Metal-Organic Gels of Silver Salts with a α,β-Unsaturated Ketone: Influence of Anions and Solvents on Gelation

Debarati Das and Kumar Biradha*

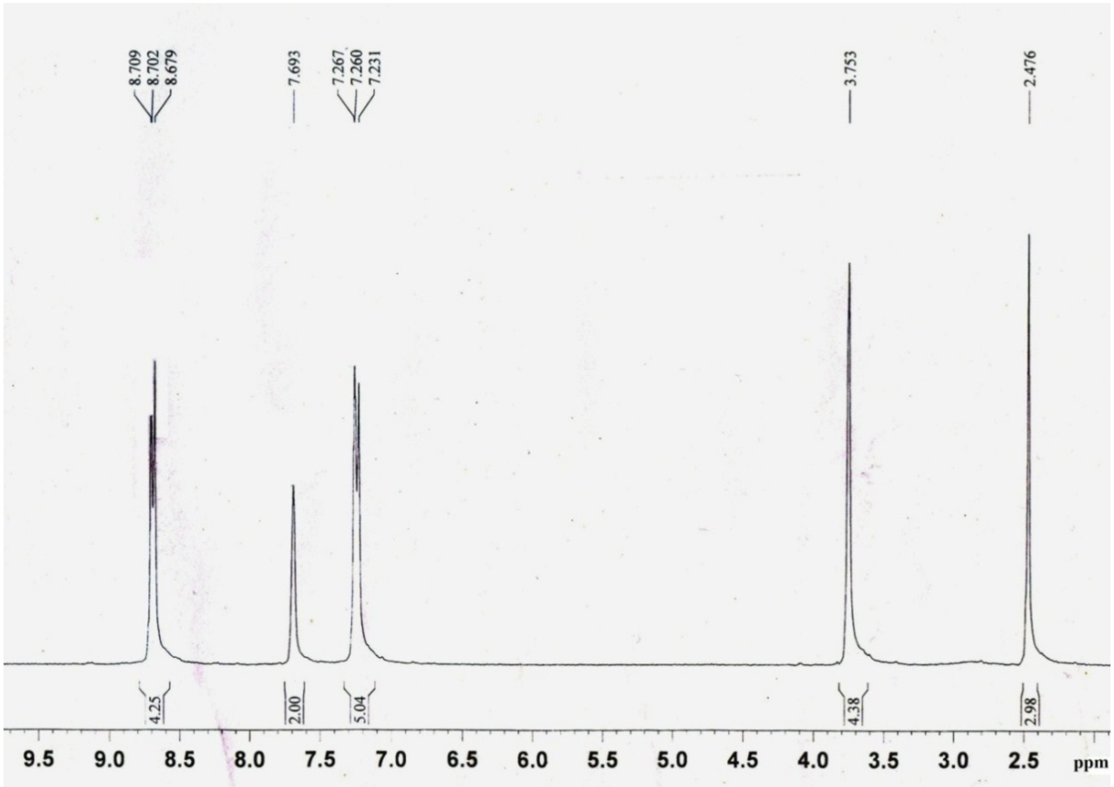
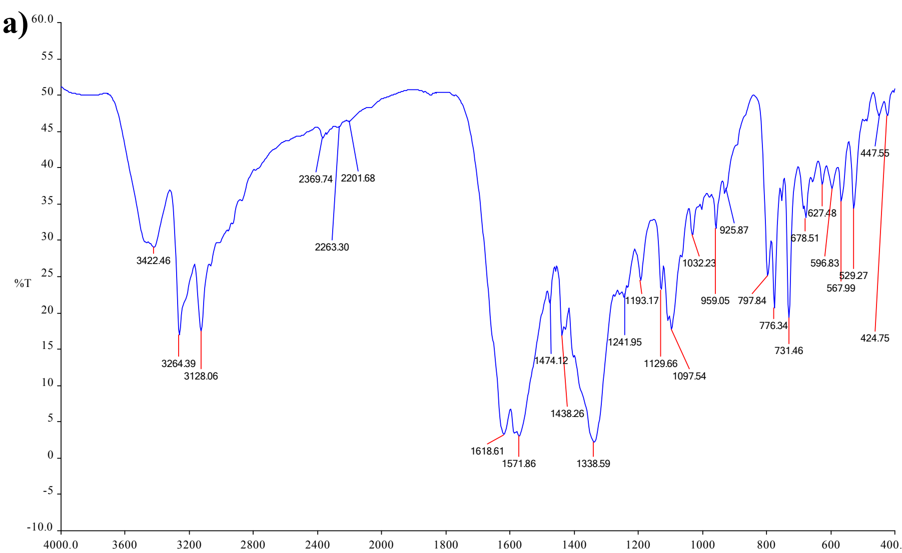


Figure S1: NMR spectrum of **L**.

a)



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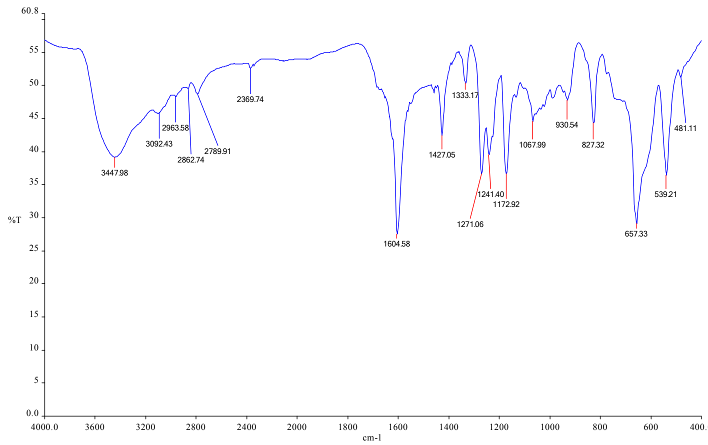
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55
50
45
40
35
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15
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5
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%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
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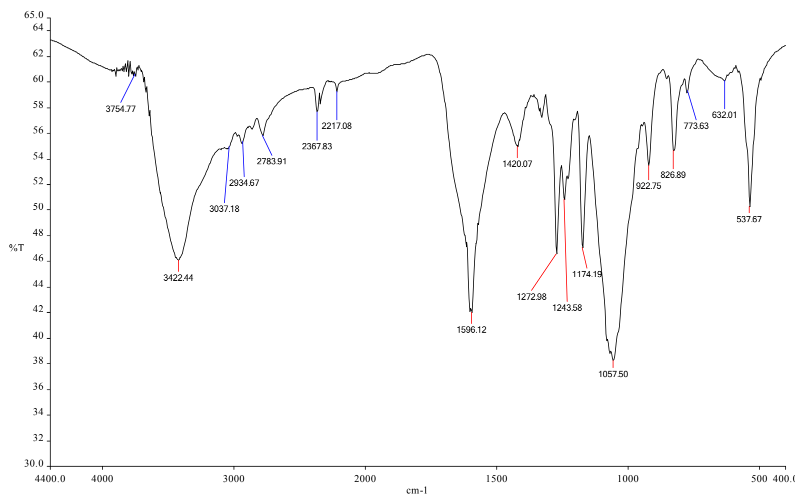
800
600
400.0
cm-1
3447.98
3092.43
2963.58
2862.74
2789.91
2369.74
1604.58
1427.05
1333.17
1271.06
1241.40
1172.92
1067.99
930.54
827.32
657.33
539.21
481.11

c)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%T
4400.0
4000
3000
2000
1500
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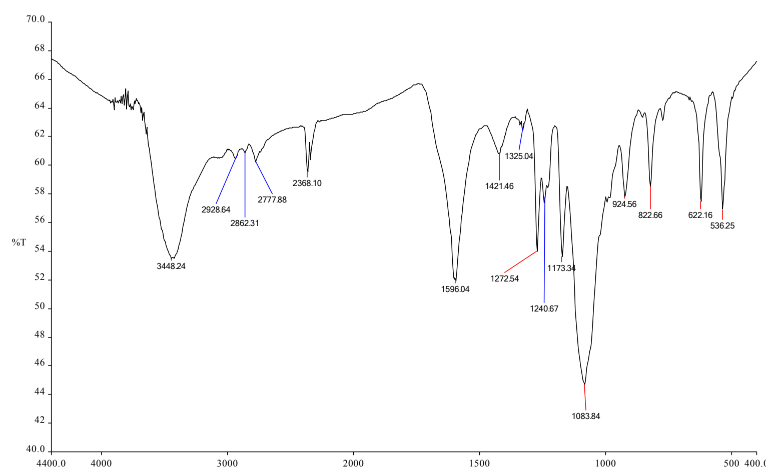
500
400.0
cm-1
3754.77
3422.44
3037.18
2934.67
2783.91
2367.83
2217.08
1596.12
1420.07
1272.98
1243.58
1174.19
1057.50
922.75
826.89
773.63
632.01
537.67

