Electronic Supplementary information (ESI):

Hydrogen-bond mediated columnar liquid crystalline assemblies of C_3-symmetric heptazine derivatives at ambient temperature

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1. Experimental Section

a) Materials and reagents. Commercially available chemicals were used in p.a. quality as obtained from the suppliers. 4-decylaniline, 4-hexylaniline, 1,10-Dibromodecane, 1,12-Dibromododecane, 1,16-Dibromohexadecane, triethylamine (NEt_3) were purchased from Sigma-Aldrich. THF was bought from Merck and dried in a lab by using benzophenone and sodium. Column chromatographic separations were performed on silica gel (60-120) and neutral alumina gel. Thin layer chromatography (TLC) was performed on alumina sheets pre-coated with silica gel (Merck, Kieselgel 60, F254).

b) Instrumentation

Structural characterization. ^{1}H NMR and ^{13}C NMR (Bruker Biospin Switzerland Avance-iii 400 MHz and 100 MHz spectrometers respectively), UV-VIS-NIR spectrophotometer (Agilent Technologies UV-Vis-NIR Spectrophotometer). NMR spectra were recorded using deuterated chloroform ($CDCl_3$) and tetramethylsilane (TMS) as an internal standard.

Polarised Optical Microscopy Textural observations of the mesophase were performed with Nikon Eclipse LV100POL polarising microscope provided with a Linkam heating stage (LTS 420). All images were captured using a Q-imaging camera.

DSC Study The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (Perkin Elmer DSC 8000 coupled to a controlled liquid nitrogen accessory (CLN 2)) which was operated at a scanning rate of 10 °C min^{-1} both on heating and cooling.

X-ray diffraction studies X-ray diffraction (XRD) was carried out using Cu Kα (λ=1.54 Å) radiation from a source (GeniX 3D, Xenocs) operating at 50 kV and 0.6 mA. The diffraction patterns were collected on a two module Pilatus detector.

Photophysical studies Fluorescence emission spectra were performed on Horiba Scientific Fluoromax spectrofluorometer 4.

Correlation length (ξ): The correlation length (ξ) measures the degree of order within the mesophases. It can be calculated by using the Scherrer's equation:

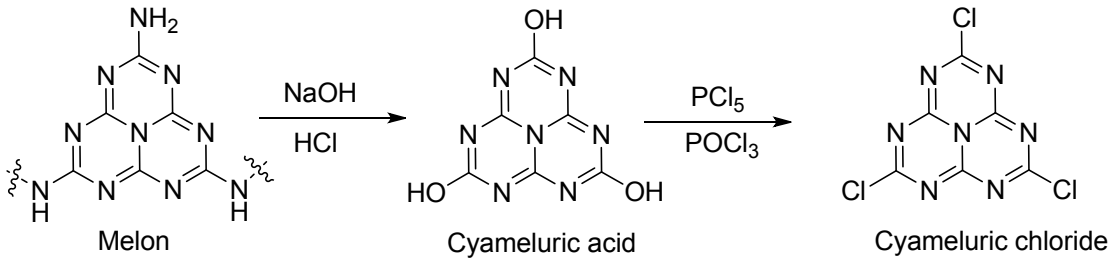
$$\xi = [k\ 2\pi]/[(\Delta q)] \text{ which is equivalent to, } \xi = [k\ \lambda]/[(\Delta 2\theta)\cos\theta]$$

Here, k is the shape factor whose typical value is 0.89, λ is the wavelength of the incident X-ray, Δ2θ is the broadening in 2θ at half the maximum intensity (FWHM) in radian unit, and θ is the maximum of the reflection. q is the scattering vector ($q=4\pi\text{Sin}\theta/\lambda$) and Δq is the broadening in q at half the maximum intensity. Δq is obtained by Lorentzian fitting of the diffraction pattern.

2. Synthesis and Characterization

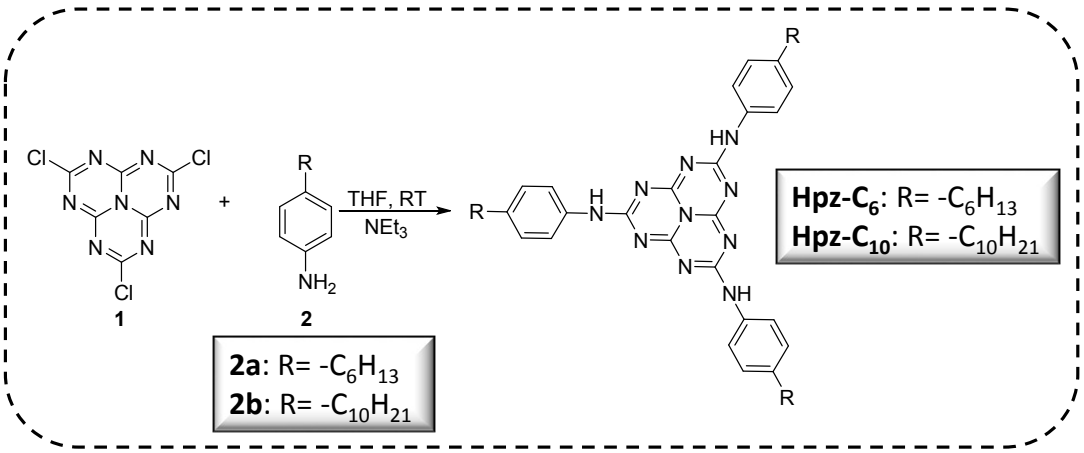
Synthesis of Heptazine (Cyameluric) Chloride from melon:

Cyameluric chloride was synthesized according to the previous reports.[1]



Scheme S1. Synthesis of Cyameluric chloride.

Synthesis of Heptazine derivatives (Hpz-$C_{m=6,10}$) from melon:



Scheme S2. Synthetic route of fluorophore component **Hpz-C_n** (n=6, 10).

Heptazine (cyameluric chloride):

^{13}C NMR: δ 159.55 (CN_3), 176.29 ($CClN_2$); FTIR (ATR, cm-1): 1600, 1500, 1300, 1200, 938, 822, 648. UV-Vis (λ in nm): 310. Photoluminescence (λ in nm): 468.

Characterization details of Hpz-$C_{m=6,10}$

Compound Hpz-C_6:

FT-IR (cm^{-1}): 3351.20, 3288.86, 3230.57, 3187.17, 3130.07, 3103.01, 2954.46, 2924.31, 2853.40, 1633.08, 1604.96, 1587.96, 1531.28, 1463.00, 1418.69, 1367.08, 1319.29, 1304.25, 1238.75, 1190.54, 1157.84, 1140.92, 1021.37, 856.94, 806.11, 737.28, 617.70.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 7.63 (s, 3H, -NH protons), δ 7.51-7.47 (m, 6H, aromatic protons), δ 7.18-7.15 (m, 6H, aromatic protons), δ 2.61-2.57 (t, 6H, J= 7.46 Hz), δ 1.63 (s, 6H), δ 1.32 (s, 12H), δ 1.27 (s, 8H), δ 0.92-0.89 (t, 9H, J= 5.70 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 177.86, 154.86, 129.06, 124.50, 121.52, 114.08, 68.40, 64.16, 43.16, 35.43, 31.95, 29.72, 22.72, 22.65, 14.14.

Compound Hpz-C_{10}:

FT-IR (cm^{-1}): 3360.00, 3286.61, 3224.42, 3096.19, 2956.41, 2922.96, 2853.06, 1703.98, 1632.35, 1603.99, 1593.24, 1512.06, 1470.16, 1422.36, 1390.67, 1368.43, 1316.01, 1299.22, 1245.21, 1190.16, 1157.52, 1139.56, 1121.49, 1019.30, 984.32, 887.65, 831.83, 805.49, 611.28.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 7.52 (s, 3H, -NH protons), δ 7.49-7.47 (d, 6H, aromatic protons, J= 4.04 Hz), δ 7.17-7.15 (d, 6H, aromatic protons, J= 7.96 Hz), δ 2.61-2.57 (t, 6H, J= 7.56 Hz), δ 1.31-1.28 (m, 46H), δ 0.92-0.89 (t, 9H, J= 6.14 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 162.29, 12913, 128.95, 128.2, 121.41, 35.41, 35.12, 31.99, 31.94, 29.67, 29.38, 22.73, 14.16.

Synthesis of 3,4,5-trialkoxybenzoic acids (**A10**, **A12** & **A16**):

3,4,5-trialkoxybenzoic acids were prepared from the starting material gallic acid monohydrate according to the previously reported procedures.[2]

Compound A10:

FT-IR (cm^{-1}): 2955.13, 2924.78, 2854.79, 1685.00., 1587.00, 1504.13, 1468.06, 1433.16, 1382.11, 1330.88, 1265.83, 1229.76, 1117.35, 987.65, 931.74, 867.30, 768.55.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.35 (s, 2H), 4.08-4.03 (m, 6H), 1.86-1.77 (m, 6H), 1.54-1.46 (m, 6H), 1.33-1.30 (m, 36H), 0.92-0.89 (t, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 171.67, 152.84, 143.10, 123.62, 108.49, 73.57, 69.17, 31.97, 31.94, 30.35, 29.76, 29.70, 29.66, 29.61, 29.58, 29.43, 29.41, 29.38, 29.28, 26.10, 26.06, 14.15.

Compound A12:

FT-IR (cm^{-1}): 2954.20, 2920.73, 2850.62, 1685.23, 1587.41, 1504.44, 1468.14, 1432.25, 1385.24, 1333.47, 1275.38, 1228.04, 1121.59, 864.03, 767.69.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.34 (s, 2H), 4.08-4.03 (m, 6H), 1.86-1.77 (m, 6H), 1.53-1.46 (m, 6H), 1.32-1.29 (m, 48H), 0.92-0.89 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 152.87, 143.11, 108.51, 73.57, 69.18, 31.98, 31.96, 30.35, 29.79, 29.77, 29.73, 29.69, 29.67, 29.59, 29.42, 29.40, 29.29, 26.11, 26.07, 22.73, 14.16.

Compound A16:

FT-IR (cm^{-1}): 2954.48, 2917.92, 2849.42, 1685.01, 1587.02, 1504.94, 1468.76, 1429.99, 1381.01, 1334.10, 1275.39, 1227.27, 1123.20, 984.81, 969.88, 863.06, 767.13.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.34 (s, 2H), 4.08-4.03 (m, 6H), 1.88-1.73 (m, 6H), 1.53-1.46 (m, 6H), 1.37-1.28 (m, 72H), 0.92-0.88 (t, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 171.67, 152.84, 143.10, 123.62, 108.49, 73.57, 69.17, 31.97, 31.94, 30.35, 29.76, 29.70, 29.66, 29.61, 29.58, 29.43, 29.41, 29.38, 29.28, 26.10, 26.06, 14.15.

Characterization data of Heptazine-Acid complexes:

Complex Hpz-C_6/A10:

FT-IR (cm^{-1}): 3310.11, 3303.32, 3087.23, 2954.60, 2924.44, 2854.57, 1695.00, 1619.28, 1611.57, 1587.57, 1529.65, 1511.07, 1467.22, 1428.64, 1391.39, 1329.13, 1225.96, 826.60, 767.45, 720.24.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 9.55-9.45 (m, 2H), 9.01-8.95 (m, 1H), 7.75-7.60 (m, 6H), 7.38 (s, 6H), 7.21-7.19 (d, 6H, *J*= 7.60 Hz), 4.08-4.04 (m, 18H), 2.63-2.58 (m, 6H), 1.88-1.75 (m, 24H), 1.52-1.49 (m, 18H), 1.30 (broad s, 126H), 0.92-0.89 (t, 36H, *J*= 6.48 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 171.22, 152.86, 142.97, 128.86, 124.15, 121.13, 108.56, 73.57, 69.22, 35.54, 31.95, 31.81, 31.95, 31.81, 30.39, 29.77, 29.72, 29.69, 29.64, 29.62, 29.48, 29.44, 29.40, 29.38, 26.16, 26.10, 22.74, 22.72, 22.69, 14.16.

Complex Hpz-C_6/A12:

FT-IR (cm^{-1}): 3310.11, 3303.65, 3088.50, 2955.39, 2922.78, 2853.11, 1695.32, 1611.01, 1587.79, 1529.90, 1511.34, 1468.02, 1428.74, 1391.54, 1330.14, 1259.99, 1226.25, 1154.28, 1121.39, 1018.99, 864.48, 825.70, 799.88, 765.92, 720.76.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 9.46 (broad s, 2H), 8.96 (s, 1H), 7.74-7.62 (m, 6H), 7.38 (s, 6H), 7.21-7.19 (d, 6H, *J*= 7.36 Hz), 4.08-4.04 (m, 18H), 2.63-2.57 (m, 6H), 1.88-1.76 (m, 24H), 1.51-1.44 (m, 18H), 1.29 (broad s, 163H), 0.92-0.89 (t, 36H, *J*= 6.52 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 171.20, 152.86, 142.97, 128.86, 124.15, 121.16, 108.56, 73.57, 69.22, 35.55, 31.98, 31.96, 30.39, 29.79, 29.77, 29.75, 29.74, 29.71, 29.61, 29.63, 29.48, 29.44, 29.41, 29.38, 26.17, 26.11, 22.73, 22.69, 14.16.

