Electronic Supporting Information

Cooperative Effects of Na^+ and Citrates on Dissolution of Calcium Oxalate Crystals

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1.1 Gravimetry

CaOx dissolution was quantified by gravimetric measurements by weighing the undissolved CaOx remaining in the beaker after the treatment of sample solution (trisodium citrate, citric acid etc.) The details of experiment methods were illustrated in Fig. 2.

0.3000 g of CaOx was accurately weighed and transferred into Beakers. To this, 50 ml of sample solution in distilled water was added. Then the 2 beakers were sonicated for 3 minutes using a fast clean ultrasonic cleaner .Then the suspension was incubated for 3 hours, so as to allow the precipitate of CaOx to settle for about 2 hours. Decant the clear solution through a quantitative ashless (whatman No: 40) filter paper. Wash the precipitate left in the beaker and glass rod with cold water with minimum quantity of distilled water (approximately 15 ml), allow the precipitate to settle and decant the clear solution through the same filter paper. Repeat this process several times. Now transfer the precipitate completely to the filter paper. Remove any precipitate sticking to the sides of the beaker and glass rod carefully using a rubber- tipped glass rod and transfer it to the filter cone. Allow the filter paper to become dry.

Fold the moist filter paper carefully around the precipitate and place it in a silica crucible which has been previously ignited to constant weight. Cover the crucible loosely with its lid, place it on a clay pipe triangle kept on a tripod and gently heat it in a small non-luminous flame so that the filter paper first dries and then chars slowly without catching fire. When the charring is complete, increase the burner flame and heat the crucible at dull redness with free access of

air so that carbon is completely burnt off. Heat the crucible at red heat for about 30 minutes and then allow it to cool. Transfer it to a desiccator, cool and weigh. Repeat heating, cooling, and weighing till the weight becomes constant.

1.2 Complexometric titration method

The dissolution of CaOx was analyzed by estimating the Ca^{2+} concentration in filterate by EDTA titrations using Eriochrome Black T as indicator.

10 ml of this filterate solution is pipette out into a conical flask. 2 ml of buffer solution of pH 10 and 6 drops of Eriochrome Black T indicator are added. The solution is shaken well and titrated against the EDTA solution which is set in the burette, until the color of the solution changes from wine red to blue at the endpoint. The titration is repeated for concordant titre values.

1.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) experiments were conducted on a TG Instruments model Perkin Elmer, STA 6000. Samples (90 mg) were heated to 1000 C under air, and weight gain was recorded isothermally as a function of time. Air was introduced at a flow rate of 100 ml/min, and the temperature was increased at a rate of 10 ^{o}C/min up to 1000 ^{o}C with 20 min holding time. The sample preparation was carried out by filtering dispersed CaOx in (1) distilled water (2) 0.1 M Trisodium citrate solution at various time 1, 2 and 3 h.

