ROM Polymerization−Capture−Release: Application to the Synthesis of Unsymmetrical Porphyrazinedithiols and Peripherally Metalated Derivatives

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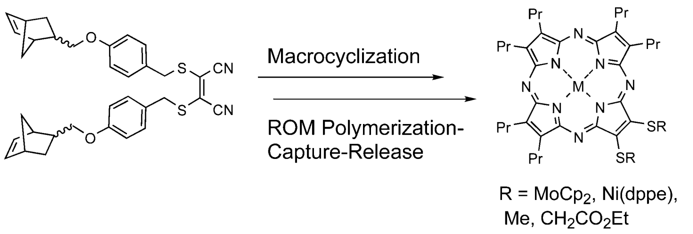

Crossover Linstead macrocyclization of a doubly norbornenyl-functionalized dimercaptomaleonitrile with dipropylmaleonitrile gave a crude mixture of porphyrazines containing the hexapropylporphyrazinedithiol magnesium complex. The mixture was subjected to ring-opening metathesis polymerization to yield the insoluble porphyrazinedithiol-functionalized polymers. Cleavage from the polymer backbone using mercury(II) acetate followed by reaction with electrophiles gave access to a range of thioporphyrazinedithiol derivatives including solitaire porphyrazines. Studies into the possible uses of hexapropyl-2,3-di-(carboxymethylthio)porphyrazine in sensing metal cations in solution are described.

Introduction

Compounds possessing tetrapyrrolic macrocyclic ring systems can be divided into two distinct categories, namely porphyrins and tetraazaporphyrins. The latter differ merely by the presence of *meso* nitrogen atoms and can be further divided into porphyrazines and phthalocyanines. Porphyrazines present a unique opportunity in respect to the other two tetrapyrrolic systems in that direct heteroatom substitution of the β-pyrrole positions is possible.[1] *meso*-Aza-substitution has a strong influence on the chemical behavior[2] and the overall aromaticity and the size of the central cavity.[3] In addition, peripheral heteroatom substitution has profound effects on the electronic structure and optical properties of the porphyrazine framework.[4] Barrett, Hoffman, and co-workers have published extensively on the synthesis of porphyrazines bearing thiols, amines, or alcohols as ring substituents and with the conversion of these polydentate ligands into a variety of coordination complexes.[5,6] Porphyrazines containing peripheral thiols constitute an important subclass of these immensely flexible macrocycles. Since our initial publication in 1980,[1] we have demonstrated the synthesis of numerous porphyrazinedithiol, -tetrathiol, -hexathiol, and -octathiols and their multimetallic complexes, including star porphyrazines,[7−9] Gemini porphyrazines,[10] solitaire systems,[11−13] octathioporphyrazine crown ethers,[14−16] and

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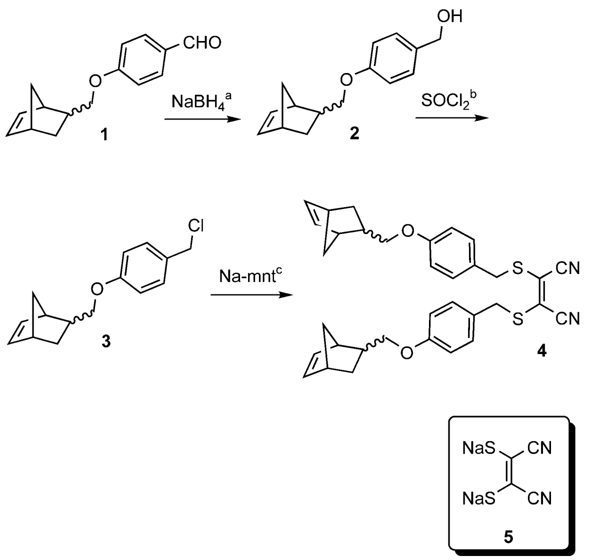
trimetallic porphyrazine dimers.[17] Furthermore, we have attached porphyrazinedithiol and -tetrathiol derivatives to gold surfaces and investigated the effect of orientation on the porphyrazine redox potential.[18] Many of the porphyrazinedithiols and -tetrathiols are fluorescent and are of potential use as biomedical agents.[19,20] Following our studies on purification-minimized parallel synthesis using ring-opening metathesis (ROM) polymerization[21] and impurity annihilation[22] and related studies by Hanson,[23,24] we sought to use ROM polymerization methods to improve the syntheses of polyfunctional porphyrazines. The principle of employing a norbornenyl-functionalized dinitrile with solution-phase Linstead macrocyclization and subsequent selective capture of the desired porphyrazine by ROM polymerization is appealing. Cleavage of the macrocycle from the ROM polymer should deliver the pure porphyrazine without the need for extensive chromatography. Ruthenium alkene metathesis catalysts, developed by Grubbs,[25,26] have been previously applied to the synthesis of polymeric porphyrazine structures[27] and, therefore, should be ideal for this application. Recently, we published initial studies on a ROM polymerization−capture−release strategy for the chromatography-free synthesis of amino-porphyrazines.[28] We now report an significant extension of the method for the preparation of unsymmetrical porphyrazinedithiols. This new procedure should assist in the parallel synthesis of novel multimetallic porphyrazines, with possible applications in electronic and magnetic materials and as chemical sensors, nanomaterials, and biomedical agents.

