Supporting Information

Photophysicochemical and Electrochemical Properties of Pyrene-BODIPY Platforms

İpek Ömeroğlu[a], Baybars Köksoy[b], Dilek Öztürk[a], Lubna Salah[c], Saad Maksheed[c], Mahmut Durmuş[a*]

[a]*Gebze Technical University, Department of Chemistry, 41400, Gebze, Kocaeli, Türkiye*

[b]*Bursa Technical University, Department of Chemistry, 16130, Bursa, Türkiye*

[c]*Kuwait University, Department of Chemistry, 5969, Safat 13060, Kuwait*

**Corresponding Author: Mahmut Durmuş*

Email: durmus@gtu.edu.tr

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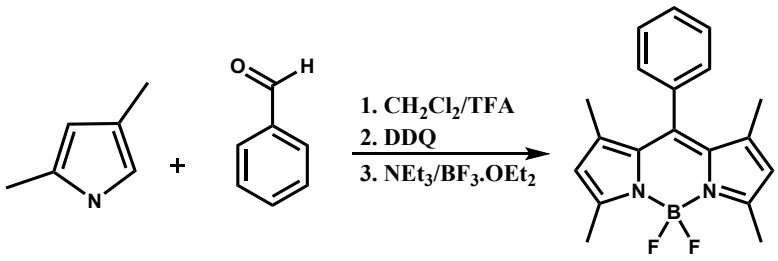
1. Characterization of BODIPY compounds (1-5)

1.1. 4,4'-Difluoro-8-(phenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (1)



(1)

An orange solid. Chemical formula $C_{19}H_{19}BF_2N_2$, (780 mg, 51%). FT-IR (ν, cm^{-1}): 3100-3025 (Aromatic-CH), 2955-2851 (Aliphatic-CH), 1462 (B-N). ^1H NMR (500 MHz, $CDCl_3$) δ, ppm: 7.51-7.50 (m, 3H, Ar-H), 7.31-7.30 (m, 2H, Ar-H), 6.00 (s, 2H, Pyrrole-H), 2.58 (s, 3H, $-CH_3$), 1.40 (s, 3H, $-CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ, ppm: 155.46, 143.19, 141.76, 135.03, 131.46, 130.03, 129.15, 128.96, 127.97, 121.21, 14.34. ^{11}B NMR (160 MHz, $CDCl_3$) δ, ppm: 0.79 (t, *J:* 66.21 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ, ppm: -146.29 (q, *J:* 98.68 Hz).

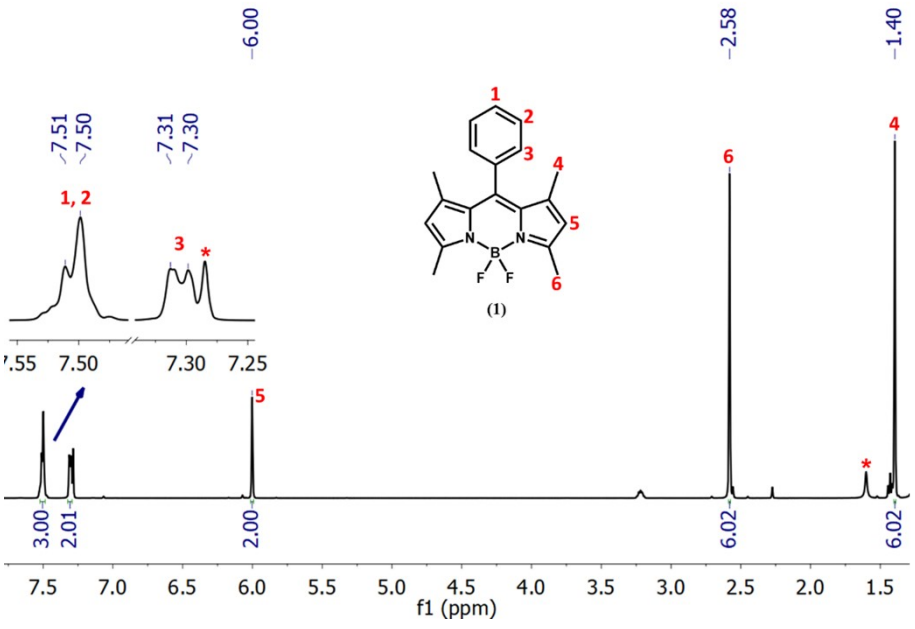


Fig. S1. ^1H-NMR spectrum of compound **1** in $CDCl_3$.

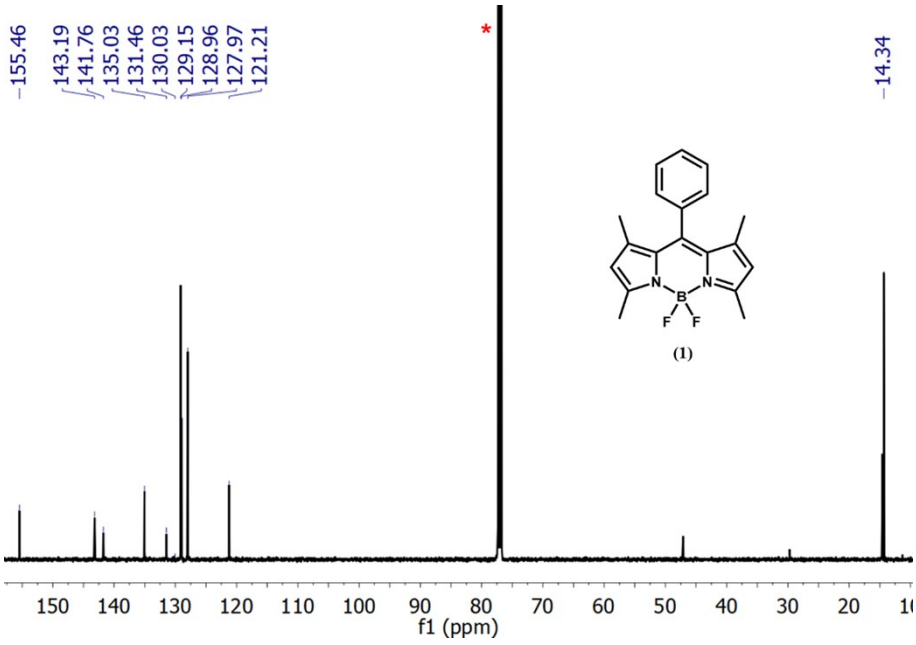


Fig. S2. ^{13}C-NMR spectrum of compound **1** in $CDCl_3$.

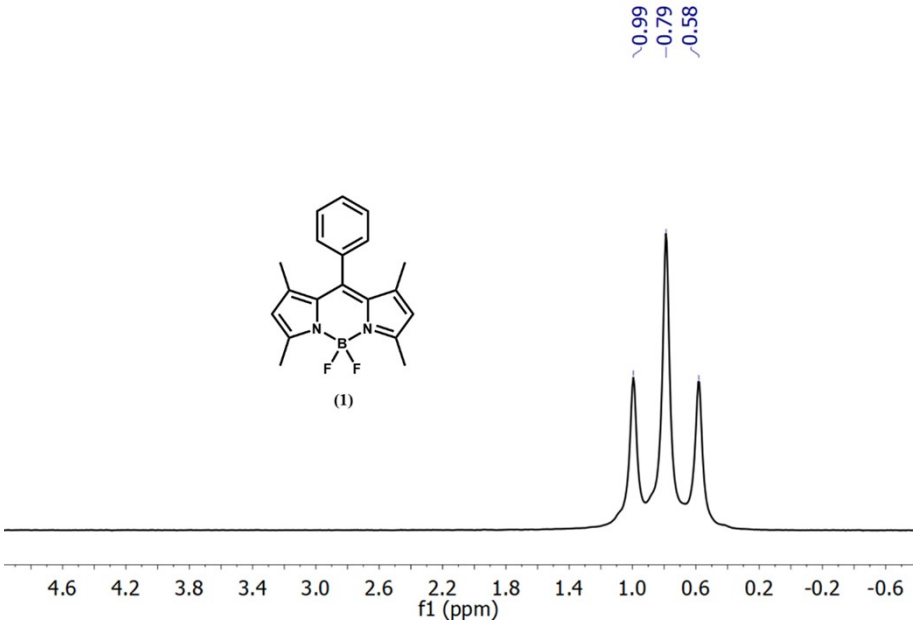


Fig. S3. ^{11}B-NMR spectrum of compound **1** in $CDCl_3$.

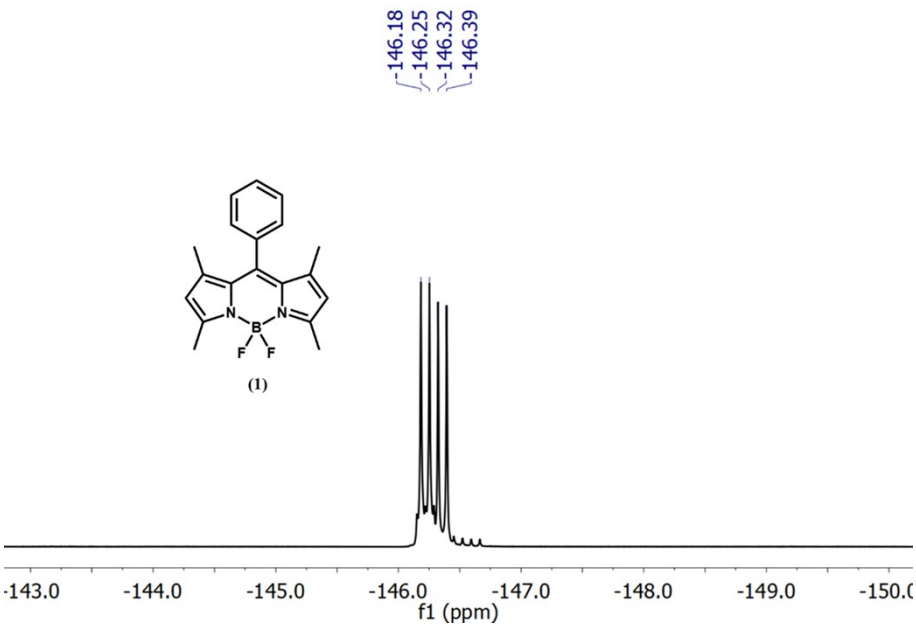
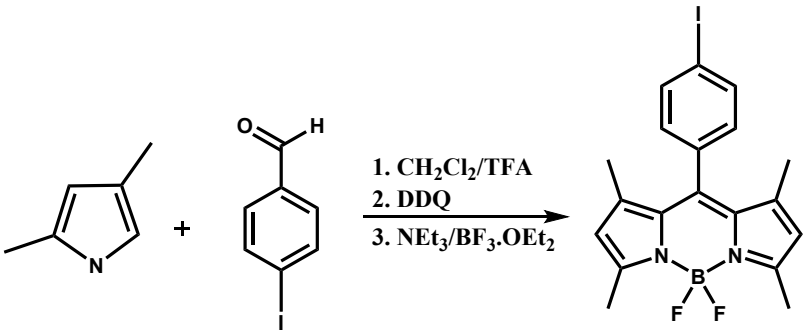


Fig. S4. ^{19}F-NMR spectrum of compound **1** in $CDCl_3$.

