Supporting Information

A Twist in the Non-Slanted H-mers to Control π-Conjugation in 2-Dimensions and Optical Properties

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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 the synthesis were purchased from Fisher, Acros, Alfa Aesar and Sigma Aldrich. 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, $KMnO_4$ stain and yellow dip stain. Silica gel of particle size 230-400 mesh was used for flash chromatography. Unless otherwise stated, all starting materials and reagents were used without further purification. Centrifuge was conducted using Eppendorf 5415r Centrifuge.

^1H 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, $(CD_3)_2SO$: 2.50, (7.96, 2.94, 2.78 DMF in $(CD_3)_2SO$), 8.02 ($CHCl_3$ in $(CD_3)_2SO$) and MeOH-D4: 3.31, 2.03 (acetonitrile in MeOH-D4) for ^1H. 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), ddd(doublet of doublets of doublets), dq(doublet of quartets), m(multiplet), and q(quartet). High resolution TOF-EI+ and High resolution MALDI mass spectra were recorded in the Mass Spectrometry laboratory, School of Chemical Sciences at University of Illinois Urbana-Champaign. UV-vis absorption spectra were recorded on Agilent Technologies Cary Series 5000 UV-vis-NIR Spectrophotometer. Fluorescence absorption spectra were recorded on Horiba Scientific Fluoromax-4 Spectrophotometer. The column chromatography of UV active compounds was performed on Biotage Isolera one 3.0.

The fluorescence quenching studies of H-mer 3 were performed in the solution state by adding different concentrations of quencher (TCNE) in v/v to the 40 μM solution of H-mer solution in chlorobenzene and emission spectra were recorded. PXRD data was collected on a

Rigaku R-Axis Rapid-S diffractometer equipped with a curved image plate detector and a three-circle goniometer. Data was collected using a Cu k-alpha (λ = 1.5418 Å) fine-focus sealed tube source with a graphite monochromator. S2 Samples were packed into a 0.3mm kapton film capillary which was mounted onto the goniometer head.
Fluorescence lifetime decay measurements were conducted following the reported protocols.[1] The fluorescence lifetime decay measurements were performed using a Q-25 Lifetime add-on to the PTi Photon Technology International Fluorometer QuantaMaster 40. The samples were excited with a PTi-L375 Class 1 LED source (375 nm) and observed at their respective emission maxima. The instrument response function (IRF) was recorded with respect to a dilute LUDOX (Sigma-Aldrich) AS-40 colloidal silica suspension in water. Fluorescence lifetime exponential fits were all executed using Felix32 version 4.9 software.

Quantum yields were determined by making four solutions of each H-mer in chloroform such that their maximum absorbance was below 0.1. The emission spectra of these solutions were recorded by irradiating them at their corresponding λ_{max}^{abs}. The resulting emission spectra were then integrated. The integration value of each solution was then plotted against the respective absorption.

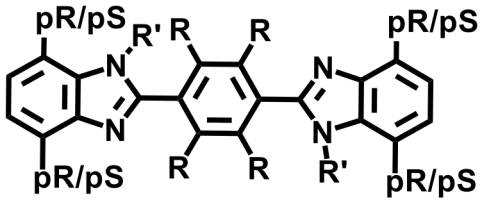
Four solutions of 9,10-diphenylanthracene were made in ethanol such that the maximum absorbance at the λ_{max}^{abs} of the corresponding H-mer was below 0.1. The emission spectra of these solutions were then recorded (using the same experimental parameters as the corresponding H-mer) by exciting at the λ_{max}^{abs} of the corresponding H-mer. The resulting spectra were integrated. The integration value of each solution was then plotted against the respective absorption.

To obtain the quantum yield, the following equation was used:

$$Q_s = Q_r \left(\frac{m_s}{m_r}\right)\left(\frac{n_s}{n_r}\right)^2$$

Where
Q = quantum yield
m = slope of generated plots
n = refractive index of the solvent
“s” and “r” refer to the sample and reference, respectively

NMR experiments: Due to the planar chirality both pR and pS cyclophanes are formed during the synthesis hence the all the monosubstituted cyclophane compounds are racemic in nature. The racemic cyclophane is used to make H-mers. Since each H-mer contains four cyclophanes there is a possibility of formation of 16 stereoisomers for each H-mer. Some of them will be meso compounds, hence each H-mer is a mixture of at least 10 diastereomers. Approximately close chemical shifts of the protons of various diastereomers result in broad peaks for each proton. The combination of all the diastereomer peaks together result in broad peaks for each proton.



H-mer 1: R = H, R' = H
H-mer 2: R = H, R' = Me
H-mer 3: R = F, R' = Me

H-mer containing 4 cyclophanes. Each cyclophane could be either pR or pS chirality

Due to lower solubility limit of H-mers and presence of at least 10 diastereomers there are fewer carbon peaks in H-mers. Also, due to lower solubility, the tetrafluoro intermediates (9b and 10b) showed very few or no peaks in the carbon NMR. Saturated solutions of H-mers are prepared for NMR studies. The solubility of H-mers in DMSO increased with increase in temperature.

Procedures for the synthesis of H-mers:

Synthesis of compounds 2 – 5 were reported by us previously.[2]

Procedure for the Synthesis of 2-bromo-1,4-bis(bromomethyl)benzene[3]:

The synthesis of (2-bromo-1,4-bis(bromomethyl)benzene) was performed using a modified procedure from literature. Benzene was used as the solvent. (30% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 1.8 Hz, 1H), 7.43 (d, J = 7.9 Hz, 1H), 7.32 (dd, J = 7.9, 1.8 Hz, 1H), 4.58 (s, 2H), 4.41 (s, 2H).

Procedure for the Synthesis of (±)-5^2-bromo-3,7-dithia-1(5,7)-adamantana-5(1,4)-benzenacyclooctaphane (**6**):

A benzene solution of 2-bromo-1,4-bis(bromomethyl)benzene (3.75 g, 10.95 mmol, 1.0 equiv.) and adamantane-1,3-diyl)dimethanethiol (**5**) (2.5 g, 10.95 mmol, 1.0 equiv.) was added dropwise over period of 48 h into a solution of KOH (1.35 g, 24.09 mmol, 2.2 equiv.) in absolute ethanol (1 L) using dilution. The solution was refluxed for another 24 h and the whole reaction mixture was concentrated *in vacuo*. The crude residue was separated

chromatographically on silica gel with CH_2Cl_2/*n*-hexanes gradient (0 to 20% CH_2Cl_2) as the eluent to yield **6** as a white crystalline solid (1.57 gm, 35% yield). R_f = 0.50 (10% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.27 (m, 2H), 7.08 (d, J = 44.2 Hz, 1H), 3.95 – 3.59 (m, 2H), 3.54 – 3.32 (m, 2H), 2.64 (s, 2H), 1.98 – 1.64 (m, 4H), 1.57 – 1.31 (m, 5H), 1.24 – 0.87 (m, 6H), -0.23 (d, J = 66.7 Hz, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 142.62, 138.84, 134.30, 132.38, 129.61, 124.64, 44.51, 42.86, 38.78, 37.97, 36.60, 36.53, 33.89, 33.83, 29.07, 29.01. HRMS (TOF MS-EI+) m/z 408.0572 $[M]^+$; calculated for $[C_{20}H_{25}BrS_2]^+$: 408.0581.

Procedure for the Synthesis of (((±)-3,7-dithia-1(5,7)-adamantana-5(1,4)-benzenacyclooctaphane-5^2-yl)ethynyl)trimethylsilane (**7**):

In an oven dried Schlenk flask, compound **6** (530 mg, 1.294 mmol, 1.0 equiv.) was taken and brought into the glovebox. Bis(tri-*tert*-butylphosphine)palladium(0) (33 mg, 0.064 mmol, 5 mol %) and copper (I) iodide (25 mg, 0.129 mmol, 10 mol %) were added along with degassed piperidine (4 mL). TMS-acetylene (272 µL, 1.941 mmol, 1.5 equiv.) was added subsequently and the reaction mixture was stirred at 50°C for 1h. The crude mixture was evaporated and the residue was separated chromatographically on silica gel with CH_2Cl_2/*n*-hexanes gradient (0 to 15% CH_2Cl_2) as the eluent to yield **7** as a white solid (485 mg, 88% yield). R_f = 0.51 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 0H), 7.43 (d, J = 75.3 Hz, 2H), 7.03 (s, 1H), 4.29 (d, J = 12.3 Hz, 1H), 3.68 (s, 1H), 3.46 (d, J = 13.6 Hz, 2H), 2.73 – 2.49 (m, 2H), 2.24 (d, J = 12.3 Hz, 1H), 1.83 (d, J = 44.5 Hz, 3H), 1.42 (s, 3H), 1.12 (s, 4H), 0.98 – 0.84 (m, 2H), 0.26 (s, 9H), -0.18 (s, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 143.24, 140.61, 134.45, 133.88, 133.69, 132.23, 132.13, 130.81, 130.59, 128.64, 128.52, 124.29, 123.04, 104.05, 98.99, 44.83, 44.46, 42.83, 38.84, 38.27, 36.61, 35.17, 33.90, 29.10, 29.05, 0.35, 0.12, 0.07, -0.21.; HRMS (TOF MS-EI+) m/z 426.1859 $[M]^+$; calculated for $[C_{25}H_{32}S_2Si]^+$: 426.1871.

Procedure for the Synthesis of (±)-5^2-ethynyl-3,7-dithia-1(5,7)-adamantana-5(1,4)-benzenacyclooctaphane (**8**):

Compound **7** (480mg, 1.125 mmol, 1.0 equiv.) was taken in THF and cooled to 0 °C. Tetrabutylammonium fluoride (1.23 mL, 1.237 mmol, 1.1 equiv.) was added and the reaction mixture was stirred for 30 min at room temperature. The solvent was evaporated and the crude product was purified by column chromatography on silica gel with CH_2Cl_2/*n*-hexane gradient (0 to 15% CH_2Cl_2) as the eluent to **8** as a white solid (386 mg, 97% yield). R_f = 0.48

(10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.31 (m, 2H), 7.25 – 6.96 (m, 1H), 4.36 – 4.00 (m, 1H), 3.71 (d, J = 13.5 Hz, 1H), 3.57 – 3.15 (m, 3H), 2.80 – 2.43 (m, 2H), 2.15 (d, J = 14.4 Hz, 1H), 1.83 (d, J = 43.6 Hz, 3H), 1.57 – 1.31 (m, 4H), 1.12 (s, 4H), 0.92 (s, 2H), 0.00 – (-0.42) (m, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 143.32, 140.78, 134.76, 134.31, 130.93, 123.11, 121.95, 83.03, 81.49, 44.83, 44.56, 42.81, 38.77, 38.20, 36.54, 35.13, 33.84, 33.77, 29.02.; HRMS (TOF MS-EI+) m/z 354.1470 $[M]^+$; calculated for $[C_{22}H_{26}S_2]^+$: 354.1476.

Procedure for the Synthesis of 1,4-bis(4,7-dibromo-1H-benzo[d]imidazol-2-yl)benzene (9a):

In an oven dried round-bottom flask 3,6-dibromo-1,2-benzenediamine (250 mg, 0.94 mmol, 1.0 equiv.) and terepthaldehyde (63 mg, 0.47 mmol, 0.5 equiv.) were taken in chloroform (60 mL). Zirconium (IV) chloride (88 mg, 0.376 mmol, 0.4 equiv.) was added and the reaction was stirred at room temperature for 12 h. The solvent was evaporated and the crude product was purified by column chromatography on silica gel with CH_2Cl_2/CH_3OH gradient (5 to 16% CH_2Cl_2) as the eluent. The product was recrystallized from acetonitrile and Et_2O (1:1) to synthesize **9a** as a yellow solid (220 mg, 32% yield). R_f = 0.1 (10% CH_3OH in CH_2Cl_2). **^{1}H NMR (**400 MHz, DMSO-D_6) δ: 8.51 (s, 4H), 7.40 (s, 4H). **^{13}C NMR** (400 MHz, DMSO) δ 152.28, 138.95, 130.71, 127.88, 126.45, 112.72, 107.06, 102.51.; HRMS (TOF MS-EI+) m/z 621.7642 $[M]^+$; calculated for $[C_{20}H_{10}Br_4N_4]^+$: 621.7639.

Procedure for the Synthesis of H-mer 1:

In an oven dried Schlenk flask, **9a** (30 mg, 0.048 mmol, 1.0 equiv.) and **8** (118 mg, 0.33 mmol, 7.0 equiv.) were taken and brought into the glovebox. Bis(tri-*tert*-butylphosphine)palladium(0) (6 mg, 0.009 mmol, 0.2 equiv.) and copper (I) iodide (3 mg, 0.019 mmol, 0.4 equiv.) were added along with degassed DMF and piperidine. The reaction mixture was stirred at 100°C for 14h. The crude mixture was evaporated and washed with approximately 5 ml of water and centrifuged. The process was repeated again and after removal of water, the mixture was dissolved in ethyl acetate. The residue was separated chromatographically on silica gel with EtOH/n-hexanes gradient (0 to 40% EtOH), followed by MeOH/CH_2Cl_2 (5 to 10% MeOH) as the eluent to obtain **H-mer 1** as a yellow solid (20 mg, 25% yield). R_f = 0.15 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, DMSO-D6) δ 8.65 (s, 4H), 7.48 (s, 17H), 3.76 (s, 7H), 3.60 (s, 7H), 3.09 (s, 4H), 1.34 (ddd, J = 196.8, 151.9, 44.5 Hz, 55H), -0.13 (s, 8H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 133.84, 123.35, 109.79, 42.88,

40.00, 37.24, 33.94, 32.07, 29.84, 29.80, 29.50, 22.83, 14.26.; HRMS (MALDI-DCTB matrix) m/z 1719.6636 $[M+H]^+$; calculated for $[C_{108}H_{110}N_4S_8]^+$: 1718.6496.

Procedure for the Synthesis of 1,4-bis(4,7-dibromo-1-methyl-1H-benzo[d]imidazol-2-yl)benzene (10a):

In an oven dried round bottom flask, **9a** (100 mg, 0.16 mmol, 1.0 equiv.) was taken. K_2CO_3 (154 mg, 1.12 mmol, 7.0 equiv.) and MeI (114 mg, 0.80 mmol, 5.0 equiv.) were added along with DMF (3 mL). The reaction mixture was stirred at 25°C for 24h. The crude mixture was evaporated and the residue was separated chromatographically on silica gel with CH_2Cl_2/*n*-hexanes gradient (10 to 45% CH_2Cl_2) as the eluent to yield **10a** as a white compound (54 mg mg, 52% yield). R_f = 0.12 (75% EtOAc in hexane). **^{1}H NMR** (400 MHz, DMSO-D_6) δ: 8.03 (s, 4H), 7.44 (s, 4H),4.13 (s, 6H). **^{13}C NMR** (400 MHz, DMSO) δ 155.14, 142.69, 133.62, 130.74, 130.16, 128.31, 126.22, 112.29, 102.60, 34.87.; HRMS (TOF MS-EI+): m/z 649.7925 $[M]^+$; calculated for $[C_{22}H_{14}Br_4N_4]^+$: 649.7952.

Procedure for the Synthesis of H-mer 2:

H-mer 2 was synthesized from compound **10a** using the same procedure used for H-mer 1. The residue was separated chromatographically on silica gel with EtOH/n-hexanes gradient (0 to 40% EtOH), followed by MeOH/ CH_2Cl_2 (5 to 10% MeOH) as the eluent to obtain **H-mer 2** as a yellow solid (28 mg, 37% yield). R_f = 0.25 (10% MeOH in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 3H), 7.77 – 7.30 (m, 19H), 4.39 (s, 6H), 4.16 – 4.07 (m, 2H), 3.84 – 3.35 (m, 13H), 2.67 (s, 6H), 1.90 (s, 6H), 1.58 (s, 7H), 1.41 (s, 19H), 1.11 (d, J = 20.2 Hz, 18H), 0.91 – 0.83 (m, 24H), -0.13 (d, J = 54.3 Hz, 8H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 32.07, 29.85, 29.51, 22.84, 14.27.; HRMS (MALDI-DCTB matrix) m/z 1747.6710 $[M+H]^+$; calculated for $[C_{110}H_{114}N_4S_8]^+$: 1746.6809.

