# Supporting Information

# for

# "Estimating the shape and size of supramolecular assemblies by variable temperature diffusion ordered spectroscopy"

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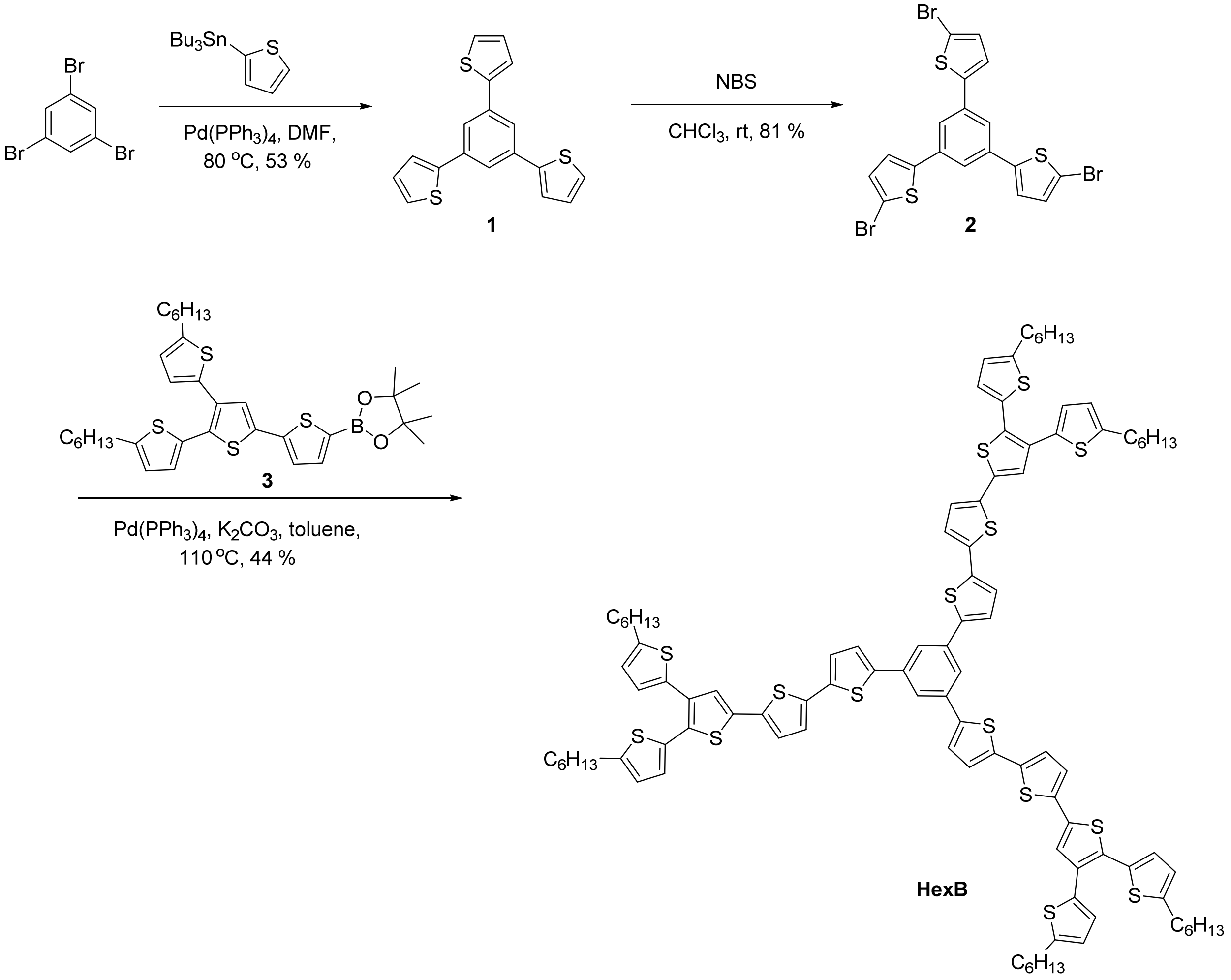
## General remarks

All reagents were purchased from Sigma Aldrich (St. Louis, MO, USA). Deuterated solvents (toluene-$d_8$, $CDCl_3$, DMSO-$d_6$, and THF-$d_8$) were purchased from Cambridge Isotope Laboratories, Inc. and used without further purification. DMF was degassed in 20 L drums and passed through two sequential purification columns (activated molecular sieves) under a positive argon atmosphere. Thin layer chromatography (TLC) was performed on $SiO_2$-60 $F_{254}$ aluminum-backed plates with visualization by UV light or staining. Flash column chromatography was performed using silica gel technical grade, pore size 60 Å, 230−400 mesh particle size, 40−63 µm particle size from Sigma-Aldrich.

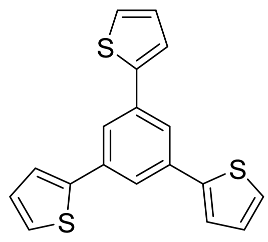
## Synthetic details

Preparation of **HexBQPH**,[1] **HexBQPME**,[1] 1,3,5-tri(thiophen-2-yl)benzene (**1**),[2, 3] 1,3,5-tris(5-bromothiophen-2-yl)benzene (**2**),[2] 4,4,5,5-tetramethyl-2-(5''-hexyl-5'-(5-hexylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)-1,3,2-dioxaborolane (**3**),[1] and **HexB**[4] were based on previously published procedures.

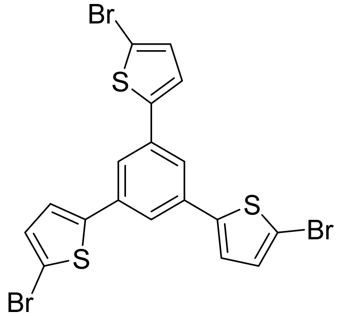
Reported below are the full synthetic details for the preparation of **HexB**, where some deviation from the literature reported methods was made.



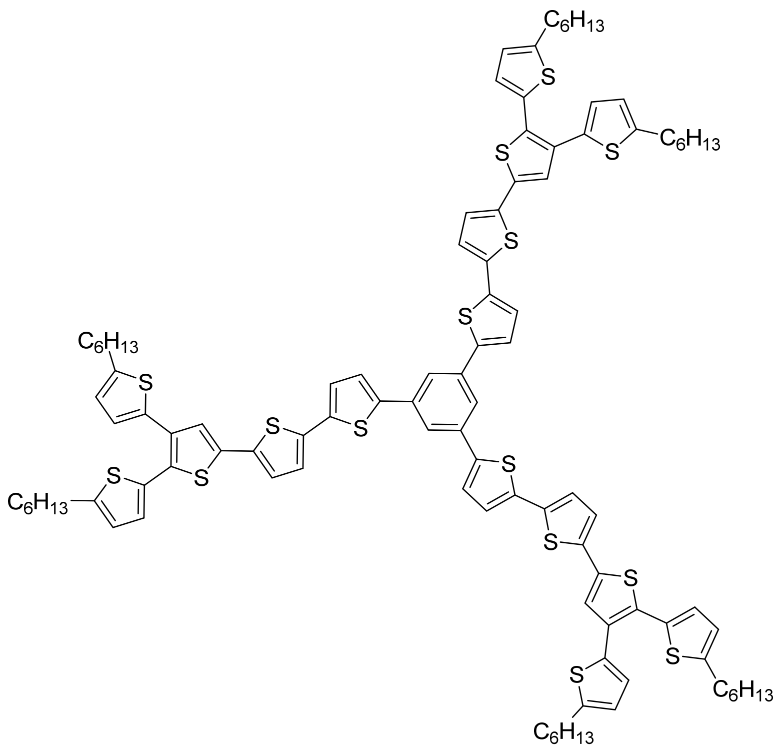
**Scheme S1.** Synthesis of **1**, **2**, and **HexB**.



**1,3,5-Tri(thiophen-2-yl)benzene** (**1**). 2-(Tributylstannyl)thiophene (1.50 mL, 4.71 mmol) was added to a solution of 1,3.5-tribromobenzene (0.501 g, 1.60 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.271 g, 0.237 mmol) in anhydrous DMF (10 mL). The resulting mixture was heated to 100 °C for 16 h. After cooling to room temperature, the mixture was poured into water and extracted with methylene chloride. The organic layers were combined, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (EtOAc:hexanes, 0:100 → 50:50) to afford the title compound as a beige solid (0.301 g, 58 %); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.78 (s, 3H), 7.44 (d, $J$ = 3.6 Hz, 3H), 7.36 (d, $J$ = 4.4 Hz, 3H), 7.15 (dd, $J$ = 4.4; 3.6 Hz, 1H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 143.3, 135.5, 127.9, 125.2, 123.7, 122.5 ppm. The $^1$H and $^{13}$C NMR data matches that found in the literature.[3]



**1,3,5-Tris(5-bromothiophen-2-yl)benzene** (**2**). In the absence of light, **1** (0.102 g, 0.314 mmol) was added to a solution of *N*-bromosuccinimide (0.184 g, 1.04 mmol) in chloroform/acetic acid (10 mL of a 1:1 solution). The resulting solution was stirred at 0 °C for 1 h. The mixture was then allowed to warm to rt and stirred for an additional 12 h. The reaction was quenched with aqueous NaOH. The organic layer was separated, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield a beige solid that was subsequently washed with hexanes (0.142 g, 81 %): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.52 (s, 3H), 7.12 (d, $J$ = 3.6, 3H), 7.07 (d, $J$ = 3.6, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 144.2, 135.1, 130.9, 124.1, 122.0, 112.3 ppm. The $^1$H and $^{13}$C NMR data matches that found in the literature.[2]



**1,3,5-Tris(5'''-hexyl-5''-(5-hexylthiophen-2-yl)-[2,2':5',2'':4'',2'''-quaterthiophen]-5-yl)benzene** (**HexB**). Under argon, degassed toluene (15 mL) was added to a suspension of 4,4,5,5-tetrahexyl-2-(5''-hexyl-5'-(5-hexylthiophen-2-yl)-[2,2':4',2''-terthiophen]-5-yl)-1,3,2-dioxaborolane (**3**) (0.313 g, 0.501 mmol), potassium carbonate (0.189 g, 1.37 mmol), deionized water (1.0 mL), tetrakis(triphenylphosphine)palladium(0) (0.042 g, 0.036 mmol), and **2** (0.076 g , 0.135 mmol). The solution was heated to reflux for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with methylene chloride. The organic layers were combined, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by recrystallization from acetone and obtained as an amber solid in 44 % yield (0.107 g): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.67 (bs, 3H), 7.33 (bs, 3H), 7.19 (bs, 6H), 7.12 (bs, 3H), 7.10 (bs, 3H), 6.95 (bs, 3H), 6.92 (bs, 3H), 6.69 (bs, 6H), 2.80 (m, 12H), 1.71 (m, 12H), 1.35 (m, 36H), 0.93 (m, 18H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 147.8, 146.6, 142.3, 137.3, 136.5, 136.0, 135.5, 134.9, 134.7, 132.7, 132.4, 131.1, 127.7, 126.7, 126.4, 124.7, 124.7, 124.4, 124.2, 121.8, 31.7, 31.6, 30.4, 28.9, 22.7, 14.2 ppm. The $^1$H and $^{13}$C NMR data matches that found in the literature.[4]

## Equipment, materials, and sample preparation for VT-NMR and VT-DOSY

Spectra were collected on an INOVA 500 MHz spectrometer equipped with a 5 mm Varian indirect-detection, triple resonance ($^1$H-$^{19}$F)/$^{13}$C/($^{31}$P-$^{15}$N)PFG probe and Vnmrj v3.51 software using a gradient compensated stimulated echo ("DgcsteSL_cc") pulse sequence with convection correction. Temperature was varied using a FTS Systems TC-84 temperature controller.

