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Constructing a self-assembling C_3-symmetric covalently linked (fused) donor-acceptor-type molecule containing hexaazatriphenylene core

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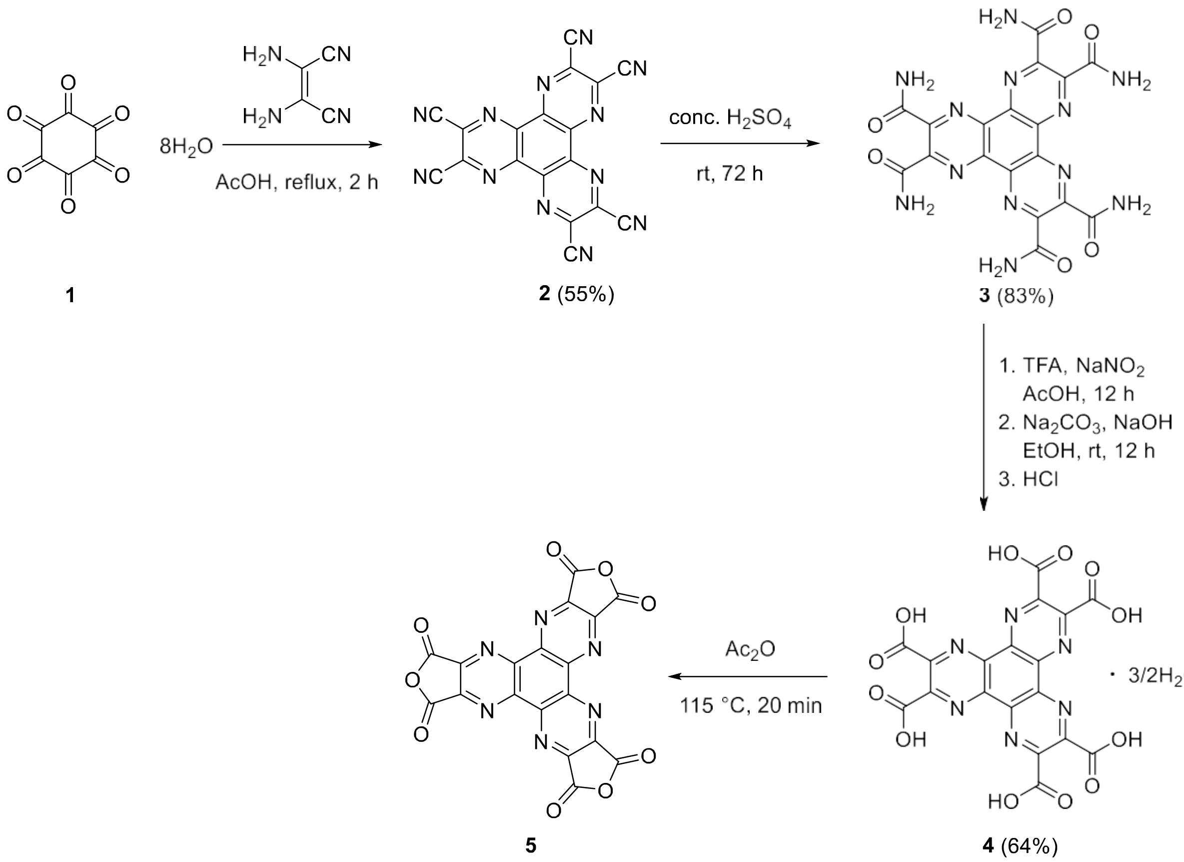
Experimental details

General methods: All the chemicals were reagent grade and used as purchased. Moisture-sensitive reactions were performed under an inert atmosphere of dry nitrogen with dried solvents. Reactions were monitored by thin-layer analysis (TLC) analysis using Merck 60 F_{254} aluminium-coated plates and the spots were visualized under ultraviolet (UV) light. Column chromatography was carried out on silica gel (60–120 mesh). Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument. NMR spectra were recorded on a Bruker Avance-III 400 spectrometer in $CDCl_3$ and DMSO-D_6. UV-Visible absorption spectra were recorded on Jasco V-630 spectrophotometer using quartz cuvette. The steady-state fluorescence spectra were recorded on Jasco FP 6300 spectrofluorometer using quartz cuvette. CV data were obtained with CH Instruments model of CHI 600C with three electrode (Pt disc/glassy carbon as the working electrode, platinum as the counter electrode, and nonaqueous Ag/$AgNO_3$ as the reference electrode) cells in anhydrous THF solution containing 50 mM tetra-n-butylammonium hexafluorophosphate at a scan rate of 100 mV/s under an N_2 atmosphere. Thermo-Gravimetric Analysis (TGA) of the polymer was done on Exstar SII TG/DTA 6300 using N_2 as an inert gas. Differential Scanning Calorimetry (DSC) of the polymer was performed with Mattler Toledo DSC822^e under N_2 atmosphere. Polarizing Optical Microscopy was performed on Leica DM 2500P with variable heat platform. DLS studies were performed on the Brookhaven Instrumentation Corporation made a particle size analyzer, model 90 plus. Elemental analysis was performed on Perkin Elmer C/H/N Analyser, 2400 series II.



Scheme S1 Synthesis of compound **5** (HAT-trisanhydride)

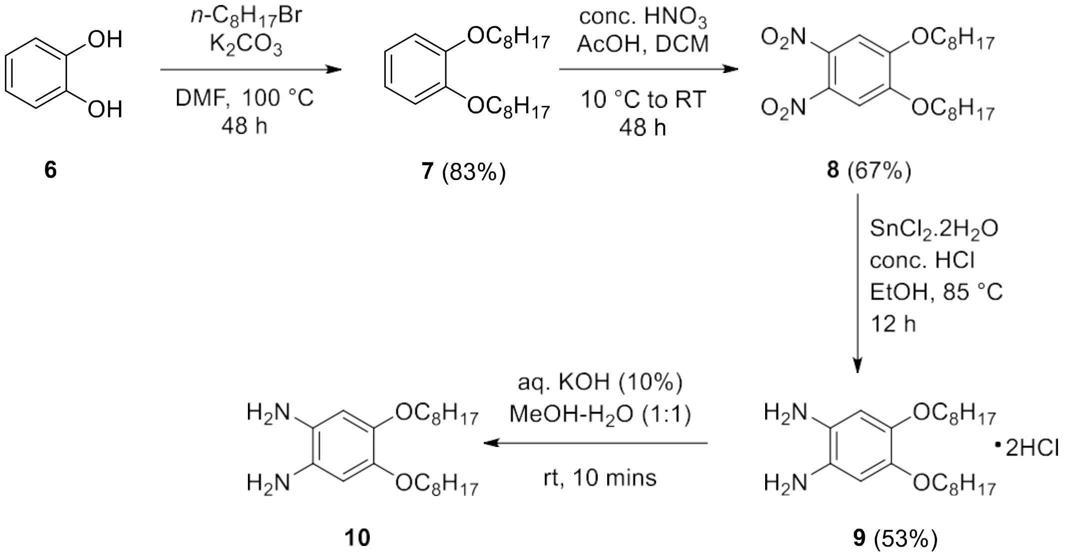
Compound **2, 3, 4** and **5** were synthesized according to the procedure reported in the literature[1].

Compound **2** (hexaazatriphenylenehexacarbonitrile): Yellow solid; ^{13}C NMR (DMSO-D$_6$, 100 MHz): 114.1, 135.3, 141.5.

Compound **3** (hexaazatriphenylenehexacarboxamide): Beige yellow solid; ^{13}C NMR (DMSO-D$_6$, 100 MHz): 141.0, 148.7, 166.3.

