Electronic Supplementary Information

Probing the nature of peripheral boryl groups within luminescent tellurophenes

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S1. Computational Methods and Results

Ground state geometry optimizations were performed using density functional theory (DFT). For **B-Te-6-B**, both the hybrid B3LYP[1,2] and the meta hybrid M06-2X[3] functionals were used for the geometry optimizations; for **ImMe$_2^i$Pr$_2$•B-Te-6-B**, only the B3LYP functional was utilized. The cc-pVTZ/cc-pVTZ-PP(Te) and cc-pVDZ/cc-pVDZ-PP (Te) basis sets[4-6] were used for the geometry optimizations; these shall be referred to as cc-pVXZ-(PP) [X = D or T] in the subsequent discussions. The basis sets and corresponding effective core potential (ECP) for tellurium were obtained from the Basis Set Exchange library.[7,8] Harmonic vibrational frequencies were computed at the same level of theory to characterize the stationary points as true minima, representing equilibrium structures on the potential energy surfaces. The geometry for the lowest-lying triplet state for each molecule was optimized using spin-unrestricted B3LYP (UB3LYP); for **B-Te-6-B**, the triplet state geometry was also determined using UM06-2X. The geometry optimizations for the triplet state used the same basis sets as for the corresponding singlet state geometry optimizations. In previous computations for the triplet states of **2,4-TeC$_4$(BPin)$_2$Ph$_2$** and **2,5-TeC$_4$(BPin)$_2$Ph$_2$**,[9] geometries determined using UB3LYP versus restricted open-shell B3LYP (ROB3LYP) were shown to have bond lengths within < 0.01 Å and bond angles

within 1°; at the triplet state optimized geometry, the ROB3LYP relative triplet state energies compared to the singlet state (B3LYP) were, not surprisingly, about 0.1 eV larger than their UB3LYP counterparts.

For the tellurophenes, there is interest in both the absorption (corresponding to S_0 to S_1 excitation) and phosphorescence (estimated as T_1 to S_0 energy difference) energies. In the present work, the absorption (vertical excitation) energies were predicted using time-dependent density functional theory (TD-DFT) for the lowest three singlet and triplet states. The phosphorescence energies can be estimated from the singlet to triplet energy gap at the optimized geometry for the triplet state; alternatively one can perform TD-DFT computations at this geometry to determine the energy differences keeping in mind known limitations for TD-DFT in determining triplet state energies relative to singlet ones, see for example discussion in Ref. 11. Note that this model assumes that the system geometry can fully relax before phosphorescence. In our initial report,[10] the low-lying singlet and triplet excited states for **B-Te-6-B** were determined at the B3LYP/6-31G(2d,p) [LANL2DZ for Te] level of theory in the gas-phase. Through comparison with the non-emissive **B-S-6-B** and **B-Se-6-B** analogues, the emission seen in **B-Te-6-B** was attributed to the small S_1 to T_3 energy gap (< 0.1 eV), as compared to the much larger gaps (> 0.8 eV) in the analogues, as well as the expected larger spin-orbit coupling due to the presence of tellurium. In the present work, we have investigated the sensitivity of this interpretation due to (1) choice of basis set, (2) choice of functional, and (3) inclusion of solvation effects as the experiments are carried out in THF/H_2O mixtures (in addition to the aggregated state); examining alternate methodologies to DFT and TD-DFT are on-going. The DFT and TD-DFT computations were performed using Gaussian 09 (G09).[12]

For **B-Te-6-B**, the vertical excitation energies were computed at the TD-B3LYP level of theory, at the B3LYP/cc-pVDZ-(PP) geometry optimized in the gas-phase, using the cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, and jun-cc-pVTZ[13] basis sets; for all computations, the corresponding basis sets incorporating the effective core potential (ECP) for Te were used, see Table S1. Relative to the computations with the largest basis set (jun-cc-pVTZ), the mean average difference (MAD) for the six states considered is < 0.1 eV. Moreover, the S_1 to T_3 energy gap remains small (< 0.1 eV) for all basis sets considered. The predicted vertical excitation energies to S_1 are slightly larger than the measured peak absorption at

350 nm (3.5 eV) but well within the expected error for TD-DFT. Hence, computations, even with the fairly modest cc-pVDZ basis set, should be suitable for examining the photophysical properties of the tellurophenes although cc-pVTZ or aug-cc-pVDZ would be preferred.

For **B-Te-6-B**, the vertical excitation energies were computed using TD-DFT, at the B3LYP/cc-pVDZ-(PP) geometry optimized in the gas-phase, using the M06-2X[3] and CAM-B3LYP[14] functionals, *i.e.,* a hybrid meta-GGA and a range-separated hybrid functional. These computations used the cc-pVDZ basis set. As seen in Table S2, the general energy ordering is similar; however, both M06-2X and CAM-B3LYP place the S_1 state higher in energy than T_3 but this shift moves the computed vertical excitation energy to S_1 further from the experimental measurement of the UV-Vis absorption maximum. With M06-2X, the energies of the lowest lying triplet states are significantly increased but this change seems to be strongly basis set dependent, see discussion of Table S4 below. Overall from the vertical excitation energies alone, there does not appear to be a strong preference for using one functional versus another; thus, the present work primarily focuses on using the B3LYP functional.

To assess the role of solvation on the vertical excitation energies for **B-Te-6-B**, they were re-computed at the TD-B3LYP/cc-pVDZ-(PP) level of theory using the polarizable continuum model (IEF-PCM[15,16] and universal force field (UFF) atomic radii) with parameters for THF and water; the computations were at the B3LYP/cc-pVDZ-(PP) geometry optimized in the gas-phase, see Table S3. The MAD for the lowest six states, when compared to the gas-phase results, is less than 0.03 eV in both water and THF. Hence, gas-phase computations should be suitable for interpreting the photophysical properties.

To determine (approximately) the phosphorescence energies, the lowest-lying triplet state for **B-Te-6-B** was optimized using the UB3LYP/cc-pVTZ-(PP) and UM06-2X/cc-pVDZ-(PP) levels of theory. The phosphorescence energy can then be estimated using the energy difference to the ground S_0 state at the T_1 geometry or, alternatively, determined from the TD-DFT energies at this geometry, see Table S4. As expected from our previous computations,[9] the phosphorescence energies are under-estimated from the T_1 (UB3LYP) to S_0 (B3LYP) values; similar under-estimation comes from the TD-B3LYP results. On the

other hand, the phosphorescence energies are over-estimated from the T_1 (UM06-2X) to S_0 (M06-2X) values; the TD-M06-2X/cc-pVTZ-(PP) result under-estimates the phosphorescence energy albeit the value is closer to the experimental measurement (2.32 eV) than from TD-B3LYP. In the TD-M06-2X/cc-pVDZ-(PP) computations, the T_1 and T_2 electronic states are near-degenerate, as seen previously at the S_1 geometry, see Table S2. This near-degeneracy does not appear for other computations, and, therefore, care must be taken using the modest cc-pVDZ-(PP) basis set with the M06-2X functional.

Spin-orbit coupling was considered using the time-dependent density functional theory framework[17-20] within the Amsterdam Density Functional (ADF) software package.[21] The ground state and triplet state optimized structures were determined at B3LYP/TZ2P (UB3LYP/TZ2P) level of theory.[1,2,22] The computations include scalar relativistic (ZORA)[23] and spin–orbit relativistic (SO) methods. Vertical excitation energies were determined via TD-DFT at the B3LYP/TZ2P level of theory. All studies were performed in the gas-phase. The TD-DFT results without spin-orbit coupling for the lowest three singlet and triplet states are provided in Table S5. The lowest energy "singlet" states at the S_1 geometry and the lowest energy "triplet" states at the T_1 geometry are provided in Table S6; these are the spin-orbit mixed states that have the largest contributions from the S_1 and T_1 states, respectively (the three components for the triplet state are grouped into a single contribution). For the absorption step, one sees that the S_1 and T_3 states are strongly mixed, and thus, as expected solely from the energetic arguments presented previously,[9,10] excitation provides access to the triplet manifold for phosphorescence. At the T_1 geometry, the lowest "triplet" states, and the ground state, have modest T_3 contributions, which provide the required oscillator strength (f) for de-excitation, see Table S6 for the small (but non-zero) oscillator strengths. Further analysis of computations including spin-orbit coupling for other tellurophenes is underway. However, it is clear that computations excluding spin-orbit coupling can be utilized to provide reasonable explanations for absorption and phosphorescence wavelengths.

Table S1. The excitation energies[a] (in eV) of the three lowest-lying singlet and triplet states for **B-Te-6-B** with different basis sets[b] at the TD-B3LYP level of theory at the gas-phase S_0 geometry (as determined at the B3LYP/cc-pVDZ-(PP) level of theory).

Excited state	Ref. 10[c]	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	jun-cc-pVTZ
T_1	2.5894	2.6987	2.6682	2.6659	2.6511
T_2	2.8208	2.7228	2.6966	2.6951	2.6928
S_1	3.8070	3.6916	3.6021	3.6279	3.5955
T_3	3.8668	3.7444	3.6848	3.6864	3.6597
S_2	4.2826	4.2002	4.0958	4.1451	4.0982
S_3	4.3186	4.3031	4.2295	4.2546	4.2262
MAD[d]	0.1475	0.0729	0.0097	0.0252	---

a) Results reported to 4 decimal places to facilitate present and future computational comparison.

b) For Te, the basis set employs the corresponding ECP.

c) 6-31G(2d,p)/LanL2DZ for Te.

d) Mean absolute difference relative to the jun-cc-pVTZ results.

