Supporting Information

Solid or Gel? Which one Works Better for [2+2] Photochemical Polymerization in Pyridine Appended Flexible Phenylene 1,4-bis-olefins by Ag(I) Templation

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Experimental details and synthesis of compounds

General

FTIR spectra were recorded with a Perkin Elmer Instrument Spectrum Rx Serial No. 73713. Powder XRD patterns were recorded with a BRUKER-AXS-D8-ADVANCE diffractometer (Cu target). ^{1}H-NMR (400MHz) spectra were recorded on a BRUKER-AC 400 MHz. spectrometer. MALDI-TOF experiment was done by a BRUKER ULTRAFLEXTREME MALDI TOF/TOF mass spectrometer by using 2,5-Dihydroxybenzoic acid as matrix.

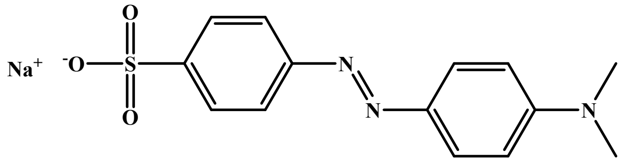
Synthesis of (2E,2'E)-3,3'-(1,4-phenylene)bis(N-(pyridin-3-ylmethyl)acrylamide (1)

In a round bottom flask, *p*-phenylene diacrylic acid (1.09 g, 5 mmol) and pyridine (15 mL) were taken and 3-picolyl amine (1.02 ml, 10 mmol) was added to the reaction mixture and stirred for 15-20 minutes. After that triphenylphosphite (2.95 mL, 10.5 mmol) was added to it and the reaction mixture was refluxed for (8-10) hours. It was cooled to room temperature. Then excess pyridine was distilled out to reduce the volume upto 5 mL. It was kept overnight standing. After washing with water, solid product was filtered and washed with acetone. The white solid product was recrystallized from MeOH-H_2O (1:1).[S1]

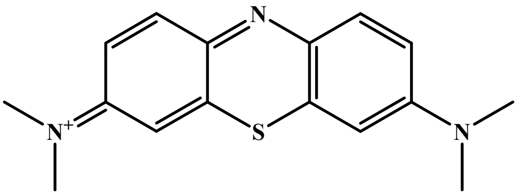
Synthesis of (2E,2'E)-3,3'-(1,4-phenylene)bis(N-(pyridin-4-ylmethyl)acrylamide (2)

The compound **2** was synthesized from *p*-phenylene diacrylic acid (1.09 g, 5 mmol) and 4-picolyl amine (1.02 g, 10 mmol) in presence of pyridine (15 mL) and triphenyl phosphite (2.95 mL, 10.5 mmol) using the same procedure as described for **1.** The white solid product was recrystallized from EtOH-H_2O (1:1) solvent mixture.

Chemical diagrams of dyes



Methyl Orange(MO)



Methyelene Blue (MB)

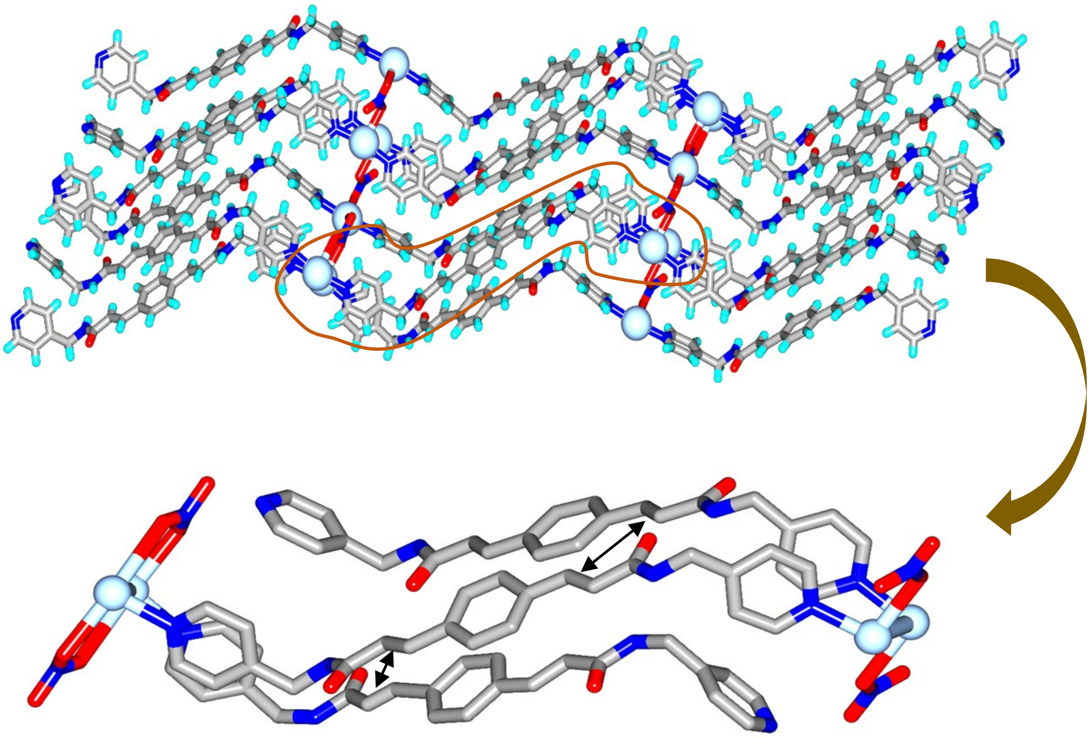


Fig. S1 Illustration for the crystal structure of CP-**2**: (a) Overall 2D-layer; (b) Ag···Ag interactions templated by nitrates and distance between the centroids of the olefins (H atoms have been removed for clarity).

