

*Electronic Supplementary Information for*  
**Microporous organic polymer-induced gel electrolytes  
for enhanced operation stability of electrochromic devices**

Ju Hong Ku,<sup>‡a</sup> Hyunjae Lee,<sup>‡a</sup> Jaewon Choi,<sup>a</sup> June Young Jang,<sup>a</sup> Sang Moon Lee,<sup>b</sup> Hae Jin Kim,<sup>b</sup> Yoon-Joo Ko,<sup>c</sup> and Seung Uk Son<sup>\*a</sup>

<sup>a</sup>Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea

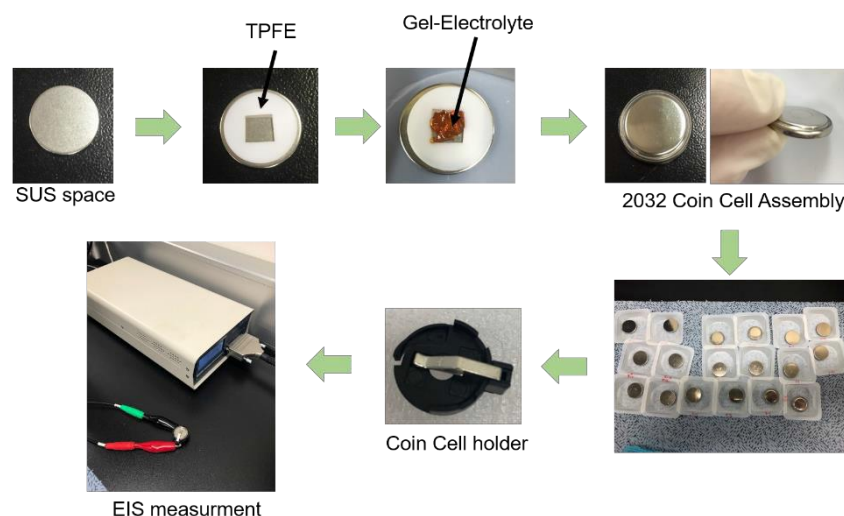
<sup>b</sup>Korea Basic Science Institute, Daejeon 350-333, Korea

<sup>d</sup>Laboratory of Nuclear Magnetic Resonance, National Center for Inter-University Research Facilities(NCIRF),  
Seoul National University, Seoul 08826, Korea

<sup>‡</sup> These authors contributed equally to this work.

**Experimental Sections**

Infrared (IR) absorption spectroscopy was conducted using a Bruker VERTEX 70 FT-IR spectrometer. N<sub>2</sub> adsorption-desorption isotherm curves were obtained at 77K using a Micromeritics ASAP2020. The pore size distribution of analyzed by the density functional theory. Solid state <sup>13</sup>C nuclear magnetic resonance spectroscopy was conducted in the CPTOSS mode using a 500 MHz Bruker ADVANCE II NMR spectrometer at the NCIRF of Seoul National University. A 4 mm magic angle spinning probe was used. The spinning rate was 5 kHz. Powder X-ray diffraction studies were conducted using a Rigaku MAX-2200 (filtered Cu-Ka radiation). Thermogravimetric analysis was conducted using a Seiko Exstar 7300. UV/vis absorption spectroscopy was conducted using an Ocean optics flame spectrophotometer. Electrochemical impedance spectroscopy was conducted using a WonAtech ZIVE SP1 potentiostat at 25°C. The 2032 coin cell assemblies were used for the EIS studies. For the 2032 coin cell assemblies, the following procedures were applied. On the SUS space disc (16Φ =16 mm diameter/1t=1mm thickness, Welcos Co. Ltd), poly(tetrafluoroethylene) (PTFE, 0.5t) film with a square-shaped hole of 0.5 cm × 0.5 cm size was loaded. The square hole was filled with gel electrolytes (33 mg) and another SUS space disc was loaded on the PTFE film. Using the 2032 coin cell caps, the coin cells were assembled. Frequency range was 0.01~1000000 Hz. The amplitude was 5 mV.



