

Controlled Synthesis of Subnano Pd Cluster Catalysts by Fine Tuning of Dendrimers

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ABSTRACT

We succeeded in fine control of the Pd cluster sizes in wide range using the fifth generation poly(propylene imine) (PPI) dendrimers. Preorganization of Pd ions within the PPI dendrimer with butanediamine core and successive reduction lead to the formation of precisely defined Pd clusters of Pd₄, Pd₈, and Pd₁₆, respectively, as determined by Pd K-edge XAFS analysis. These Pd clusters shows the size dependent catalytic activity in hydrogenation of olefins, where the TOF increases with increasing the cluster size.

Keywords: dendrimer, subnano Pd clusters, hydrogenation, XAFS

1 INTRODUCTION

The size and shape selective syntheses of metal nanoparticles are of much interest in the areas of materials physics and chemistry, because of their high potential for catalysts, optics, and electronics [1]. Among naked metal nanoparticles, small clusters ranging in diameters less than 1 nm, "subnano metal clusters", are highly expected to open a new realm in materials science [2], since they bridge the gap between mononuclear metal atoms and nanoparticles [3]. However, the subnano metal clusters are prone to aggregate into larger particles or bulk metals, which obstructs their study under practical conditions. Size-controlled synthesis of the subnano metal clusters is a current topic in the development of highly functionalized materials[4].

Palladium is at the heart of catalytic molecular transformations in areas of organic synthesis and environmental pollution control [5]. One of the promising synthetic methodologies for producing subnano Pd clusters is by reduction of Pd ions in the presence of stabilizing agents such as polymer micelles [4a], zeolites [4b], and clays [4c]. Such hosts have subnano ordered spaces to protect the small nuclei from aggregation. However, systematic control over the nuclearity of *naked* subnano Pd clusters by bottom-up process has not been achieved yet [6].

Dendrimers are highly branched molecules with monodispersed molecular weight having the following characteristics: 1) tunable chemical and physical properties by designing core, branch and surface units, 2) sterically confined nano voids, and 3) a highly congested surface with increasing generation [7]. Due to the above combination of attributes, dendrimers have been attracting attention as

unimolecular capsules for entrapping metal nanoparticles [8]. Although there are many reports on dendrimer-encapsulated metal nanoparticles with diameters ranging from 1 nm to 3 nm [9], the precise control of the cluster sizes within the confined nanovoids is still challenging.

We describe here a selective synthesis of Pd clusters in the subnanometer range (Pd_y; y denotes the numbers of Pd atoms) using a fifth generation poly(propylene imine) (PPI) dendrimer functionalized with 3,4,5-triethoxybenzamide (TEBA) groups on the periphery and their catalytic performances in hydrogenation of olefins. The size dependent catalytic activity in hydrogenation of olefins was observed, where the TOF increased with increasing the cluster size [10].

2 EXPERIMENTAL

The third generation (G₃) of poly(propylene imine) (PPI) dendrimer was purchased from SyMO-Chem B.V. The fourth (G₄) and the fifth (G₅) generations of the PPI dendrimers were synthesized from the G₃ PPI dendrimer by the divergent method. Surface modification of the PPI dendrimers with TEBA groups were carried out by the reported procedure (Figure 1) [9d, 11]. Other chemicals were commercially available from Wako Pure Chemicals, Tokyo Kasei Co., and Aldrich Inc. and were used after appropriate purification.

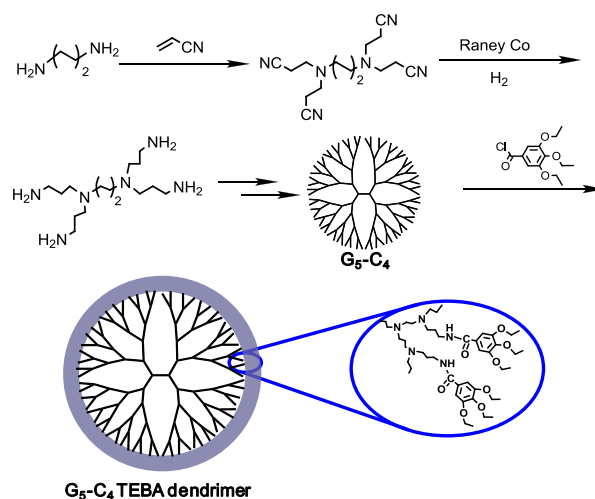


Figure 1: Synthesis of the fifth generation PPI dendrimers functionalized with 3,4,5-triethoxybenzoic acid chloride (G₅-C₄-TEBA).

