

# Purification of deteriorated liquid crystals by employing porous metal–organic–framework/polymer composites

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**Abstract:** This study demonstrates the effectual purification of degraded nematic liquid crystals (LCs) by introducing metal–organic framework (MOF) into the copolymer with either negatively charged 2-acrylamido-2-methylpropane sulfonic acid (AMPS) or positively charged (vinylbenzyl) trimethylammonium chloride (VBTA). Experimental results show that the ion elimination is primarily achieved by the nanoporous MOF itself while AMPS or VBTA plays an important role in functionalizing MOF with hydrophilicity. It was found that the overall ion-removal efficacy of either MOF/polymer-AMPS or MOF/polymer-VBTA composite is higher than that of the pristine MOF counterpart.

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## 1. Introduction

Liquid crystal displays (LCDs) are currently the most dominant type of flat-panel displays on the markets. Applications of human-machine interfaces increase numerous in a variety of commercially electronic and information-content products, such as digital cameras, mobile phones, notebooks, tablets, personal computers, and high-definition televisions. With growing popularity of LCD-related products, the increasing amount of waste materials, especially those received as leftovers from the production line, has emerged as one of critical issues in LC and related industries due to cost consideration and environmental protection [1]. In view of the fabrication process of LCDs, a certain amount of LC remnants or spills is inevitable in the stage of panel-filling procedure regardless of the injection approach used. Such LC leftovers, in contact with the surrounding environment, are often contaminated as evidenced by the increasing content of ion impurities, most likely originating from the dissemination of atmospheric moistures and dust particles from air into LCs. It has been elucidated that the pollutants in degraded LCs are primarily composed of hydrogen cations and hydroxyl anions dissociated from water molecules as well as of metal cations [2-4]. Consequently, severe migration of mobile ions under an applied voltage could generate a considerable ionic effect in a LCD, causing image sticking and, in turn, detrimental display performance [5-8]. Although the adoption of LC materials with high resistivity as well as low ion density is the most reliable strategy to reduce the unwanted ionic effect in LCDs, the LC leftovers from the production line are not reusable in consideration of their loss of material integrity. Thus far, several potential non-synthesis approaches involving trapping or restraining the transport of ions have been extensively reported through the dispersion of specific nanomaterials in ion-rich LCs [9-15]. Disadvantageously, nanodopants suspended in LCs over time have a strong tendency to aggregate, implying that their long-term stability would be challengeable.

With the purpose toward the purification and recycle of LC leftovers obtained from flat-panel production lines, we have demonstrated in our previous work that soaking porous metal-organic frameworks (MOFs) as desiccants in LCs is a simple, feasible and cost-effective approach for the recovery of electrical or electrically resistive properties of degraded LCs [3]. Owing to the unusual nanoporous structures and excellent water-sorption ability, it has been confirmed that MOFs can serve as useful purifiers for effective absorption of ion

impurities in LCs. Nevertheless, when a MOF material in the powder form is immersed in LC for a period of time, an additional fine filtrating procedure must be performed to extract the purified LC from the LC–MOF “mixture”. To further enhance the properties and make them suitable for applications, MOF is introduced into some active components by microwave-assisted polymerization [16]. The resulting globular, MOF-containing polymer grains incorporate unaltered MOF skeletons homogeneously mixed in the polymer networks. The efficacy of various MOF composites on the removal of ion impurities of a degraded LC is discussed in accordance with the calculated ion densities and the results of inductively coupled plasma mass spectrometry (ICP-MS). The MOF composites as sorbents (or drying agents) not only reduce the MOF used but show distinctly superior purification power.