d)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48
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42
40.0
%T
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4000
3000
2000
1500
1000
500
400.0
cm-1
3448.24
2928.64
2862.31
2777.88
2368.10
1596.04
1421.46
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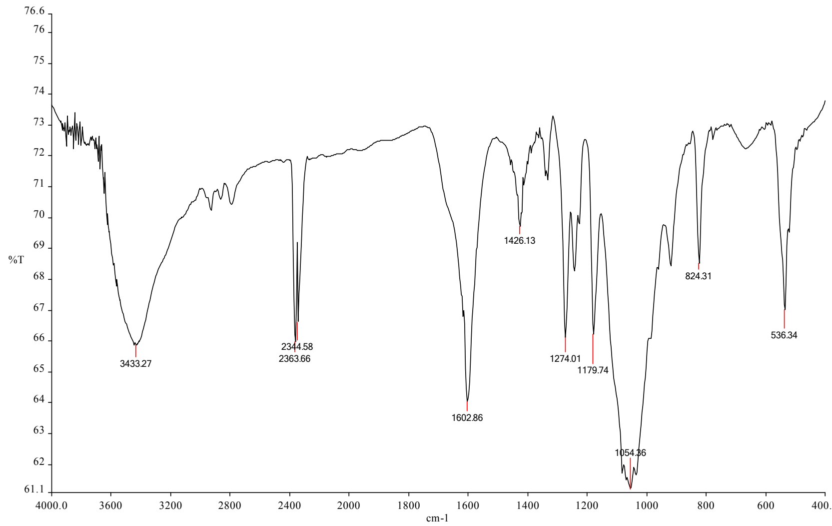
1272.54
1240.67
1173.34
1083.84
924.56
822.66
622.16
536.25

e)



f)

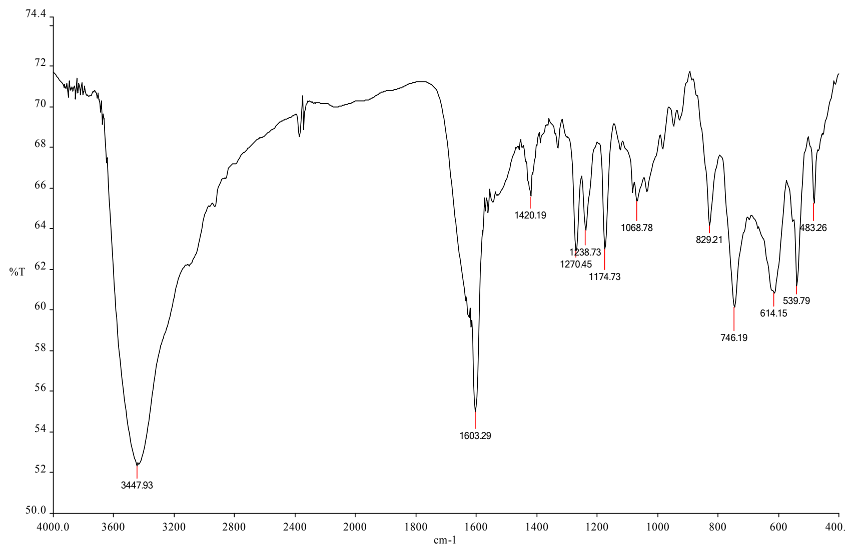


Figure S2: IR spectra of (a) CP-**1**, (b) CP-**2**, c-h) xerogels of MOG **1-4**.

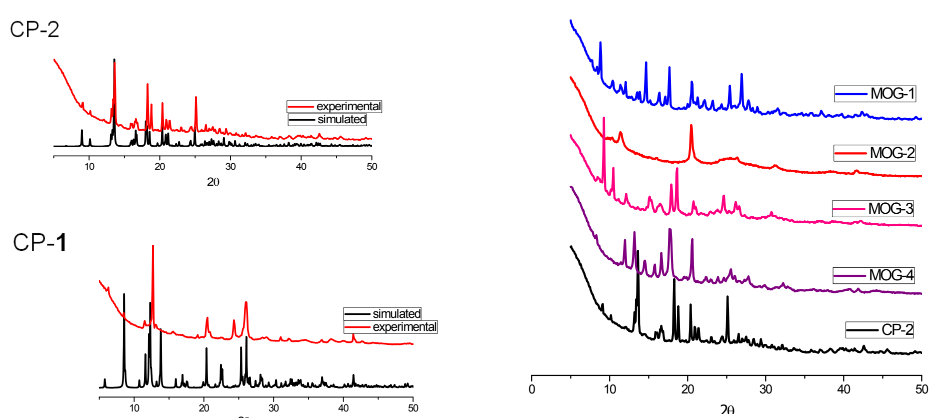


Figure S3. PXRD patterns of xerogels and CPs.

MOG-1

MOG-2

MOG-3

MOG-4

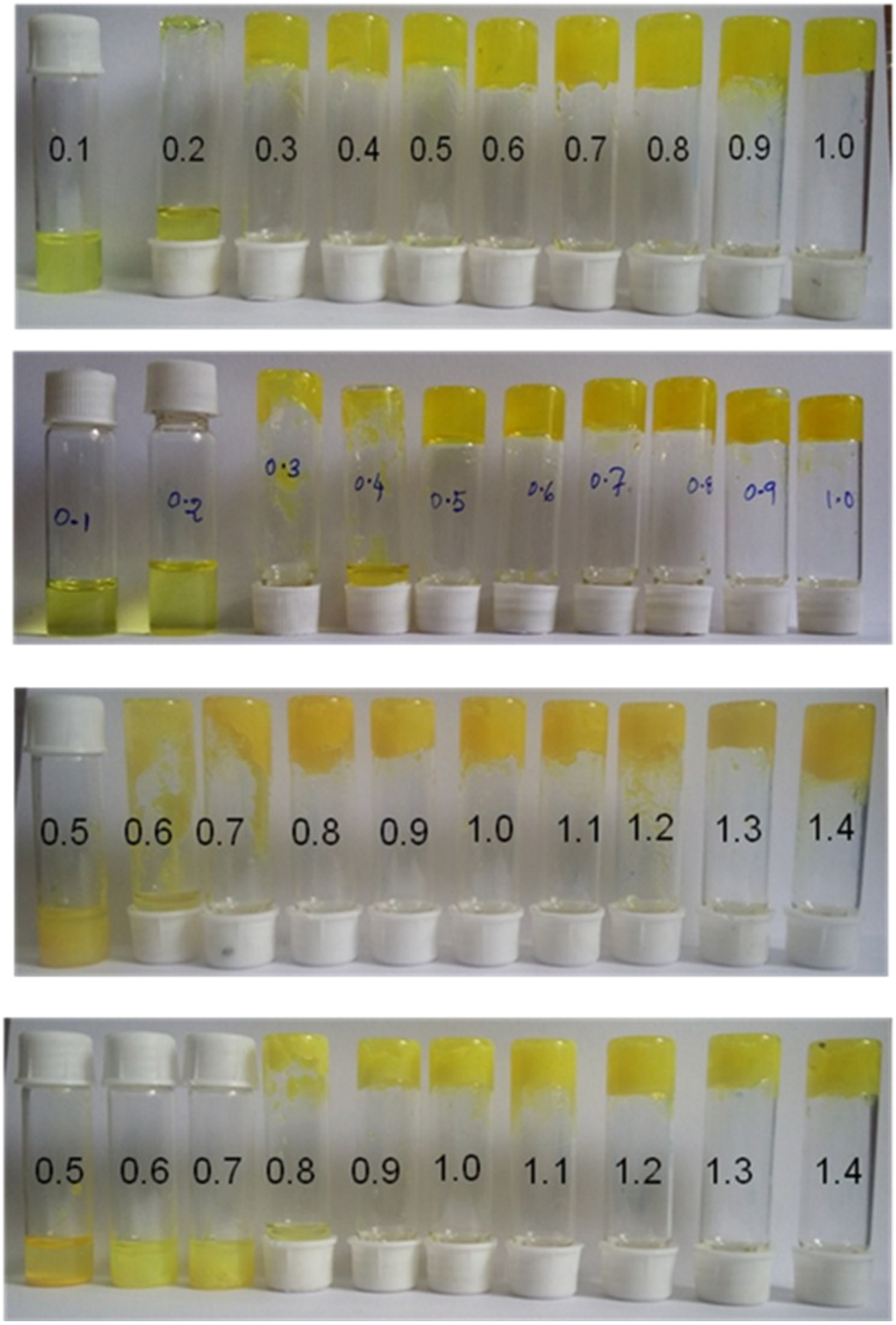


Figure S4: Illustration of the inverted vials for the gel formation reactions: formation of MOGs at various ratios of the metal and ligand.

