Synthesis, Structure, and Spectroscopy of Phenylacetylenylene Rods Incorporating *meso*-Substituted Dipyrrin Ligands

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Abstract: The synthesis, structure, and spectroscopic characterization of a series of phenylacetylenylene rodlike molecules containing dipyrromethene (dipyrrin) ligands are described. The combination of the phenylacetylenylene groups with the porphyrinogenic dipyrrin moieties results in a rich absorption spectroscopy for these compounds, although the fluorescence of the phenylacetylenylene moiety is quenched by presence of the dipyrrin chelator. The Cu^{2+} and Fe^{3+} complexes of these ligands have been prepared and three of these compounds have been structurally characterized by using single-crystal X-ray diffraction. Unlike other octahedral metal-dipyrrin complexes described to date, one of the iron complexes demonstrates ideal threefold symmetry in the solid-state. The elongated structure and high symmetry of these complexes suggests the use of these *meso*-substituted phenylacetylenylene ligands as an interesting class of extended, branched molecules for the construction of supramolecular architectures.

Keywords: copper · iron · ligand design · N ligands · supramolecular chemistry

Introduction

Rigid phenylacetylenylene building blocks have gathered considerable attention for use in a variety of supramolecular systems. Macrocyclic phenylacetylenylenes have been used to prepare a number of liquid-crystalline materials,[1, 2] and heteroatom-substituted systems have been synthesized to generate several novel metal-binding macrocycles.[3] Branched phenylacetylenylene-based molecules have been described in the construction of light-harvesting dendrimers[4–6] and decorating the surface of metal-cluster-based dendrimers.[7] Smaller branched systems have been derivatized with peripheral metal-binding groups to construct molecular solids[8–10] and even to link together metal nanoparticles.[11, 12] These conjugated molecules have also been tethered to surfaces for study as 'molecular-scale wires'[13] and surface-immobilized catalysts.[14, 15] Clearly, these investigations show that the phenylacetylenylene unit has found widespread incorporation into various supramolecular systems.

Dipyrromethene (dipyrrin) ligands are aromatic, planar ligand systems that are porphyrinogenic in nature.[16–20] The dipyrrin ligand offers a number of desirable features for utilization in supramolecular coordination chemistry including relative ease of synthesis, intense optical absorptions, and a propensity to form stable, neutral complexes with a variety of metal ions. Previous efforts have taken advantage of these properties by synthesizing both simple coordination compounds and supramolecular clusters that are easily purified by conventional silica flash chromatography.[21, 22] Earlier studies by Dolphin and co-workers utilized α- and β- linked dipyrrins for the synthesis of metallohelicates and metal-containing cyclic trimers.[21, 22] These multinuclear complexes clearly demonstrate the advantages of dipyrrin ligands as described above, but the complexes described to date have been limited to only a few different supramolecular topologies.[23, 24] In contrast, the use of *meso*-substituted dipyrrins has the advantage of allowing for the rational design of directional bonding[24, 25] and exploration of new molecular architectures with these intriguing ligand systems.

In an effort to exploit the phenylacetylenylene building block motif and provide new compounds for the synthesis of supramolecular structures, we have prepared a series of *meso*-substituted dipyrrin ligands fused with a variety of phenylacetylenylene backbones. The cupric and ferric metal complexes of these ligands have been synthesized, and the spectroscopic properties of these compounds have been examined. The compounds prepared show that metal ions can be used to spatially organize phenylacetylenylene units in a defined stoichiometry. The highly symmetric architecture of these complexes makes them excellent candidates for incorporation of transition-metal centers into many of the supramolecular systems where phenylacetylenylene-derived compounds have found utility.

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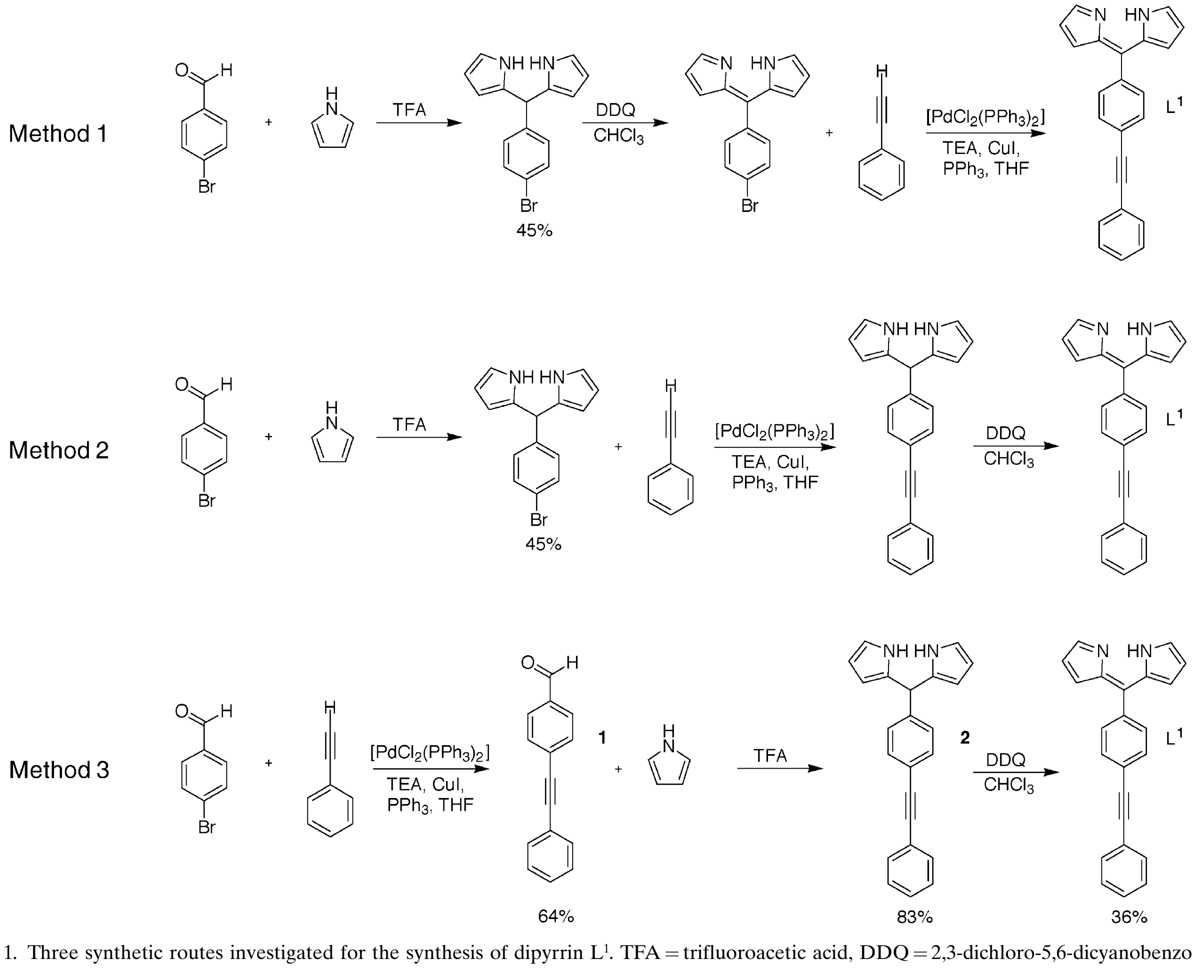
DOI: 10.1002/chem.200305041

