LETTER

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Preparation of α,β-unsubstituted *meso*-arylbidipyrrins *via* metal-templated, oxidative coupling of dipyrrins†

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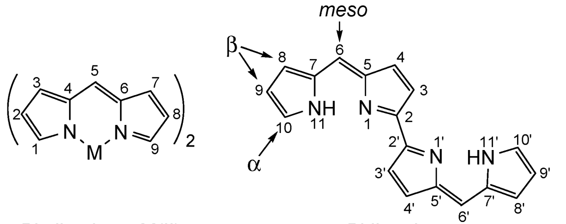
A three-step, one-pot procedure provides *meso*-aryl-α,β-unsubstituted bisdipyrrinato nickel complexes; oxidative coupling of these ligands followed by demetallation affords an unprecedented class of *meso*-aryl-α,β-unsubstituted bidipyrrins.

Oxidative biaryl coupling reactions have been employed in the preparation of numerous classes of compounds, including polycyclic aromatic hydrocarbons,[1a] fused porphyrin arrays,[1b] and natural products.[1c] Direct carbon-carbon bond-forming reactions are among the most challenging transformations in synthetic chemistry, often requiring harsh reaction conditions and unpleasant metal reagents or expensive catalysts. Furthermore, due to the lack of regiospecificity, intermolecular dehydrogenation reactions of aromatic compounds frequently result in polymers or complex product mixtures, unless directing or protecting groups are utilized. Inspired by the successful oxidative biaryl coupling methodology recently employed for the synthesis of large, flat porphyrins,[2] we were interested in applying these concepts to a divergent area of synthetic chemistry. In this system, a late transition metal was incorporated into the macrocycle to lower the oxidation potential of the ligand, and the pre-organization of the carbons to be coupled facilitated the cyclo-dehydrogenation under very mild oxidative conditions. With these issues in mind, we examined the reactivity of metal complexes with *meso*-aryl-α,β-unsubstituted bidipyrrins (Fig. 1) since coupling of two of the α-carbons would produce a bidipyrrin, a difficult molecule to prepare by known methodology.

Bidipyrrins represent the class of bile pigments with two dipyrromethene units linked directly by α-carbons. With an eye towards utilizing these tetrapyrroles as synthons for corrole forming reactions, Johnson and Price first described their preparation in 1960,[3] but little work was pursued with this ligand prior to the report of a dimeric zinc complex (M_2L_2) by Dolphin and co-workers in 1998.[4] In the following years, Bröring and co-workers isolated a similar metal-free octaalkylbidipyrrin using modified procedures,[5] and they expanded the scope of their methodology to include the preparation of the previously unprecedented *meso*-arylbidipyrrins. Their approach, employing diacylbipyrroles, represents the only synthetic scheme for the preparation of *meso*-arylbidipyrrins to date. Unfortunately, the reaction requires harsh conditions, involving a reflux in neat $POCl_3$, and the methodology is not compatible with either reactive *meso*-aryl groups or with the preparation of α- or β-unsubstituted *meso*-arylbidipyrrins.



Bisdipyrinato M(II) Bidipyrrin

Fig. 1 General bidipyrrin and bisdipyrrinato compounds and their respective numbering schemes.

For reasons enumerated by Bröring, *meso*-arylbidipyrrins offer advantages over their *meso*-unsubstituted analogs.[5] Aryl moieties incorporated at the *meso*-positions of bidipyrrins provide points for synthetic elaboration, allow for the fine-tuning of steric and electronic properties. The range of aryl substituents that may be incorporated at the bidipyrrin *meso*-positions by the methodology of Bröring is limited to *para*- and *meta*-substituted aryl moieties, as *ortho*-substituted aryl groups hinder the acylation reaction.[6] In addition, the absence of α-alkyl substituents on bidipyrrins is a desirable feature for many applications, including monomers for electropolymerization, and the ability to further derivatize at these free α positions may allow for the preparation of macrocycles.

