**Supporting Information**

**Controlled Release of 5-Fluorouracil by a Novel L-Lysine Based Polyesterurethane Material Synthesized from Epoxide and CO2 via a Novel Dicopper Salen Catalyst**

**Arunangshu Kundu a,b , Gobinda Chandra De\* b , Sushobhan Ghosh\* a ,**

**a: Department of Chemistry, Alipurduar College, Westbengal, India. Email:** [**sushobhan.iisc@gmail.com**](mailto:sushobhan.iisc@gmail.com)**;**

**b: Dept of Chemistry, Coochbehar Panchanan Barma University, Westbengal, India. Email:** [**degobinda@yahoo.com**](mailto:degobinda@yahoo.com) **(\*marked as corresponding author)**

Methods and Materials:

All synthetic procedures were performed under normal atmospheric conditions. 1H NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer. 1H NMR spectra were referenced internally to residual solvent peaks, and chemical shifts are expressed relative to tetramethylsilane, SiMe4 (δ = 0 ppm). Fourier transform infrared (FTIR) spectra were recorded with an IRAffinity-1S Shimadzu spectrophotometer. ESI MS was recorded in high resolution mass spectrometer, AGILENT QTOF 6520. Microanalyses were carried out with a Perkin–Elmer 2400 CHN analyzer. SEM analysis was performed with a Sigma 300 Zeiss machine. All solvents were purchased from local chemical company and were dried via standard procedure prior to use. Tetrabutyl ammonium bromide and the epoxide 2-(phenoxymethyl)oxirane were purchased from Sigma Aldrich. Copper nitrate, Benzene 1, 3, 5 tricarbonyl trichloride ( trimesoyl chloride), 5 fluro uracil, 5 bromo 2 hydroxy benzaldehyde, Pd(PPh3)2Cl2, 1,2 diamino benzene, Copper acetate, 1,3 dihydroxy propane, di-tert-butyl dicarbonate, sodium hydride were also purchased from Sigma Aldrich Chemical company. 1, 8 diethynyl anthracene1 and 1-Boc-O-4-bromo-2-([1,3]dioxan)benzene2 were synthesized according to the previously reported literature procedures.

**Synthesis of the Polyesterurethane** **1**: In a 100 mL round bottom flask the ring opened diol **3** (250 mg ; 0.46 mmol ;1.5 equivalent) was suspended in 10 ml dry THF. To this 78 mg trimesyl chloride (0.30 mmol; 1 equvalent) dissolved in 5 ml dry THF and 2 ml triethyl amine was added. The mixture was heted at 1200 c for 1 hour under the slow N2 flow and further heated at this temperate for 1 hour under vacume and cooled slowly at room temperature. After that the mass was dissolved in chloroform and washed with brine solution (2times) and distilled water (1time). This gave a highly viscous brown product. Yield: 200 mg. 1H NMR( 300 MHz, DMSO-*d6*);δ = 8.61 (brs); 7.27 (m), 6.91 (m), 4.86 (brs), 4.37 (brs), 3.99 – 2.94 (m), 1.81 (m), 1.55 (m), 1.38 (m) ppm. 13C NMR (75 MHz, DMSO-d6); δ = 179.68, 167.65, 159.38, 135, 133.32, 130.06, 121.29, 115.03, 69.66, 67.66, 65.4, 63.4, 60.14, 53.38, 45.86, 29.82, 23.8 ppm. IR (KBr) wave number = 3320, 2915, 2852, 1689, 1629, 1528, 1222, 1033 cm-1.

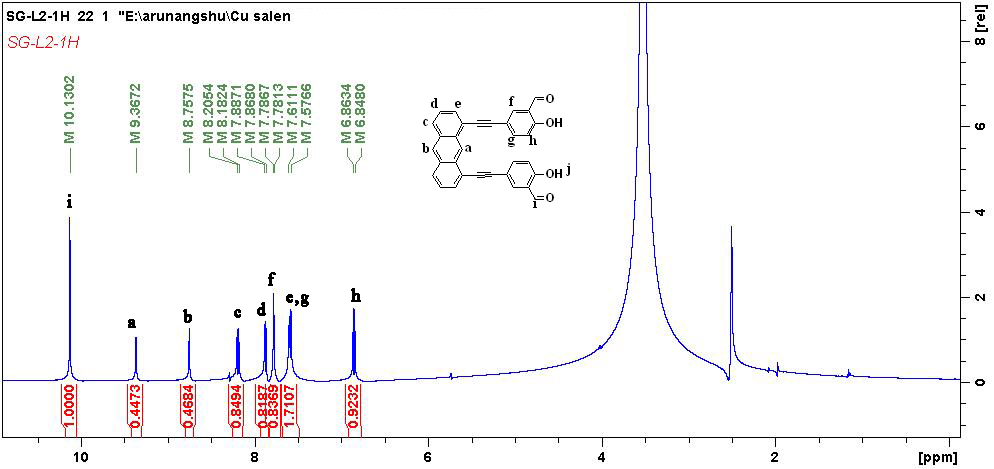
**Synthesis of the ring opened diol** **3**: Cyclic carbonate **2** (500 mg ; 2.57 mmol; 2 equvalent) was taken in a RB and melted at 1200 c. To this 188 mg lysine (1.28 mmol; 1 equvalent) dissolved in 4 ml H20:MeOH mixture(1:1) was added and the solution was stirred for 1 hour at 1200 C. Then the reaction mixture was evaporated to dryness to get the gel type product. Yield= 0.736 mg (54 %) 1H NMR( 300 MHz, CDCl3);δ= 7.2 – 7.15 (m, 4H, Ph-H), 6.88 – 6.82 (m, 6H, Ph-H), 4.0-3.8 (m, 8H), 3.63 – 3.45 (m, 4H), 3.33 – 3.22 (m, 1H), 2.93 – 2.87 (m, 1H), 2.79 – 2.75 (m, 1H), 1.57 – 1.45 (m, 4H), 1.32 – 1.19 (m, 4H) ppm. 13C NMR( 75 MHz, CDCl3);δ 178.73, 157.96, 157.83, 157.73, 129.54, 121.29, 114.65, 69.80, 68.17, 62.08, 54.77, 38.89, 31.62, 28.29, 26.46, 21.53 ppm. IR (KBr) wave number = 3290, 2909, 2852, 1678, 1571, 1487, 1230, 1035 cm-1. HRMS (ESI-): calcd. for C26H33N2O10 [M-H]- 533.2135, found 533.1476.

