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Supporting Information for:

Stable Room Temperature Ferroelectricity in Hydrogen-bonded Supramolecular Assemblies of Ambipolar π -Systems

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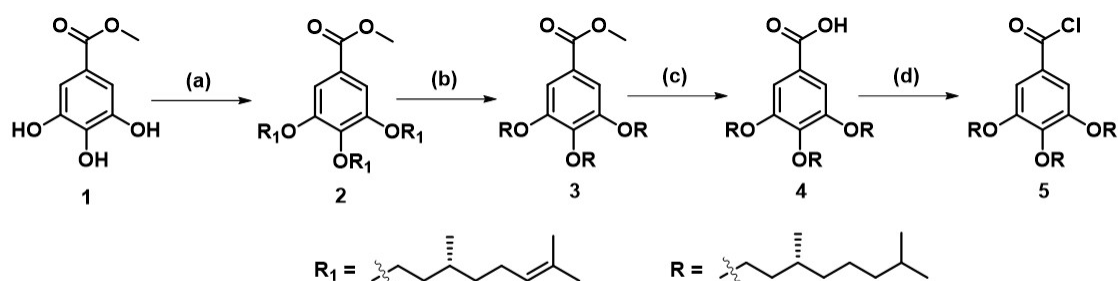
Table S1. Ferroelectric properties of the AD_nA molecules.

Entry	Ferroelectricity		
	P _s (μC/cm ²)	P _r (μC/cm ²)	E _c (kV/cm)
AD ₁ A	1.1	1.0	2.8
AD ₂ A	1.9	0.7	1.6
AD ₃ A	0.7	0.3	1.7
AD ₄ A	0.07	0.06	2.7

Experimental Procedures

Materials and methods

Reagents and solvents were purchased from available commercial sources and purified by standard protocols as reported in the literature.¹ Spectroscopy grade solvents were used for all physical and spectroscopy studies. ¹H and ¹³C NMR spectra were recorded in Bruker DPX-400 MHz and Bruker DPX-300 MHz spectrometer and peaks were calibrated against TMS as the internal standard. HRMS experiments were carried out on Electron spray ionization (ESI) technique Q-tof-micro quadrupole mass spectrometer (Micro mass). Matrix-Assisted Laser Desorption Ionization (MALDI) mass were recorded on a Bruker ultrafleXtreme MALDI-TOF/TOF system. FT-IR spectra were recorded in a Perkin Elmer Spectrum 100FT-IR spectrometer. UV-Vis experiments were performed in a JASCO V-750 UV-visible spectrometer. AFM images were captured in Bruker Innova-S 2 instrument in tapping mode. TEM images were recorded in JEOL-2010EX instrument operating at an accelerating voltage of 200 KV. Electrochemical (CV) measurements were performed using a CHI620E electrochemical analyzer (CH Instruments, USA). Multicell micro-DSC from TA instrument was used for examining the thermodynamic properties at a heating rate of 1 °C/min under N₂ atmosphere. PXRD of the dropcast films were recorded using a Rigaku SmartLab X-ray diffractometer (Cu K α radiation, λ = 1.54 Å) with a voltage of 40 kV and current of 110 mA.



Reagents and conditions : (a) S-citronellyl bromide, K₂CO₃, KI, dry CH₃CN, 90 °C, 36 h, 81%; (b) H₂- Pd, 50 psi, 6 h, quantitative yield; (c) KOH, EtOH, 80 °C, 8 h, 93%; (d) SOCl₂, dry DCM, 0°C-rt, 6 h, quantitative yield.

Synthesis.

Scheme S1 Synthesis of the chiral wedge.

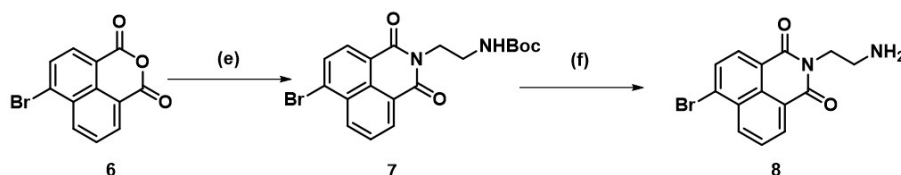
Compound 2: Commercially available methyl 3,4,5-trihydroxybenzoate (1.0 gm, 5.43 mmol), (S)-(+)-citronellyl bromide (3.73 gm, 17 mmol), anhydrous K₂CO₃ (3.75 gm, 27.15 mmol) and catalytic amount of KI were taken in a 100 ml round bottom flask together with 20 ml dry

CH₃CN and the reaction mixture was stirred at 90 °C for 36 h under inert atmosphere. After that, the reaction was stopped, cooled to room temperature and poured into 100 mL water and extracted with ethyl acetate (3 x 30 ml). The organic layer was washed with brine (3 x 10 ml), dried over anhydrous Na₂SO₄ and concentrated under vacuum to get the crude product as brown oil which was purified by column chromatography using basic alumina as the stationary phase and 2% ethyl acetate/hexane as the eluent to get the pure product as colourless oil. Yield: 2.6 gm (81%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 7.25 (s, 2H), 5.10 (t, 3H), 4.10-4.01 (m, 6H), 3.89 (s, 3H), 2.05-1.21 (m, 39H), 0.97 (m, 9H). HRMS (ESI): [M+H]⁺ calculated for C₃₈H₆₂O₅: 599.4605; found: 599.4710.

Compound 3: To a solution of compound **2** (2.6 g, 4.35 mmol) in 20 mL ethyl acetate, activated palladium-charcoal (10%, 260 mg) was added and the reaction mixture was stirred at rt in a high-pressure reaction vessel under 50 psi pressure of hydrogen gas for 12 h. After that, the solution was passed through short celite column to remove the catalyst and the filtrate was concentrated in vacuum to obtain the desired amine as light-yellow oil which was used in the next step without any further purification. Yield = 2.63 g (quantitative yield). ¹H NMR (CDCl₃, 300 MHz, TMS): δ (ppm) = 7.25 (s, 2H), 4.11-4.00 (m, 6H), 3.89 (s, 3H), 1.88- 1.12 (m, 30H), 0.92-0.85 (m, 27H). HRMS (ESI): [M+H]⁺ calculated for C₃₈H₆₈O₅: 605.5075; found: 605.5225.

Compound 4: To a solution of compound **3** (2.6 gm, 4.3 mmol) in ethanol (15 ml), aqueous KOH solution (1.5 g in 10 ml H₂O) was added and the reaction mixture was refluxed for 6 h at 80 °C. The reaction mixture was allowed to cool to rt and acidified with cold dil. HCl solution (50 ml). A white precipitate came out, which was filtered and washed with distilled water and dried under vacuum to get the crude product as white solid which was used for the next step without further purification. Yield: 2.35 g (93%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 7.31 (s, 2H), 4.15-4.03 (m, 6H), 1.90-1.16 (m, 30H), 0.96-0.85 (m, 27H). HRMS (ESI): [M+K]⁺ calculated for C₃₇H₆₆O₅: 629.4546; found: 629.4547.

Compound 5: To a solution of compound **4** (2.35 g, 4.0 mM) in 20 ml DCM, freshly distilled thionyl chloride (4.76 g, 2.9 ml, 40.0 mM) was added dropwise at 0 °C with constant stirring. After that, the reaction mixture was allowed to come to room temperature and stirred for



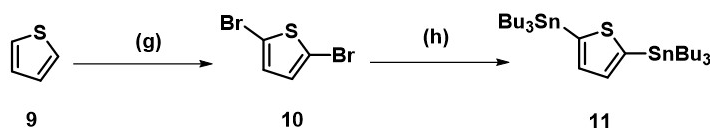
Reagents and conditions : (e) (Boc)N-ethylene diamine, EtOH, 70 °C, 82%; (f) TFA-DCM, 3h, rt, quantitative yield.

another 12 h under inert atmosphere. Then, thionyl chloride was removed by distillation and the brownish pasty mass was dried under vacuum for 6 h which was used for the next step without further purification. Yield: 2.44 g (quantitative yield).

Scheme S2 Synthesis of compound 8.

Compound 7: Commercially available 4-Bromo-1,8-naphthalic anhydride (2.0 g, 7.22 mmol) and mono Boc-protected ethylene diamine (1.28 g, 8.0 mmol) were taken together in a 100 mL round bottom flask equipped with a reflux condenser and a magnetic stirring bar. The reaction mixture was dispersed in 20 ml of ethanol and stirred at 70 °C for 12 h. Then the reaction mixture was allowed to cool down to room temperature and diluted by 20 ml of ethanol further. The resulting solid precipitate was filtered and washed with ethanol a few times and dried under vacuum to get compound **7** as a white solid. Yield = 2.48 g (82%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.62 (d, 1H), 8.60 (d, 1H), 8.52 (d, 1H), 8.37 (d, 1H), 8.00 (d, 2H), 7.82-7.77 (dd, 1H), 4.99 (s, 1H), 4.34-4.30 (t, 2H), 3.52- 3.50 (m, 2H), 1.27 (s, 9H). HRMS (ESI): [M+Na]⁺ calculated for C₁₉H₁₉BrN₂O₄: 441.0426; found: 441.0427.

Compound 8: To a solution of compound **7** (1.5 g, 3.58 mmol) in 10 ml dry DCM, trifluoroacetic acid (1.0 ml) was added dropwise at 0 °C with constant stirring. After that, the reaction mixture was allowed to come to room temperature and stirred under inert atmosphere for



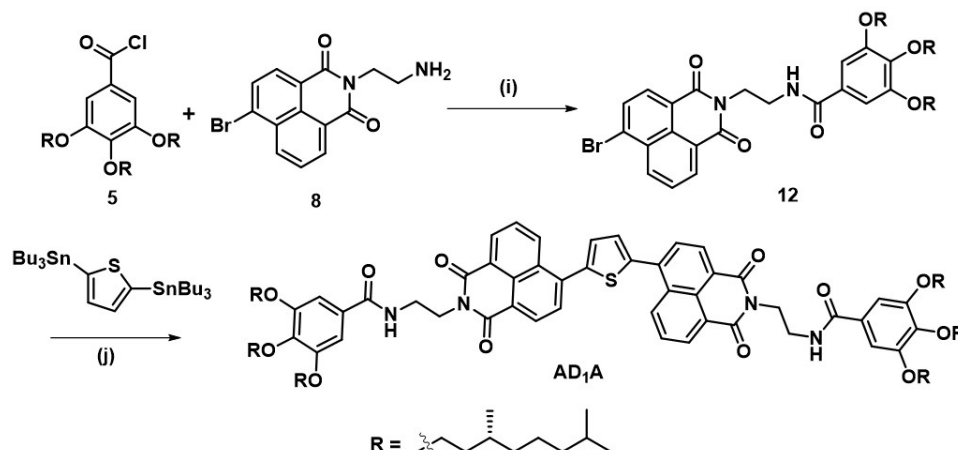
Reagents and conditions : (g) NBS, dry DMF, 16 h, rt, 95%; (h) nBuLi, dry THF, Bu₃SnCl, 8h, -78°C-rt, 91%.

3h. Then, the solvent was evaporated to obtain the desired product as white solid which was used in the next step without further purification. Yield: 1.14 g (quantitative yield). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.71-8.65 (m, 3H), 8.13 (d, 1H), 7.94-7.89 (m, 1H), 4.60 (s, 2H), 3.62 (s, 2H). HRMS (ESI): [M+H]⁺ calculated for C₁₄H₁₁BrN₂O₂: 318.0012; found : 319.0079.

Scheme S3 Synthesis of compound 11.

Compound 10: A solution of compound **9** (1.0 g, 11.89 mmol) in 5 ml dry DMF was stirred overnight under inert atmosphere along with N-bromosuccinimide (2.12 g, 11.9 mol) at room temperature. After that, the reaction mixture was poured into 100 mL water and extracted with ethyl acetate (3 x 30 ml). The organic layer was washed with brine (3 x 10 ml), dried over anhydrous Na₂SO₄ and concentrated on vacuum to get the crude product as brown oil which was used in the next step without further purification. Yield: 2.73 g (95%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 6.84 (s, 2H). HRMS (ESI): [M+H]⁺ calculated for C₄H₂Br₂S: 240.8252; found: 240.8281.

Compound 11: To a solution of compound **10** (2.0 g, 8.27 mmol) in 20 ml dry THF at -78 °C, was added 10.4 ml of n-BuLi (2.0 M) under Ar atmosphere. After that, tributyltinchloride (5.28g, 4.5 ml, 16.54 mmol) was added dropwise and then the reaction mixture was stirred overnight at room temperature. After that, the reaction mixture was diluted by adding 50 ml of hexane. Then the organic part was washed with brine (2 x 10 ml), dried over anhydrous Na₂SO₄ and concentrated under vacuum to get the crude product as light brown oil. Further



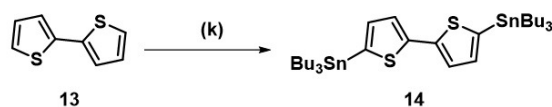
Reagents and conditions : (i) Et₃N, dry DCM, 12h, 0°C-rt, 84%; (j) Pd(PPh₃)₄, dry toluene, 24h, 90°C, 81%.

purification was done by column chromatography (1:9 DCM/Hexane) to obtain compound **11** as yellow oil. Yield: 4.98 g (91%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 7.34 (s, 2H), 1.60-1.55 (m, 12H), 1.37-1.27 (m, 12H), 1.13-1.09 (m, 12H), 0.95-0.83 (m, 18H). HRMS (ESI): [M]⁺ calculated for C₂₈H₅₆SSn₂: 664.2147; found: 664.2366.

