

Triggered Formation of Thixotropic Hydrogels by Balancing Competitive Supramolecular Synthons

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Supplementary Material

Table S1 Gelation behaviours of **1** and **2** in polar solvents

Solvent	1a	1b	1c	1d	2a	2b	Solvent	1a	1b	1c	1d	2a	2b
H ₂ O	P	P	P	P	I	I	Cyclohexanone	P	P	P	P	P	G
Methanol	P	P	P	P	P	G	Cyclopentanone	P	P	P	P	P	G
Ethanol	P	P	P	P	P	G	Diethylene glycol	P	P	P	P	I	G
1-Butanol	P	P	P	P	P	G	Acetone	P	P	P	P	I	VS
2-Butanol	P	P	P	P	P	G	Acetonitrile	I	I	I	I	I	VS
1-Propanol	P	P	P	P	P	G	1,4-Dioxane	I	I	I	I	I	VS
2-Propanol	P	P	P	P	P	WG	DMF	S	S	S	S	S	S
1-Pentanol	P	P	P	P	P	G	DMSO	S	S	S	S	S	S

Table S2 Gelation behaviours of **1a** and dicarboxylic acids in polar solvents

[illegible]

Table S3 Gelation behaviours of **1b** and dicarboxylic acids in polar solvents

[illegible]

Table S4 Gelation behaviours of **1c** and dicarboxylic acids

[illegible]

Table S5 Gelation behaviours of **1d** and dicarboxylic acids

[illegible]

Table S6 Gelation behaviours of **2a** and dicarboxylic acids

[illegible]

Table S7 Gelation behaviours of **2b** and dicarboxylic acids

Solvent	2b+a		2b+b		2b+c		2b+d		2b+e	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H ₂ O	VS	I	PG	I	P	I	G	I	G	I
Methanol	-	-	-	-	-	-	-	-	-	-
Ethanol	-	-	-	-	-	-	-	-	-	-
1-Butanol	-	-	-	-	-	-	-	-	-	-
2-Butanol	-	-	-	-	-	-	-	-	-	-
1-Propanol	-	-	-	-	-	-	-	-	-	-
2-Propanol	-	-	-	-	-	-	-	-	-	-
1-Pentanol	-	-	-	-	-	-	-	-	-	-
Cyclohexanone	-	-	-	-	-	-	-	-	-	-
Cyclopentanone	-	-	-	-	-	-	-	-	-	-
Diethylene glycol	-	-	-	-	-	-	-	-	-	-
Acetone	P	I	G	G	G	G	P	G	G	VS
Acetonitrile	P	I	P	G	PG	PG	G	PG	P	I
1,4-dioxane	P	P	G	VS	G	VS	G	VS	G	VS
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Solvent	2b+f		2b+g		2b+h		2b+i		2b+j	
	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C	Sonication	H-C
H ₂ O	VS	I	TUS	I	VS	I	VS	I	P	I
CH ₃ OH	-	-	-	-	-	-	-	-	-	-
CH ₃ CH ₂ OH	-	-	-	-	-	-	-	-	-	-
1-Butanol	-	-	-	-	-	-	-	-	-	-
2-Butanol	-	-	-	-	-	-	-	-	-	-
1-Propanol	-	-	-	-	-	-	-	-	-	-
2-Propanol	-	-	-	-	-	-	-	-	-	-
1-Pentanol	-	-	-	-	-	-	-	-	-	-
Cyclohexanone	-	-	-	-	-	-	-	-	-	-
Cyclopentanone	-	-	-	-	-	-	-	-	-	-
Diethylene glycol	-	-	-	-	-	-	-	-	-	-
Acetone	PG	I	TUS	I	G	I	VS	VS	P	I
Acetonitrile	G	P	TUS	TUS	G	VS	P	I	P	I
1,4-Dioxane	P	P	P	P	VS	I	P	I	P	I
DMF	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S

Notes: “-” referred to the gel systems of pure **2b** without any dicarboxylic acid

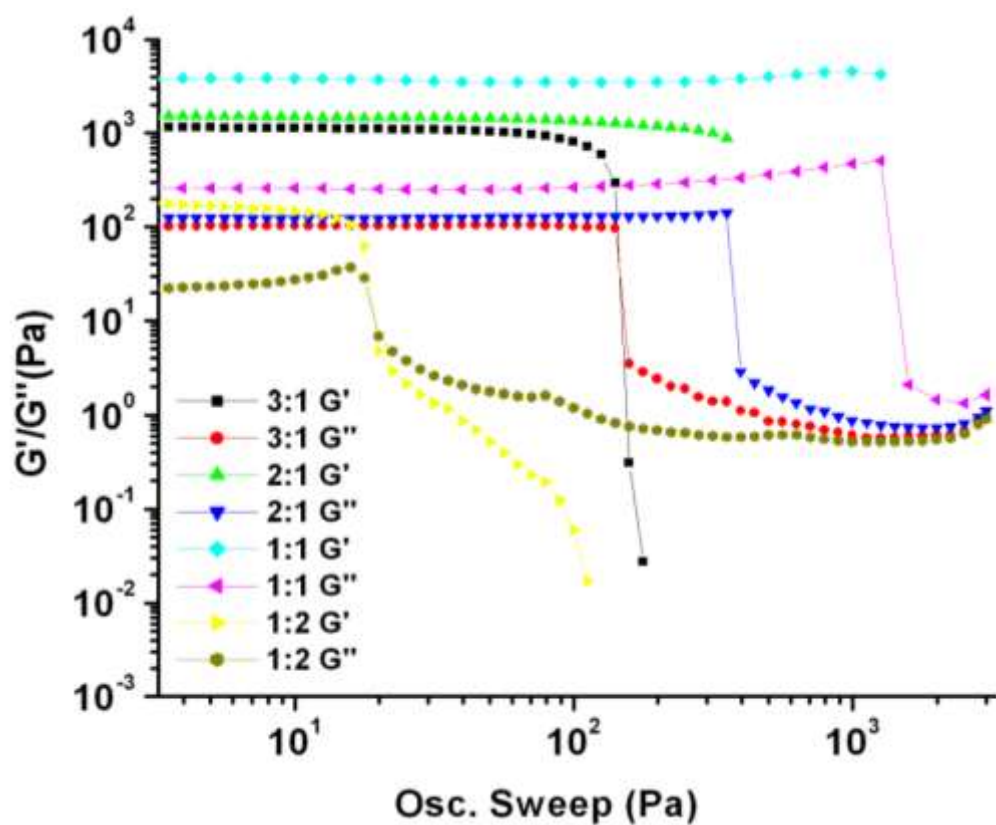


Figure S1 Stress sweeps of 2a/oxalic acid hydrogels at different ratios (2.0 wt/vol %)

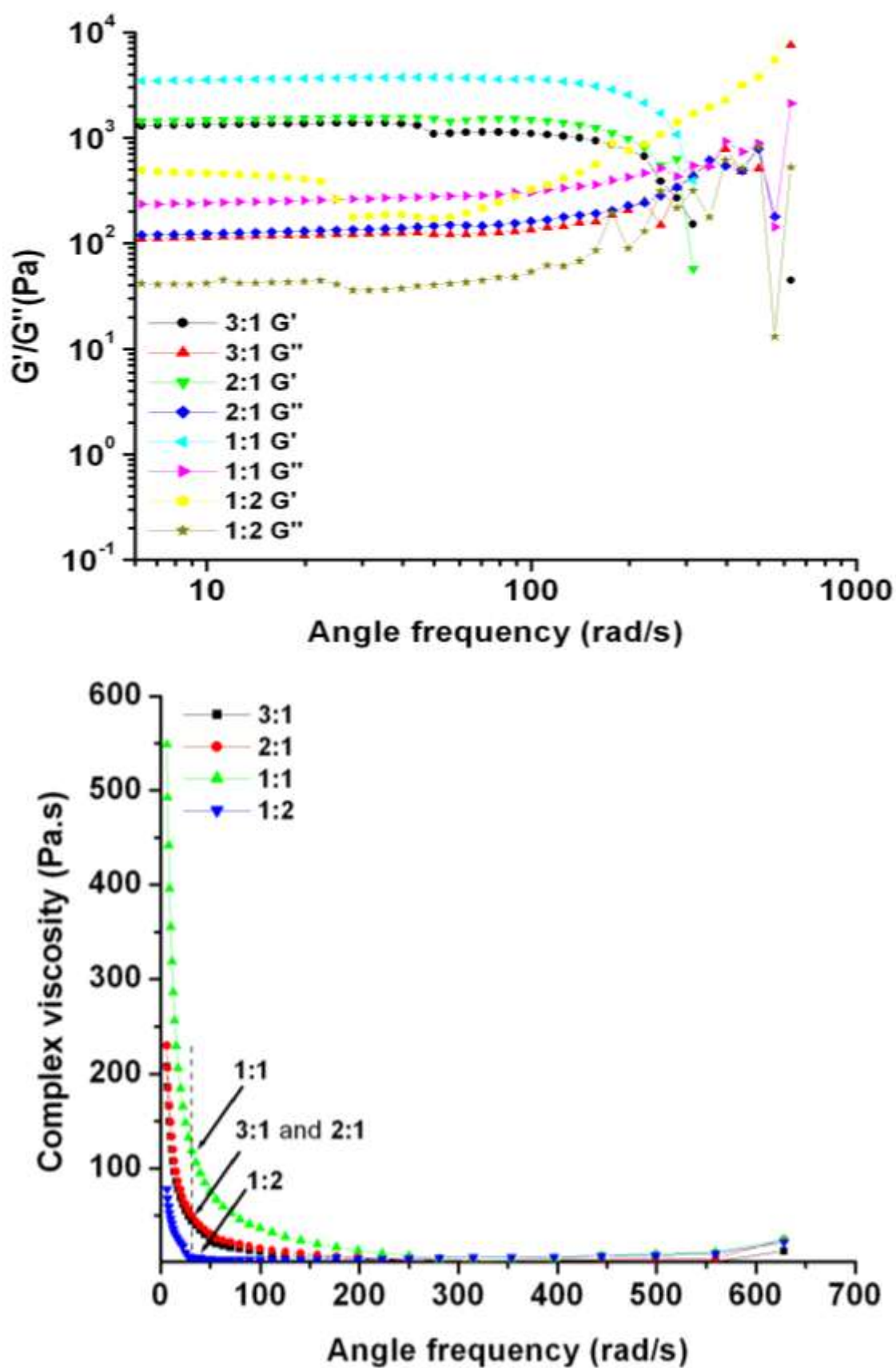


Figure S2 Angle frequency sweep (top) and complex viscosity (bottom) of supramolecular gels at different ratio (3:1, 2:1, 1:1 and 1:2) between **2a** and oxalic acid in water

