Disruption of a binary organogel by the chemical warfare agent soman (GD) and common organophosphorus simulants.

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Electronic Supplementary Information

Experimental

General remarks: All reactions were performed under slight positive pressure of nitrogen using oven-dried glassware. NMR spectra were determined on a Bruker AVII 400 spectrometer with the chemical shifts reported in parts per million (ppm), calibrated to the centre of the solvent peak set. All solvents and starting materials were purchased from chemical stores where available. Low resolution mass spectra were recorded on a Waters Acquity UHPLC-MS system. High resolution mass spectra were recorded on a Bruker Maxis ESI-TOF system by the mass spectrometry service at the University of Southampton.

Organogel breakdown experiments initiated by the addition of liquid simulant or GD: Gels (1 mL) were formed at various concentrations in a vial, 1.2 cm in diameter, by heating a sample of compound **1** in cyclohexane and then cooling the sample to 15 ºC. The sample was then allowed to come to room temperature (19-20 ºC). The vials were then inverted to check organogel formation. Nine identical samples were prepared for each addition of DCP/DMMP, three samples to act as a blank and three for the addition of each simulant. The DCP/DMMP was added carefully to the surface of the organogel with the minimal disturbance. This was taken as time = 0. At set intervals (2 minutes, 5 minutes, 10 minutes) one of the experiments containing either DMMP, DCP or no addition of simulant was halted the solution created from the gel-to-sol transition could be extracted and the volume recorded and translated into a percentage of the total volume of organogel plus DCP/DMMP. The results of this set of experiments are given in Figure S3.

Organogel breakdown experiments initiated by the addition of simulant vapours: The general experimental set up is illustrated in Figure 8. A sample of the organogel (1 mL) containing compound **1** (1 mg/mL) in cyclohexane was prepared as previously mentioned in a 2.3 cm diameter, 25 cm^3 volume vial. This vial was the inverted over a sample of DMMP/DCP and the vial was the sealed. The time at which the organogel sample was inverted over the DCP/DMMP sample was taken as time = 0. The time taken for the gel-to-sol transition to take place was then observed. If a gel-to-sol transition was identified then the experiment was repeated three times. A control experiment was conducted without the presence of either DCP or DMMP and no change was noted to the organogel over a 30 minute period. The same experiment repeated in the presence of DMMP did not show a gel-to-sol transition over a 30 minute period.

Table 1 Amount of gelator; compound **1** (mmol) and added phosphonate (mmol)

Gelator	**Amount of gelator in 1 mL of organogel (mmol)**			
	20.0 mg	5.0 mg	2.5 mg	1.0 mg
1	0.053	0.013	0.007	0.003
Phosphonate	**Amount of phosphonate added (mmol)**			
	0.100 mL	0.050 mL	0.010 mL	0.001 mL
DCP	0.695	0.348	0.070	0.007
DMMP	0.923	0.461	0.092	0.009
GD	-	0.281	0.056	-

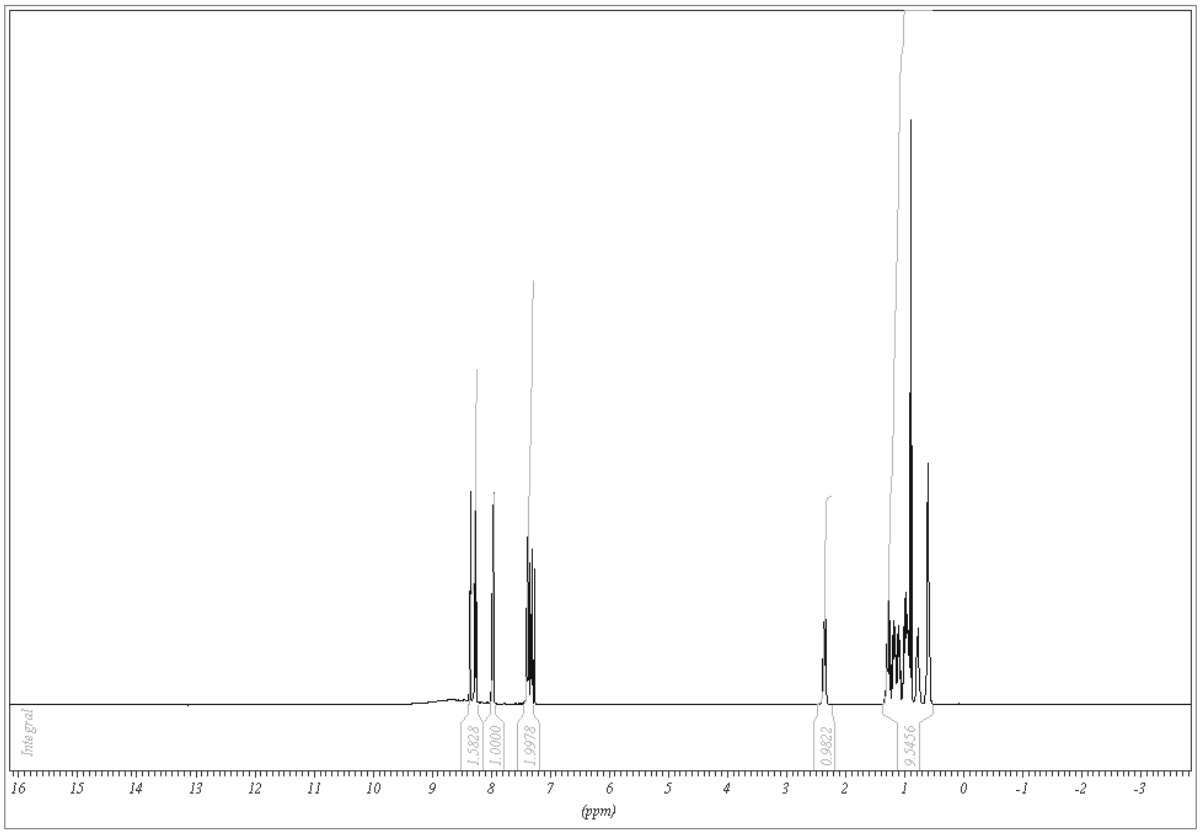


Figure S1 ^{1}H NMR of compound **1** in $CDCl_3$.

