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Emissive Tellurophenes

Coaxing Solid-State Phosphorescence from Tellurophenes**

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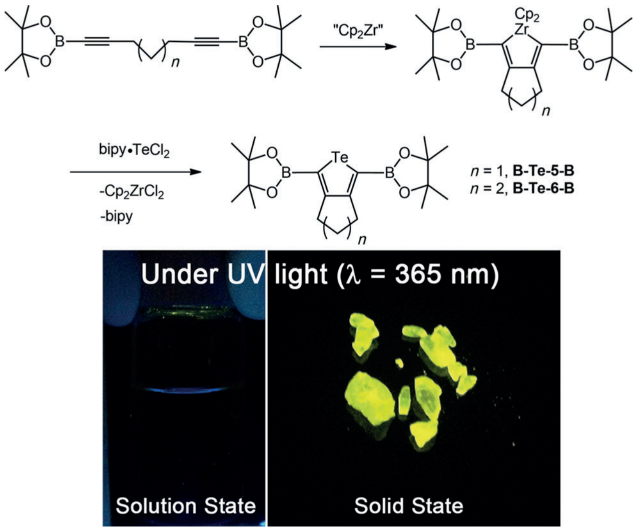
Abstract: *The synthesis of the first examples of tellurophenes exhibiting phosphorescence in the solid state and under ambient conditions (room temperature and in air) is reported. Each of these main-group-element-based emitters feature pinacolboronates (BPin) as ring-appended side groups. The nature of the luminescence observed was also investigated using computational methods.*

The discovery of new phosphorescent materials that are efficient light emitters in the solid state is of paramount importance in advancing organic light-emitting diode (OLED) technologies, as higher internal emission quantum efficiencies can be obtained in relation to ubiquitous fluorescent systems (100% vs. 25%).[1] However, molecules that exhibit efficient emission in solution are often non-luminescent in the solid state owing to aggregation-caused quenching (ACQ).[2] As the ACQ effect is detrimental to many practical applications (for example, requiring dilution of the emitter in a host material for OLEDs), there have been numerous efforts to tackle this problem. In 2001, Tang and co-workers uncovered aggregation-induced emission (AIE), whereby a restriction of intramolecular motions in the solid state suppresses the ACQ effect by limiting non-radiative decay pathways, leading to intense emission in both the solid and aggregated states;[3] however in the vast majority of reported cases, only fluorescence was noted.[4]

Tellurophenes are attracting increasing attention from the scientific community with respect to the development of new optoelectronic materials as a result of their lower optical band gaps, deeper LUMO levels, and potentially higher charge carrier mobilities relative to their well-studied thiophene counterparts.[5] Notably, the Seferos and Rivard groups have prepared a series of polytellurophenes for consideration as photovoltaic materials with the aid of improved synthetic approaches.[6] In each case, the reported polytellurophenes were non-emissive owing to the "heavy-metal effect"[7] whereby heavy elements encourage singlet-to-triplet crossing, leading to the formation long-lived triplet excited states that are prone to internal (self) or external (oxygen or solvent-mediated) quenching. For example, the Navarrete group noted that Te-substituted benzodichalcogenophenes were non-emissive, whereas fluorescence was observed for the lighter S and Se analogues.[8] Herein, we report that the previously known boronic ester-capped tellurophene B-Te-6-B[6c] displays intense green phosphorescence in the solid state (Scheme 1[9]). Furthermore, B-Te-6-B readily forms emissive host-free films that can be cast directly from THF solution. The development of inexpensive tellurophene phosphors is of added interest given that most phosphorescent materials feature precious metal Ir or Pt complexes diluted in accompanying host materials.[10] To the best of our knowledge, this is the first example of luminescence from a tellurophene under ambient conditions,[11] and the photophysical data of comparative inorganic rings are provided to extract the nature of light emission from B-Te-6-B.



Scheme 1. Synthesis of pinacolboronate-capped tellurophenes, and emission characteristics of B-Te-6-B in solution and in the solid state.

