

Controlling Light Emitting Properties in Bis(pyrenyl)-di-imines by Tuning Chemical Functionality of Spacer Group

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Experimental Details

General

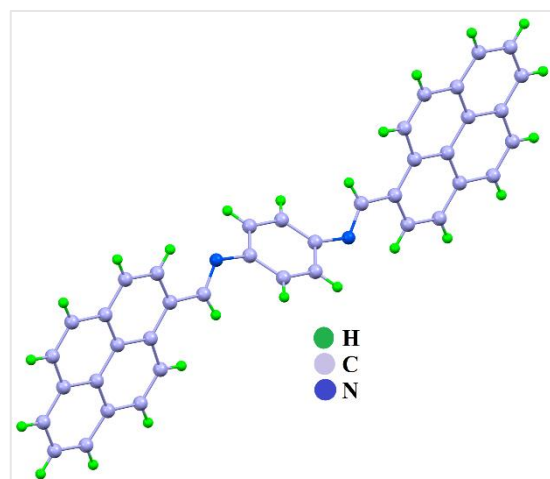
^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. FTIR spectra were obtained from Shimadzu IRAffinity-1S system. Powder X-Ray Diffraction (XRD) data was collected using a Rigaku miniflex II, $\lambda = 1.54 \text{ \AA}$, Cu $K\alpha$. UV-Visible and fluorescence spectra were recorded on Jasco V-650 spectrophotometer and Fluorimax-4 0426C0809 respectively. Absolute quantum yield was measured by using quanta ϕ instrument.

Single Crystal XRD

The single-crystal XRD analysis of **L1** was done at Narendrapur Ramkrishna Mission, Kolkata, using a Bruker AXS D8 QUEST ECO diffractometer equipped with monochromatic Mo-target rotating anode X-ray and graphite monochromator α radiation with $\lambda = 0.71073 \text{ \AA}$ by ω and ϕ scan technique. The integrated diffraction data, unit cell, and data correction were performed using Bruker SAINT system, SMART, and SADABS respectively. The structure was solved by SHELXS-97 through the direct method and refined by full-matrix least-squares based on F^2 through SHELXS-2018/3.¹ The hydrogen atoms were added at determined positions as riding atoms and non-H atoms were refined anisotropically.

Synthesis of (1*E*,1'*E*)-*N,N'*-(1,4-phenylene)bis(1-(pyren-1-yl)methanimine) (**L1**)²

p-Phenylene diamine (0.270 g, 2.5 mmol) and catalytic amount of trifluoroacetic acid (TFA, 2-3 drops) were added to the solution of 1-pyrenecarboxaldehyde in dimethylacetamide (DMA) (1.15 g, 5 mmol). The mixture was refluxed for 24 hours. Bright yellow precipitate was removed by filtration and recrystallized from chloroform. Yield: 59%; Melting point: 315 - 316 °C; IR (cm^{-1}): 3047 (w), 2360 (w),

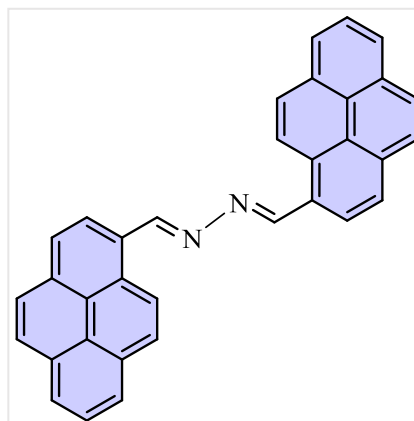


1597 (s), 1481 (m), 1203 (m), 964 (m), 895 (m), 849 (m), 763 (m), 710 (s), 610 (w), 502 (w) (Figure S1); ^1H NMR (400MHz, $\text{DMSO-}d_6$) δ ppm: 9.80 (2H, s, imine CH), 9.37 (2H, d, $J = 9.4 \text{ Hz}$, ArH), 8.88 (2H, d, $J = 8.1 \text{ Hz}$, ArH), 8.55 – 8.13 (14H, br, ArH), 7.71 (4H, s, ArH) (Figure S2); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ ppm: 150.24, 133.43, 131.19, 130.56, 130.16,

130.15, 129.43, 128.59, 127.69, 127.65, 127.23, 126.87, 125.43, 125.30, 124.43, 124.36, 123.76, 123.38, 115.10 (Figure S3).

Synthesis of (1*E*,2*E*)-1,2-bis(pyren-1-ylmethylene)hydrazine (L2)²

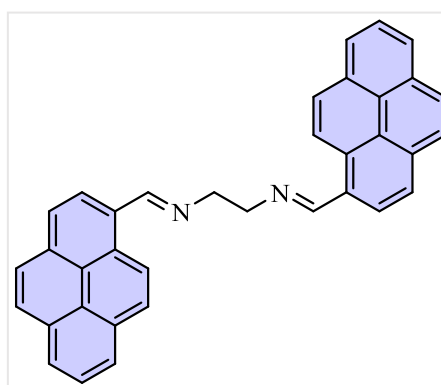
Hydrazine hydrate (0.121 mL, 2.5 mmol) was added dropwise to ethanolic solution of 1-pyrenecarboxaldehyde (1.15 g, 5 mmol), then catalytic amount of TFA (2-3 drops) was added to this solution. The mixture was refluxed for 24 hours. Pale yellow precipitate was removed by filtration and recrystallized from chloroform. Yield: 52%; Melting point: 308-309 °C; IR (cm⁻¹): 3099 (w), 2360 (w), 1913 (w), 1597 (s), 1388 (w), 1311 (w),



1242 (m), 1804 (m), 887 (w), 817 (s), 748 (m), 709 (m), 678 (w), 509 (m) (Figure S4); ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm: 9.94 (2H, s, imine CH), 9.30 (2H, d, *J* = 9.2 Hz, ArH), 8.86 (2H, d, *J* = 8.0 Hz, ArH), 8.53 – 8.42 (6H, m, ArH), 8.41 – 8.28 (6H, m, ArH), 8.19 (2H, t, *J* = 7.7 Hz, ArH) (Figure S5); ¹³C NMR (100 MHz, DMSO-*d*₆) δ ppm: 150.89, 133.19, 131.28, 130.65, 129.93, 129.84, 129.44, 128.55, 127.73, 127.51, 127.05, 126.69, 125.38, 124.99, 124.74, 124.46, 123.89 (Figure S6).

Synthesis of (1*E*,1'*E*)-*N,N'*-(ethane-1,2-diyl)bis(1-(pyren-1-yl)methanimine) (L3)³

Ethylene diamine (0.167 mL, 2.5 mmol) was added dropwise to ethanolic solution of 1-pyrenecarboxaldehyde (1.15 g, 5 mmol) then catalytic amount of TFA (2-3 drops) was added to this solution. The mixture was refluxed for 24 hours. Dark orange precipitate was removed by filtration and recrystallized from chloroform. Yield: 48%; Melting point: 225 - 226 °C; IR (cm⁻¹): 1627 (s), 1435 (w), 1242 (w), 1064 (w),

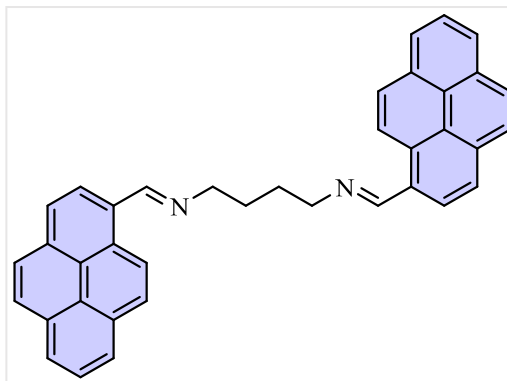


972 (w), 840 (s), 756 (m), 717 (m), 609 (m) (Figure S7); ¹H NMR (400 MHz, CDCl₃) δ ppm: 9.35 (2H, s, imine CH), 8.71 (2H, d, *J* = 9.3 Hz, ArH), 8.54 (2H, d, *J* = 8.0 Hz, ArH), 8.23 – 7.77 (14H, m, ArH), 4.38 (4H, s, 2×CH₂) (Figure S8); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 162.43, 135.58, 131.43, 131.13, 130.99, 130.88, ¹³C NMR (100 MHz, Chloroform-*d*) δ 162.43, 135.58, 131.43, 131.13, 130.99, 130.88,

130.75, 130.47, 127.47, 127.24, 127.09, 126.87, 126.60, 124.73, 124.59, 124.12, 123.07, 47.34 (Figure S9).

Synthesis of (1*E*,1'*E*)-*N,N'*-(butane-1,4-diyl)bis(1-(pyren-1-yl)methanimine) (L4)⁴

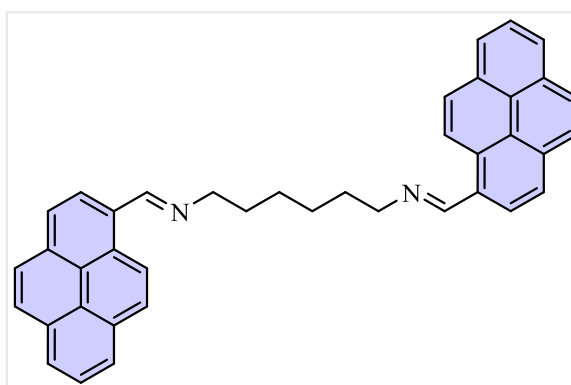
1,4-Diaminobutane (0.251 mL, 2.5 mmol) was added dropwise to ethanolic solution of 1-pyrenecarboxaldehyde (1.15 g, 5 mmol) then catalytic amount of TFA (2-3 drops) was added to this solution. The mixture was refluxed for 24 hours. Bright red precipitate was removed by filtration and recrystallized from chloroform. Yield: 54%; Melting point: 231-232 °C; IR (cm⁻¹): 3741



(w), 3039 (w), 2360 (w), 1743 (s), 1620(m), 1535 (w), 1458 (w), 1365 (w), 1234 (s), 1080 (s), 856 (s), 717 (m), 632 (m) (Figure S10); ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm: 9.45 (2H, s, imine CH), 9.12 (2H, d, *J* = 9.4 Hz, ArH), 8.58 (2H, d, *J* = 8.1 Hz, ArH), 8.39 – 8.19 (12H, m, ArH), 8.12 (2H, t, *J* = 7.6 Hz, ArH), 3.94 (4H, br, 2×CH₂), 1.95 (4H, br, 2×CH₂) (Figure 11); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 159.79, 132.74, 131.29, 130.62, 128.82, 129.79, 128.58, 128.45, 127.47, 126.32, 126.07, 125.80, 125.56, 124.97, 124.88, 124.69, 122.65, 62.61, 29.16 (Figure S12); HRMS: *m/z* calcd for C₃₈H₂₈N₂ (M+H)⁺ = 513.2325, found 513.2302 (Figure S13).

