Electronic Supporting Information

Ultrastructure of metallopeptide-based soft spherical morphologies

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1. Crystallization and X-ray diffraction analysis:

The complex was grown by slow evaporation of **4** (1 equiv) and $CuSO_4.5H_2O$ (3 equiv) solutions in methanol. Blue colored crystals were obtained in a month's time.

1.1. Crystal Structure Determination and Refinements: Single Crystal of **4**+Cu(II) was coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature apparatus and intensity data was collected using graphite-monochromated Mo Kα radiation. The data integration and reduction were processed with the SAINT software.[1] An absorption correction was applied.[2] Structure was solved by the direct method using SHELXS-97 and refined on F^2 by a full-matrix least-squares technique using the SHELXL-97 program package.[3] Non-hydrogen

atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters. Crystal structure refinement parameters are given in Table 1, whereas H-bonding parameters are provided in Table 2.

CCDC contains the supplementary crystallographic data for this paper with deposition number of CCDC 1005702 for **4**+Cu(II) Complex. Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK. [Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

Table S1: Crystallographic Data for $Cu_2$4$_2$ metallopeptide

Identification code	Cu(II)+4 Complex
Empirical formula	C_{90} H_{94} Cu_2 N_{10} O_{28}
*M*r	1890.83
crystal system	Triclinic
space group	P1
a/Å	12.0316 (8)
b/Å	13.9710 (10)
c/Å	15.7586 (11)
α/°	73.2190 (10)
β/°	80.012 (4)
γ/°	74.696 (2)
Volume/ Å^3	2432.6 (3)
Z	1
Dx /Mg m^{-3}	1.291
F(000)	986
μ/ mm^{-1}	0.516
θ range for data collection/ °	2.11 to 28.37
Limiting indices	-16<=h<=10, -18<=k<=14, -21<=l<=19
Reflections collected	20414
unique reflections	15130
R(int)	0.0333
Completeness to θ	98.5
T_{max} / T_{min}	0.9038/ 0.8905
Data / restraints / parameters	15130 / 3 / 1179
Goodness-of-fit on F^2	1.043
*R*1 and *R*2 [$I>2\sigma(I)$]	0.0767, 0.1859

*R*1 and *R*2 (all data)	0.1220, 0.2129
Largest diff. peak and hole/e.A^{-3}	1.281 and -0.906
CCDC No.	**1005702**

Table S2: Selected hydrogen bonding distances (Å) and bond angles (°) in **4**+Cu(II) Complex

D—H…A[#]	D…A	H…A	D—H…A
4+Cu(II)			
N(2)—H(2')…O(25)	3.0652	2.26	157
N(2)—H(2')…N(1)	2.7046	2.33	107
N(3)—H(3')…O(1)^{iv}	2.9319	2.12	156
N(4)—H(4')…O(25)	2.9659	2.17	153
N(4)—H(4')…N(1)	2.6849	2.32	106
N(5)—H(5')…O(25)	2.9582	2.14	158
N(5)—H(5')…O(25)	2.8091	2.47	104
N(7)—H(7')…O(23)	3.1644	2.38	152
N(7)—H(7')…N(6)	2.7078	2.33	107
N(8)—H(8')…O(23)	2.8942	2.04	174
N(9)—H(9')…O(23)	3.0987	2.32	151
N(9)—H(9')…N(6)	2.6703	2.31	106
N(10)—H(10')…O(9)^{i}	2.9467	2.11	164
O(17)—H(17A)…O(5)^{ii}	2.7168	1.95	155
O(18)—H(18)…O(13)^{iii}	2.6308	1.84	162
O(23)—H(23A)…O(2)	2.6828	1.87	170
O(27)—H(27)…O(25)	2.7654	1.98	162
C(7)—H(7)…O(13)	2.7789	2.35	105
C(9)—H(9)…O(14)	2.7856	2.36	105
C(18)—H(18B)…O(16)	2.8189	2.47	101
C(26)—H(26)…O(1)^{iv}	3.1833	2.34	144
C(26)—H(26)…O(9)	2.8182	2.42	103
C(37)—H(37B)…O(10)	3.1060	2.58	115
C(50)—H(50)…O(5)	2.8214	2.39	106
C(52)—H(52)…O(6)	2.8131	2.38	106
C(61)—H(61B)…O(8)	2.8617	2.50	102
C(69)—H(69)…O(1)	2.8265	2.43	104
C(69)—H(69)…O(9)^{i}	3.3506	2.50	146
C(77)—H(77)…O(6)^{i}	3.4802	2.57	166
C(80)—H(80B)…O(4)	2.9624	2.57	105

#Symmetry of A: (i) x,1+y,z (ii) -1+x,y,z (iii) 1+x,y,z (iv) x,-1+y,z ; where A= acceptor and D= donor.

