

Photoregulated Complexation, Redox Behavior, and Photoluminescence of a Supramolecular Polymer Solution

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ABSTRACT: Reported in this paper is a new finding based on a spectroscopic and electrochemical study of a supramolecular polymer in dilute solution. Dissolved in a mixture of dichloromethane and acetonitrile, zinc-tetraphenylporphyrin (ZnTPP) can complex with a polymethacrylate bearing an azopyridine moiety (AzPy) through the axial coordination between the metal and pyridyl group. The self-assembled polymer (PAzPy-ZnTPP) displays different photoluminescence and redox behaviors compared with those of noncomplexed ZnTPP. Moreover, the reversible trans-cis-photoisomerization of azopyridine upon UV and visible light irradiation was found to alter the equilibrium of

the axial coordination between azopyridine and ZnTPP in solution, resulting in photoregulable redox potentials and fluorescence emission of the metalloporphyrin. The results suggest that supramolecular polymer solutions could enhance the mechanism of photoinduced change in the degree of complexation, which gives rise to a phenomenon of photoregulation of the electrochemical and optical properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 744–750, 2006

Key words: supramolecular polymer; azo polymer; photoregulation; photoluminescence; self-assembly

INTRODUCTION

Molecular self-assembly through noncovalent chemical bonding such as H-bond, coordination interaction, and π - π stacking has become a powerful tool in developing new functional polymers.^{1–5} Such supramolecular polymers sometimes may exhibit interesting properties arising from the dynamic nature of the noncovalent interactions.^{6,7} We have recently studied polymers bearing an azopyridine moiety in the side-chain.^{8,9} While retaining the trans-cis-photoisomerization characteristic of azobenzene and its derivatives, the azopyridine moiety enables self-assembly through H-bonding between the pyridyl group and H-bond donors and through coordination between pyridine and transition metal containing compounds. Our previous studies showed that the complexation of an amorphous azopyridine polymer with various commercially available carboxylic acids can readily transform the polymer into a series of photoactive liquid crystalline polymers with different LC phases and properties.⁸ Moreover, using the amorphous azopyridine polymer as a building block for block copolymers, the easy complexation with acids or zinc-tetra-

phenylporphyrin (ZnTPP) gives rise to multifunctional block copolymers that are photoactive and liquid crystalline (H-bonding with acids), or photoactive and electroactive (coordination with the metalloporphyrin).⁹

In this article, we report a new finding issued from a spectroscopic and electrochemical study of the supramolecular polymer PAzPy-ZnTPP in dilute solution, which is different from previous works^{8,9} dealing with polymers in the solid state. The present study finds that in solution, the polymer with azopyridine in the trans-form does not have the same complexation degree (via the axial coordination) with ZnTPP as the polymer with azopyridine in the cis-form (Fig. 1). This difference results in reversible changes in the redox and photoluminescence properties of the polymer solution upon UV and visible light irradiation. Photoinduced regulation or modulation of luminescence of small-molecules in solution has been much studied,^{10–13} However, few examples are known for polymers, and in those known systems,^{14,15} a fluorophore and a photoisomerizable chromophore are covalently linked together in the polymer structure. We are not aware of reports on supramolecular polymers such as PAzPy-ZnTPP studied in this work, which displays photoregulable redox and fluorescence as a result of changes in equilibrium of the dynamic, labile axial coordination between the fluorophore (ZnTPP) and the photoisomerizable chromophore (azopyridine) in solution.

