

Switchable structural modification accompanying altered optical properties of a zwitterionic polysquaraine

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ABSTRACT

Active metals induce a variation of the conformation of zwitterionic conducting polymer poly(3-octylpyrrole)squaraine in solution. Evidence from infrared, visible and photoluminescent spectra and from small-angle X-ray scattering profiles unambiguously confirms the isomerization of this polysquaraine induced by the surfaces of active metals. Unlike the irreversible change induced by cations in solution, the folded conformation induced by active metals reverts to its original structure on eliminating contact between the metals and the solution. Accompanied by altered optical properties, this reversible structural modification of the zwitterionic polysquaraine induced by active metals represents a new chemical and physical process.

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1. Introduction

Conducting polymers (CP, sometimes called conjugated polymers) attract increasing attention because of their novel electrical, optical and magnetic properties, which might be translated into diverse applications [1–3]. Developing a CP allows a great flexibility for synthetic manipulation; a common approach involves use of organic dyes as building blocks. Among these CP, polysquaraines are zwitterionic dyes containing squaraines and π -conjugated polymers that are characterized by intense red absorption [4,5]; these compounds are suitable for the design of conducting polymers with small optical band gaps [6–9]. This possession of unique optical, physical and chemical properties has made polysquaraines suitable materials for technical applications such as in solar cells [10–13], xerographic sensitizers [14], optical data storage [15], photodynamic therapeutics [16,17] and chemical sensors [8,18–21].

The optical, physical and electronic properties of CP are affected strongly by a variation of the polymer conformation because of excitonic interaction among the constituent chromophores [22]. To optimize the performance, controlling the conformation is a critical issue for applications based on these materials. Preceding workers have investigated the variation of the structural conformation for squaraine-based materials through solvent concentration [23,24], solvent polarity [23,25–27], temperature [23,28], metal ions [29–31] and other conditions. Besides induction by

these external stimuli, other techniques might control the conformation of polysquaraine.

We synthesized the target CP poly(3-octylpyrrolyl)squaraine to possess mostly zwitterionic repeating units. Accompanied by color changes, the conformational structure of the carrier was altered on adding metal ions to solutions of the polymer and also induced by some active metals. The conformation of this zwitterionic poly(3-octylpyrrole)squaraine induced by active metals reverted to its original structure on removing contact with the metals; this observation has no precedent.

2. Experiments

2.1. Materials

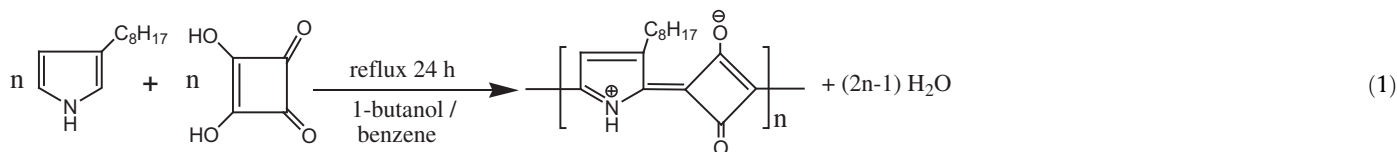
Reagents 3-octylpyrrole (99.5%) and squaric acid (99.0%) (T.C.I.), solvents 1-butanol (99.9%), benzene (99.8%), and trichloromethane (99.4%) (Merck); copper perchlorate hexahydrate (98%) (Acros), calcium perchlorate tetrahydrate (98%) (Acros), copper foils (99.98%) (Sigma–Aldrich) and copper gauze (Alfa Aesar) were obtained from the indicated suppliers.

2.2. Preparation of poly(3-octylpyrrole)squaraine

For our target polysquaraine, we reacted 3-octylpyrrole (1.1224 g, 6.26 mmol) with squaric acid (0.714 g, 6.26 mmol) in equimolar proportions in an azeotropic solution of 1-butanol and benzene, under continuously flowing N₂ for 24 h to produce poly(3-octylpyrrole)squaraine as shown in Eq. (1) [32–34].

