ACS APPLIED MATERIALS & INTERFACES

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Receptor-Free Poly(phenylenevinylene) Fibrous Membranes for Cation Sensing: High Sensitivity and Good Selectivity Achieved by Choosing the Appropriate Polymer Matrix

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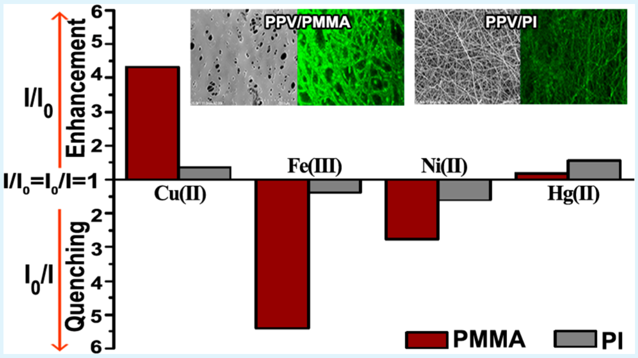
Ⓢ *Supporting Information*

ABSTRACT: Poly(phenylenevinylene)/polyimide (PPV/PI) and poly(phenylenevinylene)/ polymethylmethacrylate (PPV/PMMA) fibrous membranes without any deliberately introduced receptors were prepared as fluorescence sensing materials through electrospinning, followed by thermal treatment. Both of these membranes displayed higher sensitivity toward most cations compared to the corresponding spin-coated films. PPV/PMMA membranes were more sensitive than PPV/PI membranes toward Cu^{2+} and Fe^{3+}. About 4.5 fold of intensity enhancement upon 20 nM of Cu^{2+}, 80% of quenching upon 20 nM of Fe^{3+} with fast response and simple regeneration were realized for PPV/PMMA membrane. The preliminary investigation into the mechanism revealed that the properties of the polymer matrix and thermal treatment of the membrane played important roles in the sensing performance.



KEYWORDS: *poly(phenylenevinylene), electrospinning, receptor-free, fluorescence, sensing*

1. INTRODUCTION

There is a growing need for the real-time detection of metal cations in biological or environmental systems because of the ever-increasing healthcare issues and environmental concerns. Fluorescence-based analysis for cations has many advantages over other methods such as ease of measurement, fast response, and low-cost in determining the presence of trace metal cations.[1−3] Conjugated polymers have been widely used as fluorescent sensing material because of its distinctive molecular-wire-effect enhanced sensitivity, as well as the structural modifiability according to the application requirements and the processability.[4−6] Tremendous solution-based sensory systems have been developed for various applications.[4−11] Recently, considerable efforts have been devoted to employ solid fluorescent materials as the key sensing element because of the great demanding of portable and reusable sensory devices.[12−20] Such portability is very necessary for the "on-site" field detection as well as the reusability for the reduction of resource wastage, which rarely can be realized in solution-based systems. The nano/microfibrous membrane produced by electrospinning may bring higher sensitivity relative to conventional films because of the higher surface-to-volume ratio.[18−20]

Fluorescence sensing is usually completed according to the following sequence of events: recognition of analytes, transduction of the recognition event to a directly observable phenomenon, or readable/reportable data and finally the readout.[1−3] The function of receptor is to interact with the analytes, bring them close to the fluorophore and make energy or electron transfer between the analytes and fluorophore possible. Thus introduction of receptor onto the conjugated polymers for the recognition step is indispensable in most systems, which usually requires many synthetic efforts. Many nanofibrous sensing materials have been fabricated and they always have receptors, or sometimes part of the fluorophore molecule itself can interact with the analytes.[18−20] In addition, most of such materials were used for gas sensing. Different from the literature, we proposed a strategy for preparation of receptor-free sensing material, shown in Figure 1, which was developed on the basis of our experience in conjugated polymers[6−9,21−23] and electrospinning technique.[24−26] Poly(*p*-phenylenevinylene) (PPV), without any apparent interaction site with cations, was incorporated into polymer fibers with polyimide (PI) or polymethylmethacrylate (PMMA) matrix, as our first proof-of-concept attempts of this receptor-free strategy. The initial consideration for preparing PPV/PI membrane is to take advantage of the high adsorbability of fibers, which may hold the cations within the fluorophore's "sphere of action".[27] Additionally, PI has been demonstrated to be a good supporting matrix for certain functional nano/microfibrous

