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(excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135522. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Highly Conductive Macrocycle-Linked Metallophthalocyanine Polymer**

Richard P. Kingsborough and Timothy M. Swager*

Phthalocyanines are among the most extensively investigated chemical species because of their uses in chemical sensors,^[1] low-dimensional conductors,^[2–6] nonlinear optics,^[7] liquid crystals,^[8–12] as well as their utility as catalysts and dyes.^[13] Clearly, these properties are derived from the exceptional stability and delocalized electronic nature of the macrocycle. The vast majority of metallophthalocyanine-containing polymers are composed of axially connected phthalocyanines that possess conductivities (σ) of 10⁻³–10⁻¹ Scm⁻¹ when oxidatively doped.^[5, 14–17] These polymers, however, cannot be exploited for catalytic applications because of the lack of vacant coordination sites. Previous work directed toward the preparation of one- and two-dimensional and macrocycle-linked phthalocyanine polymers resulted in moderately conductive (σ = 10⁻⁸–10⁻² Scm⁻¹), intractable materials that have not been studied electrochemically.^[18–21] Electrochemical polymerization of designed phthalocyanine macrocycles offers a number of advantages over existing systems, including the deposition of thin electroactive films wherein the electronic states of the macrocycle π system mix with those of the polymer backbone. After considering all the desirable attributes that phthalocyanine ligands offer we chose them as ideal moieties from which to design electroactive metal-containing polymers.^[22–26] Herein we report the synthesis of a novel highly electroactive polythiophene–metallophthalocyanine hybrid material that exhibits conductivities more than three orders of magnitude higher than previously synthesized macrocycle-connected polymers.

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Our synthetic procedures were designed to favor the preparation of macrocycles with electrochemically polymerizable thiophene moieties on alternating subunits. This arrangement should give nearly linear polymer backbones with the metal center in direct electronic communication with the conjugated polymer backbone (Scheme 1). Hoffman and co-workers have recently developed methodologies to preferentially prepare *trans*-[M{pz(A₂;B₂)}] (where pz(A;B) denotes the porphyrazines contain two differently substituted heterocyclic rings) porphyrazines through the use of steric bulk on one of the condensation components.^[27] We have further endowed our macrocycle polymers with rigid, three-dimensional scaffolds to prevent the cofacial aggregation of the macrocycles which would otherwise limit monomer solubility and the accessibility of ligands to the metal centers in the polymer. For this scaffold we utilize iptycene groups, which have previously been demonstrated to create porous highly soluble materials.^[28, 29]

The synthesis of the iptycene-containing phthalocyanine monomers is shown in Scheme 1. Quinone **1** was converted into **2** by reaction with bromine in chloroform. Reduction of the quinone **2** to the hydroquinone **3** was carried out using Na₂S₂O₄ in a biphasic Et₂O/H₂O solvent system. Alkylation of the hydroquinone **3** afforded **4** in high yield. Cyanation of **4** with CuCN in DMF yielded the dicyano derivative **5** in moderate yields. Conversion into the diiminoisoindoline **6** was carried out by bubbling ammonia through a suspension of **5** in ethylene glycol at 140 °C with a catalytic amount of Na for 5 h. Compound **6** (A) was then cyclized then with 4-iodophthalonitrile^[30] (B) in a refluxing Mg(OBu)₂ suspension in BuOH. After trifluoroacetic acid treatment, the free bases of the three isomers, 2H[pz(A₃;B)], *cis*-2H[pz(A₂;B₂)], and *trans*-2H[pz(A₂;B₂)] were obtained. Consistent with our synthetic design the alternating mixed-ring phthalocyanines (precursors to **9-Ni**) were the major products. Numerous attempts to separate these isomers failed. Subsequently, the crude mixture was metalated with [Ni(acac)₂] in refluxing THF. The crude metallophthalocyanine mixture was then treated with 2-tributylstannyl-3,4-ethylenedioxythiophene in DMF at 60 °C in