1.2. 4,4'-Difluoro-8-(4-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (2)



An orange solid. Chemical formula $C_{19}H_{18}BF_2IN_2$, (285 mg, 33%). FT-IR (ν, cm^{-1}): 3107-3050 (Aromatic-CH), 2959-2852 (Aliphatic-CH), 1466 (B-N). ^{1}H NMR (500 MHz, $CDCl_3$) δ, ppm: 7.87 (d, 2H, Ar-H, *J:*7.65 Hz), 7.07 (d, 2H, Ar-H, *J:*7.63 Hz), 6.01 (s, 2H, Pyrrole-H), 2.57 (s, 6H, -CH_3), 1.44 (s, 6H, -CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ, ppm: 155.92, 142.95, 140.10, 138.38, 134.59, 131.16, 129.99, 121.46, 94.76, 14.67. ^{11}B NMR (160 MHz, $CDCl_3$) δ, ppm: 0.73 (t, *J:* 65.80 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ, ppm: -146.26 (q, *J:* 98.84 Hz).

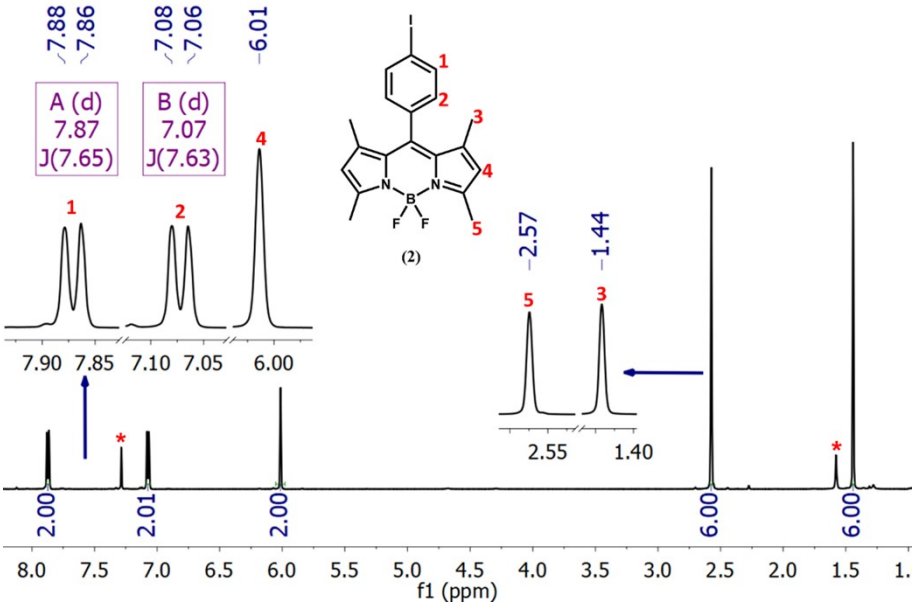


Fig. S5. ^{1}H-NMR spectrum of compound **2** in $CDCl_3$.

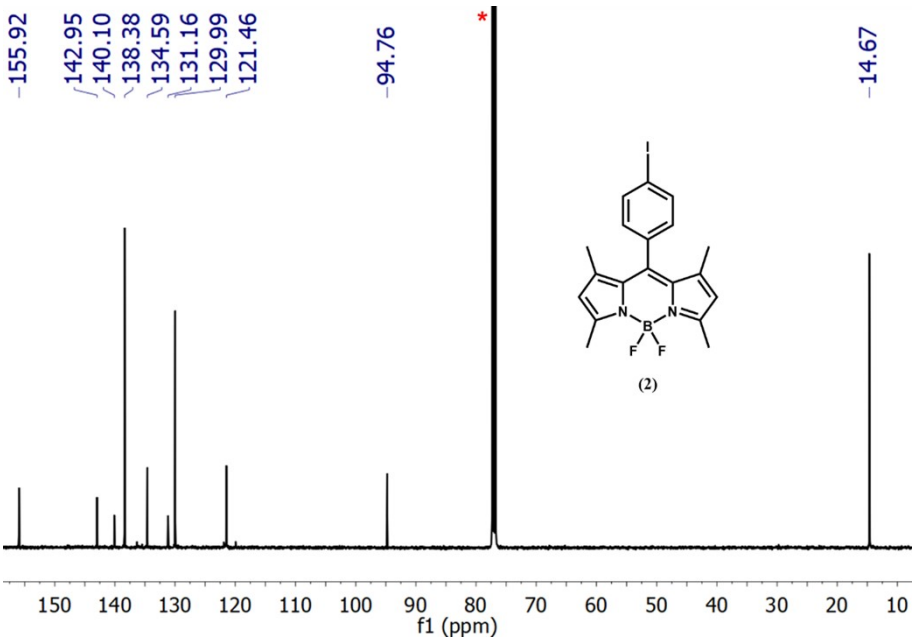


Fig. S6. ^{13}C-NMR spectrum of compound **2** in $CDCl_3$.

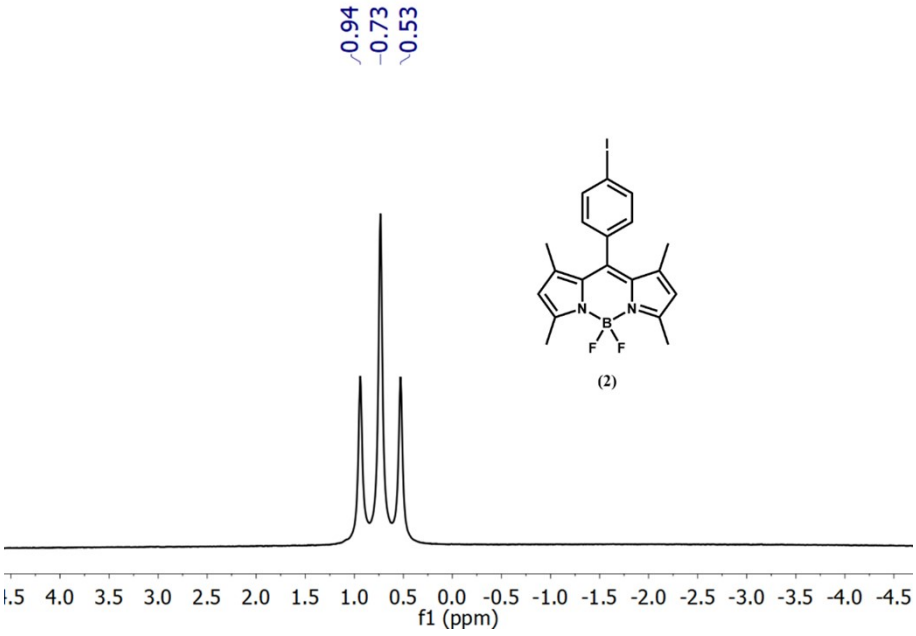


Fig. S7. ^{11}B-NMR spectrum of compound **2** in $CDCl_3$.

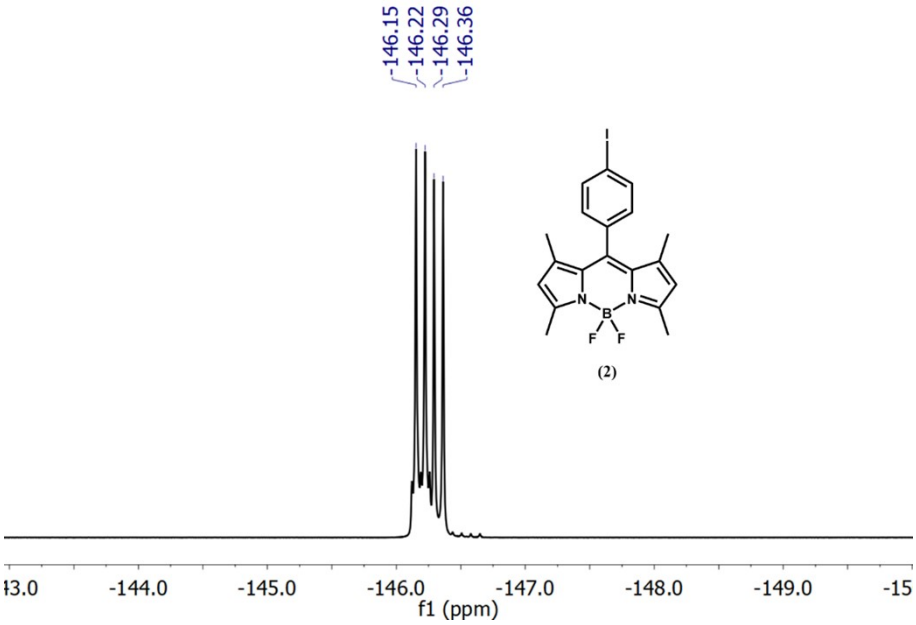
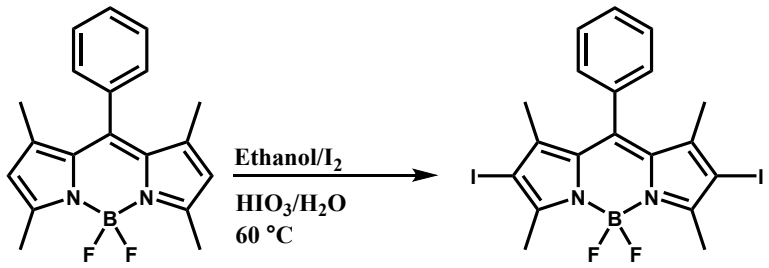


Fig. S8. ^{19}F-NMR spectrum of compound **2** in $CDCl_3$.

1.3. 4,4'-Difluoro-8-(phenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (3)



A dark red solid. Chemical formula $C_{19}H_{17}BF_2I_2N_2$, (175 mg, 78.8%). FT-IR (ν, cm^{-1}): 3070-3018 (Aromatic-CH), 2959-2844 (Aliphatic-CH), 1479 (B-N). ^1H NMR (500 MHz, $CDCl_3$) δ, ppm: 7.55-7.54 (m, 3H, Ar-H), 7.28-7.27 (m, 2H, Ar-H), 2.67 (s, 6H, $-CH_3$), 1.41 (s, 6H, $-CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ, ppm: 156.80, 145.40, 141.40, 134.76, 131.32, 129.56, 127.80, 85.69, 29.72, 16.96, 16.05. ^{11}B NMR (160 MHz, $CDCl_3$) δ, ppm: 0.58 (t, *J:* 64.46 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ, ppm: -145.64 (q, *J:* 97.09 Hz).

