Supporting Information for

Using Molecular Straps to Engineer Conjugated Porous Polymers Growth, Chemical Doping and Conductivity

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Table of Contents

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 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 or inside glove box. Thin layer chromatography was performed using Silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, $KMnO_4$ 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.

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Varian 400-MR NMR. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak. $CDCl_3$: 7.26 for ^{1}H; and 77.36 for ^{13}C; CD_2Cl_2: 5.32 for ^{1}H; and 54.00 for ^{13}C; 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).

Solid-state ^{13}C and ^{31}P cross-polarization magic-angle spinning (CP-MAS) NMR[i] of monomers and CPPs were collected on 11.75-T (proton radio frequency of 500 MHz) Bruker Avance NEO with a double resonance HX probe at ambient temperature. The samples were contained in a 3.2-mm outer diameter zirconia rotor with Kel-F endcap. ^{13}C-CP-MAS NMR spectra were collected at a spectrometer frequency of 125.7 MHz with magic-angle spinning (MAS) at 8 and 10 kHz. ^{31}P-CPMAS NMR spectra were collected at a spectrometer frequency of 202.5 MHz with MAS at 10 and 18 kHz. Proton-carbon and proton-phosphorus matched cross-polarization ramp was at 50 kHz with 2-ms contact time. The proton dipolar decoupling was achieved by applying continuous wave spinal64[ii] on the ^{1}H channel during acquisition. The π pulse length was 2.5 μs for ^{1}H and the recycle delay was 5s. The line broadening for the spectrum was 50 Hz.

ATR-IR spectra of the trimers and CMPs were obtained using PerkinElmer FT-IR spectrometer with an ATR attachment by directly loading the samples on to the ATR crystal.

Dynamic Light Scattering (DLS) measurements were performed using LS spectrometer by LS instruments using a single laser beam at 631 nm wavelength at 90^o angle.

Thermogravimetric analysis (TGA) was conducted on a TA Instruments Q5000IR TGA. 100 μL platinum pans were used for the analysis and the heating rate was maintained at 5 °C/minute.

Gas adsorption studies were conducted on a Quantachrome Instruments Autosorb-1 sorption analyzer for all samples using a 6 mm bulb cell. Sample activation was performed at 100 ^oC under vacuum using the integrated setup available on the autosorb.

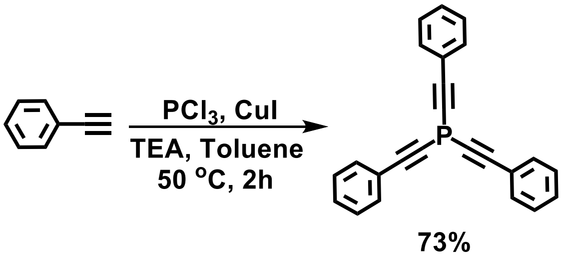
UV-vis absorption spectra were recorded on Agilent Technologies Cary Series 5000 UV-vis-NIR spectrophotometer and Genesys 10S UV−vis spectrophotometer.

Cyclic voltammetry experiments were done using PGZ402 and data was analyzed by Voltamaster 4. Glassy Carbon (3.0mm diameter), platinum wire, silver wire in 0.1M AgNO3 were used as working, auxiliary and reference electrodes respectively.

Electrical Conductivity measurements were performed using a custom-designed multipin framework with gold channels by measuring the I-V responses over -2 V to 2 V using a Keithley source meter (2604B, dual-channel, 40V SMU).

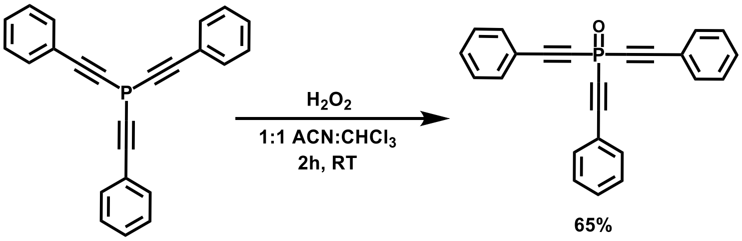
2. Synthesis of trimers, CPPs and S-LP

2.1 Procedure for Synthesis of NS-trimer



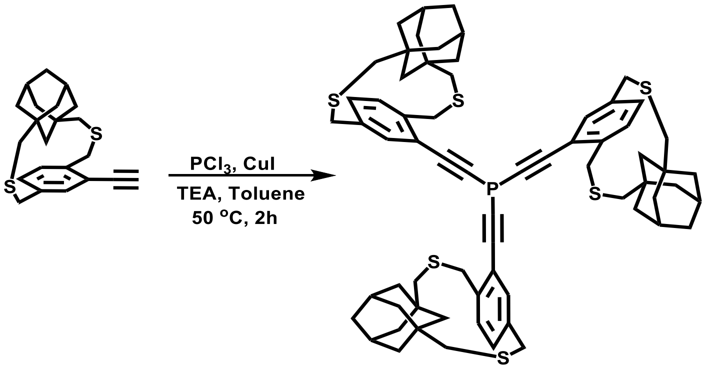
In an oven dried Schlenk flask phenyl acetylene (1 g, 9.79 mmol, 3.5 equiv.) was taken and brought into the glove box, copper (I) iodide (79 mg, 0.41 mmol, 15 mol%), degassed triethylamine (3.9 ml, 28 mmol, 10 equiv.) were added along with dry toluene (12 mL). Then phosphorous trichloride (245 µL, 2.79 mmol, 1 equiv.) was added and the reaction mixture was stirred at room temperature for 2 hours. After removing the solvents by evaporation under reduced pressure, the crude reaction mixture was purified using silica gel column chromatography with 2 to 5% ethyl acetate in hexane as eluent to obtain a white solid as product (680 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.9 Hz, 6H), 7.42 – 7.30 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.82 (d, *J* = 1.9 Hz), 132.07, 130.99, 124.76 (d, *J* = 1.4 Hz), 108.30 (d, *J* = 11.3 Hz), 82.08 (d, *J* = 6.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ -91.30

2.2 Procedure for oxidation of NS-trimer



In an oven dried round bottom flask NS-trimer (280 mg, 0.83 mmol, 1 equiv.) was dissolved in 5ml of 1:1 acetonitrile: $CHCl_3$ mixture and 130µL of 30% (1.67 mmol, 2 equiv.) hydrogen peroxide was added dropwise and the reaction mixture was stirred for 2 hours at room temperature. After removing the solvents by evaporation under reduced pressure, the crude reaction mixture was purified using silica gel column chromatography with 10 to 15% ethyl acetate in hexane as eluent to obtain an offwhite solid as product (190 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (dt, *J* = 7.1, 1.6 Hz, 6H), 7.52 – 7.45 (m, 3H), 7.41 – 7.36 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.48, 135.45, 133.69, 131.25, 122.18, 122.13, 105.21, 104.75, 87.16, 84.78. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -53.86 (d, *J* = 2.7 Hz).

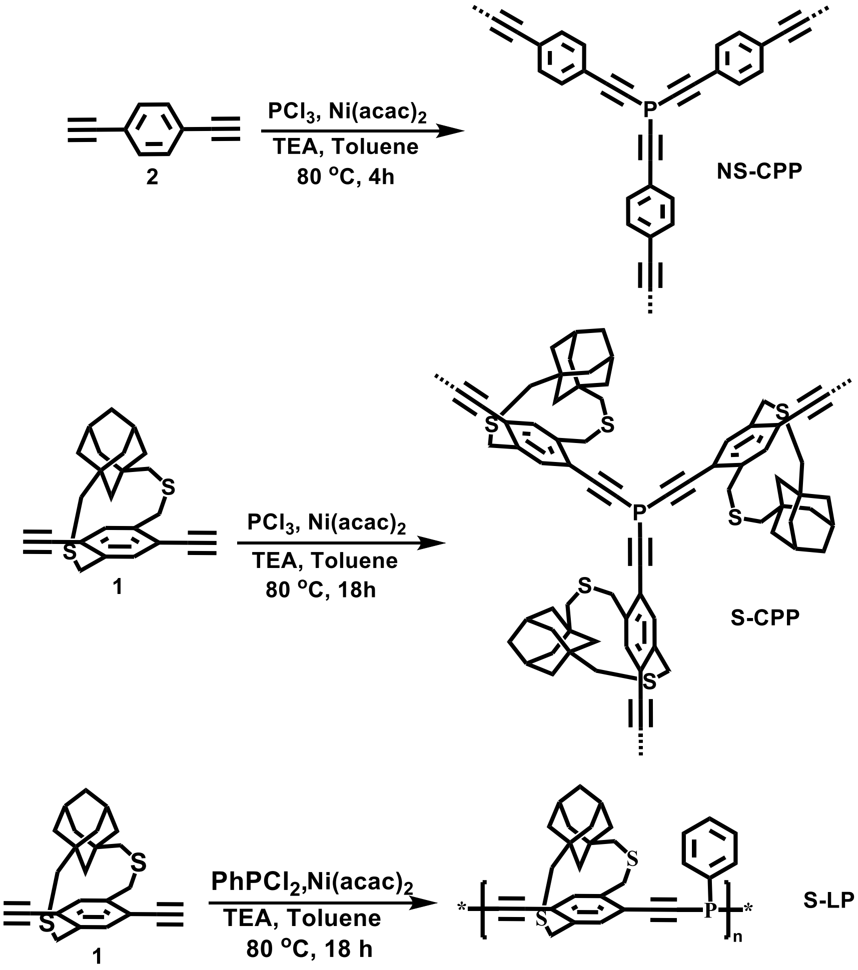
2.3 Procedure for Synthesis of S-trimer



65%

In an oven dried Schlenk flask cyclophane acetylene (540 mg, 1.52 mmol, 3.2 equiv.) was taken and brought into the glove box, copper (I) iodide (29 mg, 0.07 mmol, 15 mol%), degassed triethylamine (640 µL, 4.6 mmol, 10 equiv.) were added along with dry toluene (10 mL). Then phosphorous trichloride (40 µL, 0.46 mmol, 1 equiv.) was added and the reaction mixture was stirred at room temperature for 2 hours. After removing the solvents by evaporation under reduced pressure, the crude reaction mixture was purified using silica gel column chromatography with 2 to 5% ethyl acetate in hexane as eluent to obtain a white solid as product (325 mg, 65% yield). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.65 (s), 7.43 (s), 7.34 (s), 7.17 (d, *J* = 16.8 Hz): 9H]; [4.31 (d, *J* = 13.6 Hz), 4.11 (dd, *J* = 14.5, 7.2 Hz) 3H]; [3.73 (d, *J* = 13.6 Hz), 3.61 – 3.41 (m), 9H]; 2.65 (d, *J* = 13.8 Hz, 6H); 2.23 (d, *J* = 14.5 Hz, 2H); 1.88 (m, 10H); 1.44 (m, 12H); 1.15 (m, 12H); 0.91 (dd, *J* = 15.1, 8.7 Hz, 6H); -0.13 (q, *J* = 13.2, 12.3 Hz, 6H); **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 146.53, 143.82, 136.80 (d, *J* = 74.8 Hz), 135.57 – 132.74 (m), 124.88 (d, *J* = 132.5 Hz), 106.86, 86.73 (d, *J* = 119.2 Hz), 62.86, 47.23, 45.41, 41.00 (d, *J* = 75.6 Hz), 40.11, 39.11, 37.87, 36.40 (d, *J* = 5.7 Hz), 31.80; **^{31}P NMR** (162 MHz, $CDCl_3$) δ -90.62 (d, *J* = 85.7 Hz). **HRMS** (ESI) m/z: 1091.4009 $[M+H]^+$; calculated for $[C_{66}H_{75}PS_6+H]^+$: 1091.39

2.4 General procedure for the synthesis of CPPs and S-LP



CPP	Equivalence of PCl$_3$ w.r.t. diacetylene	Time (h)	Yield (%)
NS-CPP	0.66	4	38
S-CPP-1	0.66	18	48
S-CPP-2	1	18	34
S-CPP-3	1.33	18	43

Table S1: CPP synthesis details

In an oven dried Schlenk flask, diacetylene (1 or 2) precursor was weighed, brought into the glove box and was dissolved in dry toluene. Then 6 mol% of Nickel (II) acetylacetonate and 6 equivalents of degassed triethylamine with respect to the diacetylene (strut) were added, followed by addition of required amount of phosphorous trichloride (knot) (Table S1). The reaction mixture was stirred at 80 °C and stopped when the solvodynamic radius reached roughly 200 nm *(DLS measurement was done after diluting the reaction mixture ~10 times with $CHCl_3$)* or after 18 hours. After removing the solvents by evaporation under reduced pressure, 10 ml of THF (for 1g diacetylene batch) was added into crude reaction mixture, sonicated for 2 minutes and reprecipitated by adding 150 ml of MeOH, filtered and vacuum dried. The obtained brown powder was further purified by Soxhlet with MeOH (18 hours) and then vacuum dried to obtain CPPs and was used for further characterization.

