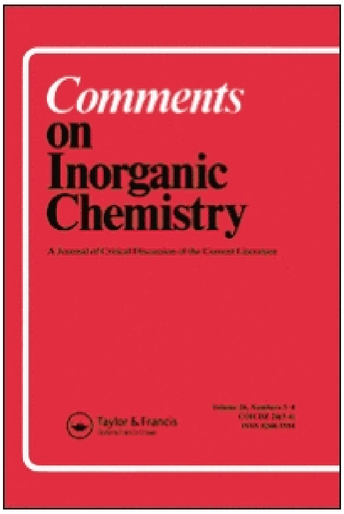

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SYNTHESIS, STUDY, AND APPLICATIONS OF POLYMERIC N-HETEROCYCLIC CARBENES

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SYNTHESIS, STUDY, AND APPLICATIONS OF POLYMERIC N-HETEROCYCLIC CARBENES

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A brief review of our work on orthogonally-positioned NHC metallopolymers is highlighted herein. Some pertinent literature is presented, followed by the synthetic strategy employed as well as comprehensive electrochemical analyses. Derivatization of a suitable diimine into a electropolymerizable gold (I) NHC complex resulted in the first orthogonally-positioned NHC metallopolymer. Extension of this methodology to prepare analogous group 11, iridium and sulfur-substituted metallopolymers generated thin films with electrochromic activity that could be tuned by proper selection of the metal center.

Keywords: electrochromism, electropolymerization, metallopolymer, N-heterocyclic carbene

Abbreviations: tetrahydrothiophene (tht), X-ray photoelectron spectroscopy (XPS), saturated calomel electrode (SCE), decamethylferrocene (Fc*)

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My first meeting with Gordon Stone took place at his former home in Bristol, UK. The University of Bristol had been selected as the location of an international meeting on organometallic chemistry in the mid-1960s. A large tent had been erected in the Stones' back garden to provide hospitality for his distinguished guests – a category to which I certainly did not belong! I was under the mistaken impression that all the conferees had been invited. Once there, I realized that I had made a terrible mistake and started a retreat to my humble dormitory room when I came across Gordon's late wife, Judith. Truly a charming lady, she escorted me back to the infamous tent and introduced me to Gordon. As you can imagine, this initial meeting did not exactly put a smile on Gordon's face! So, from this rather odd beginning Gordon and I became very good friends and I have a particularly happy memory of visiting the Stones at their Bristol home along with my family. Moreover, he has been very helpful in terms of my own career and for this I am extremely grateful. Gordon has had a tremendous impact on inorganic chemistry in general and at the University of Bristol and Baylor University in particular. Indeed, he has earned his place as one of the greats in inorganic chemistry.

Well-defined transition metal complexes supported by N-heterocyclic carbenes (NHCs) have found tremendous utility in a broad range of catalytic[1] and medicinal applications over the past several decades.[2] However, relatively less attention has been directed toward polymeric materials containing NHCs. Due to their unique electronic and/or physical properties, such materials hold promise for enabling the aforementioned applications, in addition to creating new ones.[3] As illustrated in Figure 1, three types of polymeric NHCs are currently known.

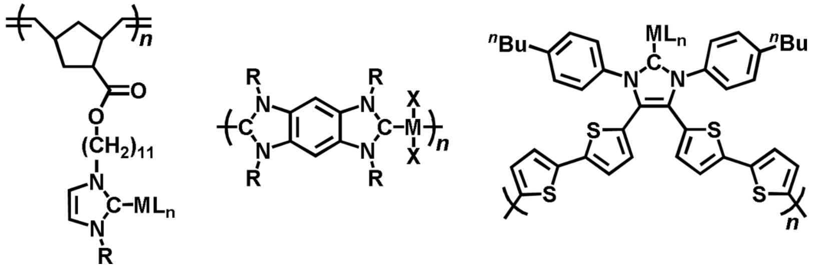

Figure 1. General examples of transition metal complexes supported by three different classes of poly(NHC)s. ML_n = transition metal complex. R = aryl or alkyl.

