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Photocurrent responsive films prepared from nickel-dithiolate compound with directly bonded pyridyl group

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Because the pyridyl group can act as a proton acceptor and a coordination biting unit, electrodes with films of dithiolene complex [n-Bu$_4$N][Ni(4-pedt)$_2$] (**1**) (4-pedt = 1-(pyridine-4-yl) ethylene-1,2-dithiolate) are prepared to investigate the photocurrent response behaviours of metal dithiolene compound upon protonation and transition metal coordination. The morphologies of films **1** are characterized by SEM analysis. Photoelectrochemical measurements are carried out with the electrodes of films **1**. The results are as follows: (1) The stronger the medium acidity is, the weaker the photocurrent becomes. (2) Photocurrent intensities of Mn(II), Co(II) and Zn(II) treated film **1** are increased in comparison with that of the original film **1** due to the polymeric coordination. (3) When film **1** is treated by Fe(III) ion, it is oxidized to neutral [Ni(4-pedt)$_2$] film that shows weaker photocurrent response. In addition, a new ionic pair compound MV[Ni(4-pedt)$_2$]$_2$ (**2**) (MV^{2+} = methylviologen dication) synthesized by cation exchange shows good photocurrent responsive property due to the improvement of electron transfer.

1. Introduction

Researchs on metal complexes with 1,2-dithiolene ligands, a kind of famous classical redox active molecules,[1] are recrudesced now due to their increasing potential in energy conversion, non-linear optics, bioinorganic, and catalysis chemistry.[2] Recently, cobalt dithiolene complexes were found to be an active catalyst for the electrocatalytic and photocatalytic reduction of protons from water;[3] thin films of indole-substituted nickel dithiolene complexes were utilized to fabricate field-effect transistors and bulk heterojunction photovoltaic devices;[4] a layered photoresponse device based on nickel dithiolene complexes can be used to detect periodic light signals and is applicable for optical communication;[5] metal dithiolates were applied to thermoelectric devices with low thermal conductivities;[6] and a series of dithiolene complexes were synthesized lately and their chemical and phisical properties were studied.[7] We have studied intra-molecular charge transfer properties of a nickel dithiolene complex [n-Et$_4$N][Ni(4-pedt)$_2$] (4-pedt = 1-(pyridine-4-yl)-ethylene-1,2-dithiolate, the anion see chart 1).[8] The electronic state of the dithiolene can be modified not only by the oxidation states, but also by the charge transfer states.

Although various structures, properties and potential applications of transition metal dithiolene complexes have been investigated, studies on photocurrent response property of the dithiolene materials are limited.[4,5,9] We use nickel dithiolene complex [n-Bu$_4$N][Ni(4-pedt)$_2$] (**1**) as the film material to prepare photoactive electrode for photoelectro-chemical studies. Taking advantage of the pyridyl group of complex **1** that can act both as a proton acceptor[8] and a coordination ligand[10], photocurrent responses of film **1** to different acidity mediums and transition metal ions are investigated and discussed.

By cation exchange of **1**, a new dithiolene compound MV[Ni(4-pedt)$_2$]$_2$ (**2**) (MV^{2+} = methylviologen dication) is also prepared to investigate the photocurrent response. As a famous photo and electronic active organic electron acceptor, MV^{2+} has been frequently used as cations of charge transfer salts. Photochemical redox properties, energy conversion and photocatalyzation were studied recently.[11,12] Although a structure–property relationship of nickel dithiolene complexes with viologen derivatives was established,[13] there are still few reports concerned with MV-dithiolene system for studies of photoelectron responses or photocurrent conversion. We find MV-dithiolene is a good photocurrent responsive system.

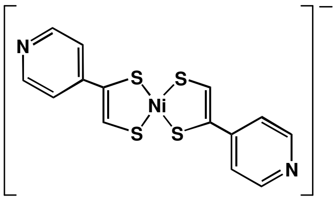

Chart 1. The monoanionic structure of [Ni(4-pedt)$_2$]$^-$.

