reaction conditions: **1** (1 equiv.) and **2** (1 equiv.) for 10 minutes in CH_2Cl_2 at room temperature. [b]Conversion ratio and product distribution were determined by ^{1}H NMR.

Table 2. Screening of solvents for halogenation of **1**[a]

Entry	**2**	Solvent	Conversion ratio (%)[b]	Product distribution (%)[b]			
				3		**4**	
1	**2a**	Dichloromethane	74	**3a**	94	**4a**	6
2	**2b**	Dichloromethane	70	**3b**	87	**4b**	13
3	**2a**	Ethyl acetate	73	**3a**	85	**4a**	15
4	**2b**	Ethyl acetate	60	**3b**	73	**4b**	27
5	**2a**	Tetrahydrofuran	59	**3a**	85	**4a**	15
6	**2b**	Tetrahydrofuran	58	**3b**	85	**4b**	15
7	**2a**	Methanol	62	**3a**	80	**4a**	20
8	**2b**	Methanol	45	**3b**	48	**4b**	52
9	**2a**	Acetone	42	**3a**	66	**4a**	34
10	**2b**	Acetone	58	**3b**	62	**4b**	38
11	**2a**	*n*-Hexane	48	**3a**	95	**4a**	5
12	**2b**	*n*-Hexane	35	**3b**	62	**4b**	38

[a]Reaction conditions: **1** (1 equiv.), **2** (1 equiv.) and $FeCl_3$ (1 mol %) for 10 minutes at room temperature. [b]Conversion ratio and product distribution were determined by ^{1}H NMR.

conversion ratio and the product distribution by using ^{1}H NMR, we firstly obtained the analytical samples of compounds **3**-**8** from the halogenations of **1** with 1-7 equivalents of **2** in the presence of $FeCl_3$ (1 mol %) in CH_2Cl_2 at room temperature. After the establishment of the structures for **3a**-**8a** and **3b**-**8b** by using elemental analysis, IR, NMR and HRMS, we determined the conversion ratio and the product distribution by using the reference proton signals of ^{1}H NMR for each compound; the reference signals for **3a** (δ 7.26-7.24 ppm, $1H^5$), **4a** (δ 6.68-6.85 ppm, $2H^{4,4''}$), **5a** (δ 6.82 ppm, $1H^{4''}$), **6a** (δ 6.74 ppm, $2H^{4,4''}$), **7a** (δ 7.13 ppm, $1H^{3'}$), **8a** (δ 6.91 ppm, $2H^{4,4''}$), **3b** (δ 7.24-7.22 ppm, $1H^3$), **4b** (δ 6.91-6.90 ppm, $2H^{4,4''}$), **5b** (δ 6.97-6.96 ppm, $1H^3$), **6b** (δ 7.28 ppm, $2H^{4',3'}$), **7b** (δ 7.28 ppm, $1H^{3'}$), and **8b** (δ 7.08 ppm, $2H^{4,4''}$).

First, we chlorinated 2,2',5',2''-terthiophene (**1**) with 1-7 equivalents of **2a** under the optimized conditions. Chlorination of **1** with one equivalent of **2a** for 10 minutes under the optimized conditions gave two products (**3a**/**4a** = 94:6 ratio) (Entry 1 in Table 3). When 2-5 equivalents of **2a** was used, we detected three products, respectively: **3a**/**4a**/**5a** (25:71:4 ratio) for 2 equivalents; **4a**/**5a**/**6a** (12:66:22 ratio) for 3 equivalents; **5a**/**6a**/**7a** (14:63:23 ratio) for 4 equivalents; **6a**/**7a**/**8a** (22:63:15 ratio) for 5 equivalents (Entries 2-5 in Table 3). 2,2',5',2''-Terthiophene (**1**) was chlorinated with six equivalents under the same optimized condition to give **7a** and **8a** (57:43 ratio) (Entry 6 in Table 3). Chlorination of **1** with seven equivalents of **2a** under the same conditions afforded only hexabromoterthiophene **8a** (Entry 7 in Table 3), however, hepta- and octachloroterthiophenes, did not detected. The chlorination of **1** with 1 or 7 equivalents of **2a** under our conditions gave regioselectively compound **3a** or **8a**.

