

Co-based Metal-Organic Nanostructures for Vis-to-NIR Electrochromic Display

Chanchal Chakraborty^{1,2}, Sayan Halder¹

Chanchal@hyderabad.bits-pilani.ac.in

¹Department of Chemistry, Birla Institute of Technology & Science (BITS) Pilani, Hyderabad Campus, Samirpet, Hyderabad, Telangana 500078, India

²Materials Center for Sustainable Energy & Environment (McSEE), Birla Institute of Technology and Science, Hyderabad Campus, Hyderabad 500078, India

Keywords: Electrochromism, Co(II), Metal-organic hybrid, Vis-to-NIR.

ABSTRACT

Vis-to-NIR electrochromism is highly demanding as it can regulate solar irradiation by blocking the NIR lights to control indoor cooling. In this regard, the Co (II)-based different dimensional metal-organic nanostructures are developed to exhibit the Vis-to-NIR electrochromism when used as electrochromic (EC) displays, and their EC parameters are thoroughly compared.

1 Introduction

To control the solar heat gain inside the building indoors and to improve the building energy consumption in smart buildings, Visible-to-near infrared (vis-to-NIR) electrochromic materials (ECMs) based electrochromic displays (ECDs) are very demanding.¹⁻² According to the data shared by National Renewable Energy Laboratory (NREL), the invisible NIR radiation, which is widened from 700 nm to 2500 nm, accounts for ~50% of the total solar energy reaching the earth's surface and is responsible for interior heating of the earth as well as an overheated and unpleasant indoor environment.³⁻⁴ The NIR radiation has no contribution toward daylight but contributes significantly to solar heating. The nonstop passage and absorption of the solar irradiation containing NIR radiations through the window and building blocks cause the overheating of building indoors and provide unpleasant weather conditions. This weather condition forces us to use the air conditions, which consume substantial electrical energy, mainly from burning fossil fuel. So, preventing the NIR radiation from passing the window can directly reduce energy consumption and indirectly the emission of greenhouse gases.

Different materials, like phase-transfer materials, thermochromic materials, aero-gels, organic liquid crystals, etc., have been developed to contribute to window technology.³ However, most of these materials have limitations regarding climate change and consequently suffer from the lack of durability when used in windows.⁵ However, the ECMs in ECDs can smartly adjust the solar heat passing through it during daytime by controlling the light spectra only upon optimized external voltage.⁶ These ECMs are not vulnerable to other abovementioned stimuli.⁷ In this regard, the widely studied ECMs are metal

oxides, small organic molecules, organic polymers, transition metal complexes, and co-ordination metallo-supramolecular polymers (MSPs).⁸⁻¹³ Nevertheless, these MSPs are in high demand as they possess good film-forming ability and can produce the durable ECDs with good coloration efficiency, less switching time, long-term EC stability, high optical contrast, etc.¹²⁻¹⁵

Although MSPs are very effective as ECMs, they are mostly restricted to visible-EC devices, owing to the metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) absorption that falls mainly in the visible region.¹²⁻¹⁴ To date, the mixed-valence organometallic materials are considered primarily for generating intervalence charge transfer (IVCT) between their multiple redox states to generate the NIR-electrochromism.¹⁶ Sometimes, organic ligands like triphenylamine (TPA)-based moieties that produce stable radical ions can have the NIR-EC because of π -polaron transitions.¹⁷ Nevertheless, developing MSP-based vis-to-NIR ECMs using only the redox of the metal center is very challenging. Only Hsu et al. have developed black-to-transmissive Co(II) based MSP with vis-to-NIR EC behavior.¹⁸ However, the EC in that MSP was completely dependent on the pH of the electrolyte and was restricted only to an aqueous alkaline solution. We have also developed a Co(II) based coordination nanosheet with a terpyridine-based tri-armed ligand to produce transparent-to-greenish black EC behavior with Vis-to-NIR absorption.¹⁹ So, there is a vast scope to develop low-cost vis-to-NIR ECMs based on MSPs that can exhibit the EC behavior only owing to the metal center redox in aqueous and non-aqueous media for wide-spread applications.

In this report, we have developed two different Co(II)-based MSPs (Co-NS-1 and Co-NS-2) with two dissimilar thiazolothiazole containing ligand structures as shown in Fig. 1. The linear and network, both the polymers exhibited nanosheet morphology and exhibited the vis-to-NIR EC behavior when used in thin-film based EC devices.

