Supplementary Information

Hydrogen bonding self-assemblies with 1-D linear, dimeric and hexagonal nanostructures of *meso*-pyridyl-substituted dipyrromethanes

Hiromitsu Maeda,* Masahiro Hasegawa, and Atsushi Ueda

Department of Bioscience and Biotechnology, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu 525–8577, Japan, Department of Materials Molecular Science, Institute for Molecular Science (IMS), Okazaki 444–8787, Japan. Fax: +81 77 561 2659; Tel: +81 77 561 5969; E-mail: maedahir@se.ritsumei.ac.jp

Table of Contents

1. Synthetic procedures and spectroscopic data for 1 and 2

General Procedures. Starting materials were purchased from Wako Chemical Co., Nacalai Chemical Co., and Aldrich Chemical Co. and used without further purification unless otherwise stated. NMR spectra used in the characterization of products were recorded on a JEOL ECA-600HR 600 MHz spectrometer. All NMR spectra were referenced to solvent. Fast atom bombardment mass spectrometric studies (FAB-MS) were made using JOEL-GCmate instruments in the positive ion mode with a 3-nitrobenzylalcohol matrix. TLC analyses were carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on Sumitomo alumina KCG-1525, Wakogel C200, and C300. Compounds **3** and **3'** were synthesized by the modified procedures following the literature methods.[S1]

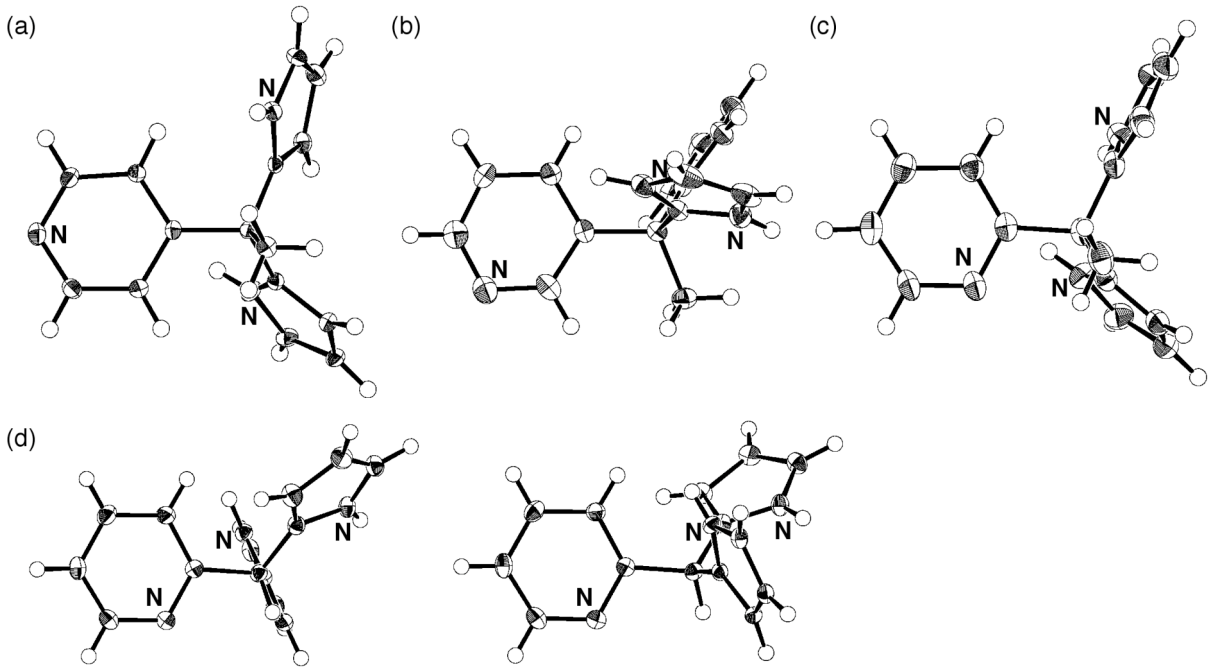
***p*-Pyridyl-substituted dipyrromethane, 1.** After a mixture of 4-acetylpyridine (1.20 g, 9.9 mmol), pyrrole (2.78 g, 40.2 mmol), and EtOH (10 mL) was stirred for 5 min, methanesulfonic acid (0.2 mL) was added and the solution was refluxed for 4 d. The solvent was removed by vacuum distillation with heating. The residual viscous solid was purified by column chromatography (Wakogel C300; $CHCl_3$) and recrystallized from CH_2Cl_2/hexane to afford **1** (620 mg, 26%) as a light gray solid. R_f = 0.50 (5% MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C); δ (ppm) 8.51 (d, J = 5.4 Hz, 2H, ArH), 7.84 (br, 2H, NH), 7.04 (d, J = 5.4 Hz, 2H, ArH), 6.72 (s, 2H, pyrrole-H), 6.19 (d, J = 2.4 Hz, 2H, pyrrrole-H), 5.95 (s, 2H, pyrrole-H), 2.04 (s, 3H, *meso*-CH_3). FABMS: *m/z* (% intensity): 237.2 (32, M^+), 238.2 (100, M^++1). Calcd for $C_{15}H_{15}N_3$: 237.13.

