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Emission Behavior of Secondary Thioamide-Based Cationic Pincer Platinum(II) Complexes in the Aggregate State

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Cationic pincer platinum(II) complexes bearing secondary thioamide units showed aggregation-induced emission (AIE) activity in chloroform/hexane and methanol/water mixtures.

Hydrogen bonding of the thioamide units and interionic interactions contributed to the AIE activities.

Introduction

The emission of conventional luminophores such as perylene and rhodamine is often quenched if their molecules are aggregated (aggregation-caused quenching, ACQ).^[1] However, recently, Tang and co-workers and other researchers reported luminophores exhibiting efficient emission in the aggregate and solid states.^[1-4] This unusual luminescent phenomenon is termed aggregation-induced emission (AIE). AIE-active compounds have received considerable attention because of their potential applications in organic light-emitting diodes and sensors.^[5] Studies have revealed that the main cause of AIE activity is the restriction of molecular motion in the aggregate state.^[2,3a] In some AIEactive compounds, hydrogen-bonding interactions also induce suppression of the molecular motion.^[3b,3c] Yam and Che reported AIE-active platinum(II) complexes.^[6] The emission color and intensity of the Pt^{II} complexes depend on the extent of the Pt…Pt and π - π interactions, that is, metal-metal-to-ligand charge transfer (MMLCT) in the aggregate and the solid states.^[6,7]

In previous work, we found that the emission intensity of a neutral Pt^{II} complex bearing secondary thioamide units [Pt(^{Bn}S^C^S)Cl] (1, ^{Bn}S^C^S = N,N'-dibenzyl-1,3benzenedicarbothioamide, Figure 1) increased upon adding tetra-*n*-butylammonium chloride to the solution.^[8] Efficient emission was caused by the suppression of molecular motion resulting from hydrogen-bonding interactions between the N–H moiety in the secondary thioamide group and the chloride anion. This result suggested that hydrogen-bonding interactions of thioamide contribute to AIE activity. In addition to hydrogen bonding, the introduction of ionic interactions into thioamide-based complexes should effectively suppress the molecular motion. Therefore, it is expected that secondary thioamide-based cationic Pt^{II} complexes should exhibit AIE activity because of the restriction of the molecular motion owing to intermolecular hydrogenbonding and ionic interactions with the counteranions. Herein, we report AIE-active cationic Pt^{II} complexes having secondary thioamide units and the effects of hydrogenbonding and ionic interactions on the AIE activities.



Figure 1. Structures of complexes 1-3.

Results and Discussion

 $[Pt(^{Bn}S^C^S)(PPh_3)]Cl$ (2-Cl, Figure 1) was synthesized to investigate the effects of hydrogen bonding of the secondary thioamide sites and the ionic interactions on AIE. In addition, complex $1^{[8]}$ (Figure 1), which is neutral, and

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 $[Pt(^{Pi}S^C^S)(PPh_3)]C1 \{3-Cl, ^{Pi}S^C^S = 1,3-bis(1-piperid$ $inothiocarbonyl)benzene\}$ with tertiary thioamide units were prepared^[9] as control samples to compare the emission behavior in the aggregate states.

Complexes 2-Cl and 3-Cl exhibited good solubility in chloroform. To examine the emission behavior of 2-Cl and 3-Cl in the aggregate state, aggregates were prepared by adding hexane (a poor solvent) into the respective chloroform solutions. Because aggregate states are usually prepared by use of a poor solvent,^[1a,2a] hexane was used to induce the formation of nanoparticles of 2-Cl and 3-Cl. Aggregation was confirmed by dynamic light scattering (DLS). DLS measurements in 90 vol.-% hexane showed the formation of aggregates with particle sizes of 518 and 573 nm for 2-Cl and 3-Cl, respectively (Figure S1, Supporting Information). The absorption and emission spectra were obtained immediately after preparing the aggregates because the nanoparticles began to precipitate within 15 min.

The absorption spectra of 2-Cl and 3-Cl in chloroform solution and as chloroform/hexane mixtures are shown in Figure S2. Tailing was apparent in the long-wavelength region of the absorption spectra of the chloroform/hexane mixtures. These tails were attributed to light scattering by the nanoparticles of the complex molecules.^[2b] As shown in Table S1 and Figure 2, 2-Cl ($\lambda_{em} = 589$ nm) and 3-Cl ($\lambda_{em} = 663$ nm) exhibited weak luminescence in the chloroform solutions. However, a significant enhancement in the emission of 2-Cl and 3-Cl was observed if their hexane fractions were above 80 and 85%, respectively, in the chloroform/hexane mixtures. If the volume fraction of hexane was 90%, the corresponding emission intensities of 2-Cl ($\lambda_{em} = 577$ nm) and 3-Cl ($\lambda_{em} = 660$ nm) were approximately 46 and 9 times higher than those in the chloroform solution,

respectively. These results indicate that 2-Cl and 3-Cl are AIE active in the chloroform/hexane mixtures. In addition, the emission wavelength of 2-Cl in the chloroform/hexane (90 vol.-%) shifted to higher energy (12 nm) relative to that in the chloroform solution.

To examine the effects of solvents on the AIE properties of the complexes, water was used as a poor solvent in combination with dimethylformamide (DMF) for 1 or methanol for 2-Cl and 3-Cl as good solvents. These good solvents were selected by considering the solubility of each complex and their compatibility with water. DLS measurements in 90 vol.-% water showed the formation of aggregates with particle sizes of 91, 63, and 73 nm for 1, 2-Cl, and 3-Cl, respectively (Figure S3, Supporting Information). As shown in Figure 3 (a), the addition of water (>50 vol.-%) into a methanol solution of 2-Cl led to a redshift in the absorption bands. The emission spectrum of 2-Cl exhibited an increase in the emission intensity accompanied by a redshift (from 585 to 640 nm) upon increasing the proportion of water in the methanol/water mixtures (Figure 3, b). The emission intensity of the mixture with 70% water fraction was approximately 11 times higher than that in the methanol solution, whereas negligible AIE activity of 1 and 3-Cl was observed in the aggregate states with water (Figures S4 and S5, Supporting Information). The absorption and emission wavelength shift of 3-Cl were small in comparison with those of 2-Cl. Notably, the AIE activities of the complexes depended on the solvent systems; complexes 2-Cl and 3-Cl were AIE active in the chloroform/hexane systems, whereas only complex 2-Cl showed AIE activity in the methanol/water system. The luminescence decay time (τ) of **2**-Cl in the solution $(\tau_{chloroform} = 3.1 \,\mu s, \tau_{methanol} = 3.1 \,\mu s)$ and aggregate states $(\tau_{\text{chloroform/hexane}} = 6.3 \,\mu\text{s}, \tau_{\text{methanol/water}} = 3.3 \,\mu\text{s})$ were exam-



Figure 2. Emission spectra of (a) 2-Cl (λ_{ex} = 384 nm) and (b) 3-Cl (λ_{ex} = 404 nm) in chloroform/hexane mixtures (5 × 10⁻⁵ M).



Figure 3. (a) Absorption and (b) emission spectra of 2-Cl in methanol/water mixtures (5×10^{-5} M, $\lambda_{ex} = 400$ nm).



ined (Table S2 and Figure S6, Supporting Information). The long emission life time indicates that **2**-Cl exhibited phosphorescent emissions.

One of the factors of AIE-active Pt^{II} complexes is MMLCT^[6] and their emission shift to lower energies upon cooling (77 K) because of the enhancement in the metalmetal interactions.^[6b] To determine the main cause of the AIE activities of 2-Cl and 3-Cl, the photoluminescence spectra of 2-Cl and 3-Cl were obtained in CH₂Cl₂/THF (3:2 v/v) solution at room temperature and at 77 K. Because CH₂Cl₂ and THF are good solvents for 2-Cl and 3-Cl, the formation of aggregates was not observed. The emission bands of 2-Cl and 3-Cl in solution shifted to higher energies at 77 K (glass matrix) relative to those obtained at room temperature (Figure S7, Supporting Information); emission originating from MMLCT was not observed. X-ray crystallographic analysis of 2-Cl^[10] was consistent with the photoluminescence data, which indicated the absence of d^8-d^8 metal-metal interactions because the Pt-Pt distance between adjacent complexes was 9.66 Å. Thus, it is postulated that the AIE activities of 2-Cl and 3-Cl originate primarily from the suppression of molecular motion in the aggregate state, as proposed by Tang and other researchers.^[1–3] Electrostatic interactions promote the tendency to aggregate and enhance the AIE activity.^[11] X-ray crystallographic analysis of 2-Cl revealed that the thioamide group of 2-Cl forms hydrogen-bonding interactions with the counteranion (N-H···Cl⁻, 2.45 Å, Figure 4, a). The results suggest that the AIE activity of 2-Cl is induced by these hydrogen-bonding interactions.

As mentioned above, in the water system only complex 2-Cl showed AIE activity. These results indicate that water molecules interrupt the ionic interactions but that the hydrogen-bonding interactions in 2-Cl remain. The hydrogen-bonding interactions in 2-Cl in the presence of water were evaluated from a crystal structure of 2-BF_4 instead of 2-Cl, because the crystals of the latter could not be obtained (Figure 4, b).^[12] The thioamide groups of 2-BF_4 have hydrogen-bonding interactions with the counteranion (N–H···F, 1.95 Å) and the water molecule (N–H···O, 2.06 Å). Because 2-BF_4 also exhibited AIE activity in the methanol/water system (Figure S8, Supporting Information), it was deduced that the hydrogen-bonding interactions of the secondary thioamide contribute to the AIE activities of 2-Cl.

To consider the blue- and redshifts in the emission spectra of 2-Cl in the chloroform/hexane and methanol/water mixtures relative to the pure solutions, we focused on the origin of absorption in the long-wavelength region and on the emission of 2-Cl. Time-dependent DFT calculations of 2^+ , which was used as a model complex for 2-Cl, revealed that the absorption band in the long-wavelength region (380–500 nm) was assigned as metal-to-ligand charge transfer (MLCT) and ligand-centered (LC) transitions (Figure S9 and Table S3, Supporting Information). This assignment is consistent with the thioamide-based pincer complexes reported previously.^[8,13] These results suggested that MLCT excited states were involved in the emission of 2-Cl.



Figure 4. Hydrogen-bonding networks of (a) 2-Cl·CHCl₃ and (b) 2-BF₄·H₂O·MeOH. Chloroform, methanol, and hydrogen atoms except for N–H are omitted for clarity.

In addition, the origin of emission of 2-Cl in the aggregate state was also supposed to be MLCT, because the decay lifetime curves of 2-Cl in the solution state (methanol) were similar to those in the aggregate state (methanol/water; see Figure S6, Supporting Information). It was reported that the wavelength of emission through MLCT excited states depends on solvent polarity.^[14] Because the emission wavelength of 2-Cl shifted to lower energy with an increase in the solvent polarity (positive solvatochromism; Figure S10, Supporting Information),^[14] a blueshift or redshift in the emission spectra of 2-Cl in the aggregate states could be induced by changes in the solvent polarities around the complex molecules. To confirm the effect of the hydrogenbonding interactions on the emission wavelength, the emission behavior of 2-BF₄ in the crystal state was examined, because the crystal structure exhibited the presence of hydrogen-bonding interactions with water molecules (Figure 4, b). The emission wavelength of $2-BF_4$ in the crystal state was much shorter (588 nm) than that of 2-Cl in the aggregate state in methanol/water (640 nm) and was almost the same as that of 2-Cl in chloroform solution (589 nm; see Figure S11, Supporting Information). Therefore, the effect of hydrogen bonding on the emission wavelength is negligible. These results suggested that the redshift in the aggregate state in methanol/water was due to positive solvatochromism induced by the solvent polarity around the complex.



Conclusions

In summary, cationic complex 2-Cl bearing secondary thioamide units exhibited AIE activity induced by hydrogen-bonding and interionic interactions. The origin of the AIE in the pincer platinum(II) complexes differs from that of conventional AIE-active platinum(II) complexes, which occurs by metal-metal interactions. These results should provide valuable information for the design of AIE-active complexes by exploiting hydrogen-bonding and ionic interactions with counteranions.

Experimental Section

General Procedures: All NMR spectra were obtained with a Bruker Avance-400S with tetramethylsilane or [D₃]phosphoric acid solution as an internal standard. MALDI-MS spectra were recorded with a Kratos-Shimadzu AXIMA-CFR plus MALDI-TOF MS. Elemental analyses were performed with a Perkin–Elmer 2400 CHN Elemental Analyzer. Average particle sizes of the aggregates were measured by dynamic light scattering (FDLS3000, Otsuka Electronics). Absorption spectra were recorded with a JASCO V-630 spectrometer. The emission spectra at room temperature were measured with a JASCO FP-6200 spectrophotometer. The emission spectra at room temperature and 77 K were measured with a Hitachi F-2700 spectrophotometer. The temporal profiles of the luminescence decay were recorded by using a microchannel plate photomultiplier (Hamamatsu, R3809U) equipped with a TCSPC computer board module (Becker and Hickl, SPC630).

Synthetic Methods: Complex $1^{[8]}$ and 1,3-bis(1-piperidinothiocarbonyl)phenyl{C²,S,S'}chloroplatinum(II)^[9] were synthesized according to methods reported in the literature.

Synthesis of Complex 2-Cl: A mixture of complex 1 (151.5 mg, 0.25 mmol) and triphenylphosphine (78.7 mg, 0.30 mmol) was stirred by ultrasound in acetone (100 mL) for 1 h at 40 °C. The solvent was evaporated under reduced pressure. The residue was washed with hexane and extracted with chloroform. Recrystallization from chloroform/hexane gave complex 2-Cl (204.7 mg, 94%). ¹H NMR (400 MHz, [D₆]DMSO): δ = 12.17 (s, 2 H), 8.32 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.62–7.53 (m, 9 H), 7.49–7.44 (m, 7 H), 7.39–7.29 (m, 10 H), 4.89 (s, 4 H) ppm. ³¹P{¹H} NMR (162 MHz, [D₆]DMSO): δ = 19.64 [*J*(Pt,P) = 2227.9 Hz] ppm. MALDI-TOF-MS: calcd. for C₄₀H₃₄N₂PPtS₂ [M – Cl + H]²⁺ 833.2; found 833.1. C₄₀H₃₄ClN₂PPtS₂ (868.4): calcd. C 55.33, H 3.95, N 3.23; found C 54.94, H 4.04, N 3.27.

Synthesis of Complex 3-Cl: Synthesized in the same manner as complex **2-**Cl, except that 3-bis(1-piperidinothiocarbonyl)phenyl{C2,S,S'}chloroplatinum(II) was used instead of complex **1**, yield 31.6 mg, 70%. ¹H NMR (400 MHz, [D₆]DMSO): δ = 7.65 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.56–7.58 (m, 9 H), 7.45–7.50 (m, 6 H), 7.34 (t, *J* = 8.0 Hz, 1 H), 4.24 (br. s, 4 H), 4.06 (br. s, 4 H), 1.79 (br. m, 12 H) ppm. ³¹P{¹H} NMR (162 MHz, [D₆]DMSO): δ = 18.95 [*J*(Pt,P) = 1135.8 Hz] ppm. MALDI-TOF-MS: calcd. for C₃₆H₃₈N₂PPtS₂ [M – Cl]⁺ 788.2; found 788.1. C₃₆H₃₈ClN₂PPtS₂· 1.5H₂O (851.4): calcd. C 50.79, H 4.85, N 3.29; found C 50.73, H 4.82, N 3.19.

Crystal Structure Determination: Intensity data were collected with a Rigaku R-AXIS RAPID and a Bruker APEX-II CCD diffractometer with Mo- K_{α} radiation. A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic ther-

mal parameters method by the SHELXL-97 program. Hydrogen atoms except for H1 and H2 were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. H1 and H2 of 2-Cl and 2-BF₄ were determined by difference Fourier map and refined isotropically.

CCDC-957173 (for 2-Cl) and -957174 (for 2-BF_4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: The geometrical structures were optimized at the B3LYP level for 2^+ with the LANL2DZ basis set implemented in the Gaussian 09 program suite.^[15] By using the optimized geometries, time-dependent DFT calculations were performed at the B3LYP level for 2^+ to predict their absorptions.

Supporting Information (see footnote on the first page of this article): Size distribution, absorption spectra, and emission spectra of 1-3; luminescence decay time of 2-Cl; and DFT calculations for 2^+ .

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- a) Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Soc. Rev.* 2011, 40, 5361–5388; b) S. Kamino, Y. Horio, S. Komeda, K. Minoura, H. Ichikawa, J. Horigome, A. Tatsumi, S. Kaji, T. Yamaguchi, Y. Usami, S. Hirota, S. Enomoto, Y. Fujita, *Chem. Commun.* 2010, 46, 9013–9015.
- [2] a) Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Commun.* 2009, 4332–4353; b) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.* 2001, 1740–1741.
- [3] a) G.-G. Shan, D.-X. Zhu, H.-B. Li, P. Li, Z.-M. Su, Y. Liao, Dalton Trans. 2011, 40, 2947–2953; b) T. Zhou, F. Li, Y. Fan, W. Song, X. Mu, H. Zhang, Y. Wang, Chem. Commun. 2009, 3199; c) J. Kuwabara, Y. Ogawa, A. Taketoshi, T. Kanbara, J. Organomet. Chem. 2011, 696, 1289–1293.
- [4] a) K. Umakoshi, T. Kojima, K. Saito, S. Akatsu, M. Onishi, S. Ishizaka, N. Kitamura, Y. Nakao, S. Sakaki, Y. Ozawa, *In*org. Chem. **2008**, 47, 5033–5035; b) Y. Chen, W.-C. Xu, J.-F. Kou, B.-L. Yu, X.-H. Wei, H. Chao, L.-N. Ji, *Inorg. Chem.* Commun. **2010**, 13, 1140–1143; c) N. Komiya, M. Okada, K. Fukumoto, D. Jomori, T. Naota, J. Am. Chem. Soc. **2011**, 133, 6493–6496.
- [5] a) Y. Dong, J. W. Y. Lam, A. Qin, J. Liu, Z. Li, B. Z. Tang, J. Sun, S. Kwok, *Appl. Phys. Lett.* **2007**, *91*, 011111; b) L. J. Grove, J. M. Rennekamp, H. Jude, W. B. Connick, *J. Am. Chem. Soc.* **2004**, *126*, 1594–1595; c) G.-G. Shan, L.-Y. Zhang, H.-B. Li, S. Wang, D.-X. Zhu, P. Li, C.-G. Wang, Z.-M. Su, Y. Liao, *Dalton Trans.* **2012**, *41*, 523–530.
- [6] a) V. W.-W. Yam, K. M.-C. Wong, N. Zhu, J. Am. Chem. Soc. 2002, 124, 6506–6507; b) V. W.-W. Yam, K. H.-Y. Chan, K. M.-C. Wong, N. Zhu, Chem. Eur. J. 2005, 11, 4535–4543; c) W. Lu, Y. Chen, V. A. L. Roy, S. S.-Y. Chui, C.-M. Che, Angew. Chem. Int. Ed. 2009, 48, 7621–7625; Angew. Chem. 2009, 121, 7757–7761.
- [7] E. Rossi, A. Colombo, C. Dragonetti, D. Reberto, F. Demartin, M. Cocchi, P. Brulatti, V. Fattori, J. A. G. Williams, *Chem. Commun.* 2012, 48, 3182–3184.



