Supramolecular Hair Dyes: A New Application of Cocrystallization

Electronic Supplementary Information:

SI-1) Crystallographic details

Crystal Structure Refinement

Good quality crystals were selected using an optical microscope, glued to a glass fibre by using an adhesive, and mounted on the goniometer for data collection. X-ray diffraction intensities were collected using a Bruker Apex II diffractometer with an Incotec IμS microsource (using Mo *K*α radiation (λ=0.71073 Å)). All the crystals diffracted well. The data was integrated by Bruker SAINT suite of program. [1] It was followed by absorption correction by multi-scan methods, (*SADABS*; Bruker, 2007).[1] The structures were solved by using SHELXS[1] and refined by full-matrix least-squares against F^2 using all data (SHELXL). [1] In the **PPD**-Lawsone salt, substitutional disorder was found in a hydrogen atom and a hydroxyl group of the lawsone molecule. The disorder was solved by placing both of these groups (H and OH) on the same carbon with half the occupancy. All the structural refinements converged to good R factors.

SI-Table 1 (Crystallographic Tables)

	p-Phenylenediamine + sebacic acid	p-Phenylenediamine + trimesic acid + methanol	p-Phenylenediamine + lawsone
Crystal data			
Chemical formula	$C_{10}H_{16}O_4·2(C_6H_9N_2)$	$C_9H_5O_6·C_6H_9N_2·CH_4O$	$2(C_{10}H_5O_3)·C_6H_{10}N_2$
M_r	418.53	350.32	456.44
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$	Monoclinic, $C2/m$
Temperature (K)	-150.15	-150.15	-150.15
a, *b*, *c* (Å)	9.1366 (7), 6.2639 (6), 20.6631 (16)	3.9902 (2), 17.0520 (9), 23.5518 (12)	14.204 (3), 8.573 (2), 8.3934 (19)
α, β, γ (°)	90, 94.489 (5), 90	90, 90, 90	90, 91.851 (13), 90
V (Å^3)	1178.94 (17)	1602.49 (14)	1021.5 (4)
Z	2	4	2
μ (mm^{-1})	0.08	0.12	0.11
Crystal size (mm)	0.45 × 0.40 × 0.36	0.40 × 0.20 × 0.15	0.20 × 0.15 × 0.12
Data collection			
T_{min}, T_{max}	0.611, 0.746	0.683, 0.746	0.537, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8666, 2570, 2257	13202, 3235, 3031	4626, 985, 737
R_{int}	0.031	0.029	0.066

$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.642	0.625	0.602
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.072, 0.189, 1.21	0.030, 0.074, 1.06	0.098, 0.257, 1.13
No. of reflections	2570	3235	985
No. of parameters	204	298	90
No. of restraints	0	0	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	All H-atom parameters refined	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 2.1065P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 0.299P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 10.3813P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.32, -0.32	0.15, -0.18	0.40, -0.56
Absolute structure	-	Flack x determined using 1143 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons and Flack (2004), Acta Cryst. A60, s61).	–
Absolute structure parameter	-	-0.2 (4)	–

	N-Phenyl-p-phenylenediamine + diglycolicacid (Form1)	N-Phenyl-p-phenylenediamine + diglycolicacid (Form2)
Crystal data		
Chemical formula	$2(C_{12}H_{12}N_2)\cdot 2(C_4H_6O_5)$	$2(C_{12}H_{12}N_2)\cdot 2(C_4H_6O_5)$
M_r	636.65	636.65
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pca2_1$
Temperature (K)	-150.15	22.85
a, b, c (Å)	19.0949 (19), 9.2904 (9), 17.9875 (19)	17.9195 (15), 9.1323 (8), 18.7653 (15)
α, β, γ (°)	90, 110.543 (5), 90	90, 90, 90
V (Å^3)	2988.0 (5)	3070.9 (4)
Z	4	4
μ (mm^{-1})	0.11	0.10
Crystal size (mm)	0.45 × 0.20 × 0.10	0.40 × 0.20 × 0.15
Data collection		

$T_{\min}$, $T_{\max}$	0.556, 0.745	0.727, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	47123, 5913, 4108	41535, 5837, 5545
R_{int}	0.059	0.027
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.619	0.626
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.242, 1.63	0.027, 0.065, 1.05
No. of reflections	5913	5837
No. of parameters	555	523
No. of restraints	0	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 0.5084P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rangle_{\max}$, $\Delta\rangle_{\min}$ (e Å^{-3})	0.45, -0.39	0.18, -0.17
Absolute structure	–	Flack x determined using 2341 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons and Flack (2004), Acta Cryst. A60, s61).
Absolute structure parameter	–	0.25 (19)

Computer programs: Bruker *APEX2*, Bruker *SAINT*, *SHELXS97* (Sheldrick, 2008), *SHELXS97* (Sheldrick 2008), *SHELXL97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013), Bruker *SHELXTL*.

SI-2) Experimental Details

SI-2a) Materials Used

All the chemicals were purchased from Sigma-Aldrich, and used as such without purification.

SI-2b) Small scale Liquid-assisted grinding (LAG) experiments:

Small scale **LAG** experiments were carried out using Retsch MM400 ball and mill. The reactants were mixed in the grinding jars containing two 8mm diameter steel balls, in the ratios shown in SI-Table 2. The jars were tightly closed after adding 50μL of methanol. The grinding was done for 90 minutes at a frequency of 30Hz/sec. The materials were recovered by scratching the jars with the help of a spatula.

SI - Table 2: The quantities of each component material used in LAG experiments in mg.

LAG experiment between **PPD** and Sebacic acid (**SebA**)		
Ratio of **PPD** & **SebA**	Weight of **PPD**	Weight of **SebA**
2:1	216mg	202mg
LAG experiment between **PPD** and trimesic acid (**TMA**)		
Ratio of **PPD** & **TMA**	Weight of **PPD**	Weight of **TMA**
1:1	108mg	210mg
LAG experiment between **PPD** and Lawsone (**L**)		
Ratio of **PPD** & **L**	Weight of **PPD**	Weight of **L**
1:2	108mg	348mg
LAG experiment between **NPPPD** and Diglycolic acid (**DGA**)		
Ratio of **PPD** & **DGA**	Weight of **NPPPD**	Weight of **DGA**
1:1	184mg	134mg
SI-Table 2		

SI-2c) Bulk preparation of PPD-SebA salt by Liquid-assisted grinding (LAG):

Fifty 12mm balls were put in the milling jar of Griffin and George vibratory ball mill containing 144g of **PPD**, 134.66 g of **SebA** and 10ml of methanol for grinding. The milling experiment was carried out for 90 minutes with vibratory frequency of 1450 revolutions per minutes. At the end of the experiment pinkish-white material was recovered using spatula.

SI-2d) Bulk preparation of PPD-SebA salt by solution crystallization:

144g of **PPD** and 134.66 g of **SebA** were separately dissolved in 500ml of methanol by heating (50°C) and stirring and later mixed together. The solution was kept at ambient temperature till full evaporation, which resulted in blackish-blue crystals.

