SUPPORTING INFORMATION

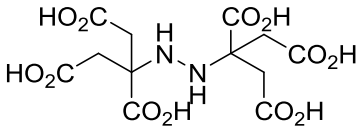
Bio-based Additives as Renewable Alternatives for Polyvinylchloride Formulations and Application in Paper Coatings

Ellana Beard, Michelle Ledward and Natalia Sergeeva*

CONTENT

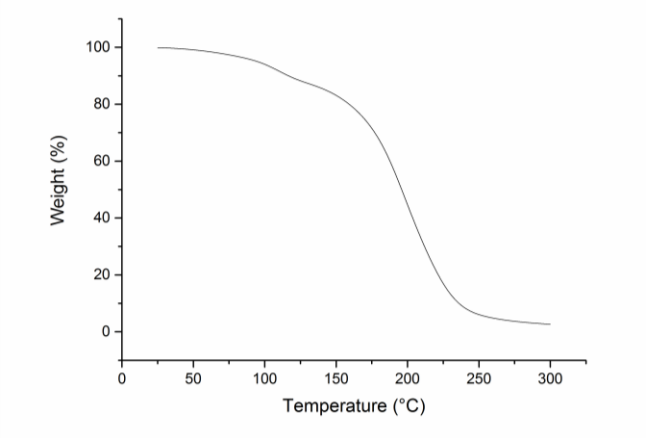
Materials. Citric acid, triethyl citrate, hydrazine monohydrate and phenyl hydrazine were all reagent grade (97 %+) and purchased from Alfa Aesar (UK). PVC plastisol type (commercial code: 1122D) was supplied by G&B Ltd. (UK). Ethanol, acetone and chloroform were all reagent grade and purchased from VWR International (UK)

2,2'-Hydrazobiscitric acid (Compound 1)

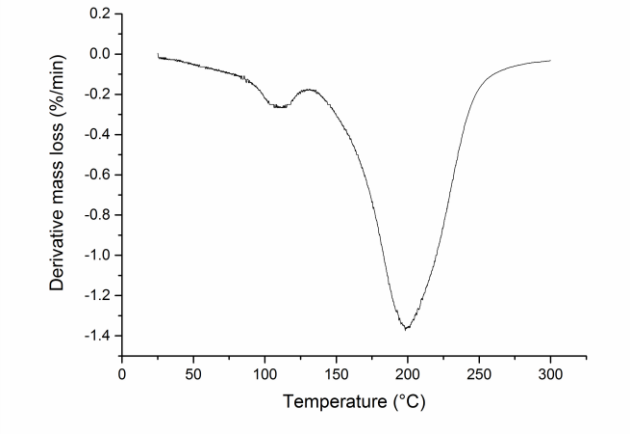


Citric acid (16.52 g, 86 mmol) was dissolved in ethanol (95 mL) with vigorous stirring for 10 minutes. Hydrazine monohydrate (2.2 mL, 43 mmol) was added dropwise to the solution over 15 minutes. The resulting reaction was left to stir for 24 hours at 25 °C to give an off white suspension. The solid impurities were filtered and washed with acetone (3 x 10 mL). The filtrate was concentrated under reduced pressure to yield 2,2'-hydrazobiscitric acid as yellow oil **1** (13.86 g, 36.5 mmol, 85%).

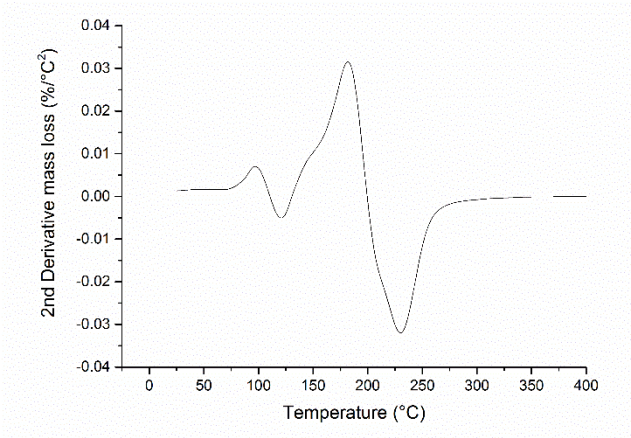
$C_{12}H_{16}O_{12}N_2$. IR (neat): 3436 cm^{-1} (w), 2981 cm^{-1} (w), 2591 cm^{-1} (w), 1704 cm^{-1} (s), 1653 cm^{-1} (w), 1367 cm^{-1} (m); δ_H (500 MHz, D_2O): δ 2.58 (dd, 8H, J = 58.08, 15.23 Hz); δ_C (126 MHz, $CDCl_3$): δ 179.9, 176.6, 74.4, 44.5; ESI-MS: m/z 402.8871 [M+Na].



