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Synthesis of 5,5′-diarylated 2,2′-bithiophenes via palladium-catalyzed arylation reactions

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Abstract—2,2′-Bithiophene and 3,3′-dicyano-2,2′-bithiophenes are diarylated directly with aryl bromides at the 5- and 5′-positions accompanied by C–H bond cleavage in the presence of $Pd(OAc)_2$ and a bulky phosphine ligand using Cs_2CO_3 as base. In the reaction using (2,2′-bithiophen-5-yl)diphenylmethanol as the substrate, monoarylation at the 5-position via C–C bond cleavage occurs selectively to give 5-aryl-2,2′-bithiophenes and the subsequent arylation with a different aryl bromide affords the corresponding unsymmetrically 5,5′-diarylated products.

1. Introduction

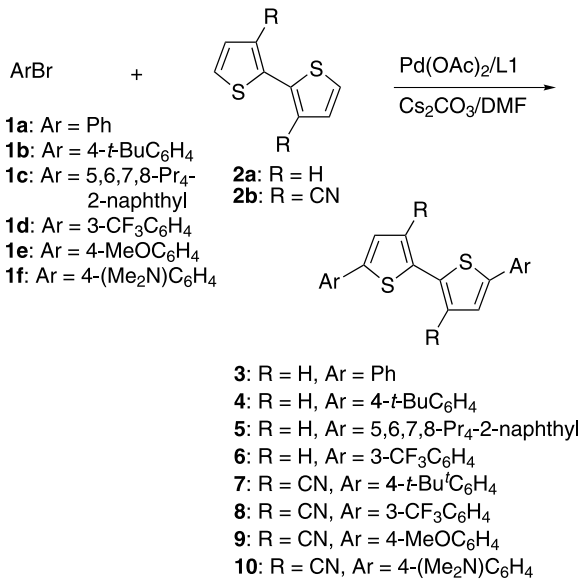
Poly- and oligoaryl compounds involving a thiophene unit have attracted much attention as the organic components of electronic devices.[1] Among the most useful methods to prepare such arylheterocycles is the palladium-catalyzed cross-coupling of either heteroaryl halides with arylmetals or aryl halides with heteroarylmetals. Thus, the reaction has been extensively studied.[2]

Meanwhile, it is known that aryl halides can couple directly with a number of five-membered heteroaromatics[3] including thiophenes[3,4] at their 2- and/or 5-position(s) in the presence of a palladium catalyst. The method has a significant advantage, not requiring stoichiometric metalation of the heterocycles. We recently reported that thiophenes[5a] as well as thiazoles[5b] are effectively arylated with aryl bromides in the presence of $Pd(OAc)_2$ and a bulky phosphine ligand using Cs_2CO_3 as base.

5,5′-Diaryl-2,2′-bithiophenes have been shown to be useful compounds as organic semiconductors[1c,d] and fluorescent materials.[1e,f] Consequently, we have examined the direct arylation of 2,2′-bithiophene as well as its 3,3′-dicyano derivative by means of palladium catalysis. It has also been undertaken to prepare unsymmetrically 5,5′-diarylated 2,2′-bithiophenes using diphenyl(2,2′-bithiophen-5-yl)diphenylmethanol as the strating substrate; the first step is based on our method recently developed for preparing unsymmetrical biaryls by the palladium-catalyzed arylation of *tert*-benzylalcohols via C–C bond cleavage.[6] The results are reported herein.

2. Results and discussion

The arylation of 2,2′-bithiophene (**2a**) (1 mmol) was first carried out with bromobenzene (**1a**) (4 mmol) in the presence of $Pd(OAc)_2$ (0.1 mmol) and P(biphenyl-2-yl)-(*t*-Bu)$_2$ (L1)[7] (0.2 mmol) using Cs_2CO_3 as base in DMF at 150 °C for 48 h. As expected, 5,5′-diphenyl-2,2′-bithiophene (**3**) was obtained in 60% yield (Scheme 1 and entry 1 in Table 1).



Scheme 1.

Keywords: Arylation; Aryl halides; Palladium and compounds; Thiophenes.
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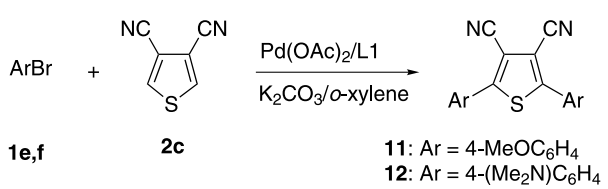
Table 1. Diarylation of 2,2′-bithiophene (**2a**), 3,3′-dicyano-2,2′-bithiophene (**2b**), and 3,4-dicyanothiophene (**2c**) with aryl bromides **1a**–**f**[a]

Entry	Bromide	Thiophene	Conditions[b]	Time (h)	Product, yield[c] (%)
1	**1a**	**2a**	A[d]	48	**3**, 60
2	**1b**	**2a**	A	8	**4**, 60
3	**1c**	**2a**	B	48	**5**, 87
4	**1d**	**2a**	A	8	**6**, 91
5	**1b**	**2b**	B	4	**7**, 66
6	**1d**	**2b**	B	4	**8**, 93
7	**1e**	**2b**	B	1	**9**, 96
8	**1e**	**2b**	B[e]	4	**9**, 87
9	**1f**	**2b**	B	4	**10**, 94
10	**1e**	**2c**	B[e,f]	8	**11**, 76
11	**1f**	**2c**	B[e,f]	18	**12**, 62

[a] The reaction was carried out in DMF under N_2 unless otherwise noted.
[b] A: [**1**]:[**2**]:[$Pd(OAc)_2$]:[L1]:[Cs_2CO_3]=2.4:1:0.1:0.2:2.4 (in mmol). B: [**1**]:[**2**]:[$Pd(OAc)_2$]:[L1]:[Cs_2CO_3]=1.2:0.5:0.05:0.1:1.2 (in mmol). L1=P(biphenyl-2-yl)(*t*-Bu)$_2$.
[c] Isolated yield.
[d] [**1**]:[**2**]:[Cs_2CO_3]=4:1:4.
[e] Reaction in *o*-xylene.
[f] K_2CO_3 was used in place of Cs_2CO_3.