**Synthesis of the cyclic carbonate** **2**: Epoxide 2-(phenoxymethyl)oxirane (2 gm, 13.33 mmol), catalyst **L1Cu2** (10 mg, 0.0083 mmol) and Bu4NBr (10 mg, 0.0311 mmol) were placed in a stainless steel autoclave fitted with a magnetic stirrer bar, and the reactor was heated to 80°C after being charged with 10 bar pressure of carbon dioxide. The reaction mixture was stirred for 24 h at this temperature and pressure. The conversion of epoxide to cyclic carbonate was determined by analysis of a sample by 1H NMR spectroscopy.1H NMR( 300 MHz, CDCl3);δ= 7.34-7.27(m, 2H, PhH); 7.04-7.02(m , 1H, PhH); 6.93- 6.90,(m, 2H, PhH); 5.07-5.02(m, 1H, OCH); 4.65-4.52(m, 2H, CH2 ); 4.27- 4.22(dd, 1H, OCH2) ppm. 13C NMR( 300 MHz, CDCl3);δ = 157.65(Ph-OC), 154.68(C=O), 129.7(Ph-C), 121.93(Ph-C), 114.50(Ph-C), 74.06(CH2), 66.73(OCH), 64.20(OCH2) ppm. IR (KBr) wave number = 2926, 2875, 1793, 1595, 1492 cm-1. HRMS (ESI+): calcd. for C10H10O4 [M+H]+195.18, found 195.07.

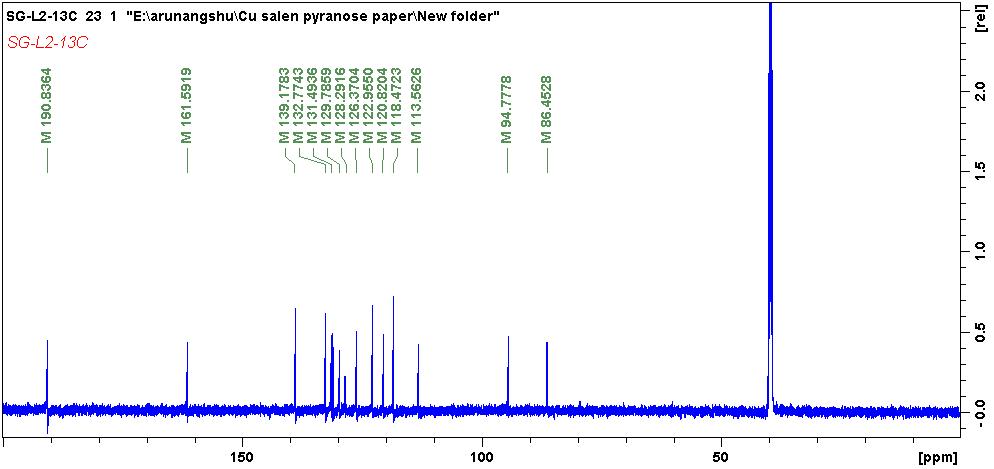
**Synthesis of the salen proligand** **L**: A mixture of 1-Boc-O-4-bromo-2-([1,3]dioxan)benzene (100 mg, 0.28 mmol), CuI (1.3 mg, 0.009 mmol), and Pd(PPh3)2Cl2 (5.3 mg, 0.014 mmol) was stirred for 1 hour under vacuum in a flame-dried Schlenk flask. A degassed solution of 1,8-diethynyl anthracene (31.65 mg, 0.14 mmol), triethylamine (0.3 ml), and dioxane (1 ml) was added and the mixture was stirred for 24 hours at 50 ºC under an argon atmosphere. The reaction mixture was allowed to cool to room temperature, filtered through a pad of celite® and the residue was partitioned between CH2Cl2 (15 ml) and water (10 ml). The organic layer was separated and the aqueous phase was extracted twice with CH2Cl2 (10 ml). The combined organic phase was dried (MgSO4) and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, 40 % CH2Cl2 in pentane) to yield 86 mg (45 %) of the (anthracene-1,8-diylbis(ethyne-2,1-diyl))bis(2-(1,3-dioxan-2-yl)-4,1-phenylene) di-tert-butyl bis(carbonate) as a yellow solid after removal of the solvent.

(anthracene-1,8-diylbis(ethyne-2,1-diyl))bis(2-(1,3-dioxan-2-yl)-4,1-phenylene) di-tert-butyl bis(carbonate) (75 mg, 0.095 mmol) was dissolved in a mixture of CH2Cl2 (4 ml) and CF3COOH (1 ml) and was stirred for 3 hours at room temperature. The reaction mixture was poured into CH2Cl2 (40 ml) and extracted with saturated NaHCO3 (2 x 15 ml) and water (2 x 10 ml). The organic phase was dried over (MgSO4) and the solvent was removed in vacuo to yield 35 mg (88 %) of the desired product as a shiny yellow solid. 1 H NMR (400 MHz, DMSO-d6) δ 10.13 (s, 2H, CHO), 9.36 (s, 1H, Ph-H), 8.75 (s, 1H, Ph-H), 8.2 (d, J = 8 Hz, 2H, Ph-H), 7.88 (d, J = 8 Hz, 2H, Ph-H), 7.78 (d, J = 2 Hz, 2H, Ph-H), 7.61 – 7.57 (m, 4H, Ph-H), 6.86 (d, J = 8 Hz, 2H, Ph-H) ppm.13C NMR (100 MHz, DMSO-d6) δ, 190.83, 161.59, 139.17, 132.77, 131.49, 129.78, 128.29, 126.37, 122.95, 120.82, 118.47, 113.56, 94.77, 86.45 ppm. IR (KBr) wave number = 1666, 1490, 1417, 1290, 1199, 1163, 896, 840, 746 cm-1. ESI MS negative mode ( m/e calcd for C32H17O4 (M-H) 465.1127, found 465.0635.