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The synthesis of B-Te-6-B is outlined in Scheme 1 and involves the initial formation of the zirconacycle, B-Zr-6-B, followed by an efficient Zr/Te transmetalation reaction with bipy·$TeCl_2$[12] to give B-Te-6-B as a pale yellow-green solid.[6c] B-Te-6-B is non-emissive when dissolved in organic solvents such as THF, but in the solid state shows bright green luminescence ($\lambda_{emis.} = 535$ nm; Scheme 1). Furthermore, B-Te-6-B undergoes a dramatic change from a non-emissive state in THF to highly emissive aggregated states in THF/water mixtures when the water content exceeded 80 vol% (Figure 1); this observation is a hallmark of the AIE effect.[3c]

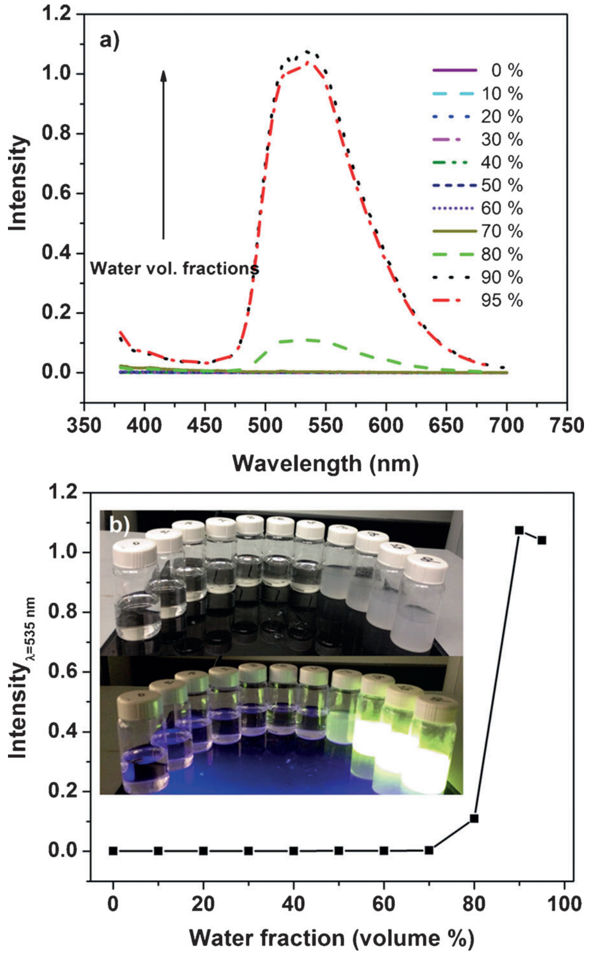
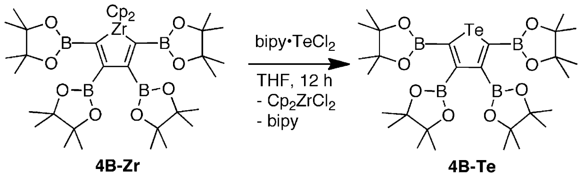


Figure 1. a) Photoluminescence (PL) spectra of B-Te-6-B in different THF/water ratios; b) emission intensity of B-Te-6-B as the THF/water ratio is altered. Inset: aggregates under UV light ($\lambda_{excit.} = 365$ nm); [B-Te-6-B] = 600 μM. See the Supporting Information, Figures S15 and S16 for SEM images of the aggregates.[9]

The emission profile is independent of the aggregation state, and we were able to make emissive films of B-Te-6-B (1–10 wt%) in PMMA (Supporting Information, Figure S13).[9] A weighted mean luminescence lifetime of 166 μs was found for pure films of B-Te-6-B drop-coated from THF (Supporting Information, Figure S17 and Table S12)[9] (quantum yield $\Phi \approx 11.5$ %), indicating that light emission is phosphorescence.[13] Furthermore, the large Stokes shift (170 nm) found in B-Te-6-B lends added support for the presence of phosphorescence. This observation is noteworthy given that efficient phosphorescence in neat films at room temperature is generally very difficult to achieve, as triplet excited states are highly susceptible to intermolecular triplet–triplet annihilation and quenching by oxygen.[1d,14]