2. Experimental Section

2.1 General Remarks

The materials of [n-Bu$_4$N][Ni(4-pedt)$_2$] (**1**)[14] and [n-Bu$_4$N][Ni(Phdt)$_2$] (**3**) (Phdt = 1-(phenyl)-ethylene-1,2-dithiolate)[15] were synthesized according to reported literatures. Neutral [Ni(4-pedt)$_2$] was synthesized following the method reported by Zuo.[10] All the other reagents for syntheses and analyses were of analytical grade. The FTIR spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Elemental analyses of C, H, and N were performed using a VARIO EL III elemental analyzer. Electronic absorption spectra were measured on a Shimadzu UV-3150 spectrometer. Cyclic voltammetry (CV) experiments were performed on a CHI650 electrochemistry workstation in a three-electrode system that was run under inert atmosphere, a Pt plate working electrode, a saturated calomel electrode (SCE) as reference electrode, and a Pt wire as the auxiliary electrode. Solid-state EPR spectra were recorded by an EMX-10/12 spectrometer at 110 K. The morphologies of the films were observed with a JSM-5600LV scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) was collected on a D/MAX-3C diffractometer using a Cu tube source (Cu-Kα, λ = 1.5406 Å).

2.2 Synthesis of MV[Ni(4-pedt)$_2$]$_2$ (2)

To a degassed solution of 4-pyridyl-1,3-dithiol-2-one (80 mg, 0.4 mmol) in absolute methanol (15 mL) was added a degassed methoxide solution (0.2 mol·L^{-1}, 4 mL) under an argon atmosphere. After 0.5 h of stirring, the degassed solution of $NiCl_2·6H_2O$ (48 mg, 0.2 mmol) in 5 mL absolute methanol was added dropwise. After complete addition of the $NiCl_2·6H_2O$ solution, the color of the reaction mixture turned from yellow to dark red. The solution was continuously stirred for 0.5 h followed by the addition of [MV]I$_2$ (220 mg, 0.5 mmol) in 2 mL degassed water. The color of the reaction mixture turned from dark red to dark brown. The final mixture was stirred for 2 h under argon atmosphere and then the reaction vial was opened to air overnight at 4 °C. During which time dark brown precipitate was formed. Then the precipitate was filtered and washed with MeOH and dried in vacuo. Yield 68 mg (70%). Anal. Calcd for $C_{40}H_{34}N_6Ni_2S_8$: C, 49.49; H, 3.53; N, 8.66. Found: C, 49.67; H, 3.71; N, 8.55. Important IR data (cm^{-1}, KBr pellet): 3050w, 1640w, 1586vs, 1495w, 1450w, 1408m, 1202w, 988w, 798w, 670w, 614m.

Compound **2** can also be prepared by cation exchange reaction from [*n*-Bu$_4$N][Ni(4-pedt)$_2$] (**1**). Starting material **1** (0.01 mmol, 6.3 mg) in acetone (4.0 ml) was dropwise added to [MV]I$_2$ (2.2 mg, 0.005 mmol) in mixed solvent of acetonitrile (3.0 ml) and DMF (1.0 ml). The color of the solution turned dark brown. The mixture was filtered and microcrystals of **2** were obtained after 2 days from the filtrate by controlled evaporation of the solvent. Yield 5.5 mg (22.6%). Growth of large crystals of **2** was tried by two layers solution diffusion method in glass tube. Flower-like crystals of **2** were observed from the interface in 2 days.

2.3 Preparation of the films and electrodes.

The films of **1** were prepared by wet solution coating method. Compound **1** (0.01 mmol) was dissolved in 3 mL different solvents and the resulting solutions were coated on a pre-cleaned glass substrate. The solvents were removed by evaporation to yield the respective films. The metal ion treated films were prepared by immersing the film in $Mn(ClO_4)_2$, $Co(ClO_4)_2$, $Zn(ClO_4)_2$ and $Fe(ClO_4)_3$ aqueous solution (0.10 mol·L^{-1}), respectively in 2 days, and then rinsed and dried for measurements (CAUTION: All metal perchlorates must be regarded as potentially explosive. Only a small amount of compound should be handled with caution). The photoelectrodes of the films were prepared by the same method as those of the preparation of the films except that the glass substrate is replaced by the ITO substrate (100 Ω/□).