**Synthesis of the catalyst L1Cu2:** To a stirred solution of proligand **L** (60 mg, 0.129 mmol) and orthophenylene diamine ( 14 mg, 0.129 mmol) in 20 mL methanol copper acetate monohydrate (25.7 mg, 0.13 mmol) was added and the brownish yellow solution was refluxed for 3 hrs. The supramolecular catalyst **L1Cu2** precipitated from the solution which was filtered and washed with methanol and diethyl ether to give 70 mg (yield 85%) of the catalyst **L1Cu2** as light brown powder. FT IR 1610, 1581, 1408, 1390, 1384, 1170, 881, 837, 742 cm-1. Elemental analysis for C76H40Cu2N4O4 calculated C 76.05, H 3.36, and N 4.67 found C 76.23, H 3.54, and N 4.39. MS (MALDI-TOF) m/e calcd for C76H40Cu2N4O4 (M+) 1200.27, found 1200.07.



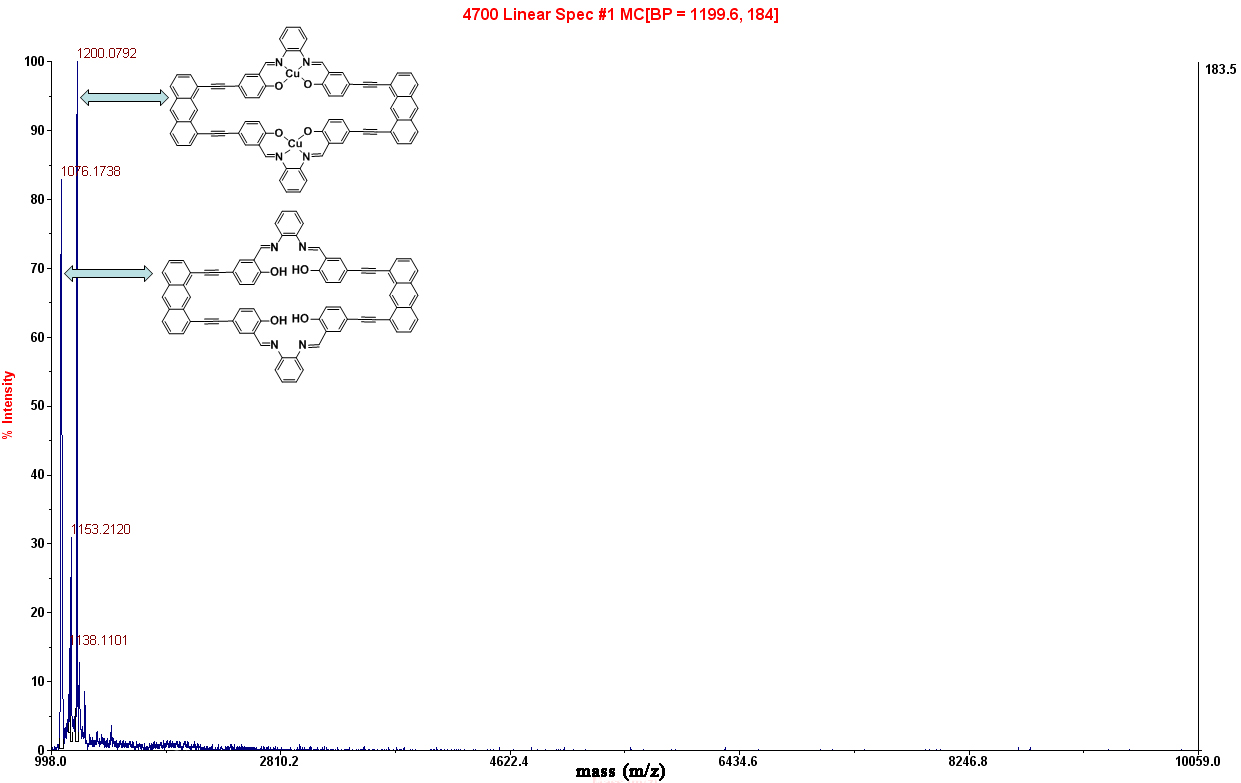
**Figure S1: 1H NMR of the proligand L.**

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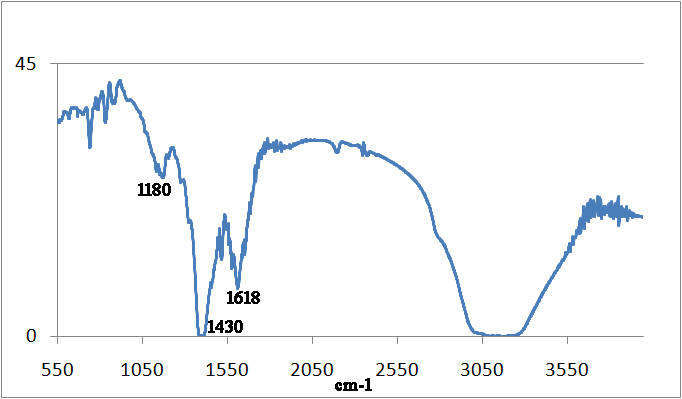
**FigureS2: 13C NMR of the proligand L.**

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**Figure S3: ESI MS in negative mode for the proligand L.**

