

Supporting Information

Photo Responsive Metal-Organic Gels of Rigid Phenylene-1,3-di-Substituted Angular Diene with Metal Halides: Gel-to-Gel Transformation triggered by [2+2] Polymerization

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Table S1 Gelation in different solvents for **MOG1-5**.

| Gels | (M:L) | Solvent (Total vol =2ml) |
|-------------|-------------------------------|----------------------------------|
| MOG1 | CdCl₂ (1:1) | MeOH |
| MOG2 | CdBr₂ (1:1) | MeOH |
| MOG3 | HgCl₂ (4:1) | MeOH:H₂O (1:1) |
| MOG4 | HgBr₂ (4:1) | MeOH:H₂O (1:1) |
| MOG5 | HgI₂ (4:1) | MeOH:H₂O (1:1) |

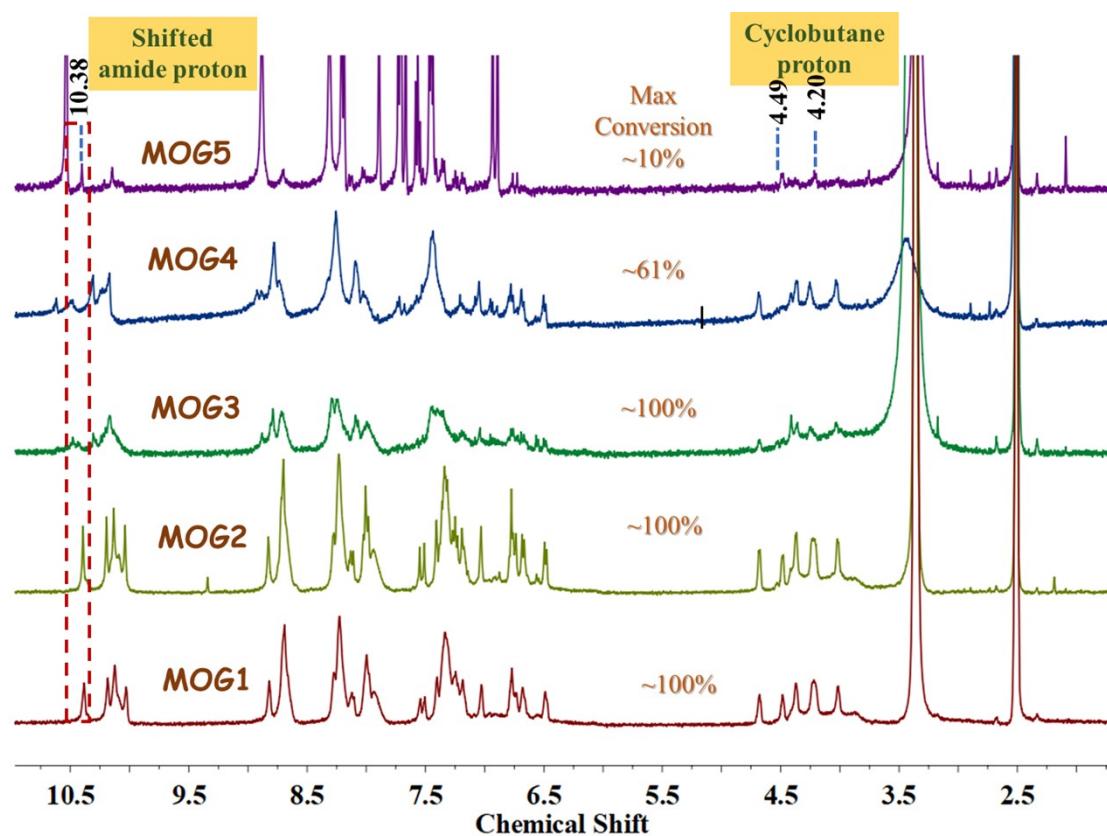


Fig. S1 ¹HNMR spectra in DMSO-*d*₆ and % conversion of **MOG1-5** after 24h of UVA irradiation.

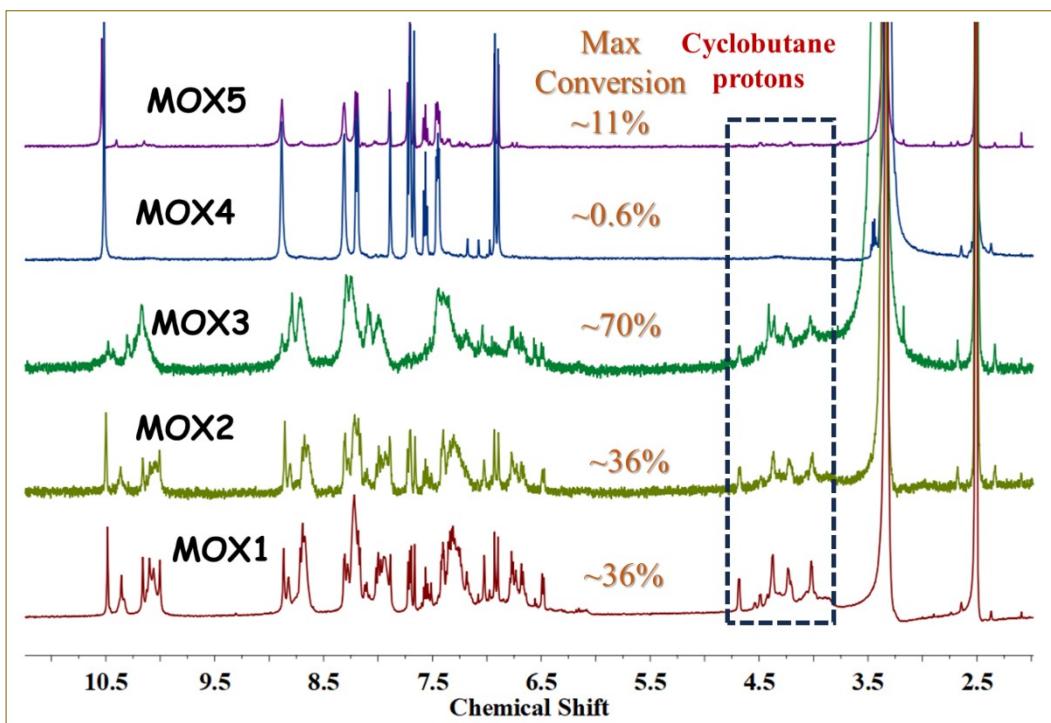


Fig S2 ^1H NMR spectra in $\text{DMSO}-d_6$ of xerogels of **MOG1-5** at 24h of irradiation. Yield of the reaction has been calculated by taking into account the integration ratios of unreacted olefinic protons appearing at 6.89 ppm with newly formed cyclobutane peak at 4.21 ppm.¹

