A Straightforward Synthesis to Novel 1,10-Phenanthrolines with Fused Thiophene Structure

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Abstract We report here a straightforward synthesis for a series of new structures with fused 1,10-phenanthroline-thiophene connection. They are synthesized with a modified Hinsberg thiophene procedure, followed by successive modification to yield several 5,7-disubstituted thieno[3,4-f][1,10]phenanthrolines, most notable thiophene-substituted compounds that could be potentially of use for organic electronics applications. For some selected examples, crystal structures were obtained, showing a nearly coplanar arrangement around the fused connection, also beneficial for an effective electron transfer in organic electronics or solar cells.

Key words thiophene, 1,10-phenanthroline, fused thiophene, semiconductor, organic solar cells

Thiophenes are versatile compounds that are used in many different fields and they are gaining much interest during the last years.¹ They are often used in research areas like organic electronics as semiconductors,²,³ organic light-emitting diodes (OLEDs)⁴,⁵ or solar cells⁶ and as bioimaging materials.⁷,⁸ In these applications, the thiophene compounds are mostly based on π-conjugated polymer structures. Some of these polymers contain fused thiophene rings or organic structures that are fused with the thiophene backbone like 3,4-ethylenedioxythiophene (EDOT).⁹ Through the conjugated structure they possess the ability to transfer electrons within the organic framework. While most fused thiophene structures are based on fusion at the 2,3-position, a novel procedure to generate a fusion of 1,10-phenanthroline at the 5,6-position with a thiophene ring at 3,4-position is presented here.

The structural motif of interest is shown in Scheme 1. It is generally unknown from literature studies, except for a patent by Jung-Sub Lee, describing the fusion of a 2,9-phenanthroline to thiophene.⁹ Their proposed protocol did not yield the desired 5,7-disubstituted thieno[3,4-f][1,10]phenanthrolines. Another structure, which shows the highest similarity with the systems reported here possess a 1,10-phenanthroline with a fused imide ring at the [3,4-f]-position.¹⁰ These pyrrole-containing molecules were synthesized based on a procedure described by Lash or Ono, who used 5-nitro-1,10-phenanthroline, DBU, and different isocyanatoacetates to isolate the fused pyrrole structure.

We therefore chose the well-established Hinsberg thiophene synthesis to prepare compound 1 as precursor for further 5,7-disubstituted thieno[3,4-f][1,10]phenanthrolines. The according reaction scheme is shown in Scheme 1. Following the literature procedure¹¹ that uses NaOt-Bu for the deprotonation of the thiodiacetate and t-BuOH as solvent only 1,10-phenanthroline-5,6-diol was obtained instead of the desired product 1. Consequently, a screening of reaction parameters was carried out to realize the synthesis of 1.¹² The individual reaction components are summarized in Table 1. Exchange of NaOt-Bu by KOt-Bu led to the
desired product, but only with a very low yield of 1.7 % (Table 1, entry 1). Contrary, changing the solvent to MeOH and the base to KOMe increased the yield up to 96 % (Table 1, entry 9). Isolation of the dicarboxylic acid required a workup under strongly acidic conditions, which led to the precipitation of the product.

Additional screening was performed to ascertain the ideal conditions for the C–C cross-coupling reaction of 5 with 2-thienylmagnesium bromide (Table 2, entries 1–5), 2-thienyl boronic acid (Table 2, entries 6–10), and 2-(tributylstannyl)thiophene (Table 2, entry 11). The summarized screening results are collected in Table 2. It was not possible to isolate the desired extended thiophene structure 6 with a Ni- or Fe-catalyzed Kumada coupling, while every Suzuki coupling yielded the desired product 6, but with varying yields of 14.6–54.3 %.

The best result with a yield of 54.9 % was obtained with the Stille coupling utilizing Pd(PPh3)4 as catalyst, and a solvent mixture of toluene and DMF (4:1; Table 2, entry 11).

