Electronic Supplementary Information (ESI)

Pyridyne Cycloaddition of Graphene: "External" Active Sites for Oxygen Reduction Reaction

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Table of Contents

1. General Experimental Section

1.1 Materials

Graphene sheets (99%) were purchased from Nanjing XianFeng Nano Material Technology Co.,Ltd, China.

Cesium fluoride (99%) and Acetonitrile (99.9%) were purchased from J&K Scientific Ltd.

20 wt% Pt/C were purchased from Alfa Aesar.

Unless otherwise stated, all chemicals were used as received without further purification.

De-ionized water (18.2 MΩ) was used throughout the experiments.

1.2 Instruments

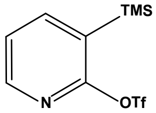
Transmission electron microscopy (TEM) images were performed on Tecnai G2F30S-Twin electron microscope operating at 300 kV. Scanning electron microscopy (SEM) images were performed on Hitachi S4700. Thermogravimetric analysis (TGA) was measured under an argon atmosphere to 900 °C with a Perkin Elmer Thermal Analyzer at a heating rate of 10 °Cmin^{-1}. Atomic force microscopy (AFM) images were recorded with Tapping mode in a commercial Nanoscope VIII MultiMode SPM system (Bruker, Santa Barbara, CA) under ambient conditions (temperature, 24 C; humidity, 44%). X-ray photoelectron spectroscopy (XPS) analysis was carried on Kratos AXIS Ultra DLD X-ray photoelectron spectrometer. Raman spectra were obtained by inVia Reinishaw confocal spectroscopy with 633nm laser excited. X-ray diffraction (XRD) measurements were performed on a PANalytical-X'Pert PRO generator.

Cyclic voltammetry (CV) experiments were performed on CHI660D Electrochemical analyzer (CHI Instrument Corp. Shanghai). Rotating disk electrode (RDE) measurements were performed on CHI 760C and MSR Electrode Rotator from Pine Research Instrumentation.

1.3 Materials synthesis

Pyridyne precursors were prepared according to literature procedures.[1]

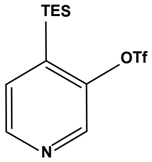
2, 3-pyridyne precursor: 3-Trimethylsilyl-2-pyridyl Trifluoromethanesulfonate



^{1}H NMR (CDCl3) δ: 8.32 (dd, J) 1.8, 4.8 Hz, 1H), 7.94 (dd, J) 1.8, 7.2 Hz, 1H), 7.32 (dd, J) 4.8, 7.2 Hz, 1H), 0.38 (s, 9H).

^{13}C NMR (CDCl3) δ: 160.8, 148.7, 146.9, 125.2, 123.1, 119.8, 117.2 (d, Jcf) 317 Hz), -1.68.

3, 4-pyridyne precursor: 4-(Triethylsilyl)pyridin-3-yl Trifluoromethanesulfonate



^{1}H NMR ($CDCl_3$) δ: 8.3 (s, 1H), 8.0 (d, J) 4.5 Hz, 1H), 7.3 (d, J) 4.8 Hz, 1H), 0.95 (m, 15H).

^{13}NMR ($CDCl_3$) δ: 152.2, 147.8, 141.0, 140.3, 130.8, 119.7 (d, J) 320 Hz), 7.0, 2.8.

Pyridynes Cycloaddition of Graphene (PyNGs)

Typically, 2,3-pyridyne precursor (5 mmol, 2.5 equiv. per graphene carbon) was added to an acetonitrile solution of the pristine graphene sheets (Gs) (24 mg, 2mmol) and CsF (10 mmol, 5 equiv. per graphene carbon), the mixture was stirred at 80℃ for 24 h. After completion of the reaction, the 2,3-pyridyne cycloaddition of graphene (PyNG-2) were separated from the mixture by filtration, washed thoroughly with N,N-dimethylformamide (DMF), water and ethanol, in order to ensure that no residual pyridine and by-product remains, then collected and dried in vacuo.

For the purpose of comparsion, in the similar way, the PyNG-3 was also prepared by using 3,4-pyridyne precursor.

1.4 Electrochemical characterization

5 mg of the graphene samples were dispersed in a solution containing 4.8 ml of deionized water (18.2 MΩ) and 0.2 ml of 5 wt.% Nafion aqueous solution (1mg.ml-1). The mixtures were ultrasonicated for 10 minutes to obtain a homogenous catalyst ink.

To prepare the working electrode for electrochemical measurements, 10 μl of the ink was dipped on a glass carbon electrode (3 mm in diameter). For comparison, a commercially available catalyst of 20 wt% Pt/C was used and 1 mg.ml-1 suspension was also prepared as the same procedure described above. The electrode is allowed to dry at room temperature before measurement.

Cyclic voltammetry (CV) experiments：the working electrode was inserted into the cell setup, which is composed of a platinum counter electrode, an Ag/AgCl/KCl (3 M) reference electrode and a 30 ml glass cell containing 20 ml of 0.1 M KOH aqueous electrolyte. Before test, electrolyte was saturated with O_2/N_2 by bubbling O_2/N_2 prior to the start of each experiment. A flow of O_2/N_2 was maintained over the electrolyte during the recording of CVs in order to ensure its continued O_2/N_2 saturation. The potential range is cyclically scanned between -1.2 and +0.2 V at different scan rate of 100 mV s-1 at the ambient temperature.

Rotating disk electrode (RDE) measurement: the same amount of catalyst was loaded on a rotating glass carbon electrode (3mm in diameter). A Pt sheet and an Ag/AgCl/KCl (3 M) were used as the counter and reference electrodes, respectively. The linear sweep voltammograms of the modified glass carbon electrode were recorded in O_2 saturated 0.1 M KOH with a scan rate of 10 mV s^{-1} at various rotating speeds from 400 to 2025 rpm. After each scan, the electrolyte was saturated with O_2 again for 20 minutes.

As a matter of fact, in order to get more accurate and reliable data, the samples was tested 3 times to avoid any incidental error.

The Koutecky-Levich plots were obtained by linear fitting of the reciprocal rotating speed versus reciprocal current density collected at different potentials form -0.4 V to -0.8 V. The overall electron transfer numbers per oxygen molecule involved in a typical ORR process weere calculated from the slopes of Koutecky-Levich plots using the following equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

where j is the current, j_k is the kinetic current, ω is the electrode rotating speed in rpm, and B is the Levich slope, which was determined from the slope of Koutecky-Levich plots based on Levich equation as followed:

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6}$$

where n is the number of electrons transferred per oxygen molecule, F is the Faraday constant （96485 C mol^{-1}）, D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10-5 cm s^{-1}), ν is the kinetic viscosity, and C_0 is the concentration of O_2 (1.2×10^{-3} mol L^{-1}). The constant 0.2 is adopted when the rotating speed is in rpm.

