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Electronic Supplementary Information

Donor-acceptor interaction-driven folding of linear naphthalene-glycol oligomers templated by a rigid bipyridinium rod

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Compound 1. 3,6-dichloropyridazine (2.0g, 13.5mmol) and 4,4'-bipyridine (10.5 g, 67.3 mmol) was placed in a 25 mL Shrek tube, which was then degassed and recharged with argon and sealed. The mixtures were heated to 120^{o}C for 2 days. After being cooled to room temperature, the resulting solid was washed with acetone and diethyl ether and further recrystallized in CH_3OH to give compound **1** as a grey solid (4.0 g, 64%). ^{1}H NMR (400MHz,CD_3OD): δ 9.96 (d, *J* = 8.0 Hz, 4H), 9.16 (s, 2H), 8.94 (t, 8 H), 8.18 (d, *J* = 4.0 Hz, 4H). ^{13}C NMR (125MHz, CD_3OD): δ 159.29, 159.27, 152.07, 145.30, 142.97, 128.54, 127.34 and 123.85. MS(ESI): *m/z* 195.2 $[M-2Cl]^{2+}$. HRMS(MALDI): Calcd. for $C_{24}H_{18}N_6$: 390.1587. Found: 390.1585.

Compound PBDV. Compound **1** (0.46 g, 1.0 mmol), anhydrous CH_3CN (15 mL) and CH_3I (2.4 mL) were mixed in a 25 mL Shrek tube and was then heated to 60^{o}C for 4 days after being degassed and recharged with argon. When the reaction completed (monitored by TLC), the mixture was cooled to room temperature and the resulting precipitate was washed with acetone to give a red solid. It was further dissolved in H_2O (60 mL) and NH_4PF_6 (1.3 g, 8.0 mmol) was added and the mixture stirred for 2h. The resulting precipitates were filtrated and washed with a small amount of water and dried to give compound **PBDV** as a light yellow solid (0.86 g, yield 86%).^{1}H NMR (400 MHz, CD_3CN): δ 9.68 (d, *J* = 4.0 Hz, 4 H), 8.94 (d, *J* = 8.0 Hz, 4 H), 8.84 (s, 2 H), 8.78 (d, *J* = 4.0Hz, 4 H), 8.53 (d, *J* = 8.0 Hz, 4 H), 4.46 (s, 6 H).^{13}C NMR (125 MHz, CD_3CN): δ 158.76, 147.57, 145.37, 128.82, 128.13 and 49.67. MS (ESI): *m/z* 420.1 $[M - 4PF_4]^{+}$. HRMS(MALDI): Calcd. for $C_{26}H_{24}N_6$: 420.2057. Found: 420.2053.

Compound 3.[1] 1,5-dioxynaphthalene (1.0 g, 6.25mmol), K_2CO_3 (1.034 g, 7.5 mmol), CH_3I (0.43 mL, 6.24 mmol) and acetone (20 mL) were mixed in a 50 mL flask. The mixture was heated to reflux for 24h and filtrated after cooling to room temperature. The filtrate was evaporated and the resulting residue was dissolved in ethyl acetate, which was further washed with H_2O and brine and dried over $MgSO_4$. Column chromatography (acetone/PE = 1:5) was further used to give pure compound **3** as an yellow-green solid (0.4 g, yield 37%).^{1}H NMR (300 MHz, acetone-d_6): δ 8.90 (s,1 H), 7.81 (d, *J*=6.3 Hz,1 H), 7.71 (d, *J*=6.0Hz, 1 H), 7.36 (t, *J* = 6.0 Hz, 1 H), 7.27 (t, *J* = 6.0 Hz, 1 H), 6.94 (d, *J* = 6.0 Hz, 2 H), 4.00 (s,1 H). MS (EI): *m/z* 174$[M]^{+}$.

Compound 5.[2] 1,5-dioxynaphthalene (5.0 g, 31 mmol) and K_2CO_3 (1.8 g, 12.9 mmol) were placed in a 250 mL three-necked flask, which was then degassed and recharged with argon. Acetone (60 mL) was added and the mixture was heated to 50^{o}C. Compound **4**[3] (2.6 g, 5.17 mmol, dissolved in 50 mL acetone) was then added slowly into the above reaction mixture. The mixture was refluxed for 12h and then cooled to room temperature. After being filtrated, the filtrate was evaporated and the resulting residue was dissolved in ethyl acetate, which was further washed with H_2O and brine and dried over $MgSO_4$ and concentrated under reduced pressure. The crude was purified by column chromatography (PE/EA = 2:1) to give compound **5** (1.13 g, yield 45%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J*=6.3 Hz, 2 H), 7.72 (d, *J*=6.3 Hz,2 H), 7.31 (t, *J*=6.3 Hz, 2 H), 7.21 (t, *J*=6.3 Hz,2 H), 6.80 (d, *J*=5.4 Hz,2 H), 6.75 (d, *J*=5.4 Hz,2 H), 5.78 (s, 2 H), 4.22 (t, *J* = 3.6 Hz, 4 H), 3.95 (t, *J* = 3.6 Hz, 4 H), 3.78 (t, *J* = 1.5 Hz, 4 H), 3.72 (t, *J* = 1.8 Hz, 4 H). MS (ESI): *m/z* 477.2 $[M-H]^-$.

Compound 6.[4] Prepared in 40% yield as a light purple oil from compound **4** and 1,5-dioxynaphthalene according to a procedure similar to that described for compound **5**. ^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.7 Hz, 2 H), 7.77 (d, *J* = 8.4 Hz, 4 H), 7.31 (t, *J* = 6.6 Hz, 6 H), 6.83 (d, *J* = 7.8 Hz, 2 H), 4.28 (t, *J* = 4.6 Hz, 4 H), 4.12 (t, *J* = 4.8 Hz, 4 H), 3.98 (t, *J* = 4.9 Hz, 4 H), 3.78 (dd, J_1 = 3.8 Hz, J_2 = 5.4 Hz, 4 H), 3.67-3.57 (m,16 H), 2.40 (s,6 H). MS (ESI): *m/z* 843.4 $[M + Na]^+$.

Compounds7[5] and D_1[6]. K_2CO_3 (3.0 g, 23 mmol) and compound **3** (1.0 g, 5.75 mmol) were mixed in acetone (100 mL) and heated to reflux. Compound **4** (8.6 g, 17.2 mmol, dissolved in 60 mL acetone) was then added to the above reaction mixture slowly. The reaction mixture was refluxed for 24h. After being cooled to room temperature, the mixture was filtrated. The filtrate was evaporated and the resulting residue was dissolved in CH_2Cl_2, which was further washed with H_2O and brine and dried over $MgSO_4$. After being concentrated, the residue was subjected to column chromatography (acetone/PE = 1:5 to 1:3) to give compound **7** as a viscous oil (2.4 g, yield 83%) and compound $\mathbf{D_1}$ as a white solid (0.24 g, yield 16%).

Compound 7. ^1H NMR (300 MHz, $CDCl_3$): δ 7.82 (dd, J_1 = 3.6 Hz, J_2 = 8.7 Hz, 2 H), 7.75 (d, *J* = 8.1 Hz, 2 H), 7.33-7.26 (m, 5 H), 6.81 (d, *J* = 7.5 Hz, 2 H), 4.26 (t, *J* = 4.8 Hz, 2 H), 4.09 (t, *J* = 4.5 Hz, 2 H), 3.96 (t, *J* = 2.4 Hz, 5 H), 3.74 (t, *J* = 2.4 Hz, 2 H), 3.64-3.52 (m,8 H). MS (ESI): *m/z* 527.4 $[M+Na]^+$.

Compound $\mathbf{D_1}$. ^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (dd, J_1 = 1.5 Hz, J_2 = 8.1 Hz, 4 H), 7.34 (m,4 H), 6.81 (d, *J*= 5.7 Hz,4 H), 4.26 (t, *J* = 3.6 Hz, 4 H), 3.96 (t, *J* = 3.6 Hz, 10 H), 3.78 (t, *J* = 1.8 Hz, 4 H), 3.72 (t, *J* = 1.8 Hz, 4 H). MS (ESI): *m/z* 529.5 $[M + Na]^+$.