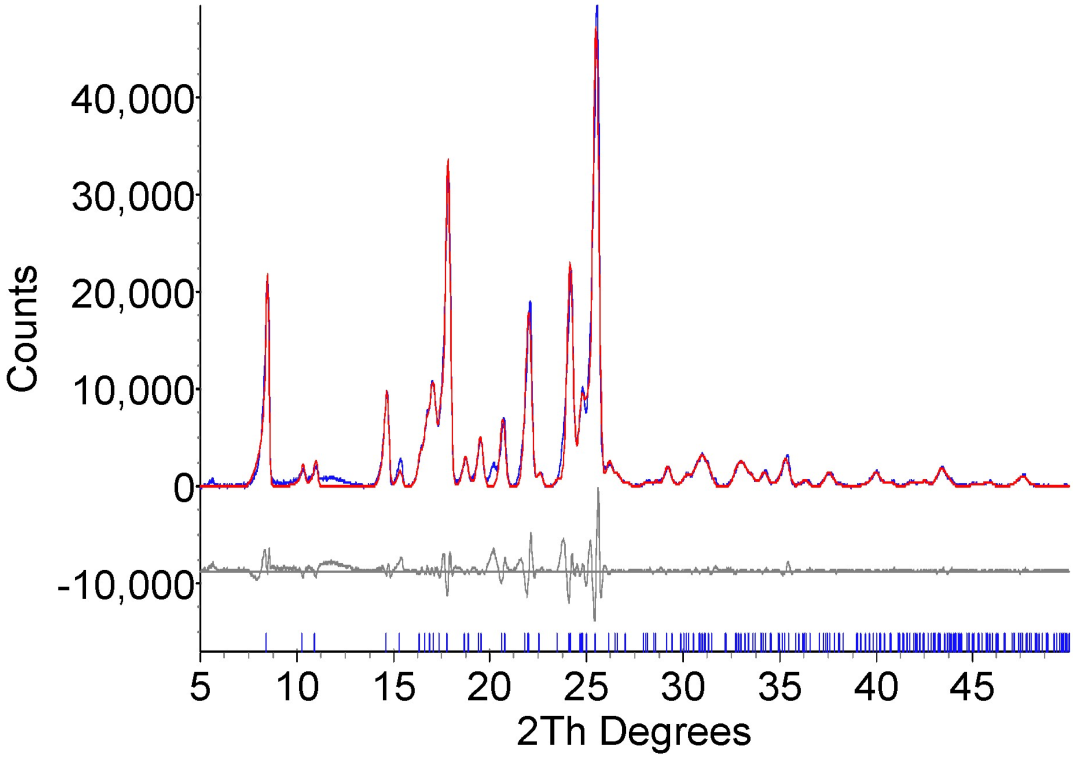
SI-2e) Preparation of concentrated methanolic solution of PPD-SebA salt:

Dissolved 10.5g of **PPD- SebA** salt (obtained from the bulk solution crystallization from methanol as a solvent) in 30ml of methanol by stirring at room temperature. The solution was kept for evaporation for 4 days. After the 4 days some material precipitated. The supernatant liquid was used in the formation of hair dye paste formulation.

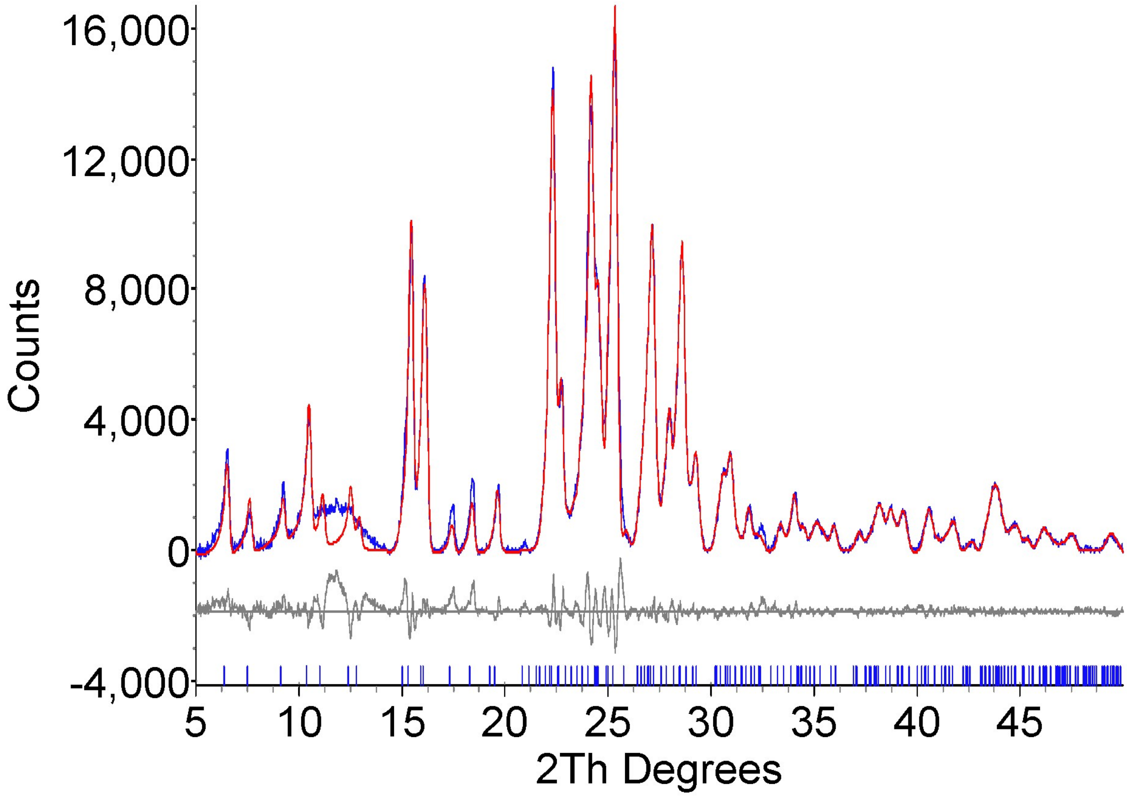
SI-2f) Absorption Spectroscopy: Absorption spectra were collected in the range of 380 to 800 nm using Cary® 50 UV-Vis spectrophotometer. The samples were prepared in methanol (by dissolving 8-10mg of sample in 10ml of methanol) and the solvent corrections were applied.

SI-2g) SEM: Scanning electron microscopy (SEM) was carried out in a Hitachi SU6600 field emission electron gun set at an accelerating voltage of 20keV. The hairs were gold coated before analysis.

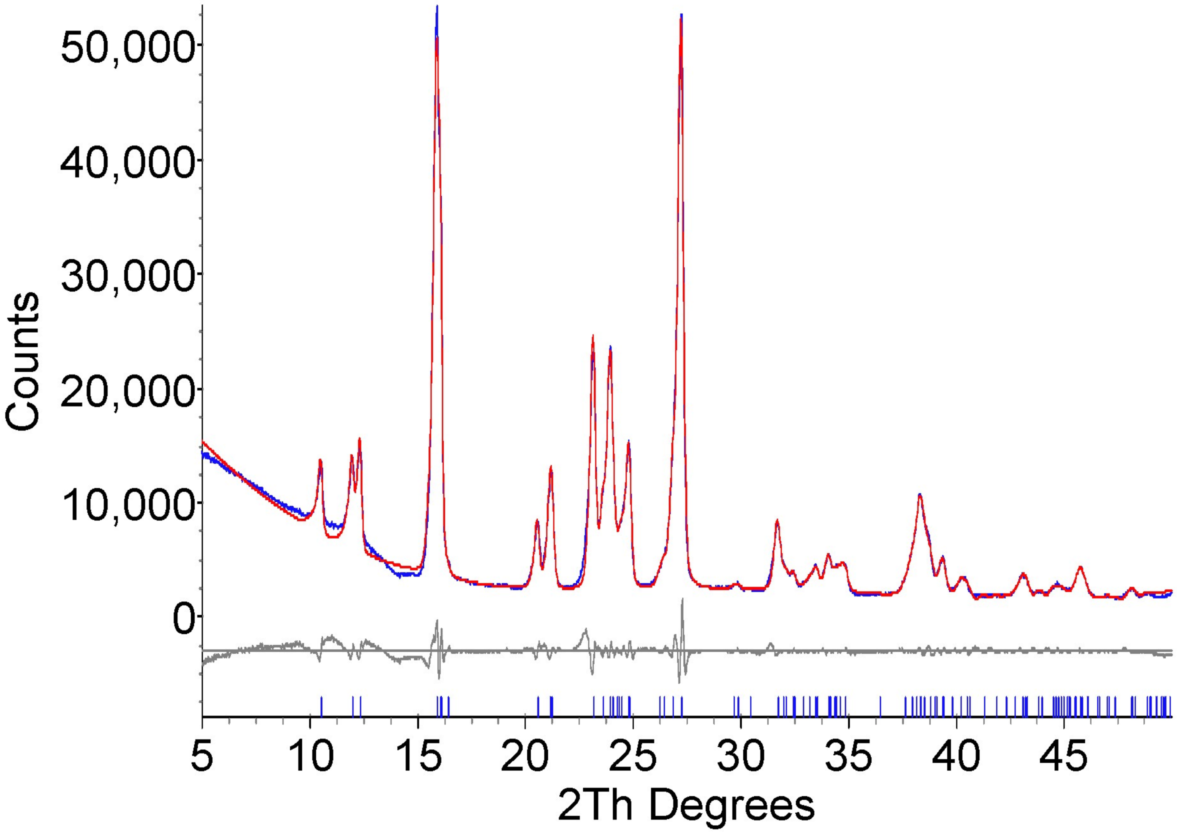
SI-3) PXRD patterns: The samples were thoroughly ground using a mortar and pestle before analysis. PXRD patterns were measured in the 2θ range of 5-50° (scan size 0.15°sec^{-1}) at ambient temperature using BRUKER D8 ADVANCE with DAVINCI (2010) instrument. A Cu (λ = 1.56 Å) X-ray source was used and the X-ray tube was set to 40kV and 40mA. The experimentally observed PXRD patterns (Blue) were Pawley fitted with the PXRD pattern generated (red) using the unit cell information obtained from the crystal structures[2]. The difference plot (Yobs-Ycalc) are shown in black. The peaks matched well in all the cases, as shown in the difference plots. There are slight humps in the background at ~10° 2θ that could be attributed to the potential amorphisation of our material as we ground the samples. Table SI-3 shows the refined unit cell parameters for each of the bulk phases and compare favourably with those parameters from the single crystal experiment.



