Coordination Polymers of Organic Polymers via Photopolymerization in Single Crystals: Two-dimensional Hydrogen Bonding Layers with Amazing Shock Absorbing Nature

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Supporting Information

Experimental details and characterization of the compounds by ¹H-NMR spectra, FTIR spectra,PXRD patterns, MALDI-TOF mass spectroscopy, Thermal analysis and Crystallographic data and refinement details

General

FTIR spectra were recorded with a Perkin Elmer Instrument Spectrum Rx Serial No. 73713. Powder XRD patterns were recorded with a BRUKER-AXS-D8-ADVANCE defractometer (Cu target). ¹H NMR (200/400 MHz) spectra were recorded on a BRUKER-AC 200/400 MHz. spectrometer. Elemental analyses were carried out by Perkin Elmer Series II 2400 and melting points were recorded using a Fisher Scientific melting point apparatus cat. No.12-144-1. MALDI-TOF experiment was done by a Voyager-DE PRO MALDI-TOF mass spectrometer (Applied Biosystem, USA) in N₂ laser (λ =337 nm) operating at a pulse rate of 20 Hz. The total acceleration potential was 20 kv. Delayed extraction was done with delay time of 300 nsec.Spectrum was collected in the positive ion reflection mode as average of 100 laser shot.

Synthesis of 3-pyridineacrylic acid

In a round bottom flask malonic acid (2.45 g, 0.024 mol) and pyridine (3 ml) were taken and then 3-pyridinecarboxaldehyde (2.2 ml, 0.028 mol) followed by 4-5 drops of piperidine were added to the reaction mixture. It was then refluxed for 10-12 hours. It was cooled to room temperature and cold water was added to it. The white solid product was filtered and washed with cold water and then with acetone. It was dried in oven. Yield (3.14g, 88%). M.P. 232°C.

Synthesis of N, N'-bis(3-(3-pyridyl)acryloyl)ethylenediamine (1a)

In a round bottom flask 3-pyridineacrylic acid (1.21 g, 0.008 mol) and pyridine (15 mL) were taken and ethylenediamine (0.267 ml, 0.004 mol) was added to the reaction mixture and stirred for about 15-20 minutes. After that triphenyl phosphite (2.25 ml, 0.0086 mol) was added to it and the reaction mixture was refluxed for 7-8 hours. It was cooled to room temperature, pyridine was distilled out to reduce the volume up to 5 ml which was kept standing overnight to obtain a solid mass. The solid mass was washed with EtOH several times. The white solid product was recrystallized from MeOH and DCM mixture. For **1a**, Yield (0.97 g, 75%); Found C, 66.5; H, 6.7; N, 16.7. Calc. for C₁₈H₁₈N₄O₂ (322.36): C, 67.1; H, 5.6, N, 17.4. M.P. 230°C; IR v_{max}/cm^{-1} ; 3222, 3041, 2935, 2374, 1675, 1598, 1577, 1348, 1224, 974; ¹H-NMR δ_{ppm} (200 MHz; D⁶-DMSO): 3.26(s, 4H), 6.65(d, *J* = 16 Hz, 2H), 7.39(m, 2H), 7.92(d, *J* = 8Hz, 2H), 8.25(s, 1H)., 8.47(m, 2H), 8.67(d, *J* = 8Hz, 2H).

Synthesis of N,N'-bis(3-(3-pyridyl)acryloyl)butanediamine (1b)

1b was synthesized from β-(3-pyridyl)-*trans*-acrylic acid (1.21 g, 8 mmol) and 1, 4butanediamine (0.267 ml, 4 mmol) following the same synthetic procedure as described for compound 1a. The white solid product was recrystallized from MeOH. For 1b, Yield (0.87 g 60%). Found C, 67.74; H, 6.63; N, 14.96. Calc. for C₂₀H₂₂N₄O₂ (350.41): C, 68.55; H, 6.33; N, 15.99; M.P.; 249°C; IR v_{max}/cm^{-1} 2895-3291, 1555-1657, 1343-1475, 1296, 1245-1231, 983, 872-520. ¹H-NMR δ_{ppm} (200 MHz; D⁶-DMSO): 1.38 (s,4H); 3.09 (m, 4H); 6.61 (d, *J* = 16 Hz, 2H); 7.32 (m, 4H); 7.85 (d, *J* = 6Hz, 2H); 8.08 (s, 1H); 8.43(d, *J* = 6Hz, 2H), 8.64 (s, 2H).