Procedure for the Synthesis of 2,2'-(perfluoro-1,4-phenylene)bis(4,7-dibromo-1H-benzo[d]imidazole) (9b):

Compound **9b** was synthesized from 3,6-dibromo-1,2-benzenediamine and tetrafluoroterephthaldehyde using the same procedure used for compound **9a**. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/CH_3OH gradient (5 to 16% CH_2Cl_2) as the eluent. The product was recrystallized from acetonitrile and Et_2O (1:1) to obtain **9b** as a white solid (117 mg, 45% yield). R_f = 0.15 (75% EtOAc in hexane). **^{1}H NMR** (400 MHz,

MeOH-D_4) δ: 7.54 (s, 4H). **^{13}C NMR** (400 MHz, DMSO) δ 140.43.; HRMS (TOF MS-EI+): m/z 693.7288 $[M]^+$; calculated for $[C_{20}H_6Br_4F_4N_4]^+$: 693.7262.

Procedure for the Synthesis of 2,2'-(perfluoro-1,4-phenylene)bis(4,7-dibromo-1-methyl-1H-benzo[d]imidazole) (10b):

Compound **10b** was synthesized from compound **9b** using the same procedure used for compound **10a.** The crude mixture was evaporated and the residue was separated chromatographically on silica gel with CH_2Cl_2/*n*-hexanes gradient (10 to 45% CH_2Cl_2) as the eluent to yield **10b** as a yellow solid (54 mg, 52% yield). **^{1}H NMR** (400 MHz, DMSO-D_6) δ 7.54 (d, J = 3.8 Hz, 4H), 4.17 – 3.98 (m, 6H). **^{13}C NMR** could not be taken because of limited solubility. HRMS (TOF MS-EI+): m/z 721.7562 $[M]^+$; calculated for $[C_{22}H_{10}Br_4F_4N_4]^+$: 721.7575.

Procedure for the Synthesis of H-mer 3:

H-mer 3 was synthesized from compound **10b** using the same procedure used for **H-mer 1**. The residue was separated chromatographically on silica gel with EtOH/n-hexanes gradient (0 to 40% EtOH), followed by MeOH/ CH_2Cl_2 (5 to 10% MeOH) as the eluent to obtain **H-mer 3** as a yellow solid (30 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.29 (m, 13H), 7.13 (d, J = 52.1 Hz, 4H), 4.15 (s, 6H), 3.83 – 3.39 (m, 11H), 3.15 (d, J = 45.9 Hz, 5H), 2.88 (s, 3H), 2.67 (s, 5H), 2.33 (d, J = 44.1 Hz, 2H), 1.89 (s, 10H), 1.44 – 1.04 (m, 37H), 0.98 – 0.85 (m, 10H), -0.13 (d, J = 53.6 Hz, 8H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 142.79, 141.23, 140.65, 135.33, 133.98, 132.28, 132.18, 132.07, 132.04, 128.69, 128.57, 125.16, 44.85, 42.94, 39.20, 38.90, 38.36, 37.23, 36.78, 36.70, 36.54, 34.01, 33.97, 32.89, 32.34, 32.06, 30.17, 29.87, 29.83, 29.79, 29.49, 29.15, 29.06, 27.22, 26.87, 26.53, 24.05, 23.56, 22.83, 19.87, 19.37, 14.26.; HRMS (MALDI- DCTB matrix) m/z 1947.8053 $[M+8O+H]^+$; calculated for $[C_{110}H_{110}F_4N_4S_8]^+$: 1818.6432.

Figure S1: High temp and room temp NMR of H-mer 1 (DMSO-D6)

7.95, 2.94, 2.78ppm peaks correspond to DMF; 8.30ppm peak corresponds to $CHCl_3$ in $(CD_3)_2SO$

