

Electronic Supplementary Information for MS:

**Solid- and Solution-State Structural Transformations
In Flexible Lead(II) Supramolecular Polymers**

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Experimental

Materials and Physical Techniques: All reagents for the Syntheses and analysis were commercially available and used as received. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. The thermal behavior was measured with a PL-STA 1500 apparatus with the rate of 10 °C.min⁻¹. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo-K_α radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F². X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer of X'pert company with monochromated Cu-k_α radiation. The samples were characterized with a scanning electron microscope with gold coating.

Synthesis of [Pb₂(Q-2-c)₂(OAc)₂(MeOH)₂]_n (1) and preparation of its single crystals.

This complex was synthesized according to reported procedure.¹ Lead(II) acetate trihydrate (1 mmol, 0.379 g) and quinoline-2-carboxylic acid (1 mmol, 0.173 g) were loaded into one arm of a branch tube and both of the arms were filled slowly by methanol. The chemical-bearing arm was immersed in an oil bath kept at 60 °C. Crystals were formed on the inside surface of the arm kept at ambient temperature after a few days, d.p. = 235 °C, Yield: 0.414 g (88% based on final product), Anal. calc. for C₂₆H₂₆N₂O₁₀Pb₂: C, 33.19; H, 2.79; N, 2.98 found; C, 33.11; H, 2.82, N, 3.05%.

(1) Mohammadnezhad, G.; Ghanbarpour, A. R.; Amini, M. M.; Ng, S. W. *Acta Crystallogr., Sect. E*, **2010**, E66, m963.

Synthesis of [Pb₂(Q-2-c)₂(OAc)₂(EtOH)₂]_n (2) and preparation of its single crystals.

This complex was synthesized according to reported procedure.² Lead(II) acetate trihydrate (1 mmol, 0.379 g) and quinoline-2-carboxylic acid (1 mmol, 0.173 g) were

loaded into one arm of a branch tube and both of the arms were filled slowly by ethanol. The chemical-bearing arm was immersed in an oil bath kept at 60 °C. Crystals were formed on the inside surface of the arm kept at ambient temperature after a few days, d.p. = 226 °C, Yield: 0.412 g (85% based on final product), Anal. calc. for $C_{28}H_{30}N_2O_{10}Pb_2$: C, 34.71; H, 3.13; N, 2.89 found; C, 34.65; H, 3.04, N, 2.95%.

(2) Najafi, E.; Amini, M. M.; Ng, S. W. *Acta Crystallogr., Sect. E*, **2011**, E67, m264.

Synthesis of $[Pb_2(Q-2-c)_2(OAc)_2]_n$ (3) and preparation of its single crystals.

In order to obtain single crystals of compound **3** in a single crystal to single crystal transformation, we placed the block crystals of compounds **1** and **2** in electric furnace at 100 °C for 5 hours. Both samples lose their transparency and were found not suitable for single crystal X-ray crystallography. Both of these samples have the same XRD patterns which differed from those of **1** and **2** (Figure S3). Anal. calc. for $[Pb_2(Q-2-c)_2(OAc)_2]_n$ (**3**) with the proposed molecular formula of $C_{24}H_{18}N_2O_8Pb_2$: C, 32.87; H, 2.07; N, 3.19 found; C, 32.79; H, 2.12, N, 3.15% for **3** which obtained from **1** and C, 32.94; H, 1.99, N, 3.21% for **3** which obtained from **2**. Thus single crystals of compound **3** were obtained from another reaction; Lead(II) acetate trihydrate (1 mmol, 0.379 g) and quinoline-2-carboxylic acid (1 mmol, 0.173 g) were loaded into one arm of a branch tube and both of the arms were filled slowly by acetonitrile. The chemical-bearing arm was immersed in an oil bath kept at 60 °C. Crystals were formed on the inside surface of the arm kept at ambient temperature after four weeks, d.p. = 230 °C, Yield: 0.333 g (76% based on final product), Anal. calc. for $C_{24}H_{18}N_2O_8Pb_2$: C, 32.87; H, 2.07; N, 3.19 found; C, 32.90; H, 2.02, N, 3.23%. CCDC 901757 contains the supplementary crystallographic data for this complex.

Synthesis of $[Pb(Q-2-c)_2]_n$ (4) and preparation of its single crystals.

White powder of compound **4** was obtained by solution-state structural transformation of **1**, **2** and **3** in water (Figures S5 and S6). Anal. calc. for $[Pb(Q-2-c)_2]_n$ (**4**) with the proposed molecular formula of $C_{20}H_{12}N_2O_4Pb$: C, 43.55; H, 2.20; N, 5.08 found; C,

43.65; H, 2.25; N, 5.13%, C, 43.48; H, 2.16; N, 5.14% and C, 43.51; H, 2.21; N, 5.10% for **4** which obtained from **1**, **2** and **3**, respectively. White powder of **4** could be also obtained from solution-state structural transformation of **1** and **2** in EtOH and MeOH, respectively (Figures S9 and S10). Anal. calc. for $[\text{Pb}(\text{Q-2-c})_2]_n$ (**4**) with the proposed molecular formula of $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_4\text{Pb}$: C, 43.55; H, 2.20; N, 5.08 found; C, 43.61; H, 2.23; N, 5.11% and C, 43.48; H, 2.19; N, 4.99% for **4** which obtained from **1** and **2**, respectively. But in order to obtain single crystals of compound **4**, we performed the reaction of Lead(II) acetate trihydrate (1 mmol, 0.379 g) and quinoline-2-carboxylic acid (1 mmol, 0.173 g) in a branch tube, which both of its arms were filled slowly by distilled water. The chemical-bearing arm was immersed in an oil bath kept at 60 °C. Crystals were formed on the inside surface of the arm kept at ambient temperature after three weeks, d.p. = above 300 °C, Yield: 0.358 g (65% based on final product), Anal. calc. for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_4\text{Pb}$: C, 43.55; H, 2.20; N, 5.08 found; C, 43.60; H, 2.17, N, 5.12%. CCDC 896831 contains the supplementary crystallographic data for this complex. It should be also mentioned that after we did structural analyses of this compound, we found out that this complex was previously reported by S. W. Ng et al, too.³

(3) Mohammadnezhad, G.; Ghanbarpour, A. R.; Amini, M. M.; Ng, S. W. *Acta Crystallogr., Sect. E*, **2010**, E66, m946.

Experimental conditions of solid-state and solution-state structural transformations.

For investigation thermal desolvation of compounds **1** and **2** to **3**, we heated 0.5 mmol crystal samples from each of them at 100°C in an electric furnace and static atmosphere of air. For gas-solid reactions, we placed 0.5 mmol of compound **3** powder (0.438 g) upon exposure to MeOH and EtOH vapors in an enclosed vessel for 5 hours. Solution-state structural transformations were also considered by immersing 0.5 mmol crystal samples from each of **1-3** in appropriate solvents (MeOH, EtOH, MeCN or water) for 12 hours. In the case of gas-solid reaction of **3** with MeOH vapors, the crystalline sample did not miss its transparency and this transformation occurs in a SCSC manner.