Rheological properties were studied using a rheometer (ARES-G2, TA instruments Co.). Electrochromic studies were conducted using a CH1604e potentiometer and an Ocean optics flame spectrophotometer.

### ***Synthetic procedure for MOP-G electrolytes***

For the preparation of MOP-G-3, LiClO<sub>4</sub> (33 mg, 0.31 mmol), (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (0.9 mg, 1.3 μmol), CuI (0.2 mg, 1.3 μmol), 1,4-diazabicyclo[2,2,2]octane (DABCO, 29 mg, 0.26 mmol) were added to a 20 mL vial. After N-methylpyrrolidone (NMP, 3 mL) was added, the mixture was sonicated for 40 min. Tetrakis(4-ethynylphenyl)methane was prepared following the procedures in the literature.<sup>1</sup> Tetrakis(4-ethynylphenyl)methane (55 mg, 0.13 mmol) and 1,4-diiodobenzene (86 mg, 0.26 mmol) dissolved in NMP (1 mL) were added to the mixture. After standing at 25°C without stirring for 2 days, the gel material was obtained. For other MOP-G materials described in Table 1 in text were prepared by using various total volumes of NMP and LiClO<sub>4</sub>. The amount of (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>, CuI, DABCO, tetrakis(4-ethynylphenyl)methane, and 1,4-diiodobenzene were fixed. For the preparation of MOP-G-1, 33 mg of LiClO<sub>4</sub> and 2 mL of NMP were used. For the preparation of MOP-G-2, 33 mg of LiClO<sub>4</sub> and 3 mL of NMP were used. For the preparation of MOP-G-4, 99 mg of LiClO<sub>4</sub> and 4 mL of NMP were used. For the preparation of MOP-G-5, 330 mg of LiClO<sub>4</sub> and 4 mL of NMP were used. For the preparation of MOP-G-6, 1 g of LiClO<sub>4</sub> and 4 mL of NMP were used.

### ***Fabrication procedures of electrochromic cells and electrochromic studies***

Indium tin oxide electrode (ITO on glass, 1.1T, 10 Ω) was cut to an area size of 1.4 cm × 1.8 cm. TiO<sub>2</sub> paste (PST-18NR, Lot No, FF06, JGC catalysts and Chemicals Ltd.) was silk screen-printed on the ITO/glass electrode with an area size of 1 cm × 1 cm. The TiO<sub>2</sub>-paste/ITO/glass was treated at 500°C for 3 hours. 1,1'-Bis(2-phosphonoethyl)-4,4'-bipyridinium hexafluorophosphate was prepared by following the procedures in the literature.<sup>2</sup> In a 20 mL vial wrapped with an aluminium foil, the TiO<sub>2</sub>/ITO/glass electrode was dipped in methanol solution (4.0 mM, 10 mL) of 1,1'-bis(2-phosphonoethyl)-4,4'-bipyridinium hexafluorophosphate (27 mg, 0.041 mmol) for 2 days. The viologen-grafted TiO<sub>2</sub>/ITO/glass was washed with methanol, dried under air, and used as a working electrode. Using a Surlyn tape (thickness: 0.10 mm), the working electrode was sandwiched with an ITO/glass electrode with an area size of 1.4 cm × 1.8 cm. *N*-butylphenothiazine was prepared by following the procedures in the literature.<sup>3</sup> In the solution for the preparation of gel or liquid electrolytes, the *N*-butylphenothiazine (51 mg, 0.20 mmol) was added. Electrolytes were added to the sandwich cells using a syringe. In the case of gel electrolytes, after standing the electrolyte solution for 1 day, the semi-gel materials were added to the sandwich cells by a syringe. Then, the sandwich cells were put aside for 4 days to induced the formation of gel electrolytes. We confirmed that the excess semi-gel materials were became gels after 1 day. For the electrochromic studies, the potentials were applied using a CH1604e potentiometer. In a chronoamperometry mode, the alternating potentials of -1.65 (coloring) and +0.5 V (de-coloring) were applied for 30 seconds each. The color changes were recorded using an Ocean optics flame spectrophotometer. The maximum absorptions in the range of 500~800 nm were measured as 550 and 528 nm, respectively, for the electrochromic cells fabricated using MOP-G-2~5 and liquid electrolytes. Thus, ΔA values at

500 and 528 nm were recorded for the electrochromic cells fabricated using MOP-G-2~5 and liquid electrolytes, respectively. In our studies, the response time was defined as the time taken to reach 90% of the maximum  $\Delta A$  values.

