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Synthesis and photophysical properties of 3,5-diaryl-2-heteroarylthiophenes

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ABSTRACT

A series of 3,5-diaryl-2-heteroarylthiophenes have been synthesized via Fiesselmann type reaction between alkynones and easily available heteroarylmethanethiols or heteroarylmethyl carbamimidothioates. A correlation between compounds structure and efficiency of luminescence has been established. These compounds exhibited photoluminescence with quantum yields up to 83%. An evidence of twisted intramolecular charge transfer and singlet emissive states have been demonstrated.

1. Introduction

Substituted thiophenes represent an important class of building blocks for the development of new pharmaceuticals [1,2] and optical materials [3–7]. There are numerous reports on the optoelectronic applications of thiophene-containing oligomeric or polymeric materials [8–13]. In contrast, the literature on the optoelectronic properties of monomeric thiophenes is relatively scarce. Although there are a few reports on the emissive properties of monomeric thiophenes [14], and these studies have led to the application of thiophenes in aggregation induced emission [15] and three-dimensional optical storage [16], the relationship between the structure and emissive behavior of monomeric thiophenes has not been systematically studied. It has been only shown that the introduction of benzimidazole (or structurally related phenanthroimidazole) [14] in the position 2 of the thiophene ring has helped to increase photoluminescence quantum yields (PLQY) to near unity in solution [14b]. In addition, Mueller has also demonstrated that aryl substituents that are not conjugated with the thiophene core have almost no effect on the emissive properties of oligomeric thiophenes [13]. Hence, we decided to utilize the beneficial effect of benzimidazole in position 2 and aryl substituents in positions 3 and 5 of thiophene scaffold in our study of emissive properties. The relationship between electronic and emissive properties of 2,3,5-trisubstituted thiophenes was systematically explored by the introduction of electron withdrawing groups (EWG) or electron donating groups (EDG) in aryl moieties (Fig. 1.). We were pleased to find that the proper choice of EWGs in the R_1 and R_2 positions and EDG in the R_3 position of 2,3,5-trisubstituted thiophenes allowed for PLQY of 83% to be achieved in solutions (Fig. 1).

Among a variety of methods for the synthesis of 2,3,5-trisubstituted thiophenes, Fiesselmann reaction is especially suitable. Early examples of Fiesselmann reaction involved a base-catalyzed condensation of acetylene dicarboxylates with mercaptoacetate to furnish 2,3,5-trisubstituted thiophenes (Scheme 1) [17]. The reaction experienced a renaissance in the late 90ties, when a tandem Michael addition/intramolecular Knoevenagel condensation between the appropriate 1,3-disubstituted propynones and mercaptoacetates was reported (Scheme 1) [18]. Later developments were mostly focused on various approaches for the *in situ* generation of ynones/ynoates under the Fiesselmann reaction conditions. Accordingly, Mueller elaborated the Fiesselmann reaction as a three-component or pseudo-five-component synthesis of 2,3,5-trisubstituted thiophenes and oligothiophenes [11–13] and Wu recently reported a four-component Fiesselmann reaction [19]. Importantly, easy-to-oxidize and relatively toxic mercaptans have been used as sulphur-containing building blocks in most of the above mentioned examples. Herein we report the use of heteroaryl substituted S-functionalized thioureas as a stable, non-toxic and easy-to-handle alternative to thiols [20] in the Fiesselmann reaction (Scheme 1).

2. Experimental section

2.1. General information

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100.6 MHz with Bruker Ascend™ spectrometer. Chemical shifts are reported in parts per million (ppm) using the residual protic solvent resonance as

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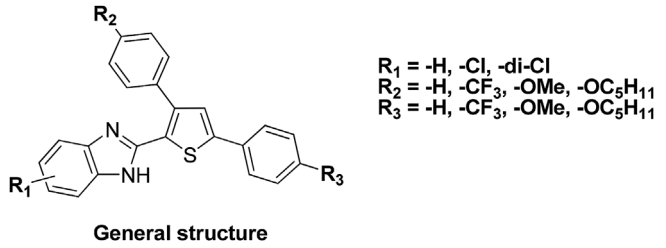


Fig. 1. General structure of luminescent 2,3,5-trisubstituted thiophenes.

the internal standard ($CHCl_3$: δ 7.28 (77.0), DMSO: δ 2.50 (39.5)) unless otherwise stated. Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration). Mass spectra were recorded with a TSQ Endura™ spectrometer (electrospray ionization) in positive mode. Melting points of synthesized compounds were monitored in open capillary with "Stuart SMP 10" apparatus. Reaction process was monitored by TLC using Silicagel 60 F_{254} Merc plates. For purification Silicagel 60 (40–63 μm), hexane or petroleum ether (PE), ethyl acetate (EA), toluene (Tol), chloroform ($CHCl_3$), acetonitrile (MeCN) and their mixtures were used as eluents. Hexane and petroleum ether were distilled before use.

The solution absorption and emission, as well as solid state emission spectra were measured on the FS5-*Edinburgh instruments* spectrofluorometer in ambient atmosphere and room temperature. The PLQYs were determined by the absolute method at ambient temperature using an integrating sphere. Compounds were excited in the wavelength they absorbed in. The temperature measurements were conducted in a cryostat using EtOH/liquid nitrogen as coolant.

2.2. Synthesis of compounds

2.2.1. Synthesis of starting materials

1,3-Diarylpropynones **1a-f** were synthesized according to known procedure [21] from corresponding alkynes and aroyl chlorides. (1*H*-benzo[*d*]imidazol-2-yl)methanethiols were prepared according to known procedure [22] in cyclization of aryl-1,2-diamine and mercaptoacetic acid and various substituted methyl carbamimidothioates were synthesized from corresponding alcohols in two step synthesis according the literature procedures [23] in good to excellent yield.

2.2.2. Synthesis of 3,5-diaryl-2-heteroarylthiophenes (3) and 2-heteroaryl-3,5-diaryl-2,3-dihydrothiophen-3-ols (4). General procedure

To the 25 ml round bottomed flask the corresponding heteroarylmethanethiol or heteroarylmethyl carbamimidothioate (0.45 mmol) and 36 mg NaOH (0.9 mmol) were added followed by 5 ml of ethanol. Reaction mixture was refluxed 1 h under argon atmosphere, then the corresponding 1,3-diarylpropynone **1** (0.3 mmol) was added and refluxing was continued until full completion (monitored by TLC). The solvent was evaporated under reduced pressure; the residue was portioned between DCM and water. The organic layer was separated, then washed with water, dried with sodium sulfate and concentrated under reduced pressure. The resulting solid material was purified by crystallization or column chromatography.