Complex Hpz-C_6/A16:

FT-IR (cm^{-1}): 3303.11, 3087.32, 2954.68, 2919.87, 2851.56, 1696.14, 1621.71, 1612.55, 1530.63, 1513.08, 1468.28, 1428.90, 1392.16, 1329.64, 1225.07, 1121.07, 823.68, 796.52, 763.51, 720.98.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 9.36 (s, 2H), 8.92 (s, 1H), 7.73-7.59 (m, 6H), 7.38 (s, 6H), 7.21-7.20 (d, 6H, *J*= 7.00Hz), 4.08-4.04 (m, 18H), 2.63-2.58 (m,6H), 1.88-1.75 (m, 24H), 1.51-1.47 (m, 18H), 1.28 (s, 234H), 0.92-0.88 (t, 36H, *J*= 6.66 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 171.20, 152.86, 142.97, 128.88, 108.55, 73.57, 69.21, 35.55, 31.97, 31.81, 30.39, 29.77, 29.70, 29.64, 29.48, 29.42, 29.38, 26.17, 26.11, 22.73, 22.69, 14.16.

Complex Hpz-C_{10}/A10:

FT-IR (cm^{-1}): 3310.11, 3303.05, 3090.36, 2955.69, 2923.65, 2853.73, 1696.11, 1620.97, 1612.884, 1588.31, 1529.92, 1511.85, 1467.64, 1429.15, 1391.32, 1329.40, 1226.48, 1116.59, 823.82, 765.54, 720.00.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 9.39-9.32 (m, 2H), 8.91 (s, 1H), 7.72-7.59 (m, 6H), 7.38 (s, 6H), 7.21-7.19 (d, 6H, *J*= 7.80 Hz), 4.08-4.04 (m, 18H), 2.63-2.57 (m, 6H), 1.88-1.75 (m, 24H), 1.52-1.47 (m, 18H), 1.30 (broad s, 150H), 0.92-0.89 (t, 36H, *J*= 6.60 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 171.09, 152.86, 142.96, 128.88, 108.56, 73.57, 69.23, 35.55, 31.98, 31.95, 30.39, 29.77, 29.72, 29.69, 29.64, 29.62, 29.48, 29.44, 29.40, 29.38, 26.16, 26.10, 22.74, 22.72, 14.15.

Complex Hpz-C_{10}/A12:

FT-IR (cm^{-1}): 3310.11, 3303.12, 3082.17, 2954.98, 2920.14, 1696.41, 1620.42, 1610.39, 1588.61, 1527.97, 1511.36, 1467.93, 1429.30, 1390.86, 1331.01, 1259.82, 1227.41, 1150.18, 1020.65, 862.86, 801.12, 764.89, 722.25.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 9.26 (s, 3H), 7.71-7.61 (m, 6H), 7.36 (s, 6H), 7.21-7.19 (d, 6H, *J*= 8.00 Hz), 4.08-4.03 (m, 18H), 2.63-2.55 (m, 6H), 1.85-1.74 (m, 24H), 1.60-1.50 (m, 18H), 1.29 (broad s, 186H), 0.91-0.88 (t, 36H, *J*= 6.00 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 173.27, 152.86, 143.39, 128.91, 110.23, 108.55, 73.57, 69.2, 31.96, 30.38, 29.78, 29.74, 29.70, 29.69, 29.61, 29.43, 29.41, 29.36, 26.15, 26.09, 22.73, 14.16.

Complex Hpz-C_{10}/A16:

FT-IR (cm^{-1}): 3310.11, 3303.21, 3090.33, 2954.93, 2920.14, 2852.39, 1695.00, 1621.21, 1614.68, 1530.48, 1512.67, 1468.76, 1429.20, 1392.41, 1329.68, 1225.79, 1120.15, 795.49, 720.88.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 9.32-9.30 (d, 3H, *J*= 8.12 Hz), 7.72-7.61 (m, 6H), 7.37 (s, 6H), 7.21-7.19 (d, 6H, *J*= 8.20 Hz), 4.08-4.03 (m, 18H), 2.60-2.57 (m, 6H), 1.87-1.74 (m, 24H), 1.50-1.47 (m, 18H), 1.28 (broad s, 258H), 0.92-0.89 (t, 36H, *J*= 6.68 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 171.06, 152.87, 142.99, 128.88, 124.11, 121.18, 108.57, 73.56, 69.23, 35.54, 31.96, 31.63, 30.40, 29.80, 29.77, 29.71, 29.64, 29.49, 29.41, 26.17, 26.11, 22.72, 14.15.

NMR spectra of the compounds:

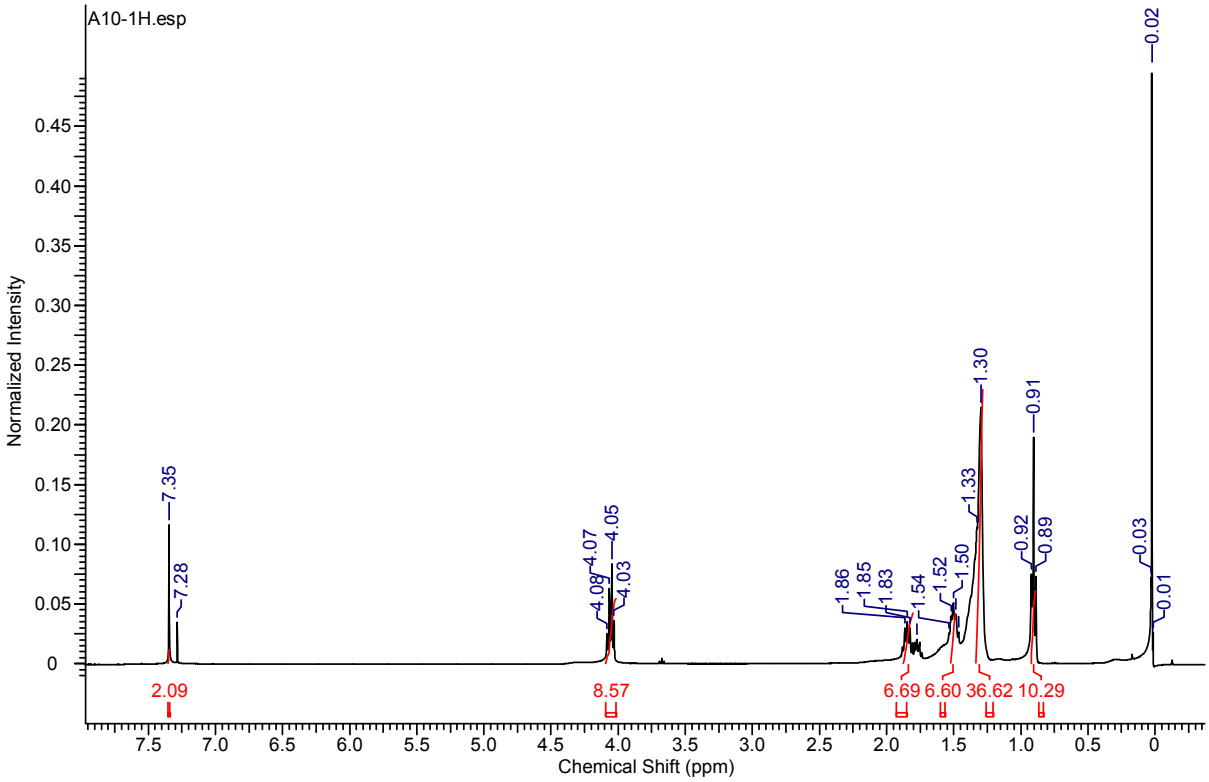


Figure S1. ^{1}H NMR spectra of compound **A10**

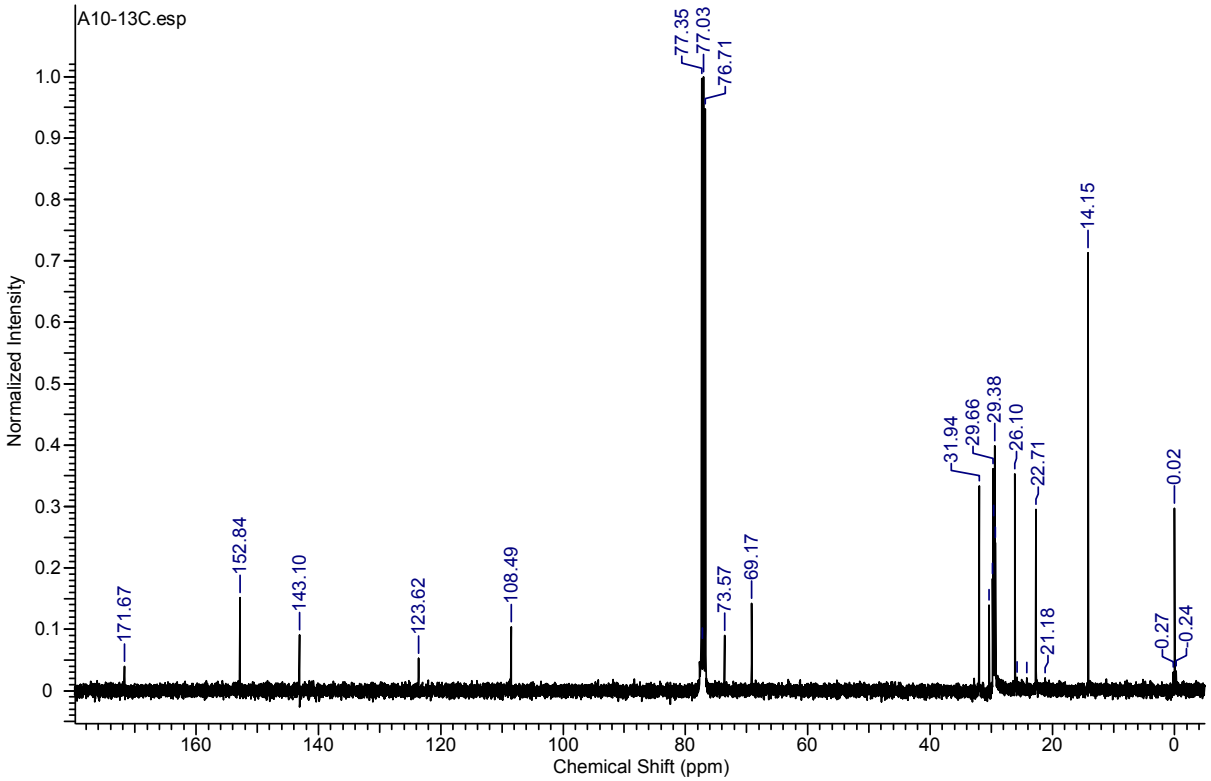


Figure S2. ^{13}C NMR spectra of compound **A10**

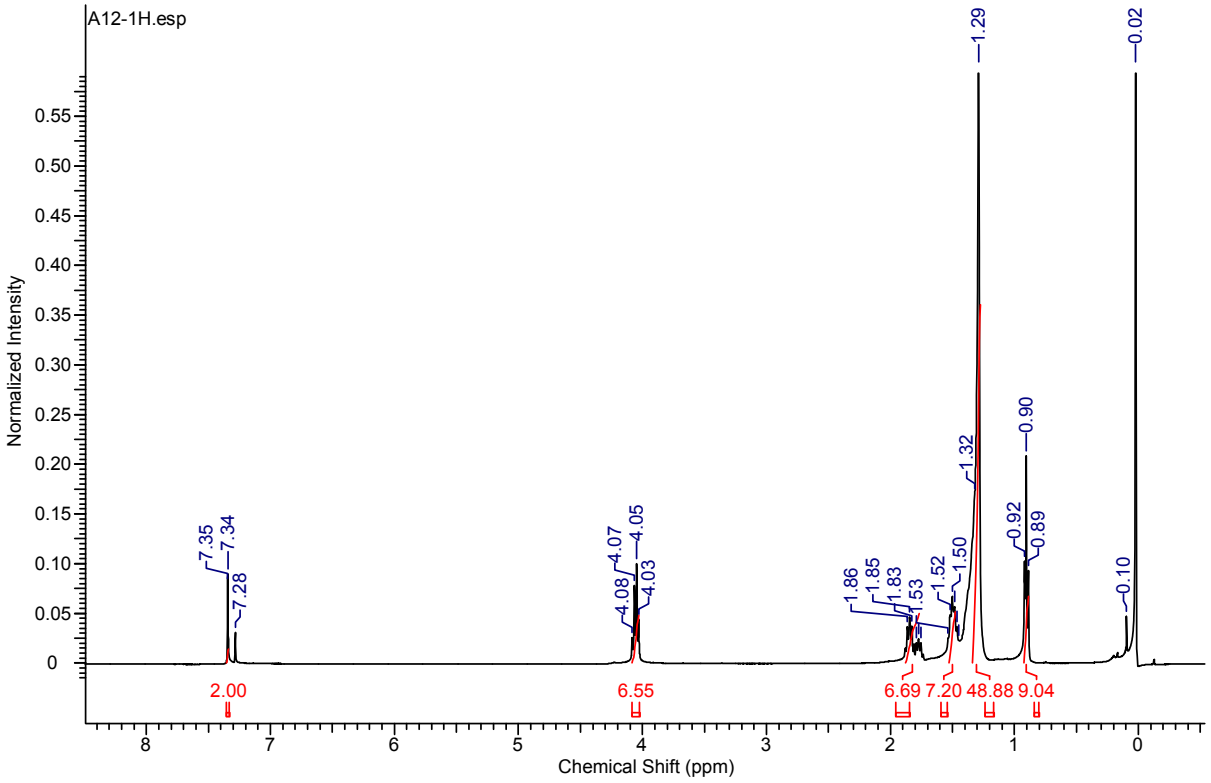


Figure S3. ^{1}H NMR spectra of compound **A12**

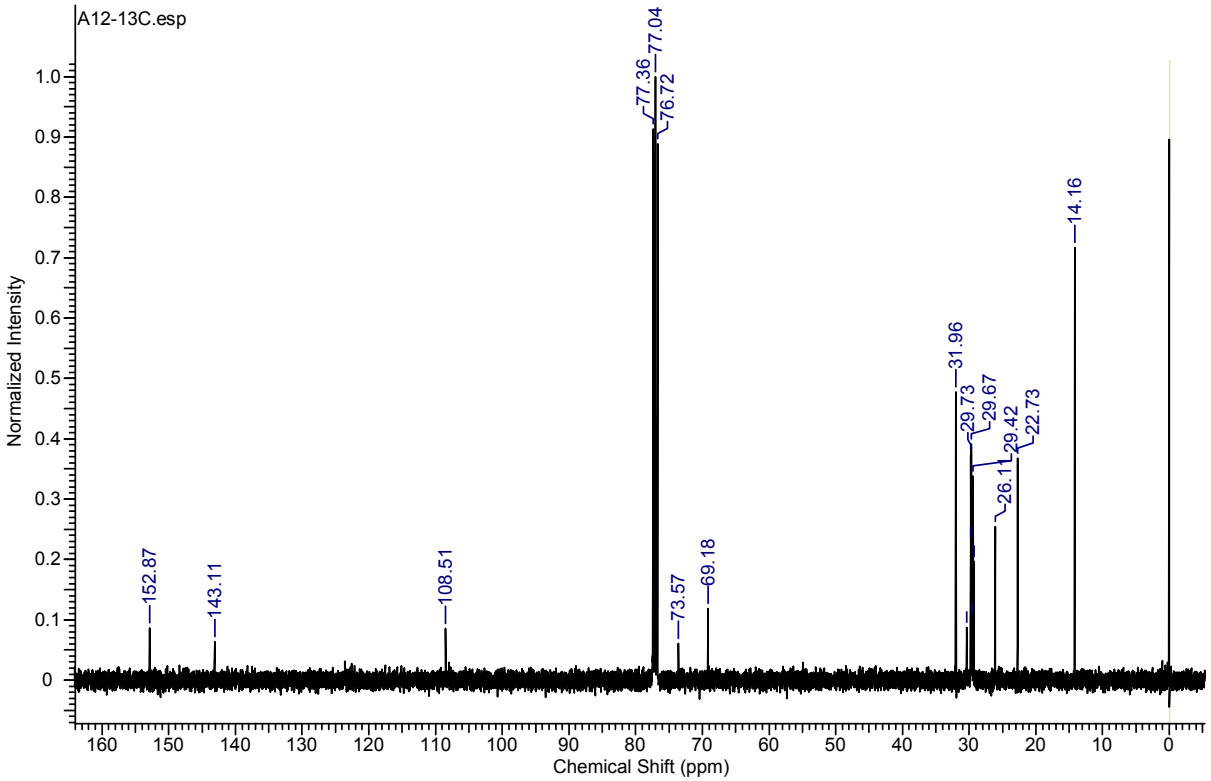


Figure S4. ^{13}C NMR spectra of compound **A12**

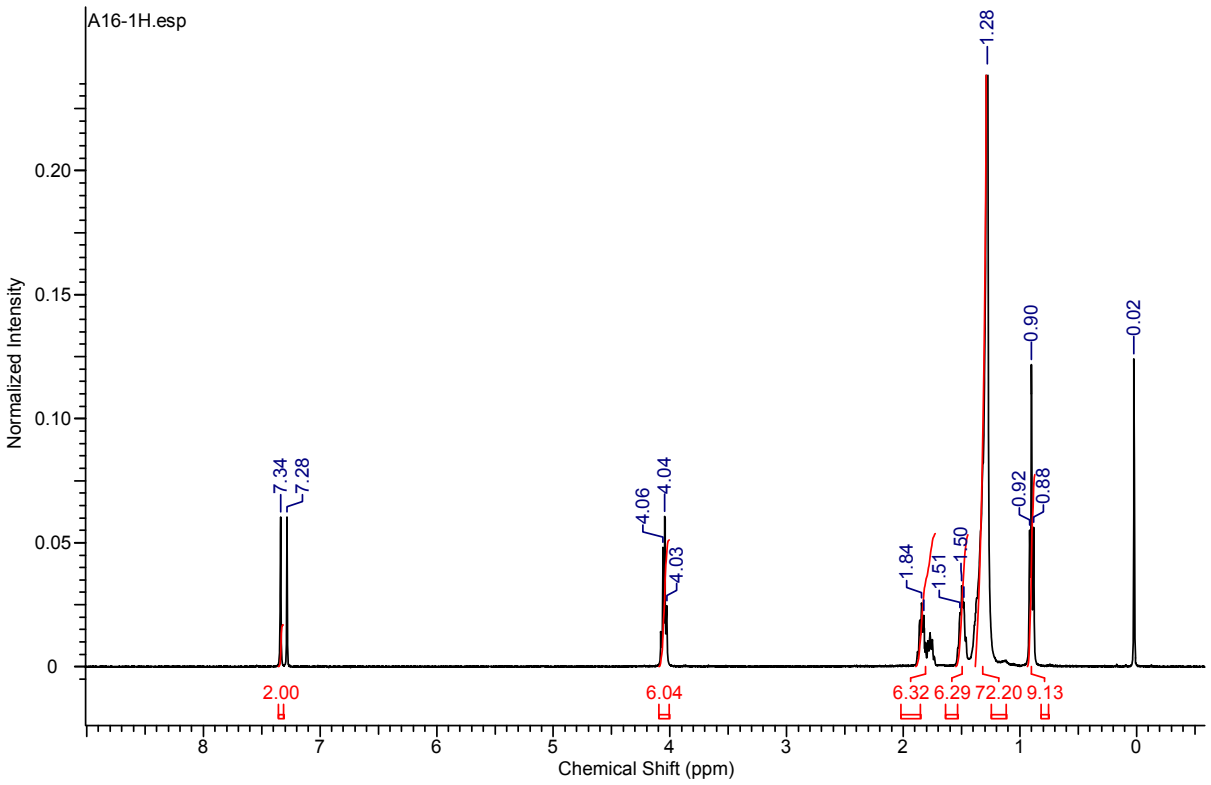


Figure S5. ^{1}H NMR spectra of compound **A16**

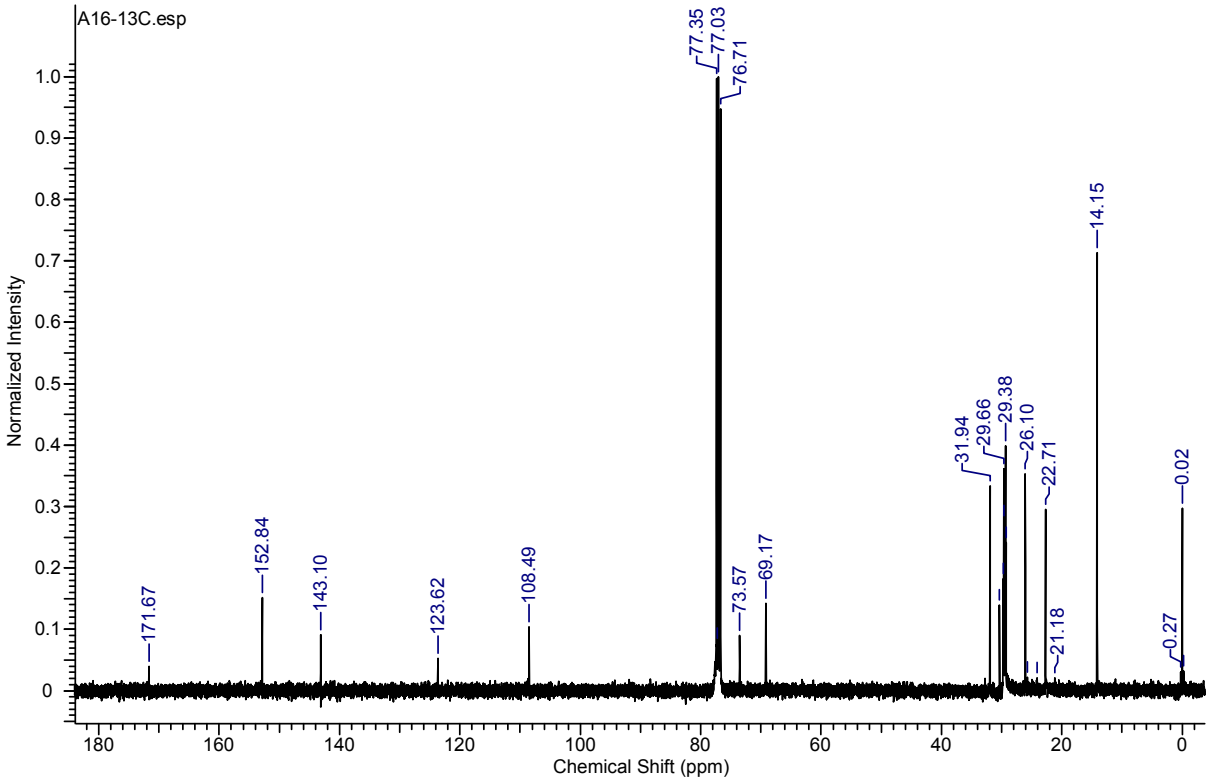


