

**Supplementary Table S1** Information of the milk-allergic human sera samples

Serum No.	Age & gender	milk-specific IgE (kU/L) *
PL 21527	27 (NA)	403.9
PL 21902	32 (M)	43.6
PL 25830	66 (F)	92.9
PL 25880	24 (M)	78.7
PL 26248	28 (F)	20.8
PL 26024	24 (M)	≥100
PL 23320	30 (M)	91.0
PL 25329	66 (F)	≥100
PL 20838	31 (M)	30.5
PL 26655	33 (M)	50.3

NA, not available.

\*Tested by the ImmunoCap® FEIA system against the cow milk allergen.

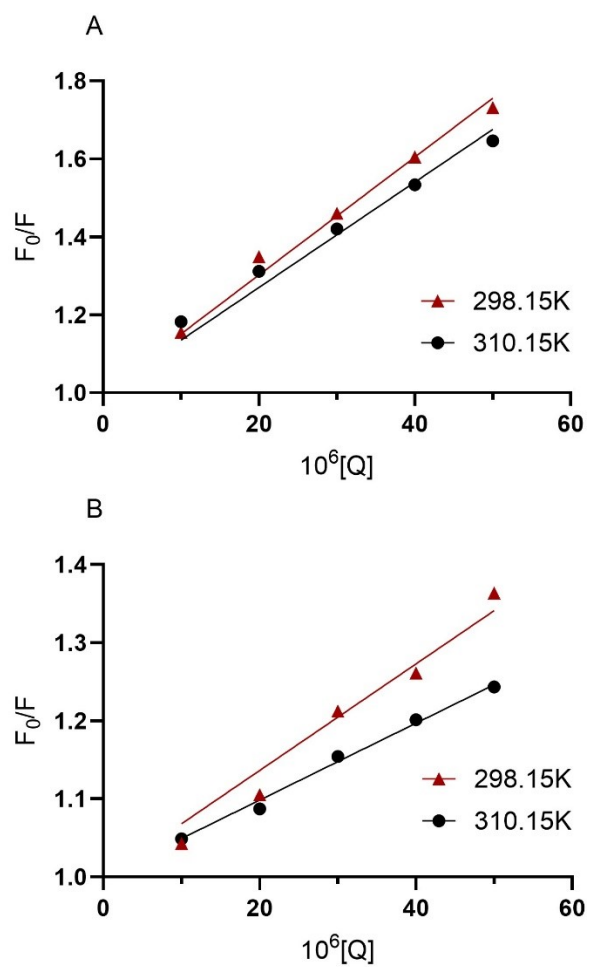
**Supplementary Table S2** PDI values of  $\alpha$ -CN–C3G and  $\beta$ -LG–C3G non-covalent and covalent complexes.

	C3G/protein molar	Pdl	
	ratio	Non-covalent	Covalent
$\alpha$ -CN	0	0.46a $\pm$ 0.08	0.52a $\pm$ 0.14
	10	0.46a $\pm$ 0.09	0.53a $\pm$ 0.13
	20	0.49a $\pm$ 0.05	0.44a $\pm$ 0.02
	30	0.43a $\pm$ 0.06	0.47a $\pm$ 0.15
	40	0.41a $\pm$ 0.06	0.52a $\pm$ 0.06
	50	0.43a $\pm$ 0.07	0.42a $\pm$ 0.05
$\beta$ -LG	0	0.45abc $\pm$ 0.05	0.44abc $\pm$ 0.01
	10	0.38bc $\pm$ 0.08	0.41abc $\pm$ 0.05
	20	0.45abc $\pm$ 0.05	0.53ab $\pm$ 0.03
	30	0.52ab $\pm$ 0.01	0.49abc $\pm$ 0.04
	40	0.43abc $\pm$ 0.07	0.43abc $\pm$ 0.02
	50	0.55a $\pm$ 0.04	0.36c $\pm$ 0.06

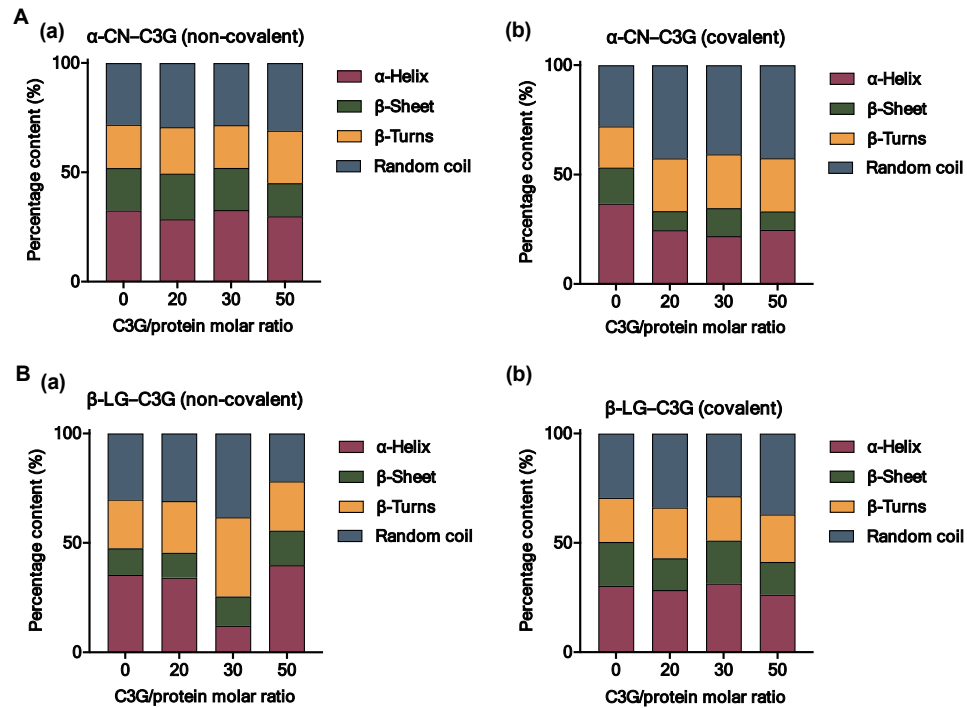
$\alpha$ -CN,  $\alpha$ -casein;  $\beta$ -LG,  $\beta$ -lactoglobulin; C3G, cyanidin-3-*O*-glucoside;

Significance analysis was performed for each protein under both complexation conditions. Values are expressed as the mean  $\pm$  SD and different superscript letters in the same group indicate significant difference ( $p < 0.05$ , Tukey's test).

**Supplementary Figure S1** Stern-Volmer plots for the quenching of (A)  $\alpha$ -CN and (B)  $\beta$ -LG by C3G at different temperatures (298 and 310 K).



**Supplementary Figure S2** Calculated secondary structural composition of  $\alpha$ -CN (A) and  $\beta$ -LG (B) non-covalently and covalently interacted with C3G.  $\alpha$ -CN,  $\alpha$ -casein;  $\beta$ -LG,  $\beta$ -lactoglobulin; C3G, cyanidin-3-*O*-glucoside.



**Supplementary Figure S3** Pearson correlation analysis revealed the transition between certain ordered secondary components and random coil in  $\alpha$ -CN/ $\beta$ -LG-C3G complexes. (A) random coil vs.  $\alpha$ -helix; (B) random coil vs.  $\beta$ -sheet; (C) random coil vs.  $\beta$ -turn.

