

A high contrast mechanochromic luminescent diacetylene-linked bis-benzothiadiazole derivative

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S1. General Information

Proton and carbon NMR spectra. Proton and carbon NMR spectra were recorded on Bruker AC 300 spectrometer (^1H 300MHz, ^{13}C 75 MHz). Samples were recorded as solution in deuterated NMR solvents as stated and chemical shifts (δ) are quoted in parts per million, referenced to residual solvent.

Linear Spectroscopy: UV-vis in solution studies were carried out on a PerkinElmer Lambda XLS+ spectrometer. UV-is in solid state were carried out on a Shimadzu UV-2401 PC spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse spectrophotometer.

Cyclic Voltammetry Measurements. Cyclic voltammetry (CV) experiments were performed on a Bioanalytical Systems Inc. (BASi) Epsilon electrochemical workstation in a three-electrode cell at room temperature under nitrogen atmosphere. Electrochemical measurements were carried out in CH_2Cl_2 solution ($c = 1 \times 10^{-3}$ M) containing 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF_6) of supporting electrolyte at a scan rate 100 mV/s. A three electrode setup was used including a platinum working electrode, a Ag/AgCl (3 M NaCl) reference electrode, and a platinum wire auxiliary electrode.

X-ray structure determinations: Crystal of **4** showing well defined faces were mounted Bruker Kappa Apex II (X8 APEX) diffractometer equipped with a Mo INCOATED microsource. Diffraction data were collected exploring over a hemisphere of the reciprocal space in a combination of ϕ and ω scans to reach a resolution of 0.86 Å, using a Bruker APEXII software suite (APEX2; Bruker-AXS: Madison, WI, 2006). The structures were solved by the Multan and Fourier methods. Most of the calculations were carried out with APEXII software for data collection and reduction, and OLEX2 for structure solution and refinements.

S2 Synthesis and characterization of 3-5

Synthesis of 4-ethynyl-7-(4-nonylphenyl)benzo[*c*][1,2,5]thiadiazole (3).

A mixture of **2** (200 mg, 0.48 mmol), CuI (4.6 mg, 0.024mmol) and Pd(dppf)₂Cl₂ (17.6 mg, 0.024mmol) in 6 ml of a 1:1 mixture triethylamine:THF was degassed, and then, ethynyl trimethylsilane (0.73ml, 0.52 mmol) was added. The solution was irradiated with an Anton Paar microwave irradiator (CEM) at 120°C (80W) for 120 min. After cooling to room temperature, the mixture was diluted with CH₂Cl₂, washed with water, and dried (MgSO₄); the solvent was then evaporated and the residue was purified by chromatography with CH₂Cl₂/hexane (1:3) to give a yellow solid 4-(4-nonylphenyl)-7-((trimethylsilyl)ethynyl)benzo[*c*][1,2,5]thiadiazole (177 mg, 85%).

¹H NMR (300 MHz, CDCl₃) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.86 – 1.56 (m, 2H), 1.51 – 1.16 (m, 12H), 1.00 – 0.80 (m, 3H), 0.35 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 144.0, 135.2, 134.4, 134.1, 129.3, 128.9, 127.2, 115.5, 101.6, 100.7, 35.9, 32.0, 31.5, 29.9, 29.7, 29.5, 22.8, 14.2, 0.1. UV (CH₂Cl₂, 25 °C) λ_{max} (log ε) 275(4.98), 392(4.63). FAB MS *m/z* 434.71 (M⁺); HRMS (FAB) calcd for C₂₆H₃₄N₂SSi: 434.2212, found: 434.2205.

A mixture of 4-(4-nonylphenyl)-7-((trimethylsilyl)ethynyl)benzo[*c*][1,2,5]thiadiazole (100mg, 0.23mmol) and KF (138mg, 3.45mmol) was stirred for 12h at room temperature in 8 ml of a 1:1 mixture of THF:MeOH. Then the mixture was diluted with CH₂Cl₂, washed with water, and dried (MgSO₄); the solvent was then evaporated to give a yellow solid (**3**) (75 mg, 90%). ¹H NMR (300 MHz, CDCl₃) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.61 (s, 1H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.03 (t, *J* = 7.1 Hz, 2H), 1.41 – 1.17 (m, 12H), 0.88 (t, *J* = 6.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 144.2, 139.4, 135.8, 134.2, 129.3, 129.0, 127.2, 123.7, 114.2, 83.6, 79.7, 36.0, 34.0, 32.1, 31.5, 29.8, 29.7, 29.5, 29.3, 29.1, 22.8, 14.2. UV (CH₂Cl₂, 25 °C) λ_{max} (log ε) 267(3.34), 383(3.05). FAB MS *m/z* 362.53 (M⁺); HRMS (FAB) calcd for C₂₃H₂₆N₂S: 362.1817, found: 362.1825.

