SUPPORTING INFORMATION

Carbon(sp3) Tetrel Bonding Mediated BODIPY Supramolecular Assembly via Unprecedented Synergy of $C_{sp3}\cdots N$ and $C_{sp3}\cdots F$ pair interactions.

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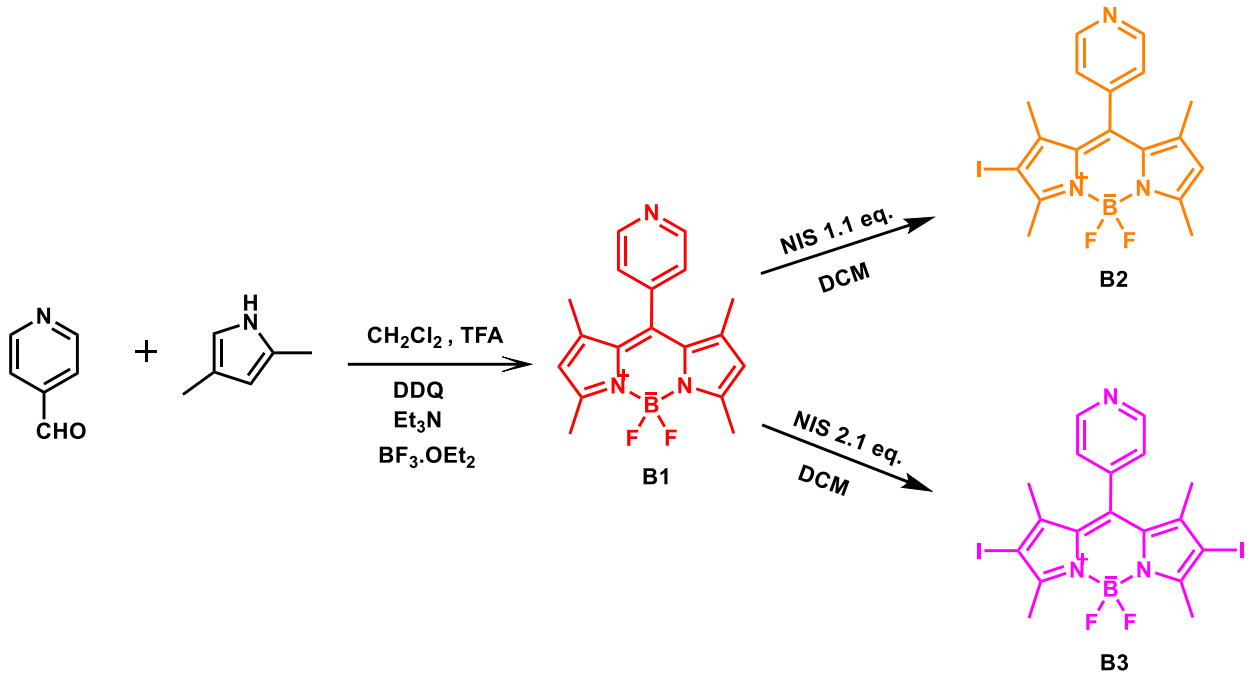

Scheme S1: Synthetic pathway of compounds **B1-B3**

1. Experimental Section

1.1. Materials and Methods

All reagents were purchased from commercial sources and used without any further purification unless otherwise noted. ^{1}H, ^{11}B, ^{13}C, ^{19}F NMR spectra analyses of the compounds were performed in $CDCl_3$ on a Varian INOVA 500 MHz spectrometer (West Sussex, UK) using TMS as an internal reference for ^{1}H and ^{13}C measurements. Bruker MS MALDI TOF spectrometer (Bremen, Germany) was used for mass analyses.

2. Synthesis

The compounds **B1** and **B3** were synthesized and purified according to literature procedure (Scheme S1). [1,2]

2.1. Synthesis of Compound B1

CH_2Cl_2 (300 ml) was placed in a 1 L of round bottom reaction flask and it was purged with argon gas for 15 min. 4-Pyridinecarboxaldehyde (1000 mg, 9.34 mmol) and 2,4-Dimethylpyrrole (1.3 mL, 12.5 mmol) were added to the medium, respectively. The color of the solution turned to red after the addition of 3 drops of trifluoroacetic acid. The reaction mixture was stirred at room temperature for 12 h. After 12 h, DDQ (2.04 g, 8.9 mmol) was added to the reaction medium and the mixture was stirred at room temperature for a further 30 min. Then, triethyl amine (5 mL) and boron trifluoride diethyl etherate ($BF_3.OEt_2$) (5 mL) were added, sequentially. The reaction mixture was stirred at room temperature for further 3 hours. Then, it was extracted with CH_2Cl_2 and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using CH_2Cl_2 as mobile phase. Fraction containing **B1** was collected then the solvent was removed under reduced pressure (600 mg, 19.8 %). MALDI TOF (m/z) calc. 325.16, found: 326.176 [M^+], 306.337 [M^+-F]. ^{1}H NMR (500 MHz, Chloroform-d) δ_H = 8.80 (d, J = 4 Hz, 2H, Ar-CH), 7.32 (d, J = 4.1 Hz, 2H, Ar-CH), 6.03 (s, 2H, Ar-CH), 2.58 (s, 6H, CH_3), 1.43 (s, 6H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 156.476, 150.659, 143.591, 142.663, 137.662, 137.604, 130.356, 123.314, 121.809, 14.636, 14.606 ppm

2.4. Synthesis of Compound B2

B1 (150 mg, 0.461 mmol) was dissolved with 50 mL of CH_2Cl_2. N-Iodo-succinimide (NIS) (114 mg, 0.507 mmol, 1.1 eq) was added to the previous reaction mixture and it was stirred for 30 minutes. According to thin layer chromatography tests, it was stirred additional 3 hours and then solvent of the reaction was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using n-hexane–Ethyl acetate (2:1) as mobile phase. Fraction

containing **B2** was collected then the solvent was removed under reduced pressure (124 mg, 60%). MALDI TOF (m/z) calc. 451.07, found: 451.305 [M^+], 432.368 [M^+-F]. ^{1}H NMR (500 MHz, Chloroform-d) δ_H = 8.83 (s, 2H, Ar-CH), 7.32 (d, J = 3.1 Hz, 2H, Ar-CH), 6.09 (s, 1H, Ar-CH), 2.66 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.59 (s, 6H, CH_3), 1.44 (s, 6H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 158.89, 155.79, 150.89, 144.69, 143.65, 137.57, 130.92, 129.92, 123.38, 123.02 17.09, 14.98 ppm

