

Halochromism of a Polythiophene Derivative Induced by Conformational Changes and Its Sensing Application of Carbon Dioxide

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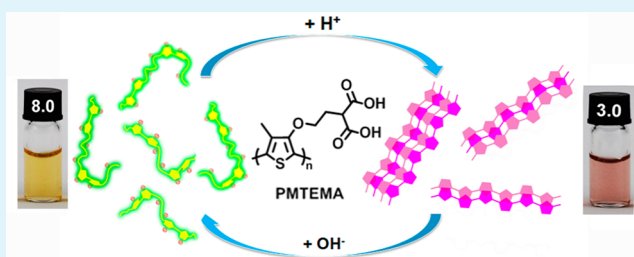
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S Supporting Information

ABSTRACT: We report the design and synthesis of a halochromic polythiophene derivative, whose conformation can be alternated between random coil and rodlike phase by adjusting the pH of the solution. Distinct solution color changes associated with the pH-induced conformational transitions can be used to construct a colorimetric probe for sensing carbon dioxide. This probe can be recovered by bubbling nitrogen gas into carbon dioxide-treated solutions for over 20 cycles.

KEYWORDS: halochromism, polythiophene, conformation, sensor, carbon dioxide



INTRODUCTION

The design and construction of optical sensing platforms based on conjugated polyelectrolytes (CPEs) have attracted broad interest because of the signal amplification effects of the polymer backbone and the potential in sensing biomolecules.^{1–8} Among various CPEs, water-soluble poly(3-alkoxy-4-methylthiophene)s (P3RO-4MeTs) have received extensive attention in recent years because of their colorimetric and fluorometric dual-output.^{9–13} The colorimetric mode provides advantages of visual detection and real-time in situ responses for P3RO-4MeTs,^{14,15} while other CPEs mostly rely on a signal intensity change upon analyte binding. As reported previously, the mechanism of the color changes of P3RO-4MeTs can be attributed to the transitions of their chain conformations induced by external stimuli such as temperature,¹⁶ ionic strength,¹⁷ light,¹⁸ solvent,¹⁹ and certain analytes.^{20–25} However, colorimetric probes based on P3RO-4MeTs that can be responsive to pH changes, one of the most common stimuli, have not been reported to date. As part of our interest in investigating stimuli-induced chromism of polythiophenes (PTs), herein we report the halochromism of one type of P3RO-4MeTs induced by conformational changes of the polymer backbone. This new mechanism is in stark contrast to the conventional halochromism caused by conjugated electronic structure changes upon protonation or deprotonation of small molecules.²⁶

For this purpose, we designed and synthesized a novel anionic polythiophene derivative, poly(2-(2-(4-methylthiophen-3-yloxy)-ethyl)malonic acid) (PMTEMA, Scheme 1). In this polymer, we introduced a malonic acid moiety to the side chain of the polymer backbone. The double carboxyl groups

not only make PMTEMA highly soluble in aqueous phase, but also maintain electrostatic repulsion between polymer chains under basic conditions and thus prevent polymer aggregation. On the basis of this structure, we anticipate that the PMTEMA will adopt a random-coiled conformation at high pH corresponding to a yellow solution, whereas at low pH, it might form aggregates via π - π stacking together with hydrogen bonding upon the protonation of carboxyl groups,²⁷ resulting in a pink solution (Scheme 1). The experimental results validated our proposed strategy, and the details are discussed below.

EXPERIMENTAL SECTION

Materials. All chemicals were purchased from Aldrich and Beijing Chem. Reagents Co. (Beijing, China) and were used as received. Water-soluble polythiophene derivative, PMTEMA, was synthesized and purified as described in the Supporting Information.

Sample Preparation. In a typical procedure, the probe solution was prepared by diluting PMTEMA aqueous stock solution (5 mM based on the repeating unit) to a given concentration with the specified buffer. In the experiments of gas sensing, CO₂, SO₂, and N₂ were directly bubbled into a dilute solution of PMTEMA with the given concentration. The corresponding spectroscopic measurements were carried out immediately.