Results and Discussion

To extend the ROM polymerization−capture−release strategy to the synthesis of porphyrazinedithiols, a suitable protected derivative of dimercaptomaleonitrile, tagged with a norbornenyl linker was needed. Simmons and co-workers reported the synthesis of the monosodium salt of mercapto(methylthio)maleonitrile,[29] in two steps from the readily available disodium dimercaptomaleonitrile (Na-mnt) **5**,[30] a starting material frequently employed in the synthesis of porphyrazinedithiols.[5] However, in our hands, monofunctionalization of **5** gave low yields and mixtures of mono-, di-, and unsubstituted compounds. We therefore focused on the synthesis of doubly norbornenyl-functionalized mercaptomaleonitrile **4**. Aldehyde **1**[28] was reduced using sodium borohydride to provide alcohol **2** (97%). Although preparation of the tosylate proved problematic due to its facile solvolysis, conversion of alcohol **2** into the corresponding chloride **3** proceeded smoothly by treatment with thionyl chloride. Subsequent reflux of an acetone solution containing dinitrile **5** and chloride **3** catalyzed by sodium iodide resulted in the formation of dinitrile **4** (68% yield) (Scheme 1).

SCHEME 1[a]



[a] Reagents and conditions: (a) NaBH$_4$, MeOH, (97%); (b) SOCl$_2$, Tol, 0 °C to Δ(96%); (c) **5**, Me$_2$CO, cat. NaI, Δ(68%).

Mixed Linstead macrocyclization of dinitrile **4** with dipropylmaleonitrile **6** (10 equiv)[31] gave a crude mixture of dyes containing the porphyrazines **7** and **8**, as identified by FAB mass spectrometry. Filtration of this crude mixture, followed by treatment with Grubbs' second-generation catalyst **13**[25,26] and cross-linker **14**, under the previously reported conditions,[28] resulted in the formation of ROM polymer **9** as an insoluble blue solid (Scheme 2).

ROM polymer **9** was stable to the previously established cleavage acidic system (10% TFA in dichloromethane).[28] This is not too surprising since the analogous *p*-methoxybenyl protecting group has been reported to be relatively stable to TFA when used as a protecting group for cysteine amino acids.[32] However, treatment of ROM polymer **9** under more potent Brønsted acidic

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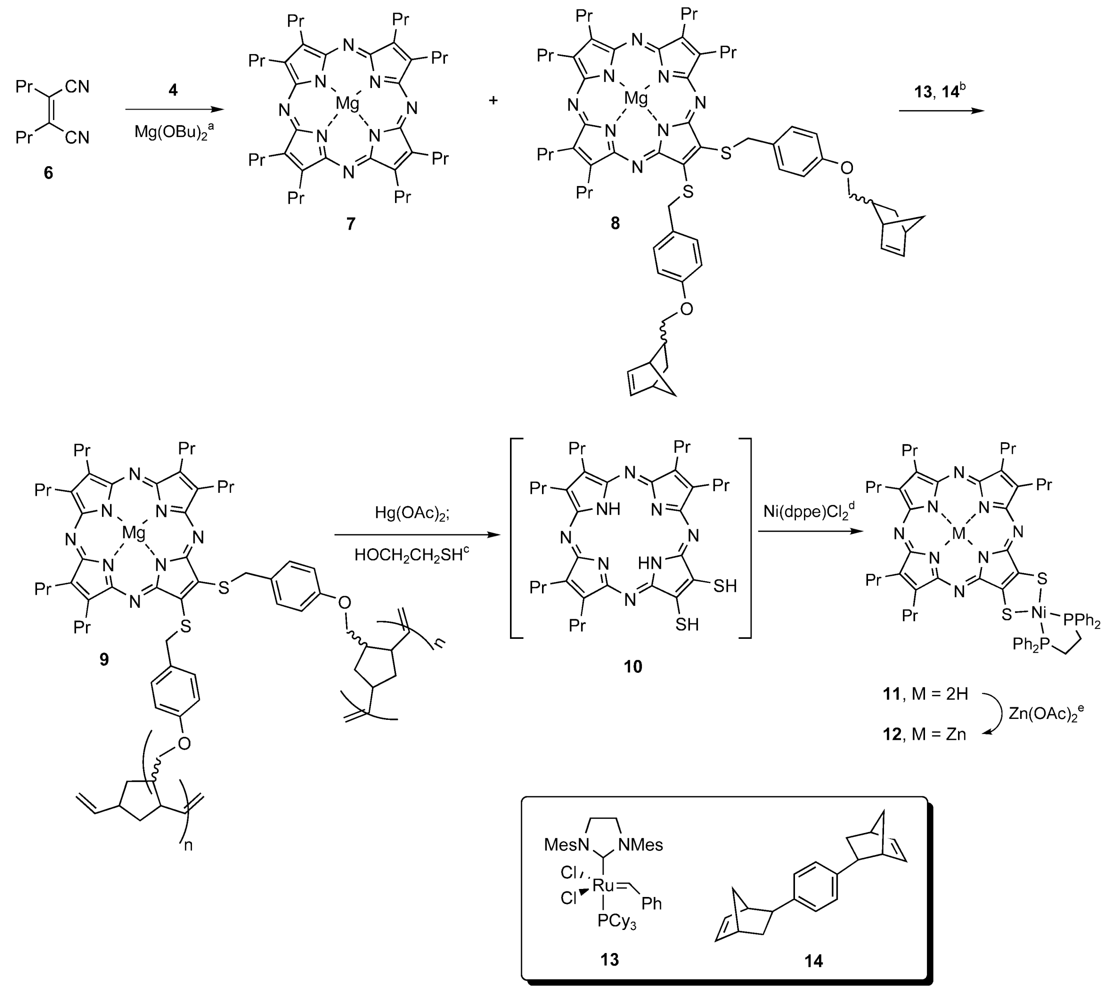
SCHEME 2[a]



