Supporting Information

Butterfly Architecture of NIR Aza-BODIPY Small Molecules Decorated with Phenothiazine or Phenoxazine

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1. Materials and methods

All the precursor materials were purchased directly from commercial sources and used as such without any further purification and solvents were dried under vacuum by following standard procedure. UV-vis spectrophotometer used to record absorption spectra in dichloromethane (DCM) solution. NMR (¹H and ¹³C) spectra were measured with Advance ACP-400 or AMX2-500 spectrometers at 400 and 500 MHZ respectively, using tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were measured on a Shimadzu LCMS-2010 EV model with ESI probe. Cyclic voltammetry was performed on a CH Instruments with a three electrode system consisting of Ag/AgCl reference electrode, a working electrode and a platinum wire counter-electrode. The redox potentials of the dyes were measured in DCM containing 0.1 M Bu₄NHClO₄ at a scan rate of 100 mV s⁻¹.

2. Synthetic route:

Reagents: a) KOH/Ethanol and H₂O. b) CH₃NO₂, (CH₃-CH₂)₂ NH/Ethanol c) NH₄OAc, DIPEA, BF₃-OEt₂, DCM

The intermediates 1a and 1b was synthesized following previous reports.¹ The intermediates 2a and 2b were synthesized in good yield by the well-known Knoevenagel condensation by the chemical reaction of 1a, 1b, and B intermediates in the presence water and ethanol as solvent and KOH as base. The intermediates 3a and 3b were prepared by Michel addition reaction using nitromethane and diethylamine as base in very good yield. Finally the desired molecules AZA-PTZ-BOD and AZA-POZ-BOD were prepared with ammonium acetate (NH₄OAc), N,N-diisopropylethylamine (DIPEA) and boron trifluoride complex (BF₃-OEt₂) in dichloromethane solution.
Scheme S1: Preparation of AZA-PTZ-BOD and AZA-POZ-BOD molecule

Fig. S1: Molar extinction coefficient spectra of AZA-PTZ-BOD and AZA-POZ-BOD

Fig. S2: Cyclic voltammogram of dyes in DCM
6. Device fabrication and characterization:

The organic solar cells were fabricated with a conventional device structure of ITO/PEDOT:PSS/SMs:PC$_{71}$BM/PFN/Al. The ITO glass substrates were cleaned in ultrasonic bath with detergent, de-ionized water, acetone, and isopropyl alcohol, sequentially and dried in vacuum oven at the temperature of 50 °C for overnight. A thin layer (about 40 nm) of PEDOT:PSS was then spin coated on the onto the ITO glass at 3500 rpm and annealed at 110 °C for 20 min. The mixers of AZA-POZ-BOD or AZA-PTZ-BOD/PC$_{71}$BM in different weight ratios were dissolved in chloroform solution and stirred for overnight and spin coated on top of the PEDOT:PSS layer for form the active BHJ layer of about 85-90 nm and dried in atmospheric environment. For solvent vapor annealing (SVA) treatment, optimized thin films were placed in the petri-disc in the THF environment for 40 s and then dried at room temperature. PFN solution (methanol with some traces of acetic acid) was then spin coated as electron transport layer. Finally, aluminum (Al) electrode was thermally evaporated under 1x10$^{-5}$ Pa and device area was 26 mm$^2$ was defined by a shadow mask. The current -voltage characteristics were measured with a Keithley 2400 source meter unit under stimulated 100 mW/cm$^2$ irradiation for a solar simulator. The incident photon to current conversion efficiency spectra was recorded using a IPCE measurement unit (Benthem make).

