

Supporting Information

for

**$\pi$ -Face Strapped Monomers Enable Self-Stabilized Hyperbranched  $\pi$ -  
Conjugated Polymer Particles**

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## 1. General information

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under nitrogen atmosphere and were stirred with teflon-coated magnetic stirring bars. Reagents used for synthesis were purchased from Fisher, Acros, Alfa Aesar, Ambeed, A2B and Sigma Aldrich. Unless otherwise stated, all starting materials and reagents were used without further purification. All air or moisture-sensitive reactions were performed under nitrogen atmosphere using standard Schlenk techniques. Thin layer chromatography was performed using Silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, KMnO<sub>4</sub> stain and other stains as required. Silica gel of particle size 230-400 mesh was used for flash chromatography. The column chromatography of UV active compounds was performed on Biotage Isolera one 3.0 unless otherwise specified.

**<sup>1</sup>H and <sup>13</sup>C NMR spectra** were recorded on Varian 400-MR NMR. Chemical shifts are reported in  $\delta$  (ppm) relative to the residual solvent peak. CDCl<sub>3</sub>: 7.26 for <sup>1</sup>H; and 77.36 for <sup>13</sup>C; CD<sub>2</sub>Cl<sub>2</sub>: 5.32 for <sup>1</sup>H; (CD<sub>3</sub>)<sub>2</sub>CO: 2.05 for <sup>1</sup>H. Coupling constants (*J*) are expressed in Hertz (Hz). Splitting patterns are designated as s(singlet), br(broad signal), d(doublet), t(triplet), dd(doublet of doublets), dt(doublet of triplets), dq(doublet of quartets), m(multiplet), and q(quartet).

**Infra-Red spectra** of the polymers were obtained using PerkinElmer FT-IR spectrometer with an ATR attachment by directly loading the samples onto the ATR crystal.

**Atomic Force Microscopy (AFM)** images of the HBPs were obtained using NT-MDT NTEGRA Prima (ver 1.0) by drop casting the sample dispersions onto a clear glass slide.

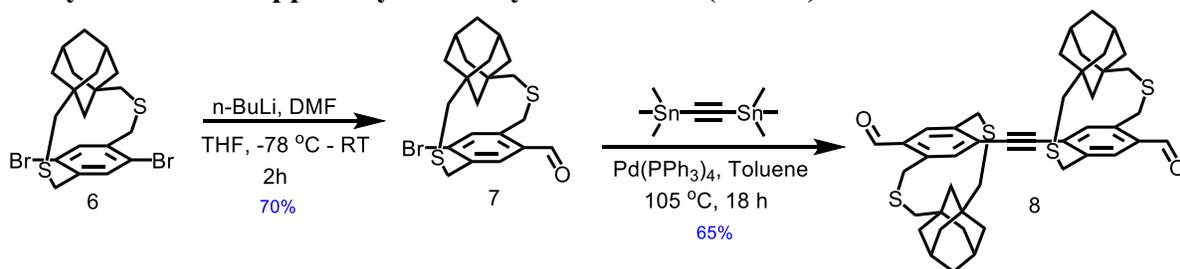
**UV-vis absorption spectra** were recorded on Agilent Technologies Cary Series 5000 UV-vis-NIR Spectrophotometer.

**Photoluminescence (PL) spectra** were recorded on Horiba Scientific Fluoromax-4 Spectrophotometer.

**Single Crystal X-ray diffraction** was obtained using a Bruker D8 Quest equipped with a Mo K $\alpha$  microfocus source, a Photon100 detector, and an Oxford 700 Cryostream.

**Powder X-ray diffraction (PXRD)** patterns were collected in transmission mode on an APEX II DUO diffractometer with a CCD detector employing Cu-K $\alpha$  radiation ( $\lambda = 1.54187 \text{ \AA}$ ) generated from an *I $\mu$ S* source. Samples were mounted in 0.8 mm polyimide capillaries produced by Cole-Palmer®. PowDLL3, Panalytical X'Pert Highscore Plus2, convert, process, analyze and compare the PXRD patterns.

## 2. Synthesis of strapped aryl dialdehyde monomer (DADA)



**Scheme S1: Synthesis of DADA (8), compound 6 was synthesized by following our previous report.<sup>i</sup>**

### 2.1 Procedure for synthesis of compound 7

In an oven dried Schlenk flask 1 g (2.04 m.moles) of compound 6 was dissolved in dry THF under nitrogen atmosphere. The mixture was cooled to -78 °C using dry ice. Then 2.6 ml (2.66 m.moles) of 1 M n-butyl lithium solution was added drop wise and stirred for 1 hour. Then 0.32 ml (4.09 m.moles) of N,N-dimethyl formamide was added dropwise into the reaction mixture and continued stirring at -78 °C. After 2 hours, the dry ice was removed, and the reaction was allowed to stir at room temperature for overnight. The reaction was quenched by slowly adding a few drops of saturated ammonium chloride solution and worked up with ethyl acetate and brine. The organic layer was extracted, dried and concentrated under reduced pressure. Crude product was purified using column chromatography (0-10% ethyl acetate in hexane as eluent) to obtain compound 2 as a white solid. R<sub>f</sub> value: 0.75 with 10% ethyl acetate in hexane. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 10.29 (s, 1H), 7.64 (s, 1H), 7.40 (s, 1H), 4.59 (d, *J* = 28.6 Hz, 1H), 3.92 (s, 1H), 3.58 (d, *J* = 13.7 Hz, 1H), 3.36 (d, *J* = 13.8 Hz, 1H), 2.80 – 2.61 (m, 2H), 1.97 – 1.72 (m, 4H), 1.31 (s, 4H), 1.15 (d, *J* = 15.0 Hz, 3H), 0.98 (d, *J* = 40.8 Hz, 3H), -0.22 (s, 1H), -0.41 (s, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 192.35, 147.61, 142.80, 138.62, 136.35, 135.67, 133.71, 47.90, 47.32, 45.32, 41.59, 41.24, 40.17, 38.91, 37.61, 36.50, 36.37, 31.46, 31.36.

