Supplementary Material (ESI) for Chemical Communications

Anion Bridge Nano-Sheet from Self-Assembled G-Quadruplexes

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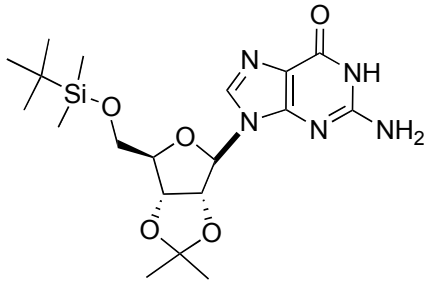
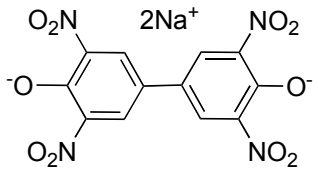
Supporting Information

General Information: Unless otherwise noted all commercial materials and solvents were purchased from Acros Fisher Chemical Company and used without further purification. TLC analysis of reaction mixtures was preformed on Merck silica gel 60 F254 TLC plates. Chromatography was carried out on Merck 60 silica gel (32-63 μm). ^{1}H and ^{13}C NMR spectra were recorded with 600 MHz Varian Inova NMR spectrometer and referenced to d_6-DMSO unless otherwise noted. Mass spectra were obtained from the Micro-Mass/Analytical Facility operated by the Department of Chemistry, West Virginia University. Atomic force microscope (AFM) measurement was carried out on Molecular Imaging (PICOPLUS) in Department of Mechanical & Aerospace Engineering. Solid-state NMR spectra were recorded at 11.75 T on a Bruker Avance-500 spectrometer. XRD measurement was performed on Bruker D8 Advance diffractometer using CuKa radiation (scan rate 0.1 deg/min, scan step 0.02 deg).

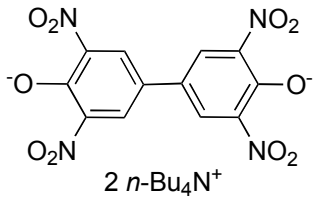
General procedures for nano-sheet preparation: Guanosine **G-1** and Na_2TNBP were prepared following published methods.[1, 2].



G-1. ^{1}H NMR (600 MHz, d_6-DMSO): δ 10.45 (br, s, 1 H, NH1), 7.89 (s, 1 H, H8), 6.51 s, 2 H, NH_2), 5.91 (d, 1H, H1', J = 2.4Hz), 5.24 (dd, 1H, H2', J = 6.0, 2.4 Hz), 4.88 (dd, 1 H, H3', J = 6.0, 2.8Hz), 4.13 (m, 1 H, H4', J = 10.0, 2.4Hz), 3.69 (m, 2 H, H5', J = 11.2, 6.0 Hz), 1.50 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 0.81 (s, 9 H, t-Bu), -0.03 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (600 MHz d_6-DMSO) δ -5.63, 17.85, 25.18, 25.63, 26.88, 63.39, 80.89, 83.62, 86.84, 88.36, 112.90, 116.75, 135.68, 150.49, 153.68, 156.71.



Na_2TNBP: ^{1}H NMR (600 MHz, d_6-DMSO): δ 8.00 (s, 4 H, 3,5,3',5' H). ^{13}C NMR (600 MHz d_6-DMSO) δ 115.19, 127.54, 143.92, 158.96.



$(Bu_4N)_2$•TNBP: The Bu_4NF (250 mg, 0.958 mmol) was dissolved in distilled water (20 mL) followed by the addition of addition of Na_2TNBP (500 mg, 1.22 mmol) to form a dark red clear solution. After stirring for 10 minutes, the solution was extracted by CH_2Cl_2 (20 ml). The dark red organic solution was then washed by distilled water (20 ml ×3) to remove NaF. The solution was than dried by Na_2SO_4 and solvent was removed under vacuum giving black solid (763 mg, 90%). ^{1}H NMR (600 MHz, d_6-DMSO): δ 7.93 (s, 4 H, TNBP), 3.18-3.12 (m, 16 H, CH_2–α), 1.61-1.49 (m, 16 H, CH_2-β), 1.33-1.25 (m, 16 H, CH_2-γ), 0.92 (t, 24 H, CH_3, J = 7.5). ^{13}C NMR (600 MHz d_6-DMSO) δ 13.42, 19.14, 22.99, 57.43, 113.95, 126.62, 143.26, 157.87.

Approach I: The guanosine monomer **G-1** (200 mg, 428 umol) was dissolved in CH_2Cl_2 (5 mL) forming a colorless, clear solution. The bridging salt Na_2TNBP (51 mg, 125 umol) was dissolved in distilled water (5 mL) as a transparent, dark red solution. The two resulting solutions were mixed together at room temperature and a red precipitate was observed at the interface of two the solutions after 10 minutes. The heterogeneous reaction mixture was left overnight and the solid was filtered followed by the washing with CH_2Cl_2 (20 ml×2) and distilled water (20 ml×2) respectively. The remaining red solid (233 mg, 93%) was dried under vacuum and used for the AFM measurement and NMR studies.

