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Pyrrole-Terminated Diaminobutane (DAB) Dendrimer Monolayers on Gold: Oligomerization of Peripheral Groups and Adhesion Promotion of Poly(pyrrole) Films[†]

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In this study, the formation of oligomerized monolayers on Au of poly(propylene imine) dendrimers[1] with a diaminobutane core and pyrrole termini (DAB-Py$_X$, X = 4, 8, 16)[2] is demonstrated. In the case of DAB-Py$_{16}$, adsorption on Au (DAB-Py$_X$/Au) leads to a dendrimer structure wherein the pyrrole termini are sufficiently close to each other[3] that electrooxidation of the pyrroles yields a dendrimer monolayer containing intramolecularly (intradendrimer) coupled oligo(pyrroles). In addition, poly(1-methylpyrrole) and poly(1-*H*-pyrrole) films electrodeposited onto DAB-Py$_X$/Au are more adherent to the Au substrate and are topographically smoother than poly(pyrrole)s deposited onto bare Au or Au surfaces coated with *tert*-butoxycarbonyl-protected poly(proplene imine) dendrimers (DAB-BOC$_X$).[4a]

Our interests are directed at the construction of dendrimers,[1,5−8] which have at their periphery conducting, conjugated pyrrole oligomers that can have their molecular structure changed in a controlled and reversible fashion by a stimulus, such as a change in oligomer oxidation state (redox switching).[9] The stimulated structural change would result in large changes in the geometry of the oligomer[10,11] and thus the steric barrier presented to molecules at the periphery of the dendrimer, which would in turn lead to a dendrimer whose permeability[8] can be manipulated. To form such oligomers at the periphery of the dendrimers, the low-generation, pyrrole-terminated dendrimers are adsorbed on Au, thereby placing the terminal monomer groups in close proximity to each other,[3a,6a,d] such that the coupling of the monomers is highly favored.[12] We are aware of only two investigations targeting similar research with solution-phase dendrimers,[7] and in only one case involving a phenyl ether dendrimer terminated with olefinic groups was the degree of connectivity shown to be substantial.[7b] Finally, the pyrrole-terminated dendrimers may also be used to fabricate conducting polymer-coated surfaces.[13,14]

Electrochemical[15] oxidation of the DAB-Py$_X$[2] layers on Au[16] was carried out using Au-coated microscope slides.[17] The potential of the DAB-Py$_X$/Au samples was cycled from 0.0 to +1.5 V or 0.0 to +1.6 V vs Ag/Ag$^+$ and then back to 0.0 V before further evaluation. All of the DAB-Py$_X$/Au (X = 4, 8, 16) exhibited a broad, chemically irreversible oxidation peak, $E_{p,ox} = +1.1$ V,[4c] on the first anodic scan, indicative of pyrrole radical cation formation and subsequent follow-up reactions.[11,12a] After the first potential excursion, only in the case of DAB-Py$_{16}$/Au (*ox*-DAB-Py$_{16}$/Au) was there observed any voltammetric peaks in subsequent scans; a set of voltammetric peaks centered at +0.94 V was noted.[4c] The potential of the voltammetric peaks for *ox*-DAB-Py$_{16}$/Au (+0.94 V) is near that of oligo(1-methylpyrroles) containing three to six pyrrole repeats;[18] thus, we attribute the voltammetric waves at +0.94 V to the oxidation and reduction of oligomeric pyrroles on the Au surface.

To provide further proof that the *ox*-DAB-Py$_{16}$/Au surfaces are composed of intramolecularly oligomerized pyrrole dendrimers, a spectroscopic end-group analysis method[19] was implemented.[12a] The pyrrole oligomer length can be estimated by comparing the intensity of the monomer "tail" C−H out-of-plane deformation band (*T*-mode) at roughly 720 cm^{-1} to that of the oligomer "backbone" C−H out-of-plane deformation band (*B*-mode) which appears at 800 cm^{-1} for dimers and at lower energies with increasing oligomer repeat length (765 to 750 cm^{-1}).[19] Separate DAB-Py$_{16}$/Au samples were each electrochemically oxidized by scanning the potential from 0 V to either +1.5 or +1.6 V vs Ag/Ag$^+$ and then back to 0 V. The spectra of these *ox*-DAB-Py$_{16}$/Au samples (Figure 1) exhibit bands in the 765 to 750 cm^{-1} range, indicating the presence of intradendrimer-coupled[20] oligo(pyrroles) containing an average of roughly seven monomer repeats.[19] However, observation of the band at 800 cm^{-1} points to the fact that there are also some dimeric pyrroles present on the surface, although their number is smaller for the sample that

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[†] This paper is ninth in a series of contributions from LSU entitled Monomers on Electrode Surfaces.

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(16) The DAB-Py$_X$/Au surfaces were prepared by exposing Au substrates to 0.5 mM dendrimer solutions (anhydrous CH_2Cl_2) for 5 h.