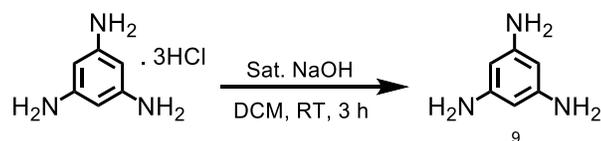
### 2.2 Procedure for synthesis of ((±, meso) 8, (DADA))

Under nitrogen atmosphere, 500 mg (1.14 m.moles) of compound 7, Bis(trimethylstannyl) acetylene (200 mg, 0.57 m.moles) and tetrakis(triphenylphosphine)palladium(0) (265 mg, 0.23 m.moles) were taken in a Schlenk flask and dissolved in dry toluene. The reaction mixture was stirred at 105 °C for 18 hours. After the reaction was completed, toluene was removed, and the residue was dissolved in ethyl acetate and washed with brine. The organic layer was extracted, dried using sodium sulfate and concentrated under reduced pressure. Crude product was purified using column chromatography (5-15% ethyl acetate in hexane as eluent) to obtain DADA as yellow solid. R<sub>f</sub> value: 0.5 with 10% ethyl acetate in hexane. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 10.35 (s, 1H), 7.70 (s, 1H), 7.41 – 7.33 (m, 2H), 4.61 (s, 1H), 4.28 (d, *J* = 12.8 Hz, 0H), 4.13 (s, 0H), 3.65 – 3.58 (m, 2H), 3.44 (d, *J* = 13.2 Hz, 1H), 2.70 (d, *J* = 21.8 Hz, 3H),

1.88 (s, 3H), 1.81 (s, 2H), 1.42 (s, 2H), 1.34 (d,  $J = 11.6$  Hz, 1H), 1.15 (d,  $J = 14.7$  Hz, 1H), 1.04 (s, 0H), 0.91 (s, 3H), -0.12 (s, 1H), -0.37 (s, 0H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  192.51, 146.61, 146.15, 138.24, 137.75, 136.15, 135.15, 133.00, 130.75, 130.60, 98.83, 47.98, 47.55, 45.26, 41.27, 40.18, 38.94, 37.93, 36.53, 36.43, 31.55, 31.39.

### 3. Synthesis of model imine trimer

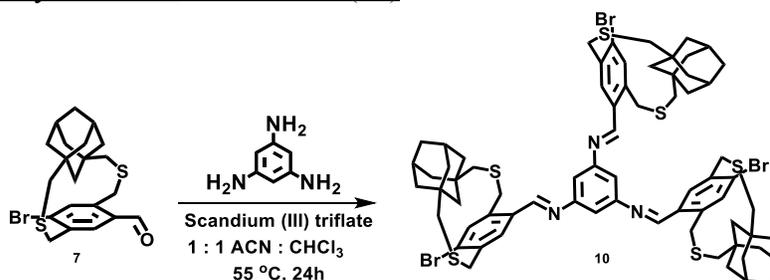
#### 3.1 Procedure for synthesis of Benzene-1,3,5-triamine (9)



**Scheme S2: Synthesis of benzene-1,3,5-triamine (9)**

In an oven dried Schlenk flask, 20 ml of 1:1 DCM: Saturated NaOH solution was prepared and 200 mg of benzene-1,3,5-triamine trihydrochloride was added. The dispersion was stirred at room temperature for 3 hours. The organic layer was extracted, dried using sodium sulfate and concentrated under reduced pressure. Crude products were directly used for the next steps.  $^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ )  $\delta$  5.37 (s, 3H), 3.96 (br s, 6H).

