

## Doping of Conducting Polymers by Sulfonated Fullerene Derivatives and Dendrimers

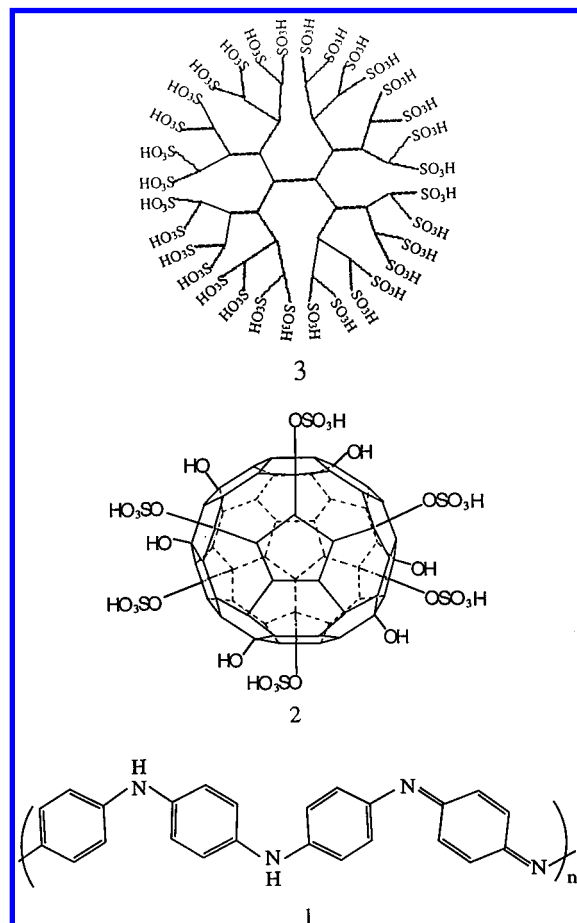
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We report here the use of sulfonated fullerene derivatives and dendrimers with multiple  $-(O)SO_3H$  groups as protonic acid dopants for polyaniline emeraldine base (PANI-EB). While doping of PANI-EB films with the sulfonated dendrimers gives conductivities up to ca. 10 S/cm, the hydrogensulfated fullerenol-doped materials show metallic characteristics with room-temperature conductivities as high as 100 S/cm—about 6 orders of magnitude higher than the typical value for fullerene-doped conducting polymers. This, coupled with the anticipated photoinduced charge-transfer effects characteristic of fullerene  $C_{60}$  and potential biomedical applications of dendrimers, could make these highly conducting materials useful in many advanced optoelectronic and/or biomedical devices.

In 1985, Kroto et al.<sup>1</sup> discovered that buckminsterfullerene  $C_{60}$  has a soccer-ball-like structure faced symmetrically with 12 pentagons and 20 hexagons. This discovery, together with the large-scale synthesis of fullerenes reported by Krätschmer and Huffman<sup>2</sup> in 1990, has had a significant impact on both applied and fundamental research in many fields.<sup>3</sup> Owing to their unusual molecular symmetry, fullerenes and their derivatives have been shown to possess interesting photonic, electronic, superconducting, magnetic, and biomedical properties.<sup>3</sup> On the basis of these findings, a wide range of potential applications have been proposed for fullerenes and their derivatives. To mention but a few examples: fullerene thin films, or certain  $C_{60}$ -containing conjugated polymers, have been doped into superconducting states by alkali metals at a relatively “high” temperature ( $T_c \leq 40$  K);<sup>4</sup> photovoltaic cells with significantly improved conversion efficiencies have been devised using interpenetrating network composites consisting of poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylenevinylene] (MEH-PPV) and  $C_{60}$  derivatives;<sup>5</sup>  $C_{60}$ -doped photoconducting films with performances comparable to some of the best commercial photoconductors (e.g., thiapyrylium dye aggregates) have been prepared by liquid-phase mechanical mixing of poly(9-vinylcarbazole) with fullerenes (a mixture of  $C_{60}$  and  $C_{70}$ );<sup>6</sup> and fullerene  $C_{60}$  has been shown to exhibit third-order nonlinear optical responses comparable to those of certain conjugated polymers.<sup>7</sup> The use of  $C_{60}$  as a p-type dopant for conducting polymers, however, was shown to only marginally improve the dark conductivities of conducting polymers (up to about  $10^{-4}$  S/cm),<sup>8</sup> presumably owing to a relatively weak charge-transferring capability associated with  $C_{60}$  at the ground state. Indeed, a theoretical study has indicated that the lowest unoccupied molecular orbital (LUMO) of  $C_{60}$  is located between the top of the valence band and the bottom of the conduction band (i.e., in the forbidden gap) of those conducting polymers, indicating that fullerenes are weak charge-transfer dopants.<sup>9</sup> Chemical modification of  $C_{60}$  has opened up a new era in synthetic chemistry and materials science involving the carbon clusters.<sup>10</sup> In particular, the recent synthesis of hydrogensulfated fullerene derivatives with multiple  $-OSO_3H$  groups<sup>10d</sup> prompted us to



