

**Figure 1.** X-ray powder diffraction results. Patterns a-c were obtained on powders heated for 4 h at the specified temperature under argon. Patterns d and e are the calculated diffraction pattern for cubic GaN and the experimental pattern for hexagonal GaN, respectively.

smaller, more gradual weight loss (1.7%) between 210 and 500 °C. Mass spectrometric studies indicated that hydrogen was the only product evolved at temperatures greater than 200 °C, but that hydrogen, ammonia, and some gallium were detected during the initial weight loss. Due to the involatility of elemental Ga, its appearance in the mass spectrum indicates the occurrence of a small amount of sublimation of starting material. The precipitous loss of hydrogen from cyclotrigallazane may be facilitated by its crystal structure in which the nearest intermolecular contact to each hydride ligand is a nitrogen-bound proton. During the overall conversion, the white starting material is transformed to a dark gray solid. Figure 1 illustrates the X-ray powder diffraction patterns obtained after treating three separate samples of cyclotrigallazane for 4 h under argon at the specified temperatures. Surprisingly, the onset of crystallinity is evident even in the sample treated at 180 °C. Figure 1 also includes a graphical representation of the known diffraction pattern for hexagonal GaN. The notable absence in our patterns of several reflections of *h*-GaN,<sup>13</sup> coupled with the similarity to the patterns of GaP and other cubic (sphalerite) structures,<sup>14</sup> suggested that we had formed cubic GaN. The elemental analyses suggest<sup>15</sup> that the cubic phase may be nonstoichiometric having the formula GaN<sub>0.83</sub>, a value that corresponds closely to the overall weight loss observed in the TGA experiments. Our calculated powder diffraction pattern for cubic GaN (a = 4.50 (2) Å) agrees well with the experimental results. The lattice constants of the various thin films of cubic GaN range from 4.52 to 4.55 Å.<sup>5-7</sup> The cubic GaN was found to convert to the hexagonal phase; however, the phase transition is slow. After 120 h at 900 °C under Ar, the transition is approximately 50% complete.

(13) Powder Diffraction File, International Center for Diffraction Data, Swarthmore, PA, card no. 2-1078.

(14) Powder Diffraction File, International Center for Diffraction Data, Swarthmore, PA, card no. 32-397.

(15) Anal. Calcd for GaN<sub>1.00</sub>: Ga, 83.27; N, 16.73. Found: Ga, 85.99; N, 14.31; H, < 0.5; C, < 0.5 (Galbraith Laboratories).

Why the cubic phase of GaN should form remains unexplained. On one hand this GaN synthesis is conducted at temperatures well below those typically used, perhaps in a temperature range where the cubic phase is thermodynamically favored. Alternatively the synthesis may well lead to a kinetically trapped, metastable phase. Experiments addressing this fundamental issue are in progress.

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**Supplementary Material Available:** Description of the structural solution, tables of atomic positional and thermal parameters and crystallographic data, and an ORTEP drawing of the molecule (7 pages); a list of the structure factors (4 pages). Ordering information is given on any current masthead page.

## Ferrocene Polymers with "Polyaniline" Backbones

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Transiton-metal complex polymer modified electrodes have become an area of intense research activity as practical applications may exist for these unique polymers.<sup>1</sup> Polymers containing ferrocene covalently bonded to the polymer<sup>2</sup> or immobilized within a host polymer matrix<sup>3</sup> have been used for practical applications and fundamental studies. Polymer films of poly(vinylferrocene) often are used in these studies. Recent reports have appeared in which pyrrole units have been appended to one or both of the cyclopentadienyl rings.<sup>4,5</sup> Synthetically, attaching the pyrrole to the cyclopentadienyl ring(s) can be difficult, and good-quality polymers generally result when the mo-

