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A Chromo-Fluorogenic Tetrazole-Based $CoBr_2$ Coordination Polymer Gel as a Highly Sensitive and Selective Chemosensor for Volatile Gases Containing Chloride

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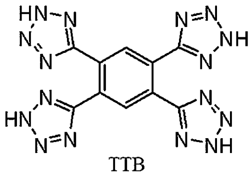
Crystalline coordination polymers are a newer class of organic–inorganic hybrid nanomaterials created by infinitely extending metal–ligand coordination interactions. These polymers show promise in a broad range of applications, including gas storage, molecular sieves, ion exchange, sensing, magnetism, and catalysis.[1,2] Recently, a rational-design strategy for supramolecular gels based on the concept of coordination polymers is attracting interest.[3–6] In particular, recent studies have demonstrated that simple bridging organic units can facilitate the formation of coordination polymer gels in the absence of auxiliary moieties (e.g., urea, sugar, cholesterol, long alkyl chains), offering new possibilities to produce functional soft materials from structurally simple building blocks.[7] Although the literature includes several reports on the synthesis and characterization of bulk coordination polymer gels, there are only a few examples of such gels used in practical catalysis applications.[8] Also, to best of our knowledge, there is no report on the usage of coordination polymer gels as chemosensors or adsorbents for toxic gases. Coordination polymer gels feature easy preparation and handling, good stability, and recyclability. As such, they will act as very useful chemosensors if they can bind to specific toxic gases.

To design a chemosensor, we chose tetrazole-appended benzene as the framework to attach ligands because of its well-defined and extensively developed metal–organic framework (MOF).[9] A tetrazole derivative, with multibinding sites, promotes cross-linking to form a polymer network, which is a critical condition for gelation. Herein, we describe the preparation, morphology, fluorescence, and lifetime of a tetrazole-appended coordination polymer gel incorporating Co^{2+} ions. In addition, we tested the $CoBr_2$ coordination polymer gel (**1**) as a selective chemosensor for chloride gas, such as HCl, $SOCl_2$, $(COCl)_2$, and $COCl_2$. Upon the addition of several gases containing chloride atoms, gel **1** changed from red to blue in the gel state through interconversion. This is a new phenomenon that has never before been reported for coordination polymer gels.


TTB

$$\mathrm{TTB} + \mathrm{CoBr_2} \xrightarrow[\text{gel formation}]{} [(\mathrm{TTB})_2\mathrm{CoBr_2(MeOH)(DMF)}]_n$$

1

$$\mathrm{TTB} + \mathrm{CoCl_2} \xrightarrow[\text{gel formation}]{} [(\mathrm{TTB})_2\mathrm{CoCl_2}]_n$$

2

In a typical experiment, 1,2,4,5-tetra(2*H*-tetrazole-5-yl)-benzene (TTB) was dissolved in organic solvent and the Co^{2+} salt was dissolved in the same solvent. The Co^{2+} solution was then added to the TTB solution without heating. The molar ratios of metal ions to TTB was in the range of 1–5:1, and the amount of the coordination polymer in the gel ranged from 1 to 5 wt%, corresponding to a molar ratio of gelator/solvent of $\approx 1{:}10^4$. TTB immediately formed a gel upon addition of Co^{2+} salts of ClO_4^-, OAc^-, Cl^-, Br^-, I^-, or NO_3^- in polar solvents, such as DMF, DMA, and DMF/methanol (1:1 v/v, Figure 1A, as well as Figure S1 and Table S1 in the Supporting Information). Except for the solution containing Cl^-, these gels exhibited a red color, as will be discussed in detail shortly. Figure 1B shows a field-emission scanning electron microscope (FE-SEM) image of **1**. A spherical structure is seen with 20–30 nm diameter particles. The sample uniformity and narrow diameter were

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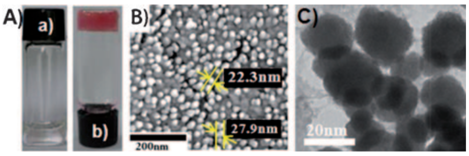

Figure 1. A) Photograph of TTB in solution (a, 20 mM) and **1** (b, 20 mM, 3.0 equiv). B) SEM and C) TEM images of **1**.

confirmed by TEM as shown in Figure 1 C. In addition, TEM images of the coordination polymer gels obtained with different anions than Br^- show a spherical structure with 20–30 nm diameter particles (Figure S2 in the Supporting Information). These findings suggest that the morphology of **1** does not strongly depend on the nature of the anion.