7. Hole and Electron Mobility of Device:
The hole/electron mobilities for as cast active layer are about $7.56 \times 10^{-5}/2.34 \times 10^{-4}$ cm$^2$/Vs and $8.97 \times 10^{-5}/2.38 \times 10^{-4}$ cm$^2$/Vs for AZA-PTZ-BOD:PC$_{71}$BM and AZA-POZ-BOD:PC$_{71}$BM with electron to hole mobility ratio of 3.09 and 2.65, respectively, indicating that there is an unbalanced charge transport in the as cast active layer leading to low value of FF in these OPVs. However, both the hole and electron mobility were increased after the SVA treatment and hole/electron mobility’s are about $9.86 \times 10^{-5}/2.45 \times 10^{-4}$ cm$^2$/Vs and $1.24 \times 10^{-4}/2.52 \times 10^{-4}$ cm$^2$/Vs with electron to hole mobility ratio of 1.97 and 2.48 for AZA-PTZ-BOD:PC$_{71}$BM and AZA-POZ-BOD:PC$_{71}$BM blended films, respectively reduced electron to hole mobility ratio is consistent with the high value of FF for SVA treated OPV Moreover, the high value of FF for AZA-PTZ-BOD:PC$_{71}$BM based OPV as compared to AZA-POZ-BOD:PC$_{71}$BM counterpart may also be attributed to the lowest value of electron to hole mobility ratio, indicating that in AZA-PTZ-BOD:PC$_{71}$BM film the charge transport is more balanced as compared to other devices, resulting the high values of both $J_{sc}$ and FF.\(^9\)

![Fig. S4: Dark J-V characteristics of (a) hole only and (b) electron only devices for the optimized active layers (SVA).](image)

8. X-ray diffraction (XRD) Study:
Both the active layer showed two diffraction peaks located at $2\theta = 5.04^\circ$ (same of both active layers) and $2\theta = 23.34^\circ$ and $23.84^\circ$ for AZA-POZ-BOD:PC$_{71}$BM and AZA-PTZ-BOD:PC$_{71}$BM, respectively. The peak at $2\theta = 5.04^\circ$ corresponds to lamellar (100) signal with d-spacing of about 1.78 nm. The peak at $2\theta = 23.34^\circ$ and $23.84^\circ$ corresponds to $\pi-\pi$ stacking (010) with distance of 0.394 nm and 0.373 nm for AZA-POZ-BOD: PC$_{71}$BM and AZA-PTZ-BOD:PC$_{71}$BM active layer respectively. In addition to these peaks, there is a wide peak around $2\theta - 18.23^\circ$ corresponds to the PC$_{71}$BM. It can be seen from XRD pattern that the intensity of the lamellar signal for the active layer based on AZA-PTZ-BOD is higher than that for AZA-POZ-BOD is an indication of higher crystallinity for former than later. The higher crystallinity and reduced $\pi-\pi$ sacking distance is beneficial for the better charge transport and reduced recombination and resulting high values of FF and $J_{sc}$.

![X-ray diffraction patterns](image)

