Controlled Synthesis of Optically Active Polyaniline Nanorods and Nanostructured Gold Microspheres Using Tetrachloroaurate as an Efficient Oxidant of Aniline

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Received January 19, 2008; In Final Form March 10, 2008;
Revised Manuscript Received March 10, 2008

ABSTRACT: Optically active polyaniline nanorods and hierarchically structured gold microspheres are synthesized using tetrachloroaurate as an efficient oxidant of aniline in the presence of a chiral inducing agent camphorsulfonic acid. The chiral organization of the resultant polyaniline nanorods is strongly affected by the ratio of aniline to $AuCl_4^-$, with the highest optical activity being observed for the ratio around 5:2. The particle size and size distributions of the gold microspheres are influenced by the concentration of the oxidant tetrachloroaurate.

Introduction

The synthesis and properties of individual components for applications in nanoscale optoelectronics have attracted intense interest in recent years.[1] Much attention is focused on nanoscale structures, which mimic aspects of traditional microscale circuitry, such as conducting nanowires[2] and/or metal nanoparticles.[3]

Optically active (chiral) conducting polymers are promising building blocks for such structures due to their potential applications in chiroptical electroluminescence devices and surface-modified electrodes.[2] Among conducting polymers, chiral polyaniline is desirable because it is inexpensive and environmentally stable.[4] Furthermore, it can be readily doped and dedoped using simple acid–base stimuli.[5] Chiral polyaniline is usually synthesized by the enantioselective oxidative polymerization of aniline in the presence of an optically active acid, which acts as a chiral inducing agent by interacting with the amines on the growing polyaniline chain.[4] By controlling the synthetic conditions, a few chiral polyaniline nanostructures have been synthesized with a range of controlled morphologies: spherical,[6] tubular,[7] or fibrillar.[8] Although many oxidizing agents,[9] including chloroauric acid,[10] have been used to polymerize aniline, the influence of oxidizing agents on the optical activity of the resultant chiral polyaniline has not been explored.

The oxidative polymerization of aniline with $AuCl_4^-$ leads to the simultaneous formation of Au nanoparticles.[10] Au nanoparticles are also intriguing components for application in optoelectronic devices.[3] It has been widely demonstrated that gold nanoparticles can be synthesized in a reproducible and controllable way with well-defined nanoscale dimensions.[11] The optical properties, such as surface plasmon resonance, are well-known to depend on the dimensions of the nanoparticles, and it is therefore possible to synthetically tune the physical behavior of these nanoscale building blocks.[12] Recently, hierarchical gold particles with microscale dimensions self-assembled from nanoparticles have started to attract attention, as such gold microparticles might find important applications in catalysis, sensing, surface-enhanced Raman spectroscopy (SERS), and photonics.[13,14] For example, porous gold microspheres have been synthesized using preformed gold nanoparticles as building blocks and porous organic beads as templates[13] and quasi-monodisperse raspberry-like gold microspheres have been prepared in a straightforward way from a commercial gold plating solution.[14]

Herein, we report a new method for the controlled synthesis of chiral polyaniline nanorods using tetrachloroaurate ($AuCl_4^-$) to oxidize aniline in the presence of a chiral inducing agent (1*S*)-(+)-10-camphorsulfonic acid ((*S*)-(+)-CSA) or its enantiomer (*R*)-(−)-CSA. The optical activity of the chiral polyaniline varies as a function of the molar ratio of aniline to $AuCl_4^-$, with the highest optical activity observed at the ratio of 5:2. Intriguingly, Au(0) reduced from the oxidant $AuCl_4^-$ by the aniline monomer further self-assembles into monodispersed hierarchical microspheres in the presence of the chiral polyaniline nanofibers.

Results and Discussion

The asymmetric synthesis of chiral polyanilines in their doped states has been achieved by oxidizing aniline in the presence of either (*S*)-(+)-CSA or (*R*)-(−)-CSA. Initially, we employed an aniline:$KAuCl_4$ molar ratio of 5:2. Figure 1a presents the absorption spectra of aqueous suspensions of the products, which are typical of the emeraldine salt of polyaniline with absorption bands around 345 and 435 nm and a polaron band in the near IR.[15] The CD spectra in Figure 1b confirm the strong optical activity of the polyaniline synthesized in the presence of either (*S*)-(+)-CSA or (*R*)-(−)-CSA. As expected, the CD spectra of polyaniline prepared in the presence of the opposite CSA enantiomers display an inverse relationship, indicating the efficient transfer of chiral information from CSA to the polyaniline nanostructure. All bands observed in these spectra, except for that at 300 nm, result from the induced optical activity of the polyaniline chains. The peak at ca. 300 nm can probably be ascribed to the weak Cotton effect[16] associated with the interaction between polyaniline and CSA itself.