Synthesis of Complex 2

The complex **2** was prepared by directly mixing **1a** (0.0161 g, 0.05 mmol) and AgClO₄ (0.0103 g, 0.05 mmol) in EtOH. The direct mixing initially resulted in a white precipitate which was dissolved with one drop of NH₃ solution. The clear and colourless solution was kept in dark by wrapping aluminium foil at room temperature. The formed white crystals are separated from vial after 48-72 hours and allowed to dry in dark condition. Yield (0.0237 g, 90%), Found C, 51.1; H, 4.5, N, 13.2. Calc. for $C_{18}H_{18}AgClN_4O_6$ (527.68); C, 50.2; H, 4.2; N, 13.0; IR v_{max}/cm^{-1} ; 3284, 1661, 1623, 1559, 1414, 1335, 1240, 1120, 1087, 972, 805, 635

Synthesis of Complex 3

The Complex **3** was prepared same as Complex **2** by taking **1b** (0.0175 g, 0.05 mmol) and AgClO₄ in ethanol (0.0103 g, 0.05mmol). Yield (0.02502 g, 90%); Found C, 43.2; H, 3.7, N, 10.2. Calc. for $C_{20}H_{22}AgClN_4O_6$ (558.06); C, 43.0; H, 4.0; N, 10.0; IR v_{max}/cm^{-1} ; 3288, 2946, 1659, 1616, 1540, 1332, 1227, 1089, 968, 806, 627

Synthesis of Complex 4

The complex **4** was also prepared by directly mixing **1a** (0.0161 g, 0.05 mmol) and AgNO₃ (0.0085 g, 0.05 mmol) in MeOH-DCM and the mixing resulted in a white precipitate which was dissolved by adding one drop of NH₃ solution. The clear and colourless solution was kept in dark by wrapping aluminium foil. The white crystals separated from vial after 48-72 hours and allowed to dry in dark condition. Yield (0.0209 g, 85%), Found C, 42.6; H, 4.1; N, 14.8. Calc. for $C_{36}H_{36}Ag_2N_{10}O_{10}$ (984.49). C, 43.9; H, 3.7; N, 14.2; **IR** v_{max}/cm^{-1} ; 3281, 3071, 1654, 1618, 1559, 1383, 1232, 1128, 1023, 975, 807, 680.

Synthesis of Complex 5

The Complex **5** was prepared same as complex **4**: **1b** (0.0175 g, 0.05 mmol) and AgClO₄ (0.0103 g, 0.05 mmol) are mixed in MeOH-DCM solvent mixture. Yield (0.0208 g, 80%), Found C, 52.6; H, 3.0; N, 12.8. Calc. for $C_{20}H_{22}AgN_5O_5$ (520.30). C, 53.4; H, 3.1; N, 12.4; IR v_{max}/cm^{-1} ; 3287, 3035, 2946, 2871, 1654, 1615, 1539, 1473, 1417, 1383, 1333, 1255, 1226, 1025, 967-630.

Irradiation process

The crystals were irradiated in sunlight in a smooth Petri-dish for 72 hours. After irradiation crystals turned to light yellowish from colourless. Crystal structure determinations of the irradiated complex of **2**, **3**, **4** were conducted using single crystal diffraction. The crystal structure of irradiated crystals of **5** could not be conducted due to poor crystal quality. Further, all the above complexes were prepared by dry grinding process and the irradiation of those grounded materials found to result in similar type materials like conventionally grown crystals. Solid MALDI-Tof Mass experiments were conducted to determine the molecular weights of the organic polymers.

Separation of Irradiated complex

1g of irradiated complex of **2** was taken in 10 mL of water and then acidified with 2(N) HCl up to pH 2-3. The resulted precipitate of AgCl was removed by celiate filtration until AgCl was removed from the solution completely; the filtrate was carefully neutralized

by drop wise addition of dilute NaOH. The resulted solid product was isolated by filtering and dried in oven. 1 H- NMR was recorded in D₂O for the characterization of organic polymer.





Figure S1. ¹H-NMR spectrum for 1a (200MHz, D⁶ DMSO)



Figure S2. ¹H-NMR spectrum for 1b (200MHz, D⁶ DMSO)



Figure S3. ¹H-NMR spectrum for 1a polymer after separation (400MHz, D_2O & 1 drop HCl))



FTIR Spectra

Figure S4. FTIR spectra of (a) 2 and (b) 2'

687.84 635.98

600

400



Figure S7. FTIR spectra of (a) 5 and (b) 5'

PXRD Patterns

Figure S8. PXRD patterns of complex **2** before irradiation (a) calculated, (b) observed, (c) grinding and after irradiation (d) calculated, (e) observed, (f) grinding.

Figure S9. PXRD patterns of complex **3** before irradiation (a) calculated, (b) observed, (c) grinding and after irradiation (d) calculated, (e) observed, (f) grinding.

Figure S10. PXRD patterns of complex **4** before irradiation (a) calculated, (b) observed, (c) grinding and after irradiation (d) calculated, (e) observed, (f) grinding.

Figure S11. PXRD patterns of complex **5** before irradiation (a) calculated, (b) observed, (c) grinding and after irradiation (d) observed, (e) grinding.

MALDI-TOF mass spectra

Sample preparation for solvent free MALDI-TOF analysis:

10 mg of irradiated complex, 10 mg 2, 5 di-hydroxy benzoic acid (DBH) and 1 mg of sodium tri-fluro acetate with KBr were grinded thoroughly in a mortar-pestle. Thin palate of this mixture was prepared with pressure similar to the palate preparation for FTIR analysis. Small pieces of the palate was attached on the MALDI probe tip with the double side tape and introduced in the laser source.