2.5. Synthesis of Compound B3

B1 (150 mg, 0.461 mmol) was dissolved with 50 mL of CH_2Cl_2. N-Iodo-succinimide (NIS) (310 mg, 1.40 mmol 3eq) was added to the previous reaction mixture and it was stirred for 30 minutes. According to thin layer chromatography tests, it was stirred additional 3 hours and then solvent of the reaction was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using n-hexane–Ethyl acetate (2:1) as mobile phase. Fraction containing **B3** was collected then the solvent was removed under reduced pressure (185 mg, 70%). MALDI TOF (m/z) calc. 576.95, found: 577.837 [M^+], 557.845 [M^+-F]. ^{1}H NMR (500 MHz, Chloroform-d) δ_H = 8.82 (d, J = 5.8 Hz, 2H, Ar-CH), 7.28 (d, J = 5.9 Hz, 2H, Ar-CH), 2.65 (s, 3H, CH_3), 1.42 (s, 6H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 158.25, 151.30, 145.22, 143.76, 143.57, 137.50, 130.61, 123.47, 17.65, 16.55 ppm

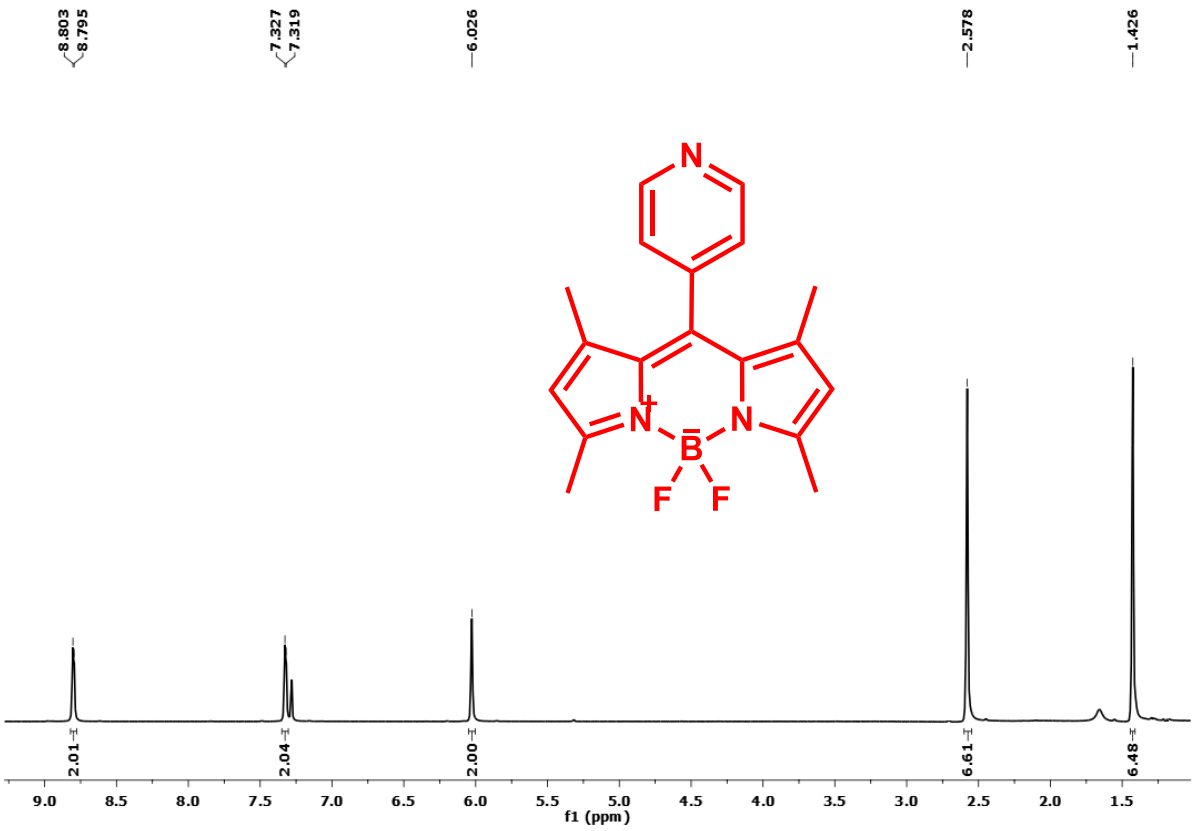

Figure S1: ^{1}H NMR Spectrum of Compound **B1**

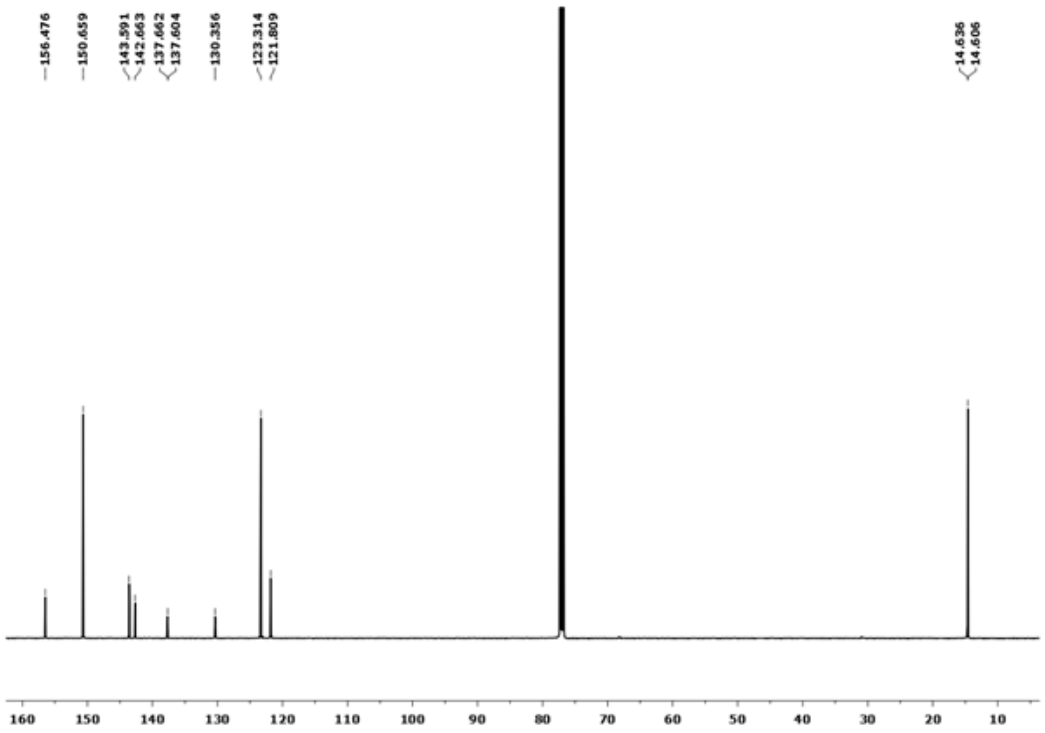

Figure S2: ^{13}C NMR Spectrum of Compound **B1**

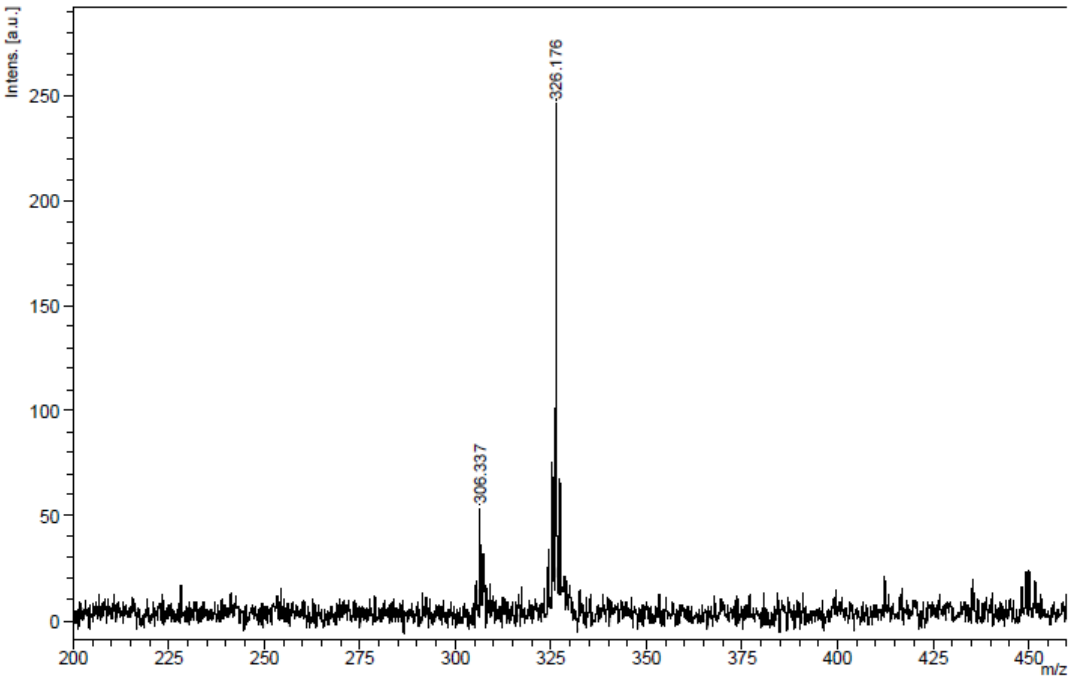

Figure S3: Mass Spectrum of Compound **B1**

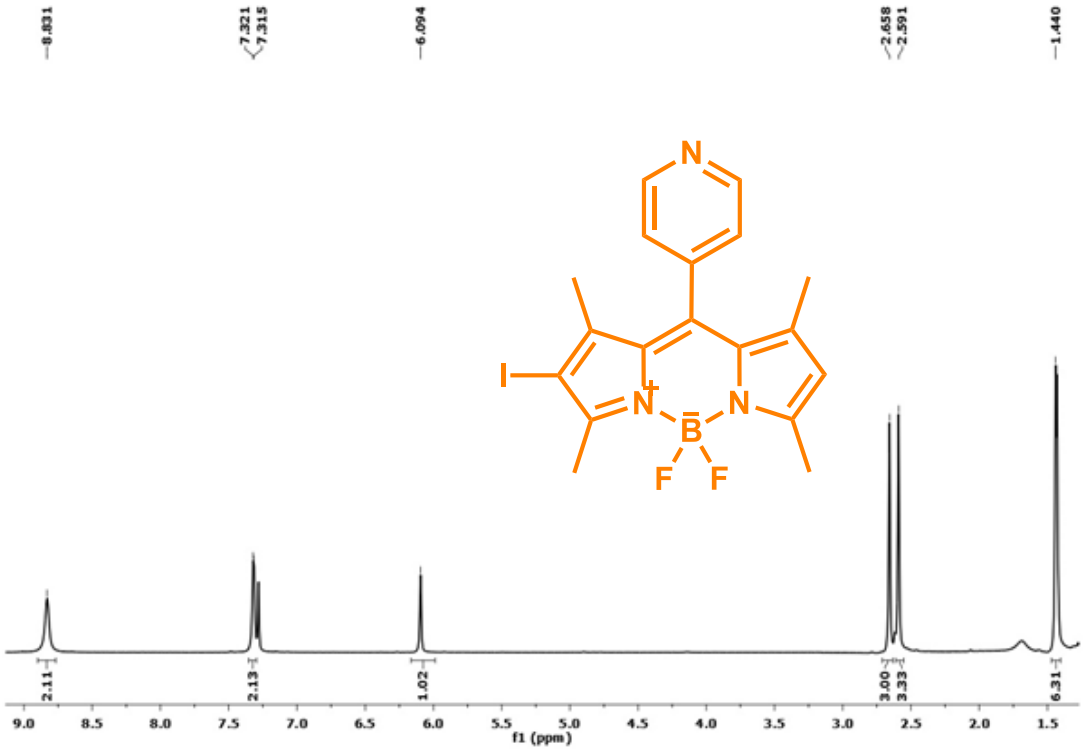