#### 3.2 Procedure for synthesis of imine trimer (10)

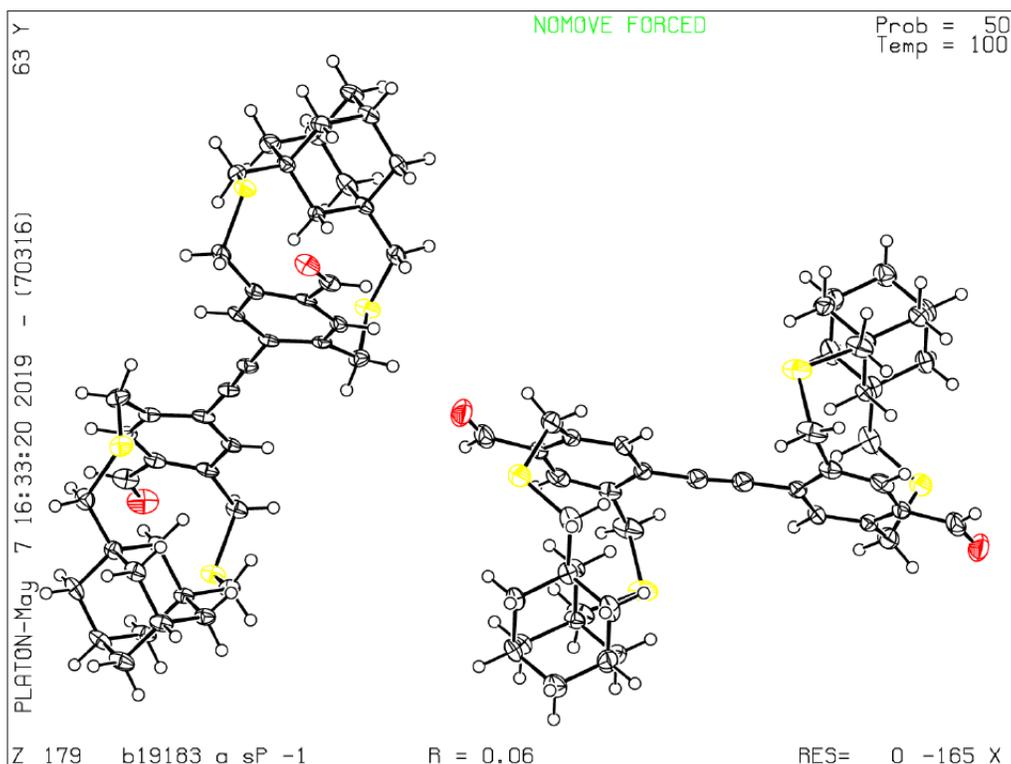


**Scheme S3: Synthesis of model imine trimer (10)**

25 mg (0.20 m.moles) of benzene-1,3,5-triamine was dissolved in 10 ml of 1:1 DCM : ACN solution taken in a vial equipped with stir bar. 355 mg (0.81 m.moles) of compound 7 and 600 mg (1.2 m.moles) of Scandium (III) triflate added to the solution and the mixture was left stirring at 55 °C for 24 hours. Solvent was removed under reduced pressure and the crude product was subjected to column chromatography using neutralized (by passing 5% triethyl amine in hexanes) silica as stationary phase and 0-10% ethyl acetate in hexane as mobile phase to obtain the imine trimer (10) as an off-white powder. Rf value: 0.5 with 10% ethyl acetate in hexane.  $^1\text{H}$  NMR (400 MHz, Methylene Chloride- $d_2$ )  $\delta$  8.78 (s, 3H), 7.97 (s, 3H), 7.42 (s, 3H), 6.50 (d,  $J = 16.2$  Hz, 3H), 4.37 (s, 2H), 3.95 (s, 4H), 3.68 – 3.44 (m, 6H), 2.72 (d,  $J = 13.2$  Hz, 6H), 1.90 (d,  $J = 13.6$  Hz, 8H), 1.46 (s, 6H), 1.29 (s, 8H), 1.23 – 1.06 (m, 12H), 0.99 – 0.88 (m, 8H), -0.19 (s, 6H). HRMS: (ESI)  $m/z$ : 1382.2161  $[\text{M}+\text{H}]^+$ ; calculated for  $[\text{C}_{69}\text{H}_{78}\text{Br}_3\text{N}_3\text{S}_6+\text{H}]^+$ : 1382.48

#### 4. Single crystal XRD of DADA

Single crystals of DADA (Compound 8) were mounted under mineral oil on Mitegen micromounts and placed under a cold nitrogen stream at 100(2) K prior to data collection. Data for compound DADA (Compound 8) was collected on a D8 Quest equipped with a Photon100 detector and Mo K $\alpha$  microfocus source ( $\lambda = 0.7107 \text{ \AA}$ ). Data was integrated with the Bruker SAINT program. Structure solutions were performed using the SHELXTL/PC suite. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABS. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions.



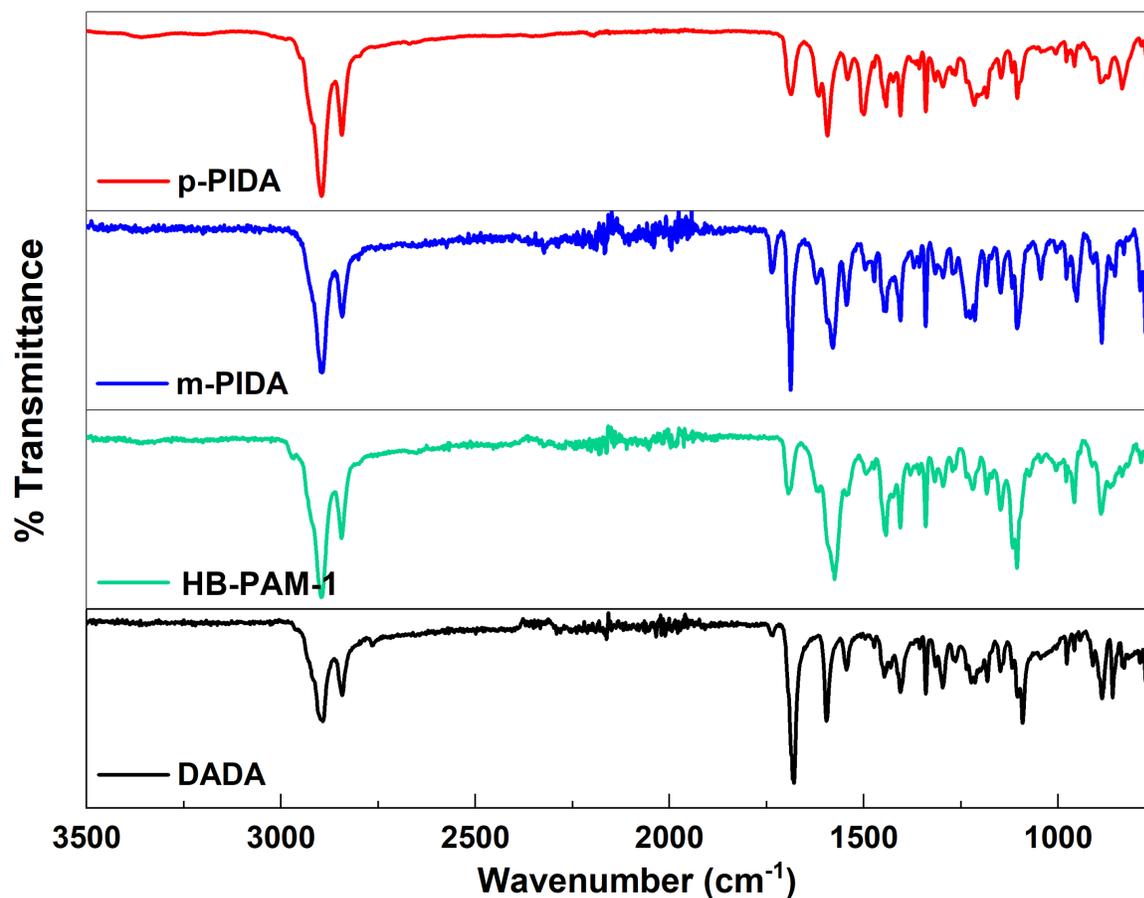
*Figure S1: Single crystal XRD of DADA*

***Table 1. Crystal data and structure refinement for diadamantano dialdehyde (DADA).***

|                        |   |
|------------------------|---|
| CCDC deposition number | 2266289   |
| Empirical formula      | C <sub>44</sub> H <sub>50</sub> O <sub>2</sub> S <sub>4</sub> |
| Formula weight         | 739.08  |
| Temperature            | 100(2) K  |
| Wavelength             | 0.71073 Å   |
| Crystal system         | Triclinic   |
| Space group            | P-1   |
| Unit cell dimensions   | a = 9.6958(3) Å      a = 85.106(2)°.                          |