Compound 8.[5] Prepared in 45% yield as an oil from 1,5-dioxynaphthalene and compound **7** according to a procedure similar to that described for compound **5**. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86-7.73 (m, 4 H), 7.36-7.19 (m, 4 H), 6.82-6.74 (m,4 H), 6.10 (s,1 H), 4.22 (dd, J_1 = 3.0 Hz, J_2 = 3.6 Hz, 4 H), 3.96 (d, *J* = 4.2 Hz, 7 H), 3.78 (d, *J* = 3.9 Hz, 4 H), 3.72 (t, *J* = 3.6 Hz, 4 H). MS (ESI): *m/z* 515.2 $[M + Na]^+$.

Compound 9.[5] Prepared in 80% yield as an oil from compound **3** and compound **6**

according to a procedure similar to that described for compound **5**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86-7.76 (m,6 H), 7.36-7.29 (m, 6 H), 6.80 (dd, J_1 = 1.8 Hz, J_2 = 5.7 Hz, 4 H), 4.26 (dd, J_1 = 1.8 Hz, J_2 = 6.6 Hz, 6 H), 3.97 (t, J = 3.6 Hz, 9 H), 3.80-3.76 (m, 8 H), 3.73-3.70 (m, 4 H), 3.66-3.64 (m, 4 H), 3.59-3.55 (m, 4 H), 2.40 (s, 3 H). MS (ESI): *m/z* 845.4 $[M + Na]^+$.

Compound 10.[5] Prepared in 76% yield as an oil from compound **6** and compound **8** according to a procedure similar to that described for compound **5**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86-7.81 (m,6 H), 7.77 (d, J = 6.0 Hz, 2 H), 7.36-7.28 (m, 8 H), 6.79 (t, J = 6.0 Hz, 6 H), 4.27-4.22 (m, 10 H), 3.98 (d, J = 3.6 Hz, 14 H), 3.79-3.75 (m, 11H), 3.72-3.70 (m, 8 H), 3.66-3.63 (m, 4 H), 3.58-3.55 (m, 4 H), 2.40 (s,3 H). MS (ESI): *m/z* 1141.7 $[M + H]^+$.

Compound D_2.[6] Prepared in 55% yield from compound **5** and compound **7** according to a procedure similar to that described for compound **5**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (t, J= 7.8 Hz, 8 H), 7.35 (m,8 H), 6.78 (t, J= 8.1 Hz, 8 H), 4.24 (dd, J_1 = 4.5 Hz, J_2 = 4.8 Hz, 12 H), 3.96 (s, 18 H), 3.79-3.70 (m, 24 H). MS (ESI): *m/z* 1166.0 $[M + Na]^+$.

Compound D_3. Prepared in 40% yield from compound **5** and compound **9** according to a procedure similar to that described for compound **5**. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.84 (t, J = 12.0 Hz,12 H), 7.36-7.29 (m, 12 H), 6.81-6.77 (m,12 H), 4.26-4.22 (m, 20 H), 3.98-3.94 (m, 26 H), 3.79-3.77 (m, 20 H), 3.72-3.70 (m, 20 H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.31, 154.51, 154.47, 126.90, 126.86, 126.78, 125.25, 125.20, 114.75, 114.54, 105.83, 105.79, 104.63, 71.14, 69.95, 68.03 and 55.66. MS (MALDI): *m/z* 1803.9 $[M + Na]^+$. HRMS(MALDI): Calcd. for $C_{102}H_{122}O_{27}Na$: 1801.8051. Found: 1801.8065.

Compound D_4. Prepared in 50% yield from compound **5** and compound **10** according to a procedure similar to that described for compound **5**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (t, J = 12.0 Hz, 16 H), 7.34-7.29 (m, 16 H), 6.81-6.77 (m, 16 H), 4.26-4.22 (m, 26 H), 3.97-3.94 (m, 32 H), 3.79-3.77 (m, 30 H), 3.72-3.70 (m, 30 H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.18, 154.38, 154.34, 126.77, 126.72, 126.64, 125.15, 125.11, 114.62, 114.40, 105.70, 105.67, 104.52, 70.98, 69.80, 67.88 and 55.52. MS (MALDI): *m/z* 2439.8 $[M + Na]^+$. HRMS(MALDI): Calcd. for $C_{138}H_{166}O_{37}Na$: 2438.1013. Found: 2438.1000.

Typical procedures for the spectroscopic experiments

^{1}H NMR experiments

Compound **PBDV**, DAN oligomers **D_1-D_4** and their equivalent molar mixtures were dissolved in a binary solvent $CD_3CN/CDCl_3$ (4:1), respectively. All the samples were treated with ultra-sonication and the resulting homogeneous solutions were then subjected to a Bruker Advance 400 MHz spectrometer at ambient temperature.

The UV-vis titrations and evaluation of binding constants

Aliquots of a stock solution of compound **PBDV (**1.0 mM) in a binary solvent $CH_3CN/CHCl_3$ (4:1) were added to the solutions of DAN oligomers **D_1-D_4** (1.0×10^{-5} M) in $CH_3CN/CHCl_3$ (4:1), respectively. The mixtures were subjected to a Unico-4802 UV-vis double beam spectrophotometer at 25 ℃ and the spectra were then recorded. The association constants for the 1:1 complexes were determined by Benesi-Hildebrand (B-H) plots (O. K. Abou-Zied, *Spectrochimica Acta Part A*, 2005, **62**, 245-251.).

The fluorescence titrations and Job's plots

Aliquots of a stock solution of compound **PBDV** (2.0 mM) in a binary solvent $CH_3CN/CHCl_3$ (4:1) were added to the solutions of DAN oligomers **D_1-D_4** (3.0×10^{-6} M) $CH_3CN/CHCl_3$ (4:1), respectively, and the fluorescence spectra were recorded with a F-4600 FL spectrophotometer at 25 ℃. The excitation wavelength was 329 nm with the slit of a = b = 5.0 nm under a voltage of 400 V. For the Job's plots, the fluorescence emissions of the solutions of DAN oligomers **D_1-D_4** were reordered in the presence of varied ratio of compound **PBDV** (9:1~1:9) in a binary solvent $CH_3CN/CHCl_3$ (4:1), with a total concentration of ([**D_n**] + [**PBDV**]) to be 1.5×10^{-7} M at 25^{o}C. The differences in emission intensity (ΔInt) of the DAN oligomers in the presence and absence of compound **PBDV** were plotted against [**D_n**]/([**D_n**] +[**PBDV**]) to generate the Job's plots.

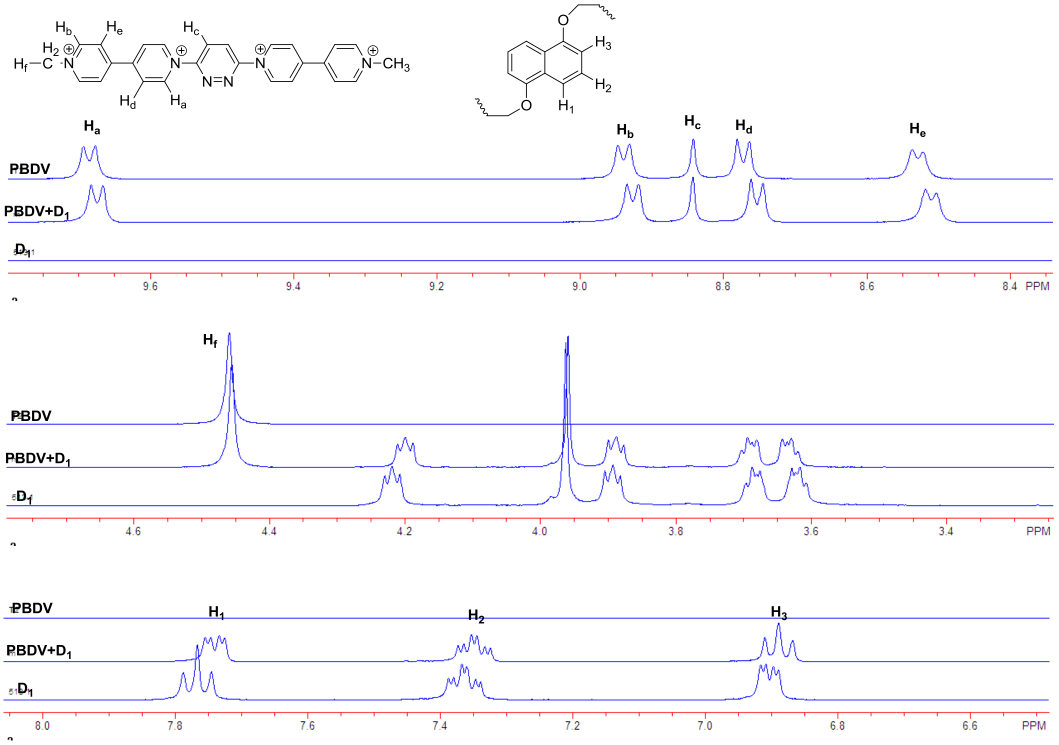

Figure S1 Partial ^{1}H NMR spectra of **PBDV**, **D_1** and their 1:1 mixture in $CD_3CN/CDCl_3$ (4:1, 3.0 mM).

