*Organic*
LETTERS

Selective Functionalization of Tetrathiafulvalene Using Mg- and Zn-TMP-Bases: Preparation of Mono-, Di-, Tri-, and Tetrasubstituted Derivatives

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Ⓢ *Supporting Information*
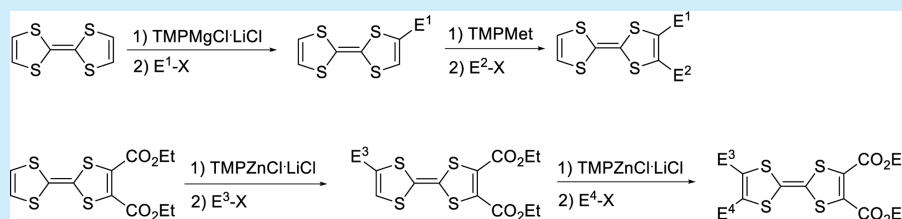
ABSTRACT: The tetrathiafulvalene-scaffold (TTF) reacts selectively in allylation, acylation, arylation, halogenation, and thiolation reactions via magnesium or zinc derivatives that are obtained by a direct metalation with Mg- and Zn-TMP-bases (TMP = 2,2,6,6-tetramethylpiperidyl). This stepwise functionalization provides access to a range of new mono-, di-, tri-, and tetra-functionalized TTF-derivatives and allows for fine-tuning of their energy levels.

Pioneered by the discovery of Wudl,[1] tetrathiafulvalenes (TTFs) have emerged into an important class of organic materials[2] owing to their unique optical, electronic, and magnetic properties.[3] Much effort has been made to functionalize the TTF-scaffold,[4] including C–H arylation[5] and direct metalations.[6] Although the lithiation of TTF (1) allows for an efficient functionalization with robust substituents, the preparation of TTFs featuring sensitive functional groups remains difficult due to the high reactivity of the carbon–lithium bond. Recently, we have reported a set of new metallic amides[7] derived from 2,2,6,6-tetramethylpiperidine (TMP-H), such as TMPMgCl·LiCl (2),[8] TMP$_2$Mg·2LiCl,[9] TMPZnCl·LiCl (3),[10] and TMP$_2$Zn·2MgCl$_2$·2LiCl (4).[11] These bases are highly kinetically active due to the steric hindrance of the TMP-moiety and tolerate a wide range of functional groups.

Herein, we report the selective functionalization of the TTF-skeleton using Mg- and Zn-TMP-bases (2–4) and demonstrate the potential of the resulting new polyfunctionalized TTFs as molecular semiconductors.

Thus, the magnesiation of TTF (1) is conveniently achieved by the addition of TMPMgCl·LiCl (2, 1.1 equiv) at 25 °C within 1 h leading to the magnesiated-TTF (5). This magnesium derivative can be treated with various electrophiles (E^1–X) providing a range of TTF-derivatives of type 6 in 55–92% yield (Scheme 1 and Table 1).

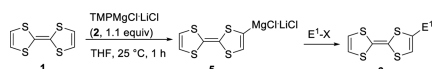**Scheme 1. Preparation of Functionalized TTFs (6) via the Magnesiation of TTF (1) with TMPMgCl·LiCl (2)**

Table 1. Preparation of 4-Substituted TTF-Derivatives of Type 6 by Magnesiation of TTF (1) with TMPMgCl·LiCl (2)

