Supplementary Information

Dithienylethene metallodendrimers with high photochromic efficiency

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Table of Contents

1. General Information

All reagents were commercially available and used as supplied without further purification. TLC analyses were performed on silica-gel plates, and flash chromatography was conducted using silica-gel column packages purchased from Qing-dao Haiyang Chemical Co (China). Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA).

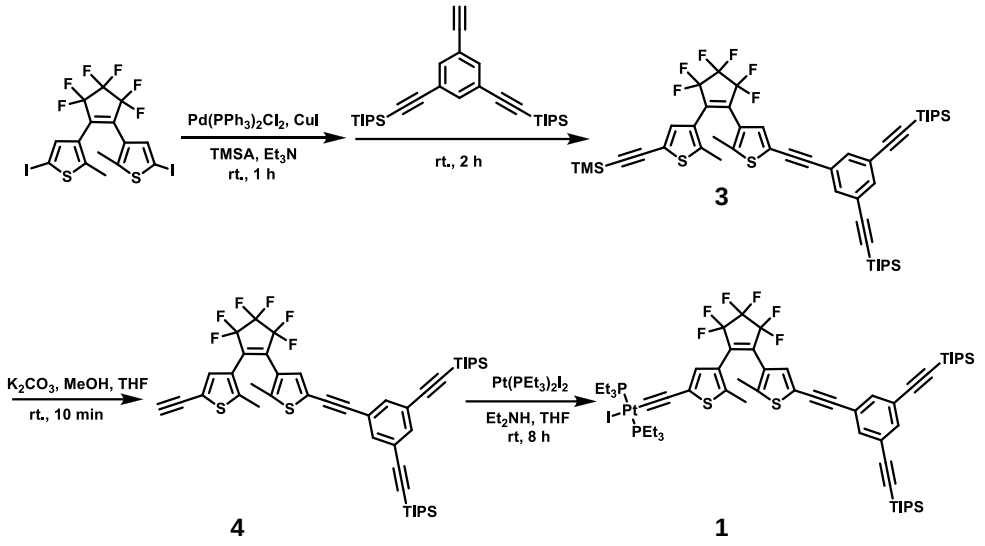
NMR spectra were recorded on a Bruker DRX 400 (400 MHz) or 500 (500 MHz) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and $^{31}P\{^{1}H\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). The two-dimensional diffusion-ordered NMR spectroscopy (2D-DOSY) was recorded on a Bruker DRX500 spectrometer. AFM images were obtained on a Dimension FastScan (Bruker), using ScanAsyst mode under ambient condition. UV−vis spectra were recorded in a quartz cell (light path 10 mm) on a Cary 50Bio UV-Visible spectrophotometer. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Cary Eclipse fluorescence spectrophotometer.

The MALDI MS experiments were carried out on a Bruker UltrafleXtreme MALDI TOF/TOF Mass Spectrometer (Bruker Daltonics, Billerica, MA), equipped with smart beam-II laser. All spectra were measured in positive reflectron or linear mode.

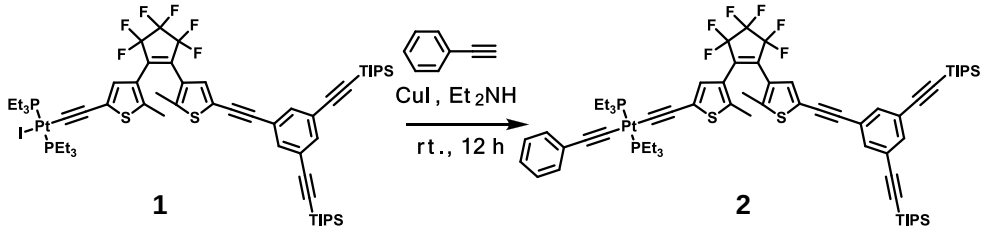
Broadband transient absorption (TA) spectra were acquired on a commercial transient absorption spectrometer (Helios-EOS fire, Ultrafast System) with and 1 kHz Ti:sapphire laser amplifier system (Astrella, Coherent Inc.) with 120 fs time resolution. A magic angle (54.7°) was set between the polarization of pump and probe beams. The samples were hold in a 2-mm quartz cell and continuously stirred by a magnetic bar.

2. Synthesis and Characterization of Precursors and DTE Dendrimers Gn.

2.1 Synthesis of key building block platinum-acetylide complexes **1** and **2**.



Scheme S1. The synthesis route of platinum-acetylide complex **1**.



Scheme S2. The synthesis route of platinum-acetylide model complex **2**.

Synthesis of 3: A Schlenk flask was charge with 1,2-bis(5-iodo-2-methylthiophen-3-yl)cyclopentene (2.1 g, 3.39 mmol), $Pd(PPh_3)_2Cl_2$ (238 mg, 0.34 mmol) and CuI (65 mg, 0.34 mmol). The Schlenk flask was then evacuated via reduced pressure and backfilled with N_2 for three times. Next, Et_3N (50 mL) was added via syringe. The resultant solution was stirred for 5.0 min. Then TMSA (333 mg, 3.39 mmol) was added to the mixture, and the mixture was allowed to stir for 1.0 h. Then 1,3-bis(ethynyltriisopropylsilane)-5-ethynylbenzene (2.35 g, 5.08 mmol) was added to the mixture. The solvent was then removed by reduced pressure, and the compound was purified by column chromatography on silica gel (eluent: petroleum ether): 940 mg (30% yield) of a white oil was

afforded. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (m, 2H), 7.50 (m, 1H), 7.24 (s, 1H), 7.22 (s, 1H), 1.93 (s, 3H), 1.89 (s, 3H), 1.13 (s, 42H) , 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 143.4, 135.0, 134.4, 132.0, 131.8, 124.9, 124.5, 124.3, 122.9, 121.8, 121.3, 105.0, 100.1, 96.2, 92.5, 92.4, 82.5, 18.7, 14.6, 14.5, 11.3, 0.24. MS (ESI): Calculated for $C_{50}H_{62}F_6Si_3S_2$ $[M + H]^+$: 925.35; Found: 925.44.

Synthesis of 4: A round-bottom flask was charged with **3** (500 mg, 0.54 mmol). 20 mL of a THF/MeOH solution (v/v, 1:1) was added to the round-bottom flask. Then K_2CO_3 (298 mg, 2.16 mmol) was added to the resultant solution. The mixture was allowed to stir for 10 min. The solvent was then removed by reduced pressure, and the compound was purified by column chromatography (eluent: petroleum ether): 437 mg (95% yield) of a white oil was afforded. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (m, 2H), 7.51 (m, 1H), 7.25 (s, 1H), 3.36 (s, 1H), 1.93 (s, 6H), 1.13 (s, 42H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 143.7, 135.0, 134.4, 132.6, 131.8, 124.8, 124.6, 124.3, 122.9, 121.4, 120.6, 105.0, 92.5, 92.4, 82.4, 82.3, 75.8, 18.7, 14.5, 14.4, 11.3. MS (ESI): Calculated for $C_{47}H_{54}F_6Si_2S_2$ $[M + H]^+$: 853.31; Found: 853.37.

Synthesis of 1: A Schlenk flask was charge with **4** (400 mg, 0.47 mmol) and $Pt(PEt_3)_2I_2$ (967 mg, 1.41 mmol). The Schlenk flask was then evacuated via reduced pressure and backfilled with N_2 for three times. Next, THF (30 mL) and Et_2NH (15 mL) was added via syringe. The resultant solution was stirred for 5.0 min. Then CuI (4.5 mg, 1.41 mmol) was added to the mixture under N_2 atmosphere, and the mixture was allowed to stir overnight. The solvent was then removed by reduced pressure, and the compound was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, v/v, 20:1 to 5:1): 417 mg (63% yield) of a blue oil was afforded. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.54 (m, 2H), 7.52 (m, 1H), 7.26 (s, 1H), 6.77 (s, 1H), 2.18 (m, 12H), 1.98 (s, 1H), 1.89 (s, 1H), 1.14 (m, 60H); ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 10.82 (J = 2300.6 Hz); ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 144.6, 139.4, 134.6, 134.1, 132.6, 128.1, 126.7, 125.1, 124.4, 123.9, 123.5, 120.7, 104.9, 98.0, 92.4, 91.6, 91.1, 82.2, 18.1, 16.5, 13.7, 13.6, 11.1, 7.7.

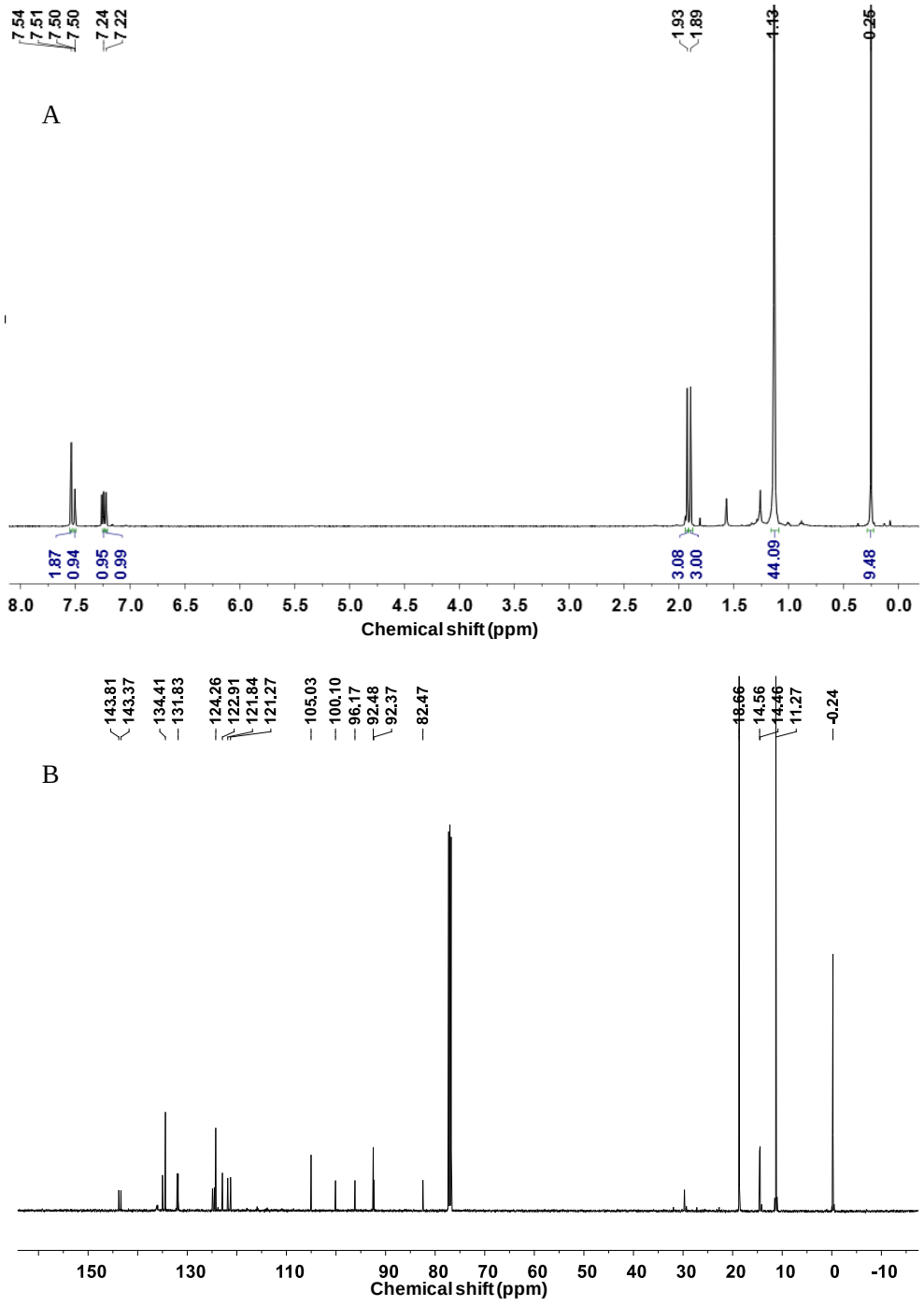


Figure S1. (A) ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz), and (B) ^{13}C NMR spectrum ($CDCl_3$, room temperature, 100 MHz) of **3**.