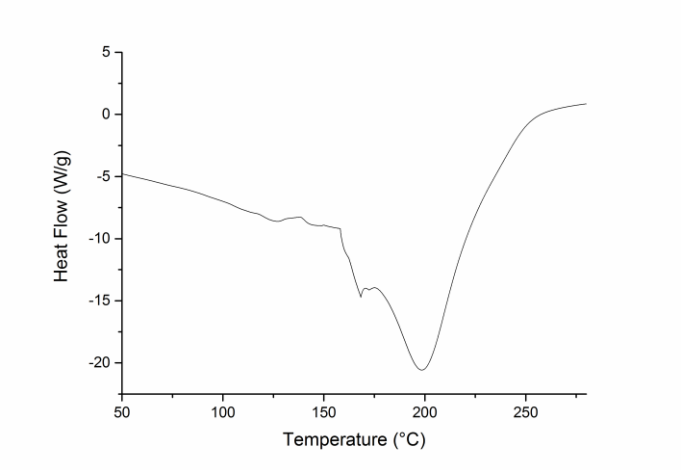
SI Figure 1 TGA graph of compound **1**.



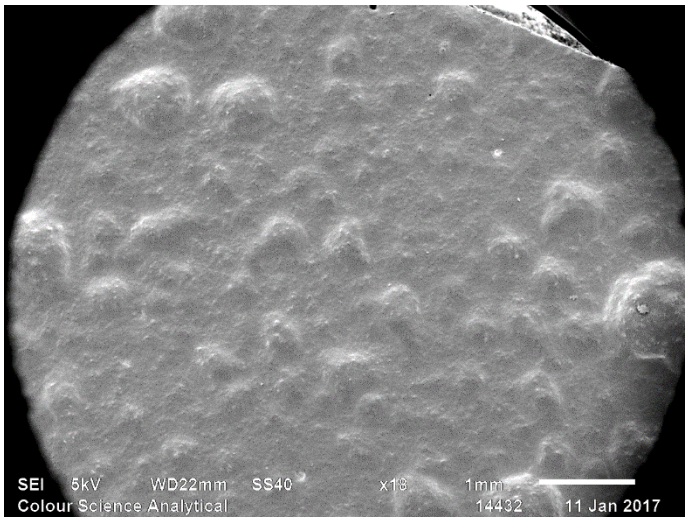
SI Figure 2 DTG graph of compound **1**.



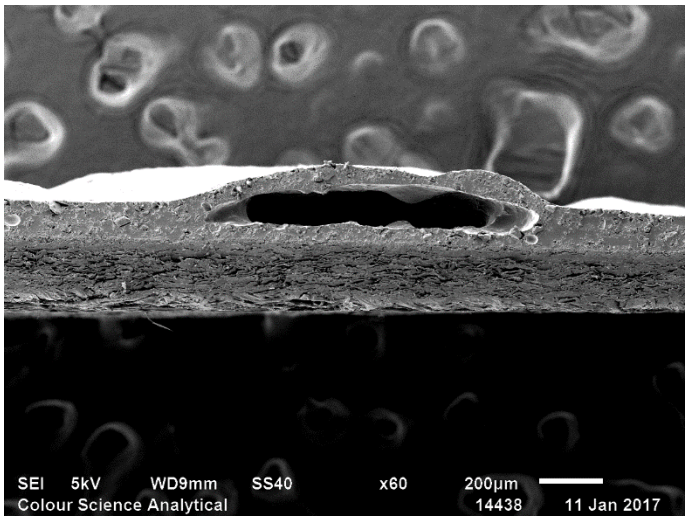
SI Figure 3 D2TG graph of compound **1**.



