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Isolation and Characterization of Pr@C$_{82}$ and Pr$_2$@C$_{80}$

Junqi Ding and Shihe Yang*

Contribution from the Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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Abstract: Pr@C$_{82}$ and Pr$_2$@C$_{80}$ have been isolated with a purity of >99.0% by an efficient solvent extraction procedure, followed by HPLC separation. UV−VIS−NIR spectra of the metallofullerenes were measured in the wavelength range from 300 to 2100 nm. The X-ray photoelectron spectra of Pr@C$_{82}$ and Pr$_2$@C$_{80}$ suggest that the Pr atoms inside the carbon cages all exist in a cationic form represented by Pr^{3+}.

I. Introduction

During the last few years, a wealth of information has been generated on endohedral metallofullerenes.[1] However, most studies were focused on metallofullerenes involving Sc, Y, La, and Gd due to the successful isolation of these species in milligram quantities.[2−20] In order to provide a more global picture of the electronic structure of these exotic molecules, it is necessary to investigate other congeners of metallofullerenes, e.g., metallofullerenes with other metal atoms encaged. This would provide important information as to how the properties of metallofullerenes change as a function of the identity of their respective metal atoms. The barrier prohibiting researchers from investigating the family of endohedral metallofullerenes with different encapsulated metal atoms perhaps lies in the lack of an efficient isolation method.

We have recently reported on a method of high-yield separation of Ce@C$_{82}$ and Nd@C$_{82}$ and their spectroscopic characterization.[21,22] Ce and Nd were both shown to possess an oxidation state of +3.[21,22] This new method also allowed separation and characterization of a new dimetallofullerene Ce$_2$@C$_{80}$,[23] which was detected in early laser desorption mass spectrometry experiments.[24] In this contribution, we will report on the separation of Pr@C$_{82}$ and Pr$_2$@C$_{80}$ as well as the spectroscopic probe of these metallofullerenes including UV−VIS−NIR absorption spectroscopy and X-ray photoelectron spectroscopy (XPS). We are aware that some preliminary studies have already been reported on the crude extract of Pr$_m$@C$_{2n}$ by techniques such as mass spectrometry,[20,25] and UV−VIS−NIR of isolated Pr@C$_{82}$ has been measured.[20] However, isolation of Pr$_2$@C$_{80}$ has not been carried out and the physical properties of both Pr@C$_{82}$ and Pr$_2$@C$_{80}$ remain largely uncharacterized.

II. Experimental Section

The metallofullerene separation procedures used in this study were described previously.[21] Only a brief description is given here. Soot-containing metallofullerenes was produced by the standard arc vaporization method using a composite anode which contains graphite and praseodymium oxide (Pr$_6$O$_{11}$) in an atomic ratio of $\mathrm{Pr/C} \approx 0.01$. The composite rod was then subjected to a DC contact-arc discharge as an

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* To whom correspondence should be addressed.

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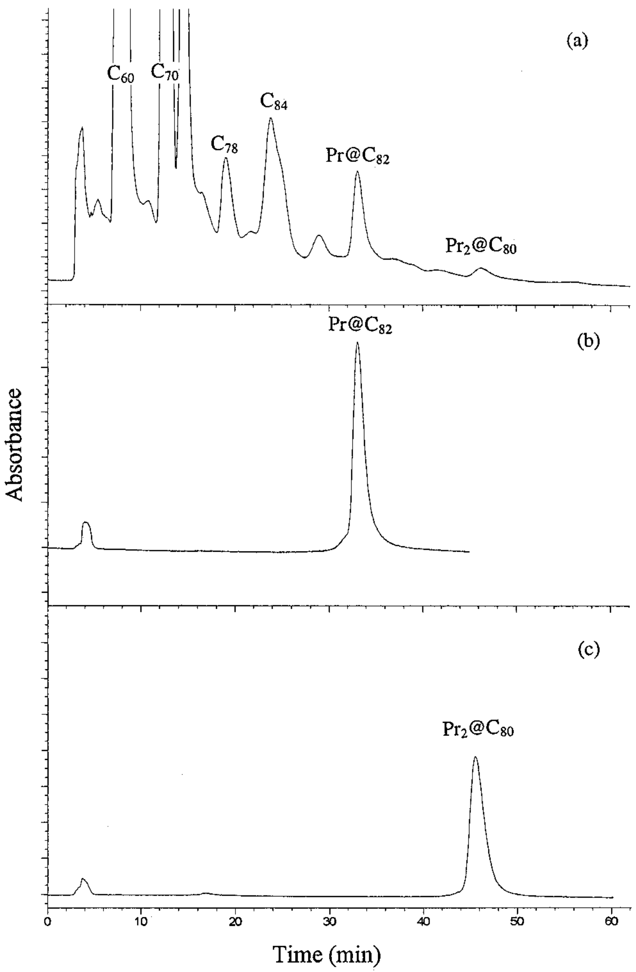

