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Conducting Polyaniline/Calixarene Salts: Synthesis and Properties

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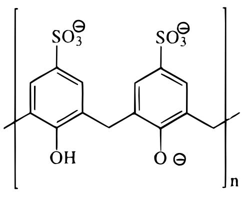
ABSTRACT: Emeraldine base has been doped with the sulfonated calixarene host species, calix[4]-*p*-tetrasulfonic and calix[6]-*p*-hexasulfonic acid in water or DMSO solvents, yielding novel colloidal conducting emeraldine salts PAn.calix[4]SO_3H and PAn.calix[6]SO_3H. The colloidal polyaniline products were characterized by UV−vis and FTIR spectra, cyclic voltammetry, particle size analysis, and transmission electron microscopy. The polyelectrolyte dopants conferred enhanced stability on the emeraldine salts toward alkaline dedoping, with only partial conversion to emeraldine base occurring even at pH 14. The emeraldine salts could, however, be readily oxidized by persulfate ion at pH 2 to the pernigraniline salt forms, while oxidation at pH 12 generated pernigraniline base. Reduction at pH 12 using hydrazine hydrate yielded the fully reduced leucoemeraldine base.

1. Introduction

Polyaniline (PAn) in its emeraldine oxidation state has attracted considerable interest due to its environmental stability and electrical conductivity[1−3] and has emerged as a promising material for applications in various areas.[4−6] Unlike other conducting polymers, PAn can also be reversibly modified by pH changes (with the conducting emeraldine salt being dedoped by base to the insulating emeraldine base form) as well as oxidized and reduced to pernigraniline and leucoemeraldine forms (Scheme 1).

Although polyaniline salts have been extensively investigated, applications are currently limited due to their poor solubility in common organic solvents and water. *N*-Alkyl or alkyl/methoxy ring substituted polyanilines possess enhanced organic solvent solubility. Water solubility of polyanilines has also recently been achieved via the incorporation of sulfonate groups on the aniline rings or amine nitrogen atoms.[7−10] This has usually been achieved post-polymerization via attack on preformed emeraldine or leucoemeraldine base substrates, although the polymerization of sulfonated monomers such as 2-methoxyaniline-5-sulfonic acid has also been reported.[11] However, these synthetic routes are frequently tedious, and the presence of substituents on the aniline rings or N atoms usually decreases the electrical conductivity. Simple synthetic routes to water-soluble (or water-dispersible) parent polyanilines have recently been described, including chemically[12a,b] and enzymatically[12c] controlled processes leading to conducting PAn/poly(styrenesulfonate) colloids.

Recently, sulfonated calixarenes have been described and shown to function as water-soluble anionic sensing host species.[13] Their incorporation into polypyrrole and polythiophene conducting polymers has been reported.[14−17] We report here, for the first time, the use of sulfonated calixarenes for the synthesis of water-dispersible conducting polyanilines. This facile route involves the acid doping of emeraldine base (EB) with calix[4]-*p*-tetrasulfonic acid (**1**) or calix[6]-*p*-hexasulfonic acid (**2**) in water to give emeraldine salts (Scheme 1, where A^- is the anionic form of the dopant acid). These colloidal polyaniline products, PAn.calix[4]SO_3H (**3**) and PAn.calix[6]SO_3H (**4**), could also be readily generated in DMSO solvent.



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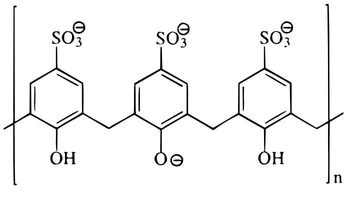

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2. Experimental Section

2.1. Reagents. Emeraldine base (EB) was synthesized via the chemical oxidation of aniline in 1.0 M HCl and subsequent alkaline dedoping, according to a literature procedure.[18] Calix[4]-*p*-tetrasulfonic acid hexahydrate (**1**) and calix[6]-*p*-hexasulfonic acid (**2**) were obtained from Acros. Hydrazine hydrate and ammonium persulfate from Aldrich were used without further purification. Aniline was purchased from Aldrich and distilled under nitrogen gas prior to use. Dimethyl sulfoxide solvent was purchased from Crown Scientific. Aqueous reactions and dialyses employed Milli-Q water (18 MΩ cm). Dialysis tubing (2000 mol wt cutoff) was obtained from Sigma.

2.2. Preparation of Colloidal Emeraldine Salt Polymers 3 and 4 in Dimethyl Sulfoxide. EB (10 mg, 0.03 mmol, on the basis of tetramer repeat unit) in 3.0 mL of DMSO was combined with calix[4]-*p*-tetrasulfonic acid (**1**) (62 mg, 0.074 mmol) (equivalent to a 4-fold molar excess of sulfonate groups compared to that required to fully dope the EB tetramer repeat unit). The mixture was stirred until the reaction had gone to completion (6 h) as evidenced by UV−vis spectroscopy. Filtration through a sintered glass funnel, followed by a 0.22 μm membrane, gave a colloidal solution of the polymer product **3** that was employed for subsequent characterization studies.

