Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Natural hybrid-mediated long-lived room temperature phosphorescence of milk powder

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Experimental Section

Materials. MP was purchased from Mengniu Dairy, goat MP (GMP) was purchased from Flevomel, moderately hydrolyzed MP (MHMP) was purchased from Nestle, sweetened MP (SMP) was purchased from Yili, AND infant formula MP (IFMP) was purchased from Friso. Casein phosphopeptide (CPP), acid hydrolyzed casein (AHC), lactalbumin were purchased from Macklin. Casein was purchased from Bidepharm. Water was purified with a Millipore system, combining inverse osmosis membrane (Milli-R) and ion-exchange resins (Milli-Q).

Measurements and methods. Steady-state photoluminescence spectra were measured using a Horiba Fluoromax-4C-L instrument. The excitation-dependent emission spectra, steady state and time-resolved emission spectra, temperature-dependent photoluminescence spectra, fluorescence and phosphorescence lifetime, as well as photoluminescence quantum efficiency were obtained on Edinburgh FLS 1000 fluorescence spectrophotometer equipped with a xenon lamp, an EPLED, a microsecond flash-lamp and an integrating sphere. All photographs and videos were taken by a digital camera (Canon EOS R6) or a mobile phone (Huawei Mate 40 pro). Inductively coupled plasma optical emission spectrometer (ICP-OES) was adopted using a Shimadzu ICPE-9800 instrument.

Calculation details. According to the given amino acid sequence, Robetta was used to construct the structure model of the peptide. The obtained structure was dynamically optimized by Chimera software based on Amber force field parameters (default parameters) to obtain a reasonable peptide structure. Discovery Studio was used to analysis the interaction between amino acid residues in the peptide structure. Autodock4 was used to docking the peptide with calcium ion. The center of the docking box was set as (X= 3, Y=-1, Z=3), the box size was X= 17.25 Å, Y= 16.5 Å, Z= 16.5 Å, and other parameters were default. Lamarck genetic algorithm was used to docking and study the interaction.

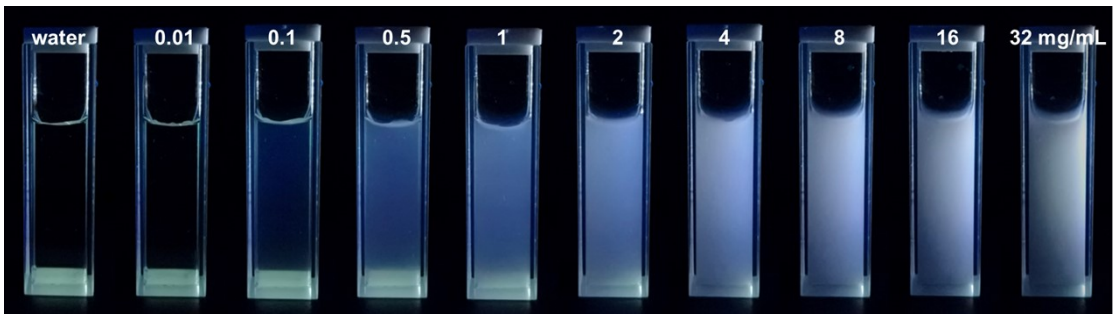

Fig. S1. Photographs for milk powder aqueous solutions with varying concentrations (λ_{ex} = 254 nm).

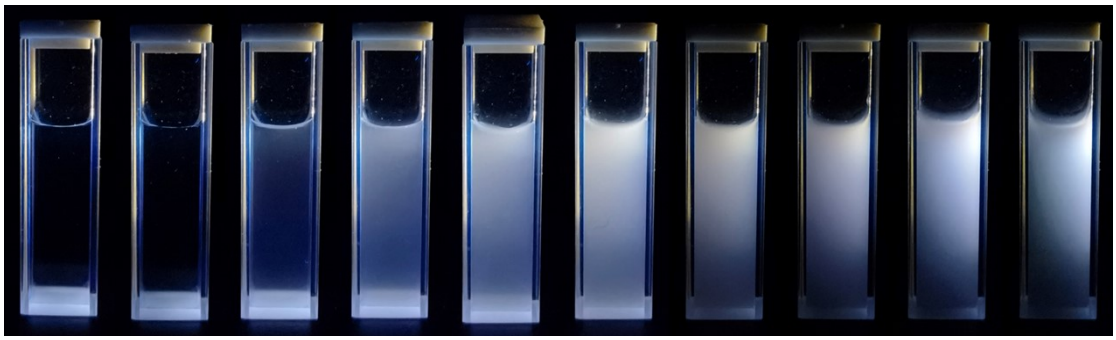

Fig. S2. Photographs for milk powder aqueous solutions with varying concentrations (λ_{ex} = 310 nm).