Figure S6. ^{13}C NMR spectra of compound **A16**

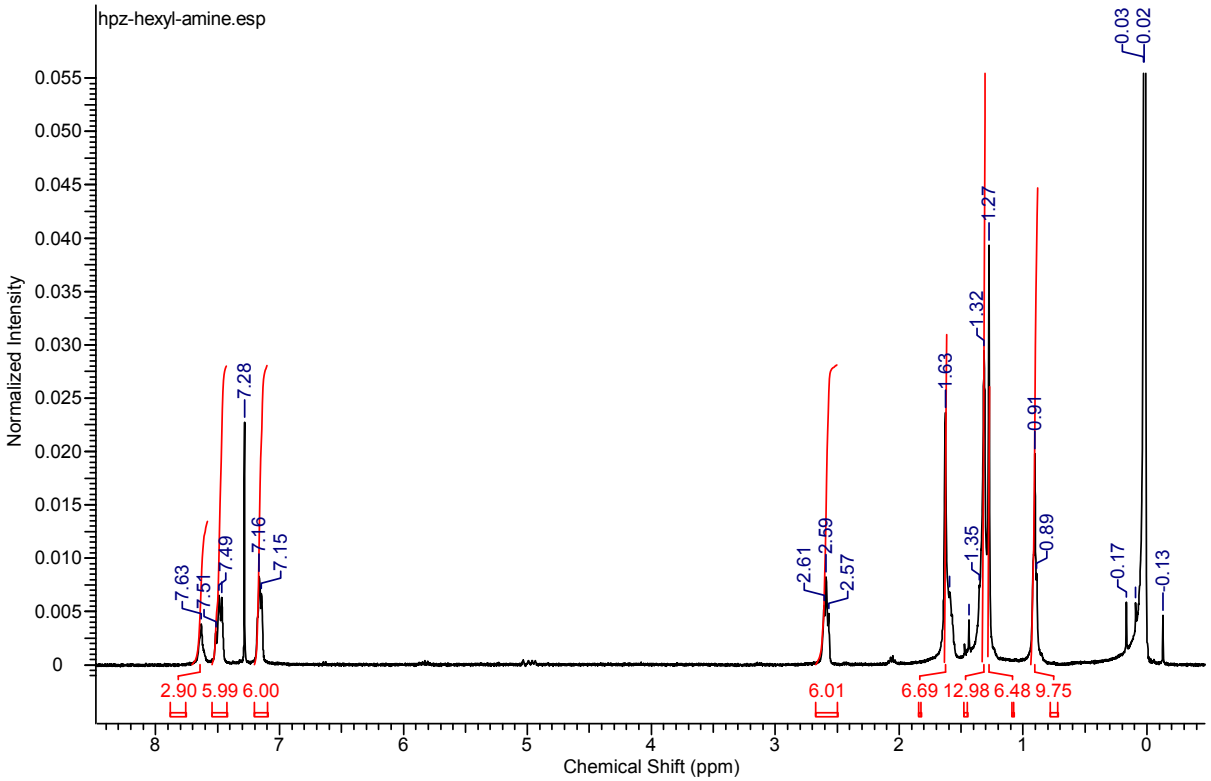


Figure S7. ^{1}H NMR spectra of compound **Hpz-C_6**

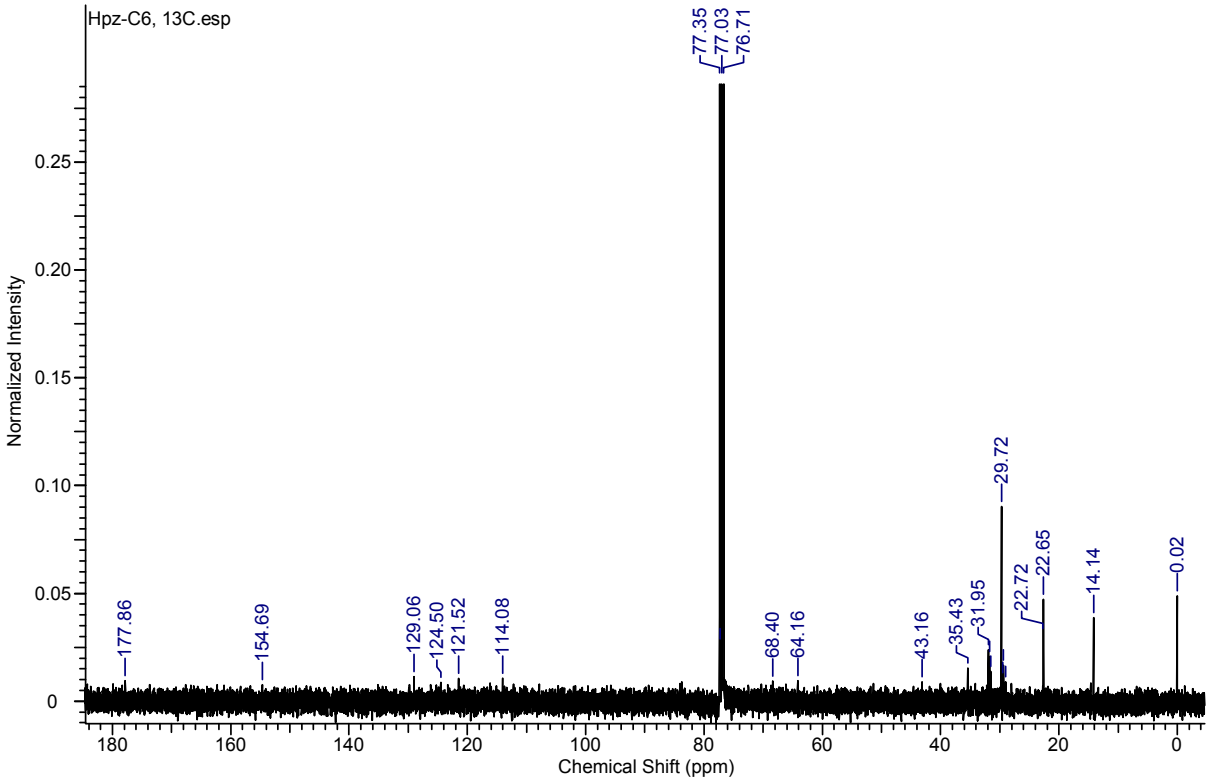


Figure S8. ^{13}C NMR spectra of compound **Hpz-C$_6$**

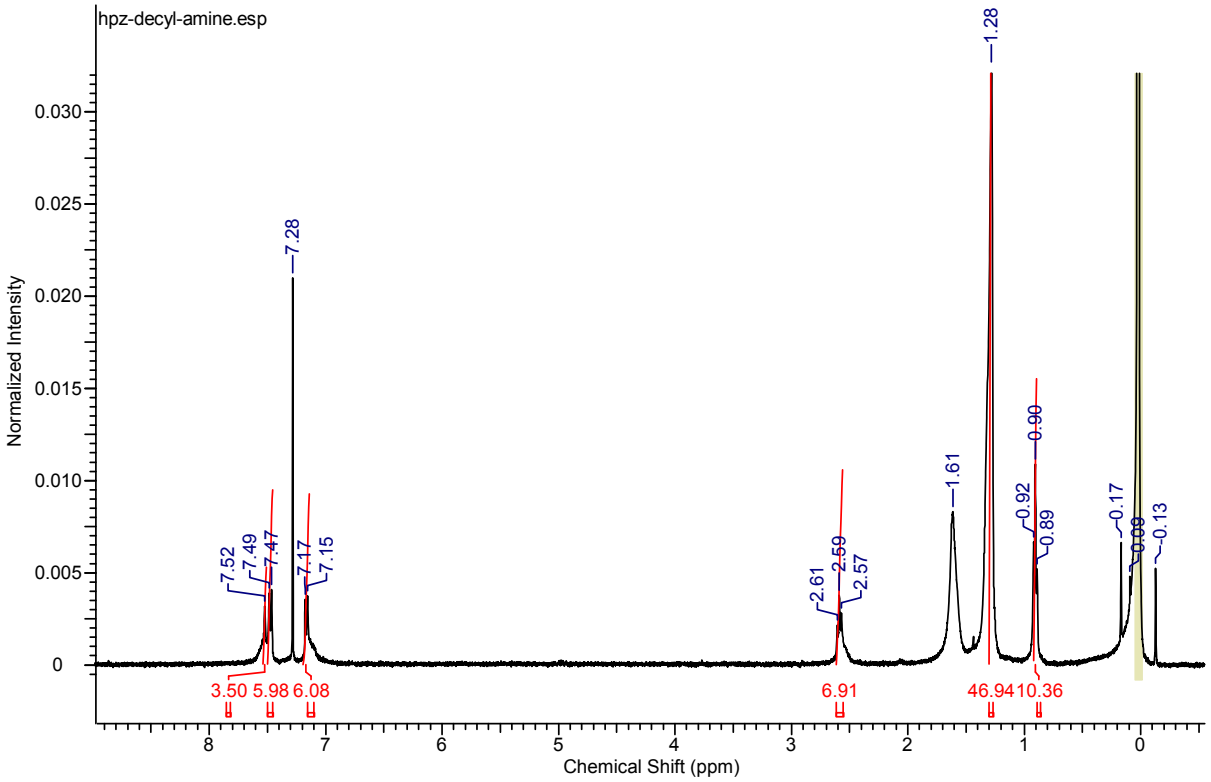


Figure S9. ^{1}H NMR spectra of compound **Hpz-C$_{10}$**

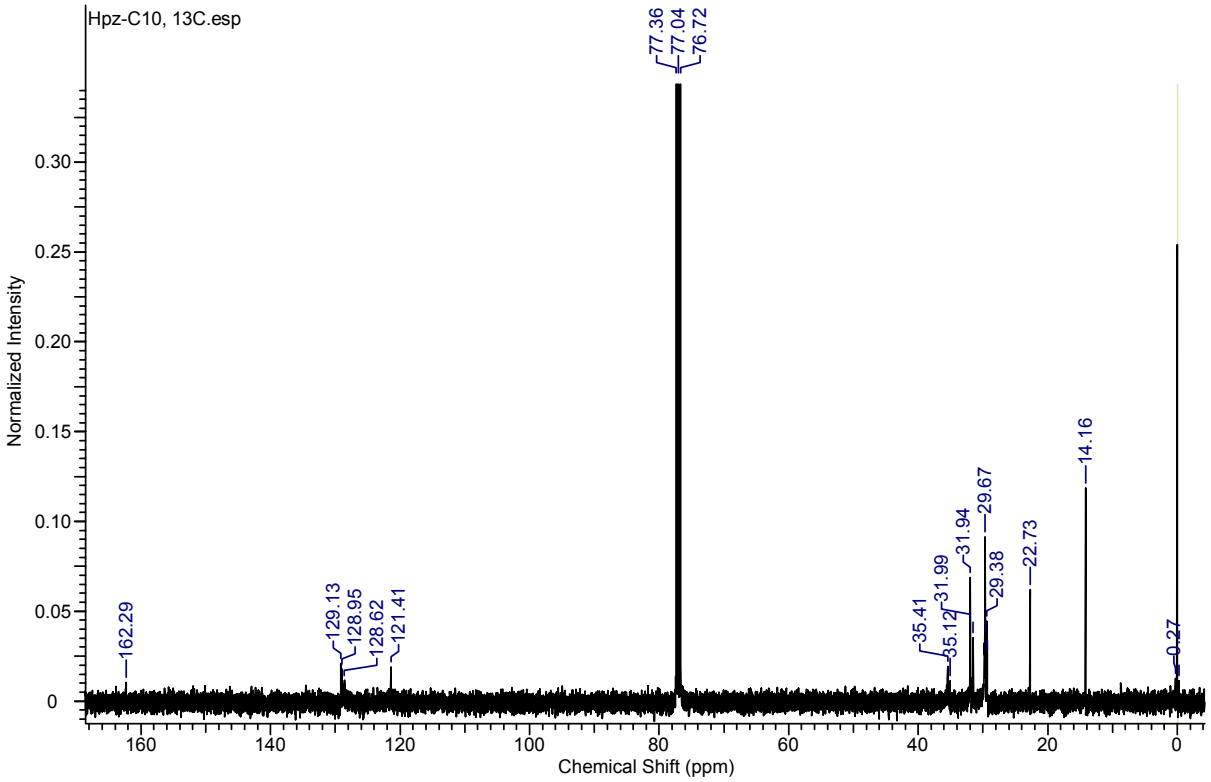


Figure S10. ^{13}C NMR spectra of compound **Hpz-C$_{10}$**