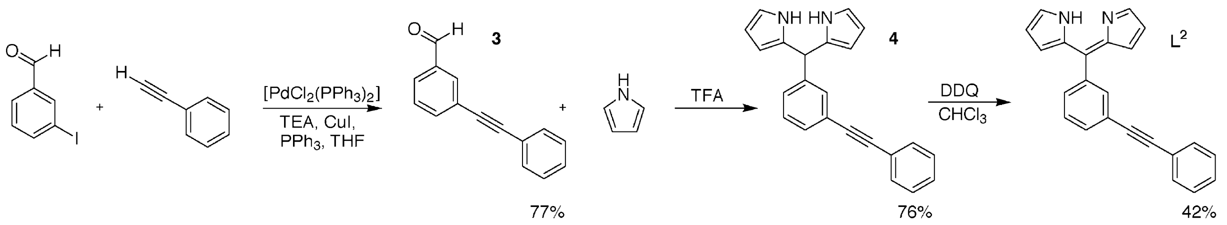
Results and Discussion

Ligand synthesis: Three different approaches were envisaged for the preparation of dipyrrin phenylacetylenylene ligands. These three synthetic strategies are outlined in Scheme 1. Method 1 begins first with the preparation of an arylhalide-substituted dipyrrin that can be subsequently coupled to phenylacetylenylene. Method 1 was abandoned due to the difficulty involved in purifying the dipyrrin products via column chromatography (vide infra). Method 2 involved the preparation of an arylhalide-substituted dipyrromethane, followed by Sonogashira coupling[26] to phenylacetylenylene, and finally oxidation to the dipyrrin ligand.[17, 18] Although a plausible route based on the large amounts of dipyrromethane that could be prepared (despite the modest yield), repeated attempts of the Sonogashira coupling were unsuccessful, presumably due to an incompatibility with the dipyrromethane moiety. Finally, method 3 was applied, which involves the synthesis of a phenylacetylenylene-extended aldehyde followed by subsequent preparation of the dipyrromethane and the dipyrrin, respectively. Method 3 was found to be the most efficient route to L^1 and was subsequently applied to all of the ligands described herein. This route provided good yields for all of the intermediates, although the isolated yields of the dipyrrin products remained relatively low. Scheme 2 shows the synthesis of a *meta*-substituted dipyrrin phenylacetylenylene ligand (L^2) that was also synthesized via a phenylacetylenylene-substituted aldehyde prior to formation of the dipyrrin. Scheme 3 shows the synthesis of two 'extended' ligands (L^3, L^4) that contain an additional phenylacetylenylene unit relative to L^1 and L^2. The synthesis of these extended ligands proceeds via an iodoarylaldehyde intermediate that is ultimately converted to the dipyrrin ligand at the end of the synthesis in a manner analogous to ligands L^1 and L^2 described above. All of the final dipyrrin ligands can be isolated as yellow, glassy solids, however isolation of the dipyrrins was not required for the synthesis of the desired metal complexes. Indeed, synthesis of the metal complexes was found to be more facile when prepared by a one-pot reaction starting with the dipyrromethane precursors.[16–18]

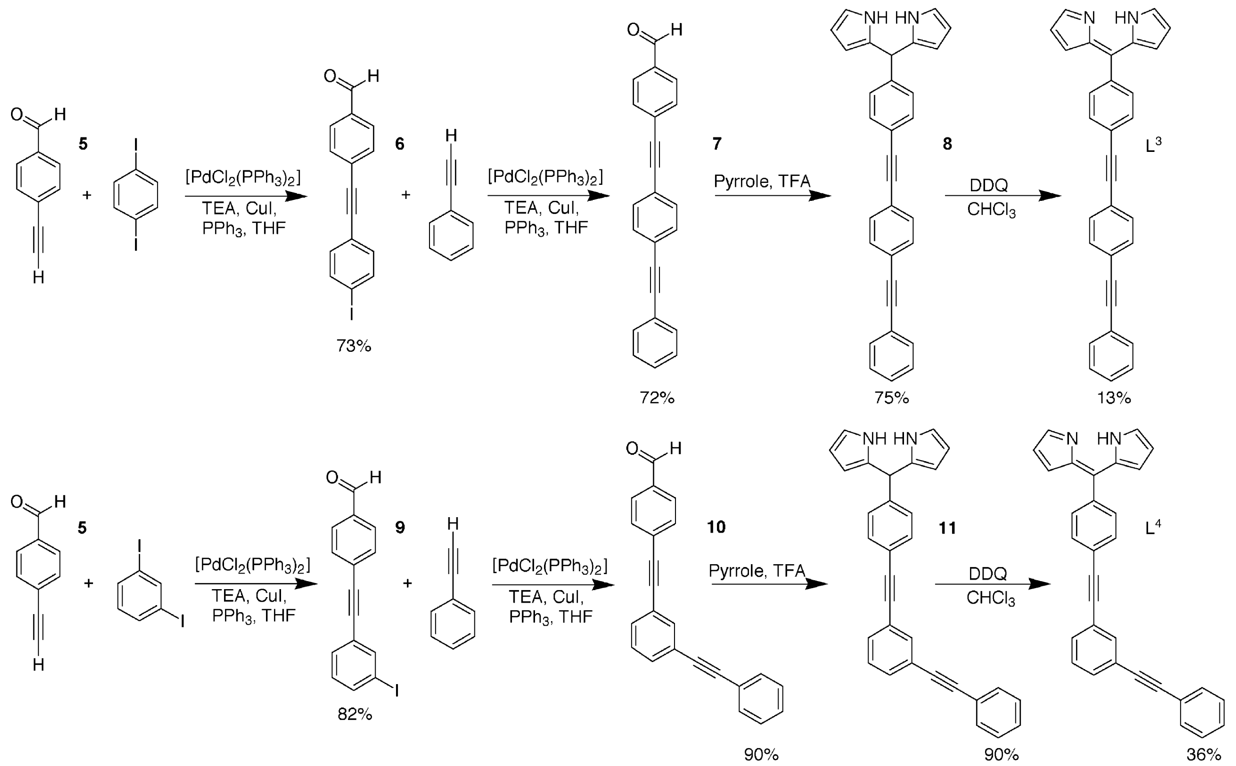
Synthesis of metal complexes: Copper(II) and iron(III) complexes of ligands L^1–L^4 were synthesized from solutions of the ligand prepared in situ. This approach was used, as purification of the free dipyrrin ligands was rather tedious, while isolation of the metal complexes was found to be facile. In addition, the free dipyrrin ligand could be isolated later by demetalation methods (vide infra).[27, 28] In a typical reaction (Scheme 4), the dipyrromethane precursor (**2**, **4**, **8**, **11**) was oxidized in ice cold $CHCl_3$ by the addition of a benzene



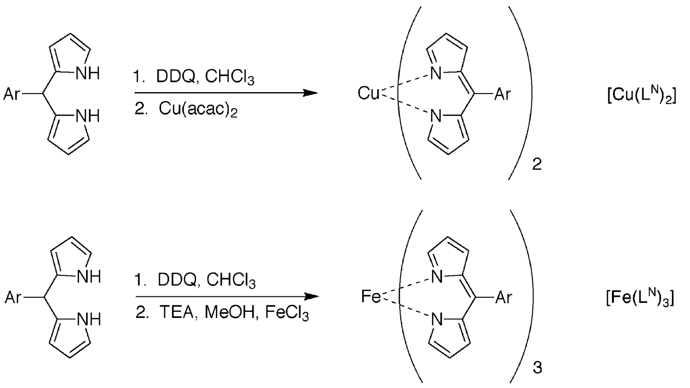
Scheme 1. Three synthetic routes investigated for the synthesis of dipyrrin L^1. TFA = trifluoroacetic acid, DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone, TEA = triethylamine.



Scheme 2. Synthetic route for ligand L^2.



Scheme 3. Synthetic route for ligands L^3 and L^4.



Scheme 4. Synthesis of metal complexes from ligands L^1–L^4.

solution containing an equimolar amount of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). After the addition was complete, partial removal of solvent, followed by addition of the metal salt resulted in formation of the desired complexes as judged by thin-layer chromatography. All of the metal complexes were easily purified by flash silica chromatography, where the compounds were followed as bright red bands on the column. Subsequent isolation of the free ligands could be obtained by treating the purified copper complexes ([Cu(L^N)$_2$]) with excess KCN in a ~3:1 THF/water solution. Subsequent removal of solvent and re-dissolution of the resulting residue in CH_2Cl_2 was followed by several aqueous washes resulting in isolation of the metal-free ligands (L^1–L^4). A notable difference was found in the solubility of complexes prepared with the 'linear' ligands (L^1, L^3) versus the 'bent' ligand systems (L^2, L^4). The complexes [Cu(L^2)$_2$], [Fe(L^2)$_3$], [Cu(L^4)$_2$], and [Fe(L^4)$_3$] were soluble in most organic solvents including acetone, MeOH, EtOH, CH_2Cl_2, $CHCl_3$, benzene, pentane, hexanes, and diethylether. However, the linear ligand complexes [Cu(L^1)$_2$], [Fe(L^1)$_3$], [Cu(L^3)$_2$], and [Fe(L^3)$_3$] were generally only soluble in CH_2Cl_2, $CHCl_3$, and benzene. Notably, the complex [Cu(L^3)$_2$] after being purified by column chromatography, using $CHCl_3$ as solvent, became difficult to redissolve in all solvents, including the aforementioned CH_2Cl_2, $CHCl_3$, and benzene. The reason for the low solubility of the 'linear' ligand complexes is unclear, but may be related to interligand stacking and subsequent aggregation.

