DOI: 10.1002/anie.201402141

Polymer Films

Controlled Synthesis of Conjugated Microporous Polymer Films: Versatile Platforms for Highly Sensitive and Label-Free Chemo- and Biosensing**

*Cheng Gu, Ning Huang, Jia Gao, Fei Xu, Yanhong Xu, and Donglin Jiang**

Abstract: *Conjugated microporous polymers (CMPs), in which rigid building blocks form robust networks, are usually synthesized as insoluble and unprocessable powders. We developed a methodology using electropolymerization for the synthesis of thin CMP films. The thickness of these films is synthetically controllable, ranging from nanometers to micrometers, and they are obtained on substrates or as freestanding films. The CMP films combine a number of striking physical properties, including high porosity, extended π conjugation, facilitated exciton delocalization, and high-rate electron transfer. We explored the CMP films as versatile platforms for highly sensitive and label-free chemo- and biosensing of electron-rich and electron-poor arenes, metal ions, dopamine, and hypochloroic acid, featuring rapid response, excellent selectivity, and robust reusability.*

Conjugated microporous polymers (CMPs) are a class of organic porous polymers that inherently combine π-conjugated skeletons with permanent nanopores, in sharp contrast to other porous materials that are not π-conjugated and conventional conjugated polymers that are nonporous.[1–3] As an emerging materials platform, CMPs feature a high flexibility in molecular design of conjugated skeletons and nanopores. Because of high surface areas and the microporous character, CMPs have emerged as a new class of porous materials for gas adsorption and storage.[1–3] The pores are accessible to various guest molecules and metal ions, which allow the construction of supramolecular structures and organic–inorganic hybrids.[1–3] Significantly, CMPs allow the complementary utilization of π conjugation and porosity to explore novel functions and have shown their high potential in the challenging of energy and environmental issues, as exemplified by their excellent performances in superabsorption,[3h] light emitting,[1,3e,g] chemosensing,[3f] light harvesting,[3a] catalysis,[1,2,3b,c] and electric energy storage.[3d,k]

However, CMPs are usually obtained as powders, they are insoluble in any solvents, and it is difficult to obtain thin films of them.[1–4] A few approaches, including surface-initiated growing,[4a] layer-by-layer crosslinking,[4b] and hyperbranched structuring,[4c] have been reported to fabricate CMP films. However, these methods are tedious with regard to synthesis and structural control; the films thus prepared are nonporous. The development of a methodology for the synthesis of thin films with retained π conjugation and porosity is highly desired for the further advancement, but remains a substantial challenge.[1a] The difficulty to process CMPs hampers their applications in organic electronics; processability and device integration are highlighted as bottleneck issues of "paramount importance" in recent reviews of the CMP field.[1a,3a] Herein, we report an electrochemical approach to the synthesis of CMP films. Our CMP films combine intriguing physical properties, including extended π conjugation, facilitated exciton delocalization, and high porosity. We highlight that this methodology allows the control of thickness, size, and shape of the films, and affords freestanding thin films. To demonstrate the utility, we prepared photoactive CMP films, which are luminescent and exhibit fluorescence on/off chemo- and biosensing with rapid response, sensitivity, selectivity, and reusability.

We fabricated our CMP films using electropolymerization with concurrent polymer film deposition (Supporting Information), which has been proven to be an especially useful method for the preparation of electroactive and conducting polymer films.[5] Generally, in this method, the precursors are oxidized electrochemically and the coupling reaction between the precursors occurs at the electrode surface with deposition of the crosslinked polymer network film onto the electrode. We synthesized the CMP precursor TPBCz, which bears a 1,3,5-triphenylbenzene focal core with three N-substituted carbazole groups at the periphery (Scheme 1 a). The N-substituted carbazole is well established as a highly electroactive compound, which has a relatively low oxidative potential. It enables the effective coupling reaction between its oxidative species (radical carbazyl cation) and produces only dimers.[5] These unique characteristics allow the precise control of the structure and properties of resulting CMP films. TPBCz with its triangular, twisted, and rigid focal structure was designed to bear three N-substituted carbazole groups linked in a C_3 geometry, which upon electrochemical reaction guarantee the growth of thin films with a three-dimensional conjugated network, high porosity, and uniform pore distribution.[6]

The TPBCz-CMP films were fabricated by multicycle cyclic voltammetry (CV) of TPBCz (1.25×10^{-3} M) in a mixture

