Synthesis H. Yorimitsu et al. Short Review

Catalytic C–H Arylation of Tetrathiafulvalenes for the Synthesis of Functional Materials

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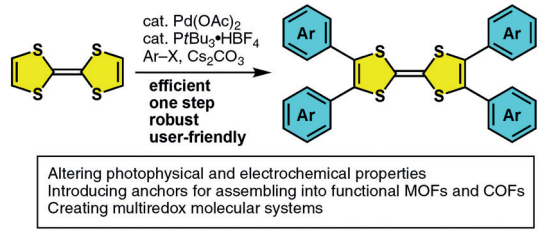

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Abstract Sulfur-containing functional π-conjugated cores play key roles in materials science, mostly due to their unique electrochemical and photophysical properties. Among these, the excellent electron donor tetrathiafulvalene (TTF) has occupied a central position since the emergence of organic electronics. Peripheral C–H modification of this highly useful sulfur-containing motif has resulted in the efficient creation of new molecules that expand the applications of TTFs. This Short Review begins with the development of the palladium-catalyzed direct C–H arylation of TTF. Subsequently, it summarizes the applications of this efficient C–H transformation for the straightforward synthesis of useful TTF derivatives that are employed in a variety of research fields, demonstrating that the development of a new reaction can have a significant impact on chemical science.

1 Introduction
2 Development of the Palladium-Catalyzed Direct C–H Arylation of TTF
3 Synthesis of TTF-Based Tetrabenzoic Acid and Tetrapyridine for MOFs
4 Synthesis of TTF-Based Tetrabenzaldehyde and Tetraaniline for COFs
5 Tetraarylation of TTFAQ
6 Synthesis of Multistage-Redox TTF Derivatives
7 Miscellaneous Examples
8 Conclusions

Key words C–H arylation, tetrathiafulvalene, sulfur, palladium catalysis, metal-organic framework, covalent organic framework, supramolecular chemistry, redox-active material

Hideki Yorimitsu obtained his Ph.D. in 2002 from Kyoto University under the tutelage of Professor Koichiro Oshima. He then served as a JSPS postdoctoral fellow with Professor Eiichi Nakamura at the University of Tokyo. Subsequently, he became Assistant Professor (2003) and Associate Professor (2008) in the Graduate School of Engineering, Kyoto University. In 2009, he moved to the Graduate School of Science, Kyoto University, where he was promoted to Full Professor in 2015. He received the Chemical Society of Japan Award for Young Chemists in 2009, the Young Scientists' Prize from MEXT in 2011, the Mukaiyama Award in 2016, the JSPS Prize in 2020, and the Japan Academy Medal in 2020. His research focuses on the development of new organic transformations in order to create new molecules, phenomena, and concepts.

1 Introduction

Conjugated π-electronic molecular systems are important in organic electronics due to their unique photophysical and electrochemical properties.[1] Polyaromatic hydrocarbons (PAHs) such as acenes and fullerenes have been extensively investigated in order to characterize the highly useful properties that originate from their interesting structures. Conjugated π-electronic systems that bear heteroatom(s)

are also intriguing, as the presence of heteroatoms can endow such systems with characteristics that are not observed for PAHs. Among the typical heteroatoms, the third-row element sulfur occupies a unique position. Sulfur has a high natural abundance and is particularly attractive for several reasons: 1. Compared to elements in the second row, the larger size and weaker hybridization of the s and p orbitals of sulfur lead to longer C–S bonds and smaller C–S–C angles. The aromaticity of sulfur-containing heteroarenes such as thiophene is thus moderate; and 2. the effective shielding of its inner 1s, 2s, and 2p electrons allows sulfur to easily donate and accept electron density, endowing sulfur-containing molecules with redox activity. Thus, sulfur-containing conjugated π-electronic systems have been widely investigated, resulting in the creation of molecules with highly useful properties,[2] such as tetrathiafulvalene (TTF).[3]

The functionality of such sulfur-containing compounds is governed by the conjugated π-electronic cores. The peripheral modification of these cores has attracted great attention, as this approach can effectively alter the electronic and steric properties and peripheral reactivity of the parent core to create new π-extended molecules with unique properties. Cross-coupling reactions have traditionally been employed as the key tool for this purpose.[4] This strategy usually requires either a metalated or halogenated core as a precursor, which is often laborious and/or difficult to achieve. Recently, direct catalytic modifications of C–H bonds on aromatic rings have emerged in organic synthesis as an inherently more efficient tool for this purpose.[4c,5–8] This straightforward strategy should also be applicable for the peripheral modification of conjugated π-electronic cores[7] such as TTF in order to prepare novel π-extended molecules with unique functionality.

This Short Review discusses the catalytic peripheral C–H arylation of TTF and its analogues to alter the electronic properties of the parent cores. More importantly, the arylation of the cores can provide peripheral functionality to create hybrid molecules with applications in research fields other than conventional organic electronics, such as materials sciences, coordination chemistry, supramolecular chemistry, and catalysis; these applications are also briefly summarized in this Short Review.

2 Development of the Palladium-Catalyzed Direct C–H Arylation of TTF

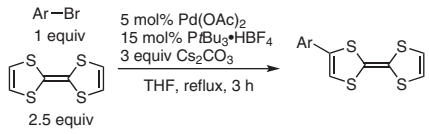
Tetrathiafulvalene, which contains two 7π-1,3-dithiole units connected to each other at the 2-position, is a good electron donor due to the favorable formation of aromatic 1,3-dithiolium rings upon one- and two-electron oxidation. TTF has thus become a key component in a variety of functional organic electronic materials.[3] In addition to TTF itself, peripherally functionalized TTF derivatives are also important, as they exhibit different characteristic properties derived from their substituents. It is thus hardly surprising that peripherally modified TTFs have been extensively synthesized and investigated.[3] Among these, aryl-substituted TTFs are particularly attractive because the aromatic substituents can considerably alter the electronic nature of TTF via outward extension of its π-conjugation. However, the conventional synthesis of peripherally arylated TTFs involves the laborious preparation of metalated or halogenated TTF (or similar precursors) prior to the palladium-catalyzed cross-coupling arylation.[3c,f,m,o,9] The pre-activation/cross-coupling sequence is especially disadvantageous for the synthesis of multiply arylated TTFs.

In 2011, Yorimitsu and co-workers developed a more straightforward synthetic route to arylated TTFs.[10] Their application of a palladium-catalyzed direct C–H arylation to the peripheral arylation of TTF greatly simplified the functionalization of TTF and related analogues, and expanded the application range of TTF derivatives.

This approach is based on the treatment of TTF with aryl bromide in the presence of cesium carbonate and catalytic amounts of palladium acetate and tri-*tert*-butylphosphonium tetrafluoroborate in refluxing THF or dioxane, which results in the peripheral arylation of TTF (Table 1 and Table 2). Several points regarding this reaction are worth noting: 1. The reaction conditions are similar to those applied during the multiple arylation of cyclopentadiene reported by Miura;[11] 2. The protons in TTF are sufficiently acidic to allow peripheral H/D exchange to occur in the presence of MeONa in MeOD even at room temperature.[12] The high efficiency of the combination of the palladium catalyst and highly basic cesium carbonate indicates that the concerted metalation-deprotonation mechanism[13] can be expected to work in the palladation of TTF; 3. As commercially available and air-stable tri-*tert*-butylphosphonium tetrafluoroborate is used instead of air-sensitive tri-*tert*-butylphosphine,[14] the experimental procedure is very simple and thus practical, which has led to the adoption of this protocol by non-synthetic organic chemists (vide infra). As tri-*tert*-butylphosphine is generated in situ due to the presence of cesium carbonate, a glove box is not necessary. 4. As far as we have investigated, aryl bromides reacted the most efficiently among aryl halides and triflates. However, chlorides and iodides are also worth examining, as shown in Schemes 5, 11, and 13 (vide infra), while all our attempts to use aryl triflates have failed; 5. When aryl bromide is the limiting reagent and an excess of TTF is used (Table 1), monoarylation predominates. However, the yield of the monoarylated products is usually moderate because competitive multiple arylation occurs; 6. Due to the high efficiency of the C–H arylation, the tetraarylation of TTF proceeds in high yield when an excess of aryl bromide, a larger amount of the catalyst, and a longer reaction time are used (Table 2). Prior to the development of this reaction, only two examples of the synthesis of tetraaryl TTFs had been

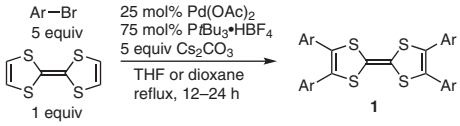
reported, which were either very inefficient or employed harsh conditions;[15] and 7. This powerful new protocol enabled the creation of a wide variety of new tetraaryl TTFs, which allowed systematic structure-property investigations of the photophysical and electrochemical properties of aryl TTFs. Since its development, this protocol has been recognized as the most efficient method for exploiting TTF-based functional materials.

