Electronic Supplementary Information (ESI)

Tb^{3+}-Trigged luminescence supramolecular gel and its fluorescence chemoprobe for proteins containing alanine

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Experimental Section

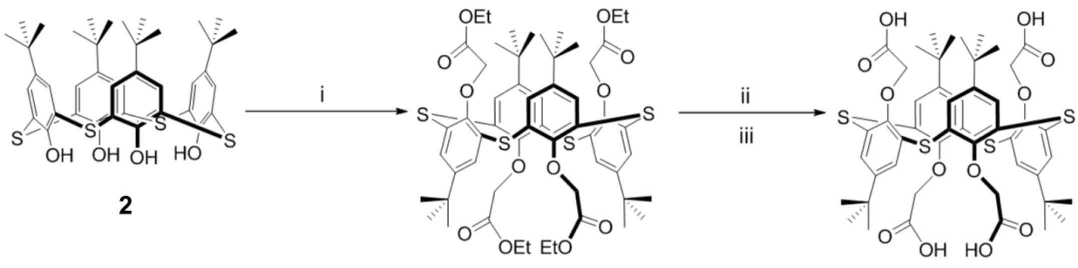
Characterization. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX 300 apparatus. Mass spectra were obtained by a JEOL JMS-700 mass spectrometer. The optical absorption spectra of the samples were obtained at 298K using a UV–Vis spectrophotometer (Thermo Evolution 600). All fluorescence spectra were recorded in RF-5301PC spectrophotometer. Elemental analyses were performed with a Perkin Elmer 2400 series II.

SEM observations. For Scanning electron micrographs of the samples were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG). The accelerating voltage of SEM was 5–15 kV and the emission current was 10 μA.

Preparation of metal coordination polymer gels. A solution of terbium salt [150 μL, 1−5 equiv. in H_2O (0.1 M NaOH)/DMF (1:6, v/v%)] was added to a solution of ligand **1** [5.0 wt % in H_2O (0.1 M NaOH)/DMF (1:6, v/v%)] in a vial at pH = 11.0. The metal coordination polymeric gel formed upon standing at ambient temperature. The gelation state of the material was evaluated by the criterion of "stable-to-inversion" performed in the test tube.

Synthesis of compound 3: Compound **2** (5 g, 4.7 mmol) was suspended in acetone (200 mL) containing anhydrous cesium carbonate (15.3 g, 47 mmol) and ethyl bromoacetate (3.8 mL, 23.5 mmol). The mixture was heated under nitrogen for 24 h at room temperature. After cooling to room temperature, the solid residue was removed by filtration. The residue was extracted with chloroform (100 mL × 2). The combined extracts were washed with water (80 mL × 2) and saturated brine (20 mL), dried ($MgSO_4$), and condensed under reduced pressure. The product was purified by recrystallization from hexane/dichloromethane (33.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (36H, s, $C(CH_3)_3$), 1.28 (12H, t, J = 7.2 Hz, CH_3), 4.22 (8H, q, J = 7.2 Hz, $COOCH_2$), 4.60 (8H, s, OCH_2CO), 7.51 (8H, s, ArH). ESI-MS. Calcd for $C_{56}H_{72}O_{12}S_4$: *m/z* 1064.4, 1065.5 ($[M + 1]^+$). FT-IR: 2960 (CH), 1764 and 1736 (CO) cm^{-1}. Elem anal. Calcd for $C_{56}H_{72}O_{12}S_4$: C, 63.13; H, 6.81; S, 12.04. Found: C, 63.12; H, 6.72; S, 12.11.

Synthesis of ligand 1: The ligand **1** was prepared according to a literature procedure.[1] Compound **3** (2.0 g, 1.88 mmol) was dissolved in 150 mL of ethanol/tetrahydrofuran, and a solution of potassium hydroxide (KOH; 2.1 g, 37.5 mmol) in distilled water (3 mL) was added. The reaction mixture was stirred for 6 h at reflux. The solvent was then removed by vacuum evaporation. Then, the residue was dissolved in water and acidified with HCl. The white precipitate was collected by filtration and dried in a vacuum to yield the desired product in quantitative yield (60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (36H, s, tBu), 4.66 (8H, s, OCH_2), 7.39 (8H, s, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.1 153.2 150.3 129.2 127.8 65.3 34.6 30.9. ESI-MS. Calcd for $C_{48}H_{56}O_{12}S_4$: *m/z* 953.22, 975.1 ($[M + Na]^+$). FT-IR: 3421 (OH), 1695 (CO) cm^{-1}. Elem anal. Calcd for $C_{48}H_{56}O_{12}S_4$: C, 60.48; H, 5.92; S, 13.46. Found: C, 60.35; H, 5.72; S, 13.55.