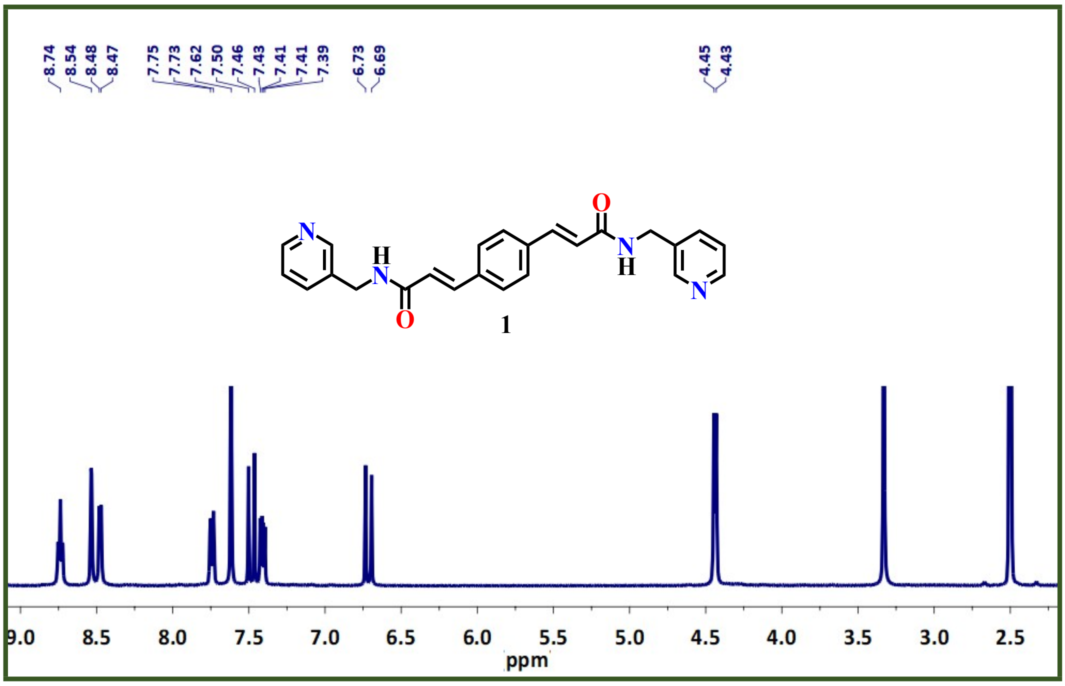


Fig. S2 ^{1}H NMR of **1** in DMSO-d_6.

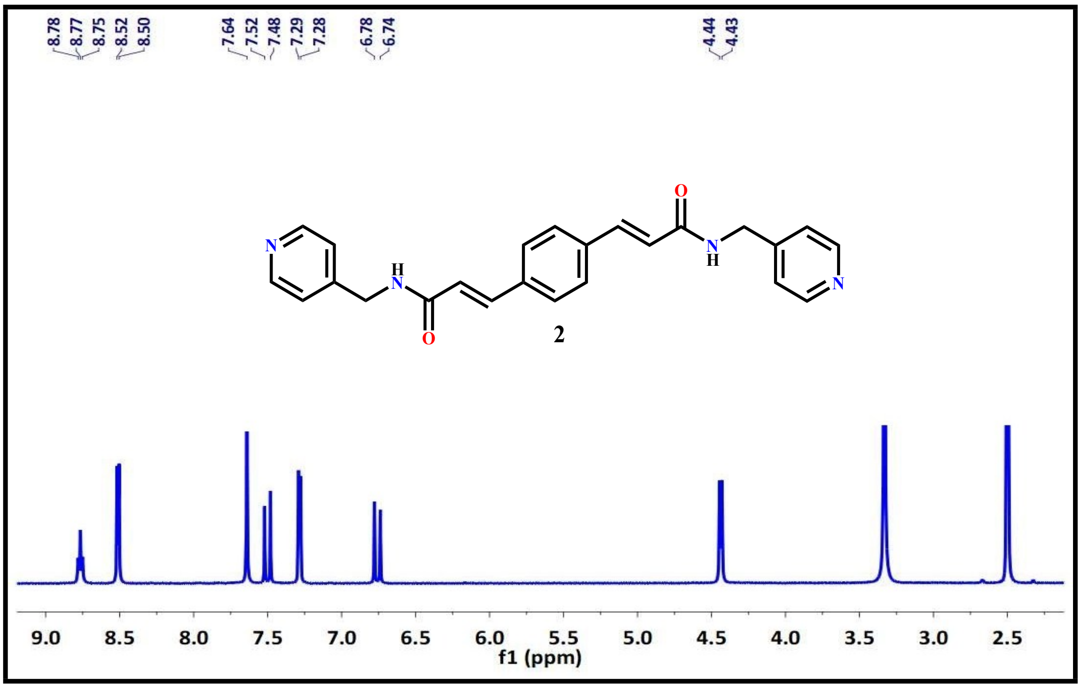


Fig. S3 ^{1}H NMR of **2** in DMSO-d_6.

