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Efficient HPLC Purification of Endohedral Metallofullerenes on a Porphyrin–Silica Stationary Phase

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Endohedral metallofullerenes are among the most fascinating materials to emerge from ongoing efforts to produce and characterize closed-cage carbon compounds. Compounds of the general formula $M@C_n$ (M = group IIIA and rare earth metals) have been prepared;[1–6] however, the difficulty in isolating them from the matrix of empty fullerenes in which they are produced has been a major impediment to full characterization of these unique compounds. In this paper, we describe the use of a new tetraphenylporphyrin–silica support material for efficient HPLC purification of the metallofullerenes from crude soot extract.

Metallofullerenes are typically produced in a standard carbon arc reactor using a composite anode which contains graphite and the target metal or its oxide or carbide.[1–6] Extraction of the resulting soot produces a mixture of empty fullerenes along with some of the more robust metallofullerenes, notably $M@C_{82}$,[1,4–9] $M_2@C_n$ (n = 74, 80, 82, 84),[3–6] and $M_3@C_{82}$.[2,3] The small quantities of metallofullerenes generated, coupled with their similarity in size and shape to empty fullerenes, makes chromatographic purification a challenge. To date, most HPLC purifications for metallofullerenes have involved two stages, such as the methods reported by Shinohara et al.[7] for Sc_2C_n and Kikuchi et al.[10] for $La@C_{82}$. More recently, Yamamoto et al.[11] reported the first successful single-stage isolation of $La@C_{82}$ on a 20 mm × 250 mm 2-(1-pyrenyl)ethylated silica column, using toluene as the mobile phase. However, the $La@C_{82}$ fraction needed to be reinjected to enhance purity.

To enhance the efficiency in purifying large quantities of metallofullerenes it would be desirable to perform high-yield single-stage HPLC separations using mobile phases that consist of very strong solvents for fullerenes (e.g., pure toluene, carbon disulfide, *p*-xylene, etc.).[12] Toward this goal, we recently demonstrated that columns packed with a (*p*-carboxyphenyl)-triphenylporphyrin–silica (CPTPP) stationary phase (metalated or unmetalated) offer the best selectivity to date for separating C_{60} and C_{70} with pure toluene as the eluent (α = 4.8).[13] These columns have also proven to be useful in the shape-selective separation of polycyclic aromatic hydrocarbons (PAHs).[14] In both cases, the unique selectivity appears to result from strong π–π interactions between the solutes and the silica-bound porphyrins. We now take advantage of this selectivity to efficiently purify $La@C_{82}$ and $Y@C_{82}$ from crude soot extract with a toluene/carbon disulfide mobile phase (3:1). As reported previously,[15] the porphyrin–silica stationary phase was synthesized and packed into a 4.6 mm × 250 mm HPLC column. Metallofullerene soot was prepared by the arc vaporization of graphite/metal oxide rods in a standard arc reactor.[1] The soot was first Soxhlet extracted for 24 h with toluene and then Soxhlet extracted for an additional 24 h with pyridine. The pyridine extract was dried and partially redissolved in toluene, producing a mixture enriched in metallofullerenes. This mixture was injected through the HPLC system. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and electron paramagnetic resonance (EPR) measurements were used to characterize the various bands that eluted from the column.

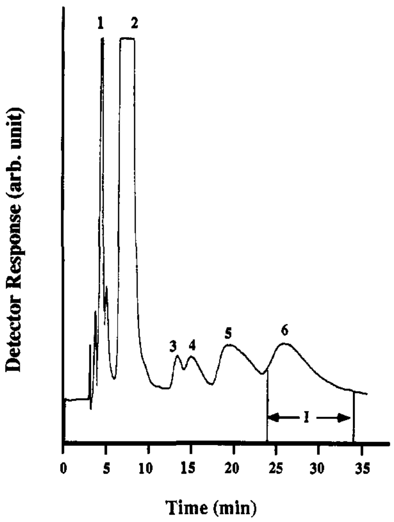

Figure 1. HPLC chromatogram of the crude extract containing $La@C_{82}$ on a 4.6 mm × 250 mm Zn–CPTPP–silica column. Mobile phase: 25% CS_2/75% toluene. Injection volume: 150 μL. Flow rate: 1 mL/min. Detection: UV at 482 nm (0.150 AUFS). Temperature: ambient. Peak identity: (1) C_{60}, (2) C_{70}, (3) C_{76}, (4) C_{78}, (5) C_{82} and C_{84}, and (6) $La@C_{82}$. Fraction I was collected as shown.