Scheme S4 Synthesis of compound AD₁A.

Compound 12: A solution of compound **5** (1.0 g, 1.64 mmol) in 10 ml of dry DCM was added dropwise to an ice-cold mixture of compound **8** (523 mg, 1.64 mmol) and triethylamine (165 mg, 0.23 ml, 1.64 mmol) in 5 ml dry DCM. After the addition was completed, the reaction mixture was stirred at room temperature for 12 h under inert atmosphere. Then it was diluted with 30 ml DCM and washed with H₂O (2 x 10 ml) followed by saturated NaHCO₃ solution (1 x 30 ml) and brine (1 x 30 ml). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under vacuum to get the crude product as brown pasty mass which was purified by column chromatography using silica gel (100-200) as a stationary phase and 1% MeOH/DCM as eluent to get the pure product as light-yellow solid. Yield: 1.23 gm (84%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.67-8.58 (m, 2H), 8.42 (d, 1H), 8.05 (d, 1H), 7.87-7.82 (m, 1H), 6.95 (s, 2H), 4.55-4.51 (t, 2H), 4.06-3.95 (m, 6H), 3.87-3.82 (m, 2H), 1.90-1.28 (m, 30H), 0.96-0.85 (m, 27H). HRMS (ESI): [M+H]⁺ calculated for C₅₁H₇₅BrN₂O₆: 891.4817; found : 891.4922.

AD₁A: Compound **11** (185 mg, 0.28 mmol) and compound **12** (500 mg, 0.56 mmol) were dissolved together in anhydrous toluene (5 ml) and bubbled with Ar gas for 10 min. After that, it was transferred into a 50 ml Schlenk tube. Tetrakis(triphenylphosphine) palladium (Pd(PPh₃)₄) (64 mg, 0.056 mmol) was added and the reaction mixture was heated at 90 °C for 24h under N₂ atmosphere. Then the solution was filtered through celite pad and concentrated under vacuum to get crude product which was purified by column chromatography using silica gel as the stationary phase and 2% MeOH/DCM as the eluent to obtain AD₁A as a red solid. Yield: 345 mg (81%). Melting point: 112±2 °C. ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.70-8.59 (m, 4H), 7.93-7.76 (m, 6H), 7.49 (s, 2H), 7.03 (bs, 2H), 6.99 (s, 4H), 4.57 (m, 4H),



Reagents and conditions : (k) nBuLi, dry THF, Bu₃SnCl, 8h, -78°C-rt-65°C, 93%.

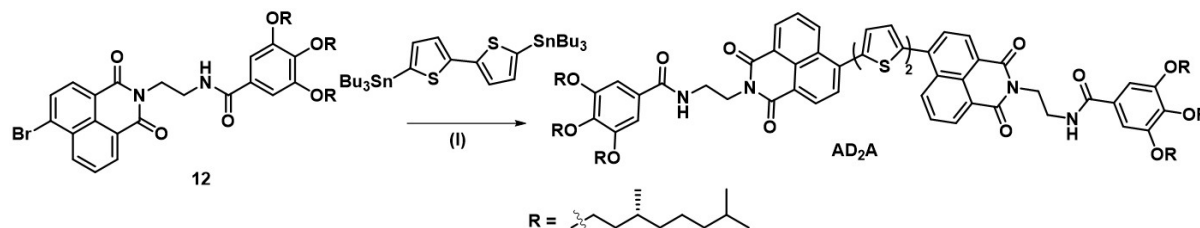
4.07- 3.95 (m, 12H), 3.87 (m, 4H), 1.88-1.10 (m, 60 H), 0.94-0.79 (m, 54 H). ¹³C NMR (75 MHz, CDCl₃, TMS): δ (ppm) = 167.5, 165.1, 164.8, 153.1, 142.1, 140.9, 138.8, 134.5, 132.7, 132.0, 131.7, 131.1, 130.0, 129.9, 129.17, 128.9, 127.7, 127.1, 122.9, 122.2, 105.4, 71.8, 71.8, 67.5, 40.6, 39.7, 39.5, 39.4, 37.6, 37.5, 36.5, 30.0, 29.8, 28.1, 24.9, 24.8, 22.84, 22.74, 19.74, 19.69. MALDI TOF (Matrix - DHB): [M+Na]⁺ calculated for C₁₀₆H₁₅₂N₄O₁₂S: 1728.1025; found : 1727.1802.

Scheme S5 Synthesis of compound 14.

Compound 14: To a solution of compound **13** (500 mg, 3.0 mmol) in 10 ml dry THF at -78 °C, was added 2.8 ml of n-BuLi (2.0 M) under Ar atmosphere. After a white precipitate appeared, the reaction mixture was allowed to reach to room temperature and tributyltinchloride (1.98 g, 1.65 ml, 6.1 mmol) was added dropwise. Then the reaction mixture was stirred at refluxing condition for 1 h. After that, the reaction mixture was allowed to come to room temperature and diluted by adding 30 ml of hexane. Then the organic part was washed with 1 (M) Na₂CO₃ and dried over anhydrous Na₂SO₄ and concentrated on vacuum to get the crude product as light brown oil. Further purification was done by column chromatography (1:9 DCM/Hexane) to obtain compound **14** as brown oil. Yield: 2.0 g (93%). ¹H NMR (300 MHz, CDCl₃,

TMS): δ (ppm) = 7.29 (d, 2H), 7.05 (d, 1H), 1.60-1.53 (m, 12H), 1.38-1.26 (m, 12H), 1.14-1.08 (m, 12H), 0.94-0.86 (m, 18H). HRMS (ESI): $[M]^+$ calculated for $C_{32}H_{58}S_2Sn_2$: 746.2024; found: 746.2311.

AD₂A: Compound **14** (208.4 mg, 0.28 mmol) and compound **12** (500 mg, 0.56 mmol) were dissolved together in anhydrous toluene (5 ml) and bubbled with Ar gas for 10 min. After that, it was transferred into a 50 ml Schlenk tube. Tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$) (64 mg, 0.056 mmol) was added and the reaction mixture was heated at 90 °C for 24h under N_2 atmosphere. Then the solution was filtered through celite pad and concentrated under high vacuum to get crude product which was purified by column chromatography

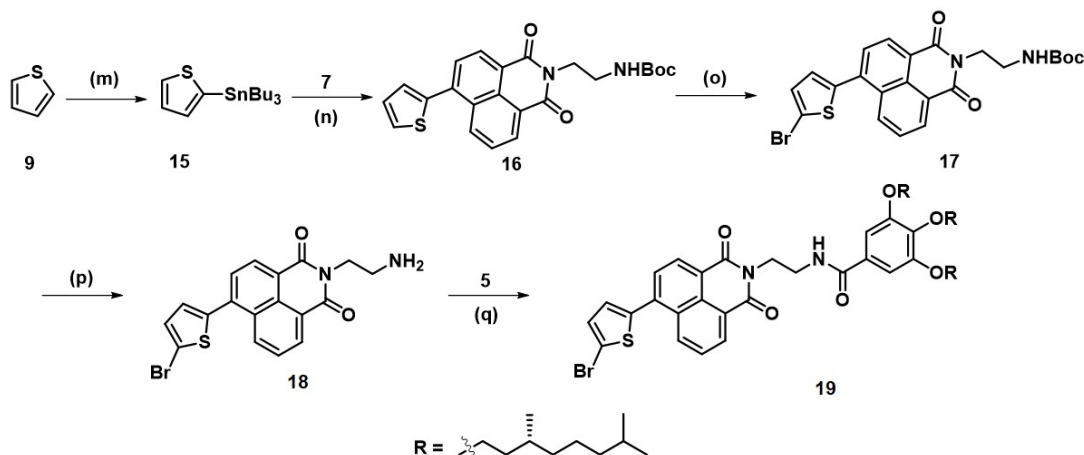


Reagents and conditions : (l) $Pd(PPh_3)_4$, dry toluene, 24h, 90°C, 80%.

using silica gel as the stationary phase and 2% MeOH/DCM as the eluent to obtain AD₂A as red solid. Yield: 400 mg (80%). Melting point: 115±2 °C. ¹H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 8.74-8.59 (m, 4H), 7.87-7.54 (m, 6H), 7.42-7.28 (m, 4H), 7.09 (bs, 2H), 6.99 (s, 4H), 4.57-4.55 (m, 4H), 4.07-3.98 (m, 12H), 3.87-3.86 (m, 4H), 1.89-1.14 (m, 60 H), 0.97-0.79 (m, 54 H). ¹³C NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 167.6, 165.2, 164.9, 153.1, 140.7, 139.3, 139.9, 138.7, 132.3, 132.2, 131.9, 131.7, 131.1, 130.2, 130.0, 129.3, 129.2, 128.7, 128.6, 128.2, 127.6, 127.5, 127.1, 125.5, 125.3, 124.6, 122.9, 121.6, 105.4, 71.8, 67.5, 40.6, 39.5, 39.4, 37.6, 37.5, 36.5, 30.1, 29.8, 28.1, 24.9, 22.7, 19.7. MALDI TOF (Matrix - DHB): $[M+K]^+$ calculated for $C_{110}H_{154}N_4O_{12}S_2$: 1826.0642; found : 1825.9937.

Scheme S6 Synthesis of compound AD₂A.

Compound 15: To a solution of compound **9** (1.0 g, 11.88 mmol) in 20 ml of dry THF at -78 °C, was added 4.75 ml of n-BuLi (2.0 M) under Ar atmosphere. After 30 min, tributyltinchloride (4.25 g, 3.5 ml, 13.07 mmol) was added dropwise and the reaction mixture was stirred at room temperature for 8 h. After that, the reaction mixture was diluted by adding 30 ml of hexane. Then the organic part was washed with 1 (M) Na_2CO_3 and dried over anhydrous Na_2SO_4 and concentrated under vacuum to get the crude product as light brown oil which was used in the next step without further purification. Yield: 3.95 g (89%). ¹H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 7.64 (d, 1H), 7.26 (t, 1H),



Reagents and conditions : (m) nBuLi, dry THF, Bu_3SnCl , 8h, -78°C-rt, 89%. (n) $Pd(PPh_3)_4$, dry toluene, 24h, 90°C, 87%; (o) NBS, dry DMF, 3 h, 0°C-rt, 92%; (p) TFA-DCM, 3h, rt, quantitative yield; (q) Et_3N , dry DCM, 12 h, 0°C-rt, 82%.

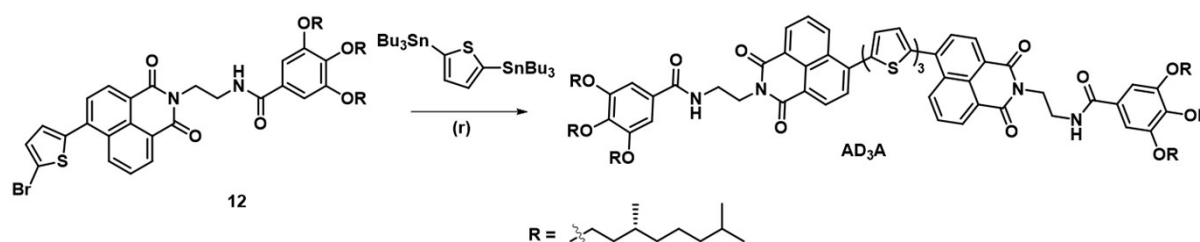
7.19 (d, 1H). HRMS (ESI): $[M]^+$ calculated for $C_{16}H_{30}SSn$: 374.1090; found: 374.0131.

Scheme S7 Synthesis of compound 19.

Compound 16: Compound **7** (1.0 g, 2.38 mmol) and compound **16** (1.0g, 2.85 mmol) were taken together in a 50 ml round bottom flask and dissolved in 10 ml anhydrous toluene and bubbled with Ar gas for 10 min. After that, it was transferred into a 50 ml Schlenk tube. Tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$) (34 mg, 0.029 mmol) was added and the reaction mixture was heated at 90 °C for 24h under N_2 atmosphere. Then the solution was filtered through celite pad and concentrated under vacuum to get crude product which was purified by column chromatography using silica gel as the stationary phase and 1% MeOH/DCM as the eluent to obtain compound **16** as yellow solid. Yield: 864 mg (87%). ¹H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 8.64 (m, 2H), 7.76 (m, 1H), 7.68 (m, 1H), 7.57 (m, 1H), 7.49 (m, 1H), 7.35 (d, 1H), 7.25 (t, 1H), 4.99 (bs, 1H), 4.38 (t, 2H), 3.56-3.54 (m, 2 H), 1.30 (s, 9 H). HRMS (ESI): $[M+Na]^+$ calculated for $C_{23}H_{22}N_2O_4S$: 445.1198; found : 445.1199.

Compound 17: A solution of N-bromosuccinimide (370 mg, 2.0 mmol) in DMF (4.0 ml) was added dropwise to a solution of compound **16** (800 mg, 1.9 mmol) in DMF (6 ml) at 0 °C while being stirred. The reaction mixture was allowed to come to room temperature and stirred for 2 h under inert atmosphere in dark condition. Then it was poured into ice water and the aqueous phase was extracted with EtOAc (3 x 30 ml). The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The obtained crude product was purified by column chromatography using silica gel as the stationary phase and 1% MeOH/DCM as the eluent to obtain compound **17** as yellow solid. Yield: 876 mg (92%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.62 (m, 2H), 7.78 (m, 1H), 7.67 (m, 1H), 7.48 (m, 1H), 7.20 (d, 1H), 7.11 (d, 1H), 4.94 (bs, 1H), 4.38 (t, 2H), 3.55 (m, 2H), 1.29 (m, 9H). HRMS (ESI): [M+Na]⁺ calculated for C₂₃H₂₂N₂O₄S: 523.0303; found : 523.0306.