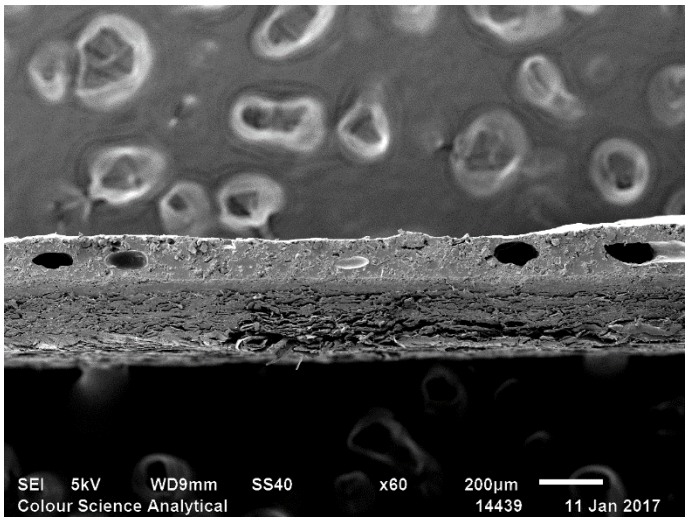
SI Figure 4 DSC graph of compound **1**.



SI Figure 5 SEM image of compound **1** surface.

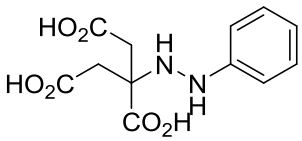


SI Figure 6 SEM image of compound **1** cross section.



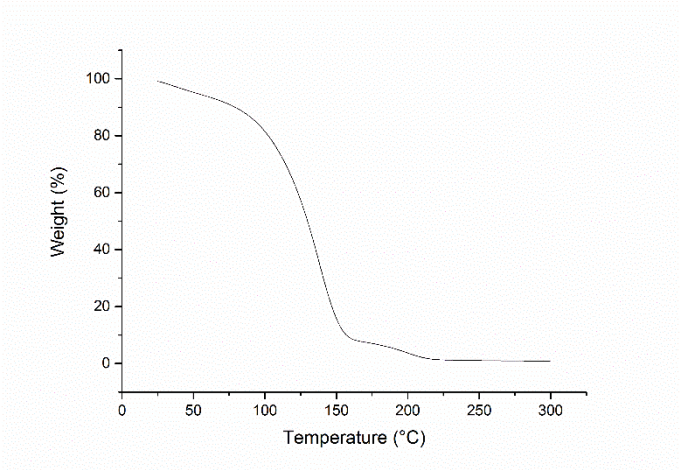
SI Figure 7 SEM image of compound **1** cross section.

2-(2-Phenylhydrazinyl)citric acid (Compound 2)

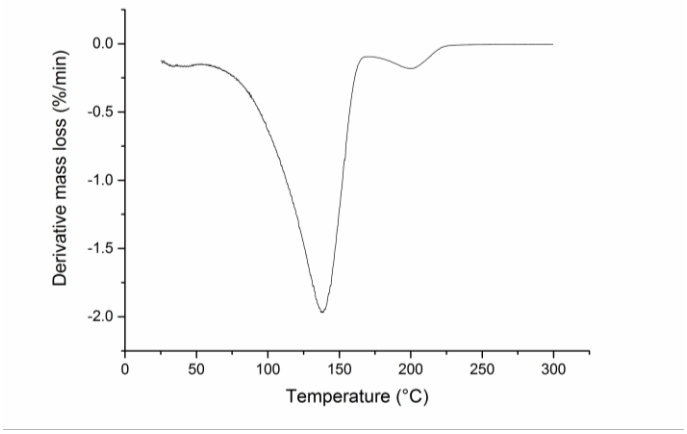


Citric acid (3.83 g, 20 mmol) was dissolved in ethanol (30 mL) under vigorous stirring. Phenyl hydrazine (2.5 mL, 20 mmol) was added dropwise and the solution was left to stir for 18 hours at 25 °C. The solvent was removed under reduced pressure to give crude mixture. This crude product was further dried of organic solvent impurities in a vacuum oven at 60 °C for 96 hours. 2-(2-Phenylhydrazinyl)citric acid was isolated as dark orange oil **2** (5.03 g, 17.8 mmol, 89%).