A similar procedure was followed to synthesize the related colloidal emeraldine salt PAn.calix[6]SO_3H (**4**), commencing

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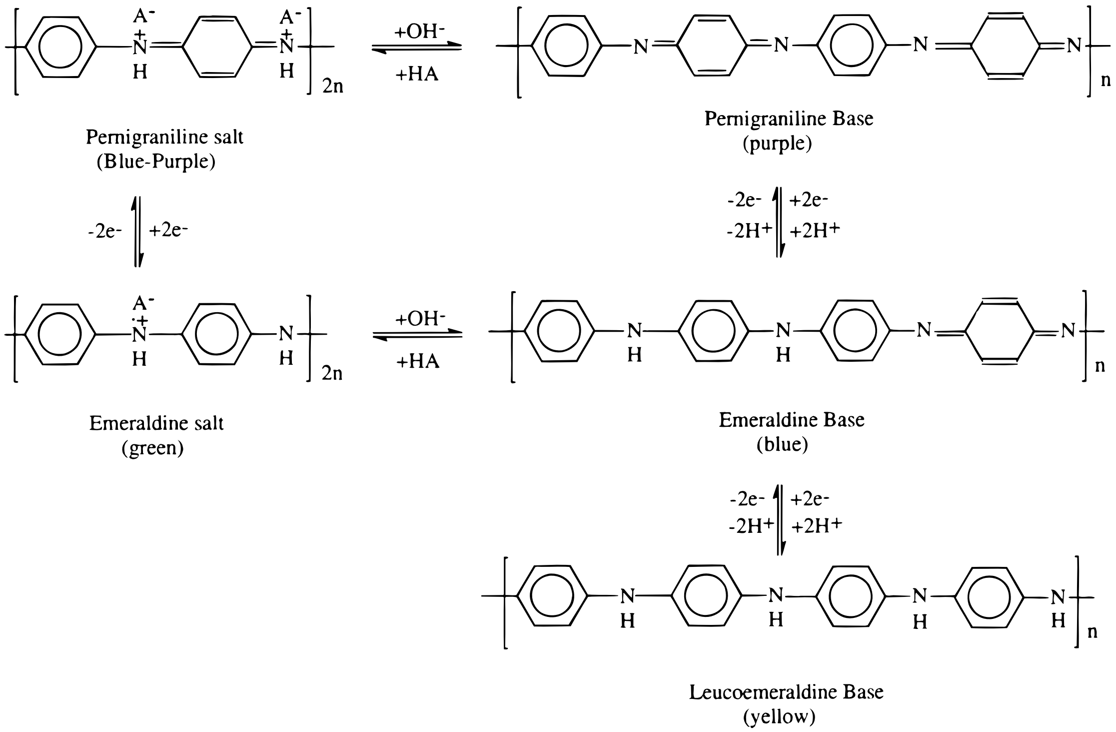
Scheme 1



with calix[6]-*p*-hexasulfonic acid (**1**) (71 mg, 0.063 mmol) and 10 mg (0.03 mmol) of EB.

2.3. Preparation of Colloidal Emeraldine Salt Polymers 3 and 4 in Water. Initial UV–vis spectroscopic studies of the doping of EB with the calixarenesulfonic acid dopants **1** and **2** in water, carried out by stirring EB (10 mg, 0.03 mmol) with varying molar excesses of the dopants, showed that full doping occurred using a ≥2:1 molar excess of **1** or **2**.

The colloidal emeraldine salts **3** and **4** were prepared and isolated via analogous procedures, illustrated below for the PAn.calix[4]SO_3H case: EB (10 mg, 0.03 mmol) in water (7.5 mL) was mixed with calix[4]-*p*-tetrasulfonic acid (**1**) (62 mg, 0.073 mmol), and the reaction mixture was stirred for 48 h at room temperature. Samples were withdrawn at periodic intervals for the first 8 h to monitor the progress of the reaction via UV–vis spectroscopy. The mixture was then filtered through a sintered glass funnel and the filtrate dialyzed with water for 24 h using 2000 mol wt cutoff dialysis tubing. Following centrifugation at 49K rpm for 90 min, the solid emeraldine salt product **3** was separated and dried for a week in a desiccator (yield 59 mg, 86%).

A similar procedure commencing with 10 mg (0.03 mmol) of EB and 71 mg (0.064 mmol) (a 6-fold molar excess of SO_3H groups for full doping of EB) of calix[6]-*p*-hexasulfonic acid gave 61 mg (85% yield) of emeraldine salt **4**.

2.4. Characterization Techniques and Instrumentation. UV–vis spectra of colloidal aqueous and DMSO dispersions of **3** and **4** were obtained utilizing a Shimadzu UV-1601 spectrophotometer. Infrared spectra of the dried polyanilines **3** and **4** in KBr disks were recorded using a Bomem MB-100 Fourier transform infrared spectrophotometer. pH measurements were made with a Metrohm 360 pH meter.