IR spectra description

To confirm the solid-state and solution-state structural transformations of compounds **1-4**, IR spectra were recorded for them during these transformations. The IR spectra of **1** and **2** show characteristic absorption bands for the Q-2-c⁻ and OAc⁻ (Figure S2). The absorption bands with similar intensity in the frequency range of 1340-1620 cm⁻¹ correspond to carboxylate groups of Q-2-c⁻ and OAc⁻. It seems that the absorption bands in the frequency range of 1560-1565 cm⁻¹ and 1615-1620 cm⁻¹ correspond to $\nu_{as(C-O)}$ of OAc⁻ and uncoordinated C=O groups of Q-2-c⁻, respectively. The broad absorption band in the frequency range of 1300-1500 cm⁻¹ correspond to the overlap of $\nu_{sym(C-O)}$ of OAc⁻ and coordinated C-O groups of Q-2-c⁻. In addition, the characteristic absorption peaks of coordinated MeOH and EtOH could be observed in the frequency range of 1015-1045 cm⁻¹ (ν_{C-O}) and 2750-3600 cm⁻¹ (ν_{O-H}). Appearance of broad peak in the frequency range of 2750-3600 cm⁻¹ attributes to the formation of hydrogen bonding interaction between –OH hydrogen atom of MeOH (in **1**) and EtOH (in **2**) and one oxygen atom of coordinated acetate anion. A comparison between the IR spectra of **1** and **2** with **3** indicates that the appearance positions of carboxylate group in **3** (1340 and 1611 cm⁻¹) do not have any difference with those in **1** and **2**, which indicate similar coordination mode and strength of Q-2-c⁻ carboxylate group in **3** in comparison with **1** and **2**. But the positions of OAc⁻ carboxylate group are changed in **3** and appear close to each other as the two peaks which overlap with each other in **1** and **2** (in the frequency range of 1300-1500 cm⁻¹) separate from each other. Probably the coordination mode of carboxylate group of OAc⁻ in **3** is more symmetric than that in **1** and **2**. On the other hand, disappearance of MeOH and EtOH characteristic bands (1015-1045 cm⁻¹ and 2750-3600 cm⁻¹) approved the removal of these coordinated solvents. The IR spectrum of **4** is approximately different from those observed in **1-3** and absence of the sharp absorption bands in frequency range of 1400-1570 cm⁻¹ approved that no OAc⁻ anion exists in **4**.

Thermogravimetric and differential thermal analyses (TG-DTA).

Thermogravimetric analyses (TGA) were recorded for the crystal samples of **1-4** (Figure S14). Compounds **1** and **2** are stable up to 93 and 112 °C, respectively, at which temperature the coordinated MeOH and EtOH molecules begin to be removed up to 138 and 140 °C, respectively. The TG curve of **1** shows a mass loss *ca.* 6.50% (calcd 6.80%) between 93-138°C which could be related to removal of coordinated MeOH molecules. In **2**, the TG curve shows a mass loss *ca.* 9.00% (calcd 9.50%) between 112-140 °C which could be related to removal of coordinated EtOH molecules. In both compounds, the solid residue formed at around 140 °C is suggested to be the MeOH-free and EtOH-free compound, $[\text{Pb}_2(\text{Q-2-c})_2(\text{OAc})_2]_n$ (**3**). Above a temperature of 140 °C the graphs of compounds **1** and **2** in comparison with **3** are basically superimposable. In Compounds **1-3**, removal of Q-2-c⁻ and OAc⁻ species take a place in two steps between about 200-500 °C. The TG curve of **4** is wholly different from those observed in **1-3** and shows that the crystalline form is stable up to 335 °C (Figure S14), at which temperature removal of two coordinated Q-2-c⁻ ligands starts up to 470 °C.

Table S1 Crystal data and structure refinement of [Pb₂(Q-2-c)₂(OAc)₂]_n (**3**) and [Pb(Q-2-c)₂]_n (**4**).

	3	4
Identification code	3	4
Empirical formula	C ₂₄ H ₁₈ N ₂ O ₈ Pb ₂	C ₂₀ H ₁₂ N ₂ O ₄ Pb
Formula weight	876.78	551.51
Temperature	293(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 2 ₁ /c	P 2 ₁ /c
Unit cell dimensions	a = 9.3030(3) Å b = 5.1690(2) Å c = 24.7981(8) Å α = 90.00° β = 98.872(2)° γ = 90.00°	a = 16.581(6) Å b = 7.331(3) Å c = 14.377(6) Å α = 90.00° β = 109.247(6)° γ = 90.00°
Volume	1178.20(7) Å ³	1649.9(11) Å ³
Z	2	4
Density (calculated)	2.471 g.cm ⁻³	2.220 g.cm ⁻³
Absorption coefficient	14.325 mm ⁻¹	10.257 mm ⁻¹
F(000)	808	1040
Crystal size	0.16 × 0.12 × 0.06 mm ³	0.33 × 0.26 × 0.21 mm ³
Theta range for data collection	2.97 to 30.22°	2.85 to 25.10°
Index ranges	-13 ≤ h ≤ 13 -7 ≤ k ≤ 7 -34 ≤ l ≤ 35	-19 ≤ h ≤ 19 -8 ≤ k ≤ 7 -17 ≤ l ≤ 17
Reflections collected	8468	8468
Independent reflections	41978 [R(int) = 0.0362]	2891 [R(int) = 0.0230]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.3168 and 0.7460	0.2219 and 0.1329
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	3479 / 0 / 164	2891 / 0 / 245
Goodness-of-fit on F ²	1.323	1.082
Final R indices [I > 2σ(I)]	R ₁ = 0.0470 wR ₂ = 0.0899	R ₁ = 0.0316 wR ₂ = 0.1095
R Indices (all data)	R ₁ = 0.0523 wR ₂ = 0.0916	R ₁ = 0.0356 wR ₂ = 0.1187
Largest diff. Peak, hole	2.400 and -2.037 e.Å ⁻³	1.576 and -1.588 e.Å ⁻³

Table S2 Bond lengths /Å and angles /° for [Pb₂(Q-2-c)₂(OAc)₂]_n (**3**).

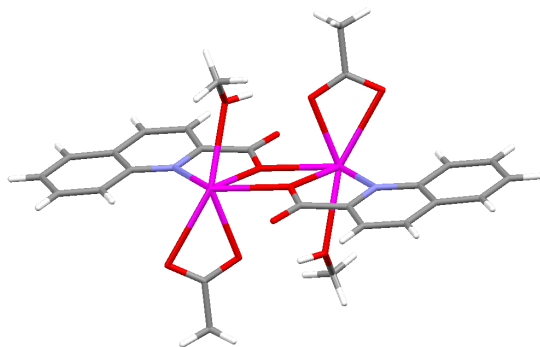
Pb(1)-O(1)	2.364(5)	O(1)-Pb(1)-O(3)	75.2(2)
Pb(1)-O(3)	2.433(6)	O(1)-Pb(1)-N(1)	66.39(18)
Pb(1)-N(1)	2.537(6)	O(3)-Pb(1)-N(1)	78.7(2)
Pb(1)-O(1)#1	2.572(5)	O(1)-Pb(1)-O(1)#1	68.7(2)
Pb(1)-O(4)	2.581(8)	O(3)-Pb(1)-O(1)#1	76.5(2)
		N(1)-Pb(1)-O(1)#1	132.76(19)
		O(1)-Pb(1)-O(4)	122.4(2)
		O(3)-Pb(1)-O(4)	51.1(2)
		N(1)-Pb(1)-O(4)	82.4(3)
		O(1)#1-Pb(1)-O(4)	110.6(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1

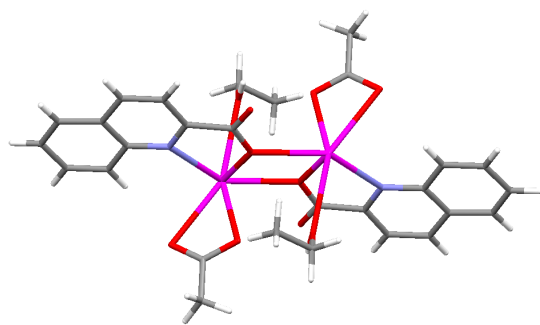
Table S3 Bond lengths /Å and angles /° for [Pb(Q-2-c)₂]_n (**4**).