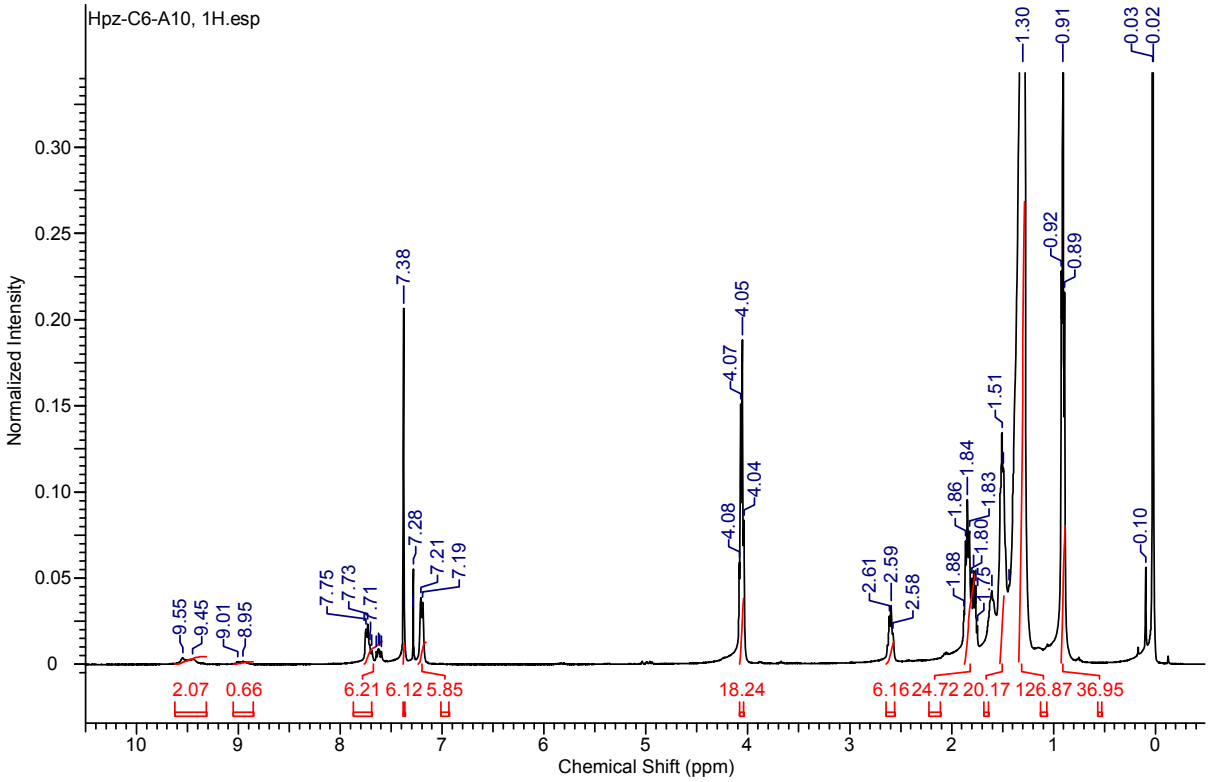


Figure S11. ^{1}H NMR spectra of compound **Hpz-C$_6$/A10**

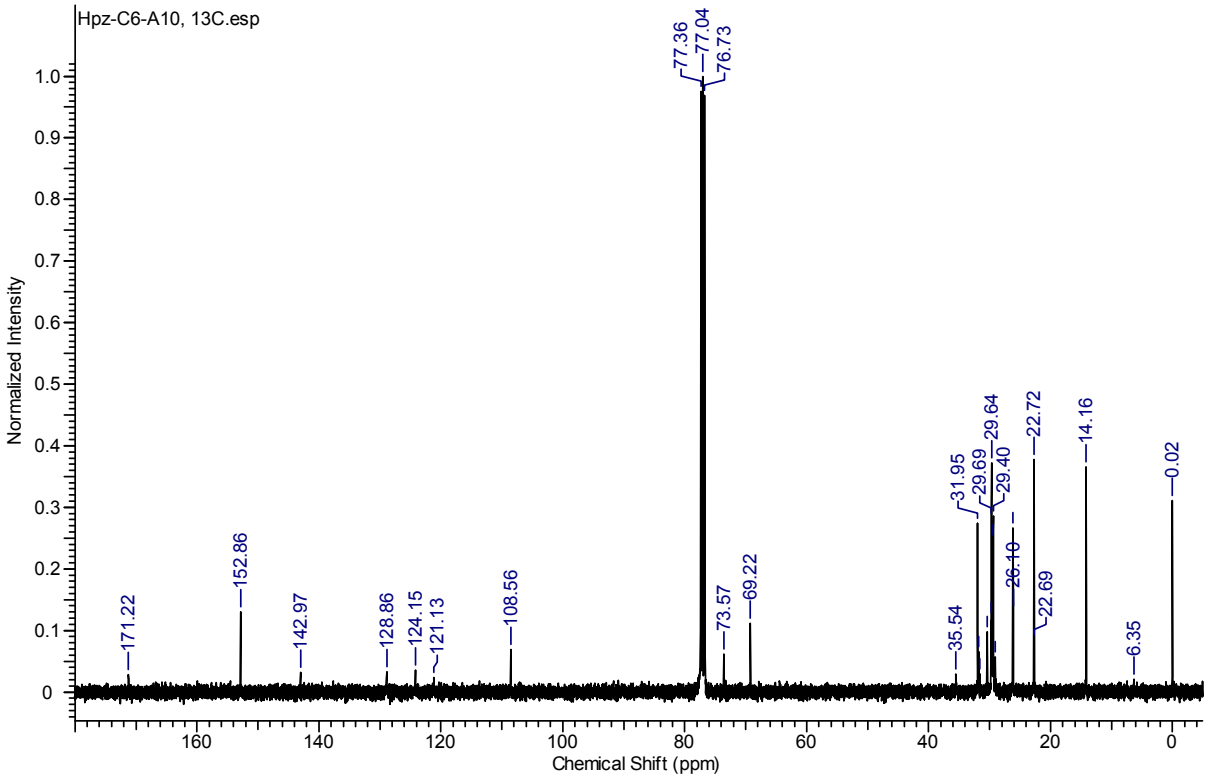


Figure S12. ^{13}C NMR spectra of compound **Hpz-C$_6$/A10**

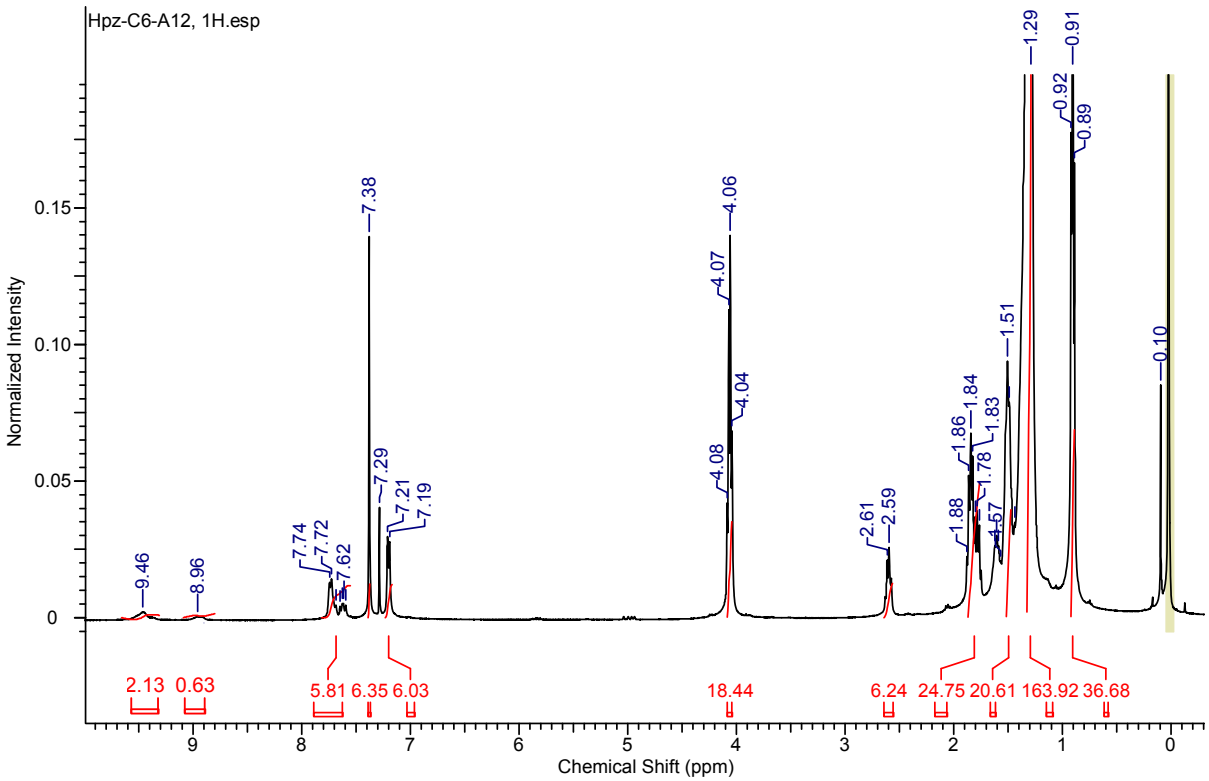


Figure S13. ^{1}H NMR spectra of compound **Hpz-C$_6$/A12**

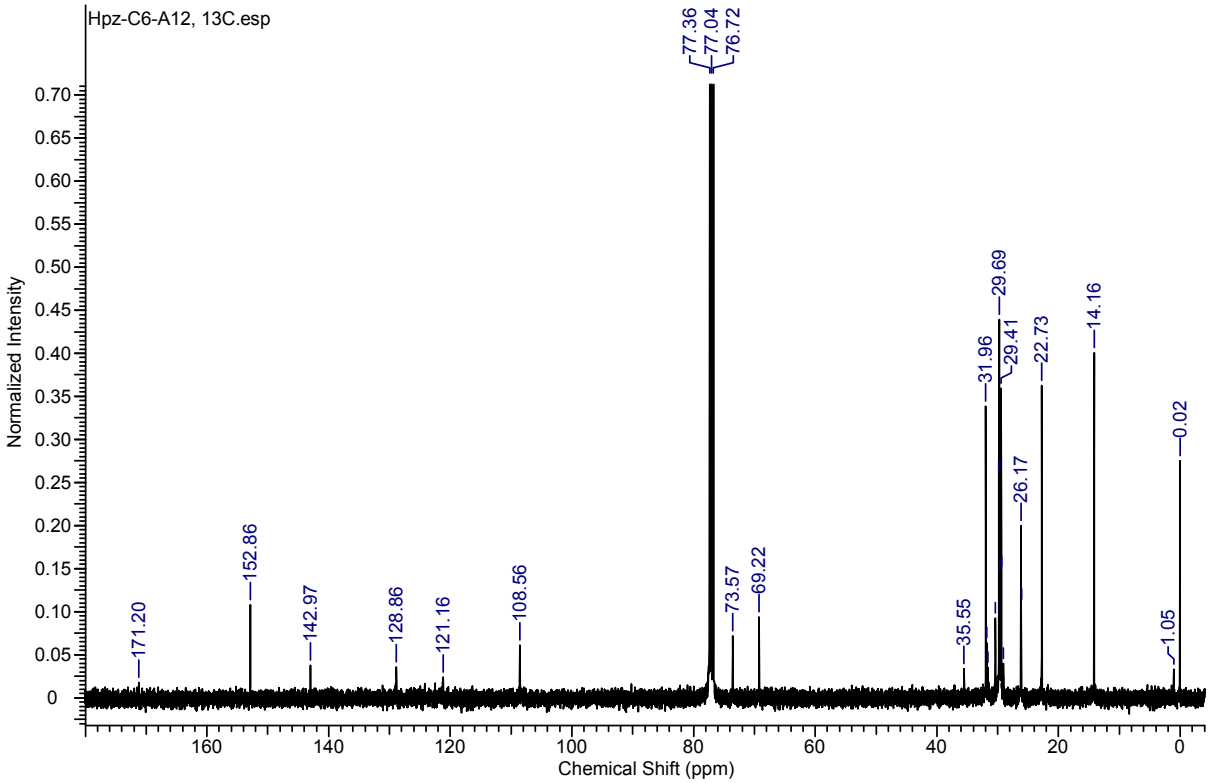


Figure S14. ^{13}C NMR spectra of compound **Hpz-C$_6$/A12**

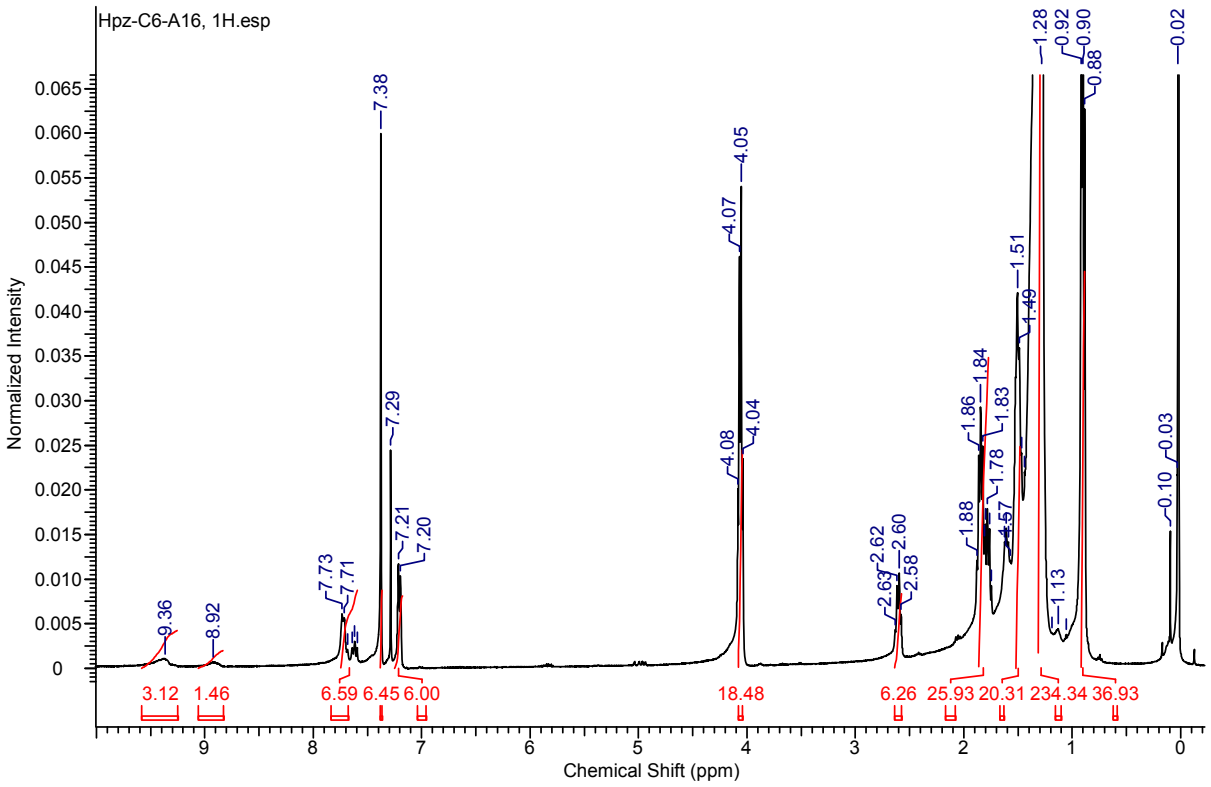


Figure S15. ^{1}H NMR spectra of compound **Hpz-C$_6$/A16**

