Supporting information to accompany

Molecular Design of Viologens to Exhibit Low-Order Liquid-Crystalline Phases

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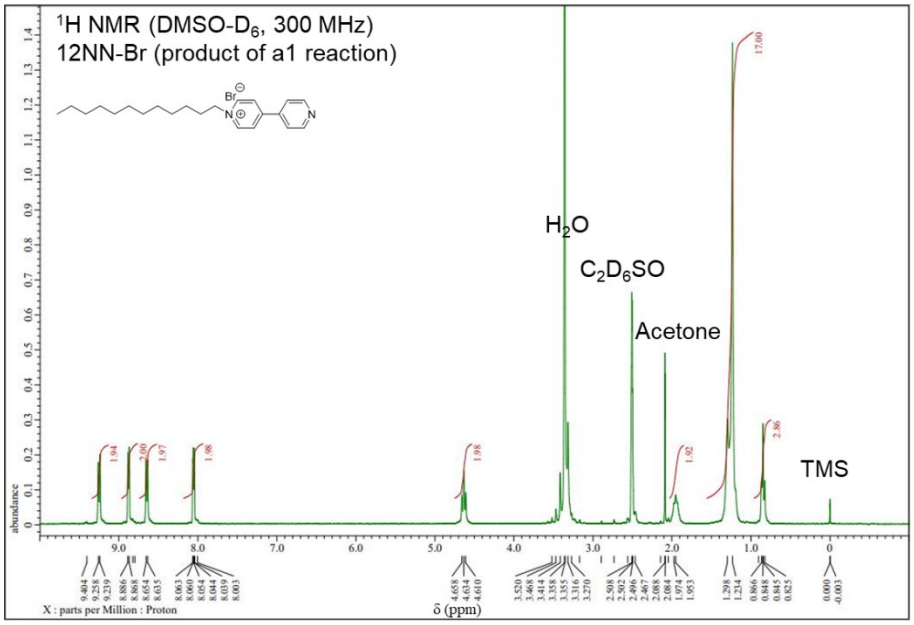
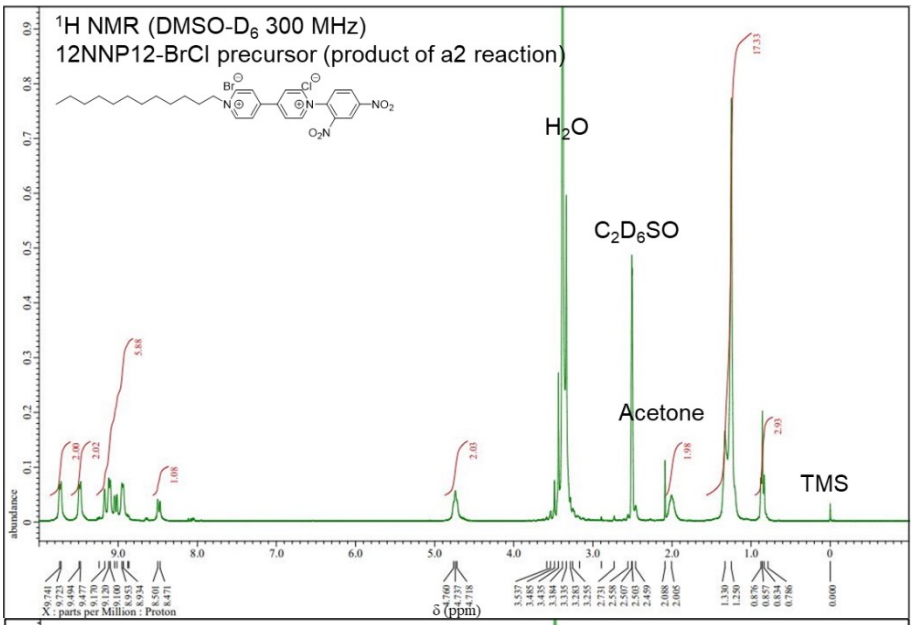
1. Confirmation of synthesis by NMR spectroscopy

The progress of the reaction was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy. The NMR spectra of each reaction for all compound are described below.

Synthesis of 12NNP12

(Step a1) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.25 (d, J = 5.8 Hz, 2H), 8.89-8.80 (m, 2H), 8.64 (d, J = 5.8 Hz, 2H), 8.06-8.00 (m, 2H), 4.63 (t, J = 7.2 Hz, 2H), 1.96 (d, J = 6.5 Hz, 2H), 1.27 (d, J = 19.3 Hz, 18H), 0.90-0.83 (m, 3H)
(Step a2) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.73 (d, J = 5.5 Hz, 2H), 9.49 (d, J = 5.2 Hz, 2H), 9.24-8.86 (m, 6H), 8.49 (d, J = 8.9 Hz, 1H), 4.74 (s, 2H), 2.01 (s, 2H), 1.29 (d, J = 24.1 Hz, 18H), 0.88-0.79 (m, 3H)
(Step a3) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.64 (d, J = 5.5 Hz, 2H), 9.43 (d, J = 5.5 Hz, 2H), 8.90 (t, J = 6.9 Hz, 4H), 7.87 (d, J = 7.9 Hz, 2H), 7.62 (d, J = 7.9 Hz, 2H), 4.72 (s, 2H), 2.76 (d, J = 7.2 Hz, 2H), 2.00 (s, 2H), 1.64 (d, J = 6.9 Hz, 2H), 1.29 (d, J = 22.0 Hz, 36H), 0.92-0.84 (m, 6H)
(Step a4) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.65 (s, 2H), 9.39 (s, 2H), 8.90 (s, 4H), 7.86 (d, J = 6.5 Hz, 2H), 7.61 (d, J = 7.9 Hz, 2H), 4.69 (s, 2H), 2.73 (s, 2H), 1.99 (s, 2H), 1.64 (s, 2H), 1.28 (d, J = 21.7 Hz, 36H), 0.85 (d, J = 6.9 Hz, 6H). ^{13}C-NMR (500 MHz, DMSO- d_6) δ 149.2, 148.3, 146.6, 145.8, 145.7, 140.1, 130.0, 126.7, 126.5, 124.6, 123.3, 120.7, 118.2, 115.6, 61.0, 34.6, 31.3, 30.8, 29.1, 29.0, 28.9, 28.9, 28.8, 28.7, 28.6, 28.4, 25.5, 22.1, 13.9.

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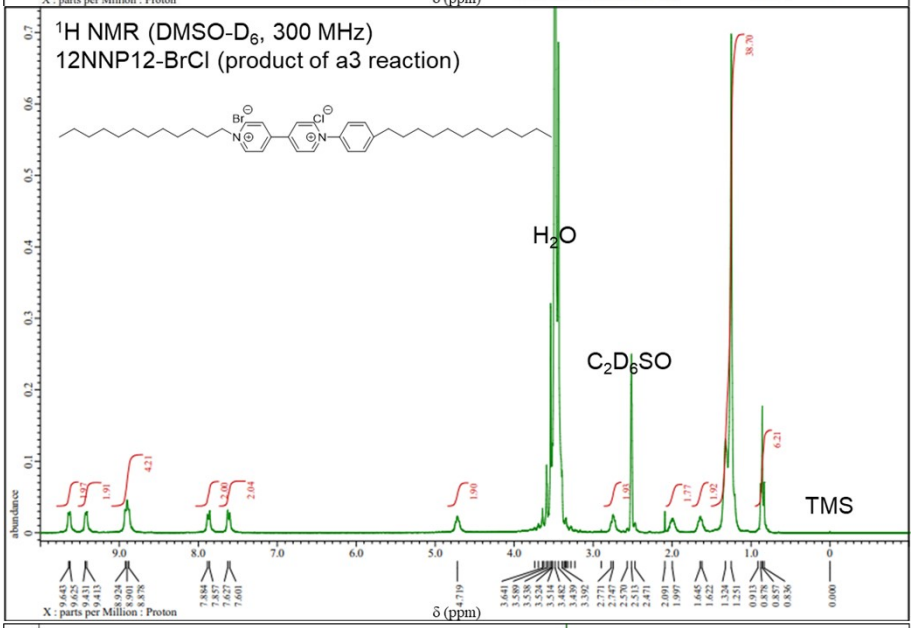
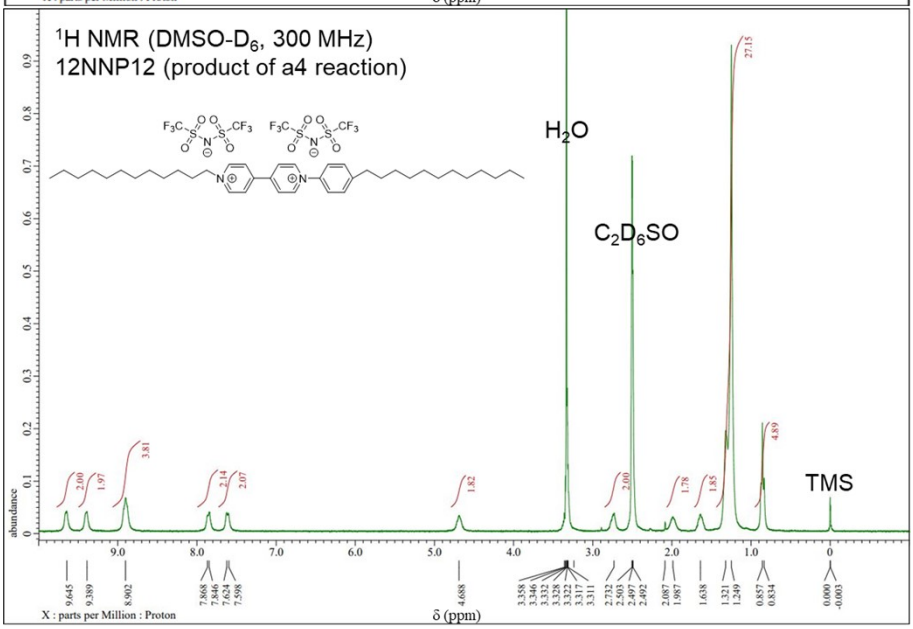
12NNP12-BrCl precursor (product of a2 reaction)
H2O
C2D6SO
Acetone
TMS
abundance
X : parts per Million : Proton
δ (ppm)


1H NMR (DMSO-D6, 300 MHz)
12NNP12-BrCl (product of a3 reaction)
H2O
C2D6SO
TMS
abundance
X : parts per Million : Proton
δ (ppm)


1H NMR (DMSO-D6, 300 MHz)
12NNP12 (product of a4 reaction)
H2O
C2D6SO
TMS
abundance
X : parts per Million : Proton
δ (ppm)

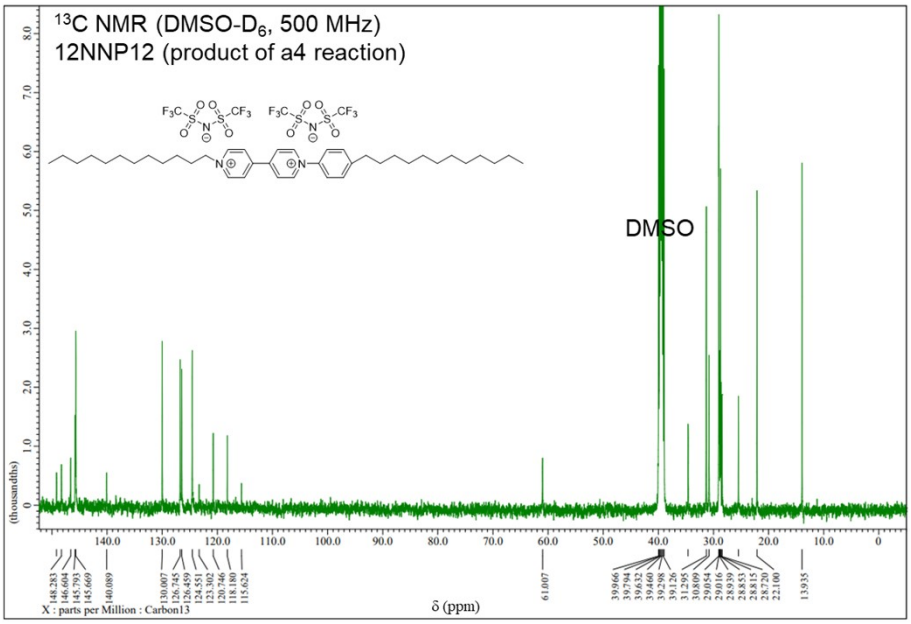
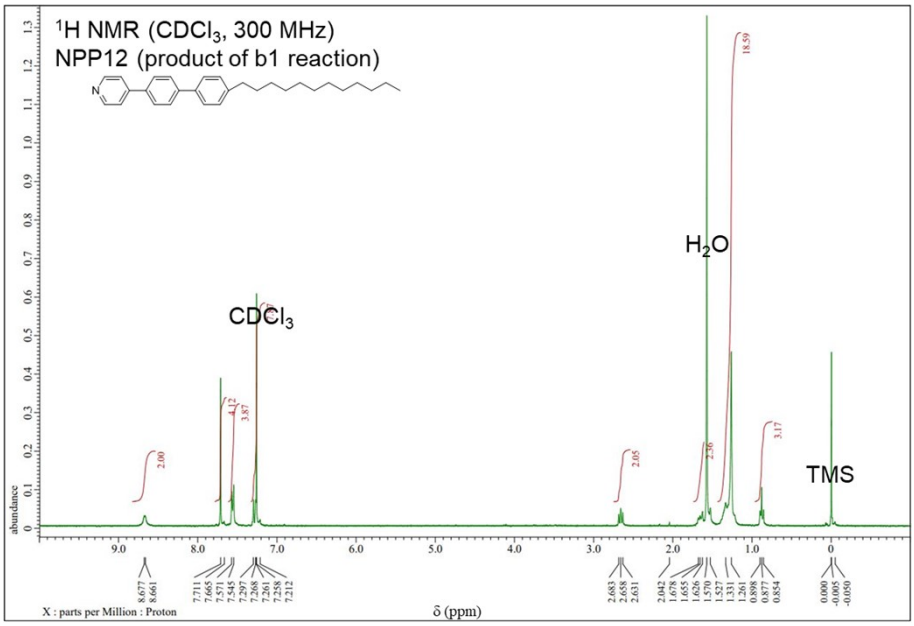


Figure SI-1 ^{1}H- and ^{13}C-NMR spectra of 12NNP12.

