

Light cured networks containing metal organic frameworks as efficient and durable polymer electrolytes for dye-sensitized solar cells

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SUPPORTING INFORMATION

1. Materials

As regards the preparation of polymer membranes, polyethylene glycol diacrylate (PEGDA, average M_n : 575) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, average M_n : 475) were obtained by Aldrich; 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) from Ciba Specialty Chemicals was used as the free radical photoinitiator. Liquid electrolyte was prepared with acetonitrile (CH_3CN), sodium iodide (NaI), 1-methyl-3-propylimidazolium iodide (MPII), 4-*tert*-butylpyridine (TBP), and iodine (I_2), all purchased from Sigma-Aldrich.

For the synthesis of Mg-MOF, benzene tricarboxylic acid (BTC) and tetrabutylammonium tetrafluoroborate (TBATFB), from Acros Organics, were analytical grade. Methanol was HPLC grade (Sisco Research Laboratories). Mg-plates with 99.9% purity (John Mathew, India) were used as electrode material.

As regards DSSC devices, they were assembled using conducting glass plates (FTO glass, sheet resistance $7 \Omega \text{ cm}^{-2}$, Solaronix), which were cut into $2 \times 2 \text{ cm}^2$ sheets and used as a substrate for the deposition of a TiO_2 porous film from a paste (DSL 18NR-AO, Dyesol) and for the fabrication of platinized counter-electrodes. Sensitizing dye *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (N719, Ruthenizer 535 bis-TBA) was purchased from Solaronix.

2. Preparation and characterization of Mg-MOF

Mg-MOF was prepared by electrochemical route. Two Mg electrodes having similar area (5.25 cm^2) were used as an anode and cathode for the synthesis of $\text{Mg}_3(\text{BTC})_2$. The organic linker (0.1 M BTC) and supporting electrolyte (TBATFB) were dissolved in 50 mL of methanol in an electrochemical cell and stirred for 15 min. Electrolysis was carried out under constant voltage for 2.5 h to complete the reaction. Finally, the colorless precipitate of $\text{Mg}_3(\text{BTC})_2$ was collected and allowed to dry in a hot air oven at $120 \text{ }^\circ\text{C}$ for 12 h. The yield of the product, corresponding to the amount of weight loss in the magnesium anode, was 97%.

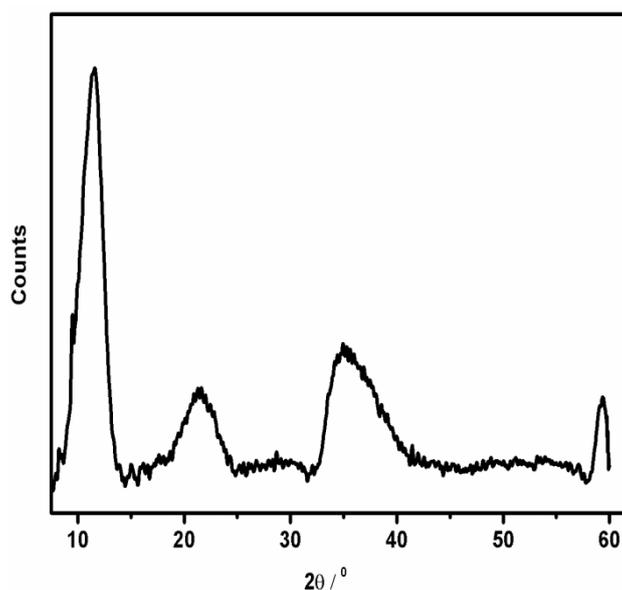


Fig. S1 X-ray diffraction pattern of as-synthesized Mg-MOF.