Figure S12. MALDI-Tof mass spectra of irradiated complex 2', the intense peaks are defined as $[nM+K]^+$ and highest molecular peak is ~ 7-mer unit

Figure S13. MALDI-Tof mass spectra of irradiated complex **3'**, the intense peaks are defined as $[nM+Na]^+$ and highest molecular peak is ~ 9-mer unit

Figure S14. MALDI-Tof mass spectra of irradiated complex 4', the intense peaks are defined.as $[nM+Na]^+$ and highest molecular peak is ~ 8-mer unit

Figure S15. MALDI-Tof mass spectra of irradiated complex 5', the intense peaks are defined as $[nM+K]^+$ and highest molecular peak is ~ 7-mer unit

Figure S16. MALDI-Tof mass spectra of irradiated complex 2' (grinding process) the intense peaks are defined as $[nM+K]^+$ and highest molecular peak is ~ 6-mer unit

Figure S17. MALDI-Tof mass spectra of irradiated complex **3'** (grinding process) the intense peaks are defined as $[nM+K]^+$ and highest molecular peak is ~ 6-mer unit

Figure S18. MALDI-Tof mass spectra of irradiated complex 4' (grinding process) the intense peaks are defined as $[nM+K]^+$ and highest molecular peak is ~ 4-mer unit

Figure S19. MALDI-Tof mass spectra of irradiated complex 5' (grinding process) the intense peaks are defined as $[nM+Na]^+$ and highest molecular peak is ~ 5-mer unit.

Figure S20. Thermal gravimetric analysis of 4 and 4'

Crystallographic data and refinement details

Crystal Structure Determination: All the single-crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo K α radiation ($\mu = 0.71073$ Å) at room temperature (293 K) by the hemisphere method. The structures were solved by direct methods and refined by least-squares methods on F² usingSHELX-97.^{S1} Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model.

	2	2'	3	3'	4	4'	5
CCDC	965790	965791	965792	965793	965794	965795	965796
Formula	C ₁₈ H ₁₈ AgCl	(C ₁₈ H ₁₈ AgClN ₄	C ₂₀ H ₂₂ AgCl	(C ₂₀ H ₂₂ AgCl	(C ₃₆ H ₃₆ Ag ₂ N	(C ₁₈ H ₁₈ AgN ₅	(C ₂₀ H ₂₂ AgN ₅
	N ₄ O ₆	O ₆) _n	N ₄ O ₆	N ₄ O ₆)	10O10)	O ₅) _n	O ₅) _n
MW	529.68	1589.05	557.74	557.74	492.24	984.49	520.30
Cryst. System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	C ₂ /c	C ₂ /c	C ₂ /c	C ₂ /c	P-1	P-1	C ₂ /c
a (Å)	19.799(2)	20.677(2)	20.838(4)	19.871(2)	10.839(5)	9.458(8)	20.667(3)
b (Å)	9.647(1)	9.6611(7)	9.757(2)	9.841(1)	11.156(5)	10.001(8)	9.479(2)
c (Å)	11.2675(11)	30.357(2)	12.759(3)	23.807(2)	17.108(7)	11.102(9)	13.454(4)
α (°)	90.00	90.00	90	90	76.789(13)	75.79(2)	90
β(°)	113.439(2)	107.503(2)	121.463(8)	110.762(3)	80.643(13)	65.02(2)	126.546(4)
γ (°)	90.00	90.00	90	90	69.187(12)	89.24(3)	90
Vol. (Å ³)	1974.5(3)	5783.5(7)	2212.8(8)	4352.9(8)	1874.9(1)	917.9(1)	2117.4(6)
Ζ	4	4	4	8	4	1	4
D _{cal} (mg/m ³)	1.782	1.825	1.674	1.702	1.774	1.781	1.632
R ₁	0.0637	0.0605	0.0386	0.0708	0.0791	0.0960	0.0600
[I>2(σI))]							
wR ₂ (onF ² ,al	0.2558	0.1776	0.0920	0.2057	0.1889	0.2377	0.1071
l data)							

Table S1. Crystallographic Data

Compound	Centroid to centroid distance (d, Å)	C=CC=C torsion angle (θ, \circ)
2	3.714	0.00
3	3.931	0.00
4	3.633, 3.642	0.00, 1.48
5	3.922	0.00

 Table S2. Geometrical parameters for double bond orientation

Figure S21. (a) The CPOP square grid network exhibited by the crystal structure 3'; Illustrations of two dimensional hydrogen bonded layers: (b) in 2 (c) in 2' (d) in 3 and (e) in 3'. Notice the differences in the H-bonded amide groups (encircled) in 2 & 2' and 3 & 3'.

References:

1. Sheldrick, G. M. SHELX-97, Program for the Solution and Refinement of Crystal Structure; University of Göttingen, Germany, 1997.