Supporting Information

Utilizing heterocyclic effect towards high contrast ratio of mechanoresponsive luminescence based on aromatic aldehydes

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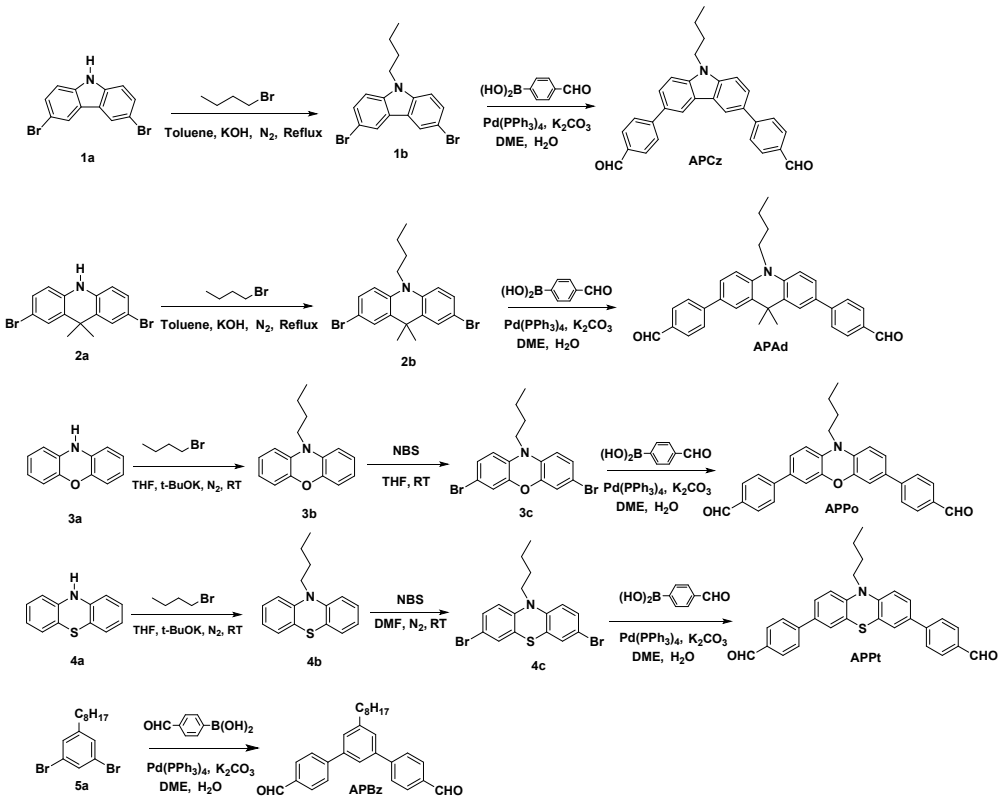
1. Experimental section

Materials and characterizations

All solvents and reagents, unless otherwise stated, were of high purity quality and used as received. Starting chemicals and reagents were purchased from commercial sources and used as received without further purification. Reactions were monitored by TLC silica plate (60F-254). NMR spectra measurements were carried out at Bruker 600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR, using chloroform-d as solvent. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm). Splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). Mass spectra measured on Microflex MALDI-TOF MS. UV-Vis spectra were recorded in a HITIACH U-3900 spectrometer. Photoluminescent (PL) spectra were recorded in a HORIBA FluoroMax-4 spectrometer. The absolute fluorescence quantum yields of solutions (10 μM) and solid powders were measured on HORIBA FluoroMax-4 by using a calibrated integrating sphere. The quartz cuvettes used were of 1 cm path length. Single-crystal X-ray diffraction data were collected on an Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer. The crystal was kept at 173.00(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Powder X-ray diffraction (XRD) of the samples was characterized using a Philips high resolution X-ray diffraction system (model PW1825). Differential scanning calorimetry (DSC) experiments were recorded on a NETZSCH DSC 204 instrument at a scanning rate of 5 K min^{-1}. The transient photoluminescence decay profiles of the solids were recorded using an Edinburgh Instrument FLS980 spectrometer equipped with an EPL-375 picosecond pulsed diode laser.

Synthesis



Scheme S1 Synthetic routes to **APCz**, **APAd**, **APPo**, **APPt** and **APBz**.

Synthesis of 1b (3,6-dibromo-9-butyl-9H-carbazole)

3.6-dibromocarbazole (3.25 g, 10 mmol), 1-bromobutane (2.06 g, 15 mmol) tetrabutylammonium bromide (160 mg, 0.5 mmol) and KOH (2.8 g, 50 mmol) were dissolved in a mixture of toluene (20 mL) and H_2O (6 mL), and subsequently refluxed for 5 h. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were washed with water and dried over anhydrous $MgSO_4$. The product was then obtained by column chromatography on silica gel with petroleum ether/ethyl acetate (10 : 1 by volume) eluent as a white solid (3.12 g, 82%).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 1.9 Hz, 2H), 7.55 (dd, J = 8.7, 1.9 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 4.25 (t, J = 7.2 Hz, 2H), 1.81 (dd, J = 15.0, 7.5 Hz, 2H), 1.35 (dd, J = 15.2, 7.5 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 139.25, 128.95, 123.28, 111.89, 110.34, 43.05, 30.94, 20.45, 13.80. MALDI-TOF: m/z $[M]^+$ cacld. $C_{16}H_{15}Br_2N$, 381.9551; found: 381.9549.

Synthesis of 2b (2,7-dibromo-10-butyl-9,9-dimethyl-9,10-dihydroacridine)

The procedure is similar to the synthesis of **1b** but using **2a** instead of **1a**. Compound **2b** was obtained as white crystal by silica gel column chromatography (petroleum ether) in an 53% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.3 Hz, 2H), 7.29 (dd, *J* = 8.7, 2.3 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.87 – 3.82 (m, 2H), 1.77 (dt, *J* = 15.5, 7.7 Hz, 2H), 1.49 – 1.46 (m, 8H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.45, 133.97, 129.47, 127.42, 114.27, 113.10, 45.85, 36.53, 28.58, 27.84, 20.39, 13.87. MALDI-TOF: m/z $[M]^+$ cacld. $C_{19}H_{21}Br_2N$, 423.0020; found: 423.0019.

Synthesis of 3b (10-butyl-10H-phenoxazine)

10H-phenoxazine (1.83 g, 10 mmol), potassium tert-butoxide (1.68 g, 15 mmol), 1-bromobutane (2.06 g, 15 mmol) were dissolved in THF (30 mL). After stirring the mixture under an ice-water bath for 0.5 h under nitrogen atmosphere, then turn the temperature into 25 °C for 3 h. The obtained reaction mixture was filtered and removed using a rotary evaporator. The crude product was then subjected to column chromatography on silica gel (petroleum ether) to afford 1.9 g yellowish oil liquid of **3b** in a yield of 80%.^{1}H NMR (600 MHz, $CDCl_3$) δ 6.68 (dd, *J* = 7.7, 5.6 Hz, 2H), 6.54 (d, *J* = 13.2 Hz, 4H), 6.37 (d, *J* = 7.9 Hz, 2H), 3.37 (s, 2H), 1.57 – 1.52 (m, 2H), 1.34 (dt, *J* = 14.5, 7.4 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.05, 133.46, 123.62, 120.68, 115.33, 111.29, 43.83, 27.04, 20.21, 13.96. MALDI-TOF: m/z $[M]^+$ cacld. $C_{16}H_{17}NO$, 239.1310; found: 239.1308.

Synthesis of 4b (10-butyl-10H-phenothiazine)

The procedure is similar to the synthesis of **3b** but using **4a** instead of **3a**. Compound **4b** was obtained as yellowish oil liquid by silica gel column chromatography (petroleum ether) in an 80% yield. ^{1}H NMR (600 MHz, DMSO) δ 7.17 – 7.13 (m, 2H), 7.10 (dd, *J* = 7.6, 1.5 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.90 (td, *J* = 7.5, 1.1 Hz, 2H), 3.82 (t, *J* = 7.0 Hz, 2H), 1.65 – 1.59 (m, 2H), 1.35 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 129.08, 128.27, 127.46, 127.20, 122.34,

115.43, 47.11, 29.06, 20.24, 13.88. MALDI-TOF: m/z $[M]^+$ cacld. $C_{16}H_{17}NS$, 255.1082; found: 255.1081.

Synthesis of 3c (3,7-dibromo-10-butyl-10H-phenoxazine)

Syntheses of **3c** was carried out by the reaction with **3b** (2.39 g, 10 mmol) and *N*-bromosuccinimide (NBS) (4.45 g, 25 mmol) in THF (40 mL). After stirring the mixture under an ice-water bath for 0.5 h, then turn the temperature into 25 °C for 1.5 h. The crude product was purified by column chromatography on silica gel using (petroleum ethe), a white crystal with a yield of 75% (2.97 g) was obtained. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (dd, J = 5.2, 3.1 Hz, 2H), 6.73 (s, 2H), 6.30 (d, J = 8.3 Hz, 2H), 3.40 (s, 2H), 1.58 (d, J = 5.3 Hz, 2H), 1.45 – 1.39 (m, 2H), 1.01 – 0.97 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.21, 132.20, 126.54, 118.57, 112.42, 112.19, 43.99, 26.79, 20.10, 13.87. MALDI-TOF: m/z $[M]^+$ cacld. $C_{16}H_{15}Br_2NO$, 396.9500; found: 396.9487.

Synthesis of 4c (3,7-dibromo-10-butyl-10H-phenothiazine)

A potion of 4.45 g (25 mmol) of N-bromosuccinimide (NBS) in 15 mL of N, N'-dimethylformamide (DMF) was added dropwise to a solution of compound **4b** (2.55 g, 10 mmol) in 30 mL of DMF under the nitrogen atmosphere under an ice-water bath then stirred for 30 min. The reaction mixture was stirred for another 10 hours at room temperature. The mixture was poured into water and extracted with CH_2Cl_2 with several times. The combined organic layer was washed with aqueous sodium bisulfite (10 wt %) and then dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator. The crude product was purified by column chromatography on silica gel using (petroleum ether/ ethyl acetate 2/1, v/v), a white powder with a yield of 47% (1.9 g) was obtained. ^{1}H NMR (600 MHz, DMSO) δ 8.22 (d, J = 2.4 Hz, 2H), 7.86 (dd, J = 9.1, 2.4 Hz, 2H), 7.67 (d, J = 9.2 Hz, 2H), 4.34 – 4.31 (m, 2H), 1.73 (dd, J = 15.0, 7.7 Hz, 2H), 1.43 (dd, J = 15.1, 7.5 Hz, 2H), 0.92 (d, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.21, 132.20, 126.54, 118.57, 112.42, 112.19, 43.99, 26.79, 20.10, 13.87. MALDI-TOF: m/z $[M]^+$ cacld. $C_{16}H_{15}Br_2NS$, 412.9271; found: 412.9269.

Synthesis of APCz (4,4'-(9-butyl-9H-carbazole-3,6-diyl)dibenzaldehyde)

A mixture of 4-formylphenylboronic acid (2.73 g, 22 mmol), **1c** (3.81g, 10 mmol), tetrakis(triphenylphosphine) palladium (0) ($Pd(PPh_3)_4$) (576 mg, 0.5 mmol) and K_2CO_3 (6.9 g, 50 mmol) in 1,2-glycol dimethyl ether (DME) (100 mL) was stirred at 90 °C for 12 h. After cooling to room temperature, the mixture was poured into H_2O and extracted with chloroform. The extracts were dried over anhydrous $MgSO_4$. After filtration and concentration under reduced pressure, product **APCz** was obtained as a light yellow solid power using silica gel column chromatography (petroleum ether/ ethyl acetate 5/1, v/v) (3.1 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.08 (s, 2H), 8.45 (d, *J* = 1.7 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 4H), 7.90 (d, *J* = 8.2 Hz, 4H), 7.81 (dd, *J* = 8.5, 1.8 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 1.95 – 1.90 (m, 2H), 1.45 (dd, *J* = 15.2, 7.5 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.75, 150.84, 144.05, 137.54, 133.95, 133.26, 130.45, 128.55, 126.49, 122.30, 112.46, 46.13, 34.08, 23.46, 16.76. Anal. Cacld for $C_{30}H_{25}NO_2$: C, 83.50; H, 5.84; N, 3.25; O, 7.42. Found: C, 83.49; H, 5.85; N, 3.23; O, 7.43. MALDI-TOF: m/z $[M]^+$ cacld. $C_{30}H_{25}NO_2$, 431.5550; found: 431.5548.

