Electronic Supporting Information (ESI)

Efficient capturing of hydrogen peroxide in dilute aqueous solution by co-crystallization with amino acids

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Table S1 Graph set analyses for co-crystals of H_2O_2 and L-Phe, DL-Phe or DL-Asn

a. Patterns in period 1 (D⋯A)

	a	b	c	d	e	f	g	h	i	j
L-Phe·H_2O_2·0.5H_2O	$D^1_1(2)$	$D^1_1(2)$	$C^1_1(5)$	$D^1_1(2)$	$D^1_1(2)$	$D^1_1(2)$				
	$N\cdots O_a$	$N\cdots O_b$	$N\cdots O_2$	$O_a\cdots O_1$	$O_b\cdots O_2$	$O_w\cdots O_1$				
DL-Phe·H_2O_2	$D^1_1(2)$	$D^1_1(2)$	$C^1_1(5)$	$D^1_1(2)$	$D^1_1(2)$	$C^1_1(5)$	$D^1_1(2)$	$D^1_1(2)$	$D^1_1(2)$	$D^1_1(2)$
	$N_1\cdots O_b$	$N_1\cdots O_b$,	$N_1\cdots O_2$	$N_2\cdots O_b$,	$N_2\cdots O_b$	$N_2\cdots O_4$	$O_a\cdots O_1$	$O_b\cdots O_2$	O_a,$\cdots O_3$	O_b,$\cdots O_4$
DL-Phe·0.5H_2O_2	$D^1_1(2)$	$C^1_1(5)$	$D^1_1(2)$	$D^1_1(2)$	$C^1_1(5)$	$D^1_1(2)$	$D^1_1(2)$	$D^1_1(2)$		
·0.5H_2O	$N_1\cdots O_b$	$N_1\cdots O_2$,	$N_2\cdots O_w$	$N_2\cdots O_b$	$N_2\cdots O_4$	$O_a\cdots O_1$	$O_b\cdots O_2$	$O_w\cdots O_4$		
DL-Asn·H_2O_2	$S^1_1(6)$	$D^1_1(2)$	$D^1_1(2)$	$C^1_1(6)$	$D^1_1(2)$	$R^2_2(8)$	$R^2_2(8)$	$D^1_1(2)$	$D^1_1(2)$	
	$N_1\cdots O_3$	$N_1\cdots O_a$	$N_1\cdots O_a$	$N_1\cdots O_3$	$N_1\cdots O_b$	$N_2\cdots O_3$	$N_2\cdots O_1$	$O_b\cdots O_2$	$O_a\cdots O_1$	

b. Graph set matrix in period 2

L-Phe·H_2O_2·0.5H_2O

	a	b	c	d	e	f
a						
b	$C^2_2(5)$					
	>a<b					
c	$D^3_3(10)$	$D^3_3(10)$				
	<a>c>a	<b>c>b				
d	$R^4_4(14)$	$C^2_2(8)$	$D^3_3(10)$			
	>a>d>a>d	>b>d	>d>c<d			
e	$C^2_2(8)$	$C^2_2(7)$	$D^2_3(8)$	$C^2_2(7)$		
	>a>e	>b>e	>e>c<e	>d<e		
f	$D^2_2(7)$	$D^2_2(7)$	$C^3_3(11)$	$D^1_2(3)$	$D^2_2(5)$	$D^2_2(5)$
	>f>a	>f>b	>c<f>f	>d<f	>e<f	<f>f
	$D^3_3(10)$	$D^3_3(10)$		$D^2_3(6)$	$D^3_3(8)$	
	<a<f>f	<b<f>f		>d<f>f	>e<f>f	

DL-Phe·H_2O_2

	a	b	c	d	e	f	g	h	i	j
a										
b	$D^2_2(5)$									
	<a>b									
c	$D^3_3(10)$	$D^3_3(10)$								
	<a>c>a	<b>c>b								
d		$D^1_2(3)$								
		>b<d								
e	$D^1_2(3)$			$D^2_2(5)$						
	>a<e			<d>e						
f				$D^3_3(10)$	$D^3_3(10)$					
				<d>f>d	<e>f>e					
g	$C^2_2(8)$	$D^2_2(7)$	$D^3_3(10)$		$D^2_2(5)$					
	>a>g	>g>b	>g>c<g		>e>g					
h	$C^2_2(7)$	$D^2_2(7)$	$D^2_3(8)$		$D^2_2(4)$		$C^2_2(7)$			
	>a>h	>h>b	>h>c<h		>e>h		>g<h			
i		$D^2_2(5)$		$C^2_2(8)$	$D^2_2(7)$	$D^3_3(10)$				
		>b>i		>d>i	>i>e	>i>f<i				
j		$D^2_2(4)$		$C^2_2(7)$	$D^2_2(7)$	$D^2_3(8)$			$C^2_2(7)$	
		>b>j		>d>j	>j>e	>j>f<j			>i<j	