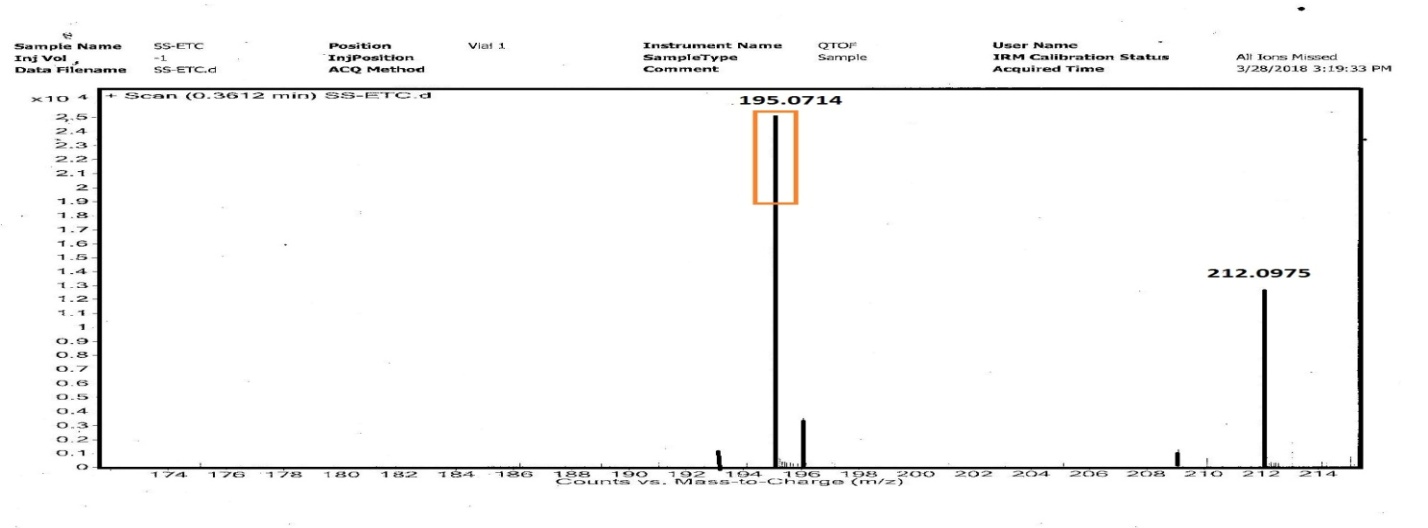
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**Figure S4: MALDI mass of the copper salen catalyst L1Cu2.**

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**Figure S5: IR spectra of the salen catalyst L1Cu2.**

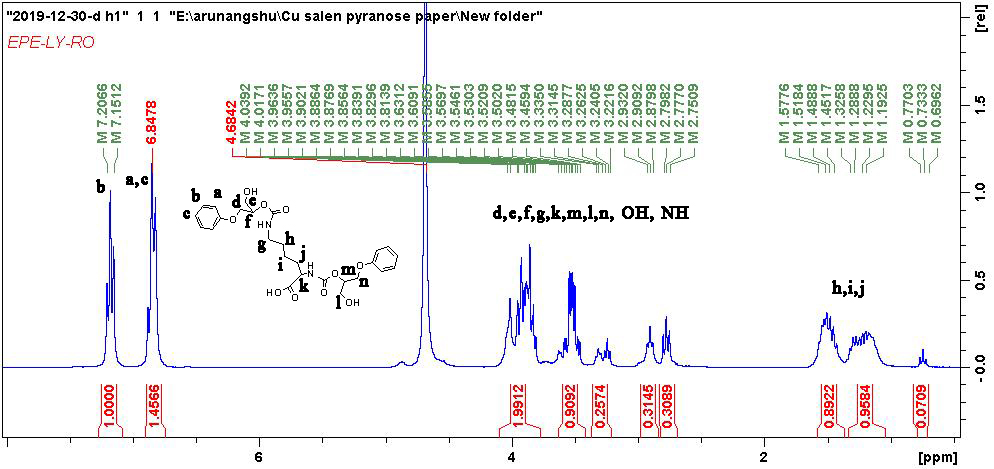
**Figure S6: IR spectra of the cyclic carbonate 2 as taken from the catalysis reaction.**

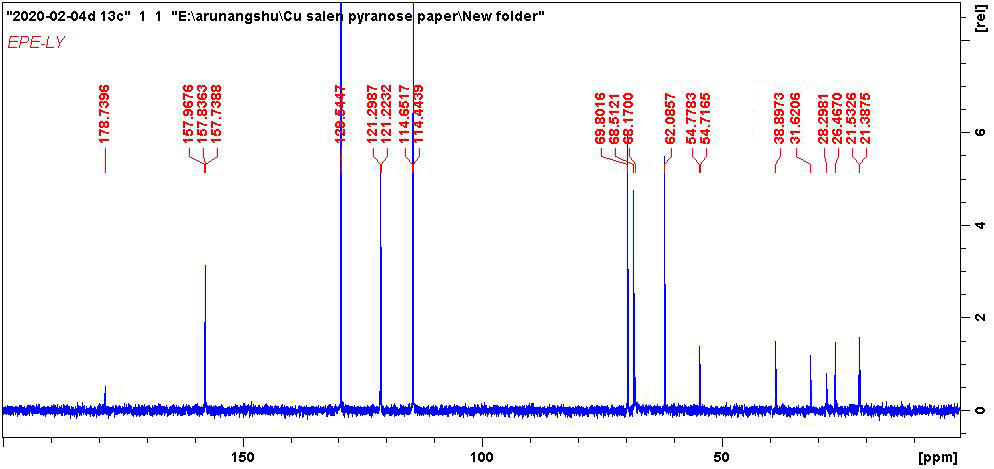
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**Figure S7: 1H NMR of the cyclic carbonate 2.**