Synthesis of APAd (4,4'-(10-butyl-9,9-dimethyl-9,10-dihydroacridine-2,7-diyl) dibenzaldehyde)

The procedure was similar to the synthesis of **APCz** but using **2b** instead of **1b**. Compound **APAd** was afforded as yellow solid power by using silica gel column chromatography (petroleum ether/ CH_2Cl_2 2/1, v/v) in 63% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.05 (s, 2H), 7.95 (d, *J* = 8.2 Hz, 4H), 7.77 (d, *J* = 8.2 Hz, 4H), 7.73 (d, *J* = 2.2 Hz, 2H), 7.55 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 4.04 – 4.01 (m, 2H), 1.91 (s, 2H), 1.61 – 1.50 (m, 8H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.68, 150.03, 143.44, 137.49, 135.48, 134.71, 133.26, 130.92, 129.70, 128.80, 126.63, 116.19, 48.87, 39.45, 32.45, 31.08, 23.35, 16.80. Anal. Cacld for $C_{33}H_{31}NO_2$: C, 83.69; H, 6.60; N, 2.96; O, 6.76. Found: C, 83.70; H, 6.59; N, 2.95; O, 6.76. MALDI-TOF: m/z $[M]^+$ cacld. $C_{33}H_{31}NO_2$, 437.6160; found: 437.6157.

Synthesis of APPo (4,4'-(10-butyl-10H-phenoxazine-3,7-diyl) dibenzaldehyde)

The procedure is similar to the synthesis of **APCz** but using **3c** instead of **1b**. Compound **APPo** was afforded as red solid power by using silica gel column

chromatography (petroleum ether/ CH_2Cl_2 2/1, v/v) in 52% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.02 (s, 2H), 7.92 – 7.90 (m, 4H), 7.68 – 7.66 (m, 4H), 7.14 (dd, *J* = 8.3, 2.2 Hz, 2H), 6.97 (d, *J* = 2.2 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 3.58 – 3.55 (m, 2H), 1.71 (t, *J* = 7.9 Hz, 2H), 1.50 (dt, *J* = 14.8, 7.5 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.53, 148.57, 148.04, 137.73, 136.09, 135.26, 133.22, 129.26, 125.62, 116.90, 114.71, 80.14, 79.93, 79.72, 46.81, 30.15, 23.08, 16.79. Anal. Cacld for $C_{30}H_{25}NO_3$: C, 80.51; H, 5.63; N, 3.13; O, 10.73. Found: C, 80.54; H, 5.61; N, 3.10; O, 10.75. MALDI-TOF: m/z $[M]^+$ cacld. $C_{30}H_{25}NO_3$, 447.5340; found: 447.5337.

Synthesis of APPt (4,4'-(10-butyl-10H-phenothiazine-3,7-diyl) dibenzaldehyde)

The procedure was similar to the synthesis of **APCz** but using **4c** instead of **1b**. Compound **APPt** was was obtained as a yellow solid power using silica gel column chromatography (petroleum ether/ ethyl acetate 2/1, v/v) (2.3 g, 50%). ^{1}H NMR (600 MHz, DMSO) δ 9.97 (s, 2H), 7.89 (d, *J* = 8.3 Hz, 4H), 7.82 (d, *J* = 8.3 Hz, 4H), 7.29 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.09 (d, *J* = 2.1 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.65 – 3.62 (m, 2H), 1.55 (dd, *J* = 14.9, 7.5 Hz, 2H), 1.42 (dd, *J* = 15.0, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.51, 147.73, 140.86, 138.28, 136.41, 135.00, 134.81, 134.53, 133.34, 131.38, 130.01, 127.82, 119.47, 50.98, 31.39, 22.99, 16.69. Anal. Cacld for $C_{30}H_{25}NO_2S$: C, 77.72; H, 5.44; N, 3.02; O, 6.90; S, 6.92. Found: C, 77.71; H, 5.45; N, 3.07; O, 6.84; S, 6.93. MALDI-TOF: m/z $[M]^+$ cacld. $C_{30}H_{25}NO_2S$, 463.5950; found: 463.5947.

Synthesis of APBz (2,5-Bis(4-formylphenyl)-3-octyl-phenyl): The procedure was similar to the synthesis of **APCz** but using **5a** instead of **1b**. Compound **APBz** as white solid was obtained by silica gel column chromatography (petroleum ether/ dichloromethane=5/1, v/v) in a 48% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.08 (s, 2H), 7.98 (d, *J* = 8.2 Hz, 4H), 7.81 (d, *J* = 8.2 Hz, 4H), 7.69 (s, 1H), 7.50 (s, 2H), 2.79 – 2.75 (m, 2H), 1.72 (dt, *J* = 15.4, 7.6 Hz, 2H), 1.34 (ddd, *J* = 25.7, 13.1, 6.6 Hz, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.70, 149.91, 147.59, 143.53, 138.34, 133.19, 130.76, 130.52, 126.85, 39.03, 34.78, 34.48, 32.36, 32.29, 32.15, 25.56, 16.99. Anal. Cacld for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59; O, 8.03. Found: C, 84.36; H, 7.57; O, 8.07. MALDI-TOF: m/z $[M]^+$ cacld. $C_{28}H_{30}O_2$, 398.5460; found: 398.5458.

2. Figures

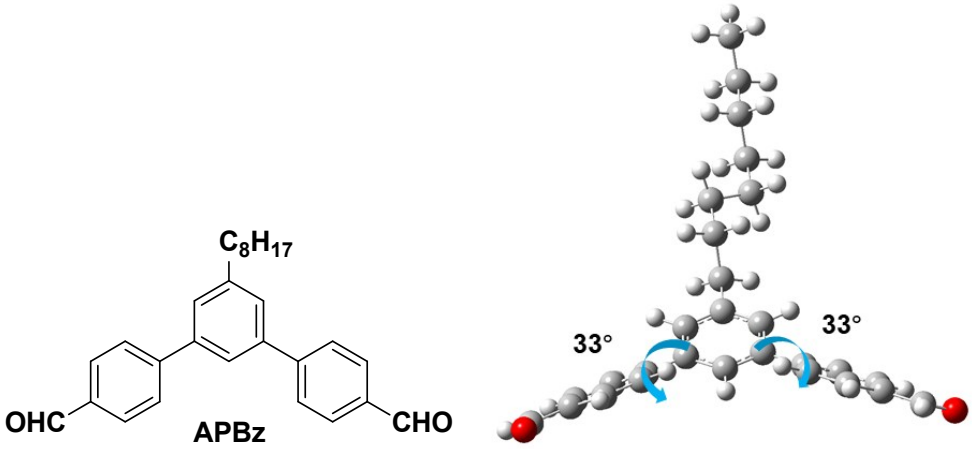


Fig. S1 Molecular structure and geometrically optimized 3D molecular model of **APBz**.

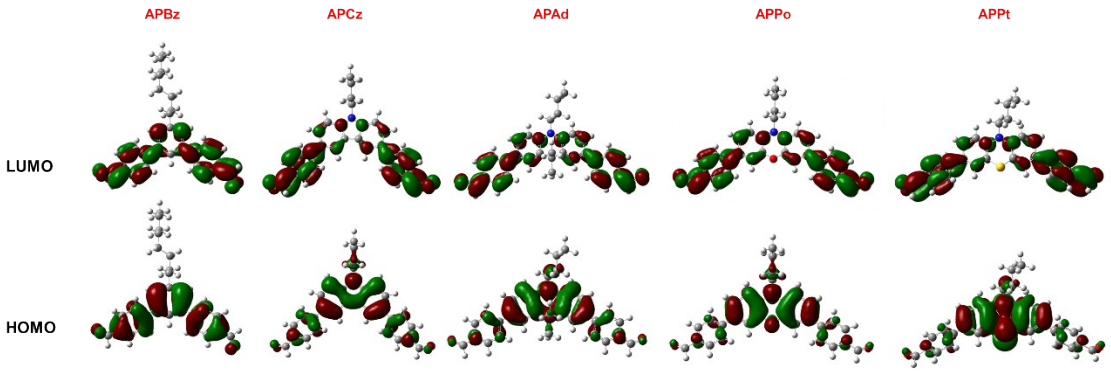


Fig. S2 HOMO and LUMO spatial distributions of **APBz**, **APCz**, **APAd**, **APPo**, and **APPt** by TD-DFT B3LYP/6-31G(d) calculation.

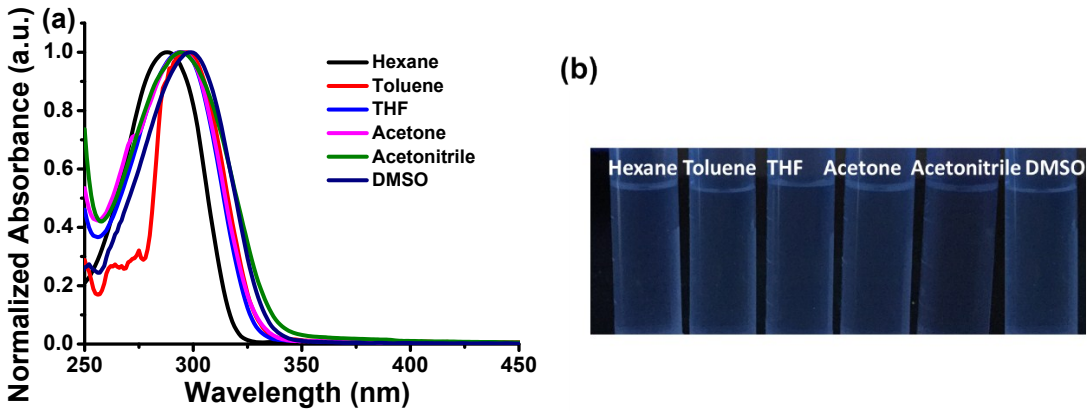


Fig. S3 (a) UV-Vis absorption spectra of **APBz** in various solvents (10 μM) and (b) Luminescence photographs of **APBz** in various solvents (10 μM) under UV irradiation at 365 nm.

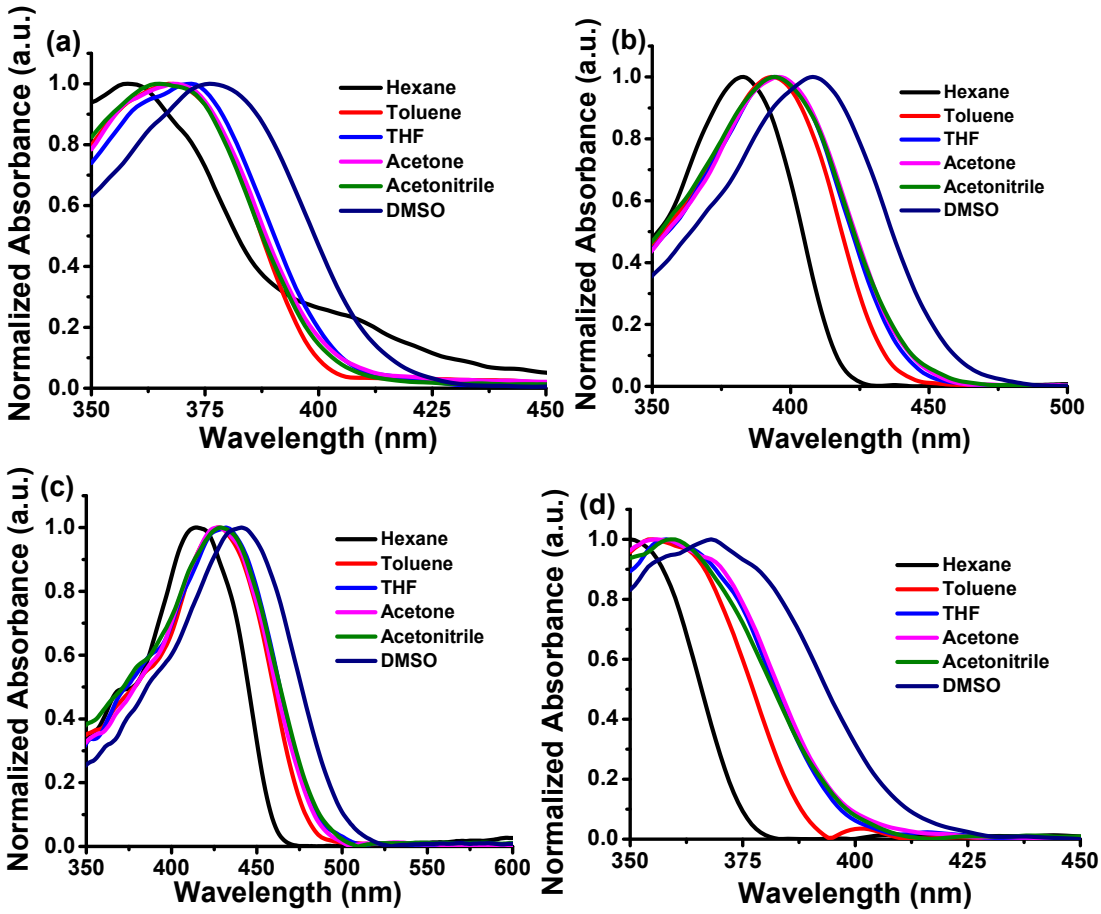


Fig. S4 UV-Vis absorption spectra of (a) **APCz**, (b) **APAd**, (c) **APPo**, and (d) **APPt** in various solvents (10 μM).