***m*-pyridyl-substituted dipyrromethane, 2.** After a mixture of 3-acetylpyridine (1.20 g, 9.9 mmol), pyrrole (2.78 g, 40.2 mmol), and EtOH (10 mL) was stirred for 5 min, methanesulfonic acid (0.2 mL) was added and the solution was refluxed for 4 d. The solvent was removed by vacuum distillation with heating. The residual viscous solid was purified by column chromatography (Wakogel C300; $CHCl_3$) and recrystallized from CH_2Cl_2/hexane to afford **2** (1.19 g, 51%) as a white solid. R_f = 0.50 (5%MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C); δ (ppm) 8.48 (d, J = 4.8 Hz, 1H, ArH), 8.40 (s, 1H, ArH), 7.85 (br, 2H, NH), 7.38 (d, J = 7.8 Hz, 1H, ArH), 7.20 (dd, J = 8.4 and 4.2 Hz, 1H, ArH), 6.71 (s, 2H, pyrrole-H), 6.18 (d, J = 3.0 Hz, 2H, pyrrole-H), 5.94 (s, 2H, pyrrole-H), 2.07 (s, 3H, *meso*-CH_3). FABMS: *m/z* (% intensity): 237.2 (20, M^+), 238.2 (100, M^++1). Calcd for $C_{15}H_{15}N_3$: 237.13.

[S1] G. Gao, I. Korobkov, and S. Gambarotta, *Inorg. Chem.*, 2004, **43**, 1108.

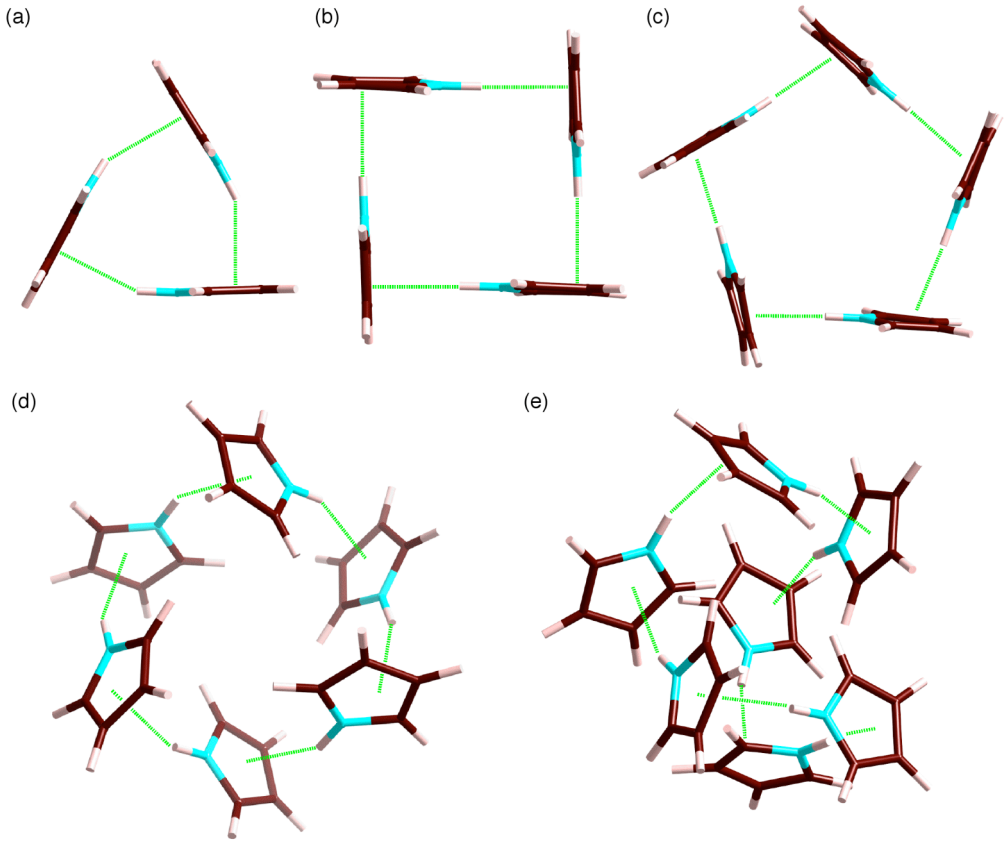
2. X-ray analysis of 1–3 and 3'