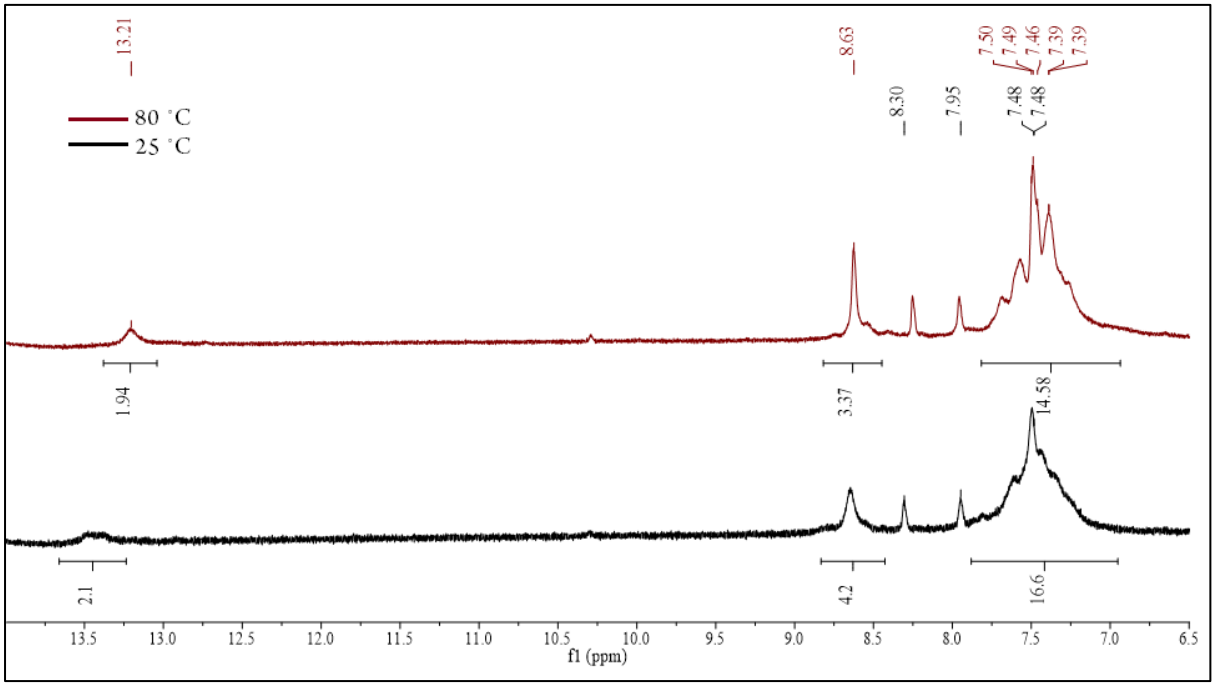


Figure S2: ^1H NMR (400 MHz, DMSO) of H-mer 1 at 80°C

5.71ppm corresponds to CD_2Cl_2 peaks in $(CD_3)_2SO$

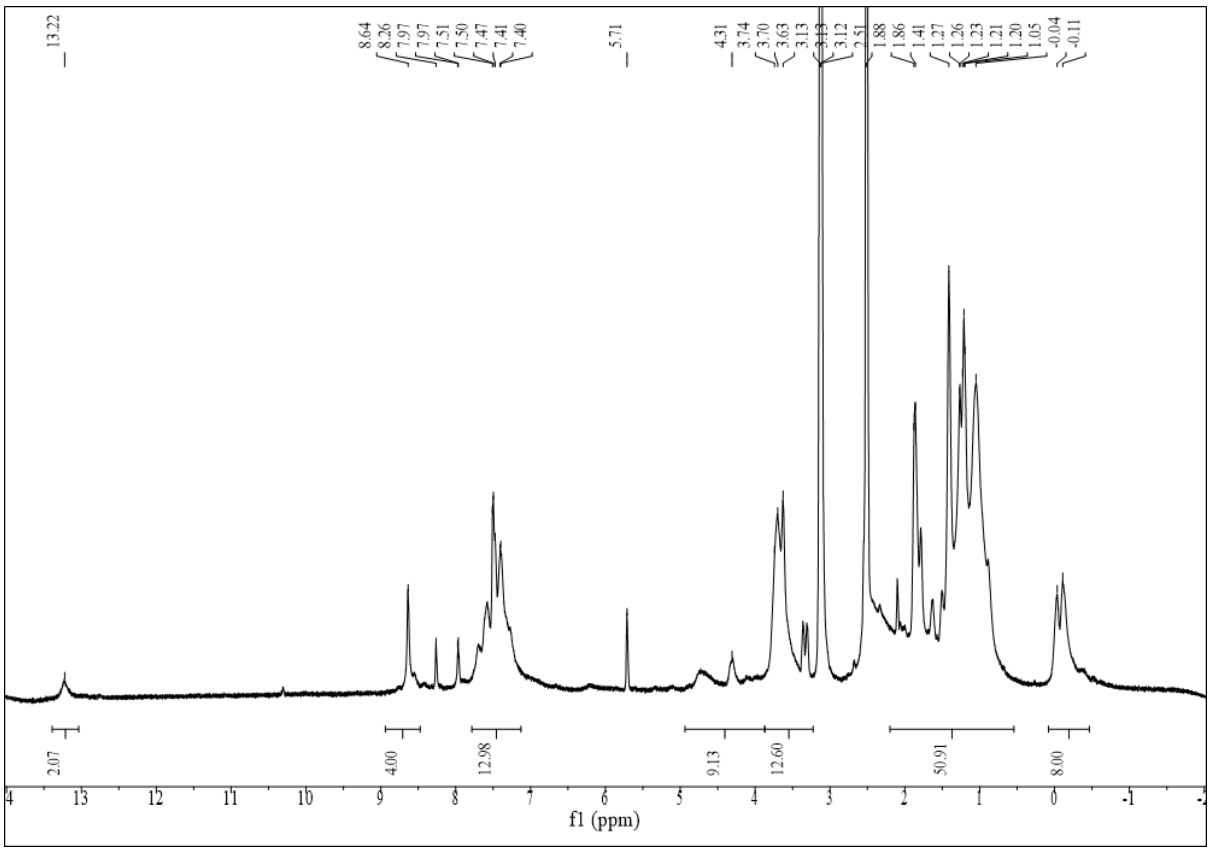


Figure S3: ^{1}H NMR (400 MHz, DMSO) of H-mer 2 at 25˚C and 80˚C

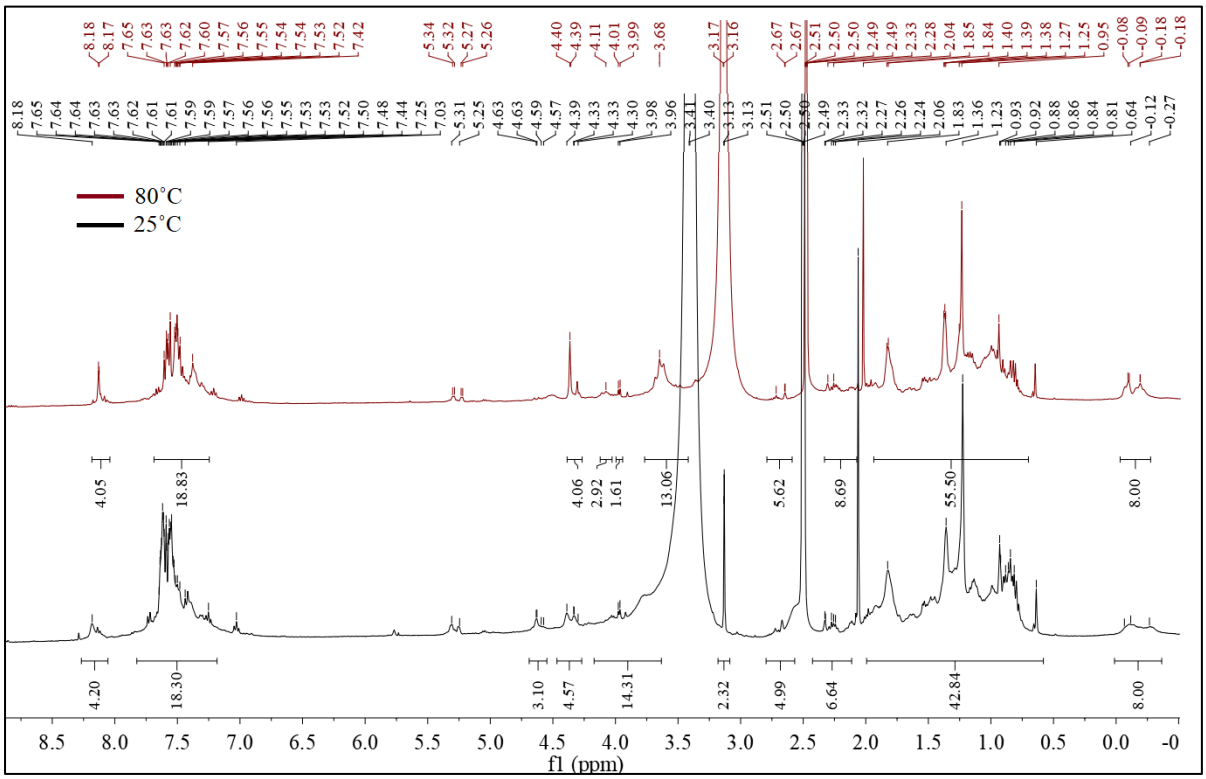


Figure S4: ^{1}H NMR (400 MHz, DMSO) of H-mer 3 at 25˚C and 80˚C

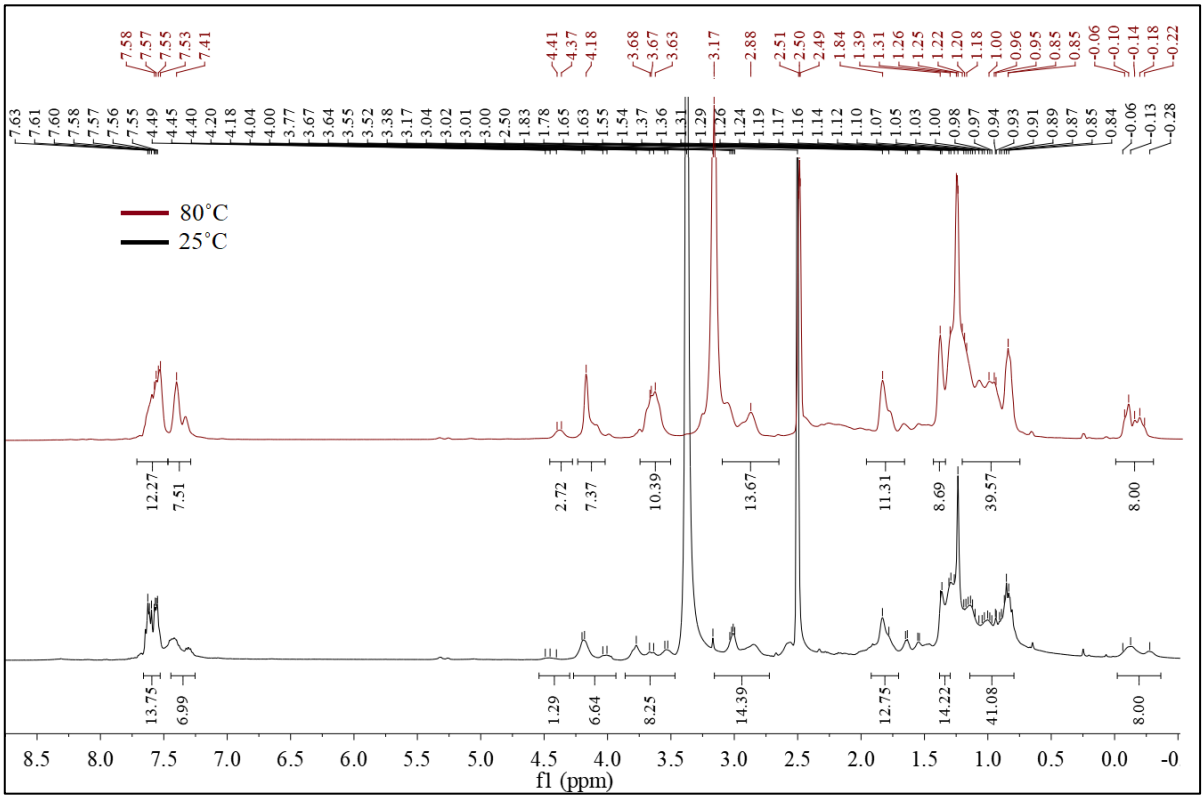


Figure S5: High temperature absorption spectra of H-mer 1

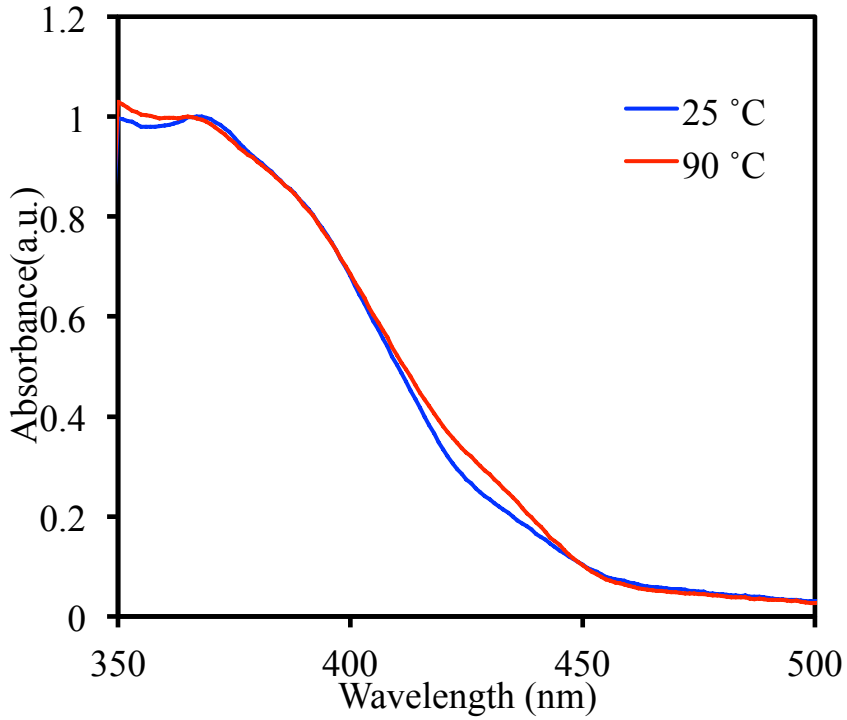


Figure S6: High temperature absorption spectra of H-mer 2

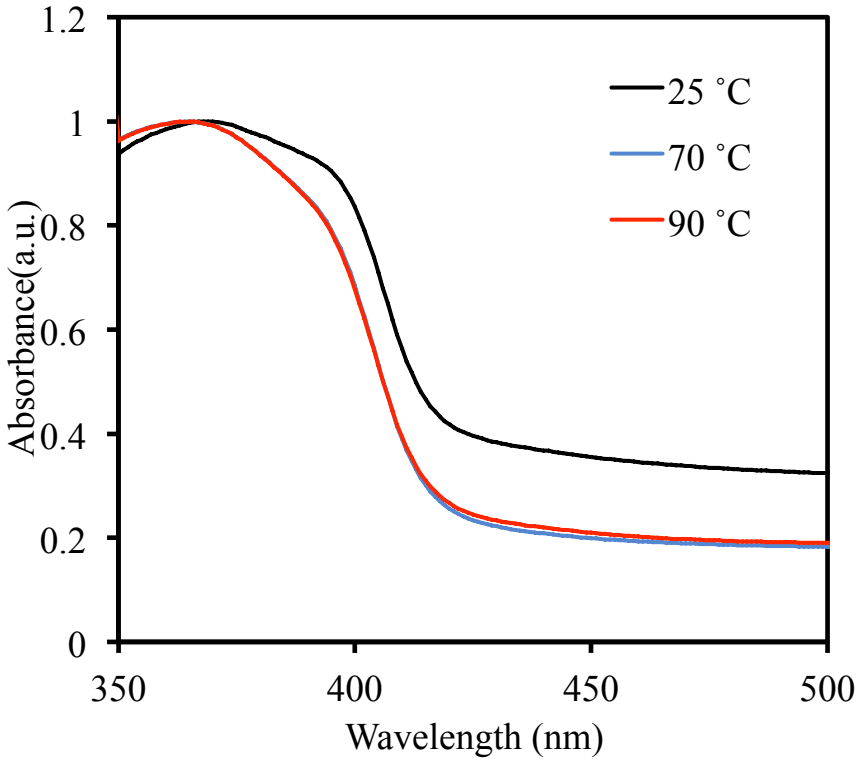