Using less volatile 1-bromo-4-*tert*-butylbenzene (**1b**) (2.4 mmol), the same yield of the corresponding product **4** was attained after 8 h (entry 2). The symmetrically diarylated compounds **3** and **4** are relatively less soluble, and therefore, they were isolated by filtration through a silica gel pad and extraction with hot toluene. Use of 2-bromo-5,6,7,8-tetrapropylnaphthalene (**1c**)[8] as arylating reagent afforded 5,5′-bis(5,6,7,8-tetrapropylnaphthalen-2-yl)-2,2′-bithiophene (**5**), which was readily soluble in ether and isolated in a higher yield (entry 3). The reaction with 1-bromo-3-(trifluoromethyl)benzene (**1d**) also gave a relatively soluble compound **6** (entry 4). While the reaction with 4-bromoanisole (**1e**) proceeded, isolation of the product in pure state was not successful due to its insolubility.

It has been reported that 3,3′-dicyano-2,2′-bithiophene (**2b**) exhibits a high fluorescence quantum yield (Φ=0.995), while its molar extinction coefficient is relatively low (log ε=3.86).[9] On the other hand, 3-cyanothiophene was found to be readily arylated by the direct method.[3c,4,5a] Thus, we next examined the diarylation of **2b**. Treatment of **2b** with **1b**,**d**,**e** and 4-bromo-*N*,*N*-dimethylaniline (**1f**) gave 5,5′-diaryl-3,3′-dicyano-2,2′-bithiophenes **7**–**10** in good yields (Scheme 1 and entries 5–9 in Table 1). For the comparison of their properties, 2,5-di(4-methoxyphenyl)-(**11**) and 2,5-bis[4-(dimethylamino)phenyl]-3,4-dicyanothiophenes (**12**) were also prepared by the reaction of 3,4-dicyanothiophene (**2c**) with **1e** and **1f** (Scheme 2 and entries 10 and 11, the optical properties are described later). For the reaction of **2c**, K_2CO_3 and *o*-xylene were used as base and solvent, respectively. The products appeared to be unstable

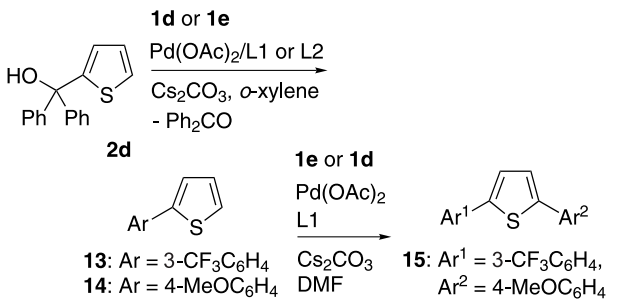


Scheme 2.

in the presence of Cs_2CO_3 in DMF, although the reaction of **2b** proceeded more efficiently in DMF than in *o*-xylene (entries 7 vs 8).

While the above direct method is useful for the symmetrical diarylation, it is not successful for the monoarylation, since a mixture of mono- and diarylated products is formed even with a limited amount of an aryl bromide. Thus, another strategy is required to furnish the unsymmetrical 5,5′-diarylation, especially for the initial step. We have recently reported that the palladium-catalyzed arylation of *tert*-benzylalcohols with aryl halides efficiently occurs accompanied by C–C bond cleavage to give unsymmetrical biaryls along with the corresponding ketones.[6] In order to see applicability of this new cross-coupling method to a bithiophene system, we have undertaken the reaction of (2,2′-bithiophen-5-yl)diphenylmethanol (**2e**).

Before beginning the examination with **2e**, the reaction of diphenyl(thiophen-2-yl)methanol (**2d**) was carried out in order to obtain appropriate conditions (Scheme 3 and Table 2).



Scheme 3.

Table 2. Arylation of diphenyl(thiophen-2-yl)methanol (**2d**) and 2-arylthiophenes **13** and **14** with aryl bromides **1d** and **1e**[a]

Entry	Bromide	Thiophene	Ligand[b]	Solvent	Time (h)	Product, yield[c] (%)
1[d]	**1d**	**2d**	L1	*o*-xylene	2	**13**, 62
2[e]	**1d**	**2d**	L2	*o*-xylene	1	**13**, 91 (71)
3[f]	**1e**	**2d**	L1	*o*-xylene	1.5	**14**, 88
4[d]	**1e**	**2d**	L1	DMF	2	**14**, 59
5[e]	**1e**	**2d**	L2	*o*-xylene	1	**14**, 88 (82)
6[g]	**1e**	**13**	L1	DMF	8	**15**, 85 (64)
7[g]	**1d**	**14**	L1	DMF	24	**15**, 72