The subnano Pd clusters were prepared as follows: An appropriate amount of aqueous solution of Na_2PdCl_4 was added to a chloroform solution of the G_x , giving $\text{G}_x\text{-C}_4\text{-Pd}_y$ dendrimers where y represents the number of Pd ions in one dendrimer ($y = 4, 8, 16, \text{ and } 32$). The $\text{G}_x\text{-C}_4\text{-Pd}_y$ dendrimers were further treated with aqueous solution of KBH_4 under vigorous stirring. The light brown solution turned dark brown indicating the formation of Pd(0) clusters (Figure 2).

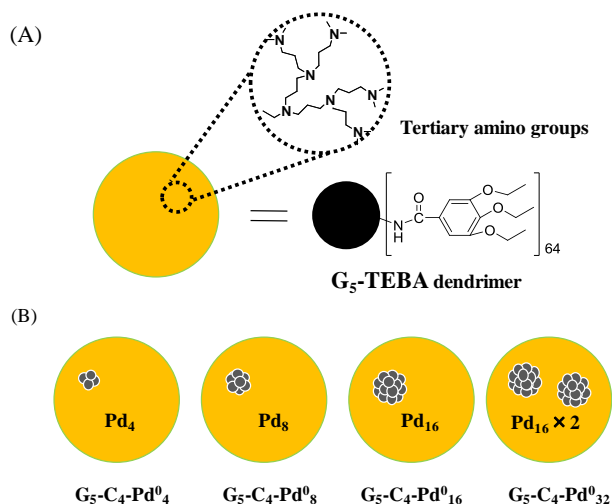


Figure 2: Schematic illustration of (A) structure of $\text{G}_5\text{-TEBA}$ dendrimers and (B) $\text{G}_5\text{-C}_4\text{-Pd}_y^0$ ($y = 4, 8, 16, \text{ and } 32$) and subnano Pd clusters within $\text{G}_5\text{-TEBA}$.

^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were obtained using a JEOL GSX-270 or JNM-AL400 spectrometer with tetramethylsilane as an internal standard. Infrared spectra were measured using a JASCO FTIR-410. The Pd K-edge X-ray absorption data were collected in the quick mode and recorded at room temperature in transmission mode at the BL01B1 and BL14B2 stations attached to the Si(311) monochromator at SPring-8 (JASRI), Harima, Japan. Data analyses were performed using REX2000 ver. 2.5.7 (Rigaku). Coordination numbers (CN) and interatomic distances (R) were estimated by curve-fitting analysis using Pd-Pd, Pd-Cl, and Pd-N shell parameters extracted from $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$, PdCl_2 , and Pd foil as reference samples. The sizes of the Pd clusters were calculated from the CN values based on the relationship between CN and diameter [12].

Hydrogenation of 1,3-cyclooctadiene (1,3-COD) catalyzed by $\text{G}_5\text{-C}_4\text{-Pd}_y^0$ were performed under an atmospheric pressure of hydrogen. To a toluene solution (2 mL) of $\text{G}_5\text{-C}_4\text{-Pd}_y^0$ (1.25 μmol of Pd) was added 1,3-COD (0.5 mmol) under 1 atm of H_2 at 313 K, and the mixture was vigorously stirred. The initial turnover frequency (TOF) was defined as the initial rate at 20% conversion, normalized by the number of surface Pd atoms in the subnano clusters [10]. The TOF was calculated using the following equation 1.

$$\text{TOF (min}^{-1}\text{)} = \frac{\text{H}_2 \text{ consumption (mol)}}{\text{Surface Pd atoms (mol)} \times \text{Time (min)}} \quad (1)$$

3 RESULTS AND DISCUSSION

The PPI dendrimer was used as a nano-capsule on the basis of its high compatibility with Pd^{2+} ions. The primary amino groups of the third to fifth generations of PPI dendrimers were functionalized with triethoxybenzoic acid chloride to construct unimolecular capsules having congested shell on the surface. An appropriate amount of aqueous solution of Na_2PdCl_4 was added to a chloroform solution of the G_x ($x = 3\text{-}5$), giving $\text{G}_x\text{-C}_4\text{-Pd}_y$ dendrimers where y represents the number of Pd ions in one dendrimer ($y = 4, 8, 16, \text{ and } 32$). The $\text{G}_x\text{-C}_4\text{-Pd}_y$ dendrimers were further treated with aqueous solution of KBH_4 under vigorous stirring. The light brown solution turned dark brown indicating the formation of Pd(0) clusters.

