Electronic Supplementary Information for

Meso-N-linker engineering of benzo[cd]indole cyanines for mid-band (850–950 nm) near-infrared absorption and film implementation

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Supporting Information includes:

S1. Supporting Figures

- Supporting Figures S1 ~ S7
- Supporting Table S1~S2

S2. Supporting experimental section

- Schemes S1 ~ S6
- Supporting Figures S8 ~ S20

S1. Supporting Figures

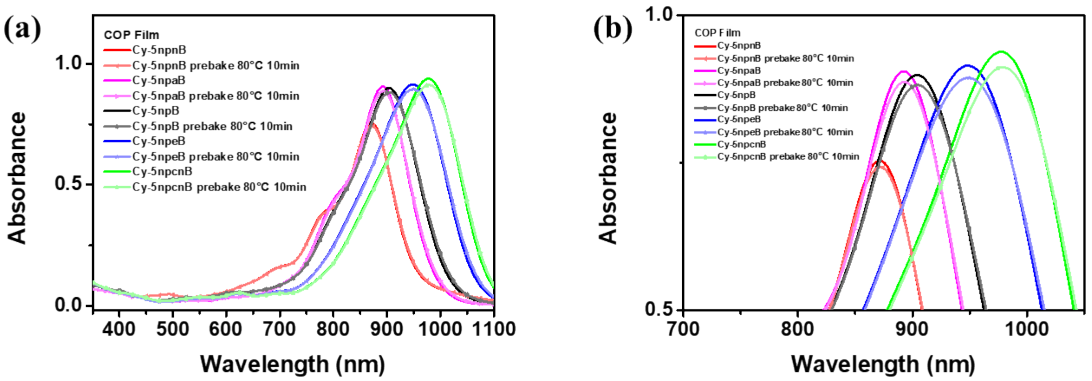


Fig. S1. Change in relative absorbance of NIR-absorbing films before prebaking (deep color) and after prebaking (light color). (a) shows the overall absorbance graph, and (b) is an enlarged view around the maximum absorption wavelength.

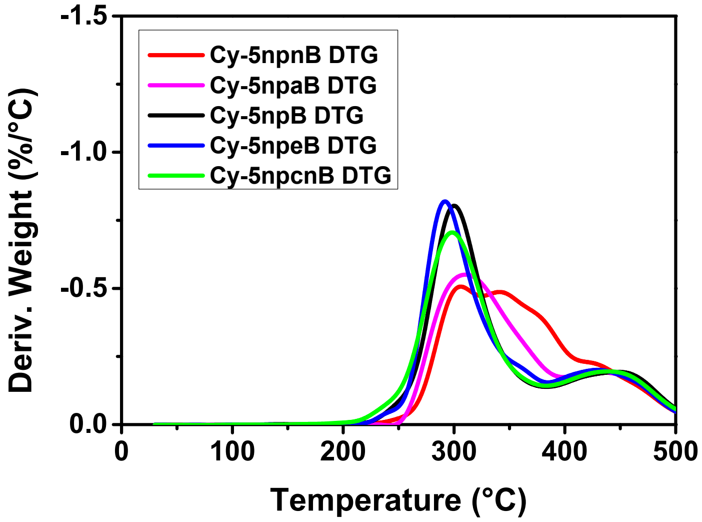


Fig. S2. First derivative TG curves in the full range.

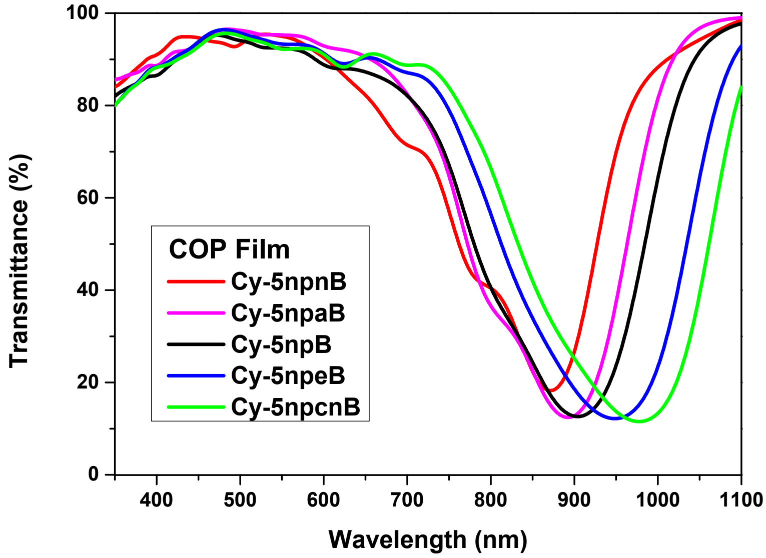


Fig. S3. UV-Vis-NIR transmittance spectra of fabricated NIR absorbing films (COP)

Table S1 Average visible transmittance of the prepared film (400-700nm)

NIR absorbing films	Average visible transmittance
Cy-5npnB	89.7%
Cy-5npaB	92.7%
Cy-5npB	90.3%
Cy-5npeB	92.1%
Cy-5npcnB	91.7%

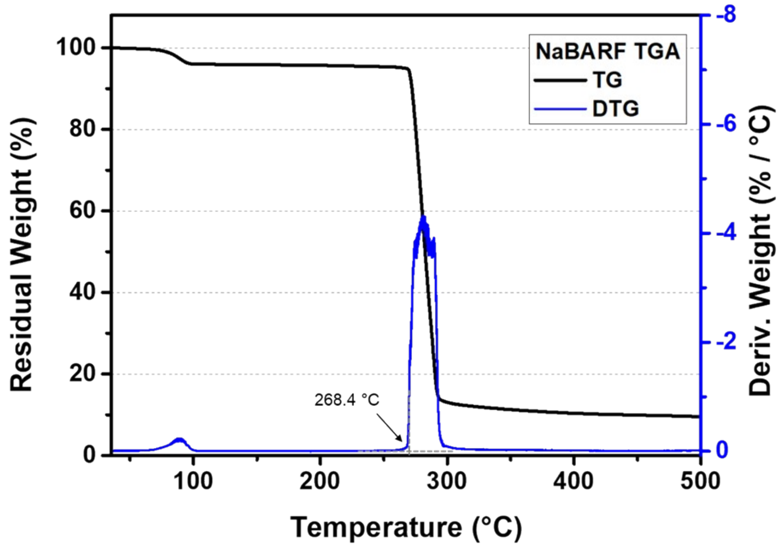


Fig. S4. TGA curve (black) and first derivative TG curve (blue) of NaBARF.

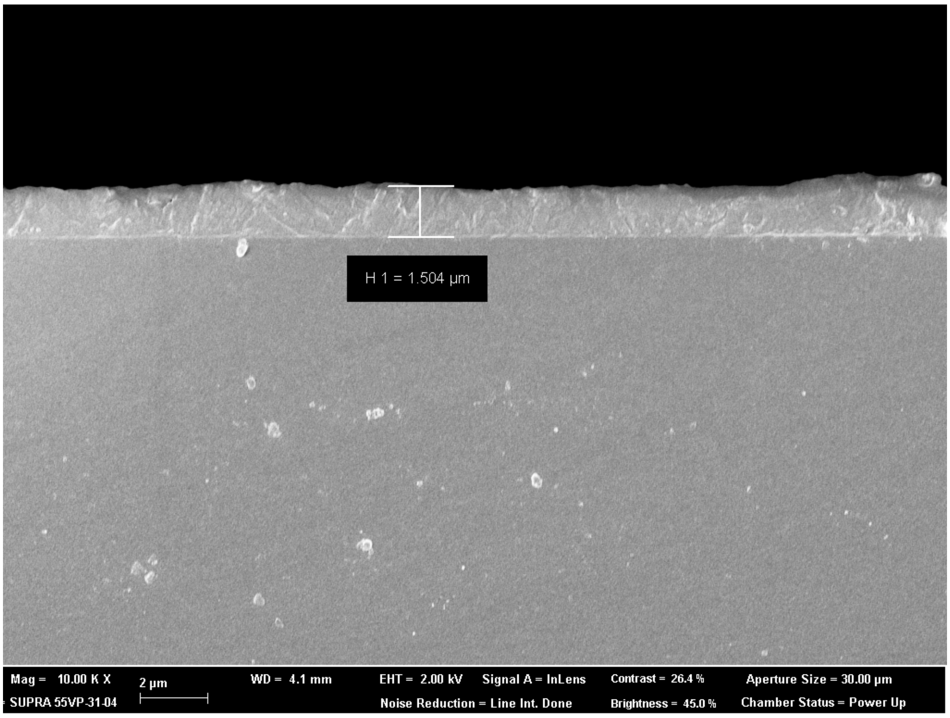


Fig. S5. Cross-sectional SEM image of COP film.