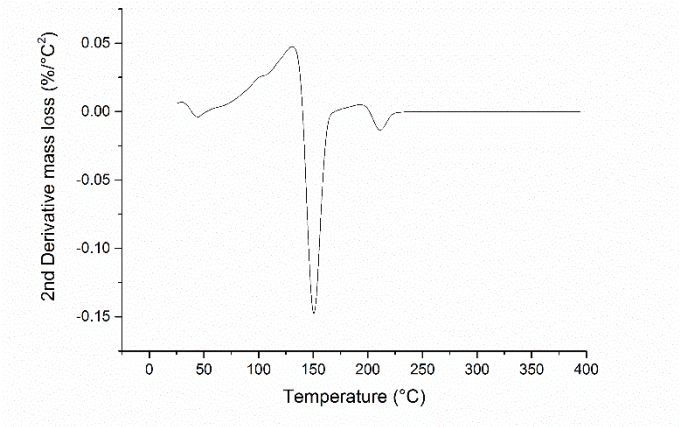
$C_{12}H_{14}O_6N_2$. IR (neat): 2971 cm^{-1} (w), 2691 cm^{-1} (w), 1931 cm^{-1} (w), 1702 cm^{-1} (m), 1603 cm^{-1} (s), 1551 cm^{-1} (s), 1497 cm^{-1} (s); δ_H (500 MHz, $CDCl_3$): δ 7.36 (t, 2H, *J* = 8.03 Hz), 7.1 (t, 1H, *J* = 7.36 Hz), 7.0 (d, 2H, *J* = 8.53 Hz), 2.65-2.80 (dd, 4H, *J* = 15.4, 56.4 Hz); δ_C (126 MHz, $CDCl_3$): δ 129.8, 129.3, 128.3, 76.7, 58.5, 18.4; ESI-MS: *m/z* 355.14 [M+3Na+2H_2].



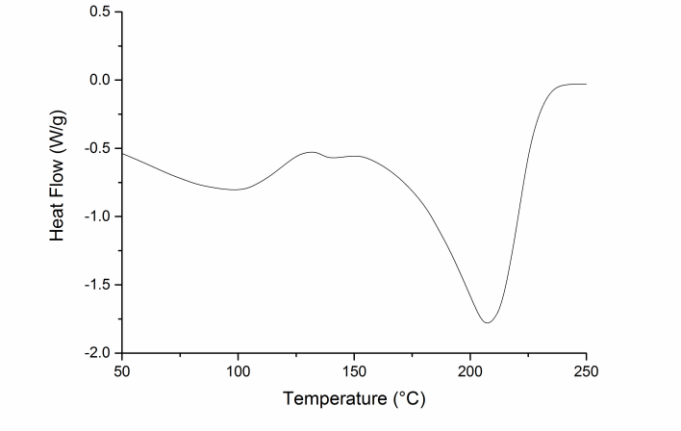
SI Figure 8 TGA graph of compound **2**.



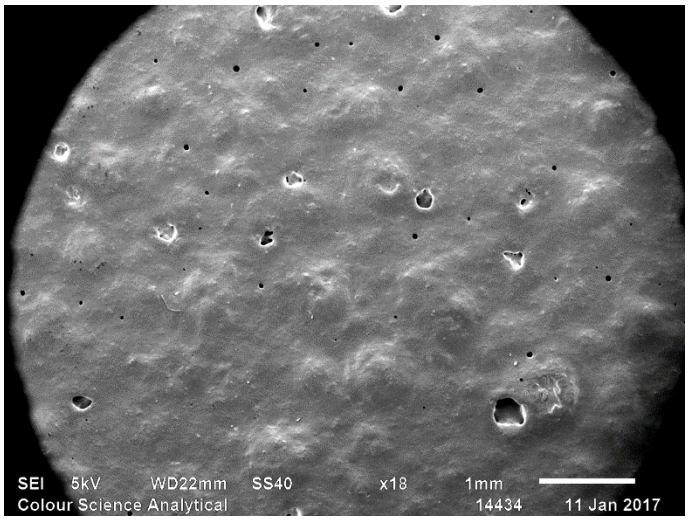
SI Figure 9 DTG graph of compound **2**.