2.4 Photocurrent measurement.

A 150-W high pressure xenon lamp, positioned 15 cm far from the surface of the ITO electrode, was employed as a light source. The photocurrent experiments were measured on a CHI650 electrochemistry workstation and parallel performed in a three-electrode system, a sample coated (in Φ = 0.7 cm area) ITO glass plate as the working electrode, a Pt plate auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. An aqueous solution of Na_2SO_4 (100 mL, 0. 1 mol·L^{-1}) was used as the medium in a quartz cell.

3. Results and Discussion

3.1 Preparation and characterization

Compound MV[Ni(4-pedt)$_2$]$_2$ (**2**) can be prepared by both cation exchange method and direct synthetic method. The crystal samples were obtained from [*n*-Bu$_4$N][Ni(4-pedt)$_2$] (**1**) and [MV]I$_2$ by two layers solution diffusion method in glass tube in mixed solvent. After some days flower-like crystals of **2** were obtained (Figure S1, Supporting Materials). Unfortunately, the crystals are too thin to be measured by single crystal structural analysis. Compound **2** can also be synthesized directly from 4-pyridyl-1,3-dithiol-2-one by following the similar procedure to **1**.[14a] Instead of [*n*-Bu$_4$N]Br, [MV]I$_2$ is added and used as the cation source. The XRD of the powder sample obtained by direct synthetic method is the same as that of the crystal sample (Figure S2). The best solvent for compound **2** is a DMF/acetonitrile mixed solvent (4:1 by volume) that is used in all the measurments in solution.

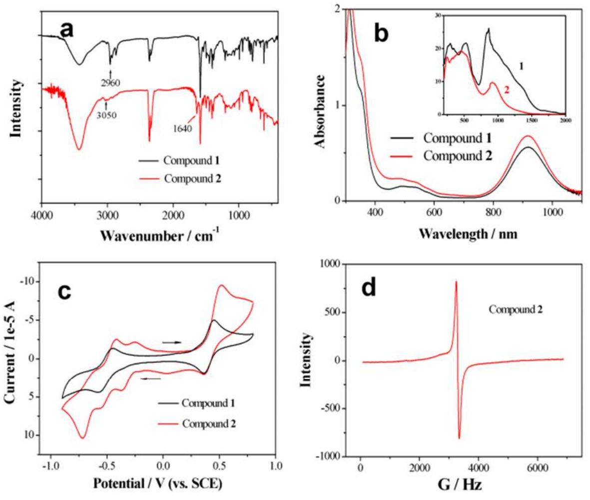

Fig. 1. (a) FTIR spectra of **1** and **2.** (b) UV-vis-NIR absorption spectra of **1** and **2** in solution and solid state (inserted)**.** (c) Cyclic voltammogram of **1** and **2** (1.0 × 10^{-3} mol·L^{-1}) in DMF / CH_3CN (4:1 by volume). (d) ESR spectra of **2** at 110K.