Synthesis of 12NPP12

(Step b1) ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.67 (d, J = 4.8 Hz, 2H), 7.69 (d, J = 13.8 Hz, 4H), 7.56 (d, J = 7.9 Hz, 4H), 7.297 (s, 2H), 2.66 (t, J = 7.7 Hz, 2H), 1.68-1.63 (m, 2H), 1.30 (d, J = 21.0 Hz, 18H), 0.88 (t, J = 6.7 Hz, 3H)
(Step b2) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.10 (d, J = 6.9 Hz, 2H), 8.57 (d, J = 6.9 Hz, 2H), 8.19 (d, J = 8.3 Hz, 2H), 7.95 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 4.57 (t, J = 7.2 Hz, 2H), 2.66-2.56 (m, 2H), 1.96 (d, J = 6.9 Hz, 2H), 1.61 (s, 2H), 1.27 (d, J = 19.6 Hz, 36H), 0.87-0.82 (m, 6H)
(Step b3) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.09 (d, J = 6.9 Hz, 2H), 8.57 (d, J = 6.9 Hz, 2H), 8.19 (d, J = 8.6 Hz, 2H), 7.94 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 4.57 (t, J = 7.2 Hz, 2H), 2.64 (t, J = 7.6 Hz, 2H), 1.95 (d, J = 7.2 Hz, 2H), 1.61 (t, J = 7.1 Hz, 2H), 1.30-1.19 (m, 36H), 0.87-0.80 (m, 6H). ^{13}C-NMR (500 MHz, DMSO- d_6)δ 154.1, 144.8, 143.7, 143.1, 135.9, 132.0, 129.2, 128.8, 127.5, 126.9, 124.2, 120.8, 118.3, 60.0, 34.9, 31.4, 31.0, 30.7, 29.1, 29.0, 28.9, 28.9, 28.8, 28.7, 28.5, 25.5, 22.2, 14.0



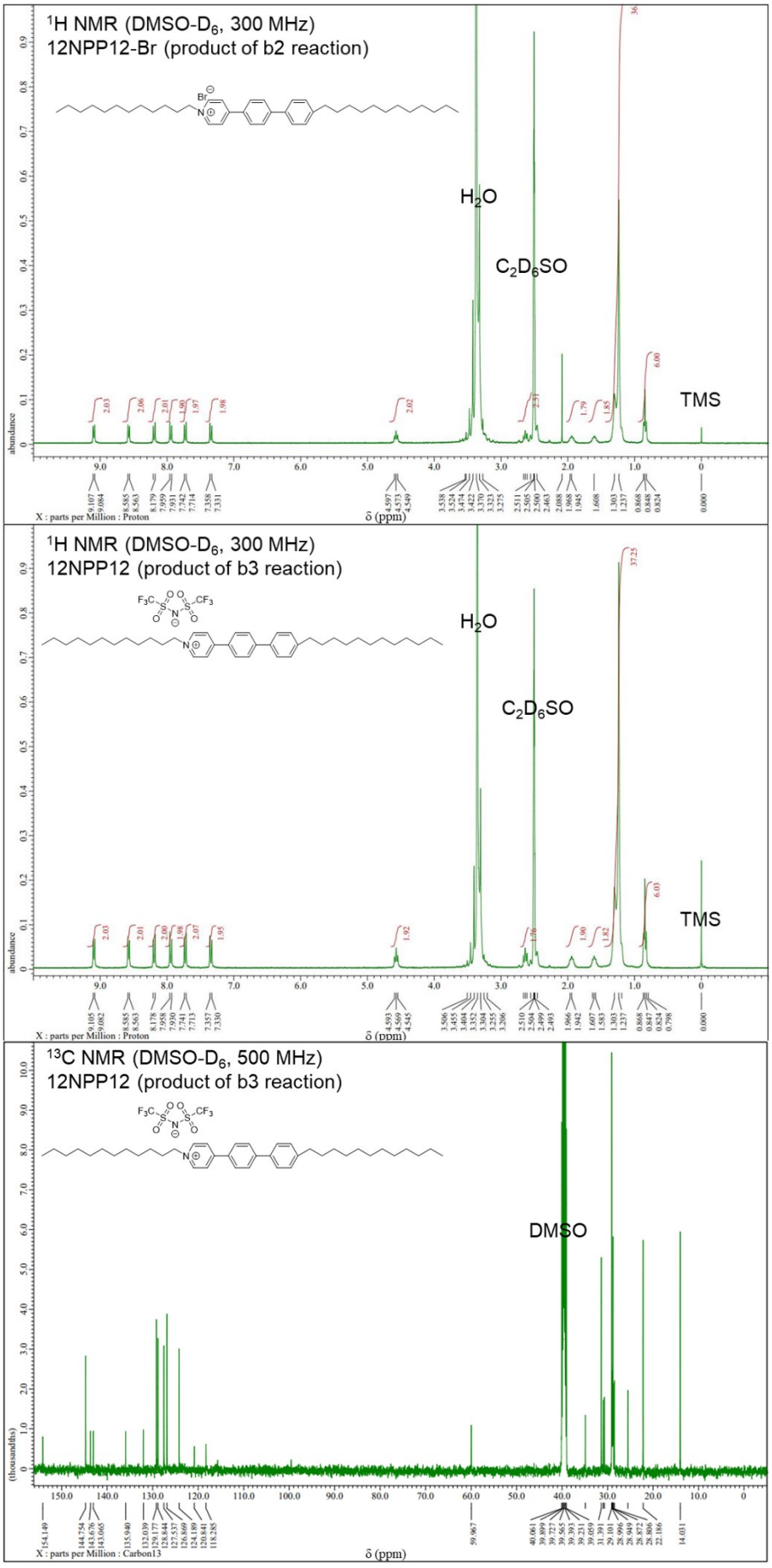
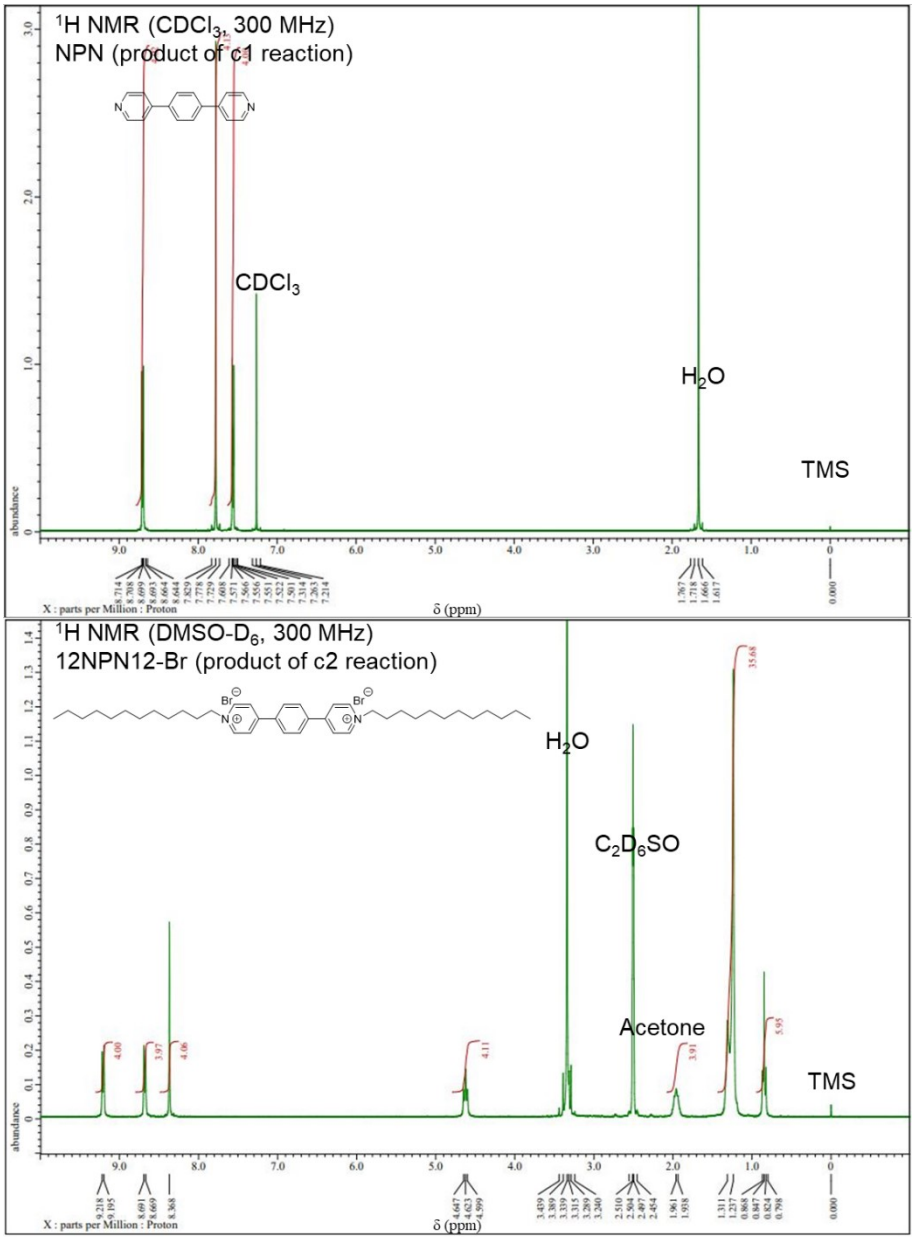


Figure SI-2 ^{1}H- and ^{13}C-NMR spectra of 12NPP12.

Synthesis of 12NPN12

(Step c1) ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.71-8.64 (m, 4H), 7.78 (t, J = 15.0 Hz, 4H), 7.61-7.50 (m, 4H)
(Step c2) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.21 (d, J = 6.9 Hz, 4H), 8.68 (d, J = 6.5 Hz, 4H), 8.37 (s, 4H), 4.62 (t, J = 7.2 Hz, 4H), 1.95 (d, J = 6.9 Hz, 4H), 1.27 (d, J = 22.0 Hz, 36H), 0.87-0.80 (m, 6H)
(Step c3) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.19 (d, J = 6.5 Hz, 4H), 8.66 (d, J = 6.9 Hz, 4H), 8.36 (s, 4H), 4.61 (t, J = 7.2 Hz, 4H), 1.96 (s, 4H), 1.27 (d, J = 22.0 Hz, 36H), 0.84 (t, J = 6.7 Hz, 6H). ^{13}C-NMR (500 MHz, DMSO- d_6)δ 153.4, 145.1, 136.7, 129.4, 125.2, 120.9, 118.4, 60.4, 31.5, 30.9, 29.2, 29.1, 29.0, 28.9, 28.6, 25.6, 22.3, 14.1.



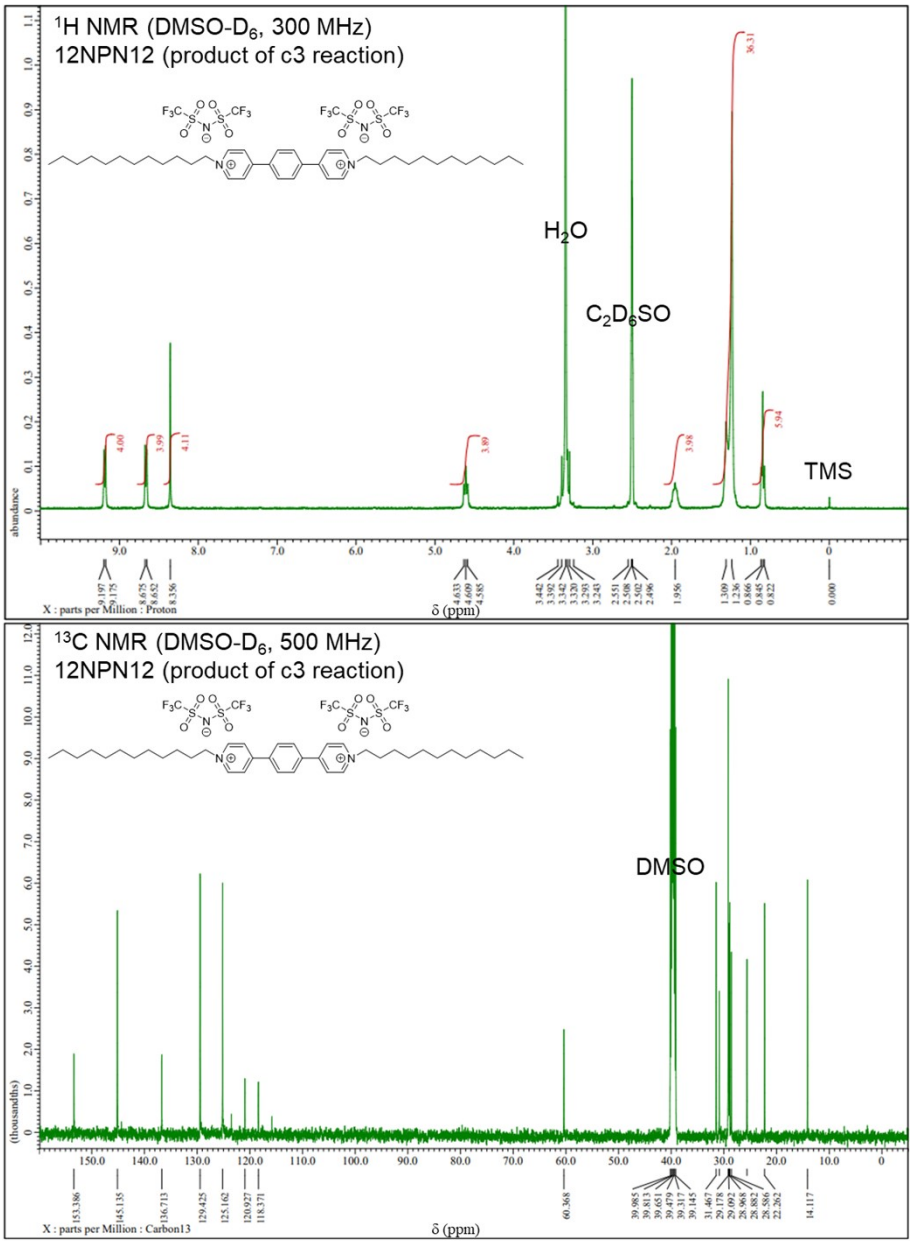
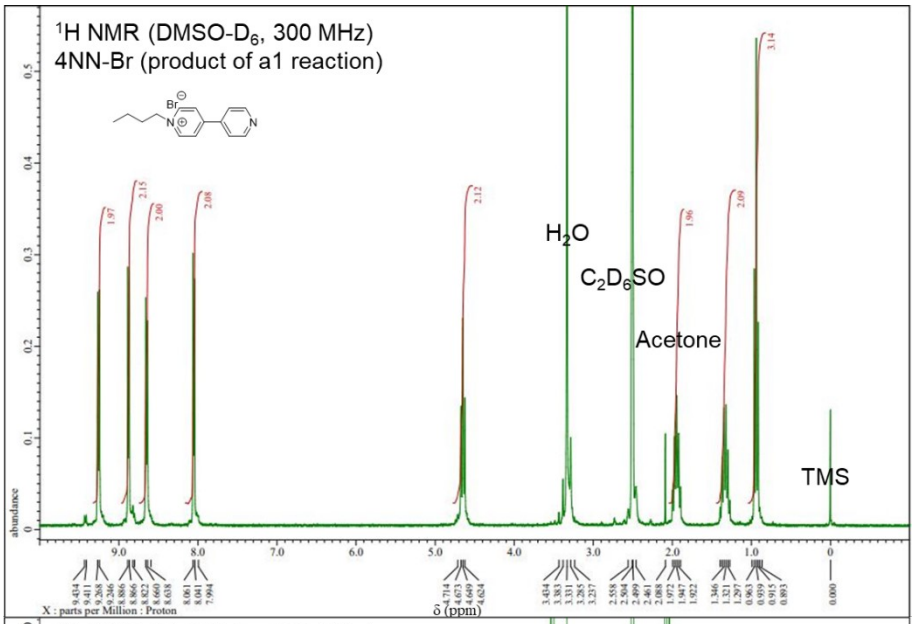
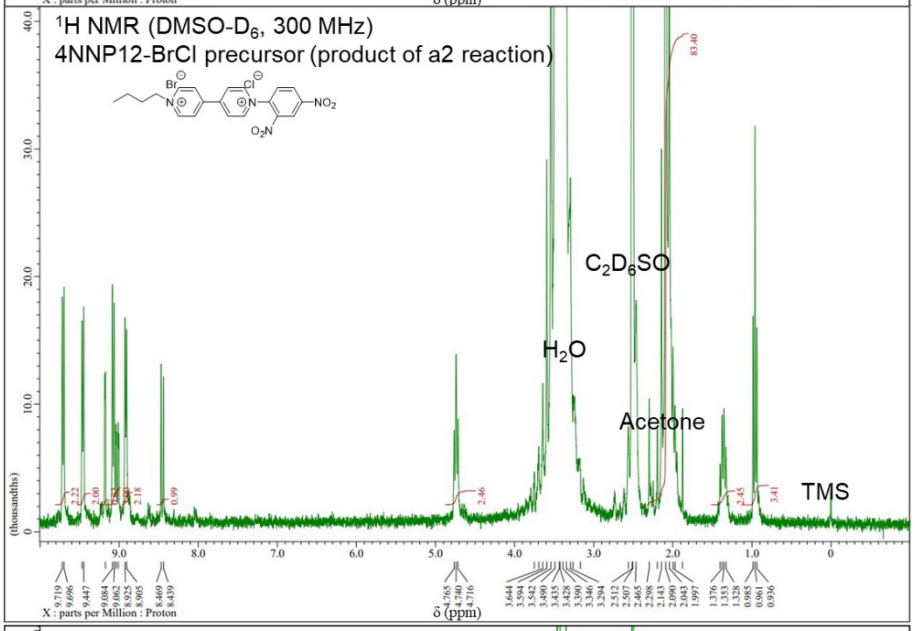


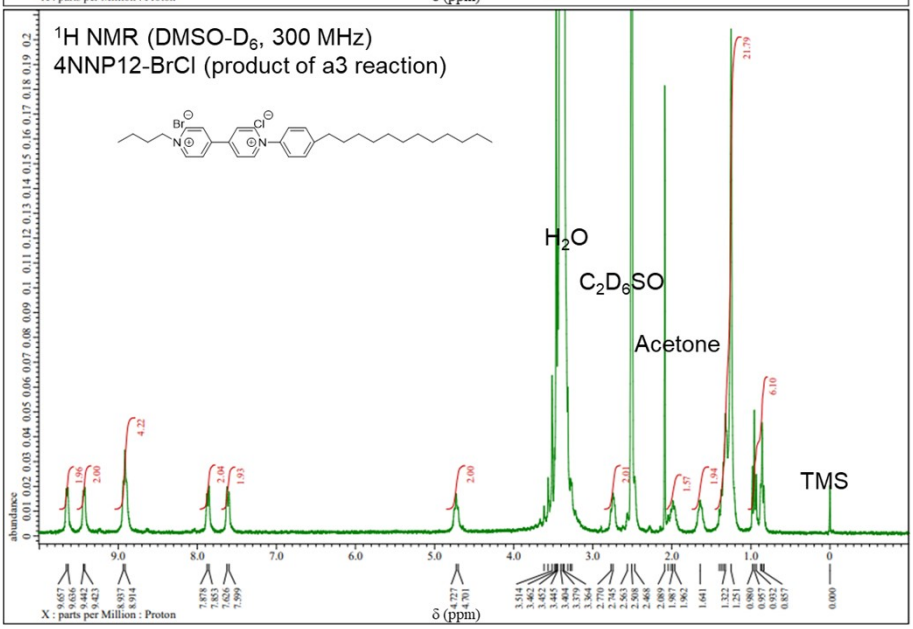
Figure SI-3 ^{1}H- and ^{13}C-NMR spectra of 12NPN12.