Samples of **3** and **4** for electrical conductivity studies were dried at room temperature and pressed into pellets and their conductivities measured using the conventional four-point probe method.

Hydrodynamic diameter and zeta potential measurements were made on samples of **3** and **4** redispersed in water, using a Zetasizer 3000 (Malvern Instruments).

TEM micrographs of **3** and **4**, obtained by evaporating their aqueous dispersion onto a Cu support grid, were recorded using a JEOL 2000 (160 kV) transmission electron microscope.

Cyclic voltammetry studies of aqueous dispersions of salts **3** and **4** in 0.10 M $NaNO_3$ were conducted in a three-electrode cell, utilizing a Ag/AgCl (NaCl, 3.0 M) reference electrode, platinum mesh auxiliary electrode, and a glassy carbon (0.07 cm^2 area) working electrode. The potential scan range was -0.2 to $+0.8$ V for both emeraldine salts, with a scan rate of 100 mV s^{-1}. The cyclic voltammetry data were collected using a MacLab/400 A/D and D/A data collection system (AD Instruments).

2.5. Dedoping/Redoping Experiments on Salts 3 and 4. Aqueous dispersions of **3** and **4** (initially at a pH of ca. 2) were dedoped by titrating with 1.0 M NaOH until the pH was raised to 14. UV–vis spectra were recorded immediately after each addition of NaOH. The reaction mixtures were continually stirred utilizing a magnetic stirrer.

The emeraldine base dispersions formed in the above alkaline dedoping reactions were subsequently redoped by titration with 1.0 M HCl to generate the emeraldine salt PAn.HCl. UV–vis spectra were recorded immediately after each addition of acid.

2.6. Redox Reactions on Salts 3 and 4. The aqueous polyaniline colloids **3** and **4** were each oxidized in two different pH regimes: (i) pH 2—dispersions of the emeraldine salts in water exhibited a pH of ca. 2. Solid ammonium persulfate was then added sufficient to give 0.10 M oxidant. (ii) pH 12—aqueous dispersions of polymers **3** and **4** were also raised to pH 12 (with NaOH) prior to initiating oxidation with 0.10 M ammonium persulfate.

The corresponding reductions of the aqueous colloids **3** and **4** were carried out at an initial pH of 12 via the addition of hydrazine hydrate sufficient to give 0.10 M reductant.

The redox reactions were monitored by withdrawing samples at regular intervals from the stirred reaction mixtures for UV–vis spectral analysis.

3. Results and Discussion

3.1. Formation of Polymers 3 and 4 in Dimethyl Sulfoxide.

The acid doping of EB with the calixarenesulfonic acids **1** and **2** was investigated in a range of organic solvents such as *N*-methylpyrrolidinone, dimethylformamide, dimethyl sulfoxide (DMSO), chloroform, acetone, and toluene. However, the only organic

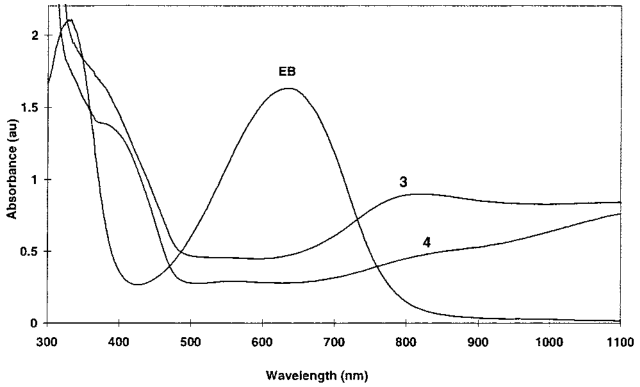
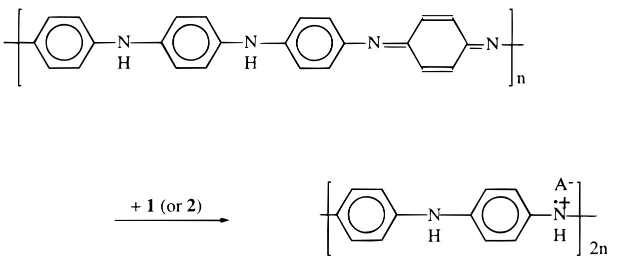


Figure 1. UV−vis spectra of EB solution, PAn.calix[4]SO_3H **(3)** colloids, and PAn.calix[6]SO_3H **(4)** colloids in DMSO solution.

medium that facilitated the conversion of EB to colloidal emeraldine salts was DMSO, due to the low solubility of the calixarenes in the other solvents. The blue color of EB when dissolved in DMSO changed to green within 30 min upon addition of **1** or **2**, indicating the formation of the emeraldine salts PAn.calix[4]SO_3H **3** and PAn.calix[6]SO_3H **4,** as in eq 1.