Structure: The structures of [Cu(L^1)$_2$], [Fe(L^1)$_3$], and [Fe(L^3)$_3$] were determined by single-crystal X-ray diffraction methods (Table 1). The crystals were produced by solvent diffusion methods by using a solution of the metal complex into which either hexanes or cyclohexane was slowly diffused. Like other metal complexes based on dipyrrin ligands, the complexes prepared here produced deeply colored crystals that appeared either red and/or a lustrous deep green. The copper complex [Cu(L^1)$_2$] displays the expected four-coordinate distorted square-planar coordination geometry (Figure 1), with a twist angle between the two dipyrrin planes of ~46°. The Cu–N bond lengths are all comparable at 1.942, 1.951, 1.947, and 1.943 Å. The phenylacetylenylene moieties lie out of the plane of the dipyrrin chelating groups, as is typically found for *meso*-substituted dipyrrins with aryl substituents in this position.[16–18] The angle between the planes of the two aromatic systems is 59° in one ligand and 55° in the other. The phenylacetylenylene groups are essentially linear for both ligands attached to the copper center.

Table 1. Crystal data for [Cu(L^1)$_2$], [Fe(L^1)$_3$], and [Fe(L^3)$_3$].

	[Cu(L^1)$_2$]	[Fe(L^1)$_3$]	[Fe(L^3)$_3$]
empirical formula	$C_{52}H_{36}N_4Cu$	$C_{75}H_{51}N_6Fe$	$C_{99}H_{69}N_6Fe$
crystal system	triclinic	rhombohedral	monoclinic
space group	$P\bar{1}$	$R\bar{3}c$	$P2_1/c$
unit cell dimensions			
a [Å]	9.378(1)	14.455(1)	28.896(2)
α [°]	104.721(2)	84.738(1)	90
b [Å]	13.821(1)	14.455(1)	15.122(1)
β [°]	99.250(2)	84.738(1)	91.484(1)
c [Å]	16.635(2)	14.455(1)	17.094(1)
γ [°]	104.753(2)	84.738(1)	90
volume [Å^3], Z	1957.2(3), 2	2984.2(2), 2	7466.7(8), 4
crystal size [mm]	0.21 × 0.20 × 0.20	0.34 × 0.32 × 0.12	0.48 × 0.35 × 0.03
temperature [K]	100(2)	100(2)	100(2)
reflections collected	16330	24747	45623
independent reflections	8499	2298	16911
R(int)	0.0253	0.0326	0.0426
data/restraints/parameters	8499/0/514	2298/0/119	16911/0/955
goodness-of-fit on F^2	1.034	1.075	1.023
final R indices $I > 2\sigma(I)$			
$R1$	0.0518	0.0393	0.0510
$wR2$	0.1445	0.0999	0.1164
R indices (all data)			
$R1$	0.0551	0.0497	0.0821
$wR2$	0.1477	0.1043	0.1292
largest peak/hole difference [e Å^{-3}]	2.215/ – 0.631	0.339/ – 0.267	0.699/ – 0.473

The iron complex [Fe(L^1)$_3$] crystallized as small hexagons, suggestive of a high-symmetry complex. Indeed, the metal center displays a perfect octahedral coordination geometry with the metal center occupying a special position in the crystal lattice (Figure 2). The high symmetry of this complex in the solid state is unlike similar octahedral complexes of α,β-unsubstituted dipyrrins reported to date, where the geometry at the metal center is typically distorted such that no threefold axis is present.[16, 17] The idealized symmetry of the complex generates a Fe–N distance of 1.959 Å and an interplane angle between the dipyrrin and phenylacetylenylene π systems of 73°. Although the phenyl groups of each ligand are twisted relative to one another, the phenylacetylenylene units are overall linear in structure with no apparent bending along the ligand axis. The rigid structure and high symmetry of this complex suggests that appropriately substituted derivatives may be very useful for preparing heterometallic honeycomb framework molecular solids.[8, 9]

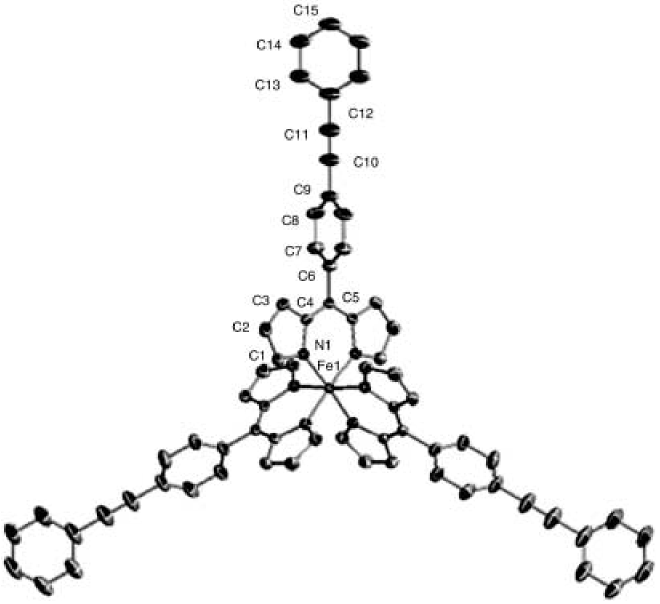


Figure 2. Structural diagram of [Fe(L^1)$_3$] with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms and disordered solvent have been omitted for clarity.

Crystals of the iron complex [Fe(L^3)$_3$] were obtained as thin hexagonal plates by slow evaporation from benzene. Although this morphology was suggestive of a high-symmetry complex (vide supra), a structure from these crystals was not achieved due to their extremely

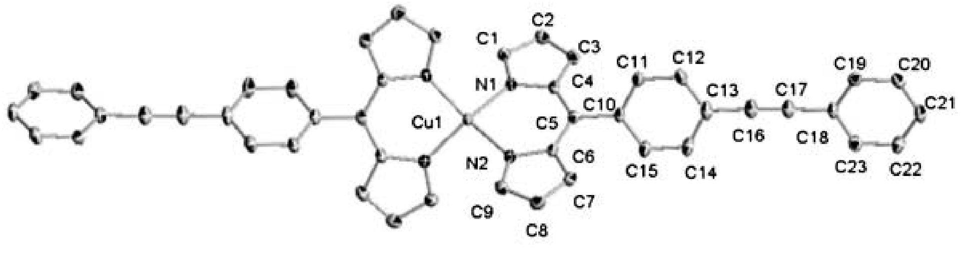


Figure 1. Structural diagram of [Cu(L^1)$_2$] with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent have been omitted for clarity.

thin dimension and fragility. Ultimately, the structure of [Fe(L^3)$_3$] was determined from thin plates (which did not show a hexagonal morphology), grown from solvent diffusion methods. The structure shows the expected distorted octahedral complex (Figure 3) lacking the perfect three-fold symmetry observed in [Fe(L^1)$_3$]. The average Fe–N bond length is 1.960 Å and the twist angles between the dipyrrin and phenyl π systems for each ligand are 65°, 67°, and 84°. A notable feature of the structure is the bending observed along the axis of the coordinated ligands (Figure 3).

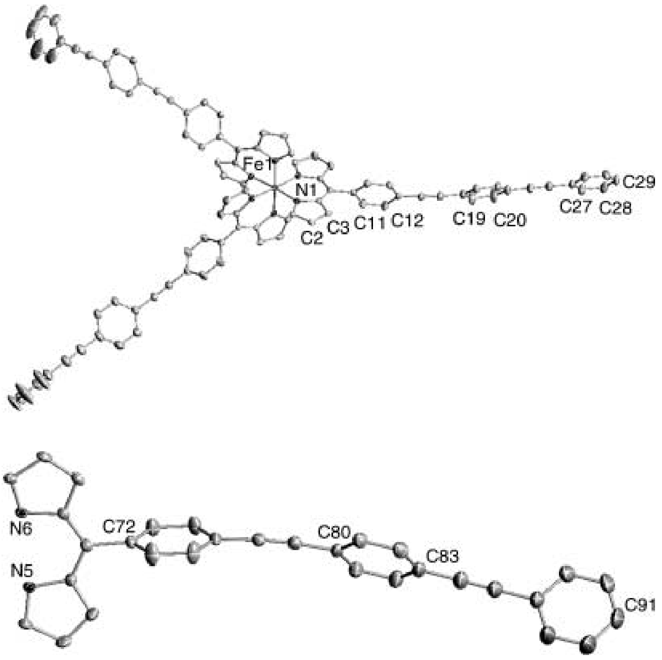


Figure 3. Structural diagram of [Fe(L^3)$_3$] (top) with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Structural diagram of one ligand from [Fe(L^3)$_3$] (bottom) with partial atom numbering schemes (ORTEP, 50% probability ellipsoids), showing the notable bending of the phenylacetylenylene portion of the ligand. Hydrogen atoms and solvent have been omitted for clarity.

