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出版情報：Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 206, pp.112-119, 2019-01-05. Elsevier
バージョン：
権利関係：

Infrared spectroscopic and computational studies on formamide solutions of Ca^{2+}. Vibrational frequencies of formamide and modes of coordination to Ca^{2+}

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Supplementary material

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Table S1

Natural charges on Ca, O, C, and N atoms for selected species evaluated from Natural Bond Orbital (NBO) analysis.

species	Ca	O	C	N
FA		–0.710	0.508	–0.858
1-O-i	1.977	–0.821	0.537	–0.809
1-O-ii	1.978	–0.827	0.543	–0.810
1-N	1.987	–0.643	0.533	–0.964
1-ON	1.971	–0.623	0.562	–1.087
2-O-i	1.959	–0.811	0.535	–0.814
2-O-ii	1.959	–0.815	0.540	–0.815
4-O-vii*	1.856	–0.758 – –0.770	0.513 – 0.533	–0.838 – –0.844
4-O-viii*	1.822	–0.764 – –0.768	0.531 – 0.533	–0.849 – –0.850
4-ON-i*	1.860	–0.696 – –0.701	0.523 – 0.534	–0.925 – –0.928
4-ON-ii*	1.811	–0.682 – –0.695	0.525 – 0.527	–0.929 – –0.943
4-N*	1.915	–0.642	0.534	–0.957 – –0.961
4-O-i	1.899	–0.813	0.537	–0.814
5-O-i	1.859	–0.793 [a] –0.803 – –0.815 [b]	0.532 [a] 0.534 – 0.537 [b]	–0.820 [a] –0.807 – –0.815 [b]
6-O-i	1.815	–0.782 [a] –0.797 – –0.810 [b]	0.531 [a] 0.534 – 0.536 [b]	–0.822 [a] –0.809 – –0.816 [b]
7-O-i	1.812	–0.777 – –0.789	0.529 – 0.533	–0.820 – –0.825
7-O-ii	1.812	–0.777 – –0.790	0.528 – 0.532	–0.820 – –0.825
7-O-iii	1.818	–0.755 – –0.763	0.522 – 0.527	–0.830 – –0.835
7-O-iv	1.817	–0.756 – –0.762	0.521 – 0.526	–0.829 – –0.833
8-O-i	1.810	–0.771	0.528	–0.825
8-O-ii	1.810	–0.770	0.526	–0.827
8-O-iii	1.808	–0.752	0.529	–0.839
8-O-iv	1.811	–0.751	0.525	–0.838

[a] Values for FA molecule(s) in axial position.

[b] Values for FA molecules in equatorial position.

Table S2

Scaled ν_{CO} frequency, IR intensity, and Raman scattering activity for the lowest-energy isomers of $Ca^{2+}(FA)_7$ and $Ca^{2+}(FA)_8$.

	Scaled frequency cm^{-1}	IR intensity km/mol	Raman activity $Å^4$/amu
7-O-i	1663.9	100.6837	7.7959
	1666.2	123.8318	7.4470
	1667.8	39.8974	18.4808
	1675.5	2071.3942	1.0619
	1676.0	1832.0728	1.1653
	1677.0	2107.0784	1.3970
	1700.1	65.6390	19.2363
8-O-i	1667.8	0.0417	20.4643
	1667.9	0.0698	20.5280
	1671.8	0.7176	3.4359
	1671.9	0.3776	3.4096
	1678.3	520.5404	0.0011
	1683.3	3350.4924	0.0005
	1683.4	3348.9603	0.0011
	1708.8	0.0264	31.4342

