

## Supplementary materials

# Crystal structure and bonding analysis of the first dinuclear calcium(II)-proton pump inhibitor (PPI) ‘molecular butterfly’: a combined microcrystal synchrotron and DFT study

*Hengjiang Cong*

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

Correspondence e-mail: conghj@whu.edu.cn

### Figure Captions:

Figure **S1** (a) TDOS, (b) PDOS and (c) COOP spectra. (Atoms are partitioned into six groups: ca, py, ms, so, bi and ak, which correspond to calcium, pyridine, methylsulfinyl, solvent, benzofuroimidazole and alkoxy arm, respectively.)

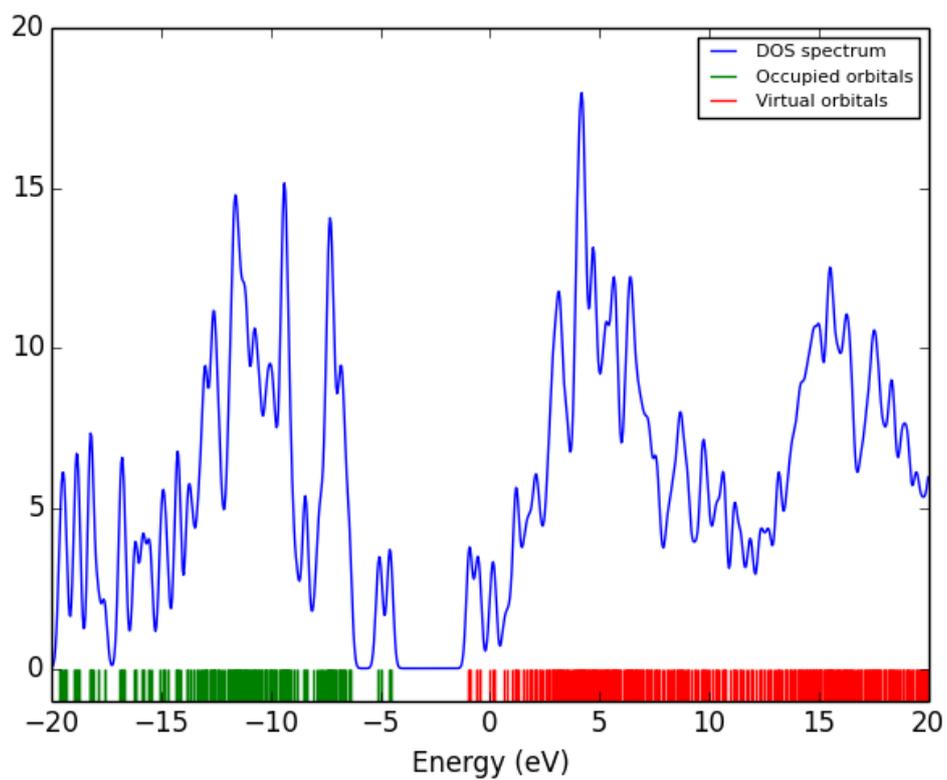
Figure **S2** Theoretical (a) infrared (b) Raman vibrational spectra.

### Table Captions:

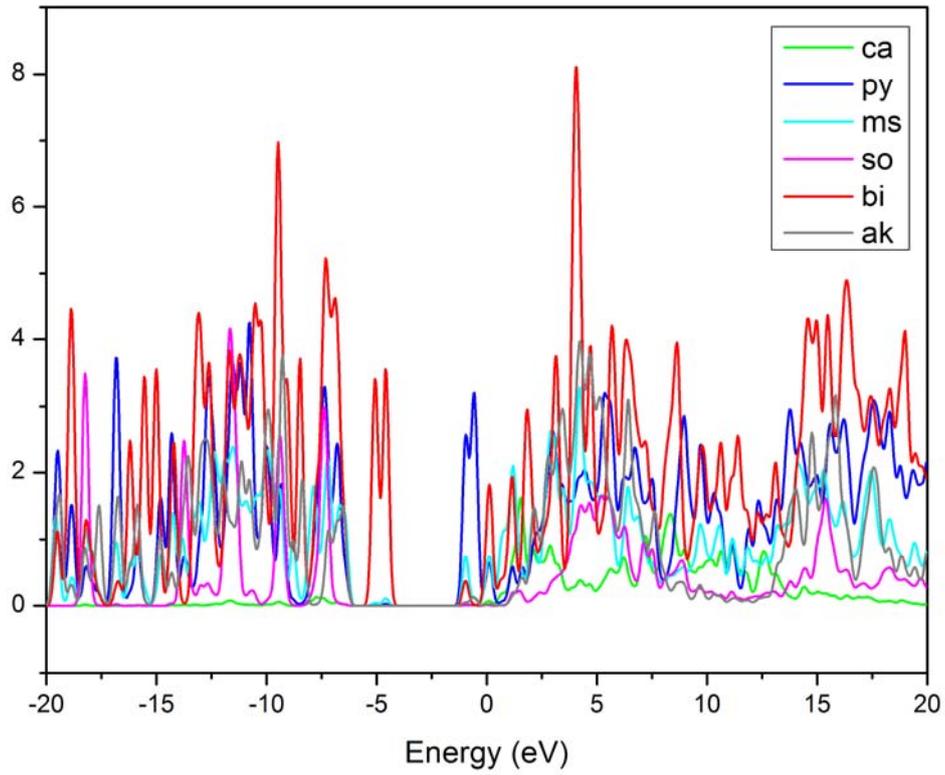
Table **S1** Comparison of (1) X-ray and (2) DFT results for important bond lengths (Å) in the ‘molecular butterfly’.

Table **S2** The energy and group decompositions of typical frontier molecular orbitals. (The abbreviations of ca, py, ms, so, bi and ak denote calcium, pyridine, methylsulfinyl, solvent, benzofuroimidazole and alkoxy arm, respectively.)

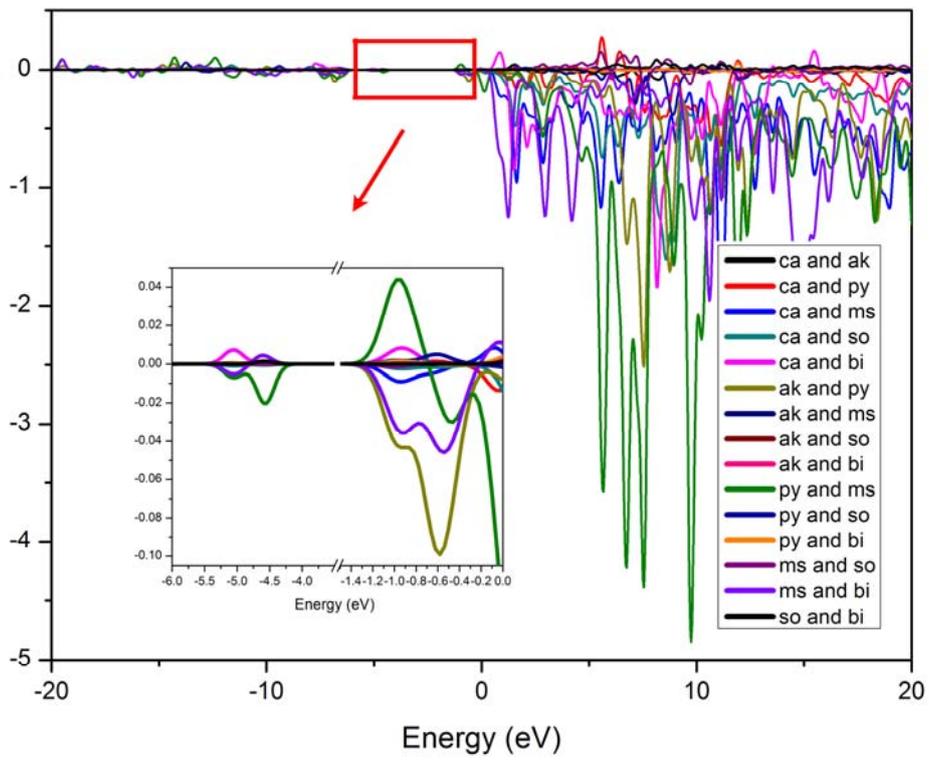
Figure S1 (a) TDOS, (b) PDOS and (c) COOP spectra. (Atoms are partitioned into six groups: ca, py, ms, so, bi and ak, which correspond to calcium, pyridine, methylsulfinyl, solvent, benzofuroimidazole and alkoxy arm, respectively.)



(a)

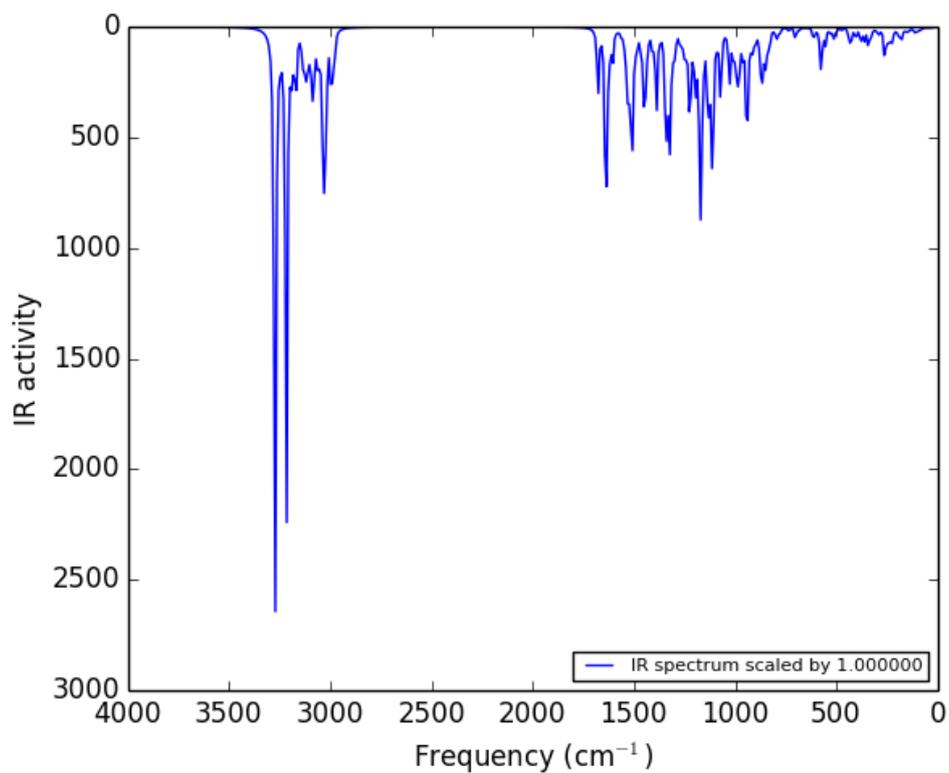


(b)

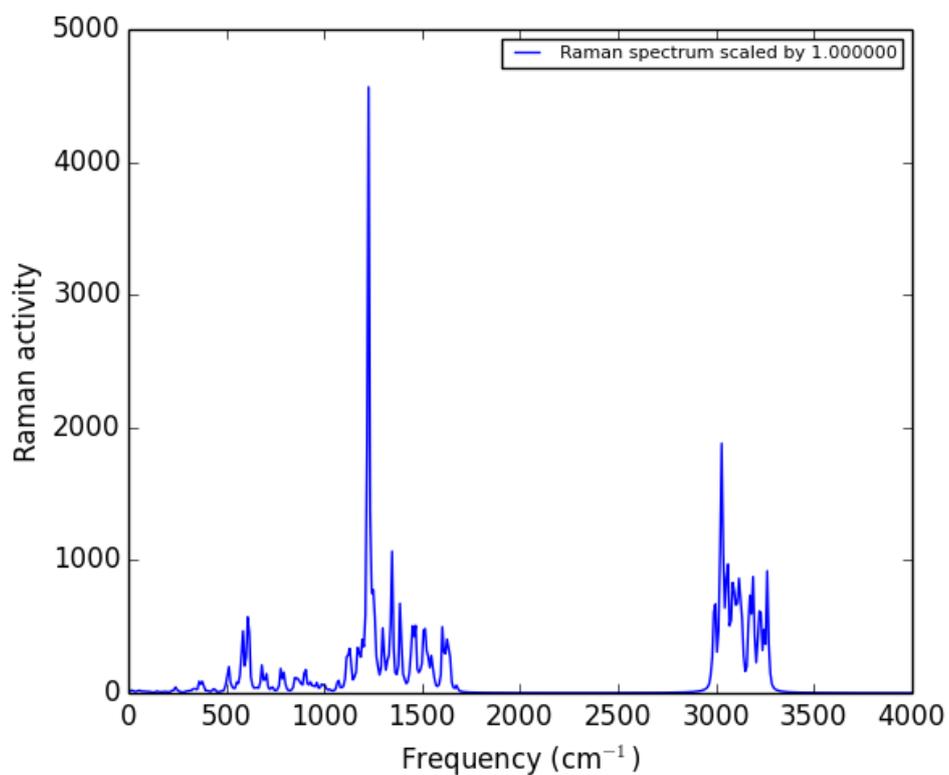


(c)

Figure S2 Theoretical (a) infrared (b) Raman vibrational spectra.



(a)



(b)

Table S1 Comparison of (1) X-ray and (2) DFT results for important bond lengths (Å) in the ‘molecular butterfly’.

	(1)	(2)		(1)	(2)
Ca1—O10	2.362 (2)	2.451	O2—C6	1.455 (6)	1.443
Ca1—O5	2.3920 (18)	2.483	O3—C14	1.362 (14)	1.353
Ca1—O9	2.3986 (19)	2.472	O6—C27	1.426 (4)	1.377
Ca1—O1	2.4225 (19)	2.520	O6—C26	1.533 (8)	1.443
Ca1—O1 <sup>i</sup>	2.4814 (17)	2.580	O7—C37	1.442 (3)	1.436
Ca1—N2 <sup>i</sup>	2.507 (2)	2.558	O8—C40	1.404 (5)	1.412
Ca1—N5	2.516 (2)	2.605	O9—C41	1.425 (3)	1.427
S1—O1	1.5277 (17)	1.563	N1—C1	1.327 (3)	1.331
S1—C1	1.771 (2)	1.775	N1—C2	1.388 (3)	1.380
S1—C10	1.820 (3)	1.872	N2—C9	1.386 (3)	1.381
S2—O5	1.5129 (17)	1.546	N2—Ca1 <sup>i</sup>	2.507 (2)	2.558
S2—C21	1.775 (2)	1.779	N4—C21	1.331 (3)	1.329
S2—C30	1.832 (3)	1.880	N5—C21	1.339 (3)	1.353
O1—Ca1 <sup>i</sup>	2.4814 (17)	2.580	N6—C32	1.327 (4)	1.337
O2—C7	1.385 (4)	1.376	N6—C31	1.350 (3)	1.351
C1—N2	1.345 (3)	1.353	C28—C27	1.380 (4)	1.381
C2—C3	1.406 (4)	1.410	C29—N5	1.386 (3)	1.382
C3—C4	1.383 (5)	1.381	C29—C28	1.405 (4)	1.411
C4—C5	1.526 (9)	1.513	C31—C30	1.494 (4)	1.501
C6—C5	1.558 (11)	1.545	C32—C33	1.383 (4)	1.391
C7—C4	1.396 (6)	1.418	C34—O7	1.352 (3)	1.355
C8—C7	1.382 (4)	1.381	C34—C33	1.388 (4)	1.399
C9—C2	1.409 (4)	1.433	C35—C31	1.395 (3)	1.402
C9—C8	1.411 (4)	1.411	C35—C34	1.406 (4)	1.414
C11—N3	1.313 (9)	1.351	C35—C36	1.505 (4)	1.511
C11—C10	1.508 (4)	1.503	C38—C37	1.516 (4)	1.522

C12—N3	1.334 (10)	1.333	C39—O8	1.419 (4)	1.416
C13—C12	1.379 (9)	1.389	C39—C38	1.514 (4)	1.525
C14—C13	1.387 (12)	1.400	C42—O10	1.471 (9)	1.427
C15—C11	1.397 (4)	1.401			
C15—C14	1.438 (10)	1.413			
C15—C16	1.494 (4)	1.509			
C17—O3	1.448 (15)	1.438			
C18—C17	1.468 (11)	1.520			
C18—C19	1.500 (6)	1.527			
C19—O4	1.391 (6)	1.415			
C20—O4	1.471 (9)	1.416			
C22—N4	1.385 (3)	1.382			
C22—C23	1.409 (3)	1.409			
C22—C29	1.415 (4)	1.433			
C24—C23	1.372 (5)	1.382			
C24—C27	1.403 (5)	1.417			
C24—C25	1.448 (4)	1.514			
C25—C26	1.595 (11)	1.545			

Table S2 The energy and group decompositions of typical frontier molecular orbitals. (The abbreviations of ca, py, ms, so, bi and ak denote calcium, pyridine, methylsulfinyl, solvent, benzofuroimidazole and alkoxy arm, respectively.)

MO	Energy (eV)	% of composition					
		ca	ak	py	ms	so	bi
LUMO+10	1.33	22	5	4	53	3	13
LUMO+9	1.19	24	6	18	24	8	21
LUMO+8	1.17	4	2	6	40	1	47
LUMO+7	0.97	10	1	5	51	0	33
LUMO+6	0.63	11	0	3	55	1	29

LUMO+5	0.19	3	1	20	23	0	53
LUMO+4	-0.01	4	0	22	28	1	45
LUMO+3	-0.48	0	3	91	5	0	1
LUMO+2	-0.63	0	5	93	1	1	0
LUMO+1	-0.89	1	1	68	21	0	10
LUMO	-1	0	2	67	20	0	11
HOMO	-4.52	0	0	1	3	0	96
HOMO -1	-4.62	0	0	1	3	0	96
HOMO -2	-4.99	0	0	0	1	0	98
HOMO -3	-5.12	0	0	0	1	0	98
HOMO-4	-6.39	1	2	21	57	1	19
HOMO-5	-6.48	0	64	2	2	0	32
HOMO -6	-6.62	1	3	23	40	1	33
HOMO -7	-6.71	0	22	27	17	0	34
HOMO -8	-6.74	1	10	23	10	0	55
HOMO -9	-6.8	1	11	31	8	0	49
HOMO -10	-6.88	0	24	31	4	0	40

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