Synthesis of 4NNP12

(Step a1) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.26 (d, J = 6.5 Hz, 2H), 8.84 (dd, J = 19.3, 6.2 Hz, 2H), 8.66-8.59 (m, 2H), 8.06-7.99 (m, 2H), 4.71-4.62 (m, 2H), 2.00-1.90 (m, 2H), 1.33 (td, J = 14.8, 7.3 Hz, 2H), 0.99-0.87 (m, 3H)
(Step a2) ^{1}H-NMR (300MHz, DMSO-d_6) δ 9.71 (d, J = 6.9 Hz, 2H), 9.46 (d, J = 6.9 Hz, 2H), 9.17 (s, 1H), 9.08-9.01 (m, 3H), 8.92 (d, J = 6.2 Hz, 2H), 8.45 (d, J = 8.9 Hz, 1H), 4.74 (t, J = 7.4 Hz, 2H), 2.30-1.88 (m, 2H), 1.36 (q, J = 7.5 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H)
(Step a3) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.65 (d, J = 6.2 Hz, 2H), 9.43 (d, J = 5.5 Hz, 2H), 8.93 (d, J = 6.9 Hz, 4H), 7.87 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 4.71 (d, J = 7.9 Hz, 2H), 2.76 (d, J = 7.6 Hz, 2H), 2.05-1.96 (m, 2H), 1.64 (s, 2H), 1.40-1.25 (m, 18H), 0.98-0.83 (m, 6H)
(Step a4) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.59 (d, J = 47.5 Hz, 2H), 9.43 (d, J = 36.1 Hz, 2H), 8.90-8.74 (m, 4H), 7.85 (s, 2H), 7.57 (d, J = 54.4 Hz, 2H), 4.66 (d, J = 49.8 Hz, 2H), 2.87-2.68 (m, 2H), 1.98 (s, 2H), 1.64-1.58 (m, 2H), 1.38-1.17 (m, 18H), 0.96 (t, J = 7.2 Hz, 3H), 0.91-0.84 (m, 3H). ^{13}C-NMR (500 MHz, DMSO-d_6) δ 149.2, 148.3, 145.8, 145.7, 140.1, 130.0, 126.8, 126.5, 124.6, 123.3, 120.8, 118.2, 115.6, 60.8, 34.6, 32.7, 31.3, 30.8, 29.1, 28.9, 28.7, 28.6, 22.1, 18.8, 14.0, 13.3.


1H NMR (DMSO-D6, 300 MHz)
4NN-Br (product of a1 reaction)
H2O
C2D6SO
Acetone
TMS
abundance
X : parts per Million : Proton
δ (ppm)


1H NMR (DMSO-D6, 300 MHz)
4NNP12-BrCl precursor (product of a2 reaction)
C2D6SO
H2O
Acetone
TMS
(thousandths)
X : parts per Million : Proton
δ (ppm)


1H NMR (DMSO-D6, 300 MHz)
4NNP12-BrCl (product of a3 reaction)
H2O
C2D6SO
Acetone
TMS
abundance
X : parts per Million : Proton
δ (ppm)

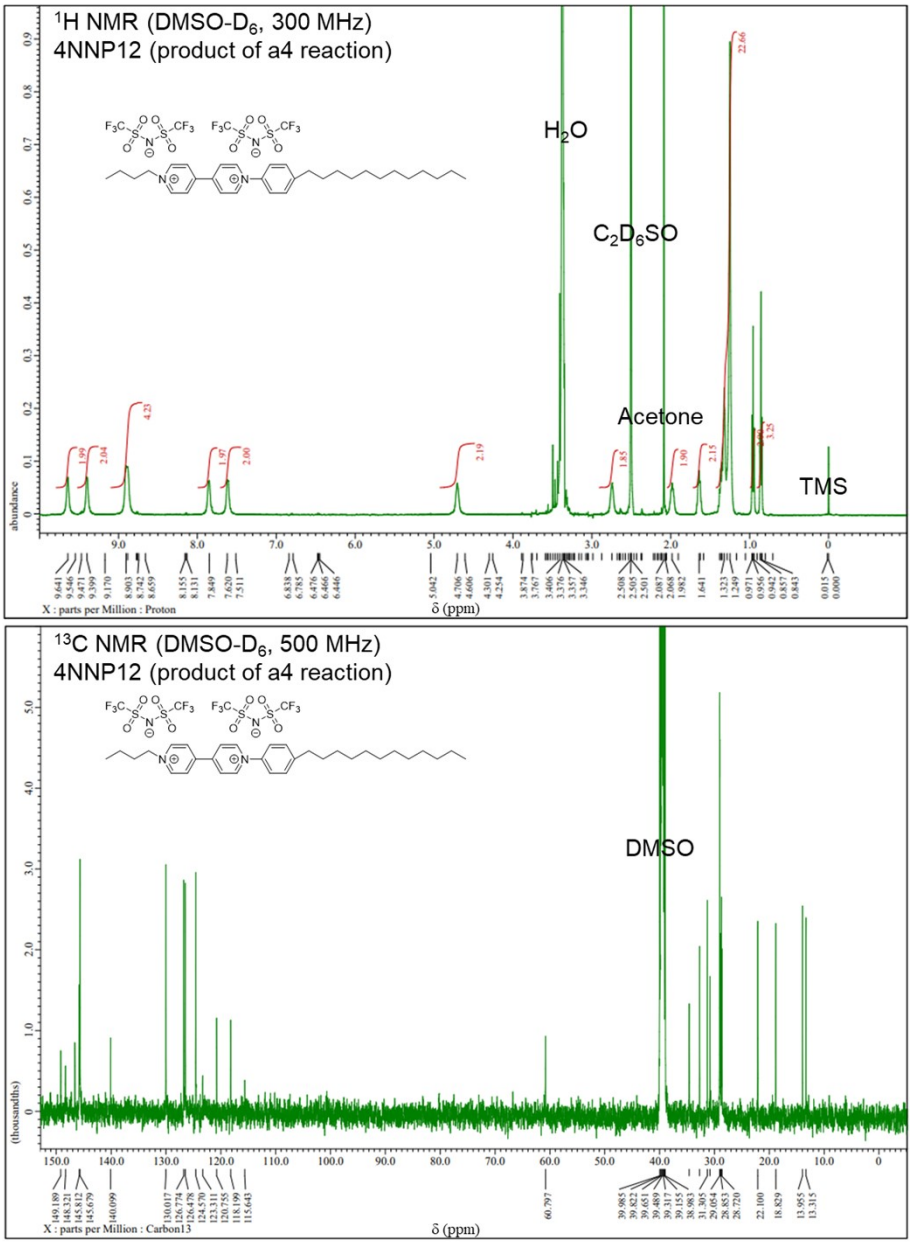
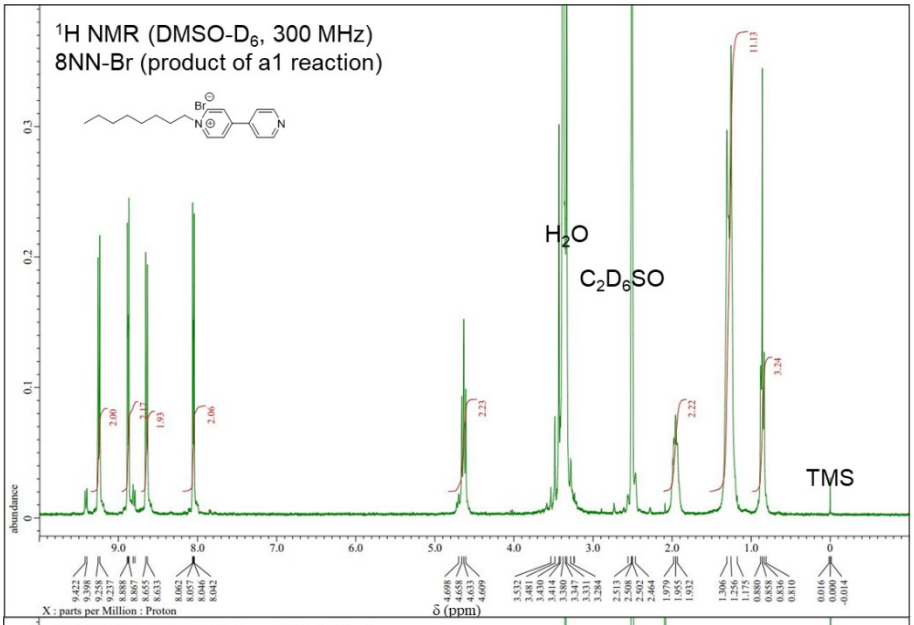
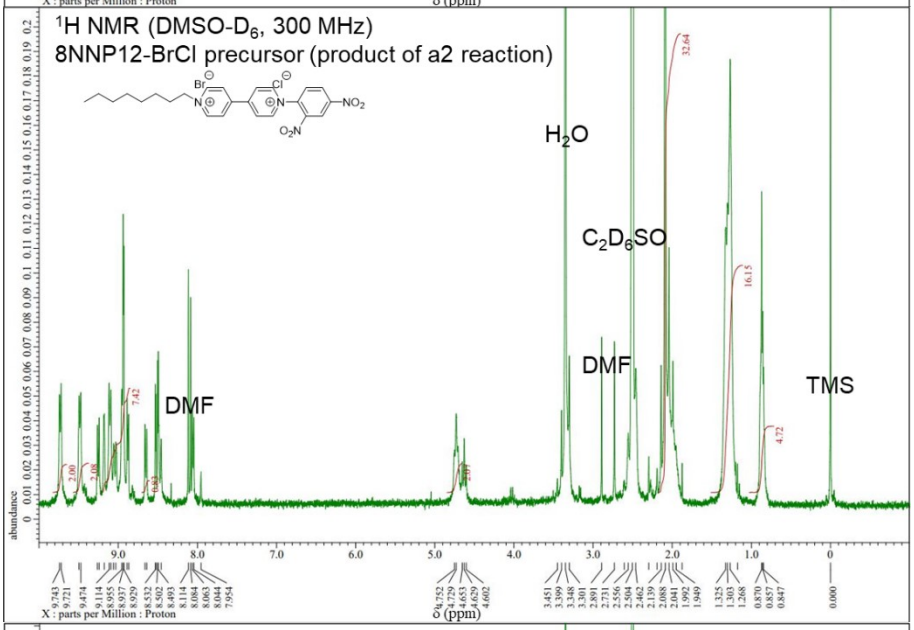


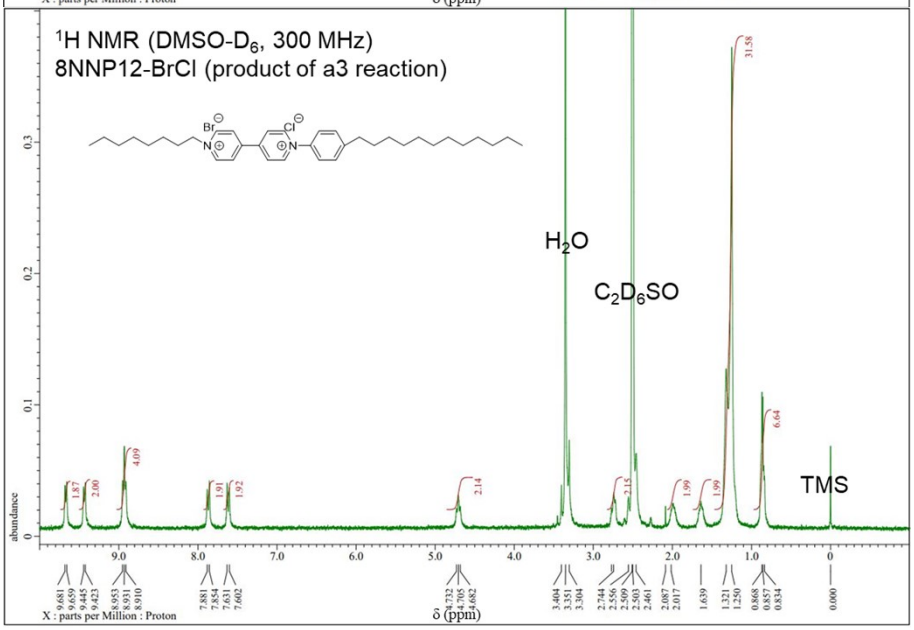
Figure SI-4 ^{1}H- and ^{13}C-NMR spectra of 4NNP12.

Synthesis of 8NNP12

(Step a1) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.25 (d, J = 6.5 Hz, 2H), 8.89-8.79 (m, 2H), 8.64 (d, J = 6.5 Hz, 2H), 8.05 (d, J = 4.6, 1.5 Hz, 2H), 4.70-4.61 (m, 2H), 1.96 (t, J = 7.1 Hz, 2H), 1.31-1.18 (m, 10H), 0.85 (q, J = 7.0 Hz, 3H)
(Step a2) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.73 (d, J = 6.5 Hz, 2H), 9.48 (d, J = 6.5 Hz, 2H), 9.18-8.87 (m, 6H), 8.65 (d, J = 6.9 Hz, 1H), 4.74 (d, J = 6.9 Hz, 2H), 2.14-1.95 (m, 2H), 1.33-1.17 (m, 10H), 0.86 (t, J = 3.4 Hz, 3H)
(Step a3) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.67 (d, J = 6.5 Hz, 2H), 9.43 (d, J = 6.5 Hz, 2H), 8.93 (t, J = 6.4 Hz, 4H), 7.87 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 4.71 (t, J = 7.4 Hz, 2H), 2.76 (d, J = 7.6 Hz, 2H), 2.02 (s, 2H), 1.64 (s, 2H), 1.29 (m, J = 21.3 Hz, 28H), 0.87-0.83 (m, 6H)
(Step a4) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.64 (s, 2H), 9.40 (s, 2H), 8.89 (s, 4H), 7.85 (s, 2H), 7.62 (s, 2H), 4.70 (s, 2H), 2.75 (d, J = 7.9 Hz, 2H), 2.00 (s, 2H), 1.63 (d, J = 6.9 Hz, 2H), 1.29 (m, J = 21.7 Hz, 28H), 0.88-0.83 (m, 6H). ^{13}C-NMR (500 MHz, DMSO-d_6) δ 149.2, 148.3, 146.6, 145.8, 145.7, 140.1, 130.0, 128.5, 126.7, 126.5, 124.6, 120.7, 118.2, 114.0, 61.0, 34.6, 31.3, 31.2, 30.8, 29.0, 28.9, 28.7, 28.6, 28.5, 28.4, 25.5, 22.1, 22.1, 13.9.