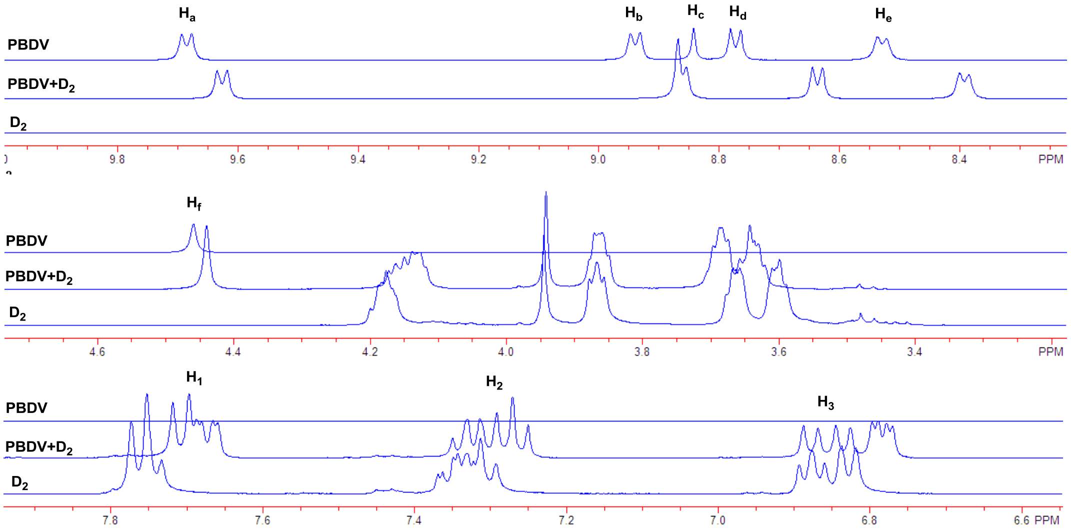

Figure S2 Partial ^{1}H NMR spectra of **PBDV**, **D_2** and their 1:1 mixture in $CD_3CN/CDCl_3$ (4:1, 3.0 mM).

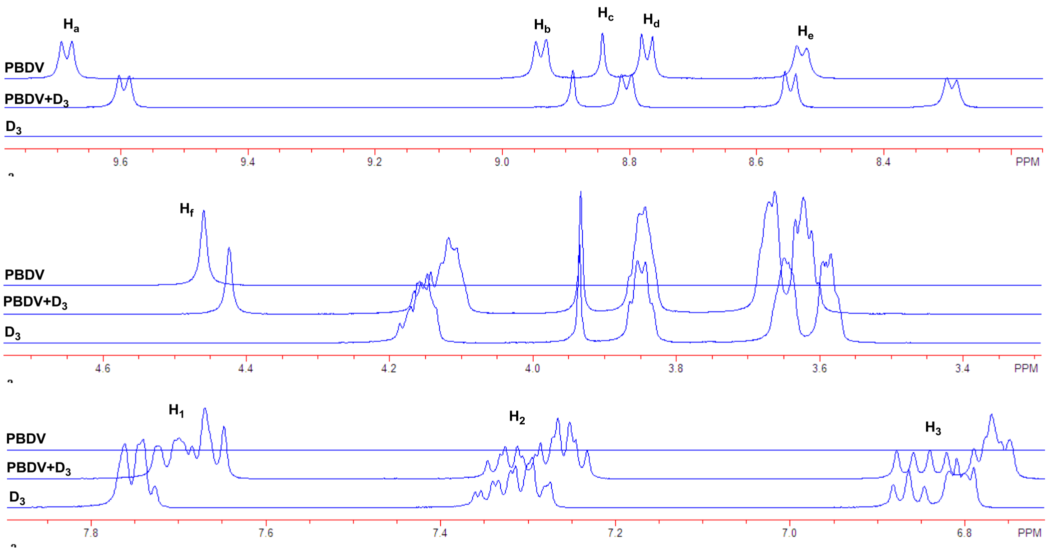

Figure S3 Partial ^{1}H NMR spectra of **PBDV**, **D_3** and their 1:1 mixture in $CD_3CN/CDCl_3$ (4:1, 3.0 mM).

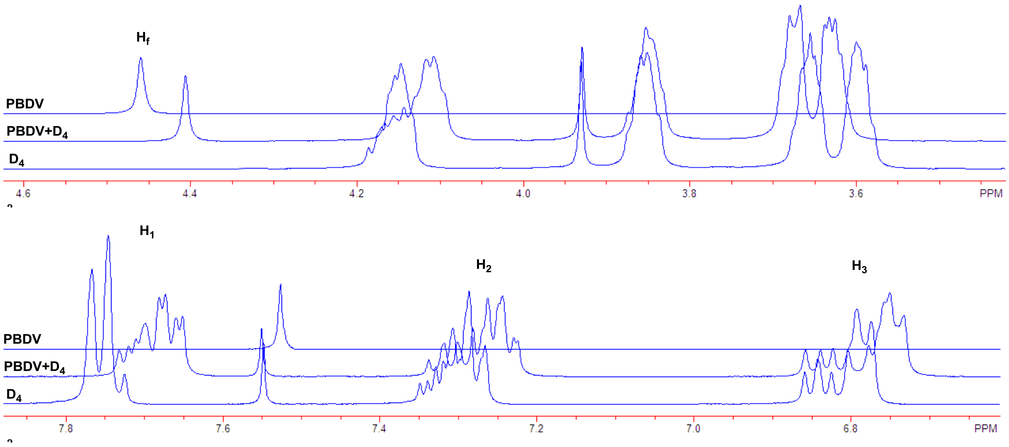

Figure S4 Partial ^{1}H NMR spectra of **PBDV**, **D_4** and their 1:1 mixture in $CD_3CN/CDCl_3$ (4:1, 3.0 mM).

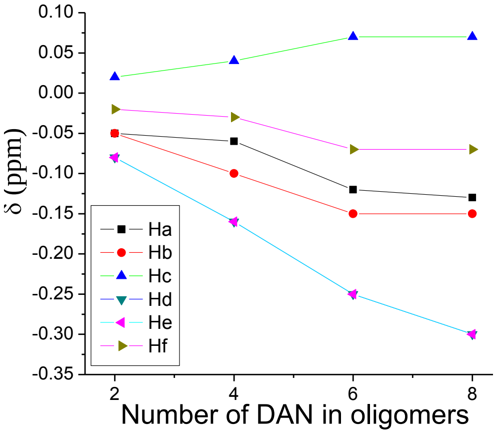

Figure S5 Chemical shift changes of the protons of **PBDV** after being mixed with equivalent DAN oligomers in $CD_3CN/CDCl_3$ (4:1). The concentration of DAN unit was 3.0 mM.

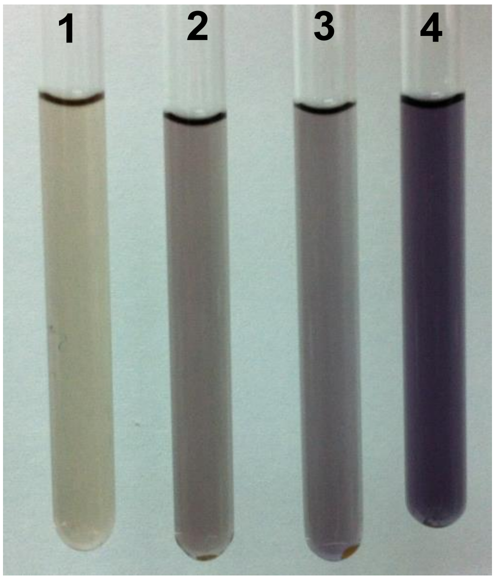

Figure S6 Color of the mixtures of equivalent **PBDV** and DAN oligomers in $CD_3CN/CDCl_3$ (4:1, 3.0 mM) at 25 °C.

