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Isolation and Monitoring of the Endohedral Metallofullerenes $Y@C_{82}$ and $Sc_3@C_{82}$: On-Line Chromatographic Separation with EPR Detection

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The direct coupling of high-performance liquid chromatography (HPLC) with on-line electron paramagnetic resonance (EPR) detection is demonstrated for monitoring separations of endohedral metallofullerenes ($M@C_{2n}$). The HPLC-EPR approach readily permits detection of the paramagnetic species, such as $Y@C_{82}$ and $Sc_3@C_{82}$, in the presence of the dominant empty-cage fullerenes (C_{60}, C_{70}) and diamagnetic metallofullerenes (e.g., $M_2@C_{2n}$). The results indicate that on-line EPR provides a noninvasive, selective detector for HPLC metallofullerene separations that is readily adaptable to air-sensitive and/or labile compounds. Specifically, the "EPR-active" metallofullerenes, $Y@C_{82}$ and $Sc_3@C_{82}$, are selectively monitored on-line for an initial separation of the metallofullerene fraction from the dominant empty-cage fullerenes utilizing a combination of polystyrene columns. This preparative "cleanup" procedure is followed by HPLC-EPR separation and monitoring of $Y@C_{82}$ and $Sc_3@C_{82}$ species using a selective tripodal π-acidic-phase column (Trident-Tri-DNP) for the final stages of isolation.

The recent discovery and macroscopic preparation of the endohedral metallofullerenes ($M@C_{2n}$),[1,2-8] consisting of transition metals (M = Sc, Y, La, etc.) encapsulated in fullerene carbon cages (C_{2n}, n = 30–53), have generated considerable interest in these unusual molecules. Solid metallofullerenes would constitute a class of tunable materials with possible electronic or optical applications. However, investigation into the properties of metallofullerenes has been hindered by the difficulty in obtaining pure samples. Production yields for $M@C_{2n}$ species from the usual electric arc synthesis are estimated to be <1% with empty-cage fullerenes (C_{60}, C_{70}) dominating the soluble product distribution. Separation and isolation of the metallofullerenes from their empty-cage counterparts is difficult because of their low abundance and uncertain chemical stability in aerobic environments.[4] Strategies for $M@C_{2n}$ separations have included sublimation techniques[9] and chromatography.[10,11]

Historically, liquid chromatography coupled with on-line electron paramagnetic resonance (HPLC-EPR) was demonstrated in 1975 for the separation of stable organic radicals.[12] Subsequently, HPLC-EPR has been utilized in the separation of spin adducts,[13–17] metal complexes,[18,19] and spin-trapped amino acids.[20,21] One of the advantages of utilizing flow EPR as a detector in $M@C_{2n}$ separations is the high specificity for endohedral metallofullerenes with an odd number of encapsulated metal atoms. Several of these species have been shown to be "EPR active" (e.g., $Sc@C_{82}$, $Sc_3@C_{82}$, $Y@C_{82}$, $La@C_{82}$, etc.).[2,7,8,22–25] In contrast, HPLC with conventional UV detection is not generally selective since strong UV absorption occurs for both the $M@C_{2n}$ and empty-cage fullerenes. Monitoring the EPR-active species as chromatographic conditions and stationary phases are optimized is readily achieved with on-line HPLC-EPR. The recovery of valuable samples and coupling to other HPLC detectors is straight-

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forward. Since HPLC-EPR monitors the eluting metallofullerenes in a controlled *anaerobic environment*, air-sensitive metallofullerenes are not compromised. However, the selectivity of EPR for paramagnetic species can be a disadvantage if one wishes to isolate metallofullerenes of the type $M_2@C_{2n}$ (e.g. $Y_2@C_{84}$). All of the latter species examined to date have been diamagnetic.

In this article, on-line EPR detection is shown to be a powerful technique for monitoring all stages of HPLC separations for the EPR-active endohedral metallofullerenes. Accurate chromatographic retention times for $Y@C_{82}$ and $Sc_3@C_{82}$ are readily established *by direct observation of the on-line HPLC-EPR spectra* as a function of time (i.e., EPR stacked plot). The on-line HPLC-EPR approach is demonstrated for a two-stage separation process utilizing a relatively nonselective polystyrene phase followed by a selective tripodal π-acidic phase (Trident-Tri-DNP) developed by Welch and Pirkle.[26]

EXPERIMENTAL SECTION

Yttrium and scandium metallofullerene-containing samples were prepared by electric arc burning Y_2O_3- and Sc_2O_3-packed graphite rods.[27] Specifically, 6-mm-diameter cored-carbon rods were packed with a mixture of metal oxide (Y_2O_3 or Sc_2O_3) in graphite powder and burned at a pressure of 200 Torr of helium with ~100 A dc current. A relatively high metal-to-carbon ratio was used for preparation of the scandium extract (3–5 scandium atoms per 100 carbons). Fullerene and $M@C_{2n}$ species were extracted from the arc-generated soot with carbon disulfide under a N_2 atmosphere.