1H NMR (DMSO-D6, 300 MHz)
8NN-Br (product of a1 reaction)
H2O
C2D6SO
TMS
abundance
X : parts per Million : Proton
δ (ppm)


1H NMR (DMSO-D6, 300 MHz)
8NNP12-BrCl precursor (product of a2 reaction)
H2O
C2D6SO
DMF
DMF
TMS
abundance
X : parts per Million : Proton
δ (ppm)


1H NMR (DMSO-D6, 300 MHz)
8NNP12-BrCl (product of a3 reaction)
H2O
C2D6SO
TMS
abundance
X : parts per Million : Proton
δ (ppm)

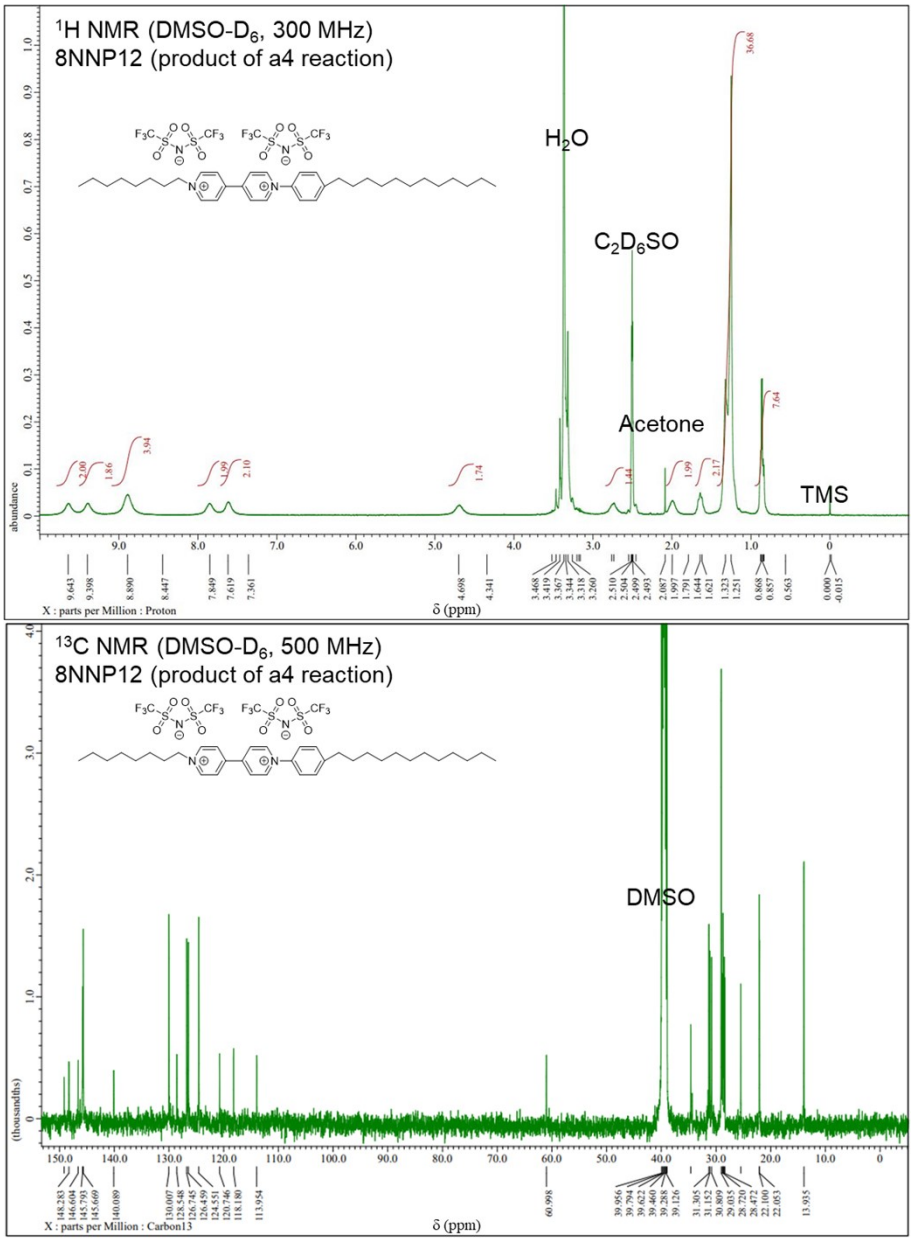
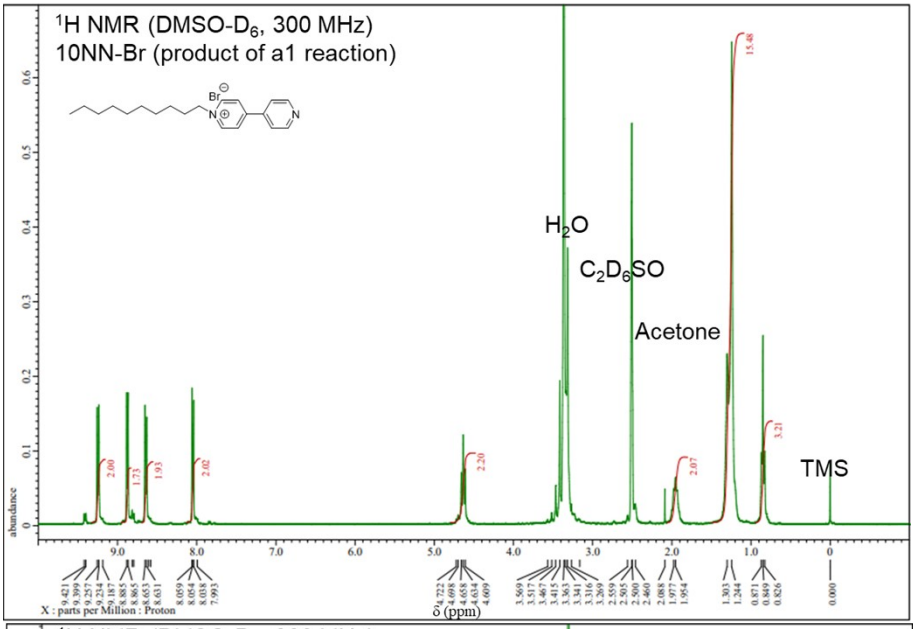
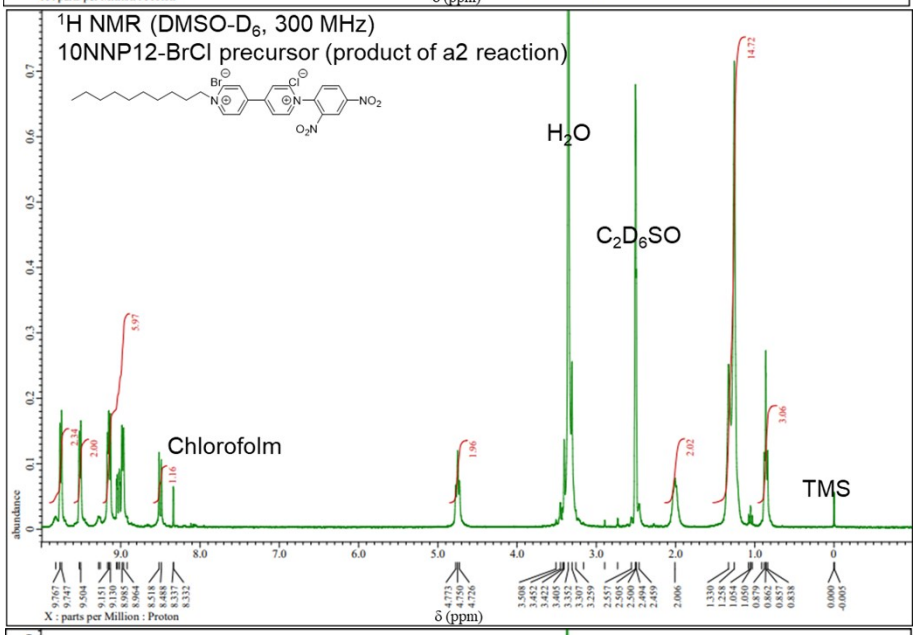


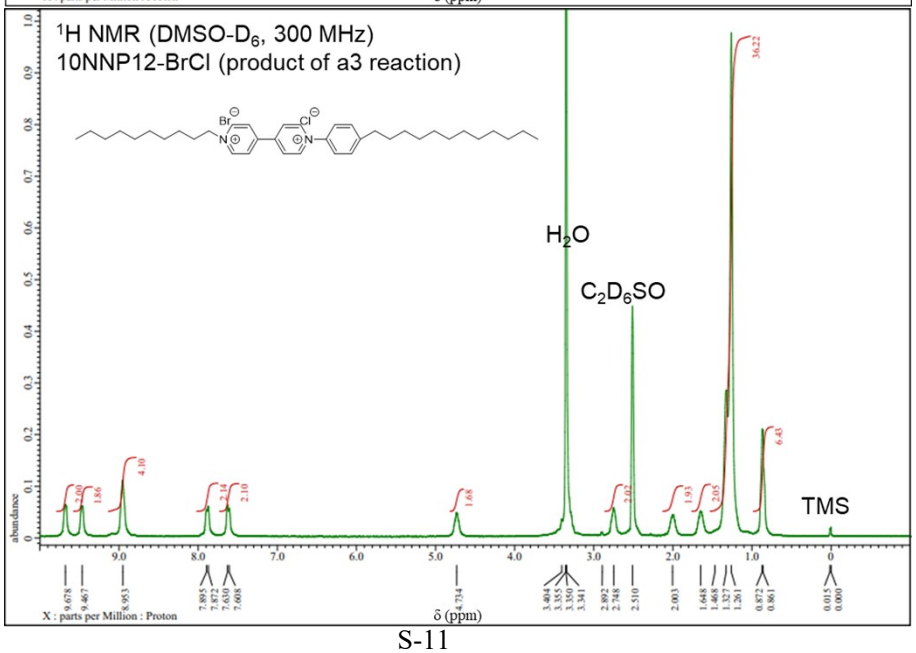
Figure SI-5 ^{1}H- and ^{13}C-NMR spectra of 8NNP12.

Synthesis of 10NNP12

(Step a1) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.26-9.19 (m, 2H), 8.87 (d, J = 6.2 Hz, 2H), 8.62 (q, J = 7.2 Hz, 2H), 8.06-7.99 (m, 2H), 4.72-4.61 (m, 2H), 1.97 (d, J = 6.9 Hz, 2H), 1.27 (d, J = 17.5 Hz, 14H), 0.85 (t, J = 6.7 Hz, 3H)
(Step a2) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.82-9.75 (m, 2H), 9.51 (d, J = 5.8 Hz, 2H), 9.17-8.92 (m, 6H), 8.50 (d, J = 8.9 Hz, 1H), 4.75 (t, J = 7.1 Hz, 2H), 2.01 (s, 2H), 1.29 (d, J = 21.7 Hz, 14H), 0.91-0.84 (m, 3H)
(Step a3) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.68 (s, 2H), 9.47 (s, 2H), 8.95 (s, 4H), 7.88 (d, J = 6.9 Hz, 2H), 7.62 (d, J = 6.5 Hz, 2H), 4.73 (s, 2H), 2.75 (s, 2H), 2.00 (s, 2H), 1.65 (s, 2H), 1.47-1.26 (m, 32H), 0.87 (d, J = 3.4 Hz, 6H)
(Step a4) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.65 (s, 2H), 9.39 (s, 2H), 8.90 (s, 4H), 7.86 (d, J = 6.5 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 4.69 (s, 2H), 2.75 (s, 2H), 1.99 (s, 2H), 1.64 (s, 2H), 1.29 (d, J = 21.0 Hz, 32H), 0.85 (d, J = 6.5 Hz, 6H). ^{13}C-NMR (500 MHz, DMSO-d_6) δ 149.2, 148.4, 146.7, 145.9, 145.8, 140.2, 130.1, 126.8, 126.5, 124.6, 123.4, 120.8, 118.3, 115.7, 61.1, 34.7, 31.4, 30.9, 29.1, 29.0, 28.9, 28.9, 28.8, 28.7, 28.5, 25.6, 22.2, 14.0.


¹H NMR (DMSO-D6, 300 MHz)
10NN-Br (product of a1 reaction)
H2O
C2D6SO
Acetone
TMS
abundance
X : parts per Million : Proton
δ (ppm)


¹H NMR (DMSO-D6, 300 MHz)
10NNP12-BrCl precursor (product of a2 reaction)
H2O
C2D6SO
Chlorofolm
TMS
abundance
X : parts per Million : Proton
δ (ppm)


¹H NMR (DMSO-D6, 300 MHz)
10NNP12-BrCl (product of a3 reaction)
H2O
C2D6SO
TMS
abundance
X : parts per Million : Proton
δ (ppm)