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The hot rich pink solutions obtained were filtered; the filtrates were concentrated with vacuum distillation and poured into diethyl ether. The crude products were collected on filtration and washed with diethyl ether, before being redissolved in trichloromethane to yield solutions that were filtered again; the filtrates were evaporated to dryness in an open fume cupboard to eliminate HCCl_3 . The precipitates were finally washed again with diethyl ether and dried in a vacuum chamber near 25°C for 2 days. This product was obtained in a yield 65%.

This polycondensation was amenable to experimental control such that the poly(3-octylpyrrole)squaraine was synthesized with predominantly zwitterionic repeating units (>97%) [32]. The molar masses of the polymers were measured with a gel-permeation chromatograph (GPC, Viscotek-TDA) at 25°C using trichloromethane as eluent and polystyrene as the standard reference; the molecular masses are $M_n = 21$ kDa and $M_w = 38$ kDa. The characterization of the poly(3-octylpyrrole)squaraine as synthesized can be found in our previous report [32].

2.3. Methods

Visible absorption (Ocean Optics UV-Visible spectrophotometer), photoluminescent (Jobin-Yvon Model Fluorolog-3 spectrophotometer) and IR absorption (Nicolet Magna 860 FTIR, attached to IR beamline 14A1 at NSRRC with a HgCdTe for $500\text{--}4000\text{ cm}^{-1}$ or DTGS detector for $400\text{--}4000\text{ cm}^{-1}$) spectra were recorded with the indicated instruments. The IR spectra were typically measured with resolution 0.5 cm^{-1} and 200–512 scans. Small-angle X-ray scattering (SAXS) curves were recorded with the 15-keV beam (ca. $0.2 \times 0.2\text{ mm}$) from beam line 23A at NSRRC [35]; the target polymers were dissolved in trichloromethane, then injected into the stainless-steel or copper cell (diameter 5 mm, thickness 2.2 mm) with Kapton windows for incident X-ray.

3. Results and discussion

Zwitterionic organic dyes act as ligands and react with metal ions to form stable complexes, resulting in altered optical properties. As synthesized, poly(3-octylpyrrole)squaraine reacts thus with metal ions; the color of its solution alters concurrently. On reaction of our poly(3-octylpyrrole)squaraine, as synthesized, with Cu^{2+} cation in trichloromethane solution, the absorption maximum gradually shifted with time from 543.6 nm to 524.3 nm; the intensity of the former band correspondingly decreased, as shown in Figure 1A. For this reaction we prepared a saturated solution of Cu^{2+} in HCCl_3 over $\text{Cu}(\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$. The curves of these spectra intersect at 531.2 nm, an isosbestic point. Thus either poly(3-octylpyrrole)squaraine reacted with Cu^{2+} ion in trichloromethane or the metal ion altered the structure of this zwitterionic polymer, in either case to shift the absorption band of poly(3-octylpyrrole)squaraine. To compare with other cations, we also added Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Be^{2+} , Mg^{2+} , and Ca^{2+} into the trichloromethane solution containing the target polymer. In these experiments, there was no spectral change on adding these metal cations except Ca^{2+} . In the case of Ca^{2+} , the isosbestic point is located about 525 nm, significantly distinct from that with Cu^{2+} at 531.2 nm. As mentioned above, the zwitterionic polymers react with metal ions to

form stable complexes, resulting in altered optical properties. The extension of the optical change depends not only on the metal ions but also on their solubilities in solvents; for example, the solubility of calcium perchlorate tetrahydrate might be less soluble than copper perchlorate hexahydrate in trichloromethane. This phenomenon of a color change for a polysquaraine induced by a metal ion implies a prospective practical technical application as a sensor [29–31,36,37].