[a] Reagents and conditions: (a) $Mg(O^nBU)_2$, ^nBuOH, Δ; (b) 1 mol % of **13**, **14**, CH_2Cl_2, 40 °C; (c) $Hg(OAc)_2$, CH_2Cl_2, MeOH, 20 °C; $HOCH_2CH_2SH$, 20 °C; (d) $Ni(dppe)Cl_2$, EtN, CH_2Cl_2, 20 °C, 24 h, 15%; (e) $Z(OAc)_2$, PhMe, DMF, 85 °C (98%).

conditions (1 M triflic acid, 2 M TFA)[28] resulted in the formation of the purple pigment **10**, which was not characterized but allowed to react with (diphos)$NiCl_2$ and triethylamine. This resulted in the formation of solitaire porphyrazine **11** in 6% overall yield (from **4**) (Scheme 2). Unfortunately, significant decomposition was observed throughout the reaction and the isolation of the highly air-sensitive macrocycle **10** was not conducive to isolation of the product in reasonable yield. Therefore, an alternative cleavage strategy was examined. Recently, the 4-methoxybenyl protecting group has been utilized in the synthesis of porphyrazinedithiols, with subsequent cleavage by mercury(II) acetate, to give the air-sensitive free porphyrazinedithiolate complex.[33] With this in mind, ROM polymer **9** was allowed to react sequentially with mercury(II) acetate, 2-hydroxyethanethiol, and (diphos)-$NiCl_2$ in the presence of triethylamine in a one-pot reaction. Purification by chromatography on a single flash column gave the solitaire porphyrazine **11**. Optimization showed that use of an excess of mercury(II) acetate was important and resulted in the production of **11** in good yield (15% from **4**) (Scheme 2). This result compares favorably with a structurally related nickel solitaire porphyrazine, which was obtained by the standard solution phase methods in approximately 5% overall yield from the maleonitrile.[11] The product contained traces of dppe/dppe oxide from the excess (dppe)$NiCl_2$ utilized. Likewise, the synthesis of a molybdocene solitaire porphyrazine, using the *p*-methoxybenyl protecting group was achieved in a low 5% yield from the precursor dinitrile.[33]

Excess mercury(II) acetate was presumably needed to compensate for oxymercuration of the unsaturated ROMP backbone and the slow rates commonly observed for solid supported reactions. However, interestingly, hydrogenation of the ROM polymer backbone[34] or demetalation (1:1 acetic acid/dichloromethane) of the polymer supported macrocycle **9** failed to increase the yield of the cleavage reaction. The unexpected in situ demetalation of **9** observed, giving the delicate porphyrazinedithiol **10**, arose from acetic acid mediated demetalation. Remetalation of the free-base solitaire **11** furnished the pure

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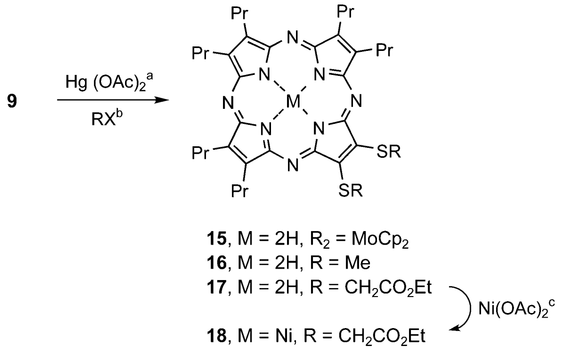
SCHEME 3[a]



