Supporting Information for

On the Structural Evolution, Magnetic Modulation, and Spectroscopic Characteristics of Cobalt Phosphide Clusters: A DFT Investigation

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Table S1. Theoretical ADE (in eV) values of Co_3^- at various theoretical levels, and the experimental data is also included for comparison.

Co_3^-		Theor.	Exp.
Functionals	Basic sets	ADE	ADE
TPSSH	def2-TZVP	0.92	1.40[a]
	LANL2DZ	0.61	
	SDD	0.68	
M06L	def2-TZVP	0.94	
	LANL2DZ	0.67	
	SDD	0.94	
BPW91	def2-TZVP	**1.34**	
	LANL2DZ	1.18	
	SDD	1.50	
BPBE	def2-TZVP	1.32	
	LANL2DZ	0.73	
	SDD	1.46	
B3LYP	def2-TZVP	0.91	
	LANL2DZ	0.93	
	SDD	0.96	
PBE	def2-TZVP	1.47	
	LANL2DZ	1.26	
	SDD	1.54	

[a] Experimental data extracted from Phys. Rev. B., 64 (2001) 153402.

Table S2. Cartesian coordinates of optimized Co_4P_n (n = 1-10) clusters.

n = 1

Co	-1.10603300	-0.72244400	0.00000000
Co	0.16882300	-0.04321800	1.81674500
Co	0.16882300	1.29069000	0.00000000
Co	0.16882300	-0.04321800	-1.81674500
P	1.07921300	-0.86725800	0.00000000

n = 2

Co	1.25236500	0.00000000	-0.62499600
Co	0.00000000	1.11244100	1.13953800
Co	-1.25236500	0.00000000	-0.62499600
Co	0.00000000	-1.11244100	1.13953800
P	0.00000000	1.74997600	-0.92617500
P	0.00000000	-1.74997600	-0.92617500

n = 3

Co	1.25236500	0.00000000	-0.62499600
Co	0.00000000	1.11244100	1.13953800
Co	-1.25236500	0.00000000	-0.62499600
Co	0.00000000	-1.11244100	1.13953800
P	0.00000000	1.74997600	-0.92617500
P	0.00000000	-1.74997600	-0.92617500

n = 4

Co	0.88046000	0.88046000	0.88046000
Co	-0.88046000	-0.88046000	0.88046000
Co	-0.88046000	0.88046000	-0.88046000
Co	0.88046000	-0.88046000	-0.88046000
P	1.23562100	-1.23562100	1.23562100
P	-1.23562100	-1.23562100	-1.23562100
P	1.23562100	1.23562100	-1.23562100
P	-1.23562100	1.23562100	1.23562100

n = 5

Co	0.00000000	1.34966900	0.58707100
Co	1.28646100	0.00000000	-1.08217100
Co	-1.28646100	0.00000000	-1.08217100
Co	0.00000000	-1.34966900	0.58707100
P	0.00000000	1.67453200	-1.54775100
P	-1.69175500	0.00000000	1.13646600
P	0.00000000	-1.67453200	-1.54775100
P	0.00000000	0.00000000	2.60493000
P	1.69175500	0.00000000	1.13646600

n = 6

Co	0.82186300	-0.02308300	-1.26557800
Co	-0.84832500	-1.35976900	0.00040900
Co	-0.79629100	1.36260800	0.00212700
Co	0.82384800	-0.02648500	1.26446900
P	1.42782300	1.70508300	0.00078400
P	-1.40175100	0.00654000	-1.70795800
P	2.86115700	0.03022600	0.00076300
P	1.34263900	-1.73957600	-0.00385800
P	-2.83080500	0.07795400	-0.00076000
P	-1.40103400	0.00388500	1.70846100

n = 7

Co	-1.06666000	0.71989000	0.72792100
Co	0.74733700	-0.96156900	1.01081500
Co	1.06718800	0.72081400	-0.72700900
Co	-0.74786700	-0.95991600	-1.01235500
P	-0.00000700	2.63858400	0.00133700
P	-2.79074100	-0.53561300	-0.02524100
P	2.79072000	-0.53609700	0.02503900
P	-1.40076700	-1.63686100	1.17264800
P	1.07706500	1.28412700	1.49421800
P	-1.07642600	1.28703800	-1.49340700
P	1.40015900	-1.63577300	-1.17346200

n = 8

Co	0.01899000	-1.25989500	-0.78190900
Co	-1.35794600	-0.06762900	0.82245900
Co	-0.03550600	1.25107800	-0.80661200
Co	1.31915200	0.08541900	0.83182500