The Pd K-edge X-ray absorption fine structure (XAFS) of $\text{G}_x\text{-C}_4\text{-Pd}_8$ ($x = 3\text{-}5$) was examined before addition of KBH_4 : the $k^3\chi(k)$ Fourier transforms of these dendrimers showed peaks at 1.6 \AA and 1.9 \AA corresponding to Pd-Cl and Pd-N shells (Table 1). Curve-fitting analyses suggest that the Pd^{2+} species are surrounded by two Cl and two N atoms, i.e. the PdCl_2 species are immobilized at the two nitrogen atoms of the dendritic branch.

Table 1. Curve-fitting results of the Pd K-edge EXAFS ^a

sample	shell	CN ^b	$R / \text{\AA}$ ^c	$\sigma^2 / \text{\AA}^2$ ^d	N^e	d / nm ^f
$\text{G}_5\text{-C}_4\text{-Pd}_{16}^0$	Pd-N ^g	1.9	2.08	0.0004	-	-
	Pd-Cl ^g	1.8	2.29	0.0048	-	-
$\text{G}_5\text{-C}_4\text{-Pd}_8^0$	Pd-Pd	3.1	2.73	0.0069	4	0.50
	Pd-N ^g	2.0	2.05	0.0034	-	-
$\text{G}_5\text{-C}_4\text{-Pd}_4^0$	Pd-N ^g	2.1	2.05	0.0044	-	-
	Pd-Cl ^g	1.9	2.26	0.0074	-	-
$\text{G}_5\text{-C}_4\text{-Pd}_8^0$	Pd-Pd	4.6	2.76	0.0074	8	0.76
$\text{G}_5\text{-C}_4\text{-Pd}_{16}^0$	Pd-Pd	5.9	2.73	0.0092	16	0.97
$\text{G}_4\text{-C}_4\text{-Pd}_8^0$	Pd-Pd	5.1	2.75	0.0074	10	0.84
$\text{G}_3\text{-C}_4\text{-Pd}_8^0$	Pd-Pd	6.0	2.75	0.0076	17	0.99

^a The region of 1.0-2.9 \AA in FT of the reduced samples was inversely transformed. ^b Coordination number. ^c Interatomic distance. ^d Debye-Waller factor. ^e Number of Pd atoms in a cluster. ^f Diameter of Pd clusters. ^g Before addition of aqueous KBH_4 solution.

Addition of KBH_4 yielded Pd(0) clusters having a new peak at 2.5 \AA attributable to a Pd-Pd bond, accompanied by the diminution of the peak from the Pd-Cl shell. Coordination numbers (CN) of the Pd-Pd shell of $\text{G}_x\text{-C}_4\text{-Pd}_8^0$ were calculated as 6.0, 5.1, and 4.6 for $x = 3, 4, \text{ and } 5$, respectively. Diameters of the Pd clusters for $\text{G}_x\text{-C}_4\text{-Pd}_8^0$ were estimated to be less than 1 nm, i.e. 0.99, 0.84, and 0.76 nm for $x = 3, 4 \text{ and } 5$, respectively (Table 1). Interestingly, in the case of the fifth generation of the dendrimer ($\text{G}_5\text{-C}_4\text{-Pd}_8^0$), the Pd cluster of 0.76 nm can be determined to contain 8 Pd atoms which is the same as that of the preorganized Pd^{2+} ions within one dendrimer before the KBH_4 reduction.