S-LP was synthesized and purified by following similar procedure as above. Dichlorophenyl phosphine (122 µL, 0.9 mmole, 1 eqiv.) was reacted with adamatane diacetylene (1) (340 mg, 0.9 mmole, 1 eqiv.) in presence of 6 mol% of Nickel (II) acetylacetonate and 6 equivalents of degassed triethylamine in toluene at 80 °C for 18 hours. After reaction, solvents were removed, reprecipitated the residue in MeOH, filtered and further purified by Soxhlet with MeOH (18 hours). ^1H NMR (Figure S35) (400 MHz, $CDCl_3$) δ 8.11-7.91 (d, 2H), 7.58 (s, 2H), 7.48 – 7.41 (m, 4H), 4.00 (m, 2H), 3.43 (m, 2H), 2.62 (brs, 2H), 2.05-0.89 (m, 14H) -0.20 (s, 2H). Molecular weight of the THF soluble fraction was 3 kDa with respect to polystyrene standards.

3. Solid State ^{13}C-CP-MAS NMR spectra of CPPs

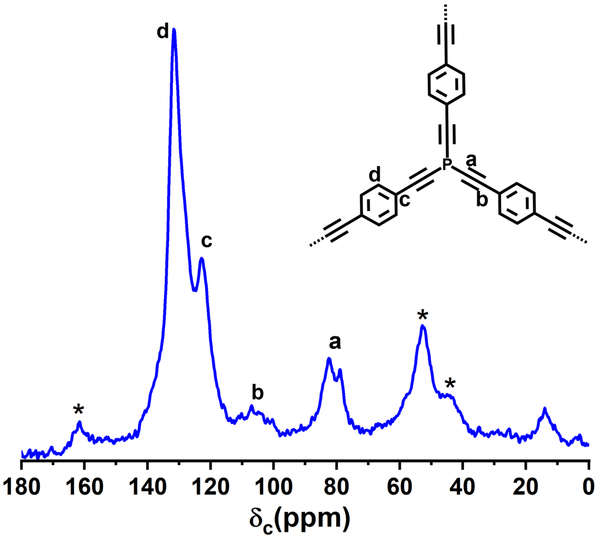


Figure S1: Solid state ^{13}C CPMAS NMR (10MHz) spectrum of NS-CPP, *(* peaks represent the spinning side bands)*

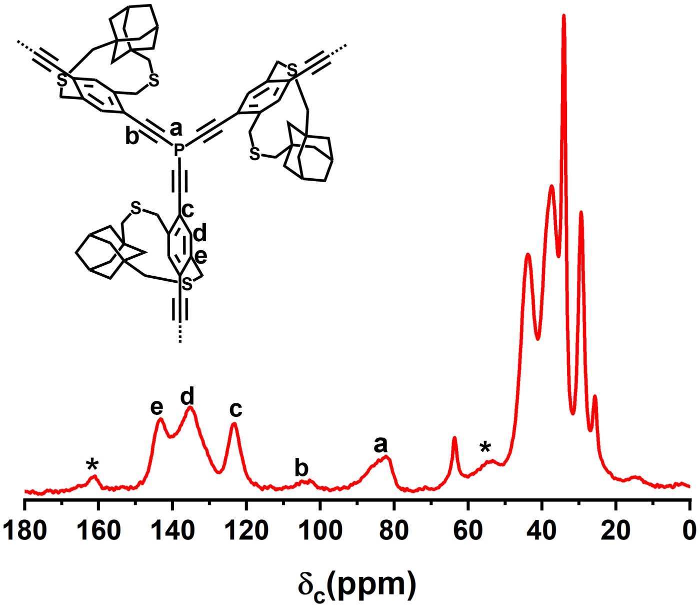


Figure S2: Solid state ^{13}C CPMAS NMR (10MHz) spectrum of S-CPP-1, *(* peaks represent the spinning side bands)*

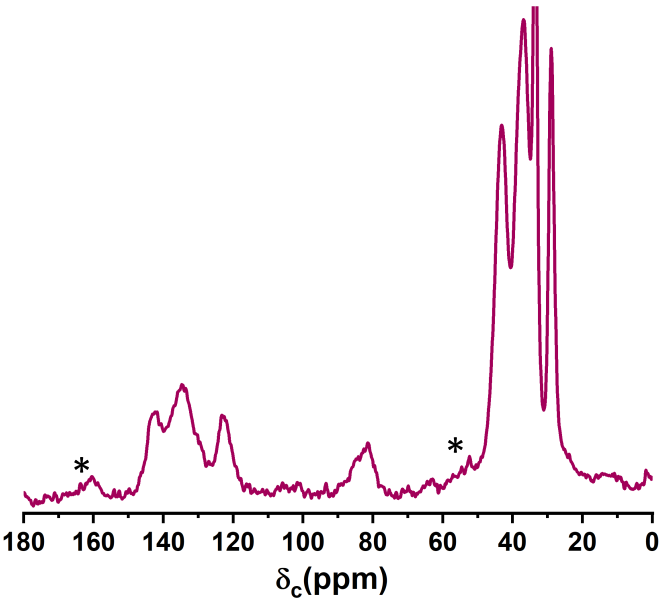


Figure S3: Solid state ^{13}C CPMAS NMR (10MHz) spectrum of S-CPP-2, *(* peaks represent the spinning side bands, peak assignment same as Figure S2)*

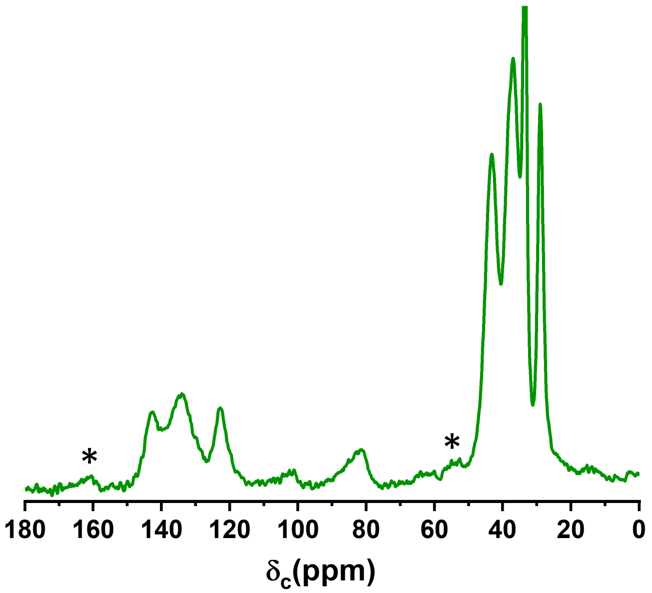


Figure S4: Solid state ^{13}C CPMAS NMR (10MHz) spectrum of S-CPP-3, *(* peaks represent the spinning side bands, peak assignment same as Figure S2)*