A stock solution containing ~3 mg/mL of the metallofullerene-containing extract was prepared with mobile phase as the solvent. On-line HPLC-EPR metallofullerene separations were performed by utilizing a N_2-degassed solvent system, 80% toluene (Fisher)/20% decalin (Aldrich Chemical Co.), to maintain an anaerobic environment. The chromatographic separation of the metallofullerene fraction incorporated two polystyrene columns connected in series, with a Perkin-Elmer, 25 cm × 10 mm PL gel, 10-μm, 1000-Å column, followed by a 25 cm × 10 mm PL gel, 5-μm, 500-Å column. Conditions for the polystyrene separations were 1.0 mL/min with UV detection at 340 nm. In the second stage, a semipreparative Trident-Tri-DNP HPLC column[26] ("Buckyclutcher", 25 cm × 10 mm i.d.; Regis Chemical) was utilized for final isolation of $Y@C_{82}$ and $Sc_3@C_{82}$ fractions. A Hitachi L-4000 UV detector (340 nm) and D-2500 Chromato-Integrator recorder were attached on-line to an IBM 200D-SRC EPR spectrometer with a Bruker microwave bridge operating at 9.54 GHz. A block diagram of the HPLC-EPR design is presented in Figure 1.

The selection of EPR operating parameters (sweep time, modulation, attenuation, time constant, gain) were optimized to increase the signal-to-noise ratio at the expense of resolution. Specifically, high modulation amplitude (~1–1.5 G) and microwave power (~10 mW) was employed with fairly rapid scanning (4–7 G/s). The home-built EPR glass flow cell had

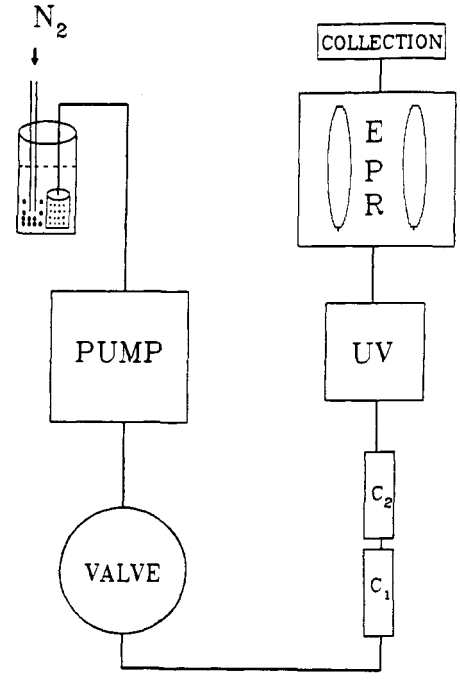

Figure 1. Diagram of the on-line LC-EPR apparatus utilized in metallofullerene separations. The two polystyrene columns are C_1 and C_2.

a measured detection volume of 250 μL. The flow cell was placed in the front side of a dual TE_{102} microwave cavity. Connections to the EPR flow cell incorporated PEEK tubing (0.010-in. i.d.; Upchurch Sci.).

On-line EPR spectral profiles were obtained for 20-s magnetic field sweeps with a spectral window of 90–130 G. Although a smaller spectral window could have been employed for observation of the $Y@C_{82}$ species, a relatively large spectral window was necessary for observation of the expected 22-line pattern for $Sc_3@C_{82}$.[7,822,25] Signal averaging of three to four scans per file was performed with on-line EPR spectra stored in an Aspect 2000 computer. In this manner, a stacked plot of EPR activity versus elution time was readily obtained, with each plot corresponding to 1–3-min segments of elution time.