Table S2. The excitation energies[a] (in eV) of the three lowest-lying singlet and triplet states for **B-Te-6-B** at the TD-B3LYP, TD-CAM-B3LYP, and TD-M06-2X levels of theory with the cc-pVDZ-(PP) basis set at the gas-phase S_0 geometry (as determined at the B3LYP/cc-pVDZ-(PP) level of theory). Change relative to TD-B3LYP results given in parenthesis.

Excited state	B3LYP	CAM-B3LYP	M06-2X
T_1	2.6987	2.5288 (-0.1699)	3.0331 (0.3344)
T_2	2.7228	2.8214 (0.0986)	3.0350 (0.3122)
S_1	3.6916	3.8938 (0.2022)	3.9857 (0.2941)
T_3	3.7444	3.7095 (-0.0349)	3.7046 (-0.0398)
S_2	4.2002	4.2174 (0.0172)	4.1652 (-0.0350)
S_3	4.3031	4.4743 (0.1712)	4.5532 (0.2501)

a) Results reported to 4 decimal places to facilitate present and future computational comparison.

Table S3. The excitation energies[a] (in eV) of the three lowest-lying singlet and triplet states for **B-Te-6-B** at the TD-B3LYP/cc-pVDZ-(PP) level of theory for different solvents (THF and H_2O treated with IEF-PCM) at the gas-phase S_0 geometry (as determined at the B3LYP/cc-pVDZ-(PP) level of theory). Change relative to gas-phase results given in parenthesis.

Excited state	Gas-phase	H_2O	THF
T_1	2.6987	2.7051 (0.0064)	2.7033 (0.0046)
T_2	2.7228	2.8041 (0.0813)	2.7884 (0.0656)
S_1	3.6916	3.7172 (0.0256)	3.6967 (0.0051)
T_3	3.7444	3.7896 (0.0452)	3.7820 (0.0376)
S_2	4.2002	4.2259 (0.0257)	4.2166 (0.0164)
S_3	4.3031	4.2717 (-0.0314)	4.2639 (-0.0392)
MAD[b]	---	0.0097	0.0252

a) Results reported to 4 decimal places to facilitate present and future computational comparison.
b) Mean absolute difference compared to the gas-phase results.

Table S4. The excitation energies[a] (in eV) using various levels of theory for **B-Te-6-B** at the optimized T_1 geometry. Experimental phosphorescence energy is 2.32 eV.

Excited state	TD-B3LYP/ cc-pVTZ-(PP)[b]	TD-M06-2X/ cc-pVTZ-(PP)[b]	TD-M06-2X/ cc-pVDZ-(PP)[c]
T_1	1.9196 (2.12)[d]	2.0915 (2.5452)[e]	2.7200
T_2	2.5294	2.7311	2.7560
T_3	3.6373	3.6558	3.8695
S_1	3.3673	3.5257	3.7091
S_2	3.8360	4.0168	4.3207
S_3	4.4945	4.1080	4.3260

a) Results reported to 4 decimal places to facilitate present and future computational comparison.
b) T_1 geometry determined at the UB3LYP/cc-pVTZ-(PP) level of theory.
c) T_1 geometry determined at the UM06-2X/cc-pVDZ-(PP) level of theory.
d) Energy computed as difference between UB3LYP/B3LYP triplet/singlet state energies.
e) Energy computed as difference between UM06-2X/M06-2X triplet/singlet state energies.

Table S5. The excitation energies[a] (in eV) at the TD-B3LYP/TZVP/ZORA of theory for **B-Te-6-B** at the specified geometries. Experimental phosphorescence energy is 2.32 eV.

Excited state	S_1 geometry	T_1 geometry
T_1	2.7340	1.9784
T_2	2.8010	2.5624
T_3	3.6356	3.6261
S_1	3.6510	3.4282
S_2	4.0748	3.8139
S_3	4.2947	4.0117

a) Results reported to 4 decimal places to facilitate present and future computational comparison.

Table S6. The excitation energies[a] (in eV) to the lowest-energy "singlet" state (at the S_1 geometry) and "triplet" states (at the T_1 geometry) at the TD-B3LYP/TZVP/ZORA [+ spin-orbit coupling] level of theory for **B-Te-6-B**. Also, included are the oscillator strength (f) and the contributions of the spin-states (the three components of the triplet state have been collected into a single contribution). Experimental phosphorescence energy is 2.32 eV.

Geometry	Energy	Contributing States[b]	f	Contributions to ground state
S_1	3.5636	$0.5509\ S_1 + 0.4298\ T_3$	0.4362E-01	$0.9960\ S_0 +$
	3.7354	$0.4287\ S_1 + 0.5524\ T_3$	0.3394E-01	$0.0030\ T_3$
T_1	1.9876	$0.9967\ T_1 + 0.0014\ T_3$	0.1277E-07	$0.9962\ S_0 +$
	1.9879	$0.9970\ T_1 + 0.0013\ T_3$	0.2539E-05	$0.0020\ T_3$
	1.9889	$0.9908\ T_1 + 0.0008\ T_3$	0.1370E-05	

a) Results reported to 4 decimal places to facilitate present and future computational comparison.

Table S7. The excitation energies[a] (in eV) at the TD-B3LYP level of theory with the cc-pVDZ-(PP) and cc-pVTZ-(PP) basis sets for **ImMe$_2$^{i}Pr$_2$•B-Te-6-B** at the specified geometries

Excited state	cc-pVDZ-(PP)[b]	cc-pVDZ-(PP)[c]	cc-pVTZ-(PP)[b]	cc-pVTZ-(PP)[d]
T$_1$	2.7257	2.5938	2.7200	2.7133
T$_2$	3.0698	2.9938	2.7560	3.0068
T$_3$	4.1075	3.9026	3.8695	4.0369
S$_1$	3.9333	3.8245	3.7091	3.8618
S$_2$	4.3030	4.1452	4.3207	4.2594
S$_3$	4.4045	4.3242	4.3260	4.3565

a) Results reported to 4 decimal places to facilitate present and future computational comparison.

b) At the reported X-ray structure.

c) At the B3LYP/cc-pVDZ-(PP) optimized geometry for S$_0$.

d) At the B3LYP/cc-pVTZ-(PP) optimized geometry for S$_0$.

Table S8. The excitation energies[a] (in eV) at the TD-B3LYP level of theory with the cc-pVDZ-(PP) and cc-pVTZ-(PP) basis sets for **ImMe$_2$^{i}Pr$_2$•B-Te-6-B** at the specified geometries.

Excited state	cc-pVDZ-(PP)[b]	cc-pVTZ-(PP)[c]
T$_1$	1.6107	1.6702
T$_2$	2.7651	2.7427
T$_3$	3.5077	3.5536
S$_1$	3.3709	3.3595
S$_2$	3.6973	3.6966
S$_3$	3.8773	3.9357

a) Results reported to 4 decimal places to facilitate present and future computational comparison.

b) At the UB3LYP/cc-pVDZ-(PP) optimized geometry for T$_1$.

c) At the UB3LYP/cc-pVTZ-(PP) optimized geometry for T$_1$.

Figure S1. HOMO (top) and LUMO (bottom) of **ImMe$_2$^{i}Pr$_2$•B-Te-6-B** for the S$_0$ state at the (B3LYP/cc-pVDZ-(PP)) S$_0$ equilibrium geometry as determined at the B3LYP/cc-pVDZ-(PP) level of theory in the gas-phase.
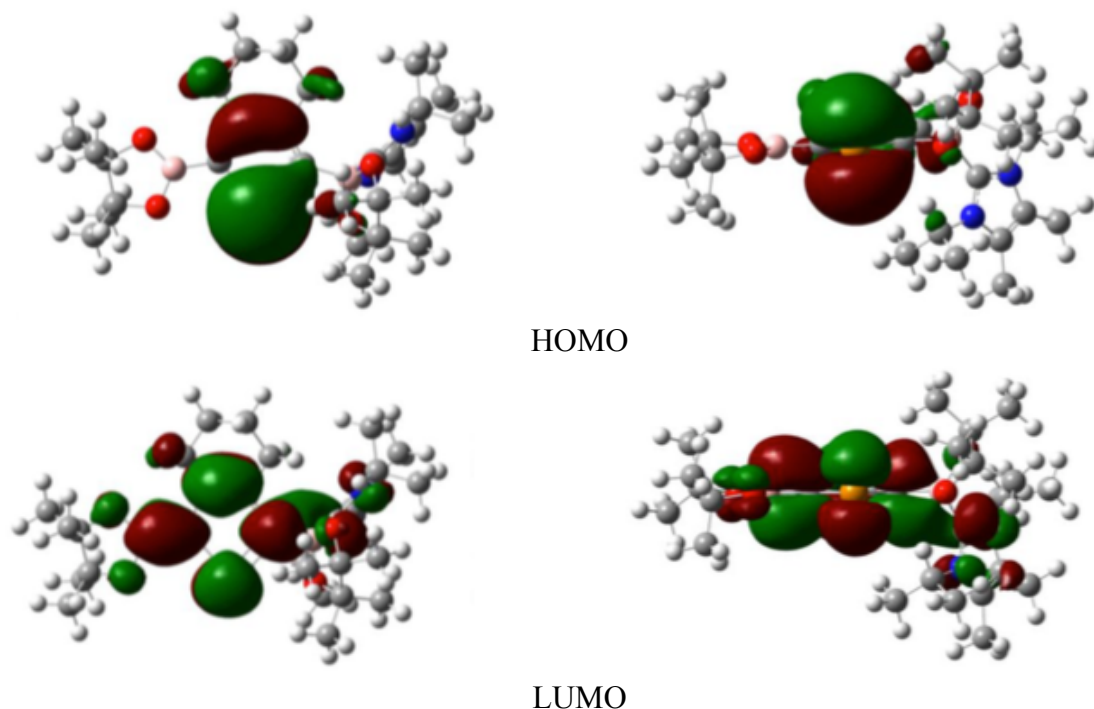
HOMO

LUMO

Figure S2. HOMO (top) and LUMO (bottom) of **ImMe$_2$^{i}Pr$_2$•B-Te-6-B** for the S$_0$ state at the (B3LYP/cc-pVDZ-(PP)) T$_1$ equilibrium geometry as determined at the B3LYP/cc-pVDZ-(PP) level of theory in the gas-phase.