Pb(1)-O(3)	2.287(6)	O(3)-Pb(1)-O(1)	90.1(2)
Pb(1)-O(1)	2.291(6)	O(3)-Pb(1)-N(2)	68.35(19)
Pb(1)-N(2)	2.533(6)	O(1)-Pb(1)-N(2)	76.89(19)
Pb(1)-N(1)	2.574(6)	O(3)-Pb(1)-N(1)	78.0(2)
		O(1)-Pb(1)-N(1)	67.3(2)
		N(2)-Pb(1)-N(1)	130.2(2)

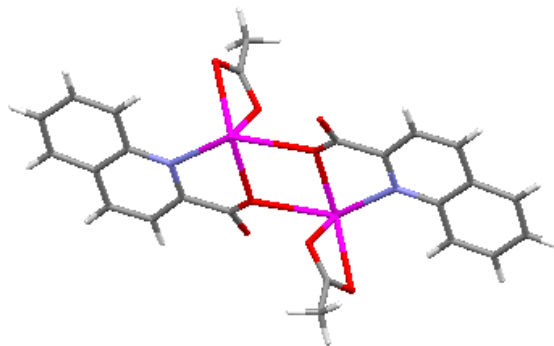
a



b



c



d

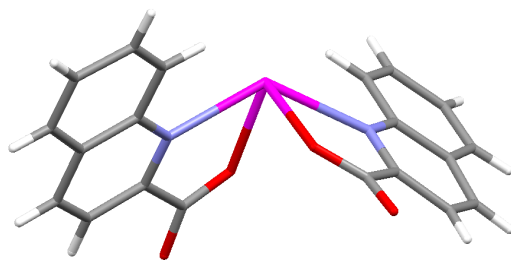


Figure S1. Showing the structures of the basic polymeric building blocks of compounds **1** (a), **2** (b), **3** (c) and **4** (d), (Pb = violet, O = red, N = blue, C = gray and H = white).

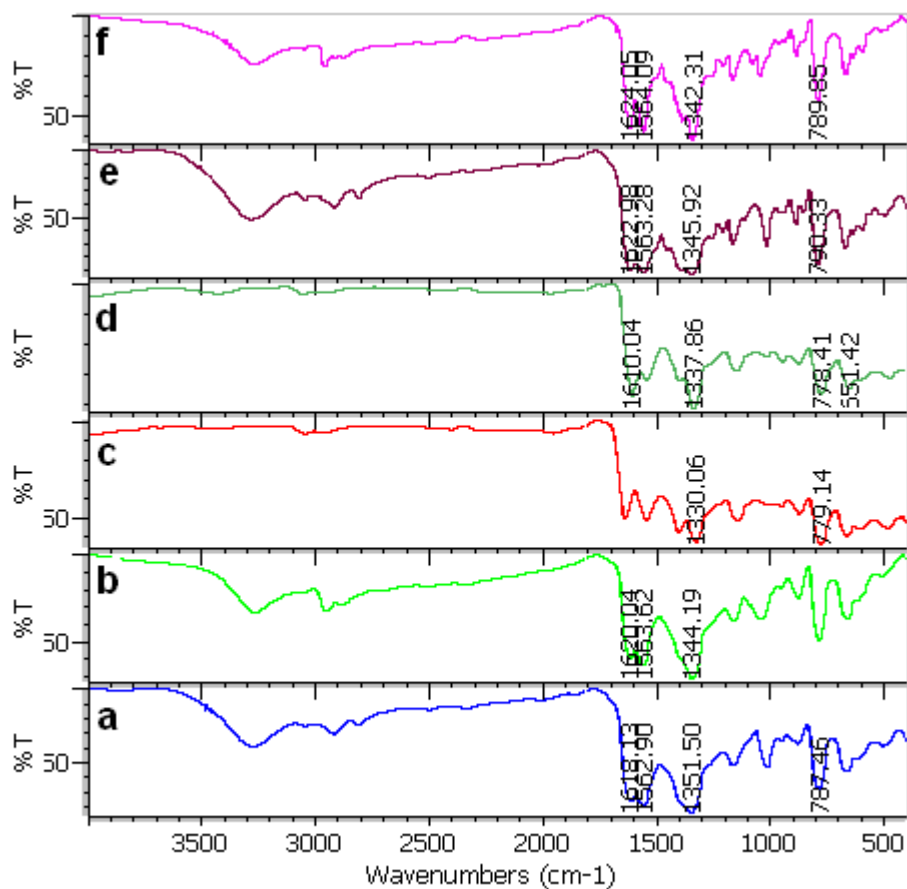


Figure S2. IR spectra of a) compound **1** crystals prepared by branch tube method, b) compound **2** crystals prepared by branch tube method, c) compound **3** sample obtained by heating of compound **1** crystals at 100 °C for 12 hours, d) compound **3** sample obtained by heating of compound **2** crystals at 100 °C for 12 hours, e) compound **1** prepared from solid-gas reaction of **3** with MeOH vapors and f) compound **2** prepared from solid-gas reaction of **3** with EtOH vapors.