Figure S4: ^{1}H NMR Spectrum of Compound **B2**

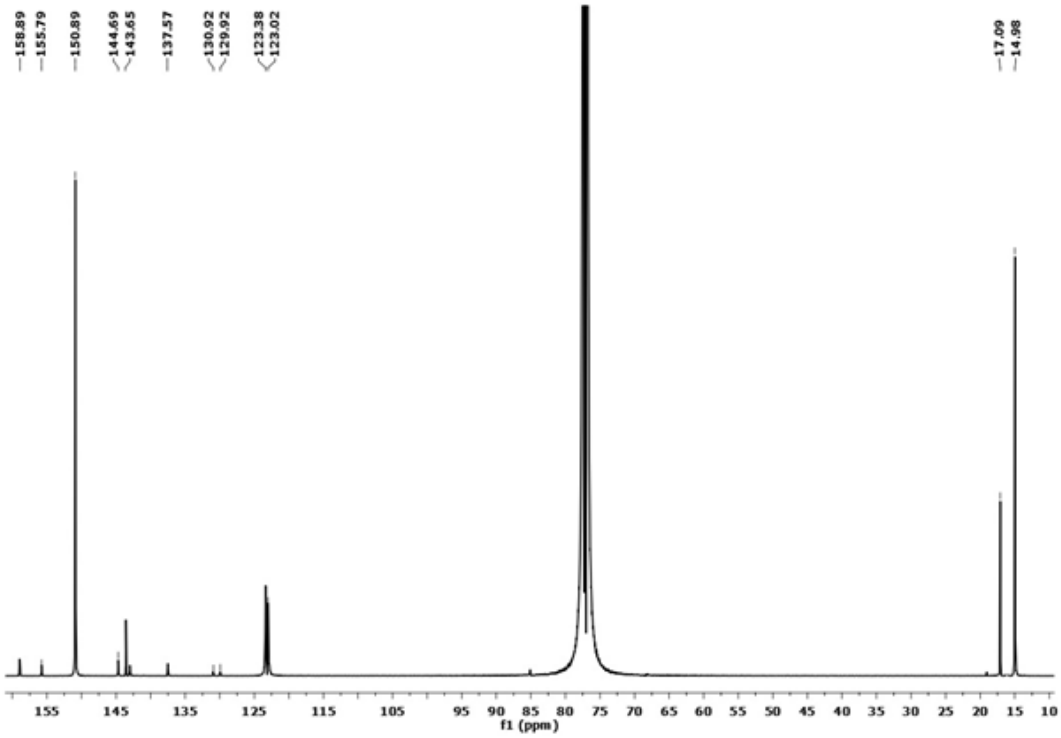

Figure S5: ^{13}C NMR Spectrum of Compound **B2**

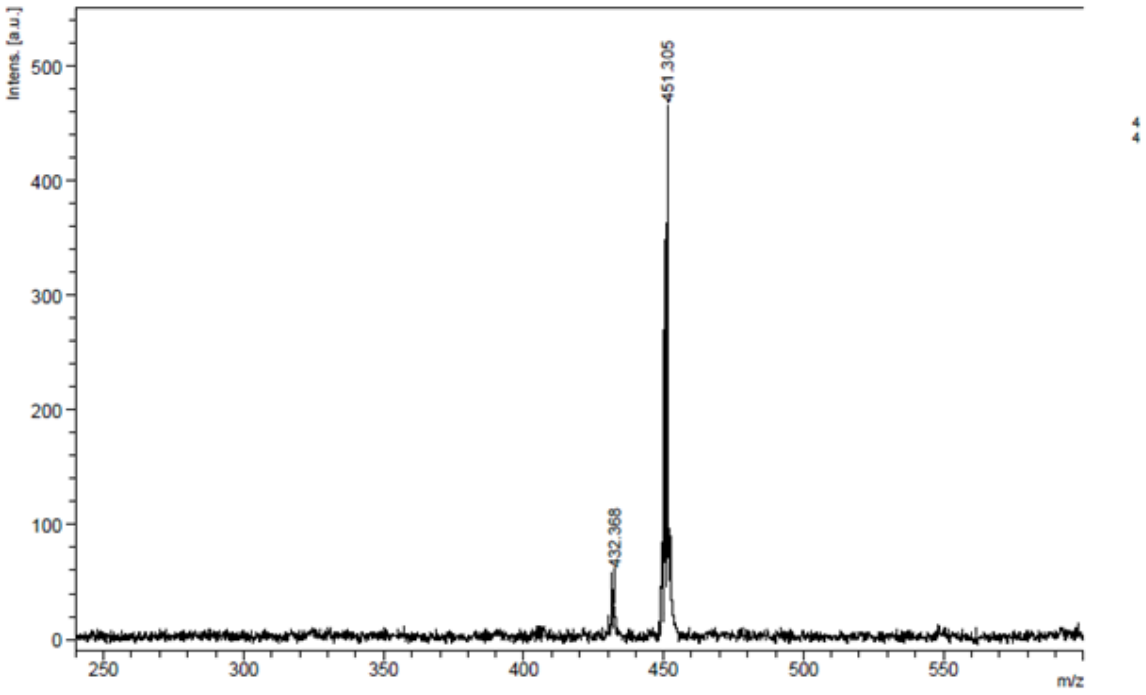

Figure S6: Mass Spectrum of Compound **B2**

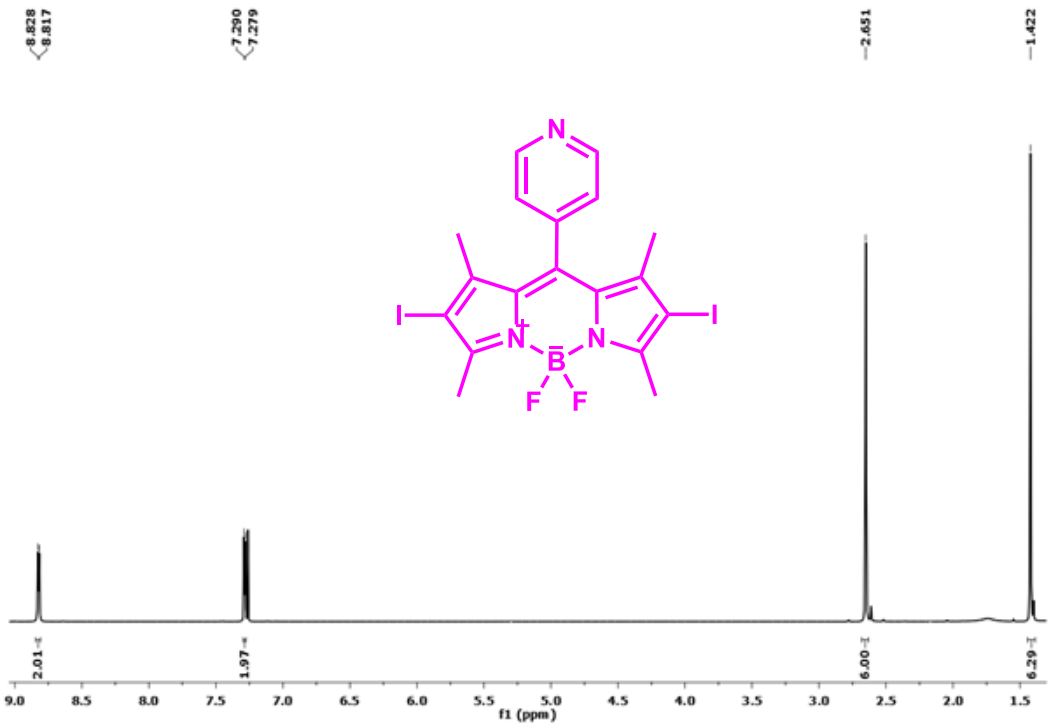

Figure S7: ^{1}H NMR Spectrum of Compound **B3**

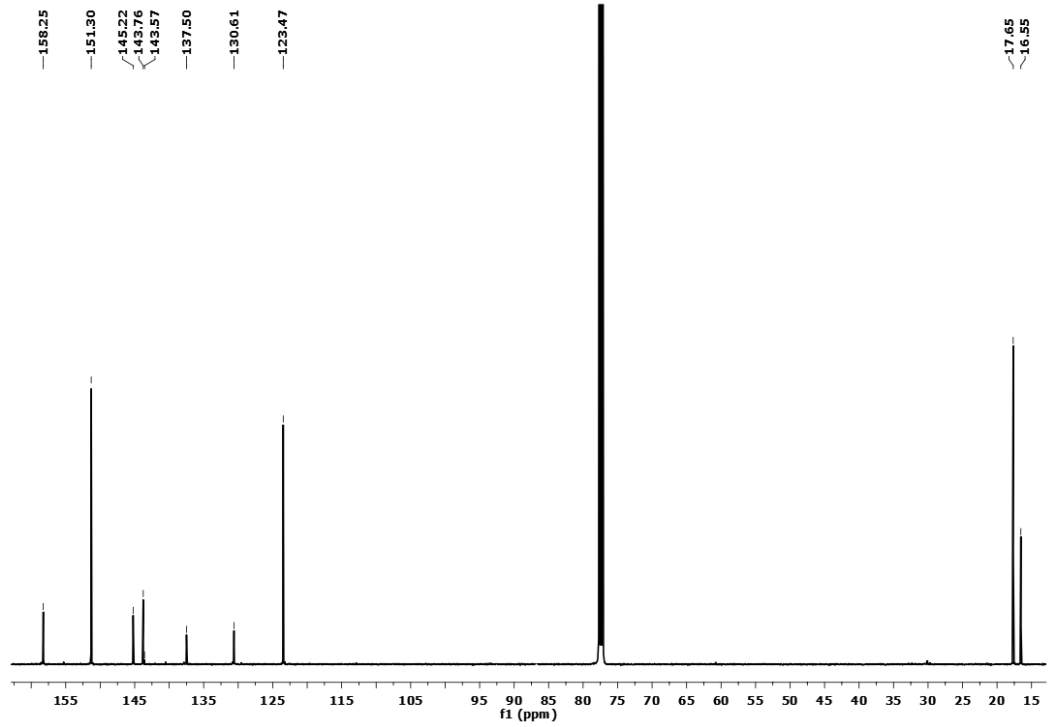

Figure S8: ^{13}C NMR Spectrum of Compound **B3**

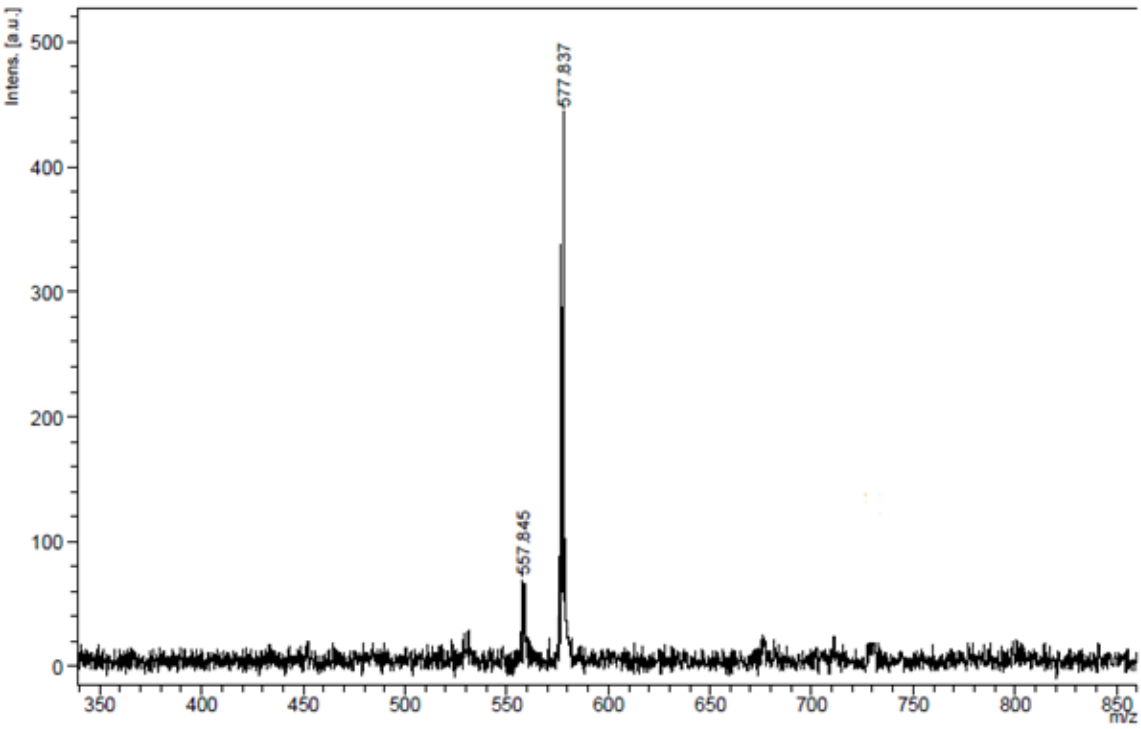

Figure S9: Mass Spectrum of Compound **B3**

X-ray Crystallography

Data was obtained with Bruker APEX II QUAZAR three-circle diffractometer. Indexing was performed using APEX2[3]. Data integration and reduction was carried out with SAINT[4]. Absorption correction was performed by multi-scan method implemented in SADABS[5]. The structure was solved using SHELXT[6] and then refined by full-matrix least-squares refinements on F^2 using the SHELXL[6] in Olex2 Software Package[7]. Aromatic and aliphatic C-bound H atoms were positioned geometrically and refined using a riding mode. Crystallographic data and refinement details of the data collection for BODIPY derivatives are in Table S1. Crystal structure validations, geometrical calculations and crystal packing analysis were performed using Platon software.