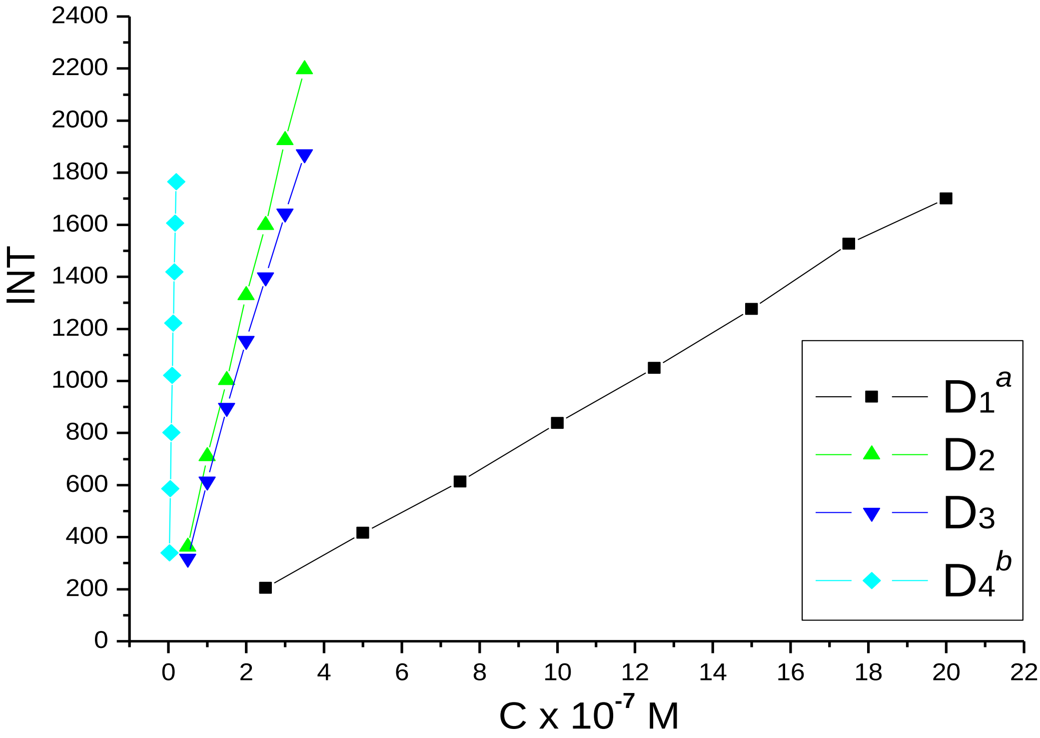

Figure S7 Fluorescence intensity titration plots (Ex at 329 nm) of **D_1-D_4** *vs* concentration in CH_3CN at 25 °C. Slit *a*: 5.0 nm; *b*: 10.0 nm.

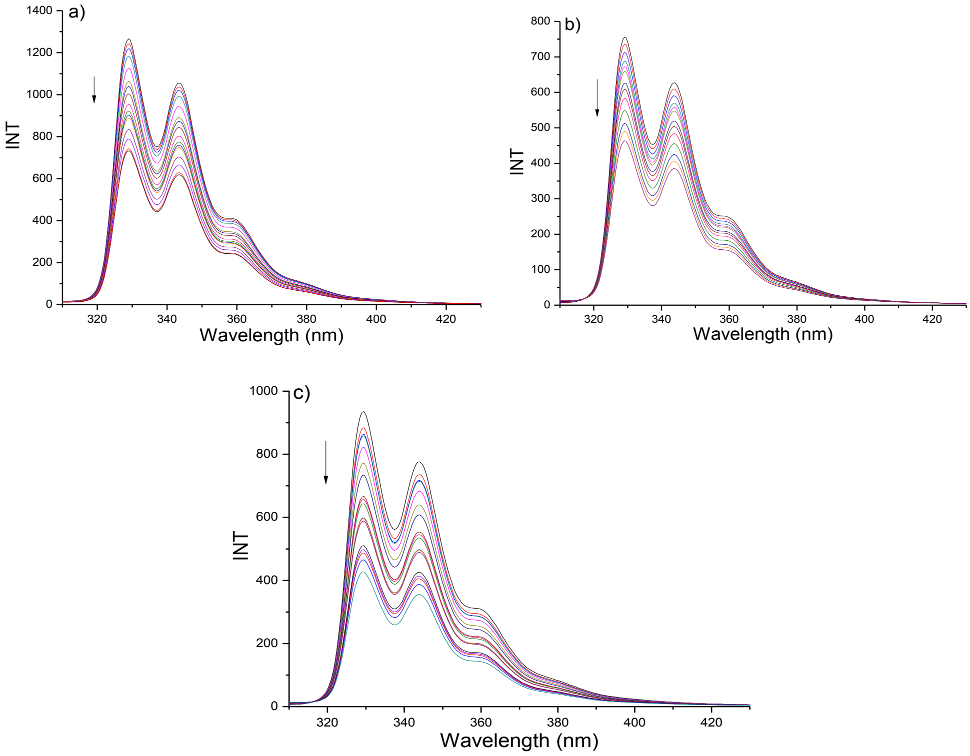

Figure S8 Fluorescence titration spectra of (a) $\mathbf{D_1}$, (b) $\mathbf{D_2}$, and (c) $\mathbf{D_3}$ with **PBDV** in CH_3CN at 25°C. The concentration of DAN unit was 3.0×10^{-6} M.

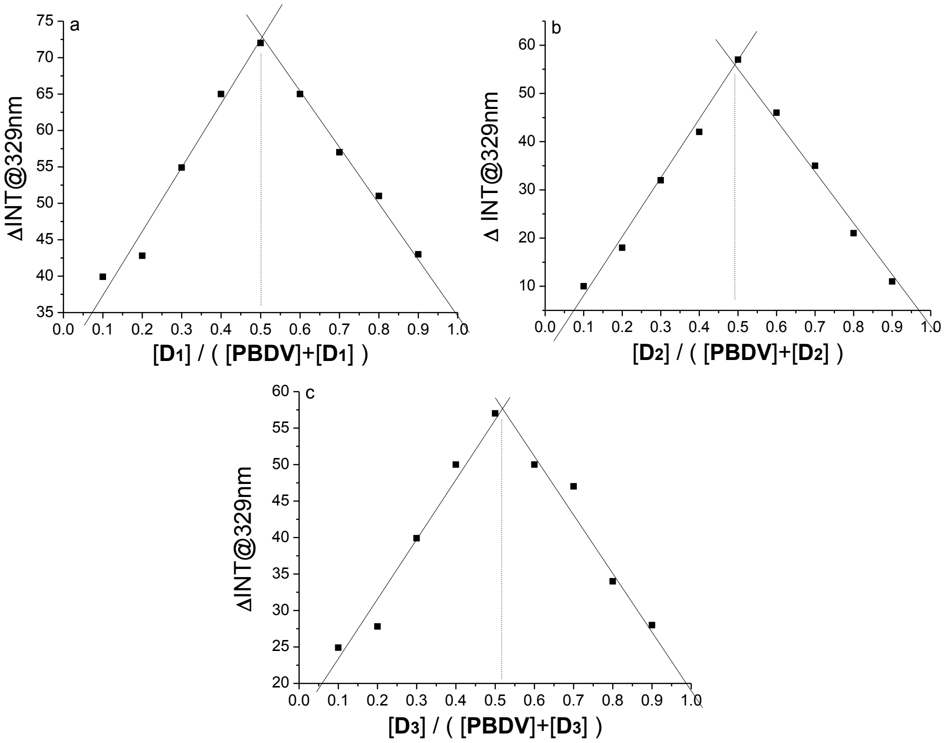

Figure S9 Job's plots of (a) **PBDV** + $\mathbf{D_1}$, (b) **PBDV** + $\mathbf{D_2}$, and (c) **PBDV** + $\mathbf{D_3}$ generated by fluorescence spectroscopy.