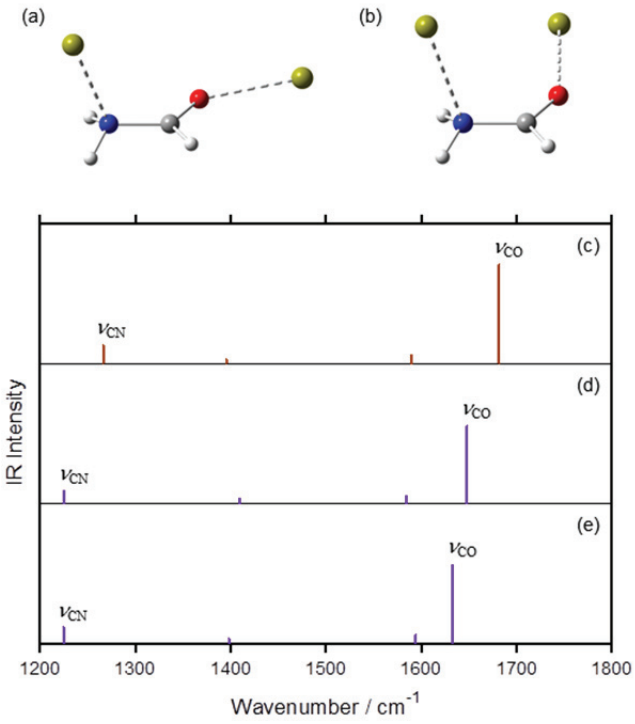

Fig. S1. Geometries of $(Ca^{2+})_2(FA)_1$ complexes in which one Ca^{2+} is bound to the N atom and the other to the O atom of FA with (a) 'trans' configuration, 2-1-i* and (b) 'cis' configuration, 2-1-ii*. Theoretical IR spectra for (c) FA monomer, (d) 2-1-i*, and (e) 2-1-ii*. Geometries of both 2-1-i* and 2-1-ii* have 1 imaginary-frequency vibration. The $Ca^{2+}\cdots O/Ca^{2+}\cdots N$ distances are 2.45/2.31 Å in 2-1-i* and 2.55/2.64 Å in 2-1-ii*.

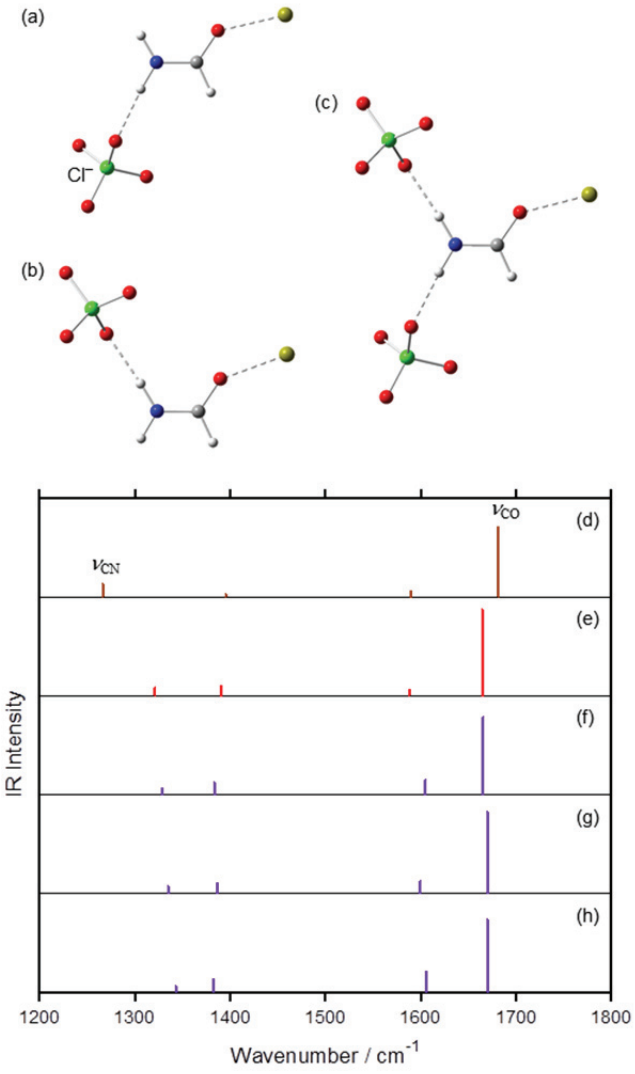

Fig. S2. Optimized structures of solvent-separated ion pairs of the form $Ca^{2+}(FA)_1(ClO_4^-)_m$: (a) m = 1, 1-T; (b) m = 1, 1-C; and (c) m = 2, 1-TC. Theoretical IR spectra for (d) FA monomer, (e) 1-O-i of $Ca^{2+}(FA)_1$, (f) 1-T, (g) 1-C, and (h) 1-TC. Substructure of the $Ca^{2+}(FA)_1$ unit in the ion pairs is similar to 1-O-i. Ca^{2+} and ClO_4^- are on the opposite sides of the CN bond in 1-T while on the same side in 1-C.

