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Colorimetric and Fluorescent Changes for Transition Metal ions and Nitroaromatic Compounds Based on a Nano-Spongy Continuous Structure of LB-PANI-Amide-Py System

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On account of their nano-scale size, large aspect ratio and high conductivity, conducting polymer have emerged as an attractive choice for conducting composite materials.[1-3] As part of drive towards finding applications, an examination of the charge transfer (CT) between the conducting polymers and metal species is needed.[4,5] Morrow *et al.*[6] have reported on the metal properties of cyclen-based ligand containing *N*-propionamide donor groups since acetamide oxygen donor is much stronger donor than the alcoholic oxygen. Amide donor is also of tremendous interest because peptide oxygen donors bind K^+ in K^+-ion channels.[7] However, there is no work related with chemosensor properties by metal or electronic interactions for amide-fluorophore-introduced conducting polymer. Among the conducting polymer, polyaniline (PANI) is a unique conjugated polymer in that it can be tailored for specific applications through acid/base doping process.[8] PANI nanostructures are of great current interest since they have a reactive-NH group in the polymer chain flanked on either side by phenylene rings.[9] We have recently shown that PANIs can provide a very high chemical flexibility for the complexation of metal ions.[10] Mechanisms of chemical interactions between PANI and transition metals are also intensively discussed by T. Hirao *et al.* and relate to the importance of metal ion sensing in biology, medicine, and the environment. Most colorimetric or luminescent chemosensors for transition metal ions are designed by employing intramolecular charge transfer (ICT) or photoinduced electron transfer (PET) mechanism.[11] One significant advantages of nanoporous polyaniline conducting particles is that appropriate design combined with reactive binding sites in EB or LB could allow efficient control of colorimetric and conducting changes by metal complexation. In order to demonstrate the above proposal, two structurally similar EB (two imine and two NH groups for four aromatic rings) and LB (four NH groups for four aromatic rings) type PANIs were designed on the basis of the terms of coordination via the nitrogen lone pairs.

Meanwhile, fluorescent pyrene (Py)-fuctionalized copolymers has been evaluated as a sensor for embedded between PANI leucoemeraldine base (LB) and Py, which could display colorimetric change in the presence of the metal nitroaromatic explosive materials (NAC) to give fluorescence quenching by π-π-stacked complexes.[12] In addition, the interest in these materials has been driven by the ability of the conjugated polymers to create large signal amplification relative to small molecule chemosensors due to the delocalization and rapid diffusion of excitons throughout the individual polymer chains, so-called molecular wire effect or one point contact and multipoint response effect, in solution.[13-15] This encouraged us to develop multi-chemosensor based on amide bond ions as well as fluorescent quenching by electron poor NAC species.

Experimental Section

Nanoporous LB-Amide-Py Preparation. The nanoporous PANI-EB (3.0 g) form was reduced by hydrazine hydrate solution (10 mL aqueous 10%) to give PANI-LB of reduced form. To a solution of PANI-LB (2.5 g, 7 mmol) and 5 mL of triethylamine in 50 mL of *N*-methylpyrrolidinone (NMP) was added slowly 1-pyrenebutyric acid *N*-hydroxysuccinimide ester (8 mmol) in 10 mL of NMP at room temperature. The mixture was stirred for 12 h at 100 °C. The reaction mixture was filtered, and the filterate solution was precipitated into methanol and dried to give a polymer (LB-Amide-Py) as pale dark blue powders in 2.1 g (yield 51%). The morphology and size of the conducting particles were characterized by scanning electron micrographs (FE-SEM, JEOL LTD; JSM-600F). Fluorescence spectroscopic studies were performed on a Varian (Cary Eclipse) spectrophotometer. UV-vis spectra were obtained on a Varian Carry-100 spectrophotometer. FT-IR spectra were recorded using a Thermo Mattson Satellite spectrometer.