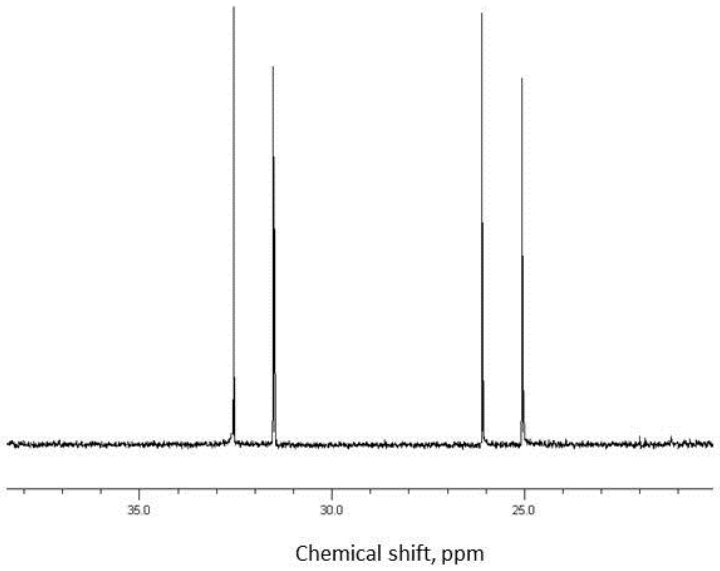


Figure S2 ^{31}P NMR of GD in $CDCl_3$. © Crown Copyright, Dstl.

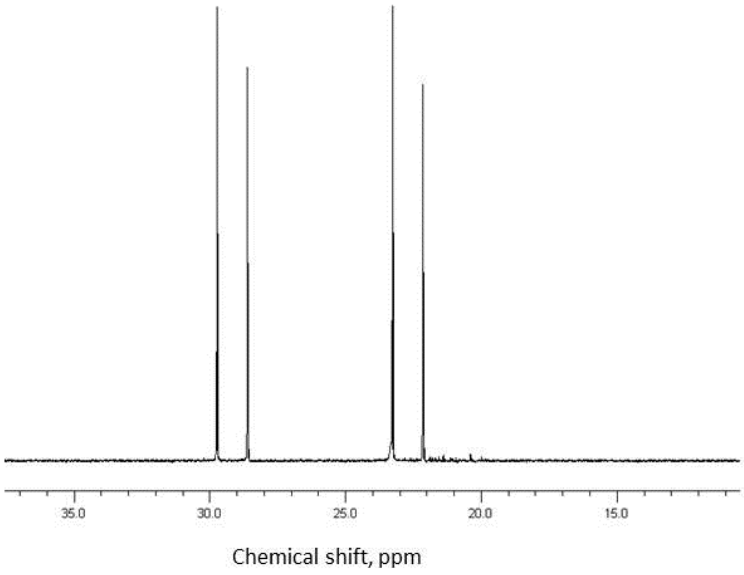


Figure S3 ^{31}P NMR of compound **1** (approximately 1 mg/mL) in cyclohexane-d_{12} with the addition of GD (approximately 2 mg/mL). This NMR spectrum was obtained after the solution was allowed to stand for 20 minutes. © Crown Copyright, Dstl.

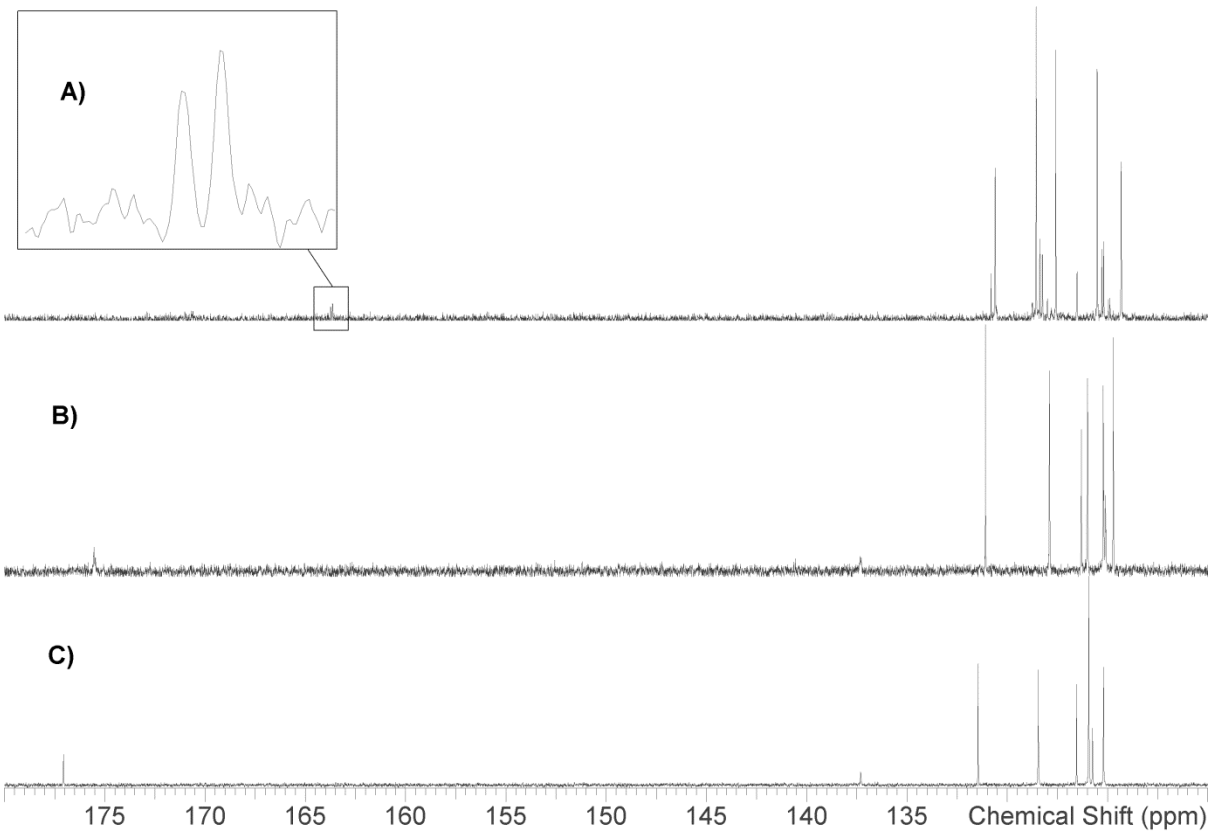


Figure S4 ^{13}C NMR stack plot of compound **1** in $CDCl_3$ with A) the addition of DCP (the expanded area of the spectrum shows a doublet that is likely to be due to the reaction of DCP with carboxylate, B) the addition of DMMP and C) no addition of simulant.

