- Electronic Supplementary Information -

Photoluminescent responses of graphene quantum dots toward organic bases and an acid

Kaho Suzuki, Kairi Yamato, Ryo Sekiya, and Takeharu Haino*

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526 Japan

*To whom correspondence should be addressed.

haino@hiroshima-u.ac.jp

Contents

Experimental Section

Supporting Figures and Tables

Cartesian Coordinates

References

Experimental Section

General

All chemicals and solvents were purchased from Kanto Chemical Co., Ltd., Wako Pure Chemical Co., Ltd., Tokyo Kasei Kogyo Co., Ltd., and Sigma-Aldrich Co., Ltd., and were used as received without further purification. ^{1}H, and ^{13}CNMR spectra were recorded on a VARIAN 300 MHz spectrometer. Chemical shifts are quoted as parts per million (ppm) relative to chloroform (CDCl$_3$, δ = 7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C). IR absorption spectra were recorded on a JASCO FT/IR-4600 spectrometer using pellets in KBr. UV/vis absorption spectra were recorded on a JASCO V-560 spectrophotometer. Emission spectra were recorded on a JASCO FP-6500 spectrophotometer. GQD-**1** were synthesized by the method reported previously.[1]

Computational Details

Geometry optimizations for **2**–**6** were performed by *Gaussian 09* using B3LYP/6-31G level of theory.[2] The energy levels of the HOMO and LUMO of **2**–**6** are listed in Table S1. The Cartesian coordinates of the energy-minimized conformations of **2**–**6** are listed in Tables S2-S6.

Supporting Figures and Tables
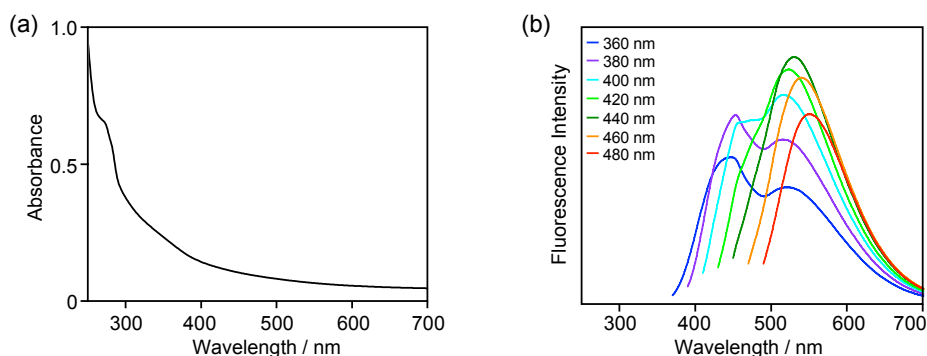
Figure S1. (a) UV/vis absorption and (b) photoluminescence (λ_{ex} = 360, 380, 400, 420, 440, 460, and 480 nm) spectra of GQD-**1** in 1,2-dichlroethane at 293 K.