Metal ions play a key role in the structural transformation of zwitterionic polymers in solution; without cations, such an altered structure for these CP generally does not occur. To investigate this structural transformation by other processes, we performed experiments using poly(3-octylpyrrole)squaraine involving a heterogeneous, rather than homogeneous, mechanism, such as that involving the metal ions described above. We inserted metal plates or gauzes into the solution of poly(3-octylpyrrole)squaraine, but observed no color change for metals Al, Co, Ni, Mo, Pd, Sn, Ta, W, Re, Au and stainless-steel, whereas metals Fe, Cu, Zn, Rh, Pt, Ag and Pb produced a change. With metal plates of Zn, Pt, Ag, and Pb, the absorption spectra altered slightly over a protracted period. For example with an Ag plate, after 40 h the intensity of the band at

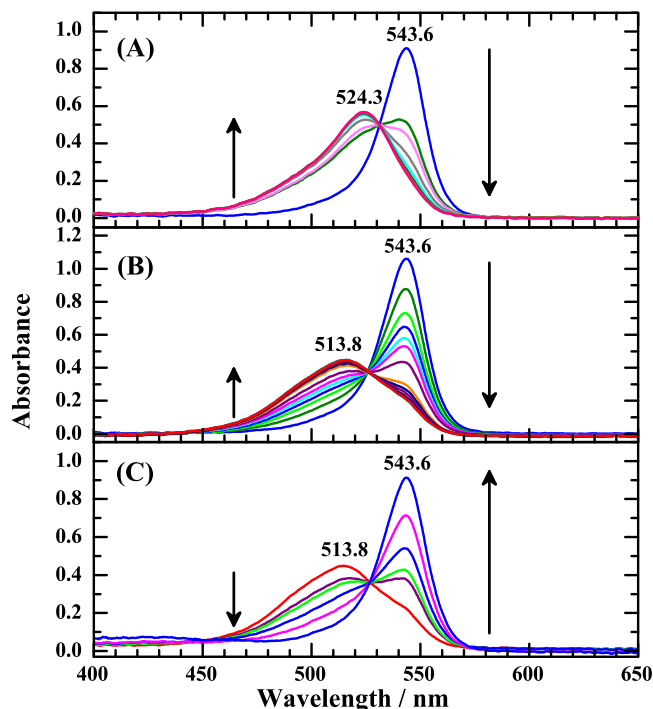


Figure 1. Temporal variation of the visible absorption spectrum of poly(3-octylpyrrole)squaraine in trichloromethane (concentration 3.5 mg/L) in a silica cell (optical path 1 cm), (A) to which was added a saturated solution (10 μL) of Cu^{2+} in trichloromethane: before addition (blue curve) and 180 min after addition (red curve); (B) copper gauze was added to the solution: before addition (blue curve) and 60 min after addition (red curve); (C) after removal of copper gauze from process (B) following ultrasonic agitation (40 kHz, 25 min): before agitation (red curve) and after agitation (blue curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

543.6 nm decreased about 10% and the intensity near 500 nm increased perceptibly.

For added metal plates or gauzes of Fe, Cu and Rh, the visible absorption spectrum of the polymer solutions altered markedly. With Cu gauze (100 mesh, diameter 0.11 mm and mass 2.133 g) in a cell (concentration 3.5 mg/L, liquid volume 3 mL, optical path 1.0 cm) for example, a pronounced variation over 60 min at 23 °C shows that the original feature (maximum at 543.6 nm) gradually decreased, becoming replaced with another broad feature (maximum at 513.8 nm), as shown in Figure 1B. All these absorption spectra retain an isosbestic point at 525.8 nm. The rates of intensity decrease at 543.6 nm and intensity increase at 513.8 nm are sensitive to temperature, increasing with increasing temperature. With the same quantity of copper gauze, the color change was completed in less than 30 min at 50 °C.