[8] Mercury software was used for visualization of the cif files.[9] Additional crystallographic data with CCDC reference numbers 2011924-2011926 for **B1**, **B2**, and **B3** have been deposited within the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/deposit.

Table S1. Crystal data and refinement parameters for **BODIPY** compounds.

Compound	**B1**	**B2**	**B3**
CCDC	2011924	2011925	2011926
Empirical Formula	$C_{18}H_{18}BF_2N_3$	$C_{18}H_{17}BF_2IN_3$	$C_{18}H_{16}BF_2I_2N_3$
Formula weight/g. mol^{-1}	325.16	451.05	576.95
Temperature/K	296.15	296.15	120
Radiation, Wavelength (Å)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	*Cmcm*
a/Å	24.878(4)	14.9264(12)	16.724(2)
b/Å	6.8029(13)	11.4332(9)	15.302(2)
c/Å	20.937(4)	10.9861(8)	7.6345(10)
α/°	90	90	90
β/°	114.088(9)	107.745(4)	90
γ/°	90	90	90
Crystal size/mm^3	0.27 × 0.22 × 0.18	0.39 × 0.24 × 0.09	0.05 × 0.18 × 0.19
Volume/Å^3	3234.9(10)	1785.6(2)	1953.7(4)
Z	8	4	4
ρ_{calcd} (g. cm^{-3})	1.335	1.678	1.961
μ (mm^{-1})	0.096	1.818	3.244
***F*(000)**	1360	888	1096
2θ range for data collection/°	1.794 to 49.994	4.572 to 50.042	6.442 to 49.968
