

C₈₀ Encaging Four Different Atoms: The Synthesis, Isolation, and Characterizations of ScYErN@C₈₀Ning Chen,^{†,‡} Er-Yun Zhang,^{†,‡} and Chun-Ru Wang^{*,†}*Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100080, China, and Graduate School of CAS, Beijing, China**Received: May 16, 2006; In Final Form: June 8, 2006*

The synthesis, isolation, and spectroscopic characterizations of an endohedral fullerene with four heteroatoms encapsulated (ScYErN@C₈₀) are reported for the first time. The isomeric structure and electronic properties of this molecule are studied by various spectrometry methods such as high-performance liquid chromatography (HPLC), laser desorption time-of-flight (LD-TOF) mass spectroscopy, cyclic voltammetry, Fourier transform infrared (FTIR) spectroscopy, and visible-near infrared (vis-NIR) absorption spectroscopy. The carbon cage of ScYErN@C₈₀ is assigned as *I_h*-C₈₀, and the four-membered ScYErN cluster is suggested to rotate rapidly inside the fullerene cage. Six electrons are transferred from the nuclear cluster ScYErN to the fullerene cage, which leads to a closed-shell electronic structure of the *I_h*-C₈₀ and results in excellent stability of this molecule.

Introduction

For many years, endohedral fullerenes have attracted great interest due to the potential to obtain new spherical molecules by encapsulating various species inside fullerene cages.¹ Up to now, dozens of endohedral fullerenes^{2–5} with 1–6 encaged atoms or clusters have been reported, for example, La@C₈₂,⁶ La₂@C₈₀,⁷ Sc₂C₂@C₈₄,⁸ and Sc₂C₄@C₈₀,⁹ and more new species are being continuously reported. Extensive applications^{10–19} are revealed for endohedral fullerenes in the fields of optics, electronics, medicine, material sciences, and so forth.

In 1999, the discovery of Sc₃N@C₈₀ led to an endohedral fullerene family known as trimetallic nitride template (TNT) endohedral fullerenes,²⁰ which are famous due to their relative higher yields compared with other endohedral fullerenes. For TNT fullerenes, it was revealed that the carbon cages are mainly C₈₀, C₇₈, and C₆₈, and the encaged metals are flexible among Sc, Y, Lu, Gd, Er, Ho, and so forth.^{21–27} As the electronic properties of endohedral fullerenes depend not only on the carbon cages but also on the encaged species, TNT fullerenes containing one nitrogen atom and three alterable encaged metal atoms provide a prototype model for exploring how the encaged moieties influence the properties of endohedral fullerenes. Herein, we report the first synthesis, isolation, and spectroscopic characterizations of ScYErN@C₈₀ in which four heteroatoms are encapsulated in the C₈₀ cage.

Experimental Section

The sample was prepared by the Krätschmer–Huffman arc-burning method under a 98% He/1% N₂ atmosphere at 300 Torr. A fine powder mixture consisting of Sc/Ni alloy, Y/Ni alloy,

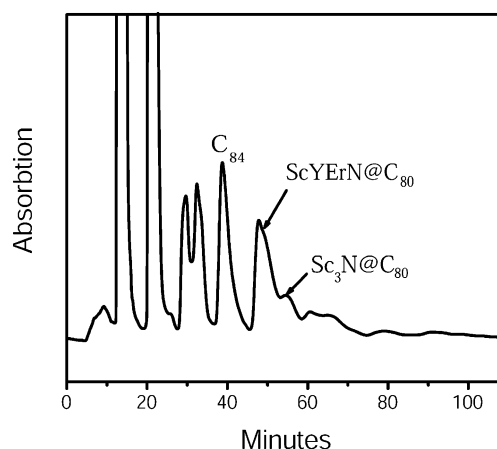


Figure 1. First stage HPLC profile of the soot extract by employing a Buckyprep column ($\Phi 20 \times 250$ mm, $12 \text{ mL} \cdot \text{min}^{-1}$ toluene flow rate, and UV detection at 310 nm), which separates fullerenes and endohedral fullerenes based on their different sizes.