X-ray Single-Crystal Analysis. A single crystal of **1** was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **1** in sealed vials. The data crystal was a colorless prism of approximate dimensions 0.30 × 0.20 × 0.20 mm. Data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71075 Å), and structure was solved by direct method. A single crystal of **2** was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **2** in sealed vials. The data crystal was a colorless prism of approximate dimensions 0.50 × 0.40 × 0.25 mm. Data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71075 Å), and structure was solved by direct method. A single crystal of **3** was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **3** in sealed vials. The data crystal was an orange-colored prism of approximate dimensions 0.40 × 0.05 × 0.05 mm. Data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71075 Å), and structure was solved by direct method. A single crystal of **3'** was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **3'** in sealed vials. The data crystal was a colorless prism of approximate dimensions 0.55 × 0.30 × 0.20 mm. Data were collected at 123 K on Bruker SMART CCDC diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), and structure was solved by direct method. In each case, the non-hydrogen atoms were refined anisotropically. The calculations were performed using the Crystal Structure crystallographic software package of Molecular Structure Corporation. CIF files (CCDC-637498–637501 for **1**, **2**, **3**, and **3'**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Supporting Figure 1 Ortep drawings (top and side view) of X-ray single crystal structures of (a) **1**, (b) **2**, (c) **3**, and (d) **3'** (two conformations). Thermal ellipsoids are scaled to the 50% probability level.

3. Optimized structures of cyclic oligomers of pyrrole



Supporting Figure 2 Optimized structures of cyclic oligomers of pyrrole: (a) trimer, (b) tetramer, (c) pentamer, (d) hexamer (based on the crystal structure of **3**), and (e) heptamer.

Cartesian Coordination of Pyrrole Monomer
-210.1763299 hartree
C,-0.9880426763,0.0005038184,-0.6328512949
C,-0.9585072424,0.0006505494,0.7449039893
C,0.4099784993,-0.0022154578,1.1431583043
C,1.1730772849,-0.0005824413,-0.0041944843
H,0.5937618963,0.0191518109,-2.0438689597
H,2.2434483403,-0.0049012687,-0.1448935027
H,0.7882158586,-0.0062226062,2.1558535432
H,-1.8216109222,-0.0006763433,1.3953334289
H,-1.8148648225,0.0095014164,-1.3271345312
N,0.3131449223,-0.0009988317,-1.077341295

Cartesian Coordination of Pyrrole Trimer
-630.5533312 hartree
C,-2.5781416954,-1.758552572,-0.8208916662
C,-2.6594585212,-1.7077691359,0.6037645632
C,-1.3675678602,-1.7960954962,1.0885851387
C,-1.2400475634,-1.8754858057,-1.1484173444
C,-0.2302126895,3.1752948998,0.5448185824
C,-0.1555921821,3.1015482678,-0.8786137702
C,-0.8804866249,1.9921716879,-1.2671035375
C,-1.0018294204,2.1071225657,0.9683201773
C,2.8049663555,-1.2702326425,-0.6560975016
C,2.8223709246,-1.513517497,0.7507193551
C,2.2591176112,-0.4084584781,1.3619527275
C,2.2303104598,-0.0281348187,-0.848478631
H,0.4927622417,-1.9123221236,0.0754426734
H,-1.9118606097,0.5316984668,-0.1231632183
H,1.4075559674,1.3521926312,0.5370833477
H,2.0190303361,0.5278827651,-1.7485951758
H,2.0889040524,-0.1865980611,2.4049359488
H,3.2212913273,-2.38266969,1.2549053646
H,3.1836925729,-1.9208947404,-1.4318995655
H,-1.3072184456,1.8009622551,1.957627564
H,-1.0743273127,1.5777072059,-2.2448068104
H,0.3596041809,3.78723962,-1.5365011193
H,0.2039887205,3.9354182178,1.1795816436
H,-0.9875459596,-1.7961127771,2.099010633
H,-0.747451142,-1.9419402807,-2.1066356288
H,-3.5578393074,-1.6363942109,1.2008964009
H,-3.4025959367,-1.7315818769,-1.5196181634
N,-0.5201514034,-1.9019786857,0.0171477821
N,-1.3904034565,1.4018610828,-0.1398880644
N,1.90933151,0.4841271383,0.3813670745