HOMO

LUMO
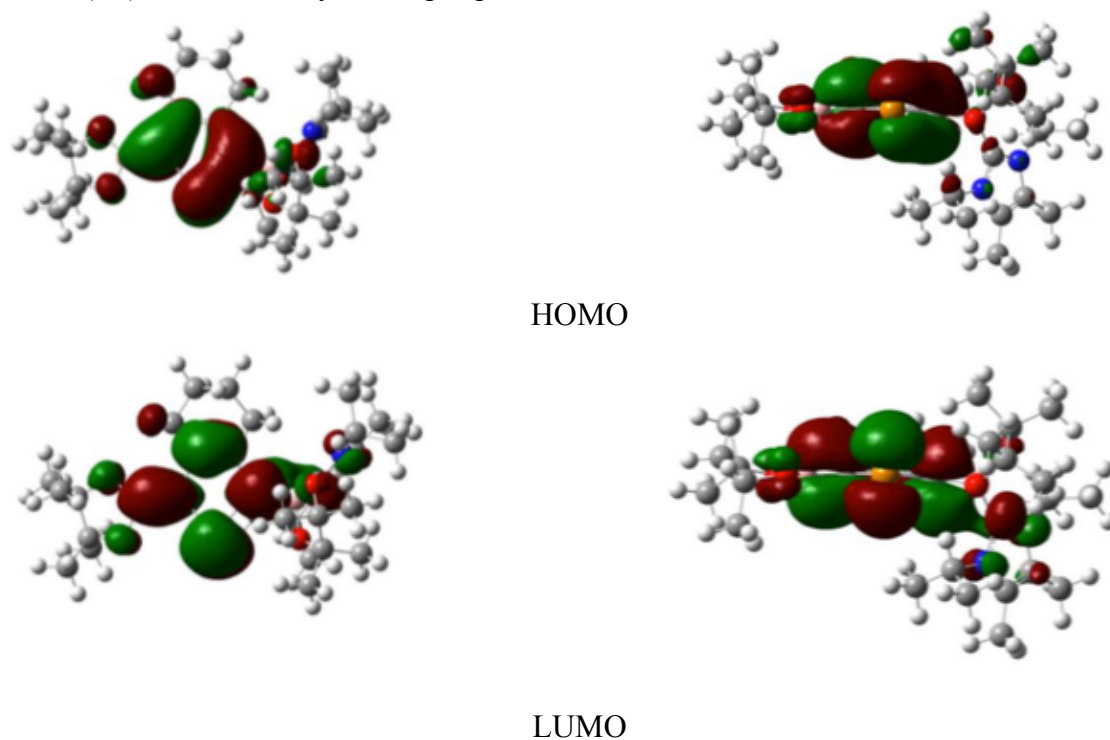
Table S9. Gas phase B3LYP/cc-pVDZ (cc-pVDZ-PP Te) determined xyz coordinates (in Å) for **B-Te-6-B** at S_0 equilibrium geometry

1	52	0	0.000524	-1.250603	0.053919
2	6	0	-1.369569	0.297140	-0.135014
3	6	0	1.370218	0.298198	-0.129520
4	6	0	-0.723961	1.497220	-0.285378
5	6	0	0.724360	1.497815	-0.282222
6	8	0	3.355365	-1.295015	0.034683
7	8	0	3.897185	0.924784	-0.122844
8	5	0	2.882767	-0.005758	-0.076013
9	6	0	5.135874	0.193513	-0.278449
10	6	0	4.770570	-1.208571	0.309326
11	6	0	6.237478	0.928789	0.465208
12	1	0	7.170785	0.346057	0.444489
13	1	0	6.425198	1.896710	-0.019882
14	1	0	5.958167	1.116263	1.508958
15	6	0	5.436382	0.145679	-1.774297
16	1	0	5.466845	1.173463	-2.160894
17	1	0	6.403695	-0.336182	-1.975381
18	1	0	4.649328	-0.401874	-2.312653
19	6	0	5.474878	-2.379901	-0.353709
20	1	0	6.565710	-2.287028	-0.241709
21	1	0	5.157684	-3.316592	0.125115
22	1	0	5.230018	-2.440617	-1.420919
23	6	0	4.932894	-1.273069	1.826010
24	1	0	4.456829	-2.193011	2.191689
25	1	0	5.992502	-1.282784	2.118308
26	1	0	4.439972	-0.416222	2.307658
27	6	0	0.771101	3.836881	0.581924
28	1	0	1.158755	4.844033	0.370436
29	1	0	1.133571	3.566846	1.584807
30	6	0	-0.779005	3.839669	0.572786
31	1	0	-1.153724	3.578907	1.573671
32	1	0	-1.160459	4.846616	0.349264
33	6	0	-1.381214	2.844493	-0.434974
34	1	0	-1.193313	3.210842	-1.459382
35	1	0	-2.467544	2.767651	-0.312324
36	6	0	1.380738	2.846315	-0.425633
37	1	0	2.466407	2.771328	-0.296612
38	1	0	1.196849	3.215401	-1.449890
39	5	0	-2.882120	-0.007364	-0.087369
40	8	0	-3.353782	-1.286105	0.112561
41	8	0	-3.897731	0.912594	-0.227556
42	6	0	-4.776523	-1.259732	-0.133737
43	6	0	-5.128850	0.240983	0.128202
44	6	0	-5.457632	-2.245768	0.799796
45	6	0	-4.982910	-1.668612	-1.590079
46	6	0	-6.254487	0.790418	-0.730954
47	6	0	-5.384525	0.537471	1.603641
48	1	0	-6.551516	-2.177810	0.700352
49	1	0	-5.150681	-3.268194	0.539609
50	1	0	-5.182640	-2.060994	1.845174
51	1	0	-4.516336	-2.650260	-1.749316
52	1	0	-6.050636	-1.739391	-1.841679
53	1	0	-4.505713	-0.947142	-2.268968
54	1	0	-7.184562	0.230596	-0.550200
55	1	0	-6.431561	1.844158	-0.474692
56	1	0	-6.006404	0.733518	-1.797627
57	1	0	-5.408521	1.626549	1.745651
58	1	0	-6.343160	0.116696	1.938693
59	1	0	-4.579233	0.125750	2.229047

Table S10. Gas phase UB3LYP/cc-pVDZ (cc-pVDZ-PP Te) determined xyz coordinates (in Å) for **B-Te-6-B** at T_1 geometry

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Te   0.000917  -1.183550   0.038050
C   -1.428225   0.353675  -0.138595
C    1.428266   0.354445  -0.125505
C   -0.714610   1.555219  -0.273081
C    0.714223   1.555594  -0.269225
O    3.336227  -1.305830   0.033299
O    3.954362   0.910160  -0.094392
B    2.894392   0.012157  -0.065932
C    5.154770   0.132881  -0.273578
C    4.746491  -1.253965   0.321115
C    6.300082   0.822197   0.448838
H    7.208305   0.201293   0.416638
H    6.520514   1.780138  -0.042631
H    6.044163   1.025606   1.495757
C    5.430099   0.065793  -1.774388
H    5.488349   1.090154  -2.167125
H    6.376340  -0.450323  -1.991334
H    4.613753  -0.456553  -2.294245
C    5.427942  -2.448723  -0.324803
H    6.520256  -2.381961  -0.207649
H    5.085957  -3.373626   0.160562
H    5.187732  -2.513390  -1.393027
C    4.900293  -1.305046   1.839972
H    4.395920  -2.206478   2.214628
H    5.957189  -1.341933   2.140482
H    4.429751  -0.426711   2.305467
C    0.772596   3.914687   0.551845
H    1.156879   4.914486   0.302612
H    1.140767   3.681372   1.561526
C   -0.776711   3.912350   0.551606
H   -1.144206   3.673847   1.560403
H   -1.163807   4.912109   0.306524
C   -1.384799   2.891285  -0.426342
H   -1.227210   3.241012  -1.462759
H   -2.467820   2.797240  -0.280182
C    1.384131   2.891711  -0.422239
H    2.466712   2.799293  -0.272116
H    1.228407   3.239498  -1.459687
B   -2.894508   0.009806  -0.090170
O   -3.334838  -1.295851   0.117741
O   -3.955927   0.894743  -0.235429
C   -4.752472  -1.305283  -0.136625
C   -5.148834   0.180607   0.144115
C   -5.412786  -2.323386   0.778025
C   -4.946835  -1.693964  -1.600916
C   -6.314574   0.695064  -0.683638
C   -5.384634   0.450590   1.628809
H   -6.508008  -2.281692   0.677534
H   -5.080443  -3.334316   0.503232
H   -5.144650  -2.147894   1.826964
H   -4.451427  -2.658647  -1.777799
H   -6.011404  -1.792083  -1.857417
H   -4.490237  -0.944089  -2.263250
H   -7.220277   0.100613  -0.489227
H   -6.523848   1.739597  -0.413572
H   -6.086885   0.657967  -1.755865
H   -5.437734   1.536837   1.784671
H   -6.322499  -0.002912   1.980277
H   -4.552687   0.056177   2.230383
```

Table S11. Gas phase B3LYP/cc-pVTZ (cc-pVTZ-PP Te) determined xyz coordinates (in Å) for **B-Te-6-B** at S_0 equilibrium geometry