A search of the Cambridge Structural Database[29] revealed only 17 structures containing a linear (central *para* substitution) phenyl-acetylene-phenyl-acetylene-phenyl oligomer, several of which demonstrated bending along the acetylene axis. Surprisingly, of these 17 compounds only one was found to be a metal complex; a thiol-terminated oligomer that was appended to a tris(osmium) cluster.[30] As such, the system reported here represents the first structurally characterized metal complex that contains multiple, chelating ligands appended with these extended molecular units.

Attempts to crystallize the complexes containing the ligands L^2 or L^4 were not successful. The high solubility of these complexes in a variety of organic solvents (vide supra) precluded the use of solvent diffusion methods. Attempts to grow crystals by slow evaporation always resulted in formation of thin films, never the desired crystalline materials.

Electrochemistry: The electrochemical behavior of the iron complexes was examined by cyclic voltammetry. Similar to previously reported iron–dipyrrin compounds,[16] complexes [Fe(L^N)$_3$] ($N = 1$, 2, 3, or 4) display quasireversible redox couples centered around −1.152 V (−0.692 V versus SCE) with an average ΔE_p value of 0.119 V for all four complexes. Table 2 summarizes the individual electrochemical results for each compound. Based on this data the phenylacetylenylene moiety does not significantly contribute to the electrochemical behavior of the metal center. The electrochemical behavior of these complexes may serve as a useful tool to examine the incorporation of these building blocks in supramolecular structures.

Table 2. Electrochemical data for [Fe(L^1)$_3$], [Fe(L^2)$_3$], [Fe(L^3)$_3$], and [Fe(L^4)$_3$].

Compound	Potential versus Fc [V]	Potential versus SCE [V]	ΔE_p [V]
[Fe(L^1)$_3$]	−1.156	−0.697	0.105
[Fe(L^2)$_3$]	−1.147	−0.687	0.086
[Fe(L^3)$_3$]	−1.155	−0.695	0.145
[Fe(L^4)$_3$]	−1.150	−0.690	0.140

UV/Vis spectroscopy: The combination of the phenylacetylenylene groups with the dipyrrin chelators provides these ligands and the resulting metal complexes with a rich absorption spectroscopy. Absorption spectra were collected for all of the phenylacetylenylene-substituted aldehydes, dipyrromethanes, dipyrrins, and metal complexes synthesized. The absorption spectra of the aldehydes and dipyrromethanes for each phenylacetylenylene system generally displayed fairly similar broad, high energy transitions below 350 nm. For example, compounds **3** and **4** had similar absorption spectra with maxima at 282/298 nm and 284/302 nm, respectively. These broad, intense features are assigned to π–π* transitions of the phenylacetylenylene systems.[5] Compounds **7** and **8** display the most significantly red-shifted spectra with maxima at 338 nm and 324/346 nm, respectively. This is consistent with the extended π-conjugation of this system due to the *para* substitution pattern at the central benzene ring.[5] Compounds **10** and **11** do not display this large red-shift, indicating that the *meta* substitution pattern on the central benzene ring disrupts the extended conjugation of the π system. Upon oxidation with DDQ, all of the compounds display a new absorption band centered around 435 nm, which is ascribed to the π–π* transition of the dipyrrin aromatic system.[17, 18] In addition to the new band at 435 nm, dipyrrins L^1 and L^4 display a second, less intense band centered at 342 nm for L^1 and 332 nm for L^4. This new band is not seen in L^2, but does appear to be present in L^3, as a shoulder feature of a more intense, higher energy absorption. These spectra indicate that this transition only appears in dipyrrins where the *meso*-phenyl group has *para* versus *meta* substitution, and that the feature is not solely due to the formation of a dipyrrin moiety. Additionally, this transition is affected by the coordination of metal ions. In the copper and iron complexes of L^1 this band becomes better defined and shifts to slightly lower energy at 356 and 348 nm, respectively (Figure 4). In the complex [Cu(L^4)$_2$] this band shifts to lower energy at 354

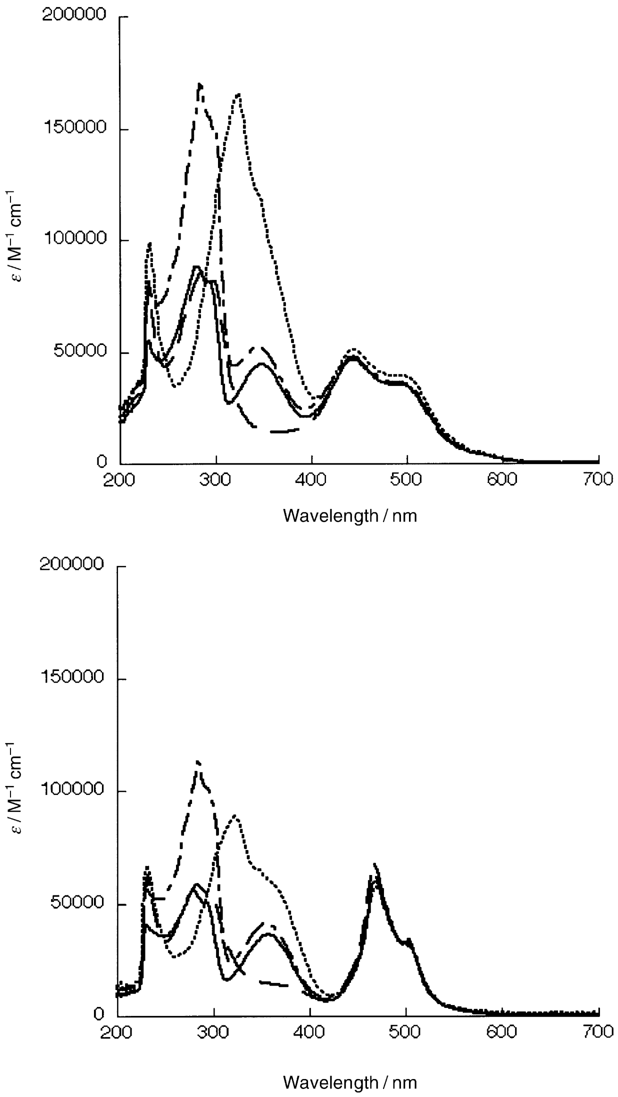


Figure 4. UV/Vis spectra for dipyrrin-metal complexes ([Fe(L^N)$_3$] top, [Cu(L^N)$_2$] bottom) as determined in CH_2Cl_2 solution; complexes: ——: L^1; – – –: L^2; ••••: L^3; •–•–: L^4.

and in [Fe(L^4)$_3$] to 344 nm. Based on these observations, this transition is tentatively assigned as a $\pi-\pi^*$ charge transfer process between the π system of the phenylacetylenylene group and the π system of the dipyrrin moiety. Continuing studies of *meso*-substituted phenyl dipyrrins will be required to more concretely elucidate the nature of this absorption feature.