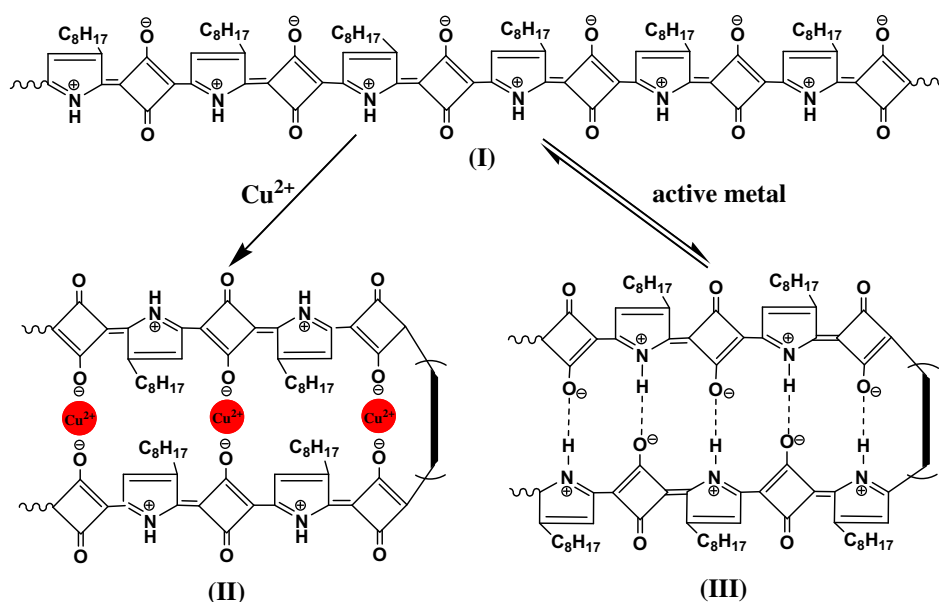
As the spectral variations shown in Figure 1A and B are similar, they likely share a common cause, although the former was induced with metal ion and the latter with a metal surface. To interpret the color transformation of organic dyes and related polymers induced by metal ions, authors have proposed altered structures: the molecular carrier of the spectrum dissolves as a linear form, which turns into a folding structure on binding with a metal ion [28–31]. In this similar case, as the interaction between squaraine and the metal ion produces distinct optical properties, the color change reveals the extent of the transformation, which accounts for the altered spectra in Figure 1A. Scheme 1 illustrates the proposed transformation of the molecular structure of poly(3-octylpyrrole)squaraine caused by Cu^{2+} ; the linear backbone of this polymer represented as formula I converts to a folded complex with Cu^{2+} ion as formula II. In such modification of conformation caused by a cation, the metal ion plays a key role.

The visible absorption spectra of solution samples containing the monomers did not change by adding the metal ions or in the presence of active metals. Then, how can one explain the different optical phenomena for the target polymer induced by a metal surface in contact with the solution? The spectral changes imply that an alteration of the polymer's conformation is occurring in these separate processes. One plausible explanation of this phenomenon is that the presence of a heterogeneous metal causes the polysquaraine to pack in such a way so as to induce aggregation; such aggregation would lead to a blue-shift and broadening of the

absorption spectrum. However, the observation of spectral changes for the target polysquaraine is not associated to aggregation of polysquaraine. As mentioned above, the rates of spectral changes induced by active metals are sensitive to temperature, increasing with increasing temperature. Therefore, this temperature effect of the spectral change excludes the possible route from aggregation; which should reveal the different temperature behavior of the spectral changing rates, decreasing with increasing temperature. Then, folding closure accompanied spectral changes of this polymer might occur induced by metal surface. From analysis of the detailed temperature dependent experiments induced by active metals, the relative rates ($\ln k$) of spectral changes vs. temperature factor (T^{-1}) followed the linear relationship, consistent with a barrier of activation for the process accompanying the conformational isomerization.