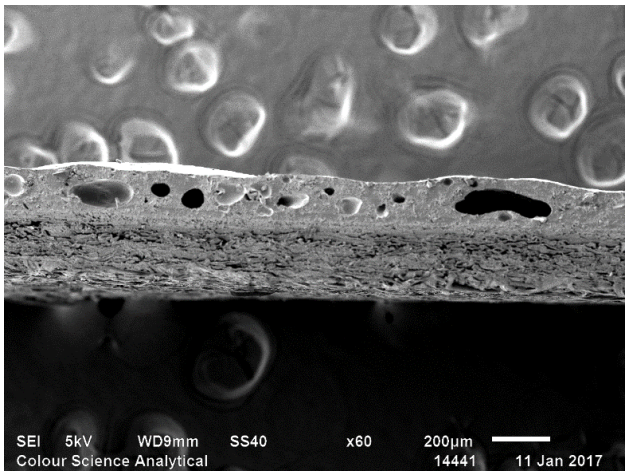
SI Figure 10 D2TG graph of compound **2**.



SI Figure 11 DSC graph of compound **2**.

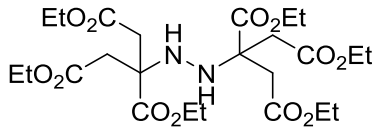


SI Figure 12 SEM image of compound **2** surface.



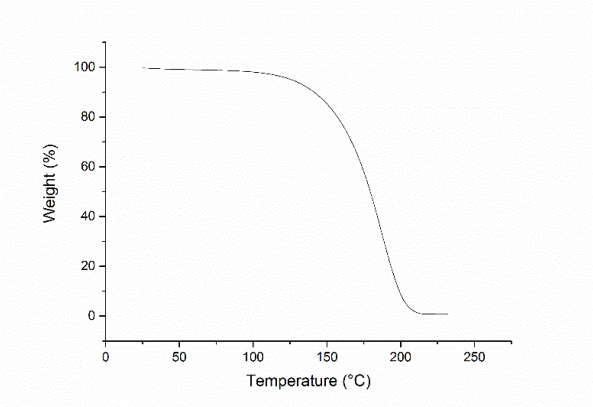
SI Figure 13 SEM image of compound **2** cross section.

2,2'-Hydrazobistriethyl citrate (Compound 3)

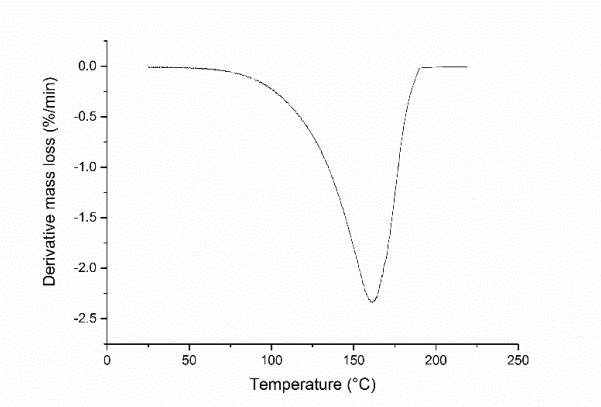


Triethyl citrate (10 mL, 41.2 mmol) was dissolved in ethanol (50 mL). Hydrazine monohydrate (1 mL, 20.6 mmol) was added dropwise over 15 minutes. The mixture was left to stir for 72 hours at 25 °C to give an yellowish suspension. The solid impurities were filtered and washed with chloroform (75 mL). The filtrate was concentrated and concentrated under vacuum to yield 2,2'-hydrazobistriethyl citrate as a yellow oil **3** (9.35 g, 17.1 mmol, 83%).