(**3**, A^- = anion of **1**) (1)
(**4**, A^- = anion of **2**)

Conversion of EB to the colloidal emeraldine salts **3** and **4** was confirmed by the UV−vis spectral changes shown in Figure 1. The exciton band at 630 nm for the initial EB disappeared and was replaced by bands at ≥800 nm characteristic of emeraldine salts.[19] In the case of the PAn.calix[4]SO_3H (**3**) product, a high wavelength polaron band was observed at ca. 800 nm together with significant near-infrared absorption. For the related colloidal PAn.calix[6]SO_3H (**4**) product, the high wavelength polaron band became only a weak shoulder (at ca. 850 nm) superimposed on a strong free carrier tail in the near-infrared.

On the basis of earlier analyses of emeraldine salt spectra,[20,21] these spectroscopic features for polymer **4** indicate extensive delocalization of the high wavelength polaron band and the adoption of an "expanded coil" conformation by the polyaniline chains. A mixture of "compact coil" and "expanded coil" conformations may be similarly assigned to the polyaniline chains in the related polymer **3** involving the smaller calix[4]-*p*-tetrasulfonic acid dopant.

For both the emeraldine salts **3** and **4**, a shoulder was also observed at ca. 400 nm which may be assigned to the expected second polaron band.[19] Observation of the $\pi-\pi^*$ band below 350 nm was obscured by intense absorption by the DMSO solvent.

3.2. Formation of Polymers 3 and 4 in Water.

Initial spectroscopic studies of the doping reaction (eq 1) in water were carried out by stirring solid EB for 48 h with varying molar ratios of the calixarenesulfonic acid dopants **1** and **2** (see Experimental Section). For both dopants, a 2:1 [dopant]/[EB] ratio was found to be sufficient to ensure full doping of the EB to give the colloidal emeraldine salts **3** and **4**. These dopant/EB molar ratios provided a 4:1 and 6:1 molar excess of SO_3H groups from the dopants **1** and **2**, respectively.

Subsequent studies of the doping reaction (eq 1) in water used a dopant/EB molar ratio of ca. 2:1. UV−vis spectra recorded periodically over 48 h showed that the reaction proceeded at very similar rates for dopants **1** and **2**, which was reflected in the similar yields of the isolated colloidal products **3** and **4** (86% and 85%, respectively).

Formation of the colloidal emeraldine salts **3** and **4** was confirmed by the appearance of a broad, high wavelength polaron band at ca. 850 nm in each case, together with bands at ca. 440 and 350 nm (br) assignable as the expected low wavelength polaron band and the $\pi-\pi^*$ transition, respectively. The presence also of significant near-infrared absorption for both emeraldine salts **3** and **4** suggests that the polyaniline chains adopt a mixture of "compact coil" and "expanded coil" conformations.

Interestingly, the very similar final (48 h) spectra for the colloidal emeraldine salt products **3** and **4** in water contrast with the behavior in DMSO solvent, where the dopant **2** led to a more "expanded coil" conformation for the emeraldine salt product than with the related dopant **1**.

3.3. Morphology/Particle Sizes.

A Tyndall effect could be seen when light was passed through aqueous dispersions of **3** and **4** salts. Hydrodynamic diameter analysis showed the size of the colloid particles (of **3)** to be 517 ± 59 nm, while colloid particles (of **4)** were considerably smaller (279 ± 8 nm). These differences in particle size for the two emeraldine salt dispersions may be due to the differing doping modes by the two sulfonate dopants. However, they are both within the range observed (30−600 nm) for other colloidal polyaniline dispersions.[22−29] The particles for both colloidal salts **3** and **4** exhibited negative zeta potentials (−28 ± 1 and −43 ± 5 mV, respectively), consistent with negative groups from the calixarenesulfonate dopants being on the surface of the particles.

Transmission electron microscope (TEM) images for deposited **3** indicated that small discrete particles (ca. 50−100 nm in diameter) were present and held together to produce a larger raspberry morphology of comparable size to the particles identified above in aqueous dispersions (Figure 2a). Similar raspberry morphologies have been previously reported for PAn colloids stabilized with silica.[27,30] TEM images of **4** showed a similar range of particles but were more disperse and displayed a ricelike morphology (Figure 2b). This morphology has also been reported for PAn colloids stabilized with poly(2-vinylpyridine-*co*-*p*-aminostyrene)[22] and poly(1-vinylimidazole).[23]

3.4. Electrical Conductivity.

The solid-state conductivities for pressed dried pellets of **3** and **4** were found to be 3.2×10^{-4} and 2.9×10^{-4} S cm^{-1}, respectively. These conductivities are low compared to those of most PAn.HA salts reported to date[22−25] and are most likely due to the insulating nature of the large calixarene dopants. Similar low conductivity values have been found for emeraldine salts stabilized by poly(vinyl alcohol),[26] colloidal silica,[27] and both poly(styre-