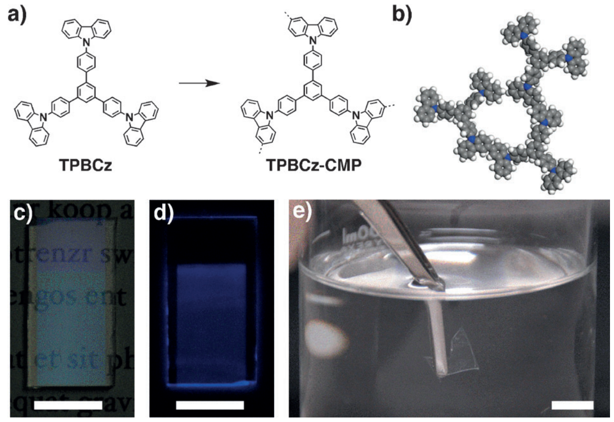
---

[*] Dr. C. Gu,[+] N. Huang,[+] J. Gao, F. Xu, Dr. Y. Xu, Prof. Dr. D. Jiang
Department of Materials Molecular Science, Institute for Molecular Science, National Institutes of Natural Sciences
5-1 Higashiyama, Myodaiji, Okazaki 444-8787 (Japan)
E-mail: jiang@ims.ac.jp
Homepage: //groups.ims.ac.jp/organization/jiang_g/Welcome.html

[+] These authors contributed equally to this work.

[**] This work was supported by a Grant-in-Aid for Scientific Research (A) from MEXT (Japan; 24245030).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201402141.



Scheme 1. a) Schematic representation of the electrochemical synthesis of TPBCz-CMP films. b) Elementary pore of the film. Photos of c) a film on an ITO substrate (0.5×1.5 cm^2), d) the film under UV light, and e) a 100 nm thick freestanding film (0.5×1 cm^2) in acetonitrile. Scale bars: 0.5 cm.

of acetonitrile and water (3/2 *v*/*v*) containing $LiClO_4$ as electrolyte in a potential range from −0.8 to 0.7 V at room temperature (Supporting Information). In the first cycle of the positive CV scan, the onset oxidative potential of TPBCz appeared at 0.64 V, which was attributed to the oxidation of carbazole (Figure 1 a).[5] At a scan potential of higher than 0.64 V, the anode current increased rapidly, indicating more carbazoles were oxidized. Previous studies have shown that upon oxidation, N-substituted carbazole transforms into the cationic radical, which effectively couples with another cationic radical to form a dimeric carbazole cation.[5,7] During the negative scan, an obvious reductive peak was observed at a potential of 0.63 V, which can be assigned to the reduction of dimeric carbazole cations. In the second cycle of a continuous CV scan (shown in Figure 1 b), a new oxidative band appears at 0.60 V, which is due to the oxidation of dimeric carbazoles on the electrode.[5,7] A distinct feature is that the current increases with the number of cycles, thus demonstrating the gradual growth of the TPBCz-CMP film on the electrode (Figure 1 b). After ten CV cycles, the CMP films are transparent and exhibit a light-blue color (Scheme 1 c). The high reactivity and efficient coupling reaction of carbazoles are key to the synthesis of structurally well-defined CMP films, which are further studied by the following experimental investigations. First, the electronic absorption and infrared spectral analysis showed that the films are free of monomeric carbazole units (Figures S1 and S2 in the Supporting Information). Second, the films are insoluble in organic solvents irrespective of polarity, which clearly reflects their highly crosslinked structure, in contrast to TPBCz, which is highly soluble in organic solvents such as acetonitrile (>50 mg mL^{-1}).

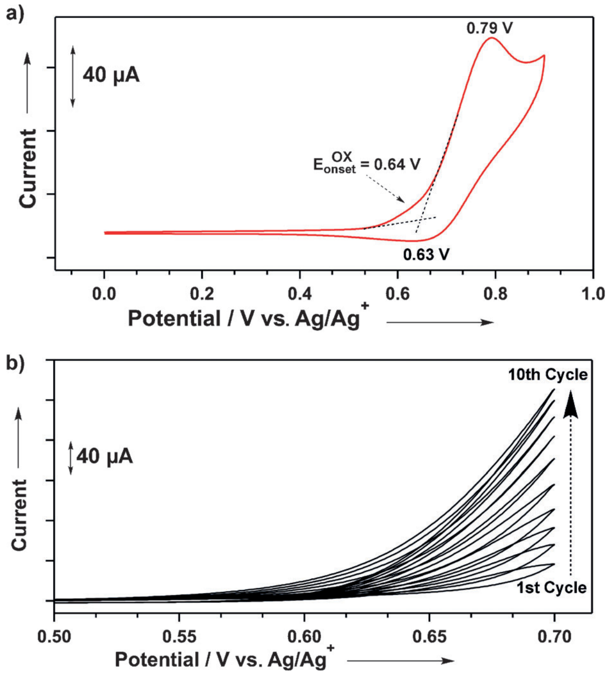


Figure 1. CV profiles of a) the 1st cycle and b) the 1st to 10th cycle of a solution of TPBCz in acetonitrile/water (3/2 *v*/*v*) in the presence of $LiClO_4$ as electrolyte at 25 °C.

