ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2015, **51**, 5444

Received 19th August 2014, Accepted 15th October 2014

DOI: 10.1039/c4cc06529h

www.rsc.org/chemcomm

Phosphorescence within benzotellurophenes and color tunable tellurophenes under ambient conditions†

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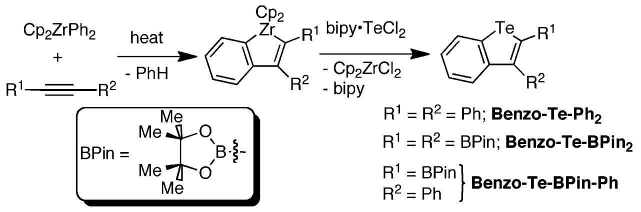
The zirconium-mediated syntheses of pinacolboronate (BPin) appended benzo[*b*]tellurophenes and two phenyl/BPin substituted tellurophene isomers with different colors of emission have been achieved. These species are new additions to an emerging class of inorganic heterocycles that display visible phosphorescence in the solid state under ambient conditions.

Despite the advancements made in organic light-emitting diode (OLED) technologies during last several decades, there is still a need for efficient phosphorescent materials that operate in the solid state.[1] One complication is that many compounds that display strong luminescence in solution are often non-emissive in the condensed phase due to aggregation-caused quenching.[2] By disrupting close intermolecular contacts and limiting intramolecular motions, enhanced luminescence can transpire; this effect has been termed aggregation-induced emission (AIE),[3] and AIE has been employed to yield solid state emitters for OLEDs and sensing applications.[4]

Tellurophenes and their polymeric analogues have attracted attention recently due to their novel electronic properties (*i.e.* low-electronic band gaps),[5] yet these species are generally non-emissive.[6] This behavior can be traced to the "heavy-metal effect" whereby heavy elements encourage singlet-to-triplet crossing, leading to the formation of long-lived triplet excited states that are prone to self or external (oxygen and/or solvent-mediated) quenching.[5] Recently, we prepared a new class of pinacolboronate (BPin)-capped tellurophenes which show efficient green phosphorescence in the solid state at room temperature and in the presence of water and oxygen.[7] A key advance in this field would be to access new Te-based phosphors featuring a wider color palette of emitted light in a controlled fashion. Accordingly, in this communication we report new phosphorescent BPin-substituted benzo[*b*]tellurophenes and related tellurophenes, and show in the latter systems that variation of the emission color is possible.

The synthesis of functionalized benzo[*b*]tellurophenes is outlined in Scheme 1 and begins with the elimination of benzene from Cp_2ZrPh_2 in the presence of alkynes to yield isolable benzo[*b*]zirconocenes.[8] These orange-red metallacycles can be readily converted into yellow crystalline benzo[*b*]tellurophenes, **Benzo-Te-Ph$_2$**, **Benzo-Te-BPin-Ph** and **Benzo-Te-BPin$_2$**, *via* Zr/Te exchange with bipy·$TeCl_2$ (bipy = 2,2′-bipyridine).[9,10] Of note, **Benzo-Te-BPin-Ph** was obtained as a single regioisomer with a BPin group positioned adjacent to the Te center, as confirmed by single-crystal X-ray crystallography.[11] The pinacolboronate group in **Benzo-Te-BPin-Ph** is nearly coplanar (Fig. 1) with respect to the planar benzotellurophene unit [O1-B-C1-C2 torsion angle = −176.4(3)°], while the Ph group is canted by *ca.* 62°.



Scheme 1 Synthesis of benzo[*b*]tellurophenes *via* metallacycle transfer.

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† Electronic supplementary information (ESI) available: Full experimental, computational and crystallographic details. CCDC 1019615–1019619. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc06529h

‡ Prof. Eric Rivard: principal investigator, designed the concept and co-wrote the manuscript. Prof. Alex Brown: principal investigator responsible for the computational studies. Prof. Karthik Shankar: principal investigator responsible for luminescence measurements. Dr Gang He and Mr Paul Choi: conducted all chemical syntheses and Dr Gang He co-wrote the manuscript. Mr Benjamin Wiltshire and Mr Arash Mohammadpour: conducted solid-state photoluminescence measurements. Mr Aliaksandr Savin and Mr Shuai Sun: conducted the TD-DFT and DFT computational studies. Ms Samira Farsinezhad: conducted bulk X-ray diffraction (XRD) studies. Drs Michael Ferguson and Robert McDonald: conducted single-crystal X-ray diffraction measurements and structure refinements.