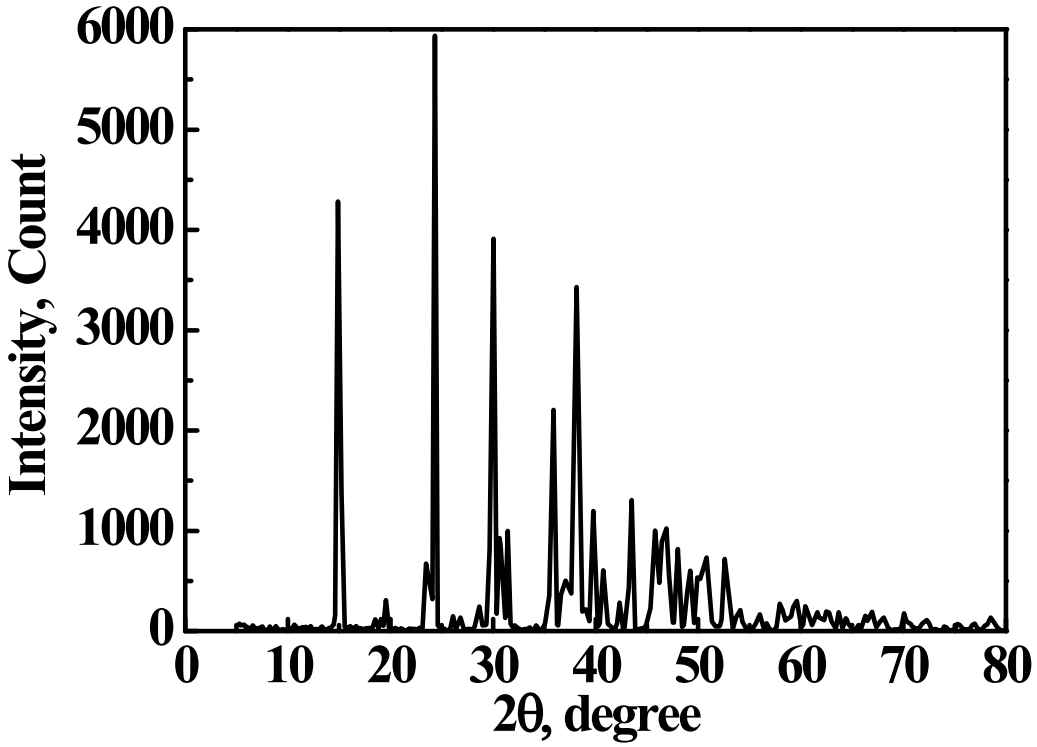

Fig. S1. XRD spectra of purified calcium oxalate monohydrate crystals used for the dissolution studies.

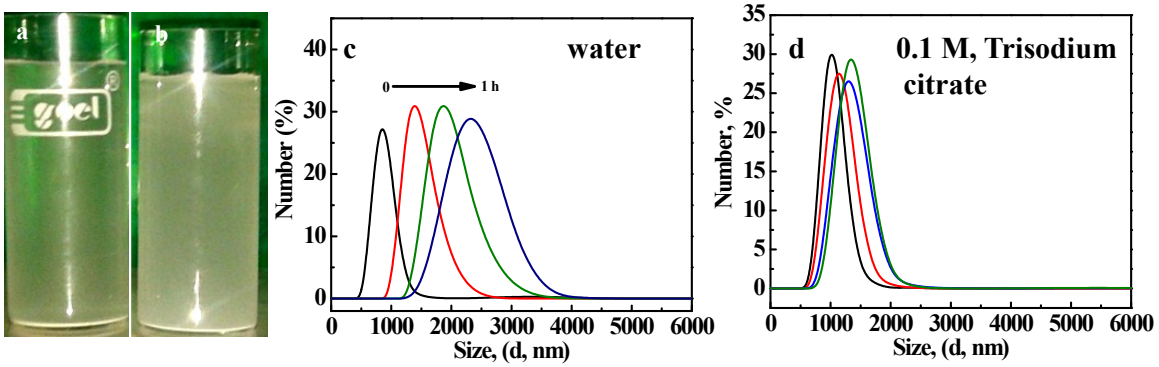

Fig.S2. Photograph shows the CaOx dispersion after 1h in (a) distilled water and (b) 0.1 M trisodium citrate solution. Dynamic light scattering spectra of CaOx dispersion in distilled water (c) and 0.1M trisodium citrate solution (d) plotted number percentage Vs Size.