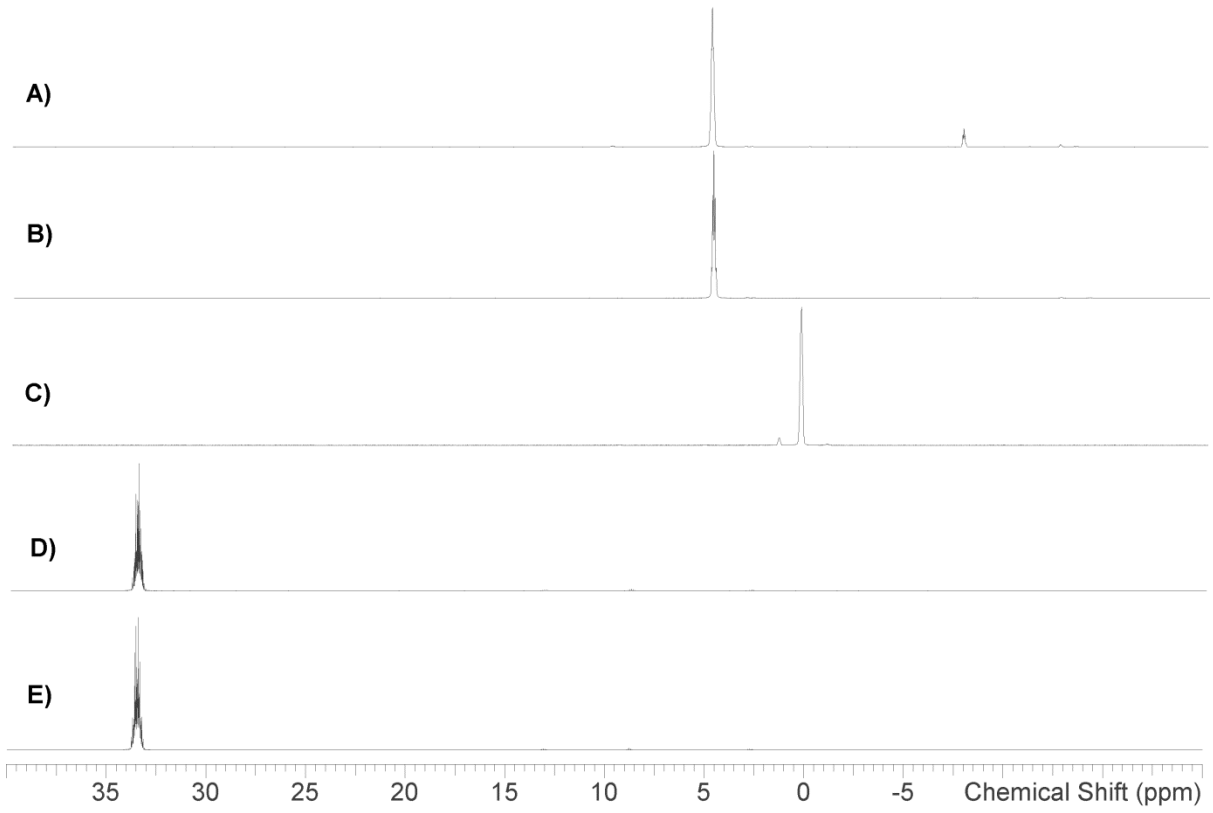


Figure S5 ^{31}P NMR stack plot in $CDCl_3$ of A) compound **1** with the addition of DCP, B) DCP only, C) DHP only (containing a phosphoric acid stabiliser), D) compound **1** with the addition of DMMP and E) DMMP only.

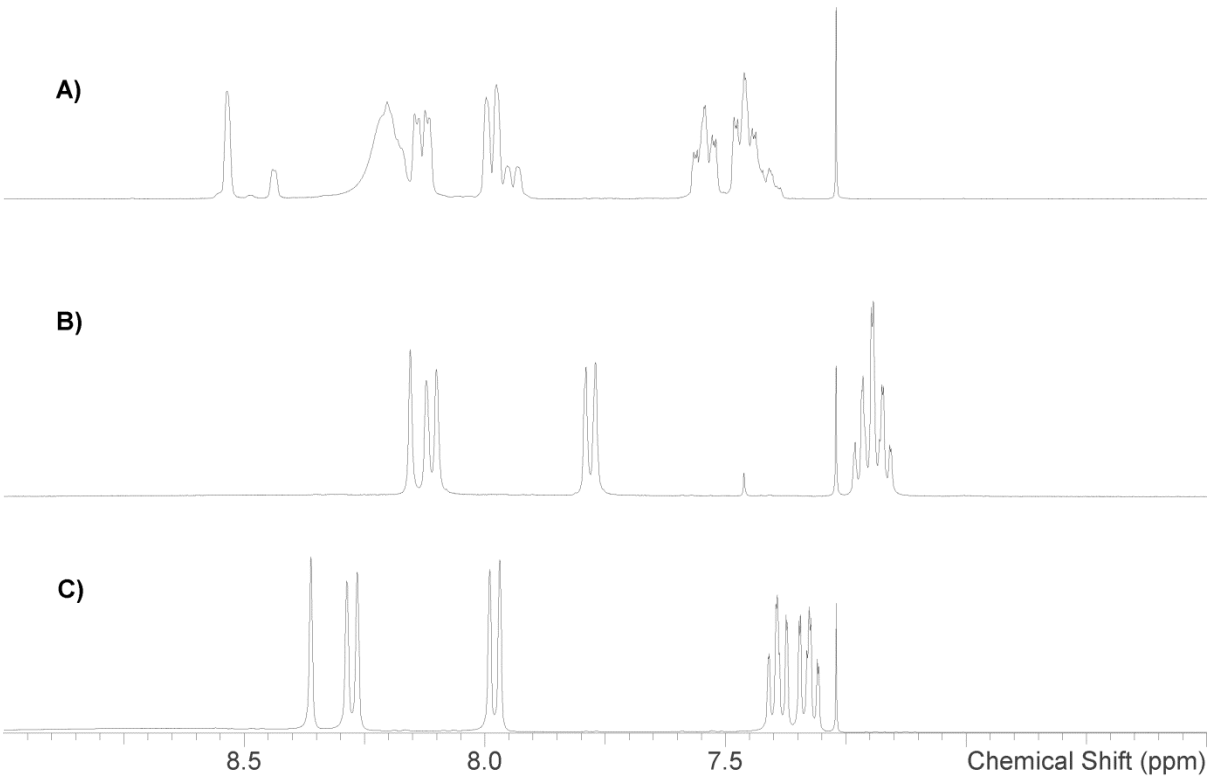


Figure S6 ^{1}H NMR stack plot of compound **1** in $CDCl_3$ with A) the addition of DCP, B) the addition of DMMP and C) compound **1** only.