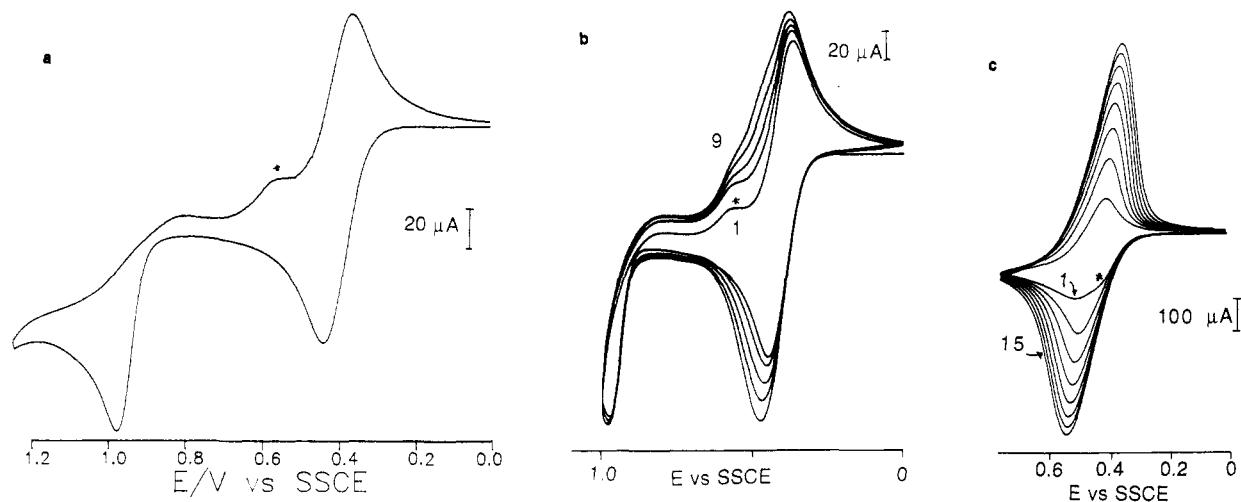
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**Figure 1.** (a) Single-potential sweep for 6.4 mM solution of **1a**, 100 mV/s. The asterisk denotes a new reduction process resulting from the irreversible oxidation at  $E_{p,ox} = 975$  mV. (b) Electropolymerization of a 6.5 mM solution of **1a**, 20 mV/s. The first scan and every second scan are shown. (c) Electropolymerization of a 4.9 mM solution of **1b**, 50 mV/s. The first scan and every second scan are shown. The asterisk denotes oxidation of the aromatic amine. All voltammograms were obtained in 0.1 M TBAP/CH<sub>3</sub>CN on a Pt electrode ( $A = 0.15$  cm<sup>2</sup>) and  $E/V$  vs SSCE.

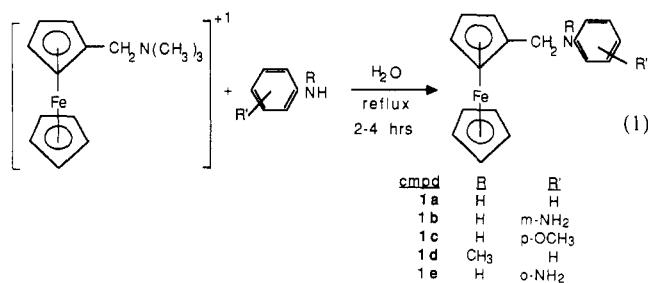
**Table I. Electrochemical Data<sup>a</sup>**

compd	$E^\circ_{\text{ferr}}$ , mV	$E_{\text{ox,amine}}$ , mV
<b>1a</b>	406	975
<b>1b</b>		410
<b>1c</b>	405	770
<b>1d</b>	414	945
<b>1e</b>	455	410
poly- <b>1a</b>	465	
poly- <b>1b</b>	430	