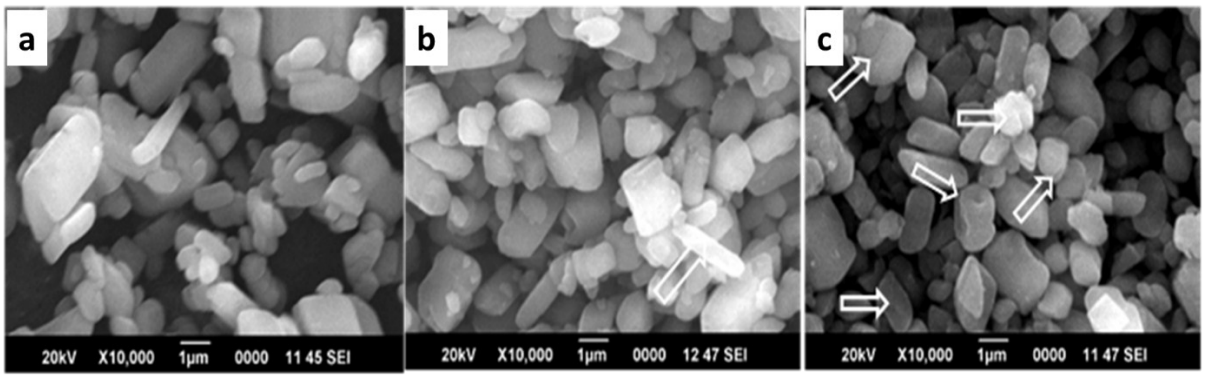

Fig. S3. SEM images of calcium oxalate crystals after the 3 h treatment of (a) distilled water, (b) potassium citrate (0.3M), (c) sodium citrate (0.3M).

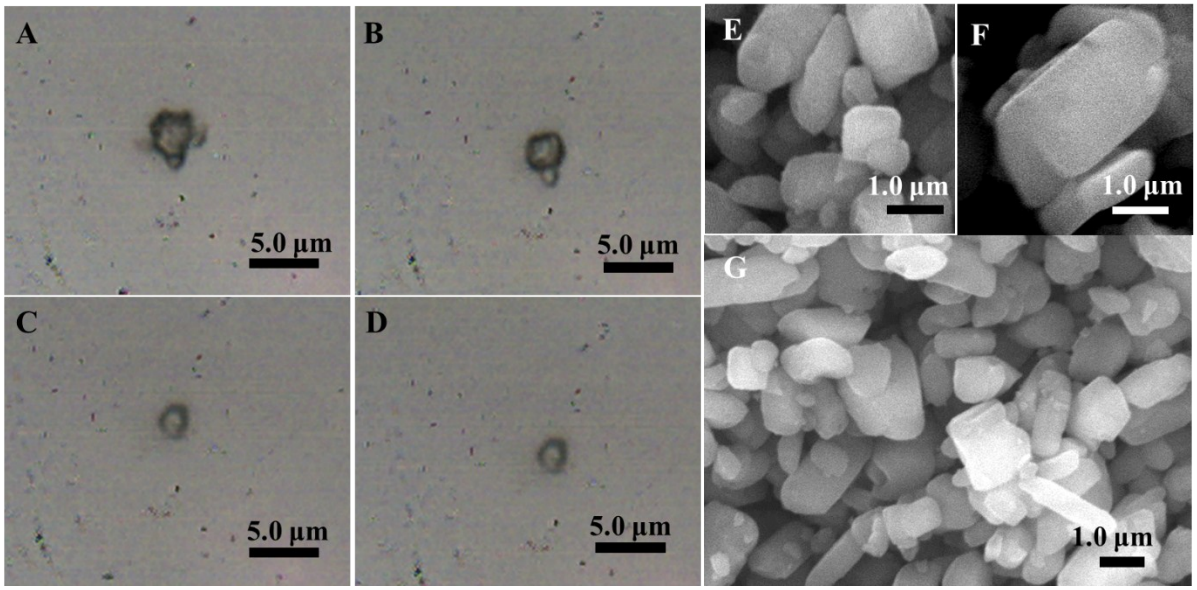

Fig. S4. Morphological effects of potassium citrate (0.3M) on calcium oxalate crystals. (A-D) Optical microscopic images of CaOx crystal immersed in the 0.3 M potassium citrate solution at various time of dissolution. (E-G) SEM images of calcium oxalate crystals after the 3 h treatment of potassium citrate.