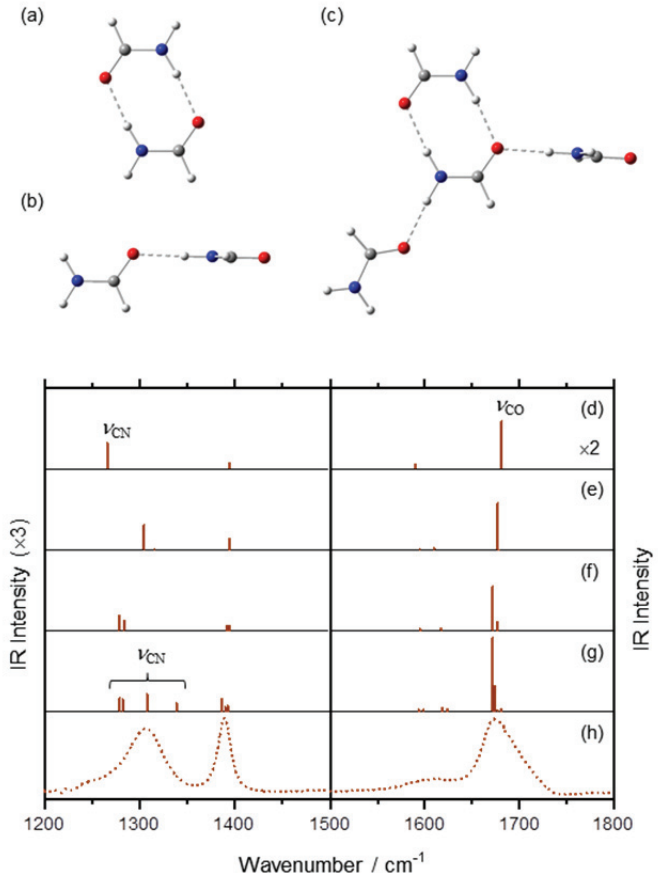

Fig. S3. Optimized structures of FA clusters: (a) 2R, (b) 2L, and (c) 4RL. Theoretical IR spectra of (d) FA monomer, (e) 2R, (f) 2L, and (g) 4RL. (h) Experimental IR spectrum of neat FA liquid. Amplitude of the spectra in the 1200–1500 cm^{-1} region is magnified by a factor of 3. Amplitude of the spectrum of FA monomer is magnified by a factor of 2. 2R is a ring dimer of C_{2h} symmetry with two NH···O hydrogen bonds. 2L is a linear dimer with a single NH···O hydrogen bond. 4RL is a tetramer consisting of a ring dimer and a linear chain. Scaled frequencies for ν_{CN} and ν_{CO} of FA monomer in PCM are 1266 and 1681 cm^{-1}, respectively. The ν_{CN} and ν_{CO} transitions of 2R are located at 1305/1316 and 1677/1678 cm^{-1}, respectively, but the latter of both modes has zero IR intensity. The ν_{CN} and ν_{CO} transitions of 2L are located at 1279/1284 and 1672/1677 cm^{-1}, respectively. For 4RL, the ν_{CN} transitions are located at 1279, 1282, 1308, and 1339 cm^{-1} with an average value of 1302 cm^{-1} and the strongest ν_{CO} transition is located at 1672 cm^{-1} with a weaker one at 1674 cm^{-1}.

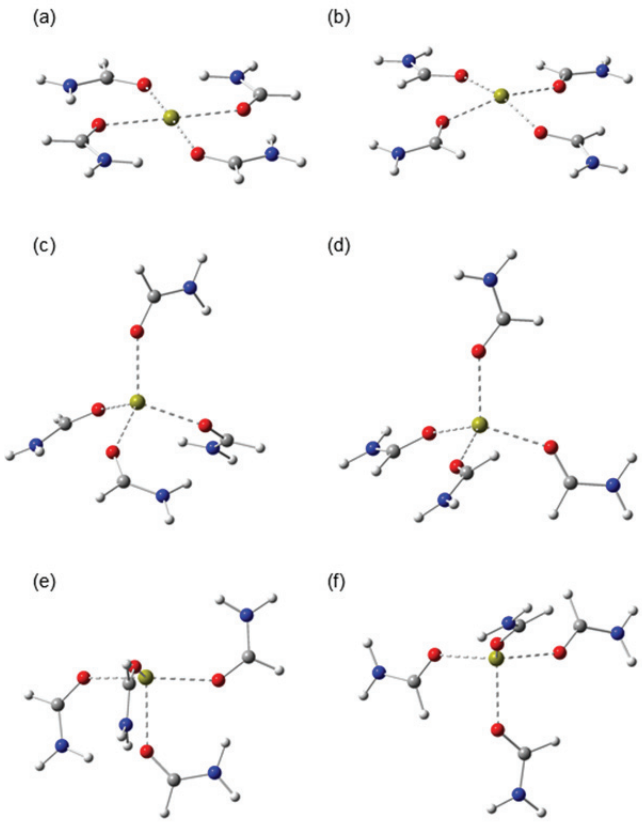

Fig. S4. Optimized structures of O-bound isomers of $Ca^{2+}(FA)_4$: (a) 4-O-i, (b) 4-O-ii, (c) 4-O-iii, (d) 4-O-iv, (e) 4-O-v, and (f) 4-O-vi. Four O atoms of FA molecules adopt a square-planar coordination in 4-O-i and 4-O-ii, a tetrahedral coordination in 4-O-iii and 4-O-iv, and a square-pyramidal coordination with one vacancy in 4-O-v and 4-O-vi. All FA molecules are bound to Ca^{2+} with 'cis' configuration in 4-O-i, 4-O-iii, and 4-O-v, while 'trans' configuration in 4-O-ii, 4-O-iv, and 4-O-vi.