The FTIR spectra of **1** and **2** in 400–4000 cm^{-1} range are showed in Figure 1a. The alkyl C–H vibrations of the quaternary amonium of **1** at about 2960 cm^{-1} almost disappear and the 3050 cm^{-1} of the pyridyl C–H vibration of $[\mathrm{MV}]^{2+}$ in **2** appears due to the cation replacement. The characteristic absorption peaks of MV^{2+} are observed at 1640 cm^{-1} (ν_{ring}) and 798 cm^{-1} (Figure S3).[16] Electronic spectra of **1** and **2** were measured at room temperature. As shown in Figure 1b, an intense absorption band of **1** appears in NIR (920 nm), which is the character of the nickel dithiolene compounds and related to the redox state of the central metal dithiolene.[8] The spectrum of **2** is similar to that of **1**. The inserted is their solid state spectra calculated from the diffuse-reflection. As reported previous, the monoanion $[\mathrm{Ni(4\text{-}pedt)}_2]^-$ of compound **1** shows two typical quasi reversible redox waves.[8] The $E_{1/2}(1)$ and $E_{1/2}(2)$ in DMF/acetonitrile mixed solvent are at –0.516 V and 0.405 V vs SCE, respectively, corresponding to the two steps redox couples (Figure 1c). Two sets additional waves $E_{1/2}(1)_{\mathrm{MV}}$ and $E_{1/2}(2)_{\mathrm{MV}}$ of compound **2** appeared in negative potential side, –0.320 V and –0.682 V, respectively, which are assigned to the redox of the MV^{2+} cation.[12] The radical property of **2** was recorded by ESR spectrum at low temperature (110 K) shown in Figure 1d. The *g* value 2.060 is similar to that of **1**[8] near that of the free radical 2.003.

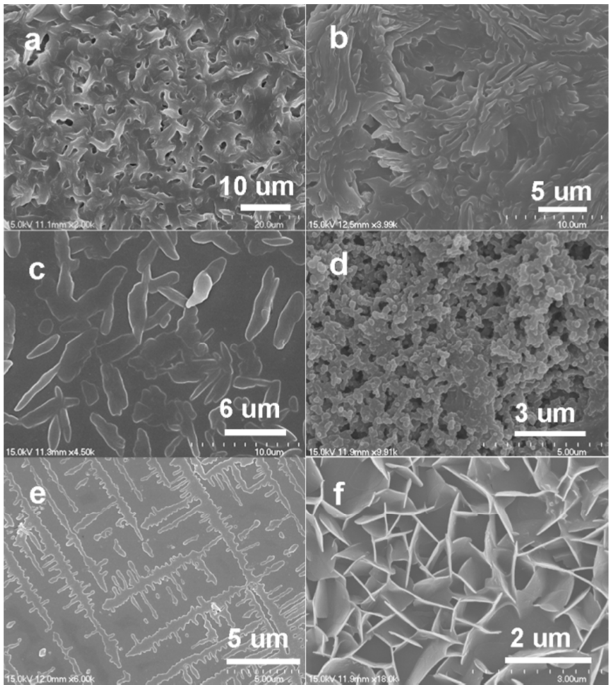

Figure 2. SEM images of the morphologies of **1** in (a) acetone, (b) methanol, (c) dichloromethane, and (d) THF. SEM images of the morphologies of **2** in (e) acetonitrile, (f) DMF-methanol (4:1by volume).

3.2 Morphologies of various $[\mathrm{Ni(4\text{-}pedt)}_2]^-$ films

The self-assembly films of **1** were prepared by coating the solutions with different solvents on a pre-cleaned glass substrate, and then the solvents were removed by evaporation. The films were subjected to scanning electron microscope (SEM) analysis. Figure 2a–d show the SEM images of the morphologies obtained in different solvents. The film prepared in acetone is well-distributed with irregular petal-like pattern. The film morphology prepared in methanol is similar to that prepared in acetone, but futher fused. lump-like and fused particle-like morphologies are appeared for films prepared in dichloromethane and THF, respectively. All the films of **1** discussed later are prepared using acetone solution unless otherwise indicated. Films of **2** can be also obtained by direct solution coating method (Figure 2e and 2f). The film prepared by acetonitrile solution of **2** shows regular branching pattern, in which the branches are grown in right angle. Using DMF-methanol (4:1 by volume) mixed solution of **2**, a uniform structure assembled by interlocked plates (1~2 μm in width) is observed. The obvious difference in pattens between **1** and **2** is related to the good crystallinity of **2**.