The chiral polyanilines can be dedoped using 1 M NaOH aqueous solution. This reaction could be visually monitored by the color change of the aqueous suspension of the polyaniline from green to indigo and was further confirmed by the absorption spectra shown in Figure 1a, where the dedoped state exhibits the disappearance of the band at 435 nm and a blue shift of the band in the near IR. The dedoping process can also be monitored by CD spectroscopy. In particular, the CD band at ca. 382 nm blue shifts with a decrease in intensity.

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10.1021/ma800134w CCC: $40.75
Published on Web 04/29/2008

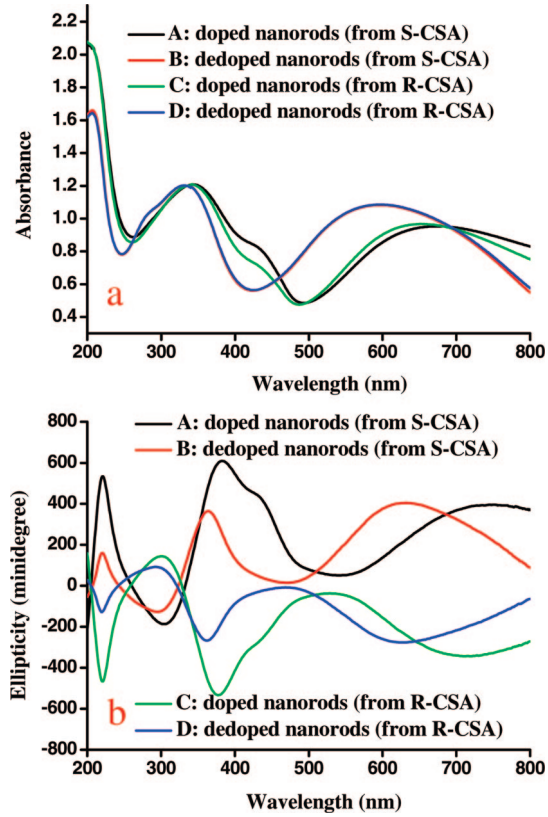

Figure 1. UV (a) and CD (b) spectra of water-dispersed chiral polyaniline nanorods synthesized in the presence of either (*S*)-(+)-CSA or (*R*)-(−)-CSA by using potassium tetrachloroaurate as an oxidant. (The molar ratio of aniline to $AuCl_4^-$ was 2.5).

The structures and morphologies of the products were characterized by electron microscopy. The scanning and transmission electron microscopy (SEM and TEM) images (Figure 2a,b) reveal that chiral polyaniline forms rods ca. 50 nm in diameters and over 1 μm long. These nanorods twist and tangle to form a random porous mat similar to the structure reported elsewhere.[8] Interestingly, no nanosized gold, which might be expected from the reduction of the oxidant $AuCl_4^-$[10], was observed in the rods. This can be most clearly seen in the TEM image of an individual nanorod (inset in Figure 2b), where the presence of gold nanoparticles would have been visible as dark regions. There was also no evidence for the presence of Au nanoparticles in the UV–vis spectra (Figure 1a), where a surface plasmon resonance peak centered at ca. 520 nm may be expected in the dedoped polyaniline.[17] Furthermore, energy dispersive X-ray spectroscopy (EDX) confirmed the absence of signals for gold in the sample of chiral polyaniline nanofibers.

Interestingly, we found that the polyaniline rods in this reaction do not protect gold nanoparticles from aggregation. Indeed, the reduced gold objects were observed to be sufficiently large to sediment from solution. This made it possible to separate the reaction mixture into polyaniline and gold by a repeated dispersion−precipitation process. SEM images (Figure 2c) revealed that the reduced gold is uniformly spherical, with dimensions of several microns in diameter. Closer observation indicates that these gold microspheres are self-assembled from apparently gold nano-objects as shown in Figure 2d. These gold microspheres are intriguing hierarchical structures and may have interesting properties.