Er/Ni alloy, and the graphite was pressed to make the Sc/Y/Er/C composite rods. The molar ratio of the four elements (Sc/Y/Er/C) is 1:1:1:36. The as-produced soot was Soxhlet-extracted by toluene for 24 h, and multistage recycling high-performance liquid chromatography (HPLC) was employed to isolate and purify the ScYErN@C₈₀. Two complementary columns, that is, Cosmosil Buckyprep and Cosmosil Buckyprep-M, were used with toluene eluent.

For the first HPLC stage, as shown in Figure 1, the Buckyprep column was used to separate fullerenes and endohedral fullerenes according to their size. Figure 2 is the mass spectrum of the ScYErN@C₈₀-containing fraction (retention times of 45–52 min) that contains also empty fullerenes C₈₈–C₉₂ and other TNT endohedral fullerenes, for example, Y₃N@C₈₀, Sc₂YN@C₈₀, ScY₂N@C₈₀, ScEr₂N@C₈₀, Er₂YN@C₈₀, and ErY₂N@C₈₀.

* Corresponding author. Phone and fax: (+86)10-62652120. E-mail: crwang@iccas.ac.cn.

[†] Institute of Chemistry, Chinese Academy of Sciences (CAS).

[‡] Graduate School of CAS.

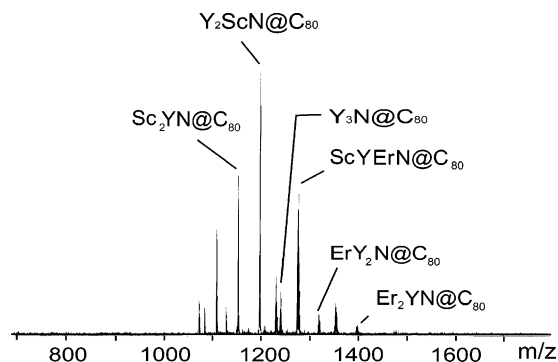


Figure 2. MALDI-TOF mass spectrum of the TNT-fullerene-containing fraction collected between 45 and 52 min in Figure 1.

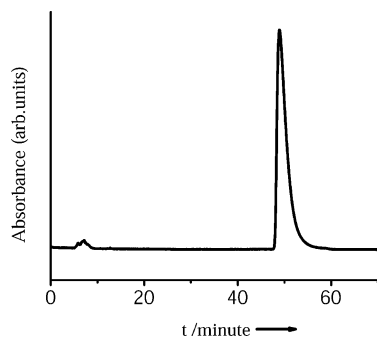


Figure 3. HPLC chromatogram of the purified ScYErN@C₈₀ on a Φ20×250 mm Buckyprep column (1 mL injection volume, toluene flow rate of 12 mL·min⁻¹).

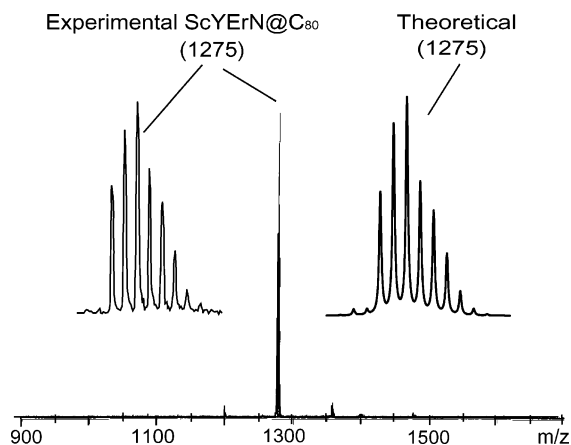


Figure 4. MALDI-TOF mass spectrum of the purified ScYErN@C₈₀.