Synthesis of 7,7'-bis(4-nonylphenyl)-4,4'-bibenzo[*c*][1,2,5]thiadiazole. (4)

A mixture of **2** (150mg, 0.37mmol), Pd(OAc)₄ (4.1 mg, 0.02 mmol), K₂CO₃ (54.6 mg, 0.4mmol) and polyethylene glycol (PEG 4000, 359 mg, 0,09 mmol) in 2 ml of a dimethylformamide was stirred for 24h at 120°C. Then the mixture was diluted with Diethyl ether, washed with water, and dried (MgSO₄); the solvent was then evaporated and the residue was purified by chromatography with CH₂Cl₂/Hexane (1:2) to give a yellow solid **4** (53 mg, 45%). ¹H NMR (300 MHz, CDCl₃) δ 8.41 (d, *J* = 7.4 Hz, 2H), 7.93 (d, *J* = 6.9 Hz, 4H), 7.90

(d, $J = 6.1$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 4H), 2.71 (t, $J = 7.8$ Hz, 4H), 1.78 – 1.60 (m, 4H), 1.45 – 1.26 (m, 24H), 0.90 (d, $J = 6.4$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 154.31, 154.15, 143.65, 134.64, 134.43, 131.18, 129.20, 128.80, 128.53, 127.65, 35.87, 31.94, 31.50, 29.60, 29.46, 29.39, 22.72, 14.18. FAB MS m/z 674.35 (M^+); HRMS (FAB) calcd for $\text{C}_{42}\text{H}_{51}\text{N}_4\text{S}_2$: 675.3550, found: 675.3548 ($\text{M}+1$)

Synthesis of 1,4-bis(7-(4-nonylphenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)buta-1,3-diyne. (5)

A mixture of **5** (100mg, 0.27mmol) and $\text{Cu}_2(\text{OAc})_4 \cdot \text{H}_2\text{O}$ (40.4mg, 0.20mmol) in 10ml of a 1:1 mixture of Piperidine: CH_2Cl_2 was stirred for 12h at room temperature. Then the mixture was diluted with CH_2Cl_2 , washed with water, and dried (MgSO_4); the solvent was then evaporated and the residue was purified by chromatography with CH_2Cl_2 /Hexane (1:3) to give a yellow solid **5** (57 mg, 58%). ^1H NMR (300 MHz, CDCl_3) δ 7.95 (d, $J = 7.4$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 7.4$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 2.70 (t, $J = 7.7$ Hz, 2H), 1.82 – 1.60 (m, 2H), 1.44 – 1.18 (m, 12H), 1.00 – 0.78 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 155.8, 153.3, 144.4, 136.3, 135.0, 134.2, 129.3, 129.0, 127.3, 114.0, 80.2, 80.0, 36.0, 32.0, 31.5, 29.7, 29.5, 22.8, 14.3. MALDI MS m/z 722.4 (M^+)HRMS (MALDI) calcd for $\text{C}_{49}\text{H}_{50}\text{N}_4\text{S}_2$: 722.3471, found: 722.3472.