The thickness of CMP films can be precisely controlled by the numbers of scan cycles, with each cycle producing approximately 2.5 nm of film thickness using an oxidative potential of 0.7 V (Figure S3). By employing this technique, we prepared a series of films with thicknesses ranging from several nanometers to several micrometers. When the thickness became larger than 50 nm, the films could automatically peel off the electrode to give freestanding CMP films (Scheme 1 e). The freestanding films only grew on the electrode and were of the same size and shape as the employed electrodes; in our studies, films with a size of up to 0.5×1.5 cm^2 were produced. The present method produces high quality films either on electrodes or in a freestanding form, with synthetically controlled thickness, size, and shape. We conducted Kr sorption isotherm measurements and found that these CMP films are highly porous and have a Brunauer-Emmett-Teller surface area of as high as 1450 m^2 g^{-1} (Figure S4 a). The thickness of the CMP films used for Kr sorption measurements was about 1 μm, which corresponds to a mass of 120 μg (two films on ITO (indium tin oxide)). We measured the Kr sorption curves for four lots of samples to assure the reproducibility. On the other hand, the BET surface area of a bulk CMP sample prepared through oxidation polymerization in solution was much lower with only 135 m^2 g^{-1} (Figure S4 b). High-resolution transmission electron microscopy supports the porous texture of the films (Figure S5).

A spin-coated film of TPBCz monomers exhibited an absorption band at 338 nm, assignable to the $\pi\rightarrow\pi^*$ transition of the triphenylbenzene focal unit, and a band at 288 nm, assignable to the $\pi\rightarrow\pi^*$ transition of the N-substituted carbazole group (Figure S1). In the TPBCz-CMP films, the dimeric carbazole unit displayed an absorption band at 300 nm, which is 12 nm red-shifted compared to the spin-coated TPBCz film, and features a greatly enhanced absorption coefficiency. In this case, the band resulting from the focal triphenylbenzene unit was superimposed by the broad band resulting from the carbazole dimers. These results indicate an extended π conjugation in the CMP films. Upon excitation at 340 nm, the CMP film emitted a deep-blue luminescence (Scheme 1 d) with two peaks at 374 and 399 nm, respectively (Figure S6). The absolute fluorescence quantum yield is 10 %. In contrast, the spin-coated TPBCz film gave a fluorescence spectrum similar to that of the CMP film, but its fluorescence quantum yield is only 1 %. The network structure in the CMP film greatly enhances the light-emitting activity.[3e] Since the CMP film allows an extended π conjugation, we further investigated the fluorescence depolarization profiles of the CMP films, which are considered to reflect the occurrence of photochemical events in the microporous network. The suppression of Brownian motion in a viscous medium should result in fluorescence depolarization occurring predominantly by exciton migration along the conjugated chain. The TPBCz monomer showed a fluorescence depolarization value of 0.044 in poly(ethylene glycol) (Figure S7). In contrast, the CMP film exhibited a significantly depolarized fluorescence with an extremely low depolarization value of 0.002. This observation demonstrates that the CMP film facilitates exciton migration over the network, which endows the film with a collective response, a key factor to enhance the sensitivity.

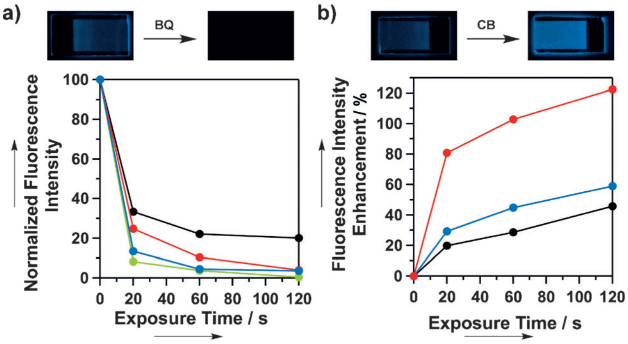


Figure 2. a) Normalized fluorescence intensity of the CMP films upon exposure to vapors of benzonitrile (BN, black line), 1,2-dinitrobenzene (DNB, red line), hexafluorobenzene (HFB, blue line), and 1,4-benzoquinone (BQ, green line) for different periods of time. Photos: fluorescence quenching by BQ vapor. b) Enhancement of fluorescence intensity of the CMP films upon exposure to vapors of toluene (black line), benzene (blue line), and cholorobenzene (CB, red line) for different periods of time. Photos: enhancement of fluorescence intensity upon exposure to CB vapor.

Chemosensing experiments were conducted by exposing CMP films to arene vapors for specific periods of time at 25 °C followed by monitoring with fluorescence spectroscopy. The air was not removed from the micropores of the CMP films prior to their exposure to arene vapors. We first investigated the effect of the thickness of CMP films on the chemosensing properties. As shown in Figure S8, the CMP film with a thickness of 10 nm exhibited the best performance. For each chemosensing experiment, several individual CMP films with a thickness of 10 nm were used in parallel experiments, and the results showed excellent reproducibility.