Figure 3 shows the SEM images of the morphologies of the metal ion treated film **1** (originally prepared in acetone), by immersing the film into metal salt solutions in 2 days. Based on the SEM images, the morphologies are completely changed. When the metal ion replaces the $[n\text{-}\mathrm{Bu_4N}]^+$ cation, films with fused particles are formed, which is attributed to the formation of polymeric compound $\{\mathrm{M[Ni(4\text{-}pedt)_2]_2}\}_n$ (M = Mn(II), Co(II) and Zn(II)) through the metal-pyridyl coordination. Different from the Mn(II), Co(II) and Zn(II) treated films, the morphology of Fe(III) ion treated film shows grass-like microstructure. The difference is reasonable due to their different reaction products. When the film of **1** is treated by Fe(III) ion, an oxidation reaction occurs and the product is the neutral $[\mathrm{Ni(4\text{-}pedt)_2}]$ based on the knowledge of Ni-dithiolene chemistry and previous research.[8] FTIR spectra of the metal ion treated films are showed in Figure S4. The alkyl C–H vibrations of **1** at about 2960 cm^{-1} are weakened and the 1586 cm^{-1} of the pyridyl C–H vibration is shifted to 1600 cm^{-1} due to the metal coordination. EDS spectra were measured to further confirm the result (Figure S5). The data reveal that the element ratios of Ni:Mn, Ni:Co and Ni:Zn are 1:0.36, 1:0.47 and 1:0.31, respectively for the Mn(II), Co(II) and Zn(II) treated films (theoretically, 1:0.5). No Fe signal was detected for the Fe(III) treated film.

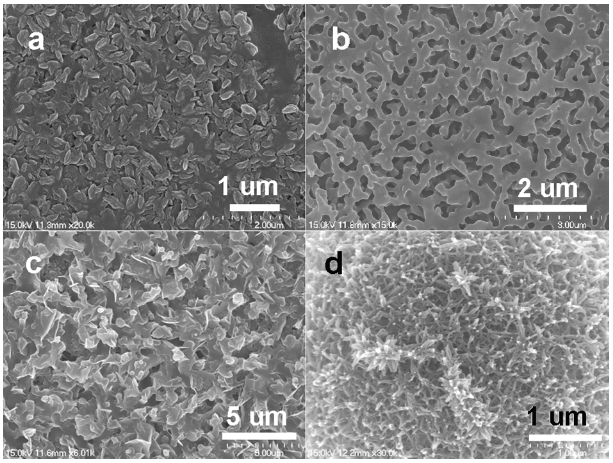

Figure 3. SEM images of the morphologies of the metal ions treated film **1**, (a) Mn(II), (b) Co(II), (c) Zn(II), and (d) Fe(III).

3.3 Photocurrent response properties

Besides showing various morphologies in different solvents, compound **1** is unique among the Ni-dithiolene derivatives in that the pyridyl group can act as a proton acceptor and a coordination biting unit, therefore, the effects of morphologies, protonation and metal coordination on photocurrent response properties are investigated. Film **1** coated ITO electrode and the metal ion treated film **1** electrodes are used as working electrodes in a photoelectrochemical cell for measurements. Furthermore, the MV^{2+} cation has been widely used in photoelectrochemical cells as an auxiliary reagent added in solution for photocurrent generation.[17] To understand the function of MV^{2+} cation in photocurrent response of MV-dithiolene hybrid material, compound **2** coated ITO electrode is also studied in comparison with **1**. All the experiments were carried out in 0.10 mol·L^{-1} Na_2SO_4 electrolyte solution under irradiation with a 150-W high pressure xenon lamp. The selected applied potential is 0.5 V based on the IV curve (Figure S6). A more detailed description is given in the experimental section.