Figure S2. (a) UV/vis absorption and (b) photoluminescence (λ_{ex} = 360 nm) titration experiments of GQD-**1** in 1,2-dichloroethane at 293 K. Amine: 1,8-diazabicyclo[5.4.0]undec-7-ene (**3**). (c) Stern-Volmer plot of GQD-**1** (λ = 450 nm) upon addition of **3**.
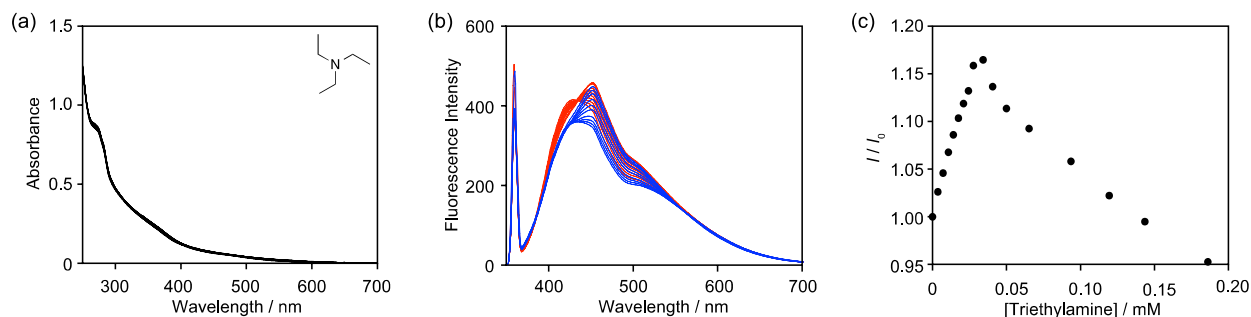
Figure S3. (a) UV/vis absorption and (b) photoluminescence (λ_{ex} = 360 nm) titration experiments of GQD-**1** in 1,2-dichloroethane at 293 K. Amine: triethylamine (**4**). (c) Stern-Volmer plot of GQD-**1** (λ = 450 nm) upon addition of **3**.
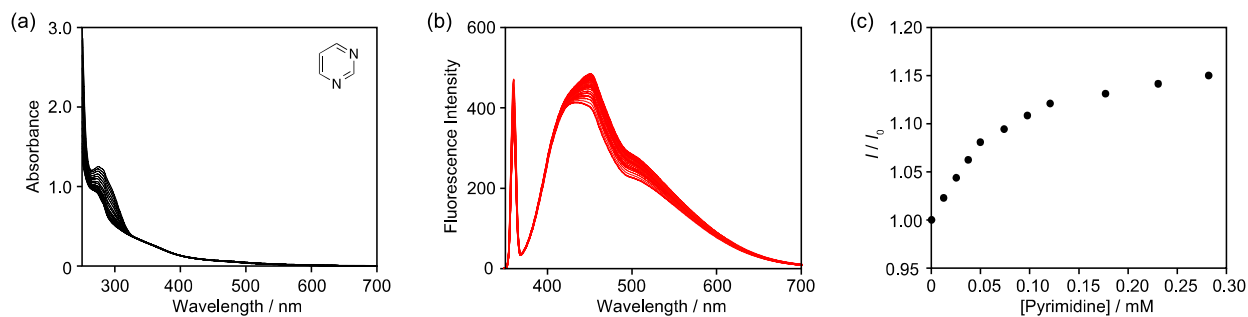
Figure S4. (a) UV/vis absorption and (b) photoluminescence (λ_{ex} = 360 nm) titration experiments of GQD-**1** in 1,2-dichloroethane at 293 K. Amine: pyrimidine (**6**). (c) Stern-Volmer plot of GQD-**1** (λ = 450 nm) upon addition of **6**.