4. ATR-IR spectra of oxidized NS-trimer and S-LP

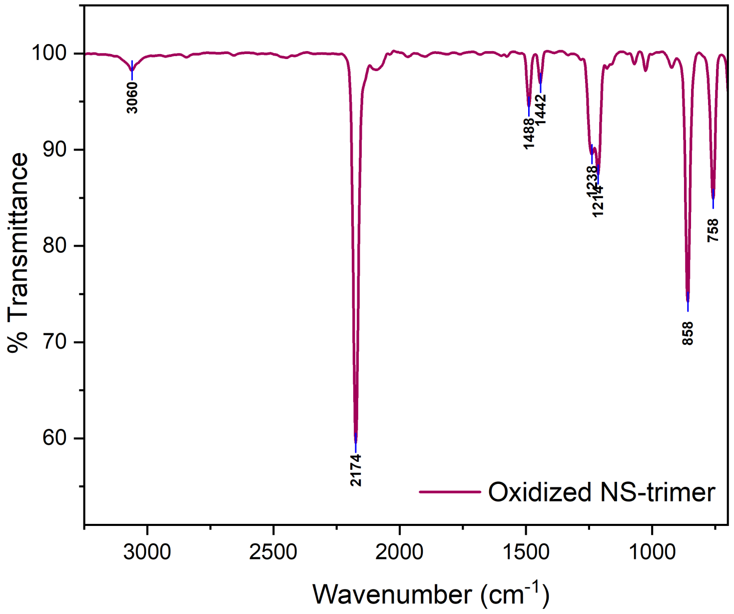


Figure S5: ATR-IR spectrum of Oxidized NS-trimer

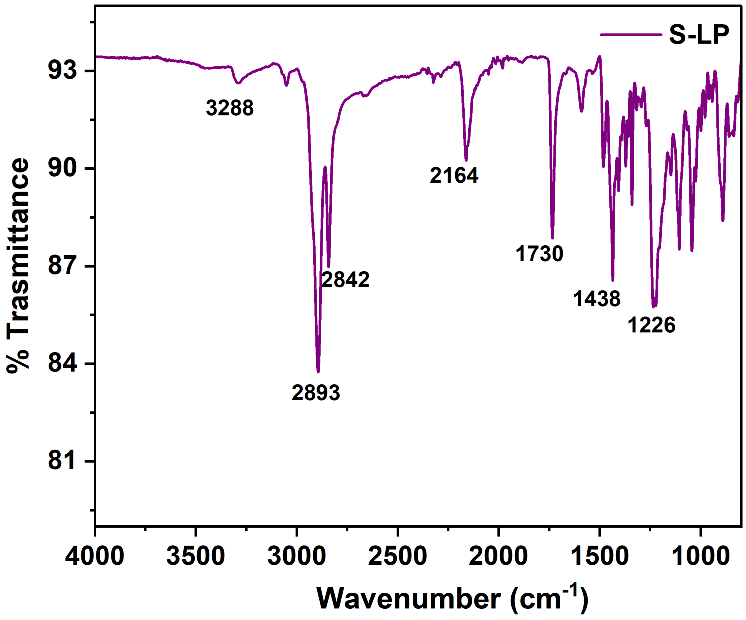


Figure S6: ATR-IR spectrum of S-LP

5. TGA plots of CPPs

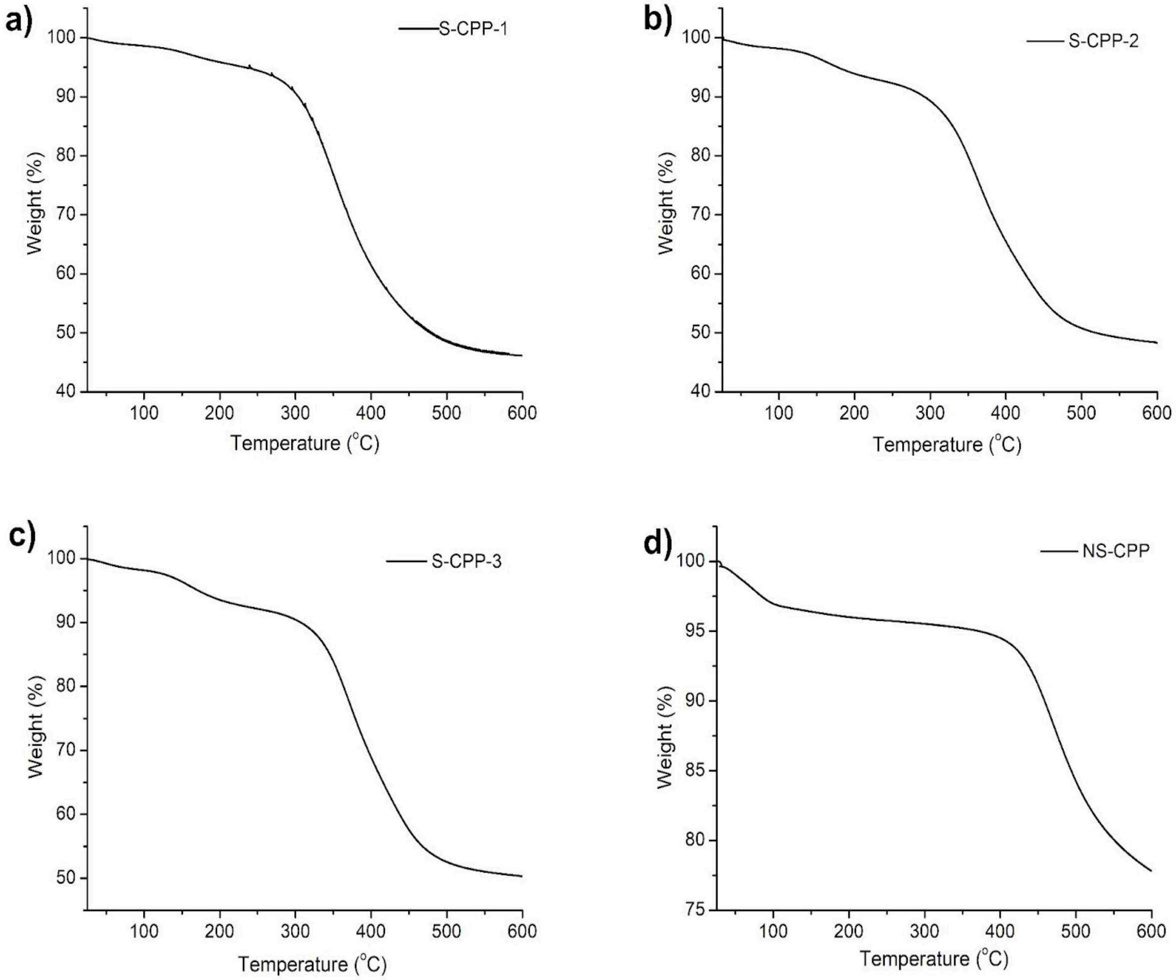


Figure S7: TGA traces of a) S-CPP-1; b) S-CPP-2; c) S-CPP-3 d) NS-CPP from 25 °C to 600 °C at 5 °C/min ramping rate

CPP	Temperature at which 5% weight loss occurs (°C)
S-CPP-1	215
S-CPP-2	175
S-CPP-3	170
NS-CPP	365

Table S2: Thermal stability of CPPs

6. Nitrogen adsorption isotherms and BET surface areas of CPPs

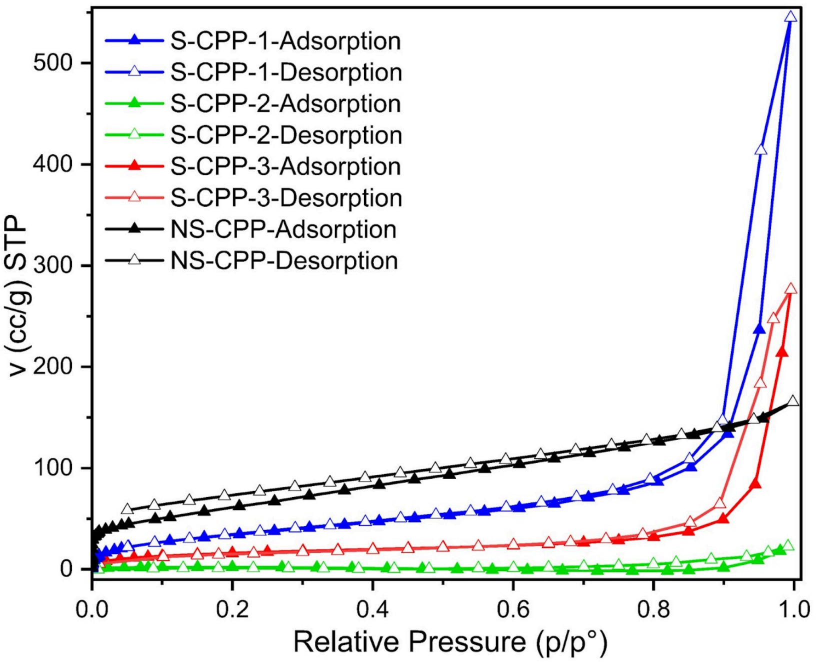


Figure S8: Nitrogen adsorption isotherms of CPPs

CPPs	BET-Surface Area (m^2/g)
S-CPP-1	128
S-CPP-2	8.5
S-CPP-3	47
NS-CPP	221

Table S3: BET surface areas of CPPs

7. Percentage of strut / B_2 conversion

Once the polymer was filtered out from the reaction mixture, the filtrate was collected, concentrated and dried under high vacuum. ^{1}H NMR spectra of the filtrate was recorded with Anthracene as an internal standard. Percentage of unreacted starting material was estimated based on the ratio of integration between two protons of anthracene at 8.43 ppm and two free acetylene protons of the strut (B_2) at 3.35 ppm. All spectra were referenced at 8.43 ppm and integration limits were kept same across all samples for consistency.

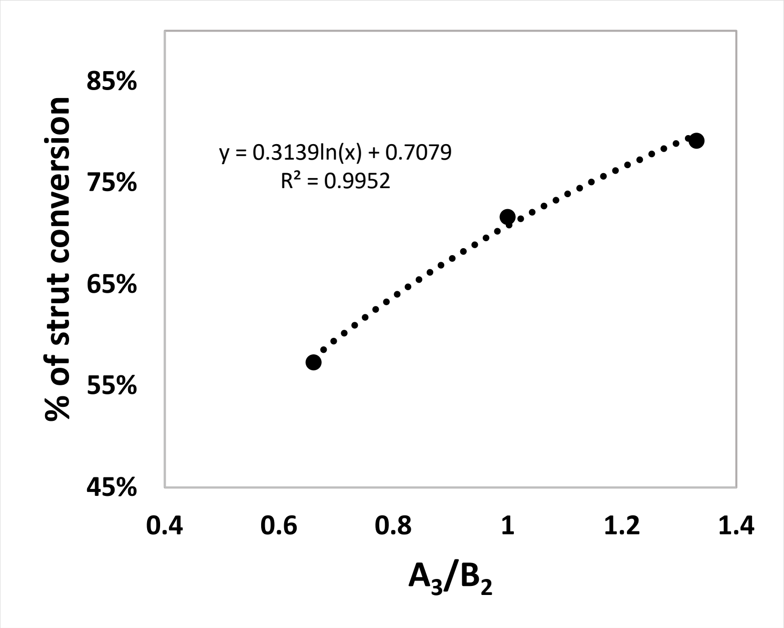
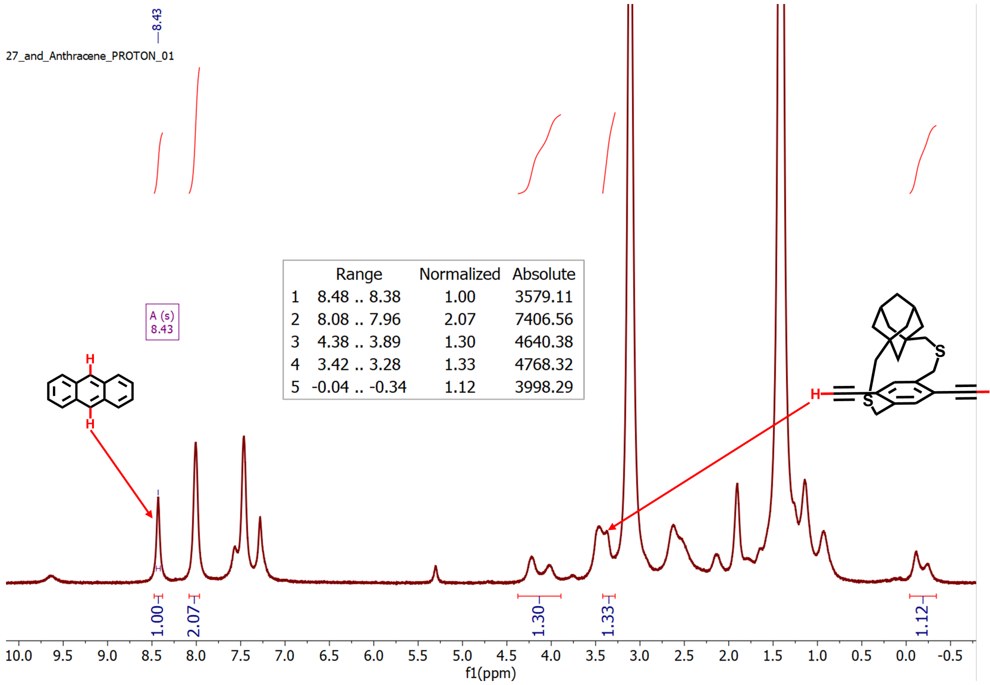
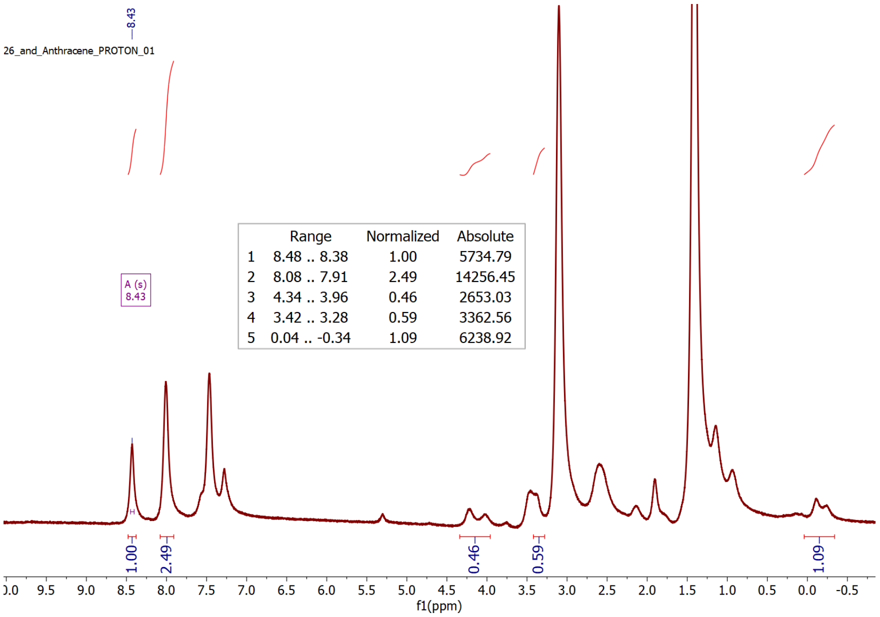