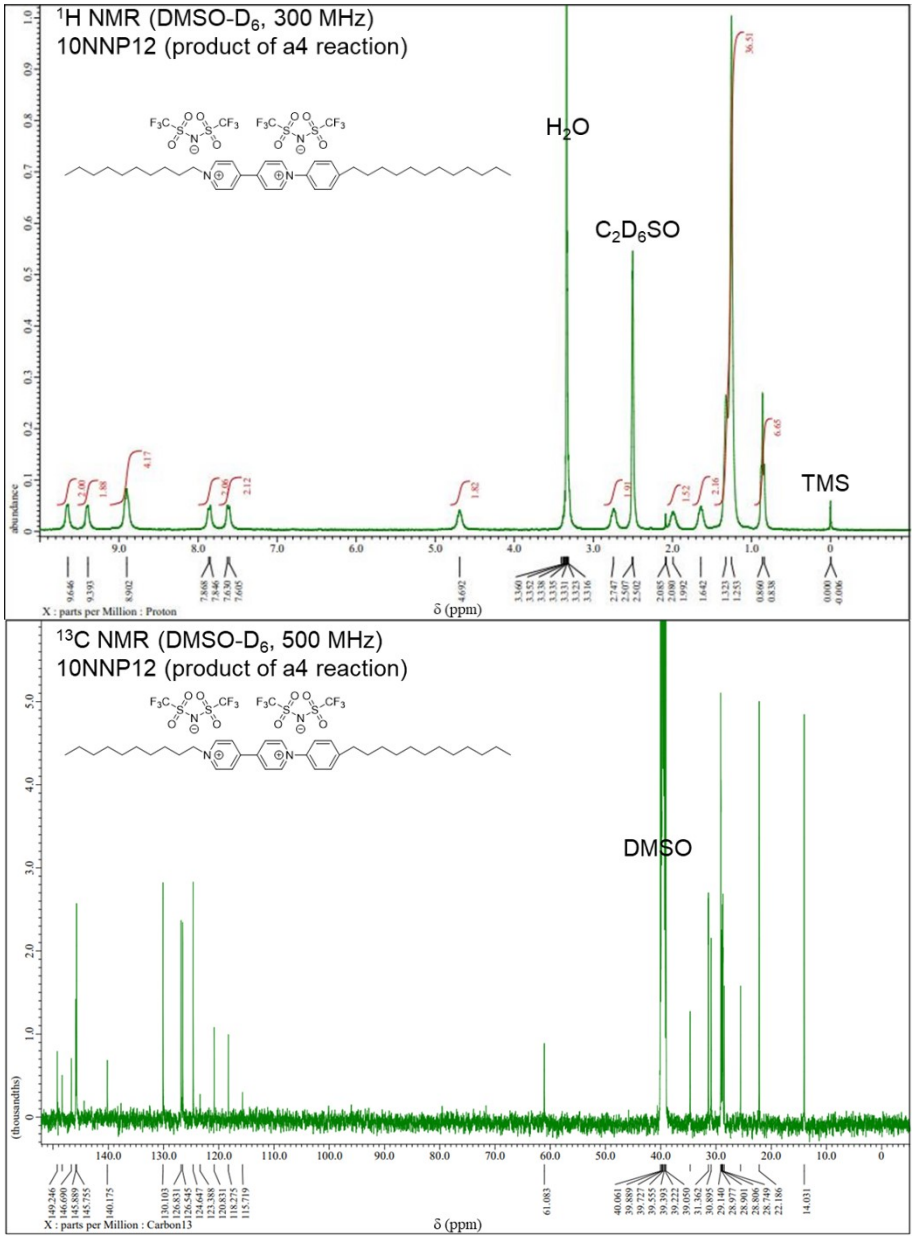
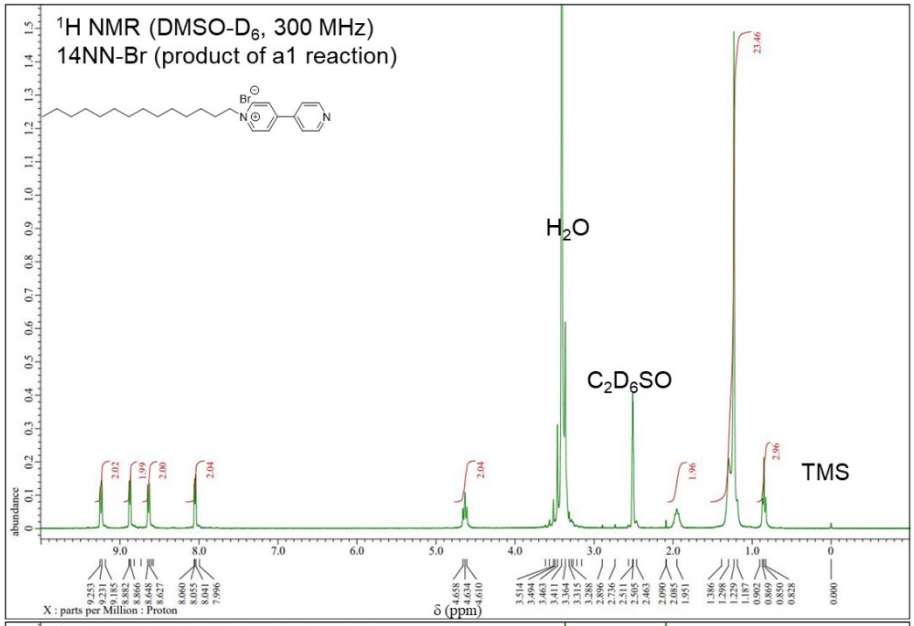
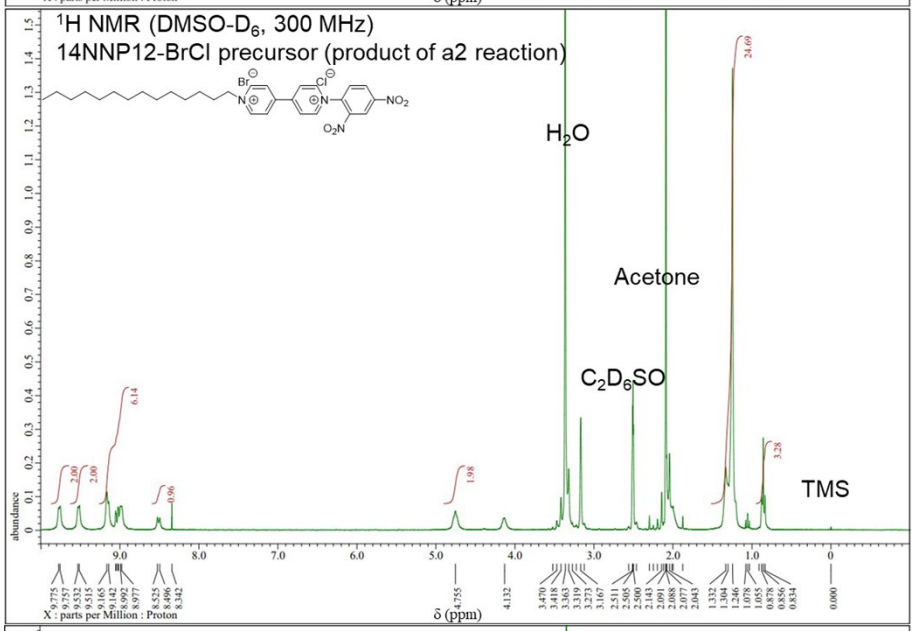


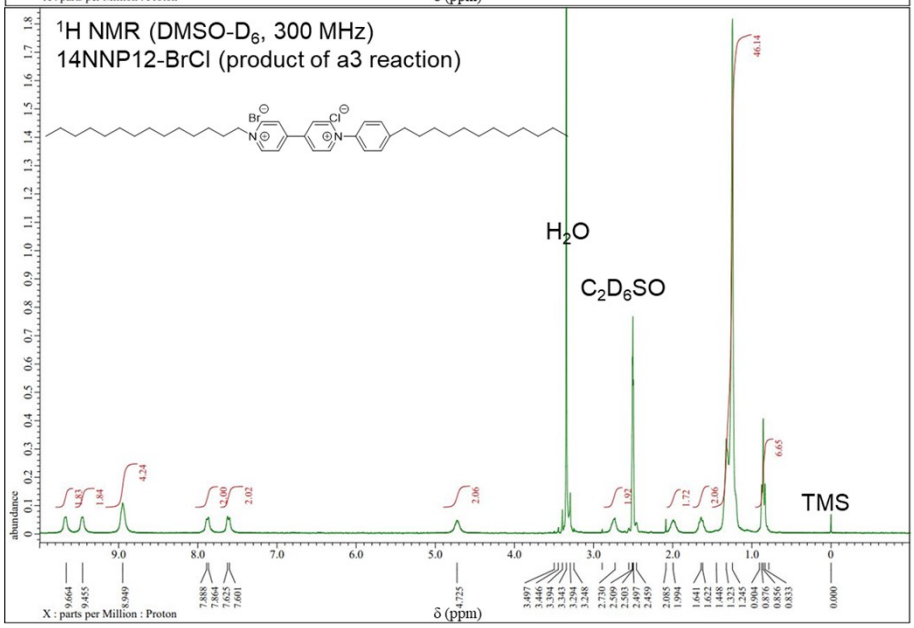
Figure SI-6 ^{1}H- and ^{13}C-NMR spectra of 10NNP12.

Synthesis of 14NNP12

(Step a1) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.25-9.19 (m, 2H), 8.89-8.82 (m, 2H), 8.61 (q, J = 7.0 Hz, 2H), 8.06-8.00 (m, 2H), 4.63 (t, J = 7.2 Hz, 2H), 1.95 (s, 2H), 1.39-1.19 (m, 22H), 0.90-0.83 (m, 3H)
(Step a2) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.77 (d, J = 5.2 Hz, 2H), 9.52 (d, J = 5.2 Hz, 2H), 9.16-8.98 (m, 6H), 8.51 (d, J = 8.6 Hz, 1H), 4.75 (s, 2H), 1.33-1.25 (m, 22H), 0.91-0.83 (m, 3H)
(Step a3) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.66 (s, 2H), 9.46 (s, 2H), 8.95 (s, 4H), 7.88 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 7.2 Hz, 2H), 4.72 (s, 2H), 2.73 (s, 2H), 1.99 (s, 2H), 1.63 (d, J = 5.8 Hz, 2H), 1.45-1.25 (m, 40H), 0.90-0.79 (m, 6H)
(Step a4) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.64 (d, J = 6.2 Hz, 2H), 9.39 (d, J = 5.5 Hz, 2H), 8.89 (t, J = 7.6 Hz, 4H), 7.85 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 7.9 Hz, 2H), 4.71-4.66 (m, 2H), 2.74 (t, J = 7.4 Hz, 2H), 1.99 (s, 2H), 1.64 (s, 2H), 1.29 (d, J = 21.3 Hz, 40H), 0.87-0.79 (m, 6H). ^{13}C-NMR (500 MHz, DMSO-d_6) δ 149.4, 148.5, 146.8, 146.0, 145.9, 140.3, 130.2, 126.9, 126.6, 124.8, 123.5, 120.9, 118.4, 115.8, 61.2, 34.8, 31.5, 31.0, 29.3, 29.2, 29.1, 29.1, 28.9, 28.8, 28.6, 25.7, 22.3, 14.1.


1H NMR (DMSO-D6, 300 MHz)
14NN-Br (product of a1 reaction)
H2O
C2D6SO
TMS
X : parts per Million : Proton
δ (ppm)


1H NMR (DMSO-D6, 300 MHz)
14NNP12-BrCl precursor (product of a2 reaction)
H2O
Acetone
C2D6SO
TMS
X : parts per Million : Proton
δ (ppm)


1H NMR (DMSO-D6, 300 MHz)
14NNP12-BrCl (product of a3 reaction)
H2O
C2D6SO
TMS
X : parts per Million : Proton
δ (ppm)

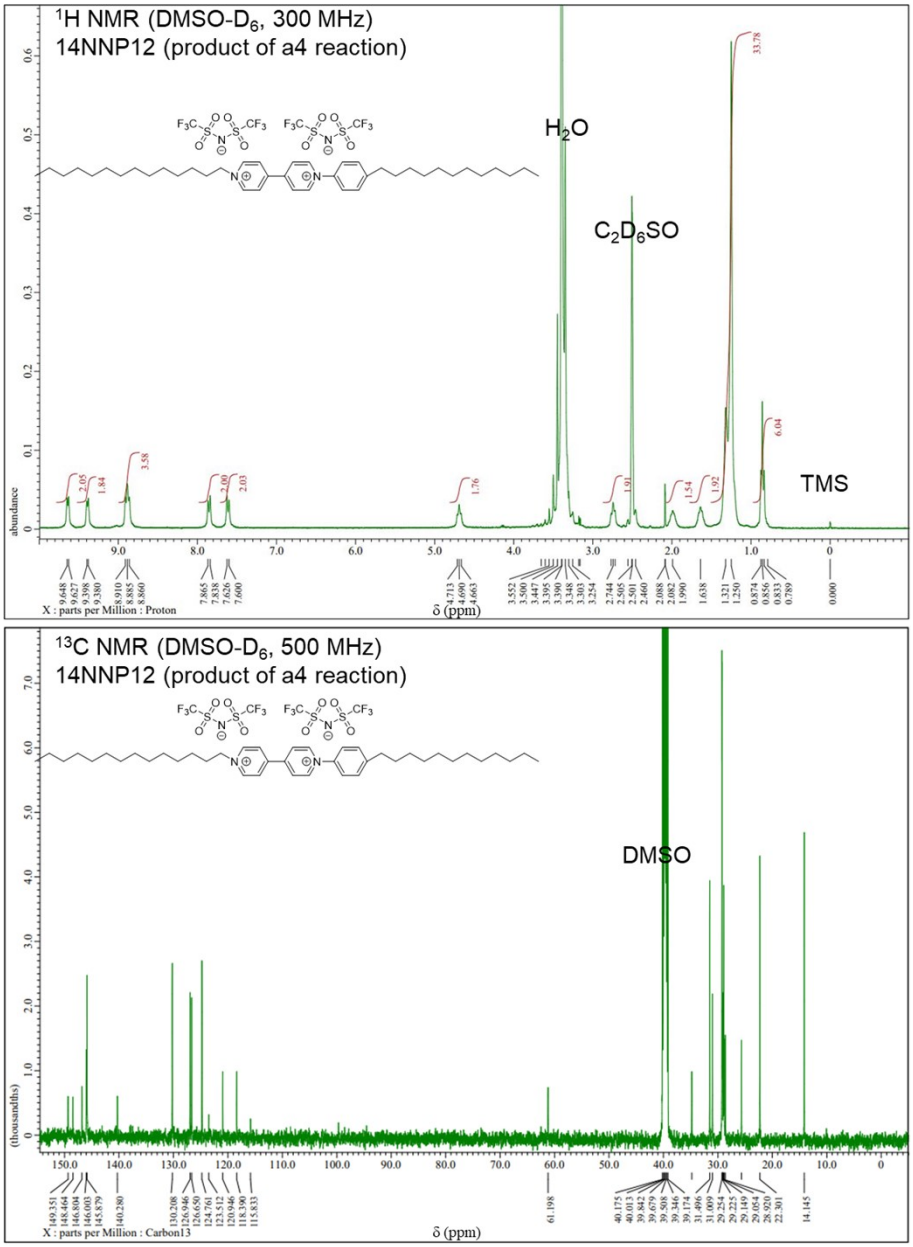
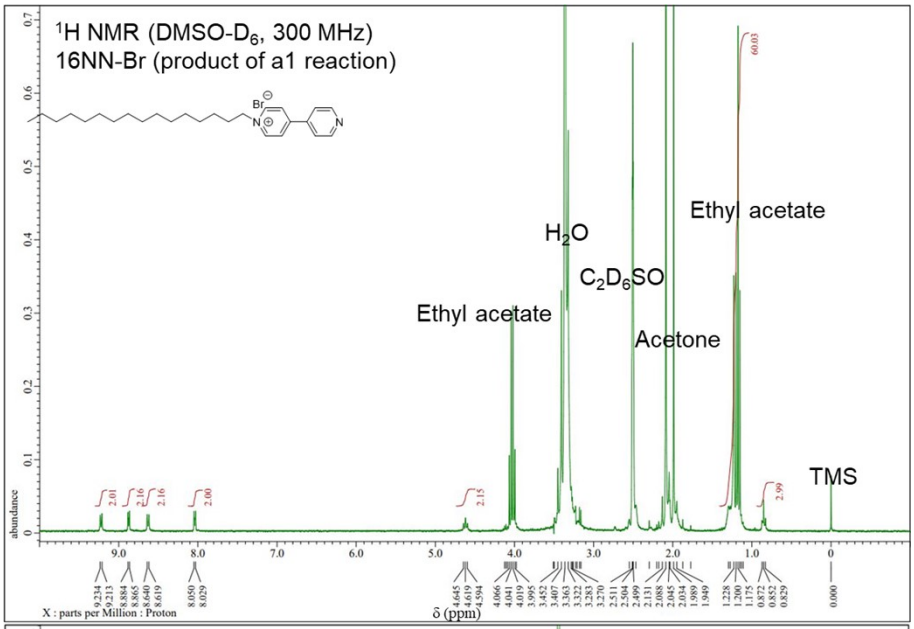
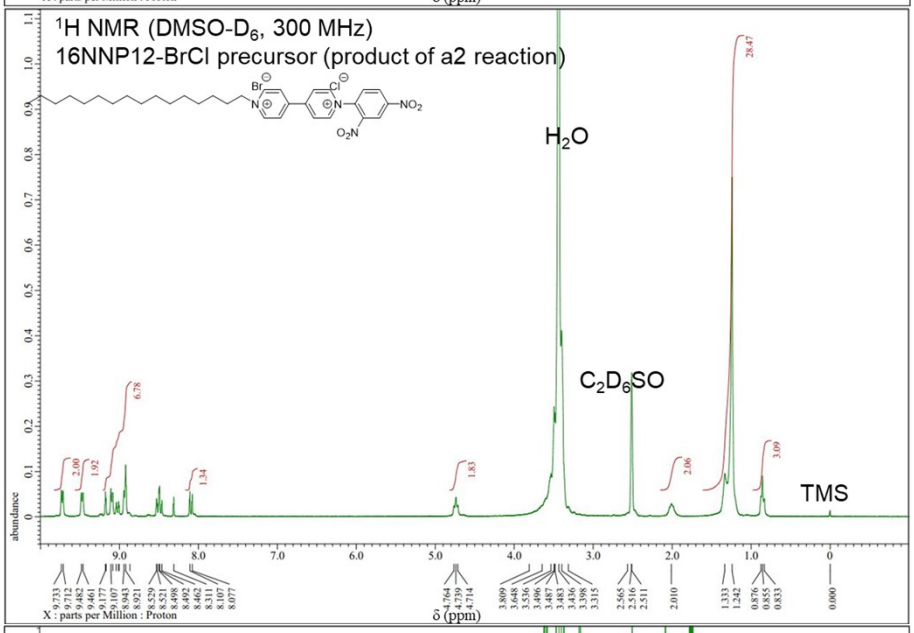