**Fig. S5:** X-ray diffraction patterns of the optimized active layers

9. **Computational Details of the AZA-BODIPY Dyes.**
Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) calculations were performed using Gaussian 09 software program package. TDDFT calculations were performed at B3LYP /6-311g (d,p) level of theory in DCM solvent by means of the Polarizable Continuum Model (PCM), as implemented in Gaussian 09. Singlet-singlet excitations at S\textsubscript{0} optimized geometry are calculated. The software GaussSum were used to simulate the major portion of the absorption spectrum and to interpret the nature of transitions. The molecular orbital surfaces are visualized with Gaussview, and the molecular orbital were calculated using GaussSum.
Table S1: Molecular orbital of **AZA-POZ-BOD** calculated at B3LYP/6-311g (d,p) level of theory in DCM solvent.
<table>
<thead>
<tr>
<th>Excited State</th>
<th>Wavelength (nm)</th>
<th>Osc. Strength</th>
<th>Major contribs</th>
<th>Minor contribs</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>695.7196</td>
<td>0.7853</td>
<td>HOMO-&gt;LUMO (93%)</td>
<td>H-2-&gt;LUMO (4%)</td>
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<tr>
<td>S2</td>
<td>571.5664</td>
<td>0.6308</td>
<td>H-1-&gt;LUMO (94%)</td>
<td>H-10-&gt;LUMO (2%)</td>
</tr>
<tr>
<td>S3</td>
<td>522.9194</td>
<td>0.242</td>
<td>H-2-&gt;LUMO (90%)</td>
<td>HOMO-&gt;LUMO (3%)</td>
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<tr>
<td>S4</td>
<td>394.8541</td>
<td>0.2013</td>
<td>H-3-&gt;LUMO (97%)</td>
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</tr>
<tr>
<td>S5</td>
<td>373.4801</td>
<td>0.0171</td>
<td>H-6-&gt;LUMO (27%), H-4-&gt;LUMO (36%)</td>
<td>H-13-&gt;LUMO (5%), H-7-&gt;LUMO (9%), H-2-&gt;LUMO (4%)</td>
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<tr>
<td>S6</td>
<td>362.4209</td>
<td>0.0259</td>
<td>H-6-&gt;LUMO (23%), H-4-&gt;LUMO (54%)</td>
<td>H-9-&gt;LUMO (9%), H-7-&gt;LUMO (4%)</td>
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<tr>
<td>S7</td>
<td>357.7155</td>
<td>0.0263</td>
<td>H-10-&gt;LUMO (18%), H-5-&gt;LUMO (62%)</td>
<td>H-14-&gt;LUMO (5%), H-11-&gt;LUMO (3%), H-8-&gt;LUMO (6%), H-1-&gt;LUMO (2%)</td>
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<tr>
<td>S8</td>
<td>330.2898</td>
<td>0.0119</td>
<td>H-17-&gt;LUMO (38%), H-6-&gt;LUMO (15%)</td>
<td>H-18-&gt;LUMO (8%), H-16-&gt;LUMO (3%)</td>
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<tr>
<td>S9</td>
<td>320.9614</td>
<td>0.0306</td>
<td>H-10-&gt;LUMO (25%), H-8-&gt;LUMO (20%), H-5-&gt;LUMO (20%)</td>
<td>H-14-&gt;LUMO (4%), H-11-&gt;LUMO (9%), HOMO-&gt;L+3 (5%)</td>
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<tr>
<td>S10</td>
<td>316.133</td>
<td>0.0041</td>
<td>H-17-&gt;LUMO (16%), H-7-&gt;LUMO (41%), H-6-&gt;LUMO (13%)</td>
<td>H-18-&gt;LUMO (4%), H-12-&gt;LUMO (3%), H-8-&gt;LUMO (5%)</td>
</tr>
</tbody>
</table>

**Table S2.** Major allowed transitions of **AZA-POZ-BOD** calculated at B3LYP/6-311g (d,p) level of theory in DCM solvent.
Fig. S6: Normalized plots of experimental and simulated absorption spectra of AZA-POZ-BOD