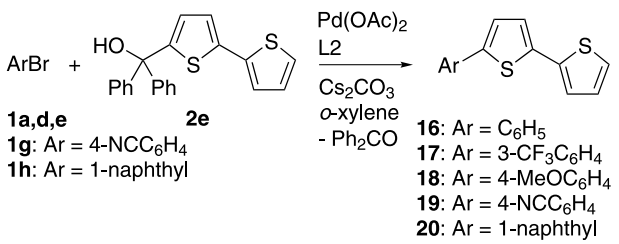
[a] The reaction was carried out at 150 °C under N_2.
[b] L1=P(biphenyl-2-yl)(*t*-Bu)$_2$, L2=P(cyclohexyl)$_3$.
[c] Determined by GLC abalysis. Value in parenthesis is isolated yield.
[d] [**1**]:[**2**]:[$Pd(OAc)_2$]:[L]:[Cs_2CO_3]=1:1:0.025:0.05:1 (in mmol).
[e] [**1**]:[**2**]:[$Pd(OAc)_2$]:[L]:[Cs_2CO_3]=1.5:1.5:0.025:0.05:1 (in mmol).
[f] [**1**]:[**2**]:[$Pd(OAc)_2$]:[L]:[Cs_2CO_3]=1.8:1.5:0.025:0.05:1 (in mmol).
[g] [**1**]:[**13** or **14**]:[$Pd(OAc)_2$]:[L]:[Cs_2CO_3]=0.6:0.5:0.05:0.1:0.6 (in mmol).

The reactions of **2d** with **1d** in *o*-xylene using L1 and P(cyclohexyl)$_3$ (L2) indicated that L2 is superior than L1, as was observed in the reaction of triphenylmethanol (entry 2 vs 1).[6] In the reaction with **1e**, however, the ligand effect was not important (entries 3 and 5). The origin of this discrepancy between **1d** and **1e** is not definitive at the present stage. DMF as solvent was not effective for the

reaction (entry 4 vs 3). This may be attributed to the fact that coordination of the oxygen of the alcohol to metal center is the key for the coupling.[6]

The obtained 2-arylthiophenes **13** and **14** were then treated with **1e** and **1b** in DMF as for the reaction of **2a**. Both the reactions gave 2-(4-methoxyphenyl)-5-(3-trifluoromethylphenyl)thiophene (**15**), while **13** reacted more efficiently (entries 6 and 7 in Table 2). The electron-withdrawing group in **13** seems to promote the deprotonation in the catalytic cycle.[4a] An attempt to use 2-(2-thienyl)-2-propanol in place of **2d** was unsuccessful.

Based on the above results, alcohol **2e** was reacted with **1a**,**d**,**e**, 1-bromo-4-cyanobenzene (**1g**) and 1-bromonaphthalene (**1h**) using L2 in *o*-xylene (Scheme 4). As shown in Table 3, 5-aryl-2,2′-bithiophenes **16**–**20** were obtained in good yields.



Scheme 4.

Table 3. Arylation of (2,2′-bithiophen-5-yl)diphenylmethanol (**2e**) with aryl bromides **1a**,**d**,**e**,**g**,**h**[a]

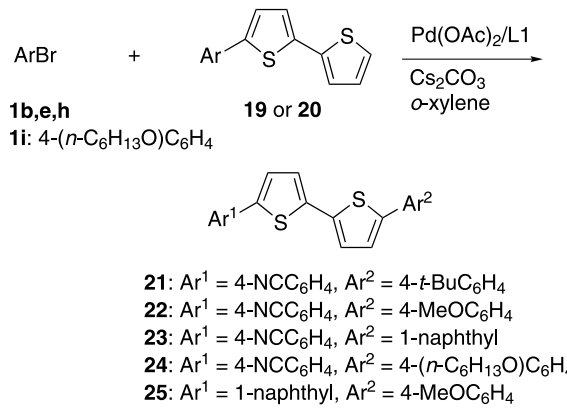
Entry	Bromide	Conditions[b]	Time (h)	Product, yield[c] (%)
1	**1a**	A	1	**16**, 96 (94)
2	**1d**	A	1	**17**, 75 (60)
3	**1e**	A	2	**18**, 71
4	**1e**	B	24	**18**, 71 (55)
5	**1g**	B	1	**19**, 99 (91)
6	**1h**	B	1	**20**, 76 (74)

[a] The reaction was carried out in *o*-xylene at 150 °C under N_2.
[b] A; [**1**]:[**2e**]:[$Pd(OAc)_2$]:[L2]:[Cs_2CO_3]=0.525:0.5:0.025:0.05:0.525 (in mmol). B; [**1**]:[**2e**]:[$Pd(OAc)_2$]:[L2]:[Cs_2CO_3]=1.575:1.5:0.025:0.05:1.575 (in mmol). L2=P(cyclohexyl)$_3$.
[c] Determined by GLC abalysis. Value in parenthesis is isolated yield.

Then, the arylation reactions of **19** with **1b**,**e**,**h** and 1-bromo-4-hexyloxybenzene (**1i**) and of **20** with **1e** were conducted as for that of **13** (Scheme 5 and Table 4). The unsymmetrically disubstituted bithiophenes **21**–**25** could be extracted with ethyl acetate or chloroform and were relatively tractable.

Shown in Table 5 are the optical properties of diarylated bithiophenes and thiophenes measured for the corresponding chloroform solutions under ambient conditions.

The optical band gap E_{00} was estimated from the interception of the absorption and emission spectra; the influence of Stokes shifts was neglected.[9] It can be seen that fine-tuning of the gap of 5,5′-diaryl-2,2′-bithiophene (compounds **3**–**10** and **21**–**25**) is possible by substituent effects; it is perturbed in a range of 2.33–3.22 eV. The emission spectra of compounds **3**–**6**, **21** and **23** showed two



Scheme 5.