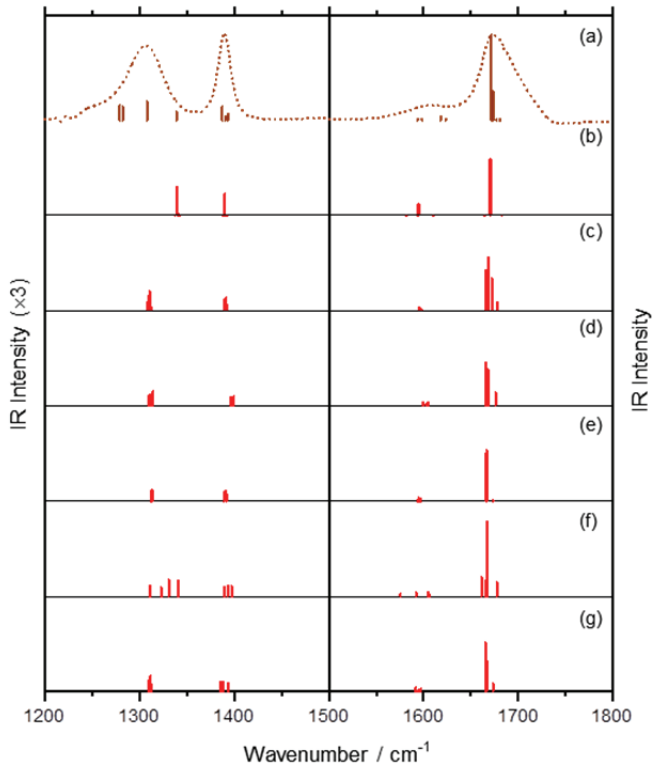

Fig. S5. Theoretical IR spectra of (a) 4RL of $(FA)_4$ and O-bound isomers of $Ca^{2+}(FA)_4$: (b) 4-O-i, (c) 4-O-ii, (d) 4-O-iii, (e) 4-O-iv, (f) 4-O-v, and (g) 4-O-vi. Dashed curve in (a) stands for experimental IR spectrum of neat FA liquid. Location of the strongest ν_{CO} transition is as follows: 1671.9 cm^{-1} (4RL), 1670.4 cm^{-1} (4-O-i), 1668.7 cm^{-1} (4-O-ii), 1666.2 cm^{-1} (4-O-iii), 1667.0 cm^{-1} (4-O-iv), 1667.6 cm^{-1} (4-O-v), and 1665.4 cm^{-1} (4-O-vi).

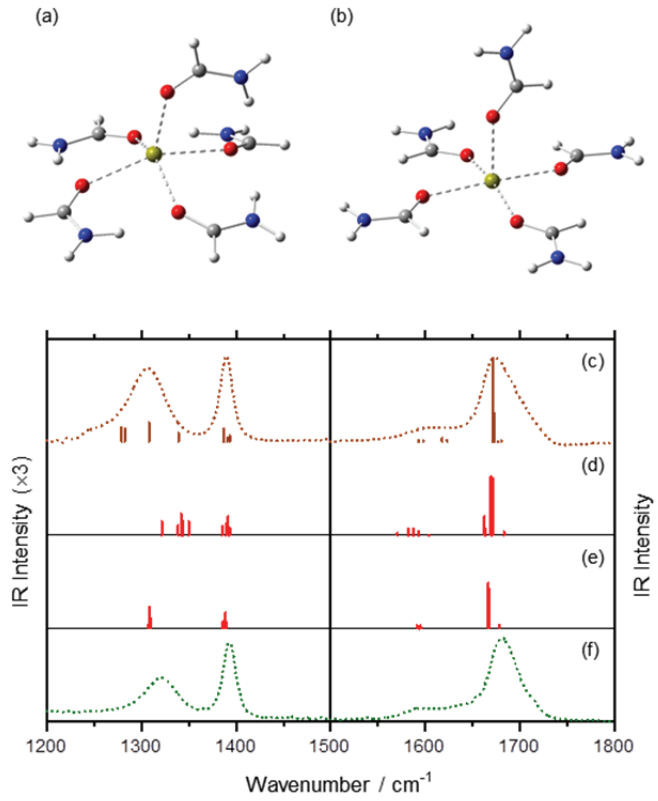

Fig. S6. Optimized structures of O-bound isomers of $Ca^{2+}(FA)_5$: (a) 5-O-i and (b) 5-O-ii. Theoretical IR spectra of (c) 4RL of $(FA)_4$, (d) 5-O-i, and (e) 5-O-ii. Dashed curves in (c) and (f) stand for experimental IR spectra of neat FA liquid and 4.0 M solution, respectively. In both 5-O-i and 5-O-ii, five O atoms of FA molecules adopt a square-pyramidal coordination. All FA molecules are bound to Ca^{2+} with 'cis' configuration in 5-O-i, while 'trans' configuration in 5-O-ii.