In order to couple dipyrrinato groups, two properties are important for the metal template: a propensity towards square-planar coordination and the formation of charge neutral complex with both the bisdipyrrinato and bidipyrrinato ligands. Nickel offers several advantages over metals such as palladium or platinum for this purpose. The stronger Lewis acidity of Ni(II) weakens the C–H bonds of coordinated ligands to a greater degree than Pd(II) or Pt(II), and the small ionic radius of Ni(II) brings the α-hydrogens of bisdipyrrinato Ni(II) complexes into close contact (2.481 and 2.532 Å), as illustrated in the solid-state structure of **Ni-2b** depicted in Fig. 2. Additionally, the removal of the metal template should be facile, since Ni(II) complexes are typically easier to demetallate than analogous chelates of Pd(II) or Pt(II).

α,β-Unsubstituted-5-aryldipyrromethanes are needed for the synthesis presented in Fig. 3. These readily available molecules offer several desirable attributes for precursors, including their

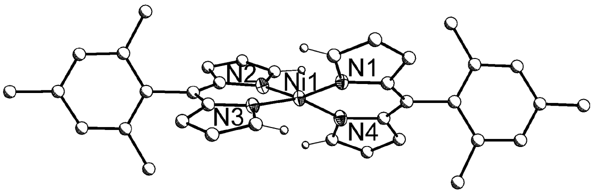


Fig. 2 Solid-state structure of **Ni-2b** (40% ellipsoids). Carbon atoms are drawn with arbitrary radii and hydrogen atoms other than those on the α-carbons have been omitted for clarity.

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† Electronic supplementary information (ESI) available: ^1H NMR spectra for all compounds and magnetic analysis of **Ni-2b** (χT *vs.* T plot). See http://www.rsc.org/suppdata/nj/b4/b412620c/

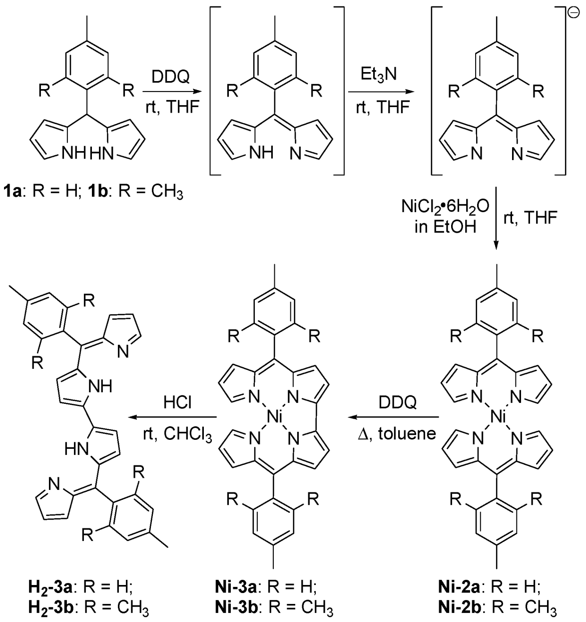

Fig. 3 Illustration of the three-step, one-pot reaction sequence employed for the preparation of bisdipyrrinato Ni(II) complexes followed by oxidation and demetallation to afford dibipyrrins.

ease of preparation, numerous choices for aryl functional groups, and the well-established coordination chemistry of their 2H$^+$, 2e$^-$ oxidized dipyrromethene derivatives.[7,8] Preparations of α,β-unsubstituted-5-arylbisdipyrrinato M(II) complexes have been recently described by the groups of both Dolphin and Lindsey.[8b,e] For the preparations of **Ni-2a** and **Ni-2b**, a room temperature, three-step, one-pot procedure similar to that utilized by Lindsey and co-workers was employed (Fig. 3). Isolation of the resulting bisdipyrrinato Ni(II) complexes is straightforward and the complexes **Ni-2a** and **Ni-2b** are obtained in good yields as crystalline solids, despite the multi-step nature of the synthetic methodology.