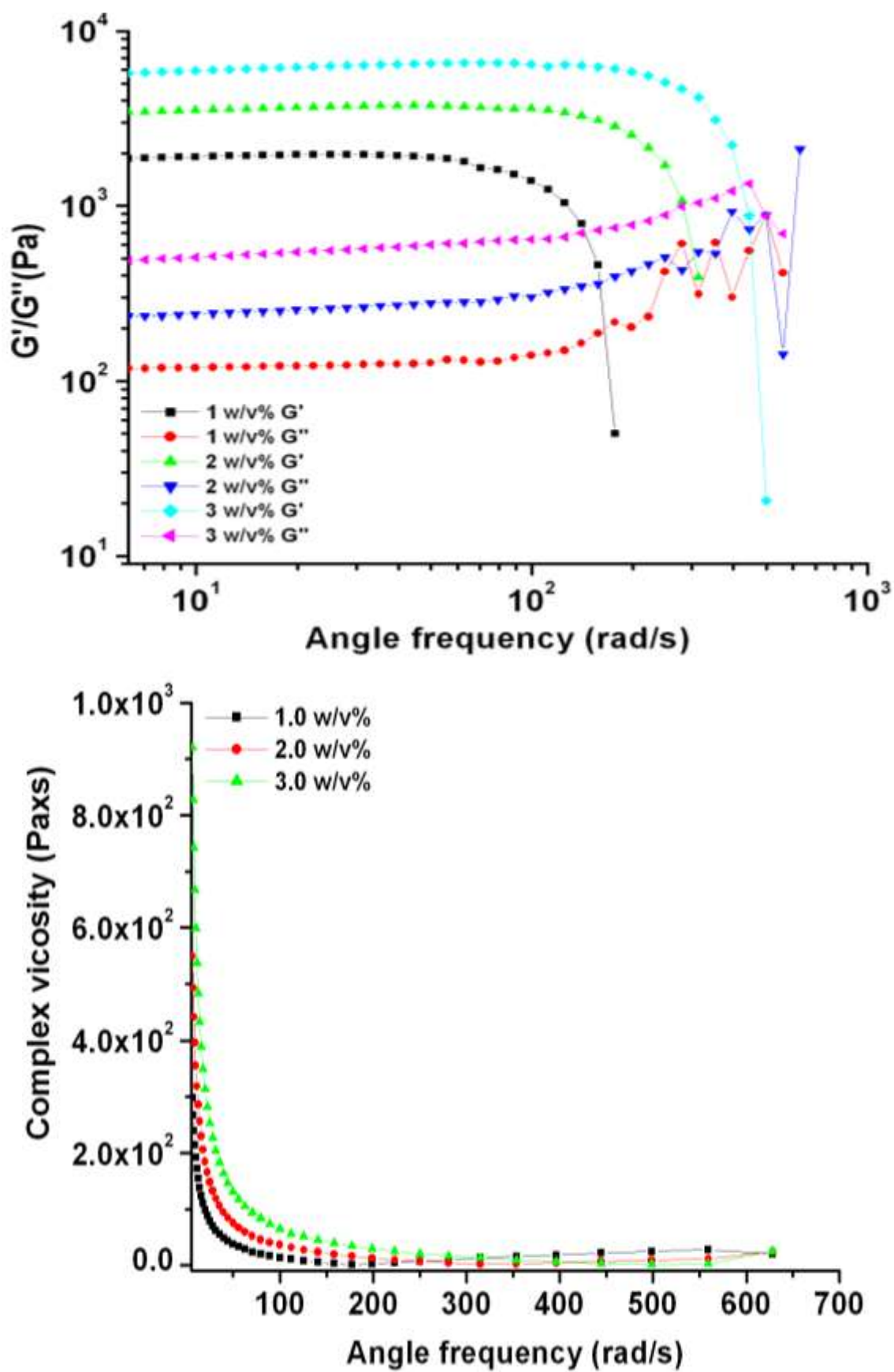


Figure S3 Angle frequency sweep (top) and complex viscosity (bottom) of supramolecular gels of **2a** and oxalic acid at different concentration (1:1 ratio)

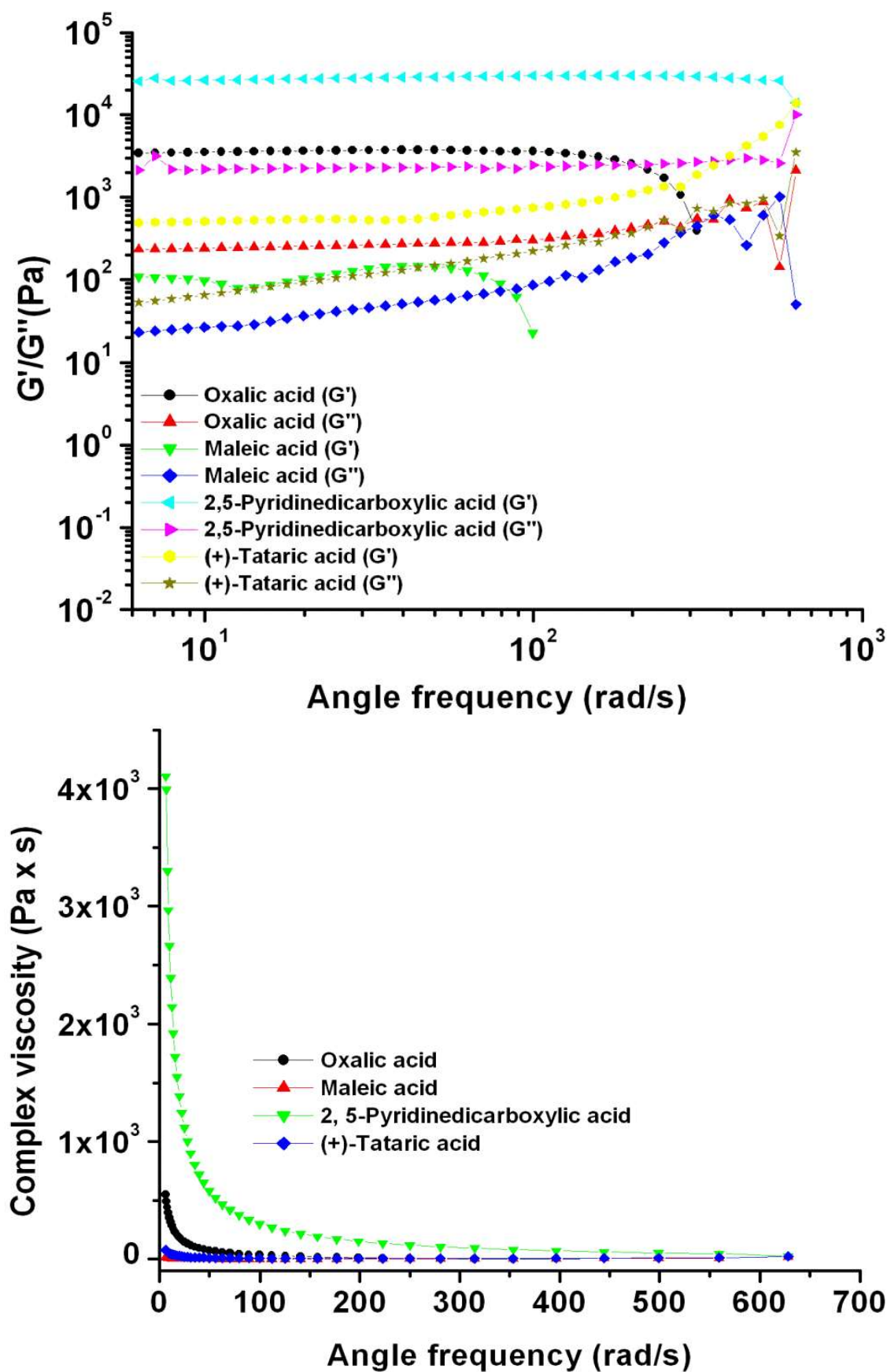


Figure S4 Angle frequency sweep (top) and complex viscosity (bottom) of hydrogels of different dicarboxylic acid systems (1:1, 2.0 w/v%)