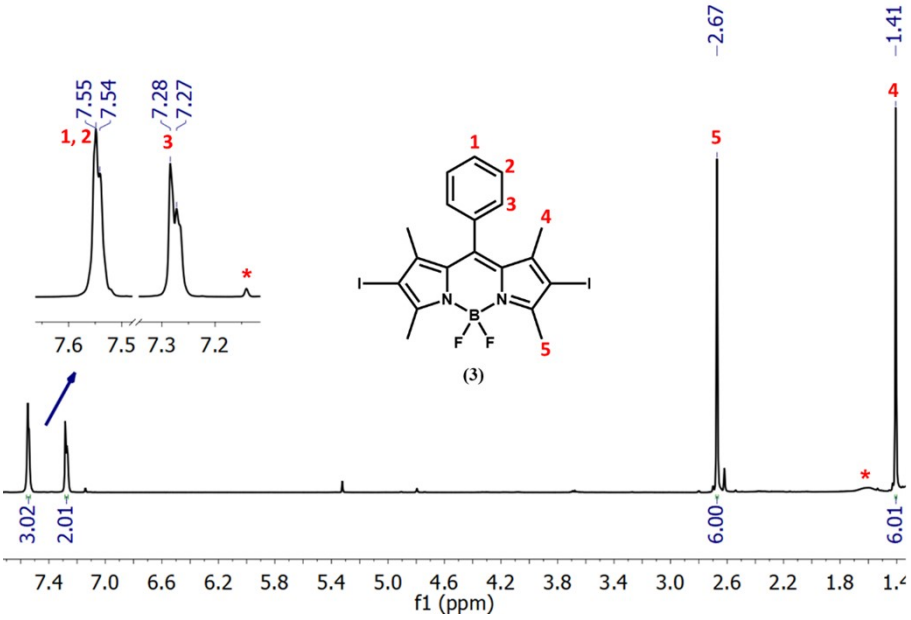


Fig. S9. ^1H-NMR spectrum of compound **3** in $CDCl_3$.

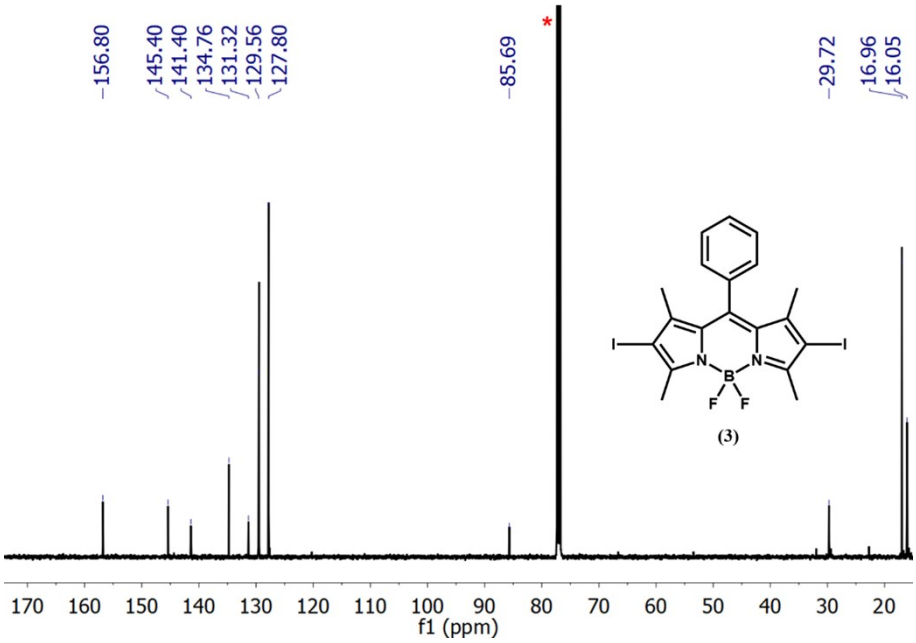


Fig. S10. ^{13}C-NMR spectrum of compound **3** in $CDCl_3$.

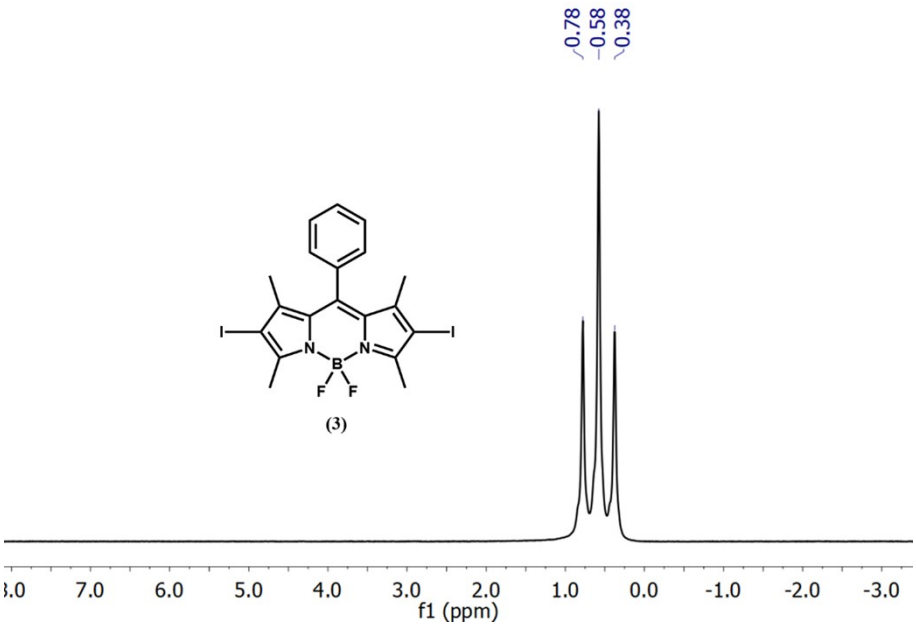


Fig. S11. ^{11}B-NMR spectrum of compound **3** in $CDCl_3$.

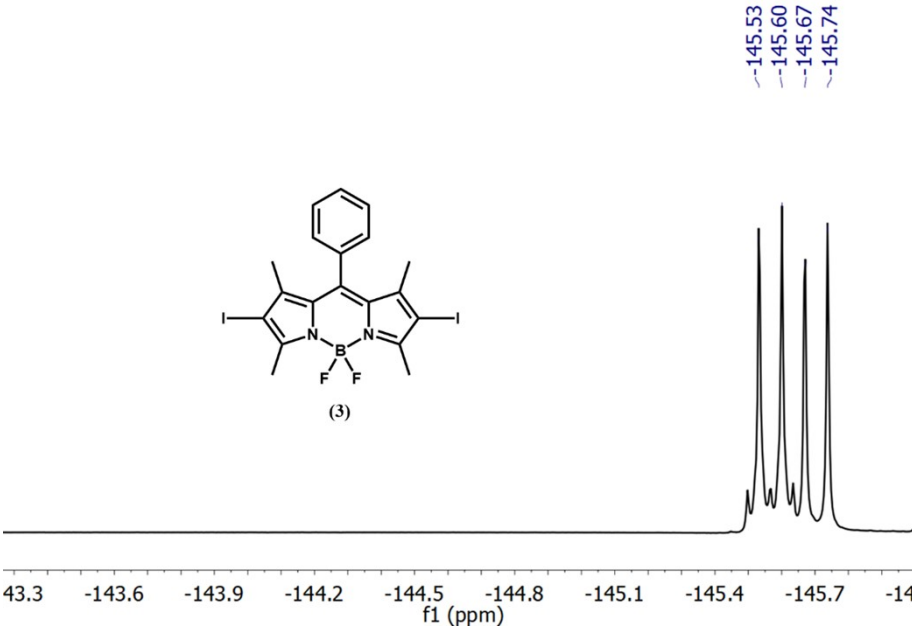
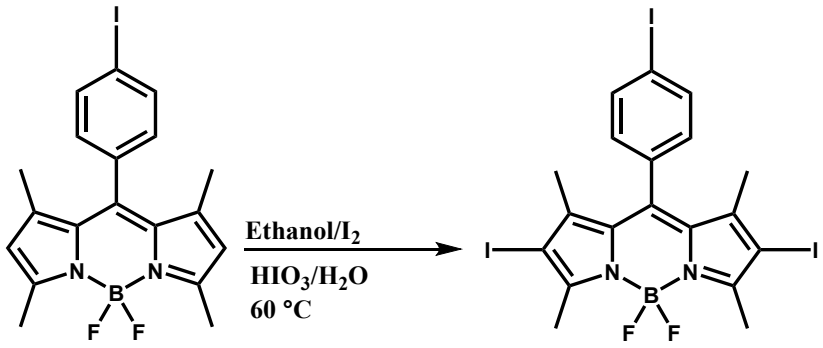


Fig. S12. ^{19}F-NMR spectrum of compound **3** in $CDCl_3$.

1.4. 4,4'-Difluoro-8-(iodophenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (4)



A dark red solid. Chemical formula $C_{19}H_{16}BF_2I_3N_2$, (187 mg, 60%). FT-IR (ν, cm^{-1}): 3055-3037 (Aromatic-CH), 2962-2851 (Aliphatic-CH), 1454 (B-N). ^{1}H NMR (500 MHz, $CDCl_3$) δ, ppm: 7.91 (d, 2H, Ar-H, *J:*7.80 Hz), 7.04 (d, 2H, Ar-H, *J:*7.63 Hz), 2.66 (s, 6H, -CH_3), 1.45 (s, 6H, -CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ, ppm: 157.7, 145.15, 139.71, 138.71, 134.31, 131.03, 129.75, 95.39, 85.98, 17.30, 16.09. ^{11}B NMR (160 MHz, $CDCl_3$) δ, ppm: 0.53 (t, *J:* 64.06 Hz). ^{9}F NMR (470 MHz, $CDCl_3$) δ, ppm: -145.64 (q, *J:* 95.91 Hz).

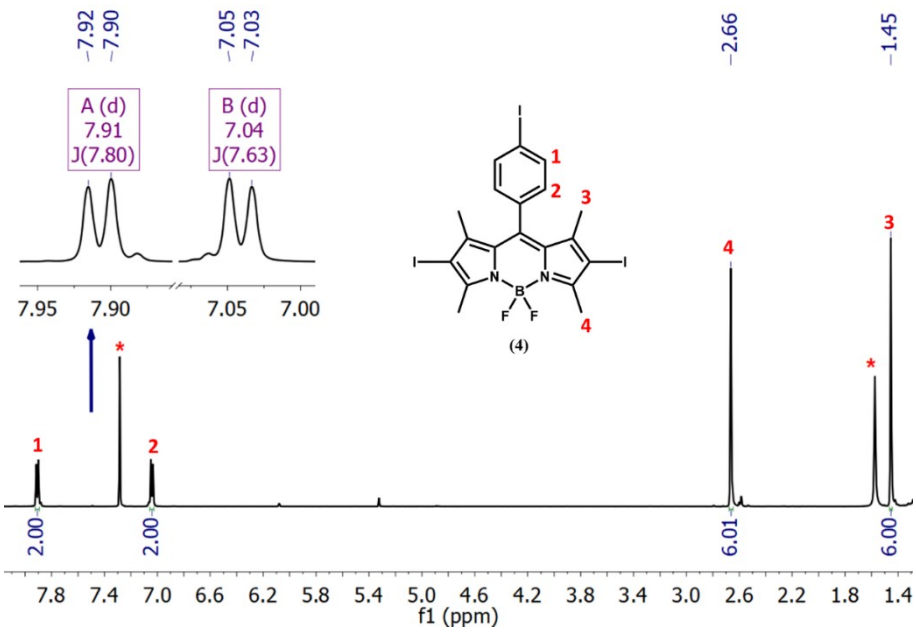


Fig. S13. ^{1}H-NMR spectrum of compound **4** in $CDCl_3$.