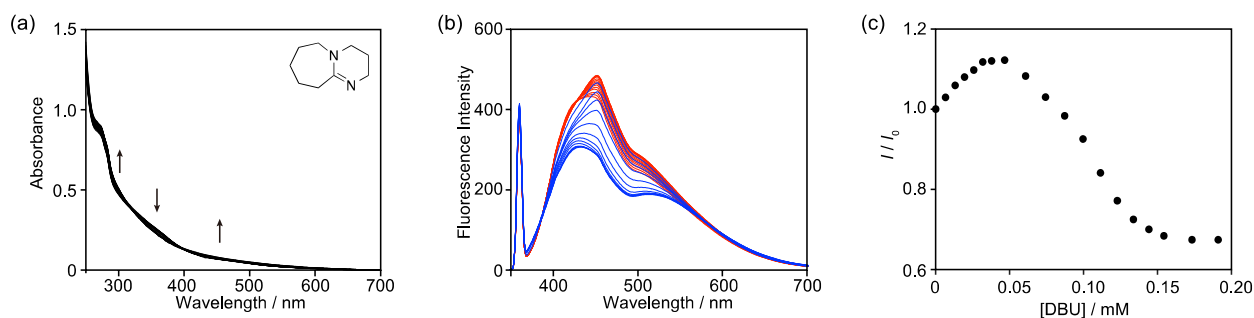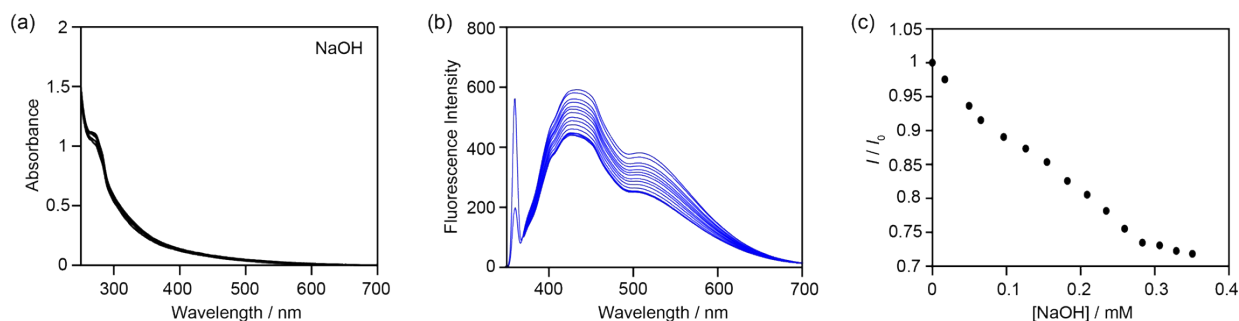**Figure S5.** (a) UV/vis absorption and (b) photoluminescence (λ_{ex} = 360 nm) titration experiments of GQD-**1** in a mixed solvent of THF and ethanol at 293 K. Base: sodium hydroxide. (c) Stern-Volmer plot of GQD-**1** (λ = 450 nm) upon addition of base.
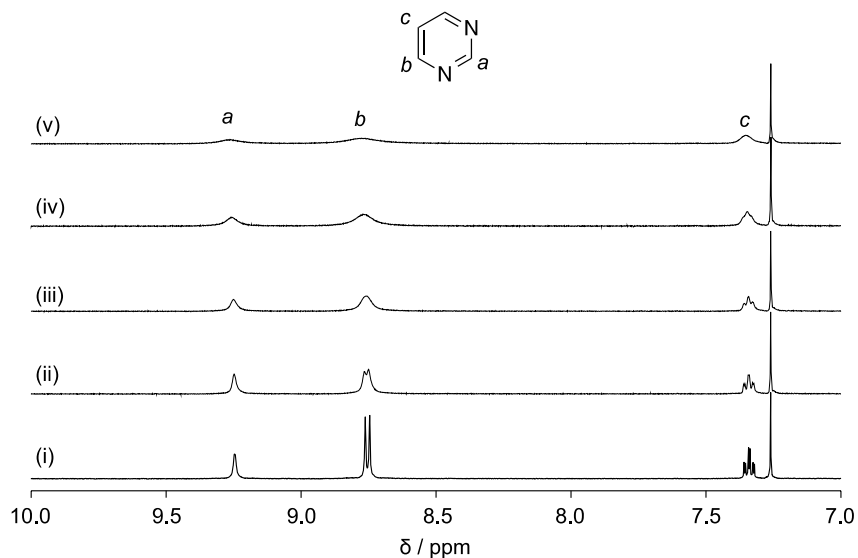
Figure S6. ^{1}H NMR (300 MHz, 293 K, chloroform-d_1) titration experiment of GQD-**1**. Amine: pyrimidine (**6**). The concentration of **6** was 31.84 mM throughout the experiment. The concentration of GQD-**1** were (i) 0, (ii) 0.46, (iii) 0.93, (iv) 1.87, and (v) 3.74 mg mL^{-1}.
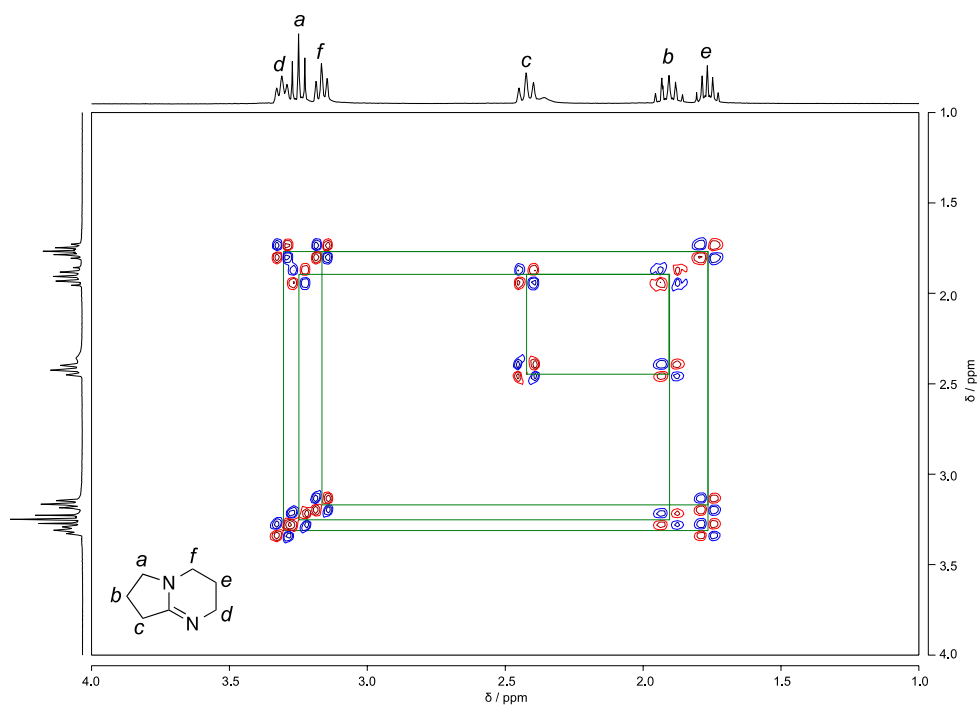
Figure S7. DQF-COSY (300 MHz, 293 K, chloroform-d_1) of 1.5-diazabicyclo[4.3.0]non-5-ene (**2**).
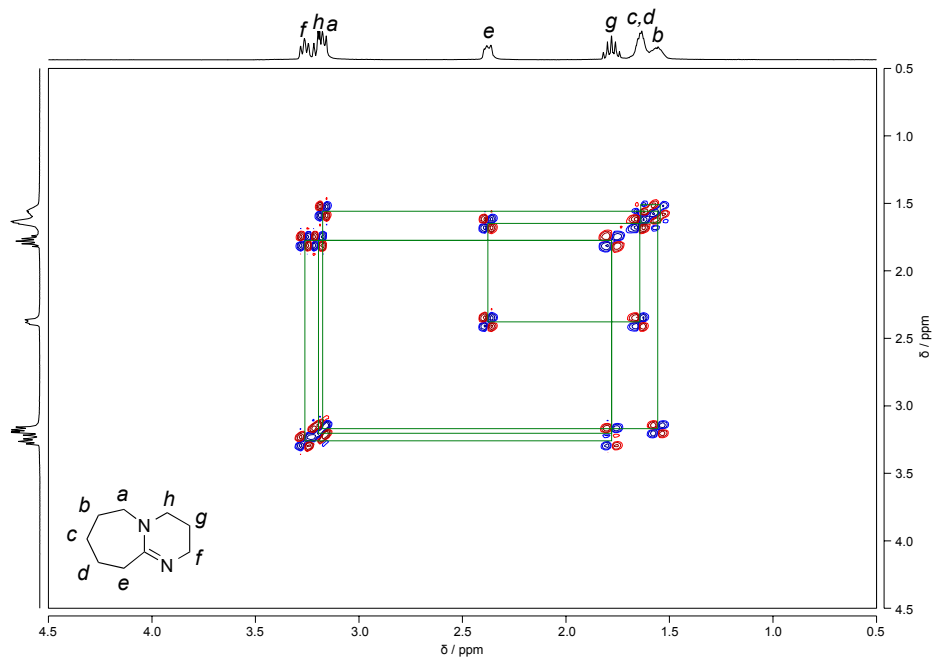
Figure S8. DQF-COSY (300 MHz, 293 K, chloroform-d_1) of 1,8-diazabicyclo[5.4.0]undec-7-ene (**3**).

Table S1. The energy levels of the HOMO+1, HOMO, LUMO, and LUMO+1 of **2–6** calculated by *Gaussian 09* using B3LYP/6-31G(d,p) level of theory.

Base	HOMO+1 / hartree	HOMO / hartree	LUMO / hartree	LUMO+1 / hartree
2	−0.22446	−0.19968	+0.04325	+0.08584
3	−0.22085	−0.19642	+0.04519	+0.06936
4	−0.32065	−0.20417	+0.09184	+0.10894
5	−0.26185	−0.25251	−0.02312	−0.01034
6	−0.28997	−0.25465	−0.04299	−0.03085
	HOMO+1 / eV	HOMO / eV	LUMO / eV	LUMO+1 / eV
2	−6.1078	−5.4335	+1.1769	+2.3358
3	−6.0095	−5.3448	+1.2297	+1.8874
4	−8.7272	−5.5557	+2.4991	+2.9644
5	−7.1252	−6.8710	−0.6291	−0.2814
6	−7.8904	−6.9293	−1.1698	−0.8395

1 harteree = 27.211 eV

Cartesian Coordinates

Table S2. Cartesian coordinates of the optimized structure of **2** at the B3LYP/6-31G(d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	1.569684	1.181220	-0.185106
2	6	0	2.466481	0.017521	0.281678
3	6	0	1.631262	-1.234551	-0.048824
4	1	0	1.717559	2.096642	0.400465
5	1	0	1.754772	1.433012	-1.243911
6	1	0	3.445932	0.027126	-0.202544
7	1	0	2.624038	0.091484	1.362366
8	1	0	1.776956	-2.066039	0.643780
9	1	0	1.852512	-1.608035	-1.056050
10	6	0	-2.137407	-0.830842	-0.128515
11	6	0	-2.151260	0.617143	0.390968
12	6	0	-0.979572	1.412396	-0.197876
13	1	0	-2.857008	-1.429573	0.442885
14	1	0	-2.490102	-0.855156	-1.170943
15	1	0	-2.055792	0.613129	1.482959
16	1	0	-3.099539	1.108096	0.146885
17	1	0	-0.880798	2.388299	0.293786
18	1	0	-1.143677	1.606501	-1.271522
19	6	0	0.195403	-0.738670	-0.025297
20	7	0	0.232516	0.647547	0.015242
21	7	0	-0.834288	-1.497659	-0.065289

Table S3. Cartesian coordinates of the optimized structure of **3** at the B3LYP/6-31G(d,p) level.