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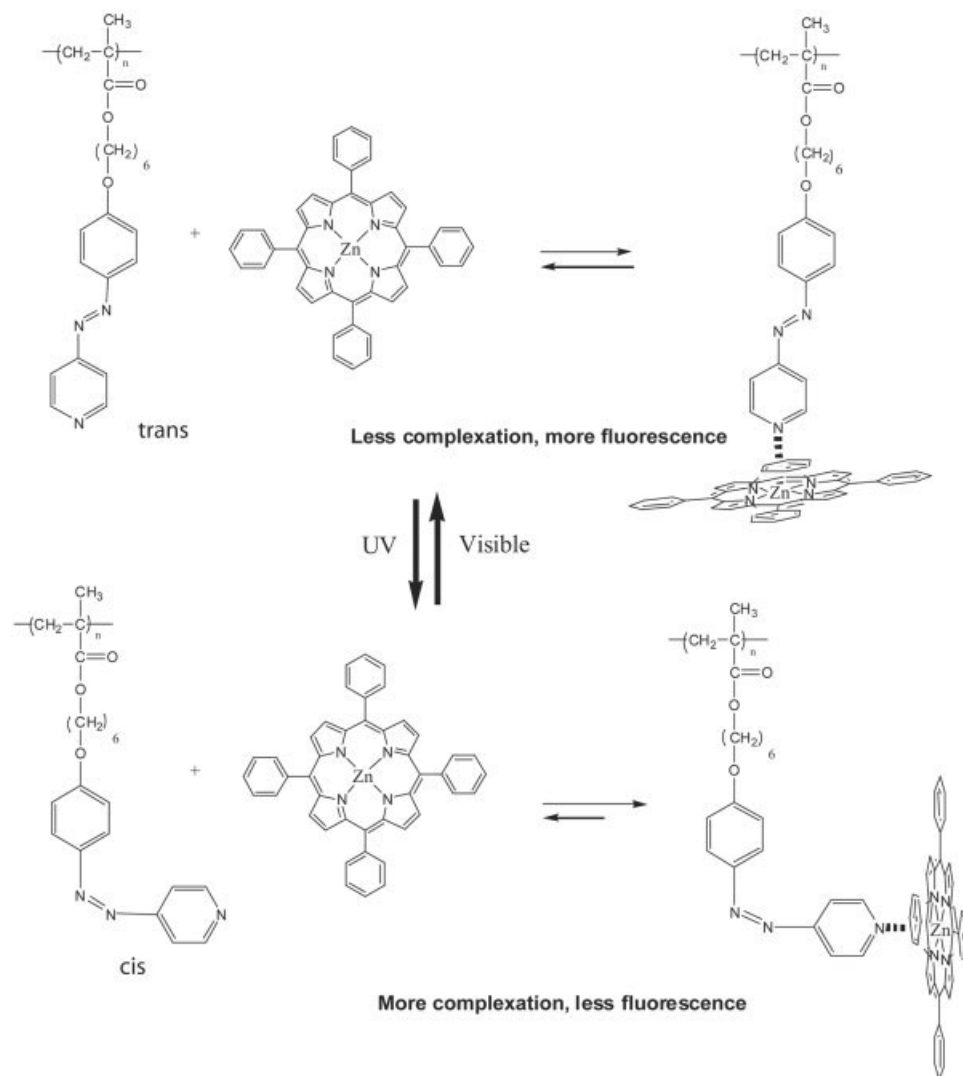


Figure 1 Self-assembly of the supramolecular polymer PAzPy-ZnTPP in dilute solution through axial coordination of zinc-tetraphenylporphyrin (ZnTPP) with the azopyridine polymer (PAzPy); the photoisomerization of azopyridine between trans- and cis-isomers upon UV and visible light irradiation being found to affect the complexation degree.

EXPERIMENTAL

The synthesis of the side-chain azopyridine polymer PAzPy was previously reported.⁸ The sample used in this study has $T_g = 33^\circ\text{C}$ (measured using DSC, scan rate = $10^\circ\text{C}/\text{min}$), $M_n = 12,600$ g/mol and $M_w/M_n = 1.8$ (data of GPC, using polystyrene standards and THF as eluent). The complexation of PAzPy with zinc-tetraphenylporphyrin (ZnTPP, purchased from Aldrich) was investigated by first dissolving ZnTPP in a mixture of dichloromethane (CH_2Cl_2) and acetonitrile (CH_3CN) (1/5 v/v), at a concentration $1.0 \times 10^{-6}\text{M}$ for optical measurements and $1.4 \times 10^{-4}\text{M}$ for cyclic voltammetry (CV) measurements, which was followed by adding a CH_2Cl_2 solution of PAzPy (concentration: 1 mg/mL) to reach a predetermined molar ratio of azopyridine groups to ZnTPP molecules (AzPy/ZnTPP). Before all measurements, the compl-

exation was allowed to reach the equilibrium by thoroughly mixing the two solutions under stirring.

UV-Vis absorption spectra of the solutions were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. The solution was placed in a standard cuvette that was closed to prevent the solvent evaporation during the measurement. Steady-state fluorescence emission spectra were obtained using a SPEX Fluorolog-2 photofluorometer. Fluorescence emission lifetimes were measured using a nanosecond N_2 laser system from PTI model GL-3300 pumping a dye laser (fwhm ~ 1500 ps). The excitation wavelength was 555 nm and the emission wavelength was 605 nm for ZnTPP. Samples for these measurements were prepared under inert atmosphere (in a glovebox, $\text{P}_{\text{O}_2} < 1\text{--}3$ ppm) by dissolution of different compounds in the mixed solvent used. CV was performed