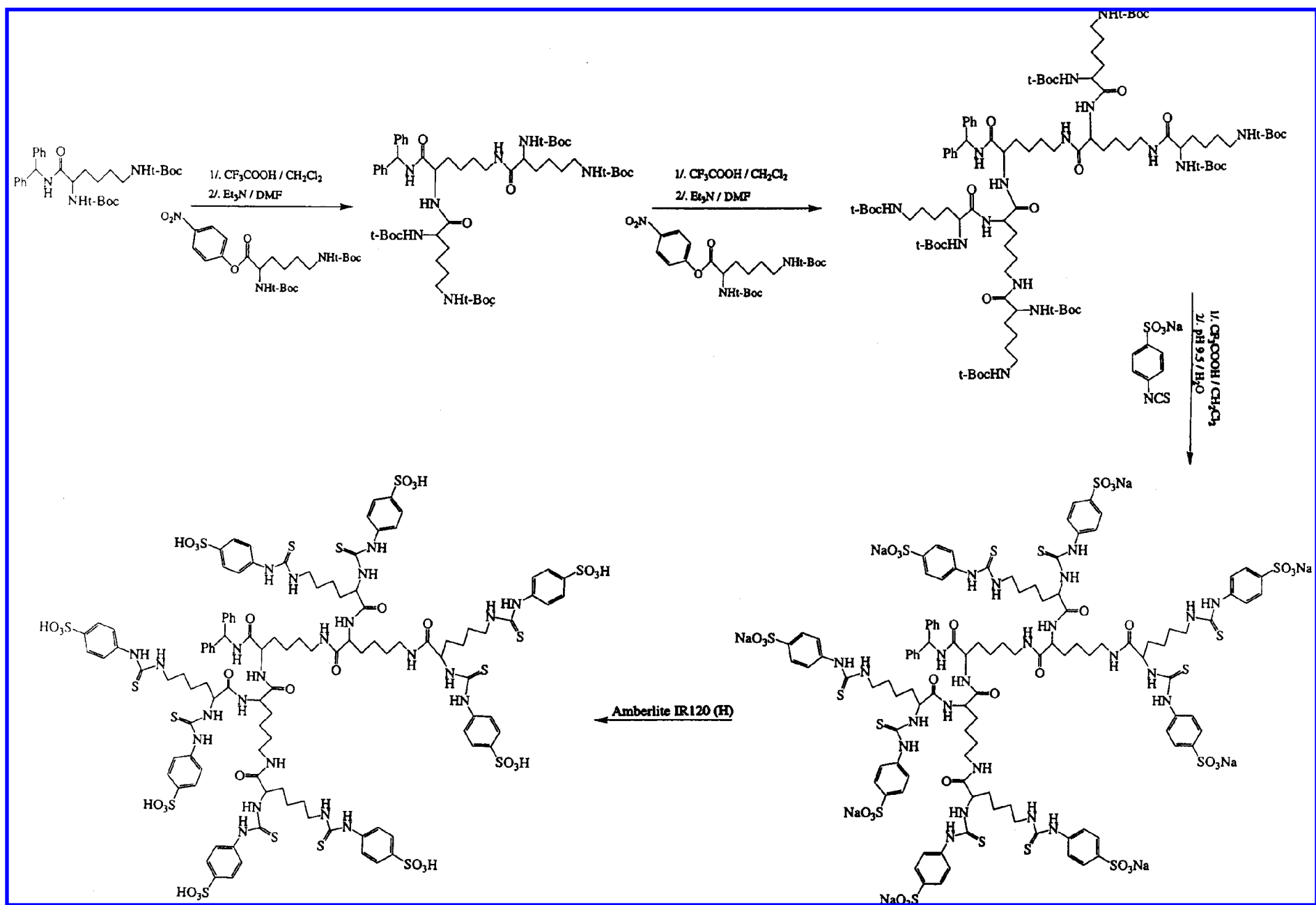
**Figure 1.** Molecular structure of the polymer and dopants used in this study: (1) polyaniline emeraldine base; (2) hydrogensulfated fullerene; (3) sulfonated dendrimer.