Table 1 Monoarylation of TTF



Ar	Yield (%)	Ar	Yield (%)
4-MeC_6H_4	50	4-$NO_2C_6H_4$	60
2-naphthyl	53	3-$MeOC_6H_4$	64
4-FC_6H_4	51	3-$CF_3C_6H_4$	56
4-$MeOC_6H_4$	48	4-$MeCOC_6H_4$	51
4-$Me_2NC_6H_4$	42	4-CNC_6H_4	50
4-$CO_2EtC_6H_4$	64		

Table 2 Tetraarylation of TTF

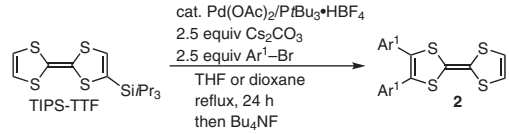


Ar	1	Yield (%)	Ar	1	Yield (%)
4-MeC_6H_4	**1a**	97	4-$CF_3C_6H_4$	**1h**	80[a]
2-naphthyl	**1b**	85	3-$CF_3C_6H_4$	**1i**	86
4-FC_6H_4	**1c**	60	3-$MeOC_6H_4$	**1j**	86
4-$MeOC_6H_4$	**1d**	78	3,5-$(MeO)_2C_6H_3$	**1k**	82
4-$Me_2NC_6H_4$	**1e**	60	4-CNC_6H_4	**1l**	60[a]
4-$CO_2EtC_6H_4$	**1f**	91[a]	3-pyridyl	**1m**	63
4-$NO_2C_6H_4$	**1g**	60[a]	4-biphenylyl	**1n**	90

[a] Using 30 mol% $Pd(OAc)_2$, 90 mol% $PtBu_3{\cdot}HBF_4$, and 6 equiv Cs_2CO_3.

Yorimitsu also synthesized triisopropylsilyl-substituted TTF (TIPS-TTF) as a potential platform for the synthesis of low-symmetry TTF derivatives.[16] The bulky TIPS group tolerates basic conditions, which allows the selective palladium-catalyzed C–H diarylation of the unsilylated dithiole ring. Subsequent fluoride-mediated 'deprotection' provides unilaterally diarylated TTFs **2** (Table 3), which can undergo further C–H diarylation to yield low-symmetry tetraaryl TTFs **3** (Table 4). The conditions also accommodate a TIPS-ethynyl group (**3e**), which would be useful for Sonogashira coupling reactions and Cu-mediated dimerization after desilylation. Low-symmetry tetraaryl TTF **3b**, which exhibits a strong push-pull substitution pattern, showed, as expected, interesting electrochemical properties. This method represented the first selective synthesis of low-symmetry tetraaryl TTFs. The synthesis involves only three steps starting from TTF and hence has the potential to expand the variety of low-symmetry TTF derivatives.

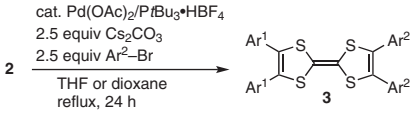
Table 3 Synthesis of Unilaterally Diarylated TTFs from TIPS-TTF



Ar^1	2	Yield (%)	Ar^1	2	Yield (%)
4-MeC_6H_4	**2a**	96	4-$NO_2C_6H_4$	**2f**	86
2-naphthyl	**2b**	85	4-$CO_2MeC_6H_4$	**2g**	63[a]
4-$MeOC_6H_4$	**2c**	86	4-$MeSC_6H_4$	**2h**	79
4-$Me_2NC_6H_4$	**2d**	76	4-ClC_6H_4	**2i**	69
4-$CF_3C_6H_4$	**2e**	67	3-pyridyl	**2j**	62

[a] Cs_2CO_3: 3 equiv.

Table 4 Synthesis of Low-Symmetry Tetraaryl TTFs **3**

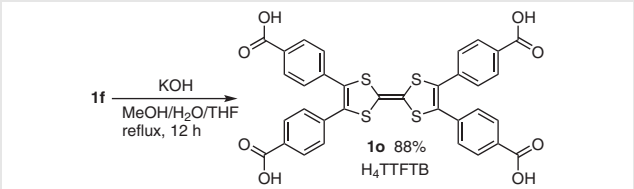


2	Ar^1	Ar^2	3	Yield (%)
2d	4-$Me_2NC_6H_4$	Ph	**3a**	99
2d	4-$Me_2NC_6H_4$	4-$NO_2C_6H_4$	**3b**	60
2e	4-$CF_3C_6H_4$	Ph	**3c**	91
2e	4-$CF_3C_6H_4$	4-$MeOC_6H_4$	**3d**	63
2e	4-$CF_3C_6H_4$	4-(TIPSC≡C)C_6H_4	**3e**	62
2f	4-$NO_2C_6H_4$	Ph	**3f**	99

3 Synthesis of TTF-Based Tetrabenzoic Acid and Tetrapyridine for MOFs

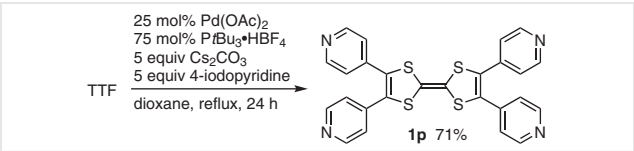
The development of the user-friendly direct C–H arylation of TTF in 2011[10] had a significant beneficial impact on other research fields, particularly coordination chemistry and supramolecular chemistry.[17] The introduced peripheral substituents can facilitate the assembly of multiple TTF-based molecules with strong interactions between the TTF units, while the TTF core endows the TTF-based assemblies with redox activity.

This approach was the first applied to the field of metal-organic frameworks (MOFs) in 2013 by Dincă and co-workers, who synthesized TTF-based tetrabenzoic acid **1o** (H_4TTFTB) via the saponification of **1f**, and used it in the synthesis of Zn_2(TTFTB), that is, a MOF that is composed of columnar stacks of TTF and benzoate-lined one-dimensional channels (Scheme 1).[18] Zn_2(TTFTB) is the first example of a permanently porous MOF with high charge mobility. Following this discovery, several groups including Dincă's used the TTF-based ligand TTFTB for the synthesis of various redox-active MOFs,[19] two-dimensional hydrogen-bonded organic frameworks (HOFs),[20] and charge-transfer supra-amphiphiles.[21] Tetrabenzoic acid **1o** also found application as a hole-transport layer in conventional polymer solar cells.[22] TTFTB-based MOFs are now one of most important classes of redox-active MOFs.



Scheme 1 Dincă's synthesis of **1o** (H_4TTFTB) by saponification of ethyl ester **1f**

Tetra-4-pyridyl TTF (**1p**, $TTFpy_4$) was synthesized from TTF and 4-iodopyridine by Sallé and co-workers in 2014.

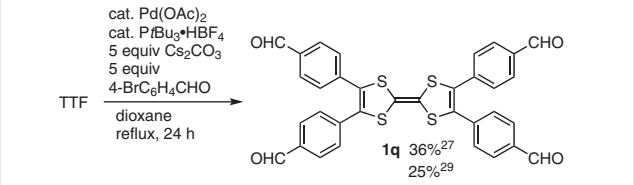


Scheme 2 Sallé's synthesis of TTF-based tetrapyridine **1p**

Since then, it has been used for the synthesis of redox-active arene-ruthenium architectures[23] and M_8L_4 cages (M = Pt or Pd)[24] (Scheme 2). Recently, **1p** was employed for the synthesis of a dodecanuclear molecular rhenium box that displays luminescence in the solid state.[25] Compound **1p** can also be used to construct redox-active MOFs[26] and is expected to find additional applications in coordination chemistry as a neutral ligand complementary to tetraanionic TTFTB.

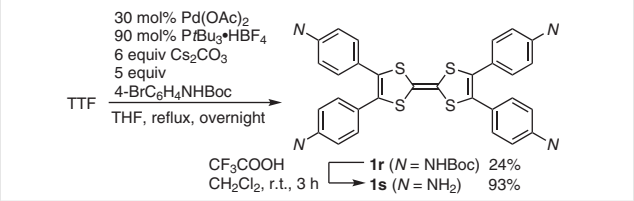
4 Synthesis of TTF-Based Tetrabenzaldehyde and Tetraaniline for COFs

Tetraaryl TTFs also provide a core structure for the construction of redox-active covalent organic frameworks (COFs). Jiang,[27] Wang, and Zhang,[28] as well as Zhang and Liu[29] simultaneously reported the preparation of tetra(4-formylphenyl) TTF (**1q**) (Scheme 3) for the synthesis of two-dimensional COFs by condensation with 1,4-diaminobenzene or related aromatic diamines through imine formation. Such COFs can be prepared on a surface where they align with the underlying substrate lattice.[30] The condensation of **1q** with tetraaminoadamantane or tetra(aminophenyl)methane affords three-dimensional TTF-based COFs with high crystallinity, permanent porosity, and large specific surface area.[31] Interestingly, the condensation of **1q** with *meso*-tetraaminophenyl metalloporphyrins forms crystalline porphyrin–TTF COFs that act as excellent photocatalysts for the reduction of CO_2 with H_2O without an additional photosensitizer, reductant, or co-catalyst.[32] Thus, the future of TTF-based COFs seems promising.