Dilute solutions of **HexBQPH** (20 mM and 27 mM) were prepared by dissolving 13.2 mg in 1.0 mL of toluene-$d_8$ and 13.2 mg in 0.75 mL of DMSO-$d_6$, respectively. Dilute solutions of

**HexBQPME** (20 mM and 24 mM) were prepared by dissolving 13.8 mg in 1.0 mL of toluene-$d_8$ and 13.8 mg in 0.75 mL of DMSO-$d_6$, respectively. Dilute solutions of **HexBQPME** (18 mM and 30 mM) were prepared by dissolving 33.5 mg in 1.0 mL of toluene-$d_8$ and 38.6 mg in 1.0 mL of THF-$d_8$, respectively.

**Solvent van der Waals radii and viscosity**

Solvent van der Waals volumes were estimated from molecular models (prepared and MM2 minimized in Chem3D Pro) using Accelrys Discovery Studio 3.5. The volumes were then converted to the van der Waals radius (in Å) through:

$$r_{vdW} = \sqrt[3]{\frac{3(vdW_{vol})}{4\pi}}$$

| **Solvent** | **Van der Waals volume** (Å$^3$) | $r_{\mathrm{vdW}}$ (Å) |
|---|---|---|
| DMSO | 68.75 | 2.541 |
| THF | 73.25 | 2.596 |
| toluene | 92.48 | 2.805 |

Temperature-specific viscosities for toluene-$d_8$ (Figure S8) and DMSO-$d_6$ (Figure S9) were estimated from fitted curves of reported viscosity versus temperature data (see references herein). Temperature-specific viscosities for THF-$d_8$ were estimated by the following equation:[5]

$$\log \eta = -3.670 + \frac{395}{T}$$

Viscosity values are calculated in Poise and then converted to Pascal-seconds (1 Poise = 0.1 Pascal-seconds).

Changes in solvent viscosity with solute aggregation are assumed to be negligible given the range of concentrations evaluated.

**Diffusion coefficient data collection procedure**

First, a normal $^1$H NMR spectrum was taken in order to determine the correct parameters (acquisition time, acquisition delay, spectral width, etc.) for obtaining an accurate 1D spectrum at room temperature. Then, those spectral parameters were transferred to an empty experimental window. In that same window, the DOSY pulse sequence (DgcsteSL_cc) was loaded so that the optimal parameters for collecting 1D spectra were adopted for the DOSY sequence.

Upon the loading of the sequence, the lower and upper limits of gradient strength were set at 1000 and 31000 respectively. Both diffusion gradient length (default = 2.0 ms) and diffusion delay (default = 100.0 ms) were adjusted such that the peak heights in the final spectrum in the array were ~ 10–30% of the peak heights in the first spectrum. Either seven (7) or fifteen (15) spectra were used to determine the diffusion coefficients of the samples—if seven were used, a software calculation correction was used. Once all spectra were collected, they were batch processed and baseline corrected. Then, diffusion coefficients were calculated based on peak integrals of the arrayed decay spectra. Where possible, the solvent diffusion coefficient was also included as a point of comparison. This data was collected as a 2D-DOSY spectrum where chemical shift (x-axis) was plotted against diffusion coefficient (y-axis), and the temperature was recorded. An important consequence of using the peak integrals as the fitting parameter (and using DOSY NMR in general) is that while each chemical shift peak should have an identical diffusion coefficient, the reality is measured diffusion coefficients vary slightly from peak to peak. Therefore, the overall diffusion coefficient of the compound was selected from the chemical shift with the smallest calculated error from decay fitting.

After the necessary data was compiled, the temperature of the instrument was raised by using the temperature controller in increments of roughly 10 °C. The next spectrum was collected at least an hour later to minimize convection. At the new temperature, the diffusion parameters were changed to again match the previously stated requirements, and the spectra were collected using the same methodology. Acknowledged is a rapid exchange between monomer and aggregate on the NMR time scale; therefore, the observed diffusion coefficients reflect a weighted average of the species in solution.

## Variable-temperature $^1$H NMR spectra of HexBQPH

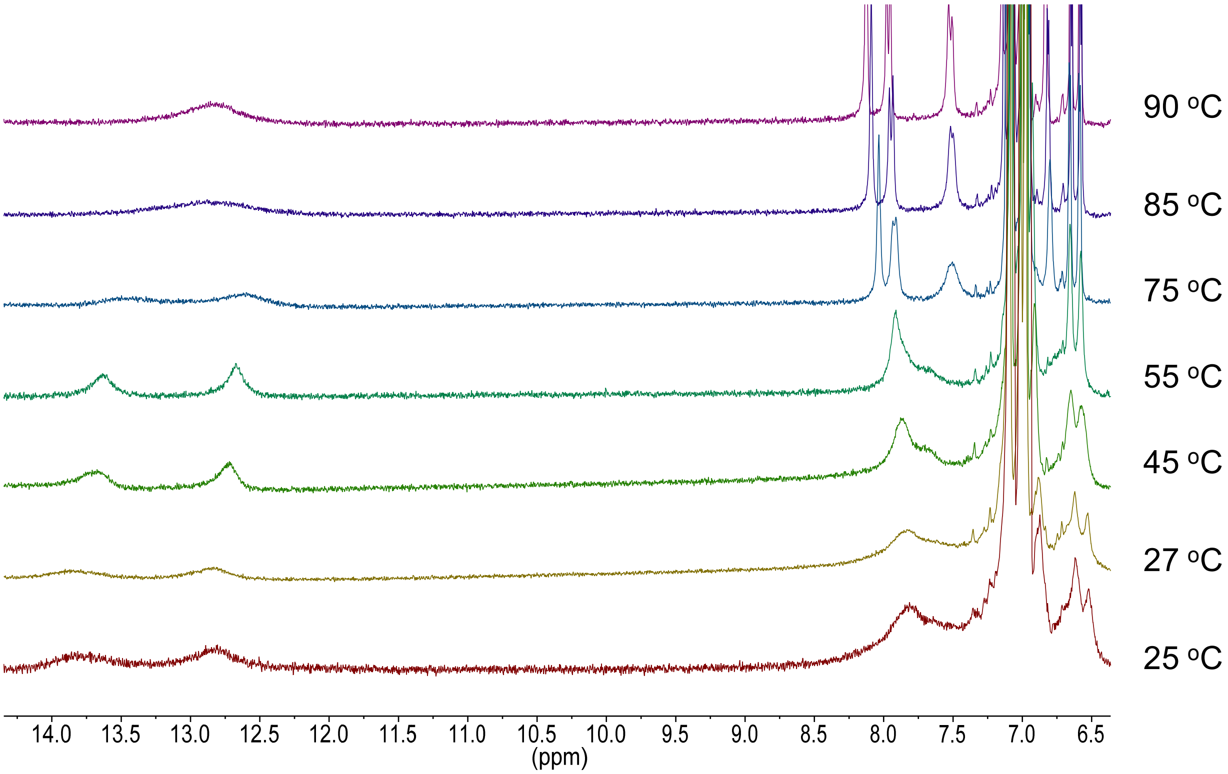


**Figure S1.** Variable-temperature $^1$H NMR spectra of a 10 mM toluene-$d_8$ solution of **HexBQPH**.

## Variable-temperature $^1$H NMR spectra of HexB

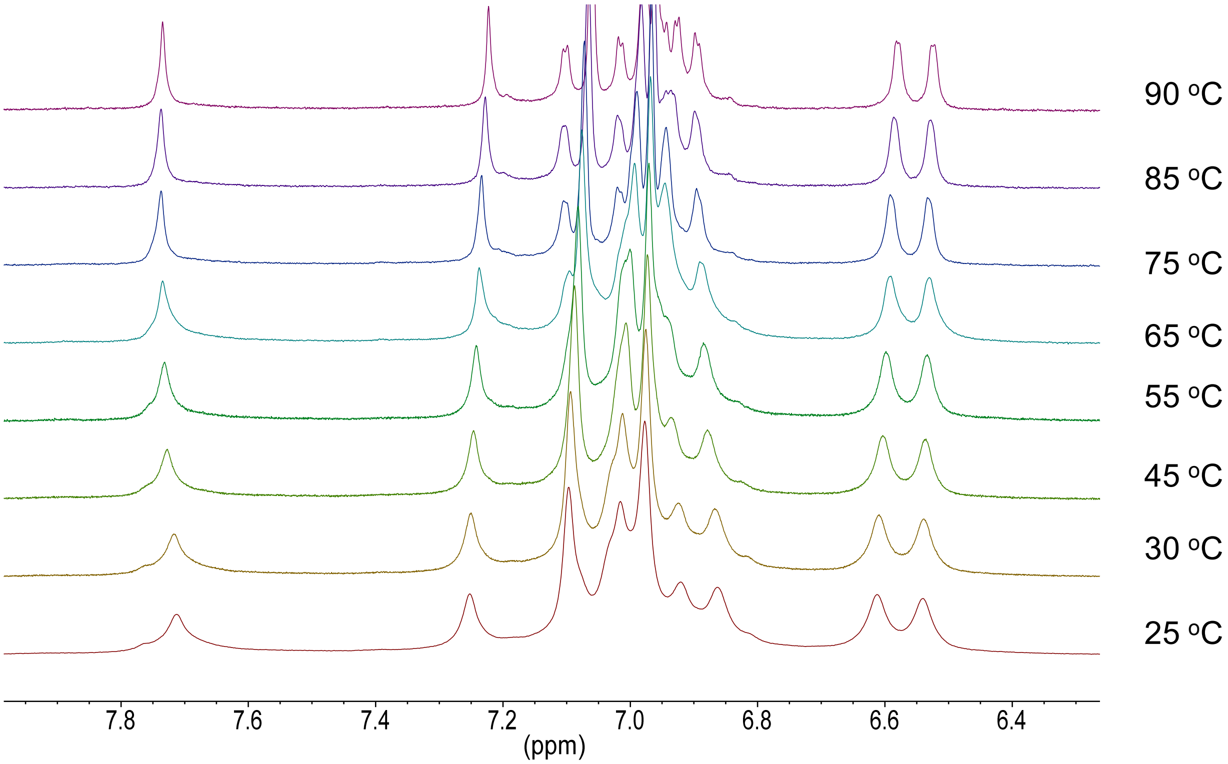


**Figure S2.** Variable-temperature $^1$H NMR spectra of a 10 mM toluene-$d_8$ solution of **HexB**; downfield shoulder at 7.77 ppm results from an unidentified minor impurity.

## Estimation of molecular and assembly size by computation

Approximate molecular and supramolecular dimensions for **HexBQPH** were obtained using the AMBER* forcefield (as implemented in MacroModel v. 9.1). Geometries were obtained from a conformational search (10,000 iterations max, 0.01 convergence threshold, max 10 conformers reported, energy window = default) using the MacroModel v 9.1 application within the Maestro v7.0.110 interface.