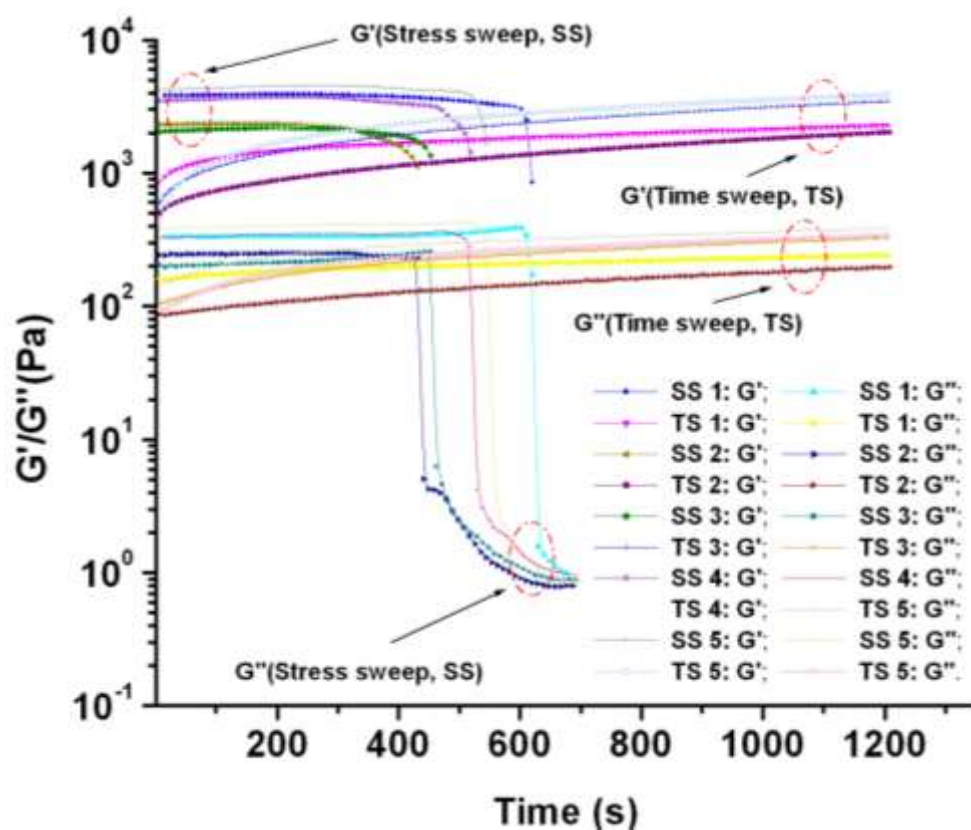


Figure S5 Five cycles of stress sweep (deformation, SS) and time sweep (formation, TS) for the **2a**-oxalic acid hydrogel (1:1, 2.0 w/v%)

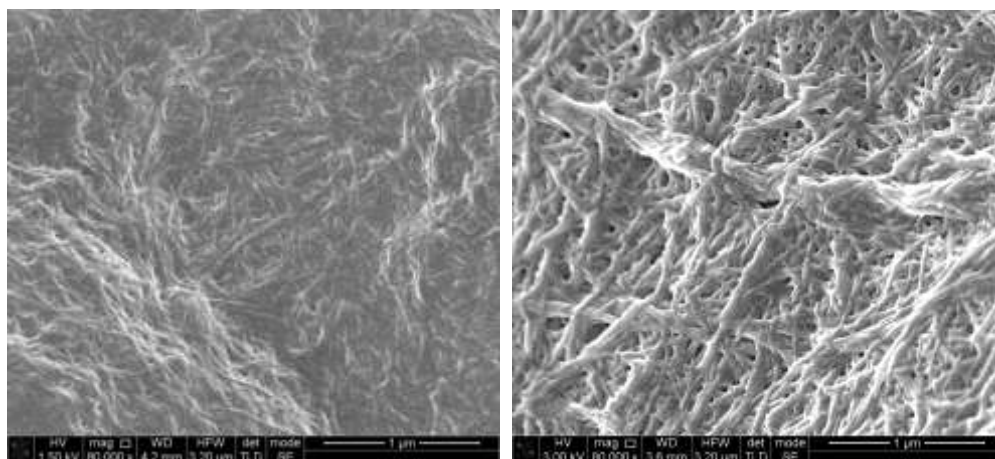


Figure S6 Morphologies of dried hydrogels of **2a**/oxalic acid (1:1) at concentrations of (left) 1.0 w/v% and (right) 3.0 w/v%

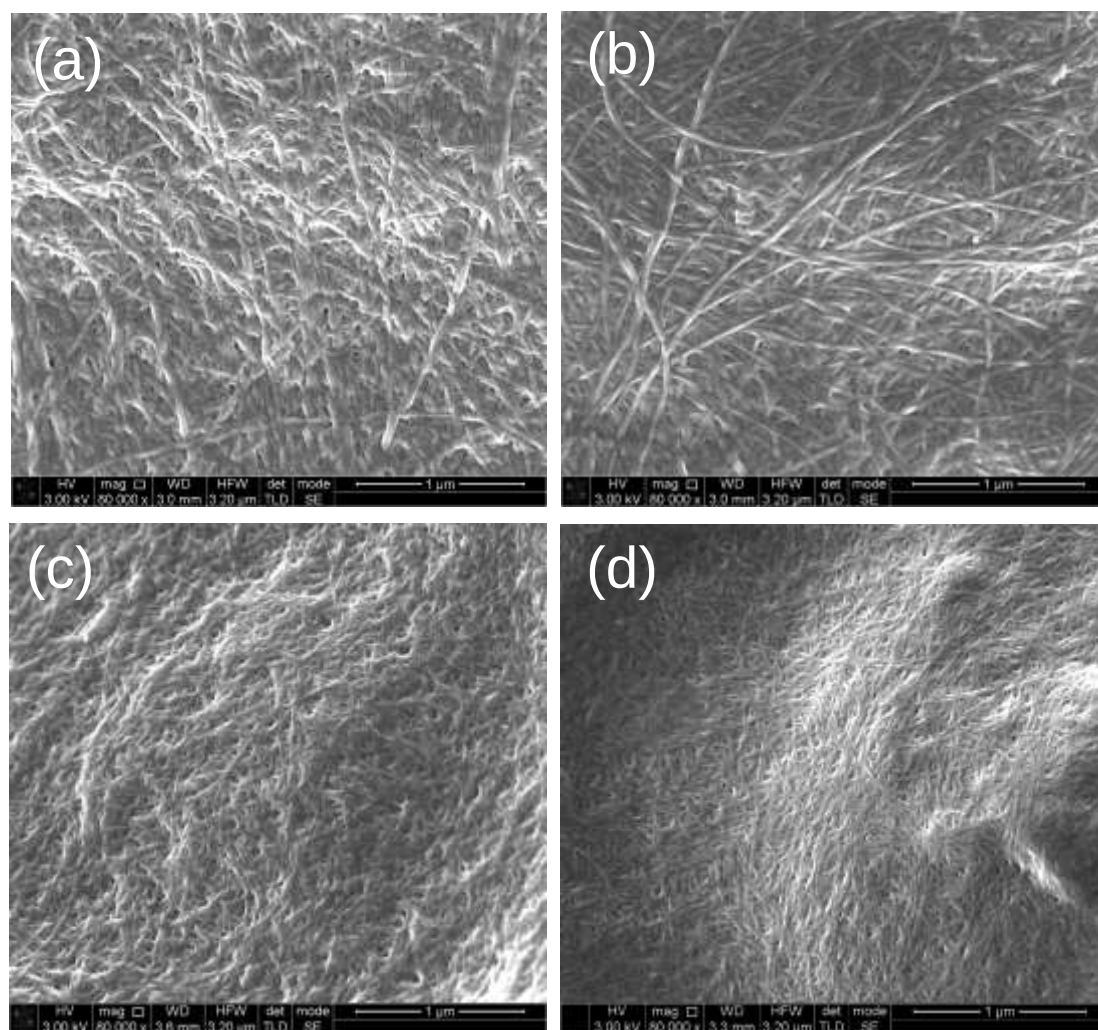


Figure S7 Morphologies of dried hydrogels of **2a**/oxalic acid (a), maleic acid (b), 2,5-pyridinecarboxylic acid (c) and (+)-tartaric acid (d) at 2.0 w/v% (1:1 ratio)

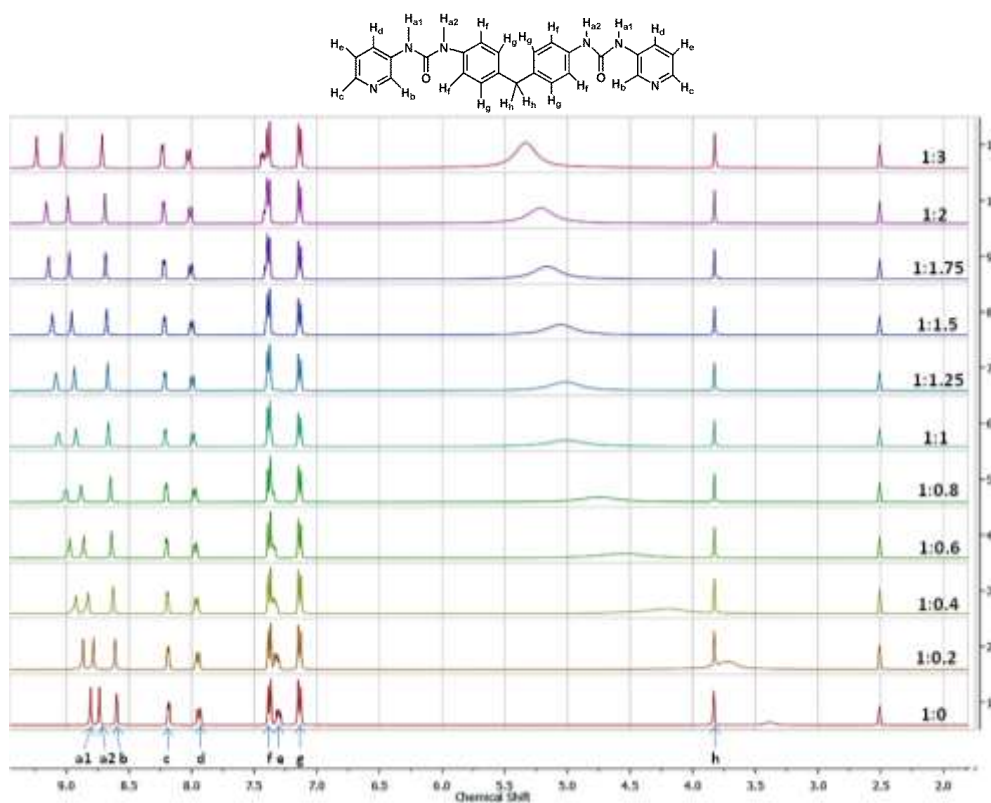


Figure S8 ^1H NMR spectroscopic titration of oxalic acid into **2a**/ d_6 -DMSO solution