Tethered poly(NHC) complexes typically feature catalytically-active complexes connected via alkyl linkers to the main chains of synthetic polymers or Merrifield resins.[4] One notable advantage of these materials is that they can be conveniently recovered from various reaction mixtures and re-used. Another example is main-chain poly(NHC)s where carbene-metal complexes are integral components of the polymer main-chain. Certain derivatives of these materials have been shown to be thermally-reversible, which has helped to establish new concepts in self-healing electronics, self-assembly, and catalysis.[5] Recently, we reported the first examples of poly(NHC) complexes in which the carbene functionalities are orthogonally connected to the main chains of the respective polymers.[6] These materials feature a backbone analogous to polythiophene, which renders them attractive for use as components in molecular electronics and redox-switchable catalysts.[3,7]

The synthetic strategy used to prepare the latter class of polymers was based on a series of thiophene-substituted diimine ligands that were previously reported[8] by our group (see Figure 2). Due to their ability to accept up to two electrons, these diimine ligands and their transition metal complexes were envisioned to undergo electropolymerizaton. However, these species were found to be too unstable under oxidative conditions to be electropolymerized. Subsequent cyclic voltammetry studies revealed that the installation of electron-donating groups lowered the oxidation potential of the aforementioned diimines. Hence, it was surmised that the incorporation of bithiophene moieties might sufficiently lower the oxidation potential to facilitate electropolymerization.

A bithiophene-substituted diimine (**1**) was synthesized in 77% overall yield by dimerizing and then oxidizing the monoimine formed from

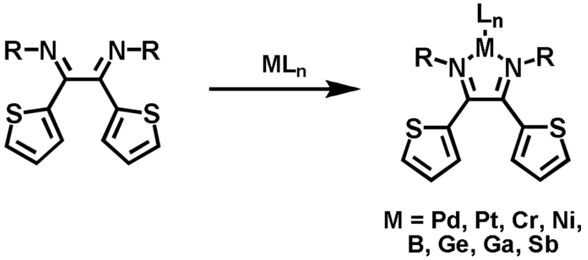

Figure 2. Metallation of thiophene-substituted diimines with various main-group and transition metal complexes.

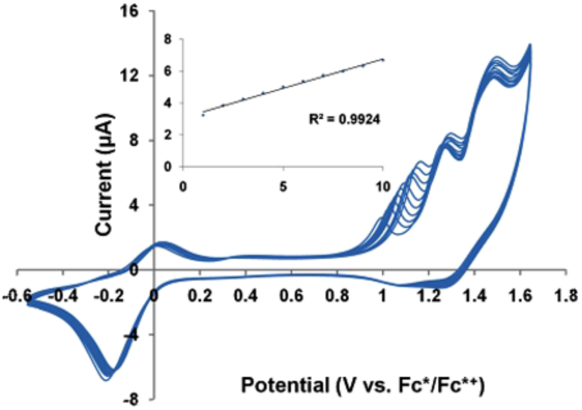

Figure 3. Overlay of continuous cyclic voltammograms of diimine **1** over time. Inset: plot of current maxima vs. number of cycles. Conditions: CH_2Cl_2, $[(n\text{-Bu})_4N^+]$ $[PF_6^-]$ (0.1 M), $[\mathbf{1}]_0 = 1 \times 10^{-3}$ M, $\nu = 100\,\text{mV}\,\text{s}^{-1}$. The potentials were referenced to SCE by shifting Fc^{*0}/Fc^{*+} to -0.057 V. (Figure appears in color online.)

the condensation of 2,2′-bithiophene carboxaldehyde with 4-*n*-butylaniline. Continuous electrochemical cycling of a CH_2Cl_2 solution of **1** in a three-electrode cell resulted in the deposition of a yellow film of polymer. While the relationship between the oxidative current and the scan rate was found to be linear, an indicator that good films were being electrodeposited,[9] a reduction feature was observed at −0.2 V (see Figure 3) and the overall profile did not resemble that of a standard thiophene polymerization. Hence, the material appeared to undergo decomposition