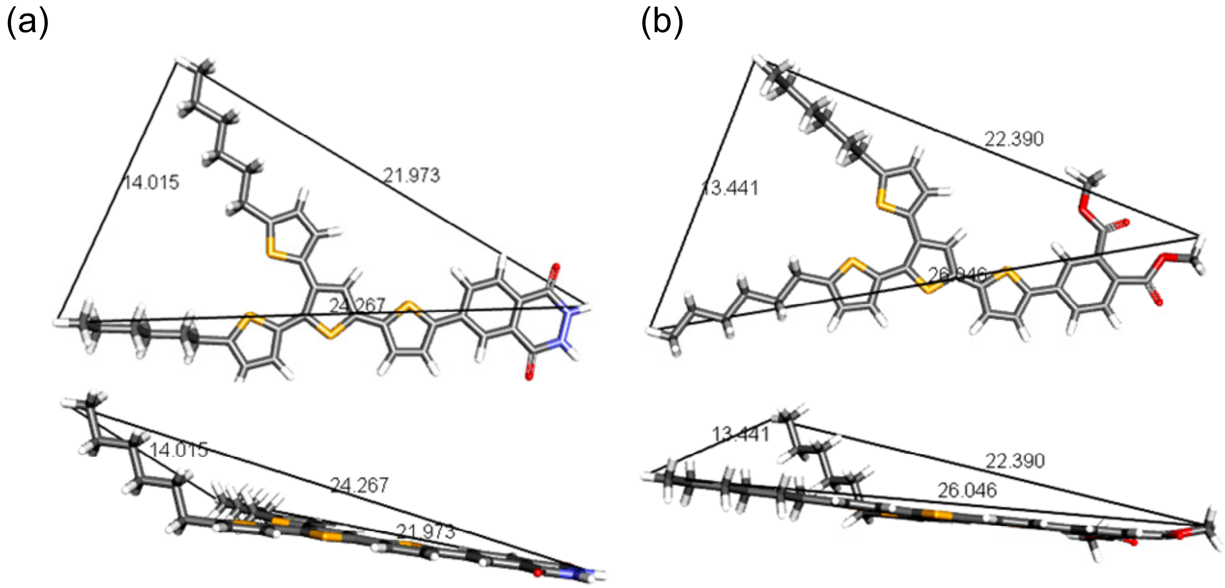


**Figure S3.** Computationally derived molecular dimensions of (a) a monomeric **HexBQPH** (AMBER*; see details above) and (b) **HexBQPME** (MM2 as implemented in Chem3D Pro 13.0).

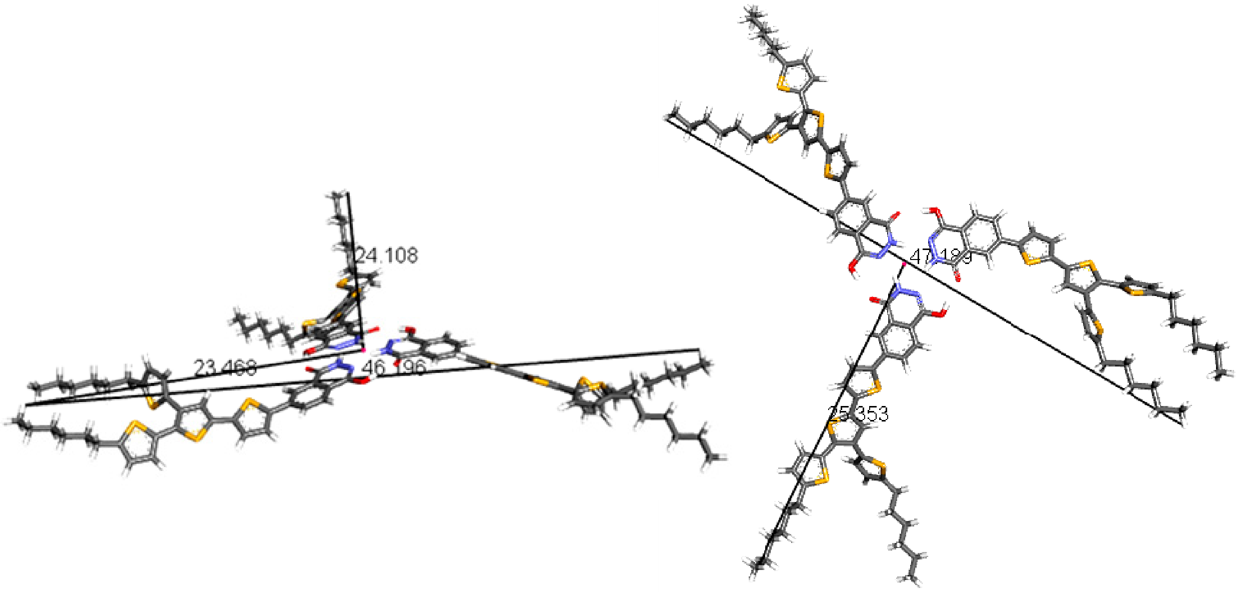


**Figure S4.** Computationally derived molecular dimensions of a discrete trimeric aggregate of **HexBQPH** (AMBER*; see details above)

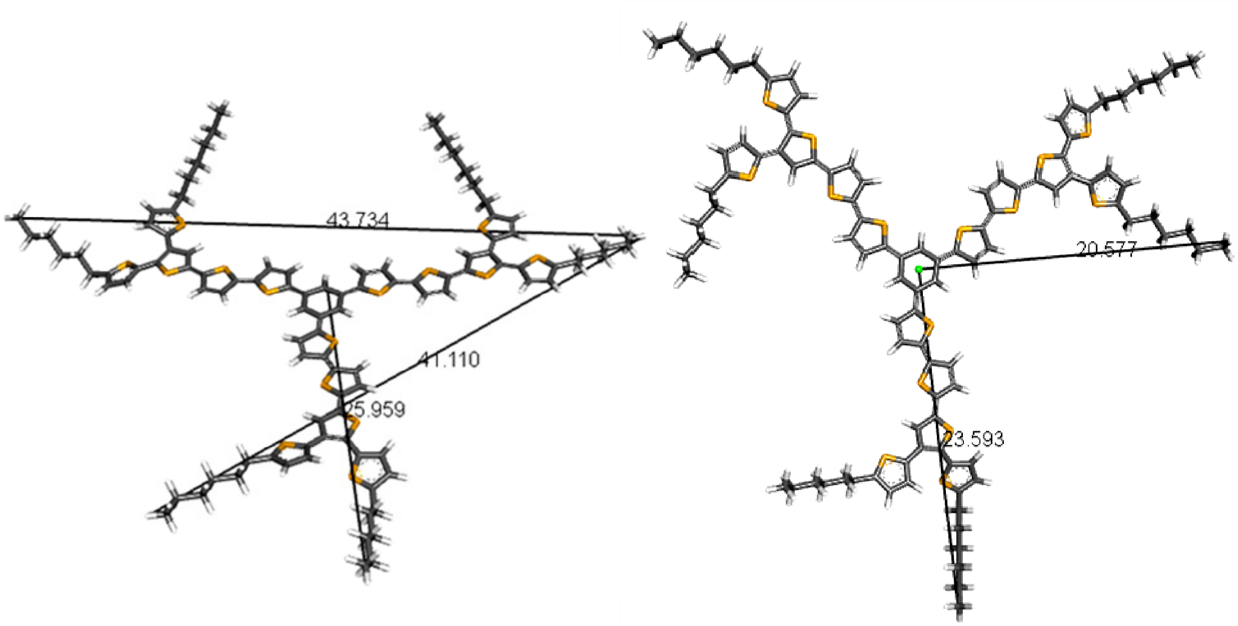
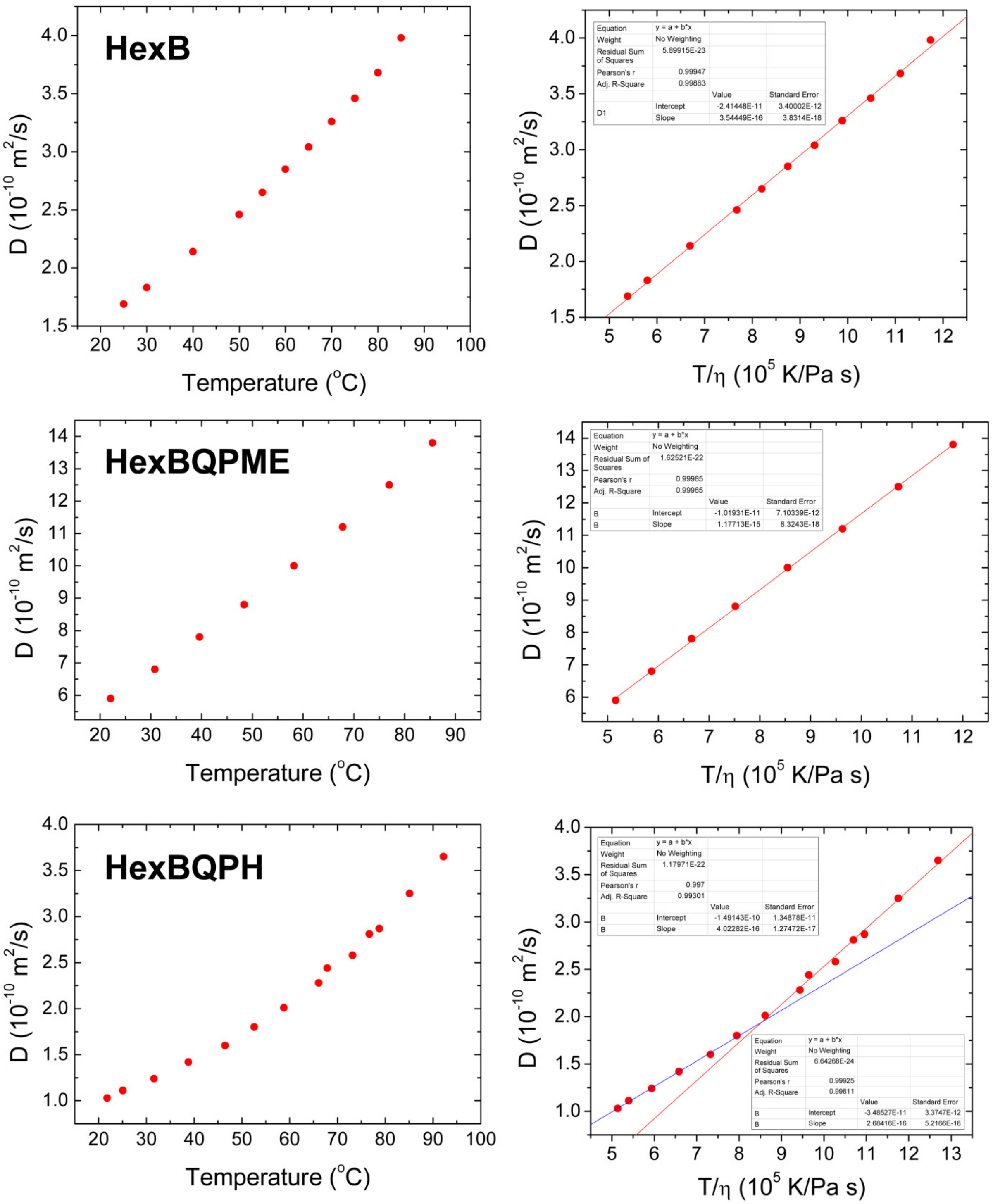