The UV/visible absorption spectrum was obtained with a Perkin-Elmer Lambda-6 spectrophotometer, which permitted a scanning range of 190–900 nm. A VG 7070E-HF mass spectrometer (VG Analytical, Manchester, UK) with negative-ion chemical ionization was utilized. All metallofullerene samples were evaporated onto the DCI probe filament, which was ramped 0 to 1 A at a rate of 0.05 A/s. Methane was employed as the carrier gas.

RESULTS AND DISCUSSION

The starting stock solutions of yttrium and scandium metallofullerene extracts represent a complex mixture of dominant empty-cage fullerenes with only <1% of the desired metallofullerenes ($Y@C_{82}$, $Sc_3@C_{82}$). Using this stock solution, ~8 mg of raw extract was injected onto two polystyrene columns in series (Figure 1). The high sample loading was employed in order to initially exceed the detection limits for $Y@C_{82}$ in the flow HPLC-EPR experiment. This large "sample throughput" is possible due to the relatively high solubility of the $M@C_{2n}$ extract in toluene/decalin.

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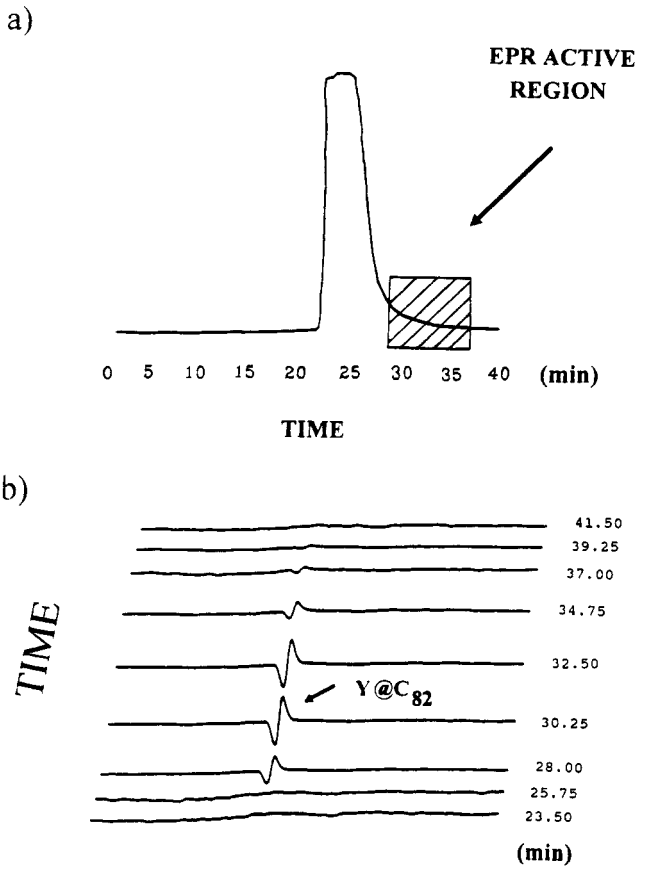

Figure 2. (a) HPLC-UV trace (340 nm), Y@C_{2n} extract, first pass with the two polystyrene columns, 1 mL/min, degassed 80:20 toluene/decalin, and ~8 mg injected. (b) On-line HPLC-EPR stacked plot, sweep width 130 G, and sweep time 20 s. A broad singlet was observed under low resolution conditions (see Experimental Section).