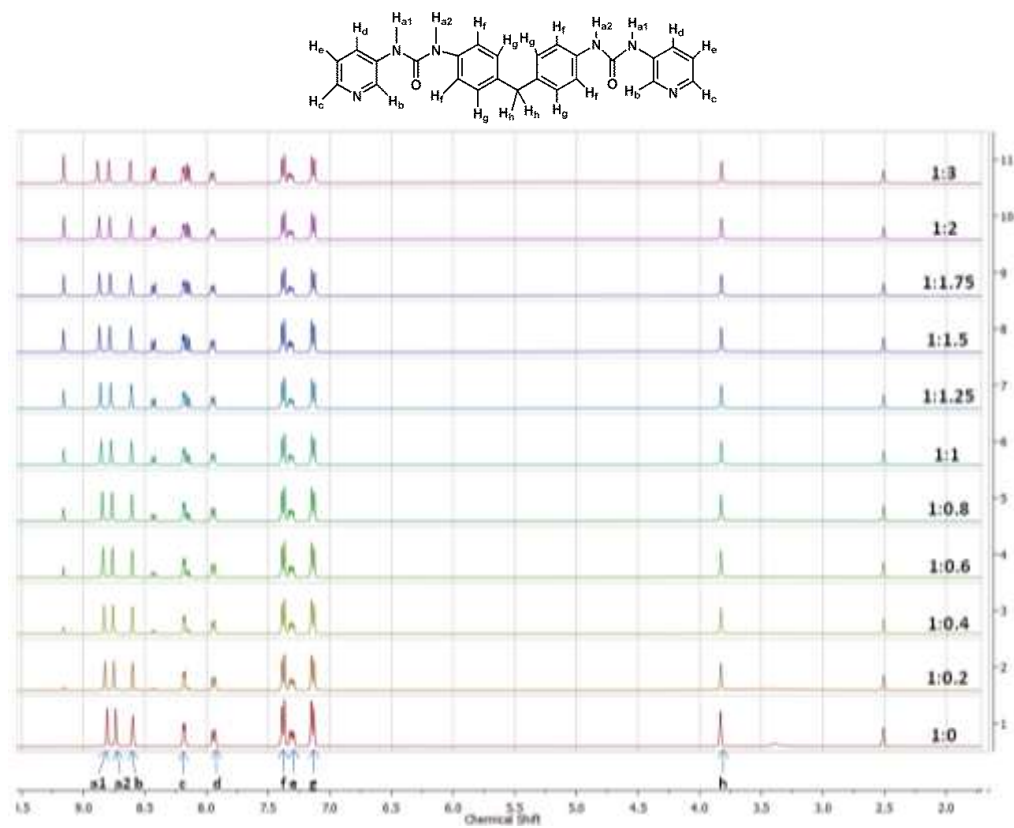


Figure S9 ^1H NMR spectroscopic titration of 2, 5-pyridinedicarboxylic acid into **2a**/ d_6 -DMSO solution

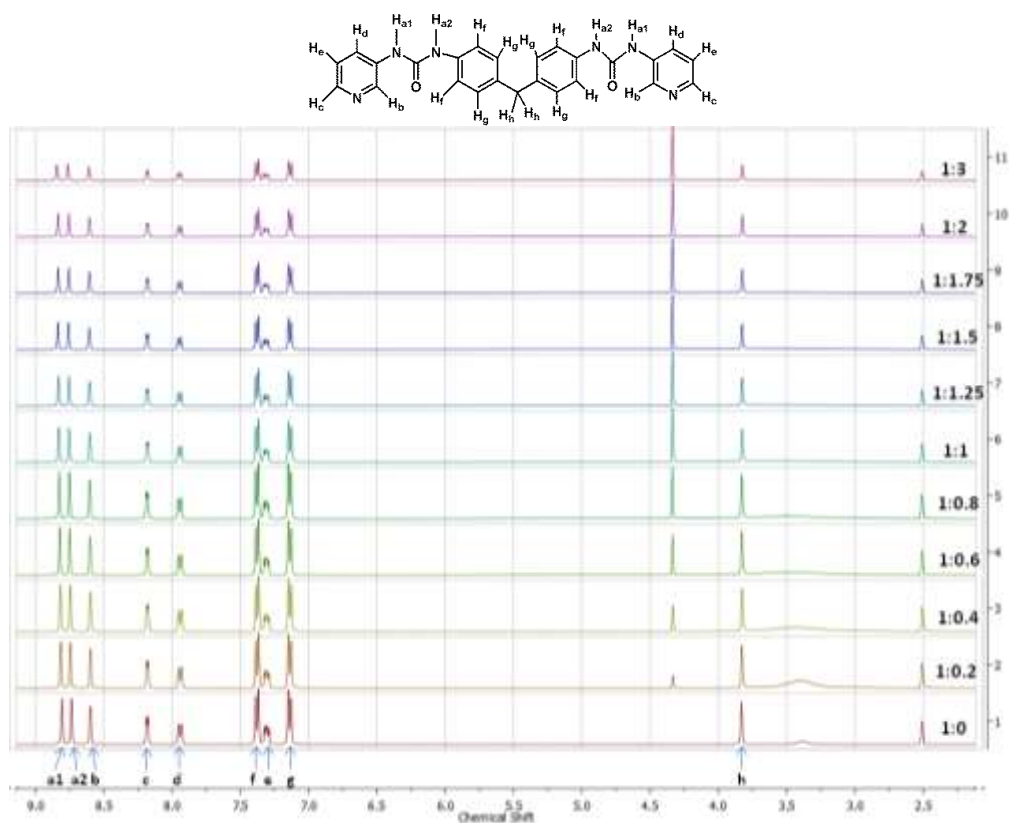


Figure S10 ^1H NMR spectroscopic titration of (+)-tartaric acid into **2a**/ d^6 -DMSO solution

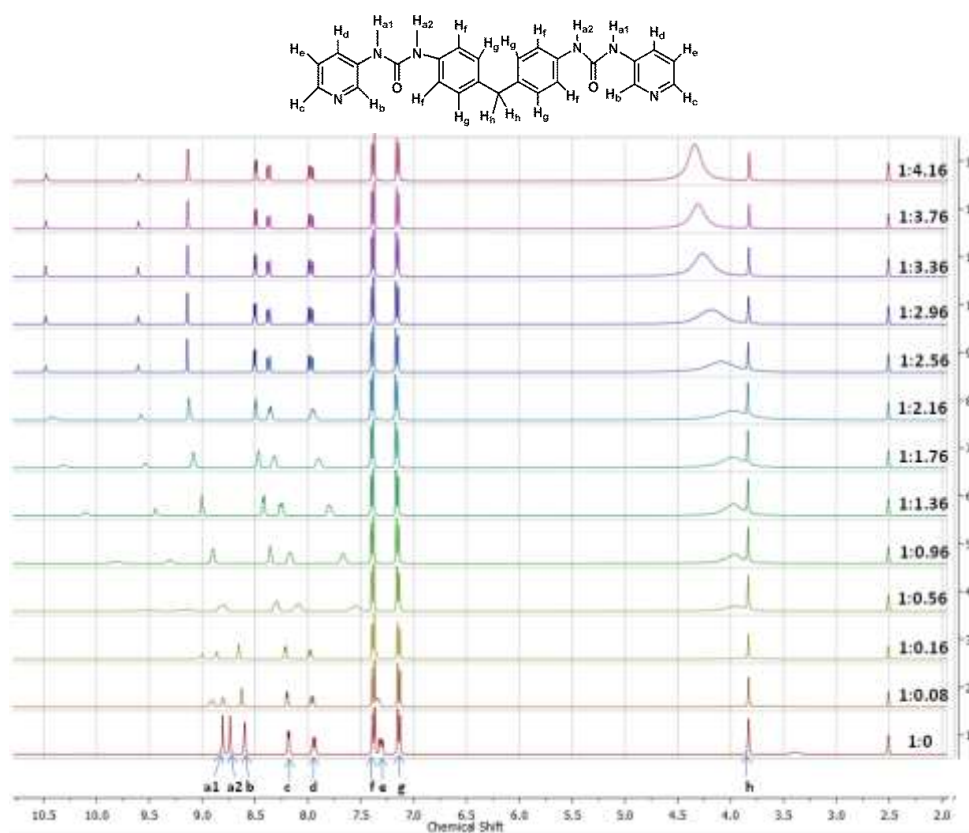


Figure S11 ^1H NMR spectroscopic titration of DCl into **2a**/ d^6 -DMSO solution