Approach II: The guanosine monomer **G-1** (200 mg, 428 umol) was dissolved in CH_2Cl_2 (5 mL) forming a clear solution, followed by the addition of NaSCN aqueous solution (5ml, 25.2 mmol/L). The mixture was stirred for 5 hrs. The organic layer was separated and washed by distilled water (10 ml×2). The organic solution was treated by flowing through a pipette column filled with Na_2SO_4 to remove the trace amount of water. The solution of $(\mathbf{G\text{-}1})_{16}$•$Na_4$•$SCN_4$ complex was then prepared. Dissolving the $(Bu_4N)_2$•TNBP (106 mg, 125 umol) in CH_2Cl_2 (5 mL) giving the dark-red TBA-TNBP solution. The two solutions of $(\mathbf{G\text{-}1})_{16}$•$Na_4$•$SCN_4$ and $(Bu_4N)_2$•TNBP were mixed together. Within 1 min, the clear solution turned turbid. The red precipitate suspension was formed in 5 hours. After vacuum filtration, the red precipitate was washed by CH_2Cl_2 (20ml × 4) to remove the remaining free $(Bu_4N)_2$•SCN and $(\mathbf{G\text{-}1})_{16}$•$Na_4$•$SCN_4$. The red solid was dried under vacuum (198 mg, 88%) and used for the AFM measurement and NMR studies.

AFM measurement

The nano-sheets were observed with an atomic force microscope (AFM) (Molecular Imaging, PICOPUS). The suspensions of nano-sheet particles were prepared in various solvents, including CH_2Cl_2, CH_3CN, MeOH and deionized H_2O. The AFM images shown below were prepared in the deionized water, which produced best quality of pictures of nano-sheet without severe aggregation. The nano-sheet was first suspended

in deionized water and stirred for 3hrs. The suspension was then filtered through a tissue-packed pipette. This process removed the large aggregated nano-particles and the non-aggregated/less-aggregated nano-particle can go through to form a nano-particle "solution" (suspension). The resulting clear "solution" was transferred to the surface of mica substrate (SPI, V4 grade). The mica with sample was then dried in the desiccator prior to AFM measurement. AFM measurement was performed on the nano-sheet sample under tapping mode with the Si tip (Applied Nanostructure, Model ACT) with a resonance frequency of ~300 kHz and spring constant of 40 N/m. During scanning, the tip was kept at a distance from the sample at which the oscillation amplitude was dampened by the intermolecular repulsive force with sample to 90% of its free amplitude. The scanning speed was 2um/s.