Table 4. Arylation of 5-aryl-2,2′-bithiophenes **19** and **20** with aryl bromides **1b**,**e**,**h**,**i**[a]

Entry	Bromide	Thiophene	Time (h)	Product, yield[b] (%)
1	**1b**	**19**	8	**21**, 57
2	**1e**	**19**	4	**22**, 51
3	**1h**	**19**	4	**23**, 63
4	**1i**	**19**	4	**24**, 91
5	**1e**	**20**	8	**25**, 53

[a] The reaction was carried out in DMF at 150 °C under N_2. [**1**]:[**19** or **20**]:[$Pd(OAc)_2$]:[L1]:[Cs_2CO_3]=0.75:0.5:0.05:0.1:0.75 (in mmol). L1=P(biphenyl-2-yl)(*t*-Bu)$_2$.
[b] Isolated yield.

maxima; such a behavior has been reported to be often characteristic for 5,5′-diaryl-2,2′-bithiophene. It is worth noting that the introduction of two cyano groups to the 3,3′-positions of 5,5′-di(4-*tert*-butylphenyl)-2,2′-bithiophene (**4**) increased the quantum yield as expected (compound **7** versus **4**). 3,3′-Dicyano-5,5′-di(4-methoxyphenyl)-2,2′-bithiophene (**9**) also showed a relatively high quantum yield. In the case of the bis[3-(trifluoromethyl)phenyl] derivative **8**, however, it was significantly low (compound **8** versus **6**). The introduction of strongly electron-donating 4-*N*,*N*-dimethylamino group allowed a remarkable red-shift

Table 5. Optical absorption and emission maxima, extinction coefficient, fluorescent quantum yield, and optical band gap of diarylated bithiophenes **3**–**10**, **21** and **23**–**25** and those of diarylated thiophenes **11**, **12**, and **15**[a]

Compound	λ_{abs} (nm)	λ_{em} (nm)	log ε	Φ[b]	E_{00} (eV)
3	373	431, 455	4.54	0.17	2.98
4	377	436, 462	4.51	0.16	2.94
5	399	462, 491	4.72	0.29	2.78
6	374	431, 455	4.57	0.17	2.98
7	394	478	4.35	0.33	2.73
8	309	429	4.12	0.01	3.22
9	407	497	4.39	0.42	2.64
10	460	565	4.44	0.12	2.33
21	396	467, 476	4.63	0.12	2.80
23	384	469, 478	4.59	0.21	2.84
24	400	491	4.63	0.12	2.80
25	369	461	4.53	0.18	2.92
11	348	436	4.38	0.08	3.13
12	412	488	4.59	0.04	2.70
15	338	414	4.49	0.32	3.25

[a] Absorption and emission spectra were measured as a chloroform solution (5×10^{-5} M and 0.1 to 2.5×10^{-6} M, respectively).
[b] Determined by comparison of quinine sulfate (Φ=0.546).

(compound **10**). The fluorescent efficiencies of 2,5-diaryl-3,4-dicyanothiophenes **11** and **12** were low. While the relation of structures of the dicyanothiophenes with the emission properties can not be rationalized, it is remarkable that compounds **7** and **9** having a larger torsion angle around the C2–C2′bond show relatively high emission efficiencies.

In summary, we have described that 2,2′-bithiophene and 3,3′-dicyano-2,2′-bithiophene can be directly and effectively diarylated at the 5- and 5′-positions by means of palladium catalysis. The diarylated 3,3′-dicyano-2,2′-bithiophenes with aryl bromides having an electron-donating substituent shows relatively high fluorescent efficiency. Using (2,2′-bithiophen-5-yl)diphenylmethanol as the substrate, 5-aryl-2,2′-bithiophenes can be obtained selectively and the successive direct arylation affords unsymmetrically 5,5′-diarylated products. Thus, the arylation method accompanying C–C bond cleavage as well as that via C–H bond cleavage we reported previously can be applied effectively to bithiophene systems.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. MS analysis was made by EI. GC analysis was carried out using a Silicone OV-17 glass column (i.d. 2.6 mm×1.5 m).

3.2. Preparation of thiophenes 2

Bithiophene **2a** was commercially available. Thiophenes **2b**,[10] **2c**[11] and **2d**[6b] were prepared according to the methods reported previously.

3.2.1. (2,2′-Bithiophen-5-yl)diphenylmethanol (2e). In a 200 cm^3 three-necked flask were added 2,2′-bithiophene (3.34 g, 20 mmol) and THF (50 cm^3). Then, BuLi in hexane (1.57 M, 13 ml) and TMEDA (3 cm^3, 20 mmol) was added with srirring at −78 °C under N_2 (balloon) and allowed to warm to room temperature. After stirring 30 min, the mixture was cooled to −10 °C and benzophenone (3.09 g, 17 mmol) in THF (10 cm^3) was added. Then, the mixture was stirred at room temperature for 15 h, after which it was poured into aq. NH_4Cl, extracted with ethyl acetate and dried over Na_2SO_4. Evaporation of the solvents and column chromatography on silica gel using hexane–toluene (8:2, v/v) as eluent gave compound **2e** (5.74 g, 97%): Viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (s, 1H), 6.62 (d, J=3.7 Hz, 1H), 6.98 (dd, J=3.7, 5.1 Hz, 1H), 7.00 (d, J=3.7 Hz, 1H), 7.11 (dd, J=1.1, 3.7 Hz, 1H), 7.18 (dd, J=1.1, 5.1 Hz, 1H), 7.28–7.42 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.12, 122.94, 123.69, 124.41, 127.24, 127.48, 127.72, 127.76, 128.05, 137.27, 137.67, 146.16, 151.03; HR-MS m/z (M^+). Calcd for $C_{21}H_{16}OS_2$ 348.0643. Found 348.0648.