P	1.89467400	-0.11942800	-1.42379800
P	-1.85875800	0.03331500	-1.48281400
P	1.86784000	-2.06863800	0.39446400
P	0.02329200	-1.79050100	1.47795500
P	-1.83075100	2.09191500	0.38518800
P	0.01830800	1.84861600	1.44474500
P	2.13307600	1.80324700	-0.49152400
P	-2.14812500	-1.81467700	-0.42259100

n = 9

Co	0.08778300	-0.74992600	1.19214400
Co	-1.40662400	0.86461900	0.00101800
Co	0.08763000	-0.75115200	-1.19061500
Co	1.14535900	1.13056400	-0.00187900
P	1.62075200	-2.09753900	0.00052900
P	-1.09593400	-2.39678700	0.00104500
P	2.39000200	-0.30095300	1.20454600
P	-0.16586000	1.50085500	1.84787200
P	-2.24591600	-0.83241500	-1.21699800
P	-0.16994300	1.49536900	-1.84933300
P	2.39111200	-0.30244300	-1.20442000
P	-2.24710700	-0.83327000	1.21679100
P	-0.32257300	2.87779400	-0.00123400

n = 10

Co	-0.30294900	-0.75206400	1.24132600
Co	1.29063200	0.76552600	-0.08449700
Co	-1.21447400	1.11067800	-0.00663900
Co	-0.33347400	-0.85170500	-1.20239900
P	-1.81475400	-2.09297100	0.07457200
P	0.15287900	1.64566500	1.77902700
P	1.05429000	-2.17048800	0.08167400
P	3.01650100	-0.84610800	0.03875200
P	0.24408300	2.88037700	-0.12785200
P	0.02466900	1.51988800	-1.89407200
P	-2.61228300	-0.29700700	-1.12677100
P	1.75719900	-0.28482100	1.90494500
P	1.77131300	-0.61545200	-1.85016900
P	-2.58542000	-0.22946500	1.21386800

Table S3. Theoretical and experimental VDEs of the ground state structures of $CoSi_n^-$ (n = 3-5) are obtained from their photoelectron spectra.

Cluster	VDE (eV)		ΔVDE
	Theor.	[a]Exp.	
$CoSi_3^-$	2.01	2.03	0.02
$CoSi_4^-$	2.14	2.16	0.02
$CoSi_5^-$	2.75	2.72	0.03

[a]Experimental data extracted from Phys. Chem. Chem. Phys., 21 (2019) 6207-6215.

Table S4. Theoretical first VDE values of $Co_4P_n^-$ with n = 1-10. All energies are in eV.

Clusters	VDE (eV)
$Co_4P_1^-$	0.51
$Co_4P_2^-$	1.84
$Co_4P_3^-$	2.25
$Co_4P_4^-$	2.56
$Co_4P_5^-$	2.40
$Co_4P_6^-$	2.37
$Co_4P_7^-$	2.94
$Co_4P_8^-$	2.93
$Co_4P_9^-$	2.72
$Co_4P_{10}^-$	2.88

Table S5. Spin contamination analysis of the Co_4P_n (n = 1-10) clusters.

Clusters	Configuration	Theoretical $\langle \hat{S}^2 \rangle$	Calculated $\langle \hat{S}^2 \rangle$	$\Delta\langle \hat{S}^2 \rangle$
Co_4P	Octet (S = 8)	15.7500	15.7524	0.0024
Co_4P_2	Septet (S = 7)	12.0000	12.0028	0.0028
Co_4P_3	Octet (S = 8)	15.7500	15.7523	0.0023
Co_4P_4	Triplet (S = 3)	2.0000	2.0485	0.0485
Co_4P_5	Doublet (S = 2)	0.7500	0.7925	0.0425
Co_4P_6	Triplet (S = 3)	2.0000	2.0085	0.0085
Co_4P_7	Octet (S = 8)	15.7500	15.7518	0.0018
Co_4P_8	Quintet (S = 5)	6.0000	6.0106	0.0106
Co_4P_9	Doublet (S = 2)	0.7500	0.7955	0.0455
Co_4P_{10}	Quintet (S = 5)	6.0000	6.0037	0.0037
Threshold	-	-	-	<0.1000

a. Theoretical $\langle \hat{S}^2 \rangle = S(S+1)$

b. $\Delta\langle \hat{S}^2 \rangle$ = Calculated $\langle \hat{S}^2 \rangle$ – Theoretical $\langle \hat{S}^2 \rangle$. Values <0.10 indicate negligible spin contamination.