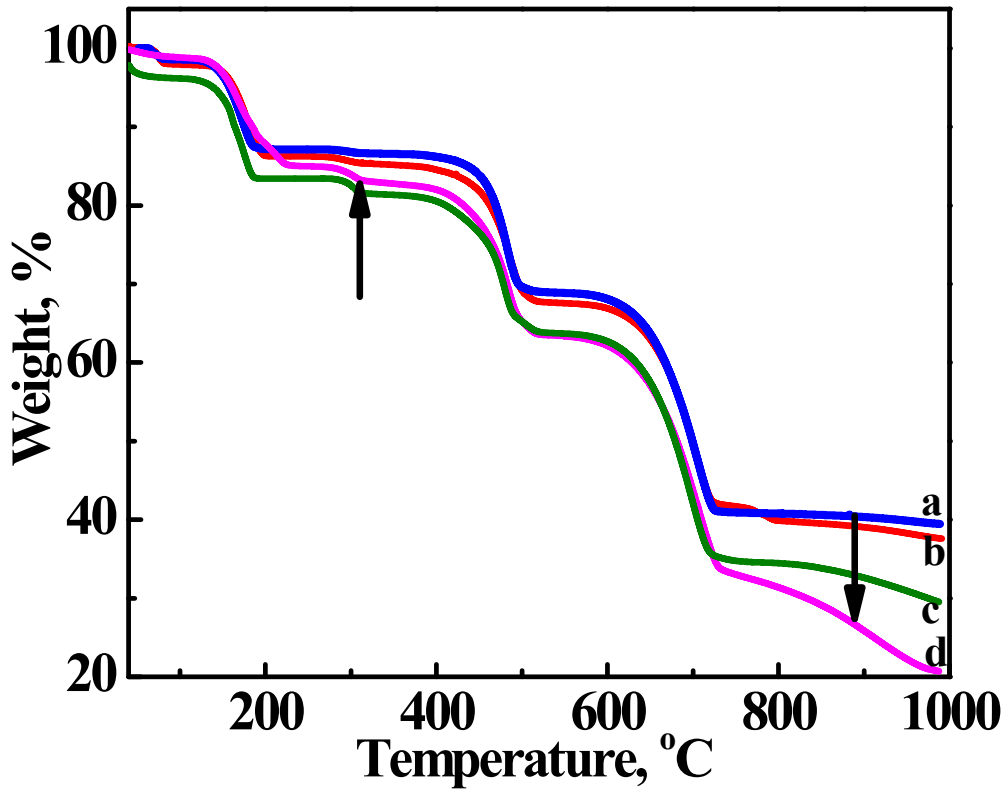

Fig. S5. TGA curves under air atmosphere for the pyrolysis of (a) CaOx treated with distilled water, (b-d) CaOx treated with 0.3M trisodium citrate for 1-3 h.

Table S1. Weight loss as a function of the temperature (°C) of CaOx nH_2O, CaOx nH_2O treated with trisodium citrate (0.3 M) for 3 h.

Compound	**Temperature range (°C)**	**ΔWt %**	**Compound**	**Temperature range (°C)**	**ΔWt %**
CaOx nH_2O	60 - 200	12.4 (removal of water)	CaOx nH_2O + Trisodium citrate (0.3 M) after 3h incubation	60 - 200	15.4
	-	-		**250- 350**	**3.0**
	386-532	17.7		386-532	19
	558-767	28.1		558-767	31.3
	-	-		**770-980**	**11.8**