Compound **4** (hexaazatriphenylenehexacarboxylic acid): Bright yellow solid; ^{13}C NMR (DMSO-D$_6$, 100 MHz): 142.7, 148.0, 165.2.

Compound **5** (HAT-trisanhydride) was synthesized from its synthetic precursor, compound **4** (hexaazatriphenylenehexacarboxylic acid) by heating the suspension of later in acetic anhydride at 115-117 ^{o}C for 15-20 min. The yellow suspension turned into an orange-brown clear solution, after which heating was discontinued and the reaction mixture was allowed to cool at room temperature. The excess of acetic anhydride was removed under vacuum and the crude HAT-trisanhydride thus obtained was subjected to the condensation reaction with 4,5-diamino-1,2-dioctyloxybenzene.



Scheme S2 Synthesis of compound **10** (4,5-diamino-1,2-dioctyloxybenzene)

Compound **7**, **8**, **9** and **10** were synthesized according to the literature procedure[2].

Compound **7** (1,2-dioctyloxybenzene): Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): 6.90 (s, 2H), 3.99-4.02 (t, J = 6.8 Hz, 2H), 1.80-1.87 (m, 2H), 1.44-1.52 (m, 2H), 1.30-1.38 (m, 8H) 0.88-0.92 (t, J = 6.8 Hz, 3H). ESI-MS 334.03 [M+].

Compound **8** (1,2-dinitro-4,5-dioctyloxybenzene): Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.31 (s, 1H), 4.10-4.13 (t, J = 6.4 Hz, 2H), 1.85-1.92 (m, 2H), 1.46-1.54 (m, 2H), 1.33-1.40 (m, 8H), 0.91-0.94 (t, J = 7.2 Hz, 3H). ESI-MS 424.51 [M+].

Compound **9** (1,2-diamino-4,5-dioctyloxybenzene).2HCl: Off white solid; ^{1}H NMR ($CDCl_3$+CD_3OD 1:1, 400 MHz): 6.71 (s, 1H), 3.87-3.95 (m, 2H), 1.72-1.77 (m, 2H), 1.20-1.42 (m, 10H), 0.83 (br s, 3H).

Note: The hydrochloride salt being unstable was stored as suspension in diethylether and was neutralized to compound **10** just prior to the condensation reaction with HAT-trisanhydride.

For the characterization purpose, *N,N'*-(4,5-dioctyloxy-1,2-phenylene)bistrifluoroacetamide was synthesized from compound **10** using trifluoroacetic anhydride and DMAP.

N,N'-(4,5-dioctyloxy-1,2-phenylene)bistrifluoroacetamide; White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): 8.47 (s, 1H), 6.91 (s, 1H), 3.97-4.00 (m, 2H), 1.80-1.87 (m, 2H), 1.44-1.50 (m, 2H), 1.34-1.38 (m, 8H), 0.91-0.94 (m, 3H).

Compound **10** (1,2-diamino-4,5-dioctyloxybenzene) was synthesized as follow. Compound **9** was dissolved in methanol:chloroform (1:1) and to this solution was added 10% aqueous KOH solution drop-wise. After stirring at room temperature for 15 min, the bulk was extracted multiple times with aliquots of dichloromethane. A combined organic layer was washed with brine and finally with water to remove traces of alkali and evaporated to dryness under vacuum to yield compound **10** as dark yellow to orange solids. The crude product being unstable was forwarded to the next step without any purification.

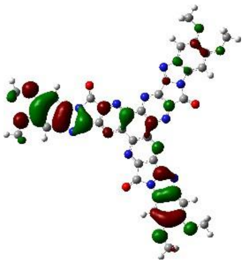
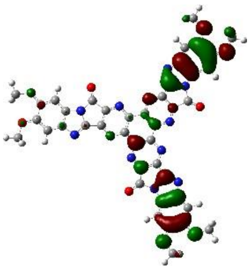
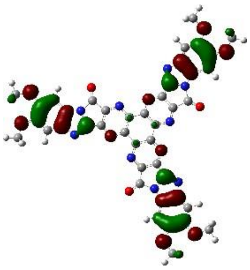
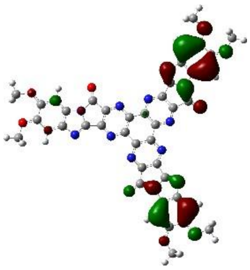
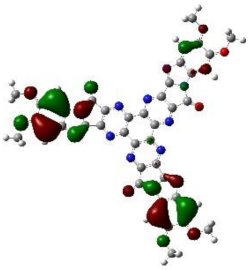
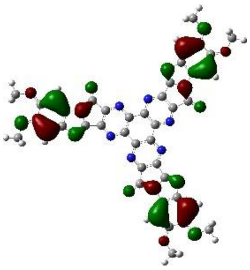
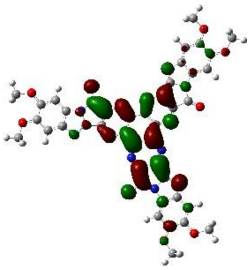
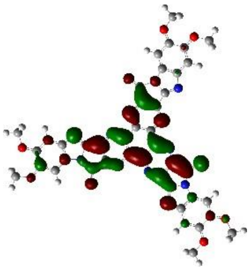
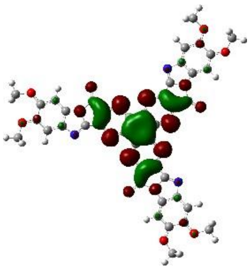
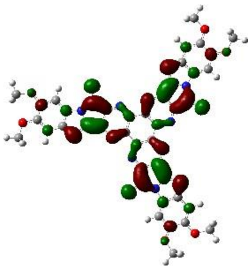
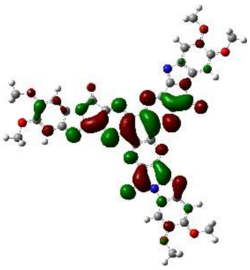
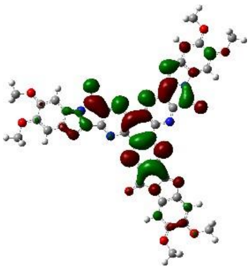
		
HOMO (-5.5827 eV)	**HOMO-1 (-5.5830 eV)**	**HOMO-2 (-5.6592 eV)**
		
HOMO-3 (-6.3999 eV)	**HOMO-4 (-6.4004 eV)**	**HOMO-5 (-6.4072 eV)**
		
LUMO (-3.0352 eV)	**LUMO+1 (-3.0349 eV)**	**LUMO+2 (-2.7078 eV)**
		
LUMO+3 (-2.3007 eV)	**LUMO+4 (-1.8675 eV)**	**LUMO+5 (-1.8670 eV)**

Figure S1 DFT (B3LYP6-31G(d)) calculated energies and topologies of frontier orbitals.[3]