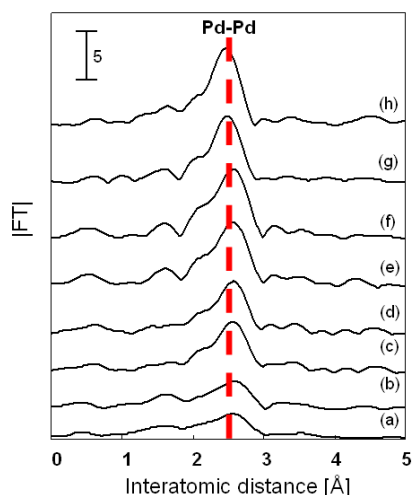


Figure 3: Fourier transforms of k^3 -weighted Pd K-edge EXAFS experimental data for (a) $G_5-C_4-Pd_4^0$, (b) used $G_5-C_4-Pd_4^0$, (c) $G_5-C_4-Pd_8^0$, (d) used $G_5-C_4-Pd_8^0$, (e) $G_5-C_4-Pd_{16}^0$, (f) used $G_5-C_4-Pd_{16}^0$, (g) $G_5-C_4-Pd_{32}^0$, and (h) used $G_5-C_4-Pd_{32}^0$.

Next, it was attempted to control the number of Pd atoms in the subnano clusters by using the G_5-C_4 dendrimer ($G_5-C_4-Pd_y$) as a unimolecular capsule (Table 1 and Figure 2). For $y = 4$ and 16, subnano Pd clusters having diameters of 0.50 and 0.97 nm were obtained, which correspond to the clusters composed of 4 and 16 Pd atoms, respectively. In the cases of $y = 32$, the CN for the Pd-Pd shell were close to that for the $G_5-C_4-Pd_{16}^0$ asserting to the formation of Pd clusters having 0.97 nm in diameter. Transmission Electron Micrograph (TEM) images of the $G_5-C_4-Pd_{16}^0$ and $G_5-C_4-Pd_{32}^0$ also show formation of Pd clusters having *ca.* 0.9 nm diameter. These results showed that two subnano Pd clusters having 16 Pd atoms were encapsulated within one G_5 dendrimer (Table 1 and Figure 2B). In hydrogenation of olefins (*vide infra*), the similar turnover frequencies (TOFs) obtained for the $G_5-C_4-Pd_{16}^0$ and $G_5-C_4-Pd_{32}^0$ also supports the existence of the Pd_{16} clusters within one dendrimer. It should be noted that *the subnano clusters composed of specific number of Pd atoms (i.e., Pd_4 , Pd_8 , Pd_{16}) were obtained by preorganization of Pd ions within one dendrimer molecule, respectively.*

Surface congestion and nano voids derived from the regulated branching units of the dendrimers play important roles in the fine control of size of the subnano Pd clusters. Introduction of the bulky TEBA groups on the surface makes a highly congested shell on the G_5 PPI dendrimer. This then affords a unimolecular capsule capable of sterically confining the Pd clusters within the G_5 dendrimer. In the cases of higher loading of the Pd ions over 16 within one dendrimer, e.g. $G_5-C_4-Pd_{32}^0$, the nucleation of Pd atoms affords other Pd_{16} clusters without growing into larger aggregates over Pd_{16} . The internal void spaces segregated by the branch units of the G_5 dendrimer seem to fit the size of the Pd_{16} cluster. In the cases of the G_3 and G_4 dendrimers, the relatively loose surface shell allows the bimolecular

nucleation process that results in the formation of larger Pd clusters together with empty dendrimers.

The catalytic performances of the dendrimer-encapsulated subnano Pd clusters $G_5-C_4-Pd_y^0$ ($y = 4, 8, 16,$ and 32) were examined in the hydrogenation of 1,3-COD (Figure 4). All $G_5-Pd_y^0$ tested promoted hydrogenation selectively, giving cyclooctene in over 99% yield. Interestingly, the initial turnover frequency (TOF/ min^{-1}), normalized to the total number of surface Pd atoms in the Pd clusters within $G_5-C_4-Pd_y^0$, increased with increasing Pd cluster size; the TOFs of $G_5-C_4-Pd_y^0$ ($y = 4, 8,$ and 16) were 10, 31, and 62, respectively (Figure 4). Moreover, the TOF of $G_5-C_4-Pd_{32}^0$ (65) was similar to that of Pd_{16}^0 (62), which is consistent with the presence of two Pd_{16} clusters within one dendrimer (*vide supra*).