S3. Copy of the ^1H NMR and ^{13}C NMR spectra of compounds 3-5

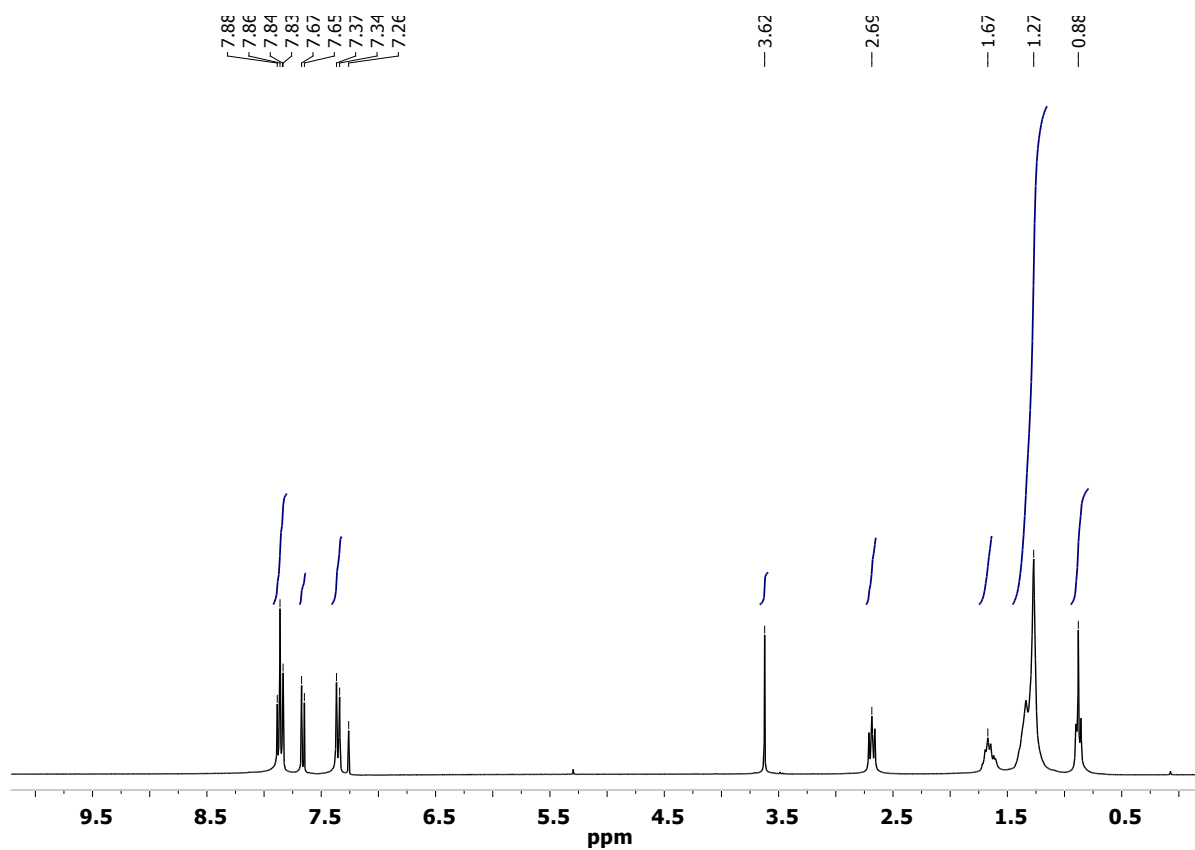


Figure S1. Copy of ^1H NMR (300MHz, CDCl_3) experimental spectra for 3.

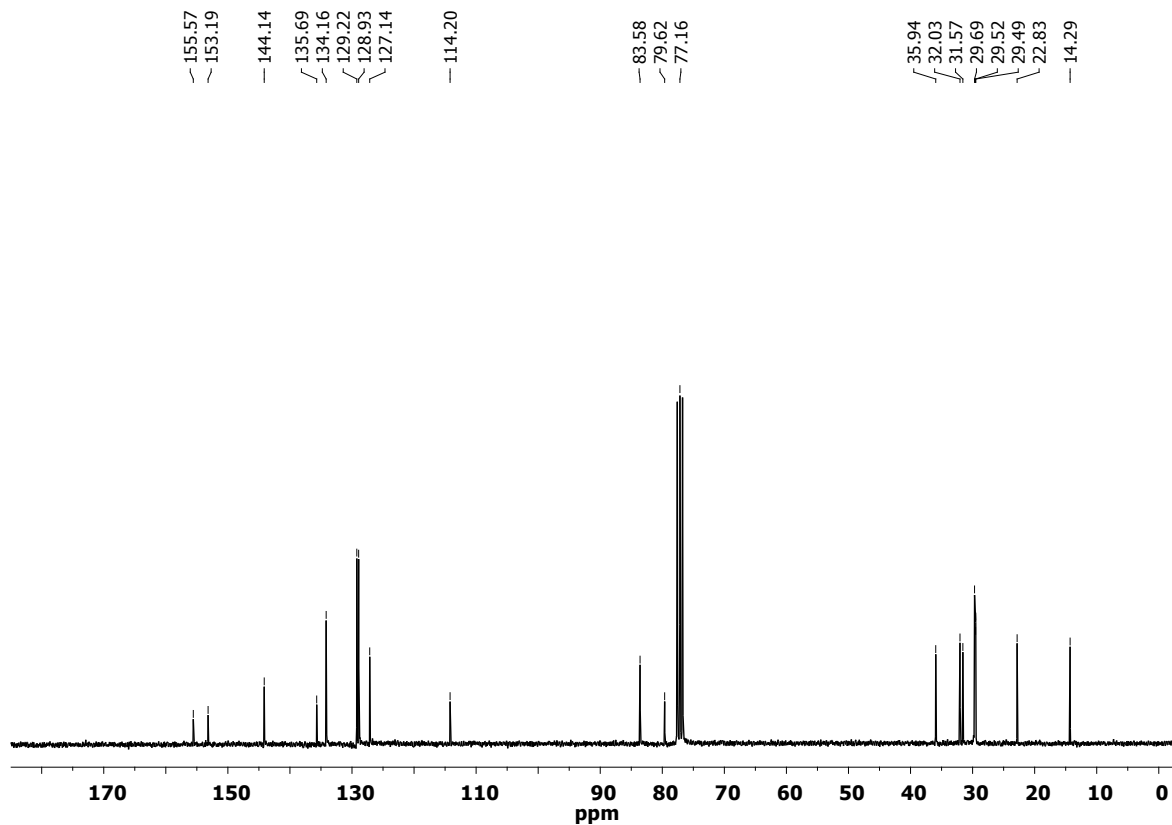


Figure S2. Copy of ^{13}C NMR(75MHz, CDCl_3) experimental spectra for 3.