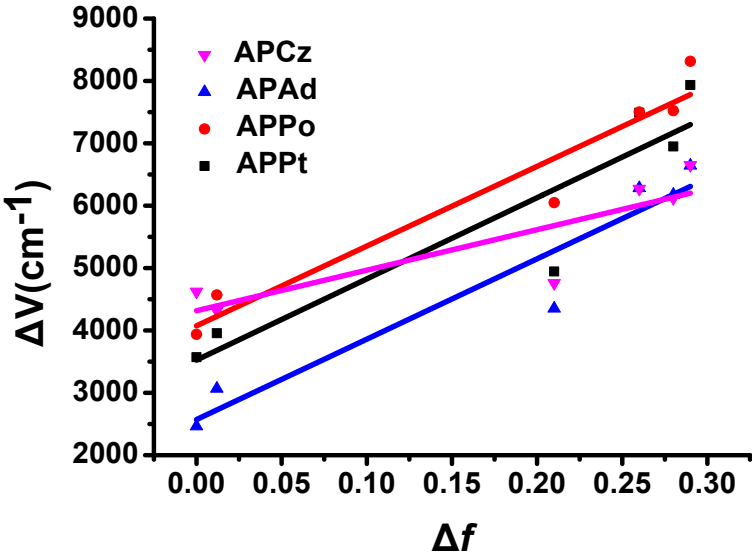


Fig. S5 Linear correlation of the orientation polarization (Δf) of solvent media with the Stokes shifts ($\Delta \nu$) for **APCz**, **APAd**, **APPo** and **APPt**.

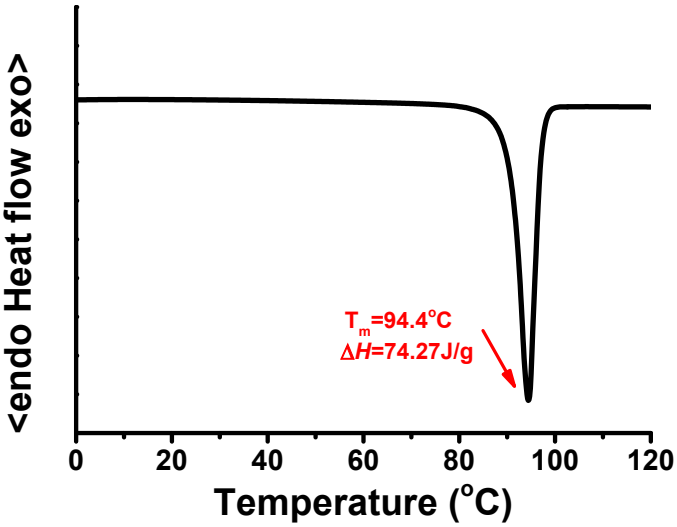


Fig. S6 DSC curves of **APBz** in pristine state.

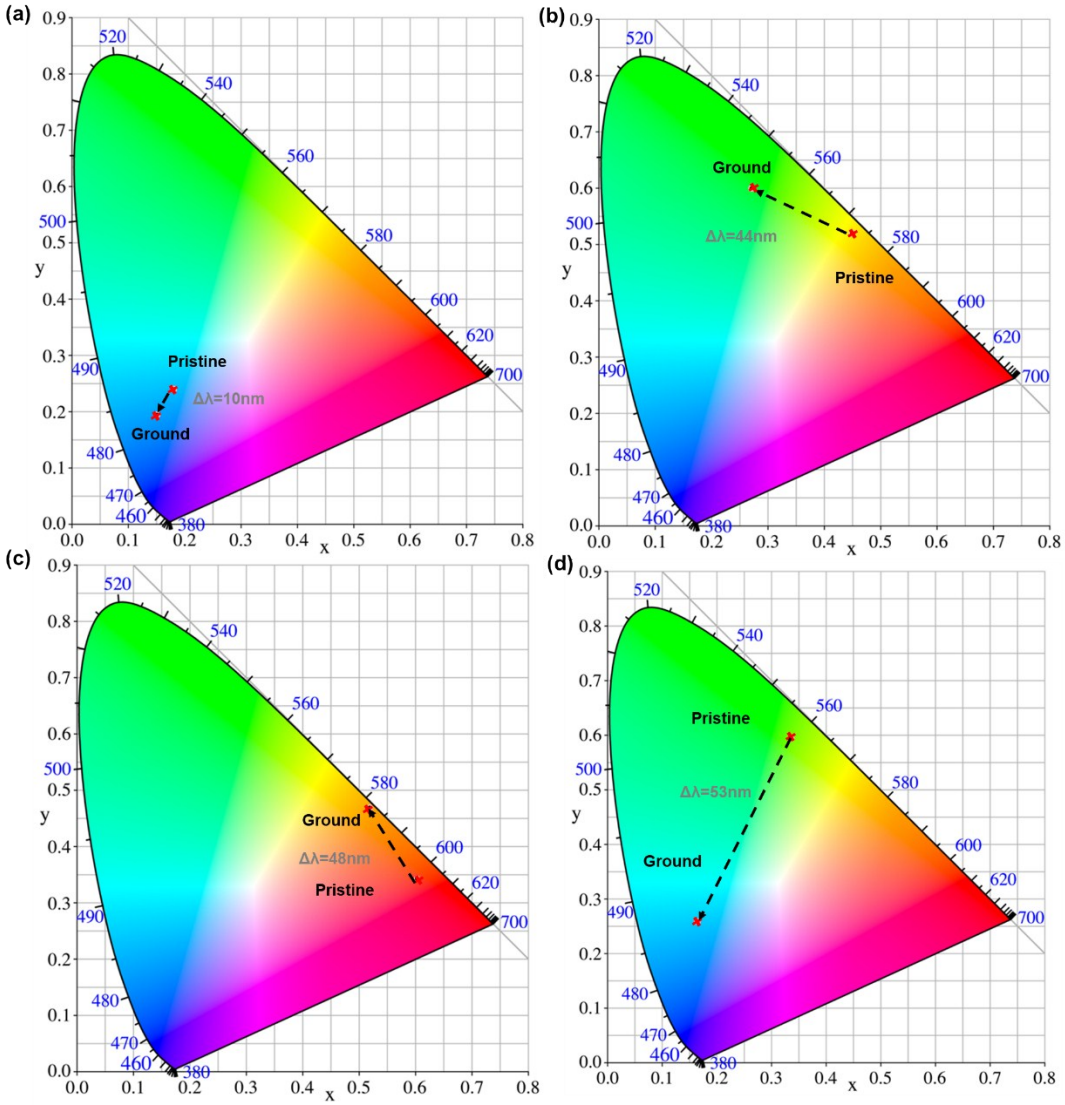


Fig. S7 CIE color coordinates of (a) **APCz**, (b) **APAd**, (c) **APPo** and (d) **APPt** in different solid states on the chromatic diagram.

3. Tables

Table S1 Crystal data and structure refinement for **APCz CCDC: 1842477**

Identification code	**APCz**
Empirical formula	$C_{30}H_{25}NO_2$
Formula weight	431.51
Temperature/K	173.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.8799(7)
b/Å	13.3532(8)
c/Å	17.0824(10)
α/°	101.465(5)
β/°	97.263(5)
γ/°	109.371(6)
Volume/Å^3	2244.3(2)
Z	4
ρ_{calc}g/cm^3	1.277
μ/mm^{-1}	0.079
F(000)	912.0
Crystal size/mm^3	0.21 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.5 to 52.04
Index ranges	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-21 \leq l \leq 20$
Reflections collected	15843
Independent reflections	8844 [R_{int} = 0.0366, R_{sigma} = 0.0685]
Data/restraints/parameters	8844/24/625
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0603, wR_2 = 0.1315
Final R indexes [all data]	R_1 = 0.1014, wR_2 = 0.1608
Largest diff. peak/hole / e Å^{-3}	0.21/-0.22

Table S2 Crystal data and structure refinement for **APAd CCDC: 1847380**

Identification code	**APAd**
Empirical formula	$C_{30}H_{25}NO_2$

Formula weight	473.59
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	Cc
a/Å	22.7890(12)
b/Å	11.8841(7)
c/Å	38.1493(18)
α/°	90.00
β/°	104.566(5)
γ/°	90.00
Volume/Å^3	9999.7(9)
Z	16
ρ_{calc}g/cm^3	1.258
μ/mm^{-1}	0.077
F(000)	4032.0
Crystal size/mm^3	0.21 × 0.15 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.64 to 52.04
Index ranges	$-17 \leq h \leq 28$, $-14 \leq k \leq 14$, $-45 \leq l \leq 47$
Reflections collected	18934
Independent reflections	12789 [R_{int} = 0.0475, R_{sigma} = 0.0909]
Data/restraints/parameters	12789/2/1309
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0730, wR_2 = 0.1444
Final R indexes [all data]	R_1 = 0.1294, wR_2 = 0.1876
Largest diff. peak/hole / e Å^{-3}	0.34/-0.27
Flack parameter	-1(3)

Table S3 Crystal data and structure refinement for **APPo CCDC: 1847379**

Identification code	**APPo**
Empirical formula	$C_{30}H_{25}NO_3$
Formula weight	447.51
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	9.3553(5)
b/Å	25.1617(13)
c/Å	9.5973(5)
α/°	90
β/°	95.653(5)
γ/°	90
Volume/Å^3	2248.2(2)
Z	4
ρ_{calc}g/cm^3	1.322
μ/mm^{-1}	0.085
F(000)	944.0
Crystal size/mm^3	0.24 × 0.21 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.608 to 52.044
Index ranges	$-9 \leq h \leq 11$, $-15 \leq k \leq 31$, $-11 \leq l \leq 11$
Reflections collected	10095
Independent reflections	4524 [R_{int} = 0.0399, R_{sigma} = 0.0622]
Data/restraints/parameters	4524/0/348
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0730, wR_2 = 0.1888
Final R indexes [all data]	R_1 = 0.1184, wR_2 = 0.2220
Largest diff. peak/hole / e Å^{-3}	0.37/-0.24

Table S4 The summary of different kinds of noncovalent interactions for compound **APCz**, **APAd** and **APPo** in a crystal cell.