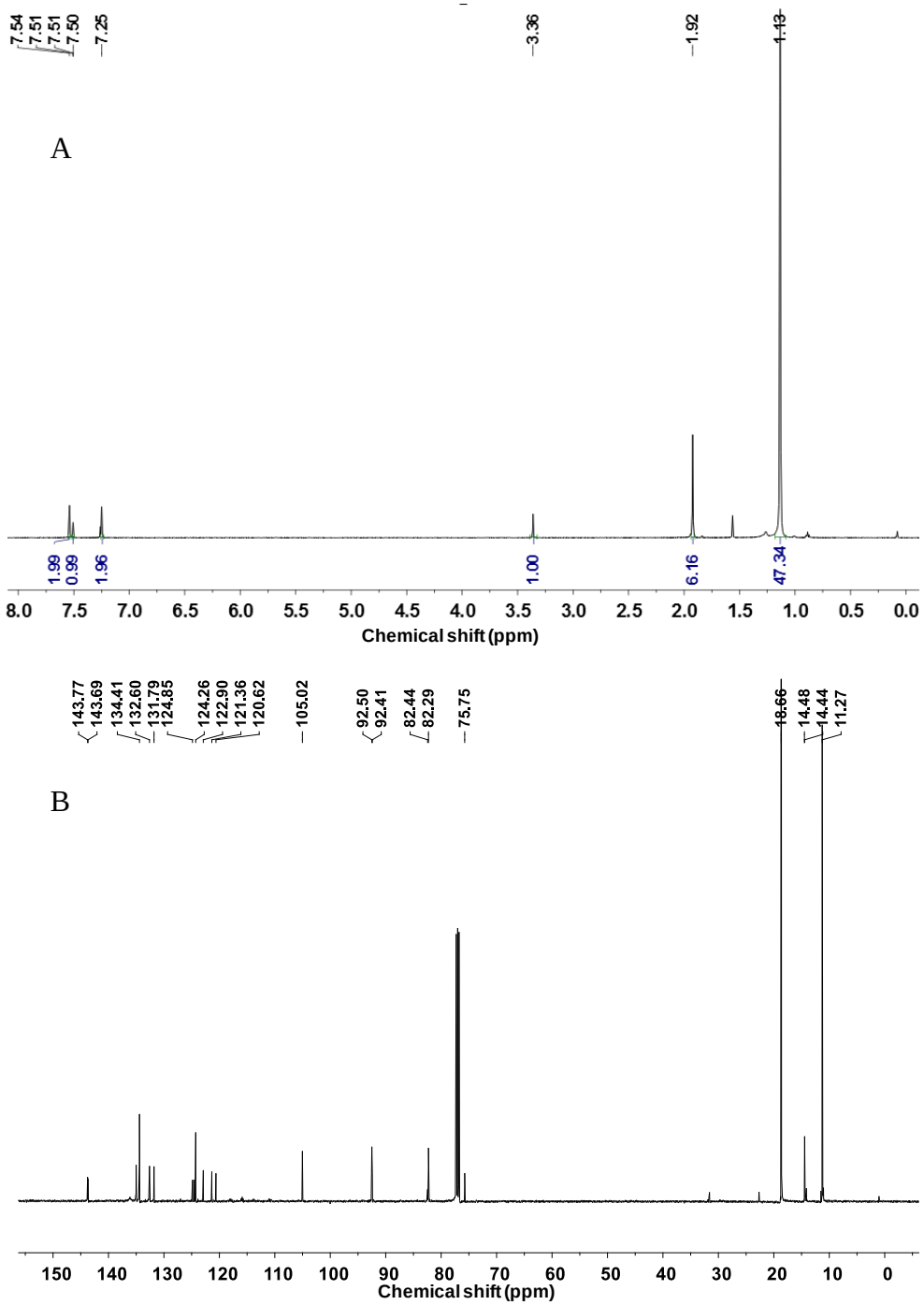
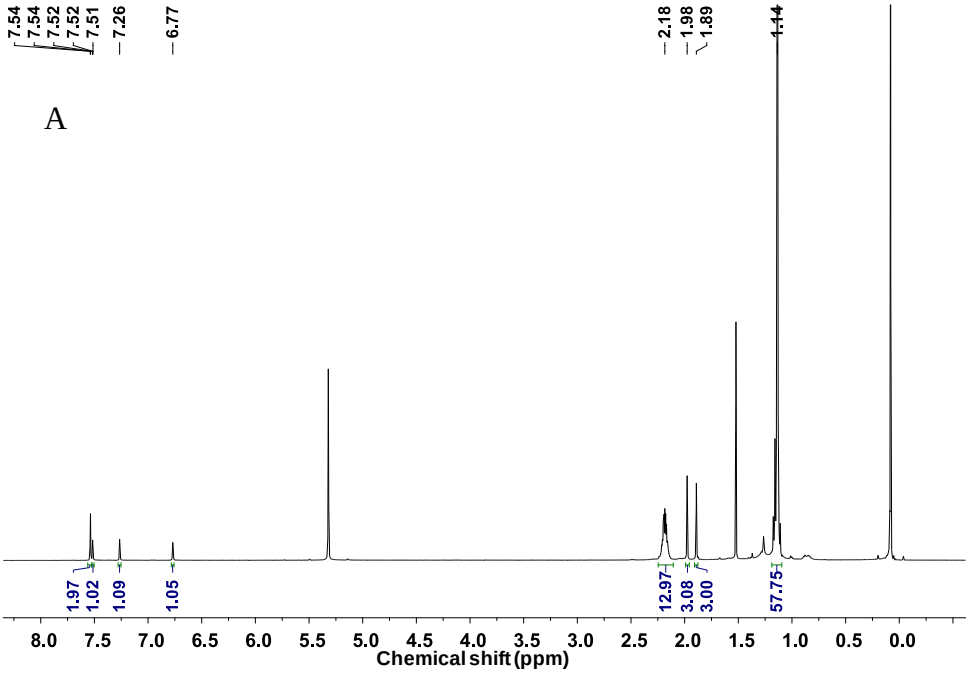


Figure S2. (A) ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz), and (B) ^{13}C NMR spectrum ($CDCl_3$, room temperature, 100 MHz) of **4**.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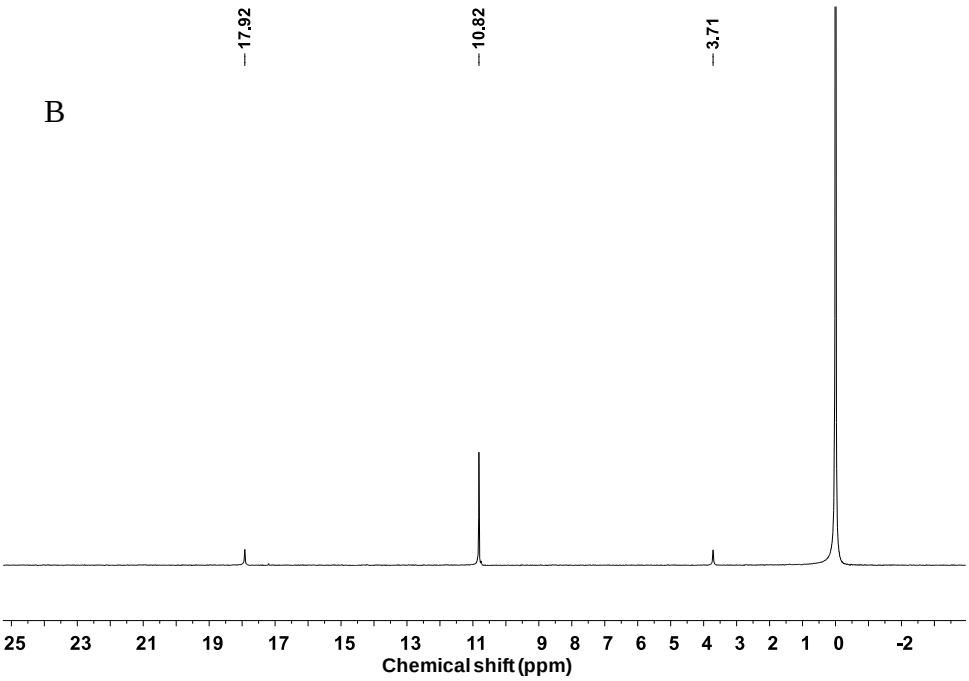
7.54
7.54
7.52
7.52
7.51
7.26
6.77
2.18
1.98
1.89
1.14
1.97
1.02
1.09
1.05
12.97
3.08
3.00
57.75
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)


B
17.92
10.82
3.71
25 23 21 19 17 15 13 11 9 8 7 6 5 4 3 2 1 0 -2
Chemical shift (ppm)

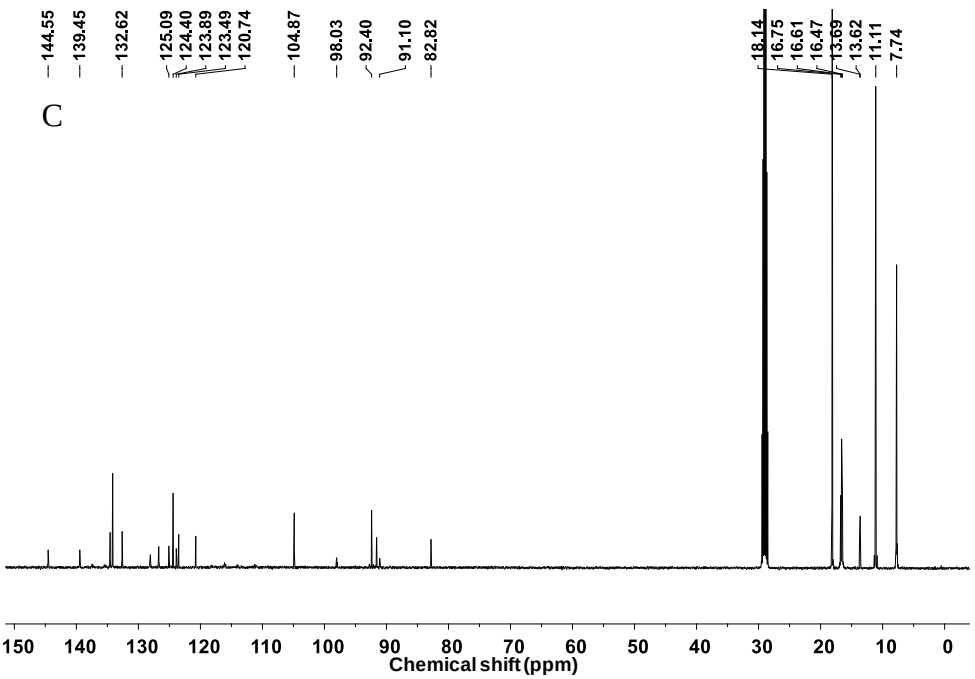
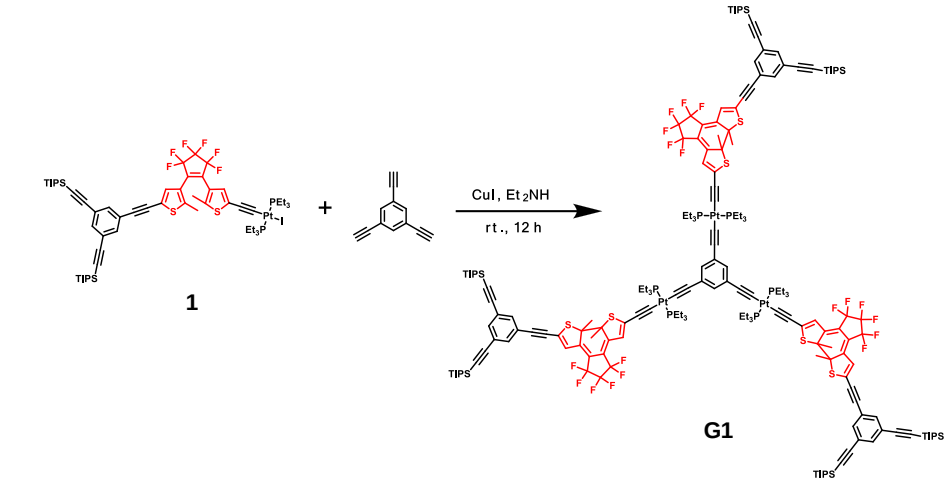
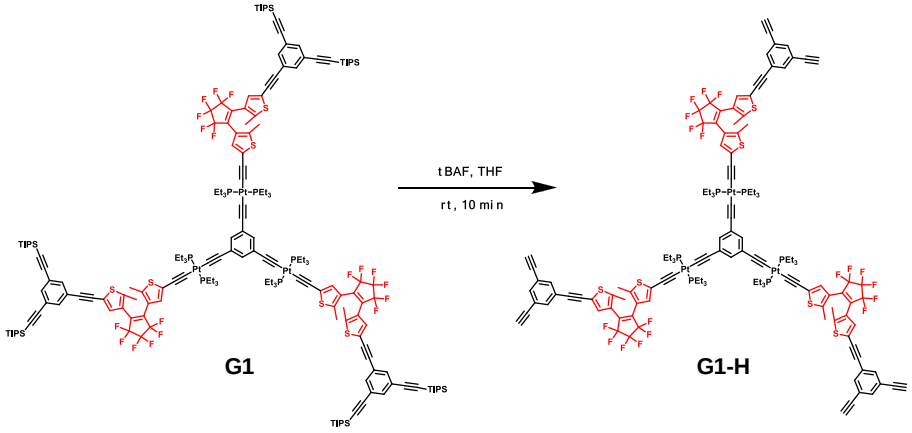
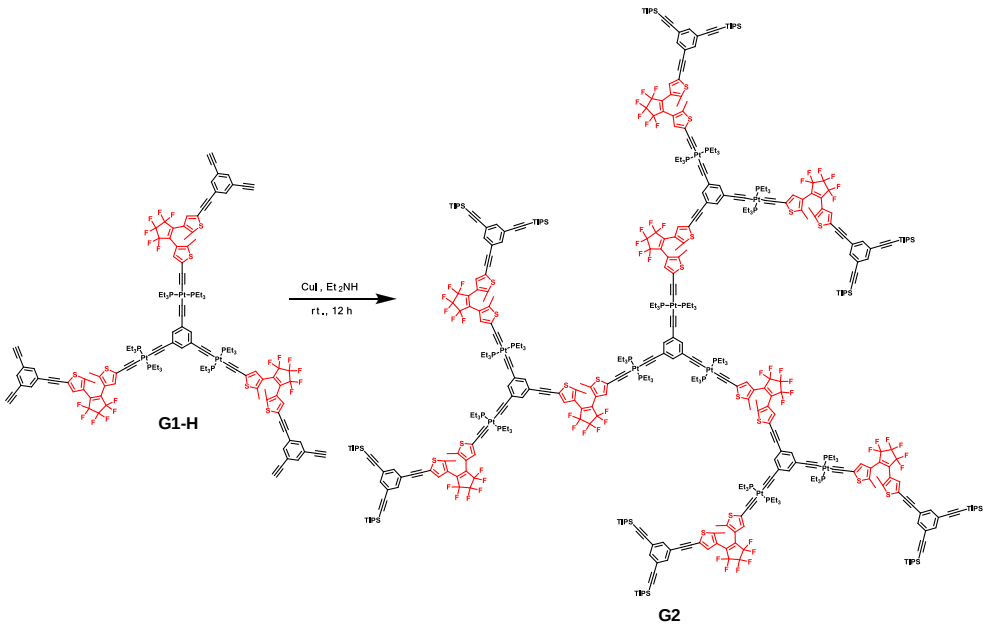