**Figure S5.** Computationally derived molecular dimensions of **HexB** (MM2 as implemented in Chem3D Pro 13.0).



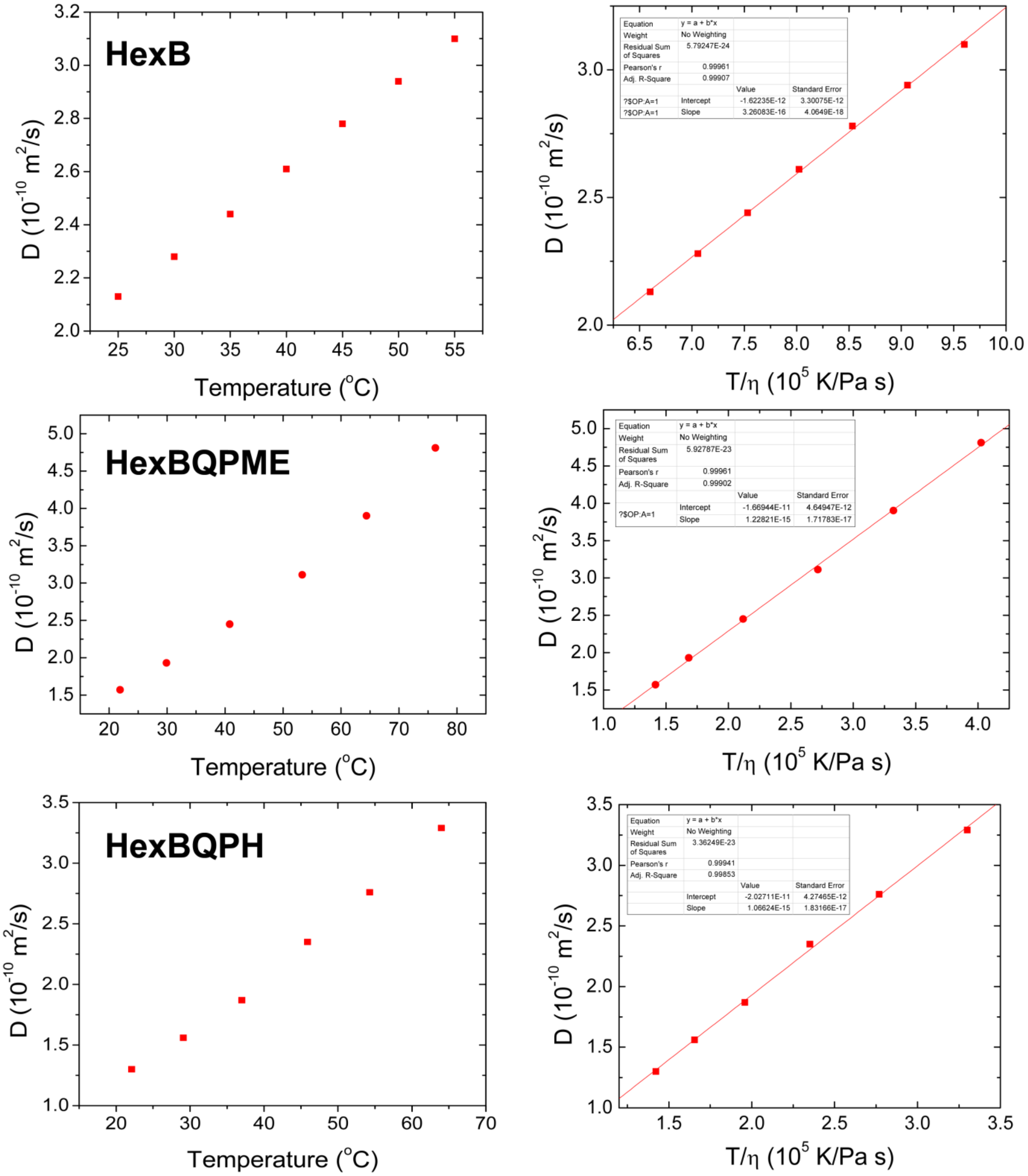
| | | | |
|---|---|---|---|
| Equation | y = a + b*x | | |
| Weight | No Weighting | | |
| Residual Sum of Squares | 5.89915E-23 | | |
| Pearson's r | 0.99947 | | |
| Adj. R-Square | 0.99883 | | |
| | | Value | Standard Error |
| D1 | Intercept | -2.41448E-11 | 3.40002E-12 |
| | Slope | 3.54449E-16 | 3.8314E-18 |

| | | | |
|---|---|---|---|
| Equation | y = a + b*x | | |
| Weight | No Weighting | | |
| Residual Sum of Squares | 1.62521E-22 | | |
| Pearson's r | 0.99985 | | |
| Adj. R-Square | 0.99965 | | |
| | | Value | Standard Error |
| B | Intercept | -1.01931E-11 | 7.10339E-12 |
| B | Slope | 1.17713E-15 | 8.3243E-18 |

| | | | |
|---|---|---|---|
| Equation | y = a + b*x | | |
| Weight | No Weighting | | |
| Residual Sum of Squares | 1.17971E-22 | | |
| Pearson's r | 0.997 | | |
| Adj. R-Square | 0.99301 | | |
| | | Value | Standard Error |
| B | Intercept | -1.49143E-10 | 1.34878E-11 |
| B | Slope | 4.02282E-16 | 1.27472E-17 |

| | | | |
|---|---|---|---|
| Equation | y = a + b*x | | |
| Weight | No Weighting | | |
| Residual Sum of Squares | 6.64268E-24 | | |
| Pearson's r | 0.99925 | | |
| Adj. R-Square | 0.99811 | | |
| | | Value | Standard Error |
| B | Intercept | -3.48527E-11 | 3.3747E-12 |
| B | Slope | 2.68416E-16 | 5.2166E-18 |

**Figure S6.** (left) Diffusion versus temperature plot and (right) linearized diffusion versus temperature plot for **HexB**, **HexBQPME**, and **HexBQPH** in toluene-$d_8$.



| Equation | y = a + b*x | | |
|---|---|---|---|
| Weight | No Weighting | | |
| Residual Sum of Squares | 5.79247E-24 | | |
| Pearson's r | 0.99961 | | |
| Adj. R-Square | 0.99907 | | |
| | | Value | Standard Error |
| ?$OP:A=1 | Intercept | -1.62235E-12 | 3.30075E-12 |
| ?$OP:A=1 | Slope | 3.26083E-16 | 4.0649E-18 |

| Equation | y = a + b*x | | |
|---|---|---|---|
| Weight | No Weighting | | |
| Residual Sum of Squares | 5.92787E-23 | | |
| Pearson's r | 0.99961 | | |
| Adj. R-Square | 0.99902 | | |
| | | Value | Standard Error |
| ?$OP:A=1 | Intercept | -1.66944E-11 | 4.64947E-12 |
| | Slope | 1.22821E-15 | 1.71783E-17 |

| Equation | y = a + b*x | | |
|---|---|---|---|
| Weight | No Weighting | | |
| Residual Sum of Squares | 3.36249E-23 | | |
| Pearson's r | 0.99941 | | |
| Adj. R-Square | 0.99853 | | |
| | | Value | Standard Error |
| | Intercept | -2.02711E-11 | 4.27465E-12 |
| | Slope | 1.06624E-15 | 1.83166E-17 |

**Figure S7.** (left) Diffusion versus temperature plot and (right) linearized diffusion versus temperature plot for **HexB** in THF-$d_8$, **HexBQPME** and **HexBQPH** in DMSO-$d_6$.

**Table S1.** Diffusion versus temperature data with estimated viscosities for **HexBQPH** in toluene-$d_8$.

| Temperature (°C) | Temperature (K) | Viscosity, $\eta$ ($\times 10^{-4}$ Pa s)[a] | $T/\eta$ ($\times 10^{5}$ K/Pa s) | $D$ ($\times 10^{-10}$ m$^2$/s)[b] |
|---|---|---|---|---|
| 21.8 | 294.95 | 5.74 | 5.14 | 1.03 |
| 25.1 | 298.25 | 5.52 | 5.40 | 1.11 |
| 31.6 | 304.75 | 5.13 | 5.94 | 1.24 |
| 38.8 | 311.95 | 4.74 | 6.59 | 1.42 |
| 46.5 | 319.65 | 4.36 | 7.33 | 1.60 |
| 52.6 | 325.75 | 4.10 | 7.95 | 1.80 |
| 58.8 | 331.95 | 3.85 | 8.62 | 2.01 |
| 66.1 | 339.25 | 3.60 | 9.44 | 2.28 |
| 67.9 | 341.05 | 3.54 | 9.64 | 2.44 |
| 73.2 | 346.35 | 3.37 | 10.3 | 2.58 |
| 76.7 | 349.85 | 3.27 | 10.7 | 2.81 |
| 78.8 | 351.95 | 3.21 | 11.0 | 2.87 |
| 85.1 | 358.25 | 3.05 | 11.7 | 3.25 |
| 92.2 | 365.35 | 2.88 | 12.7 | 3.65 |

[a] Based on values derived from Figure S-8. [b] Estimated error for diffusion coefficients = ± 3%.

**Table S2.** Diffusion versus temperature data with estimated viscosities for **HexBQPH** in DMSO-$d_6$.

| Temperature (°C) | Temperature (K) | Viscosity, $\eta$ ($\times 10^{-3}$ Pa s)[a] | $T/\eta$ ($\times 10^{5}$ K/Pa s) | $D$ ($\times 10^{-10}$ m$^2$/s)[b] |
|---|---|---|---|---|
| 22.1 | 295.25 | 2.08 | 1.42 | 1.30 |
| 29.1 | 302.25 | 1.83 | 1.66 | 1.56 |
| 37.0 | 310.15 | 1.58 | 1.96 | 1.87 |
| 45.9 | 319.05 | 1.36 | 2.35 | 2.35 |
| 54.3 | 327.45 | 1.18 | 2.77 | 2.76 |
| 64.0 | 337.15 | 1.02 | 3.30 | 3.29 |

[a] Based on values derived from Figure S-9. [b] Estimated error for diffusion coefficients = ± 3%.

**Table S3.** Diffusion versus temperature data with estimated viscosities for **HexBQPME** in toluene-$d_8$.

| Temperature (°C) | Temperature (K) | Viscosity, $\eta$ ($\times 10^{-4}$ Pa s)[a] | $T/\eta$ ($\times 10^{5}$ K/Pa s) | $D$ ($\times 10^{-10}$ m$^2$/s)[b] |
|---|---|---|---|---|
| 22.1 | 295.25 | 5.72 | 5.16 | 5.90 |
| 30.8 | 303.95 | 5.18 | 5.87 | 6.80 |
| 39.6 | 312.75 | 4.70 | 6.66 | 7.80 |
| 48.4 | 321.55 | 4.28 | 7.52 | 8.80 |
| 58.2 | 331.35 | 3.88 | 8.55 | 10 .0 |
| 67.8 | 340.95 | 3.54 | 9.63 | 11.2 |
| 77 | 350.15 | 3.26 | 10.7 | 12.5 |
| 85.5 | 358.65 | 3.04 | 11.8 | 13.8 |

[a] Based on values derived from Figure S-8. [b] Estimated error for diffusion coefficients = ± 3%.

**Table S4.** Diffusion versus temperature data with estimated viscosities for **HexBQPME** in DMSO-$d_6$.

| Temperature (°C) | Temperature (K) | Viscosity, $\eta$ ($\times 10^{-3}$ Pa s)[a] | $T/\eta$ ($\times 10^{5}$ K/Pa s) | $D$ ($\times 10^{-10}$ m$^2$/s)[b] |
|---|---|---|---|---|
| 21.9 | 295.05 | 2.08 | 1.42 | 1.57 |
| 29.9 | 303.05 | 1.80 | 1.68 | 1.93 |
| 40.8 | 313.95 | 1.48 | 2.12 | 2.45 |
| 53.3 | 326.45 | 1.20 | 2.72 | 3.11 |
| 64.4 | 337.55 | 1.02 | 3.32 | 3.90 |
| 76.3 | 349.45 | 0.868 | 4.02 | 4.81 |

[a] Based on values derived from Figure S-9. [b] Estimated error for diffusion coefficients = ± 3%.