DL-Phe·0.5H_2O_2·0.5H_2O

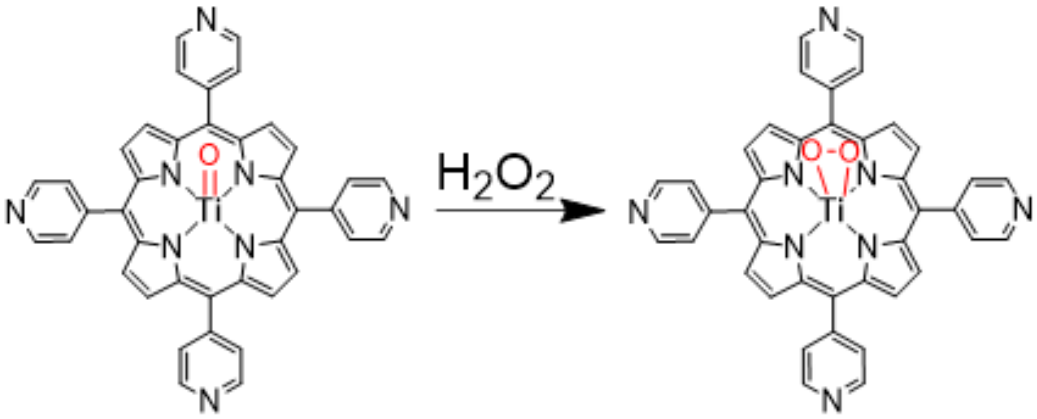
	a	b	c	d	e	f	g	h
a								
b	$D^3_3(10)$							
	<a>b>a							
c								
d	$D^1_2(3)$		$D^2_2(5)$					
	>a<d		<c>d					
e			$D^3_3(10)$	$D^3_3(10)$				
			<c>e>c	<d>e>d				
f	$C^2_2(8)$	$D^3_3(10)$		$D^2_2(5)$				
	>a>f	>f>b<f		>d>f				
g	$C^2_2(7)$	$D^2_3(8)$		$D^2_2(4)$		$C^2_2(7)$		
	>a>g	>g>b<g		>d>g		>f<g		
h			$C^2_2(7)$	$D^2_2(7)$	$D^2_3(8)$			
			>c>h	>h>d	>h>e<h			

DL-Asn·H_2O_2

	a	b	c	d	e	f	g	h	i	j
a										
b										
c		$R^2_4(8)$ >b<c>b<c								
d		$D^3_3(11)$ <b>d>b	$D^3_3(11)$ <c>d>c							
e		$C^2_2(5)$ >b<e	$R^4_4(10)$ >c<e>c<e	$D^3_2(9)$ <e>d>e						
f		$D^3_3(15)$ <b>f>b	$D^3_3(15)$ <c>f>c	$R^2_4(16)$ >d<f>d<f $C^3_4(18)$ >d>f<d<f $R^3_4(18)$ >d>f>d<f $R^4_4(20)$ >d>f>d>f $R^4_6(28)$ >d>d<f>d>d<f $R^5_6(30)$ >d>d>f>d>d<f $R^6_6(32)$ >d>d>f>d>d>f	$D^3_3(15)$ <e>f>e					

Table S2 Crystallographic parameters for co-crystals of H_2O_2 and L-Phe, DL-Phe, or DL-Asn, and that of H_2O and L-Asn