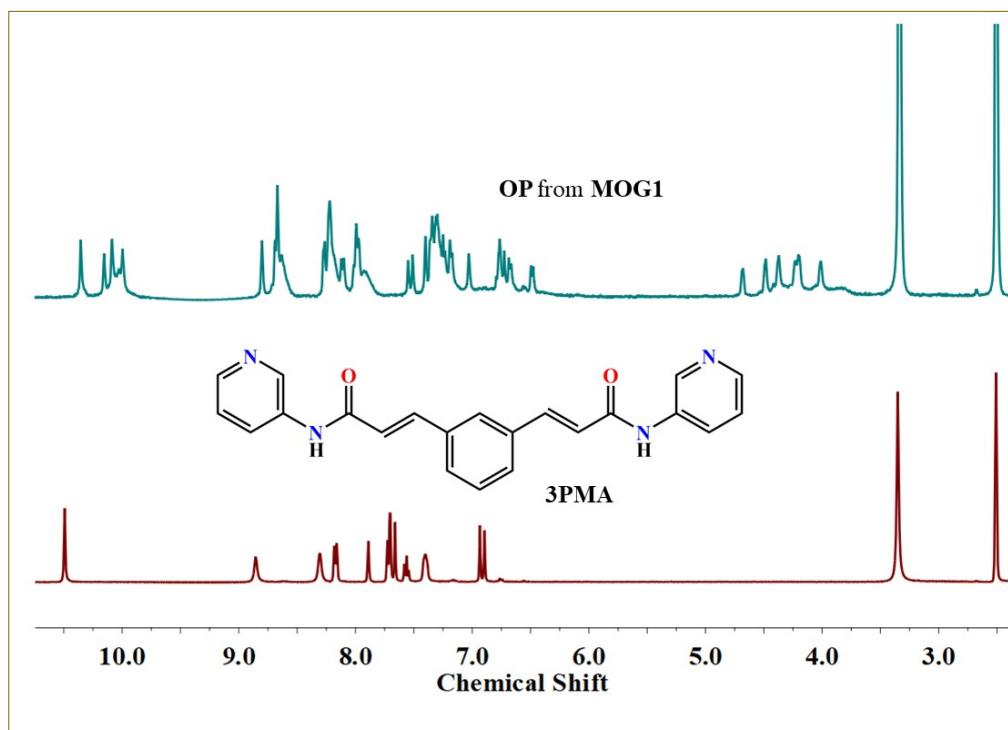


Fig. S3 ^1H NMR spectra of **3PMA** and the separated organic polymer in $\text{DMSO}-d_6$.

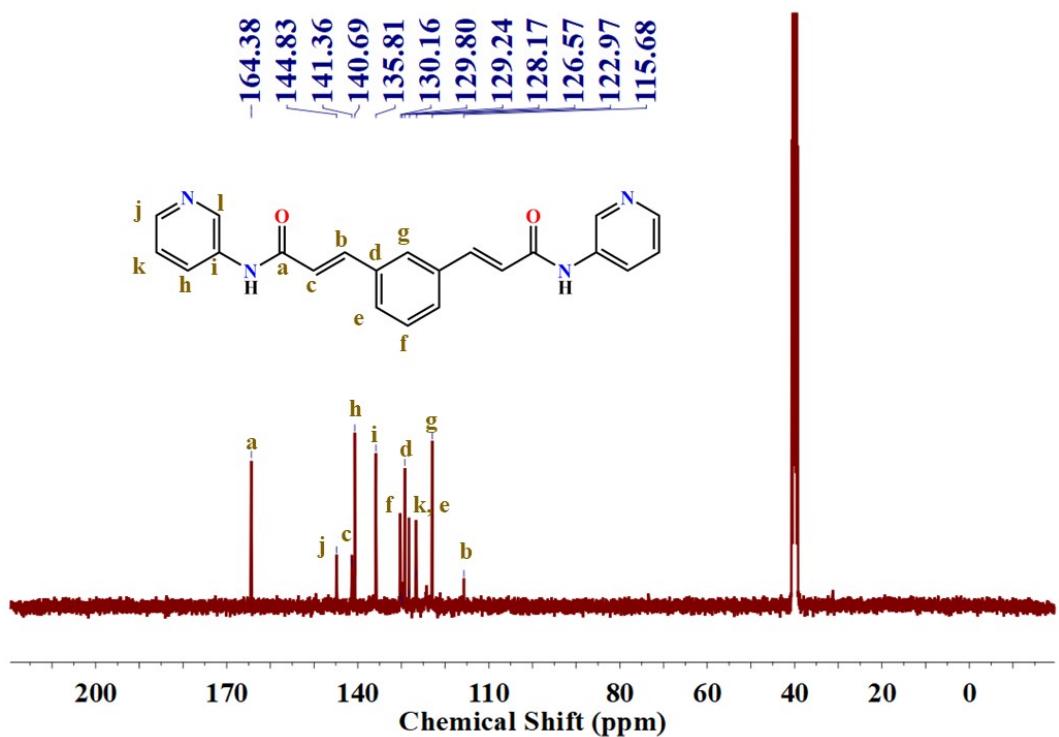


Fig. S4 ¹³CNMR spectra of **3PMA** in DMSO-*d*₆.

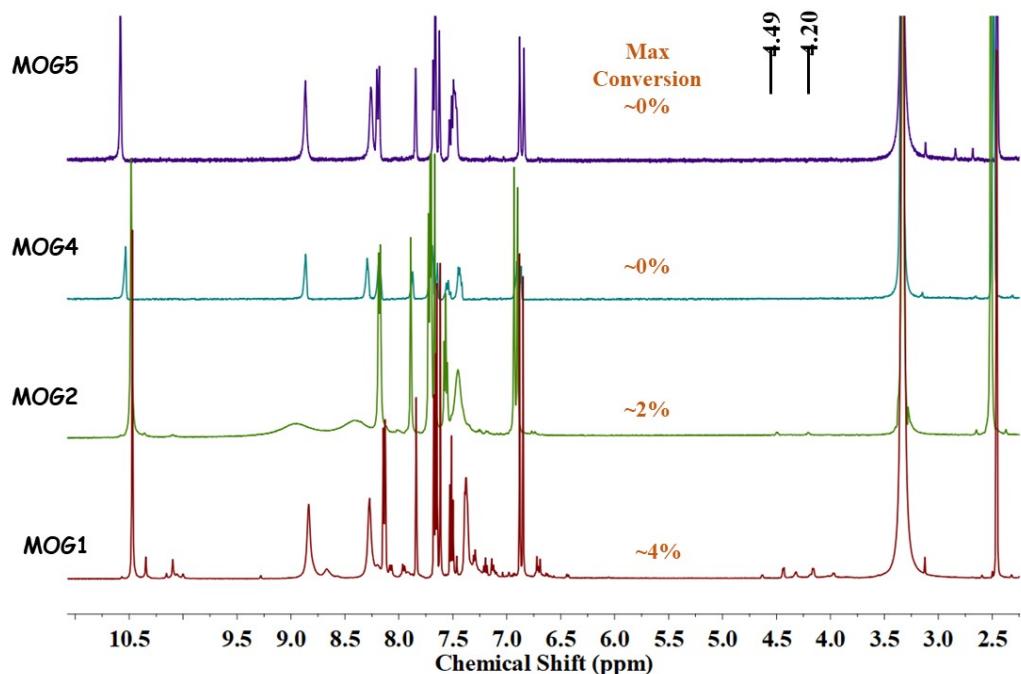


Fig. S5 ¹HNMR spectra illustrating % conversion of **MOG1-2** and **MOG4-5** upto the point of self-persistent nature in DMSO-*d*₆.