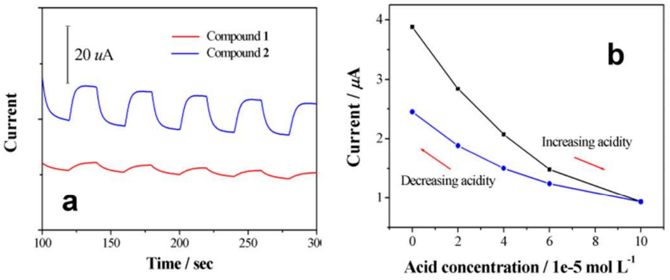

Figure 4. (a) Photocurrent responses of compounds **1** and **2**, in a 0.1 mol·L^{-1} Na_2SO_4 aqueous solution with 0.5 V applied potential. (b) Effect of the acidity on the photocurrent of **1**.

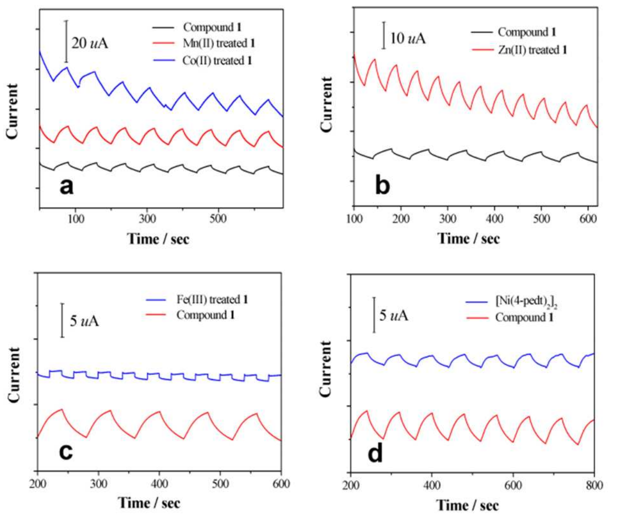

Figure 5. Photocurrent responses (a) of **1** and of Mn(II) and Co(II) treated **1**, (b) of **1** and of Zn(II) treated **1**, (c) of **1** and of Fe(III) treated **1**, and (d) of **1** and neutral [Ni(4-pedt)$_2$].

The photocurrent responses of **1** to the morphologies obtained in different solvents acetone, methanol, acetonitrile and THF are shown in Figure S7. The results display no distinguishable difference in μA scale. Figure 4a shows the photocurrent responses of **1** and **2** measured under the same conditions. The anodic photocurrents are 4 μA for **1** and 12 μA for **2** about three times of **1**. The current intensity is increased when the quaternary ammonium cation is replaced by electroactive MV^{2+} cation. It should be noted that controlled test of the MVI_2 sole system shows no response in the same intensity scale. The result indicates that a dithiolene-MV donor-acceptor system is in favor of the photocurrent generation. Figure 4b shows the photocurrent responses of film **1** to different acidity mediums. The concentration of $HClO_4$ is gradually increased from 0.0 to 1.0×10^{-4} mol·L^{-1} with the interval of 2.0×10^{-5} mol·L^{-1}. The photocurrent intensity is decreased when the acidity is increased. It is reversible when the acid is neutralized by [*n*-Bu_4N]OH, but not comletely recovered.

Photocurrent responses of the metal ion treated electrodes of **1** were studied in comparison with that of the untreated electrode (Figure 5). Some conclusions can be deduced from the experimental results. (1) Photocurrent intensities of the Mn(II), Co(II) and Zn(II) treated films are better than that of the original electrode prepared from **1** (Figure 5a and 5b). (2) The morphologies of the films also seem to have no obvious effect on the photocurrent intensity. (3) Photocurrent intensity of the Fe(III) ion treated film is decreased comparing with that of **1** (Figure 5c). The Fe(II) ion treated film **1** is also tested, the risult is comparable to those of the other M(II) ions treated films (Figure S8). All the conclusions are based on repeated experiments. Therefore, the nature of the compound itself is the main factor in influencing the photocurrent response property.