Buckyprep-M is similar to the Buckyclutsch column in nature which separates endohedral fullerenes from fullerenes by the difference in molecular polarity, so in HPLC stage 2, the Buckyprep-M column was employed to remove empty fullerenes C₈₈–C₉₂ from TNT endohedral fullerenes. In HPLC stage 3, the mixture of TNT fullerenes collected in stage 2 were injected into the Buckyprep column again and recycling HPLC was performed. ScYErN@C₈₀ was separated and purified thoroughly from Y₃N@C₈₀, ScEr₂N@C₈₀, Er₂YN@C₈₀, Sc₂YN@C₈₀, and ScY₂N@C₈₀ in this stage. It should be mentioned that the retention time of ScYErN@C₈₀ is very close to that of Sc₂YN@C₈₀ and ScY₂N@C₈₀, so HPLC stage 3 may be repeated several times until a high purity of the ScYErN@C₈₀ is confirmed by both a single peak appearing in the HPLC profile (Figure 3), and a single peak showing in the mass spectrum (Figure 4) of the purified sample. Moreover, the left inset of Figure 4 shows the measured isotopic distribution of the purified ScYErN@C₈₀ which is quite consistent with that

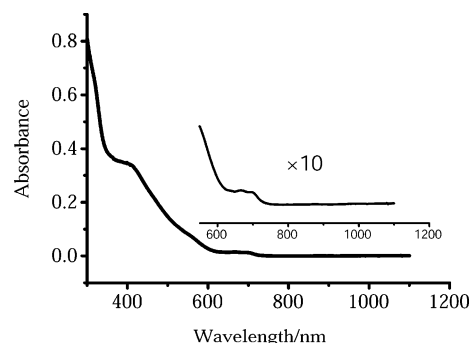


Figure 5. vis-NIR absorption spectrum of the purified ScYErN@C₈₀.

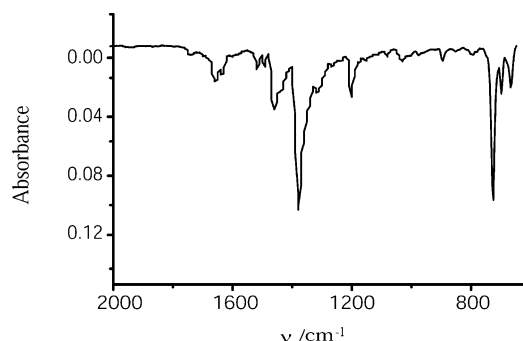


Figure 6. FTIR spectrum of the purified ScYErN@C₈₀ (500 accumulations, 2 cm⁻¹ resolution).

of the theoretical simulation, further confirming the isolation of ScYErN@C₈₀. Around 1 mg of ScYErN@C₈₀ was prepared from ~100 mg of fullerene extract for further spectroscopic characterizations.

Results and Discussion

The purified ScYErN@C₈₀ sample shows a reddish-brown color in toluene. Figure 5 is the visible-near infrared (vis-NIR) spectrum of ScYErN@C₈₀, which has a major absorption peak at ~403 nm. In fact, the main features of the spectrum closely resemble those of other TNT fullerenes such as Sc₃N@C₈₀,²⁸ Y₃N@C₈₀,²⁹ and Gd₃N@C₈₀,²⁴ suggesting that this molecule shares also the I_h-C₈₀ cage as those previously studied Sc₃N@C₈₀, Y₃N@C₈₀, and Gd₃N@C₈₀, and the electronic structure is (ScYErN)⁶⁺@C₈₀⁶⁻. This result confirms Campanera's theoretical prediction that³⁰ the closed-shelled electronic structure of C₈₀⁶⁻ plays a crucial role in the high stability and special electronic property of TNT fullerenes.

The vis-NIR spectrum of ScYErN@C₈₀ shows the absorption onset at ~755 nm, corresponding to an optical gap at 1.65 eV for this molecule. This value is larger than those of most known endohedral fullerenes,^{1,31–35} for example, 0.54 eV for La@C₈₂,³⁶ 0.7 eV for Ce@C₈₂(I),³¹ and 0.7 eV for Pr@C₈₂.³⁵ Therefore, it is safe to classify ScYErN@C₈₀ as a large band-gap fullerene.