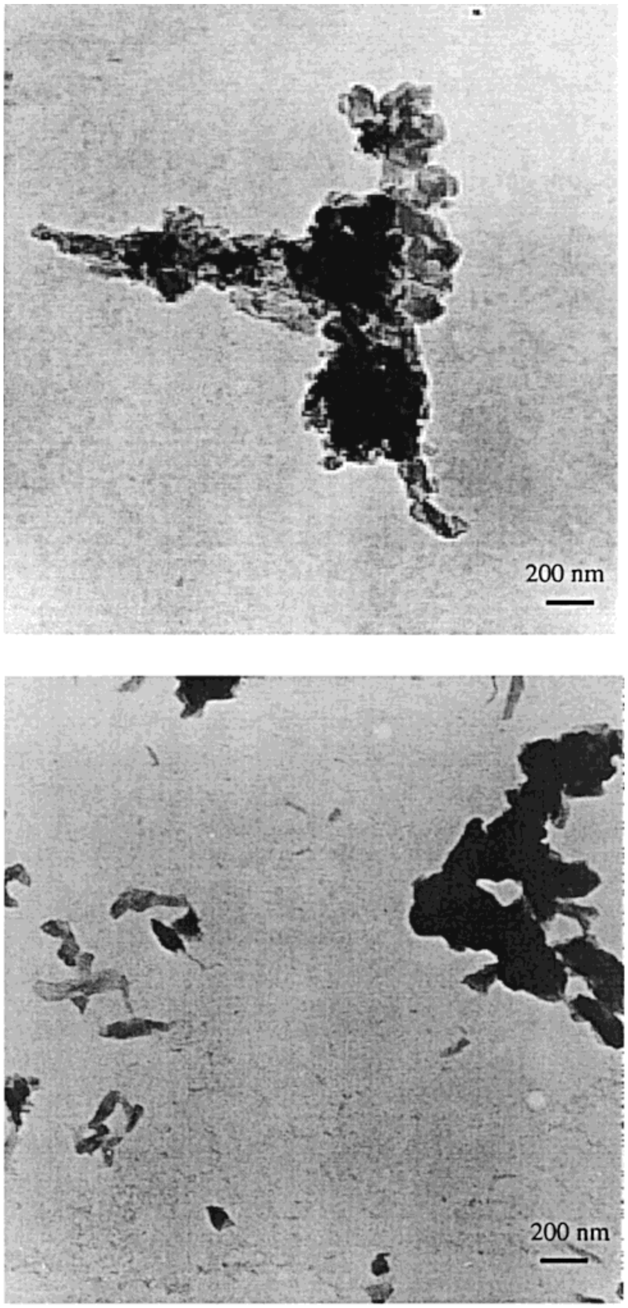


Figure 2. Transmission electron micrographs of (a, top) PAn.calix[4]SO$_3$H (**3**) and (b, bottom) PAn.calix[6]SO$_3$H (**4**).

nesulfonate) and poly(2-(dimethylamino)ethyl methacrylate) polyelectrolytes.[28]

3.5. Infrared Spectra. The two emeraldine salts **3** and **4** exhibited very similar infrared spectra (see Table 1 for assignments)[31a] that confirmed the incorporation of the dopants **1** and **2**. The symmetric −OH stretch of the phenol groups at the base of the calixarene dopants was observed at ca. 3300 cm^{-1}, while the dopant −CH$_2$ asymmetric stretch and deformation bands were seen at ca. 2930 and 1480 cm^{-1}, respectively. A strong asymmetric S=O band was also observed at ca. 1350 and 1115 cm^{-1}, while bands at ca. 1040, 800, and 620 cm^{-1} are attributed to S−O−C stretching. Benzene ring (C=C) deformation peaks were also observed at ca. 1435 cm^{-1}.[31b]

3.6. Cyclic Voltammetry. Aqueous dispersions of the PAn.calix[4]SO$_3$H (**3**) and PAn.calix[6]SO$_3$H (**4**) salts in 0.10 M NaNO$_3$ were electroactive, as seen from their cyclic voltammograms in Figure 3. For both colloidal polymers, two oxidation peaks were observed in the anodic sweep and two corresponding reduction peaks in the reverse cathodic sweep. In keeping with previous studies on PAn.HA films,[1,7,32,33] the anodic peaks $E_{1(ox)}$ and $E_{2(ox)}$ may be assigned to the oxidations of leucoemeraldine to emeraldine salt and of emeraldine salt to pernigraniline, respectively, as depicted in Scheme 2. The cathodic peaks $E_{1(red)}$ and $E_{2(red)}$ arise from the corresponding reductions. The effect of *iR* drop should have been minimized by the presence of the 0.10 M NaNO$_3$ supporting electrolyte.

Table 1. FTIR Band Assignments for Polymers 3 and 4

Pan.calix[4]SO$_3$H (**3**)			Pan.calix[6]SO$_3$H (**4**)		
λ^{-1} (cm^{-1})	rel int[a]	assignt	λ^{-1} (cm^{-1})	rel int[a]	assignt
3286	v	ν_s(OH)	3332	v	ν_s(OH)
2942	w	ν_{as}(CH$_2$)	2925	w	ν_{as}(CH$_2$)
1483	s	δ(CH$_2$)	1477	s	δ(CH$_2$)
1449	s	δ(C=C)	1426	s	δ(C=C)
1348	w	ν_{as}S(=O)$_2$	1350	s	ν_{as}S(=O)$_2$
1117	s	ν_{as}S(=O)$_2$	1111	s	ν_{as}S(=O)$_2$
1042	s	ν_s(S−O−C)	1036	s	ν_s(S−O−C)
802	s	ν_s(S−O−C)	802	s	ν_s(S−O−C)
619	s	ν_s(S−O−C)	613	s	ν_s(S−O−C)

[a] v = very strong, s = strong, w = weak, s = symmetric, as = asymmetric, ν = stretching mode, δ = deformation mode.

