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Supporting Information

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‘Conformational’ Solvatochromism: Spatial Discrimination of Nonpolar Solvents Using a Supramolecular Box of a [illegible]-Conjugated Zinc Bisporphyrin Rotamer

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1. Materials

Most reagents and solvents were used as received from commercial sources without further purification. *o*-, *m*-, and *p*-Xylene (98%, 99%, and 99%, respectively), γ- and α-terpinene (>95% and >90%, respectively), myrcene (>70%), and terpinolene (>85%) were purchased from Tokyo Kasei Co. (TCI). Compounds $\mathrm{ZnP}(\equiv)_1$ and $\mathrm{ZnP}(\equiv)_4$ were prepared by the procedures reported previously,[1,2] and unambiguously characterized by means of ^{1}H NMR, absorption, and emission spectroscopy, along with MALDI-TOF mass spectrometry. For column chromatography, Wakogel C-300HG (particle size 40–60 mm, silica), C-400HG (particle size 20–40 mm, silica), aluminum oxide 90 standardized (Merck), and Bio-Beads*TM* S-X1 (BIO RAD) were used.

2. Measurements

Electronic absorption and fluorescence spectra were recorded on a JASCO type V-570 UV/VIS/NIR spectrometer equipped with a JASCO type ETC-505T temperature/stirring controller and a JASCO type FP-777W spectrometer equipped with a JASCO type ECT-271 temperature/stirring controller, respectively. ^{1}H NMR spectra were recorded on a JEOL model EX-270 or GSX-500 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane (TMS) as an internal standard. Preparative size-exclusion chromatography (SEC) was carried out on a JASCO Type PU-2080 analytical HPLC pump with MD2015 multi wavelength UV-Vis detector, equipped with a column set consisting of TSK-Gel $\mathrm{GMH_{XL}}$ (exclusion limit 4×10^8) and $\mathrm{G5000H_{XL}}$ (exclusion limit 4×10^6), using $\mathrm{CHCl_3}$ as an eluent at a flow rate of 1.0 mL min^{-1}. Matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF-MS) spectrometry was performed with 9-nitroanthracene as a matrix on an Applied Biosystems BioSpectrometry Workstation*TM* model Voyager-DE*TM* STR spectrometer.

3. Synthesis

$H_2P(\equiv)_2$: To a CH_2Cl_2 solution (200 mL) of the zinc complex of 5-(3,5-didodecyloxyphenyl)-10-ethynyl-15-(4-pyridyl)porphyrin (75 mg, 82 μmol) was successively added tetramethylenediamine (TMEDA; 1.23 mL, 8.2 mmol) and CuCl (813 mg, 8.2 mmol), and the mixture was stirred for 30 min at room temperature. Then, the reaction mixture was washed with water and extracted with CH_2Cl_2, and the combined organic extract was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue dissolved into $CHCl_3$ was treated with 6 N aq. HCl, washed with aq. $NaHCO_3$ and water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was chromatographed on silica gel with $CHCl_3$ as an eluent, where the first fraction was collected and recrystallized from CH_2Cl_2/MeCN to give $H_2P(\equiv)_2$ as green solid in 30% yield (45 mg, 25 μmol). MALDI–TOF MS m/z 1709, Calcd for $C_{114}H_{136}N_{10}O_4$ 1709; UV/Vis ($CHCl_3$): λ_{max} = 451, 483, 624, and 726 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ –2.45 (s, 4H, NH), 0.69 (t, J = 6.8 Hz, 12H, alkyl), 1.21 (br. s, 56H, alkyl), 1.90 (m, 8H, alkyl), 4.16 (t, J = 6.5 Hz, 8H, alkyl), 6.93 (s, 2H, Ar), 7.40 (d, J = 1.9 Hz, 4H, Ar), 8.21 (d, J = 5.7 Hz, 4H, Py), 8.89 (d, J = 4.9 Hz, 2H, pyrrole-β), 9.00 (d, J = 4.9 Hz, 2H, pyrrole-β), 9.08 (d, J = 4.9 Hz, 2H, pyrrole-β), 9.08 (d, J = 5.7 Hz, 4H, Py), 9.19 (d, J = 4.9 Hz, 2H, pyrrole-β), 9.29 (d, J = 4.9 Hz, 2H, pyrrole-β), 9.32 (d, J = 4.9 Hz, 2H, pyrrole-β), 9.99 (d, J = 4.9 Hz, 2H, pyrrole-β), 10.02 (d, J = 5.0 Hz, 2H, pyrrole-β), and 10.20 (s, 2H, meso).