2. Supplementary Results

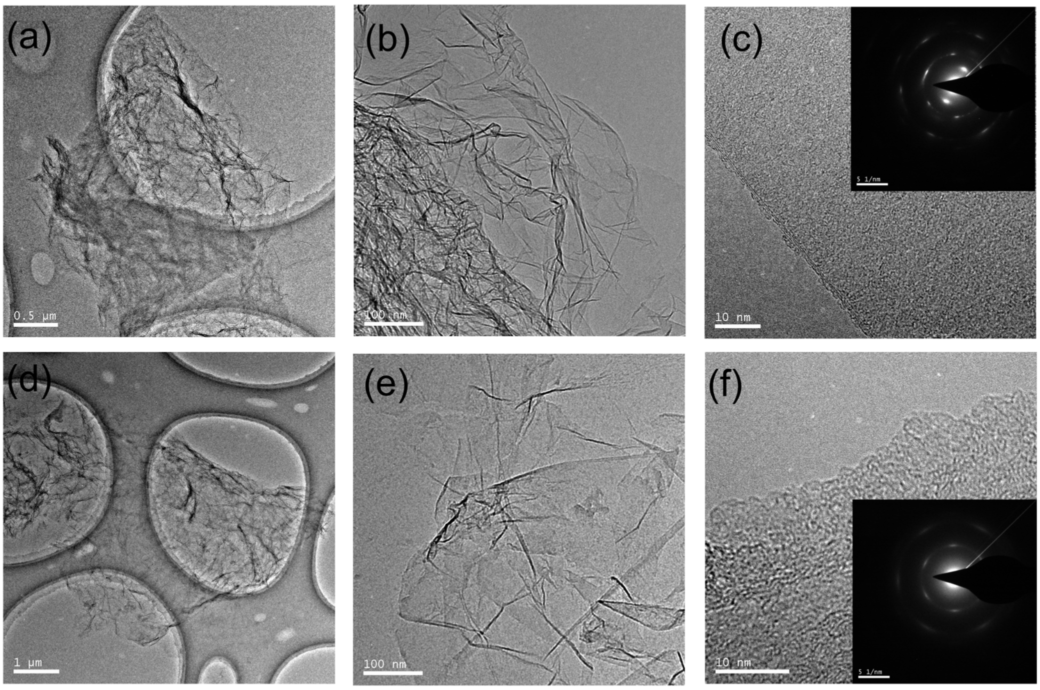


Figure S1. TEM images of (a), (b) and (c): Gs; (d), (e) and (f): PyNG-3.

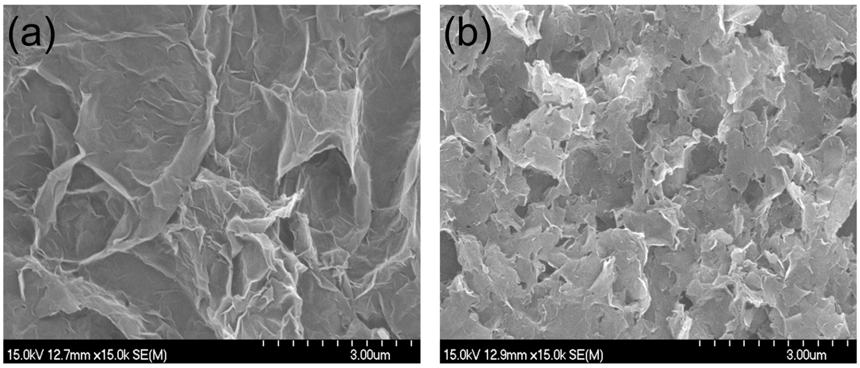


Figure S2. SEM images of (a): Gs and (b): PyNG-3.

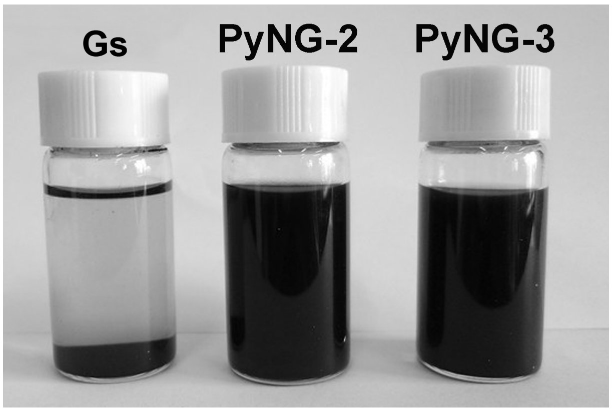


Figure S3. Photographs of Gs and PyNGs dispersions in DMF.

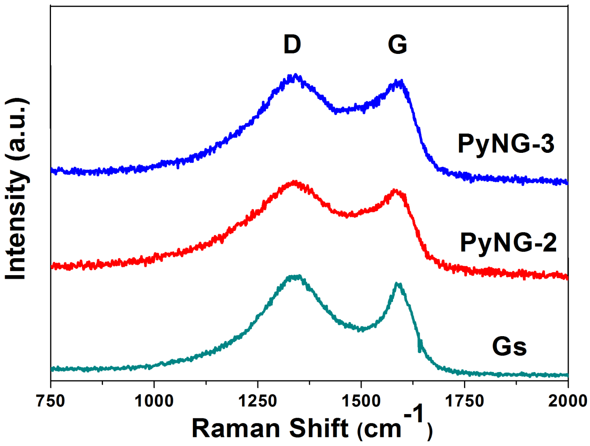


Figure S4. Raman spectra of Gs, PyNG-2, and PyNG-3.

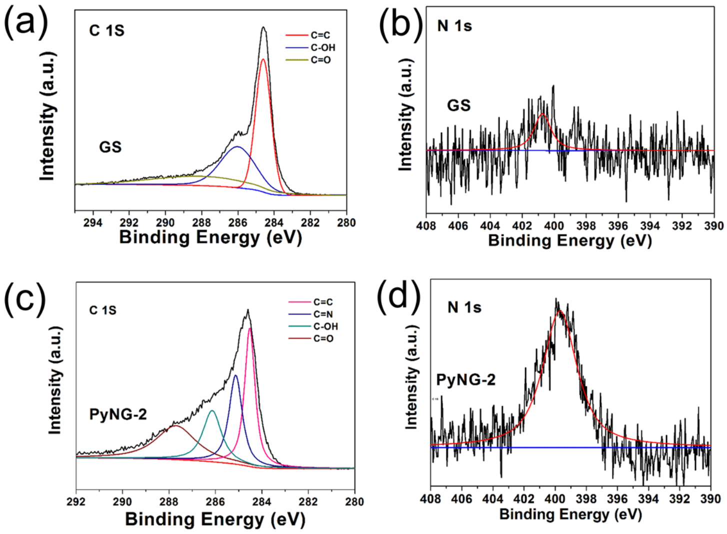


Figure S5. C1s and N1s XPS spectra of (a) and (b): Gs; (c) and (d): PyNG-2.

Table S1: The calculated mass concentrations of different atoms in Gs and PyNGs.

	C%	**N%**	**O%**
Gs	86.05	0.44	13.51
PyNG-2	80.29	5.87	13.84
PyNG-3	81.77	5.06	13.17

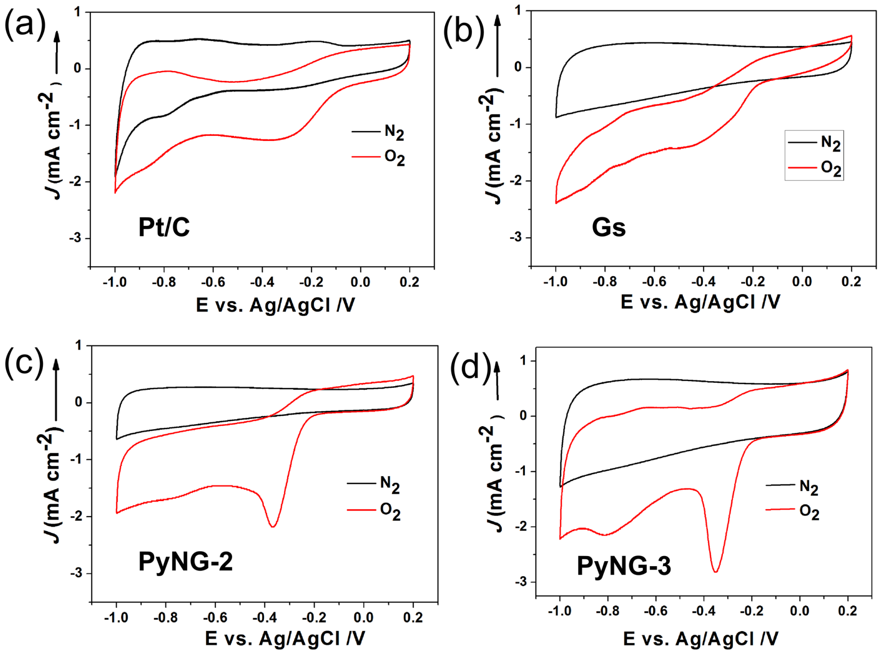


Figure S6. CVs of (a) commercial Pt/C, (b) Gs, (c) PyNG-2 and (d) PyNG-3 in N_2 saturated 0.1 M KOH, O_2-saturated 0.1 M KOH.

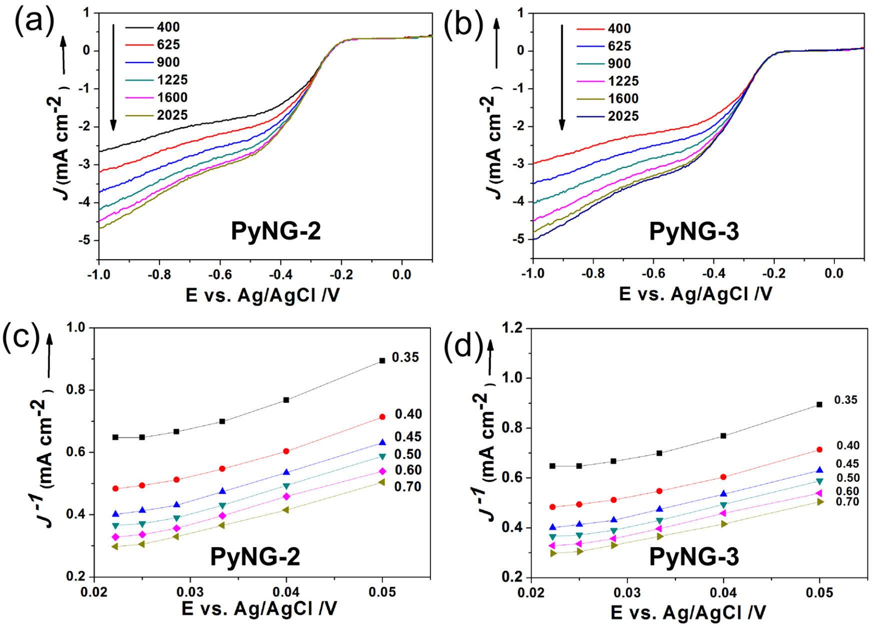


Figure S7. LSV of (a) PyNG-2, (b) PyNG-3 on RDE at different rotating rates (400 to 2,025 rpm). Corresponding Koutecky–Levich plot of (c) PyNG-2 and (d) PyNG-3 at different potentials.

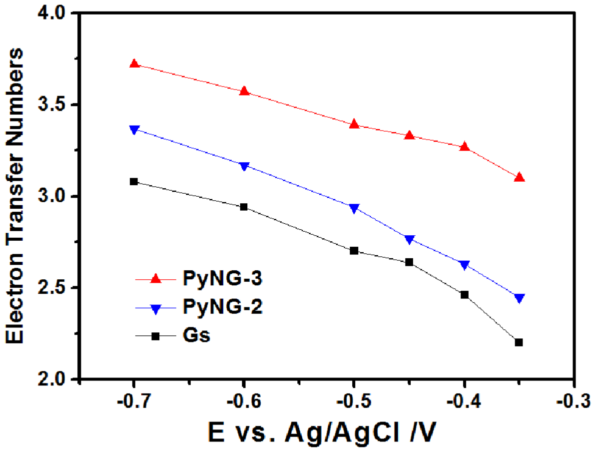


Figure S8. Electron transfer numbers as a function of the overpotential of Gs and PyNGs.

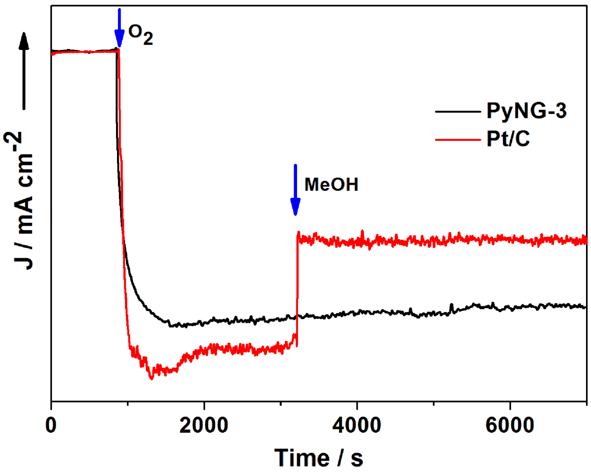


Figure S9. Methanol crossover tolerance test of PyNG-3 and 20% Pt/C conducted by chronoamperometric response at -0.35 V vs Ag/AgCl in 0.1 M KOH aqueous electrolyte.

3. Computational Calculation Section

3.1 Models and Method

A 32 carbon atoms graphene cluster was used in this study, the doping concentration is similar with the experimental one. The terminated carbon was saturated with hydrogen. The geometry optimization of molecule (pyridine), radical (OOH) and graphene (pristine graphene, aryne-doped and PyNG-2, PyNG-3) clusters were carried out by using spin polarized Density Functional Theory method of Gaussian 03 software.[2] All the calculations were performed using the level of UB3LYP/6-31g (d, p). The adsorption energy was typically calculated as follow: E_a = E (OOH/PyNG) – E (PyNG) – E (OOH). Moreover, NBO[3] population analysis was also performed for pure and OOH adsorbed PyNG-2, PyNG-3 systems.