The Fourier transform infrared (FTIR) spectrum of ScYErN@C₈₀ is shown in Figure 6. It clearly shows the fingerprint absorptions of I_h-C₈₀⁶⁻ between 1600 and 1200 cm⁻¹, confirming the (ScYErN)⁶⁺@C₈₀⁶⁻ electronic structure derived from the above vis-NIR absorption spectral analysis. Interestingly, the main vibrational bands of ScYErN@C₈₀ at 1379, 1460, and 1202 cm⁻¹ are downshifted several wavenumbers compared with that of the archetypal Sc₃N@C₈₀,²⁸ implying a slight distortion of the I_h-C₈₀ cage due to the relative larger size of the ScYErN cluster compared with that of Sc₃N.

Electrochemical cyclic voltammetry (CV) of ScYErN@C₈₀ was used to further characterize the molecular electronic

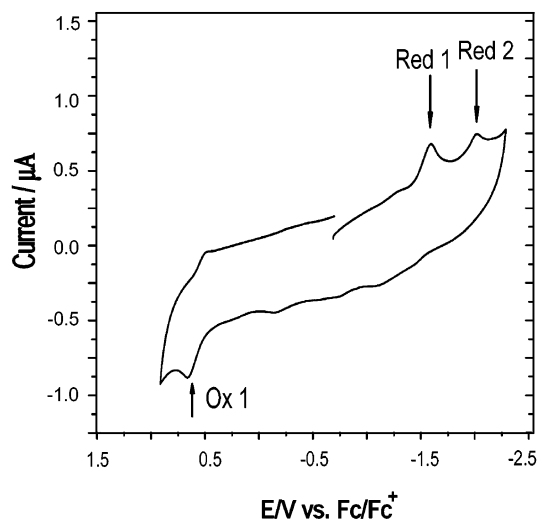


Figure 7. Cyclic voltammogram of the purified ScYErN@C₈₀ (*o*-dichlorobenzene, 0.1 mol·L⁻¹ TBABF, 50 mV·s⁻¹ scan rate). The redox stages of ScYErN@C₈₀ are labeled, and the formal redox potentials are marked by arrows.

property. The experiment was performed in *o*-dichlorobenzene solution with 0.1 mol·L⁻¹ tetrabutylammonium fluoroborate (TBABF) as the supporting electrolyte and with a 50 mV·s⁻¹ scan rate. The measured cyclic voltammogram is shown in Figure 7, in which all of the potentials refer to Fc/Fc⁺ (Fc = ferrocene). The cyclic voltammogram of ScYErN@C₈₀ showed two irreversible reduction steps at $E_{1/2}(\text{Red 1}) = -1.55$ V and $E_{1/2}(\text{Red 2}) = -1.97$ V and one reversible oxidation step at $E_{1/2}(\text{Ox 1}) = 0.64$ V, which is comparable to that of Sc₃N@C₈₀²⁸ with two irreversible reduction steps at -1.24 and -1.62 V and one reversible oxidation step at 0.62 V, respectively. In theory, the highest occupied molecular orbitals (HOMOs) of TNT fullerenes are mainly contributed from the I_h -C₈₀ cage, and the lowest unoccupied molecular orbitals (LUMOs) are from the hybridizations of M₃N and C₈₀.³⁷ ScYErN@C₈₀ and Sc₃N@C₈₀ share the same C₈₀ cage but different nuclear M₃N clusters, so it is reasonable for them to show a high resemblance in the oxidation part and large differences in the reduction part of their cyclic voltammograms.

Ever since Sc₃N@C₈₀ was isolated and characterized in 1999,²⁰ it has been found that the M₃N nuclei undergo rapid rotational motion within the C₈₀ cage, which helps to maintain the high molecular symmetry of the TNT fullerenes. ScYErN@C₈₀ closely resembles Sc₃N@C₈₀ in various spectroscopy features such as in the optical absorption spectra, the IR spectra, and the electrochemical cyclic voltammograms, strongly suggesting that the ScYErN nucleus rotates also inside the C₈₀ cage; otherwise, the strong electrostatic interactions between C₈₀ and ScYErN would seriously distort the C₈₀ cage and lead to large differences in their spectroscopic behavior. Note the large difference of Sc, Y, and Er in their atomic weights; it is a great challenge for both experimental and theoretical scientists to learn how the very asymmetrical ScYErN cluster balances itself while rapidly rotating within a uniform C₈₀ cage.