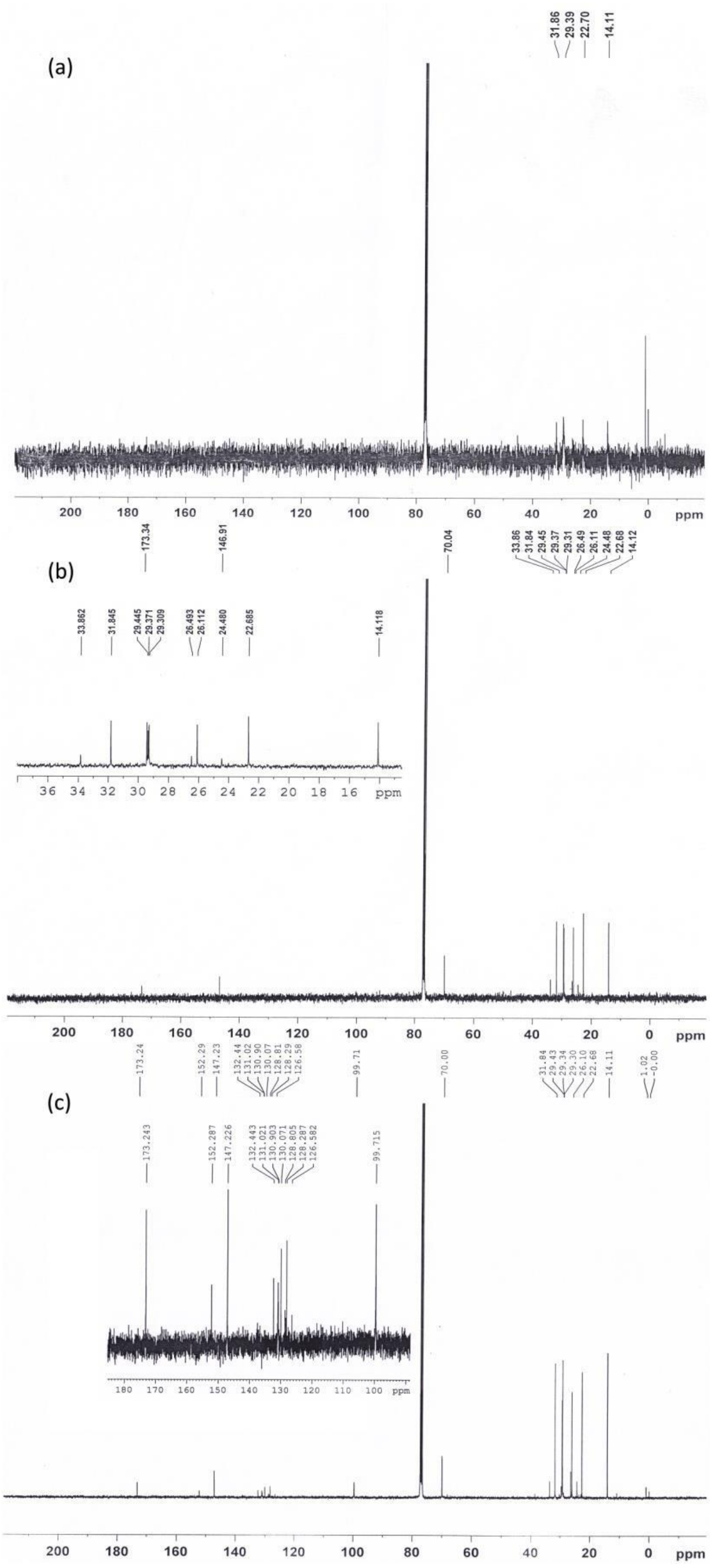


Figure S2 ^{13}C NMR of HAT-IPN ($CDCl_3$) recorded at different delay time (D1) and scan rate (NS), exhibiting one-dimensional π-stacking; (a) D1 2 sec, NS 1024 (b) D1 5 sec, NS 1024 and (c) D1 5 sec, NS 6144.