Fig. S7: Normalized plots of experimental and simulated absorption spectra of AZA-PTZ-BOD
<table>
<thead>
<tr>
<th>AZA-PTZ-BOD</th>
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<td><strong>HOMO</strong></td>
<td><strong>LUMO</strong></td>
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<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
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<tr>
<td><strong>HOMO-1</strong></td>
<td><strong>LUMO+1</strong></td>
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<td><img src="image4.png" alt="Image" /></td>
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<tr>
<td><strong>HOMO-2</strong></td>
<td><strong>LUMO+2</strong></td>
</tr>
<tr>
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<td><img src="image6.png" alt="Image" /></td>
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<tr>
<td><strong>HOMO-3</strong></td>
<td><strong>LUMO+3</strong></td>
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<tr>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Table** S3: Molecular orbital of **AZA-PTZ-BOD** calculated at B3LYP/6-311g (d,p) level of theory in DCM solvent.
<table>
<thead>
<tr>
<th>Excited state</th>
<th>Wavelength (nm)</th>
<th>Osc. Strength</th>
<th>Major contribs</th>
<th>Minor contribs</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>642.2388</td>
<td>0.9525</td>
<td>HOMO-&gt;LUMO (92%), H-2-&gt;LUMO (5%)</td>
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<tr>
<td>S2</td>
<td>514.1799</td>
<td>0.5889</td>
<td>H-1-&gt;LUMO (91%), H-8-&gt;LUMO (3%)</td>
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<tr>
<td>S3</td>
<td>505.3154</td>
<td>0.0796</td>
<td>H-2-&gt;LUMO (84%), H-7-&gt;LUMO (5%), H-4-&gt;LUMO (3%),</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>399.9232</td>
<td>0.1904</td>
<td>H-3-&gt;LUMO (96%)</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>381.2669</td>
<td>0.0259</td>
<td>H-7-&gt;LUMO (12%), H-4-&gt;LUMO (63%)</td>
<td>H-13-&gt;LUMO (3%), H-8-&gt;LUMO (3%), H-2-&gt;LUMO (7%)</td>
</tr>
<tr>
<td>S6</td>
<td>368.5947</td>
<td>0.0415</td>
<td>H-8-&gt;LUMO (13%), H-5-&gt;LUMO (68%)</td>
<td>H-14-&gt;LUMO (3%), H-11-&gt;LUMO (3%), H-9-&gt;LUMO (2%), H-1-&gt;LUMO (4%)</td>
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<tr>
<td>S7</td>
<td>365.951</td>
<td>0.0235</td>
<td>H-7-&gt;LUMO (17%), H-6-&gt;LUMO (47%), H-4-&gt;LUMO (19%)</td>
<td>H-13-&gt;LUMO (2%), H-10-&gt;LUMO (3%), H-8-&gt;LUMO (4%)</td>
</tr>
<tr>
<td>S8</td>
<td>333.7664</td>
<td>0.0049</td>
<td>H-20-&gt;LUMO (19%), H-7-&gt;LUMO (17%), H-6-&gt;LUMO (29%)</td>
<td>H-21-&gt;LUMO (8%), H-13-&gt;LUMO (5%), H-12-&gt;LUMO (6%), H-9-&gt;LUMO (2%)</td>
</tr>
<tr>
<td>S9</td>
<td>327.4115</td>
<td>0.0017</td>
<td>H-8-&gt;LUMO (51%), H-5-&gt;LUMO (18%)</td>
<td>H-14-&gt;LUMO (7%), H-11-&gt;LUMO (5%), H-9-&gt;LUMO (2%), H-6-&gt;LUMO (3%)</td>
</tr>
<tr>
<td>S10</td>
<td>321.5691</td>
<td>0.0083</td>
<td>H-21-&gt;LUMO (10%), H-20-&gt;LUMO (32%), H-7-&gt;LUMO (24%)</td>
<td>H-16-&gt;LUMO (2%), H-10-&gt;LUMO (4%), H-6-&gt;LUMO (8%), H-4-&gt;LUMO (5%)</td>
</tr>
</tbody>
</table>

**Table S4.** Major allowed transitions of **AZA-PTZ-BOD** calculated at B3LYP/6-311g (d,p) level of theory in DCM solvent.
10. Experimental Section

Synthesis:

10-(2-ethylhexyl)-10H-phenothiazine-3-carbaldehyde (1a), 10-(2-ethylhexyl)-10H phenoxazine-3-carbaldehyde (1b), 1-(napthalen-1-yl) ethanone (B) was synthesized according to literature procedure.

(E)-3-(10-(2-ethylhexyl)-10H-phenothiazin-2-yl)-1-(napthalen-2-yl)prop-2-en-1-one (2a):

To a stirred solution of compound 1a (4g, 9.4 mmol), KOH (2.28g, 56 mmol) in water 20 ml and ethanol 70 ml, compound B (2.44g, 14.34 mmol) in ethanol (25 mL) was added dropwise. The reaction mixture was stirred for 6 h at room temperature. The solid was filtrated and carefully washed to neutral with cold water. The crude product was purified by column chromatography (eluent: EtOAc/hexane 1:4) to furnish 2a (3.923g, 85%) as a yellowish liquid.

1H NMR (300 MHz, CDCl3): δ (ppm) = 8.30 - 8.27 (m, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.92 - 7.89 (m, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.56 - 7.52 (m, 3H), 7.40 (d, J = 15.9 Hz, 1H), 7.06 (d, J = 15.8 Hz, 1H), 6.95 (dd, J = 8.4, 1.8 Hz, 1H), 6.87 (s, 1H), 6.82 - 6.76 (m, 1H), 6.71 - 6.61 (m, 2H), 6.55 (d, J = 7.9 Hz, 1H), 6.48 (d, J = 8.4 Hz, 1H), 3.44 (d, J = 7.2 Hz, 2H), 1.90 - 1.83 (m, 1H), 1.38 - 1.25 (m, 8H), 0.95 - 0.86 (m, 6H). 13C NMR (101 MHz, CDCl3): δ (ppm) 195.7, 145.3, 145.2, 144.7, 137.7, 136.9, 133.8, 132.6, 131.1, 130.5, 128.4, 127.2, 126.7, 126.4, 125.7, 124.5, 124.1, 123.6, 121.8, 115.7, 113.6, 112.5, 111.7, 47.7, 36.7, 30.74, 29.7, 28.8, 24.1, 23.1, 14.0, 11.0. HRMS [M + H]+ (m/z):calcd.forC33H33NOS, [M + H]+ m/z 491.68, found 492.23.