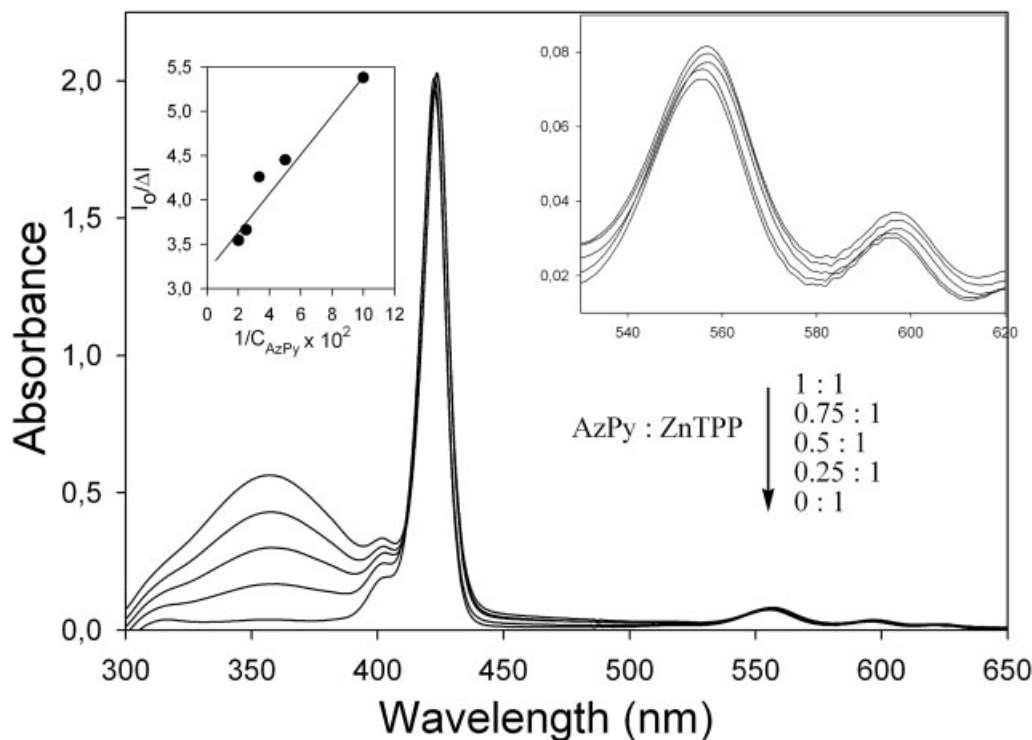


Figure 2 UV-Vis spectra of ZnTPP and PAzPy-ZnTPP in dilute solution (concentration of ZnTPP = $1.0 \times 10^{-6} M$, the amount of polymer added is indicated by the molar ratio of AzPy/ZnTPP). Inset on the right corner shows the red-shift of the Q-bands of ZnTPP due to the axial coordination, while inset on the left corner is a plot of changes in absorbance of the Soret band of ZnTPP as a function of the concentration of azopyridine groups, being used to estimate the coordination constant (see text for details).

on a potentiostat/galvanostat (Princeton Applied Research, model 263A) controlled by an external PC (Research Electrochemistry software 4.23), to which was connected a three-electrode system; the working electrode was a vitreous carbon disk (5 mm diameter), which was polished with an aqueous alumina slurry and sonicated in distilled water and rinsed with acetone after each polishing step. The CV measurements were conducted in the $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solution with 0.1M of tetrabutylammonium perchlorate (TBAP), scan rate being 100 mV/s. Irradiation of samples was performed using an UV and visible spot curing system (Novacure 2100) combined with interference filters (10 nm bandwidth, Oriol). UV light at $\lambda = 365$ nm (~ 20 mW/cm²) and visible light at $\lambda = 440$ nm (~ 17 mW/cm²) were used for irradiations.

RESULTS AND DISCUSSION

Figure 2 shows the UV-Vis spectra of ZnTPP in solution and its mixture with the polymer at various molar ratios of AzPy/ZnTPP. As more PAzPy is added in the solution of ZnTPP, the absorption of azopyridine groups in the *trans*-form around 355 nm (π - π^* transition) becomes more prominent. The occurrence of the axial coordination in the dilute solution between

the metal center and the pyridyl group, leading to the supramolecular polymer PAzPy-ZnTPP (Fig. 1), is indicated by the characteristic red-shift, better visible in the insert, of the Q-bands (~ 556 and 595 nm) as well as an increase in intensity and red-shift of the Soret band (~ 423 nm) of ZnTPP.^{16,17} Another inset of Figure 2 shows the plot of $I_o/\Delta I$ versus concentration of pyridine groups, I_o and ΔI being the absorbance of the Soret band of neat ZnTPP and the increment of absorbance in the presence of PAzPy. From this Benesi-Hildebrand plot¹⁸, the association constant of ZnTPP with *trans*-PAzPy in this dilute solution (Fig. 1) was found to be about $4.6 \times 10^2 M^{-1}$, which indicates an equilibrium between ZnTPP coordinated with PAzPy and free ZnTPP.¹⁷