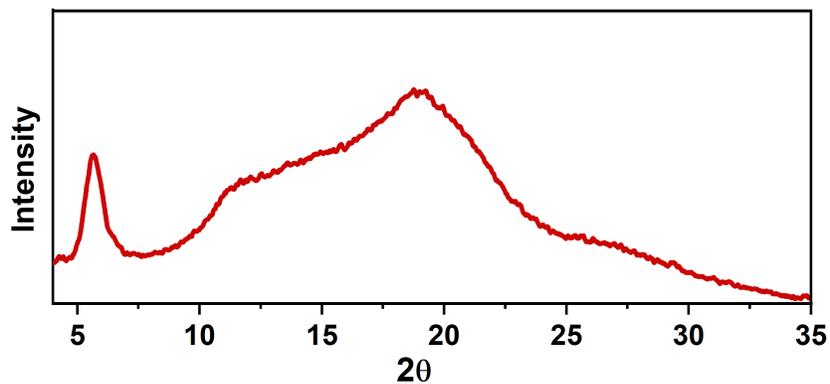
|  |  |                       |
|--|--|-----------------------|
|  | $b = 17.1453(5) \text{ \AA}$                                       | $b = 77.072(2)^\circ$ |
|  | $c = 18.5627(6) \text{ \AA}$                                       | $g = 78.794(2)^\circ$ |
| Volume                                 | $2947.43(16) \text{ \AA}^3$  |                       |
| Z                                      | 3  |                       |
| Density (calculated)                   | $1.249 \text{ Mg/m}^3$   |                       |
| Absorption coefficient                 | $0.278 \text{ mm}^{-1}$  |                       |
| F(000)                                 | 1182   |                       |
| Crystal size                           | $0.320 \times 0.073 \times 0.019 \text{ mm}^3$                     |                       |
| Theta range for data collection        | $2.191$ to $25.464^\circ$  |                       |
| Index ranges                           | $-11 \leq h \leq 11$ , $-20 \leq k \leq 20$ , $-22 \leq l \leq 22$ |                       |
| Reflections collected                  | 89166  |                       |
| Independent reflections                | 10864 [R(int) = 0.1494]  |                       |
| Completeness to theta = $25.242^\circ$ | 100.0 %  |                       |
| Absorption correction                  | Semi-empirical from equivalents                                    |                       |
| Max. and min. transmission             | 0.99415 and 0.94680  |                       |
| Refinement method                      | Full-matrix least-squares on $F^2$                                 |                       |
| Data / restraints / parameters         | 10864 / 0 / 676  |                       |
| Goodness-of-fit on $F^2$               | 1.012  |                       |
| Final R indices [ $I > 2\sigma(I)$ ]   | R1 = 0.0559, wR2 = 0.1169  |                       |
| R indices (all data)                   | R1 = 0.1073, wR2 = 0.1388  |                       |
| Extinction coefficient                 | n/a  |                       |
| Largest diff. peak and hole            | $0.411$ and $-0.337 \text{ e.\AA}^{-3}$                            |                       |

## 5. ATR-IR spectra of DADA, PAMs and HB-PAM-1



*Figure S2: ATR-IR spectra of DADA, PAMs and HB-PAM-1*

## 6. PXRD of HB-PAM-1



*Figure S3: PXRD of HB-PAM-1*

## 7. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of monomers and polymers

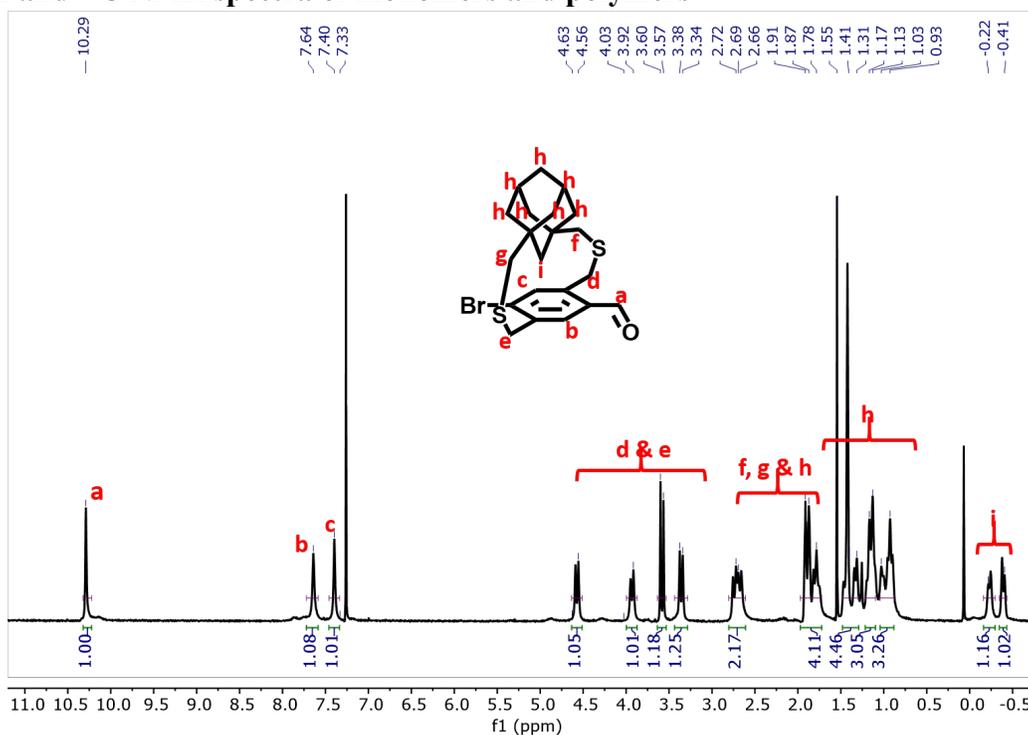


Figure S4:  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*) spectra of compound 7

