Inorganic Chemistry

Article

pubs.acs.org/IC

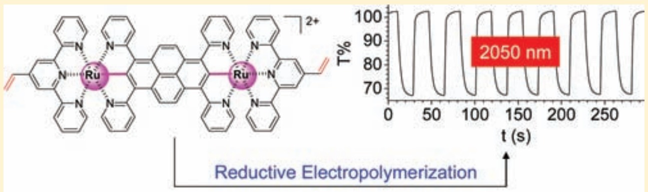
Metallopolymeric Films Based on a Biscyclometalated Ruthenium Complex Bridged by 1,3,6,8-Tetra(2-pyridyl)pyrene: Applications in Near-Infrared Electrochromic Windows

Chang-Jiang Yao, Jiannian Yao, and Yu-Wu Zhong*

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

S Supporting Information

ABSTRACT: A biscyclometalated ruthenium complex bridged by the 2,7-deprotonated form of 1,3,6,8-tetra(2-pyridyl)pyrene was deposited onto indium−tin oxide glass electrodes by reductive electropolymerization. The resulting metallopolymeric films exhibited tricolor electrochromic behavior in the near-infrared region upon switching of the two well-separated $Ru^{II/III}$ processes at low potentials. A good contrast ratio (35%) at 2050 nm and a long memory time up to 100 min were recorded for this electrochromic behavior. The response time is typically of a few seconds.



INTRODUCTION

Electrochromic materials have been the focus of intensive research activities because of their potential for applications such as smart windows/mirrors, dynamic camouflage, and information display devices.[1] Inorganic metal oxides such as WO_3 are typical materials for electrochromic uses.[2] However, they sometimes have poor coloration efficiency, high cost, and low response time. Organic conjugated polymers are another promising material for electrochromic devices.[3] Recently, coordination polymers have received increasing interest for this purpose by manipulating charge-transfer transitions between metals and ligands.[4] In contrast to the frequently studied electrochromism in the visible region, compounds that can be deposited on electrode surfaces and exhibit distinct near-infrared (NIR) absorption spectral changes are much less well-known.[5] Materials that show electrochromic behavior beyond 2000 nm are even more scarce,[6] although these NIR chromophores are very useful in many civilian and military aspects.[7] NIR electrochromism is useful for applications such as photodynamic therapy, optical fiber-based telecommunication, optical data storage, and aerospace and military camouflage.[5−7] New electrochromic materials with good contrast ratios and short response times are still in great demand.

Transition-metal complexes often exhibit well-defined redox events and intense charge-transfer transitions in the visible/NIR region. More importantly, the spectroscopic changes accompanying corresponding redox events are usually very distinct. These features make transition-metal complexes good candidates for electrochromic uses. However, we have to admit that most reported examples are only concerned with their electrochromic behavior in the solution state. In order to be useful for practical applications, they must be deposited onto electrode surfaces in a controllable way. Reductive polymerization of transition-metal complexes containing vinylpolypyridine ligands is useful in producing an adhesive polymeric film on electrode surfaces.[8] This method has previously been demonstrated to produce metallopolymeric films aimed at electrochromic uses, but only very limited examples are available.[9] We previously reported that polymeric films obtained via reductive polymerization of a vinyl-containing biscyclometalated ruthenium complex bridged by the 3,6-deprotonated form of 1,2,4,5-tetra(2-pyridyl)benzene showed appealing electrochromic behavior in the NIR region,[10] including multicolor switching, good contrast ratio (around 40% at 1165 nm), short response time (around 5 s), low switching voltage, and remarkably long memory time. Considering the presence of a vast number of transition-metal complexes that have exhibited appealing electrochromic behavior in solution, it would be of interest and importance to expand this strategy to other complexes to prove its generality. In this paper, we present electropolymerization of a new biscyclometalated ruthenium complex, $\mathbf{1}^{2+}$ (Figure 1), bridged by the 2,7-deprotonated form of 1,3,6,8-tetra(2-pyridyl)pyrene (tppyr) and the electrochromic behavior of the resulting metallopolymeric films.