[a] Reagents and conditions: (a) $Hg(OAc)_2$, CH_2Cl_2, MeOH, 20 °C; $HOCH_2CH_2SH$, 20 °C; (d) Cp_2MoCl_2 or MeI or $BrCH_2CO_2Et$, Et_3N, CH_2Cl_2, 20 °C (4−6%); (c) $Ni(OAc)_2$, DMF, 100 °C (80%).

zinc(II) macrocycle **12** (98%), highlighting both the stability of the solitaire porphyrazines and the usefulness in this methodology in the synthesis of multi-metallic systems (Scheme 2). The range of functionalized porphyrazines obtained from the above cleavage reaction was extended by reaction of the porphyrazinedithiol **10** with a variety of electrophiles to provide pure samples of the solitaire porphyrazine **15**, methylated macrocycle **16** and porphyrazine diester **17** (4%, 6% and 6% overall yield respectively) (Scheme 3). Macrocycle **17** was subsequently metalated using nickel(II) acetate to yield porphyrazine **18** (80%).

Previously, we have demonstrated the binding and sensing of various cationic metal salts using octathioporphyrazine crown ethers,[14−16] porphyrazine-appended thiacrown ethers,[15] and polyetherol appended porphyrazines.[35] For these reasons, we examined the binding of soft metal ions within the binding pocket of nickel porphyrazine **18**. A solution of macrocycle **18** was titrated against silver(I) tetrafluoroborate, mercury(II) perchlorate, lead(II) nitrate, cadmium(II) chloride, and cadmium(II) perchlorate. No evidence of binding was observed for lead(II) or cadmium(II); however, in the case of silver(I) and mercury(II) changes in the UV−vis spectra were apparent (Figure 1).

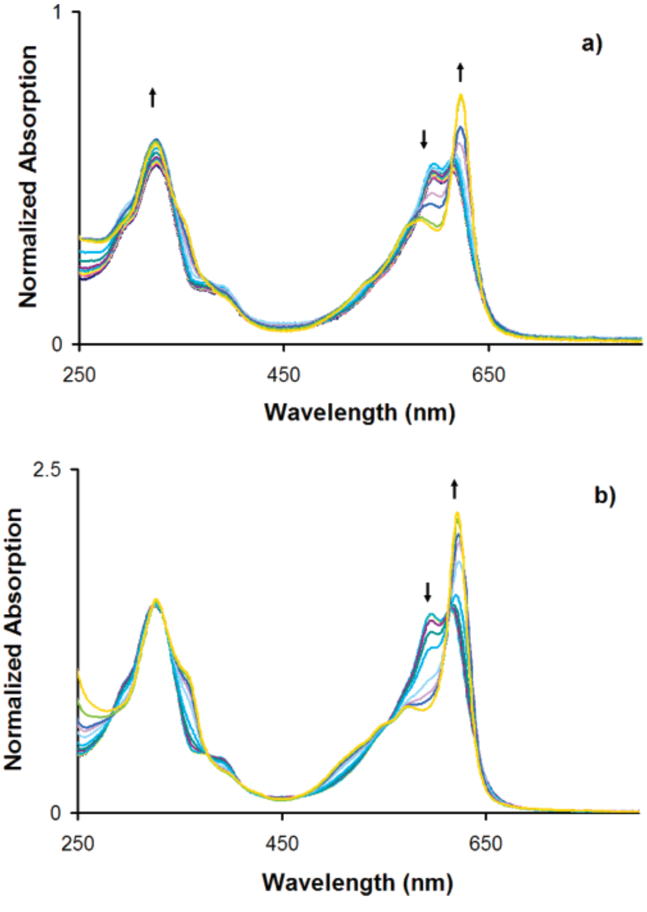


FIGURE 1. UV−vis spectra during titration of **18** in $CHCl_3$ and MeOH (3:1) using (a) $AgBF_4$, (b) $Hg(ClO_4)_2$.

