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Electrochemical Survey: The Effect of the Cage Size and Structure on the Electronic Structures of a Series of Ytterbium Metallofullerenes

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Abstract: The electrochemical properties of a series of metallofullerenes with different cages, namely, Yb@C_{74}(II), Yb@C_{76}(I, II), Yb@C_{78}, Yb@C_{80}, Yb@C_{82}(I, II, III), and Yb@C_{84}(II, III, IV), have been systematically investigated by cyclic and differential pulse voltammetry experiments for the first time. This article discusses the electronic structures of these metallofullerenes based on the results from these experiments. From previous electrochemical work and the above discussion, it is concluded that the nondegenerate LUMO is a common characteristic of the electronic structures of the higher fullerenes and monometallofullerenes. In addition, the effect of the cage on the electronic structure and properties of the metallofullerene is estimated from the plot of the reduction potential versus the carbon number of the metallofullerene. This estimation shows that usually the electronic structure and properties of the metallofullerene vary with cage size and structure. The cage structure is of particular importance for determining the electronic structure and properties. Moreover, an explanation concerning the abundance and stability of C_{82}-based trivalent monometallofullerenes is given from an electronic structural standpoint.

Keywords: electrochemistry · electronic structure · metallofullerenes · voltammetry · ytterbium

Introduction

Metallofullerenes have been attracting much attention since the first report of this kind of material, namely, La@C_{82},[1] and great effort has been made in their synthesis and in structural investigations.[2] Characterization of metallofullerenes by electrochemical methods is of special importance because their electrochemical behavior provides a direct measure of their electronic structure. In fact, the electrochemical measurements of La@C_{82} and Y@C_{82} were performed as soon as the two metallofullerenes were isolated in a pure form.[3–5] In the following years, the electrochemical behaviors of some other metallofullerenes were reported, most of which concern C_{82}-based metallofullerenes, that is, M@C_{82} (in this article, M = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu), Sc_3@C_{82}, Tm@C_{82}, and Sm@C_{82}.[6–13] The difference in electrochemical properties of M@C_{82} with different metals is very small because the metals donate three electrons to the fullerene cage in each case, resulting in similar electronic structures. Several metallofullerenes based on other fullerene cages, such as Eu@C_{74}, Tm@C_{78}, and La_2@C_{80}, were also characterized by means of electrochemistry.[14,15] The previous electrochemical investigations, most of which focused on the metallofullerenes with different encapsulated metals and the same cages, demonstrated that the metal had only a subtle influence on the electronic structure of the metallofullerene. However, the electronic structures of metallofullerenes with different cages, and therefore the effect of the cage, have not been discussed as there is no systematic electronic structural data of metallofullerenes that are based on the same encaged metals with different cages.

Here we report the electrochemical behaviors of a series of ytterbium-containing metallofullerenes, namely, Yb@C_{74}(II), Yb@C_{76}(I, II), Yb@C_{78}, Yb@C_{80}, Yb@C_{82}(I, II, III), and Yb@C_{84}(II, III, IV), providing a full electrochemical data set of metallofullerenes based on different cages for the first time. We then discusses the electronic structures of these metallofullerenes and the effect of the cage on their electronic properties.

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains the CV and DPV curves of the blank solutions, Yb@C_{74}(II), Yb@C_{78}, and Yb@C_{80}, and additional discussions on the electronic structures of these metallofullerenes.