Figure S7: Thin film absorption spectra of H-mer 2 & 3

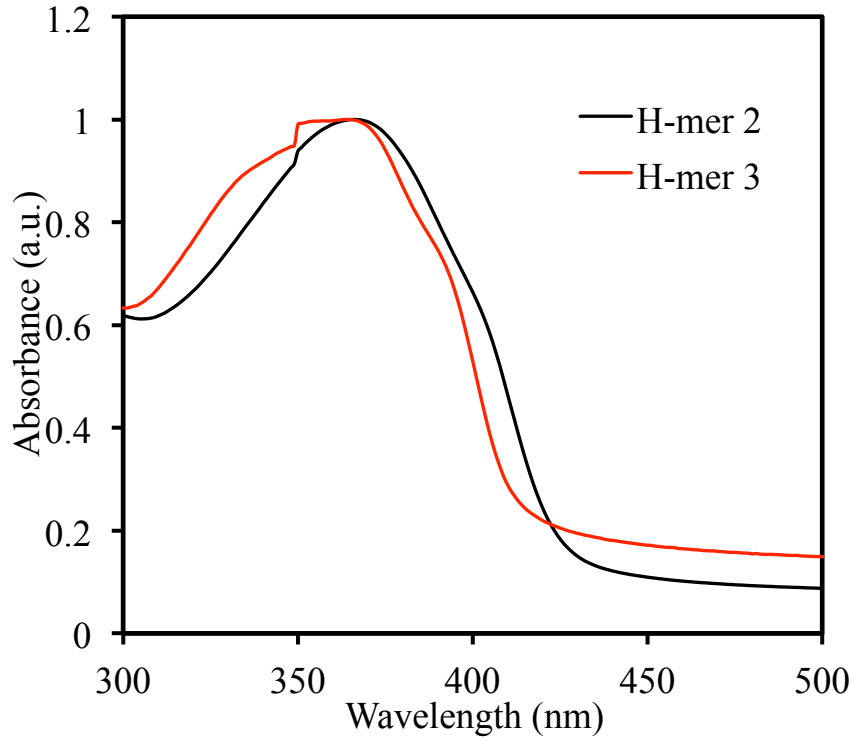
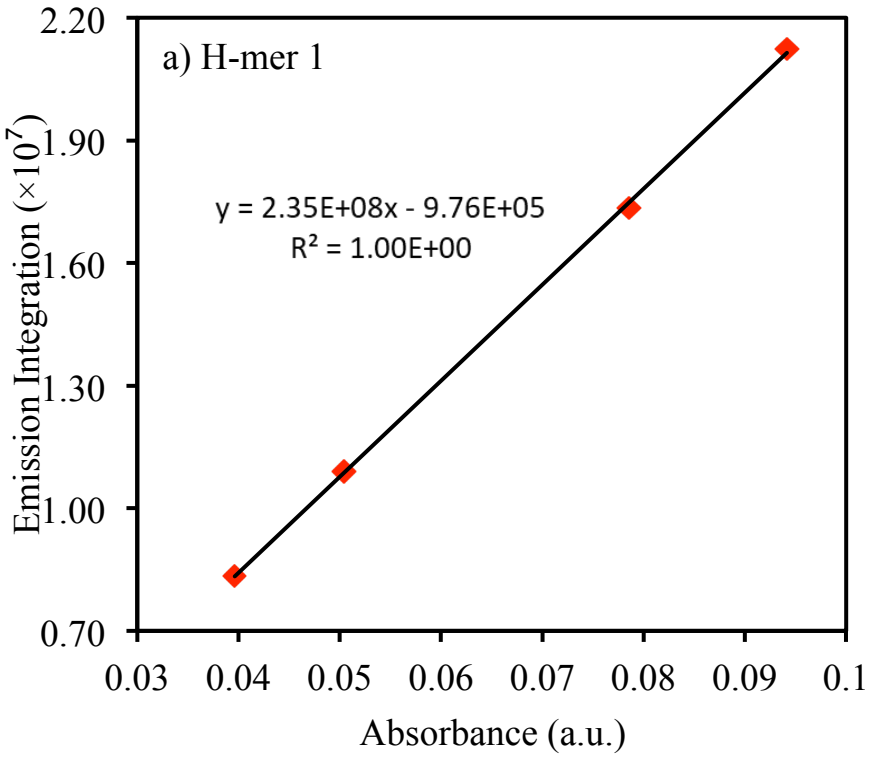
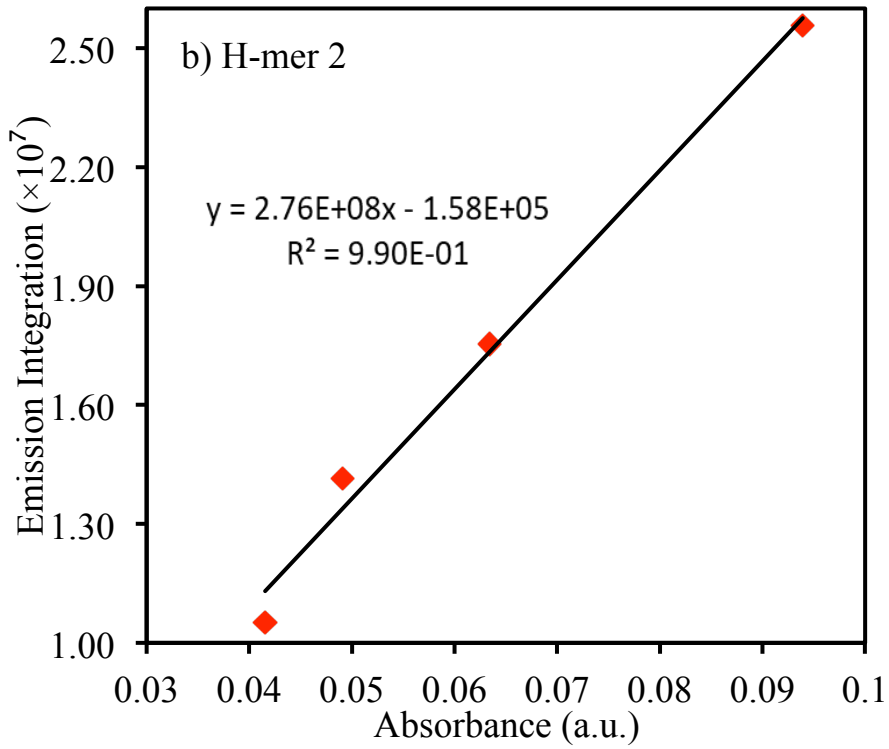


Figure S8: Quantum yields of H-mers relative to 9,10-diphenylanthracene




b) H-mer 2
y = 2.76E+08x - 1.58E+05
R² = 9.90E-01
Emission Integration (×10⁷)
2.50
2.20
1.90
1.60
1.30
1.00
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
Absorbance (a.u.)

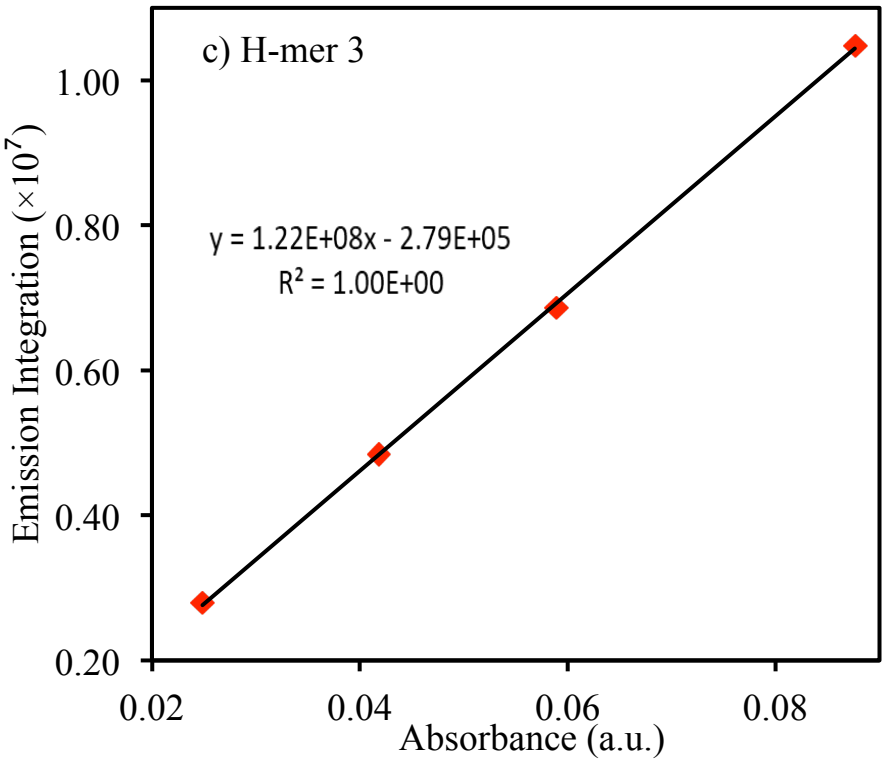

c) H-mer 3
y = 1.22E+08x - 2.79E+05
R² = 1.00E+00
Emission Integration (×10⁷)
1.00
0.80
0.60
0.40
0.20
0.02
0.04
0.06
0.08
Absorbance (a.u.)