$ZnP(\equiv)_2$: A $CHCl_3$ solution of $H_2P(\equiv)_2$ was stirred in the presence of excess $Zn(OAc)_2$ for 1 h and evaporated to dryness under reduced pressure. The residue was extracted with $CHCl_3$/water, and the combined organic extract was dried over anhydrous Na_2SO_4 and evaporated to dryness. Recrystallization of the residue from $CHCl_3$/MeCN gave **ZnP(≡)$_2$** as green solid (46 mg, 25 μmol) quantitatively. MALDI–TOF MS m/z 1837, Calcd for $C_{114}H_{132}N_{10}O_4Zn_2$ 1837; UV/Vis ($CHCl_3$): λ_{max} (ε/$M^{-1}cm^{-1}$) = 446 (321000), 480 (43400), 625 (34400), and 685 (12600) nm; Fluorescence ($CHCl_3$, λ_{ext} = 450 nm): λ_{max} = 630, and 690 nm; ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, perpendicular/planar = 2.5): **[⊥ZnP(≡)$_n$]$_4$** δ 0.70 (t, *J* = 7.4 Hz, 12H, alkyl), 0.75–1.40 (m, 56H, alkyl), 1.44 (m, 8H, alkyl), 1.64 (m, 8H, alkyl), 1.81 (m, 8H, alkyl), 2.20 (d, *J* = 6.0 Hz, 2H, Py), 2.77 (d, *J* = 5.5 Hz, 2H, Py), 3.99-4.10 (m, 8H, alkyl), 6.20 (d, *J* = 5.5 Hz, 2H, Py), 6.43 (d, *J* = 5.5 Hz, 2H, Py), 6.81 (s, 2H, Ar), 7.33 (s, 4H, Ar), 7.38 (s, 2H, Ar), 7.50 (d, *J* = 4.3 Hz, 2H, pyrrole-β), 7.90 (d, *J* = 4.3 Hz, 2H, pyrrole-β), 8.97 (d, *J* = 4.3 Hz, 2H, pyrrole-β), 9.09 (d, *J* = 4.3 Hz, 2H, pyrrole-β), 9.16 (d, *J* = 4.3 Hz, 2H, pyrrole-β), 9.28 (d, *J* = 4.3 Hz, 2H, pyrrole-β), 9.71 (d, *J* = 4.3 Hz, 2H, pyrrole-β), 9.96 (d, *J* = 4.3 Hz, 2H, pyrrole-β), and 10.08 (s, 2H, meso); **[//ZnP(≡)$_n$]$_4$** δ 0.65 (t, *J* = 7.4 Hz, 12H, alkyl), 0.75–1.40 (m, 56H, alkyl), 1.44 (m, 8H, alkyl), 1.64 (m, 8H, alkyl), 2.00 (m, 8H, alkyl), 2.20 (d, *J* = 6.0 Hz, 2H, Py), 2.83 (d, *J* = 5.5 Hz, 2H, Py), 3.99–4.10 (m, 8H, alkyl), 6.26 (d, *J* = 6.0 Hz, 2H, Py), 6.43 (d, *J* = 5.5 Hz, 2H, Py), 6.85 (s, 2H, Ar), 7.34 (s, 2H, Ar), 7.44 (s, 2H, Ar), 7.53 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 7.78 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 8.92 (d, *J* = 4.5 Hz, 2H, pyrrole-β), 9.10 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 9.24 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 9.27 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 9.67 (d, *J* = 4.0 Hz, 2H, pyrrole-β), 10.04 (d, *J* = 4.5 Hz, 2H, pyrrole-β), and 10.03 (s, 2H, meso).