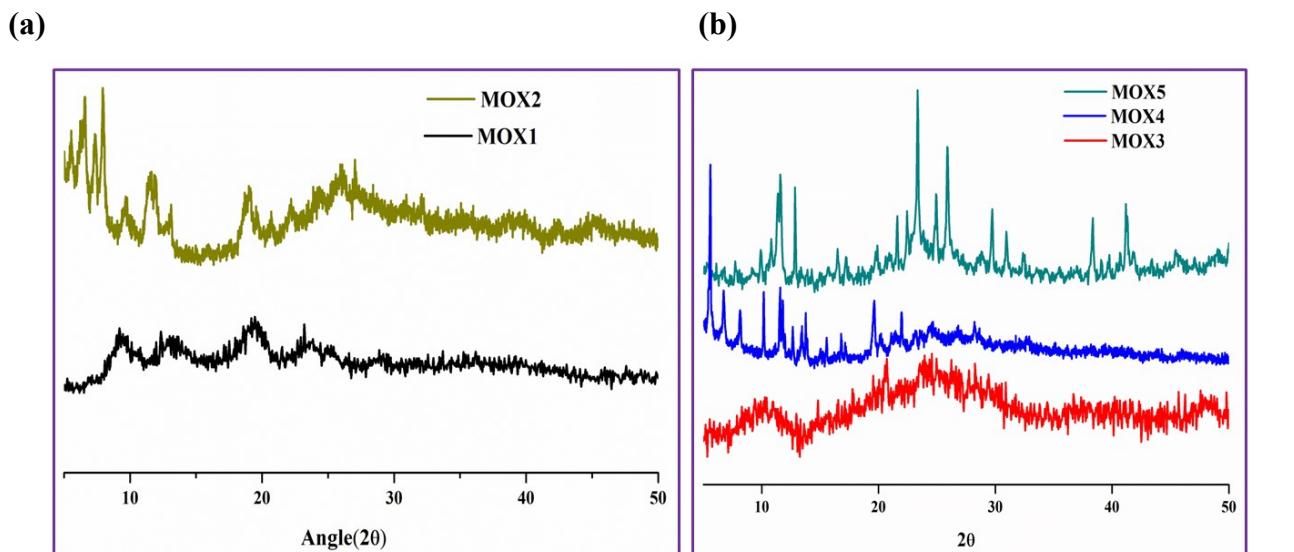


Fig. S6 XRPD pattern for all the xerogels of: (a) Cd(II) MOGs (b) Hg(II) MOGs.

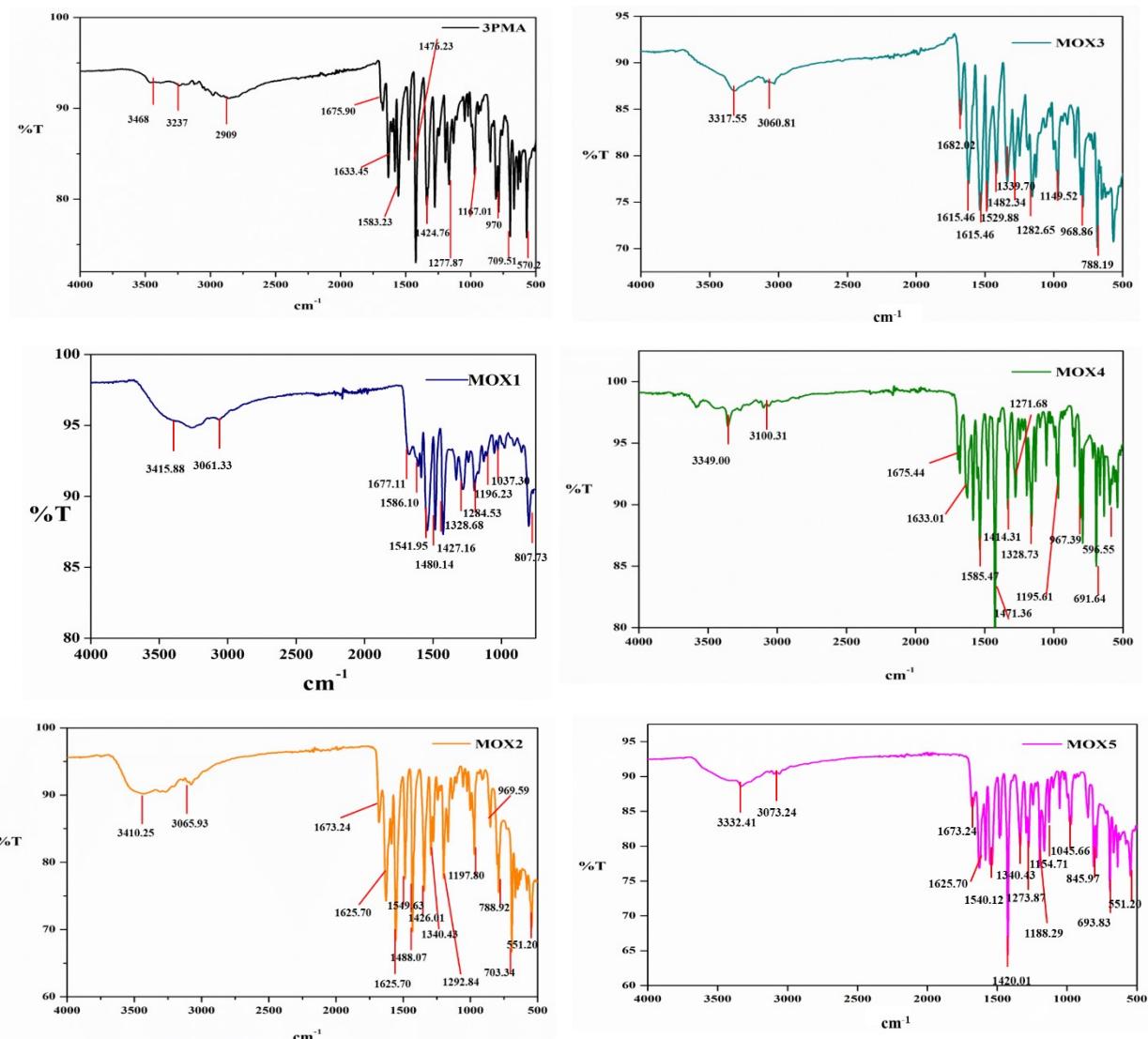


Fig. S7 FT-IR spectra of 3PMA and xerogel of MOG1-5.

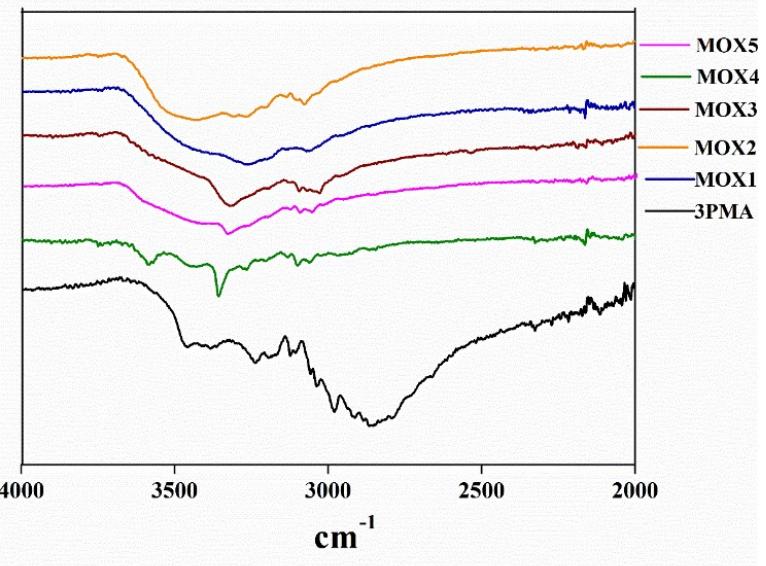


Fig. S8 FT-IR spectra of 3PMA xerogel of MOG1-5 in 4000-2000 cm^{-1} region. Notice the effect of intramolecular H bonding on secondary amine band.