Synthesis of (1*E*,1'*E*)-*N,N'*-(hexane-1,6-diyl)bis(1-(pyren-1-yl)methanimine) (L5)⁴

Hexamethylene diamine (0.346 mL, 2.5 mmol) was added dropwise to ethanolic solution of 1-pyrenecarboxaldehyde (1.15 g, 5 mmol) then catalytic amount of TFA (2-3 drops) was added to this solution. The mixture was refluxed for 24 hours. Light yellow precipitate was removed by filtration and recrystallized from chloroform. Yield: 65%;



Melting point: 153-154 °C; IR (cm⁻¹): 3039 (w), 2360 (m), 1627 (m), 1308 (w), 1242 (w), 1804 (w), 1026 (w), 848(s), 748 (m), 678 (w) (Figure S14); ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm: 9.39 (2H, s, imine CH), 9.11 (2H, d, *J* = 9.4 Hz, ArH), 8.53 (2H, d, *J* = 8.1 Hz, ArH), 8.43 – 8.15 (12H, br, ArH), 8.11 (2H, t, *J* = 7.6 Hz, ArH), 3.84 (4H, br, 2×CH₂), 1.90 – 1.77

(4H, br, 2×CH₂), 1.64 – 1.52 (4H, br, 2×CH₂) (Figure S15); ¹³C NMR (100 MHz, DMSO-*d*₆) δ ppm: 160.17, 132.56, 131.25, 130.57, 129.57, 129.05, 129.01, 128.93, 127.84, 126.97, 126.86, 126.46, 126.14, 125.43, 124.48, 124.22, 123.47, 61.86, 31.19, 27.26 (Figure S16); HRMS: m/z calcd for C₄₀H₃₂N₂ (M+H)⁺ = 541.2638, found 541.2615 (Figure S17).