4. Size-exclusion chromatography of $[ZnP(\equiv)_n]_4$ (n = 1, 2, and 4) and $H_2P(\equiv)_2$

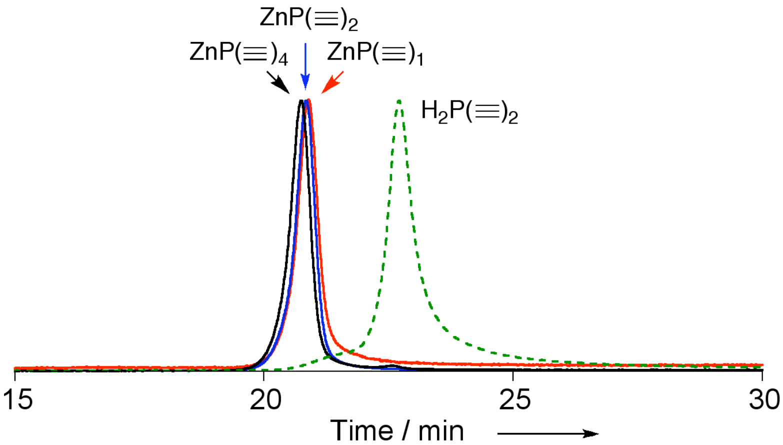
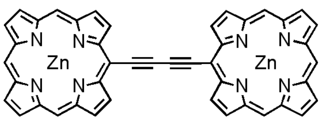


Figure S1. Size-exclusion chromatograms (SEC), using $CHCl_3$ as an eluent, of self-assembled $ZnP(\equiv)_n$ (n = 1, 2, and 4), together with that of free-base $H_2P(\equiv)_2$ as a non-assembled reference.

5. Calculation of absorption spectral profiles of ZnP(≡)$_2$*



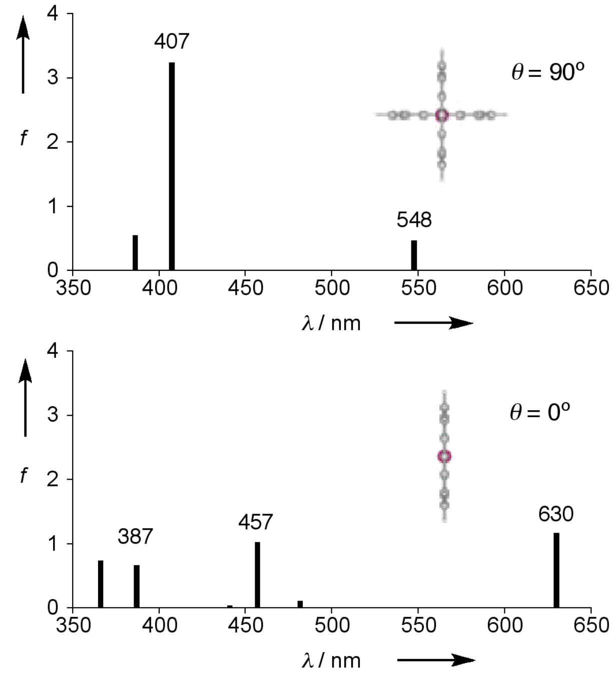


Figure S2. Simulated absorption bands of reference rotamer ZnP(≡)$_2$* with dihedral angles of $\theta = 0$ and 90 degrees, obtained by (TD)DFT calculations (B3LYP/6-31G*) with a Gaussian 03 program package.[3]

6. Absorption spectroscopy of $H_2P(\equiv)_2$ in benzene and CCl_4

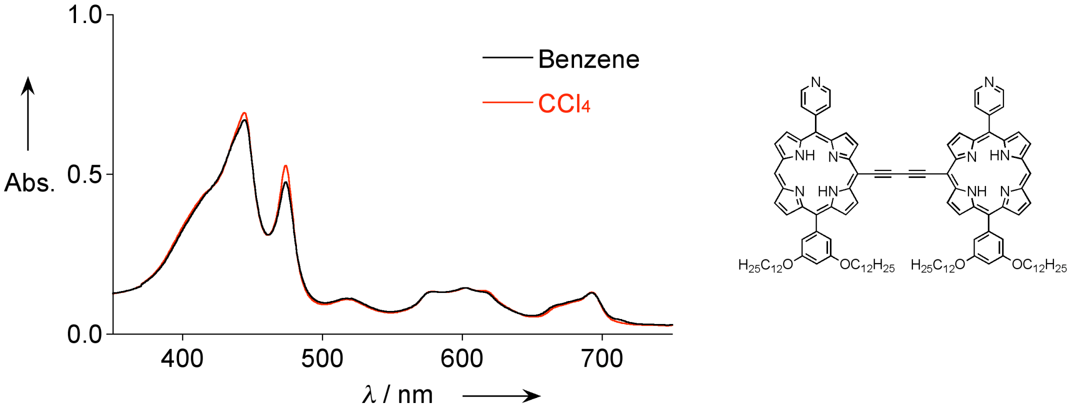


Figure S3. Absorption spectra of $H_2P(\equiv)_2$ in benzene (black curve) and CCl_4 (red curve) at 20 °C (**little solvatochromic response**).

7. Absorption spectroscopy of $[ZnP(\equiv)_1]_4$ and $[ZnP(\equiv)_4]_4$ in benzene and CCl_4

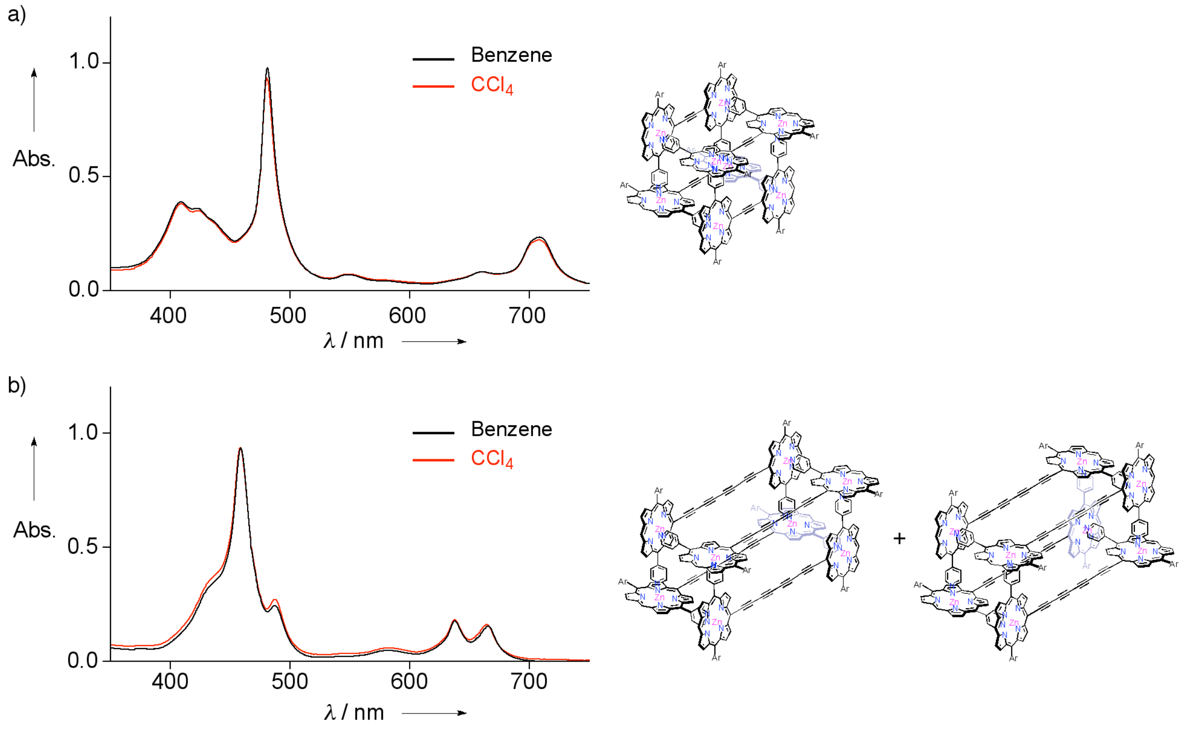


Figure S4. Absorption spectra of a) $ZnP(\equiv)_1$ (7.7×10^{-6} M) and b) $ZnP(\equiv)_4$ (5.9×10^{-6} M) in benzene (black curves) and CCl_4 (red curves) at 20 °C (**no solvatochromic responses**).

8. Dihedral angle-dependent potential energies of ZnP(≡)$_n$* (n = 2 and 4)

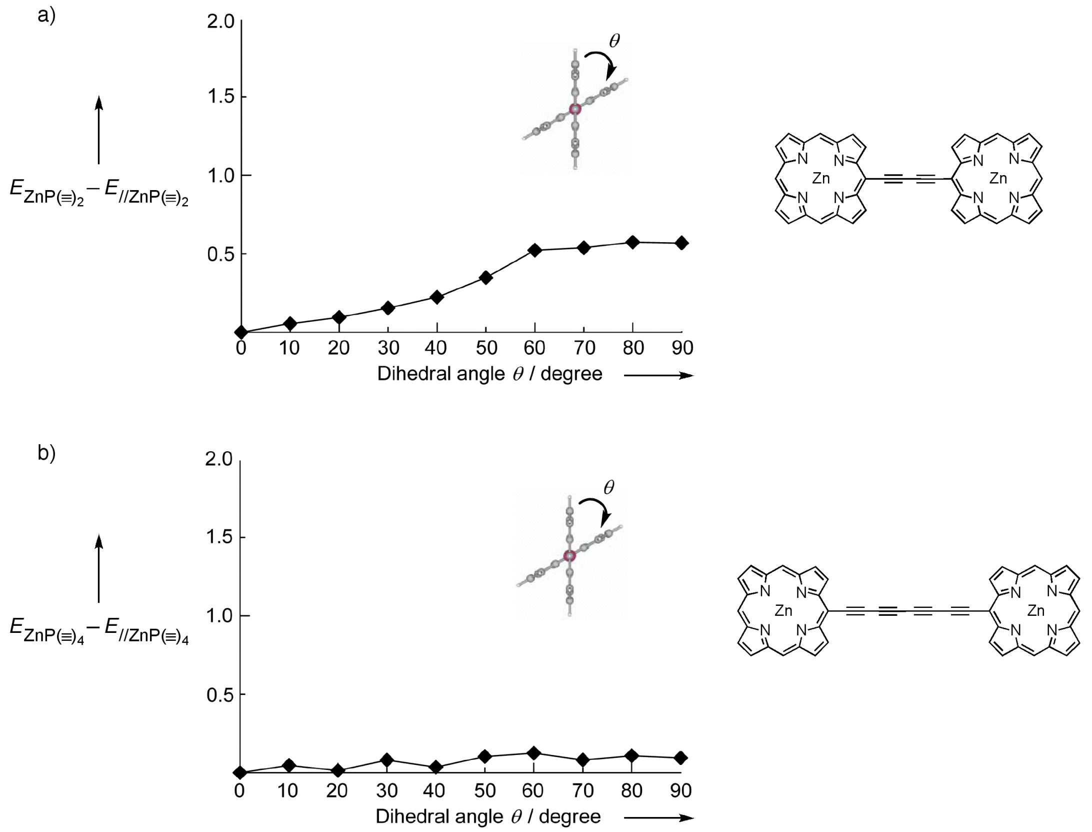


Figure S5. Potential energies (E) of ZnP(≡)$_n$* (n = 2 and 4) relative to those of //ZnP(≡)$_n$* as a function of dihedral angle θ (0–90°), obtained by DFT calculations (B3LYP/6-31G*) with a Gaussian 03 program package.[3]