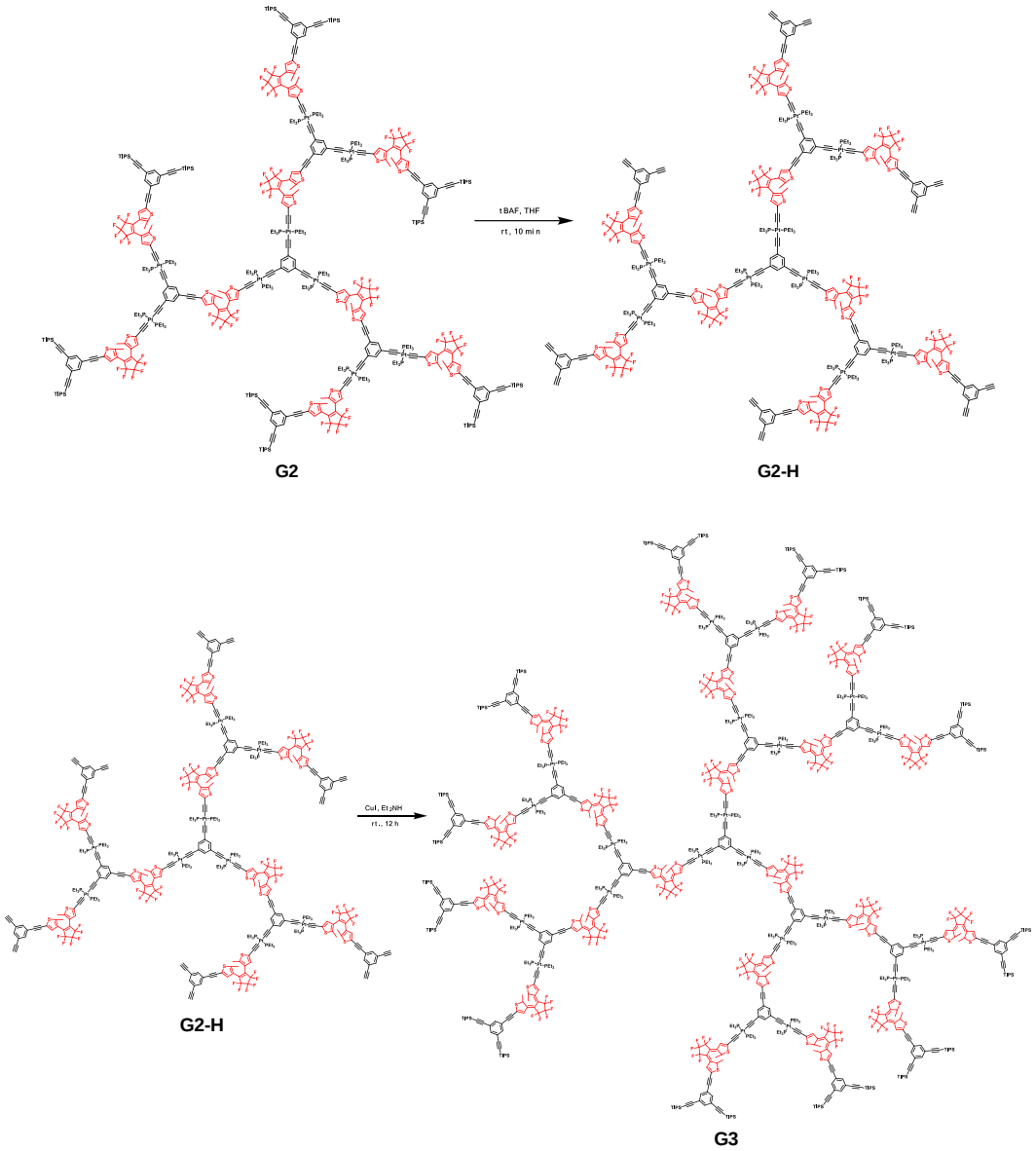
Figure S3. (A) ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 400 MHz), (B) ^{31}P NMR spectrum (CD_2Cl_2, room temperature, 161.9 MHz), and (C) ^{13}C NMR spectrum (CD_2Cl_2, room temperature, 125 MHz) of **1**.

2.2 Synthesis of DTE dendrimers **Gn** and **Gn-H**.









Scheme S3. The synthesis route of DTE dendrimers **Gn** and **Gn-H**.

Synthesis of G1: A Schlenk flask was charge with 1,3,5-triethynylbenzene (44.4 mg 0.296 mmol) and **1** (800 mg, 0.932 mmol). The Schlenk flask was then evacuated via reduced pressure and backfilled with N_2 for three times. Next, Et_2NH (10 mL) was added via syringe. The solution was stirred for 5 min. Then CuI (9 mg) was added to the mixture under N_2 atmosphere, and the mixture was allowed to stir overnight. The solvent was then removed by reduced pressure, and the compound was purified by alumina column chromatography (eluent: ether/dichloromethane (2:1)): 620 mg (67% yield) of a slight yellow solid was afforded. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.54 (br, 6H), 7.51 (br, 3H), 7.27 (s, 3H), 6.91 (s, 3H), 6.74 (s, 3H), 2.13 (m, 36H), 1.98 (s, 9H), 1.87 (s, 9H), 1.20 (m, 54H), 1.13 (s, 126H); ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 11.51 (J = 2351.6 Hz); ^{13}C

NMR (CD_2Cl_2, 100 MHz): δ 144.6, 138.9, 134.5, 134.2, 132.7, 128.6, 124.4, 123.5, 120.7, 116.7, 109.1, 106.2, 104.9, 99.7, 92.4, 91.6, 82.8, 18.1, 16.4, 13.6, 11.1, 7.9. MS (MALDI-TOF-MS): Calculated for $C_{189}H_{252}F_{18}P_6Pt_3S_6Si_6$ $[M]^+$: 3994.37; Found: 3999.1.

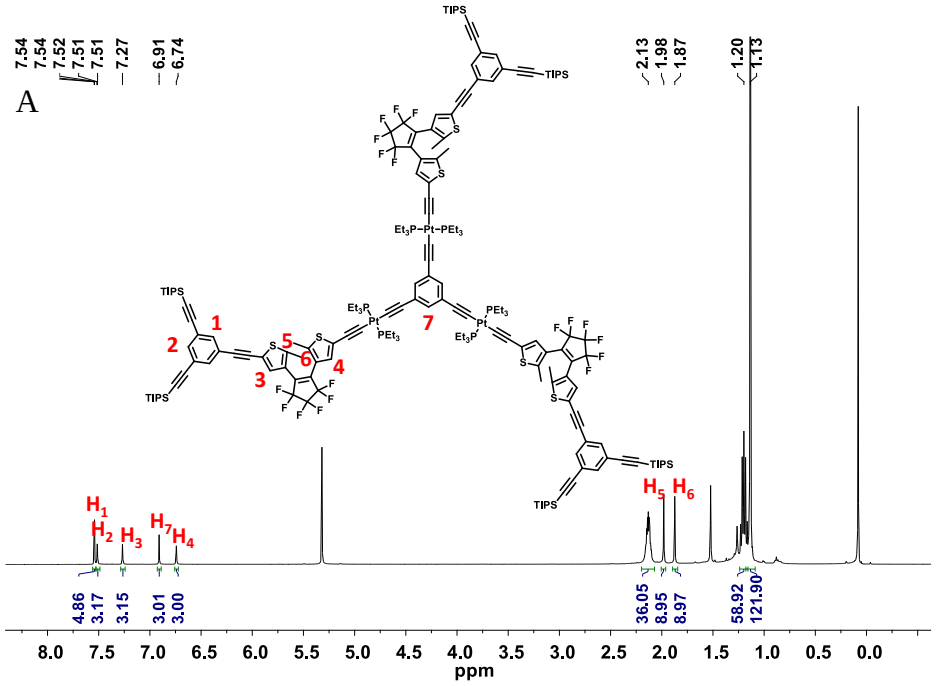
Synthesis of G1-H: A solution of the **G1** (150 mg, 0.053 mmol) in THF was cooled in ice bath, and a solution of Bu_4NF (0.48 mmol) in THF (1.0 M) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 10 min. The solvent was removed under reduced pressure and the residue was purified by alumina column chromatography with dichloromethane: 85 mg (85% yield) of a slight yellow solid was afforded. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.59 (br, 9H), 7.28 (s, 3H), 6.91 (s, 3H), 6.74 (s, 3H), 3.05 (s, 6H), 2.15 (m, 48H), 1.99 (s, 9H), 1.98 (s, 9H), 1.20 (m, 72H); ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 11.75; ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 143.9, 140.8, 131.2, 130.2, 127.6, 126.3, 125.3, 123.9, 110.9, 109.4, 94.53, 93.27, 16.5, 16.3, 7.91.

Synthesis of G2: G1-H (60 mg 0.0318 mmol) and **1** (204 mg, 0.200 mmol) were reacted in a similar manner to that of the preparation of G1. Column chromatography on silica gel was performed with dichloromethane as eluent: 800 mg (87% yield) of a slight yellow solid was afforded. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.54 (s, 6H), 7.51 (s, 12H), 7.28 (br, 9H), 7.13 (br, 9H), 6.92 (s 3H), 6.78 (s 3H), 6.74 (s 6H), 2.13 (m, 108H), 1.98 (s, 18H), 1.94 (s, 9H), 1.88 (s, 18H), 1.84 (s, 9H), 1.20 (m, 162H), 1.13 (s, 252H); ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 12.07, 11.96; ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 144.3, 143.7, 139.2, 134.8, 134.2, 132.2, 128.9, 128.2, 124.2, 123.9, 123.1, 120.8, 116.1, 104.9, 92.6, 91.9, 82.6 18.4, 16.4, 14.3, 11.3, 8.1. MS (MALDI-TOF-MS): Calculated for $C_{489}H_{624}F_{54}P_{18}Pt_9S_{18}Si_{12}$ $[M]^+$: 10746.23; Found: 10780.5.