Figure S9: Percentage conversion of strut (B_2) with respect to A_3 : B_2 ratio in strapped CPPs



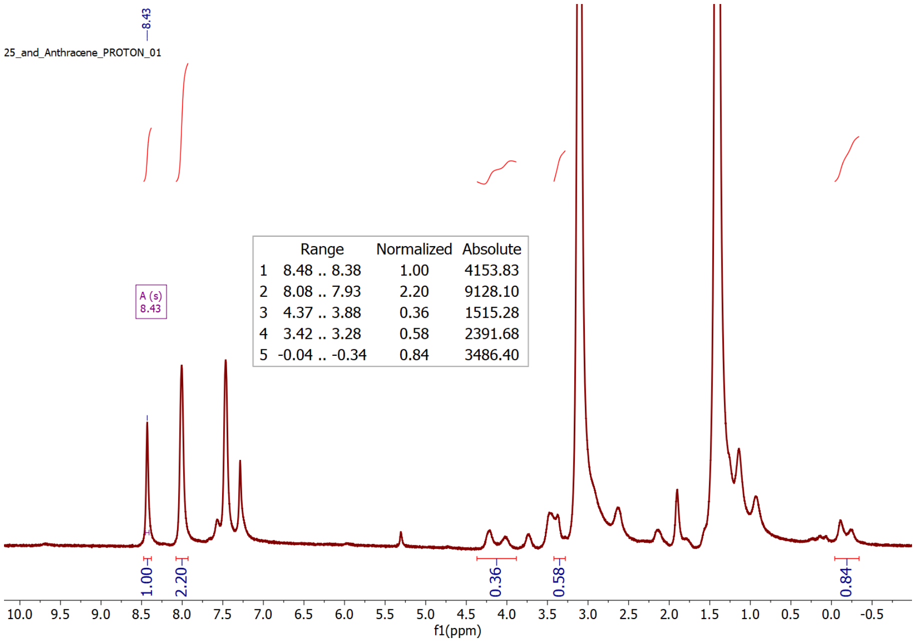
	Range	Normalized	Absolute
1	8.48 .. 8.38	1.00	3579.11
2	8.08 .. 7.96	2.07	7406.56
3	4.38 .. 3.89	1.30	4640.38
4	3.42 .. 3.28	1.33	4768.32
5	-0.04 .. -0.34	1.12	3998.29

Figure S10: ^{1}H NMR spectrum of filtrate obtained after S-CPP-1 synthesis with Anthracene as internal standard; *(peaks used for calculation are shown: 8.43 ppm from anthracene and 3.35 ppm from the strut / B_2)*



	Range	Normalized	Absolute
1	8.48 .. 8.38	1.00	5734.79
2	8.08 .. 7.91	2.49	14256.45
3	4.34 .. 3.96	0.46	2653.03
4	3.42 .. 3.28	0.59	3362.56
5	0.04 .. -0.34	1.09	6238.92

Figure S11: ^{1}H NMR spectrum of filtrate obtained after S-CPP-2 synthesis with Anthracene as internal standard, *(peak assignment same as Figure S8)*



	Range	Normalized	Absolute
1	8.48 .. 8.38	1.00	4153.83
2	8.08 .. 7.93	2.20	9128.10
3	4.37 .. 3.88	0.36	1515.28
4	3.42 .. 3.28	0.58	2391.68
5	-0.04 .. -0.34	0.84	3486.40

Figure S12: ^{1}H NMR spectrum of filtrate obtained after S-CPP-3 synthesis with Anthracene as internal standard, *(peak assignment same as Figure S8)*

8. DLS of CPPs

CPP suspensions (~2mg/ml) were prepared by sonicating them either in ACN, THF, $CHCl_3$ or o-DCB for 30-40 mins at 50 ^{O}C. The obtained dispersions were centrifuged at 14000 rpm for 2 minutes. The supernatant was collected and DLS was done at room temperature.

9. Dispersibility limit of CPPs

A concentration (mg/ml) dependent absorbance plot was generated for each CPP by recording UV-vis absorption spectra at different concentrations.

Saturated dispersions of CPPs were prepared by sonicating excess of CPPs in $CHCl_3$ for 30 minutes at 50 ^{O}C. The obtained dispersions were centrifuged at 14000 rpm for 2 minutes and the supernatant was further diluted to obtain the absorbance at specific wavelength. The amount of CPP dispersed was the back-calculated using the concentration dependent absorbance plot.

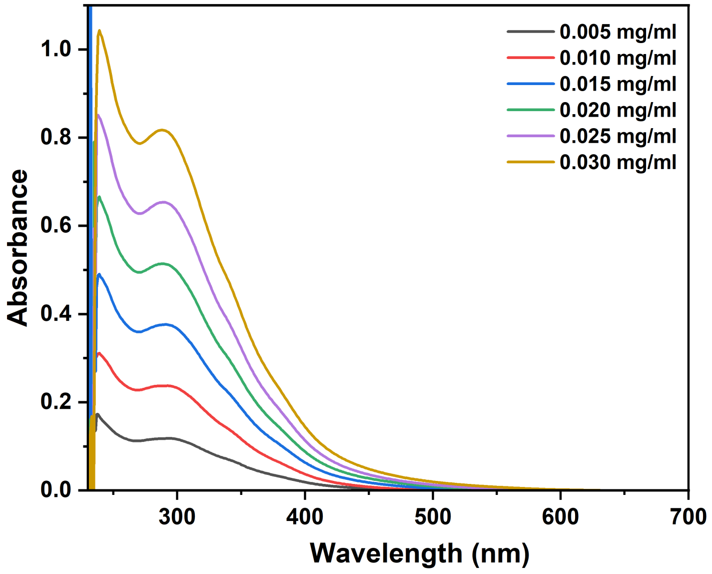
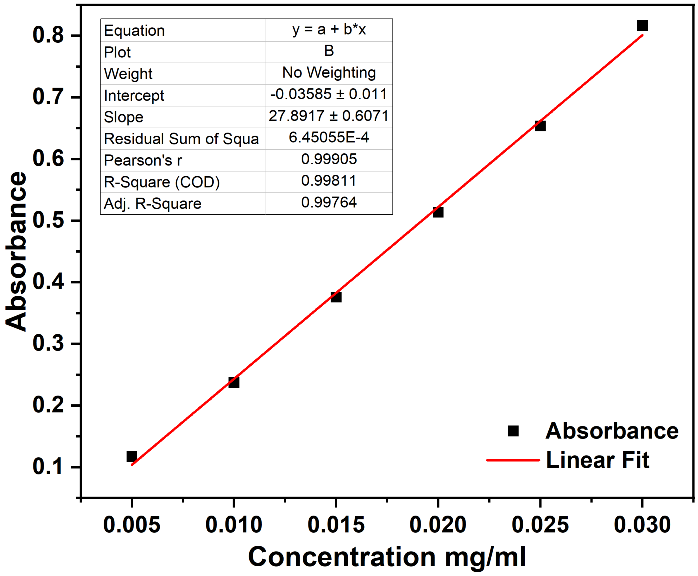


Figure S13: Concentration dependent absorbance spectra of S-CPP-1



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	-0.03585 ± 0.011
Slope	27.8917 ± 0.6071
Residual Sum of Squa	6.45055E-4
Pearson's r	0.99905
R-Square (COD)	0.99811
Adj. R-Square	0.99764

Figure S14: Absorbance vs concentration of S-CPP-1 at 290nm

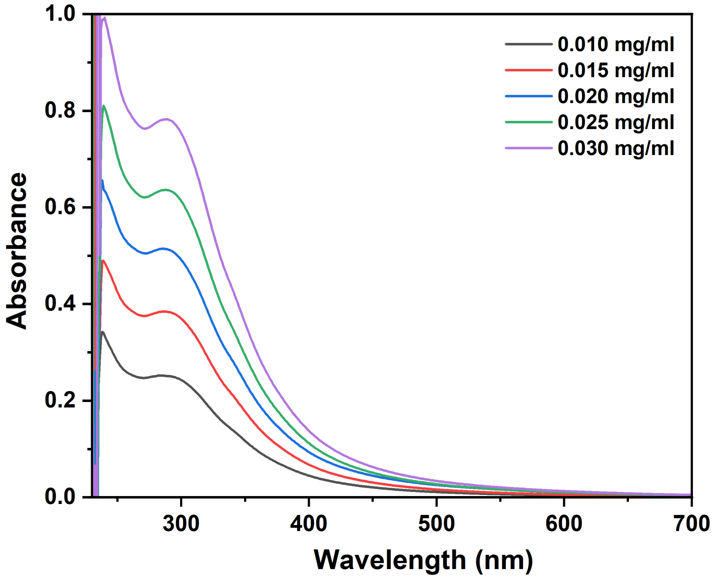
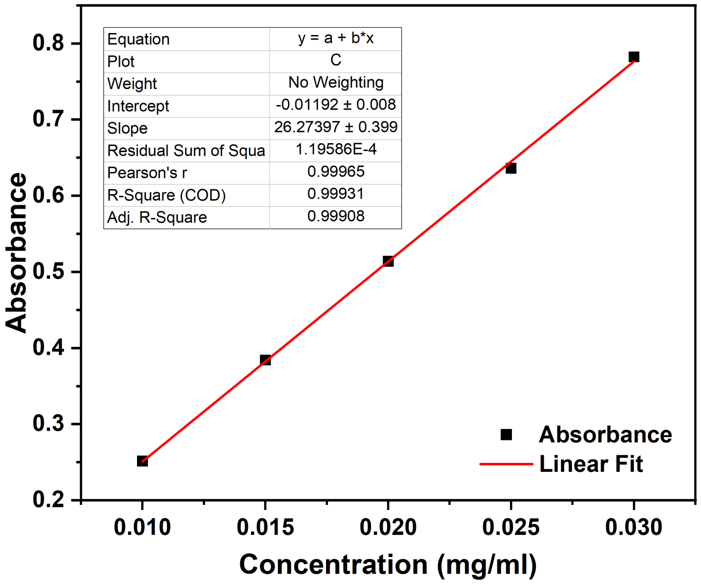


Figure S15: Concentration dependent absorbance spectra of S-CPP-2



Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	-0.01192 ± 0.008
Slope	26.27397 ± 0.399
Residual Sum of Squa	1.19586E-4
Pearson's r	0.99965
R-Square (COD)	0.99931
Adj. R-Square	0.99908