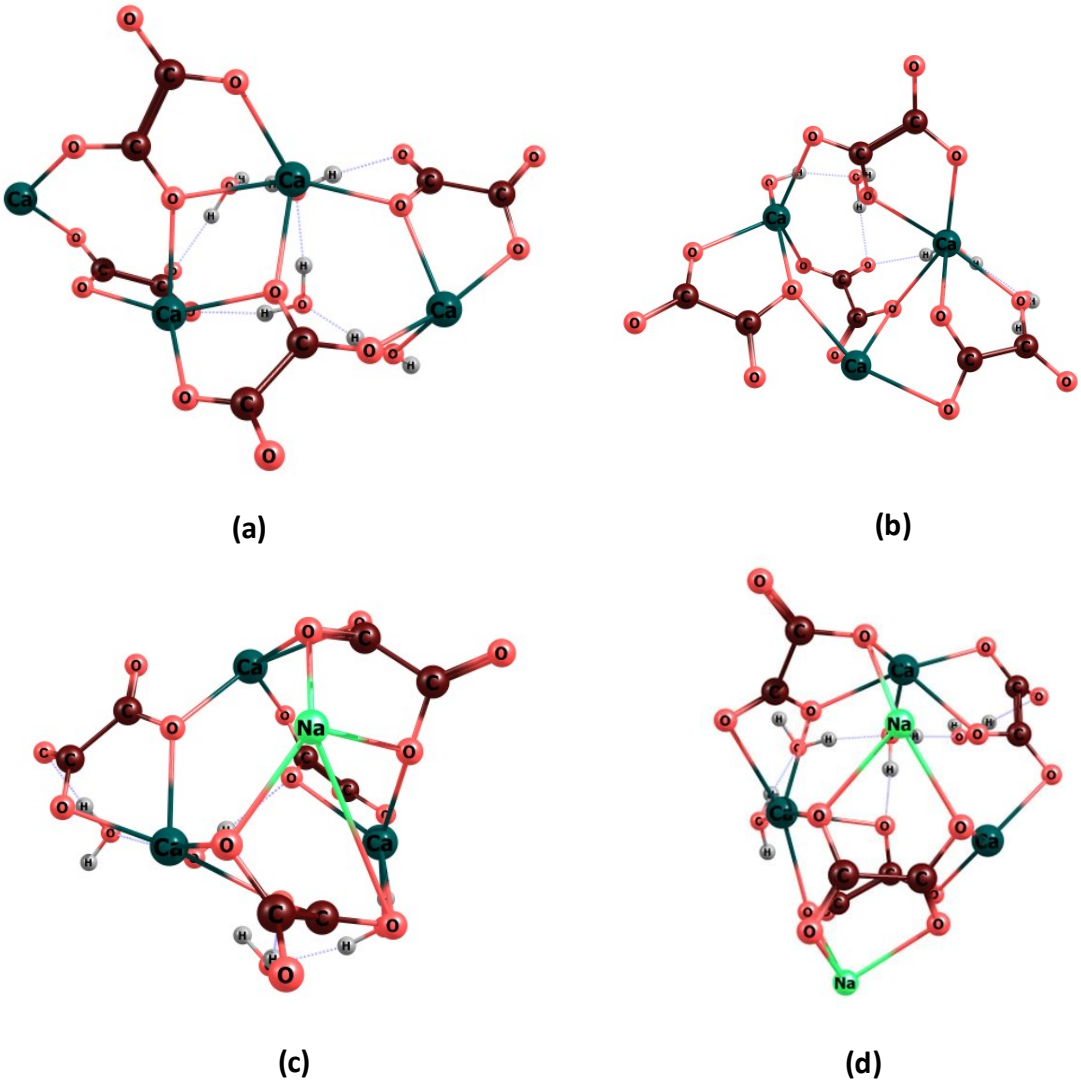

Fig. S5: Optimised goemteries of (a) Calcium oxalate monohydrate structure (b) Calcium oxalate monohydrate structure with one Ca^{2+} ion is removed (c) Calcium oxalate monohydrate structure with one Ca^{2+} is replaced by one Na^{+} ion (d) Calcium oxalate monohydrate structure with one Ca^{2+} is replaced by two Na^{+} ions

1.7 Density Functional Calculations

All DFT calculations were performed in the gas phase with the Gaussian 16software package.For each structures, vibrational frequencies were fully performed to characterise local minimum on the potential energy surface.