The results from the titration indicate complex binding behavior. In the case of titration with Ag^+ there was initially no significant change in the UV−vis spectrum (0−2.5 equiv $AgBF_4$). At higher concentrations (>2.5 equiv), the Soret band (325 nm) gradually increased in intensity and the small band at 385 nm disappeared. The Q-band exhibited complex behavior; the peak at 600 nm underwent broadening with a blue shift, whereas the peak at 618 nm underwent sharpening with a red shift. No further changes were observed at greater than 10 equiv. The initial minimal effects on the spectrum have been previously observed for certain porphyrazine appended crown and thiacrown ethers.[36] The authors suggested a cooperative binding process was in operation. Alternatively, binding to the carboxyl groups without binding to the ring sulfur atoms may have been occurring, which would have been UV−vis invisible. As with $AgBF_4$, $Hg(ClO_4)_2$ displayed more complex binding behavior than expected, although the observable changes appeared qualitatively similar to those of Ag(I). With Hg(II), spectroscopic changes were observed from the start of the titration (<1 equiv Hg(II)) with the changes complete at around 5 equivalents. No real change was observed for the Soret band (325 nm) whereas the Q-band exhibited complex behavior. The peak at 600 nm was broadened and blue shifted whereas the peak at 618 nm was sharpened and red shifted. From these initial results it is difficult to draw any firm conclusions regarding the binding of metal cations by porphyrazine **18**, apart from the fact that Hg^{2+} is bound more strongly than Ag^+. The exact nature the binding has yet to be established and further studies are underway.

Conclusions

An extension to the ROM polymerization−capture−release strategy for the synthesis of novel porphyrazinedithiols and derived solitaire complexes is described. This synthetic strategy therefore has potential for application to the synthesis of novel electronic and magnetic materials. In addition, the nickel(II) porphyrazine **18** showed complex binding behavior with silver(I) and mercury(II) salts in solution, whereas no binding was

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observed for cadmium(II) and lead(II). Therefore, derivatives of **18** could find application in the production of selective chemical sensors. Further applications of this methodology will be the subject of future reports.

Experimental Section

5-(4-(Hydroxymethyl)phenoxymethyl)bicyclo[2.2.1]hept-2-ene (2). Aldehyde **1**[28] (5.0 g, 21.9 mmol) in MeOH (10 mL) was added slowly to $NaBH_4$ (2.0 g, 52.9 mmol) in MeOH (30 mL) at 0 °C under N_2, and the mixture was allowed to warm to 20 °C over 30 min. HCl (1 M, 30 mL) was added, and the resulting solution extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and rotary evaporated. Chromatography (SiO_2, hexanes/EtOAc, 6:4) gave alcohol **2** (4.89 g, 97%), a clear oil, as a mixture of isomers: R_f 0.44 (hexanes/EtOAc 6:4); IR (neat) 3339, 1612, 1513, 1468, 1243, 1173, 1029, 826 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 0.62 (m, 1H), 1.26−1.51 (m, 2H), 1.91 (m, 1H), 2.56 (m, 1H), 2.86 (s, 1H) 3.05 (s, 1H), 3.55 (t, J = 9.0 Hz, 1H), 3.72 (t, J = 9.0 Hz, 1H), 4.60 (s, 2H), 5.96−6.18 (m, 2H), 6.88 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.1, 38.4, 42.3, 43.9, 49.5, 65.1, 71.6, 114.6, 128.7, 132.4, 132.9, 137.6, 158.8; MS (CI) m/z 230 $[M]^+$; HRMS (CI) calcd for $C_{15}H_{18}O_2$ $[M^{+\bullet}]$ 230.1307, found $[M^{+\bullet}]$ 230.1300. Anal. Calcd for $C_{15}H_{17}ClO$: C, 78.23; H, 7.88. Found: C, 78.05; H, 7.75.

5-(4-(Chloromethyl)phenoxymethyl)bicyclo[2.2.1]hept-2-ene (3). Thionyl chloride (0.62 mL, 8.6 mmol) in PhMe (5 mL) was added dropwise with vigorous stirring to alcohol **2** (1.0 g, 4.3 mmol) and Et_3N (0.6 mL, 4.5 mmol) in PhMe (20 mL) at 0 °C under N_2. Once the addition was complete, the mixture was allowed to warm to 20 °C and stirred for 2 h. Finally, the mixture was heated at reflux for 30 min to complete the transformation. The solution was allowed to cool to 20 °C and further cooled to 0 °C, and H_2O (20 mL) was slowly added. The resulting layers were separated, and the organic layer was washed with 10% 2 M HCl (20 mL) and saturated aqueous $NaHCO_3$ (20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and rotary evaporated. Chromatography (SiO_2, hexanes/EtOAc, 9:1) gave chloride **3** (1.03 g, 96%), a clear oil, as a mixture of isomers: R_f 0.67 (hexanes/EtOAc, 9:1); IR (neat) 1611, 1513, 1467, 1246, 1175, 1025, 830 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 0.64 (m, 1H), 1.28−1.53 (m, 2H), 1.95 (m, 1H), 2.58 (m, 1H), 2.89 (s, 1H), 3.07 (s, 1H), 3.57 (t, J = 9.0 Hz, 1H), 3.74 (t, J = 9.0 Hz, 1H), 4.60 (s, 2H), 5.97−6.22 (m, 2H), 6.89 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.1, 38.6, 42.3, 43.9, 46.1, 49.5, 71.5, 114.7, 129.4, 130.1, 132.4, 137.6, 159.3; MS (CI) m/z 248 $[M]^+$; HRMS (CI) calcd for $C_{15}H_{17}ClO$ $[M^{+\bullet}]$ 248.0968, found $[M^{+\bullet}]$ 248.0964. Anal. Calcd for $C_{15}H_{17}ClO$: C, 72.43; H, 6.89. Found: C, 72.29; H, 6.73.