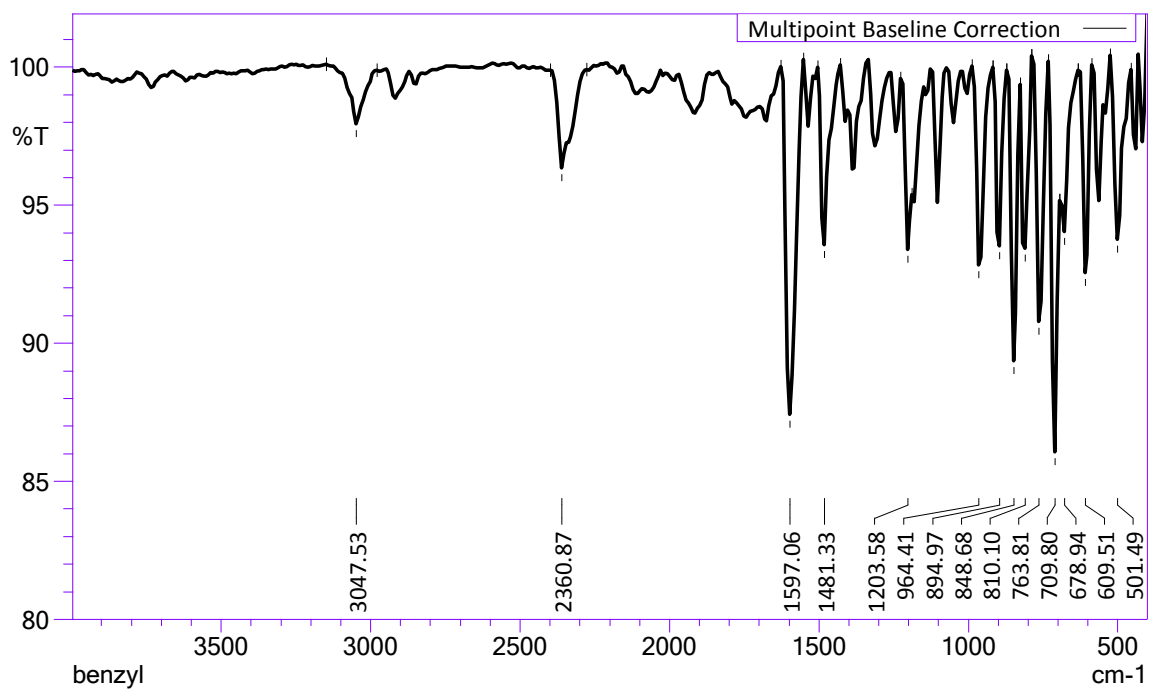


Figure S1: IR spectrum of **L1**

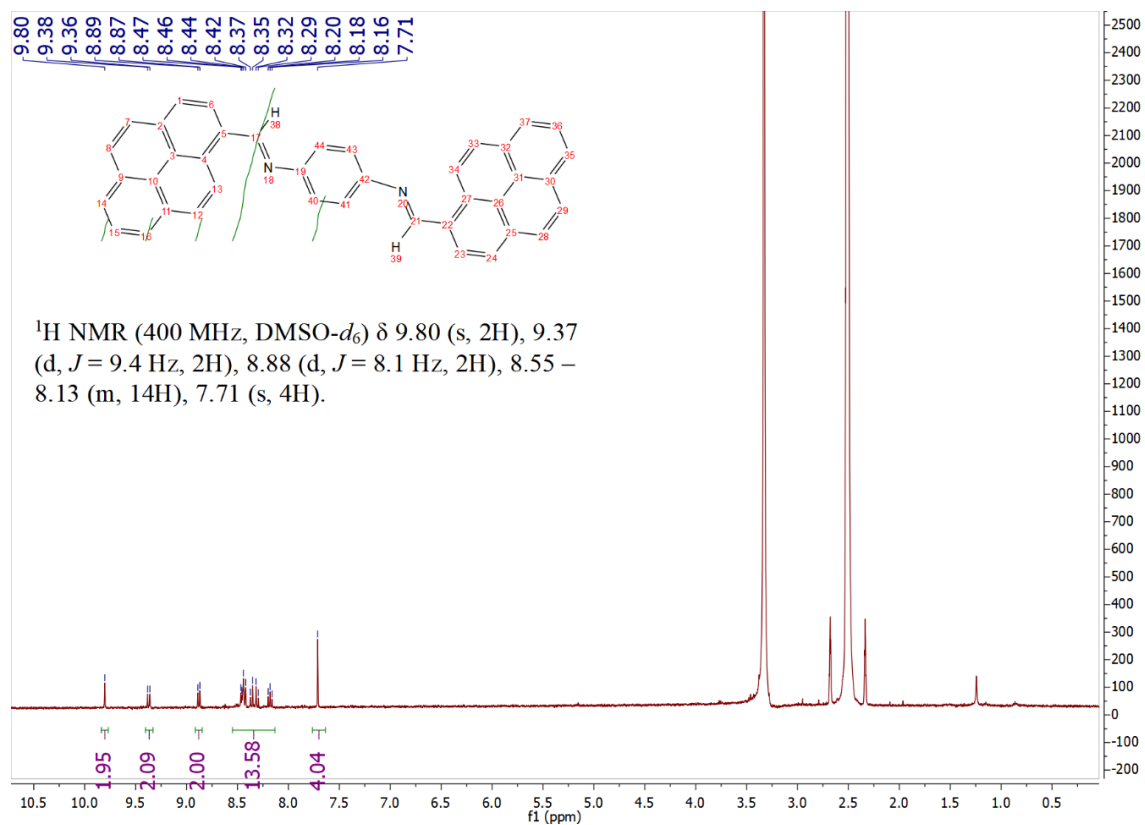


Figure S2: ¹H NMR spectrum of L1

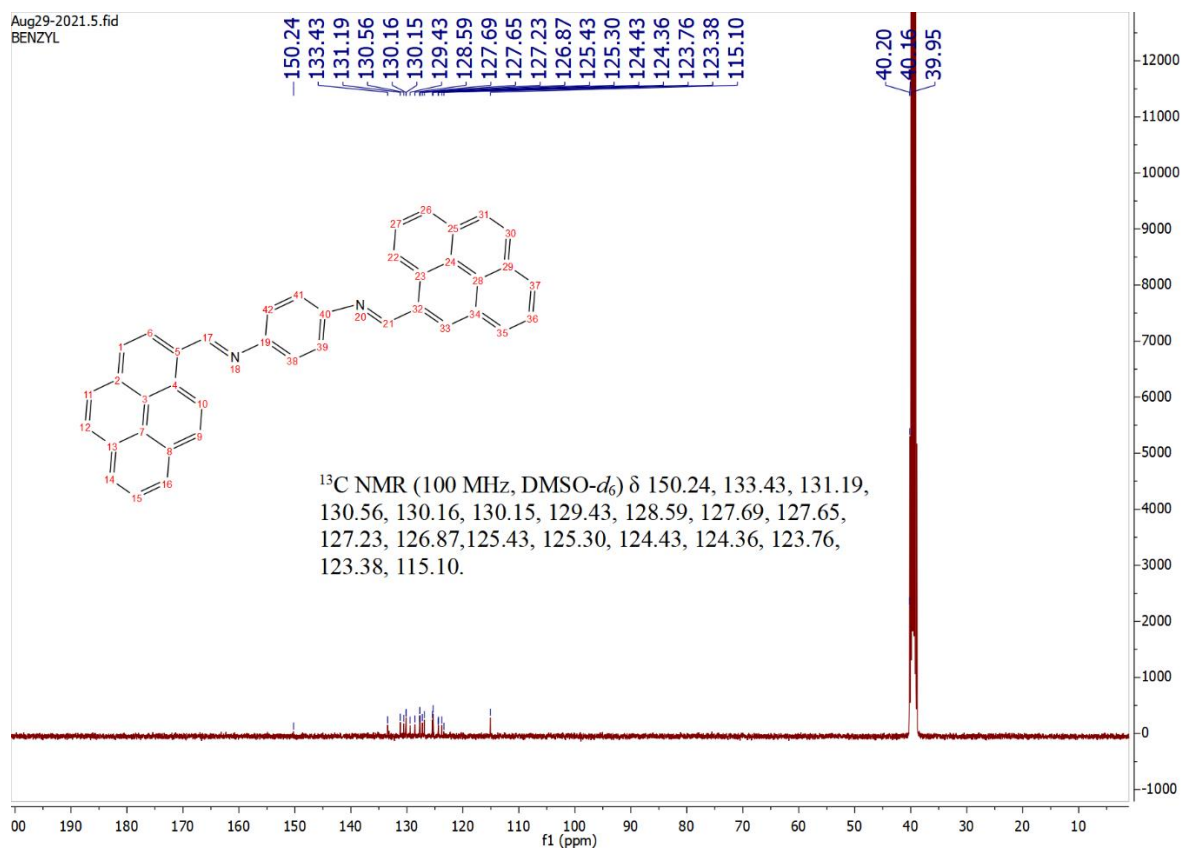


Figure S3: ¹³C NMR spectrum of L1

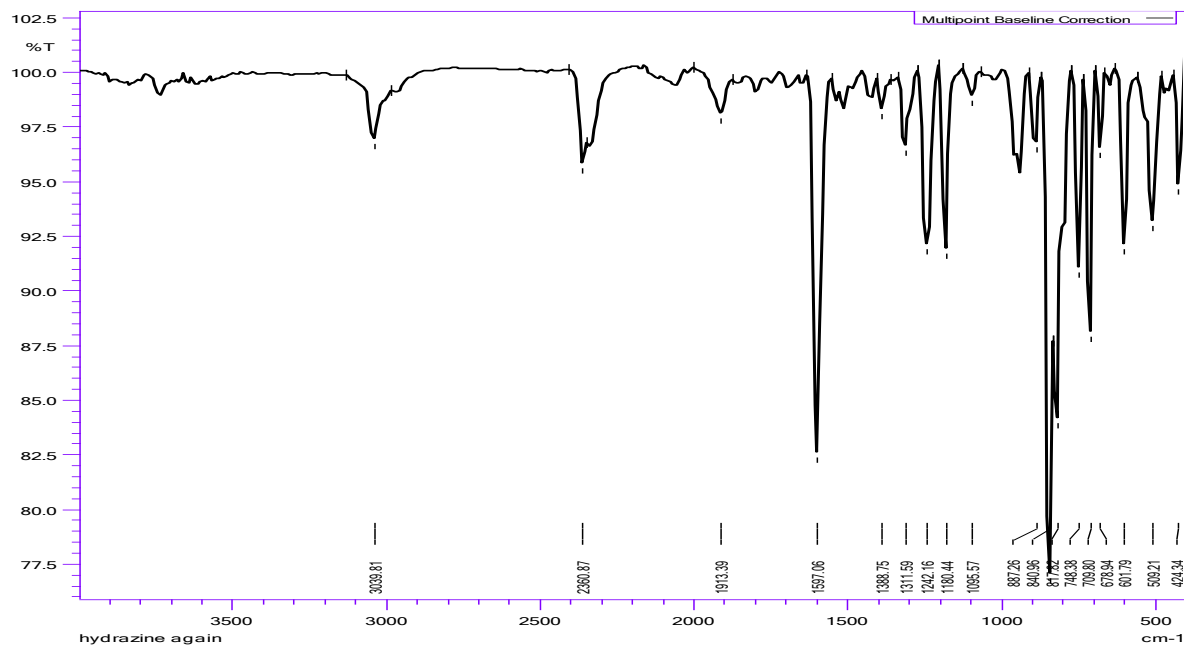


Figure S4: IR spectrum of L2

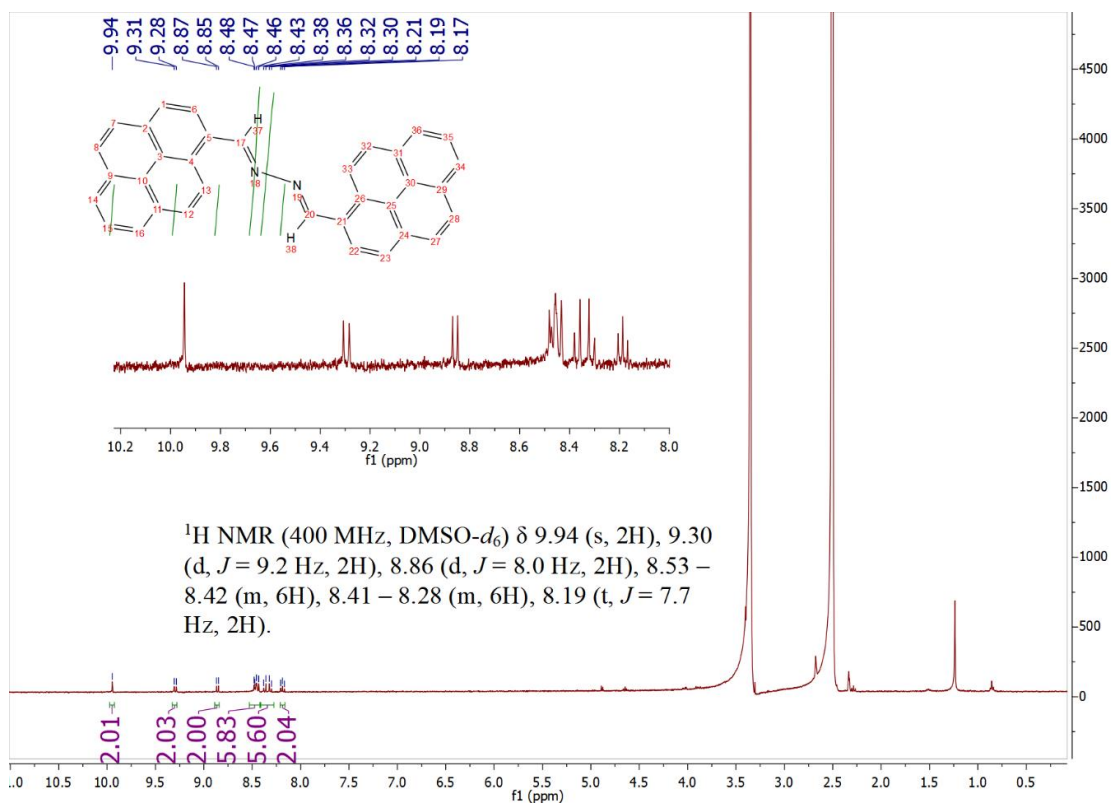


Figure S5: ¹H NMR spectrum of L2

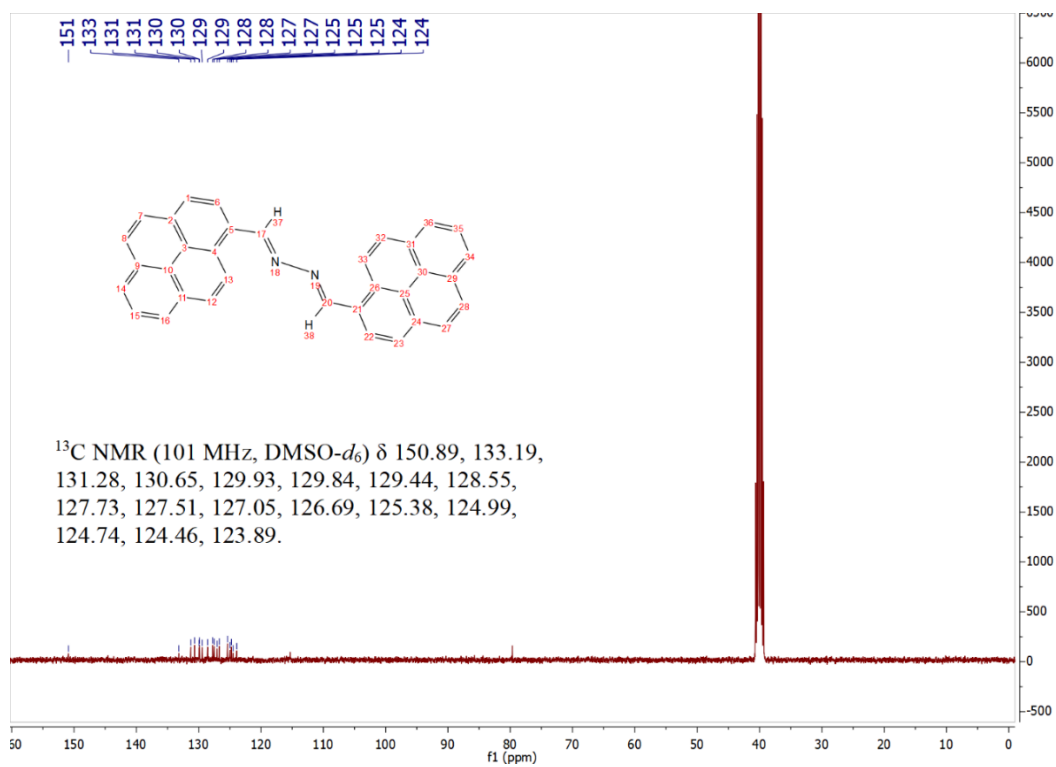


Figure S6: ¹³C NMR spectrum of **L2**