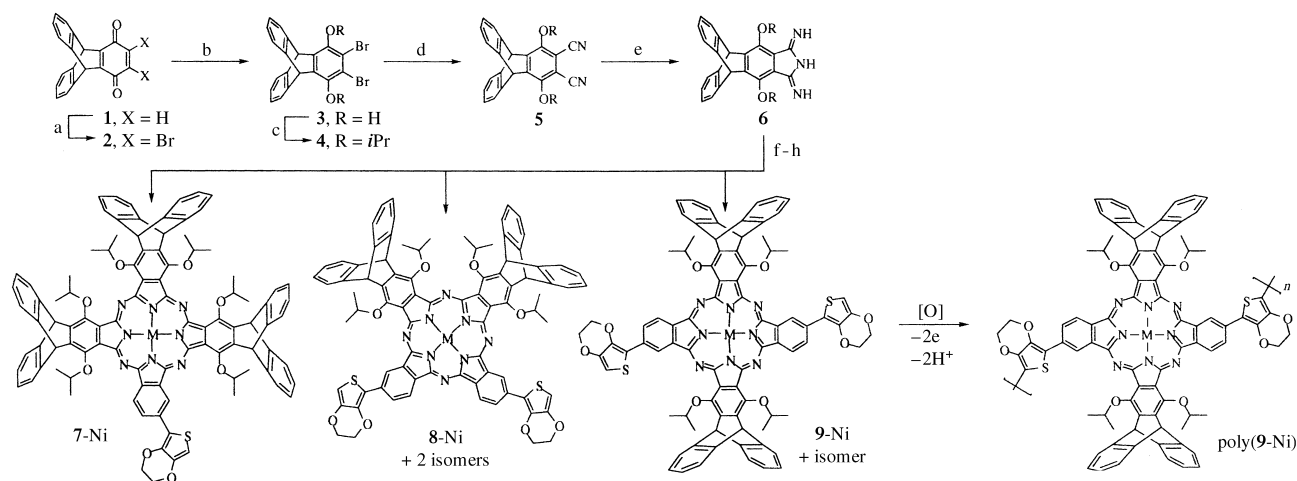
the presence of a catalytic amount of [PdCl₂(PPh₃)₂]. Separation of the three isomers **7-Ni**, **8-Ni**, and **9-Ni** (see Table 1) was easily accomplished by flash chromatography. Compound **7-Ni** with a single thiophene group is incapable of forming polymers and was not studied further. Corey–Pauling–Koltun (CPK) space-filling models indicate that the iptycene architecture should create a pocket at the metal center in all the metal containing species.

The electrochemical characteristics of both the *cis* and *trans* isomers and their polymers were investigated. Electropoly-

Table 1. Spectroscopic and analytical data for selected compounds.^[a]