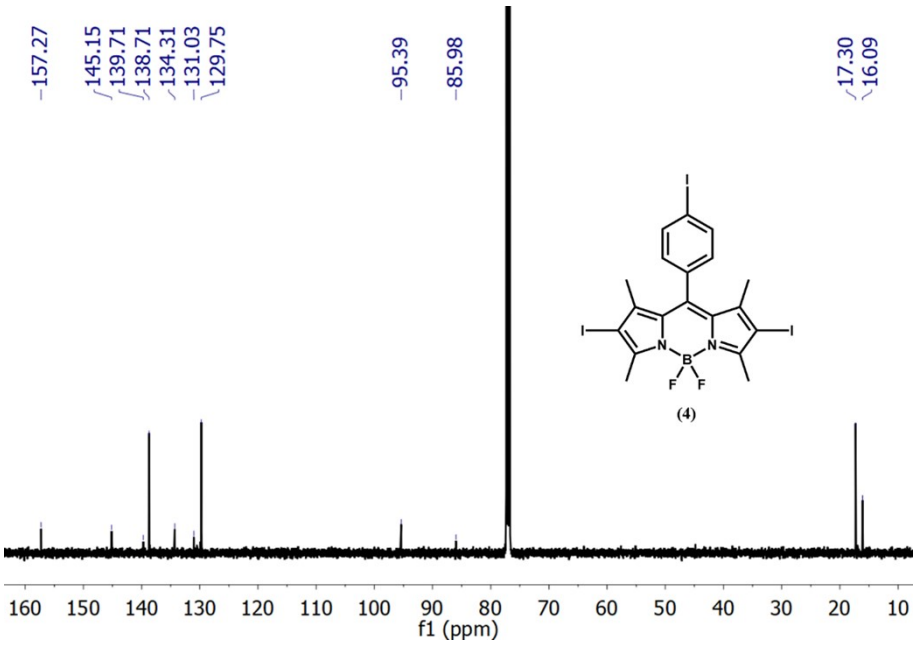


Fig. S14. ^{13}C-NMR spectrum of compound **4** in $CDCl_3$.

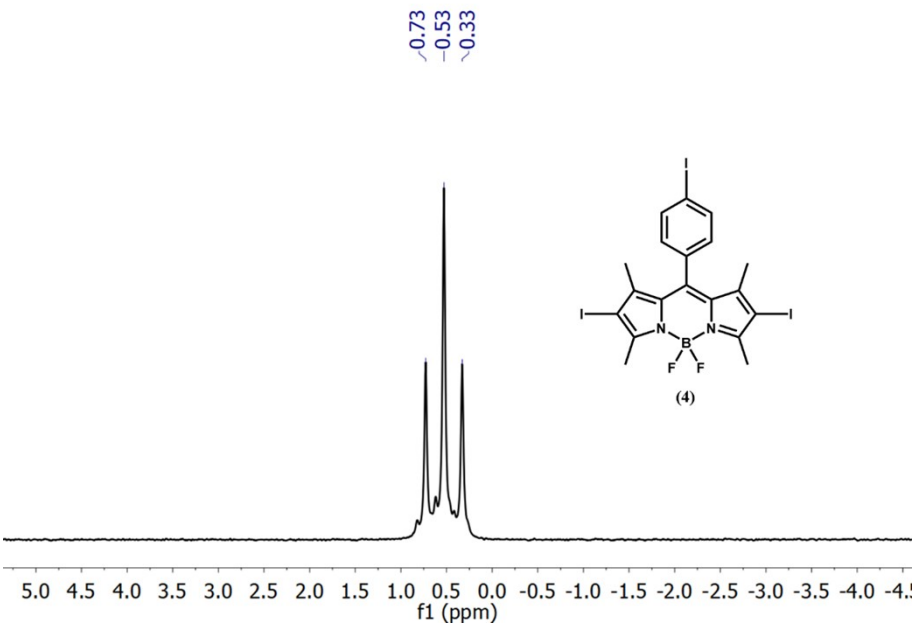


Fig. S15. ^{11}B-NMR spectrum of compound **4** in $CDCl_3$.

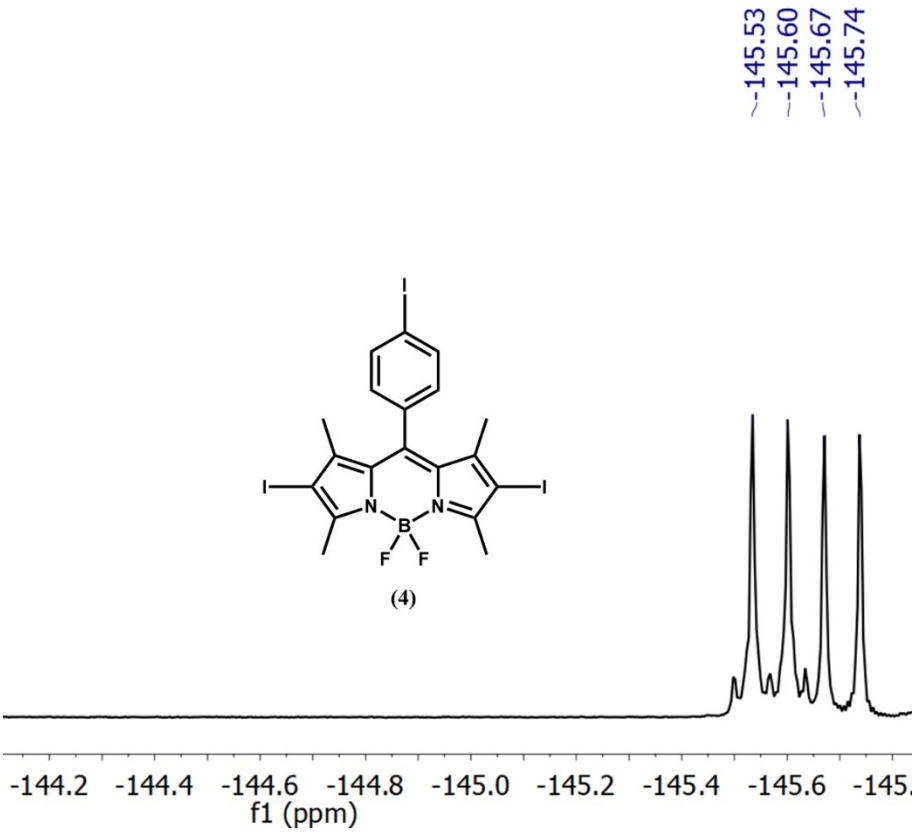
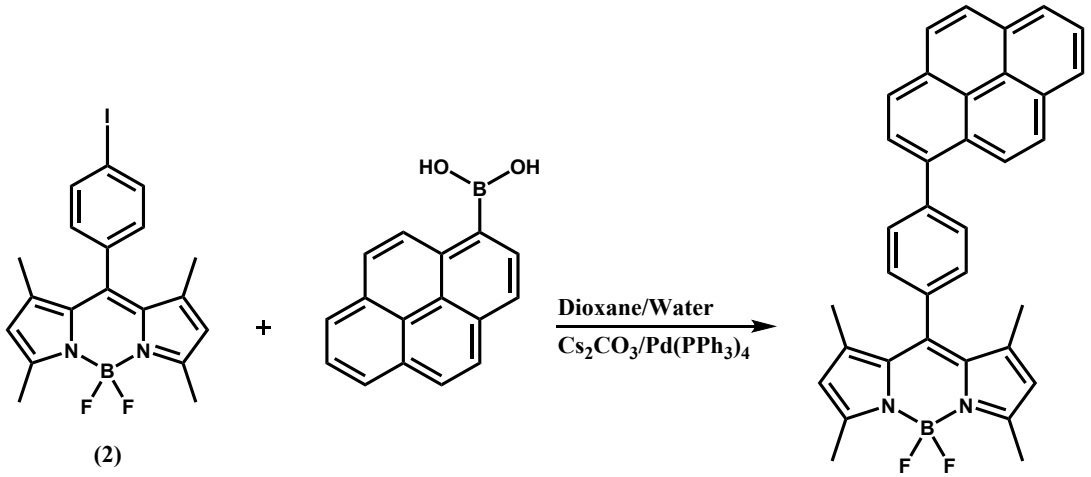


Fig. S16. ^{19}F-NMR spectrum of compound **4** in $CDCl_3$.

1.5. 4,4'-Difluoro-8-(4-pyrenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (5)



(2) **(5)**

An orange solid. Chemical formula $C_{35}H_{27}BF_2N_2$, (93.21 mg, 80%). FT-IR (ν, cm^{-1}): 3107-3030 (Aromatic-CH), 2962-2848 (Aliphatic-CH), 1467 (B-N). ^{1}H NMR (500 MHz, $CDCl_3$) δ, ppm: 8.29-8.22 (m, 3H, Pyrene-H), 8.16-8.05 (m, 6H, Pyrene-H), 7.79 (d, 2H, Ar-H, *J:*7.62 Hz), 7.52 (d, 2H, Ar-H, *J:*7.60 Hz), 6.09 (s, 2H, Pyrrole-H), 2.63 (s, 6H, $-CH_3$), 1.65 (s, 6H, $-CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ, ppm: 155.64, 143.14, 142.12, 136.67, 134.01, 131.52, 131.34, 130.94, 128.44, 128.14, 127.94, 127.73, 127.63, 127.44, 126.20, 125.43, 125.08, 125.04, 124.71, 124.68, 121.40, 14.65. ^{11}B NMR (160 MHz, $CDCl_3$) δ, ppm: 0.86 (t, *J:* 65.44 Hz). ^{9}F NMR (470 MHz, $CDCl_3$) δ, ppm: -146.22 (q, *J:* 99.51 Hz).