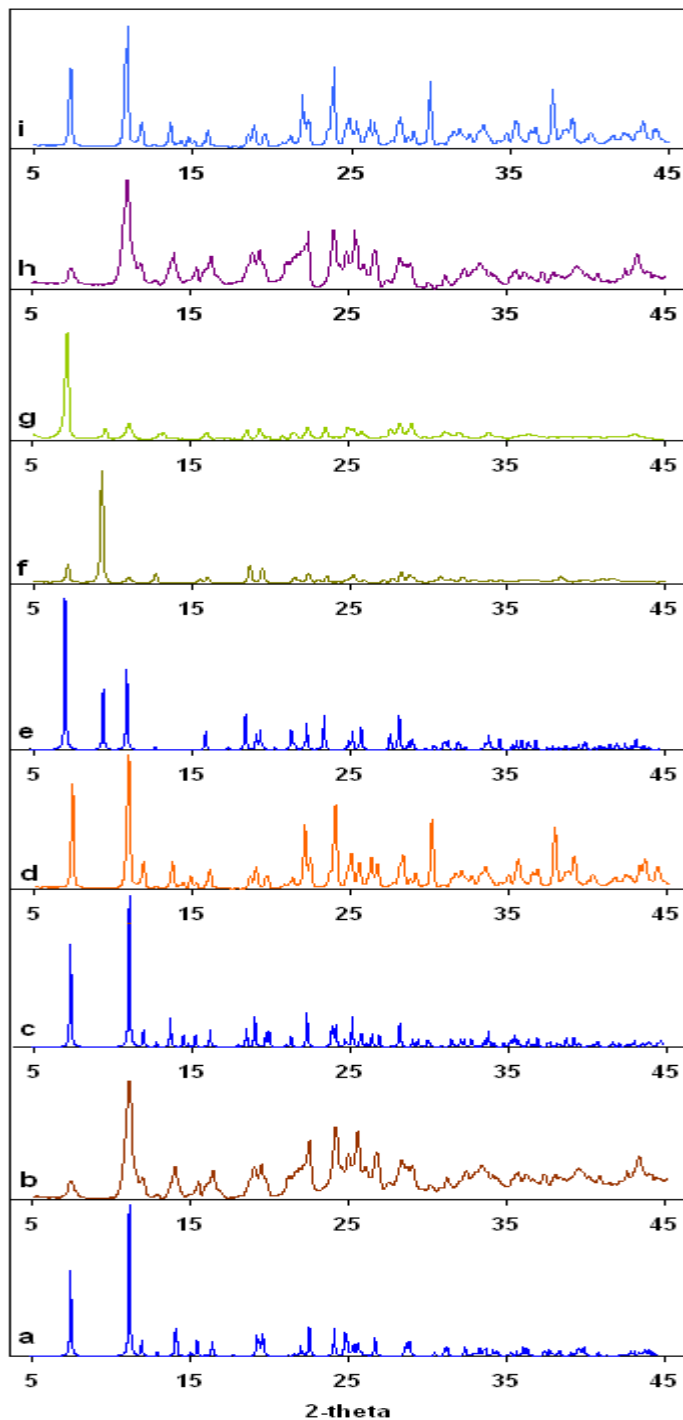


Figure S3. The XRD patterns of (a) simulated from single crystal X-ray data of compound **1**, (b) compound **1** single crystals prepared by branch tube method, (c) simulated from single crystal X-ray data of compound **2**, (d) compound **2** single crystals prepared by branch tube method, (e) simulated from single crystal X-ray data of compound **3**, (f) compound **3** sample obtained by heating of compound **1** crystals at 100 °C for 12 hours, (g) compound **3** sample obtained by heating of compound **2** crystals at 100 °C for 12 hours, (h) compound **1** prepared from solid-gas reaction of **3** with MeOH vapors and (i) compound **2** prepared from solid-gas reaction of **3** with EtOH vapors.

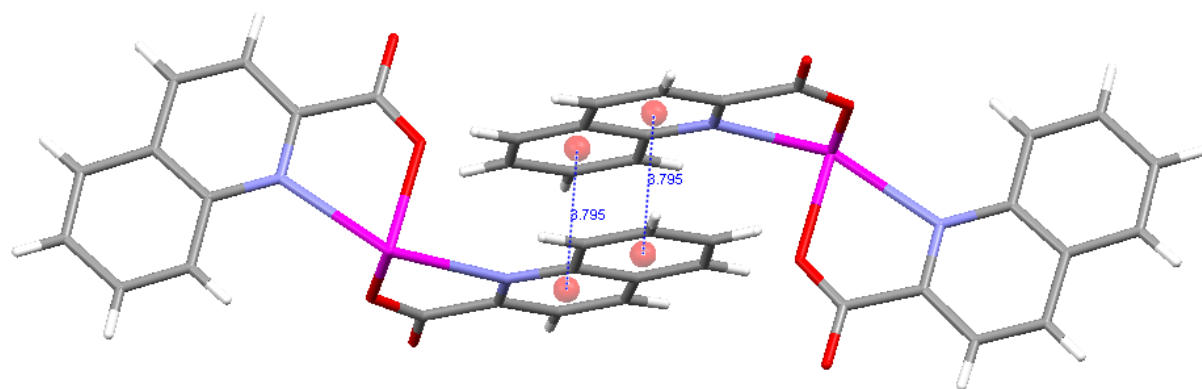


Figure S4. Showing the π - π stacking interactions exist in **4**, (Pb = violet, O = red, N = blue, C = gray and H = white).

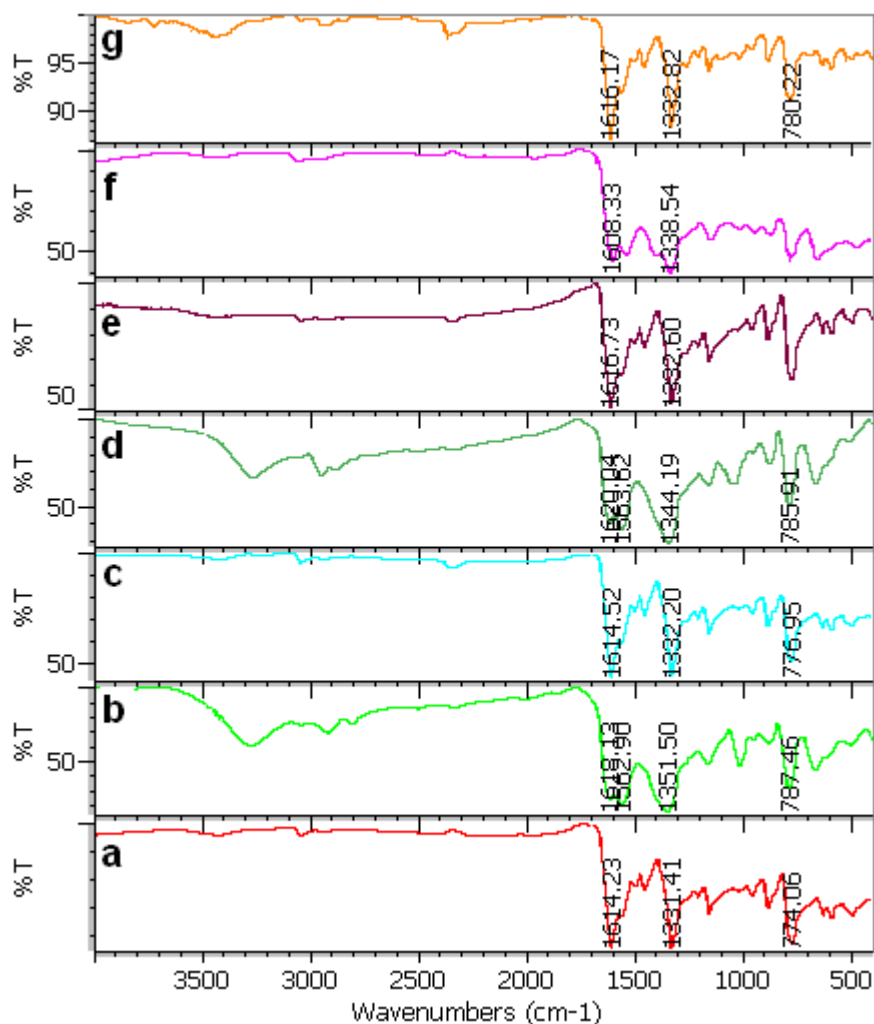


Figure S5. IR spectra of a) compound **4** crystals prepared by branch tube method, b) compound **1** crystals prepared by branch tube method, c) compound **4** sample obtained by solution-state structural transformation of **1** in distilled water, d) compound **2** crystals prepared by branch tube method, e) compound **4** sample obtained by solution-state structural transformation of **2** in distilled water, f) compound **3** crystals prepared by branch tube method, g) compound **4** sample obtained by solution-state structural transformation of **3** in distilled water.