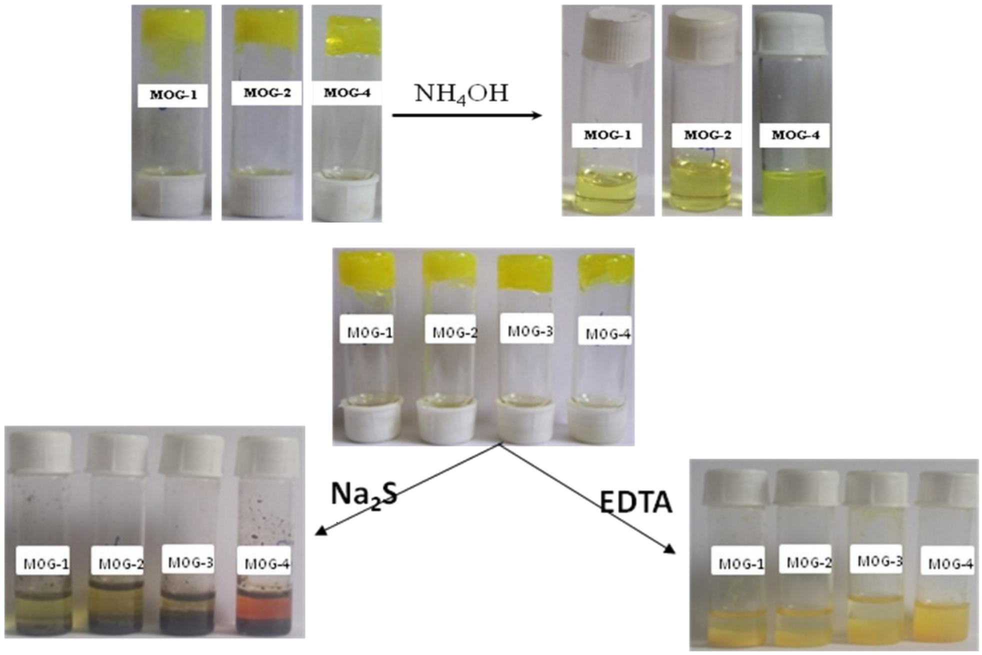


Figure S5: Chemical responsive behavior of the MOGs.

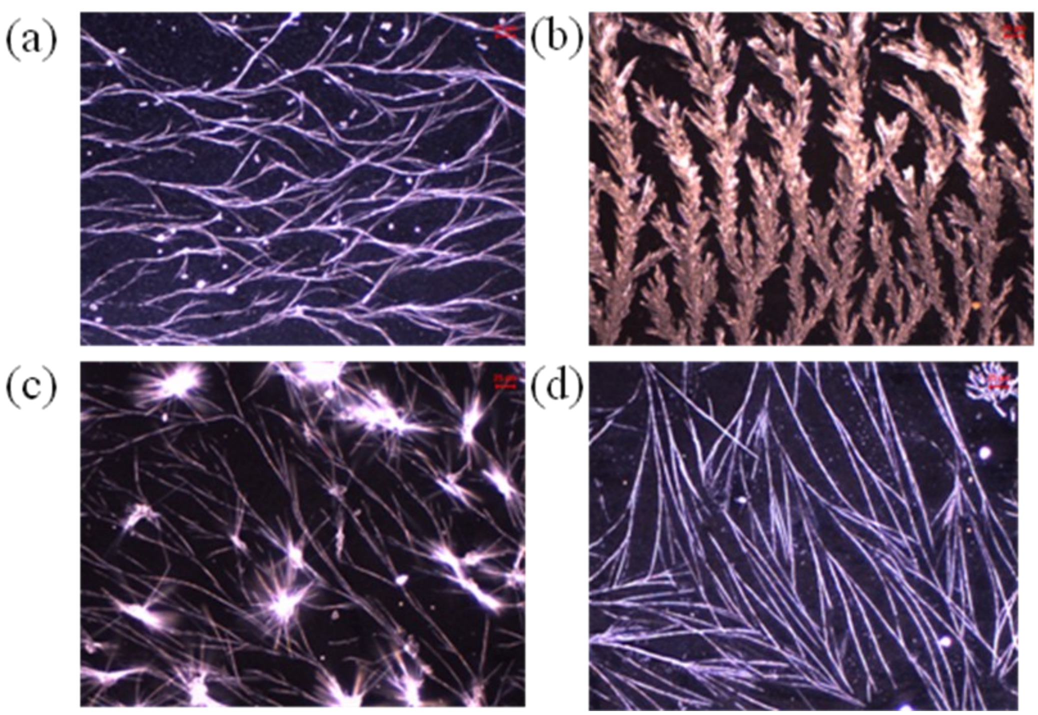


Figure- S6: Illustrations of microscopic studies: POM images of a) MOG-**1**, b) MOG-**2**, c) MOG-**3**, d) MOG-**4**.

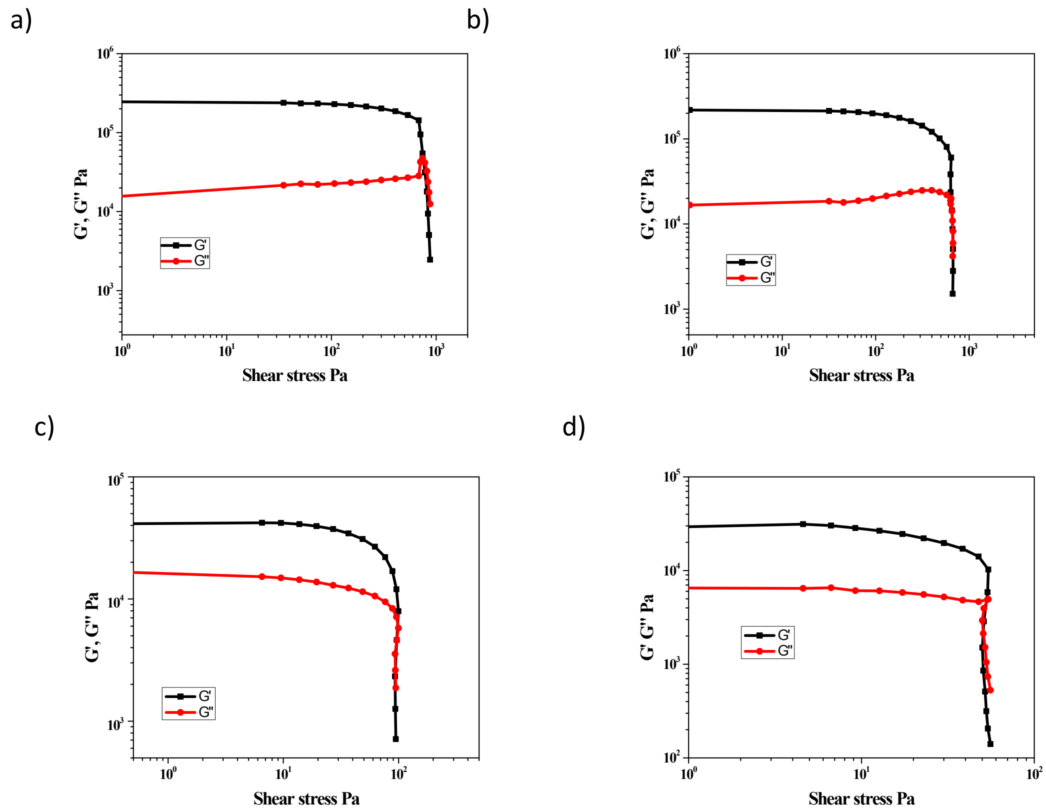


Figure- S7: Rheological experiment: Variation of the storage modulus (G′) and loss modulus (G′′) with shear stress for a) MOG-**1**, b) MOG-**2**, c) MOG-**3**, d) MOG-**4**.