```
Te        0.00048400   -1.23448400    0.06067700
C        -1.37682400    0.32070700   -0.11886600
C         1.37720800    0.32155400   -0.11652100
C        -0.72029000    1.51659900   -0.26167300
C         0.72026000    1.51711200   -0.25982500
O         3.34563800   -1.29272100    0.01828700
O         3.90756500    0.91888200   -0.10672900
B         2.88082800    0.00152600   -0.07142500
C         5.15796600    0.18843000   -0.25931600
C         4.77482400   -1.24376300    0.27572800
C         6.23856800    0.90969100    0.53408300
H         7.17914400    0.35775900    0.49923000
H         6.41092700    1.89507900    0.10175100
H         5.95248100    1.04407000    1.57429000
C         5.49989800    0.20858900   -1.75031800
H         5.55591500    1.24421300   -2.08375600
H         6.46030200   -0.26730800   -1.94856100
H         4.73527600   -0.29474200   -2.34081000
C         5.43834200   -2.40600000   -0.45020300
H         6.52274100   -2.36773700   -0.33562300
H         5.08806000   -3.34647800   -0.02561600
H         5.19985400   -2.40697500   -1.51087100
C         4.95697500   -1.39702800    1.78718000
H         4.48755400   -2.32761200    2.10404200
H         6.01068300   -1.43316700    2.06382000
H         4.48354300   -0.57982600    2.33010800
C         0.77271900    3.88694700    0.56932600
H         1.15577200    4.87946800    0.32570400
H         1.13424600    3.65740300    1.57298000
C        -0.77835900    3.88879800    0.56304400
H        -1.14804000    3.66580600    1.56525000
H        -1.15703600    4.88092200    0.31103200
C        -1.38337400    2.86253400   -0.41472100
H        -1.22500800    3.21342400   -1.44107500
H        -2.45809100    2.78766800   -0.27526300
C         1.38254600    2.86407000   -0.40874700
H         2.45665900    2.79080300   -0.26450000
H         1.22628700    3.21701700   -1.43481900
B        -2.88034400    0.00018300   -0.07732900
O        -3.34472900   -1.28018700    0.13298000
O        -3.90770700    0.90342300   -0.23812600
C        -4.77697500   -1.28824200   -0.11159800
C        -5.15511800    0.22824400    0.09138600
C        -5.43019500   -2.25585400    0.86572500
C        -4.97724900   -1.77817300   -1.54722500
C        -6.24631400    0.75401600   -0.83070300
C        -5.47846900    0.58444400    1.54360200
H        -6.51598800   -2.24248900    0.75896100
H        -5.08425000   -3.26842400    0.65958500
H        -5.17843300   -2.01838400    1.89632900
H        -4.51035600   -2.75687200   -1.65164900
H        -6.03419700   -1.87437900   -1.79576800
H        -4.51159000   -1.10509800   -2.26615600
H        -7.18618300    0.22677800   -0.65980600
H        -6.41332600    1.81212500   -0.63039900
H        -5.97377400    0.64893000   -1.87788500
H        -5.53301600    1.66862300    1.63564100
H        -6.43521400    0.16604100    1.85615900
H        -4.70551200    0.22675000    2.22278100
```

Table S12. Gas phase UB3LYP/cc-pVTZ (cc-pVTZ-PP Te) determined xyz coordinates (in Å) for **B-Te-6-B** at T_1 geometry

Te	- 0.02330600	-1.27092700	0.00000000
C	-1.38842700	0.27364800	-0.12626400
C	1.42137500	0.36070000	-0.11479200
C	-0.66055000	1.56609000	-0.24717000
C	0.72030100	1.57667500	-0.23705200
O	3.34623500	-1.27675700	0.04332600
O	3.95420900	0.92997800	-0.08150200
B	2.90650400	0.03024100	-0.05398500
C	5.18658900	0.17140500	-0.23324700
C	4.77430300	-1.25028200	0.30902400
C	6.28513000	0.87156200	0.55459900
H	7.21289800	0.29825300	0.52101800
H	6.47894500	1.85062700	0.11700400
H	6.00375700	1.01767200	1.59452600
C	5.52674800	0.17566600	-1.72508400
H	5.60342400	1.20806000	-2.06436200
H	6.47675500	-0.32111800	-1.92233300
H	4.75080800	-0.31516700	-2.31142500
C	5.42256700	-2.42913500	-0.40391000
H	6.50672000	-2.40814200	-0.28275700
H	5.05398600	-3.36046200	0.02539400
H	5.19076600	-2.43391200	-1.46607300
C	4.94427400	-1.39490300	1.82301200
H	4.45592600	-2.31412900	2.14435900
H	5.99547100	-1.44813500	2.10635600
H	4.48293000	-0.56429300	2.35592900
C	0.74720100	3.94330600	0.57077200
H	1.19553600	4.92586200	0.41224000
H	0.98612100	3.65691700	1.59650400
C	-0.78694400	4.01873600	0.39919300
H	-1.26266300	4.00901400	1.38063500
H	-1.07259300	4.96219400	-0.06892200
C	-1.38108400	2.86330400	-0.44404600
H	-1.29430300	3.12825100	-1.50730900
H	-2.44455000	2.75579800	-0.24956500
C	1.40422400	2.91877800	-0.36787200
H	2.46681800	2.83282600	-0.15616500
H	1.31963400	3.26727700	-1.40443000
B	-2.87465300	-0.02159600	-0.06569700
O	-3.36012600	-1.31074900	0.09105100
O	-3.90200600	0.90437900	-0.15432400
C	-4.79263600	-1.28020700	-0.13031800
C	-5.14322000	0.22506300	0.17718900
C	-5.44866800	-2.29935300	0.79171200
C	-5.02805200	-1.66873800	-1.59206600
C	-6.26046400	0.81712800	-0.67114300
C	-5.41289800	0.49202100	1.65986100
H	-6.53572700	-2.26084800	0.70479800
H	-5.12424000	-3.30190900	0.51363100
H	-5.17584100	-2.13474900	1.83118500
H	-4.58032300	-2.64564900	-1.77119000
H	-6.09082600	-1.73032000	-1.82688300
H	-4.56317700	-0.95571200	-2.27203600
H	-7.19944200	0.28770100	-0.50172100
H	-6.40999000	1.86188200	-0.39910500
H	-6.02434800	0.77622200	-1.73161900
H	-5.44750100	1.56887100	1.82215200
H	-6.36489900	0.06743500	1.97884000
H	-4.62254200	0.08108500	2.28692500

Table S13. Gas phase M06-2X/cc-pVDZ (cc-pVDZ-pp Te) determined xyz coordinates (in Å) for **B-Te-6-B** at S_0 equilibrium geometry

```
Te   0.000524  -1.250603   0.053919
C   -1.369569   0.297140  -0.135014
C    1.370218   0.298198  -0.129520
C   -0.723961   1.497220  -0.285378
C    0.724360   1.497815  -0.282222
O    3.355365  -1.295015   0.034683
O    3.897185   0.924784  -0.122844
B    2.882767  -0.005758  -0.076013
C    5.135874   0.193513  -0.278449
C    4.770570  -1.208571   0.309326
C    6.237478   0.928789   0.465208
H    7.170785   0.346057   0.444489
H    6.425198   1.896710  -0.019882
H    5.958167   1.116263   1.508958
C    5.436382   0.145679  -1.774297
H    5.466845   1.173463  -2.160894
H    6.403695  -0.336182  -1.975381
H    4.649328  -0.401874  -2.312653
C    5.474878  -2.379901  -0.353709
H    6.565710  -2.287028  -0.241709
H    5.157684  -3.316592   0.125115
H    5.230018  -2.440617  -1.420919
C    4.932894  -1.273069   1.826010
H    4.456829  -2.193011   2.191689
H    5.992502  -1.282784   2.118308
H    4.439972  -0.416222   2.307658
C    0.771101   3.836881   0.581924
H    1.158755   4.844033   0.370436
H    1.133571   3.566846   1.584807
C   -0.779005   3.839669   0.572786
H   -1.153724   3.578907   1.573671
H   -1.160459   4.846616   0.349264
C   -1.381214   2.844493  -0.434974
H   -1.193313   3.210842  -1.459382
H   -2.467544   2.767651  -0.312324
C    1.380738   2.846315  -0.425633
H    2.466407   2.771328  -0.296612
H    1.196849   3.215401  -1.449890
B   -2.882120  -0.007364  -0.087369
O   -3.353782  -1.286105   0.112561
O   -3.897731   0.912594  -0.227556
C   -4.776523  -1.259732  -0.133737
C   -5.128850   0.240983   0.128202
C   -5.457632  -2.245768   0.799796
C   -4.982910  -1.668612  -1.590079
C   -6.254487   0.790418  -0.730954
C   -5.384525   0.537471   1.603641
H   -6.551516  -2.177810   0.700352
H   -5.150681  -3.268194   0.539609
H   -5.182640  -2.060994   1.845174
H   -4.516336  -2.650260  -1.749316
H   -6.050636  -1.739391  -1.841679
H   -4.505713  -0.947142  -2.268968
H   -7.184562   0.230596  -0.550200
H   -6.431561   1.844158  -0.474692
H   -6.006404   0.733518  -1.797627
H   -5.408521   1.626549   1.745651
H   -6.343160   0.116696   1.938693
H   -4.579233   0.125750   2.229047
```

Table S14. Gas phase UM06-2X/cc-pVDZ (cc-pVDZ-pp Te) determined xyz coordinates (in Å) for **B-Te-6-B** at T_1 geometry