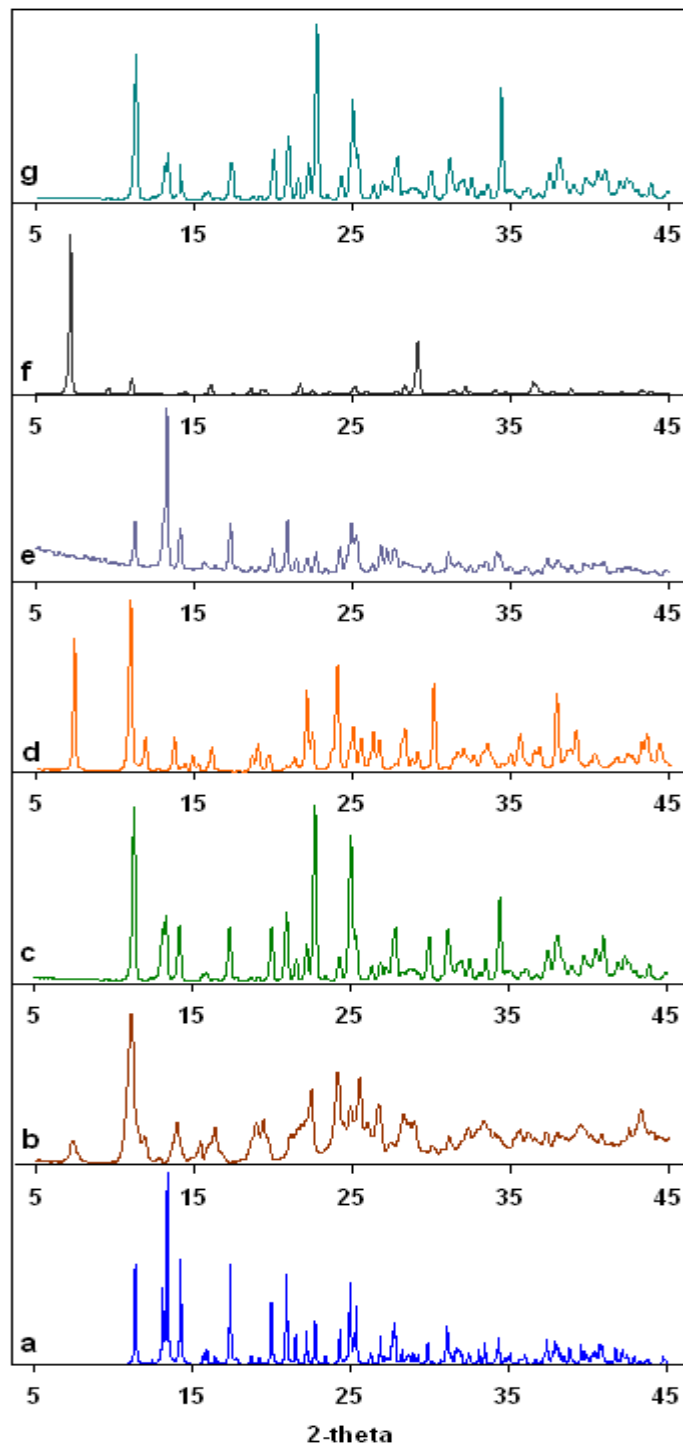


Figure S6. The XRD patterns of (a) simulated from single crystal X-ray data of compound **4**, (b) compound **1** crystals prepared by branch tube method, (c) compound **4** sample obtained by solution-state structural transformation of **1** in distilled water, (d) compound **2** crystals prepared by branch tube method, (e) compound **4** sample obtained by solution-state structural transformation of **2** in distilled water, (f) compound **3** crystals prepared by branch tube method, (g) compound **4** sample obtained by solution-state structural transformation of **3** in distilled water.

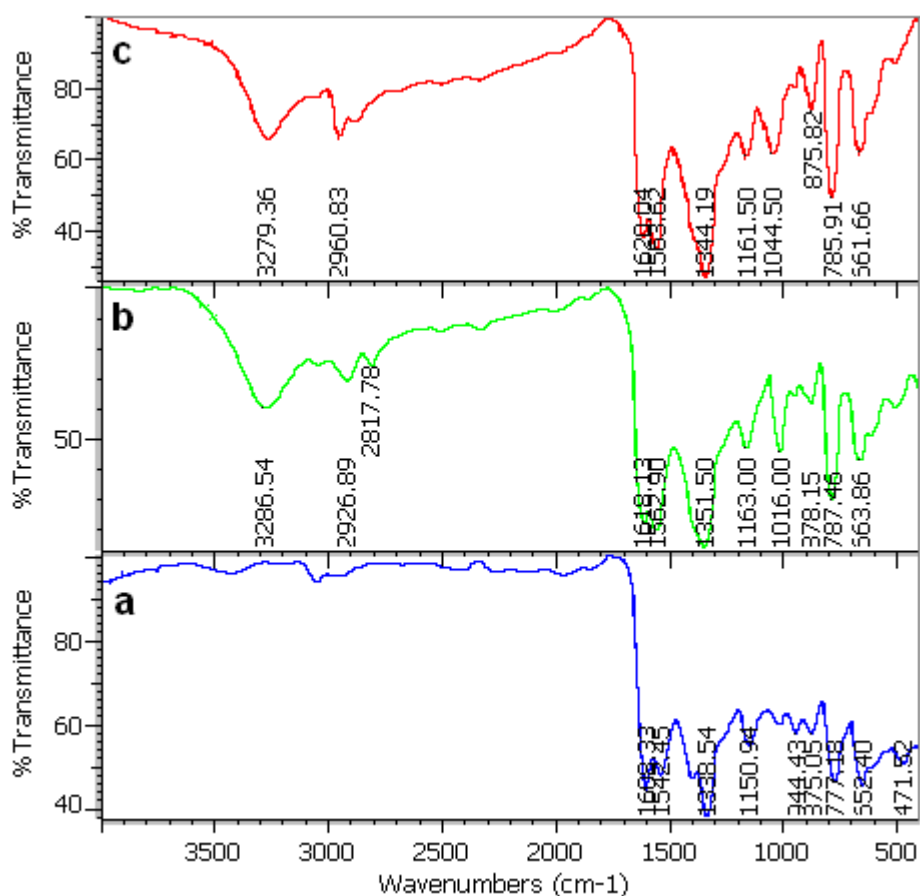


Figure S7. IR spectra of a) compound **3** crystals prepared by branch tube method, b) compound **1** sample obtained by solution-state structural transformation of **3** in MeOH and c) compound **2** sample obtained by solution-state structural transformation of **3** in EtOH.