The formation of highly monodisperse Au microspheres during polyaniline synthesis is unusual. The narrow size distribution can be explained by one of the two possible mechanisms: (i) a templating effect of the polyaniline fibers, which could stabilize a particular microparticle size or (ii) the confinement of the nucleation of Au particles to the short initial period of the reaction, together with the absence of nucleation during microsphere growth, ensuring monodispersity. In order to distinguish between these mechanisms, we recorded SEM images of Au microspheres prepared using different amounts of Au(III) in the reaction and then measured the particle sizes and their distributions as shown in Figure 3a. An increased concentration of Au(III) initially led to increased particle size. We believe this is consistent with the nucleation-growth mechanism (e.g., mechanism (ii) above). Particle size is determined by the growth of initially formed nuclei, and hence, increased Au(III) concentration leads to bigger particle size. However, it should be noted that the particle sizes became smaller again at the highest Au(III) concentration; we argue that under these conditions there is insufficient aniline to completely reduce the excess Au(III).

To better understand the role of the oxidant $KAuCl_4$ in determining the optical activity of the chiral polyaniline nanorods, we first replaced it with equivalent amounts of other oxidants as shown in Figure 4a and monitored the products by CD spectroscopy. The rate of polymerization increased when ammonium cerium nitrate or ammonium persulfate was used as the oxidant. However, a slower reaction rate was observed when iron(III) chloride or hydrogen peroxide was used. The polyaniline synthesized using ammonium cerium nitrate, ammonium persulfate, or iron(III) chloride as oxidant showed a dramatically reduced optical activity in comparison with the product made using $KAuCl_4$ as the oxidant, as shown in Figure 4a. When hydrogen peroxide was used as the oxidant, the reaction rate was so low that no products were collected after the same reaction time. We therefore believe that using $AuCl_4^-$ as the oxidant plays a crucial role in determining the high optical activity of the resulting chiral polyaniline nanorods.

We then monitored the effect of the molar ratio of aniline to $AuCl_4^-$ on the polyaniline nanorods, with the products again being monitored by CD spectroscopy. Figure 4b reveals that the optimum molar ratio for obtaining chiral polyaniline nanorods with the highest optical activity is 5:2. The use of a slightly higher or lower amount of oxidant $AuCl_4^-$ leads to a decreased ellipticity value of the chiral polyaniline nanorods, as illustrated by the cases of the molar ratios 5:1 and 5:3, respectively, in Figure 4b. On further changing the ratio closer to 1 (e.g., 5:4 or 5:5 in Figure 4b), the resulting polyaniline shows almost no optical activity. Clearly, the molar ratio of aniline to $AuCl_4^-$ plays a significant role in controlling the optical activity of the resulting chiral polyaniline nanorods.

Although the underlying mechanism concerning the influence of the oxidant $AuCl_4^-$ on the optical activity of the resultant chiral polyaniline is not clearly understood at this time, we hypothesize that the short chain oligo-aniline, initially formed by the reaction between aniline and $AuCl_4^-$, governs the helical growth of the chiral polyaniline macromolecules. It has been reported,[4,8] that during the polymerization of aniline in the presence of the chiral inducing agent CSA, the optical activity of the resultant chiral polyaniline can be greatly enhanced by adding a small amount of oligo-aniline into the reaction mixture. Due to the lower oxidation potential of the oligoaniline, aniline preferentially polymerizes at the end of the preformed oligomer.[4,8] This favors the helical growth of the chiral polyaniline macromolecules and, thus, enhances the optical activity of the resulting polymer.[8] When Au(III) is used as an oxidant, the oligoaniline species (probably formed during the nucleation of Au microparticles) may be stabilized by the adsorption on the surface of Au particles.[18] Au is known to have an affinity for aniline;[10] this is further confirmed by the attachment of polyaniline rods to Au microspheres, as observed in SEM