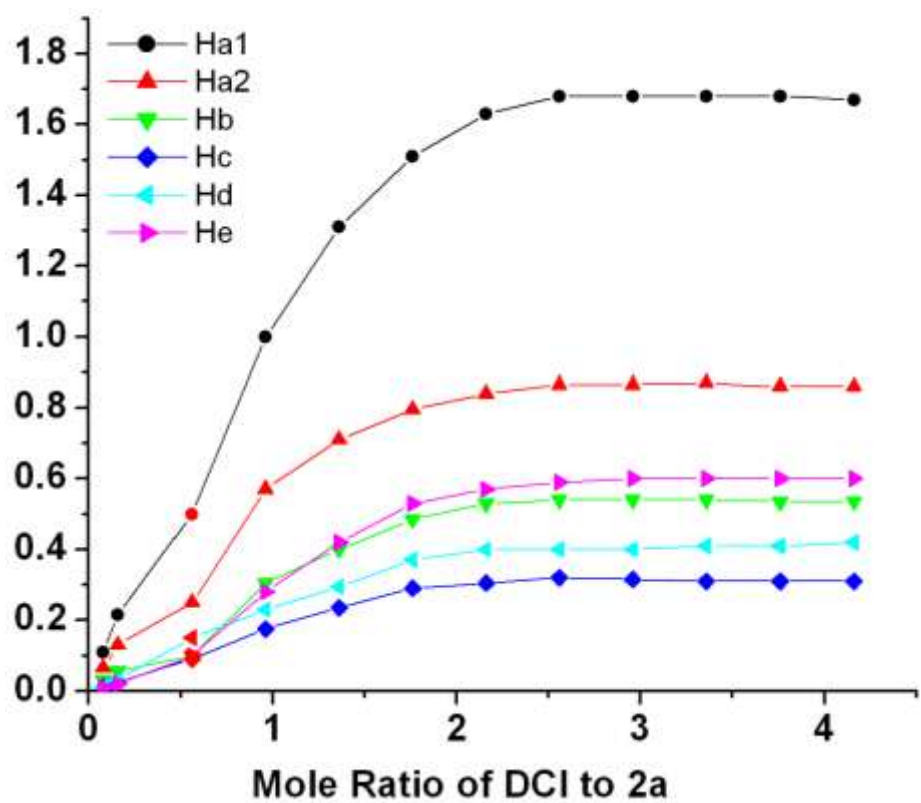


Figure S12 Dependence of chemical shift on mole ratio of DCl to 2a in d^6 -DMSO

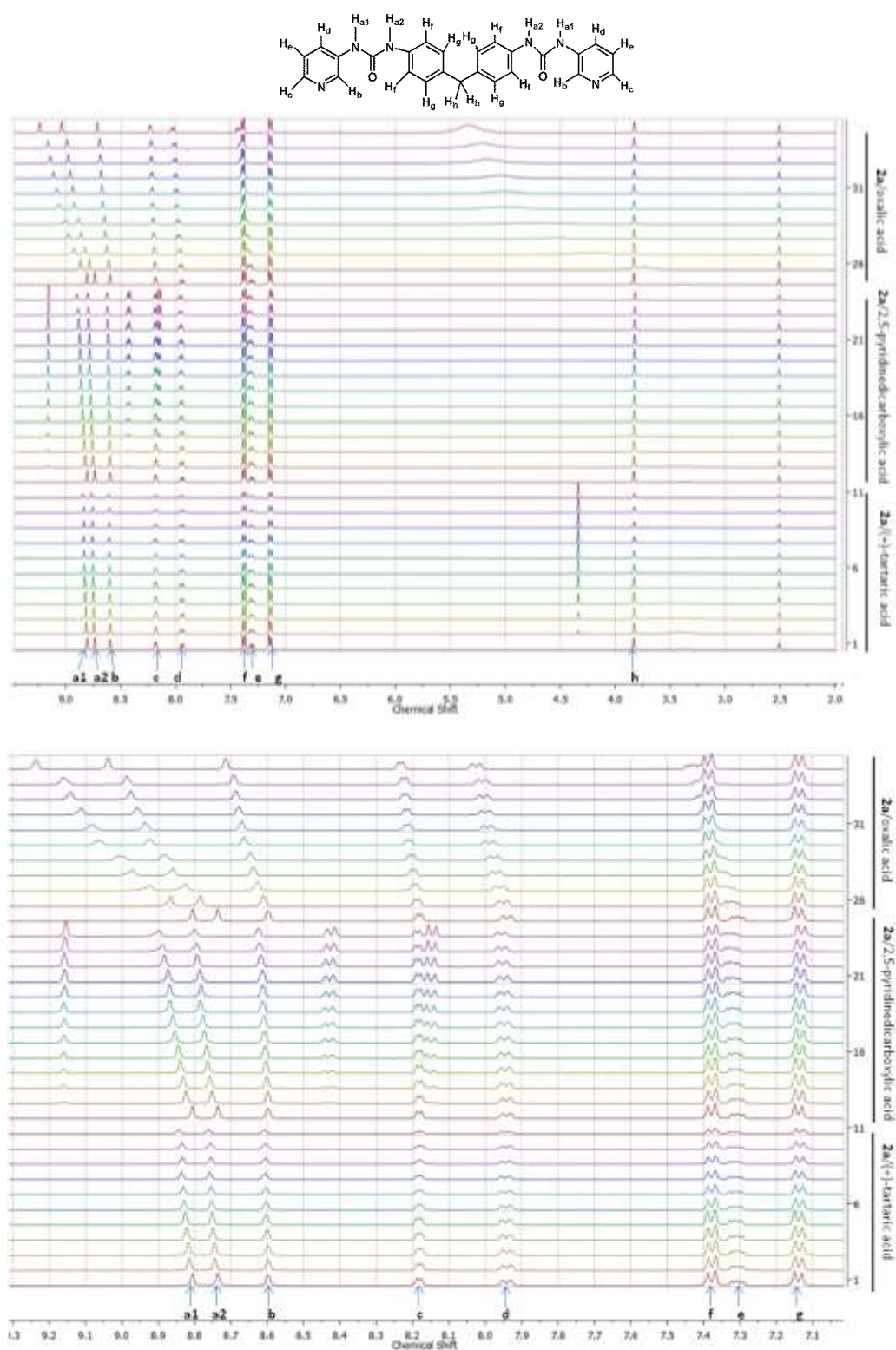


Figure S13 ^1H NMR spectroscopic titration of oxalic acid, (+)-tartaric acid, and 2, 5-pyridinedicarboxylic acid into **2a**/ d_6 -DMSO solution

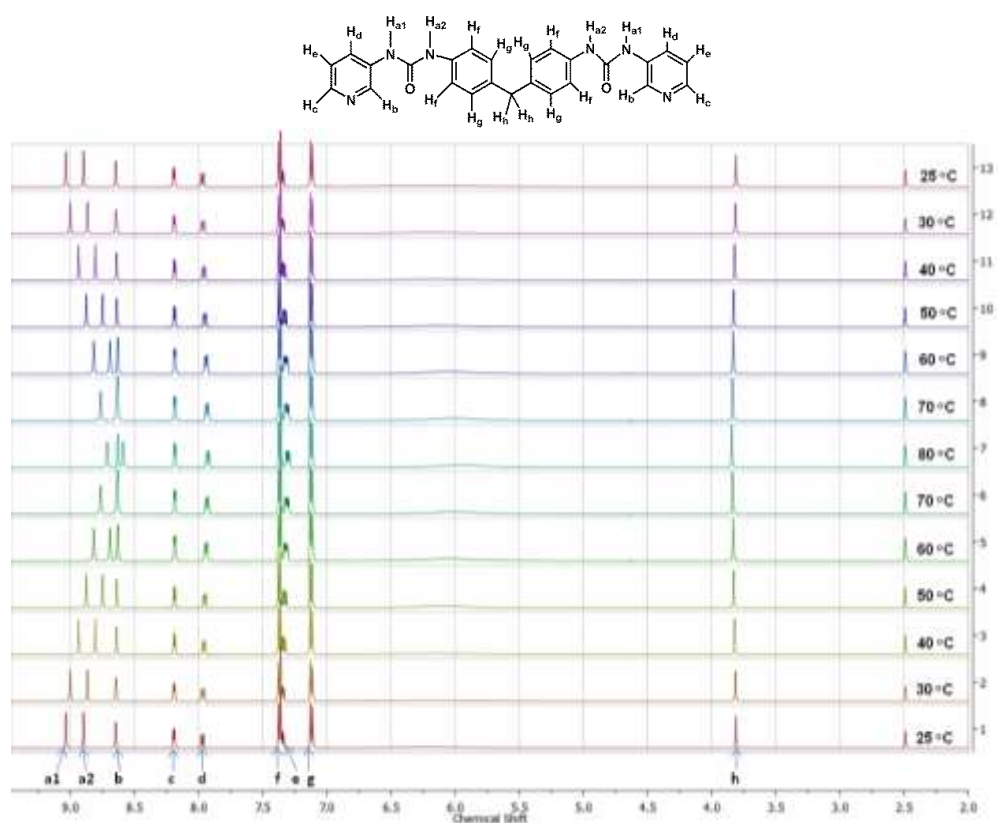


Figure S14 Temperature-dependent ^1H NMR spectra of **2a**/oxalic acid in d^6 -DMSO (ratio is 1:1, temperature is change 25 °C to 80 °C, and then down to 25 °C)