The CMP films are extremely sensitive to arenes, as shown in Figures 2 and S9. For example, upon exposure to the vapor of benzonitrile (BN) for only 20 s, the fluorescence of the CMP films was significantly quenched (Figure 2 a, black line), and only 33 % of the intensity of the pristine CMP film remained. As the exposure time was prolonged, further quenching was observed, and the fluorescence gradually settled at 20 % of its original intensity. Interestingly, the fluorescence-off chemosensing was not specific to BN, but was widely applicable to other electron-deficient arenes. The CMP films exhibited an enhanced response to 1,2-dinitrobenzene (DNB) with 75 % of the fluorescence quenched upon exposure for 20 s (Figure 2 a, red line). Notably, 87 % of the fluorescence was quenched upon exposure to hexafluorobenzene (HFB) for 20 s (Figure 2 a, blue line). The most explicit quenching of fluorescence was observed with 1,4-benzoquinone (BQ). A 20 s exposure resulted in a 92 % loss of fluorescence (Figure 2 a, green line and photos). After 120 s exposure, the fluorescence of CMP films was completely quenched. The degree of fluorescence quenching is in good agreement with the trend in the lowest unoccupied molecular orbital (LUMO) of arenes, as a result of an enhanced driving force for photoinduced electron transfer from the CMP films to arenes.[8] Therefore, a lower LUMO energy level gives a higher detection sensitivity. In contrast, spin-coated TPBCz films, which are nonporous and do not have an extended π conjugation, exhibited a maximum quenching percentage of only 43 % after 120 s exposure under otherwise identical conditions (Figure S10). These results indicate that the function of the CMP films is multifold: the extended π-conjugation network allows exciton migration, the porous skeleton provides a broad interface for electron transfer, and the micropores hold the arene molecules. These features cooperate to facilitate the signaling process and improve the response. The CMP films offer a practical platform for fabricating chemosensors, which feature a precisely controlled structure and a simple fabrication process together with excellent reproducibility and high performance.

The CMP films are also sensitive to electron-rich arenes. In contrast to electron-deficient arenes that quench fluorescence, electron-rich arenes enhanced the fluorescence intensity of the CMP films, thus allowing fluorescence-on sensing (Figure S11). For example, upon exposure to toluene vapor for 20 s, the fluorescence intensity of the CMP films increased by 20 % (Figure 2 b, black line). As the exposure time was prolonged, further enhancement was observed, whereas the fluorescence intensity reached a 46 % increment upon 120 s exposure. Similarly, benzene vapor triggered a 59 % enhancement on 120 s exposure (Figure 2 b, red line). Remarkably, upon exposure to chlorobenzene (CB) vapor, the fluorescence intensity was increased by 81 % in 20 s, and by 122 % in 120 s (Figure 2 b, blue line and inset). In contrast, spin-coated TPBCz films exhibited a very limited change in fluorescence intensity with only 19 % enhancement for CB after 120 s exposure under otherwise identical conditions (Figure S12). The flow of electrons of arenes to the conduction band of TPBCz-CMP enhances the fluorescence intensity, as observed for bulk CMP solids.[3f]

Time-resolved fluorescence spectroscopy was utilized to investigate the kinetics of electron transfer. The CMP film exhibited a fluorescence lifetime (τ_0) of 3.25 ns, which was decreased to 1.03 and 1.86 ns (τ_{DA}) upon exposure to BQ or CB vapor for 20 s, respectively (Figure 3 a, Table S1). The

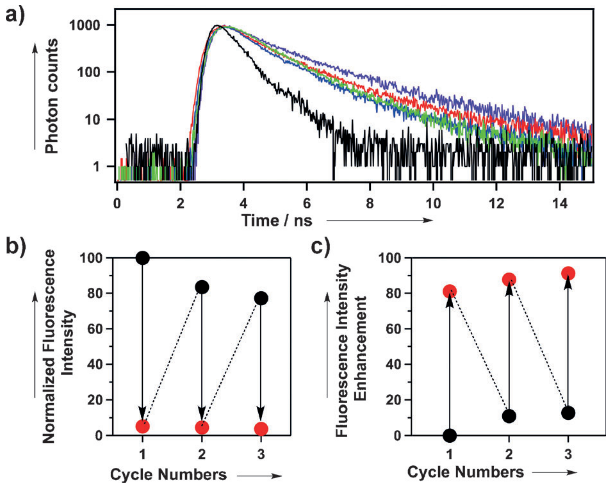


Figure 3. a) Fluorescence-decay profiles of the original CMP film (purple) and the films upon exposure to BQ (red curve), CB (blue curve), and Fe^{3+} (green curve). The black curve represents the IRF (instrument response function) profile. Cycling test of the CMP films upon 20 s exposure to vapors of b) BQ and c) CB.

pseudo-first-order rate constant of electron transfer from the film to BQ or from CB to the film was estimated to be 6.63×10^{8} or $2.30\times10^{8}\,s^{-1}$, respectively, by using τ_{DA}^{-1}-τ_{0}^{-1}. On the other hand, the lifetime of spin-coated TPBCz film was decreased from 4.65 to 3.32 or 3.79 ns, on contact with BQ or CB vapor for 20 s (Figure S13). The electron-transfer rate constants from the TPBCz film to BQ and from CB to the film were 8.62×10^{7} and $4.88\times10^{7}\,s^{-1}$, respectively. Therefore, the electron transfer of the CMP films is much faster than that of the monomer films.