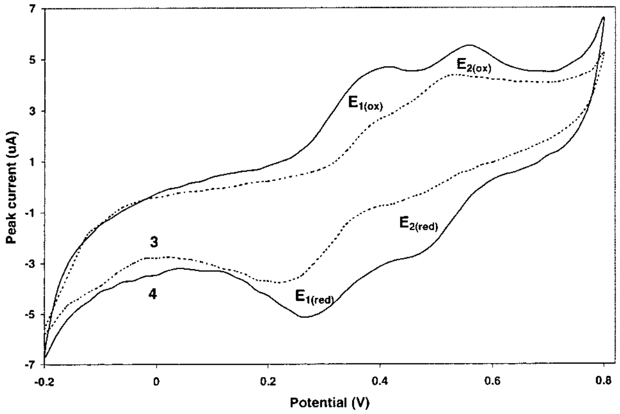


Figure 3. Cyclic voltammograms of aqueous colloidal dispersions of PAn.calix[4]SO$_3$H (**3**) and PAn.calix[6]SO$_3$H **(4)** (both 0.45 g) in 5 mL of 0.10 M NaNO$_3$ using a glassy carbon electrode. Scan rate = 100 mV s^{-1}.

The redox potentials for the two colloidal salts **3** and **4** are similar (Table 2). Interestingly, their $E_{1(ox)}$ values (0.40 V) are significantly more positive than those typically observed for PAn.HA films,[31a,34] while the $E_{2(ox)}$ potentials (0.55 V) are considerably less positive. This results in a narrower potential range of redox stability for the emeraldine state of these colloids compared to those of typical PAn.HA films. That is, the emeraldine salt is both more readily oxidized to pernigraniline and more easily reduced to leucoemeraldine.

In addition, the cyclic voltammograms of dispersions of polymers **3** and **4** showed a larger peak current for polymer **4**, indicating this colloid is more electroactive. The reason for this is not clear at present. It may have been anticipated that calix[4]-*p*-tetrasulfonic acid **(1)**, being a smaller and probably more mobile dopant than **2**, would have facilitated easier oxidation and reduction of polymer **3** compared to **4**.

3.7. Dedoping and Redoping of 3 and 4 Dispersions. Aqueous dispersions of both the PAn.calix[4]-

Scheme 2

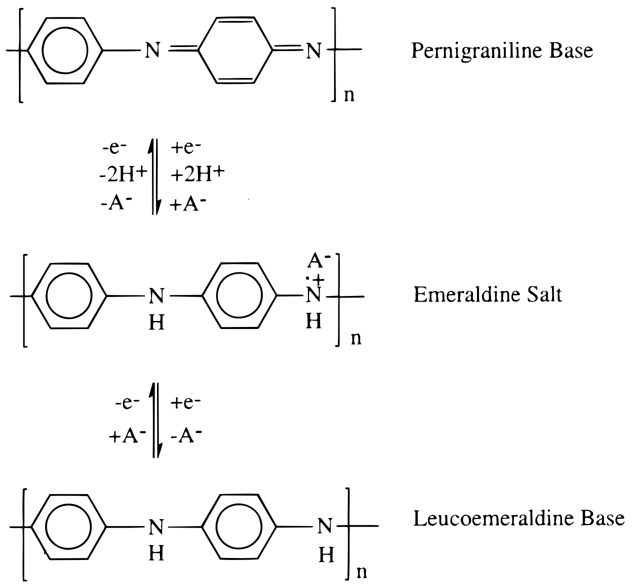


Table 2. Redox Potentials Observed for Aqueous Colloidal Dispersions of the Emeraldine Salts 3 and 4[a,b] **in 0.10 M NaNO$_3$**

salt	redox potentials (V vs Ag/AgCl)			
	$E_{1(ox)}$	$E_{2(ox)}$	$E_{1(red)}$	$E_{2(red)}$
PAn.calix[4]SO$_3$H (**3**)	0.40	0.55	0.20	0.45
PAn.calix[6]SO$_3$H (**4**)	0.40	0.55	0.25	0.45

[a] Cyclic voltammograms recorded at ca. pH 2. [b] The calixarenesulfonic acid dopants **1** and **2** themselves have been shown[48] to be electroinactive over the potential range studied here.