Compound 18: To a solution of compound **17** (850 mg, 1.7 mmol) in 10 ml dry DCM, trifluoroacetic acid (1 ml) was added dropwise at 0 °C while stirring. After that, the reaction mixture was allowed to come to room temperature and stirred under inert atmosphere for 3h. Then, the solvent was evaporated to obtain the desired product as yellow solid which was used in the next step without further purification. Yield: 680 mg (quantitative yield). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.62 (m, 2H), 7.81 (m, 1H), 7.65 (m, 1H), 7.53 (m, 1H), 7.22 (d, 1H), 7.11 (d, 1H), 4.60 (m, 2H), 3.61 (m, 2H). HRMS (ESI): [M+H]⁺ calculated for C₁₈H₁₃BrN₂O₂S: 400.9889; found : 400.9922.

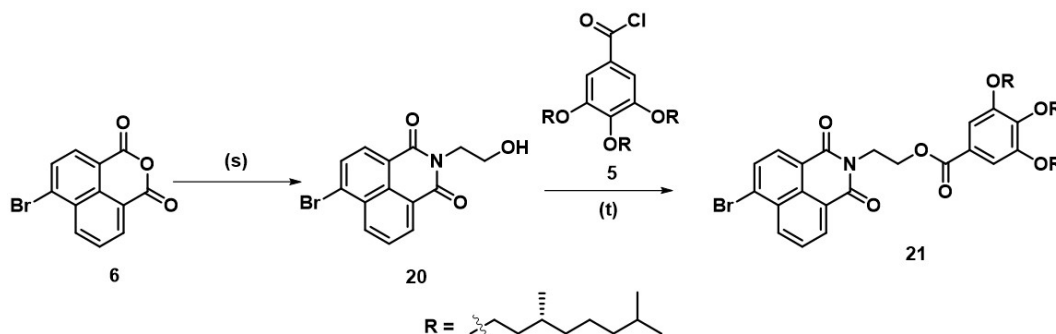


Reagents and conditions : (r) Pd(PPh₃)₄, dry toluene, 24h, 90°C, 78%.

Compound 19: A solution of compound **5** (760 mg, 1.24 mmol) in 8.0 ml of dry DCM was added dropwise to an ice-cold mixture of compound **18** (500 mg, 1.24 mmol) and triethylamine (125 mg, 0.17 ml, 1.24 mmol) in 5 ml dry DCM. After the addition was complete, the reaction mixture was stirred at room temperature for 12 h under inert atmosphere. Then it was diluted with 30 ml DCM and washed with H₂O (2 x 10 ml) followed by saturated NaHCO₃ solution (1 x 30 ml) and brine (1 x 30 ml). The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuum to get the crude product as brown pasty mass which was purified column chromatography using silica gel (100-200) as a stationary phase and 1.5% MeOH/DCM as eluent to get the pure product as brownish-red solid. Yield: 990 mg (82%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.62 (m, 3H), 7.77 (m, 2H), 7.21 (d, 1H); 7.10 (d, 1H), 7.05 (bs, 1H, amide), 6.97 (s, 2H), 4.56 (m, 2H), 4.05 (m, 6H), 3.86 (m, 2H) 1.90-1.13 (m, 30H), 0.96-0.85 (m, 27H). HRMS (ESI): [M+H]⁺ calculated for C₅₅H₇₇BrN₂O₆S: 973.4694; found : 973.4766.

Scheme S8 Synthesis of AD₃A.

AD₃A: Compound **11** (170 mg, 0.256 mmol) and compound **19** (500 mg, 0.51 mmol) were dissolved together in anhydrous toluene (5 ml) and bubbled with Ar gas for 10 min. After that, it was transferred into a 50 ml Schlenk tube. Tetrakis(triphenylphosphine) palladium (Pd(PPh₃)₄) (59 mg, 0.051 mmol) was added and the reaction mixture was heated at 90 °C for 24h under N₂ atmosphere. Then the solution was filtered through celite pad and concentrated under high vacuum to get crude product which was purified by column chromatography using silica gel as the stationary phase and 2% MeOH/DCM as the eluent to obtain AD₃A as red solid. Yield: 374 mg (78%). Melting point: 117±2 °C. ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.76-8.57 (m, 4H), 7.85-7.62 (m, 4H), 7.52-7.43 (m, 2H), 7.36-7.24 (m, 6H), 7.04 (s, 2H), 6.99 (s, 4H), 4.57 (d, 4H), 4.08- 3.98 (m, 12H), 3.87 (t, 2H, J = 8 MHz), 1.89-1.10 (m, 60 H), 0.96-0.80 (m, 54 H). ¹³C NMR (75 MHz, CDCl₃, TMS): δ (ppm) = 167.5, 165.2, 164.9, 153.1, 140.8, 139.6, 138.8, 133.1, 132.2, 131.9, 131.1, 130.0, 129.3, 128.8, 128.7, 128.6, 128.2, 128.1, 128.0, 127.5, 125.5, 125.2, 124.8, 124.6, 122.7, 121.6, 105.4, 71.8, 67.5, 40.7, 39.6, 39.5, 37.6, 37.5, 36.5, 30.0, 29.8, 28.1, 24.9, 22.7, 19.7.



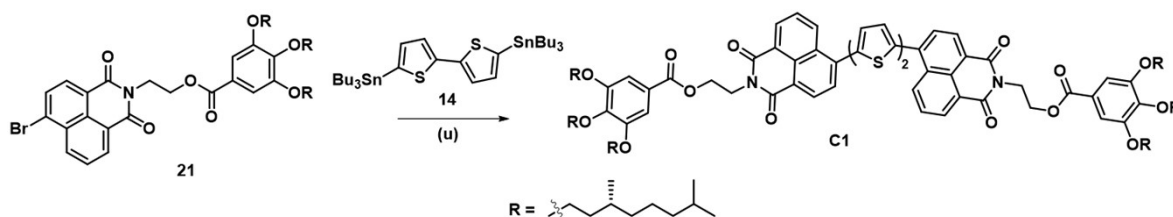
Reagents and conditions : (s) Ethanolamine, EtOH, 70 °C, 85%; (t) EDC, DMAP, dry DCM, 24h, 0°C-rt, 73%.

MALDI TOF (Matrix - DHB): [M+Na]⁺ calculated for C₁₁₀H₁₅₄N₄O₁₂S₂: 1892.078; found : 1892.3368.

Scheme S9 Synthesis of compound 21.

Compound 20: Commercially available 4-Bromo-1,8-naphthalic anhydride (500 mg, 1.80 mmol) and ethanolamine (131 mg, 2.16 mmol) were taken together in a 50 mL round bottom flask equipped with a reflux condenser and a magnetic stirring bar. The reaction mixture was dispersed in 10 ml of ethanol and stirred at 70 °C for 12 h. Then the reaction mixture was allowed to cool down to room temperature and diluted by 10 ml of ethanol further. The resulting solid precipitate was filtered and washed with ethanol a few times and dried under vacuum to get compound **20** as a yellowish-white solid. Yield = 480 mg (85%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.63 (d, 1H), 8.58 (d, 1H), 8.41 (d, 1H), 8.04 (d, 2H), 7.86-7.81 (dd, 1H), 4.46-4.42 (m, 2H), 3.99- 3.96 (m, 2H). HRMS (ESI): [M+Na]⁺ calculated for C₁₄H₁₀BrNO₃: 341.9742; found: 341.9107.

Compound 21: Compound **20** (400 mg, 1.25 mmol) and compound **5** (740 mg, 1.25 mmol) was dissolved together in 10 ml dry DCM followed by the addition of DMAP (25 mg, 0.2 mmol) and stirred at 0 °C for 15 mins. Subsequently, a solution of EDC (290 mg, 1.5 mmol) in 5 ml dry DCM was added dropwise for 15 mins. After the addition was complete, the reaction mixture was stirred at room temperature for 24 h under inert atmosphere. Then it was diluted with 30 ml DCM and washed with 1 (N) HCl (2 x 10 ml) followed by brine (1 x 30 ml). The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuum to get the crude product as brown pasty mass which was purified column chromatography using silica gel (100-200) as a stationary phase and 1% MeOH/DCM as eluent to get the pure product as yellowish-white solid. Yield: 738 mg (73%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.61 (1H, d), 8.53 (1H, d), 8.37 (1H, d), 7.99 (1H, d),

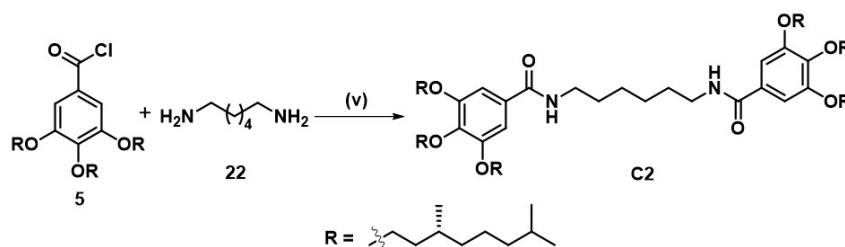


Reagents and conditions : (u) Pd(PPh₃)₄, dry toluene, 24h, 90°C, 77%.

7.78 (1H, d), 7.18 (1H, s), 4.39-4.36 (2H, m), 4.01-3.89 (8H, m), 1.90-1.28 (m, 30H), 0.96-0.85 (m, 27H). HRMS (ESI): [M+H]⁺ calculated for C₅₁H₇₄BrNO₇: 892.4657; found : 892.4617.

Scheme S10 Synthesis of C1.

Compound C1: Compound **21** (400 mg, 0.45 mmol) and compound **14** (172 mg, 0.23 mmol) were dissolved together in anhydrous toluene (5 ml) and bubbled with Ar gas for 10 min. After that, it was transferred into a 50 ml Schlenk tube. Tetrakis(triphenylphosphine) palladium (Pd(PPh₃)₄) (52 mg, 0.045 mmol) was added and the reaction mixture was heated at 90 °C for 24h under N₂ atmosphere. Then the solution was filtered through celite pad and concentrated under vacuum to get crude product which was purified by column chromatography using silica gel as the stationary phase and 1.5% MeOH/DCM as the eluent to obtain AD1A as a red solid. Yield: 317 mg (77%). Melting point: 108±2 °C. ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 8.72-8.57 (m, 6H), 7.95-7.78 (m, 4H), 7.40 (s, 2H), 7.01 (s, 4H), 4.67 (m, 4H), 4.06- 3.96 (m, 12H), 3.87 (m, 4H), 1.88-1.10 (m, 60 H), 0.94-0.79 (m, 54 H). ¹³C NMR (75 MHz, CDCl₃, TMS): δ (ppm) = 166.3, 164.7, 154.1, 142.4, 141.1, 138.9, 134.7, 132.9, 132.5, 131.9, 131.5, 129.7, 128.9, 127.8, 127.2, 125.1, 123.7, 108.4, 71.8, 67.6, 62.7, 40.7, 39.8, 39.5, 37.6, 36.5, 30.0, 28.1, 24.9, 24.8, 22.84, 22.74, 19.74, 19.69. MALDI TOF (Matrix - DHB): [M+Na]⁺ calculated for C₁₁₀H₁₅₂N₂O₁₄S₂: 1812.0583; found :



Reagents and conditions : (v) Et₃N, dry DCM, 0°C-rt, 6 h, 80%.

1811.8828.

Scheme S11 Synthesis of C2.

Compound C2: A solution of compound **22** (39 mg, 0.33 mmol) in 1.0 ml of dry DCM was added dropwise to an ice-cold mixture of compound **5** (400 mg, 0.66 mmol) and triethylamine (70 mg, 0.1 ml, 0.66 mmol) in 2.0 ml dry DCM. After the addition was complete, the reaction mixture was stirred at room temperature for 12 h under inert atmosphere. Then it was diluted with 30 ml DCM and washed with H₂O (2 x 10 ml) followed by saturated NaHCO₃ solution (1 x 20 ml) and brine (1 x 20 ml). The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuum to get the crude product as brown pasty mass which was purified column chromatography using silica gel (100-200) as a stationary phase and 1% MeOH/DCM as eluent to get the pure product as off-white solid. Yield: 333 mg (80%). ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 7.01 (s, 4H), 6.29 (t, 2H, amide), 4.026 (m, 12H), 3.44 (m, 4H), 1.87-1.13 (m, 68H), 0.93-0.85 (m, 54H). ¹³C NMR

(75 MHz, CDCl₃, TMS): δ (ppm) = 167.6, 153.2, 141.2, 129.7, 105.8, 71.8, 67.8, 39.5, 39.4, 37.6, 36.5, 29.9, 29.8, 28.1, 25.8, 24.9, 22.8, 19.7. HRMS (ESI): [M+H]⁺ calculated for C₈₀H₁₄₄N₂O₈: 1262.0931; found : 1262.1016.