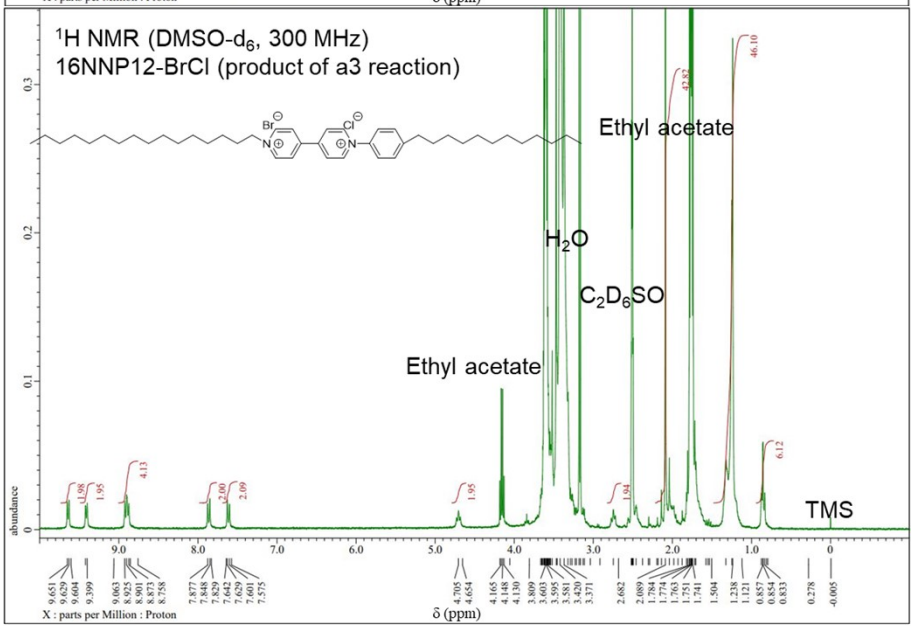
Figure SI-7 ^{1}H- and ^{13}C-NMR spectra of 14NNP12.

Synthesis of 16NNP12

(Step a1) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.22 (d, J = 6.5 Hz, 2H), 8.87 (d, J = 5.8 Hz, 2H), 8.63 (d, J = 6.5 Hz, 2H), 8.04 (d, J = 6.2 Hz, 2H), 4.62 (t, J = 7.6 Hz, 2H), 1.30-1.11 (m, 26H), 0.85 (t, J = 6.5 Hz, 3H)
(Step a2) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.72 (d, J = 6.5 Hz, 2H), 9.47 (d, J = 6.2 Hz, 2H), 9.18-8.87 (m, 6H), 8.09 (d, J = 8.9 Hz, 1H), 4.74 (t, J = 7.4 Hz, 2H), 2.01 (s, 2H), 1.29 (d, J = 27.5 Hz, 26H), 0.85 (t, J = 6.4 Hz, 3H)
(Step a3) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.63 (t, J = 7.1 Hz, 2H), 9.41 (d, J = 6.5 Hz, 2H), 8.93-8.76 (m, 4H), 7.88-7.83 (m, 2H), 7.64-7.57 (m, 2H), 4.68 (d, J = 15.5 Hz, 2H), 2.71 (d, J = 20.0 Hz, 2H), 2.20-1.93 (m, 43H), 1.32-1.12 (m, 46H), 0.88-0.79 (m, 6H)
(Step a4) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.65 (s, 2H), 9.38 (s, 2H), 8.90 (d, J = 1.0 Hz, 4H), 7.84 (s, 2H), 7.63 (s, 2H), 4.69 (s, 2H), 2.64-2.86 (2H), 1.99 (s, 2H), 1.64 (s, 2H), 1.32-1.15 (m, 44H), 0.85 (t, J = 6.4 Hz, 6H). ^{13}C-NMR (500 MHz, DMSO-d_6) δ 149.2, 148.3, 146.6, 145.8, 145.7, 140.1, 130.0, 126.8, 126.5, 124.6, 123.3, 120.8, 118.2, 115.7, 61.0, 34.6, 31.3, 30.8, 29.1, 29.0, 28.9, 28.7, 28.7, 28.5, 25.5, 22.1, 13.9.


^{1}H NMR (DMSO-D$_6$, 300 MHz)
16NN-Br (product of a1 reaction)
Br
N
N
H$_2$O
C$_2$D$_6$SO
Ethyl acetate
Acetone
Ethyl acetate
TMS
abundance
δ (ppm)
X : parts per Million : Proton


^{1}H NMR (DMSO-D$_6$, 300 MHz)
16NNP12-BrCl precursor (product of a2 reaction)
Br
Cl
N
N
NO$_2$
O$_2$N
H$_2$O
C$_2$D$_6$SO
TMS
abundance
δ (ppm)
X : parts per Million : Proton


^{1}H NMR (DMSO-d$_6$, 300 MHz)
16NNP12-BrCl (product of a3 reaction)
Br
Cl
N
N
Ethyl acetate
H$_2$O
C$_2$D$_6$SO
Ethyl acetate
TMS
abundance
δ (ppm)
X : parts per Million : Proton

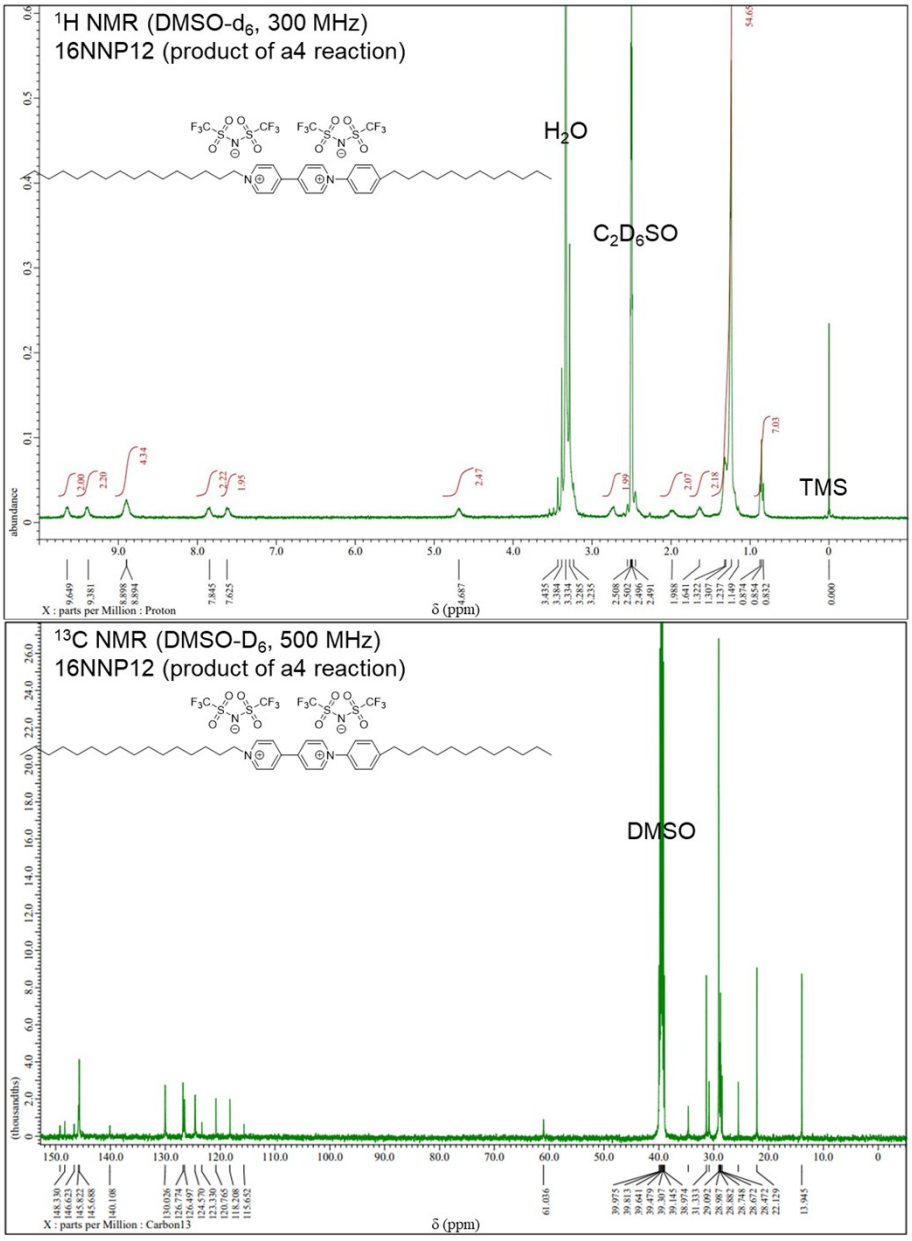


Figure SI-8 ^{1}H- and ^{13}C-NMR spectra of 16NNP12.

Synthesis of 12NN12

(Step 1) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.41 (d, J = 6.2 Hz, 4H), 8.80 (d, J = 6.2 Hz, 4H), 4.70 (t, J = 7.1 Hz, 4H), 1.94 (d, J = 23.7 Hz, 4H), 1.27 (d, J = 20.3 Hz, 36H), 0.87-0.78 (m, 6H)
(Step 2) ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.37 (d, J = 6.5 Hz, 4H), 8.76 (d, J = 6.5 Hz, 4H), 4.67 (t, J = 7.4 Hz, 4H), 1.97 (s, 4H), 1.28 (d, J = 20.0 Hz, 36H), 0.85 (t, J = 6.7 Hz, 6H). ^{13}C-NMR (500 MHz, DMSO-d_6) δ 148.8, 145.8, 126.7, 123.4, 120.9, 118.3, 115.8, 61.1, 31.4, 30.9, 30.8, 29.1, 29.1, 28.9, 28.8, 28.5, 25.6, 22.2, 14.1.

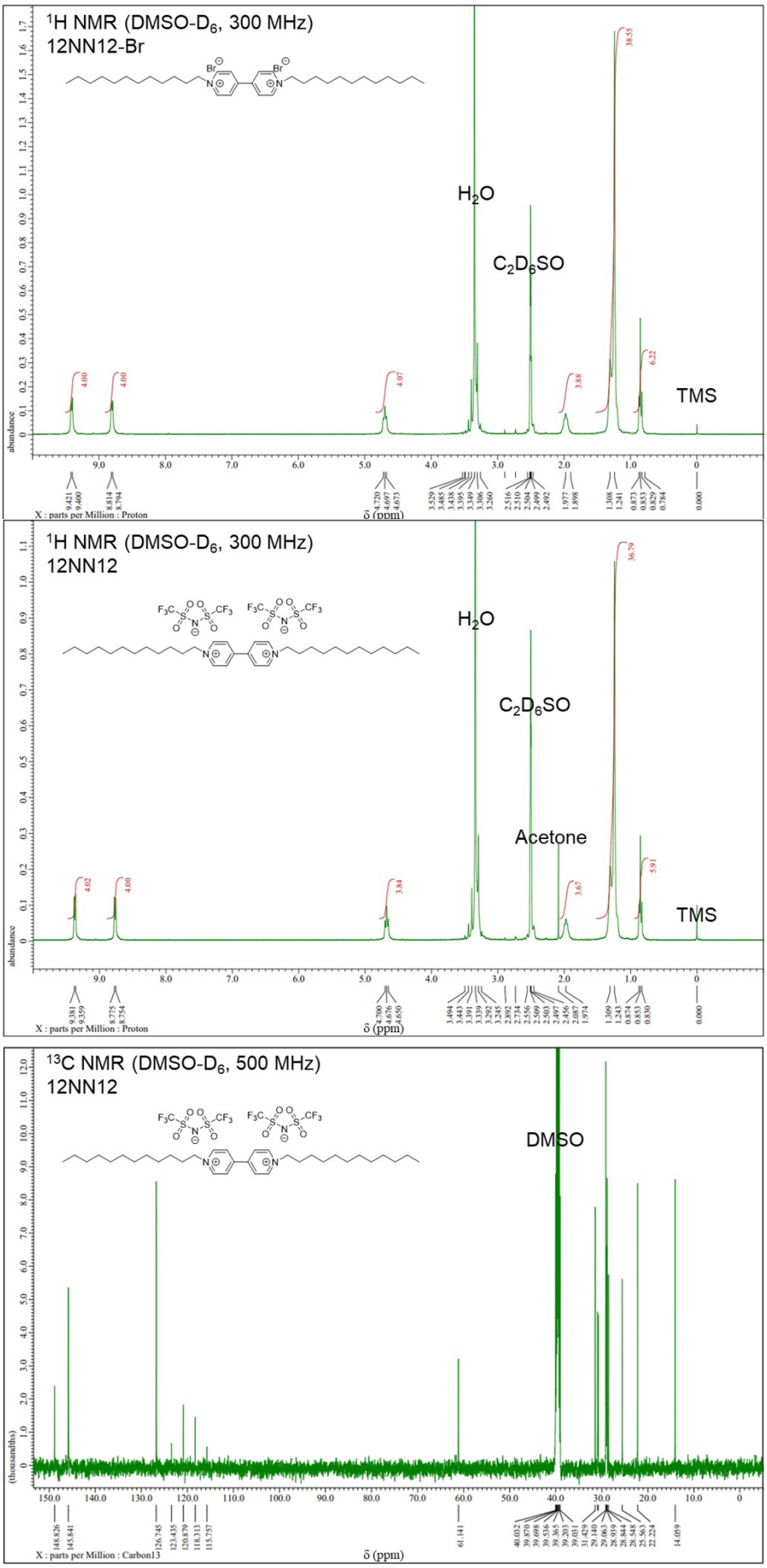
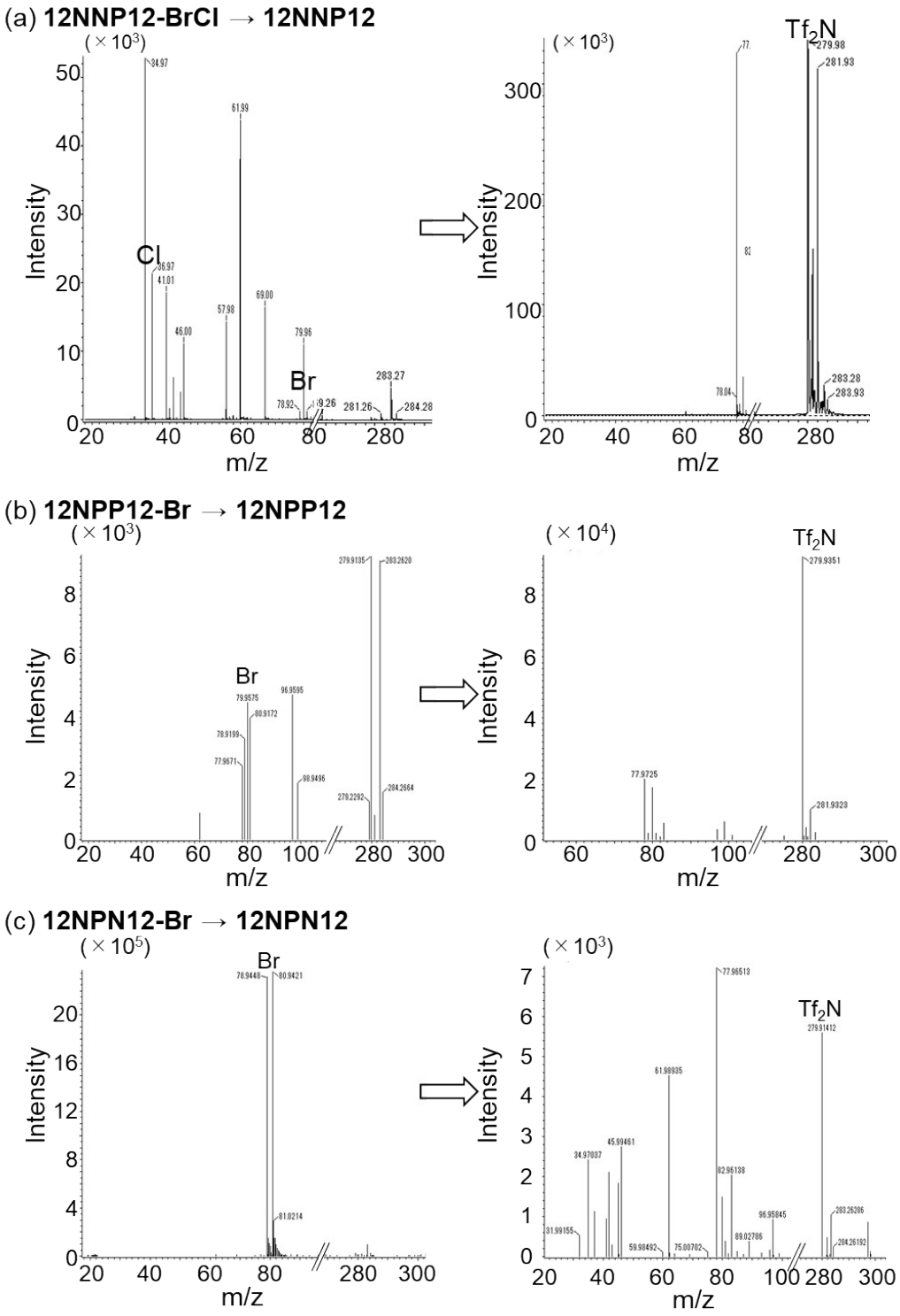


Figure SI-9 ^{1}H- and ^{13}C-NMR spectra of 12NN12.