The steady-state fluorescence emission spectra of ZnTPP of the same solutions as in Figure 2 are shown in Figure 3. At the used excitation wavelength of $\lambda_{\text{ex}} = 555$ nm, azopyridine has no absorption. The fluorescence intensity of ZnTPP decreases with increasing the amount of the azopyridine polymer. This result is consistent with a previous report that 4-(phenylazo)pyridine, which is the azopyridine moiety in the polymer without the substituent at the para position of the benzyl ring, is an effective fluorescence quencher for ZnTPP if axially coordinated to the metalloporphyr-

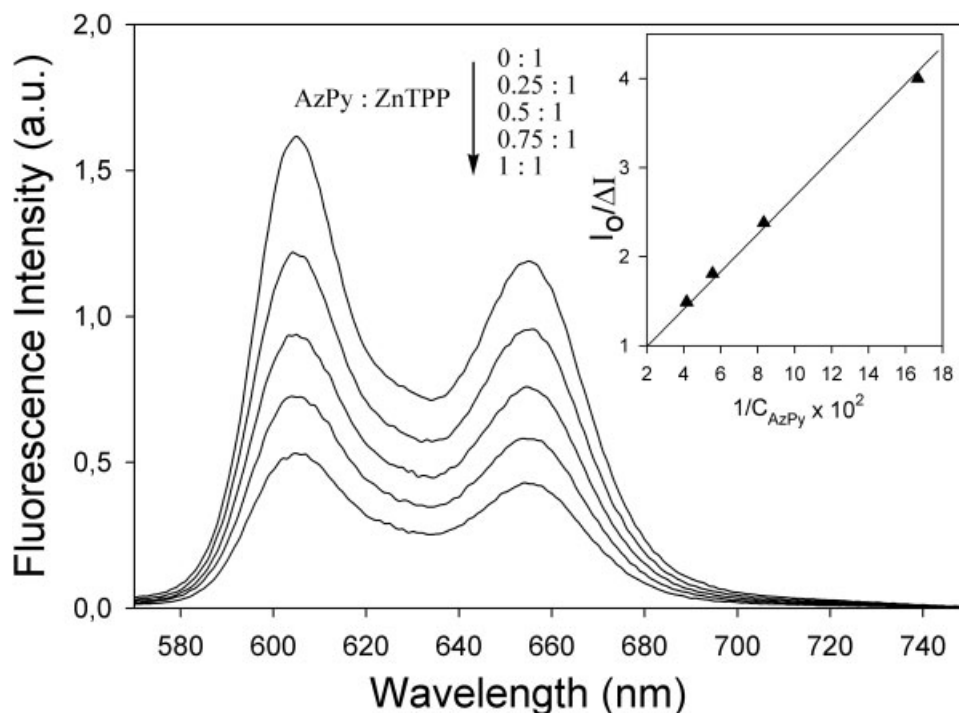


Figure 3 Fluorescence emission spectra of the same solutions of ZnTPP and PAzPy-ZnTPP as in Figure 2 (excitation at 555 nm). Inset is a plot of changes in fluorescence intensity as a function of the concentration of azopyridine groups, being used to estimate the coordination constant (see text for details).

rin.¹⁹ A process of electron transfer from excited ZnTPP to azopyridine was suggested as what causes the fluorescence quenching of ZnTPP, even though the actual mechanism remains unclear.¹⁹ The continuous decrease in fluorescence of ZnTPP with the successive addition of the polymer reaching AzPy/ZnTPP = 1 indicates that as more azopyridine groups became available more ZnTPP molecules were complexed with PAzPy through axial coordination, forming the supramolecular polymer even in the dilute solution. The association constant can also be obtained from changes in fluorescence by plotting $I_0/\Delta I$ versus concentration of pyridine, where I_0 is the fluorescence intensity of neat ZnTPP and ΔI is the decrease of fluorescence in the presence of PAzPy.¹⁷ The result shown in the inset gives an association constant of $5.0 \times 10^2 M^{-1}$, which is very similar to that measured from UV-Vis spectra (Fig. 2). In yet another control experiment aimed at making sure that the fluorescence quenching was due to the complexation, ZnTPP was dissolved in an azobenzene (not azopyridine) polymer solution at 1:1M ratio of Azo/ZnTPP; no fluorescence quenching of ZnTPP was observed. We note that similar UV-Vis and fluorescence spectral changes due to the complexation between ZnTPP and PAzPy were also observed with other solvents such as CH_2Cl_2 , chloroform, and THF.