Types of non-covalent interactions	**APCz**		**APAd**		**APPo**	
	distance	number	distance	number	distance	number
C-H…O=C	2.531 Å, 2.393 Å, 2.718 Å	3	2.554 Å, 2.623 Å, 2.555 Å, 2.717 Å, 2.718 Å, 2.718 Å, 2.669 Å, 2.635 Å, 2.704 Å, 2.697 Å, 2.605 Å, 2.623 Å	11	2.531 Å, 2.393 Å, 2.718 Å	3
C-H…π	2.886 Å, 2.874 Å, 2.857 Å, 2.843 Å, 2.845 Å	5	2.871 Å, 2.855 Å, 2.884 Å, 2.868 Å, 2.841 Å, 2.852 Å	6	2.885 Å, 2.765 Å	2
C-H…H-C	2.314 Å, 2.239 Å	2	2.297 Å	1	/	/
π…π	3.293 Å,3.334 Å,3.387 Å	3	/	/	/	/

4. ^{1}H NMR and ^{13}C NMR

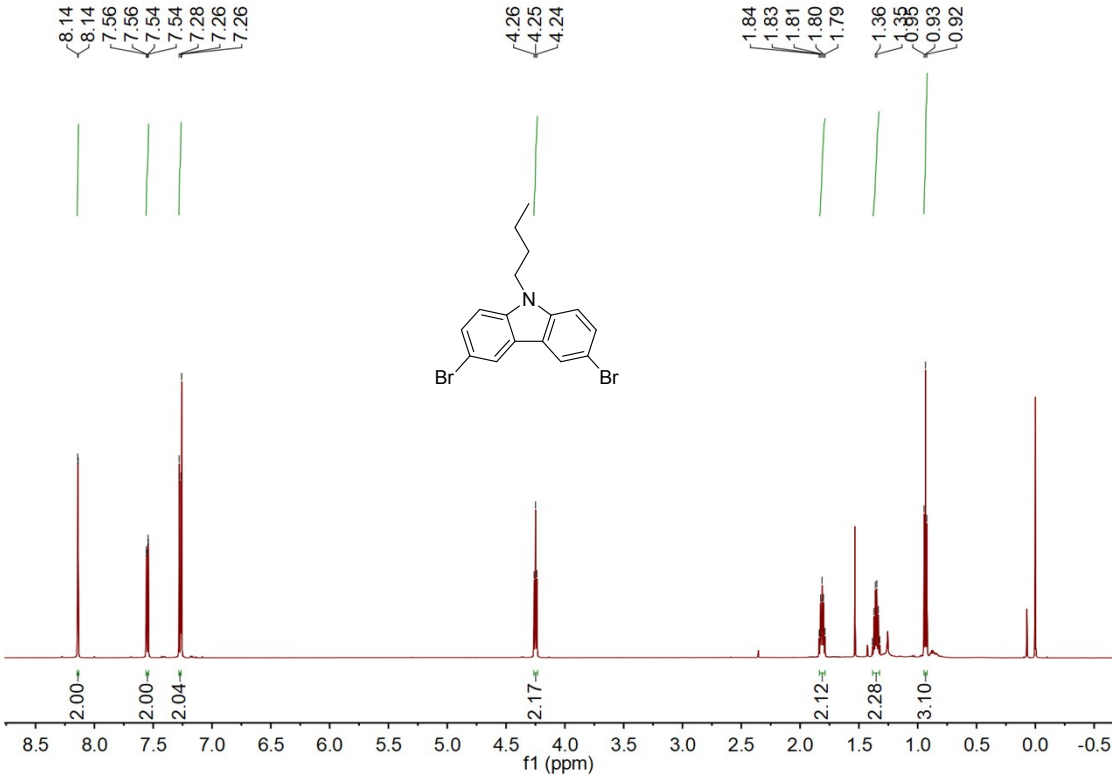


Fig. S8 ^{1}H NMR spectrum of 1b.

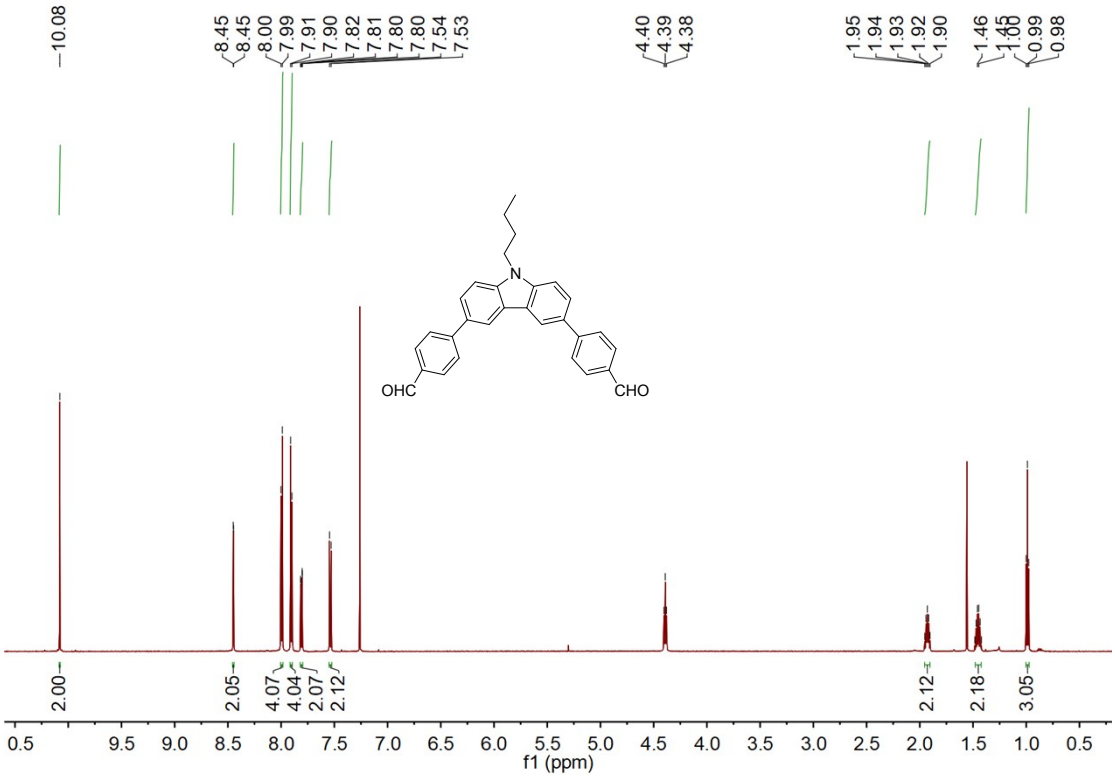


Fig. S9 ^{1}H NMR spectrum of **APCz**.

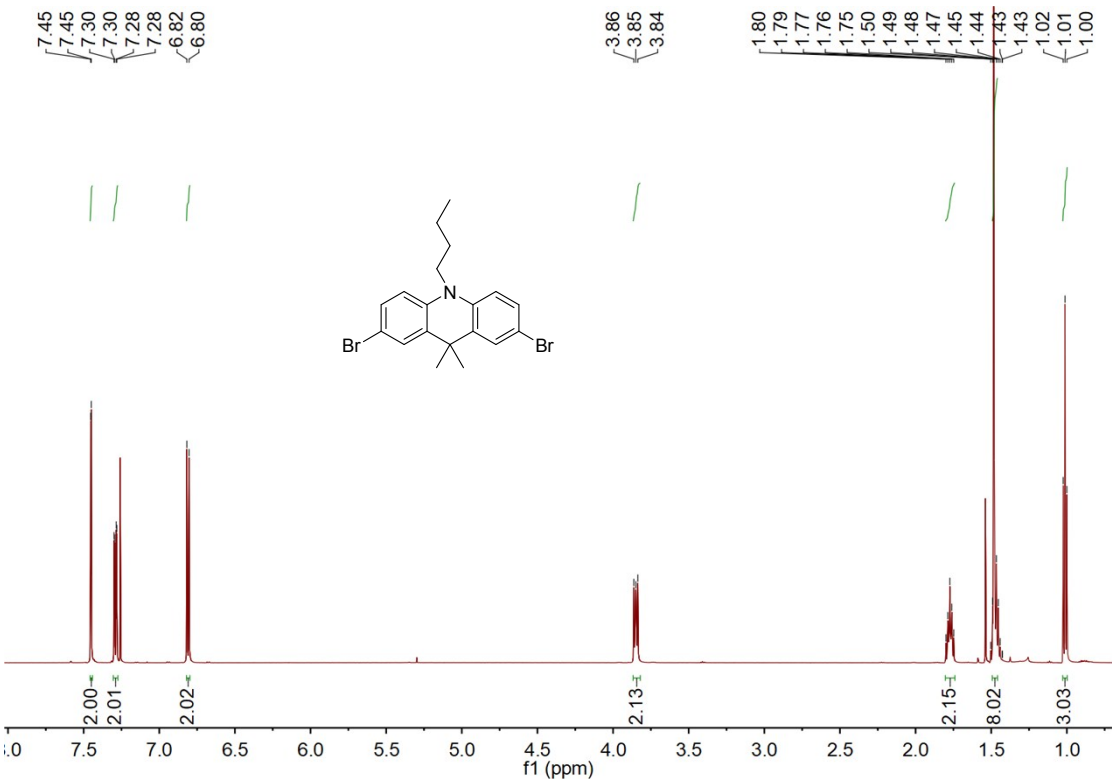


Fig. S10 ^{1}H NMR spectrum of 2b.

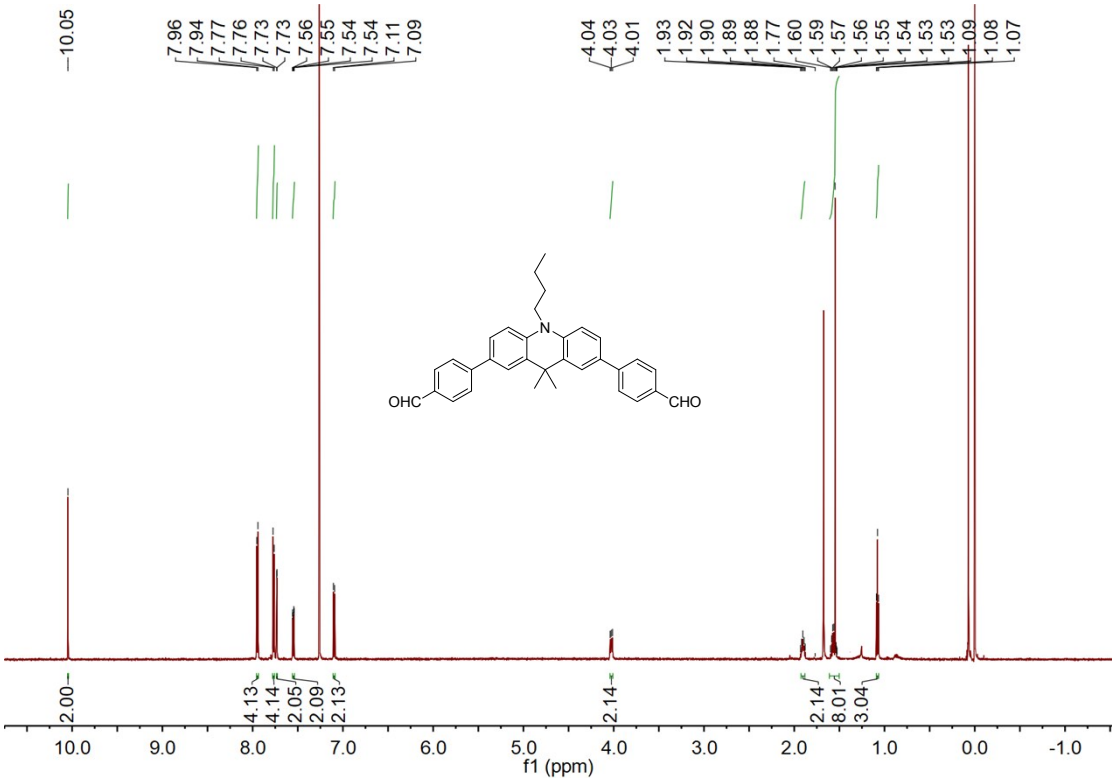


Fig. S11 ^{1}H NMR spectrum of **APAd**.

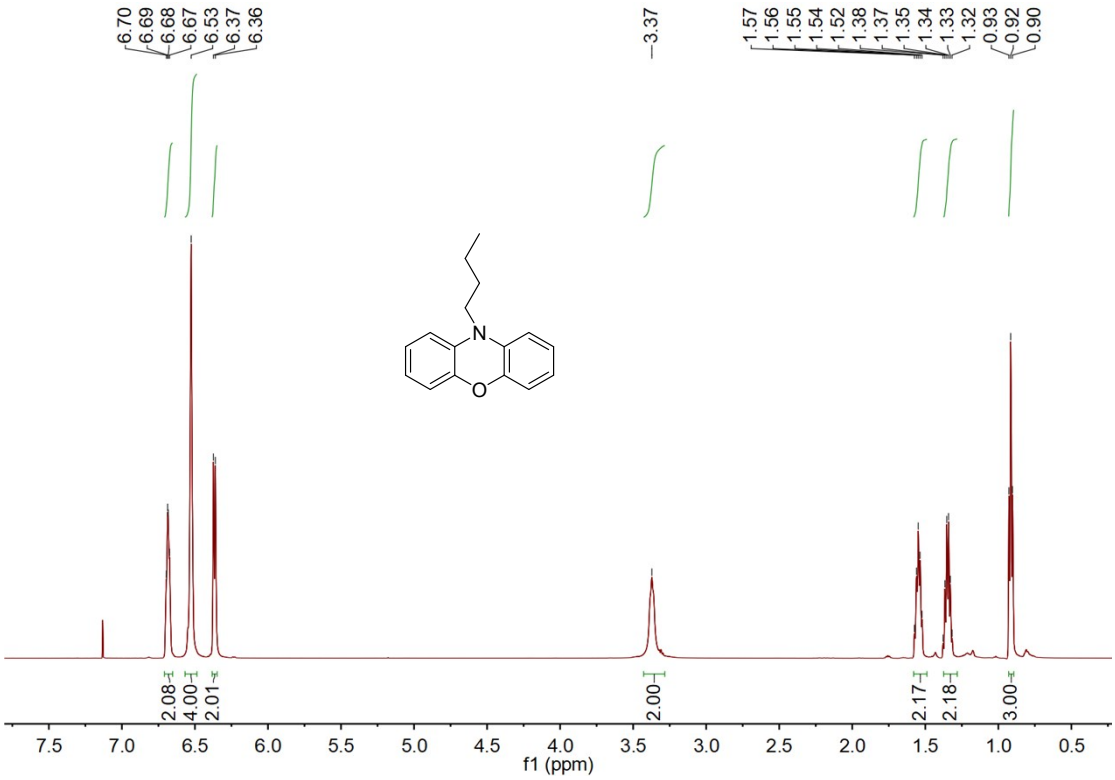


Fig. S12 ^{1}H NMR spectrum of 3b.