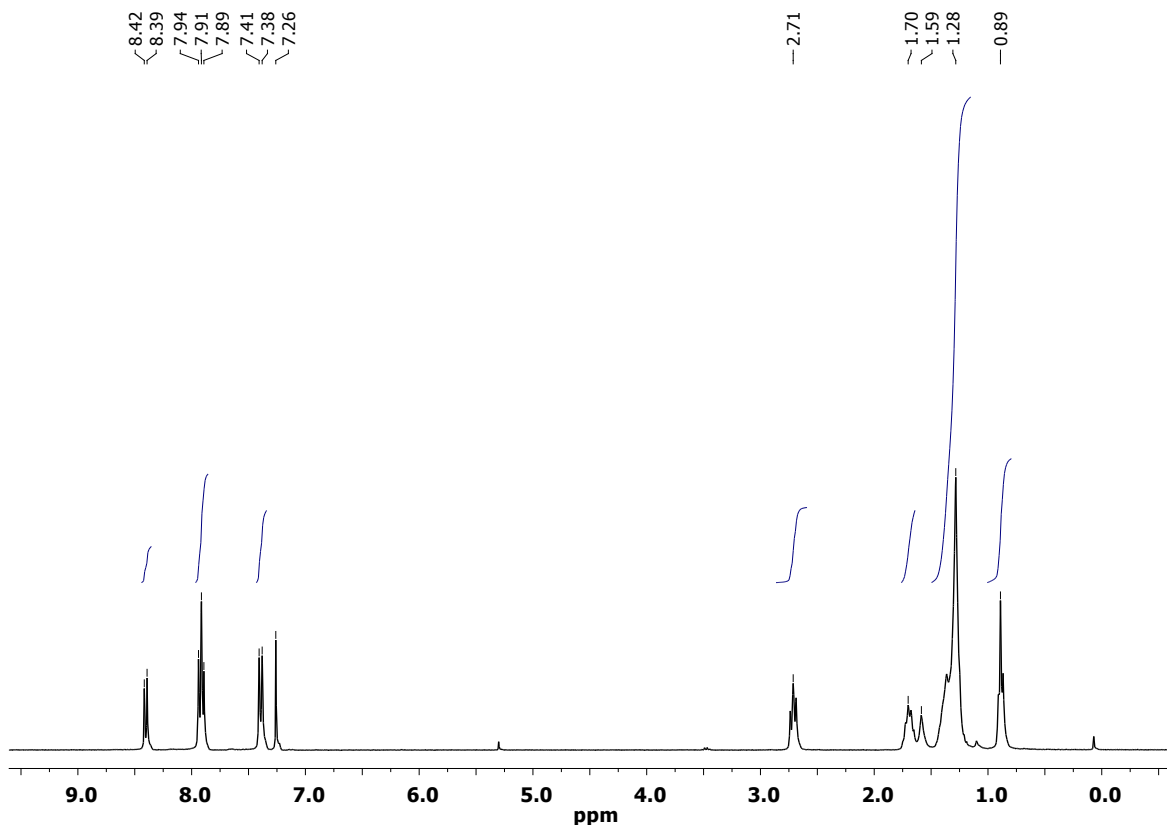


Figure S3. Copy of ^1H NMR (300MHz, CDCl_3) experimental spectra for 4.