```
Te    0.000917  -1.183550   0.038050
C    -1.428225   0.353675  -0.138595
C     1.428266   0.354445  -0.125505
C    -0.714610   1.555219  -0.273081
C     0.714223   1.555594  -0.269225
O     3.336227  -1.305830   0.033299
O     3.954362   0.910160  -0.094392
B     2.894392   0.012157  -0.065932
C     5.154770   0.132881  -0.273578
C     4.746491  -1.253965   0.321115
C     6.300082   0.822197   0.448838
H     7.208305   0.201293   0.416638
H     6.520514   1.780138  -0.042631
H     6.044163   1.025606   1.495757
C     5.430099   0.065793  -1.774388
H     5.488349   1.090154  -2.167125
H     6.376340  -0.450323  -1.991334
H     4.613753  -0.456553  -2.294245
C     5.427942  -2.448723  -0.324803
H     6.520256  -2.381961  -0.207649
H     5.085957  -3.373626   0.160562
H     5.187732  -2.513390  -1.393027
C     4.900293  -1.305046   1.839972
H     4.395920  -2.206478   2.214628
H     5.957189  -1.341933   2.140482
H     4.429751  -0.426711   2.305467
C     0.772596   3.914687   0.551845
H     1.156879   4.914486   0.302612
H     1.140767   3.681372   1.561526
C    -0.776711   3.912350   0.551606
H    -1.144206   3.673847   1.560403
H    -1.163807   4.912109   0.306524
C    -1.384799   2.891285  -0.426342
H    -1.227210   3.241012  -1.462759
H    -2.467820   2.797240  -0.280182
C     1.384131   2.891711  -0.422239
H     2.466712   2.799293  -0.272116
H     1.228407   3.239498  -1.459687
B    -2.894508   0.009806  -0.090170
O    -3.334838  -1.295851   0.117741
O    -3.955927   0.894743  -0.235429
C    -4.752472  -1.305283  -0.136625
C    -5.148834   0.180607   0.144115
C    -5.412786  -2.323386   0.778025
C    -4.946835  -1.693964  -1.600916
C    -6.314574   0.695064  -0.683638
C    -5.384634   0.450590   1.628809
H    -6.508008  -2.281692   0.677534
H    -5.080443  -3.334316   0.503232
H    -5.144650  -2.147894   1.826964
H    -4.451427  -2.658647  -1.777799
H    -6.011404  -1.792083  -1.857417
H    -4.490237  -0.944089  -2.263250
H    -7.220277   0.100613  -0.489227
H    -6.523848   1.739597  -0.413572
H    -6.086885   0.657967  -1.755865
H    -5.437734   1.536837   1.784671
H    -6.322499  -0.002912   1.980277
H    -4.552687   0.056177   2.230383
```

Table S15. Gas phase B3LYP/TZ2P/ZORA determined xyz coordinates (in Å) for **B-Te-6-B** at S_0 equilibrium geometry

Te	0.001581	-1.294725	-0.114863
C	1.385860	0.278798	0.071905
C	-1.385909	0.276201	0.067650
C	0.721802	1.475700	0.211448
C	-0.724436	1.473673	0.214545
O	-3.415869	-1.267074	-0.230606
O	-3.895573	0.907603	0.322409
B	-2.903601	-0.015740	0.051704
C	-5.157826	0.187394	0.439664
C	-4.860316	-1.139991	-0.370092
C	-6.276345	1.058487	-0.132752
H	-7.230147	0.522189	-0.117436
H	-6.385046	1.958930	0.476963
H	-6.065583	1.366385	-1.157420
C	-5.398122	-0.055516	1.937473
H	-5.406099	0.906800	2.454864
H	-6.357230	-0.549581	2.112447
H	-4.604980	-0.666693	2.374515
C	-5.522618	-2.398562	0.189344
H	-6.612672	-2.307296	0.158720
H	-5.237434	-3.260984	-0.418150
H	-5.216823	-2.592546	1.217817
C	-5.157395	-1.011832	-1.871764
H	-4.753086	-1.885936	-2.387812
H	-6.232202	-0.963456	-2.063987
H	-4.686529	-0.122130	-2.296439
C	-0.781814	3.843187	-0.641127
H	-1.169407	4.840410	-0.410277
H	-1.143942	3.592880	-1.643123
C	0.776081	3.849899	-0.634404
H	1.148983	3.612958	-1.635505
H	1.152931	4.847945	-0.390112
C	1.380494	2.831445	0.361779
H	1.210329	3.188444	1.386830
H	2.457797	2.758875	0.229433
C	-1.385447	2.828902	0.359208
H	-2.462985	2.754562	0.229238
H	-1.217016	3.190402	1.382918
B	2.903476	-0.013578	0.067045
O	3.407300	-1.299583	0.049777
O	3.902732	0.940877	0.087060
C	4.840144	-1.223818	0.298886
C	5.176282	0.263815	-0.128158
C	5.543470	-2.305077	-0.521264
C	5.048197	-1.484536	1.798559
C	6.248794	0.952765	0.716960
C	5.514129	0.407363	-1.619618
H	6.629090	-2.232911	-0.404083
H	5.229114	-3.290973	-0.170278
H	5.300966	-2.229602	-1.581760
H	4.622004	-2.458722	2.049948
H	6.109438	-1.494128	2.059538
H	4.545475	-0.729754	2.407792
H	7.205416	0.428561	0.629091
H	6.390668	1.976784	0.362385
H	5.969104	0.994588	1.770116
H	5.547537	1.469668	-1.873611
H	6.486967	-0.032962	-1.852646
H	4.756183	-0.066145	-2.247927

Table S16. Gas phase UB3LYP/TZ2P/ZORA determined xyz coordinates (in Å) for **B-Te-6-B** at T_1 geometry

Te	-0.023812	-1.343939	0.109135
C	-1.389504	0.212358	-0.059682
C	1.413048	0.281859	-0.053402
C	-0.660153	1.506247	-0.158307
C	0.709902	1.511564	-0.160763
O	3.419065	-1.270768	0.124429
O	3.900888	0.940312	-0.252431
B	2.909962	-0.001448	-0.060356
C	5.155260	0.227386	-0.427719
C	4.858676	-1.146674	0.284284
C	6.274369	1.050491	0.195691
H	7.222745	0.512488	0.145780
H	6.386761	1.985039	-0.354619
H	6.064387	1.293888	1.234845
C	5.383162	0.091030	-1.934743
H	5.385429	1.085698	-2.380815
H	6.339434	-0.385949	-2.151392
H	4.588147	-0.487316	-2.405523
C	5.528413	-2.357819	-0.349283
H	6.614875	-2.259832	-0.310435
H	5.249409	-3.256796	0.200502
H	5.225857	-2.487938	-1.385894
C	5.138213	-1.117240	1.788414
H	4.732330	-2.022462	2.239623
H	6.208454	-1.079111	1.993239
H	4.660112	-0.260304	2.263111
C	0.781033	3.859219	0.720627
H	1.180043	4.854252	0.513727
H	1.119620	3.588081	1.721938
C	-0.766139	3.877060	0.682925
H	-1.159855	3.686956	1.682332
H	-1.132124	4.861405	0.385111
C	-1.365083	2.823124	-0.277230
H	-1.245586	3.179081	-1.309622
H	-2.432031	2.717034	-0.111600
C	1.390709	2.855619	-0.276476
H	2.460608	2.764949	-0.119417
H	1.254845	3.234205	-1.296271
B	-2.886591	-0.041435	-0.076709
O	-3.431324	-1.306326	0.051514
O	-3.859668	0.931525	-0.222277
C	-4.848150	-1.209553	-0.248091
C	-5.147479	0.312916	0.032235
C	-5.604939	-2.186174	0.641675
C	-5.022052	-1.596188	-1.718540
C	-6.182404	0.947516	-0.887825
C	-5.500469	0.602448	1.493101
H	-6.681767	-2.087987	0.491983
H	-5.318998	-3.206788	0.386920
H	-5.381818	-2.025762	1.694131
H	-4.621848	-2.599000	-1.867542
H	-6.072930	-1.597236	-2.009398
H	-4.477738	-0.915668	-2.373424
H	-7.152266	0.459968	-0.772826
H	-6.300888	2.000299	-0.629710
H	-5.882545	0.888270	-1.931743
H	-5.506783	1.682033	1.645002
H	-6.485944	0.213479	1.750763
H	-4.764347	0.170959	2.171374

Table S17. Gas phase B3LYP/cc-pVDZ-(PP) determined xyz coordinates (in Å) for **ImMe$_2$^{i}Pr$_2$•B-Te-6-B** at the S$_0$ equilibrium geometry

Te   -1.246347   1.230044   0.408746
O   1.769411   1.946058   0.432184
O   2.448991   1.045589   -1.622956
O   -4.593237   0.776356   0.545621
O   -4.879556   -1.239282   -0.512781
N   3.817922   -1.238556   -0.010100
N   2.720342   -0.735304   1.796826
C   -0.240566   -1.034655   -1.049358
C   -1.676956   -1.257109   -0.986020
C   -2.308554   -2.455468   -1.683216
H   -2.773043   -2.101046   -2.623283
H   -3.139819   -2.844946   -1.079040
C   -1.309289   -3.565537   -2.024753
H   -0.992982   -4.088815   -1.102435
H   -1.798150   -4.320004   -2.663695
C   -0.080380   -2.975100   -2.715531
H   -0.402858   -2.419401   -3.615502
H   0.601365   -3.770500   -3.062230
C   0.664152   -2.033903   -1.761303
H   1.184075   -2.650969   -1.002472
H   1.446694   -1.484255   -2.305108
C   0.294423   0.085105   -0.447094
C   2.523517   2.957920   -0.245582
C   2.492364   2.474753   -1.749357
C   1.849652   4.310304   0.002824
H   2.353809   5.116330   -0.555641
H   0.791031   4.291544   -0.287559
H   1.900753   4.558875   1.074861
C   3.943656   2.990982   0.348239
H   4.556068   3.804089   -0.073002
H   3.868124   3.149643   1.435601
H   4.470696   2.039760   0.182643
C   1.239751   2.942726   -2.510021
H   1.270725   4.021722   -2.731871
H   1.188254   2.396516   -3.464702
H   0.319942   2.723658   -1.951148
C   3.732164   2.853894   -2.565998
H   3.843742   3.948718   -2.632408
H   4.652957   2.437282   -2.136133
H   3.631855   2.464798   -3.591745
C   -2.451598   -0.324413   -0.321137
C   -5.977831   0.408873   0.780601
C   -6.218834   -0.708669   -0.309073
C   -6.842220   1.659034   0.631404
H   -7.911720   1.413845   0.734312
H   -6.582384   2.382864   1.418961
H   -6.685189   2.148167   -0.338870
C   -6.060390   -0.117740   2.219736
H   -7.095790   -0.352466   2.511745
H   -5.446231   -1.021106   2.350933
H   -5.674305   0.654387   2.902122
C   -6.683143   -0.149837   -1.660461
H   -7.723950   0.207214   -1.619904
H   -6.041280   0.679825   -1.991989
H   -6.619863   -0.948126   -2.415194
C   -7.130728   -1.854136   0.124516
H   -8.143075   -1.485312   0.356073
H   -7.215640   -2.587896   -0.691693
H   -6.737000   -2.376034   1.006635
C   2.814936   -0.447675   0.469758