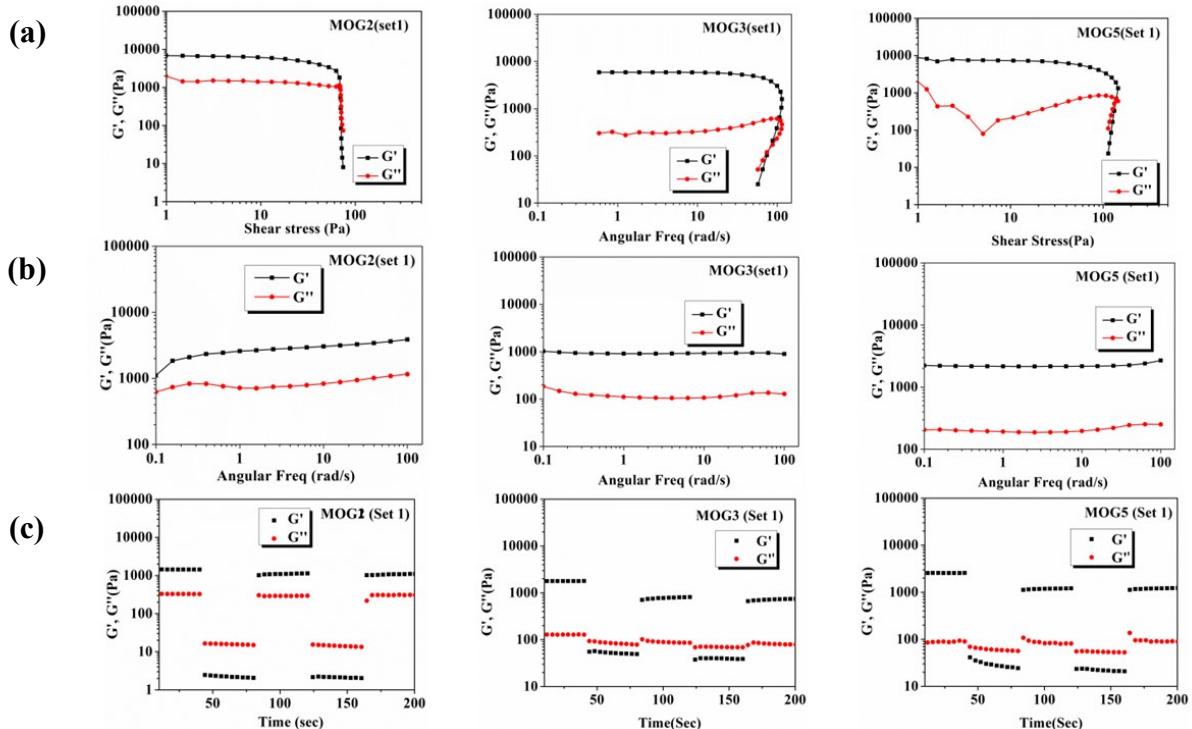


Fig. S9 Rheological analysis for MOG2, MOG3 and MOG5 before irradiation: variation of storage modulus (G') and loss modulus (G'') with: (a) shear stress (b) frequency and (c) step-strain hysteresis loop.

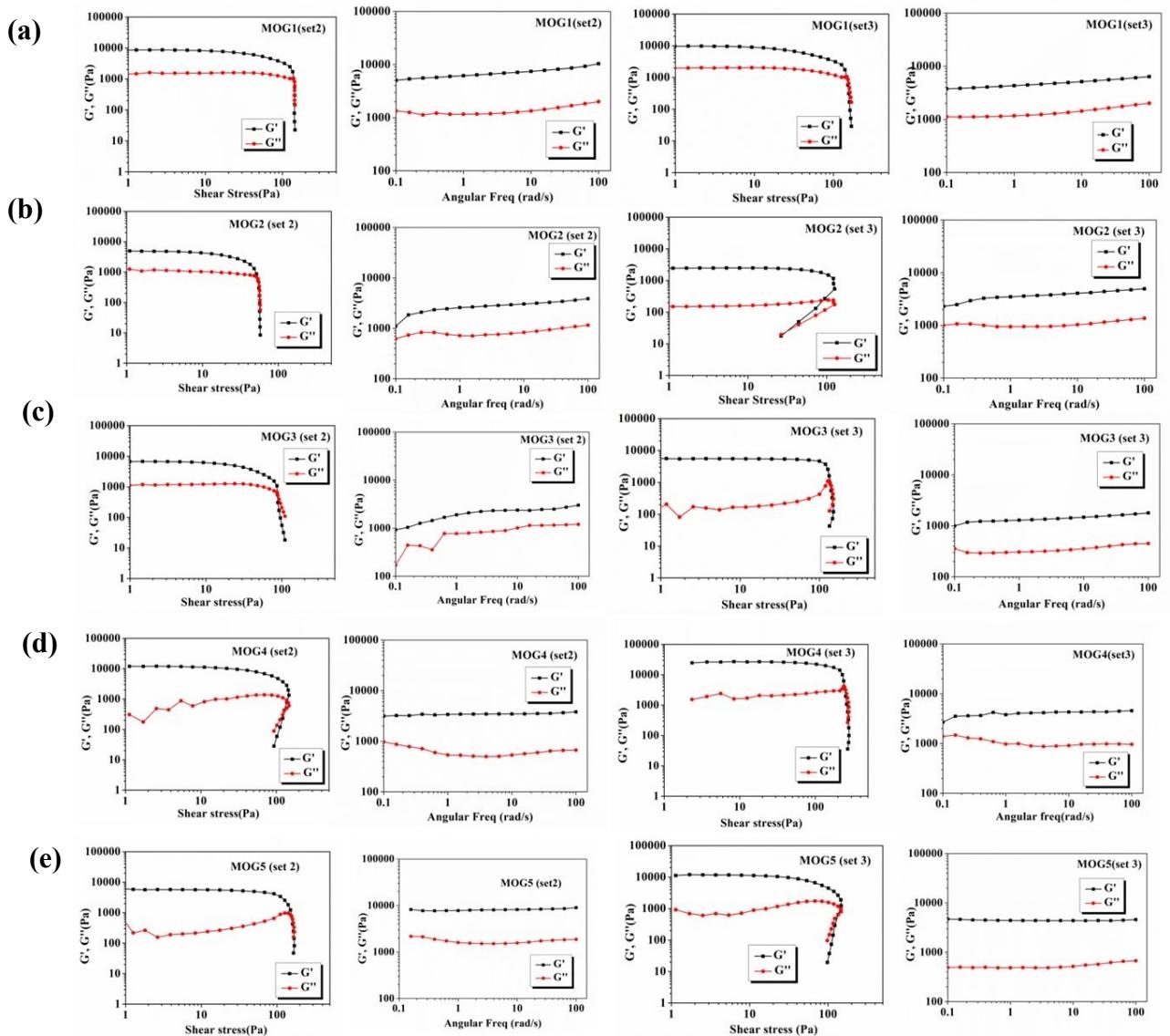


Fig. S10 Rheological data reproducibility for **MOG1-5** before irradiation: variation of storage modulus (G') and loss modulus (G'') with: shear stress and frequency for (a) **MOG1**, (b) **MOG2**, (c) **MOG3**, (d) **MOG4** and (e) **MOG5** (set 2 and set 3 denotes data for two different batches of sample).