3.3. Synthesis of 5,5′-diaryl-2,2′-bithiophenes

The following experimental procedures may be regarded as typical in methodology and scale.

3.3.1. 5,5′-Di(4-*tert*-butylphenyl)-2,2′-bithiophene (4). In a 100 cm^3 two-necked flask was placed Cs_2CO_3 (2.4 mmol, 782 mg), which was then dried at 150 °C in vacuo for 2 h. Then, $Pd(OAc)_2$ (0.1 mmol, 22.4 mg), P(biphenyl-2-yl)(*t*-Bu)$_2$ (L1) (0.2 mmol, 40.5 mg), 1-bromo-4-*tert*-butylbenzene (**1b**) (2.4 mmol, 511 mg), 2,2′-bithiophene (**2a**) (1 mmol, 166 mg), 1-methylnaphthalene (ca. 100 mg) as internal standard and DMF (5 cm^3) were added. The resulting mixture was stirred under N_2 (balloon) at 150 °C for 8 h. The reaction mixture was filtered through a silica gel pad (ca. 20 g) with hot toluene. After evaporation of the solvents, the residue was washed with hexane and recrystallized with toluene to give compound **4** (256 mg, 60%).

3.3.2. 5,5′-Di(4-*tert*-butylphenyl)-3,3′-dicyano-2,2′-bithiophene (7). In a 100 cm^3 two-necked flask was placed Cs_2CO_3 (1.2 mmol, 391 mg) and dried as above. Then, $Pd(OAc)_2$ (0.05 mmol, 11.2 mg), P(biphenyl-2-yl)(*t*-Bu)$_2$ (L1) (0.1 mmol, 20.3 mg), 1-bromo-4-*tert*-butylbenzene (**1b**) (1.2 mmol, 256 mg), 3,3′-dicyano-2,2′-bithiophene (**2b**) (0.5 mmol, 108 mg) and DMF (5 cm^3) were added. The resulting mixture was stirred under N_2 (balloon) at 150 °C for 4 h. After cooling, the reaction mixture was extracted with ethyl acetate. Column chromatography on silica gel using hexane–ethyl acetate (98.5:1.5, v/v) gave compound **7** (159 mg, 66%).

3.3.3. 5-(4-*tert*-Butylphenyl)-5′-(4-cyanophenly)-2,2′-bithiophene (21). In a 100 cm^3 two-necked flask was placed Cs_2CO_3 (1.575 mmol, 513 mg) and dried as above. Then, $Pd(OAc)_2$ (0.025 mmol, 5.6 mg), P(cyclohexyl)$_3$ (L2) (0.05 mmol, 14 mg), 1-bromo-4-cyanobenzene (**1g**) (1.575 mmol, 286 mg), diphenyl(2,2′-bithiophen-5-yl)methanol (**2e**) (1.5 mmol, 522 mg), 1-methylnaphthalene (ca. 100 mg) as internal standard and *o*-xylene (5 cm^3) were added. The resulting mixture was stirred under N_2 (balloon) at 150 °C for 1 h. After cooling, the reaction mixture was extracted with ethyl acetate. After evaporation of the solvents, the residue was washed with hexane to give compound **19** (364 mg, 91%). Then, **19** (130 mg, 0.5 mmol) was treated with 1-bromo-4-*tert*-butylbenzene (**1b**) (136 mg, 0.75 mmol) in the presence of $Pd(OAc)_2$ (0.05 mmol, 11.2 mg), P(biphenyl-2-yl)(*t*-Bu)$_2$ (L1) (0.1 mmol, 20.3 mg) and Cs_2CO_3 (0.75 mmol, 244 mg) in DMF (5 cm^3) under N_2 at 150 °C for 8 h. Compound **21** (114 mg, 57%) was obtained by extraction with chloroform, washing with hexane and recrystallization with toluene.

3.4. Characterization data of products

3.4.1. 5,5′-Diphenyl-2,2′-bithiophene (3).[12] Mp 239.5–240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J=4.0 Hz, 2H), 7.25 (d, J=4.0 Hz, 2H), 7.29 (t, J=7.3 Hz, 2H), 7.39 (t, J=7.7 Hz, 4H), 7.61 (d, J=7.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.80, 124.48, 125.62, 127.61, 128.96, 134.04, 136.72, 143.16; MS m/z 318 (M^+).

3.4.2. 5,5′-Di(4-*tert*-butylphenyl)-2,2′-bithiophene (4). Mp 282–283 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 18H), 7.15 (d, J=3.8 Hz, 2H), 7.20 (d, J=3.8 Hz, 2H), 7.41 (d, J=8.6 Hz, 4H), 7.54 (d, J=8.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.26, 34.63, 123.35, 124.30, 125.35,

125.86, 131.31, 136.37, 143.10, 150.76; HR-MS *m/z* (M^+). Calcd for $C_{28}H_{30}S_2$ 430.1780. Found 430.1789.