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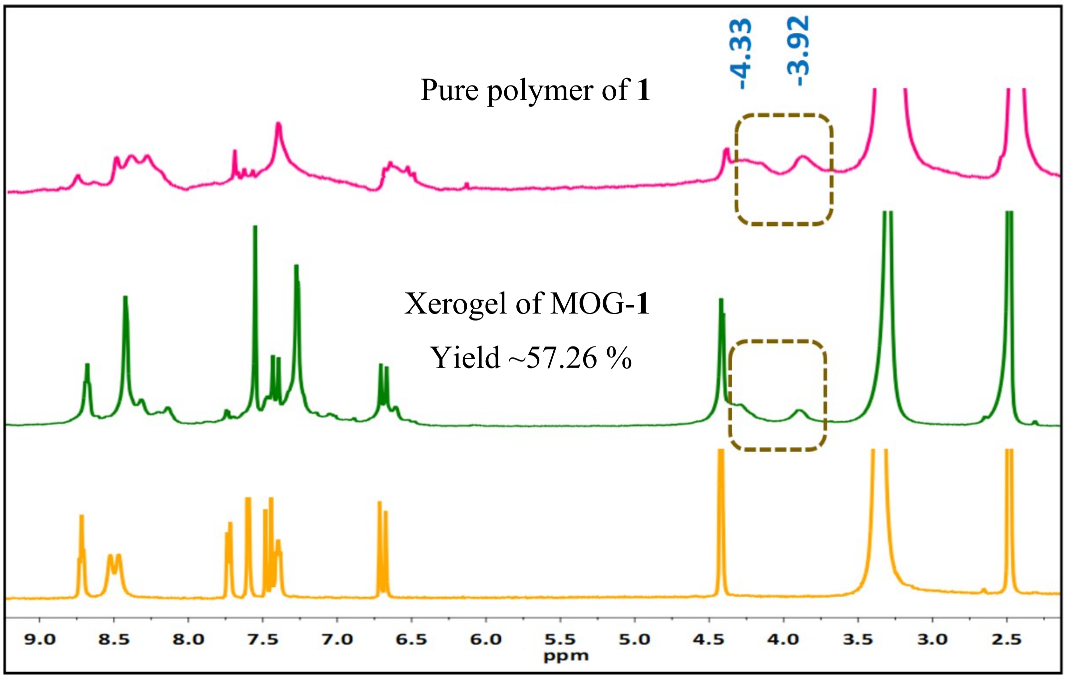


Fig. S4 ^{1}H NMR in DMSO-d_6 for irradiated xerogel of MOG-**1** and pure polymer of **1**.

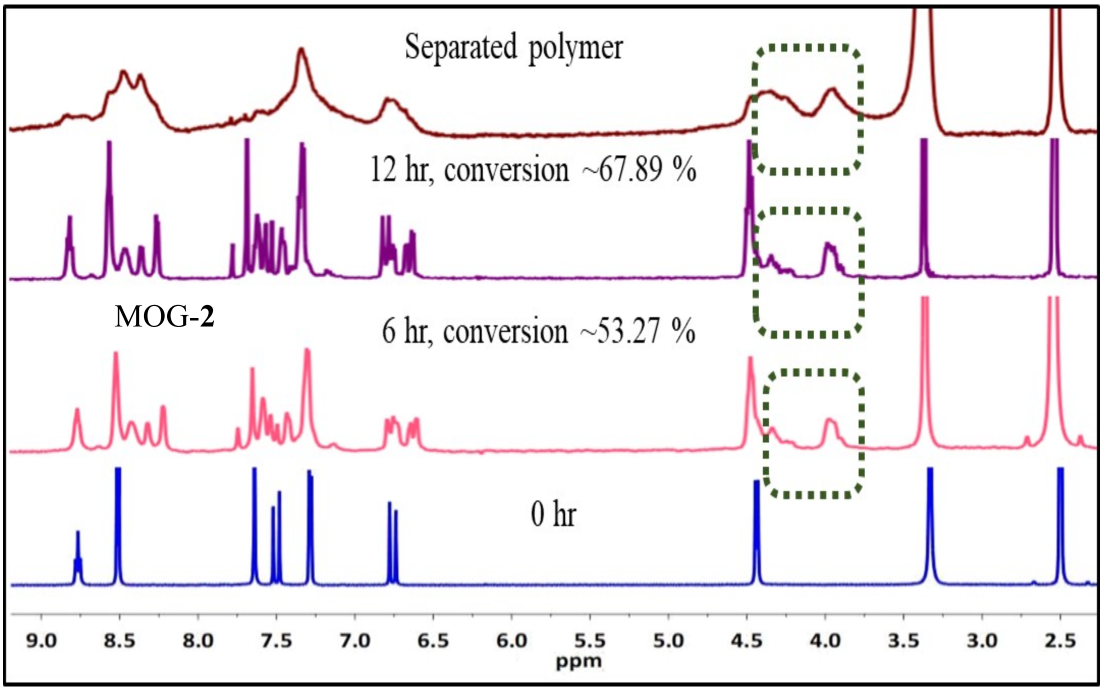


Fig. S5 ^{1}H NMR in DMSO-d_6 for MOG-**2**. at various time of irradiation.