```
C    4.351147  -2.023963   1.019575
C    3.657724  -1.707176   2.156781
C    4.315271  -1.187005  -1.415686
H    3.598751  -0.526412  -1.914316
C    4.301927  -2.554305  -2.108102
H    4.398444  -2.396172  -3.193896
H    5.134336  -3.203769  -1.800145
H    3.356421  -3.086522  -1.931935
C    5.684219  -0.501910  -1.497981
H    5.938023  -0.334337  -2.556778
H    5.664331   0.477416  -0.999078
H    6.494724  -1.101927  -1.055542
C    5.449051  -3.029700   0.867058
H    6.330818  -2.617833   0.355960
H    5.124336  -3.918924   0.303697
H    5.778794  -3.369710   1.857795
C    3.855899  -2.254704   3.535513
H    4.506676  -3.138292   3.494171
H    2.911315  -2.567885   4.001332
H    4.332173  -1.524477   4.209136
C    1.716147  -0.098535   2.694454
H    1.262825   0.673836   2.069160
C    0.621612  -1.084373   3.110550
H   -0.179374  -0.530546   3.623995
H    0.175751  -1.563340   2.226860
H    0.983430  -1.864782   3.798223
C    2.369764   0.631869   3.871345
H    1.609166   1.265816   4.353557
H    2.767256  -0.045229   4.641614
H    3.179990   1.289333   3.521429
B    1.816193   0.680521  -0.340583
B   -3.969997  -0.275908  -0.105825
```

Table S18. Gas phase UB3LYP/cc-pVDZ-(PP) determined xyz coordinates (in Å) for **ImMe$_2$^{i}Pr$_2$•B-Te-6-B** at the T$_1$ equilibrium geometry

```
Te  -1.258241   1.360307   0.325123
O    1.820401   1.920771   0.504667
O    2.578714   1.054617  -1.541833
O   -4.574366   0.779024   0.557256
O   -4.827037  -1.241885  -0.513698
N    3.785065  -1.318594   0.085325
N    2.574095  -0.845205   1.828127
C   -0.238848  -0.954440  -1.245818
C   -1.597656  -1.166194  -1.203480
C   -2.280028  -2.294010  -1.938983
H   -2.866881  -1.864877  -2.776883
H   -3.037582  -2.756111  -1.285291
C   -1.303489  -3.350185  -2.469514
H   -0.972252  -3.998033  -1.636451
H   -1.816153  -4.005262  -3.193521
C   -0.078777  -2.687996  -3.102350
H   -0.405595  -2.036500  -3.933312
H    0.596710  -3.443662  -3.538512
C    0.674707  -1.849394  -2.063633
H    1.226196  -2.522237  -1.377941
H    1.437234  -1.223583  -2.554497
C    0.347393   0.149281  -0.513708
C    2.628278   2.929158  -0.114392
C    2.644291   2.485937  -1.629952
C    1.981190   4.292591   0.143897
```

```
H    2.528642    5.098648   -0.372181
H    0.934763    4.310906   -0.188190
H    1.996051    4.511573    1.223428
C    4.024039    2.905783    0.534483
H    4.673010    3.715393    0.164267
H    3.909430    3.030653    1.622749
H    4.531966    1.946403    0.357200
C    1.424495    2.990939   -2.419167
H    1.477593    4.074477   -2.612736
H    1.395665    2.469743   -3.388671
H    0.482408    2.774764   -1.895168
C    3.917835    2.865792   -2.392469
H    4.050397    3.959824   -2.422887
H    4.815133    2.420002   -1.942263
H    3.847344    2.507700   -3.431864
C   -2.438752   -0.211095   -0.424682
C   -5.926681    0.345149    0.850598
C   -6.172497   -0.759861   -0.250597
C   -6.851995    1.557692    0.771412
H   -7.903628    1.262344    0.918095
H   -6.587300    2.275712    1.562732
H   -6.762663    2.074022   -0.193404
C   -5.916713   -0.215277    2.279593
H   -6.925975   -0.499160    2.616339
H   -5.260720   -1.095019    2.358787
H   -5.528497    0.557490    2.960068
C   -6.708030   -0.190406   -1.571268
H   -7.758316    0.128715   -1.484270
H   -6.108449    0.668220   -1.908368
H   -6.646164   -0.970550   -2.344982
C   -7.029961   -1.942302    0.195061
H   -8.043488   -1.611180    0.473811
H   -7.124145   -2.663047   -0.631747
H   -6.584568   -2.467631    1.050213
C    2.777076   -0.510070    0.524380
C    4.214650   -2.161209    1.118556
C    3.450975   -1.861840    2.215146
C    4.382144   -1.229380   -1.278521
H    3.727952   -0.519796   -1.795221
C    4.360338   -2.564288   -2.030663
H    4.552507   -2.367380   -3.097250
H    5.131887   -3.268717   -1.686820
H    3.378383   -3.052910   -1.954629
C    5.779635   -0.600279   -1.238103
H    6.113280   -0.402506   -2.269217
H    5.763965    0.359078   -0.701253
H    6.533290   -1.250433   -0.766946
C    5.285785   -3.200170    1.003854
H    6.216711   -2.801401    0.576234
H    4.973655   -4.053584    0.381051
H    5.529161   -3.591704    2.000528
C    3.530073   -2.465258    3.582332
H    4.164646   -3.361141    3.557207
H    2.545876   -2.773658    3.961627
H    3.966747   -1.771412    4.318299
C    1.515592   -0.217466    2.667855
H    1.126816    0.588576    2.040645
C    0.370675   -1.190971    2.958313
H   -0.459955   -0.633663    3.417722
H   -0.007254   -1.634397    2.025569
H    0.656875   -1.999744    3.648805
C    2.088545    0.453205    3.919744
```