RESULTS AND DISCUSSION

The model compound $[(tpy)Ru(tppyr)Ru(tpy)]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) without two vinyl groups has been previously reported by us[11] and showed two stepwise $Ru^{II/III}$ processes with some involvement of the ligand oxidation at +0.44 and +0.65 V vs Ag/AgCl. The one-electron-oxidized species $[(tpy)Ru(tppyr)Ru(tpy)]^{3+}$ exhibited intense charge-transfer transitions around 2100 nm with ε_{max} of 3.2 × 10^4 M^{-1} cm^{-1}, and this band was not observable in $[(tpy)Ru(tppyr)Ru(tpy)]^{2+}$ and $[(tpy)Ru(tppyr)Ru(tpy)]^{4+}$. We conjectured that complex $\mathbf{1}^{2+}$ with two pendant

Received: February 29, 2012
Published: May 14, 2012

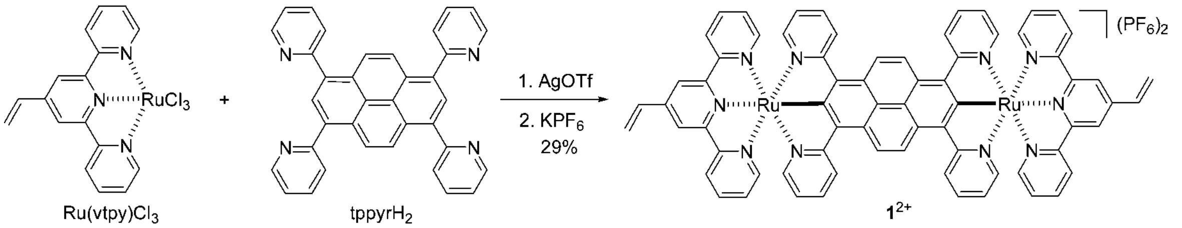


Figure 1. Biscyclometalated ruthenium complex **1**.

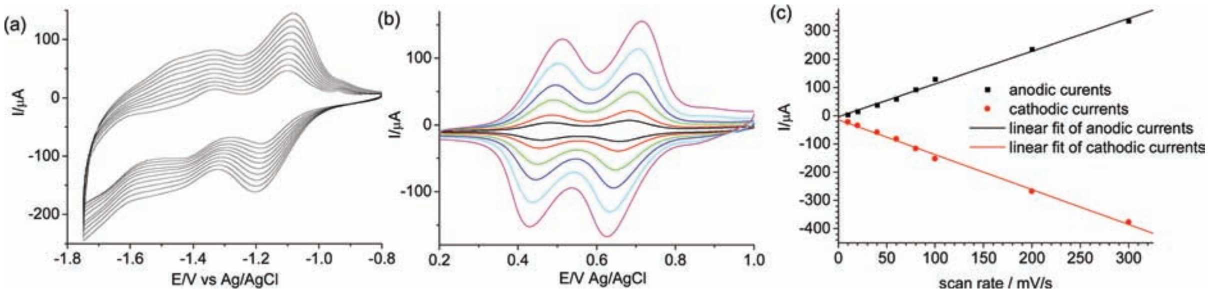


Figure 2. (a) Reductive electropolymerization of $\mathbf{1}^{2+}$ (0.5 mM in acetonitrile) on an ITO glass (25 mm × 8 mm) by 10 repeated potential scan cycles (−0.8 V → −1.75 V → −0.8 V) at 100 mV s^{-1}. (b) CV profiles of the polymeric films obtained in part a at different scan rates (10, 20, 40, 60, 80, and 100 mV s^{-1}, respectively). (c) Linear dependence on the scan rates of the peak currents of the polymeric film obtained in part a.

vinyl groups could be electropolymerized by reductive polymerization, and the resulting polymeric films were able to realize electrochromism beyond 2000 nm. As shown in Figure 1, complex $\mathbf{1}^{2+}$ was synthesized by the reaction of Ru(vtpy)Cl_3 (vtpy = 4′-vinyl-2,2′;6′,2″-terpyridine) with the neutral ligand tppyrH_2 in the presence of AgOTf, followed by anion exchange with KPF_6 (see details in the Experimental Section).