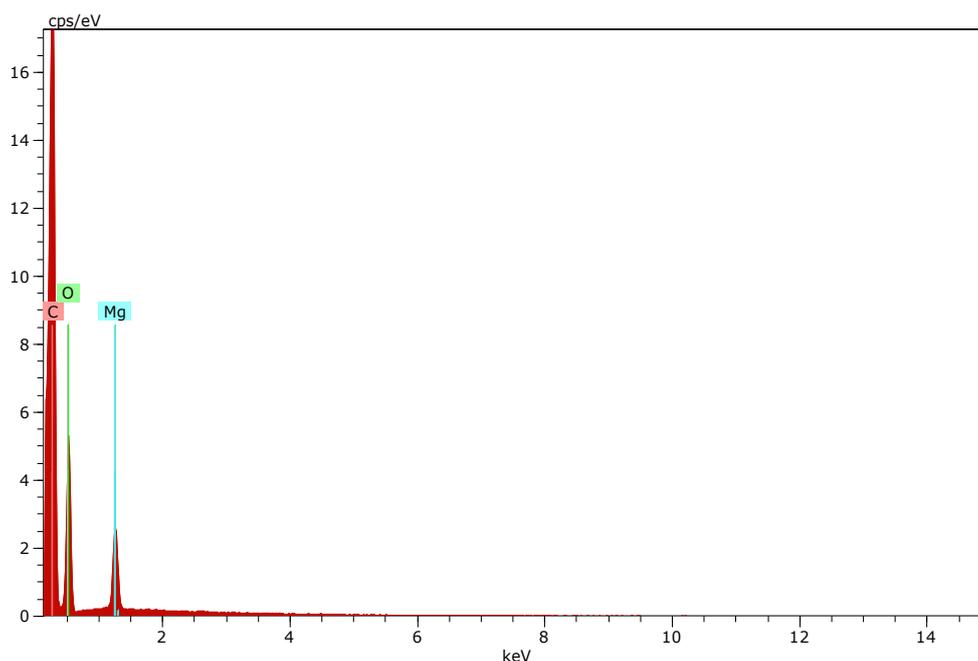


Fig. S2 Energy-dispersive X-ray (EDAX) spectrum of as-synthesized Mg-MOF.

3. Preparation and characterization of polymer electrolyte membranes

UV-curable reactive mixtures were prepared by mixing PEGMA and PEGDA (80:20 weight ratio), and adding Mg-MOF powder in different amounts (i.e., 0-1-2-3 wt%). The complete dispersion was achieved by mechanical mixing with Ultra-Turrax for 3 min. Each mixture was sandwiched between two UV-transparent glasses, separated by a 100 μm -thick tape, and UV cured under N_2 flux by using a medium vapour pressure Hg lamp (Helios Italquartz), with an irradiation intensity on the surface of 25 mW cm^{-2} . After 3 minutes, membranes were peeled off from the glass plates, and were activated by soaking them in the liquid electrolyte swelling solution previously described. Higher quantities of Mg-MOF (5%, 10%, ...) have also been tried, but the dispersion within the polymer matrix was no longer homogeneous, and this gave rise both to the formation of macroscopic aggregates that made the material inhomogeneous, both to fragility and loss of flexibility.

The kinetics of the photo-polymerization was determined by Real-Time FTIR spectroscopy (RT-FTIR), employing a Thermo-Nicolet 5700 instrument. A thin coating with the reactive mixtures was deposited on silicon wafers and exposed simultaneously to the UV beam (which induced the polymerization) and to the IR beam (which analyzed *in situ* the extent of the reaction). The conversion of acrylate/methacrylate double bonds at any time was calculated monitoring the peak area under the 1634 cm^{-1} band (acrylate C=C signal), normalized by a constant signal in the spectra (C=O peak at 1726 cm^{-1}).

The gel content was determined on the cured membranes by measuring the weight loss after 24 h extraction in chloroform at room temperature, according to the standard test method ASTM D2765-84.

The final thickness of the membranes was measured with a Mitutoyo Series 547 Thickness Gauge, equipped with an Absolute Digimatic Indicator (model IDC112XBS), with a resolution of $\pm 1 \mu\text{m}$ and a max measuring force of 1.5 N.

The glass transition temperature (T_g) of the materials was evaluated by differential scanning calorimetry (DSC) with a METTLER DSC-30 instrument, equipped with a low temperature probe.

The thermal stability of the UV-cured gel-polymer membranes was tested by thermogravimetric analysis (TGA), with a TGA/SDTA-851 instrument from Mettler, over a temperature range of 25-600 $^\circ\text{C}$ under N_2 flux at a heating rate of 10 $^\circ\text{C min}^{-1}$.

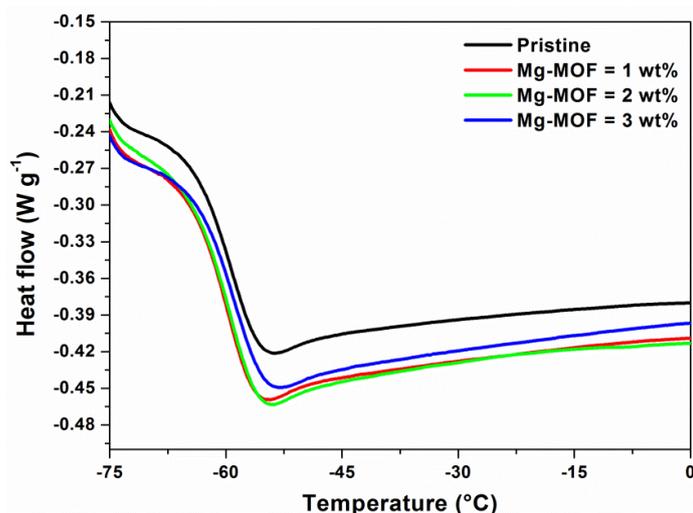


Fig. S3 DSC traces of the series of the Mg-MOF/PEGMA/PEGDA polymer membranes prepared.