2.2.2.1. 2-(3,5-diphenylthiophen-2-yl)-1H-benzo[d]imidazole (3aa).

Yellowish powder, m.p. 210–215 °C (*i*PrOH). Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.89 (1H, s), 7.79 (1H, d, J = 7.8 Hz), 7.69 (2H, d, J = 7.3 Hz), 7.62–7.49 (5H, m), 7.43 (2H, t, J = 7.5 Hz), 7.39–7.31 (2H, m), 7.29–7.23 (1H, m), 7.20 (2H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.0, 143.1, 141.8, 136.0, 133.4, 129.4, 129.1, 129.0, 128.8, 128.4, 126.6, 125.8, 123.3, 122.6, 119.5, 110.5 ppm. HRMS (ESI) calcd. for $C_{23}H_{17}N_2S$ (MH^+): 353.1106; found 353.1109.

2.2.2.2. 5-Chloro-2-(3,5-diphenylthiophen-2-yl)-1H-benzo[d]imidazole (3ab).

Yellowish powder, m.p. 205–209 °C (*i*PrOH). Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.29 (1H, s), 7.82 (2H, d, J = 7.3 Hz), 7.78 (1H, s), 7.73–7.35 (10H, m), 7.22 (1H, d, J = 8.1 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.7, 145.3, 142.8, 135.2, 133.3, 129.8, 129.2, 129.1, 129.0, 128.7, 128.5, 127.5, 126.9, 126.0, 123.1, 120.5, 118.4, 113.5 ppm. HRMS (ESI) calcd. for $C_{23}H_{16}ClN_2S$ (MH^+): 387.0717; found 387.0719.

2.2.2.3. 5,6-Dichloro-2-(3,5-diphenylthiophen-2-yl)-1H-benzo[d]imidazole (3ac).

Yellowish powder, m.p. 232–233 °C (*i*PrOH). Yield: 60%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.32 (1H, br. s), 7.89–7.68 (5H, m), 7.56–7.31 (8H, m) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 148.9, 145.7, 143.2, 139.5, 135.1, 133.2, 129.8, 129.2, 129.1, 129.1, 128.6, 127.6, 126.1, 125.6, 125.1, 116.8 ppm. HRMS (ESI) calcd. for $C_{23}H_{15}Cl_2N_2S$ (MH^+): 421.0328; found 421.0332.

2.2.2.4. 4-(3,5-diphenylthiophen-2-yl)pyridine (3ad).

Yellowish plates, m.p. 107–110 °C (EtOH). Yield: 67%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.50 (2H, d, J = 5.0 Hz), 7.79–7.75 (2H, m), 7.70 (1H, s), 7.47 (2H, t, J = 7.6 Hz), 7.43–7.34 (6H, m), 7.22 (2H, dd, J = 4.6, 1.5 Hz) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 150.5, 144.2, 141.7, 141.4, 135.8, 134.0, 133.3, 129.7, 129.3, 129.2, 128.8, 128.3, 128.0, 125.9, 123.2 ppm. HRMS (ESI) calcd. for $C_{21}H_{16}NS$ (MH^+): 314.0998; found 314.0998.

2.2.2.5. 2-(3,5-bis(4-methoxyphenyl)thiophen-2-yl)-1H-benzo[d]imidazole (3ba).

Yellow crystals, m.p. 255–258 °C (EtOH). Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.18 (1H, br. s), 7.56 (2H, d, J = 8.0 Hz), 7.50–7.42 (4H, m), 7.20–7.13 (3H, m), 6.99 (2H, d, J = 8.0 Hz), 6.91 (2H, d, J = 4.8 Hz), 3.85 (3H, s), 3.83 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.8, 146.8, 145.9, 141.8, 130.1, 128.1, 127.1, 126.2, 125.6, 122.8, 114.7, 114.4, 55.3 ppm. HRMS (ESI) calcd. for $C_{25}H_{21}N_2O_2S$ (MH^+): 413.1318; found 413.1322.

2.2.2.6. 2-(3,5-bis(4-methoxyphenyl)thiophen-2-yl)-5-chloro-1H-benzo[d]imidazole (3bb).

Yellow powder, m.p. 235–237 °C (EtOH). Yield: 58%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.03 (1H, br. s), 7.72 (2H, d, J = 8.6 Hz), 7.60–7.53 (2H, m), 7.50 (1H, d, J = 8.3 Hz), 7.41 (2H, d, J = 8.6 Hz), 7.19 (1H, dd, J = 8.5, 1.6 Hz), 7.03 (2H, d, J = 8.7 Hz), 6.98 (2H, d, J = 8.6 Hz), 3.81 (3H, s), 3.79 (3H, s) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 160.0, 159.6, 148.1, 145.2, 142.5, 130.3, 127.7, 127.7, 127.4, 127.4, 126.8, 126.3, 126.0, 124.1, 124.1, 122.7, 122.7, 115.1, 114.6, 55.8, 55.6 ppm. HRMS (ESI) calcd. for $C_{25}H_{20}ClN_2O_2S$ (MH^+): 447.0928; found 447.0934.

2.2.2.7. 2-(3,5-bis(4-methoxyphenyl)thiophen-2-yl)-5,6-dichloro-1H-benzo[d]imidazole (3bc).