## 2. Experimental

The investigated LC materials are designated G1U (i.e., a G1 leftover from a local panel manufacturer) and G1N (i.e., the brand-new nematic G1 found in the current LCD market, dielectric anisotropy  $\Delta\epsilon = 7.9$ ). The resistivity of the TFT-grade nematic G1N is  $\sim 10^{13}$   $\Omega\cdot\text{cm}$  and that of G1U  $\sim 10^{12}$   $\Omega\cdot\text{cm}$ . The MOF material employed in this study is MIL-101(Cr),  $[\text{Cr}_3\text{F}(\text{H}_2\text{O})\text{O}(\text{BDC})_3]\cdot m\text{H}_2\text{O}$ , where BDC is benzene dicarboxylate and  $m \sim 25$ . It is a mesoporous chromium terephthalate fabricated with metal oxygen central cage clusters interconnected by multifunctional organic linkers, forming three-dimensional (3-D) porous networks with high inner surface areas ranging from 2800 to 4230  $\text{m}^2/\text{g}$  and large pore volumes up to 34  $\text{\AA}$  in size [3]. This material has superior chemical and solvent stabilities [17,18]. In our previous work, the water-sorption capacity of MIL-101(Cr) has been demonstrated to be higher than the other MOF materials [3]. In this study, two comparative MOF/copolymer composites were prepared by dispersing 8.5-mg MIL-101(Cr) in the mixture of 7.2- $\mu\text{L}$  butyl methacrylate (BMA), 10.2- $\mu\text{L}$  ethylene dimethacrylate (EDMA), 1-mg initiator 2,2'-azobisisobutyronitrile (AIBN), a trace amount of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) or (vinylbenzyl) trimethylammonium chloride (VBTA) weighing 0.5, 1.0, and 2.0 mg, and a porogenic solvent composed of 70  $\mu\text{L}$  ionic-liquid (1-hexyl-3-methylimidazolium tetrafluoroborate;  $\text{C}_6\text{BF}_4$ ) and 6 $\mu\text{L}$  water. The chemical structures of the four monomers used are illustrated in Fig. 1. Note that AMPS tends to become electronegative whereas VBTA often exhibits electropositivity. Incidentally, the sulfonic acid group ( $\text{HSO}_3^-$ ) of AMPS and the quaternary ammonium group ( $\text{R}_4\text{N}^+\text{Cl}^-$ ) of VBTA both belong to hydrophilic groups. The MOF/copolymer blends were obtained by means of *in situ* polymerization [16] using microwave-assisted heating for 5 min. The porous polymer matrix with uniformly mixed MOF was achieved after several washing processes.

Before the experiments, all MOF composites were put in a vacuum oven at temperature of 150  $^\circ\text{C}$  for 12 h. This activation process is to remove the pre-absorbed contaminants, especially combined and coordinated moistures. 0.5-wt.% of each MOF or MOF composite, functioning as a regenerating agent, was individually immersed into a G1U bottle. All the experimental bottles were then sealed and put undisturbed for 24 h to accomplish the purifying step. The treated (i.e., purified) G1U in each bottle was extracted out using a syringe and a syringe filter with an aperture size of 0.22  $\mu\text{m}$ . It was then filled into a  $6.6 \pm 0.5$   $\mu\text{m}$ -thick, planar-antiparallel-aligned cell by the capillary action.

Powder X-ray diffraction (XRD) patterns of all samples were taken to identify the porous structure of the single-component MOF and MOF composites after *in situ* polymerization. The ion-removal ratio for each MOF sample was obtained from the calculated ion density, which was deduced from low-frequency dielectric spectroscopic data of the corresponding purified LC cell [9–11]. The frequency regime of the LCR meter (HIOKI 3522-50) was set between  $10^{-1}$  and  $10^5$  Hz and the probe voltage was 0.5  $V_{\text{rms}}$  in the sinusoidal waveform.

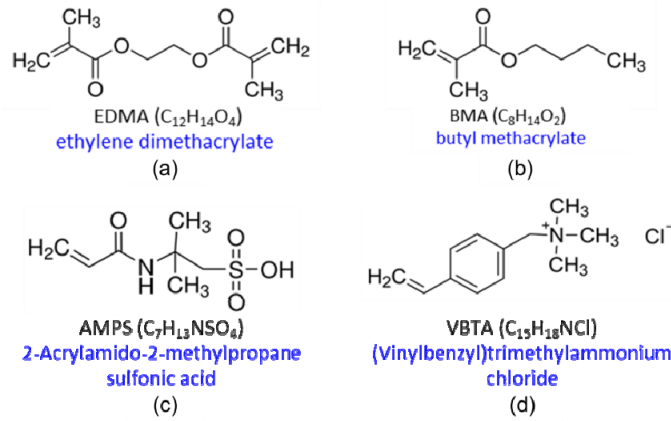


Fig. 1. Molecular structures of (a) BMA, (b) EDMA, (c) AMPS, and (d) VBTA.