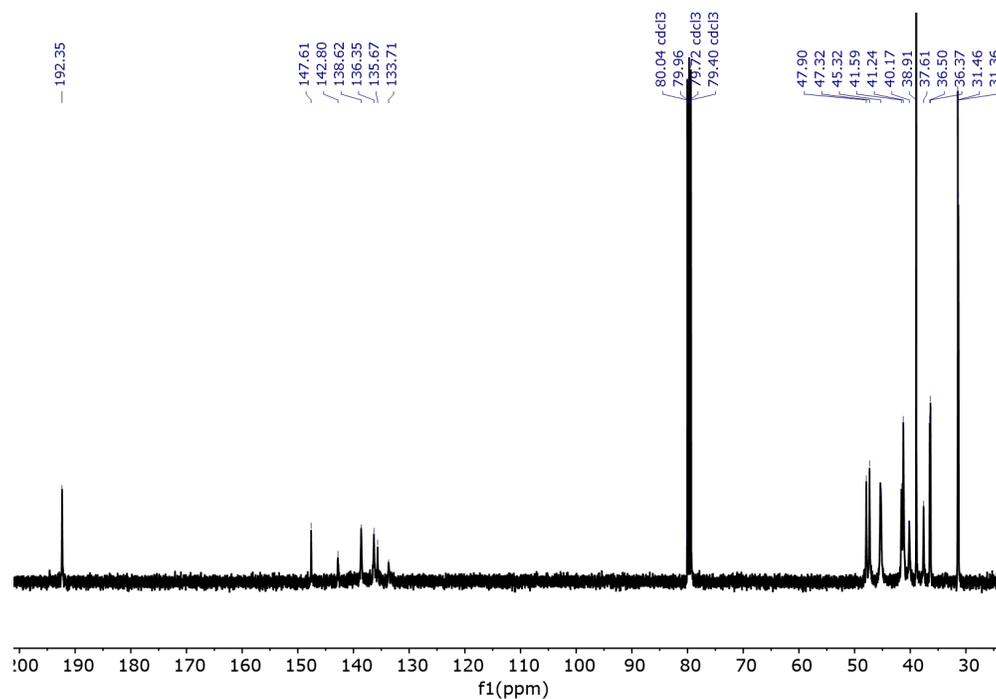


Figure S5:  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*) spectra of compound 7

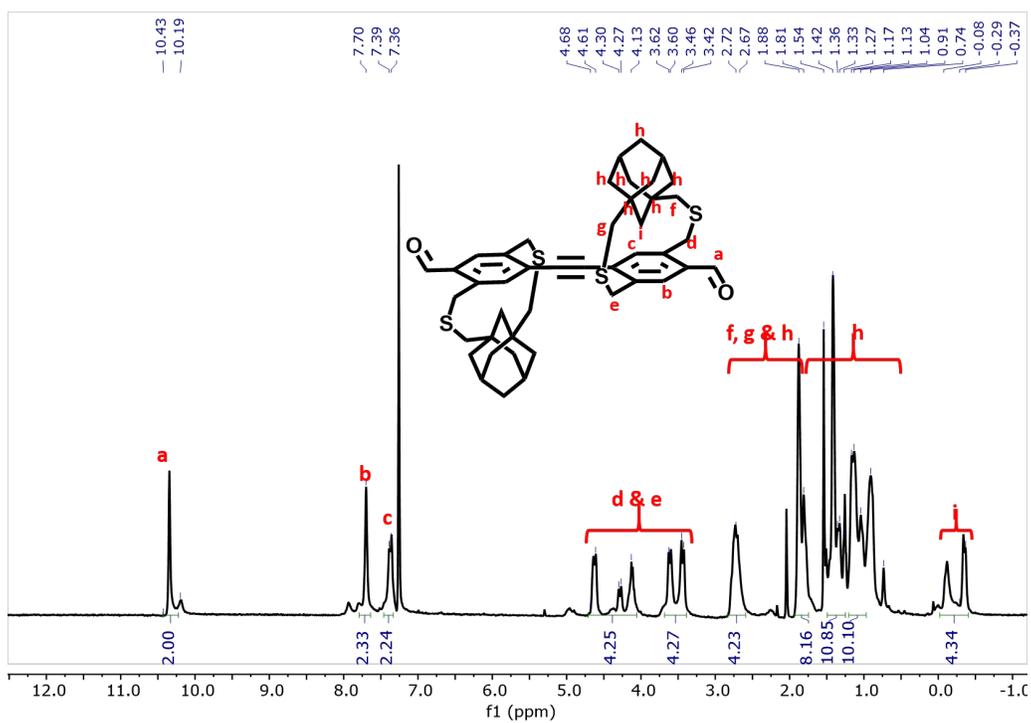


Figure S6:  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) spectra of compound 8 (DADA)