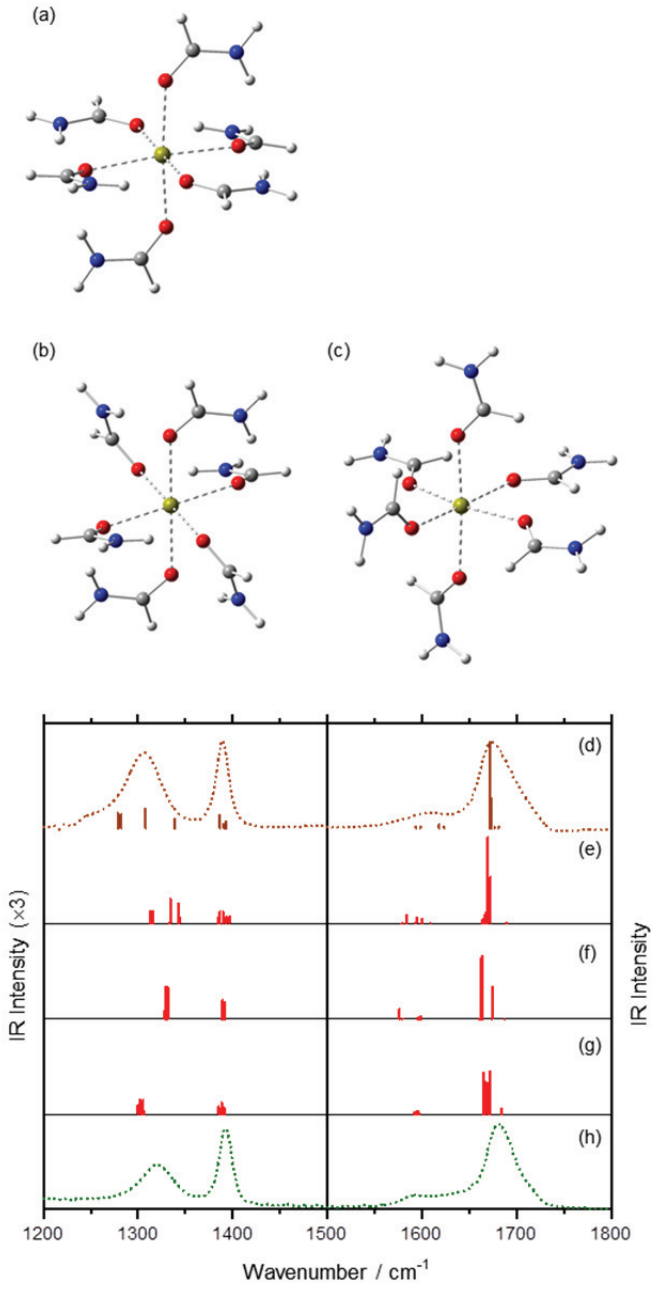

Fig. S7. Optimized structures of O-bound isomers of $Ca^{2+}(FA)_6$: (a) 6-O-i, (b) 6-O-ii, and (c) 6-O-iii. Theoretical IR spectra of (d) 4RL of $(FA)_4$, (e) 6-O-i, (f) 6-O-ii, and (g) 6-O-iii. Dashed curves in (d) and (h) stand for experimental IR spectra of neat FA liquid and 4.0 M solution, respectively. In all isomers, six O atoms of FA molecules adopt an octahedral coordination. 6-O-i is formed by adding two FA molecules over and under the Ca^{2+} ion in 4-O-i. All FA molecules are bound to Ca^{2+} with 'cis' configuration in 6-O-i and 6-O-ii, while 'trans' configuration in 6-O-iii.