7-Ni : ¹ H NMR (500 MHz, CDCl ₃): δ = 9.64 (s, 2H), 9.26 (d, <i>J</i> = 8 Hz, 2H), 8.45 (d, <i>J</i> = 7.5 Hz, 2H), 7.61 (dd, <i>J</i> = 5.25, 3 Hz, 4H), 7.08 (dd, <i>J</i> = 5.75, 2.5 Hz, 4H), 6.51 (s, 2H), 6.45 (s, 4H), 5.83 (sept, <i>J</i> = 6 Hz, 4H), 4.55–4.54 (m, 4H), 4.43–4.42 (m, 4H), 1.79 (d, <i>J</i> = 5.5 Hz, 6H), 1.78 (d, <i>J</i> = 5.5 Hz, 6H), 1.76 (d, <i>J</i> = 5.5 Hz, 6H), 1.76 (d, <i>J</i> = 5.5 Hz, 6H); ¹³ C NMR (125 MHz, CDCl ₃): δ = 147.0, 146.9, 146.8, 146.5, 146.4, 145.9, 145.55, 145.5, 145.46, 143.6, 143.54, 143.52, 143.4, 143.2, 140.0, 138.7, 135.8, 135.5, 129.3, 129.0, 128.9, 128.8, 127.9, 127.0, 126.98, 125.0, 123.1, 119.8, 118.6, 99.9, 77.9, 65.7, 65.3, 49.8, 30.4, 24.4, 24.3; UV/Vis (CH ₂ Cl ₂) λ _{max} [nm] (lgε) = 319 (4.71), 730 (4.94); MS: <i>m/z</i> : 1588 ([M+H] ⁺); HR-MS (FAB): calcd for C ₉₈ H ₈₁ N ₈ NiO ₈ S: 1587.5252 ([M+H] ⁺); found: 1587.5288 ([M+H] ⁺)
8-Ni : ¹ H NMR (300 MHz, CDCl ₃): δ = 9.62 (s, 1H), 9.51 (s, 1H), 9.30–9.05 (m, 2H), 8.42–8.16 (m, 2H), 7.68–7.61 (m, 4H), 7.13–7.08 (m, 4H), 6.49–6.45 (m, 6H), 5.90–5.77 (m, 2H), 5.43–5.35 (m, 2H), 4.58–4.32 (m, 8H), 1.82–1.79 (m, 6H), 1.70 (d, <i>J</i> = 5.7 Hz, 6H), 1.50–1.45 (m, 12H); suitable ¹³ C NMR spectra could not be obtained; UV/Vis (CH ₂ Cl ₂) λ _{max} [nm] (lgε) = 318 (4.42), 718 (4.73); MS: <i>m/z</i> : 1436 ([M+H] ⁺); HR-MS (FAB): calcd for C ₈₄ H ₆₅ N ₈ NiO ₈ S ₂ : 1435.3720 ([M+H] ⁺); found: 1435.3673 ([M+H] ⁺)
9-Ni : ¹ H NMR (500 MHz, CDCl ₃): δ = 9.61 (s, 1H), 9.26 (d, <i>J</i> = 7.5 Hz, 1H), 9.50 (dd, <i>J</i> = 8, 1.5 Hz, 1H), 7.65 (dd, <i>J</i> = 5.25, 3 Hz, 4H), 7.63–7.60 (m, 8H), 7.11 (dd, <i>J</i> = 5.25, 3 Hz, 4H), 7.10–7.07 (m, 8H), 6.52 (s, 1H), 6.46 (s, 2H), 6.44 (s, 2H), 6.42 (s, 2H), 5.85 (sept, <i>J</i> = 6.5 Hz, 1H), 5.78 (sept, <i>J</i> = 6.5 Hz, 1H), 5.32 (spt, <i>J</i> = 6.5 Hz, 2H), 5.14 (sept, <i>J</i> = 6.5 Hz, 2H), 4.56–4.54 (m, 2H), 4.42–4.41 (m, 2H), 1.81 (d, <i>J</i> = 6 Hz, 6H), 1.78, (d, <i>J</i> = 6 Hz, 6H), 1.46 (d, <i>J</i> = 6 Hz, 12H), 1.40 (d, <i>J</i> = 6 Hz, 12H); ¹³ C NMR (125 MHz, CDCl ₃): δ = 145.89, 145.86, 145.80, 145.6, 145.55, 145.50, 142.7, 139.4, 134.6, 129.2, 128.2, 128.1, 125.5, 125.4, 124.5, 124.46, 124.4, 77.4, 65.2, 64.8, 49.3, 49.1, 24.0, 23.9, 23.3, 23.2; UV/Vis (CH ₂ Cl ₂) λ _{max} [nm] (lgε) = 325 (4.65), 715 (5.05); MS: <i>m/z</i> : 1436 ([M+H] ⁺); HR-MS (FAB): calcd for C ₈₄ H ₆₅ N ₈ NiO ₈ S ₂ : 1435.3720 ([M+H] ⁺); found: 1435.3688 ([M+H] ⁺)

[a] For full experimental details and characterization for the compounds reported see Supporting Information (7 pages).



Scheme 1. a) Br₂ (2 equiv), CHCl₃, RT, 3 d (87%); b) Na₂S₂O₄ (4 equiv), 1:1 Et₂O:H₂O, RT, 24 h (90%); c) K₂CO₃ (5 equiv), (CH₃)₂CHBr (8 equiv), DMF, 60 °C, 3 d (93%); d) CuCN (6 equiv) DMF, 140 °C, 2 d (71%); e) cat. Na, NH₃(g), ethylene glycol, 140 °C, 5 h (87%); f) Mg(OBu)₂, BuOH, reflux, 12 h then 4-iodophthalonitrile, 1 d; g) [Ni(acac)₂], THF, reflux, 12 h; h) [Bu₃SnEDOT], [PdCl₂(PPh₃)₂], DMF, 60 °C, 12 h.

merization of **9**-Ni on 2 μm -interdigitated microelectrodes^[31–34] resulted in the deposition of dark green films of poly(**9**-Ni). The polymerization proceeds by oxidative coupling of the pendant thiophenes (Scheme 1), there is extensive literature precedent for this process,^[2] and we find that related macrocycles without pendant thiophenes do not oxidatively polymerize. The cyclic voltammogram of this polymer in fresh (monomer free) electrolyte on the interdigitated microelectrodes (Pt button electrodes give identical results) is shown in Figure 1.^[36]