### References

- 1 S. Yuan, S. Kirklín, B. Dorney, D. -J. Liu and L. Yu, *Macromolecules* 2009, **42**, 1554-1559.
- 2 M. Felderhoff, S. Heinen, N. Molisho, S. Webersinn and L. Walder, *Helv. Chim. Acta.* 2000, **83**, 181-192.
- 3 A. K. Sanap, K. K. Sanap, G. S. Shankarling, *Dyes Pigm.* 2015, **120**, 190-199.

**Table S1.** Synthetic conditions and properties of MOP-G electrolytes<sup>a</sup>.

Entry	LiClO <sub>4</sub> (mg)	NMP (mL)	Code Name	Conductivities (mS/cm)
1	33	2	MOP-G-1	-
2	33	3	MOP-G-2	-
3	33	4	MOP-G-3	2.56
4	66	4	MOP-G-3.5	2.98
5	99	4	MOP-G-4	3.94
6	132	4	MOP-G-4.5	4.46
7	330	4	MOP-G-5	6.33
8	495	4	MOP-G-5.5	9.69

<sup>a</sup>Reaction conditions: tetrakis(4-ethynylphenyl)methane (0.13 mmol), 1,4-diiodobenzene (0.26 mmol), (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (1.3 μmol), CuI (1.3 μmol), DABCO (0.26 mmol), 2 days, room temperature, no stirring. <sup>b</sup>Ionic conductivities of gel electrolytes.

Fig. S1 PXRD patterns of MOP-G-3~5, the MOP material isolated from MOP-G-3, and LiClO<sub>4</sub>.