Conclusions

In conclusion, we have synthesized, isolated, and characterized the first endohedral TNT fullerene (ScYErN@C₈₀) in which four different atoms are incarcerated. Various spectroscopic characterizations such as HPLC, laser desorption time-of-flight mass spectroscopy (LD-TOF MS), cyclic voltammetry, vis-NIR

absorption spectroscopy, and FTIR spectroscopy confirmed the encapsulating nature of the ScYErN@C₈₀ molecule. Six electrons were assigned to transfer from the encapsulated species to the carbon cage I_h -C₈₀; that is, the molecular electronic structure is (ScYErN)⁶⁺@C₈₀⁶⁻.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (nos. 50225206, 90206045, 20121301, and 20573121), the Major State Basic Research Program of China "Fundamental Investigation on Micro-Nano Sensors and Systems based on BNI Fusion" (grant 2006CB300402), and the National Center for Nanoscience and Technology of China. The authors thank Dr. Louzhen Fan for her help in the electrochemical measurements.

References and Notes

- (1) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843–892.
- (2) Nagase, S.; Kobayashi, K.; Akasaka, T.; Wakahara, T. In *Fullerenes: Chemistry, Physics, and Technology*; Kadish, K. M., Ruoff, R. S., Eds.; John Wiley and Sons: New York, 2000; pp 395–436.
- (3) Olmstead, M. M.; Lee, T. M.; Duchamp, J. C.; Stevenson, S.; Marciu, D.; Dorn, H. C.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 900–903.
- (4) Kanai, M.; Porfyrakis, K.; Briggs, A. D.; Dennis, T. J. S. *Chem. Commun.* **2004**, *2*, 210–211.
- (5) Nikawa, H.; Kikuchi, T.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Rahman, G. M. A.; Akasaka, T.; Maeda, Y.; Yoza, K.; Horn, E.; Yamamoto, K.; Mizorogi, N.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 9684–9685.
- (6) Johnson, R. D.; Devries, M. S.; Salem, J.; Bethune, D. S.; Yannoni, C. S. *Nature* **1992**, *355*, 239–240.
- (7) Akasaka, T.; Nagase, S.; Kobayashi, K.; Walchli, M.; Yamamoto, K.; Funasaka, H.; Kako, M.; Hoshino, T.; Erata, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1643–1645.
- (8) Wang, C. R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 397–399.
- (9) Tan, K.; Lu X.; Wang, C. R. *J. Phys. Chem. B* **2006**, *110*, 11098–11102.
- (10) Guha, S.; Nakamoto, K. *Coord. Chem. Rev.* **2005**, *249*, 1111–1132.
- (11) Kobayashi, K.; Nagase, S. *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2002; p 99.
- (12) Martin, N.; Altable, M.; Filippone, S.; Martin, D. A.; Echegoyen, L.; Cardona, C. M. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 110–114.
- (13) Bolskar, R. D.; Benedetto, A. F.; Husebo, L. O.; Price, R. E.; Jackson, E. F.; Wallace, S.; Wilson, L. J.; Alford, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 5471–5478.
- (14) Toth, E.; Bolskar, R. D.; Borel, A.; Gonzalez, G.; Helm, L.; Merbach, A. E.; Sitharaman, B.; Wilson, L. J. *J. Am. Chem. Soc.* **2005**, *127*, 799–805.
- (15) Wilson, L. J.; Cagle, D. W.; Thrash, T. P.; Kennel, S. J.; Mirzadeh, S.; Alford, J. M.; Ehrhardt, G. J. *Coord. Chem. Rev.* **1999**, *192*, 199–207.
- (16) Kanbara, T.; Shibata, K.; Fujiki, S.; Kubozono, Y.; Kashino, S.; Urisu, T.; Sakai, M.; Fujiwara, A.; Kumashiro, R.; Tanigaki, K. *Chem. Phys. Lett.* **2003**, *379*, 223–229.
- (17) Kobayashi, S.; Mori, S.; Iida, S.; Ando, H.; Takenobu, T.; Taguchi, Y.; Fujiwara, A.; Taninaka, A.; Shinohara, H.; Iwasa, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8116–8117.
- (18) Nagano, T.; Kuwahara, E.; Takayanagi, T.; Kubozono, Y.; Fujiwara, A. *Chem. Phys. Lett.* **2005**, *409*, 187–191.
- (19) Nishikawa, T.; Kobayashi, S.; Nakanowatari, T.; Mitani, T.; Shimoda, T.; Kubozono, Y.; Yamamoto, G.; Ishii, H.; Niwano, M.; Iwasa, Y. *J. Appl. Phys.* **2005**, *97*, 104509–104514.
- (20) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maitra, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. *Nature* **1999**, *401*, 55–57.
- (21) Olmstead, M. M.; de Bettencourt-Dias, A.; Duchamp, J. C.; Stevenson, S.; Dorn, H. C.; Balch, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 12220–12226.
- (22) Iezzi, E. B.; Duchamp, J. C.; Fletcher, K. R.; Glass, T. E.; Dorn, H. C. *Nano Lett.* **2002**, *2*, 1187–1190.
- (23) Wolf, M.; Müller, K. H.; Skourski, Y.; Eckert, D.; Georgi, P.; Krause, M.; Dunsch, L. *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 290–293.
- (24) Krause, M.; Dunsch, L. *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 1557–1160.
- (25) Stevenson, S.; Phillips, J. P.; Reid, J. E.; Olmstead, M. M.; Rath, S. P.; Balch, L. *Chem. Commun.* **2004**, *24*, 2814–2815.