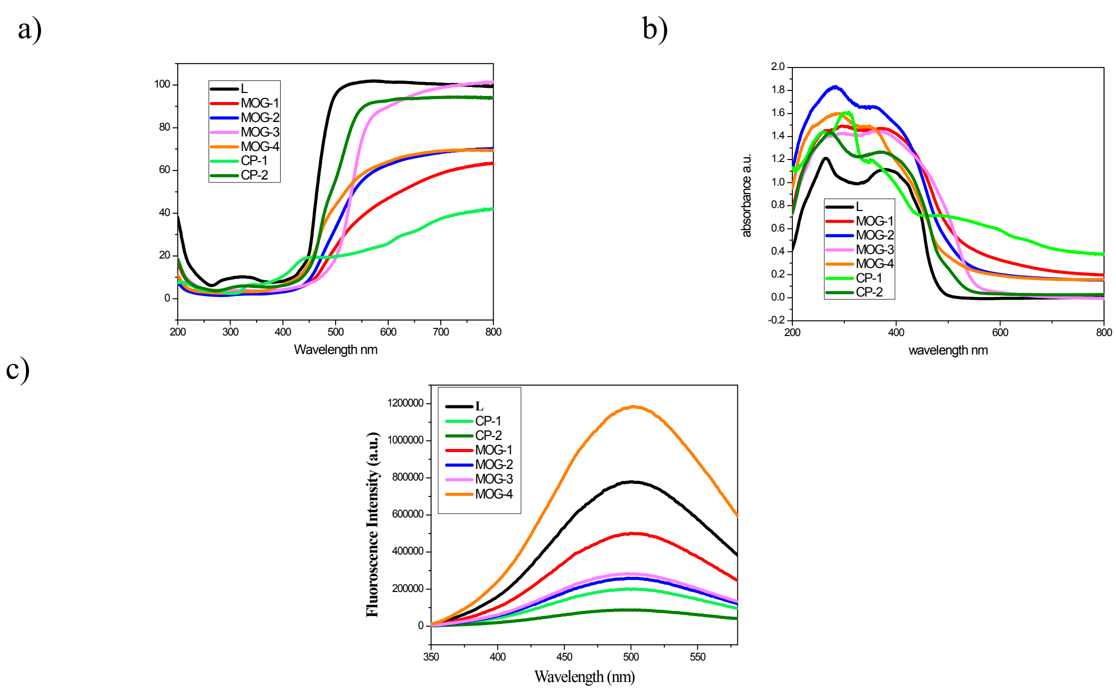
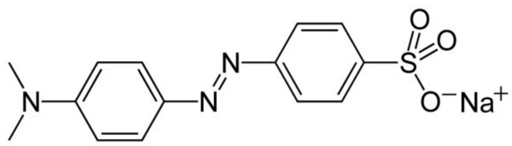
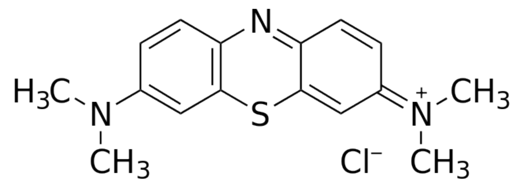


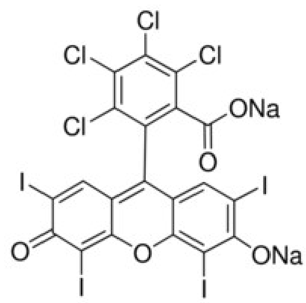
Figure-S8: (a. b) DRS study and (c) Solid state fluorescence study for all the CPs and MOGs along with **L**.



MO



MB



Rose Bengal

Figure S9. Structure of dyes used for study dye adsorption.

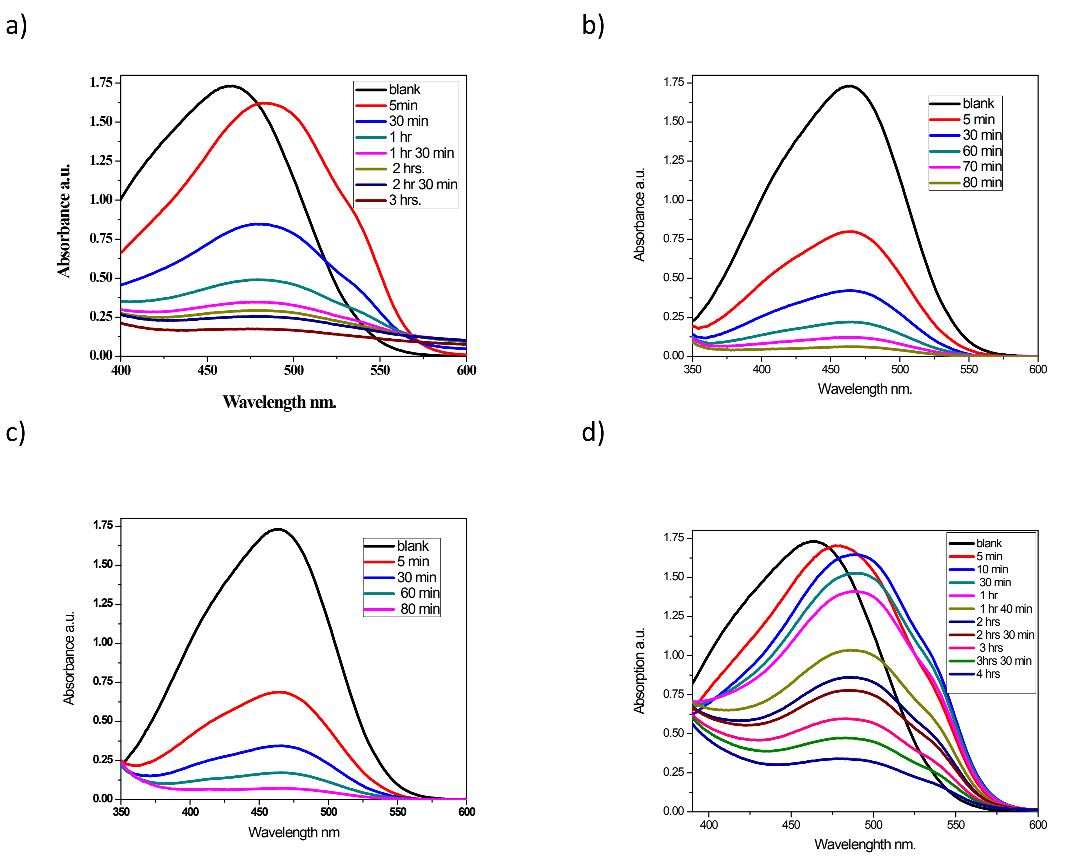


Figure S10: Dye removal from aq. solution of MO of all the xerogels of a) MOG-**1**, **b)** MOG-**2**, **c)** MOG- **3**, d) MOG-**4**.

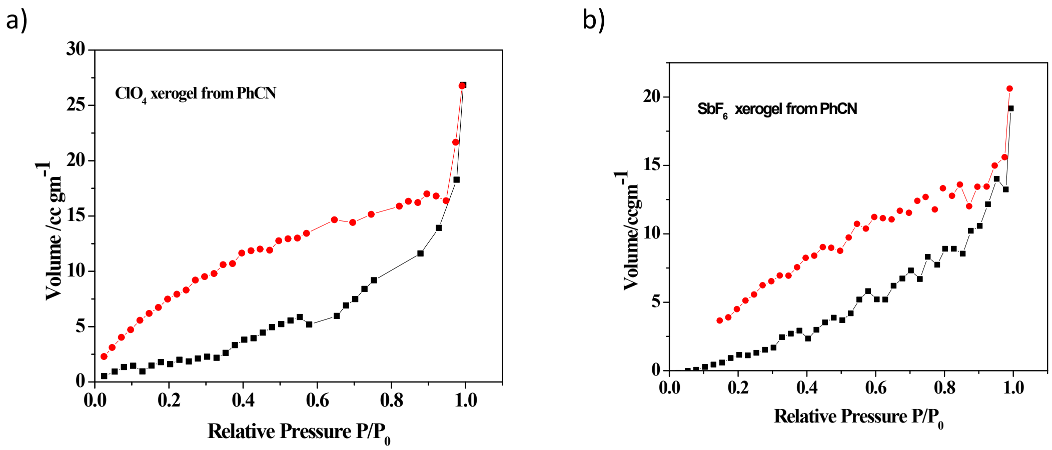


Figure S11: Gas adsorption isotherm for xerogels of MOGs (a) MOG-**2** (b) MOG-**4.**

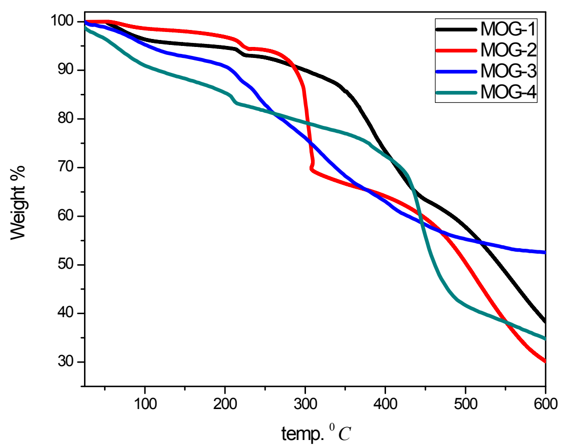
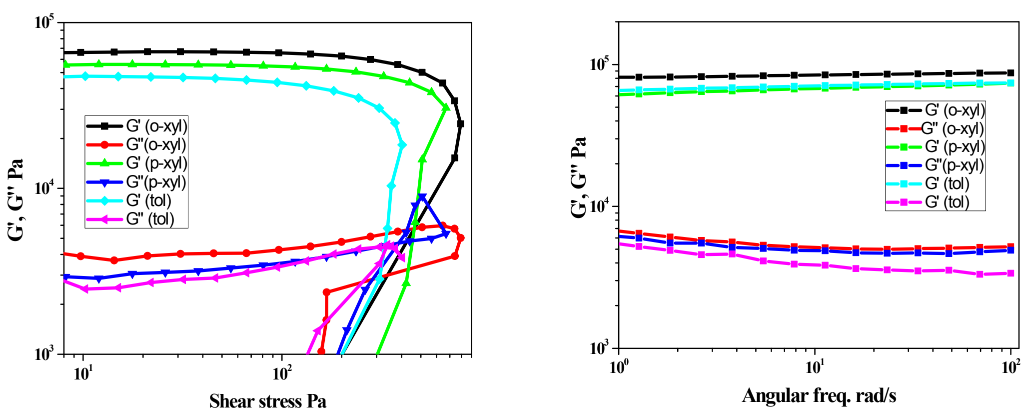


Figure S12: TGA of all the xerogels.