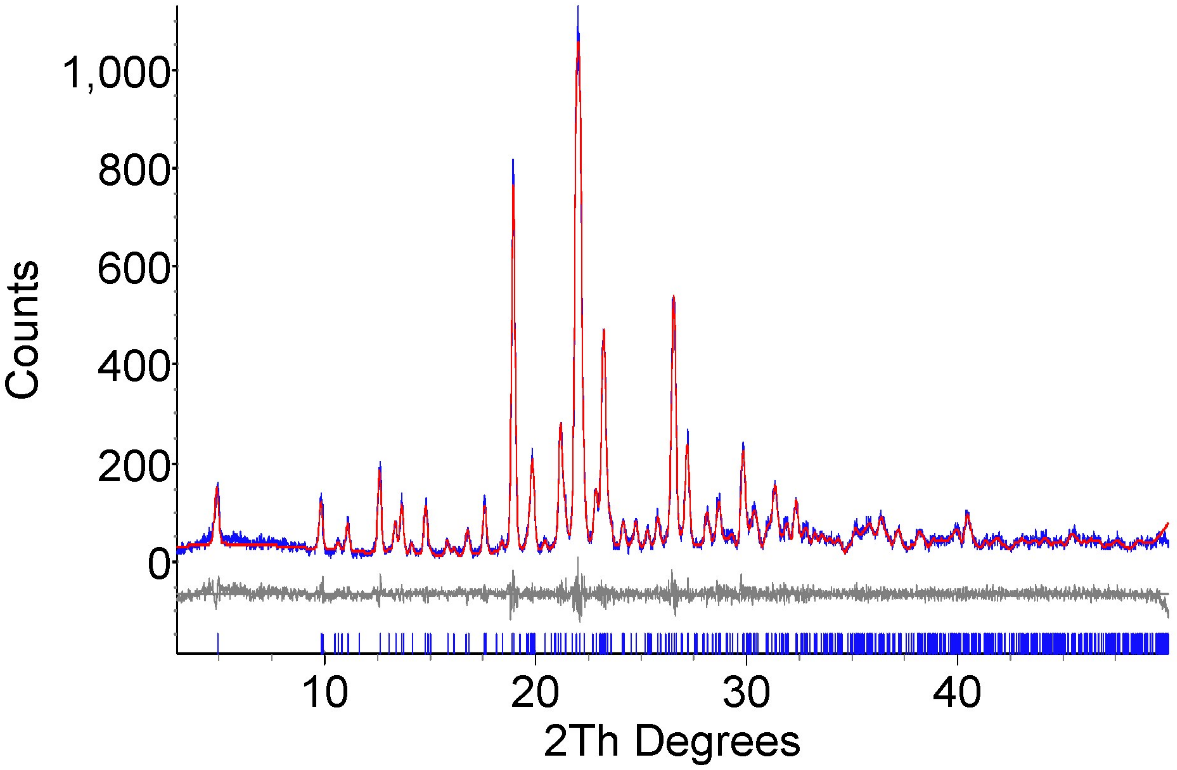
SI-3a: Pawley fitted PXRD patterns of salt between **PPD** and Sebacic acid.



SI-3b: Pawley fitted PXRD patterns of salt between **PPD** and Trimesic acid.



SI-3c: Pawley fitted PXRD patterns of salt between **PPD** and Lawsone.



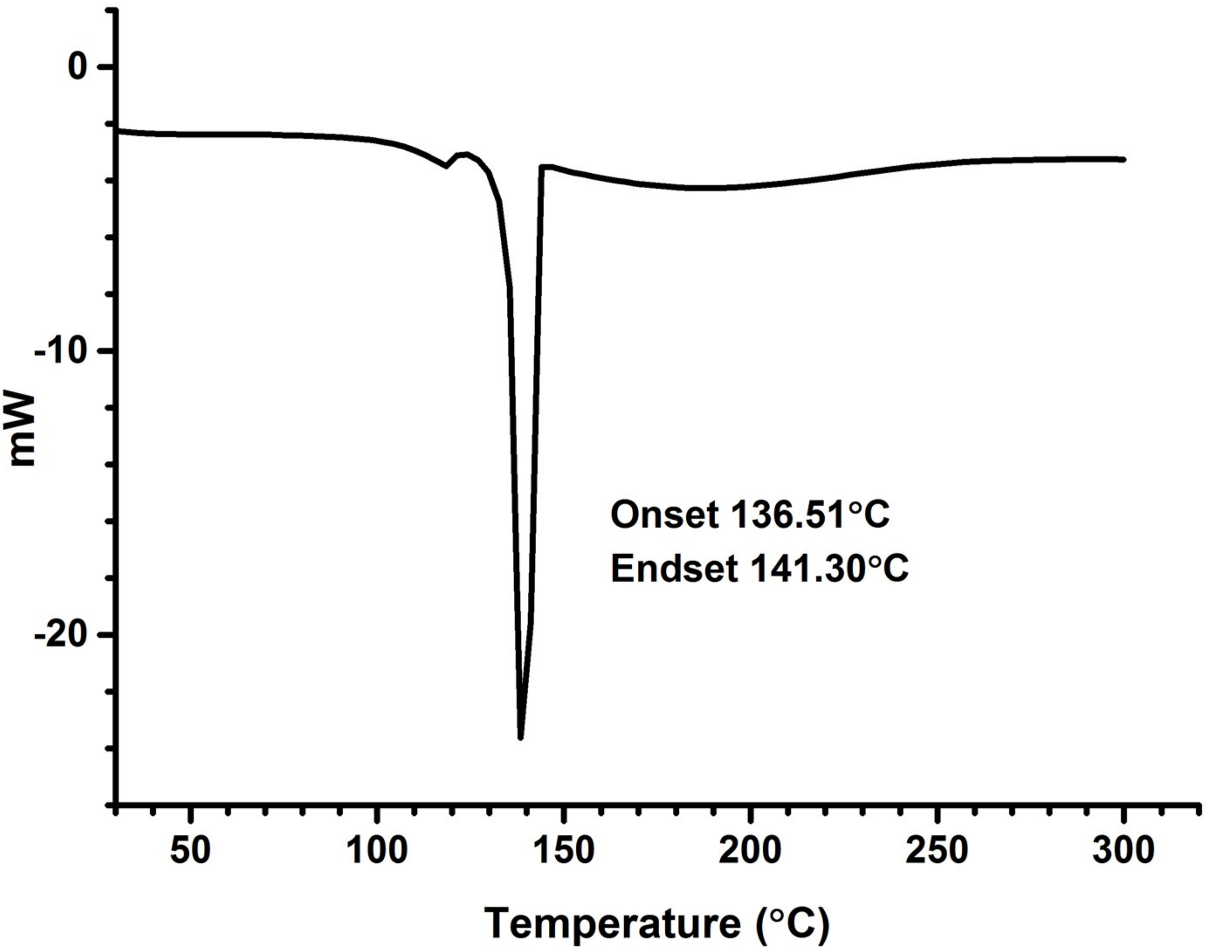
SI-3d: Pawley fitted PXRD patterns of salt between **NPPPD** and Diglycolic acid.