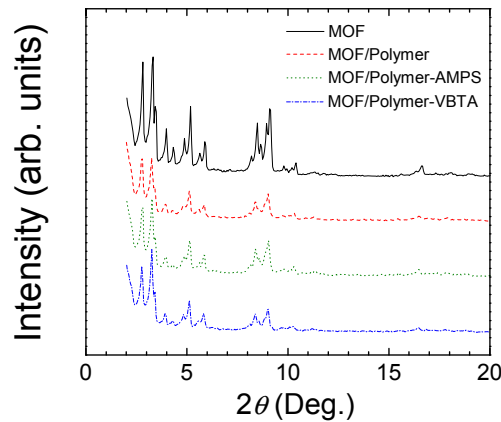


Fig. 2. XRD patterns of the as-synthesized MIL-101(Cr) and MIL-101(Cr)/copolymer.

Owing to the motion of mobile ions, the variation of complex dielectric data with frequency  $f$  was observed below  $10^3$  Hz. The charge density  $n$  can be deduced by fitting the real-part ( $\epsilon'$ ) and imaginary-part ( $\epsilon''$ ) dielectric functions via the following two equations [3,19,20]:

$$\epsilon'(f) = \frac{nq^2 D^{3/2}}{\pi^{3/2} \epsilon_0 d k_B T} f^{-3/2} + \epsilon'_b, \quad (1)$$

and

$$\epsilon''(f) = \frac{nq^2 D}{\pi \epsilon_0 k_B T} f^{-1}, \quad (2)$$

where  $q$  is the electric charge,  $D$  is the diffusion coefficient of the ions,  $\epsilon_0$  is the permittivity in free space,  $d$  is the cell gap,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\epsilon'_b$  represents the intrinsic dielectric constant (in the high-frequency limit) of the LC bulk. In addition to the charge density discussed, the ion-removal ratio was further calculated [21], which was defined as the ratio of the difference between the charge density in G1U and LC samples treated by MOF composites to that in G1U.

### 3. Results and discussion

The XRD patterns of MIL-101(Cr) and various MIL-101-polymer composites are shown in Fig. 2. The five diffraction peaks of the composites located at  $2\theta = 2.8^\circ, 3.3^\circ, 5.2^\circ, 8.5^\circ,$  and  $9.1^\circ$  resemble those of the pristine MOF and conform to the inherent characteristic features of crystalline 3-D MIL-101(Cr) in the literature [22,23]. It confirms that the porous structures and porous sizes of the MOF in the composites are not changed during the *in situ* polymerization process.

Figure 3 depicts the water-absorbing efficiencies of the neat MOF, its three composites (MOF/polymer, MOF/polymer-AMPS and MOF/polymer-VBTA), polymer-VBTA (BMA-co-EDMA with VBTA), and silica gel obtained from their time-varying weight gains. The silica gel, a reference for comparison, is a well-known and commercially available desiccant.

To perform the water-sorption kinetics measurement, each pre-dried sample, stored in an uncovered Petri dish, was put, together with a beaker of water, in an unplugged and closed dry cabinet at the temperature of  $26 \pm 1^\circ\text{C}$  and relative humidity of  $50 \pm 5\%$  for 24 h. The weight gain of each absorbent was determined by the formula:

$$W_{\text{gain}} = \frac{W_{\text{total}} - W_{\text{dried}}}{W_{\text{dried}}} \times 100\%, \quad (3)$$

where  $W_{\text{total}}$  and  $W_{\text{dried}}$  ( $= 5 \text{ gw}$ ) stand for the total and dry weights of the material, respectively. Figure 3 reveals the excellent water absorption ability of the MOF (i.e., MIL-101(Cr)) used and the reduced water-absorption capacities of all the polymeric agents. These data imply the following facts: First, the polymer-VBTA is comparatively inefficient to absorb moistures since its weight gain is only about 4.5%. The reason is that the surface area and porosity of polymer-VBTA were relatively low (Brunauer–Emmett–Teller (BET) surface  $\sim 5 \text{ m}^2\text{g}^{-1}$ ) [16]. Secondly, the weight gain of MOF/polymer-VBTA is much higher than that of polymer-VBTA; we infer that the water intake is primarily attributed to the skeletal MOF. Thirdly, when adding 1 mg of AMPS (VBTA) in the monomers, the saturated weight gain of these MOF composites increases by nearly 1%. It is because AMPS (VBTA) contains the sulfonic acid (the quaternary ammonium) group, which is more hydrophilic than BDC (linker of MIL-101(Cr), the partition constant,  $\log P$ , of AMPS, VBTA and BDC is  $-2.049, -0.460$  and  $1.788$ , respectively) and expected to help trap moisture. Fourthly, the saturated weight gain of the MOF composites (i.e., MOF/polymer, MOF/polymer-AMPS, and MOF/polymer-VBTA) is roughly 20%. The main reason is that the amount of MOF in the composites is only one-third that of the pure MOF sample. One can thus conclude that the MOF component itself dominates the water-absorption level and the MOF embedded in polymer networks remains its water absorption capacity.