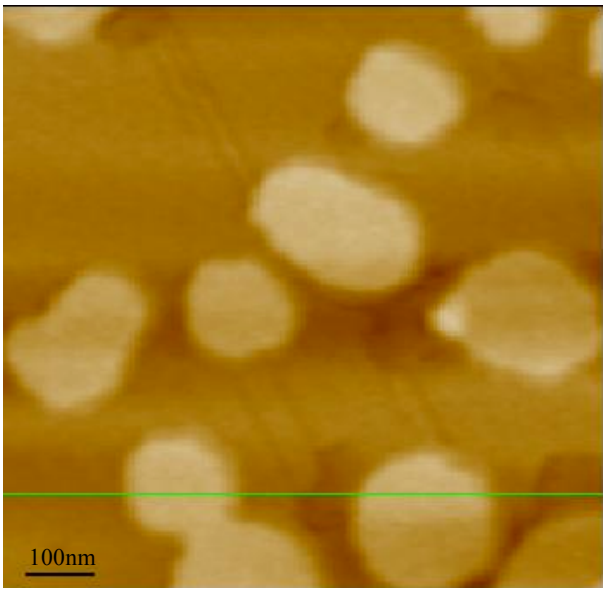


Figure1. AFM 2D image

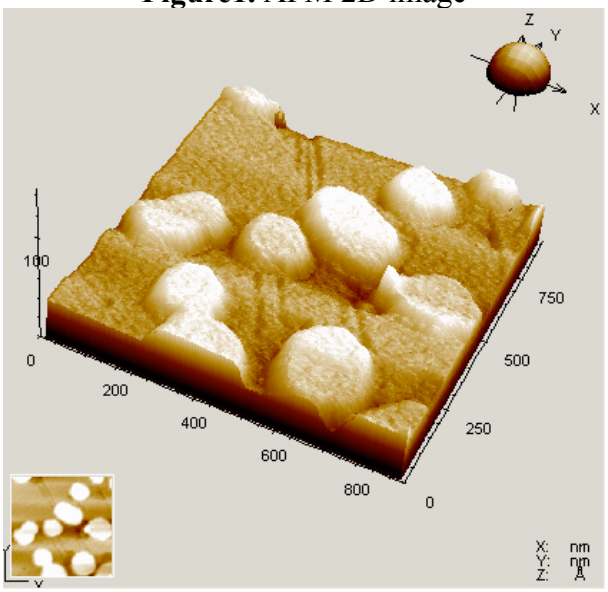


Figure2. AFM 3D image

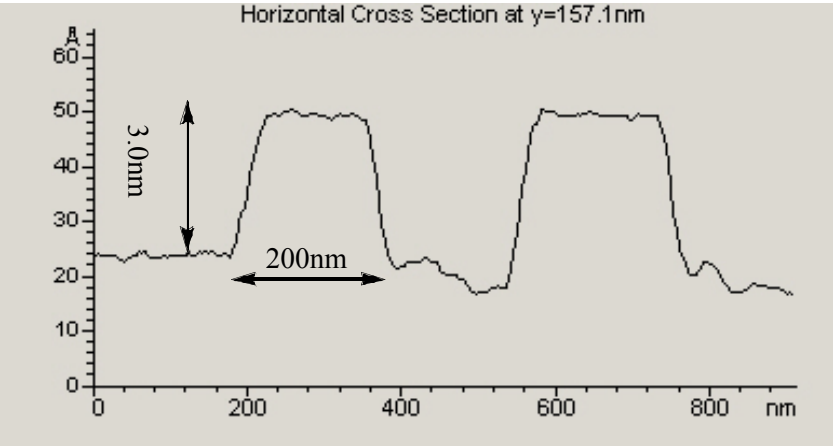
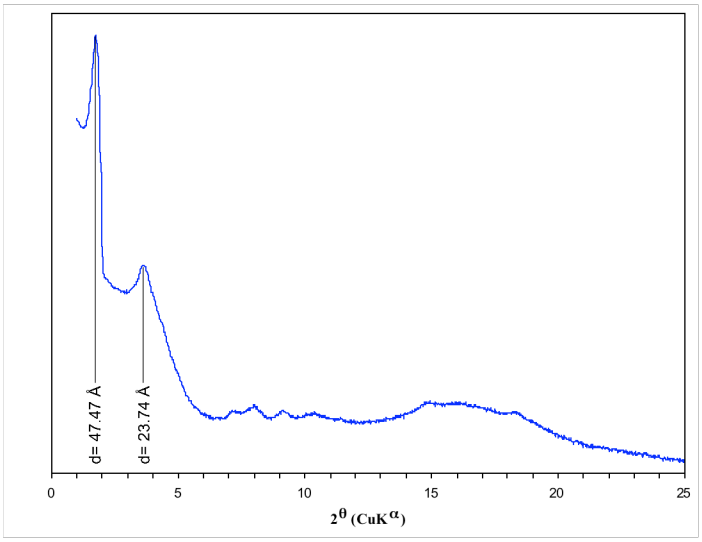


Figure3. Cross Section profile over the line indicated (green line)

Powder X-ray determination

The powder X-ray diffraction was measured using Bruker D8 Discover equipped with HiStar 2D detector and Göbel mirror. Two 2D frames were measured using CuKa radiation for 10 min each and integrated resulting XRD pattern shown below.



The powder X-ray pattern reveals two low angles peaks observed at d-spacing 47.5 Å and 23.75 Å, which suggest 1st and 2nd orders (e.g. 100 and 200). This result indicates the presenting of large unit cell. The other smaller peaks cannot be interpreted from this pattern due to broadening and overlapping of the peaks. In the supporting information of **reference 3**, the unit cells of guanosine hexadecamer have been determined, which is around 47 Å. For example, the unit cell for $(\mathbf{G\text{-}1})_{16}\bullet Ba_2\bullet(\text{P-OME-2,6-DNP})_4$ hexadecamer is:

a=46.662 Å $\alpha = 90^o$
b=24.259 Å $\beta = 93.139^o$
c=45.111 Å $\gamma = 90^o$