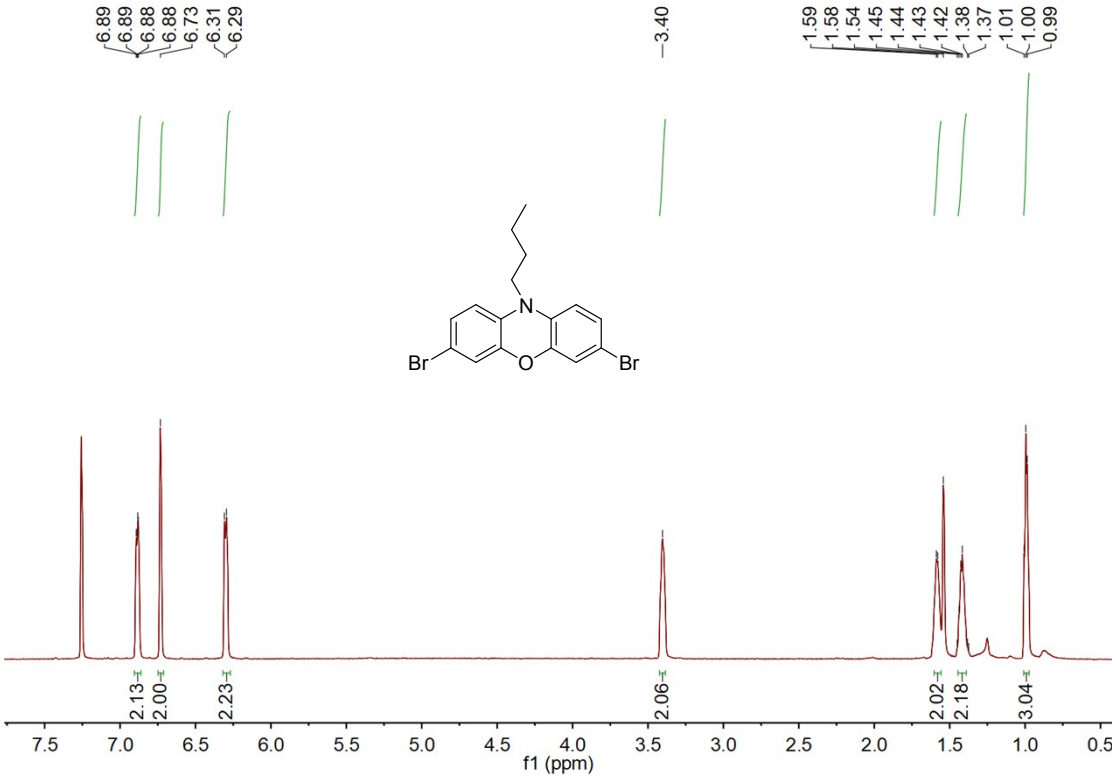


Fig. S13 ^{1}H NMR spectrum of 3c.

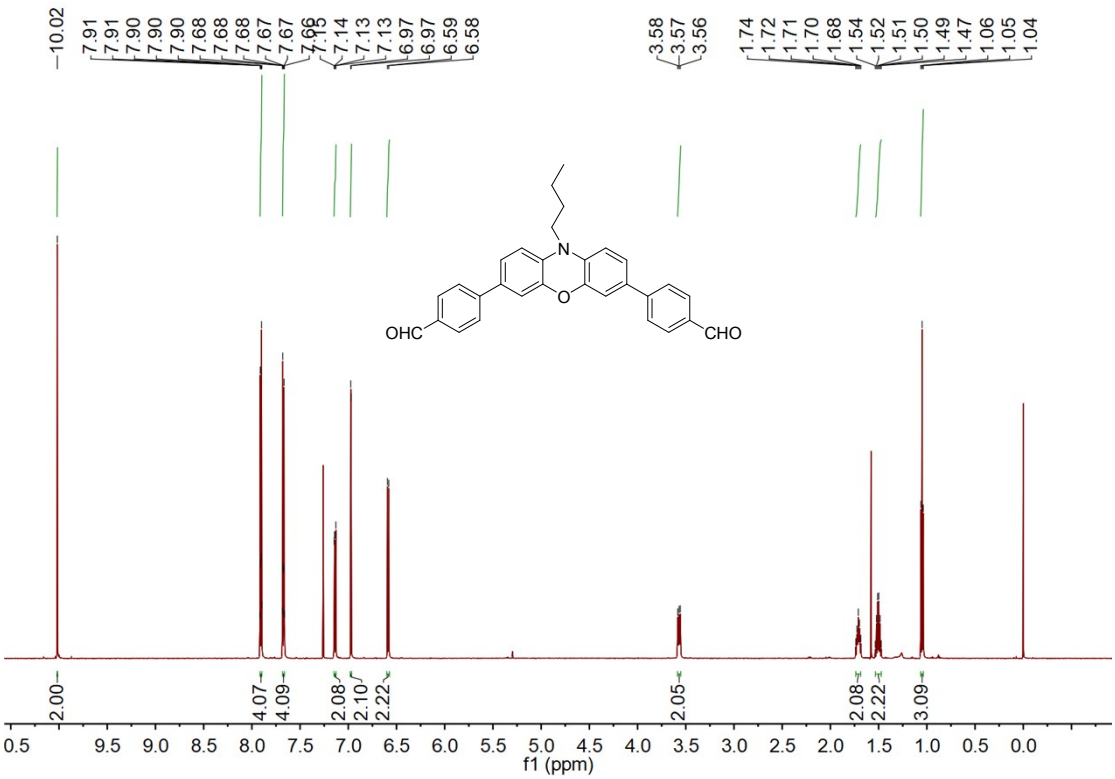


Fig. S14 ^{1}H NMR spectrum of **APPo**.

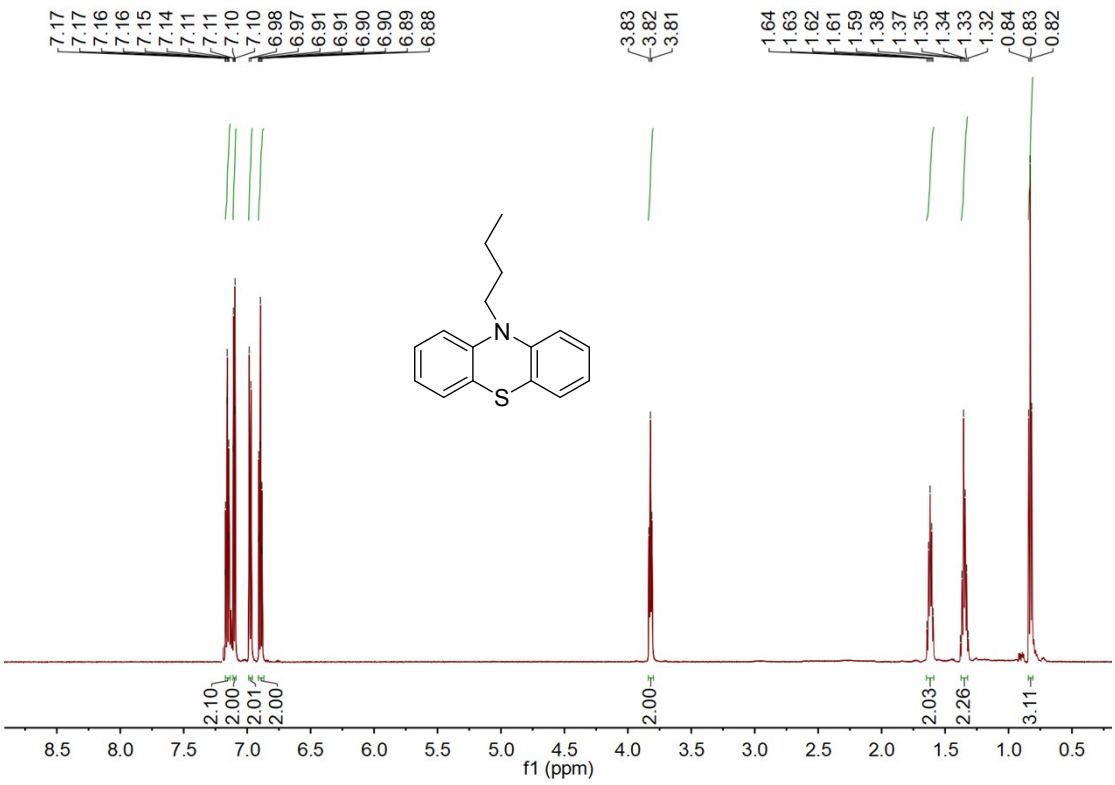


Fig. S15 ^{1}H NMR spectrum of 4b.

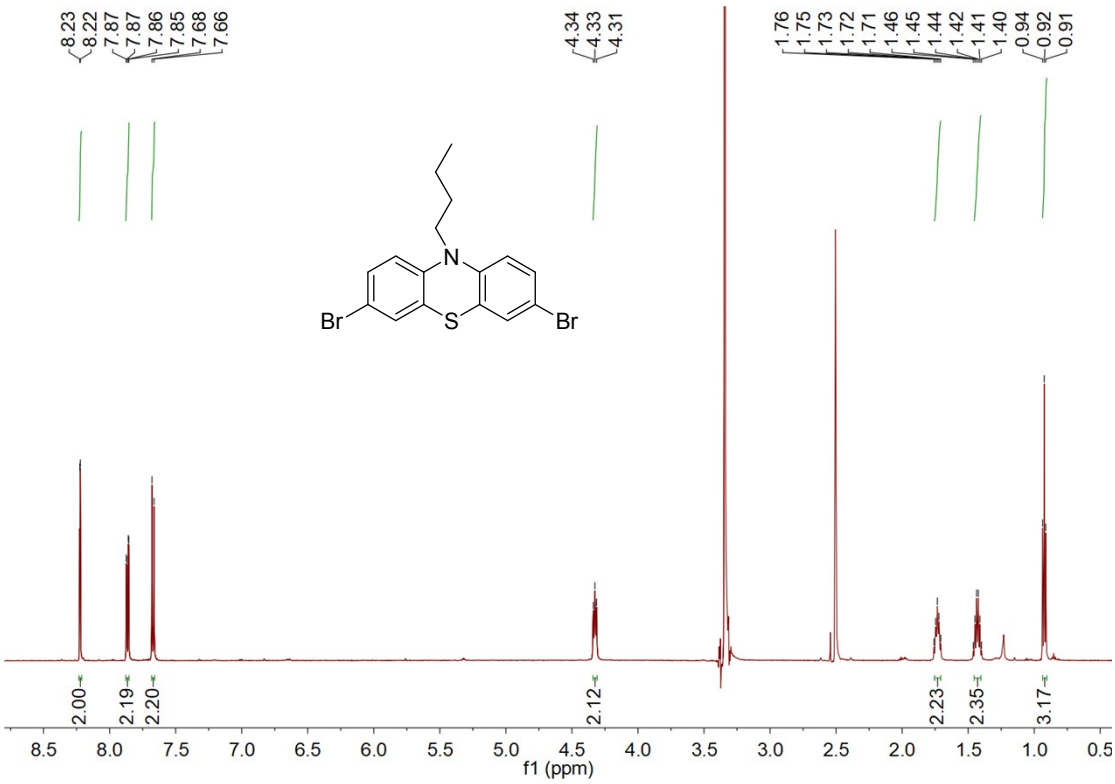


Fig. S16 ^{1}H NMR spectrum of 4c.