h*/*k*/*l	-29 ≤ h ≤ 24, -8 ≤ k ≤ 8, -24 ≤ l ≤ 24	-17 ≤ h ≤ 15, -9 ≤ k ≤ 13, -13 ≤ l ≤ 12	-19 ≤ h ≤ 19, -18 ≤ k ≤ 18, -8 ≤ l ≤ 9
Reflections collected	25315	9432	7350
Independent reflections	5674 [R_{int} = 0.0887, R_{sigma} = 0.0810]	3148 [R_{int} = 0.0289, R_{sigma} = 0.0300]	967 [R_{int} = 0.0543, R_{sigma} = 0.0363]
Data/restraints/parameters	5674/0/442	3148/0/230	967/0/86
Goodness-of-fit on F^2 (S)	1.083	1.045	1.127
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0767, wR_2 = 0.1958	R_1 = 0.0290, wR_2 = 0.0736	R_1 = 0.0298, wR_2 = 0.0790
R indices (all data)	R_1 = 0.1334, wR_2 = 0.2158	R_1 = 0.0345, wR_2 = 0.0769	R_1 = 0.0309, wR_2 = 0.0798
Largest diff. peak/hole / e Å^{-3}	0.29/-0.27	0.79/-0.54	0.69/-1.72

3.1. Analysis of studied structures

The solid-state structures and geometries of BODIPY compounds (**B1**, **B2**, and **B3**) were determined using single-crystal X-ray structural analysis. ORTEP representations of these three structures are shown in Fig. S1. Compounds **B1** and **B2** crystallize in the monoclinic crystal system with a $P2_1/c$ space group, whereas compound **B3** have different crystal system, which is orthorhombic *Cmcm* space group.