Results and Discussion

The voltammograms of the ytterbium metallofullerenes: The cyclic voltammetries (CV) and differential pulse voltammetries (DPV) of Yb@C_{74}(II), Yb@C_{76}, Yb@C_{78}, Yb@C_{80}, Yb@C_{82}, and Yb@C_{84} were conducted in the potential range of -3.0 to 1.3 V. No oxidation peaks were observed in this range. However, there has been an oxidation peak observed for M@C_{82} in previous studies.[8–11] It was attributed to the fact that the encapsulated metal M donates three electrons to the C_{82} cage, resulting in an unpaired electron in the HOMO. However, the encapsulated ytterbium atom donates two electrons to the surrounding fullerene cage, forming a closed-shell electronic configuration. In addition, it seems that the solvent used has a profound effect on the metallofullerene-based oxidations. In this work and our previous work (MeCN/$C_6H_5CH_3$ used as the solvent), the oxidations of Yb@C_{2n} and Sm@C_{82} were not observed. But, according to the report by Dunsch, two irreversible oxidations were recorded for Eu@C_{74} when *o*-dichlorobenzene was used as the solvent.[11,13] However, Dunsch et al. also failed to record the oxidation of Tm@C_{82} even with *o*-dichlorobenzene as the solvent.[12] This indicated the relatively bigger HOMO–LUMO gaps of Tm@C_{82}. In contrast, the metallofullerene-based reductions are easier to observe. In the present work, we succeeded in recording four or five reduction peaks for each isomer. The reduction processes were reversible even after several recycles. Note that the peak that has a potential around -2.2 V is assigned to an impurity from the toluene used as the HPLC solvent. Fortunately, the impurity does not interfere with the redox processes of the metallofullerenes. For a detailed discussion see the Supporting Information.

The voltammograms of Yb@C_{76}, Yb@C_{82}, and Yb@C_{84} are presented in Figures 1, 2, and 3, respectively. The others (e.g., Yb@C_{74}, Yb@C_{78}) are presented in the Supporting Information. To the best of our knowledge, it is the first time that the electrochemical behaviors of metallofullerenes based on C_{76} and C_{84} cages have been reported. In Figure 1, four reduction peaks are clearly observed. The signal of the impurity is also obvious due to the low concentration of the two metallofullerenes. But in the curves of the more abundant metallofullerenes (thus higher concentration), the impurity peak is barely visible, as seen in Figures 2 and 3. It is noteworthy that there are five reduction peaks recorded in the potential window for each isomer of Yb@C_{82} and Yb@C_{84}. The fifth of which should be attributed to the metallofullerene because the corresponding region is featureless in the voltammogram of a blank solution containing the impurity (see the lower curve in Figure S1a in the Supporting Information). Therefore, it is clear that the higher metallofullerenes, that is, Yb@C_{82} and Yb@C_{84}, accept the fifth electron easier than the lower metallofullerenes, such as Yb@C_{74}(II), Yb@C_{76}, Yb@C_{78}, and Yb@C_{80}. The voltammograms of Yb@C_{84}(IV) are not well-defined due to a low current intensity and limited sample. For the same reason, we failed to record the voltammograms of Yb@C_{74}(I) and Yb@C_{84}(I).

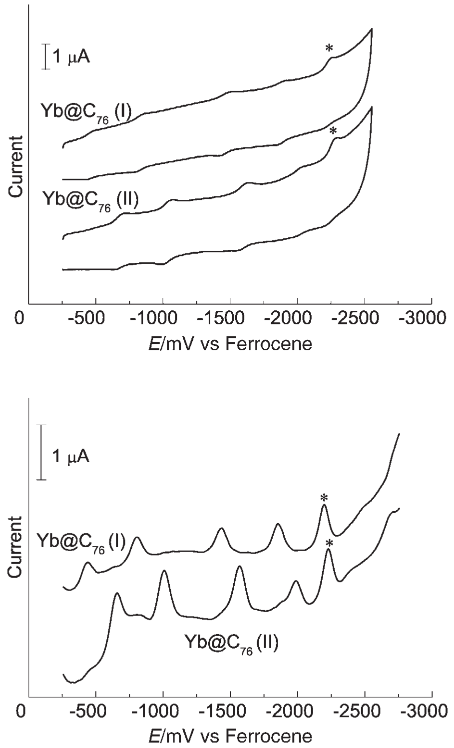

Figure 1. Cyclic (top) and differential pulse (bottom) voltammograms of Yb@C_{76}(I, II) in MeCN/$C_6H_5CH_3$ (1:4 v/v) containing $(n\mathrm{Bu})_4\mathrm{NClO}_4$ (0.1 M). The peak ($E=-2.23$ V) labeled with an asterisk is assigned to an impurity.