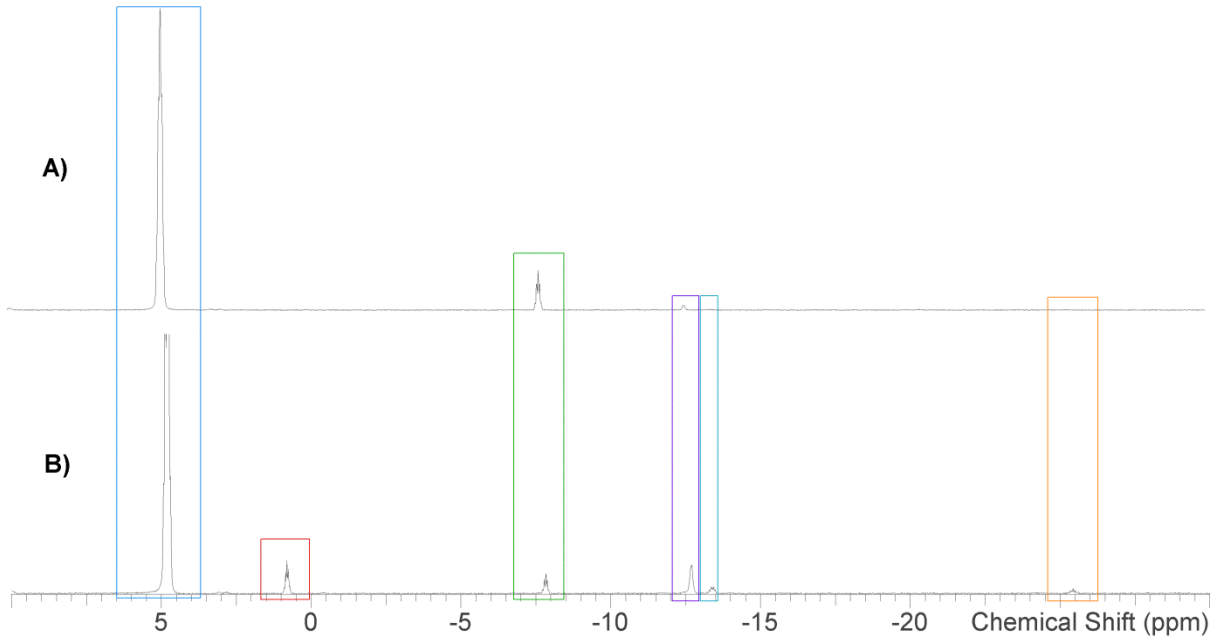


Figure S7a ^{31}P NMR stack plot in $CDCl_3$ of A) compound **1** with the addition of DCP and B) same sample left to stand at room temperature for a greater period of time showing further break down of the DCP.

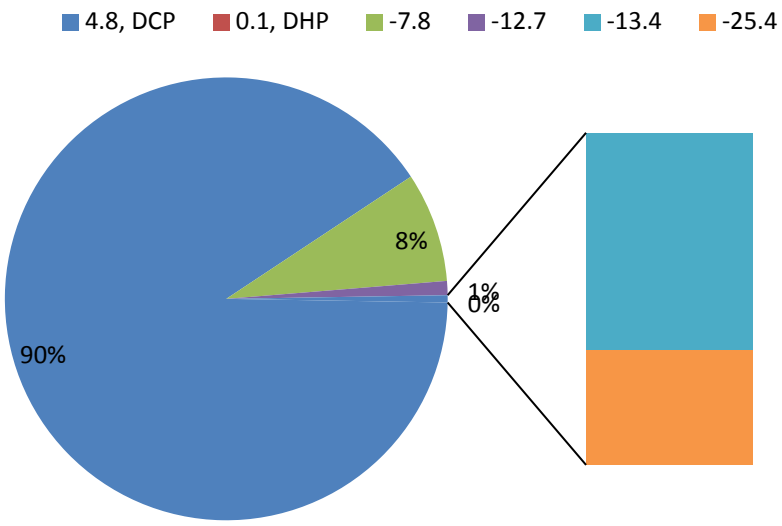


Figure S7b Pie chart showing the proportion of different phosphorus species in solution as shown in Figure S7a A. The different Phosphorus species have been labelled in accordance with their chemical shift given in ppm.

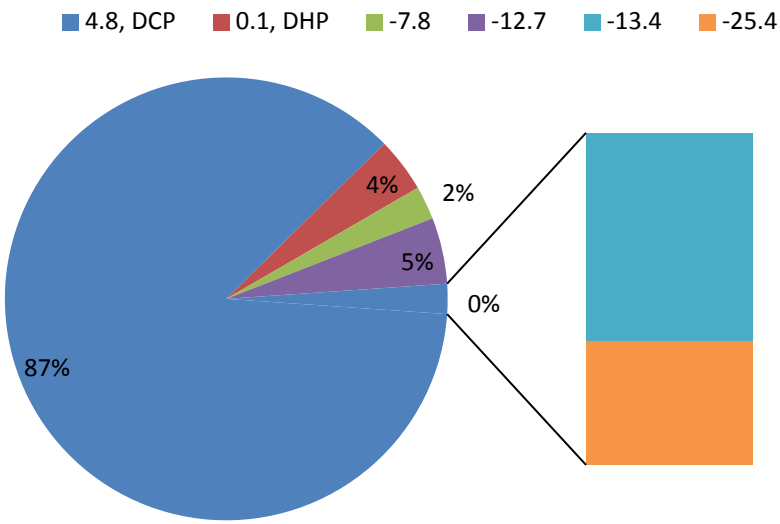


Figure S7c Pie chart showing the proportion of different phosphorus species in solution as shown in Figure S7a B. The different Phosphorus species have been labelled in accordance with their chemical shift given in ppm.