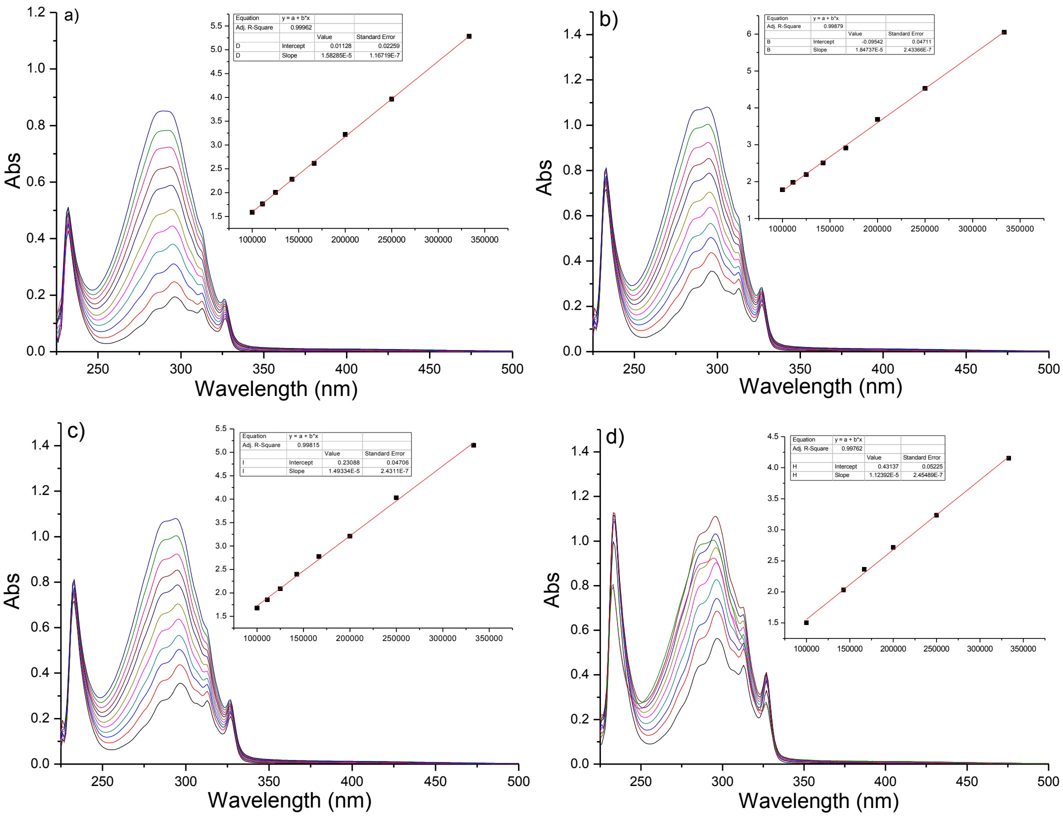

Figure S10. UV-*vis* titration spectra of (a) $\mathbf{D_1}$, (b) $\mathbf{D_2}$, (c) $\mathbf{D_3}$, and (d) $\mathbf{D_4}$ with **PBDV** in $CH_3CN/CHCl_3$ (4:1) at 25°C. Inset: B-H plots. The concentration of DAN oligomer was 1.0 ×10^{-5} M.

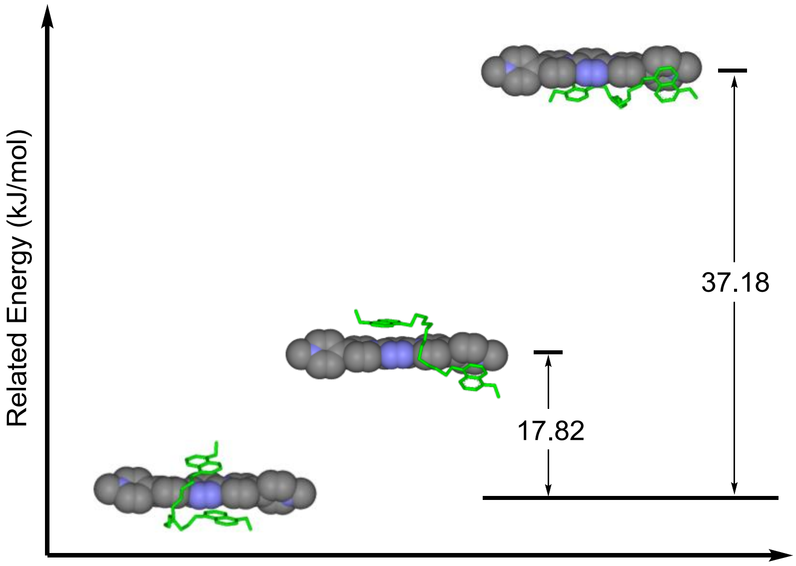

Figure S11 Energy diagram of representative optimized structures of (**PBDV** + $\mathbf{D_1}$) obtained by DFT calculations at B3LYP/6-31G level.

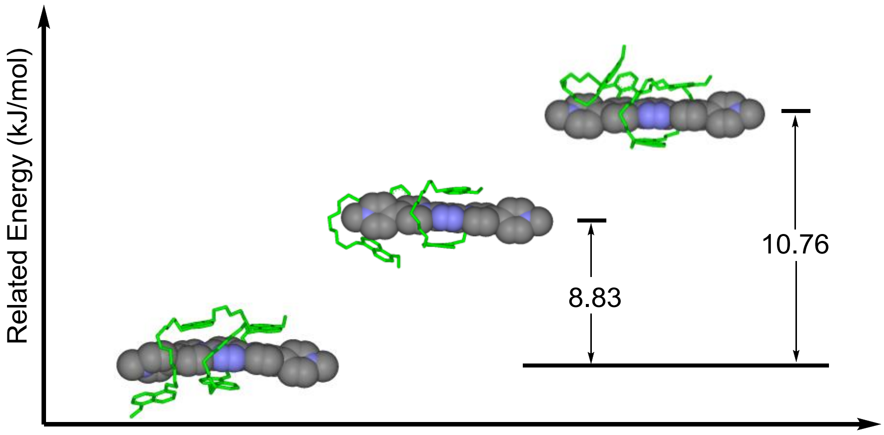

Figure S12 Energy diagram of representative optimized structures of (**PBDV** + **D**$_2$) obtained by DFT calculations at B3LYP/6-31G level.

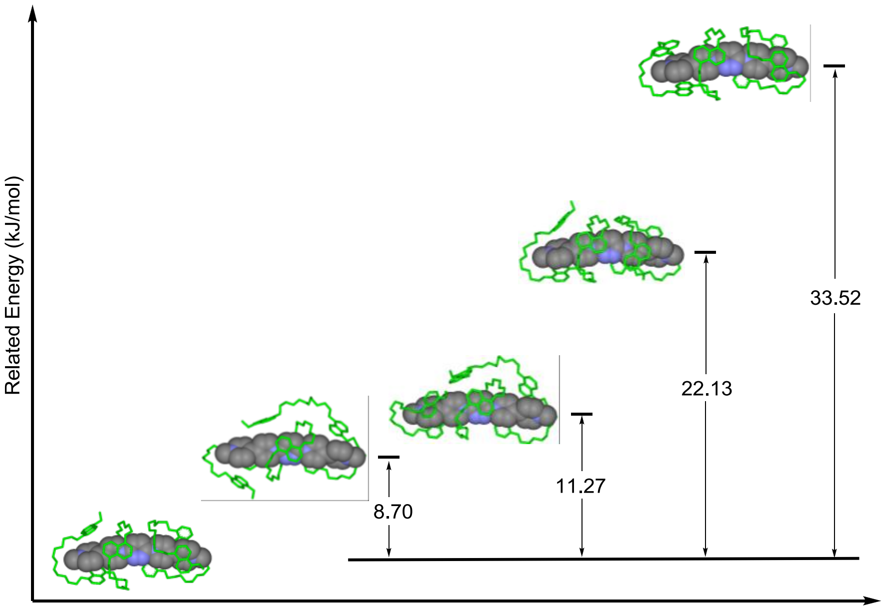

Figure S13 Energy diagram of representative optimized structures of (**PBDV** + **D**$_3$) obtained by DFT calculations at B3LYP/6-31G level.