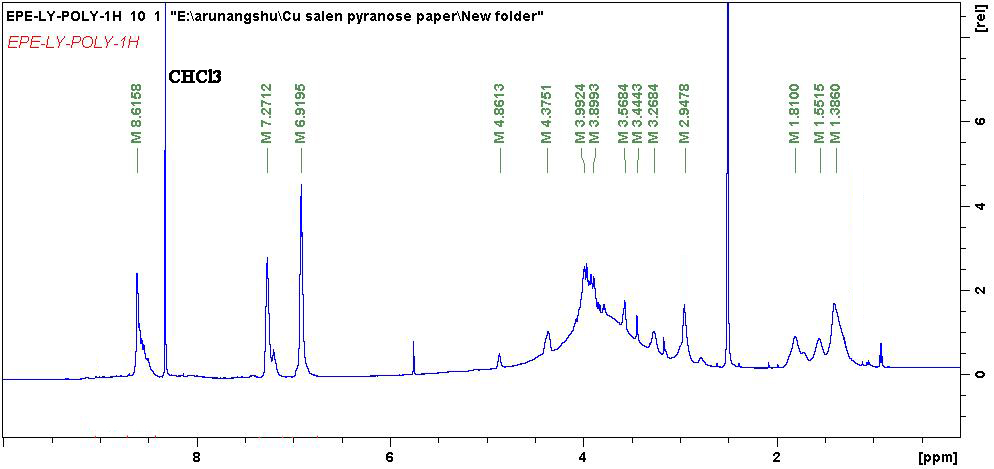
**Figure S8: ESI MS of the cycliccarbonate 2.**

**Figure S9: 1H NMR spectra of the ring opened diol 3 in D2O.**

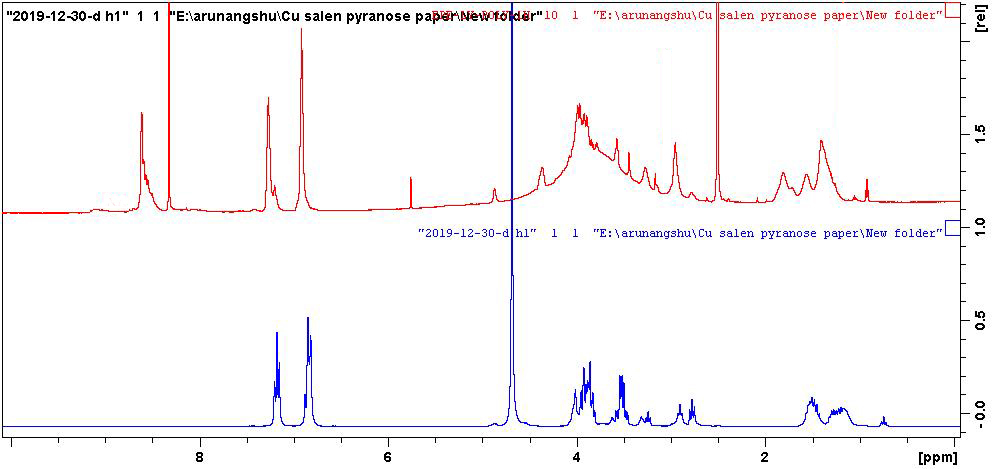
**Figure S10: 13C NMR spectra of the ring opened diol 3 in D2O.**

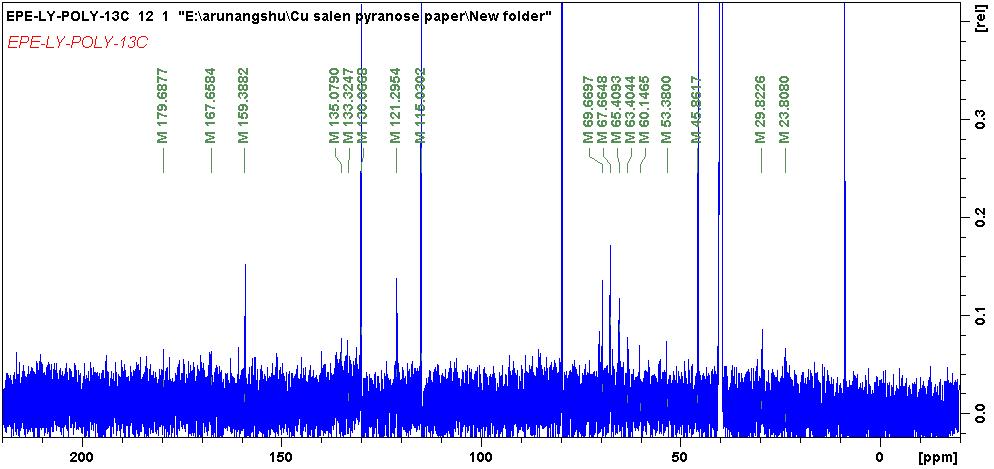
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**Figure S11: ESI MS spectra of the ring opened diol 3 in the negative mode ( peak at 1067.3440 corresponds to dimer of 3).**

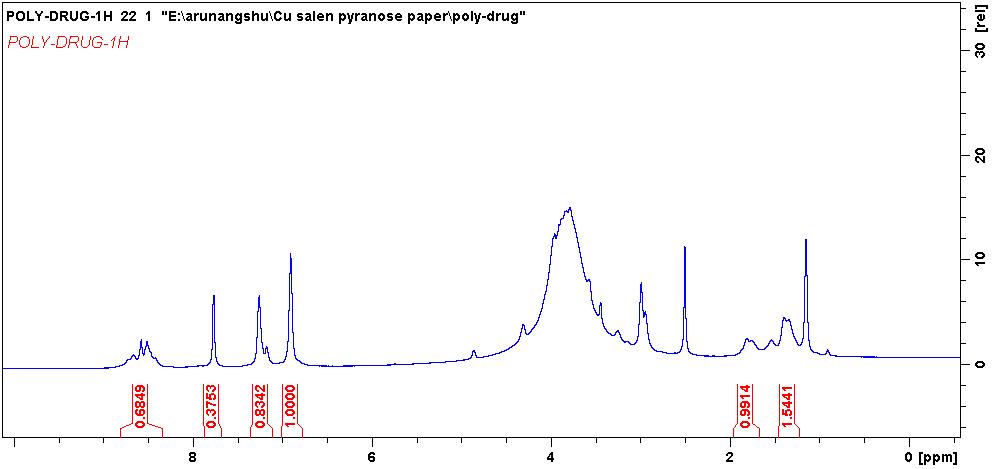
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**Figure S12: 1H NMR spectra of the polyesterurethane polymer 1 in DMSO-d6.**