In solution, the metal complexes of these ligands appear bright red, while in the solid state they are either deep red or lustrous green in color. The absorption spectroscopy of the metal complexes (Figure 4) preserves some of the features found in the free ligands and generates additional charge transfer transitions. The maintained transitions are those associated with the phenylacetylenylene $\pi-\pi^*$ transitions and the cautiously assigned $\pi-\pi^*$ charge transfer process between the phenylacetylenylene and dipyrrin π systems as described above. However the strong absorption features associated solely with the dipyrrin $\pi-\pi^*$ transitions, centered at ~435 nm is lost in favor of new features. The new bands are dependent on the nature of the metal center,[17, 18] but not on the nature of the phenylacetylenylene group as would be anticipated for a metal–dipyrrin charge transfer process. For the iron complexes, two new broad absorptions appear centered at around 444 and 490 nm. These two new transitions are relatively close in intensity with extinction coefficients of 47900 and 36200 M^{-1} cm^{-1}, respectively. In the copper complexes, two new transitions also arise, centered at 468 and 500 nm, but the intensities of these transitions differ more significantly from one another (61700 versus 32600 M^{-1} cm^{-1}). These spectral features of these metal complexes are consistent with similar compounds reported in the literature.[16–18]

Fluorescence spectroscopy: The use of phenylacetylenylene[4–6] and boron-dipyrrin (BODIPY) groups[31, 32] in light-harvesting systems prompted the examination of the fluorescence properties of the compounds prepared in this study. The fluorescence emission of the phenylacetylenylene aldehydes, dipyrromethanes, dipyrromethenes, and metal complexes were examined as solutions in CH_2Cl_2. Of all the aldehydes (**1**, **3**, **7**, **10**) and dipyrromethanes synthesized (**2**, **4**, **8**, **11**), only the *para*-substituted compounds **7** and **8** exhibited a significant fluorescence emission (Figure 5). The emission from the dipyrromethane **8** was considerably stronger than that observed from aldehyde **7**, probably due to the known quenching properties of aldehyde substituents.[33, 34] The fluorescence spectrum of **8** exhibited emission maxima at 352 and 368 nm consistent with the known emission features of the extended phenylacetylenylene functionality.[30] In addition a strong emission centered at ~460 nm was observed; the exact origin of this band has not been determined, but the feature appears to have some concentration dependent behavior and may be related to solution aggregation. The dipyrrin oxidation products were all found to be virtually non-fluorescent, and subsequently, none of the metal complexes showed any emission properties.

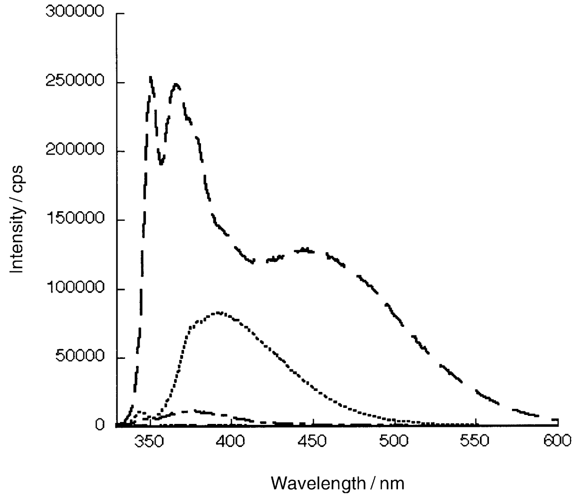


Figure 5. Fluorescence spectra for compounds **7** (••••), **8** (– – –), L^3 (•–•–), [Cu(L^3)$_2$] (——, no significant emission), and [Fe(L^3)$_3$] (- - - -, no significant emission). Only compounds **7** and **8** show significant fluorescence emission. Excitation wavelength = 320 nm.

Conclusion

Several routes have been explored for the preparation of a new series of phenylacetylenylene compounds that contain a dipyrrin porphrinoid unit. These studies have led to a general method for the synthesis of metal-chelating ligands containing these extended unsaturated groups. Eight different metal complexes have been prepared and their electrochemical and spectroscopic features have been studied. Three of these metal complexes have been structurally characterized clearly demonstrating that the metal centers can assemble and organize these 'molecular rods' in a stoichiometric and spatially defined fashion. The high symmetry and extended structure of these complexes suggest their use as components for supramolecular assembly; efforts to utilize these compounds in expanded structures and molecular solids are currently underway.

Experimental Section

General: Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Mass spectrometry was performed either at the University of California, San Diego Mass Spectrometry Facility in the Department of Chemistry and Biochemistry, or at University of Arizona Mass Spectrometry Facility in the Department of Chemistry. Elemental analysis was performed at the University of California, Berkeley Analytical Facility. ^{1}H/^{13}CNMR spectra were recorded on a Varian FT-NMR spectrometer running at 400 MHz at the Department of Chemistry and Biochemistry, University of California, San Diego. UV/Vis spectra were recorded in CH_2Cl_2 using a Hewlett-Packard 4582A spectrophotometer under PC control using the ChemStation software suite.

4-(Phenylacetylenyl)benzaldehyde (1): A mixture of 4-bromobenzaldehyde (0.150 g, 0.81 mmol), phenylacetylenylene (0.331 g, 3.24 mmol), triethylamine (0.123 g, 1.22 mmol), $[Pd(PPh_3)_2Cl_2]$ (0.028 g, 0.04 mmol), triphenylphosphine (0.005 g, 0.02 mmol), CuI (0.002 g, 0.008 mmol), and dry THF (15 mL) was stirred under nitrogen for 24 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 0.1 M EDTA (50 mL) and brine (50 mL), and then dried over Mg_2SO_4. The Mg_2SO_4 was removed by vacuum filtration, and the filtrate was evaporated to dryness. The resulting brown oil was purified by column chromatography (SiO_2; hexanes/CH_2Cl_2, 4:1) to afford a yellow solid. Yield: 64% (0.107 g). ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta = 7.34-7.36$ (m, 3H), 7.51–7.54 (m, 2H), 7.67 (d, 2H, $J = 8.0$ Hz), 7.85 (d, 2H, $J = 8.4$ Hz), 9.99 ppm (s, 1H, CHO); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta = 88.4$, 93.7, 122.6, 128.7, 129.2, 129.7, 132.0, 132.2, 132.6, 135.5, 191.4 ppm; APCI-MS: *m/z*: 207.2 $[M+H]^+$; $\lambda_{max} = 312$, 326 nm.

5-(4-Phenylacetylenylphenyl)dipyrromethane (2): Aldehyde **1** (0.107 g, 0.52 mmol) was dissolved in neat pyrrole (10 mL) and degassed by bubbling with nitrogen for 20 min. Trifluoroacetic acid (0.01 mL, 0.09 mmol) was added. The solution was stirred for 10 min. It was diluted with CH_2Cl_2 (50 mL), washed with 0.1 M NaOH (50 mL) and water (50 mL) then dried over Mg_2SO_4. The Mg_2SO_4 was removed by vacuum filtration and the filtrate was evaporated to remove CH_2Cl_2. The remaining pyrrole was removed by vacuum distillation with gentle heating. The product was purified by column chromatography (SiO_2; hexanes/CH_2Cl_2, 1:1) to afford a yellow foam. Yield: 83% (0.139 g). ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta = 5.46$ (s, 1H) 5.95 (s, 2H), 6.23 (q, 2H, $J = 2.8$ Hz, $J = 2.8$ Hz), 6.71 (m, 2H), 7.23 (d, 2H, $J = 8.4$ Hz), 7.39–7.41 (m, 3H), 7.55 (d, 2H, $J = 8.4$ Hz), 7.58–7.61 (m, 2H), 7.88 ppm (bs, 2H, NH); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta = 44.2$, 89.5, 89.8, 107.7, 108.7, 117.7, 122.1, 123.4, 128.5, 128.6, 128.7, 131.8, 132.0, 132.2, 142.6 ppm; APCI-MS: *m/z*: 323.1 $[M+H]^+$, 256.3 $[M-\text{pyrrole}]^+$; $\lambda_{max} = 288$, 306 nm.

5-(4-Phenylacetylenylphenyl)-4,6-dipyrromethene (L^1):

Method 1: Dipyrromethane **2** (0.080 g, 0.25 mmol) was dissolved in $CHCl_3$ (150 mL) and stirred in an ice bath. DDQ (0.057 g, 0.25 mmol) was dissolved in benzene (100 mL) and added slowly dropwise over the course of 1 h. The solvent was then evaporated and the product was purified by column chromatography (SiO_2; $CHCl_3$) to afford a yellow film. Yield: 30% (0.024 g). ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta = 6.43$ (d, 2H, $J = 4.4$ Hz, pyrH), 6.63 (d, 2H, $J = 4.4$ Hz), 7.38–7.41 (m, 3H), 7.52 (d, 2H, $J = 8.1$ Hz), 7.58–7.60 (m, 2H), 7.64 (d, 2H, $J = 8.1$ Hz), 7.66 ppm (bs, 2H); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta = 88.8$, 90.7, 117.6, 122.8, 123.8, 128.2, 128.3, 128.4, 130.6, 130.7, 131.5, 137.0, 140.5, 140.8, 143.6 ppm; ESI-MS: *m/z*: 321.3 $[M+H]^+$; $\lambda_{max} = 286$, 342, 436 nm.