Received: February 7, 2013
Accepted: May 6, 2013
Published: May 6, 2013

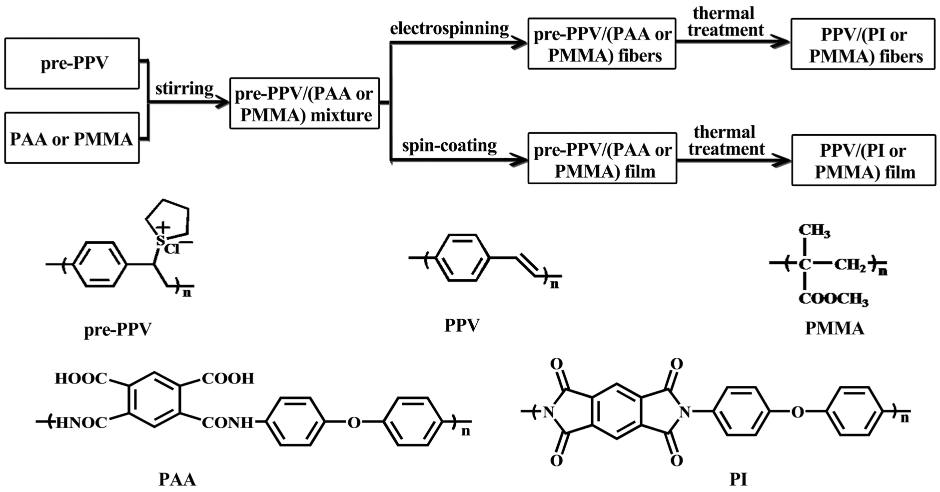


Figure 1. Schematic diagram for preparation of PPV/PI and PPV/PMMA fibers and films. The reaction schemes are shown in the Supporting Information. The thermal treatment was carried out at 120 °C in vacuum for 1 h.

membranes.[24,25] PPV/PMMA fibers were prepared for comparison since PMMA is well-known for its optically transparency and photophysical inertness. Surprisingly, among the two PPV membranes, the PPV/PMMA fibrous membrane was found to have higher selectivity and sensitivity toward Cu^{2+} and Fe^{3+} cations, with opposite effect on the emission intensity. Here we present our detailed study on the sensing performance of this receptor-free PPV/PMMA material and preliminary investigation into the origin of these interesting findings.

2. RESULTS AND DISCUSSION

2.1. Preparation. The schematic illustration of material preparation is shown in the Figure 1. Based on the consideration of the limited solubility of PI or PPV in most solvent under ambient temperature may pose some challenge for direct processing, PAA and pre-PPV (the precursors for PI and PPV) synthesized according to the literatures,[22,24] were used for electrospinning or spin-coating. PI and PPV formed after the thermal treatment. PMMA was directly used for electrospining or spin-coating because of its good processability. All the experimental parameters were selected after optimization, based on the comprehensive consideration on the easiness for processing, apparent uniformity, and mechanical performance as well as photophysical properties of the resulting materials. The specific experimental details and related discussions are presented in the Supporting Information.

2.2. Cation Sensing. The excitation and emission spectra of the two PPV membranes are shown in Figure S1 in the Supporting Information. The cation-responsive properties of the PPV fibrous membranes and films were investigated by different cations in aqueous solution. The experiments were performed according to the following procedure, mimicking the "on-site" field detection. The membrane or film on the quartz slide was fit into a cuvette and ultrapure water was added into the cuvette. The fluorescence emission was recorded as the starting point of the cation sensing measurements. After removing the water by pipet, the cation solution was added and the emission was recorded. The whole process should be carried out very carefully to avoid the shifting in the position of the membrane or film, since small nonuniformity inherently exists for solid materials. Figure 2 shows the fluorescence intensity changes of the membranes or films, upon 20 nM of Cu^{2+}, Fe^{3+}, Ni^{2+}, and Hg^{2+} cations in aqueous solution. All the intensity changes in Figure 2 were average values from 3 measurements for the same cations with materials produced from different batches. All the emission were recorded 3 min after the membranes or films were immersed in the solution to ensure the adsorption or diffusion of cations are equilibrated and thus all the data are comparable, though it seemed that the equilibrium was reached right after the immersion for the fibrous membranes. The original emission spectra are shown in Figures S2 and S3 in the Supporting Information.