The cyclic voltammograms measured for the bisdipyrrinato nickel complexes revealed irreversible oxidative processes at 1.10 V for **Ni-2a** and 1.08 V for **Ni-2b** (*vs.* Ag/AgCl). Various reaction conditions were attempted to affect this oxidative change chemically, but the nickel complexes proved to be incompatible with the Lewis acids often employed for dehydrogenation reactions. Due to this difficulty, alternative procedures were pursued; treatment of **Ni-2a** or **Ni-2b** with a slight excess of DDQ in refluxing toluene afforded the desired bidipyrrinato nickel complexes (Fig. 3). Filtration through a plug of silica, followed by recrystallization, provides **Ni-3a** and **Ni-3b** as purple microcrystalline solids. Treatment of CHCl$_3$ solutions of **Ni-3a** and **Ni-3b** with HCl results in an immediate color change from wine-red to bright-green. Aqueous workup causes a change in color to indigo upon deprotonation and solvent removal provides the metal-free ligands, **H$_2$-3a** and **H$_2$-3b**, in nearly quantitative yields.

Typically, tetrahedral Ni(II) complexes have an $S = 1$ ground state while square-planar Ni(II) complexes are diamagnetic, and often Ni(II) complexes with an intermediate geometry will exhibit temperature-dependent spin equilibrium.[9] Other than **Ni-2a**, **Ni-2b**, and the related phenyl and *p*-nitrophenyl-α-unsubstituted analogs described by Dolphin and co-workers,[8b] all reported bisdipyrrinato nickel complexes bear methyl or phenyl groups at their α-carbons. The steric clash between these groups induces a severe distortion towards tetrahedral geometry and the complexes are paramagnetic.[10] Based upon these precedents and the realization that even hydrogen atoms on the α-carbons sterically preclude a square-planar environment, Dolphin and co-workers were surprised to observe sharp signals in the ^{1}H and ^{13}C NMR spectra of the phenyl and *p*-nitrophenyl complexes.[8b] The dihedral angle between the planes containing N(1)–Ni(1)–N(4) and N(2)–Ni(1)–N(3) indicates the degree of tetrahedral distortion for square-planar complexes, and the structural characterization of the phenyl derivative revealed a dihedral angle of 38.5°, which is considerably smaller than the tetrahedral angle of 76.3° calculated from the X-ray structure of [bis(1,3,7,9-tetramethyldipyrrinato)]Ni(II).[10c] In view of the properties of the phenyl and *p*-nitrophenyl congeners, **Ni-2a** and **Ni-2b** were expected to be diamagnetic, low-spin complexes and the ^{1}H NMR spectrum of **Ni-2a** (see electronic supplementary information, ESI) did indeed exhibit sharp signals. In contrast, the resonances in the spectrum of **Ni-2b** were broadened and many were shifted downfield relative to their analogous positions in the spectrum of **Ni-2a** (see ESI). The α-carbon protons experienced the most significant shift, from a value of 9.23 ppm in **Ni-2a** to 15.62 ppm in **Ni-2b**. When Ni(II) complexes adopt geometries in an intermediate range between square planar and tetrahedral, they often exhibit a temperature-dependent magnetic moment; in the structure of **Ni-2b** the angle between N(1)–Ni(1)–N(4) and N(2)–Ni(1)–N(3) planes has opened up in comparison to the phenyl derivative to a value of 49.6°.[8b] This 11.1° increase is apparently sufficient to induce thermal population of a paramagnetic state for the d^8 Ni(II) ion and preliminary magnetic data is consistent with this observation.[11]

The coupling of the α-carbons upon going from **Ni-2b** to **Ni-3b** appears to relieve some of the steric strain in the complex; the Ni(II) cation assumes a coordination geometry closer to square planar (Fig. 4), with a smaller angle between the planes containing N(1)–Ni(1)–N(2) and N(3)–Ni(1)–N(4) for **Ni-3b** (11.8°) in comparison to **Ni-2b** (38.3°). As apparent from the sharp signals in the ^{1}H NMR spectrum of **Ni-3b**, the paramagnetism observed for **Ni-2b** is lost and the resonance for the hydrogens on the uncoupled α-carbons experiences a dramatic change upon conversion to **Ni-3b**, changing from a broad singlet at 15.62 ppm to a doublet of doublets at 6.02 ppm (see ESI). Although conversion to the bidipyrrin causes a slight increase in the separation of the uncoupled α-carbons from 3.025 Å to 3.093 Å, their associated hydrogens are brought in closer proximity to each other (2.284 Å for **Ni-3b**) relative to the α-protons in the uncoupled complex (2.507 Å for **Ni-2b**).