entry	electrophile	product	yield (%)[a]
		(R at 4-position)	
1	I$_2$	**6a**: R = I	55
2	(BrCl$_2$C)$_2$	**6b**: R = Br	67
3	PhSO$_2$Cl	**6c**: R = Cl	65
4	MeSO$_2$SMe	**6d**: R = SMe	89
5	Me$_2$N=CH$_2$OCOCF$_3$	**6e**: R = CH$_2$NMe$_2$	55
		(acyl R)	
6	DMF	**6f**: R = H	60
7	NC-CO$_2$Et	**6g**: R = OEt	72
8	tBuCOCl	**6h**: R = tBu	76[b]
9	3-Cl-C$_6$H$_4$COCl	**6i**: R = 3-Cl-C$_6$H$_4$	83[c]
	(aryl R)	*(aryl R)*	
10	R = 4-Cl	**6j**: R = 4-Cl	86[d]
11	R = 4-CO$_2$Et	**6k**: R = 4-CO$_2$Et	87[d]
12	R = 4-OMe	**6l**: R = 4-OMe	61[d]
13	R = 3-CF$_3$	**6m**: R = 3-CF$_3$	92[d]

[a]Isolated yield of analytically pure product. [b]CuCN·2LiCl solution was added. [c]Pd-catalyzed acylation reaction using 10 mol % Pd(PPh$_3$)$_4$. [d]Cross-coupling conditions: ZnCl$_2$ transmetalation, 3 mol % Pd-(dba)$_2$, 6 mol % tfp.

The halogenation of **5** (iodolysis, bromination, and chlorination) proceeds in moderate yields (55−67% yield; Table 1, entries 1−3) due to the limitated stability of the heterocyclic halides (**6a−c**). Methylthiolation of **5** is performed using MeSO₂SMe affording the thioether (**6d**) in 89% yield (entry 4). An aminomethylation of **5** using the iminium salt Me₂NCH₂OCOCF₃[12] provides the amine **6e** in 55% yield (entry 5). The acylation of **5** can be directly achieved by the addition of DMF or ethyl cyanoformate leading to the aldehyde **6f** and the ester **6g** in 60−72% yield (entries 6−7; for single-crystal X-ray structure analysis of **6g**, see the Supporting Information, Figure S3). A copper-catalyzed acylation with pivaloyl chloride provides the ketone **6h** (76% yield; entry 8), whereas a Pd-catalyzed Negishi-acylation[13] furnishes the ketone **6i** in 83% yield (entry 9). The arylation of **5** is achieved by a transmetalation with zinc chloride followed by a Negishi cross-coupling using 3 mol % Pd(dba)₂ (dba = dibenzylidene-acetone) and 6 mol % tfp (tri-2-furylphosphine)[14] as a catalyst and an aryl iodide as an electrophile. Interestingly, electron-withdrawing, as well as electron-donating, groups can be attached to the electron-rich TTF-core producing the corresponding arylated TTF-derivatives (**6j−m**) in 61−92% yield (entries 10−13).

The preparation of symmetrically and asymmetrically disubstituted TTF-derivatives of type **7** can be achieved by a selective metalation of various monofunctionalized TTF-derivatives. The presence of an electron-withdrawing substituent, such as a chlorine or an acyl or a carboethoxy group, on the TTF-core directs the second metalation to the adjacent position.[15] In the case of a chloride (**6c**) or a carboethoxy group (**6g**), the metalation is best performed with TMPMgCl·LiCl (**2**). Thus, the treatment of 4-chloro-TTF (**6c**) with TMPMgCl·LiCl (**2**) at 0 °C (0.5 h) followed by the copper-catalyzed allylation reaction with ethyl 2-(bromomethyl)-acrylate[16] furnishes the disubstituted TTF **7a** in 85% yield (Table 2, entry 1). After transmetalation with zinc chloride, a Pd-catalyzed Negishi acylation reaction with benzoyl chloride and Negishi cross-coupling reactions with aryl iodides are achieved leading to 4,5-disubstituted TTF-derivatives (**7b−d**) in 78−92% yield (entries 2−4). Magnesiation of the ester **6g** is performed using TMPMgCl·LiCl (**2**; 1.1 equiv) at −20 °C (0.5 h). Subsequent trapping with ethyl cyanoformate leads to the diester-TTF (**7e**) in 65% yield (entry 5). The thioethers **7f−7g** were obtained in 59−65% yield by quenching the magnesiated TTF-derivative of **6g** with PhSO₂SPh and MeSO₂SMe (entries 6−7). In the case of a benzoyl substituent (**7e**), a metalation with a magnesium base is too harsh and leads to unwanted side reactions. However, a zincation with TMP₂Zn·2MgCl₂·2LiCl (**4**; 1.1 equiv, THF, 0 °C, 0.5 h) leads to the corresponding zincated TTF in quantitative yield. After iodolysis, the corresponding iodide **7h** is obtained in 83% yield (entry 8).

