gem-DiBromovinyl Boron Dipyrrins: Synthesis, Spectral Properties and Crystal Structures

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Electronic Supplemental Information (ESI)

Fig. S1 Crystal structure packing of 2 (top) \textit{b}-axis (bottom) \textit{c}-axis
Fig. S2 Crystal structure packing 9.
Fig. S3 Crystal structure packing of 10.
Fig. S4 Crystal structure packing of 12.
Fig. S5 Crystal structure packing of 16.
Fig. S6 Crystal structure packing of 19.
Fig. S7 Crystal structure packing of 20.
**Hirshfeld crystal surface analysis.** Hirshfeld surfaces in the crystal structure and the associated 2D-fingerprint plots were calculated using the Crystal-Explorer17.5 program, which accepts CIF format file structure input. Hirshfeld surfaces and their associated two-dimensional fingerprint plots using **Crystal-Explorer (Version 3.1)**, [S.K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka, M.A. Spackman, Eur. J. Inorg. Chem.; 2012: 2653-2662], were employed to quantify the various intermolecular interactions. The Hirshfeld surface fingerprint plots of the molecules are mapped using the descriptor $d_{\text{norm}}$, which encompasses $d_e$ (the distance of any surface point nearest to the internal atoms), $d_i$ (the distance of the surface point nearest to the exterior atoms and also with the van der Waals radii of the atoms). These data were generated using this pair of coordinates. The Hirshfeld surfaces mapped over $d_{\text{norm}}$ (range of -0.1-1.6 Å) are displayed in Fig S8. The value of $d_{\text{norm}}$ is negative or positive depending on whether the intermolecular contacts are shorter or longer than the van der Waals separations.
Fig. S9 Hirshfeld surfaces (HSs) and 2D fingerprint plots of gem-dibromovinyl BODIPYs
Fig. S10 Relative percentage contributions of various non-covalent intermolecular contacts on the basis of Hirshfeld surface in BODIPYs.

**General method for the synthesis of gem-dibromovinyl boron dipyrrins.**

For 1 or 5: To a solution of BODIPY aldehyde (1 mmol) 7, 8, 11, 13, 15, 17, 18 and 22 in CH$_2$Cl$_2$ (4 mL) at 0 °C and CBr$_4$ (2 mmol) was added dropwise a solution of the corresponding phosphines, triphenyl phosphine (4 mmol) or P(Oi-Pr)$_3$ (3 mmol). After 30 min, the reaction was warmed to r.t. and extracted with CH$_2$Cl$_2$ (20-50 mL). After drying over MgSO$_4$, solvent was removed under vacuum and the product was purified over silica gel column. On elution using either a mixture of CH$_2$Cl$_2$-Hexane or EtOAc-hexane, bright coloured products were obtained. HPLC purification using a C$_{18}$ reversed column in CH$_3$CN-H$_2$O furnished analytically pure products.
Fig S11. $^1$H NMR spectrum of compound 2 in CDCl$_3$.

Fig S12. $^{13}$C NMR spectrum of compound 2 in CDCl$_3$. 
Fig S13. $^{19}$F NMR spectrum of compound 2 in CDCl$_3$

Fig S14. $^{11}$B NMR spectrum of compound 2 in CDCl$_3$
Fig S15. $^1$H-$^{13}$C HSQC 2D NMR spectrum for compound 2 in CDCl$_3$
Fig S16. ESI-MS spectrum of compound 2.
Fig S17. $^1$H NMR spectrum of compound 6 in CDCl$_3$

Fig S18. $^{13}$C NMR spectrum of compound 6 in CDCl$_3$
Fig S19. $^{19}$F NMR spectrum of compound 6 in CDCl$_3$

Fig S20. $^{11}$B NMR spectrum of compound 6 in CDCl$_3$
Fig S21. $^1$H-$^{13}$C HSQC 2D NMR spectrum for compound 6 in CDCl$_3$

Fig S22. ESI-MS spectrum of compound 6
Fig S23. $^1$H NMR spectrum of compound 9 in CDCl$_3$
Fig S24. $^1$H NMR spectrum of compound 9 in DMF$_d$$_7$

Fig S25. $^{13}$C NMR spectrum of compound 9 in CDCl$_3$
Fig S26. $^{19}$F NMR spectrum of compound 9 in CDCl$_3$

Fig S27. $^{11}$B NMR spectrum of compound 9 in CDCl$_3$
Fig S28. $^1$H-$^{13}$C HSQC 2D NMR spectrum for compound 9 in CDCl$_3$. 