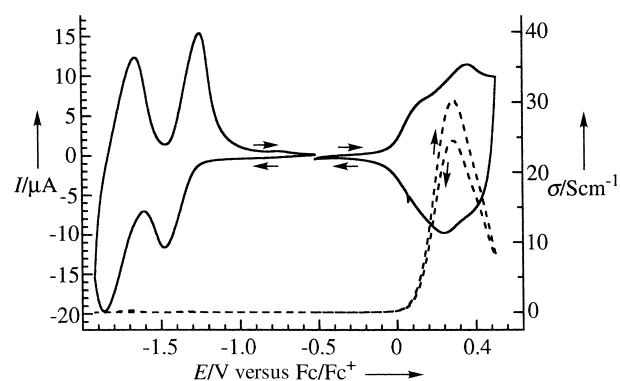


Figure 1. Cyclic voltammograms (solid lines) and conductivity profiles (dashed lines) of poly(**9**-Ni) in 0.1M $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ on 2 μm -interdigitated microelectrodes. Sweep rates are 100 mV s^{-1} for cyclic voltammograms and 5 mV s^{-1} with a 40 mV offset potential for conductivity measurement.

The cyclic voltammogram of poly(**9**-Ni) displays prominent features in the reductive region at -1.35 and -1.75 V (Figure 1). Based upon comparisons of cyclic voltammograms with those of the *cis* derivative **8**-Ni, we assign the first one-electron wave to a $\text{Ni}^+/\text{Ni}^{2+}$ redox process and the second to a ligand-centered process. The oxidative region of the cyclic voltammogram of poly(**9**-Ni) consists of a single broad redox wave centered at 0.3 V with a leading shoulder at 0.1 V. The conductivity trace obtained in situ^[35] (Figure 1) shows significant conduction associated only with the polymer backbone and not the metal-centered and ligand-centered reductive processes. This later fact is consistent with our previous studies that demonstrate the need for redox-matching of the polymer with square planar Co species to produce high levels of metal centered electroactivity and redox conductivity.^[22a] The maximum conductivity is observed at the half-wave potential of the polymer film ($\sigma_{\text{max}} = 30 \text{ Scm}^{-1}$) and decreases rapidly at higher applied potentials.

Complex **8**-Ni did not afford films when subjected to the standard electrochemical polymerization conditions. During this process, oxidation of the ethylenedioxythiophene, EDOT, moieties is observed along with a ligand-based oxidation. However, the expected reduction waves associated with an immobilized polymer film were not detected, perhaps because of the higher solubility of the polymer. Cyclic voltammograms of the monomeric species in solution closely resemble those of **9**-Ni. Two metal- and ligand-based reductive processes are observed, with the first corresponding almost exactly to that

of **9**-Ni, which allows (see above) for the assignment as the $\text{Ni}^+/\text{Ni}^{2+}$ redox process.

We have prepared a highly conductive phthalocyanine-containing hybrid polymer. This polymer shows both metal-centered electroactivity as well as high conductivity. The $\text{Ni}^+/\text{Ni}^{2+}$ redox wave does not contribute to the conductivity.

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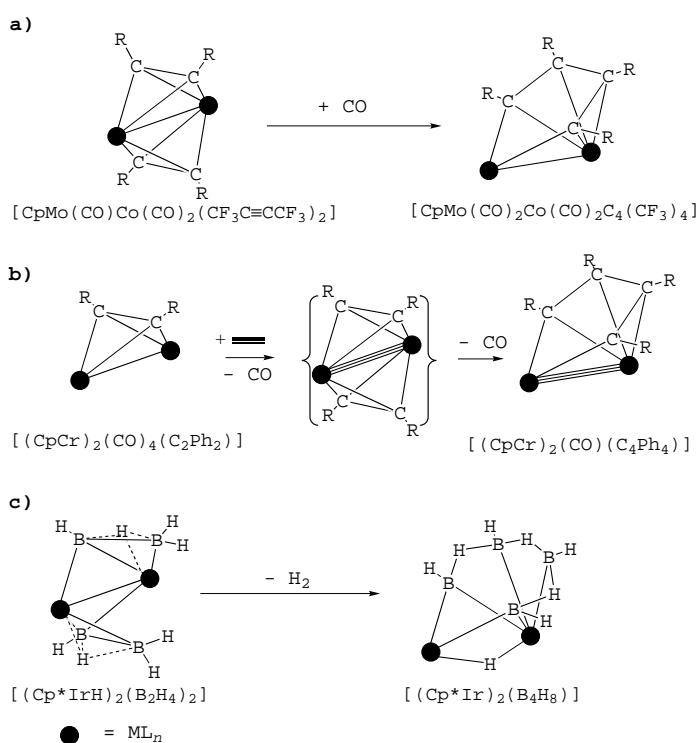
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 [36] Unless noted all potentials are referenced to the Fc/Fc⁺ redox couple.