Synthesis of G2-H: A solution of the **G2** (130 mg, 0.018 mmol) in THF was cooled in ice bath, and a solution of Bu_4NF (0.32 mmol) in THF (1.0 M) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 10 min. The solvent was removed under reduced pressure and the residue was purified by alumina column chromatography with dichloromethane: 87 mg (91% yield) of a slight yellow solid was afforded. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.59 (br, 18H), 7.14 (br, 9H), 6.95 (s, 3H), 6.78 (s, 3H), 6.78 (s, 3H), 6.75 (s, 6H), 3.05 (s, 12H), 2.15 (m, 144H), 1.99 (s, 18H), 1.95 (s, 9H), 1.89 (s, 18H), 1.86 (s, 9H), 1.21 (m, 216H); ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 11.77, 11.72; ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 143.9, 143.8, 140.9, 140.6, 131.2, 130.0, 127.6, 125.6, 123.8, 121.7, 109.7, 108.7, 107.5, 1002, 93.6, 80.7, 16.3, 16.0,

14.1, 8.11.

Synthesis of G3: G2-H (50 mg 0.0093 mmol) and **1** (119 mg, 0.117 mmol) were reacted in a similar manner to that of the preparation of **G2**. Alumina column chromatography was performed with dichloromethane as eluent: 79 mg (53% yield) of a slight yellow solid was afforded. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.54 (s, 27H), 7.28 (br, 9H), 7.28 (br, 21H), 6.92 (s, 6H), 6.81 (s, 6H), 6.79 (s, 6H), 6.74 (s, 6H), 2.13 (m, 288H), 1.98 (s, 36H), 1.94 (s, 18H), 1.92 (s, 9H), 1.88 (s, 36H), 1.85 (s, 18H), 1.82 (s, 9H), 1.20 (m, 432H), 1.13 (s, 441H); ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 12.23, 12.21; ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 144.3, 143.7, 139.3, 131.5, 126.2, 124.2, 123.1, 120.1, 116.1, 108.4, 104.9, 100.1, 92.5, 91.8, 82.6, 80.9, 18.7, 16.5, 16.3, 14.3, 14.2, 12.8, 11.3, 8.1. MS (MALDI-TOF-MS): Calculated for $C_{1089}H_{1368}F_{126}P_{42}Pt_{21}S_{42}Si_{24}$ $[M]^+$: 24249.93; Found: 24396.2.



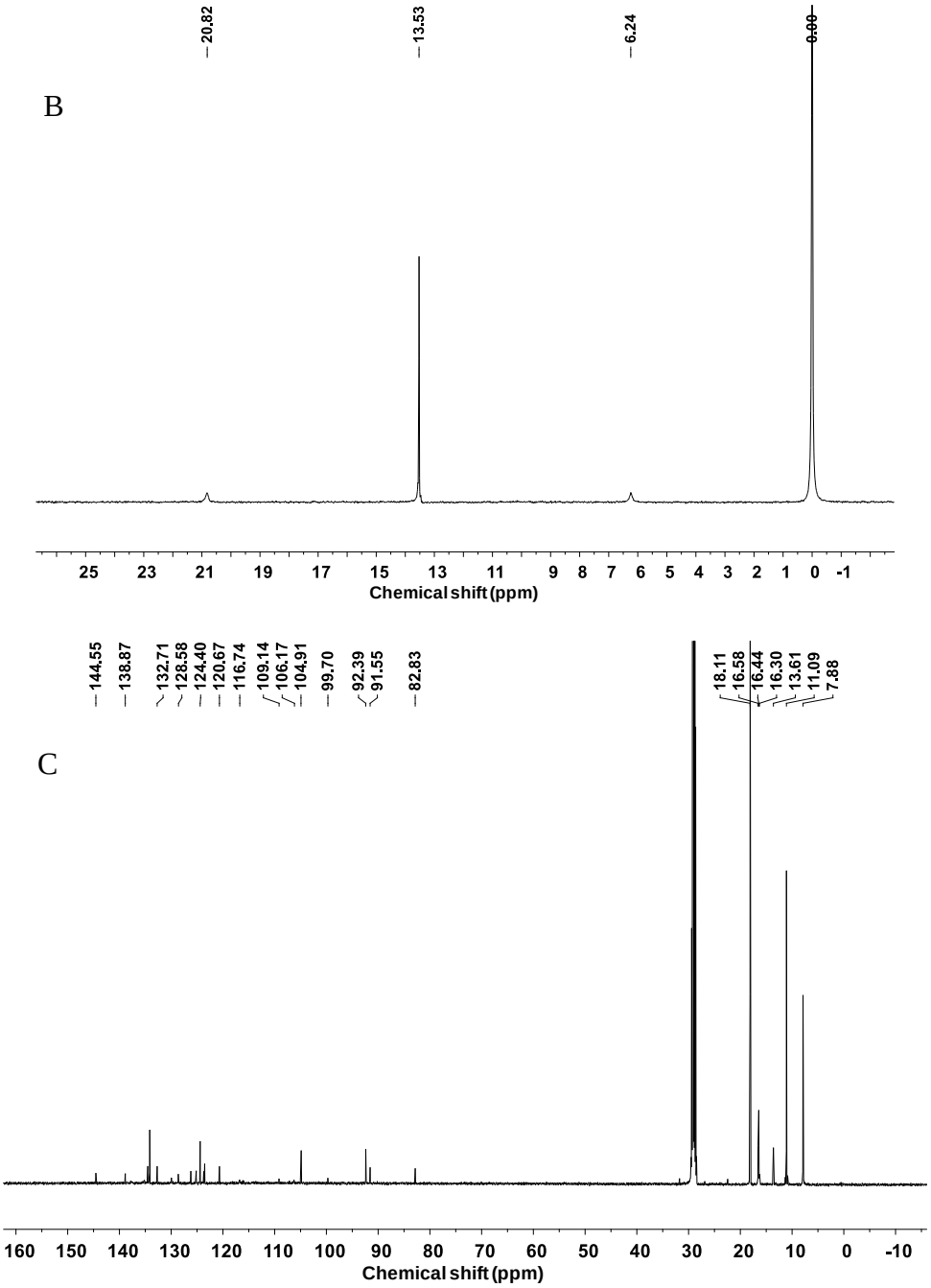
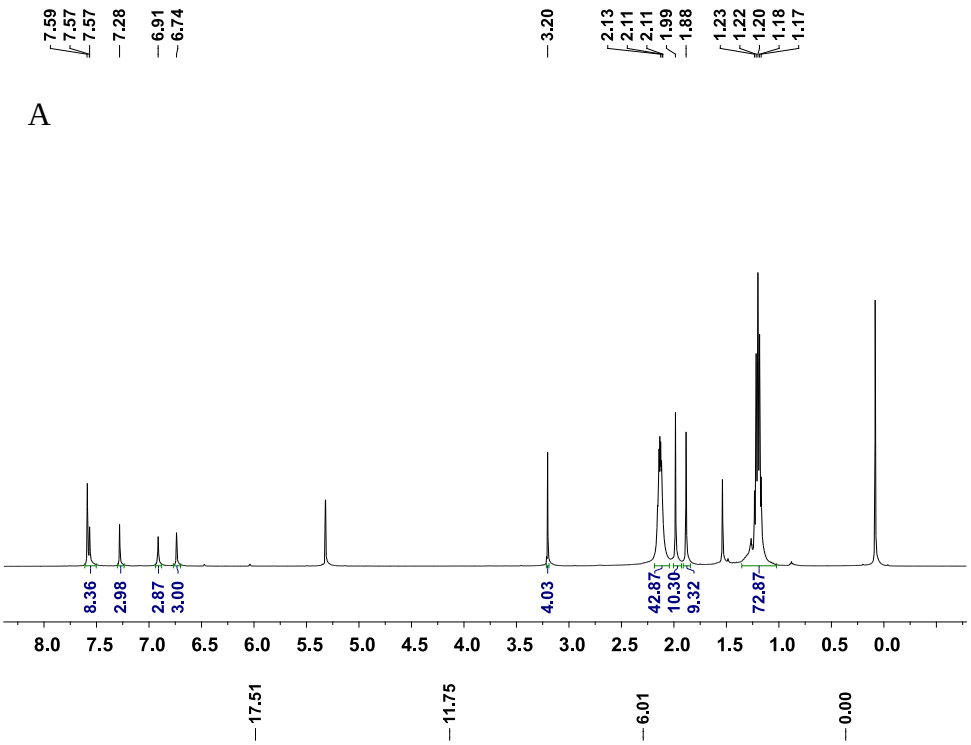


Figure S4. (A) ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 500 MHz), (B) ^{31}P NMR spectrum (CD_2Cl_2, room temperature, 161.9 MHz), and (C) ^{13}C NMR spectrum (CD_2Cl_2, room temperature, 125 MHz) of **G1**.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7.57
7.57
7.28
6.91
6.74
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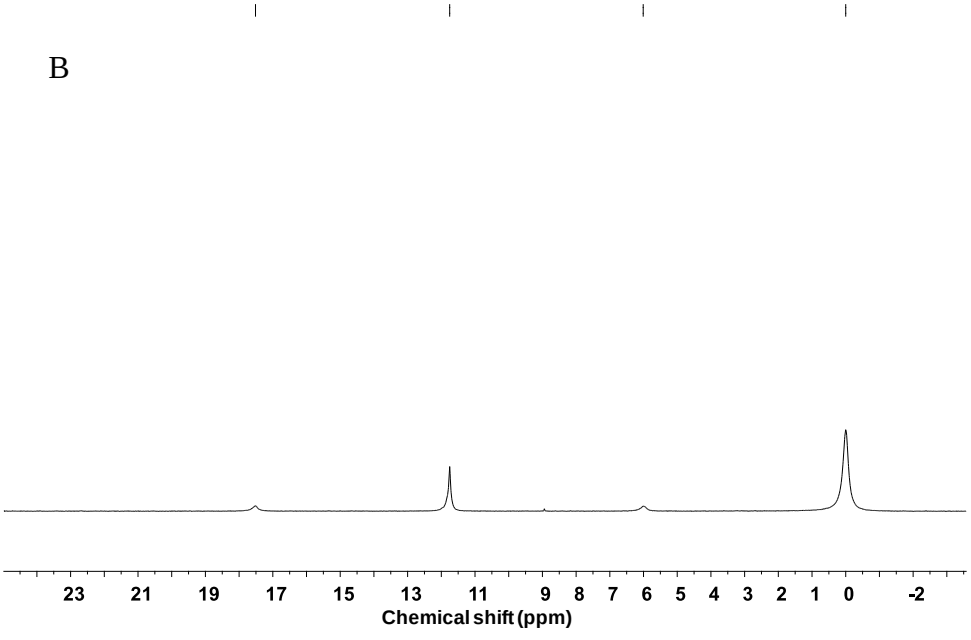
2.13
2.11
2.11
1.99
1.88
1.23
1.22
1.20
1.18
1.17
8.36
2.98
2.87
3.00
4.03
42.87
10.30
9.32
72.87
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

A


17.51
11.75
6.01
0.00
23 21 19 17 15 13 11 9 8 7 6 5 4 3 2 1 0 -2
Chemical shift (ppm)