SI-Table 3: Unit cell parameters from the Pawley fits of the four compounds under study. These data were taken at 25°C.

	a (Å)	b (Å)	c (Å)	β (°)	Vol (Å^3)	R_{wp}
PPD-SebA	9.117(6)	6.333(4)	21.07(2)	94.93(4)	1211.7(15)	30.25
PPD-TMA	4.105(2)	17.054(14)	23.592(17)	90	1652(2)	30.45
PPD-L	14.3277(16)	8.6238(9)	8.397(2)	91.132(11)	1037.3(3)	6.67
NPPPD-DGA	19.135(6)	9.355(2)	17.948(12)	110.21(5)	3013(3)	14.12

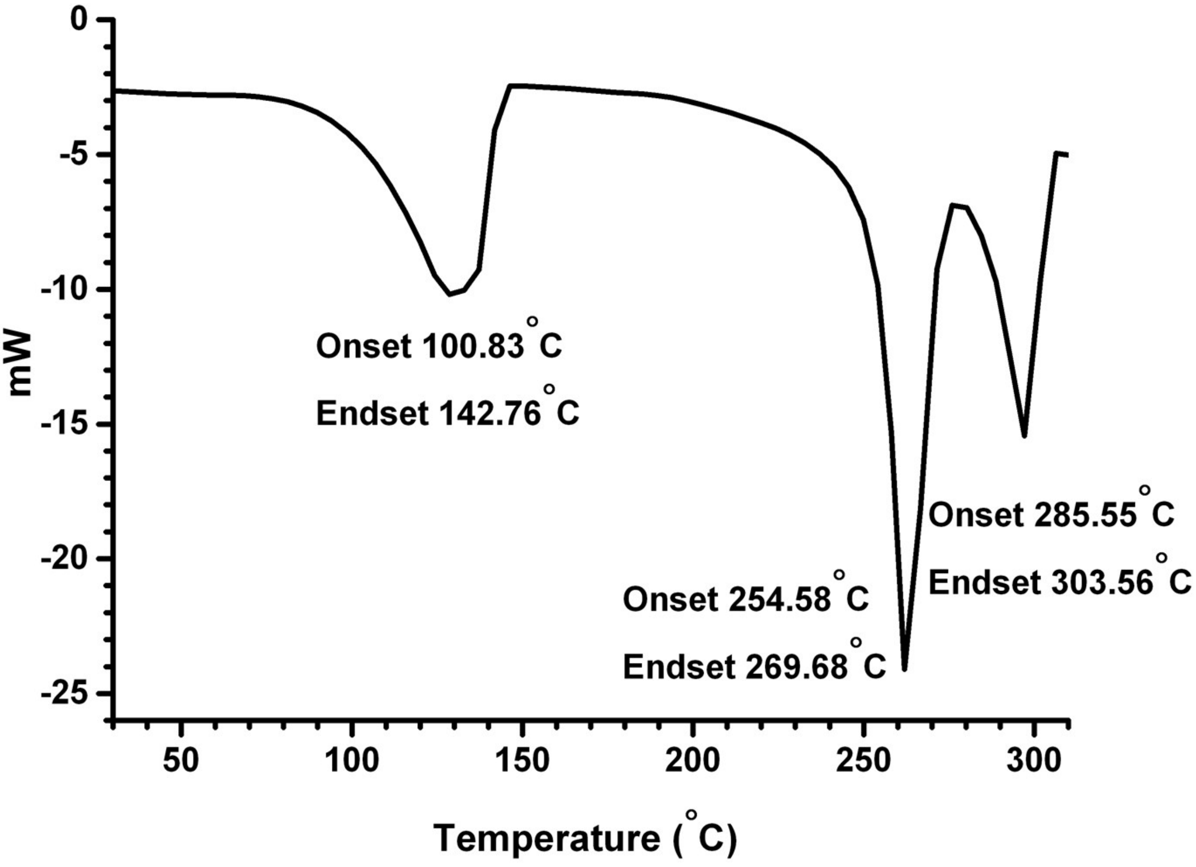
SI-4) DSC Spectra: Finely ground samples of **PPD-SebA** (4.41mg), **PPD-TMA** (9.80 mg), **PPD-L** (8.46mg), and **NPPPD-DGA** (9.71 mg) were weighed into a 40 µL aluminium pan before loading onto a Mettler Toledo DSC822e/400/Rc instrument. All the samples (except **PPD-TMA** which was heated from 30-310 °C) were heating from 30-300 °C at a ramp rate of 10 K min^{-1}. N_2 gas purge was started 30 minutes before the start of the experiment to create the inert atmosphere and was continued throughout the experiment. The trace was analysed in STARe software and OriginPro 9.0.

PPD-SebA shows a sole endothermic event having onset at 136°C which can be assigned to the melting point of the complex (Figure SI-4a) after which there is decomposition that is indicated in the TGA profile (Figure SI-5a). The melting points of **PPD** and sebacic acid are 145 and 131°C, respectively. There is a small event prior to this that may be due some solvent from the crystallisation.



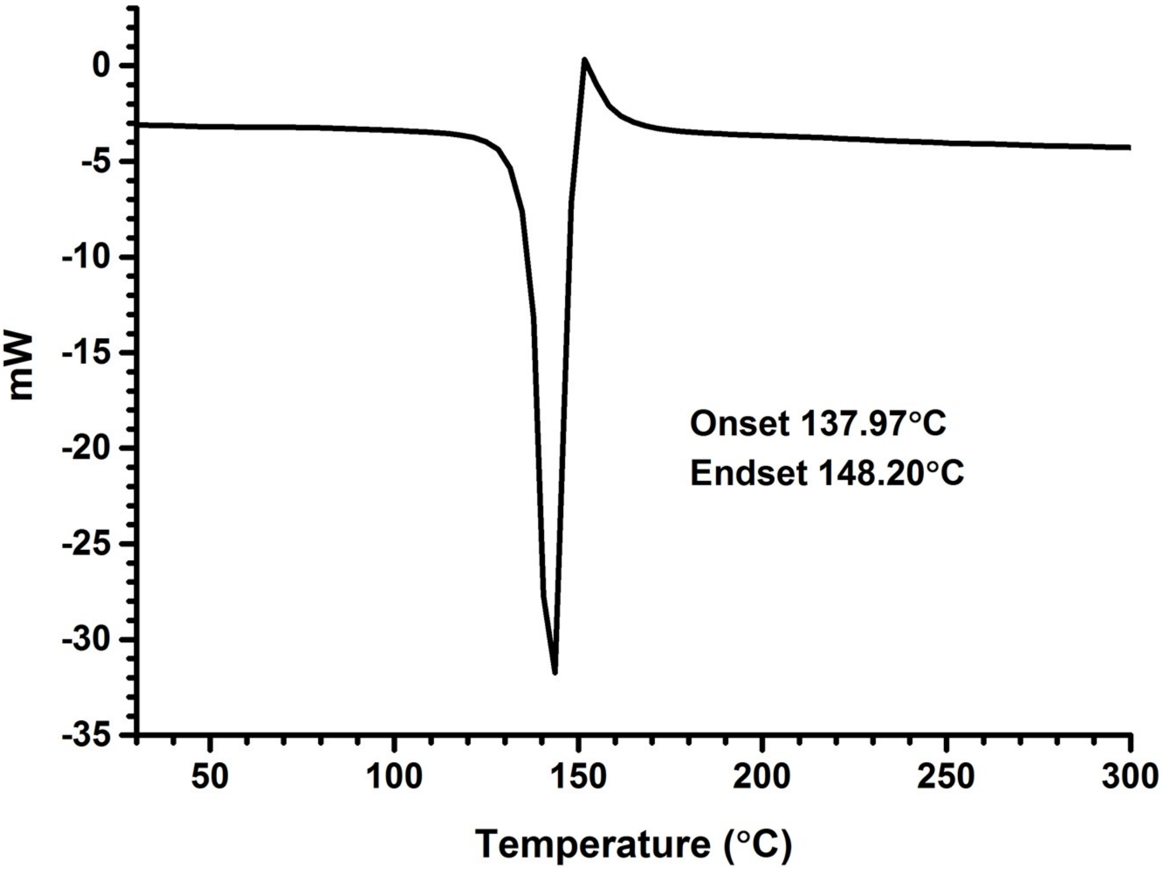
SI-4a: DSC pattern of **PPD** and Sebacic acid.