To understand the coordination behavior between TTB and Co^{2+}, we attempted to obtain crystal structures of the related complexes, but were not successful. As an alternative, we obtained the X-ray powder diffraction (XRD) patterns of freeze-dried **1**. The tetrazole groups serve as multibinding sites to form a 2D- or 3D-coordination polymer in the presence of an excess of metal ions.[9,10] As shown in Figure S3 in the Supporting Information, the XRD pattern of **1** reveals a crystalline structure. The crystallinity of TTB may be due to the formation of a highly ordered 2D-coordination polymer structure.[9,10]

To obtain the coordination structure for Co^{2+} with Br^-, MeOH, and DMF, we carried out DFT calculations with Becke's three parameterized Lee–Yang–Parr exchange functional (B3LYP) implemented with the 6-31G* basis sets with a suite of Gaussian 03 programs.[11] We used the octahedral coordination structure as an initial geometry in which Co^{2+} was coordinated by two *trans* oriented TTB ligands, two *trans* oriented Br^- ions, one MeOH, and one DMF. The optimized structure is shown in Figure 2. Even though the two bromides may have *cis* orientation, the expanded geometry seems to be equivalent to the *trans* orientation as shown in Figure 2. The coordinated distances between the cobalt atom and the TTB ligand, bromide anions, MeOH, and DMF were 1.98, 2.52, 2.25, and 2.09 Å, respectively. Referring to the previously reported crystal structure in a similar system,[9,10] we generated the expanded framework by assembling the optimized structure. As shown in Figure S4 in the Supporting Information, the intercobalt(II) distance was approximated to 14.43 Å. This cavity size gives at least a reasonable assembled structure in the 2D space.

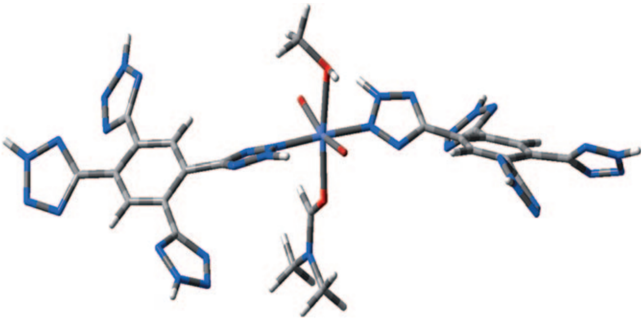

Figure 2. Optimized structure for $[(TTB)_2CoBr_2(MeOH)(DMF)]$ calculated with B3LYP/6-31G.

The absorption and emission properties of TTB and **1** in solution were studied by UV/Vis spectroscopy and fluorometry. The UV/Vis absorption band of **1** appears at 475 nm (Figure 3 A), which is a typical π–π* absorption band.[4] In contrast, the π–π* absorption band of TTB shows a large blueshift of $\lambda = 300$ nm. The fluorescence spectrum of **1** (20 mM) upon excitation at $\lambda = 300$ nm is shown in Figure 3 B. Gel **1** exhibits strong blue emission with a maximum at 375 nm. The fluorescence intensity is greatly enhanced compared to TTB. The photoluminescence of **1** can be seen by the naked eye under UV light. Interestingly, the fluorescence intensity of **1** gradually increased up to the addition of three equivalents of Co^{2+} ions (Figure S5 in the Supporting Information) and then remained constant above this concentration.