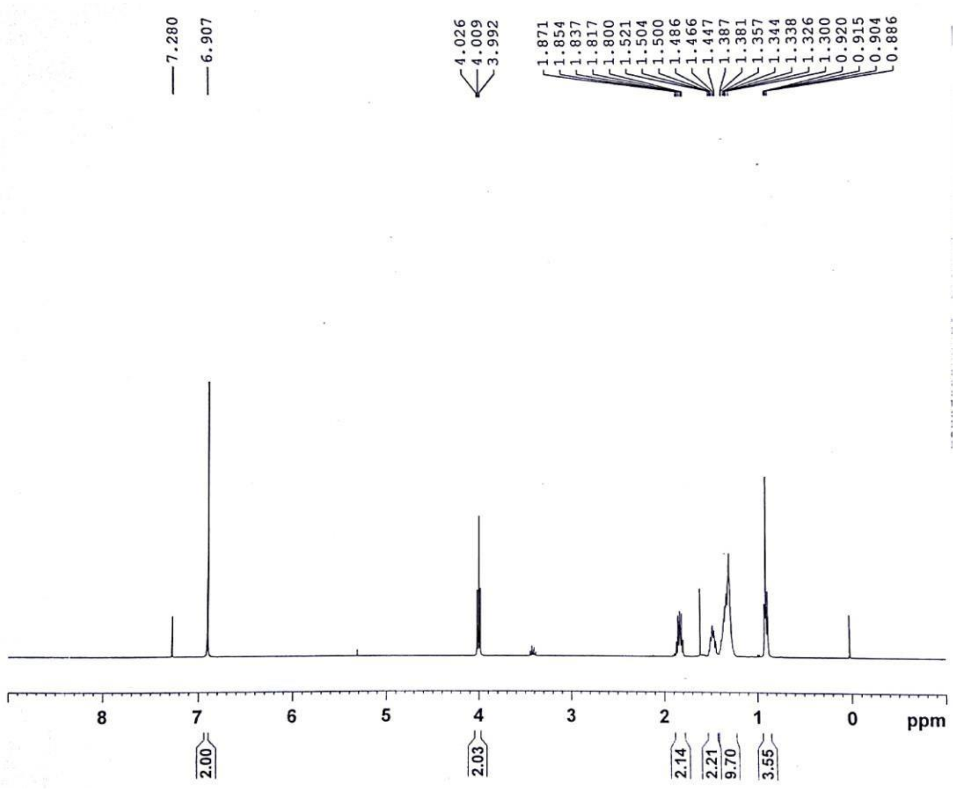


Figure S3 ^{1}H NMR (CDCl$_3$) spectra of compound **7**

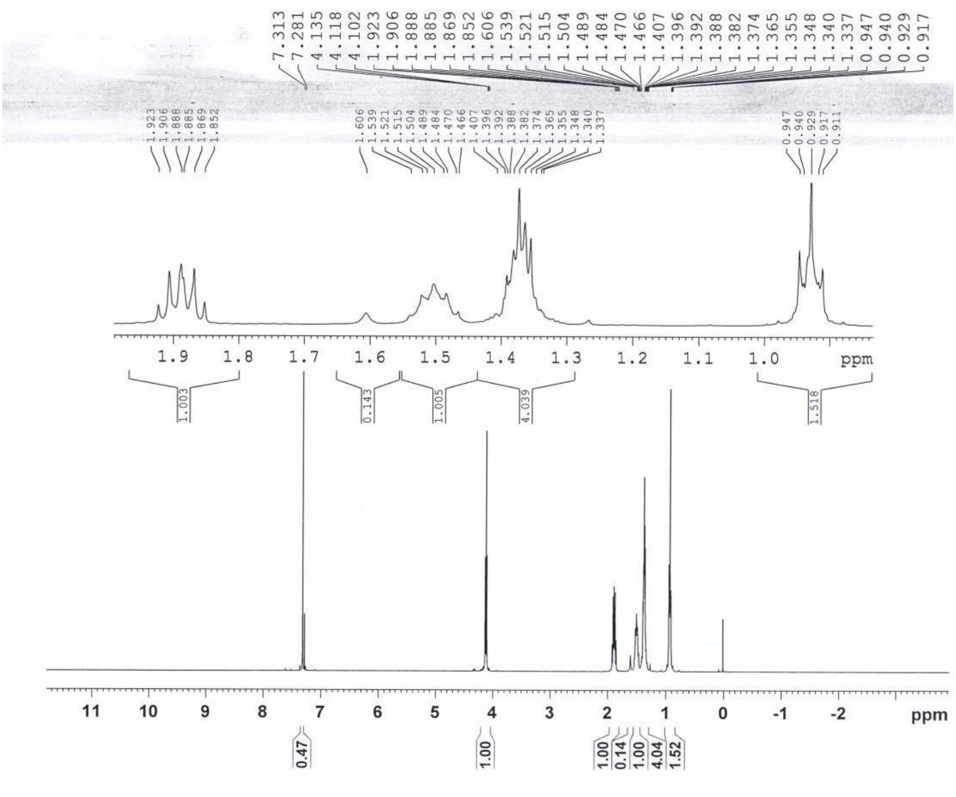


Figure S4 ^{1}H NMR (CDCl$_3$) spectra of compound **8**

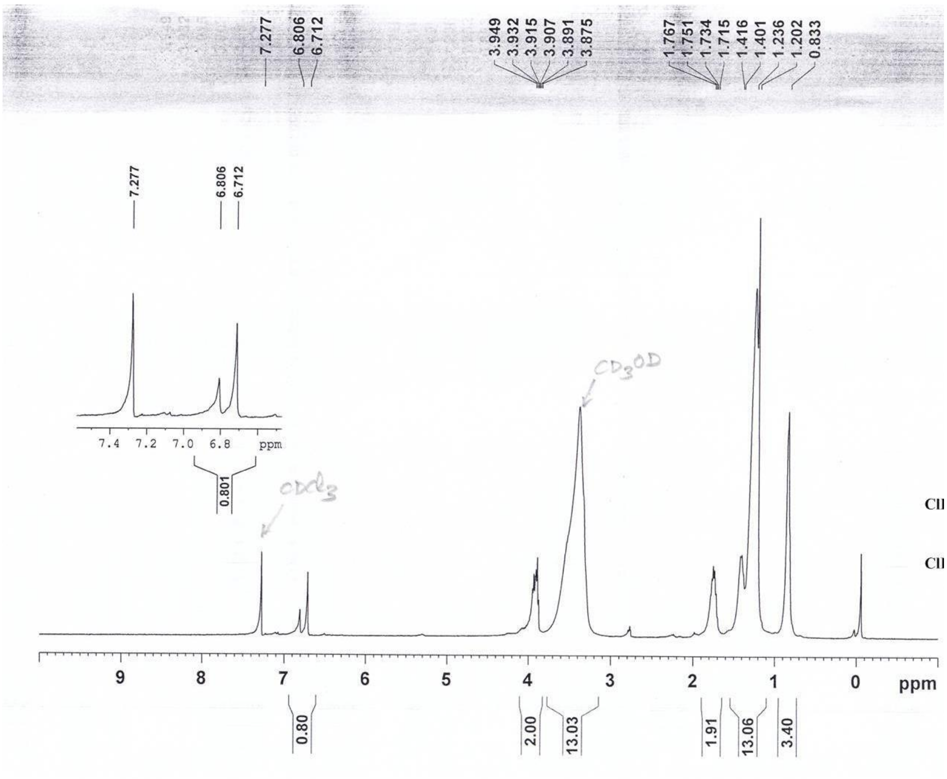


Figure S5 ^{1}H NMR (1:1 $CDCl_3$:CD_3OD) spectra of compound **9**

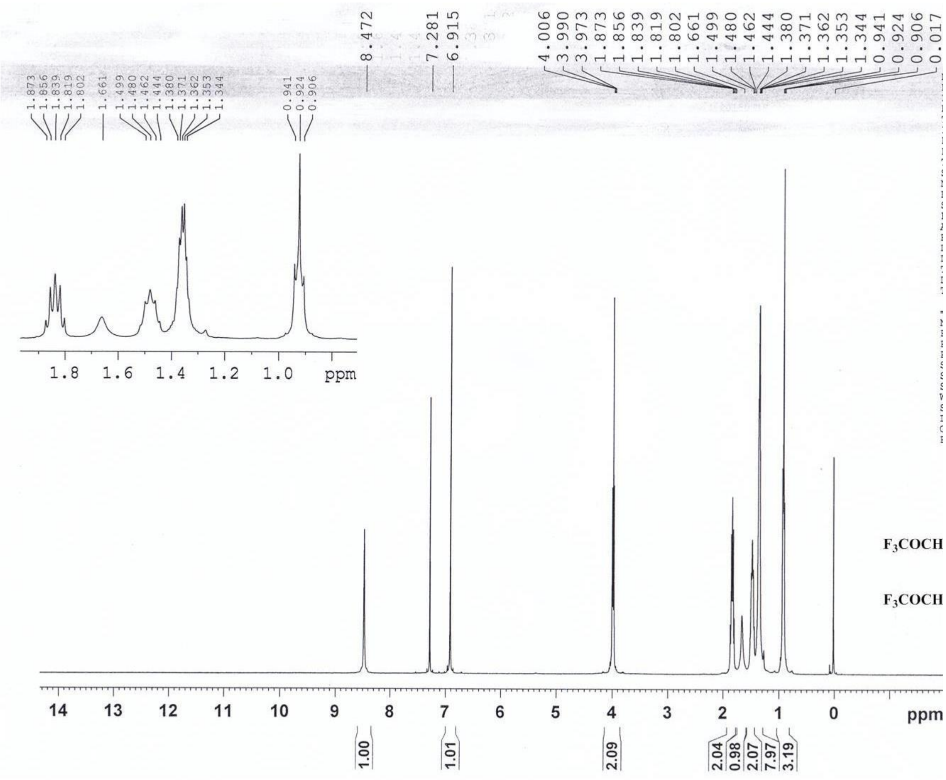


Figure S6 ^{1}H NMR ($CDCl_3$) spectra of *N,N'*-(4,5-dioctyloxy-1,2 phenylene) bistrifluoroacetamide