PPD-TMA shows quite a bit of activity in the DSC patterns (Figure SI-4b). The **PPD-TMA** crystal structure has a methanol in the structure as a solvent of crystallisation. Methanol is approximately 9% of the weight of the material but we only observe 5% leaving as part of the initial loss at ~100°C (Figure SI-5b). This is followed by two endothermic events in quick succession at 254 and 285°C, each with a loss of weight (15% and 8%, respectively). These losses do not correspond to a particular molecular species. The event which started at 285°C may correspond to the decomposition of the salt.



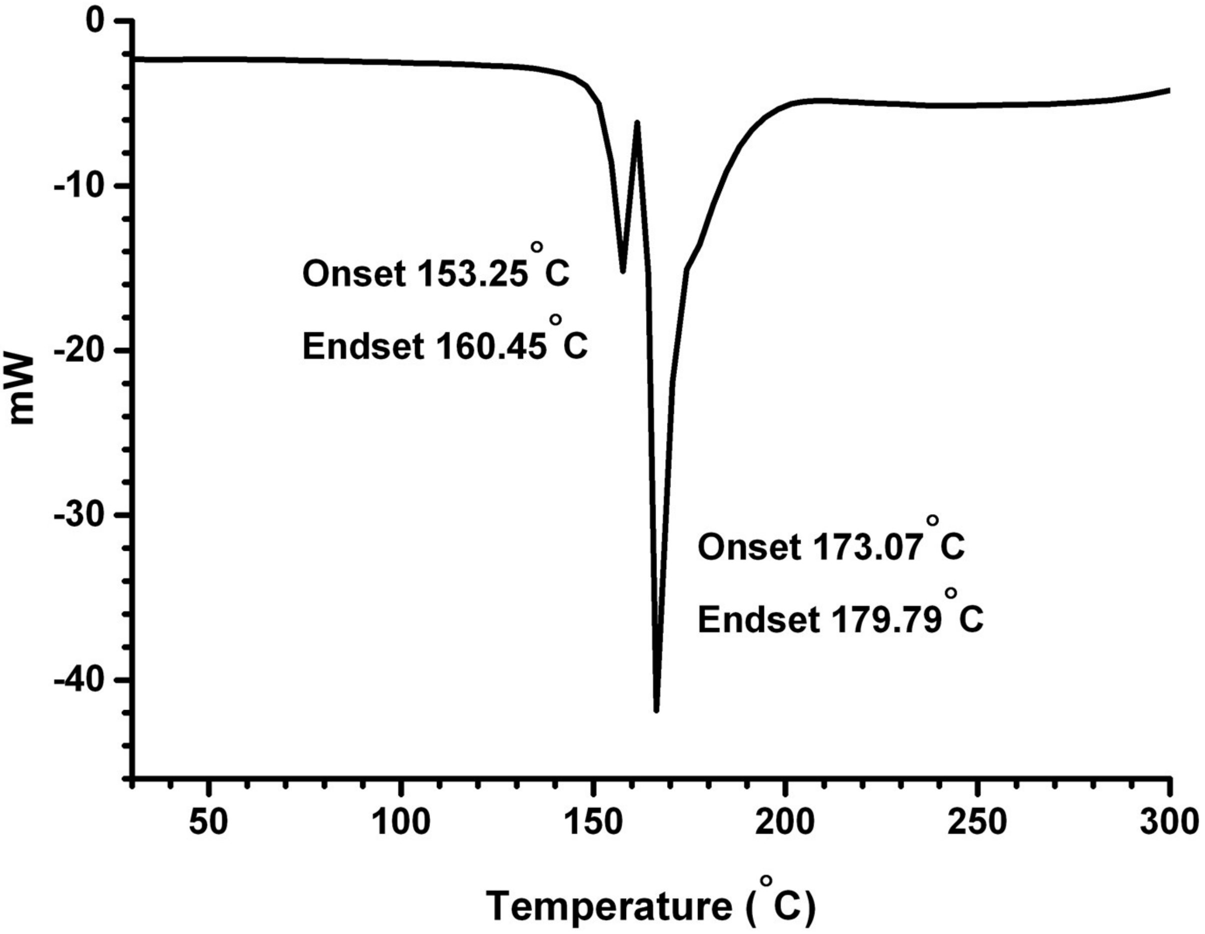
SI-4b: DSC pattern of **PPD** and Trimesic acid.

PPD-L shows only one endothermic peak (having onset at 137.97°C) on heating with 9.42% weight loss, which indicates towards a chemical reaction between **PPD** and lawsone. After this event, a gradual weight loss was observed, which may be either due to the decomposition or gradual evaporation of the material.



SI-4c: DSC pattern of **PPD** and Lawsone.

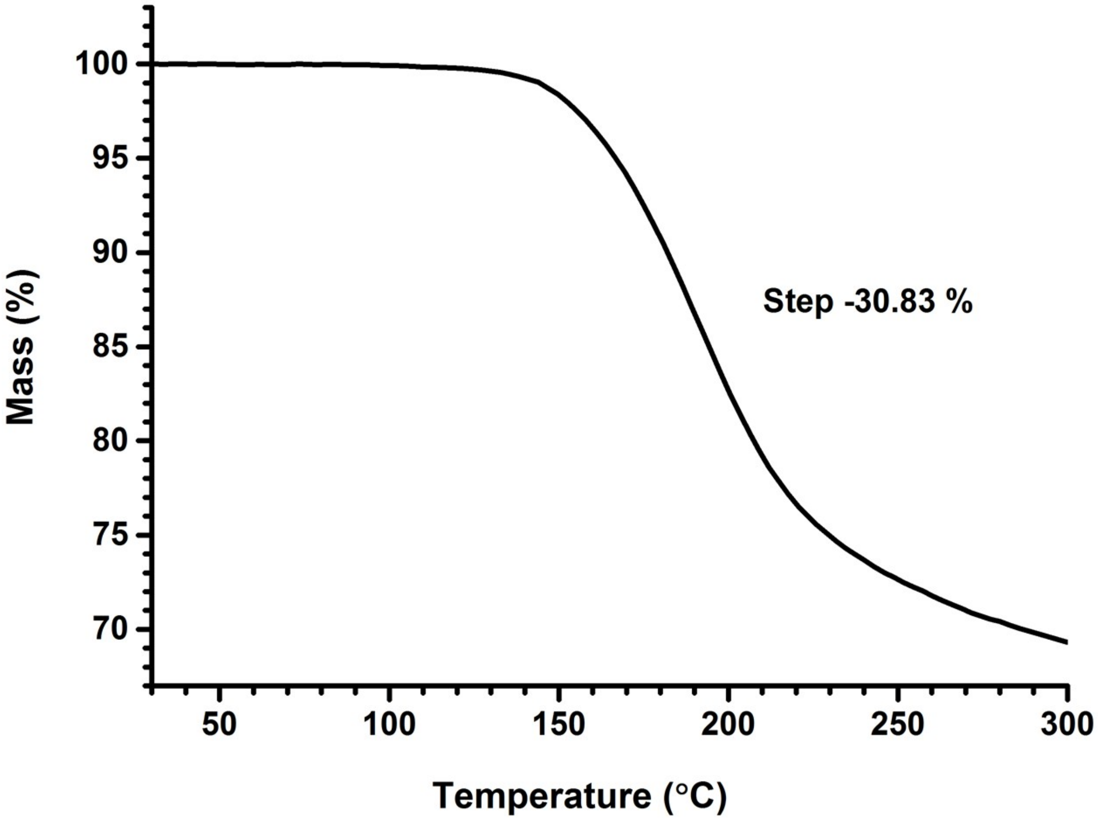
NPPPD-DGA exhibits a main endothermic peak at 173°C but a small one just prior to it at 153°C. From this melting process there is a sharp loss of weight. As with many of the other compounds this loss is not specific to the loss of a particular molecule and so can be attributed to a decomposition product from the reactants e.g. carbon dioxide from the diglycolic acid. After this initial loss the compound appears to have a continual loss of material until the maximum temperature reached.