Table S6. Analysis of the composition of the superatomic orbitals of the Co_4P_4 cluster.

Orbitals	Co_4(%)	P_4(%)
57-1S	25.97	74.03
58-1P	15.95	84.05
59-1P	15.20	84.80
60-1P	17.23	82.77
61-2S	65.88	34.12
62-1D	59.90	40.10
64-1D	58.76	41.24
65-2P	56.09	43.91
66-2P	55.72	44.28
67-2P	54.14	45.86
68-1D	68.32	31.68
69-1D	67.12	32.88
70-1F	66.03	33.97
71-1F	62.57	37.43
72-1F	64.23	35.77
73-3S	50.89	49.11
74-1D	57.96	42.04
75-2D	61.59	38.41
76-1F	90.70	9.30
77-1F	80.55	19.45
79-2D	76.75	23.25
80-2D	73.93	26.07
81-1F	94.92	5.08
82-1F	94.90	5.10
84-2D	68.26	31.74
85-2D	69.84	30.16

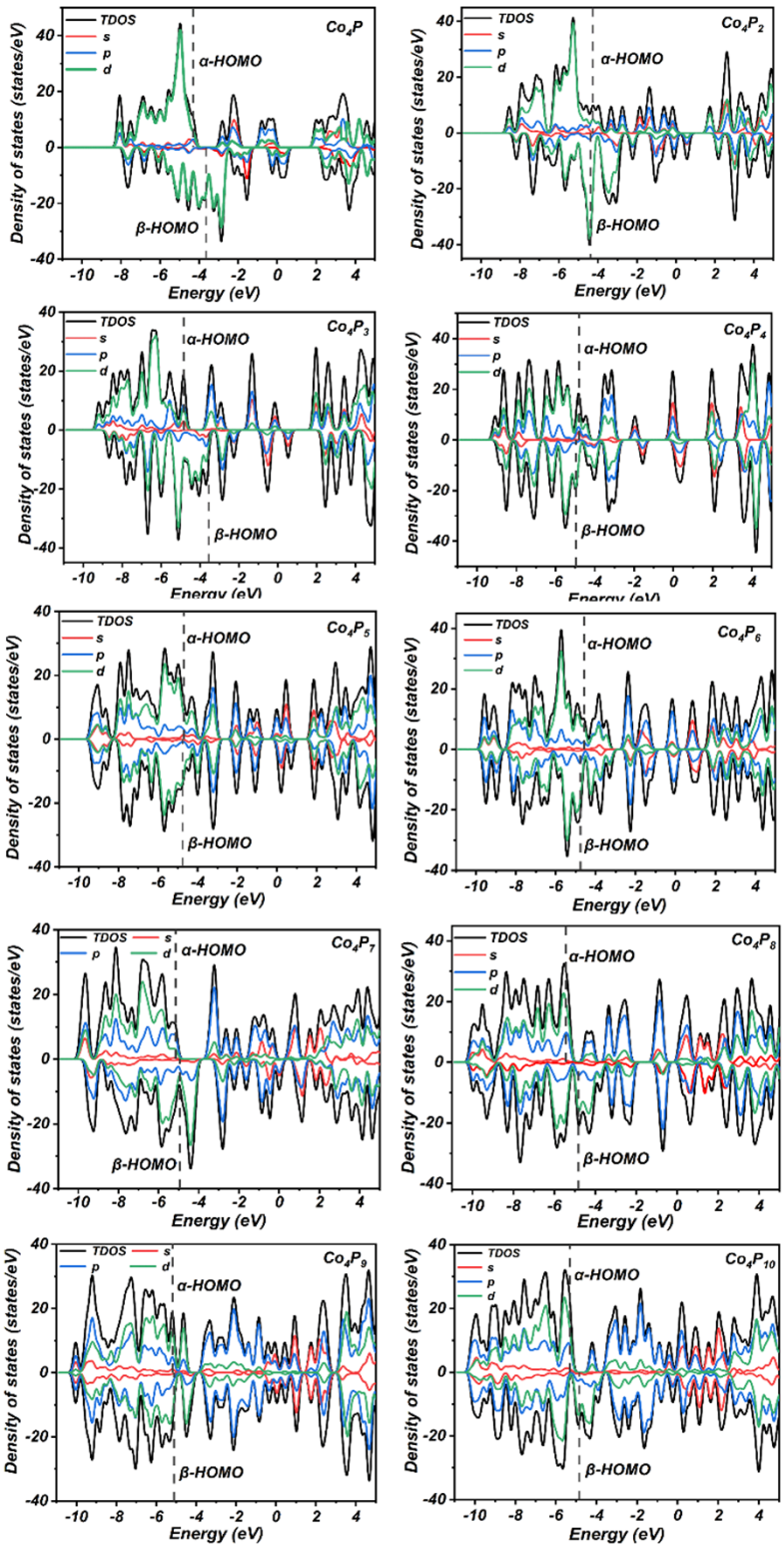

Fig. S1. Calculated TDOS and PDOS for the ground states of Co_4P_n (n = 1-10). Lorentzian broadening of FWHM is 0.01 eV. The dotted lines on the topside refer to the position of α-HOMOs and the bottom side refer to β-HOMOs.

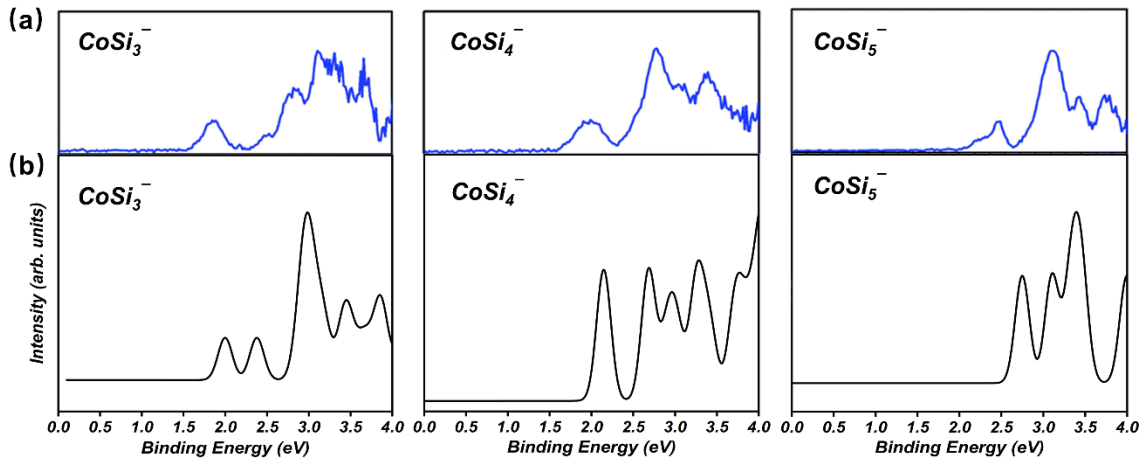

Fig. S2. Comparison of (a) experimental and (b) theoretical PES for the lowest-energy structures of the $CoSi_n^-$ (n = 3-5) clusters. Experimental data are adapted from Phys. Chem. Chem. Phys., 21 (2019) 6207-6215.