Figure S16: Absorbance vs concentration of S-CPP-2 at 288nm

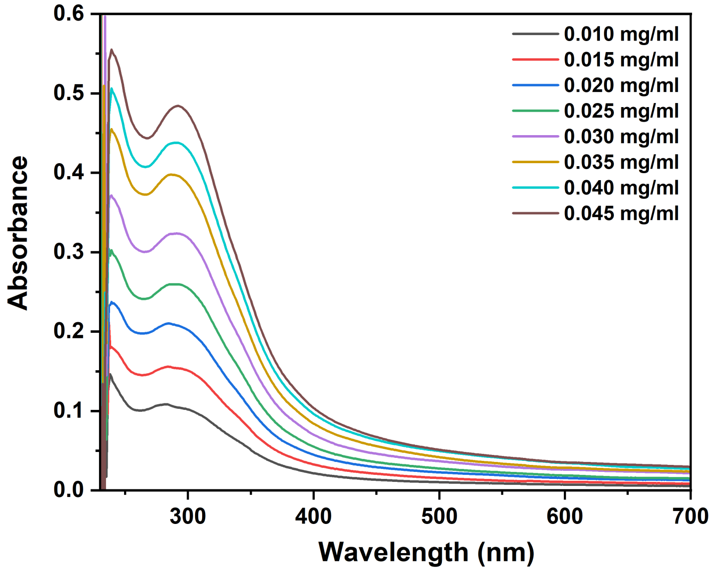
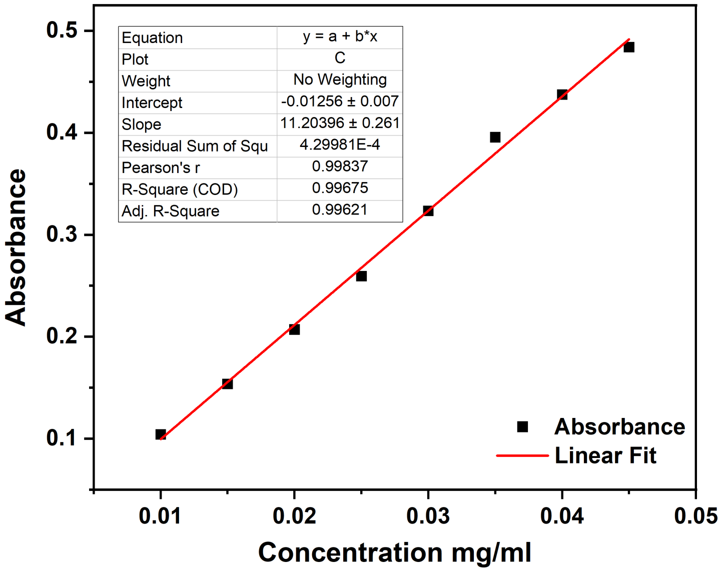


Figure S17: Concentration dependent absorbance spectra of S-CPP-3



Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	-0.01256 ± 0.007
Slope	11.20396 ± 0.261
Residual Sum of Squ	4.29981E-4
Pearson's r	0.99837
R-Square (COD)	0.99675
Adj. R-Square	0.99621

Figure S18: Absorbance vs concentration of S-CPP-3 at 289nm

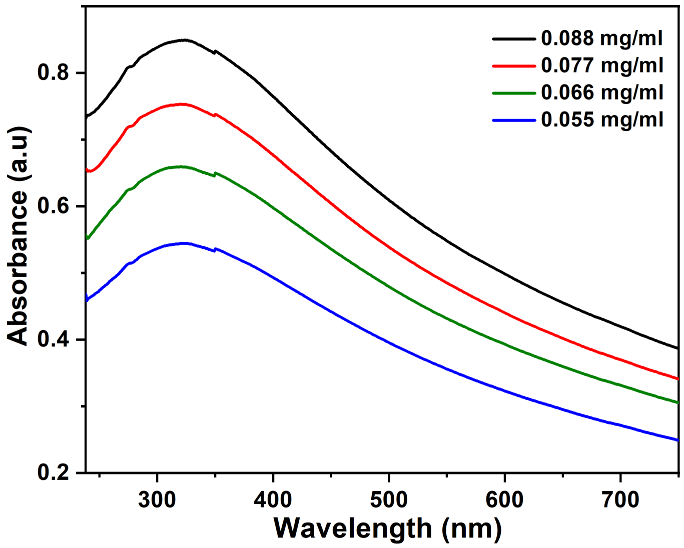
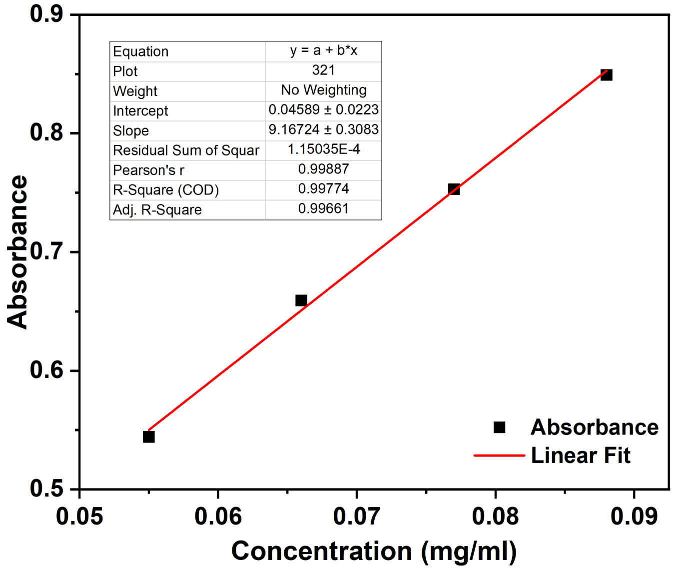


Figure S19: Concentration dependent absorbance spectra of NS-CPP



Equation	y = a + b*x
Plot	321
Weight	No Weighting
Intercept	0.04589 ± 0.0223
Slope	9.16724 ± 0.3083
Residual Sum of Squar	1.15035E-4
Pearson's r	0.99887
R-Square (COD)	0.99774
Adj. R-Square	0.99661

Figure S20: Absorbance vs concentration of NS-CPP at 321nm

10. Cyclic Voltammograms of CPPs

1mg/ml dispersions of CPPs were prepared in 0.1M tetrabutylammonium hexafluorophosphate in DMF. CV measurements were performed from -2 to +1 V potential starting from open circuit potential at three different scan rates. HOMO values of S-CPPs were calculated using the equation, $E_{HOMO} = -[4.8 - E_{1/2\ Fc,Fc} + E_{OX,\ onset}]$

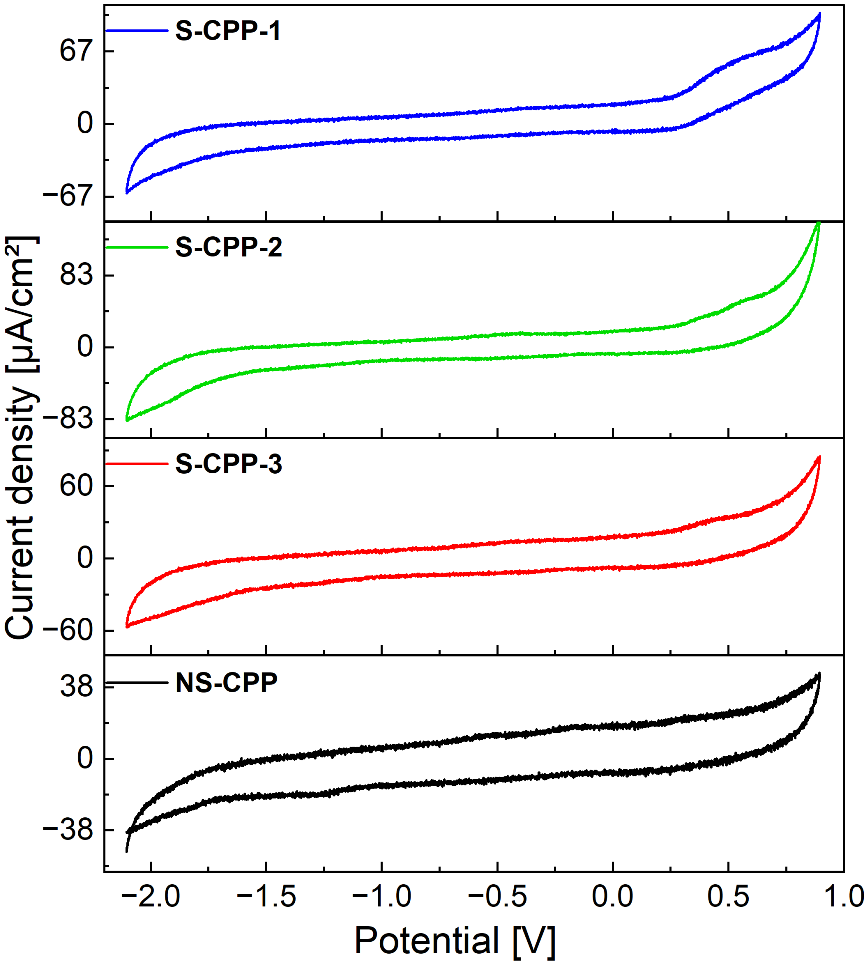


Figure S21: Cyclic Voltammograms of CPPs (scan rate 100mV/s, cycle 2)

11. Doping of CPPs with F_4TCNQ

Under nitrogen atmosphere, dispersions of 0.6 mg/ml CPP and 0.6 mg/ml of F_4TCNQ in anhydrous deoxygenated chlorobenzene was prepared in separate vials by sonicating for 30 minutes at 50 °C. Required amount of F_4TCNQ solution was mixed with the CPP dispersions and transferred into a quartz cuvette, and UV-vis-NIR spectra was recorded. The formation of F_4TCNQ anion was quantified using its reported molar extinction co-efficient.[iii] Doping efficiency is reported as amount of F_4TCNQ radical anion formed with respect to the F_4TCNQ loaded. The values were normalized respect to the doping efficiency of the strapped linear polymer (S-LP).

