Chemical Science

EDGE ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: Chem. Sci., 2017, 8, 4527

Received 14th March 2017
Accepted 6th April 2017

DOI: 10.1039/c7sc01162h

rsc.li/chemical-science

Versatile telluracycle synthesis *via* the sequential electrophilic telluration of C(sp^2)–Zn and C(sp^2)–H bonds†

Bin Wu, Melvina, Xiangyang Wu, Edwin Kok Lee Yeow and Naohiko Yoshikai *

We report herein a new approach for the synthesis of tellurium-bridged aromatic compounds based on the sequential electrophilic telluration of C(sp^2)–Zn and C(sp^2)–H bonds with tellurium(IV) chlorides. A combination of transition metal-catalyzed (migratory) arylmetalation of alkynes and sequential telluration allows for the expedient construction of a library of functionalized benzo[*b*]tellurophenes. Furthermore, a variety of heteroarene-fused benzotellurophenes and other novel tellurium-embedded polycyclic aromatics can be readily synthesized from the corresponding 2-iodoheterobiaryls.

Introduction

Tellurophene has gained growing interest as a structural element of polymeric materials for organic electronics and other applications with features such as narrow band gaps, low LUMO levels, high charge carrier mobilities, the redox capability of Te, and Te–Te interactions.[1,2] Studies of tellurophene-containing small molecules focused on their redox and photochemical reactivity,[3] photoluminescence properties,[4] and anion recognition ability through chalcogen bonds[5] have also emerged (Chart 1). In these studies, the synthesis and functionalization of substituted tellurophenes have been achieved using a variety of methods, such as the cyclization of 1,3-diyne with sodium telluride[6] and zirconacyclopentadiene transfer to $TeCl_2$·bpy.[2c,7]

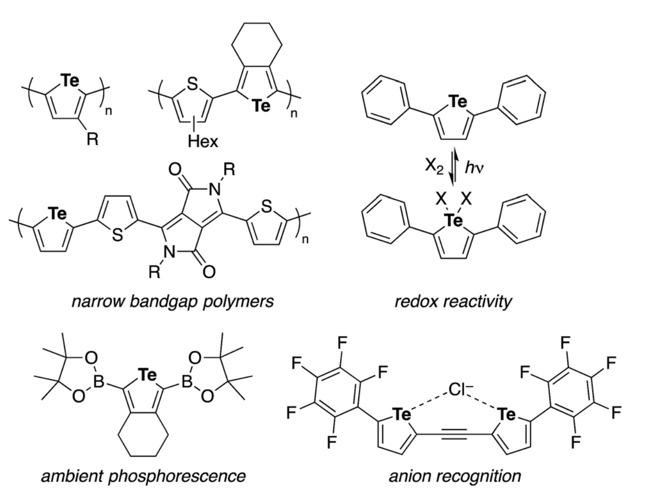
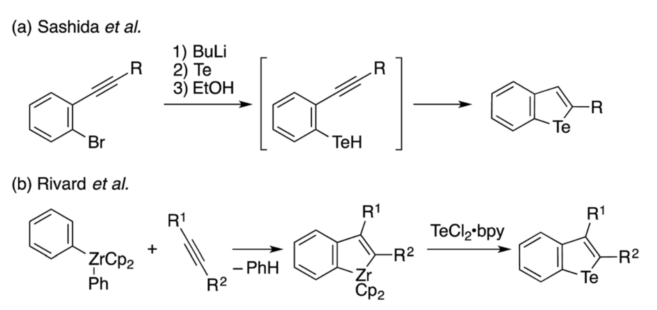


Chart 1 Examples of tellurophene-based polymers and small molecules.

In contrast to the extensive studies on tellurophenes, benzo-fused tellurophenes and other tellurium-bridged aromatic systems, unlike their sulfur and selenium congeners,[8] have been much less explored.[4b,9] Indeed, there remains a scarcity of synthetic methods for making such tellurium compounds,[10] as the C–S and C–Se bond-forming methods can not always be extended to C–Te bond formation.[11] Sashida developed a benzo[*b*]tellurophene synthetic route *via* the trapping of *ortho*-alkynylaryllithium with elemental tellurium and subsequent intramolecular cyclization (Scheme 1a).[12] Rivard extended the zirconacycle transfer method to achieve benzo[*b*]tellurophene synthesis *via* a zirconaindene intermediate (Scheme 1b).[4b] However, these methods may not be suitable for the rapid preparation of diversely functionalized benzotellurophenes. Likewise, synthetic methods for making other tellurium-bridged (hetero)aromatic systems remain scarce.[9a,13]