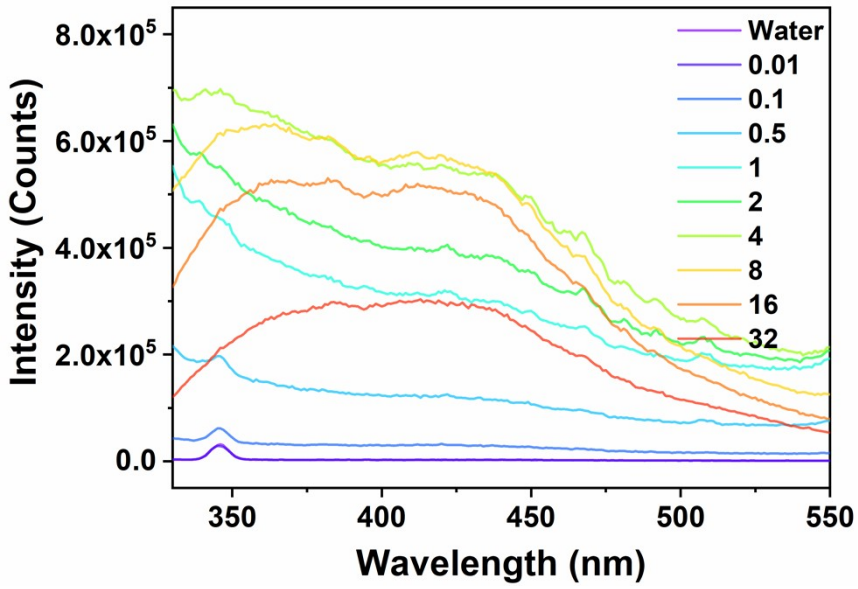

Fig. S3. PL spectra for milk powder aqueous solutions with varying concentrations (λ_{ex} = 310 nm).

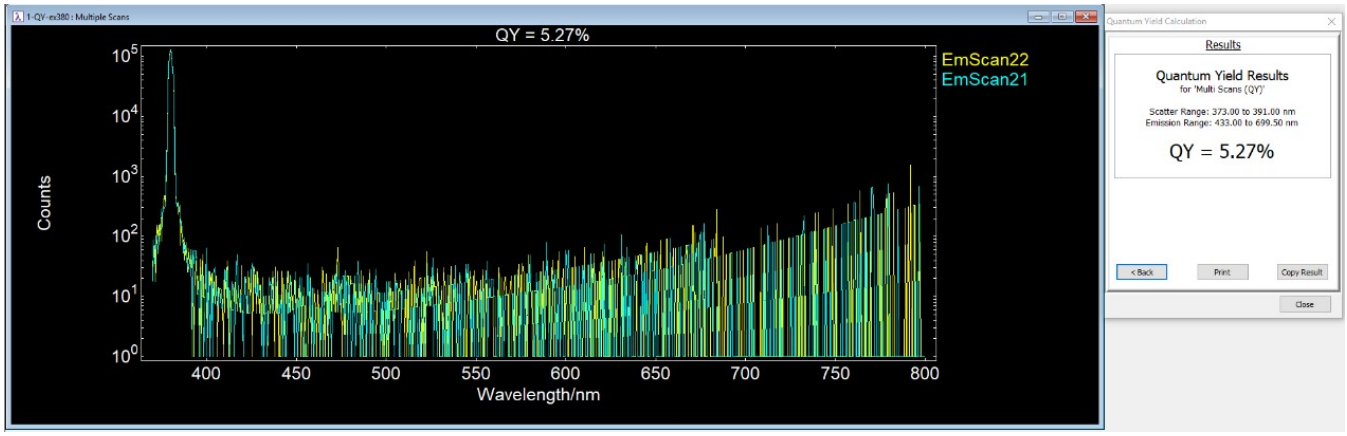

Fig. S4. Fluorescence quantum efficiency of milk powder aqueous solution with a concentration of 2 mg/mL.