**Table S5.** Diffusion versus temperature data with estimated viscosities for **HexB** in toluene-$d_8$.

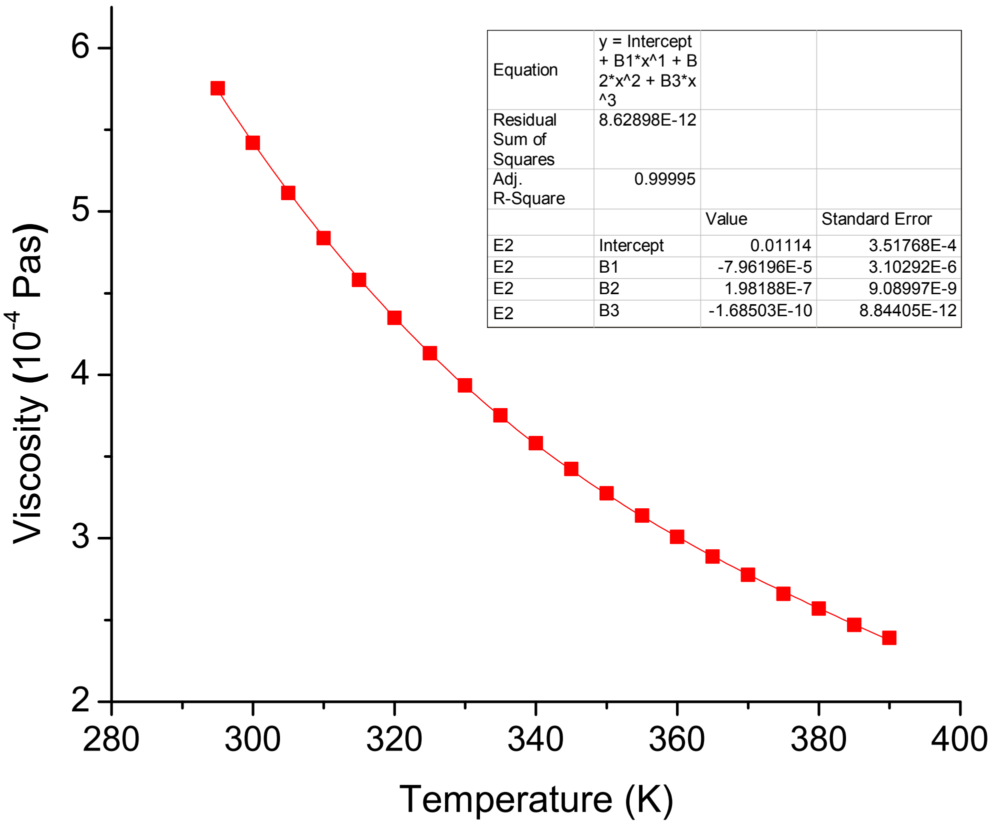
| Temperature (°C) | Temperature (K) | Viscosity, $\eta$ ($\times 10^{-4}$ Pa s)[a] | $T/\eta$ ($\times 10^{5}$ K/Pa s) | $D$ ($\times 10^{-10}$ m$^2$/s)[b] |
|---|---|---|---|---|
| 25.0 | 298.15 | 5.53 | 5.39 | 1.69 |
| 30.0 | 303.15 | 5.22 | 5.80 | 1.83 |
| 40.0 | 313.15 | 4.68 | 6.70 | 2.14 |
| 50.0 | 323.15 | 4.21 | 7.68 | 2.46 |
| 55.0 | 328.15 | 4.00 | 8.20 | 2.65 |
| 60.0 | 333.15 | 3.81 | 8.75 | 2.85 |
| 65.0 | 338.15 | 3.63 | 9.31 | 3.04 |
| 70.0 | 343.15 | 3.47 | 9.89 | 3.26 |
| 75.0 | 348.15 | 3.32 | 10.5 | 3.46 |
| 80.0 | 353.15 | 3.18 | 11.1 | 3.68 |
| 85.0 | 358.15 | 3.05 | 11.7 | 3.98 |

[a] Based on values derived from Figure S-8. [b] Estimated error for diffusion coefficients = ± 3%.

**Table S6.** Diffusion versus temperature data with estimated viscosities for **HexB** in THF-$d_6$

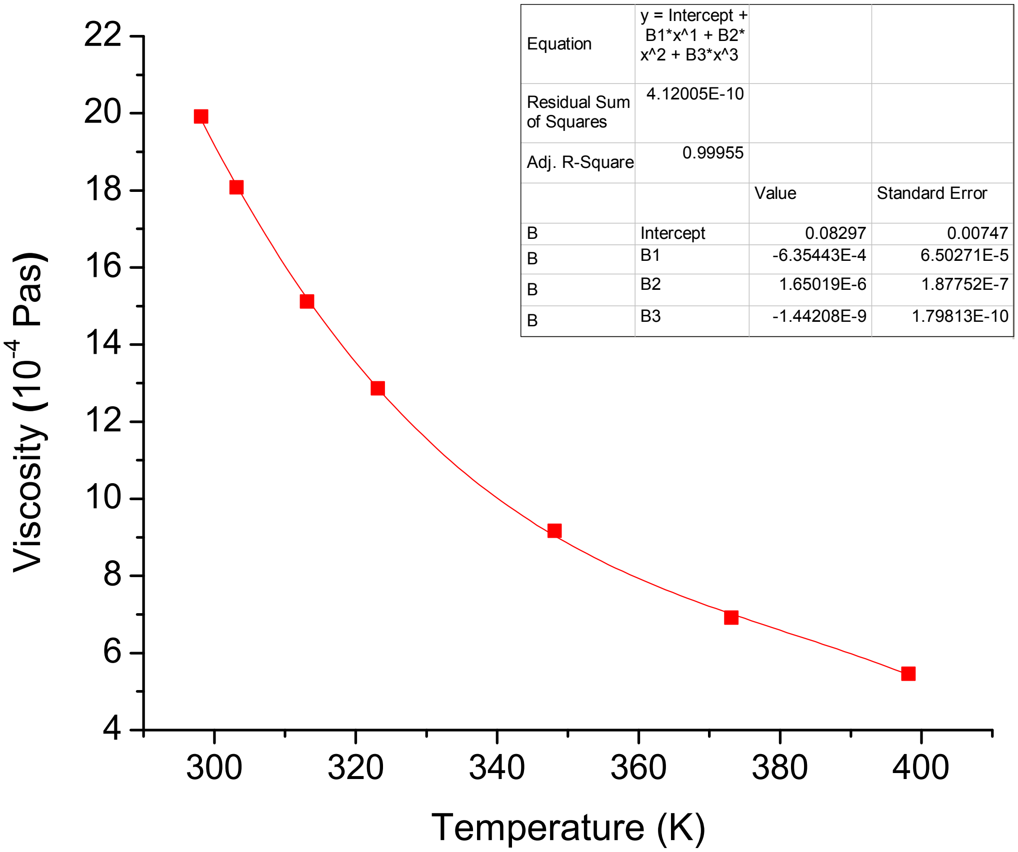
| Temperature (°C) | Temperature (K) | Viscosity, $\eta$ ($\times 10^{-4}$ Pa s)[a] | $T/\eta$ ($\times 10^{5}$ K/Pa s) | $D$ ($\times 10^{-10}$ m$^2$/s)[b] |
|---|---|---|---|---|
| 25 | 298.15 | 4.52 | 6.60 | 2.13 |
| 30 | 303.15 | 4.29 | 7.06 | 2.28 |
| 35 | 308.15 | 4.09 | 7.53 | 2.44 |
| 40 | 313.15 | 3.90 | 8.02 | 2.61 |
| 45 | 318.15 | 3.73 | 8.53 | 2.78 |
| 50 | 323.15 | 3.57 | 9.06 | 2.94 |
| 55 | 328.15 | 3.42 | 9.60 | 3.10 |

[a] Based on values derived from the equation shown on page S6. [b] Estimated error for diffusion coefficients = ± 3%.



| | | | |
|---|---|---|---|
| Equation | y = Intercept + B1*x^1 + B2*x^2 + B3*x^3 | | |
| Residual Sum of Squares | 8.62898E-12 | | |
| Adj. R-Square | 0.99995 | | |
| | | Value | Standard Error |
| E2 | Intercept | 0.01114 | 3.51768E-4 |
| E2 | B1 | -7.96196E-5 | 3.10292E-6 |
| E2 | B2 | 1.98188E-7 | 9.08997E-9 |
| E2 | B3 | -1.68503E-10 | 8.84405E-12 |

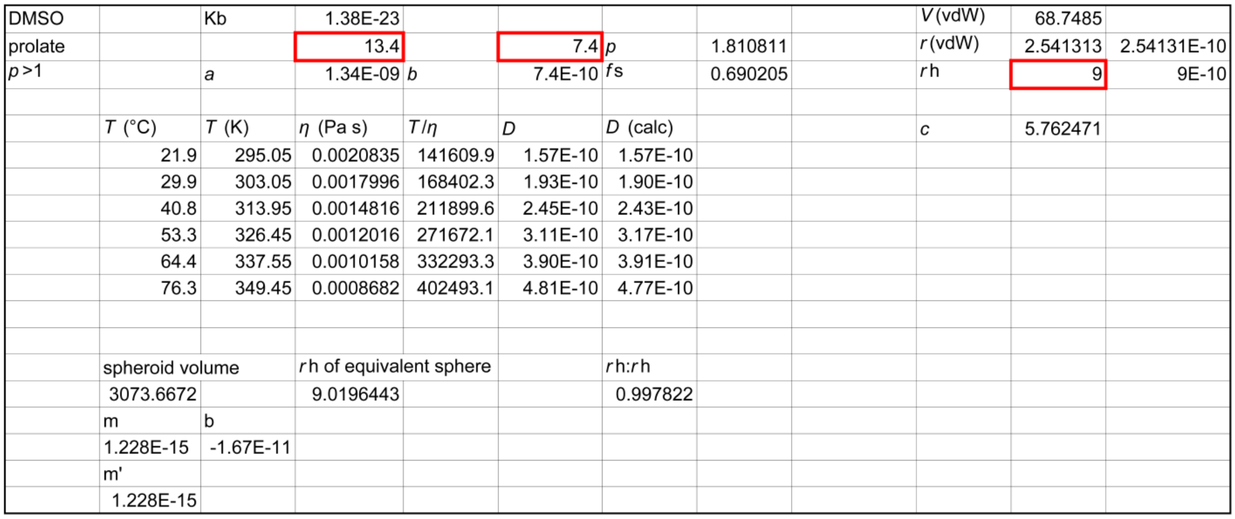
**Figure S8.** Cubic fitting of viscosity versus temperature data for toluene based on values found in the literature.[6]



|  |  |  |  |
|---|---|---|---|
| Equation | y = Intercept + B1*x^1 + B2*x^2 + B3*x^3 |  |  |
| Residual Sum of Squares | 4.12005E-10 |  |  |
| Adj. R-Square | 0.99955 |  |  |
|  |  | Value | Standard Error |
| B | Intercept | 0.08297 | 0.00747 |
| B | B1 | -6.35443E-4 | 6.50271E-5 |
| B | B2 | 1.65019E-6 | 1.87752E-7 |
| B | B3 | -1.44208E-9 | 1.79813E-10 |

**Figure S9.** Cubic fitting of viscosity versus temperature data for DMSO based on values found in the literature.[7]

## Sample fitting procedure to derive $a$, $b$, and $r_h$



| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| DMSO | | Kb | 1.38E-23 | | | | | | $V$(vdW) | 68.7485 | |
| prolate | | | 13.4 | | 7.4 | $p$ | 1.810811 | | $r$(vdW) | 2.541313 | 2.54131E-10 |
| $p$>1 | | $a$ | 1.34E-09 | $b$ | 7.4E-10 | $f$s | 0.690205 | | $r$h | 9 | 9E-10 |
| | | | | | | | | | | | |
| | $T$ (°C) | $T$ (K) | $\eta$ (Pa s) | $T/\eta$ | $D$ | $D$ (calc) | | | $c$ | 5.762471 | |
| | 21.9 | 295.05 | 0.0020835 | 141609.9 | 1.57E-10 | 1.57E-10 | | | | | |
| | 29.9 | 303.05 | 0.0017996 | 168402.3 | 1.93E-10 | 1.90E-10 | | | | | |
| | 40.8 | 313.95 | 0.0014816 | 211899.6 | 2.45E-10 | 2.43E-10 | | | | | |
| | 53.3 | 326.45 | 0.0012016 | 271672.1 | 3.11E-10 | 3.17E-10 | | | | | |
| | 64.4 | 337.55 | 0.0010158 | 332293.3 | 3.90E-10 | 3.91E-10 | | | | | |
| | 76.3 | 349.45 | 0.0008682 | 402493.1 | 4.81E-10 | 4.77E-10 | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | spheroid volume | | $r$h of equivalent sphere | | | $r$h:$r$h | | | | | |
| | 3073.6672 | | 9.0196443 | | | 0.997822 | | | | | |
| | m | b | | | | | | | | | |
| | 1.228E-15 | -1.67E-11 | | | | | | | | | |
| | m' | | | | | | | | | | |
| | 1.228E-15 | | | | | | | | | | |

**Figure S10.** Screenshot of Microsoft Excel spreadsheet used to fit **MeBQPME** in DMSO-$d_6$ using the prolate spheroid model.