When a clean indium−tin oxide (ITO) glass electrode was placed in a solution of $\mathbf{1}^{2+}$ containing 0.1 M Bu_4NClO_4 as the supporting electrolyte and the potential was repeatedly scanned between −0.8 and −1.75 V vs Ag/AgCl, the current was found to increase gradually and continuously (Figure 2a), which indicated that electropolymerization of $\mathbf{1}^{2+}$ proceeded smoothly on the electrode surface. The typical geometrical dimensions of the polymeric films are 20 mm × 8 mm. Figure 2b shows the cyclic voltammetry (CV) profiles of the thus-obtained polymeric film at different scan rates (from 10 to 100 mV s^{-1}) in a clean supporting electrolyte solution, which evidence two stepwise and well-defined redox couples at +0.47 and +0.67 V. The potentials and separation difference between two waves of the polymeric film are very similar to those observed in the model compound $[(tpy)Ru(tppyr)Ru(tpy)]^{2+}$, which indicates that the basic electrochemical properties of the dimetallic unit are retained after electropolymerization. The peak separation between the anodic and cathodic waves of each couple is 20 mV at a scan rate of 10 mV s^{-1}. However, this separation became bigger with increasing scan rate. For instance, the separation increased to 82 mV at a scan rate of 100 mV s^{-1}, which was possibly caused by the nonohmic contact between the polymer and electrode. It should be pointed out that both anodic and cathodic currents of the film are linearly dependent on the scan rate (Figure 2c), which is characteristic of redox processes confined on an electrode surface.

The surface coverage of the polymeric film can be easily varied by changing the number of potential cycles during electropolymerization (Figures S1 and S2 in the Supporting Information). As can be clearly seen from Figure 3a, the CV profiles of the polymeric films (at the same scan rate of 10 mV s^{-1}) expand considerably with increasing electropolymerization cycles from 10, 20, 40, to 80 cycles. The surface coverage of each film is 6.2 × 10^{-10}, 15 × 10^{-10}, 25 × 10^{-10}, and 38 × 10^{-10} mol cm^{-2}, respectively. Figure 3b shows that the current

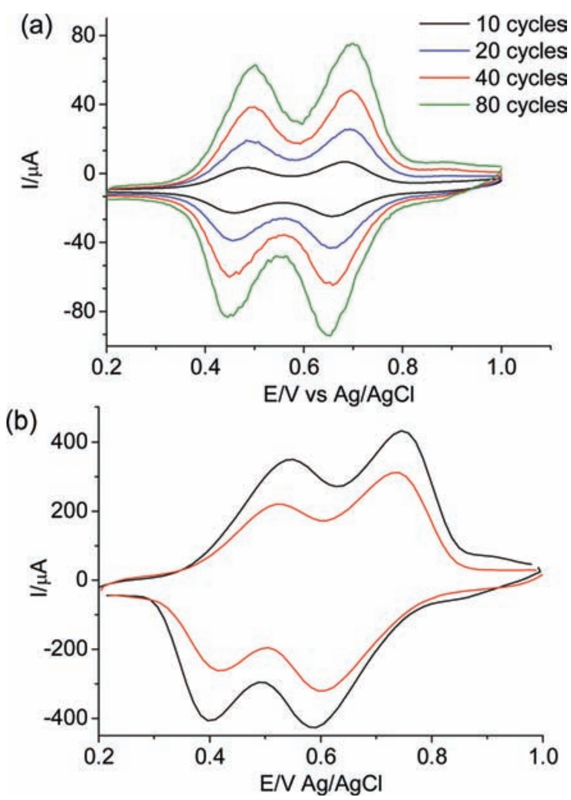


Figure 3. (a) CV profiles of polymeric films obtained after 10, 20, 40, and 80 electropolymerization cycles. The scan rate is 10 mV s^{-1}. The surface coverage of each film is 6.2 × 10^{-10}, 15 × 10^{-10}, 25 × 10^{-10}, and 38 × 10^{-10} mol cm^{-2}, respectively. (b) CV profiles of a polymeric film obtained after 20 electropolymerization cycles before (black line) and after 500 potential cycles at 100 mV s^{-1} (red line).

of the CV profile of a film after 500 potential cycles drops to 72% of its original value. However, the shapes of two redox couples are well preserved. This attests to the good stability of the polymeric film.