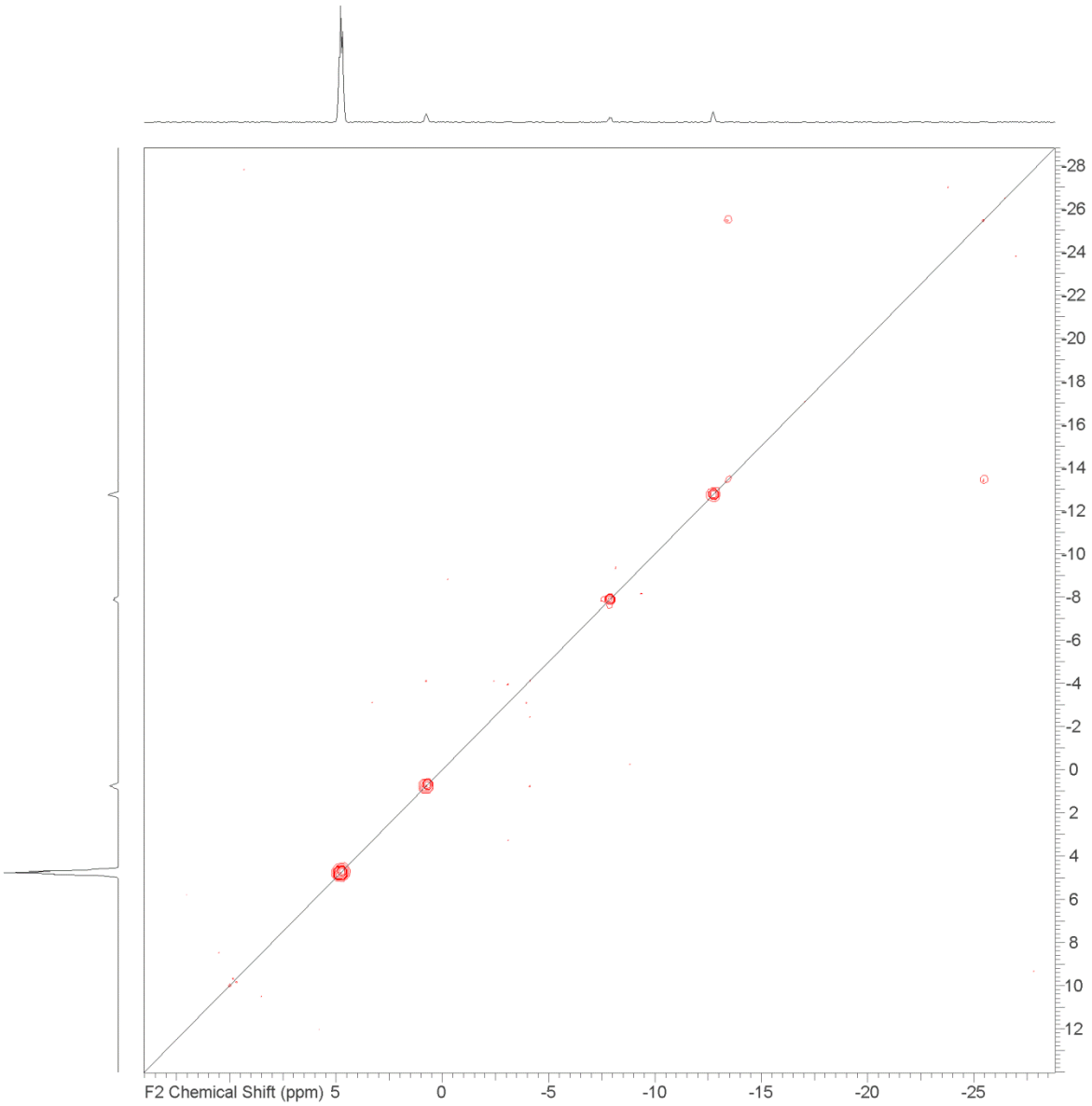


Figure S8 ^{31}P COSY of compound **1** in $CDCl_3$ with the addition of DCP.