As depicted in Fig. 4, the solid-state structure of **Ni-3b** reveals a helical complex, consistent with the structures of other known Ni bidipyrrins.[12] Interestingly, the degree of helicity, as described by the angle between the planes containing N(1)–Ni(1)–N(4) and N(2)–Ni(1)–N(3), is only 11.9° for **Ni-3b**. This interplanar angle is slightly smaller than the 13.0° measured for the only other α-unsubstituted bidipyrrinato Ni(II) complex reported and significantly smaller than the 19.9° measured for an α-methyl bidipyrrinato Ni(II) complex.[12]

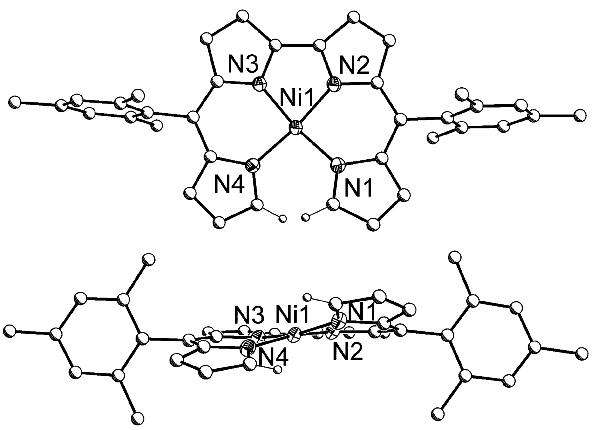

Fig. 4 Solid-state structure of **Ni-3b** (40% ellipsoids). Carbon atoms are drawn with arbitrary radii; hydrogen atoms other than those on the α-carbons have been omitted for clarity.

The average Ni–N bond length of 1.873(2) Å is consistent with other bidipyrrinato Ni(II) complexes in the literature.[12] The relatively short bond between the coupled α-carbons of 1.437(3) Å is indicative of its partial double-bond character, as can be envisioned from the resonance form placing the two imine nitrogens in one dipyrromethene moiety.

Electrochemical investigations of **Ni-3b** and **H_2-3b** were undertaken to provide insight into the stability and electronic properties of these chromophores. Comparable to redox processes observed for numerous porphyrin species,[13] the cyclic voltammogram of **Ni-3b** exhibits two reversible oxidations at 0.80 and 1.09 V, as well as two reversible reductions at 0.89 and 1.60 V (*vs.* Ag/AgCl). These observations are consistent with a series of measurements reported by Bröring and co-workers, which also show two reversible processes in both the oxidative and reductive directions for most compounds of this type.[14] In addition to a reversible reduction at −1.05 V, **H_2-3b** also undergoes an irreversible oxidation at 0.94 V *versus* Ag/AgCl, indicating that alkylation of the pyrrolic carbons is not required for stability over this broad potential range.

The electronic absorption spectra of these compounds change substantially on going from **Ni-2** to **Ni-3** to **H_2-3** in both series as illustrated by the spectra of the mesityl series shown in Fig. 5. Compounds **Ni-2a** and **Ni-2b** exhibit one broad absorption maximum around 471 and 478 nm, respectively, which are slightly higher in energy than transitions reported for other bisdipyrrinato Ni(II) complexes.[8c,10] The absorption spectra become more complex after coupling: the main absorption bands of **Ni-3a** and **Ni-3b** are bathochromically shifted in comparison to their precursors, but they also exhibit electronic transitions at longer wavelengths (above 550 nm). Upon demetallation, an additional low-energy feature emerges in the electronic spectra of **H_2-3a** and **H_2-3b**. The metal-free compounds **H_2-3a** and **H_2-3b** show fluorescence emissions at 687 and 648 nm, with quantum yields of 1% and 5%, respectively. The higher value for **H_2-3b** is consistent with the observation that rigid substituents such as mesityl groups at the *meso*-position in bisdipyrrinato Zn(II) complexes significantly increase the quantum yields for emission.[15]