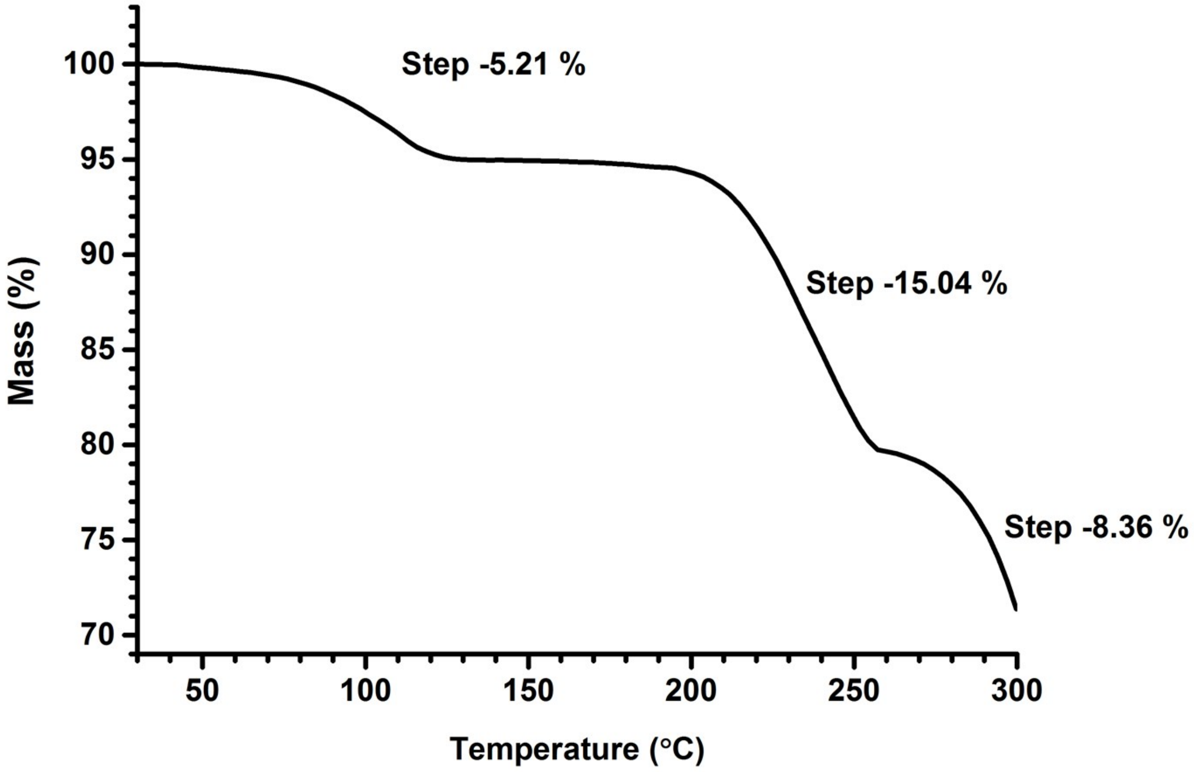
SI-4d: DSC pattern of NP**PPD** and Diglycolic acid.

SI-5) TGA Spectra: Finely ground samples of **PPD-SebA** (8.59mg), **PPD-TMA** (8.45mg), **PPD-L** (6.79mg) were weighed into a 70 µl aluminium pan and loaded into a Mettler Toledo TGA851e/LG/RO instrument (samples) and heating from 30-300 °C at a ramp rate of 10 K min^{-1}. The trace was analysed in STARe software and OriginPro 9.0.

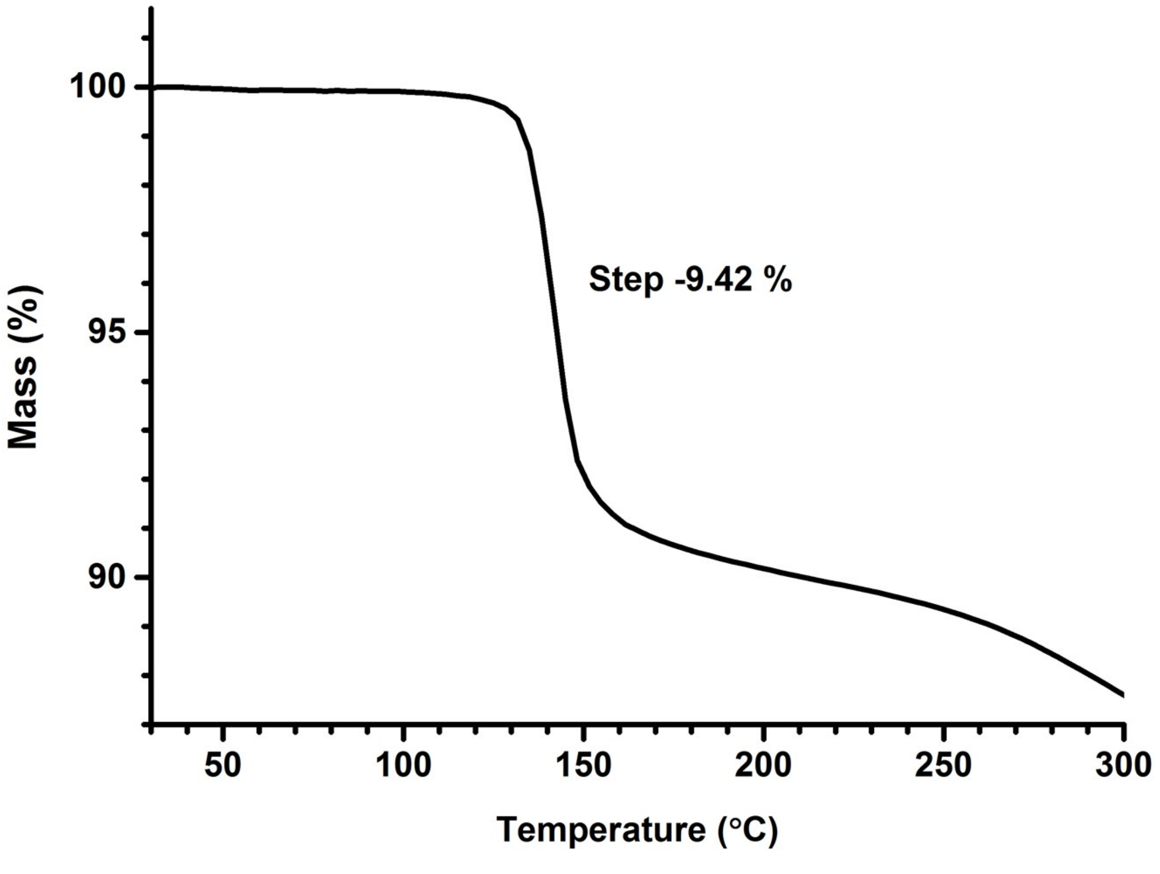
Samples of **NPPPD-DGA** (3.4mg) were weighted into a 40 µL aluminium pan and analysed for TGA in a in the temperature range 30-300 °C at a ramp rate of 10 K min^{-1} using NETSZCH STA 449 F1 Jupiter ® instrument and analysed using OriginPro 9.0