2 Experiment

2.1 Materials

The reagents like dithiooxamide and 4-pyridinecarboxaldehyde, 4-([2,2':6',2''-terpyridin]-4'-yl)benzaldehyde, cobalt chloride, cobalt acetate, etc. were purchased from Sigma Aldrich as used as received. The extra-pure solvents like dry dimethyl formamide (DMF), ethanol, methanol, acetonitrile, etc., were bought from Sisco Research Laboratories (SRL) Pvt. Ltd. – India and used as received. Indium tin oxide (ITO)-coated glass slides ($R \approx 20 \Omega$) were obtained from Shilpa Enterprises.

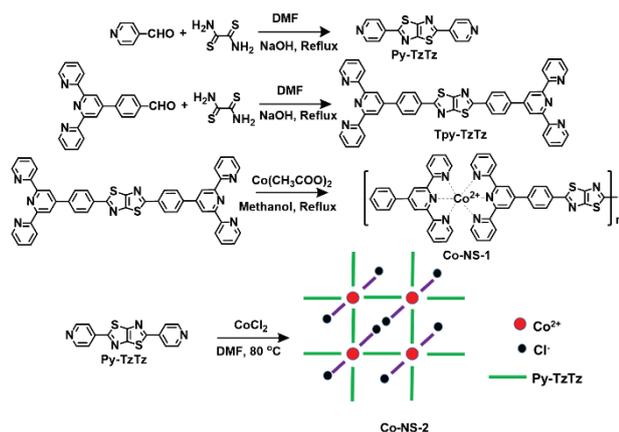


Fig. 1. Synthesis of the Co-containing MSPs.

2.2 Synthesis of materials

The thiozolothiazole (TzTz) and pyridine-containing ligand Py-TzTz was synthesized by taking dithiooxamide and 4-pyridinecarboxaldehyde (1:2 molar ratio) in DMF and refluxing the mixture for 12 h. Finally, the Co(II) containing polymeric structure Co-NS-2 was prepared by taking the mixture of CoCl_2 and P-TzTz (1:2 ratio) in dry DMF in a sealed tube and heating the mixture at 80°C for 48 h without stirring. A pale-yellow solid was finally filtered and dried in the oven as Co-NS-2.

The thiozolothiazole (TzTz) and terpyridine-containing ligand Tpy-TzTz were synthesized similarly, as stated earlier. The dithiooxamide and 4-([2,2':6',2''-terpyridin]-4'-yl)benzaldehyde (1:2 molar ratio) was mixed in DMF and refluxed for 12 h. The precipitation was collected and dried as Tpy-TzTz. The linear MSP Co-NS-1 was synthesized by refluxing the Tpy-TzTz ligand and Cobalt (II) acetate in methanol at an equimolar ratio for 24 h. Finally, the solvent was removed under a vacuum, and deep yellowish polymer Co-NS-1 was obtained.

2.3 Instrumentations

The morphological study of the MSPs was determined by field emission scanning electron microscopy (FESEM) using FEI, Apreo SEM instrument with 30 kV operating voltage. For the experiment, the surface of the compound was gold-coated by sputtering for 30 s to reduce the

surface potential. The Electrochromism study was performed using Autolab PGSTAT128N potentiostat in a three-electrode electrochemical cell where the sample-modified ITOs were used as working electrodes and Ag/AgCl in sat. KCl, platinum wire, and 0.1 M TBAP in acetonitrile were used as reference electrode, a counter electrode, and electrolyte. The transmission changes of the EC films in different potentials were measured with an Ocean Optics UV-vis spectrophotometer (USB4000, Ocean Optics).

3 Results

The morphology of the synthesized polymers, Co-NS-1 and Co-NS-2, was analyzed using SEM imaging, and the results are provided in Fig. 2a-b. Both the MSPs revealed the 2D sheet morphology in SEM imaging.

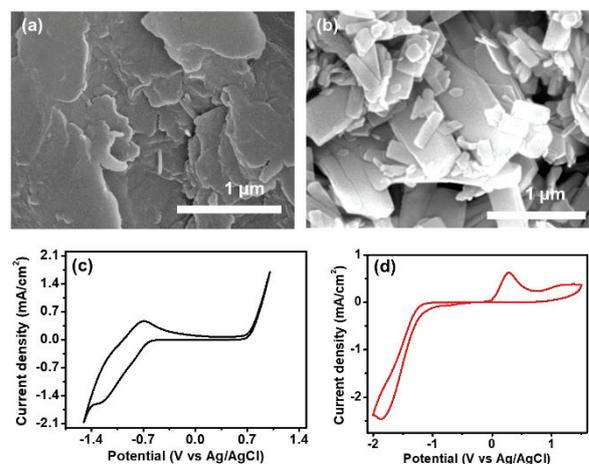


Fig. 2. The SEM images of (a) Co-NS-1 and (b) Co-NS-2. The CV study of the (c) Co-NS-1 and (d) Co-NS-2 taking the thin film on ITO as the working electrode.