Figure S9: UV/Vis absorption in the presence of TFA

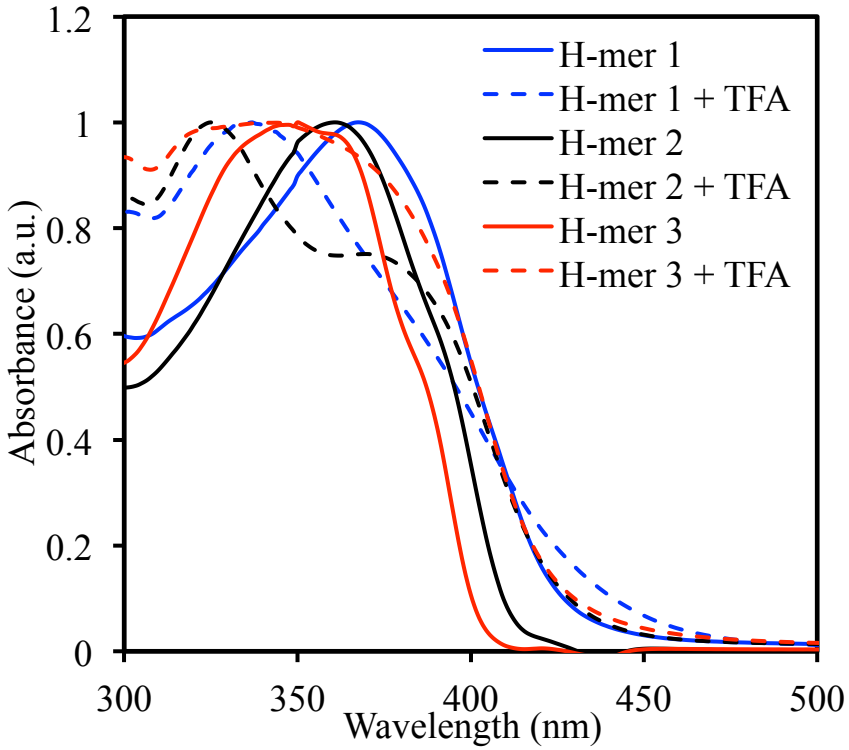
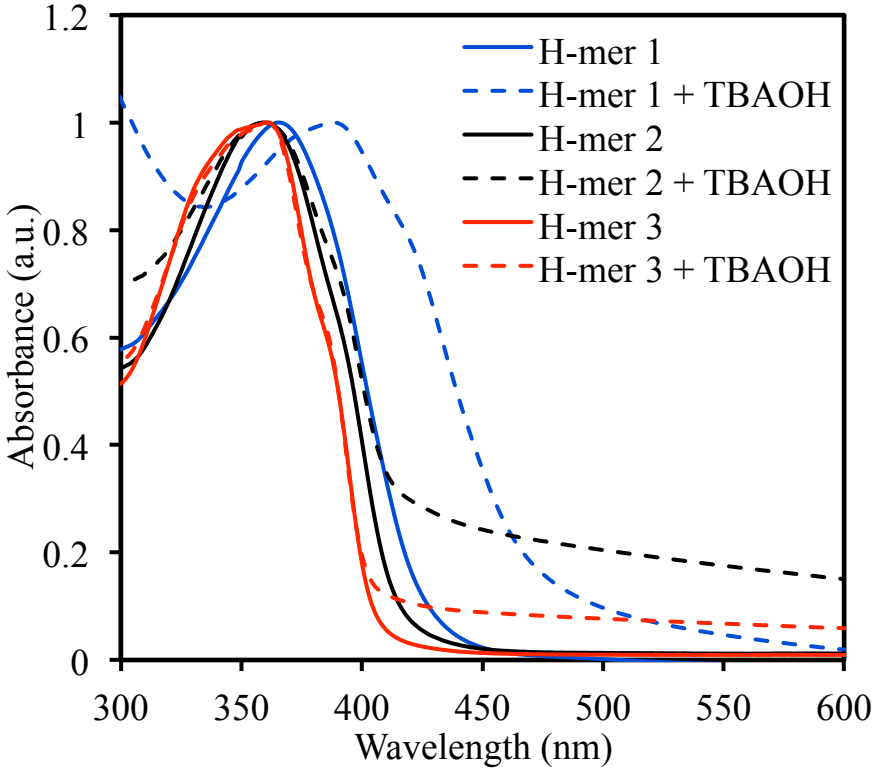
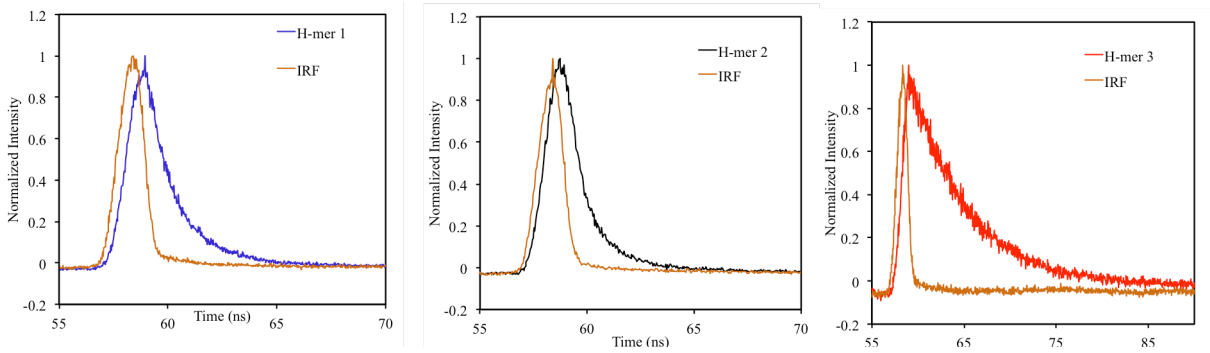


Figure S10: UV/Vis absorption in the presence of TBAOH



Lifetimes of H-mer 1 – 3

Figure S11: PL lifetime measurements for H-mers.



Sample preparation for lifetime studies:

20 µM samples of each H-mer were prepared (H-mer-1 and H-mer-2 in $CHCl_3$, H-mer-3 in Hexanes). The samples were diluted to obtain an intensity value between 5 and 8. H-mer 3 did not emit as strongly, so we used the maximum intensity we could get without sacrificing resolution. The intensity of the IRF was made to match the intensity of the H-mer in question.

Table S1: HOMO/LUMO values from DFT Studies:

	H-mer 1	H-mer 2	H-mer 3
LUMO (eV)	-2.143	-1.974	-2.054
HOMO (eV)	-5.166	-5.096	-5.167
Electronic energy (Hartree)	-2533.02	-2611.62	-3008.53

Calculations performed using methyl substituent instead of adamantane cycloalkyl group.

Calculations performed at the DFT B3LYP/6-31G* level of theory.

All three H-mers had zero imaginary frequencies.

Table S2: Atomic coordinates of H-mers 1-3

H-mer 1				
Tag	Symbol	X	Y	Z
1	C	3.811685	5.957128	4.920554
2	C	4.082348	4.867342	4.094163
3	C	4.89937	6.6342	5.489786
4	C	5.402268	4.450103	3.827602
5	C	6.209278	6.231099	5.233688
6	C	6.494144	5.142358	4.406073
7	C	5.616006	3.32989	2.976196

8	C	5.77195	2.369344	2.244492
9	C	5.948681	1.251728	1.393281
10	C	4.844425	0.571845	0.822123
11	C	7.223493	0.756057	1.069195
12	C	5.032998	-0.54335	-0.02758
13	C	7.397223	-0.34349	0.226928
14	H	8.095751	1.248616	1.486311
15	C	6.317888	-1.03647	-0.35771
16	H	8.401846	-0.68564	0.000141
17	C	6.560926	-2.13733	-1.22185
18	C	6.828042	-3.06922	-1.96052
19	C	7.134348	-4.15908	-2.82518
20	C	8.463785	-4.63528	-2.93771
21	C	6.106017	-4.76637	-3.57426
22	C	8.700472	-5.70712	-3.80215
23	C	6.355337	-5.8354	-4.43357
24	H	5.094554	-4.38113	-3.47563
25	C	7.674284	-6.29911	-4.53645
26	H	9.714774	-6.08662	-3.90178
27	N	3.756519	-0.94692	-0.38211
28	N	3.504737	0.841865	0.97474
29	C	2.891448	-0.06483	0.246922
30	C	1.424615	-0.13012	0.114654
31	C	0.783805	-0.11815	-1.12948
32	C	0.601874	-0.12857	1.248425
33	C	-0.60187	-0.12855	-1.24842
34	C	-0.7838	-0.11816	1.129489
35	C	-1.42461	-0.13012	-0.11465
36	C	-2.89145	-0.06482	-0.24692
37	N	-3.75652	-0.94692	0.382099
38	N	-3.50473	0.841888	-0.97472
39	C	-5.033	-0.54334	0.027574
40	C	-4.84442	0.571866	-0.82211
41	C	-6.31789	-1.03647	0.35769
42	C	-5.94867	1.25176	-1.39326
43	C	-7.39722	-0.34348	-0.22694
44	C	-6.56093	-2.13733	1.221812
45	C	-5.77194	2.369389	-2.24446
46	C	-7.22349	0.756086	-1.06919
47	H	-8.40185	-0.68562	-0.00016
48	C	-6.82806	-3.06924	1.96047
49	C	-5.61599	3.329946	-2.97614
50	H	-8.09575	1.248652	-1.4863
51	C	-7.13437	-4.15911	2.825108
52	C	-5.40225	4.450172	-3.82753
53	C	-8.46382	-4.63526	2.937672

54	C	-6.10603	-4.76646	3.57414
55	C	-4.08233	4.867419	-4.09407
56	C	-6.49412	5.142433	-4.406
57	C	-8.70052	-5.70712	3.802095
58	C	-6.35536	-5.8355	4.433429
59	H	-5.09456	-4.38125	3.475478
60	C	-3.81166	5.957218	-4.92045
61	H	-3.26604	4.315059	-3.63696
62	C	-7.67432	-6.29917	4.536341
63	H	-9.71483	-6.08659	3.901748
64	C	-4.89934	6.634295	-5.48968
65	C	-6.20925	6.231187	-5.2336
66	H	-7.03352	6.774921	-5.68964
67	H	3.266063	4.314987	3.63705
68	H	7.033554	6.774827	5.689729
69	C	9.583978	-4.0045	-2.14984
70	H	9.396114	-4.06176	-1.07077
71	H	10.53689	-4.5012	-2.35606
72	H	9.694908	-2.94083	-2.39375
73	C	5.242922	-6.47611	-5.23106
74	H	4.281969	-5.98765	-5.04171
75	H	5.439261	-6.4186	-6.3088
76	H	5.132119	-7.53862	-4.98109
77	C	-2.39254	6.403953	-5.18639
78	H	-2.18195	7.370048	-4.70965
79	H	-1.66747	5.68067	-4.80077
80	H	-2.20604	6.527702	-6.25988
81	C	-7.9146	4.714034	-4.13691
82	H	-8.08885	3.680629	-4.46067
83	H	-8.14697	4.750396	-3.06559
84	H	-8.6257	5.359547	-4.66158
85	C	-9.58402	-4.00442	2.14986
86	H	-9.3962	-4.06166	1.070787
87	H	-10.5369	-4.50109	2.356107
88	H	-9.6949	-2.94076	2.393798
89	C	-5.24294	-6.47628	5.230861
90	H	-5.43925	-6.4188	6.308607
91	H	-5.13218	-7.53878	4.980846
92	H	-4.28198	-5.98784	5.041501
93	C	2.392568	6.403857	5.18652
94	H	2.206082	6.527606	6.260013
95	H	2.18197	7.36995	4.709777
96	H	1.667499	5.68057	4.80091
97	C	7.914622	4.713966	4.136961
98	H	8.088878	3.680556	4.460706
99	H	8.146981	4.750344	3.06564

100	H	8.625728	5.359473	4.661635
101	F	1.13221	-0.14748	2.473807
102	F	-1.5184	-0.09909	2.255167
103	F	-1.13221	-0.14745	-2.4738
104	F	1.518398	-0.09907	-2.25516
105	C	-3.39759	-2.1067	1.188396
106	H	-2.36555	-2.38364	0.9677
107	H	-3.48999	-1.88963	2.256032
108	H	-4.05234	-2.94039	0.934156
109	C	3.397584	-2.1067	-1.18842
110	H	2.365535	-2.38361	-0.96775
111	H	3.49001	-1.88961	-2.25605
112	H	4.052318	-2.94039	-0.93417
113	H	-7.90117	-7.13176	5.19873
114	H	-4.71975	7.486609	-6.14167
115	H	4.71979	7.486503	6.141796
116	H	7.901128	-7.13169	-5.19885

H-mer 2				
Tag	Symbol	X	Y	Z
1	C	3.22412	-6.80609	4.193872
2	C	3.588418	-5.70178	3.424786
3	C	4.239057	-7.67929	4.609738
4	C	4.930033	-5.45791	3.066888
5	C	5.569471	-7.44919	4.262257
6	C	5.947551	-6.34697	3.491605
7	C	5.242169	-4.31272	2.281441
8	C	5.485581	-3.32664	1.609885
9	C	5.770473	-2.17826	0.831146
10	C	4.740938	-1.32983	0.355225
11	C	7.087135	-1.8208	0.489052
12	C	5.039388	-0.18384	-0.41838
13	C	7.369634	-0.68593	-0.27095
14	H	7.903703	-2.44655	0.834353
15	C	6.364832	0.180257	-0.7516
16	H	8.401787	-0.44304	-0.50201
17	C	6.72292	1.33729	-1.49455
18	C	7.090105	2.318523	-2.11737
19	C	7.512885	3.467331	-2.84588
20	C	8.879859	3.649895	-3.16998
21	C	6.563212	4.429243	-3.24625
22	C	9.232005	4.79667	-3.88623
23	C	6.927433	5.569493	-3.96082
24	H	5.520583	4.270035	-2.98391
25	C	8.282636	5.739609	-4.2765

26	H	10.27681	4.953923	-4.14405
27	N	3.809291	0.389	-0.70498
28	N	3.385079	-1.44662	0.538245
29	C	2.85436	-0.41589	-0.09098
30	C	1.404457	-0.17102	-0.11939
31	C	0.835114	1.114692	-0.09695
32	C	0.544529	-1.28178	-0.09786
33	C	-0.54456	1.281784	-0.09783
34	H	1.470448	1.992856	-0.04524
35	C	-0.83515	-1.11469	-0.09694
36	H	0.980241	-2.27449	-0.06471
37	C	-1.40449	0.171024	-0.11935
38	H	-0.98027	2.274486	-0.06466
39	H	-1.47048	-1.99286	-0.04522
40	C	-2.85439	0.415886	-0.0909
41	N	-3.80934	-0.389	-0.70487
42	N	-3.3851	1.446615	0.538353
43	C	-5.03943	0.183834	-0.41824
44	C	-4.74096	1.329822	0.355367
45	C	-6.36488	-0.18026	-0.75143
46	C	-5.77048	2.178249	0.831321
47	C	-7.36967	0.685926	-0.27074
48	C	-6.72299	-1.33729	-1.49437
49	C	-5.48557	3.326617	1.610062
50	C	-7.08715	1.820785	0.489258
51	H	-8.40183	0.443032	-0.50178
52	C	-7.09018	-2.31851	-2.1172
53	C	-5.24213	4.312701	2.281609
54	H	-7.90371	2.446536	0.834586
55	C	-7.51297	-3.46731	-2.84573
56	C	-4.92994	5.457883	3.06704
57	C	-8.87995	-3.64988	-3.1698
58	C	-6.56329	-4.4292	-3.24614
59	C	-3.5883	5.701746	3.424869
60	C	-5.94743	6.34696	3.491811
61	C	-9.23209	-4.79664	-3.88608
62	C	-6.92752	-5.56944	-3.96072
63	H	-5.52066	-4.26999	-2.98382
64	C	-3.22395	6.80605	4.193938
65	H	-2.8305	5.00031	3.08695
66	C	-8.28272	-5.73956	-4.27639
67	H	-10.2769	-4.9539	-4.14388
68	C	-4.23886	7.679258	4.609858
69	C	-5.5693	7.449173	4.262447
70	H	-6.33629	8.142629	4.599962
71	H	2.830589	-5.00036	3.086907