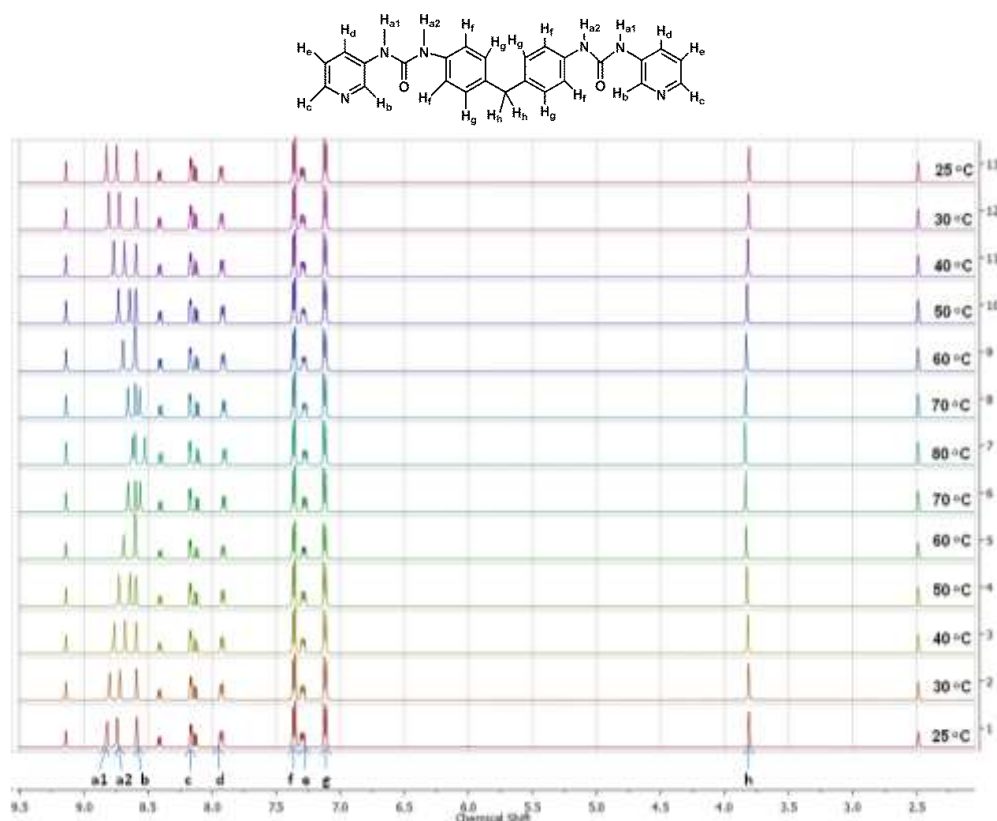


Figure S15 Temperature-dependent ^1H NMR spectra of **2a**/2, 5-pyridinedicarboxylic acid in d^6 -DMSO (ratio is 1:1, temperature is change 25 °C to 80 °C, and then down to 25 °C)

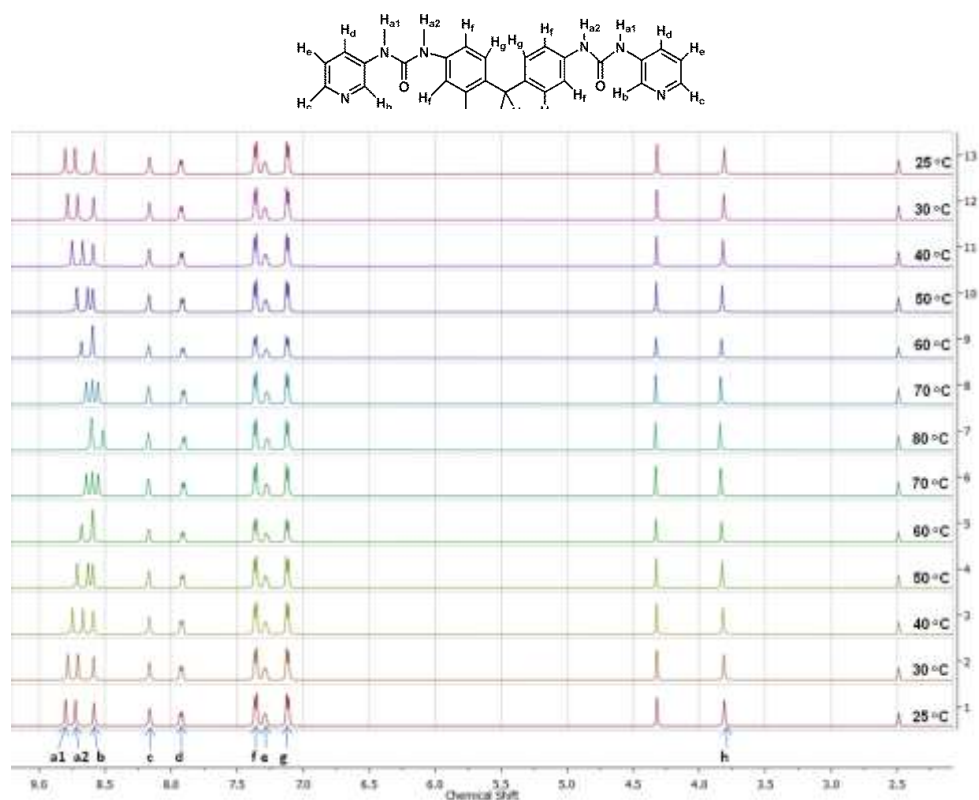


Figure S16 Temperature-dependent ^1H NMR spectra of **2a**/(+)-tartaric acid in d^6 -DMSO (ratio is 1:1, temperature is change 25 °C to 80 °C, and then down to 25 °C)

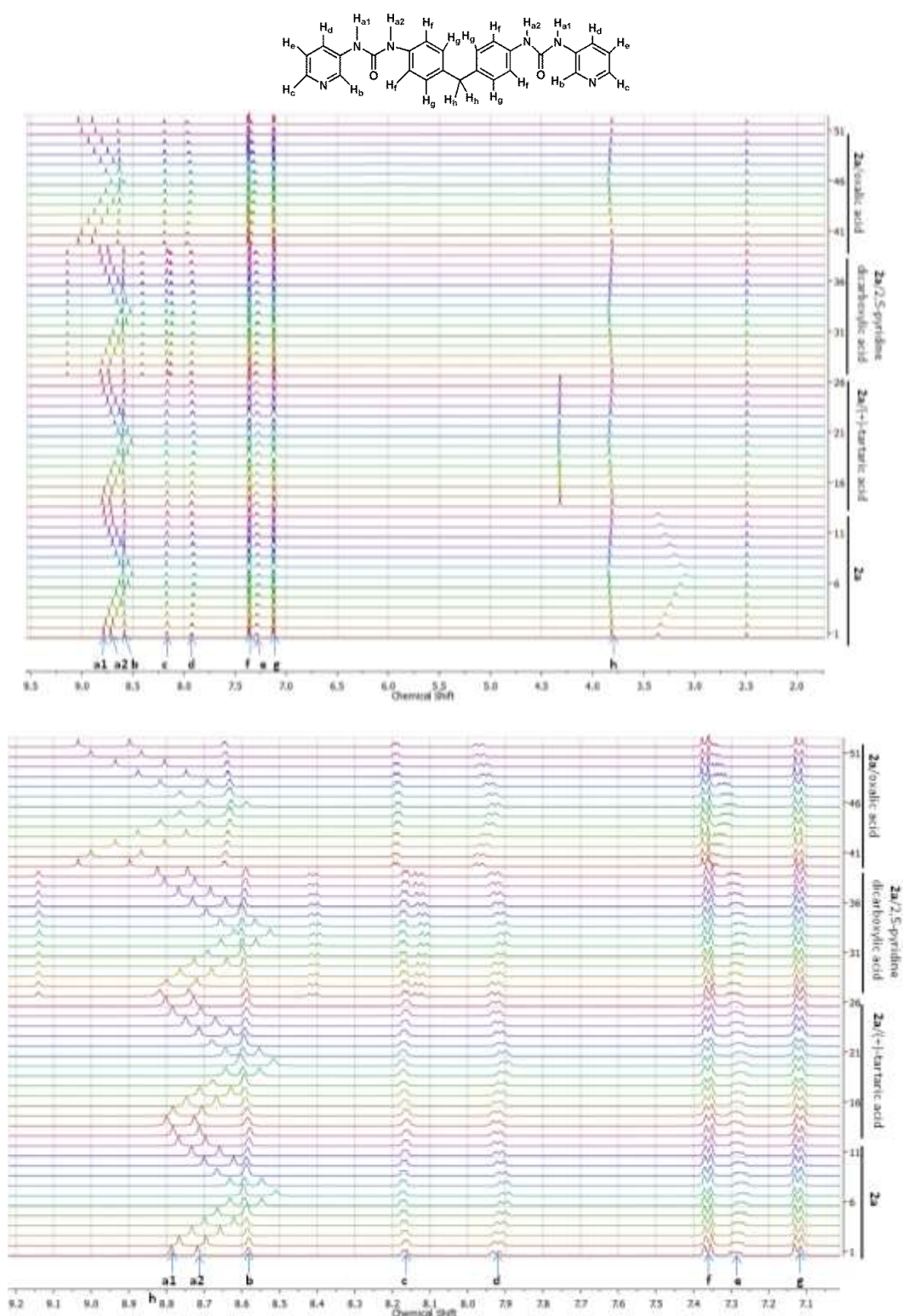


Figure S17 Temperature-dependent ¹H NMR spectra of 2a/oxalic acid, 2, 5-pyridinedicarboxylic acid and (+)-tartaric acid in d⁶-DMSO (ratio is 1:1, temperature is change 25 °C to 80 °C, and then down to 25 °C)