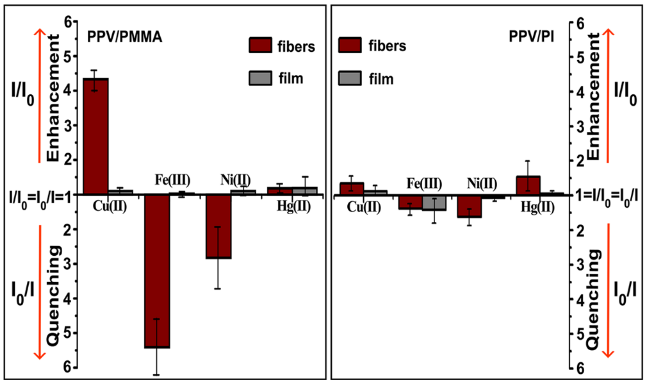


Figure 2. Fluorescence intensity change at the emission maximum for PPV/PMMA (left) and PPV/PI (right) fibrous membranes and films upon various 20 nM of cations in aqueous solution relative to the same material in pure water, at room temperature. The error bars show the data deviations from the average value.

As expected, the films displayed very small emission changing upon the cations tested. The highest enhancement is less than 1.2 fold and the quenching is less that 25% of the initial intensity. However, the fibrous membranes, displayed very different response toward these cations. PPV/PMMA was found to have higher sensitivity toward Cu^{2+} and Fe^{3+} than PPV/PI in the form of membrane, though such differences were not apparent in the form of film. About 4.5 fold of intensity enhancement at the emission maximum of PPV/PMMA fibrous membrane was found upon addition 20 nM of Cu^{2+}, and 80% of quenching upon addition of 20 nM of Fe^{3+}. In addition, 36% of quenching upon 20 nM of Ni^{2+} was also found for PPV/PMMA membrane. In the case of PPV/PI membrane, only about 1.35 fold enhancement for Cu^{2+}, and 28 and 35% quenching for Fe^{3+} and Ni^{2+} were obtained. No significant shifting in the wavelength and change in the profile of the spectra were observed, indicating no new emission species produced.

For comparison, PPV with the same chemical structure were dissolved in THF and the similar cation sensing were carried out. Negligible emission change was found for PPV/THF solution upon cations confirmed no direct interaction between PPV and cations (see Figure S4 in the Supporting Information). However, higher sensitivity and better selectivity for some cations achieved by the fibrous membranes relative to the films with the same composition, as discussed above, suggesting the "receptor-free" strategy worked well. Even without the presence of any receptor, the high adsorbability of the fibrous structure is able to catch the analytes and hold them tightly enough to influence the emission of the PPV fluorophore greatly. In addition, PPV/PMMA membrane was more selective and sensitive toward Cu^{2+} and Fe^{3+}, compared to PPV/PI membrane, indicating the polymer matrix plays a very important role for the cation sensing, which will be discussed later.

To further investigate the sensing performance of PPV/PMMA membrane, we recorded the continuous responses of PPV/PMMA membrane toward Cu^{2+} and Fe^{3+}, respectively, with increased concentration. The spectra and the trend of intensity changes are shown in Figure 3. Interestingly, Cu^{2+} displayed a significant fluorescence enhancement effect, which is very different from most reported fluorescence sensing systems, where Cu^{2+} usually showed a quenching behavior.[4,8,14,28−30] With only 1 nM of Cu^{2+}, the intensity was enhanced by 2-fold and enhancement almost reached equilibrium for about 4-fold upon 20 nM of cation. Interestingly, Fe^{3+} showed an opposite influence on emission. With addition of 1 nM of Fe^{3+}, the fluorescence was quenched for more than 20%. The fluorescence keep decreasing by increasing the concentration of Fe^{3+}, and about 80% were quenched by addition of 20 nM of cations. Thus, PPV/PMMA fibrous membrane not only had opposite response toward Cu^{2+} and Fe^{3+} but also displayed very high sensitivity. The sensitivity achieved here is far beyond that in the literature reports about conjugated polymer film sensors for Cu^{2+} or Fe^{3+}, which detected cations on the micromolar (μM) level with the similar value of the intensity change.[13,14]