Figure 1. (a) HPLC chromatogram of the redissolved crude DMF extract from the metallofullerene soot; (b) HPLC chromatogram of $Pr@C_{82}$ collected from (a) (note that only one clean peak appears corresponding to $Pr@C_{82}$); (c) HPLC chromatogram of $Pr_2@C_{80}$ collected from (a) (note that only one clean peak appears corresponding to $Pr_2@C_{80}$). The peaks at 3.5 min in (a) and (b) are due to the solvent. 330-nm UV detection was used.

anode under an He atmosphere of 50 Torr. The raw soot was collected and extracted in a Soxhlet extractor using *N*,*N*-dimethylformamide (DMF, 99.9%, BDH) at its boiling temperature for 8 h. After removing the DMF by evaporation, a black powder (~1% of the raw soot) was obtained. The soluble fraction was dissolved in toluene and injected into an HPLC. A buckyprep column (4.6 mm × 250 mm; Cosmosil, Nacalai Tesque Inc.) similar to the PYE column was used, and the mobile phase was toluene. The injection volume was 1 mL and the elution rate was 1 mL per min. The purity of $Pr@C_{82}$ and $Pr_2@C_{80}$ collected from HPLC was checked by DCI negative ion mass spectrometry (Finnigan TSQ7000) as shown in Figure 2. Judging from the mass spectrum and the HPLC profile in Figure 1, the purity of $Pr@C_{82}$ and $Pr_2@C_{80}$ is estimated to be >99%.

The UV−VIS−NIR absorption spectrum of $Pr@C_{82}$ and $Pr_2@C_{80}$ in toluene solution was recorded with a Perkin-Elmer spectrometer (Lambda 19). A 1-cm-thick cuvette was used for the sample cell, and the resolution of the spectrometer was set at 1 nm. For XPS study, we prepared films of $Pr@C_{82}$ and $Pr_2@C_{80}$ on a polycrystalline Au substrate. To obtain a clean Au surface, we used town gas flame to pretreat a gold foil. After heating, the Au foil was dipped into methanol and dried in N_2 gas. Several drops of a concentrated metallofullerene solution in toluene were transferred to the Au foil. The evaporation of the solvent left uniform films of $Pr@C_{82}$ and $Pr_2@C_{80}$ on the substrate in an area of ~0.5 cm^2. These films were dried and washed with *n*-hexane. XPS measurements were taken using monochromatized Al Kα radiation ($h\nu = 1486.6$ eV) with an energy resolution of ~0.6 eV.