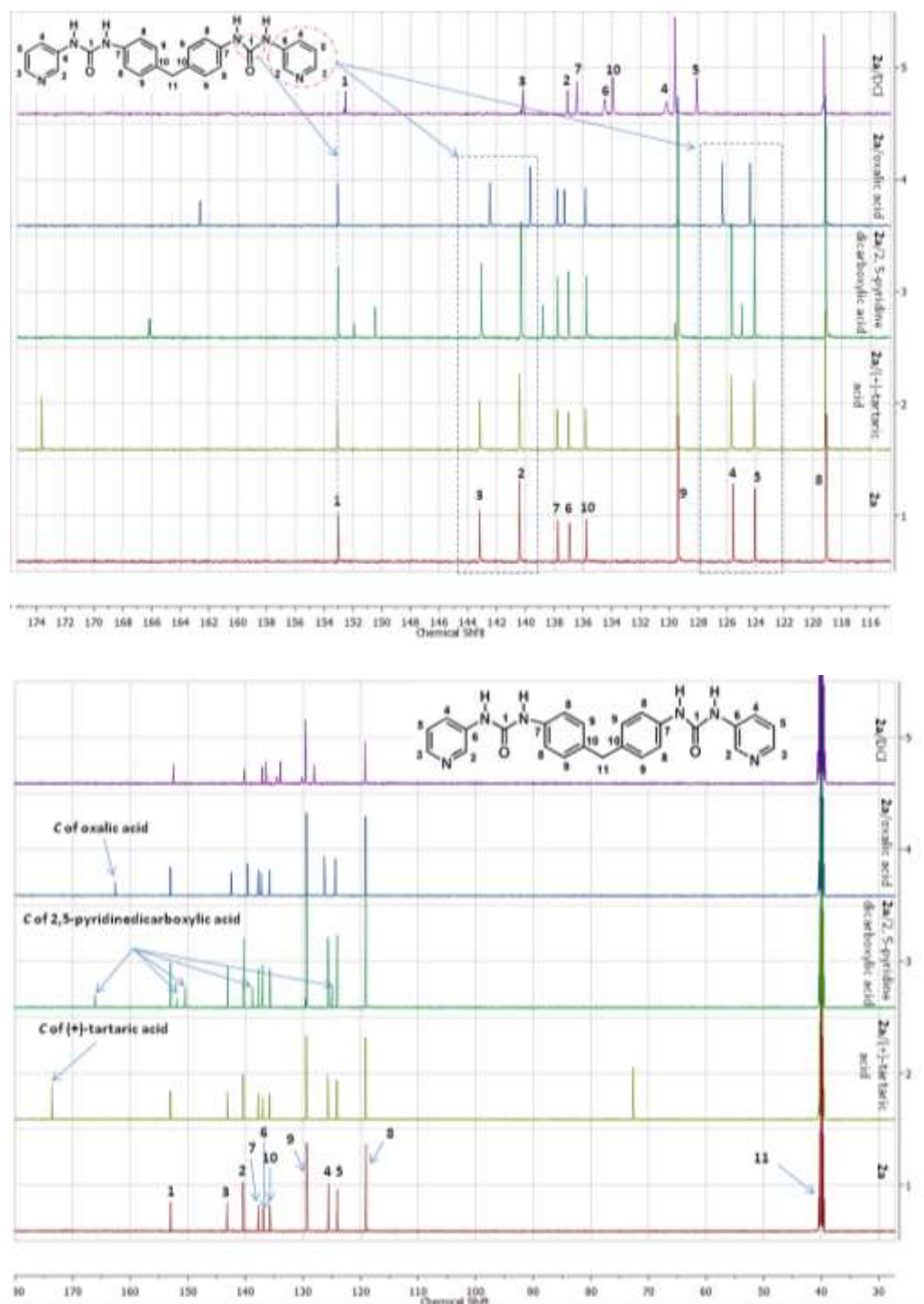


Figure S18 Full and partial ^{13}C NMR spectra of **2a**, **2a/oxalic acid**, **2a/2,5-pyridinedicarboxylic acid**, **2a/(+)-tartaric acid** and **2a/DCl** in d^6 -DMSO (1:1)

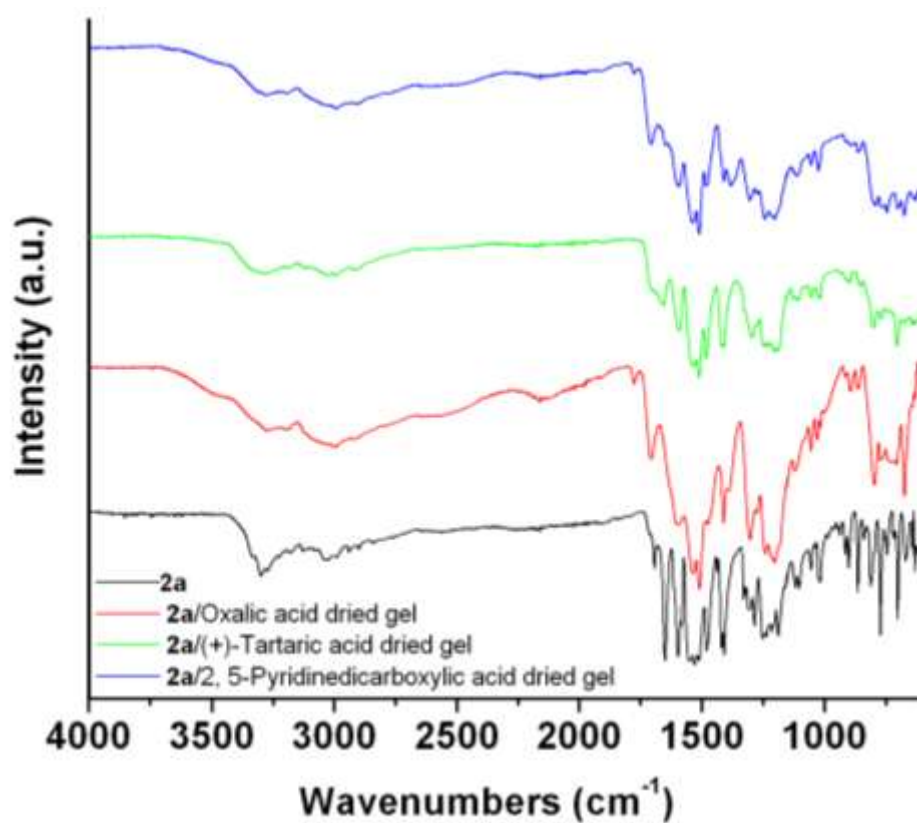
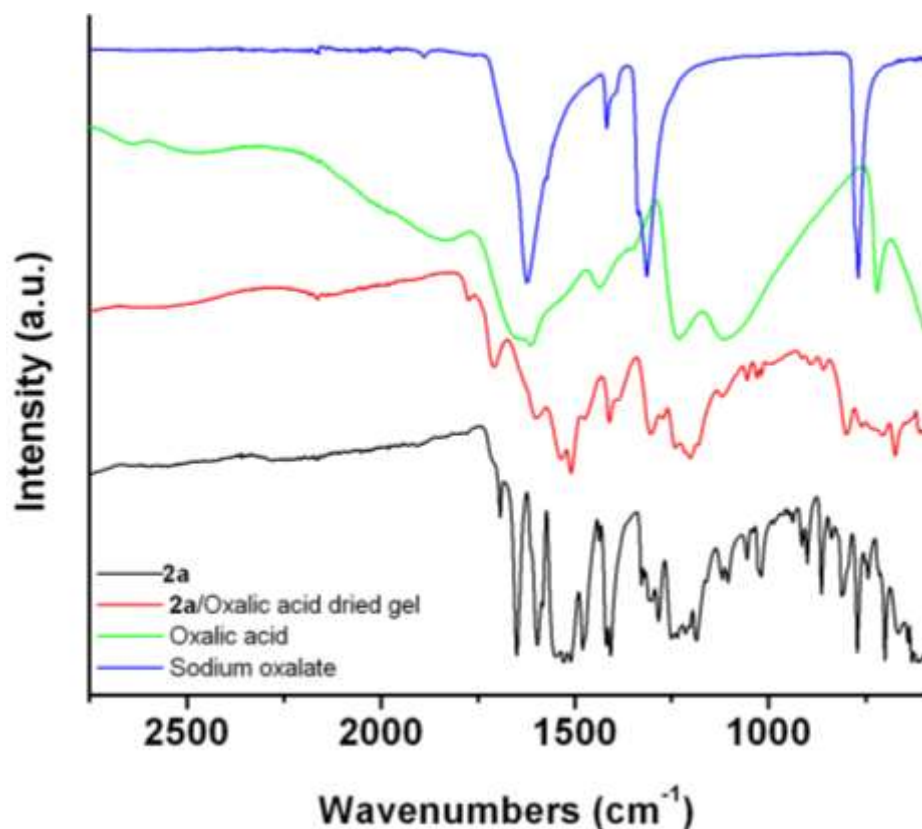
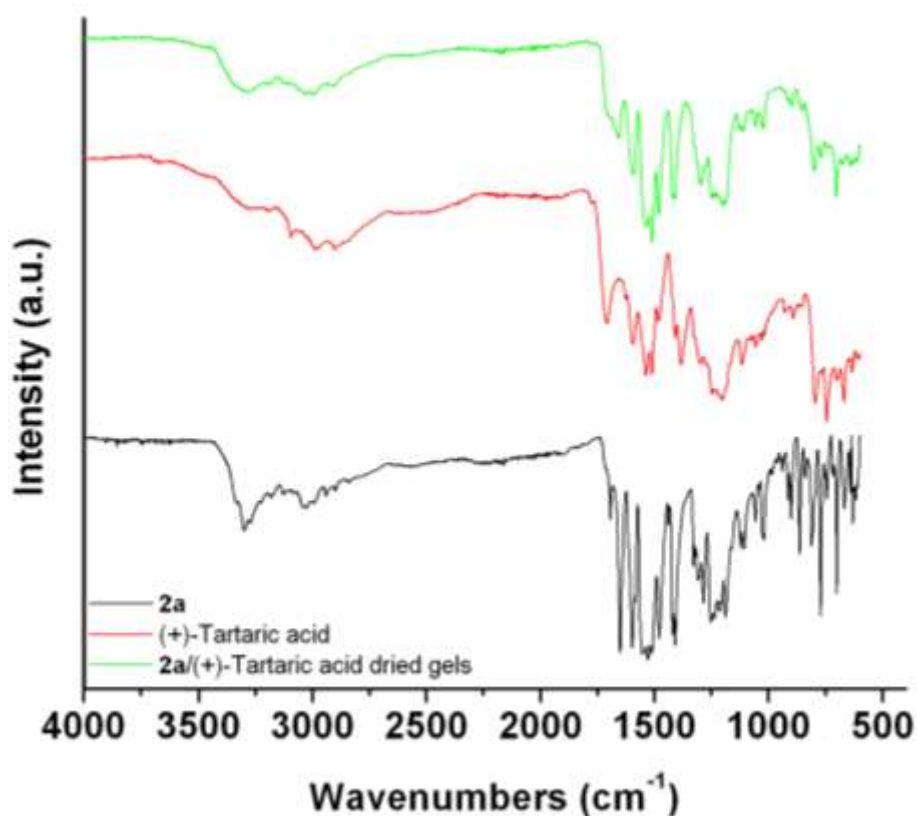