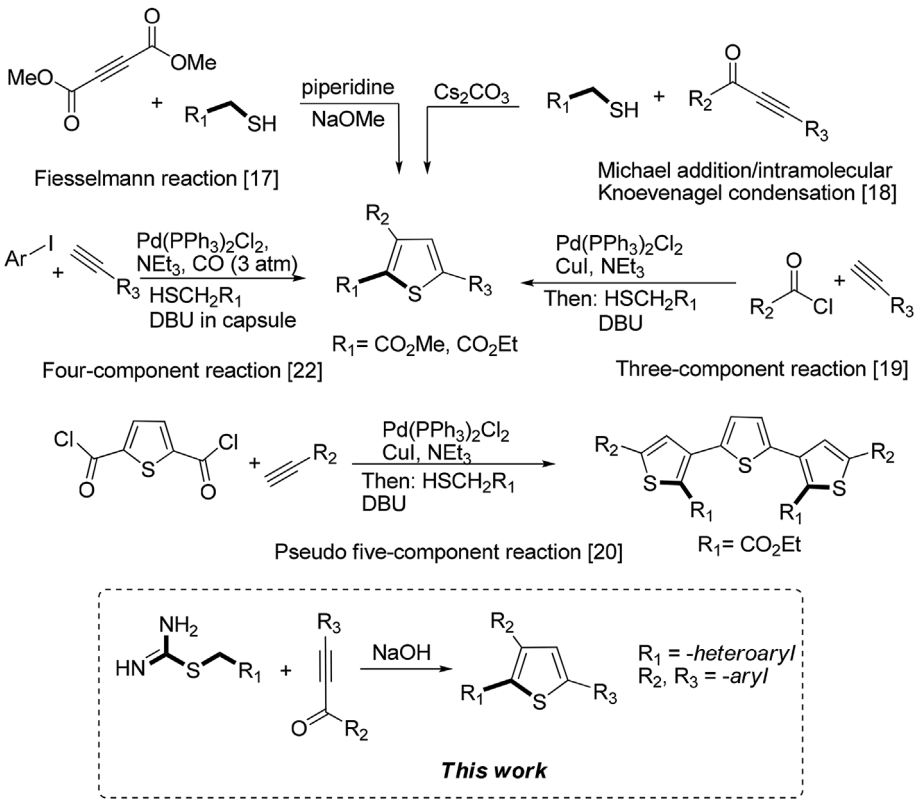
Yellow crystals, m.p. 122–127 °C (R_f = 0.3, PE:EA = 4:1). Yield 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (1H, br. s), 7.79 (1H, s), 7.59 (2H, d, J = 8.4 Hz), 7.43 (2H, d, J = 8.8 Hz), 7.31 (1H, s), 7.14 (1H, s), 7.05 (2H, d, J = 8.4 Hz), 6.94 (2H, d, J = 8.8 Hz), 3.90 (3H, s), 3.85 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.1, 160.0, 148.9, 146.8, 142.7, 132.7, 130.1, 127.8, 127.2, 126.0, 125.7, 124.6, 120.2, 114.9, 114.5, 111.8, 55.4 ppm. HRMS (ESI) calcd. for $C_{25}H_{19}Cl_2N_2O_2S$ (MH^+): 481.0539; found 481.0545.

2.2.2.8. 4-(3,5-bis(4-methoxyphenyl)thiophen-2-yl)pyridine (3bd).

Yellow crystals, m.p. 120–125 °C (R_f = 0.5, Tol:EA = 1:1). Yield: 89% ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (2H, br. s), 7.57 (2H, d, J = 8.0 Hz), 7.24–7.22 (2H, m), 7.20–7.17 (3H, m), 6.94 (2H, d, J = 8.0 Hz), 6.89 (2H, d, J = 8.0 Hz), 3.84 (6H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.8, 159.2, 149.9, 144.5, 142.3, 141.3, 137.9, 132.5, 132.5, 130.1, 128.5, 127.1, 126.4, 114.5, 114.2, 55.4, 55.3 ppm. HRMS (ESI) calcd. for $C_{23}H_{19}NO_2S$ (MH^+): 374.1209; found 374.1212.

2.2.2.9. 2-(3,5-bis(4-methoxyphenyl)thiophen-2-yl)-1-methyl-1H-imidazole (3be).

Brown oil (R_f = 0.6, Tol:EA = 1:1). Yield: 30%. ^{1}H



Scheme 1. Fiesselmann reaction.

NMR (400 MHz, $CDCl_3$) δ: 7.55 (2H, d, J = 8.0 Hz), 7.38 (1H, s), 7.16–7.15 (2H, m), 7.14 (1H, s), 6.91 (2H, d, J = 8.0 Hz), 6.84–6.83 (2H, m), 6.81 (1H, s), 3.81 (3H, s), 3.77 (3H, s), 3.00 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6, 159.0, 145.4, 142.2, 141.5, 129.0, 128.9, 128.6, 127.1, 126.6, 123.4, 123.1, 121.7, 114.4, 114.2, 55.4, 55.2, 33.3 ppm. HRMS (ESI) calcd. for $C_{22}H_{21}N_2O_2S$ (MH^+): 377.1318; found 377.1312.

2.2.2.10. 2-(5-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)thiophen-2-yl)-1H-benzo[d]imidazole ***(3ca)***. Yellow crystals, m.p. 260–270 °C (R_f = 0.4, PE:EA = 3:1). Yield: 42%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.62 (1H, s), 7.82–7.67 (7H, m), 7.65–7.59 (1H, m), 7.44–7.36 (1H, m), 7.26–7.14 (2H, m), 7.05 (2H, d, J = 8.7 Hz), 3.81 (3H, s) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 160.1, 145.9, 145.4, 143.9, 140.6, 139.6, 135.3, 129.9, 128.5 ($^2J_{C\text{-}F}$ = 31.3 Hz), 127.5, 126.9, 126.2, 126.0 ($^3J_{C\text{-}F}$ = 3.7 Hz), 125.8, 124.8 ($^1J_{C\text{-}F}$ = 270.0 Hz), 123.3, 122.3, 119.2, 115.2, 112.1, 55.8 ppm. HRMS (ESI) calcd. for $C_{25}H_{18}F_3N_2OS$ (MH^+): 451.1086; found 451.1091.

2.2.2.11. 5-Chloro-2-(5-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl) thiophen-2-yl)-1H-benzo[d]imidazole ***(3 cb)***. Yellow crystals, m.p. 200–205 °C (R_f = 0.2, $CHCl_3$:MeCN = 98:2). Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.03 (1H, br. s), 7.72 (2H, d, J = 8.0 Hz), 7.69 (1H, s), 7.61 (2H, d, J = 8.0 Hz), 7.55 (2H, d, J = 8.4 Hz), 7.26–7.15 (3H, m), 7.16 (1H, s), 6.92 (2H, d, J = 8.0 Hz), 3.84 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.1, 147.1, 140.6, 139.4, 139.4, 130.6 ($^2J_{C\text{-}F}$ = 32.6 Hz), 130.6, 129.3, 127.2, 126.2 ($^3J_{C\text{-}F}$ = 3.5 Hz), 125.9, 125.7, 125.2, 125.1, 123.8 ($^1J_{C\text{-}F}$ = 270.6 Hz), 114.6, 113.7, 55.4 ppm. HRMS (ESI) calcd. for $C_{25}H_{17}ClF_3N_2OS$ (MH^+): 485.0697; found 485.0701.