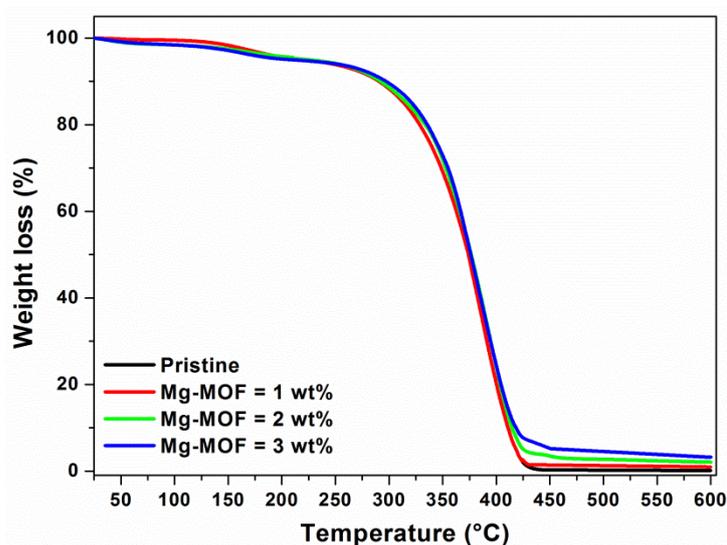


Fig. S4 TGA measurements the series of the Mg-MOF/PEGMA/PEGDA polymer membranes prepared.

4. DSSC fabrication and testing

As regards the preparation of photoanodes, FTO covered glasses were rinsed with acetone and ethanol in an ultrasonic bath for 10 min. A TiO₂ film was deposited on FTO by doctor-blade technique and dried at 70 °C for 30 min on a hot plate. A sintering process at 525 °C for 30 min allowed the formation of a nanoporous TiO₂ layer with a mean thickness of 9.0 μm, measured by profilometry (P.10 KLA-Tencor Profiler). The sensitization of the photoelectrodes was performed by soaking into a 0.35 mM N719 dye solution in ethanol for 12 h at room temperature, followed by a washing procedure in ethanol to remove the unadsorbed dye.

Counter electrode FTO glasses were cleaned with the same rinsing method described above and a 5 nm Pt thin film was deposited by thermal evaporation.

A quasi-solid state DSSC was assembled by positioning the polymer electrolyte membrane above the sensitized photoanode circular surface. Then, photoanode and cathode were clipped together, and cyanoacrylate glue was used as a sealant.

The active area of the cell was 0.78 cm^2 and the photovoltaic measurements were performed with a 0.22 cm^2 rigid black mask. I - V electrical characterizations under AM1.5 illumination (100 mW cm^{-2}) were carried out using a class A solar simulator (91195A, Newport) and a Keithley 2440 source measure unit. The photoelectric performances (i.e. fill factor FF and light-to-electricity energy conversion efficiency η) were calculated by the following equations:

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}}$$

$$\eta(\%) = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100$$

where V_{oc} is the open-circuit voltage (V), J_{sc} the short-circuit current density (mA cm^{-2}), P_{in} the incident light power density (mW cm^{-2}); V_{max} (V) and J_{max} (mA cm^{-2}) are the voltage and the current density in the J - V curves, respectively, at the point of maximum power output.