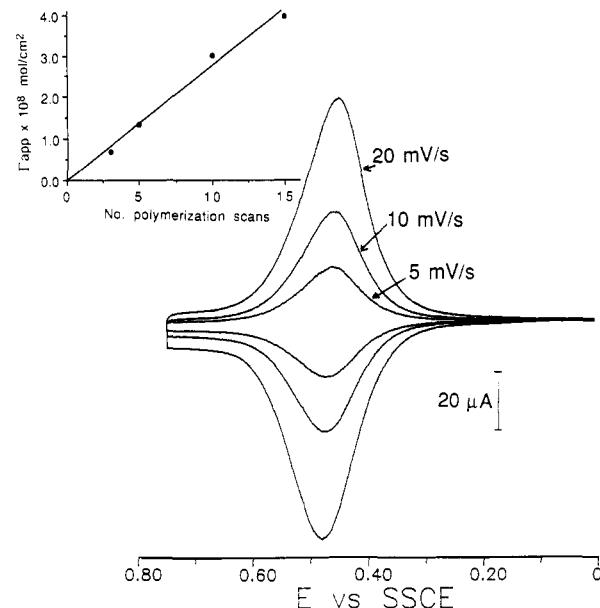
<sup>a</sup> Pt electrode in 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN.

nomers are copolymerized with pyrrole. These polymers have complicated electrochemistry with components arising from a polypyrrole backbone and a ferrocene portion.

We now report a simple method for preparing electro-polymerized ferrocene polymer films from monomeric materials such as **1** (eq 1). The oxidative polymerization



of the pendant aniline moieties on **1** comprises the polymer backbone in a manner analogous to other metal complexes with similar aromatic amine substituents.<sup>6</sup> Synthesis<sup>7</sup> and isolation of compounds **1a**–**e** are straightforward. Furthermore the electrochemical properties for the resulting polymer films are similar to the poly(vinylferrocene)-based



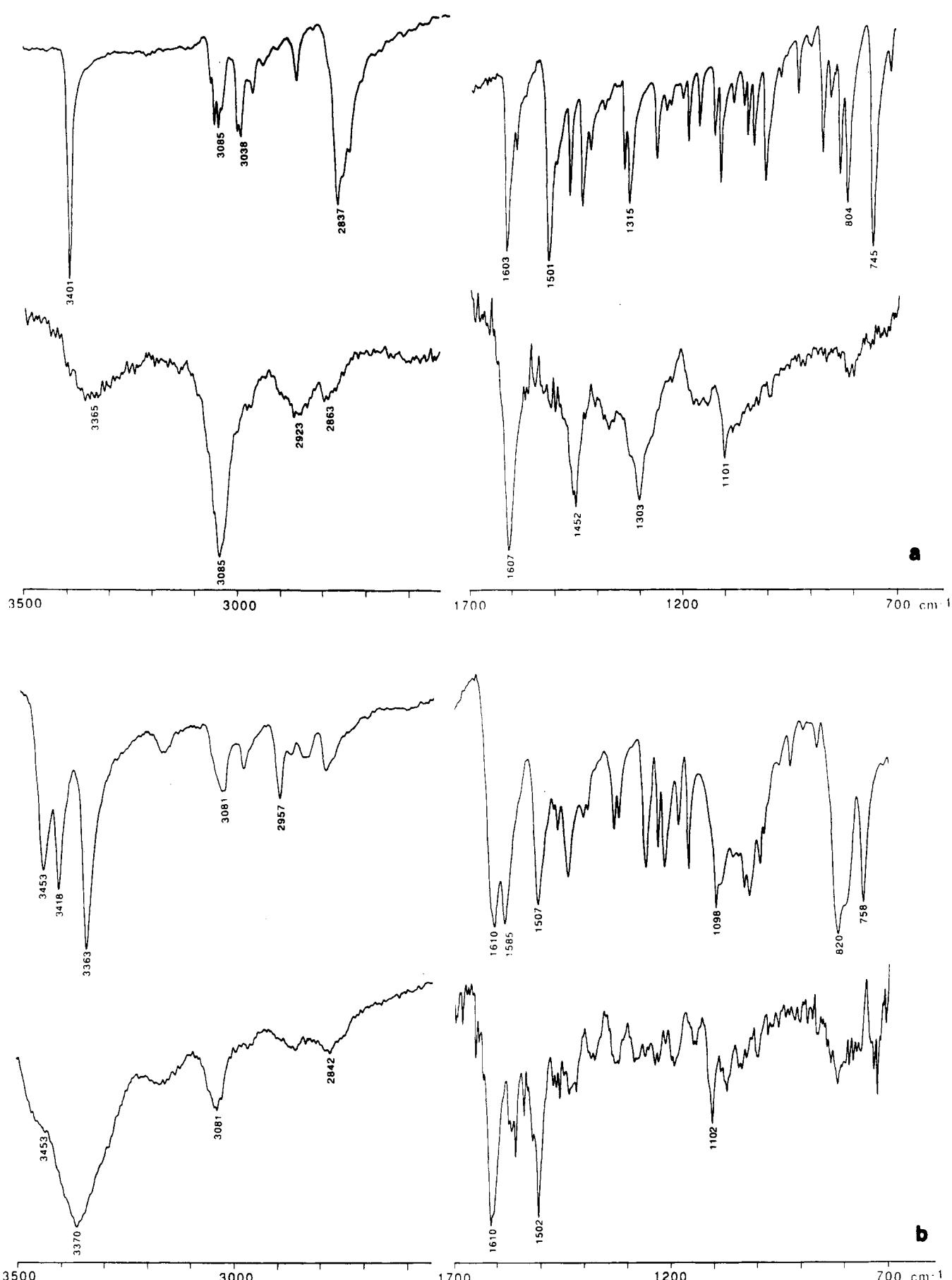
**Figure 2.** Voltammetric response of poly-**1a** at the various scan rates shown on the figure. Insert is  $\Gamma_{\text{app}}$  (determined at 5 mV/s) vs number of polymerization scans to form a film. Films were grown by cycling the potential between 0 and 1.0 V at 20 mV/s using conditions shown in Figure 1b. The voltammetry of poly-**1b** is similar to that of poly-**1a**.