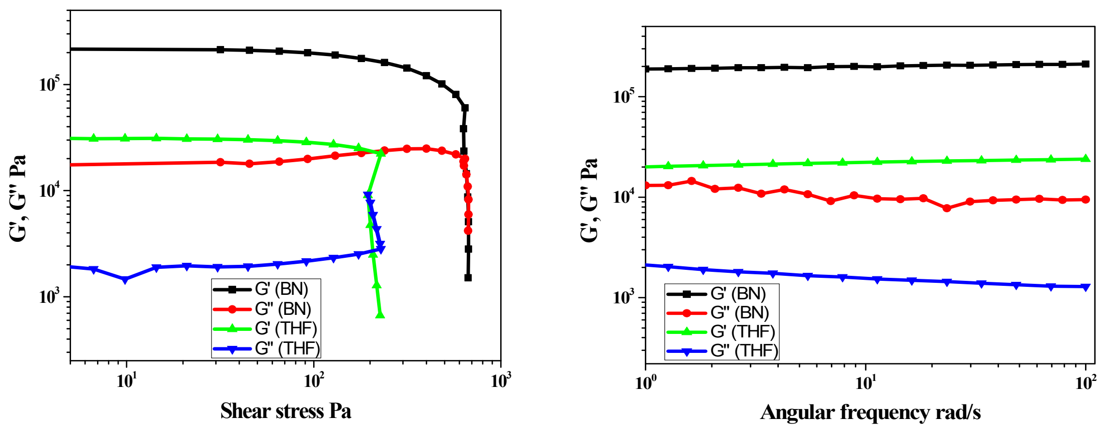


Figure S13: Rheological plots of ClO_4 anion**.**

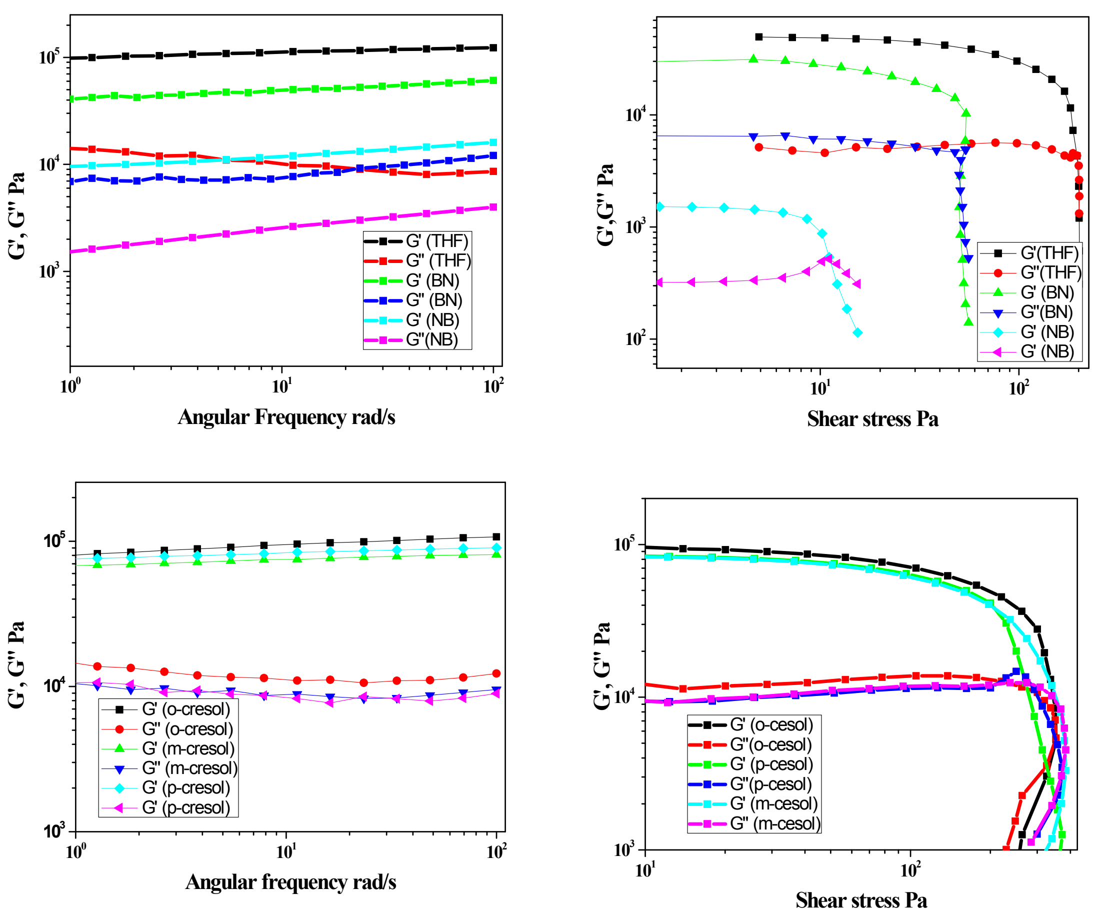


Figure S14: Rheological plots of anion SbF_6.

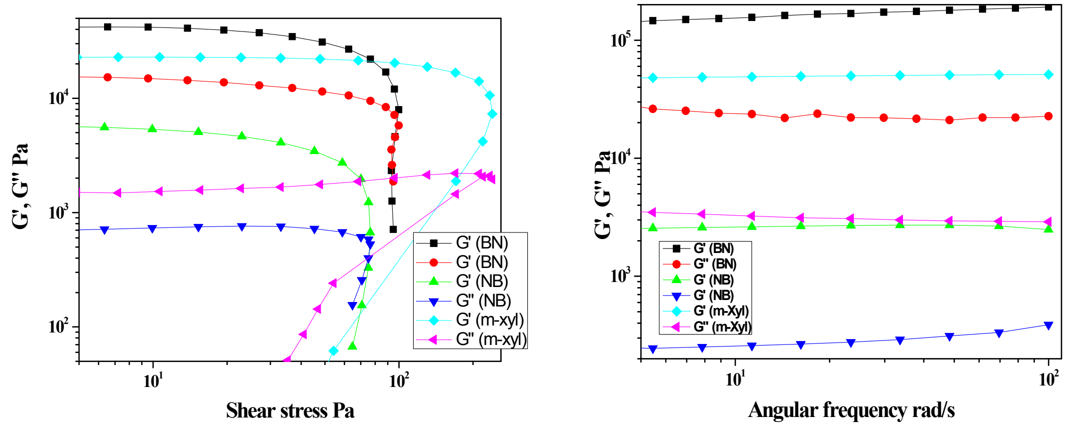


Figure S15: Rheological plots of anion OTf in different solvent.