The in situ spectroelectrochemical measurement of the above-obtained polymeric film was carried out to monitor its visible/NIR spectral changes (Figure 4). When the applied potential was stepwise increased from +0.2 to +0.56 V vs Ag/AgCl to induce the first one-electron oxidation, the metal-to-ligand charge-transfer transitions in the visible region gradually decreased. Concomitantly, a distinct absorption band in the NIR region (centered at 1900 nm) developed. The color of the film changed from blue to brown. When the potential was further increased to +0.85 V to enable the second one-electron oxidation, the new NIR absorption was found to decrease gradually until it disappeared completely (Figure 4b). The emergence of a new band around 800 nm was evident during this process, which was ascribed to the ligand-to-metal charge-transfer transition. As a result of these spectral changes, the color of the film changed from brown to orange. These two-step processes are totally reversible, and the same color changes could be observed during cyclic potential scans on films in Figure 3.

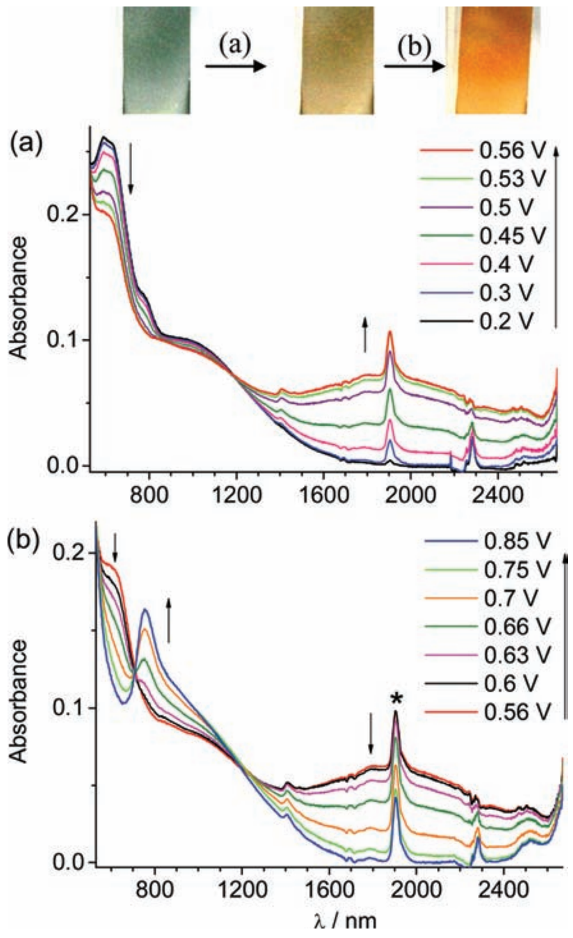


Figure 4. Visible/NIR absorption spectral changes of a polymeric film of $\mathbf{1}^{2+}$ on ITO glass (surface coverage = 20×10^{-10} mol cm^{-2}) upon stepwise application of potentials (a) from +0.2 to +0.56 V and (b) from +0.56 to +0.85 V vs Ag/AgCl. The inset in part a shows corresponding color changes of the film during these two processes. *: Artifacts due to a nonperfect compensation of the background.