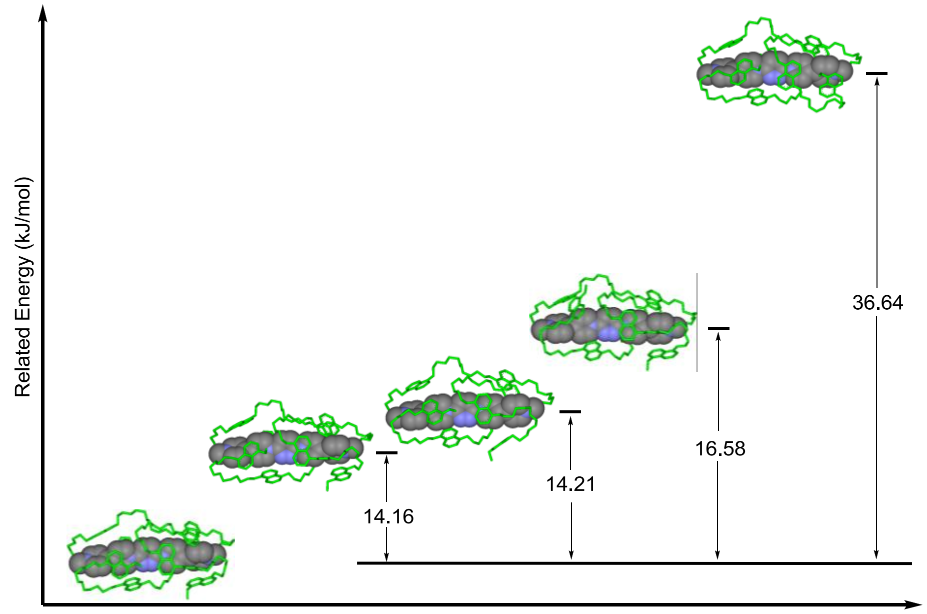

Figure S14 Energy diagram of representative optimized structures of (**PBDV + D_4**) obtained by DFT calculations at B3LYP/6-31G level.

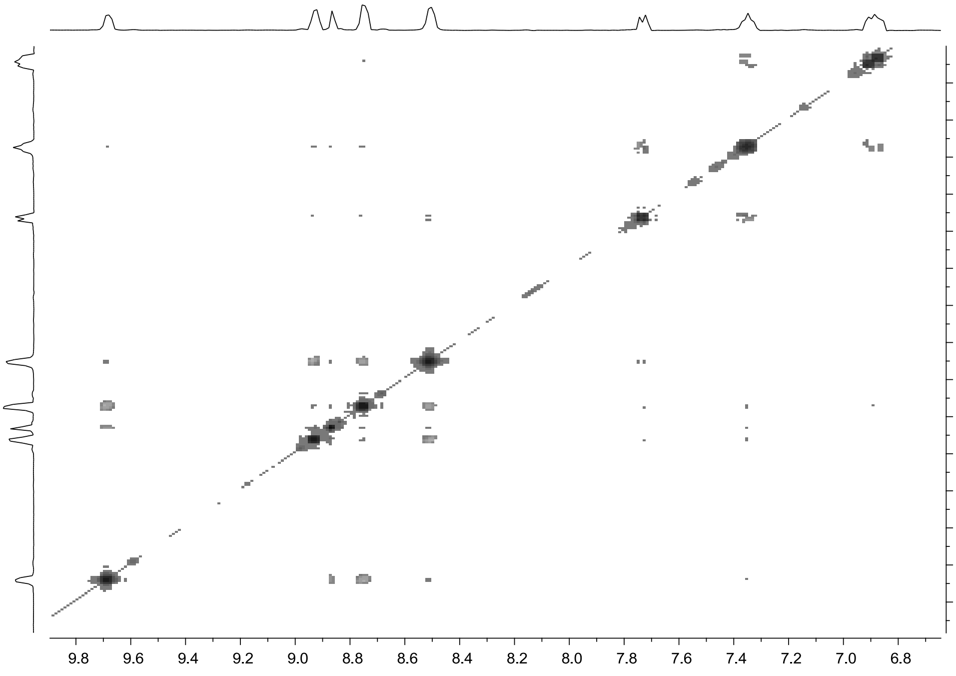

Figure S15 Partial ^{1}H NMR 2D NOESY spectrum of (**PBDV + D_1**, 1:1) in $CD_3CN/CDCl_3$ (4:1, 3.0 mM).

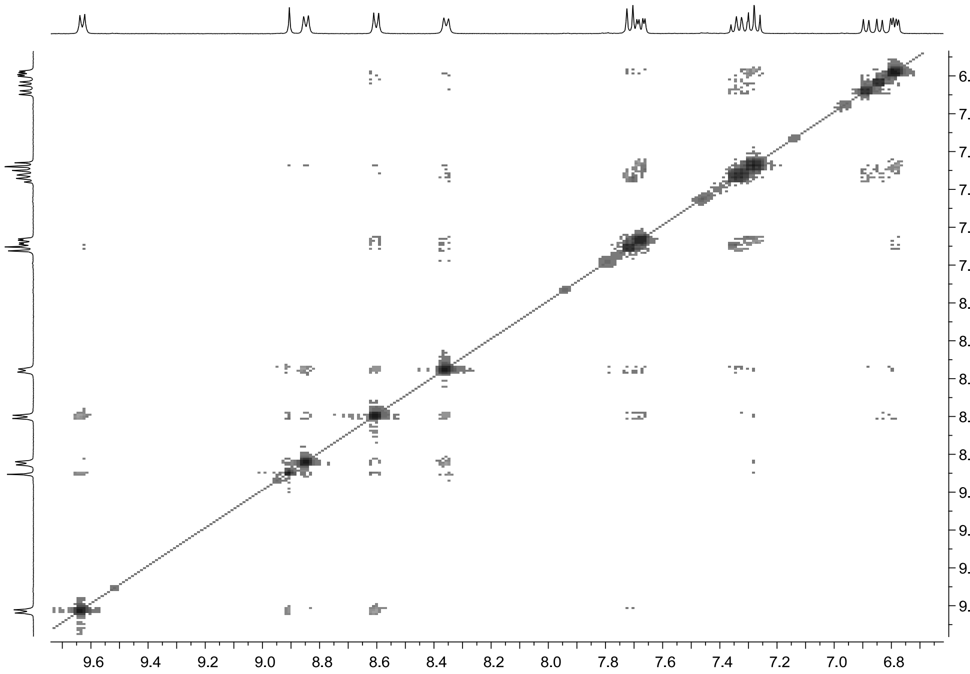

Figure S16 Partial ^{1}H NMR 2D NOESY spectrum of (**PBDV** + **D$_2$**, 1:1) in $CD_3CN/CDCl_3$ (4:1, 3.0 mM).

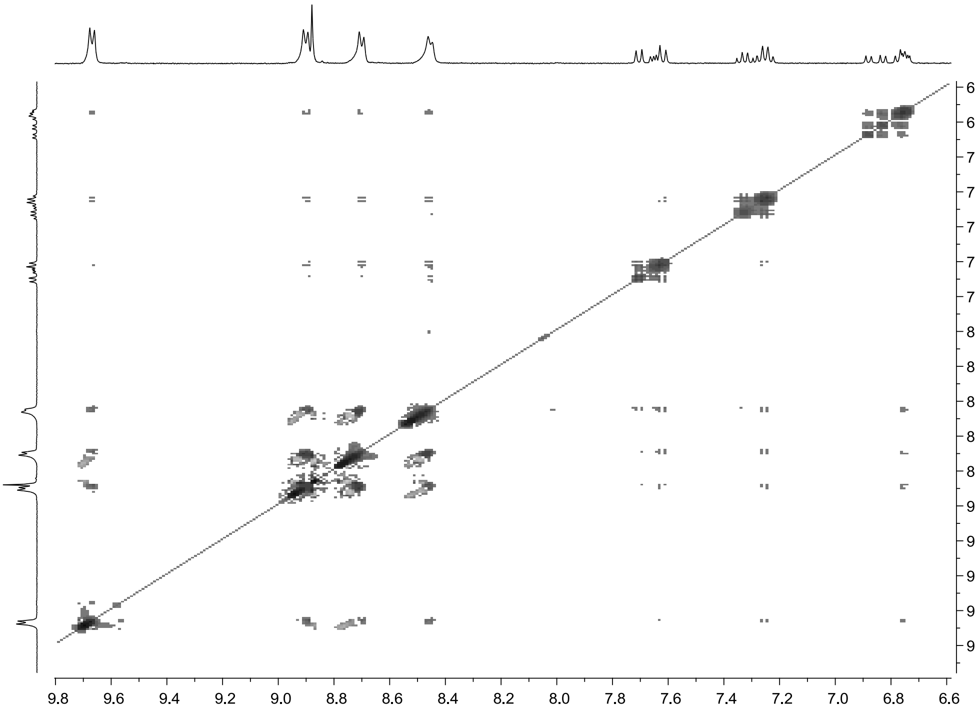

Figure S17 Partial ^{1}H NMR 2D NOESY spectrum of (**PBDV** + **D$_3$**, 1:1) in $CD_3CN/CDCl_3$ (4:1, 3.0 mM).