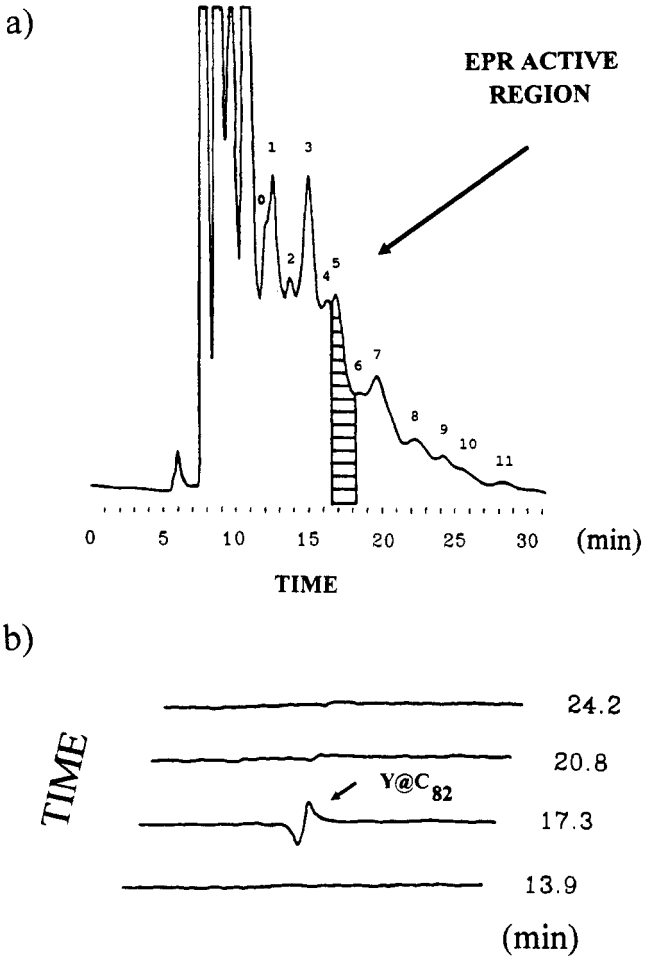

Figure 3. (a) HPLC-UV trace (340 nm), concentrated Y@C_{2n} fraction after two polystyrene passes, Buckyclutcher column, 2.0 mL/min, degassed 80:20 toluene/decalin, and 250-μL injection. (b) On-line HPLC-EPR stacked plot, 9.56 GHz, 3 scans/file, and sweep time 20 s. The EPR time dimension represents an average time of 1.7 min for a given file. Alternate files are not shown.

It is not obvious by examination of the UV chromatogram (Figure 2a) where any of the metallofullerenes elute relative to the empty-cage fullerenes. Although the HPLC-UV trace would indicate a lack of chromatographic resolution of even empty-cage fullerenes, a significant initial separation of Y@C_{82} (relative to C_{60} and C_{70}) is clearly illustrated from the EPR dimension (Figure 2b). It should be noted that the EPR-active chromatographic region of Y@C_{82} occurs from 28 to 37 min. In contrast, the empty-cage fullerenes (C_{60}, C_{70}) elute with significantly shorter retention times (23–27 min). This large difference in retention times (5–10 min) can be attributed to weak "π–π" interactions between the polystyrene substrate and the M@C_{2n} species. Since the EPR-active region (tailing portion of the UV trace) was not clearly resolved from the empty-cage fullerenes, it was necessary to recover and reinject the Y@C_{82} EPR-active fraction (28–37 min) several times into the polystyrene columns to improve the separation. An alternative automated procedure was also employed.[27] After two initial passes with the polystyrene columns, mass spectral data for this EPR-active fraction suggested the presence of Y@C_{82}, Y_2@C_{80}–Y_2@C_{104}, and higher mass empty-cage fullerenes (C_{84}–C_{120}). Mass spectra of pre- and postfractions to the EPR-active region revealed that monitoring Y@C_{82} also served as a "marker" for the overall metallofullerene fraction. It should also be noted that these polystyrene separations were not based on size exclusion chromatography and are consistent with the work of Meier et al.[28] where the elution order was also C_{60}, C_{70}, C_{84}.

The second stage in the yttrium separation required a more selective chromatographic phase for isolation of specific metallofullerenes (e.g., Y@C_{82}). Welch and Pirkle[26] have described a novel chromatographic "Buckyclutcher" phase which employs tripidal ligands (2,4-dinitrophenyl groups) for highly selective "π–π" complexation with fullerenes and metallofullerenes.[10]

To demonstrate the high selectivity inherent in EPR detection, a solution of this concentrated EPR-active Y@C_{2n} metallofullerene fraction vide supra was further separated by utilizing the Buckyclutcher column. The UV trace (Figure 3a) resulting from an injection of this M@C_{2n}-enriched solution indicates at least 10 separate peaks. Although UV detection again was not selective for Y@C_{82}, on-line HPLC-EPR readily identified the Y@C_{82} fraction (Figure 3b). The retention time of Y@C_{82} in the UV trace (peak 5) corresponds to the EPR-active region (16.5–18.2 min). *It is important to emphasize that on-line HPLC-EPR directly identified fraction 5 as containing Y@C_{82} without the necessity of off-line*