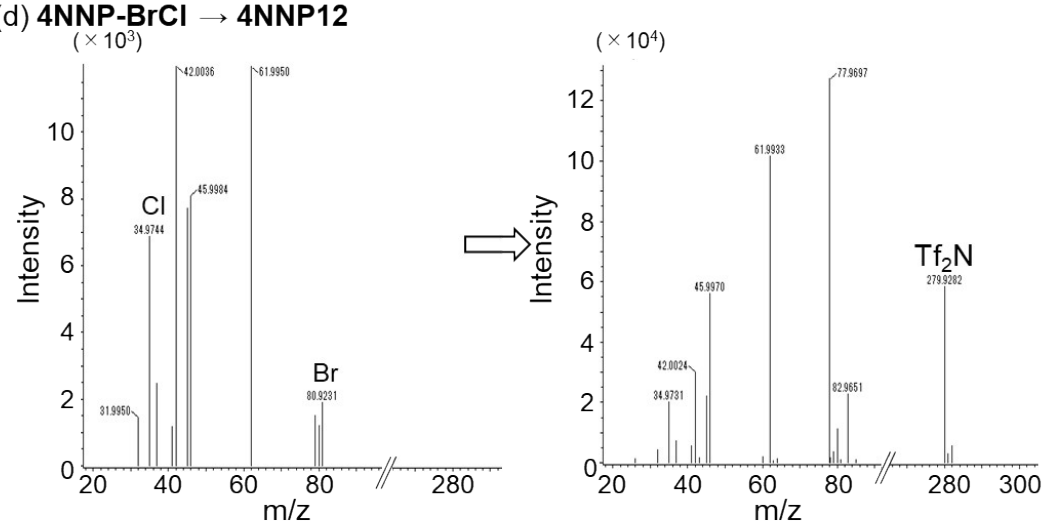
2. Confirmation of the progress of the ion exchange reaction

In the ion-exchange reaction, a slight chemical shift in the ^{1}H-NMR spectrum was observed for all compounds. However, it is not possible to determine from the ^{1}H-NMR spectrum whether there is insufficient ion exchange. Therefore, we confirmed that the halogen (Br^- or Cl^-) disappeared and Tf_2N appeared after the reaction by ESI-TOF-MS measurement. FT-IR measurements also confirmed the appearance of peaks originating from the S=O and C-F stretching vibrations of Tf_2N after the reaction. The results of ESI-TOF-MS and FT-IR measurements are shown below. The purity of the final product was checked by elemental analysis as shown in Experimental section of main text.

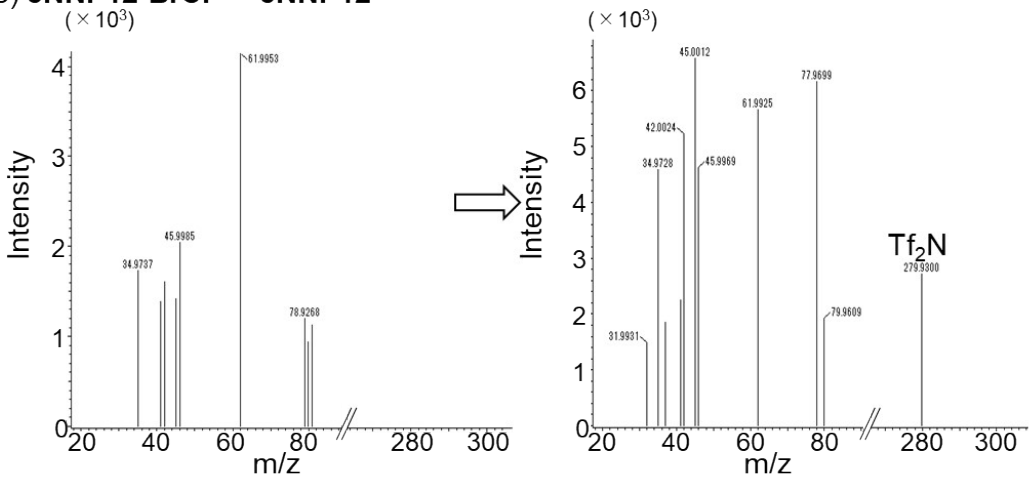
ESI-TOF-MS



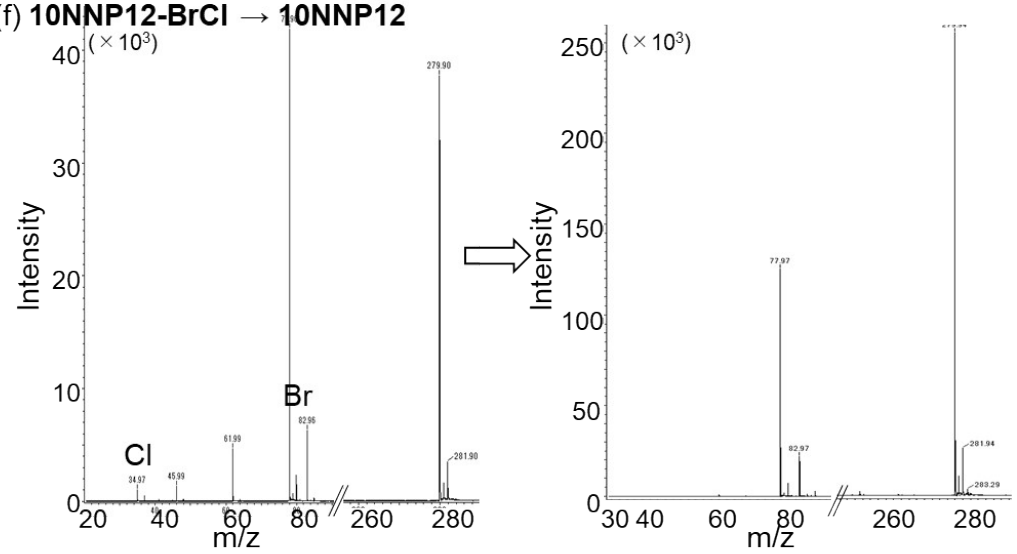
(d) **4NNP-BrCl → 4NNP12**



(e) **8NNP12-BrCl → 8NNP12**



(f) **10NNP12-BrCl → 10NNP12**



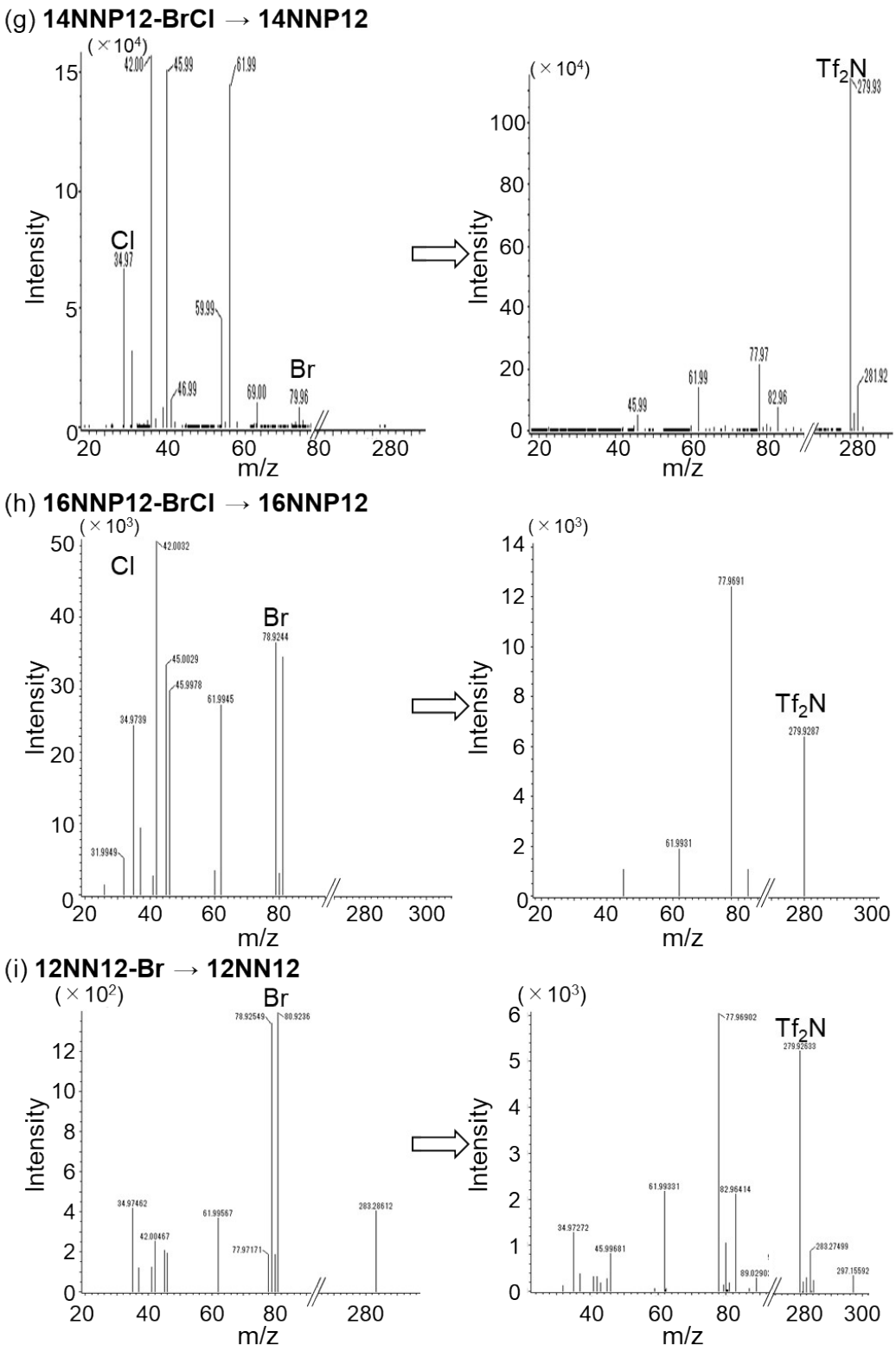


Figure SI-10 ESI-TOF-Mass spectrometry of 12NNP12 (a), 12NPP12 (b), 12NPN12 (c), 4NNP12 (d), 8NNP12 (e), 10NNP12 (f), 14NNP12 (g), 16NNP12 (h), and 12NN12 (i) before and after ion exchange reaction.

FT-IR spectra

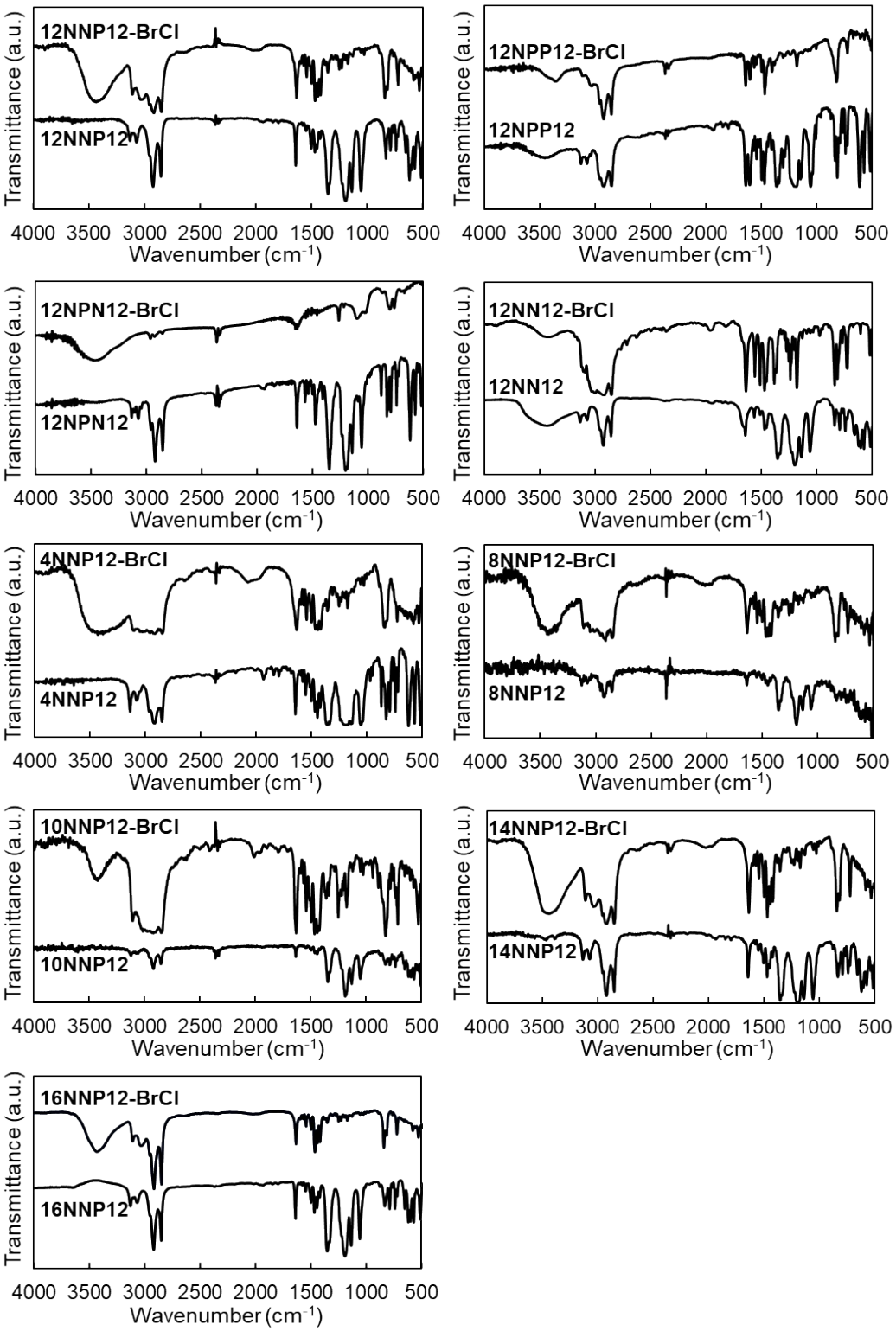


Figure SI-11 FT-IR spectra of 12NNP12, 12NPP12, 12NPN12, 12NN12, 4NNP12, 8NNP12, 10NNP12, 14NNP12, and 16NNP12 before and after ion exchange reaction.