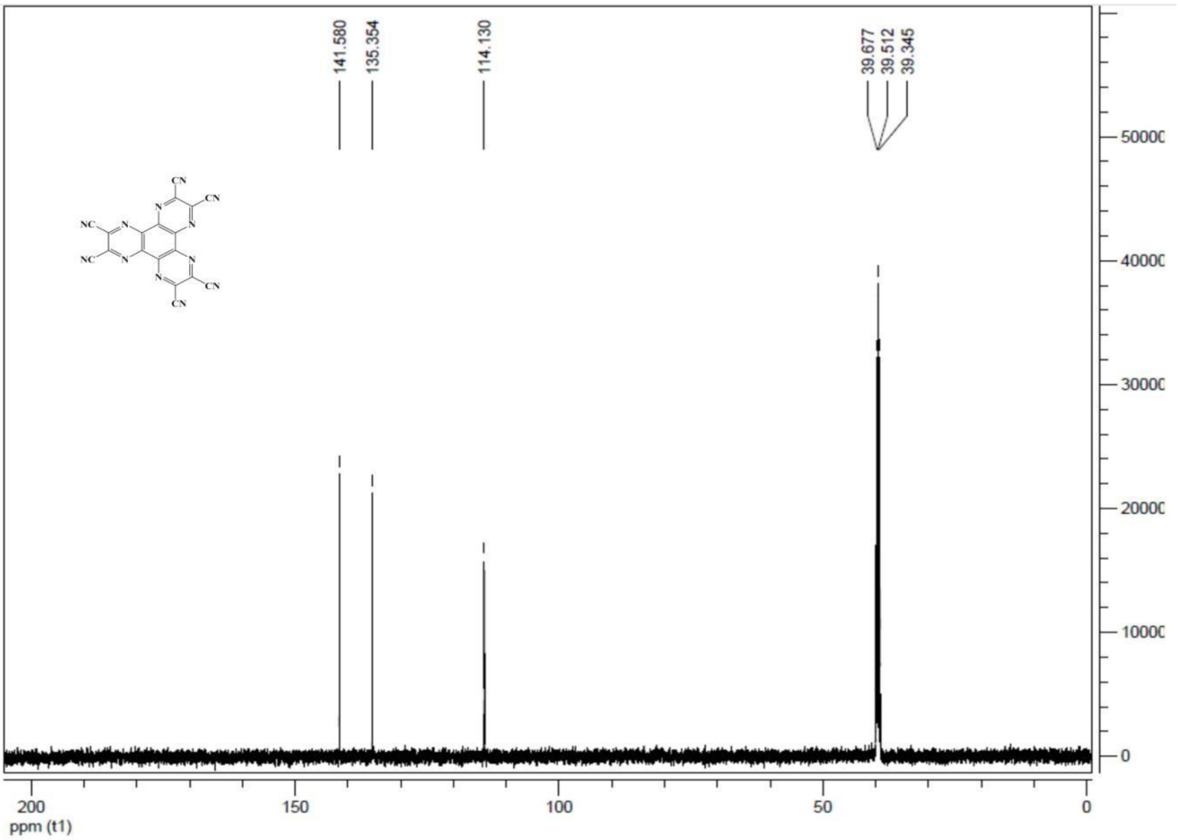


Figure S7 ^{13}C NMR (DMSO-D$_6$) spectra of compound **2**

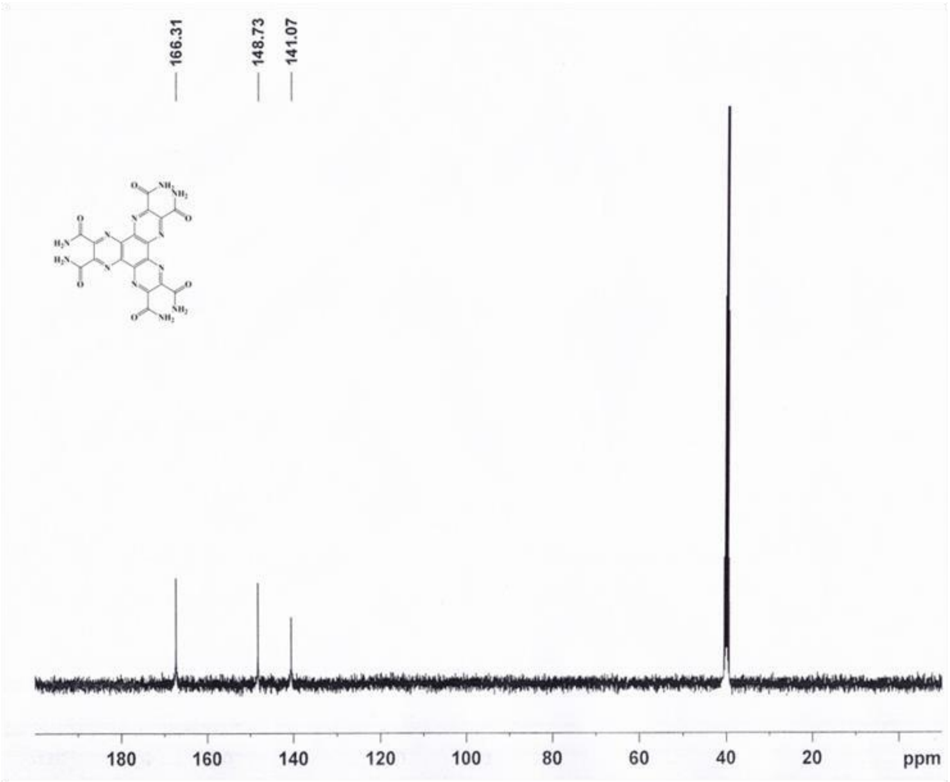


Figure S8 ^{13}C NMR (DMSO-D$_6$) spectra of compound **3**

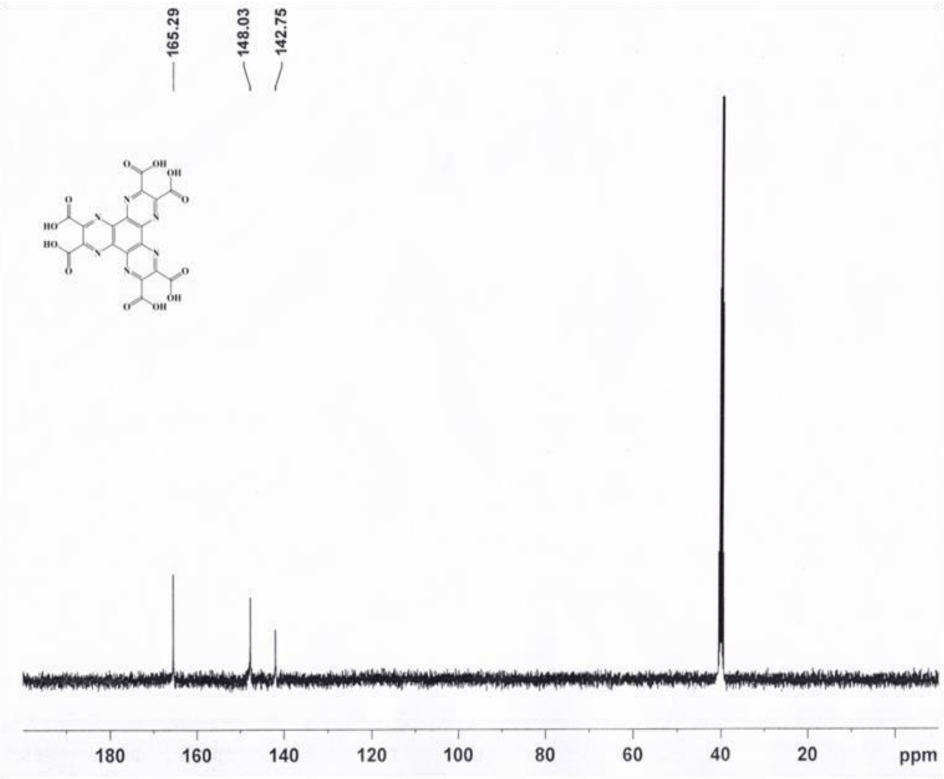


Figure S9 ^{13}C NMR (DMSO-D$_6$) spectra of compound **4**

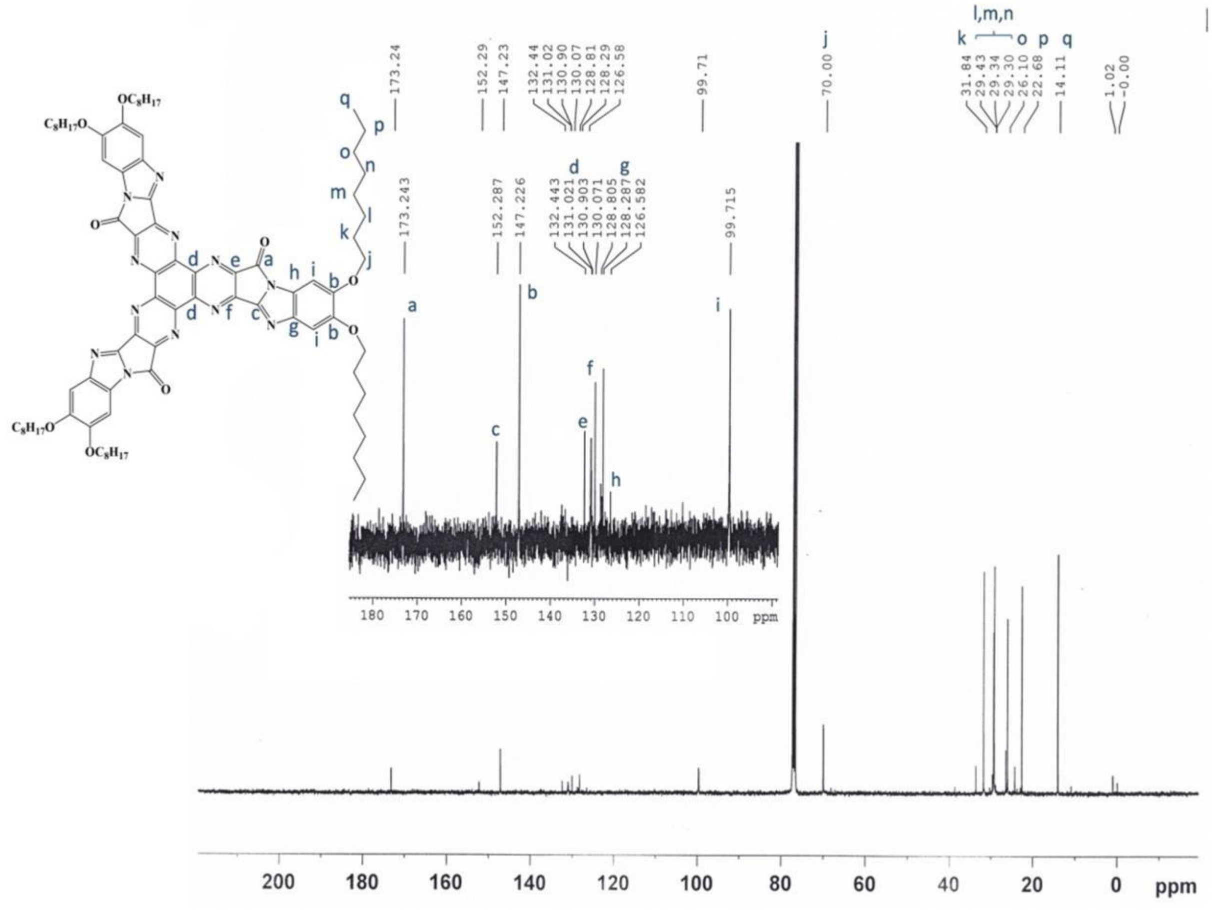
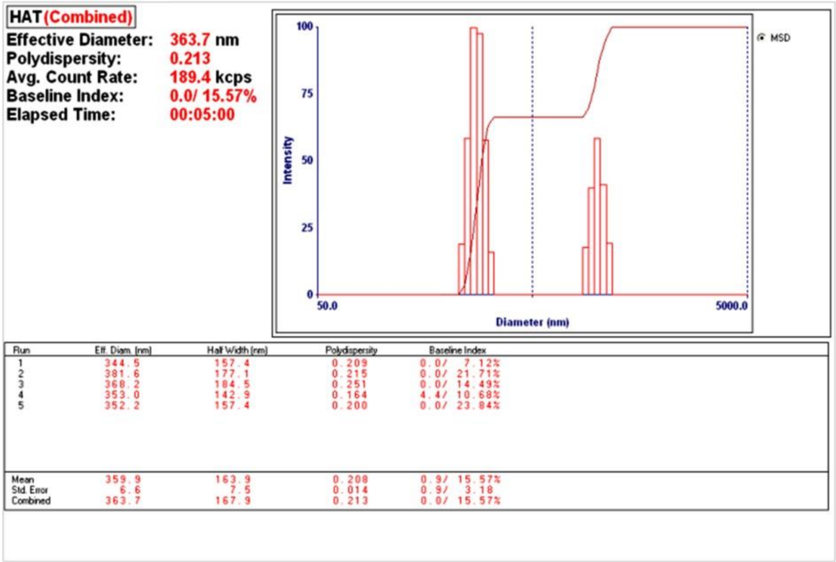


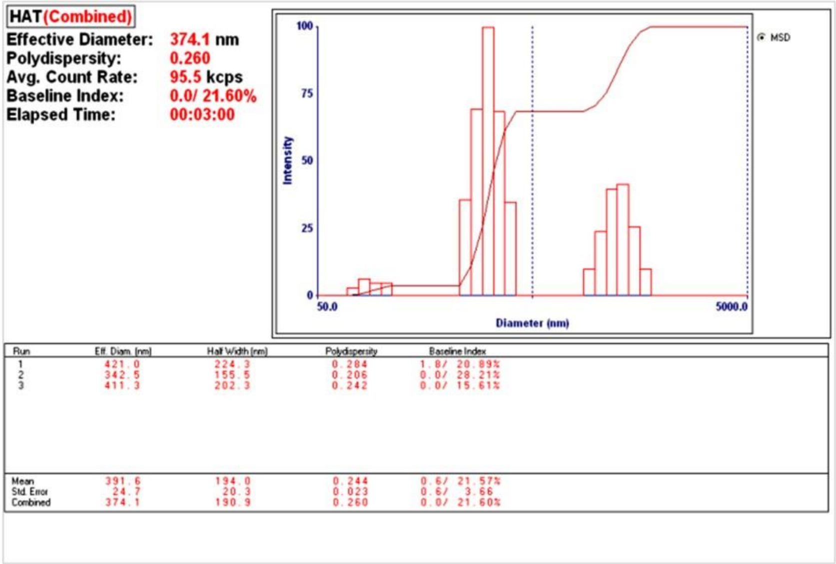
Figure S10 ^{13}C NMR spectrum of HAT-IPN in CDCl$_3$



HAT(Combined)