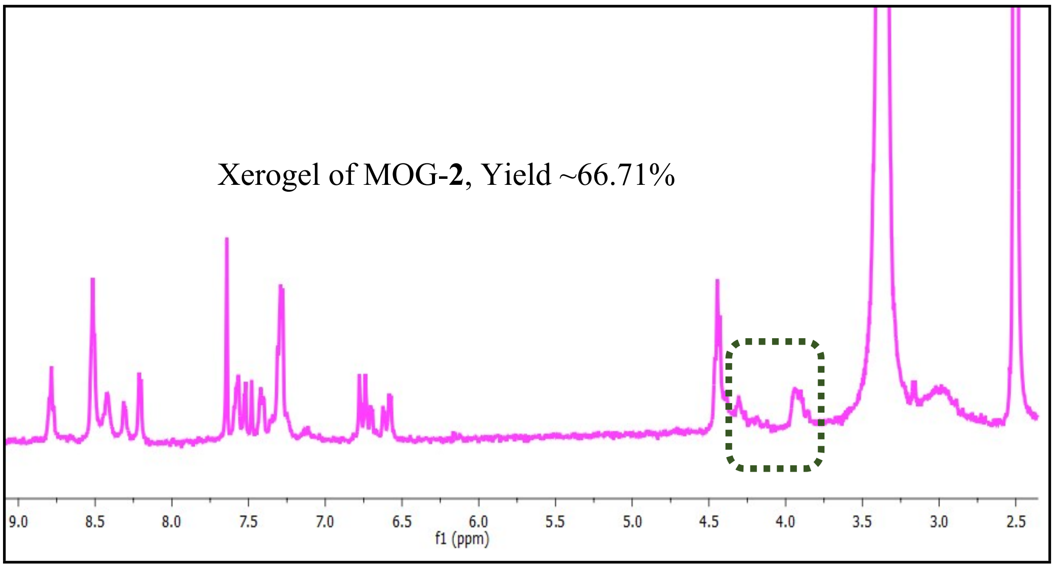


Fig. S6 ^{1}H NMR in DMSO-d_6 for irradiated xerogel of MOG-**2**.

Yield calculation for the polymerization reactions

The yields were calculated based on the integration ratios of newly formed cyclobutane protons in the polymer (MOG-**1**: 3.92 & 4.33 ppm; MOG-**2**: 3.96 & 4.37 ppm) with the unreacted olefinic protons (MOG-**1**: 6.71 & 7.42 ppm; MOG-**2**: 6.76 & 7.29 ppm).