Figure 1 shows a typical chromatogram obtained using the Zn(II)–CPTPP–silica column after the injection of lanthanofullerene soot extract. Even with a relatively small and inefficient analytical column (4.6 mm i.d. × 250 mm length; 800 theoretical plates) and a rather strong fullerene solvent mixture as the mobile phase (75% toluene/25% CS_2), a fairly good separation of $La@C_{82}$ from empty fullerenes was achieved within a reasonable time frame (30 min). Although the extract was enriched in higher fullerenes and metallofullerenes, C_{60} (band 1) and C_{70} (band 2) are still the predominant components in the extract. As shown, the $La@C_{82}$ (band 6) elutes after C_{82} and C_{84} (band 5). Fraction I originating from band 6 was collected and concentrated. The EPR and mass spectra of this fraction (see Figure 2) clearly confirm that band 6 contains relatively pure $La@C_{82}$ along with minor amounts of C_{90} and $La@C_n$. Similar results were obtained with a pyridine extract of Y-containing soot, with $Y@C_{82}$ eluting at about 25 min. The retention behavior of $La@C_{82}$ and $Y@C_{82}$ observed on the CPTPP–silica column correlates with a previous

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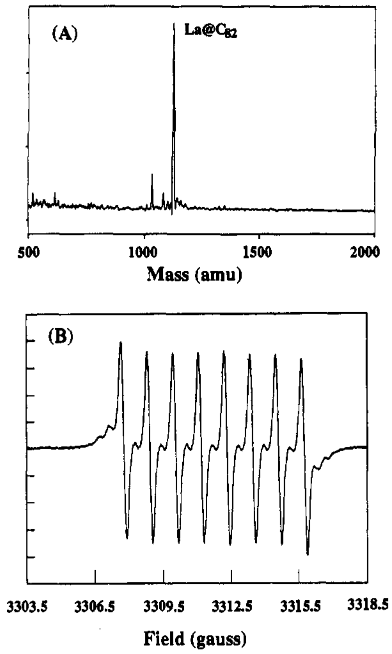

Figure 2. MALDI-TOF mass spectrum (A) and X-band EPR spectrum (B) of fraction I of the chromatogram shown in Figure 1.

report[11] where La@C_{82} eluted between coeluted C_{84} and C_{86} bands and a C_{88} band on another π-acidic stationary phase (2-(1-pyrenyl)ethylated silica) with toluene as the mobile phase. However, in contrast to data reported in ref 11, no further purification procedure or reinjection of the initial M@C_{82} fraction was performed prior to obtaining the MS and EPR data reported here (Figure 2). Clearly, efficient large-scale purifications of M@C_{82} as well as other metallofullerenes should be possible on the CPTPP–silica stationary phase.

The ability to efficiently separate metallofullerenes on CPTPP–silica columns appears to stem from the three-dimensional relationship between the immobilized porphyrin and the fullerenes. It is known from single-crystal X-ray studies[17] that the four phenyl rings of tetraphenylporphyrin are perpendicular to the porphyrin ring. Thus, as shown in Figure 3, the immobilized tetraphenylporphyrin possesses a cavity with approximately the same diameter as a typical fullerene cage ($<C_{100}$). It is, therefore, likely that π electrons on the fullerene surface can interact not only with the porphyrin ring through face-to-face π–π interactions but also with the meso phenyl rings through face-to-edge π–π interactions. Consequently, simultaneous face-to-face and face-to-edge π–π interactions between fullerenes and the immobilized tetraphenylporphyrin probably play a key role in the unique selectivity and strong retention observed with the porphyrin–silica stationary phase.

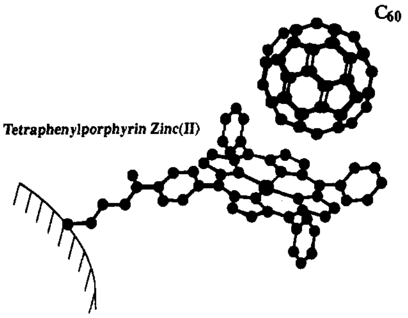

Figure 3. Three-dimensional structures of immobilized zinc(II) tetraphenylporphyrin (ZnTPP) and buckminsterfullerene (C_{60}).

The retention position of La@C_{82} and Y@C_{82} relative to C_{82} on the CPTPP–silica column substantiates the notion that π basicity of a given fullerene along with its size (i.e., larger surface interaction area) controls the affinity of fullerenes for the immobilized porphyrin. Indeed, XPS and EPR studies suggest that a substantial charge transfer from the metal atom to the fullerene cage occurs in metallofullerenes and that these compounds can formally be expressed as M^{3+}@$C_{82}{}^{3-}$.[2,18] This means that the presence of lanthanum within the C_{82} cage increases the number of π electrons on the C_{82} surface by 3, a 3.7% increase in π-electron density. In terms of the π electrons on the fullerene surface, La@C_{82} is an electronic analog of the hypothetical C_{85} structure, not C_{82}, with an electron density somewhat greater than that of C_{85}. This may explain why the M@C_{82} species are retained on the porphyrin column (as well as on the previously reported 2-(1-pyrenyl)ethylated-silica column[11]) longer than C_{82} and C_{84}. In addition, metallofullerenes may possess a substantial dipole moment which could also contribute to the longer retention times for La@C_{82} and Y@C_{82} compared to C_{82}.

The true single-stage separation of La@C_{82} and Y@C_{82} from pyridine extracts, as reported here, demonstrates the unique chemical selectivity exhibited by employing π-electron-rich tetraphenylporphyrin–silica stationary phases in chemical purifications. Because the CPTPP column used was rather inefficient ($N = 800$), it is likely that further improvements in fullerene and metallofullerene separations can be achieved by increasing the amount of porphyrin immobilized on the silica, altering the structure of the immobilized porphyrin species (i.e., by adding electron withdrawing substituents to *meso*-phenyl groups, etc.), by using smaller diameter silica particles, and by more effectively packing columns with the resulting porphyrin–silica stationary phases (increasing the number of theoretical plates). Such efforts are currently in progress in these laboratories.

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