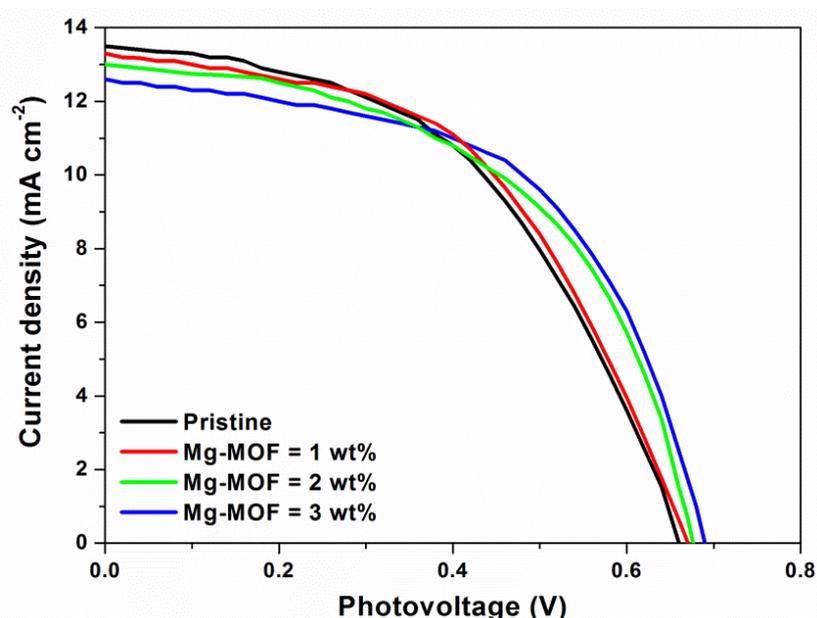


Fig. S5 J-V curves for quasi-solid DSSCs fabricated with different Mg-MOF/PEGMA/PEGDA polymer membranes.