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	2.597149	-0.768363	0.205507
2	6	0	2.372454	0.645508	0.751839
3	6	0	1.445136	1.410606	-0.190834
4	1	0	3.190301	-1.358311	0.914302
5	1	0	3.192533	-0.716371	-0.719964
6	1	0	3.317311	1.187828	0.866653
7	1	0	1.909875	0.577503	1.743879
8	1	0	1.991041	1.707496	-1.099981
9	1	0	1.095356	2.334524	0.285903
10	6	0	-0.954865	1.279000	-0.904078
11	6	0	-1.987395	1.355563	0.243144
12	6	0	-2.036377	0.078357	1.095710
13	6	0	-2.133165	-1.242760	0.314053
14	6	0	-0.970595	-1.524010	-0.685107
15	1	0	-0.691459	2.286213	-1.242645
16	1	0	-1.404643	0.783745	-1.770343
17	1	0	-1.753906	2.204079	0.898480
18	1	0	-2.971937	1.565241	-0.195488
19	1	0	-1.138388	0.042189	1.723521
20	1	0	-2.884604	0.145070	1.787568
21	1	0	-3.087177	-1.285592	-0.226322
22	1	0	-2.162870	-2.055599	1.047834
23	1	0	-1.292922	-1.290500	-1.706801
24	1	0	-0.714870	-2.584181	-0.672416
25	7	0	0.283078	0.594132	-0.545363
26	6	0	0.325256	-0.786474	-0.398075
27	7	0	1.354175	-1.483832	-0.058513

Table S4. Cartesian coordinates of the optimized structure of **4** at the B3LYP/6-31G(d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	-1.928636	1.524753	-0.437753
2	1	0	-2.682909	0.732182	-0.407871
3	1	0	-2.411997	2.449403	-0.104492
4	1	0	-1.615405	1.649359	-1.478300
5	7	0	0.000386	0.000789	0.019178
6	6	0	-0.359628	-2.431266	-0.437579
7	6	0	-0.684318	-1.225974	0.446370
8	1	0	-1.762407	-1.045772	0.395705
9	1	0	-0.464477	-1.461749	1.506140
10	6	0	-0.720303	1.207405	0.444637
11	1	0	-0.026345	2.051689	0.390897
12	1	0	-1.032634	1.137021	1.505111
13	6	0	1.405104	0.021527	0.446450
14	1	0	1.787512	-1.002486	0.397501
15	1	0	1.499269	0.331248	1.505816
16	6	0	2.287595	0.903367	-0.438446
17	1	0	3.329389	0.858894	-0.103187
18	1	0	1.981007	1.953775	-0.414234
19	1	0	2.240218	0.565026	-1.477521
20	1	0	-0.918696	-3.311642	-0.102794
21	1	0	0.703644	-2.689910	-0.412060
22	1	0	-0.627752	-2.221432	-1.477029

Table S5. Cartesian coordinates of the optimized structure of **5** at the B3LYP/6-31G(d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.197699	0.674071	0.000001
2	6	0	1.143063	-0.720627	0.000000
3	6	0	-1.141366	-0.723246	0.000001
4	6	0	-1.199052	0.671840	0.000001
5	6	0	-0.001591	1.385366	0.000000
6	1	0	2.155685	1.184559	-0.000001
7	1	0	2.061707	-1.304941	0.000001
8	1	0	-2.059013	-1.309161	0.000001
9	1	0	-2.158359	1.179842	-0.000002
10	1	0	-0.002449	2.471638	-0.000005
11	7	0	0.001416	-1.420909	-0.000001

Table S6. Cartesian coordinates of the optimized structure of **6** at the B3LYP/6-31G(d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.309629	0.003347	-0.000036
2	6	0	0.619154	-1.186117	0.000006
3	6	0	1.356270	-0.003120	0.000001
4	6	0	0.625619	1.182843	0.000003
5	1	0	-2.397929	0.005936	0.000085
6	1	0	1.113687	-2.156099	-0.000004
7	1	0	2.440825	-0.006311	-0.000024
8	1	0	1.124174	2.150744	0.000008
9	7	0	-0.719246	-1.197288	0.000007
10	7	0	-0.713503	1.200717	0.000006

References

[1] R. Sekiya, Y. Uemura, H. Naito, K. Naka, and T. Haino, *Chem. Eur. J.* **2016**, *22*, 8198–8206.

[2] *Gaussian 09*, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; 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.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.