B

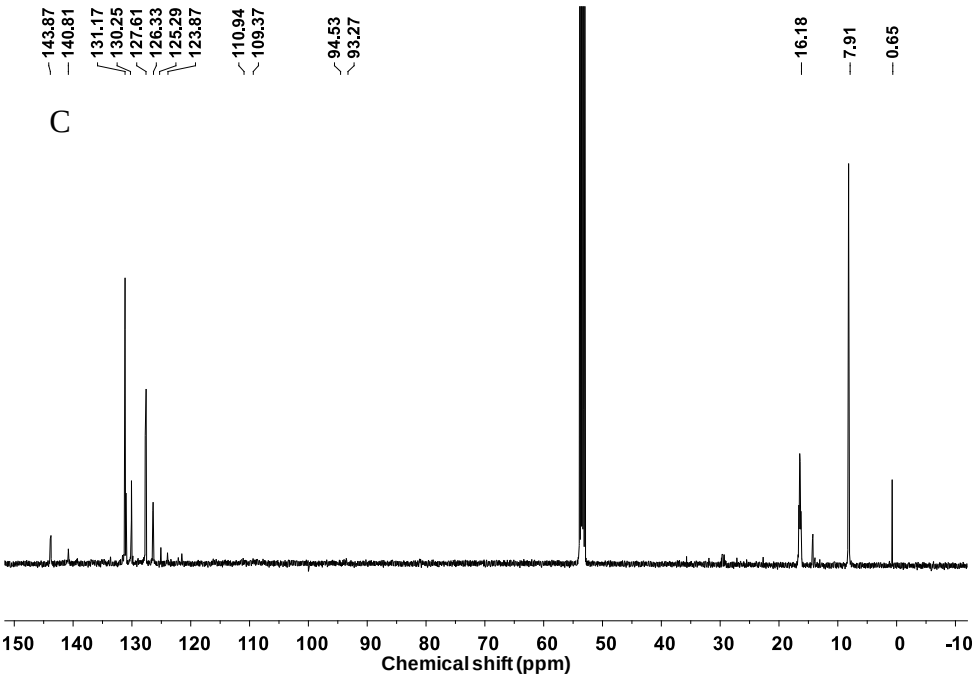
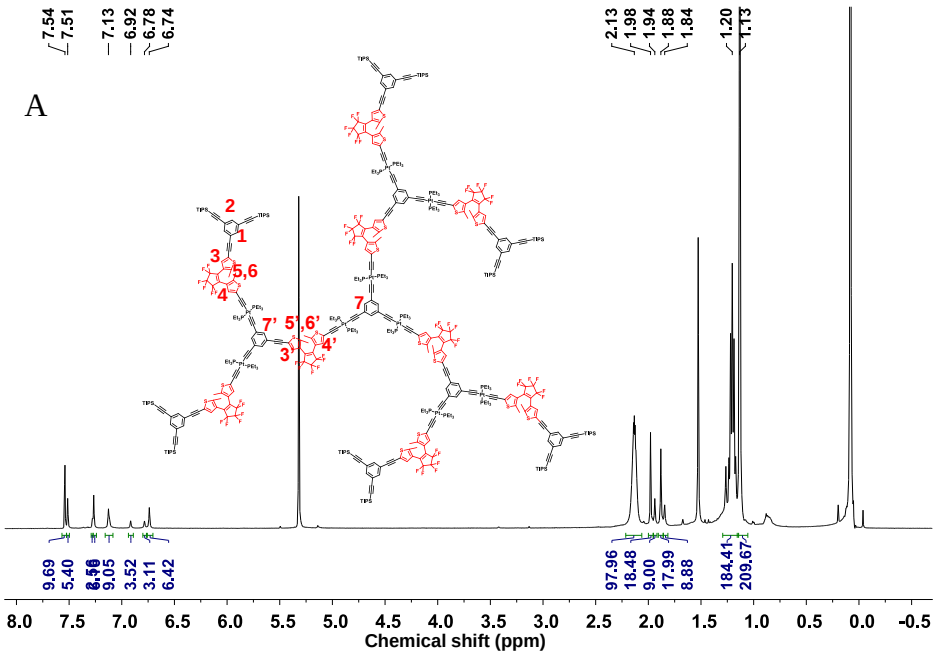


Figure S5. (A) ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 500 MHz), (B) ^{31}P NMR spectrum (CD_2Cl_2, room temperature, 161.9 MHz), and (C) ^{13}C NMR spectrum (CD_2Cl_2, room temperature, 125 MHz) of **G1-H**.



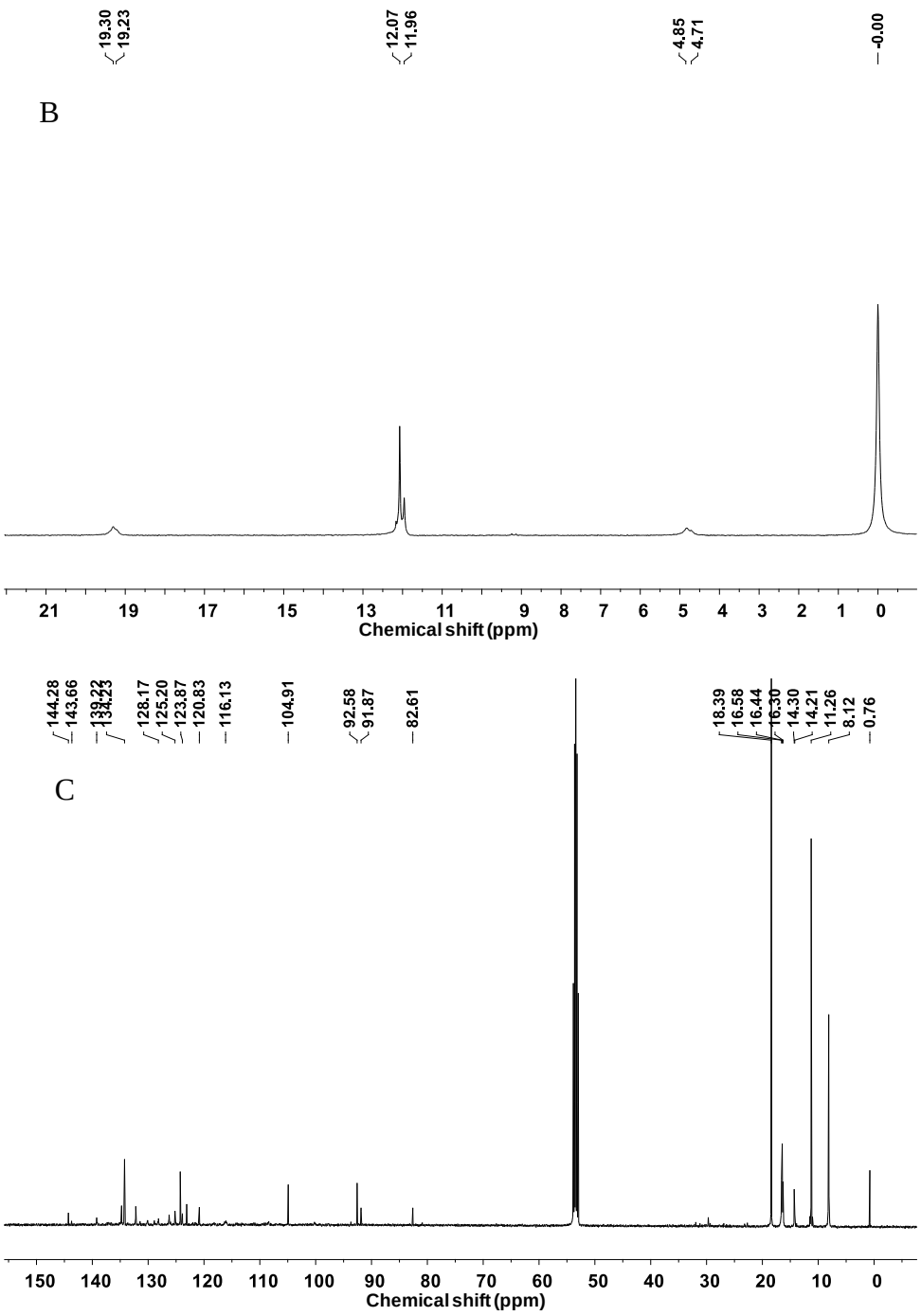
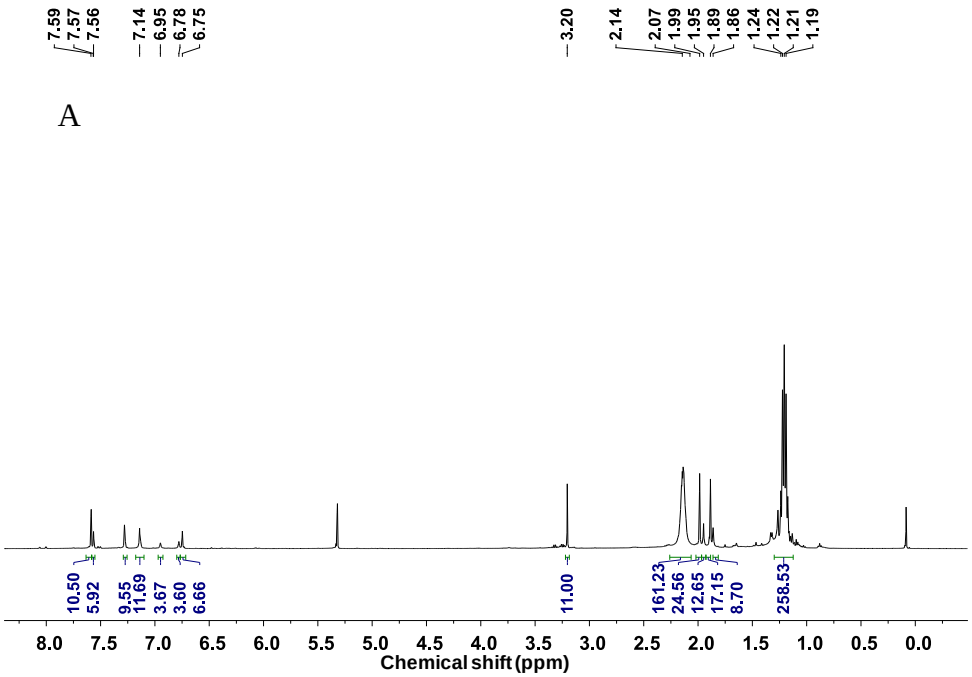


Figure S6. (A) ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 500 MHz), (B) ^{31}P NMR spectrum (CD_2Cl_2, room temperature, 161.9 MHz), and (C) ^{13}C NMR spectrum (CD_2Cl_2, room temperature, 125 MHz) of **G2**.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7.56
7.14
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6.78
6.75
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2.07
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1.24
1.22
1.21
1.19
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11.69
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3.60
6.66
11.00
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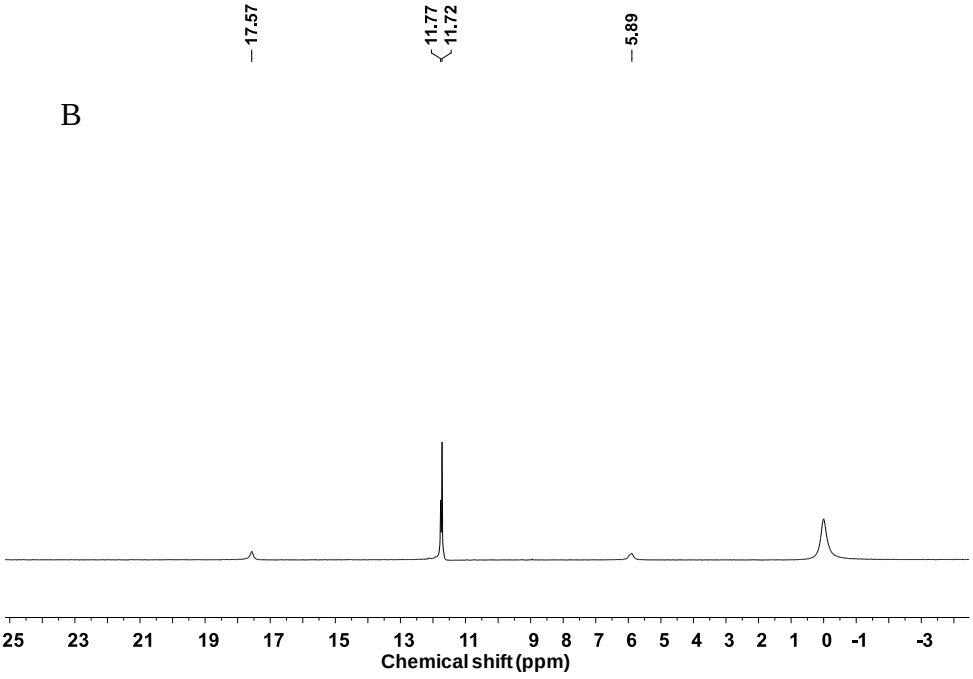
12.65
17.15
8.70
258.53
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

A


17.57
11.77
11.72
5.89
25 23 21 19 17 15 13 11 9 8 7 6 5 4 3 2 1 0 -1 -3
Chemical shift (ppm)