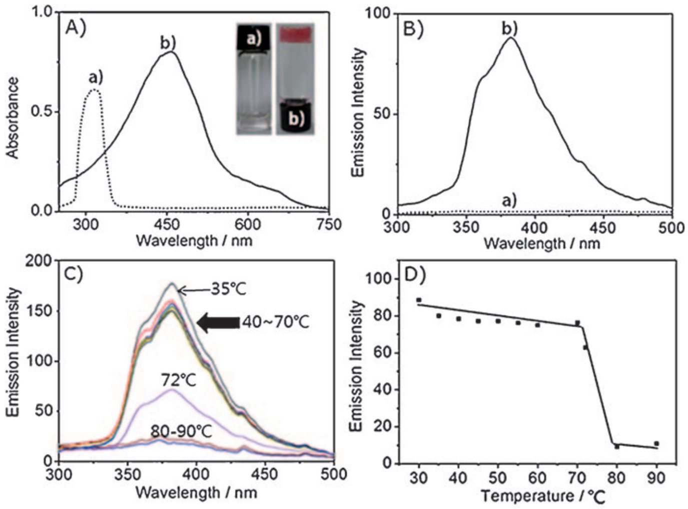

Figure 3. A) UV/Vis spectra of TTB (a, 20 mM) and **1** (b, 20 mM, 3.0 equiv) in DMF/MeOH (1:1 v/v). B) Fluorescence spectra of TTB (a, 20 mM) in DMF/MeOH (1:1 v/v) and **1** (b, 20 mM, 3.0 equiv) upon excitation at $\lambda = 300$ nm. C) Fluorescence spectra of **1** at different temperatures upon excitation at $\lambda = 300$ nm. D) Plot of emission intensities of **1** at $\lambda = 375$ nm versus temperature.

Controlled experiments were conducted to investigate whether the fluorescence enhancement is related to the gel formation or to the complexation with Co^{2+}. The emission properties of a solution of TTB (20 mM) upon addition of Co^{2+} were studied. No significant change in fluorescence intensity was observed upon excitation at $\lambda = 300$ nm. This finding indicates that complexation of Co^{2+} ion with TTB did not result in a fluorescence enhancement compared with the free ligand.

Variable-temperature fluorescence spectra of **1** are shown in Figure 3 C and 3 D. No significant spectral changes were observed as the temperature was increased from 25 to 70 °C. A slight decrease in fluorescence intensity was seen when **1** was heated to 72 °C. Further increase in temperature resulted in decreasing emission. These results suggest that the emission of **1** decreases as it starts to melt at 72–80 °C. These findings indicate that the optimal emission of TTB occurs when the gel is completely formed and that the emission of the coordination polymer gel decreases as it melts at higher temperatures. This striking observation may be attributed to the rigidification of the media upon gelation, a process that slows down nonradiative decay mechanisms, leading to fluorescence enhancement.

Additional experiments were carried out to gain insight into the luminescence properties of **1** by time-resolved fluorescence confocal microscopy. The emission decay profiles were monitored at $\lambda = 375$ nm (Figure S 6 in the Supporting Information). The fluorescence decay of **1** was fitted with a single-exponential component to yield a lifetime of 3.23 ns, indicating that this emission is fluorescence. This result suggests that **1**, in the aggregate state, increases the rigidity and restricts the rotational and vibrational movements of molecules.[12]

We investigated the sensing ability of **1** as a selective chemosensor for toxic gases containing chloride, that is, HCl, $SOCl_2$, $(COCl)_2$, and $COCl_2$ (phosgene) by using UV/Vis spectroscopy. The UV/Vis spectrum of **1** exhibits an absorption band at 475 nm with a red color, suggesting the formation of octahedral (O_h) complexes (Figure 4 A).[13] Introduction of a small amount of $COCl_2$ (phosgene) gas causes a redshift of 195 nm, resulting in a new band at 670 nm with blue color (Figure 4 A and Figure S 7 in the Supporting Information). It is likely that the bromide anions were replaced with chloride anions stemming from the phosgene that decomposed in the gel matrix.[14] An absorption band at 670 nm is characteristic of the tetrahedral Co^{2+} complex (T_d, $^4A_2 \rightarrow {}^4T_1(P)$).[13] In addition, the fluorescence intensity of **1** gradually decreases with exposure to phosgene gas (Figure 4 B). Introduction of HCl, $SOCl_2$, and $(COCl)_2$ gases in **1** also induced a color change from red to blue (Figure S 8 in the Supporting Information). These results indicate that the octahedral structure of **1** changed to a tetrahedral coordination polymer gel with chloride ligands (**2**). This is the first example of a chemosensor for detection of chloride and for conversion in the gel state. Furthermore, ESI-MS data were in agreement with the presence of octahedral and tetrahedral structures, respectively (Figure S 9 in the Supporting Information).