72	H	6.336495	-8.14264	4.599731
73	C	9.918061	2.63871	-2.75397
74	H	9.700425	1.647401	-3.16982
75	H	10.91489	2.937988	-3.09177
76	H	9.948691	2.522391	-1.6637
77	C	5.897769	6.591708	-4.38381
78	H	4.894807	6.313324	-4.04544
79	H	6.125414	7.582765	-3.97223
80	H	5.863872	6.697407	-5.47532
81	C	-1.7805	7.061269	4.562375
82	H	-1.66298	7.209316	5.642652
83	H	-1.13951	6.224637	4.267613
84	H	-1.3956	7.963964	4.070513
85	C	-7.38987	6.106882	3.123956
86	H	-7.52681	6.085376	2.035919
87	H	-7.74352	5.140382	3.503312
88	H	-8.03543	6.890115	3.533202
89	C	-9.91815	-2.63871	-2.75375
90	H	-9.70053	-1.64739	-3.16958
91	H	-10.915	-2.93799	-3.09153
92	H	-9.94876	-2.52242	-1.66347
93	C	-5.89785	-6.59164	-4.38376
94	H	-6.12547	-7.5827	-3.97217
95	H	-5.86399	-6.69733	-5.47527
96	H	-4.89488	-6.31324	-4.04542
97	C	1.780684	-7.06133	4.562388
98	H	1.395784	-7.96405	4.070591
99	H	1.66322	-7.20932	5.642679
100	H	1.139662	-6.22472	4.267613
101	C	7.389977	-6.10688	3.123673
102	H	7.526858	-6.08536	2.03563
103	H	7.743634	-5.14038	3.50302
104	H	8.035564	-6.89011	3.532879
105	C	-3.5771	-1.47806	-1.64725
106	H	-2.57116	-1.3874	-2.058
107	H	-3.68415	-2.45595	-1.16534
108	H	-4.3025	-1.41136	-2.45847
109	C	3.577026	1.478067	-1.64735
110	H	2.571074	1.387401	-2.05807
111	H	3.684092	2.455948	-1.16544
112	H	4.302411	1.41136	-2.45858
113	H	8.598626	6.619279	-4.83308
114	H	3.986204	-8.54847	5.213395
115	H	-8.59872	-6.61922	-4.83298
116	H	-3.98597	8.548432	5.213505

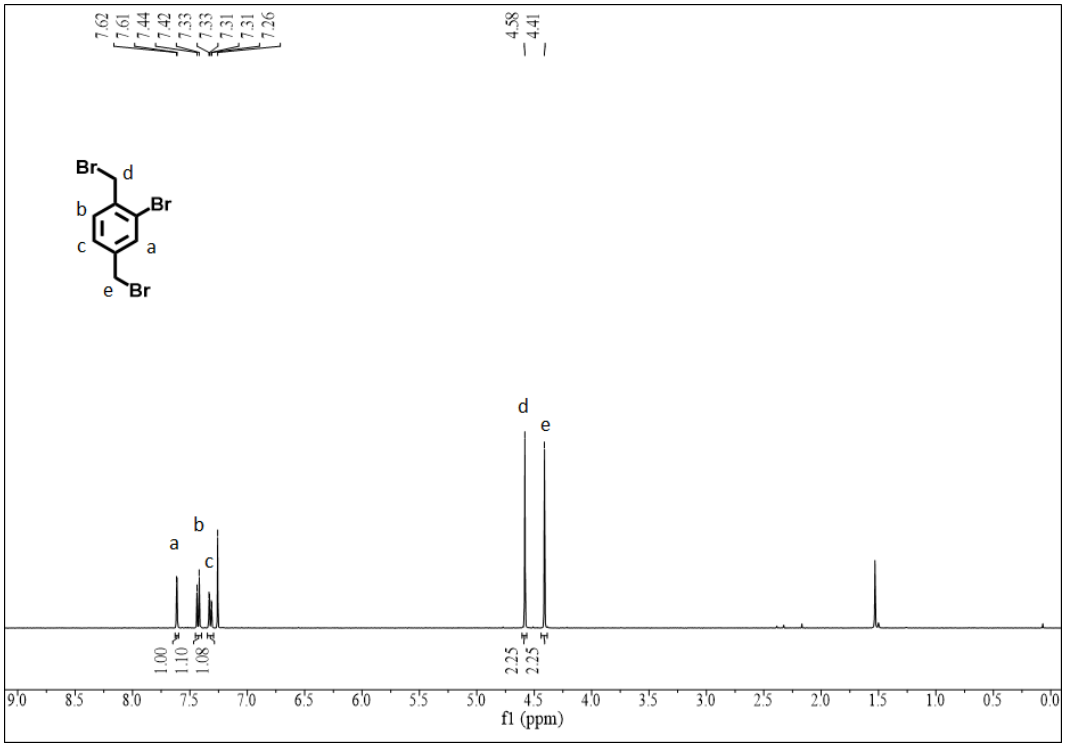
H-mer 3				
Tag	Symbol	X	Y	Z
1	C	3.811685	5.957128	4.920554
2	C	4.082348	4.867342	4.094163
3	C	4.89937	6.6342	5.489786
4	C	5.402268	4.450103	3.827602
5	C	6.209278	6.231099	5.233688
6	C	6.494144	5.142358	4.406073
7	C	5.616006	3.32989	2.976196
8	C	5.77195	2.369344	2.244492
9	C	5.948681	1.251728	1.393281
10	C	4.844425	0.571845	0.822123
11	C	7.223493	0.756057	1.069195
12	C	5.032998	-0.54335	-0.02758
13	C	7.397223	-0.34349	0.226928
14	H	8.095751	1.248616	1.486311
15	C	6.317888	-1.03647	-0.35771
16	H	8.401846	-0.68564	0.000141
17	C	6.560926	-2.13733	-1.22185
18	C	6.828042	-3.06922	-1.96052
19	C	7.134348	-4.15908	-2.82518
20	C	8.463785	-4.63528	-2.93771
21	C	6.106017	-4.76637	-3.57426
22	C	8.700472	-5.70712	-3.80215
23	C	6.355337	-5.8354	-4.43357
24	H	5.094554	-4.38113	-3.47563
25	C	7.674284	-6.29911	-4.53645
26	H	9.714774	-6.08662	-3.90178
27	N	3.756519	-0.94692	-0.38211
28	N	3.504737	0.841865	0.97474
29	C	2.891448	-0.06483	0.246922
30	C	1.424615	-0.13012	0.114654
31	C	0.783805	-0.11815	-1.12948
32	C	0.601874	-0.12857	1.248425
33	C	-0.60187	-0.12855	-1.24842
34	C	-0.7838	-0.11816	1.129489
35	C	-1.42461	-0.13012	-0.11465
36	C	-2.89145	-0.06482	-0.24692
37	N	-3.75652	-0.94692	0.382099
38	N	-3.50473	0.841888	-0.97472
39	C	-5.033	-0.54334	0.027574
40	C	-4.84442	0.571866	-0.82211
41	C	-6.31789	-1.03647	0.35769
42	C	-5.94867	1.25176	-1.39326
43	C	-7.39722	-0.34348	-0.22694
44	C	-6.56093	-2.13733	1.221812

45	C	-5.77194	2.369389	-2.24446
46	C	-7.22349	0.756086	-1.06919
47	H	-8.40185	-0.68562	-0.00016
48	C	-6.82806	-3.06924	1.96047
49	C	-5.61599	3.329946	-2.97614
50	H	-8.09575	1.248652	-1.4863
51	C	-7.13437	-4.15911	2.825108
52	C	-5.40225	4.450172	-3.82753
53	C	-8.46382	-4.63526	2.937672
54	C	-6.10603	-4.76646	3.57414
55	C	-4.08233	4.867419	-4.09407
56	C	-6.49412	5.142433	-4.406
57	C	-8.70052	-5.70712	3.802095
58	C	-6.35536	-5.8355	4.433429
59	H	-5.09456	-4.38125	3.475478
60	C	-3.81166	5.957218	-4.92045
61	H	-3.26604	4.315059	-3.63696
62	C	-7.67432	-6.29917	4.536341
63	H	-9.71483	-6.08659	3.901748
64	C	-4.89934	6.634295	-5.48968
65	C	-6.20925	6.231187	-5.2336
66	H	-7.03352	6.774921	-5.68964
67	H	3.266063	4.314987	3.63705
68	H	7.033554	6.774827	5.689729
69	C	9.583978	-4.0045	-2.14984
70	H	9.396114	-4.06176	-1.07077
71	H	10.53689	-4.5012	-2.35606
72	H	9.694908	-2.94083	-2.39375
73	C	5.242922	-6.47611	-5.23106
74	H	4.281969	-5.98765	-5.04171
75	H	5.439261	-6.4186	-6.3088
76	H	5.132119	-7.53862	-4.98109
77	C	-2.39254	6.403953	-5.18639
78	H	-2.18195	7.370048	-4.70965
79	H	-1.66747	5.68067	-4.80077
80	H	-2.20604	6.527702	-6.25988
81	C	-7.9146	4.714034	-4.13691
82	H	-8.08885	3.680629	-4.46067
83	H	-8.14697	4.750396	-3.06559
84	H	-8.6257	5.359547	-4.66158
85	C	-9.58402	-4.00442	2.14986
86	H	-9.3962	-4.06166	1.070787
87	H	-10.5369	-4.50109	2.356107
88	H	-9.6949	-2.94076	2.393798
89	C	-5.24294	-6.47628	5.230861
90	H	-5.43925	-6.4188	6.308607

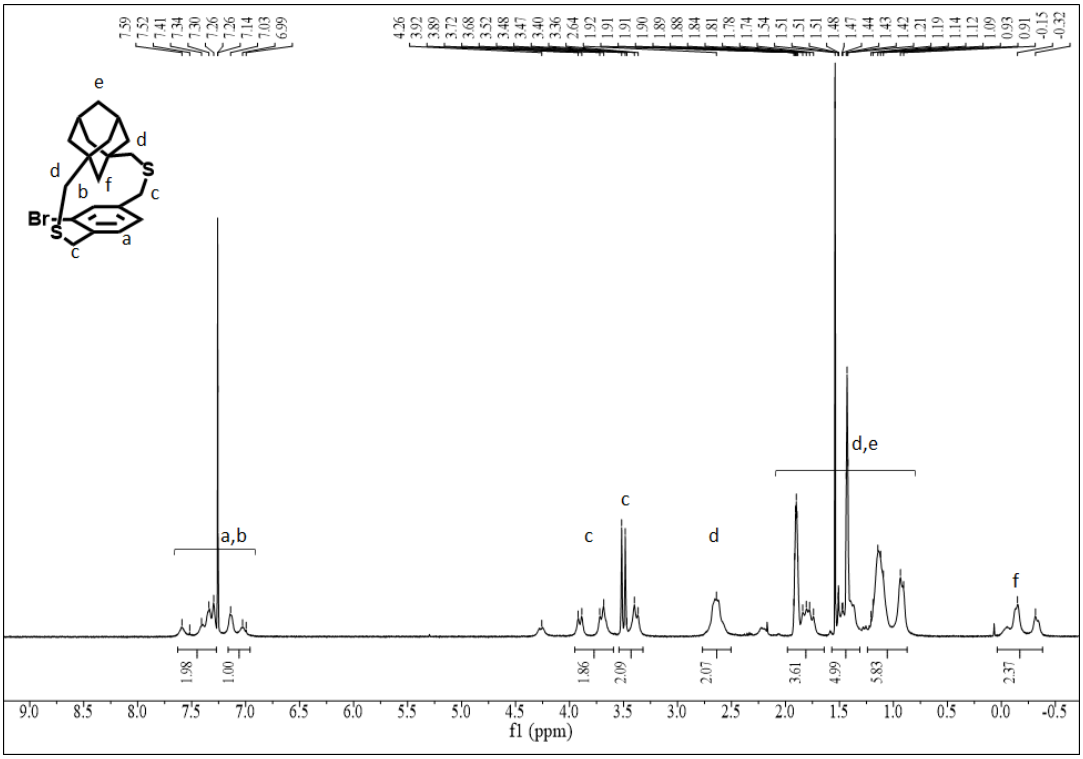
91	H	-5.13218	-7.53878	4.980846
92	H	-4.28198	-5.98784	5.041501
93	C	2.392568	6.403857	5.18652
94	H	2.206082	6.527606	6.260013
95	H	2.18197	7.36995	4.709777
96	H	1.667499	5.68057	4.80091
97	C	7.914622	4.713966	4.136961
98	H	8.088878	3.680556	4.460706
99	H	8.146981	4.750344	3.06564
100	H	8.625728	5.359473	4.661635
101	F	1.13221	-0.14748	2.473807
102	F	-1.5184	-0.09909	2.255167
103	F	-1.13221	-0.14745	-2.4738
104	F	1.518398	-0.09907	-2.25516
105	C	-3.39759	-2.1067	1.188396
106	H	-2.36555	-2.38364	0.9677
107	H	-3.48999	-1.88963	2.256032
108	H	-4.05234	-2.94039	0.934156
109	C	3.397584	-2.1067	-1.18842
110	H	2.365535	-2.38361	-0.96775
111	H	3.49001	-1.88961	-2.25605
112	H	4.052318	-2.94039	-0.93417
113	H	-7.90117	-7.13176	5.19873
114	H	-4.71975	7.486609	-6.14167
115	H	4.71979	7.486503	6.141796
116	H	7.901128	-7.13169	-5.19885

^{1}H NMR spectra

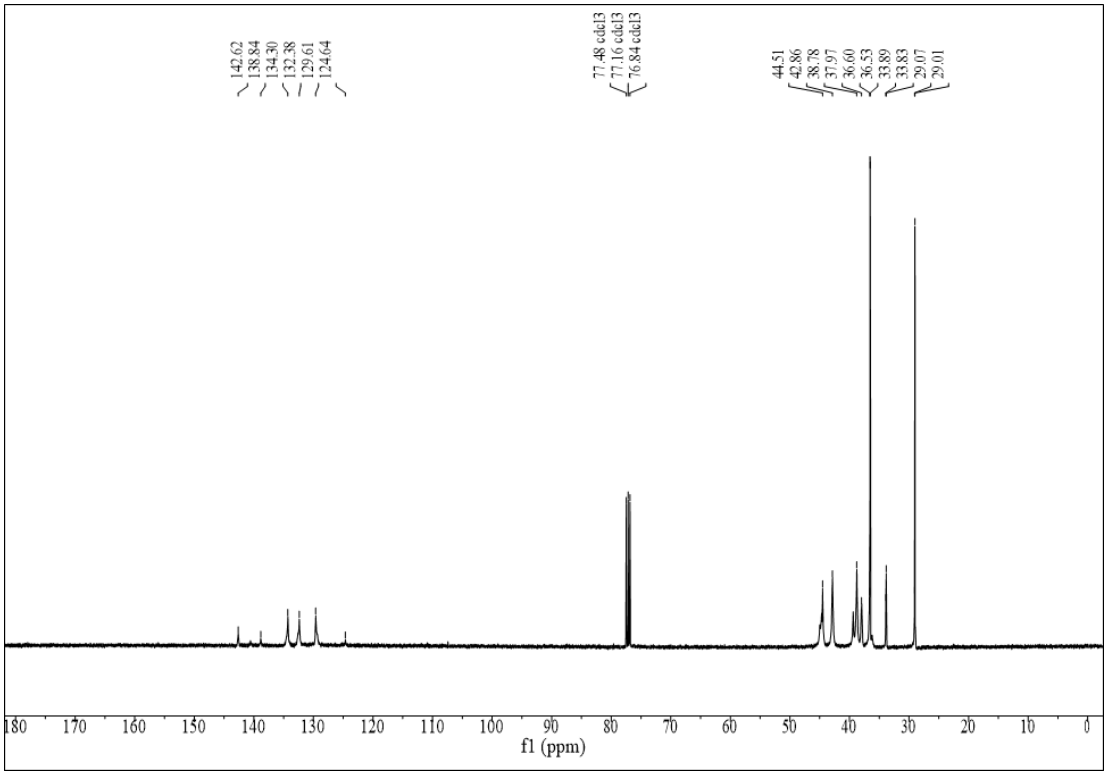
^{1}H NMR (400 MHz, $CDCl_3$) of 2-bromo-1,4-bis(bromomethyl)benzene