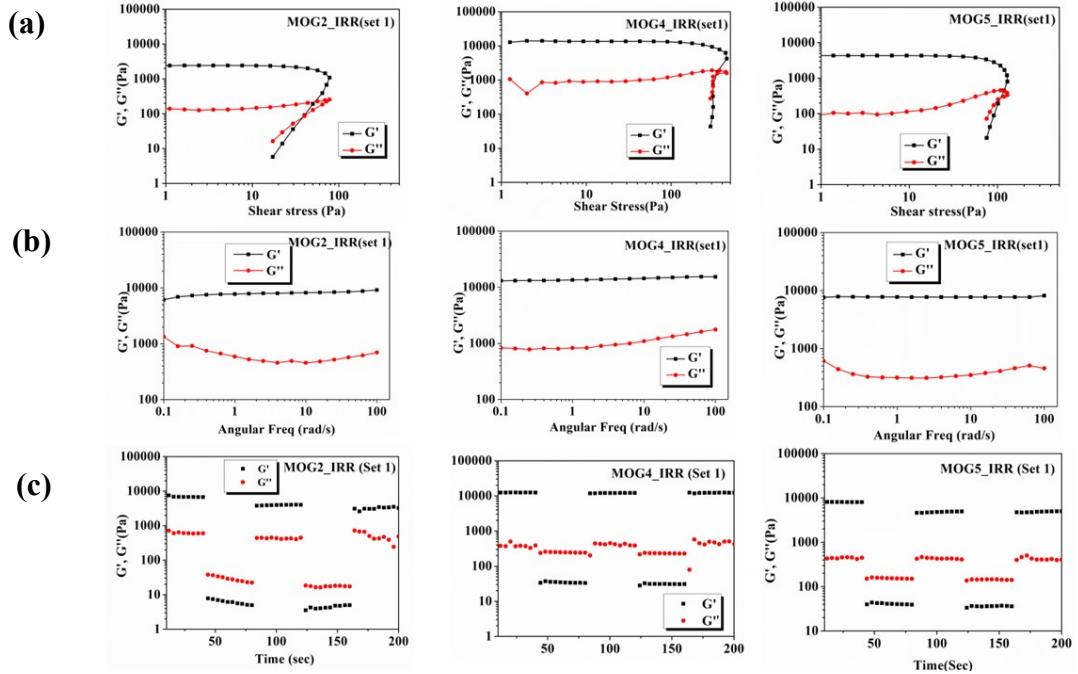


Fig. S11 Rheological analysis for MOG2, MOG4, & MOG5 after 24 hrs of UVA irradiation: variation of storage modulus (G') and loss modulus (G'') with: (a) shear stress (b) frequency and (c) step-strain hysteresis loop.

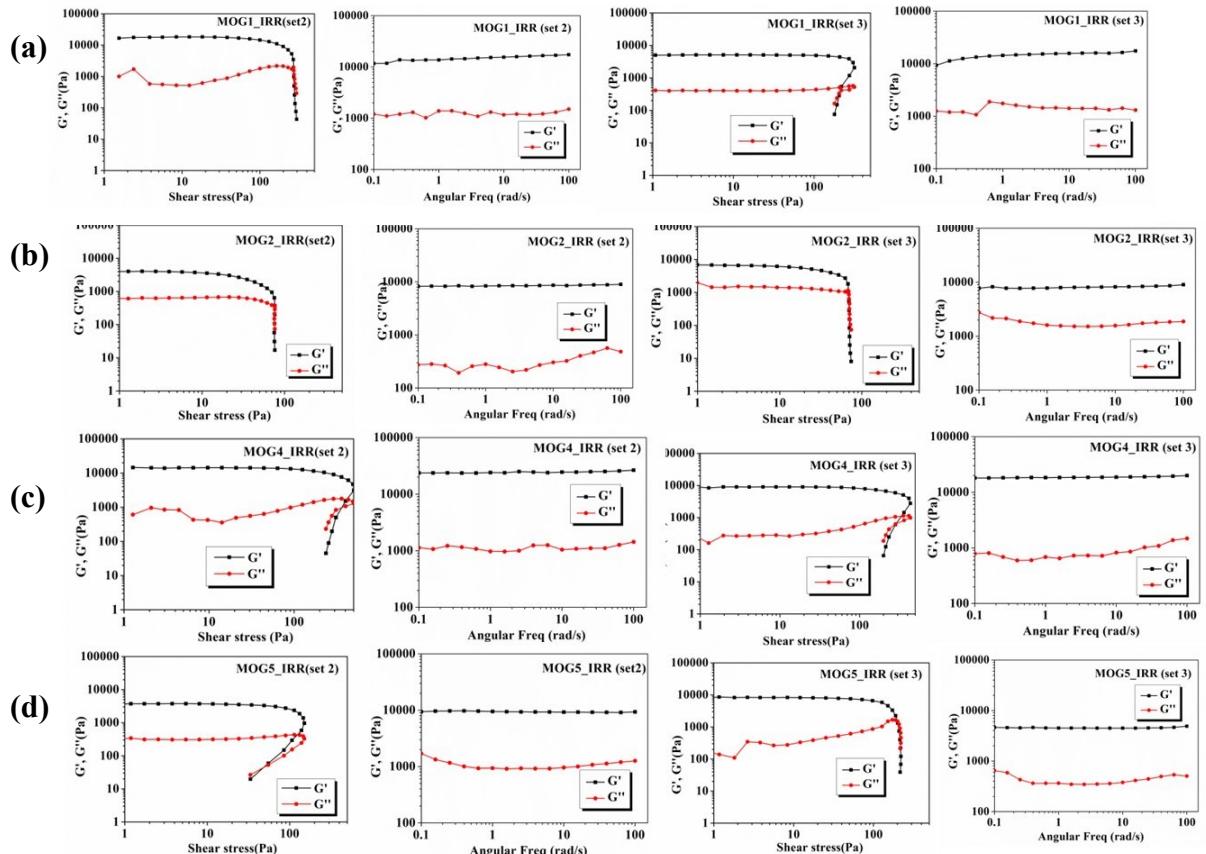


Fig. S12 Rheological data reproducibility for MOG1-5 after irradiation: variation of storage modulus (G') and loss modulus (G'') with: shear stress and frequency for (a) MOG1, (b) MOG2, (c) MOG3 and (d) MOG4 (set 2 and set 3 denotes data for two different batches of sample).