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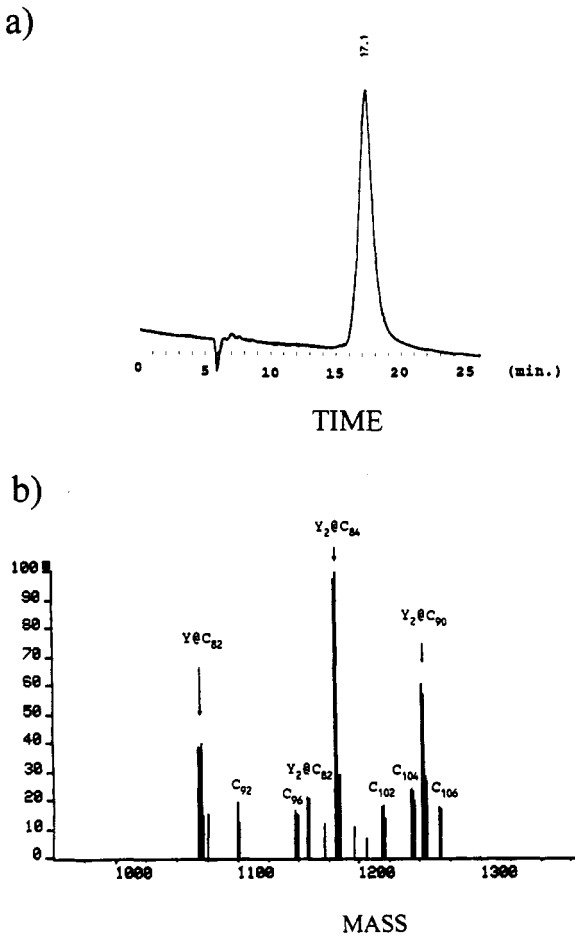

Figure 4. (a) HPLC-UV trace (340 nm), $Y@C_{2n}$, Buckyclutcher, 2.0 mL/min, and 5-μL injection of peak 5. (b) Negative-ion CI mass spectrum (peak 5).

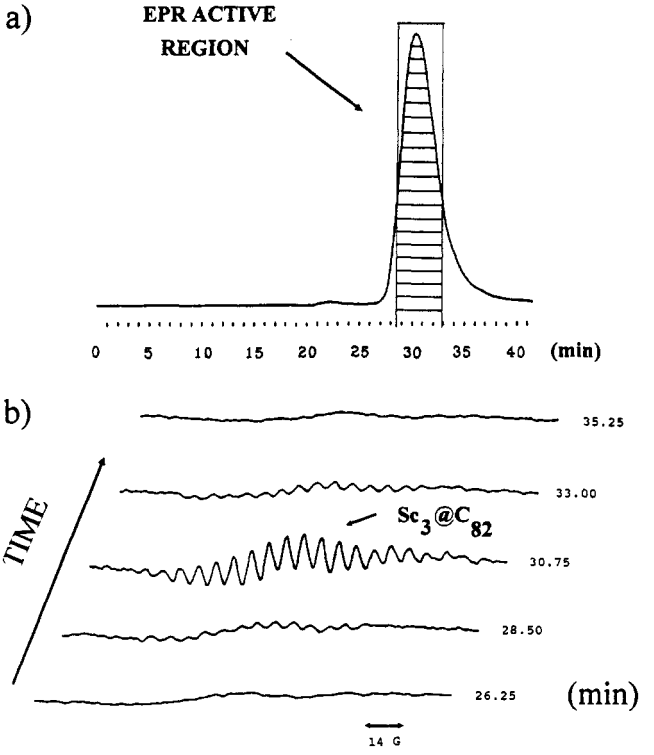

Figure 5. (a) HPLC-UV trace (340 nm) for the fifth polystyrene pass, 410-μL injection of the $Sc@C_{2n}$ EPR active fraction, 1 mL/min, and 80:20 degassed toluene/decalin. (b) On-line HPLC-EPR profile, 9.55 GHz, 4 scans/file, and 20 s/sweep.

fraction collection. As noted in Figures 2b and 3b, a broad singlet is observed in the flow EPR spectra for $Y@C_{82}$ in the present study. Although a doublet in the EPR spectrum ($I = {}^1/_2$, 0.48 G) has been reported[2,24,25] for $Y@C_{82}$ under high resolution static conditions, the EPR on-line spectra in the present study were optimized for S/N, and this relatively small hyperfine coupling was not observed. Wilson et al.[29] have also reported on-line chromatographic monitoring of $Y@C_{82}$, but their study was accomplished at a constant magnetic field without an observable spectral window.

