Supporting Information

Title: Construction of First Anion-Assisted Helix inside a Helix Network

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Experimental:

Materials and general methods

Methylene bis (3,5-dimethylpyrazole) (H_2MDP) was synthesized via a published procedure[9]. All reagents and chemicals were purchased from commercial sources and were used without further purification. FT-IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. C, H and N microanalyses were carried out with a 2400 Series-II CHN Analyzer, Perkin–Elmer, USA.

Syntheses of 1& 2:

Synthesis of 1 :

In a methanolic solution of H_2MDP, HTFA (0.001M aqueous solution) was added drop wise and stirred for 30 min. The solution was then kept in a $CaCl_2$ desiccator. After few days colorless block shaped crystals of compound **1** were separated out with 60% yield based on H_2MDP.

Anal.calcd (found) for $C_{15}H_{18}F_6N_4O_4$ (**1**) (%): C, 41.67 (41.00); H, 4.20 (3.80); N, 12.96 (12.55); O, 14.80 (14.68); F, 26.37 (26.30).

IR (400-4000cm-1): 3310m, 2929.67w, 1676.03s, 1583.45m, 1444.58s, 1296.0m, 1203.5m, 844.76m, 727.11m.

Synthesis of 2 :

Compound **2** was prepared in similar way except that HTFA was replaced by perchloric acid. Cube shaped white crystals were obtained in 50% yield (based on H_2MDP).

Anal.calcd (found) for $C_{11}H_{18}C_{l2}N_4O_8$ (**2**): C, 32.61 (32.00); H, 4.48 (4.50); N, 13.83 (13.90); O, 31.59 (31.65); Cl, 17.50 (17.55).

IR (400-4000cm-1): 3417.63w, 2829.38w, 1585.38s, 1436.87w, 1265.22s, 1143.71s, 1112.85s, 1089.71s, 883.34w, 756.04m, 628.75s.

Hydrogen bonding geometries in Form-A, Form-B, 1 and 2.

Interaction	*D*/Å	*d*/Å	*θ*/deg
	Form-A		
N_1-H_{111}…. N_4	1.89(3)	2.913(2)	159(3)
N_3-H_{333}…. N_2	1.72(3)	2.860(2)	170(3)
	Form-B		
N_1-H_{111}.... N_3	2.15(3)	2.9566(15)	156(3)
N_2-H_{222}…. N_2	2.10(3)	2.9306(16)	175(3)
N_3-H_{333}…. N_1	2.08(3)	2.9566(15)	173(3)
N_4-H_{444}…. N_4	2.10(3)	2.9538(17)	178(4)
	Complex 1		
N_1-H_{111}…. O_4	1.71(4)	2.661(3)	173(3)
N_2-H_{222}…. O_1	1.84(3)	2.678(3)	171(4)
N_3-H_{333}…. O_3	1.77(3)	2.665(3)	173(3)
N_4-H_{444}…. O_2	1.80(4)	2.670(3)	174(4)
C_{10}-H_{10B}…. O_2	2.58(4)	3.365(4)	150(3)
	Complex 2		
N_1-H_{111}…. O_6	1.92(3)	2.767(3)	176(2)
N_2-H_{222}…. O_1	1.99(3)	2.786(2)	169(3)
N_3-H_{333}…. O_4	2.15(3)	2.823(3)	158(3)
N_4-H_{444}…. O_5	1.94(3)	2.753(3)	179(3)
C_9-H_{9B}…. O_7	2.369(2)	3.288(3)	160.09(14)
C_{11}-H_{11B}….O_1	2.563(2)	3.293(3)	132.95(15)