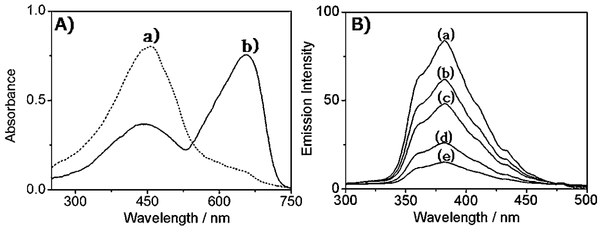

Figure 4. A) UV/Vis spectra of **1** (10 mM) before (a) and after (b) diffusion of phosgene gas (10 mM). B) Fluorescence spectra of **1** ($\lambda_{ex} = 300$ nm) upon diffusion of phosgene gas; 0 (a), 5 (b), 10 (c), 15 (d), and 20 ppb (e).

The complex stability of the coordination polymers prepared in this work would be determined mainly by the following factors: 1) the thermal stability of the coordination structures, 2) interactions between solvent molecules and anions, 3) electrostatic interactions between the polymer complex and the counter anions, and 4) π–π stacking of aromatic rings. The configurational equilibrium between octahedral and tetrahedral structures of the Co^{2+} ion is affected by several factors, including crystal-field stabilization, properties of ligands (chemical structure, polarizability, π receptor capacity), and crystal packing. Octahedral coordination is favored in the solution phase, whereas tetrahedral coordination is favored in the gel-like state.[13,15]

The sol–gel transition temperature of **2** was slightly higher than that of **1** (Figure S 10 in the Supporting Information), indicating that the tetrahedral structure of **2** is more stable. On the other hand, no significant color changes were observed for an excess of other anions, namely, HF, HBr, HI, HNO_3, and H_2SO_4 (Figure S 11 in the Supporting Information). These findings indicate that **1** is useful as a chemosensor and adsorbent for chloride ions.

To extend the performance described above to a portable chemosensor kit, gel **1** was coated in a capillary with 50 μm inner diameter (Figure 5 A). Then, both ends of the capillary were closed with membrane filters of 1–2 μm pore size. Figure 5 shows the **1**-coated capillary before and after exposure to phosgene gas. The color of the capillary coated with **1** was red before exposure(Figure 5 B: a). As expected, gel **1** only changed from red to blue when exposed to chloride

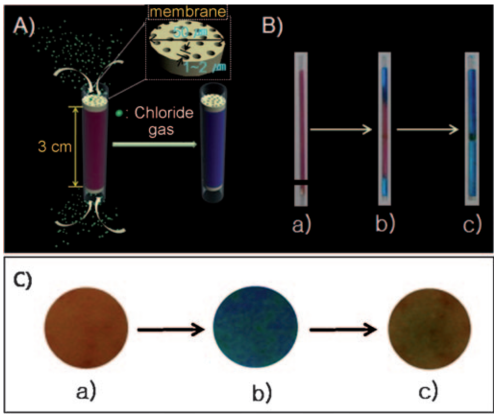

Figure 5. A) Representation of a **1**-coated capillary as the portable chemosensor. B) Photographs of a **1**-coated (20 mM) capillary before (a), after 10 (b), and 30 s (c) of exposure to chloride gas (100 mM). C) Photographs of disktype pellets of dried **1** before (a) and after (b) exposure to phosgene gas, and after rinsing the pellet with DMF and methanol containing 100 mM HBr (c).

atoms, such as HCl, $SOCl_2$, $(COCl)_2$, and $COCl_2$ (Figure 5B: b and c). With the **1**-coated capillary, it is hence possible to detect low concentrations of chloride in gas in the gel by the naked eye. The result implies that capillaries coated with **1** are applicable as portable colorimetric sensors for detection of chloride atoms in the environment. Furthermore, a disk-type pellet prepared from dried gel **1** was prepared (Figure 5C). The red color of the disktype pellet of dried **1** was changed to blue within 10 s when exposed by phosgene gas. The color change was fully reversible when the pellet was rinsed by DMF and methanol containing HBr.

The absorption and fluorescence changes of **1** were found to correspond to the range of 1–20 ppb of phosgene (Figure 4B and Figure S12 in the Supporting Information). The limit of detection of **1** for phosgene gas was determined to ≈1.0 ppb, more than sufficient to sense the phosgene concentration in the atmosphere according to the American conference of governmental industrial hygienists' (ACGIH) limit (100 ppb). An evaluation of the time course for the absorption intensity of gel **1** at 670 nm indicated that immediately after the addition of phosgene gas, the absorption-band intensity of **1** started to increase, and after 60 s the band was almost saturated (Figure S13 in the Supporting Information). Thus, the response time of this system is less than 1 min, making it a rapid and convenient method for quantitative analysis of phosgene.

In conclusion, we have demonstrated the first example of a selective chemosensor for the detection of chloride by conversion of a coordination gel. The gel is produced by mixing a tetrazole-appended ligand with Co^{2+} ions. The photophysical studies showed that the coordination polymer gel exhibits a typical π–π^* transition and gives rise to a highly fluorescence behavior. Upon the formation of the coordination polymer gel with a 2D structure, the complex shows a pronounced fluorescence enhancement with a long lifetime compared with the ligand. More interestingly, a $CoBr_2$ coordination polymer gel with octahedral structure selectively recognizes toxic gases, such as HCl, $SOCl_2$, $(COCl)_2$, and $COCl_2$ containing chloride atoms. The results suggest that coordination polymer gels may offer useful applications in chemical sensing.

Experimental Section

Microscopy observations: For TEM, a piece of the gel was placed on a carbon-coated copper grid (400 mesh) and removed after one min, leaving some small patches of the sample on the grid. The species were examined with a JEOL JEM-2010 transmission electron microscope operating at 200 kV with an accelerating voltage of 100 kV and a 16 mm working distance. Scanning electron micrographs of the samples were taken with a FE-SEM (Philips XL30 S FEG). The accelerating voltage of the SEM was 5–15 kV and the emission current was 10 μA.

Fluorescence lifetime microscopy: Fluorescence lifetime images were acquired by an inverse time-resolved fluorescence microscope (MicroTime-200, PicoQuant GmbH). The excitation wavelength, the spatial resolution, and the time resolution were 375 nm, 0.3 μm, and 60–70 ps, respectively. The samples were prepared on one side of microscope cover glasses. The manufacturer's software was used to analyze the data and calculate the lifetime maps.

Photophysical studies: UV/Vis absorption and emission spectra in the range of 200–800 nm of the gel dispersed in 1:1 DMF/MeOH were run at room temperature. The absorption properties of **1** were studied extensively. UV/Vis absorption of **1** ([**1**] = 20 mM) were observed in the presence of Co^{2+} (0–5 equiv).

Differential scanning calorimetry: Differential scanning calorimetry was performed on a Seiko DSC6100 high-sensitivity differential scanning calorimeter equipped with a liquid-nitrogen cooling unit. Samples of Co^{2+} coordination polymer gels were hermetically sealed in a silver pan and measured against a pan containing alumina as the reference. The thermograms were recorded at a heating rate of 0.5 °C min^{-1}.

Preparation of the gel: In a vial, a solution of the metal salt (150 μL, 3 equiv in MeOH) was added to solution of the gelator (150 μL, 1–5 wt % in DMF). The metal-coordination polymeric gel was formed immediately upon standing in ambient temperature. The resulting reaction mixture was sonicated. The gelation state of the material was evaluated by turning the test tube upside down.