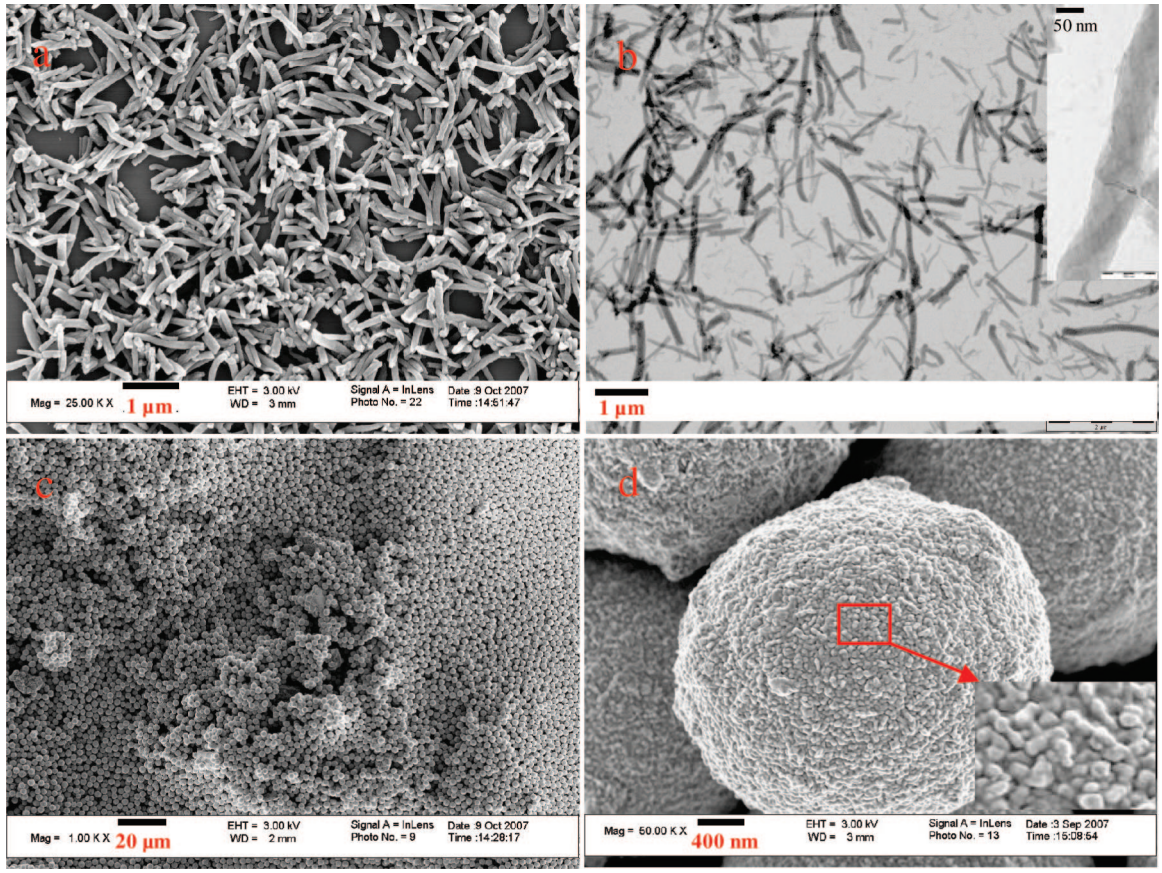

Figure 2. SEM (a) and TEM (b) images of the chiral polyaniline nanorods synthesized using tetrachloroaurate as an oxidant. SEM images of gold microspheres, formed during polymerization, at low (c) and high (d) magnification.

images (Figure 3b). However, this attachment is rather weak, and polyaniline can be completely removed from the particle surface with thorough washing.

Obviously, there is an optimal molar ratio of aniline to $AuCl_4^-$ to produce, in situ, an appropriate amount of the oligoaniline for the helical growth of chiral polyaniline. If the ratio is too high (e.g., 5:1 in Figure 4b), a smaller amount of oligoaniline will be produced, which leads to poor optical activity. If the ratio is too low (e.g., 5:5 in Figure 4b), too much oligoaniline will be produced, which again leads to a reduction of chirality. The critical role of oligomers in determining the nanofiber chirality was further verified by adding the dimer, *N*-phenyl-1,4-phenylenediamine, as an oligomer model into the reaction mixture. The supposedly optimal molar ratio of aniline to $AuCl_4^-$ was employed, but a significant reduction in the optical activity of polyaniline nanorods was observed when 6% of the aniline monomer was replaced by *N*-phenyl-1,4-phenylenediamine (Figure 4c). Indeed, the nanorods showed no optical activity at all if the monomer was completely replaced with *N*-phenyl-1,4-phenylenediamine during the synthesis. The observed decrease in ellipticity value can be ascribed to the excess amount of oligoaniline disfavoring the helical growth of the chiral polyaniline macromolecules.