The NIR electrochromism of the polymeric film of $\mathbf{1}^{2+}$ was examined by double-potential-step chronoamperometry in conjunction with monitoring of the transmittance (T %) changes of a polymeric film at 2050 nm (Figure 5). When the

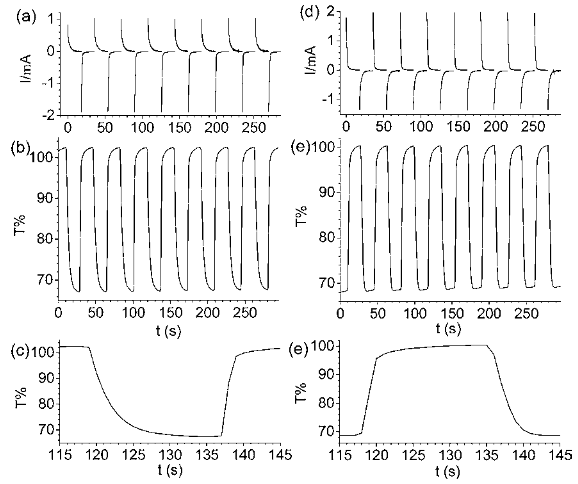


Figure 5. Electrochromic switching of a polymeric film of $\mathbf{1}^{2+}$ on ITO glass (surface coverage = 41×10^{-10} mol cm^{-2}) (a–c) between +0.2 and +0.56 V and (d–f) between +0.56 and +0.85 V vs Ag/AgCl with an interval of 18 s in 0.1 M Bu_4ClO_4/CH_3CN. (a and d) Current assumption. (b, c, e, and f) Transmittance changes monitored at 2050 nm as a function of time.

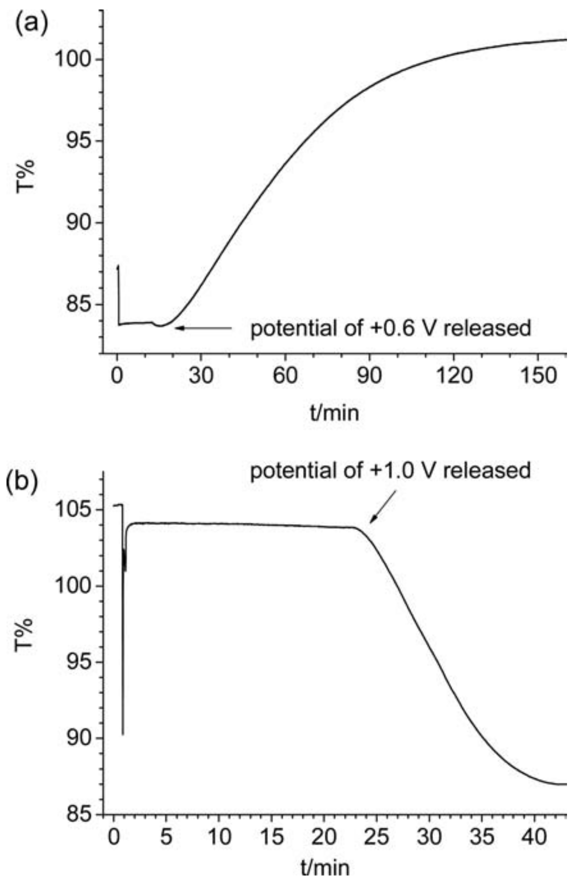


Figure 6. Optical memory effect of a polymeric film of $\mathbf{1}^{2+}$ on ITO glass (surface coverage = 20×10^{-10} mol cm^{-2}) after the potential at (a) +0.6 V or (b) +1.0 V vs Ag/AgCl was released.

applied potential was switched stepwise between +0.2 and +0.56 V, which corresponded to the first one-electron oxidation process (Figure 5a−c), a contrast ratio (ΔT %) of 35% was acquired. The response times for the contrast ratio to reach over 90% of its maximum are 6 and 2 s for the oxidation and reverse reduction processes, respectively. The coloration efficiency (CE) at 2050 nm for this process is calculated to be 220 $cm^2\ C^{-1}$ according to the equation $CE(\lambda) = \Delta OD/Q_d$, where $\Delta OD = \log[T_b/T_c]$, OD is the optical density, Q_d is the injected/ejected charge density ($C\ cm^{-2}$), and T_b and T_c are the transmittance values in the bleached and colored states at the indicated wavelength. In the second one-electron oxidation process (Figure 5d−f), the contrast ratio (32%) and response time for the oxidation and reverse reduction processes (2 and 6 s, respectively) are comparable to those observed in the first oxidation process.