prepare novel conducting polymer systems through protonic acid doping<sup>11</sup> of polyaniline emeraldine base (PANI-EB) **1** with molecule **2** (Figure 1).

Dendritic macromolecules resemble the molecule **2** in that they contain a large number of terminal groups surrounding a central core.<sup>12</sup> Dendrimers have recently attracted a great deal of interest for various potential applications ranging from

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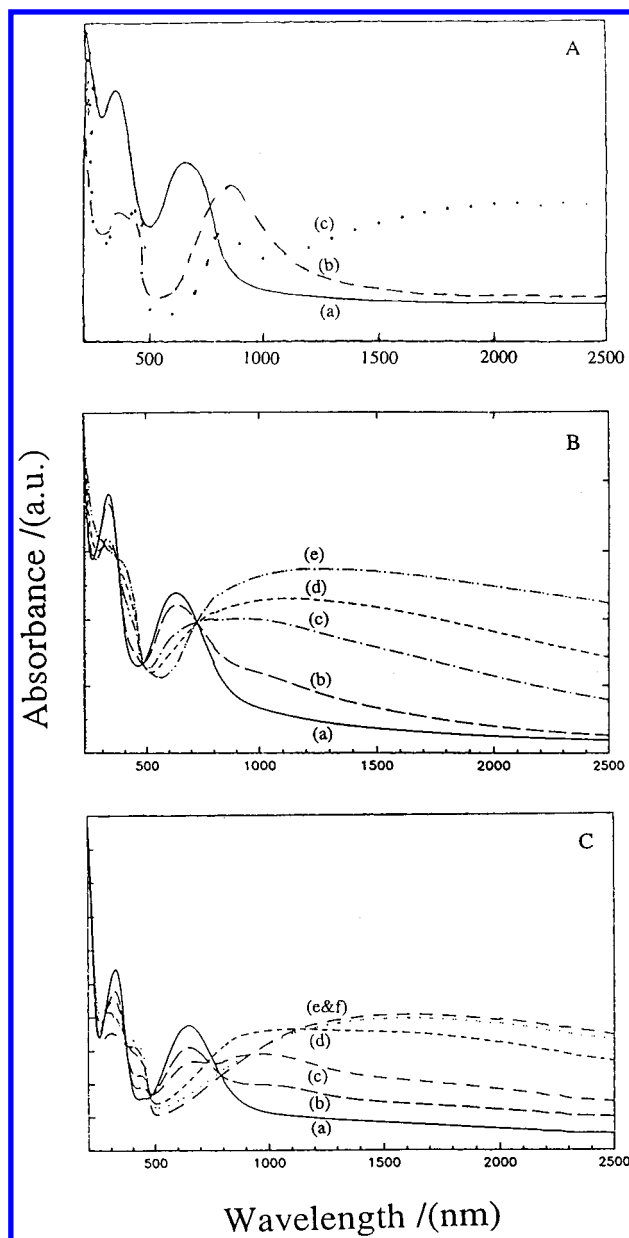
SCHEME 1: Synthetic Route to the Sulfonated Dendrimer (cf. Reference 12h)