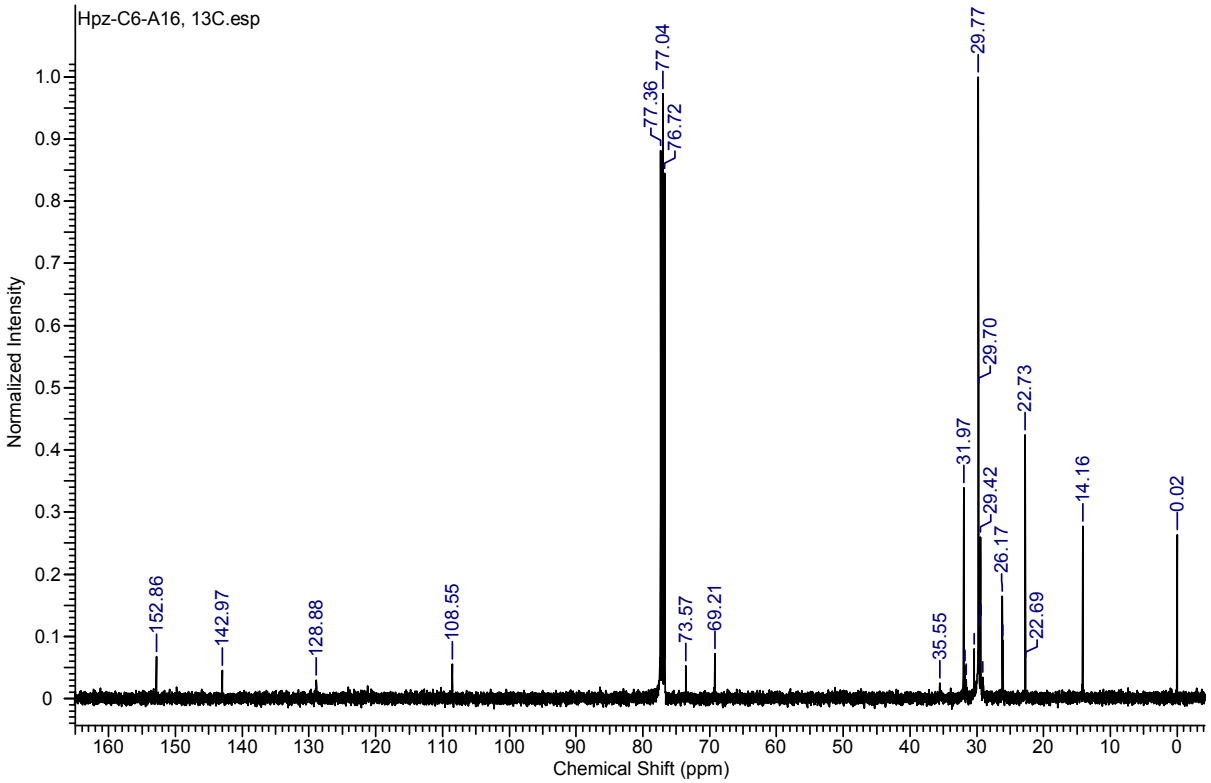


Figure S16. ^{13}C NMR spectra of compound **Hpz-C$_6$/A16**

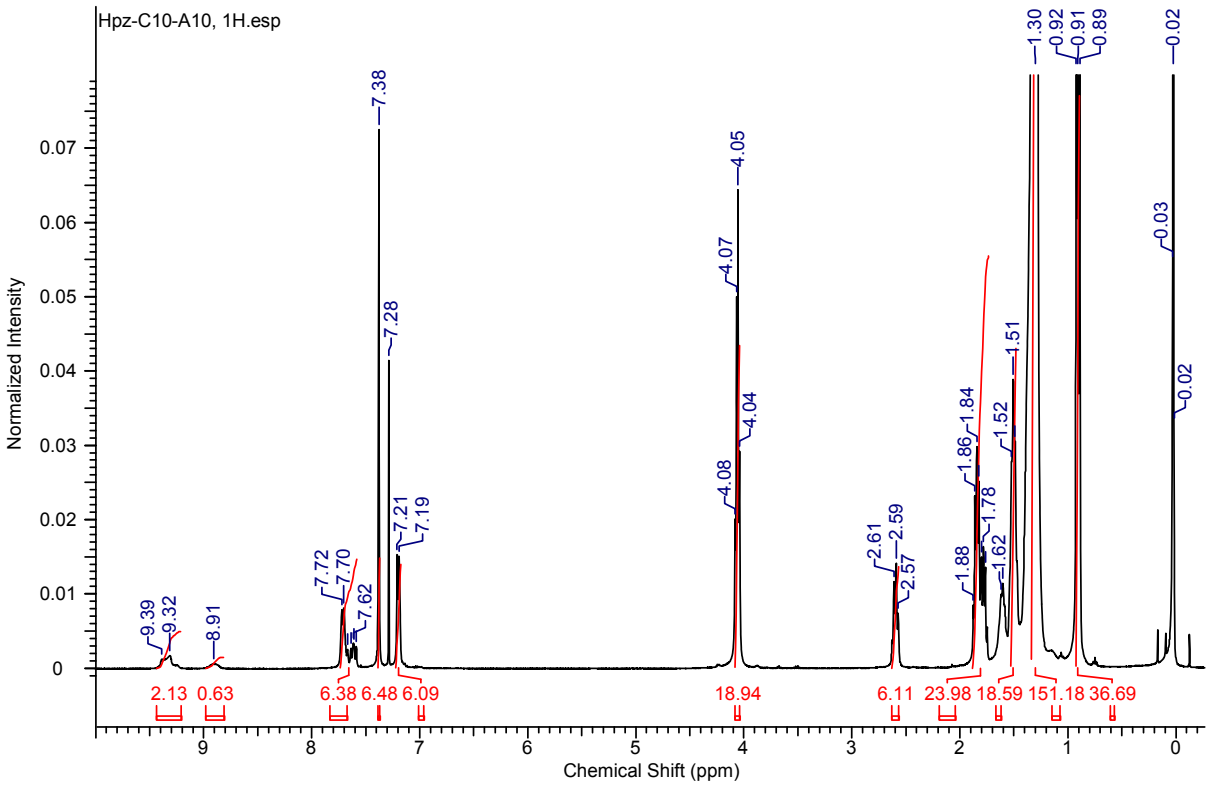


Figure S17. ^{1}H NMR spectra of compound **Hpz-C$_{10}$/A10**

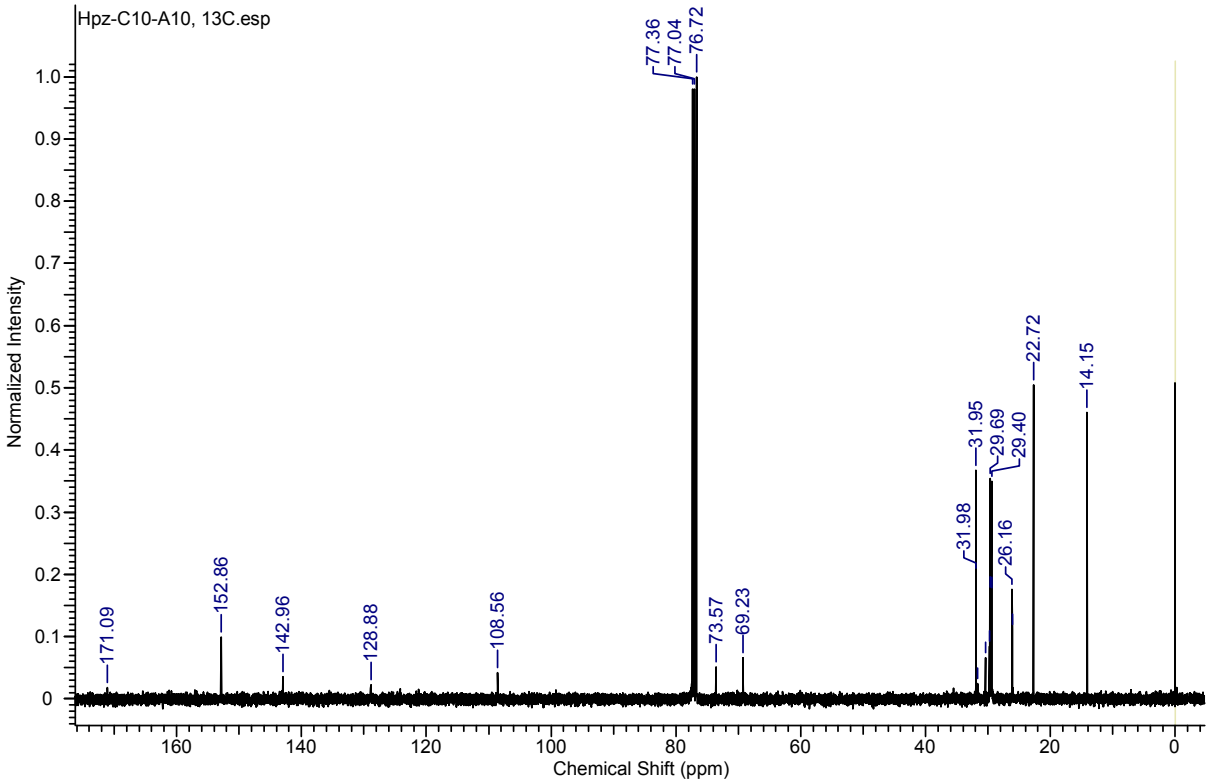


Figure S18. ^{13}C NMR spectra of compound **Hpz-C$_{10}$/A10**

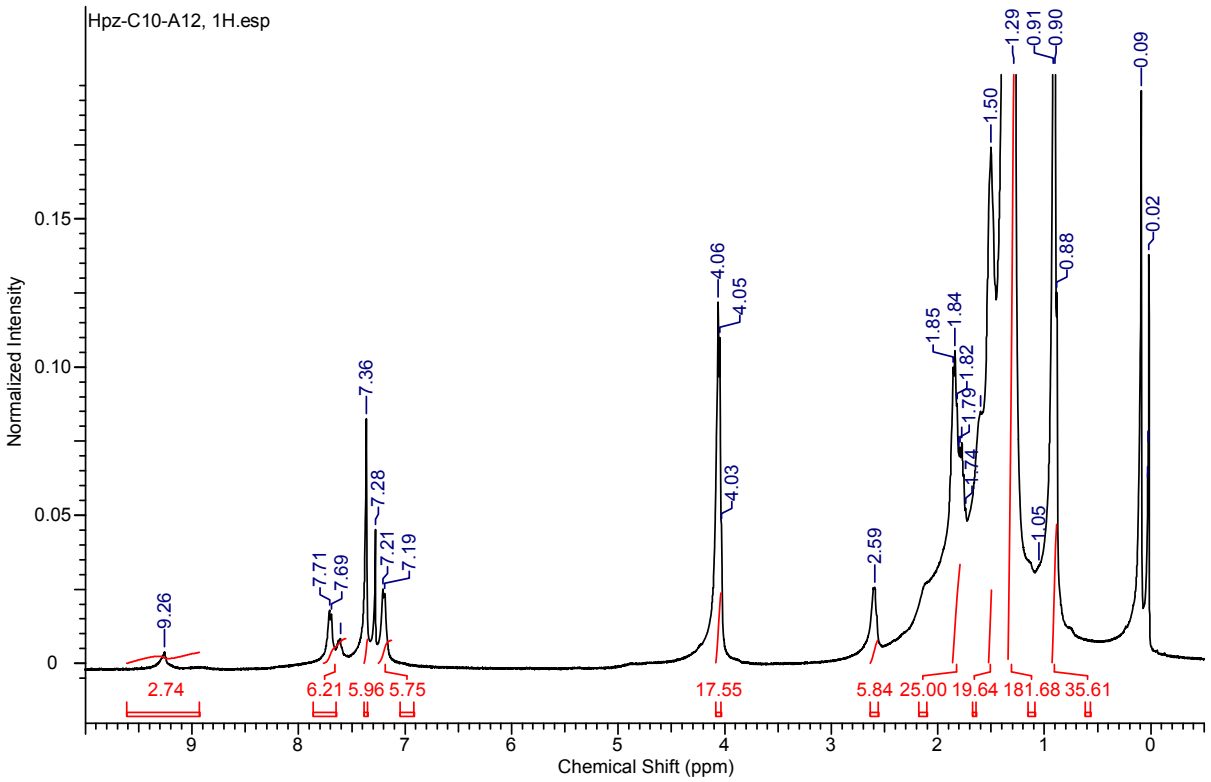


Figure S19. ^{1}H NMR spectra of compound **Hpz-C$_{10}$/A12**

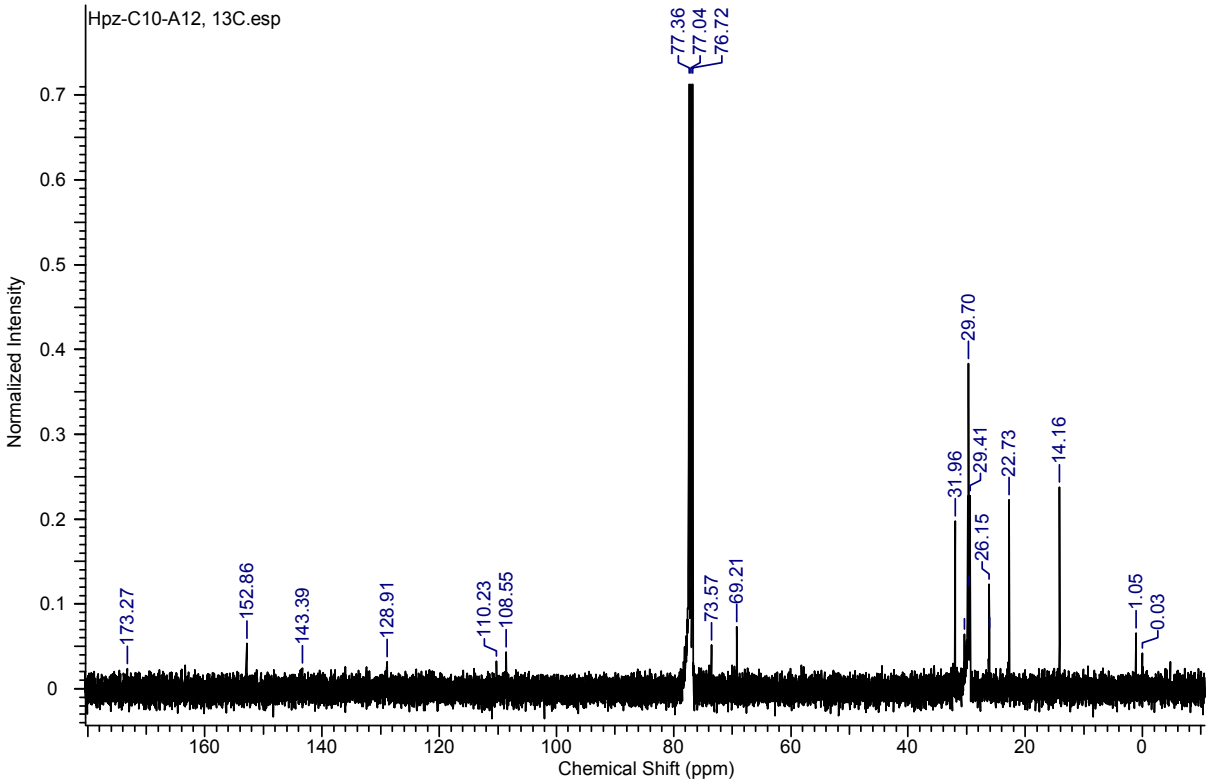