The CMP films can be used repetitively. For example, upon exposure to BQ vapor for 20 s, the CMP film exhibited the same degree of fluorescence quenching after each cycle, and the fluorescence intensity recovered to a similar level when the BQ vapor was removed (Figure 3b). The CMP films exhibited a similar degree of the enhancement in fluorescence intensity upon repetitive exposure to CB vapor for 20 s in the cycling test (Figure 3c). Because of their highly crosslinked network skeletons, the CMP films achieve outstanding stability and can be used repetitively, while retaining a high sensitivity and rapid response.

The carbazole groups in the CMP films can be oxidized chemically or electrochemically, providing a possibility for sensing redox-active ions. For instance, Fe^{3+}, an essential ion in biological systems, has a standard electrode potential of 0.77 V ($E_{Fe(III)/Fe(II)}$),[5a] which is higher than the oxidative potential of dimeric carbazoles (0.6 V) in our CMP films. We found that when the CMP films were immersed in an aqueous Fe^{3+} solution, the dimeric carbazoles in the CMP films were oxidized to form cations, which quenched the fluorescence of the CMP films. Based on this result, the CMP films were utilized to detect different concentrations of Fe^{3+} (Figure S14). As shown in Figure 4a, when the CMP films were immersed for 20 s in aqueous solutions of Fe^{3+} in concentrations ranging from 10^{-3} to 10^{-5} M, the degree of fluorescence quenching exceeded 90%. Remarkably, as the concentration of Fe^{3+} decreased to 10^{-6} and 10^{-7} M, over 80% of the fluorescence was quenched. Even when the Fe^{3+} concentration was decreased to 10^{-8} M, the degree of fluorescence quenching was as high as 50%. The CMP films with such a high sensitivity for reporting Fe^{3+} outperform other Fe^{3+} chemosensors thus far reported.[9] In contrast, the spin-coated TPBCz films exhibited a low sensitivity for Fe^{3+} by showing a degree of fluorescence quenching of only 41% when immersed in a 10^{-5} M solution for 60 s (Figure S15). The rate constant of electron transfer from the CMP film to Fe^{3+} was $5.85\times10^{8}\,s^{-1}$ (Figure 3a).

We further investigated the scope of ion species that can be sensed (Figure S16). Compared to Fe^{3+} ions, the CMP films exhibited low sensitivity and torpid response to other non-oxidative metal ions (Figure 4b). For example, the fluorescence was slightly quenched with a degree of only 17% when immersed for 60 s in an aqueous solution of Fe^{2+} with a concentration of 10^{-4} M. Similarly, the CMP films are not sensitive to other transition metals, such as Co^{2+}, Cu^{2+}, and Ni^{2+}. As for alkali metal ions, we examined K^{+}, Ca^{2+}, and

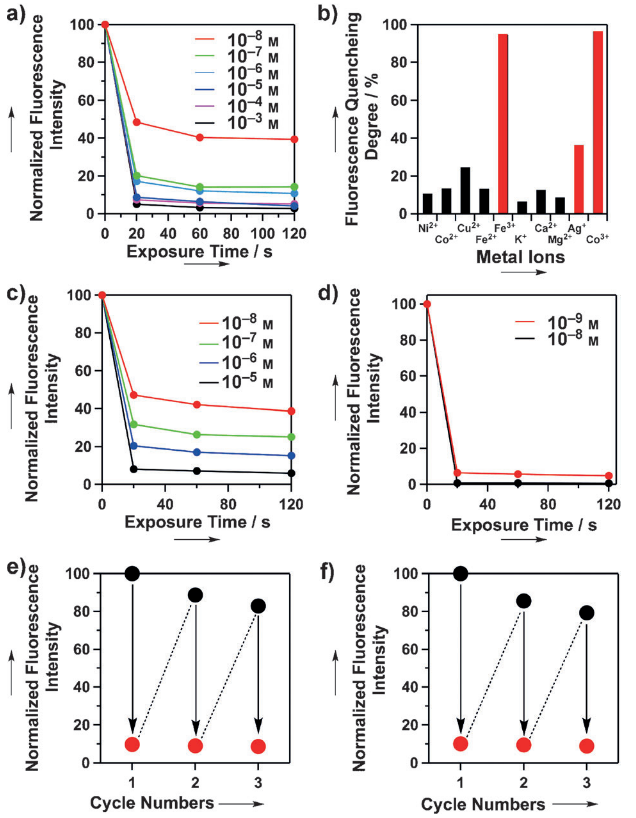


Figure 4. a) Normalized fluorescence intensity of the CMP films upon immersion in aqueous solutions of Fe^{3+} at different concentrations (10^{-3} to 10^{-8} M) for different periods of time. b) Degree of fluorescence quenching of the CMP films upon 60 s immersion in aqueous solutions of different metal ions (10^{-4} M). Red bars are for Fe^{3+}, Ag^{+}, and Co^{3+}. Normalized fluorescence intensity of the CMP films upon immersion in saline solutions of c) dopamine and d) HOCl at different concentrations for different periods of time. Recycle test of the CMP films for biosensing saline solutions (10^{-8} M) of e) dopamine and f) HOCl.