Scheme 3 Synthesis of tetra(4-formylphenyl) TTF (**1q**)

Tetra(4-aminophenyl) TTF (**1s**) was synthesized via Boc-protected **1r** and forms imine-linked COFs with terephthalaldehyde via imine formation in an inverse manner, where the amine groups reside on the periphery of **1r** (Scheme 4).[33]



Scheme 4 Synthesis of tetra(4-aminophenyl) TTF (**1s**)

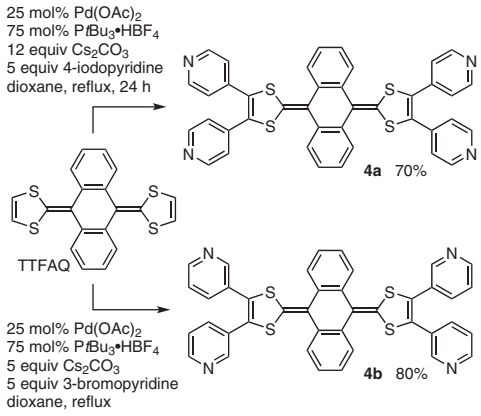
In the field of one-dimensional polymers, di(4-formylphenyl) TTF undergoes condensation with difunctional acylhydrazines to afford hydrazone-based polymers.[34]

5 Tetraarylation of TTFAQ

An extended TTF with an anthraquinoid spacer (hereafter abbreviated as TTFAQ) has emerged as a unique electron donor, showing simultaneous two-electron oxidation accompanied by a drastic conformational change from a folded saddle-like conformation to a stretched conformation, in which the two 1,3-dithiolium rings are oriented perpendicular to the central anthracene moiety with orthogonal twists between the central anthracene moiety and the two 1,3-dithiolium rings.[35] TTFAQ and its derivatives are promising prospective functional materials, for example, sensitizers in organic photovoltaics[36] and positive electrode

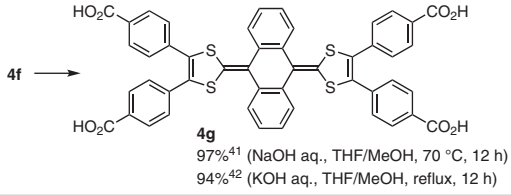
materials for rechargeable batteries.[37,38] Therefore, the peripheral modification of TTFAQ to obtain a variety of new TTFAQ derivatives is important.

In 2013, Goeb, Sallé, and co-workers found that the direct C–H arylation of TTF was also applicable to the peripheral arylation of TTFAQ, which resulted in the preparation of TTFAQ-based tetrapyridine **4a** (Scheme 5).[39] This finding highlights the robustness of the original synthetic protocol for the tetraarylation of TTF. Redox-active self-assembled coordination cages were formed via the complexation of neutral saddle-like **4a** with Pd^{2+} or Pt^{2+} cations,[40] and an Ag-based MOF was prepared using the stretched conformation of cationic **4a**.[40f] A similar 3-pyridyl-substituted TTFAQ (**4b**) was also synthesized and used as a switchable guest with redox-controlled encapsulation/release in a tetragonal Zn-porphyrin-based prismatic nanocage.[40e]



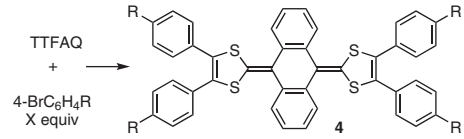
Scheme 5 Synthesis of TTFAQ-based tetrapyridines **4a** and **4b** according to Goeb and Sallé

Misaki and co-workers reported the synthesis of several tetraaryl TTFAQ derivatives via the direct C–H arylation (Table 5),[41] wherein optimal reaction conditions depend on the electronic nature of the aryl bromide used. Ester-containing **4f** undergoes saponification to afford TTFAQ-based tetrabenzoic acid **4g** (Scheme 6). Almost at the same time, Saha and co-workers reported the synthesis of **4f** and **4g** using the same strategy.[42] Misaki and Saha independently applied **4g** to the construction of double-helical MOFs upon complexation with Co^{2+} and Zn^{2+}, respectively.



Scheme 6 Synthesis of H_4TTFAQTB (**4g**) by saponification of **4f**

Table 5 Tetraarylation of TTFAQ According to Misaki[a] and Saha[b]

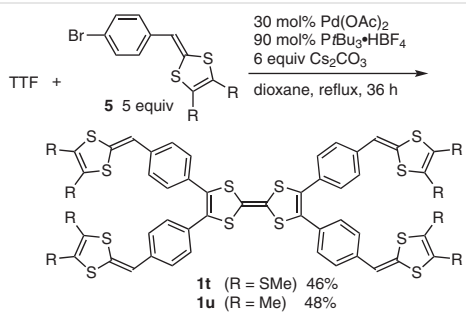


Conditions	R	X (equiv)	Time (d)	4	Yield (%)
Ref. 41[a]	Me	5	0.5	**4c**	75
Ref. 41[a]	MeO	12	6	**4d**	67
Ref. 41[a]	NO_2	6	0.67	**4e**	92
Ref. 41[a]	CO_2Et	6	3	**4f**	80
Ref. 42[b]	CO_2Et	5	7	**4f**	80

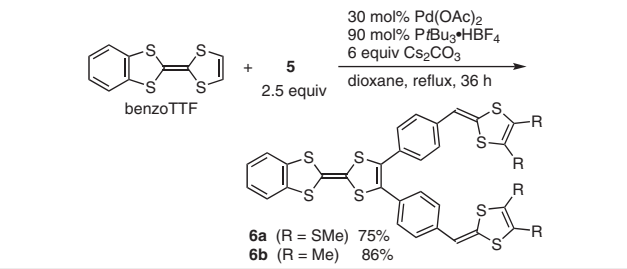
[a] 30 mol% $Pd(OAc)_2$, 90 mol% $PtBu_3{\cdot}HBF_4$, 6 equiv Cs_2CO_3, dioxane, reflux.
[b] 40 mol% $Pd(OAc)_2$, 120 mol% $PtBu_3{\cdot}HBF_4$, 9 equiv Cs_2CO_3, THF, reflux.

6 Synthesis of Multistage Redox TTF Derivatives

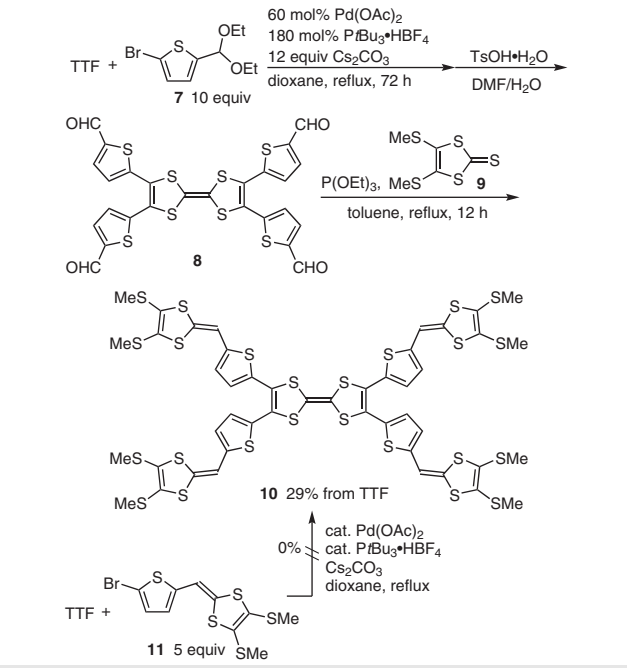
The group of Misaki has been interested in the development of multistage redox-active TTF derivatives and synthesized tetraphenyl TTFs **1t** and **1u**, which feature additional 1,3-dithiafulvene units on the four phenyl groups, by C–H arylation (Scheme 7).[43] BenzoTTF also undergoes diarylation with high efficiency (Scheme 8). Tetrathienyl analogue **10** is accessible starting from the C–H thienylation of TTF with 5-bromo-2-thiophenecarbaldehyde diethyl acetal (**7**) (Scheme 9). Subsequent deprotection and $P(OEt)_3$-mediated coupling with **9** yield **10**. This indirect route is necessary because the ideal precursor, dithiafulvene-substituted bromothiophene **11**, is unstable under these reaction conditions.



Scheme 7 Synthesis of tetraphenyl TTFs that bear additional dithiafulvene groups on the four phenyl groups

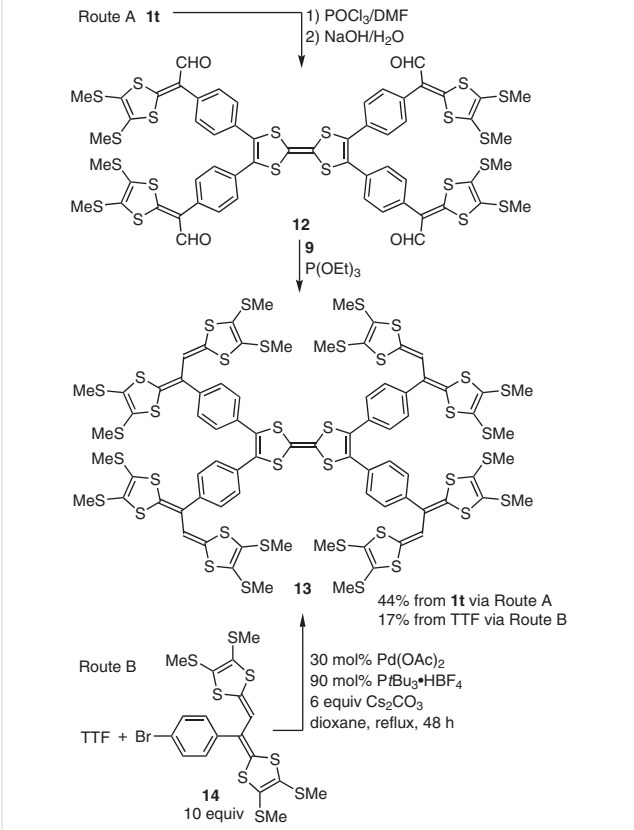


Scheme 8 Synthesis of diphenyl benzoTTFs that bear additional dithiafulvene groups on the two phenyl groups

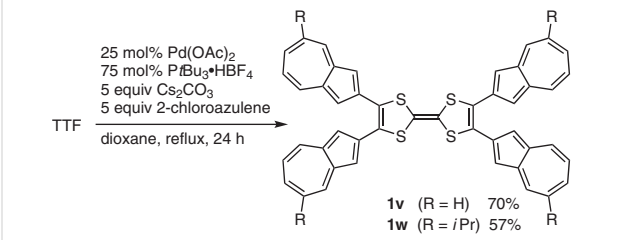


Scheme 9 Synthesis of tetrathienyl TTFs that bear additional dithiafulvene groups on the four thienyl groups

Misaki and co-workers have also focused on cross-conjugated systems with 1,3-dithiole rings, which are attractive as novel multistage redox systems and as donor components for organic conductors.[3,44,45] Palladium-catalyzed C–H arylation offers two approaches to the new cross-conjugated molecule **13**, which bears vinyl-extended TTF moieties (EBDT) (Scheme 10).[43] Route A begins with the Vilsmeier–Haack reaction of **1t** (Scheme 7), followed by $P(OEt)_3$-mediated coupling of the resulting **12** with **9**. Route B uses a C–H arylation with the 'all-in-one' precursor **14**, which bears an EBDT moiety. Even though precursor **14** and product **13** contain many catalytically poisonous sulfur atoms and electronically flexible π-systems, the four-fold arylation proceeds with acceptable efficiency. Interestingly, the measurement and digital simulation of the cyclic voltammogram of **13** revealed that three pairs of redox waves and suggested that, surprisingly, ten stages of one-electron transfer can be expected in total.



Scheme 10 Synthesis of tetraphenyl TTFs that bear EBDT groups



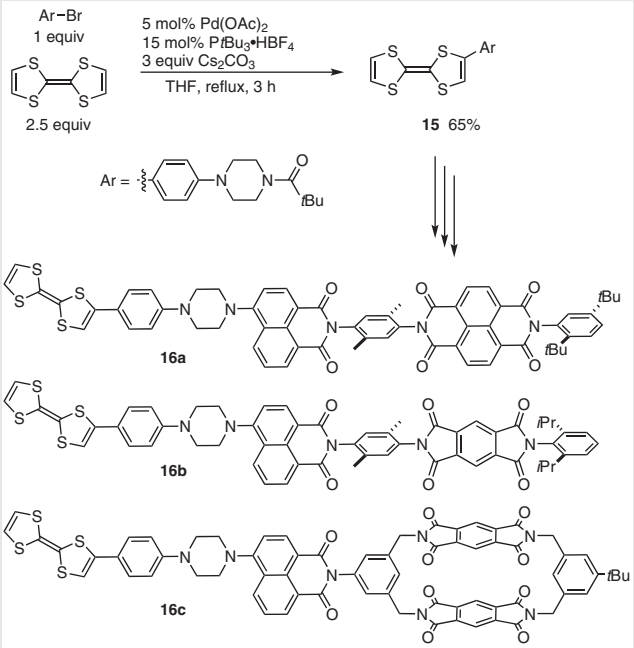
Scheme 11 Synthesis of TTF-azulene hybrids according to Shoji

7 Miscellaneous Examples

Shoji and co-workers have synthesized TTFs that bear 2-azulenyl groups via a direct functionalization of TTF with 2-chloroazulenes (Scheme 11).[46] Due to the optoelectronic nature of the azulene units, **1v** and **1w** show significant spectral change in the visible region under redox conditions.

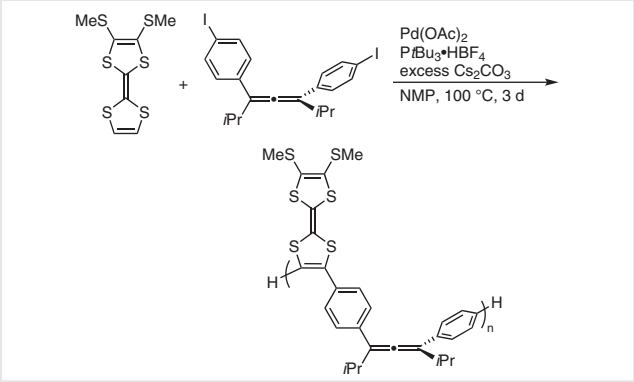
With the C–H arylation method, Wasielewski and co-workers have synthesized covalently linked electron donor-acceptor molecules **16** that consist of TTF as the donor part and a bisimide unit as the acceptor part via intermediate **15** (Scheme 12).[47] Photo-driven intramolecular electron trans-

fer reactions of **16** form well-defined spin-correlated radical pairs, which can find applications in research on bulk-ensemble quantum information processing.



Scheme 12 Synthesis of TTF-bisimide-based donor-acceptor molecules

Hasegawa, Mazaki, and co-workers successfully applied the C–H arylation method to the synthesis of chiral (1,3-diphenylallene)-TTF-based copolymers (Scheme 13) and investigated the chiroptical properties of the resulting polymers.[48] Conventional cross-coupling reactions cannot be applied to the synthesis of such polymers given the difficulties associated with the preparation of doubly metalated 3,4-$(MeS)_2$TTF.



Scheme 13 Co-polymerization of 3,4-$(MeS)_2$TTF and chiral di(iodophenyl)allene

8 Conclusions

The efficient, robust, and operationally facile direct peripheral catalytic C–H arylation of TTF and TTFAQ has paved the way for the creation of TTF-based functional materials. The peripheral arylation of TTF derivatives not only alters their redox properties, but more importantly, allows the installation of peripheral substituents such as carboxylate, pyridine, and formyl, which in turn permits such multiaryl TTFs to assemble into MOFs, COFs, or other supramolecular architectures. Moreover, multiredox molecular systems are readily accessible by integrating dithiole units into one molecule using C–H arylation strategies. Considering the importance of TTF for organic electronics, the peripheral arylation of TTF will continue to facilitate the exploitation of the potential of TTF-based molecules in various fields of chemical science.

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References

(1) (a) Zhang, G.; Zhao, J.; Chow, P. C. Y.; Jiang, K.; Zhang, J.; Zhu, Z.; Zhang, J.; Huang, F.; Yan, H. *Chem. Rev.* **2018**, *118*, 3447. (b) Cheng, P.; Li, G.; Zhang, X.; Yang, Y. *Nat. Photonics* **2018**, *12*, 131. (c) Nielsen, C. B.; Holliday, S.; Chen, H.-Y.; Cryer, S. J.; McCulloch, I. *Acc. Chem. Res.* **2015**, *48*, 2803. (d) Mishra, A.; Bäuerle, P. *Angew. Chem. Int. Ed.* **2012**, *51*, 2020. (e) Lin, Y.; Li, Y.; Zhan, X. *Chem. Soc. Rev.* **2012**, *41*, 4245. (f) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. *Chem. Rev.* **2012**, *112*, 2208. (g) Figueira-Duarte, T. M.; Müllen, K. *Chem. Rev.* **2011**, *111*, 7260. (h) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Adv. Mater.* **2011**, *23*, 268. (i) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem. Int. Ed.* **2008**, *47*, 4070.

(2) (a) Takimiya, K.; Nakano, M. *Bull. Chem. Soc. Jpn.* **2018**, *91*, 121. (b) Turkoglu, G.; Cinar, M. E.; Ozturk, T. *Top. Curr. Chem.* **2017**, *375*, 84. (c) Takimiya, K.; Osaka, I.; Mori, T.; Nakano, M. *Acc. Chem. Res.* **2014**, *47*, 1493. (d) Takimiya, K.; Shinamura, S.; Osaka, I.; Miyazaki, E. *Adv. Mater.* **2011**, *23*, 4347. (e) Iwanaga, T.; Yamada, Y.; Yamauchi, T.; Misaki, Y.; Inoue, M.; Yamada, H. *Chem. Lett.* **2018**, *47*, 760; and references cited therein.

(3) (a) *TTF Chemistry*; Yamada, J.; Sugimoto, T., Ed.; Kodansha-Springer: Tokyo, **2004**. (b) Hasegawa, M.; Iyoda, M. *In Organic Redox Systems*; Nishinaga, T., Ed.; Wiley: New Jersey, **2016**, Chap. 4, 89. (c) Segura, J. L.; Martín, N. *Angew. Chem. Int. Ed.* **2001**, *40*, 1372. (d) Bendikov, M.; Wudl, F.; Perepichka, D. F.

Chem. Rev. **2004**, *104*, 4891. (e) Yamada, J.; Akutsu, H.; Nishikawa, H.; Kikuchi, K. *Chem. Rev.* **2004**, *104*, 5057. (f) Iyoda, M.; Hasegawa, M.; Miyake, Y. *Chem. Rev.* **2004**, *104*, 5085. (g) Jérome, D. *Chem. Rev.* **2004**, *104*, 5565. (h) Gorgues, A.; Hudhomme, P.; Sallé, M. *Chem. Rev.* **2004**, *104*, 5151. (i) Otsubo, T.; Takimiya, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 43. (j) Saito, G.; Yoshida, Y. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1. (k) Misaki, Y. *Sci. Technol. Adv. Mater.* **2009**, *10*, 024301. (l) Canevet, D.; Sallé, M.; Zhang, G.; Zhang, D.; Zhu, D. *Chem. Commun.* **2009**, 2245. (m) Lorcy, D.; Bellec, N.; Fourmigué, M.; Avarvari, N. *Coord. Chem. Rev.* **2009**, *253*, 1398. (n) Bergkamp, J. J.; Decurtins, S.; Liu, S.-X. *Chem. Soc. Rev.* **2015**, *44*, 863. (o) Pop, F.; Avarvari, N. *Chem. Commun.* **2015**, *52*, 7906.