Method 2: Dipyrromethane **2** (0.139 g, 0.43 mmol) was dissolved in $CHCl_3$ (150 mL) and stirred in an ice bath. DDQ (0.109 g, 0.48 mmol) was dissolved in benzene (100 mL) and added slowly dropwise. The solvent was then evaporated to one-half the volume and $Cu(acac)_2$ (0.068 g, 0.26 mmol) was added to form the copper complex, which was purified by column chromatography (vide infra). The copper complex was dissolved in THF (75 mL). Potassium cyanide (0.200 g, 3.07 mmol) dissolved in H_2O (20 mL) was added to the copper complex, and the mixture was stirred overnight. The solution turned from red to orange. The reaction mixture was evaporated to dryness and the resulting residue was dissolved in CH_2Cl_2 (50 mL), washed with brine (50 mL) and H_2O (50 mL), dried with Mg_2SO_4, vacuum filtered, and the filtrate evaporated to dryness to afford a yellow film. Yield: 36% (0.050 g, from **2**; 57% from $[Cu(L^1)_2]$).

$[Cu(L^1)_2]$: Dipyrromethane **2** (0.139 g, 0.43 mmol) was dissolved in $CHCl_3$ (150 mL) and stirred in an ice bath. DDQ (0.109 g, 0.48 mmol) was dissolved in benzene (100 mL) and added slowly dropwise. The solvent was then evaporated to one-half the volume and $Cu(acac)_2$ (0.068 g, 0.26 mmol) was added and the solution was stirred at room temperature for 5–10 min. The reaction mixture was then evaporated to dryness and the resulting residue was purified by column chromatography (SiO_2; $CHCl_3$) to afford a dichroic red/green film. Yield: 63% (0.095 g). m.p. >300 °C. APCI-MS: *m/z*: 702.1 $[M+H]^+$; elemental analysis calcd (%) for $C_{46}H_{30}N_4Cu \cdot H_2O \cdot$ benzene: C 78.22, H 4.80, N 7.02; found: C 78.40, H 4.66, N 6.99; $\lambda_{max} = 282$, 292, 356, 468, 502 nm.

$[Fe(L^1)_3]$: Dipyrromethane **2** (0.150 g, 0.47 mmol) was dissolved in $CHCl_3$ (150 mL) and stirred in an ice bath. DDQ (0.117 g, 0.51 mmol) was dissolved in benzene (100 mL) and added slowly dropwise. After addition, the reaction mixture was then evaporated to dryness and the resulting dark residue was redissolved in a 1:1 mixture of $CHCl_3$/MeOH (100 mL). Triethylamine (2 mL) and $FeCl_3 \cdot 6H_2O$ dissolved in MeOH (5 mL) was added to the $CHCl_3$/MeOH solution. The resulting mixture was heated to reflux overnight (~14 h). The solution was evaporated to dryness and the product was purified by column chromatography (SiO_2; $CHCl_3$) to afford a dichroic red/green film. Yield: 59% (0.092 g); m.p. 204 °C. APCI-MS: *m/z*: 1013.7 $[M+H]^+$; analysis calcd (%) for $C_{69}H_{45}N_6Fe \cdot H_2O \cdot$ hexane: C 80.56, H 5.50, N 7.52; found: C 80.37, H 5.18, N 7.66; $\lambda_{max} = 280$, 292, 348, 444, 490 nm.

3-(Phenylacetylenyl)benzaldehyde (3): The same procedure was used as in the synthesis of **1**, starting from 3-iodobenzaldehyde (0.250 g, 1.08 mmol). Yield: 77% (0.171 g); ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta = 7.35-7.37$ (m, 3H), 7.49 (t, 1H, $J = 15.6$ Hz), 7.54–7.56 (m, 2H), 7.74–7.76 (dt, 1H, $J = 8.4$ Hz), 7.80–7.83 (dt, 1H, $J = 8.0$ Hz), 8.01 (t, 1H, $J = 1.2$ Hz), 9.99 ppm (s, 1H, CHO); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta = 88.0$, 91.1, 122.7, 124.6, 128.5, 128.8, 128.9, 129.2, 131.7, 133.0, 136.5, 137.1, 191.5 ppm; GC-EIMS: *m/z*: 206.1 $[M^{\bullet}]^+$; $\lambda_{max} = 282$, 298 nm.

5-(3-Phenylacetylenylphenyl)dipyrromethane (4): The same procedure was used as in the synthesis of **2**, starting from **3** (0.171 g, (0.83 mmol). Yield: 76% (0.204 g); ^{1}H NMR (CD_2Cl_2 400 MHz, 25 °C): $\delta = 5.48$ (s, 1H), 5.96 (m, 2H), 6.23 (q, 2H, $J = 2.8$, Hz $J = 2.4$ Hz), 6.73 (q, 2H, $J = 2.0$, Hz $J = 2.4$ Hz), 7.26 (d, 1H, $J = 8.4$ Hz), 7.38 (t, 1H, $J = 7.6$ Hz), 7.42–7.45 (m, 3H), 7.47 (s, 1H), 7.52 (d, 1H, $J = 8.0$ Hz), 7.60–7.62 (m, 2H), 7.99 ppm (bs, 2H, NH); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta = 44.1$, 89.5, 89.6, 107.5, 108.6, 117.7, 123.3, 123.6, 128.5, 128.6, 128.7, 128.9, 130.3, 131.5, 131.8, 132.3, 143.1 ppm; APCI-MS: *m/z*: 323.1 $[M+H]^+$, 256.3 $[M-\text{pyrrole}]^+$; $\lambda_{max} = 284$, 302 nm.

5-(3-Phenylacetylenylphenyl)-4,6-dipyrromethene (L^2): The same procedure was used as in the synthesis of L^1 (Method 1), starting from **4** (0.204 g, 0.63 mmol). Yield: 42% (0.086 g); ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta = 6.42$ (d, 2H, $J = 2.8$ Hz), 6.62 (d, 2H, $J = 2.8$ Hz), 7.33–7.34 (m, 3H), 7.42–

7.43 (m, 2H), 7.51–7.53 (m, 2H), 7.64–7.66 (m, 2H), 7.70 ppm (t, 2H, $J=1.2$ Hz); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta=88.6$, 90.1, 117.6, 122.7, 122.8, 127.6, 128.2, 128.3, 129.6, 130.4, 131.4, 131.5, 132.0, 133.4, 137.2, 139.3, 143.7 ppm; APCI-MS: *m/z*: 321.3 $[M+H]^+$; $\lambda_{max}=288$, 434 nm.

[Cu(L^2)$_2$]: The same procedure was used as in the synthesis of **[Cu(L^1)$_2$]**, starting from purified L^2 (0.034 g, 0.11 mmol). Yield: 81 % (0.030 g); m.p. 146 °C; MALDI-TOF-MS: *m/z*: 702.58 $[M+H]^+$; elemental analysis calcd (%) for $C_{46}H_{30}N_4Cu$: C 78.67, H 4.31, N 7.98; found: C 78.85, H 4.42, N 7.68; $\lambda_{max}=284$, 298, 468, 500 nm.

[Fe(L^2)$_3$]: The same procedure was used as in the synthesis of **[Fe(L^1)$_3$]**, starting from purified L^2 (0.026 g, 0.081 mmol). Yield: 91 % (0.025 g); m.p. 176 °C; APCI-MS: *m/z*: 1013.8 $[M+H]^+$; elemental analysis calcd (%) for $C_{69}H_{45}N_6Fe$: C 81.73, H 4.47, N 8.29; found: C 81.70, H 4.55, N 8.22; $\lambda_{max}=284$, 300, 444, 496 nm.

4-(Ethynyl)benzaldehyde (5): 4-[(Trimethylsilyl)ethynyl]benzaldehyde (1.00 g, 4.94 mmol) was dissolved in methanol (50 mL) to which K_2CO_3 (0.500 g, 3.62 mmol) was added. The reaction mixture was stirred for 15 min at which point the starting material was completely consumed as judged by TLC and GC-MS. The reaction mixture was evaporated to dryness and dissolved in CH_2Cl_2 (50 mL), washed with aqueous sodium bicarbonate (50 mL), and dried over Mg_2SO_4. The Mg_2SO_4 was removed by vacuum filtration, and the filtrate was evaporated to dryness to afford a yellow solid. Yield: 96 % (0.617 g). ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta=3.30$ (s, 1H), 7.57 (d, 2H, $J=8.0$ Hz), 7.78 (d, 2H, $J=8.4$ Hz), 9.94 ppm (s, 1H, CHO); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta=81.5$, 82.9, 128.3, 129.6, 132.8, 136.0, 191.3. GC-EIMS: *m/z*: 130.7 $[M^{\cdot}]^+$.