Mg^{2+}, which could not effectively quench the fluorescence of the CMP films.

To investigate whether the CMP films are sensitive to other oxidative metal ions, we conducted sensing experiments with Ag^+ and Co^{3+}, which are known as oxidative metal species. The CMP films exhibited a significant fluorescence quenching when exposed to an aqueous solution of Ag^+ (10^{-4} M) for only 60 s (Figure S16 h). A more sensitive quenching was observed with Co^{3+}; the fluorescence of the films was quenched almost completely (Figure S16 i). The degree of fluorescence quenching was 36 % and 96 % for Ag^+ and Co^{3+}, respectively (Figure 4 b). These results clearly demonstrate that the CMP films are responsive to oxidative metal ions, such as Fe^{3+}, Co^{3+}, and Ag^+ (Figure 4 b).

The reported chemosensors for the detection of metal ions usually utilize probe molecules that coordinate with metal ions to cause spectral change.[10] However, such methods suffer from the interference of other transition-metal ions,[10] such as Ni^{2+}, Co^{2+}, Cu^{2+}, and Fe^{2+}. To show the difference, we further examined the chemosensing of a mixture of Fe^{3+} and Co^{2+} (each 10^{-7} M) using the CMP film (Figure S17), which exhibited a high degree of fluorescence quenching, as observed for a solution of Fe^{3+}. Even in the case of a physiological saline solution containing Fe^{3+} (10^{-7} M), the CMP film displayed a high sensitivity and quick response (Figure S18). Because of less interference, the CMP films are promising for real-time biosensing of oxidative ion species.[11] The CMP films were recyclable for Fe^{3+} sensing (Figure S19) by immersion into a solution of $NaBH_4$, which can reduce the dimeric carbazyl cations to their neutral states and recover the fluorescence.

Dopamine (DA, 3,4-dihydroxyphenethylamine) is an important neurotransmitter,[12,13] and malfunction of DA-responsive neurons has been implicated in a number of diseases, including Parkinson's disease. This has sparked significant interest for the development of detection methods for DA. However, the low sensitivity and complexity of various analytical methods, such as electrochemical techniques and HPLC, make it a great challenge to provide technically simple and label-free DA detection. We found that the electron-donating CMP films serve as a new type of sensors, featuring high sensitivity and label-free detection of DA as a result of high-rate electron transfer (Figure S20). When the CMP films were immersed in the saline solutions of DA with a concentration of 10^{-5} and 10^{-6} M for only 20 s, the fluorescence was quenched by 90 % and 80 %, respectively (Figure 4 c, black and blue dots). The DA concentration could be decreased to 10^{-8} M (red dot), upon which the fluorescence of the film was quenched to 50 % after only 20 s exposure. This high sensitivity makes our CMP films superior to other DA sensors thus far reported. The fluorescence decay profiles revealed that the rate constant of the electron transfer from the CMP film to DA is as high as $3.8 \times 10^8\,s^{-1}$ (Figure S21).

Hypochlorous acid (HOCl) is a highly active antibacterial agent and a key compound involved in biological defence.[14] Because the dimeric carbazole units can be oxidized by HOCl, the CMP films can serve as an outstanding sensor for HOCl (Figure S22). When the CMP films were immersed in the saline solutions of HOCl with a concentration of 10^{-8} M for only 20 s, the fluorescence of the films was completely quenched (Figure 4 d, black dots). Remarkably, even when the HOCl concentration was decreased to as low as 10^{-9} M, the quenching degree still exceeded 90 % (red dots). The exceptionally sensitive fluorescence quenching is beyond the photon-counting instrument for a fluorescence decay measurement. The CMP films are recyclable for biosensing DA and HOCl. By rinsing with a $NaBH_4$ solution and deionized water, the films recovered the fluorescence and were reused for sensing (Figure 4 e,f).