3-(10-(2-ethylhexyl)-10H-phenothiazin-2-yl)-1-(napthalen-1-yl)-4-nitrobutan-1-one (3a):

A mixture of a compound 2a (3.80 g, 7.73 mmol), nitromethane (2.35g, 38.61 mmol) and diethylamine (2.817g 38.6 mmol) dissolved in ethanol (100 mL) was heated to reflux for 6-12 h. After cooling at room temperature, the solvent was removed in vacuum and the oily
residue obtained was dissolved in ethyl acetate and washed with water. The combined organic layers were washed with brine solution, dried over sodium sulphate, and concentrated. Further purification by column chromatography on silica eluting with CH$_2$Cl$_2$/hexane (1:1) and evaporation of the solvent gave the target compound as colourless oily residue (2.90 g, 68%).$^1$H NMR (300 MHz, CDCl$_3$): $\delta$(ppm) 8.44 (d, $J = 7.6$ Hz, 1H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.83 (dd, $J = 15.3$, 6.8 Hz, 2H), 7.58 - 7.45 (m, 3H), 6.76 (t, $J = 8.4$ Hz, 1H), 6.67 - 6.56 (m, 3H), 6.50 (d, $J = 9.7$ Hz, 2H), 6.39 (d, $J = 8.3$ Hz, 1H), 4.79 - 4.73 (m, 1H), 4.67 - 4.60 (m, 1H), 4.10 - 4.06 (m, 1H), 3.44 (d, $J = 7.1$ Hz, 2H), 3.34 (d, $J = 7.3$ Hz, 2H), 1.82 - 1.80 (m, 1H), 1.40 - 1.25 (m, 8H), 0.88 (m, $J = 8$ Hz).$^{13}$C NMR (101 MHz, CDCl$_3$):$\delta$(ppm) 201.0 , 145.3 , 144.7 , 135.3 , 133.9 (d, $J = 10.9$ Hz), 133.1 , 131.0 , 130.0 , 128.4 , 128.1 , 127.6 , 126.6 , 125.6 , 124.3 , 123.6 , 122.7 , 120.9 , 115.4 , 114.2 , 112.0 , 79.6, 47.8, 44.7, 39.0, 36.6, 30.7, 28.8, 24.1, 23.1, 14.0, 11.0. HRMS (ESI) m/z calcd. for C$_{34}$H$_{36}$N$_2$O$_3$SNa: m/z [M+Na]$^+$ 552.72, found 553.25.

1,9-bis(10-(2-ethylhexyl)-10$^H$-phenothiazin-2-yl)-5,5-difluoro-3,7-di(naphthalen-1-yl)-5$^H$-dipyrrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-4-ium-5-uide (AZA-PTZ-BOD):

A 500 mL round-bottomed flask was charged with compound 3a (2.80 g, 5.07 mmol) and ammonium acetate (20.20 g, 200 mmol), and t-butanol 80 ml the mixture was heated at 130 °C for 12 h. The reaction mixture in the round-bottomed flask was allowed to cool to room temperature. Then CH$_2$Cl$_2$ (200 mL) and water (50mL) was added. The organic layer was separated, washed with water (3×50 mL) and dried over sodium sulphate. The solvent was evaporated to give the product as a dark blue solid which was used in the next step without further purification. The crude product was dissolved in dry CH$_2$Cl$_2$ (80 mL), treated with diisopropyl ethyl amine (1.3 mL, 10.12 mmol) and boron tri-fluoride diethyletherate (1.5mL, 12.68 mmol), and stirred at room temperature under N$_2$ for 24 h. The mixture was washed
with water (50 mL), and organic layer was dried over sodium sulphate and evaporated to dryness. Purification by column chromatography on silica eluting with CH₂Cl₂/hexane (2:3) and evaporation of the solvent gave the product green amorphous solid (0.16 g, 30%).