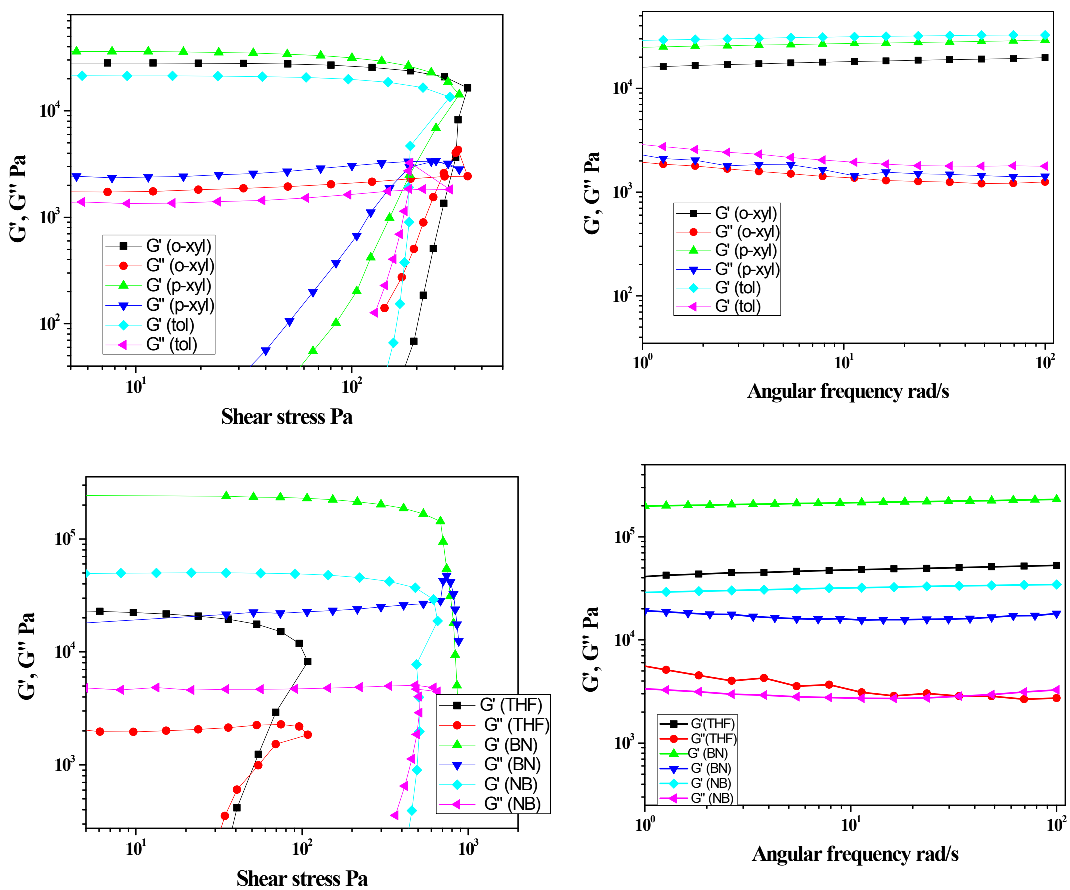


Figure S16: Rheological plots of anion BF_4

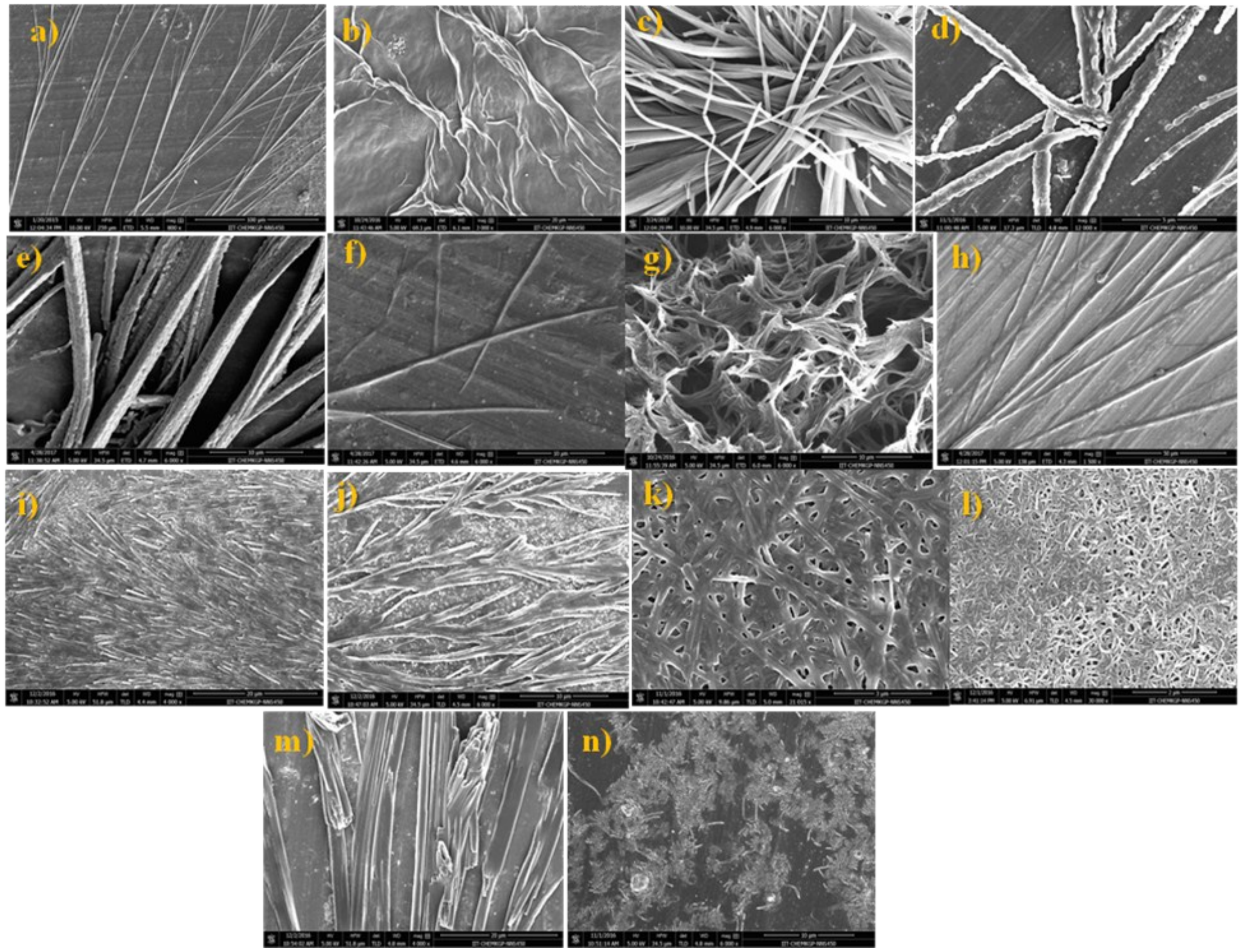
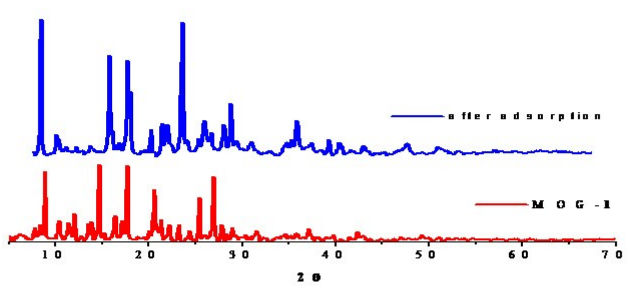


Figure S17: Illustration of FESEM images of xerogels with the four anions in different solvents: a) BF_4 in THF, b) BF_4 in NB, c) BF_4 in *p*-Xylene, d) BF_4 in toluene, e) BF_4 in *o*-Xylene, f) ClO_4 in *o*-Xylene, g) ClO_4 in NB, h) ClO_4 in THF, i) ClO_4 in toluene, j) ClO_4 in *p*-xylene, k) OTf in NB, l) OTf in *m*-xylene, m) SbF_6 in THF, n) SbF_6 in NB.

a)



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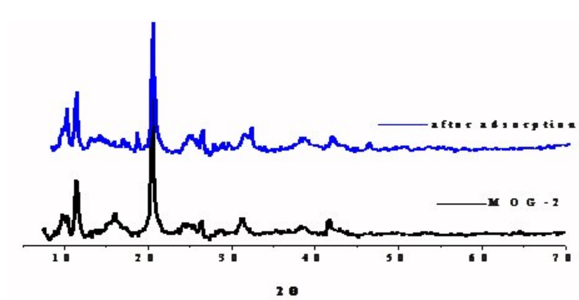
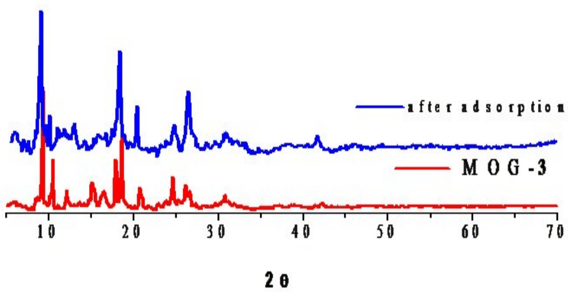


c)



d)

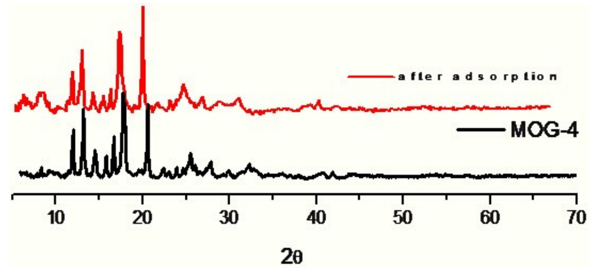
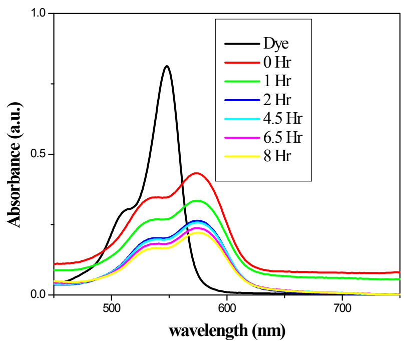
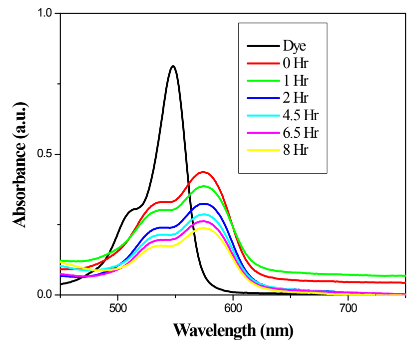


Figure S18: PXRD pattern of xerogels before and after dye adsorption: a) MOG-**1**, b) MOG-**2**, c) MOG-**3**, d) MOG-**4**.