After recovery of peak 5 and reinjection with the Buckyclutcher column, a relatively symmetric UV peak is observed for this purified fraction (Figure 4a). The off-line mass spectrum of the fraction (Figure 4b) still indicates the presence of other metallofullerenes (e.g., $Y_2@C_{84}$ and $Y_2@C_{90}$) and minor amounts of higher fullerenes. Nevertheless, the HPLC-EPR profile (Figure 3b) allows a highly selective cut of the $Y@C_{82}$ fraction to be made, which is not possible by monitoring the corresponding UV profile (Figure 4a). In this manner, a sample enriched in the $Y@C_{82}$ species was obtained. However, an insufficient quantity of sample was available for further spectroscopic characterization. Although recovery of fractions and examination by off-line EPR is an alternative approach,[27] the extra handling and possible contamination (atmospheric oxygen) make that approach less attractive, especially with limited quantities of sample. This point is even more relevant if more labile metallofullerenes are encountered in future $M@C_{2n}$ studies. Because of limited quantities of the $Y@C_{82}$ purified fraction, we proceeded to utilize the HPLC-EPR approach for isolation of the EPR-active scandium metallofullerene ($Sc_3@C_{82}$).[7,8,22,25]

To further demonstrate the on-line HPLC-EPR approach, a $Sc@C_{2n}$ stock solution (~3 mg/mL) enriched in $Sc_3@C_{82}$[27] was prepared and separated with the polystyrene columns. Analogous to the $Y@C_{82}$ polystyrene separations, the elution order of C_{60} and C_{70} (23–27 min) was significantly earlier than the EPR-active $Sc_3@C_{82}$ fraction (28.5–38.0 min). To efficiently remove the empty-cage higher fullerenes (C_{84}–C_{120}), five separate passes of the EPR-active $Sc_3@C_{82}$ fraction were necessary with the polystyrene columns. The UV profile following this fifth polystyrene injection is shown in Figure 5a. The EPR activity of $Sc_3@C_{82}$ maximizes at 30.75 min as indicated by the HPLC-EPR profile (Figure 5b). The characteristic pattern expected for $Sc_3@C_{82}$[7,8,22,25] is clearly indicated from the on-line EPR spectra, although not all 22 lines are observed. In this case, the 6.8-G hyperfine interaction is clearly resolved and provides interpretative data as well as on-line monitoring. However, it should be noted that the amount of monoatomic scandium metallofullerene ($Sc@C_{82}$) was not significant in this sample because of the high metal-to-carbon ratio used in the electric arc production of this sample.

The $Sc_3@C_{82}$ fraction (after five polystyrene passes) was further characterized using the Buckyclutcher column. The UV trace (Figure 6a) reveals at least 10 separate fractions which might contain $Sc_3@C_{82}$, but the flow EPR profile

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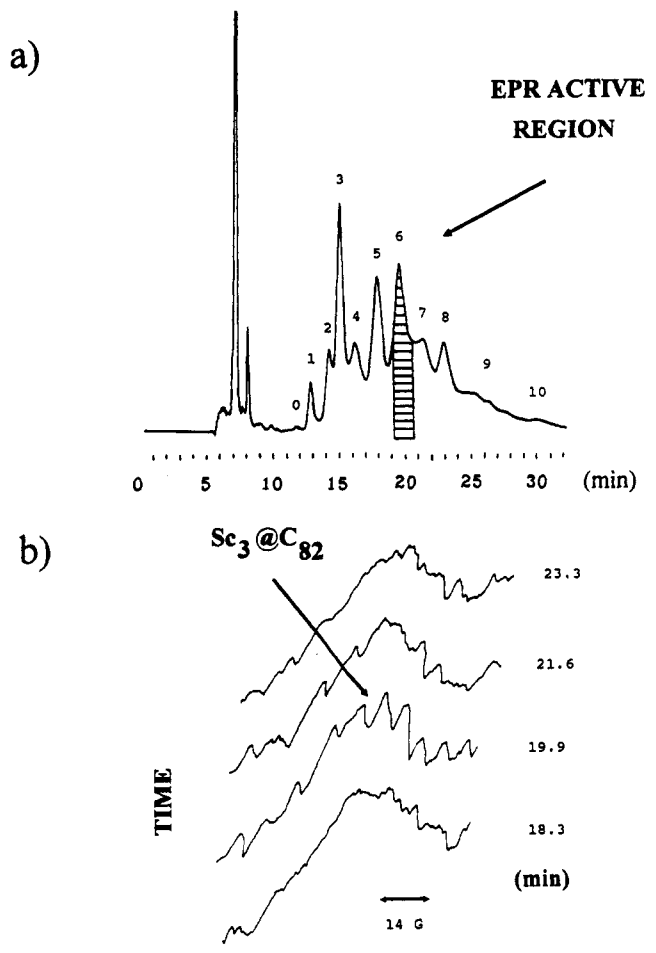