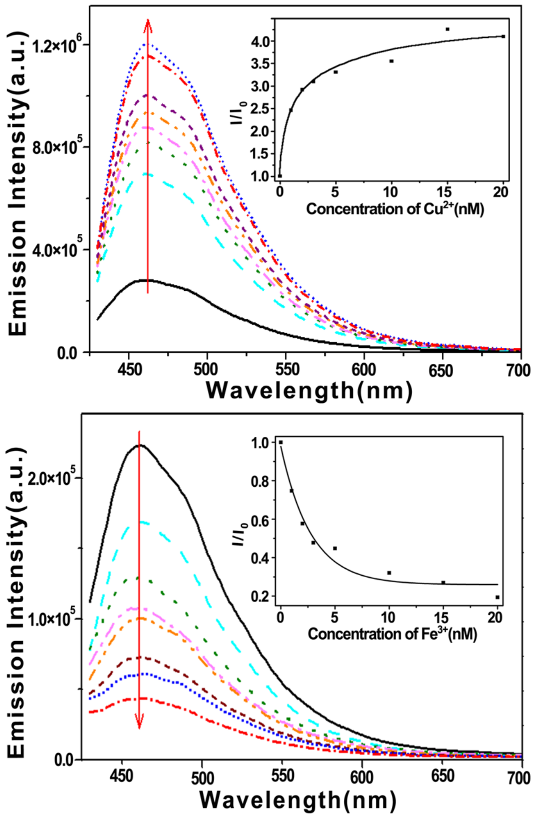


Figure 3. Fluorescence spectra of PPV/PMMA in different concentration of Cu^{2+} (top) and Fe^{3+} (bottom) aqueous solution. The excitation was set at 410 nm. The insets show the relationship between the intensity changing (I/I_0) and cation concentration.

2.3. Reversibility Study. The reusability of material is very important for incorporating them into a sensing device or directly using them as a reusable test strip, which requires that the sensing behavior should be reversible. The reversibility study of sensing Cu^{2+} and Fe^{3+} (20 nM) was carried out for PPV/PMMA membrane. As shown in Figure 4, reversibility for both Cu^{2+} enhancement and Fe^{3+} quenching were realized, though both enhancement and quenching decreased a little after the first two cycles. The variances in the enhancing factor or quenching efficiency could be partly attributed to the inherent nonuniformity of the solid materials as well as possible small degree of photobleaching. Nevertheless, even after 6 cycles, the enhancing factor for Cu^{2+} and quenching efficiency for Fe^{3+} were still relatively high. The imperfectness in the reversibility may require further improvement for the real-life application. However, some applications only require an "on—off" response. In those cases, if the threshold value falls in the range of the intensity change maintained after many cycles, the materials are still promising for those applications. The PPV/PMMA membrane has very fast response toward external aqueous environment. Each time the emission intensity was measured right after the liquid (cation solution or pure water) inside cuvette was changed. It is worth mentioning that the regeneration of the material can be simply realized by immersing it in the pure water. This further suggests our receptor-free strategy is very advantageous over other sensing systems, where certain specific compounds are usually required to wash the analytes off the sensing materials.

2.4. Preliminary Investigation into the Mechanism. It is very interesting that PPV/PMMA displayed better sensitivity and selectivity compared to PPV/PI in the fibrous membrane form, while the corresponding films did not exhibit such obvious difference as shown in Figure 2 and Figure S3 in the Supporting Information. According to the chemical structure, neither PMMA nor PI has any receptor or apparent active site to direct interaction with cations. Thus the difference in the chemical structure between PMMA and PI, cannot be the main reason for the great difference in sensing performance observed from the membrane. Based on the initial consideration using the adsorbability of the materials to catch the cations, The surface morphology study of the membranes was carried out, as shown in Figure 5. PPV/PI membrane displayed a yellowish color, whereas PPV/PMMA is transparent (top), which are consistent with the macroscopic appearance of the matrix. SEM images (middle) shows that well-defined fibrous structure with diameter around 300 nm, was maintained in PPV/PI membrane while the fibrous structure of PPV/PMMA was more complicated than that of PPV/PI. Some secondary structure appeared for PPV/PMMA. The fibers became very