(4) (a) Nishihara, Y. *Applied Cross-Coupling Reactions*; Springer: Heidelberg, **2013**. (b) *Science of Synthesis, Cross Coupling and Heck-Type Reactions, Vol. 1, C–C Cross Coupling Using Organometallic Partners*; Molander, G. A.; Larhed, M.; Wolfe, J. P., Ed.; Thieme: Stuttgart, **2013**. (c) *Metal-Catalyzed Cross-Coupling Reactions and More*; de Meijere, A.; Bräse, S.; Oestreich, M., Ed.; Wiley-VCH: Weinheim, **2014**. (d) Xu, S.; Kim, E. H.; Wei, A.; Negishi, E.-i. *Sci. Tech. Adv. Mater.* **2014**, *15*, 0442010. (e) Zani, L.; Dessì, A.; Franchi, D.; Calamante, M.; Reginato, G.; Mordini, A. *Coord. Chem. Rev.* **2019**, *392*, 177.

(5) For selected books, see: (a) *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Heidelberg, **1999**. (b) Hartung, C. G.; Snieckus, V. In *Modern Arene Chemistry, Chap. 10;* Astruc, D., Ed.; Wiley-VCH: Weinheim, **2002**, 330. (c) *Activation and Functionalization of C–H Bonds*; Goldberg, K. I.; Goldman, A. S., Ed.; Oxford University Press: Oxford, **2004**. (d) *Handbook of C–H Transformations*; Dyker, G., Ed.; Wiley-VCH: Weinheim, **2005**. (e) *Directed Metalation*; Chatani, N., Ed.; Springer: Heidelberg, **2007**. (f) *C–H Activation*; Yu, J.-Q.; Shi, Z., Ed.; Springer: Heidelberg, **2010**. (g) *Science of Synthesis, Cross Coupling and Heck-Type Reactions, Vol. 3, Metal-Catalyzed Heck-Type Reactions and C—C Cross Coupling via C–H Activation*; Molander, G. A.; Larhed, M.; Wolfe, J., Ed.; Thieme: Stuttgart, **2013**. (h) *C–H Bond Activation in Organic Synthesis*; Li, J. J., Ed.; CRC Press: Boca Raton, **2015**. (i) *Science of Synthesis, Catalytic Transformations via C–H Activation, Vol. 1*; Yu, J.-Q., Ed.; Thieme: Stuttgart, **2015**. (j) *Science of Synthesis, Catalytic Transformations via C–H Activation, Vol. 2*; Yu, J.-Q., Ed.; Thieme: Stuttgart, **2015**. (k) *C–H Bond Activation and Catalytic Functionalization, Vol. I*; Dixneuf, P. H.; Doucet, H., Ed.; Springer: Heidelberg, **2016**. (l) *C–H Bond Activation and Catalytic Functionalization, Vol. II*; Dixneuf, P. H.; Doucet, H., Ed.; Springer: Heidelberg, **2016**.

(6) For selected reviews, see: (a) Raj, S.; Ano, Y.; Chatani, N. *Chem. Rev.* **2020**, *120*, 1788. (b) Zhao, Q.; Meng, G.; Nolan, S. P.; Szostak, M. *Chem. Rev.* **2020**, *120*, 1981. (c) Kuang, G.; Liu, G.; Zhang, X.; Lu, N.; Peng, Y.; Xiao, Q.; Zhou, Y. *Synthesis* **2020**, *52*, 993. (d) Gandeepan, P.; Müller, T.; Zell, D.; Cera, G.; Warratz, S.; Ackermann, L. *Chem. Rev.* **2019**, *119*, 2192. (e) Kuroda, Y.; Nakao, Y. *Chem. Lett.* **2019**, *48*, 1092. (f) Murai, M.; Takai, K. *Synthesis* **2019**, *51*, 40. (g) Antermite, D.; Bull, J. A. *Synthesis* **2019**, *51*, 3171. (h) Le Bras, J.; Muzart, J. *Synthesis* **2019**, *51*, 2871. (i) Maraswami, M.; Loh, T.-P. *Synthesis* **2019**, *51*, 1049. (j) Kancherla, S.; Jørgensen, K. B.; Fernández-Ibáñez, M. Á. *Synthesis* **2019**, *51*, 643. (k) Sambiagio, C.; Schönbauer, D.; Blieck, R.; Dao-Huy, T.; Pototschnig, G.; Schaaf, P.; Wiesinger, T.; Zia, M. F.; Wencel-Delord, J.; Besset, T.; Maes, B. U. W.; Schnürch, M. *Chem. Soc. Rev.* **2018**, *47*, 6603. (l) Minami, Y.; Hiyama, T. *Chem. Lett.* **2018**, *47*, 1. (m) Li, Z.-K.; Jia, X.-S.; Yin, L. *Synthesis* **2018**, *50*, 4165. (n) Zhou, W.-J.; Zhang, Y.-H.; Gui, Y.-Y.; Sun, L.; Yu, D.-G. *Synthesis* **2018**, *50*, 3359. (o) Verbitskiy, E. V.; Rusinov, G. L.; Chupakhin, O. N.; Charushin, V. N. *Synthesis* **2018**, *50*, 193. (p) Chatani, N. *Bull. Chem. Soc. Jpn.* **2018**, *91*, 211. (q) Yoshino, T.; Matsunaga, S. *Asian J. Org. Chem.* **2018**, *7*, 1193. (r) Kommagalla, Y.; Chatani, N. *Coord. Chem. Rev.* **2017**, *350*, 117. (s) Shang, R.; Ilies, L.; Nakamura, E. *Chem. Rev.* **2017**, *117*, 9086. (t) Murakami, K.; Yamada, S.; Kaneda, T.; Itami, K. *Chem. Rev.* **2017**, *117*, 9302. (u) Fuse, S.; Morita, T.; Nakamura, H. *Synthesis* **2017**, *49*, 2351. (v) Yoshino, T.; Matsunaga, S. *Adv. Synth. Catal.* **2017**, *359*, 1245. (w) Yamaguchi, J.; Itami, K. *Bull. Chem. Soc. Jpn.* **2017**, *90*, 367. (x) Gensch, T.; Hopkinson, M. N.; Glorius, F.; Wencel-Delord, J. *Chem. Soc. Rev.* **2016**, *45*, 2900. (y) Davies, H. M. L.; Morton, D. *J. Org. Chem.* **2016**, *81*, 343. (z) Bheeter, C. B.; Chen, L.; Soulé, J.-F.; Doucet, H. *Catal. Sci. Technol.* **2016**, *6*, 2005. (aa) Miao, J.; Ge, H. *Eur. J. Org. Chem.* **2015**, 7859. (ab) Daugulis, O.; Roane, J.; Tran, L. D. *Acc. Chem. Res.* **2015**, *48*, 1053. (ac) Chen, Z.; Wang, B.; Zhang, J.; Yu, W.; Liu, Z.; Zhang, Y. *Org. Chem. Front.* **2015**, *2*, 1107. (ad) Iwai, T.; Sawamura, M. *ACS Catal.* **2015**, *5*, 5031. (ae) Castro, L. C. M.; Chatani, N. *Chem. Lett.* **2015**, *44*, 410. (af) Rossi, R.; Bellina, F.; Lessi, M.; Manzini, C. *Adv. Synth. Catal.* **2014**, *356*, 17. (ag) El Kazzouli, S.; Koubachi, J.; El Brahmi, N.; Guillaumet, G. *RSC Adv.* **2015**, *5*, 15292. (ah) Giri, R.; Thapa, S.; Kafle, A. *Adv. Synth. Catal.* **2014**, *356*, 1395. (ai) Rossi, R.; Bellina, F.; Lessi, M.; Manzini, C.; Perego, L. A. *Synthesis* **2014**, *46*, 2833. (aj) Rouquet, G.; Chatani, N. *Angew. Chem. Int. Ed.* **2013**, *52*, 11726. (ak) Shibahara, F.; Murai, T. *Asian J. Org. Chem.* **2013**, *2*, 624. (al) Nishino, M.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 4457. (am) Yamaguchi, J.; Muto, K.; Itami, K. *Eur. J. Org. Chem.* **2013**, 19. (an) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879. (ao) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788. (ap) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (aq) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740. (ar) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (as) Nakao, Y. *Synthesis* **2011**, 3209. (at) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (au) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (av) Satoh, T.; Miura, M. *Chem. Eur. J.* **2010**, *16*, 11212. (aw) Roger, J.; Gottumukkala, A. L.; Doucet, H. *ChemCatChem* **2010**, *2*, 20. (ax) Kulkarni, A. A.; Daugulis, O. *Synthesis* **2009**, 4087. (ay) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242. (az) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2009**, *48*, 5094. (ba) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem. Int. Ed.* **2009**, *48*, 9792. (bb) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, 3013. (bc) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (bd) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. (be) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3. (bf) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826. (bg) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (bh) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(7) For reviews on C–H functionalization reactions for the synthesis of discrete π-conjugated materials, see: (a) Ito, H.; Segawa, Y.; Murakami, K.; Itami, K. *J. Am. Chem. Soc.* **2019**, *141*, 3. (b) Ito, H.; Ozaki, K.; Itami, K. *Angew. Chem. Int. Ed.* **2017**, *56*, 11144. (c) Hiroto, S.; Miyake, Y.; Shinokubo, H. *Chem. Rev.* **2017**, *117*, 2910. (d) Besson, T.; Fruit, C. *Synthesis* **2016**, *48*, 3879. (e) Shi, Y.; Ni, Z.; Zhen, Y.; Dong, H.; Hu, W. *Chin. J. Org. Chem.* **2016**, *36*, 1741. (f) Kuninobu, Y.; Sueki, S. *Synthesis* **2015**, *47*, 3823. (g) Shinokubo, H. *Proc. Jpn. Acad., Ser. B* **2014**, *90*, 1. (h) Wencel-Delord, J.; Glorius, F. *Nat. Chem.* **2013**, *5*, 369. (i) Yorimitsu, H.;

Osuka, A. *Asian J. Org. Chem.* **2013**, *2*, 356. (j) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 8960. (k) Shinokubo, H.; Osuka, A. *Chem. Commun.* **2009**, 1011.

(8) For reviews on C–H arylation reactions for the synthesis of polymers, see: (a) Amna, B.; Siddiqi, H. M.; Hassan, A.; Ozturk, T. *RSC Adv.* **2020**, *10*, 4322. (b) Blaskovits, J. T.; Leclerc, M. *Macromol. Rapid Commun.* **2019**, *40*, 1800512. (c) Kuwabara, J.; Kinbara, T. *Bull. Chem. Soc. Jpn.* **2019**, *92*, 152. (d) Wakioka, M.; Ozawa, F. *Asian J. Org. Chem.* **2018**, *7*, 1206. (e) Gobalasingham, N. S.; Thompson, B. C. *Prog. Polym. Sci.* **2018**, *83*, 135. (f) Yang, Y.; Nishiura, M.; Wang, H.; Hou, Z. *Coord. Chem. Rev.* **2018**, *376*, 506. (g) Bura, T.; Blaskovits, J. T.; Leclerc, M. *J. Am. Chem. Soc.* **2016**, *138*, 10056. (h) Pouliot, J.-R.; Grenier, F.; Blaskovits, J. T.; Beaupré, S.; Leclerc, M. *Chem. Rev.* **2016**, *116*, 14225. (i) Okamoto, K.; Zhang, J.; Housekeeper, J. B.; Marder, S. R.; Luscombe, C. K. *Macromolecules* **2013**, *46*, 8059. (j) Mercier, L. G.. Leclerc M. *Acc. Chem. Res.* **2013**, *46*, 1597.

(9) For selected examples, see: (a) Iyoda, M.; Kuwatani, Y.; Ueno, N.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1992**, 158. (b) Iyoda, M.; Fukuda, M.; Yoshida, M.; Sasaki, S. *Chem. Lett.* **1994**, 2369. (c) Kux, U.; Iyoda, M. *Chem. Lett.* **1994**, 2327. (d) Iyoda, M.; Fukuda, M.; Sasaki, S.; Yoshida, M. *Synth. Met.* **1995**, *70*, 1171. (e) Nakatsuji, S.; Satoki, S.; Suzuki, K.; Enoki, T.; Kinoshita, N.; Anzai, H. *Synth. Met.* **1995**, *71*, 1819. (f) Skabara, P. J.; Müllen, K.; Bryce, M. R.; Howard, J. A. K.; Batsanov, A. S. *J. Mater. Chem.* **1998**, *8*, 1719. (g) Nakazaki, J.; Matsushita, M. M.; Izuoka, A.; Sugawara, T. *Tetrahedron Lett.* **1999**, *40*, 5027. (h) Iyoda, M.; Hasegawa, M.; Kuwatani, Y.; Nishikawa, H.; Fukami, K.; Nagase, S.; Yamamoto, G. *Chem. Lett.* **2001**, 1146. (i) Moore, A. J.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K.; Khodorkovsky, V.; Shapiro, L.; Shames, A. *Eur. J. Org. Chem.* **2001**, 73. (j) Bouguessa, S.; Gouasmia, A. K.; Golhen, S.; Ouahab, L.; Fabre, J. M. *Tetrahedron Lett.* **2003**, *44*, 9275. (k) Murata, T.; Morita, Y.; Fukui, K.; Sato, K.; Shiomi, D.; Takui, T.; Maesato, M.; Yamochi, H.; Saito, G.; Nakasuji, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 6343. (l) Nishida, S.; Morita, Y.; Fukui, K.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 7277. (m) Wang, L.; Zhang, B.; Zhang, J. *Inorg. Chem.* **2006**, *45*, 6860. (n) Kanato, H.; Narutaki, M.; Takimiya, K.; Otsubo, T.; Harima, Y. *Chem. Lett.* **2006**, *35*, 668. (o) Chahma, M.; Wang, X.; van der Est, A.; Pilkington, M. *J. Org. Chem.* **2006**, *71*, 2750. (p) Lamère, J. F.; Malfant, I.; Sornia-Saquet, A.; Lacroix, P. G.; Fabre, J. M.; Kaboub, L.; Abbaz, T.; Gouasmia, A. K.; Asselberghs, I.; Clays, K. *Chem. Mater.* **2007**, *19*, 805. (q) Abbz, T.; Gouasmia, A.-K.; Fujiwara, H.; Hiraoka, T.; Sugimoto, T.; Taillefer, M.; Fabre, J.-M. *Synth. Met.* **2007**, *157*, 508. (r) Murata, T.; Morita, Y.; Yakiyama, Y.; Fukui, K.; Yamochi, H.; Saito, G.; Nakasuji, K. *J. Am. Chem. Soc.* **2007**, *129*, 10837. (s) Fujiwara, H.; Sugishima, Y.; Tsujimoto, K. *Tetrahedron Lett.* **2008**, *49*, 7200. (t) Wang, Y.; Cui, S.; Li, B.; Zhang, J.; Zhang, Y. *Cryst. Growth Des.* **2009**, *9*, 3855. (u) Carmieli, R.; Mi, Q.; Ricks, A. B.; Giacobbe, E. M.; Mickley, S. M.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2009**, *131*, 8372. (v) Riobé, F.; Avarvari, N.; Grosshans, P.; Sidorenkova, H.; Berclaz, T.; Geoffroy, M. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9650. (w) Bouguessa, S.; Gouasmia, A. K.; Ouahab, L.; Golhen, S.; Fabre, J.-M. *Synth. Met.* **2010**, *160*, 361. (x) Lee, S. C.; Ueda, A.; Kamo, H.; Takahashi, K.; Uruichi, M.; Yamamoto, K.; Yakushi, K.; Nakao, A.; Kumai, R.; Kobayashi, K.; Nakao, H.; Murakami, Y.; Mori, H. *Chem. Commun.* **2012**, *48*, 8673. (y) Pointillart, F.; Bourdolle, A.; Cauchy, T.; Maury, O.; Gal, Y. L.; Golhen, S.; Cador, O.; Ouahab, L. *Inorg. Chem.* **2012**, *51*, 978. (z) Hasegawa, M.; Daigoku, K.; Hashimoto, K.; Nishikawa, H.; Iyoda, M. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 51. (aa) Poddutoori, P. K.; Zarrabi, N.; Moiseev, A. G.; Gumbau-abrisa, R.; Vassiliev, S.; van der Est, A. *Chem. Eur. J.* **2013**, *19*, 3148. (ab) Tsujimoto, K.; Ogasawara, R.; Fujiwara, H. *Tetrahedron Lett.* **2013**, *54*, 1251. (ac) Lee, S. C.; Ueda, A.; Nakao, A.; Kumai, R.; Nakao, H.; Murakami, Y.; Mori, H. *Chem. Eur. J.* **2014**, *20*, 1909. (ad) Tsunashima, R.; Iwamoto, Y.; Baba, Y.; Kato, C.; Ichihashi, K.; Nishihara, S.; Inoue, K.; Ishiguro, K.; Song, Y.-F.; Akutagawa, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 11228. (ae) Hayward, J. J.; Gumbau-Brisa, R.; Alberola, A.; Clarke, C. S.; Rawson, J. M.; Pilkington, M. *CrystEngComm* **2014**, *16*, 7268. (af) Kobayakawa, K.; Hasegawa, M.; Sasaki, H.; Endo, J.; Matsuzawa, H.; Sako, K.; Yoshida, J.; Mazaki, Y. *Chem. Asian J.* **2014**, *9*, 2751. (ag) Geng, Y.; Pop, F.; Yi, C.; Avarvari, N.; Grätzel, M.; Decurtins, S.; Liu, S.-X. *New. J. Chem.* **2014**, *38*, 3269. (ah) Ayadi, A.; Alamy, A. E.; Alévêque, O.; Allain, M.; Zouari, N.; Bouachrine, M.; El-Ghayoury, A. *Beilstein J. Org. Chem.* **2015**, *11*, 1379. (ai) Nafe, J.; Auras, F.; Karaghiosoff, K.; Bein, T.; Knochel, P. *Org. Lett.* **2015**, *17*, 5356. (aj) Nafe, J.; Knochel, P. *Synthesis* **2016**, *48*, 103. (ak) Okino, R.; Yamaguchi, M.; Fujiwara, H. *Dalton Trans.* **2017**, *46*, 4912. (al) Kanetou, T.; Tsunashima, R.; Hoshino, N.; Akutagawa, T. *RSC Adv.* **2017**, *7*, 6236. (am) Kishi, Y.; Cornet, L.; Pointillart, F.; Riobé, F.; Lefeuvre, B.; Cador, O.; Guennic, B. L.; Maury, O.; Fujiwara, H.; Ouahab, L. *Eur. J. Org. Chem.* **2018**, 458. (an) Stetsiuk, O.; Petrusenko, S. R.; El-Ghayoury, A.; Kokozay, V. N.; Avarvari, N. *Inorg. Chim. Acta* **2018**, *475*, 172. (ao) Zarrabi, N.; Lim, G. N.; Bayard, B. J.; D'Souza, F.; Poddutoori, P. K. *Phys. Chem. Chem. Phys.* **2019**, *21*, 19612. (ap) Yoshimura, A.; Kimura, H.; Handa, A.; Hashimoto, N.; Yano, M.; Mori, S.; Shirahata, T.; Hayashi, M.; Misaki, Y. *Tetrahedron Lett.* **2020**, *61*, 151724.

(10) Mitamura, Y.; Yorimitsu, H.; Oshima, K.; Osuka, A. *Chem. Sci.* **2011**, *2*, 2017.

(11) (a) Dyker, G.; Heiermann, J.; Miura, M.; Inoh, J.-I.; Pivsa-Art, S.; Satoh, T.; Nomura, M. *Chem. Eur. J.* **2000**, *6*, 3426. (b) Miura, M.; Pivsa-Art, S.; Dyker, G.; Heiermann, J.; Satoh, T.; Nomura, M. *Chem. Commun.* **1998**, 1889.

(12) Dolphin, D.; Pegg, W.; Wirz, P. *Can. J. Chem.* **1974**, *52*, 4078.

(13) (a) Lapointe, D.; Fagnou, K. *Chem. Lett.* **2010**, *39*, 1118. (b) Lafrance, M.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 16496. (c) García-Cuadrado, D.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 1066. (d) García-Cuadrado, D.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2007**, *129*, 6880.

(14) Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295.

(15) (a) Lengthy synthesis: Charlton, A.; Underhill, A. E.; Williams, G.; Kalaji, M.; Murphy, P. J.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. A. *Chem. Commun.* **1996**, 2423. (b) Condensation of diarylacetylene with carbon disulfide under 4500 atm: Nagawa, T.; Zama, Y.; Okamoto, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2035.

(16) Ueno, R.; Fujino, D.; Yorimitsu, H.; Osuka, A. *Chem. Eur. J.* **2013**, *19*, 7156.

(17) (a) Sun, L.; Campbell, M. G.; Dincă, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 3566. (b) Wang, H.-Y.; Cui, L.; Xie, J.-Z.; Leong, C. F.; D'Alessandro, D. M.; Zuo, J.-L. *Coord. Chem. Rev.* **2017**, *345*, 342. (c) Jana, A.; Bähring, S.; Ishida, M.; Goeb, S.; Canevet, D.; Sallé, M.; Jeppesen, J. O.; Sessler, J. L. *Chem. Soc. Rev.* **2018**, *47*, 5614. (d) Calbo, J.; Golomb, M. J.; Walsh, A. *J. Mater. Chem. A* **2019**, *7*, 16571.

(18) Narayan, T. C.; Miyakai, T.; Seki, S.; Dincă, M. *J. Am. Chem. Soc.* **2012**, *134*, 12932.

(19) (a) Park, S. S.; Hontz, E. R.; Sun, L.; Hendon, C. H.; Walsh, A.; Van Voorhis, T.; Dincă, M. *J. Am. Chem. Soc.* **2015**, *137*, 1774. (b) Chen, B.; Lv, Z.-P.; Leong, C. F.; Zhao, Y.; D'Alessandro, D. M.; Zuo, J.-L. *Cryst. Growth. Des.* **2015**, *15*, 1861. (c) Sun, L.; Park, S. S.; Sheberla, D.; Dincă, M. *J. Am. Chem. Soc.* **2016**, *138*, 14772.

(d) Park, S. S.; Hendon, C. H.; Fielding, A. J.; Walsh, A.; O'Keeffe, M.; Dincă, M. *J. Am. Chem. Soc.* **2017**, *139*, 3619. (e) Su, J.; Yuan, S.; Wang, H.-Y.; Huang, L.; Ge, J.-Y.; Joseph, E.; Qin, J.; Cagin, T.; Zuo, J.-L.; Zhou, H.-C. *Nat. Commun.* **2017**, *8*, 2008. (f) Park, S. S.; Rieth, A. J.; Hendon, C. H.; Dincă, M. *J. Am. Chem. Soc.* **2018**, *140*, 2016. (g) Souto, M.; Romero, J.; Calbo, J.; Vitórica-Yrezábal, I. J.; Zafra, J. L.; Casado, J.; Ortí, E.; Walsh, A.; Espallargas, G. M. *J. Am. Chem. Soc.* **2018**, *140*, 10562. (h) Souto, M.; Santiago-Portillo, A.; Palomino, M.; Vitórica-Yrezábal, I. J.; Vieira, B. J. C.; Waerenborgh, J. C.; Valencia, S.; Navalón, S.; Rey, F.; García, H.; Mínguez Espallargas, G. *Chem. Sci.* **2018**, *9*, 2413. (i) Leong, C. F.; Wang, C.-H.; Ling, C. D.; D'Alessandro, D. M. *Polyhedron* **2018**, *154*, 334. (j) Su, J.; Hu, T.-H.; Murase, R.; Wang, H.-Y.; D'Alessandro, D. M.; Kurmoo, M.; Zuo, J.-L. *Inorg. Chem.* **2019**, *58*, 3698. (k) Pattengale, B.; Neu, J.; Ostresh, S.; Hu, G.; Spies, J. A.; Okabe, R.; Brudvig, G. W.; Schmuttenmaer, C. A. *J. Am. Chem. Soc.* **2019**, *141*, 9793. (l) Castells-Gil, J.; Mañas-Valero, S.; Vitórica-Yrezábal, I. J.; Ananias, D.; Rocha, J.; Santiago, R.; Bromley, S. T.; Baldoví, J. J.; Coronado, E.; Souto, M.; Mínguez Espallargas, G. *Chem. Eur. J.* **2019**, *25*, 12636. (m) Cadiau, A.; Xie, L. S.; Kolobov, N.; Shkurenko, A.; Qureshi, M.; Tchalala, M. R.; Park, S. S.; Bavykina, A.; Eddaoudi, M.; Dincă, M.; Henden, C. H.; Gascon, J. *Chem. Mater.* **2020**, *32*, 97. (n) Wang, F.; Wang, J.; Maehrlein, S. F.; Ma, Y.; Liu, F.; Zhu, X.-Y. *J. Phys. Chem. Lett.* **2020**, *11*, 762. (o) Su, J.; He, W.; Li, X.-M.; Sun, L.; Wang, H.-Y.; Lan, Y.-Q.; Ding, M.; Zuo, J.-L. *Matter* **2020**, *2*, 711.

(20) (a) Hisaki, I.; Affendy, E. N. Q.; Tohnai, N. *CrystEngComm* **2017**, *19*, 4892. (b) Zheng, X.; Xiao, N.; Long, Z.; Wang, L.; Ye, F.; Fang, J.; Shen, L.; Xiao, X. *Synth. Met.* **2020**, *263*, 116365.

(21) Lv, Z.-P.; Chen, B.; Wang, H.-Y.; Wu, Y.; Zuo, J.-L. *Small* **2015**, *11*, 3597.

(22) Liu, L.; Zhou, S.; Zhao, C.; Jiu, T.; Bi, F.; Jian, H.; Zhao, M.; Zhang, G.; Wang, L.; Li, F.; Xiao, X. *J. Energy Chem.* **2020**, *42*, 210.

(23) Vajpayee, V.; Bivaud, S.; Goeb, S.; Croué, V.; Allain, M.; Popp, B. V.; Garci, A.; Therrien, B.; Sallé, M. *Organometallics* **2014**, *33*, 1651. In this paper, ruthenium complexes of tetra(3-pyridyl) **1m** were also reported.

(24) Goeb, S.; Bivaud, S.; Croué, V.; Vajpayee, V.; Allain, M.; Sallé, M. *Materials* **2014**, *7*, 611.

(25) Tzeng, B.-C.; Hsiao, Y.-J.; Lee, G.-H.; Wang, H.-Y.; Leong, C. F.; D'Alessandro, D. M.; Zuo, J.-L. *Dalton Trans.* **2019**, *48*, 7946.

(26) (a) Wang, H.-Y.; Wu, Y.; Leong, C. F.; D'Alessandro, D. M.; Zuo, J.-L. *Inorg. Chem.* **2015**, *54*, 10766. (b) Wang, H.-Y.; Ge, J.-Y.; Hua, C.; Jiao, C.-Q.; Wu, Y.; Leong, C. F.; D'Alessandro, D. M.; Liu, T.; Zuo, J.-L. *Angew. Chem. Int. Ed.* **2017**, *56*, 5465. (c) Wang, H.-Y.; Su, J.; Ma, J.-P.; Yu, F.; Leong, C. F.; D'Alessandro, D. M.; Kurmoo, M.; Zuo, J.-L. *Inorg. Chem.* **2019**, *58*, 8657. (d) Yu, Q.; Su, J.; Ma, J.-P.; Leong, C. F.; D'Alessandro, D. M.; Wang, H.-Y.; Kurmoo, M.; Zuo, J.-L. *Cryst. Growth Des.* **2019**, *19*, 3012.

(27) Jin, S.; Sakurai, T.; Kowalczyk, T.; Dalapati, S.; Xu, F.; Wei, H.; Chen, X.; Gao, J.; Seki, S.; Irle, S.; Jiang, D. *Chem. Eur. J.* **2014**, *20*, 14608.

(28) Ding, H.; Li, Y.; Hu, H.; Sun, Y.; Wang, J.; Wang, C.; Wang, C.; Zhang, G.; Wang, B.; Xu, W.; Zhang, D. *Chem. Eur. J.* **2014**, *20*, 14614.

(29) Cai, S.-L.; Zhang, Y.-B.; Pun, A. B.; He, B.; Yang, J.; Toma, F. M.; Sharp, I. D.; Yaghi, O. M.; Fan, J.; Zheng, S.-R.; Zhang, W.-G.; Liu, Y. *Chem. Sci.* **2014**, *5*, 4693.