Cartesian Coordination of Pyrrole Tetramer
-840.7395412 hartree

C,-3.2640418216,2.0966191649,-0.4531140642
C,-3.1706023479,2.0028846563,0.9686649594
C,-1.8351128527,2.1375773124,1.2984278967
C,-1.9807520085,2.2853639536,-0.9340030969
C,1.9974450052,3.2769898994,-0.7626991043
C,2.0968254267,3.1896853998,0.6587250304
C,2.3663156139,1.8690092246,0.9679185066
C,2.2101989807,2.006287908,-1.2645829454
C,3.2224796014,-2.0221192585,0.7199710082
C,3.2286880678,-2.0833026471,-0.706591482
C,1.9185394171,-2.2648530484,-1.112196682
C,1.909994273,-2.1677948335,1.1277356995
C,-2.056713631,-3.230381824,0.6308284488
C,-2.0415581029,-3.2309729256,-0.7967161085
C,-2.2847853296,-1.9332784524,-1.2068886495
C,-2.3085931743,-1.931918606,1.0350425124
H,-0.1233017855,2.4443102863,0.0807699179
H,2.6255386376,0.1702851689,-0.2755360594
H,0.1271938834,-2.4535280834,0.0104607948
H,-2.6428714208,-0.1623557989,-0.0874552486
H,-2.4096645666,-1.5010859182,2.0196771416
H,-2.3618691246,-1.5054850809,-2.1952414757
H,-1.8815541234,-4.0824304521,-1.4433341845
H,-1.9121055398,-4.0815061163,1.281550067
H,1.471568888,-2.1830966746,2.1142028256
H,1.4887406483,-2.3707000773,-2.0969032321
H,4.0915883181,-2.021912439,-1.3551652049
H,4.0793760321,-1.8989511369,1.3674767738
H,2.2281416947,1.6397342975,-2.2800444313
H,2.5218692608,1.3783602222,1.9167525703
H,1.9940048033,3.9997973289,1.3671476224
H,1.8032543331,4.1662565929,-1.3459619189
H,-1.3368716082,2.13006533,2.2561431876
H,-1.6118874145,2.4126503467,-1.9406383059
H,-3.9865837903,1.8665846258,1.664594298
H,-4.1652019402,2.0507754436,-1.0487555862
N,-1.127333988,2.3075301567,0.1373960827
N,2.4331790712,1.1647548045,-0.2057767978
N,1.1324355358,-2.3134512539,0.0086648123
N,-2.4453274602,-1.1583399082,-0.0878371155

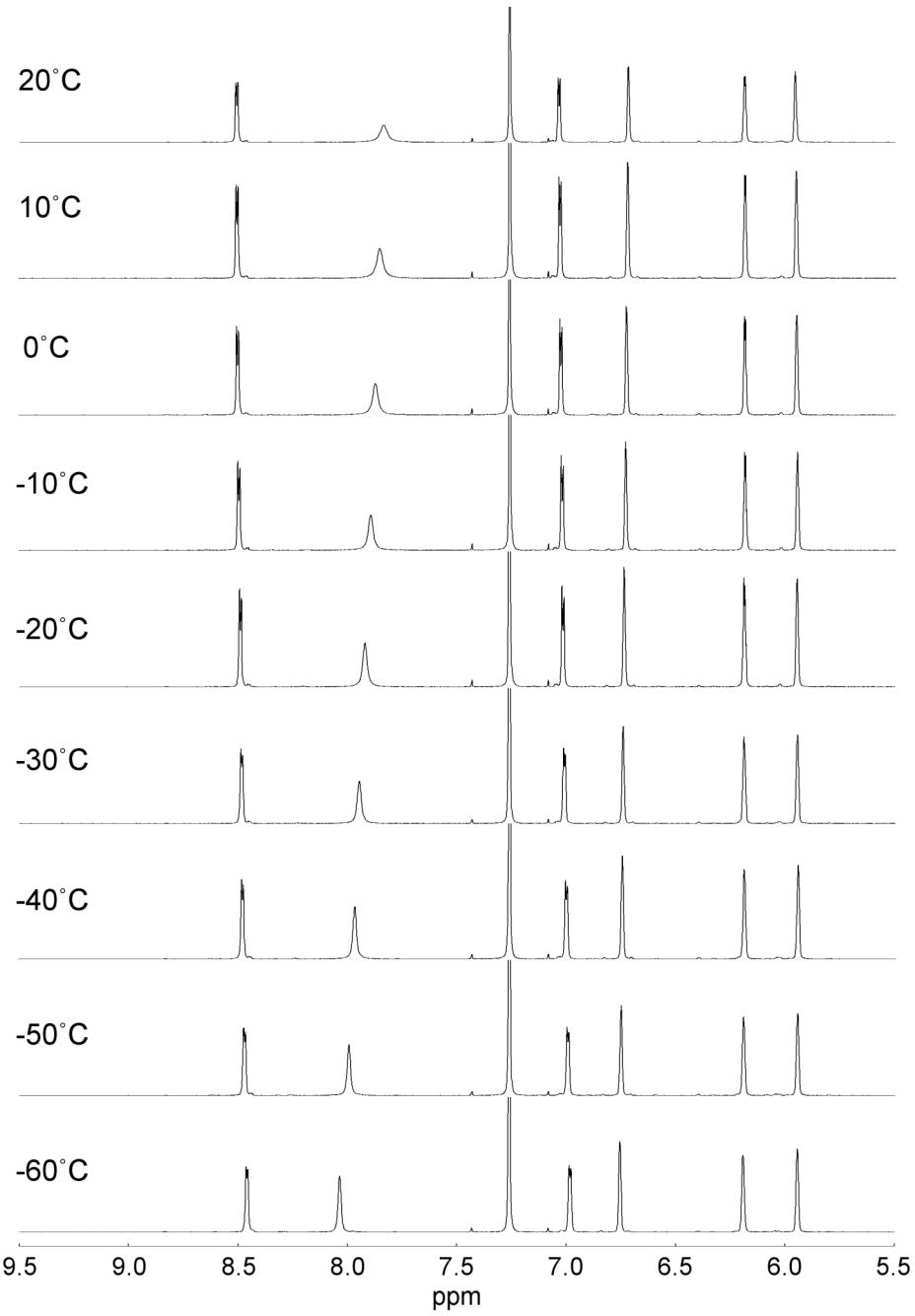
Cartesian Coordination of pyrrole pentamer
-1050.9225302 hartree
C,-4.0941724736,2.1516522089,-0.7771854221
C,-3.8926934338,2.2438350757,0.6341325977
C,-2.5854075592,2.6465716173,0.833131803
C,-2.9012527865,2.4997342118,-1.3821636311
C,0.9132855194,4.3336703152,-1.0333205437
C,0.7857337521,4.6216555502,0.3599179556
C,1.477916371,3.6410829438,1.0429362095
C,1.6800260143,3.1875853908,-1.1437976031
C,4.32794819,0.663008146,1.3438737046
C,4.5639855472,0.5296219215,-0.0587590347
C,3.8642517437,-0.5827982754,-0.4849135909
C,3.4933244775,-0.3743646903,1.7168669324
C,-3.267146612,-3.1591689231,0.6199316866
C,-3.2975280149,-3.1175955213,-0.8076586548
C,-3.3099760555,-1.7852400632,-1.1755267288
C,-3.2620122511,-1.8507094388,1.0652592292
C,1.9969074575,-4.1992066225,0.48142753
C,2.0296857668,-4.0296093511,-0.9362864364
C,0.7871309539,-3.5650903454,-1.319167798
C,0.7332002233,-3.8295031959,0.9068266929
H,-1.0474618162,3.1233001201,-0.5437917742
H,2.60683402,1.9847287435,0.3373926221
H,2.6634444521,-1.9682193459,0.5770156623
H,-3.3311189678,-0.0163113393,-0.0061759139
H,-0.9632552362,-3.1683196714,-0.1814247156
H,0.2886844339,-3.8248210583,1.8908231793
H,0.3939635315,-3.3125586088,-2.2924502195
H,2.8620117481,-4.235804211,-1.59454124
H,2.7947953598,-4.5710060102,1.1094890394
H,-3.2499853733,-1.4423957002,2.0647082063
H,-3.3421239752,-1.3173761983,-2.1479590828
H,-3.3250697107,-3.9630945448,-1.4809278981
H,-3.2674476306,-4.0424516171,1.2434868534
H,3.0846074271,-0.6425050043,2.6797034174
H,3.776068834,-1.038309923,-1.4595497721
H,5.1832977298,1.1659501933,-0.6754111194
H,4.7380390801,1.4164890206,2.0021562186
H,2.0222009866,2.6430360061,-2.011022065
H,1.6371024694,3.492358898,2.1004684976
H,0.2572154279,5.4533238137,0.8042654499
H,0.5136051766,4.912170864,-1.8549019389
H,-2.0322105988,2.8474356342,1.7379752385
H,-2.6302528724,2.5675532719,-2.4252073213
H,-4.6248292047,2.0567664643,1.4074446407
H,-5.0077607637,1.8764720118,-1.2856230527
N,-1.9970738822,2.7959164519,-0.3951248608
N,2.0133937085,2.7792243104,0.1203313693
N,3.2206546514,-1.1195231474,0.5996985131
N,-3.2869809208,-1.0302854114,-0.0321693989
N,0.0129213705,-3.4463604226,-0.1940345225

Cartesian Coordination of Pyrrole Hexamer
-1261.1142801 hartree
C,-2.0761553516,-0.7401849585,-3.7793365542
C,-2.2301191305,-0.7341937213,3.6821818975
C,4.3051517889,-0.7372864429,0.0948592365
C,2.0763756092,0.7394873758,3.779412257
C,2.2300981876,0.734842035,-3.6820659485
C,-4.3049939915,0.7369927614,-0.0951305281
C,-1.2360088737,-1.8083903948,-4.0396804708
C,-2.8779059617,-1.8055532282,3.0928593238
C,4.1175642147,-1.8119962099,0.9460834345
C,1.2364625256,1.8078591134,4.039835346
C,2.8775796243,1.8062638528,-3.0925143102
C,-4.1177209876,1.8116090416,-0.946545281
C,-0.9339356789,-2.4209673475,-2.7865572397
C,-1.946585986,-2.4243258434,2.2064795322
C,2.8825107131,-2.4267173916,0.5813907502
C,0.9345009839,2.4205844612,2.7867612766
C,1.9460348919,2.4246891921,-2.206131079
C,-2.8829482889,2.4268747312,-0.581826373
C,-1.596802481,-1.7039969878,-1.8089728334
C,-0.7673874309,-1.7086525736,2.2846672095

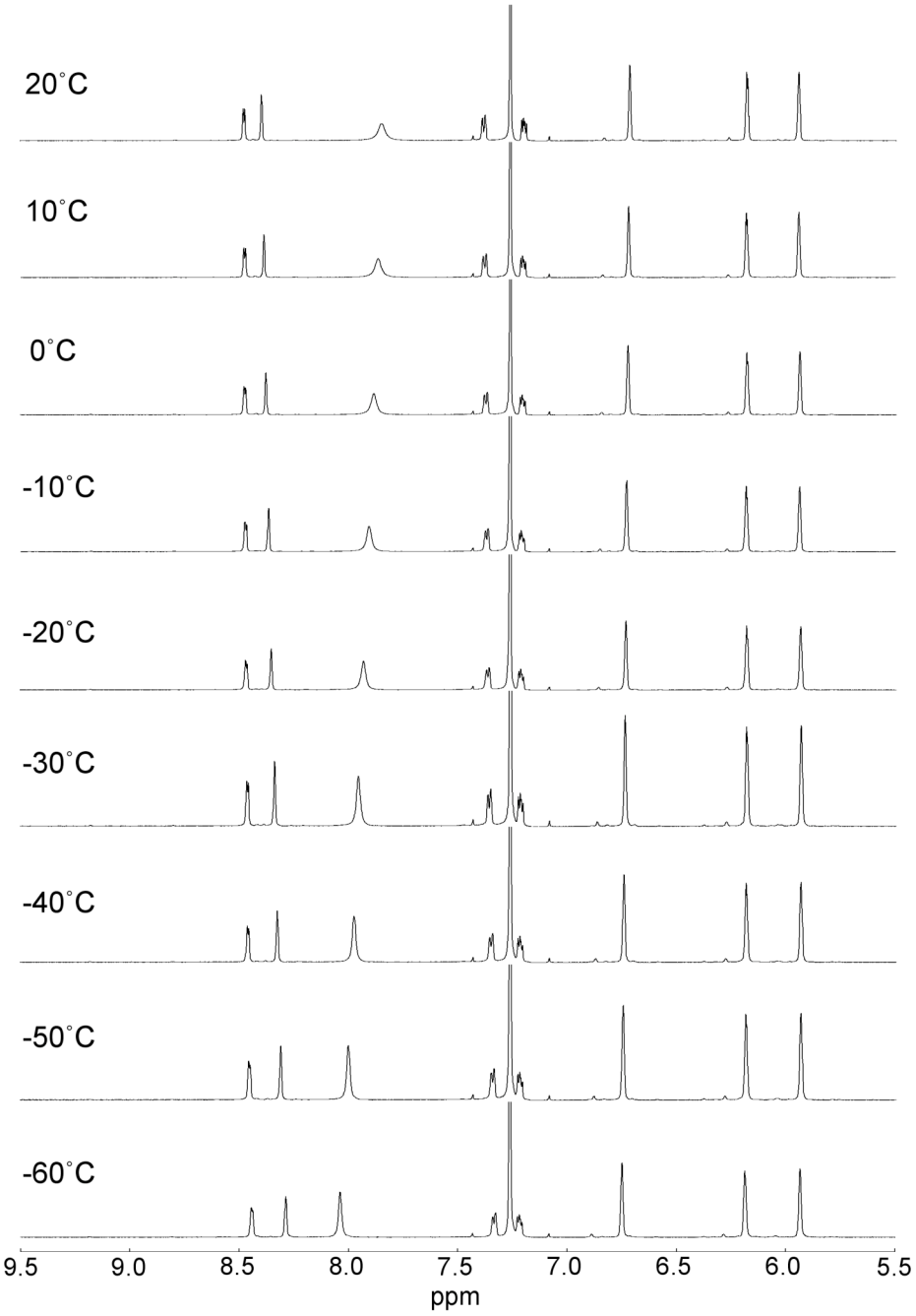
C,2.3608768653,-1.7051416278,-0.4750014319
C,1.5972913238,1.7036104241,1.8091280585
C,0.7669998767,1.7087755405,-2.2845694643
C,-2.3611765015,1.7057167307,0.4747836699
H,-2.547305163,-0.0311091509,-4.4436921859
H,-2.5677014707,-0.0200740003,4.4185701097
H,5.113742061,-0.0253547508,0.020397476
H,2.5473559095,0.0302261147,4.4436879657
H,2.5679039022,0.0209193767,-4.4185409266
H,-5.1133089248,0.0247514039,-0.0206480365
H,-2.8654717336,-0.0063452997,-1.9472173718
H,-0.2488418066,-0.0030171638,3.4412870738
H,3.1060825901,0.0006630301,-1.4982355446
H,2.8657753043,0.0058074283,1.947269067
H,0.2489628394,0.0031685974,-3.4414222246
H,-3.1059200038,-0.0001011932,1.4983393917
H,-0.9009314909,-2.1273690202,-5.0170331115
H,-3.8915610426,-2.1223592192,3.296302924
H,4.8003841185,-2.1332680306,1.720547734
H,0.9014464829,2.1268236057,5.0172146065
H,3.8911748598,2.1233381258,-3.2958410492
H,-4.8005727814,2.1324571018,-1.7211574812
H,-0.3151951859,-3.2924802494,-2.6238858649
H,-2.1175846893,-3.2998824655,1.595769014
H,2.4368715122,-3.3023973837,1.0324236444
H,0.3159162534,3.292220978,2.6241549799
H,2.1167765909,3.3001481927,-1.5952098192
H,-2.4375914588,3.3026235181,-1.0330035962
H,-1.6296526109,-1.8257865595,-0.7363829668
H,0.1769098253,-1.8337266652,1.7756483443
H,1.4466479207,-1.8252662516,-1.0372106337
H,1.6299904734,1.8253493144,0.7365300663
H,-0.1773583557,1.8335265285,-1.775584262
H,-1.4470747936,1.8264021619,1.03708082
N,-2.2815785476,-0.686897339,-2.423452951
N,-0.9539952011,-0.6852322122,3.1792713886
N,3.230912268,-0.6828875827,-0.7576931178
N,2.281883861,0.6863465837,2.4235310925
N,0.9539043818,0.6855765936,-3.1793580022
N,-3.2308560164,0.6831969182,0.7575843028

Cartesian Coordination of Pyrrole Heptamer
-1471.2980289 hartree
C,-5.2234742547,0.716647459,0.7364292674
C,-4.4008391462,1.4882035035,1.6123135946
C,-3.3689231377,0.6698553799,2.0330405334
C,-4.6621788195,-0.543412638,0.6550446689
C,4.5513678203,-2.3437362735,0.583079975
C,4.6722398021,-1.1403429645,-0.175467279
C,3.7405579771,-0.2460553314,0.3223386711
C,3.5529102357,-2.1394294113,1.5149698153
C,-1.3078424471,1.3314321064,-3.0850962336
C,-1.8400333445,2.6526673717,-3.1911942799
C,-2.7190712097,2.8227638755,-2.1368883449
C,-1.8843131517,0.7472407592,-1.9716205017
C,-1.4836982198,-3.2400021732,2.0213781733
C,-2.6042604399,-3.8382795898,1.3679558288
C,-2.3718156441,-3.7604185035,0.0086098582
C,-0.6104359123,-2.820805028,1.0337224029
C,2.987270311,3.7468507665,-0.7511421503
C,2.1318326788,4.6253419069,-0.0214953732
C,0.8357475613,4.3719874849,-0.4369391977
C,2.1827544153,2.9915440679,-1.5816297305
C,0.7029235771,-3.5594318352,-3.1756579529
C,0.2021367763,-2.222913016,-3.1372425331
C,1.0631214478,-1.4873441334,-2.3400627616
C,1.845735936,-3.5886192601,-2.4015492115
C,1.415247627,0.8774288586,3.9765177512
C,0.4173289555,0.3539549516,3.1004025185
C,0.3750150637,1.1780869281,1.9878134075
C,1.9453158286,1.9965272255,3.3673551693
H,-2.9438064555,-1.3677117385,1.5799487228
H,2.325305362,-0.4424230759,1.888453623
H,-3.3206845395,1.4931937221,-0.5959086571
H,-0.7223963358,-2.9684666299,-1.0785400693
H,0.0753646535,2.9980625403,-1.8673923033
H,2.830472191,-2.0505169466,-1.3106239223
H,1.4922478976,2.9157592971,1.5018777695
H,2.7230363766,2.6738584409,3.686732156
H,-0.2417951947,1.1435439533,1.1023243217
H,-0.2047310415,-0.5150537323,3.2640764183
H,1.7077900763,0.4805021277,4.938286595
H,2.5196662181,-4.3979817038,-2.1644488784
H,1.0462114442,-0.4465795951,-2.053942962
H,-0.6701940126,-1.8396952025,-3.6487864157
H,0.2789668015,-4.3964773246,-3.7123700444
H,2.4301330134,2.2244362933,-2.300340467
H,-0.1020516582,4.8253178364,-0.152393373
H,2.4313476884,5.3760879966,0.6969446517
H,4.0646052102,3.6878431398,-0.6856200931
H,0.3523583398,-2.3365811509,1.0932626284
H,-2.9593099618,-4.1018839518,-0.8305624046
H,-3.4693171672,-4.2829076469,1.8396851726
H,-1.3242844851,-3.1571682232,3.0878133389
H,-1.7616714992,-0.2363496929,-1.5444814638
H,-3.3384717142,3.6631895601,-1.8609970696
H,-1.622096505,3.3817483978,-3.9593052752
H,-0.6026796177,0.8595517063,-3.7552316517
H,3.1529186719,-2.7905594423,2.2777884788
H,3.5081630195,0.7714094329,0.0439072494
H,5.3727139753,-0.9451544348,-0.9757518003
H,5.1355152578,-3.2459179129,0.4674035023
H,-2.5336369273,0.8631080222,2.6893911512
H,-4.9659950992,-1.4243109146,0.1104736097
H,-4.5554972064,2.51548235,1.9119881209
H,-6.1247067954,1.0421111457,0.2357732251
N,-3.5377216311,-0.5564307019,1.4406532947
N,3.0708994597,-0.8658127961,1.3459682093
N,-2.7349586773,1.6626260006,-1.4078893193
N,-1.161826797,-3.1408483701,-0.1794842474
N,0.8815600171,3.3765106473,-1.3782470635
N,2.0509513246,-2.329110136,-1.8994046196
N,1.3094946327,2.1662194182,2.1627822606

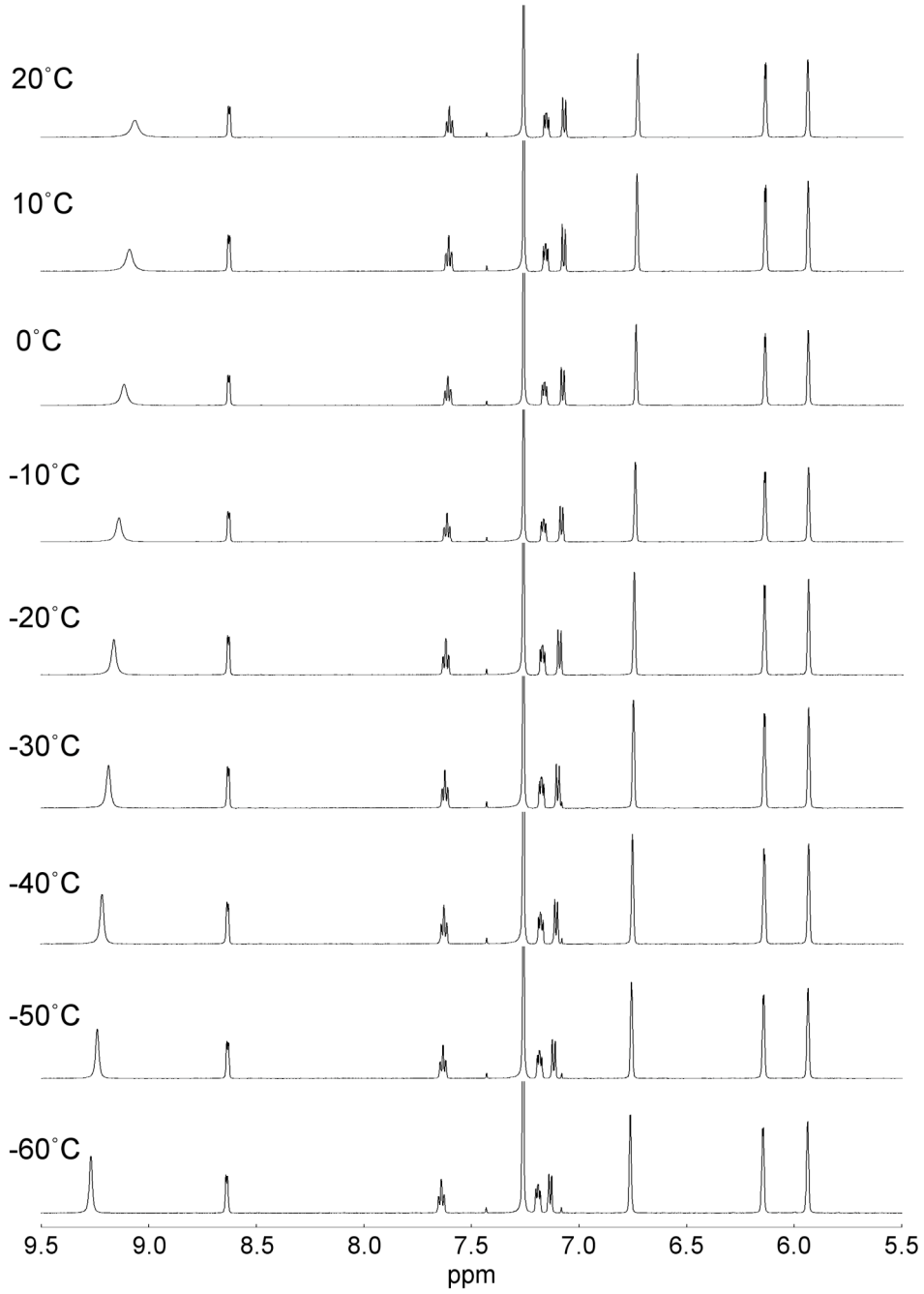
4. Solution study of 1–3



Supporting Figure 3 ^{1}H NMR spectra of **1** at various temperatures ($CDCl_3$).



Supporting Figure 4 ^{1}H NMR spectra of **2** at various temperatures ($CDCl_3$).



Supporting Figure 5 ^{1}H NMR spectra of **3** at various temperatures ($CDCl_3$).