To probe the structural requirements for light emission, metallacycle transfer chemistry[15] was used to prepare a tellurophene with a modified cycloalkane group B-Te-5-B (Scheme 1), and a tellurophene containing four ring-appended pinacolboronate esters 4B-Te [Eq. (1)].[9,16,17] Neither of these heterocycles exhibited luminescence in organic solvent; however, aggregation-induced emission (AIE) was noted in both cases with emission maxima (520 and 516 nm for B-Te-5-B and 4B-Te, respectively; Figure 2) that were slightly blue-shifted in relation to B-Te-6-B ($\lambda_{emis.} = 535$ nm).



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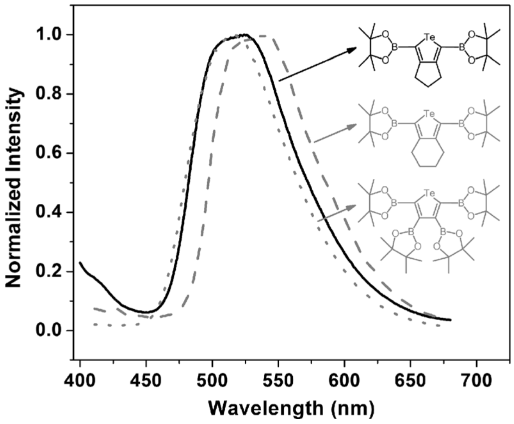

Figure 2. PL spectra of B-Te-5-B, B-Te-6-B, and 4B-Te in THF/water (5:95) mixtures; [tellurophenes] = 600 μM ($\lambda_{excit.} = 365$ nm).

The predominant mechanism of AIE is believed to be the restriction of intramolecular rotations (RIR).[3c] However, we cannot simply explain the phosphorescence in our tellurophene rings entirely by an RIR process given the involvement of singlet-to-triplet crossing. To better understand the role of Te in the noted light emission, we studied the photoluminescence of a homologous series containing the butadiene analogues, B-H-4-B, B-H-5-B, and B-H-6-B, along with the phosphorus-, sulfur-, and selenium-containing heterocycles B-PPh-6-B, B-S-6-B, and B-Se-6-B (Figure 3).[6c] Each of these species are non-emissive both in the aggregated/solid state with the exception of T-H-T (see below). Moreover the brominated tellurophene B-$TeBr_2$-B was prepared[9,17] by combining B-Te-6-B with Br_2, and this Te^{IV} heterocycle was also shown to be non-emissive. These results indicate that the

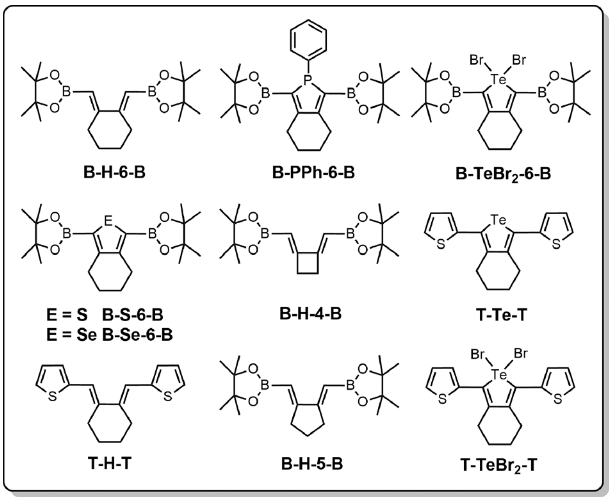

Figure 3. Structural variants of B-Te-6-B investigated.

Te^{II} center in B-Te-6-B is playing an active role in the solid-state phosphorescence.