In summary, the three-step, one-pot room temperature reaction of dipyrromethanes with DDQ, Et_3N and $NiCl_2$ described herein is a practical method to obtain *meso*-arylbisdipyrrinato Ni(II) complexes on the multigram scale. While the *para*-tolyl derivative, **Ni-2a**, showed sharp resonances in the ^1H NMR spectrum, the mesityl analog, **Ni-2b**, exhibited broad signals that were shifted downfield, indicative of temperature-dependent paramagnetism. Furthermore, the oxidative coupling of two dipyrrins by employing Ni(II) as a template is a facile procedure for the preparation of previously unreported *meso*-aryl,-α,β-unsubstituted bidipyrrins and this methodology is compatible with aryl substituents bearing methyl groups at the *ortho*-positions. Demetallation using HCl results in the metal-free bidipyrrins and these chromophores are stable over a potential range of ~2 V. Photophysical measurements of the dipyrrins reveal fluorescence in the low-energy region of the visible spectrum, with the mesityl derivative giving a higher quantum yield than the *para*-tolyl congener.

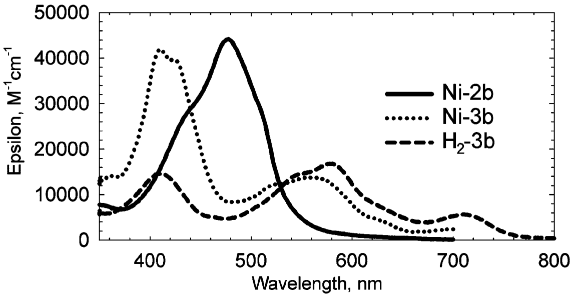

Fig. 5 Electronic absorption spectra of **Ni-2b**, **Ni-3b** and **H_2-3b**.

Experimental

General

^1H NMR spectra were recorded on a Varian Mercury spectrometer at 300 MHz in $CDCl_3$ and were referenced to the solvent residual peak. Absorption spectra were collected in CH_2Cl_2 on a Varian Cary 50 spectrophotometer. Reagents and solvents were used as received from Aldrich or Fisher Scientific. Dipyrromethanes **1a** and **1b** were prepared following modified literature procedures.[7a]

Fluorescence spectroscopy

Steady-state photoluminescence spectroscopy and quantum yield measurements were carried out using a SPEX Fluorolog 2 instrument. The standard used for quantum yield calculations was $Ru(bipy)_3Cl_2$ (Φ = 0.04). Samples **H_2-3a** and **H_2-3b** were dissolved in toluene and the concentration was adjusted so that their absorbance at the excitation wavelength (453 nm) matched that of a standard (0.2).

Electrochemistry

Electrochemical measurements were made on an EG&G PAR VersaStatII potentiostat with a Pt disc working electrode, a Pt wire counter electrode, and an aqueous Ag/AgCl reference electrode (NaCl, 3 M) fitted with a Vicor frit as a salt bridge. In all cases dry, degassed C_6H_5CN was used as the solvent and tetra-*N*-butylammoniumhexafluorophosphate, at a concentration of 0.100 M, was used for the supporting electrolyte. A small portion of ferrocene (Fc) was added to the cell after each series of measurements to confirm the potential of the reference electrode. The $E_{1/2}$ for the Fc/Fc^+ couple remained constant at 0.46(1) V *versus* Ag/AgCl. The analyte concentration was 2.5(2) mM and all measurements were made at room temperature.

X-Ray crystallography‡

Unit cell dimensions were obtained and intensity data collected on a Bruker CCD SMART diffractometer at low temperature, with monochromatic Mo-Kα radiation (λ = 0.710 73 Å). The data collections nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different ϕ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS.[16] The structure was solved and refined using the Bruker SHELXTL software package.[17]

Crystal data for Ni-2b. $C_{36}H_{34}N_4Ni$, M = 581.38, monoclinic, $C2/c$, $\mu = 0.695$ mm^{-1}, a = 30.6299(16), b = 8.0062(4), c = 26.6950(14) Å, β = 116.586(1)°, V = 5854.2(5) Å^3, Z = 8, $\rho_{\rm calcd}$ = 1.319 g cm^{-3}, T = 193(2) K, 19861 reflections collected, 6896 unique ($R_{\rm int}$ = 0.0230), R_1 = 0.0347, wR_2 = 0.0867 for all 5825 data [$I > 2\sigma(I)$].