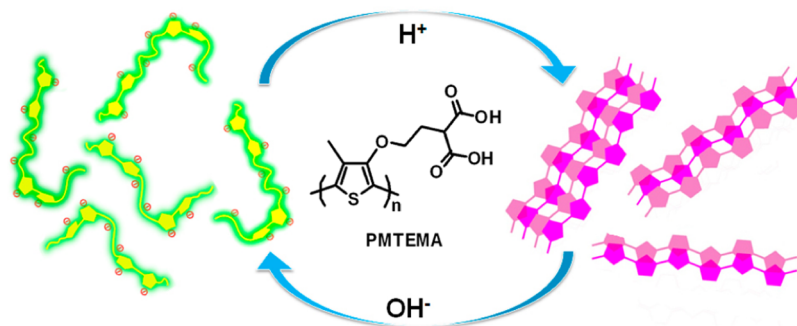
Measurements. Absorption and emission spectra were collected by using a Hitachi 3900 UV–visible spectrometer and a HORIBA Scientific Fluorolog-3 spectrofluorometer, respectively. NMR spectra were carried out on a Bruker DPX300 spectrometer. The molecular weight was determined by a Waters GPC 1515–2410. Electro spray

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Scheme 1. Chemical Structure of PMTEMA and Schematic Illustration of Its Conformational Transition Effected by pH Changes



ionization mass spectrometry (ESI-MS) results were obtained from a Shimadzu LCMS2010.

RESULTS AND DISCUSSION

We first examined the optical properties of PMTEMA in response to the changes of pH values in 20 mM phosphate buffer. At a high pH value ($\text{pH} \geq 7.0$), PMTEMA exhibits an absorption maximum at 407 nm, indicative of a random-coiled conformation of the polymer backbone.²⁸ When the pH of the solution was decreased, the absorption maximum of PMTEMA gradually red-shifted to 495 nm along with enhanced light scattering at long wavelength (Figure 1A). Simultaneously, a

groups on the side chain of PMTEMA should be in similar ranges. Hence, in a high pH (>7) phosphate buffer, all the carboxyl groups exist in the form of COO^- , resulting in a high density of negative charges on the polymer surface. These surface charges generate electrostatic repulsion between different PMTEMA molecules, which plays a key role in stabilizing the dispersion and maintaining the random-coiled conformation of the polymer chains. On the other hand, when the pH of the buffer solution decreases (<6), the carboxyl groups on the side chain would be partly protonated. As a result, the intermolecular hydrogen bonding and π - π stacking might outweigh the electrostatic repulsion between PMTEMA molecules, leading to an ordered planar conformation of the polymer backbone accompanied by the solution color change from yellow to pink. This conformational transition can also be substantiated by a set of temperature-dependent absorption spectra of PMTEMA (Supporting Information, Figure S2), of which the absorption maximum gradually blue-shifted from 495 nm (rodlike) to 407 nm (random-coiled) as the temperature was increased from 25 to 85 °C (Figure 2).

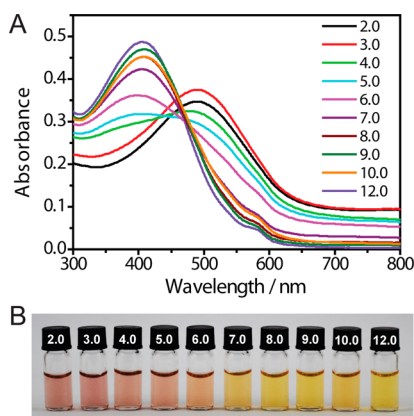


Figure 1. Absorption spectra (A) and photographs (B) of PMTEMA (1.0×10^{-4} M) in 20 mM phosphate buffer at different pH as indicated.

distinct solution color change from yellow to pink was observed (Figure 1B). This red-shift of absorption and the solution color change are attributed to the conformational stretch of the polythiophene backbone and the formation of highly ordered aggregates. The fluorescent measurements of PMTEMA at various pHs further confirmed the above speculation. When the pH of the solution was acidified stepwise from pH 12.0 to 2.0, the emission intensity of PMTEMA at 545 nm was gradually quenched and finally dropped to about only 4% of the original intensity (Supporting Information, Figure S1). These spectral results are associated with an increase in the effective conjugated length of the polythiophene backbone and imply the formation of an ordered arrangement of PMTEMA under acidic conditions.²⁸ According to CRC Handbook of Chemistry and Physics, the pK_a values of malonic acid are $\text{pK}_{a1} = 2.85$ and $\text{pK}_{a2} = 5.70$, respectively. The pK_a values of the two carboxyl

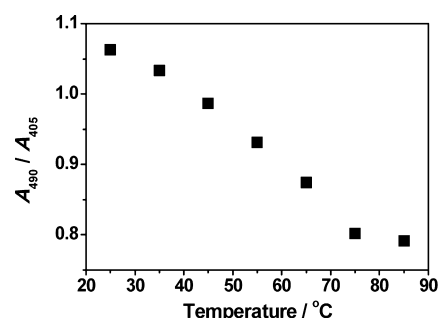


Figure 2. Temperature dependence of the relative absorbance (A_{490}/A_{405}) of PMTEMA (1.0×10^{-4} M) in 20 mM phosphate buffer (pH 4.0).