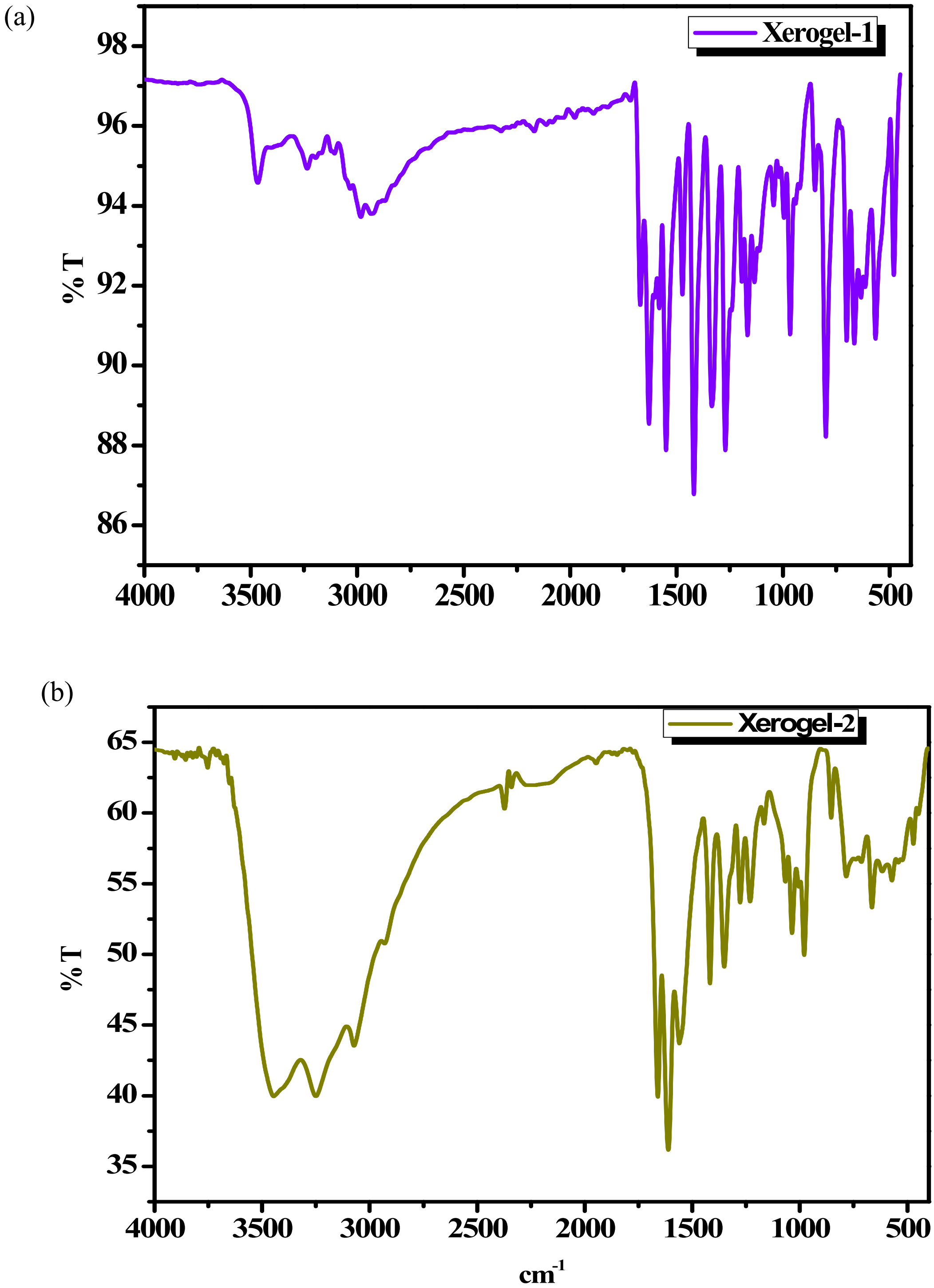


Fig. S7 FTIR spectra of xerogel of (a) MOG-**1**; (b) MOG-**2**.

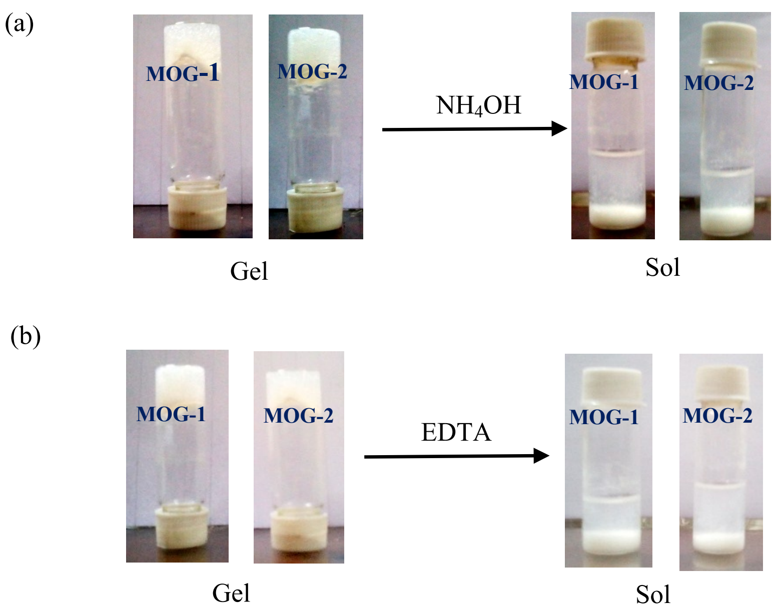


Fig. S8 Chemical responsiveness of MOG-**1** and MOG-**2**.

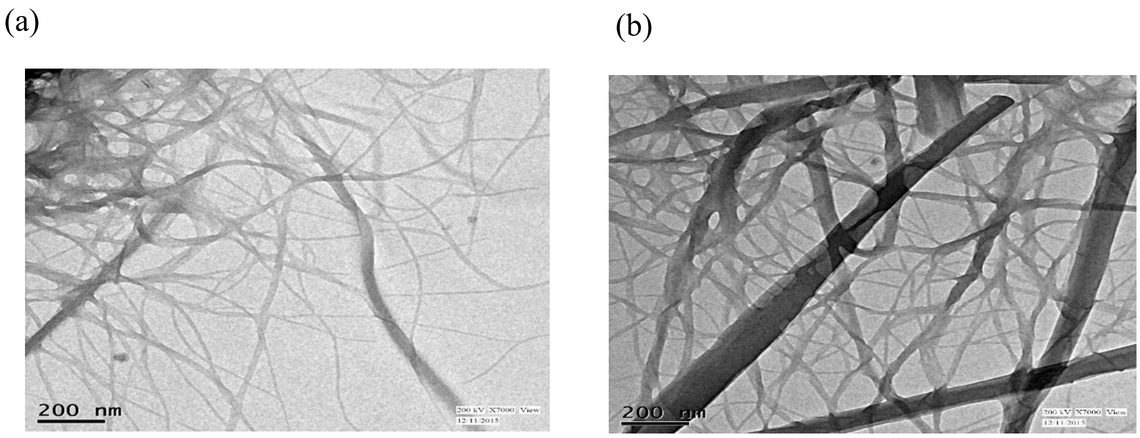


Fig. S9 Illustration for the TEM images for: (a) MOG-**1** and (b) MOG-**2**.