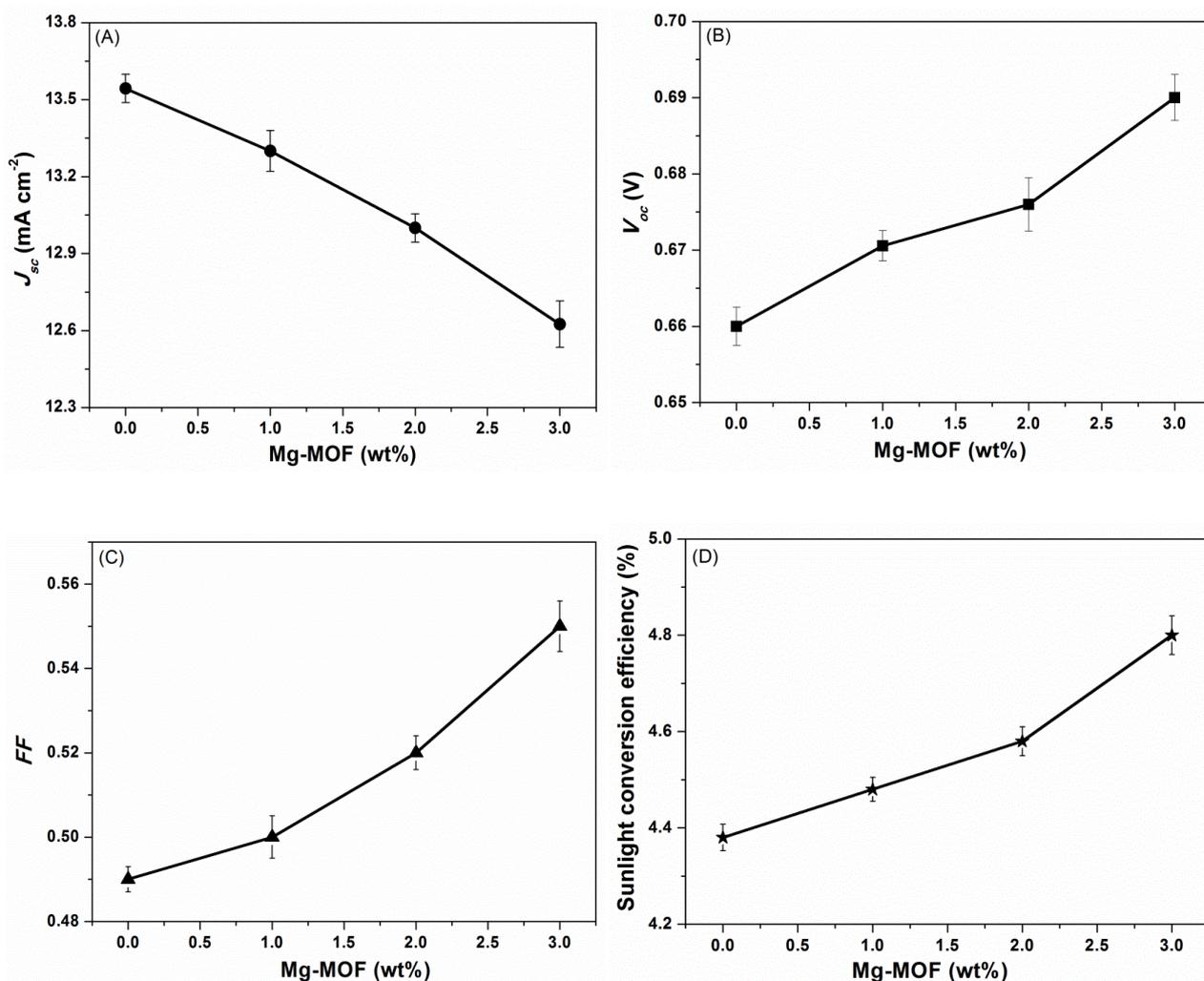


Fig. S6 Variation of photovoltaic parameters (A: J_{sc} ; B: V_{oc} ; C: FF; D: η) of quasi-solid DSSCs fabricated with different Mg-MOF/PEGMA/PEGDA polymer membranes in function of the amount of Mg-MOF.

Electrochemical impedance spectra (EIS) were collected under dark using an electrochemical workstation (760D, CH Instruments) in the frequency range 100 mHz - 20 kHz at cell open circuit voltage.

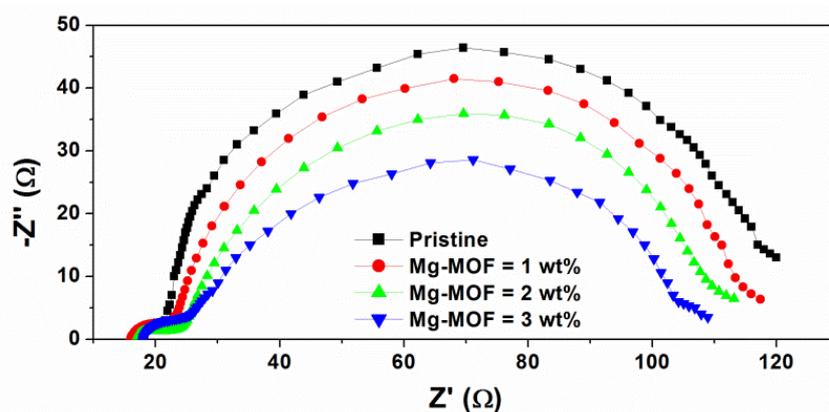


Fig. S7 EIS curves (under dark, at V_{oc}) of quasi-solid DSSCs fabricated with different Mg-MOF/PEGMA/PEGDA polymer membranes.

Measured spectra were fitted through an equivalent circuit [*], and the following terms were calculated:

$$\tau_n = (R_{CT} Q_\mu)^{1/\beta_\mu}$$

$$L_n = d(R_R/R_T)^{1/2}$$

$$D_n = L_n^2/\tau_n$$

where τ_n is the effective electron lifetime, R_{CT} is the charge transfer resistance, Q_μ is a constant phase element (CPE), β_μ is the index of the CPE Q_μ , L_n is the electron diffusion length, d is the TiO₂ thickness, R_R is the recombination resistance, R_T is the transport resistance and D_n is the electron diffusion coefficient.

Fitted data (useful to clarify the dependence of the V_{oc} on the amount of Mg-MOF present in the polymer electrolyte membranes) are reported in Table S1. First of all, it can be observed that D_n values are independent from Mg-MOF wt%; in fact, this parameter depends mainly on the properties of the photoanode, and identical TiO₂ layers were used for all the devices. On the other hand, τ_n values increased with the amount of Mg-MOF introduced in the polymer networks: this fact led to a reduction of the recombination at the interface between the TiO₂ layer and the polymer electrolyte, confirming the establishment of interactions between carboxy-terminated organic frameworks and TiO₂ surface, useful to shield the trap states of the photoelectrode. This phenomenon is responsible for the higher photovoltage exhibited by the PEGDA:PEGMA-based membranes containing high amounts of Mg-MOF. As a further result, it can be observed that the combined effect of reduction of recombination (higher τ_n values) and unchanged transport properties (D_n) brings to a slightly higher L_n values for the 3 wt% Mg-MOF-based cell respect to the others.

[*] F. Fabregat-Santiago, G. Garcia-Belmonte, J. Bisquert, A. Zaban and P. Salvador, *J. Phys. Chem. B*, 2001, **106**, 334.

Table S1 Fitted EIS parameters: D_n is the electron diffusion coefficient, τ_n is the effective electron lifetime and L_n is the electron diffusion length.

MOF (wt%)	D_n ($\text{cm}^2 \text{s}^{-1}$)	τ_n (s)	L_n (μm)
0	4.97E+04	4.24E-03	14.52
1	4.96E+04	4.40E-03	14.78
2	4.97E+04	4.56E-03	15.05
3	4.96E+04	4.70E-03	15.27