2,3-Di((4-(norborn-2-en-5-yl)methoxy)benzylthio)maleonitrile (4). A mixture containing dinitrile **5** (0.3 g, 1.65 mmol), chloride **3** (0.82 g, 3.3 mmol), and NaI (0.1 g, 0.7 mmol) in Me_2CO (10 mL) was heated to reflux for 18 h. The suspension was allowed to cool, filtered, and rotary evaporated. The residue was dissolved in CH_2Cl_2 (20 mL) and washed with H_2O (4 × 30 mL) to remove residual salts. The organic extract was dried ($MgSO_4$), filtered, and rotary evaporated. Chromatography (SiO_2, CH_2Cl_2) gave sulfide **4** (0.64 g, 68%), a viscous bright yellow oil, which crystallized over time as a mixture of isomers: R_f 0.74 (CH_2Cl_2); IR (neat) 2209, 1609, 1511, 1467, 1241, 1171, 1023, 832 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 0.64 (m, 2H), 1.28−1.51 (m, 4H), 1.93 (m, 2H), 2.56 (m, 2H), 2.87 (s, 2H), 3.05 (s, 2H), 3.55 (t, J = 9.0 Hz, 2H), 3.71 (t, J = 9.0 Hz, 2H), 4.28 (s, 4H), 5.96−6.21 (m, 4H), 6.84 (d, J = 8.0 Hz, 4H), 7.23 (d, J = 8.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.1, 38.3, 39.1, 42.3, 43.9, 49.5, 71.5, 115.0, 125.9, 130.4, 132.3, 137.7, 159.2; MS (FAB) m/z 567 $[M + H]^+$; HRMS (FAB) calcd for $C_{34}H_{35}N_2O_2S_2$ $[M + H]^+$ 567.2140, found $[M + H]^+$ 567.2156.

ROM Polymer-Supported [7,8,12,13,17,18-Hexapropyl-2,3-di((4-(norborn-2-en-5-yl)methoxy)benzylthio)porphyrazinato]magnesium(II) (9). Mg (91 mg, 3.75 mmol) and I_2 (ca. 1 crystal) in 1-butanol (20 mL) were heated to reflux for 24 h under N_2. The mixture was allowed to cool when dinitrile **4** (0.16 g, 0.28 mmol) and dipropylmaleonitrile **6**[24] (0.45 g, 2.8 mmol) in 1-butanol (10 mL) were added, and the mixture was heated to reflux for a further 24 h. Rotary evaporation and subsequent azeotrope with PhMe (2 × 50 mL) gave a residue, which was preabsorbed onto silica and added to additional silica. Elution with hexanes/EtOAc (8:2) was carried out until the intensity of the initial blue extract had decreased. After rotary evaporation, the residue was dissolved in degassed CH_2Cl_2 (2 mL) under N_2 and cross-linker **14** (8.1 mg, 0.031 mmol) in CH_2Cl_2 (0.5 mL) was added followed by catalyst **13** (2.4 mg, 2.8 μmol) and the mixture heated to 40 °C for 12 h. CH_2Cl_2 (2 mL), MeCN (1 mL), and ethyl vinyl ether (1 mL) were added, and the mixture was heated to 40 °C for 1 h. The polymer gel was filtered off and washed sequentially with CH_2Cl_2 (3 × 20 mL) and further extracted with CH_2Cl_2 (Soxhlet) for 12 h to leave the insoluble ROM polymer **9** (87 mg) as a blue solid.