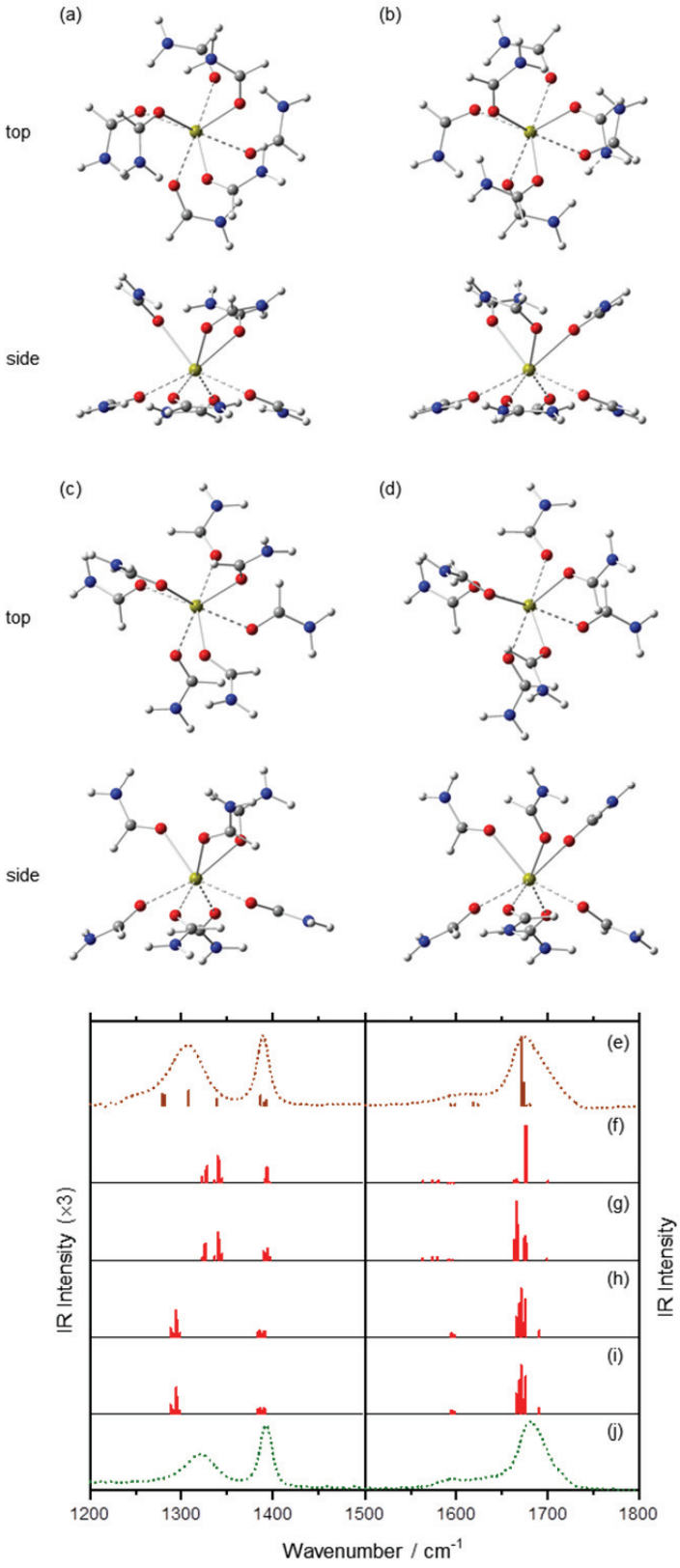

Fig. S8. Optimized structures of O-bound isomers of $Ca^{2+}(FA)_7$: (a) 7-O-i, (b) 7-O-ii, (c) 7-O-iii, and (d) 7-O-iv. Top and side views are shown for each isomer. Theoretical IR spectra of (e) 4RL of $(FA)_4$, (f) 7-O-i, (g) 7-O-ii, (h) 7-O-iii, and (i) 7-O-iv. Dashed curves in (e) and (j) stand for experimental IR spectra of neat FA liquid and 4.0 M solution, respectively.

(continued) 7-O-i and 7-O-ii are formed by squeezing two FA molecules in the upper side of Ca^{2+} in 5-O-i. 7-O-iii and 7-O-iv are formed by squeezing two FA molecules in the upper side of Ca^{2+} in 5-O-ii. All FA molecules are bound to Ca^{2+} with 'cis' configuration in 7-O-i and 7-O-ii, while 'trans' configuration in 7-O-iii and 7-O-iv. Local dipole moment vectors of the CO bonds of four FA molecules below Ca^{2+} make a left hand turn in both 7-O-i and 7-O-ii. On the other hand, the vectors of three FA molecules above Ca^{2+} make a left hand turn in 7-O-i whereas a right hand turn in 7-O-ii. In an analogous way, substructures of 7-O-iii and 7-O-iv are similar in the lower half, but different in the upper half of the complexes.