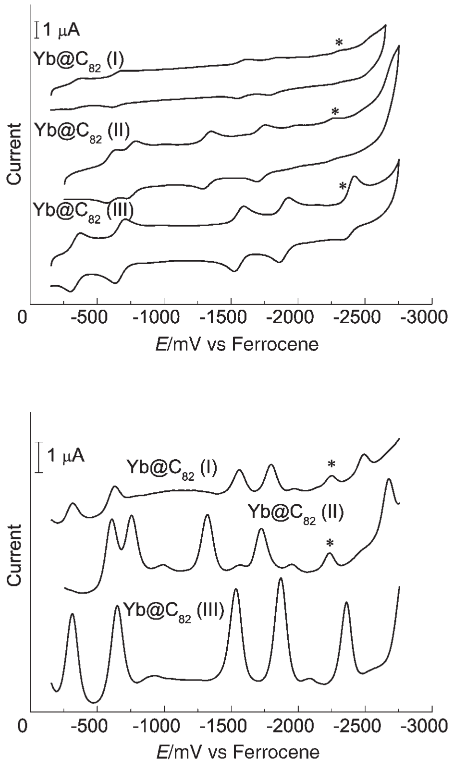

Figure 2. Cyclic (top) and differential pulse (bottom) voltammograms of Yb@C_{82}(I, II, III) in MeCN/$C_6H_5CH_3$ (1:4 v/v) containing $(n\mathrm{Bu})_4\mathrm{NClO}_4$ (0.1 M). The peak ($E=-2.23$ V) labeled with an asterisk is assigned to an impurity.

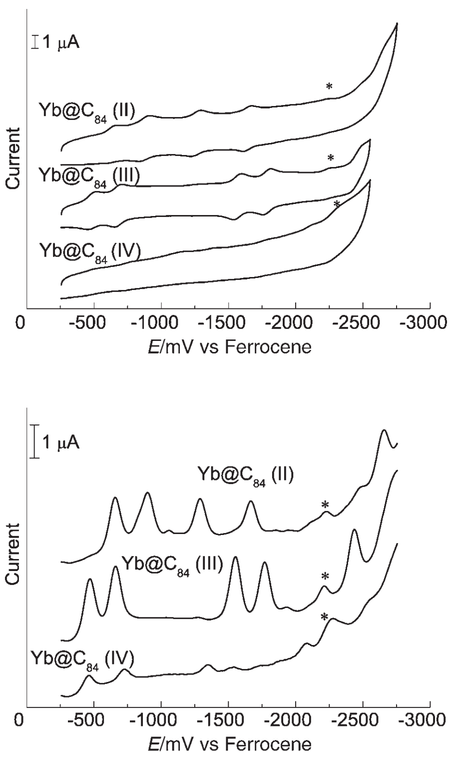

Figure 3. Cyclic (top) and differential pulse (bottom) voltammograms of Yb@C_{84}(II, III, IV) in MeCN/$C_6H_5CH_3$ (1:4 v/v) containing $(n\mathrm{Bu})_4NClO_4$ (0.1 M). The peak ($E=-2.23$ V) labeled with an asterisk is assigned to an impurity.

As mentioned above, there are quite a few reports of reversible electrochemical processes occurring for C_{82}-based metallofullerenes. We now present a comparison of the voltammograms between these previously reported metallofullerenes and Yb@C_{82}.

The cyclic voltammograms of Yb@C_{82}(I, II, III) (Figure 2) are similar to those of Tm@C_{82}(B, A, C) to some extent.[12] But the peaks in the curves of our specimens are better defined due to relatively higher purities. Their similar voltammograms indicate that they have the same electronic structures and molecular symmetries. The molecular symmetries of Tm@C_{82}(B, A, C) were determined as C_s, C_2, and C_{2v}, respectively, by using NMR spectroscopy.[16] Therefore, one can deduce that the symmetries of Yb@C_{82}(I, II, III) should be C_s, C_2, and C_{2v}, respectively. In our earlier report, the UV/Vis/near-IR absorption spectra of Yb@C_{82}(I, II, III) were given, which were very similar to those of Tm@C_{82}(B, A, C).[17] It indicated their similar electronic structures and molecular symmetries. This is in good agreement with the above conclusion. In addition, it is noteworthy that both the first reductions of Yb@C_{82}(I, III) and those of Tm@C_{82}(B, C) occur very easily. In fact, the first reduction potentials of Yb@C_{82}(I, III) are the most positive among those of the ytterbium metallofullerenes, indicating their low-lying LUMOs. Moreover, the electrochemical behaviors of Yb@C_{82}(I) and Yb@C_{82}(III) are almost identical, indicating that the frontier MOs of the two isomers are similar and nearly isoenergetic.