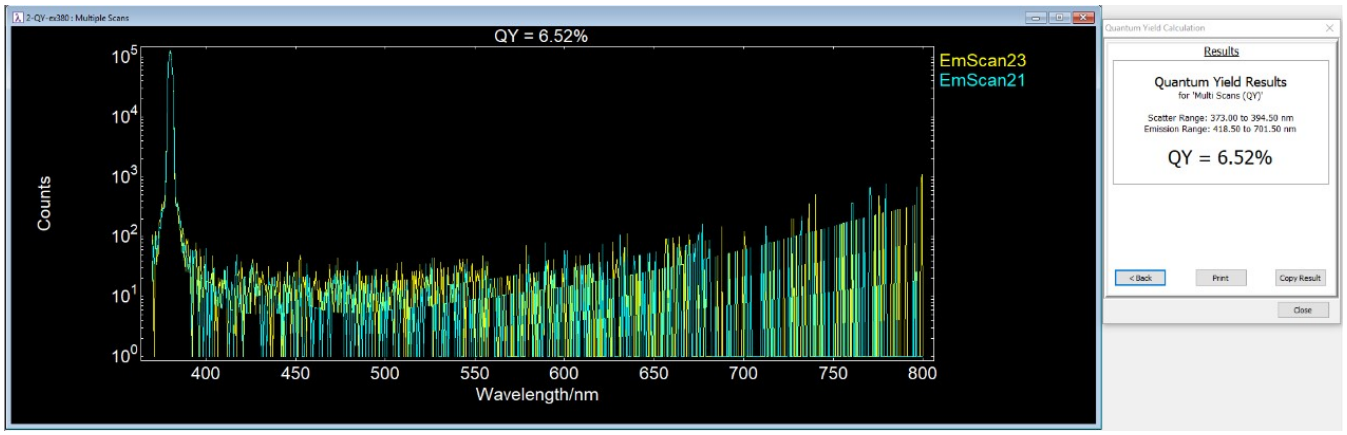

Fig. S5. Fluorescence quantum efficiency of milk powder aqueous solution with a concentration of 8 mg/mL.

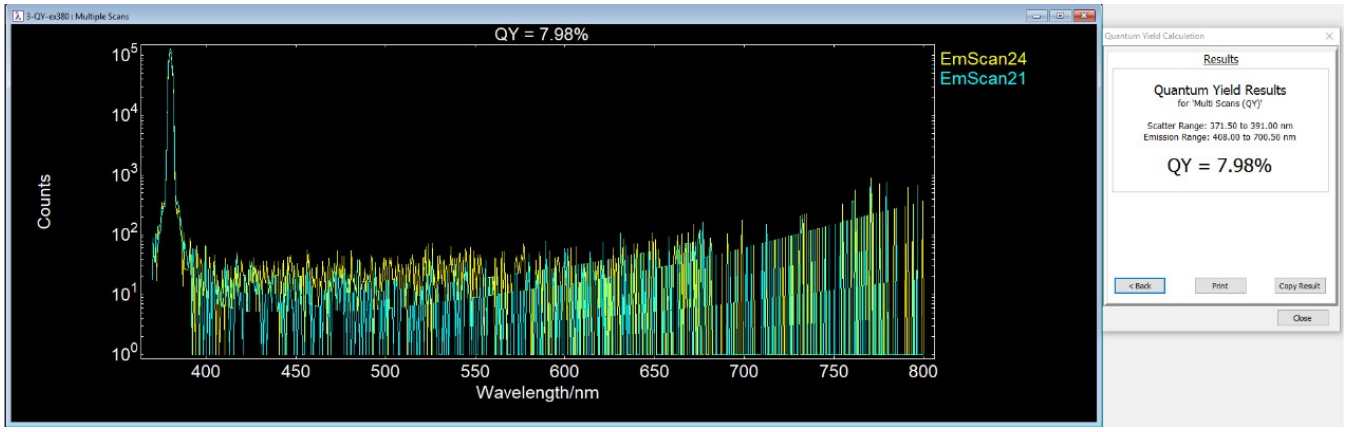

Fig. S6. Fluorescence quantum efficiency of milk powder aqueous solution with a concentration of 32 mg/mL.