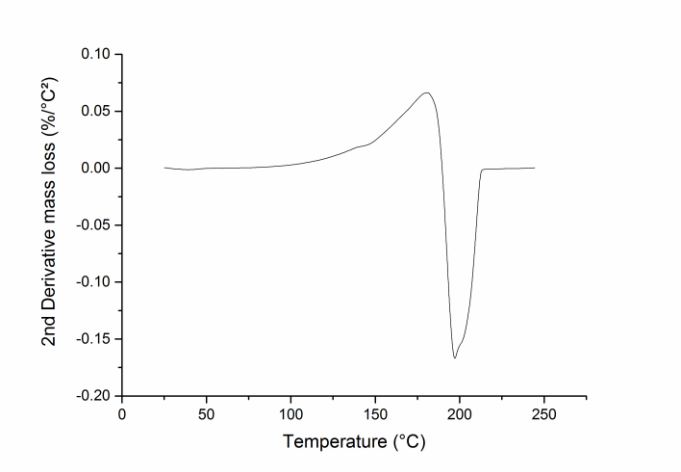
$C_{24}H_{40}O_{12}N_2$. IR v_{max}/cm^{-1} (neat): 3500 cm^{-1} (w), 2983, 2908 cm^{-1} (w), 1730 cm^{-1} (s), 1619 cm^{-1} (w), 1370 cm^{-1} (m), 1182 cm^{-1} (s); δ_H (500 MHz, $CDCl_3$): 4.22 (q, 4H, *J* = 7.1 Hz), 4.08 (q, 8H, *J* = 7.1 Hz), 2.77 (dd, 8H, *J* = 52.9, 15.5 Hz), 1.24 (t, 6H, *J* = 7.1 Hz), 1.19 (t, 12H, *J* = 7.1 Hz); δ_C (126 MHz, $CDCl_3$): 173.4, 169.7, 73.2, 62.4, 60.9, 43.4, 14.1, 14.0; ESI-MS: *m/z* 575.23 [M+Na+$2H_2$].



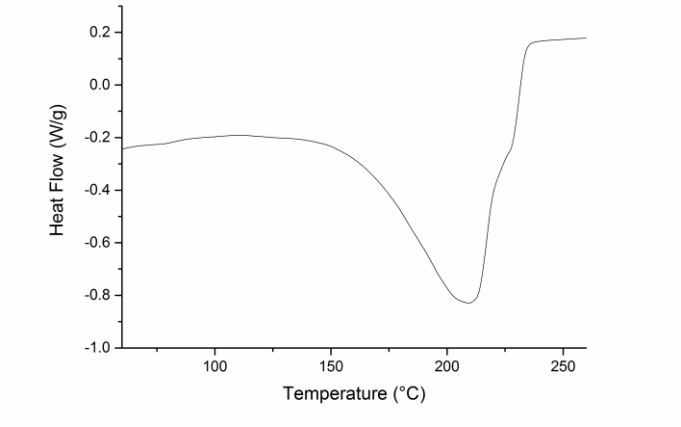
SI Figure 14 TGA graph of compound **3**.



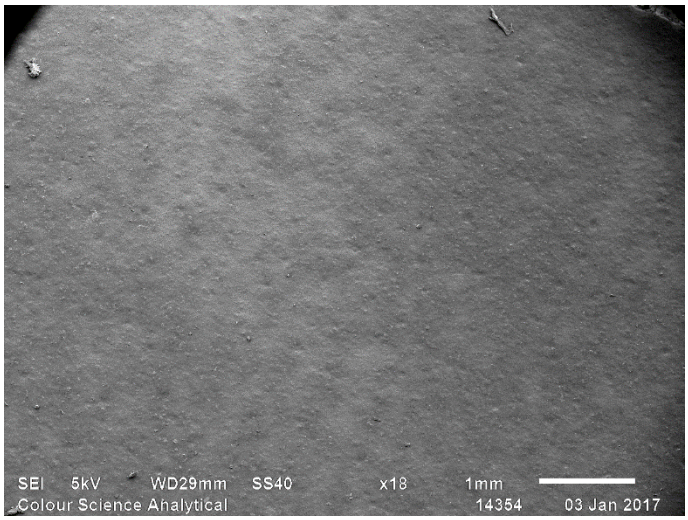
SI Figure 15 DTG graph of compound **3**.



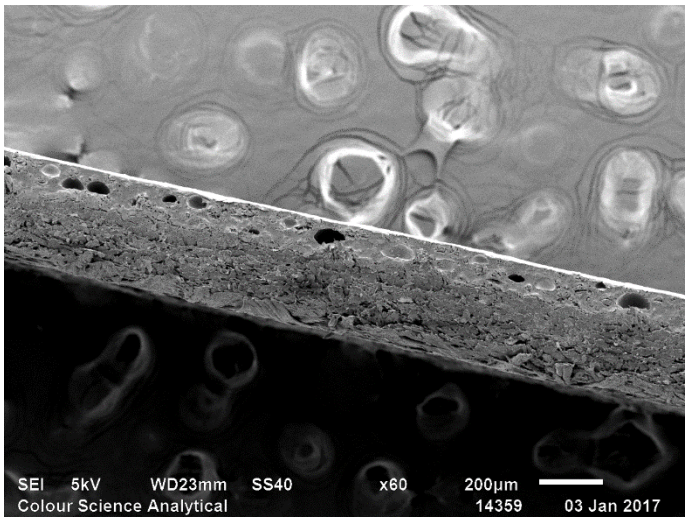
SI Figure 16 D2TG graph of compound **3**.