In some particular applications such as data storage and e-paper, electrochromic materials with long memory time are desired.[12] Thus, we examined the memory effect of the above polymeric films for both of the redox processes involved. When the applied potential of +0.6 or +1.0 V vs Ag/AgCl of a polymeric film of complex $\mathbf{1}^{2+}$ (surface coverage = 20×10^{-10} mol cm^{-2}) was released, the memory time was around 100 and 10 min, respectively (Figure 6). The memory time for the first one-electron redox event is much longer than that of most electrochromic materials examined to date. For instance, Higuchi, Kurth, and co-workers reported a longest memory time of 15 min among a series of metallosupramolecular polymers bridged by bisterpyridines.[4g]

CONCLUSION

In conclusion, biscyclometalated ruthenium complex $\mathbf{1}^{2+}$ bridged by tppyr was successfully deposited onto ITO glass electrodes by reductive electropolymerization. The resulting metallopolymeric films extend the electrochromic window beyond 2000 nm, and corresponding spectral changes were accompanied with low operation potentials, tricolor switching, good contrast ratio, long memory time, and moderate response time. These features make them promising materials for electrochromic devices. We trust that the reductive electropolymerization method will be equally useful for preparing other metallopolymeric films with electrochromic behavior. The expansion of this work to other biscyclometalated ruthenium systems[13] to adjust the electrochromic wavelength could be easily envisaged, which will be the focus of our future investigations.

EXPERIMENTAL SECTION

Electrochemistry. All electrochemical experiments were carried out using a CHI620D potentiostat. All measurements, including the spectroelectrochemical measurements, were carried out in 0.1 M Bu_4NClO_4/acetonitrile with Ag/AgCl as the reference electrode and a platinum coil as the counter electrode. A three-compartment electrochemical cell containing 0.3 mM $\mathbf{1}^{2+}$ in 10 mL of Bu_4NClO_4/acetonitrile was used in the electropolymerization experiments. The working electrode (ITO glass, <10 Ω/□) was positioned parallel and opposite to the counter electrode (platinum coil). In spectroelectrochemical and electrochromic studies, visible/NIR spectra were recorded using a PE Lambda 750 UV/visible/NIR spectrophotometer. The above-prepared ITO film was put in a conventional 1 cm quartz cell containing a clean electrolyte solution and used as the working electrode.

General Procedure for Synthesis. NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer and reported in ppm values from residual protons of a deuterated solvent. Mass spectrometry data were obtained with a Bruker Daltonics Inc. Autoflex III MALDI-TOF mass spectrometer. Microanalysis was carried out using a Flash EA 1112 analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

Synthesis of [1](PF$_6$)$_2$. To 40 mL of dry acetone were added $Ru(vtpy)Cl_3$[8a,10a] (0.1 mmol, 47 mg) and AgOTf (0.3 mmol, 78 mg). The mixture was refluxed for 5 h before cooling to room temperature. After standing for 1 h, the mixture was filtered through a pad of Celite to remove AgCl precipitates. The filtrate was concentrated to dryness. To the residue were added $tppyrH_2$[11] (0.05 mmol, 26 mg), *N*,*N*-dimethylformamide (12 mL), and *t*-BuOH (12 mL). The mixture was refluxed under microwave conditions (power = 375 W) for 30 min. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in 2 mL of methanol, followed by the addition of excess KPF_6. The resulting precipitate was collected by filtering and washing with water and Et_2O. The obtained solid was purified by chromatography on silica gel (eluent: 100:10:0.1 CH_3CN/H_2O/aqueous KNO_3) followed by anion exchange with KPF_6 to give 22 mg of $[\mathbf{1}](PF_6)_2$ as a black solid in a yield of 29%. ^1H NMR (400 MHz, CD_3CN): δ 5.86 (d, J = 10.9 Hz, 2 H), 6.60 (d, J = 17.6 Hz, 2 H), 6.81 (t, J = 6.4 Hz, 4 H), 6.89 (t, J = 6.4 Hz, 4 H), 7.15 (d, J = 5.4 Hz, 4 H), 7.25−7.30 (m, 2 H), 7.33 (d, J = 5.4 Hz, 4 H), 7.73 (t, J = 7.6 Hz, 4 H), 7.83 (t, J = 7.6 Hz, 4 H), 8.54 (d, J = 8.0 Hz, 4 H), 8.89 (s, 4 H), 8.95 (d, J = 8.3 Hz, 4 H), 9.35 (s, 4 H). MALDI-TOF (m/z): 1229.3 ($[M - 2PF_6]^{2+}$). Anal. Calcd for $C_{70}H_{46}F_{12}N_{10}P_2Ru_2 \cdot 7H_2O$: C, 51.10; H, 3.68; N, 8.51. Found: C, 50.84; H, 3.30; N, 8.17.