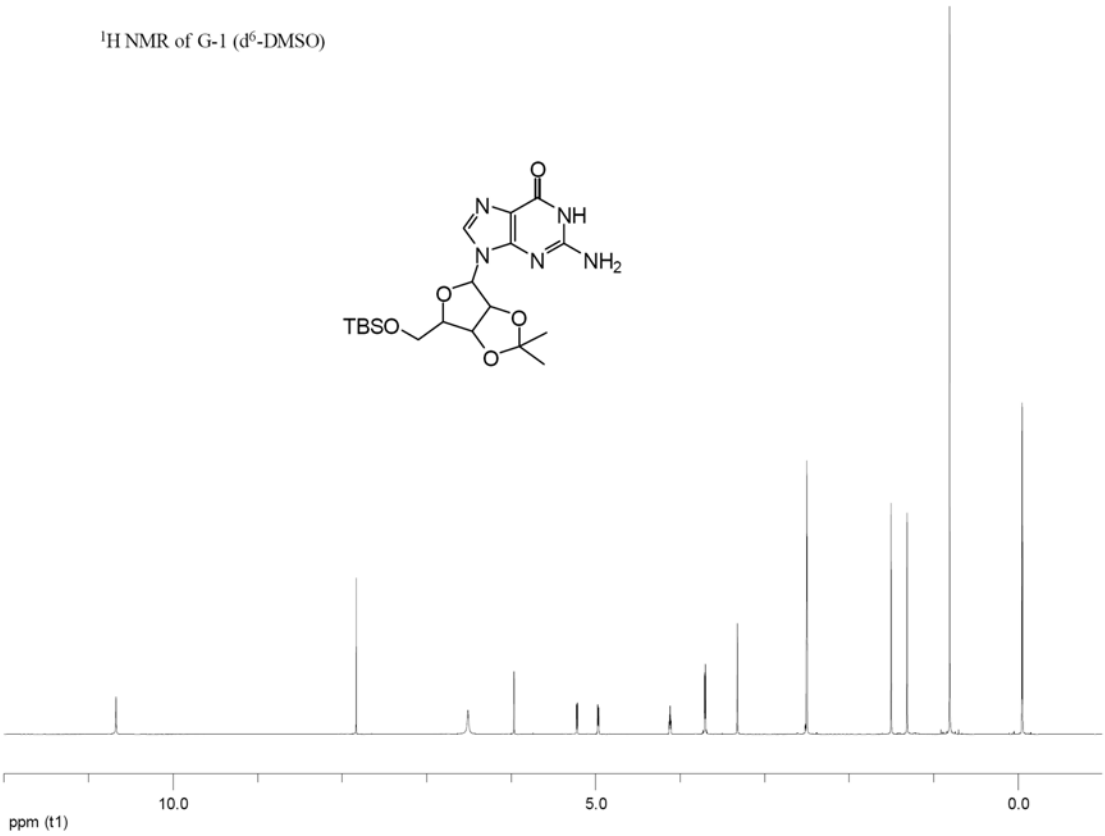
In the crystal structure, the dihedral angle between a G-quartet plane and the edge of unit cell is about 45^o. The diameter of the G-quartet formed by **G1** is around 33 Å. Therefore, the correlation is 33 X 1.414 = 47 Å, determining the size of the unit cell.

Although the information from the powder X-ray is not sufficient to determine the repeating pattern along the horizontal direction of nano-sheet, the large unit cell revealed by the powder X-ray is certainly consistent with guanosine hexadecamer and support the formation proposed nano-sheet structure.

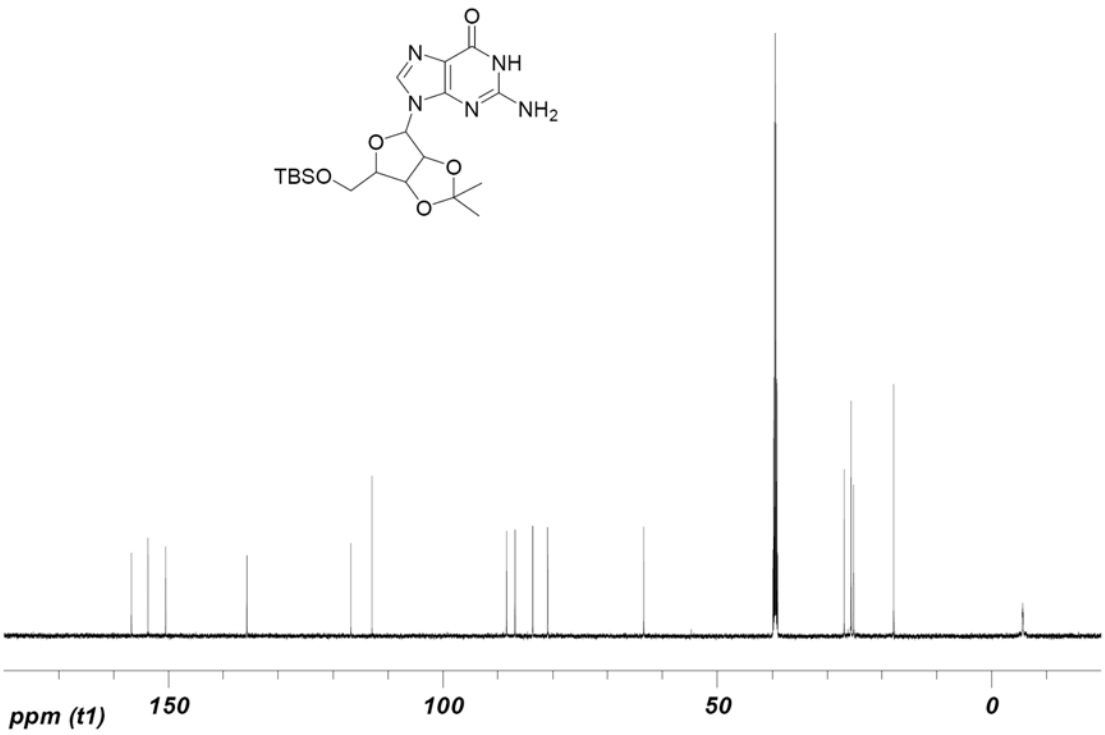
Reference:

(1) Shi, X.; Fettinger, J. C.; Davis, J. T. *Angew. Chem., Int. Ed.* 2001, *40*, 2827-2831.
(2) Nishimura, K.; Kondo, T.; Drozdova, O. O.; Yamochi, H.; Saito, G.. *J. Mater. Chem.* **2000**, *10*, 911-919.
(3) Shi, X.; Mullaugh, K. M.; Fettinger, J. C.; Jiang, Y.; Hofstadler, S. A.; Davis, J. T. *J. Am. Chem. Soc.* 2003, *125*, 10830-10841.

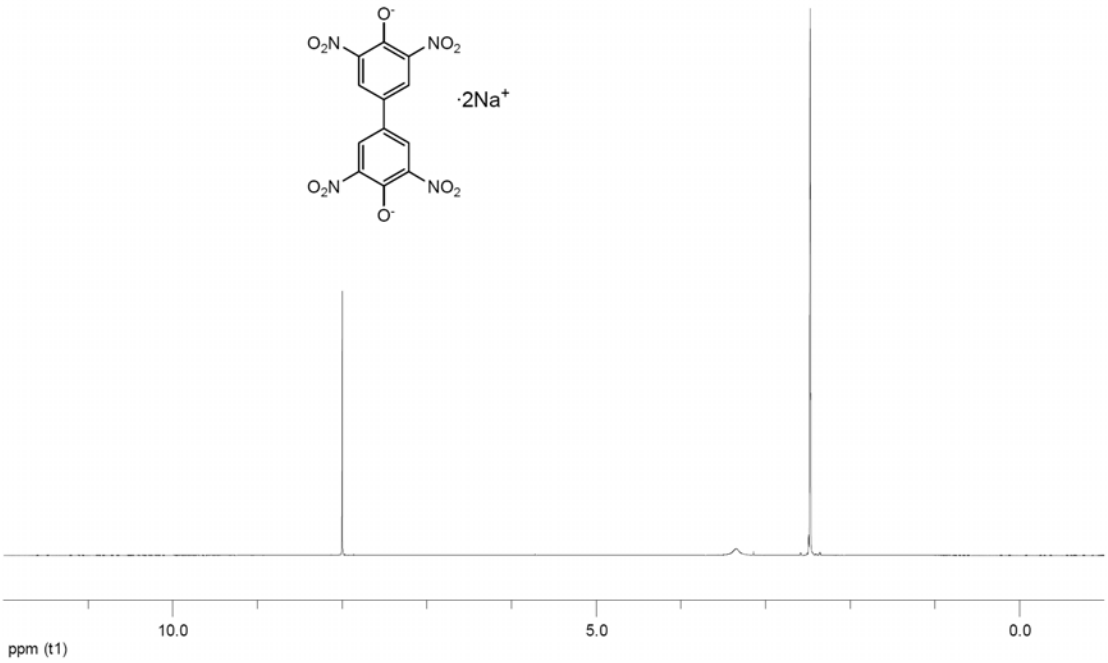
^{1}H NMR of G-1 (d^6-DMSO)



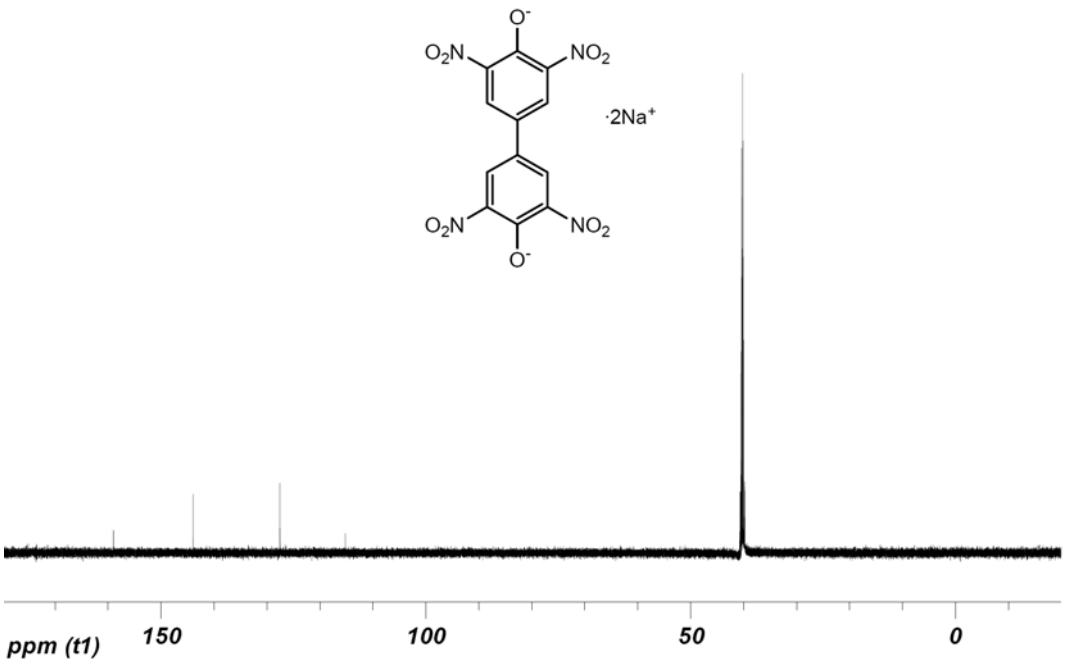
^{13}C NMR of G-1 (d^6-DMSO)