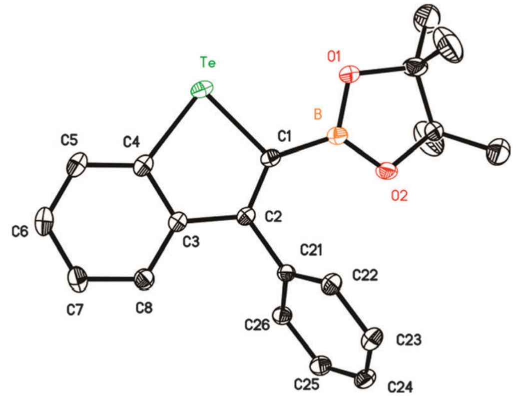
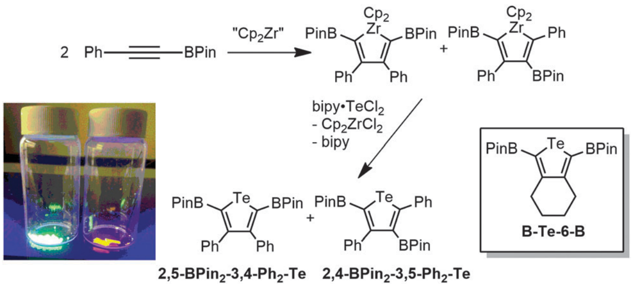


Fig. 1 Molecular structure of **Benzo-Te-BPin-Ph** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–Te 2.090(3), C(4)–Te 2.071(3), C(1)–B 1.548(4), C(2)–C(3) 1.462(3); C(1)–Te–C(4) 82.01(10), Te–C(1)–B 116.02(18), C(1)–C(2)–C(21) 121.8(2), Te–C(4)–C(5) 126.9(2).

The presence of coplanar BPin and Te heterocycles in the solid state is a common feature in the previously reported phosphorescent tellurophenes and appears to be required for luminescence.[7] The X-ray structure of the analogous diarylated benzo[*b*]tellurophene **Benzo-Te-Ph$_2$** can be found in the ESI† (Fig. S2).[11]

As expected, the newly prepared benzo[*b*]tellurophenes were non-emissive in solution, presumably due to non-radiative decay that is modulated by rotation of Ph and/or BPin residues. The BPin-substituted analogue **Benzo-Te-BPin$_2$** exhibits green luminescence in the crystalline/solid state when irradiated at 337 nm (λ_{emis} = 532 nm; Φ = 1.3%; Fig. S16, ESI†). Time-dependent luminescence measurements reveal that the nature of light emission is phosphorescence, with a lifetime (τ) of 6.1 μs observed.[12] **Benzo-Te-BPin$_2$** also exhibits telltale signs of crystallization-induced emission,[13] as this species converts from a faintly orange emissive oil to phosphorescent crystals upon standing. The related benzotellurophene **Benzo-Te-BPin-Ph** is weakly phosphorescent in the solid state (τ = 59.3 μs;[12] Φ was too low to be accurately determined), however aggregates of this species in a 5 : 95 THF–water mixture displayed bright green light emission (λ_{emis} = 520 nm) upon irradiation (Fig. S12, ESI†);[11] the weak phosphorescence from **Benzo-Te-BPin-Ph** in the neat film state is due to appreciable aggregation-induced quenching in the solid-state. Overall the optical behavior of the BPin-substituted benzotellurophenes mirrors that noted in the reported phosphorescent tellurophene **B-Te-6-B** (Scheme 2)[7] which has an emission maximum at 535 nm (τ = 170 μs) and Φ = 11.5%. **Benzo-Te-Ph$_2$** shows a very weak emission in the solid/aggregated states when irradiated at 365 nm (τ = 9.6 μs),[12] and is in line with the requisite presence of a BPin group to obtain phosphorescent tellurium heterocycles.



Scheme 2 Synthesis of the tellurophene isomers **2,5-BPin$_2$-3,4-Ph$_2$-Te** and **2,4-BPin$_2$-3,5-Ph$_2$-Te** *via* metallacycle transfer, and differing luminescence properties under 365 nm light.