4-(4-Iodophenylacetylenyl)benzaldehyde (6): A mixture of **5** (0.300 g, 2.31 mmol), 1,4-diiodobenzene (3.042 g, 9.22 mmol), triethylamine (0.349 g, 3.46 mmol), $[Pd(PPh_3)_2Cl_2]$ (0.081 g, 0.12 mmol), triphenylphosphine (0.015 g, 0.06 mmol), CuI (0.009 g, 0.05 mmol), and dry THF (15 mL) was stirred under nitrogen for four days. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 0.1 M EDTA (50 mL) and brine (50 mL), and was then dried over Mg_2SO_4. The Mg_2SO_4 was removed by vacuum filtration and the filtrate was evaporated to dryness. The remaining residue was purified by column chromatography (SiO_2; hexanes/CH_2Cl_2, 1:1) to afford a yellow solid. Yield: 73 % (0.560 g). ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta=7.28$ (d, 2H, $J=8.4$ Hz), 7.67 (d, 2H, $J=8.4$ Hz), 7.72 (d, 2H, $J=8.4$ Hz), 7.87 (d, 2H, $J=8.4$ Hz), 10.02 ppm (s, 1H, CHO); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): δ 89.8, 92.3, 95.0, 121.8, 127.7, 129.0, 129.4, 131.8, 133.0, 137.5, 191.0 ppm; GC-EIMS: *m/z*: 332.1 $[M^{\cdot}]^+$. $\lambda_{max}=320$, 334 nm.

4-[4-(Phenylacetylenyl)phenylacetylenyl]benzaldehyde (7): The same procedure was used as in the synthesis of **1**, starting from **6** (0.200 g, 0.60 mmol) and phenylacetylenylene (0.184 g, 1.8 mmol). After three days, the reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 0.1 M EDTA (50 mL) and brine (50 mL), and was then dried over Mg_2SO_4. The Mg_2SO_4 was removed by vacuum filtration and the filtrate was evaporated to dryness. The remaining residue was purified by column chromatography (SiO_2; CH_2Cl_2) to afford a yellow solid. Yield: 72 % (0.133 g); ^{1}H NMR ($CDCl_3$ 400MHz, 25 °C): $\delta=7.36$ (m, 3H), 7.54 (m, 6H), 7.69 (d, 2H, $J=8.0$ Hz), 7.89 (d, 2H, $J=8.0$ Hz), 10.03 ppm (s, 1H, CHO); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta=88.9$, 90.2, 91.6, 93.0, 122.1, 122.7, 123.8, 128.3, 128.4, 129.2, 129.5, 131.4, 131.5, 131.6, 132.0, 135.3, 191.1 ppm; GC-EIMS: *m/z*: 306.3 $[M^{\cdot}]^+$. $\lambda_{max}=338$ nm.

5-[4-((Phenylacetylenyl)phenylacetylenyl)phenyl]dipyrromethane (8): The same procedure was used as in the synthesis of **2**, starting from **7** (0.133 g, 0.43 mmol). Yield: 75 % (0.138 g); ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta=5.48$ (s, 1H), 5.93 (m, 2H), 6.19 (q, 2H, $J=2.8$ Hz, $J=3.2$ Hz), 6.71 (m, 2H), 7.22 (d, 2H, $J=8.0$ Hz), 7.37 (m, 3H), 7.49–7.57 (m, 8H), 7.90 ppm (bs, 2H, NH); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta=43.8$, 89.0, 89.1, 90.9, 91.2, 107.3, 108.4, 117.3, 121.5, 122.8, 122.9, 123.0, 128.2, 128.3, 131.3, 131.4, 131.7, 131.8, 142.3 ppm; MALDI-TOF-MS: *m/z*: 422.23 $[M+H]^+$; $\lambda_{max}=324$, 346 nm.

5-[4-((Phenylacetylenyl)phenylacetylenyl)phenyl]-4,6-dipyrromethene (L^3): The same procedure was used as in the synthesis of L^1 starting from **8** (0.202 g, 0.48 mmol). Yield: 13 % (0.026 g); ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta=6.42$ (d, 2H, $J=2.8$ Hz), 6.62 (d, 2H, $J=3.2$ Hz), 7.36–7.39 (m, 3H), 7.52 (d, 2H, $J=8.0$ Hz), 7.55–7.57 (m, 6H), 7.63 (d, 2H, $J=8.0$ Hz), 7.66 ppm (s, 2H); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): δ 89.0, 90.4, 90.6, 91.4, 117.7, 122.6, 122.8, 123.2, 123.6, 128.3, 128.4, 128.5, 130.7, 130.8, 131.3, 131.4, 131.5, 137.2, 140.5, 140.8, 143.7 ppm; ESI-MS: *m/z*: 421.3 $[M+H]^+$; $\lambda_{max}=324$, 436 nm.

[Cu(L^3)$_2$]: The same procedure was used as in the synthesis of [Cu(L^1)$_2$], starting from **8** (0.130 g, 0.31 mmol). Yield: 69 % (0.096 g). m.p. >300 °C; MALDI-TOF-MS: *m/z*: 902.40 $[M+H]^+$; analysis calcd for $C_{62}H_{38}N_4Cu$: C 82.51, H 4.24, N 6.21; found: C 82.43, H 4.58, N 5.97. $\lambda_{max}=322$, 468, 500 nm.

[Fe(L^3)$_3$]: The same procedure was used as in the synthesis of [Fe(L^1)$_3$], starting from **8** (0.340 g, 0.80 mmol). Yield: 48 % (0.170 g). m.p. 196 °C. MALDI-TOF-MS: *m/z*: 1313.44 $[M+H]^+$; analysis calcd (%) for $C_{93}H_{57}N_6Fe$: C 84.99, H 4.37, N 6.39; found: C 85.00, H 4.36, N 6.50; $\lambda_{max}=320$, 444, 490 nm.

4-(3-Iodophenylacetylenyl)benzaldehyde (9): A mixture of **5** (0.200 g, 1.54 mmol), 1,3-diiodobenzene (1.52 g, 4.61 mmol), triethylamine (0.155 g, 1.54 mmol), $[Pd(PPh_3)_2Cl_2]$ (0.054 g, 0.08 mmol), triphenylphosphine (0.010 g, 0.04 mmol), CuI (0.006 mg, 0.03 mmol), and dry THF (15 mL) was stirred under nitrogen for three days. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 0.1 M EDTA (50 mL) and brine (50 mL), and was then dried over Mg_2SO_4. The Mg_2SO_4 was removed by vacuum filtration and the filtrate was evaporated to dryness. The remaining residue was purified by column chromatography (SiO_2; hexanes/CH_2Cl_2, 1:1) to afford a yellow solid. Yield: 82 % (0.420 g). ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta=7.11$ (t, 1H, $J=8.0$ Hz), 7.52 (dt, 1H, $J=8.0$ Hz), 7.67 (d, 2H, $J=8.0$ Hz), 7.72 (dt, 1H, $J=8.0$ Hz), 7.88 (d, 2H, $J=8.4$ Hz), 7.91 (t, 1H, $J=2.0$ Hz), 10.02 ppm (s, 1H, CHO); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta=89.6$, 91.4, 93.7, 124.4, 128.8, 129.4, 129.80, 130.7, 132.0, 135.4, 137.7, 140.1, 191.1 ppm; GC-EIMS: *m/z*: 332.1 $[M^{\cdot}]^+$; $\lambda_{max}=310$, 328 nm.

4-[3-(Phenylacetylenyl)phenylacetylenyl]benzaldehyde (10): The same procedure was used as in the synthesis of **1**, starting from **9** (0.400 g, 1.20 mmol) and phenylacetylenylene (0.369 g, 3.60 mmol). After three days, the reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 0.1 M EDTA (50 mL) and brine (50 mL), and was then dried over Mg_2SO_4. The Mg_2SO_4 was removed by vacuum filtration and the filtrate was evaporated to dryness. The remaining residue was purified by column chromatography (SiO_2; CH_2Cl_2) to afford a yellow solid. Yield: 90 % (0.332 g). ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta=7.33$–7.37 (m, 4H), 7.49–7.56 (m, 4H), 7.68 (d, 2H, $J=7.6$ Hz), 7.74 (s, 1H), 7.87 (d, 2H, $J=8.0$ Hz), 10.01 ppm (s, 1H, CHO); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta=88.2$, 89.0, 90.2, 92.4, 122.6, 122.7, 123.6, 128.2, 128.3, 128.4, 129.0, 129.4, 131.2, 131.4, 131.7, 131.9, 134.5, 135.3, 191.0 ppm; GC-EIMS: *m/z*: 306.3 $[M^{\cdot}]^+$; $\lambda_{max}=286$, 304 nm.