9. CPK models of cyclic tetramer $[ZnP(\equiv)_2]_4$ without and with included benzene

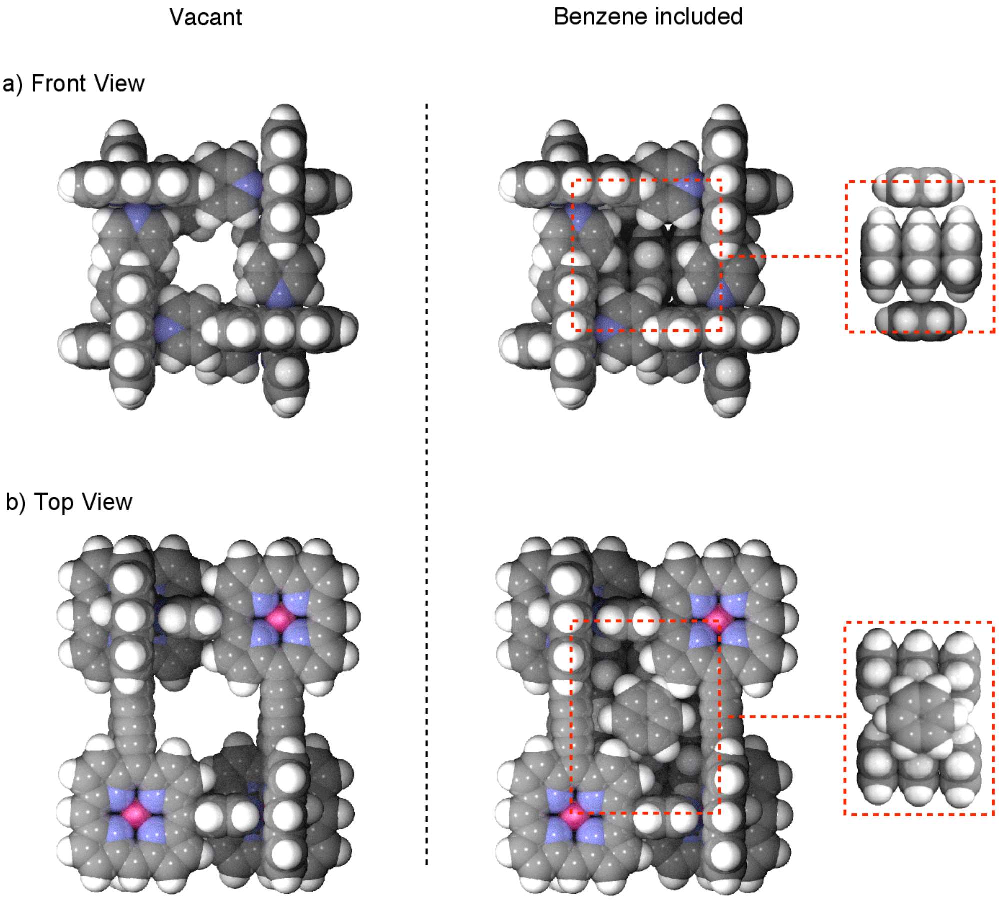


Figure S6. CPK models of, *e.g.*, $[\perp ZnP(\equiv)_2]_4$ without and with eight included benzene molecules in the cavity (1.0 × 1.0 × 1.4 nm). Red broken squares represent clustering benzene molecules caged in the cavity of $[\perp ZnP(\equiv)_2]_4$.

10. References

[1] A. Tsuda, H. Hu, R. Watanabe, T. Aida, *J. Porphyrin Phthalocyanine* **2003**, *7*, 388–393.

[2] J. Aimi, K. Oya, A. Tsuda, T. Aida, *Angew. Chem.* **2007**, *119*, 2077–2081; *Angew. Chem. Int. Ed.* **2007**, *46*, 2031–2035.

[3] Gaussian 03, revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A., Jr. Montgomery, 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, 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.: Pittsburgh, PA, 2003.