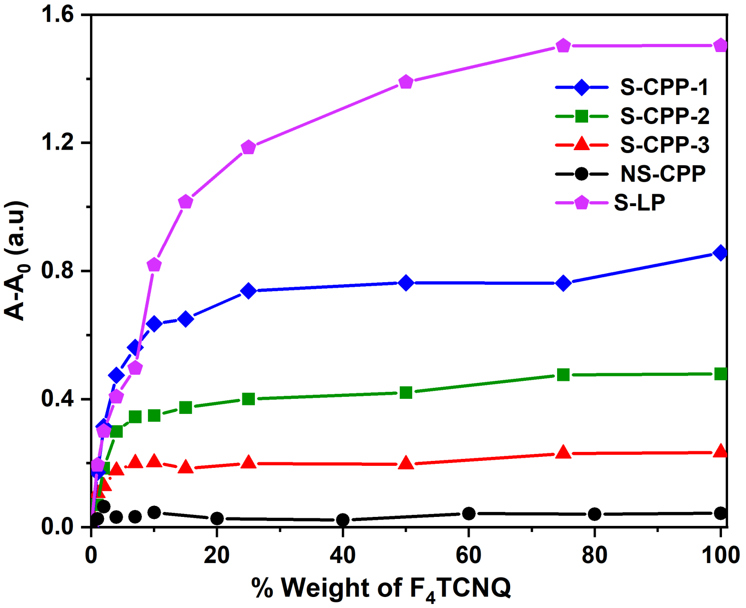


Figure S22: Change in absorbance at 873 nm with respect to % loading of F_4TCNQ (A_0: CPP absorbance at 873 nm without F_4TCNQ, A: Absorbance at 873 nm with F_4CTNQ)

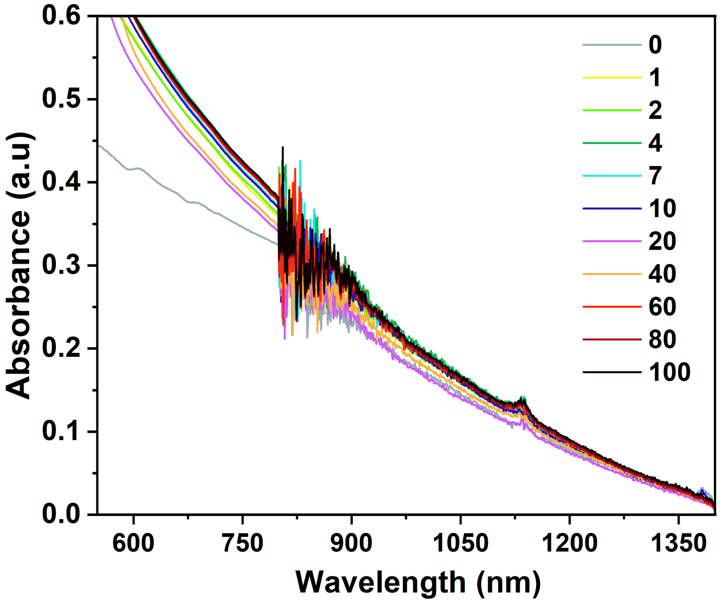


Figure S23: UV-vis absorption spectra of NS-CPP in the 550-1400 nm region with increase in %wt of F4CTNQ *(550-1400nm region is shown to highlight the formation of F4TCNQ·-)*

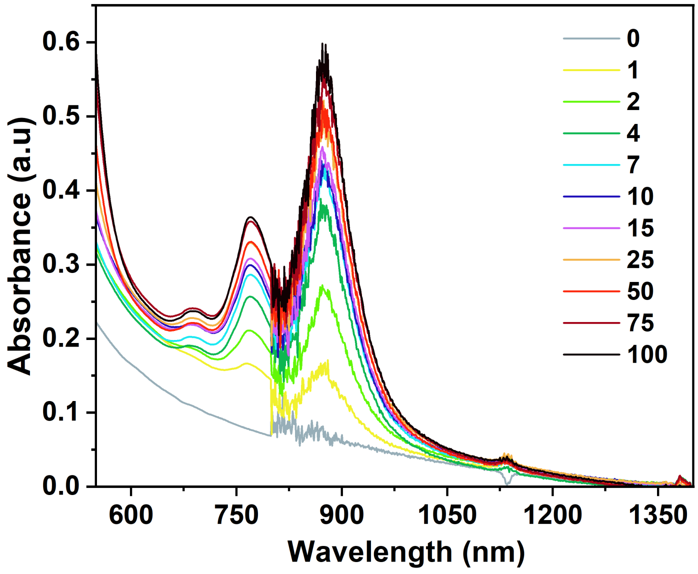


Figure S24: UV-vis absorption spectra of S-CPP-2 in the 550-1400 nm region with increase in %wt of F4CTNQ.

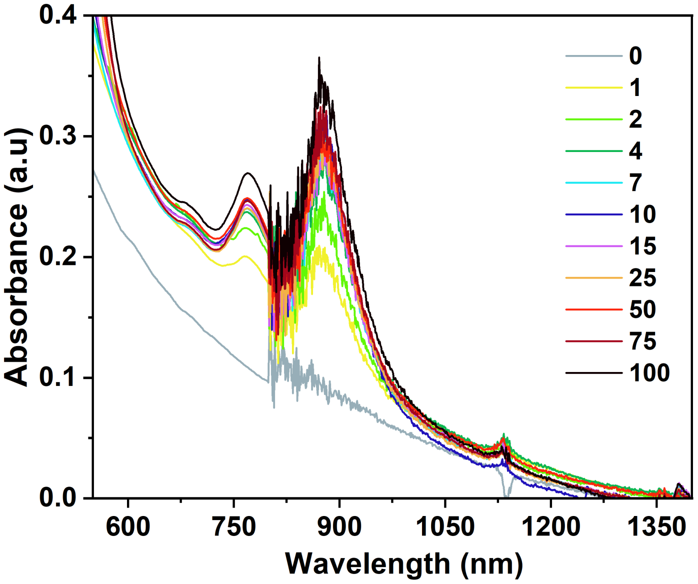


Figure S25: UV-vis absorption spectra of S-CPP-3 in the 550-1400 nm region with increase in %wt of F_4CTNQ.

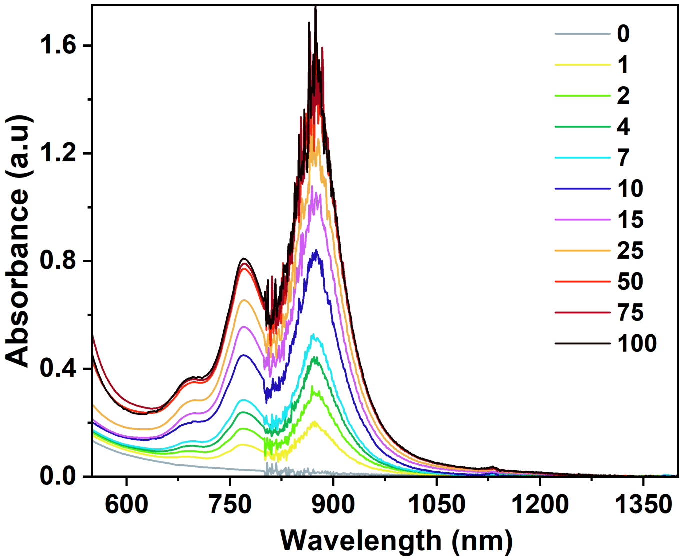


Figure S26: UV-vis absorption spectra of S-LP in the 550-1400 nm region with increase in %wt of F_4CTNQ.

12. Conductivity measurement of CPPs

Under inert conditions, dispersions of CPP (8 mg/ml) and F_4TCNQ (4 mg/ml) in chlorobenzene (CB) were prepared in separate vials by sonicating at 50°C for 20 minutes. PMMA was dissolved (4 mg/ml) in CB by heating at 70°C for 2h and then mixed with the CPP dispersion to make CPP-PMMA blend. Required amount of F_4TCNQ solution was added to the blend, stirred for few minutes to obtain the final CPP: PMMA: F_4TCNQ ratio to be 1:0.25:0.5. The electrical conductivity of drop-casted thin film (with and without doping) was evaluated using a custom-designed multipin framework.[iv] Here, a quartz-coated glass substrate with an array of gold contacts was used (Figure S24). The distance between two neighboring gold contacts ranged from 30 to 80 µm. The same blends were casted into thin films on quartz slides (20 x 15 mm) for UV-vis analysis.

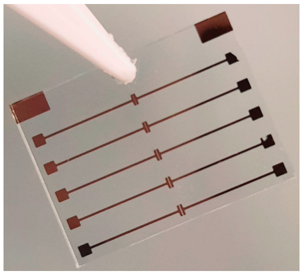


Figure S27: Prefabricated test chip with gold channels of variable channel length (30-80 µm) for thin film I-V measurement

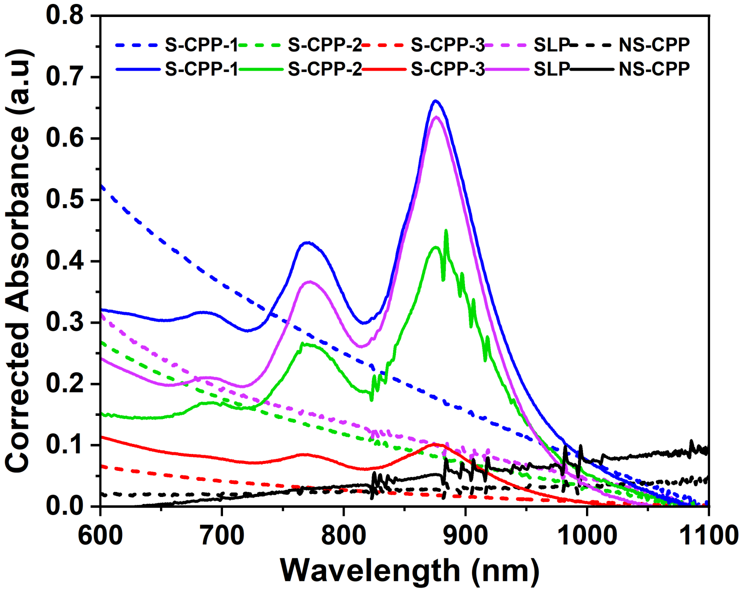


Figure S28: Thin film UV-vis absorption spectra of PMMA-CPP blends before (dotted lines) and after doping (solid lines)