Effective Diameter: 363.7 nm
Polydispersity: 0.213
Avg. Count Rate: 189.4 kcps
Baseline Index: 0.0/ 15.57%
Elapsed Time: 00:05:00

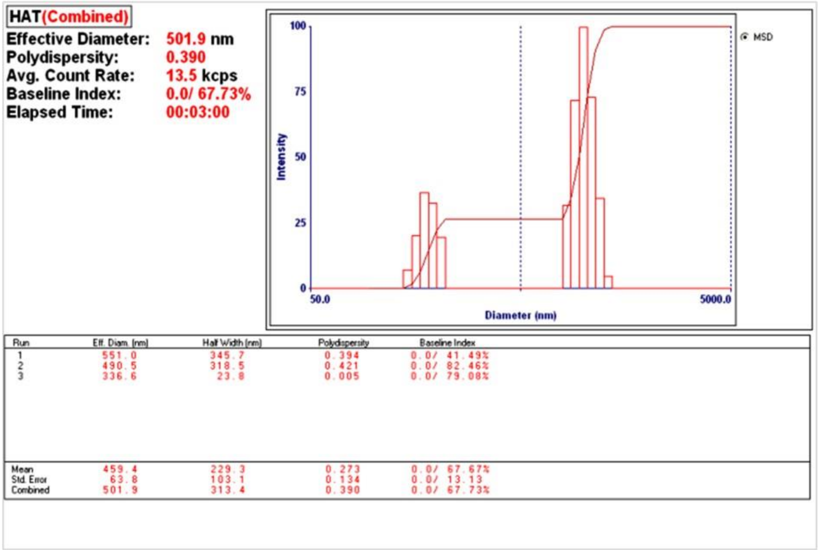
Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	344.5	157.4	0.209	0.0/ 7.12%
2	381.6	177.1	0.215	0.0/ 21.71%
3	368.2	184.5	0.251	0.0/ 14.49%
4	353.0	142.9	0.164	4.4/ 10.68%
5	352.2	157.4	0.200	0.0/ 23.84%
Mean	359.9	163.9	0.208	0.9/ 15.57%
Std. Error	6.6	7.5	0.014	0.9/ 3.18
Combined	363.7	167.9	0.213	0.0/ 15.57%