The CV measurements were performed using supramolecular polymer solutions of higher concentra-

tions (but still in the dilute regime) to have observable redox potentials of ZnTPP. The results in Figure 4 clearly reveal the effect of complexation. When compared with neat ZnTPP that displays the characteristic two peaks of oxidation/reduction,²⁰ the axial coordination with PAzPy apparently affects little the first oxidation peak (around 0.83 V, formation of radical cation) but results in important change of the second oxidation peak at about 1.15 V (formation of dication),

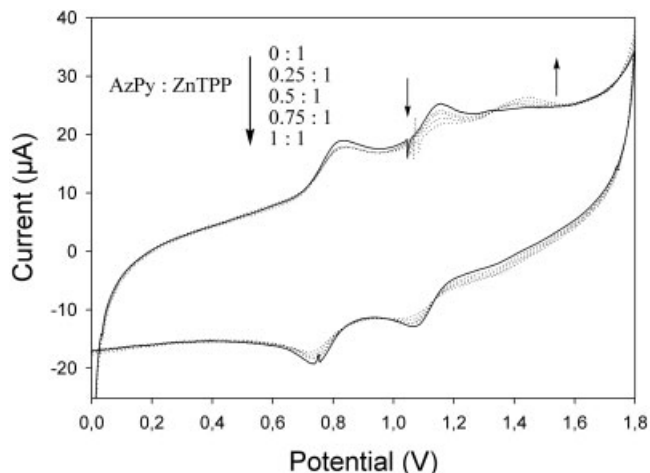


Figure 4 Cyclic voltammetry for dilute solutions of ZnTPP ($1.4 \times 10^{-4} M$) and PAzPy-ZnTPP (with the same molar ratios of AzPy/ZnTPP as in Fig. 2).

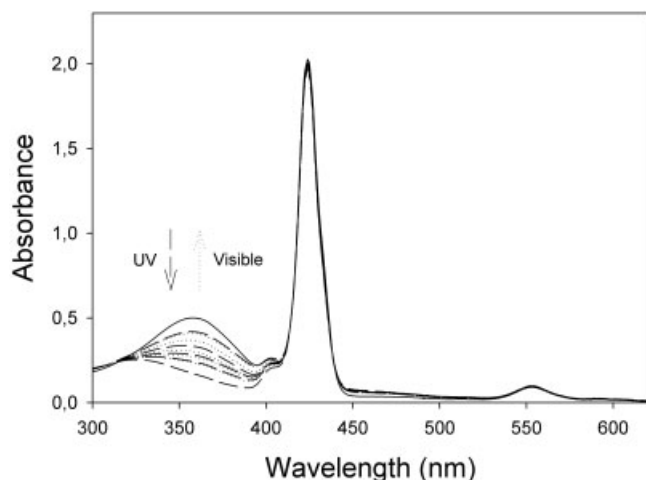


Figure 5 UV-Vis spectra of PAzPy-ZnTPP with 1:1M ratio exposed to UV and visible light irradiation (various irradiation times from 1 to 5 min), showing thorough trans-cis-photoisomerization of azopyridine in the solution.

as the latter is replaced by a new peak at higher potential of about 1.44 V. Indeed, as more ZnTPP molecules are complexed with increasing the molar ratio of AzPy/ZnTPP, the peak at 1.15 V diminishes its intensity while the peak at 1.44 V becomes more important. It appears clear that the new higher-potential peak should be attributed to ZnTPP coordinated with PAzPy, and that the remaining peak at 1.15 V is determined by the amount of noncomplexed (free) ZnTPP in solution. Upon complexation, the increase in the second oxidation potential (formation of dication from radical cation) is much greater than the shift of the first oxidation potential (formation of radical cation from neutral ZnTPP). This observation suggests that after one electron is lost from ZnTPP coordinated with PAzPy, the radical-cation of ZnTPP could have greater interaction or higher affinity with PAzPy than ZnTPP, rendering the loss of a second electron more difficult and thus requiring an increased oxidation potential. The effect of complexation can also be noticed from changes in reduction potentials though less clear. Note that under the same conditions, pure polymer PAzPy showed no oxidation/reduction peaks, indicating that azopyridine cannot be oxidized within the used range of potential.

The supramolecular polymer formed in solution thus has the azopyridine moiety linked to ZnTPP. We wanted to know if the trans-cis-photoisomerization of azopyridine could exert an effect of regulation on the fluorescence of ZnTPP. For these experiments, the complex of PAzPy-ZnTPP with the molar ratio AzPy/ZnTPP = 1 was used. Unlike in the solid state,²¹ because of the dynamic nature of the axial coordination in solution, the bulky ZnTPP cannot hamper the reversible photoisomerization of azopyridine, which results in a large geometrical change of the chro-

mophore. Indeed, the UV-Vis spectra of the solution (Fig. 5) show nearly a complete trans-to-cis photoisomerization upon UV irradiation, judging from the disappearance of the absorption peak of *trans*-azopyridine around 355 nm in the photostationary state (after 5 min UV irradiation). Upon visible light irradiation, the reverse cis-to-trans photoisomerization takes place resulting in the recovery of the absorption peak (5 min visible irradiation). The concomitant change of the low-intensity absorption peak of *cis*-azopyridine around 440 nm ($n-\pi^*$ transition) is barely noticeable in the vicinity of the intense Soret band of ZnTPP. As azopyridine undergoes the photoisomerization process, no significant changes of the absorption bands of ZnTPP could be observed.