- [8] K. Okamoto, T. Yamamoto, M. Akita, A. Wada, T. Kanbara, Organometallics 2009, 28, 3307–3310.
- [9] a) T. Kanbara, K. Okada, T. Yamamoto, H. Ogawa, T. Inoue, J. Organomet. Chem. 2004, 689, 1860–1864; b) M. Akaiwa, T. Kanbara, H. Fukumoto, T. Yamamoto, J. Organomet. Chem. 2005, 690, 4192–4196; c) R. A. Begum, D. Powell, K. Bowman-James, Inorg. Chem. 2006, 45, 964–966; d) V. A. Kozlov, D. V. Aleksanyan, Yu. V. Nelyubina, K. A. Lyssenko, E. I. Gutsul, L. N. Puntus, A. A. Vasil'ev, P. V. Petrovskii, I. L. Odinets, Organometallics 2008, 27, 4062–4070.
- [10] Å single crystal of 2-Cl·CHCl₃ was obtained from a concentrated chloroform solution of 2-Cl. Crystallographic details for 2-Cl·CHCl₃: C₄₁H₃₅N₂PPtS₂Cl₄, M = 987.74, Rigaku R-AXIS RAPID (Mo- K_{α} radiation), T = 90 K, monoclinic space group P_{2_1} , a = 11.4766(4) Å, b = 9.6619(3) Å, c = 18.1480(6) Å, $\beta = 96.764(1)^\circ$, V = 1998.3(1) Å³, Z = 2, $D_{calcd.} = 1.641$ gcm⁻³, 32342 measured reflections, 8820 independent reflections [$R_{int} = 0.0769$], $R_1[I > 2\sigma(I)] = 0.0479$, w R_2 (all data) = 0.1284, GOF = 1.059.
- [11] R.-H. Chien, C.-T. Lai, J.-L. Hong, J. Phys. Chem. C 2011, 115, 12358–12366.
- [12] A single crystal of 2-Cl could not be obtained from a methanol/ water mixture, whereas a single crystal of 2-BF₄·H₂O·CH₃OH was obtained by the slow evaporation of methanol into a methanol/water solution of 2-BF₄. Crystallographic details for 2-BF₄·H₂O·CH₃OH: C₄₁H₄₀BF₄N₂O₂PPtS₂, M = 969.77, Bruker APEX-II CCD (Mo- K_a radiation), T = 90 K, triclinic space group $P\bar{I}$, a = 10.0406(7) Å, b = 14.1142(10) Å, c =14.7104(10) Å, $a = 74.4260(10)^\circ$, $\beta = 80.2570(10)^\circ$, $\gamma =$

84.3080(10)°, V = 1976.0(3) Å³, Z = 2, $D_{\text{calcd.}} = 1.630$ gcm⁻³, 22323 measured reflections, 8612 independent reflections [$R_{\text{int}} = 0.0139$], $R_1[I > 2\sigma(I)] = 0.0208$, w R_2 (all data) = 0.0569, GOF = 1.063.

- [13] J. Kuwabara, G. Munezawa, K. Okamoto, T. Kanbara, *Dalton Trans.* 2010, 39, 6255–6261.
- [14] C.-C. Ko, J. W.-K. Siu, A. W.-Y. Cheung, S.-M. Yiu, Organometallics 2011, 30, 2701–2711.
- [15], M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, rev. B.01, Gaussian, Inc., Wallingford, CT, 2010.

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