It is worth noting here that the poor optical activity observed with persulfate or other oxidizing reagents is probably due to the generation of a suboptimal steady-state concentration of chiral oligoaniline during polymerization.

On the basis of all observations, the following mechanism for the oxidation of aniline by Au(III) can be proposed. Reaction of the aniline−CSA salt with Au(III) leads to the formation of chiral oligoaniline adsorbed on the surface of small Au particles. This step provides seeds for the growth of Au particles and polyaniline rods and is critical for achieving high optical activity of the product. Further reduction of Au(III) takes place at the surface of small Au particles and leads to the growth of both Au particles and polyaniline rods. No further nucleation occurs at these later stages of the reaction, which explains the narrow size distribution of the Au microspheres formed at the end of the reaction.

Conclusion

In summary, we have developed a one-pot synthesis of chiral polyaniline nanorods and nanostructured gold microsperes by polymerizing aniline with the tetrachloroaurate in the presence of a chiral inducing agent. The chiral organization of the resultant polyaniline nanorods was strongly affected by the ratio of aniline to $AuCl_4^-$, with the highest optical activity being observed for the ratio around 5:2. The chiral polyaniline nanorods have intriguing chiroptical properties and have potential for a diverse range of applications. The Au(0) produced in the reaction formed nearly monodisperse microspheres, which could be easily separated from the polyaniline nanorods. Once again, these hierarchically structured gold microspheres have potentially wide-ranging applications.

Experimental Section

Materials. All chemicals were purchased from Sigma-Aldrich Co. Aniline was purified by distillation before use. Other reagents were used as received without further purification.

Synthesis. One-pot synthesis of chiral polyaniline nanorods and gold microspheres: In a typical procedure, aniline (0.1 mL, 1.1 mmol) and (*S*)-(+)-CSA or (*R*)-(−)-CSA (1.75 g, 7.53 mmol) were dissolved in deionized water (0.75 mL). An aqueous solution of potassium tetrachloroaurate (0.2 mL, 2.2 mol L^{-1}) was added to the above mixture with stirring and allowed to

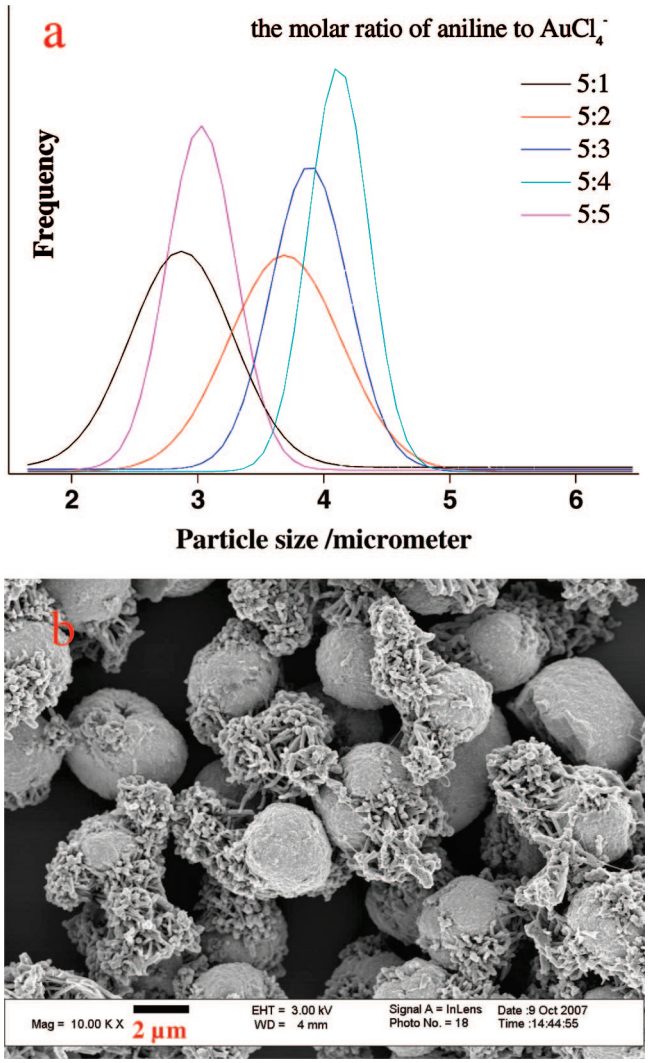

Figure 3. (a) Particle sizes and size distributions of gold microspheres prepared using different concentrations of gold salt (aniline concentration was kept constant in all experiments), and (b) SEM image of the gold microspheres with attached polyaniline nanorods.