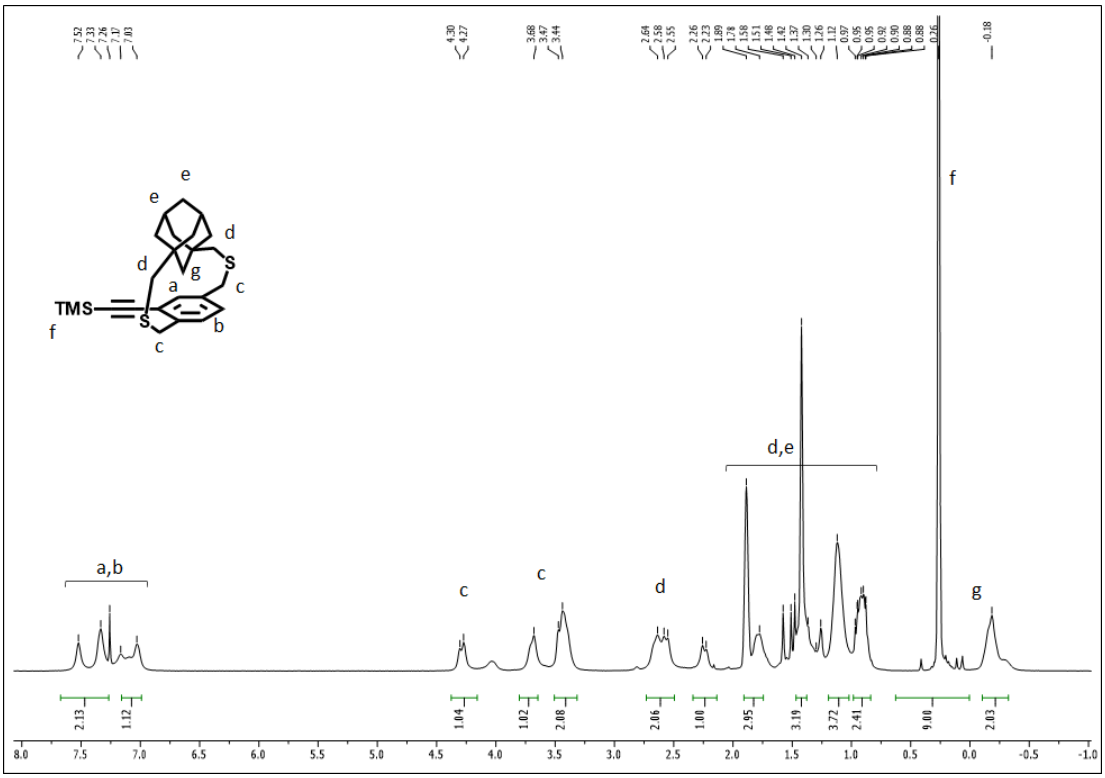
^{1}H NMR (400 MHz, $CDCl_3$) of 6



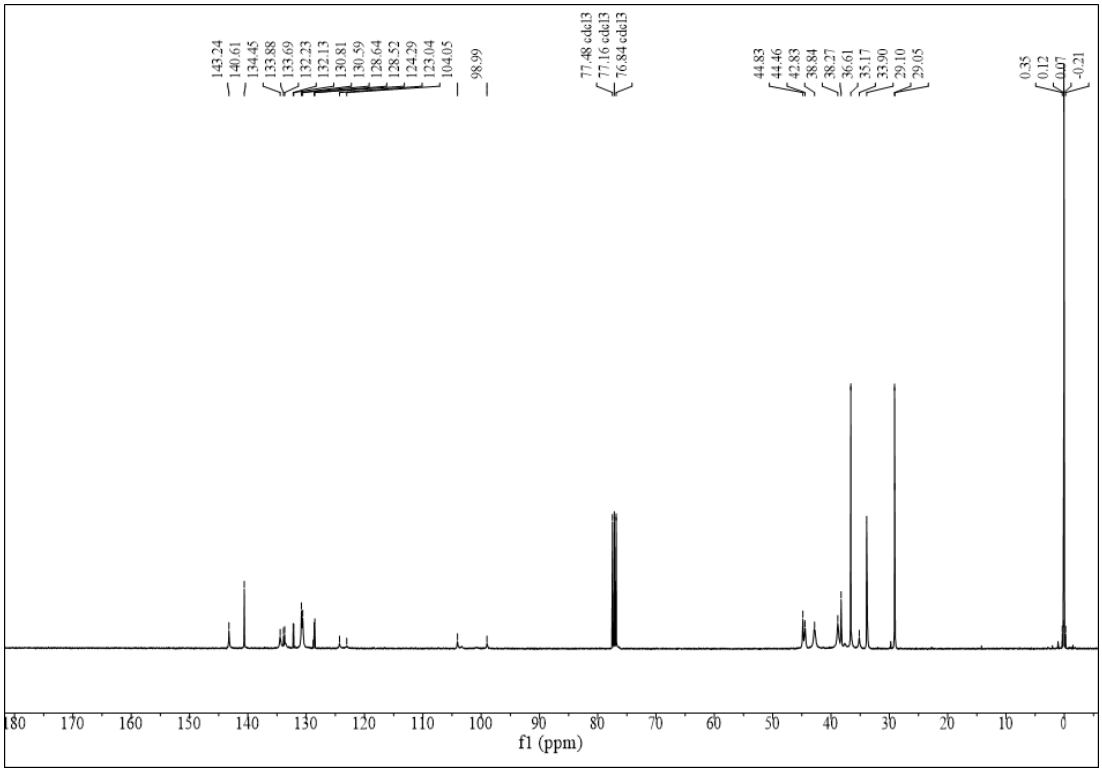
^{13}C NMR (400 MHz, $CDCl_3$) of 6



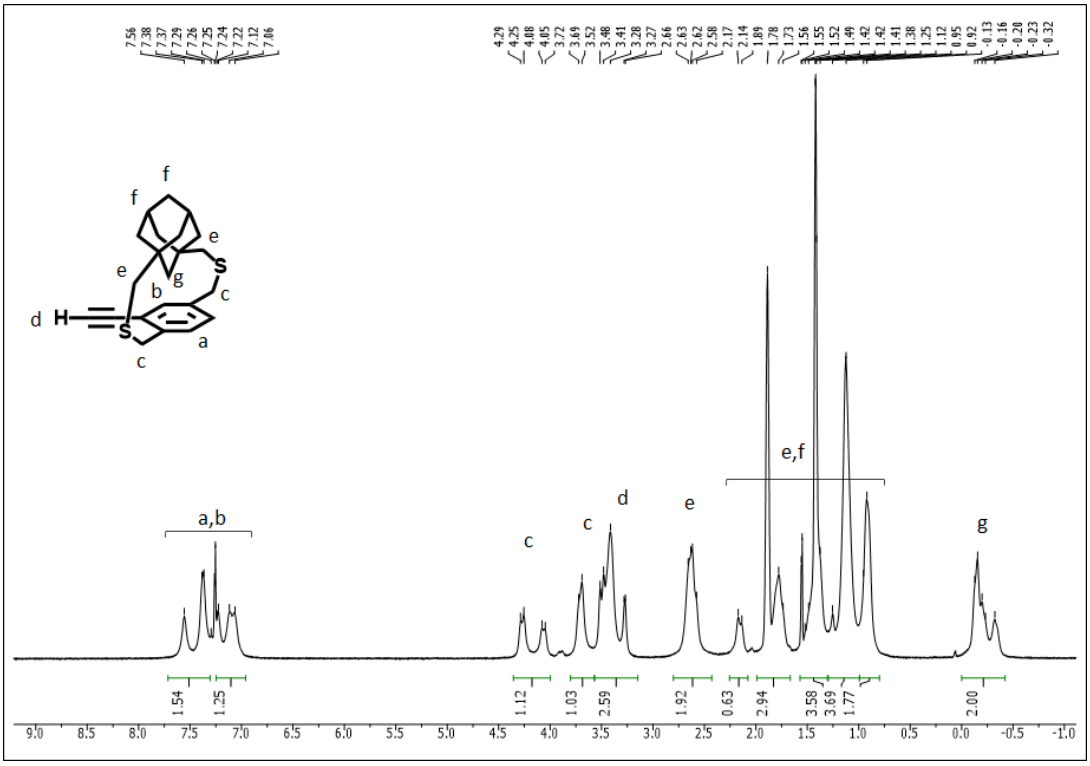
^{1}H NMR (400 MHz, $CDCl_3$) of 7



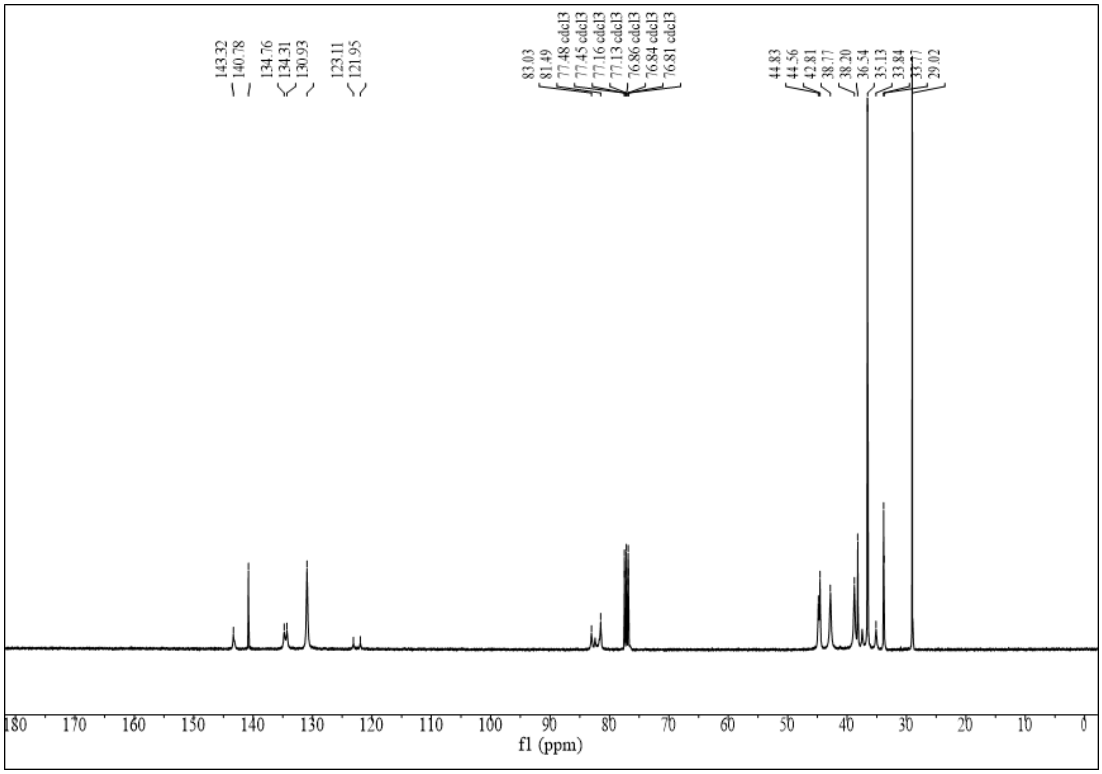
^{13}C NMR (400 MHz, $CDCl_3$) of 7



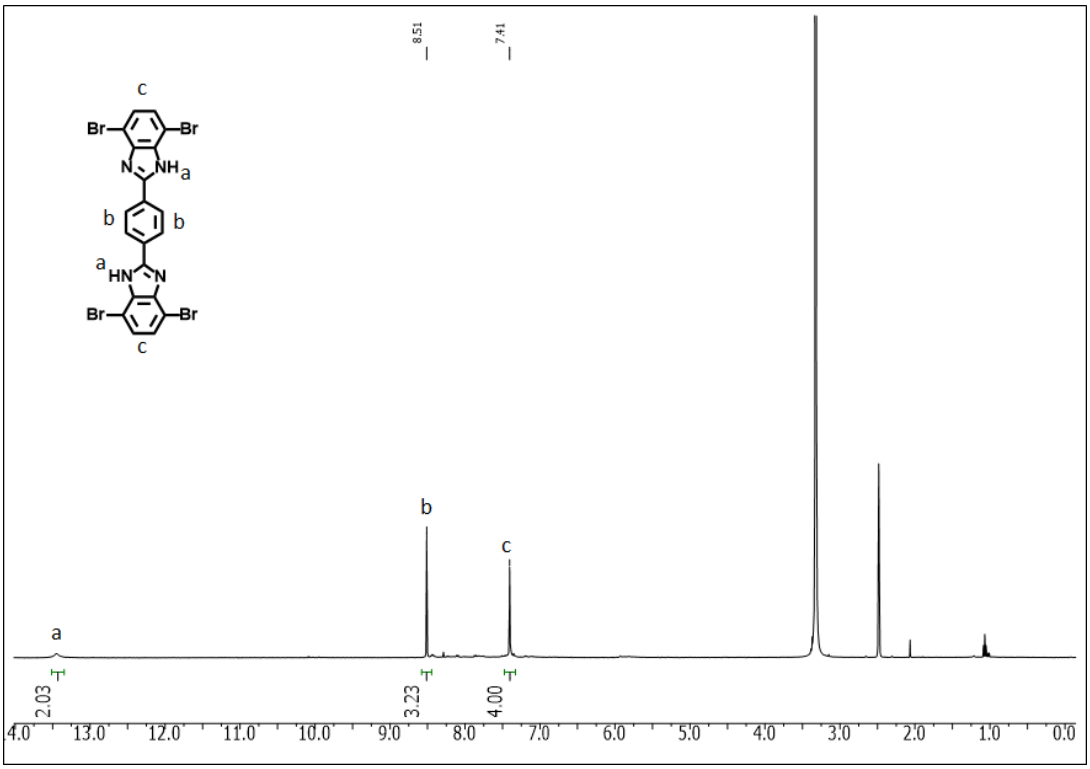
^{1}H NMR (400 MHz, $CDCl_3$) of 8



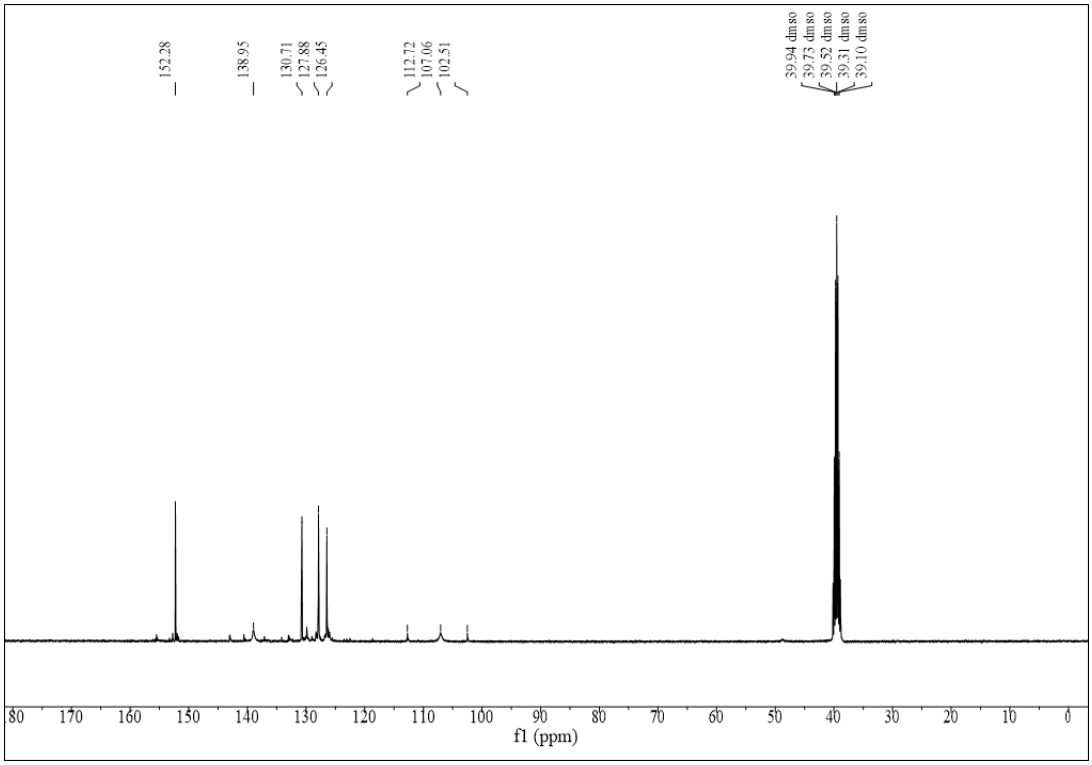
^{13}C NMR (400 MHz, $CDCl_3$) of 8



^{1}H NMR (400 MHz, DMSO) of 9a

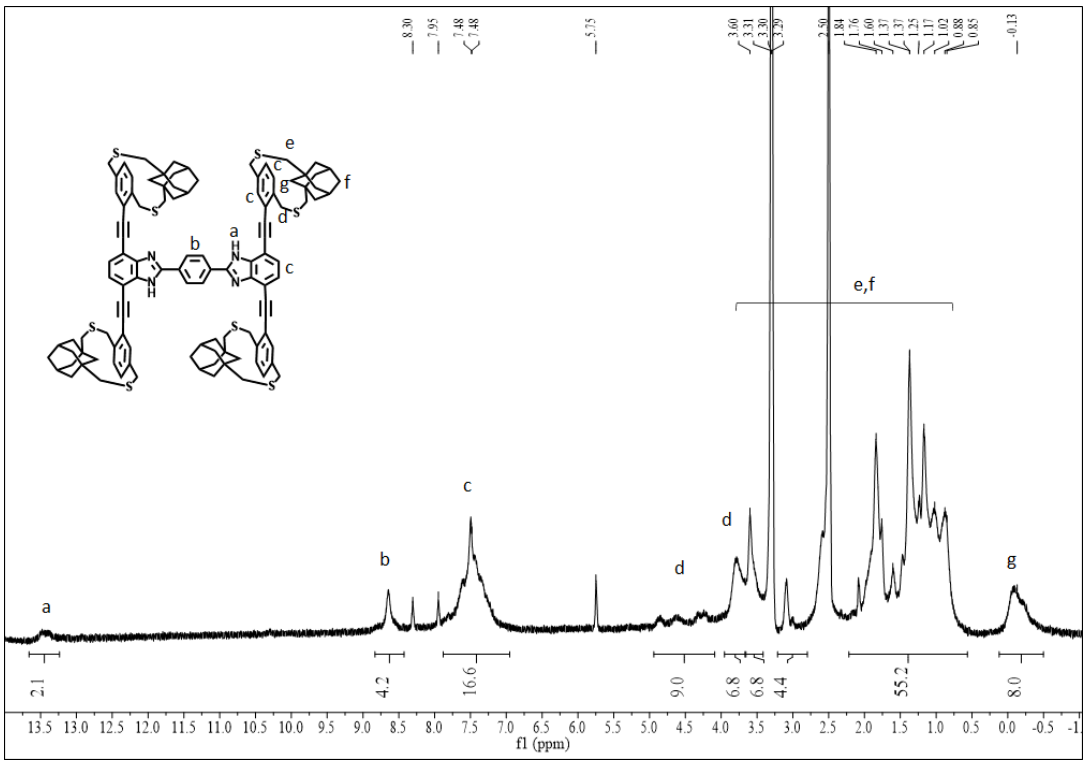


^{13}C NMR (400 MHz, DMSO) of 9a



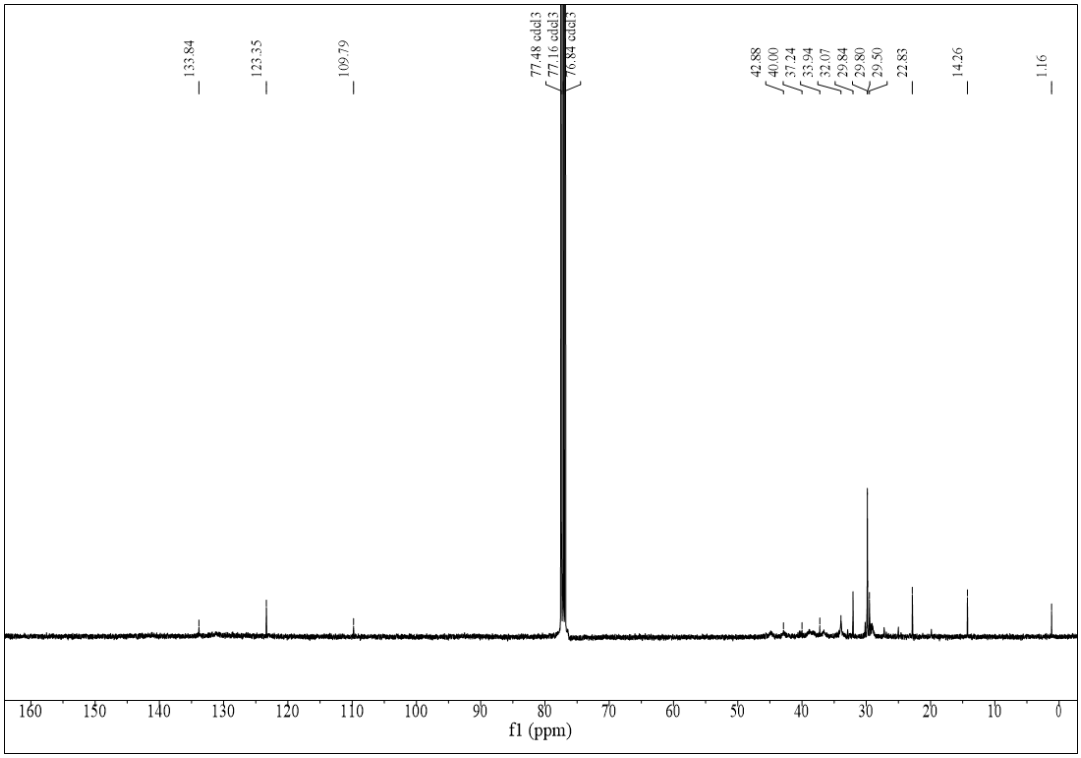
^{1}H NMR (400 MHz, DMSO) of H-mer 1

7.95, 2.94, 2.78ppm peaks correspond to DMF; 8.30ppm peak corresponds to $CHCl_3$; 5.75ppm peak corresponds to CH_2Cl_2 in $(CD_3)_2SO$