Crystal data for Ni-3b. $C_{36}H_{32}N_4Ni$, M = 579.37, monoclinic, $P2_1/c$, μ = 0.694 mm^{-1}, a = 12.1071(7), b = 31.5677(17), c = 8.0986(4) Å, β = 108.907(1)°, V = 2928.2(3) Å^3, Z = 4, $\rho_{\rm calcd}$ = 1.314 g cm^{-3}, T = 193(2) K, 19801 reflections collected, 6821 unique ($R_{\rm int}$ = 0.0247), R_1 = 0.0392, wR_2 = 0.0951 for all 5818 data [$I > 2\sigma(I)$].

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‡ CCDC reference numbers 254228 and 254229. See http://www.rsc.org/suppdata/nj/b4/b412620c/ for crystallographic data in .cif or other electronic format.

Syntheses

Ni-2a. A solution of **1a** (7.08 g, 30.0 mmol) in THF (240 ml) was treated with DDQ (6.80 g, 30.0 mmol) at room temperature. After 50 min, 10 ml of Et_3N were added. A methanolic solution containing $NiCl_2 \cdot 6H_2O$ (12 g in 30 ml) was then added to the reaction mixture. The reaction proceeded for an additional 45 min, after which the TLC indicated no uncoordinated dipyrromethene. The reaction mixture was reduced to 150 ml and was diluted with 150 ml of hexanes. This solution was filtered through a short plug of silica, with Et_2O–hexanes (1 : 1) as the eluent. The rapidly moving deep red-orange fraction was collected. Crystallization from an acetone–hexanes mixture afforded the title compound as lustrous, metallic-green crystals. Yield: 4.60 g (59%); UV-vis [CH_2Cl_2, λ_{max}/nm (log ε)]: 471 (4.73); ^1H NMR (300 MHz, $CDCl_3$): δ = 9.23 (s, 4H), 7.39 (d, 4H, J = 3.8 Hz), 7.33 (d, 4H, J = 8.1 Hz), 7.22 (d, 4H, J = 7.8 Hz), 6.77 (d, 4H, J = 4.1 Hz), 2.44 (s, 6H); anal. calcd for $C_{32}H_{26}N_4Ni$: C, 73.17; H, 4.99; N, 10.67; found C, 73.05; H, 4.84; N, 10.47; HRMS-EI (m/z): $[M + H]^+$ calcd for $C_{32}H_{27}N_4Ni$, 525.1589; found 525.1602.

Ni-2b. A portion of **1b** (1.000 g , 1.723 mmol) was treated as described above for the preparation of **Ni-2a**. Yield: 0.620 g (56%); UV-vis [CH_2Cl_2, λ_{max}/nm (log ε)]: 478 (4.64); ^1H NMR (300 MHz, $CDCl_3$): δ = 15.62 (br s, 4H), 10.86 (br s, 4H), 6.78 (s, 4H), 6.61 (s, 4H), 2.29 (s, 6H), 1.82 (s, 12H). HRMS-EI (m/z): M^+ calcd for ($C_{36}H_{34}N_4Ni$), 580.2137; found, 580.2135; anal. calcd for $C_{36}H_{34}N_4Ni$: C, 74.37; H, 5.89; N, 9.64; found C, 74.11; H, 6.02; N, 9.58.