3.4.3. 5,5′-Bis(5,6,7,8-tetrapropylnaphtalen-2-yl)-2,2′-bithiophene (5). Mp 169–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01–1.20 (m, 24H), 1.57–1.78 (m, 16H), 2.72–2.77 (m, 8H), 2.99–3.08 (m, 8H), 7.24 (d, *J*=3.6 Hz, 2H), 7.33 (d, *J*=3.6 Hz, 2H), 7.66 (d, *J*=8.7 Hz, 2H), 8.00 (d, *J*=8.7 Hz, 2H), 8.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 15.1, 15.1, 24.6, 24.7, 24.9, 24.9, 31.2, 31.2, 32.6, 32.7, 121.1, 122.5, 123.7, 124.6, 125.3, 129.9, 130.6, 131.3, 134.3, 134.4, 136.6, 137.4, 137.8, 144.2; MS *m/z* 754 (M^+). Anal. Calcd for $C_{52}H_{66}S_2$: C, 82.70; H, 8.81; S, 8.49. Found C, 82.44; H, 8.69; S, 8.60.

3.4.4. 5,5′-Di(3-trifluoromethylphenyl)-2,2′-bithiophene (6). Mp 125–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J*=4.0 Hz, 2H), 7.31 (d, *J*=4.0 Hz, 2H), 7.49–7.55 (m, 4H), 7.55–7.77 (m, 2H), 7.83 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.24 (q, *J*=3.7 Hz), 124.31 (q, *J*=3.7 Hz), 124.91, 124.93, 126.65 (q, *J*=273 Hz), 128.70, 129.50, 131.49 (q, *J*=32.2 Hz), 134.72, 137.37, 141.59; HR-MS *m/z* (M^+). Calcd for $C_{22}H_{12}F_6S_2$ 454.0285. Found 454.0293.

3.4.5. 5,5′-Di(4-*tert*-butylphenyl)-3,3′-dicyano-2,2′-bithiophene (7). Mp 275–276.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 18H), 7.44 (s, 2H), 7.47 (d, *J*=8.6 Hz, 4H), 7.55 (d, *J*=8.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.17, 34.85, 109.78, 114.86, 124.92, 126.01, 126.31, 128.71, 139.40, 147.01, 153.04; HR-MS *m/z* (M^+). Calcd for $C_{30}H_{28}N_2S_2$ 480.1694. Found 480.1697.

3.4.6. 5,5′-Di(3-trifluoromethylphenyl)-3,3′-dicyano-2,2′-bithiophene (8). Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.62 (t, *J*=7.7 Hz, 2H), 7.69 (d, *J*=7.7 Hz, 2H), 7.81 (d, *J*=7.7 Hz, 2H), 7.86 (s, 2H); ^{13}C NMR (100 MHz, DMF-d_7) δ 116.55, 119.99, 128.43 (q, *J*=4.6 Hz), 129.85 (q, *J*=272 Hz), 131.76 (q, *J*=3.7 Hz), 134.13, 135.82, 136.46, 136.55 (q, *J*=32.2 Hz), 138.22, 145.41, 150.78; HR-MS *m/z* (M^+). Calcd for $C_{24}H_{10}F_6N_2S_2$ 504.0190. Found 504.0192.

3.4.7. 5,5′-Di(4-methoxyphenyl)-3,3′-dicyano-2,2′-bithiophene (9). Mp 266–267.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.82 (s, 6H), 7.06 (d, *J*=8.8 Hz, 4H), 7.71 (d, *J*=8.8 Hz, 4H), 7.99 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 55.57, 109.91, 114.75, 115.05, 123.76, 125.45, 127.65, 137.86, 146.52, 160.51; HR-MS *m/z* (M^+). Calcd for $C_{24}H_{16}N_2O_2S_2$ 428.0653. Found 428.0650.

3.4.8. 5,5′-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3,3′-dicyano-2,2′-bithiophene (10). Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 (s, 12H), 6.72 (d, *J*=8.9 Hz, 4H), 7.26 (s, 2H), 7.47 (d, *J*=8.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.23, 109.09, 112.24, 115.33, 119.42, 122.64, 127.18, 137.98, 147.49, 151.00; HR-MS *m/z* (M^+). Calcd for $C_{26}H_{22}N_4S_2$ 454.1286. Found 454.1284.

3.4.9. 2,5-Di(4-methoxyphenyl)-3,4-dicyanothiophene (11). Mp 225.5–227.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 6H), 7.02 (d, *J*=8.8 Hz, 4H), 7.67 (d, *J*=8.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.53, 106.87, 113.43, 114.96, 122.31, 129.11, 152.40, 161.65; HR-MS *m/z* (M^+). Calcd for $C_{20}H_{14}N_2O_2S$ 346.0776. Found 346.0774.

3.4.10. 2,5-Bis[4-(*N*,*N*-dimethylamino)phenyl]-3,4-dicyanothiophene (12). Mp 228.5–230 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.01 (s, 12H), 6.85 (d, *J*=8.8 Hz, 4H), 7.65 (d, *J*=8.8 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 39.82, 103.31, 112.26, 114.45, 116.51, 128.35, 151.79, 152.09; HR-MS *m/z* (M^+). Calcd for $C_{22}H_{20}N_4S$ 372.1409. Found 372.1415.

3.4.11. 2-(3-Trifluoromethylphenyl)thiophene (13). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, *J*=3.5, 5.1 Hz 1H), 7.33 (dd, *J*=1.1, 5.1 Hz, 1H), 7.35 (dd, *J*=1.1, 3.5 Hz, 1H), 7.45–7.53 (m, 2H), 7.76 (d, *J*=8.0 Hz, 1H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.55 (d, *J*=3.7 Hz), 123.94 (q, *J*=3.7 Hz), 124.11, 125.82, 127.30 (q, *J*=297 Hz), 128.23, 129.07, 129.37, 131.34 (q, *J*=32.2 Hz), 135.20, 142.64; HR-MS *m/z* (M^+). Calcd for $C_{11}H_7F_3S$ 228.0221. Found 228.0235.