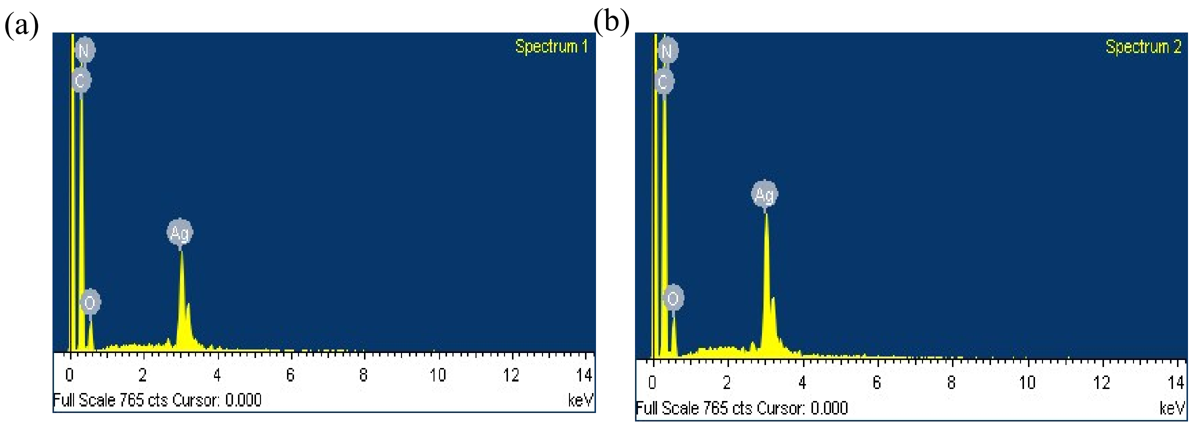
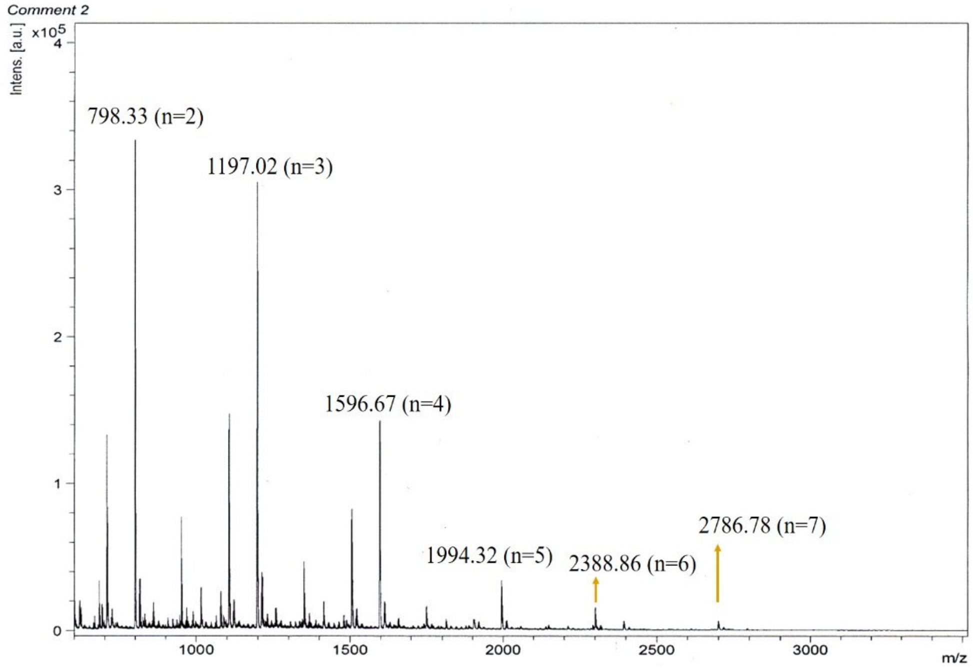


Fig. S10 EDX-elemental mapping for (a) MOG-**1** and (b) MOG-**2**.

(a)



(b)