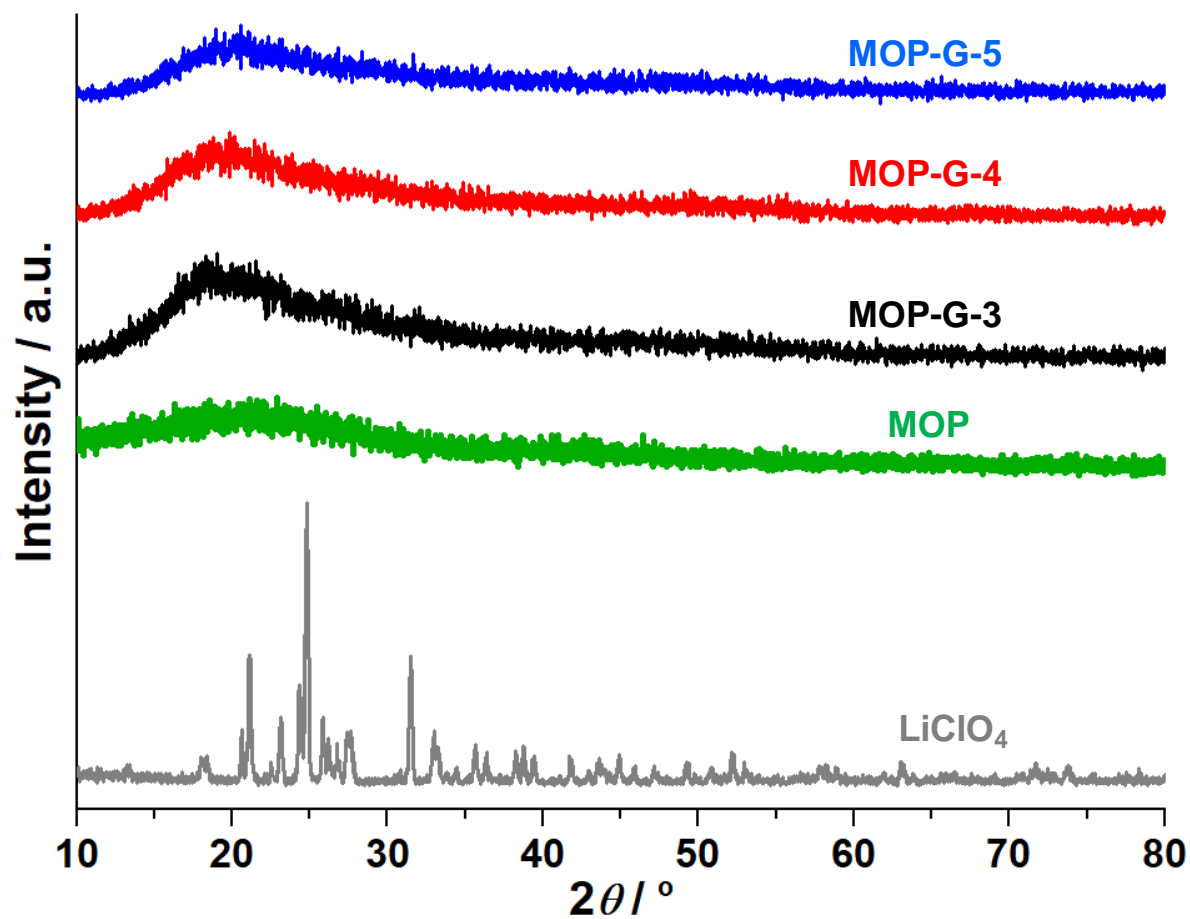
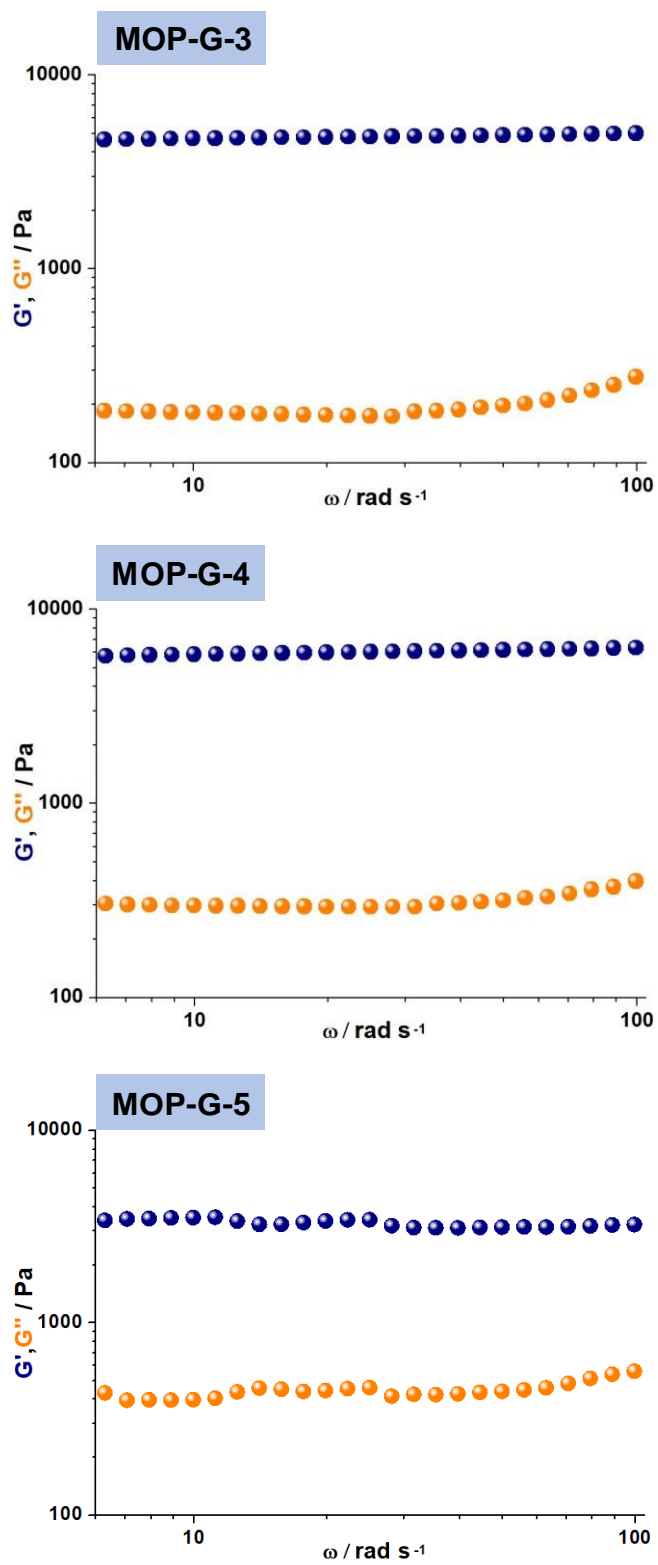