Before proceeding with the EC study, we have elucidated the redox properties of the thin films of two MSPs on ITO, and the results are depicted in Fig. 2c-d. Both the polymers exhibited the redox cycle at negative potentials. For Co-NS-1, the redox cycle appeared at -1.3 V (Co^{2+} to Co^+) and -0.7 V (Co^+ to Co^{2+}), while Co-NS-2 revealed the reduction peak for Co^{2+} to Co^+ at -1.8 V with a clear oxidation peak at 0.4 V.

The EC property of Co-NS-1 film was first investigated by a conventional three-electrode electrochemical system taking the Co-NS-1 film-coated ITO as a working electrode. The change of transmittance spectra, as shown in Fig. 3a, discovered that the MLCT peak of the pristine film at ~ 430 nm was unaltered; however, two additional peaks appeared at ~ 700 nm and 1070 nm when a potential of -1.5 V (vs. Ag/AgCl) was applied to the film. The corresponding color of the film was also changed from yellow to blackish brown, as shown in Fig. 3c. The pristine color of the film and the initial transmittance spectral pattern were recovered when the

reverse potential of 0 V (vs. Ag/AgCl) was applied to the Co-NS-1 film.

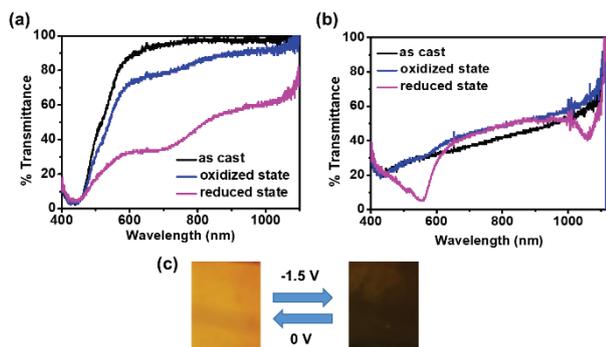


Fig. 3. Transmittance change of (a) CO-NS-1 and (b) Co-NS-2 and corresponding (c) EC color change of Co-NS-1 at different applied potentials.

The thin film of Co-NS-2 also revealed (Fig. 3b) the similar trend of the transmittance changes with applied potentials as it depicted the similar MLCT peak of the pristine film at ~430 nm was unaltered along with the generation of two additional peaks at ~580 nm and 1070 nm when a potential of -2 V (vs. Ag/AgCl) was applied to the film.

4 Discussion

The highly π - π stacking ability of the TzTz moieties of the polymers can produce the assembly between the polymer chains in Co-NS-1 and appear as the assembled nanosheet structure as shown in the SEM image. The network structure in Co-NS-2 created the 2D network with nanosheet morphology. The CV analysis revealed the Co(II)/Co(I) redox cycle in both polymers. However, the required potential was a little higher in the case of Co-NS-2. The different coordination due to the different ligands around the Co(II) ions in two polymers might be the reason for different redox potentials.

In both the polymers in transmittance spectra, the initial peak at ~430 nm in the pristine file is due to the d-d transition. The generation of the new peaks in a reduced state might be owing to the generation of new MLCT transitions.¹⁹ The new peak generation in the NIR region (1070 nm) for both polymers demonstrated the blackening of the film. These vis-to-NIR EC processes were reversible as the black state regained its original transmittance profile and color while oxidizing at 0 V.

5 Conclusions

In conclusion, we have successfully synthesized two Co(II) containing MSPs with nanosheet morphology. Both the polymer exhibited the Vis-to-NIR EC process depending on the redox cycle of Co(II)/Co(I) in negative potentials. The film showed the reversible yellow-to-black color change in the EC process. This report depicts the

potentiality of the Co(II) containing metal-organic nanosheets for excellent Vis-to-NIR electrochromism and can be used as a future material for ECDs in smart windows to restrict indoor solar heating.