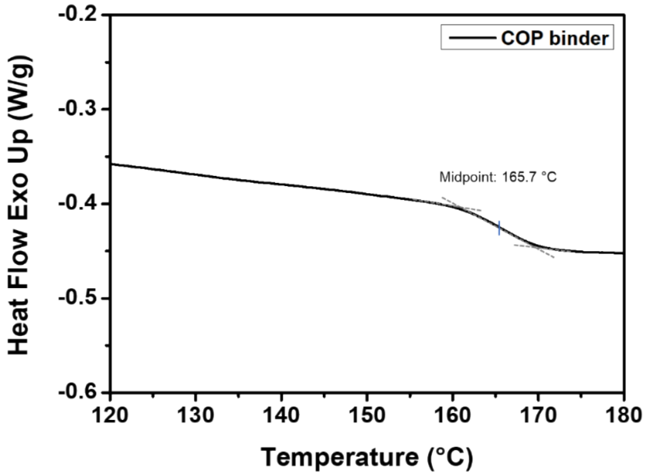


Fig. S6. Differential scanning calorimetry (DSC) curve of the selected cyclic olefin polymer (COP) binder.

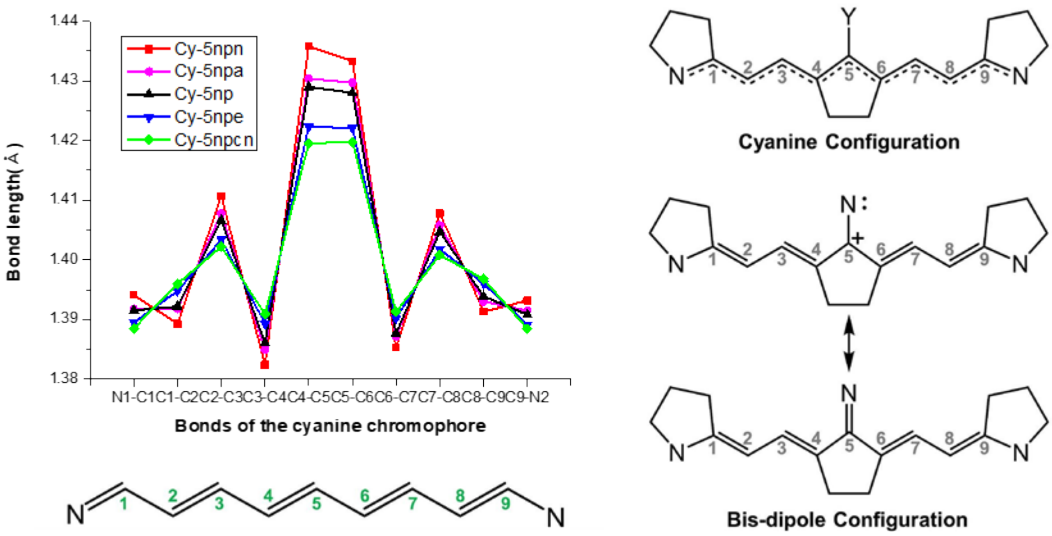


Fig. S7. Bond length of the cyanie chromophore and cyanine configuration, bis-dipole configuration.

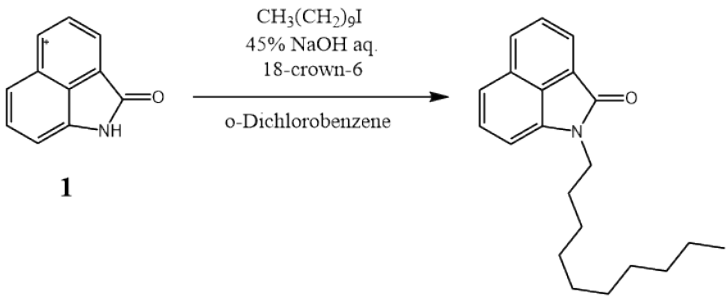
Table S2 Bond length alternation(BLA) and HOMO energy level of dyes

Dyes	BLA (pm)	HOMO (eV)
Cy-5npn	2.75	-5.270
Cy-5npa	2.27	-5.303
Cy-5np	2.10	-5.302
Cy-5npe	1.50	-5.326
Cy-5npcn	1.25	-5.346

S2. Supporting experimental section

S2.1. Synthesis of precursors of NIR cyanine dyes

S2.1.1 Synthesis of 1-decylbenzo[*cd*]indol-2(1*H*)-one (**2**)



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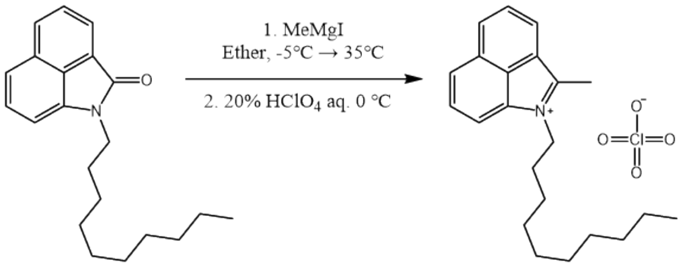
2

Scheme S1. Synthesis of 1-decylbenzo[*cd*]indol-2(1*H*)-one.

A solution of benzo[*cd*]indol-2(1*H*)-one (**1**) (5 g, 29.55 mmol) and 1-iododecane 12.61 mL (15.85 g, 59.11 mmol) in 150 mL of *o*-dichlorobenzene was added to a 500 mL three-neck flask. Subsequently, 18-crown-6 (0.146 g, 0.552 mmol) and 45% sodium hydroxide solution (120 mL) were introduced into the reaction flask and heated at 120 °C for 2 hours under vigorous stirring. Over time, the color of the solution gradually changed from yellow to orange-brown. After the reaction, the mixture was cooled to room temperature and extracted with hexane (100 mL × 3). The organic extracts were dried over anhydrous magnesium sulfate, and the solvent was removed using a rotary evaporator. The resulting crude product was purified through column chromatography on silica gel with ethyl acetate/hexane (1:7) as the eluent to afford 8.60 g of compound **2** as a bright yellow oil (Yield: 94%). LC/TOF-MS (ESI+) found: *m/z* 310.2968. Calcd for $C_{21}H_{28}NO$: [M+H], 310.2171.

S2.1.2. Synthesis of 1-decyl-2-methylbenzo[*cd*]indol-1-ium perchlorate (**3**)



2 **3**

Scheme S2. Synthesis of 1-decyl-2-methylbenzo[*cd*]indol-1-ium perchlorate.

1-Decylbenzo[*cd*]indol-2(1*H*)-one (**2**) (8 g, 25.85 mmol) was dissolved in anhydrous diethyl ether (70 mL) and cooled to −5 °C in an ice bath. Methyl magnesium iodide 16.67 mL (50 mmol, 3.0 M in diethyl ether) was placed in a 250 mL 1-neck flask, and the prepared solution of **2** was added dropwise using a syringe. After stirring for 15 min, the ice bath was removed, and the reaction flask was warmed to room temperature. Then, the reaction temperature was raised to 35 °C and stirred for 1 hour. The color gradually changed from dark yellow to dark green during this time. The flask was then returned to the ice bath and cooled to below 0 °C, followed by a slow addition of 20% perchloric acid solution (70 mL). After further stirring for 30 minutes, the resulting precipitate was filtered and washed with diethyl ether to obtain 5.695 g of compound **3** as a pale yellow solid (Yield: 54%). LC/TOF-MS (ESI+) found: *m/z* 308.3174. Calcd for $C_{22}H_{30}N$: [M–ClO_4], 308.2378.

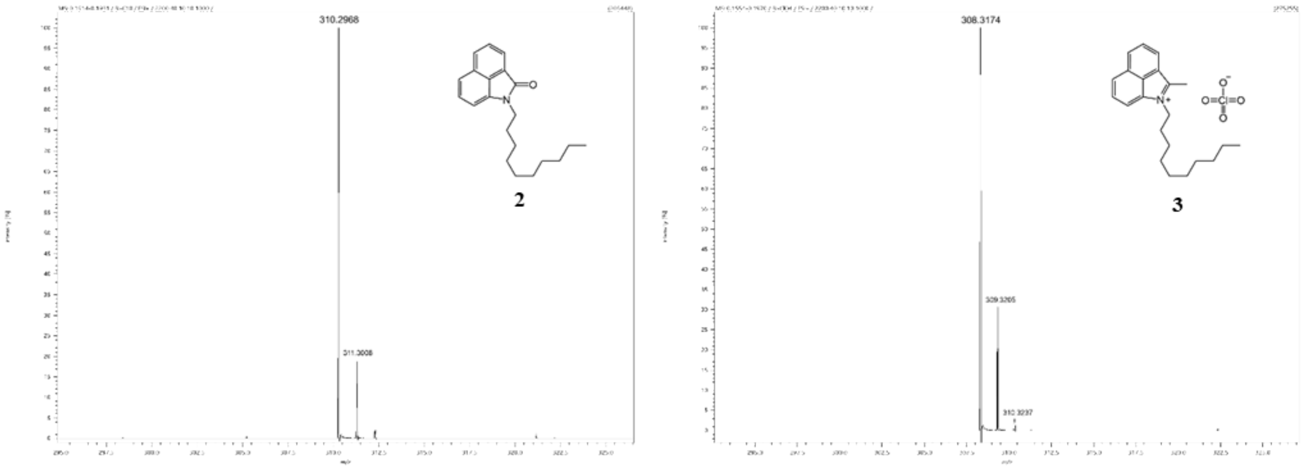
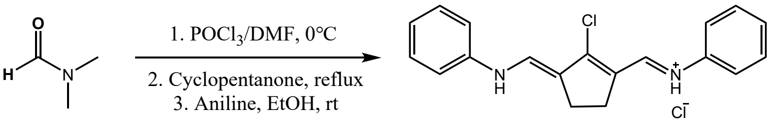


Fig. S8. LC/TOF-MS data of compounds **2** and **3**.