Tellurophenes were also synthesized wherein the pinacolboronate esters (BPin) were replaced by thiophene groups (T-Te-T and T-TeBr$_2$-T; Figure 3).[9,17] Again, no luminescence was detected, implying a cooperative interaction between the Te^{II} centers and the adjacent BPin groups[18] in B-Te-5-B, B-Te-6-B, and 4B-Te is leading to efficient light emission in the solid state. We also attempted to prepare a tellurophene wherein the capping BPin groups were replaced by BMes$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$); however, attempts to couple the diyne Mes$_2$B−C≡C−(CH$_2$)$_4$−C≡C−BMes$_2$[9,17] with “Cp$_2$Zr” (Scheme 1) have failed thus far.

Given that the BPin groups contain empty p-orbitals at boron that could mediate light emission from the excited state, we explored the luminescence of B-Te-6-B in the presence of exogenous fluoride donors.[19] Initially the reaction between B-Te-6-B and [nBu$_4$N]F was studied in THF by UV/Vis spectroscopy (Figure 4), and the resulting spectral profiles show the conversion of B-Te-6-B into a new product, with an overall F$^-$ binding constant of about $3\times10^7\,\text{M}^{-1}$ (Supporting Information, Figure S26).[20] Binding of fluoride at boron was confirmed by in situ ^{11}B NMR spectroscopy wherein the signal at 31 ppm owing to B-Te-6-B shifted to a new resonance at 6 ppm upon adding two equiv of F$^-$, consistent with the presence of four-coordinate fluoroborate environments (FB-Te-6-BF; Supporting Information, Figure S25).[9,19] Importantly, the new fluoride-bound product was non-emissive both in solution and in the solid state indicating that empty p-orbitals within the BPin units are likely involved in the light emission of B-Te-6-B. The boron-bound fluorides in FB-Te-6-BF dissociate in water, enabling the free pinacolboronate B-Te-6-B to be recovered quantitatively upon extraction of the mixture with Et$_2$O.

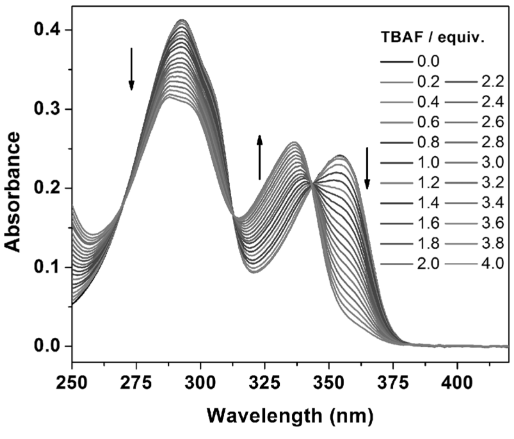

Figure 4. UV/Vis absorption spectra upon titrating B-Te-6-B (60 μM) with [nBu$_4$N]F (TBAF) in THF.

We did encounter AIE in another chalcogenophene system T-H-T (Supporting Information, Figure S24);[9,17] however, some informative differences in the luminescent properties relative to B-Te-6-B were noted. First, T-H-T exhibits discernable aggregation-induced blue light emission ($\lambda_{\text{emis.}} = 448$ nm) when a 30:70 THF/water ratio was reached (Supporting Information, Figure S24). Secondly, lifetime measurements show that the emission transpires by fluorescence ($\tau = 1.8$ ns),[3a] reinforcing the unique role that the heavy element Te has in promoting single–triplet crossing and subsequent phosphorescence-based light emission in the solid/aggregated state.