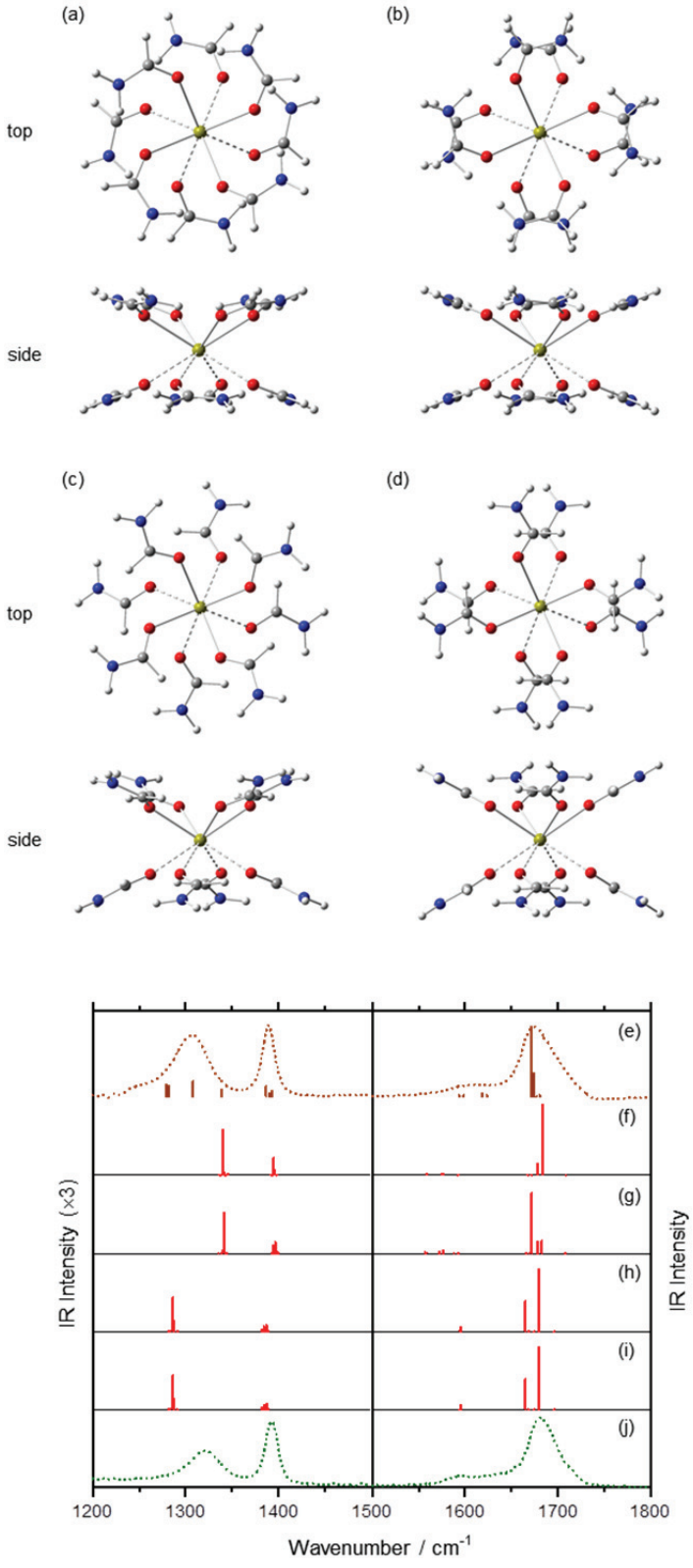

Fig. S9. Optimized structures of O-bound isomers of $Ca^{2+}(FA)_8$: (a) 8-O-i, (b) 8-O-ii, (c) 8-O-iii, and (d) 8-O-iv. Top and side views are shown for each isomer. Theoretical IR spectra of (e) 4RL of $(FA)_4$, (f) 8-O-i, (g) 8-O-ii, (h) 8-O-iii, and (i) 8-O-iv. Dashed curves in (e) and (j) stand for experimental IR spectra of neat FA liquid and 4.0 M solution, respectively.

(continued) 8-O-i and 8-O-ii are formed by squeezing three FA molecules in the upper side of Ca^{2+} in 5-O-i. 8-O-iii and 8-O-iv are formed by squeezing three FA molecules in the upper side of Ca^{2+} in 5-O-ii. All FA molecules are bound to Ca^{2+} with 'cis' configuration in 8-O-i and 8-O-ii, while 'trans' configuration in 8-O-iii and 8-O-iv. Local dipole moment vectors of the CO bonds of four FA molecules below Ca^{2+} make a left hand turn in both 8-O-i and 8-O-ii. On the other hand, the vectors of four FA molecules above Ca^{2+} make a left hand turn in 8-O-i whereas a right hand turn in 8-O-ii. In an analogous way, substructures of 8-O-iii and 8-O-iv are similar in the lower half, but different in the upper half of the complexes.