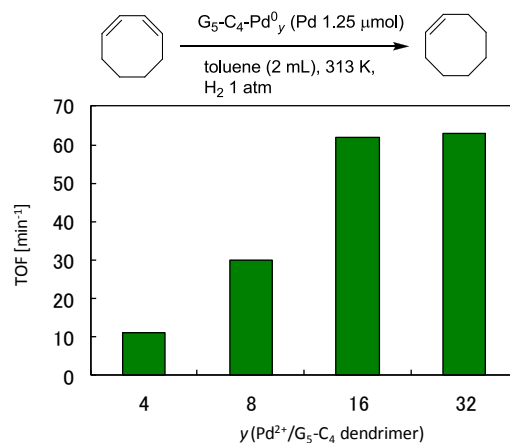


Figure 4: Hydrogenation of 1,3-cyclooctadiene catalyzed by dendrimer-encapsulated subnano Pd clusters $G_5-C_4-Pd_y^0$ ($y = 4, 8, 16,$ and 32).

After the 1,3-COD hydrogenation reaction, FT of the k^3 -weighted Pd K-edge EXAFS spectra of $G_5-C_4-Pd_y^0$ ($y = 4, 8, 16,$ and 32) gave similar peak intensities and CNs for the Pd-Pd shell to those of fresh clusters (Figure 3). Furthermore, the TOFs of $G_5-C_4-Pd_y^0$ were maintained in repeated addition of 1,3-COD. These phenomena suggest that the original sizes of the Pd clusters remain unchanged during the hydrogenation reaction.

In order to investigate the size effect of the subnano Pd clusters, preliminary kinetic studies were carried out. The initial reaction rate of the 1,3-COD hydrogenation using $G_5-C_4-Pd_y^0$ ($y = 4, 8,$ and 16) was dependent on the partial pressure of H_2 and independent of the concentration of 1,3-COD. The kinetic isotope effect was observed for the hydrogenation using D_2 ($k_H/k_D = 1.5$). From the above results, dissociative adsorption of H_2 is considered as the rate-determining step in the 1,3-COD hydrogenation [13]. $G_5-C_4-Pd_y^0$ Zhi et al. and others reported that the density functional theory (DFT) calculations of dissociative adsorption of H_2 on small Pd clusters revealed that the configuration with H atoms adsorbed on Pd three-fold hollow sites is the most stable structure [14]. In our case,

the TOF normalized to the total number of the three-fold hollow sites in the Pd cluster also increased with increasing the size of subnano Pd clusters. Namely, the size effect on catalytic activity in the hydrogenation reaction was derived from the difference of hydrogen activation ability of the three-fold hollow sites of the Pd cluster.

4 CONCLUSIONS

We have succeeded in the controlled synthesis of subnano ordered Pd clusters consisting of a specific number of Pd atoms by preorganization of Pd ions within the PPI dendrimers and subsequent reduction. The keys of this success in the size control of the subnano Pd clusters are 1) complexation of Pd²⁺ ions with the internal amino groups, 2) sterically confined nanovoids within the fifth generation of PPI dendrimers, and 3) tunable molecular structures of the PPI dendrimers as nanocapsules by changing the core and the surface units. Fine tuning of the void sizes of dendrimers by changing core and branch units will expand the tailor-made synthesis of Pd particles from subnano to nano range.

ACKNOWLEDGEMENT

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The XAFS experiments were performed at the BL01B1 and BL14B2 in the SPring-8 with approval of the Japan Synchrotron Radiation Research Institute (Nos. 2009A1856, 2009A1860, 2009B1854, 2009B1506, 2010A1781, and 2010A1788).