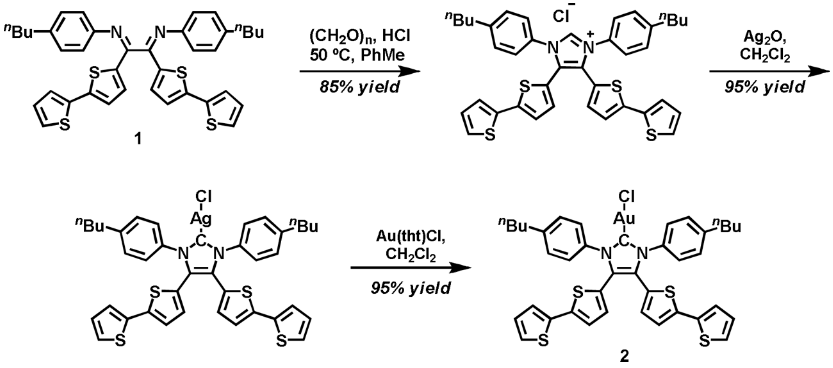

Figure 4. Synthesis of electropolymerizable gold-NHC monomer **2**.

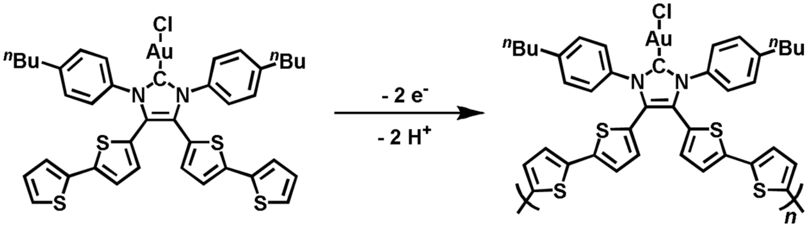

Figure 5. Oxidative electropolymerizaton of **2**.

upon deposition, precluding its use as an effective scaffold for ligating transition metals.

To overcome this limitation, the aforementioned diimine (**1**) was transformed into the NHC-gold complex **2** as summarized in Figure 4. This monomer was subsequently electropolymerized (Figure 5) onto a platinum disc in a three-electrode cell. As shown in Figure 6, features attributable to the oxidation and reduction processes were clear and easily assigned, and the current generated upon oxidation was found to vary linearly with scan rate, as anticipated. This enhancement in the electrochemical properties of the diimine upon metallation is consistent with previous reports on other systems[10] and we surmised that the ligated metals effectively assisted electron transfer processes. Regardless,

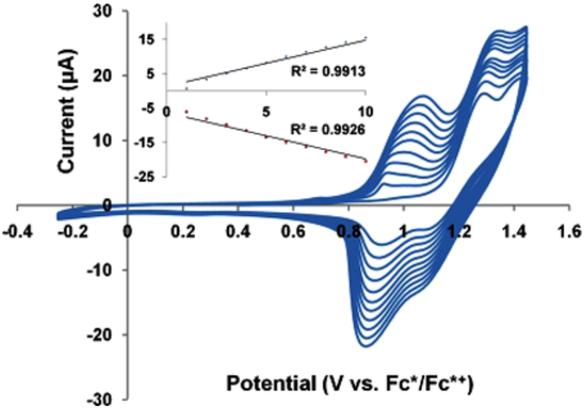

Figure 6. Overlay of continuous cyclic voltammograms of **2** over time. Inset: plot of current maxima vs. number of cycles. Conditions: CH_2Cl_2, $[(n\text{-Bu})_4N^+]$ $[PF_6^-]$ (0.1 M), $[\mathbf{2}]_0 = 1 \times 10^{-3}$ M, $\nu = 100\,\mathrm{mV\,s^{-1}}$. The potentials were referenced to SCE by shifting Fc^{*0}/Fc^{*+} to -0.057 V. (Figure appears in color online.)