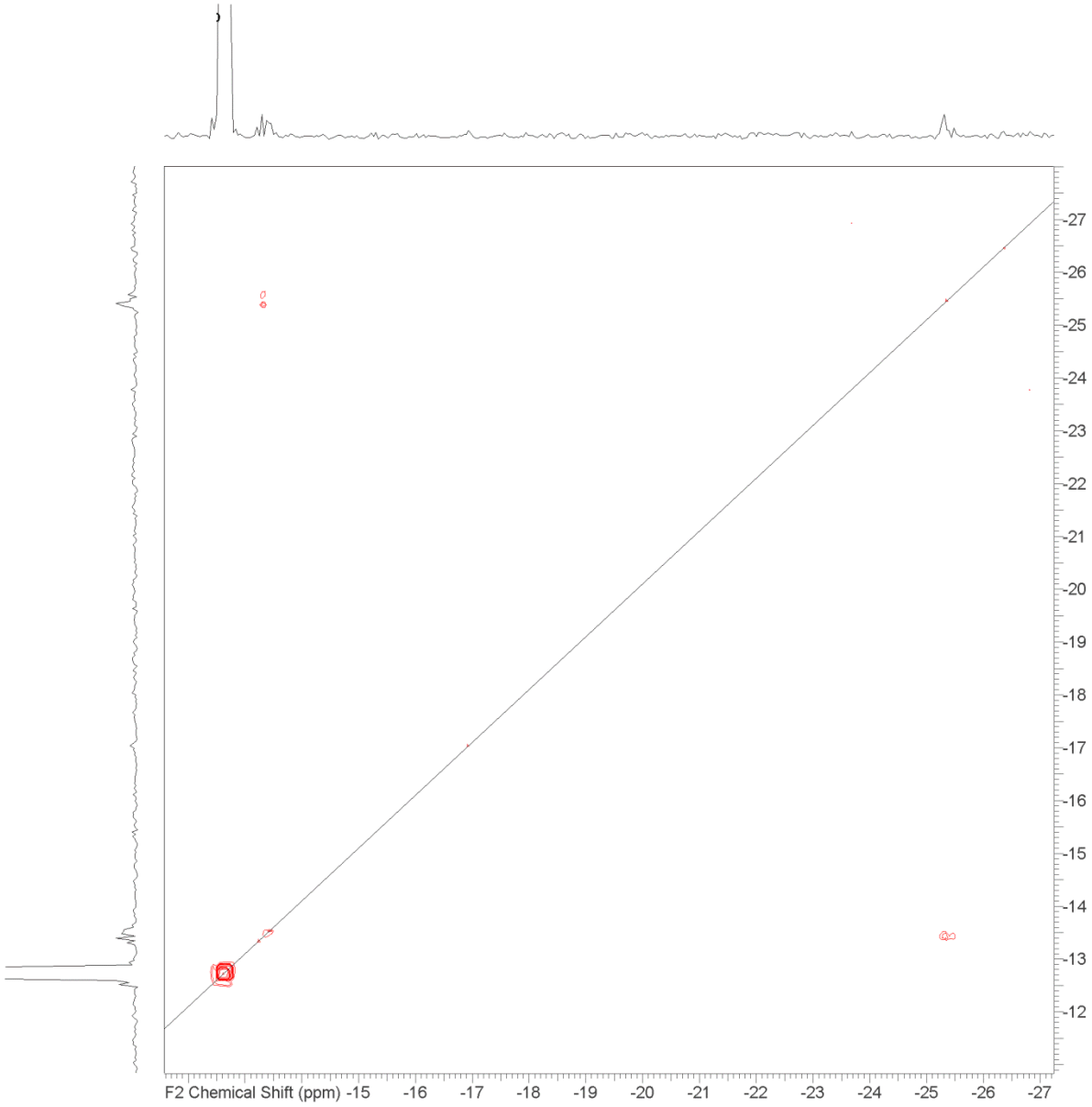


Figure S9 Expanded ^{31}P COSY of compound **1** in $CDCl_3$ with the addition of DCP.

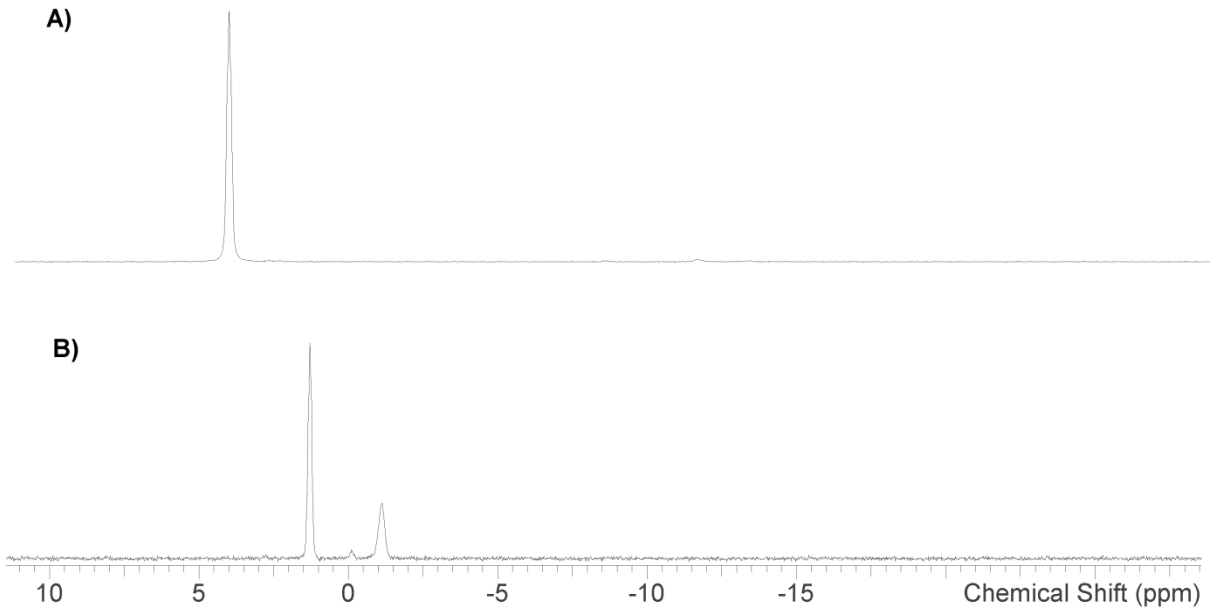


Figure S10 ^{31}P NMR stack plot in cyclohexane (1 mL) locked to external D_2O, A) with the addition of DCP and B) with the addition of DHP and a phosphoric acid stabiliser.

Table S2 High resolution mass spectrometry data obtained from the reaction of gelator **1** (10 mg/mL) and DCP (0.1 mL) in cyclohexane (1 mL). The reaction mixture was the further diluted with acetonitrile for the purpose of mass spectrum analysis.

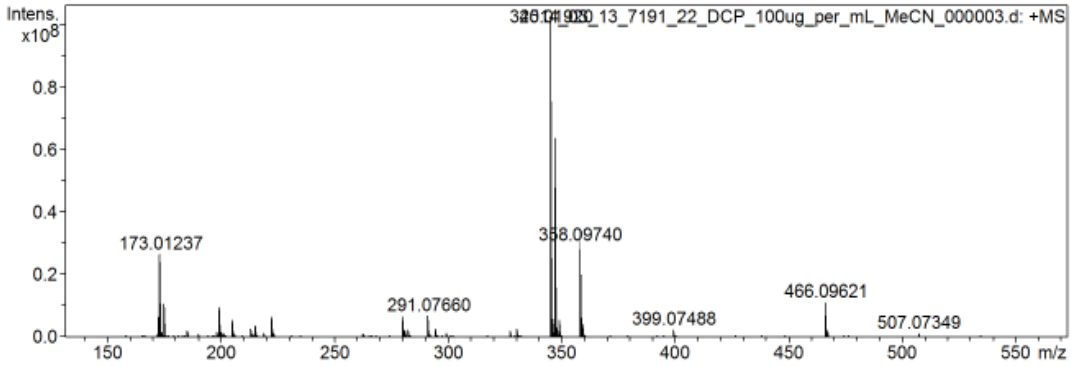
Ion	**Experimental value (m/z)**	**Calculated value (m/z)**
$[DCP + H]^+$	173.0129	173.0124
$[\mathbf{2} + H]^+$	294.2193	294.2194
$[\mathbf{2} + Na]^+$	316.2012	316.2018
$[\mathbf{4} - \cdot]^+$	358.0965	358.0974