S2.1.3 Synthesis of N-[5-Anilino-3-chloro-2,4-(propane-1,3-diyil)-2,4-pentadiene-1-ylidene] anilinium Chloride (Anilinium salt 5)



4 **5**

Scheme S3. Synthesis of anilinium salt **5**

Phosphoryl chloride (10 mL, 107 mmol) was added dropwise to anhydrous dimethylformamide (11.8 mL, 152.6 mmol) at 0 °C in a 250 mL three-necked flask and stirred for 30 min. Then, cyclopetanone (4.66 mL, 52.6 mmol) was added dropwise, and the mixture was refluxed for 1h. After it was cooled to room temperature, a solution of aniline (8.2 ml) in ethanol (100 ml) was added dropwise, and the mixture was stirred further for 1h.

The resulting mixture was poured into 1 L of ice-cold 1 M HCl solution and stirred for 2h. The precipitate was filtered and washed with copious amounts of cold water, acetone, and diethyl ether. After drying under vacuum, 10.21 g of purple crystals were obtained (Yield: 54%). The crude product was used directly for the next step without further purification. LC/TOF-MS (ESI+) of **5** found: *m/z* 309.1929. Calcd for $C_{19}H_{18}ClN_2^+$: [M−Cl], 309.1153

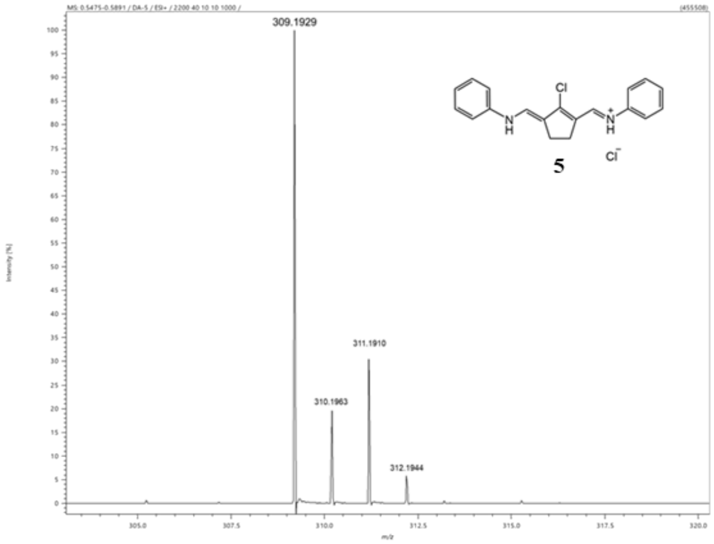
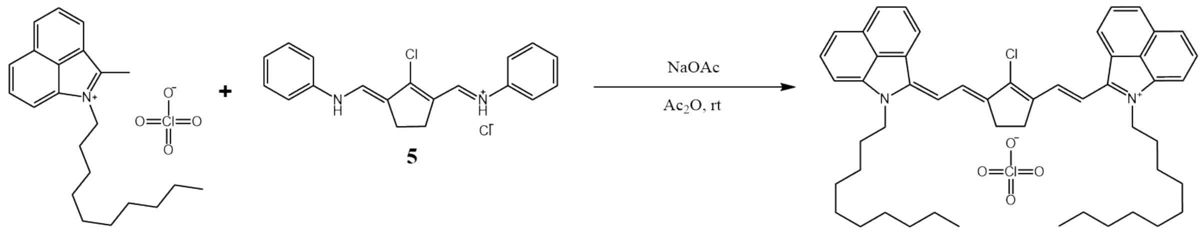


Fig. S9. LC/TOF-MS data of compound **5**.

S2.2. Synthesis of heptamethine cyanine dyes

S2.2.1 Synthesis of benzo[cd]indolenyl heptamethine cyanine dye (**Cy-5**)



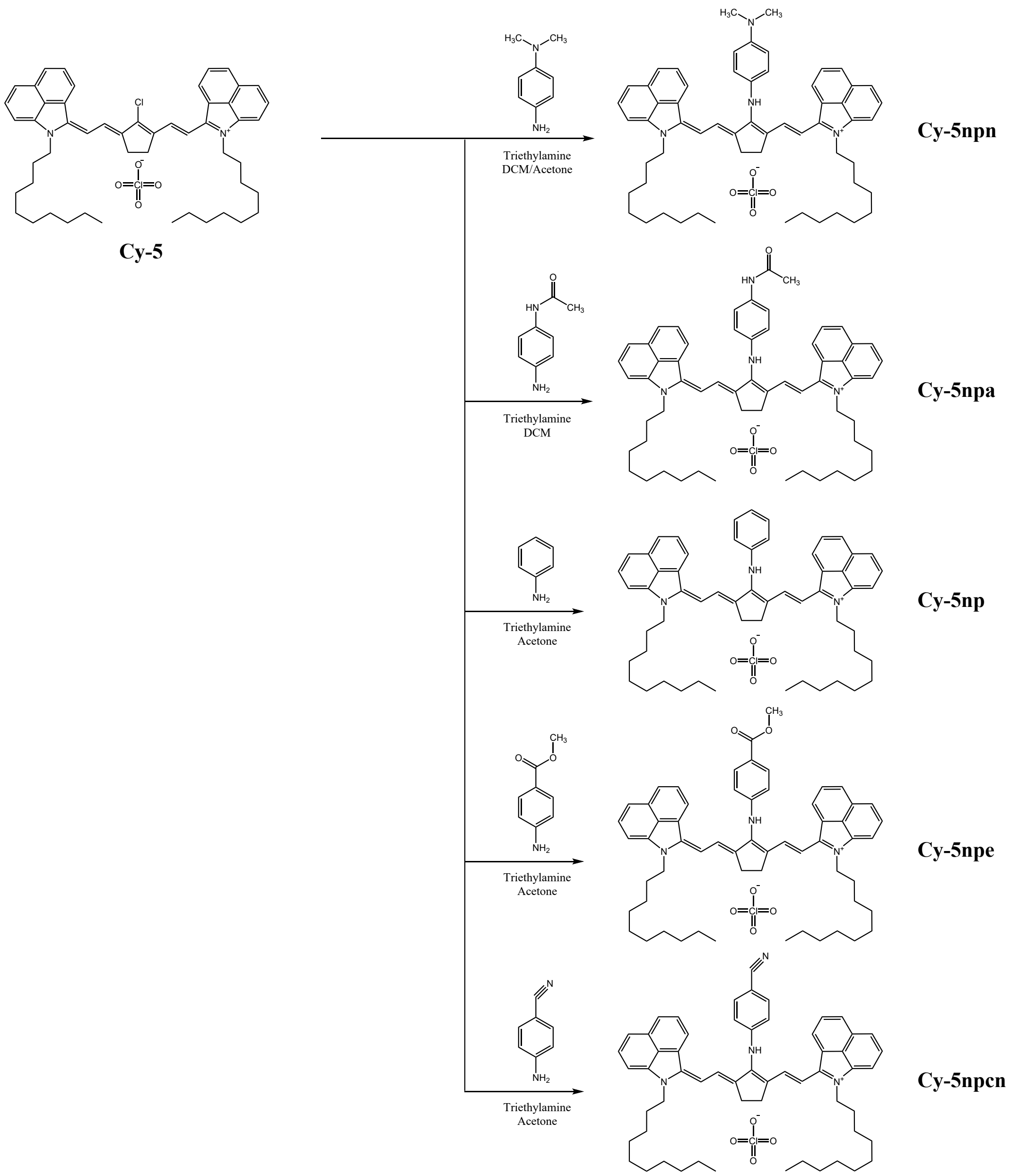
3

Cy-5

Scheme S4. benzo[cd]indolenyl heptamethine cyanine dye (**Cy-5**)

A solution of benzo[*cd*]indolenyl derivative **3** (1.5 g, 3.68 mmol) and anilinium salt **5**(0.635g, 1.84 mmol) in acetic anhydride (40 mL) was added to a 120 mL amber vial. Then, the reaction mixture was treated with anhydrous sodium acetate (0.643 g, 7.84 mmol) and stirred overnight at room temperature. The crude product was dissolved in dichloromethane and filtered to remove sodium acetate. The filtrate was then evaporated, and the resulting residue was re-dissolved in a minimum amount of dichloromethane (8 mL) and dropped into diethyl ether (500 mL) under sonication to obtain a dark brown precipitate. The precipitate was filtered, and the crude product was purified using column chromatography on silica gel with dichloromethane/methanol (50:1) as the eluent. For higher purity, the obtained products were dissolved in ethanol (70 mL) and recrystallized under sonication. 0.848g of reddish-brown powders was obtained. (Yield: 55%). GC/HRMS (FAB) found: *m/z* 737.4607. Calcd for $C_{51}H_{62}ClN_2^+$: M – ClO_4, 737.4596.