In summary, we have developed an electrochemical approach for the controlled synthesis of thin films of conjugated microporous polymers. The thickness of the CMP films can be synthetically controlled, and the films can be obtained on substrates or as freestanding films. The films are unique in that they are porous, possess extended π conjugation, allow exciton delocalization over the skeletons, and enable high-rate electron transfer. Because of these features, we developed the CMP films as versatile platforms for chemo- and biosensing. The CMP sensors feature excellent selectivity, rapid response, and high sensitivity, discriminate electron-rich and electron-poor arenes through fluorescence on/off sensing, and selectively detect oxidative ions by redox-induced fluorescence quenching. The films function as label-free sensors for the highly sensitive detection of biologically important dopamine and HOCl species. Given the structural diversity and flexibility of CMPs, we anticipate the emergence of an exciting field in designing CMP films, which would significantly expand the potential of CMPs for applications.

Received: February 7, 2014
Revised: February 28, 2014

Keywords: biosensors · chemosensors · conjugated microporous polymers · electropolymerization · thin films

---

[1] a) A. I. Cooper, *Adv. Mater.* **2009**, *21*, 1291 – 1295; b) J. X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, *Angew. Chem.* **2007**, *119*, 8728 – 8732; *Angew. Chem. Int. Ed.* **2007**, *46*, 8574 – 8578; c) J. X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak, A. I. Cooper, *J. Am. Chem. Soc.* **2008**, *130*, 7710 – 7720; d) J. T. A. Jones, D. Holden, T. Mitra, T. Hasell, D. J. Adams, K. E. Jelfs, A. Trewin, D. J. Willock, G. M. Day, J. Bacsa, A. Steiner, A. I. Cooper, *Angew. Chem.* **2011**, *123*, 775 – 779; *Angew. Chem. Int. Ed.* **2011**, *50*, 749 – 753; e) J. X. Jiang, C. Wang, A. Laybourn, T. Hasell, R. Clowes, Y. Z. Khimyak, J. L. Xiao, S. J. Higgins, D. J. Adams, A. I. Cooper, *Angew. Chem.* **2011**, *123*, 1104 – 1107; *Angew. Chem. Int. Ed.* **2011**, *50*, 1072 – 1075.

[2] a) A. Thomas, P. Kuhn, J. Weber, M. M. Titirici, M. Antonietti, *Macromol. Rapid Commun.* **2009**, *30*, 221 – 236; b) M. J. Bojdys, S. A. Wohlgemuth, A. Thomas, M. Antonietti, *Macromolecules* **2010**, *43*, 6639 – 6645.

[3] a) Y. Xu, S. Jin, H. Xu, A. Nagai, D. Jiang, *Chem. Soc. Rev.* **2013**, *42*, 8012 – 8031; b) L. Chen, Y. Yang, D. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 9138 – 9143; c) L. Chen, Y. Honsho, S. Seki, D. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 6742 – 6748; d) L. Chen, Y. Yang, Z.

Guo, D. Jiang, *Adv. Mater.* **2011**, *23*, 3149–3154; e) Y. Kou, Y. Xu, Z. Guo, D. Jiang, *Angew. Chem.* **2011**, *123*, 8912–8916; *Angew. Chem. Int. Ed.* **2011**, *50*, 8753–8757; f) Y. Xu, L. Chen, Z. Guo, A. Nagai, D. Jiang, *J. Am. Chem. Soc.* **2011**, *133*, 17622–17625; g) X. Liu, Y. Xu, D. Jiang, *J. Am. Chem. Soc.* **2012**, *134*, 8738–8741; h) Y. Xu, A. Nagai, D. Jiang, *Chem. Commun.* **2013**, *49*, 1591–1593; i) X. Liu, Y. Xu, Z. Guo, A. Nagai, D. Jiang, *Chem. Commun.* **2013**, *49*, 3233–3235; j) Y. Xu, D. Jiang, *Chem. Commun.* **2014**, *50*, 2781–2783; k) F. Xu, X. Chen, Z. Tang, D. Wu, R. Fu, D. Jiang, *Chem. Commun.* **2014**, *50*, DOI: 10.1039/C4CC01002G.

[4] a) V. Senkovskyy, I. Senkovska, A. Kiriy, *ACS Macro Lett.* **2012**, *1*, 494–498; b) M. Kim, M. Byeon, J.-S. Bae, S.-Y. Moon, G. Yu, K. Shin, F. Basarir, T.-H. Yoon, J.-W. Park, *Macromolecules* **2011**, *44*, 7092–7095; c) G. Cheng, T. Hasell, A. Trewin, D. J. Adams, A. I. Cooper, *Angew. Chem.* **2012**, *124*, 12899–12903; *Angew. Chem. Int. Ed.* **2012**, *51*, 12727–12731; <lit d> K. V. Rao, S. Mohapatra, T. K. Maji, S. J. George, *Chem. Eur. J.* **2012**, *18*, 4505–4509; e) X. Zhu, C. Tian, S. Chai, K. Nelson, K. S. Han, E. W. Hagaman, G. M. Veith, S. M. Mahurin, H. Liu, S. Dai, *Adv. Mater.* **2013**, *25*, 4152–4158; f) S.-Y. Moon, J.-S. Bae, E. Jeon, J.-W. Park, *Angew. Chem.* **2010**, *122*, 9694–9698; *Angew. Chem. Int. Ed.* **2010**, *49*, 9504–9508; g) X. Zhu, C. Tian, S. M. Mahurin, S.-H. Chai, C. Wang, S. Brown, G. M. Veith, H. Luo, H. Liu, S. Dai, *J. Am. Chem. Soc.* **2012**, *134*, 10478–10484.