With this in mind, nanoporous PANI emeraldine base (EB) and LB samples were prepared by the self-stabilized dispersion polymerization (SSDP) method as described in detail elsewhere.[16] The activated ester Py-NHS was efficiently prepared by condensation reaction between pyrene butyric acid and *N*-hydroxy succinimide in the presence of *N*-(3-Dimetylaminopropyl)-*N'*-ethyl-carbodiimide (EDC). Treatment of activated Py-NHS with LB-PANI allowed the formation of the target polymer LB-PANI-Amide-Pyrene

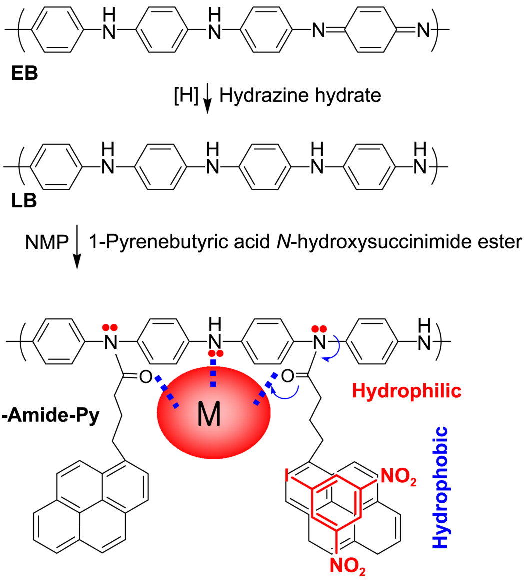

Figure 1. Synthesis of LB-PANI-Amide-Py system and interactions between LB-PANI-Amide-Py and transition metal ion or nitroaromatic compound.

(Py) under the dimethyamino pyridine (DMAP)/NMP solution as shown in Figure 1. In view of the ease with which the more soluble LB-PANI-Amide-Pyrene than EB-PANI-Amide-Pyrene in THF solvent can be produced into porous suspension solution using ethanol, this simple method for generation of nanoporous suspension is promise for various practical application; porous suspensions result in extremely small internal volumes and high surface-to-volume ratios, which lead to improved heat and mass transfer rates for analytical purposed because they provide a convenient small platform for rapid analysis and detection. Thus, dropwise addition of the NMP solution, containing LB-Amide-Py, to ethanol followed by sonication leads to efficient formation of nano-spongy continuous particles. The obtained particles were washed by sonication in ethanol for 1 hr. The aggregated solution was then filtered to remove large particles followed by centrifugation afforded the well dispersed nanoparticles in ethanol.

The structure was confirmed using FT-IR spectra and scanning electron microscopy (SEM) image as shown in Figure 2. The FT-IR spectra show characteristic carbonyl group for amide bond at 1730 cm^{-1}, the weak quinoid band (imine) for PANI at 1592 cm^{-1}, and strong benzeneoid band (NH group) at 1497 cm^{-1}, respectively. Scanning electron microscope (SEM) images, obtained following centrifugation and removal of large aggregates by filtration (2 μm), demonstrate that nano-spongy continuous structure (*ca*. 40 nm) are indeed generated in this process (Fig. 2, right).

Upon addition of ethanol solution, containing metal ions ($AgNO_3$, $Cu(NO_3)_2$, or $Cr(NO_3)_3$) to the LB-Amide-Py solution led to characteristic colorimetric changes for the different metal ions. As shown in Figure 3 (left), the 5-fold excess amount of Ag^+ (5.0 eq.) or Cu^{2+} (5.0 eq.) added to the reference solution of LB-Amide-Py (1.0 eq.) showed mild colorimetric changes, whereas the same amount of Cr^{3+} (1.0 eq.) showed a significant colorimetric change from dark blue to dark green. However, we did not found colorimetric changes upon addition of alkaline or alkaline earth metal ions such as KCl, NaCl, and $MgCl_2$. These imply that the alkaline or alkaline earth metal ions cannot interact with amine bond or NH moiety to give the metal complexation. It is noteworthy that chemosensor properties were display by the selective metal complexations by the fitness between LB-Amide-Py and transition metal ion, which show that the ionic diameter of the corresponding transition metal ion (Ag^+, Cu^{2+}, or Cr^{3+}) resemble the size of the pseudocavity formed by amide and NH group. Furthermore, the green color solution (Fig. 3(d)) returned to the original blue color (Fig. 3(a)) state when the pH was increased to 8 through the addition of aqueous NH_3. Thus, it is clear that these two stimuli (Cr^{3+} and pH) operate as distinguishable inputs to produce a reversible macroscopic output. This finding suggests that the amide and NH unit in the PANI backbone can induce significant colorimetric differences in the pH of these substances, a factor that might be useful in designing more efficient and sensitive LB-Amide-fluorophore or chromophore system. Figure 3 (right) shows the corresponding UV absorption spectral changes by metal complexation when metal ions were added to nanoporous LB-Amide-Py solution. As can be seen, the degree of absorbance of the exciton band (around 630 nm) is retained in the presence of Cr^{3+} ions (green-line), while two new bands appearing around 400 and 800 nm significantly increases with increasing the Cr^{3+} ions dose up to 1.0 equiv. These bands are usually assigned to polaron bands originated from the conducting structure of PANI, i.e., doped, emeraldindine salt structure. Thus, visual inspection of the metal-complexed solution showed green