3.4 Proposed mechanisms

Chart 2 represents the schematic drawing of the electron transfer in the photoresponsive system. Since the dithiolene complex is an electron donor and its oxidation potential is +0.405 V (see CV result), under the positive applied potential (+0.5 V), the photoexcited electron can transfer directly to the ITO electrode and anodic current is generated. The MV^{2+} cation is an electron catcher that obtains electron instantly from the dithiolene during photoexcitation and further transfers electron to the electrode. In acid solution, the py group accepts proton forming a positive charged compound, which significantly decreases the electron donor property of the dithiolene. For this reason, the current intensity is quickly decreased when the acidity is increased. The reason for photocurrent enhancement for the Mn(II), Co(II) and Zn(II) treated films should be attributed to the coordination of metal ion with the dithiolene anion. Compound **1** is a small molecular material and the non electroactive [*n*-$Bu_4N]^+$ cations obstruct the inter anion's interaction, which can be seen from the molecular packing.[14] The metal coordination drives out the [*n*-$Bu_4N]^+$ ion, which makes the material possess a close packing polymeric structure. The interaction of the dithiolene moieties are increased, which causes the π–electron moving delocalized. Therefore, the current intensity is improved.

To further understand whether the metal coordination plays a key role in the current increase or not, a nickel dithiolene complex with phenyl substitutent [n-Bu$_4$N][Ni(Phdt)$_2$] (**3**)[15] is synthesized and used as a non coordination material to do the same ion exchange experiments. IR spectra indicate that the alkyl C–H vibrations of the quaternary amonium at about 2935 cm^{-1} do not disappear and the EDS result indicates only small amount of M(II) ions exist (Fig.S9 and S10). All of these means that the [n-Bu$_4$N]$^+$ cation is not easy to be exchanged by M(II) ions for the non coordination [Ni(Phdt)$_2$]$^-$. No remarkable current increase for these metal ion treated film electrodes (Fig.S11) provides the evidence that the metal coordination is contributive to the ion exchange and hence the photocurrent enhancement.

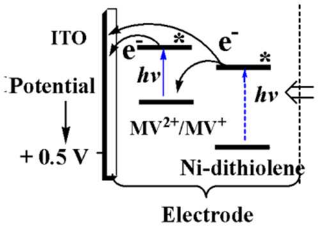

Chart 2. Schematic drawing of the electron transfer in the photoresponsive system.

It should be remembered that the nature of Fe(III) ion treated film is the neutral [Ni(4-pedt)$_2$] (see 3.2). The electron donating ability of the neutral [Ni(4-pedt)$_2$] is weaker than that of the monoanion [Ni(4-pedt)$_2$]$^-$ and for this reason only weak photocurrent was detected. To further confirm the conclusion, neutral [Ni(4-pedt)$_2$] was synthesized according to reported literature.[10] Photocurrent responsive property of the film is shown in Figure 5d. The result is in the same order of magnitude as that found for the Fe(III) ion treated film, which is also an evidence for the Fe(III) oxidization reaction.

4. Conclusions

In summary, films of nickel ditholene derivative [n-Bu$_4$N][Ni(4-pedt)$_2$] with different morphologies were prepared in different solvents. Because the pyridyl group of the anion can be protonated, photocurrent responsive property of the selected film is studied in different acidity and the result shows that the stronger the acidity is, the weaker the photocurrent becomes. Since the pyridyl group can also coordinate to metal ions, metal ion treated films are prepared. Photocurrent intensity of the Mn(II), Co(II) and Zn(II) treated films are increased comparing with that of the original film of **1** due to the polymeric coordination and cation exchange. When the film **1** is treated by Fe(III) ion, it becomes neutral [Ni(4-pedt)$_2$] film that is a weaker electron donor compared with **1** and hence shows weaker photocurrent response. By cation exchange reaction, a new MV[Ni(4-pedt)$_2$]$_2$ compound was synthesized. A MV^{2+} promoted photocurrent response for the film was observed due to the anion-cation electron transfer. All the experimental results give the consistent conclusion that the photocurrent efficiency of the dithiolene compound can be improved by increasing its electron transfer properties.

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Notes and references

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