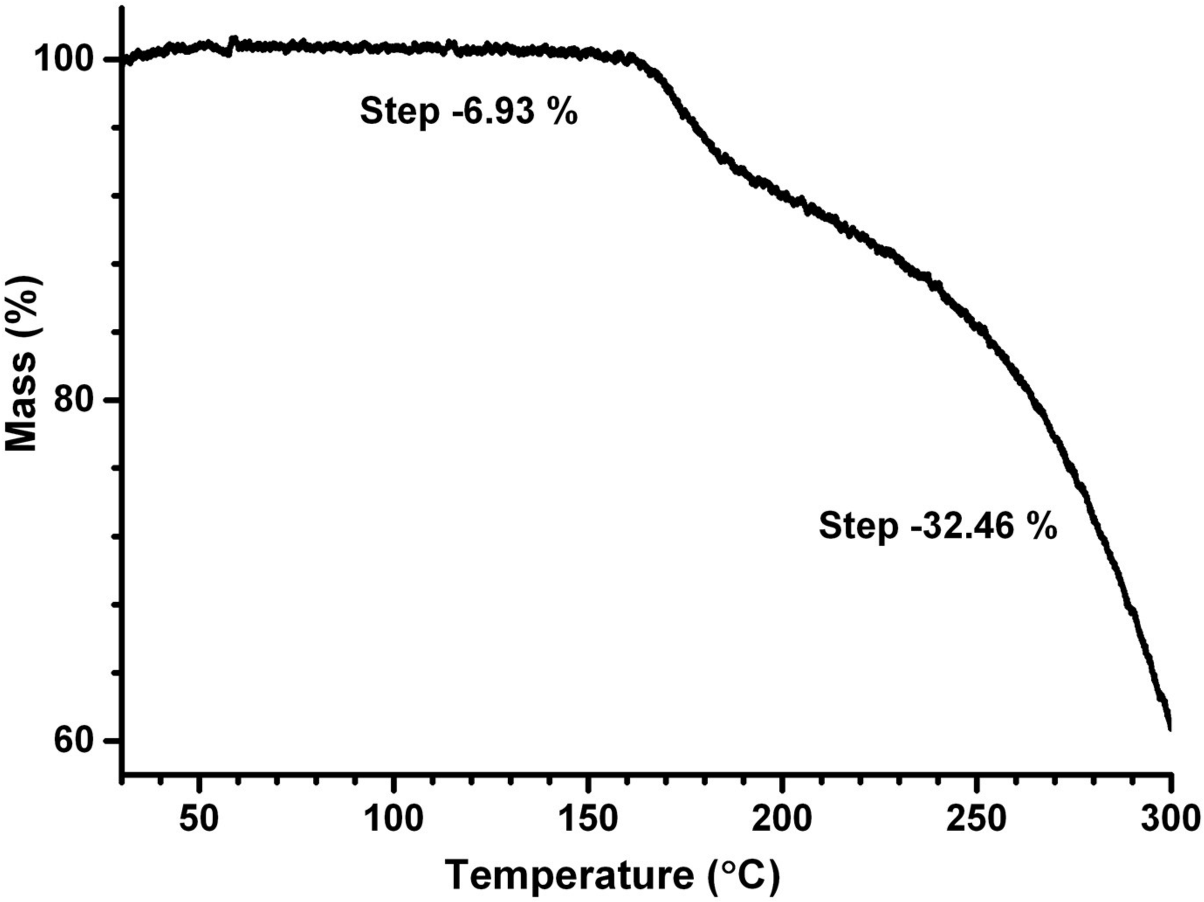
SI-5a: TGA pattern of **PPD** and Sebacic acid. The sample was stable up to melting, after which it gradually decomposed.



SI-5b: TGA pattern of **PPD** and Trimesic acid.



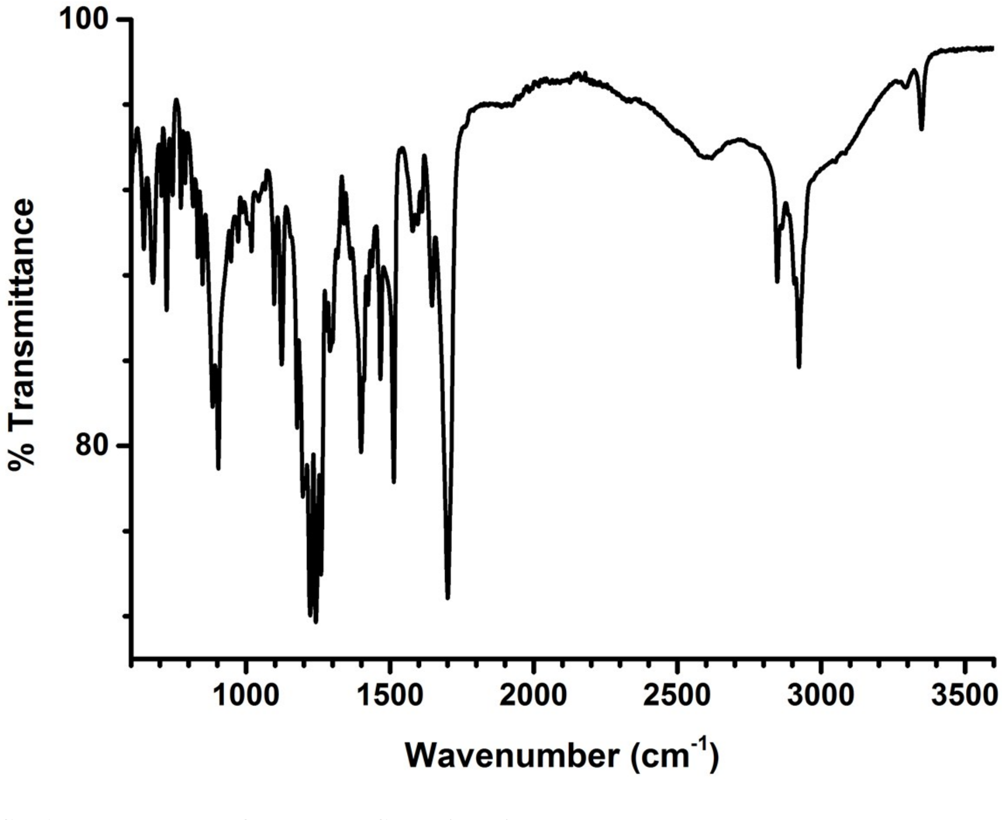
SI-5c: TGA pattern of **PPD** and Lawsone.



SI-5d: TGA pattern of NP**PPD** and Diglycolic acid.

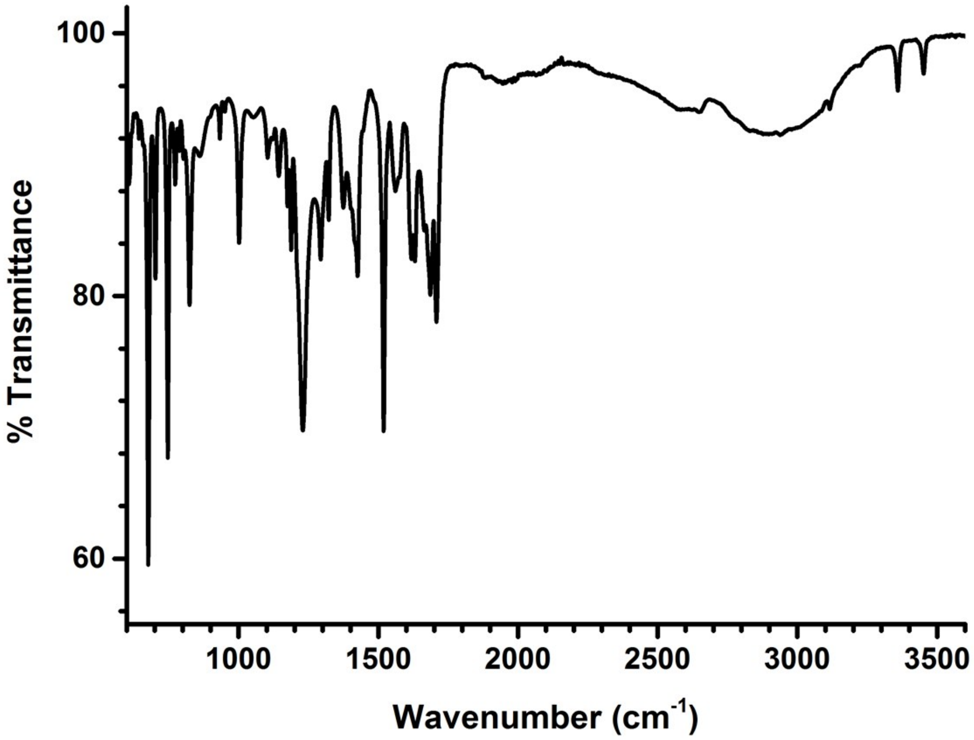
SI-6) IR Spectra: FT-IR data were collected on a ThermoFisher iS10 ATR-IR spectrophotometer in the 600-3600cm^{-1} range. The samples were analyzed by putting them directly onto the ATR crystal and their data was analysed using Omnic software and OriginPro 9.0.

The FT-IR shows the main components expected of the salt formation. The NH stretches are present at 3400 cm^{-1}. The aliphatic CH stretches are clearly apparent appearing below 3000 cm^{-1}. There is a broad underlying feature from 2400-3200 cm^{-1} that would be expected for an ammonium ions. The C=O peak associated with the carboxylic acid has moved to lower wavenumber on formation of the carboxylate salt (~1700cm^{-1}). The two stretches at 1450 and 1600 cm^{-1} that are associated with the aromatic C-C bonds PPD) are clearly represented along with a stretch for long chain carbons at ~900 cm^{-1} (sebacic acid).