S2.2.2 Synthesis of benzo[cd]indolenyl heptamethine cyanine dyes (**Cy-5npn,Cy-5npa,Cy-5np, Cy-5npe, Cy-5npcn**)



Scheme S5. benzo[cd]indolenyl heptamethine cyanine dyes (**Cy-5npn, Cy-5npa, Cy-5np, Cy-5npe, Cy-5npcn**)

Benzo[*cd*]indolenyl-substituted heptamethine cyanine dyes (Cy-5npn, Cy-5npa, Cy-5np, Cy-5npe, Cy-5npcn) were synthesized following the general procedure described below. In a 100 ml three-neck flask, N,N-dimethyl-1,4-phenylenediamine, 4'-aminoacetanilide, aniline, methyl 4-aminobenzoate or 4-aminobenzonitrile (0.96 mmol) and Cy-5 (0.4g, 0.48mmol) were dissolved in 30ml of DCM/Acetone, DCM or Acetone, and the mixture was cooled to 0°C. Then, triethylamine (0.097 g, 0.96 mmol) was slowly added into the reaction flask and stirred for 24h at room temperature. The solvent was removed under reduced pressure, and the crude product was purified using column chromatography over silica gel with dichloromethane/acetone (2:1) as the eluent. The target products (Cy-5npn, Cy-5npa, Cy-5np, Cy-5npe, Cy-5npcn) were obtained as reddish-brown powders in moderate yields. (Yield : 64%, 68%, 60%, 66%, 59% for each) GC/HRMS (FAB) of **Cy-5npn** found: *m/z* 837.5844. Calcd for $C_{57}H_{67}N_2O^+$: M – ClO_4, 837.5835, GC/HRMS (FAB) of **Cy-5npa** found: *m/z* 851.5620. Calcd for $C_{57}H_{67}N_2O^+$: M – ClO_4, 851.5628 , GC/HRMS (FAB) of **Cy-5np** found: *m/z* 794.5418. Calcd for $C_{57}H_{67}N_2O^+$: M – ClO_4, 794.5413, GC/HRMS (FAB) of **Cy-5npe** found: *m/z* 852.5461. Calcd for $C_{57}H_{67}N_2O^+$: M – ClO_4, 852.5468 , GC/HRMS (FAB) of **Cy-5npcn** found: *m/z* 819.5368. Calcd for $C_{57}H_{67}N_2O^+$: M – ClO_4, 819.5366 ,

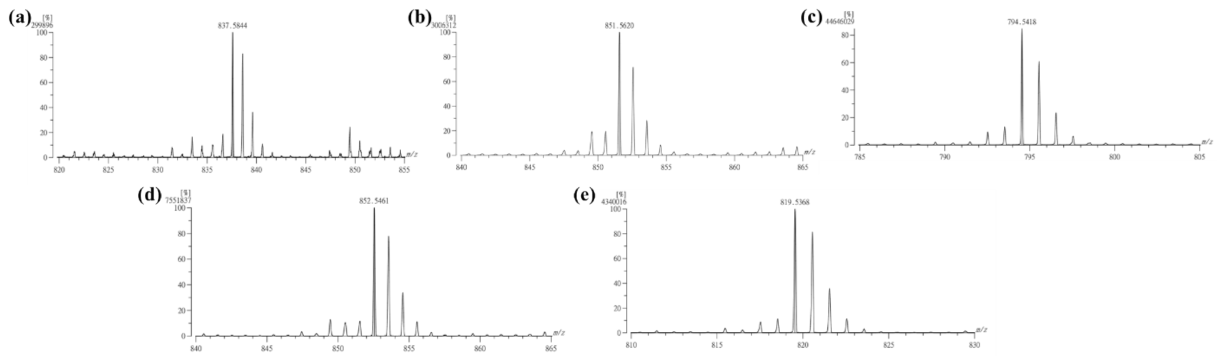
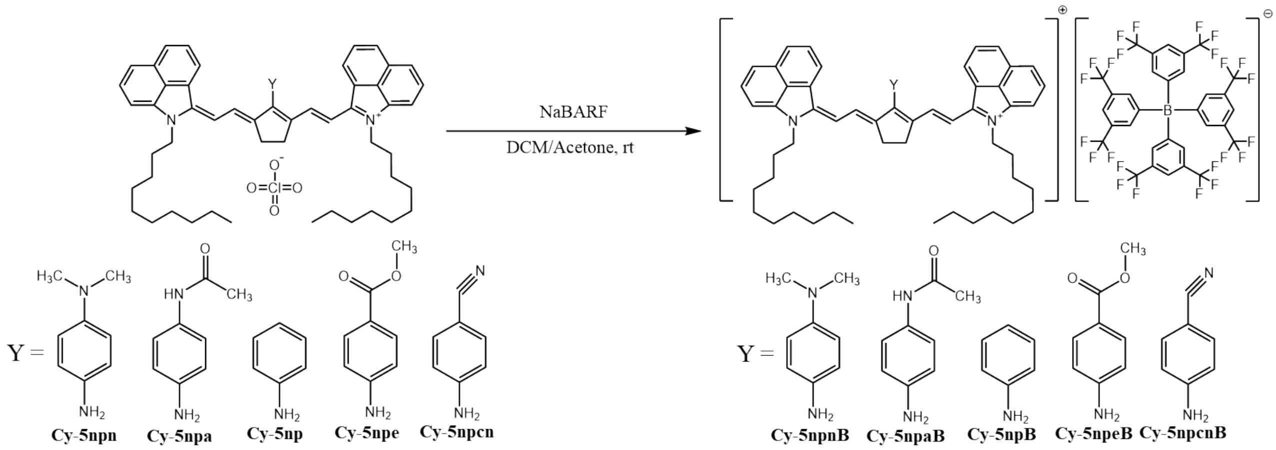


Fig. S10. HR-GC/MS data of synthesized cyanine dyes. (a) Cy-5npn, (b) Cy-5npa, (c) Cy-5np, (d) Cy-5npe, (e) Cy-5npcn.

S2.3. Synthesis of BARF-substituted heptamethine cyanine dyes



Scheme S6. Substitution of BARF anion.

BARF-substituted cyanine dyes (Cy-5npnB, Cy-5npaB, Cy-5npB, Cy-5npeB, Cy-5npcnB) were synthesized through a simple ion-exchange reaction with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF). In a 150 ml amber vial, 0.2 mmol of cyanine dyes (Cy-5npn, Cy-5npa, Cy-5np, Cy-5npe, Cy-5npcn) and NaBARF (0.24 mmol, 0.213 g) were dissolved in a 100 ml solution of acetone/dichloromethane (1:1) and stirred at room temperature for 3 hours. The mixture solution was then evaporated under reduced pressure, and the resulting solid was dissolved in dichloromethane extracted with water (3 x 15 mL). The organic extracts were dried over anhydrous magnesium sulfate, and the solvent was removed using a rotary evaporator. The residue was purified by column chromatography on silica gel using dichloromethane as the eluent. The isolated products were dissolved in 5 mL of dichloromethane and dropped into 200 mL of hexane under sonication, and the precipitated solid was collected by filtration. Cy-5npnB (0.301 g, 88% yield), Cy-5npaB (0.311 g, 90% yield) Cy-5npB (0.303 g, 91% yield) Cy-5npeB (0.323 g, 94% yield) and Cy-5npcnB (0.297 g, 88% yield) were obtained as dark violet powders.

S2.3.1. Characterization of 1-decyl-2-((E)-2-((E)-3-((E)-2-(1-decylbenzo[cd]indol-2(1H)-ylidene)ethylidene)-2-((4-(dimethylamino)phenyl)amino)cyclopent-1-en-1-yl)vinyl)benzo[cd]indol-1-ium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (**Cy-5npnB**)

^{1}H NMR of Cy-5npnB (850 MHz, $CDCl_3$): δ (ppm) 8.00–7.93 (br s, 2H), 7.82–7.74 (br s, 2H), 7.64–7.62 (br t, J = 2.2 Hz, 10H), 7.42–7.40 (m, 6H), 7.39–7.35 (m, 4H), 6.87–6.84 (br s, 2H), 6.04–5.89 (br s, 2H), 4.00–3.83 (br s, 4H), 2.94–2.92 (br s, 4H), 2.89–2.84 (br s, 4H), 2.78–2.63 (s, 1H), 1.76–1.71 (t, J = 6.9 Hz, 4H), 1.37–1.33 (m, 4H), 1.30–1.27 (m, 4H), 1.21–1.17 (m, 20H), 1.17–1.14 (m, 6H), 0.80–0.78 (t, J = 7.1 Hz, 6H).