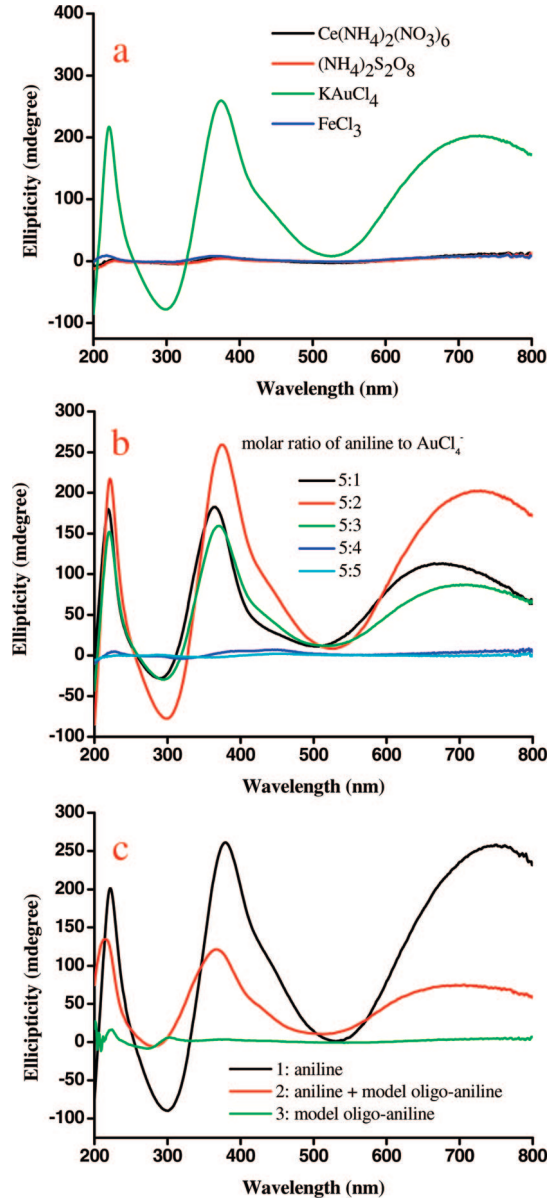

Figure 4. CD spectra of polyaniline prepared using different oxidants (a), different molar ratios of aniline to $AuCl_4^-$ (b), and in the presence of *N*-phenyl-1,4-phenylenediamine, a model oligo-aniline (c).

react overnight at room temperature. The resultant material was isolated by filtration and washed sequentially with deionized water and methanol several times. Finally, the product was separated into the pure polyaniline nanorods and gold microspheres by taking advantage of a repetitive dispersion−precipitation process, with the gold microspheres sedimenting first from the aqueous mixture.

Instrumentation. Polyaniline nanorods and Au microspheres were characterized using LEO field-emission-gun scanning electron microscope at 3 kV and FEI Tecnai G2 transmission electron microscope at 120 kV. Samples for electron microscopy were prepared by placing a droplet of the freshly made product suspension onto a silicon wafer for the field-emission-gun SEM and onto a carbon-coated copper grid for TEM, respectively. All samples were dried under ambient conditions.

Absorption spectra were obtained on a Jasco V-560 UV/vis spectrophotometer. CD spectra were acquired on a Jasco J810 spectrophotometer, calibrated with a reference standard (ammonium *d*-10-camphor sulfonate, Jasco standard) prior to the actual experiments. All the spectra were recorded in the 800–200 nm range using a 10 mm rectangular cell path length. The following parameters were used: 2 nm bandwidth, 20 nm min^{-1} scan rate, 4 s time constant, and 1 nm step size. All spectra were solvent baseline subtracted and acquired at room temperature.

Acknowledgment. This work was supported by the Engineering and Physical Science Research Council, UK (EPSRC EP/D051126/1).

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MA800134W