2.2.2.12. 5,6-Dichloro-2-(5-(4-methoxyphenyl)-3-(4-(trifluoromethyl) phenyl)thiophen-2-yl)-1H-benzo[d]imidazole ***(3 cc)***. Yellow crystals, m.p. 227–231 °C (R_f = 0.3, $CHCl_3$:MeCN = 98:2). Yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.13 (1H, br. s), 7.76 (1H, s), 7.72 (2H, d, J = 8.0 Hz), 7.60 (2H, d, J = 8.0 Hz), 7.54 (2H, d, J = 8.8 Hz), 7.34 (1H, s), 7.16 (1H, s), 6.92 (2H, d, J = 8.8 Hz), 3.84 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 148.0, 147.6, 142.6, 141.0, 139.3, 130.9 ($^2J_{C\text{-}F}$ = 32.6 Hz), 130.7, 129.3, 127.2, 126.3 ($^3J_{C\text{-}F}$ = 3.5 Hz), 125.5, 125.4, 125.2, 123.8 ($^1J_{C\text{-}F}$ = 270.9 Hz), 114.6, 112.0, 55.4 ppm. HRMS (ESI) calcd. for $C_{25}H_{16}Cl_2F_3N_2OS$ (MH^+): 519.0307; found 519.0315.

2.2.2.13. 4-(5-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)thiophen-2-yl)pyridine ***(3cd)***. Amber oil (R_f = 0.3, PE:EA = 2:1). Yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (2H, d, J = 6.0 Hz), 7.52 (2H, d, J = 8.4 Hz), 7.55 (2H, d, J = 8.8 Hz), 7.41 (2H, d, J = 8.0 Hz), 7.22 (1H, s), 7.14 (2H, d, J = 6.0 Hz), 6.93 (2H, d, J = 8.8 Hz), 3.82 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.0, 149.9, 145.4, 141.7, 139.7, 139.7, 134.1, 129.7 ($^2J_{C\text{-}F}$ = 32.3 Hz), 129.3, 127.1, 125.9, 125.7 ($^3J_{C\text{-}F}$ = 3.7 Hz), 125.6, 124.1 ($^1J_{C\text{-}F}$ = 270.5 Hz), 123.0, 114.5, 55.4 ppm. HRMS (ESI) calcd. for $C_{23}H_{17}F_3NOS$ (MH^+): 412.0977; found 412.0981.

2.2.2.14. 2-(3-(4-methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)thiophen-2-yl)-1H-benzo[d]imidazole ***(3da)***. Yellow crystals, m.p. 120–125 °C (R_f = 0.4, PE:EA = 3:1). Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.49 (1H, br. s), 7.64 (2H, d, J = 8.0 Hz); 7.56 (2H, d, J = 8.0 Hz), 7.48 (2H, br. s), 7.36 (2H, d, J = 8.4 Hz), 7.27 (1H, s), 7.23–7.20 (2H, m), 6.91 (2H, d, J = 8.8 Hz), 3.79 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.2, 143.8, 142.0, 136.7, 130.0 ($^2J_{C\text{-}F}$ = 32.6 Hz), 130.0, 127.8, 127.7, 127.5, 126.0 ($^3J_{C\text{-}F}$ = 3.6 Hz), 125.8, 124.0 ($^1J_{C\text{-}F}$ = 270.4 Hz), 123.1, 114.7, 55.3 ppm. HRMS (ESI) calcd. for $C_{25}H_{18}F_3N_2OS$ (MH^+): 451.1086; found 451.1090.

2.2.2.15. 4-(3-(4-methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)thiophen-2-yl)pyridine ***(3dd)***. Yellow crystals, m.p. 120–125°C (R_f = 0.3, Tol:EA = 2:1). Yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (2H, d,

J = 6.0 Hz), 7.74 (2H, d, J = 8.4 Hz), 7.66 (2H, d, J = 8.4 Hz), 7.41 (1H, s), 7.24 (2H, d, J = 8.8 Hz), 7.22 (2H, d, J = 6.0 Hz), 6.90 (2H, d, J = 8.8 Hz), 3.84 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 149.9, 142.4, 141.9, 141.5, 137.0, 134.9, 130.1, 129.9 ($^2J_{C-F}$ = 32.5 Hz), 128.4, 127.9, 126.1 ($^3J_{C-F}$ = 3.7 Hz), 125.8, 124.0 ($^1J_{C-F}$ = 270.1 Hz), 114.3, 55.3 ppm. HRMS (ESI) calcd. for $C_{23}H_{17}F_3NOS$ (MH^+): 412.0977; found 412.0981.

2.2.2.16. 2-(3,5-bis(4-(trifluoromethyl)phenyl)thiophen-2-yl)-1H-benzo[d]imidazole ***(3ea)***. Yellow crystals, m.p. 130–135 °C (R_f = 0.5, PE:EA = 4:1). Yield: 44%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.17 (1H, br. s), 7.53–7.49 (5H, m), 7.47–7.42 (5H, m), 7.26–7.21 (3H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.3, 144.4, 140.6, 138.6, 136.0, 130.2 ($^2J_{C-F}$ = 33.0 Hz), 130.4 ($^2J_{C-F}$ = 33.0 Hz), 128.9, 128.5, 128.3, 127.9, 127.1, 126.0 ($^3J_{C-F}$ = 3.7 Hz), 125.9 ($^3J_{C-F}$ = 3.7 Hz), 125.6, 123.8 ($^1J_{C-F}$ = 270.0 Hz), 123.7 ($^1J_{C-F}$ = 271.0 Hz), 123.5 ppm. HRMS (ESI) calcd. for $C_{25}H_{15}F_6N_2S$ (MH^+): 489.0855; found 489.0859.

2.2.2.17. 4-(3,5-bis(4-(trifluoromethyl)phenyl)thiophen-2-yl)pyridine ***(3ed)***. Yellow crystals, m.p. 115–130 °C (R_f = 0.4, Tol:EA = 2:1). Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (2H, d, J = 8.0 Hz), 7.75 (2H, d, J = 8.0 Hz), 7.68 (2H, d, J = 8.0 Hz), 7.63 (2H, d, J = 8.0 Hz), 7.44 (2H, d, J = 8.0 Hz), 7.44 (1H, s), 7.19 (2H, d, J = 8.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.1, 143.2, 141.1, 139.9, 139.1, 136.7, 136.6, 130.2 ($^2J_{C-F}$ = 33.0 Hz), 130.0 ($^2J_{C-F}$ = 32.0 Hz), 129.3, 127.8, 126.2 ($^3J_{C-F}$ = 3.7 Hz), 125.9, 125.8 ($^3J_{C-F}$ = 3.7 Hz), 124.0 ($^1J_{C-F}$ = 271.0 Hz), 124.0 ($^1J_{C-F}$ = 270.0 Hz), 123.1 ppm. HRMS (ESI) calcd. for $C_{23}H_{14}F_6NS$ (MH^+): 450.0746; found 450.0751.