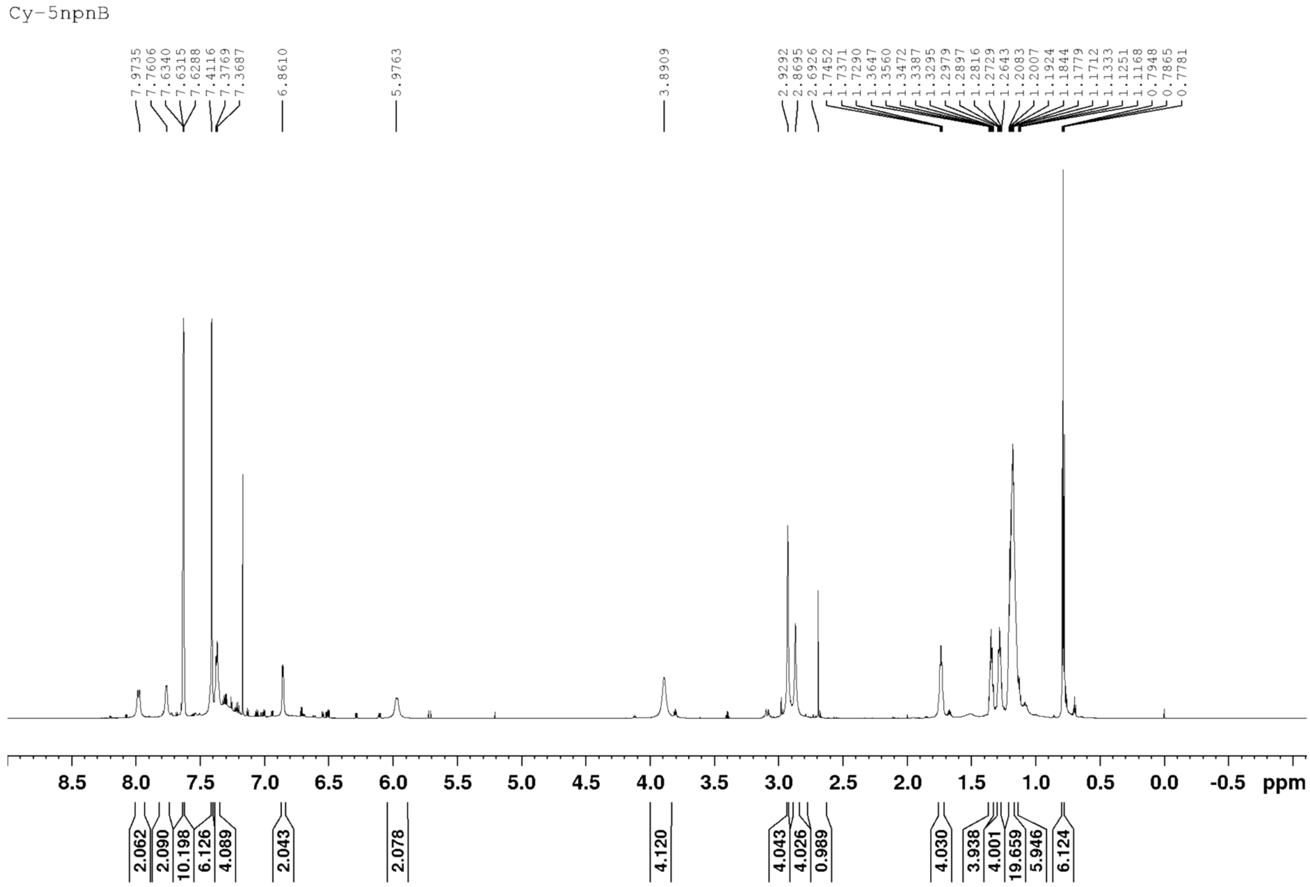


Fig. S11. ^{1}H NMR of Cy-5npnB.

S2.3.2. Characterization of 2-((E)-2-((E)-2-((4-acetamidophenyl)amino)-3-((E)-2-(1-decylbenzo[cd]indol-2(1H)-ylidene)ethylidene)cyclopent-1-en-1-yl)vinyl)-1-decylbenzo[cd]indol-1-ium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (**Cy-5npaB**)

^{1}H NMR of Cy-5npaB (850 MHz, $CDCl_3$): δ (ppm) 7.69–7.57 (m, 12H), 7.55–7.45 (br s, 4H), 7.43–7.36 (m, 6H), 7.35–7.18 (m, 4H), 7.18–7.13 (s, 2H), 2.21–1.9 (s, 4H), 1.76–1.73 (m, 4H), 1.64–1.45 (br s, 2H), 1.41–1.34 (br s, 4H), 1.34–1.26 (m, 6H), 1.26–1.21 (m, 3H), 1.21–1.17 (m, 20H), 1.17–1.06 (m, 6H), 0.80–0.78 (t, J = 7.1 Hz, 6H).

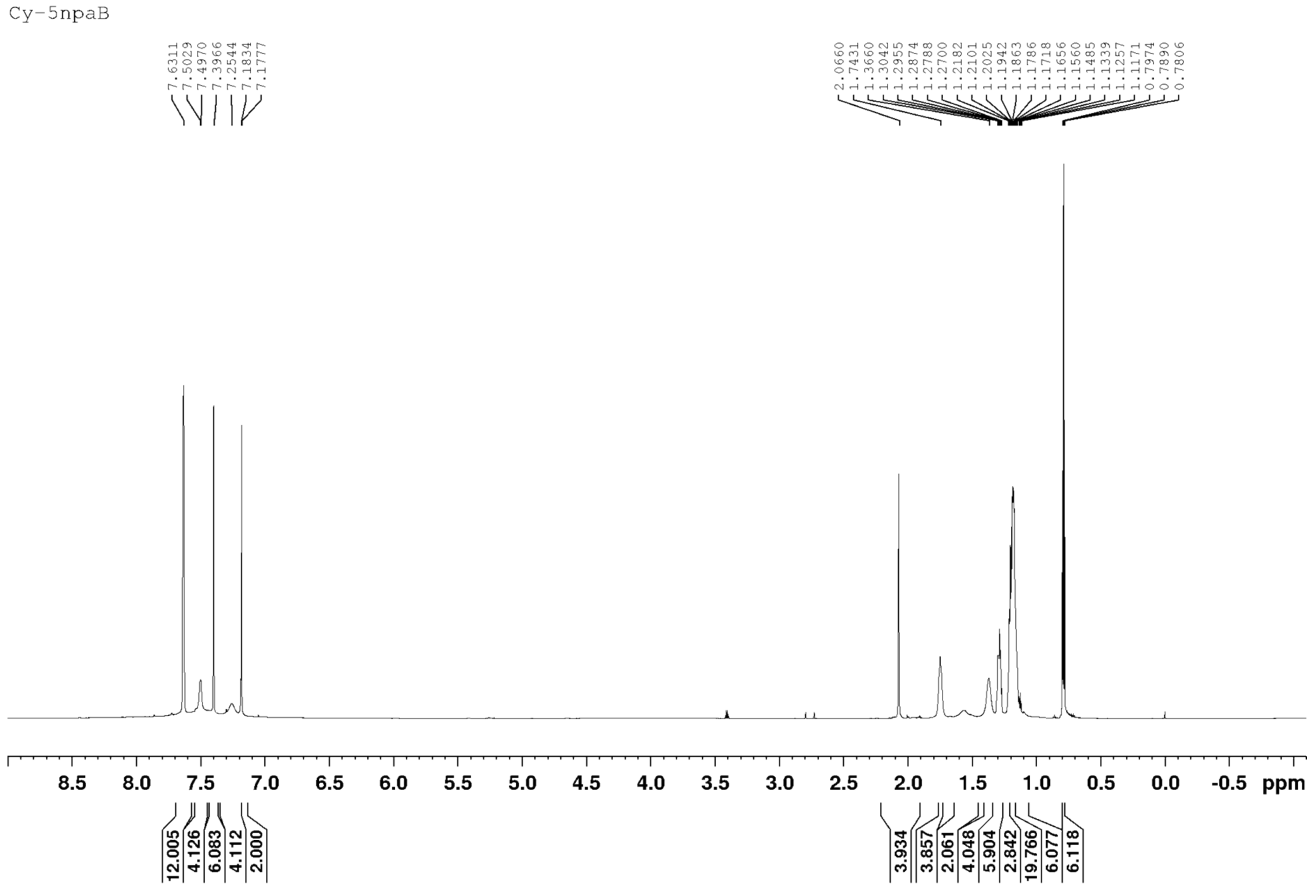


Fig. S12. ^{1}H NMR of Cy-5npaB.