From the voltammograms of the M@C_{82} metallofullerenes, one can see that the first reduction occurs readily and is followed by a substantial electrochemical gap (about 1.0 V). This gap is comparable to those between the second and third reduction potentials of Yb@C_{82}(I, III) (0.93 and 0.89 V, respectively). In addition, the first, second, and third reduction potentials of the M@C_{82} metallofullerenes are close to the second, third, and fourth potentials, respectively, of Yb@C_{82}(I, III). This means that the Yb@C_{82}^{-}(I, III) isomers are isoelectronic and isoenergetic with the M@C_{82} metallofullerenes. This result is a further indication of the divalent state of the encaged ytterbium atom.

The features of the electronic structures of the ytterbium metallofullerenes: The first four reduction potentials of all the ytterbium metallofullerenes are listed in Table 1. Both the half-cell potentials and DPV peak potentials are reported.

Table 1. Half-cell potentials[a] and DPV peak potentials[b] [V] of the Yb metallofullerenes versus Fc/Fc$^+$.

		$^{red}E_1$	$^{red}E_2$	$^{red}E_3$	$^{red}E_4$
Yb@C_{74}(II)	DPV	−0.49	−0.93	−1.52	−1.95
	CV	−0.52	−0.96	−1.55	−1.99
Yb@C_{76}(I)	DPV	−0.44	−0.81	−1.43	−1.86
	CV	−0.46	−0.83	−1.46	−1.89
Yb@C_{76}(II)	DPV	−0.66	−1.01	−1.56	−1.99
	CV	−0.68	−1.02	−1.59	-2.01
Yb@C_{78}	DPV	−0.45	−0.77	−1.44	−1.79
	CV	−0.48	−0.79	−1.46	−1.83
Yb@C_{80}	DPV	−0.56	−0.94	−1.55	−1.90
	CV	−0.57	−0.95	−1.55	−1.90
Yb@C_{82}(I)	DPV	−0.32	−0.63	−1.56	−1.80
	CV	−0.33	−0.65	−1.58	−1.81
Yb@C_{82}(II)	DPV	−0.61	−0.76	−1.32	−1.72
	CV	−0.60	−0.76	−1.33	−1.73
Yb@C_{82}(III)	DPV	−0.31	−0.65	−1.53	−1.87
	CV	−0.33	−0.67	−1.56	−1.90
Yb@C_{84}(II)	DPV	−0.66	−0.90	−1.29	−1.67
	CV	−0.63	−0.88	−1.26	−1.64
Yb@C_{84}(III)	DPV	−0.47	−0.66	−1.55	−1.77
	CV	−0.49	−0.68	−1.57	−1.79
Yb@C_{84}(IV)[c]	DPV	−0.46	−0.72	−1.34	−1.54

[a] The voltammetry experiments were conducted in MeCN/$C_6H_5CH_3$ (1:4 v/v) containing 0.1 M $(n\mathrm{Bu})_4NClO_4$; scan rate: 50 mV s^{-1}. [b] Pulse amplitude: 50 mV; pulse width: 50 ms; pulse period: 200 ms; scan rate: 10 mV s^{-1}. [c] The half-cell potentials of Yb@C_{84}(IV) are absent due to the relatively small currents produced.

Inspection of the potentials listed in Table 1 shows that there is a relatively large potential gap between the second and third reduction peaks of each voltammogram. For the Yb@C_{82} and Yb@C_{84} isomers, the gaps between the fourth and fifth reduction peaks are also remarkable. It means that the four reversible couples appear to be arranged in sets of two ($^{red}E_1$ and $^{red}E_2$, $^{red}E_3$ and $^{red}E_4$). It is widely accepted that ytterbium metallofullerenes possess closed-shell electronic structures rather than half-filled two-fold degenerate