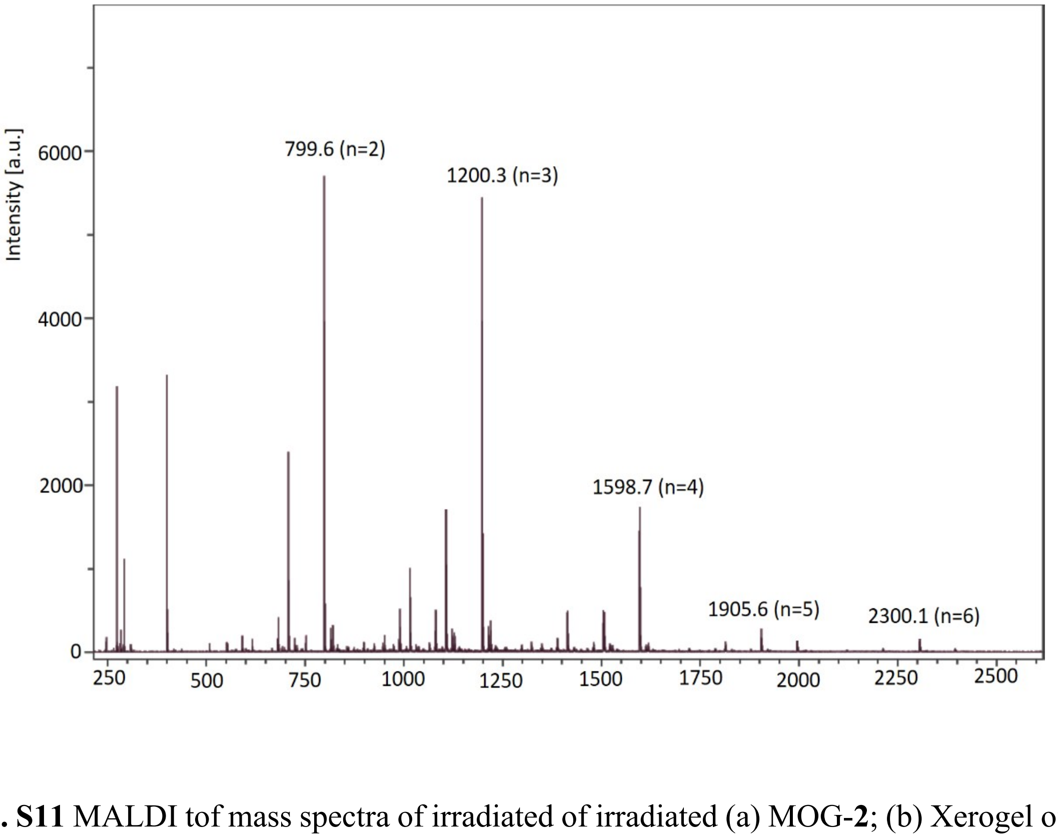


Fig. S11 MALDI tof mass spectra of irradiated of irradiated (a) MOG-**2**; (b) Xerogel of MOG-**1**.

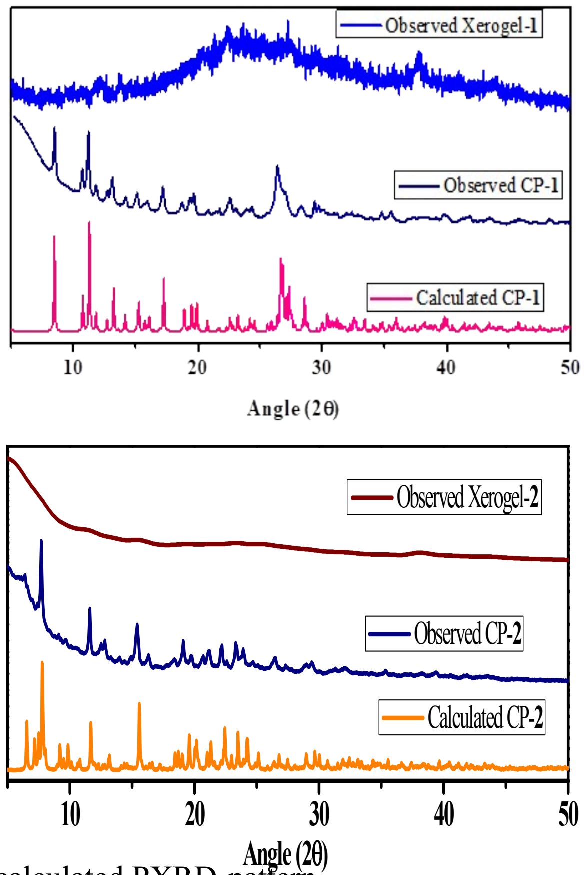


Fig. S12 Observed and calculated PXRD-pattern.

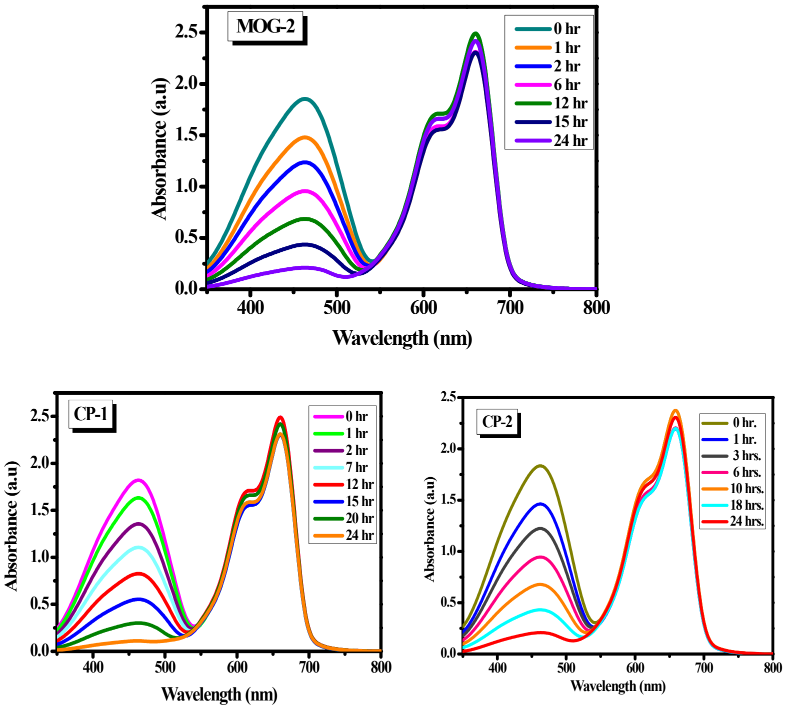


Fig. S13 UV-vis spectra of dye solutions at different time intervals during selective dye-sorption experiment.