artificial cells to drug carriers because of their molecular size and the unique way in which the outermost branches arrange themselves in the form of a dense sphere surface surrounding a relatively hollow core.<sup>12g</sup> Sulfonated dendrimers as schematically represented by **3** in Figure 1 should, in principle, be also able to dope PANI-EB into conducting states by protonation of its imine nitrogen atoms, but this possibility is as yet almost unrecognized. In this regard, we have also investigated the protonation (doping) of PANI-EB with sulfonated dendritic molecules. Results from the protonic acid doping of polyaniline by derivatives of **3** will be presented together with those from molecule **2** and be discussed on the basis of their structural characteristics.

In a typical experiment, polymer **1** and molecule **2** were chemically synthesized following the published methods of refs 11e and 10d, respectively, while the sulfonated dendrimer was prepared as shown in Scheme 1. For comparative purpose, the reaction shown in Scheme 1 was terminated at the second generation to give the sulfonated dendritic molecule of **3** with a similar number of acid groups and an equivalent molecular size as **2** (ca. 10 Å in diameter). Chemical structures of the *as-synthesized* materials and the average number of functional groups per C<sub>60</sub> moiety or dendritic molecule were confirmed by various spectroscopic measurements including ultraviolet/visible/near-infrared (UV/VIS/NIR), Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), and thermal gravimetric analyses (TGA).<sup>13</sup> Doping was achieved by immersing a quartz plate coated with a thin spin-cast film of polymer **1**, from *N,N*-dimethylformamide (DMF) or hexafluoro-2-propanol (HFIP), into a solution of **2** or **3** in chloroform (ca. 3 mg/25 mL) at room temperature (20 °C). During the doping reaction, a color change from blue to green was normally observed for the polymer film. Prior to any further studies, the doped polymer film was thoroughly rinsed with pure solvent to remove any unreacted **2** or **3** and vacuum-dried. The standard four-probe method was used to measure the dc conductivity.<sup>14</sup>

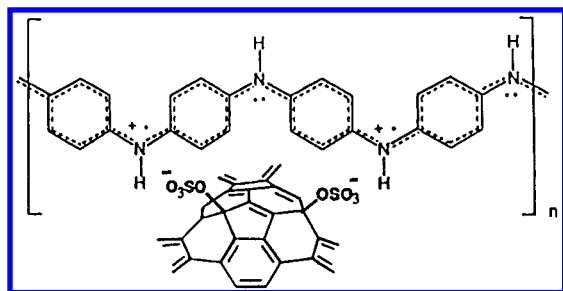
The protonation of PANI-EB by certain *monofunctionalized* protonic acids (e.g., *d,l*-camphorsulfonic acid (HCSA), *p*-CH<sub>3</sub>-(C<sub>6</sub>H<sub>4</sub>)SO<sub>3</sub>H, and (C<sub>6</sub>H<sub>5</sub>)SO<sub>3</sub>H) has been well studied previously.<sup>11</sup> The optical and electronic properties of the HCSA-doped polyaniline are briefly reviewed here, as they underpin our studies on the doping of PANI-EB by sulfonated fullerene derivatives and dendrimers containing *multiple* acid groups. Figure 2A shows the evolution in time of the UV/VIS/NIR spectrum for the as-prepared PANI-EB (curve a) after doping by HCSA (curve b) followed by exposure to *m*-cresol vapor (curve c), which is in good agreement with published results.<sup>11f</sup> The absorption peaks at 322 and 625 nm for the pristine PANI-EB (curve a) are attributable to the  $\pi$ - $\pi^*$  transition of the benzenoid rings and exciton absorption of the quinoid rings, respectively.<sup>11g,h</sup> The absorption peaks at about 420 and 800 nm seen in curve b appeared at the expense of the interband transitions and can be taken as evidence for the presence of localized polarons produced by the HCSA doping.<sup>11g,h</sup> Subsequent interaction with *m*-cresol caused the absorption band characteristic of the localized polarons to largely disappear at 800 nm, while a very intense free carrier tail commencing at ca.1000 nm developed (curve c).<sup>11g,h</sup> These spectroscopic changes have been demonstrated to arise from a conformational transition of the polymer chain from the so-called "compact coil" to "expanded coil" induced by molecular interactions between the HCSA-doped polyaniline and *m*-cresol, a process that has been widely known as "secondary doping".<sup>11f-h</sup> The observed free carrier tail in the near-infrared region was