Trifunctionalized TTF-derivatives are readily prepared starting from the 4,5-diethyl ester-TTF **7e** using the mild base TMPZnCl·LiCl (**3**; 1.3 equiv, THF, −30 °C, 0.5 h). Reactions with iodine, copper-catalyzed allylation with 3-bromocyclohexene, or Negishi cross-coupling reactions with aryl iodides produce the expected trisubstituted TTF-derivatives (**8a−e**) in 66−94% yield (Scheme 2).

Fully functionalized TTFs of type **9** are prepared by the zincation of **8c−e** using TMPZnCl·LiCl (**3**; 1.3 equiv) at 0 °C within 0.5 h. Trapping the zincated-TTF-derivative of **8c** and **8d** with iodine gives tetrasubstituted TTFs **9a** and **9b** in 76−88% yield (Table 3, entries 1 and 2). Furthermore, Negishi

Table 2. Preparation of 4,5-Disubstituted TTF-Derivatives of Type 7 by Metalation of the Monosubstituted TTFs 6c, 6g, and 6i with Mg- and Zn-TMP-Bases

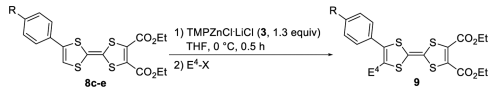| entry	substrate	electrophile	product	yield (%)[a]
1	**6c**	Br⟋CO₂Et	**7a**	85[b,c]
2	**6c**	PhCOCl	**7b**	83[b,d]
3	**6c**	R = OMe (I-Ar)	**7c**: R = OMe	78[b,e]
4	**6c**	R = CN	**7d**: R = CN	92[b,e]
5	**6g**	NC-CO₂Et	**7e**	65[f]
6	**6g**	PhSO₂SPh	**7f**: R = Ph	59[f]
7	**6g**	MeSO₂SMe	**7g**: R = Me	65[f]
8	**6i**	I₂	**7h**	83[g]

[a]Isolated yield of analytically pure product. [b]TMPMgCl·LiCl (1.1 equiv, 0 °C) was used. [c]CuCN·2LiCl solution was added. [d]ZnCl₂ solution was added. Pd-catalyzed acylation reaction using 10 mol % Pd(PPh₃)₄. [e]Cross-coupling conditions: ZnCl₂ transmetalation, 3 mol % Pd(dba)₂, 6 mol % tfp. [f]TMPMgCl·LiCl (1.1 equiv, −20 °C) was used. [g]TMP₂Zn·2MgCl₂·2LiCl (1.1 equiv, 0 °C) was used.

Scheme 2. Preparation of Trisubstituted TTF-Derivatives of Type 8 Using TMPZnCl·LiCl (3)
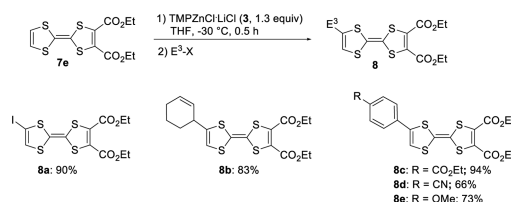
cross-coupling, copper-catalyzed allylation reaction and Pd-catalyzed Negishi acylation reaction provide tetrasubstituted TTFs **9c−h** in 53−90% yield (entries 3−8; for single-crystal X-ray structure analysis of **9c** and **9d**, see the Supporting Information, Figures S4 and S5).