However, as shown in Figure 6, reversible changes in fluorescence emission of ZnTPP do occur as a result of the reversible trans-cis-photoisomerization of azopyridine. The fluorescence intensity decreases upon UV light irradiation (with *cis*-azopyridine) and recovers, though not completely, upon visible light irradiation of the solution (with *trans*-azopyridine). After UV irradiation, the recovery of fluorescence was also observed when the solution was kept in dark for a couple of hours, during which thermal relaxation of *cis*-azopyridine occurred. These results indicate that the photoregulable fluorescence of ZnTPP was related to the photoisomerization of PAzPy. As mentioned above, prior to UV irradiation, the PAzPy-ZnTPP complex with 1:1M ratio exhibited the largest decrease in fluorescence emission, when compared with pure ZnTPP (Fig. 3) due to coordinated *trans*-azopyridine acting as a quencher for ZnTPP.¹⁹ For this complex, the observed further quenching of fluorescence

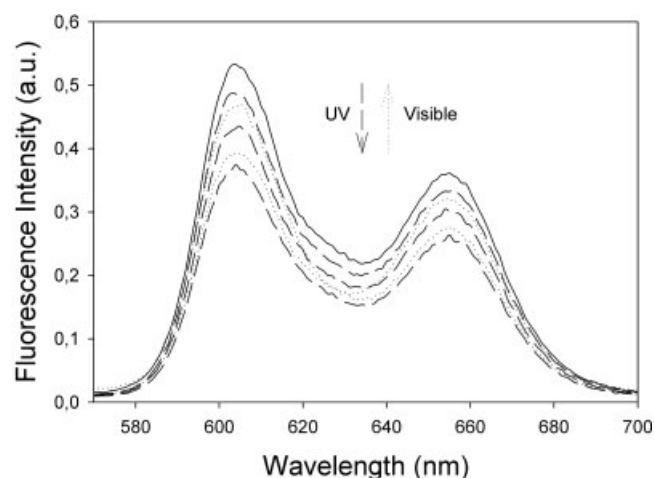


Figure 6 Fluorescence emission spectra of PAzPy-ZnTPP with 1:1M ratio exposed to UV and visible light irradiation (three UV irradiation times at 1, 3, and 5 min; two visible irradiation times at 2 and 5 min), showing the reversible change of the fluorescence of ZnTPP as a result of the photoisomerization of azopyridine.

upon UV irradiation that converts *trans*-azopyridine onto *cis*-azopyridine, may imply that coordinated azopyridine in the *cis*-form could be more efficient to quench the fluorescence of ZnTPP than azopyridine in the *trans*-form. There are, however, no experimental evidences that support this hypothesis. We measured the fluorescence lifetimes of ZnTPP in the PAzPy-ZnTPP complex solution before and after UV irradiation and found no change with PAzPy in the *trans*- and *cis*-forms within experimental errors. The fluorescence lifetime of ZnTPP in the complex was about 1.34 ns before UV irradiation and 1.30 ns after UV irradiation (either with the measurement performed on the solution right after 5 min UV irradiation or on the solution under UV irradiation during the fluorescence measurement). This result indicates that azopyridine moieties in the *trans*- and *cis*-form have a similar quenching effect on the fluorescence of ZnTPP. By contrast, the fluorescence quenching of ZnTPP due to coordinated PAzPy was reflected by the decrease in fluorescence lifetime of ZnTPP in the complex solution, when compared with pure ZnTPP under the same conditions (1.43 ns). As a matter of fact, contrary to the supramolecular polymer solution, it was reported that the photoisomerization of the small-molecule azopyridine compound, 4-(phenylazo)pyridine, axially coordinated to ZnTPP had no effect on the fluorescence quenching efficiency.¹⁹