**Figure 2.** (A) UV/VIS/NIR spectra of polymer **1** (a); after having been doped with HCSA (b); followed by exposure to *m*-cresol (c). The corresponding spectra for a polymer film of **1** spin-cast from DMF before and after doping with **2** and the sulfonated dendrimer, respectively. (B) Doping with **2**, doping level, i.e., S/N ratio (reaction time): (a) 0 (0); (b) 0.03 (15 s); (c) 0.12 (45 s); (d) 0.25 (165 s); (e) 0.50 (1800 s). (C) Doping with the sulfonated dendrimer, doping level, i.e., S/N ratio (reaction time): (a) 0 (0); (b) 0.08 (20 min); (c) 0.21 (60 min); (d) 0.40 (240 min); (e) 0.47 (720 min); (f) 0.50 (3600 min).

considered to arise from delocalization of electrons in the polaron band, leading to a concomitant increase in conductivity by up to several orders of magnitude (e.g., an increase in conductivity for a HCSA-doped polyaniline film from ca. 0.1 S/cm when cast from chloroform up to 400 S/cm when cast from *m*-cresol has been recorded<sup>11f,i,j</sup>).

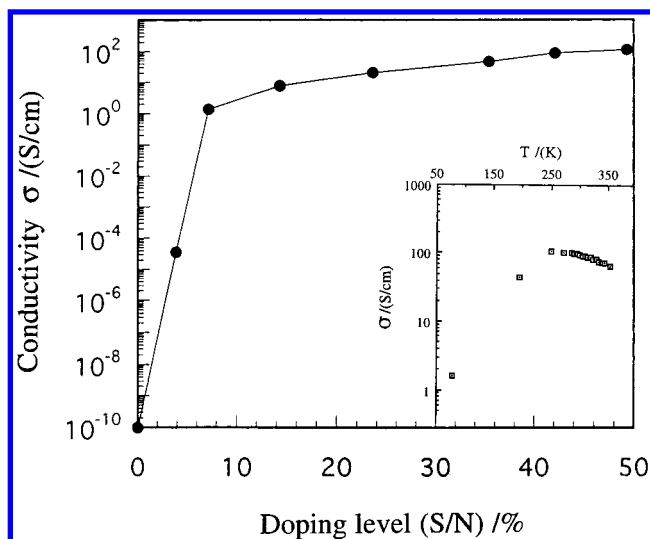
Parts B and C of Figure 2 show the corresponding changes in the UV/VIS/NIR spectrum for the PANI-EB film spin-cast from DMF upon doping with the solutions of **2** and **3**, respectively. Unlike the HCSA doping, doping polymer **1** with molecule **2** did not show any absorption peak at about 800 nm attributable to the localized polarons (Figure 2B). As the doping proceeded, however, the intense free carrier tails characteristic of delocalized states developed over 800–2500 nm and the



**Figure 3.** Schematic representation of the zipping effect by doping of polyaniline emeraldine base chains with the hydrogensulfated fullereneol derivatives containing multiple  $-\text{OSO}_3\text{H}$  groups. The interchain doping and possible crystallization of the  $\text{C}_{60}$  moieties are not shown for reasons of clarity.