On the other hand, 2,2',5',2''-terthiophene (**1**) was treated with 1-7 equivalents of **2b** under the same conditions. Treatment of 2,2',5',2''-terthiophene (**1**) with one equivalent of **2b** gave **3b** and **4b** (87:13 ratio) (Entry 1 in Table 4). When 2 or 6 equivalents of **2b** were used, we obtained two products such as **3b** and **4b** (11:89 ratio) for 2 equivalents, and **7b** and **8b** (48:52 ratio) for 6 equivalents, respectively (Entries 2 and 6 in Table 4). However, bromination of **1** with 3 or 5 equivalents of **2b** afforded three products: **4b**/**5b**/**6b** (25:65:10 ratio) for 3 equivalents; **6b**/**7b**/**8b** (19:51:30 ratio) for 5 equivalents, respectively (Entries 3 and 5 in Table 4). Specially, 2,2',5',2''-terthiophene (**1**) was reacted with 4 or 7 equivalents of **2b** under the same conditions to give only one product such as **6b** for 4 equivalents or **8b** for 7 equivalents (Entries 4 and 7 in Table 4). According to TLC

Table 3. Chlorination of 2,2',5',2''-terthiophene (**1**) with 1-7 equivalents of **2a**[a]

Entry	**2a** (equiv.)	Conversion ratio (%)[b]	Product distribution[b] (Isolated yield, %)					
			3a	**4a**	**5a**	**6a**	**7a**	**8a**
1	1	74	94 (85)	6 (3)				
2	2	100	25 (21)	71 (69)	4 (2)			
3	3	100		12 (9)	66 (57)	22 (19)		
4	4	100			14 (12)	63 (55)	23 (20)	
5	5	100				22 (18)	63 (60)	15 (13)
6	6	100					57 (53)	43 (41)
7	7	100						100 (97)

[a]Reaction conditions: **1** (1 equiv.) and $FeCl_3$ (1 mol %) for 10 minutes in CH_2Cl_2 at room temperature. 2-Halo-4,5-dichloropyridazin-3(2*H*)-one was isolated in quantitative yields. [b]The conversion ratio and the product distribution were determined by ^{1}H NMR.

Table 4. Bromination of 2,2',5',2"-terthiophene (**1**) with 1-7 equivalents of **2b**[a]

Entry	**2b** (equiv.)	Conversion ratio (%)[b]	Product distribution[b] (Isolated yield, %)					
			3b	**4b**	**5b**	**6b**	**7b**	**8b**
1	1	70	87 (82)	13 (10)				
2	2	100	11 (9)	89 (84)				
3	3	100		25 (21)	65 (60)	10 (7)		
4	4	100				100 (96)		
5	5	100				19 (14)	51[c]	30[c]
6	6	100					48[c]	52[c]
7	7	100						100 (96)

[a]Reaction conditions: **1** (1 equiv.) and $FeCl_3$ (1 mol %) for 10 minutes in CH_2Cl_2 at room temperature. 2-Halo-4,5-dichloropyridazin-3(2*H*)-one was isolated in quantitative yields. [b]The conversion ratio and the product distribution were determined by ^1H NMR. [c]Although the mixture of **7b** and **8b** were not isolated by TLC and silica gel column, the analytical sample of **7b** was seven times recrystallized from a mixed solvent (benzene/*n*-hexane = 1:10, v/v).

analysis, compound **1** was halogenated under our conditions in the following order: **1** → **3** → **4**/**5**/**6** → **7**.

Regioselectivity in the electrophilic halogenations of 2,2', 5',2"-terthiophene is well explained by a consideration of the Wheland intermediate.[1c,12] Because of the delocalization of intermediate cation, the electrophilic attack from 5- and/or 5"-positions are more favorable than from other positions in the case of 2,2',5',2"-terthiophene (**1**) and 5-halo-2,2',5',2"-terthiophene **3**. For 5,5"-dihalo- and/or 5,5",3-trihaloterthiophenes **5** and/or **6**, the electrophilic attack from 3- and/or 3"-positions are more favorable than from other positions.

In summary, we have introduced a new, effective and direct multihalogenations of 2,2',5',2"-terthiophene (**1**) under mild and ambient conditions using 2-halo-4,5-dichloropyridazin-3(2*H*)-ones **2**. The present system is a rapid and facile methods. 2-Halopyridazin-3(2*H*)-ones are easily prepared from 4,5-dichloropyridazin-3(2*H*)-one, which is commercially available, stable, and reusable.[1-11] We envision more useful cascade multihalogenation of oligothiophenes or compounds involving terthiophene moiety, and efforts in this direction are under way.

Experimental Section

Melting points were determined with a capillary apparatus and uncorrected. NMR spectra were recorded on a 300 MHz spectrometer with chemical shift values reported in δ units (ppm) relative to an internal standard (TMS). IR spectra were obtained on a Mattson Genesis Series FT-IR spectrophotometer. Mass spectra were obtained on a GC Mate 2, JEOL. The open-bed chromatography was carried out on silica gel (70 - 230 mesh, Merck) using gravity flow. The column was packed with slurries made from the elution solvent.