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Keywords: chlorine · chromophores · gels · sensors · tetrazole

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[1] a) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*; VCH, Weinheim, **1995**; b) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217; c) J. T. Hupp, K. R. Poeppelmeier, *Science* **2005**, *309*, 2008; d) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334; e) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705.

[2] a) B. L. Chen, Y. Yang, F. Zapata, G. N. Lin, G. D. Qian, E. B. Lobkovsky, *Adv. Mater.* **2007**, *19*, 1693; b) B. L. Chen, L. B. Wang, F. Zapata, G. D. Qian, E. B. Lobkovsky, *J. Am. Chem. Soc.* **2008**, *130*, 6718; c) B. L. Chen, L. B. Wang, Y. Q. Xiao, F. R. Fronczek, M. Xue, Y. J. Cui, G. D. Qian, *Angew. Chem.* **2009**, *121*, 508; *Angew. Chem. Int. Ed.* **2009**, *48*, 500; d) B. V. Harbuzaru, A. Corma, F. Rey, J. L. Jorda', D. Ananias, L. D. Carlos, J. Rocha, *Angew. Chem.* **2009**, *121*, 6598; *Angew. Chem. Int. Ed.* **2009**, *48*, 6476; e) K. L. Wong, G. L. Law, Y. Y. Yang, W. T. Wong, *Adv. Mater.* **2006**, *18*, 1051; f) B. Zhao, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan, Z. H. Jiang, *J. Am. Chem. Soc.* **2004**, *126*, 15394.

[3] F. Fages, *Angew. Chem.* **2006**, *118*, 1710; *Angew. Chem. Int. Ed.* **2006**, *45*, 1680.

[4] For selected examples of coordination polymer gels, see: a) W. L. Leong, A. Y.-Y. Tam, S. K. Batabyal, L. W. Koh, S. Kasapis, V. W.-W. Yam, J. J. Vittal, *Chem. Commun.* **2008**, 3628; b) S. K. Batabyal, W. L. Leong, J. J. Vittal, *Langmuir* **2010**, *26*, 7464; c) W. L. Leong, S. K. Batabyal, S. Kasapis, J. J. Vittal, *Chem. Eur. J.* **2008**, *14*, 8822.

[5] a) J. M. J. Paulusse, D. J. M. van Beek, R. P. Sijbesma, *J. Am. Chem. Soc.* **2007**, *129*, 2392; b) J. K.-H. Hui, Z. Yu, M. J. MacLachlan, *Angew. Chem.* **2007**, *119*, 8126; *Angew. Chem. Int. Ed.* **2007**, *46*, 7980; c) W. Weng, J. B. Beck, A. M. Jamieson, S. J. Rowan, *J. Am. Chem. Soc.* **2006**, *128*, 11663.

[6] H. J. Kim, J.-H. Lee, M. Lee, *Angew. Chem.* **2005**, *117*, 5960; *Angew. Chem. Int. Ed.* **2005**, *44*, 5810.

[7] S. Zhang, S. Yang, J. Lan, S. Yang, J. You, *Chem. Commun.* **2008**, 6170.
[8] B. Xing, M.-F. Chio, B. Xu, *Chem. Eur. J.* **2002**, *8*, 5028.
[9] M. Dincă, A. F. Yu, J. R. Long, *J. Am. Chem. Soc.* **2006**, *128*, 8904.
[10] a) M. Dincă, A. F. Yu, Y. Liu, C. M. Brown, D. A. Neumann, J. R. Long, *J. Am. Chem. Soc.* **2006**, *128*, 16876; b) M. Dincă, A. Dailly, J. R. Long, *Chem. Eur. J.* **2008**, *14*, 10280.
[11] Gaussian 03, Revision B.05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2003**.
[12] A. Kishimura, T. Yamashita, T. Aida, *J. Am. Chem. Soc.* **2005**, *127*, 179.
[13] a) F. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, **1980**; b) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, **1968**.
[14] J. G. Smith, *Organic Chemistry*, McGraw-Hill Higher Education, New York, **2006**.
[15] K. Kuroiwa, T. Shibata, A. Takada, N. Nemoto, N. Kimizuka, *J. Am. Chem. Soc.* **2004**, *126*, 2016.

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