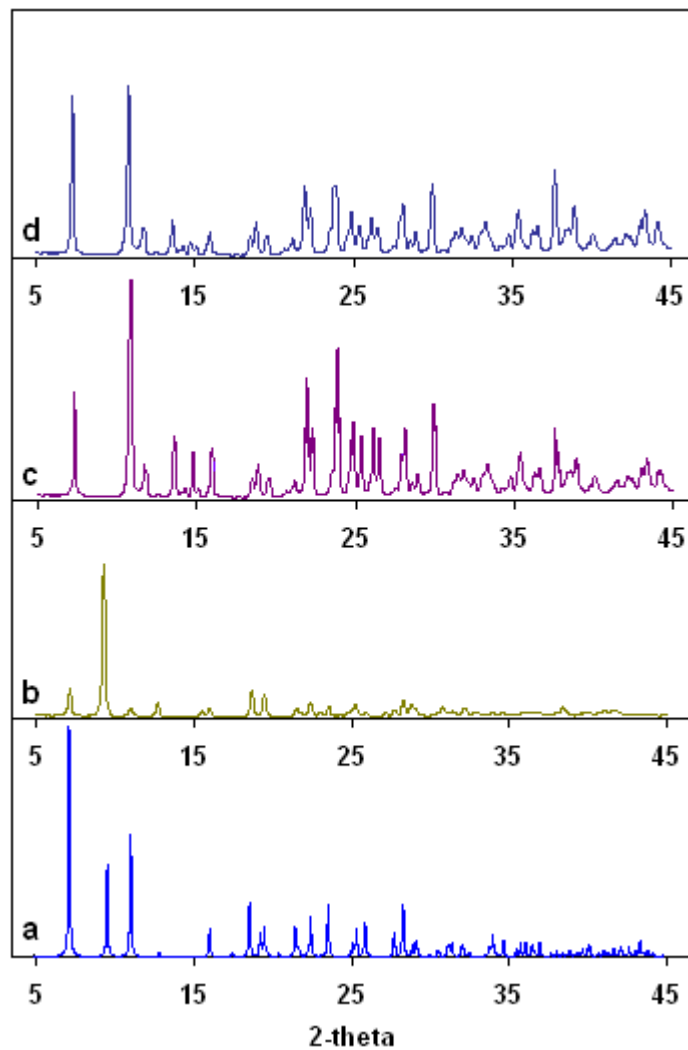


Figure S8. The XRD patterns of (a) simulated from single crystal X-ray data of compound **3**, (b) compound **3** crystals prepared by branch tube method, (c) compound **1** sample obtained by solution-state structural transformation of **3** in MeOH and (d) compound **2** sample obtained by solution-state structural transformation of **3** in EtOH.

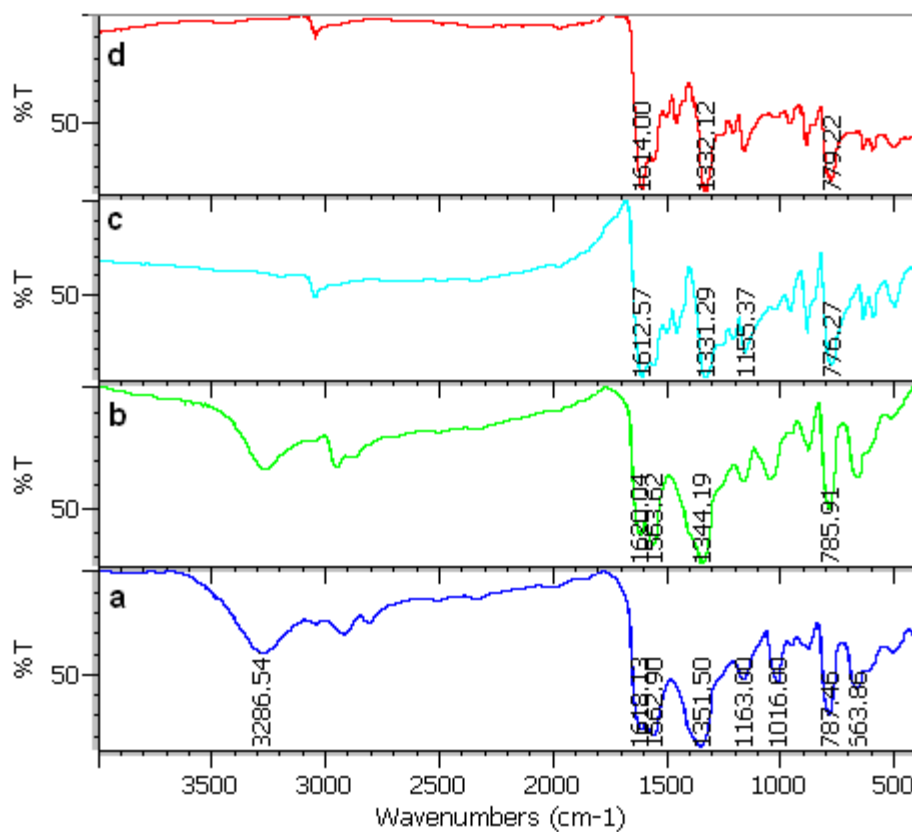


Figure S9. IR spectra of a) compound **1** crystals prepared by branch tube method, b) compound **2** crystals prepared by branch tube method, c) compound **4** sample obtained by solution-state structural transformation of **1** in EtOH and d) compound **4** sample obtained by solution-state structural transformation of **2** in MeOH.