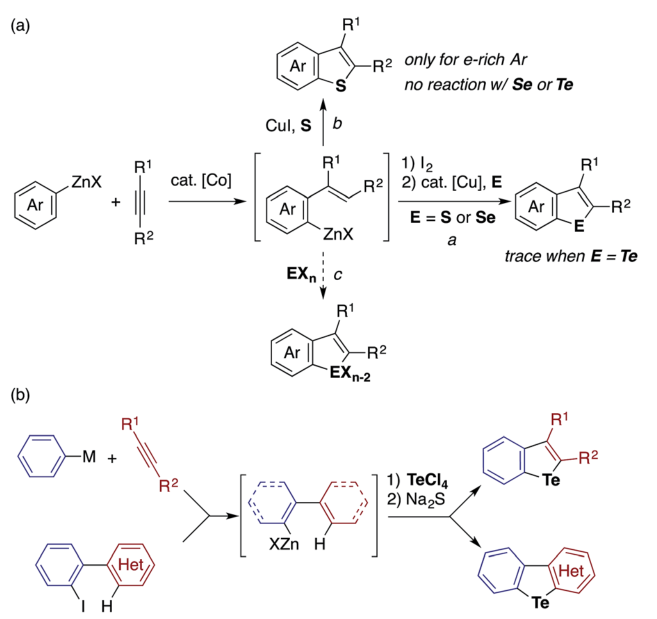
Scheme 1 Reported synthetic approaches for benzotellurophenes.

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore. E-mail: nyoshikai@ntu.edu.sg

† Electronic supplementary information (ESI) available. CCDC 1523262–1523264. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc01162h

Recently, we developed methods for the synthesis of benzothiophenes and benzoselenophenes based on the cobalt-catalyzed addition of an arylzinc reagent to an alkyne involving 1,4-cobalt migration (migratory arylzincation), which affords an *ortho*-alkenylarylzinc species as a key intermediate (Scheme 2a).[14,15] The iodination of this zinc intermediate is followed by the reaction of the resulting aryl iodide and elemental sulfur or selenium under copper-catalyzed Ullmann-type conditions, allowing for the two-step synthesis of benzothiophene or benzoselenophene (route a). Only when an electron-rich arylzinc reagent is employed can the zinc intermediate be directly converted to the corresponding benzothiophene using stoichiometric CuI and elemental sulfur (route b). Our attempt to synthesise benzotellurophene using elemental tellurium *via* route a or b was futile.

We envisioned that the above limitation in our previous benzochalcogenophene synthesis could be removed using stronger chalcogen electrophiles (EX_n), such as $TeCl_4$, $SeCl_4$, and SCl_2, to intercept the zinc intermediate (route c). If successful, the electrophilic trapping of the zinc intermediate might be followed by intramolecular dehydrohalogenative cyclization onto the olefinic moiety to furnish benzochalcogenophene.[16] Our study along this line allowed us not just to develop a modular one-pot method for benzotellurophene synthesis, but also to establish the sequential electrophilic telluration of C(sp^2)–Zn and C(sp^2)–H bonds as a general approach to tellurium-bridged aromatic systems (Scheme 2b). Being moderately nucleophilic, the C(sp^2)–Zn bond undergoes selective monosubstitution of $TeCl_4$, which is followed by the intramolecular telluration of the proximal alkenyl or (hetero)aryl C(sp^2)–H bond to form a telluracycle. A variety of functionalized benzotellurophenes can be synthesized in a one-pot manner starting from arylzinc or aryl Grignard reagents and alkynes by way of cobalt- or nickel-catalyzed (migratory) arylmetalation.[14,17] Furthermore, 2-heterobiarylzinc reagents that were generated from the corresponding iodides gave rise to a series of heteroarene-fused benzotellurophenes.



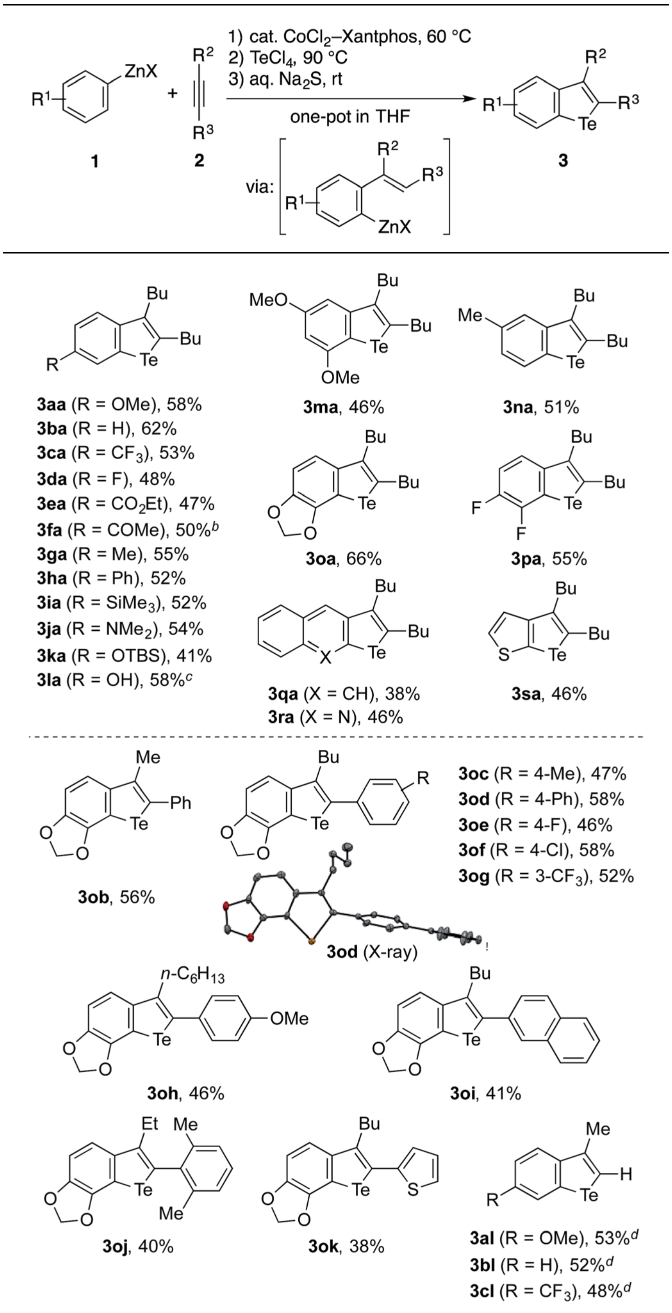
Scheme 2 Approaches to benzochalcogenophenes *via* cobalt-catalyzed migratory arylzincation (a) and a summary of the telluracycle synthesis developed in this study (b).