Infrared spectra provide information about the conformational structure of polysquaraine in solution. Figure 2 displays absorption spectra of the liquid samples. As shown in Figure 2A, although the solvent trichloromethane has strong absorption in the mid-IR region and perturbs the measurements for dissolved samples, it is still possible to obtain structural information on careful examination. The difference absorption spectra of a polysquaraine sample in trichloromethane without and with a copper plate are plotted in Figure 2B and C, respectively.

Apart from artefacts produced by imperfect subtraction of trichloromethane in both spectra, a major new feature appears at 1602 cm^{-1} , which is assigned to the functional group of the zwitterionic carbonyl of this polysquaraine sample [32,38–41]. A notable difference between these two spectra is a line at 3365 cm^{-1} that appears only in Figure 2C, and that is assigned to the OH-stretching mode of an intramolecular hydrogen bond [42]. Scheme 1 also illustrates the proposed molecular structures of the isomerization of poly(3-octylpyrrole)squaraine induced by an active metal; the intramolecular hydrogen bonds are schematically depicted in the folded conformation as in formula III. As discussed above and shown in formula I, the carrier of the polysquaraine sample exists in trichloromethane with a linear backbone structure that contains no OH functional group, consistent with its absence from Figure 2B, whereas in the presence of the copper plate or gauze this polysquaraine sample has a folded structure; the negatively charged $-\text{O}^-$ then bonds to the positively charged $-\text{NH}^+$ to form



Scheme 1. Structural transformation of poly(3-octylpyrrole)squaraine induced by Cu^{2+} and an active metal depicted in molecular structures.

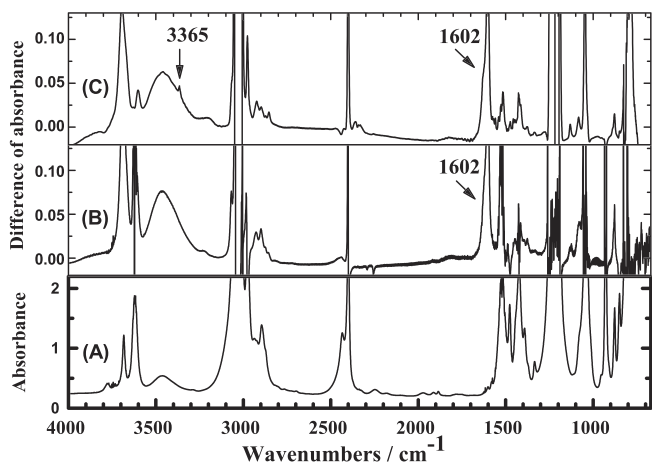


Figure 2. IR spectra: (A) absorption of trichloromethane (optical path 1 mm); difference of absorption of poly(3-octylpyrrole)squaraine in trichloromethane solution, (B) no metal plate, and (C) with a Cu plate.

an intramolecular hydrogen-bonded O–H group, revealed through its characteristic absorption at 3365 cm^{-1} in Figure 2C.

As mentioned above, this polysquaraine solution exhibited a similar variation of the conformation induced by both cations and some active metal plates, but this zwitterionic polymer might fold its structure in two distinct ways. While the polysquaraine reacts with a cation and folds its structure, the negative charge of O^- binds to the cation; in this case, no OH group is formed in the complex. The difference IR absorption spectrum of poly(3-octylpyrrole)squaraine with added Cu^{2+} cations in trichloromethane possessed no such OH band. The evidence from the IR spectra thus confirms the distinct conformational changes of this polysquaraine sample induced by cations and by the surfaces of active metals.