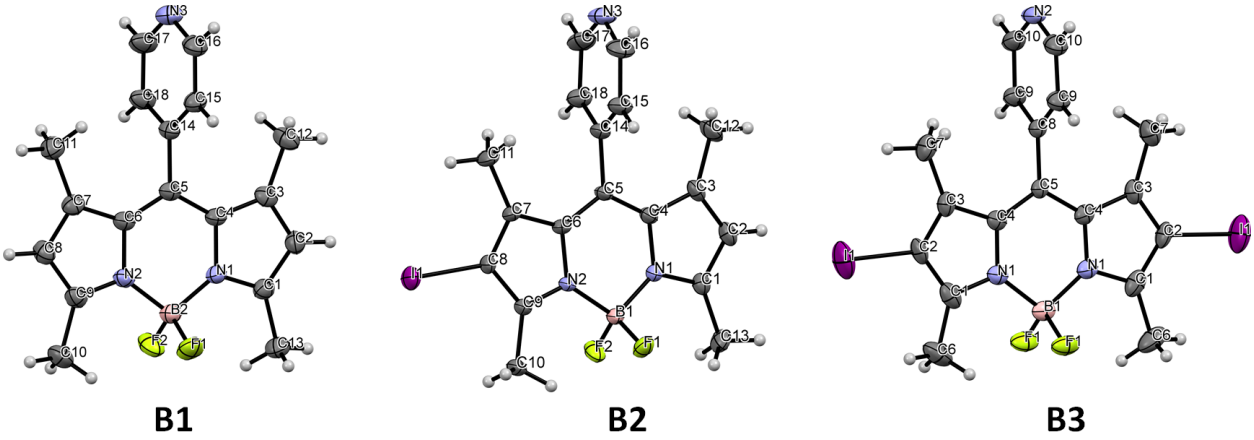

Figure S10: Molecular structures of compounds **B1**, **B2**, and **B3**, showing displacement ellipsoids at the 30% probability level. Only one molecule of the asymmetric unit of **B1** is shown.

Table S2. The intermolecular D-H···A interaction parameters (Å and °) for BODIPY compounds.

D-H···A	Symmetry	d(D-H)	d(H···A)	d(D-H···A)	D-H···A
B1					
C34-H34···F4	x, 3/2-y, 1/2+z	0.93	2.59	3.382	143.50
C18-H18···N6	-	0.93	2.63	3.428	143.97
C30-H30A···N3	x, 1/2-y, -1/2+z	0.93	2.70	3.645	167.32
C36-H36···N3	x, 3/2-y, -1/2+z	0.93	2.61	3.515	163.58
B2					
C15-H15···F2	x, 3/2-y, -1/2+z	0.93	2.49	3.364	156.62
C13-H13C···F1	x, 3/2-y, 1/2+z	0.93	2.43	3.352	161.12

$r_{vdw}(F)+ r_{vdw}(H)=2.67$ Å, $r_{vdw}(N)+ r_{vdw}(H)=2.75$ Å.

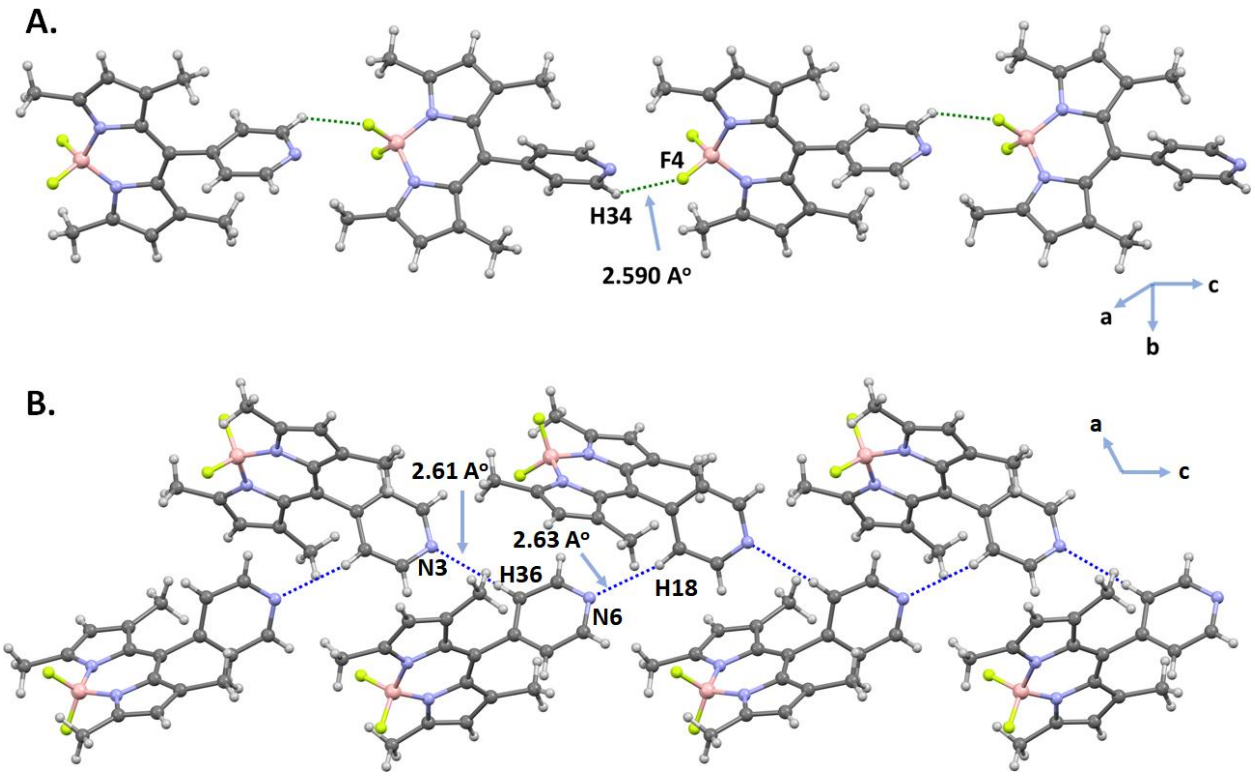

Figure S11: (A) Non-classical C-H···F and **(B)** C-H···N hydrogen bonding interactions in **B1**.