3.4.12. 2-(4-Methoxyphenyl)thiophene (14).[13] Mp 106–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.90–6.93 (m, 2H), 7.05 (dd, *J*=3.6, 5.1 Hz, 1H), 7.19 (dd, *J*=1.5, 3.6 Hz, 1H), 7.21 (dd, *J*=1.5, 5.1 Hz, 1H), 7.51–7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.34, 114.27, 122.07, 123.81, 127.22, 127.31, 127.89, 144.33, 159.18; MS *m/z* 190 (M^+).

3.4.13. 2-(4-Methoxyphenyl)-5-(3-trifluoromethylphenyl)thiophene (15). Mp 103.5–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 6.94 (d, *J*=8.7 Hz, 2H), 7.20 (d, *J*=3.8 Hz, 1H), 7.33 (d, *J*=3.8 Hz, 1H), 7.47–7.55 (m, 2H), 7.57 (d, *J*=8.7 Hz, 2H), 7.76–7.78 (m, 1H), 7.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.39, 114.39, 122.09 (q, *J*=3.8 Hz), 123.09, 123.71 (q, *J*=3.8 Hz), 124.02 (q, *J*=272 Hz), 124.97, 126.82, 127.03, 128.56, 129.38, 131.43 (q, *J*=32.7 Hz), 135.22, 140.62, 144.80, 159.51; MS *m/z* 334 (M^+). Anal. Calcd for $C_{18}H_{13}F_3OS$: C, 64.66; H, 3.92; F, 17.05; S, 9.59. Found C, 64.36; H, 3.70; F, 17.34; S, 9.70.

3.4.14. 5-Phenyl-2,2′-bithiophene (16).[14] Mp 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (dd, *J*=3.6, 5.1 Hz, 1H), 7.15 (d, *J*=3.8 Hz, 1H), 7.20 (dd, *J*=1.1, 3.6 Hz, 1H), 7.22 (dd, *J*=1.1, 5.1 Hz, 1H), 7.22 (d, *J*=3.8 Hz, 1H), 7.27–7.31 (m, 1H), 7.36–7.41 (m, 2H), 7.58–7.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.62, 123.70, 124.37, 124.59, 125.61, 127.57, 127.85, 128.93, 134.06, 136.71, 137.43, 143.12; MS *m/z* 242 (M^+).

3.4.15. 5-(3-Trifluoromethylphenyl)-2,2′-bithiophene (17). Mp 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, *J*=3.7, 5.1 Hz 1H), 7.17 (d, *J*=4.0 Hz, 1H), 7.23 (dd, *J*=1.1, 3.7 Hz, 1H), 7.25 (dd, *J*=1.1, 5.1 Hz, 1H), 7.29 (d, *J*=4.0 Hz, 1H), 7.47–7.54 (m, 2H), 7.74–7.77 (m, 1H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.19 (q, *J*=4.6 Hz), 123.96 (q, *J*=272 Hz), 124.00 (q, *J*=4.6 Hz), 124.02, 124.69, 124.77, 124.81, 127.94, 128.66, 129.45, 131.43 (q, *J*=32.2 Hz), 134.86, 136.99, 137.87, 141.12; HR-MS *m/z* (M^+). Calcd for $C_{15}H_9F_3S_2$ 310.0098. Found 310.0095.

3.4.16. 5-(4-Methoxyphenyl)-2,2′-bithiophene (18). Mp 150–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.92 (d, J=8.8 Hz, 2H), 7.02 (dd, J=3.5, 5.0 Hz, 1H), 7.10 (d, J=4.0 Hz, 1H), 7.12 (d, J=4.0 Hz, 1H), 7.17 (dd, J=1.1, 3.5 Hz, 1H), 7.20 (dd, J=1.1, 5.0 Hz, 1H), 7.52 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.36, 114.34, 122.64, 123.36, 124.10, 124.56, 126.91, 127.79, 128.05, 135.69, 137.59, 143.15, 159.30; HR-MS m/z (M^+). Calcd for $C_{15}H_{12}OS_2$ 272.0329. Found 272.0323.

3.4.17. 5-(4-Cyanophenyl)-2,2′-bithiophene (19). Mp 148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (dd, J=3.6, 5.1 Hz, 1H), 7.18 (d, J=3.8 Hz, 1H), 7.24 (dd, J=1.1, 3.6 Hz, 1H), 7.27 (dd, J=1.1, 5.1 Hz, 1H), 7.34 (d, J=3.8 Hz, 1H), 7.64–7.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.49, 118.81, 124.33, 124.85, 125.20, 125.67, 125.84, 128.02, 132.76, 136.69, 138.29, 139.13, 140.38; HR-MS m/z (M^+). Calcd for $C_{15}H_9NS_2$ 267.0176. Found 267.0171.

3.4.18. 5-(Naphthalen-1-yl)-2,2′-bithiophene (20).[15] Mp 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (dd, J=3.7, 5.1 Hz, 1H), 7.16 (d, J=3.7 Hz, 1H), 7.23 (dd, J=1.1, 3.8 Hz, 1H), 7.25–7.26 (m, 2H), 7.48–7.54 (m, 3H), 7.58–7.61 (m, 1H), 7.86 (d, J=8.4 Hz, 1H), 7.89–7.91 (m, 1H), 8.29–8.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.71, 123.98, 124.40, 125.27, 125.66, 126.08, 126.54, 127.86, 128.02, 128.07, 128.39, 128.54, 131.69, 132.03, 133.91, 137.34, 137.63, 140.80; MS m/z 292 (M^+).