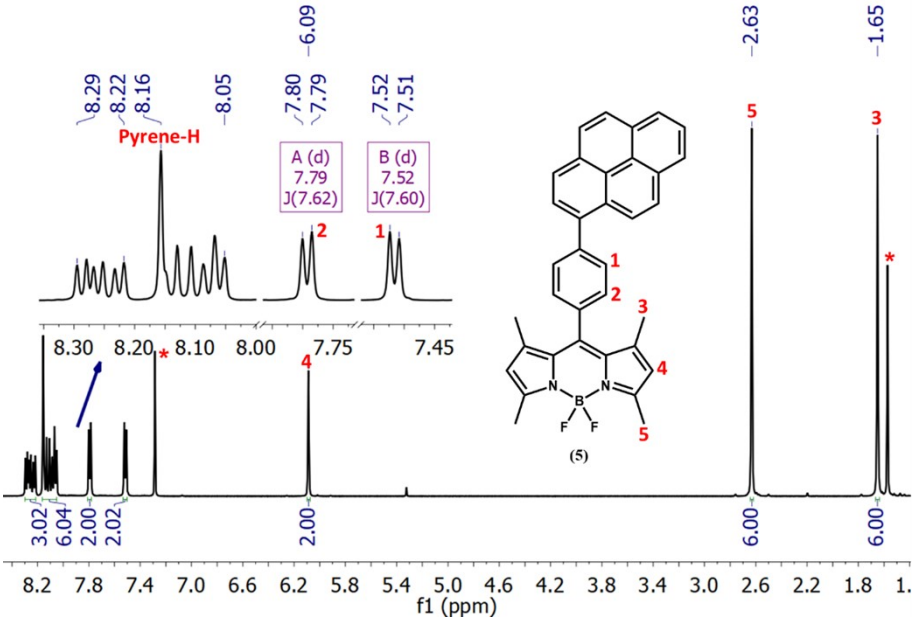


Fig. S17. ^{1}H-NMR spectrum of compound **5** in $CDCl_3$.

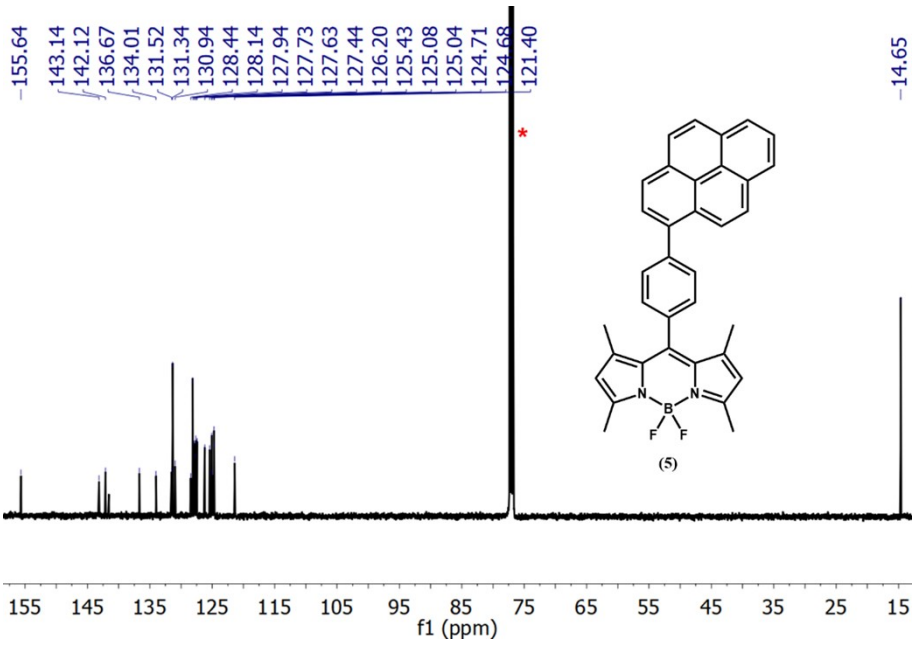


Fig. S18. ^{13}C-NMR spectrum of compound **5** in $CDCl_3$.

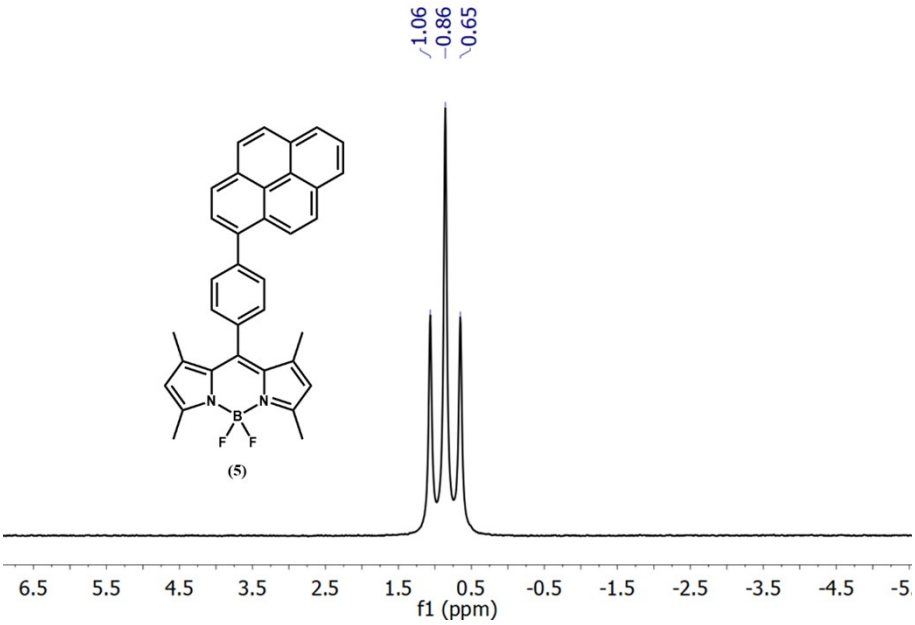


Fig. S19. ^{11}B-NMR spectrum of compound **5** in $CDCl_3$.

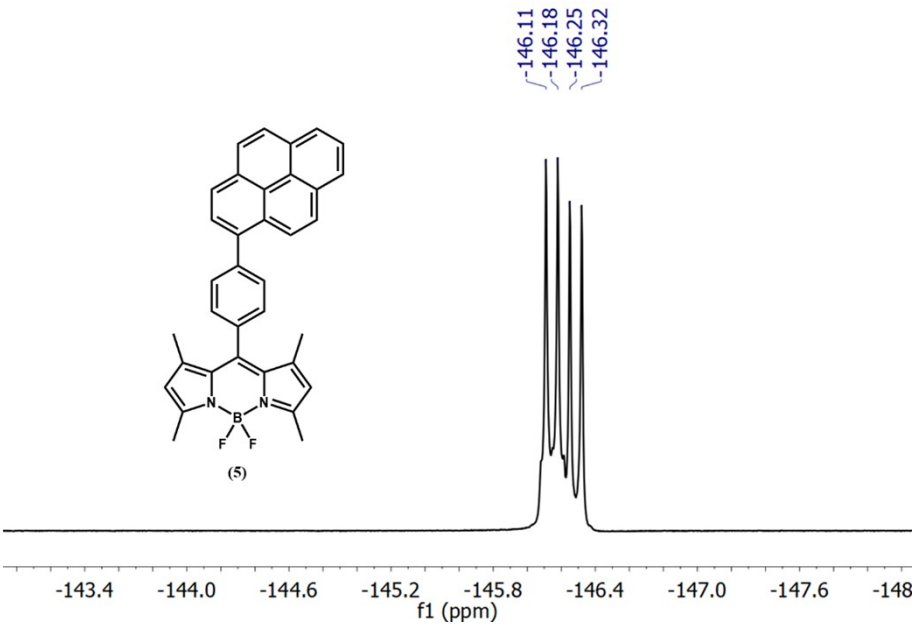


Fig. S20. ^{19}F-NMR spectrum of compound **5** in $CDCl_3$.

2. Characterization of novel pyrene-BODIPY compounds (5♦, 6, and 7)

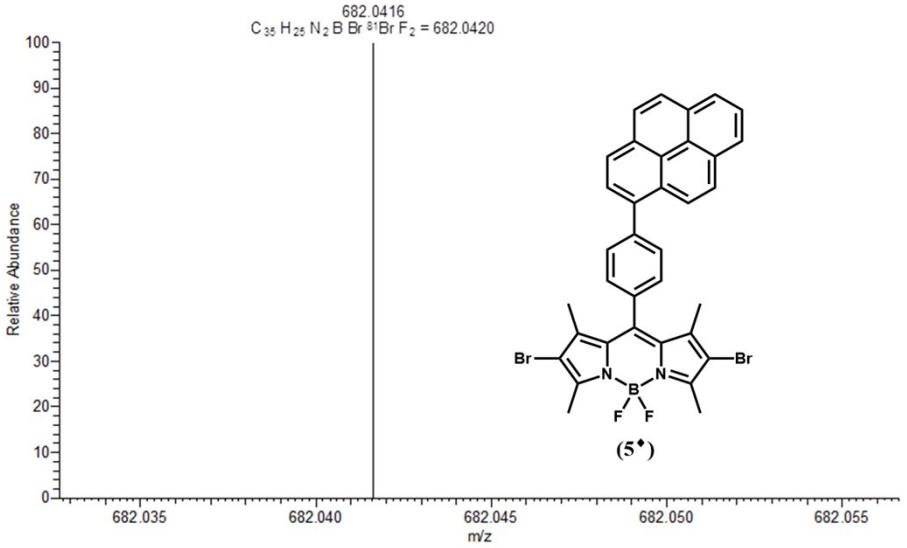


Fig. S21. HRMS spectrum of compound **5♦**.

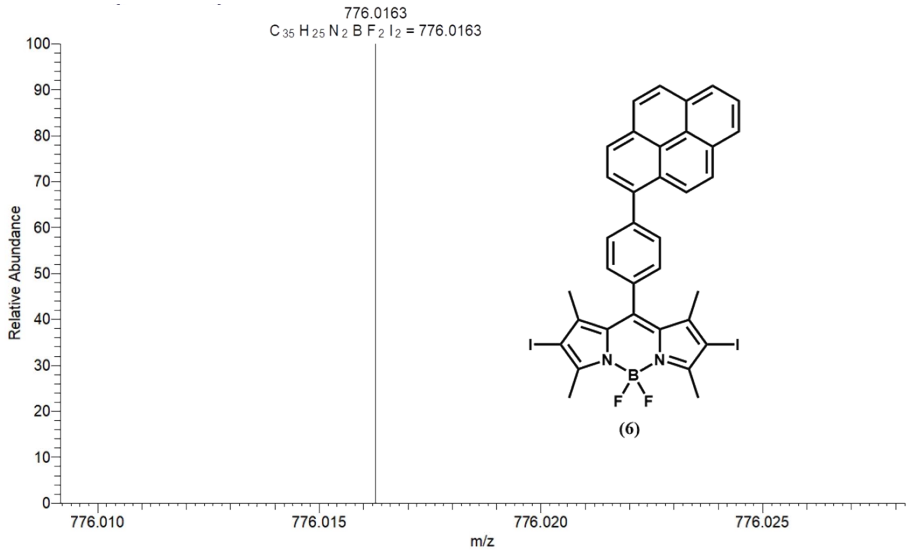


Fig. S22. HRMS spectrum of compound **6**.