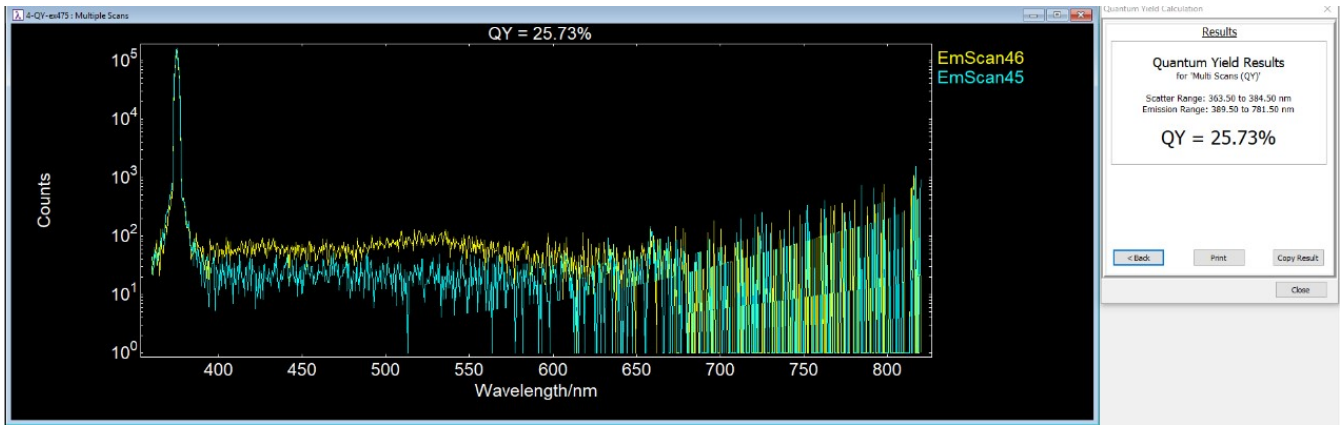

Fig. S7. Fluorescence quantum efficiency of milk powder.

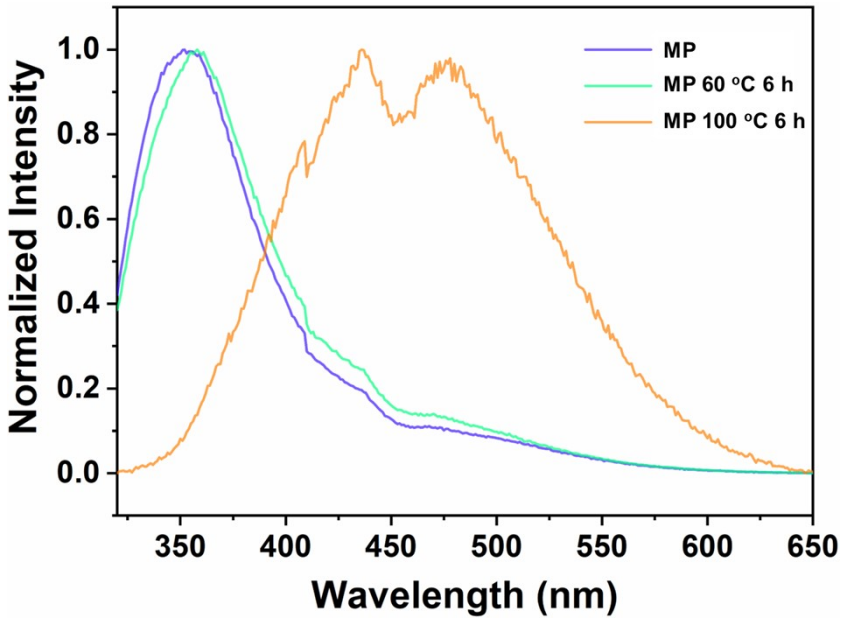

Fig. S8. PL spectra of MP placed under high temperature.