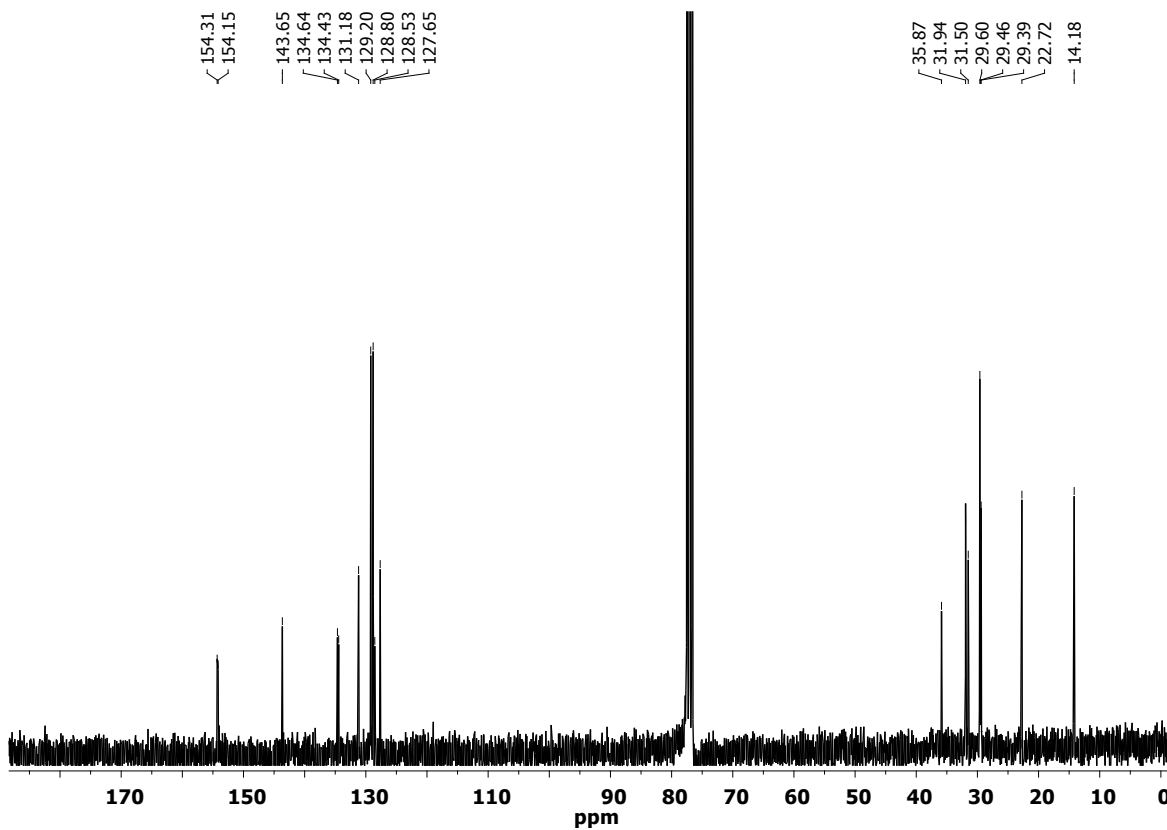


Figure S4. Copy of ^{13}C NMR(75 MHz, CDCl_3) experimental spectra for 4.

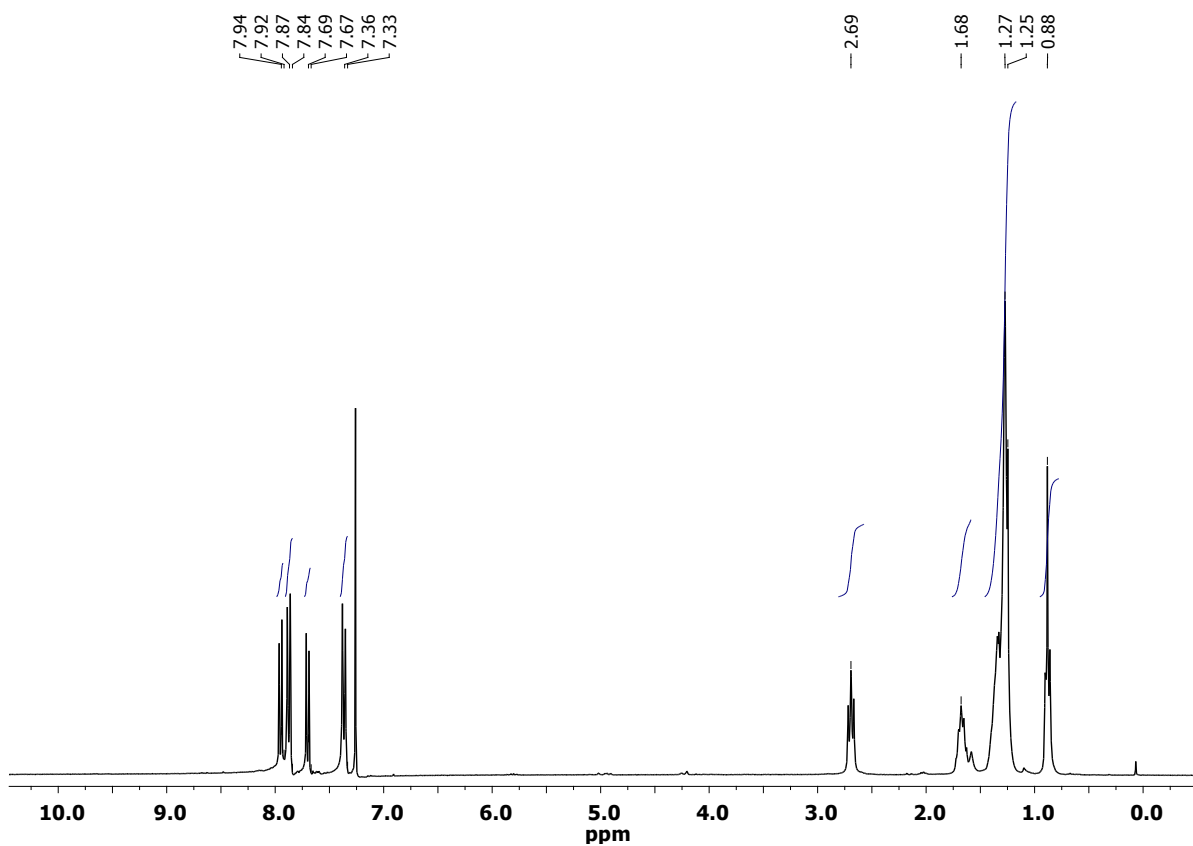


Figure S5. Copy of ^1H NMR (300MHz, CDCl_3) experimental spectra for **5**.