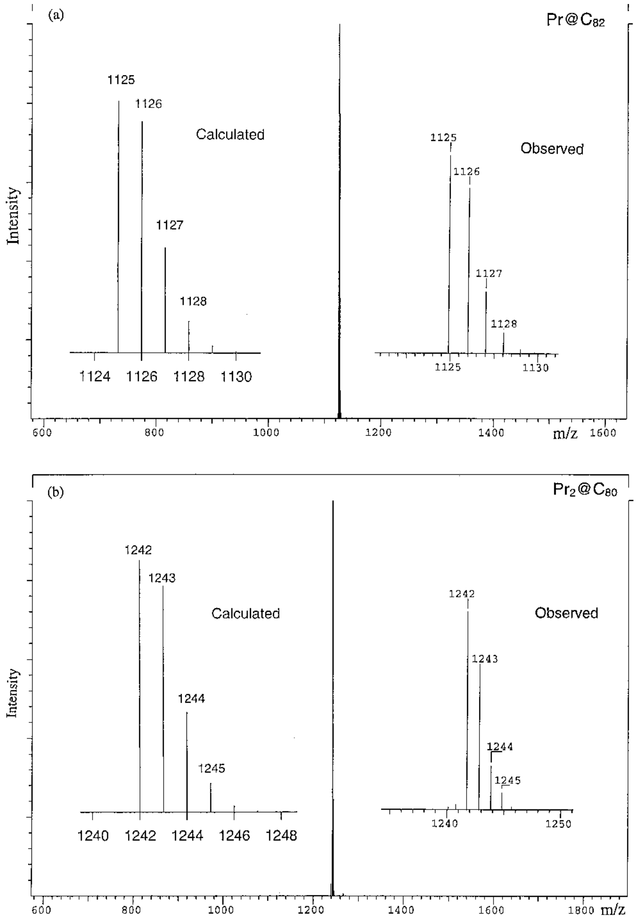

Figure 2. (a) Methane DCI negative ion mass spectrum of the sample corresponding to Figure 1b after HPLC separation; (b) methane DCI negative ion mass spectrum of the sample corresponding to Figure 1c after HPLC separation. The insets show the calculated and observed isotopic distributions for $Pr@C_{82}$ and $Pr_2@C_{80}$.

III. Results and Discussion

Shown in Figure 1a is an HPLC profile for the crude extract of the fullerene soot redissolved in toluene. A prominent peak and a relatively small peak immediately after it appear at the elution time of 33.2 and 45.6 min, respectively. These two peaks are absent for samples produced from arc-discharge of a pure carbon electrode. The prominent peak apparently corresponds to $Pr@C_{82}$ while the small peak is identified as $Pr_2@C_{80}$, as verified by mass spectrometry shown in Figure 2 which will be described below.

Figure 1b shows an HPLC profile of the collected fraction of $Pr@C_{82}$ in Figure 1a. The spectrum shows a single clean peak due to $Pr@C_{82}$, indicating the efficiency of our single-step isolation. An HPLC profile of the collected fraction of $Pr_2@C_{80}$ is shown in Figure 1c. With the type of column we are using, these two metallofullerenes can be readily separated.

Figures 2a and 2b show the mass spectra of the fractions of $Pr@C_{82}$ and $Pr_2@C_{80}$ collected after a single-step HPLC. It is remarkable that both spectra contain only a single envelope corresponding to $Pr@C_{82}$ and $Pr_2@C_{80}$, respectively. Isotopic ratio analysis is also shown along with the mass spectra in Figures 2a and 2b. Overall, the calculated isotopic distribution and the observed isotopic distribution are quite consistent. It should be pointed out that the calculated relative peak intensity for $m + 1$ (m is the smallest mass in the envelope) is larger than the observed relative peak intensity for both metallofullerenes. This is also true in the case of $Ce@C_{82}$ and $Ce_2@C_{80}$.[21,23] Such deviations seem systematic and may be related to the data treatment of mass spectra. The isotopic

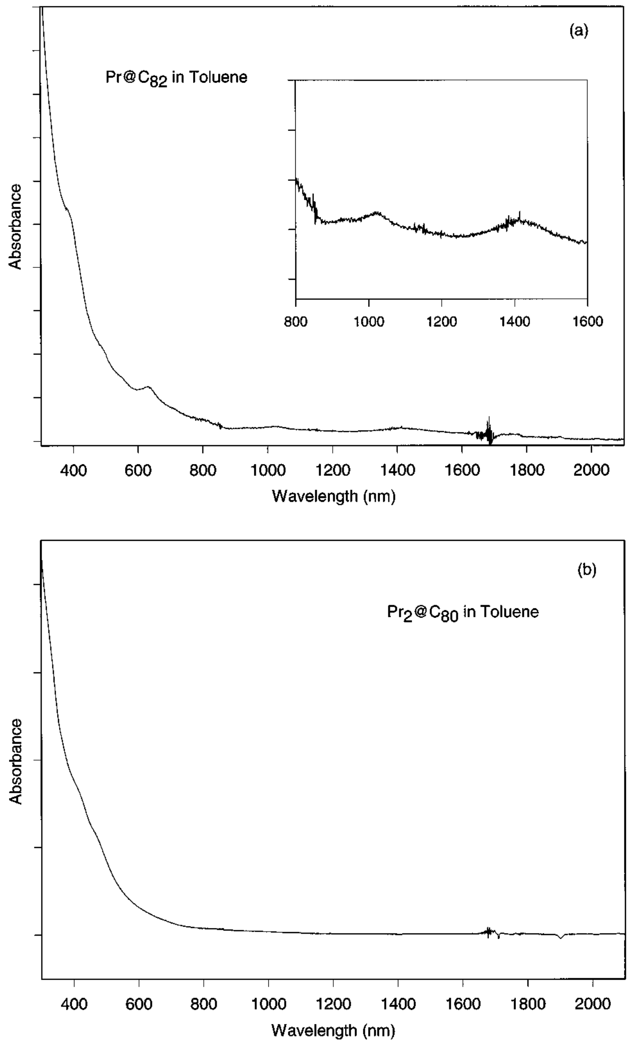

Figure 3. (a) UV−VIS−NIR absorption spectrum of Pr@C_{82} in toluene solution; (b) UV−VIS−NIR absorption spectrum of Pr_2@C_{80} in toluene solution.