B

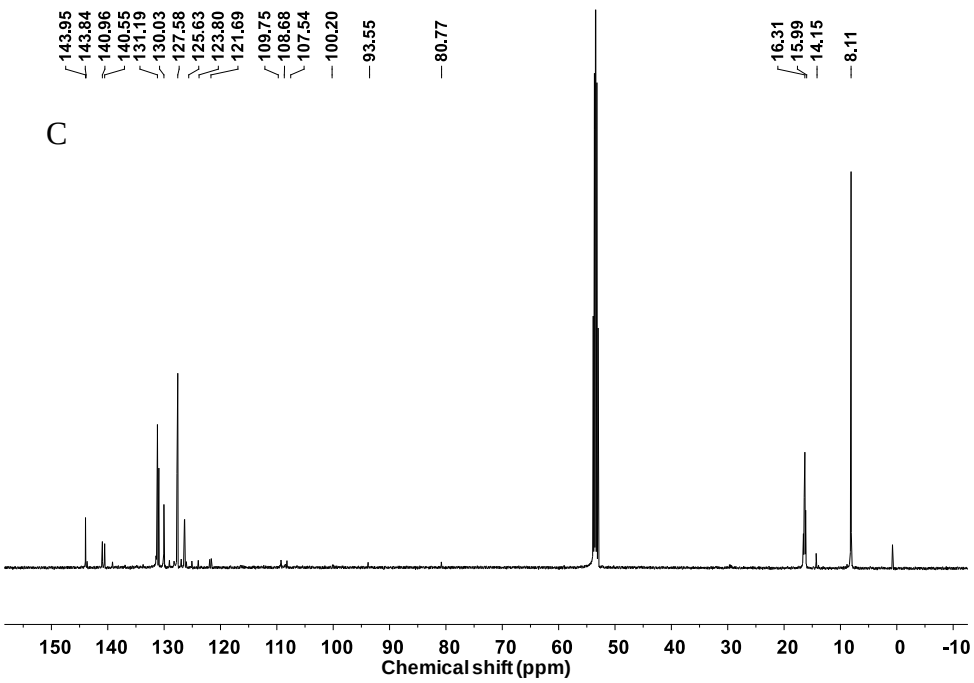
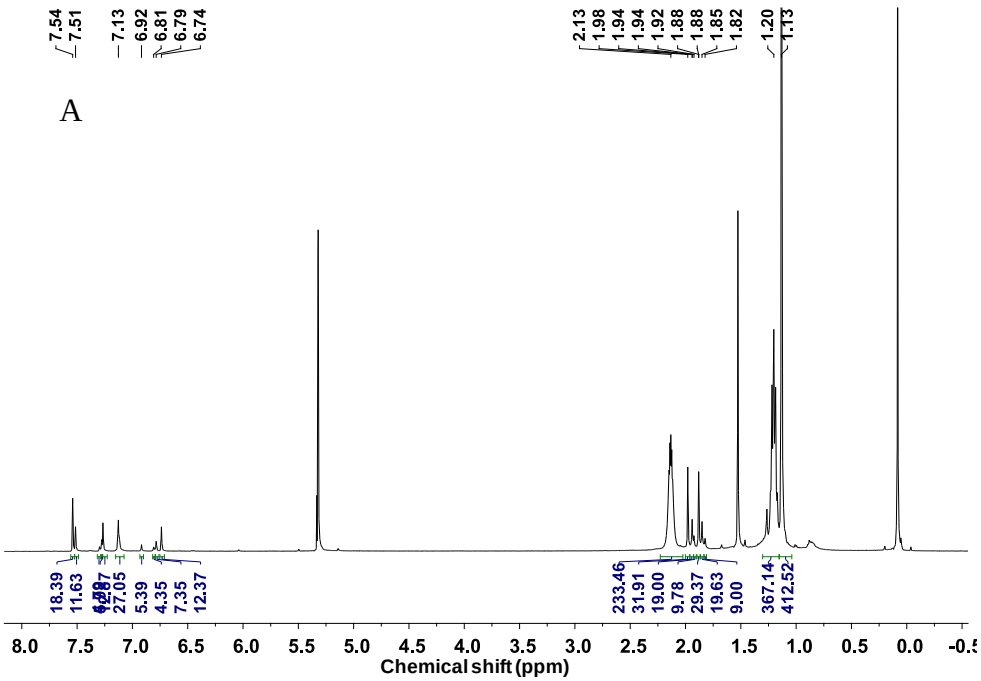


Figure S7. (A) ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 500 MHz), (B) ^{31}P NMR spectrum (CD_2Cl_2, room temperature, 161.9 MHz), and (C) ^{13}C NMR spectrum (CD_2Cl_2, room temperature, 125 MHz) of **G2-H**.



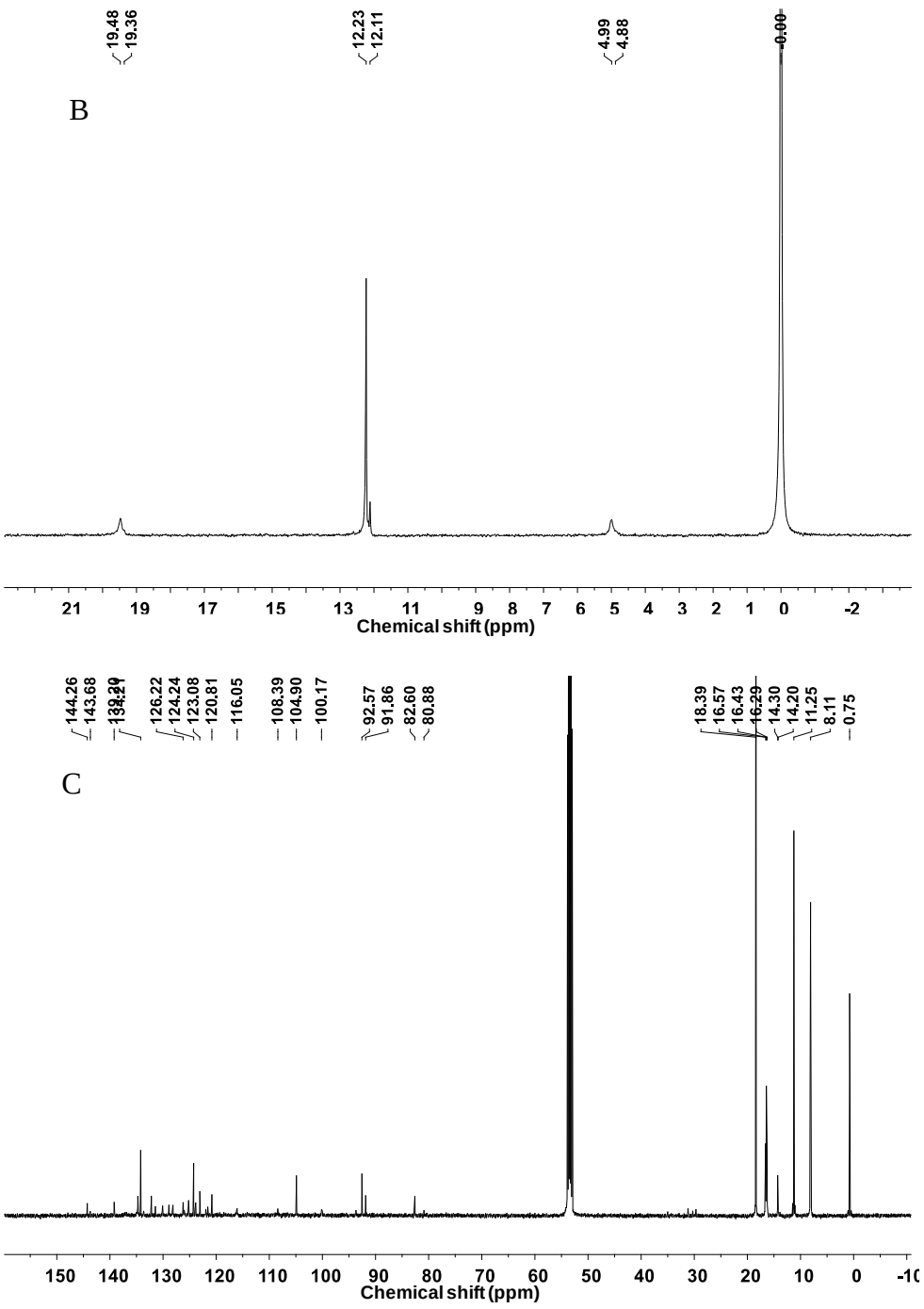
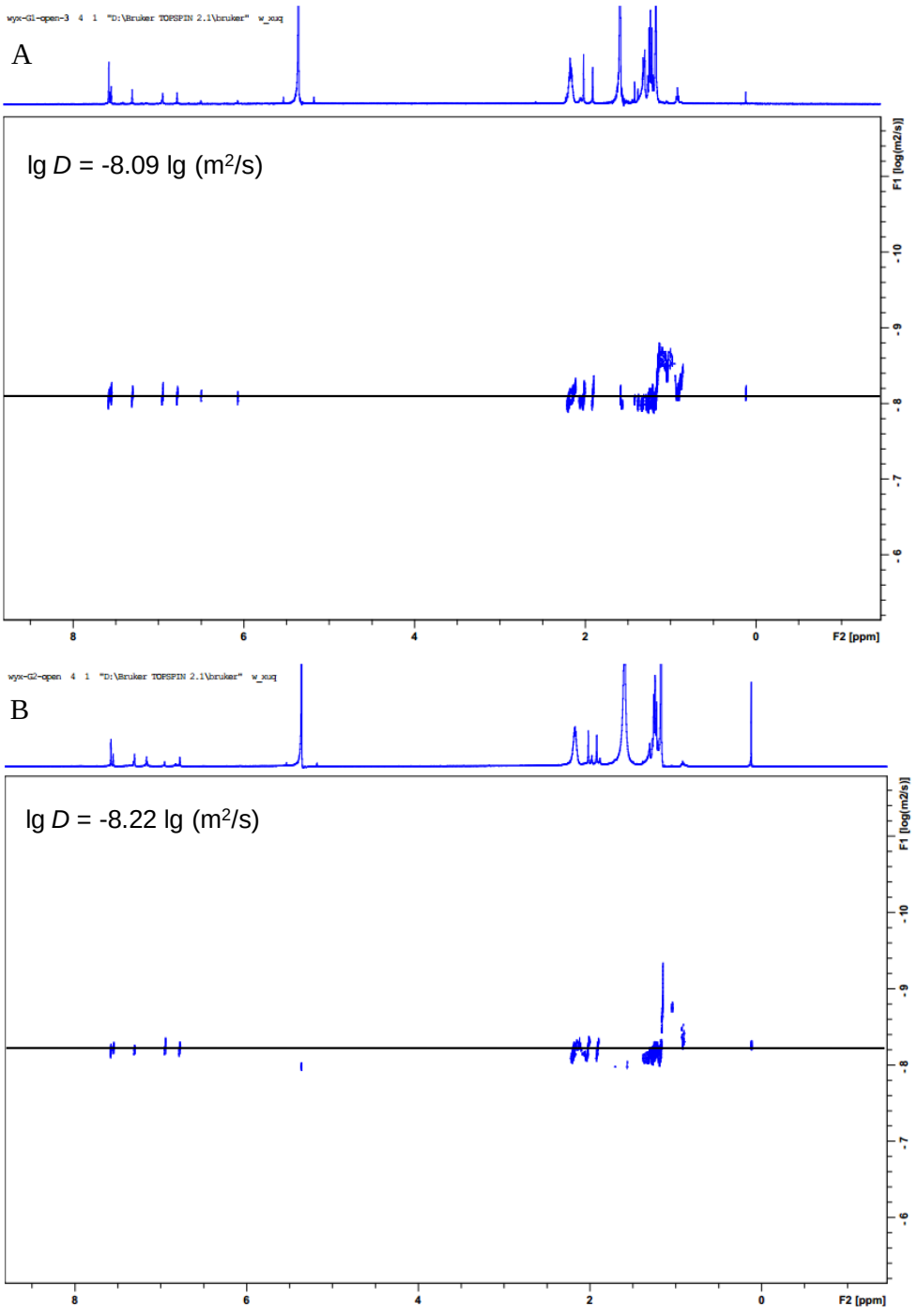


Figure S8. (A) ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 500 MHz), (B) ^{31}P NMR spectrum (CD_2Cl_2, room temperature, 161.9 MHz), and (C) ^{13}C NMR spectrum (CD_2Cl_2, room temperature, 125 MHz) of **G3**.

