

Delocalized π -Stacks Formed on Dendrimers

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In the present investigation we modified a set of poly-(amidoamine) (PAMAM) dendrimers¹ with imide electrophores,² reduced these compounds with one electron per imide group to form poly(anion radicals), and studied the aggregation of these anion radicals. Recent studies have shown that anion radicals derived from imides **1** assemble in aqueous solution to form π -dimers and π -stacks.² These soluble stacks are unusual and interesting because the π -electrons are delocalized intermolecularly along the stack. As such they are single stack analogs of solid state conductors such TTF–TCNQ.³ We imagined that similar aggregation could occur intramolecularly on modified dendrimers. Because the dendritic chains of interest are flexible, it was not clear that there would be great organizational advantage, but it seemed possible that the high density of anion radicals attached to the periphery of a higher generation dendrimer^{1c} could lead to extensive delocalization over its three dimensional surface. Polymer films containing 1^- have unusual electrical conductivity⁴ and an organized dendrimeric structure might lead to materials with unusual or even useful electrical and optical properties.

Although dendrimers are receiving extensive attention^{1c,5} there are to our knowledge no previous studies of the electrochemistry or ion radical chemistry of peripherally modified dendrimers. Oligomers connecting redox centers in a dendritic structure have been reported,⁶ one example of π -stacking of side chain ion radicals on a soluble, linear polymer is known,^{7a} and we

note a viologen trimer in which two of the three cation radicals π -dimerize in DMF, but do not form stacks.^{7b}

It has been established² that imide anion radical π -stacks are formed in aqueous solution, not organic solvents, so the experimental design required a water soluble dendrimer. Well defined PAMAM dendrimers¹ were, therefore, especially appropriate. The generations **1-6** (**3-1-3-6**, Chart 1) were derivatized using monoanhydride mono-imide **2**, which has an aliphatic, ionic substituent on nitrogen. Because the substituent is aliphatic, it was not displaced during the derivatization and it blocked cross-linking. The water soluble iodide salts (**3-1-3-6**) prepared by reaction of **2** with dendrimers in dimethylacetamide at 120° for 14 h, as well as the monomeric model **1d**, were characterized by IR, NMR, and UV–vis. Loading was assayed at 380 nm in DMF solvent using **1e** as a standard, and by coulometry in DMF, 0.1 M Et₄NBF₄, assuming 1 electron/imide unit (Table 1). Since a 5% error in measuring concentration of A units translates to a 12–17% change in loading there is acceptable agreement of data except for **3-3**. Clearly the loading is quite high. We note (Table 1) that the number of imide groups per molecule (A_n) ranges from one (**1d**) to 192 (**3-6**).

On the basis of previous experience² and control experiments which showed no evidence for formation of imide dianions, imide anion radicals (A^-) were produced on the dendrimers using a 2-fold excess per A of Na₂S₂O₄ in degassed D₂O. Vis–NIR spectra (Figure 1) were recorded. Previous studies² have shown that unaggregated A^- compounds such as **1a**⁻ in DMF have strong bands near 700 nm; π -dimers (A^-)₂ in water absorb at 1140 nm; and π -stacks at 1200–2200 nm (longer λ for larger stacks). The NIR bands of these anions are assigned to excitation along stacks. In Table 1 are data taken in dilute solution (0.25 mM) in D₂O. The model **1d**⁻ absorbs weakly at 1160 nm (π -dimer) but is mostly monomeric at this concentration. Dendrimer anion radicals show λ_{\max} 1340 nm for **3-1** and about 1420 nm for **3-2-3-6** demonstrating that π -stacks are formed. Visible spectra (λ_{\max} 450 nm) were in agreement² with this conclusion. Studies of the spectra over a large range of concentrations intended to elucidate intra- vs intermolecular stacks have thus far been complicated by insolubility (high concentration) and stability (low concentration) problems. The similarity of the six dendrimer spectra is remarkable, showing that similar π -stacks are formed for molecules which contain 12–192 electrophores.

Cyclic voltammograms were recorded using a glassy carbon electrode and either DMF, 0.1 M Et₄NClO₄, or aqueous 0.1 M Na₂SO₄. In DMF the model compound **1d** gave two reversible couples as expected. All the dendrimers gave voltammograms closely similar to that shown in Figure 2 for **3-4**. These voltammograms have very broad first “peaks”, which were shown by coulometry to correspond to one electron per A group. Reoxidation was quantitative. The current measured at –0.75 V increased linearly with v at $v > 100$ mV s⁻¹, suggesting that the dendrimers are adsorbed. Indeed, the second couple (near –0.9 V, Figure 2B), which is

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Chart 1

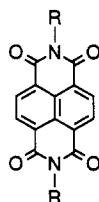
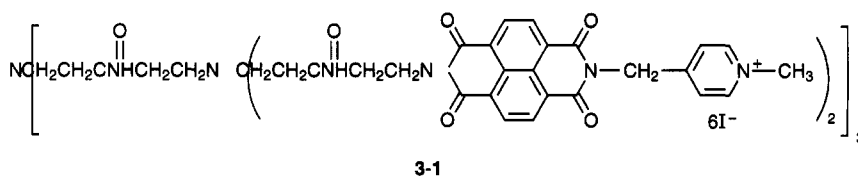
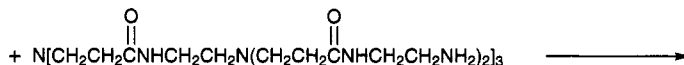
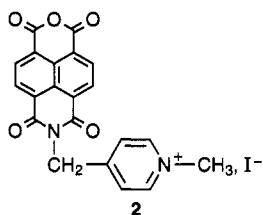
1a, R, R' = -C₆H₄SO₃⁻1b, R, R' = —[pyridinium ring]⁺—CH₂—C₆H₅1c, R, R' = -CH₂CH₂N⁺(CH₃)₃1d, R, R' = -CH₂—[pyridinium ring]⁺—CH₃1e, R = -CH₂—[pyridinium ring]⁺—CH₃, R' = *n*-C₁₂H₂₃

Table 1. Loading of Dendrimers and NIR Absorbance of Anion Radicals

compd	A _n	loading % coul ^a	loading % vis ^b	λ _{max} (nm) ^c
1d	1	1160 ^d		
3-1	6	84	100	1340
3-2	12	106	119	1410
3-3	24	80	118	1430
3-4	48	103	91	1410
3-5	96	102	92	1460
3-6	192	101	103	1420

^a Reproducibility of measurement ±10%. ^b Calculated using 1e as a standard with ε 18 800 at 380 nm. The reproducibility of absorbance was ±5%. ^c 0.25 mM in A groups, reduced in D₂O with Na₂S₂O₄. ^d The spectrum is much weaker than that for the dendrimers (Figure 1) because the monomer-dimer equilibrium favors monomer at low concentration.

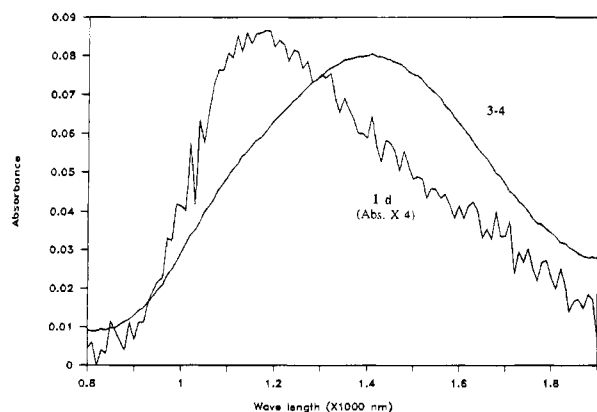


Figure 1. NIR spectra in D₂O of radical anions formed from 1d and 3-4 with Na₂S₂O₄. Both 0.25 mM in A groups; 1 mm cell.

the anion-dianion couple and is coulometrically one electron per A has the shape expected for surface confined species. Note especially that the anodic peak current of the second couple would be much smaller if

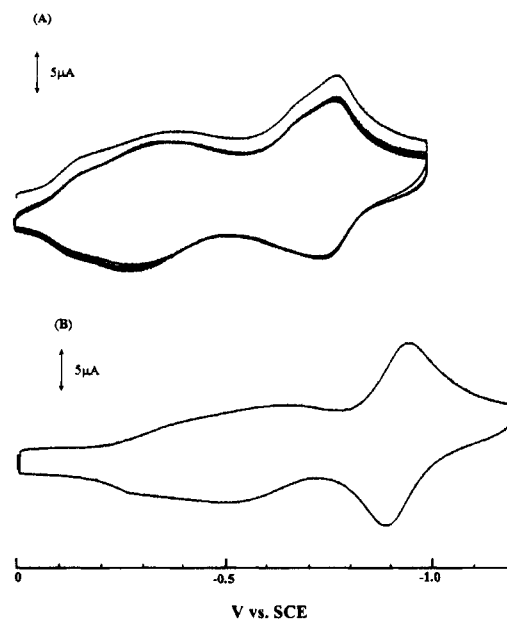


Figure 2. Cyclic voltammograms of 3-4. Glassy carbon working electrode (0.072 cm²), SCE reference, 100 mV s⁻¹: (A) H₂O, 0.1 M Na₂SO₄, 0.5 mM in A groups; (B) DMF, Et₄NClO₄, 0.3 mM in A groups.

the redox species were not surface confined but free to diffuse. In aqueous solution similarly shaped voltammograms (Figure 2) were obtained with similar sweep rate dependence. Again all six dendrimers had this basic shape with a very broad "peak" corresponding to anion radical formation. Coulometry (Table 1) was consistent with one electron per imide on fully loaded molecules and reoxidation was quantitative. Although a detailed interpretation is beyond the scope of this communication the breadth of the first peak suggests that different A groups on 3 form radical anions at

different potentials. Importantly this process begins at potentials about 150 mV more positive than that for the simpler **1d** reduction. This anodic shift can result from the stabilizing π -aggregation of anion radicals or from the stronger adsorption of the reduced compared to the neutral dendrimers.

This initial investigation has demonstrated the feasibility of generating dendrimers which are highly loaded with anion radicals and detected the assembly of the peripheral entities. The similarity of vis-NIR and CV results for the various dendrimers is striking. This may result from the intrinsic stacking character of the specific imide that was used or be determined by the dendrimer structure. Future studies will evaluate this discovery, explore the possibility of obtaining

extensive intramolecular π -delocalization in a soluble species, and investigate the material properties of solids formed from these π -stacked dendrimers.

Note Added in Proof. Dendrimers substituted with redox-active TTF units have been recently reported: Bryce, M. R.; Devonport, W.; Moore, A. J. *Angew Chem., Int. Ed. Engl.* **1994**, *33*, 1761.

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