[1,2-(Diphenylphosphino)ethyl)nickel(II)]-7,8,12,13,-17,18-hexapropyl-2,3-dithiolatoporphyrazine (11). $Hg(OAc)_2$ (36 mg, 0.11 mmol) was added to a suspension of ROM polymer **9** (10 mg) in degassed CH_2Cl_2 (3 mL) and MeOH (1 mL) under N_2. The suspension was stirred at 20 °C for 24 h. 2-Hydroxyethanethiol (48 μL, 0.68 mmol) in degassed CH_2Cl_2 (0.5 mL) was added and the resultant suspension stirred at 20 °C for 10 min. $(Diphos)NiCl_2$ (70 mg, 0.13 mmol) was added, followed by Et_3N (27 μL, 0.195 mmol) in degassed CH_2Cl_2 (0.5 mL). The resulting suspension was stirred under N_2 for 24 h and rotary evaporated. Chromatography (SiO_2, $CHCl_3$) gave solitaire **11** (5.3 mg, 15%) as a blue solid: R_f 0.41 ($CHCl_3$); IR (neat) 1481, 1462, 1435, 1104, 734 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 339 (4.68), 549 (4.38), 587 (4.44), 661 (4.34) nm; ^1H NMR (500 MHz, $CHCl_3$) δ 1.17−1.29 (m, 18H), 2.13−2.39 (m, 8H), 2.53 (m, 4H), 2.69 (m, 4H), 3.74−4.01 (m, 12H), 7.46 (m, 4H), 7.72 (m, 8H), 8.06 (m, 8H); ^{13}C NMR (125 MHz, $CHCl_3$) δ 14.9, 25.0, 27.2, 28.4, 29.7, 128.7, 129.3, 130.8, 131.0, 131.1, 132.4, 133.5, 134.0, 143.3, 165.5; MS (FAB) m/z 1085 $[M + H]^+$; HRMS (FAB) calcd for $C_{60}H_{69}N_8NiP_2S_2$ $[M + H]^+$ 1085.3915, found $[M + H]^+$ 1085.3942.

[1,2-(Diphenylphosphino)ethyl)nickel(II)][7,8,12,13,-17,18-hexapropyl-2,3-dithiolatoporphyrazinato]zinc(II) (12). Porphyrazine **11** (3.6 mg, 3.3 μmol), $Zn(OAc)_2{\cdot}2H_2O$ (3.0 mg, 13 μmol), dry DMF (0.5 mL), and PhMe (2 mL) were heated to 85 °C for 16 h under N_2. Rotary evaporation and chromatography (SiO_2, $CHCl_3$) gave solitaire **12** (3.7 mg, 98%) as a green solid: R_f 0.10 ($CHCl_3$); IR (neat) 1454, 1435, 1148, 947, 875 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 346 (4.48), 572 (4.03), 622 (4.41), 668 (3.93) nm; ^1H NMR (500 MHz, $CHCl_3$) δ 1.11−1.25 (m, 18H), 2.12 (m, 12H), 2.54 (m, 4H), 3.58 (m, 8H), 3.75 (m, 4H), 7.47 (m, 4H), 7.63 (m, 8H), 8.03 (m, 8H); ^{13}C NMR (125 MHz, $CHCl_3$) δ 14.8, 25.4, 27.2, 28.2, 29.7, 128.8, 129.2, 131.8, 132.0, 133.6, 133.9, 144.6; MS (FAB) m/z 1146 $[M^{+\bullet}]$.

[1,1′-Di(cyclopentadienyl)molybdenum(II)]-7,8,12,13,-17,18-hexapropyl-2,3-dithiolatoporphyrazine (15).[13] $Hg(OAc)_2$ (36 mg, 0.11 mmol) was added to ROM polymer **9** (10 mg) in degassed CH_2Cl_2 (3 mL) and MeOH (1 mL) under N_2 and the suspension stirred at 20 °C for 24 h. 2-Hydroxyethanethiol (48 μL, 0.68 mmol) in degassed CH_2Cl_2 (0.5 mL) was added and the resultant suspension stirred at 20 °C for 10 min. Cp_2MoCl_2 (39 mg, 0.13 mmol) was added, followed by Et_3N (27 μL, 0.195 mmol) in degassed CH_2Cl_2 (0.5 mL). The resulting suspension was stirred under N_2 for 24 h and rotary evaporated. Chromatography (SiO_2, $CHCl_3$) gave solitaire **15** (1.2 mg, 4%) as a blue solid: R_f 0.13 ($CHCl_3$); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 345 (3.87), 576 (3.76), 636 (3.56) nm; MS (FAB) m/z 856 $[M^{+\bullet}]$; HRMS (FAB) calcd for $C_{44}H_{55}MoN_8S_2$ $[M + H^+]$ 857.3045, found $[M + H^+]$ 857.3075.