	L-Phe·H_2O_2·0.5H_2O	DL-Phe·0.9675H_2O_2 ·0.0325H_2O	DL-Asn·H_2O_2	L-Asn·H_2O
Formula	$C_9H_{14}O_{4.5}$	$C_9H_{13}O_{3.9675}$	$C_4H_{10}N_2O_5$	$C_4H_{10}N_2O_4$
Formula weight	208.21	198.69	166.14	150.14
Temperature / K	150(2)	200(2)	200(2)	200(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
Space group	$C2$	$P_{ca}2_1$	$P\bar{1}$	$P2_12_12_1$
Z	4	8	2	4
a / Å	9.9671(3)	11.6333(3)	4.7744(4)	5.571(2)
b / Å	7.2000(3)	5.98690(10)	7.3961(7)	9.766(4)
c / Å	14.1385(6)	28.5029(10)	9.8715(6)	11.738(4)
α / °	90	90	90.222(5)	90
β / °	92.803(3)	90	90.124(3)	90
γ / °	90	90	101.127(6)	90
V / Å^3	1013.41(7)	1985.15(9)	342.02(5)	638.6(4)
Density	1.365	1.330	1.613	1.562
GOF	1.096	1.052	1.045	1.067
R_1 [$I > 2\sigma(I)$]	0.0505	0.0364	0.0371	0.0294
wR_2 for all data	0.1325	0.0836	0.0919	0.0775
CCDC No.	2083714	2083715	2083716	2083717



Scheme S1 Reaction of oxo[5, 10, 15, 20-tetra(4-pyridyl)porphyrinato]titanium(IV) and hydrogen peroxide

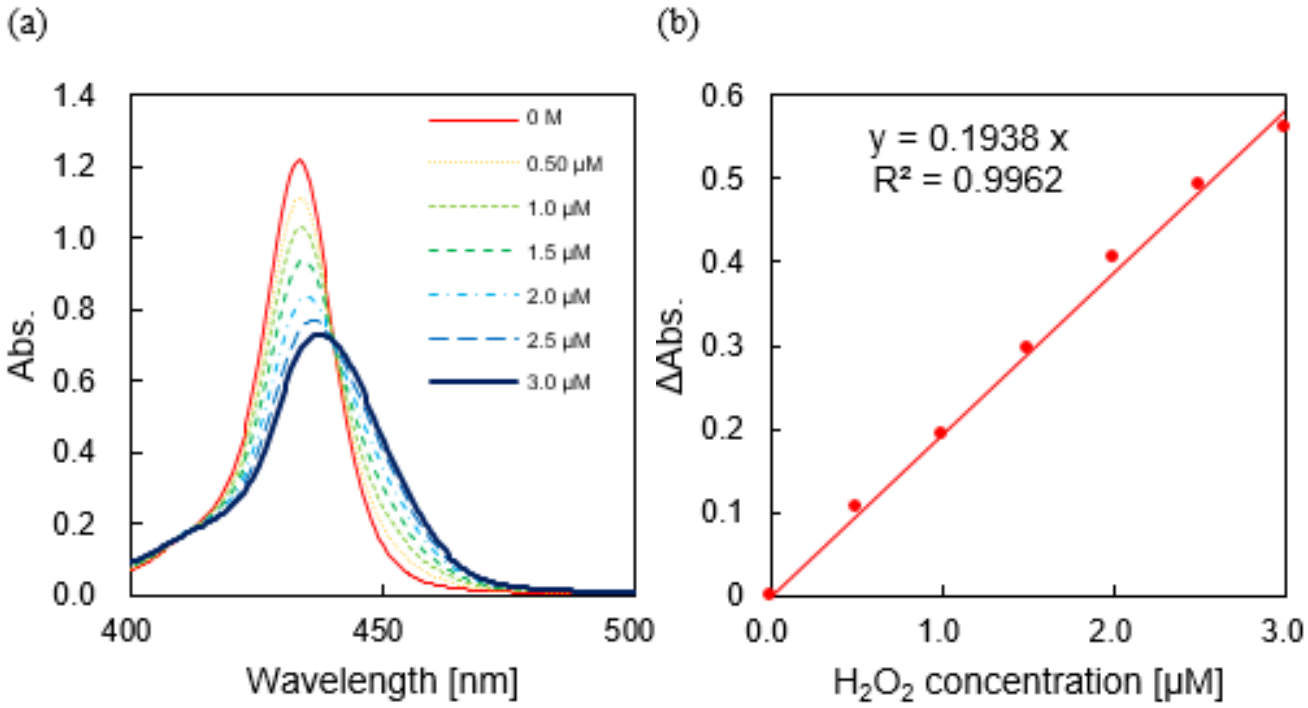
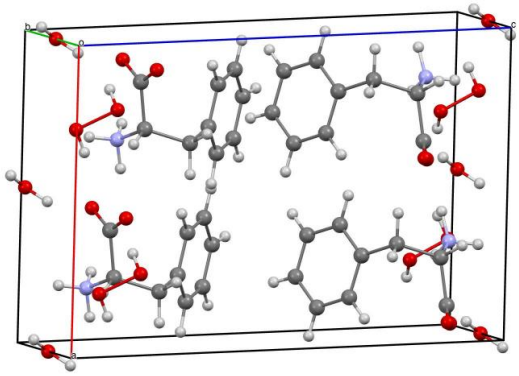
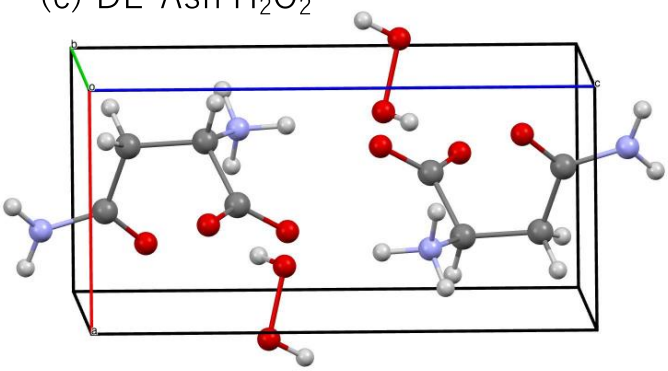