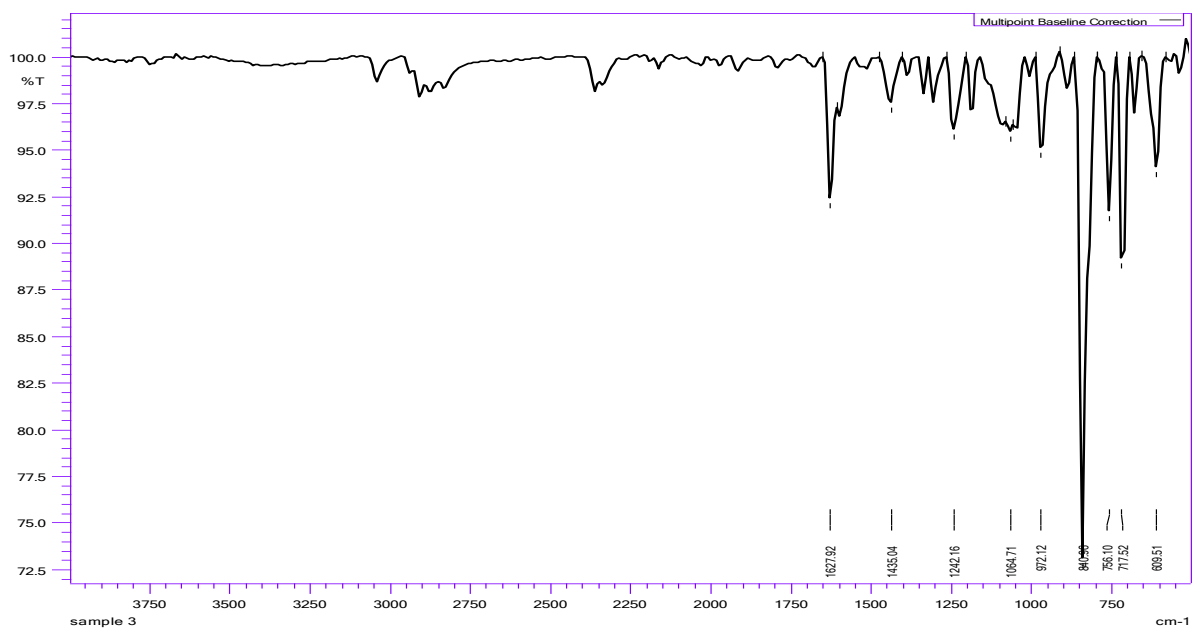


Figure S7: IR spectrum of **L3**

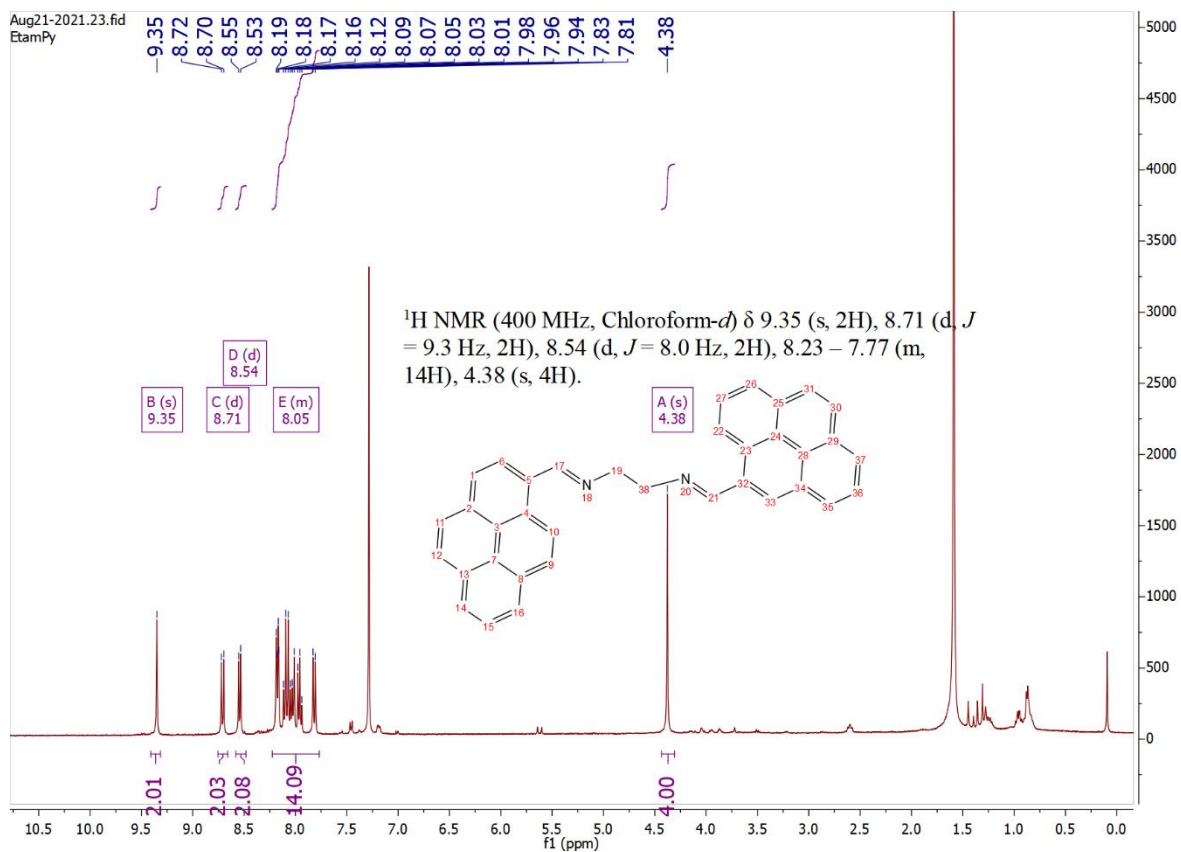


Figure S8: $^1\text{H NMR}$ spectrum of L3

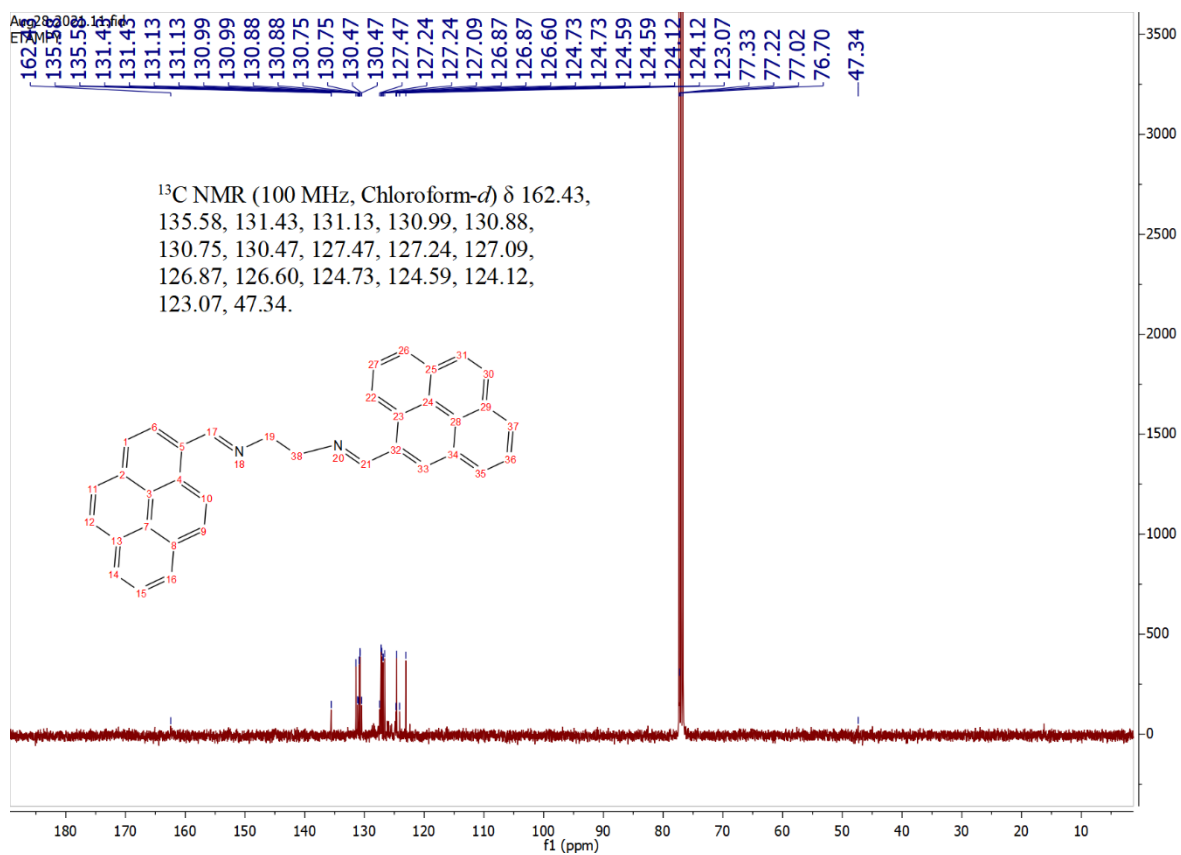


Figure S9: $^{13}\text{C NMR}$ spectrum of L3

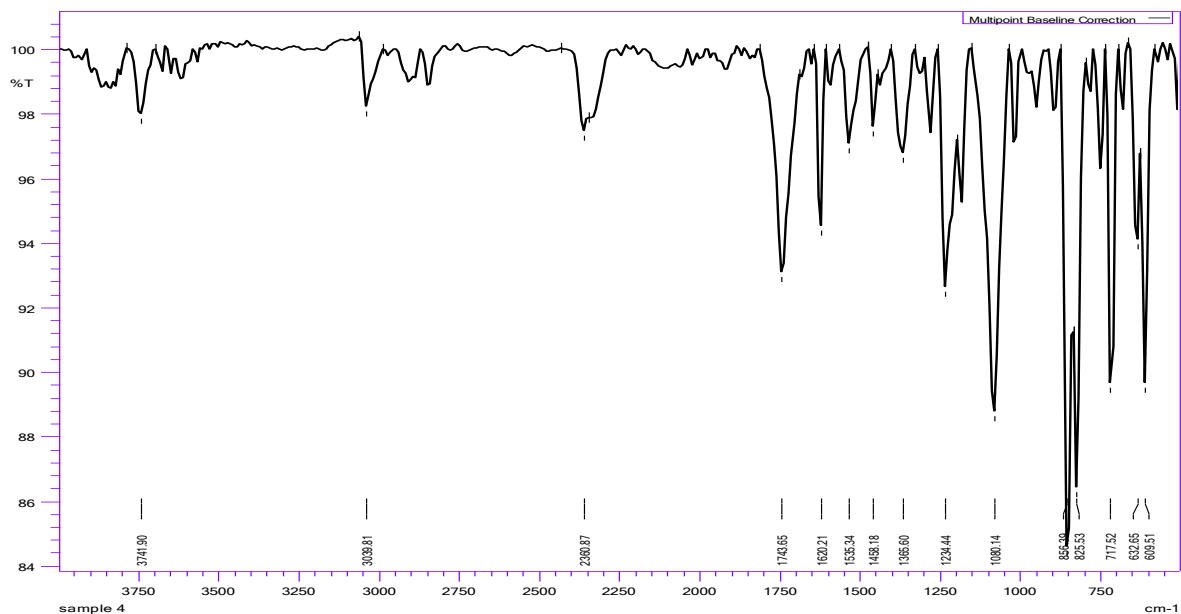


Figure S10: IR spectrum of L4

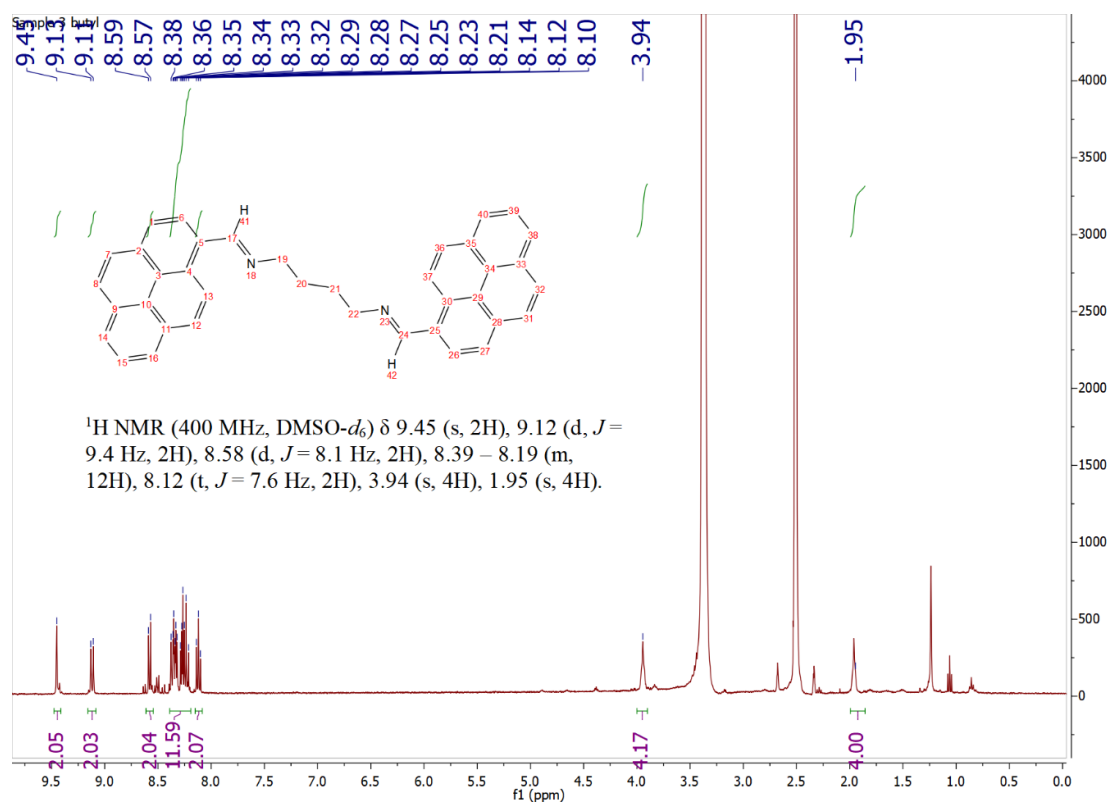


Figure S11: ¹H NMR spectrum of L4

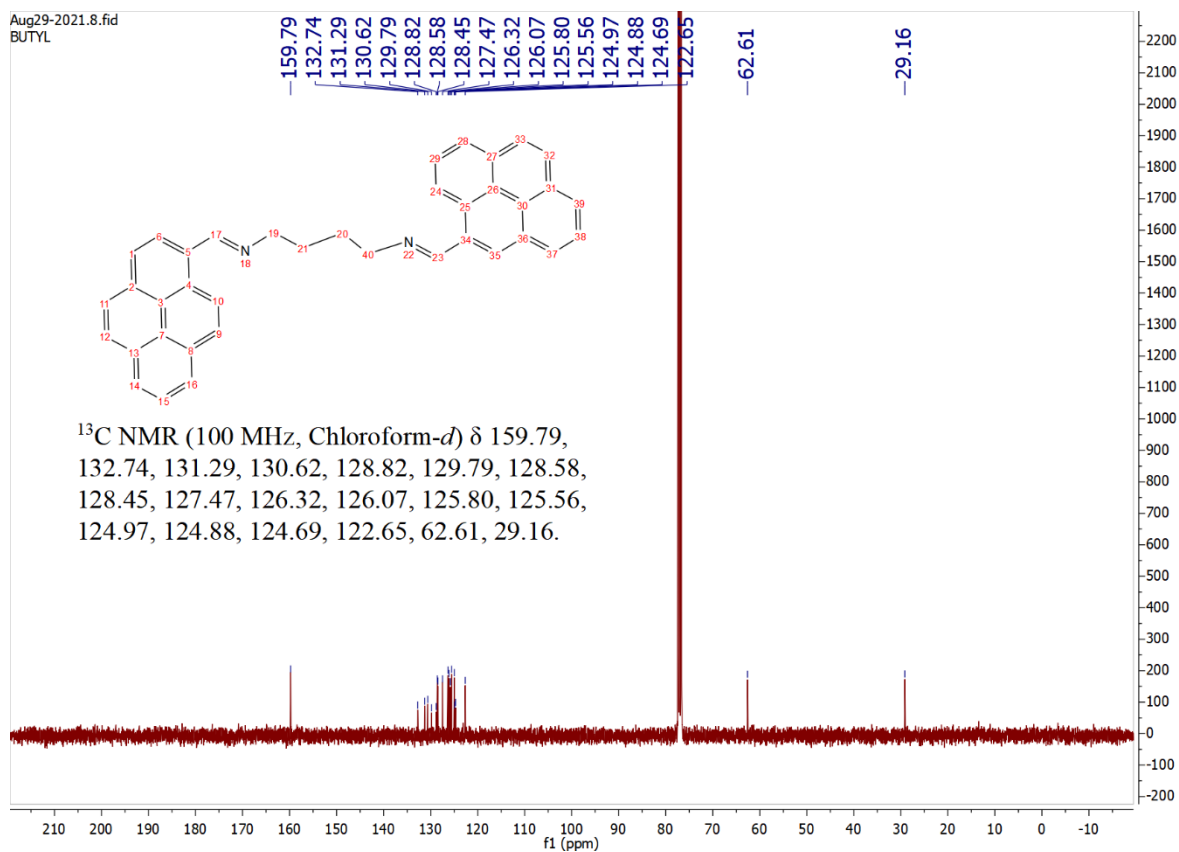


Figure S12: ¹³C NMR spectrum of L4