2.2.2.18. 2-(3,5-bis(4-(pentyloxy)phenyl)thiophen-2-yl)-1H-benzo[d]imidazole ***(3fa)***. White powder, m.p. 95–100 °C (*i*PrOH). Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (1H, br. s), 7.58 (2H, d, J = 8.6 Hz), 7.45 (2H, d, J = 8.5 Hz), 7.29 (1H, s), 7.26–7.12 (3H, m), 7.15 (1H, s), 7.02 (2H, d, J = 8.6 Hz), 6.93 (2H, d, J = 8.7 Hz), 4.08–3.95 (4H, m), 1.90–1.78 (4H, m), 1.56–1.36 (8H, m), 1.04–0.91 (6H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.5, 159.4, 147.0, 145.9, 143.2, 141.8, 133.5, 130.1, 128.0, 127.1, 126.1, 125.6, 125.6, 123.0, 122.4, 119.3, 115.3, 115.0, 110.4, 68.2, 68.1, 29.0, 28.9, 28.2, 28.2, 22.5, 22.4, 14.0, 14.0 ppm. HRMS (ESI) calcd. for $C_{33}H_{37}N_2O_2S$ (MH^+): 379.2268; found 379.2270.

2.2.2.19. (2R,3S) or (2S,3R)-2-(1H-benzo[d]imidazol-2-yl)-5-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)-2,3-dihydrothiophen-3-ol ***(4ca)***. Brown oil (R_f = 0.2, PE:EA = 4:1). Yield: 10%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62–7.60 (4H, m), 7.55–7.52 (2H, m), 7.49–7.44 (4H, m), 6.84 (2H, d, J = 8.0 Hz), 6.02 (1H, s), 5.46 (1H, s), 3.79 (3H, s) ppm.

2.2.2.20. (2R,3S) or (2S,3R)-2-(1H-benzo[d]imidazol-2-yl)-3,5-bis(4-(trifluoromethyl)phenyl)-2,3-dihydrothiophen-3-ol (4ea). Brown oil (R_f = 0.3, PE:EA = 4:1). Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64–7.58 (8H, m), 7.54–7.25 (4H, m), 6.23 (1H, s), 5.47 (1H, s) ppm.

2.2.2.21. (2R,3S) or (2S,3R)-5-(4-methoxyphenyl)-2-(1-methyl-1H-imidazol-2-yl)-3-(4-(trifluoromethyl)phenyl)-2,3-dihydrothiophen-3-ol ***(4ce)***. Brown oil (R_f = 0.4, Tol:EA = 4:1). Yield: 38%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (2H, d, J = 8.4 Hz), 7.57 (2H, d, J = 8.0 Hz), 7.50 (2H, d, J = 8.8 Hz), 7.03 (1H, s), 6.89 (2H, d, J = 8.8 Hz), 6.82 (1H, s), 6.10 (1H, s), 5.08 (1H, s), 3.83 (3H, s), 3.42 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.4, 142.7, 141.7 ($^1J_{C-F}$ = 265.0 Hz), 137.8, 129.7 ($^2J_{C-F}$ = 32.0 Hz), 128.8, 128.1, 127.2, 126.3, 125.1 ($^3J_{C-F}$ = 4.0 Hz), 123.1, 122.0, 113.9, 88.7, 55.4, 55.3, 52.4, 32.5 ppm.

2.2.2.22. (2R,3S) or (2S,3R)-3-(4-methoxyphenyl)-2-(1-methyl-1H-imidazol-2-yl)-5-(4-(trifluoromethyl)phenyl)-2,3-dihydrothiophen-3-ol ***(4de)***. Brown oil (R_f = 0.45, Tol:EA = 2:1). Yield: 44%.^{1}H NMR (400 Hz, DMSO-d_6) δ: 7.82 (2H, d, J = 8.4 Hz), 7.79 (2H, d, J = 8.8 Hz), 7.44 (2H, d, J = 8.8 Hz), 7.16 (1H, s), 6.93 (1H, s), 6.90 (2H, d, J = 8.4 Hz), 6.53 (1H, s), 5.42 (1H, s), 3.75 (3H, s), 3.46 (3H, s) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 159.0, 142.7, 138.9 ($^1J_{C-F}$ = 271.9 Hz), 137.3, 129.4 ($^2J_{C-F}$ = 31.8 Hz), 128.3, 127.5, 127.3, 126.7, 126.1 ($^3J_{C-F}$ = 3.6 Hz), 123.4, 123.1, 113.8, 88.4, 55.5, 55.5, 53.5, 33.0 ppm.

2.2.2.23. (2R,3S) or (2S,3R)-2-(1-methyl-1H-imidazol-2-yl)-3,5-bis(4-(trifluoromethyl)phenyl)-2,3-dihydrothiophen-3-ol ***(4ee)***. Brown oil (R_f = 0.3, Tol:EA = 4:1). Yield 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (2H, d, J = 8.0 Hz), 7.72–7.65 (6H, m), 7.62 (2H, d, J = 8.0 Hz), 7.07 (1H, s), 6.86 (1H, s), 6.33 (1H, s), 5.15 (1H, s), 3.47 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.3, 139.9 ($^1J_{C-F}$ = 266.0 Hz), 139.8 ($^1J_{C-F}$ = 272.0 Hz), 137.9, 136.5, 131.0 ($^2J_{C-F}$ = 32.0 Hz), 130.0 ($^2J_{C-F}$ = 32.0 Hz), 129.6, 129.0, 127.4, 127.0, 126.2, 125.6 ($^3J_{C-F}$ = 3.7 Hz), 125.2 ($^3J_{C-F}$ = 3.7 Hz), 121.6, 88.6, 52.4, 32.5 ppm.

2.2.3. Conversion of compound 4de to compound 3de

Compound **4de** (40 mg, 0.093 mmol) was refluxed in 5 ml of EtOH in the presence of 2 drops of concentrated H_2SO_4. Reaction was monitored by TLC. After the completion of reaction, solvent was evaporated under reduced pressure, the residue was treated with DCM and water. Organic layer was collected, dried with Na_2SO_4 giving 25 mg of crude oil 2-(3-(4-methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)thiophen-2-yl)-1-methyl-*1H*-imidazole **3de**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (2H, d, J = 8.0 Hz), 7.68 (2H, d, J = 8.0 Hz), 7.50 (1H, s), 7.37 (1H, d, J = 1.2 Hz), 7.17 (2H, d, J = 8.0 Hz), 6.99 (1H, d, J = 1.2 Hz), 6.89 (2H, d, J = 8.0 Hz), 3.83 (3H, s), 3.11 (3H, s) ppm.