S2.3.3. Characterization of 2-((*E*)-2-((*E*)-3-((*E*)-2-(1-(decan-2-yl)benzo[*cd*]indol-2(1*H*)-ylidene)ethylidene)-2-(phenyl amino)cyclopent-1-en-1-yl)vinyl)-1-decylbenzo[*cd*]indol-1-ium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (**Cy-5npB**)

^{1}H NMR of Cy-5npB (850 MHz, $CDCl_3$): δ (ppm) 8.01–7.92 (br s, 2H), 7.86–7.77 (br s, 2H), 7.63–7.61 (br t, J = 2.4 Hz, 8H), 7.46–7.40 (m, 8H), 7.40–7.38 (s, 4H), 7.35–7.31 (m, 3H), 7.21–7.18 (br s, overlapped, 2H), 6.98–7.85 (br s, 2H), 6.16–5.98 (br s, 2H), 4.06–3.85 (br s, 4H), 2.97–2.77 (br s, 4H), 1.79–1.73 (p, J = 7.4 Hz, 4H), 1.38–1.33 (p, J = 7.4 Hz, 4H), 1.31–1.27 (p, J=7.1 Hz, 4H), 1.22–1.16 (m, 20H), 0.80–0.78 (t, J = 7.1 Hz, 6H).

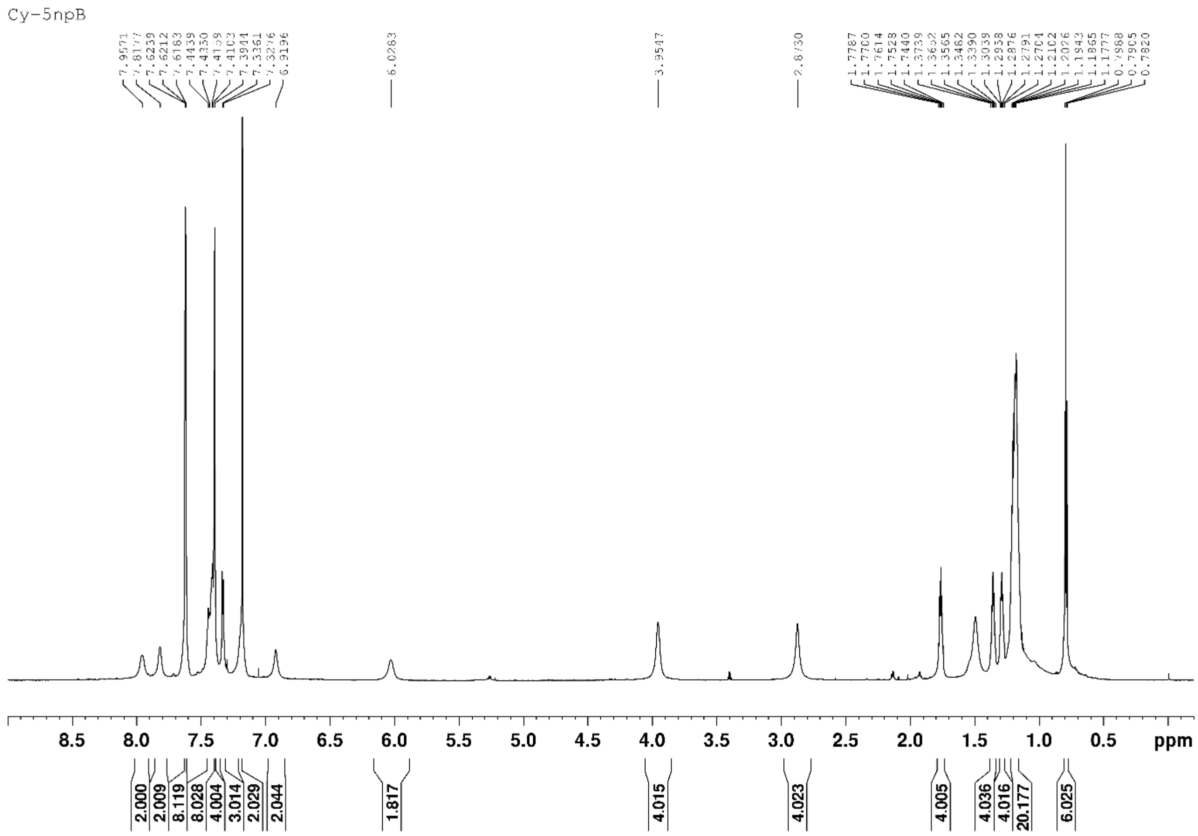


Fig. S13. ^{1}H NMR of Cy-5npB.

S2.3.4. . Characterization of 1-decyl-2-((E)-2-((E)-3-((E)-2-(1-decylbenzo[cd]indol-2(1H)-ylidene)ethylidene)-2-((4-(methoxycarbonyl)phenyl)amino)cyclopent-1-en-1-yl)vinyl)benzo[cd]indol-1-ium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (**Cy-5npeB**)

^{1}H NMR of Cy-5npeB (850 MHz, $CDCl_3$): δ (ppm) 8.04–8.00 (br s, 2H), 7.69–7.58 (m, 12H), 7.50–7.35 (m, 8H), 7.34–6.98 (m, 6H), 3.84–3.83 (s, 3H), 1.78–1.74 (br s, 4H), 1.62–1.49 (br s, 4H), 1.42–1.34 (m, 4H), 1.33–1.26 (m, 6H), 1.25–1.23 (br s, overlapped, 1H), 1.21–1.18 (m, 20H), 1.18–1.17 (m, 6H), 0.80–0.78 (t, J = 7.1 Hz, 6H).

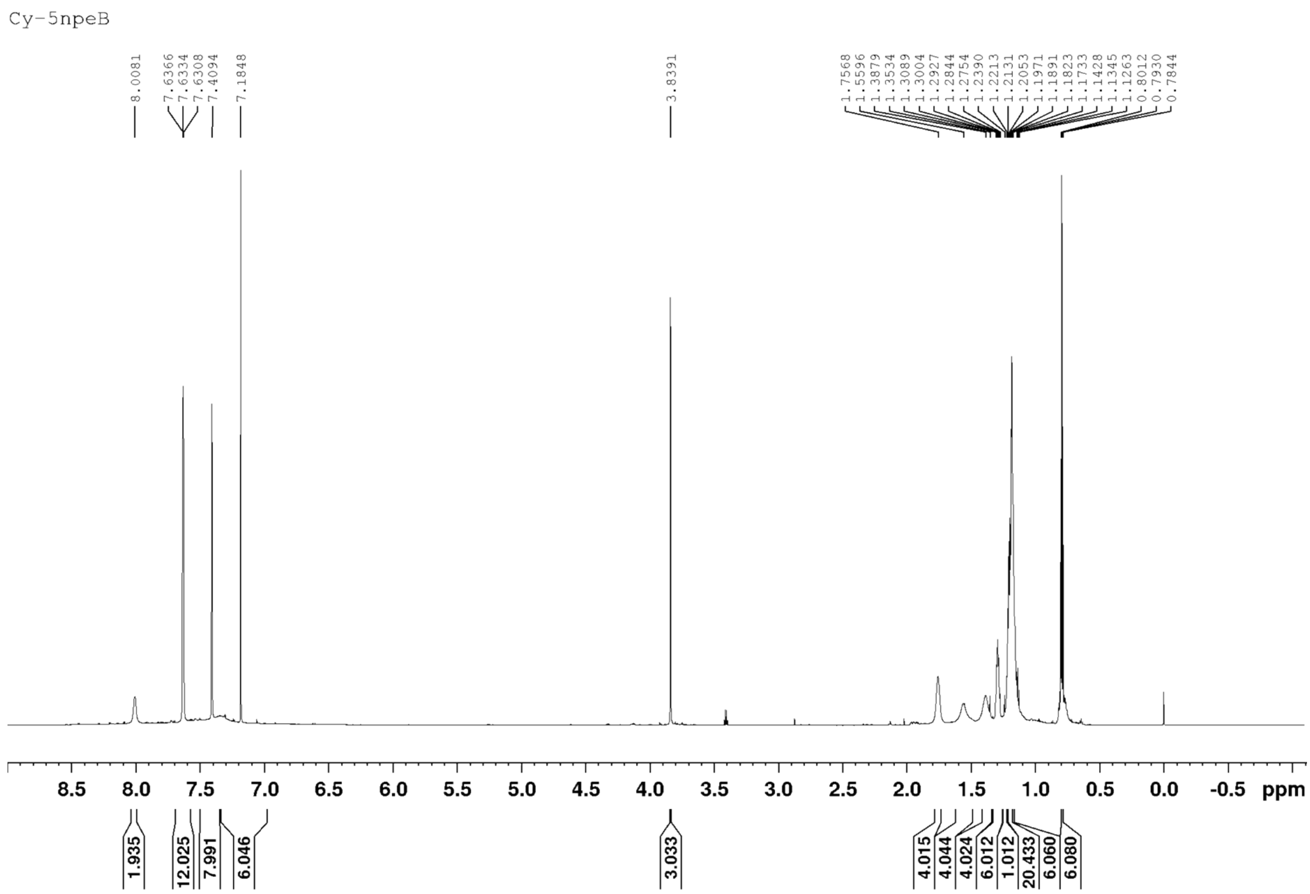


Fig. S14. ^{1}H NMR of Cy-5npeB.