The selective functionalization of tellurophenes remains a challenge as electrophilic reagents often instigate oxidization at Te.[5b] Inspired by the regioselective synthesis of **Benzo-Te-BPin-Ph**, wherein a BPin group was preferentially positioned adjacent to a Te-center, we decided to assemble PhC≡CBPin units using Negishi's reagent "Cp$_2$Zr" (prepared from Cp$_2$ZrCl$_2$ and 2 equiv. of *n*-BuLi).[14] In place of obtaining one zirconocene isomer with BPin groups at the 2- and 5-positions, an inseparable mixture of the 2,5- and 2,4-isomers was obtained (*vide infra*; Scheme 2). Treatment of this product mixture with bipy·TeCl$_2$ gave tellurophenes **2,5-BPin$_2$-3,4-Ph$_2$-Te** and **2,4-BPin$_2$-3,5-Ph$_2$-Te** (Scheme 2) as two crystalline solid products with differing luminescence properties, which enabled their manual separation under UV light. **2,5-BPin$_2$-3,4-Ph$_2$-Te** (Fig. S4, ESI†)[11] was isolated in a 21% yield (based on the moles of the Zr starting material) and emitted green light under irradiation at 365 nm. Of added interest, the other isomer **2,4-BPin$_2$-3,5-Ph$_2$-Te** (41% yield) exhibited yellow-orange photoluminescence upon irradiation (Scheme 2), showing a direct link between the placement of the BPin and Ph groups about the tellurophene and the energy of light emission. The pinacolboronate and phenyl groups at the 2- and 5-positions in **2,4-BPin$_2$-3,5-Ph$_2$-Te** (Fig. 2) are nearly coplanar with the tellurophene ring, while the remaining ring-positioned Ph and BPin groups are twisted into a propeller arrangement; a similar overall geometry exists with the tellurophene TeC$_4$(BPin)$_4$.[7]

The phosphorescence profiles of **2,5-BPin$_2$-3,4-Ph$_2$-Te** and **2,4-BPin$_2$-3,5-Ph$_2$-Te** are shown in Fig. 3, and as mentioned

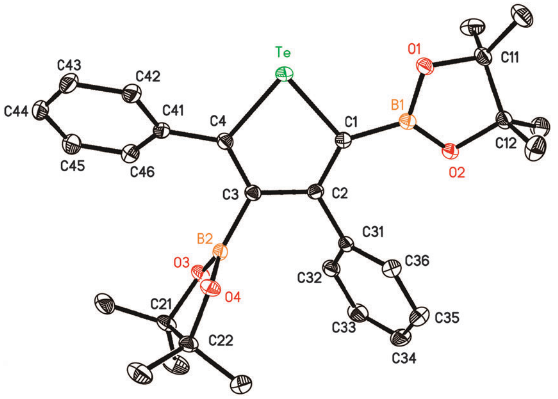


Fig. 2 Molecular structure of **2,4-BPin$_2$-3,5-Ph$_2$-Te** with thermal ellipsoids presented at a 30% probability level. Selected bond lengths [Å] and angles [°]: Te–C(1) 2.062(2), Te–C(4) 2.069(2), C(1)–B(1) 1.551(3), C(3)–B(2) 1.576(3); C(1)–Te–C(4) 82.65(9), Te–C(1)–B(1) 115.73(17). The structure of **2,5-BPin$_2$-3,4-Ph$_2$-Te** can be found in the ESI† (Fig. S4).[11]

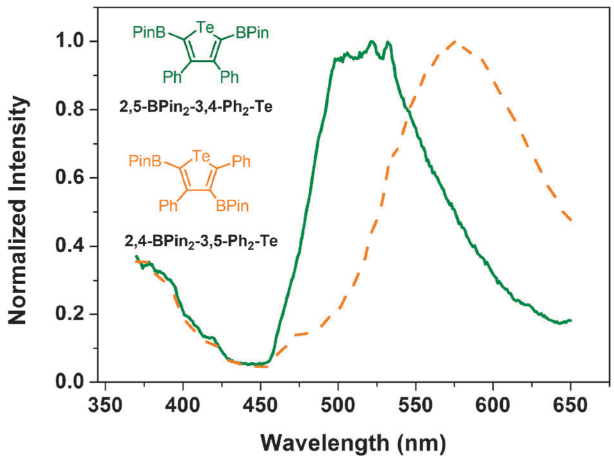


Fig. 3 PL spectra of **2,5-BPin$_2$-3,4-Ph$_2$-Te** and **2,4-BPin$_2$-3,5-Ph$_2$-Te** in the film state ($\lambda_{\text{excit.}}$ = 337 nm).