Results and discussion

The feasibility of the sequential telluration of C(sp^2)–Zn and C(sp^2)–H bonds was first demonstrated by the one-pot synthesis of benzotellurophenes from arylzinc reagents and alkynes capitalizing on the cobalt-catalyzed migratory arylzincation (Table 1).[13] As a typical example, the reaction of a 4-methoxyphenylzinc reagent (**1a**) and 5-decyne (**2a**) in the presence of a $CoCl_2$–Xantphos catalyst was followed by the treatment of the resulting *ortho*-alkenylarylzinc species with $TeCl_4$ at 90 °C and then with aqueous Na_2S at room temperature, affording a benzotellurophene **3aa** in 58% yield. Na_2S is considered to reduce Te(IV) to Te(II) in the last step.[13b] The putative Te(IV) intermediate, *i.e.*, the 1,1-dichlorobenzotellurophene derivative, was detected using mass spectrometry (ESI) analysis of the reaction mixture before the addition of Na_2S. We obtained the product **3aa** even without the addition of Na_2S, albeit in a significantly lower yield (<30% GC yield). It should be noted that the use of a Te(II) electrophile, such as $TeCl_2$·bipy instead of $TeCl_4$, resulted in an even poorer yield of **3aa** (<10% GC yield). It is also worth noting that all of the attempts using other chalcogen electrophiles such as $SeCl_4$, $SeCl_2$, S_2Cl_2, $SOCl_2$, or SO_2Cl_2 in place of $TeCl_4$ failed to produce the corresponding benzochalcogenophene derivative.[18]

A wide variety of arylzinc reagents could be employed for the one-pot cyclization with **2a** and $TeCl_4$, affording the corresponding benzotellurophenes **3ba–3qa** in moderate to good yields. In particular, the method allowed for the installation of various functional groups, both electron-donating and electron-withdrawing, to the 6-position of the benzotellurophene core. The benzotellurophenes **3na–3qa** were obtained with exclusive regioselectivity as a result of regioselective 1,4-cobalt migration to the less hindered position (for **3na** and **3qa**) or the position proximal to the ether oxygen or the fluorine atom (for **3oa** and **3pa**).[14] The reactions of 2-quinolinyl- and 3-thienylzinc reagents with **2a** allowed for the preparation of the corresponding fused tellurophenes **3ra** and **3sa** in moderate yields. Besides these 2,3-dialkylbenzotellurophenes, a series of 2-aryl-3-alkylbenzotellurophenes **3ob–3ok** could be synthesized in decent yields from the 3,4-methylenedioxyphenylzinc reagent and the corresponding aryl(alkyl)acetylenes. Furthermore, the use of 1-trimethylsilyl-1-propyne as the alkyne reactant resulted in a loss of the trimethylsilyl group during the cyclization process, thus furnishing 3-methylbenzotellurophenes **3al–3cl**. The generally moderate efficiency of the present synthesis of benzotellurophenes and other telluracycles (*vide infra*) is mainly attributed to the moderate efficiency of the electrophilic trapping of the organozinc intermediate with $TeCl_4$, which results in its protonated derivative as the major byproduct. It is worth noting that the crystal packing of the benzotellurophene **3od**

Table 1 One-pot benzotellurophene synthesis based on the Co-catalyzed migratory arylzincation of alkynes[a]



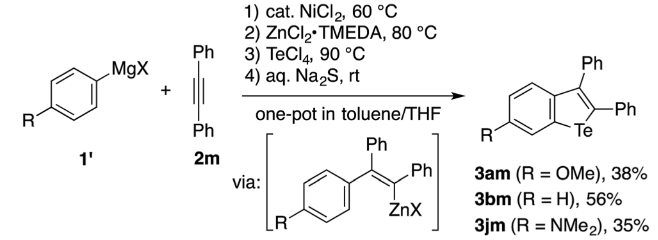
[a] The reaction was performed using 0.5 mmol of **2a** as the limiting agent. See the ESI for the detailed procedure. [b] The starting arylzinc reagent was protected in the form of *p*-anisidine imine. [c] The starting arylzinc reagent was protected with a Boc group, which was removed during the reaction. [d] 1-Trimethylsilyl-1-propyne was used as the alkyne.

displayed a rather short Te–Te distance of 3.67 Å, indicating that there were significant Te–Te interactions.[1,19]

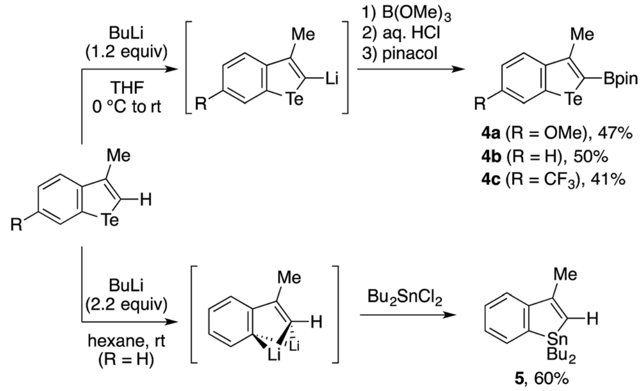
Because migratory arylzincation is not applicable to a diarylalkyne due to the substantial *E*/*Z* isomerization of the alkenylcobalt intermediate and incomplete 1,4-cobalt migration,[14] the above protocol did not allow for the synthesis of a 2,3-diarylbenzotellurophene. This gap can be filled by a modified protocol employing a normal arylmetalation reaction instead of the migratory arylzincation (Scheme 3). Thus, a one-pot sequence of the nickel-catalyzed arylmagnesiation of diphenylacetylene (**2m**),[17,20] the transmetalation of the resulting alkenylmagnesium species with $ZnCl_2 \cdot$TMEDA (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), and treatment with $TeCl_4$ and aqueous Na_2S allowed for the preparation of 2,3-diphenylbenzotellurophenes **3am**, **3bm**, and **3jm** in moderate yields. It should be noted that the Mg-to-Zn transmetalation is essential for this protocol. The omission of this step resulted in only a trace amount of the desired benzotellurophene due to multiple substitution reactions on Te(IV) with the alkenylmagnesium species, as indicated from the GCMS analysis of the crude product.

The reaction chemistry of benzotellurophene and *n*-BuLi[21] enabled the further transformations of the 3-methylbenzotellurophenes **3al–3cl** (Scheme 4). Thus, these benzotellurophenes were amenable to C2-lithiation using *n*-BuLi in THF, and the resulting 2-lithiobenzotellurophenes were readily transformed into 2-borylated benzotellurophenes **4a–4c**. Not unexpectedly, **4a–4c** and the other benzotellurophenes (Table 1 and Scheme 3) were not emissive in organic solvents.[3a,4,8d] Among **4a–4c**, only **4c** exhibited weak luminescence at 525 nm in a THF/water mixture (1 : 9), presumably due to aggregation-induced emission.[22] This luminescence was found to have a short lifetime in the order of ns (see the ESI†), and the relevance of this to the phosphorescent nature of Rivard's borylated (benzo)tellurophenes in the solid state[4] remains to be explored. A treatment of **3bl** with excess *n*-BuLi in hexane resulted in double tellurium–lithium exchange,[21] and subsequent trapping with Bu_2SnCl_2 furnished benzostannole **5** in 60% yield. The success of this conversion would hold promise for the use of benzotellurophenes as versatile precursors for different benzoheteroles,[10] such as benzosilole[23] and benzophosphole.[24]

The scope of the sequential C(sp^2)–Zn and C(sp^2)–H telluration was further extended to the synthesis of tellurium-bridged heterobiaryls starting from 2-iodoheterobiaryls, which can be readily prepared in two steps from 2-bromoaniline and heteroarylboronic acids (Table 2). Iodine–magnesium exchange with *i*-PrMgBr or *i*-PrMgCl·LiCl was followed by Mg-to-Zn transmetalation and sequential treatment with $TeCl_4$ and Na_2S, thus furnishing benzotellurophenes fused with (benzo)thiophene, (benzo)furan, indole, or benzoselenophene **6–14** in decent yields. Again, the Mg-to-Zn transmetalation proved to be a crucial step, without which the double substitution on Te(IV)

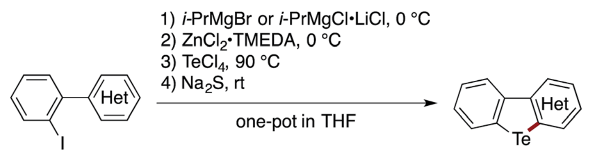


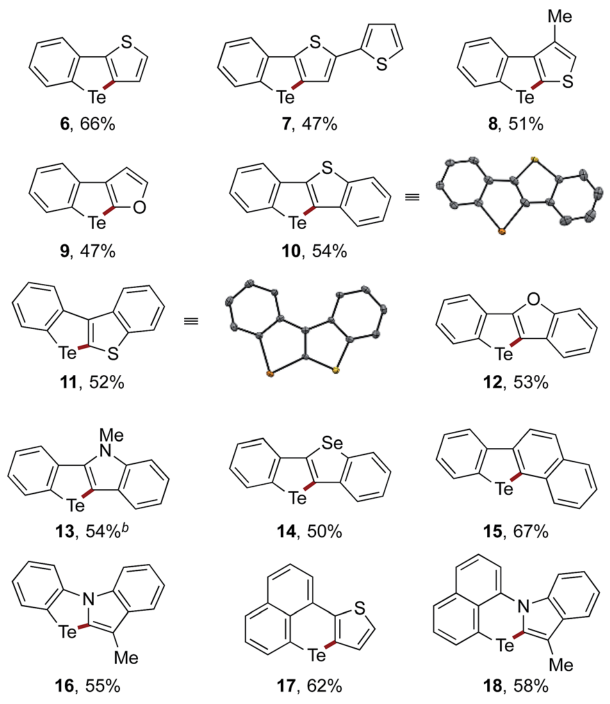
Scheme 3 One-pot benzotellurophene synthesis based on the Ni-catalyzed arylmagnesiation of diphenylacetylene.



Scheme 4 Transformations of 3-methylbenzotellurophenes.

Table 2 Conversion of 2-iodoheterobiaryls and related compounds to tellurium-bridged heteroaromatic systems[a]





[a] See the ESI for the detailed procedure. [b] *n*-BuLi was used instead of *i*-PrMgBr at −78 °C.

with the arylmagnesium species took place predominantly to afford a diaryltellurium derivative. Although the present protocol failed to convert 2-iodobiphenyl to the parent dibenzotellurophene in an appreciable yield, it allowed for the conversion of 2-(2-iodophenyl)naphthalene to benzo[*b*]naphtho[2,1-*d*]tellurophene **15** *via* the regioselective telluration of the naphthalene 1-position. Furthermore, tellurium-bridged heteroarenes **16–18**, which feature non-tellurophene-type telluracycles, could also be synthesized in reasonable yields.

The planar structures of the benzothiophene-fused derivatives **10** and **11** were confirmed using X-ray crystallographic analysis.[19] While **10** adopted a so-called sandwiched herringbone-type packing structure without significant Te–Te interactions (the shortest Te–Te distance being 6.80 Å),[25] **11** assumed a herringbone arrangement with close Te–Te contacts (3.71 Å) between the π-stacks (Fig. 1). This sharp difference suggests the importance of the molecular framework and the peripheral structures in achieving efficient Te–Te interactions in the condensed phase, which may be relevant for the potential application of tellurium-embedded polyaromatic systems in organic electronics.

We measured the UV absorption spectra of selected Te-bridged heterobiaryls, *i.e.*, compounds **10–15** and **17**, and also calculated their HOMO/LUMO levels and transition energies using TD-DFT calculations for reference (Table 3). The compounds **10**, **12**, and **14**, which can be regarded as Te/chalcogen-bridged stilbenes, exhibited a trend of increasing λ_{max} (the longest wavelength absorption maxima) upon changing the extra chalcogen atom from O to Se. This trend is in line with the trends observed for related chalcogen-bridged π-conjugated systems,[25,26] and is also consistent with the trend of the lowest transition energies, which are largely represented by the HOMO–LUMO (π–π*) transition (see the ESI† for details). Compound **11**, the cross-conjugated isomer of **10**, showed a distinctly shorter λ_{max}. Unlike the other compounds, the LUMO of **11** was found to be the C–Te σ*-orbital, with the π*-orbital being located at the LUMO+1 level. The non-tellurophene-type compound **17**, which is another structural isomer of **10**, exhibited absorption in the visible region, that is in agreement with a much lower transition energy. It is worth noting that none of these compounds were emissive in organic solvents.

The utility of the present Te-bridging protocol was further demonstrated using a stepwise synthesis of a bis-tellurium-bridged ladder molecule **22** (Scheme 5). The thiophene-fused benzotellurophene **6** was subjected sequentially to bromination, Suzuki–Miyaura coupling with a 2-aminophenylboron reagent, and diazotization–iodination to afford a new 2-iodoheterobiaryl **21**. With **21** in hand, the second tellurium bridge

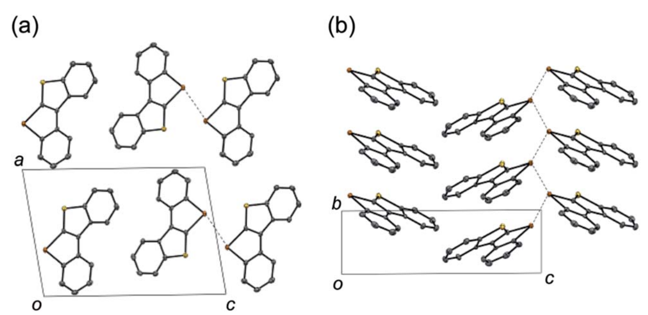
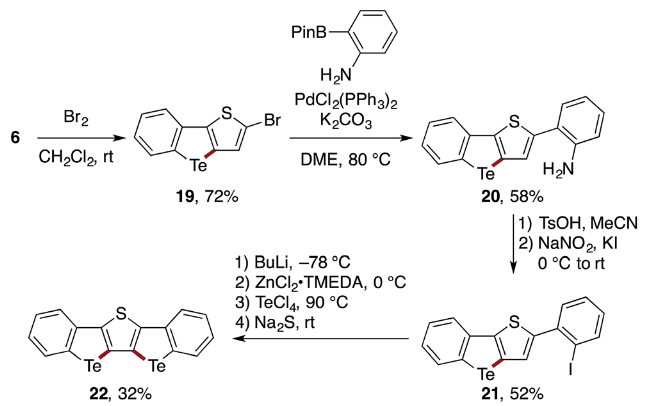


Fig. 1 Packing structures of **11** in the (a) *ac*-plane and (b) *bc*-plane. The dotted lines indicate the Te–Te contacts (3.71 Å).

Table 3 UV absorption data and the calculated HOMO/LUMO levels of Te-bridged heterobiaryls

Cmpd	$\lambda_{max}{}^{a}$ (nm)	ε^{a} (10^4 M^{-1} cm^{-1})	$E_{HOMO}{}^{b}$ (eV)	$E_{LUMO}{}^{b}$ (eV)	ΔE (f)^{c} (eV)
10	348	0.51	−5.67	−1.55	3.65 (0.0992)
11	321	0.73	−5.71	−1.49	4.08 (0.1116)
12	334	0.85	−5.66	−1.45	3.79 (0.1493)
13	348	0.68	−5.23	−1.21	3.56 (0.1878)
14	356	0.61	−5.66	−1.60	3.58 (0.0902)
15	363	0.25	−5.64	−1.54	3.58 (0.0575)
17	425	0.31	−5.10	−1.71	2.98 (0.1492)

[a] The longest wavelength absorption maxima from absorption spectra in MeOH. [b] Calculated using DFT at the level of B3LYP/6-311G* (SDD for Te). [c] The lowest significant transition energies determined using TD-DFT calculations (f > 0.05; f = oscillator strength).



Scheme 5 Synthesis of the bis-tellurium-bridged ladder molecule **22**.

was constructed using n-BuLi instead of i-PrMgBr as the metalating agent, thus affording the ladder product **22**, albeit in a modest yield.[27]

Conclusions

In summary, we have established the sequential electrophilic telluration of C(sp^2)–Zn and C(sp^2)–H bonds as a simple and versatile approach for the construction of tellurium-bridged aromatic systems. The combination of the transition metal-catalyzed (migratory) arylmetalation of alkynes and sequential telluration offers a method for the expedient synthesis of functionalized benzotellurophenes starting from arylmetal reagents and alkynes. The sequential telluration also enables the facile conversion of 2-iodoheterobiaryls into heteroarene-fused benzotellurophenes and other Te-bridged aromatics, most of which are unprecedented in the literature and have been synthesized for the first time. We envision that electrophilic aromatic telluration will open access to an even greater variety of novel Te-containing heterocycles, and that the present study will stimulate further studies on the synthesis, properties, and application of such compounds.

Acknowledgements

This work was supported by the Singapore Ministry of Education (RG 114/15), Nanyang Technological University, and JST, CREST. We thank Dr Yongxin Li and Dr Rakesh Ganguly for assistance with the X-ray crystallographic analysis.

Notes and references

1 (*a*) A. A. Jahnke and D. S. Seferos, *Macromol. Rapid Commun.*, 2011, **32**, 943–951; (*b*) E. I. Carrera and D. S. Seferos, *Macromolecules*, 2015, **48**, 297–308; (*c*) E. Rivard, *Chem. Lett.*, 2015, **44**, 730–736; (*d*) S. M. Parke, M. P. Boone and E. Rivard, *Chem. Commun.*, 2016, **52**, 9485–9505; (*e*) M. Jeffries-EL, B. M. Kobilka and B. J. Hale, *Macromolecules*, 2014, **47**, 7253–7271.

2 (*a*) A. A. Jahnke, G. W. Howe and D. S. Seferos, *Angew. Chem., Int. Ed.*, 2010, **49**, 10140; (*b*) A. A. Jahnke, B. Djukic, T. M. McCormick, E. B. Domingo, C. Hellmann, Y. Lee and D. S. Seferos, *J. Am. Chem. Soc.*, 2013, **135**, 951; (*c*) G. He, L. Kang, W. T. Delgado, O. Shynkaruk, M. J. Ferguson, R. McDonald and E. Rivard, *J. Am. Chem. Soc.*, 2013, **135**, 5360; (*d*) M. Kaur, D. S. Yang, J. Shin, T. W. Lee, K. Choi, M. J. Cho and D. H. Choi, *Chem. Commun.*, 2013, **49**, 5495; (*e*) Y. S. Park, Q. Wu, C.-Y. Nam and R. B. Grubbs, *Angew. Chem., Int. Ed.*, 2014, **53**, 10691; (*f*) E. H. Jung, S. Bae, T. W. Yoo and W. H. Jo, *Polym. Chem.*, 2014, **5**, 6545; (*g*) M. Planells, B. C. Schroeder and I. McCulloch, *Macromolecules*, 2014, **47**, 5889; (*h*) P.-F. Li, T. B. Schon and D. S. Seferos, *Angew. Chem., Int. Ed.*, 2015, **54**, 9361; (*i*) R. S. Ashraf, I. Meager, M. Nikolka, M. Kirkus, M. Planells, B. C. Schroeder, S. Holliday, M. Hurhangee, C. B. Nielsen, H. Sirringhaus and I. McCulloch, *J. Am. Chem. Soc.*, 2015, **137**, 1314; (*j*) M. Kaur, D. H. Lee, D. S. Yang, H. A. Um, M. J. Cho, J. S. Kang and D. H. Choi, *Dyes Pigm.*, 2015, **123**, 317; (*k*) A. K. Mahrok, E. I. Carrera, A. J. Tilley, S. Y. Ye and D. S. Seferos, *Chem. Commun.*, 2015, **51**, 5475; (*l*) M. Al-Hashimi, Y. Han, J. Smith, H. S. Bazzi, S. Y. A. Alqaradawi, S. E. Watkins, T. D. Anthopoulos and M. Heeney, *Chem. Sci.*, 2016, **7**, 1093; (*m*) S. Ye, M. Steube, E. I. Carrera and D. S. Seferos, *Macromolecules*, 2016, **49**, 1704.