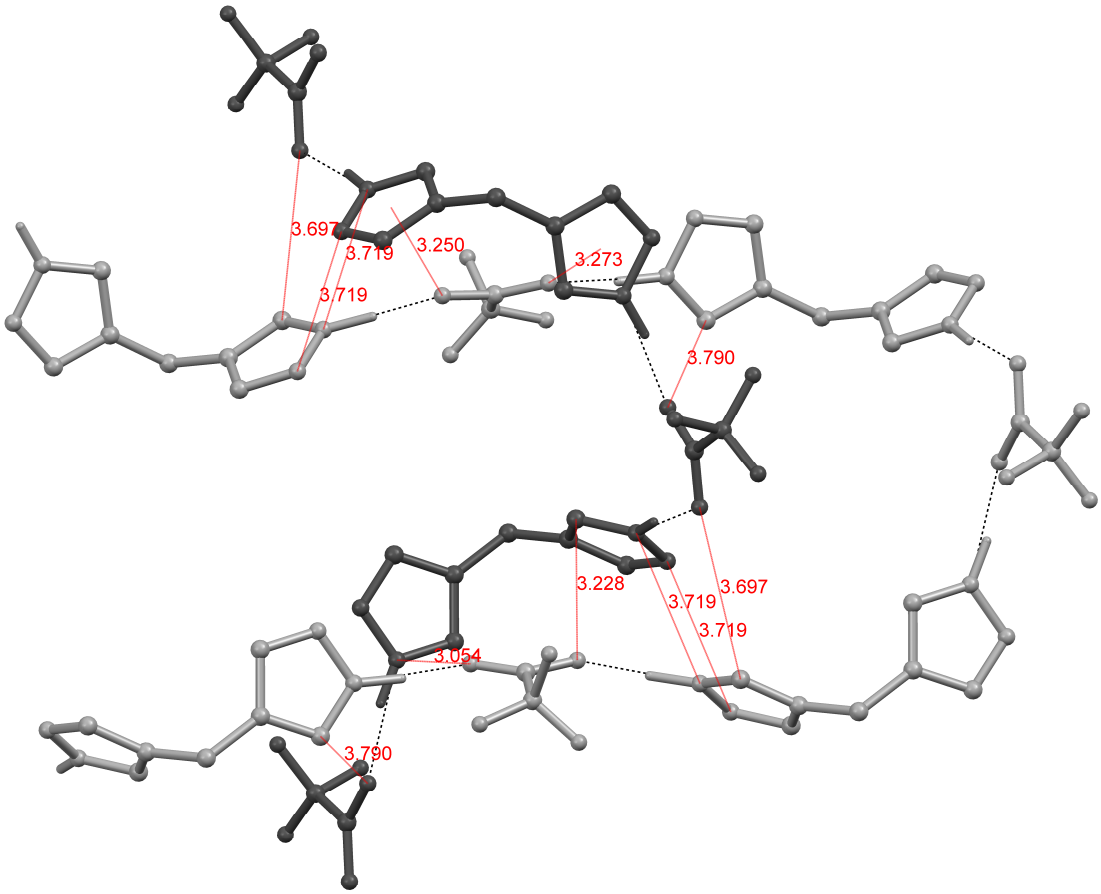

Figure SI-1. Crystal structure of 1 showing anion-π interactions and edge-to-edge π-stacking

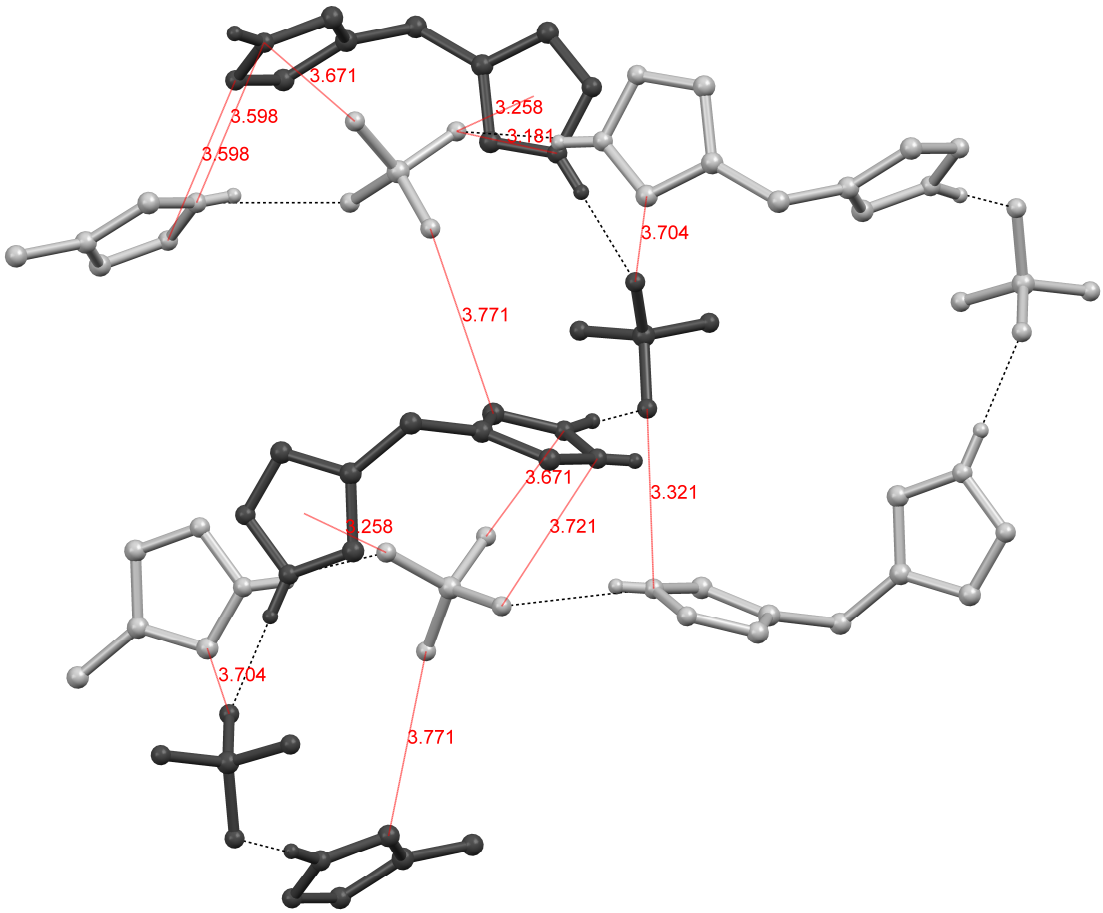

Figure SI-2. Crystal structure of 2 showing anion-π interactions and edge-to-edge π-stacking