[5] a) A. J. Bard, L. Faulkner, *Electrochemical Methods—Fundamentals and Applications*, *2nd ed.*, Wiley, New York, **2001**; b) J. Heinze, B. Frontana, S. Ludwigs, *Chem. Rev.* **2010**, *110*, 4724–4771; c) P. M. Beaujuge, J. R. Reynolds, *Chem. Rev.* **2010**, *110*, 268–320; d) C. Gu, T. Fei, Y. Lv, T. Feng, S. Xue, D. Lu, Y. Ma, *Adv. Mater.* **2010**, *22*, 2702–2705; e) C. Gu, T. Fei, L. Yao, Y. Lv, D. Lu, Y. Ma, *Adv. Mater.* **2011**, *23*, 527–530; f) C. Gu, W. Dong, L. Yao, Y. Lv, Z. Zhang, D. Lu, Y. Ma, *Adv. Mater.* **2012**, *24*, 2413–2417; g) C. Gu, Z. Zhang, S. Sun, Y. Pan, C. Zhong, Y. Lv, M. Li, K. Ariga, F. Huang, Y. Ma, *Adv. Mater.* **2012**, *24*, 5727–5731; h) C. Gu, Y. Chen, Z. Zhang, S. Xue, S. Sun, K. Zhang, C. Zhong, H. Zhang, Y. Pan, Y. Lv, Y. Yang, F. Li, S. Zhang, F. Huang, Y. Ma, *Adv. Mater.* **2013**, *25*, 3443–3448.

[6] a) Y. Yuan, F. Sun, H. Ren, X. Jing, W. Wang, H. Ma, H. Zhao, G. Zhu, *J. Mater. Chem.* **2011**, *21*, 13498–13502; b) F. Piron, P. Leriche, I. Grosu, J. Roncali, *J. Mater. Chem.* **2010**, *20*, 10260–10268.

[7] a) A. Desbene-Monvernay, P.-C. Lacaze, J.-E. Dubois, *J. Electroanal. Chem.* **1981**, *129*, 229–241; b) A. Desbene-Monvernay, P.-C. Lacaze, M. Delamar, *J. Electroanal. Chem.* **1992**, *334*, 241–246.

[8] S. Pramanik, C. Zheng, X. Zhang, T. J. Emge, J. Li, *J. Am. Chem. Soc.* **2011**, *133*, 4153–4155.

[9] a) X. Wang, C. Drew, S.-H. Lee, K. J. Senecal, J. Kumar, L. A. Samuelson, *Nano Lett.* **2002**, *2*, 1273–1275; b) S. J. Lee, J.-E. Lee, J. Seo, I. Y. Jeong, S. S. Lee, J. H. Jung, *Adv. Funct. Mater.* **2007**, *17*, 3441–3446; c) M. Shellaiah, Y.-H. Wu, A. Singh, M. V. R. Raju, H.-C. Lin, *J. Mater. Chem. A* **2013**, *1*, 1310–1318.

[10] a) J. Du, M. Hu, J. Fan, X. Peng, *Chem. Soc. Rev.* **2012**, *41*, 4511–4535; b) Y. Xiang, A. Tong, *Org. Lett.* **2006**, *8*, 1549–1552.

[11] a) A. W. Czarnik in *Fluorescent Chemosensors for Ion and Molecule Recognition*, American Chemical Society, Washington, DC, **1992**; b) D. W. Domaille, E.-L. Que, C.-J. Chang, *Nat. Chem. Biol.* **2008**, *4*, 168–175; c) T. Terai, T. Nagano, *Curr. Opin. Chem. Biol.* **2008**, *12*, 515–521; d) D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537–2574; e) S. W. Thomas III, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, *107*, 1339–1386; f) B. S. Gaylord, A. J. Heeger, G. C. Bazan, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 10954–10957; g) B. Liu, G. C. Bazan, *Chem. Mater.* **2004**, *16*, 4467–4476; h) G. D. Scholes, K. P. Ghiggino, *J. Chem. Phys.* **1994**, *101*, 1251–1261; i) S. E. Webber, *Chem. Rev.* **1990**, *90*, 1469–1482.

[12] G. S. Wilson, M. A. Johnson, *Chem. Rev.* **2008**, *108*, 2462–2481.

[13] D. W. Hatchett, M. Josowicz, *Chem. Rev.* **2008**, *108*, 746–769.

[14] Y. Yang, Q. Zhao, W. Feng, F. Li, *Chem. Rev.* **2013**, *113*, 192–270.