Figure S19 Full IR spectra of **2a** and dried gels of **2a**/oxalic acid, **2a**/(+)-tartaric acid and **2a**/2, 5-pyridinedicarboxylic acid



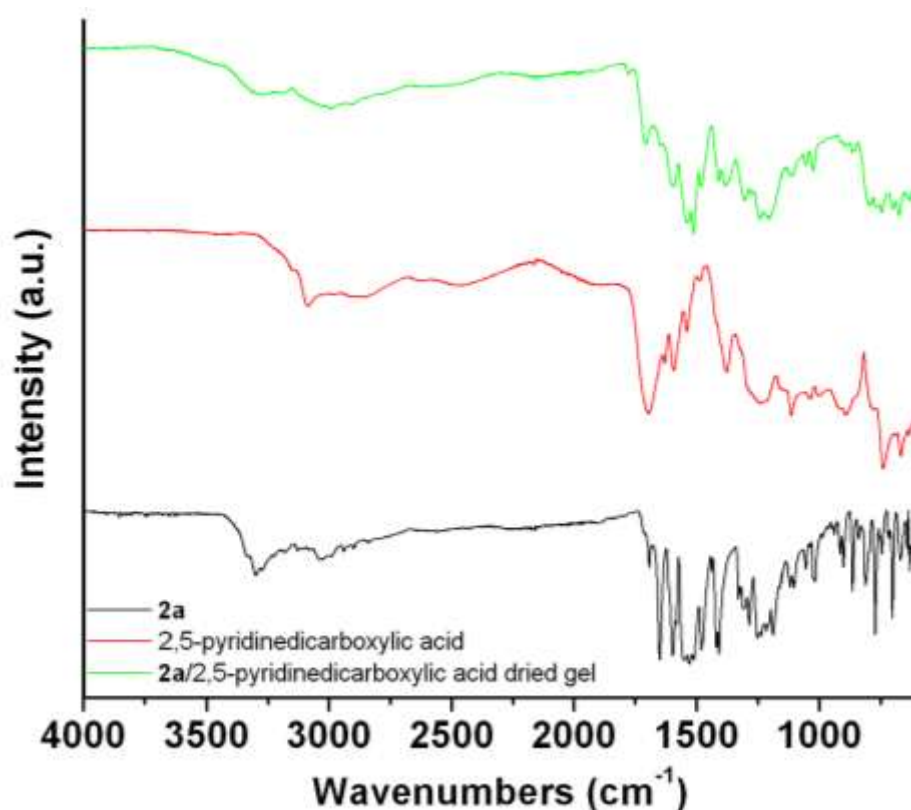
Samples	IR signals (cm ⁻¹)
2a	3297.6; 3034.8; 1692.0; 1648.2; 1593.9; 1550.1; 1552.8; 1501.7; 1474.5; 1417.1; 1404.6; 1326.5; 1282.7; 1252.5; 1184.5; 1119.6; 1103.4; 1055.6; 1019.3; 917.1; 901.8; 865.5; 812.03; 773.8; 746.1; 703.2; 668.7
2a/Oxalic acid dried gel	3278.0; 3034.8; 1776; 1709.8; 1599.06; 1535.07; 1509.28; 1472.98; 1401.9; 1303.9; 1269.5; 1239.9; 1200.8; 1119.6; 803.44; 763.33; 706.97; 677.37
Oxalic acid	3416.97; 1611.48; 1436.7; 1235.2; 1104.7; 724.17
Sodium oxalate	2935.1; 1618.04; 1414.1; 1309.9; 769.2

Figure S20 Full IR spectra of oxalic acid, sodium oxalate and **2a**/oxalic acid dried gel



Samples	IR signals (cm ⁻¹)
2a	3297.6; 3034.8; 1692.0; 1648.2; 1593.9; 1550.1; 1552.8; 1501.7; 1474.5; 1417.1; 1404.6; 1326.5; 1282.7; 1252.5; 1184.5; 1119.6; 1103.4; 1055.6; 1019.3; 917.1; 901.8; 865.5; 812.03; 773.8; 746.1; 703.2; 668.7
2a/(+)-Tartaric acid dried gel	3288.3; 1701.8; 1652.2; 1591.5; 1533.9; 1509.9; 1476.3; 1432.4; 1294.0; 1198.04; 1112.8; 1111.7; 1054.1; 1018.9; 897.4; 854.2; 799.8; 767.8; 703.9
(+)-Tartaric acid	3091.60; 2987.6; 2898.1; 1706.6; 1626.6; 1591.5; 1533.9; 1509.9; 1476.3; 1409.2; 1380.4; 1297.2; 1198.04; 1114.9; 1054.1; 793.4; 742.4; 695.9; 667.08; 631.9

Figure S21 Full IR spectra of **2a** and (+)-tartaric acid and **2a/(+)-tartaric acid** dried gel



Samples	IR signals (cm ⁻¹)
2a	3297.6; 3034.8; 1692.0; 1648.2; 1593.9; 1550.1; 1552.8; 1501.7; 1474.5; 1417.1; 1404.6; 1326.5; 1282.7; 1252.5; 1184.5; 1119.6; 1103.4; 1055.6; 1019.3; 917.1; 901.8; 865.5; 812.03; 773.8; 746.1; 703.2; 668.7
2, 5-Pyridinedicarboxylic acid	3146.6; 3086.2; 1696.6; 1628.6; 1590.8; 1536.5; 1686.6; 1374.9; 1235.9; 1113.5; 1036.5; 1003.3; 891.5; 735.9; 667.9
2a/2, 5-Pyridinedicarboxylic acid gel	3278.0; 1176.6; 1710.2; 1648.3; 1590.8; 1533.5; 1509.3; 1479.1; 1408.1; 1380.9; 1303.9; 1272.1; 1241.9; 1198.1; 1113.5; 1053.1; 1025.9; 745.0; 701.2; 674.0; 633.2

Figure S22 Full IR spectra of **2a** and 2, 5-pyridinedicarboxylic acid and **2a**/2, 5-pyridinedicarboxylic acid dried gel

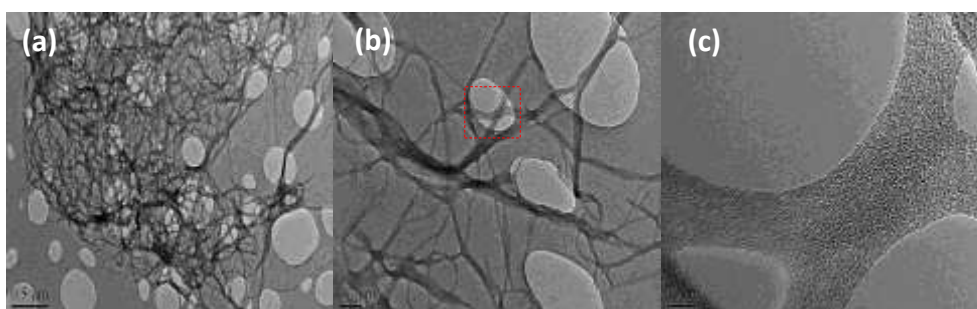


Figure S23 TEM images of the diluted sol of the **2a**-oxalic acid (1:1, 0.05 w/v%) Bar: 0.5 μ m, 0.1 μ m and 10 nm