Supramolecular assembly related experiments

Sample preparations for self-assembly studies: Stock solutions of the AD_nA-compounds and control molecules were prepared at 2.0 mM concentration by dissolving a given sample in spectroscopy-grade tetrahydrofuran (THF) by gentle heating and ultra-sonication in a hot water bath (45 °C). These solutions were diluted as per volume and strength requirements and used directly for experiments in THF solution of the monomeric dye. For experiments with aggregates in MCH solutions, measured volume of the stock solution in THF was transferred into glass vials and solvent was evaporated by blowing hot air using a hair dryer (50-55 °C). Then to this dry sample a given amount of MCH was added as per concentration and volume requirements of a particular experiment and gently sonicated in a hot water bath (~ 70 °C) for about 2-5 min and kept at room temperature for 1 h prior to any experiment. To check if there was any lag phase for self-assembly, a given sample (AD₂A) in MCH was cooled from 90 °C to rt and then its UV-Vis spectrum was checked at different time point (Fig. S4). No difference was noticed in the spectrum recorded after 1h with that recorded after 6 h, suggesting 1h was enough for equilibration, if any, and for all experiments, samples were used after 1h of sample preparation. Required information about concentration and other parameters are mentioned in the respective figure captions. For AFM experiments, solution of a given sample in MCH (concentration mentioned in the figure caption) was spin-coated on freshly cleaned mica surface and dried in the air for 24 h before imaging. For solid state UV-Vis measurements, MCH solution (c = 0.1 mM) of a given AD_nA sample was drop-casted on a quartz plate and dried for 24 h before the experiment.

Electrochemical studies and band gap calculations:

Cyclic voltammetry: Electrochemical analysis of the AD_nA compounds was carried out in THF (c = 1.0 mM) using a CHI620E electrochemical analyser (CH Instruments, USA) equipped with a three-electrode setup comprising of a glassy carbon working electrode, an auxiliary electrode of platinum wire and a silver wire as the pseudo reference electrode. Tetra-N-butyl-ammonium hexafluorophosphate (TBAPF₆) was used as the supporting electrolyte at 0.1 M concentration. Electrochemical potentials are reported in reference with the Fc/Fc⁺ couple at 298K. Calculation of the HOMO/ LUMO energy level are done using the following equations:

$$E_{\text{HOMO}} = -(E_{\text{Ox1 onset}} - E_{\text{Fc/Fc}^+ \text{ onset}}) - 4.80 \text{ eV}$$

$$E_{\text{LUMO}} = -(E_{\text{Red1 onset}} - E_{\text{Fc/Fc}^+ \text{ onset}}) - 4.80 \text{ eV}$$

$$\Delta E_{\text{CV}} = E_{\text{LUMO}} - E_{\text{HOMO}}, (E_{\text{Fc/Fc}^+ \text{ onset}} \text{ is } 0.5 \text{ vs Ag/AgCl})$$

Calculation of energy gap from UV-Vis spectroscopy: Energy gap was also estimated from the UV-Vis spectrum of AD_nA samples (either in THF or solid state) using the following standard equation:

$$\Delta E_{\text{UV}} = h\nu = hc/\lambda \quad (h = \text{Planks constant} = 6.626 \times 10^{-34} \text{ Joules.sec}; C = 3 \times 10^8 \text{ meter/sec}; \lambda = \text{wavelength at onset of absorption, } 1.0 \text{ eV} = 1.6 \times 10^{-19} \text{ Joules}).$$

Experimental details of ferroelectric studies:

Preparation of AD_nA, C1 and C2 films for ferroelectric measurements: 5.0 mM concentration solutions of AD_nA, C1 and C2 were prepared in spectroscopy grade methylcyclohexane (MCH) via. ultrasonication at rt for 1h. (5× 5) mm ITO coated glass substrates (purchased from Techinstro, India) with surface resistivity ~4 ohm-m were cleaned first with D.I water, absolute ethanol, acetone and then air dried at rt. Films were prepared by spin-coating (Apex Ltd, India, spin speed, acceleration, and time of 500rpm, 20rpm/sec, and 120sec respectively) and kept under vacuum for 24h to dry. The thicknesses of the films were around 0.1mm, as measured by a Mitutoyo Micrometer (Model No- 293-240-30).

Device fabrication for ferroelectric measurements: The ferroelectric and dielectric capacitor device structures were prepared by depositing Ag epoxy (Sigma Aldrich) electrodes (electrode diameter ~ 0.5 mm) both on top of the film and on bottom ITO/glass substrate, and successively attaching 0.1 mm Cu wires to all the Ag electrodes (both top of the film and on ITO coated conducting surface act as a bottom electrode). Several such top electrodes and one bottom Ag electrode were thereby prepared (Fig. S4). Resulting capacitor devices were dried at rt for 1h and used for the ferroelectric and dielectric measurements thereafter. Measurements were repeated for different sets of top-bottom electrodes geometry for all the films in order to obtain consistent data.

Dielectric, leakage current and ferroelectric polarization measurements: The dielectric permittivity vs. temperature measurements were carried out in an inert sealed bespoke chamber with a heating and cooling rate of 2 °C min⁻¹ (using resistor heater), while the dielectric properties were recorded between frequencies of 100 Hz and 1.0 MHz using an impedance analyzer (4100, Wayne Kerr LCR Meter). The ferroelectric properties, including the leakage current were evaluated at different temperatures with a Precision LCII Ferroelectric Tester (Radiant Technologies, Inc.) equipped with a micro-probe station. A constant standard bipolar input profile at 50 -100 Hz, with applied voltages between 5 V to 30 V was used.²⁻³ Artefacts due to dielectric loss during P-E hysteresis loop measurements were corrected by varying the measuring frequency to minimize the leakage current contribution. The leakage current densities in the film capacitors were measured at 298 K by applying a stress voltage of 10 V for a soak period of 100 ms at each voltage step. The heating was carried out using

a PID controlled heater setup (SES Instruments, India) to measure polarizations at different temperatures. The polarization data were collected independently from several top-bottom electrodes combination, and the results were found to be consistent.

Computational details

Structure optimizations of AD₂A have been performed using the Gaussian 16 suite of programs⁴ using the M06-2X^{5,6} hybrid functional with the 6-31G(d,p)⁷ basis set. Harmonic frequency calculations were performed to verify that the structures have no imaginary frequencies. Stacked oligomers of dimer, trimer, tetramer and octamer were also optimized using the same functional. Dipole moments for each of the dimer and the conglomerated units are also computed at the same level of theory. The volume is computed using “volume” keyword in Gaussian. ESP (electrostatic potential) were calculated using the “cubegen” keyword. For a better insight into the structural change in the AD₂A molecule, an oligomer containing 16 layers of AD₂A monomers was studied at higher temperature using the ReaxFF reactive force field molecular dynamics simulation. A box of dimension (70×90×60) Å³ containing an AD₂A oligomer in the centre and 1200 MCH solvent molecules surrounding it, was prepared using NVT simulation. The bond order assisted ReaxFF force fields developed by Fedkin et al.⁸ has been used to study the MCH-AD₂A system in Amsterdam Density Functional (ADF) package.⁹ In our simulation, the timestep was set to 0.25 fs for every iteration to integrate the equation of motion by velocity-verlet algorithm. The system was equilibrated first at a temperature of 300K for 50ps using the NHC thermostat with a 100 fs damping constant to control the temperature of whole system. After minimization the system annealing was done using NVE ensemble in 8 steps at a rate of 2 K/ps until the system reaches at 380 K.¹⁰

Additional Figures

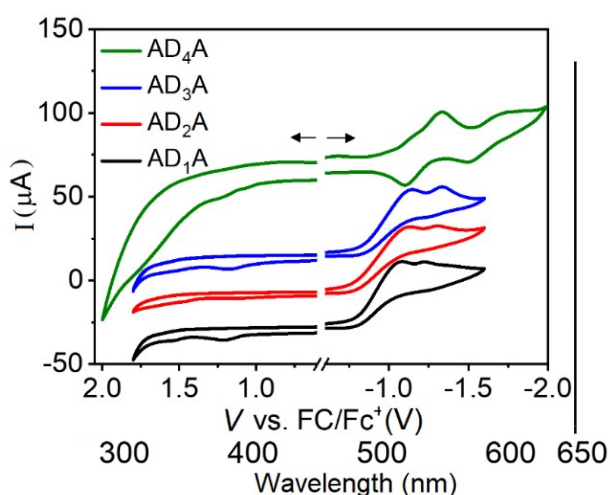
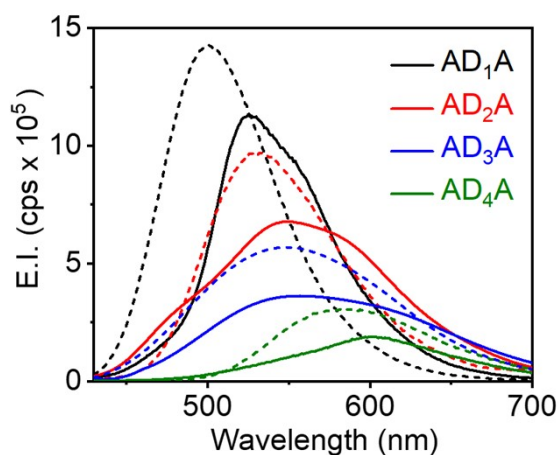


Fig. S1 Cyclic voltammogram of AD₁A, AD₂A, AD₃A and AD₄A against Fc/Fc⁺ ($c = 1.0$ mM in THF; scan rate = 100 mV/sec).

Fig. S2 Absorbance normalized UV-Vis spectra of AD₁A, AD₂A, AD₃A and AD₄A in THF and MCH at 25 °C ($c = 0.1$ mM, $l = 0.1$ cm).

Fig. S3 Emission spectra of AD₁A, AD₂A, AD₃A and AD₄A in THF (broken lines) and MCH (solid lines) at 25 °C ($c = 0.1$ mM, $l = 1.0$ cm, slit = 2/2, $\lambda_{\text{ex}} = 420$ nm).



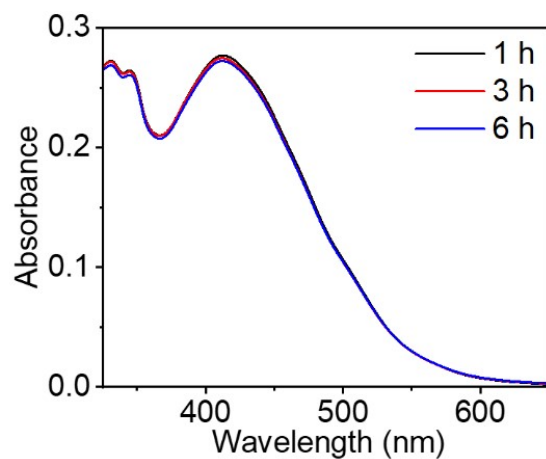


Fig. S4 Representative time dependent UV-Vis spectra of MCH solution of AD₂A at 1h, 3h and 6h after cooling down a hot solution ($c = 0.1$ mM in MCH, $l = 0.1$ cm) from 90 °C to rt.

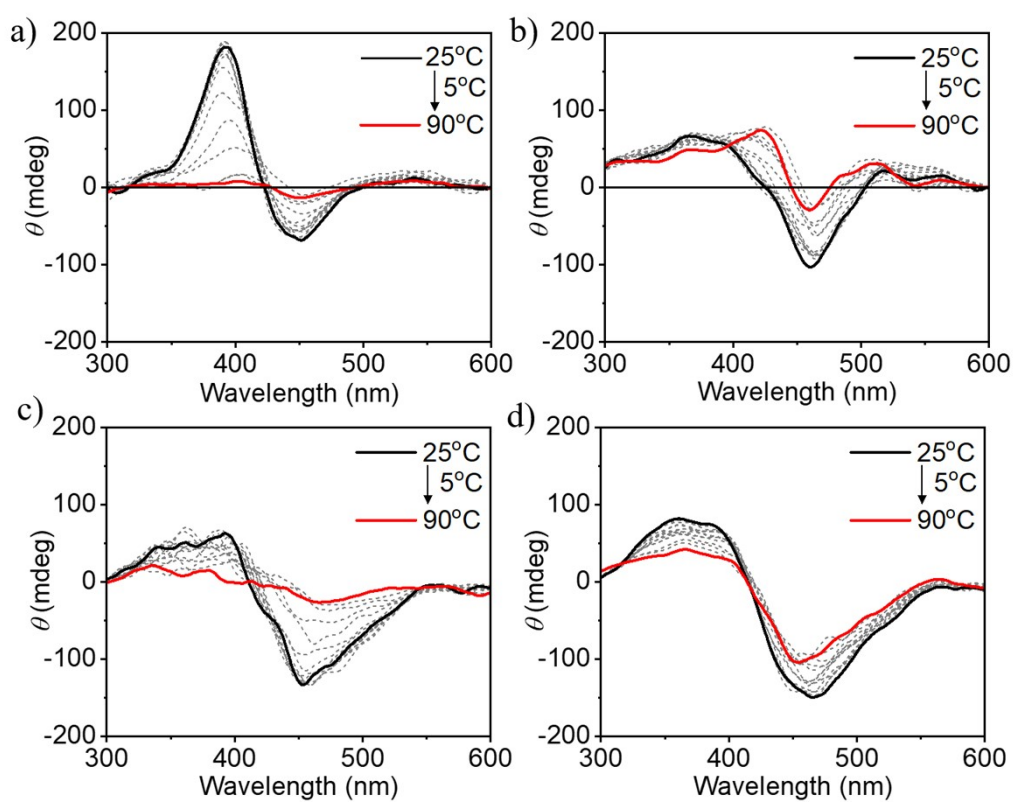


Fig. S5 Temperature dependent CD experiment of (a) AD₁A, (b) AD₂A, (c) AD₃A and (d) AD₄A in MCH ($c = 1.0$ mM, $l = 1.0$ cm) at 5 °C interval.