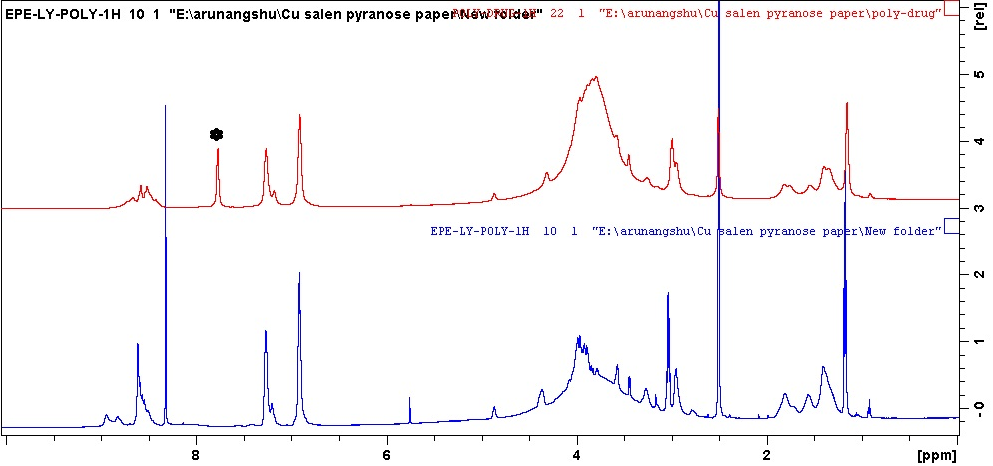
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**Figure S13: 1H NMR spectra of ring opened diol 3 (bottom) and the polyesterurethane polymer 1 (top).**

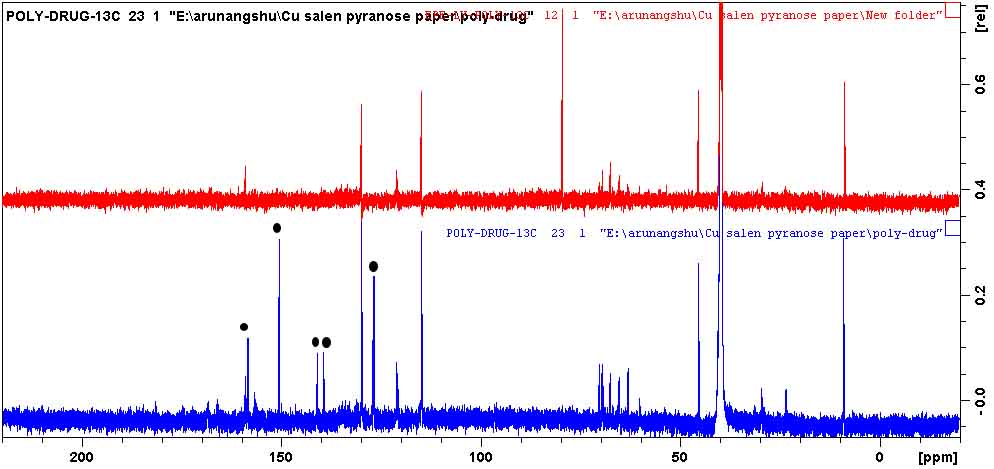
**Figure S14: 13C NMR spectra of the polyesterurethane polymer 1 in DMSO-d6.**

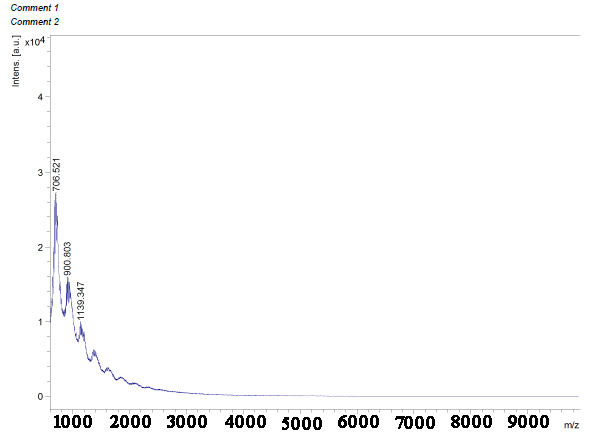
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**Figure S15: 1H NMR spectra of the 5-fluorouracil encapsulated polyesterurethane polymer 1 in DMSO-d6.**

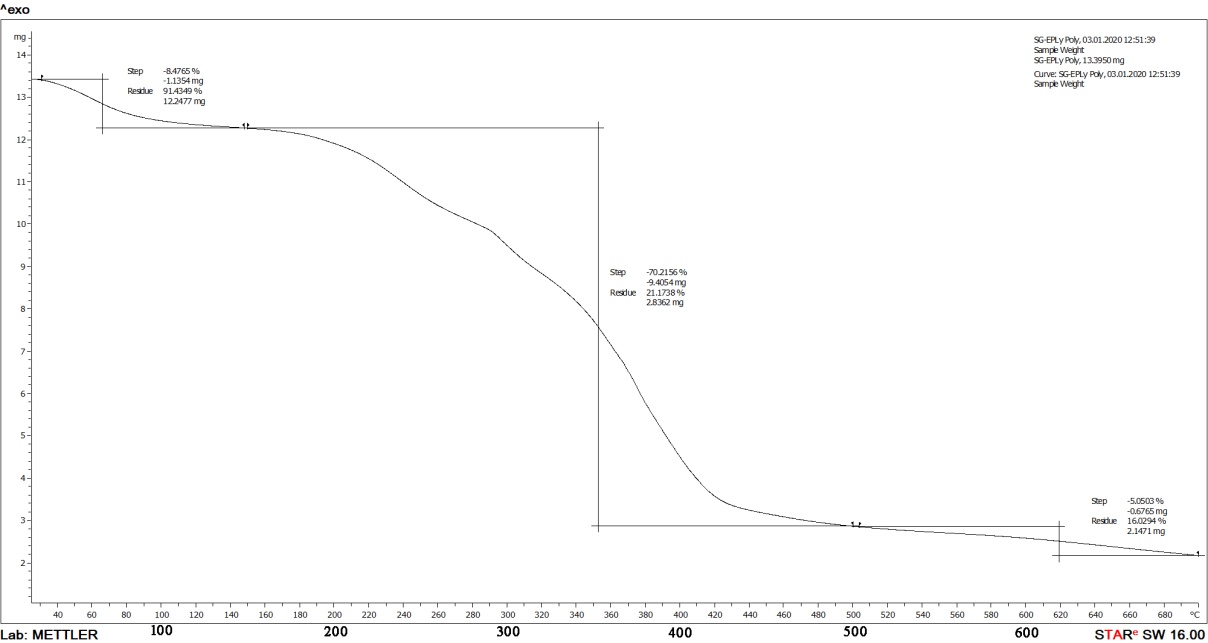
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**Figure S16: 1H NMR spectra of the 5-flurouracil encapsulated polymer 1 (above) and polyesterurethane polymer 1 (bottom) in DMSO-d6.**