Scheme S1. Synthetic route of **1**; Reagent and conditions: (i) ethyl bromoacetate, Cs_2CO_3, acetone, reflux, 24h, nitrogen; (ii) EtOH/THF, KOH in H_2O, reflux, 6h; (iii) *con*-HCl in H_2O, room temperature, 1h.

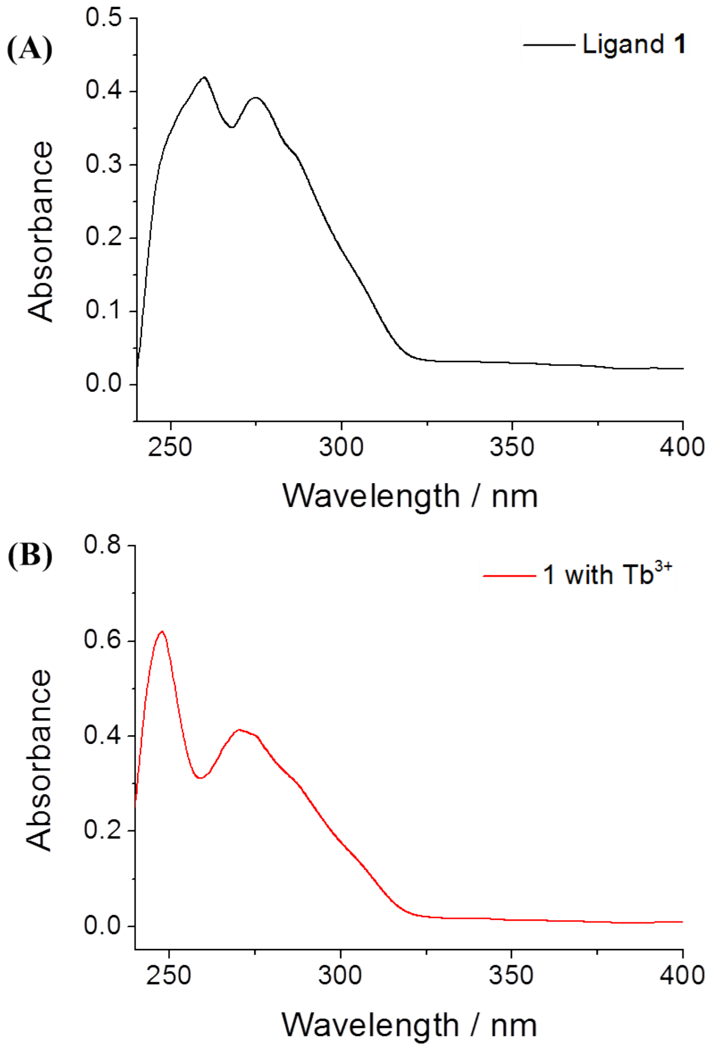


Fig. S1 Absorption spectrum of A) ligand **1** (1.0×10^{-4} M) and B) **1** with Tb^{3+} (1.0 equiv.) in DMF/water (6:1 v/v%) at pH=11.

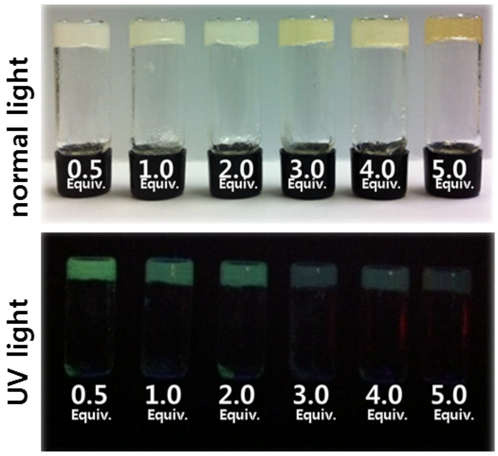


Fig. S2 Photograph of supramolecular gel (5 wt%) with various concentration of Tb^{3+} (0.5-5.0 equiv.) in DMF/water (6:1 v/v%).