3.2 Computational Calculation results

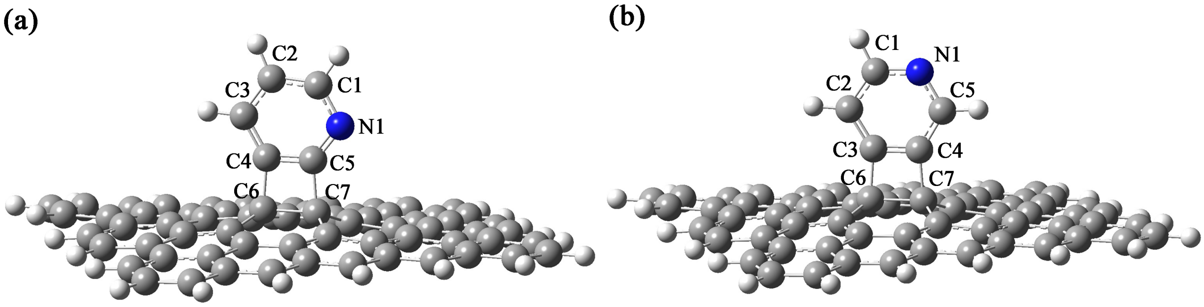


Figure S10. The optimized structures of PyNG-2 (a) and PyNG-3 (b).

Table S2. Natural Charges of Nitrogen and Carbon in PyNG-2 and PyNG-3. (The number of atom is taken from Figure S11.)

Atoms	PyNG-2	PyNG-3
N1	-0.42977	-0.4485
C1	0.01366	0.02154
C2	-0.27524	-0.26739
C3	-0.19217	0.03105
C4	-0.03596	-0.03506
C5	0.2608	0.03317
C6	-0.04497	-0.04938
C7	-0.0632	-0.04624

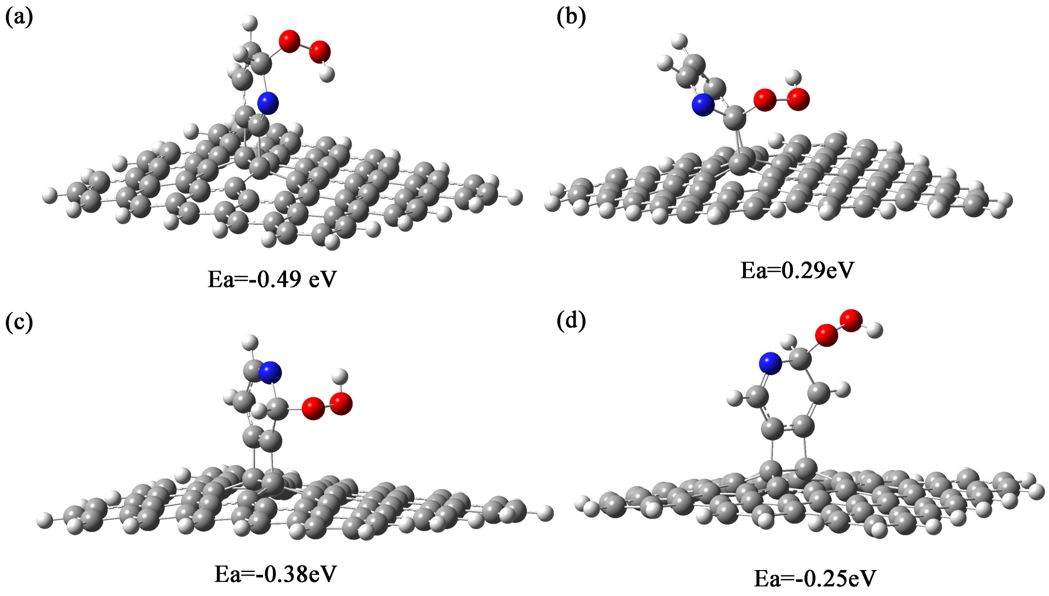


Figure S11. The stable adsorption geometries of OOH on PyNG-2 (a, b) and PyNG-3 (c, d)

4. References

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(2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J.

J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision B.05; Gaussian, Inc.: Pittsburgh PA, 2003.

(3) E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold. NBO Version 3.1.