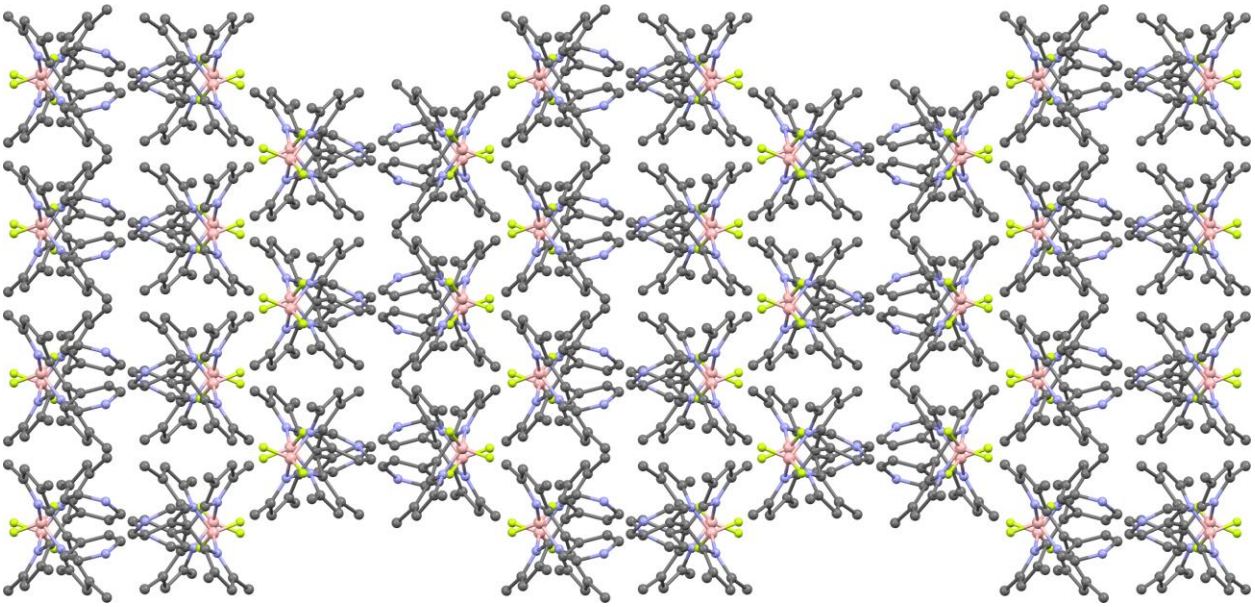

Figure S12:3D supramolecular network of **B1**.

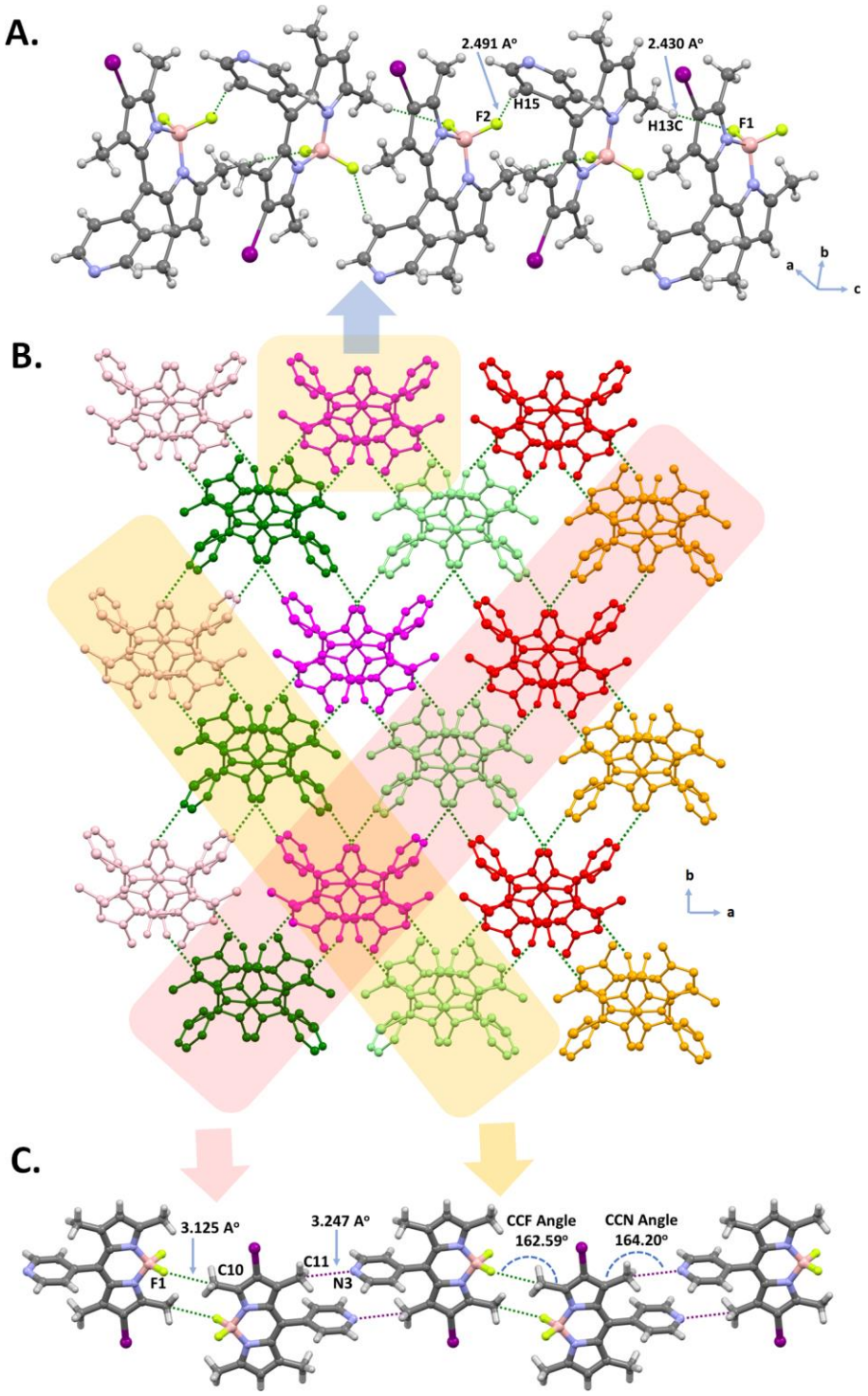

Figure S13: (A) The 1D hydrogen-bonded chain linked by intermolecular C-H···F interactions **(B)** The 3D supramolecular network of B2 **(C)** The 1D infinite chains formed by homodimer Csp3···N (3.247(6) Å) and Csp3···F (3.125(4) Å) interactions.