Figure 4 displays the measured real and imaginary parts of the dielectric functions and the corresponding ion-removal ratios in cells composed of variously treated GIU in comparison with an untreated GIU and a G1N counterpart. When the polymer-AMPS composite was used for purification, the ion-removal ratio in the treated sample is very low, which demonstrated the neat copolymer has no apparent effect on ion-trapping or ion adsorption. The ion-removal ratios in two treated-GIU samples (i.e., GIU treated with MIL-101(Cr) and with MIL-101(Cr)/polymer-AMPS) were significantly close to one. It delineates that the purification effect is determined by the MOF ingredient. Besides, although the MIL-101(Cr) has greater ability in water adsorption (Fig. 3), MIL-101(Cr)/polymer-AMPS exhibited a comparable results to the pristine MIL101(Cr) (Fig. 4). We suggested that AMPS is negatively charged as well as increasing the hydrophilicity of MIL-101(Cr)/polymer could enhance the cation/anion attraction in deteriorated LCs.

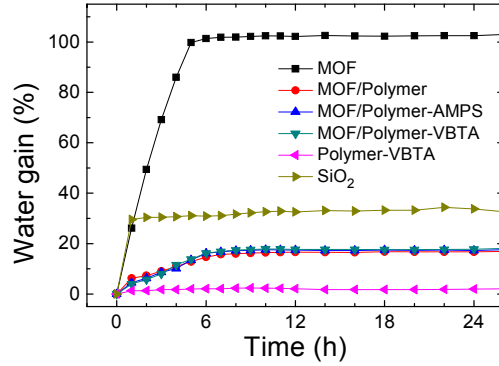


Fig. 3. Time-varying weight gains in various agents due to atmospheric water adsorption.

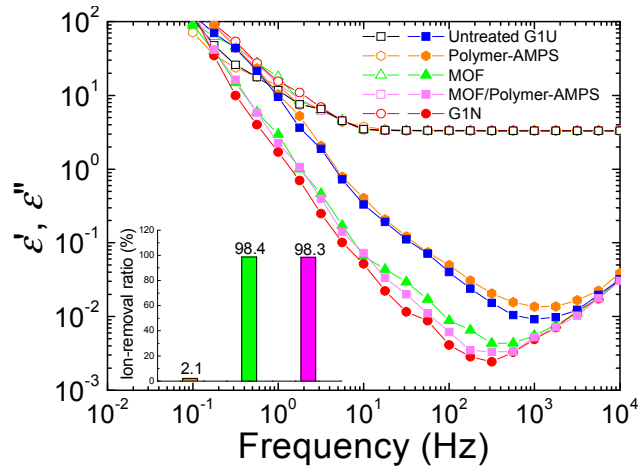


Fig. 4. Measured real (open symbols) and imaginary (filled symbols) parts of the dielectric functions in cells of untreated G1U and G1N as well as G1U treated with various agents. Inset, deduced ion-removal ratios in various LC samples.

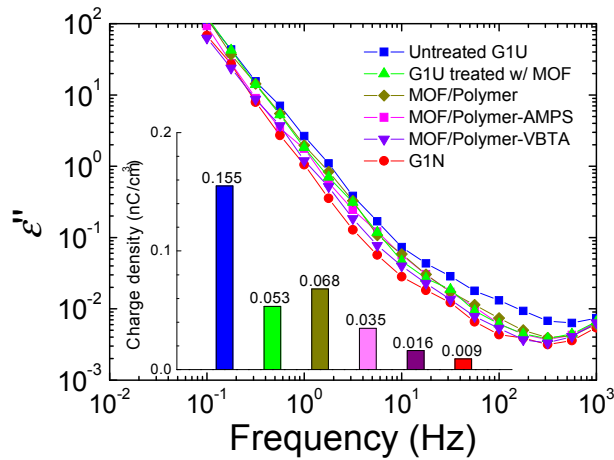


Fig. 5. Imaginary parts of the dielectric constants of an untreated G1U, various treated G1U cells and a G1N counterpart for comparison. Inset, deduced charge densities in various LC samples.