polymers and are superior to the pyrrole-substituted ferrocene polymer films owing to the simplicity of the electrochemical responses (at present, no evidence is found for electronic conduction through the presumed polyaniline backbone). Some of the interesting properties that might be displayed by these modified aniline/ferrocene polymers include mixed electronic and redox hopping conductivities, enhanced solubility of the polymer, copolymer film-forming capabilities with aniline, and others as well.

The ferrocene derivatives are prepared according to eq 1. An amine, 1.5–2 equiv, is combined with [(dimethylamino)methyl]ferrocene methiodide in water, and the solution refluxed for 2–4 h, during which time a viscous oil forms. After this is cooled to room temperature, the water is decanted from the oil, which is taken up in Et<sub>2</sub>O, dried with Na<sub>2</sub>SO<sub>4</sub>, and chromatographed on silica (1:1 ethyl

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**Figure 3.** (a) Upper trace: transmission IR spectrum of monomer **1a** taken as a KBr pellet. Lower trace: specular reflectance spectrum of poly-**1a** on a Pt electrode formed under conditions analogous to those shown in Figure 1b. (b) Upper trace: transmission IR spectrum of monomer **1b** taken as a KBr pellet. Lower trace: specular reflectance spectrum of poly-**1b** on a Pt electrode formed under conditions analogous to those shown in Figure 1c.

acetate:hexane for **1a** and 1:2 ethyl acetate:hexane for **1b**). For **1a** the first band eluted is the desired product (isolated yield 75%) while the desired product is the second band for **1b** (isolated yield 65%).<sup>8</sup> The products are stable in air at room temperature in the solid state and in solution.