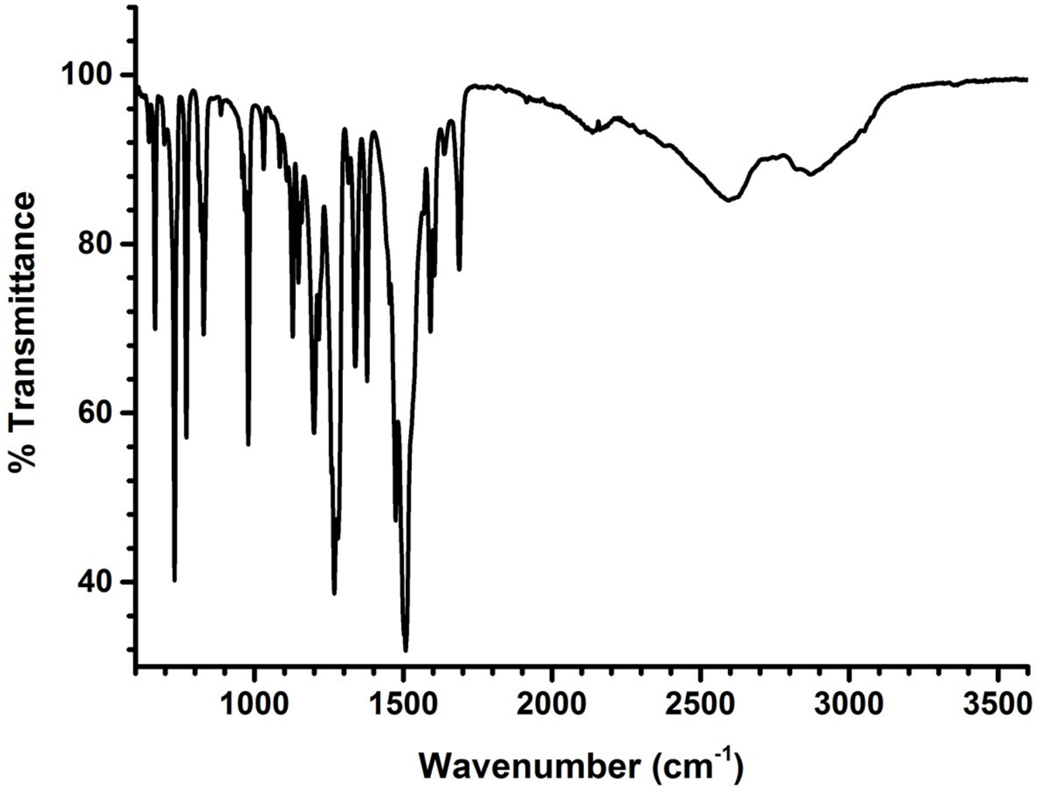
SI-6a: IR pattern of PPD and Sebacic acid.

PPD-TMA clearly shows two sharp bands associated with the amine but also the broad band that can be assigned to the ammonium ion. The area around the C=O stretch (1600-1700 cm^{-1}) shows three peaks that are associated with the acid. All three are a little lower than one would anticipate for a carboxylic acid but these are associated with the hydrogen bonding within the system hence will show a reduced energy. Only one of the acid groups has been converted into the carboxylate ion.



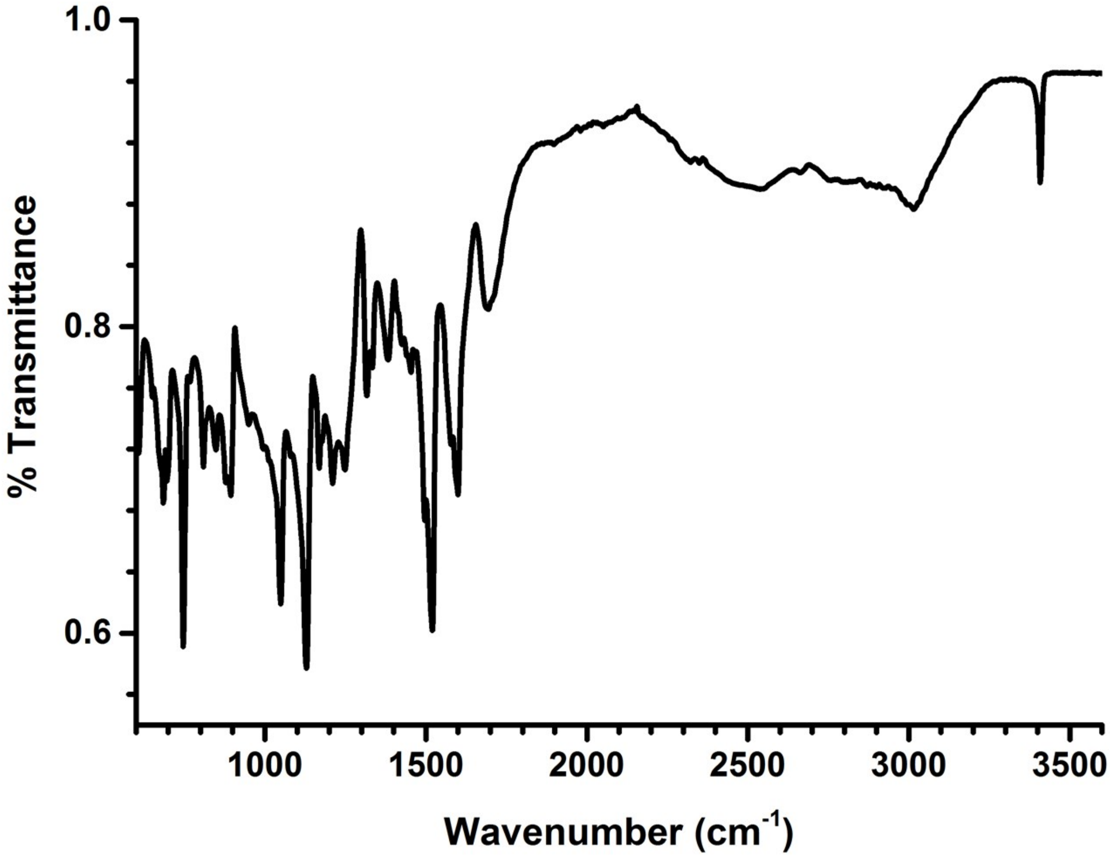
SI-6b: IR pattern of **PPD** and Trimesic acid.

The IR spectrum for **PPD-L** shows that only the ammonium ion is present. There is a representative peak for the C=O bonds in lawsone however this is lower in intensity than one would normally find (1700 cm^{-1}). In this structure there are two sources of aromatic stretches hence there are multiple overlapping peaks around the 1475 and 1600 cm^{-1} regions. The hydroxyl group of lawsone is ionised in this structure and the ionised form will increase the wavenumber of this stretch from 1200 cm^{-1} to 1500 cm^{-1}.



SI-6c: IR pattern of **PPD** and Lawsone.

NPPPD-DGA shows typical peaks for both species present e.g. a single NH stretch for the amine moiety, large extended absorbance due to the ammonium cation that is present. The peak at ~1700 cm^{-1} is broad due to the occurrence the C=O stretches from both the carboxylic acid and carboxylate groups. The presence of the 1450 & 1600 cm^{-1}stretches confirm the existence of the aromatic groups in the solid structure. The two peaks at 1000-1200 cm^{-1} can be attributed to the C-O (ether) and C-N bonds in DGA and NPPPD respectively.



SI-6d: IR pattern of **NPPPD** and Diglycolic acid.

[1] *a) Siemens, **SMART** System, Siemens Analytical X-ray Instruments Inc., Madison, WI (USA), **1995**; b) G. M. Sheldrick, **SADABS** Siemens Area Detector Absorption Correction Program, University of Gottingen, Gottingen, Germany, **1994**; c) G. M. Sheldrick, **SHELXTL-PLUS** program for crystal structure solution and refinement, University of Gottingen, Gottingen, Germany.*

[2] A. Coelho, Coelho Software, **2012**.