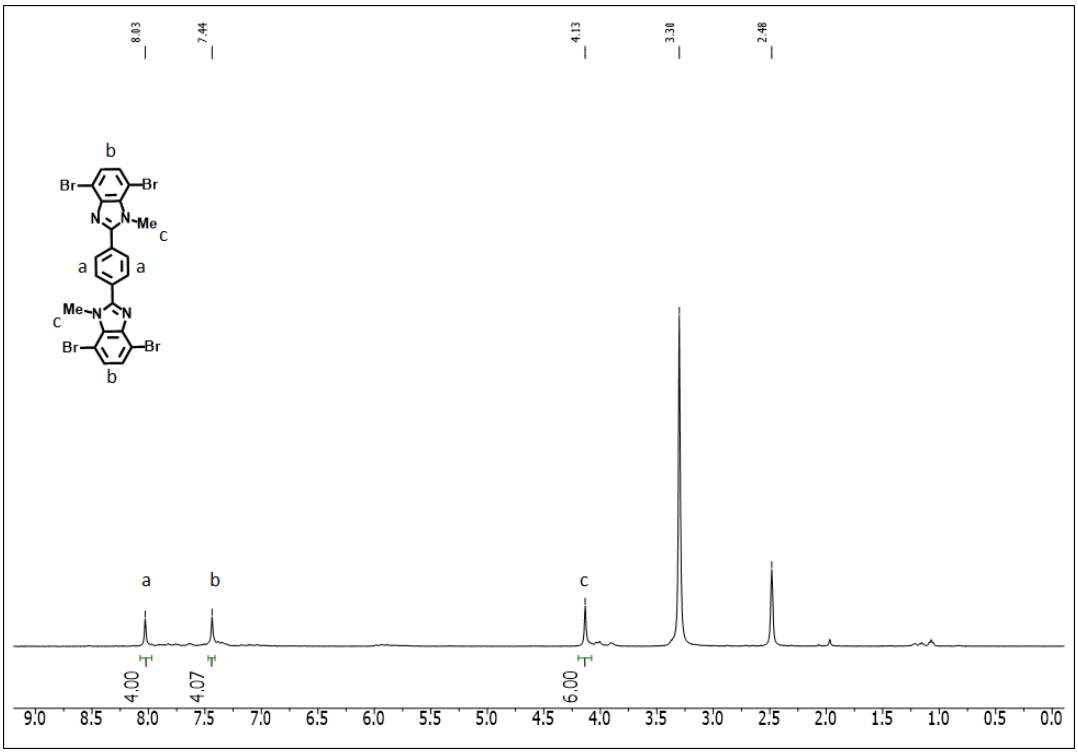


^{13}C NMR (400 MHz, $CDCl_3$) of H-mer 1

1.16ppm peak corresponds to silicone grease

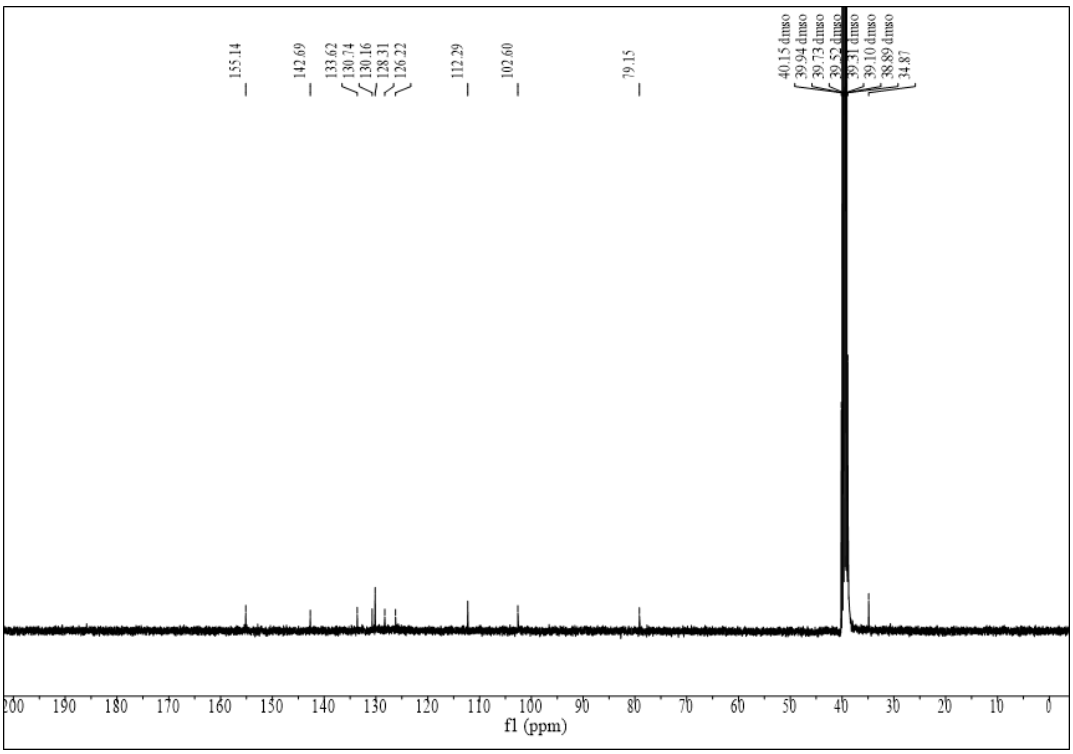


^{1}H NMR (400 MHz, DMSO) of 10a



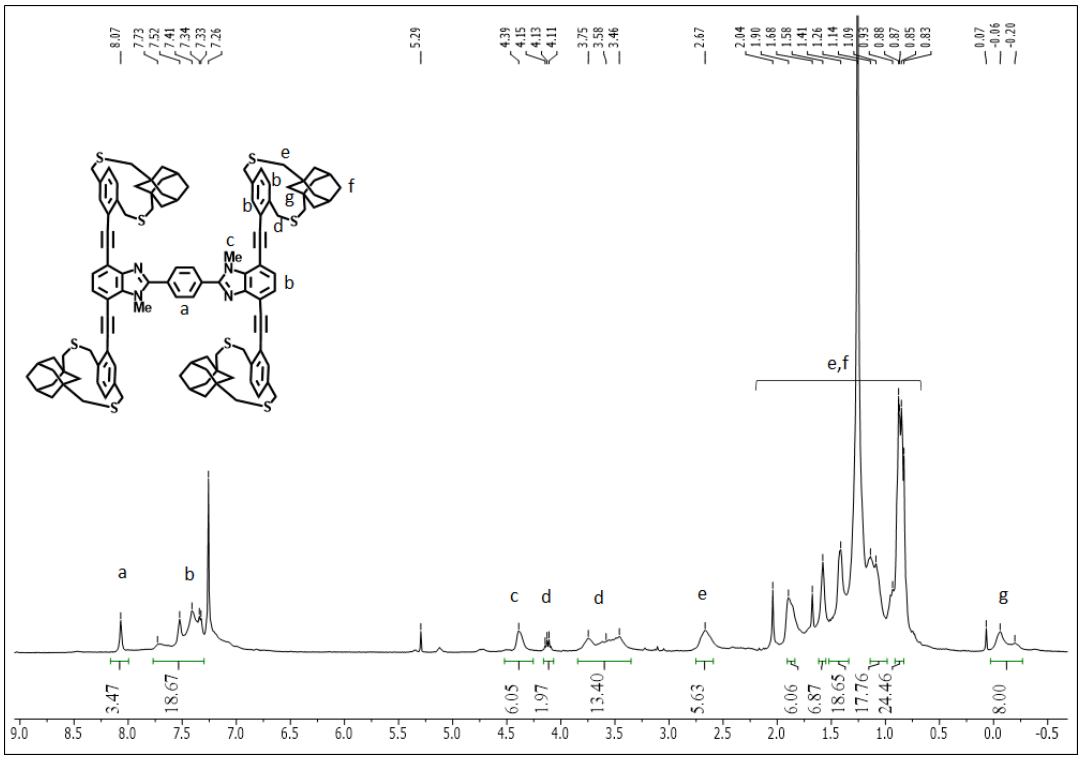
^{13}C NMR (400 MHz, DMSO) of 10a

79.15ppm peak corresponds to $CHCl_3$ in $(CD_3)_2SO$

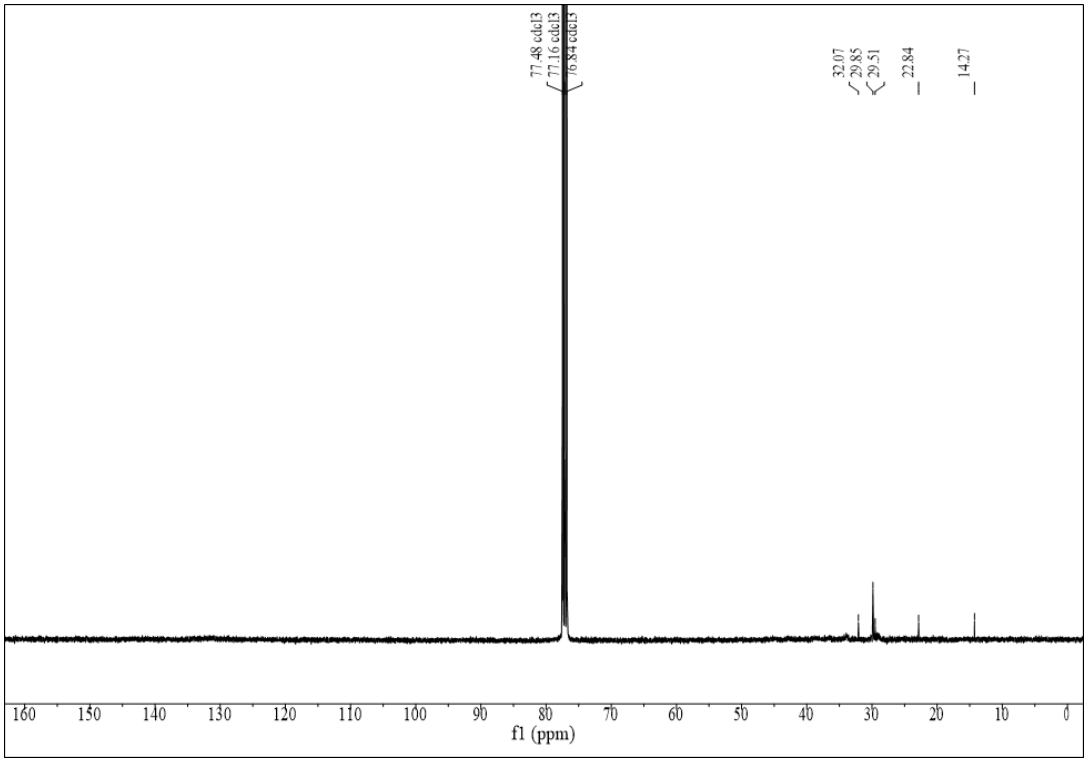


^{1}H NMR (400 MHz, $CDCl_3$) of H-mer 2

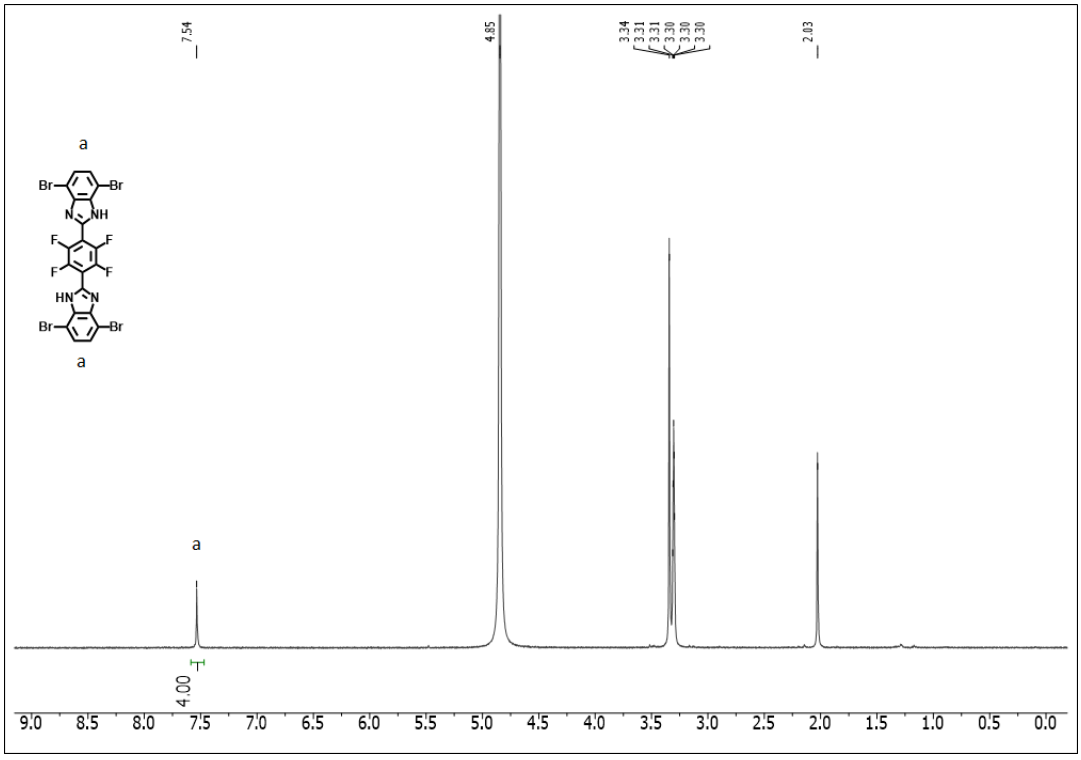
5.3ppm peak corresponds to CH_2Cl_2 in $CDCl_3$



^{13}C NMR (400 MHz, $CDCl_3$) of H-mer 2

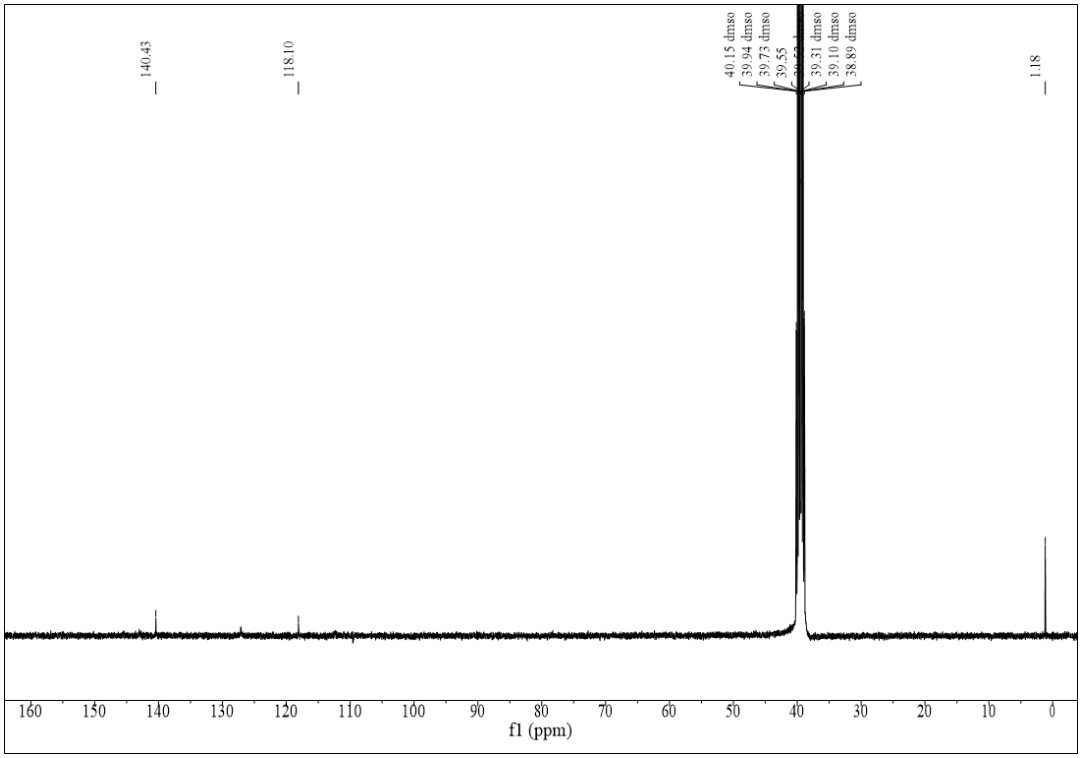


^{1}H NMR (400 MHz, MeOH-D1) of 9b



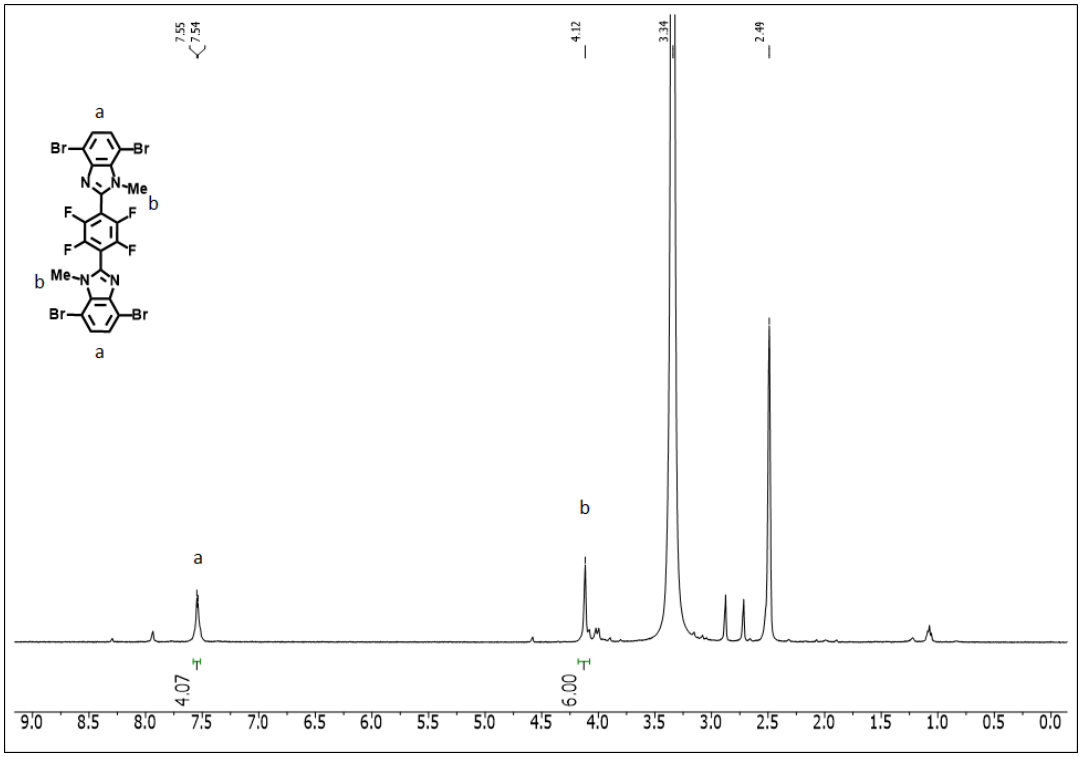
^{13}C NMR (400 MHz, DMSO) of 9b

1.18, 118.10 ppm peaks corresponds to MeCN in DMSO

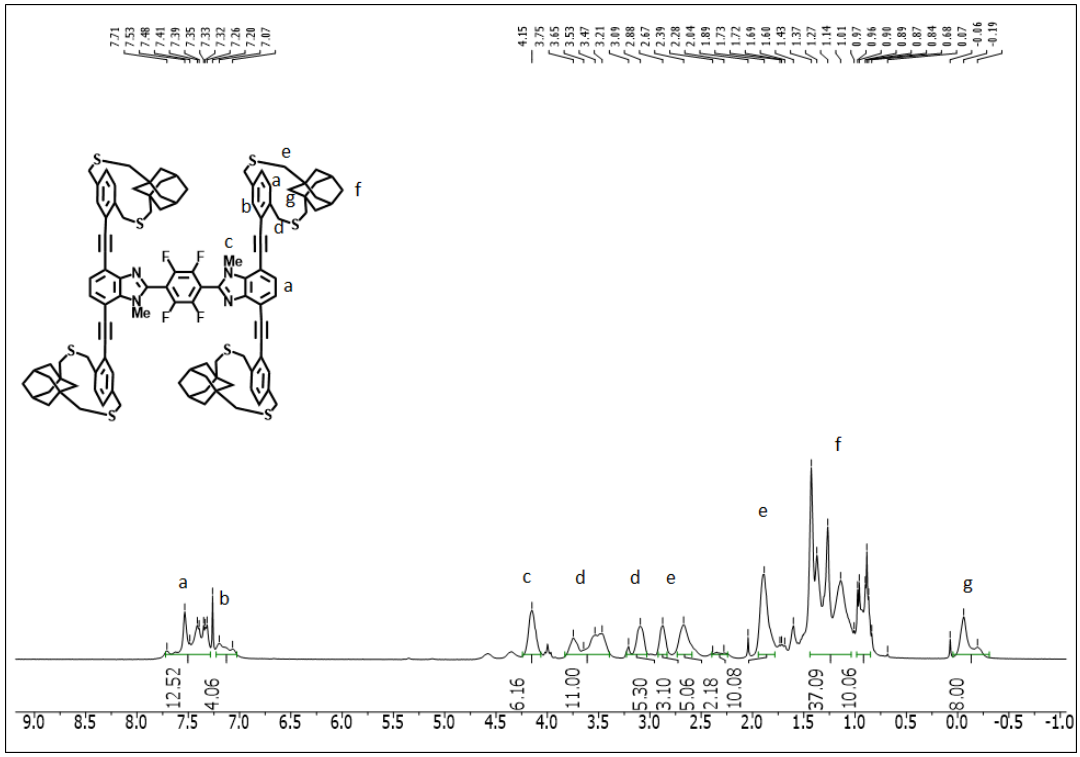


^{1}H NMR (400 MHz, DMSO) of 10b

7.95, 2.94, 2.78ppm peaks correspond to DMF in $(CD_3)_2SO$

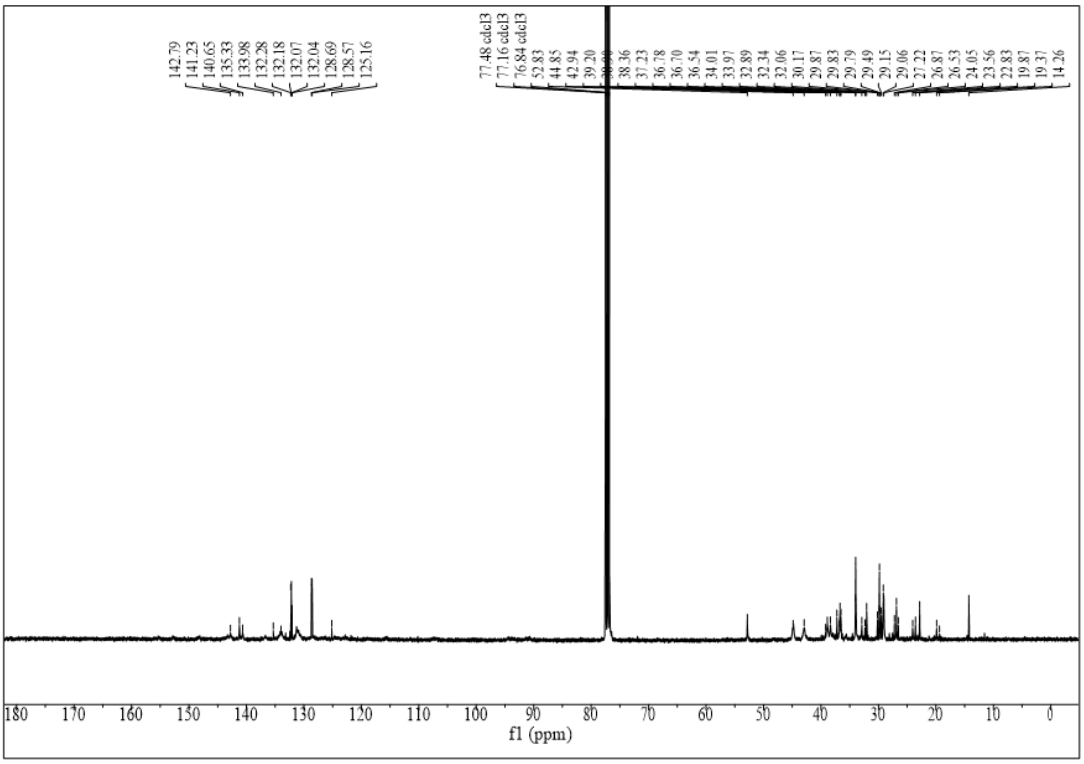


^{1}H NMR (400 MHz, $CDCl_3$) of H-mer 3



^{13}C NMR (400 MHz, $CDCl_3$) of H-mer 3

52.83ppm peaks correspond to CD_2Cl_2 in $(CD_3)_2SO$



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2. Chaudhuri, S., Mohanan, M., Willems, A. V., Bertke, J. A., Gavvalapalli, N. *Chemical science*, **2019**, *10*, 5976-5982.

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