Cyclic voltammograms for the monomers in  $\text{CH}_3\text{CN}$  [0.1 M  $\text{Bu}_4\text{NClO}_4$  (TBAP)] show a quasi-reversible ferrocene/ferricinium ( $\text{Fc}/\text{Fc}^+$ ) couple and an irreversible amine oxidation process,<sup>10</sup> Table I and Figure 1a. For **1b** the onset voltage for electropolymerization occurs *negatively* of the  $\text{Fc}/\text{Fc}^+$  couple precluding assignment of an  $E^\circ$  for this complex. However, compound **1e** does not electropolymerize, and due to their similarity we assume that complexes **1e** and **1b** have nearly the same  $E^\circ$ .

Upon continuous potential cycling between 0 and 1.0 V at 20 mV/s in a rigorously deaerated electrolysis solution of **1a**, an adherent polymer film of the ferrocene complex deposits on the Pt electrode surface (Figure 1b). The monotonic increase in both  $i_{\text{ox}}$  and  $i_{\text{red}}$  for the  $\text{Fc}/\text{Fc}^+$  couple clearly indicates polymer film formation. The reduction process marked with an asterisk in Figure 1b likely arises from an amine coupling product.<sup>10</sup> In the case of **1b** oxidation of the aromatic amine and film deposition occur under less forcing conditions than required for **1a**,  $E_{\text{ox,amine}} = 0.41$  V (Figure 1c), and deaerating the solution is not necessary.

Neither complex **1c** nor **1d** electropolymerizes under any conditions investigated since the head (amine nitrogen) to tail (para position of an adjacent benzene ring) coupling sites expected for polymerization are blocked by steric bulk, **1c**, and site occupation, **1d**. These observations strongly suggest that head-to-tail coupling of the amines constitute the polymer backbone for the ferrocene polymer.<sup>9,10</sup> Support for the head-to-tail coupling also comes from infrared (IR) specular reflectance data taken on a poly-**1a**-coated Pt electrode for which only a very weak N-H absorption ( $\nu_{\text{N-H}} = 3365 \text{ cm}^{-1}$ ) is observed (Figure 3a). For poly-**1b** polymerization most likely occurs by coupling of the primary amine nitrogen to the 4 and/or 6 position, both of which are resonance-stabilized radical cations, on an adjacent benzene ring. IR specular reflectance measurements indicate the presence of ( $\nu_{\text{N-H}} = 3370 \text{ cm}^{-1}$ ) secondary amine functionalities in poly-**1b** films and possibly also some primary amine groups (shoulder at  $\sim 3450 \text{ cm}^{-1}$ , Figure 3b). The relatively simple IR spectra observed for both polymers are somewhat unexpected, although other ferrocene polymer films also have simple IR spectra.<sup>2c,4b,11</sup>

When electrodes of either poly-**1a** or poly-**1b** are transferred to a solution containing only supporting electrolyte (0.1 M TBAP in  $\text{CH}_3\text{CN}$ ) and scanned between 0 and 0.75 V, the voltammetric responses shown in Figure 2 are obtained (Table I). Voltage excursions more positive (1.25 V) and negative (-2.0 V,  $\text{N}_2$  atmosphere) do not

degrade the films. For thin films of either polymer examined at 5 mV/s sweep rate, the peak splitting,  $\Delta E_p$ , the peak width at half-height,  $E_{\text{fwhm}}$ , can be as low as 10 and 110 mV respectively. Both quantities approach the theoretical values of 0 V and 90.5 mV for  $\Delta E_p$  and  $E_{\text{fwhm}}$ , respectively, for a surface-confined species.<sup>1a,12</sup> Thicker films and faster scan rates ( $>50 \text{ mV/s}$ ) result in both increased peak splittings and peak widths, but the nearly symmetrical wave shape observed for the  $\text{Fc}/\text{Fc}^+$  couple is maintained even at 200 mV/s. Thus the voltammetry for the  $\text{Fc}/\text{Fc}^+$  portion of these polymer films is comparable to that for poly(vinylferrocene). No obvious redox processes for the "polyaniline" backbone are detected for either polymer film.<sup>10</sup> Poly-**1b** shows a broad, weak feature at 0.5–0.6 V, which has been observed in thick films of other ferrocene derivatives.<sup>2,3</sup> In 1 M  $\text{H}_2\text{SO}_4$ , poly-**1a** shows only modified voltammetry for the ferrocene portion,<sup>1a</sup> while poly-**1b** is unstable under these conditions and appears to "dissolve" off the electrode surface. Studies are ongoing to determine if voltammetry for the polyaniline backbone can be observed under other conditions.