3. LC prperties of 12NN12

The LC property of 12NN12 was evaluated by POM observation, DSC measurement and XRD measurement. In the cooling process of DSC thermogram, the first-order phase-transition peaks appeared at 188.9 °C and 3.5 °C (Fig. SI-12(a)). A polarised optical micrograph under cross nicol was obtained at 100 °C as shown in Fig. SI-12(b). Sharp peaks (black circles) originating from the layer spacing of the smectic phase, broad peaks and small sharp peaks (arrows) originating from the intermolecular regularity appeared in the XRD pattern at 100°C. Therefore, this higher-order LC phase is likely to be the smectic layers with tetragonal symmetry as well as LC phase of 12NPN12.

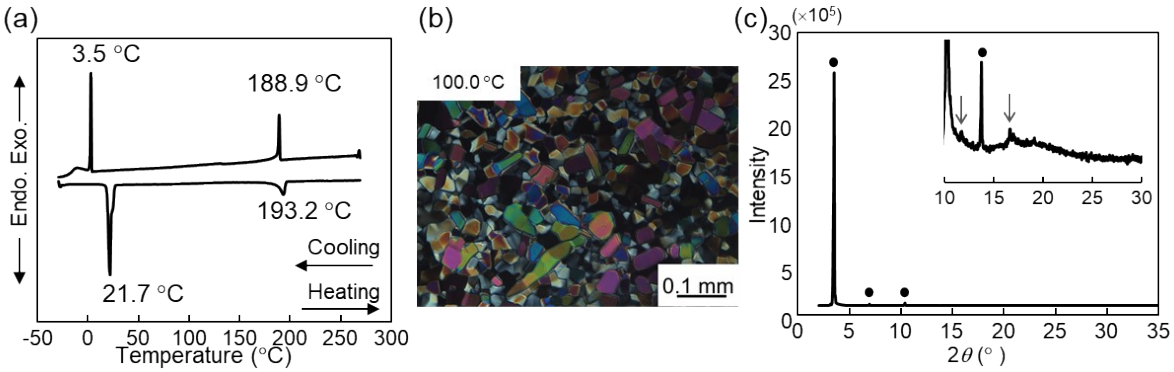


Figure SI-12 DSC thermograms (a), a polarised optical micrograph (b), and XRD patterns (c) of 12NN12. Film thickness of 12NN12 used by POM measurement is 10.4 μm.

4. DSC thermograms of 12NNP12, 12NPP12, and 12NPN12

The original data of the phase-transition temperatures of 12NNP12, 12NPP12, and 12NPN12 in Fig. 3 are shown in Fig. SI-13.

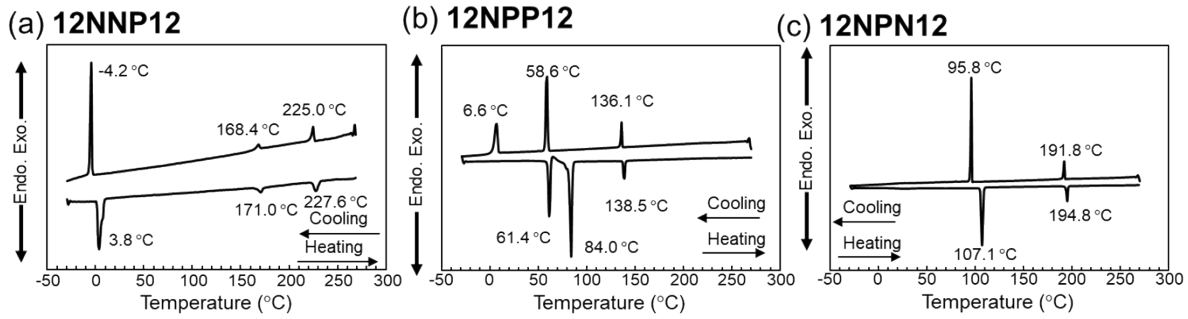


Figure SI-13 DSC thermograms of 12NNP12 (a), 12NPP12 (b), and 12NPN12 (c).

5. Original data of DSC, POM, and XRD mesurements of *n*NNP12 (*n* = 4, 8, 10, 14, 16)

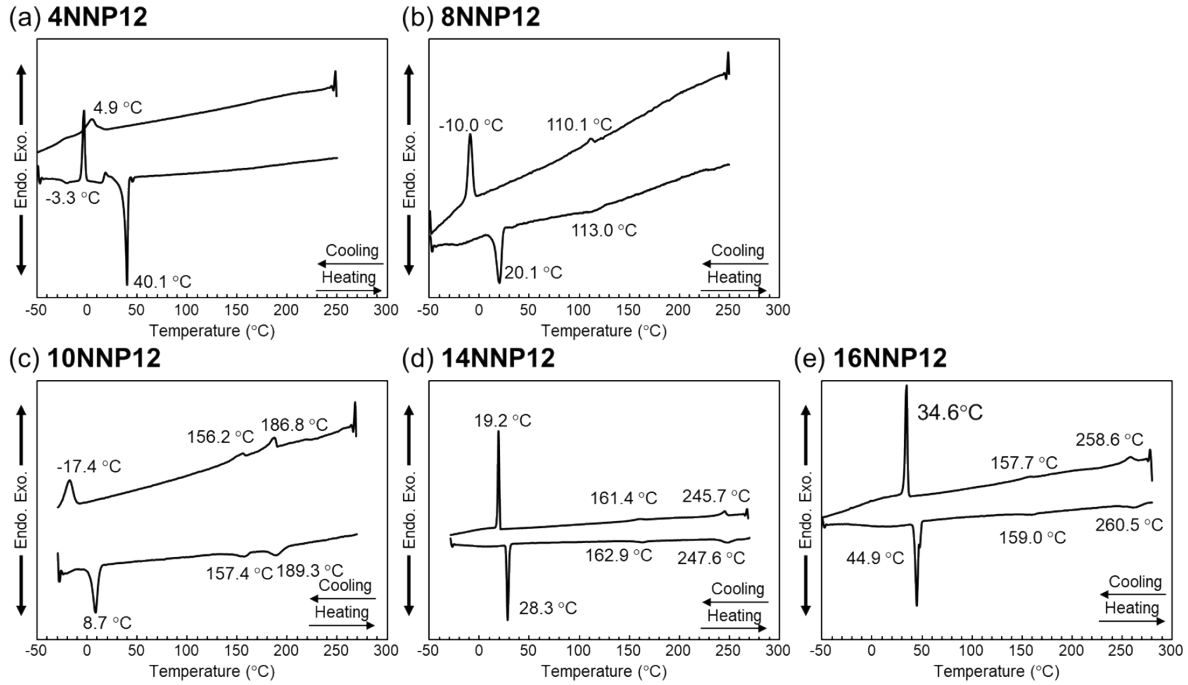


Figure SI-14 DSC thermograms of 4NNP12 (a), 8NNP12 (b), 10NNP12 (c), 14NNP12 (d), and 16NNP12 (e).

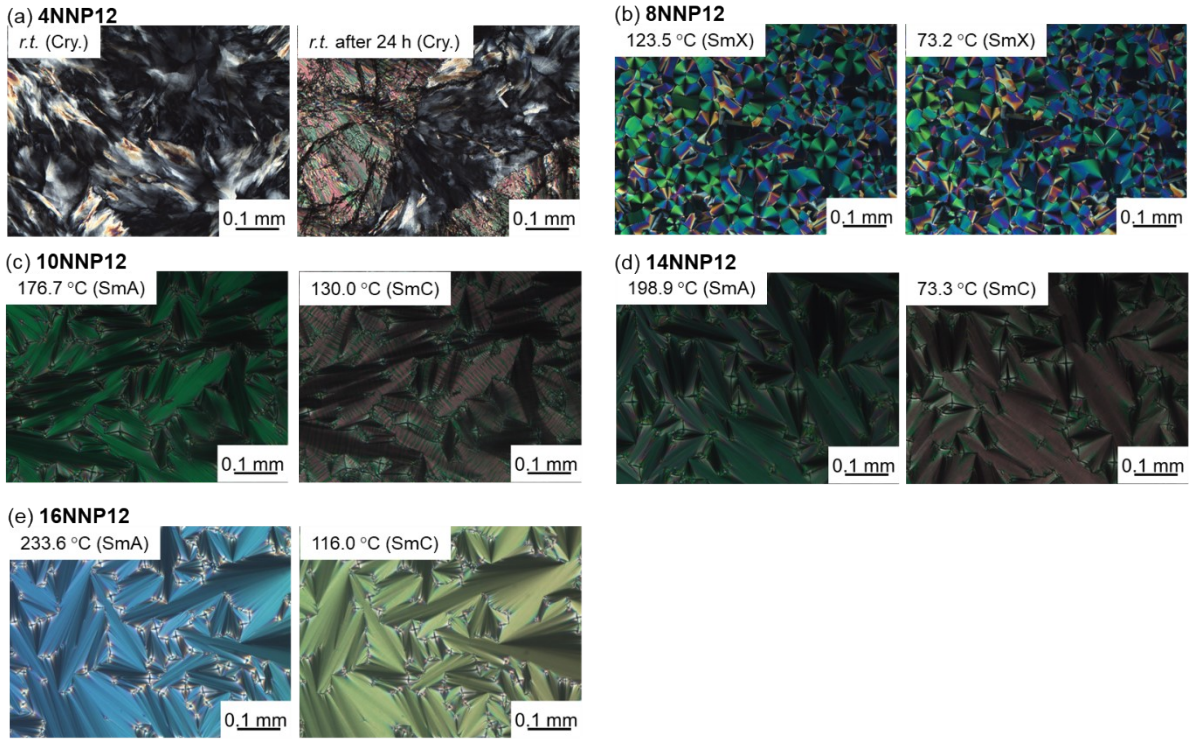


Figure SI-15 Polarised optical micrographs of 4NNP12 (a), 8NNP12 (b), 10NNP12 (c), 14NNP12 (d), and 16NNP12 (e).

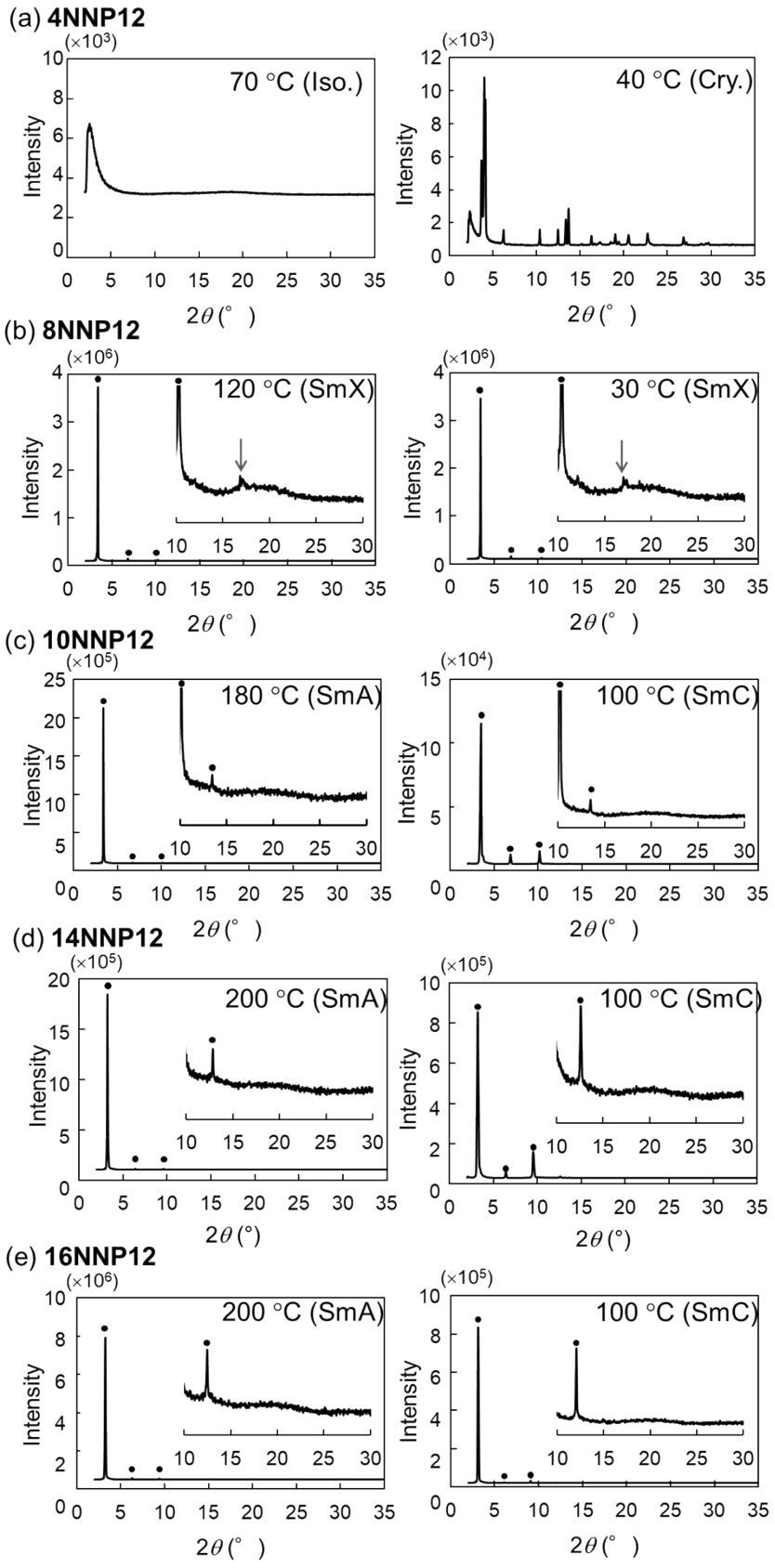


Figure SI-16 XRD patterns of 4NNP12 (a), 8NNP12 (b), 10NNP12 (c), 14NNP12 (d), and 16NNP12 (e).

6. Thermal stability

Although not mentioned in the main text, the thermal stability of obtained products was investigated by thermogravimetric analysis (TGA).

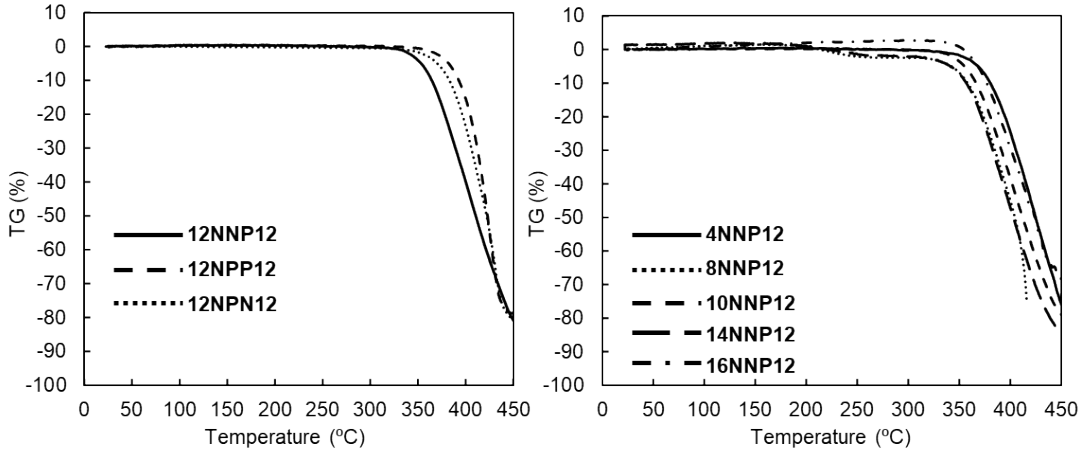


Figure SI-17 The thermogravimetric curves of compounds synthesized in this study.