To check if the halochromism of PMTEMA can be reversibly switched by adjusting the pH value of the solution, we conducted experiments with pH oscillating between 4.0 and 10.0. The solution turned pink as the pH was decreased and yellow as the pH rose. The absorption spectra are shown in the Supporting Information, Figure S3. We used the relative absorption intensity, A_{483}/A_{410} , to illustrate the system performance during the pH cycles (Figure 3). It was observed that the halochromism of PMTEMA was not compromised after five successive cycles between pH 4.0 and 10.0. Moreover, all the measurements were carried out immediately after the pH

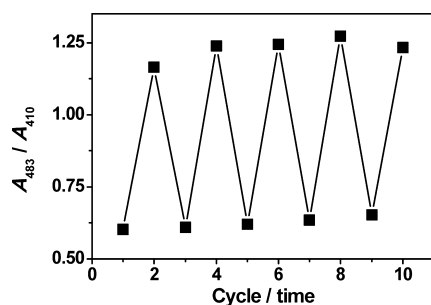


Figure 3. Relative absorbance at 483 and 410 nm of PMTEMA (1.0×10^{-4} M) upon cycling the pH between 4.0 and 10.0.

was adjusted to the given value, which implies that the conformational transition of PMTEMA is not kinetically constrained. This property makes PMTEMA a promising candidate for constructing a rapid-response sensing system.

Following the above discussion, we employed the halochromic PMTEMA for the sensing of carbon dioxide (CO_2). CO_2 is an important greenhouse gas associated with many environmental problems. Hitherto, many approaches have been developed for the detection of CO_2 such as electrochemical assay,²⁹ GC-MS,³⁰ functionalized nanomaterials,³¹ and spectroscopic techniques including surface plasmon resonance,³² fluorescence,^{33,34} IR,³⁵ etc. But there are still some limitations with the existing methods, including requirement of sophisticated and expensive equipment, excitation and emission in the UV region, the use of organic–water mixed media, and time-consuming procedures, and so forth. Therefore, it is still necessary to establish new systems that could expedite CO_2 detection with visual means and simple procedures. The color of PMTEMA solution is quite sensitive to pH changes within the range between 6.0 and 8.0; therefore it is feasible to fabricate a colorimetric probe for sensing CO_2 based on this polymer.

A solution of alkalinized PMTEMA in pure water with initial pH 9.80 showed an absorption maximum around 408 nm, which is attributed to a random-coiled conformation of the PT backbone. Upon bubbling of CO_2 gas through the solution for 5 min, the absorbance at 408 nm decreased along with the rise of absorbance at 480 nm (Figure 4A). Simultaneously, a distinct solution color change from yellow to red-orange was observed, signifying that a more planar conformation of PMTEMA was adopted after the stimuli of CO_2 (Figure 4B). These results confirmed that PMTEMA could be a practically useful probe for rapid CO_2 sensing. It is known that the gas–liquid equilibrium of CO_2 solubilization in water ($\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$) can be readily perturbed by bubbling an inert gas into the solution.³⁶ This prompted us to recover the probe by bubbling nitrogen gas (N_2) to the CO_2 -treated PMTEMA solution. To our delight, the solution color turned back to yellow after 10 min of N_2 bubbling, while the absorption maximum was also restored to its initial state. This cycle could be repeated over 20 times without any considerable loss of sensing ability of the probe (Figure 4C).

To evaluate if the sensing of CO_2 with PMTEMA could be interfered with by other acid gases, we tested the interaction of sulfur dioxide (SO_2) with the probe under identical conditions. Bubbling SO_2 to the probe solution also induced a solution color change from yellow to brownish; but the absorption maximum red-shifted to 490 nm, which was slightly different from that of CO_2 treatment. More interestingly, when we tried