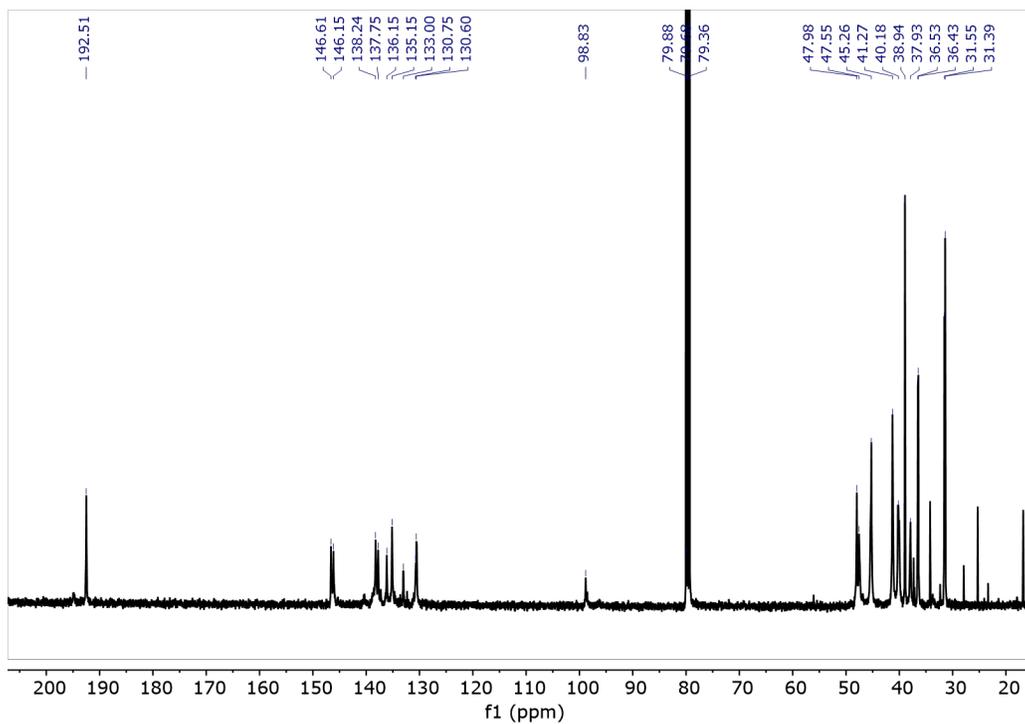


Figure S7:  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ ) spectra of compound 8 (DADA)

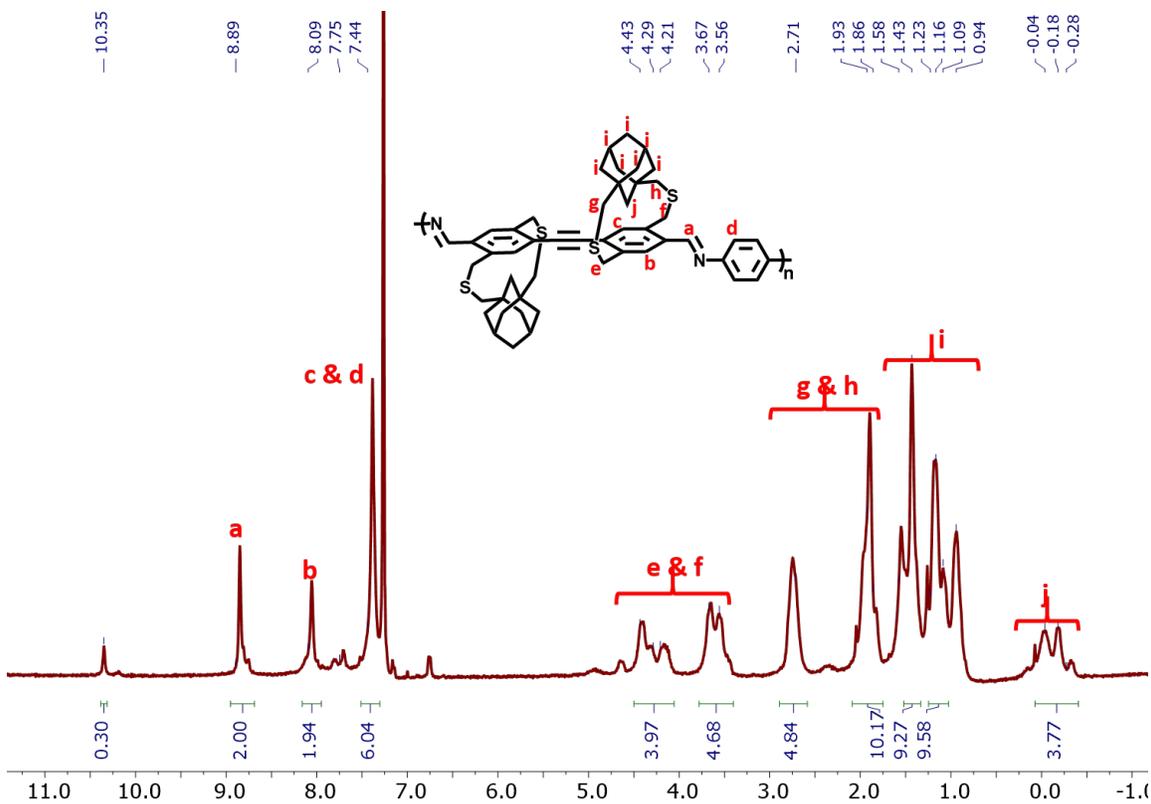


Figure S8:  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) spectra of p-PAM