Chemistry - solariX APPI Accurate Mass Report

Analysis Info

Analysis Name	D:\Data\Chemistry2014\APPI\2014_03_13_7191_22_DCP_100ug_per_mL_MeCN_000003.d	Acquisition Date	3/13/2014 4:13:00 PM
Method	APPI	Operator	
Sample Name	positive ion APPI	Instrument / Ser#	solariX -0
Comment	7191_22_DCP1mg/mL toluene positive ion		

+MS



Meas. m/z	Formula	m/z	err [ppm]	err [mDa]	# Sigma	mSigma	rdb	e¯ Conf	N-Rule
173.01237	C 4 H 11 Cl O 3 P	173.01288	2.97	0.51	1	40.8	-0.5	even	ok
358.09740	C 9 H 8 N 15 O 2	358.09799	1.65	0.59	1	9.9	13.5	even	ok
	C 10 H 14 N 8 O 7	358.09800	1.67	0.60	2	10.5	8.0	odd	ok
	C 11 H 20 N O 12	358.09800	1.68	0.60	3	17.8	2.5	even	ok
	C 20 H 15 N 4 O P	358.09780	1.11	0.40	4	51.9	16.0	odd	ok
	C 9 H 18 N 4 O 11	358.09666	-2.07	-0.74	5	53.9	3.0	odd	ok
	C 22 H 17 N O 2 P	358.09914	4.86	1.74	6	58.5	15.5	even	ok
	C 8 H 12 N 11 O 6	358.09665	-2.08	-0.75	7	58.7	8.5	even	ok
	C 7 H 6 N 18 O	358.09665	-2.10	-0.75	8	67.2	14.0	odd	ok
	C 24 H 12 N 3 O	358.09749	0.25	0.09	9	75.3	20.5	even	ok
	C 26 H 14 O 2	358.09883	4.00	1.43	10	82.1	20.0	odd	ok
	C 19 H 19 O 5 P	358.09646	-2.62	-0.94	11	104.6	11.0	odd	ok
	C 18 H 13 N 7 P	358.09646	-2.64	-0.94	12	112.8	16.5	even	ok
	C 22 H 10 N 6	358.09615	-3.50	-1.25	13	136.1	21.0	odd	ok

Figure S11 HRMS of DCP and compound **4** obtained from a reaction mixture of compound **1** (10 mg), DCP (0.1 mL) in cyclohexane (1 mL).

Chemistry - maXis HPLC-ESI Accurate Mass Report

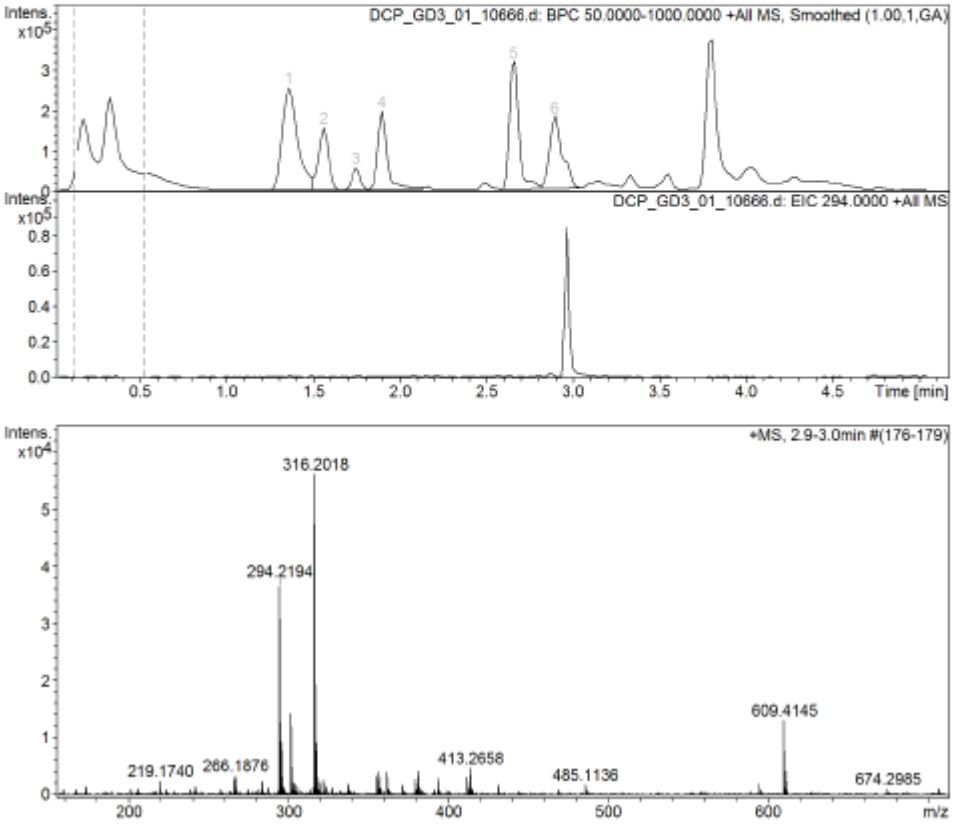
Analysis Info

Analysis Name	D:\Data\chemistry\2014\mar 14\DCP_GD3_01_10666.d	Acquisition Date	13/03/2014 16:42:53
Method	soton lcms pos 120 to 1500.m	Operator	MSWEB@SOTON.AC.UK
Sample Name	DCP	Instrument / Ser#	maXis 17
Comment	Analyst: JMH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	120 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

+MS, 2.9-3.0min #(176-179)



Meas. m/z	Formula	m/z	err [ppm]	err [mDa]	# Sigma	mSigma	rdb	e⁻ Conf	N-Rule
294.2194	C 14 H 33 N O 3 P	294.2193	-0.6	-0.2	1	15.1	-0.5	even	ok
	C 19 H 29 N Na	294.2192	-0.8	-0.2	2	21.6	5.5	even	ok
316.2018	C 14 H 32 N Na O 3 P	316.2012	-1.7	-0.5	1	2.8	-0.5	even	ok
	C 12 H 27 N 7 O P	316.2009	-2.6	-0.8	2	4.9	3.5	even	ok

Samples were analysed using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser. Samples were introduced to the mass spectrometer via a Dionex Ultimate 3000 autosampler and uHPLC pump. Gradient 20% acetonitrile (0.1% formic acid) to 100% acetonitrile (0.1% formic acid) in five minutes. Column, Acquity UPLC BEH C18 (Waters) 1.7 micron 50 x 2.1mm. High resolution mass spectra were recorded using positive/negative ion electrospray ionisation.