It is worth reminding that the amount of MOF in MOF/polymer-AMPS is only one-third amount of pure MOF; yet the reduced ion densities are almost equal. We infer that the moisture is the leading impurity in the deteriorated LC.

To clarify whether the electronegativity of AMPS contributes to the reduction in charge density in treated GIU via trapping impurity ions (precisely, metal cations), a comparative monomer with a tendency to become electropositive; i.e., VBTA, was employed to replace AMPS. We measured the dielectric data of all treated GIU samples (separately with MIL-101(Cr), MIL-101(Cr)/polymer, MIL-101(Cr)/polymer-AMPS, and MIL-101(Cr)/polymer-VBTA) and of untreated GIU and a G1N counterpart. The dielectric spectra and the deduced charge densities are plotted in Fig. 5. Among these four treated GIU samples, the one treated with MIL-101(Cr)/polymer has the highest ion density. Noticeably, when a trace amount of AMPS or VBTA is copolymerized into the MIL-101(Cr)/polymer composite, the corresponding treated GIU cell exhibits a considerable reduction in charge density. These data also confirm that the electronegative tendency of AMPS in the MIL-101(Cr)/polymer-AMPS composite does not account for the dramatic ion removal from GIU. It is clear from the Fig. 5 that the one-third amount of MIL-101(Cr) in the MIL-101(Cr)/polymer-AMPS composites with hydrophilic groups produces superior results in comparison with that of the pure MOF absorbent. Since the ion impurities in deteriorated LCs come principally from dissociated ions of moistures, the nanoporous MIL-101(Cr) as the desiccant soaked in LCs has been suggested to hold great promise for absorbing these ions owing to its proven, exceptional water absorption capacity [3]. Based on the observations, we speculate that AMPS (VBTA) with the sulfonic acid (quaternary ammonium) group would assist MOF to absorb the hydrogen cations and hydroxyl anions dissociated from water molecules in moisture-contaminated GIU. As a result, the overall ion absorption efficacy of MOF/polymer-AMPS or MOF/polymer-VBTA becomes more effective and we infer that the probability of capturing impurity ions by the trapping centers within the cage of MOF increases due to the surrounding hydrophilic network in the copolymer. Because of the addition of AMPS or VBTA, the amount of MOF can be reduced to achieve the same purification level.

The model of the mentioned mechanism is schematically shown in Fig. 6. It illustrates the transport of water molecules in LCs treated with MOF and, in comparison, a MOF composite. When MOF is immersed in a LC, the water molecules traveling in the LC have a probability to be trapped by the cage of the MOF unit cell. Once the hydrophilic group (AMPS or VBTA) exists in the polymer networks, the MOF composite has greater intermolecular attraction for water molecules and, in turn, higher ability to trap moistures compared with the pure MOF.

As mentioned above, the main ion impurities in a deteriorated LC from the panel production line is the moistures and limited content of metal ions. In order to analyze the concentration of metal ions in a degraded LC, ICP-MS (with a Perkin Elmer SCIEX ELAN 5000 spectrometer) was performed. The elements, Mg, Si, Ca and Zn, were specifically monitored because of their relative abundances in the dust particles suspended in atmosphere. These trace elements often found in LCs originate actually from dirt in the earth crust. The additional element Cr was also measured in that Cr may be released from MIL-101(Cr) in the purification processes [3]. Figure 7 shows the element concentrations in ppb of G1N, GIU and GIU treated separately with MOF, MOF/polymer-AMPS and MOF/polymer-VBTA. Since there is no trace of Cr found in the treated LCs, the MOF composites are robust and stable. However, the best overall removal of metal elements (and Si) is found in the MOF-treated sample, much better than that of LC treated with MOF/polymer-AMPS or MOF/polymer-VBTA. Since metal elements are mainly trapped and, hence, removed by nanoporous MOF, the existence of hydrophilic groups in the copolymer matrix does not seem to have an effect on capturing the metal ions.