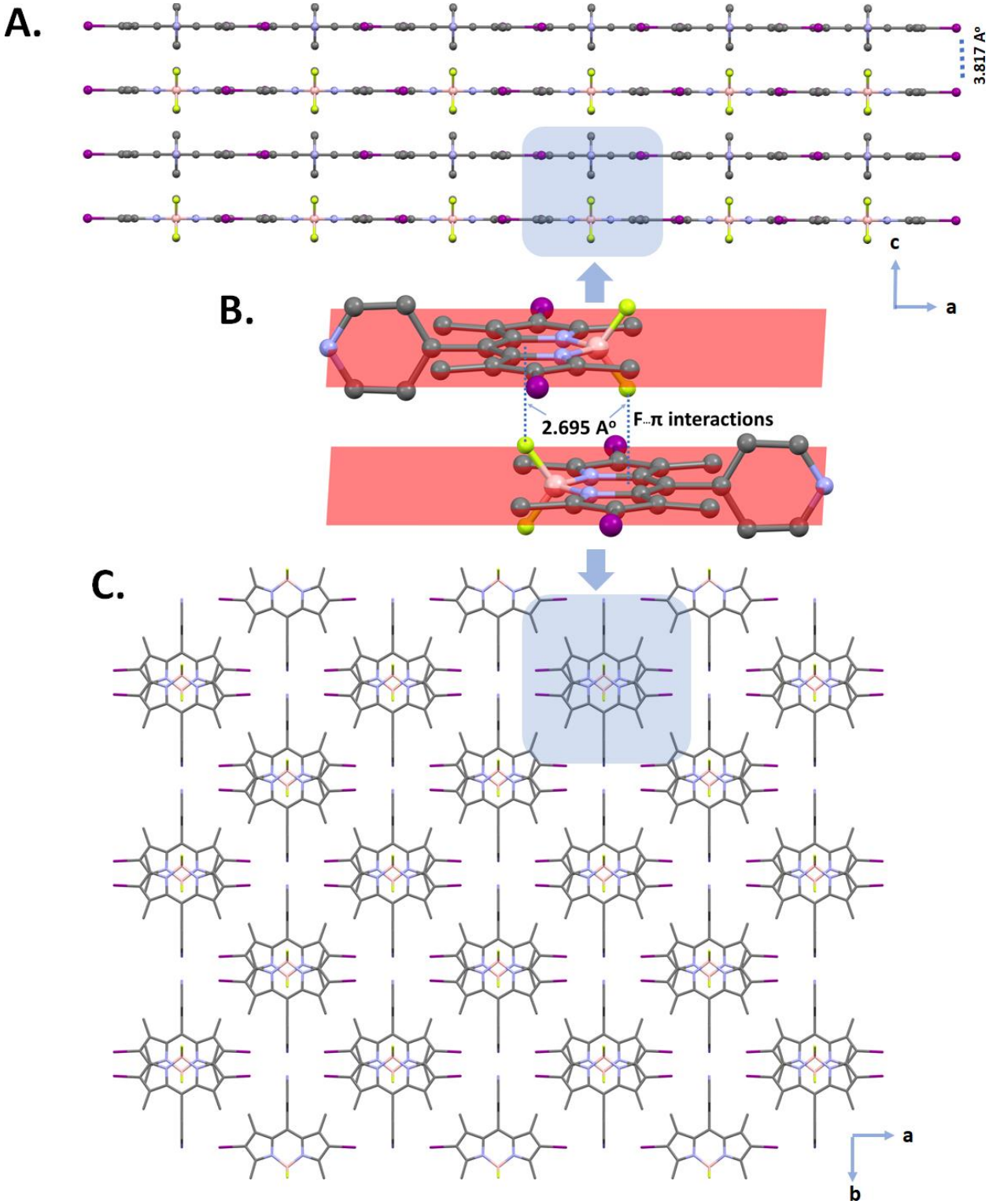
A.
3.817 Aº
c
a
B.
2.695 Aº
F···π interactions
C.
a
b

Figure S14: (A) and **(C)** Perspective view of crystal packing of **B3** along *ac* and *ab* plane. **(B)** The 1D F···$\pi_{(BODIPY)}$ interactions in **B3**.

4. Computational Methodology

Molecular electrostatic potential surfaces were calculated with the density functional M06-2X as implemented in Gaussian09.[10] For iodine, DGDZVP and for the rest of the atoms 6–31+G(d,p) basis sets were used. The atoms-in-molecules (***AIM***) topology calculations were performed with the help of Multiwfn software (v. 3.3.5),[11] using the output generated by the Gaussian 09.

The decomposition of the binding energies of studied compounds was carried out by using the symmetry-adapted perturbation theory (SAPT), which partitions the attractive forces into electrostatic (**E_{elst}**), exchange-repulsion (**E_{exch}**), induction (**E_{ind}**), dispersion (**E_{disp}**) terms and the exchange as the repulsive term.[12–14] For such decomposition, the Hamiltonian is partitioned into monomeric Fock operators, *Møller–Plesset* fluctuation operators and intermolecular interaction operators. All SAPT calculations were done with the Psi4 program using density fitting at the sSAPT0/jun-cc-pVDZ level.[15]

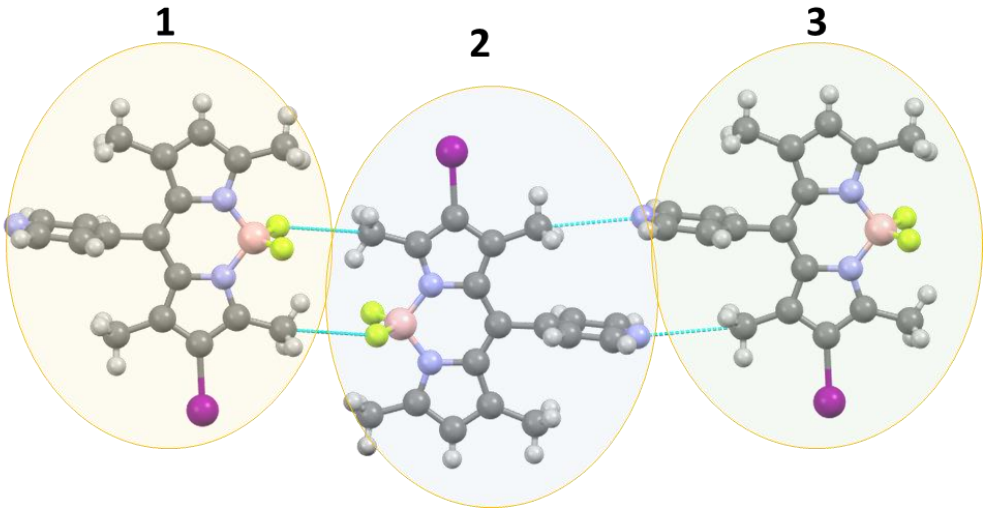

Figure S15: Trimer BODIPY unit of **B2**.

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