HAT(Combined)

Effective Diameter: 374.1 nm
Polydispersity: 0.260
Avg. Count Rate: 95.5 kcps
Baseline Index: 0.0/ 21.60%
Elapsed Time: 00:03:00

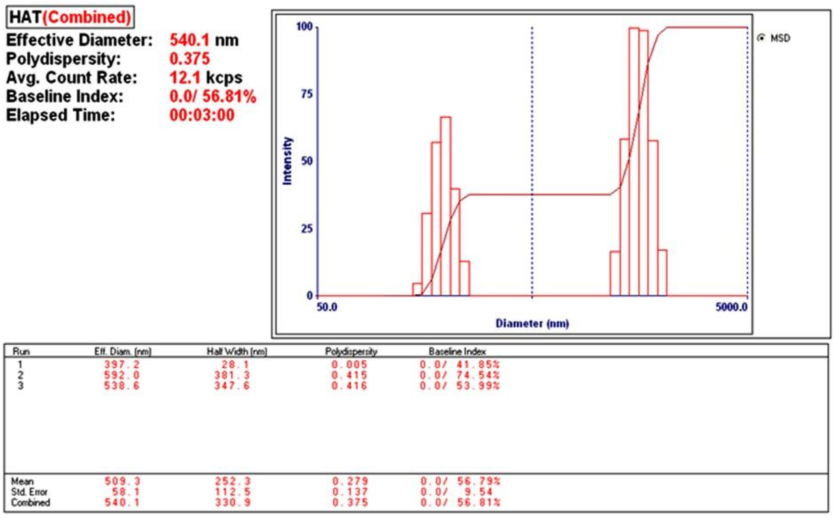
Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	421.0	224.3	0.284	1.8/ 20.89%
2	342.5	155.5	0.206	0.0/ 28.21%
3	411.3	202.3	0.242	0.0/ 15.61%
Mean	391.6	194.0	0.244	0.6/ 21.57%
Std. Error	24.7	20.3	0.023	0.6/ 3.66
Combined	374.1	190.9	0.260	0.0/ 21.60%



HAT(Combined)

Effective Diameter: 501.9 nm
Polydispersity: 0.390
Avg. Count Rate: 13.5 kcps
Baseline Index: 0.0/ 67.73%
Elapsed Time: 00:03:00

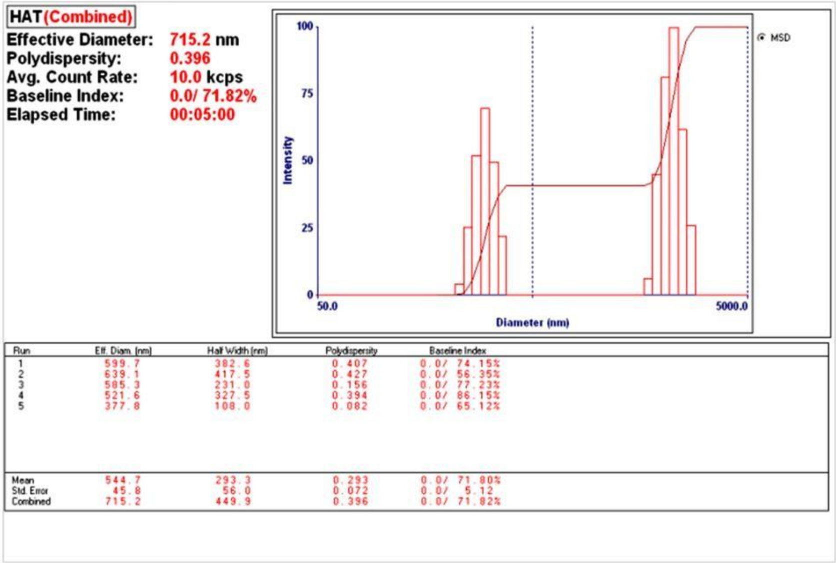
Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	551.0	345.7	0.394	0.0/ 41.49%
2	490.5	318.5	0.421	0.0/ 82.46%
3	336.6	23.8	0.005	0.0/ 79.08%
Mean	459.4	229.3	0.273	0.0/ 67.67%
Std. Error	63.8	103.1	0.134	0.0/ 13.13
Combined	501.9	313.4	0.390	0.0/ 67.73%



HAT(Combined)

Effective Diameter: 540.1 nm
Polydispersity: 0.375
Avg. Count Rate: 12.1 kcps
Baseline Index: 0.0/ 56.81%
Elapsed Time: 00:03:00

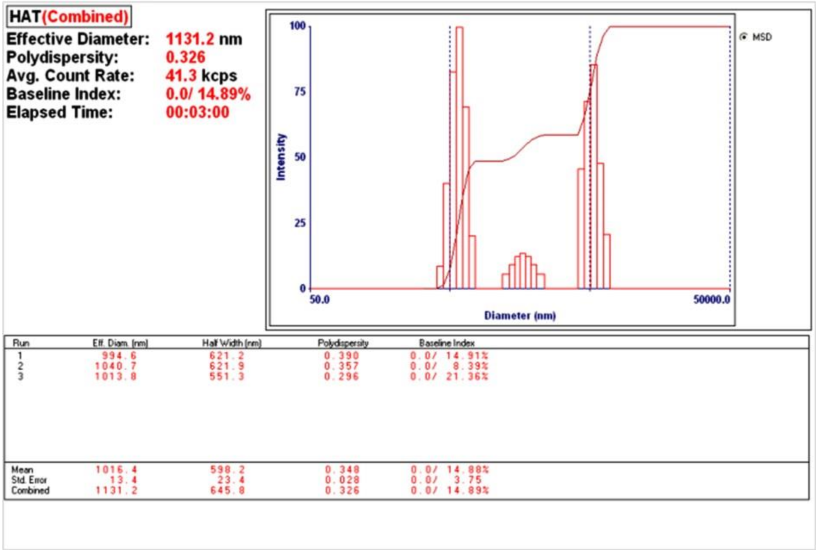
Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	397.2	28.1	0.005	0.0/ 41.85%
2	592.0	381.3	0.415	0.0/ 74.54%
3	538.6	347.6	0.416	0.0/ 53.99%
Mean	509.3	252.3	0.279	0.0/ 56.79%
Std. Error	58.1	112.5	0.137	0.0/ 9.54
Combined	540.1	330.9	0.375	0.0/ 56.81%



HAT(Combined)

Effective Diameter: 715.2 nm
Polydispersity: 0.396
Avg. Count Rate: 10.0 kcps
Baseline Index: 0.0/ 71.82%
Elapsed Time: 00:05:00