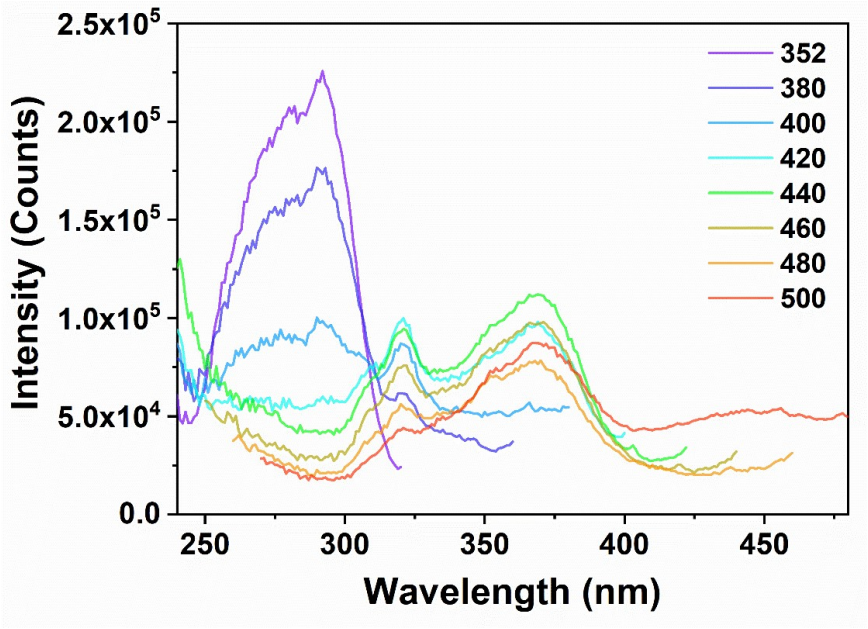

Fig. S9. Excitation spectra of the milk powder aqueous solution with a concentration of 32 mg/mL under different λ_{em}.

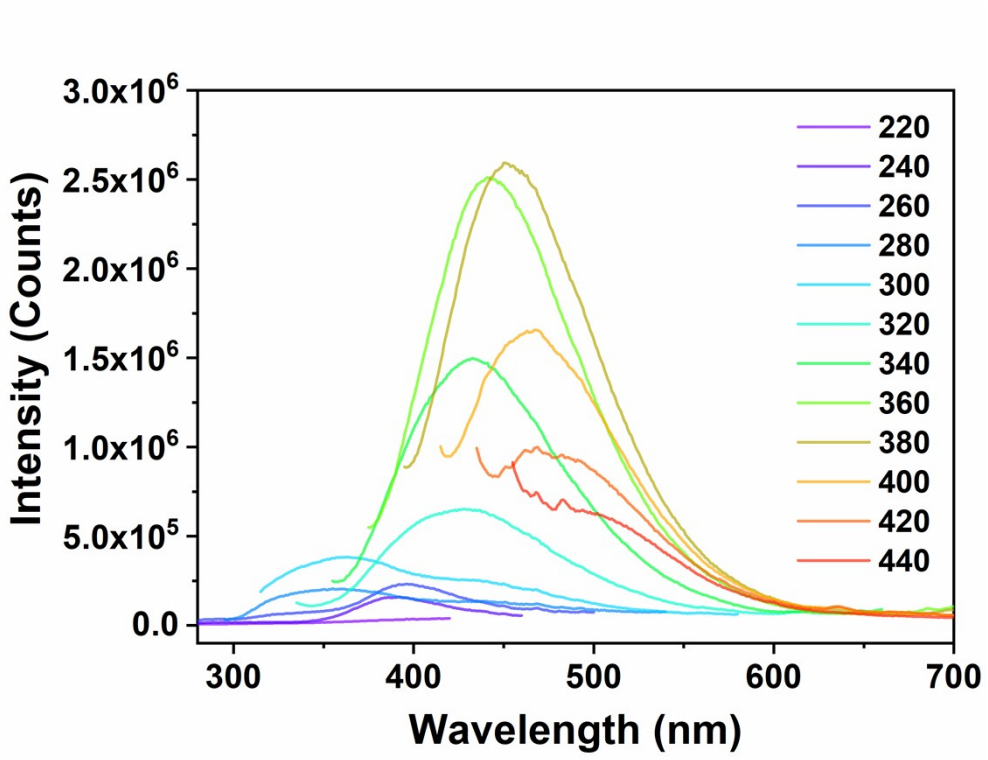

Fig. S10. PL spectra of soild lactalbumin.