ASSOCIATED CONTENT

Supporting Information

Reductive electropolymerization and ^1H NMR and MALDI mass spectra of $\mathbf{1}^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zhongyuwu@iccas.ac.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (Grant 21002104), the National Basic Research 973 program of China (Grant 2011CB932301), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry of China, and Institute of Chemistry, Chinese Academy of Sciences ("100 Talent" Program), for financial support.

REFERENCES

(1) (a) Mortimer, R. J. *Chem. Soc. Rev.* **1997**, *26*, 147. (b) Sonmez, G. *Chem. Commun.* **2005**, 5251. (c) Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268.

(2) (a) Bach, U.; Corr, D.; Lupo, D.; Pichot, F.; Ryan, M. *Adv. Mater.* **2002**, *11*, 845. (b) Lee, S.-H.; Deshpande, R.; Parilla, P. A.; Jones, K. M.; To, B.; Mahan, A. H.; Dillon, A. C. *Adv. Mater.* **2006**, *18*, 763.

(3) (a) Groenendaal, L. B.; Zotti, G.; Aubert, P.-H.; Waybright, S. M.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 855. (b) Sonmez, G.; Shen, C. K. F.; Rubin, Y.; Wudl, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 1498. (c) Li, M.; Patra, A.; Sheynin, Y.; Bendikov, M. *Adv. Mater.* **2009**, *21*, 1707. (d) Amb, C. M.; Dyer, A. L.; Reynolds, J. R. *Chem. Mater.* **2011**, *23*, 397.

(4) (a) Oh, D. H.; Boxer, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 8161. (b) Biancardo, M.; Schwab, P. F. H.; Argazzi, R.; Bignozzi, C. A. *Inorg. Chem.* **2003**, *42*, 3966. (c) Bernhard, S.; Goldsmith, J. I.; Takada, K.;

Abruña, H. D. *Inorg. Chem.* **2003**, *42*, 4389. (d) Powell, C. E.; Cifuentes, M. P.; Morrall, J. P.; Stranger, R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Heath, G. A. *J. Am. Chem. Soc.* **2003**, *125*, 602. (e) Ward, M. D. *J. Solid State Electrochem.* **2005**, *9*, 778. (f) Samoc, M.; Gauthier, N.; Cifuentes, M. P.; Paul, F.; Lapinte, C.; Humphrey, M. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7376. (g) Han, F. S.; Higuchi, M.; Kurth, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 2073. (h) Motiei, L.; Lahav, M.; Freeman, D.; van der Boom, M. E. *J. Am. Chem. Soc.* **2009**, *131*, 3468. (i) Powell, A. P.; Bielawski, C. W.; Cowley, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 10184. (j) Kaim, W. *Coord. Chem. Rev.* **2011**, *255*, 2503.