3. DOSY Spectra, MADLI-TOF-MS Spectra, AFM Images of Gn.



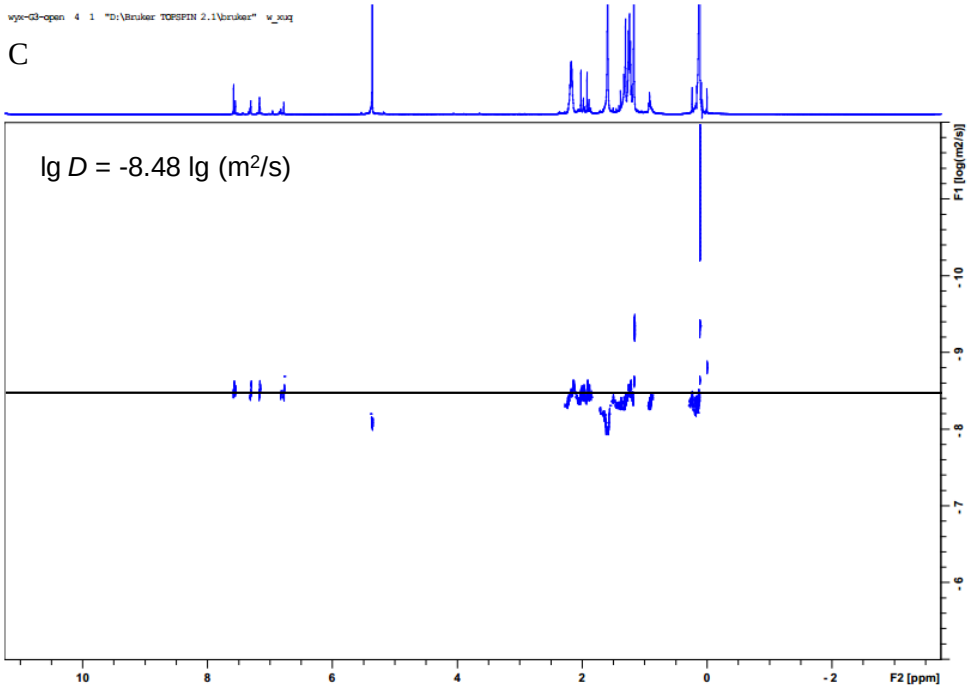
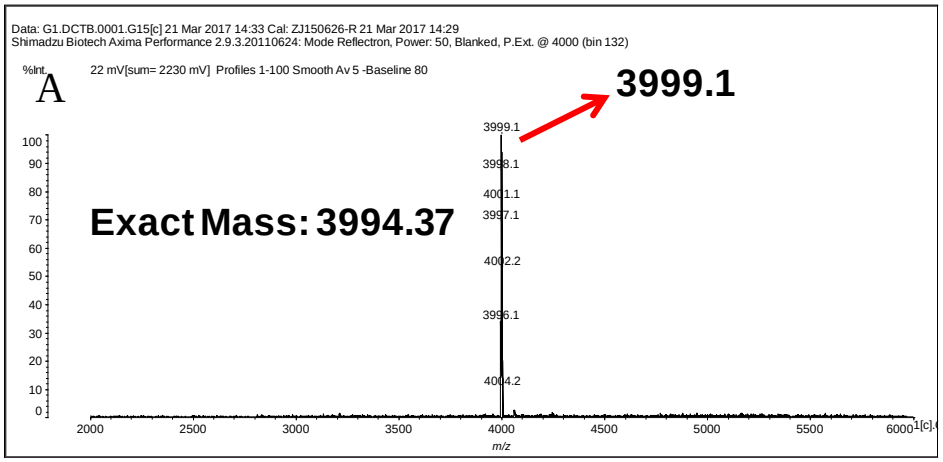
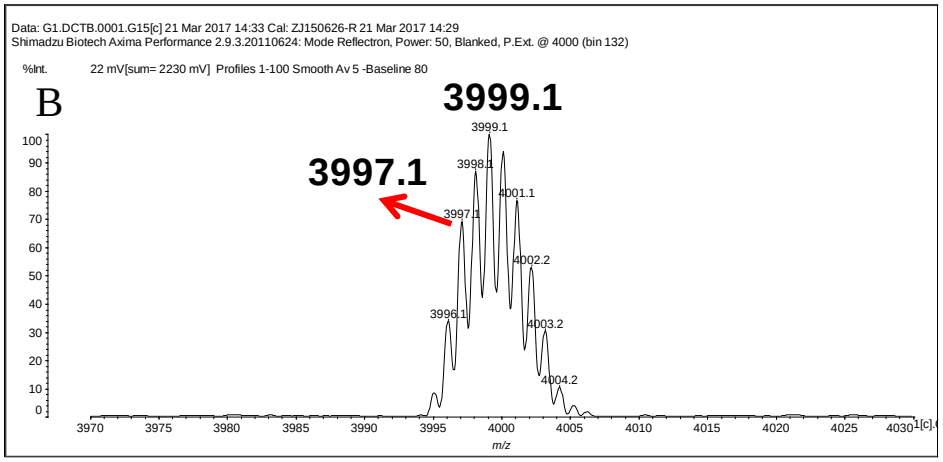
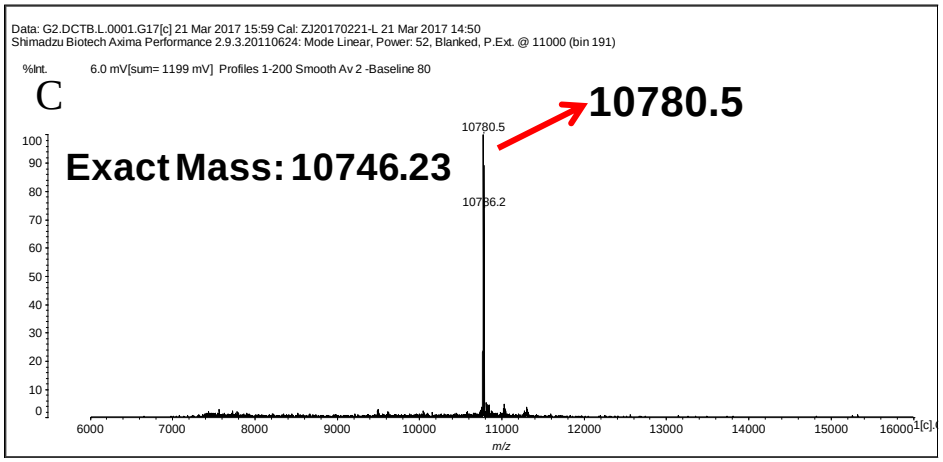


Figure S9. (A) DOSY spectra (CD_2Cl_2, room temperature, 500 MHz) of **G1** (A), **G2** (B) and **G3** (C).


Data: G1.DCTB.0001.G15[c] 21 Mar 2017 14:33 Cal: ZJ150626-R 21 Mar 2017 14:29
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron, Power: 50, Blanked, P.Ext. @ 4000 (bin 132)
%Int.
22 mV[sum= 2230 mV] Profiles 1-100 Smooth Av 5 -Baseline 80
A
3999.1
Exact Mass: 3994.37
3999.1
3998.1
4001.1
3997.1
4002.2
3996.1
4004.2
m/z


Data: G1.DCTB.0001.G15[c] 21 Mar 2017 14:33 Cal: ZJ150626-R 21 Mar 2017 14:29
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron, Power: 50, Blanked, P.Ext. @ 4000 (bin 132)
%Int.
22 mV[sum= 2230 mV] Profiles 1-100 Smooth Av 5 -Baseline 80
B
3999.1
3997.1
3999.1
3998.1
4001.1
3997.1
4002.2
3996.1
4003.2
4004.2
m/z


Data: G2.DCTB.L.0001.G17[c] 21 Mar 2017 15:59 Cal: ZJ20170221-L 21 Mar 2017 14:50
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 52, Blanked, P.Ext. @ 11000 (bin 191)
%Int.
6.0 mV[sum= 1199 mV] Profiles 1-200 Smooth Av 2 -Baseline 80
C
10780.5
Exact Mass: 10746.23
10780.5
10786.2
m/z

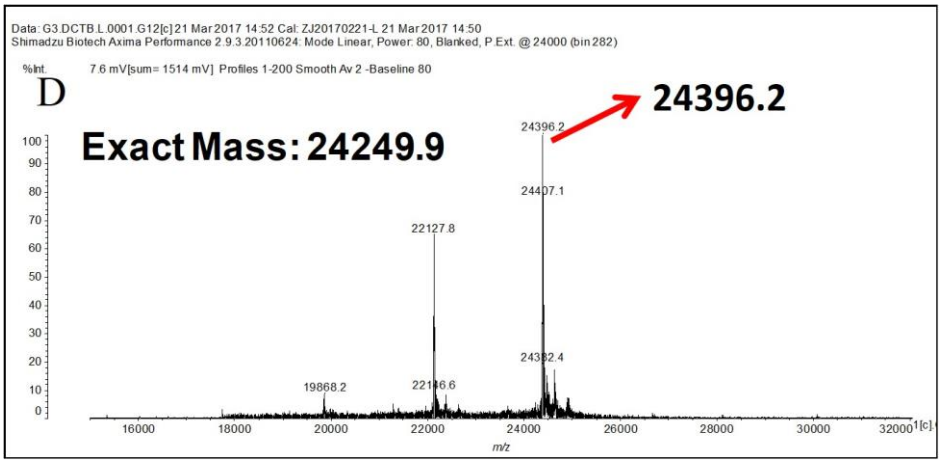
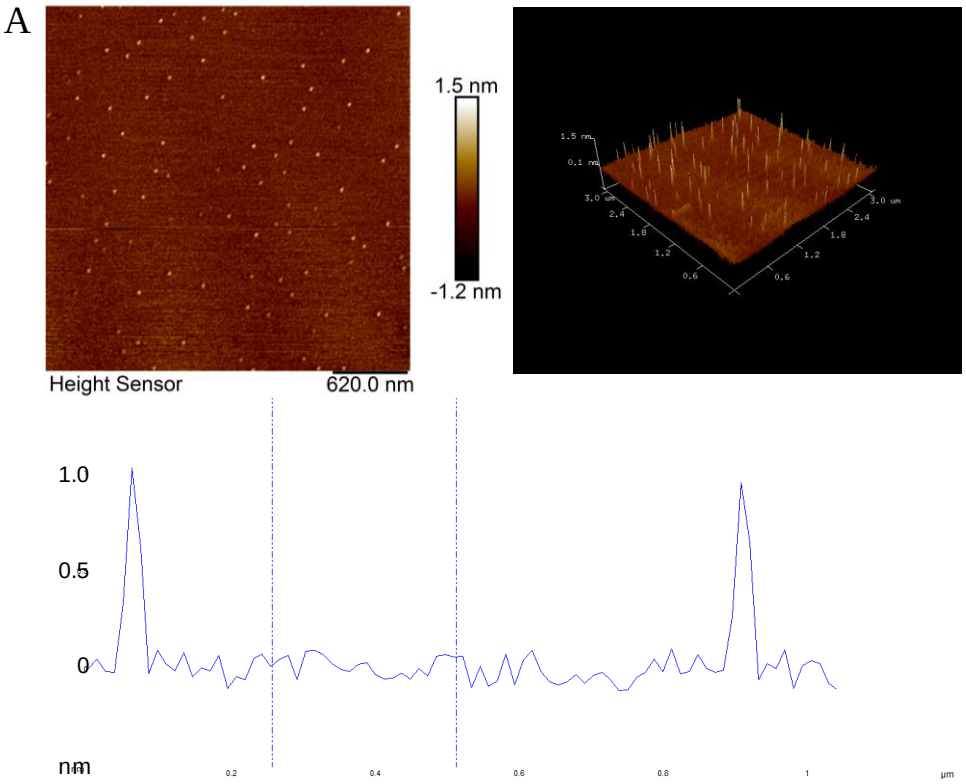


Figure S10. MADIL-TOF-MS spectra (CD_2Cl_2, room temperature, 500 MHz) of **G1** (A, B), **G2** (C) and **G3** (D).



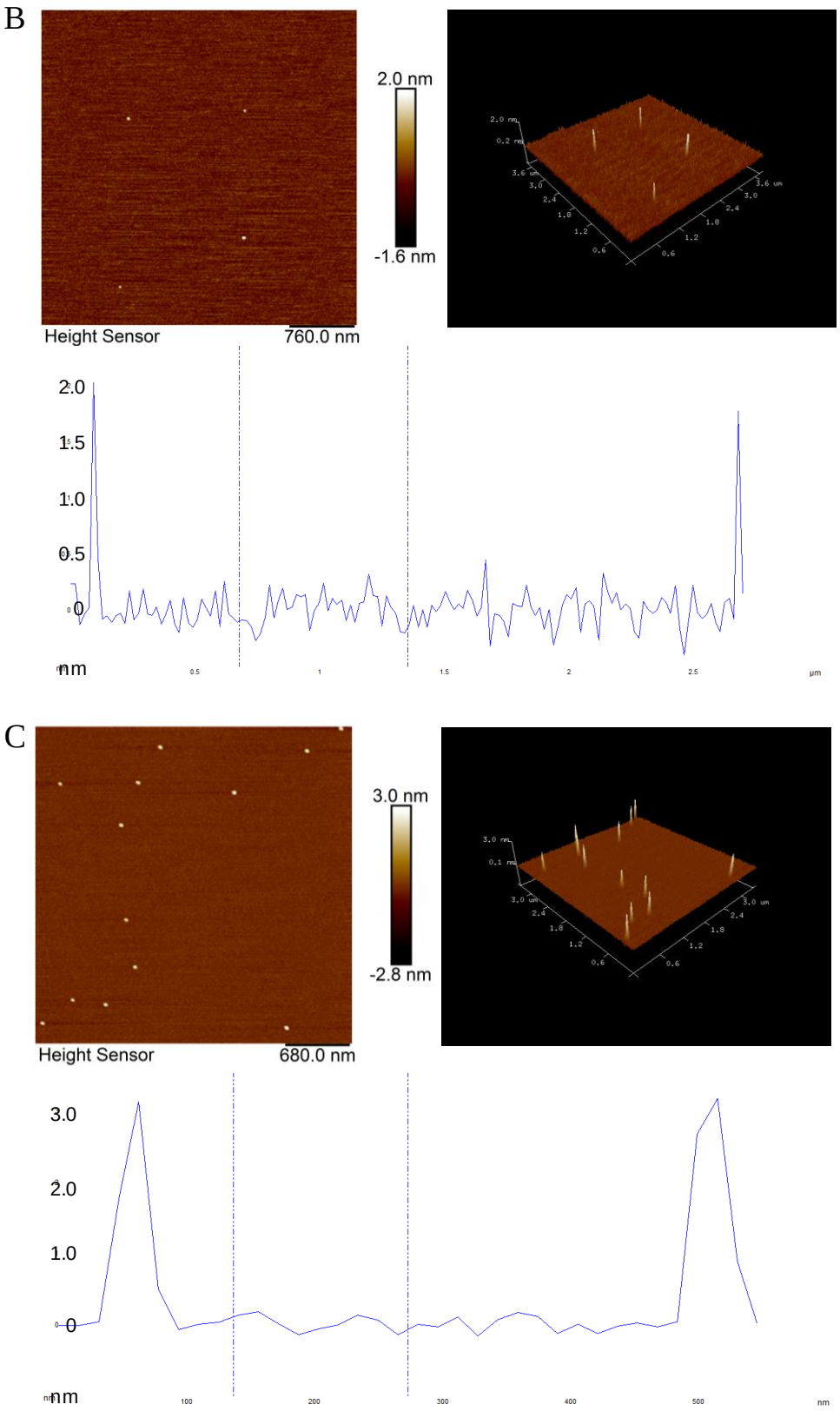


Figure S11. AFM images of **G1** (A), **G2** (B) and **G3** (C).