The previously reported structure of B-Te-6-B[6c] and those of the new luminophores B-Te-5-B and 4B-Te[9,17] each contain at least one coplanar BPin group with respect to the central tellurophene unit. The intermolecular Te−Te contacts in these compounds all lie outside of 5.5 Å (Supporting Information, Figure S27),[9] and could partially explain the retention of phosphorescence by the suppression of intermolecular quenching. To probe the phosphorescence in B-Te-6-B further, a series of TD-DFT computations were carried out at the B3LYP/6-31G(2d,p) [LANL2DZ for Te] level of theory[21] (Supporting Information, Figure S31). The calculated UV/Vis spectrum for B-Te-6-B (Supporting Information, Figure S30)[9] indicates that the dominant absorption occurring around 350 nm ($\lambda_{\text{excit.}} = 365$ nm for phosphorescence) is due to a HOMO to LUMO electronic transition. The HOMO of B-Te-6-B has significant participation from a Te lone pair (p-orbital), while the LUMO is a delocalized π-type orbital with significant B−C π-orbital overlap (Supporting Information, Figures S32 and S33). On examining the relative computed energies for the singlet (S$_n$) and triplet (T$_n$) states for the S, Se, and Te analogues (Figure 5), one striking difference was noted in the tellurophene, B-Te-6-B. In this Te heterocycle, there is a triplet state (T$_3$) which is nearly degenerate with the singlet excited state (S$_1$), while in the S and Se analogues, the T$_3$ state is about 1 eV higher in energy. Thus it appears that B-Te-6-B has energetically well-matched states to enable efficient singlet–triplet crossing to occur; once T$_3$ is populated, then relaxation through the triplet manifold to the T$_1$ state is possible, followed by emission.

Lastly, B-Te-6-B can act as a solid-state on/off sensor for organic vapor. A sample of B-Te-6-B drop-coated on a TLC plate shows bright green luminescence when irradiated with a hand-held UV lamp ($\lambda_{\text{excit.}} = 365$ nm) at room temperature. This emission is quenched when the sample is exposed to organic vapor (for example THF, hexanes, Et$_2$O, and ben-

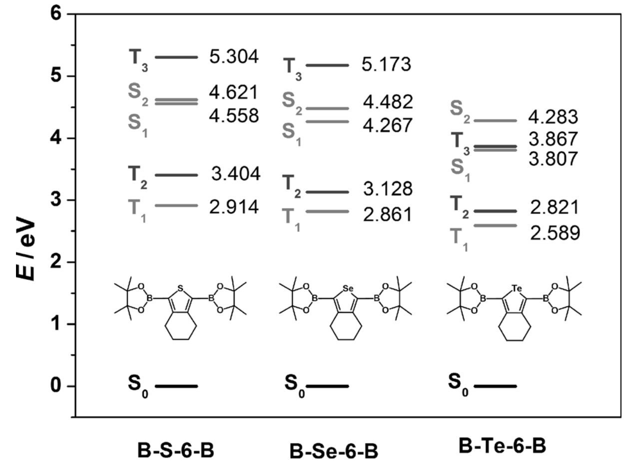

Figure 5. Computed vertical excitation energies to both singlet and triplet states at the TD-B3LYP/6-31G(2d,p) [LANL2DZ for Te] level of theory in the gas-phase, for B-S-6-B, B-Se-6-B, and B-Te-6-B.

zene; Figure 6); furthermore, removing B-Te-6-B from the organic vapor leads to renewal of light emission, demonstrating that solvent detection is reversible.

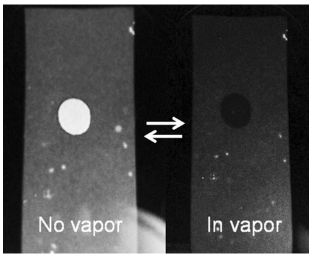

Figure 6. On/off luminescence switching of B-Te-6-B drop-coated on a TLC plate: without vapor (left) and in vapor (CH_2Cl_2) (right) under UV (365 nm) illumination at room temperature.

In conclusion, we report the unusual solid/aggregated-state phosphorescence within a series of tellurophenes bearing pinacolboronate (BPin) side groups. Our studies indicate that both Te^{II} and proximal BPin units are required for the observed room temperature phosphorescence and investigations by computational methods are presented. Furthermore, we show that reversible on/off sensing of organic vapor is possible and incorporation of these Te materials in polymer matrices (for example PMMA) leads to retention of the light-emitting properties. As our molecular emitters form high quality films directly from solution, future work will involve integrating these materials into host-free electroluminescent devices, and structural modification (by known cross-coupling strategies)[6c] to access a wider color emission palette involving this new class of molecular main-group solid-state emitter.

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