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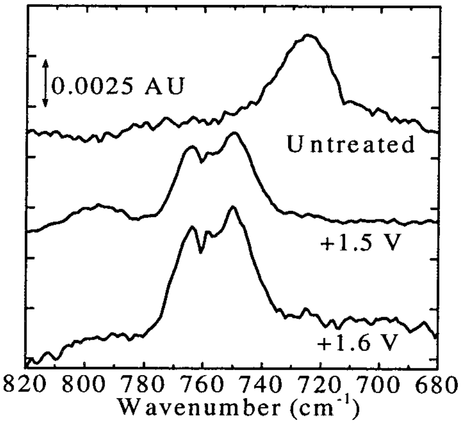
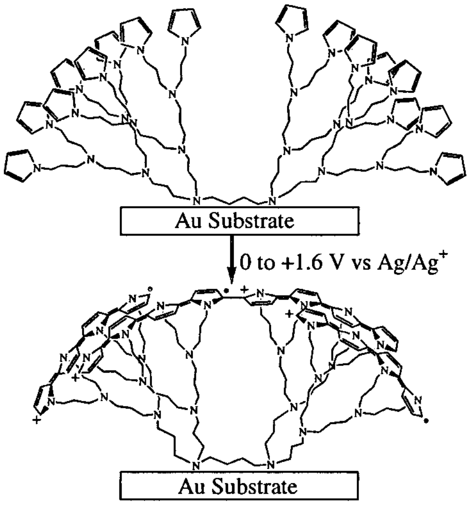


Figure 1. Ex situ RAIR spectra obtained before and after one complete voltammetric cycle between 0 and +1.5 V or 0 and +1.6 V vs Ag/Ag$^+$ at 0.1 V s^{-1} in 0.1 M Bu_4NBF_4/CH_2Cl_2.

Scheme 1. Cartoon Depicting Possible Structures of Pristine vs Electrochemically Oligomerized, Cationic DAB-Py$_{16}$/Au



was scanned to +1.6 V, as judged by the band intensities.[12a] A cartoon depicting one of the many possible structures of the surface-confined oligomers is shown in Scheme 1. We are currently studying the DAB-Py$_X$ and larger generation pyrrole-dendrimers for encapsulation and release of guests from surfaces and in solution, respectively.

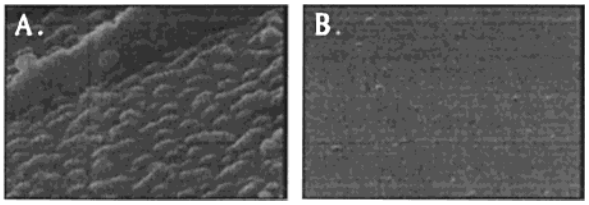


Figure 2. SEM images of poly(1-methylpyrrole) electrochemically deposited onto DAB-Py$_{16}$/Au and DAB-BOC$_{16}$/Au formed by immersing Au substrates in 0.5 mM dendrimer/CH_2Cl_2 solutions for 5 h: (A) DAB-Py$_{16}$ (200 μm × 300 μm scan area) and (B) DAB-Py$_{16}$ (15 μm × 22 μm scan area).

Thin films of poly(1-methylpyrrole) and poly(1-*H*-pyrrole) were electrochemically deposited[4d] onto DAB-Py$_{16}$/Au surfaces to probe their effect on the properties of the polymer films. DAB-Py$_{16}$/Au, DAB-BOC$_{16}$/Au,[4a] and bare Au substrates were used. Polymer films deposited on bare Au were completely removed upon rinsing with CH_2Cl_2, preventing further evaluation. The films formed on DAB-Py$_{16}$/Au were extremely scratch resistant, but they were partially removed (<25%) upon repeated (10 times) application/removal of Scotch tape.[14] However, in all cases, the polymer films deposited on DAB-BOC$_{16}$/Au were not at all scratch resistant and were *completely* removed by the tape. Scanning electron microscopy (SEM) images, Figure 2, indicate that the morphology of the poly(1-methylpyrrole) films on the DAB-Py$_{16}$/Au substrates is greatly improved when compared to that of films on DAB-BOC$_{16}$/Au. Polymer films formed from 1-*H*-pyrrole displayed similar effects. These results indicate that the DAB-Py$_{16}$/Au surfaces act as effective promoters of polymer nucleation and growth, similar to the results observed for ω-(*N*-pyrrolyl)-alkanethiol monolayers on Au.[14a] However, the synthesis of the dendrimer-based, adhesion-promotion layers[2] is considerably easier. In addition, it will be possible to readily improve the adhesion of poly(pyrrole) films to other substrates such as silica,[6d,e] military textiles,[13] and high-temperature superconductors[21] or other ceramics.

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Supporting Information Available: MALDI mass spectra of DAB-BOC$_{16}$ and electrochemical data of DAB-Py$_X$/Au (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] (a) Previous AFM studies[20b] indicate that ferrocene-terminated DAB dendrimers adsorbed on Pt do not interdigitate. More importantly, the lack of an intense infrared band at 770 cm^{-1} in the RAIR spectra of *ox*-DAB-BOC$_{16}$/Au surfaces indicates negligible *inter*dendrimer connections (2,3- or 2,4-substituted pyrroles); however, minor *inter*dendrimer coupling through the 2,5-positions cannot be ruled out.[12a] (b) Takada, K.; Díaz, D. J.; Abruña, H. D.; Cuadrado, I.; Casado, C.; Alonso, B.; Morán, M.; Losada, J. *J. Am. Chem. Soc.* **1997**, *119*, 10763–10773.

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