Figure S20. ^{13}C NMR spectra of compound **Hpz-C$_{10}$/A12**

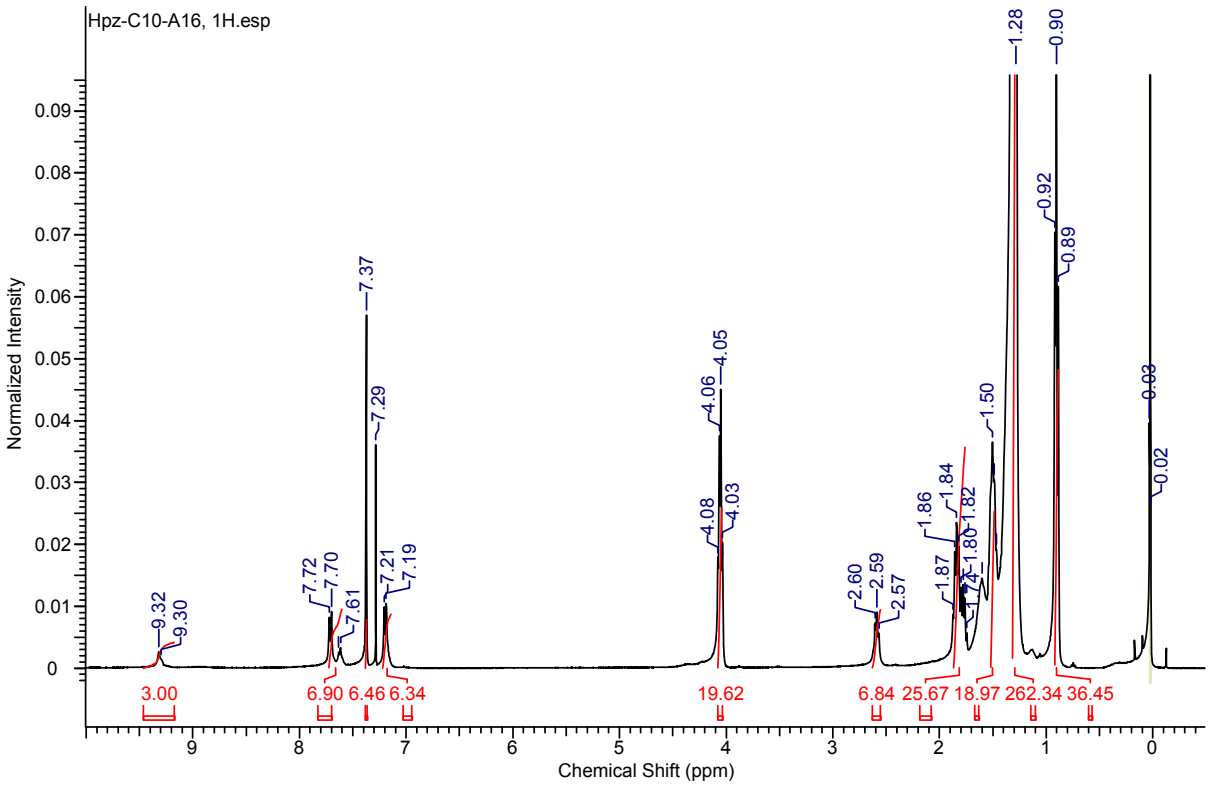


Figure S21. ^{1}H NMR spectra of compound **Hpz-C$_{10}$/A16**

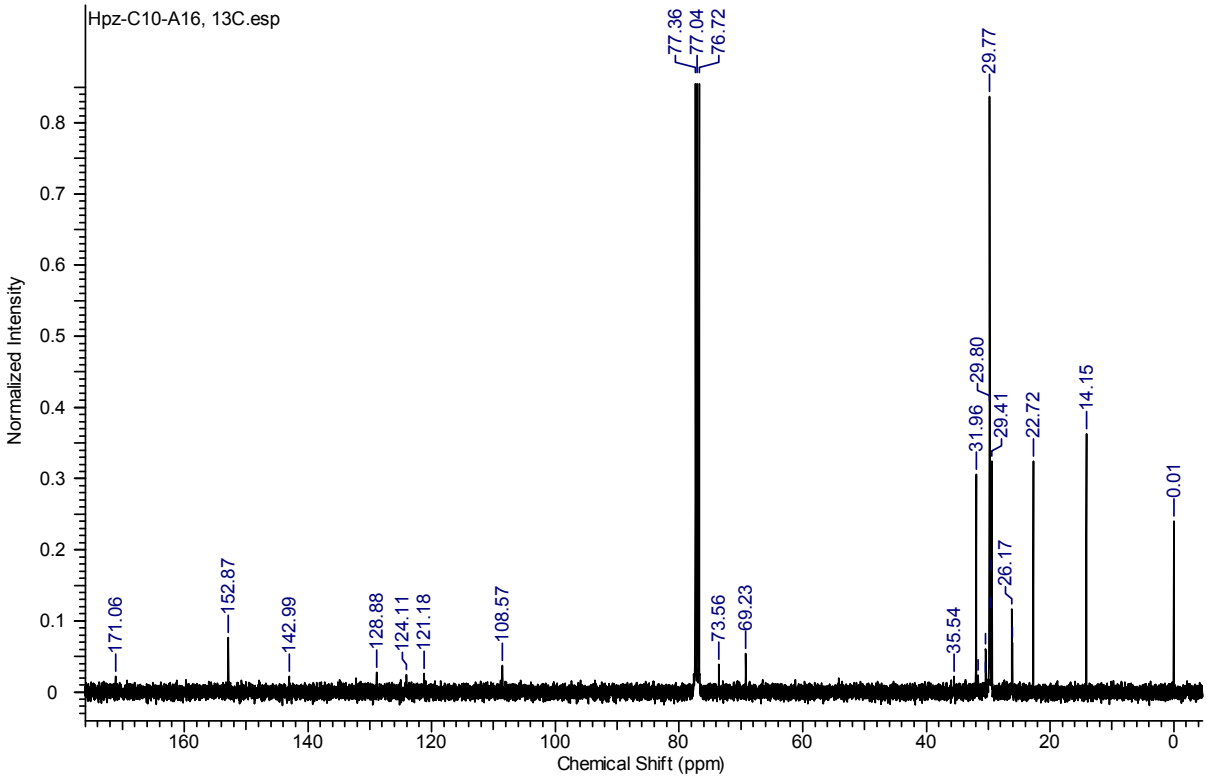


Figure S22. ^{13}C NMR spectra of compound **Hpz-C$_{10}$/A16**

HRMS Spectra

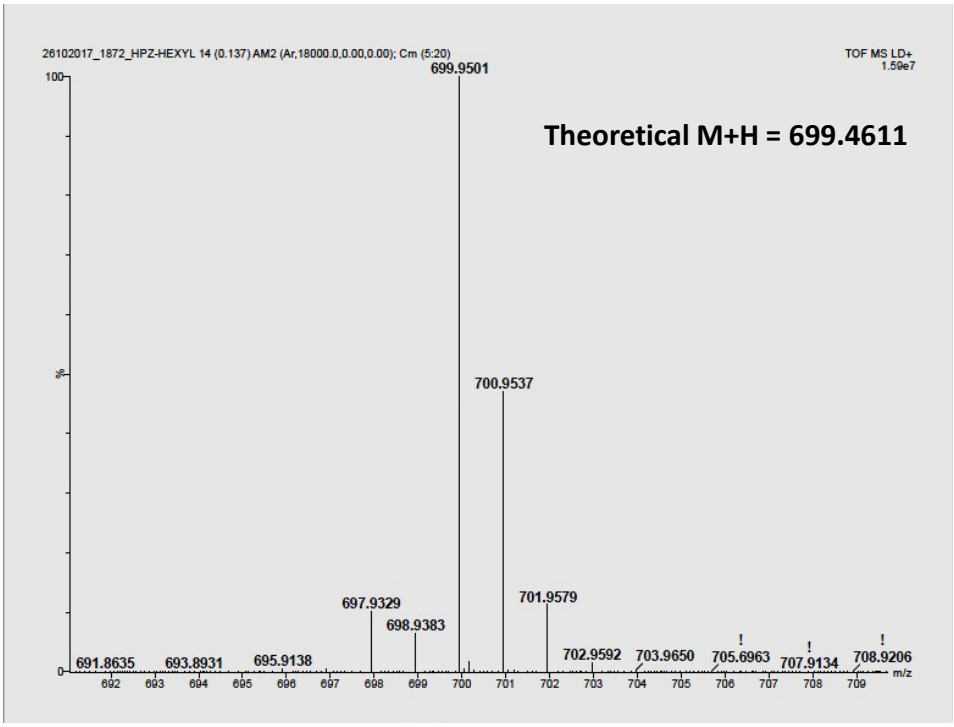


Figure S23. MALDI-TOF spectrum of compound **Hpz-C$_6$**.

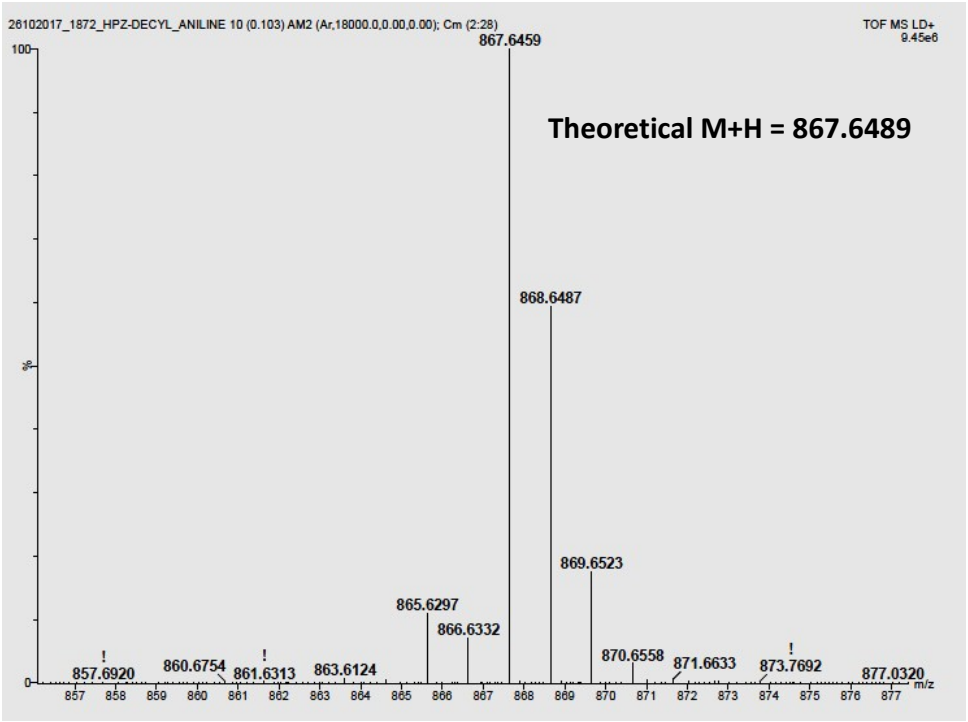


Figure S24. MALDI-TOF spectrum of compound **Hpz-C_{10}**.