Symmetrical Scission of the Coordinated Tetraborane in [(Cp*ReH₂)₂B₄H₄] on CO Addition and Reassociation of the Coordinated Diboranes on H₂ Loss**

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The formation and scission of C–H and C–C bonds within the coordination sphere of a metal lie at the heart of organometallic chemistry.^[1] For example, the cleavage of alkynes coordinated to multinuclear metal sites into separated coordinated alkylidyne fragments^[2] exhibits more than one mode of scission: dissociation of a dimetal ethyne complex (dimetallatetrahedrane) into two methylidyne complexes^[3] or ligand loss from a *nido*-trimetallaalkyne cluster to yield a *closo*-trimetalladialkylidyne cluster.^[4] The linking of alkynes at dimetal sites has been documented and, pertinent to this work, are the two systems outlined in Scheme 1 a and b. In the first, a 46 cluster valence electron (cve) bitetrahedral complex is converted into a 48 cve pentagonal-pyramidal complex containing a C₄ fragment.^[5] In the other, a μ -alkyne complex is converted into a 44 cve pentagonal-pyramidal complex with a localized Cr≡Cr bond via a postulated 46 cve bitetrahedral intermediate.^[6] Both generate a C₄ fragment from two C₂ fragments.

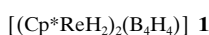
In principle, the incorporation of transition metals into the chemistry of p-block elements other than carbon permits similar manipulation of homonuclear bonding.^[7] The literature contains numerous examples for boron,^[8–11] but other elements illustrate the possibilities as well.^[12] In our own work, the elimination of H₂ from 50 cve [(Cp*IrH)₂(B₂H₄)₂] leads to the 48 cve complex [(Cp*Ir)₂(B₄H₈)] in which a B₄ fragment is generated from the fusion of two B₂ fragments (Scheme 1 c).^[13] The structure of the latter is analogous to that



Scheme 1. Examples of C–C bond formation promoted by a) CO addition to a Mo,Co complex, b) CO loss from (and C₂Ph₂ addition to) a Cr₂ complex, and c) B–B bond formation promoted by H₂ loss from an Ir₂ complex.

of the product in Scheme 1 although one reaction (C–C bond formation) is driven by ligand addition and the other (B–B bond formation) by ligand loss. Here we describe a related dirhenium system in which both B–B bond formation on ligand loss and B–B bond breaking on ligand addition are demonstrated.

The direct synthesis of **1**, from [Cp*ReCl₄] and LiBH₄, permits an examination of the chemistry of its derivatives.^[14] Thus, the chemistry of compounds of molecular formula



[(Cp*M)₂B₄H₈] as M varies from Cr^[15] to Re^[16] (and Ru^[17] to Ir^[13]) unambiguously reveals the role of the transition metal. We have reported that the reaction of 42 cve [(Cp*Cr)₂(B₄H₈)] with CO leads to 44 cve [(Cp*Cr(CO))₂(B₄H₆)] in good yield (Scheme 2).^[15] Now, the same reaction with the rhenium analogue has been explored.

Reaction of **1** with 1 atm of CO and mild heating leads (via an intermediate **2** see below) to the 44 cve complex **3**, which has been characterized spectroscopically and crystallographi-



cally (Figure 1).^[18] The core structure deduced from the data based on the electron counting rules^[19, 20] is consistent with the solid-state structure. The close analogy with the behavior of the unsaturated complex [(Cp*Cr)₂B₄H₈] is evident—each loses H₂ and adds an appropriate number of CO ligands to the

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