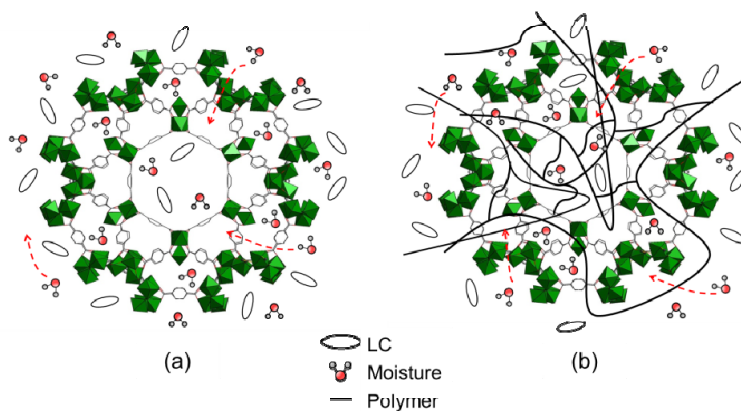


Fig. 6. Movement and interception of water molecules in LC impregnated with (a) MOF and with (b) MOF/polymer-AMPS or MOF/polymer-VBTA composite.

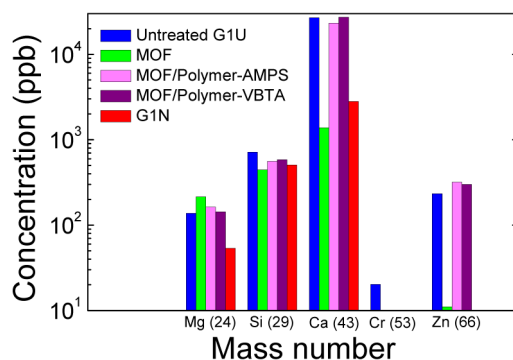


Fig. 7. Comparison of the primary elements in the G1N, G1U and G1U treated with 0.5 wt% of MOF, AMPS-Polymer/MOF/polymer-AMPS and MOF/polymer-VBTA for 24 h.

**Table 1. Ion-Removal Ratios in Cells of GIU Treated with MOF/polymer-AMPS of Various AMPS Contents**

Sample	Ion-removal ratio (%)
G1N	99.7
G1U treated with MOF/polymer-AMPS(0.5 mg)	99.4
G1U treated with MOF/polymer-AMPS(1.0 mg)	98.5
G1U treated with MOF/polymer-AMPS(2.0 mg)	94.7
G1U	0

In addition to the charge density discussed in the preceding paragraphs, the ion-removal ratio was further calculated [21]. Table 1 displays the ion-removal ratios of some specific samples. Compared with the untreated G1U, the charges of each treated G1U sample is significantly removed and adding 0.5 mg of AMPS to the MOF/polymer seems to give an optimized formula for the best ion removal. Alternatively, the similar result is also obtained for VBTA with 1.0 mg to be the preferred additive amount. Briefly, the effect of the hydrophilic groups in MOF composites is clearly manifested by the higher ion-removal ratios for regeneration of degraded LCs.

#### 4. Concluding remarks

MOF materials, known for their superior nanoporous structure, have been confirmed as potential agents for recovering the electrical properties of degraded LCs. After performing together with monomers for microwave-assisted polymerization, the efficacy of various MIL-



101(Cr) composites on the removal of ion impurities and, in turn, the regeneration of degraded LCs have been demonstrated in accordance with the dielectric data and results of ICP-MS. Experimental evidence indicates that the MIL-101(Cr) dispersed in polymer-AMPS (or -VBTA) networks still preserves its inherent features, such as high crystallinity, porous structure, and water-sorption efficacy. Additionally, due to the presence of AMPS or VBTA in the MOF composites to increase the degree of hydrophilicity, the efficiency of adsorption of the primary impurity; i.e., moisture, is greatly enhanced. As a consequence, the overall purifying efficacies of MOF/polymer-AMPS and MOF/polymer-VBTA for deteriorated LCs are more impressive than that of the pure MOF. Exploiting MOF incorporating copolymers, the amount of MOF used in the purification processes can be reduced to one-third while keeping the same efficacy. It is worth mentioning that the polymer and MIL-101(Cr) substances are quite stable up to 300 °C. Integrated with AMPS or VBTA as hybrids, the MOF-composites are proven to be robust and intact in the heating and stirring processes for LC purification. Practically speaking, the used MOF-composites can be easily regenerated by heating to remove excess water absorbed, meaning that they are desirably recyclable and reusable for purification of LC materials. The true lifetimes of these composites are not known at this moment but anticipated to be very long. This study provides LCD manufacturers new consideration for effective recycling and recovering contaminated LCs so as to reduce the cost and resolve environmental issues caused by the abandonment of waste materials.

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