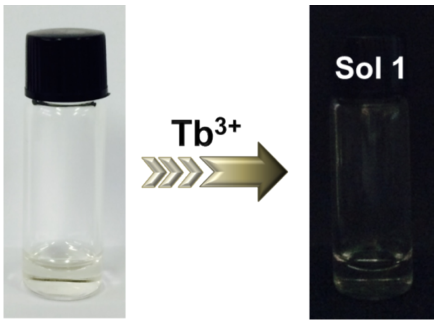


Fig. S3 Photograph of ligand **1** (left) and Sol **1** (right) with Tb^{3+} in DMF/water (6:1 v/v%).

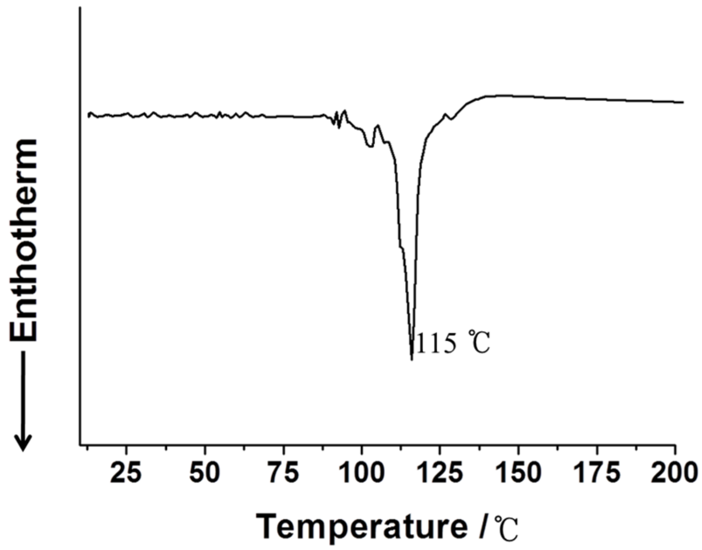


Fig. S4 DSC curve of supramolecular gel **1** (5 wt%) with Tb^{3+} (1 equiv.).

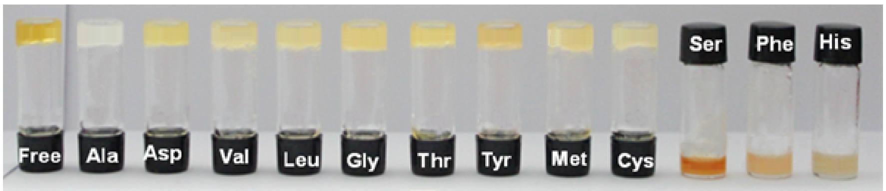


Fig. S5 Photograph of supramolecular gel **1** (5 wt%) with Tb^{3+} (1 equiv.) upon addition of amino acids(3 mM).

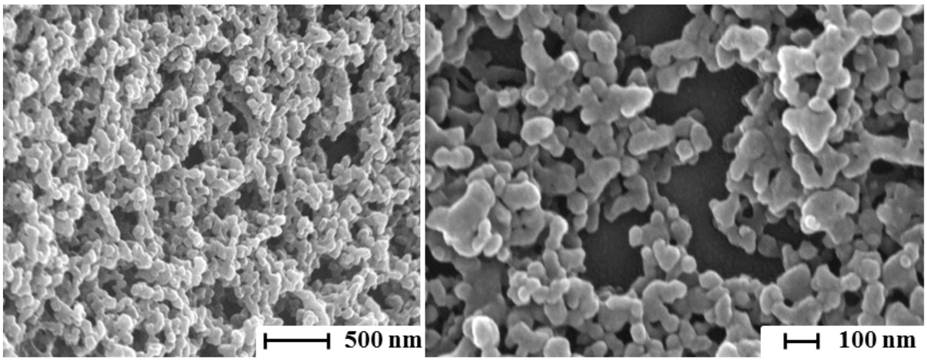


Fig. S6 SEM image of xerogel **1**(5 wt%) with Tb^{3+}(1 equiv.) upon addition of alanine(3 nM).