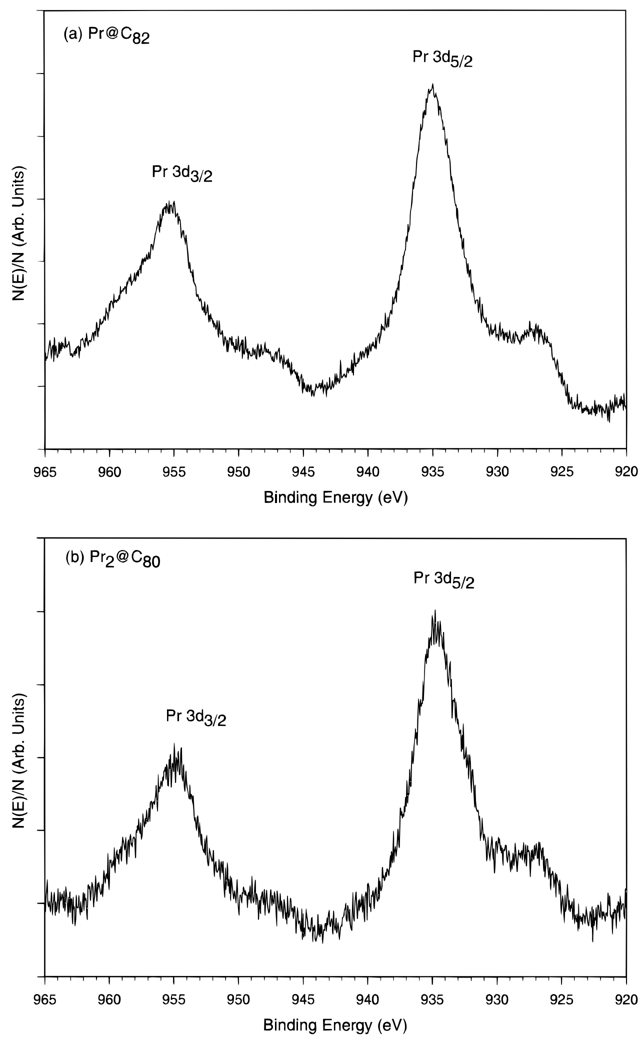

Figure 4. (a) XPS pattern of Pr@C_{82} on gold substrate in the core level region of Pr 3d; (b) XPS pattern of Pr_2@C_{80} on gold substrate in the core level region of Pr 3d.

analysis confirms that the peaks in Figures 1b and 1c are indeed pure Pr@C_{82} and Pr_2@C_{80}, respectively. The intensity of the most abundant empty fullerene C_{60} is quite low in both Figures 2a and 2b, suggesting that the purity of Pr@C_{82} and Pr_2@C_{80} is >99%. Experiments on other rare earth elements obtained similar results. Details on the separation and characterization of these metallofullerenes have been reported elsewhere.[21−23,26]

Figure 3a shows the UV−VIS−NIR absorption spectrum of Pr@C_{82}. The spectrum exhibits salient absorption peaks at 379, 632, 1020, and 1414 nm (broad). Overall, the spectrum manifests a remarkable similarity to that of other metallofullerenes with the formula of M@C_{82} (M = rare earth element) in the sense that all the peaks have a one-to-one correspondence.[1c,10−12] The similarity in the absorption spectra of the metallofullerenes M@C_{82} strongly suggests that the spectral features are derived from the cage with an open-shell electronic structure and that the cage accepts roughly the same amount of electrons from the metals for the metallofullerene family M@C_{82}, i.e., endohedral metallofullerenes have the isoelectronic structure M^{3+}@$C_{82}{}^{3-}$.