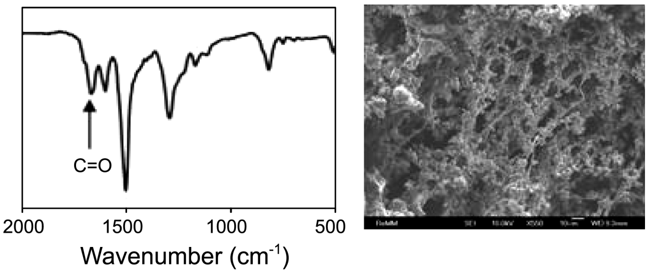

Figure 2. FT-IR spectra and SEM image of LB-Amide-Py.

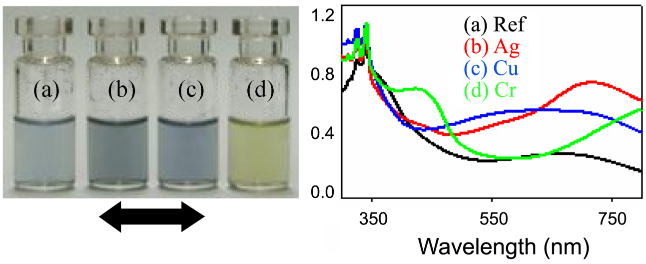

Figure 3. Colorimetric changes and UV absorption changes of the LB-PANI-Amide-Py solution (1.0×10^{-4} M) upon addition of metal ions in ethanol; (a) LB-PANI-Amide-Py only (Ref), (b) Ag^+, (c) Cu^{2+}, and (d) Cr^{3+}.

color meaning the polaron bands which can derive a stronger binding affinity as a PANI-EB-Cr complexation. These phenomena are presumably related to the fact that the more oxidized form or electron deficient species such as the Cr^{3+} ion can promote the efficient formation of polaron bands due to the classical doping process. In addition, almost no UV spectral change of all complexes involved on the pyrene functionality (around 350 nm) was observed compared with that without metal ion. This observation suggests that pyrene units did not interacted with the transition metal ions in the ground state. However, two new bands appearing around 400 and 800 nm did not showed in the presence of Ag^{+} or Cu^{2+} ions (red-line and blue-line, respectively), while the exciton band (around 630 nm) slightly increases. The increased absorbance of the exciton band at 630 nm (Fig. 3(b) and c) was similar to the classical band of the PANI-EB structure. Furthermore, visual inspection of the complexed solution (Fig. 3(b) and (c)) was similar to the dark blue color of reference sample (Fig. 3(a)). These UV spectroscopic changes could be ascribed to the formation of the EB-Amide-Py structure by the facile oxidation process of LB-Amide-Py form in the presence of Ag^{+} or Cu^{2+} ions and their related oxidation process was a known fact.[17]

Based upon the experimental results here, it is still not obvious how such binding influences the conjugated polymer to result in the observed colorimetric changes. We think that the spectral changes upon adding Ag^{+} and Cu^{2+} ions could be solely due to the oxidative doping of PANI by these species especially when they are added in 5-fold excess; indeed, electrochemical potential of Ag^{+}/Ag pair is higher than that of Cu^{2+}/Cu^{+}, which explains strong response on the former. Regarding Cr^{3+}, the total amount of added salt was 0.1 mmol; this should be enough to color the solution into green color. To investigate the sensitive colorimetric change for the Cr ion effect, we performed a control experiment where the same amounts of metal salts are added to the parent PANI-LB to observe any possible spectral changes.