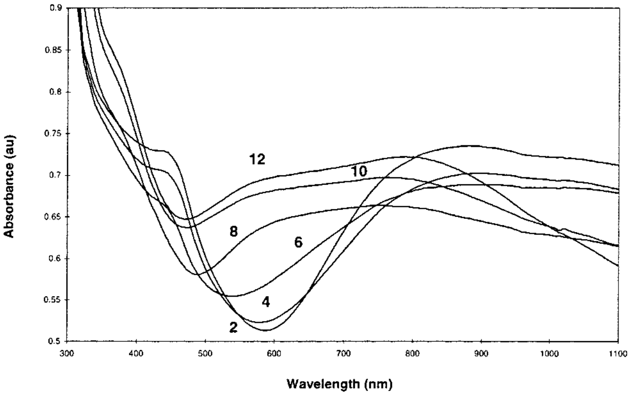


Figure 4. UV−vis spectral changes as colloidal PAn.calix[4]-SO$_3$H (**3**) is progressively dedoped with 1.0 M NaOH. Curves labeled in the range pH 2−12.

SO$_3$H (**3**) and PAn.calix[6]SO$_3$H (**4**) could be partly dedoped with NaOH to give EB and then redoped with HCl to generate the PAn.HCl salt. This was demonstrated by changes in the UV−vis spectra as aqueous dispersions of the emeraldine salt **3** or **4** were titrated with 1.0 M NaOH (e.g., Figure 4). Upon raising the pH from 2 (the natural pH of salts **3** and **4**) to 4 or 6, the broad polaron bands of the initial emeraldine salts at ≥800 nm underwent a distinct red shift (accompanied by a color change from green to turquoise). This behavior is similar to that reported recently by others[35] during the early stages of the alkaline dedoping of other PAn.HA (HA = HCl) salts in KH$_2$PO$_4$ buffered media and may be associated with a conformational change in the polyaniline backbone. The intensity of the low wavelength polaron band for the initial salts **3** and **4** at ca. 450 nm was also observed to decrease significantly as the pH was raised progressively from 2 to 4 to 6.

Upon raising the pH further to 8, significant amounts of the dedoped EB product were produced for both polymers, as evidenced by the appearance of a broad shoulder at ca. 600 nm (e.g., Figure 4). The intensity of this characteristic exciton band for EB increased upon further raising the pH to 10 and then 12 (e.g., Figure 4). The titration mixtures had also adopted a blue/violet color by this stage. However, even at pH 14, dedoping of the initial emeraldine salts was incomplete, as indicated by the retention of a broad band in the 750−800 nm region. The relative intensities of the 600 and 750−800 nm bands suggest that alkaline dedoping of the emeraldine salts is less than 50% complete at pH 12. Separate studies showed a similar result at pH 14. In contrast, typical emeraldine salts PAn.HA (e.g., HA = HCl, HClO$_4$, HPTSA) are generally fully dedoped to EB at pH > 4.[36] The exceptional inertness to alkaline dedoping by the colloidal salts **3** and **4** parallels that previously noted[12a,b,37] for PAn.HA salts where HA is a polyelectrolyte such as poly(styrenesulfonic acid) or poly(acrylic acid). It may be explained as arising from Donnan phenomenon effects arising from a high electrostatic field in the region close (10 nm) to the polyelectrolyte.[38,39]

An interesting feature of the alkaline dedoping spectra (e.g., Figure 4) is the lack of isosbestic points, which have been seen previously for the analogous dedoping of other polyaniline salts.[32,40] This may be due, in the present case, to conformational changes in either the polyaniline chains or the dopants as the pH is raised. It has been shown, for example, that the calixarenesulfonic acids **1** and **2** have a number of conformations that are pH-dependent.[31,41] At low pH the sulfonate and phenol groups are all protonated. However, at neutral and higher pH values **1** and **2** are hexaanionic and octaanionic, respectively. This is due to the removal of two protons from the phenol groups at the base of the cups of each calixarene as well as the complete deprotonation of the sulfonate groups. As a result, at neutral pH both species **1** and **2** change from a cone to a double partial-cone conformation, with several of the sulfonated phenol groups inverting and pointing down. With this occurring, the dedoping process, as evidenced by the UV−vis spectral changes, is not well-defined.

Both partially dedoped polymers could be redoped with HCl to generate the PAn.HCl emeraldine salt, as evidenced, for example, in Figure 5. Lowering the pH of the dedoped PAn.calix[4]SO$_3$H **3** from 12 to 7 caused a marked decrease in the EB absorption band at 600 nm and the appearance of a broad polaron band at $\lambda >$ 850 nm (together with significant near-infrared absorption) attributed to the formation of PAn.HCl. Addition of further HCl to give a pH of 2 caused a progressive decrease in the intensity of the absorption at 600 nm with time (over 48 h) and the appearance also of the expected second polaron band at ca. 440 nm. Accompanying these spectroscopic changes was a change in the color of the titration mixture from blue/violet (pH 12 to 6) to turquoise (pH 6 to 4) and finally to the green color characteristic of conducting emeraldine salts (at pH 4 to 2).