SI Figure 17 DSC graph of compound **3**.

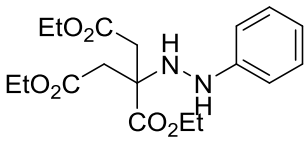


SI Figure 18 SEM image of compound **3** surface.



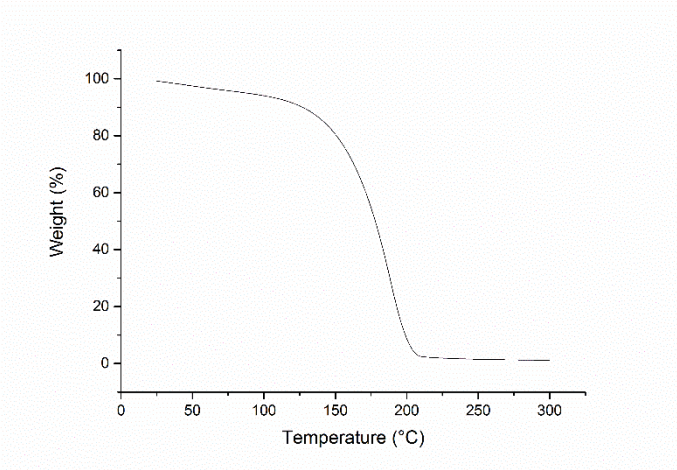
SI Figure 19 SEM image of compound **3** cross section.

2-(2-Phenylhydrazinyl)triethyl citrate (Compound 4)

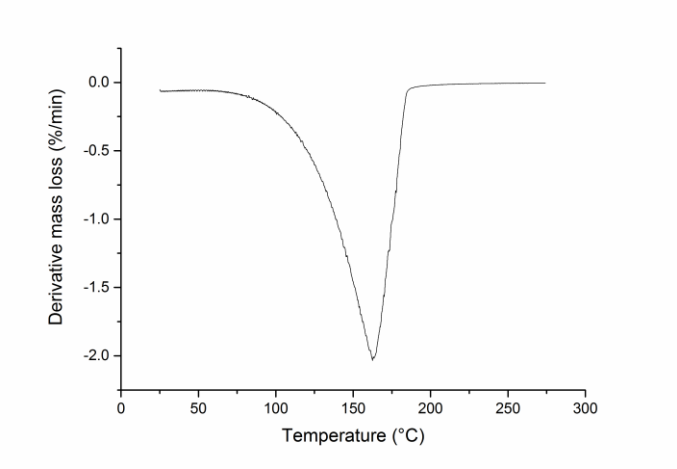


Triethyl citrate (5.60 mL, 20 mmol) was dissolved in ethanol (30 mL). Phenyl hydrazine (2 mL, 20 mmol) was added dropwise over 15 minutes and left to stir for 72 hours at 25 °C. Color change from colorless to light orange was observed. Solution was concentrated under vacuum and 2-(2-phenylhydrazinyl)triethyl citrate was isolated as yellow oil **4** (7.01 g, 19.2 mmol, 96%).

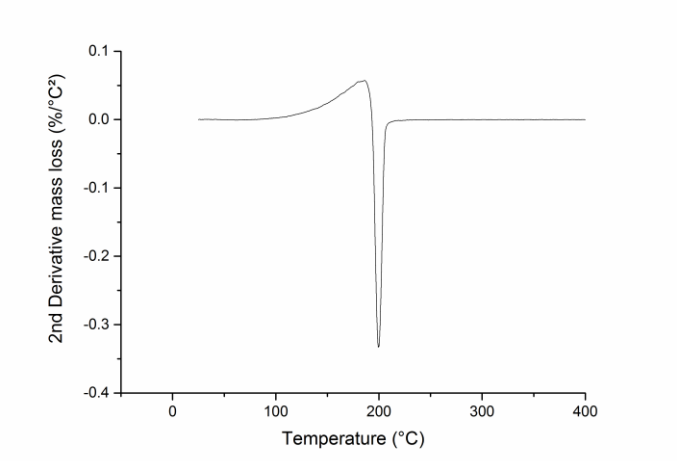
$C_{18}H_{26}O_6N_2$. IR (neat): 3368 cm^{-1} (w), 2982 cm^{-1} (w), 2056 cm^{-1} (w), 1727 cm^{-1} (s), 1601 cm^{-1} (m), 1370 cm^{-1} (m), 1180 cm^{-1} (s), 753, 695 cm^{-1} (m); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.07 (m, 2H), 6.83-6.66 (m, 3H), 4.21 (q, 2H *J* = 7.16 Hz), 4.08 (q, 4H, *J* = 7.14 Hz), 2.77 (dd, 4H, *J* = 52.91, 15.54 Hz), 1.30-1.21 (t, 3H, *J* = 8.59 Hz), 1.18 (t, 6H, *J* = 8.61 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 169.8, 151.4, 129.2, 119.5, 62.3, 61.0, 43.4, 14.1, 14.0.