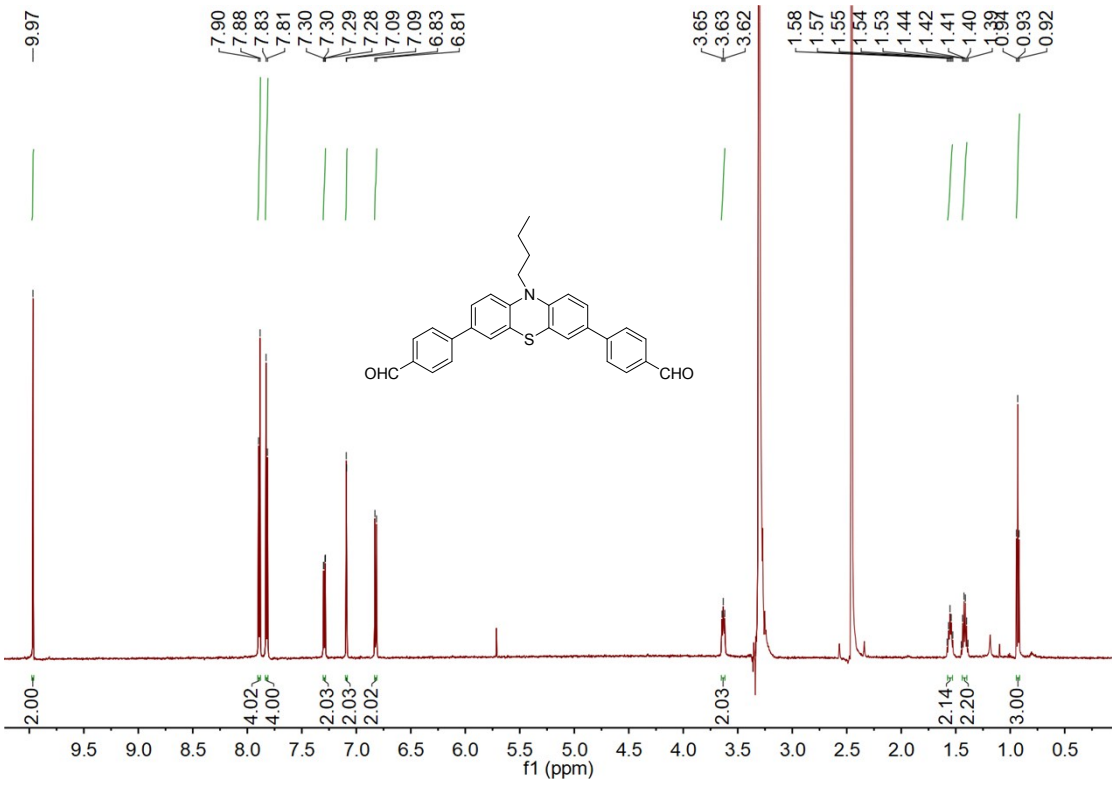


Fig. S17 ^{1}H NMR spectrum of **APPt**.

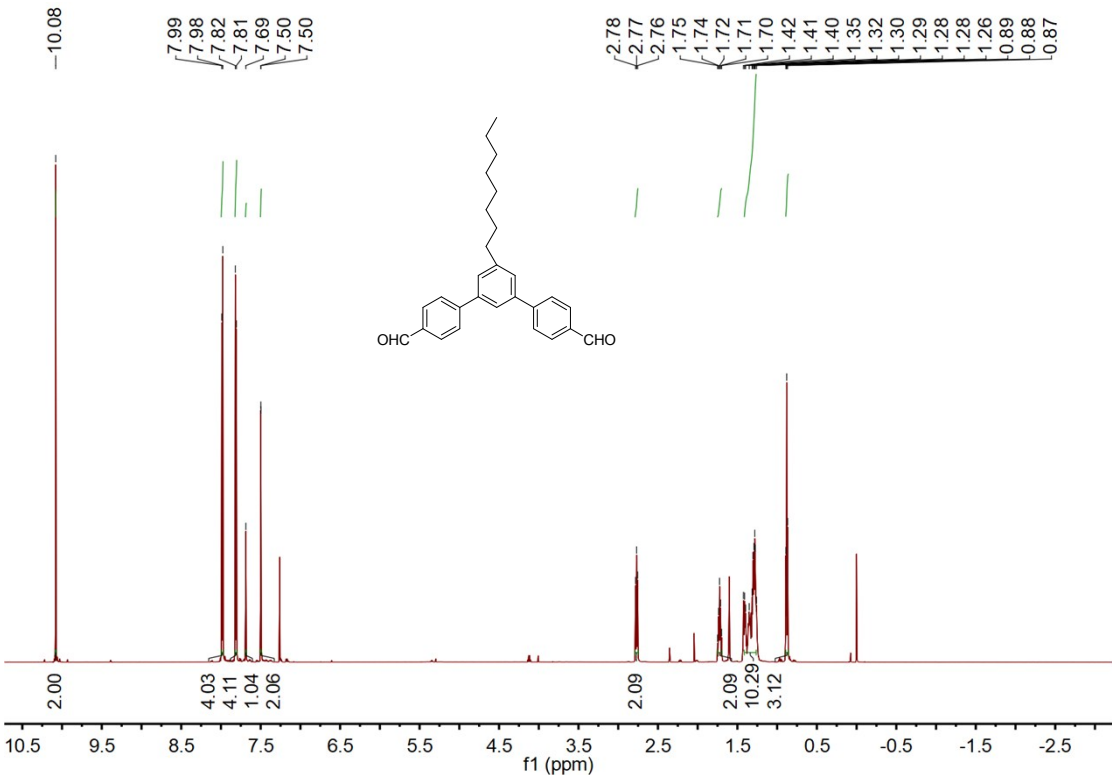


Fig. S18 ^{1}H NMR spectrum of **APBz**.

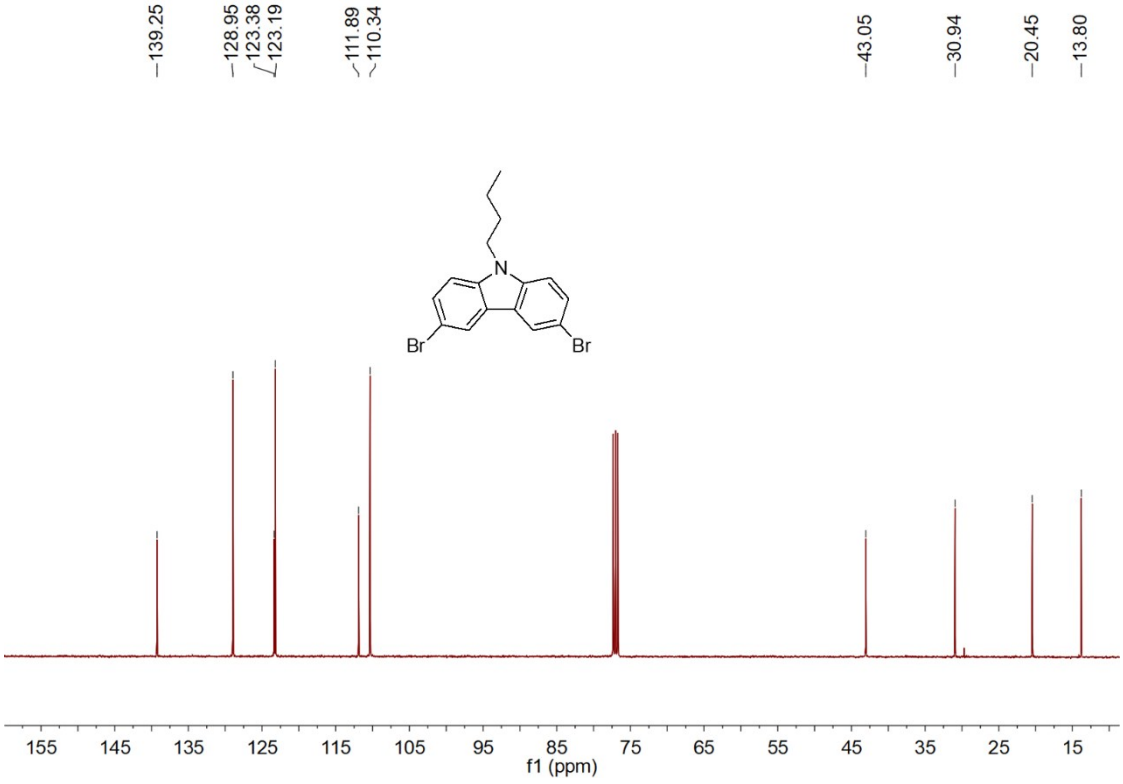


Fig. S19 ^{13}C NMR spectrum of 1b.

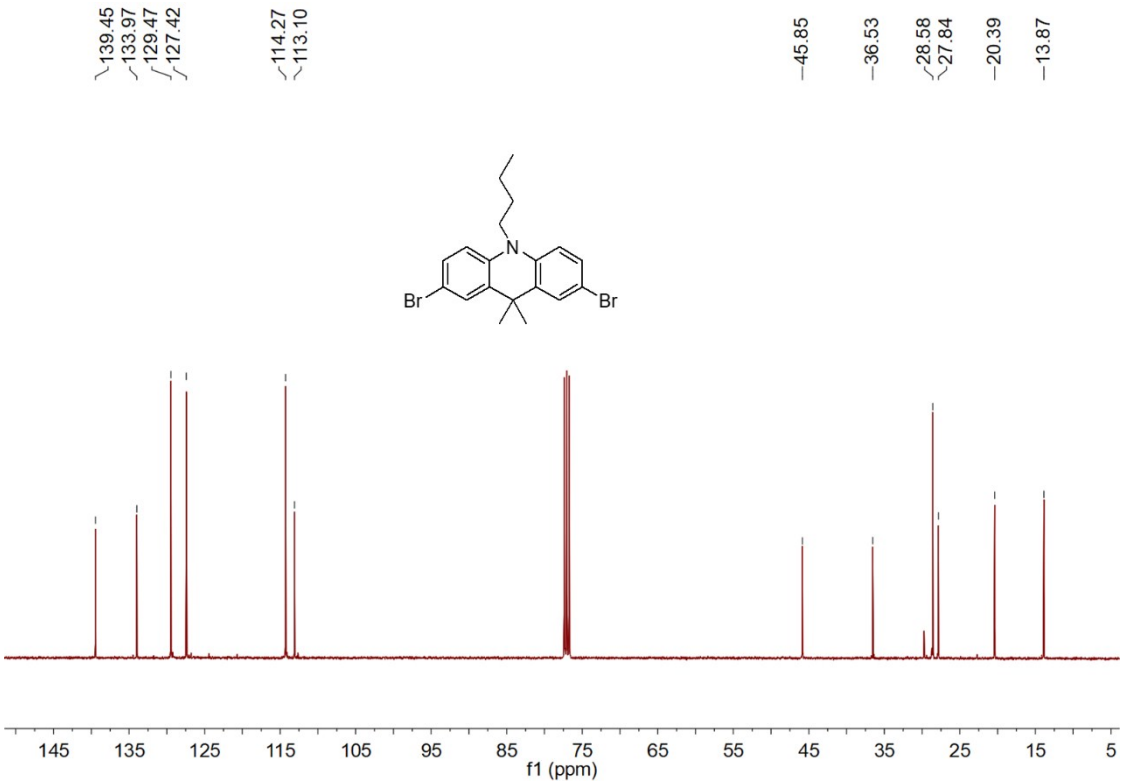


Fig. S20 ^{13}C NMR spectrum of 2b.