All TTF-derivatives feature a strong UV absorption and exhibit a broad absorption band in the visible spectral region (SI, Figure S1). While the **VIS** absorption is weak for the unsubstituted TTF, it can be significantly enhanced by attaching substituents. In particular, the nonsymmetric 1- and 3-fold substituted TTFs possess systematically higher extinction coefficients in the **VIS** region compared to their symmetrically functionalized counterparts. On the other hand, the larger conjugated π-systems of the 2- and 4-fold substituted molecules, respectively, extend the absorption further into the red.

Table 3. Preparation of Fully Functionalized TTF-Derivatives of Type 9 Using TMPZnCl·LiCl (3)

entry	substrate	electrophile	product, yield (%)[a]
1	**8c**	I_2	**9a**: R = CO_2Et, 88
2	**8d**	I_2	**9b**: R = CN, 76
3	**8c**	$R^2 = CO_2Et$	**9c**: $R^1 = R^2 = CO_2Et$, 90[b]
4	**8d**	$R^2 = CN$	**9d**: $R^1 = R^2 = CN$, 63[b]
5	**8e**	$R^2 = OMe$	**9e**: $R^1 = R^2 = OMe$, 63[b]
6	**8c**		**9f**: 85[c]
7	**8c**		**9g**: 85[d]
8	**8d**		**9h**: 80[d]

[a]Isolated yield of analytically pure product. [b]Cross-coupling conditions: 3 mol % Pd(dba)₂, 6 mol % tfp. [c]CuCN·2LiCl solution was added. [d]Pd-catalyzed acylation reaction using 10 mol % Pd(PPh₃)₄.

We then studied the effect of the nature and number of substituents on the energy levels of the TTF-derivatives using differential pulse voltammetry (DPV).[17] The highest occupied molecular orbital (HOMO) energies were extracted from scans in the oxidation direction (SI, Figure S2) and referenced to the oxidation of ferrocene ($E_{fc/fc+} = -4.80$ eV vs vacuum).

We found that indeed the substitution has a profound effect on the position of the HOMO, spanning a range of more than 200 meV (Figure 1). While a single $-CO_2Et$ or $-Cl$ substituent
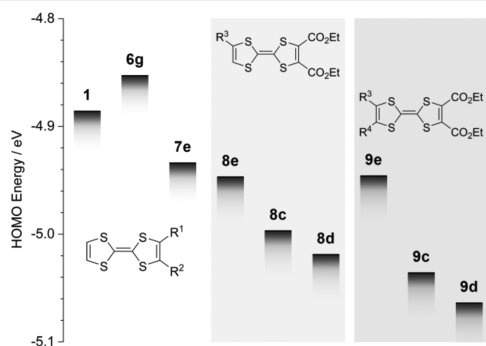
shifts the HOMO upward (SI, Figure S2k and S2l), the energy levels of all multisubstituted TTFs are significantly lower than those for bare TTF. For the series of aryl substituents, the HOMO can be further fine-tuned by adjusting the electron-accepting end group. For the molecules of type **8** and **9** we observe deeper HOMO levels as the acceptor strength is increased from $-OMe$ to $-CO_2Et$ and $-CN$. This approach for systematic fine-tuning of the energy levels allows for matching the work function of contact layers or electrodes, such as gold, silver, or indium tin oxide, which is of key importance for possible applications of these materials in electronic devices.

In summary, the use of Mg- and Zn-TMP bases allows for a selective synthesis of mono-, di-, tri-, and tetrafunctionalized TTF-derivatives. Due to the gentle reaction conditions a wide range of sensitive functional groups are tolerated leading to symmetrically, as well as asymmetrically, substituted poly-functionalized TTFs. This novel synthesis protocol allows for fine-tuning of optical properties and energy levels and thus provides a strategy for realizing tailor-made molecular semi-conductors.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02715.

> Detailed experimental procedures and characterization data for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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Figure 1. Highest occupied molecular orbital energies of selected substituted TTF-derivatives measured by differential pulse voltammetry.

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