Crystallographic data and refinement details

Crystal Structure Determination: All the single-crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo K_{α} radiation (λ= 0.71073 Å) at room temperature (293 K) by the hemisphere method. The structures were solved by direct methods and refined by least-squares methods on F^2 using SHELX-2014.[S2] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. In case of CP-**2**, two nitrate ions and one water molecule were located and refined. Whereas one of the nitrate ion and two water molecules found to be severely disordered which can't be modelled. Therefore, the final refinement was done using PLATON squeeze option.[3]

Crystallographic data

Table S1 Crystallographic parameters for CP-**1** and CP-**2**

	CP-1 **CCDC-1957462**	**CP-2** **CCDC-1957463**
Formula	$C_{24}H_{24}AgN_5O_6$	$C_{72}H_{64}Ag_3N_{14}O_{13}$
Mol.wt.	586.35	1656.99
T (K)	293(2)	293(2)
Cryst. System	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	6.8255(5)	12.0899(8)
b (Å)	8.4378(6)	13.7717(9)
c (Å)	21.0383(15)	23.2339(15)
α (˚)	92.891(2)	96.200(2)
β (˚)	94.362(2)	98.497(2)
γ (˚)	102.096(2)	97.394(2)
V (Å^3)	1178.57(15)	3762.2(4)
Z	2	2
D_{cal} (mg/m^3)	1.6523(2)	1.4627(2)
R_1 [I>2σ(I)]	0.0395	0.0580
wR_2 (on F^2, all data)	0.0968	0.2215

Formula used for calculating adsorption capacity (qt) of xerogels

The molar extinction coefficient, ε can be calculated by using a known diluted solution of MO dye, e.g. 10^{-4} (M).

According to the Beer–Lambert law, A=ε×c×l………………… (eq. 1)

Where, A = absorbance of the materials, ε= molar extinction coefficient,

c= concentration of the solution, l= path length.

Therefore, $\varepsilon = \frac{A}{c \times l}$

So, A= 2.54, c = 10^{-4}(M) and l= 1 cm

So, $\varepsilon = \frac{2.539}{10^{-4} \times 1}$ $M^{-1}cm^{-1}$,

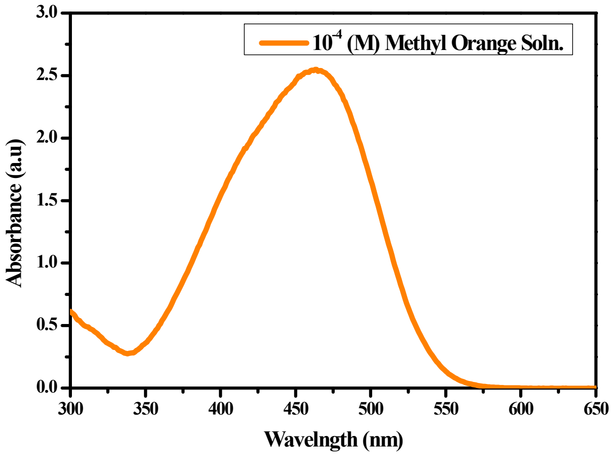
$\varepsilon = 2.54 \times 10^{4}$ $M^{-1}cm^{-1}$

Now the equation for determining absorption capacity (q_t),

$$q_t = \left(\frac{C_0 - C_t}{V} \times m\right) \quad \text{……………. (eq. 2)}$$

Where, C_0= initial concentration of dye solution, C_t= Concentration of dye solution at different time interval, V= volume of the dye solution, m= mass of absorbent

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.



Now for MOG **1**,

At t=0, A=1.82 & at t=24 hr, A= 0.11

A=ε×c×l

$c = \frac{A}{\varepsilon \times l}$

$c_0 = \{1.82/(2.54 \times 1)\} \times 10^{-4}\ M^{-1} = 0.716 \times 10^{-4}\ M^{-1}$

$c_t = \{0.110/(2.54 \times 1)\} \times 10^{-4}\ M^{-1} = 0.043 \times 10^{-4}\ M^{-1}$

So, $c_0 - c_t = \{(0.716 - 0.043)\} \times 10^{-4}\ M^{-1} = 0.673 \times 10^{-4}\ M^{-1}$

$= (0.673 \times 10^{-4} \times 327.33 \times 10^{3})$mg/L

= 22.03 mg/L

Thus, $q_t = \dfrac{22.03}{0.01} \times 0.03$ mg g^{-1}=66.09 mg g^{-1}

Similarly, for MOG **2,**

At t=0, A=1.854 & at t=24 hr, A= 0.2118

From the above equation,

$c_0=\{1.854/(2.54\times1)\}\times10^{-4}$ M^{-1}=0.73×10^{-4} M^{-1}

$c_t=\{0.21/(2.54\times1)\}\times10^{-4}$ M^{-1}=0.083×10^{-4} M^{-1}

So, c_0-c_t= $\{(0.73-0.083)\}$ $\times10^{-4}$ M^{-1}=0.647×10^{-4} M^{-1}

= $(0.647\times10^{-4}\times327.33\times10^{3})$mg/L

= 21.18 mg/L

Thus, $q_t = \dfrac{21.18}{0.01} \times 0.03$ mg g^{-1}=63.54 mg g^{-1}

Similarly, for CP-**1** and CP-**2**, q_t was calculated.

Reference

S1. C. S. Marvel, L. E.Coleman and G. P. J. Scott, *Org. Chem*. 1955, **20**, 1785-1792.

S2. G. M. Sheldrick, SHELXL-2014; University of Göttingen and Bruker AXS: Karlsruhe, 2014.

S3. A. L Spek, PLATON: A Multi Purpose Crystallographic Tool; Utrecht University, Utrecht, the Netherlands, 2002.