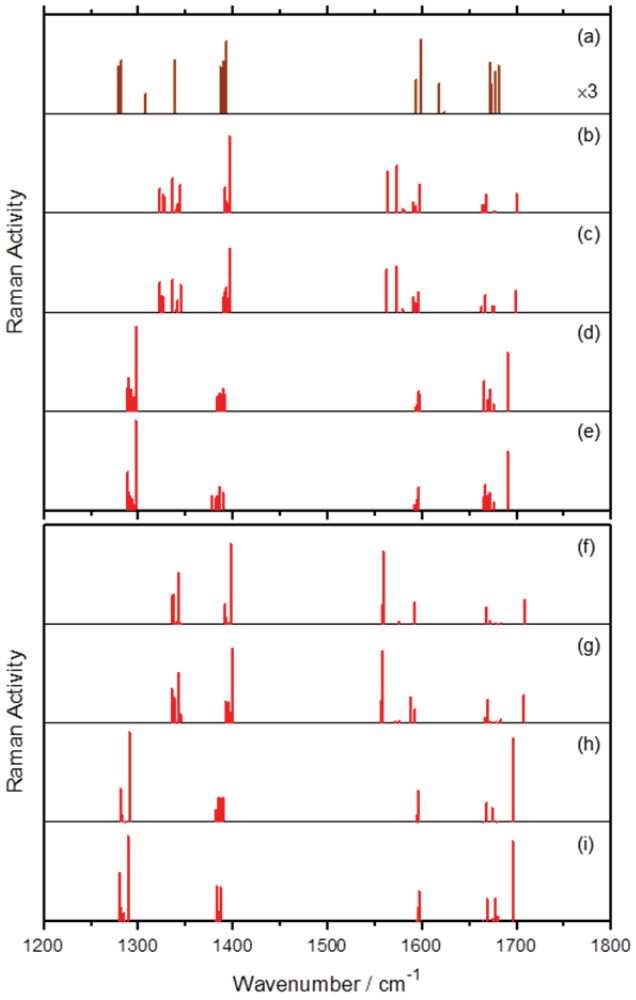

Fig. S10. Theoretical Raman spectra of (a) 4RL of $(FA)_4$; $Ca^{2+}(FA)_7$: (b) 7-O-i, (c) 7-O-ii, (d) 7-O-iii, (e) 7-O-iv; $Ca^{2+}(FA)_8$: (f) 8-O-i, (g) 8-O-ii, (h) 8-O-iii, and (i) 8-O-iv. Structures of these complexes are displayed in Figs S8a–d and S9a–d. Amplitude of the spectrum of 4RL is magnified by a factor of 3.

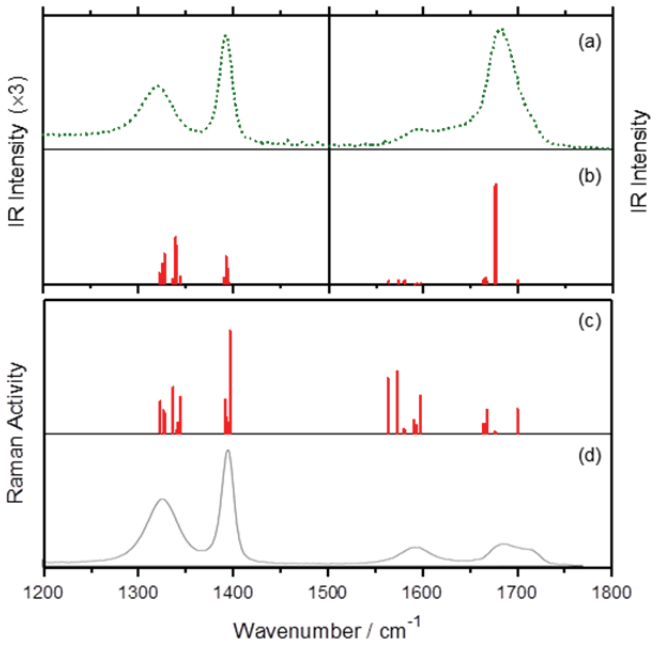

Fig. S11. Comparison of experimental (a) IR and (d) Raman spectra of 4.0 M solution with theoretical (b) IR and (c) Raman spectra predicted for 7-O-i. Experimental Raman spectrum is taken from the literature [12].

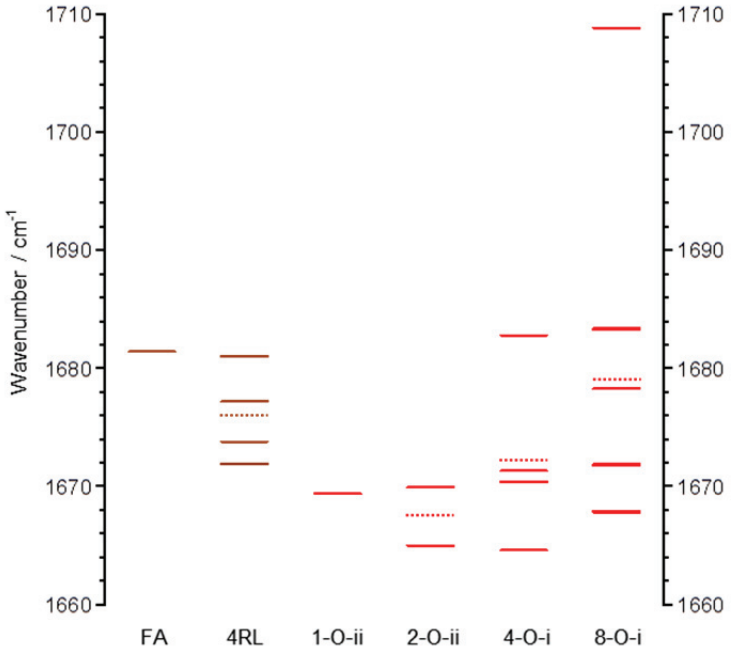

Fig. S12. Diagram of vibrational energy levels for FA monomer, 4RL of $(FA)_4$, and O-bound $Ca^{2+}(FA)_n$ (n = 1, 2, 4, and 8) complexes, in which all FA molecules are bound to Ca^{2+} with 'cis' configuration. Dashed lines indicate average values of vibrational frequencies: 1676 cm^{-1} (4RL), 1668 cm^{-1} (2-O-ii), 1672 cm^{-1} (4-O-i), and 1679 cm^{-1} (8-O-i).