Coordinates of the optimised structures shown in Fig. S5.

	(a)				(b)		
6	2.393290000	0.777159000	-2.004184000	6	-2.385203000	2.478268000	-0.567295000
6	-1.309925000	-2.576666000	-0.725551000	6	-0.954393000	-2.152651000	-1.696404000
6	1.696689000	1.706568000	-3.080507000	6	-3.948111000	2.257514000	-0.619151000
6	-0.454271000	-3.904116000	-0.830847000	6	0.130850000	-2.739643000	-2.675697000
6	3.853927000	-0.077019000	1.708756000	6	2.819469000	2.024081000	-0.866400000
6	-3.717270000	1.875354000	-0.219153000	6	0.090617000	0.749351000	2.059020000

6	2.583211000	0.115468000	2.619371000
6	-5.280845000	1.699901000	-0.152400000
8	3.657247000	0.652631000	-2.006534000
8	-0.660209000	-1.465862000	-0.560956000
8	2.431149000	2.252329000	-3.893791000
8	0.752072000	-3.767205000	-0.388534000
8	1.655080000	0.183320000	-1.149095000
8	-2.557156000	-2.625119000	-0.787664000
8	0.426146000	1.759842000	-2.934880000
8	-0.996649000	-4.890226000	-1.303725000
8	4.773950000	0.782216000	1.701730000
8	-3.152825000	2.908999000	0.155932000
8	3.852572000	-1.046232000	0.844422000
8	-3.048065000	0.820334000	-0.653712000
8	2.601489000	1.038637000	3.430930000
8	-5.986116000	2.677207000	-0.342480000
8	1.623815000	-0.681438000	2.329040000
8	-5.635055000	0.479585000	0.114154000
8	1.274410000	3.285279000	2.370327000
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8	-0.681630000	2.136670000	0.861882000
8	-3.326547000	-1.241738000	2.383945000
20	5.248864000	0.301890000	-0.522904000
20	-0.753701000	0.875179000	-1.184872000
20	1.584166000	-1.774594000	0.258741000
20	-4.073730000	-1.141402000	0.125330000
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1	-0.142167000	-0.260946000	2.875643000
1	1.730938000	2.589468000	2.895258000
1	-1.013702000	0.849957000	2.216577000
1	-1.540506000	2.639904000	0.759031000
1	-3.853135000	-1.136529000	3.190668000
1	-0.022505000	2.681824000	1.365932000
1	-2.430051000	-0.826920000	2.585720000

6	4.178140000	1.272669000	-0.693094000
6	-0.656782000	-0.506959000	2.556291000
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8	-0.520703000	-1.754010000	-0.533975000
8	-4.664581000	3.221129000	-0.896396000
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8	1.854795000	1.373527000	-1.411300000
8	0.965820000	0.530414000	1.149437000
8	5.239844000	1.891441000	-0.753826000
8	0.012525000	-1.451867000	3.047748000
8	4.004417000	0.013779000	-0.444489000
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1	-3.350203000	-1.974907000	2.227564000
1	3.244865000	-1.918881000	1.813366000
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(c)

6	1.645143000	-1.788067000	-2.412031000
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8	0.700490000	-1.102878000	-2.961978000
8	2.645885000	2.674576000	0.344675000
8	2.650255000	-0.021132000	-1.254854000
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1	2.553330000	-0.175999000	3.702458000

(d)

6	1.973710000	-0.917307000	-2.298597000
6	0.186572000	3.198925000	0.300099000
6	2.841977000	0.258352000	-1.777768000
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6	-4.177666000	-1.073447000	-0.664996000
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8	0.885487000	-0.672806000	-2.905190000
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8	2.135628000	1.227996000	-1.330159000
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				11	4.190028000	-1.795079000	-0.488070000

Reference of Gaussian 16

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. oRanasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., *Gaussian 16, Revision A.03*,Wallingford CT, 2016.