Experiments of X-ray scattering at small angles produce further evidence supporting the isomerization of the target polymer in solution induced by an active metal. We performed these measurements of poly(3-octylpyrrole)squaraine in trichloromethane solution with stainless-steel and copper cells attached to beam line 23A at NSRRRC [35]. As mentioned above, stainless-steel is not an active metal for the isomerization of this polymer in solution, consistent with the SAXS curve remaining constant with time. In contrast, the SAXS profiles of solution for poly(3-octylpyr-

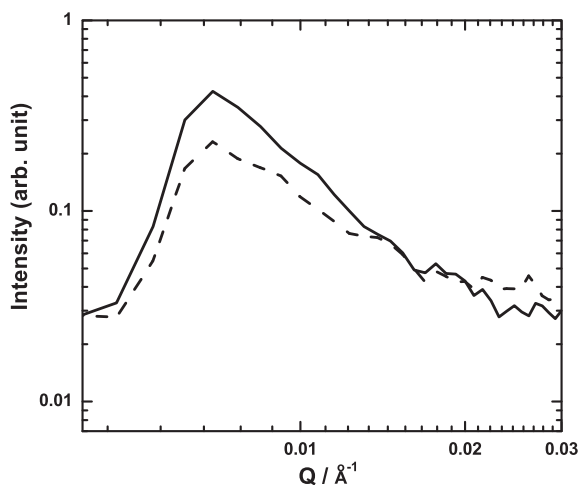


Figure 3. SAXS profiles of poly(3-octylpyrrole)squaraine in trichloromethane solution in a copper cell at initial (solid line) and final (dotted line) stages.

role)squaraine in a copper cell varied with time, as shown in Figure 3. The initial SAXS curve of polymer solution in the copper cell, displayed as a solid line, was similar to that for the stainless-steel cell, but it gradually altered and eventually became the dotted curve in Figure 3. The radius of gyration (R_g) of the polymer was determined from the plot of $\ln I(Q)$ versus Q^2 in the small- Q range; the value of R_g is extracted from the slope ($-R_g^2/3$) of this plot. By this means, we obtained the values for the polymers to be $R_g = 22 \pm 2\text{ nm}$ at the initial state and $16 \pm 2\text{ nm}$ at the final stage in the copper cell. This result unambiguously demonstrates that two conformers exist in solution, likely the linear and folded forms for this zwitterionic polymer.

One notable feature of the structural transformation of this zwitterionic polymer with metal ions is its irreversibility. Once the structure of this CP proceeds to alter through interaction with cations, it is difficult to remove the cations from the solution and so to have the structure revert to the original conformation. For the altered structure induced by metal surfaces, those surfaces are readily removed from the solution containing the zwitterionic polymer; the conformation of the polymer might then revert to its original form when the active metal is absent. On removing the metals from the solution, the visible absorption band of the solution reverted from 513.8 nm to 543.6 nm . The rates of intensity decrease at 513.8 nm and intensity increase at 543.6 nm are sensitive to temperature, increasing with increasing temperature, but the reverse process is slow: completion at 50°C required more than 24 h, but ultrasonic agitation decreases this duration. For this backward process, intra-hydrogen bonds in the folded polymer need to be broken to the O^- and the NH^+ moieties eventually by acquiring energy on collisions; without perturbation, the backward process is thus slow in the free standing solution. Figure 1C shows this phenomenon; on removing the metal plate from the solution in which it had been inserted, the absorption at 513.8 nm of the polymer solution with immersed Cu plate became replaced with the line at 543.6 nm on ultrasonic agitation for 25 min. As discussed above, the reversibility of this absorption behavior implies that the conformation of the polymer induced by the metal likewise reverted to its original structure in solution.

Reinserting the copper plate or gauze into the solution again shifted the absorption maximum of the target polymer from 543.6 nm to 513.8 nm . The conformation of the zwitterionic polysquaraine is thus reversible, back and forth, depending on the presence or absence of an active metal. We thus reversibly control the conformation of this CP with this simple heterogeneous process without altering the chemical environment in solution, whereas