3 (*a*) T. M. McCormick, A. A. Jahnke, A. J. Lough and D. S. Seferos, *J. Am. Chem. Soc.*, 2012, **134**, 3542; (*b*) E. I. Carrera, T. M. McCormick, M. J. Kapp, A. J. Lough and D. S. Seferos, *Inorg. Chem.*, 2013, **52**, 13779; (*c*) T. M. McCormick, E. I. Carrera, T. B. Schon and D. S. Seferos, *Chem. Commun.*, 2013, **49**, 11182; (*d*)

E. I. Carrera and D. S. Seferos, *Dalton Trans.*, 2015, **44**, 2092; (*e*) E. I. Carrera, A. E. Lanterna, A. J. Lough, J. C. Scaiano and D. S. Seferos, *J. Am. Chem. Soc.*, 2016, **138**, 2678; (*f*) P.-F. Li, E. I. Carrera and D. S. Seferos, *ChemPlusChem*, 2016, **81**, 917.

4 (*a*) G. He, W. T. Delgado, D. J. Schatz, C. Merten, A. Mohammadpour, L. Mayr, M. J. Ferguson, R. McDonald, A. Brown, K. Shankar and E. Rivard, *Angew. Chem., Int. Ed.*, 2014, **53**, 4587; (*b*) G. He, B. D. Wiltshire, P. Choi, A. Savin, S. Sun, A. Mohammadpour, M. J. Ferguson, R. McDonald, S. Farsinezhad, A. Brown, K. Shankar and E. Rivard, *Chem. Commun.*, 2015, **51**, 5444; (*c*) W. T. Delgado, F. Shahin, M. J. Ferguson, R. McDonald, G. He and E. Rivard, *Organometallics*, 2016, **35**, 2140; (*d*) C. A. Braun, D. Zomerman, I. de Aguiar, Y. Qi, W. T. Delgado, M. J. Ferguson, R. McDonald, G. L. C. de Souza, G. He, A. Brown and E. Rivard, *Faraday Discuss.*, 2017, **196**, 255.

5 G. E. Garrett, E. I. Carrera, D. S. Seferos and M. S. Taylor, *Chem. Commun.*, 2016, **52**, 9881.

6 (*a*) C. R. B. Rhoden and G. Zeni, *Org. Biomol. Chem.*, 2011, **9**, 1301; (*b*) V. I. Minkin and I. D. Sadekov, in *Comprehensive Heterocyclic Chemistry III*, ed. A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven and R. J. K. Taylor, Elsevier, 2008, pp. 1007–1028.

7 X. Yan and C. Xi, *Acc. Chem. Res.*, 2015, **48**, 935.

8 (*a*) P. M. Beaujuge and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2011, **133**, 20009; (*b*) K. Takimiya, S. Shinamura, I. Osaka and E. Miyazaki, *Adv. Mater.*, 2011, **23**, 4347; (*c*) C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chem. Rev.*, 2012, **112**, 2208; (*d*) J. Mei, Y. Diao, A. L. Appleton, L. Fang and Z. Bao, *J. Am. Chem. Soc.*, 2013, **135**, 6724; (*e*) K. Takimiya, M. Nakano, M. J. Kang, E. Miyazaki and I. Osaka, *Eur. J. Org. Chem.*, 2013, 217.

9 (*a*) H. Suzuki, T. Nakamura, T. Sakaguchi and K. Ohta, *J. Org. Chem.*, 1995, **60**, 5274; (*b*) K. Takimiya, Y. Konda, H. Ebata, N. Niihara and T. Otsubo, *J. Org. Chem.*, 2005, **70**, 10569; (*c*) M. Pittelkow, T. K. Reenberg, K. T. Nielsen, M. J. Magnussen, T. I. Sølling, F. C. Krebs and J. B. Christensen, *Angew. Chem., Int. Ed.*, 2006, **45**, 5666; (*d*) J. Casado, M. M. Oliva, M. C. R. Delgado, R. P. Ortiz, J. J. Quirante, J. T. L. Navarrete, K. Takimiya and T. Otsubo, *J. Phys. Chem. A*, 2006, **110**, 7422; (*e*) Y. S. Park, T. S. Kale, C.-Y. Nam, D. Choi and R. B. Grubbs, *Chem. Commun.*, 2014, **50**, 7964.