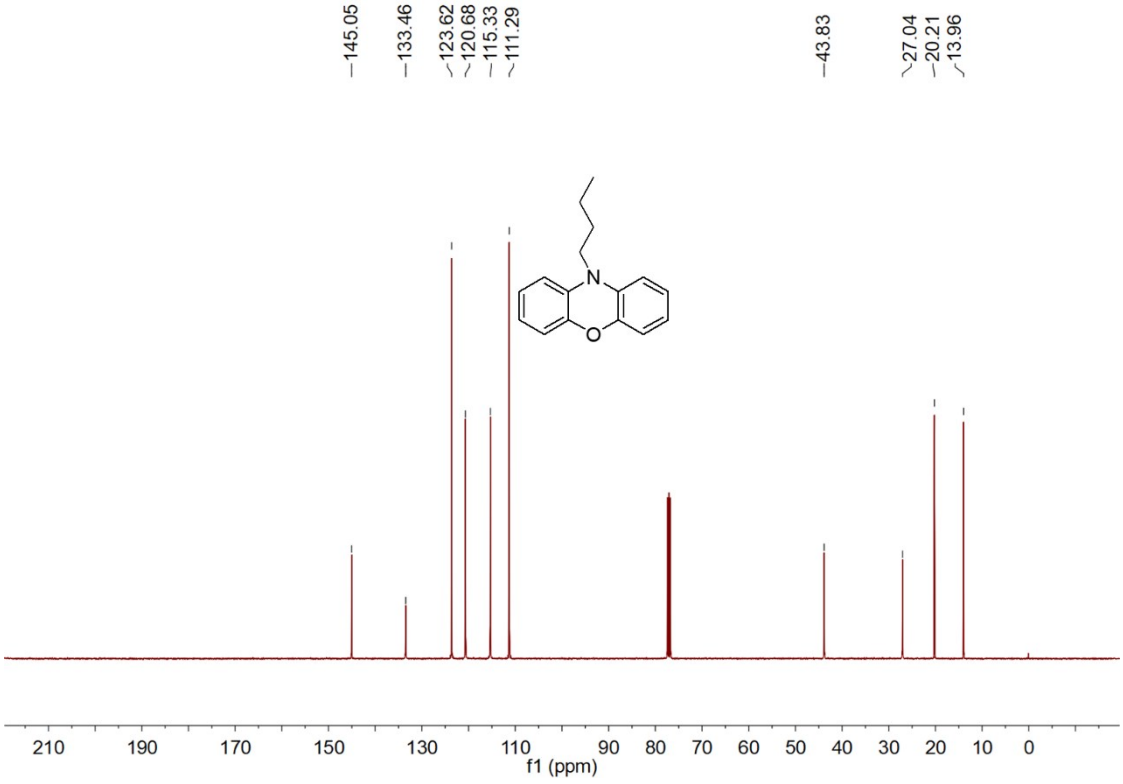


Fig. S21 ^{13}C NMR spectrum of 3b.

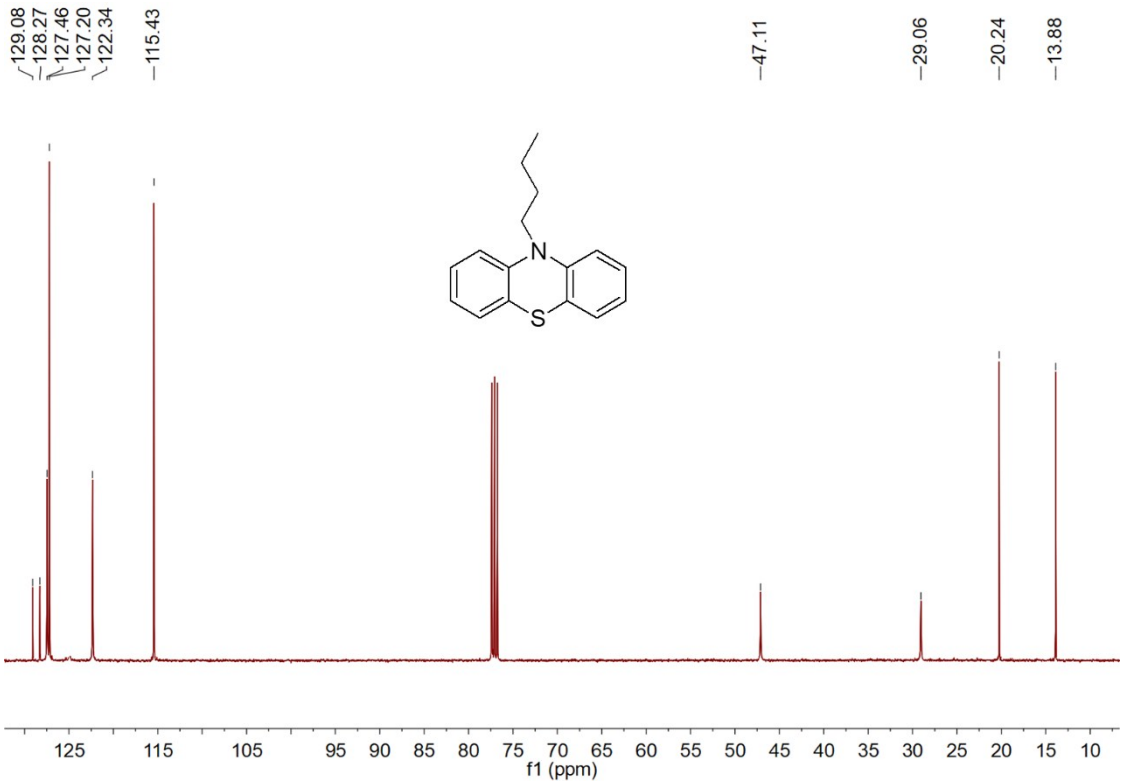


Fig. S22 ^{13}C NMR spectrum of 4b.

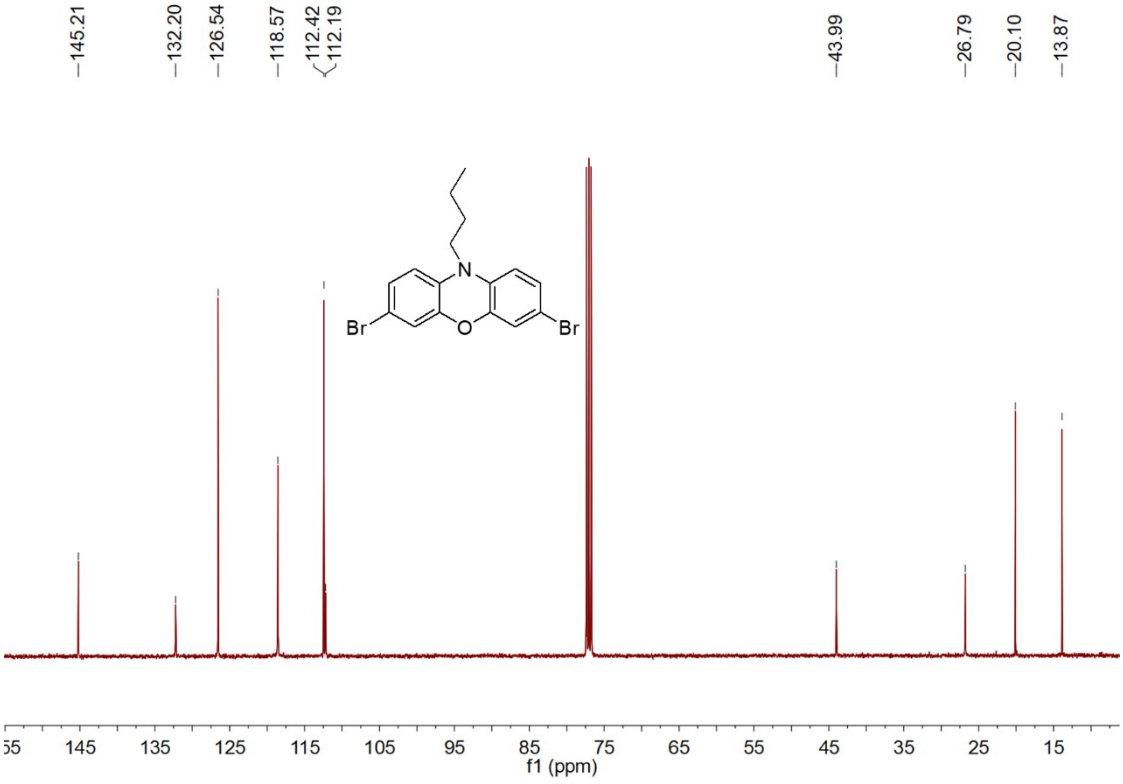


Fig. S23 ^{13}C NMR spectrum of 3c.

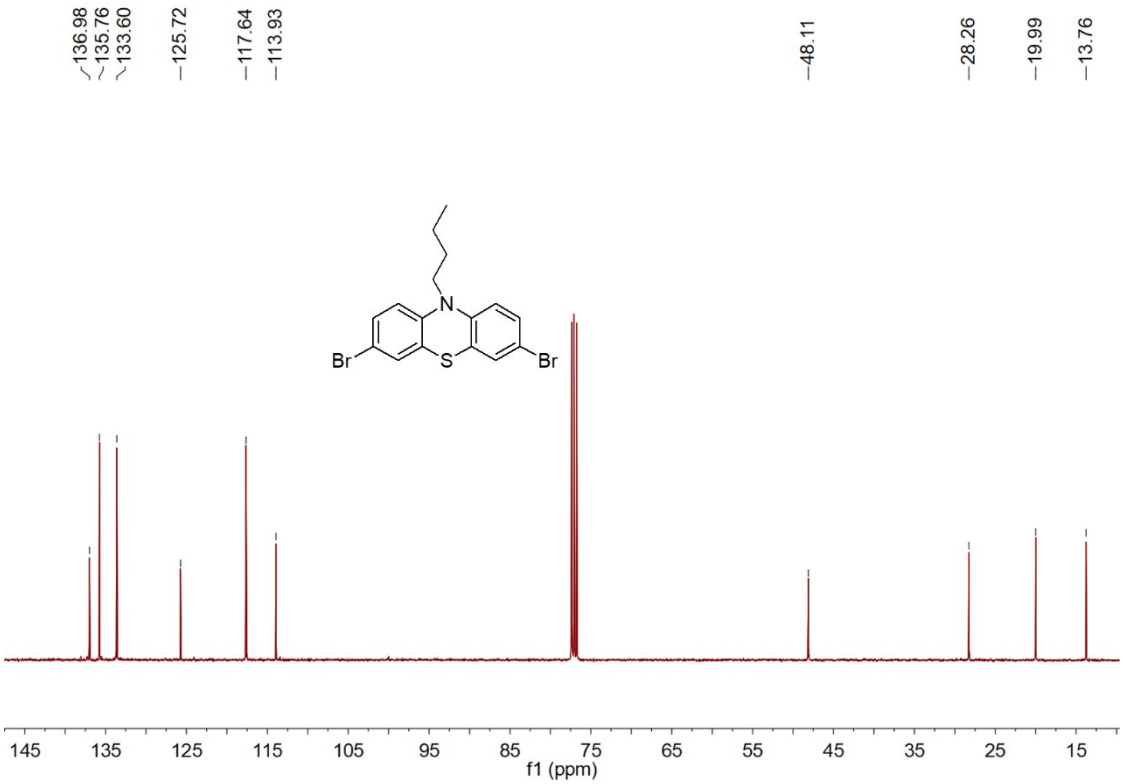


Fig. S24 ^{13}C NMR spectrum of 4c.

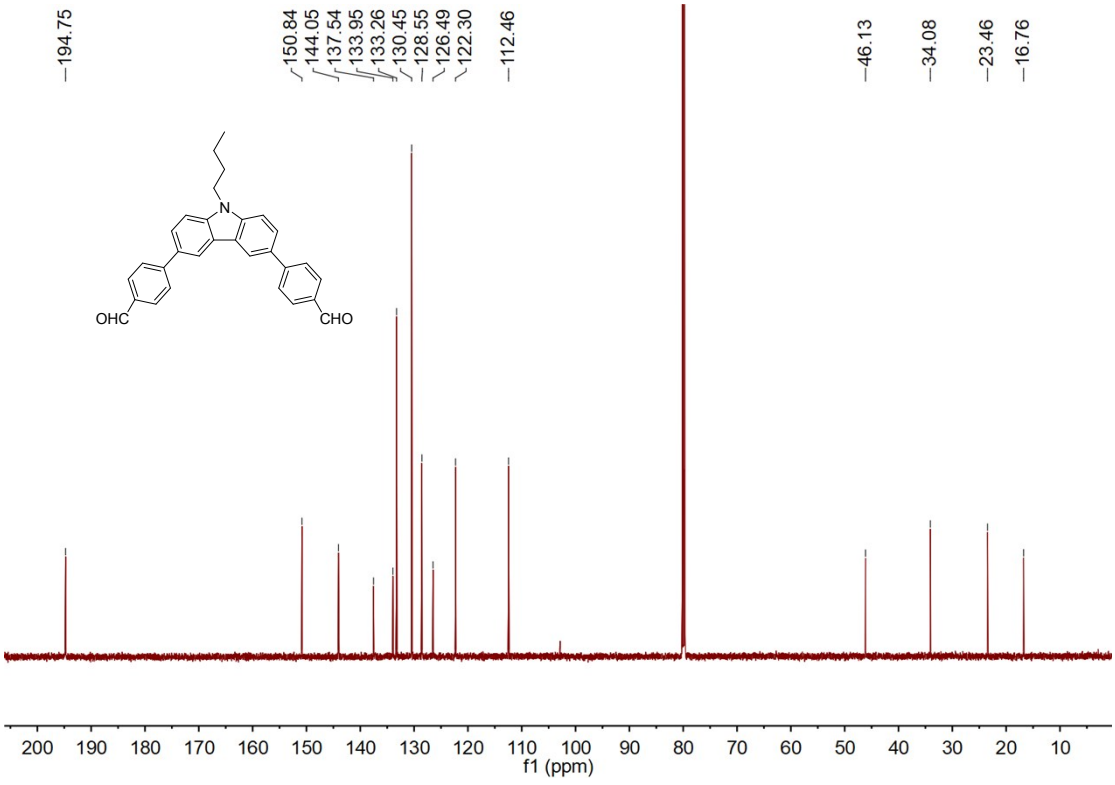


Fig. S25 ^{13}C NMR spectrum of **APCz**.