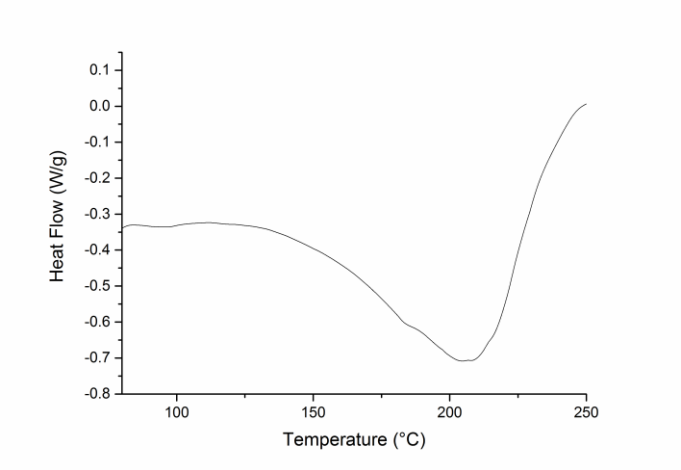
SI Figure 20 TGA graph of compound **4**.



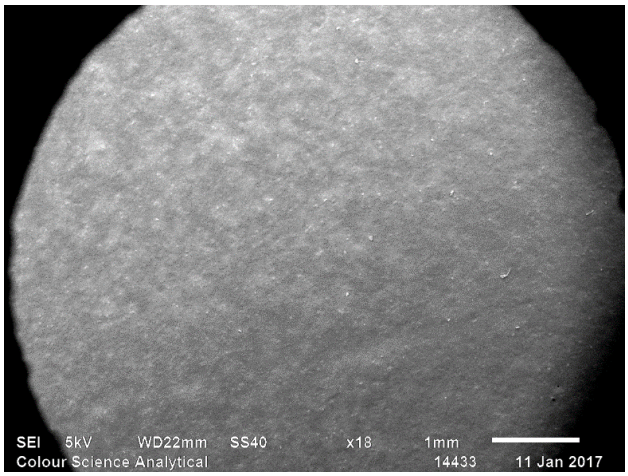
SI Figure 21 DTG graph of compound **4**.



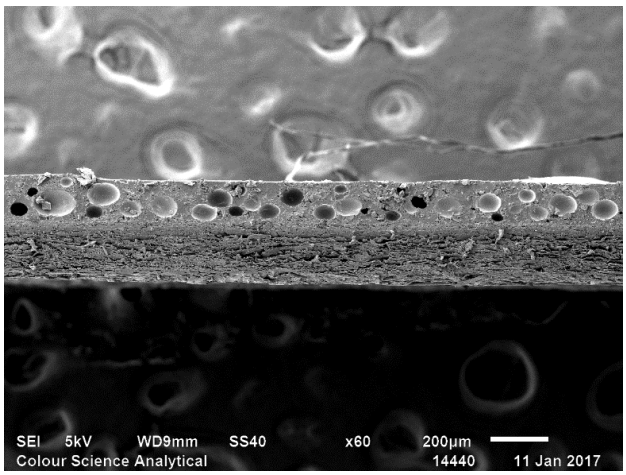
SI Figure 22 D2TG graph of compound **4**.



SI Figure 23 DSC graph of compound **4**.



SI Figure 24 SEM image of compound **4** surface.



SI Figure 25 SEM image of compound **4** cross section.