As shown in Figure 4, the same amount of Ag^{+} (5 eq.) and Cu^{2+} (5 eq.) for the reference solution of PANI-LB (1.0 eq.) showed colorimetric changes (Fig. 4(b) and (c)). It was found that the nanoporous PANI-LB solution showed similar colorimetric changes and response time with that of LB-Amide-Py. These imply that the NH functionality in polymer backbone can influence the metal complexaton and response time for Ag^{+} and Cu^{2+}; electrochemical potential of these metal ions are higher than that of Cr ion labile, and would not give the rapid color change.

To investigate the evidence of metal complexation between LB-Amide-Py and metal ions, the resulting solution was evaporated to give the resulting powder. The obtained powder was analyzed by FT-IR for spectral changes. As shown in Figure 5, the characteristic carbonyl group in the presence of Cr^{3+} ion was significantly disappeared at 1680 cm^{-1} by metal complexation between amide oxygen donor and metal ion. Thus, double bond of C=O stretch at occur 1680 cm^{-1} is more disappeared (more weak) by strong metal complexation than the case of Ag^{+} or Cu^{2+} ions Simultaneously, the corresponding strong single bond of C-O is more increased around 1120 and 1300 cm^{-1} due to the complexations or classical doping (Fig. 5(b), (c), and (d)). The new strong quinoid band at 1594 cm^{-1} was significantly appeared by oxidation process of LB-Amide-Py form in the presence of LB to give the characteristic EB-Amide-Py structure. Simultaneously, the quinoid band at 1594 cm^{-1} and benzeneoid bands at 1498 cm^{-1} were slightly shifted (weak metal complexation) to a lower wavenumber in the presence of Ag^{+} or Cu^{2+} ions (red-line and blue-line, respectively). Consequently, these interesting phenomena prove that the nanoporous LB-Amide-Py solution can serve as strong binding sites and as “naked eye” chemosensors specific for Cr^{3+}. The amide donors of LB-Amide-Py bind strongly to large metal ions such as Ag^{+}, Cu^{2+}, or Cr^{3+}, as evidenced by large carbonyl group shift in IR spectra. This resembles the metal-ion affinity patterns of binding sites in transition metal selectivity, where amide oxygen donors are present. The most important one, which is demonstrated by this study of LB-Amide-Py complexes, is that amide donors are much stronger donors than amine donor.

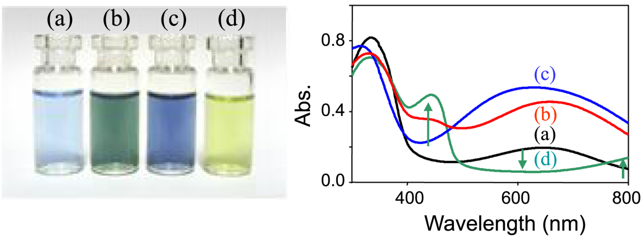

Figure 4. Colorimetric changes (left) of the PANI-LB solution (1.0×10^{-4} M) upon addition of metal ions in ethanol; (a) PANI-LB only, (b) Ag^{+} (c) Cu^{2+} and (d) Cr^{3+}. UV spectral changes (1.0×10^{-4} M) upon addition of metal ions (right); (a) PANI-LB only, (b) Ag^{+} (c) Cu^{2+} and (d) Cr^{3+}.

To investigate the interactions of LB-Amide-Py with NAC, we study the possibility of intercalative binding and hence of a strong association of electron-poor NACs such as nitrobenzene, dinitrobenzene, 1-iodo-3,5-dinitrobenzene between the pyrenyl side-groups to give fluorescent quenching by π-π-stacked complexes. Unfortunately, NACs were not easily soluble in ethanol solvent, and the complexed particles between the LB-Amide-Py and NAC were aggregated in the presence of other common organic solvents rapidly. We

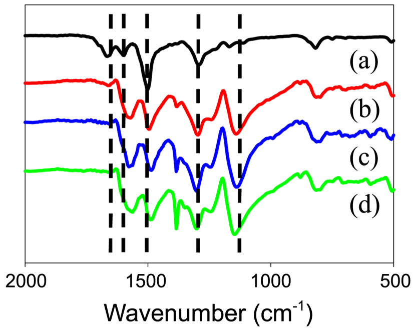

Figure 5. FT-IR changes of LB-PANI-Amide-Py upon addition of metal ions; (a) LB-PANI-Amide-Py only, (b) Ag^{+}, (c) Cu^{2+}, and (d) Cr^{3+}.