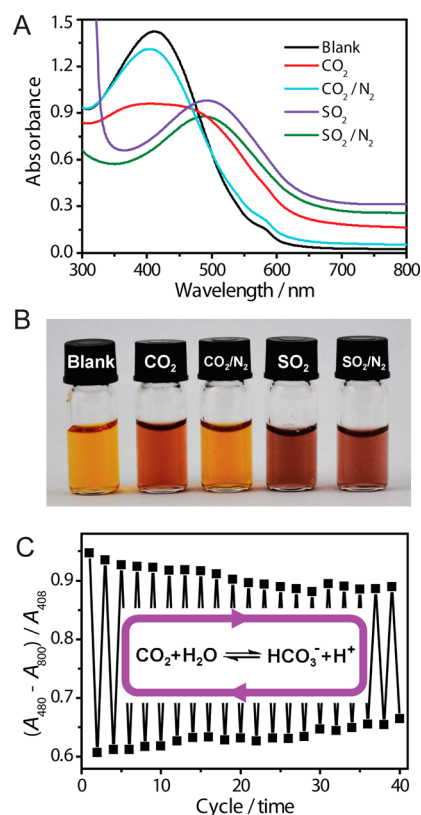


Figure 4. Absorption spectra (A) and photographs (B) of PMTEMA (3.0×10^{-4} M) in water bubbled with CO_2 , CO_2/N_2 , SO_2 , and SO_2/N_2 as indicated. (C) Relative absorbance of PMTEMA (3.0×10^{-4} M) upon alternating CO_2 and N_2 stimuli.

to recover the probe by bubbling N_2 to the solution, no changes occurred even after a prolonged attempt (Figure 4C). This might be because HSO_3^- is a much weaker base than HCO_3^- , and it fails to react with a proton to regenerate SO_2 in the presence of PMTEMA. This result can be used to discriminate these two common acid gases (CO_2 and SO_2).

As a sensor for CO_2 detection, it is of practical value to quantitatively evaluate the sensing performance of PMTEMA toward CO_2 . First, the real-time responses of PMTEMA for CO_2 at a constant flow rate ($60 \text{ cm}^3/\text{min}^{-1}$) were examined, and the absorption spectral changes were recorded. From Supporting Information, Figure S6 we can see that upon bubbling CO_2 to the probe solution (1 mL, 1×10^{-4} M) through a needle of 0.5 mm in diameter, the absorption maximum of PMTEMA gradually red-shifted from 407 to 480 nm along with the change in the solution color from yellow to red-orange. The relative absorbance of (A_{495}/A_{407}) was used to evaluate the real-time sensing ability of PMTEMA toward CO_2 (Figure 5A). It is clear that at a rate of $60 \text{ cm}^3/\text{min}^{-1}$, the equilibrium between CO_2 and the probe can be reached within 10 s which enables a rapid sensing for CO_2 . Another test was conducted to quantify the contents of CO_2 in a gas mixture while CO_2/N_2 was selected as the model system. In these experiments, a set of gas mixtures with different fractions of CO_2 were bubbled into the probe solution at a certain flow rate for a fixed period (10 s). The absorption measurements were taken immediately, and the results were depicted in Figure 5B and Supporting Information, Figure S7. The results show that increasing CO_2 contents in the gas mixture leads to an enhanced response of PMTEMA, and there is a good linear

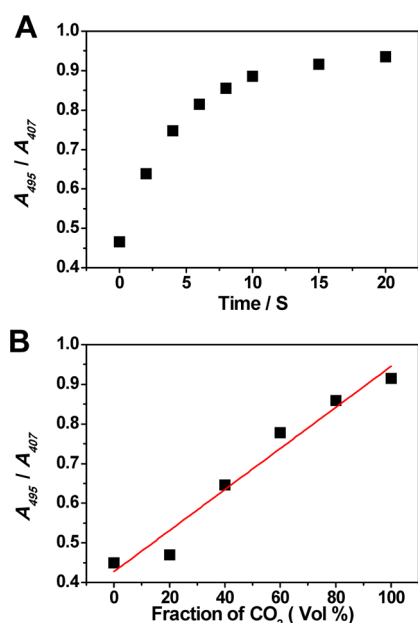


Figure 5. Plots of relative absorbance (A_{495}/A_{407}) of PMTEMA versus bubbling time (A) and fraction of CO₂ (B) in water. [PMTEMA] = 1.0×10^{-4} M.

relationship between (A_{495}/A_{407}) and the fraction of CO₂ ($R = 0.982$). It indicates that this probe is applicable to the quantitative detection of CO₂ contents over a wide concentration range in a gas mixture.

CONCLUSION

In conclusion, we have designed and developed a novel halochromic polythiophene derivative, PMTEMA. Its conformation can be alternated between random-coil and rodlike phases by adjusting the pH of the solution, along with distinct solution color changes. This pH-responsive property of PMTEMA can be used for the visual detection of CO₂ gas. Bubbling N₂ into the solution of CO₂-treated PMTEMA can recover the sensing ability of the probe even if repeated for over 20 cycles. The probe can also be applied for selective detection and quantification of CO₂. To the best of our knowledge, this is the first example that the halochromism is induced by conformational changes of a polymer backbone. We expect that the current probe not only extends the mechanism of halochromism, but also can be used to construct a colorimetric sensing platform for the detection of various analytes.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, NMR, and additional spectral data. 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.

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