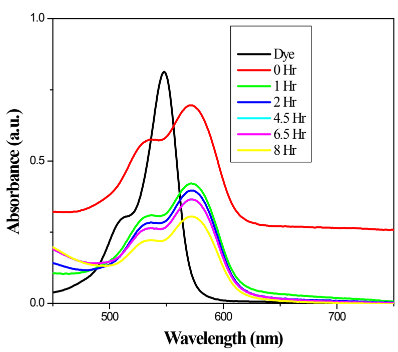
a)



b)



c)



d)

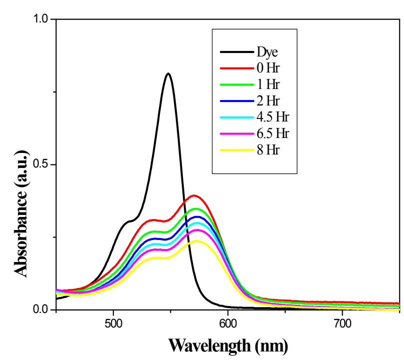


Figure S19: UV-vis adsorption spectra of xerogels of Rose Bengal dye: a) MOG-**1**, b)MOG-**2**, c) MOG-**3**, d) MOG-**4**.

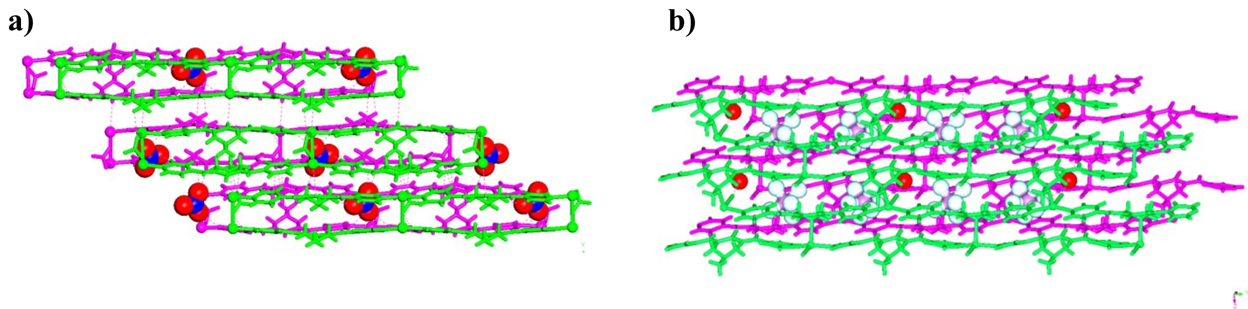


Figure S20: Illustration of crystal structures of CP-**1** and CP-**2**: a) front view of 3D-network formed by free nitrate anion *via* C-H…O hydrogen bonds in CP-**1**, b) Entrapment of SbF_6 anion and water molecule in between the brick wall network in CP-**2**.

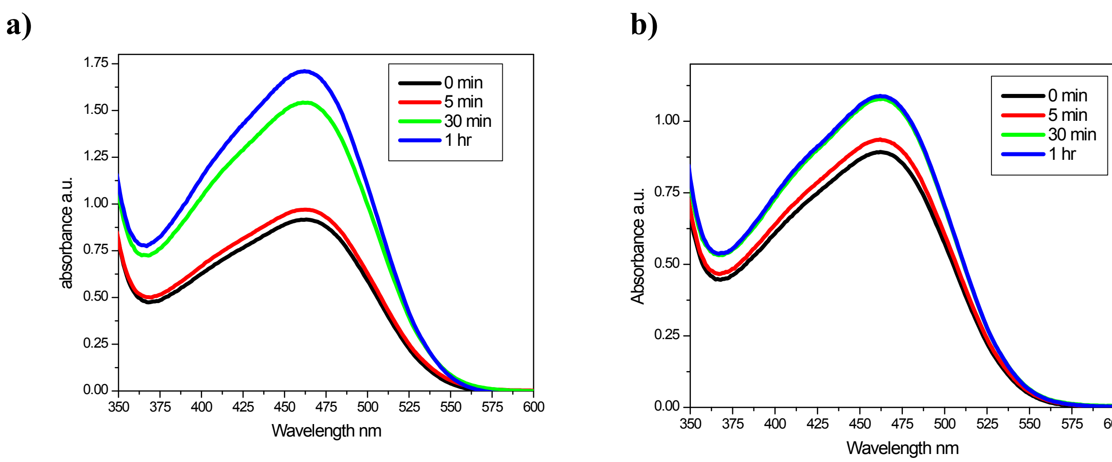
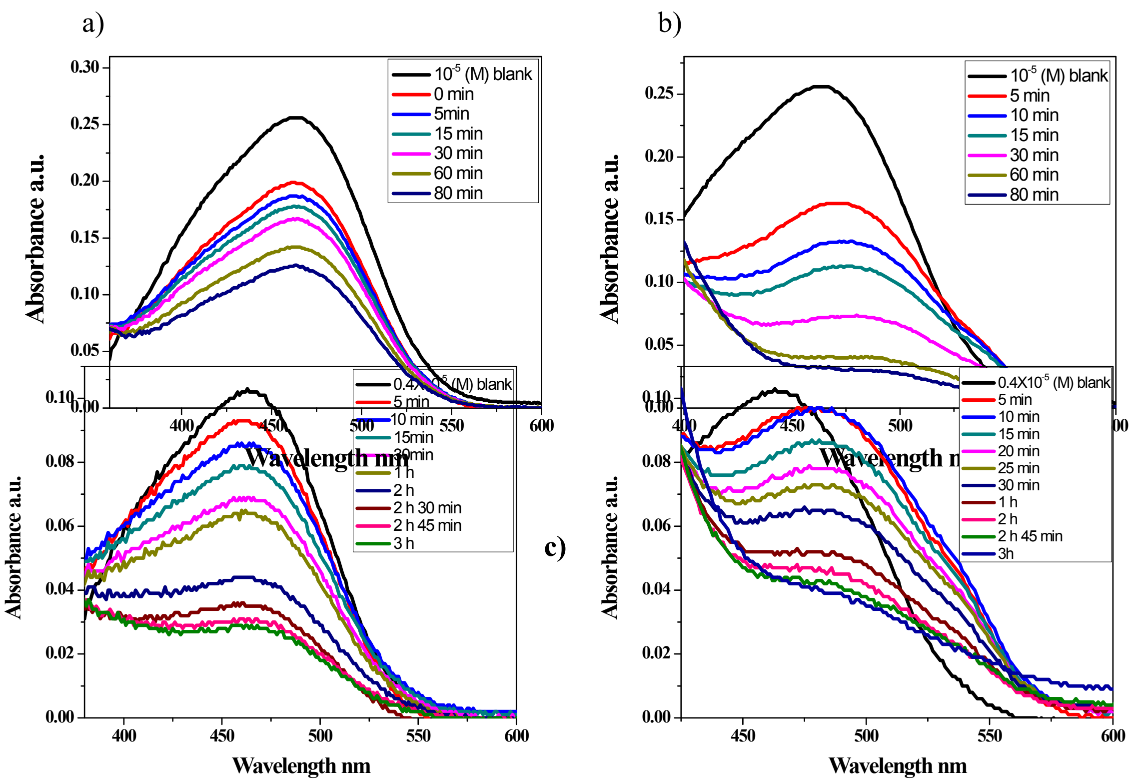


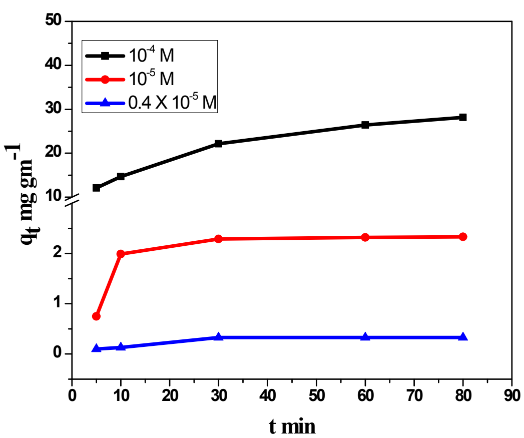
Figure S21: UV-vis desorption spectra of methyl orange adsorbed xerogels of a) MOG-**1**, b) MOG-**2**.