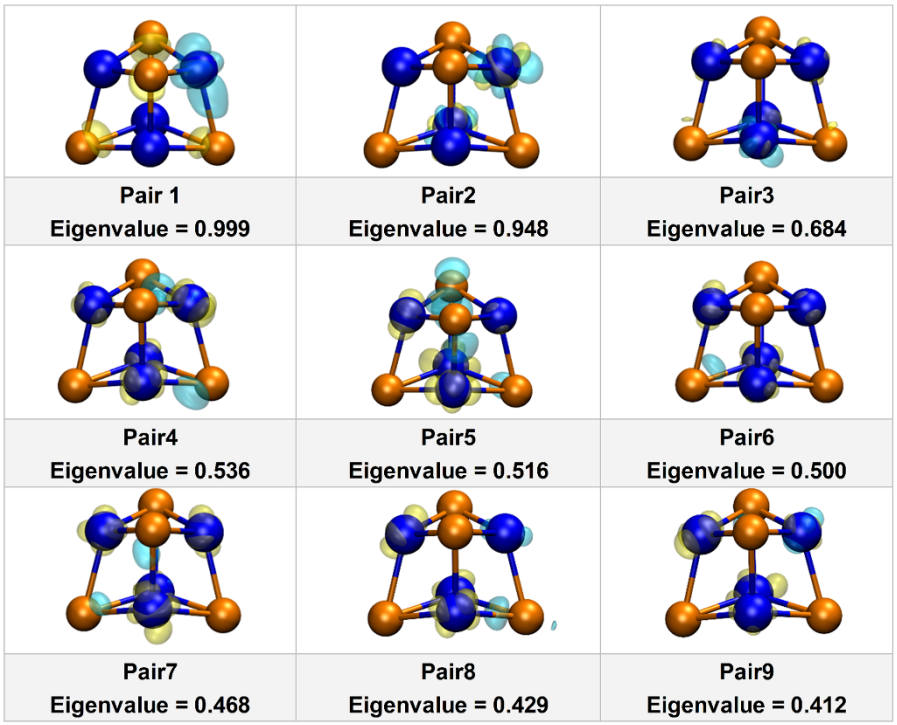

Fig. S3. Deformation density analysis of NOCV pairs (orbital contributions) based on the ETS-NOCV method. Regions of charge depletion are shown as yellow translucent surfaces and regions of charge accumulation as cyan translucent surfaces. The figure only lists eigenvalues > 0.4.

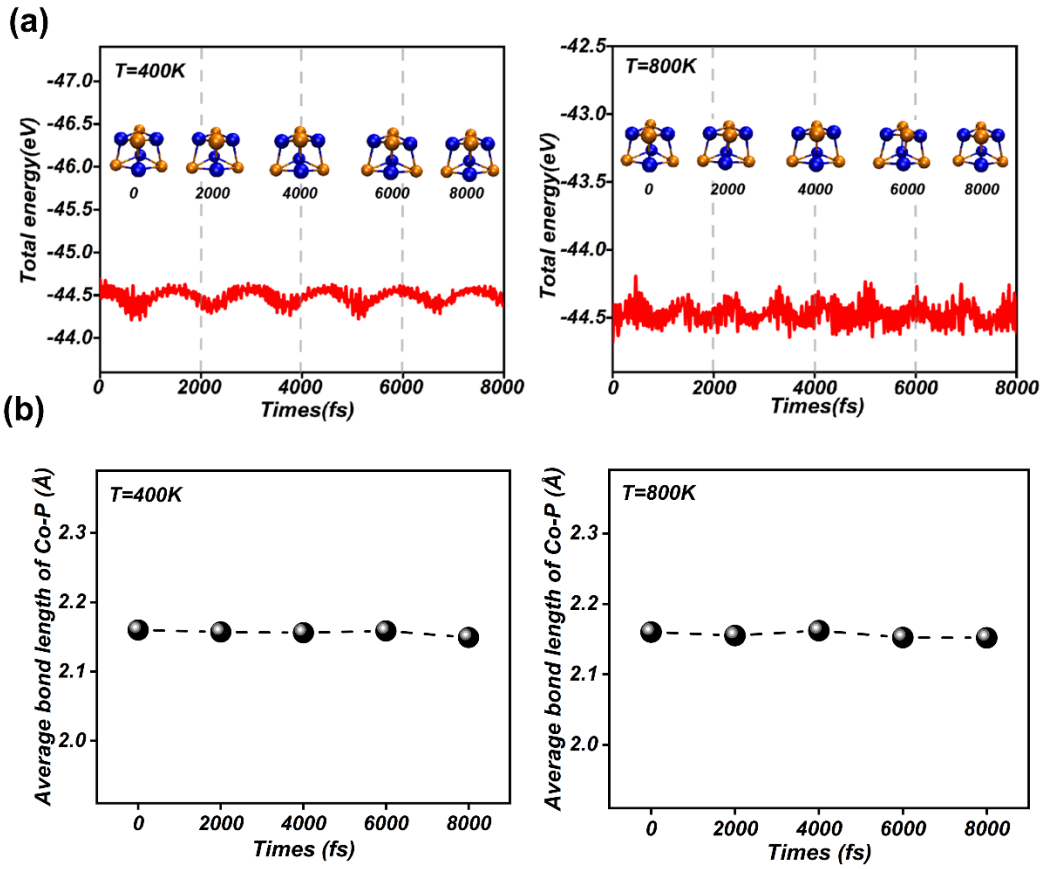

Fig. S4. (a) Variations of the total energy of Co_4P_4, and (b) average bond length of Co-P in Co_4P_4 at 400 and 800 K, respectively. The inset shows the structures of the cluster at different times.