General procedures of halogenations of 2,2',5',2"-terthiophene (1). A mixture of 2,2',5',2"-terthiophene (**1**, 1 mmol), **2** (1-7 equiv.), $FeCl_3$ (1 mol %) and solvent (20 mL) was stirred at room temperature until the **2** disappeared by TLC monitoring. After evaporating the solvent under reduced pressure, the resulting residue was applied to the top of an open-bed silica gel column (2.5 × 7 cm). The column was eluted with *n*-hexane. Fractions containing the product were combined and evaporated under reduced pressure to give the analytical samples **3**-**8** except for **7b**. The analytical sample of **7b** was obtained by seven times recrystallization of the mixture of **7b** and **8b** from a mixed solvent (benzene/*n*-hexane = 1:10 v/v). After finishing the reaction, the product distribution was also determined by ^1H NMR from the original reaction solution.

2-Chloro-2,2',5',2"-terthiophene (3a): mp 130 °C; R_f = 0.34 (*n*-hexane). IR (KBr): 3082, 3073, 1424, 1274, 1262, 1068, 1047, 1000, 833, 748, 686 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.26-7.24 (dd, 1H, *J* = 1.0, 5.1 Hz), 7.20-7.19 (dd, 1H, *J* = 1.0, 3.6 Hz), 7.09-7.08 (d, 1H, *J* = 3.8 Hz), 7.06-7.03 (dd, 1H, *J* = 5.1, 3.7 Hz) 7.03-7.01 (d, 1H, *J* = 3.8 Hz), 6.95-6.94 (d, 1H, *J* = 3.9 Hz), 6.86-6.85 (d, 1H, *J* = 3.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 136.6, 135.8, 135.2, 128.8, 127.9, 127.0, 124.7, 124.5, 124.3, 123.9, 122.8. HRMS (EI): *m*/*z* calcd for $C_{12}H_7S_3Cl$: 281.9398; found: 281.9395.

2,5"-Dichloro-2,2',5',2"-terthiophene (4a): mp 138 °C (lit.[13] mp 134 - 135 °C); R_f = 0.46 (*n*-hexane). IR (KBr): 3079, 3048, 1431, 1286, 1269, 1067, 1001, 848, 787, 733 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 2H), 6.95-6.93 (d, 2H, *J* = 3.9 Hz), 6.86-6.85 (d, 2H, *J* = 3.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 135.5, 129.1, 127.0, 124.4, 123.0. HRMS (EI): *m*/*z* calcd for $C_{12}H_6S_3Cl_2$: 315.9009; found: 315.9009.

2,4,5"-Trichloro-2,2',5',2"-terthiophene (5a): mp 73 °C; R_f = 0.54 (*n*-hexane). IR (KBr): 3002, 1503, 1455, 1375, 1274, 1260, 779, 764, 725 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19-7.18 (d, 1H, *J* = 3.9 Hz), 7.04-7.02 (d, 1H, *J* = 3.9 Hz), 6.98-6.96 (d, 1H, *J* = 3.9 Hz), 6.86-6.84 (d, 1H, *J* = 3.9 Hz), 6.82 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ137.1, 135.2, 131.8, 129.3, 128.9, 128.1, 128.0, 127.0, 126.9, 123.7, 123.2, 120.0. HRMS (EI): *m*/*z* calcd for $C_{12}H_5S_3Cl_3$: 349.8619; found: 349.8620.

2,4,3",5"-Tetrachloro-2,2',5',2"-terthiophene (6a): mp 126 °C; R_f = 0.59 (*n*-hexane). IR (KBr): 3093, 3018, 2919, 1498, 1436, 1274, 1260, 1017, 913, 857, 817, 778, 667, 617 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 2H), 6.82 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.5, 128.8, 128.4, 128.1, 126.3, 120.3 ppm. HRMS (EI): *m*/*z* calcd for $C_{12}H_4S_3Cl_4$: 383.8229; found: 383.8230.

2,4,3',3",5"-Pentachloro-2,2',5',2"-terthiophene (7a): mp 112 °C; R_f = 0.66 (*n*-hexane). IR (KBr): 3003, 2988, 1506, 1274, 1260, 912, 764, 722, 667 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (s, 1H), 6.82 (s, 1H), 6.78 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.9, 131.1, 131.0, 128.2, 127.3, 127.1, 126.5, 126.4, 125.8, 125.5, 125.0, 119.9. HRMS (EI): *m*/*z* calcd for $C_{12}H_3S_3Cl_5$: 417.7840; found: 417.7837.