CV measurements of the PAzPy-ZnTPP solution, following exposure to UV and visible light irradiations, suggest that different degrees of complexation of ZnTPP with the polymer bearing *trans*- and *cis*-azopyridine moieties were at the origin of the photo-regulation of fluorescence. The CV curves of the solution before and after UV and visible light irradiation are shown in Figure 7, with the inset highlighting the changes in the second oxidation peaks for free and coordinated ZnTPP. Though small, the effect of UV irradiation is clear and similar to that observed, by adding more polymer in the ZnTPP solution (Fig. 4), in that the second oxidation peak of free ZnTPP at 1.15 V diminishes its intensity, while the peak of coordinated ZnTPP at 1.44 V becomes more important. Upon visible light irradiation, the trend is reversed, indicating clearly that the reversible changes in oxidation potentials of ZnTPP are related to the reversible photoisomerization of coordinated azopyridine moieties. As more ZnTPP molecules are coordinated with azopyridine in the *cis*-form (after UV irradiation), the fluorescence is more severely quenched (Fig. 6). If the polymer bearing *cis*-azopyridine had the same complexation degree with ZnTPP as the polymer with *trans*-azopyridine, i.e., the number of free ZnTPP molecules remained the same in the solution exposed to UV irradiation, the second oxidation potential of free ZnTPP should not be affected by the *trans*-*cis*-photoisomerization of azopyridine. The results in Figure 7

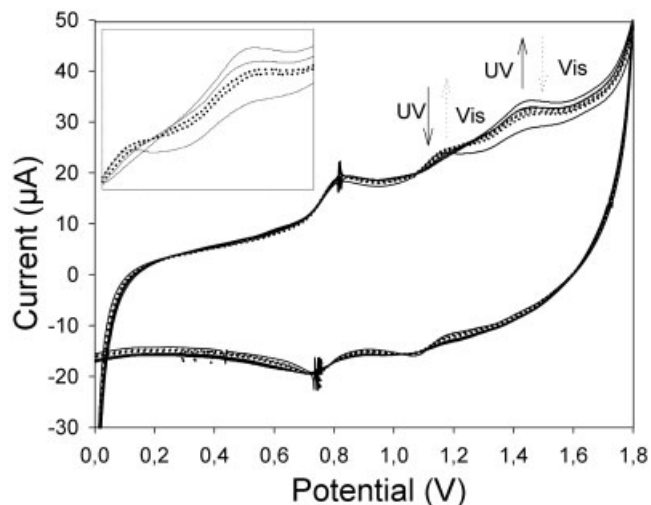


Figure 7 Cyclic voltammetry for the solution of PAzPy-ZnTPP with 1 : 1M ratio exposed to UV and visible light irradiation (two irradiation times at 3 and 5 min), showing reversible changes of the redox potentials of ZnTPP as a result of the photoisomerization of azopyridine.

show that this is not the case. We also noted that pure PAzPy solution exposed to UV light for the *trans*-to-*cis* photoisomerization of azopyridine moieties showed no redox peaks under the used conditions.

Again, the small-molecule 4-(phenylazo)pyridine axially coordinated with ZnTPP in solution displayed no effect of photoisomerization of azopyridine on the fluorescence of ZnTPP.¹⁹ The observed photoregulation of the complexation and, as a result, the redox behavior and the fluorescence of ZnTPP comes from the supramolecular polymer, whose side chain is made of the axially coordinated azopyridine moiety and ZnTPP. There are several possible explanations for a higher complexation degree with *cis*-azopyridine than with *trans*-azopyridine in the polymer solution. First, as illustrated in Figure 1, the geometrical change of azopyridine should result in a change in the position of the plane of ZnTPP relative to polymer chain backbone. Unlike small molecules, the lateral linkage of bulky ZnTPP molecules would be sensitive to the way azopyridine moieties are oriented inside the random coils of polymer chains in the dilute solution. In other words, a reduced steric hindrance with *cis*-azopyridine may favor the axial coordination. The steric effect on the complexation of small molecules, designed to reveal such effects, was used to modulate fluorescence.²² Secondly, it is known that azo polymer solutions may have their viscosity changed significantly upon the photoisomerization of the chromophore, as a result of the configurational change of azobenzene moieties (between rod-like *trans*- and bent *cis*-isomers) which, in turn, affects the polymer conformation.²³ Such a photoviscosity effect may also lead to an alteration of the equilibrium between com-

plexed and free ZnTPP in the polymer solution. Note that the photoregulation effect arising from such a mechanism would be sensitive to many factors including the concentration of the supramolecular polymer. With the dilute solutions used in this study, no NMR spectra were good enough to confirm the photoinduced change in complexation degree between ZnTPP and PAzPy; while at higher concentrations required for NMR measurements, no significant spectral changes were observed before and after UV irradiation.