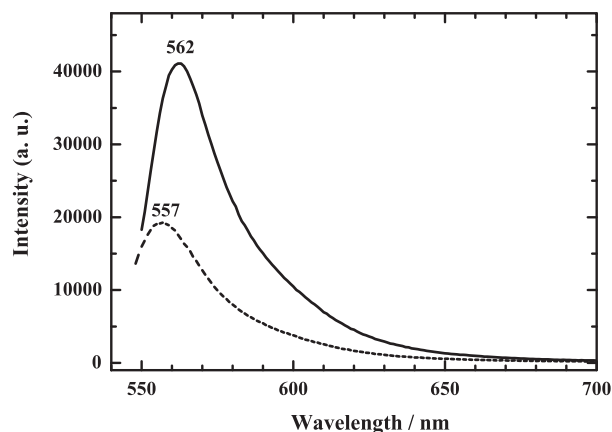


Figure 4. Photoluminescent spectra of poly(3-octylpyrrole)squaraine in trichloromethane solution: (solid line) no metal plate and (dashed line) with a Cu plate.

adding metal ions to the polymer solution causes an irreversible change of the chemical environment and the structure for this CP. The isomerization of this polysquaraine induced with a metal surface modified the optical properties, not only the visible absorption spectra described above but also the emission spectra. Figure 4 displays photoluminescent spectra of this polymer in trichloromethane; the emission maximum shifted from 562 nm to 557 nm accompanying the conformational change induced with the copper plate. The quantum yield of this polysquaraine with the linear structural conformation reduced to 47% as that of folded one. Regarding the PL yields for comparison, we used 2,3-benzanthracene as an external standard under the same optical conditions. Based on the PL intensity of 2,3-benzanthracene at 478 nm, the relative quantum yields of the linear and folded target polymers are 2.23 and 1.07, respectively. This optical-switching property of a CP induced by active metals has prospective applications. Our findings provide an impetus for the investigation of the structural modification of similar CP and the structural dynamics of their polymer chains in solution. Applying these polymer solutions to substrates, these CP might retain their specific structures in the solid after removal of a solvent. The properties and applications of these various films remain virgin territory, for which further exploration.

4. Conclusion

As synthesized, poly(3-octylpyrrole)squaraine is a conducting polymer with mostly a zwitterionic repeating unit. The visible absorption feature of polysquaraines induced by both cations and some active metal plates exhibits a similar blue-shift. This color change implies a variation of the conformation in solution; the zwitterionic polymer might fold its structure in two distinct ways. Unlike the irreversible change induced by cations in solution, the folded structure induced by active metal plates reverts to its original conformation on removal of the metal surfaces; evidence from IR, visible and photoluminescent spectra and SAXS curves unambiguously confirms the structural alteration of this polysquaraine. This observation of a reversible structural modification, accompanying altered optical properties, for the zwitterionic polysquaraine induced by active metal plates is unprecedented; it represents a new chemical and physical process, and it has a potential to lead to the discovery of significant knowledge about the interactions of polymers with metal surfaces, the dynamics and the energetics of polymer conformations.