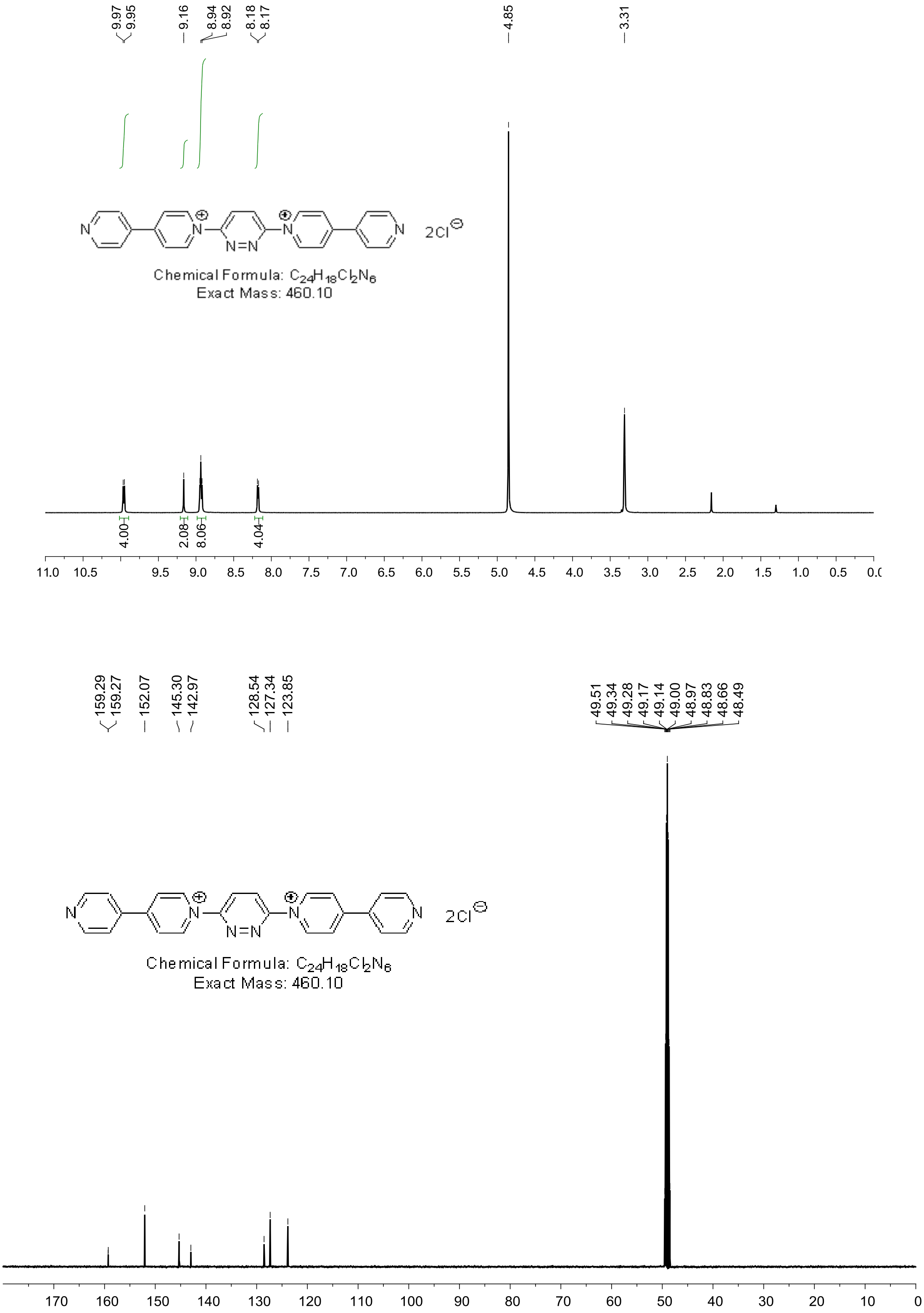

Figure S18 ^{1}H NMR and ^{13}C NMR spectra of compound **1** in CD_3OD.

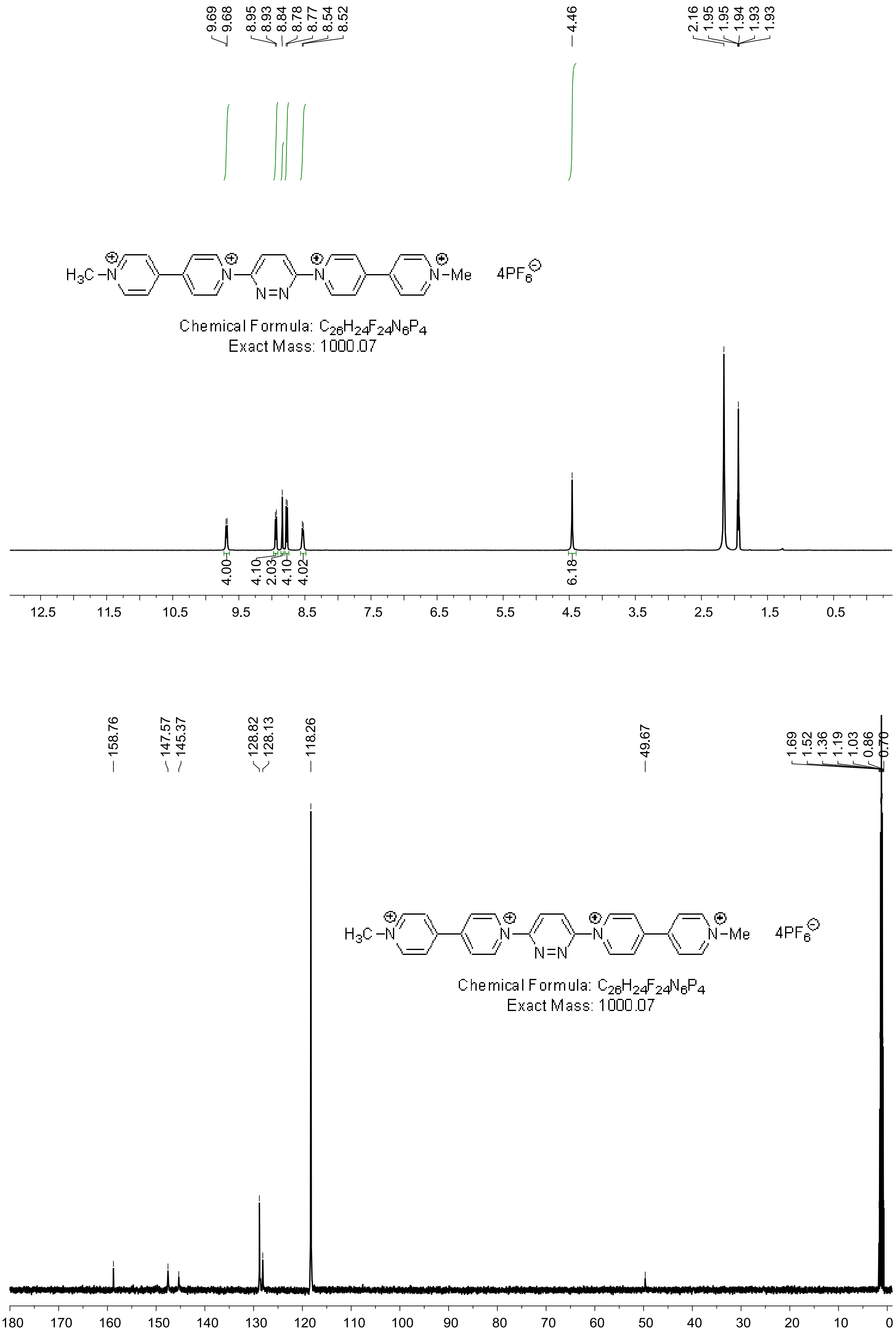

Figure S19 ^{1}H NMR and ^{13}C NMR spectra of **PBDV** in CD_3CN.