13. ^{1}H, ^{13}C, ^{31}P NMR spectra of trimers and S-LP

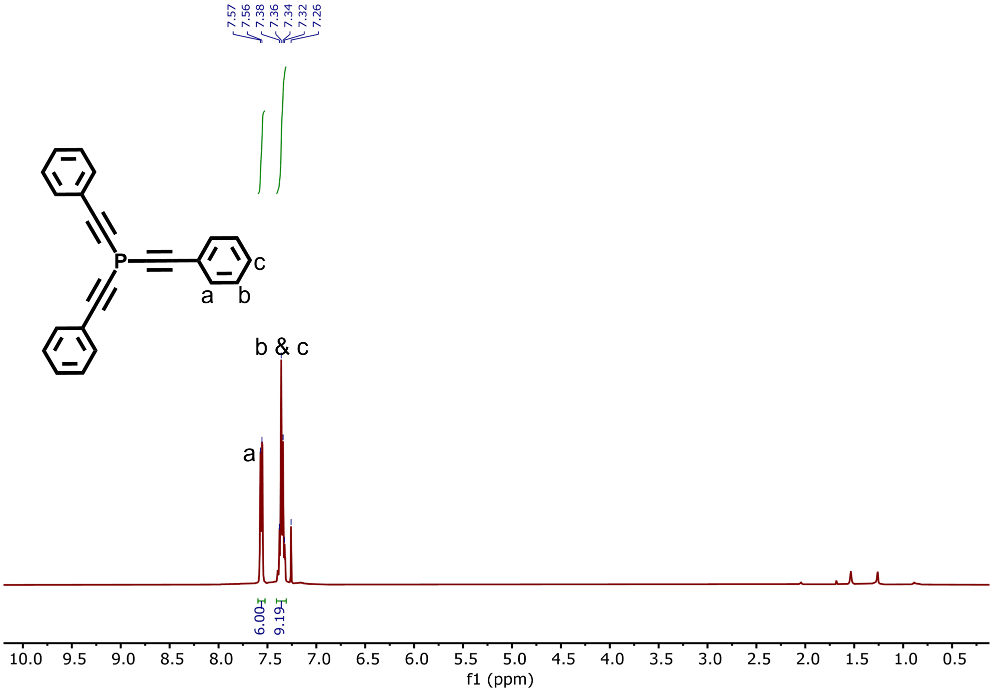


Figure S29: ^{1}H NMR (400 MHz, $CDCl_3$) of NS-trimer

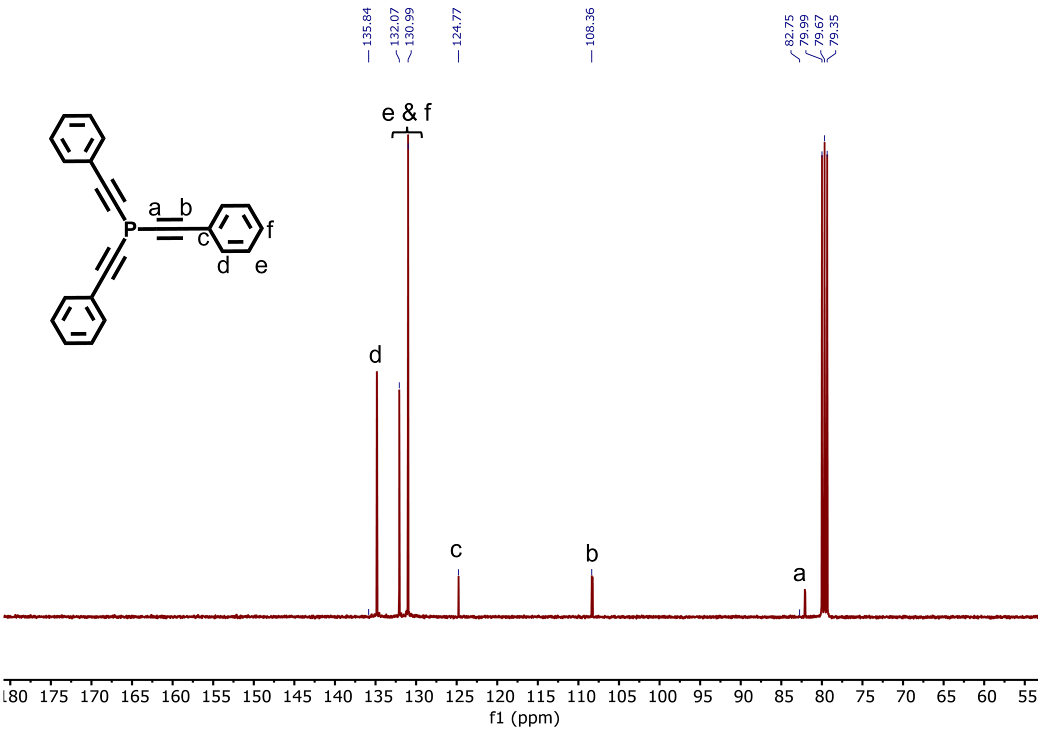


Figure S30: ^{13}C NMR (101 MHz, $CDCl_3$) of NS-trimer

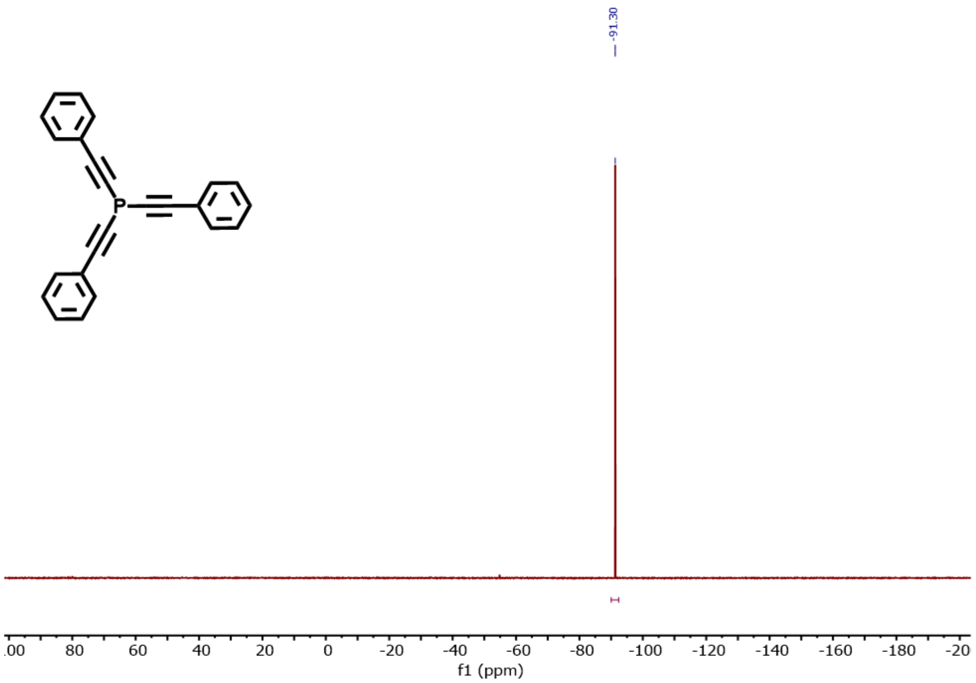


Figure S31: ^{31}P NMR (162 MHz, $CDCl_3$) of NS-trimer

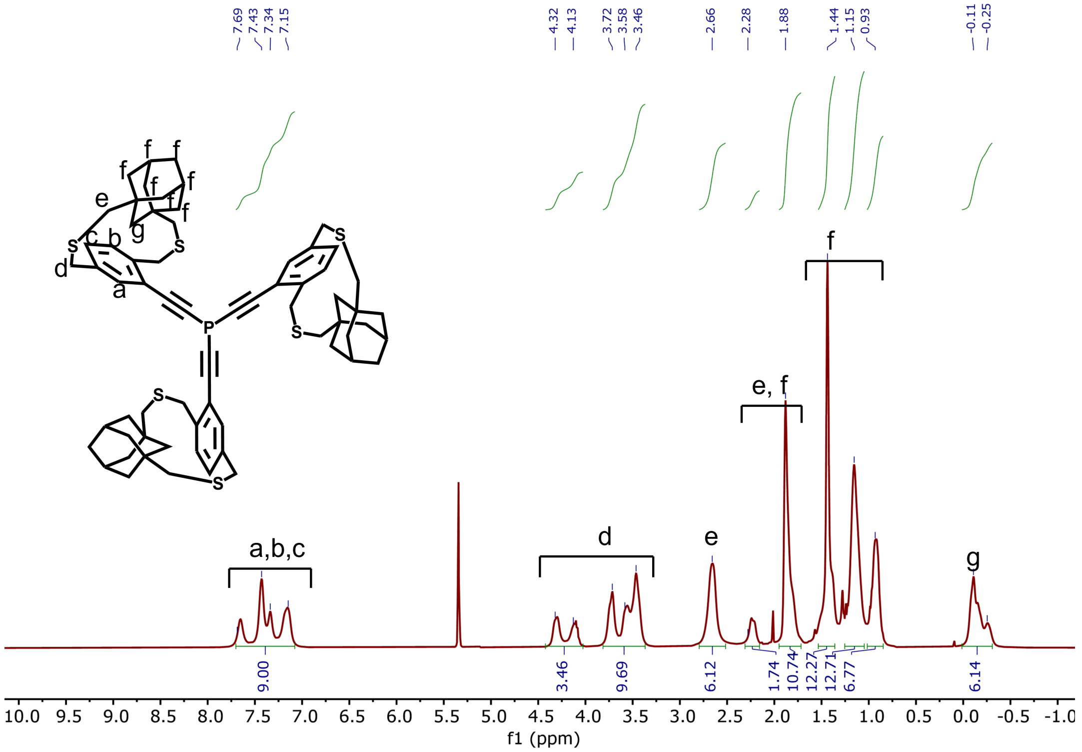


Figure S32: ^{1}H NMR (400 MHz, CD_2Cl_2) of S-trimer

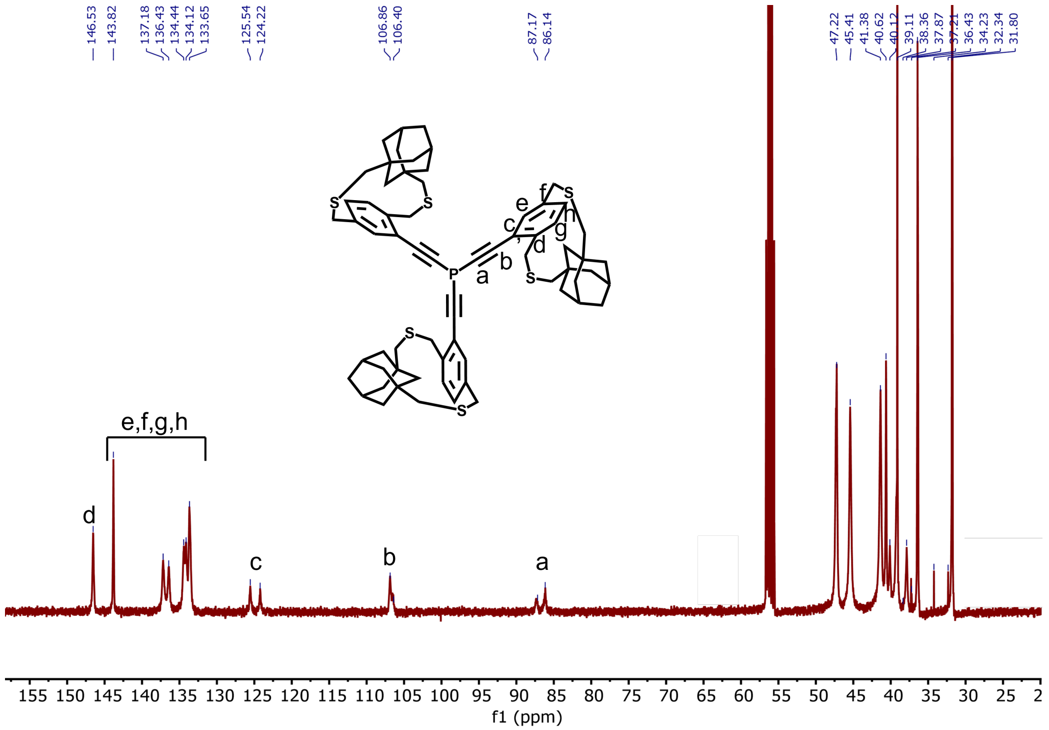


Figure S33: ^{13}C NMR (101 MHz, CD_2Cl_2) of S-trimer