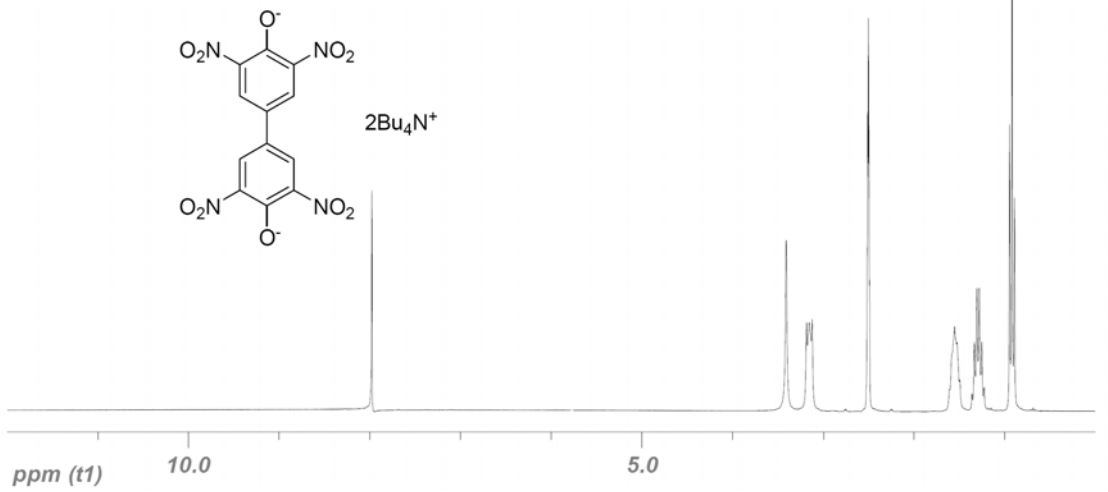
^{1}H NMR ofNa_2 TNBP (d_6-DMSO)



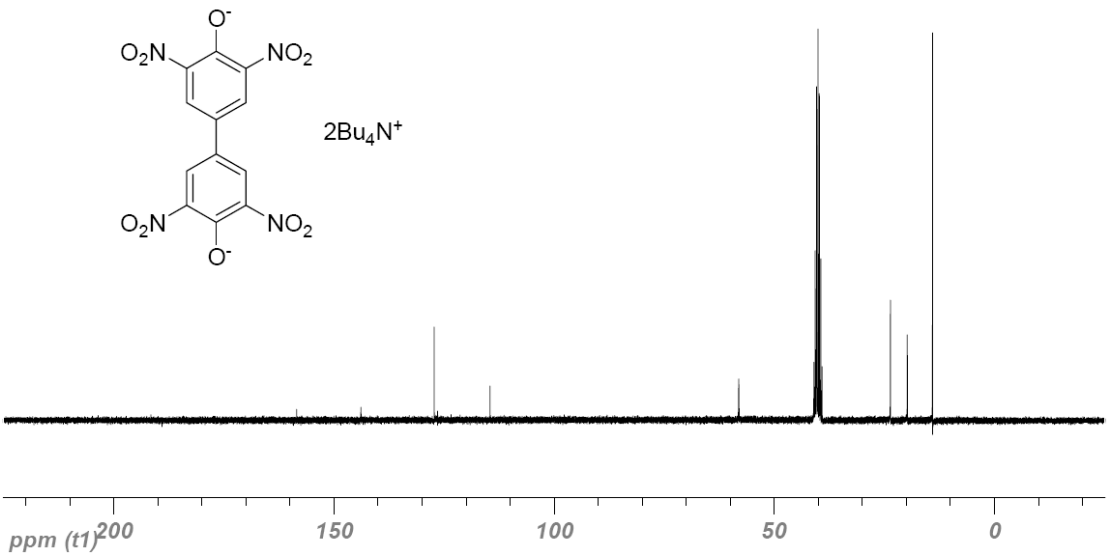
^{13}C NMR of Na_2TNBP (d_6-DMSO)