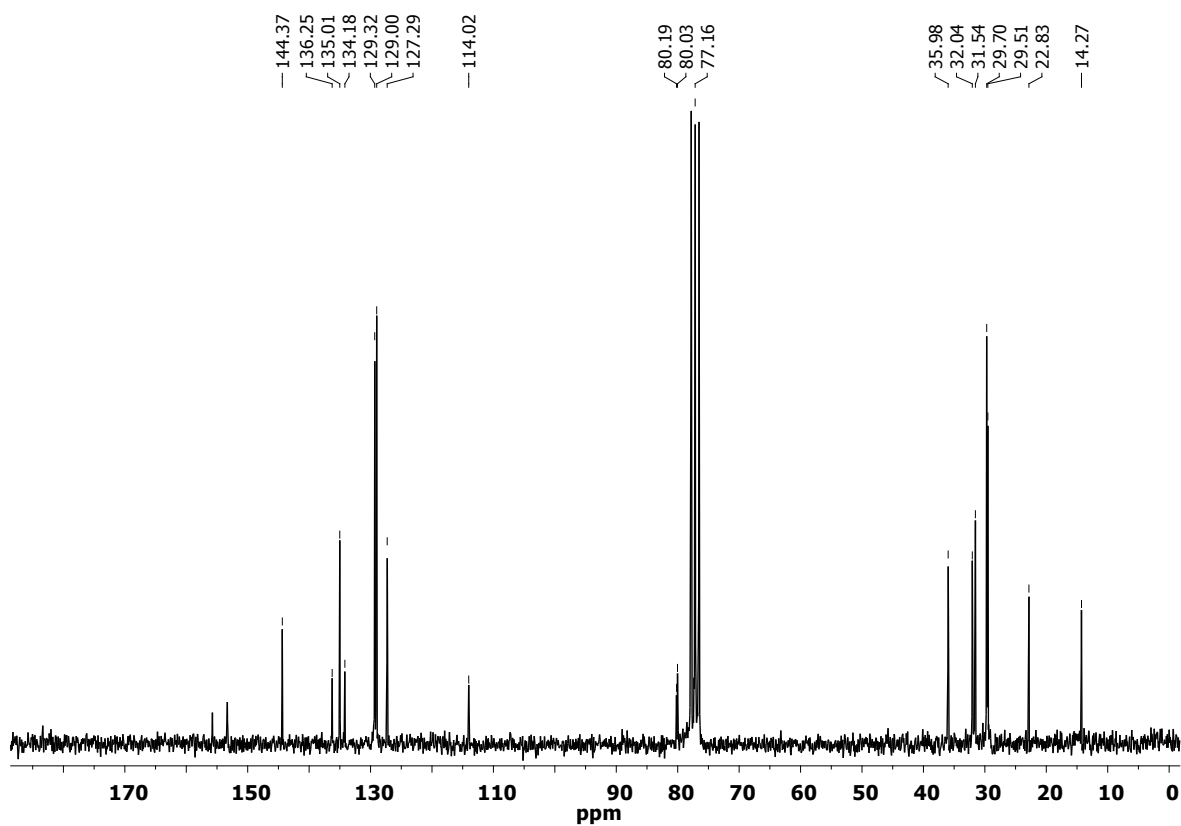


Figure S6. Copy of ^{13}C NMR (75 MHz, CDCl_3) experimental spectra for **5**.

S4. Single crystal X-ray structure determination

Crystal Structure Report of 4.

A yellow plate-like specimen of $C_{42}H_{50}N_4S_2$, approximate dimensions 0.015 mm x 0.323 mm x 0.372 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 21.50 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 134454 reflections to a maximum θ angle of 25.35° (0.83 \AA resolution), of which 34850 were independent (average redundancy 3.858, completeness = 99.5%, $R_{\text{int}} = 12.62\%$, $R_{\text{sig}} = 18.12\%$) and 11926 (34.22%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 7.7495(2) \text{ \AA}$, $b = 33.5689(8) \text{ \AA}$, $c = 39.6305(9) \text{ \AA}$, $\alpha = 68.5122(14)^\circ$, $\beta = 88.3620(15)^\circ$, $\gamma = 84.7067(16)^\circ$, volume = $9551.9(4) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 5792 reflections above $20 \sigma(I)$ with $4.941^\circ < 2\theta < 42.54^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.899. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9380 and 0.9970.

The final anisotropic full-matrix least-squares refinement on F^2 with 2171 variables converged at $R1 = 7.71\%$, for the observed data and $wR2 = 23.41\%$ for all data. The goodness-of-fit was 0.955. The largest peak in the final difference electron density synthesis was $0.253 \text{ e}/\text{\AA}^3$ and the largest hole was $-0.379 \text{ e}/\text{\AA}^3$ with an RMS deviation of $0.060 \text{ e}/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.173 g/cm^3 and $F(000)$, 3620 e⁻.