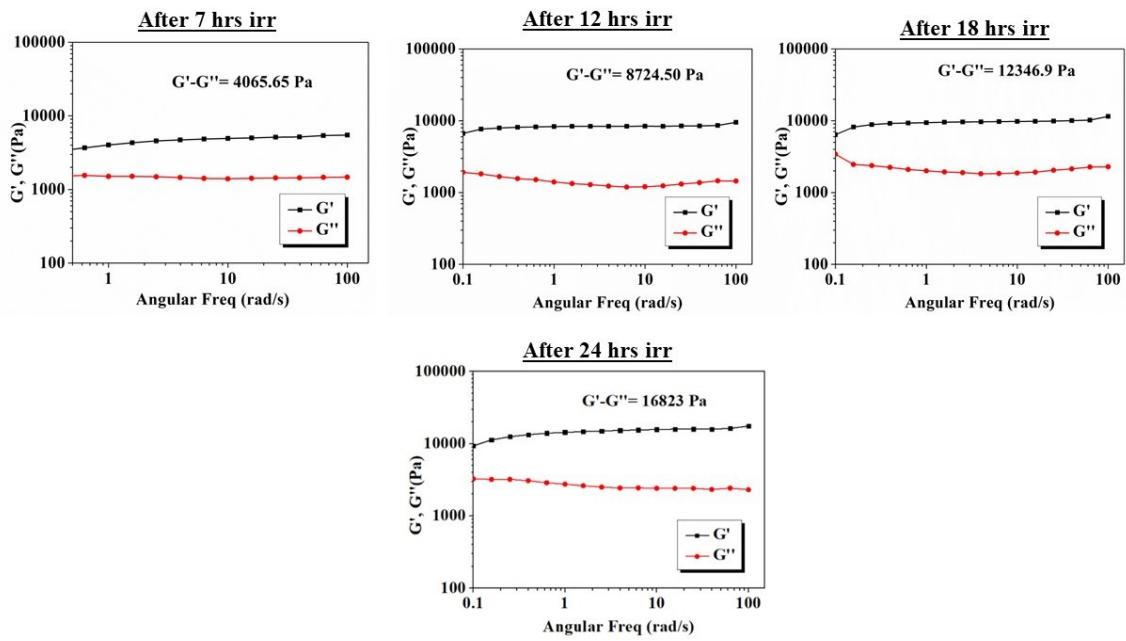


Fig. S13 Rheological analysis for **MOG1** at different course of photoreaction: variation of storage modulus (G') and loss modulus (G'') with frequency showing gradual increase in mechanical strength.

MOG5

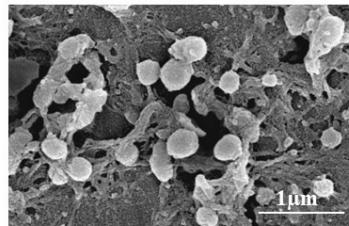


Fig. S14 Illustration of FESEM analysis of **MOG5**.

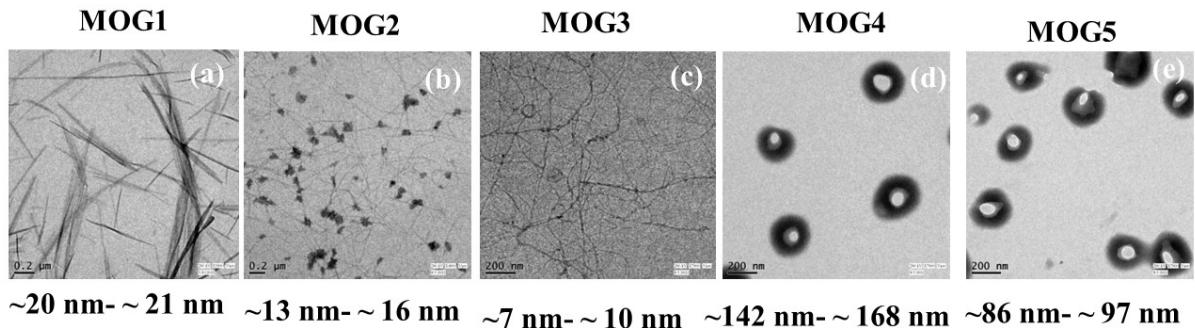


Fig. S15 (a-e) Illustration of TEM analysis of **MOG1-5**, fibril/ ring length/diameter are written at the end of the images.

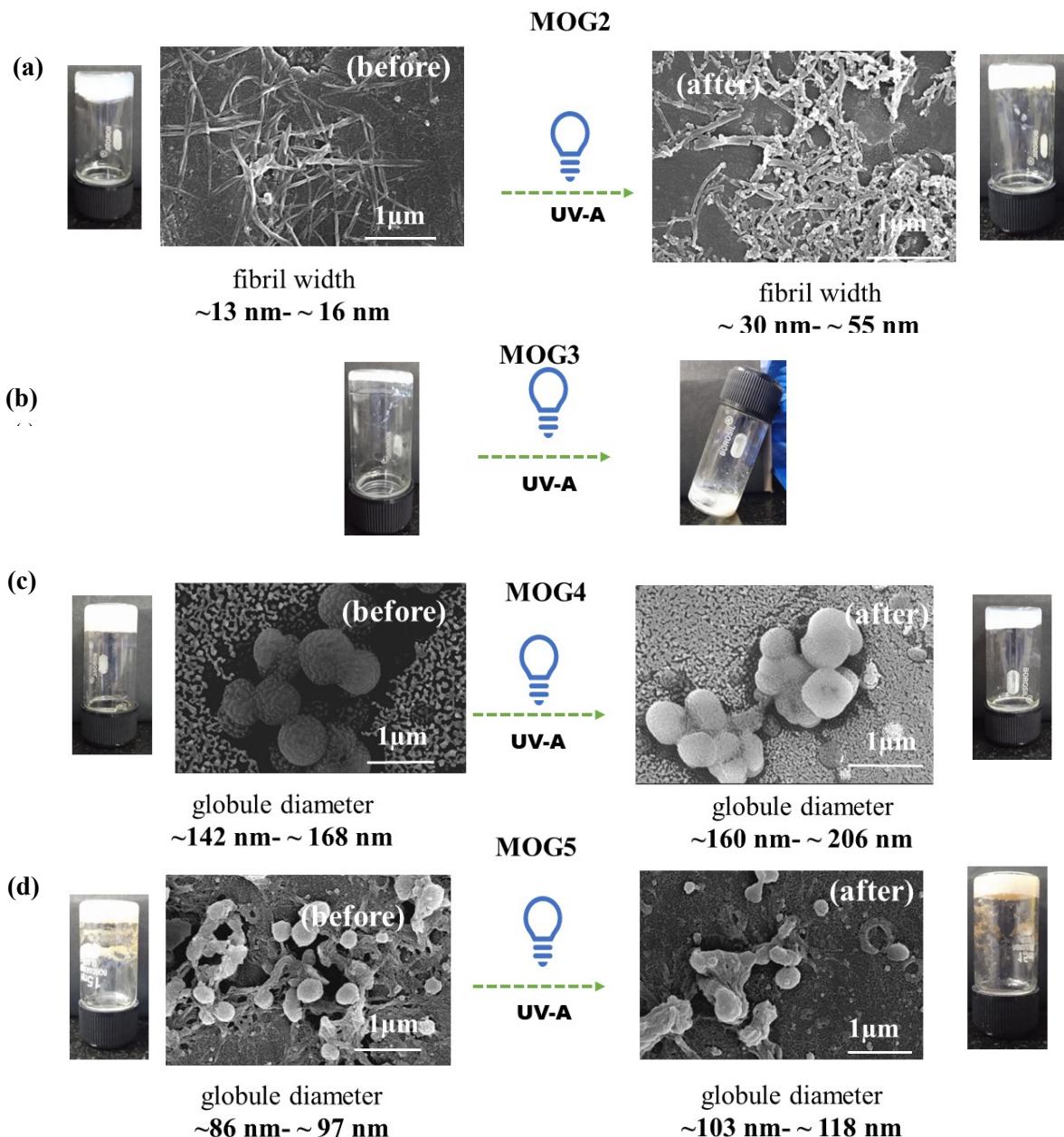


Fig. S16 Photographs showing gels in upturned vials, and FESEM showing fibre width and spheres diameter before irradiation and after 24 hours of irradiation for (a) **MOG2**, (b) **MOG3**, (c) **MOG4** and (d) **MOG5**.