## Spreadsheet details

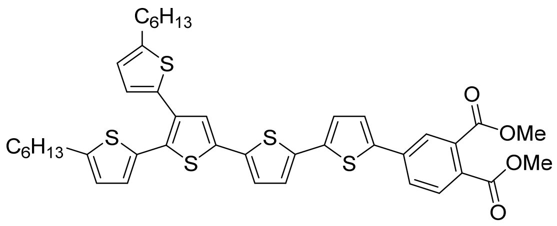
- Values in the red boxes ($a$, $b$, and $r_h$ in Å) are the only ones iteratively changed
- "Kb" is the Boltzmann constant
- "$a$" and "$b$" are the semimajor and semiminor axis values of the prolate spheroid in Å, below them is the value converted to m
- "$p$" is the aspect ratio; embedded in the cell is the ratio $a$:$b$
- "$f_s$" is the frictional coefficient derived from $a$ and $b$ for the prolate spheroid model; embedded in the cell are references to the values for $a$ and $b$ and the formula

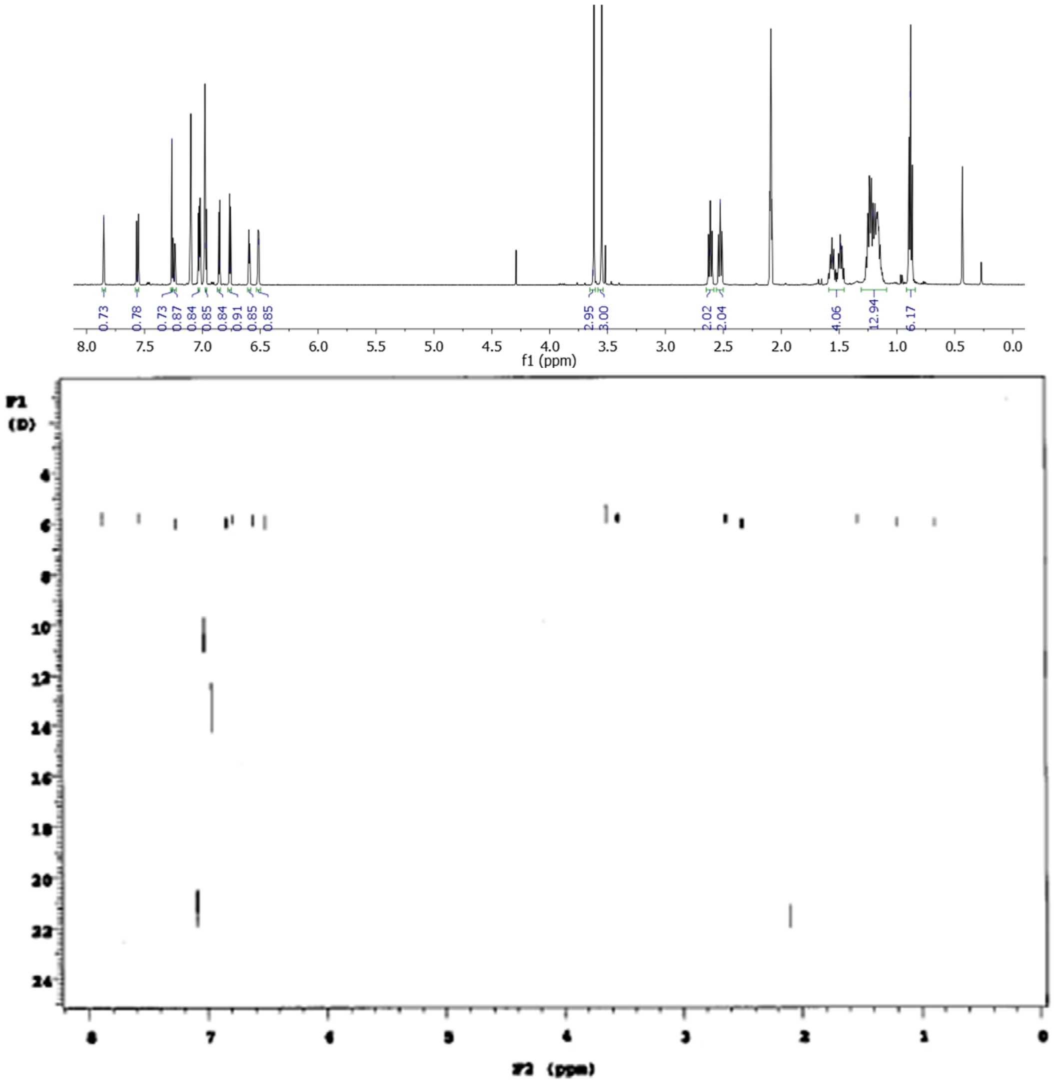
$$f_s = \frac{\left[\sqrt{1-\left(\frac{b}{a}\right)}\right]^2}{\left(\frac{b}{a}\right)^{\frac{2}{3}} \ln\left[\frac{1+\left(\sqrt{1-\left(\frac{b}{a}\right)}\right)^2}{\frac{b}{a}}\right]}$$

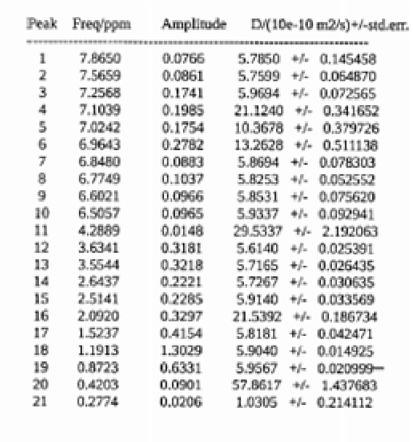
- the equation relating $f_s$ to $a$ and $b$ using the oblate spheroid model is given as equation 5 in the main text. The equation relating $f_s$ to $L$ and $d$ using the cylindrical model is given as (see main text for reference):

$$f_s = 1.0304 + 0.0193\left[\ln\left(\frac{L}{d}\right)\right] + 0.06229\left[\ln\left(\frac{L}{d}\right)\right]^2 + 0.00476\left[\ln\left(\frac{L}{d}\right)\right]^3 + 0.00166\left[\ln\left(\frac{L}{d}\right)\right]^4 + 2.66\times10^{-6}\left[\ln\left(\frac{L}{d}\right)\right]^7$$

- "*V*(vdW)" is the calculated van der Waals volume from Accelrys Discovery Studio 3.5.0 obtained from a MM2 minimized model of DMSO made in Chem3D Pro
- "*r*(vdW)" is the van der Waals radius (in Å, then m) calculated from setting the van der Waals volume equal to the volume of a sphere; embedded in the cell is the formula $r = \sqrt[3]{\frac{3V(vdW)}{4\pi}}$
- "*r*h" is the hydrodynamic radius in Å then converted to m
- "*c*" is size correction factor; embedded in the cell is are references to *r*(vdW) and *r*h and the formula $c = \frac{6}{1+0.695\left(\frac{r_{vdW}}{r_h}\right)^{2.234}}$
- "*T*" and "*D*" are the raw temperature (in °C) and diffusion coefficients (in $m^2/s$); *T* (in °C) was converted to *T* (in K) by adding 273.15
- "$\eta$" is the viscosity in Pa s derived from a reference to the temperature in K and the embedded formula $\eta = 0.08297 - 6.35443 \times 10^{-4}T + 1.65019 \times 10^{-6}T^2 - 1.44208 \times 10^{-9}T^3$ (Figure S9) where *T* is the temperature in K
- "$T/\eta$" is an embedded formula dividing temperature in K by viscosity in Pa s
- "*D*(calc)" is the derived or fitted diffusion coefficient with the modified Stokes-Einstein equation $D = \frac{k_B T}{c f_s \pi \eta r_h}$ with references to Kb, *T* (temperature in K), *c*, *f*s, viscosity ($\eta$), and *r*h that are derived in the spreadsheet
- "Spheroid volume" is the volume of the spheroid generated by *a* and *b* and has the embedded formula $V = \frac{4}{3}\pi a b^2$
- "*r*h of equivalent sphere" is the radius of a sphere with an equivalent volume as the spheroid generated by *a* and *b*; it contains a reference to the value of spheroid volume and has the embedded formula $r = \sqrt[3]{\frac{3V(spheroid)}{4\pi}}$
- "*r*h:*r*h" is the ratio of the hydrodynamic radius and the equivalent sphere radius generated by the volume of the spheroid; embedded is the ratio of "*r*h an equivalent sphere" to "*r*h" (the value in the red box); this ratio provides the data necessary to adjust *a* and *b* such that the volume generated by them matches the volume generated by *r*h