Figure 6. (a) HPLC-UV trace (340 nm), concentrated $Sc_3@C_{82}$ fraction after five polystyrene passes, Buckyclutcher column, 250-μL injection, 2.1 mL/min, and degassed 80:20 toluene/decalin; EPR-active region is peak 6. (b) On-line HPLC-EPR stacked plot, 9.54 GHz, 3 scans/file, and 20 s/sweep.

(Figure 6b) indicates the elution of $Sc_3@C_{82}$ in the 19.1–20.8-min fraction.

Additional cleanup passes with the Buckyclutcher column optimized for collection of peak 6 readily permitted isolation of purified $Sc_3@C_{82}$. An analytical injection of purified $Sc_3@C_{82}$ into the semipreparative Buckyclutcher is shown in Figure 7a. Confirmation of the assignment of $Sc_3@C_{82}$ was obtained by negative-ion mass spectral data (Figure 7b). A UV/visible absorption spectrum of $Sc_3@C_{82}$ was also obtained (Figure 7c). Characteristic absorption peaks for the isolated $Sc_3@C_{82}$ appear at approximately 396, 428, 580, 720, and 810 nm. Recently, UV/visible data have been reported for $Sc_2@C_{84}$[10] and $La@C_{82}$.[11,30] The spectral features of the $Sc_3@C_{82}$ obtained in the present study are comparative, but shifted with respect to the data reported for $Sc_2@C_{84}$, which exhibited local peak maxima at 380, 500, and 680 nm. However, the reported UV/visible spectrum for $La@C_{82}$ has a characteristic strong absorption at 637 nm which was not observed in either $Sc_3@C_{82}$ or $Sc_2@C_{84}$. In addition, strong absorption bands in the near-infrared region (1010 and 1428 nm) were reported for $La@C_{82}$. Near-infrared studies of the scandium metallofullerenes would help clarify these possible differences with the reported data for $La@C_{82}$.[11,30]

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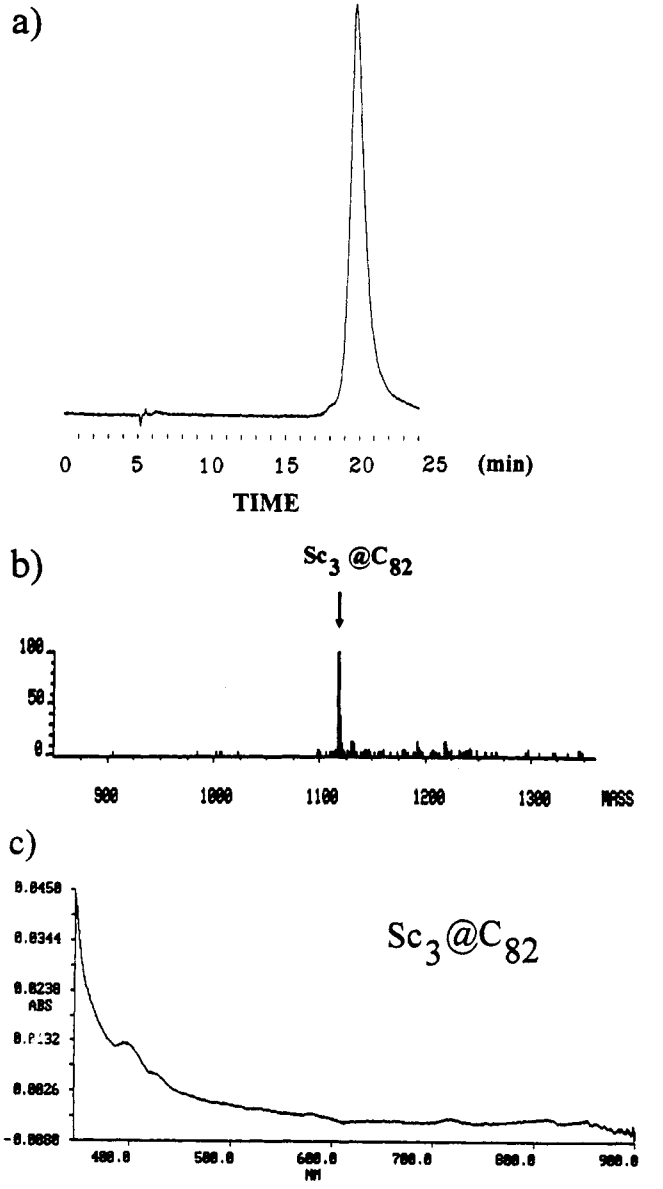