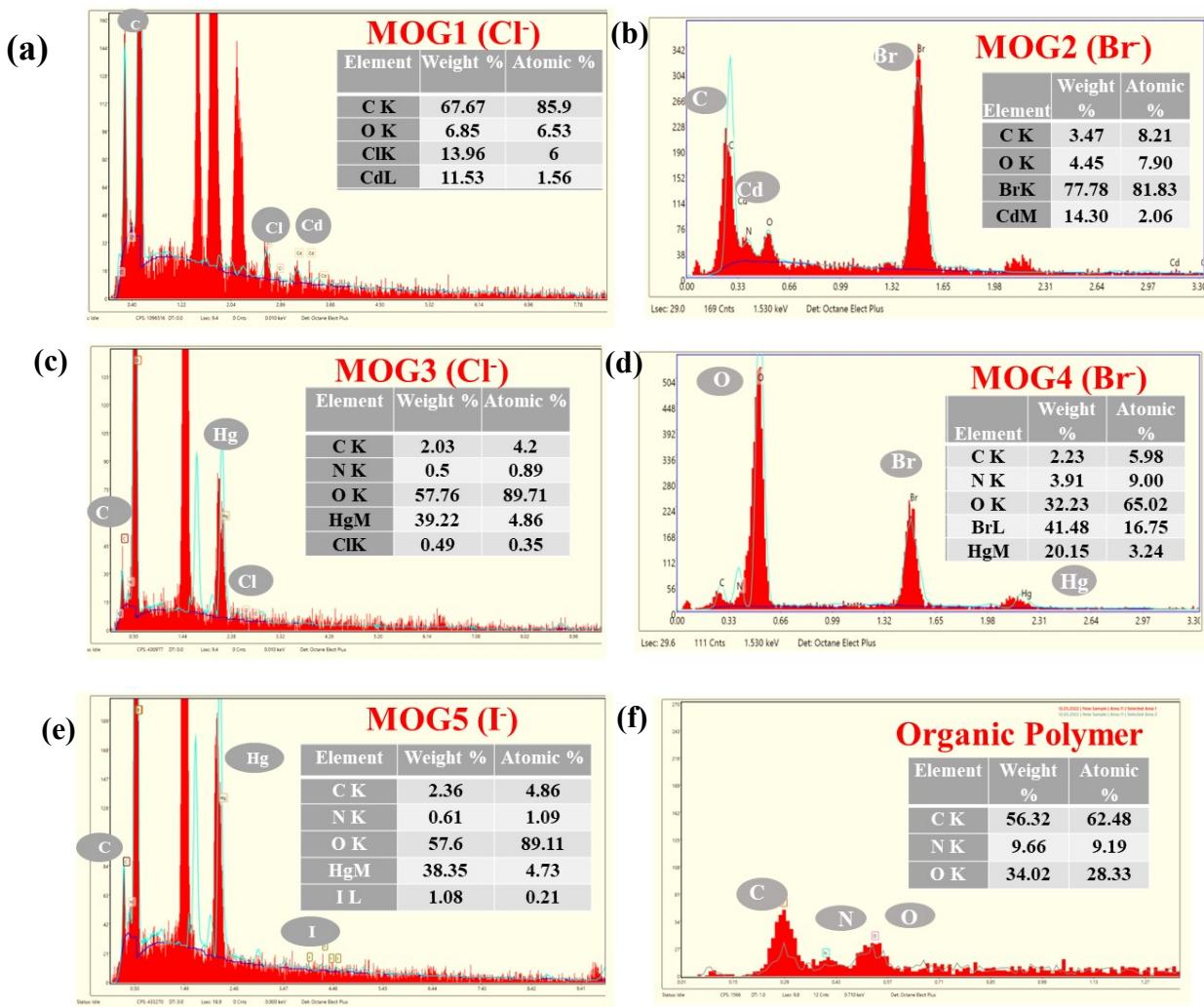


Fig. S17 EDX- elemental analysis for: (a-e) MOG1-5, (f) organic polymer extracted from MOG1

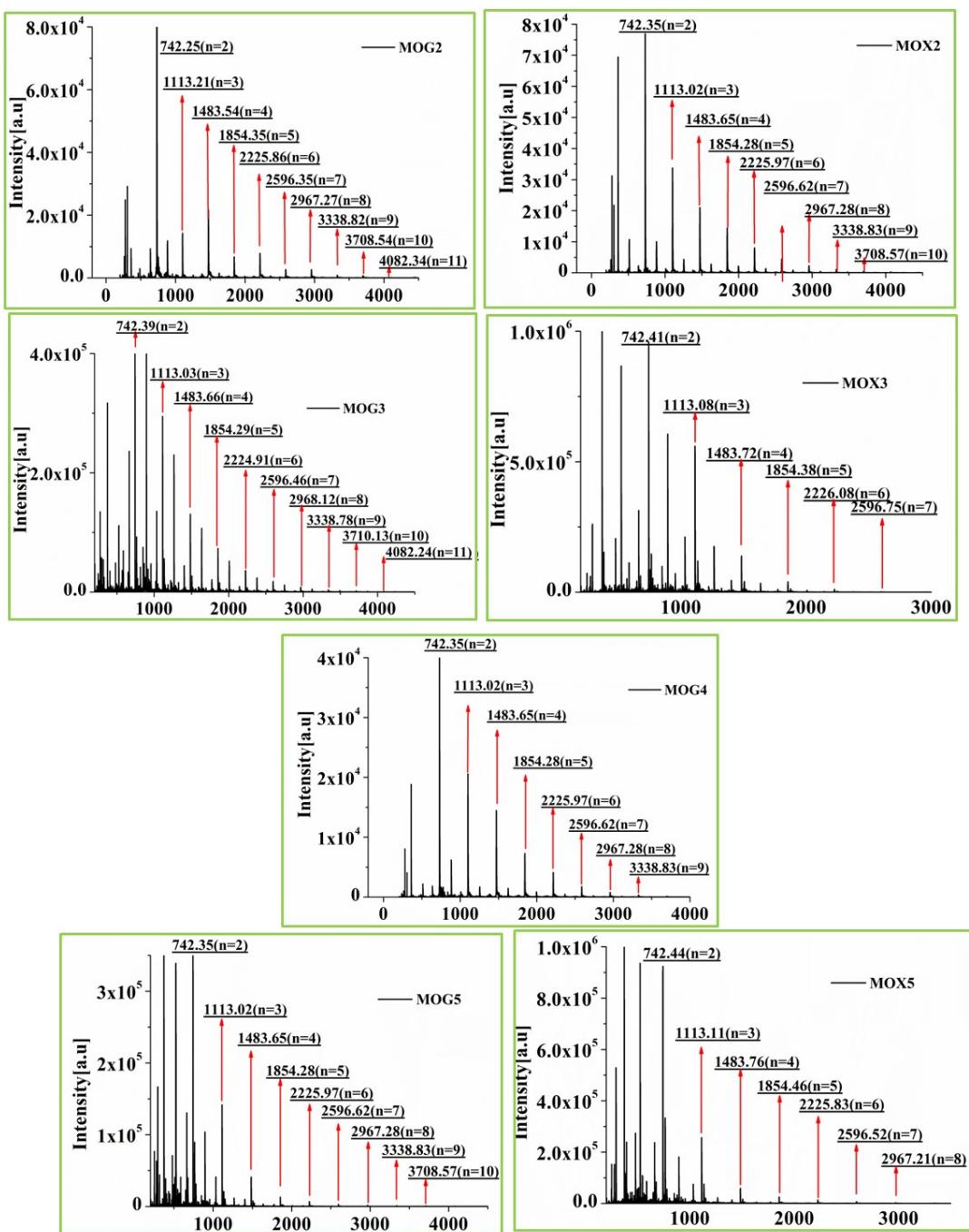


Fig. S18 MALDI-TOF analysis for **MOG1-5** and xerogel of **MOG1-3** and **MOG5**.