Table S1. Sample and crystal data for 4

Identification code	4
Chemical formula	$C_{42}H_{50}N_4S_2$
Formula weight	674.98 g/mol
Temperature	296(2) K
Wavelength	0.71073 \AA
Crystal size	0.015 x 0.323 x 0.372 mm
Crystal habit	yellow plate
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	$a = 7.7495(2) \text{ \AA}$ $\alpha = 68.5122(14)^\circ$ $b = 33.5689(8) \text{ \AA}$ $\beta = 88.3620(15)^\circ$ $c = 39.6305(9) \text{ \AA}$ $\gamma = 84.7067(16)^\circ$
Volume	$9551.9(4) \text{ \AA}^3$
Z	10
Density (calculated)	1.173 g/cm^3
Absorption coefficient	0.173 mm^{-1}
F(000)	3620

Table S2. Data collection and structure refinement for 4.

Theta range for data	1.00 to 25.35°
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collection	
Index ranges	-9<=h<=9, -40<=k<=40, -47<=l<=47
Reflections collected	134454
Independent reflections	34850 [R(int) = 0.1262]
Coverage of independent reflections	99.5%
Absorption correction	multi-scan
Max. and min. transmission	0.9970 and 0.9380
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	34850 / 0 / 2171
Goodness-of-fit on F²	0.955
Δ/σ_{\max}	0.001
Final R indices	11926 data; R1 = 0.0771, wR2 = I>2 σ (I) 0.1569 all data R1 = 0.2474, wR2 = 0.2341
Weighting scheme	w=1/[$\sigma^2(F_o^2)+(0.0903P)^2$] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	0.253 and -0.379 eÅ ⁻³
R.M.S. deviation from mean	0.060 eÅ ⁻³

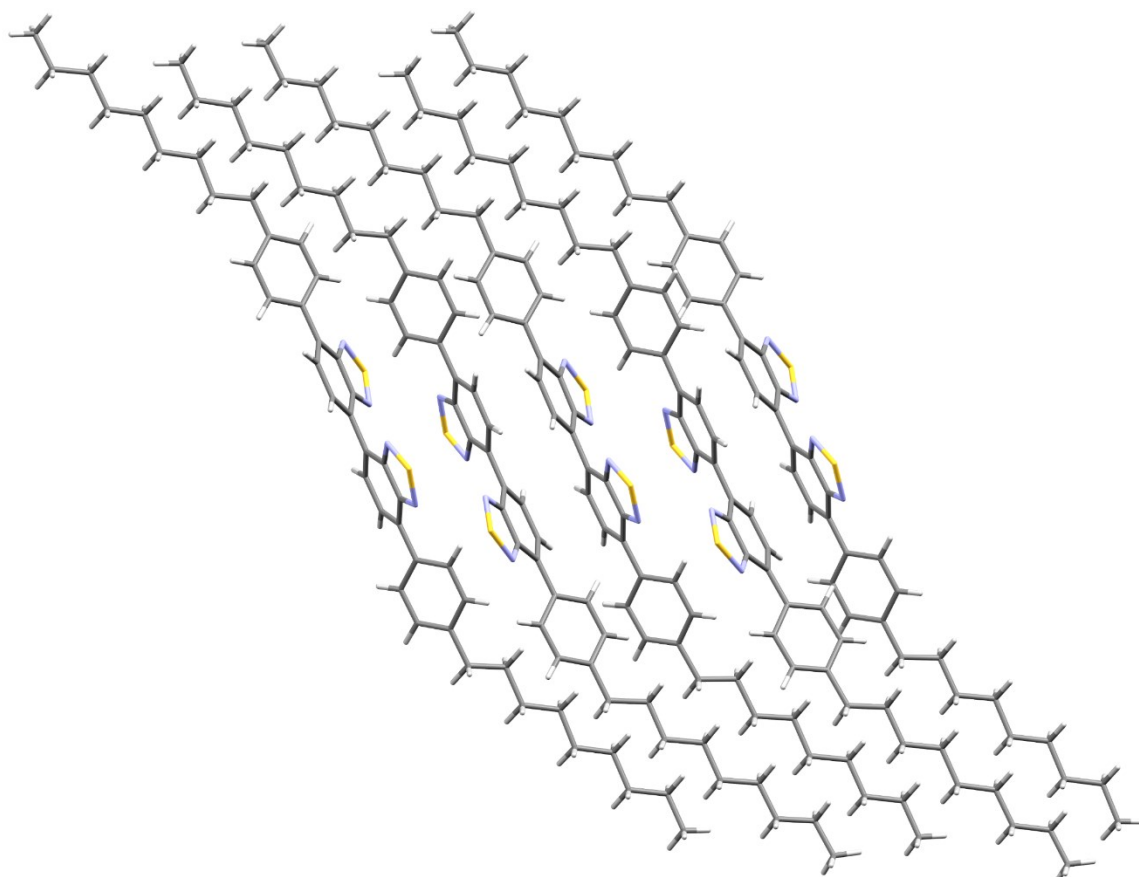


Figure S7. Five crystallographic independent molecules in the asymmetric unit cell of **4**.