Figure 7. (a) HPLC-UV trace, 10-μL injection of peak 6, semipreparative Buckyclutcher column, 2.1 mL/min, degassed 80:20 toluene/decalin, and UV 340 nm. (b) Negative-ion DCI mass spectrum of isolated peak 6. (c) UV/visible spectrum of purified $Sc_3@C_{82}$.

Figure 8a is the EPR spectrum (room temperature) for the isolated $Sc_3@C_{82}$ sample degassed by bubbling helium through the sample, All 22 lines ($I = {}^7/_2$, three equivalent Sc atoms) are readily observed for this concentrated sample, and the hyperfine coupling (6.8 G) is in agreement with previous studies.[7,8,22,25] An EPR spectrum (Figure 8b) of a more dilute $Sc_3@C_{82}$ sample was also obtained at a lower temperature (220 K). The higher resolution at lower temperatures clearly indicates the absence of $Sc@C_{82}$ (eight-line pattern) and also provides improved resolution consistent with the results of Bandow et al.[4]

CONCLUSION

On-line EPR provides a selective, noninvasive detector for monitoring HPLC separations of certain metallofullerenes with an odd number of encapsulated atoms (e.g., $M@C_{2n}$ and $M_3@C_{2n}$). Specifically, on-line HPLC-EPR has been employed to monitor $Y@C_{82}$ and $Sc_3@C_{82}$ in chromatographic

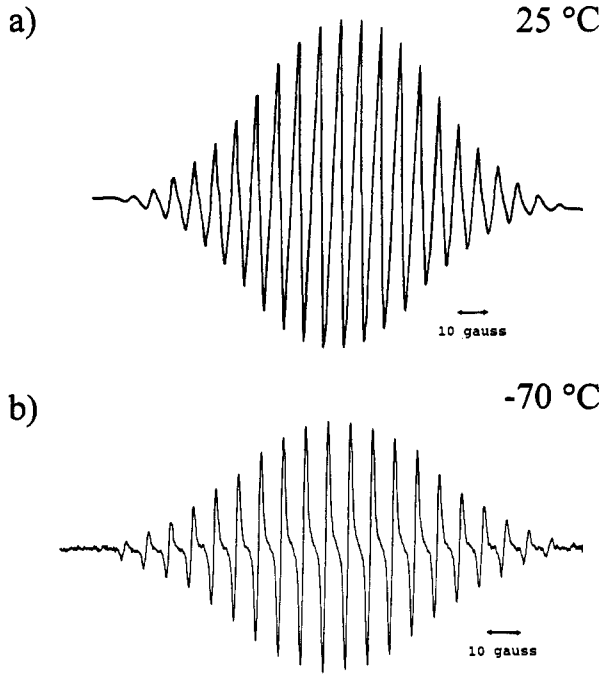

Figure 8. (a) Off-line EPR spectrum of purified peak 6 ($Sc_3@C_{82}$) in decalin, *one scan*, 9.63 GHz, sweep time 500 s, and 25 °C. (b) Off-line EPR spectrum of purified $Sc_3@C_{82}$ (less concentrated than above) in decalin, one scan, 9.63 GHz, sweep time 500 s, and −70 °C.

separations of the metallofullerene fraction from the dominant empty-cage fullerenes (C_{60}, C_{70}, etc.) using a preparative (polystyrene) column. A second stage of chromatographic separation utilizing a highly selective Buckyclutcher column has also monitored $Y@C_{82}$ and $Sc_3@C_{82}$ by utilizing on-line EPR detection. The isolation and characterization of $Sc_3@C_{82}$ has been successfully achieved with the on-line HPLC-EPR approach. In additions, the toluene/decalin solvent system provides a reasonably high sample loading for chromatographic separations. The adaptability of the HPLC-EPR technique to anaerobic conditions is clearly advantageous in the investigation and chromatography of labile and/or air-sensitive metallofullerene samples.

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