4. Partial ^{1}H NMR and ^{31}P NMR Spectra of Structural Transformation Process of Gn.

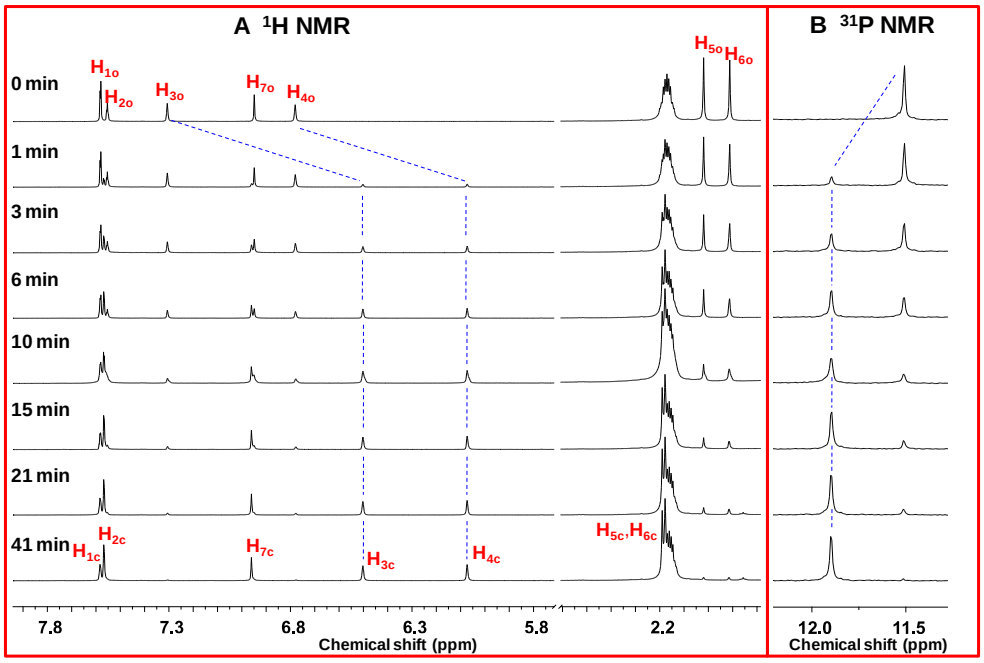


Figure S12. Partial ^{1}H NMR (A) and ^{31}P NMR (B) spectra of structural transformation process of **G1** (CD_2Cl_2, room temperature).

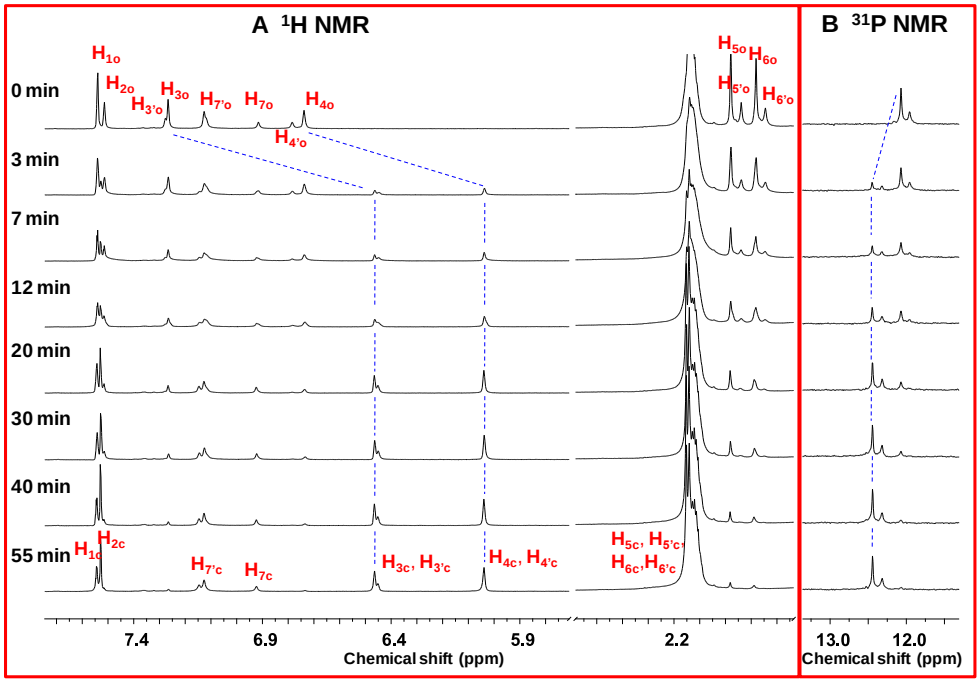


Figure S13. Partial ^{1}H NMR (A) and ^{31}P NMR (B) spectra of structural transformation process of **G2** (CD_2Cl_2, room temperature).

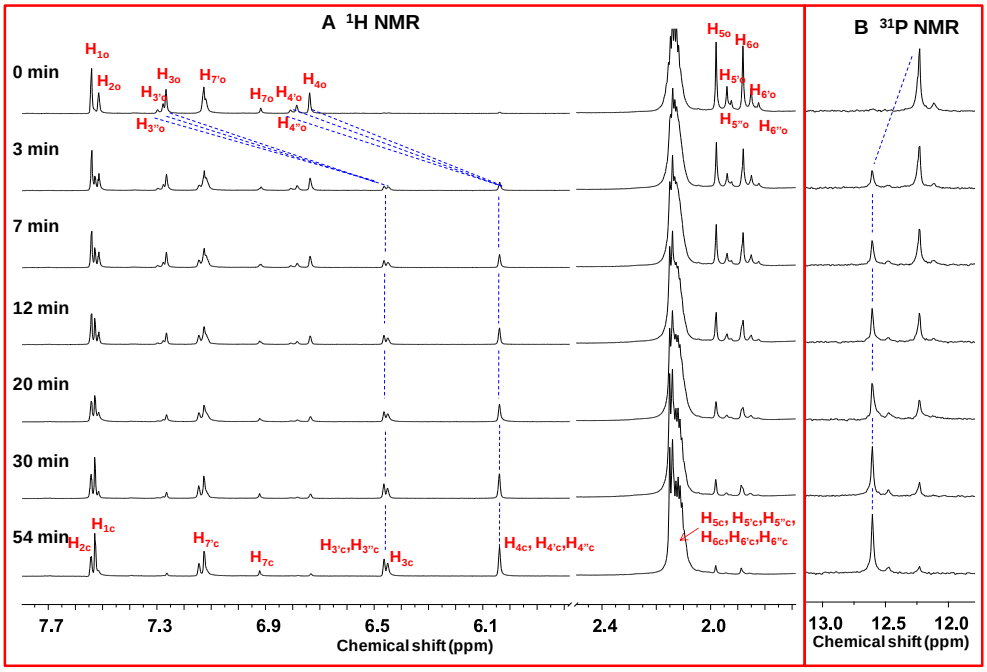


Figure S14. Partial ^{1}H NMR (A) and ^{31}P NMR (B) spectra of structural transformation process of **G3** (CD_2Cl_2, room temperature).

5. Cyclization-Cycloreversion Kinetics Studies.

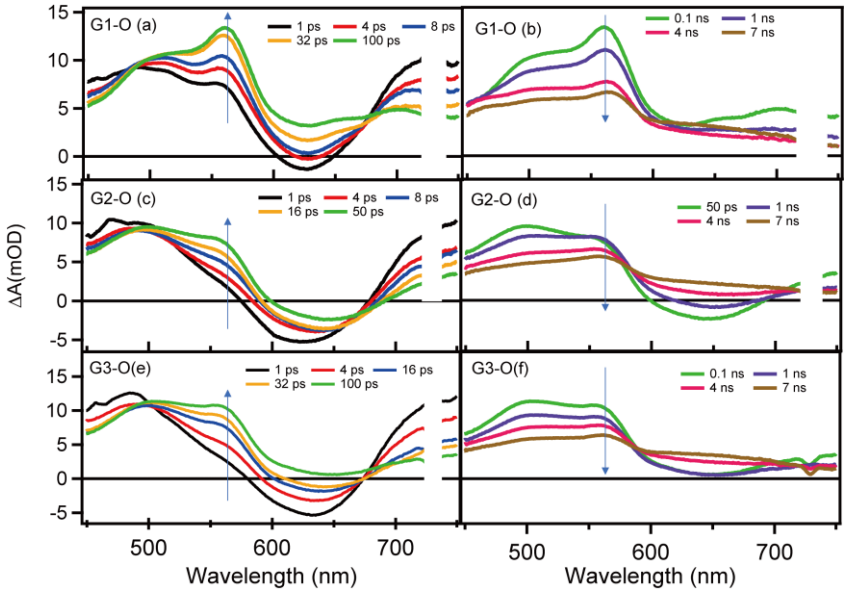


Figure S15. Femtosecond transient absorption spectra of **G1o**, **G2o** and **G3o** under 365 nm excitation.

Table S1. Best-fit parameters for kinetics show in Fig. 4f

	τ_1 (ps)	A_1(%)	τ_2 (ps)	A_2(%)	A_3(%)
2-O	0.26±0.14	8	7.4±0.8	-27	65
G1-O	0.30±0.12	13	9.9±1.5	-29	58
G2-O	0.30±0.12	11	10.8±0.8	-41	48
G3-O	0.23±0.12	12	11.4±1.1	-39	49

[a] Amplitude percentage was calculated by $A_i = A_i / \Sigma |A_n|$

6. Details of the Computational Studies.

Methods: PM6 semi-empirical molecular orbital method was used to optimize the geometries of the DTE dendrimer **G1** and TD-DFT calculations using the PBE1PBE/6-31g(d,p) (C, H, P, S, F) and SDD (Pt) was performed to investigated spectroscopic properties of it. To simplify the calculation, the ethyl groups and triisopropylsilyl (TIPS) groups were simplified to H atoms.

The HOMO and LUMO energies of **G1** in different forms were also estimated with DFT method. All the calculations were performed by using the Gaussian09 program.

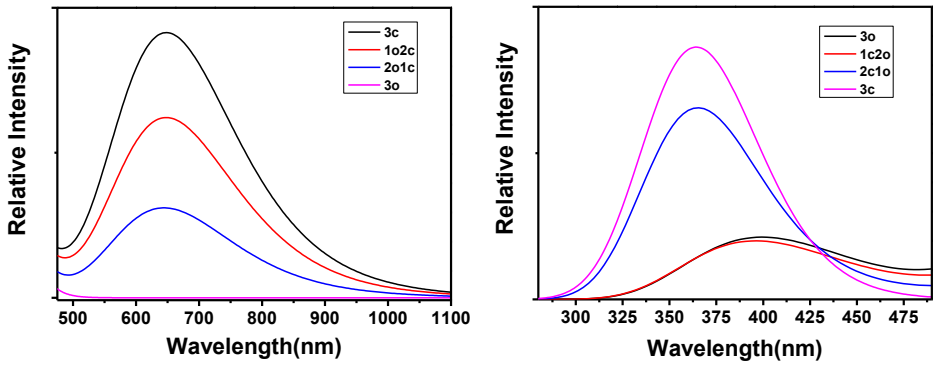


Figure S16. Simulated visible spectra for all isomers (left) and UV bands for two selected structures (right).