Fig. S1 (a) Absorption spectra of mixture of oxo[5, 10, 15, 20-tetra(4-pyridyl)porphyrinato]titanium(IV), perchloride acid (4.8 M) and H_2O_2 (0–30 μM). (b) Absorbance changes at 432 nm as a function of H_2O_2 concentrations.

(a) L-Phe·H_2O_2·0.5H_2O



(c) DL-Asn·H_2O_2



(b) DL-Phe·H_2O_2

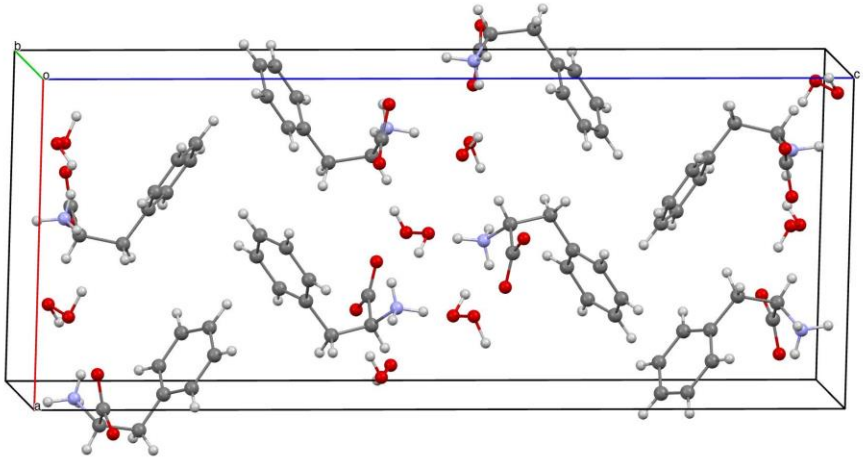


Fig. S2 Molecular packing diagrams of (a) L-Phe·H_2O_2·0.5H_2O, (b) DL-Phe·H_2O_2 and (c) DL-Asn·H_2O_2 in a unit cell. C, H, N, O atoms are color coded by gray, white, blue, and red, respectively.

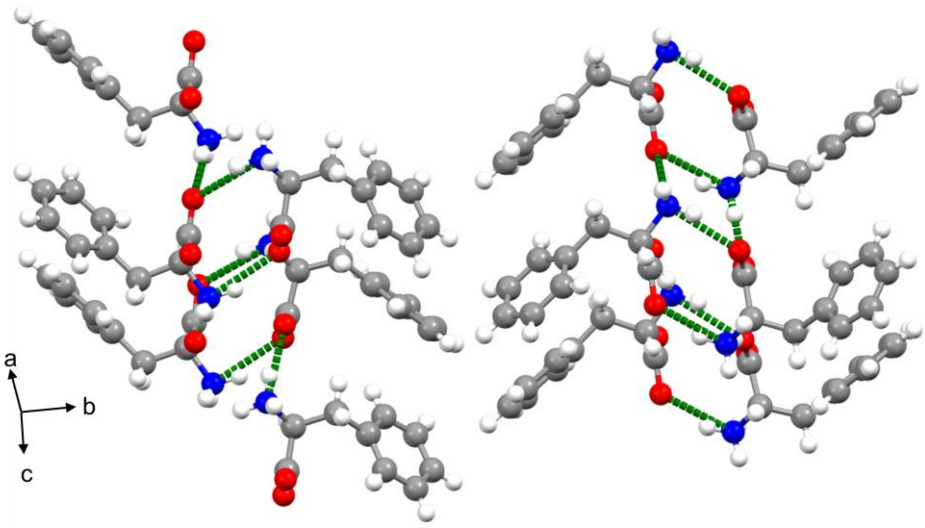


Fig. S3 Packing of L-Phe crystallized in an aqueous solution (CCDC ID: 985094).[S1] Green dotted lines represent the hydrogen bonds. C, H, N, O atoms are color coded by gray, white, blue, and red, respectively.

Reference

S1 E. Mossou, S. C. M. Teixeira, E. P. Mitchell, S. A. Mason, L. Adler-Abramovich, E. Gazite and V. T. Forsyth, *Acta Crystallogr. C*, 2014, **70**, 326.

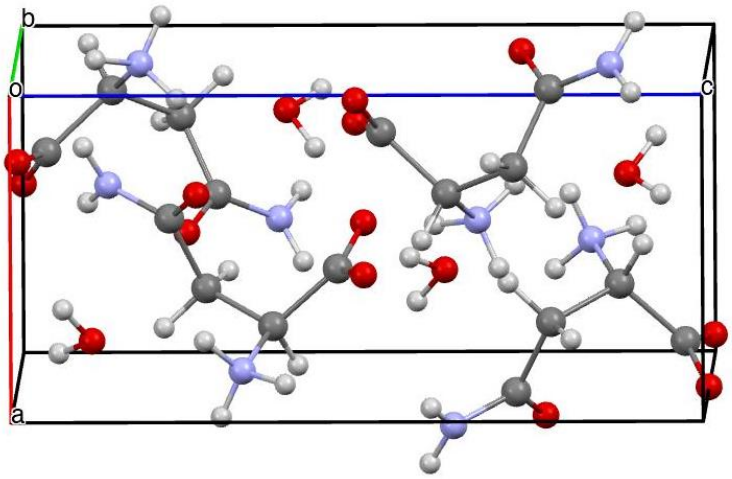


Fig. S4 Molecular packing diagram of L-Asn·H_2O in a unit cell. C, H, N, O atoms are color coded by gray, white, blue, and red, respectively.

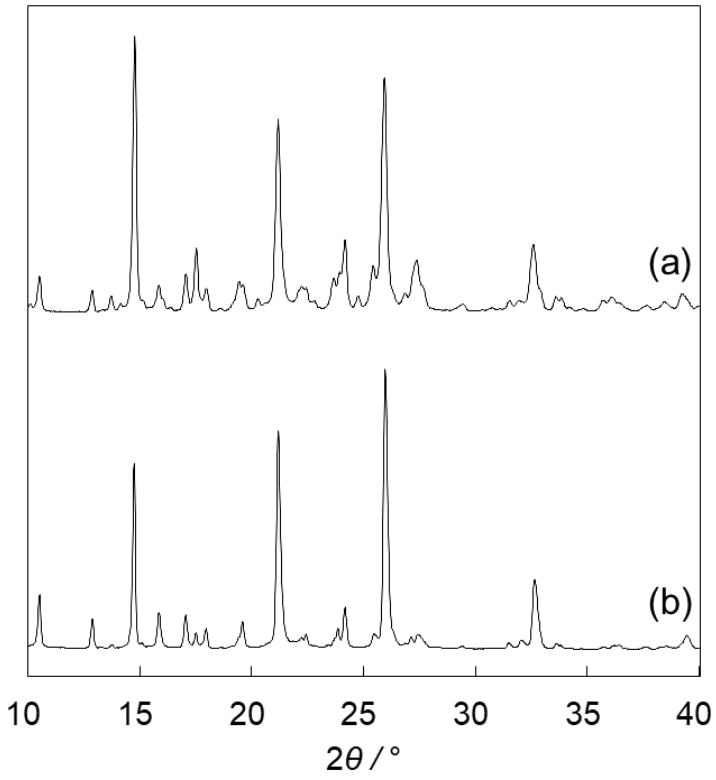


Fig. S5 Powder X-ray diffraction (PXRD) patterns of (a) co-crystals obtained at 4 °C by cooling a saturated solution of L-Phe prepared at 50 °C (H_2O_2: 20%) and (b) co-crystals obtained at 20 °C by cooling a saturated solution of L-Phe prepared at 50 °C (H_2O_2: 30%).

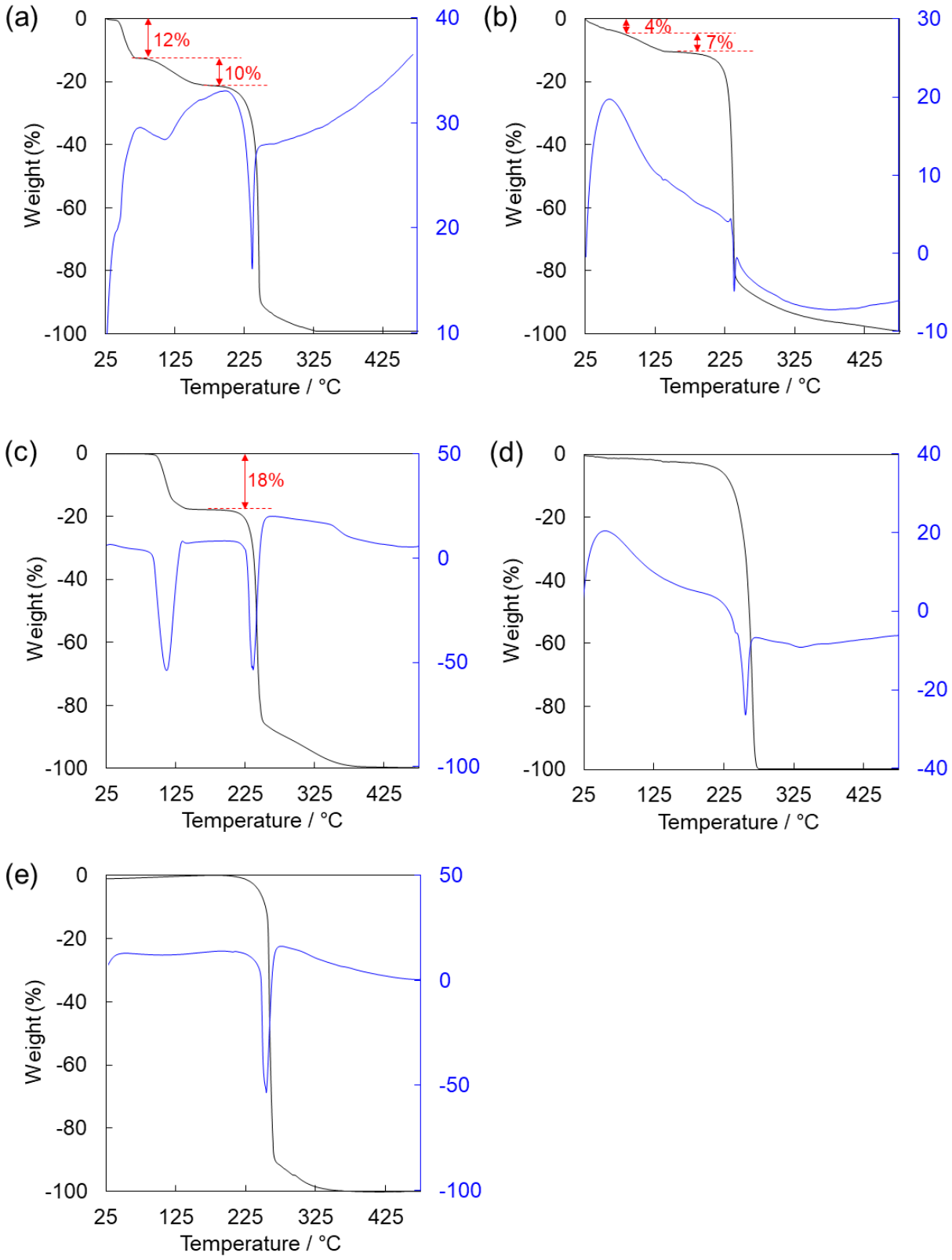


Fig. S6 Profiles of thermogravimetric and differential thermal analyses (TG/DTA) of (a) L-Phe·H_2O_2·0.5H_2O, (b) co-crystal of L-Phe and H_2O_2 prepared in an aqueous solution of 10% H_2O_2, (c) DL-Phe·H_2O_2, (d) L-Phe, and (e) DL-Phe.