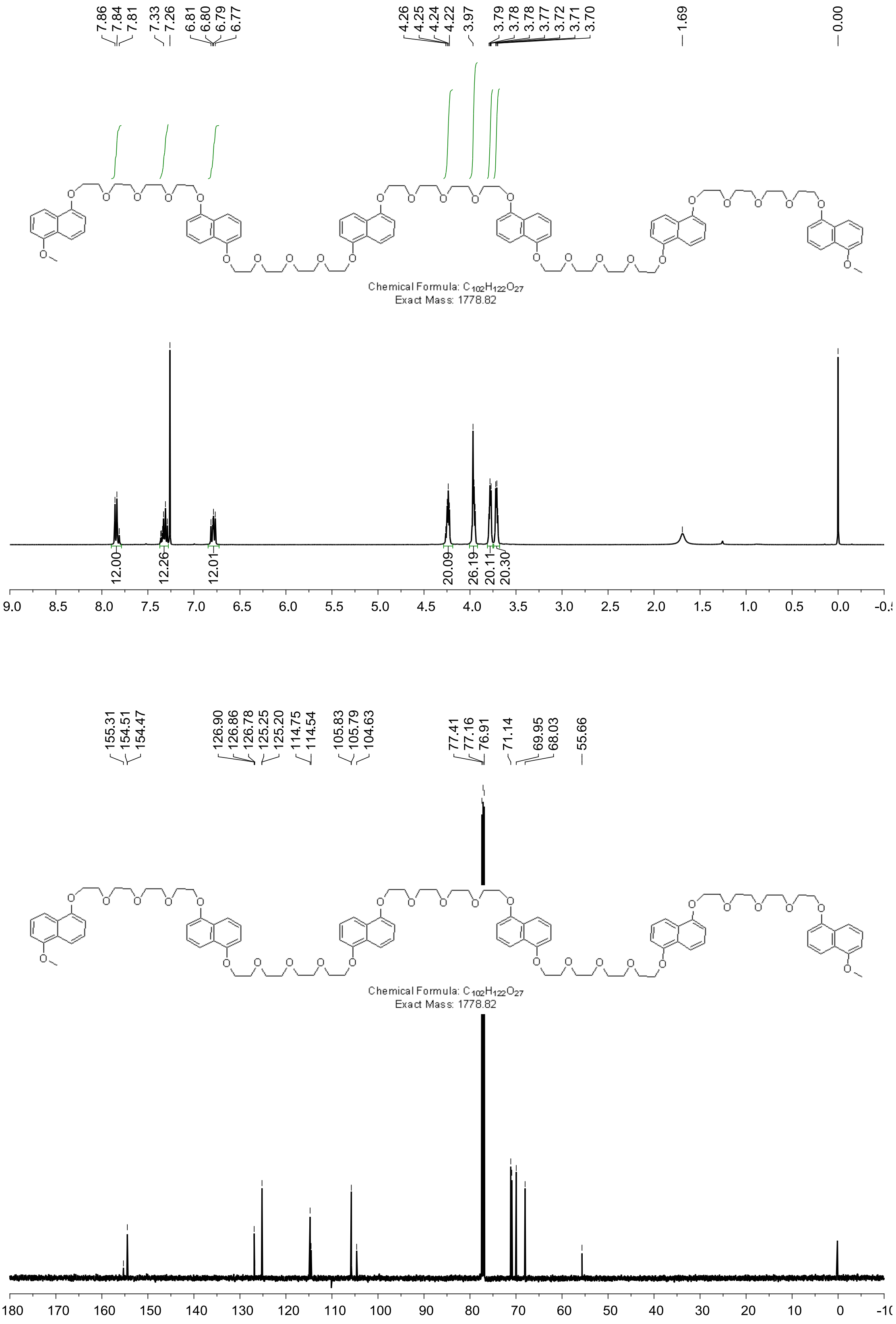

Figure S20 ^{1}H NMR and ^{13}C NMR spectra of **D_3** in $CDCl_3$.

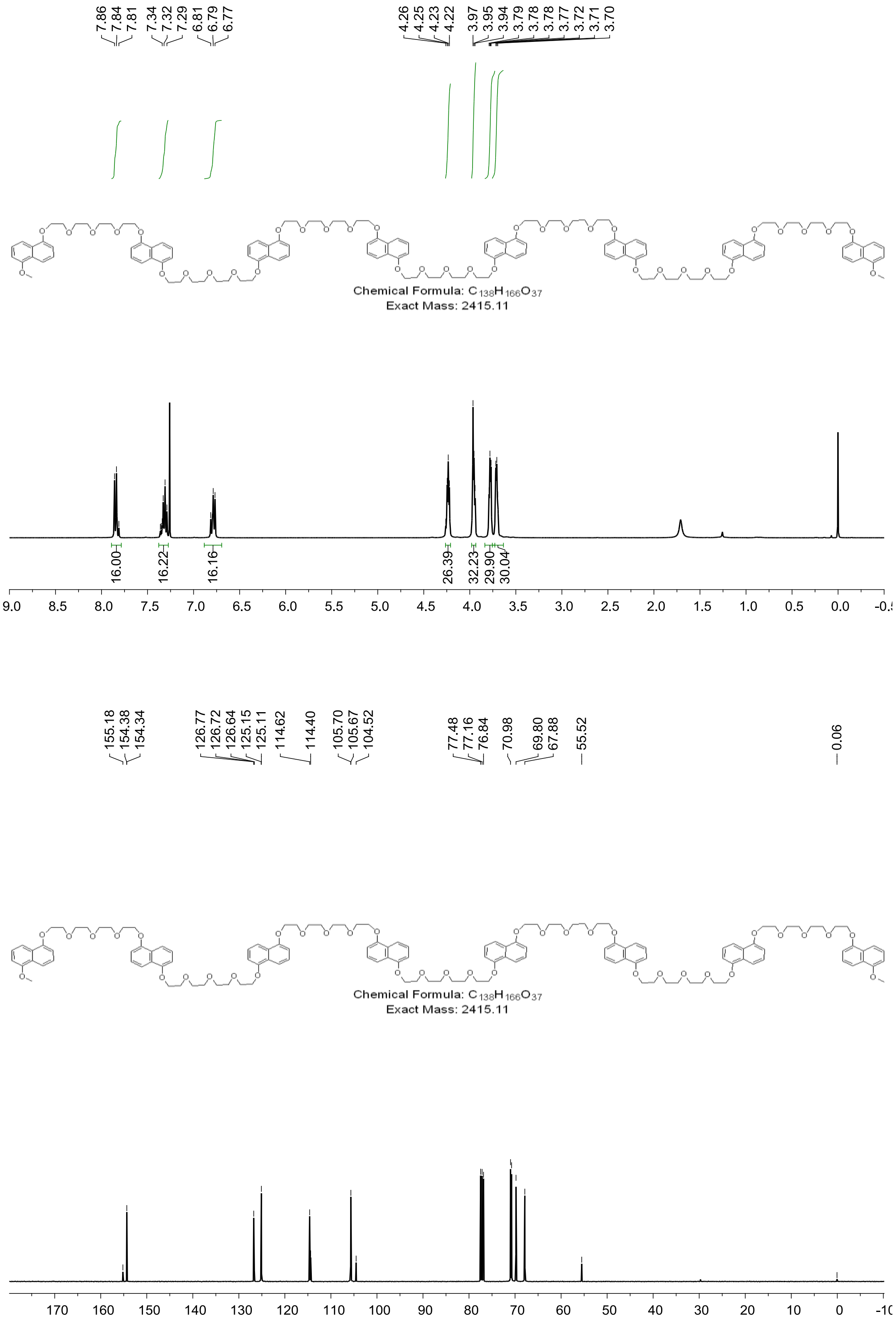

Figure S21 ^{1}H NMR and ^{13}C NMR spectra of **D_4** in $CDCl_3$.

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