HOMOs. Therefore, one can come to the conclusion that each isomer of these ytterbium metallofullerenes (so-called divalent metallofullerenes) possesses a nondegenerate LUMO and LUMO+1. Previous studies of M@C_{82} also showed that the so-called trivalent metallofullerenes possess nondegenerate LUMOs (except for Lu@C_{82} due to its low purity and the presence of other isomers).[3–5,8–10] In addition, both theoretical calculations and electrochemical measurements showed that the higher fullerenes (C_{76}, C_{78}, C_{82}, C_{84}) usually possess nondegenerate LUMOs too (except for D_2-C_{84}).[18–22] On the basis of this prior work and our experimental results, one can conclude that the nondegenerate LUMO is a common feature of the higher fullerenes and monometallofullerenes. The electronic structure with the nondegenerate LUMO seems to be uniquely favorable for the formation of the higher fullerene and monometallofullerene. This provides a clue in the study of the formation mechanism, which is still an unsolved puzzle after almost two decades of research on this kind of materials.

To demonstrate the electronic structures of the ytterbium metallofullerenes more clearly, the molecular-orbital diagrams are presented in Figure 4. The relative energy levels of the LUMO and LUMO+1 are estimated on the basis of ${}^{red}E_1$ and ${}^{red}E_3$, respectively, because ${}^{red}E_1$ and ${}^{red}E_3$ approximately simulate these two energy levels. The orbital levels of C_{76}, C_{2v}-C_{78} and D_{2d}-C_{84} are also shown for comparison, which were similarly estimated from their ${}^{red}E_1$ and ${}^{red}E_3$ potentials (as shown in Table 2).[21,23] There are some reports concerning these fullerenes which give their calculated absolute energy levels.[24–26] According to these calculations, the LUMO energy of C_{2v}-C_{78} is lower than that of C_{76} (0.056 and 0.086 hartree, respectively, predicted by using the SCF level of theory), but higher than that of D_{2d}-C_{84}. This is consistent with our estimated energy-level order. Therefore, it is believed that the orbital diagram (Figure 4) somewhat reflects the relative energy levels of the ytterbium metallofullerenes and adds some useful information to the corresponding calculation that is currently absent.[27]

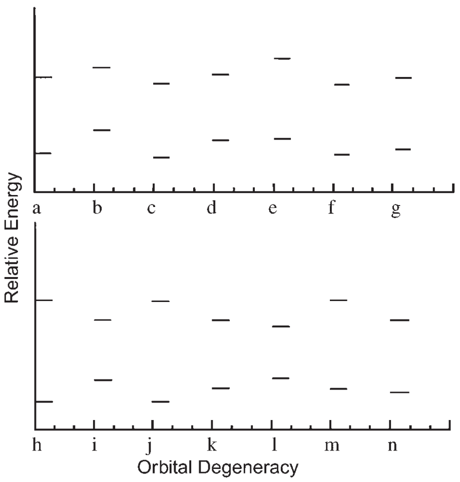

Figure 4. The LUMO (bottom line in each case) and LUMO+1 (top line in each case) relative energy levels of C_{76}, C_{2v}-C_{78}, D_{2d}-C_{84}, and the ytterbium metallofullerenes a) Yb@C_{74}(II), b) C_{76}, c) Yb@C_{76}(I), d) Yb@C_{76}(II), e) C_{2v}-C_{78}, f) Yb@C_{78}, g) Yb@C_{80}, h) Yb@C_{82}(I), i) Yb@C_{82}(II), j) Yb@C_{82}(III), k) D_{2d}-C_{84}, l) Yb@C_{84}(II), m) Yb@C_{84}(III), and n) Yb@C_{84}(IV).

Table 2. Half-cell potentials [V] of C_{76}, C_{2v}-C_{78}, and D_{2d}-C_{84}.