```
H   1.303581   1.081882   4.368367
H   2.415036  -0.262105   4.688957
H   2.933600   1.108207   3.659102
B   1.869519   0.674976  -0.298757
B  -3.935506  -0.241606  -0.138550
```

Table S19. Gas phase B3LYP/cc-pVTZ-(PP) determined xyz coordinates (in Å) for
ImMe$_2$^{i}Pr$_2$•B-Te-6-B at the S$_0$ equilibrium geometry

```
Te -1.250361   1.206537   0.415911
O    1.765277   1.943556   0.435614
O    2.431136   1.057918  -1.616115
O   -4.576860   0.764941   0.545355
O   -4.875682  -1.238151  -0.514446
N    3.816899  -1.223311  -0.011656
N    2.719889  -0.739229   1.788326
C   -0.239876  -1.025267  -1.048885
C   -1.668967  -1.252402  -0.991561
C   -2.292907  -2.445618  -1.696991
H   -2.755911  -2.090643  -2.624580
H   -3.111041  -2.841876  -1.098479
C   -1.293587  -3.547653  -2.047740
H   -0.983539  -4.076375  -1.139920
H   -1.775821  -4.287050  -2.691169
C   -0.066645  -2.949550  -2.725833
H   -0.381779  -2.393151  -3.614242
H    0.613106  -3.732730  -3.070965
C    0.667228  -2.015844  -1.762433
H    1.178133  -2.632205  -1.012748
H    1.442954  -1.465921  -2.293820
C    0.286619   0.086789  -0.444795
C    2.512886   2.957040  -0.237926
C    2.467158   2.483176  -1.740188
C    1.848699   4.307214   0.024793
H    2.345672   5.106215  -0.528995
H    0.797652   4.292953  -0.252704
H    1.912645   4.545213   1.087332
C    3.935961   2.983378   0.340135
H    4.540975   3.784095  -0.087160
H    3.871159   3.146211   1.416406
H    4.449626   2.037725   0.173833
C    1.206815   2.950601  -2.481476
H    1.229287   4.022323  -2.685227
H    1.152545   2.423819  -3.434518
H    0.302992   2.720532  -1.922373
C    3.691131   2.871557  -2.568991
H    3.789983   3.956576  -2.637585
H    4.610427   2.468310  -2.150758
H    3.581944   2.482448  -3.582063
C   -2.445130  -0.334989  -0.324810
C   -5.958560   0.402747   0.787691
C   -6.208803  -0.699673  -0.309631
C   -6.819246   1.652818   0.659796
H   -7.877669   1.410920   0.769954
H   -6.551588   2.359407   1.445195
H   -6.671939   2.145230  -0.298237
C   -6.033006  -0.138237   2.217904
H   -7.056507  -0.379115   2.506082
H   -5.419537  -1.030718   2.336405
H   -5.654710   0.622829   2.899565
C   -6.664699  -0.124656  -1.652758
```

```
H   -7.688321   0.247556   -1.605645
H   -6.014716   0.686979   -1.977411
H   -6.620835   -0.912485   -2.404050
C   -7.131840   -1.836029   0.109698
H   -8.131743   -1.462049   0.335950
H   -7.217786   -2.554252   -0.705567
H   -6.751438   -2.361825   0.982072
C   2.808666   -0.449623   0.467516
C   4.362837   -1.996019   1.014723
C   3.672106   -1.691178   2.145352
C   4.295398   -1.187280   -1.420657
H   3.573022   -0.553118   -1.919859
C   4.289436   -2.562111   -2.091335
H   4.370620   -2.418939   -3.169202
H   5.124311   -3.189696   -1.785149
H   3.361297   -3.096345   -1.897922
C   5.652162   -0.490428   -1.535740
H   5.886614   -0.343248   -2.590469
H   5.627788   0.487847   -1.060299
H   6.464925   -1.068202   -1.096571
C   5.476541   -2.978481   0.863458
H   6.332662   -2.561199   0.337089
H   5.164569   -3.876073   0.328036
H   5.825253   -3.288740   1.845409
C   3.885509   -2.230373   3.520672
H   4.560721   -3.081490   3.479864
H   2.961491   -2.575252   3.979783
H   4.330221   -1.490755   4.187584
C   1.705984   -0.128850   2.687713
H   1.220499   0.613004   2.069080
C   0.647582   -1.141231   3.122495
H   -0.158318   -0.610573   3.629021
H   0.216852   -1.641819   2.256976
H   1.033916   -1.892418   3.810525
C   2.340519   0.630413   3.852330
H   1.570203   1.237734   4.327980
H   2.758235   -0.023719   4.615696
H   3.120452   1.302396   3.496338
B   1.805497   0.685886   -0.338887
B   -3.959316   -0.285486   -0.109304
```

Table S20. Gas phase UB3LYP/cc-pVTZ-(PP) determined xyz coordinates (in Å) for **ImMe$_2$^{i}Pr$_2$•B-Te-6-B** at the T$_1$ geometry

```
Te   -1.265302   1.339435   0.321545
O   1.813366   1.914356   0.516353
O   2.568183   1.079691   -1.529796
O   -4.559768   0.776002   0.544024
O   -4.820252   -1.242747   -0.510445
N   3.786303   -1.300530   0.078212
N   2.567975   -0.858143   1.810929
C   -0.232911   -0.950349   -1.238829
C   -1.583655   -1.165556   -1.203474
C   -2.259007   -2.291483   -1.937708
H   -2.846498   -1.867446   -2.763496
H   -3.001928   -2.757295   -1.287247
C   -1.285118   -3.340788   -2.476492
H   -0.963307   -3.993761   -1.658754
H   -1.792424   -3.978109   -3.204022
C   -0.059070   -2.676586   -3.094223
H   -0.374600   -2.026281   -3.915636
H   0.613287   -3.423088   -3.524418
```

```
C    0.683637   -1.846463   -2.046820
H    1.217667   -2.519499   -1.365191
H    1.445613   -1.229676   -2.525628
C    0.341878    0.152643   -0.518701
C    2.616013    2.930076   -0.087522
C    2.624575    2.507615   -1.604903
C    1.975195    4.287906    0.192653
H    2.517023    5.091426   -0.310208
H    0.937615    4.311943   -0.131328
H    1.997256    4.488009    1.264607
C    4.012376    2.897622    0.551429
H    4.654624    3.698362    0.182470
H    3.904391    3.019877    1.629554
H    4.509094    1.945985    0.369262
C    1.398822    3.015445   -2.376425
H    1.441642    4.092577   -2.544987
H    1.371758    2.519805   -3.347131
H    0.470692    2.783188   -1.857200
C    3.885361    2.905266   -2.371741
H    4.003786    3.990181   -2.395790
H    4.780626    2.470823   -1.932794
H    3.810175    2.555247   -3.401986
C   -2.431822   -0.217588   -0.430583
C   -5.907763    0.346365    0.848337
C   -6.160808   -0.753820   -0.250430
C   -6.831644    1.555550    0.780085
H   -7.871140    1.262436    0.936878
H   -6.559822    2.264407    1.562084
H   -6.753588    2.066197   -0.176590
C   -5.888245   -0.215832    2.272571
H   -6.884852   -0.505079    2.607080
H   -5.231802   -1.082169    2.346794
H   -5.509511    0.552288    2.946057
C   -6.689665   -0.180534   -1.567798
H   -7.723736    0.152844   -1.477179
H   -6.082911    0.658577   -1.906139
H   -6.645974   -0.957556   -2.330398
C   -7.027504   -1.925564    0.191641
H   -8.029843   -1.588838    0.461571
H   -7.121284   -2.638252   -0.627696
H   -6.594532   -2.446482    1.042206
C    2.768644   -0.514329    0.515523
C    4.229380   -2.132899    1.107803
C    3.463412   -1.852973    2.196096
C    4.364040   -1.222632   -1.291011
H    3.699357   -0.542894   -1.810049
C    4.356034   -2.566861   -2.020699
H    4.525067   -2.383359   -3.082131
H    5.139089   -3.242067   -1.680610
H    3.395053   -3.068215   -1.921500
C    5.748426   -0.572257   -1.283387
H    6.061706   -0.394050   -2.312573
H    5.723960    0.387750   -0.771798
H    6.508183   -1.195519   -0.812650
C    5.322384   -3.143392    0.996257
H    6.227583   -2.731780    0.554130
H    5.026273   -4.007169    0.399663
H    5.586656   -3.506162    1.986533
C    3.555401   -2.453815    3.559070
H    4.222846   -3.311696    3.537506
H    2.592425   -2.804654    3.924389
H    3.950481   -1.749519    4.292093
```