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References

- [1] Y.J. Cheng, S.H. Yang, C.S. Hsu, *Chem. Rev.* 109 (2009) 5868.
- [2] H.A.M.V. Mullekom et al., *Mater. Sci. Eng.* 32 (2001) 1.
- [3] D.T. McQuade, A.E. Pullen, T.M. Swager, *Chem. Rev.* 100 (2000) 2537.
- [4] H.E. Sprenger, W. Ziegenbein, *Angew. Chem. Int. Ed.* 7 (1968) 530.
- [5] K.Y. Law, *J. Phys. Chem.* 91 (1987) 5184.
- [6] J. Eldo, A. Ajayaghosh, *Chem. Mater.* 14 (2002) 410.
- [7] G. Brocks, A. Tol, *J. Phys. Chem.* 100 (1996) 1838.
- [8] A. Ajayaghosh, *Acc. Chem. Res.* 38 (2005) 449.
- [9] A. Ajayaghosh, *Chem. Soc. Rev.* 32 (2003) 181.
- [10] J.H. Yum et al., *J. Am. Chem. Soc.* 129 (2007) 10320.
- [11] C. Li, W. Wang, X. Wang, B. Zhang, Y. Cao, *Chem. Lett.* 34 (2005) 554.
- [12] T. Geiger et al., *Adv. Funct. Mater.* 19 (2009) 2720.
- [13] U. Mayerhöffer et al., *Angew. Chem. Int. Ed.* 48 (2009) 8776.
- [14] K.Y. Law, *Chem. Rev.* 93 (1993) 449.
- [15] M. Emmelius, G. Pawlowski, H.W. Vollmann, *Angew. Chem. Int. Ed.* 28 (1989) 1445.
- [16] L. Beverina et al., *J. Am. Chem. Soc.* 130 (2008) 1894.
- [17] K.T. Arun, D. Ramaiah, *J. Phys. Chem. A* 109 (2005) 5571.
- [18] K.J. Wallace, *Supramol. Chem.* 21 (2009) 89.
- [19] K.D. Volkova et al., *Dyes Pigm.* 72 (2007) 285.
- [20] E. Arunkumar, P. Chithra, A. Ajayaghosh, *J. Am. Chem. Soc.* 126 (2004) 6590.
- [21] Y. Chandrasekaran, G.K. Dutta, R.B. Kanth, S. Patil, *Dyes Pigm.* 83 (2009) 162.
- [22] S. De, S. Ramakrishnan, *Macromolecules* 42 (2009) 8599.
- [23] K. Jyothish, M. Hariharan, D. Ramaiah, *Chem. Eur. J.* 13 (2007) 5944.
- [24] R.S. Stoll, N. Severin, J.P. Rabe, S. Hecht, *Adv. Mater.* 18 (2006) 1271.
- [25] C. Lorf, P. Suppan, *J. Chem. Soc. Faraday Tans.* 88 (1992) 963.
- [26] A.J. McKerrow, E. Bunce, P.M. Kazmaier, *Can. J. Chem.* 73 (1995) 1605.
- [27] K.Y. Law, *J. Phys. Chem.* 93 (1989) 5925.
- [28] E. Arunkumar, A. Ajayaghosh, J. Daub, *J. Am. Chem. Soc.* 127 (2005) 3156.
- [29] S. Yagi et al., *Org. Lett.* 9 (2007) 1999.
- [30] M.A.B. Block, S. Hecht, *Macromolecules* 37 (2004) 4761.
- [31] W. Wang, A. Fu, J. Lan, G. Gao, J. You, L. Chen, *Chem. Eur. J.* 16 (2010) 5129.
- [32] H.-C. Lu, W.-T. Whang, B.-M. Cheng, *Synth. Met.* 160 (2010) 1002.
- [33] A. Treibs, D.C.K. Jacob, *Angew. Chem. Int. Ed.* 4 (1965) 694.
- [34] C.R. Chenthamarakshan, J. Eldo, A. Ajayaghosh, *Macromolecules* 32 (1999) 251.
- [35] D.-G. Liu et al., *J. Synchr. Rad.* 16 (2009) 97.
- [36] M.C. Basheer, S. Alex, K.G. Thomas, C.H. Suresh, S. Das, *Tetrahedron* 62 (2006) 605.
- [37] J.J. McEwen, K.J. Wallace, *Chem. Commun.* (2009) 6339.
- [38] G.J. Ashwell et al., *Thin Solid Films* 327–329 (1998) 461.
- [39] D.E. Lynch, U. Geissler, K.A. Byriel, *Synth. Met.* 124 (2001) 385.
- [40] Y.Y. Chen, H.K. Hall, *Polym. Bull.* 16 (1986) 419.
- [41] D.E. Lynch et al., *J. Chem. Soc., Perkin Trans. 2* (1997) 827.
- [42] F.J. Boerio, S. Wirasate, in: N.J. Everall, J.M. Chalmers, P.R. Griffiths (Eds.), *Vibrational Spectroscopy of Polymers: Principles and Practice*, Wiley, Chichester, 2007, p. 113.