Table S2 Degree of polymerization in gel and xerogel states for **MOG1-5**.

| | No of photopolymerized gelator molecules | |
|-------------|--|-----------|
| | Gel | Xerogel |
| MOG1 | 11 | 10 |
| MOG2 | 11 | 10 |
| MOG3 | 11 | 7 |
| MOG4 | 10 | 0 |
| MOG5 | 10 | 8 |

Table S3 Overall changes in rheological moduli after 24h UV irradiation for **MOG1-5**

| Gels | Yield Stress σ_y (Pa) | | | | G'-G'' (Pa) | | | |
|-------------|------------------------------|--------|--------|--------|-------------|---------|-----------|-----------|
| | Before | | After | | Before | | After | |
| | avr | | avr | | avr | | avr | |
| MOG1 | 132.32 | | 228.06 | | 4,104.14 | | 16,823.95 | |
| | 140.13 | 140.34 | 269.08 | 238.08 | 3,925.55 | 4054.82 | 16,022.03 | 16,720.24 |
| | 148.58 | | 217.10 | | 4,134.77 | | 17,314.74 | |
| MOG2 | 53 | | 69 | | 3,896.15 | | 7,183.92 | |
| | 53.90 | 58.73 | 81.60 | 75.80 | 4,115.94 | 4091.94 | 7,126.71 | 7,406.35 |
| | 69.30 | | 76.81 | | 4,263.75 | | 7,908.43 | |
| MOG3 | 105.22 | | ... | | 802.7 | | | |
| | 87.11 | 99.89 | | | 988.12 | 959.88 | | |
| | 107.34 | | | | 1088.83 | | | |

| | | | | | | | | |
|-------------|----------------|---------------|---------------|---------------|-----------------|-----------------|------------------|------------------|
| MOG4 | 145.25 | | 358.91 | | 4,271.73 | | 20,285.25 | |
| | 119.65 | 136.01 | 417.35 | 370.64 | 4,150.92 | 3983.26 | 22,281.48 | 20,900.43 |
| | 143.15. | | 335.66 | | 3,527.14 | | 20,134.56 | |
| MOG5 | 110.80 | | 118 | | 3,915.76 | | 7,169.69 | |
| | 198.09 | 154.89 | 140.43 | 127.30 | 3,860.40 | 3,996.08 | 7,701.32 | 7,615.13 |
| | 155.78 | | 123.48 | | 4,212.09 | | 7,974.39 | |

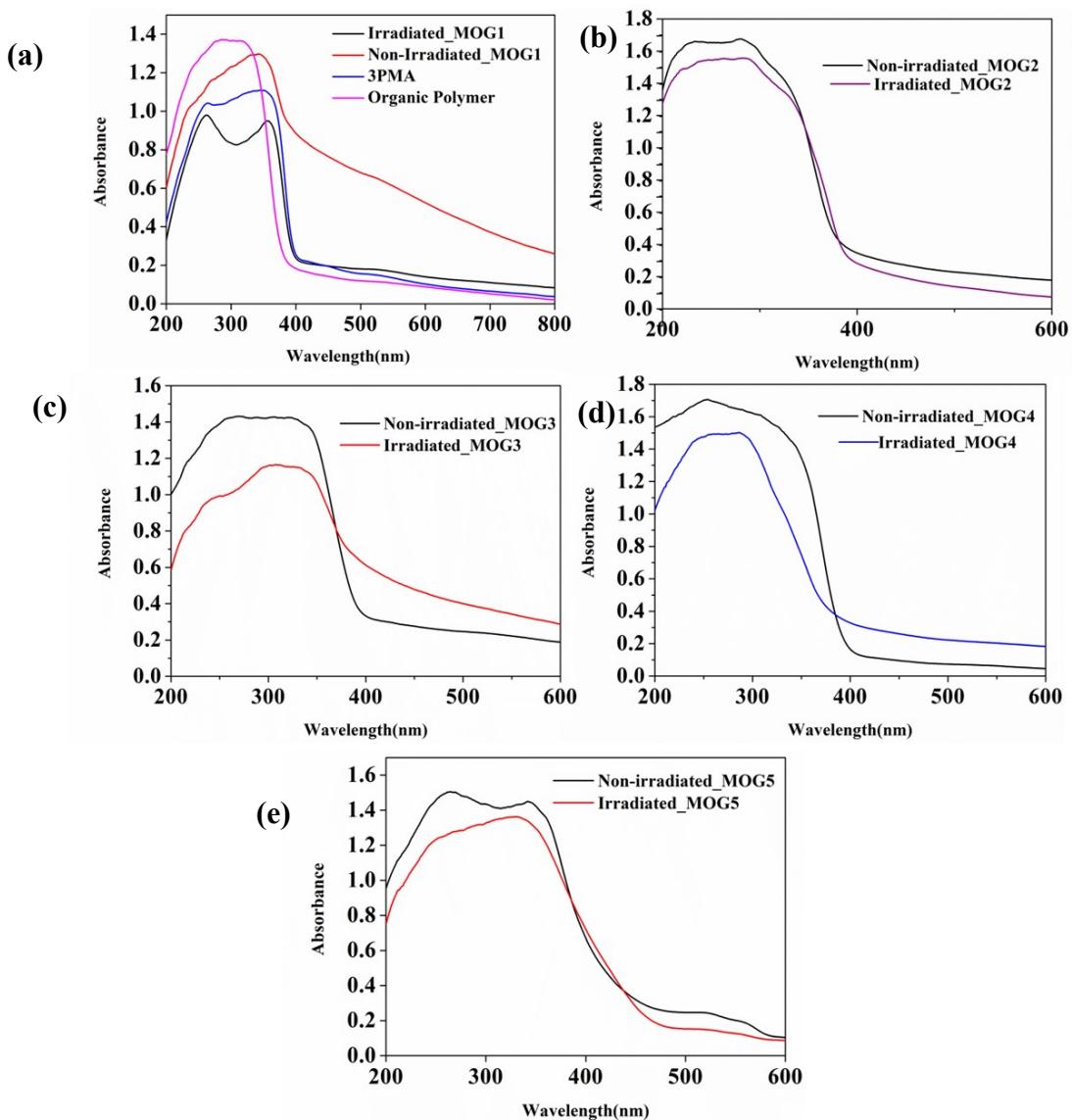


Fig. S19 Absorption spectra in solid state of (a) 3PMA, MOG1 and irradiated MOG1; (b) MOG2 and irradiated MOG2; (c) MOG3 and irradiated MOG3; (d) MOG4 and irradiated MOG4; (e) MOG5 and irradiated MOG5.

References:

- [1]. Mandal, R.; Biradha. *K. Dalton Trans.* **2020**, *49*, 13744-13752.
- [2]. Myshakina, N. S.; Ahmed, Z.; Asher, S. A. *J Phys Chem B.* **2008**, *112*, 11873-11877.