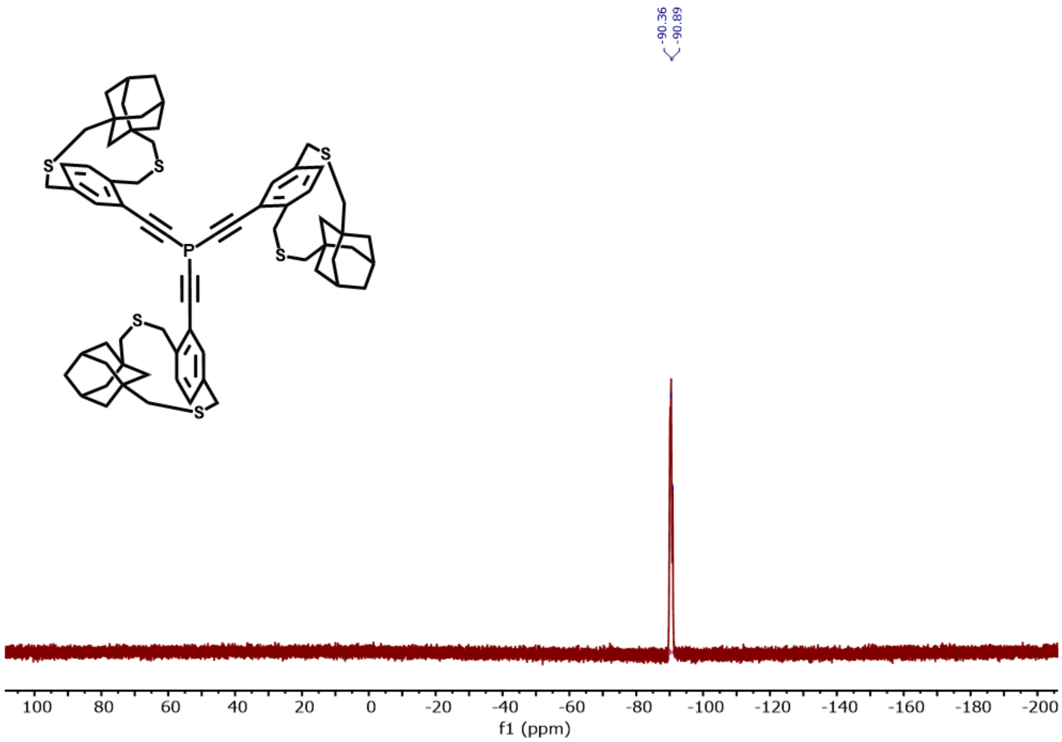


Figure S34: ^{31}P NMR (162 MHz, $CDCl_3$) of S-trimer

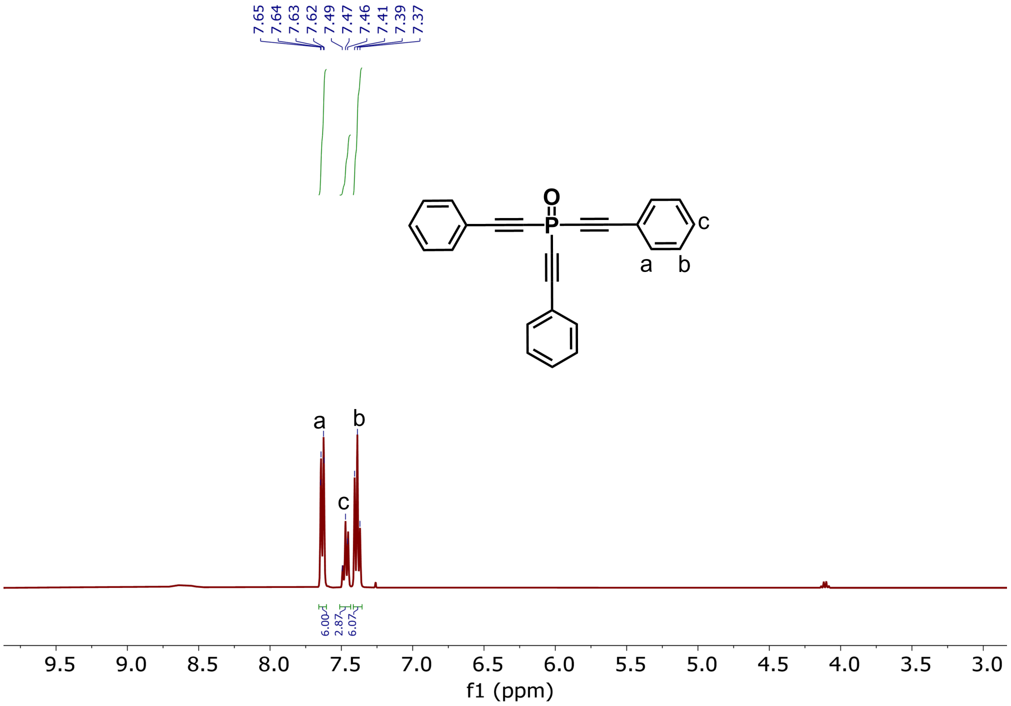


Figure S35: ^{1}H NMR (400 MHz, $CDCl_3$) of oxidized NS-trimer

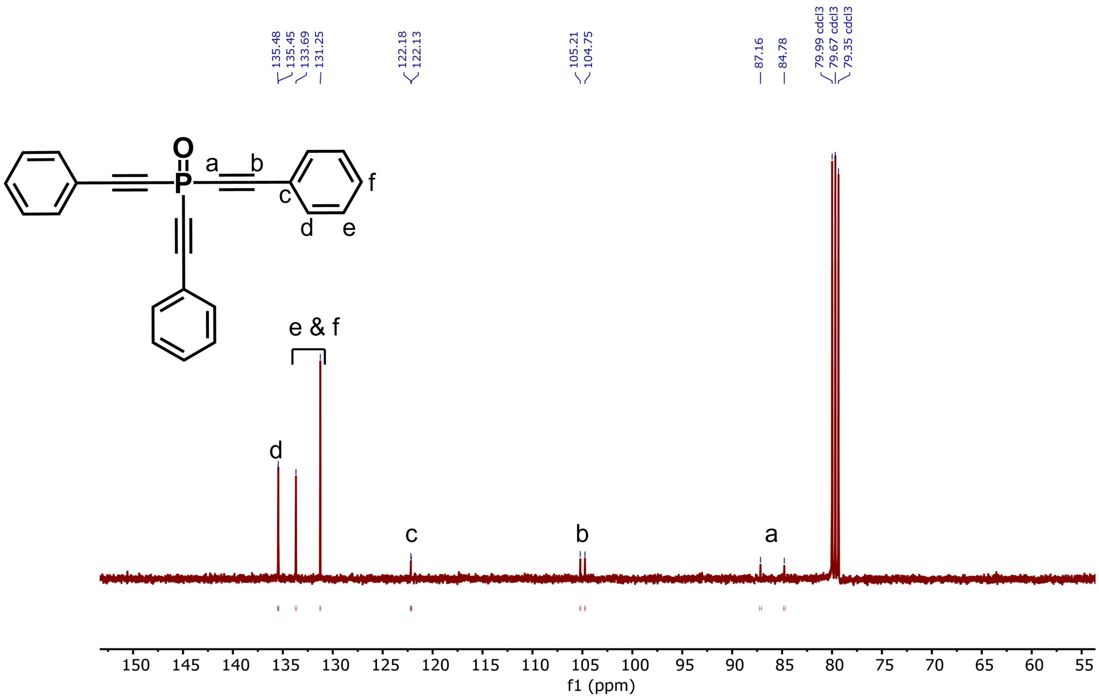


Figure S36: ^{13}C NMR (101 MHz, $CDCl_3$) of oxidized NS-trimer

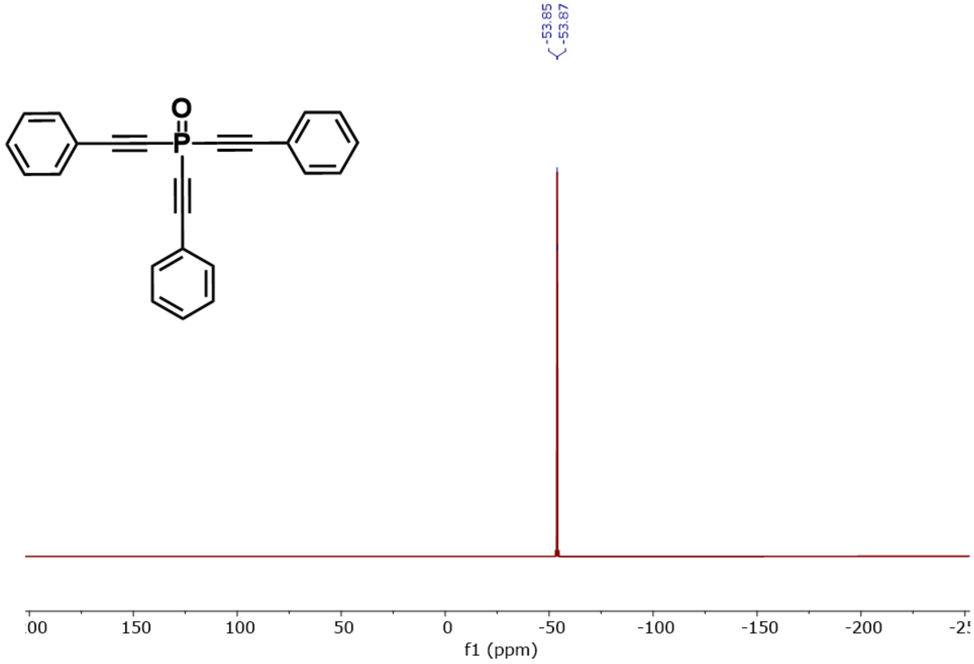


Figure S37: ^{31}P NMR (162 MHz, $CDCl_3$) of oxidized NS-trimer

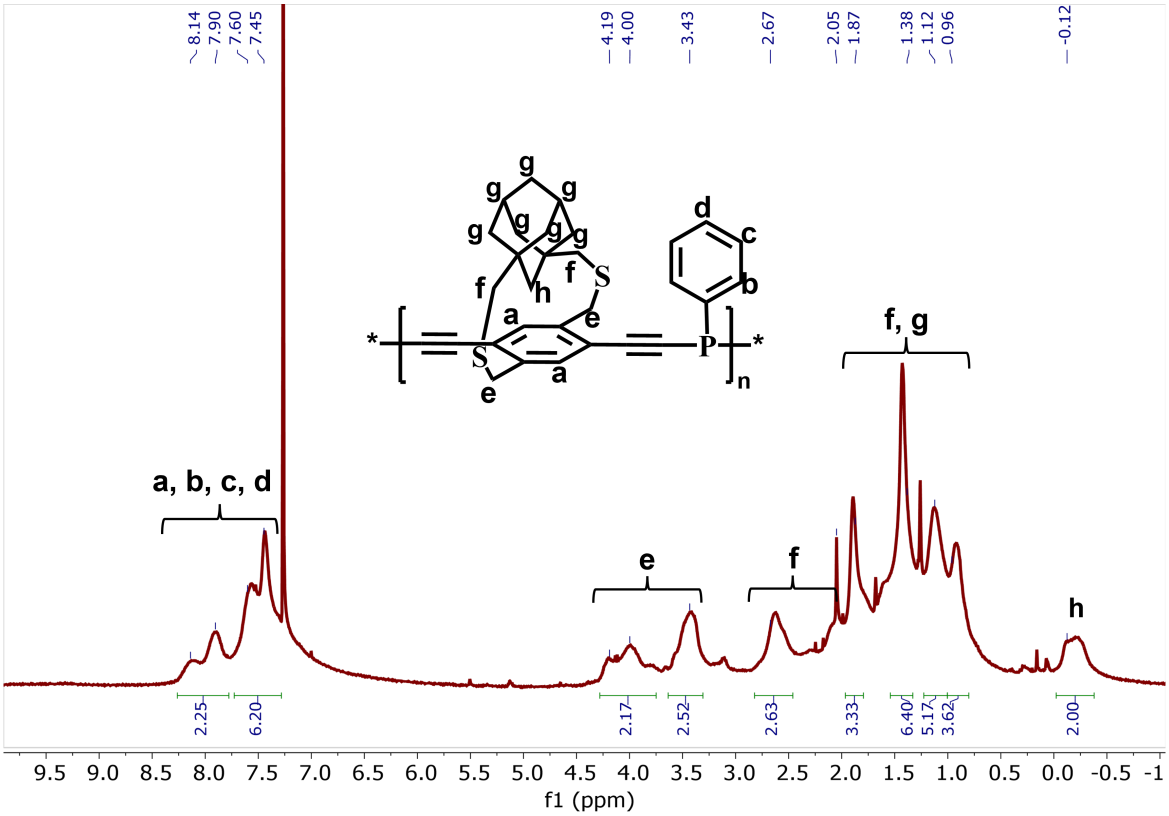


Figure S38: ^{1}H NMR (400 MHz, $CDCl_3$) of S-LP

14. References

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