Fig S29. ESI-MS spectrum of compound 9. $[M+H]^+$
Fig S30. $^1$H NMR spectrum of compound 10 in CDCl$_3$
Fig S31. $^1$H NMR spectrum of compound 10 in THF$_d$$_4$

Fig S32. $^{13}$C NMR spectrum of compound 10 in CDCl$_3$
Fig S33. $^{19}$F NMR spectrum of compound 10 in CDCl$_3$
Fig S34. ESI-MS spectrum of compound 10
Fig S35. $^1$H NMR spectrum of compound 12 in CDCl$_3$

Fig S36. $^{13}$CNMR spectrum of compound 12 in CDCl$_3$
Fig S37. $^{19}$F NMR spectrum of compound 12 in CDCl$_3$

Fig S38. $^1$H-$^{13}$C HSQC 2D NMR spectrum for compound 12 in CDCl$_3$
Fig S39. ESI-MS spectrum of compound 12
Fig S40. $^1$H NMR spectrum of compound 14 in CDCl$_3$

Fig S41. $^{13}$C NMR spectrum of compound 14 in CDCl$_3$
Fig S42. $^{19}$F NMR spectrum of compound 14 in CDCl$_3$

Fig S43. $^1$H-$^{13}$C HSQC 2D NMR spectrum for compound 14 in CDCl$_3$
Fig S44. ESI-MS spectrum of compound 14: $[M+H]^+$
Fig S45. $^1$H NMR spectrum of compound 16 in CDCl$_3$

Fig S46. $^{13}$C NMR spectrum of compound 16 in CDCl$_3$

Fig S47. $^1$H-$^{13}$C HSQC 2D NMR spectrum for compound 16 in CDCl$_3$
Fig S48. ESI-MS spectrum of compound 16

Fig S49. $^1$H NMR spectrum of compound 19 in CDCl$_3$
Fig S50. $^{13}$C NMR spectrum of compound 19 in CDCl$_3$.

Fig S51. $^{19}$F NMR spectrum of compound 19 in CDCl$_3$. 
Fig S52. $^{11}$B NMR spectrum of compound 19 in CDCl$_3$

Fig S53. $^1$H-$^{13}$C HSQC 2D NMR spectrum for compound 19 in THF
Fig S54. ESI-MS spectrum of compound 19
Fig S55. $^1$H NMR spectrum of compound 20 in CDCl$_3$

Fig S56. $^{13}$C NMR spectrum of compound 20 in CDCl$_3$
Fig S57. $^{11}$B NMR spectrum of compound 20 in CDCl$_3$

Fig S58. ESI-MS spectrum of compound 20
Fig S59. $^1$H NMR spectrum of compound 21 in CDCl$_3$

Fig S60. $^{13}$C NMR spectrum of compound 21 in CDCl$_3$
Fig S61. $^{19}$F NMR spectrum of compound 21 in CDCl$_3$

Fig S62. $^1$H-$^{13}$C HSQC 2D NMR spectrum for compound 21 in CDCl$_3$
Fig S63. ESI-MS spectrum of compound 21
Fig S64. $^1$H NMR spectrum of compound 23 in CDCl$_3$

Fig S65. $^{13}$C NMR spectrum of compound 23 in CDCl$_3$
Fig S66. $^{19}$F NMR spectrum of compound 23 in CDCl$_3$

Fig S67. $^1$H-$^{13}$C HSQC 2D NMR spectrum for compound 23 in CDCl$_3$