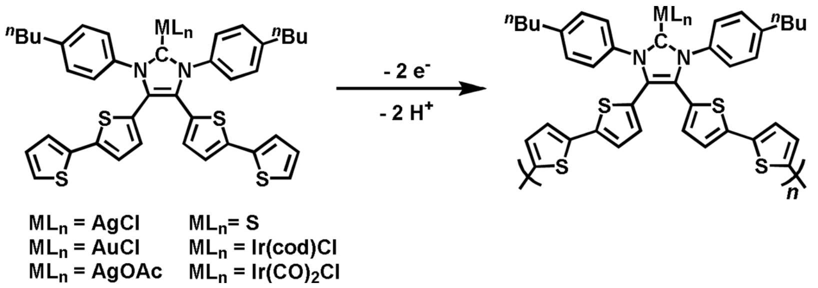

Figure 7. Oxidative electropolymerizaton of various NHC supported transition metal and main group complexes.

elemental analysis of poly(**2**) by XPS revealed the anticipated atomic ratios for sulfur, nitrogen and gold and the UV-vis profile of the polymer was shifted bathochromically with respect to its monomer, consistent with the formation of an electronically delocalized polymeric structure.

As illustrated in Figure 7, the aforementioned synthetic approach was recently extended to include five new polymeric NHCs of the general formula $[ML(NHC)]_n$.[11] These metallopolymers were found to undergo a reversible color change from yellow to blue upon electrochemical oxidation, although the stability of these materials was found to depend on the identity of the incorporated ligated transition metal complex. The $Ir(CO)_2Cl$-substitued material was found to be the most stable electrochromic material studied and was the only system capable of stabilizing

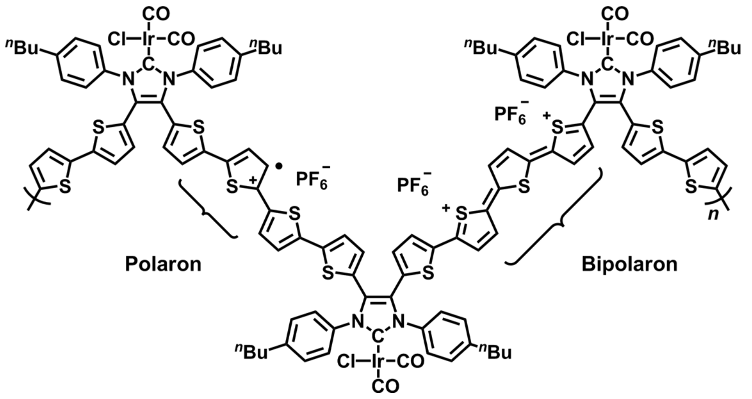

Figure 8. Formation of polaron and bipolaron excitations along the main-chain of metallopolymer containing an NHC supported $Ir(CO)_2Cl$ complex.

both polarons and bipolarons. Moreover, excitations assigned to bipolaron formation, which were observed at 1100 nm by UV-vis-NIR spectroscopy, were relatively discrete when compared to other polythiophene-based materials.[12] As shown in Figure 8, the polarons and bipolarons formed are believed to exist along the quarterthiophene chains that connect the NHC metal moieties. The metals act as electron sinks, which facilitate the formation of positive charges along the oligothiophene linkers. Although organic polymers are known to exhibit electrochromic properties,[13] analogues that contain transition metals are rare.[14] Further study of the aforementioned metallopolymers in a variety of applications is currently underway.