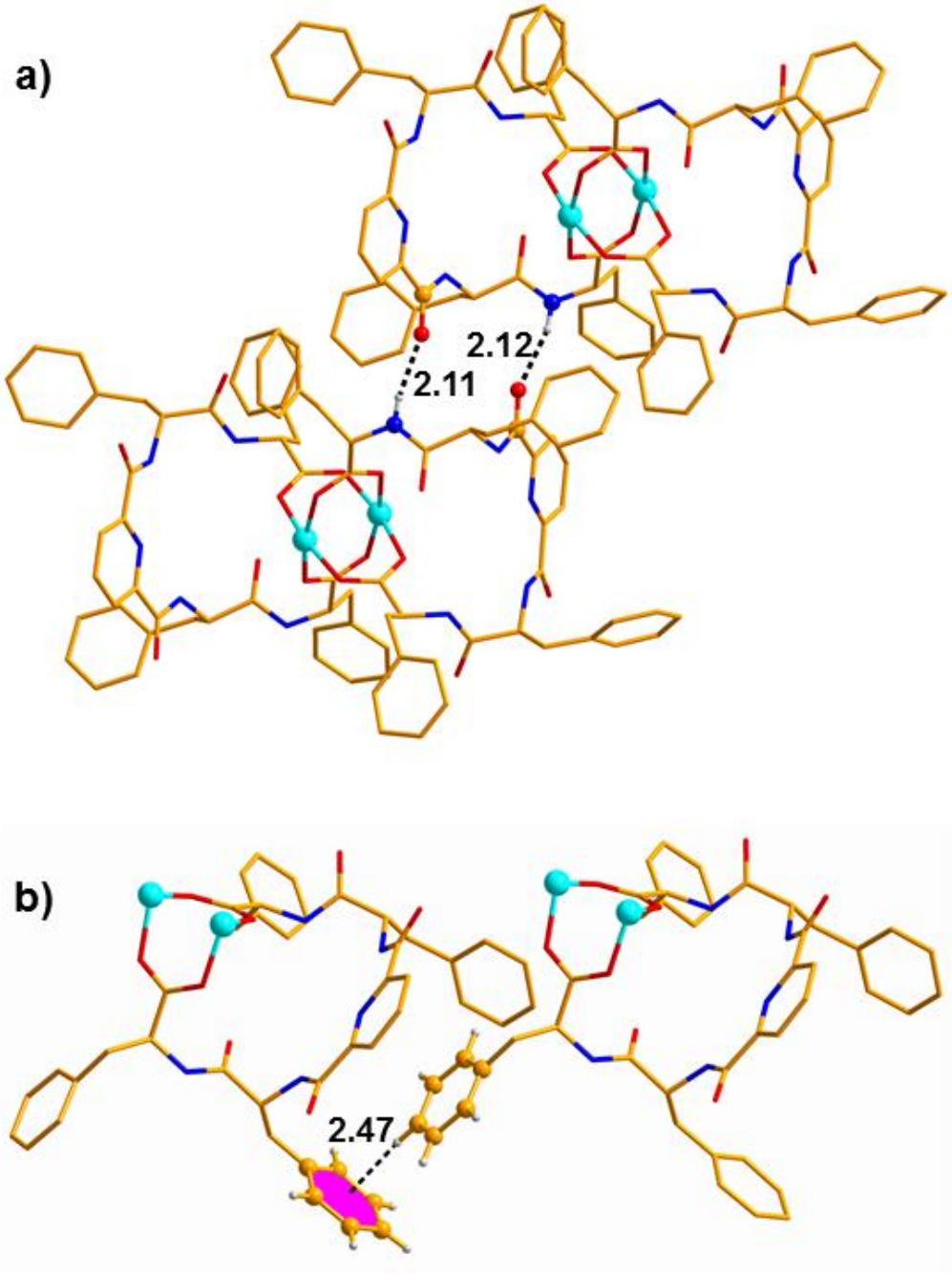

Figure S1: (a) H-bonding (Å) (b) CH-π interactions (Å) in **4**+Cu(II) complex

2. Focused Ion Beam- Scanning Electron Microscopy (FIB-SEM):

2.1. Technical terms: The milling process of peptide based soft material was depends upon: beam current, accelerating voltage and mill depth to minimize surface artifacts.

2.2. Accelerating Voltage: The interaction volume of gallium (Ga+) ions is smaller at lower voltage which may cause less damaging to the soft structure compare to higher voltage. Therefore the FIB system which is usually operates at 30 kV operates at an accelerating voltage of 20 kV in the initial milling stage. We have also used a lower accelerating voltage upto 15 kV for ion beam and electron beam.

2.3. Beam Currents: Usually the high beam current for peptide based soft structure were not applicable because, the fragile specimens may not be stable under high beam current. Due to this reason we have used a set of current in the range of 1 pA- 2.1 nA to determine least possible beam current which is less damaging in nature. Initially 2.1 nA current for 1 min used for the irradiation and effect of this irradiation causing more damage to the soft specimen, another beam current of 81 pA is also causing damage to the soft specimen under 1-2 mins time duration. Therefore a current of 37 pA for 1 min apply to mill the soft-specimen this gives a fine cutting and less damage to the specimen. Since the milling times were inversely proportional to beam current strength therefore we did not use this beam current for longer time which may cause sputtering and melting of the soft-specimen (melting due to the heat generated by ion irradiation). The optimal beam current of 10 pA for milling the specimen typically for 5 mins was used for present sample. An extremely low beam current of 1 pA is also suitable for milling propose for long time duration up to 1-2 h (lowest beam currents required impractically long exposure).

3. High Resolution Scanning Electron Microscopy (HR-SEM):

10 µL aliquots of the samples were deposited on copper grids, and allowed to dry at room temperature. Subsequently the samples were dried *in vacuo* for 30 min prior to imaging. The samples were imaged with and without (for EDX) gold coating. SEM images were acquired on Quanta 200 FEG Field Emission Gun ESEM operating at 20 kV.

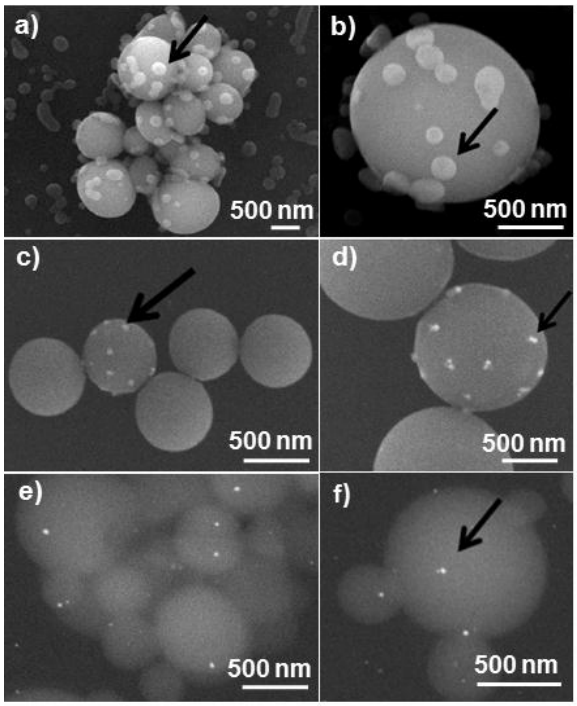

Figure S2: SEM images on copper grid after 12 h (a, b) **4**+Cu(II) complex. (c, d) **4**+Ag(I) complex. (e, f) **4**+Au(III) complex.

The solution phase study was also done in pure methanol on [surface used: silicon wafer (100)], which also showed similar results.

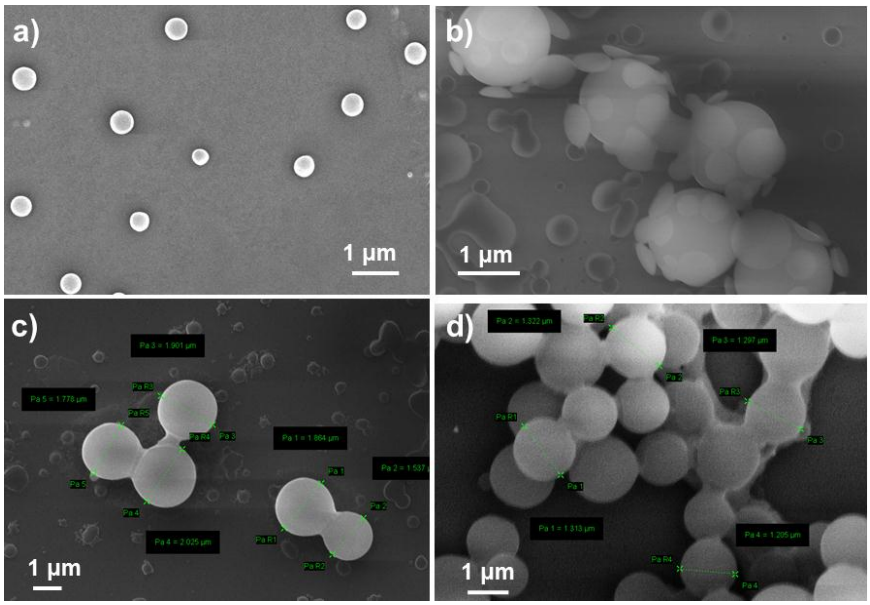

Figure S3: SEM image on Silicon Wafer (100) after 12 h of (a) **4** (b) **4**+Cu(II) complex (c) **4**+Ag(I) complex (D) **4**+Au(III) complex (solution prepared in pure methanol).

4. Spectral characterization:

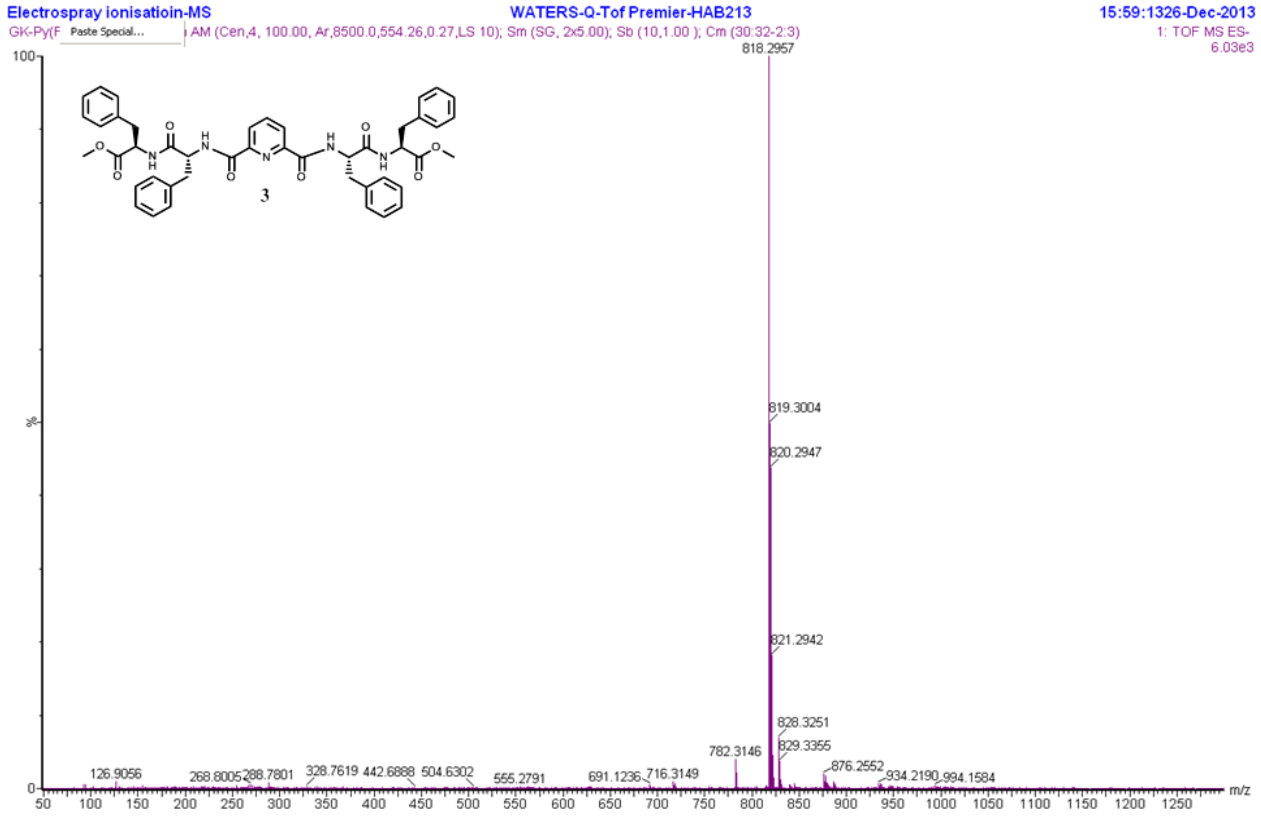

Figure S4: HRMS Spectrum of **3**

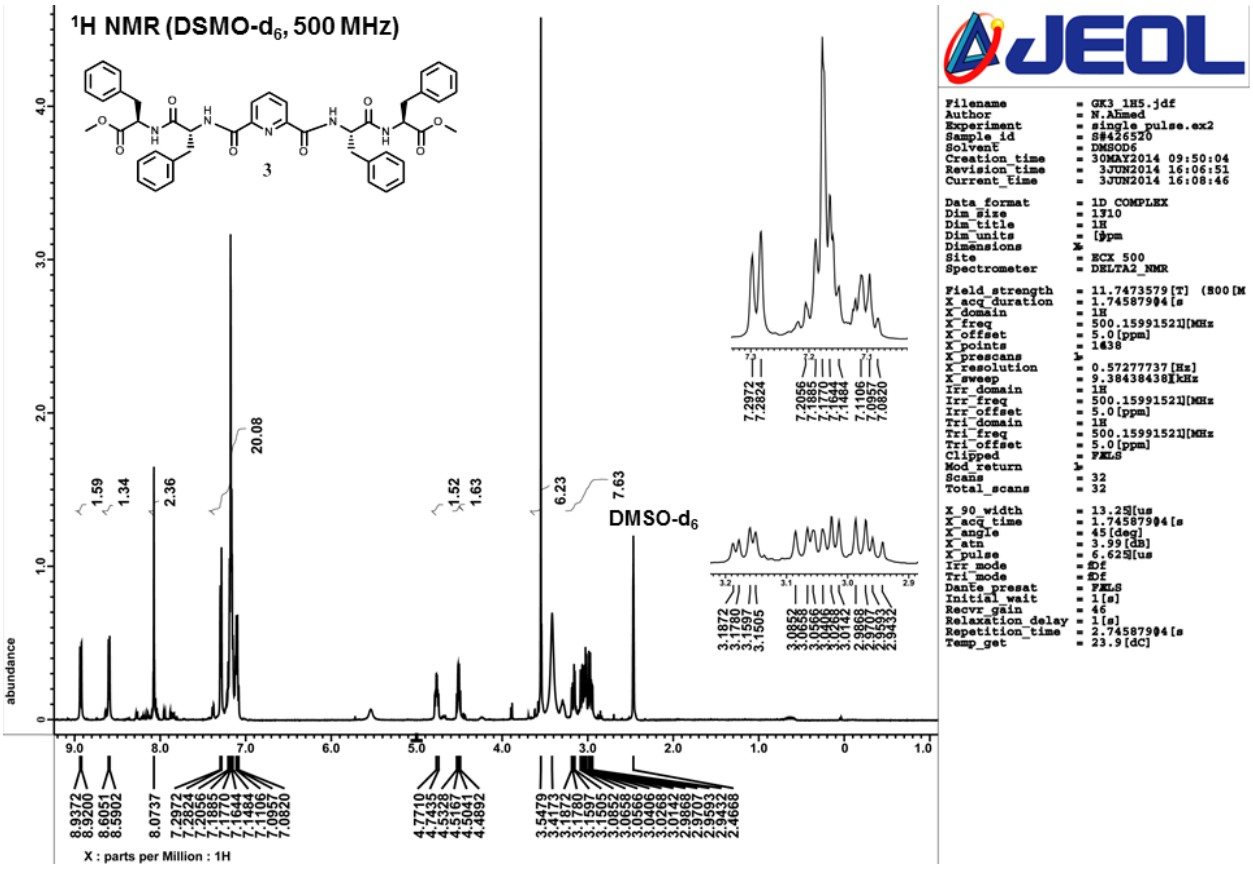

Figure S5: ^{1}H NMR Spectrum of **3**

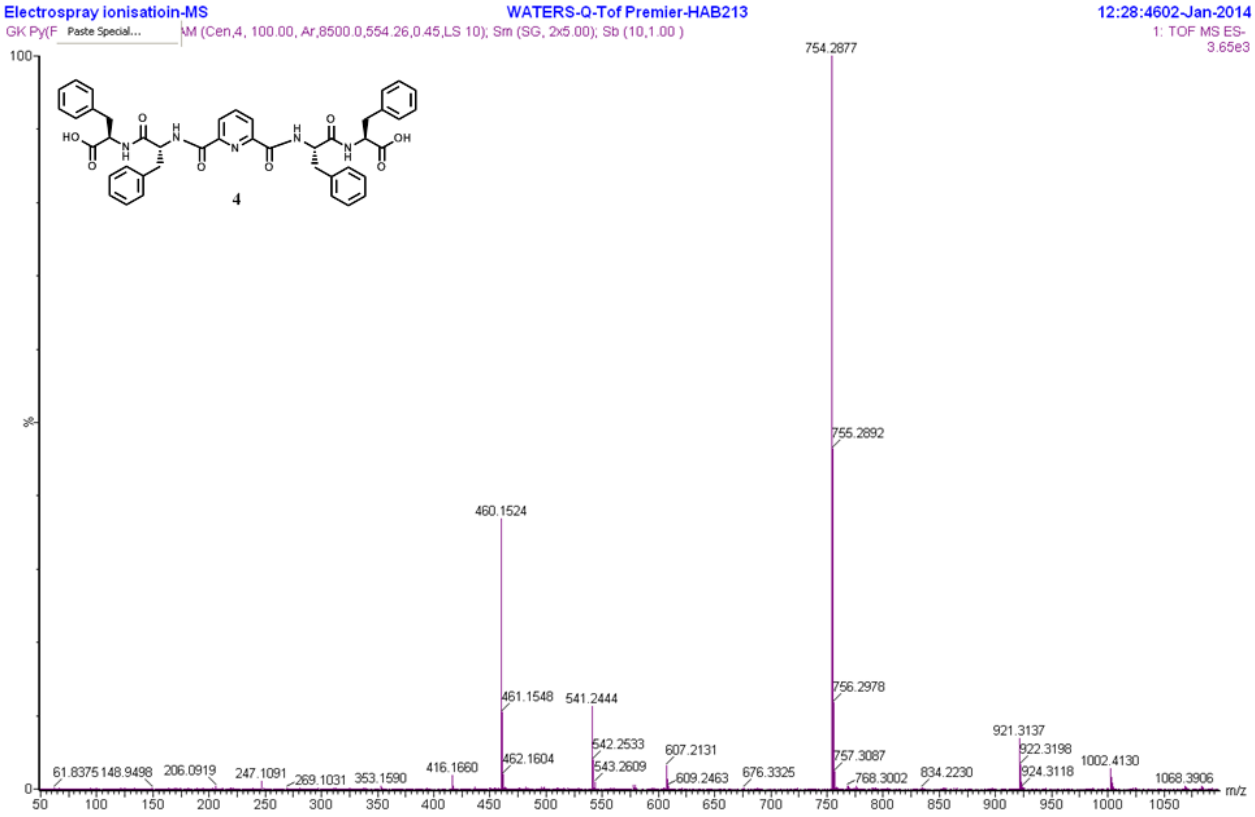

Figure S6: HRMS Spectrum of **4**

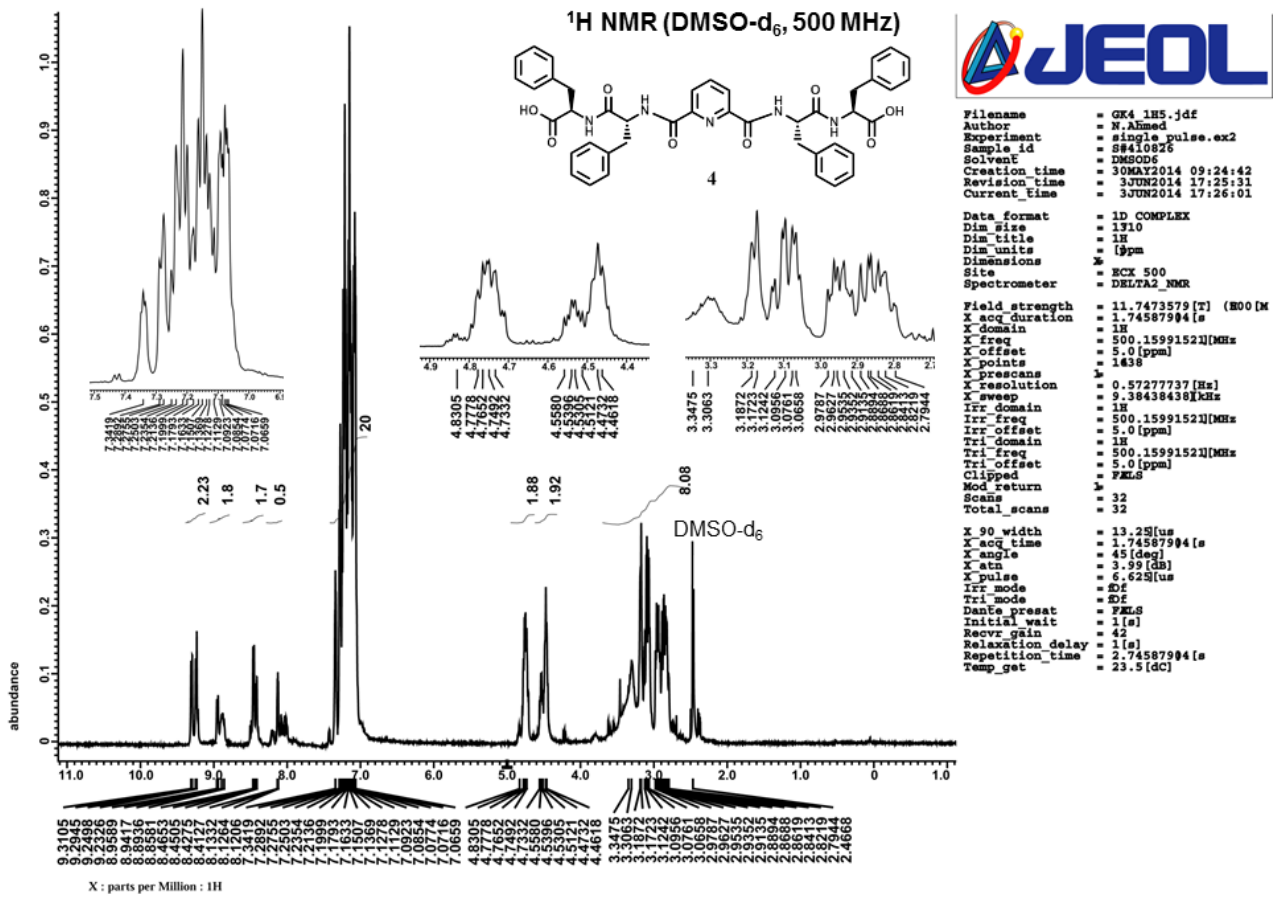

Figure S7: ^{1}H NMR Spectrum of **4**

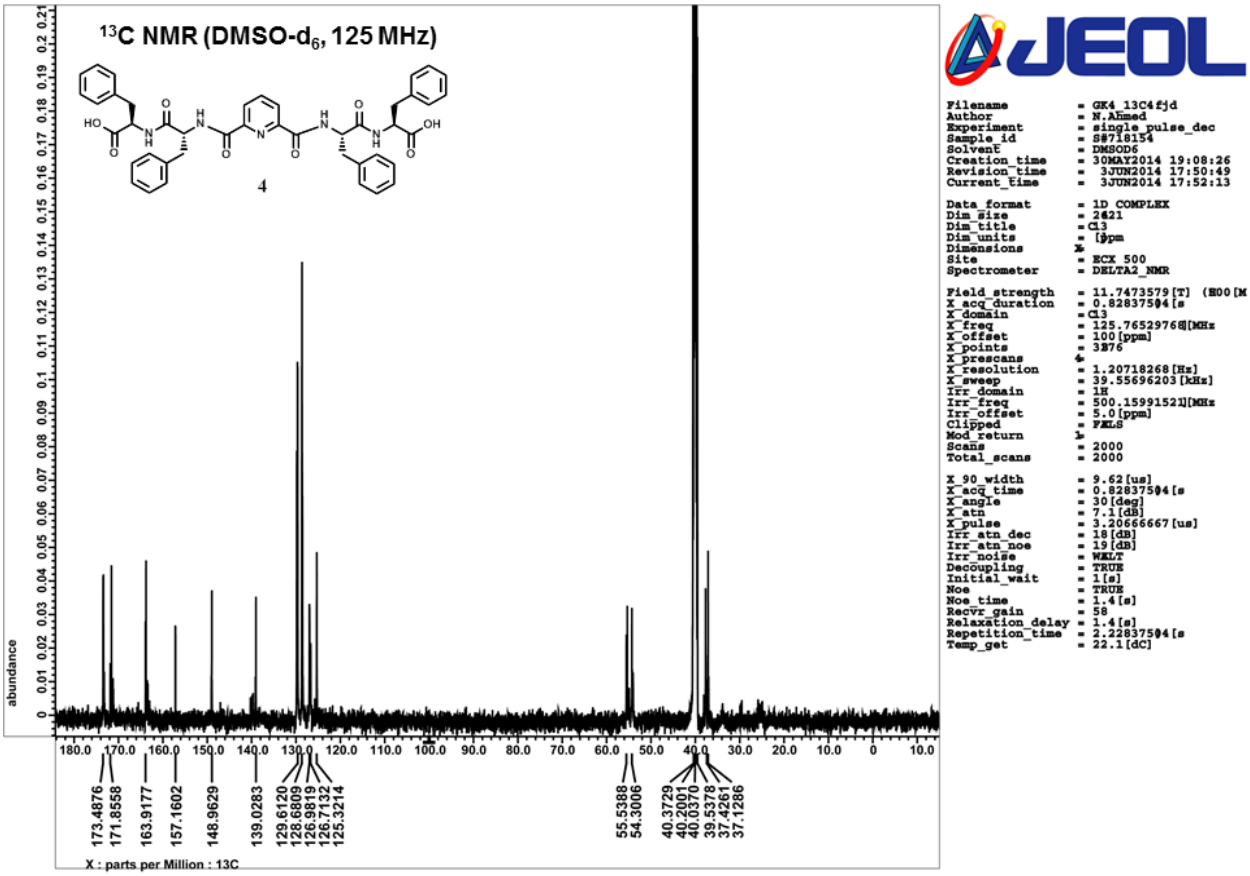

Figure S8: ^{13}CNMR Spectrum of **4**

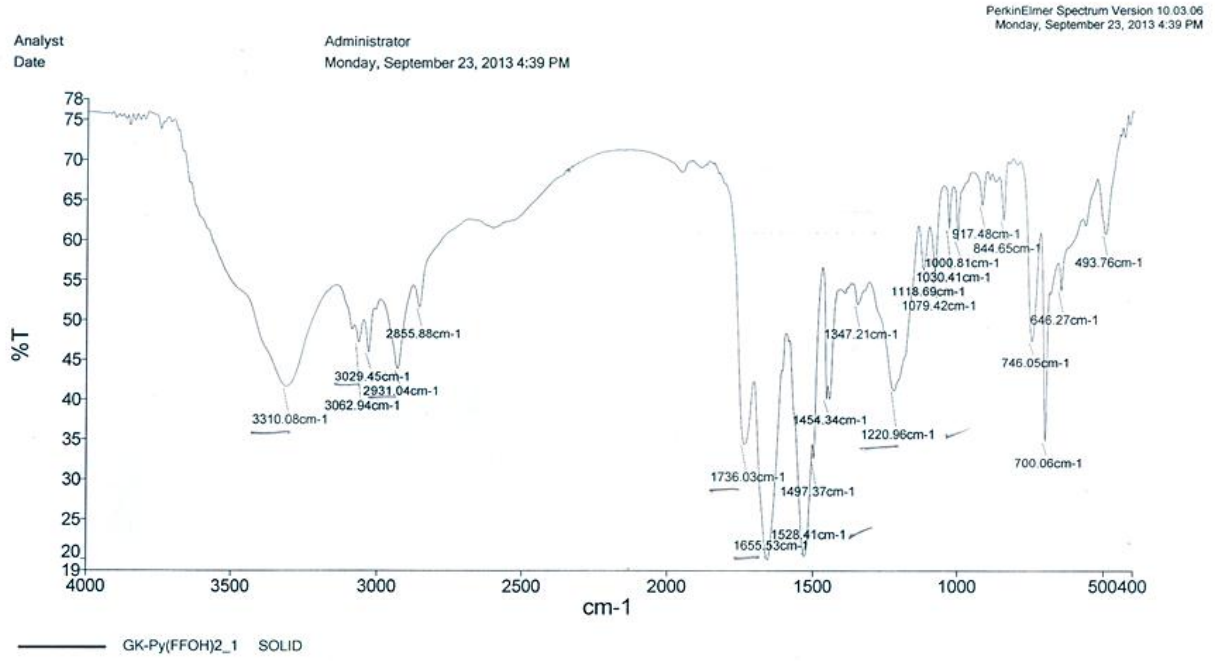

Figure S9: IR Spectrum of **4**

References:

1. SAINT+, 6.02 ed.; Bruker AXS, Madison, WI, **1999**.

2. Sheldrick, G. M. SADABS 2.0; University of Gottingen: Gottingen, Germany, **2000**

3. Sheldrick, G. M.; University of Goettingen, Germany, **1997**.