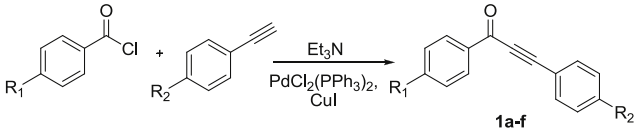
3. Results and discussion

3.1. Synthesis

The diarylalkynones **1a–f** were prepared by Sonogashira coupling reaction of commercially available aroyl chlorides with aryl alkynes [21]. The cross-coupling reaction proceeded in good to high yields with substrates containing both electron-donating and electron withdrawing substituents (Table 1). Next, the construction of thiophene ring *via* Fiesselmann-type reaction [11] between alkynones and easily available heteroarylmethanethiols was attempted.

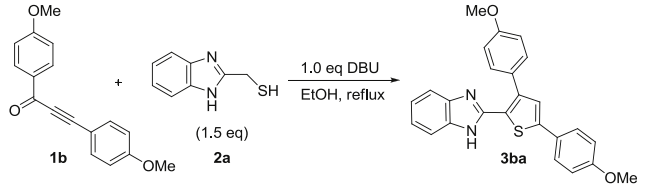
First, we performed a short screening of solvents and bases for the Fiesselmann cyclization. Although DBU is routinely used as a base in the cyclization, in our hands the reaction between alkynone **1b** and thiol **2a** in refluxing ethanol in the presence of 1 equiv. of DBU gave only 19% of the desired thiophene **3ba** (Table 2, entry 1). The yield of **3ba** was increased up to 37% and 51% when excess of thiol **2a** (3 and 6

Table 1
The synthesis of alkynones **1.**



Entry	R_1	R_2	Product (yield, %)
1	H	H	**1a** (98)
2	OMe	OMe	**1b** (78)
3	CF_3	OMe	**1c** (80)
4	OMe	CF_3	**1d** (62)
5	CF_3	CF_3	**1e** (60)
6	OC_5H_{11}	OC_5H_{11}	**1f** (71)

Table 2
Optimization of the Fiesselmann reaction conditions.



#	Deviation from initial conditions	Yield, %
1	None[a]	19
2	3 eq of **2a**	37
3	6 eq of **2a**	51
4	THF instead of EtOH	63
5	DMF instead of EtOH	54
6	NaOH instead of DBU	92

[a] Initial reaction conditions: 1.0 equiv. DBU, 1.0 equiv. **1b**, 1.5 equiv. **2a**, EtOH, reflux.

equiv, respectively) was used (Table 2, entries 2–3). However the isolation and purification of the product became challenging. Change of the solvent to THF or DMF did not improve the conversion (Table 2, entries 4–5). After extensive screening of various bases and solvents we were pleased to find that the yield of thiophene **3ba** can be increased to 92% by the use of sodium or potassium hydroxide in ethanol (Table 2, entry 6).

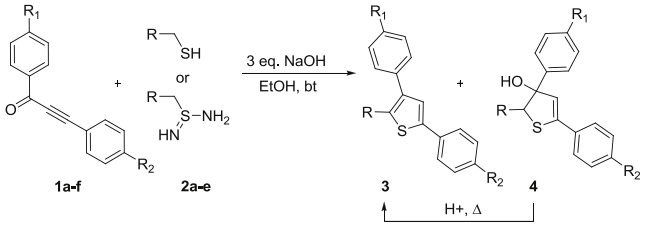
With optimized reaction conditions in hand, we elaborated on the scope of alkynones and thiols (Table 3, entries 1–9). Yields of thiophenes **3** depended on the electronic nature of both alkynones and thiols. The highest yield (92%) was observed for the most electron rich methoxy-substituted alkynone **1b** (Table 3, entry 2). In contrast, the lowest yields (42–44%) were observed for the electron deficient alkynones **1c,e** bearing trifluoromethyl substituents (Table 3, entries 3, 5). Similar relationship between electronic effects and yields of thiophenes was observed for thiols, with the more electron deficient thiol **2b** providing lower yields than **2a** (Table 3, entries 1–2 *vs* entries 7–8).

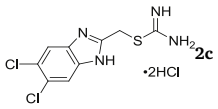
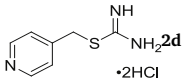
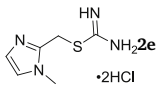
In the meantime, the use of thiols in the Fiesselmann thiophene synthesis is compromised by their inherent toxicity and propensity to oxidize to disulfide side-products that decreases yields of the desired thiophenes and complicates their purification. We were pleased to find that the more stable, easy-to-handle and readily available (see Experimental Section 2.2.1) carbamimidothioates **2c-e** can be used as an alternative to thiols in the Fiesselmann-type cyclization (Table 3, entries 10–19) affording the desired thiophenes in low to high yields. Interestingly, the reactions between alkynones **1c**,**e** and thiol **2a** (Table 3, entries 3 and 5) furnished intermediates **4ca** and **4ea** as major products. In addition, the methylimidazole (**2e**) ring–bearing starting material exclusively provided dihydrothiophen-3-ols **4ce–ee** instead of the desired thiophenes **3ce–ee** even after prolonged heating (Table 3, entries 20–22). Gratifyingly, all of the intermediates **4** can be dehydrated into the corresponding thiophenes **3** by the heating of acidified solutions (see example in Experimental Section 2.2.3). Slow dehydration process was also observed in DMSO solution after several weeks.

3.2. Photophysical properties

Photophysical properties of thiophenes **3** (Table 4) were studied in MeCN solution at *ca.* 10^{-6} M concentration. UV/Vis Absorption and emission spectra were measured under ambient atmosphere and at room temperature (for attenuation coefficients see SI page SI56). PLQY were measured using an integrating sphere. To evaluate the electronic effects on the emission in both solution and solid state, thiophene **3aa** (Table 4, entry 1) was chosen as a benchmark compound. The presence of EDG in both positions 3 and 5 resulted in a decrease in the solution

Table 3
The Fiesselmann type reaction between alkynones **1** and thiols or thioates **2**.4



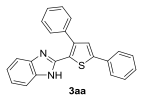
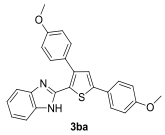
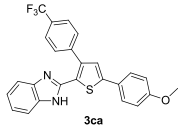
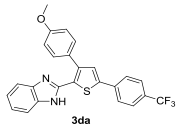
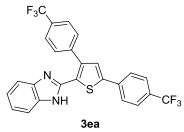
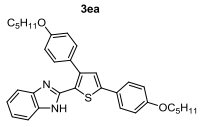
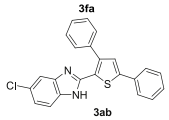
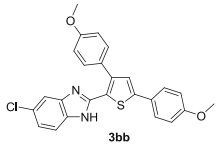
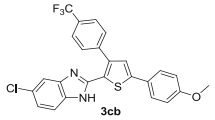
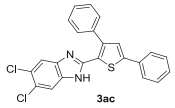
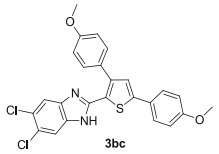
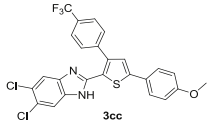
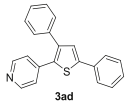
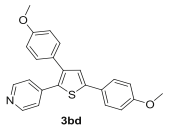
Entry	Starting material	RCH_2SX	Product (Yield, %)
1	**1a** (R_1 = R_2 = H)		**3aa** (62)
2	**1b** (R_1 = R_2 = OCH_3)		**3ba** (92)
3	**1c** (R_1 = CF_3, R_2 = -OCH_3)		**3ca** (42), **4ca** (10)
4	**1d** (R_1 = OCH_3, R_2 = CF_3)		**3da** (64)
5	**1e** (R_1 = R_2 = CF_3)		**3ea** (44), **4ea** (50)
6	**1f** (R_1 = R_2 = OC_5H_{11})		**3fa** (72)
7	**1a**		**3 ab** (55)
8	**1b**		**3bb** (58)
9	**1c**		**3 cb** (64)
10	**1a**		**3ac** (60)
11	**1b**		**3bc** (74)
12	**1c**		**3cc** (62)
13	**1a**		**3ad** (67)
14	**1b**		**3bd** (89)
15	**1c**		**3cd** (51)
16	**1d**		**3dd** (67)
17	**1e**		**3ed** (50)
18	**1a**		**3ae** (13), **4ae** (17)[a]
19	**1b**		**3be** (30)
20	**1c**		**4ce** (38)
21	**1d**		**4de** (44)
22	**1e**		**4ee** (41)

[a] Inseparable mixture, yields calculated *via* ^{1}H NMR integration.

PLQY, but a substantial increase in the solid state PLQY (Table 4, entry 2). However, the introduction of EWG in the position 3 and EDG in the position 5 resulted in a considerable increase of PLQY in the solution (Table 4, entry 3) and in the solid state PLQY. Mutual exchange of the EWG and EDG substituents resulted in a decrease in both the solution and the solid state PLQY (Table 4, entry 4). If both aryl moieties in positions 3 and 5 possess EWGs substituents, the solution PLQY is increased, but the solid state PLQY is lowered (Table 4, entry 5). Introduction of OC_5H_{11} groups in the positions 3 and 5 of aryl moieties (Table 4, entry 6) gave similar results as compared to the unsubstituted Ph groups. Thus, we can conclude that the introduction of EWG-substituted arenes in position 3 and EDG-substituted aromatic moieties in position 5 of the thiophene ring results in higher PLQY in thiophenes **3**.

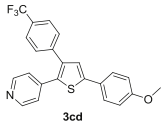
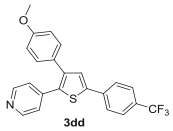
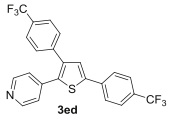
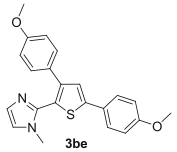
Next, the electronic properties of the benzimidazole core were altered by introducing chloro substituents (Table 4, entries 7–12). The PLQY increased when relatively electron deficient chloro-benzimidazoles **3 ab–cb** and **3ac–cc** were present in the molecule. The highest PLQY in solution (82.6%) and solid state (30.9%) was observed for **3 cc** with the most electron deficient benzimidazole core in a series. We also wanted to see whether the attachment of heterocycles other than benzimidazole to the position 2 of thiophene would affect the PLQY. Thus, the pyridine and *N*-methylimidazole was introduced in the position 2 (Table 4, entries 13–18). A sharp decrease of PLQY was observed for luminophores bearing pyridine and *N*-methylimidazole substituent, highlighting the importance of the benzimidazole subunit. However, **3cd** (Table 4, entry 15) still possessed relatively high (33.9%) PLQY in solution, possibly owing to the proper choice of EWG in the position 3

Table 4
Photophysical properties of thiophenes **3**.

Entry	Compound	λ max (abs), nm[a]	λ max (em), nm[b]	Stokes shifts (nm)	QY, % (solution)	QY, % (solid)
1	 **3aa**	237, 266, **347**	433 sn; 456 sd	86	38.9	8.5
2	 **3ba**	235, 278, **356**	445 sn; 467 sd	89	28.0	17.0
3	 **3ca**	234, 274, **358**	454 sn; 459 sd	96	77.5	22.0
4	 **3da**	238, 280, **354**	444 sn; 457 sd	90	28.6	4.5
5	 **3ea**	238, 272, **352**	442 sn; 512 sd	90	53.5	2.1
6	 **3fa**	234, 280, **356**	441 sn; 464 sd	85	33.8	1.8
7	 **3ab**	235, 266, **350**	435 sn; 459 sd	85	45.0	17.5
8	 **3bb**	234, 280, **360**	445 sn; 463 sd	85	42.5	11.6
9	 **3cb**	235, 274, **360**	460sn; 467 sd	100	77.4	30.6
10	 **3ac**	232, 268, **355**	434 sn; 475 sd	79	63.1	52.2
11	 **3bc**	234, 280, **368**	467 sn; 465 sd	99	34.6	15.1
12	 **3cc**	236, 275, **365**	462sn; 478 sd	97	82.6	30.9
13	 **3ad**	265, **329**	416 sn; 414 sd	87	2.1	2.0
14	 **3bd**	252, 280, **340**	440 sn; 538 sd	100	4.0	0.9

(*continued on next page*)

Table 4 (*continued*)

Entry	Compound	λ max (abs), nm[a]	λ max (em), nm[b]	Stokes shifts (nm)	QY, % (solution)	QY, % (solid)
15	 3cd	236, 270, **340**	460 sn; 550 sd	120	33.9	11.9
16	 3dd	242, 284, **332**	436 sn; 436, 525 sd	104	1.9	8.4
17	 3ed	240, 268, **326**	406 sn; 446 sd	80	2.0	6.1
18	 3be	236, 272, **318**	420	102	1.4	NA

[a] Absorption bands in bold correspond to the excitation wavelength.
[b] Emission spectra written in solution, otherwise indicated as Sn-in solution or Sd-in solid state.

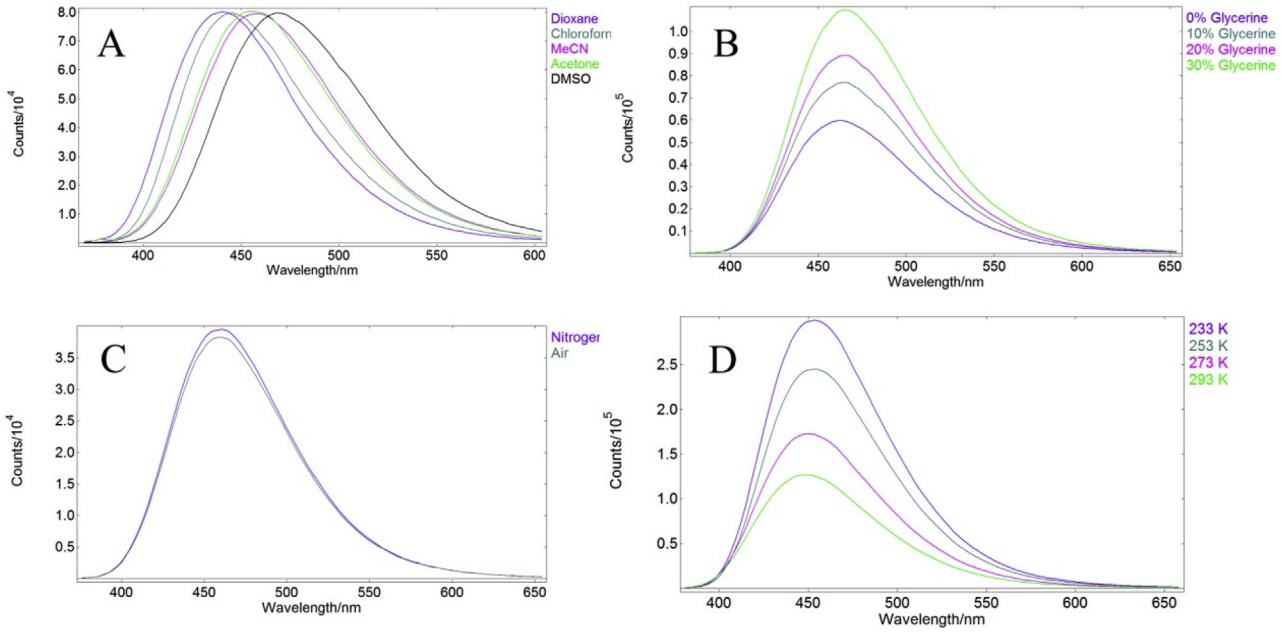


Fig. 2. Solvatochromism (A), viscosity (B), oxygen quenching (C) and variable temperature experiments (D) for **3cd**.

and EDG in the position 5 of the thiophene core. Additionally, aggregation induced emission enhancement (AIEE) was also observed for **3dd** and **3ed**.

The benzimidazole ring-containing compounds showed three characteristic absorption bands at 232–238 (band 1); 266–280 (band 2) and 347–368 (band 3) nm respectively (Table 4, entries 1–12). However, only one broad emission band with maxima at 433–467 nm was observed in MeCN solutions for these compounds. The presence of electron-donating substituent in the 5-aryl ring resulted in bathochromic shift of absorption bands 2 and 3 as well as of the emission peak maxima. This becomes clear by comparing **3ac** (Table 4, entry 10) and **3bc** (Table 4, entry 11), where introduction of electron-donating substituents results in the shift of absorption band 2 from 268 to 280 nm, and the shift of absorption band 3 from 355 to 368 nm. In addition, emission maxima were also shifted from 434 to 467 nm, when going from **3ac** to **3bc**. Similar bathochromic shifts were observed for 2-pyridinyl thiophenes bearing electron-rich 4-methoxyphenyl substituent in various positions of the thiophene subunit (Table 4, entries 14–16). Stokes shifts for all materials were in the range of 79–120 nm (see Table 4).

All thiophenes in MeCN solution feature broad emission peaks without any distinctive bands (Table 4). The broad nature of emission peaks is indicative of twisted intramolecular charge transfer (TICT) phenomenon [24]. To verify whether TICT is responsible for the observed emission, a solvatochromism study was conducted because sensitivity of TICT towards solvent effects is well-known [24,25]. Thiophene **3cd** was used in the solvatochromism study due to higher solubility and relatively high intensity of the emission (33.9% PLQY,

entry 15, Table 4). The emission maxima for **3cd** featured a shift from 440 nm in dioxane to 468 nm in DMSO (Fig. 2A), thus providing an evidence for the TICT. TICT states are also highly susceptible to viscosity of a solvent: enhanced emission is generally observed in solvents with higher viscosity [26]. Accordingly, the emission intensity of **3cd** was measured in various EtOH/glycerine mixtures (Fig. 2B). The observed correlation between the emission intensity and the viscosity of the solvent provided further support of TICT.

To verify the presence of triplet states in thiophene luminophores the intensity of **3cd** was measured in aerated and nitrogen-purged solutions. The observed similar emission intensity in both solutions (Fig. 2C) indicated that the triplet states, which would be quenched by oxygen, do not participate in the emission [27]. Furthermore, the emission intensity of **3cd** increased when temperature was lowered from 293 to 233 K (Fig. 2D). Both experiments provide evidence that singlet states are responsible for the emission and that these materials do not possess thermally activated delayed fluorescence character [28].

4. Conclusions

In summary, we have demonstrated that odorless, stable, easy-to-handle and readily available *S*-alkyl thioureas can be used as sulphur-containing building blocks for the assembly of 2,3,5-trisubstituted thiophene luminophores *via* the Fiesselmann type reaction. We have shown that the introduction of electron deficient arenes in position 3 and electron rich arenes in position 5 of the thiophene core not only results in enhancement of PLQYs to 83% for benzimidazole-containing luminophores, but also enhances PLQY of the less emissive, pyridine-containing thiophenes by more than an order of magnitude. Viscosity, solvatochromism and oxygen quenching experiments provided evidence that the observed emission of thiophenes **3** originates from TICT and singlet emissive states. Finally, we believe that the established correlation between the electronic properties of substituents and efficiency of luminescence will facilitate wider application of monomeric thiophenes in the design of luminophores.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2019.107646.

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