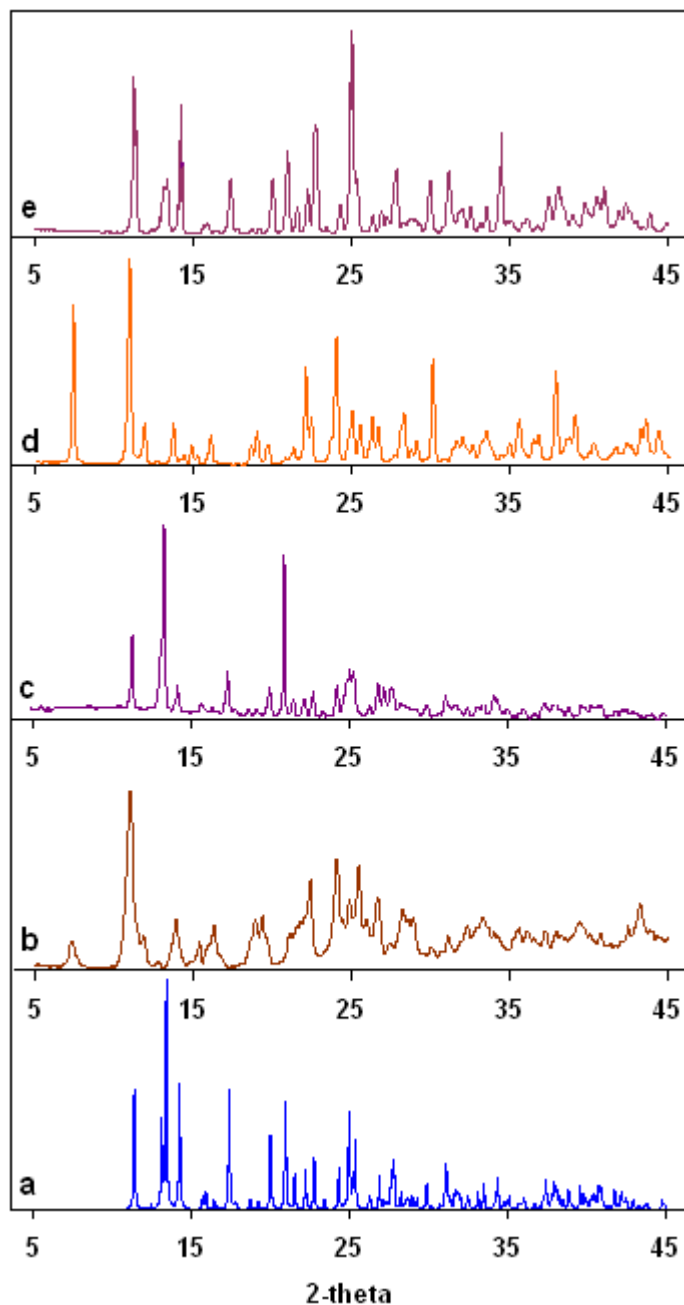


Figure S10. The XRD patterns of (a) simulated from single crystal X-ray data of compound **4**, (b) compound **1** crystals prepared by branch tube method, (c) compound **4** sample obtained by solution-state structural transformation of **1** in EtOH, (d) compound **2** crystals prepared by branch tube method and (e) compound **4** sample obtained by solution-state structural transformation of **2** in MeOH.

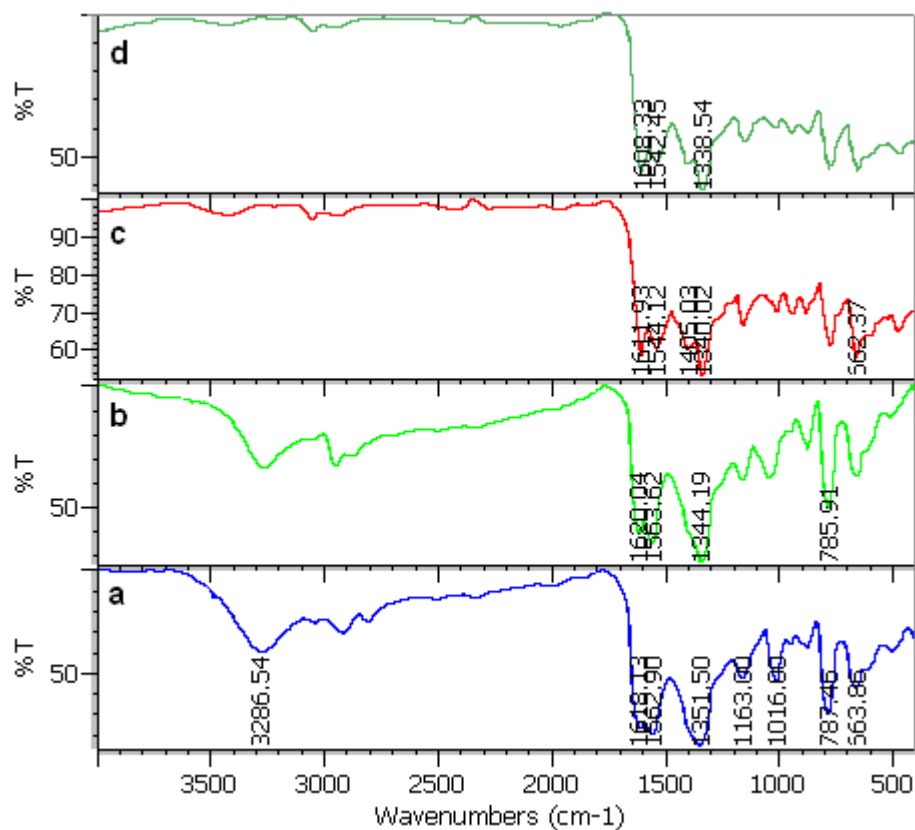


Figure S11. IR spectra of a) compound **1** crystals prepared by branch tube method, b) compound **2** crystals prepared by branch tube method, c) compound **3** sample obtained by solution-state structural transformation of **1** in MeCN and d) compound **3** sample obtained by solution-state structural transformation of **2** in MeCN.

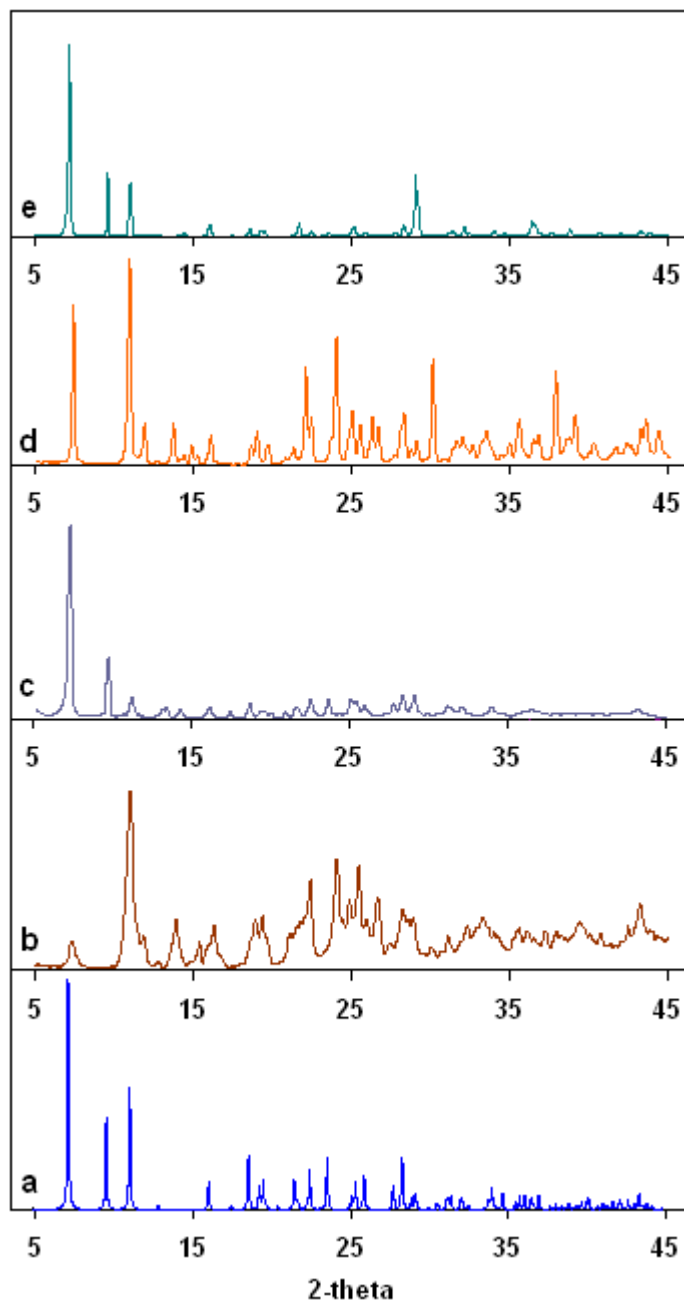


Figure S12. The XRD patterns of (a) simulated from single crystal X-ray data of compound **3**, (b) compound **1** crystals prepared by branch tube method, (c) compound **3** sample obtained by solution-state structural transformation of **1** in MeCN, (d) compound **2** crystals prepared by branch tube method and (e) compound **3** sample obtained by solution-state structural transformation of **2** in MeCN.