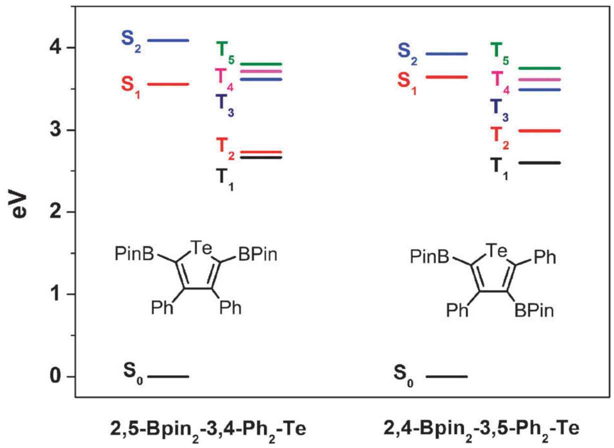


Fig. 4 Vertical excitation energies of **2,5-BPin$_2$-3,4-Ph$_2$-Te** and **2,4-BPin$_2$-3,5-Ph$_2$-Te** at their S_0 geometries. The compounds were studied using the TD-B3LYP/aug-cc-pVTZ level of theory.

above, the regioisomer with 2,5-positioned BPin groups emits in the green spectral region (λ_{emis} = 517 nm; Φ = 4.5%; τ = 51.7 μs), while the 2,4-isomer displays yellow-orange emission (λ_{emis} = 577 nm; Φ = 5.3%; τ = 17.9 μs).[12] These species are also phosphorescent when aggregated in THF–water mixtures (5 : 95) with emission maxima centered at 530 nm and 580 nm for **2,5-BPin$_2$-3,4-Ph$_2$-Te** and **2,4-BPin$_2$-3,5-Ph$_2$-Te**, respectively (Fig. S13 and S14, ESI†).[11]

Time-dependent density functional theory (TD-DFT) computations show that each isomer has similar absorption energies (Fig. 4 and Table S8, ESI†).[11] However, from DFT computations, the most salient difference between these two species is that the T_1 to S_0 energy gap at the T_1 geometry (which is related to the light emission) for the yellow-orange emitting **2,4-BPin$_2$-3,5-Ph$_2$-Te** isomer is *ca.* 0.4 eV lower in energy in relation to **2,5-BPin$_2$-3,4-Ph$_2$-Te** (Table S9, ESI†). The primary contributor to this difference appears to be the change in π-orbital conjugation between the two species[15] when going from the S_0 (absorption) to T_1 (emission) geometries (compare Fig. S18 and S19 for **2,5-BPin$_2$-3,4-Ph$_2$-Te** to Fig. S22 and S23 for **2,4-BPin$_2$-3,5-Ph$_2$-Te**, ESI†). As a result, we postulate that the synthesis of related asymmetrically-substituted heterocycles with a BPin group at one site and an electronically distinct aryl group at an opposite position, should yield a family of tellurophenes with tunable phosphorescence.

Furthermore, the emission of tellurophenes was not affected by molecular oxygen. For instance, there was no significant difference between the solid state (film) emission of **2,5-BPin$_2$-3,4-Ph$_2$Te** in N_2, air and at high pressure of O_2 (4 atm) (Fig. S30 and S31, ESI†). The emission also remained stable when the film was irradiated under ambient conditions by a strong light source (Fig. S27–S29, ESI†).[11]

New color modifiable phosphorescent tellurophenes, along with emissive benzo[*b*]tellurophenes were synthesized. In general, green light emission was observed; however, in the case of the asymmetrically substituted tellurophene, **2,4-BPin$_2$-3,5-Ph$_2$-Te**, bright yellow-orange phosphorescence in the solid state was observed. Our computations show that enhanced conjugation between ring-positioned orbitals and the Ph group adjacent to Te leads to pronounced red-shifting of the emission; thus future design of asymmetrically substituted tellurophenes with aromatic and BPin residues should enable an even wider spectral palette for emission to be attained.

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Foundation for Innovation, Alberta Innovates Technology Futures (New Faculty Award to E.R. and scholarships to B.D.W., S.F. and A.M.), and the Canada School for Energy and the Environment. We thank Prof. Y. Y. Tsui for access to his group's high-power pulsed laser for certain experiments.

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