interband transitions in the UV–visible region became obscured. Apart from the primary doping, therefore, it is most likely that molecule **2** can also act as a secondary dopant to “straighten out” the polymer chain for delocalization of polarons once formed by the protonic acid doping with the  $-\text{OSO}_3\text{H}$  groups. This was, at least partially, evidenced by the appearance of an isosbestic point at about 750 nm on the UV/VIS/NIR spectra shown in Figure 2B, which indicated that there was an interconversion of the absorption species corresponding to the interband transitions and those in the delocalized states. Subsequent exposure of the doped polyaniline film corresponding to curve e of Figure 2B to *m*-cresol vapor did not cause any significant change in either the optical absorption or conductivity, indicating that molecule **2** is a strong dopant that can induce both primary and secondary doping even without the presence of conventional secondary dopants (e.g., *m*-cresol).<sup>11f–h</sup> While the solvation of the positive charges and negative (CSA)<sup>−</sup> counterions along a HCSA-doped polyaniline chain by *m*-cresol was considered to cause the “compact coil” to “expanded coil” transition owing to an enhanced electrostatic repulsion between the positive charges on the doped polymer chain,<sup>11f–h</sup> the secondary doping effect of molecule **2** arises presumably from the “multipoint” interactions between the doped polyaniline chains and the “multiple arms” of the  $-\text{OSO}_3^-$  counterions in **2**, which could uncoil the doped polymer chains through a “zipping” mechanism (Figure 3). No primary/secondary doping effect was observed when a thin film of the pristine or HCSA-doped polymer **1** was treated with a solution of the fully hydroxylated counterpart of **2** in chloroform. Thus, the spectroscopic changes seen in Figure 2B can be unambiguously attributed to the protonic acid doping of **1** by the  $-\text{OSO}_3\text{H}$  groups in **2**.

The above conclusion was further tested by using derivatives of the sulfonated dendrimer **3** synthesized according to Scheme 1 as an alternative protonic acid dopant. As shown in Figure 2C, the overall evolution in time of the UV/VIS/NIR spectrum for a PANI-EB film upon doping with the sulfonated dendrimer is very similar to Figure 2B. Like molecule **2**, therefore, the sulfonated dendrimer can also act both as a primary and a secondary dopant. Unlike the molecule **2**, however, doping polymer **1** with the sulfonated dendrimer did produce a peaklike, broad shoulder over 800–1200 nm, especially at the initial stage of doping (curves b and c of Figure 2C). The increase in absorbance over 800–1200 nm, together with the concomitant loss of the interband transitions in the UV–visible region (curves b and c of Figure 2C), indicated the formation of localized polarons at the low doping levels, as was the case for the HCSA doping. Further doping caused delocalization of electrons in the polaron band, as reflected by the gradual disappearance of the broad shoulder over 800–1200 nm and the appearance of the free carrier tail in the near-IR region (curves d–f of Figure



**Figure 4.** Doping-level dependence of conductivity for a PANI-EB film spin-cast from HFIP upon doping with **2**. Inset shows the temperature dependence of conductivity for the 2-doped PANI-EB film at  $\text{S/N} = 0.5$ .

2C). In contrast to Figure 2C, Figure 2B shows the free carrier tail in the near-IR region without the involvement of any interconversion from absorptions characteristic of the localized polarons around 800–1200 nm. In view of the structural difference between molecule **2** and the sulfonated dendrimer, the difference seen in Figure 2B,C presumably suggests that the remaining conjugated structures in the modified  $\text{C}_{60}$  can enhance the polaron delocalization, for instance, between polymer chains. This is consistent with a higher conductivity recorded for a PANI-EB film doped with the hydrogensulfated fullereneol than the sulfonated dendrimer; vide infra.

Figure 4 depicts a plot of the doping-level (i.e., the atomic ratio of  $\text{S/N}$ , as determined by XPS) dependence of the dc conductivity for a PANI-EB film spin-cast from HFIP and doped by **2** at room temperature, which shows an increase in conductivity by ca. 12 orders of magnitude. The limiting value of ca. 100 S/cm seen in Figure 4 is much higher than that of a corresponding PANI-EB film primary-doped with HCSA (ca. 0.1 S/cm) and is very close to that of the PANI-EB after having been doped by certain benzyl-substituted sulfonic acids and subsequently treated with *m*-cresol.<sup>11f</sup> Doping the PANI-EB film with the sulfonated dendrimer gives a limiting conductivity of ca. 6 S/cm, which, though lower than that of 2-doped polyaniline, is still higher than the corresponding value for the PANI-EB primary-doped with HCSA.<sup>11f</sup> Although the limiting conductivity for the PANI-EB film spin-cast from DMF after doping with **2** is only about 40 S/cm, this is, as far as we are aware, already much higher than those reported for any other fullerene-doped conducting polymers.<sup>8</sup> PANI-EB films processed from HFIP have been previously reported to have improved conducting properties,<sup>15</sup> after doping, compared to those processed from more conventional solvents including DMF. The variable conductivities observed in the present study for the PANI-EB films cast from different solvents and/or doped by protonic acid dopants with a similar number of acid groups, but different molecular geometries, imply that there is considerable room for further increasing conductivity.

Also included in the inset of Figure 4 is the temperature ( $T$ ) dependence of the dc conductivity ( $\sigma$ ) for the PANI-EB film spin-cast from HFIP after having been fully doped with **2** (i.e.,  $\text{S/N} = 0.5$ ). As can be seen,  $\sigma$  increases with decreasing  $T$  to a maximum value of ca. 106 S/cm at 250 K and then decreases with further decrease of temperature. These changes clearly

indicate that the 2-doped polyaniline film possesses metallic characteristics with a relatively high temperature for the insulator-metal transition.<sup>16a</sup> A similar insulator-metal transition temperature has been reported for a HCSA/*m*-cresol-doped PANI after having been stretch-aligned; the high transition temperature was suggested to be related to a stretching-induced increase in the separation distance between metallic "islands".<sup>16b</sup> By analogy, therefore, the high transition temperature observed in the present study may be attributed to the large size of the C<sub>60</sub> counterions, which in turn could lead to a large interdomain distance. While relatively high dark conductivities have also been observed for PANI-EB films doped with the sulfonated fullerenes of low substitutions (e.g., ca. 10 S/cm for the dopant with about two -OSO<sub>3</sub>H groups per C<sub>60</sub> entity), the phase structure and anticipated photoinduced charge-transfer effects for polyaniline films doped by the hydrogensulfated fullerene derivatives<sup>6,17</sup> are currently under investigation.

In summary, we have demonstrated, for the first time, that sulfonated fullerene derivatives and dendrimers are effective simultaneously as both a primary and secondary dopant for polyaniline emeraldine base. The self-secondary-doping effect was shown to induce a significant enhancement in electrical properties for conducting polyanilines thus prepared. The dc conductivity measurements have revealed room-temperature conductivities up to 100 S/cm, with a metallic conduction mechanism, for polyaniline films doped by the sulfonated C<sub>60</sub>. While the highly conducting polyaniline materials obtained by doping with the hydrogensulfated fullerene derivatives could find applications in many advanced optoelectronic devices, the sulfonated dendrimer doped conducting polymers should open up avenues for making electrically controllable biomedical devices (e.g., artificial cells and/or drug delivery systems). Furthermore, the hydrogensulfated fullerene derivatives and sulfonated dendrimers described in this communication are of potential importance as useful dopants for more general applications, as many other conducting polymers,<sup>18a</sup> including polypyrrole,<sup>18b,c</sup> poly(3-alkylthiophene),<sup>18d</sup> and poly(phenylenevinylene),<sup>18e,f</sup> are also known to be susceptible to the protonic acid doping.

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## References and Notes

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