(5) (a) Qi, Y.; Desjardins, P.; Wang, Z. Y. *J. Opt. A: Pure Appl. Opt.* **2002**, *4*, S273. (b) Garcíña-Canadas, J.; Meacham, A. P.; Peter, L. M.; Ward, M. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 3011. (c) Yen, H.-J.; Lin, H.-Y.; Liou, G.-S. *Chem. Mater.* **2011**, *23*, 1874. (d) Yen, H.-J.; Lin, H.-Y.; Liou, G.-S. *J. Mater. Chem.* **2011**, *21*, 6230. (e) Lin, W.; Zheng, Y.; Zhang, J.; Wan, X. *Macromolecules* **2011**, *44*, 5146. (f) Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem., Int. Ed.* **1989**, *28*, 1445.

(6) (a) Chandrasekhar, P.; Zay, B. J.; Birur, G. C.; Rawal, S.; Pierson, E. A.; Kauder, L.; Swanson, T. *Adv. Funct. Mater.* **2002**, *12*, 95. (b) Topart, P.; Hourquebie, P. *Thin Solid Films* **1999**, *352*, 243.

(7) (a) Fabian, J.; Nakazumi, H.; Matsuoka, M. *Chem. Rev.* **1992**, *92*, 1197. (b) Qian, G.; Wang, Z. Y. *Chem.—Asian J.* **2010**, *5*, 1006. (c) Fabian, J.; Zahradnik, R. *Angew. Chem., Int. Ed.* **1989**, *28*, 677.

(8) (a) Abruña, H. D.; Denisevich, P.; Umaña, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1. (b) Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153. (c) Potts, K. T.; Usifer, D. A.; Guadalupe, A. R.; Abruña, H. D. *J. Am. Chem. Soc.* **1987**, *109*, 3961. (d) Guadalupe, A. R.; Usifer, D. A.; Potts, K. T.; Hurrell, H. C.; Mogstad, A.-E.; Abruña, H. D. *J. Am. Chem. Soc.* **1988**, *110*, 3462. (e) Nie, H.-J.; Yao, J.; Zhong, Y.-W. *J. Org. Chem.* **2011**, *76*, 4771.

(9) Leasure, R. M.; Ou, W.; Moss, J. A.; Linton, R. W.; Meyer, T. J. *Chem. Mater.* **1996**, *8*, 264.

(10) (a) Yao, C.-J.; Zhong, Y.-W.; Nie, H.-J.; Abruña, H. D.; Yao, J. *J. Am. Chem. Soc.* **2011**, *133*, 20720. (b) Yao, C.-J.; Zhong, Y.-W.; Yao, J. *J. Am. Chem. Soc.* **2011**, *133*, 15697. (c) Sui, L.-Z.; Yang, W.-W.; Yao, C.-J.; Xie, H.-Y.; Zhong, Y.-W. *Inorg. Chem.* **2012**, *51*, 1590.

(11) Yao, C.-J.; Sui, L.-Z.; Xie, H.-Y.; Xiao, W.-J.; Zhong, Y.-W.; Yao, J. *Inorg. Chem.* **2010**, *49*, 8347.

(12) (a) Sonmez, G.; Sonmez, H. B. *J. Mater. Chem.* **2006**, *16*, 2473. (b) Kondo, Y.; Tanabe, H.; Kudo, H.; Nakano, K.; Otake, T. *Materials* **2011**, *4*, 2171.

(13) (a) Gagliardo, M.; Amijs, C. H. M.; Lutz, M.; Spek, A. L.; Havenith, R. W. A.; Hartl, F.; van Klink, G. P. M.; van Koten, G. *Inorg. Chem.* **2007**, *46*, 11133. (b) Wang, L.; Yang, W.-W.; Zheng, R.-H.; Shi, Q.; Zhong, Y.-W.; Yao, J. *Inorg. Chem.* **2011**, *50*, 7074. (c) Zhong, Y.-W.; Wu, S.-H.; Burkhardt, S. E.; Yao, C.-J.; Abruña, H. D. *Inorg. Chem.* **2011**, *50*, 517. (d) Yang, W.-W.; Yao, J.; Zhong, Y.-W. *Organometallics* **2012**, *31*, 1035.