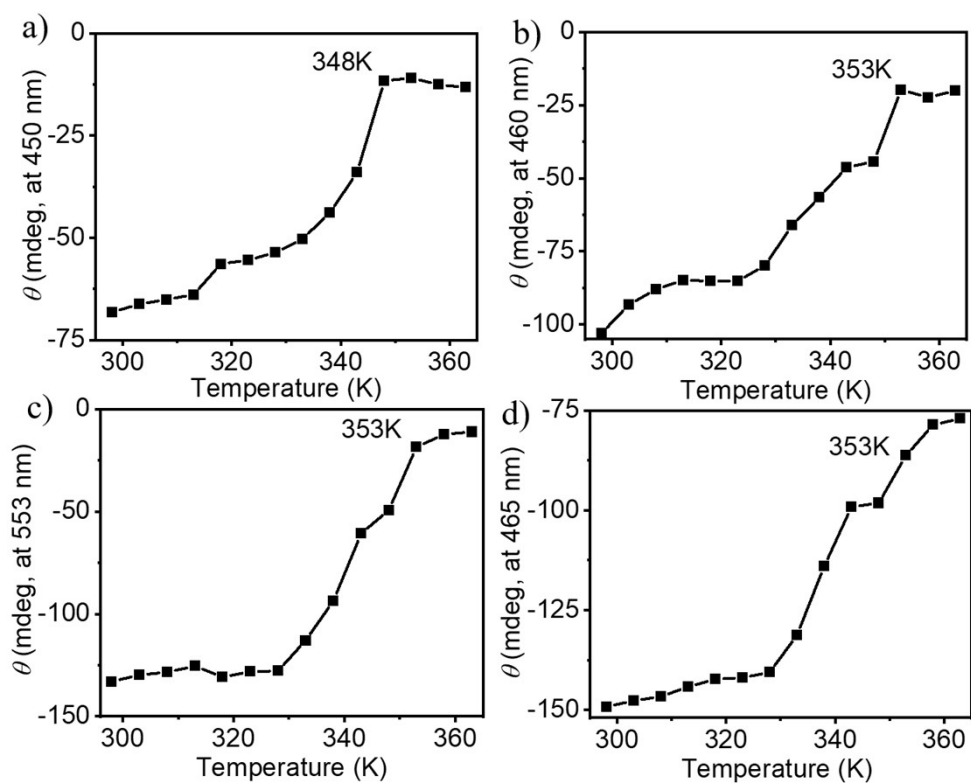


Fig. S6 Temperature dependent change in the CD band intensity of (a) AD₁A, (b) AD₂A, (c) AD₃A and (d) AD₄A in MCH (*c* = 1.0 mM, *l* = 1.0 cm) at a particular wavelength. These curves were constructed from the corresponding data shown in Fig. S5.

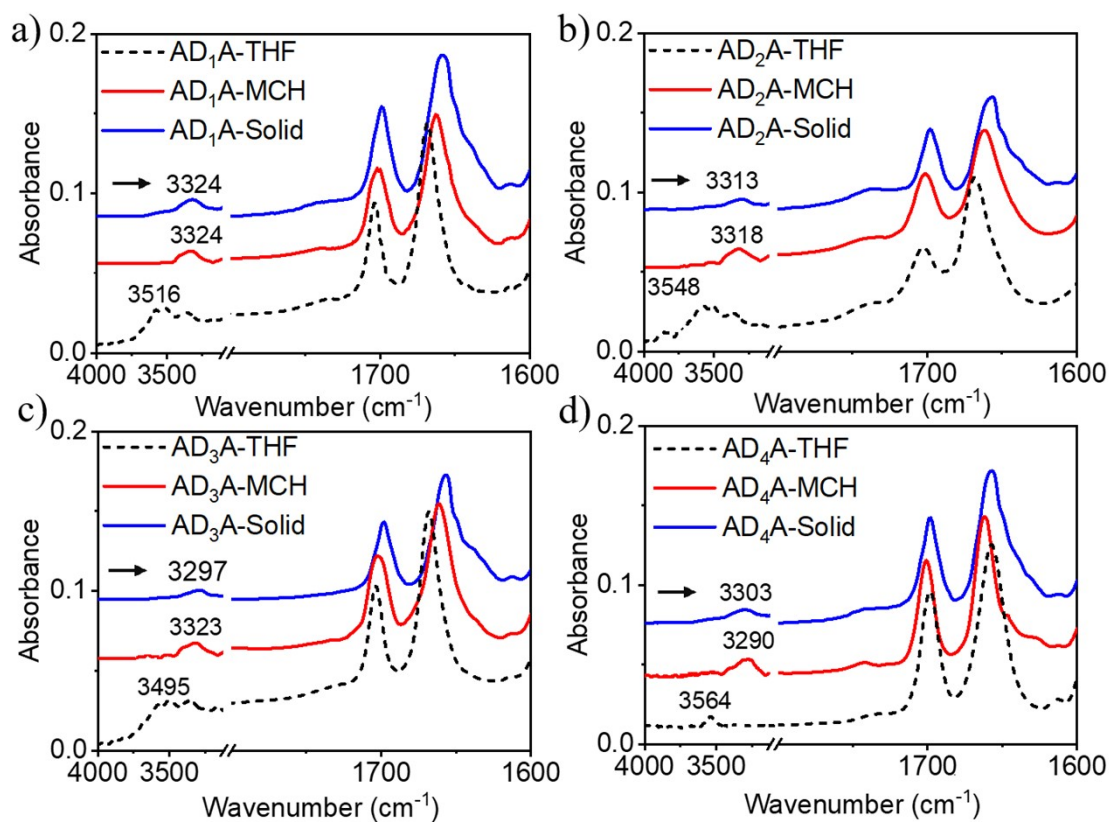


Fig. S7 FT-IR spectra (selected area is shown) of AD₁A, AD₂A, AD₃A and AD₄A in THF (*c* = 2.0 mM), MCH, *c* = 2.0 mM) and in solid state at 25 °C. The arrow indicates shifts of amide N-H stretching band to lower wavenumber in MCH/solid state compared to THF.

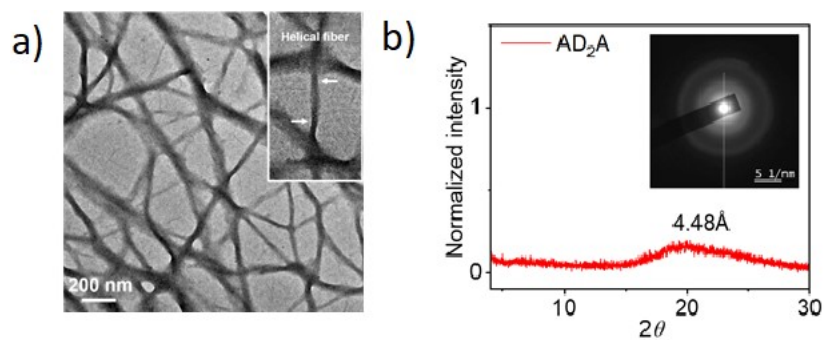


Fig. S8 a) Representative TEM images of AD₂A sample ($c = 0.1$ mM in MCH). Enlarged image in the inset shows helical fibre; b) Powder XRD pattern and SAED analysis (inset, from TEM) of a representative AD₂A sample (prepared from 1.0 mM MCH solution) suggesting lack of crystallinity of the sample.

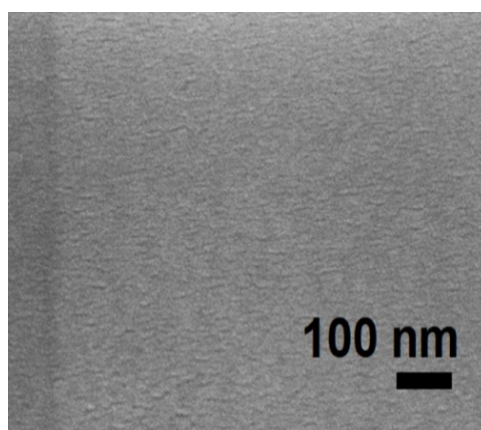


Fig. S9 Representative images of (left) solution ($c = 5.0$ mM) of AD₂A in MCH that was casted on ITO glass by spin coating and (right) film with deposited top and bottom Ag electrodes (inset) fabricated for ferroelectric and dielectric measurements.

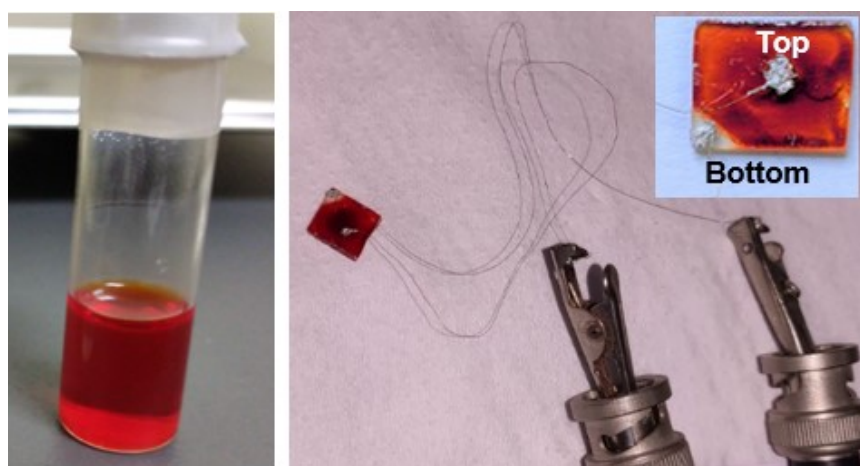


Fig. S10 A representative SEM image of AD_nA, C1, AD₄A-E films prepared by spin coating technique showing the smooth, crack-free surface morphology.

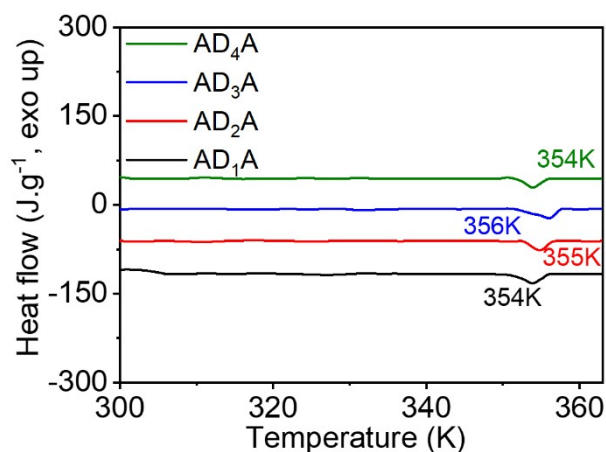
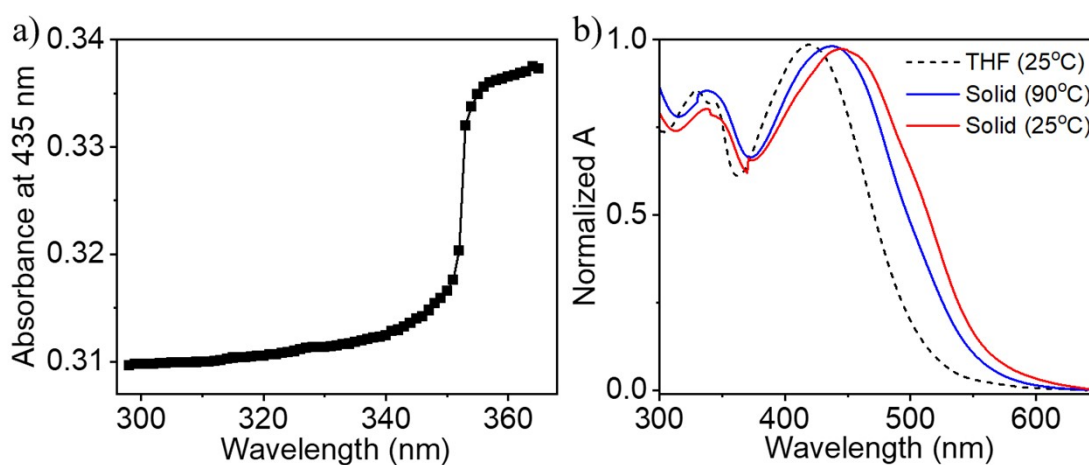


Fig. S11 Micro-DSC traces of ADnA molecules ($c = 1.0$ mM in MCH, scan rate = 1K/min) showing single endothermic peaks near the Curie temperature (T_c). Minor discrepancy between the T_c and the phase transition temperature observed in DSC may be attributed to the fact that the DSC was done in MCH while electrical measurements were done in solid state. This is also evident from slight difference in the



transition temperature observed in variable temperature UV/Vis experiments in solid state (Fig. S12) and in MCH (Fig. S13).

Fig. S12 (a) Variation of absorbance at 435 nm as a function of temperature for AD₂A film as obtained from the variable temperature UV/Vis experiments showing a transition near the T_c ; (b) UV-Vis spectra of AD₂A film at 25°C and 90°C compared to that of monomeric spectra in THF ($c = 0.1$ mM). Partial disassembly is evident at elevated temperature as the band shifts toward the monomeric band although it does not appear to be fully matching with the monomeric band.