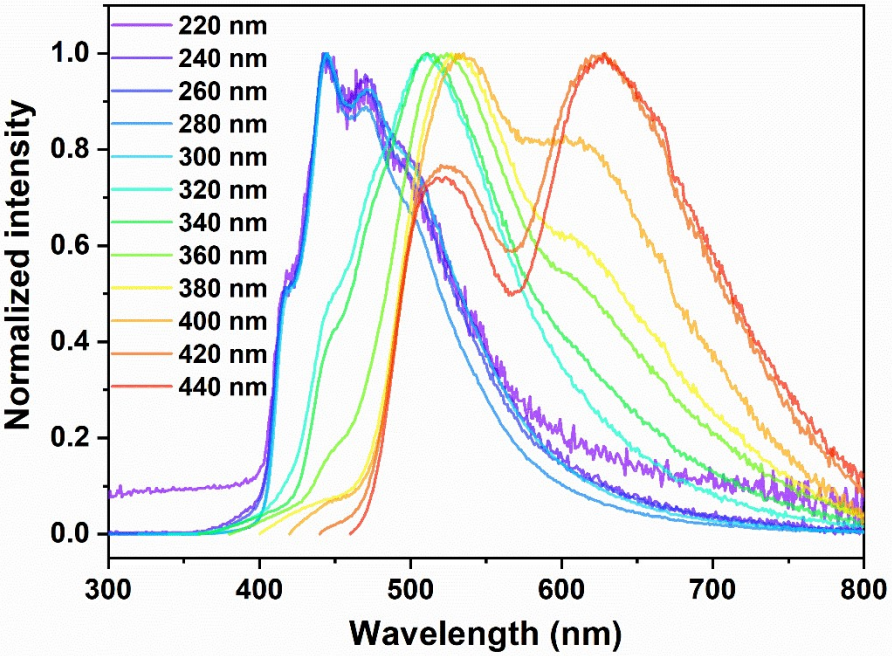

Fig. S11. Excitation-dependent delayed phosphorescence spectra of milk powder from 220 to 440 nm with a delay time of 1 ms.

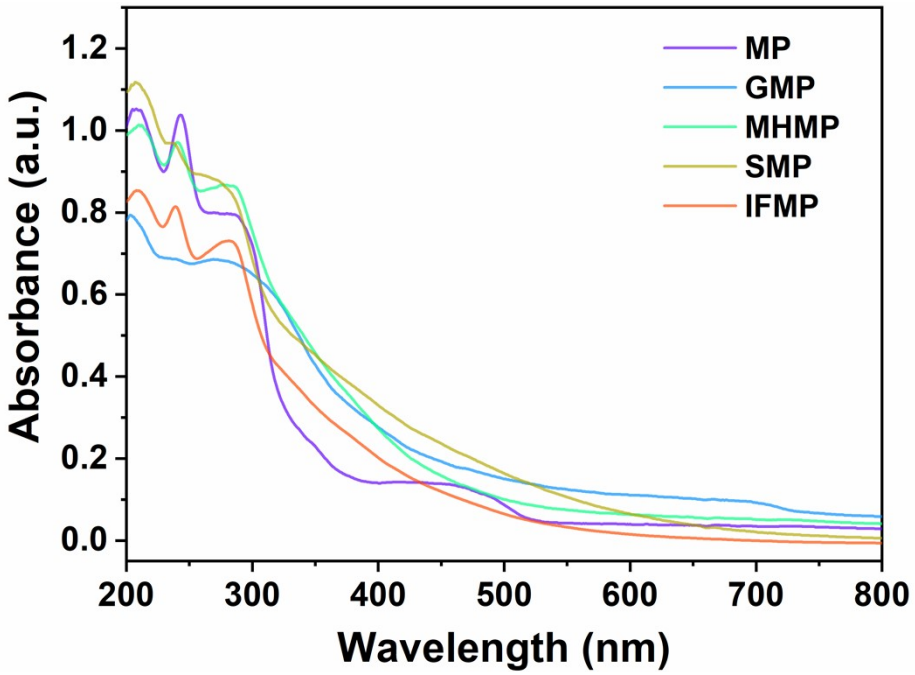

Fig. S12. UV-vis absorption of five kinds of MP.

Table S1. Phosphorescence lifetimes (τ) of MP, GMP, MHMP, SMP, IFMP, CPP, AHC, casein, and lactalbumin under ambient conditions.

Compounds	λ_{ex} (nm)	λ_{em} (nm)	Phosphorescence					
			τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)
MP	290	444	48.5	8.7	376.5	32.3	1909.8	59
GMP	290	444	45.6	7.5	343	31.7	1717.8	60.9
MHMP	290	444	49.9	3.9	463.9	21.2	2290.2	74.9
SMP	290	444	42.5	14.8	301	33.8	1659.8	51.4
IFMP	290	444	39.2	8.6	335.5	32.1	1829.1	59.3
CPP	290	444	45.4	16.3	293	38	1652.6	45.7
AHC	290	472	30.4	11.1	282.3	40.8	1686.2	48.1
casein	290	477	7.6	51.2	36.6	39.8	200	9
lactalbumin	290	476	11.8	61.9	65	25.6	582.9	12.5

Table S2. Sequence coverage of β-casein and a CPP fragment with amino acid sequence of RELEELNVPGEIVEpSLpSpSpSpEESITR.

Number	Sequence
	CASβ_BOVIN
1	MKVLILACLVALALA**RELEELNVPGEIVESLSSSEESITR**INKKIEKFQS
51	EEQQQTEDELQDKIHPFAQTQSLVYPFPGPIPNSLPQNIPPLTQTPVVVP
101	PFLQPEVMGVSKVKEAMAPKHKEMPFPKYPVEPFTESQSLTLTDVENLHL
151	PLPLLQSWMHQPHQPLPPTVMFPPQSVLSLSQSKVLPVPQKAVPYPQRD M
201	PIQAFLLYQEPVLGPVRGPFPIIV

Table S3. Analysis of the interaction between amino acid residues in the CPP fragment with amino acid sequence of RELEELNVPGEIVEpSLpSpSpSpEESITR.

Amino acid residue	Interaction	Distance（Å）	Amino acid residue	Interaction	Distance（Å）
Arg1-Glu2	NH-OH	1.82	Leu16-P2	C=O-P	2.31
Glu2-Leu3	C=O-HN	2.49	Leu16-P2	C=O-OP	1.67
Glu2-Glu5	C=O-HN	2.70	Leu16-P3	HN-O=P	2.37
Leu3-Glu4	C=O-HN	1.62	Leu16-P2	C=O-OH	1.73
Glu4-Glu5	C=O-HN	2.82	Leu16-Ser17	C=O-HC	1.80
Glu4-Glu5	HO-HN	0.98	P2-Ser17	PO-O=C	1.31,0.56
Glu5-Leu6	HO-O=C	1.80	Ser17-Ser18	C=O-HC	1,75,2.51
Glu5-Asn7	C=O-HN	2.92	P3-Ser18	PO-O=C	2.91,1.74
Leu6-Asn7	C=O-HN	2.72	Ser18-Glu21	C=O-HN	1.31
Asn7-Pro9	C=O-HC	1.88	Ser18-Glu21	C=O-HO	1.59
Val8-Pro9	C=O-HN	2.82	Glu20-Ile23	C=O-HO	2.86
Pro9-Gly10	C=O-HN	1.13	Ser22-Thr24	C=O-HN	1.74
Pro9-Glu11	C=O-HN	1.71	Ile23-Arg25	C=O-HN	2.82
Ile12-Glu14	C=O-HN	2.78	Ile23-Thr24	C=O-N	1.85
Ile12-Glu14	C=O-HO	1.94	Thr24-Arg25	C=O-HN	1.31
Glu14-P1	C=O-P	2.16	Ser22-Arg25	C=O-O=C	0.56
Glu14-P1	C=O-O-P	2.08			

Table S4. ICP-OES of mineral content in MP, CPP, Casein, AHC, and lactalbumin.

Compounds	Elements (%)				
	Ca	Mg	Na	P	Zn
MP	0.724	0.089	0.456	0.686	0.014
CPP	1.100	0.096	1.290	0.790	0.184
Casein	0.135	0.056	0.874	0.802	0.004
AHC	0.205	0.053	4.180	0.484	0.005
Lactalbumin	0.301	0.036	0.456	0.299	0.003