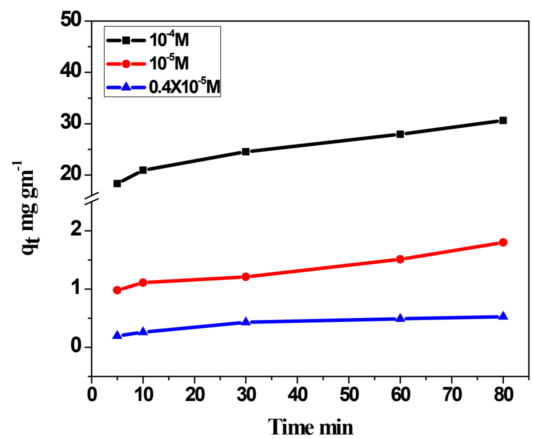
d)

Figure S22. Dye removal from high dilution of MO by xerogels of MOG-**2** and **4**.

a)



b)



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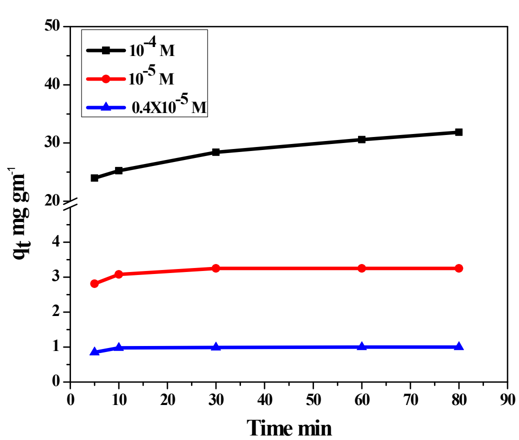

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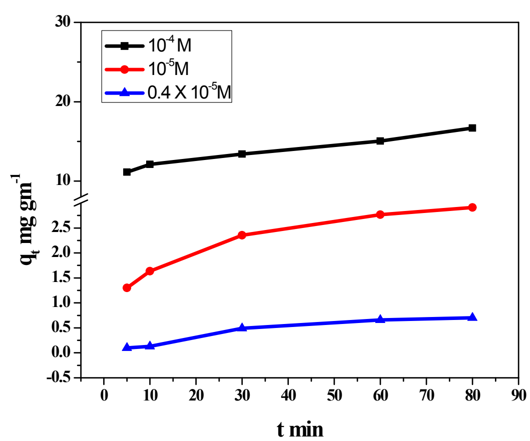


Figure S23: Plots of adsorption capacity (q_t) of MO dye *vs.* time (t) min for all the xerogels of MOGs **1**-**4** at three different concentrations.

Table S1: Rheological experiment data for all MOGs.

	Solvents	Yield stress(Pa)	G'-G"(Pa)
BF_4	BN	750.09	190754.88
	NB	488.02	28323.54
	o-xyl	310.02	16322.69
	p-xyl	198.06	24112.19
	Tol	139.72	27597.32
	THF	64.26	41283.73
ClO_4	BN	624.88	184843.44
	o-xyl	478.23	73071.32
	p-xyl	338.40	48683.57
	Tol	328.03	55609.69
	THF	194.17	16366.77
OTf	*m*-xyl	177.02	47057.41
	BN	98.22	148012.09
	NB	77.01	2355.73
SbF_6	*m*-cresol	355.01	52618.29
	o-cresol	343.39	49662.86
	p-cresol	259.70	58115.94
	THF	192.76	71973.22
	BN	51.30	46119.68
	NB	11.07	9513.78

Table S2: Surface area, pore volume and amount of nitrogen gas absorbed by the xerogels

Sample	Surface area m^2/g	Pore volume cc/g	N_2 uptake cc/gm
MOG-**4**	1.874	2.964×10^{-2}	20.74
MOG-**2**	77.586	4.151×10^{-2}	26.88

Table S3: Other Intermolecular interactions (Å) of complexes **1** and **2**

Complexes	Interactions	H···A (Å)	D···A (Å)	D−H···A (°)
1	C-H···O	2.57	3.304(14)	132
		2.55	3.248(14)	129
		2.41	3.327(12)	170
		2.43	3.292(12)	154
		2.58	3.138(13)	119
		2.60	3.512(11)	168
	C-H···O(intra)	2.27	2.705(10)	108
		2.33	2.751(11)	107
		2.26	2.703(12)	109
		2.29	2.714(10)	107
2	C-H···F	2.52	3.26(6)	136
	C-H···O(intra)	2.35	2.78(3)	108
		2.31	2.75(2)	108

Table S4: Gelation tests with some other common organic solvents.

Solvent	$AgBF_4$	$AgClO_4$	$AgSO_3CF_3$	$AgSbF_6$
MeOH	P	P	P	P
EtOH	P	P	P	P
Propan-1-ol	P	P	P	P
Butan-2-ol	P	P	P	P
Acetonitrile	P	P	P	P
Dimethyl formamide	P	P	P	P
Dimethyl sulfoxide	P	P	P	P

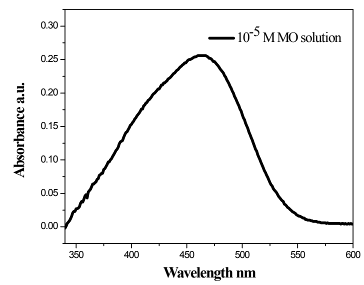
Table S5: Critical gelation concentration (wt %) of all the MOGs taking 10 mg ligand and 1 mL solvent.

Ligand	Metal salt	Solvent	Critical gelation concentration (CGC) (wt %)
	$AgBF_4$ (10 mg, 0.051 mmol)	THF (1mL)	20.0
	$AgBF_4$ (5.95 mg, 0.030 mmol)	Toluene (1mL)	15.9
	$AgBF_4$ (4.67 mg, 0.024 mmol)	*o*-xylene (1mL)	14.7
L (10 mg, 0.034 mmol)	$AgBF_4$ (4 mg, 0.020 mmol)	*p*-xylene (1mL)	14.0
	$AgBF_4$ (2 mg, 0.010 mmol)	PhCN (1 mL)	12.0
	$AgBF_4$ (5.34 mg, 0.027 mmol)	$PhNO_2$ (1 mL)	15.3
	$AgClO_4$ (10.57 mg, 0.051 mmol)	THF (1 mL)	20.6
	$AgClO_4$ (5.63 mg, 0.027 mmol)	Toluene (1mL)	15.6
	$AgClO_4$ (4.22 mg, 0.020mmol)	*o*-xylene (1mL)	14.2
	$AgClO_4$ (3.52 mg, 0.017 mmol)	*p*-xylene (1mL)	13.5
	$AgClO_4$ (3.52 mg, 0.017 mmol)	PhCN (1 mL)	13.5
	$AgSO_3CF_3$(5.24 mg, 0.020 mmol)	*m*-xylene (1mL)	15.2
L (10 mg, 0.034 mmol)	$AgSO_3CF_3$(6.93 mg, 0.027 mmol)	PhCN (1 mL)	16.9
	$AgSO_3CF_3$(13.1 mg, 0.051 mmol)	$PhNO_2$ (1 mL)	23.1
	$AgSbF_6$(4.67 mg, 0.014 mmol)	THF (1 mL)	14.7
	$AgSbF_6$(5.84 mg, 0.017 mmol)	*o*-cresol (1mL)	15.8
	$AgSbF_6$(5.84 mg, 0.017 mmol)	*m*-cresol (1mL)	15.8
	$AgSbF_6$(5.84 mg, 0.017 mmol)	*p*-cresol (1mL)	15.8
	$AgSbF_6$(10.5 mg, 0.030mmol)	PhCN (1 mL)	20.5
	$AgSbF_6$(16.35 mg, 0.048 mmol)	$PhNO_2$ (1 mL)	26.3

Formula used for calculating adsorption capacity (q_t) of xerogels

The molar extinction coefficient, ε can be calculated by using a known diluted solution of MO dye, say 10^{-5} (M).

According to the Beer–Lambert law, $A = \varepsilon \times c \times l$ (eq. 1)



Where, A = absorbance of the materials, ε = molar extinction coefficient, c = concentration of the solution, l = path length.

Therefore, $\varepsilon = A/(c \times l)$

So, A = 0.257, c = 10^{-5}(M) and l = 1 cm

So, $\varepsilon = 0.257/(10^{-5} \times 1)\ M^{-1}cm^{-1}$,

$\varepsilon = 0.257 \times 10^{5}\ M^{-1}cm^{-1}$

For different time interval, C_t were calculated by applying eq. 1 putting the value of ε. Then adsorption capacities were calculated by following eq. 2.

Adsorption Capacity $(q_t) = [(C_0 - C_t)*V] / m$ (eq. 2)

Here,

q_t= amount of dye methyl orange (MO) in mg, adsorbed into 1 g adsorbent,

C_0 and C_t are the initial and conc. of MO (mg L^{-1}) at different time interval,

V= volume of dye solution (L)

m= mass of adsorbent (g).