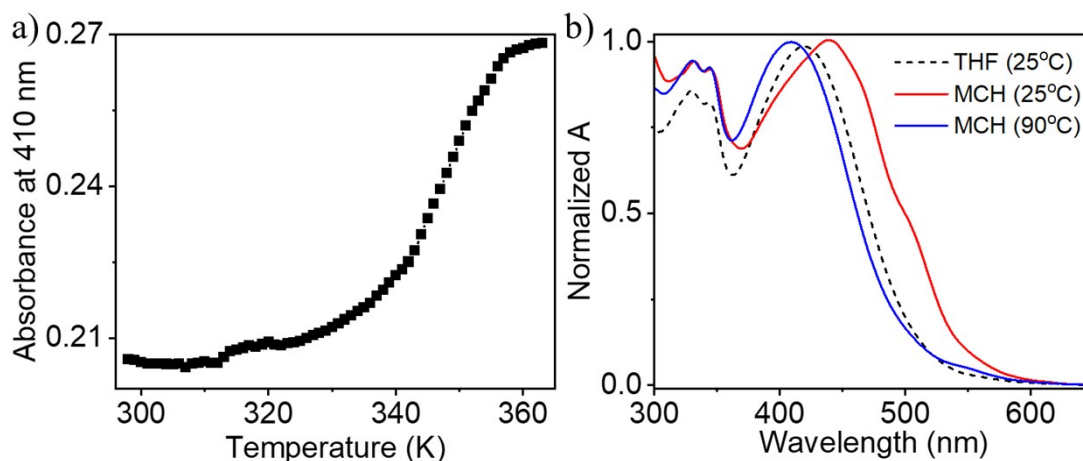


Fig. S13 (a) Variation of absorbance at 410 nm as a function of temperature of AD₂A aggregate in MCH ($c = 0.1$ mM) as obtained from the variable temperature UV-Vis experiments showing a transition similar to that observed in film state (Fig. S12) although at a slightly lower temperature; (b) UV-Vis spectra of AD₂A ($c = 0.1$ mM in MCH, $l = 0.1$ cm) at 25°C and 90°C compared to that of monomeric spectra in THF ($c = 0.1$ mM). Partial disassembly is evident at elevated temperature as the band shifts toward the monomeric band although it does not appear to be fully matching with the monomeric spectrum.

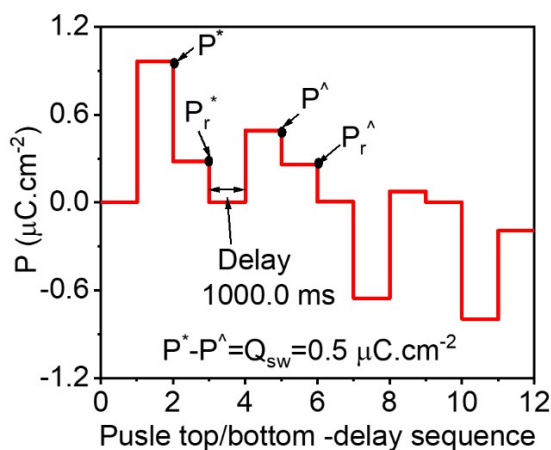


Fig. S14 PUND (Positive Up and Negative Down) sequence based on a series of five pulses, of AD_2A at 1 Hz with inset of switched charge ferroelectric density (QSW).

In PUND a series of voltage pulses are applied and current transitions are measured that result from them allows for separation of the different components of the electrical response of a ferroelectric device. The first pulse is applied to measure the total amount of polarization (P^*) (which includes the right switched charged density due to FE material and leakage current contributions), i.e. [$P^*_{\text{measured}} = P_{\text{switching}} + P_{\text{leakage}}$]. The second pulse (P^\wedge) was used to measure the total amount polarization with excluding or except the switched charged density (QSW). Third ($-P^*$) and Fourth ($-P^\wedge$) pulses are similar to first and second pulses but in negative bias of V_{max} . So that switching charge density (QSW) or contribution to the remanent polarization is extracted from the difference between P^* and P^\wedge polarization as the following equation; $Q_{sw} = (P^* - P^\wedge)$, where P^*_r , P^\wedge_r , $-P^*_r$ and $-P^\wedge_r$ represents the derivative of Positive, Up, Negative and Down voltage respectively. (Rabe et al. Modern Physics of Ferroelectrics: Essential Background in K. Rabe, C. H. Ahn, J.-M. Triscone (Eds.): Physics of Ferroelectrics: A Modern Perspective, Topics Appl. Physics 105, 1–30 (2007), Springer-Verlag Berlin Heidelberg). For AD_2A film, certain pulse width (10 ms) and pulse delay time (1000 ms) is applied to the sample under electric field (10 kV/cm) and the polarization is measured after each pulse. We calculated a Q_{sw} value of $0.5 \mu\text{C}/\text{cm}^2$, sample exhibits a good response towards the ferroelectric properties with the right value of remnant polarization as also can be observed from Figure 4a and 4b. All these evidences speak in favour of presence of switchable ferroelectric domains or presence of significant ferroelectricity in ADnA molecules, highest being observed for AD_2A .

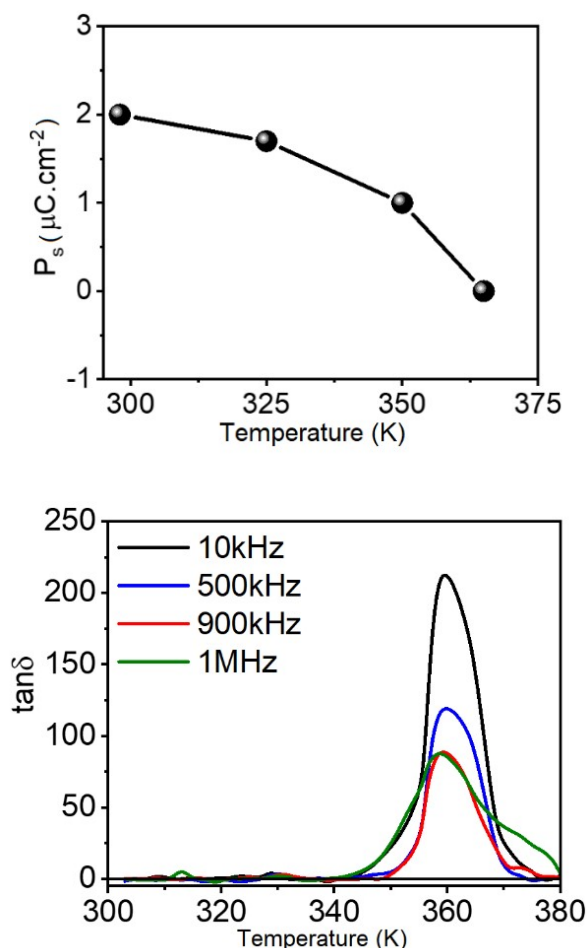


Fig. S15 Low dielectric loss at different frequencies for AD_2A molecules.

Fig. S16 Saturation polarization (P_s) of AD₂A at different temperatures at 50 Hz.

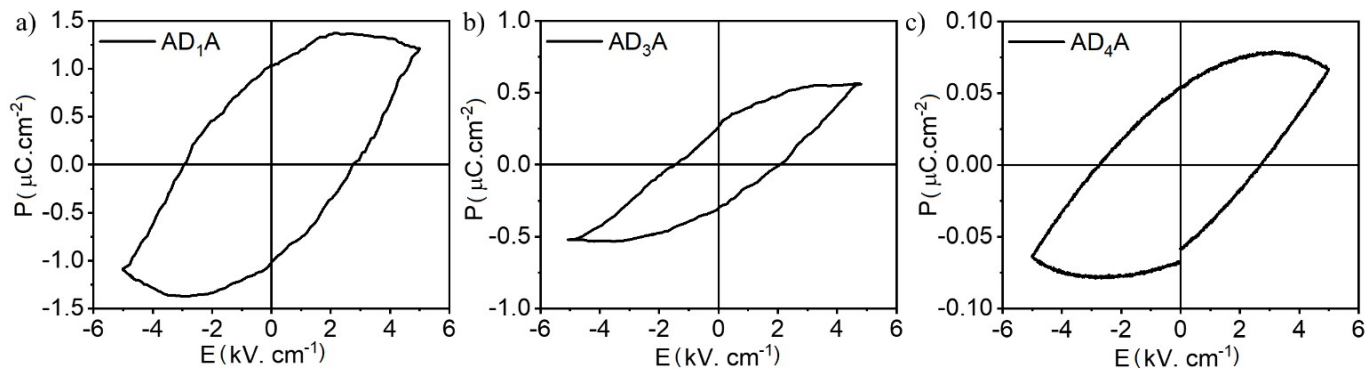


Fig. S17 P - E loops for AD₁A, AD₃A and AD₄A molecules recorded at 50 Hz ($T = 298$ K).

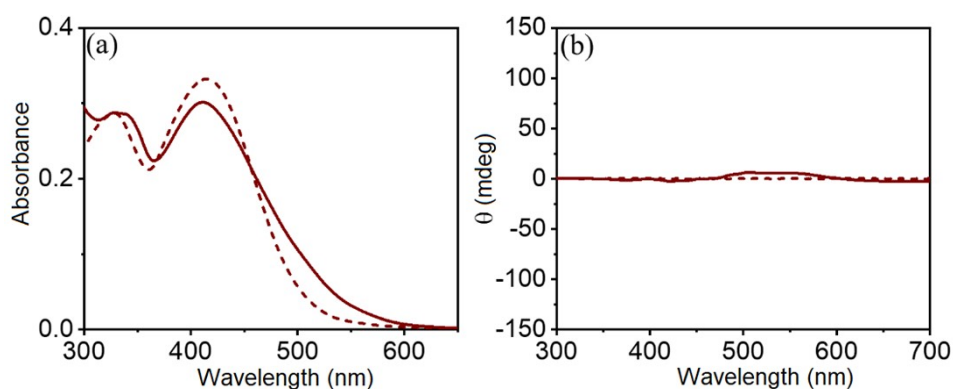


Fig. S18 Solvent dependent (a) UV-Vis ($c = 0.1$ mM, $l = 0.1$ cm) and (b) CD ($c = 1.0$ mM, $l = 0.1$ cm) spectra of C1 in THF (broken lines) and MCH (solid lines) at 25 °C. Minor changes noticed in the UV/Vis spectra is attributed to the solvetochromic effects.

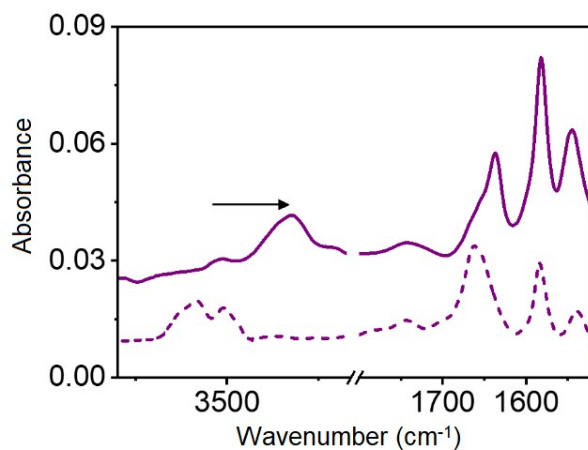


Fig. S19 Solvent dependent FT-IR spectra (selected region) of C2 in THF (broken lines) and MCH (solid lines) at 25 °C ($c = 2.0$ mM). The arrow indicates the shift of the amide N-H stretching peak to lower wavenumber in MCH.

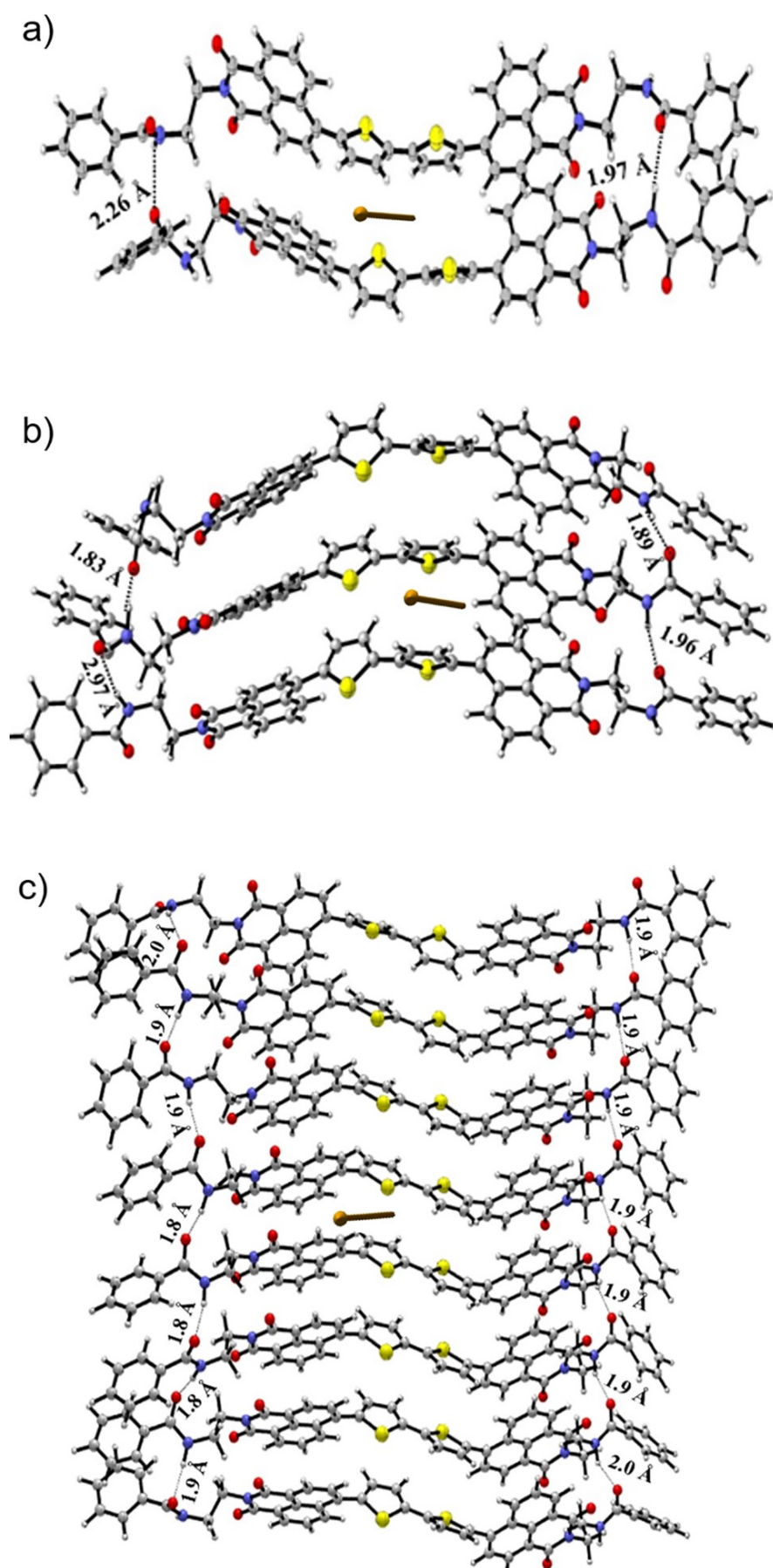


Fig. S20 Optimized structures of different AD₂A stacks, (a) dimer, (b) trimer and (c) octamer; the arrows show the direction of dipole moment in each case. Peripheral alky chains have been removed during optimization.