(30) (a) Dong, W.-l.; Wang, L.; Ding, H.-m.; Zhao, L.; Wang, D.; Wang, C.; Wan, L.-J. *Langmuir* **2015**, *31*, 11755. (b) Dong, W.-L.; Li, S.-Y.; Yue, J.-Y.; Wang, C.; Wang, D.; Wan, L.-J. *Phys. Chem. Chem. Phys.* **2016**, *18*, 17356.

(31) Li, H.; Chang, J.; Li, S.; Guan, X.; Li, D.; Li, C.; Tang, L.; Xue, M.; Yan, Y.; Valtchev, V.; Qiu, S.; Fang, Q. *J. Am. Chem. Soc.* **2019**, *141*, 13324.

(32) (a) Lu, M.; Liu, J.; Li, Q.; Zhang, M.; Liu, M.; Wang, J.-L.; Yuan, D.-Q.; Lan, Y.-Q. *Angew. Chem. Int. Ed.* **2019**, *58*, 12392. (b) Zhu, H.-J.; Lu, M.; Wang, Y.-R.; Yao, S.-J.; Zhang, M.; Kan, Y.-H.; Liu, J.; Chen, Y.; Li, S.-L.; Lan, Y.-Q. *Nat. Commun.* **2020**, *11*, 497. (c) Wu, Q.; Xie, R.-K.; Mao, M.-J.; Chai, G.-L.; Yi, J.-D.; Zhao, S.-S.; Huang, Y.-B.; Cao, R. *ACS Energy Lett.* **2020**, *5*, 1005.

(33) Cai, S.; Sun, B.; Li, X.; Yan, Y.; Navarro, A.; Garzón-Ruiz, A.; Mao, H.; Chatterjee, R.; Yano, J.; Zhu, C.; Reimer, J. A.; Zheng, S.; Fan, J.; Zhang, W.; Liu, Y. *ACS Appl. Mater. Interfaces* **2020**, *12*, 19054.

(34) Zhang, Y.-C.; Zhou, Y.; Li, Z.-T.; Zhang, D.-W. *Tetrahedron* **2015**, *71*, 605.

(35) (a) Akiba, K.-y.; Ishikawa, K.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2674. (b) Bryce, M. R.; Moore, A. J. *Synth. Met.* **1988**, *25*, 203. (c) Bryce, M. R.; Moore, A. J.; Hasan, M.; Ashwell, G. J.; Fraser, A. T.; Clegg, W.; Hursthouse, M. B.; Karaulov, A. I. *Angew. Chem. Int. Ed.* **1990**, *29*, 1450. (d) Bryce, M. R.; Finn, T.; Moore, A. J.; Batsanov, A. S.; Howard, J. A. K. *Eur. J. Org. Chem.* **2000**, 51. (e) Jones, A. E.; Christensen, C. A.; Perepichka, D. F.; Batsanov, A. S.; Beeby, A.; Low, P. J.; Bryce, M. R.; Parker, A. W. *Chem. Eur. J.* **2001**, *7*, 973. (f) Barthelmes, K.; Sittig, M.; Winter, A.; Schubert, U. S. *Eur. J. Inorg. Chem.* **2017**, 3698. (g) Hachem, H.; Vacher, A.; Dorcet, V.; Lorcy, D. *Organometallics* **2017**, *36*, 2208.

(36) (a) Martín, N.; Sańchez, L.; Herranz, M. Á.; Illescas, B.; Guldi, D. M. *Acc. Chem. Res.* **2007**, *40*, 1015. (b) Wenger, S.; Bouit, P.-A.; Chen, Q.; Teuscher, J.; Di Censo, D.; Humphry-Baker, R.; Moser, J.-E.; Delgado, J. L.; Martín, N.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2010**, *132*, 5164.

(37) (a) Ogi, D.; Fujita, Y.; Kato, M.; Yamauchi, T.; Shirahata, T.; Yao, M.; Misaki, Y. *Eur. J. Org. Chem.* **2019**, 2725. (b) Yamauchi, T.; Kato, M.; Shirahata, T.; Yao, M.; Misaki, Y. *Chem. Lett.* **2019**, *48*, 1507.

(38) For other uses, see: (a) Hardouin-Lerouge, M.; Chesneau, B.; Allain, M.; Hudhomme, P. *J. Org. Chem.* **2012**, *77*, 2441. (b) Isla, H.; Gallego, M.; Pérez, E. M.; Viruela, R.; Ortí, E.; Martín, N. *J. Am. Chem. Soc.* **2010**, *132*, 1772.

(39) Bivaud, S.; Goeb, S.; Croué, V.; Dron, P. I.; Allain, M.; Sallé, M. *J. Am. Chem. Soc.* **2013**, *135*, 10018.

(40) (a) Bivaud, S.; Goeb, S.; Croué, V.; Allain, M.; Pop, F.; Sallé, M. *Beilstein J. Org. Chem.* **2015**, *11*, 966. (b) Croué, V.; Goeb, S.; Szalóki, G.; Allain, M.; Sallé, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 1746. (c) Szalóki, G.; Croué, V.; Allain, M.; Goeb, S.; Sallé, M. *Chem. Commun.* **2016**, *52*, 10012. (d) Szalóki, G.; Croué, V.; Carré, V.; Aubriet, F.; Alévêque, O.; Levillain, E.; Allain, M.; Aragó, J.; Ortí, E.; Goeb, S.; Sallé, M. *Angew. Chem. Int. Ed.* **2017**, *56*, 16272. (e) Colomban, C.; Szalóki, G.; Allain, M.; Gómez, L.; Goeb, S.; Sallé, M.; Costas, M.; Ribas, X. *Chem. Eur. J.* **2017**, *23*, 3016. (f) Szalóki, G.; Krykun, S.; Croué, V.; Allain, M.; Morille, Y.; Aubriet, F.; Carré, V.; Voitenko, Z.; Goeb, S.; Sallé, M. *Chem. Eur. J.* **2018**, *24*, 11273.

(41) Yoshimura, A.; Henmi, K.; Kimura, H.; Sakakibara, R.; Ochi, R.; Shirahata, T.; Yorimitsu, H.; Misaki, Y. *Synthesis* **2020**, *52*, in press; DOI: 10.1055/s-0040-1707177.

(42) Gordillo, M. A.; Benavides, P. A.; Panda, D. K.; Saha, S. *ACS Appl. Mater. Interfaces* **2020**, *12*, 12955.

(43) Yoshimura, A.; Kimura, H.; Kagawa, K.; Yoshioka, M.; Itou, T.; Vasu, D.; Shirahata, T.; Yorimitsu, H.; Misaki, Y. *Beilstein J. Org. Chem.* **2020**, *16*, 974.

(44) Gholami, M.; Tykwinski, R. R. *Chem. Rev.* **2006**, *106*, 4997.

(45) (a) Sugimoto, T.; Awaji, H.; Misaki, Y.; Yoshida, Z.; Kai, Y.; Nakagawa, H.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 5792. (b) Sugimoto, T.; Misaki, Y.; Arai, Y.; Yamamoto, Y.; Yoshida, Z.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 628. (c) Misaki, Y.; Matsumura, Y.; Sugimoto, T.; Yoshida, Z.-i. *Tetrahedron Lett.* **1989**, *30*, 5289. (d) Amaresh, R. R.; Liu, D.; Konovalova, T.; Lakshmikantham, M. V.; Cava, M. P.; Kispert, L. D. *J. Org. Chem.* **2001**, *66*, 7757. (e) Rajagopal, D.; Lakshmikantham, M. V.; Cava, M. P. *Org. Lett.* **2002**, *4*, 2581. (f) Coffin, M. A.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. *J. Chem. Soc., Chem. Commun.* **1993**, 552. (g) Bryce, M. R.; Coffin, M. A.; Skabara, P. J.; Moore, A. J.; Batsanov, A. S.; Howard, J. A. K. *Chem. Eur. J.* **2000**, *6*, 1955. (h) Hasegawa, M.; Fujioka, A.; Kubo, T.; Honda, T.; Miyamoto, H.; Misaki, Y. *Chem. Lett.* **2008**, *37*, 474. (i) Horiuchi, H.; Misaki, Y. *Chem. Lett.* **2010**, *39*, 989. (j) Nishiwaki, M.; Tezuka, M.; Shirahata, T.; Misaki, Y. *Chem. Lett.* **2011**, *40*, 467. (k) Yamauchi, T.; Shibata, Y.; Aki, T.; Yoshimura, A.; Yao, M.; Misaki, Y. *Chem. Lett.* **2018**, *47*, 1176.

(46) Shoji, T.; Araki, T.; Sugiyama, S.; Ohta, A.; Sekiguchi, R.; Ito, S.; Okujima, T.; Toyota, K. *J. Org. Chem.* **2017**, *82*, 1657.

(47) (a) Nelson, J. N.; Krzyaniak, M. D.; Horwitz, N. E.; Rugg, B. K.; Phelan, B. T.; Wasielewski, M. R. *J. Phys. Chem. A* **2017**, *121*, 2241. (b) Nelson, J. N.; Zhang, J.; Zhou, J.; Rugg, B. K.; Krzyaniak, M. D.; Wasielewski, M. R. *J. Phys. Chem. A* **2018**, *122*, 9392.

(48) Hasegawa, M.; Endo, J.; Iwata, S.; Shimasaki, T.; Mazaki, Y. *Beilstein J. Org. Chem.* **2015**, *11*, 972.