```
C    1.492518   -0.265091    2.648562
H    1.066823    0.508497    2.023681
C    0.387566   -1.274624    2.955593
H   -0.455895   -0.744892    3.397571
H    0.034256   -1.748815    2.041263
H    0.699234   -2.048169    3.656579
C    2.039969    0.438290    3.889543
H    1.239086    1.031254    4.331338
H    2.395083   -0.252307    4.652593
H    2.848210    1.117850    3.622373
B    1.859592    0.682821   -0.299015
B   -3.923583   -0.247443   -0.145997
```

S2. Luminescence Measurements

Figure S3. Lifetime measurements for **ImMe$_2$^{i}Pr$_2$•B-Te-6-B** in the film state under N$_2$.
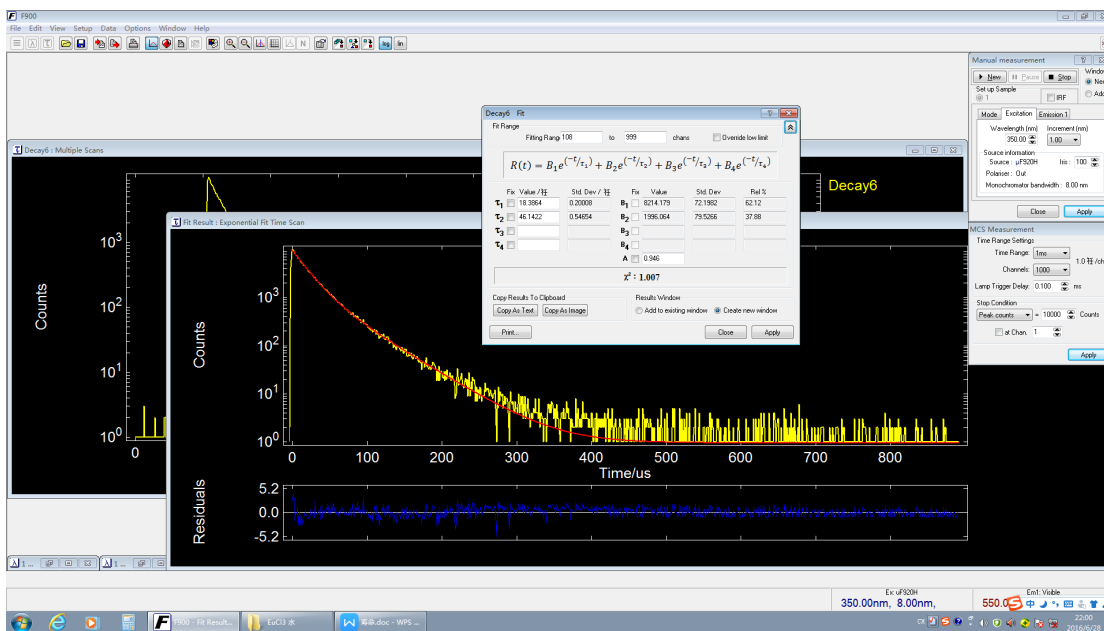
τ = 18.3864*62.12%+46.1422*37.88% = 28.90 μs

$\chi2$ = 1.007

Figure S3. Quantum yield determination for **ImMe$_2$^{i}Pr$_2$•B-Te-6-B** in the film state under N$_2$.
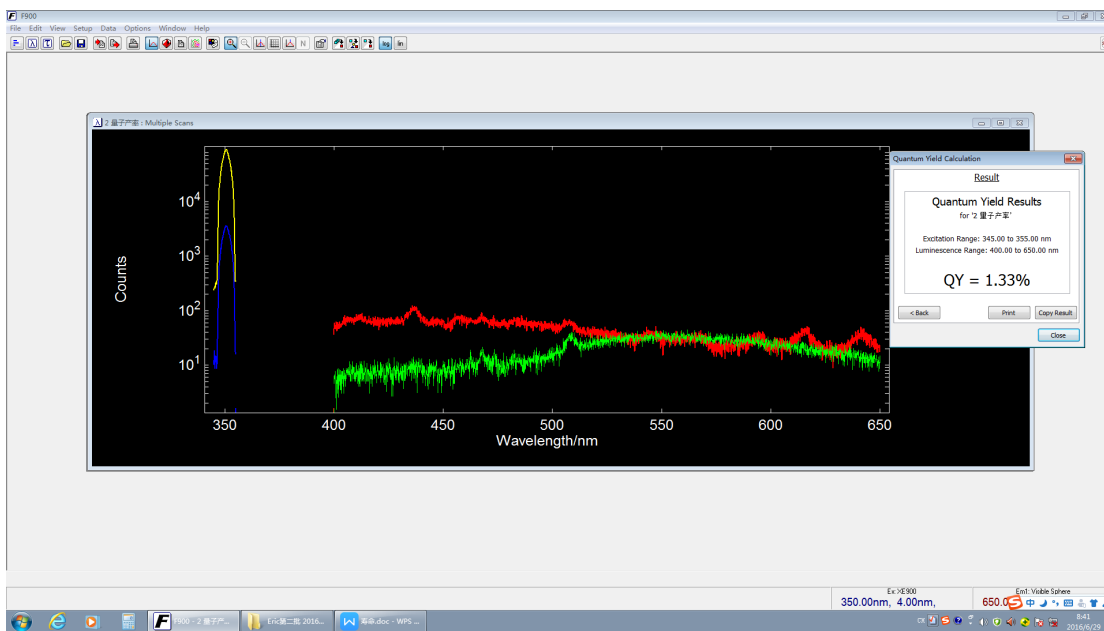
S3. Additional Crystallographic Information

Table S20. Crystallographic Experimental Details for **2**.

A. Crystal Data

formula	$C_{35}H_{40}B_2O_4$
formula weight	546.29
crystal dimensions (mm)	$0.26 \times 0.20 \times 0.03$
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	6.3523 (2)
b (Å)	8.0207 (2)
c (Å)	16.3894 (4)
α (deg)	92.3795 (18)
β (deg)	95.9413 (18)
γ (deg)	110.1138 (17)
V (Å^3)	777.24 (4)
Z	1
ρ_{calcd} (g cm^{-3})	1.167
μ (mm^{-1})	0.575

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	−100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	144.58
total data collected	5411 ($-7 \le h \le 7$, $-9 \le k \le 9$, $-17 \le l \le 19$)
independent reflections	2953 ($R_{int} = 0.0549$)
number of observed reflections (*NO*)	2310 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	1.0000–0.6597
data/restraints/parameters	2953 / 0 / 206
goodness-of-fit (*S*)[e] [all data]	1.045
final *R* indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0605
wR_2 [all data]	0.1826
largest difference peak and hole	0.462 and −0.265 e Å^{-3}

[a]Obtained from least-squares refinement of 4771 reflections with $5.44° < 2\theta < 144.30°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8. (*SHELXT-2014*)

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8. (*SHELXL-2014*)

[e]$S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; w = $[\sigma^2(F_o{}^2) + (0.0978P)^2 + 0.2157P]^{-1}$ where $P = [\text{Max}(F_o{}^2, 0) + 2F_c{}^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^4)]^{1/2}$.

Table S21. Crystallographic Experimental Details for **ImMe$_2$^{i}Pr$_2$•B-6-Te-B•ImMe$_2$^{i}Pr$_2$.**

A. Crystal Data

formula	C$_{50}$H$_{92}$B$_2$N$_4$O$_6$Te
formula weight	994.49
crystal dimensions (mm)	0.29 × 0.20 × 0.16
crystal system	monoclinic
space group	*C*2/*c* (No. 15)
unit cell parameters^a	
a (Å)	18.8131 (3)
b (Å)	11.1794 (2)
c (Å)	26.4236 (5)
β (deg)	93.0441 (6)
V (Å^3)	5549.55 (17)
Z	4
ρcalcd (g cm^{-3})	1.190
μ (mm^{-1})	4.588

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD^b
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	−100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	148.09
total data collected	19362 (-23 ≤ *h* ≤ 23, -13 ≤ *k* ≤ 13, -32 ≤ *l* ≤ 32)
independent reflections	5624 (R_{int} = 0.0136)
number of observed reflections (*NO*)	5586 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014^c*)
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014^d*)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7017–0.3735
data/restraints/parameters	5624 / 0 / 295
goodness-of-fit (*S*)^e [all data]	1.089
final *R* indices^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0212
wR_2 [all data]	0.0560
largest difference peak and hole	0.400 and −0.412 e Å^{-3}

^{a}Obtained from least-squares refinement of 9429 reflections with 9.20° < 2θ < 147.52°.

^{b}Programs for diffractometer operation, data collection, data reduction and absorption

correction were those supplied by Bruker.

[c]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8. (*SHELXT-2014*)

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8. (*SHELXL-2014*)

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0290P)^2 + 4.8857P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 22. Crystallographic Experimental Details for **ImMe₂ⁱPr₂•B-6-Te-B**.

A. Crystal Data

formula	$C_{31}H_{52}B_2N_2O_4Te$
formula weight	665.96
crystal dimensions (mm)	$0.44 \times 0.25 \times 0.12$
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	10.3086 (2)
b (Å)	15.0795 (3)
c (Å)	21.3795 (4)
β (deg)	93.2679 (7)
V (Å³)	3318.01 (11)
Z	4
ρ_{calcd} (g cm⁻³)	1.333
μ (mm⁻¹)	7.350

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	-100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	147.96
total data collected	18158 ($-11 \le h \le 12$, $-18 \le k \le 18$, $-26 \le l \le 26$)
independent reflections	6668 ($R_{int} = 0.0281$)
number of observed reflections (*NO*)	6523 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	Patterson/structure expansion (*DIRDIF–2008[c]*)
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014[d]*)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.5988–0.1784
data/restraints/parameters	6668 / 0 / 363
goodness-of-fit (*S*)[e] [all data]	1.062
final *R* indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0261
wR_2 [all data]	0.0668
largest difference peak and hole	0.468 and -1.446 e Å⁻³

[a]Obtained from least-squares refinement of 9945 reflections with $7.18° < 2\theta < 147.58°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption

correction were those supplied by Bruker.

[c]Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Granda, S.; Gould, R. O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands.

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0355P)^2 + 1.9906P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

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