S2.3.5. . Characterization of 2-((E)-2-((E)-2-((4-cyanophenyl)amino)-3-((E)-2-(1-decylbenzo[cd]indol-2(1H)-ylidene)ethylidene)cyclopent-1-en-1-yl)vinyl)-1-decylbenzo[cd]indol-1-ium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (**Cy-5npcnB**)

^{1}H NMR of Cy-5npcnB (850 MHz, $CDCl_3$): δ (ppm) 7.67–7.60 (m, 12H), 7.60–7.49 (br s, 4H), 7.45–7.40 (m, 6H), 7.40–7.08 (m, 6H), 1.79–1.75 (br s, 4H), 1.67–1.47 (br s, 3H), 1.40–1.35 (br s, 4H), 1.33–1.25 (m, 6H), 1.20–1.17 (m, 20H), 1.17–1.10 (m, 8H), 0.80–0.78 (t, J = 7.1 Hz, 6H).

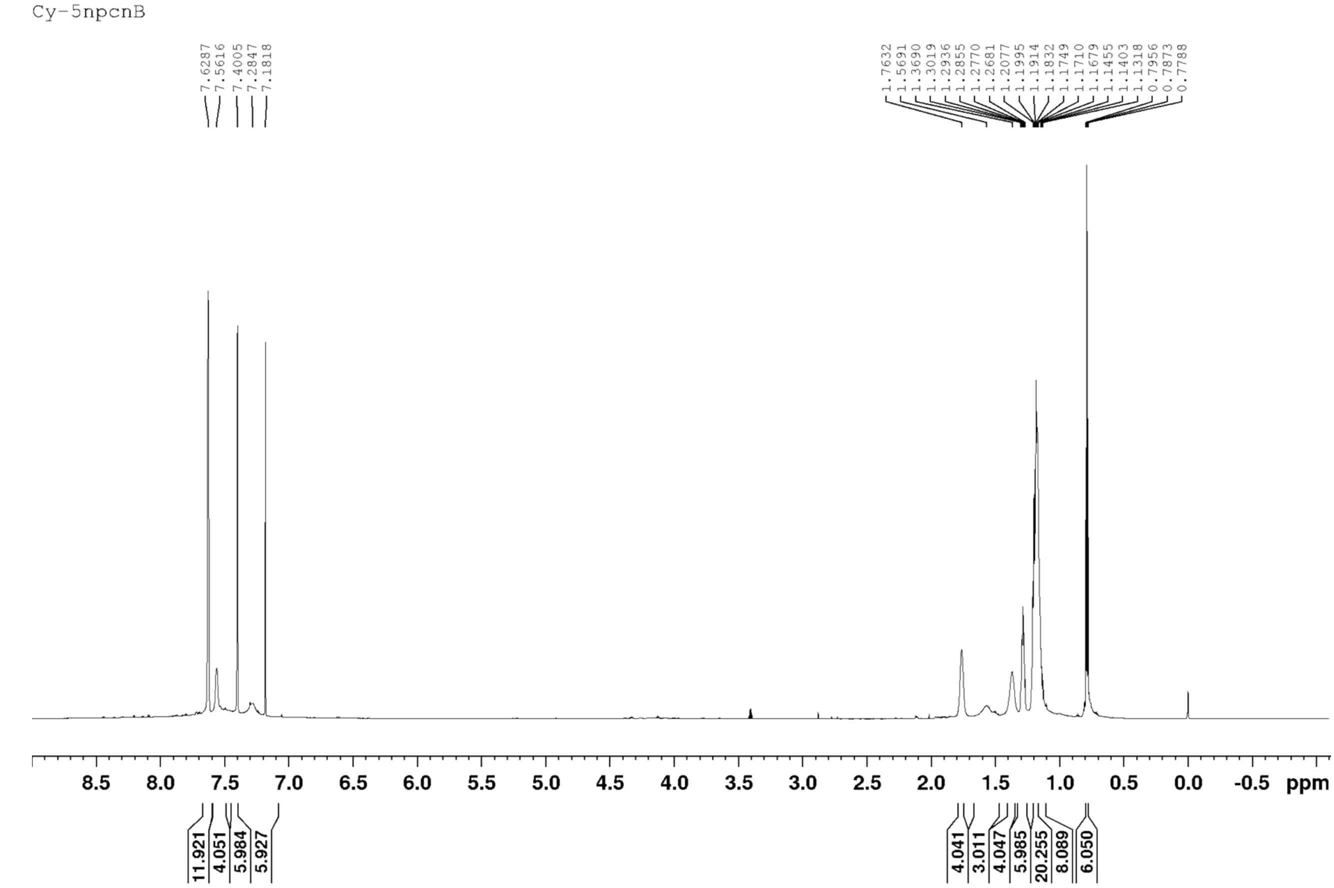


Fig. S15. ^{1}H NMR of Cy-5npcnB.

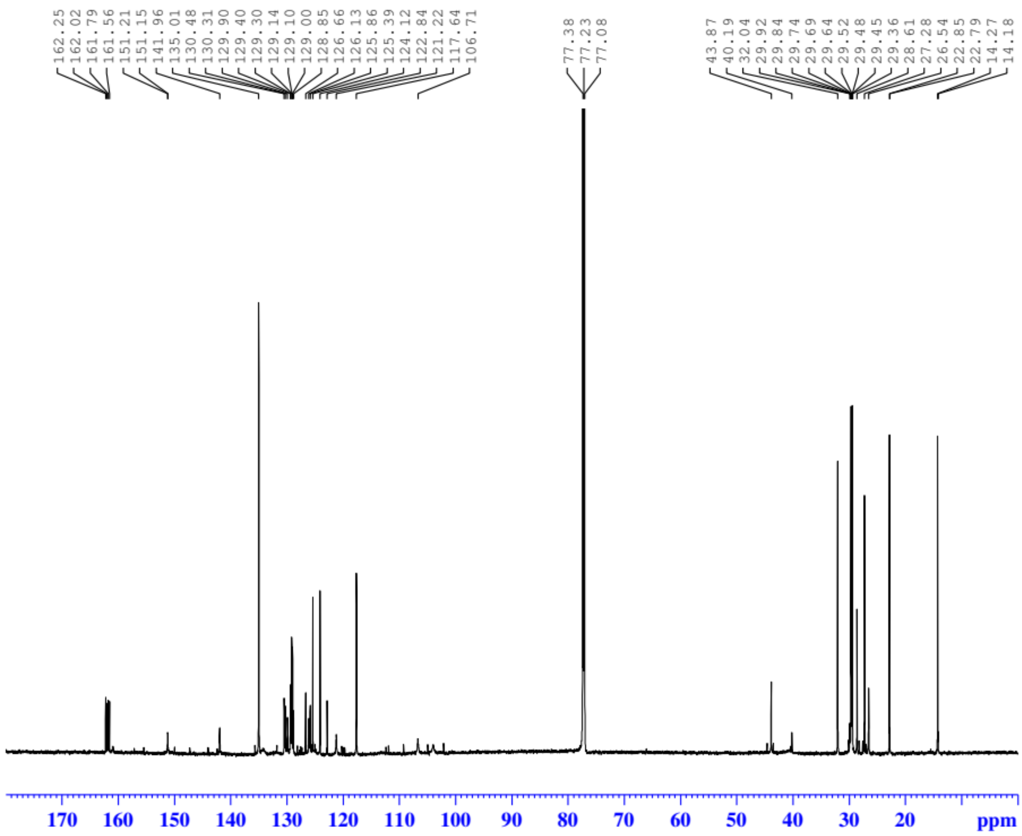


Fig. S16. ^{13}C NMR of Cy-5npnB.

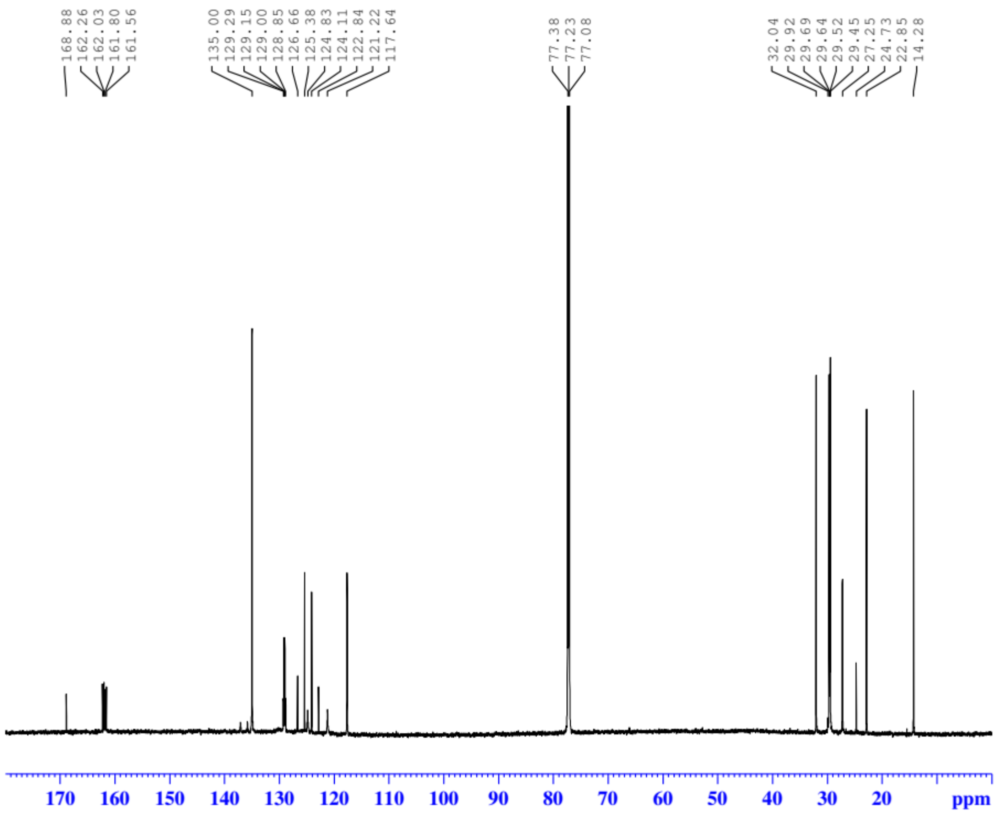


Fig. S17. ^{13}C NMR of Cy-5npaB.