- (26) Stevenson, S.; Lee, H. M.; Olmstead, M. M.; Kozikowski, C.; Stevenson, P. A.; Balch, L. *Chem.—Eur. J.* **2002**, *8*, 4528–4535.
- (27) Campanera, J. M.; Heggie, M. I.; Taylor, R. *J. Phys. Chem. B* **2005**, *109*, 4024–4031.
- (28) Krause M.; Dunsch, L. *ChemPhysChem* **2004**, *5*, 1445–1449.
- (29) Dunsch, L.; Krause, M.; Noack, J.; Georgi, P. *J. Phys. Chem. Solids* **2004**, *65*, 309–315.
- (30) Campanera, J. M.; Bo, C.; Poblet, J. M. *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 7230–7233.
- (31) Fujiki, S.; Kubozono, Y.; Rikiishi, Y.; Urisu, T. *Phys. Rev. B* **2004**, *70*, 235421–235427.
- (32) Hosokawa, T.; Fujiki, S.; Kuwahara, E.; Kubozono, Y.; Kitagawa, H.; Fujiwara, A.; Takenobu, T.; Iwasa, Y. *Chem. Phys. Lett.* **2005**, *395*, 78–81.
- (33) Nuttall, C. J.; Hayashi, Y.; Yamazaki, K.; Mitani, T.; Iwasa, Y. *Adv. Mater.* **2002**, *14*, 293–296.
- (34) Hino, S.; Takahashi, H.; Iwasaki, I.; Matsumoto, K.; Miyazaki, T.; Hasegawa, S.; Kikuchi, K.; Achiba, Y. *Phys. Rev. Lett.* **1993**, *71*, 4261–4263.
- (35) Iizumi, K.; Uchino, Y.; Ueno, K.; Koma, A.; Saiki, K.; Inada, Y.; Nagai, K.; Iwasa, Y.; Mitani, T. *Phys. Rev. B* **2000**, *62*, 8281–8285.
- (36) Yamamoto, K.; Funasaka, H.; Takahashi, T. *J. Phys. Chem.* **1994**, *98*, 2008–2011.
- (37) Campanera, J. M.; Bo, C.; Olmstead, M. M.; Balch, A. L.; Poblet, J. M. *J. Phys. Chem. A* **2002**, *106*, 12356–12364.