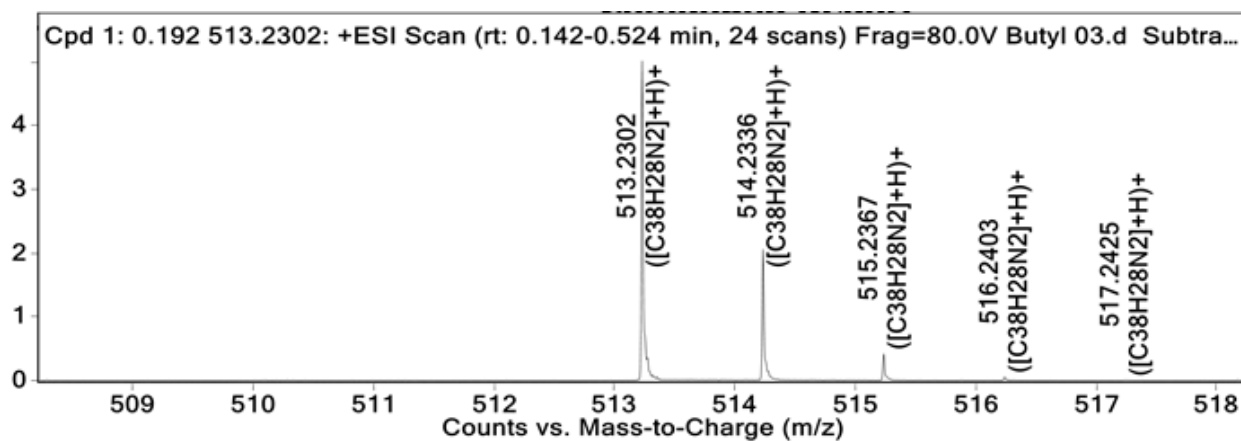


Figure S13: HRMS of L4

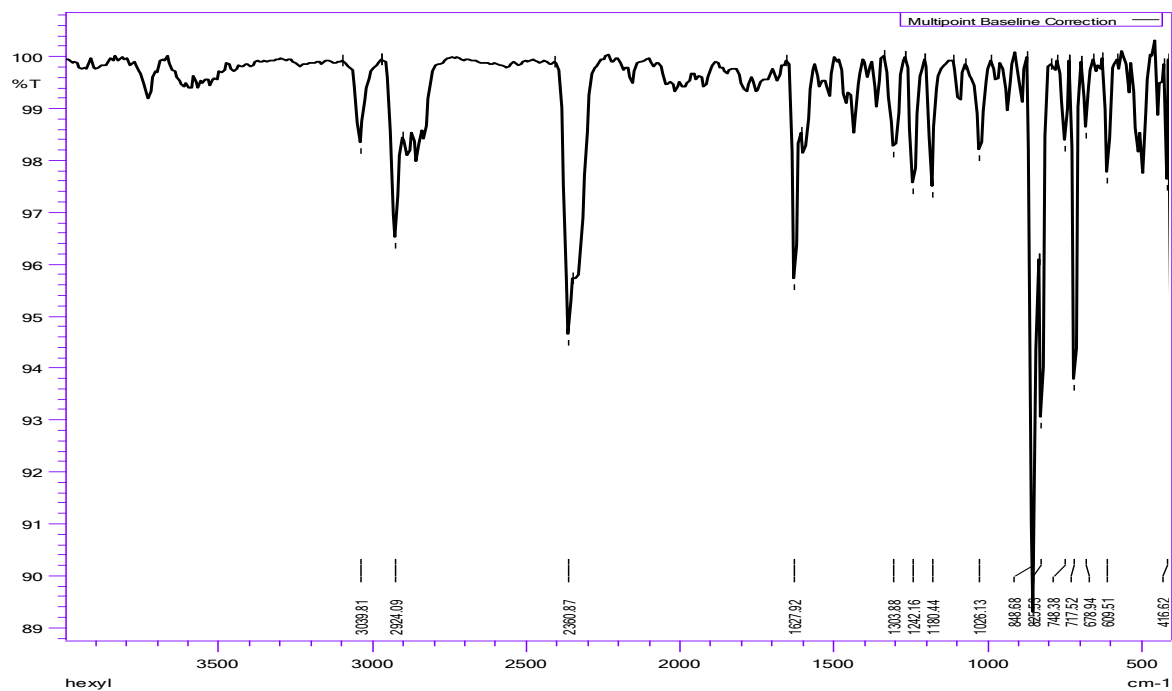


Figure S14: IR spectrum of L5

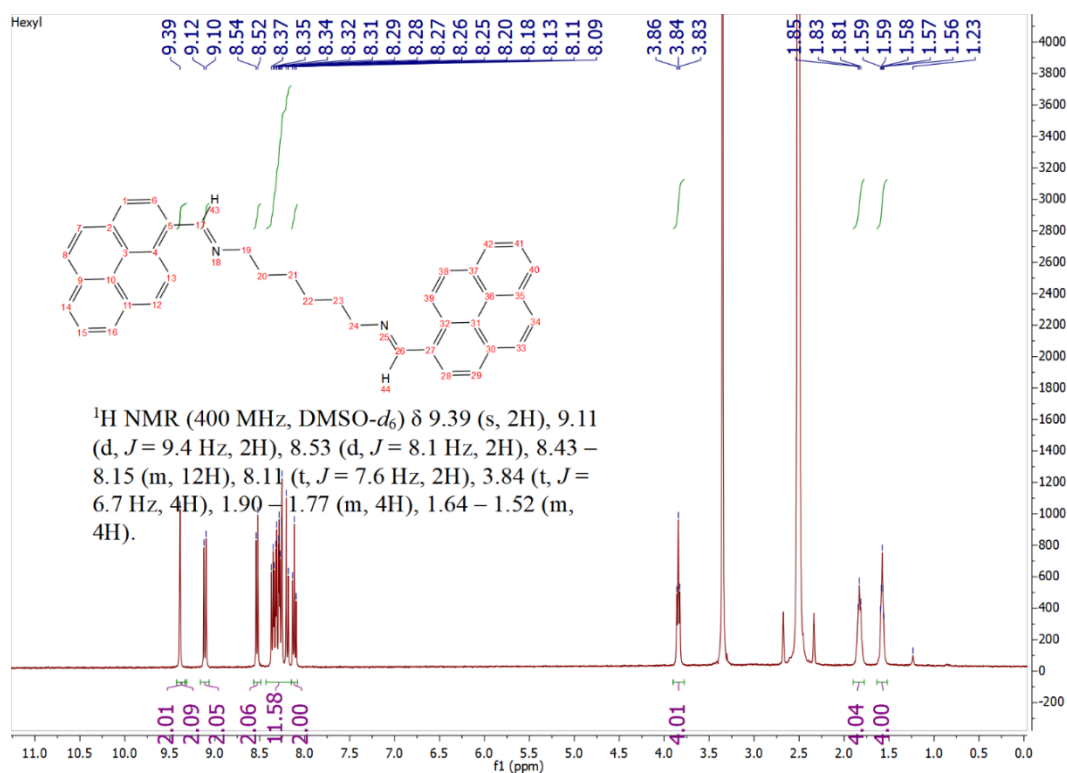


Figure S15: ^1H NMR of L5

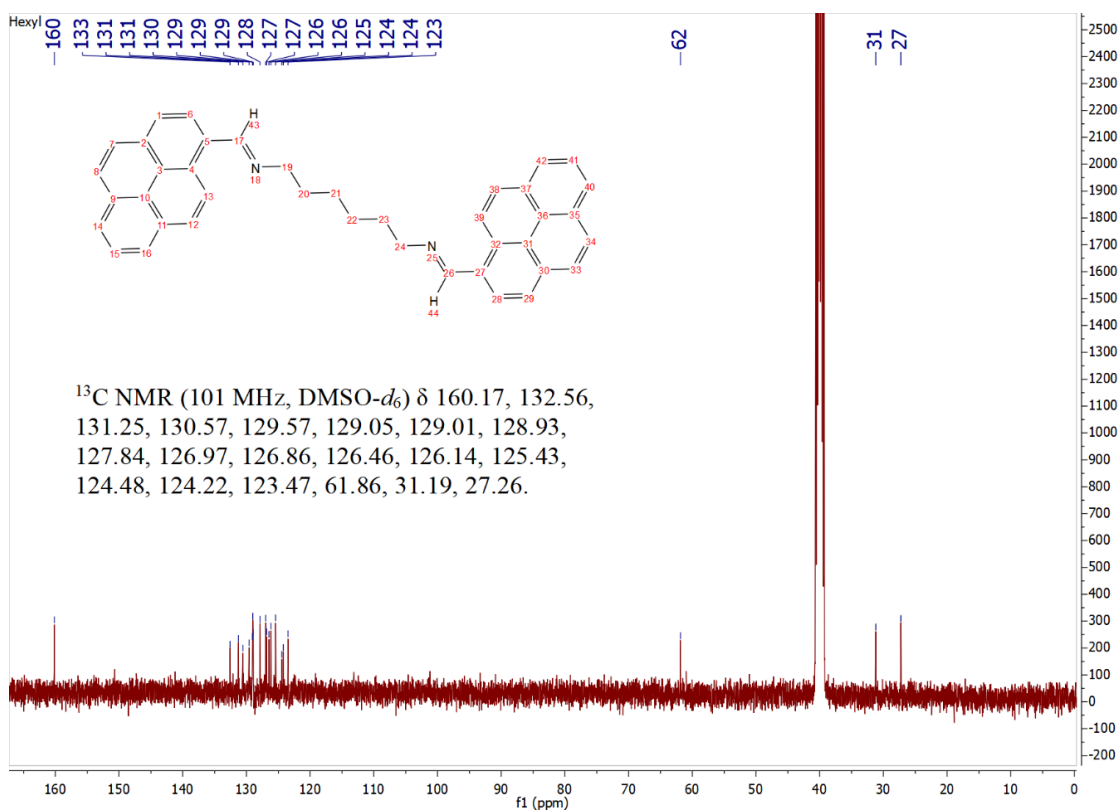


Figure S16: ^{13}C NMR of L5

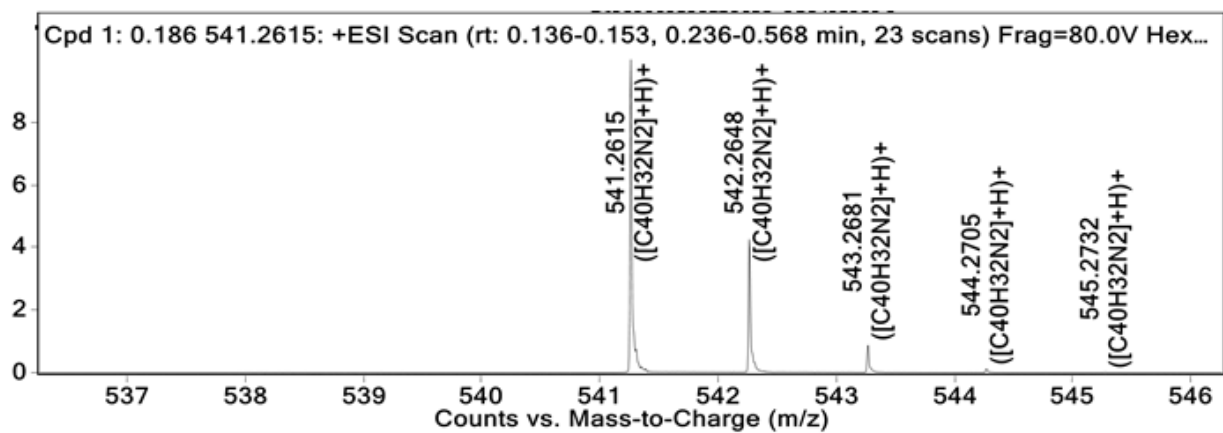


Figure S17: HRMS of L5

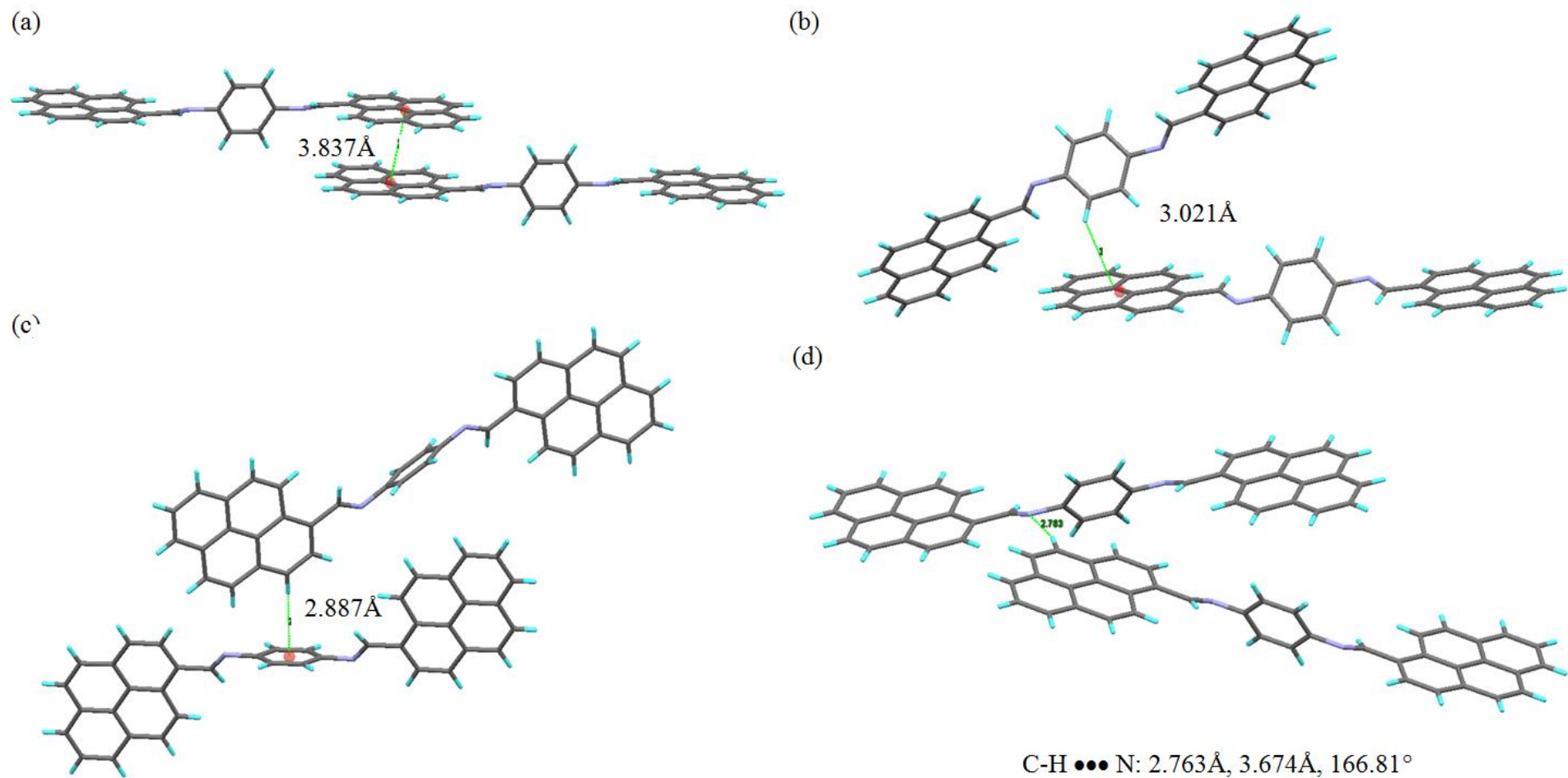


Figure S18: Illustrations of crystal structure of **L1**: (a) Aromatic $\pi \cdots \pi$ interactions between pyrene groups of two neighbouring **L1** molecules; (b) Aromatic C-H $\cdots\pi$ interactions between phenyl C-H and pyrene group; (c) Aromatic C-H $\cdots\pi$ interactions between pyrene C-H and phenyl ring; (d) Very weak C-H \cdots N interactions between pyrene C-H and imine N

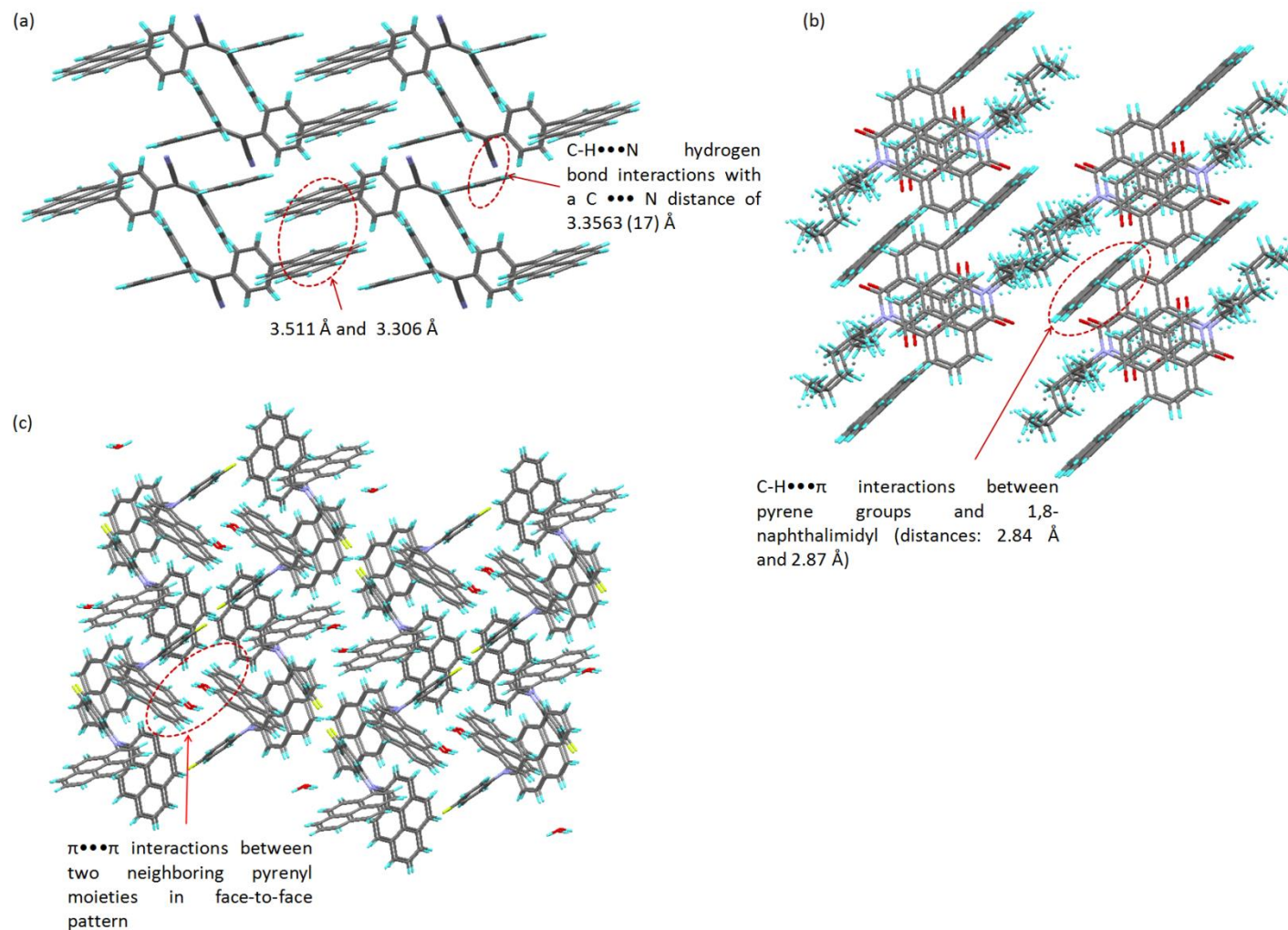


Figure S19: Literature reports on derivatives of pyrenes where aromatic interactions are responsible for holding the molecules together in the solid state; (a) Intermolecular $\pi \cdots \pi$ interactions between adjacent pyrene ring systems in a pyrene based compound (CCDC: 1834096)⁵; (b), Molecules in pyrenyl substituted 1,8-naphthalimide are linked via aromatic C-H $\cdots \pi$ interactions between the pyrene groups and 1,8-naphthalimidyl groups (CCDC 1830576)⁶; (c) Molecules in pyrenyl-based triaryl amines are linked together by $\pi \cdots \pi$ interactions (CCDC 1056680)⁷