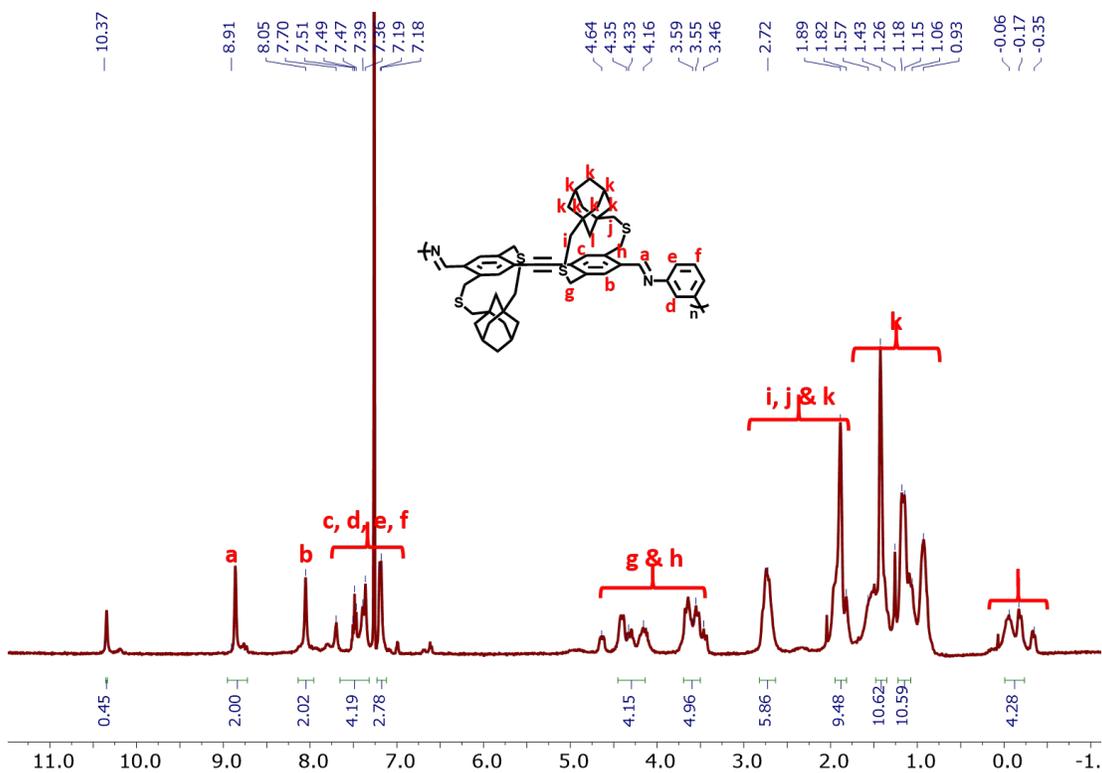


Figure S9:  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ ) spectra of m-PAM

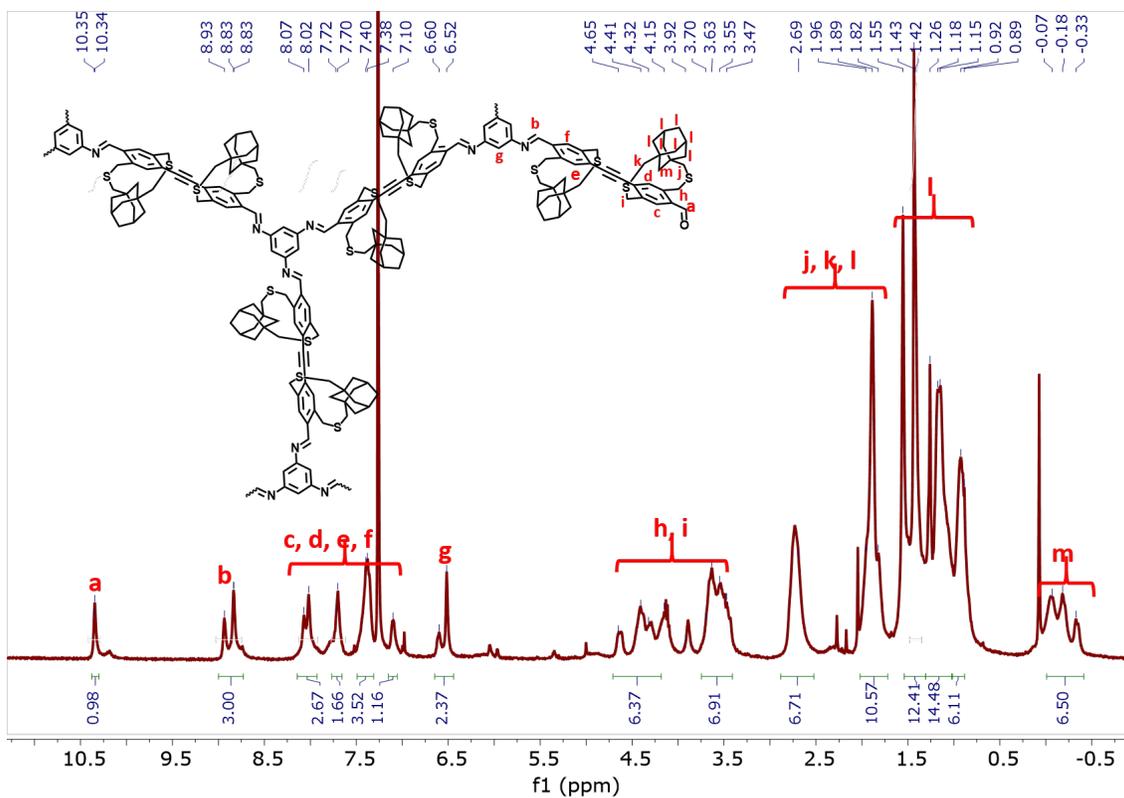


Figure S10:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of HB-PAM-1

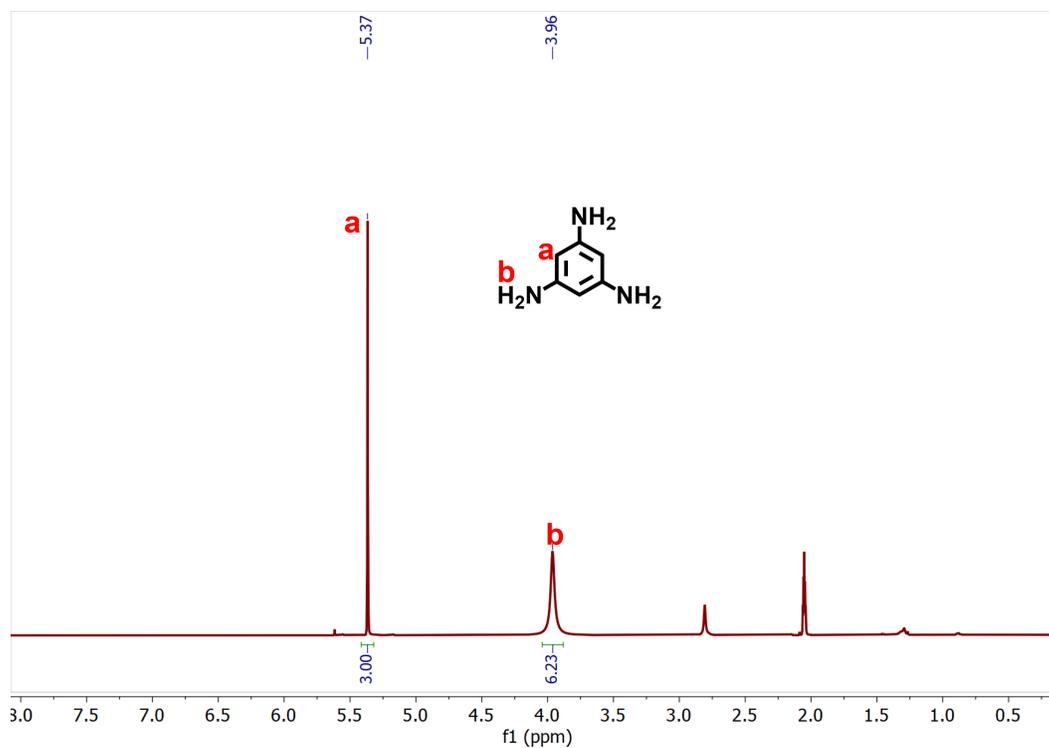


Figure S11:  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{COCD}_3$ ) spectra of benzene-1,3,5-triamine