5-[3-((Phenylacetylenyl)phenylacetylenyl)phenyl]dipyrromethane (11): The same procedure was used as in the synthesis of **2**, starting from **10** (0.330 g, 1.08 mmol). Yield: 90 % (0.410 g). ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta=5.49$ (s, 1H), 5.93 (m, 2H), 6.18 (q, 2H, $J=3.2$ Hz, $J=2.8$ Hz), 6.72 (m, 2H), 7.22 (d, 2H, $J=8.0$ Hz), 7.32–7.38 (m, 4H), 7.48–7.51 (m, 4H), 7.55–7.56 (m, 2H), 7.72 (t, 1H, $J=1.6$ Hz), 7.94 ppm (bs, 2H, NH); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta=43.9$, 88.4, 88.5, 89.6, 89.9, 107.3, 108.4, 117.3, 121.5, 122.8, 123.4, 123.5, 128.2, 128.3, 131.1, 131.5, 131.7, 134.4, 142.3 ppm; MALDI-TOF-MS: *m/z*: 421.23 $[M+H]^+$; $\lambda_{max}=286$, 302 nm.

5-[3-((Phenylacetylenyl)phenylacetylenyl)phenyl]-4,6-dipyrromethene (L^4): The same procedure was used as in the synthesis of **L^1** (Method 2), starting from **11** (0.250 g, 0.59 mmol). Yield: 36 % (0.090 g); ^{1}H NMR ($CDCl_3$ 400 MHz, 25 °C): $\delta=6.43$ (d, 2H, $J=2.8$ Hz), 6.64 (d, 2H, $J=3.2$ Hz), 7.37–7.39 (m, 4H), 7.51–7.58 (m, 6H), 7.63 (d, 2H, $J=8.8$ Hz), 7.67 (s, 2H), 7.79 ppm (s, 1H); ^{13}C NMR ($CDCl_3$ 100 MHz, 25 °C): $\delta=88.4$, 89.4, 89.9, 90.1, 117.7, 122.8, 123.2, 123.5, 123.6, 128.2, 128.3, 128.4, 128.5, 130.7, 131.1, 131.3, 131.5, 134.5, 137.2, 140.5, 140.8, 143.6 ppm; ESI-MS: *m/z*: 421.3 $[M+H]^+$; $\lambda_{max}=286$, 302, 332, 432 nm.

[Cu(L^4)$_2$]: The same procedure was used as in the synthesis of [Cu(L^1)$_2$], starting from **11** (0.250 g, 0.59 mmol). Yield: 47 % (0.125 g); m.p. 100 °C; MALDI-TOF-MS: *m/z*: 901.20 $[M+H]^+$; elemental analysis calcd (%) for $C_{62}H_{38}N_4Cu$: C 82.51, H 4.24, N 6.21; found: C 82.25, H 4.36, N 6.23; $\lambda_{max}=284$, 354, 470, 502 nm.

[Fe(L^4)$_3$]: The same procedure was used as in the synthesis of [Fe(L^1)$_3$], starting from **11** (0.150 g, 0.36 mmol). Yield: 57 % (0.088 g); m.p. 157 °C. MALDI-TOF-MS: *m/z*: 1313.38 $[M+H]^+$; analysis calcd for $C_{93}H_{57}N_6Fe$: C 84.99, H 4.37, N 6.39; found: C 84.77, H 4.55, N 6.45; $\lambda_{max}=284$, 344, 444, 494 nm.

X-ray crystallographic analysis: Data was collected on a Bruker AXS area detector diffractometer. Crystals were mounted on quartz capillaries by using Paratone oil and were cooled in a nitrogen stream (Kryo-flex controlled) on the diffractometer (−173 °C). Peak integrations were performed with the Siemens SAINT software package with absorption corrections applied using the program SADABS. Space group determinations were performed by the program XPREP and the structures were solved (by direct or Patterson methods) and refined with the SHELXTL software package.[35] Unless noted otherwise, all hydrogen atoms were fixed at calculated positions with isotropic thermal parameters; all non-hydrogen atoms were refined anisotropically.

CCDC-208199, CCDC-208200, and CCDC-208201 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

[Cu(L^1)$_2$]: Dark green blocks were grown out of a solution of the complex in a mixture of CH_2Cl_2 containing a small amount of benzene diffused with hexanes. The complex crystallized in the triclinic space group $P\bar{1}$ ($Z = 2$, $a = 9.378$, $b = 13.821$, $c = 16.635$ Å, $\alpha = 104.721$, $\beta = 99.250$, $\gamma = 104.753°$). The complex co-crystallized with one molecule of benzene in the asymmetric unit.

[Fe(L^1)$_3$]: Dark green hexagons were grown out of a solution of the complex in benzene diffused with hexanes. The complex crystallized in the rhombohedral space group $R\bar{3}c$ ($Z = 2$, $a = 14.455$ Å, $\alpha = 84.738°$). The asymmetric unit contains a molecule of highly disordered benzene. It was treated as a diffuse contribution using the program SQUEEZE (A. Spek, Platon Library). Electron count/unit cell: 92 (found), 84 (expected). The determined and calculated intensive properties include the solvent molecule, but individual atoms do not appear in the atom lists.

[Fe(L^3)$_3$]: Dark green thin plates were grown out of a solution of the complex in benzene diffused with cyclohexane. The complex crystallized in the monoclinic space group $P2_1/c$ ($Z = 4$, $a = 28.896$, $b = 15.122$, $c = 17.094$ Å, $\beta = 91.484°$). The complex co-crystallized with one molecule of cyclohexane in the asymmetric unit.

Electrochemistry: Cyclic voltammetry experiments were performed by using a Bioanalytical Systems (BAS) CV-50W voltametric analyzer under PC control.[16] Solutions were prepared by dissolving 5–15 mg of metal complex in dried, degassed CH_2Cl_2 containing 0.1 M $n\mathrm{Bu_4N(PF_6)}$. The auxiliary and reference electrodes were a platinum wire and a silver electrode ($Ag/AgCl_{(aq)}$), respectively. A platinum electrode (BAS) was used for the working electrode. Samples were purged with $N_2(g)$ for ~2 minutes before experiments were performed. Sweep rates were varied from 0.050 to 1.500 $\mathrm{V\,s^{-1}}$ to check the reversibility of the couple. All data are reported at ambient temperature (25 °C) with a sweep rate of 0.500 $\mathrm{V\,s^{-1}}$. The ferrocenium/ferrocene couple ($Fc^+/Fc°$) was measured under identical conditions for use as a reference measurement ($E_{1/2} = +0.471$ V, $\Delta E_p = 0.127$ V, 0.500 $\mathrm{V\,s^{-1}}$). All potentials are reported relative to $Fc^+/Fc°$, unless otherwise stated. Potentials reported relative to the aqueous standard calomel electrode (SCE), were adjusted using the equation $E_{1/2}^{SCE} = E_{1/2}^{Fc} + 0.46$ V, based on the data obtained here and reports in the literature[36–38] indicating that the ferrocene couple in CH_2Cl_2 with $n\mathrm{Bu_4N(PF_6)}$ electrolyte is approximately +0.46 V relative to SCE.

Fluorescence measurements: Measurements were performed on a Photon Technologies International QuantaMaster 2000 spectrophotometer. Solutions of each compound were prepared in CH_2Cl_2 to a concentration of $\sim 10^{-5}$ M; no efforts were made to exclude air or water. All reported measurements were taken in a 1.0 cm quartz cuvette at a slit width of 3 nm with an excitation wavelength of 320 nm.

Acknowledgement

We thank Jesse Mello and Prof. Nathaniel Finney (U.C. San Diego) for use and assistance with their fluorimeter, Dr. Lev N. Zakharov and Prof. Arnold L. Rheingold (U.C. San Diego) for assistance with the crystallography, Dr. Linda Breci (U. of Arizona) for assistance with obtaining several mass spectra, and Dr. Ulla Nørklit Andersen (U.C. Berkeley) for assistance with obtaining the elemental analysis. This work was supported by the University of California, San Diego, the Chris and Warren Hellman Faculty Scholar award (S.M.C.), and GAANN Fellowship Number GM-60202-03 (S.R.H.).

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Received: April 12, 2003 [F5041]