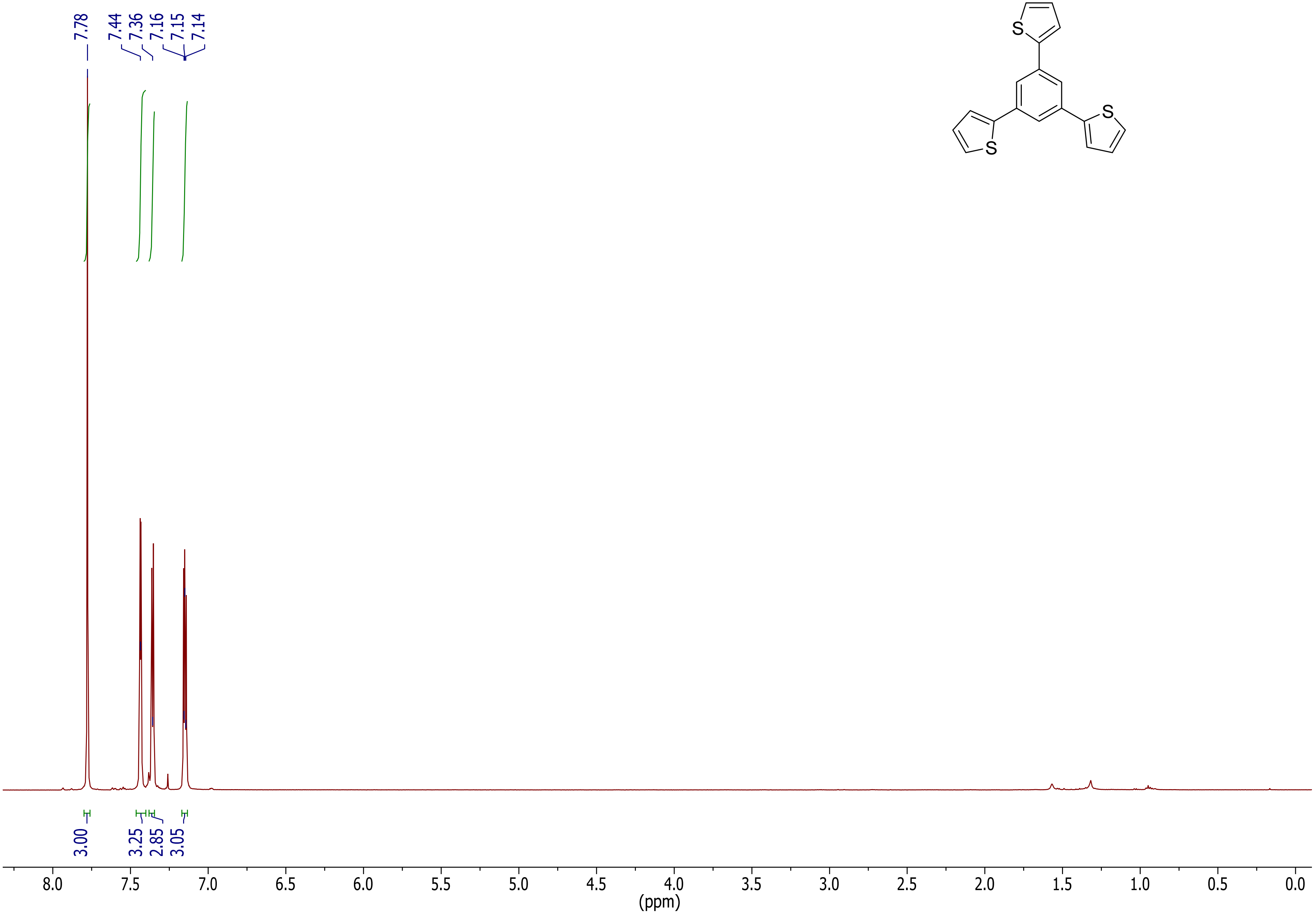


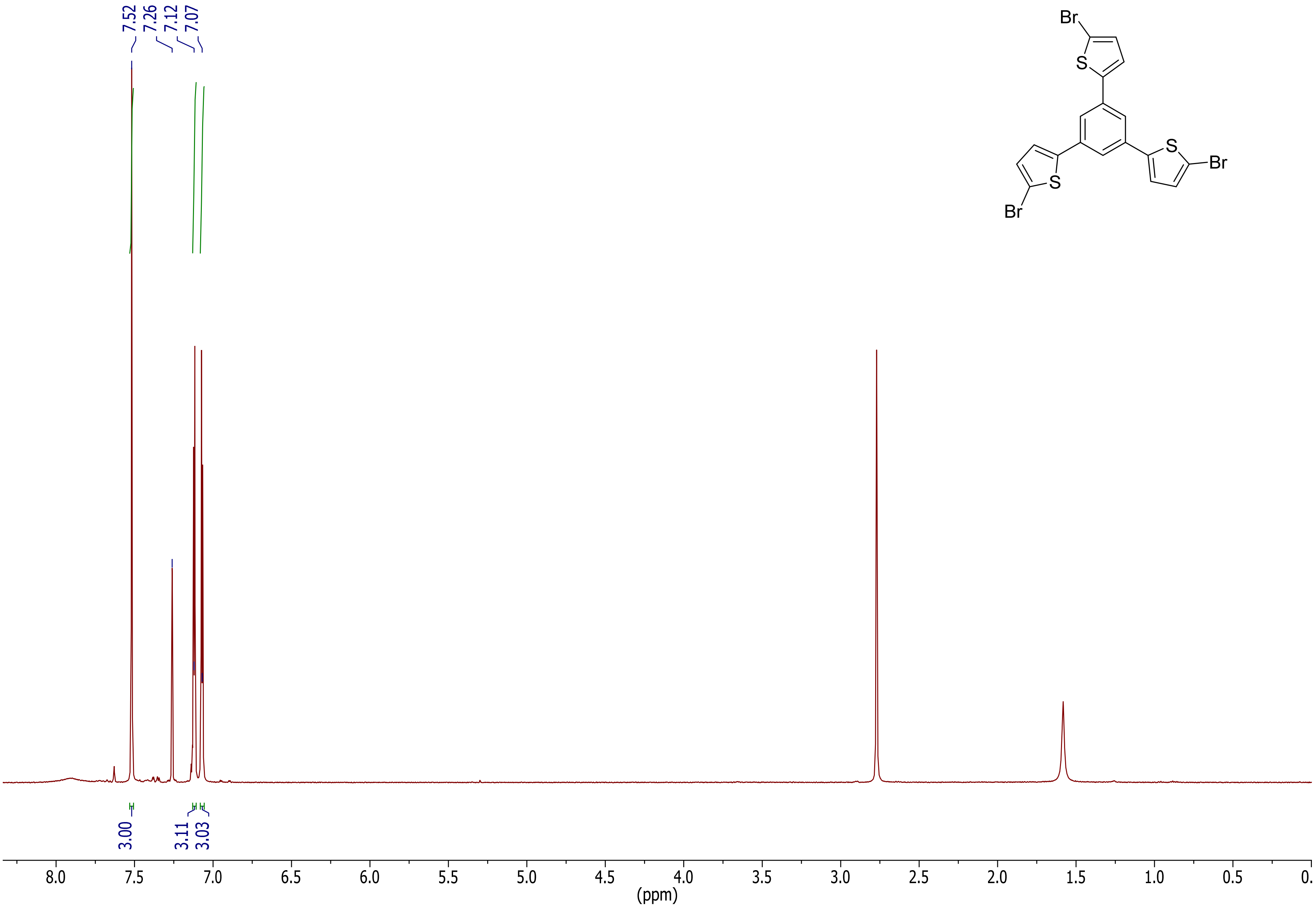


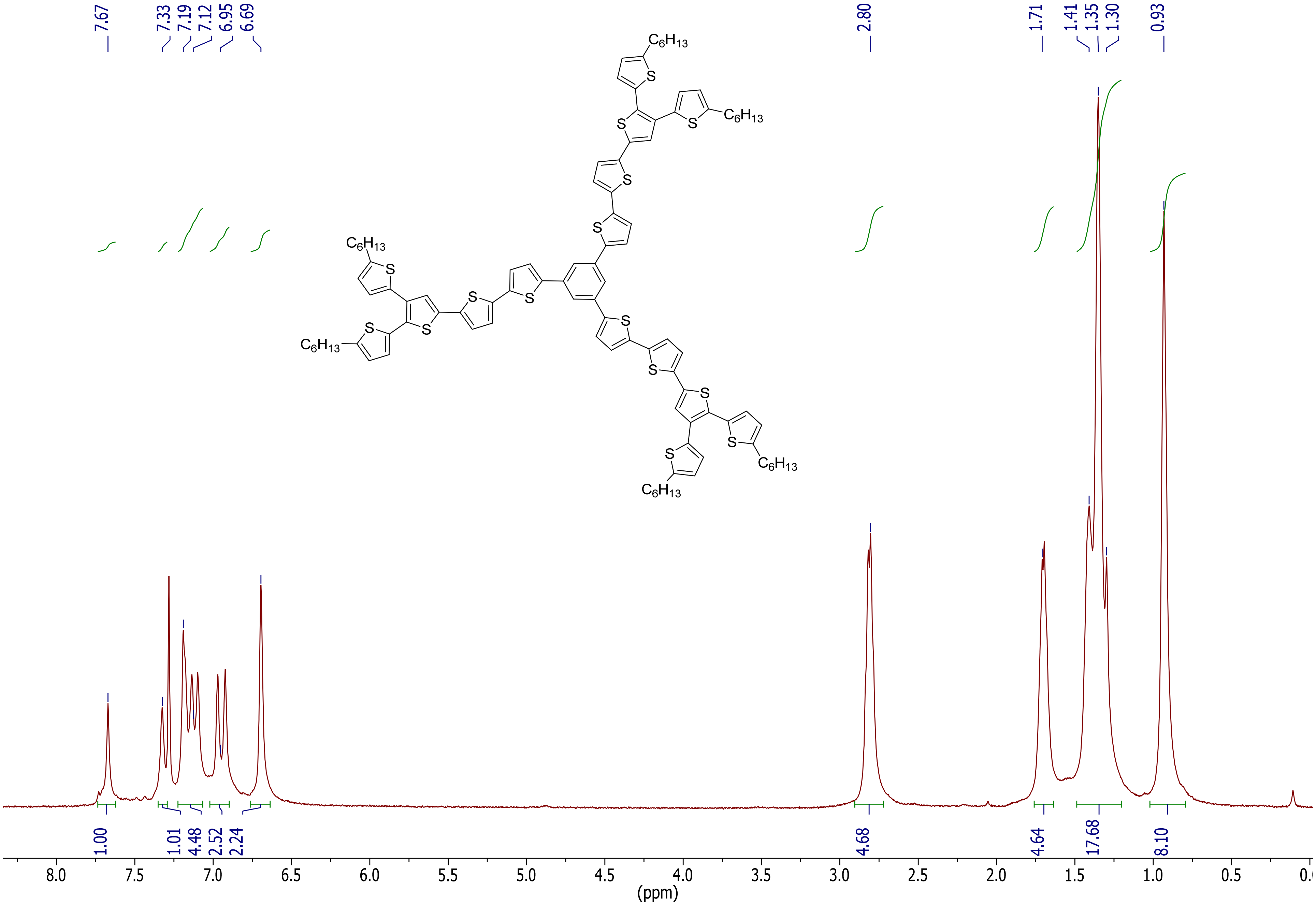


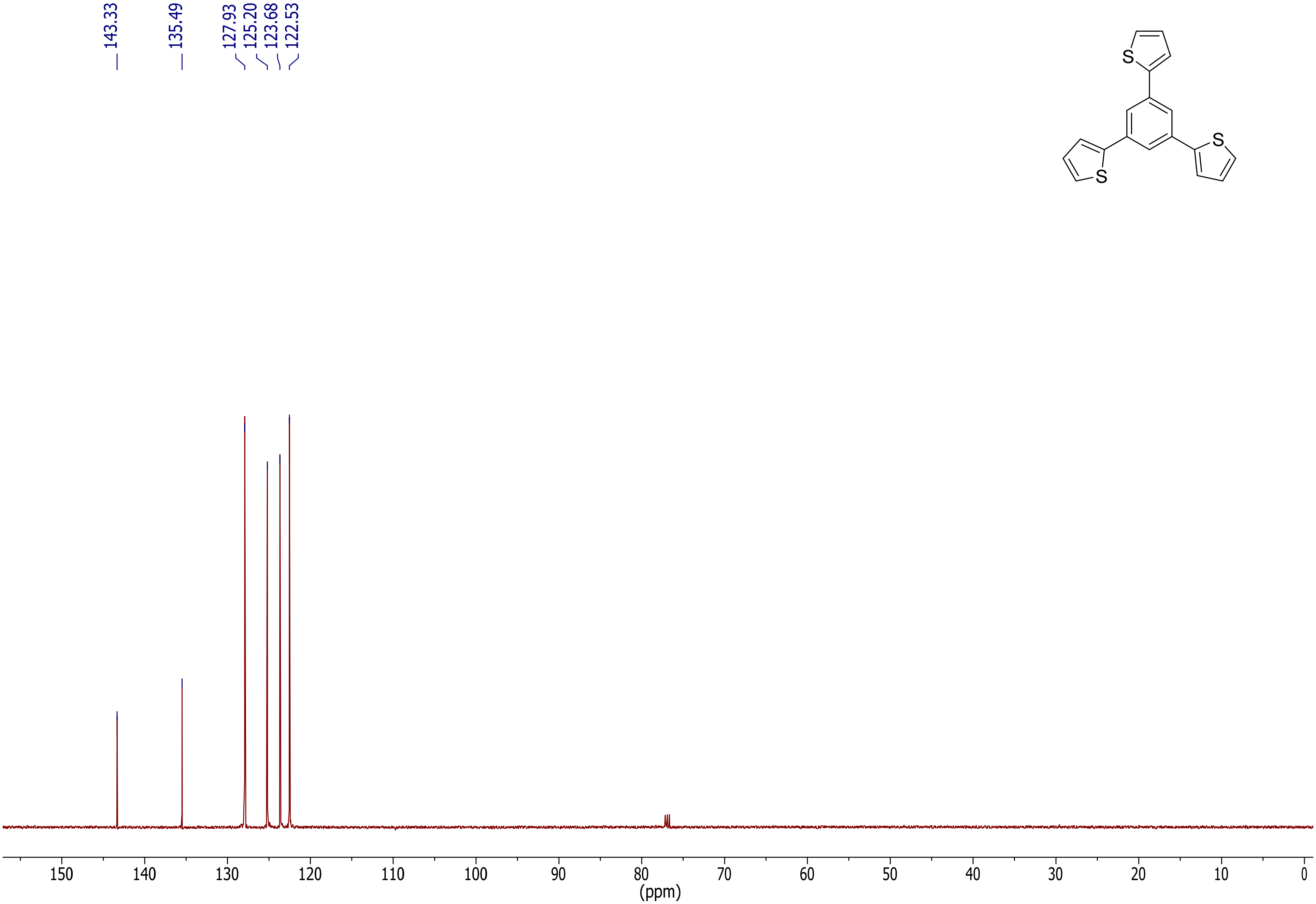
| Peak | Freq/ppm | Amplitude | D/(10e-10 m2/s)+/-std.err. | | |
|---|---|---|---|---|---|
| 1 | 7.8650 | 0.0766 | 5.7850 | +/- | 0.145458 |
| 2 | 7.5659 | 0.0861 | 5.7599 | +/- | 0.064870 |
| 3 | 7.2568 | 0.1741 | 5.9694 | +/- | 0.072565 |
| 4 | 7.1039 | 0.1985 | 21.1240 | +/- | 0.341652 |
| 5 | 7.0242 | 0.1754 | 10.3678 | +/- | 0.379726 |
| 6 | 6.9643 | 0.2782 | 13.2628 | +/- | 0.511138 |
| 7 | 6.8480 | 0.0883 | 5.8694 | +/- | 0.078303 |
| 8 | 6.7749 | 0.1037 | 5.8253 | +/- | 0.052552 |
| 9 | 6.6021 | 0.0966 | 5.8531 | +/- | 0.075620 |
| 10 | 6.5057 | 0.0965 | 5.9337 | +/- | 0.092941 |
| 11 | 4.2889 | 0.0148 | 29.5337 | +/- | 2.192063 |
| 12 | 3.6341 | 0.3181 | 5.6140 | +/- | 0.025391 |
| 13 | 3.5544 | 0.3218 | 5.7165 | +/- | 0.026435 |
| 14 | 2.6437 | 0.2221 | 5.7267 | +/- | 0.030635 |
| 15 | 2.5141 | 0.2285 | 5.9140 | +/- | 0.033569 |
| 16 | 2.0920 | 0.3297 | 21.5392 | +/- | 0.186734 |
| 17 | 1.5237 | 0.4154 | 5.8181 | +/- | 0.042471 |
| 18 | 1.1913 | 1.3029 | 5.9040 | +/- | 0.014925 |
| 19 | 0.8723 | 0.6331 | 5.9567 | +/- | 0.020999 |