Figure S12 HRMS of compound **2** obtained from a reaction mixture of compound **1** (10 mg), DCP (0.1 mL) in cyclohexane (1 mL).

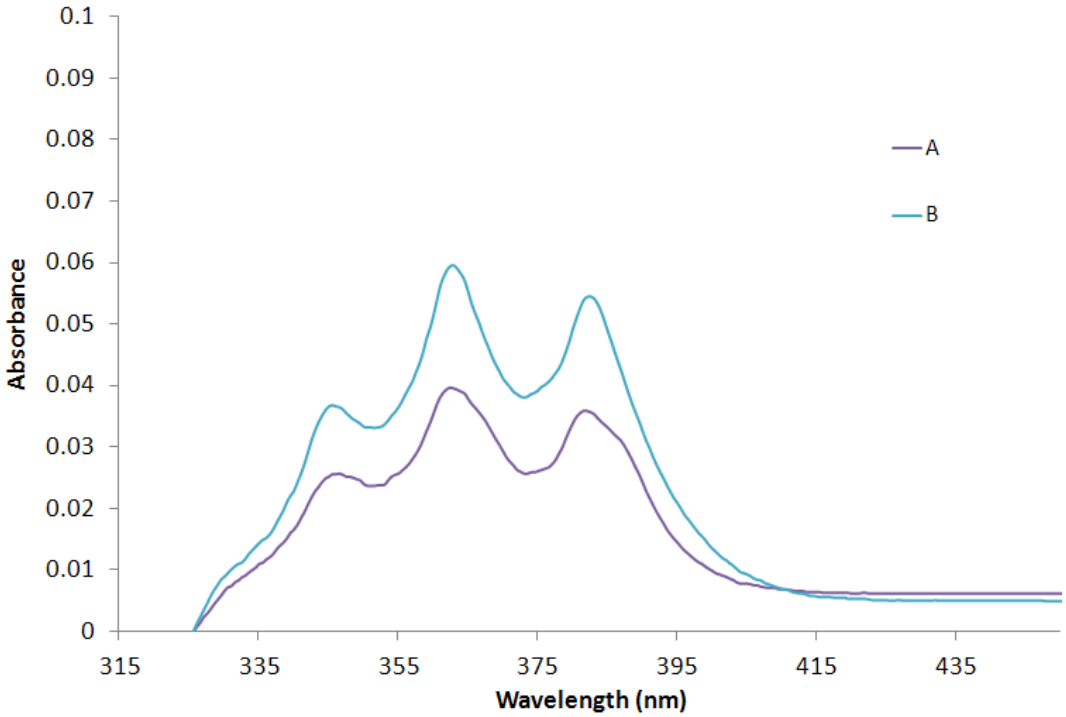


Figure S13 UV-Vis spectra of A) 0.027 mM solution of compound **1** in cyclohexane B) the sol produced from the gel-to-sol transition of a organogel containing compound **1** (9.8 mg/mL) in cyclohexane (1 mL) with the addition of DCP (0.1 mL) after a 4545 fold dilution with cyclohexane. This data was used to establish the excitation wavelength (363 nm) used in the florescence experiments as described in Figure 7.

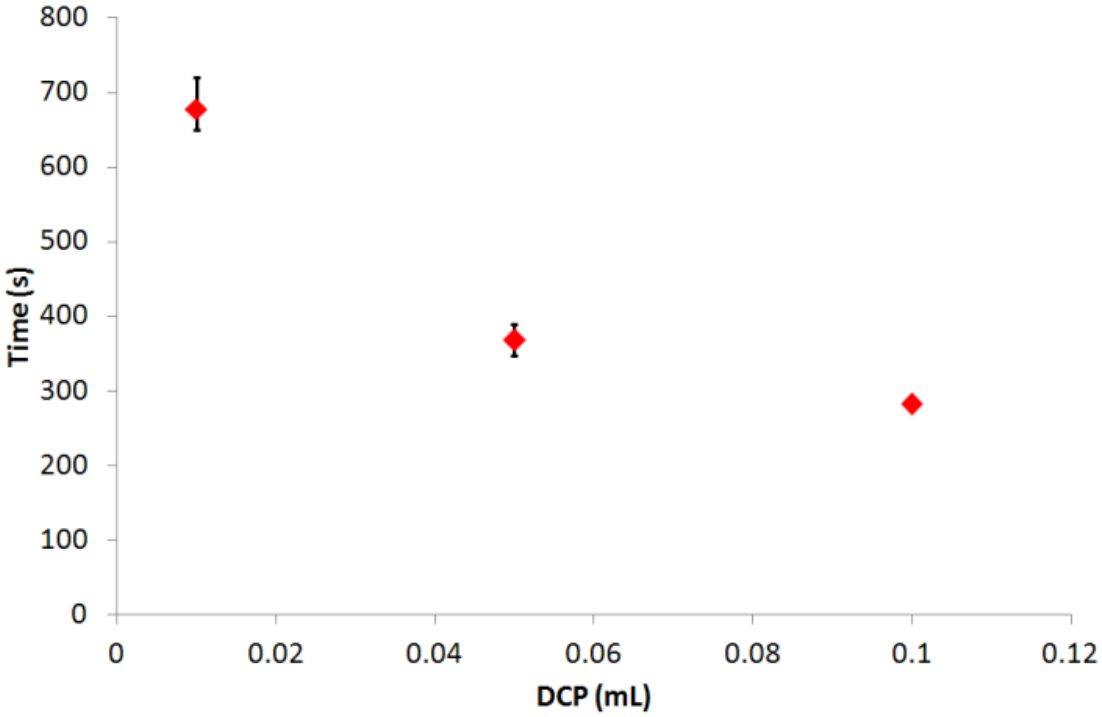


Figure S14 Time taken to dissolve organogel (1 mL) containing compound **1** (1 mg/mL) with DCP vapours. X-axis gives the amount of DCP added to the system as shown in Figure 8, included in the main publication.