** Figure S17: 13C NMR of polymer 1 (above) and 5-fluro uracil encapsulated polyesterurethane polymer 1(bottom) in DMSO-d6.**

**ep-ly-poly.tifFigure S18: IR spectra of the polyesterurethane 1.**

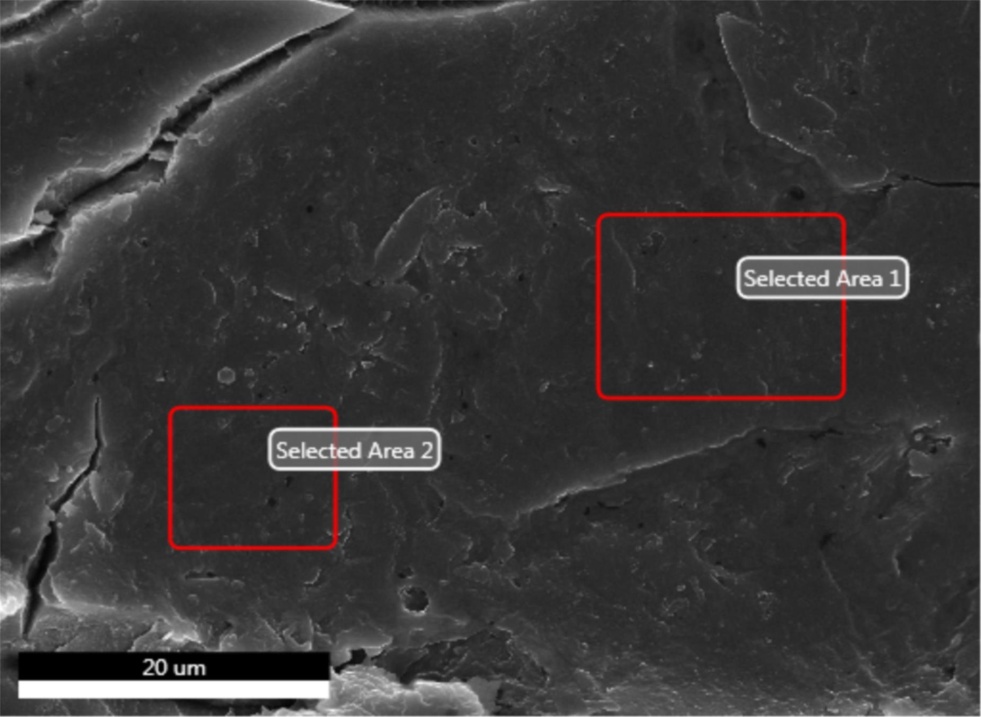
**Figure S19: MALDI Mass of the polyesterurethane 1 done in solid state with dithranol matrix in 1:1 ratio.**

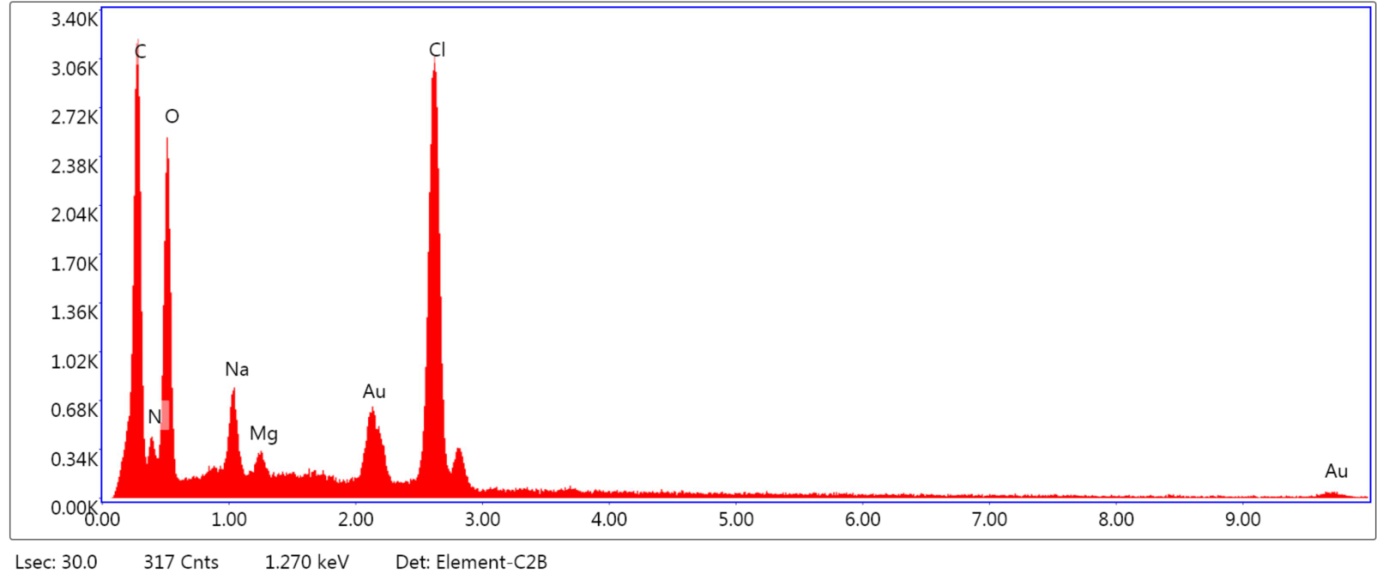
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**Figure S20: TGA data of the polyesterurethane 1.**