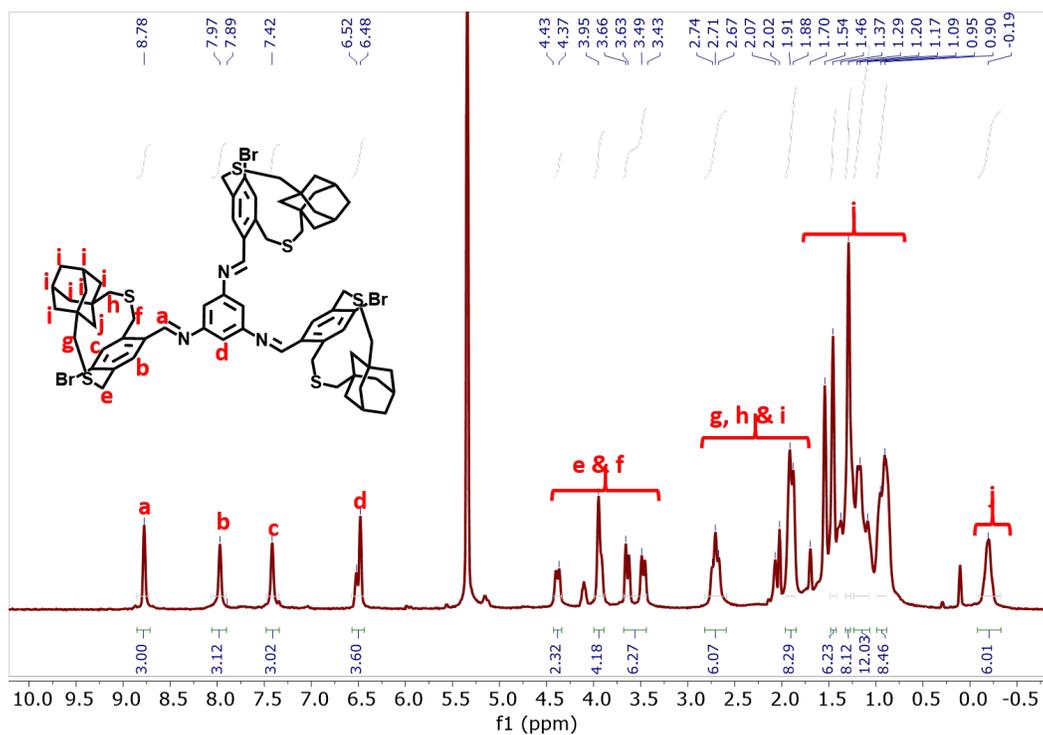


Figure S12:  $^1\text{H}$  NMR (400 MHz,  $\text{Methylenechloride-d}_2$ ) spectra of imine trimer

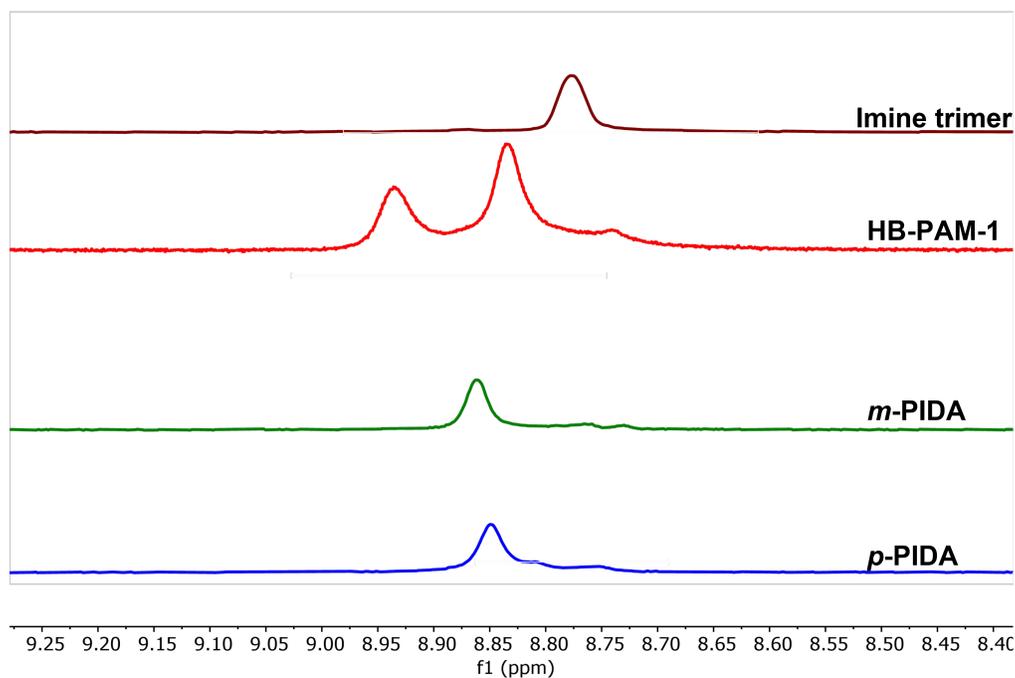


Figure S13: Stacked  $^1\text{H}$  NMR (400 MHz,  $\text{Chloroform-d}$ ) spectra of *p*-PIDA, *m*-PIDA, HB-PAM-1 and the imine model trimer highlighting the imine region.

## 8. References

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<sup>i</sup> S. Chaudhuri, M. Mohanan, A. V. Willems, J. A. Bertke and N. Gavvalapalli, *Chem. Sci.*, 2019, **10**, 5976-5982.