If the reagents were suspended and added to the base (see Table 1, order position of base: 2nd) or the base was added to the suspended reagents (see Table 1, order position of base: 1st) only minor influences on the obtained yield (91.5 % vs. 96.1 %). Compound 1 was utilized to realize a series of new 5,7-disubstituted thieno[3,4-f][1,10]phenanthrolines by using it as precursor in four different reactions. According to Scheme 2, the decarboxylated product thieno[3,4-f][1,10]phenanthroline (2), the methyl (3), and ethyl ester (4) of 1, and the 5,7-dibromo-substituted compound 5,7-dibromothieno[3,4-f][1,10]phenanthroline 5. All reactions are depicted in Scheme 2. The synthesis of 2 was carried out as a neat reaction, and the product sublimed as colorless solid in vacuum. Although the yields were quite low, esterifications of 1 to 3 and 4 produced the desired products. For the synthesis of 5, N-bromosuccinimide (NBS) was used as bromine source and water as solvent, which results in a yield of 72 %. Other solvents like CHCl3 or CH2Cl2 suffered from low solubility of 1 and did not yield any product. Until now, only molecules with electron-withdrawing groups that lower both, the HOMO and the LUMO, were prepared. Hence, a system which provides different electronic properties was also synthesized. To achieve this, 5,7-di[thiophen-2-yl]thieno[3,4-f][1,10]phenanthroline 6 with terminal thiophene rings in the 5,7-position was prepared to generate a system that is expected to feature a raised HOMO and lowered LUMO due to the extended conjugation. Additionally, 6 is theoretically capable of showing an efficient electron transfer, too. With this modification, a larger π-system is created that should be beneficial for efficient electron-transport properties. Therefore, a second screening
dimethylpyridin-3-yl)magnesium bromide and Ni(dppf)Cl₂ as catalyst failed. Hence, the synthetic strategy was altered, and we went two steps back to introduce \( \text{5} \) to Stille cross-coupling reactions with \( \text{12} \) and \( \text{13} \). These two molecules were also prepared via another Stille coupling to obtain \( \text{8} \) and \( \text{9} \), subsequent brominations to \( \text{10} \) and \( \text{11} \) that were finally converted into \( \text{12} \) and \( \text{13} \). This new synthetic route is depicted in Scheme 3. With this modified procedure it was possible to obtain the two last structures of \( \text{14} \) and \( \text{15} \). After the termination of the reaction, the products precipitated as pale-yellow solids. They are the most promising structures for novel photocatalytic systems because additional to the large \( \pi \)-system, they also possess two separate coordination sides. These can be used to obtain bimetallic systems as active photocatalytic hydrogen evolving systems.

The synthesized compounds were characterized and confirmed by NMR spectroscopy, mass spectrometry, and elemental analysis. Additionally, it was possible to collect single-crystal X-ray data for \( \text{5} \), \( \text{6} \), \( \text{7} \), and \( \text{15} \). All four structures exhibit a nearly coplanar arrangement of the 1,10-phenanthroline and the thiophene ring with a maximum torsion angle of 4.66° for structure \( \text{6} \). This plane orientation supports the assumed effective electron transfer in these compounds. The more extended structures (\( \text{6} \), \( \text{7} \), and \( \text{15} \)) show an additional twist of ca. 70–75° around the terminal thiophene rings in \( \text{6} \) and \( \text{7} \) and between the thiophene and the pyridine rings in \( \text{15} \) with angles around 45°. The molecular structure of \( \text{15} \) is shown in Figure 1, and the other crystal structures are included in the Supporting Information.

In conclusion, we have identified straightforward synthesis protocols for a series of new 5,7-disubstituted thieno[3,4-\( \text{f} \)]1,10-phenanthroline structures. The crucial step for the successful syntheses of these new structures was the modification of the Hinsberg thiophene synthesis to obtain the starting material \( \text{1} \) used for the preparation of all derivatives. It is the first time that a 1,10-phenanthroline is reported with a fused 3,4-thiophene ring in the backbone. All molecules were characterized by standard methods as well as crystal structure analysis for \( \text{5} \), \( \text{6} \), \( \text{7} \), and \( \text{15} \). Due to

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**Table 2 C–C Cross-Coupling Reaction for the Reaction to Obtain 6**

<table>
<thead>
<tr>
<th>Entry</th>
<th>THF</th>
<th>Et₂O</th>
<th>DME/H₂O</th>
<th>DMF</th>
<th>Toluene</th>
<th>Ni(dppe)Cl₂</th>
<th>Fe(acac)₃</th>
<th>Pd(dppe)₂</th>
<th>Pd(ac)₂</th>
<th>Pd(dppf)Cl₂</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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</table>

*a Entries 1–5 were conducted with 2-ThioMgBr as coupling reagent.
*b Entries 6–10 were conducted with 2-ThioB(OH)₂ as coupling reagent.
*c Na₂CO₃ was used as base in entries 6–8.
*d K₃PO₄ was used as base in entries 9 and 10.
*e Entry 11 was conducted with 2-ThioSnBu₃ as coupling reagent.

**Scheme 3 Synthetic route for the synthesis of 14 and 15**
their coplanar arrangement, these new fused systems containing thiophene rings are theoretically promising candidates for the application as molecular electronics. Although the actual application in organic electronics is not the aim of the current work, the synthesized compounds may find suitable applications in that field. However, in the near future we will report promising results obtained with these structures as ligands in photocatalytic hydrogen evolution experiments as components in two-component as well as one-component applications.

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**Supporting Information**

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611022.