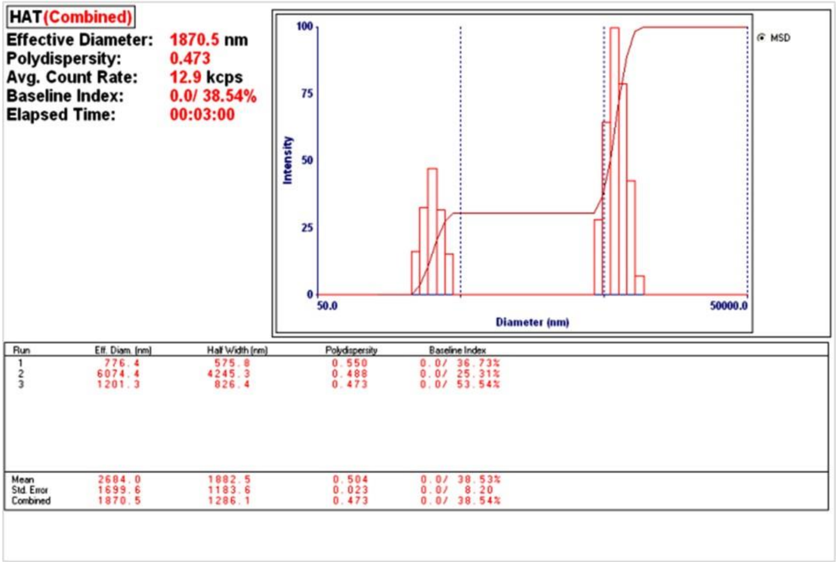
Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	599.7	382.6	0.407	0.0/ 74.15%
2	639.1	417.5	0.427	0.0/ 56.35%
3	585.3	231.0	0.156	0.0/ 77.23%
4	521.6	327.5	0.394	0.0/ 86.15%
5	377.8	108.0	0.082	0.0/ 65.12%
Mean	544.7	293.3	0.293	0.0/ 71.80%
Std. Error	45.8	56.0	0.072	0.0/ 5.12
Combined	715.2	449.9	0.396	0.0/ 71.82%



HAT(Combined)

Effective Diameter: 1131.2 nm
Polydispersity: 0.326
Avg. Count Rate: 41.3 kcps
Baseline Index: 0.0/ 14.89%
Elapsed Time: 00:03:00

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	994.6	621.2	0.390	0.0/ 14.91%
2	1040.7	621.9	0.357	0.0/ 8.39%
3	1013.8	551.3	0.296	0.0/ 21.36%
Mean	1016.4	598.2	0.348	0.0/ 14.88%
Std. Error	13.4	23.4	0.028	0.0/ 3.75
Combined	1131.2	645.8	0.326	0.0/ 14.89%

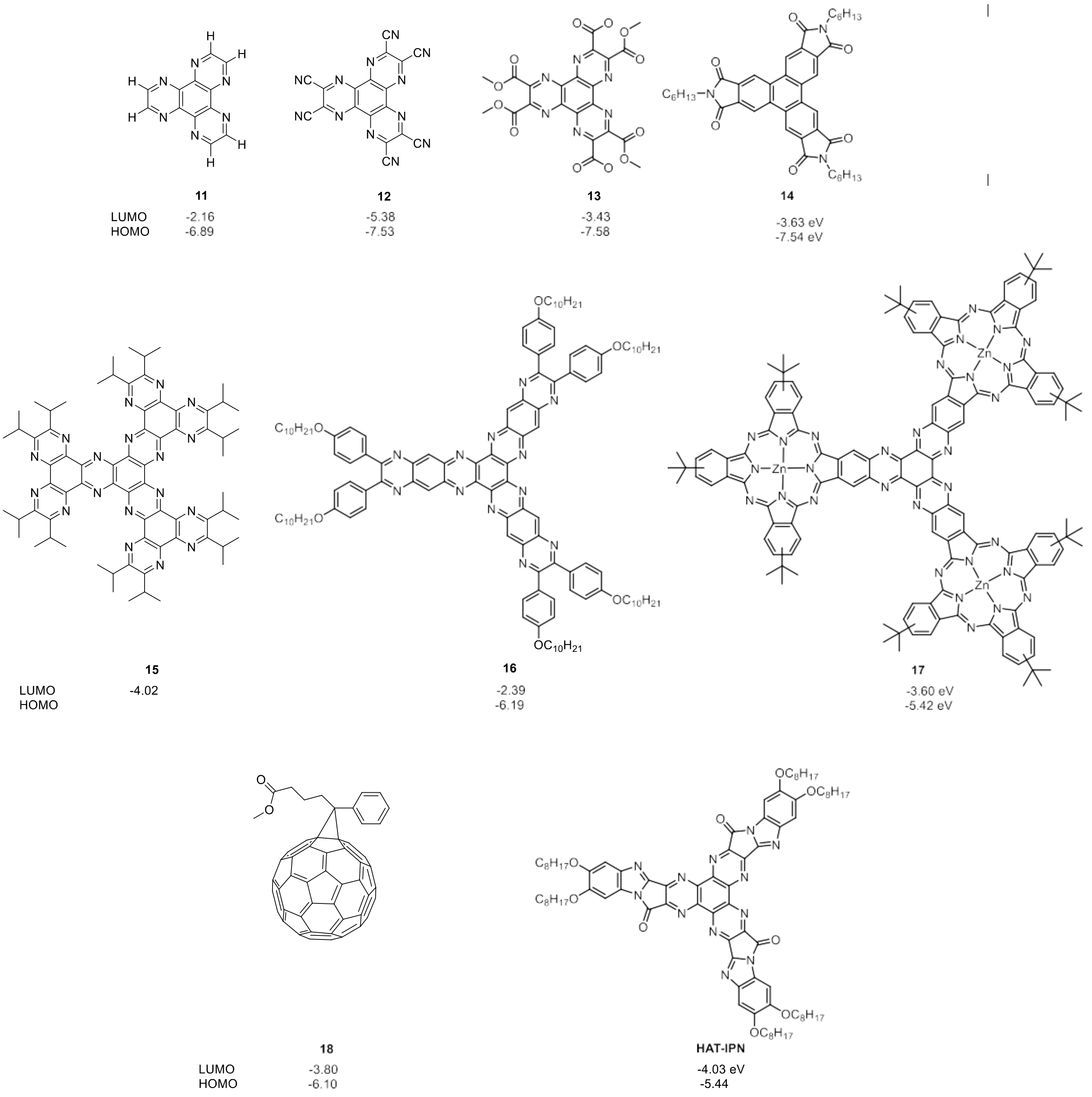


HAT(Combined)

Effective Diameter: 1870.5 nm
Polydispersity: 0.473
Avg. Count Rate: 12.9 kcps
Baseline Index: 0.0/ 38.54%
Elapsed Time: 00:03:00

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	776.4	575.8	0.550	0.0/ 36.73%
2	6074.4	4245.3	0.488	0.0/ 25.31%
3	1201.3	826.4	0.473	0.0/ 53.54%
Mean	2684.0	1882.5	0.504	0.0/ 38.53%
Std. Error	1699.6	1183.6	0.023	0.0/ 8.20
Combined	1870.5	1286.1	0.473	0.0/ 38.54%

Figure S11 DLS data of HAT-IPN solution in methanol showing increase in size of aggregates up on dilution.



	11	12	13	14
LUMO	-2.16	-5.38	-3.43	-3.63 eV
HOMO	-6.89	-7.53	-7.58	-7.54 eV

	15	16	17
LUMO	-4.02	-2.39	-3.60 eV
HOMO		-6.19	-5.42 eV

	18	HAT-IPN
LUMO	-3.80	-4.03 eV
HOMO	-6.10	-5.44

Figure S12 Comparison of HOMO and LUMO energy level of HAT-IPN with that of some reported HAT-derivatives; **11**[4], **12**[5], **13**[4], **14**[4], **15**[6], **16**[7], **17**[8] and **18**[6]

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