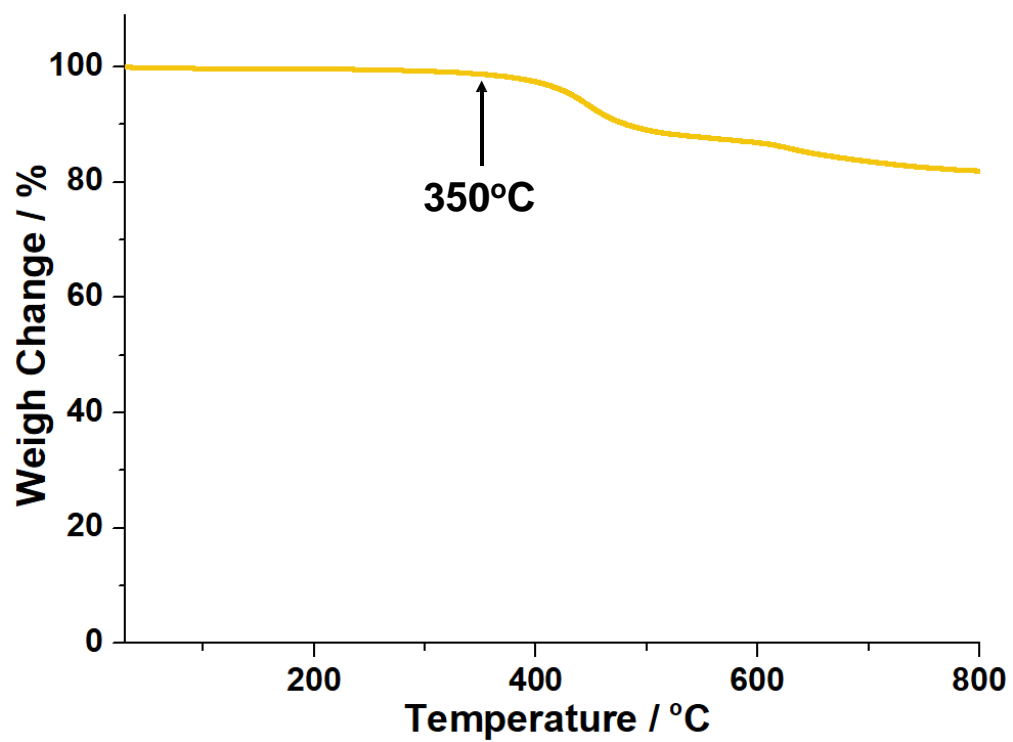