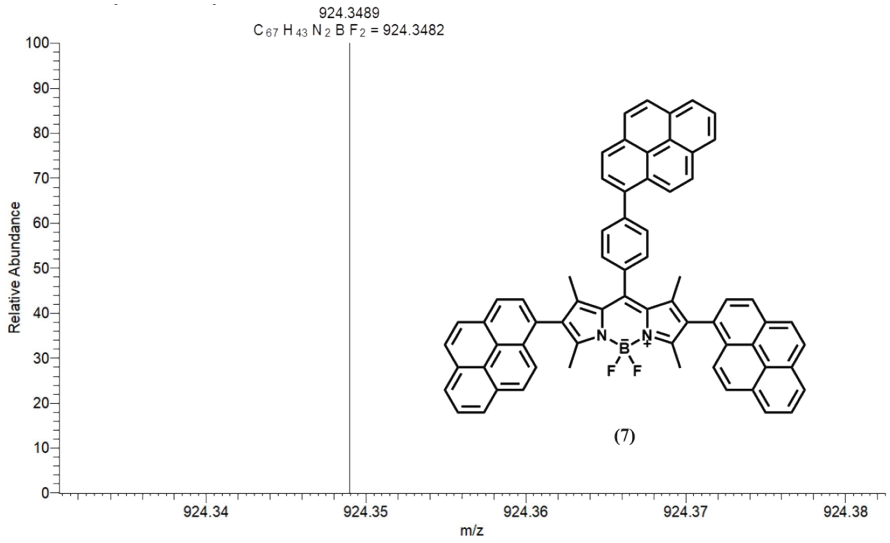


Fig. S23. HRMS spectrum of compound **7**.

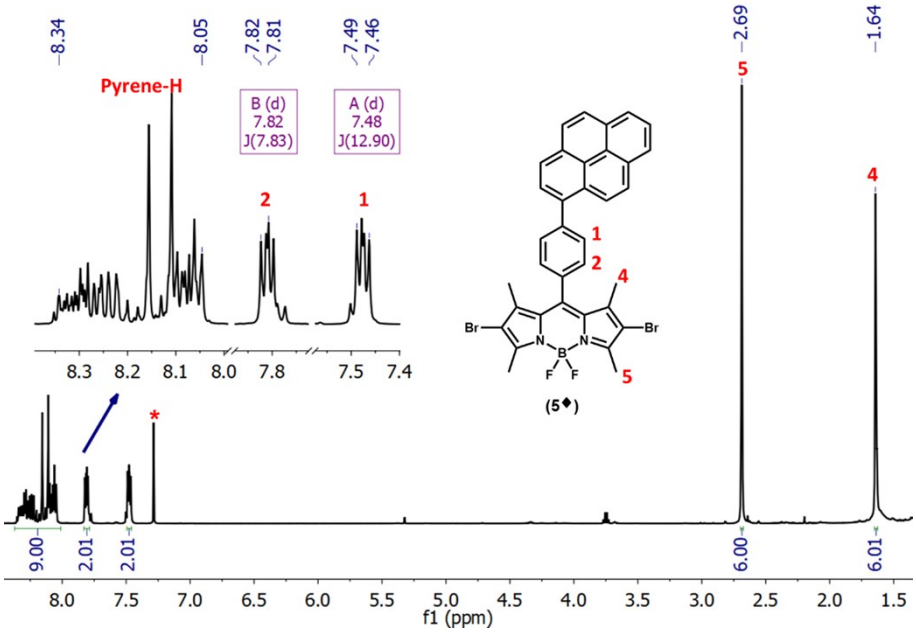


Fig. S24. ^{1}H-NMR spectrum of compound **5♦** in $CDCl_3$.

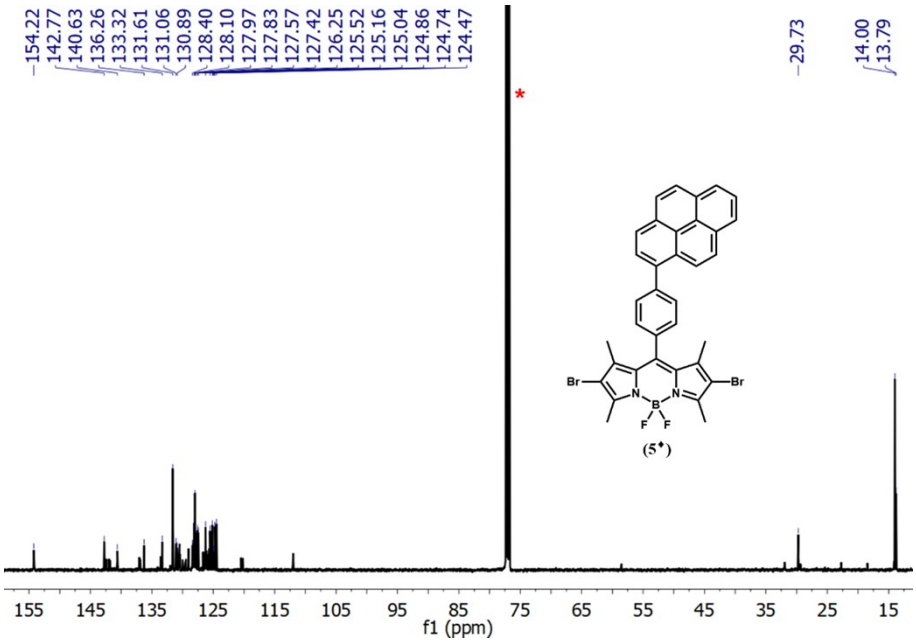


Fig. S25. ^{13}C-NMR spectrum of compound **5♦** in $CDCl_3$.

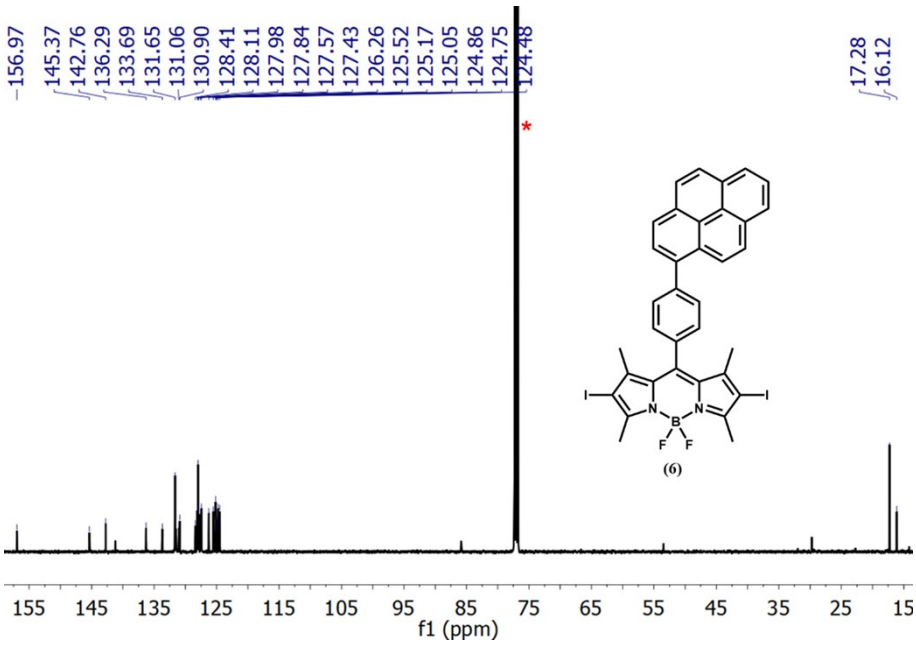


Fig. S26. ^{13}C-NMR spectrum of compound **6** in $CDCl_3$.

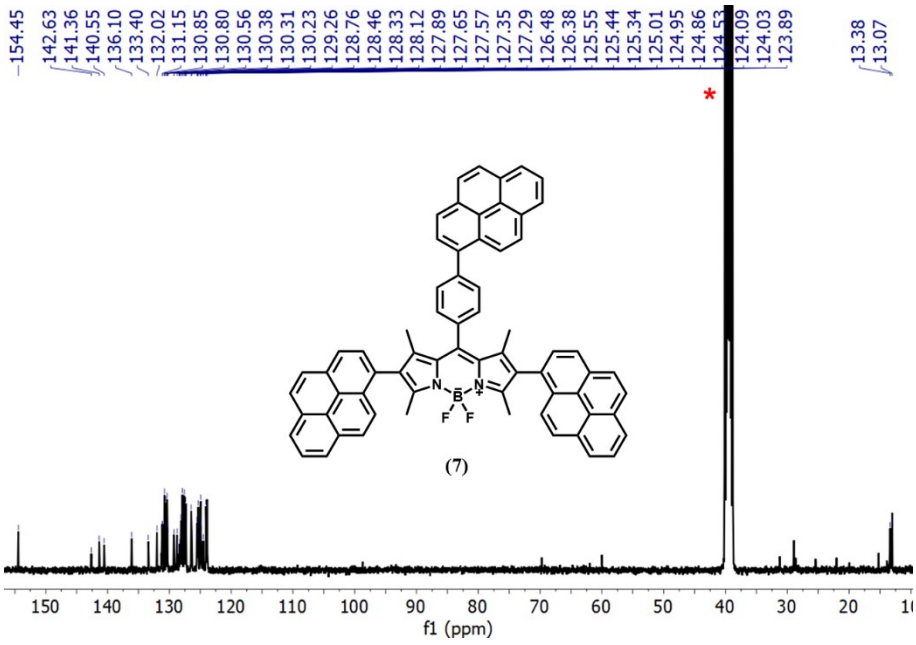


Fig. S27. ^{13}C-NMR spectrum of compound **7** in DMSO-d_6.

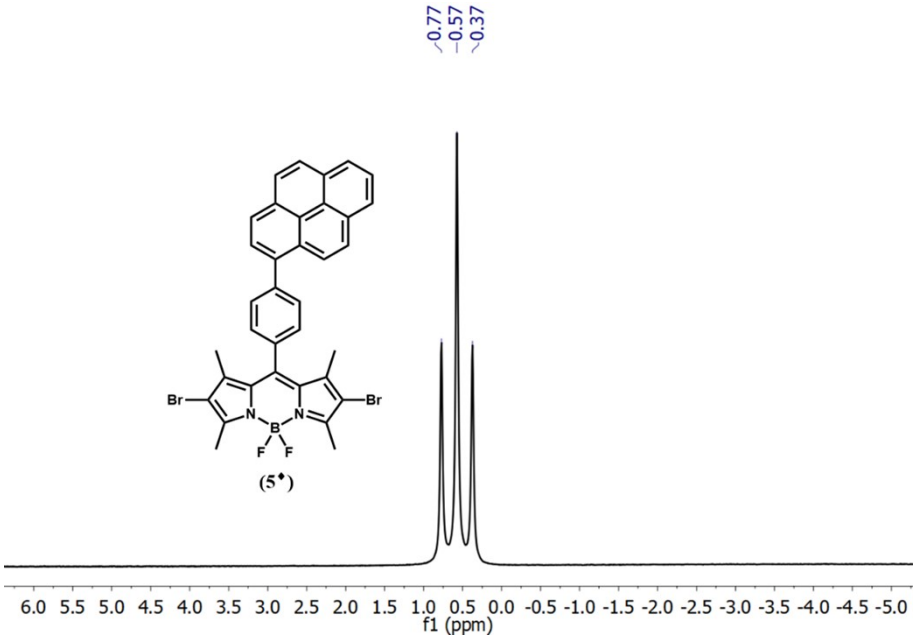


Fig. S28. ^{11}B-NMR spectrum of compound **5♦** in $CDCl_3$.