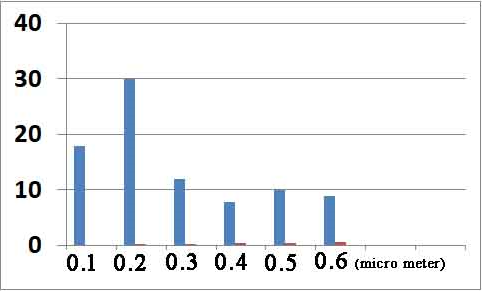
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**Figure S21: IR spectra of the 5 Fluro Uracil-polyesterurethane 1 composite.**

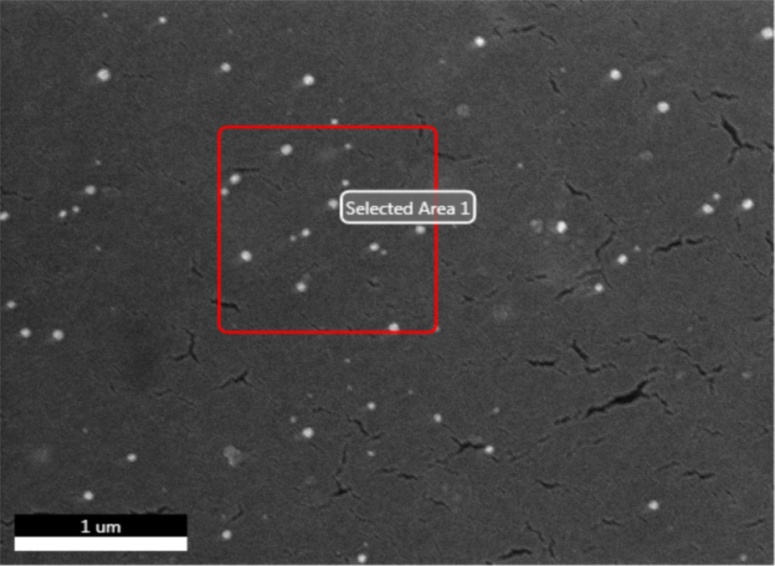
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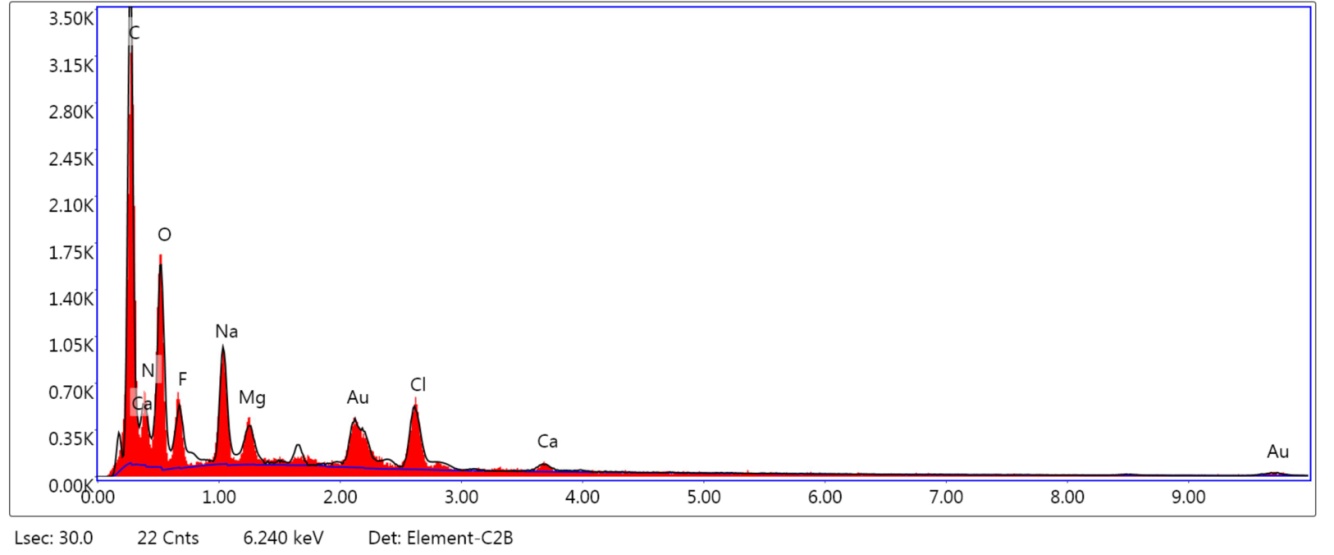
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**Figure S22: EDX spectra of the polyesterurethane 1.**

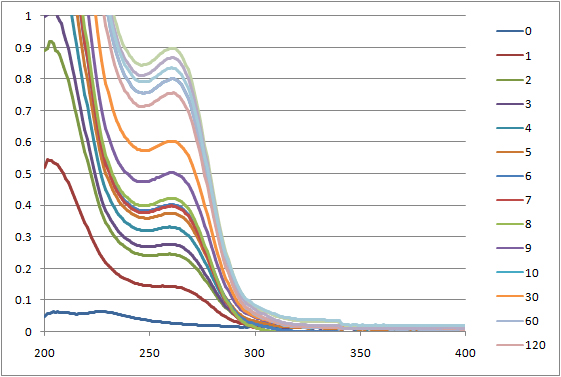
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**Figure S23: Pour size distribution of the polyesterurethane material 1**

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**Figure S24: EDX spectra of 5 Fluro Uracil-polyesterurethane composite 1.**

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**Figure S25: Kinetic study of release of 5-Fluro Uracil from 5-Fluro Uracil-Polyesterurethane 1 composite via UV vis spectroscopy.**