References

- [1] A. Llorde's, G. Garcia, J. Gazquez and D. J. Milliron, "Tunable near-infrared and visible-light transmittance in nanocrystal-in-glass composites," *Nature*, vol. 500, pp. 323–326 (2013).
- [2] B.-B. Cui, Y.-W. Zhong and J. Yao, "Three-State Near-Infrared Electrochromism at the Molecular Scale," *J. Am. Chem. Soc.*, vol. 137, No. 12, pp. 4058–4061 (2015).
- [3] H. Khandelwal, A. P. H. J. Schenning and M. G. Debije, "Infrared Regulating Smart Window Based on Organic Materials," *Adv. Energy Mater.*, vol. 7, No. 14, pp. 1602209-1602217. (2017).
- [4] E. L. Runnerstrom, A. Llorde's, S. D. Lounis and D. J. Milliron, "Nanostructured electrochromic smart windows: traditional materials and NIR-selective plasmonic nanocrystals," *Chem. Commun.*, vol. 50, pp. 10555–10572 (2014).
- [5] G. Smith, A. Gentle, M. Arnold and M. Cortie, "Nanophotonics-enabled smart windows, buildings and wearables," *Nanophotonics*, vol. 5, No. 1, pp. 55–73 (2016).
- [6] N. L. Sbar, L. Podbelski, H. M. Yang and B. Pease, "Electrochromic dynamic windows for office buildings," *Int. J. Sustainable Built Environ.*, vol. 1, No. 1, pp. 125–139 (2012).
- [7] A. Cannavale, U. Ayr, F. Fiorito and F. Martellotta, "Smart Electrochromic Windows to Enhance Building Energy Efficiency and Visual Comfort," *Energies*, vol. 13, No. 6, pp. 1449–1465 (2020).
- [8] R. J. Mortimer, "Electrochromic materials," *Chem. Soc. Rev.*, vol. 26, 147–156 (1997).
- [9] P. R. Somani and S. Radhakrishnan, "Electrochromic materials and devices: present and future," *Mater. Chem. Phys.*, vol. 77, No. 1, pp. 117–133 (2003).
- [10] C. G. Granqvist, M. A. Arvizu, I. B. Pehlivan, H.-Y. Qu, R.-T. Wen and G. A. Niklasson, "Electrochromic materials and devices for energy efficiency and human comfort in buildings: A critical review," *Electrochim. Acta*, vol. 259, No. 1, pp. 1170–1182 (2018).
- [11] E. Puodziukynaite, J. L. Oberst, A. L. Dyer and J. R. Reynolds, "Establishing Dual Electrogenerated Chemiluminescence and Multicolor Electrochromism in Functional Ionic Transition-Metal Complexes," *J. Am. Chem. Soc.*, vol. 134, No. 2, pp. 968–978 (2012).
- [12] R. Banasz and M. Wałęsa-Chorab, "Polymeric complexes of transition metal ions as electrochromic materials: Synthesis and properties,"

- Coord. Chem. Rev., vol. 389, No. 15, pp. 1–18 (2019).
- [13] M. Higuchi, "Electrochromic Organic–Metallic Hybrid Polymers: Fundamentals and Device Applications," *Polym. J.*, vol. 41, pp. 511–520 (2009).
- [14] M. Higuchi, "Stimuli-responsive metallo-supramolecular polymer films: design, synthesis and device fabrication," *J. Mater. Chem. C*, vol. 2, No. 44, 9331–9341 (2014).
- [15] S. Roy and C. Chakraborty, "Nanostructured metallo-supramolecular polymer-based gel-type electrochromic devices with ultrafast switching time and high colouration efficiency," *J. Mater. Chem. C*, vol. 7, No. 10, 2871–2879 (2019).
- [16] C.-J. Yao, Y.-W. Zhong, H.-J. Nie, H. D. Abruña and J. Yao, "Near-IR Electrochromism in Electropolymerized Films of a Biscyclometalated Ruthenium Complex Bridged by 1,2,4,5-Tetra(2-pyridyl)benzene," *J. Am. Chem. Soc.*, 2011, vol. 133, No. 51, 20720-20723 (2011).
- [17] S. Mondal, D. C. Santra, Y. Ninomiya, T. Yoshida and M. Higuchi, *ACS Appl. Mater. Interfaces*, vol. 12, No. 52, 58277-58286 (2020).
- [18] C.-Y. Hsu , J. Zhang , T. Sato , S. Moriyama and M. Higuchi , "Black-to-Transmissive Electrochromism with Visible-to-Near-Infrared Switching of a Co(II)-Based Metallo-Supramolecular Polymer for Smart Window and Digital Signage Applications," *ACS Appl. Mater. Interfaces*, vol. 7, No. 33, 18266-18272 (2015).
- [19] S. Roy and C. Chakraborty, "Transmissive to blackish-green NIR electrochromism in a Co(ii)-based interfacial co-ordination thin film," *Chem. Commun.*, vol. 57, No. 61, 7565-7568 (2021).