**NMR (400 MHz, CDCl₃):** δ (ppm) = 8.04 (d, J = 2.0 Hz, 1H), 8.02 (d, J = 2.0 Hz, 1H), 7.98 (dd, J = 9.7, 2.7 Hz, 4H), 7.88 - 7.81 (m, 6H), 7.44 (t, J = 8.2 Hz, 6H), 7.21 - 7.15 (m, 4H), 7.09 (d, J = 8.6 Hz, 2H), 6.97-6.93 (m, 4H), 6.82 (s, 2H), 3.86 (d, J = 8.6 Hz, 4H), 2.06 - 2.00 (m, 2H), 1.43 - 1.25 (m, 16H), 0.91 (t, J = 7.4 Hz, 6H), 0.86 (t, J = 7.1 Hz, 6H).

**13C NMR (126 MHz, CDCl₃):** δ (ppm) = 157.9, 147.3, 145.1, 144.6, 142.0, 133.5, 131.5, 130.2, 129.6, 129.0, 28.0, 127.6, 127.3, 126.7, 126.0, 125.3, 124.9, 122.9, 118.9, 116.2, 51.3, 36.0, 30.7, 28.5, 23.9, 23.1, 14.0, 10.5.

**(E)-3-(10-(2-ethylhexyl)-10H-phenoxazin-2-yl)-1-(naphthalen-2-yl)prop-2-en-1-one (2b):**

Followed similar procedure as 2a: **1b** (4g, 12.3 mmol), **B** (3.15g, 18.54 mmol), gave POZ-NAP (4.200 g, 71%) as a yellowish liquid gel. **NMR (300 MHz, CDCl₃):** δ (ppm) = 8.28 (d, J = 9.5 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 9.4 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.53 (dd, J = 12.2, 4.7 Hz, 3H), 7.40 (d, J = 15.8 Hz, 1H), 7.06 (d, J = 15.8 Hz, 1H), 6.94 (d, J = 8.3 Hz, 1H), 6.87 (s, 1H), 6.79 (t, J = 8.3 Hz, 1H), 6.71-6.62 (m, 2H), 6.56-6.46 (m, J = 2H), 3.44 (d, J = 5.1 Hz, 2H), 1.89-1.83 (m, 1H), 1.50-1.28 (m, 8H), 0.94 – 0.87 (m, 6H).

**13C NMR (126 MHz, CDCl₃):** δ (ppm) = 145.35, 145.14, 144.76, 137.73, 136.90, 133.85, 132.65, 131.20, 130.55, 128.41, 127.28, 126.77, 126.45, 125.80, 124.59, 124.10, 123.67, 121.88, 115.69, 113.67, 112.51, 111.75, 47.73, 36.72, 30.74, 29.75, 28.80, 24.15, 23.12, 14.08, 11.02.

**HRMS (ESI) m/z calcd. for C₃₃H₃₃NO₂, [M + H]⁺ m/z 475.20, found 475.25**

**(E)-3-(10-(2-ethylhexyl)-10H-phenoxazin-2-yl)-1-(naphthalen-1-yl)-4-nitrobutan-1-one (3b):**

Followed similar procedure as 2a: **2b** (4.00 g, 8.14 mmol), nitromethane (2.44 g, 40.70 mmol), and diethylamine (3.02g 41.50 mmol) yielded colourless oily residue (yield (2.92 g, 65%). **NMR (300 MHz, CDCl₃):** δ (ppm) = 8.44 (d, J = 8.9 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.87 - 7.80 (m, 2H), 7.57 - 7.45 (m, 3H), 6.79 - 6.74 (m, 1H), 6.67 - 6.63 (m, 3H), 6.50 (t, J = 4.8 Hz, 2H), 6.39 (d, J = 8.3 Hz, 1H), 4.79 - 4.73 (m, 1H), 4.67 - 4.61 (m, 1H), 4.11 -
4.06 (m, 1H), 3.45 (d, J = 7.1 Hz, 2H), 3.34 (d, J = 7.3 Hz, 2H), 1.89 -1.75 (m, 1H), 1.41-
1.25 (m, 8H), 0.92-0.85(m, 6H).\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) = 201.0, 145.3, 
144.7, 135.3, 133.9, 133.1, 131.0, 130.0, 128.4, 128.1, 127.6, 126.6, 125.6, 124.3, 123.6, 
122.7, 120.9, 115.4, 114.2, 112.0, 79.6, 47.8, 44.7, 39.0, 36.6, 30.7, 28.8, 24.1, 23.1, 14.0, 
11.0. HRMS (ESI) m/z calcd. for C\textsubscript{34}H\textsubscript{36}N\textsubscript{2}O\textsubscript{4}Na\([M+Na]\)\(^+\) m/z 536.26, found 536.26.