Figure 3b shows the UV−VIS−NIR absorption spectrum of Pr_2@C_{80} in a wavelength range of 300−2100 nm. Analogous to that of Ce_2@C_{80},[23] the spectrum of Pr_2@C_{80} exhibits a monotonically decreasing absorption coefficient with increasing wavelength, without well-defined sharp features. The relative featureless spectrum is in contrast to those of the empty fullerenes (ref 27) as well as single-metal-atom metallofullerenes.[1c] Whetten *et al.* proposed that in La_2@C_{80} the isomeric structure of C_{80} has I_h symmetry, resulting in an overall symmetry of D_{2h}.[24] This is supported by a recent theoretical calculation.[28] In this theoretical work, it was demonstrated that La_2@C_{80} can be formally represented by $La^{3+}{}_2$@$C_{80}{}^{6-}$, forming a closed-shell electronic structure with a HOMO-LUMO gap larger than those of M@C_{82} (M = rare earth metal). As will be shown below by XPS, C_{80} in Pr_2@C_{80} also acquires six electrons from the two Pr's, presumably forming the same electronic structure as that of C_{80} in La_2@C_{80}. The closed-shell electronic structure of $C_{80}{}^{6-}$ in Pr_2@C_{80} is likely to account for the absence of any evident NIR absorption peak in the spectrum of Pr_2@C_{80}.

Figures 4a and 4b show the XPS pattern of Pr@C_{82} and Pr_2@C_{80} in the region of Pr's $3d_{3/2}$ and $3d_{5/2}$ core levels. One immediately notices the striking similarity of the XPS patterns of the two metallofullerenes, which clearly indicates that the Pr's in both Pr@C_{82} and Pr_2@C_{80} have the same electronic structure, namely Pr^{3+} as will be shown below. Both core level features show a strong peak and a weak shoulder. Our analysis

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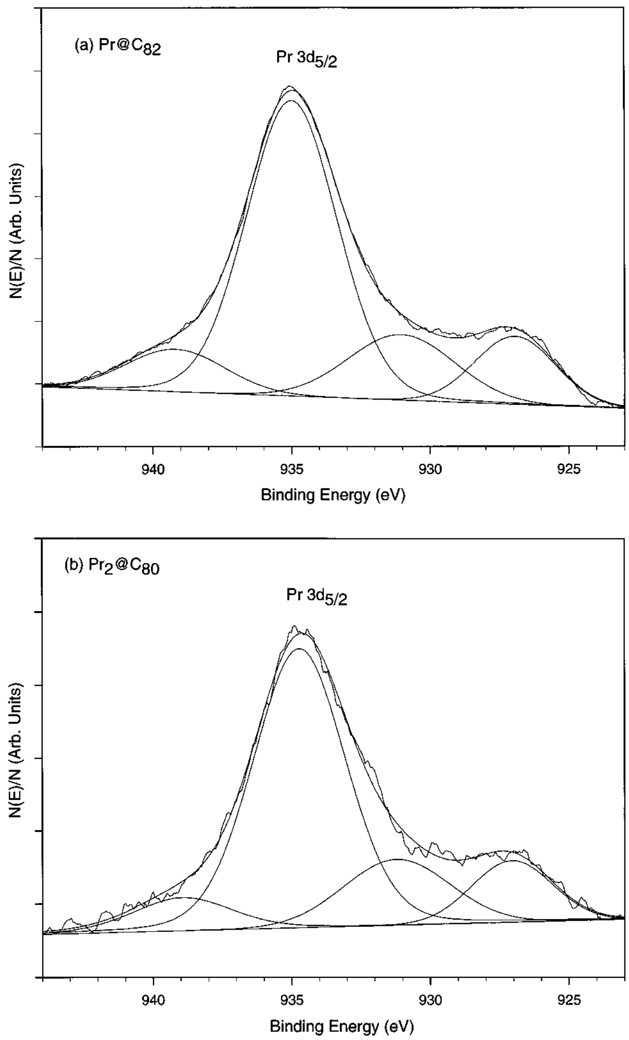

Figure 5. (a) Blow-up of Figure 4a to show the XPS of Pr 3d$_{5/2}$; (b) blow-up of Figure 4b to show the XPS of Pr 3d$_{5/2}$. The smooth line is a fitting of the spectral peaks.