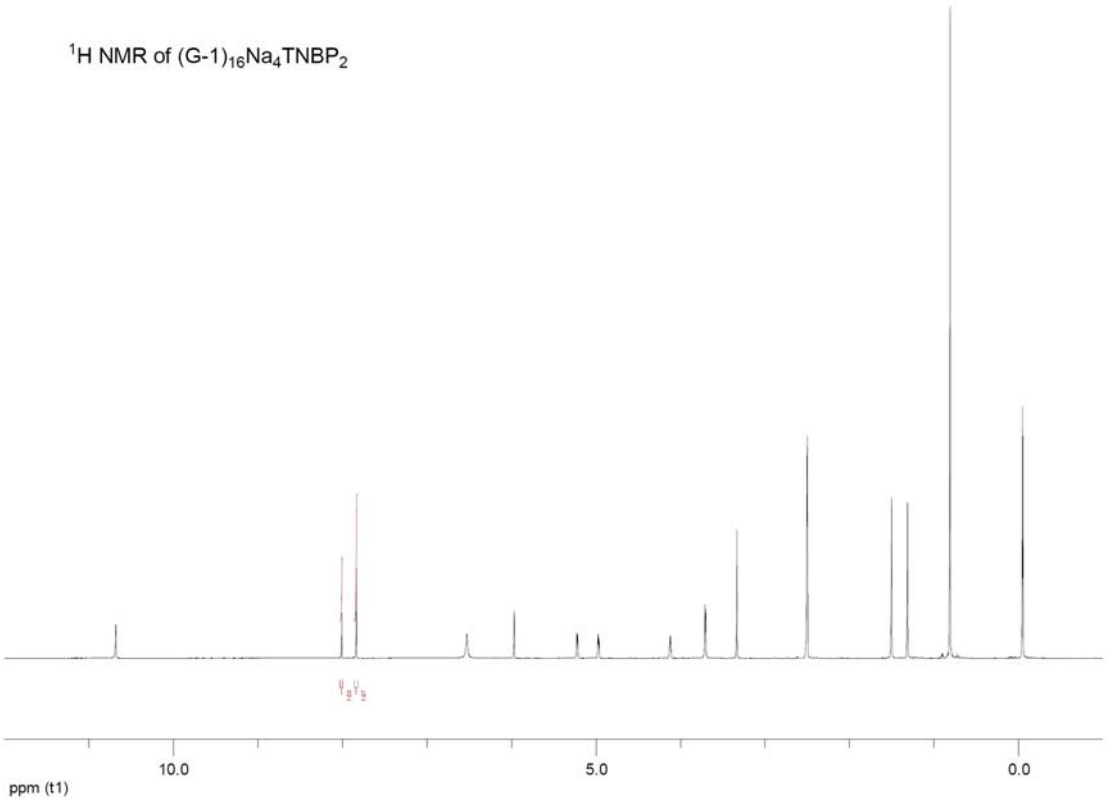
^{1}H NMR of $(Bu_4N)_2$ TNBP



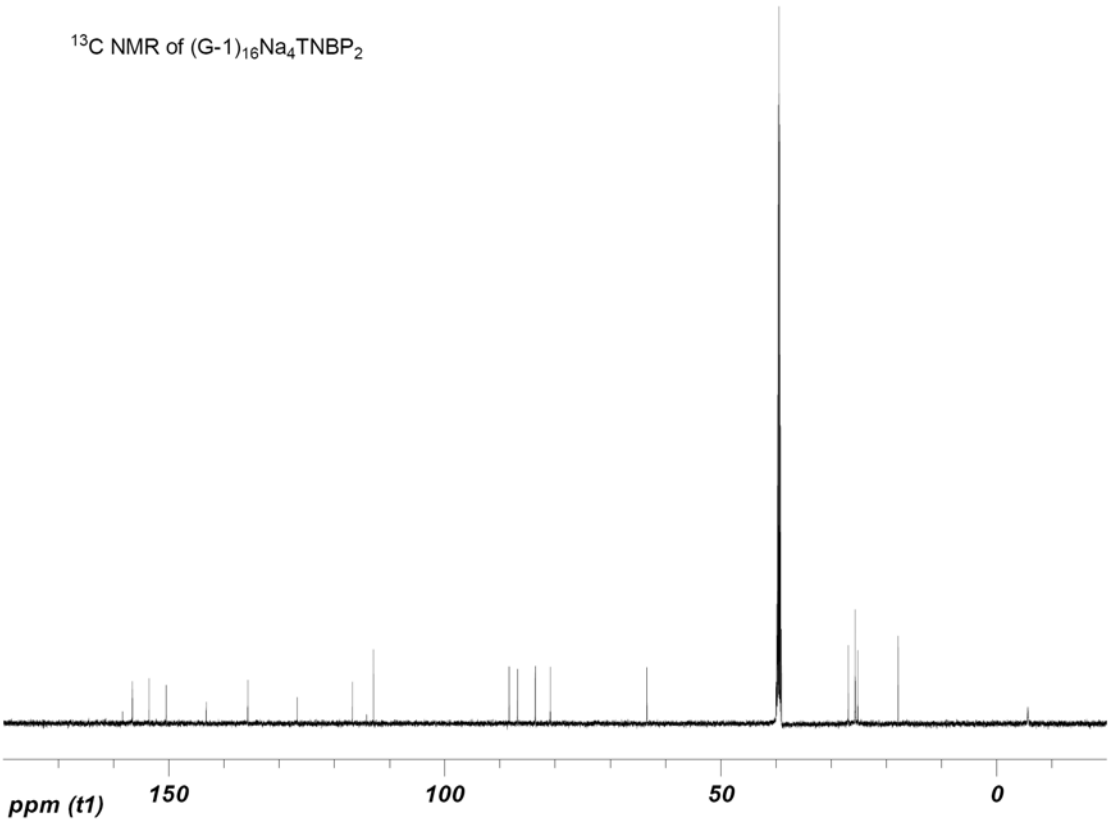
^{13}C NMR of $(Bu_4N)_2$ TNBP

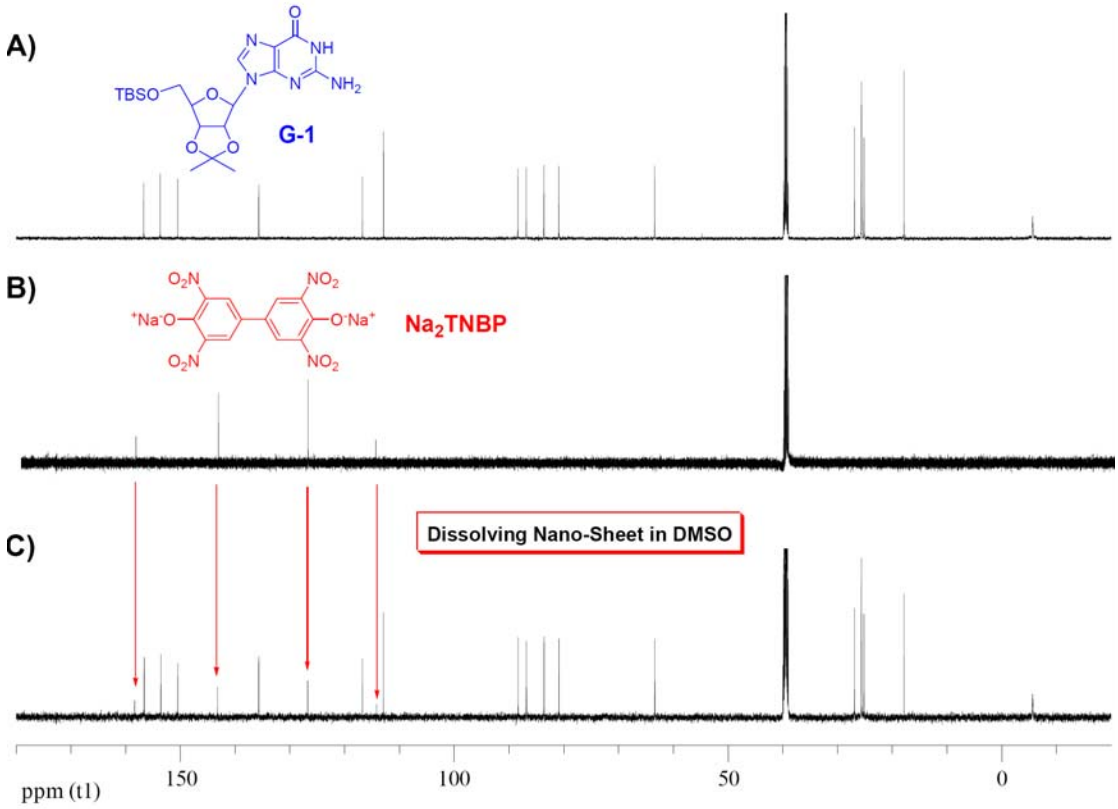


^{1}H NMR of $(G\text{-}1)_{16}Na_4TNBP_2$



^{13}C NMR of $(G\text{-}1)_{16}Na_4TNBP_2$





^{13}C NMR spectra of G-1 nano-sheet in d6-DMSO (600 mHz): A) G-1; B) Na+2TNBP2-; C) Dissolving nano-sheet in DMSO.