\(1,9\)-bis(10-(2-ethylhexyl)-10\(H\)-phenoxazin-2-yl)-5,5-difluoro-3,7-di(naphthalen-1-yl)-5\(H\)-
dipyrrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-4-ium-5-uide (AZA-POZ-BOD):

Similar procedure followed as AZA-PTZ-BOD compound 3a (2.80 g, 5.22 mmol) and 
ammonium acetate (8.03g, 20 mmol), and t-butanol 80 ml the mixture was heated at 130 \(^\circ\)C 
for 12 h. The product blue amorphous solid (0.17 g, 32\%).\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 8.77 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 7.8 Hz, 3H), 7.72 (d, J = 8.3 Hz, 1H), 7.52-7.47 
(m, 3H), 7.40-7.37 (m, 1H), 7.05 (s, 1H), 6.77 (t, J = 7.5 Hz, 1H), 6.67 – 6.59 (m, 3H), 6.55 
(d, J = 7.9 Hz, 1H), 3.46 (d, J = 6.3 Hz, 2H), 1.95 -1.88 (m, 1H), 1.37-1.28 (m, 8H), 0.92 -
0.86 (m, 6H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 201.04, 145.34, 144.76, 135.33, 
133.92, 133.15, 131.02, 130.04, 128.46, 128.13, 127.64, 126.62 , 125.62, 124.32, 123.61, 
122.72, 120.91, 115.48 , 114.21, 112.09, 79.65 , 47.87, 44.70, 39.00, 36.68, 30.77, 28.82, 
24.17, 23.14, 14.08, 11.01.MALDI-TOF calcd.for C\textsubscript{69}H\textsubscript{68}BF\textsubscript{2}N\textsubscript{5}O\textsubscript{2} m/z [M+H]\(^+\) 1031.466, 
found 1031.78
11. Copies of $^1$H-NMR and $^{13}$C-NMR Spectra:

Fig. S8: $^1$HNMR Spectra of 2a recorded in CDCl$_3$
**Fig. S9:** $^{13}$CNMR Spectra of 2a recorded in CDCl$_3$

**Fig. S10:** $^1$HNMR Spectra of 2b recorded in CDCl$_3$

**Fig. S11:** $^{13}$CNMR Spectra of 2b recorded in CDCl$_3$
Fig.S12: $^1$HNMR Spectra of 3a recorded in CDCl$_3$
Fig. S13: $^{13}$CNMR Spectra of 3a recorded in CDCl$_3$

Fig. S14: $^1$HNMR Spectra of 3b recorded in CDCl$_3$
Fig. S15: $^{13}$CNMR Spectra of 3b recorded in CDCl$_3$

Fig. S16: $^1$HNMR Spectra of AZA-PTZ-BOD recorded in CDCl$_3$
Fig. S17: $^{13}$C NMR Spectra of **AZA-PTZ-BOD** recorded in CDCl$_3$.

Fig. S18: $^1$H NMR Spectra of **AZA-POZ-BOD** recorded in CDCl$_3$. 

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S23
Fig. S19: $^{13}$CNMR Spectra of AZA-POZ-BOD recorded in CDCl$_3$

12. Copies of HRMS and MALDI-TOF

Fig. S20: HRMS spectrum of 2a

Fig. S21: HRMS spectrum of 2b
Fig. S22: HRMS spectrum of 3a

Fig. S23: HRMS spectrum of 3b
Fig. S24: MALDI-TOF spectrum of **AZA-PTZ-BOD**

Fig. S25: MALDI-TOF spectrum of **AZA-POZ-BOD**
13. References: