Toxic metal sequestration exploiting an unprecedented low molecular weight hydrogel to metallogel transformation

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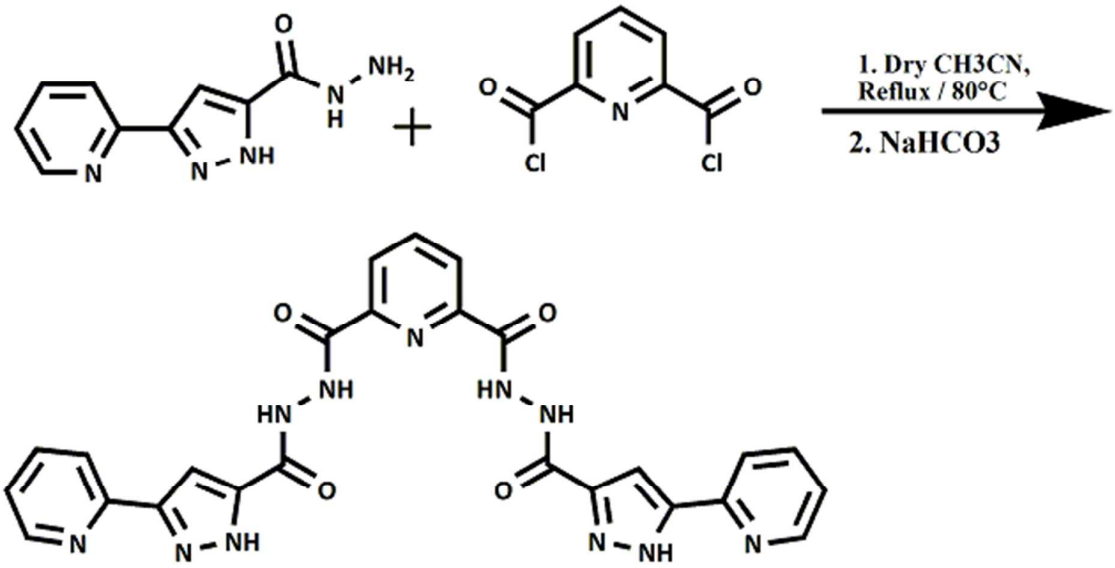
Contents

1. Synthetic procedure of BP3D:

N^2,N^6-bis(5(3)-(pyridin-2-yl)-1H-pyrazole-3(5)-carbonyl)-pyridine-2,6-dicarbohydrazide (BP3D) was prepared by the reaction of 3-(pyridin-2-yl)-1H-pyrazole-5-carbohydrazide with 2,6-Pyridinedicarbonyl dichloride. 2,6-Pyridinedicarbonyl dichloride (2.04 g, 10 mmol) was dissolved in dry acetonitrile and to it 3-(pyridin-2-yl)-1H-pyrazole-5-carbohydrazide (10.75 g, 20 mmol) was added, giving an immediate white suspension. The reaction mixture was refluxed overnight at 80°C, cooled and filtered. The precipitate was washed with acetonitrile and dried in vacuum. To the suspension of the hydrochloride salt in water, was added saturated sodium bicarbonate solution till slightly basic and stirred at room temperature overnight. The precipitated solid was filtered, washed with water, dried and purified from DMF/Water.



Scheme S1 BP3D synthesis

2. UV-Vis titration:

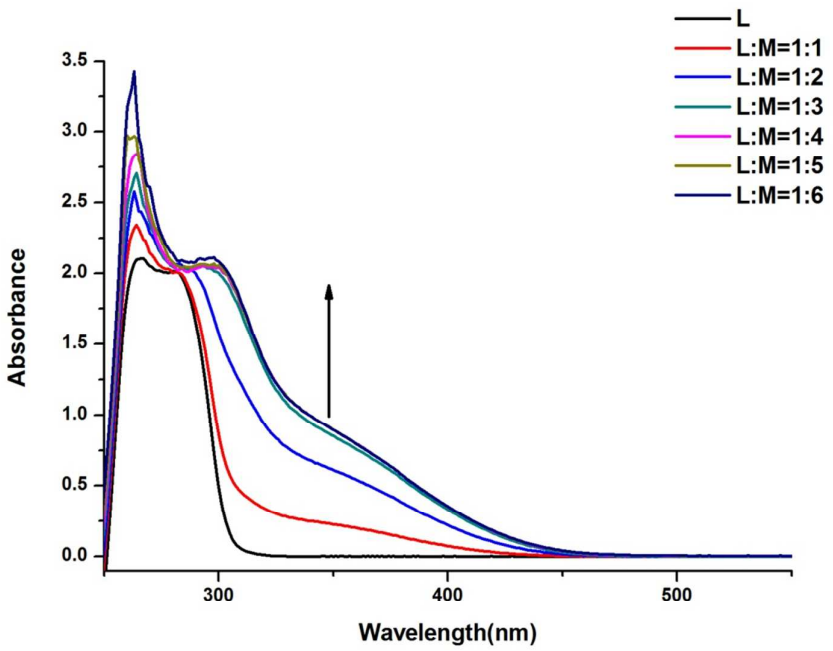


Figure S1 UV-Vis titration of BP3D with Hg plot

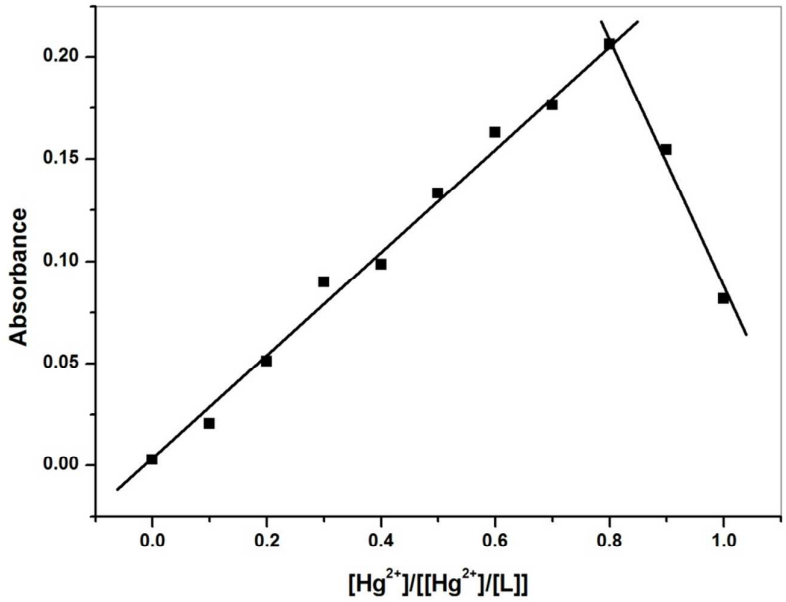


Figure S2 Job's plot of UV-Vis titration of BP3D with Hg plot

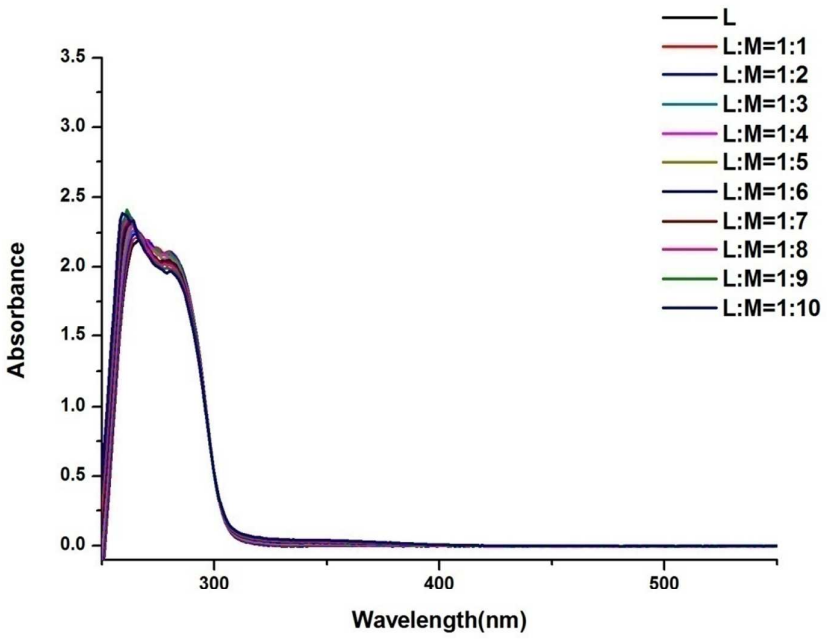


Figure S3 UV-Vis titration of BP3D with Cd plot in DMSO:Water=1:1 medium

3. IR Spectra:

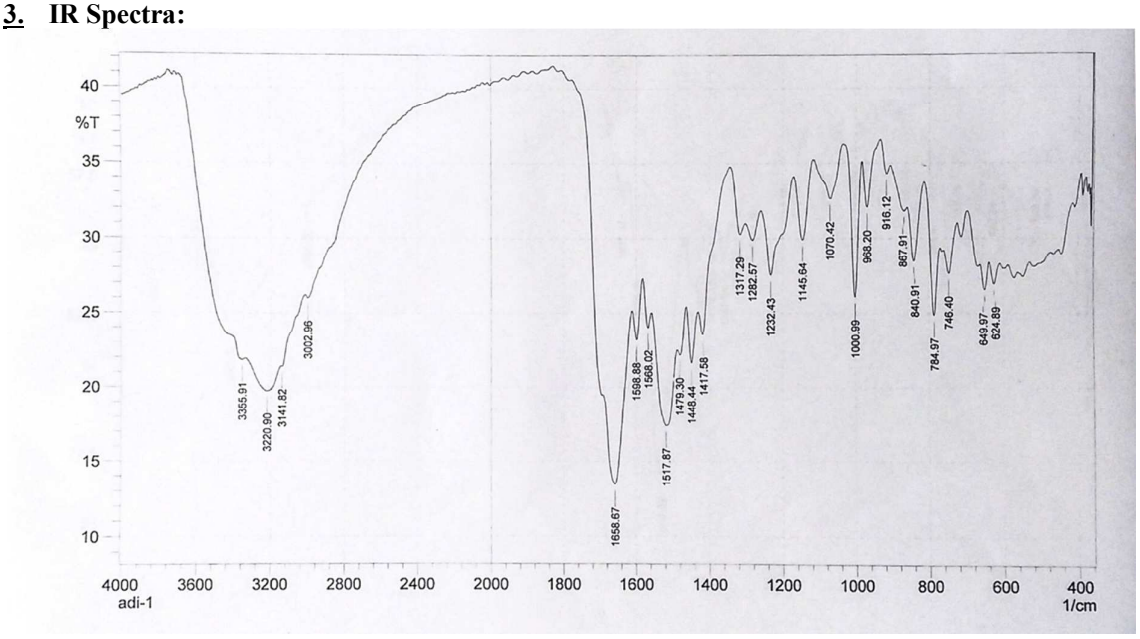


Figure S4 IR spectra of BP3DH

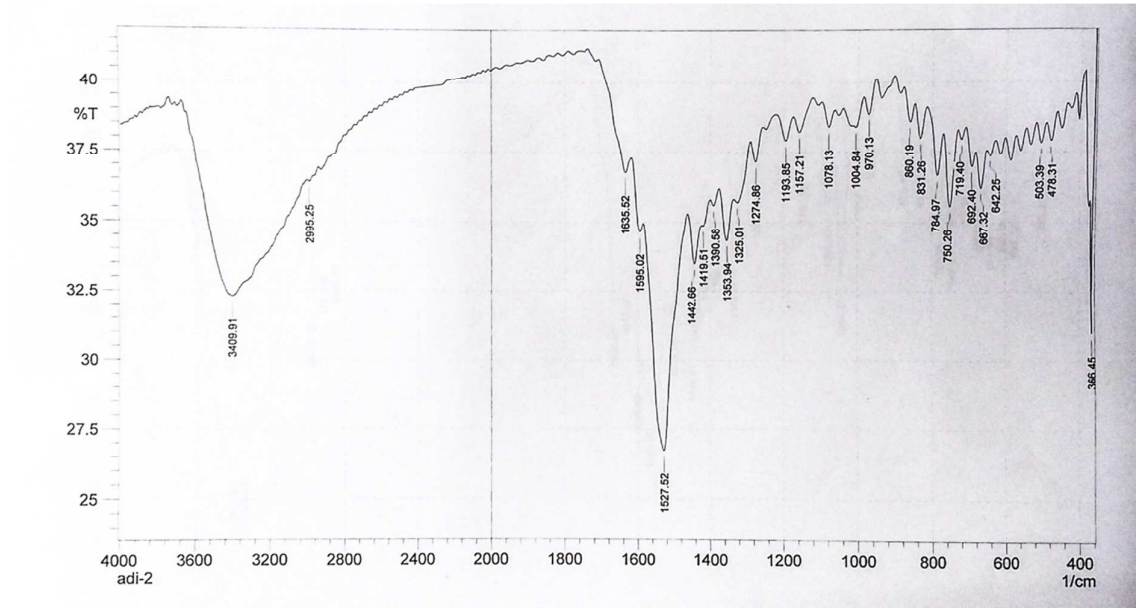


Figure S5 IR spectra of xerogels of **G-Pb**

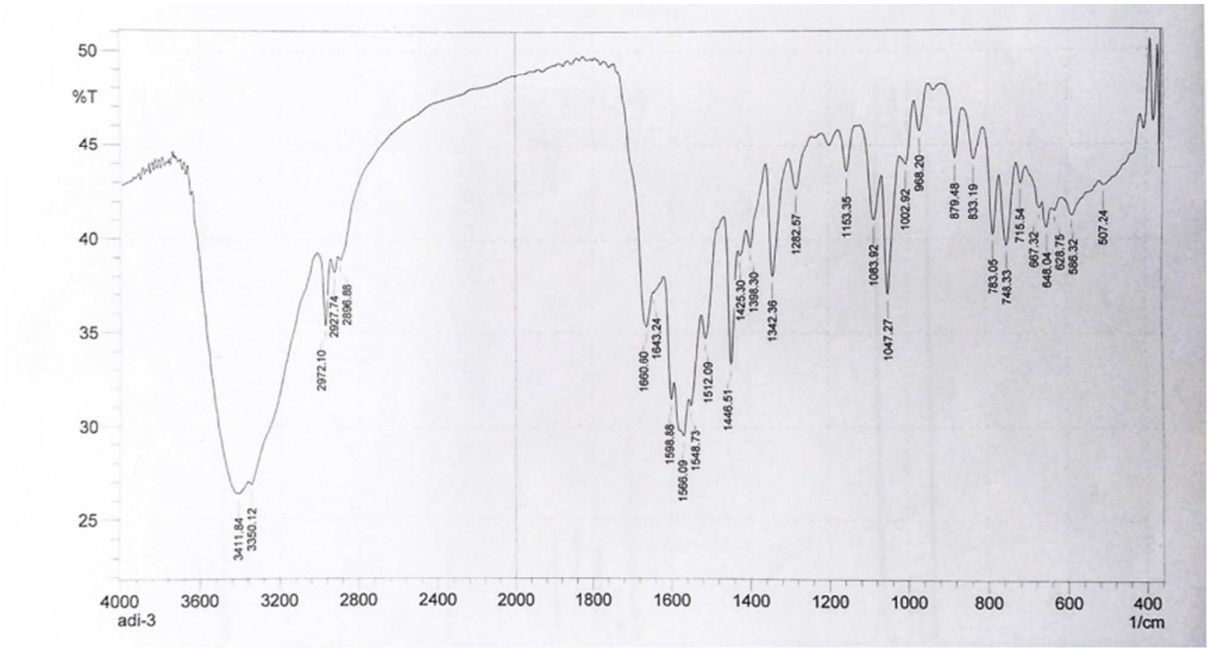


Figure S6 IR spectra of xerogels of **G-Hg**

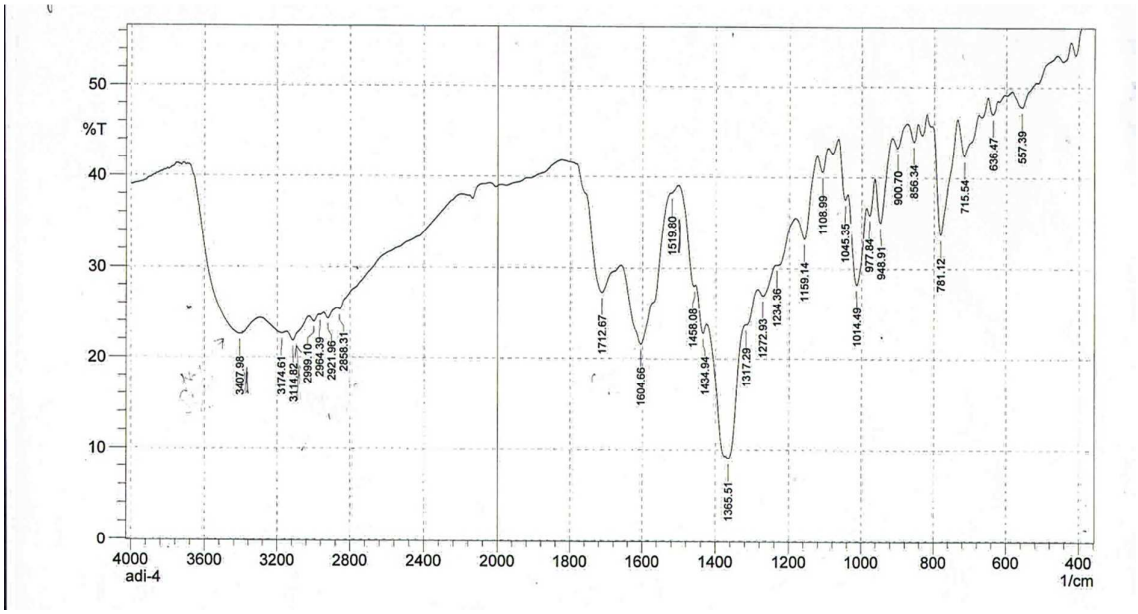


Figure S7 IR spectra of xerogels of **G-Cd**

4. NMR Spectra:

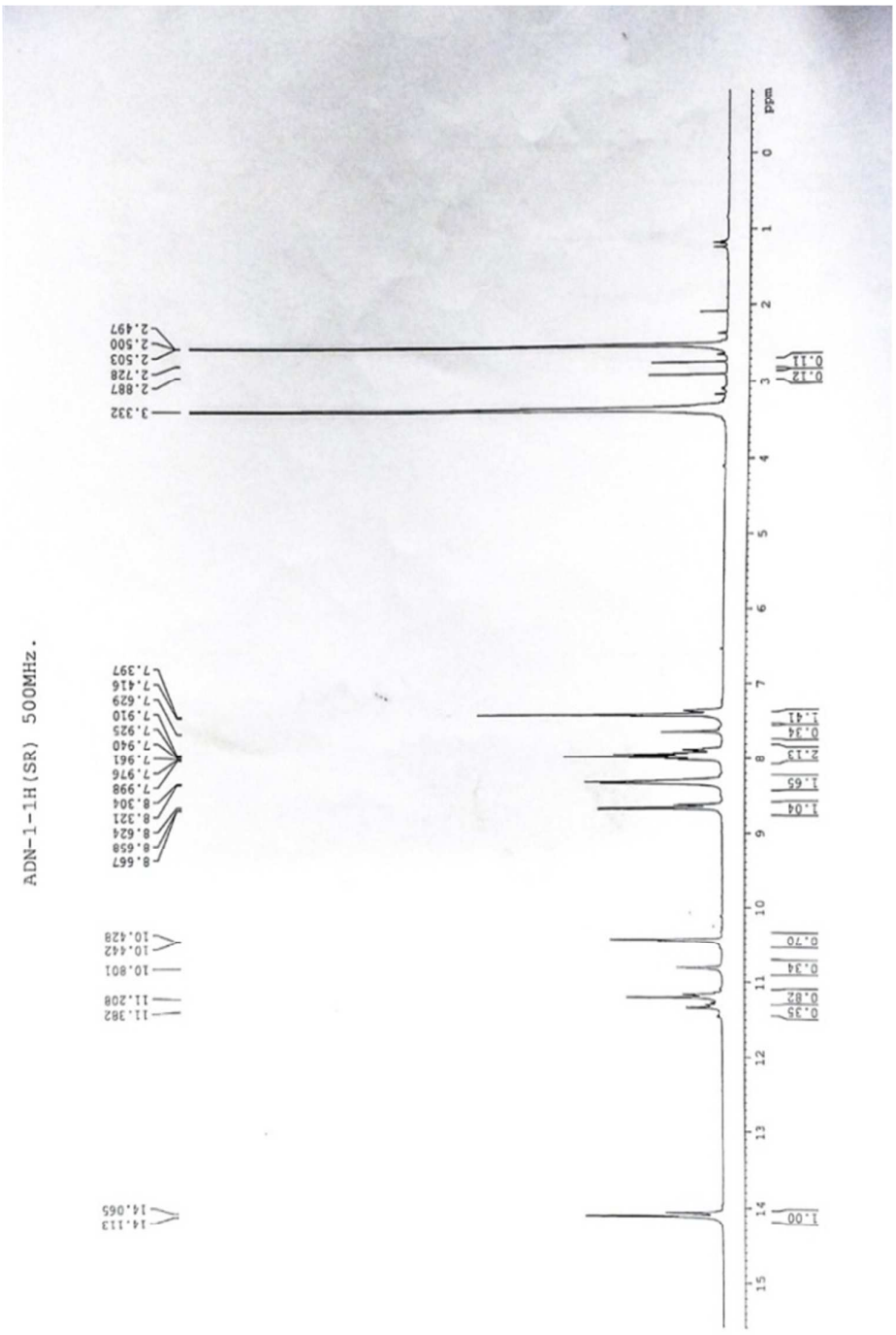


Figure S8. 1H NMR Spectra of BP3D

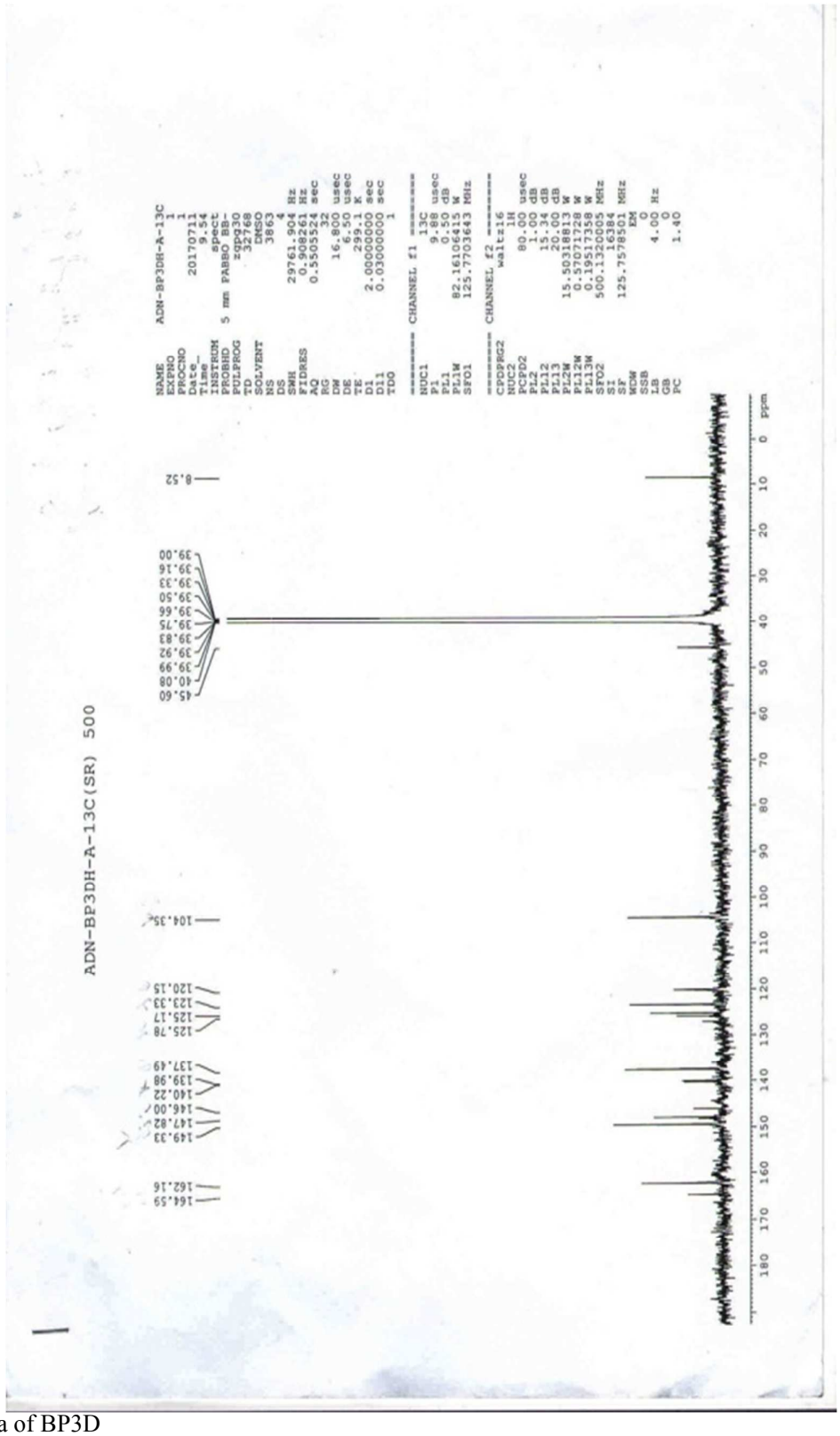


Figure S9. 13C NMR Spectra of BP3D

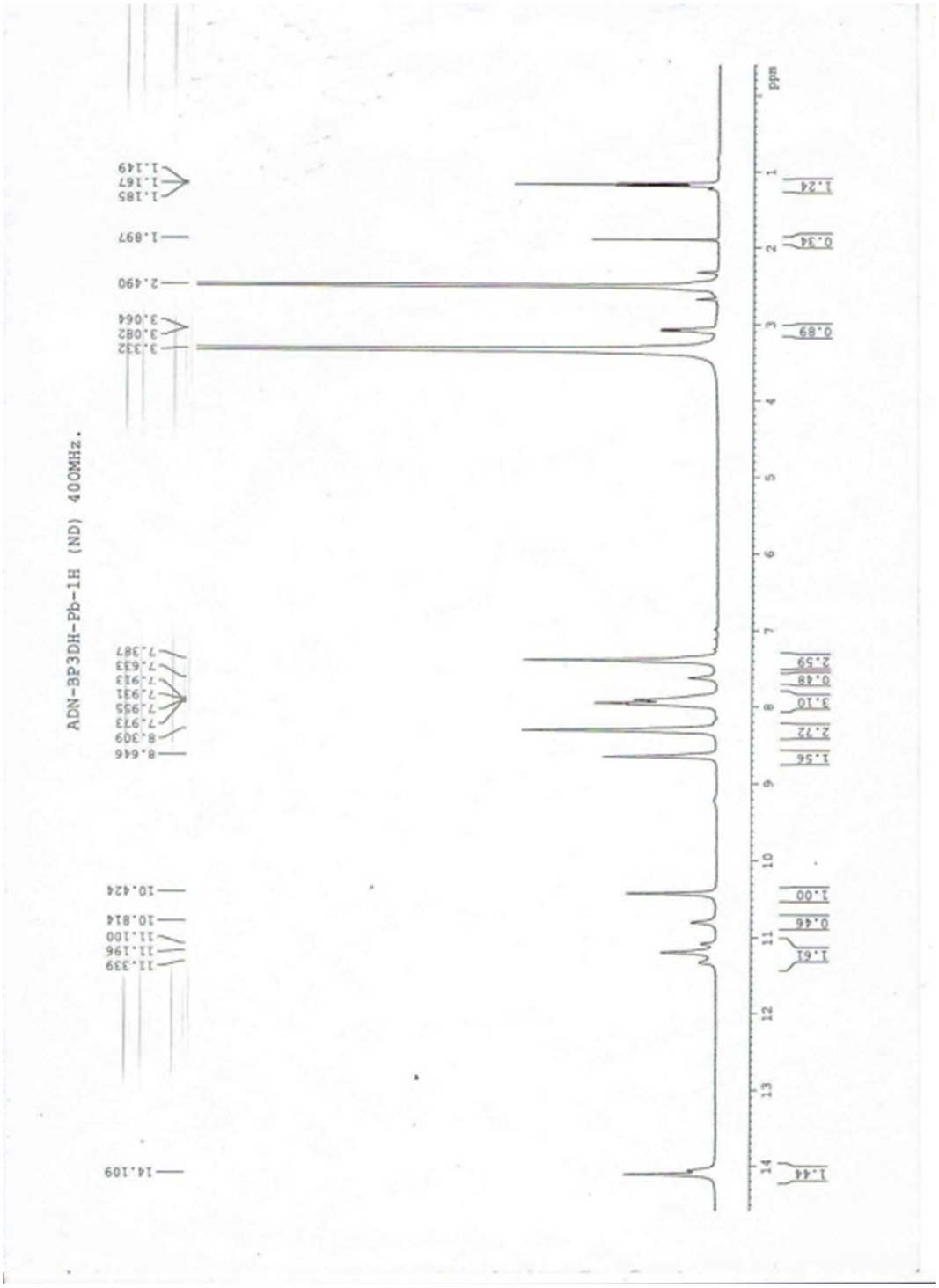


Figure S10. 1H NMR Spectra of Pb Complex of BP3D

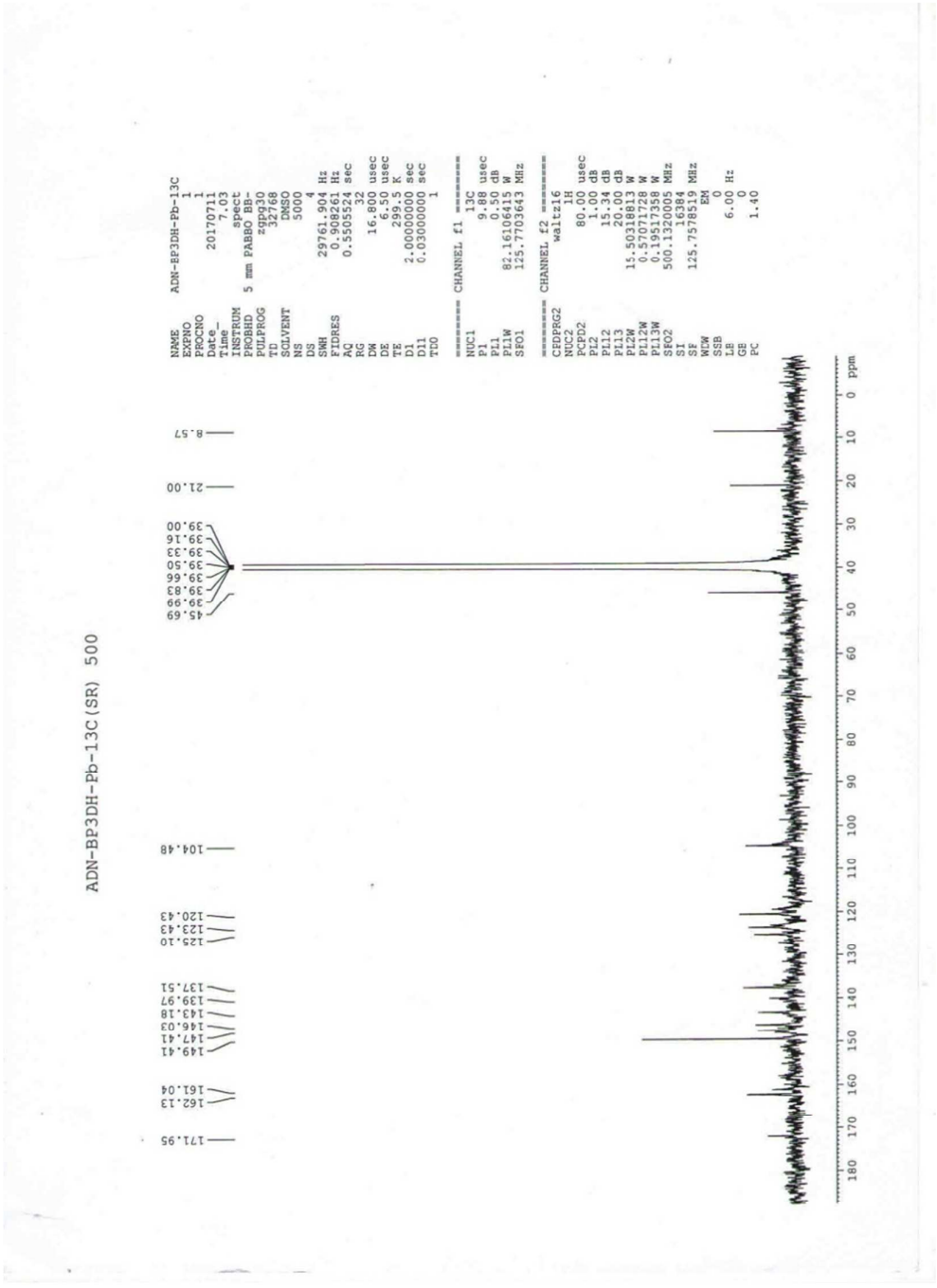


Figure S11. 13C NMR Spectra of Pb Complex of BP3D

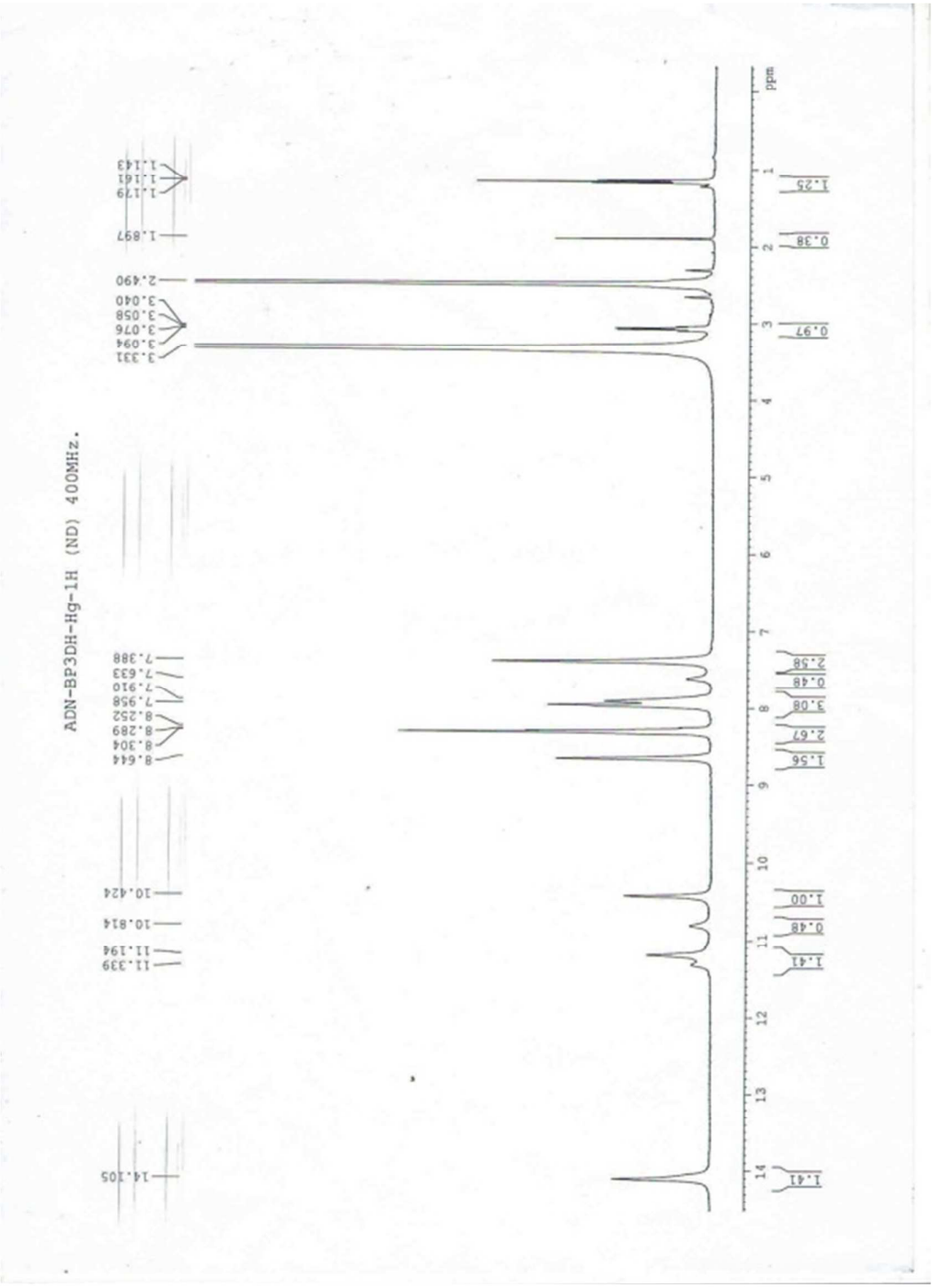


Figure S12. 1H NMR Spectra of Hg Complex of BP3D

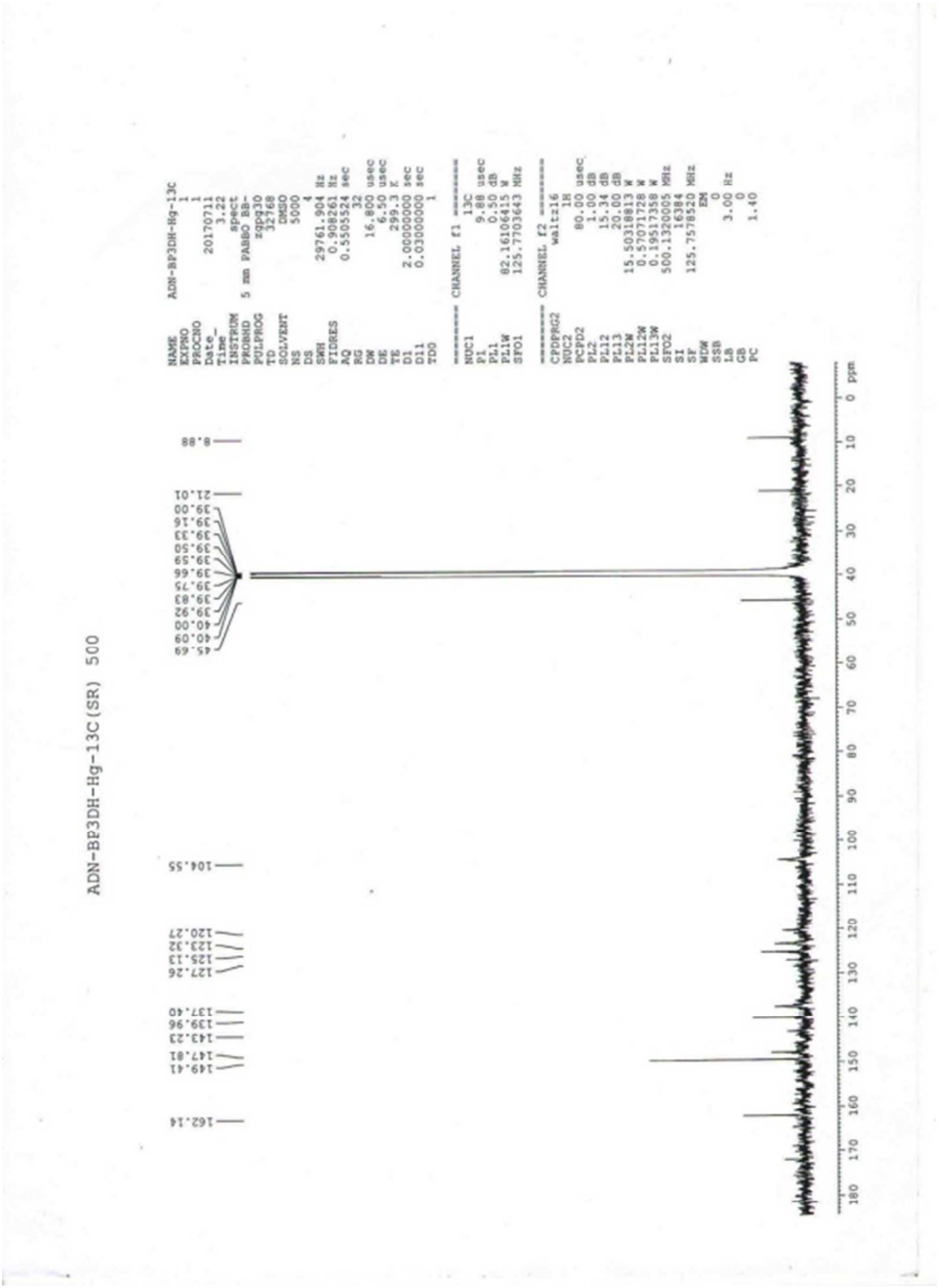


Figure S13. 13C NMR Spectra of Hg Complex of BP3D

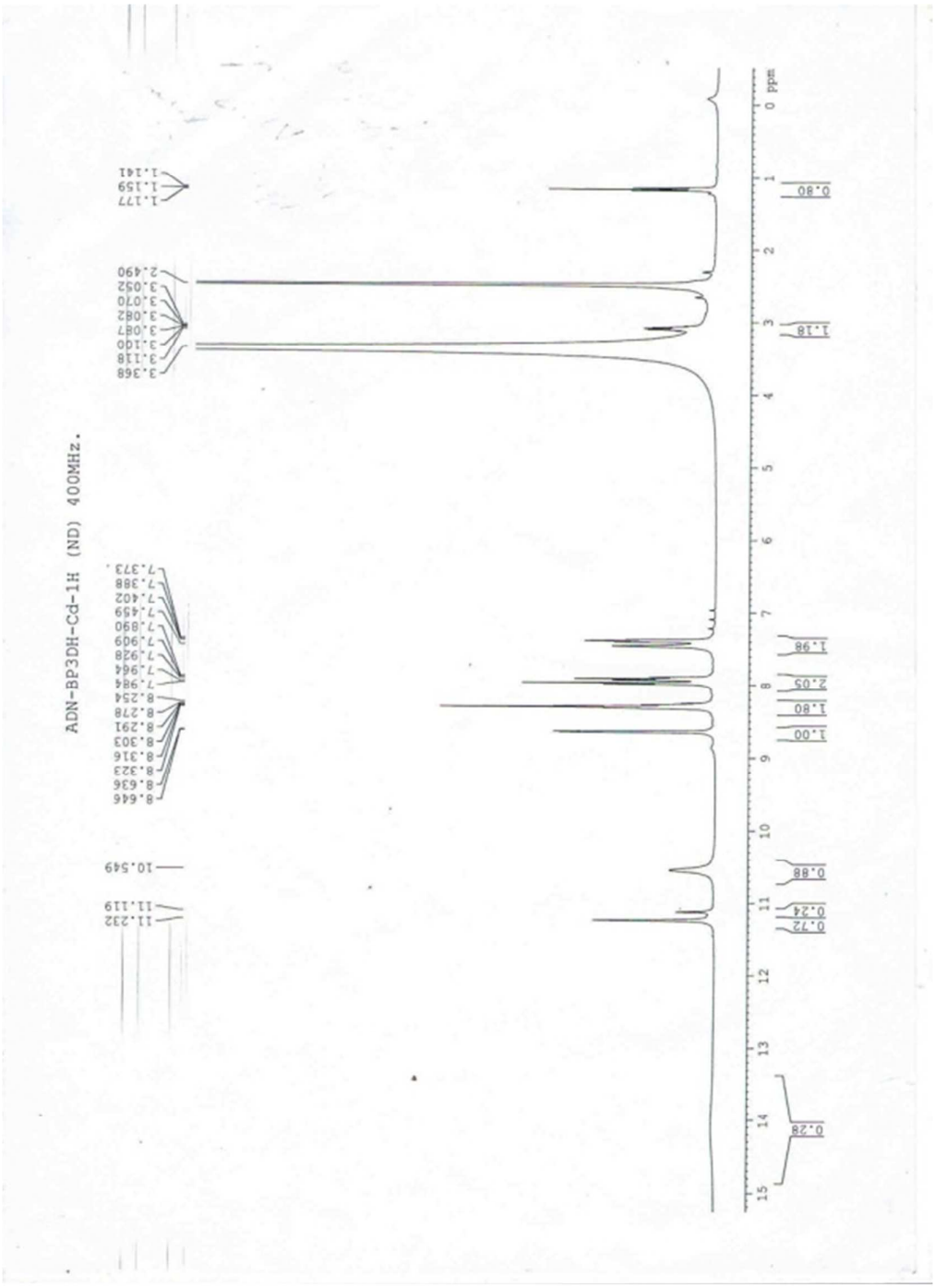


Figure S14. 1H NMR Spectra of Cd Complex of BP3D

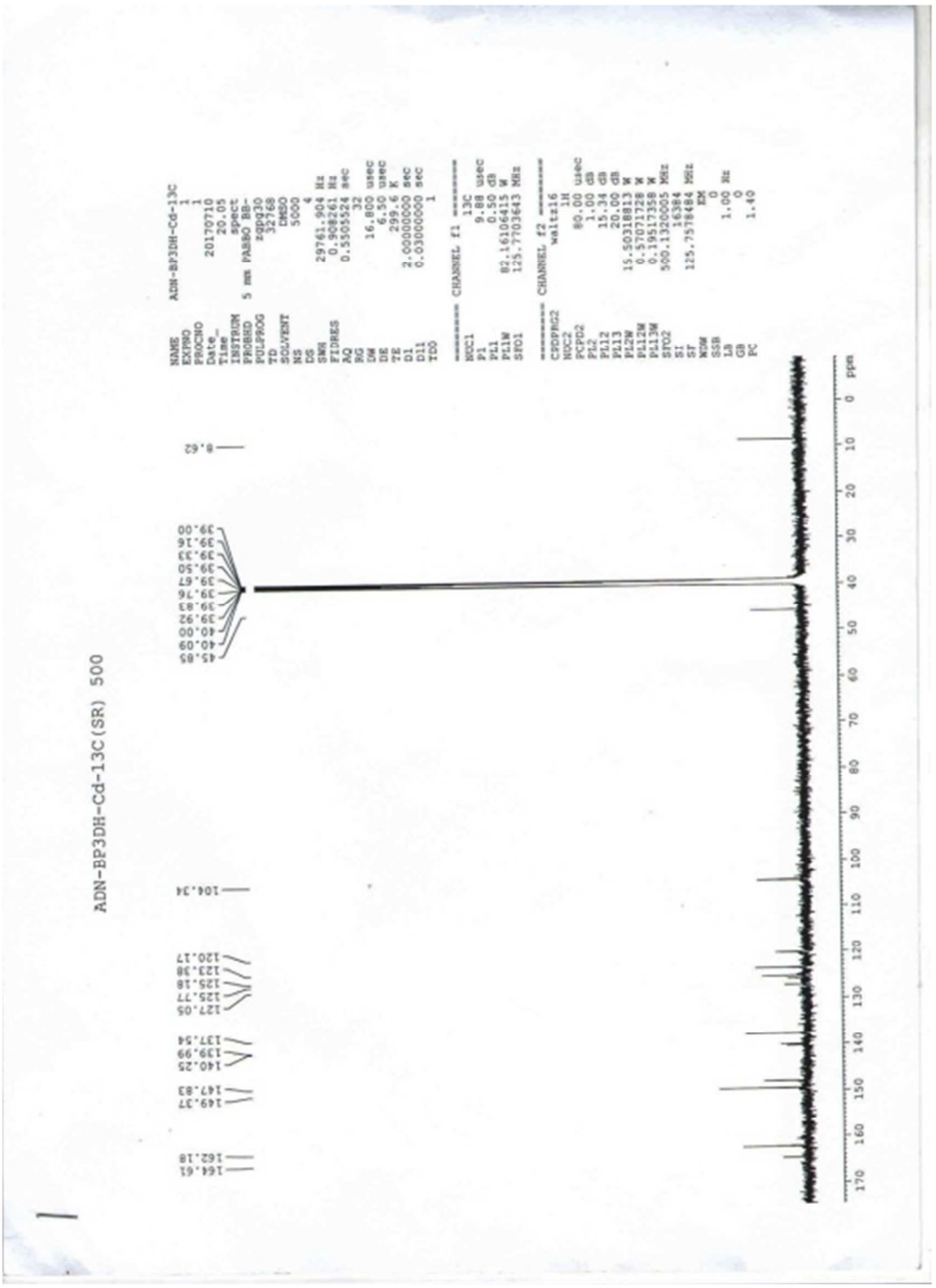


Figure S15. 13C NMR Spectra of Cd Complex of BP3D

5. SAED & EDAX data:

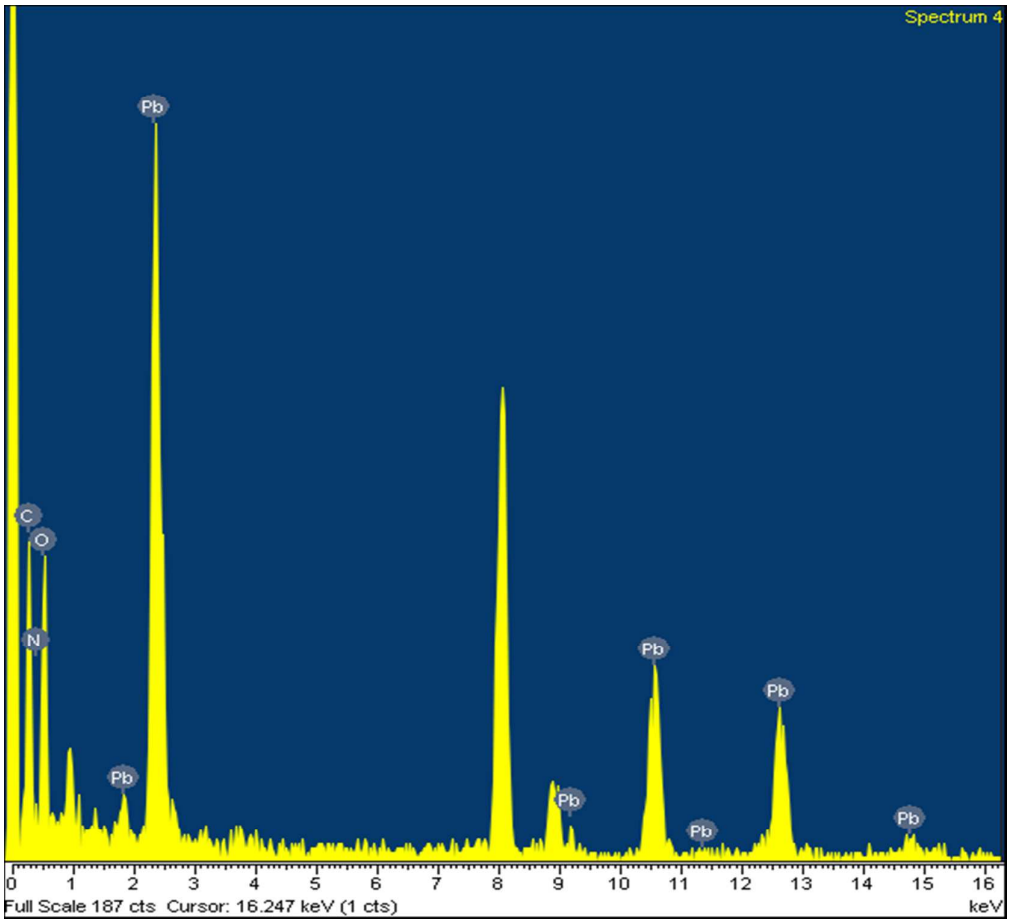


Figure S16. EDAX data of Pb NMOP

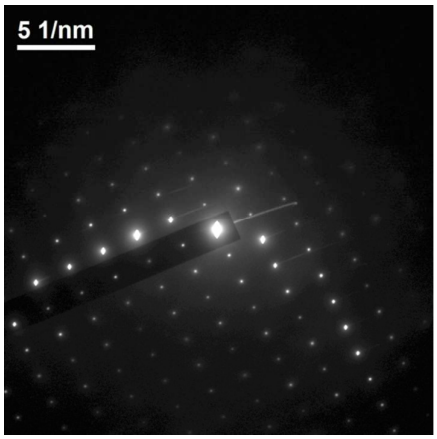


Figure S17. SAED data of Pb NMOP

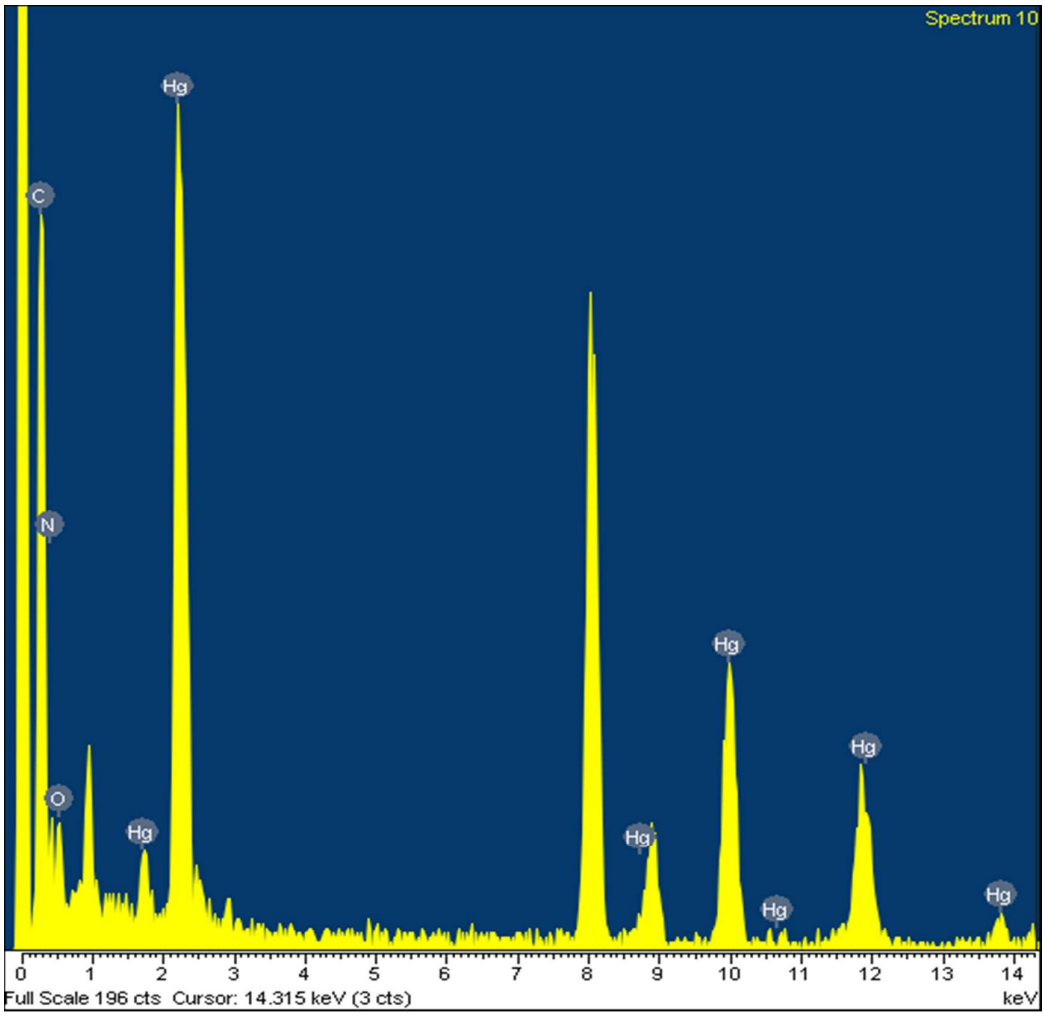


Figure S18. EDAX data of Hg NMOP

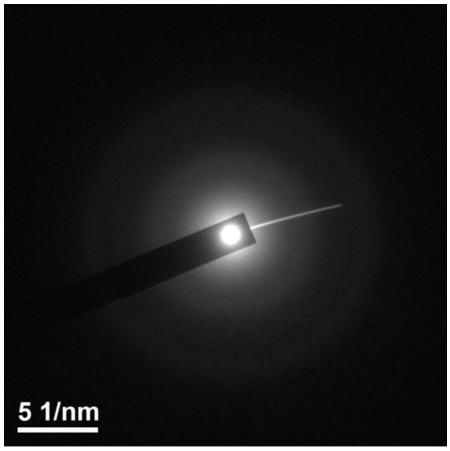


Figure S19. SAED data of Hg NMOP

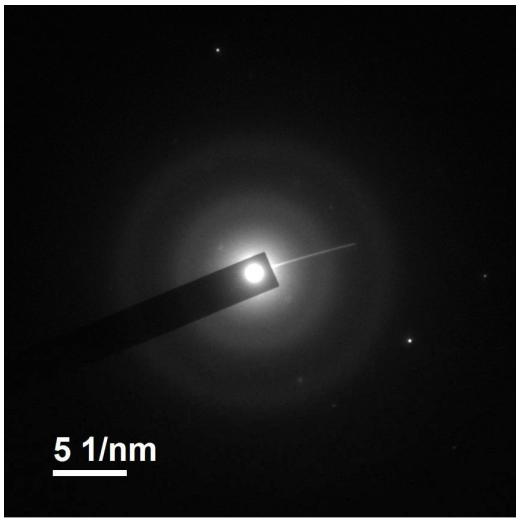


Figure S20. SAED data of Cd NMOP

6. Atomic Force Microscopic data:

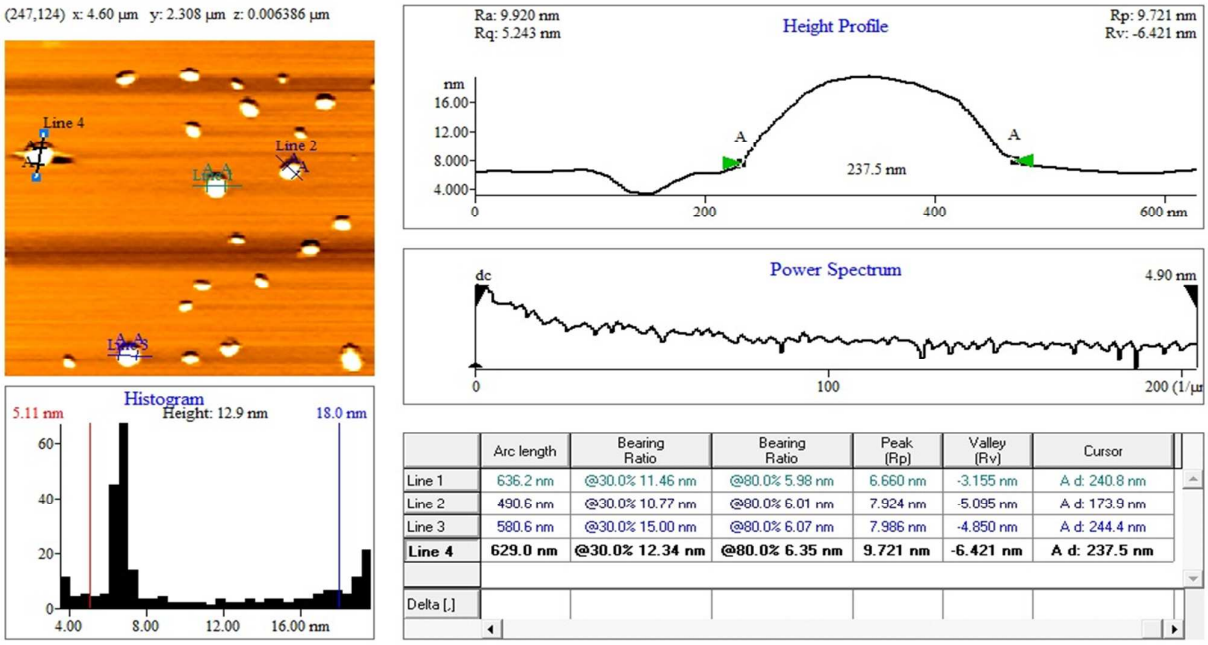


Figure S21. Height profile data of AFM images of **G-Pb**

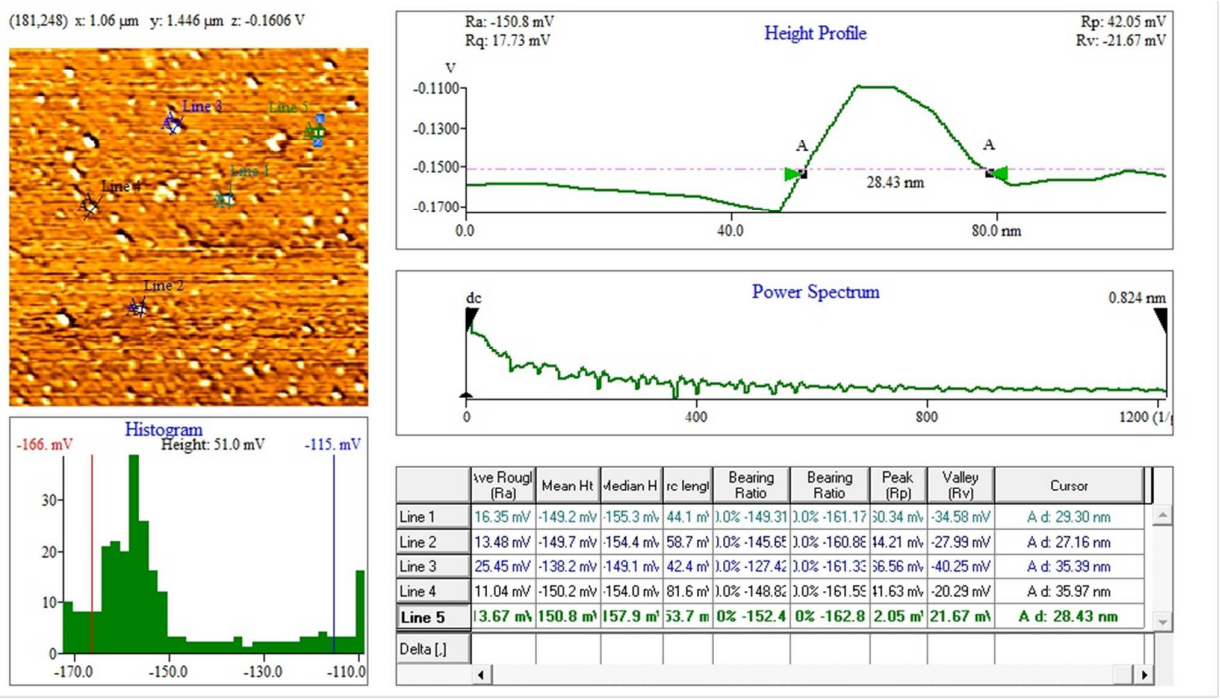


Figure S22. Height profile data of AFM images of **G-Hg**

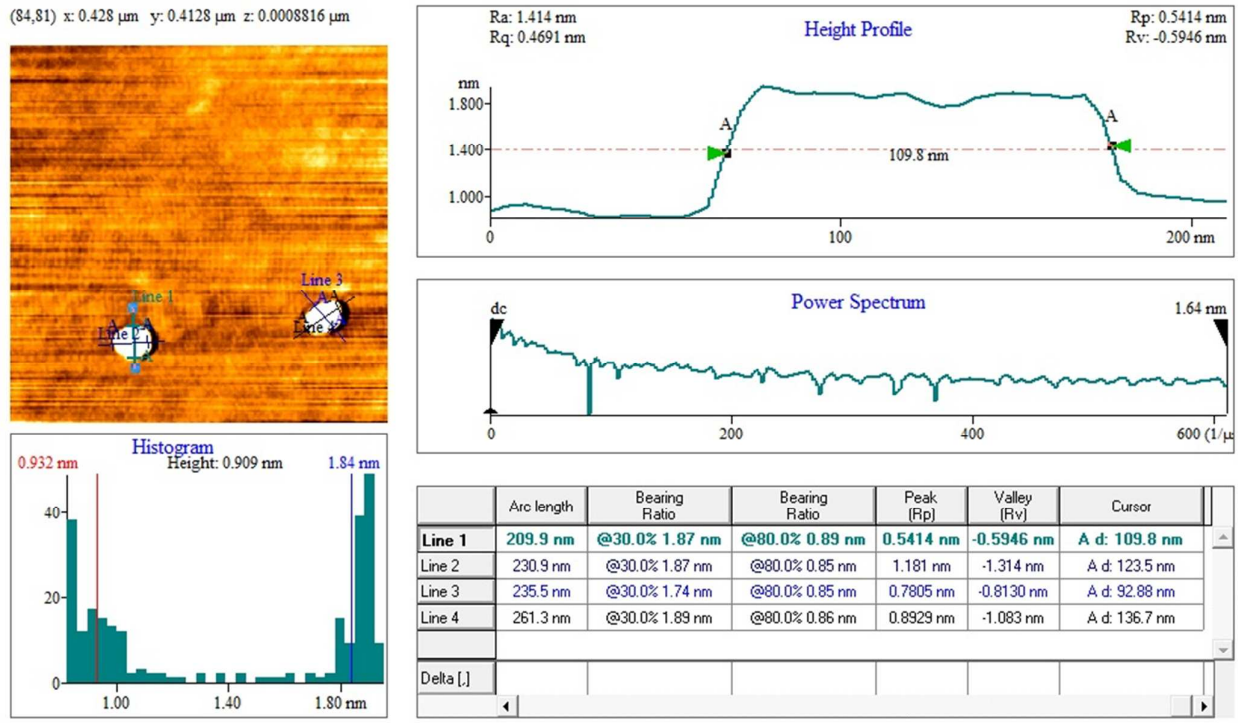


Figure S23. Height profile data of AFM images of **G-Cd**

7. Powder X-ray Diffraction Data:

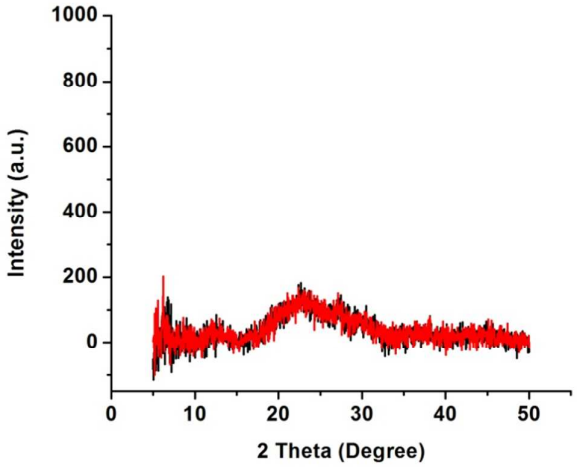


Figure S24. PXRD patterns of xerogel of **G-Pb**

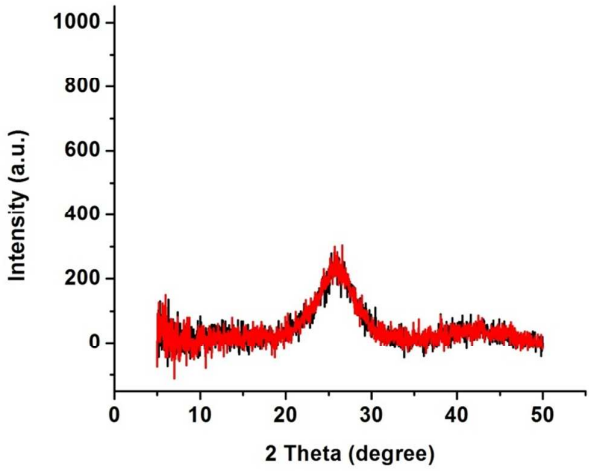


Figure S25. PXRD patterns of xerogel of **G-Hg**

8. Rheological Data:

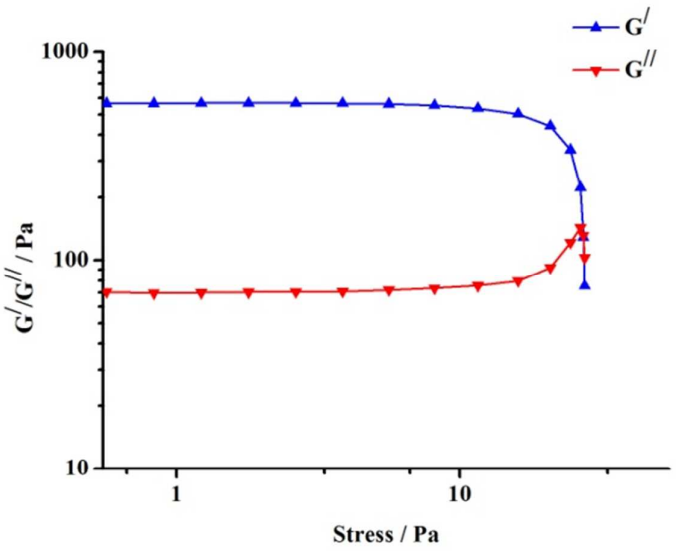


Figure S26. stress sweep data for a gel of Hydrogel

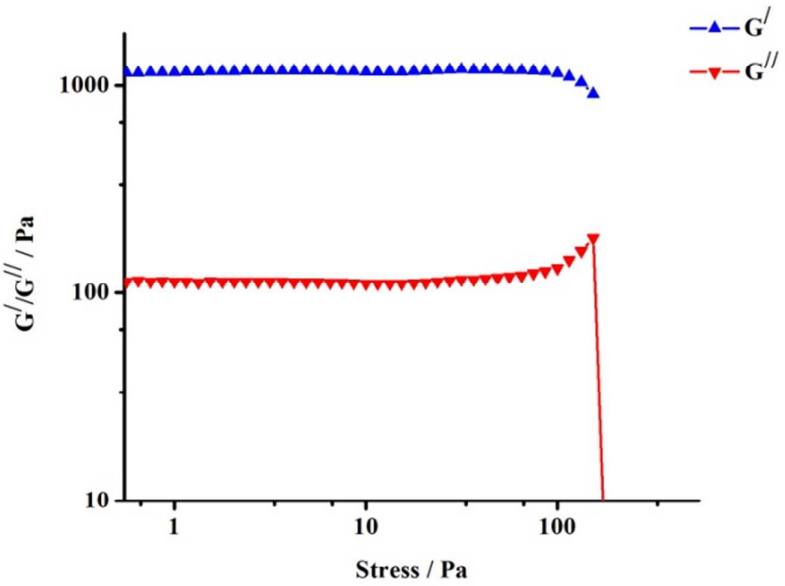


Figure S27. stress sweep data for **G-Pb**

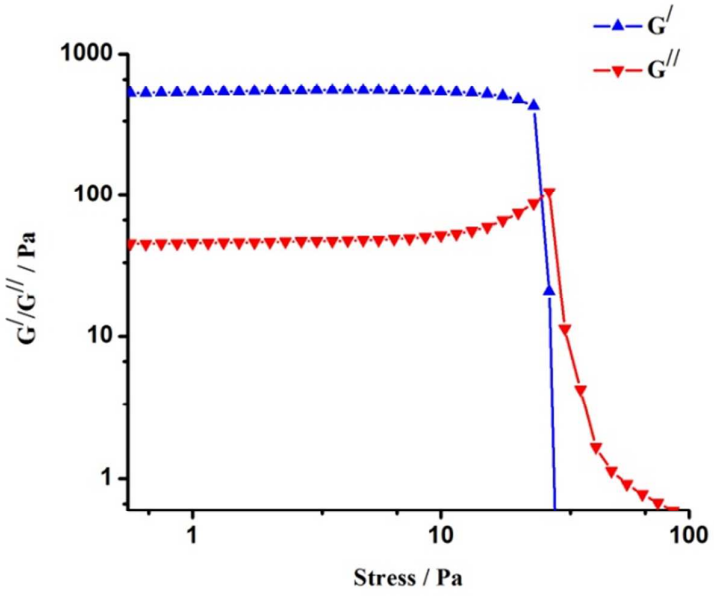


Figure S28. stress sweep data for **G-Hg**

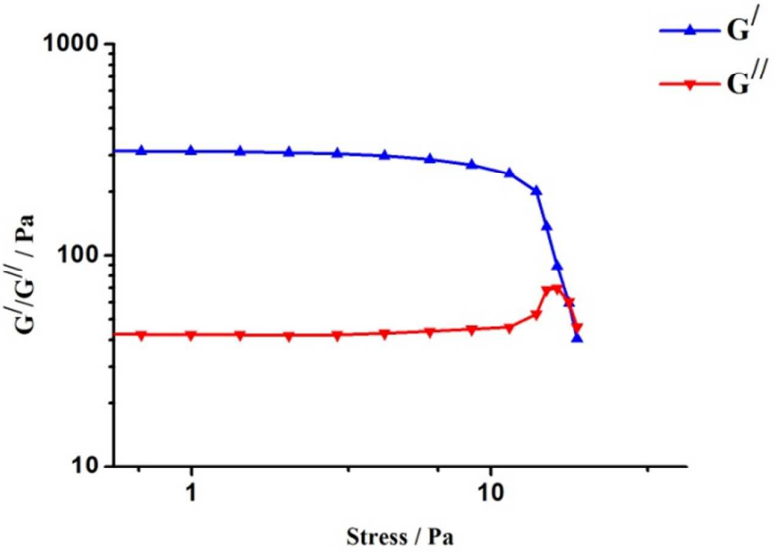


Figure S29. stress sweep data for **G-Cd**

9. Representitive Procedure for ICP Samples:

Preparation of sample for Hg estimation**:**

An aliquot of 0.1 ml of solution was taken using micropipette & it was transferred into a 15 ml glass bottle. The solvent was evaporated by heating the glass bottle in an oven at 150°C for couple of hour. It was cooled to room temperature & then 5 ml of 12% HNO_3 (prepared from 65% Suprapur Nitric acid) was added to it & it was stirred for few minutes. It was used as ICP sample for Hg estimation. 5ml standard solution (prepared from mixing 4.5 ml 12% HNO_3 solution with 0.5 ml Hg standard) was prepared & it was used for calibration.

Preparation of sample for Pb & Cd estimation**:**

Sample preparation method for Pb & Cd are same. An aliquot of 0.1 ml of solution was taken using micropipette & it was transferred into a 15 ml glass bottle. The solvent was evaporated by heating the glass bottle in an oven at 150°C for couple of hour. It was cooled to room temperature & then 5 ml of 10% HNO_3 (prepared from 65% Suprapur Nitric acid) was added to it & it was stirred for few minutes. It was used as ICP sample for Hg estimation. 5ml standard solution (prepared from mixing 4.5 ml 10% HNO_3 solution with 0.5 ml of multielement standard) was prepared & it was used for calibration.

14. Thixotropy property:

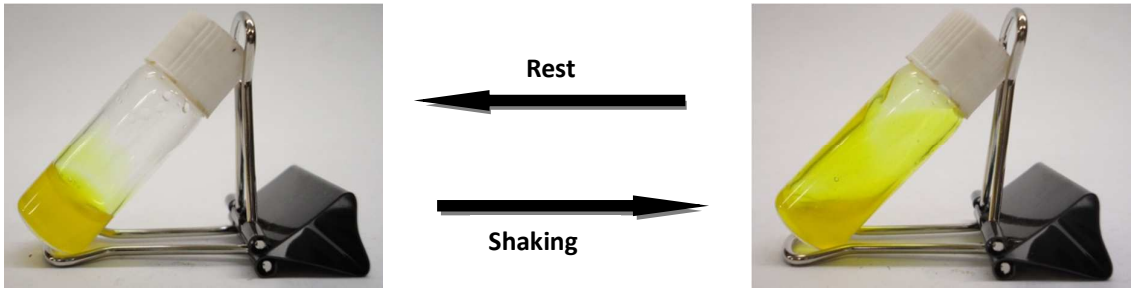


Figure S30 Images depicting thixotropic behaviour of Pb gel

15. Gelation experiment with solvent variation & metal concentration variation:

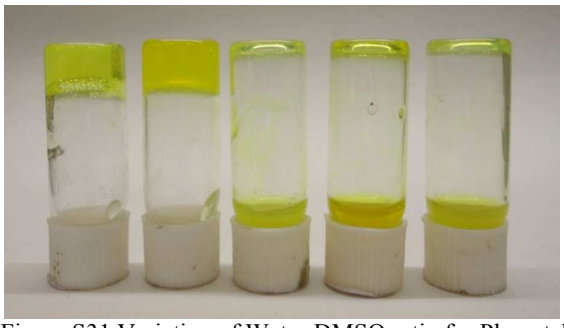


Figure S31 Variation of Water:DMSO ratio for Pb metallogelation with 1wt% BP3D & 1eqv $Pb(OAc)_2$ (Left to right- Water:DMSO = 4:1, 3:2, 1:1, 2:3, 1:4)

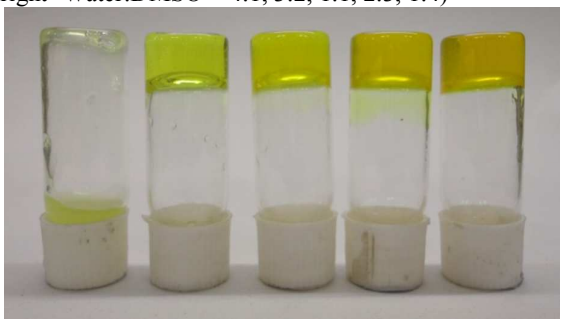


Figure S32 Variation of Pb concentration for Pb metallogelation with 1wt% BP3D & Water:DMSO =4:1 (Left to right- equivalent of $Pb(OAc)_2$= 1,2,3,4,5)

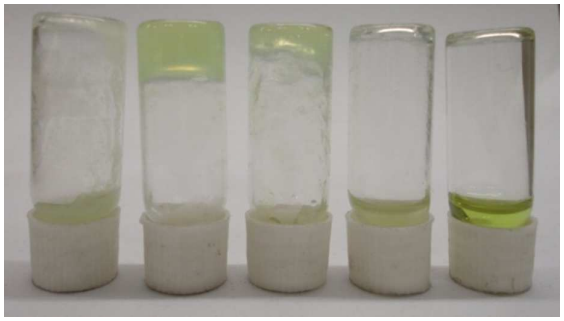


Figure S33 Variation of Water:DMSO ratio for Hg metallogelation with 1wt% BP3D & 1eqv $Hg(OAc)_2$ (Left to right- Water:DMSO = 4:1, 3:2, 1:1, 2:3, 1:4)

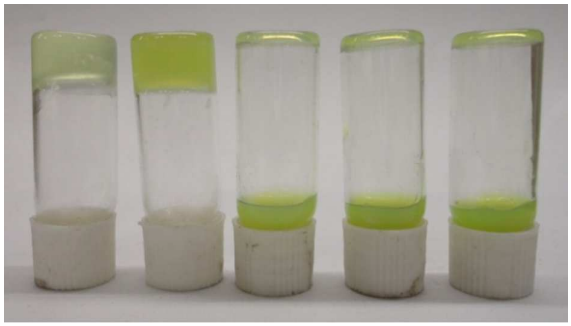


Figure S34 Variation of Hg concentration for Hg metallogelation with 1wt% BP3D & Water:DMSO =3:2 (Left to right- equivalent of $Hg(OAc)_2$= 1,2,3,4,5)

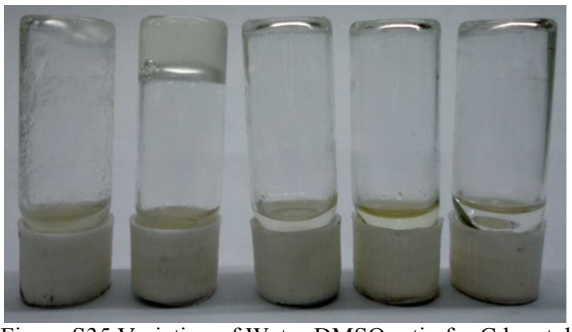


Figure S35 Variation of Water:DMSO ratio for Cd metallogelation with 1wt% BP3D & 1eqv $Cd(NO_3)_2$ (Left to right- Water:DMSO = 4:1, 3:2, 1:1, 2:3, 1:4)

Figure S36 Variation of Cd concentration for Cd metallogelation with 1wt% BP3D & Water:DMSO =3:2 (Left to right- equivalent of $Cd(NO_3)_2$= 1,2,3,4,5)

Table S1: Comparative study of the test for gelation of the ligand in presence of different Pb, Cd & Hg salts in DMSO/water medium

salt	**Appearance**
$Pb(OAc)_2$	Gel
$Pb(NO_3)_2$	Precipitate
$Hg(OAc)_2$	Gel
$Hg(NO_3)_2$	Precipitate
$HgCl_2$	Precipitate
$Cd(OAc)_2$	Precipitate
$Cd(NO_3)_2$	Gel
$Cd(ClO_4)_2$	Precipitate

16. Chemical responsiveness of organogel with Hg salt solution:

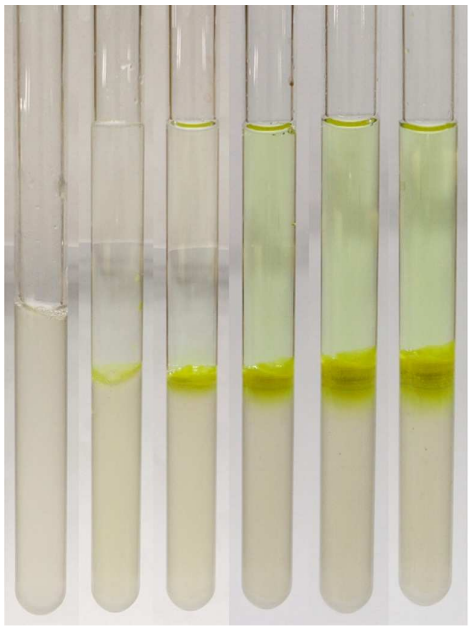


Figure S37 Set of images of effect of Hg salt solution with time (one day interval) over organogel (at righted condition with solution inside except the first one),first one is blank and second one is captured instantly after adding solution

Figure S38 Set of images of effect of Hg salt solution with time (one day interval) over organogel (at inverted condition), first one is blank and second one is captured instantly after adding solution