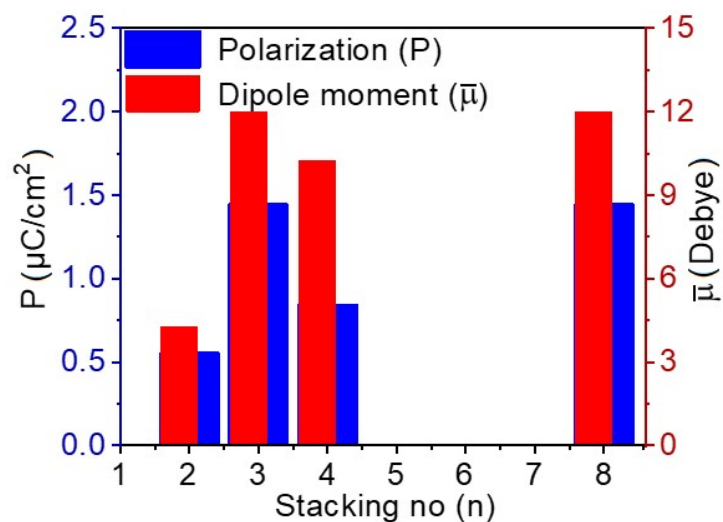


Fig. S21 Variation of the average dipole moment ($\bar{\mu}$, in Debye) and polarization (P, in $\mu\text{C}/\text{cm}^2$) for dimer, trimer, tetramer and octamer of AD_2A (Obtained from computational analysis).

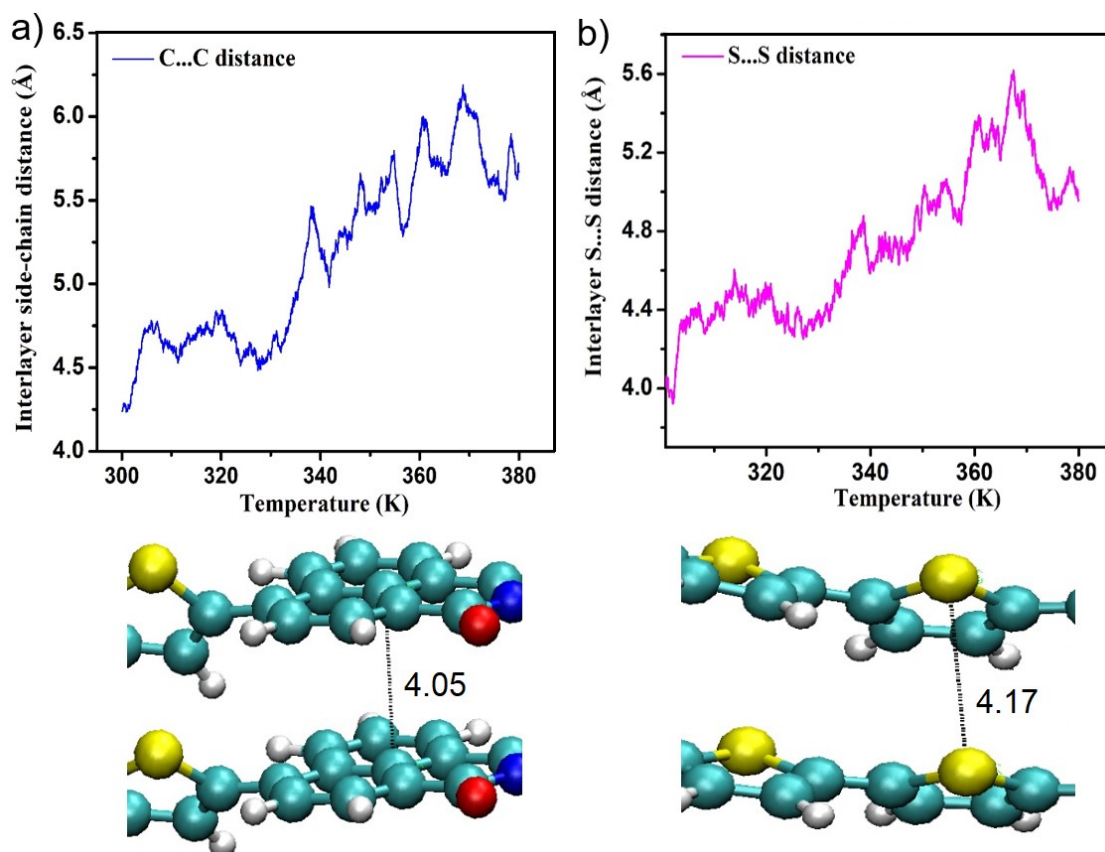


Fig. S22 Variation of the (a) stacked side-chain distances and (b) interlayer S...S distances as the system is heated from 300 K to 380K.

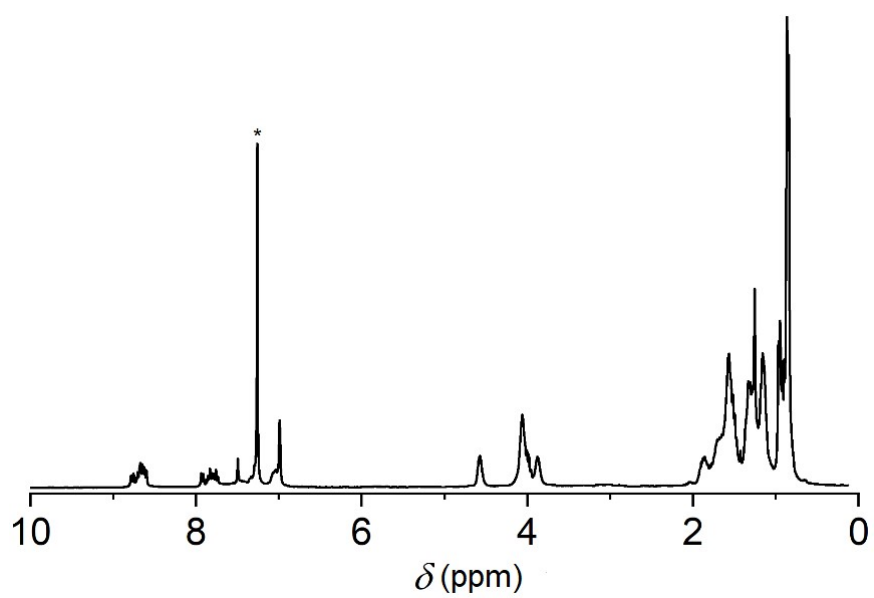


Fig. S23 ^1H NMR spectra of AD_1A in CDCl_3 . * indicates residual solvent peak.

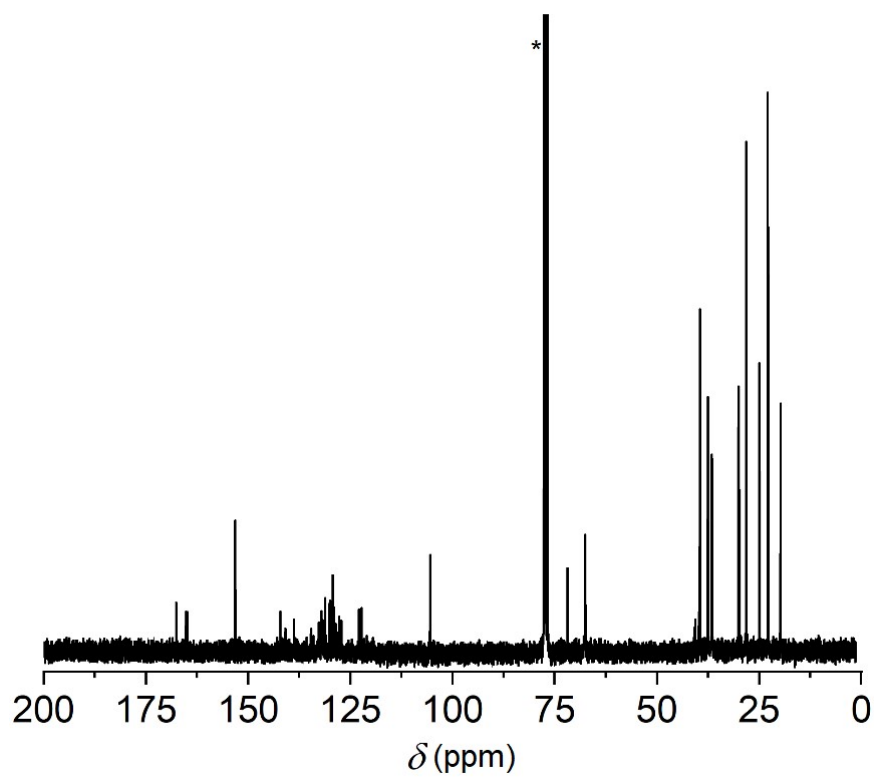


Fig. S24 ^{13}C NMR spectra of AD_1A in CDCl_3 . * indicates residual solvent peak.

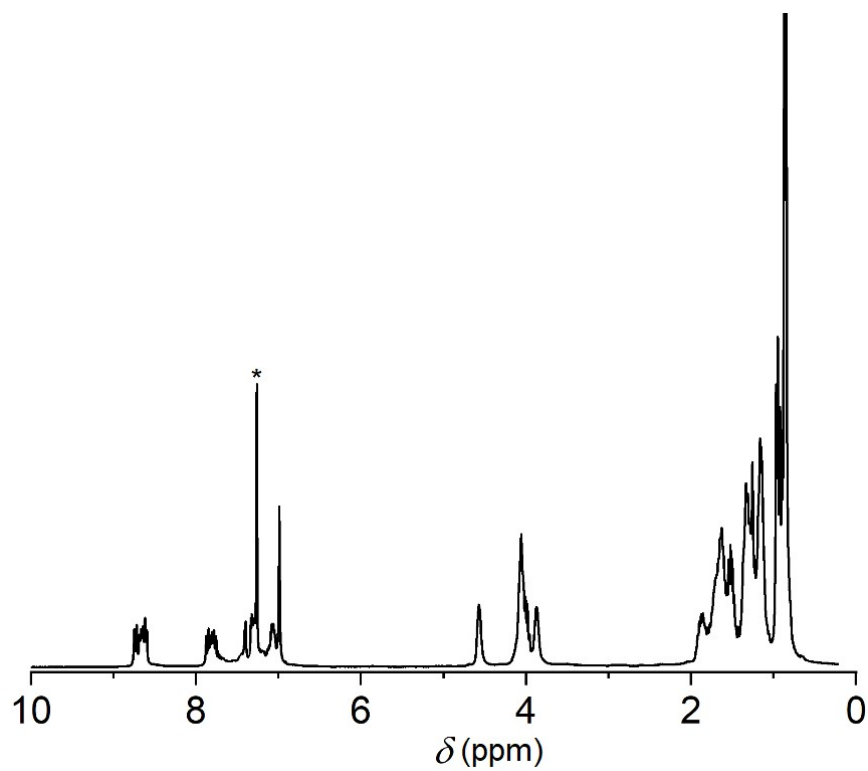


Fig. S25 ^1H NMR spectra of AD_2A in CDCl_3 . * indicates residual solvent peak.

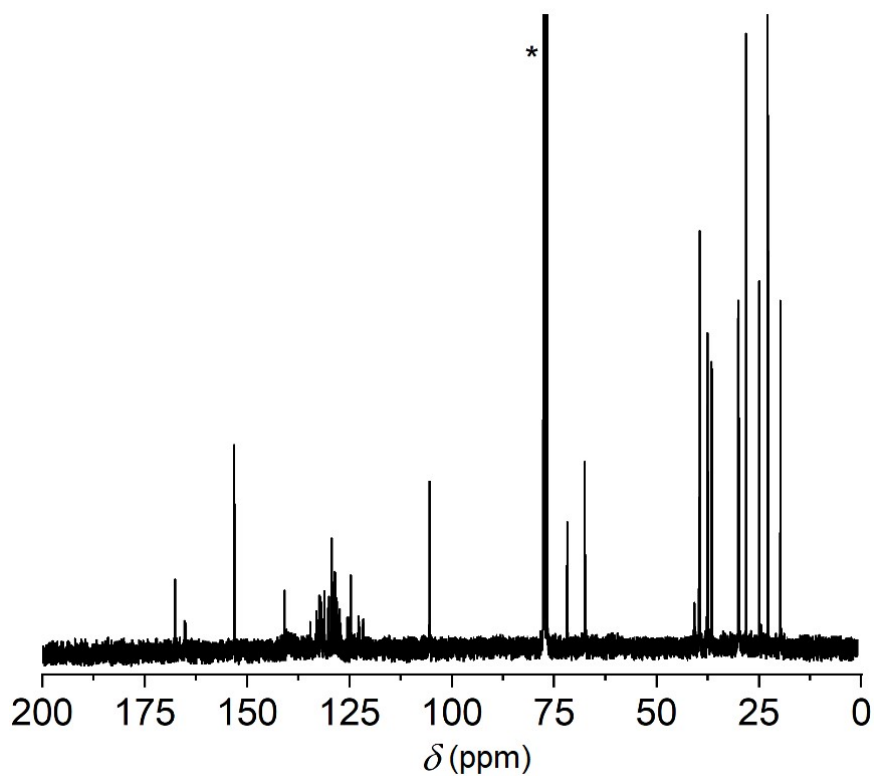


Fig. S26 ^{13}C NMR spectra of AD_2A in CDCl_3 . * indicates residual solvent peak.