REFERENCES

- [1] C. Burda, X. Chen, R. Narayana, M. A. El-Sayed, *Chem. Rev.* 105, 1025, 2005.
- [2] A. W. Castleman Jr., S. N. Khanna, *J. Phys. Chem. C*, 113, 2664, 2009.
- [3] (a) D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem. Int. Ed.* 44, 7852, 2005; (b) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* 102, 3757, 2002.
- [4] **Pd** (a) K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida, S. Kobayashi, *J. Am. Chem. Soc.* 127, 2125, 2005; (b) K. Okumura, K. Nota, K. Yoshida, M. Niwa, *J. Catal.* 231, 245, 2005; (c) T. Mitsudome, K. Nose, K. Mori, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, *Angew. Chem. Int. Ed.* 46, 3288, 2007; **Au** (d) S. Lee, L. M. Molina, M. Lopez, J. A. Alonso, B. Hammer, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, M. J. Pellin, S. Vajda, *Angew. Chem. Int. Ed.* 48, 1467, 2009; (e) Y. Negishi, H. Tsunoyama, Y. Yanagimoto, T. Tsukuda, *Chem. Lett.* 34, 1638, 2005; **Pt** (f) S. Vajda, M. J. Pellin, J. P. Greeley, C. L. Marshall, L. A. Curtiss, G. A. Ballentine, J. W. Elam, S. Catillon-Mucherie, P. C. Redfern, F. Mehmood, P. Zapol, *Nat. Mater.* 8, 213, 2009; (g) K. Yamamoto, T. Imaoka, W.-J. Chun, O. Enoki, H. Katoh, M. Takenaga, A. Sonoi, *Nature Chem.* 1, 397, 2009.
- [5] *Handbook of Organopalladium Chemistry for Organic Synthesis, Vol. 1, 2*, ed. by E. Negishi, Wiley Interscience, 2002.
- [6] The ligand-stabilized organometallic Pd cluster complexes having low nuclearity were reported: (a) T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki, H. Kurosawa, *Science* 313, 1104, 2006; (b) F. Lemaître, D. Lucas, K. Groison, P. Richard, Y. Mugnier, P. D. Harvey, *J. Am. Chem. Soc.* 125, 5511, 2003.
- [7] (a) *Dendrimers and Other Dendritic Polymers*, eds. J. M. J. Fréchet, D. A. Tomalia, Wiley & Sons, New York, 2001; (b) *Designing Dendrimers*, eds. S. Campagna, P. Ceroni, F. Puntoriero, Wiley & Sons, New Jersey, 2012.
- [8] Reviews on dendrimer catalysts, see: (a) J. K. Vohsa, B. D. Fah, *New J. Chem.* 31, 1041, 2007; (b) R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Rev.* 102, 3717, 2002.
- [9] RTypical examples of dendritic metal nanoparticles having 1-3 nm diameters, (a) M. V. Gomez, J. Guerra, A. H. Velders, R. M. Crooks, *J. Am. Chem. Soc.* 131, 341, 2009; (b) O. M. Wilson, M. R. Knecht, J. C. Garcia-Martinez, R. M. Crooks, *J. Am. Chem. Soc.* 128, 4510, 2006; (c) K. Esumi, R. Isono, T. Yoshimura, *Langmuir* 20, 237, 2004; (d) M. Ooe, M. Murata, T. Mizugaki, K. Ebitani, K. Kaneda, *Nano Lett.* 2, 999, 2002.
- [10] (a) T. Mizugaki, T. Kibata, K. Ota, T. Mitsudome, K. Ebitani, K. Jitsukawa, K. Kaneda, *Chem. Lett.* 38, 1118, 2009; (b) Z. Maeno, T. Kibata, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Lett.* 40, 180, 2011.
- [11] E. M. M. de Brabander-van den Berg, E. W. Meijer, *Angew. Chem., Int. Ed. Engl.* 32, 1308, 1993.
- [12] (a) C. Luo, C. Zhou, J. Wu, T. J. D. Kumar, N. Balakrishnan, R. C. Forrey, H. Cheng, *Inter. J. Quant. Chem.* 107, 1632, 2007; (b) C. Zhou, S. Yao, J. Wu, R. C. Forrey, L. Chen, A. Tachibana, H. Cheng, *Phys. Chem. Chem. Phys.* 10, 5445, 2008.
- [13] S. Naito, M. Tanimoto, *J. Chem. Soc., Faraday Trans. 1*, 84, 4115, 1988.
- [14] (a) N. Meiyani, Z. Zhi, *J. Mol. Struct.: THEOCHEM* 910, 14, 2009. (b) E. D. German, I. Efremenko, M. Sheintuch, *J. Phys. Chem. A*, 105, 11312, 2001 (c) J. Roques, C. L.-Dufaure, C. Mijoule, *J. Chem. Theory Comput.* 3, 878, 2007.