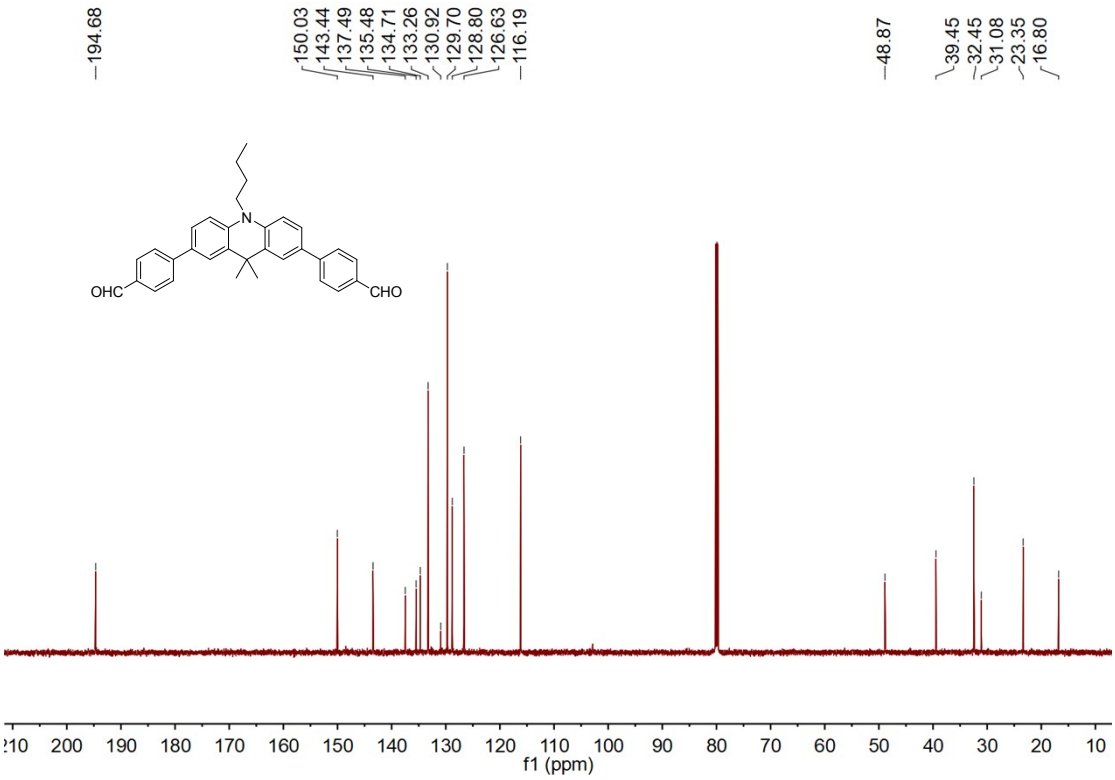


Fig. S26 ^{13}C NMR spectrum of **APAd**.

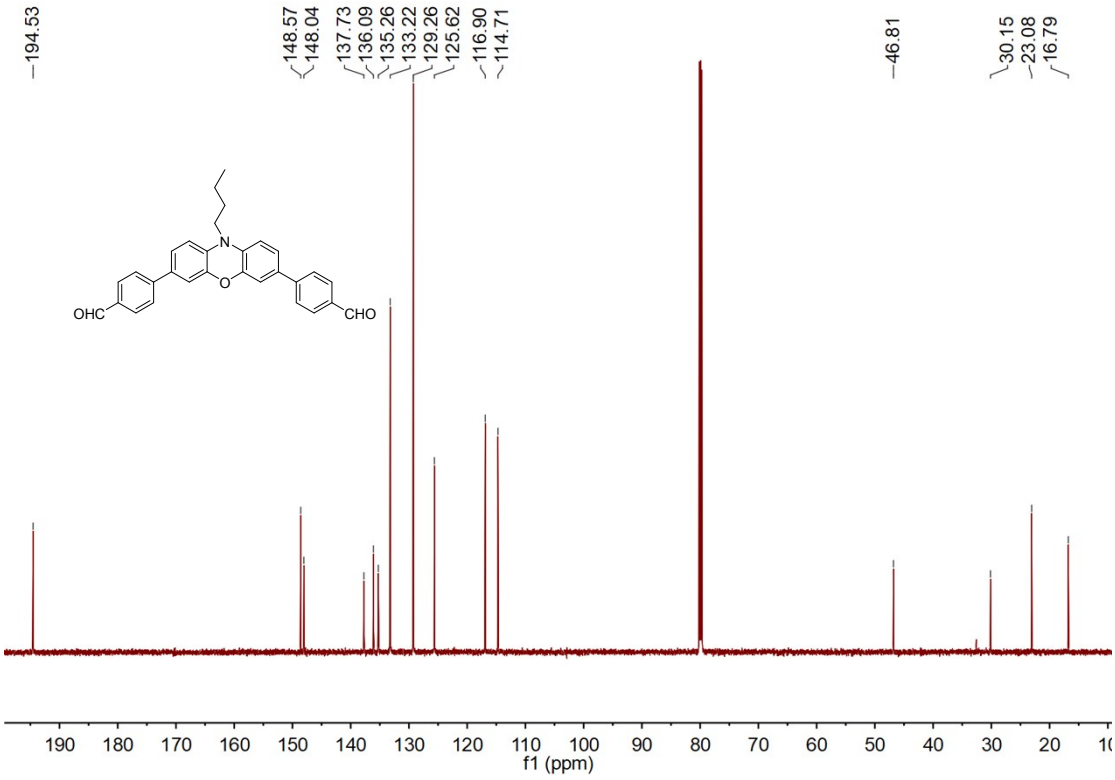


Fig. S27 ^{13}C NMR spectrum of **APPo**.

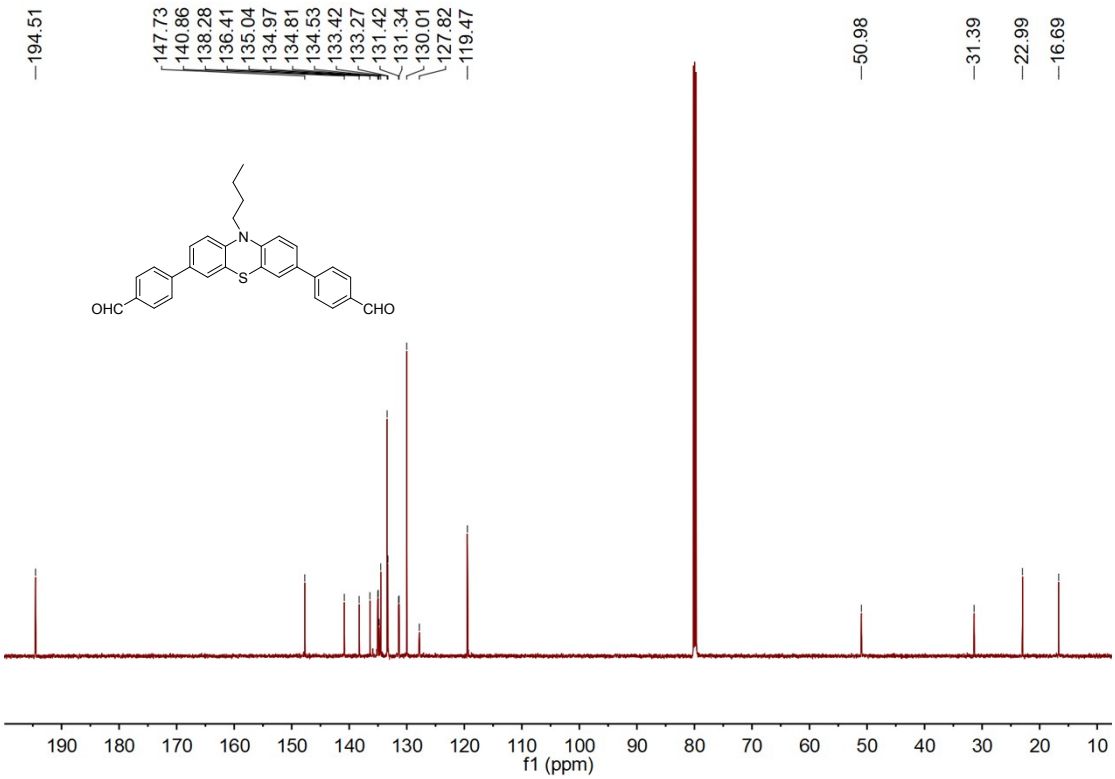


Fig. S28 ^{13}C NMR spectrum of **APPt**.

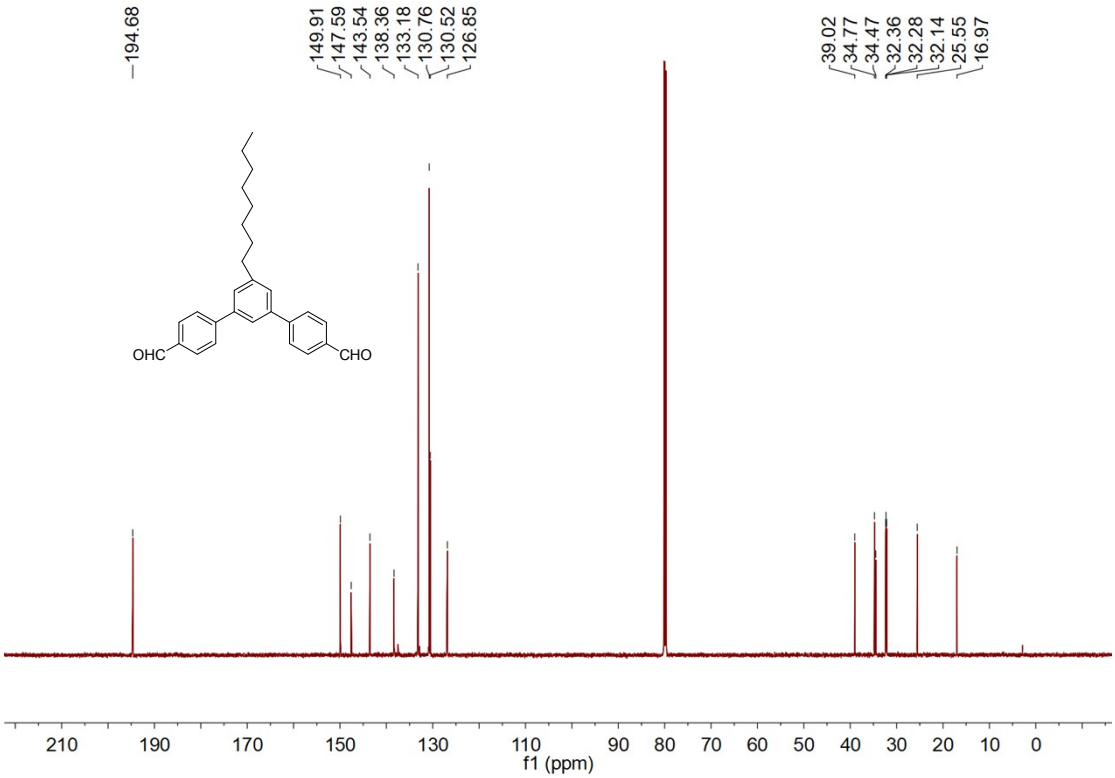


Fig. S29 ^{13}C NMR spectrum of **APBz**.