Ni-3a. A solution of **Ni-2a** (2.501 g, 4.77 mmol) in toluene (150 ml) was treated with DDQ (1.300 g, 5.72 mmol) and heated at reflux for 12 h. The reaction mixture was then diluted with 100 ml of hexanes and filtered through a short plug of silica. The plum-colored solution was further eluted with CH_2Cl_2–hexanes (2 : 1) until the eluent was almost clear. Slow removal of the solvents afforded **Ni-3a** as a dark purple microcrystalline solid. Yield: 1.768 g (71%); UV-vis [CH_2Cl_2, λ/nm (log ε)]: 833 (4.07), 757 (3.79), 566 (4.15), 427 (sh), 412 (4.64), 361 (4.47); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, 4H, J = 8.1 Hz), 7.28 (d, 4H, J = 7.7 Hz), 6.80 (dd, 2H, J_1 = 5.4 Hz, J_2 = 1.3 Hz), 6.76 (d, 2H, J = 4.3 Hz), 6.61 (d, 2H, J = 4.3 Hz), 6.42 (dd, 2H, J_1 = 4.3 Hz, J_2 = 1.7 Hz), 5.99 (dd, 2H, J_1 = J_2 = 1.5 Hz), 2.46 (s, 6H); HRMS-EI (m/z): M^+ calcd for $C_{32}H_{24}N_4Ni$, 522.1354; found 522.1365.

Ni-3b. A portion of **Ni-2b** (1.50 g, 2.58 mmol) was treated as described above for the preparation of **Ni-3a**. Yield: 1.01 g (68%); ^1H NMR (300 MHz, $CDCl_3$): δ = 6.93 (s, 4H), 6.62 (dd, 2H, J_1 = 4.8 Hz, J_2 = 1.5 Hz), 6.50 (d, 2H, J = 4.5 Hz), 6.42 (d, 2H, J = 4.2 Hz), 6.34 (dd, 2H, J_1 = 4.5 Hz, J_2 = 4.8 Hz), 6.02 (dd, J_1 = J_2 = 1.2 Hz), 2.36 (s, 6H), 2.13 (s, 12H); UV-vis [CH_2Cl_2, λ/nm (log ε)]: 555 (4.13), 409 (4.62); HRMS-EI (m/z): M^+ calcd for $C_{36}H_{32}N_4Ni$, 578.1980; found, 578.1964; anal. calcd for $C_{36}H_{32}N_4Ni$: C, 74.63; H, 5.57; N, 9.67; found C, 74.81; H, 5.69; N, 9.62.

H_2-3a. A solution of **Ni-3a** (0.50 g, 0.96 mmol) in $CHCl_3$ (100 ml) was treated with HCl (4 ml, 12 M) at room temperature for 10 min. The reaction mixture was washed sequentially with 200 ml portions of 0.2 M HCl, H_2O, $NaHCO_3$, and then H_2O. The green solution turned deep violet as the pH was increased through the second and third washings. The organic fraction was dried on Na_2SO_4 and the solvent was removed. Yield: 0.44 g (99%); Uv-vis [CH_2Cl_2, λ/nm (log ε) nm]: 710 (3.65), 588 (4.56), 558 (sh), 411 (4.40), 342 (4.27). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60 (dd, 2H, J_1 = J_2 = 1.5 Hz), 7.44 (d, 4H, J = 8.1 Hz), 7.28 (d, 4H, J = 7.8 Hz), 6.99 (d, 2H, J = 4.3 Hz), 6.80 (d, 2H, J = 4.5 Hz), 6.61 (dd, 2H, J_1 = 4.0 Hz, J_2 = 1.2 Hz), 6.41 (dd, 2H, J_1 = 4.0 Hz, J_2 = 1.9 Hz), 2.47 (s, 6H); HRMS-EI (m/z): M^+ calcd for $C_{32}H_{26}N_4$, 466.2157; found 466.2160.

H_2-3b. A portion of **Ni-3b** (71 mg, 0.12 mmol) was treated as described above for the preparation of **H_2-3a**. Yield: 63 mg (99%); UV-vis [CH_2Cl_2, λ_{max}/nm (log ε)]: 710 (3.75), 578 (4.22), 411 (4.16); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.59 (s, 2H), 6.95 (s, 4H), 6.91 (d, 2H, J = 4.2 Hz), 6.53 (d, 2H, J = 4.2 Hz), 6.35 (s, 4H), 2.37 (s, 6H), 2.13 (s, 12H); HRMS-EI (m/z): M^+ calcd for $C_{36}H_{34}N_4$, 522.2783; found 522.2780.

Acknowledgements

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