	${}^{red}E_1$	${}^{red}E_3$	Ref.
C_{76}	−0.83	−1.68	[21]
C_{2v}-C_{78}	−0.72	−1.79	[21]
D_{2d}-C_{84}	−0.51	−1.34	[23]

The effect of the cage on the electronic structures and properties of the ytterbium metallofullerenes: By considering the reduction potentials of the metallofullerenes listed in Table 1, one can see that the cage structure has an obvious influence on the electronic structure of the metallofullerene. When the cages are isomeric, the metallofullerenes usually have remarkably different reduction potentials, indicating their different frontier MO energy levels. For example, the difference in the first reduction potential of Yb@C_{76}(I) and Yb@C_{76}(II) is as large as 0.22 V. Analogously, the reduction potential differences between the Yb@C_{82}(I, III) and (II) isomers and the Yb@C_{84}(II) and (III, IV) isomers are also remarkable. An exception to this trend is the reduction potentials of the Yb@C_{82}(I, III) isomers which are almost identical. It means that the two kinds of molecules, that is, C_s and C_{2v}, have similar electronic structures. In the same way, one can see that the Yb@C_{84}(III, IV) isomers also possess similar electronic structures.

The relative electron affinities (EAs) of the metallofullerenes can be estimated from their reduction potentials. Therefore, the EA_1 of the metallofullerenes varies with the cage size and structure. The EA_1s of the isomeric metallofullerenes are usually greatly different. This is consistent with the above discussion. We now compare the relative EA_1s of the metallofullerenes with those of the corresponding fullerenes. Under the same experimental conditions, the first reduction potentials of Yb@C_{76}(I, II) and Yb@C_{78} are much more positive than those of C_{76} (−0.83 V) and C_{78} (−0.72 V, C_{2v} isomer), respectively.[21] This means that Yb@C_{76}(I, II) and Yb@C_{78} are much stronger electron acceptors than C_{76} and C_{78}, respectively. Meanwhile, under almost the same experimental conditions (different supporting electrolytes were used), the first reduction potentials of the Yb@C_{84}(III, IV) isomers (−0.49 and −0.46 V, respectively) are very close to that of D_{2d}-C_{84} (−0.51 V) and are more positive than that of D_2-C_{84} (−0.67 V). The first reduction potential of Yb@C_{84}(II) (−0.66 V) is more negative than that of D_{2d}-C_{84} and almost identical to that of D_2-C_{84}.[23] This means that the Yb@C_{84}(III, IV) isomers are better electron acceptors than D_2-C_{84}, but Yb@C_{84}(II) is a weaker electron acceptor than D_{2d}-C_{84}. Metallofullerenes used to be considered as better electron acceptors than the corresponding fullerenes. However, from the above comparison one can see that metallofullerenes are possibly weaker electron acceptors than their fullerene counterparts due to the structural influence of the cage.

Figure 5 shows the successive peak gaps of the ytterbium metallofullerenes: Gap 1 represents the gap between the first and second reductions, gap 2 is for that between the second and third reductions, and gap 3 is for that between the last two reductions. As can be seen, generally gap 1 and gap 3 are close to each other because both of them originate from the Coulomb repulsion between an exotic electron and the unpaired electron occupying a single orbital. However, gap 2 of each isomer is bigger than gap 1 and gap 3. It is noteworthy that the gap 2 values of Yb@C_{82}(I, III) (C_s and C_{2v}, respectively) and Yb@C_{84}(III) (931, 884, and 891 mV, respectively) are remarkably bigger than the gap 2 values of the other metallofullerenes reported here. Because the gap 2 value can reflect the HOMO–LUMO gap of a trivalent monometallofullerene approximately, the above phenomenon shows that C_s-C_{82}- and C_{2v}-C_{82}-based and some C_{84}-based trivalent monometallofullerenes are stable whereas the other ones are not stable as such. As is well known, there are nine IPR (isolated pentagon rule) isomers for C_{82} and the C_2-(a) isomer is considered to be the most stable.[28] However, the stabilities of the C_{82} dianion and trianion are drastically different because of the changed electronic structures. Fowler and Manolopoulos predicted the special stability of C_{82}^{2-} with C_{2v} symmetry according to the Hückel calculations.[29,30] Laasonen et al. presented a similar result.[31] In addition, according to calculations by Nagase and Kobayashi, the C_{2v}, C_s(c), and C_2(c) cages are stable for C_{82}^{2-} and the C_{2v}, C_s(c), and C_{3v}(b) cages are stable for C_{82}^{3-}.[32] Therefore, one can see that the C_{2v} and C_s cages are the most stable for both C_{82}^{2-} and C_{82}^{3-}. This could explain the stabilities of C_s-C_{82}- and C_{2v}-C_{82}-based divalent and trivalent monometallofullerenes. Our above discussion is in good agreement with this result. In addition, the first reductions of the Yb@C_{82}(I, III) isomers occur most easily among all the ytterbium metallofullerenes. From this it can be deduced that compared with other fullerenes, C_s- and C_{2v}-C_{82} most easily accept three electrons donated from the metal in the synthetic process. Therefore, one can understand that C_s- and C_{2v}-C_{82}-based trivalent monometallofullerenes are much more abundant than those based on other cages (C_{74}, C_{76}, C_{78}, C_{80}, C_{84}) in the raw soot. It is an open question in metallofullerene chemistry as to why C_{82}-based monometallofullerenes are the most abundant and stable among the so-called trivalent monometallofullerenes (M@C_{60} and M@C_{70} are not taken into consideration).[33] Our discussion shows a reasonable explanation from an electronic structural standpoint.