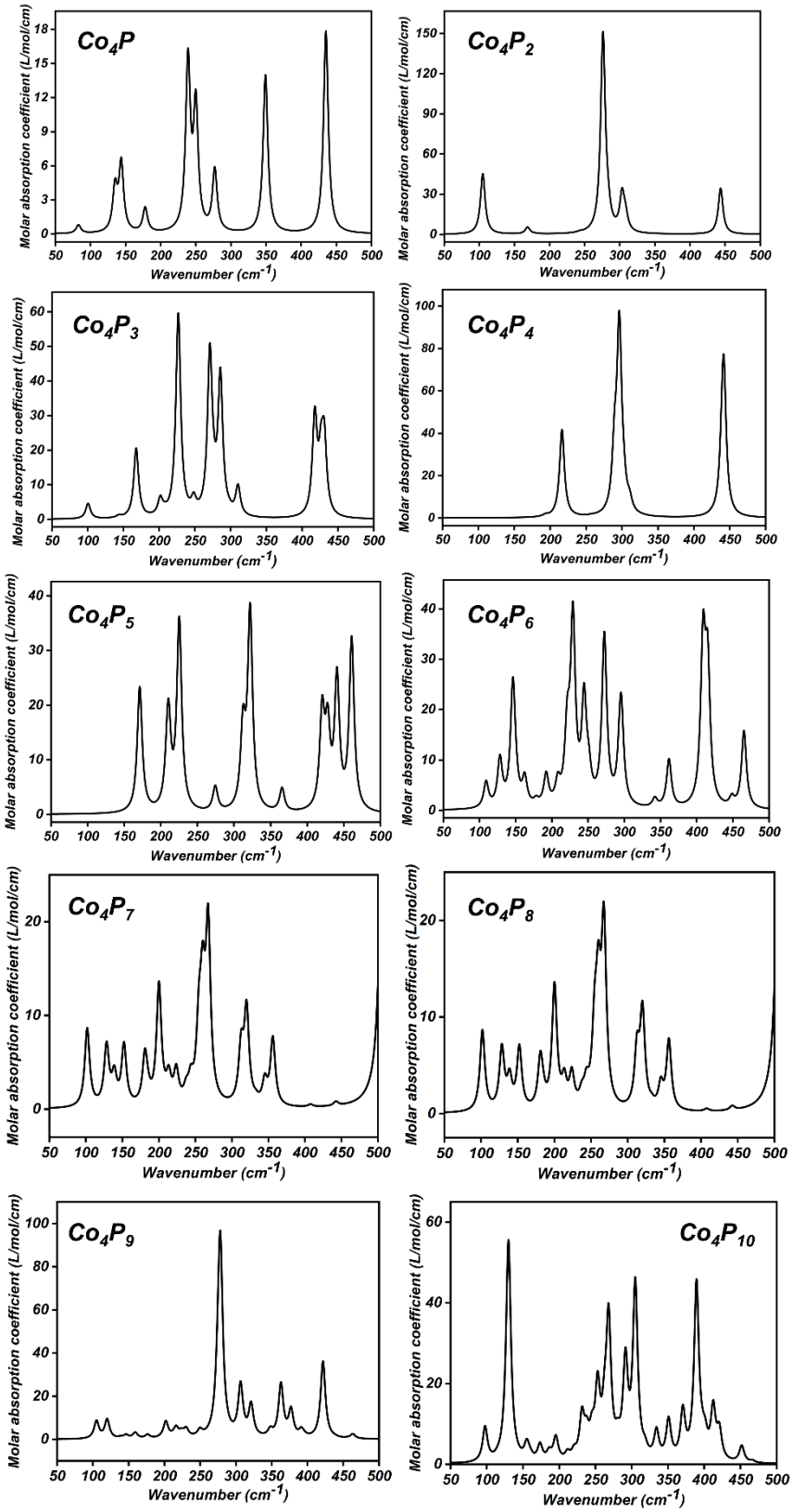

Fig. S5. Simulated infrared spectra of the Co_4P_n (n = 1-10) clusters.