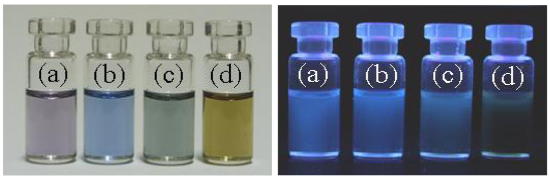

Figure 6. Visual (left) and fluorescent images (right) of LB-PANI-Amide-Py with different NACs in NMP solution under UV light; (a) LB-PANI-Amide-Py only, (b) nitrobenzene, (c) dinitrobenzene, and (d) 1-iodo-3,5-dinitrobenzene.

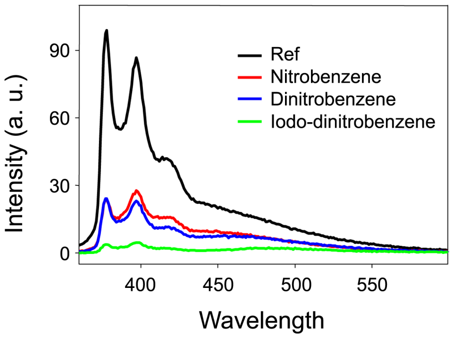

Figure 7. Fluorescent quenching experiment between LB-PANI-Amide-Py and NAC molecules in NMP solution (λ_{ex} =350 nm); (a) LB-PANI-Amide-Py only, (b) nitrobenzene, (c) dinitrobenzene, and (d) 1-iodo-3,5-dinitrobenzene.

chose the NMP solvent because it was taken place aggregation, although it was bad solvent and not relevant for possible application. Upon addition of NMP solution, containing 3 equiv of NACs (nitrobenzene, dinitrobenzene, 1,3-dinitro-5-iodobenzene), to the LB-Amide-Py solution (1 equiv) led to characteristic colorimetric changes, indicative of a CT absorption arising from complementary π-π-stacked complexation between the two species.

The solutions of LB-Amide-Py/NACs in NMP at room temperature show (Fig. 6 (left)) various color change, respectively. In the presence of light (365 nm), the LB-Amide-Py solution (Fig. 6 (right)) shows strong fluorescence but the hybrid solution reveals that fluorescent quenching is operative (Fig. 6(b) and (c)). The fluorescence intensity of the LB-Amide-Py/1,3-dinitro-5-iodobenzene decreases significantly (Fig. 6(d)).

Figure 7 shows the fluorescence quenching of the corresponding solution upon addition of NACs in NMP. The strong and fast dependence of quenching on the NACs implies that a CT process exists in the system. In such interaction systems, the light can generate electron-hole pairs. The generated excitons tend to combine; meanwhile, the electrons or holes are transferred partially to the NACs, depending on the distance and the energy barriers between LB-Amide-Py and NACs. In other words, the formation of the π-π-stacked complexes favors the electrons or holes transfer from quantum dots (donor) to the NACs (acceptor), such that the excited electrons or holes enter the NACs, rather than be emitted. The consequences of this metal complexation and π-π-stacked complexes are considerably involved with amide donor and pyrenyl functionalities that can now participate in colorimetric change and fluorescent quenching by strong association of amide donor and π-π-interactions. Noted that fluorescence quenching experiment results for maleimide-pyrene system[12] is similar compared with that of our PANI-Amide-pyrene system. However, our LB-PANI-Amide-Pyrene systems have nanoporous suspension structure, and result in extremely small internal volumes and high surface-to-volume ratios, which provide a convenient small platform for rapid analysis and detection.

In conclusion, pyrenyl pendant and amide bonded polyaniline (LB-Amide-Py) has been synthesized and used a single-component, multiple-stimulus responsive sensor that displays a colorimetric or fluorescent response toward two distinct input stimuli (metal ions and nitroaromatic explosive materials) to construct chemosensor properties. Thus, the LB-Amide-Py forms metal complexation or π-π-stacked complexes with transition metal ions and NACs as demonstrated by UV, IR spectroscopy and fluorescence quenching experiments. The molecular design of the LB-Amide-Py system allows for the facile synthesis and evaluation of wide range of fluorescent functionality and amide-derivatised polyaniline system, whose electronic conducting and fluorescent sensing properties are currently being studied.

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