REFERENCES

1. (a) Marion, N. and S. P. Nolan. 2008. *Chem. Soc. Rev.*, **37**: 1776–1782. (b) Leyva, A. and A. Corma. 2009. *J. Org. Chem.*, **74**: 2067–2074. (c) Connon, S. J. and S. Blechert. 2002. *Bioorg. Med. Chem. Lett.*, **12**: 1873–1876. (d) McGuinness, D. 2009. *Dalton Trans*, **35**: 6915–6923.
2. (a) Barnard, P. J. and S. J. Berners-Price. 2007. *Coord. Chem. Rev.*, **251**: 1889–1902. (b) Hindi, K. M., M. J. Panzer, C. A. Tessier, C. L. Cannon, and W. J. Youngs. 2009. *Chem. Rev.*, **109**: 3859–3884. (c) Hickey, J. L., R. A. Ruhayel, P. J. Barnard, V. Murray, S. J. Berners-Price, and A. Filipovska. 2008. *J. Am. Chem. Soc.*, **130**: 12570–12571. (d) Horvath, U. E. I., G. Bentivoglio, M. Hummel, H. Schottenberger, K. Wurst, M. J. Nell, C. E. J. van Rensburg, S. Cronje, and H. G. Raubenheimer. 2008. *New J. Chem.*, **32**: 533–539.
3. Mercs, L. and M. Albrecht. 2010. *Chem. Soc. Rev.*, **39**: 1903–1912.
4. (a) Sommer, W. and M. Weck. 2007. *Coord. Chem. Rev.*, **251**: 860–873. (b) Vougioukalakis, G. C. and R. H. Grubbs. 2010. *Chem. Rev.*, **110**: 1746–1787. (c) Buchmeiser, M. R. 2009. *Chem. Rev.*, **109**: 303–321.
5. (a) Boydston, A. J., K. A. Williams, and C. W. Bielawski. 2005. *J. Am. Chem. Soc.*, **127**: 12496–12497. (b) Kamplain, J. W. and C. W. Bielawski. 2006. *Chem. Commun.*, 1727–1729. (c) Boydston, A. J., J. D. Rice, M. D. Sanderson, O. L. Dykhno, and C. W. Bielawski. 2006. *Organometallics*, **25**: 6087–6098. (d) Boydston, A. J. and C. W. Bielawski. 2006. *Dalton Trans.*, 4073–4077. (e) Coady, D. J., D. M. Kharmov, B. C. Norris, A. G. Tennyson, and C. W. Bielawski. 2009. *Angew. Chem., Int. Ed.*, **48**: 5187–5190. (f) Norris, B. C. and C. W. Bielawski. 2010. *Macromolecules*, **43**: 3591–3593. (g) Tennyson, A. G., J. W. Kamplain, and C. W. Bielawski. 2009. *Chem. Commun.*, 2124–2126. (h) Williams, K. A., A. J. Boydston, and C. W. Bielawski.

2007. *J. R. Soc. Interface*, **4**: 359–362. (i) Hahn, F. E., C. Radloff, T. Pape, and A. Hepp. 2008. *Organometallics*, **27**: 6408–6410.

6. Powell, A. B., C. W. Bielawski, and A. H. Cowley. 2009. *J. Am. Chem. Soc.*, **131**: 18232–18233.
7. (a) Tennyson, A. G., V. M. Lynch, and C. W. Bielawski. 2010. *J. Am. Chem. Soc.*, **132**: 9420–9429. (b) Tennyson, A. G., E. L. Rosen, M. S. Collins, V. M. Lynch, and C. W. Bielawski. 2009. *Inorg. Chem.*, 6924–6933.
8. Powell, A. B., J. R. Brown, K. V. Vasudevan, and A. H. Cowley. 2009. *Dalton Trans.*, **14**: 2521–2527.
9. (a) Skotheim, T. A. and J. R. Reynolds. 2007. *Handbook of Conducting Polymers*, 3rd ed., CRC Press, Boca Raton, FL. (b) Farchioni, R. and G. Grosso. 2001. *Organic Electric Materials*, Springer-Verlag, Berlin.
10. Voituriez, A., M. Mellah, and E. Schulz. 2006. *Synth. Met.*, **156**: 166–175.
11. Powell, A. B., C. W. Bielawski, and A. H. Cowley. 2010. *J. Am. Chem. Soc.*, **132**: 10184–10194.
12. Milum, K. M., Y. N. Kim, and B. J. Holliday. 2010. *Chem. Mater.*, **22**: 2414–2416.
13. Beaujuge, P. M. and J. R. Reynolds. 2010. *Chem. Rev.*, **110**: 268–320.
14. Farrell, J. R., D. P. Lavoie, R. T. Pennell, A. Cetin, J. L. Shaw, and C. J. Ziegler. 2007. *Inorg. Chem.*, **46**: 6840–6842.