We emphasize that these possible explanations for the observed photoregulation of complexation, redox potentials, and fluorescence of the metalloporphyrin belong to the supramolecular polymer solution, for which the complexation through axial coordination of ZnTPP with PAzPy may be less efficient than in solutions of small molecules because of the intrinsic properties of polymers. For instance, the spatial arrangement of azopyridine moieties covalently linked to chain backbone is determined by the random-coil conformation of the polymer, and they should have a reduced mobility, when compared with small molecules. Indeed, the complexation of ZnTPP with the azopyridine monomer is much stronger (we found an association constant of about $1.8 \times 10^4 M^{-1}$ under the same conditions as in Fig. 2); however, no photoregulation of the redox behavior was observed for the small-molecule solution. Although the photoregulation effects reported in this paper are small, the results suggest a fundamentally new mechanism for photo-modulation of luminescence, which consists in using the photoisomerization of a chromophore covalently bound to polymer chain to shift the equilibrium of the labile, axial coordination between the chromophore and a fluorophore.

CONCLUSIONS

In dilute solution, ZnTPP can be linked to azopyridine side groups of a polymethacrylate through axial coordination. Thorough *trans*–*cis* photoisomerization of azopyridine can take place due to the dynamic, non-covalent linkage between the two chromophores. On the basis of the spectroscopic and electrochemical measurements and analyses, the study found that the equilibrium between the coordinated and free ZnTPP molecules in the azopyridine polymer solution could be altered by the photoisomerization of azopyridine groups. The polymer with azopyridine in the *cis*-form (upon UV light irradiation) can complex with more

ZnTPP molecules than the polymer with *trans*-azopyridine (upon visible irradiation), which results in photoregulation of redox potentials and fluorescence emission of ZnTPP. The photoregulation effect based on photoinduced changes in the complexation degree may be effective only in solutions of such supramolecular polymers, for which chain backbone-related steric hindrance as well as the solution viscosity that can affect the complexation are sensitive to geometrical changes of azopyridine side groups. This study shows that the use of supramolecular polymers offers new possibilities in the design and exploration of new materials with photoregulation luminescence.

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References

1. Lehn, J. M. *Angew Chem Int Ed Engl* 1990, 29, 1304.
2. Kato, T.; Kihara, H.; Uryu, T.; Fujishima, A.; Frechet, J. M. J. *Macromolecules* 1992, 25, 6836
3. Lohmeijer, B. G. G.; Schubert, U. S. *Angew Chem Int Ed Engl* 2002, 41, 3825
4. St. Pourcain, C. B.; Griffin, A. C. *Macromolecules* 1995, 28, 4116.
5. Folmer, B. J. B.; Cavini, E.; Sijbesma, R. P.; Meijer, E. W. *Chem Commun* 1998, 1847.
6. Kato, T.; Frechet, J. M. J. *Macromolecules* 1989, 22, 3818.
7. Chao, C. Y.; Li, X.; Ober, C.; Osuji, C.; Thomas, E. *Adv Funct Mater* 2004, 4, 364.
8. Cui, L.; Zhao, Y. *Chem Mater* 2004, 16, 2076.
9. Cui, L.; Dahmane, S.; Tong, X.; Zhu, L.; Zhao, Y. *Macromolecules* 2005, 38, 2076.
10. Prasanna de Silva, A.; Nimal Gunaratne, H. Q.; Gunnaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E.; *Chem Rev* 1997, 97, 1515.
11. Tsuchiya, S. *J Am Chem Soc* 1999, 121, 48.
12. Myles, A. J.; Branda, N. R. *J Am Chem Soc* 2001, 123, 177.
13. Otsuki, J.; Suka, A.; Yamazaki, K.; Abe, H.; Araki, Y.; Ito, O. *Chem Commun* 2004, 1290.
14. Cho, H.; Kim, E. *Macromolecules* 2002, 35, 8684.
15. Myles, A. J.; Gorodetsky, B.; Branda, N. R. *Adv Mater* 2004, 16, 922.
16. D'Souza, F.; Hsieh, Y.-Y.; Deviprasad, G. R. *Inorg Chem* 1996, 15, 5747.
17. D'Souza, F.; El-Khouly, M. E.; Gadde, S.; McCarty, A. L.; Karr, P. A.; Zandler, M. E.; Araki, Y.; Ito, O. *J Phys Chem B* 2005, 109, 10107.
18. Benesi, H. A.; Hildebrand, J. H. *J Am Chem Soc* 1949, 71, 2703.
19. Otsuki, J.; Harada, K.; Araki, K. *Chem Lett* 1999, 28, 269.
20. Kadish, K. M.; Shiue, L. R.; Rhodes, R. K.; Bottomley, L. A. *Inorg Chem* 1981, 20, 1274.
21. Smail, D.; Lasia, A.; Zhao, Y., to appear.
22. Otsuki, J.; Narutaki, K.; Bakke, J. *Chem Lett* 2004, 33, 356.
23. Kumar, G. S.; Neckers, D. C. *Chem Rev* 1989, 89, 1915.