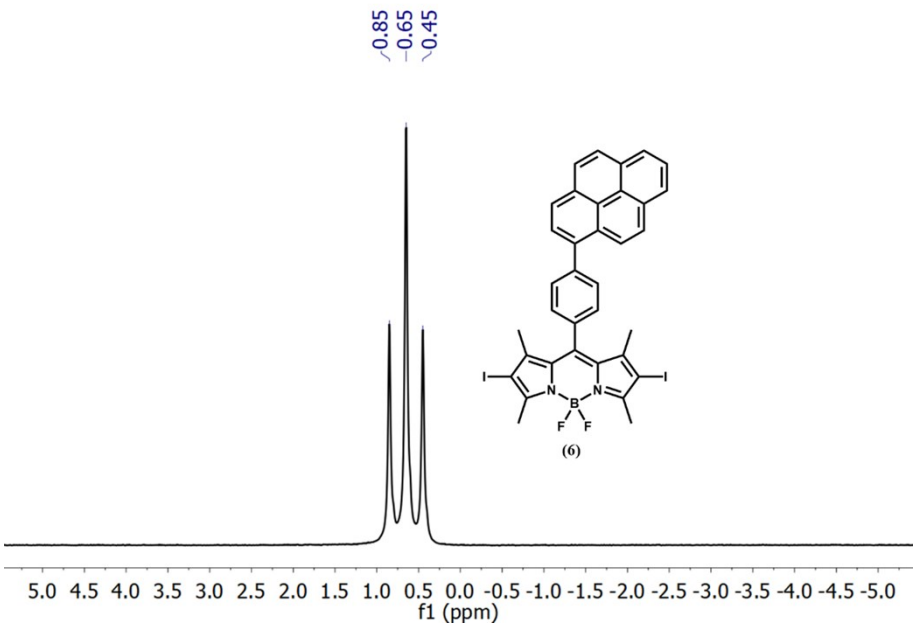


Fig. S29. ^{11}B-NMR spectrum of compound **6** in $CDCl_3$.

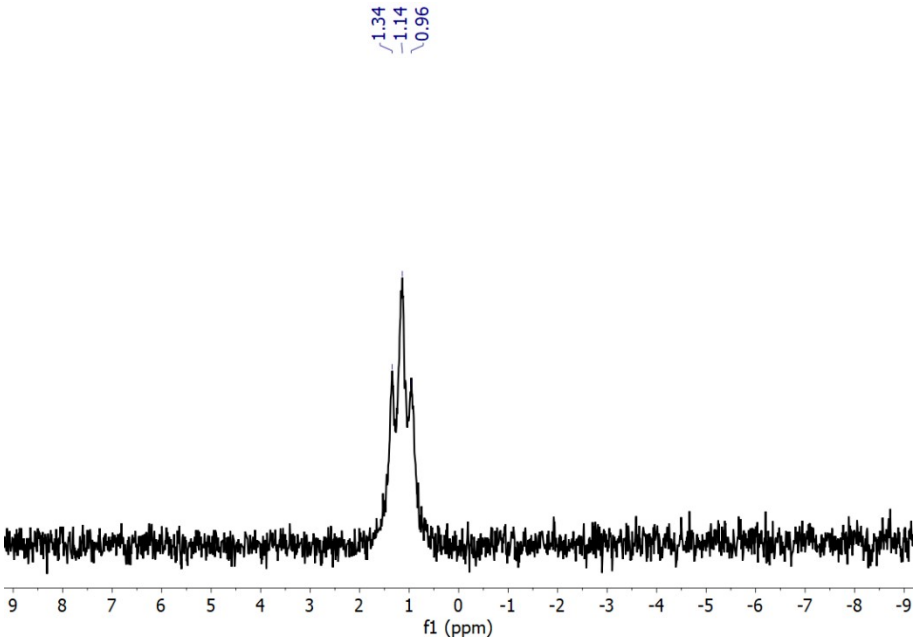


Fig. S30. ^{11}B-NMR spectrum of compound **7** in DMSO-d_6.

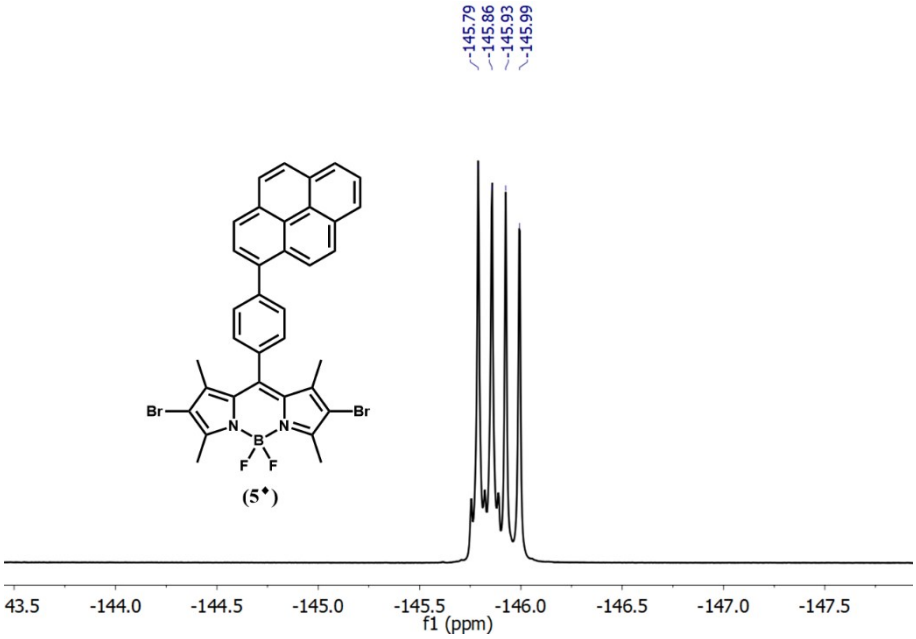


Fig. S31. ^{19}F-NMR spectrum of compound **5♦** in $CDCl_3$.

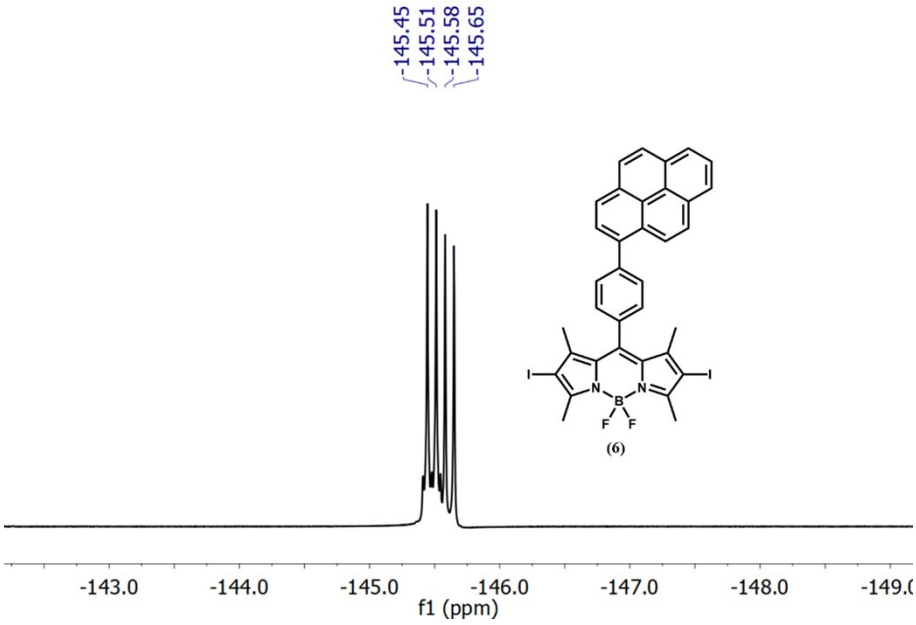


Fig. S32. ^{19}F-NMR spectrum of compound **6** in $CDCl_3$.

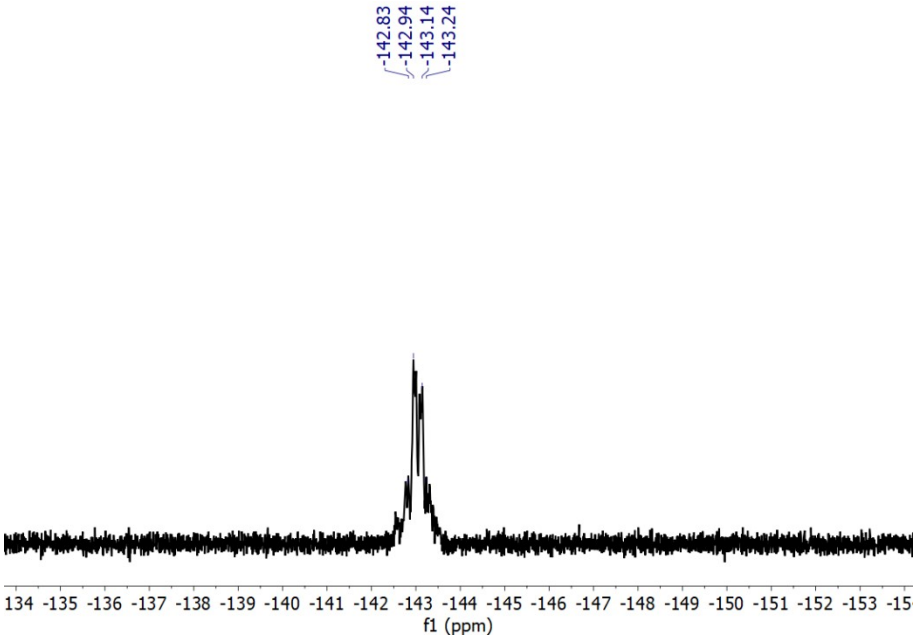


Fig. S33. ^{19}F-NMR spectrum of compound **7** in DMSO-d_6.