A linear relationship holds for apparent surface coverage,  $\Gamma_{\text{app}}$ ,<sup>13</sup> as a function of the number of polymerization scans employed to grow the film (insert in Figure 2).  $\Gamma_{\text{app}}$  also is independent of scan rate between 2 and 50 mV/s for thin films, demonstrating a reasonably high charge-transport rate through the polymer. However, at high scan rates the measured  $\Gamma_{\text{app}}$  is less than predicted from slow scan rate data.

The ease of preparation, rapid polymerization rates, and electrochemical stability [less than 5% degradation in the measured oxidative and reductive currents (50 repetitive potential cycles (0–0.75 V vs SSCE at 50 mV/s))] make these polyaniline-based ferrocene polymers potentially useful for practical applications. We are exploring the generality of the reaction shown in eq 1 to prepare new complexes for use in polymer-modified electrodes.

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**Registry No.** **1a** (homopolymer), 127356-79-0; **1b** (homopolymer), 127356-80-3.

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(13)  $\Gamma_{\text{app}}$  determined from the equation  $\Gamma_{\text{app}} = Q/(nFA)$ , where  $Q$  is the charge (area) under the oxidative wave,  $n$  is the number of electrons per metal site ( $n = 1$ ),  $F$  is Faraday's constant, and  $A$  is electrode area ( $A = 0.15 \text{ cm}^2$ ).

## Convergent Synthesis of Monodisperse Dendrimers Based upon 1,3,5-Trisubstituted Benzenes

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A growing area of materials chemistry deals with the synthesis and properties of organic structures with specific molecular architectures, including molecular rods,<sup>1</sup>

(8) Anal. for **1a** calcd (found),  $\text{C}_{17}\text{H}_{17}\text{FeN}$ : C, 70.1 (69.96); H, 5.84 (5.84); N, 4.81 (4.44).  $^1\text{H}$  NMR (**1a**,  $\text{CDCl}_3$ )  $\delta$  7.2–7.1 (m, 2 H), 6.7–6.6 (m, 3 H), 4.24 (tr,  $J = 1.8 \text{ Hz}$ , 2 H), 4.17 (s, 5 H), 4.1 (tr,  $J = 1.8 \text{ Hz}$ , 2 H), 3.99 (s, 7 H), 2.19 (br, 1 H). Anal. for **1b** calcd (found),  $\text{C}_{17}\text{H}_{18}\text{FeN}_2$ : C, 66.7 (66.20); H, 5.88 (5.86); N, 9.15 (8.76).  $^1\text{H}$  NMR (**1b**,  $\text{CDCl}_3$ )  $\delta$  7.0 (tr,  $J = 7.9 \text{ Hz}$ , 1 H), 6.0–6.15 (m, 3 H), 4.25 (tr,  $J = 1.9 \text{ Hz}$ , 2 H), 4.2 (s, 5 H), 4.16 (tr,  $J = 1.9 \text{ Hz}$ , 2 H), 3.94 (s, 2 H); 3.65 (br, 3 H).

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(11) Electrolysis of either poly-**1a** or poly-**1b** at 0.75 V vs SSCE in 0.1 M TBAP containing  $\sim 0.05 \text{ M}$  2,2'-bipyridine (bpy) results in the formation of  $[\text{Fe}(\text{bpy})_3]^{3+}$  as identified by its UV-vis spectrum and a red solution. These experiments confirm the presence of iron in both polymers.