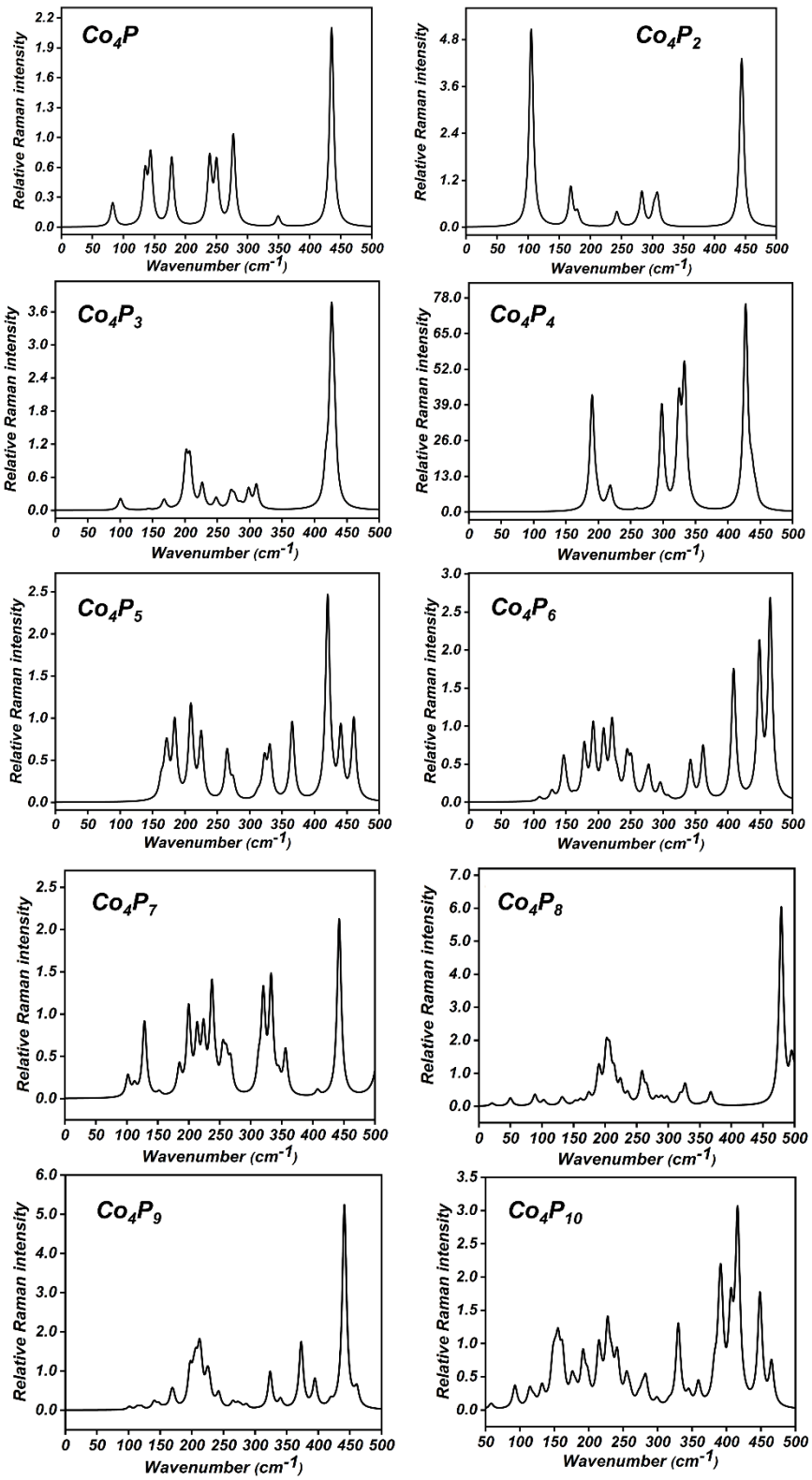

Fig. S6. Simulated Raman spectra of the Co_4P_n (n = 1-10) clusters.