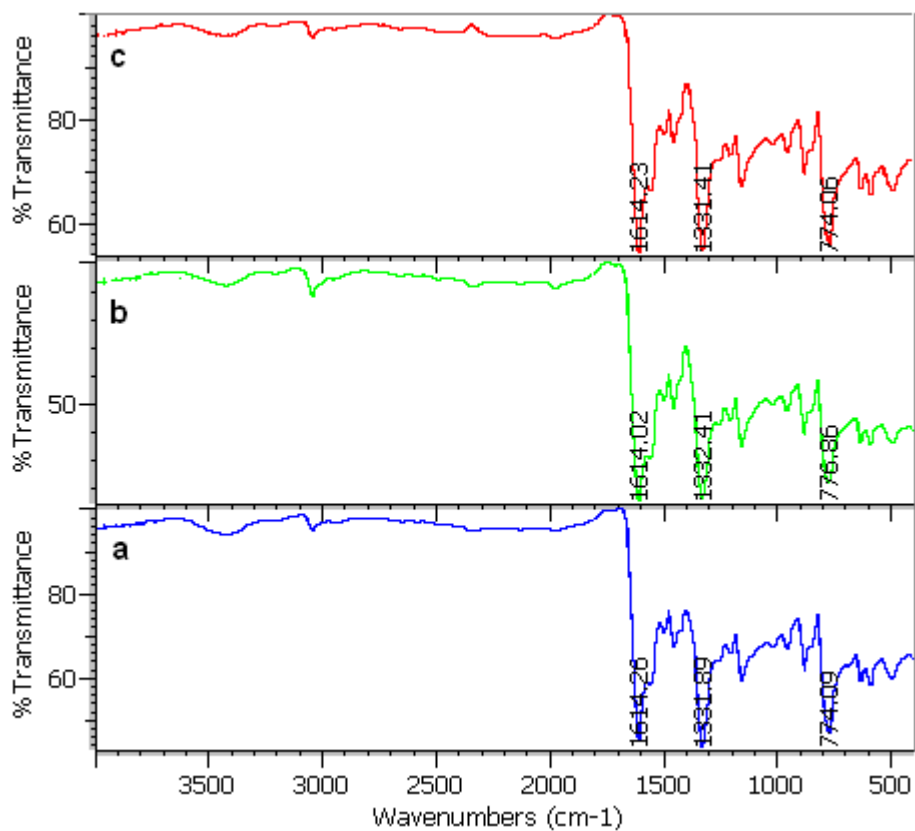


Figure S13. IR spectra of compound **4** after immersing in saturated solutions of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ in a) water, b) methanol and c) ethanol.

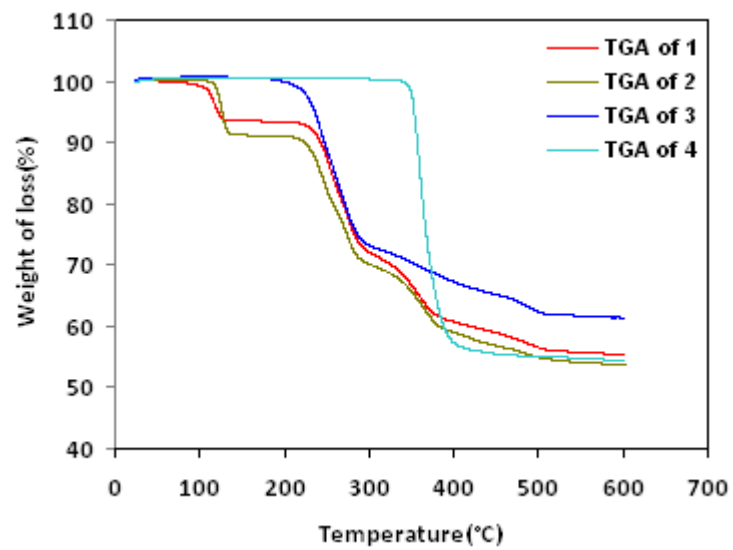


Figure S14. TGA diagrams of compounds 1-4 single crystals.

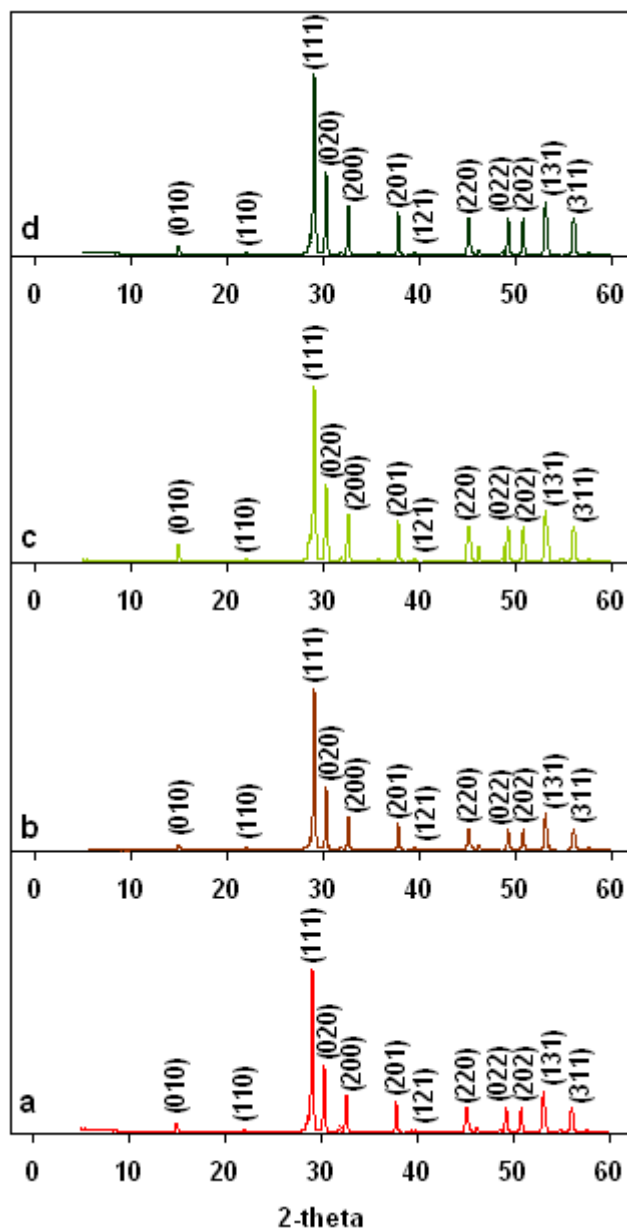


Figure S15. The XRD patterns of massicot phase of PbO (with the lattice parameters of $a = 5.4903(4)$, $b = 5.8920(4)$, $c = 4.7520(4)$ Å and $z = 4$ with JCPDS card number 38-1477) prepared from compounds (a) **1**, (b) **2**, (c) **3** and (d) **4** precursors.