Polarised optical Microscopy (POM) studies of the complexes

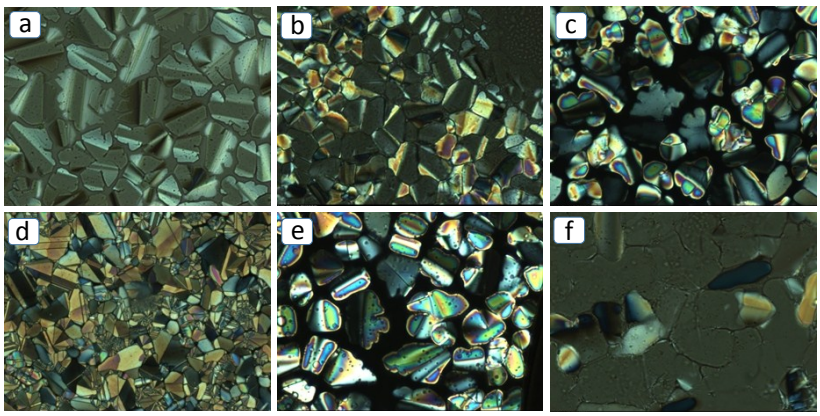


Figure S25. Optical micrograph of complexes a) **Hpz-C_6/A10** at 81.6 °C b) **Hpz-C_6/A12** at 39.5 °C c) **Hpz-C_6/A16** at 88.4 °C d) **Hpz-C_{10}/A10** at 157.2 °C e) **Hpz-C_{10}/A12** at 128.5 °C d) **Hpz-C_{10}/A16** at 130.3 °C, obtained on cooling from the isotropic liquid (scan rate 5 °C/min, crossed polarizers, magnification X 500).

DSC thermograms

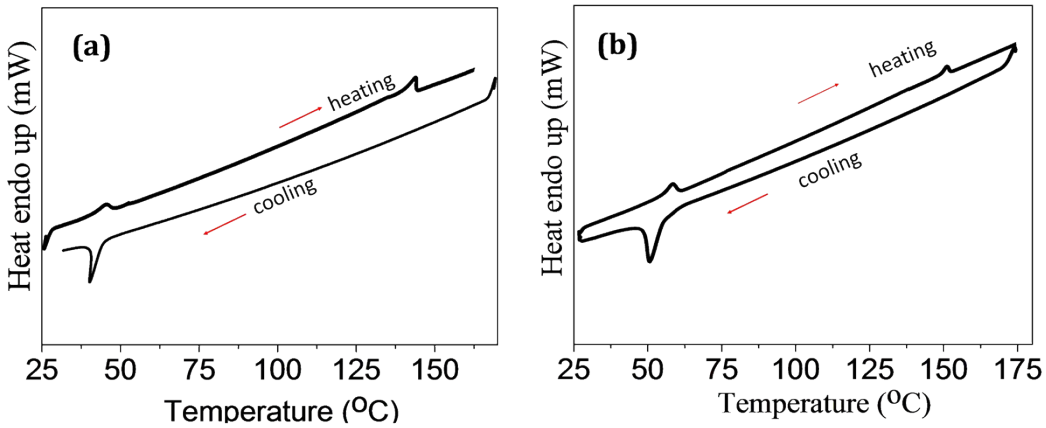


Figure S26. DSC spectra of the respective complexes of the **Hpz-C_{10}** derivative: a) **Hpz-C_{10}-A12** (1st heating & 2nd cooling); b) **Hpz-C_{10}-A16** (2nd heating and 2nd cooling) with the scan rate of 10 °C/min.

X-ray diffraction studies

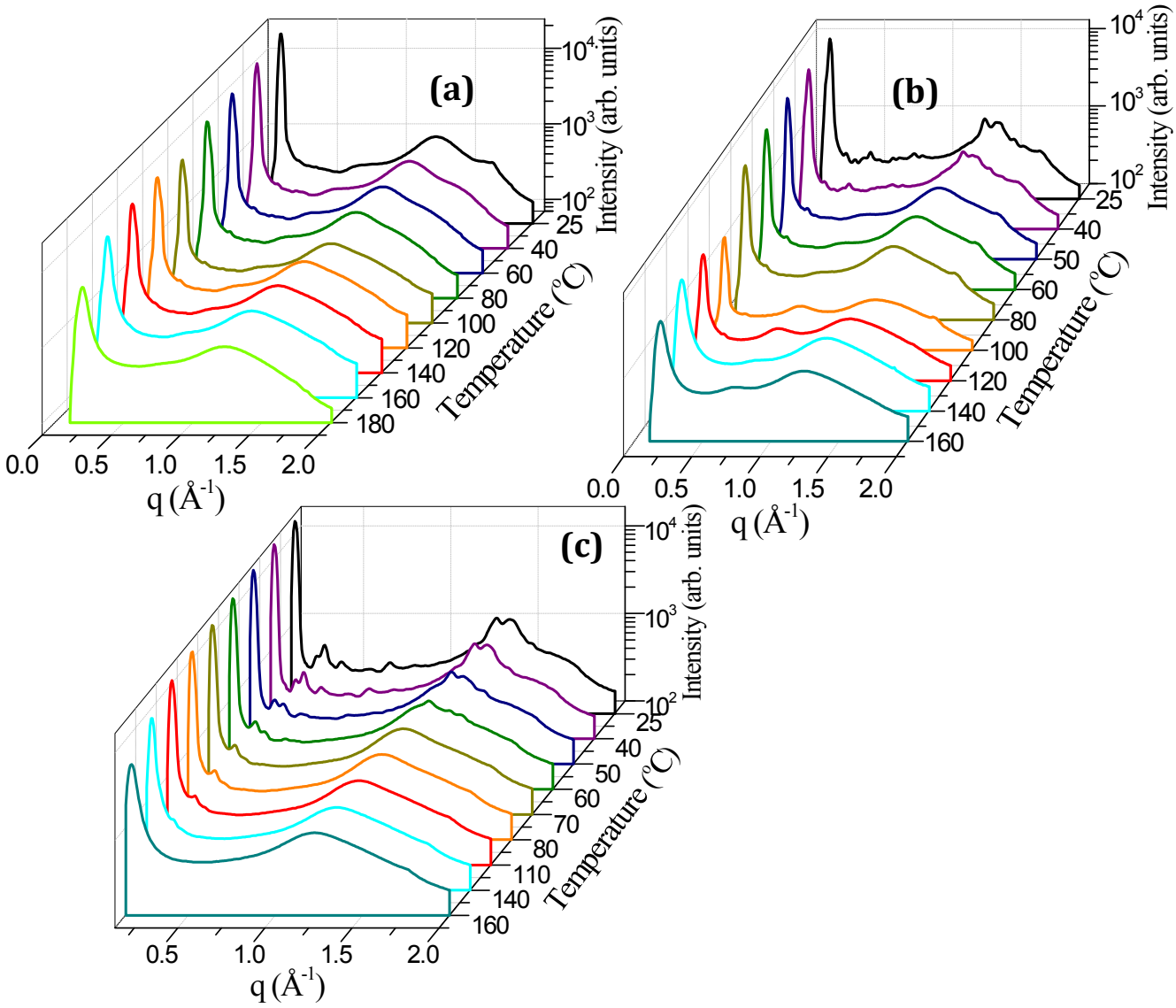


Figure S27. Systematic temperature dependent X-ray diffraction studies for **Hpz-C$_{10}$** complexes from room temperature to their respective isotropic temperatures on cooling from the isotropic phase: (a) **Hpz-C$_{10}$/A10**, (b) **Hpz-C$_{10}$/A12** and (c) **Hpz-C$_{10}$/A16**.

Calculation of number of molecules in single disk of the column:

The number of molecules in a unit cell (Z) can be calculated by using the following formula:

$$Z = (a_{hex}^2)(\sqrt{3}/2)/(h\rho N_A/M_w)$$

where a_{hex} is the hexagonal lattice parameter, h is maximum of the diffuse wide angle scattering, ρ is density assuming 1 g cm^{-3}, N_A is the Avogadro's constant, M_w is the molecular weight of the compound.

Table S1. Calculation of number of molecules (Z) in single disk[a]

Compound	a_{hex} (Å)	h (Å)	M_w ($gmol^{-1}$)	Z	
Hpz-C_6/A10	36.09	4.83	2486.73	1.32	1
Hpz-C_6/A12	38.30	4.89	2724.17	1.37	1
Hpz-C_6/A16	42.90	4.58	3229.13	1.36	1
Hpz-C_{10}/A10	39.10	4.83	2640.01	1.45	1
Hpz-C_{10}/A12	40.10	4.87	2892.49	1.41	1
Hpz-C_{10}/A16	42.90	4.97	3397.45	1.40	1

[a]Z has been calculated by using the parameters of Col_h phase.

UV and Fluorescence Studies

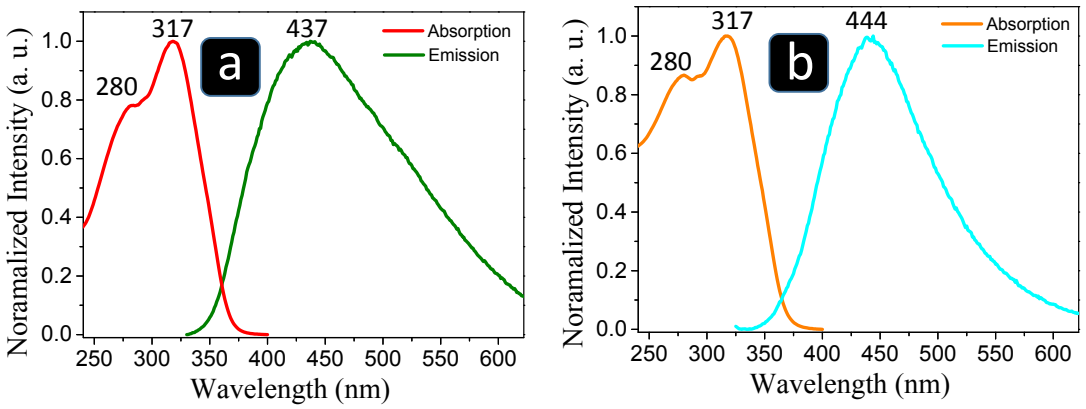


Figure S28. Absorption and emission spectra of pure compounds in chloroform solution: a) **Hpz-C$_6$**; b) **Hpz-C$_{10}$**.

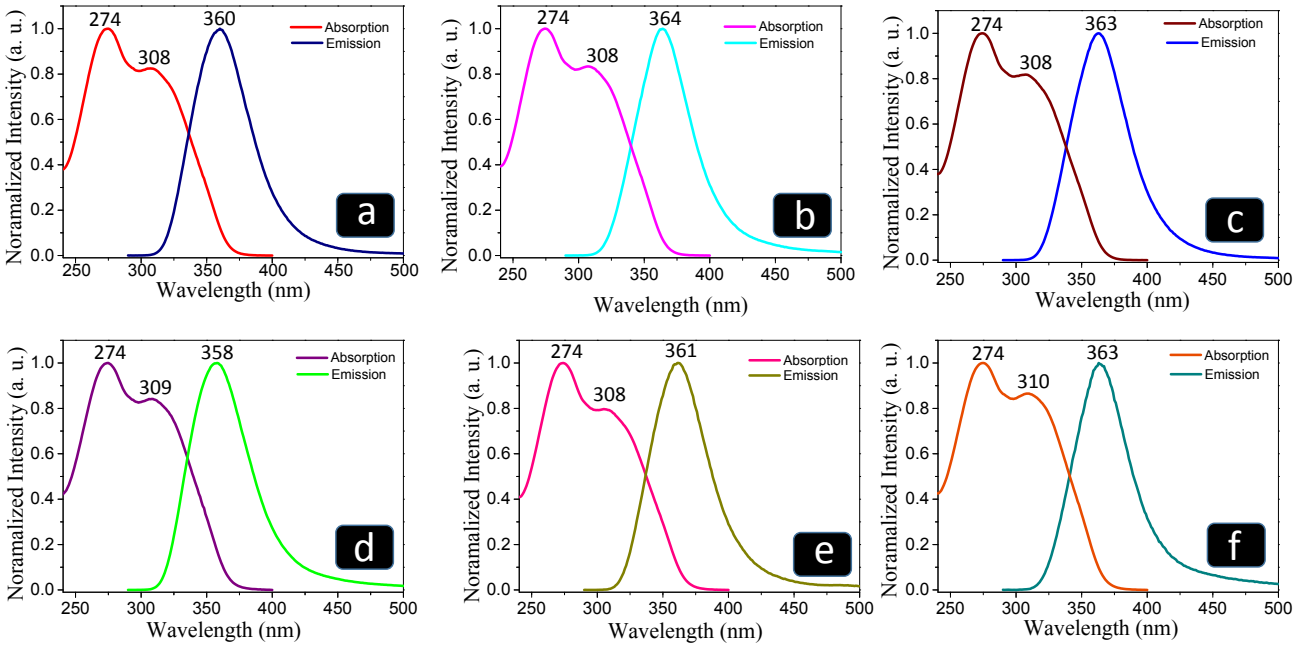


Figure S29. Absorption and emission spectra of H-bonded complexes in chloroform solution: a) **Hpz-C$_6$/A10**; b) **Hpz-C$_6$/A12**; c) **Hpz-C$_6$/A16**; d) **Hpz-C$_{10}$/A10**; e) **Hpz-C$_{10}$/A12**; f) **Hpz-C$_{10}$/A16**.

References

1. K. Kailasam, J. Schmidt, H. Bildirir, G. Zhang, S. Blechert, X. C. Wang and A. Thomas, *Macromol. Rapid Commun*, 2013, **34**, 1008-1013.

2. S. Seo, J. Park and J. Chang, *Langmuir*, 2009, **25**, 8439-8441.