7,8,12,13,17,18-Hexapropyl-2,3-di(methylthio)porphyrazine (16). $Hg(OAc)_2$ (36 mg, 0.11 mmol) was added to a suspension of ROM polymer **9** (10 mg) in degassed CH_2Cl_2 (3 mL) and MeOH (1 mL) under N_2. The suspension was stirred at 20 °C for 24 h. A solution of 2-hydroxyethanethiol (48 μL, 0.68 mmol) in degassed CH_2Cl_2 (0.5 mL) was added and the resultant suspension stirred at 20 °C for 10 min. MeI (8 μL, 0.13 mmol) was added, followed by Et_3N (27 μL, 0.195 mmol) in degassed CH_2Cl_2 (0.5 mL). The resulting suspension was stirred under N_2 for 24 h, rotary evaporated and chromatographed (SiO_2, hexanes/CH_2Cl_2, 1:1) to give sulfide **16** (1.5 mg, 6%) as a blue solid: R_f 0.89 (hexanes/CH_2Cl_2, 1:1); IR (neat) 1489, 1463, 1147, 991, 755, 717 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 348 (4.39), 550 (3.84), 584 (4.16), 634 (4.21) nm; ^{1}H NMR (500 MHz, $CHCl_3$) δ 0.89 (m, 2H), 1.28 (m, 18H), 2.33 (m, 12H), 3.55 (s, 6H), 3.80 (t, J = 7 Hz, 4H), 3.97 (t, J = 7 Hz, 8H); ^{13}C NMR (125 MHz, $CHCl_3$) δ 14.7, 25.4, 25.6, 28.1, 28.3, 29.6, 140.2, 141.9, 142.2, 145.6, 146.0, 147.4, 158.3, 163.3; MS (FAB) m/z 658 $[M^{+\bullet}]$; HRMS (FAB) calcd for $C_{36}H_{50}N_8S_2$ $[M^{+\bullet}]$ 658.3600, found $[M^{+\bullet}]$ 658.3587.

7,8,12,13,17,18-Hexapropyl-2,3-di((ethoxycarbonyl)methylthio)porphyrazine (17). $Hg(OAc)_2$ (36 mg, 0.11 mmol) was added to ROM polymer **9** (10 mg) in degassed CH_2Cl_2 (3 mL) and MeOH (1 mL) under N_2. The suspension was stirred at 20 °C for 24 h and 2-hydroxyethanethiol (48 μL, 0.68 mmol) in degassed CH_2Cl_2 (0.5 mL) was added and the resultant suspension stirred at 20 °C for 10 min. EtO_2CCH_2Br (14 μL, 0.13 mmol) was added, followed by Et_3N (27 μL, 0.195 mmol) in degassed CH_2Cl_2 (0.5 mL). The resulting suspension was stirred under N_2 for 24 h, rotary evaporated, and chromatographed (SiO_2, CH_2Cl_2) to give sulfide **17** (1.5 mg, 6%) as a blue solid: R_f 0.19 (hexanes/CH_2Cl_2, 1:1); IR (neat) 1732, 1463, 1286, 1143, 1033, 758, 722 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 348 (4.20), 592 (4.04), 632 (4.11) nm; ^{1}H NMR (500 MHz, $CHCl_3$) δ −2.23 (br s, 2H), 1.06 (t, J = 7 Hz, 6H), 1.29 (m, 18H), 2.33 (m, 12H), 3.80 (t, J = 7 Hz, 4H), 3.97 (t, J = 7 Hz, 8H). 4.10 (q, J = 7 Hz, 4H), 5.07 (s, 4H); ^{13}C NMR (125 MHz, $CHCl_3$) δ 14.0, 14.7, 25.4, 25.7, 28.1, 28.3, 37.0, 61.4, 139.0, 142.0, 142.4, 145.4, 145.9, 147.2, 158.1, 164.3, 169.8; MS (FAB) m/z 803 $[M + H]^+$; HRMS (FAB) calcd for $C_{42}H_{59}N_8O_4S_2$ $[M + H]^+$ 803.4101, found $[M + H]^+$ 803.4097.

7,8,12,13,17,18-Hexapropyl-2,3-di((ethoxycarbonyl)methylthio)porphyrazinato]nickel (II) (18). Porphyrazine **17** (2.4 mg, 0.003 mmol), $Ni(OAc)_2$ (5.0 mg, 0.03 mmol), and dry DMF (3 mL) were heated to 100 °C for 16 h under N_2. Rotary evaporation and chromatography (SiO_2, CH_2Cl_2) gave porphyrazine **18** (2.0 mg, 80%) as a deep blue solid: R_f 0.19 (hexanes/CH_2Cl_2, 1:1); IR (neat) 1732, 1454, 1284, 1155, 1026, 979, 764 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 325 (4.57), 385 (4.02), 600 (4.53), 618 (4.55) nm; ^{1}H NMR (500 MHz, $CHCl_3$) δ 1.04 (t, J = 7 Hz, 6H), 1.26 (m, 18H), 2.26 (m, 12H), 3.77 (t, J = 7 Hz, 12H), 4.08 (q, J = 7 Hz, 4H), 4.96 (s, 4H); ^{13}C NMR (125 MHz, $CHCl_3$) δ 14.0, 14.7, 25.3, 25.5, 28.1, 28.2, 37.1, 61.4, 138.0, 145.0, 145.2, 145.5, 146.1, 149.2, 151.1, 151.2, 169.6; MS (FAB) m/z 859 $[M + H]^+$; HRMS (FAB) calcd for $C_{42}H_{57}N_8NiO_4S_2$ $[M + H]^+$ 859.3298, found $[M + H]^+$ 859.3313.

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Supporting Information Available: General experimental procedures and structural data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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