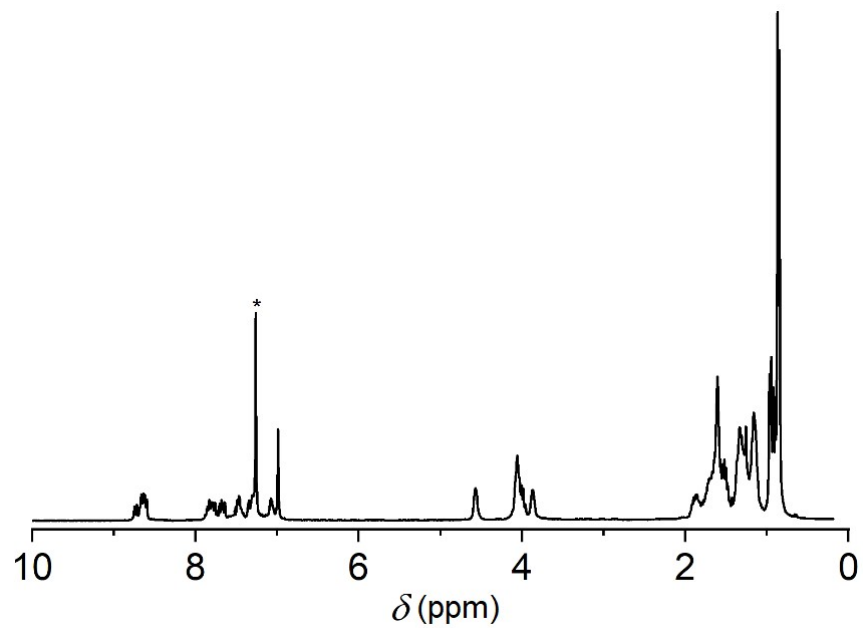


Fig. S27 ^1H NMR spectra of AD_3A in CDCl_3 . * indicates residual solvent peak.

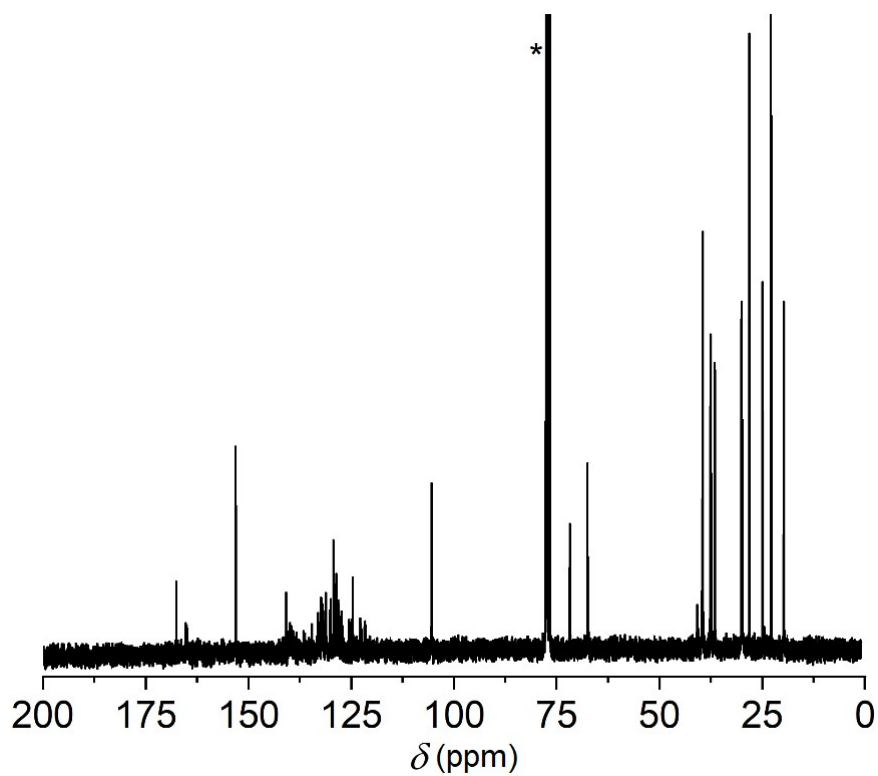


Fig. S28 ^{13}C NMR spectra of AD_3A in CDCl_3 . * indicates residual solvent peak.

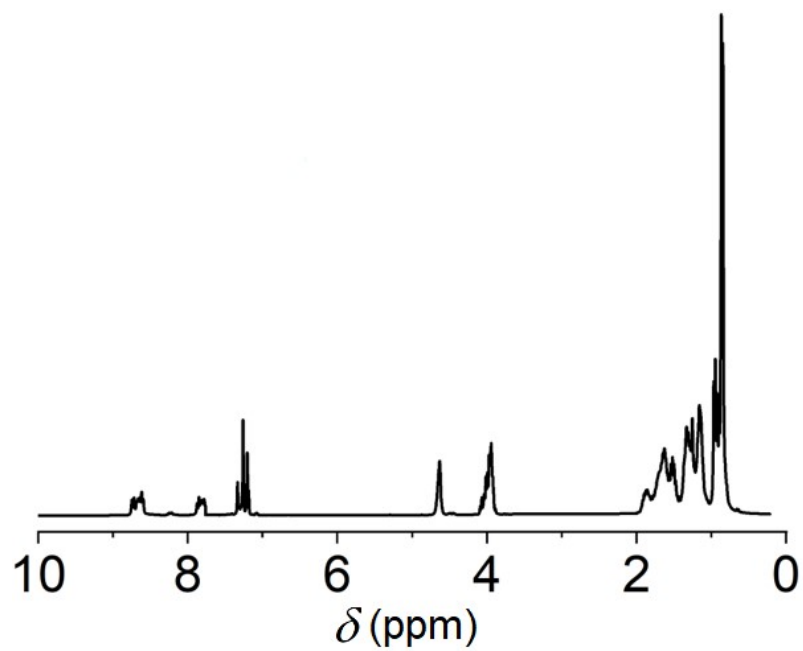


Fig. S29 ^1H NMR spectra of C1 in CDCl_3 . * indicates residual solvent peak.

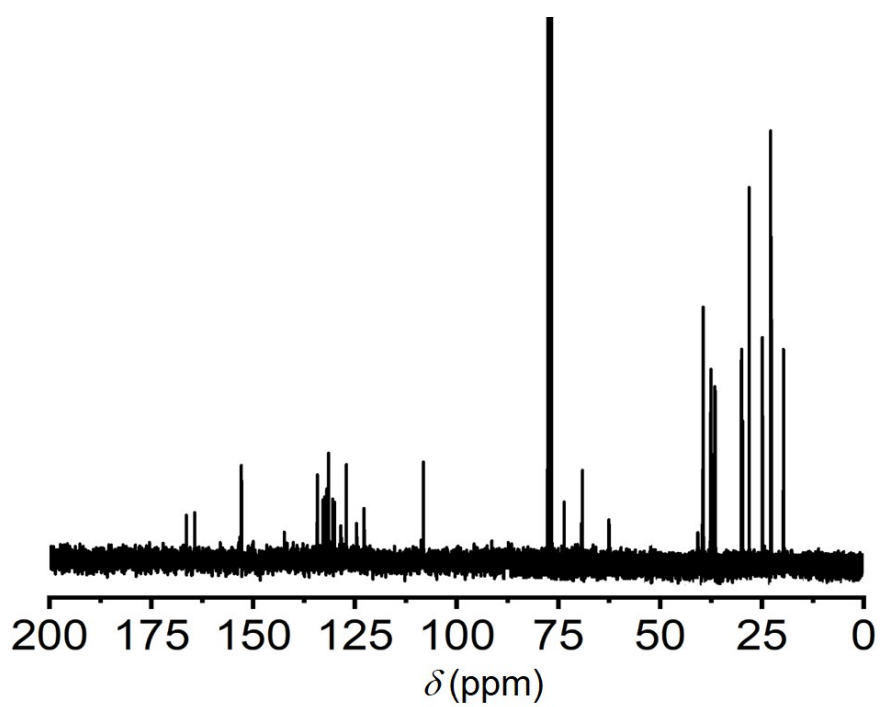


Fig. S30 ^{13}C NMR spectra of C1 in CDCl_3 . * indicates residual solvent peak.

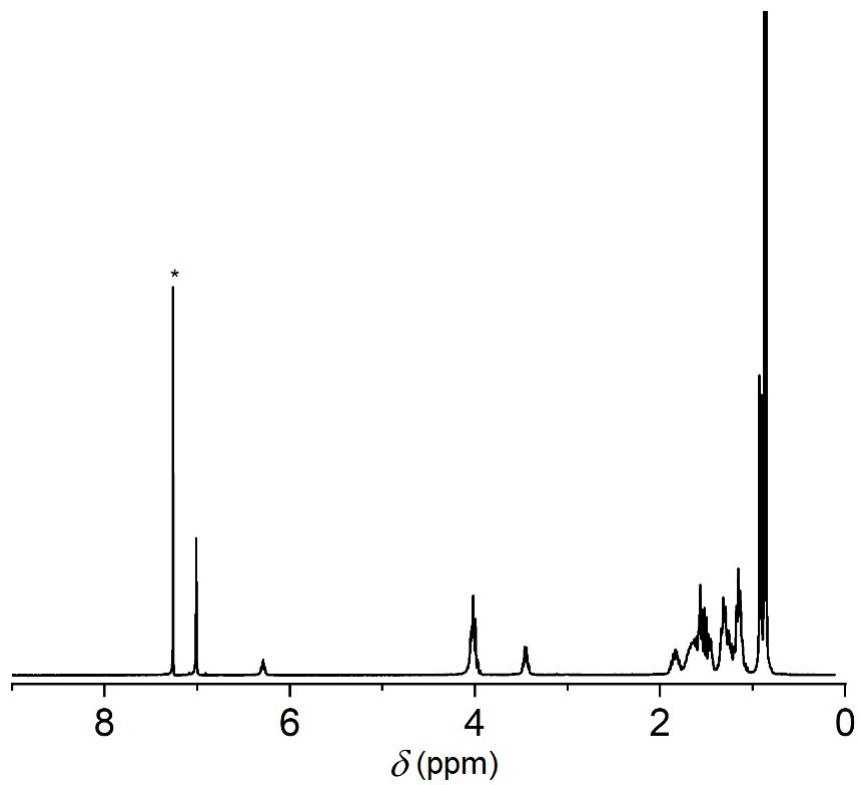


Fig. 31 ¹H NMR spectra of C2 in CDCl₃. * indicates residual solvent peak.

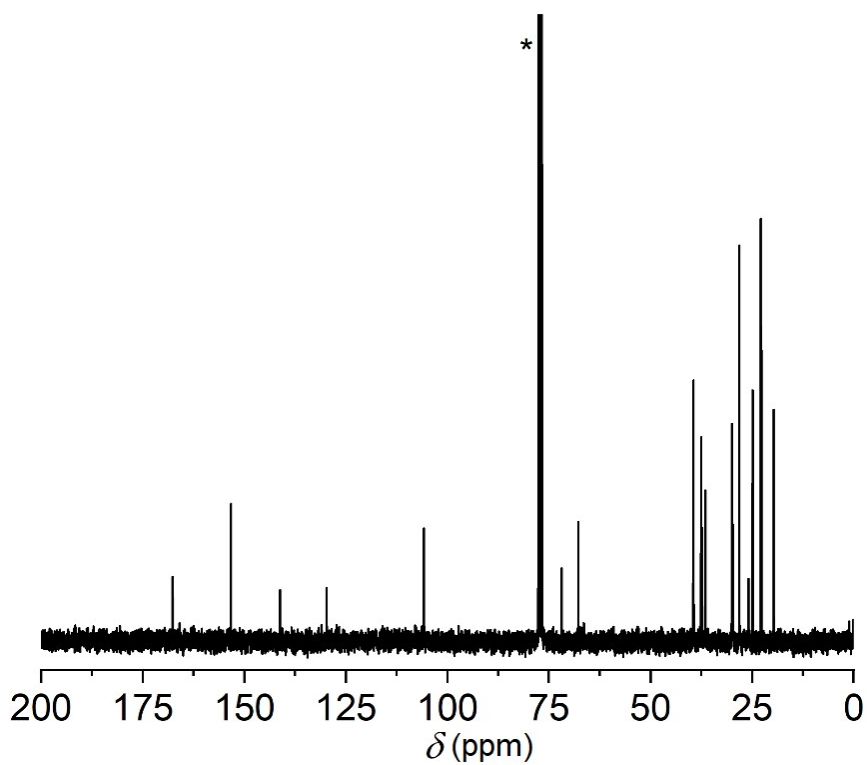


Fig. 32 ¹³C NMR spectra of C2 in CDCl₃. * indicates residual solvent peak.

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