3.4.19. 5-(4-*tert*-Butylphenyl)-5′-(4-cyanophenyl)-2,2′-bithiophene (21). Mp 285.5–286 °C; ^{1}H NMR (400 MHz, DMF-d_7) δ 1.34 (s, 9H), 7.41–7.42 (m, 2H), 7.47 (d, J=3.7 Hz, 1H), 7.50 (d, J=8.4 Hz, 2H), 7.65 (d, J=8.4 Hz, 2H), 7.71 (d, J=4.0 Hz, 1H), 7.85 (d, J=8.8 Hz, 2H), 7.91 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.41, 31.29, 110.93, 119.14, 124.83, 125.89, 125.89, 126.39, 126.47, 126.59, 127.70, 131.52, 133.61, 135.81, 138.70, 139.27, 140.96, 144.45, 151.81; HR-MS m/z (M^+). Calcd for $C_{25}H_{21}NS_2$ 399.1115. Found 399.1111.

3.4.20. 5-(4-Cyanophenyl)-5′-(4-methoxyphenyl)-2,2′-bithiophene (22). Mp 187–188 °C; ^{1}H NMR (400 MHz, DMF-d_7) δ 3.87 (s, 3H), 7.06 (d, J=8.7 Hz, 2H), 7.43–7.46 (m, 3H), 7.67 (d, J=8.7 Hz, 2H), 7.79 (d, J=8.7 Hz, 1H), 7.91 (d, J=8.7 Hz, 2H), 7.95 (d, J=8.7 Hz, 2H); ^{13}C NMR (100 MHz, DMF-d_7) δ 55.76, 110.77, 115.30, 124.25, 125.84, 126.42, 126.56, 126.92, 127.51, 127.97, 133.80, 135.10, 138.70, 139.35, 140.66, 144.42, 160.45, 162.88; HR-MS m/z (M^+). Calcd for $C_{22}H_{15}NOS_2$ 373.0595. Found 373.0599.

3.4.21. 5-(4-Cyanophenyl)-5′-(naphthalen-1-yl)-2,2′-bithiophene (23). Mp 197.5–198 °C; ^{1}H NMR (400 MHz, DMF-d_7) δ 7.41 (d, J=3.7 Hz, 1H), 7.55 (d, J=4.0 Hz, 1H), 7.61–7.66 (m, 4H), 7.71 (dd, J=1.1, 7.0 Hz, 1H), 7.83 (d, J=4.0 Hz, 1H), 7.93 (d, J=8.8 Hz, 2H), 7.98 (d, J=8.8 Hz, 2H), 8.02–8.09 (m, 2H), 8.31–8.33 (m, 1H); ^{13}C NMR (100 MHz, DMF-d_7) δ 115.89, 124.41, 130.73, 130.98, 131.24, 131.32, 131.50, 132.07, 132.70, 133.04, 133.82, 134.34, 134.65, 134.70, 136.89, 137.01, 138.84, 139.78, 142.38, 143.66, 143.98, 146.10, 146.83; HR-MS m/z (M^+). Calcd for $C_{25}H_{15}NS_2$ 393.0646. Found 393.0651.

3.4.22. 5-(4-Cyanophenyl)-5′-(4-hexyloxyphenyl)-2,2′-bithiophene (24). Mp 209.5–210.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J=6.6 Hz, 3H), 1.34–1.36 (m, 4H), 1.43–1.51 (m, 2H), 1.76–1.83 (m, 2H), 3.98 (t, J=7.0 Hz, 2H), 6.91 (d, J=7.0 Hz, 2H), 7.12–7.17 (m, 3H), 7.34 (d, J=2.9 Hz, 1H), 7.51 (d, J=7.3 Hz, 2H), 7.65 (d, J=2.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.02, 22.59, 25.70, 29.20, 31.57, 68.18, 110.37, 114.97, 118.82, 122.74, 124.39, 125.21, 125.61, 125.92, 126.40, 126.95, 132.75, 134.75, 138.33, 139.41, 139.99, 144.29, 159.14; HR-MS m/z (M^+). Calcd for $C_{27}H_{25}NOS_2$ 443.1378. Found 443.1375.

3.4.23. 5-(4-Methoxyphenyl)-5′-(naphthalen-1-yl)-2,2′-bithiophene (25). Mp 135–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 6.93 (d, J=8.8 Hz, 2H), 7.14 (d, J=3.7 Hz, 1H), 7.17 (m, 2H), 7.25 (m, 1H), 7.48–7.56 (m, 5H), 7.60 (dd, J=1.1, 7.0 Hz, 1H), 7.86 (d, J=8.1 Hz, 1H), 7.89–7.92 (m, 1H), 8.31–8.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.38, 114.38, 122.75, 123.61, 124.53, 125.29, 125.68, 126.08, 126.55, 126.94, 126.94, 128.01, 128.13, 128.40, 128.53, 131.68, 132.06, 133.93, 135.60, 137.83, 140.55, 143.22, 159.34; MS m/z 398 (M^+). Anal. Calcd for $C_{25}H_{18}OS_2$: C, 75.34; H, 4.55; S, 16.09. Found C, 75.08; H, 4.64; S, 15.83.

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