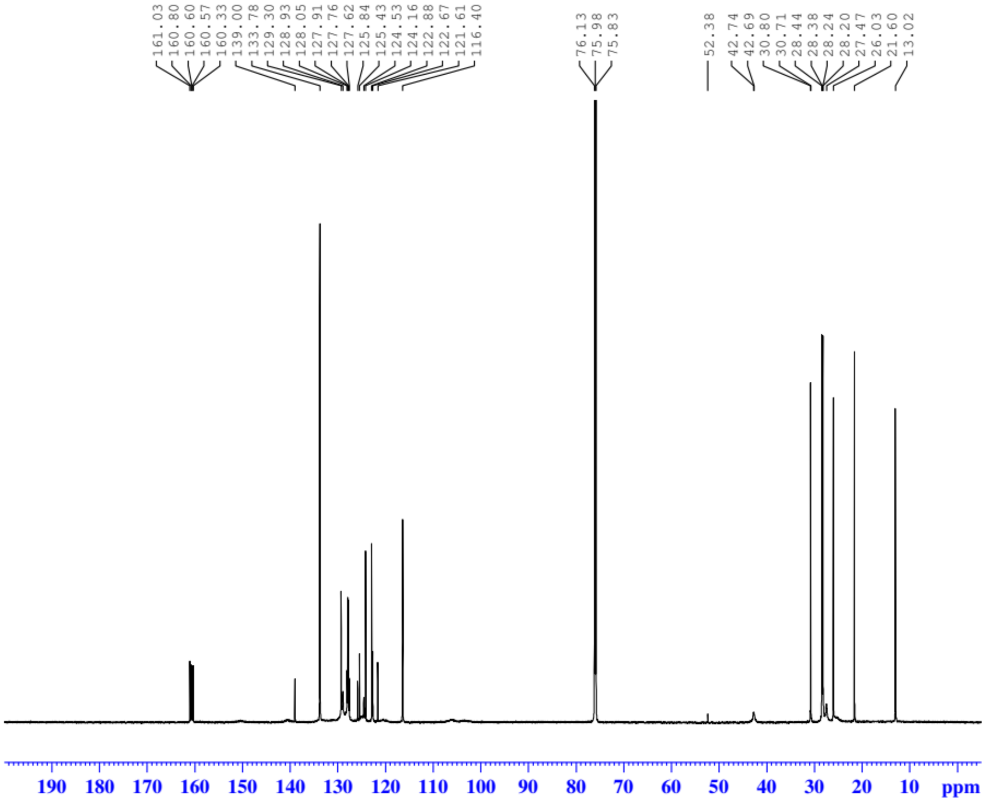


Fig. S18. ^{13}C NMR of Cy-5npB.

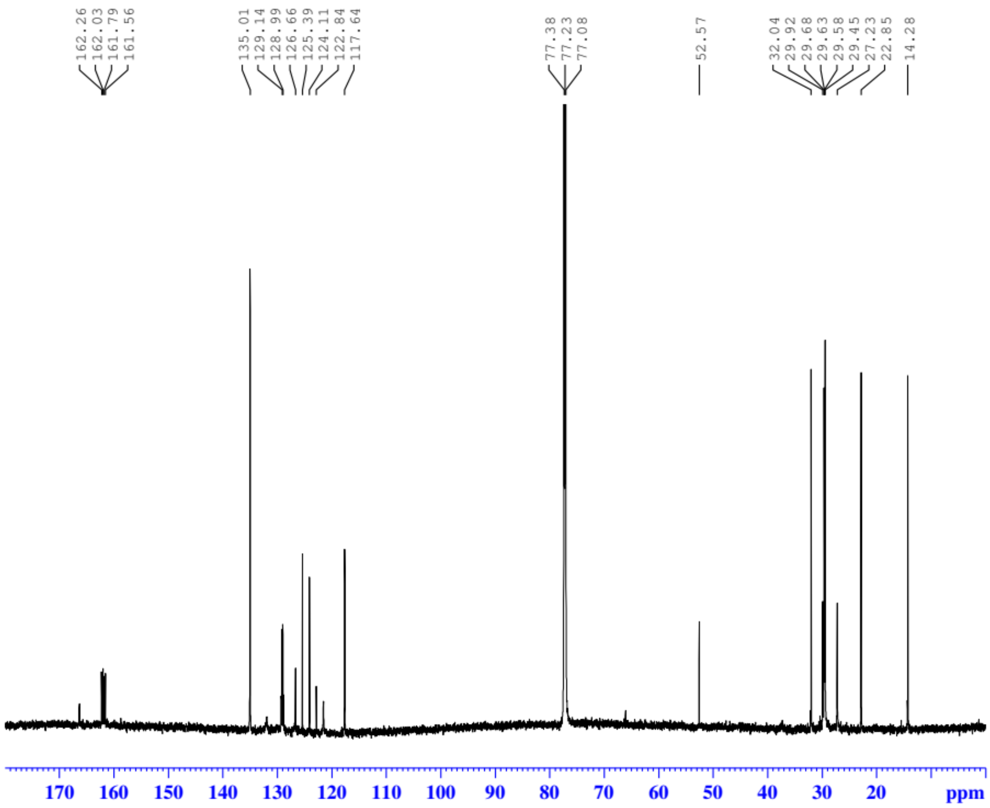


Fig. S19. ^{13}C NMR of Cy-5npeB.

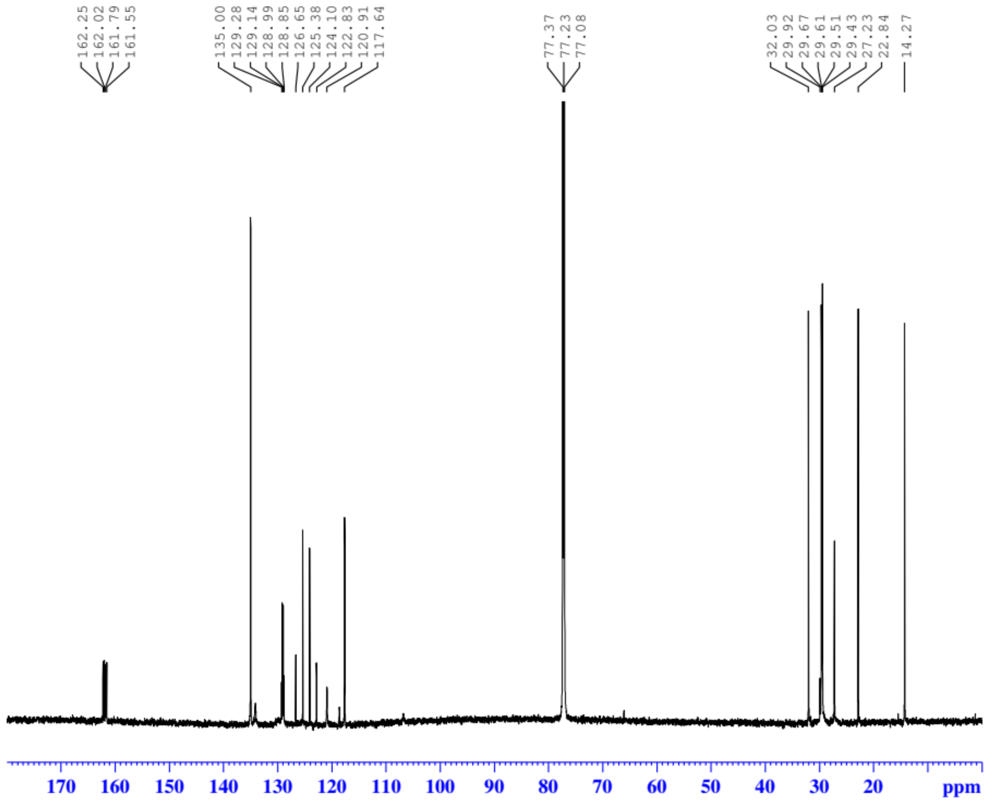


Fig. S20. ^{13}C NMR of Cy-5npcnB.