**References and Notes**


12. The reaction was conducted under inert atmosphere. Potassium (3.51 g, 89.8 mmol, 4 equiv) was dissolved in dry MeOH (15 mL). 1.10-Phenanthroline-5,6-dione (5.01 g, 23.8 mmol, 1 equiv) and diethyl-2,2’-thiodiacetate (4.99 g, 24.2 mmol, 1 equiv) were mixed in dry MeOH (40 mL) at 0 °C in a second flask. The potassium methanolate solution was added slowly. During this process, the color changed from yellow to black. The solution was stirred for 3 h at ambient temperature. After this time a solid was formed. Water (500 mL) was added to the mixture, and the reaction solution was concentrated to 250 mL. The suspension was filtered, and concentrated HCl (65 mL) was added. The obtained solid 1 was filtered, washed with diethyl ether, and dried under vacuum; yield 7.42 g (96 %). 1H NMR (500 MHz, DMSO-d6): δ = 8.18 (dd, JHH = 8.5, 4.9 Hz, 2 H), 9.15 (dd, JHH = 4.9 Hz, JHH = 1.4 Hz, 2 H), 10.00 (dd, JHH = 8.5 Hz, JHH = 1.4 Hz, 2 H) ppm. 13C NMR (125 MHz, DMSO-d6): δ = 125.7 (CH or Cq), 126.5 (Cq), 132.9 (Cq), 134.0 (Cq), 139.2 (Cq), 141.5 (CH), 147.3 (CH), 163.3 (Cq) ppm. 15N NMR (70.9 MHz, DMSO-d6): δ = 245.83 (s) ppm. MS-ESI (pos): m/z = 325.03 [M + H]+.

13. The reaction was carried out under Ar atmosphere. Compd 5 (0.16 g, 0.4 mmol, 1 equiv), 2-thienylboronic acid (0.12 g, 1.0 mmol, 2.5 equiv) and K2PO4 (0.28 g, 1.3 mmol, 3.5 equiv) were added to a Schlenk flask. Afterwards, Pd(PPh3)4 (0.06 g, 0.16 mmol, 2.5 equiv) and K3PO4 (0.28 g, 1.3 mmol, 3.5 equiv) were mixed in dry MeOH (40 mL) at −20 °C in a second flask, and the potassium methanolate solution was added slowly. After this time a solid was formed. Water (500 mL) was added to the mixture, and the potassium methanolate solution was added slowly. During this process, the color changed from yellow to black. After this time a solid was formed. Water (500 mL) was added to the mixture, and the reaction solution was concentrated to 250 mL. The suspension was filtered, and concentrated HCl (65 mL) was added. The obtained solid 1 was filtered, washed with diethyl ether, and dried under vacuum; yield 7.42 g (96 %). 1H NMR (500 MHz, DMSO-d6): δ = 8.18 (dd, JHH = 8.5, 4.9 Hz, 2 H), 9.15 (dd, JHH = 4.9 Hz, JHH = 1.4 Hz, 2 H), 10.00 (dd, JHH = 8.5 Hz, JHH = 1.4 Hz, 2 H) ppm. 13C NMR (125 MHz, DMSO-d6): δ = 125.7 (CH or Cq), 126.5 (Cq), 132.9 (Cq), 134.0 (Cq), 139.2 (Cq), 141.5 (CH), 147.3 (CH), 163.3 (Cq) ppm. 15N NMR (70.9 MHz, DMSO-d6): δ = 245.83 (s) ppm. MS-ESI (pos): m/z = 325.03 [M + H]+.
1H NMR (500 MHz, CDCl₃): δ = 2.62 (s, 6 H), 2.78 (s, 6 H), 7.10 (d, J_HH = 7.72 Hz, 2 H), 7.22 (d, J_HH = 3.65 Hz, 2 H), 7.33 (d, J_HH = 3.65 Hz, 2 H), 7.34 (d, J_HH = 4.43 Hz, 2 H), 7.70 (d, J_HH = 7.85 Hz, 2 H), 8.37 (dd, J_HH = 8.35 Hz, J_HH = 1.60 Hz, 2 H), 9.00 (dd, J_HH = 4.43 Hz, J_HH = 1.60 Hz, 2 H) ppm. 13C NMR (125 MHz, CDCl₃): δ = 24.1 (CH₃), 24.3 (CH₃), 121.1 (CH), 123.1 (CH), 125.7 (Cq), 127.9 (CH), 130.0 (CH), 130.0 (Cq), 131.0 (Cq), 132.6 (CH), 135.0 (Cq), 138.3 (CH), 144.7 (Cq), 147.1 (Cq), 149.8 (CH), 155.3 (Cq), 157.7 (Cq). 15N NMR (50.7 MHz, CDCl₃): δ = 305.9 (s), 313.1 (s) ppm. MS-ESI (pos): m/z = 633.12 [M + Na]⁺, 611.14 [M + H]⁺, 306.07 [M + 2H]²⁺. Anal. Calcd for CHN₄S₃: N, 9.17; C, 70.79; H, 4.29; S, 15.75. Found: N, 8.76; C, 69.69; H, 4.67; S, 14.5.

15) We have prepared bimetallic systems with these ligands that show high activities as hydrogen-evolving devices in photocatalytic proton reduction. The results will be published in the near future.