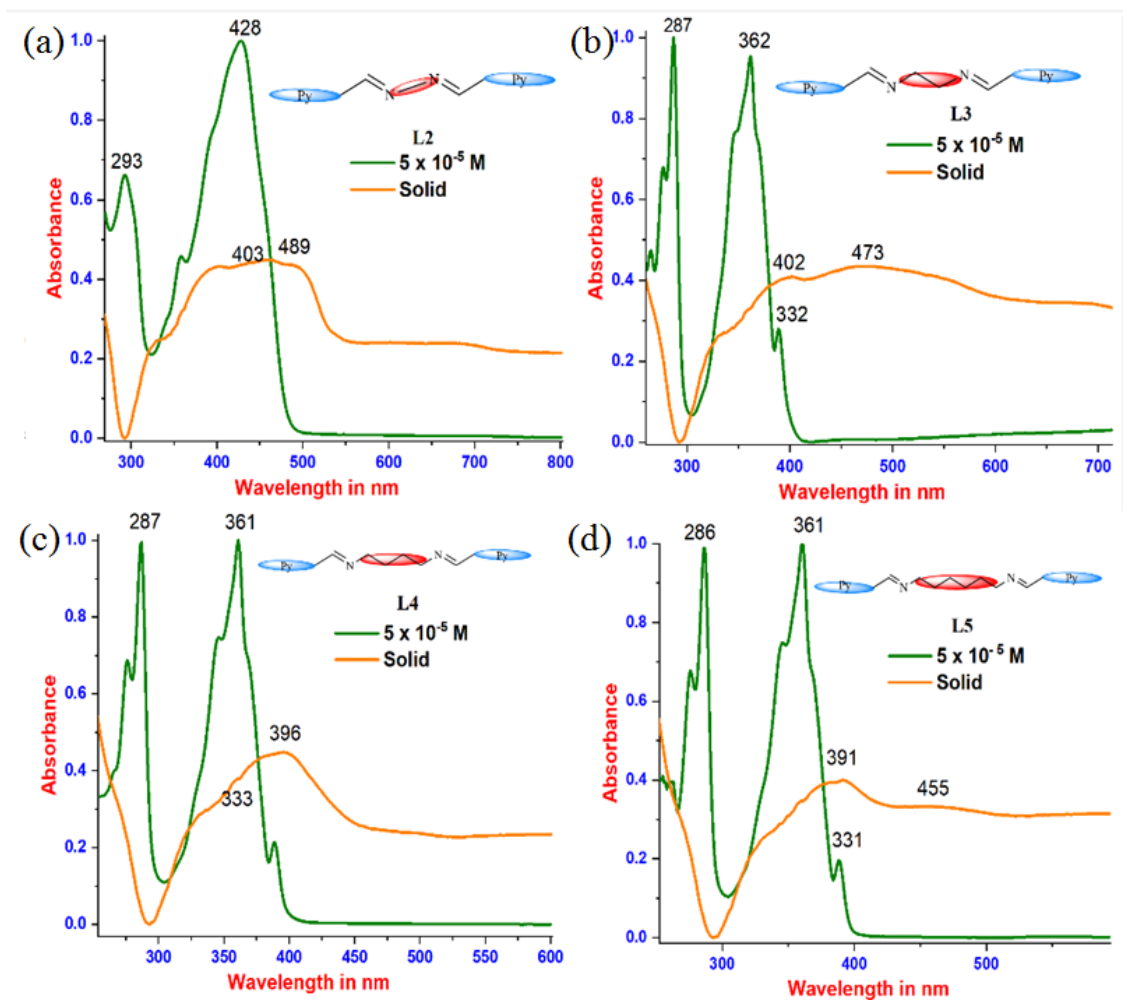


Figure S20: UV-Visible spectra in DMF and solid-state (in BaSO₄): (a) L2; (b) L3; (c) L4; (d) L5

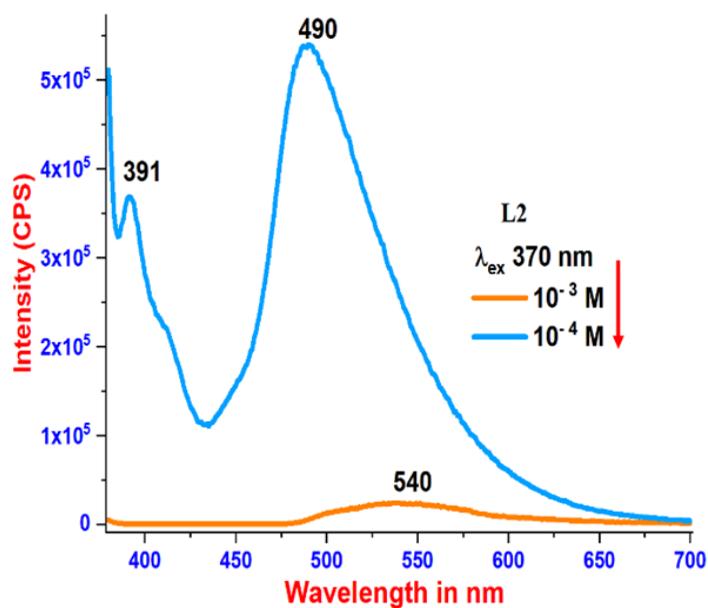


Figure S21: PL spectra of L2 (excitation wavelength 370 nm) in DMF at different concentrations (slit width 10 nm)

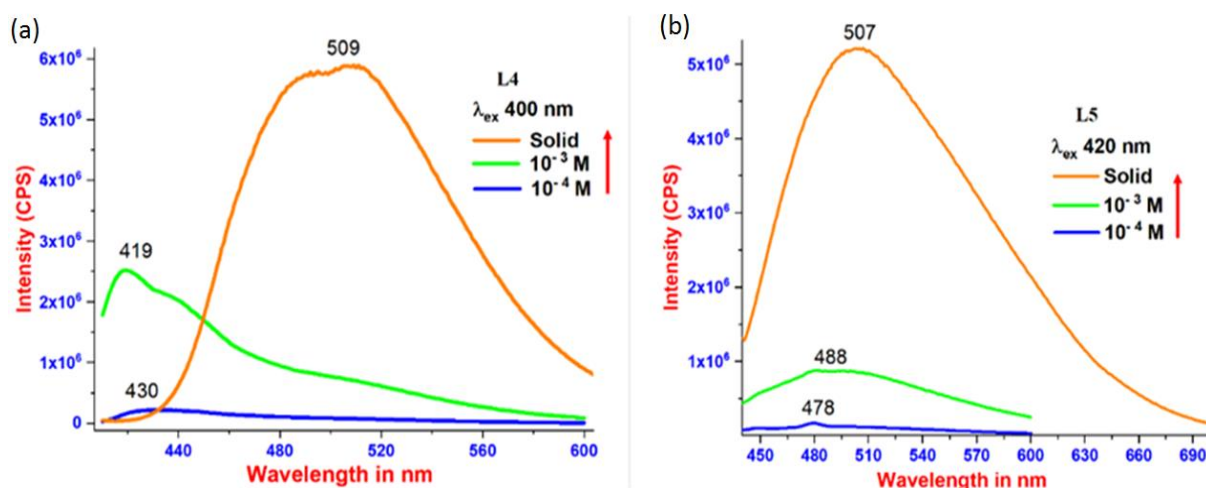


Figure S22: PL spectra of (a) **L4** (excitation wavelength 400 nm) and (b) **L5** (excitation wavelength 420 nm) in DMF at different concentrations and in solid state

Table S1: Comparison of published melting points and the spectroscopy data with the compounds synthesized in the current work

Compounds	Melting Point (Current work)	Melting Point (Literature)	¹ H-NMR (Current workt)	¹ H-NMR (Literature)	¹³ C-NMR (Current work)	¹³ C-NMR (Literature)
L1	315 - 316 °C	[317 °C] ²	9.80 (2H, s, imine CH), 9.37 (2H, d, <i>J</i> = 9.4 Hz, ArH), 8.88 (2H, d, <i>J</i> = 8.1 Hz, ArH), 8.55 – 8.13 (14H, br, ArH), 7.71 (4H, s, ArH)	[9.78 (s, 2H, CH_N), 9.35 (d, 2HAr), 8.86 (d, 2HAr), 8.44–8.16 (m, 18HAr)] ²	150.24, 133.43, 131.19, 130.56, 130.16, 130.15, 129.43, 128.59, 127.69, 127.65, 127.23, 126.87, 125.43, 125.30, 124.43, 124.36, 123.76, 123.38, 115.10	-
L2	308-309 °C	[308 °C] ² [311 °C] ⁴	9.94 (2H, s, imine CH), 9.30 (2H, d, <i>J</i> = 9.2 Hz,	[9.94 (s, 2H, CH_N), 9.03 (d, 2HAr),	150.89, 133.19, 131.28, 130.65, 129.93,	(159.3 132.4 130.4 129.9 129.3 128.4 126.7 128.3

			ArH), 8.86 (2H, d, $J = 8.0$ Hz, ArH), 8.53 – 8.42 (6H, m, ArH), 8.41 – 8.28 (6H, m, ArH), 8.19 (2H, t, $J = 7.7$ Hz, ArH)	8.85 (d, 2HAr), 8.30–8.08 (m, 14HAr)] ²	129.84, 129.44, 128.55, 127.73, 127.51, 127.05, 126.69, 125.38, 124.99, 124.74, 124.46, 123.89	126.4 126.6 126.2 125.9 125.6 125.4 124.4 123.8 122.8) ⁸
L3	225 - 226 °C	[225 °C] ³	9.35 (2H, s, imine CH), 8.71 (2H, d, $J =$ 9.3 Hz, ArH), 8.54 (2H, d, $J =$ 8.0 Hz, ArH), 8.23 – 7.77 (14H, m, ArH), 4.38 (4H, s, 2×CH ₂)	[4.35 (4H, s, CH ₂), d 7.76–8.68 (18H, m, pyrene), d 9.32 (2H, s, HC=N)] ³	162.43, 135.58, 131.43, 131.13, 130.99, 130.88, 130.75, 130.47, 127.47, 127.24, 127.09, 126.87, 126.60, 124.73, 124.59, 124.12, 123.07, 47.34	-
L4	231-232 °C	[230 °C] ⁴	9.45 (2H, s, imine CH), 9.12 (2H, d, $J =$ 9.4 Hz, ArH), 8.58 (2H, d, $J =$ 8.1 Hz, ArH), 8.39 – 8.19 (12H, m, ArH), 8.12 (2H, t, $J =$ 7.6 Hz, ArH), 3.94 (4H, br, 2×CH ₂), 1.95 (4H, br, 2×CH ₂)		159.79, 132.74, 131.29, 130.62, 128.82, 129.79, 128.58, 128.45, 127.47, 126.32, 126.07, 125.80, 125.56, 124.97, 124.88, 124.69, 122.65, 62.61, 29.16	-
L5	153-154	[150 °C] ⁴	9.39 (2H,		160.17,	-

	°C		s, imine CH), 9.11 (2H, d, $J =$ 9.4 Hz, ArH), 8.53 (2H, d, $J =$ 8.1 Hz, ArH), 8.43 – 8.15 (12H, br, ArH), 8.11 (2H, t, $J =$ 7.6 Hz, ArH), 3.84 (4H, br, 2×CH ₂), 1.90 – 1.77 (4H, br, 2×CH ₂), 1.64 – 1.52 (4H, br, 2×CH ₂)		132.56, 131.25, 130.57, 129.57, 129.05, 129.01, 128.93, 127.84, 126.97, 126.86, 126.46, 126.14, 125.43, 124.48, 124.22, 123.47, 61.86, 31.19, 27.26	
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