| 20 | 0.4203 | 0.0901 | 57.8617 | +/- | 1.437683 |
| 21 | 0.2774 | 0.0206 | 1.0305 | +/- | 0.214112 |

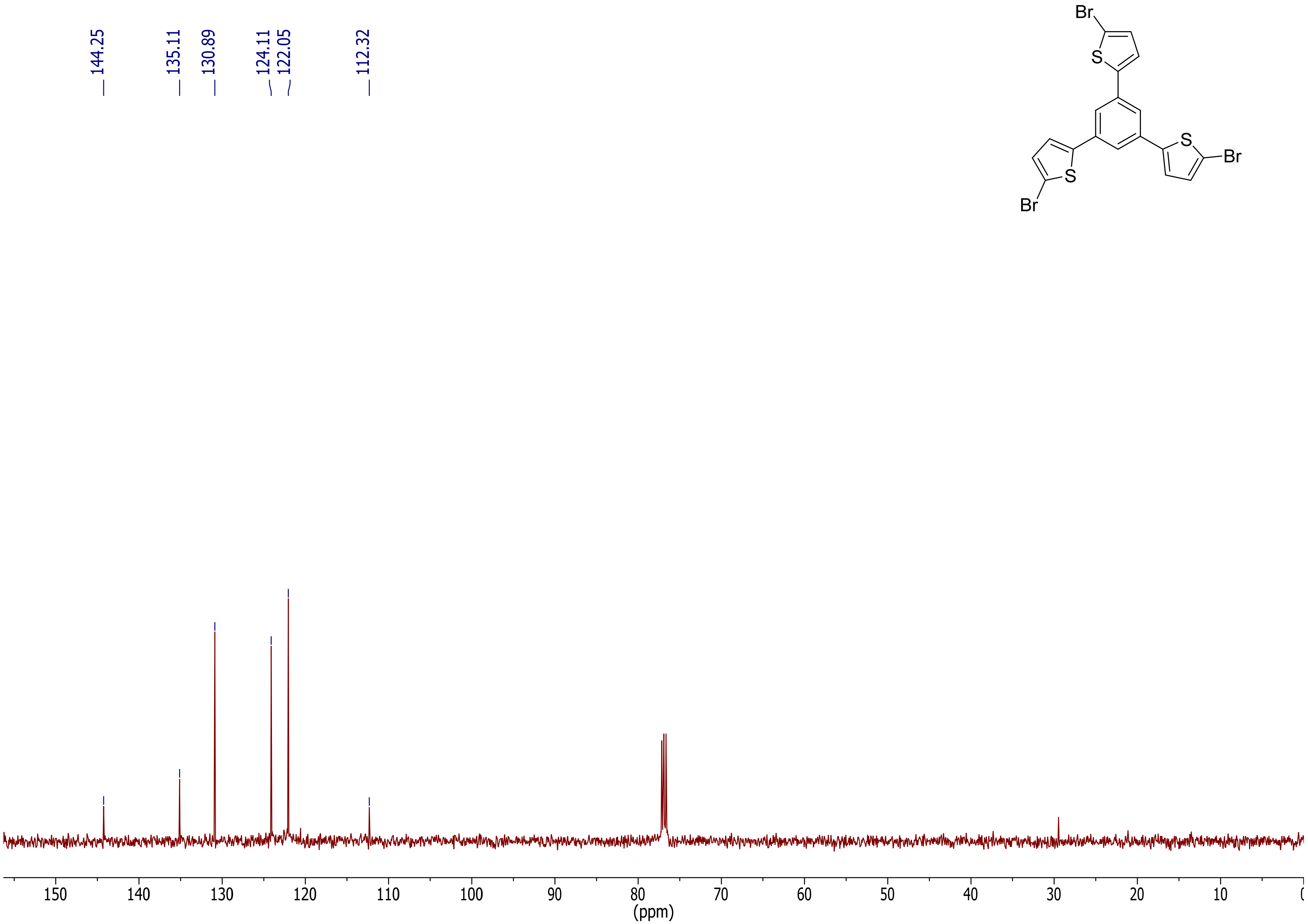
**Figure S11.** Raw diffusion coefficient data for **HexBQPME** in toluene-$d_8$ (20 mM). The $^1$H NMR and DOSY NMR spectra/data are shown.

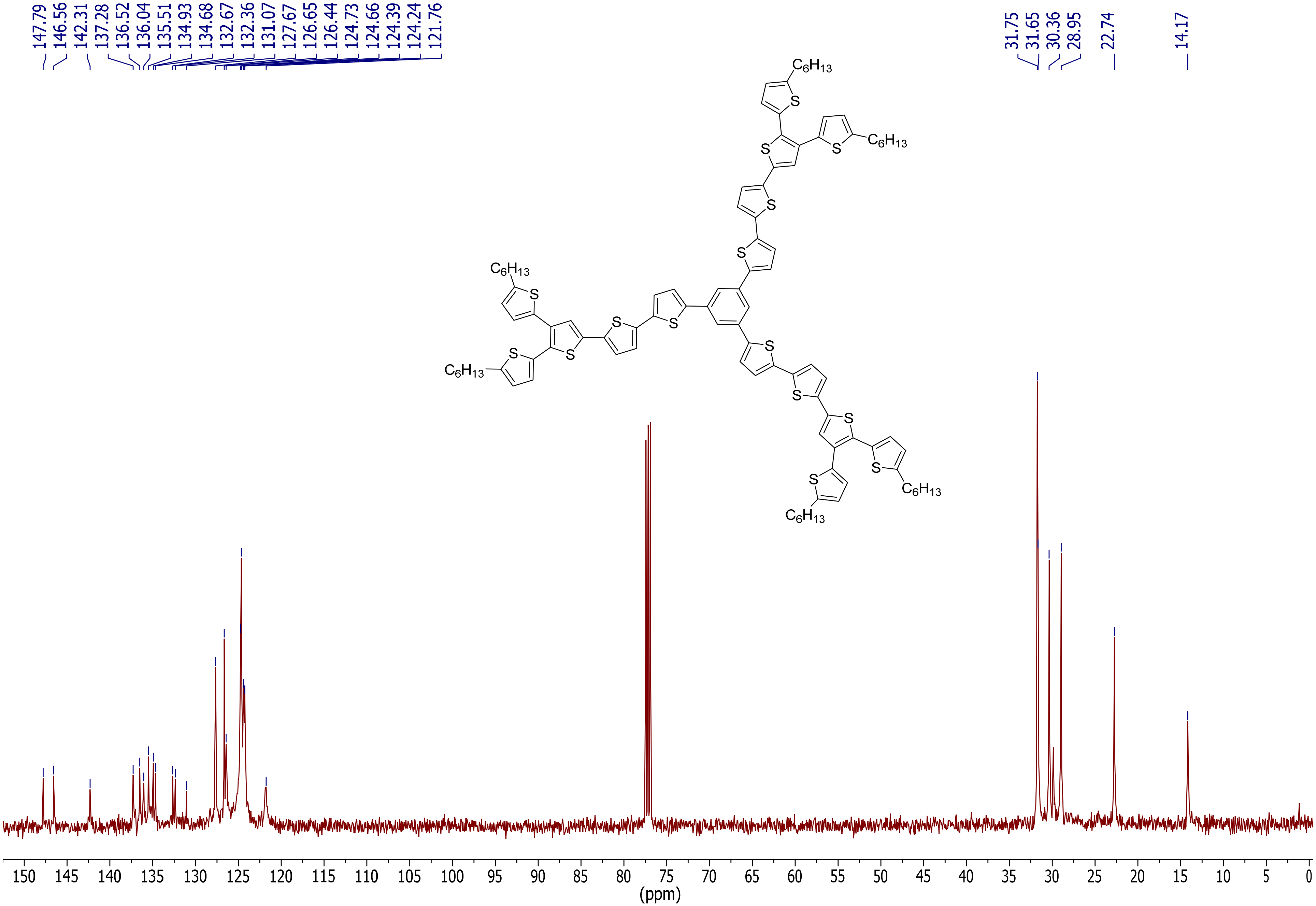

7.78
7.44
7.36
7.16
7.15
7.14
S
S
S
3.00
3.25
2.85
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


7.52
7.26
7.12
7.07
3.00
3.11
3.03
Br
S
Br
S
S
Br
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
(ppm)


7.67
7.33
7.19
7.12
6.95
6.69
2.80
1.71
1.41
1.35
1.30
0.93
1.00
1.01
4.48
2.52
2.24
4.68
4.64
17.68
8.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)
S
$C_6H_{13}$


143.33
135.49
127.93
125.20
123.68
122.53
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)
S
S
S


144.25
135.11
130.89
124.11
122.05
112.32
Br
S
Br
S
S
Br
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)


147.79
146.56
142.31
137.28
136.52
136.04
135.51
134.93
134.68
132.67
132.36
131.07
127.67
126.65
126.44
124.73
124.66
124.39
124.24
121.76
31.75
31.65
30.36
28.95
22.74
14.17
S
C6H13
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
(ppm)

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