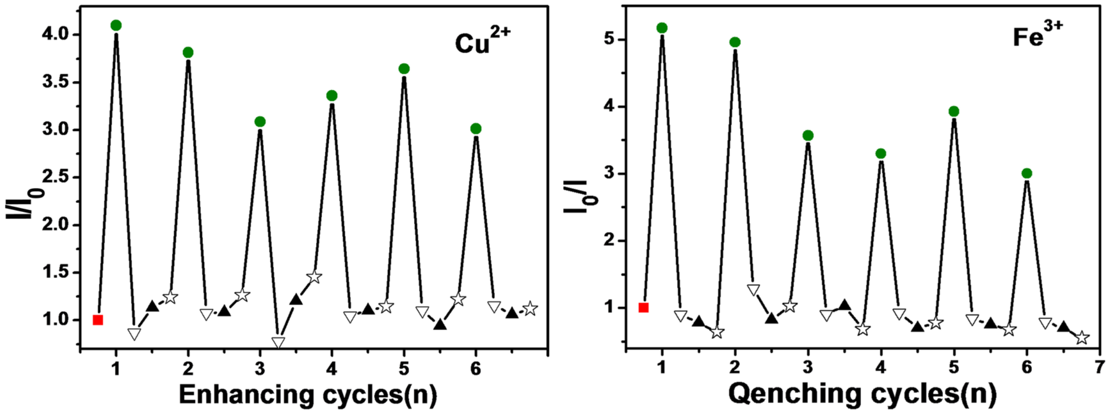


Figure 4. Reversibility study of the PPV/PMMA fibrous membrane for sensing 20 nM of Cu^{2+} and Fe^{3+}. The excitation was set at 410 nm. Orange square represents the original intensity change ($I/I_0 = I_0/I = 1$) when PPV/PMMA in H_2O and green circle represents the intensity changes (I/I_0 for enhancement and I_0/I for quenching) upon adding Cu^{2+} or Fe^{3+} aqueous solution, and ▽, ▲, ☆ represent the first, second, and third time replacing the previous liquid inside the cuvette with ultrapure water, respectively.

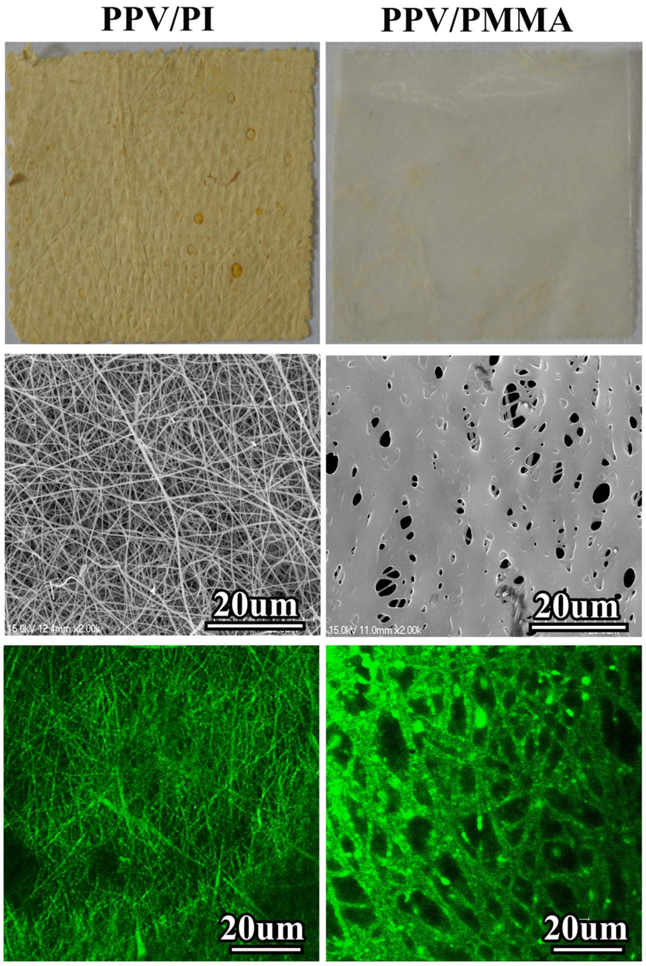


Figure 5. Digital camera pictures (top), SEM images (middle), and confocal fluorescence microscopy images (bottom) for PPV/PI (left column) and PPV/PMMA (right column) fibrous membranes.

large at the surface. Pores with various sizes dispersed among the fibers. It can also be observed that many fibers with much smaller diameter exist underneath the pores while the further inner structure is not very clear. The confocal fluorescence images (bottom) are basically consistent with the SEM images, except the relatively lower resolution. In addition, the inherent unobservability of the polymer matrix may also partly account for the small difference between the two types of images. Therefore, a provisional conclusion can be reached at this point that the secondary structure of PPV/PMMA may account greatly, if not solely, for the outstanding sensing behavior of PPV/PMMA. This finding actually is consistent with literature reports using electrospun fibers for sensing application, where the secondary or porous structures on the fibers were introduced deliberately to enhance the sensitivity using surfactant or porogen.[18−20]