shows that four peaks are required to fit each core level feature. For the clarity of our discussion, only the 3d$_{5/2}$ features along with their four-peak fittings are shown in Figures 5a and 5b. It is plausible that the main peaks (Pr@C$_{82}$: 934.98 eV; Pr$_2$@C$_{80}$: 934.76 eV) correspond to the screening by only the surrounding fullerene orbitals while the small peaks (Pr@C$_{82}$: 931.14 eV; Pr$_2$@C$_{80}$: 931.64 eV) originate from screening by charge transfer to the 4f shell.[29] These two peaks (the main peak plus a satellite peak) are remarkably similar to those of the XPS of praseodymium trihalides in terms of the peak location and shape;[30] the corresponding XPS peak positions of PrCl$_3$ are 935.2 and 931.3 eV, respectively. The only obvious difference lies in the intensity ratio of the major peak to the satellite peak which is somewhat smaller for PrCl$_3$ in comparison to those for Pr@C$_{82}$ and Pr$_2$@C$_{80}$. This difference in intensity ratio is likely to originate from the fact that the fullerene cages possess a smaller electronegativity than the Cl atom does as demonstrated for Ce@C$_{82}$ by us[22] and for La@C$_{82}$ by Weaver *et al.*[16] Therefore, the combination of the main peak and the satellite peak in the XPS patterns of Pr@C$_{82}$ and Pr$_2$@C$_{80}$ again strongly suggests an oxidation state of +3 for Pr in both metallofullerenes.

However, in marked contrast to the XPS pattern of PrCl$_3$, two extra peaks on the higher and lower binding energy sides respectively are evidently observable in the XPS of Pr@C$_{82}$ (higher energy: 939.15 eV; lower energy: 927.08 eV) and Pr$_2$@C$_{80}$ (higher energy: 938.79 eV; lower energy: 927.28 eV). It is reasonable to attribute the two extra peaks to a further "shake-down" feature on the lower binding energy side and a "shake-up" feature on the higher binding energy side given the fact that the fullerene cages are excellent multielectron acceptors and fairly good multielectron donors. In other words, the extra peak at the lower binding energy corresponds to a two-electron transfer from the fullerene cage to the 4f shell, and that at the higher binding energy is due to a one-electron transfer from the 4f shell to the fullerene cage. The final states of Pr in the XPS process are therefore 3d^{9}4f^1 and 3d^{9}4f^4 respectively for the higher binding energy peak and the lower binding energy peak. It is interesting to note that such XPS patterns with two extra shoulders in comparison with that of MCl$_3$ (M = rare earth metal) have been observed for Nd@C$_{82}$ (ref 22) but not for La@C$_{82}$,[16] Ce@C$_{82}$,[21] and Ce$_2$@C$_{80}$.[23] In the absence of any additional information, one could speculate that such XPS patterns with two extra shoulders are related to the availability of 4f electrons. An alternative explanation for the extra peaks is that they could be attributed to the presence of oxygen in the sample. Further work (e.g., prepare the metallofullerene sample by sublimation in vacuum) is needed to resolve the question.

It should be mentioned that in a previous study,[31] Bartl *et al.* proposed that Pr@C$_{82}$ can be formally represented by Pr^{4+}@C$_{82}{}^{4-}$ based on their experimental finding that Pr@C$_{82}$ is EPR silent. Our experiments and that of Ishibashi *et al.*[25] also show the negative results of the EPR response of Pr@C$_{82}$. However, the UV−VIS−NIR spectrum and XPS of Pr@C$_{82}$ all indicate that its electronic conformation is Pr^{3+}@C$_{82}{}^{3-}$. One could argue that the absence of an EPR signal in Pr@C$_{82}$ does not necessarily warrant an electronic conformation of Pr^{4+}@C$_{82}{}^{4-}$; Pr^{3+}@C$_{82}{}^{3-}$ could also be EPR silent if a strong spin−spin coupling exists between the spin of the carbon cage and that of the metal cation. Evidence for such spin−spin interaction has been provided by Boonman et al. in their EPR experiment on Er$_m$@C$_{2n}$ at low temperature.[32]

IV. Summary and Conclusions

We have reported on the successful isolation of two new endohedral metallofullerenes Pr@C$_{82}$ and Pr$_2$@C$_{80}$ with a purity of >99.0% by an efficient solvent extraction procedure, followed by HPLC separation. Their UV−VIS−NIR absorption spectra and XPS results have been presented. The UV−VIS−NIR absorption spectrum of Pr@C$_{82}$ resembles that of La@C$_{82}$, Y@C$_{82}$, Gd@C$_{82}$, and Ce@C$_{82}$, while the UV−VIS−NIR absorption spectrum of Pr$_2$@C$_{80}$ resembles that of Ce$_2$@C$_{80}$, exhibiting a monotonically decreasing function of wavelength without any sharp absorption features. The XPS patterns of both metallofullerenes are almost identical and show that the Pr atoms in both metallofullerenes are in the form of Pr^{3+}.

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