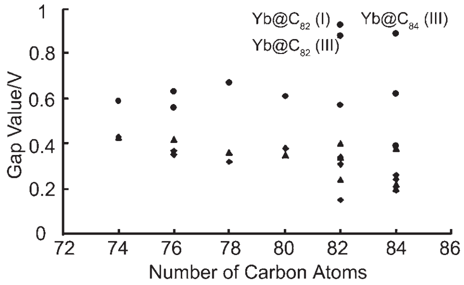

Figure 5. The successive reduction peak gaps of the Yb metallofullerenes. Gap 1 (◆) represents the gap between the first and second reductions, gap 2 (●) is for that between the second and third reductions, and gap 3 (▲) is for that between the third and fourth reductions.

Conclusion

The electrochemical behaviors of a series of ytterbium metallofullerenes based on different fullerene cages have been investigated systematically for the first time.

The electronic structures of the ytterbium metallofullerenes are discussed with respect to the voltammograms. On the basis of prior electrochemical work and our electronic structural discussion, it is proposed that an electronic structure with a nondegenerate LUMO is uniquely favorable for the formation of the higher fullerenes and monometallofullerenes. This provides a clue in the formation mechanism study of this kind of materials.

Moreover, the effect of the cage on the electronic properties of the metallofullerene is examined. Our discussion reveals that generally the electronic structure and properties of the metallofullerene vary with cage size and structure. It is concluded that the cage structure plays an important role in determining the electronic properties of the metallofullerene. Due to the influence of the cage, a metallofullerene can be a weaker electron acceptor than the corresponding fullerene. This adds new insight to the concept of the relative activities of fullerenes and metallofullerenes. In addition, an explanation about the abundance and stability of C_{82}-based trivalent monometallofullerenes is given in our discussion.

Experimental Section

The ytterbium metallofullerenes were synthesized by using an improved DC arc-discharged method and isolated in isomer-free form by using a multistep HPLC method, as described in our earlier report.[17]

A BAS-100B electrochemical analyzer was used to record cyclic voltammograms and differential pulse voltammograms of the ytterbium metallofullerenes. All the experiments were conducted in MeCN/$C_6H_5CH_3$ (1 and 4 mL, respectively) containing $(n\mathrm{Bu})_4\mathrm{NClO}_4$ (0.1 M) with a three-electrode configuration, a glassy carbon disk (4 mm in diameter) as the working electrode, a platinum wire as the auxiliary electrode, and an Ag wire coated with AgCl as the reference electrode. HPLC grade CH_3CN was used (from Fluka). Tetrabutylammonium perchlorate $(n\mathrm{Bu})_4\mathrm{NClO}_4$ (electrochemical grade) was obtained from Fluka. All the experiments were performed in an ice–water bath because the potential window can be somewhat extended at low temperatures. Cyclic voltammograms were recorded at 50 $\mathrm{mV\,s^{-1}}$ and DPV were obtained at 10 $\mathrm{mV\,s^{-1}}$ by using a pulse amplitude of 50 mV, a pulse width of 50 ms, and a pulse period of 200 ms. The electrochemical cell was purged with high purity nitrogen for about 10 min before each measurement. All the potentials in this report are with respect to the ferrocene/ferrocenium redox couple.

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