Fig. S2 Rheological properties of MOP-G-3~5.



**Fig. S3** A TGA curve of the MOP material isolated from MOP-G-3.



**Fig. S4** Cyclic voltammograms of EC devices fabricated using MOP-G-3~5.

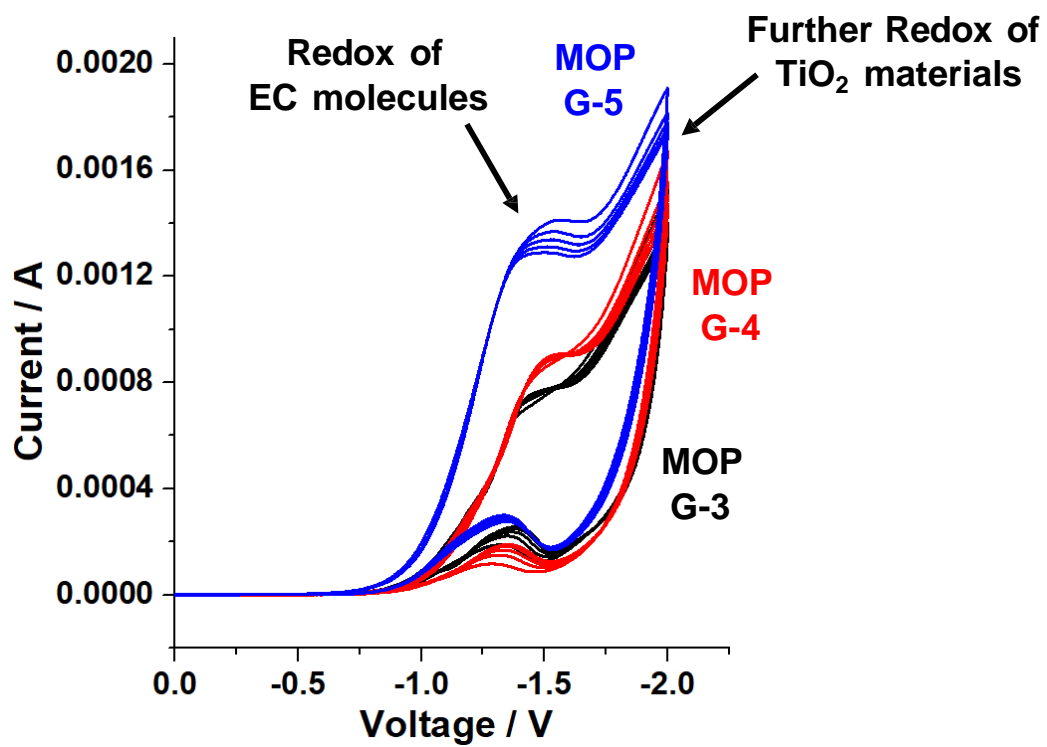
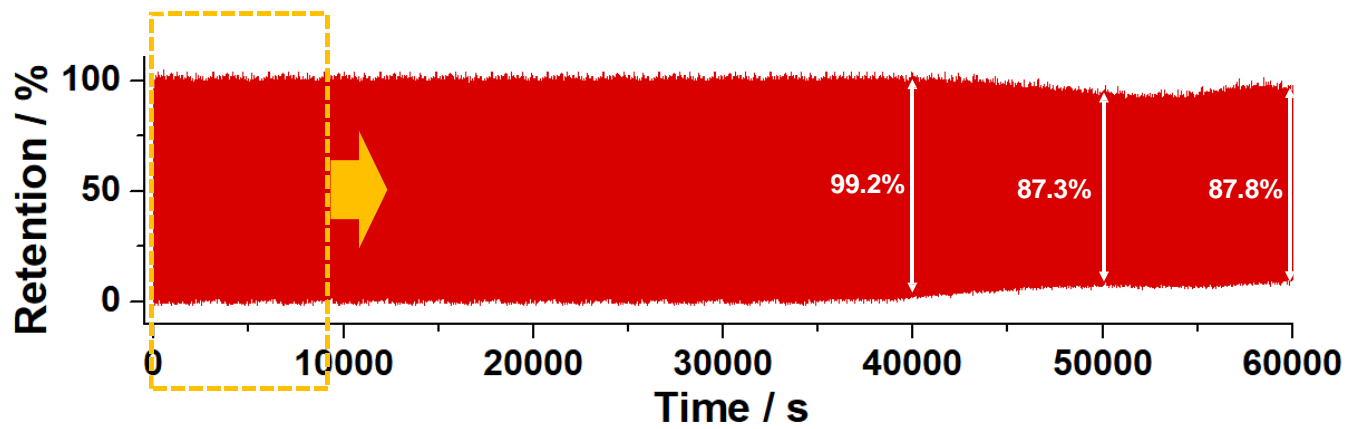
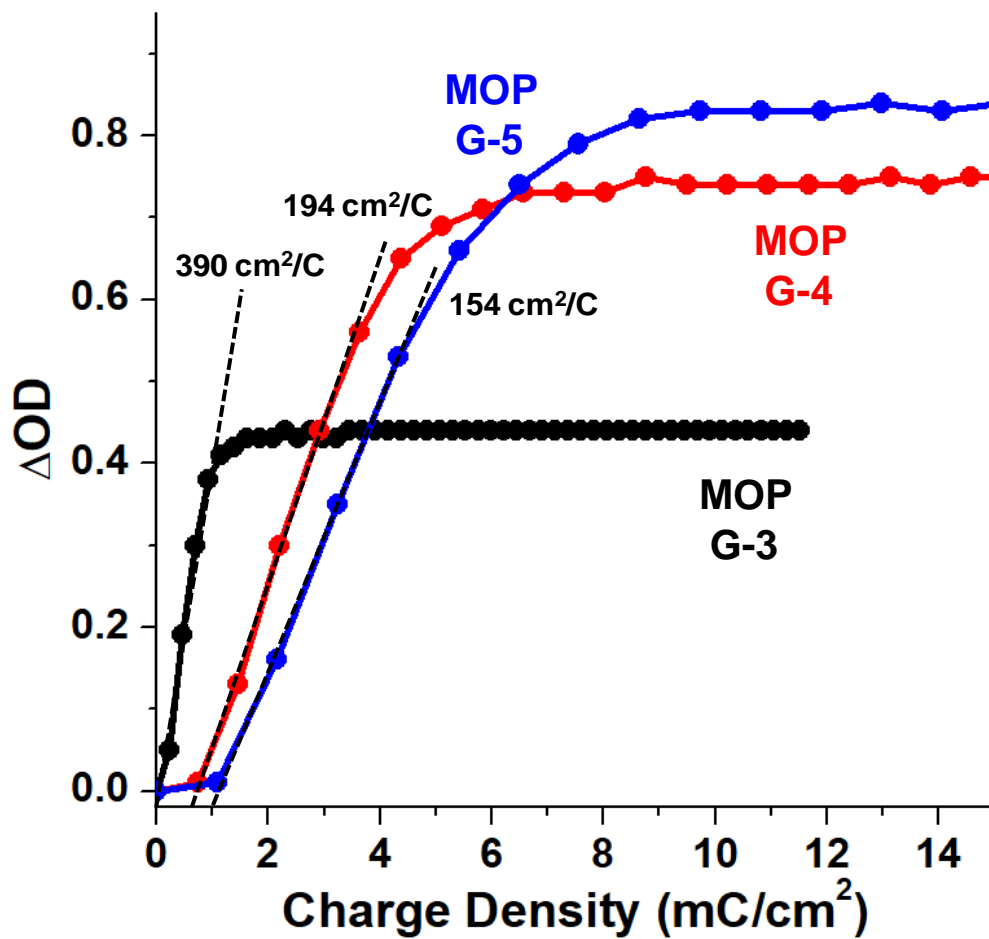




Fig. S5 Extended cycling tests of EC cell fabricated using MOP-G-4.



**Fig. S6** Color Efficiencies of EC devices fabricated using MOP-G-3~5.



**Fig. S7** (a) Performance of EC cells fabricated using conventional linear organic polymer (LOP) gel electrolytes (PMMA/LiBF<sub>4</sub>, PEO/LiClO<sub>4</sub>, PVDF/[BMI]BF<sub>4</sub>) in the literature and (b) comparison of response times and  $\Delta A$ .