10 B. Wu and N. Yoshikai, *Org. Biomol. Chem.*, 2016, **14**, 5402.

11 For an instrumental review on the uniqueness of tellurium among chalcogen elements, see: T. Chivers and R. S. Laitinen, *Chem. Soc. Rev.*, 2015, **44**, 1725.

12 H. Sashida, K. Sadamori and T. Tsuchiya, *Synth. Commun.*, 1998, **28**, 713.

13 (*a*) L. Engman, *J. Heterocycl. Chem.*, 1984, **21**, 413; (*b*) H. Sashida, M. Kaname and K. Ohyanagi, *Heterocycles*, 2010, **82**, 441.

14 B.-H. Tan, J. Dong and N. Yoshikai, *Angew. Chem., Int. Ed.*, 2012, **51**, 9610.

15 B. Wu and N. Yoshikai, *Angew. Chem., Int. Ed.*, 2013, **52**, 10496.

16 B. Wu, M. Santra and N. Yoshikai, *Angew. Chem., Int. Ed.*, 2014, **53**, 7543.

17 F. Xue, J. Zhao and T. S. A. Hor, *Chem. Commun.*, 2013, **49**, 10121.

18 SCl_2 was not examined as it was not available in Singapore.

19 ESI.†

20 B. Wu, R. Chopra and N. Yoshikai, *Org. Lett.*, 2015, **17**, 5666.

21 A. Maercker, H. Bodenstedt and L. Brandsma, *Angew. Chem., Int. Ed.*, 1992, **31**, 1339.

22 J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, 2015, **115**, 11718.

23 (*a*) L. Ilies, H. Tsuji, Y. Sato and B. Nakamura, *J. Am. Chem. Soc.*, 2008, **130**, 4240; (*b*) L. Ilies, H. Tsuji and E. Nakamura, *Org. Lett.*, 2009, **11**, 3966; (*c*) M. Tobisu, M. Onoe, Y. Kita and N. Chatani, *J. Am. Chem. Soc.*, 2009, **131**, 7506; (*d*) E. Shirakawa, S. Masui, R. Narui, R. Watabe, D. Ikeda and T. Hayashi, *Chem. Commun.*, 2011, **47**, 9714; (*e*) Y. Liang, W. Geng, J. Wei and Z. Xi, *Angew. Chem., Int. Ed.*, 2012, **51**, 1934; (*f*) K. Ouyang, Y. Liang and Z. Xi, *Org. Lett.*, 2012, **14**, 4572; (*g*) L. Xu, S. Zhang and P. Li, *Org. Chem. Front.*, 2015, **2**, 459.

24 (*a*) T. Sanji, K. Shiraishi, T. Kashiwabara and M. Tanaka, *Org. Lett.*, 2008, **10**, 2689; (*b*) H. Tsuji, K. Sato, L. Ilies, Y. Itoh, Y. Sato and E. Nakamura, *Org. Lett.*, 2008, **10**, 2263; (*c*) A. Fukazawa, Y. Ichihashi, Y. Kosaka and S. Yamaguchi, *Chem.–Asian J.*, 2009, **4**, 1729; (*d*) Y.-R. Chen and W.-L. Duan, *J. Am. Chem. Soc.*, 2013, **135**, 16754; (*e*) Y. Unoh, K. Hirano, T. Satoh and M. Miura, *Angew. Chem., Int. Ed.*, 2013, **52**, 12975; (*f*) W. Ma and L. Ackermann, *Synthesis*, 2014, **46**, 2297; (*g*) Y. Xu, Z. Wang, Z. Gan, Q. Xi, Z. Duan and F. Mathey, *Org. Lett.*, 2015, **17**, 1732; (*h*) Y. Zhou, Z. Gan, B. Su, J. Li, Z. Duan and F. Mathey, *Org. Lett.*, 2015, **17**, 5722; (*i*) V. Quint, F. Morlet-Savary, J. F. Lohier, J. Lalevee, A. C. Gaumont and S. Lakhdar, *J. Am. Chem. Soc.*, 2016, **138**, 7436; (*j*) Y. Unoh, Y. Yokoyama, T. Satoh, K. Hirano and M. Miura, *Org. Lett.*, 2016, **18**, 5436.

25 M. Matsumura, A. Muranaka, R. Kurihara, M. Kanai, K. Yoshida, N. Kakusawa, D. Hashizume, M. Uchiyama and S. Yasuike, *Tetrahedron*, 2016, **72**, 8085.

26 A. Muranaka, S. Yasuike, C.-Y. Liu, J. Kurita, N. Kakusawa, T. Tsuchiya, M. Okuda, N. Kobayashi, Y. Matsumoto, K. Yoshida, D. Hashizume and M. Uchiyama, *J. Phys. Chem. A*, 2009, **113**, 464.

27 Attempts to simultaneously construct the two tellurium bridges of **22** starting from a teraryl diiodide precursor have not been successful.