It is very important to understand the reason for the formation of such distinctive structure in PPV/PMMA membrane. More digital photographs, SEM and fluorescent images are shown in Figures S5−S7 in the Supporting Information. Before thermal treatment, pre-PPV/PMMA has very clear fibrous structure, very similar to that of pre-PPV/PAA, except the slightly larger fiber diameter. After thermal treatment, PPV/PI has almost the same structure as pre-PPV/PAA but with stronger emission. However, the morphology of PPV/PMMA is quite different from that of pre-PPV/PMMA. Considering the glass transition temperature (T_g) of PMMA is around 110 °C, chain movement and reorganization must take place during the thermal treatment at 120 °C, which resulted in the merging of the fibers. Thus the structural change was very apparent for pure PMMA, as shown in Figure S6 in the Supporting Information. Interestingly, the fibrous structure was maintained to a small degree in the case of PPV/PMMA. The presence of pre-PPV in the PMMA matrix and its transformation into PPV somehow retarded the chain reorganization of PMMA, which account for the formation of the relatively complicated morphology. Such thermal induced morphology change did not happen during the transformation of pre-PPV/PAA into PPV/PI, since this temperature (120 °C) made the imidization of PAA possible but too low to induce chain rearrangement of PI with a T_g around 300 °C.

There were some literatures about similar PPV/PMMA blends or fibrous systems,[31−33] whereas most of them were used as light emitting materials and none of them was studied for sensing application without the presence of receptors, to the best of our knowledge. The nonuniform secondary structure, formed during the thermal treatment in the PPV/PMMA fibrous membrane, seems to act as the receptor for recognizing the cations. To further confirm that the morphology is the dominating factor for the sensing performance, investigation into the influence from the temperature of thermal treatment was carried out with the same pre-PPV/PMMA membrane. A series of new PPV/PMMA fibrous membranes were prepared with post treatment at 80, 100, 110, 130, and 140 °C. The morphologies of these membrane and their sensing behaviors toward Cu^{2+} and Fe^{3+} are shown in Figures S8 and S9 in the Supporting Information. Related the morphology to the sensing performance, it is very obvious that PPV membranes with more regular and uniform fibrous structure has smaller sensitivity, even with the same PMMA matrix (detail discussed in the Supporting Information). This result is consistent with our previous arguments. Compared to the well-defined fibrous structure, secondary structures resulted from the thermal treatment, offers large surface area which may account for the higher sensitivity. The appearance of secondary structure may also change the physical interaction or shape/size match between the membrane and the analytes, which may bring the selectivity for sensing application. In addition, as a minor constituent of the polymer alloy, the conformation, aggregation state and other properties of PPV may, also be affected by thermal treatment, though no significant influence was found, at least in the emission spectra. More in-depth investigation into the role of polymer matrix, such as using polymer with different T_g, coupled with the systematic study for the influence from the thermal treatment on the membrane structure and the sensing properties, are currently ongoing in our lab.

3. CONCLUSION

Two types of PPV fibrous membranes, PPV/PI and PPV/PMMA, for cation sensing were prepared, through electrospinning the PPV polymer precursor in PI precursor or PMMA polymer matrix, followed by the thermal treatment. PPV/PMMA displayed much better sensing properties toward cations than PPV/PI. The high sensitivity, fast response, good reversibility and simple regeneration realized for PPV/PMMA membrane, are consistent with the initial design concept for the "receptor-free" fluorescence sensing materials having large surface-to-volume ratio. In addition, this material displayed high selectivity toward Cu^{2+} and Fe^{3+} with opposite responses. All these outstanding characteristics possessed by PPV/PMMA membrane, combined with the facile fabrication make it a promising sensing material for practical application. Taking account of the fact that neither PI nor PMMA has apparent interacting site with cations, and comparing with the corresponding spin-coated films, ruled out the possibility that different sensing behaviors between PPV/PMMA and PPV/PI were mainly due to the different chemical structure. Morphology study revealed the reason for PPV/PMMA surpassing PPV/PI in the sensing performance is very likely due to the more complicated surface and internal structure owned by PPV/PMMA membrane after thermal treatment. The formation of such different structures can be attributed to the different physical properties of PMMA and PI (or PAA). Therefore, the properties of polymer matrix, as well as the post-treatment, were very crucial for the sensing performance in the case of using a receptor-free conjugated polymer as the fluorophore. This finding may provide a new direction for preparing solid fluorescent sensing materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedure, reaction schemes, optimization of the experimental conditions, additional fluorescence spectra, photographs and images, as well as some related discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (20974075, 21174099) and A Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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