S4 PXRD patterns of 5

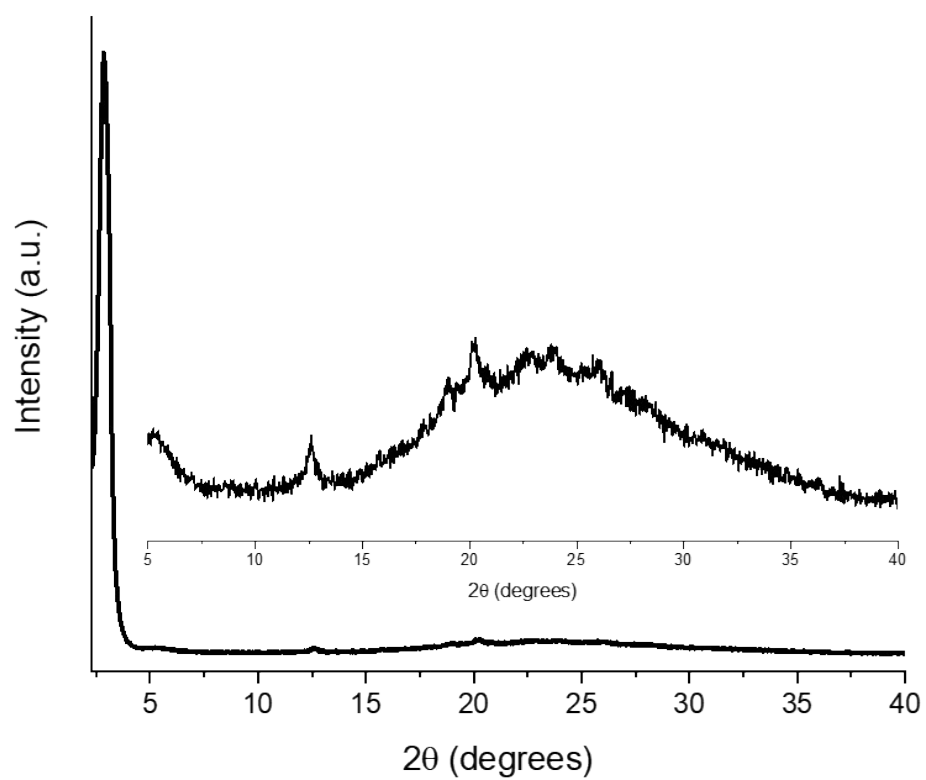


Figure S8. PXRD experimental pattern of 5a.

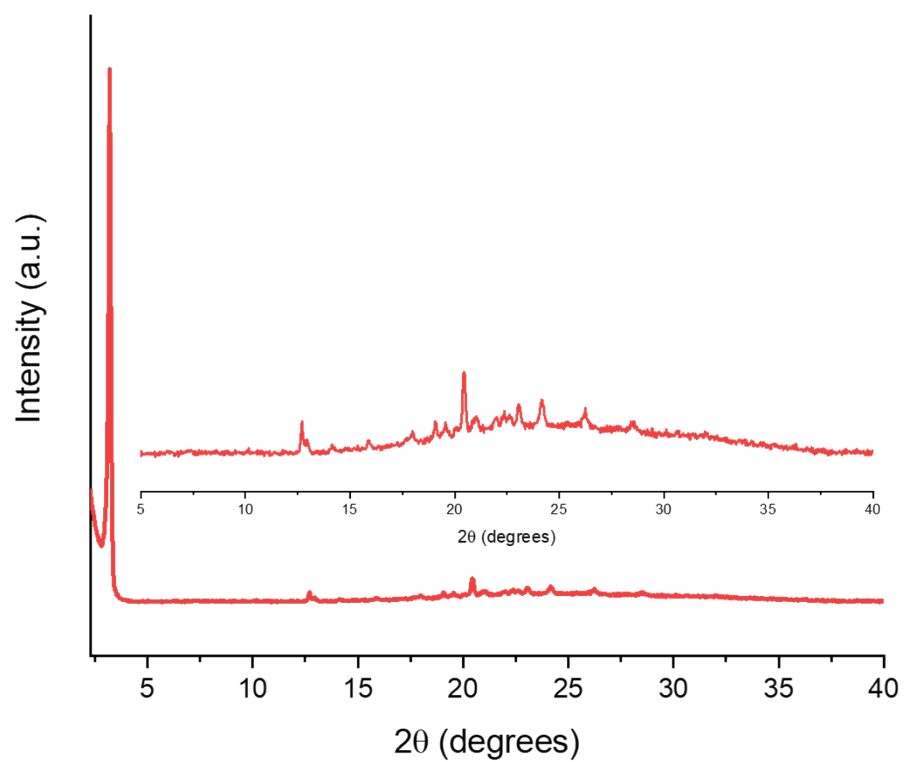


Figure S9. PXRD experimental pattern of 5β.