3. Electrochemical characterizations

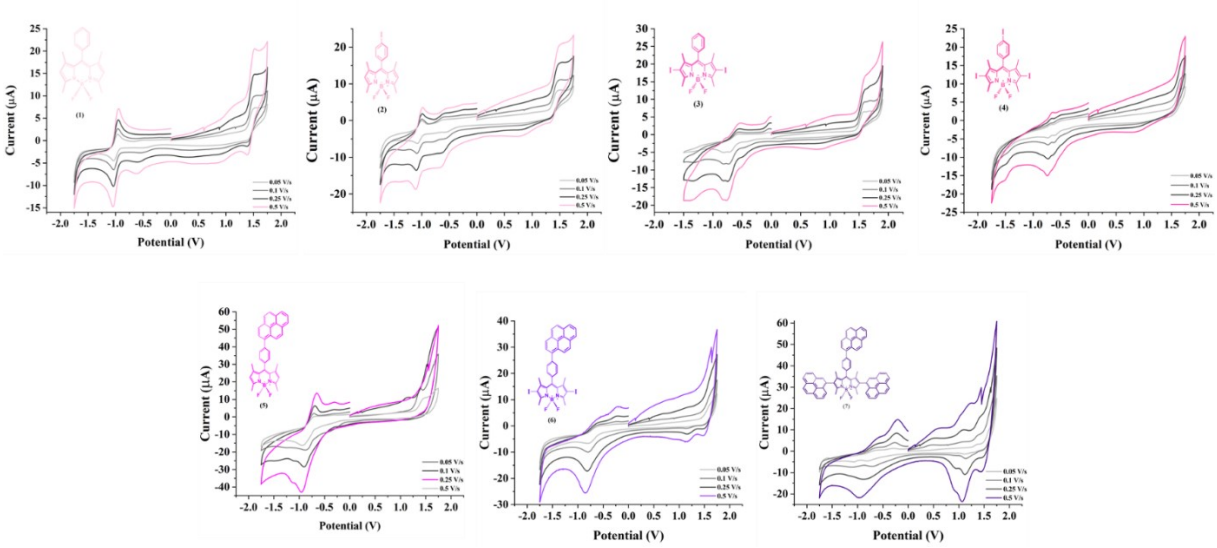


Fig. S34. Cyclic voltammograms at different scan rates of synthesized BODIPY compounds (**1-7**) in DCM with 0.1 M TBAPF6 as supporting electrolyte.

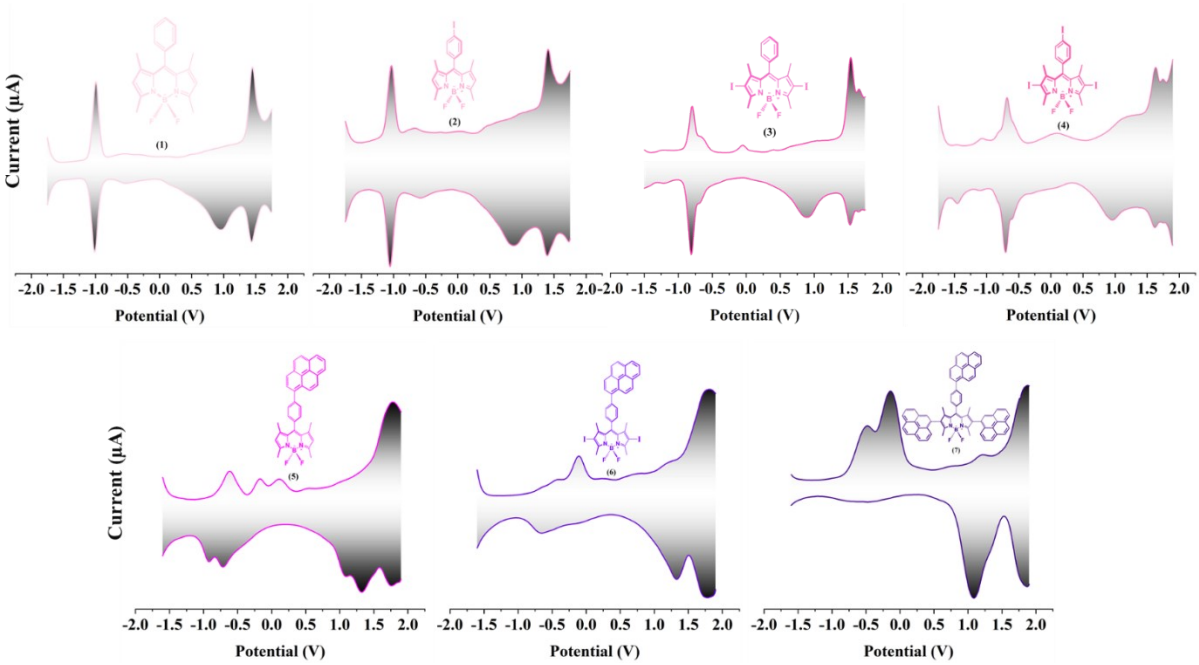


Fig. S35. Square wave voltammograms of synthesized BODIPY compounds (**1**-**7**) in DCM with 0.1 M TBAPF6 as supporting electrolyte, scan rate 0.05 V/s.

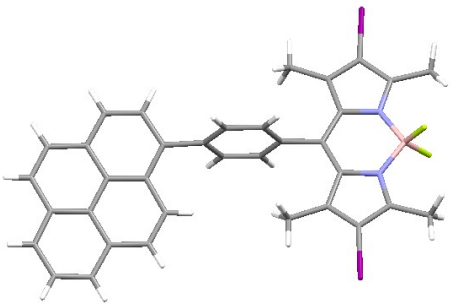
4. X-Ray study of compound 6

All starting BODIPY compounds (**1-4**) and pyrene-BODIPY (Halogen free, **5**) were not original, and their crystal structures were given in the literature before. The single crystal form of targeted pyrene-BODIPY compound **7** could not be obtained. Only compound **6** was crystalized and solved their crystal structure. The crystal structure of compound **6** was solved using single-crystal X-ray analysis and crystallographic data-refinement details given in Table S1. Suitable crystals for the X-ray diffraction study of compound **6** were obtained from recrystallization by dichloromethane-hexane solvent mixture.

The structure of compound **6** was shown in a triclinic crystal system, *P1*. As checked in the crystal structure of compound **6**, the BODIPY backbone and pyrene groups were observed at the same plane while the *meso*-phenyl group was orthogonal position to both of BODIPY center and pyrene moiety. These structural features were also compatible with the corresponding literatures including styryl-BODIPY compounds [1-3].

In addition, as the solid crystal structure of compound **1** is examined, it is seen that it has a strong pi-pi interaction (Fig. S36) and the distance between these 2 pyrene groups is 3.904 Å. This interaction is caused by the effect of electron-rich pyrene groups located on the face with face each other. These interactions hold the 2 molecules in a single packaging.

Table S1. Crystal structure and crystal data of BODIPY compound **6**

Compound	
CCDC Number	2213850
Parameters	**Compound 6**
Empirical formula	$C_{35}H_{25}BF_2I_2N_2$
Formula weight	776.18
Temperature/K	296.15
Crystal system	Triclinic
Space group	*P*1
a/Å	10.350 (3)
b/Å	11.258 (3)
c/Å	15.292 (5)
α/°	75.396 (8)
β/°	75.221 (8)
γ/°	68.248 (7)
Volume/Å^3	1575.4 (7)
Z	2
ρ_{calc}g/cm^3	1.636
μ/mm^{-1}	2.04
F(000)	756
Crystal size/mm^3	0.17 × 0.05 × 0.04
Radiation	Mo Kα (λ = 0.71073 Å)
2Θ range for data collection/°	1.4 to 25
Index ranges	$-12 \le h \le 12$, $13 \le k \le 13$, $-18 \le l \le 18$
Reflections collected	11935
Independent reflections	5464 [R_{int} = 0.044, R_{sigma} = 0.0546]
Goodness-of-fit on F^2	1.02
Final R indexes [I>=2σ (I)]	R_1 = 0.0443, wR_2 = 0.1102
Largest diff. peak/hole	0.69, −0.77

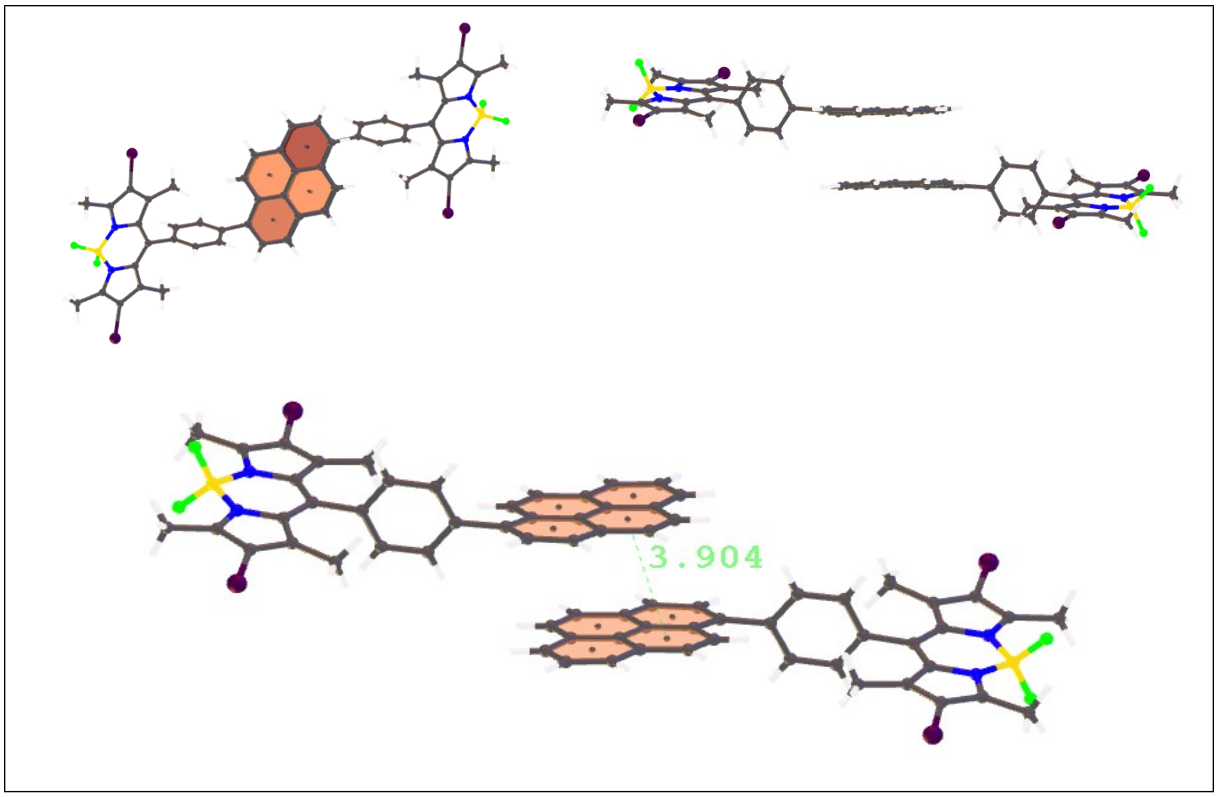


Fig. S36. π-π interaction of the solid-state crystal form of iodinated pyrene-BODIPY compound **6**.

References

1. J. Tao, D. Sun, L. Sun, Z. Li, B. Fu, J. Liu, L. Zhang, S. Wang, Y. Fang and H. Xu, *Dyes and Pigments*, 2019, **168**, 166-174.
2. C. O. Obondi, G. N. Lim, P. A. Karr, V. N. Nesterov and F. D'Souza, *Physical Chemistry Chemical Physics*, 2016, **18**, 18187-18200.
3. D. Öztürk, İ. Ömeroğlu, B. Köksoy, C. Göl and M. Durmuş, *Dyes and Pigments*, 2022, **205**, 110510.