2,4,3',4',3",5"-Hexachloro-2,2',5',2"-terthiophene (8a): mp

207 °C; R_f= 0.67 (*n*-hexane). IR (KBr): 3095, 2957, 2923, 2852, 1487, 1462, 1226, 1147, 1022, 943, 813, 789, 695 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.91 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.8, 130.8, 127.3, 126.3, 124.3, 124.2. HRMS (EI): *m/z* calcd for $C_{12}H_2S_3Cl_6$: 451.7450; found: 451.7449.

2-Bromo-2,2',5',2''-terthiophene (3b): mp 136 °C (lit.[14] mp 135 - 136 °C); R_f= 0.32 (*n*-hexane). IR (KBr): 3087, 3077, 1425, 1269, 1248, 1066, 912, 831, 790, 740, 701, 687 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.24-7.22 (dd, 1H, *J* = 1.1, 5.1 Hz), 7.18-7.16 (dd, 1H, *J* = 1.1, 3.6 Hz), 7.07-7.05 (d, 1H, *J* = 3.8 Hz), 7.03-7.01 (dd, 1H, *J* = 5.1, 3.6 Hz) 7.01-7.01 (d, 1H, *J* = 3.8 Hz), 6.98-6.96 (d, 1H, *J* = 3.8 Hz), 6.91-6.90 (d, 1H, *J* = 3.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 136.9, 136.7, 135.1, 130.7, 127.9, 124.7, 124.6, 124.3, 123.9, 123.7, 111.0. HRMS (EI): *m/z* calcd for $C_{12}H_7S_3Br$: 325.8893; found: 325.8895.

2,5''-Dibromo-2,2',5',2''-terthiophene (4b): mp 157 °C (lit.[15] mp 157 °C); R_f= 0.41 (*n*-hexane). IR (KBr): 3087, 3080, 3064, 3046, 1500, 1425, 1242, 1223, 1195, 1061, 992, 970, 845, 792, 730, 650 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 2H), 6.98-6.97 (d, 2H, *J* = 3.9 Hz), 6.91-6.90 (d, 2H, *J* = 3.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 135.6, 130.7, 124.6, 124.0, 111.3. HRMS (EI): *m/z* calcd for $C_{12}H_6S_3Br_2$: 403.7998; found: 403.7995.

2,4,5''-Tribromo-2,2',5',2''-terthiophene (5b): mp 107 °C (lit.[16] mp 105.5 - 106.5 °C); R_f= 0.44 (*n*-hexane). IR (KBr): 3087, 3062, 1494, 1432, 1425, 1263, 1236, 1129, 969, 868, 815, 780, 772, 748, 738, 606, 590 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.19 (d, 1H, *J* = 3.8 Hz), 7.02-7.01 (d, 1H, *J* = 3.8 Hz), 6.97-6.96 (d, 1H, *J* = 3.8 Hz), 6.94-6.92 (d, 1H, *J* = 3.8 Hz), 6.97 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 137.2, 134.0, 133.6, 132.5, 130.8, 127.5, 124.2, 123.9, 111.7, 111.3, 107.1. HRMS (EI): *m/z* calcd for $C_{12}H_5S_3Br_3$: 481.7104; found: 481.7105.

2,4,3'',5''-Tetrabromo-2,2',5',2''-terthiophene (6b): mp 158 °C (lit.[17] mp 156 °C); R_f= 0.45 (*n*-hexane). IR (KBr): 3097, 3086, 1516, 1487, 1456, 1433, 1131, 973, 855, 815, 791, 778, 637, 608 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 2H), 6.99 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2, 134.0, 133.4, 126.9, 111.7, 107.4 ppm. HRMS (EI): *m/z* calcd for $C_{12}H_4S_3Br_4$: 559.6209; found: 559.6213.

2,4,3',3'',5''-Pentabromo-2,2',5',2''-terthiophene (7b): mp 126 °C; R_f= 0.45 (*n*-hexane). IR (KBr): 3003, 2988, 1506, 1274, 1260, 912, 764, 722, 667 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.06 (s, 1H), 7.01 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ135.3, 134.1, 133.1, 133.0, 129.4, 115.2, 114.6, 112.8, 112.6, 112.2, 111.8, 108.2. HRMS (EI): *m/z* calcd for $C_{12}H_3S_3Br_5$: 637.5314; found: 637.5314.

2,4,3',4',3'',5''-Hexabromo-2,2',5',2''-terthiophene (8b): mp 190° C; R_f= 0.45 (*n*-hexane). IR (KBr): 3097, 1685, 1654, 1470, 1456, 1285, 1270, 1208, 983, 827, 804, 774, 756, 733, 668, 608 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.2, 130.2, 129.6, 116.9, 115.3, 112.4. HRMS (EI): *m/z* calcd for $C_{12}H_2S_3Br_6$: 715.4419; found: 715.4429.

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