3.8. Oxidation and Reduction of 3 and 4 Dispersions. a. Oxidation.

Addition of ammonium persulfate (0.10 M) to aqueous dispersions of the emeraldine salt colloids **3** or **4** at pH 2 caused a rapid change in color

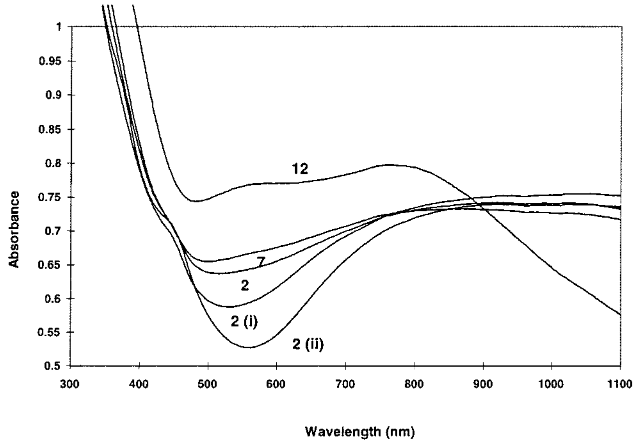


Figure 5. UV−vis spectral changes as the dedoped colloidal dispersion from Figure 4 is redoped with 1.0 M HCl. Curves labeled in the range pH 2−12. In addition, 2(i) was at pH 2 after 24 h and 2(ii) was at pH 2 after 48 h.

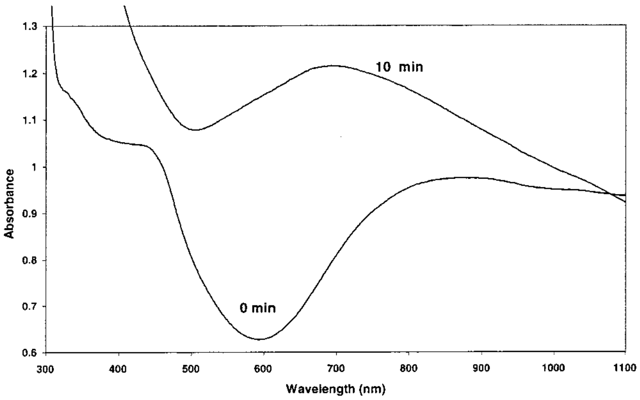


Figure 6. UV−vis spectral changes upon oxidizing an aqueous colloidal dispersion of **3** with 0.10 M ammonium persulfate at pH 2.

from green to blue/violet. Oxidation under these acidic conditions to the pernigraniline salt form (Scheme 1) was confirmed in both cases by the appearance within 10 min of a strong absorption band at ca. 700 nm characteristic of the pernigraniline salt[42,43] (e.g., Figure 6). These fully oxidized pernigraniline salts (Scheme 1, $A^- =$ anion of dopants **1** or **2**) were relatively unstable, undergoing slow decomposition over 24 h, as evidenced by the loss of the 700 nm absorption band. Similar instability has been reported[44,45] for other pernigranilines and may be associated with hydrolytic cleavage of the polyaniline backbone and/or formation of quinone type products.

In contrast, treatment with persulfate ion (0.10 M) of the emeraldine salt/emeraldine base mixture generated by partially dedoping the colloidal salt **4** at pH 12 (see section 3.7) led to rapid oxidation to the corresponding pernigraniline base (Scheme 1). This was confirmed by the appearance within 1 min of a strong absorption band at 515 nm, which may be assigned as the Peierls gap transition characteristic of pernigraniline base.[46] This fully oxidized polyaniline was again unstable with time, its distinctive 515 nm band disappearing over 4 h.

b. Reduction. Reductions of the emeraldine salt colloids **3** and **4** with hydrazine hydrate (0.10 M) were also examined at pH 12. UV−vis spectral studies showed that these reductions were relatively slow, the visible absorption bands (600−800 nm) of the initial emeraldine salt/emeraldine base mixtures gradually disappearing over 5 h. Although the expected $\pi-\pi^*$ band for the leucoemeraldine base product at ca. 300−360 nm[47] could not be detected due to strong background absorption in the reaction mixtures, the disappearance of all visible region absorption was consistent with reduction to leucoemeraldine base (Scheme 1).

4. Conclusions

Acid doping of EB with calixarenesulfonic acids **1** and **2** in Milli-Q water or DMSO leads to the facile formation of colloidal dispersions of emeraldine salts PAn.calix[4]SO_3H (**3**) and PAn.calix[6]SO_3H (**4**). The particle sizes of colloidal **3** and **4** were 517 and 279 nm, respectively, and the conductivities of the pressed dried pellets of **3** and **4** were 3.2×10^{-4} and 2.9×10^{-4} S cm^{-1}, respectively. In addition, the colloidal dispersions were electroactive and could also be chemically oxidized and reduced. Chemical dedoping with NaOH and redoping with HCl of **3** and **4** were also possible, and the results show that **3** and **4** had enhanced stability, due to the counterions **1** and **2**, toward alkaline dedoping.

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