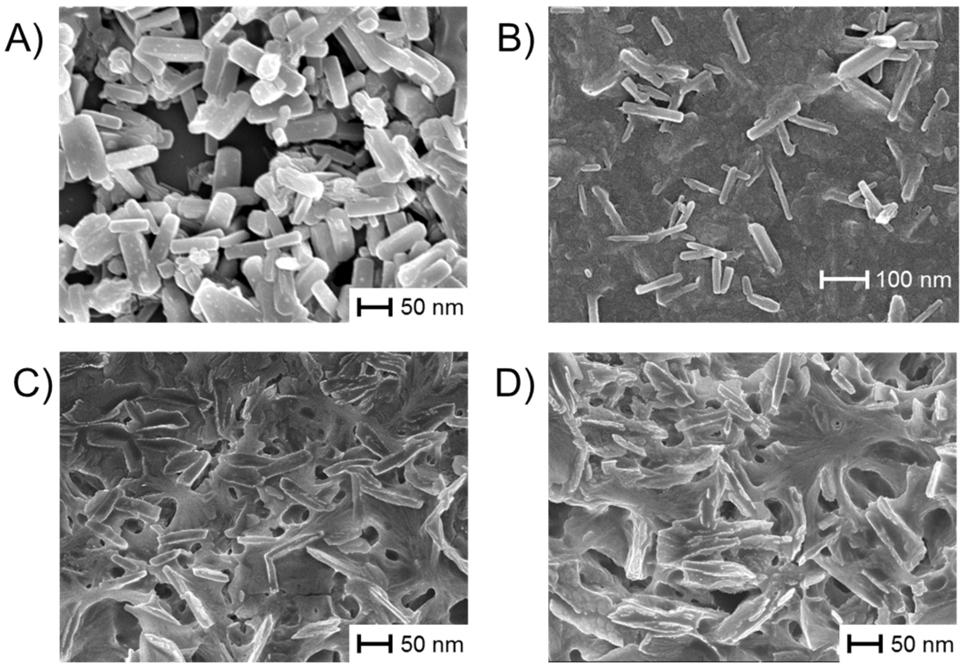


Fig. S7 SEM images of supramolecular gel **1**+Tb^{3+} upon addition of (a) Asp, (b) Val, (c) Leu and (d) Gly.

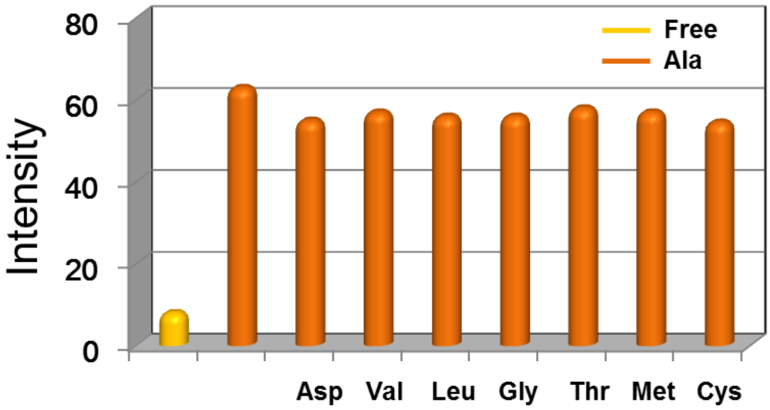


Fig. S8 Fluorescence intensity changes of supramolecular gel **1** upon addition of alanine in binary systems.

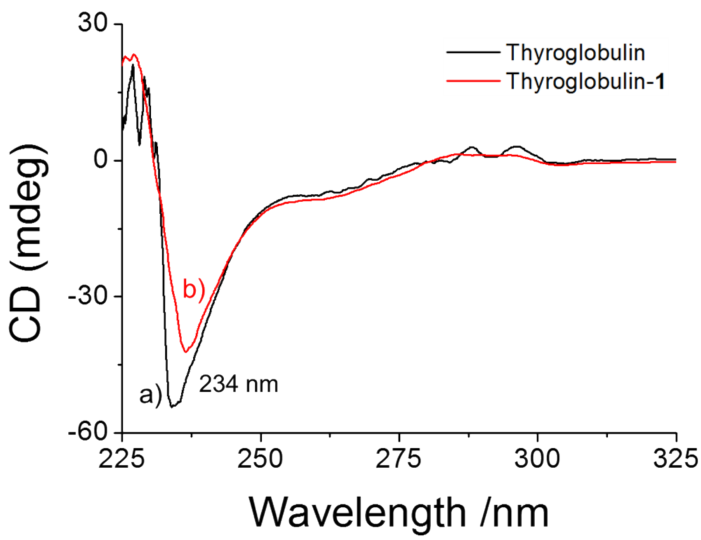


Fig. S9 CD spectra of (a) thyroglobulin (1.0×10^{-4} M) and (b) supramolecular gel **1** (1.0×10^{-4} M) with thyroglobulin.

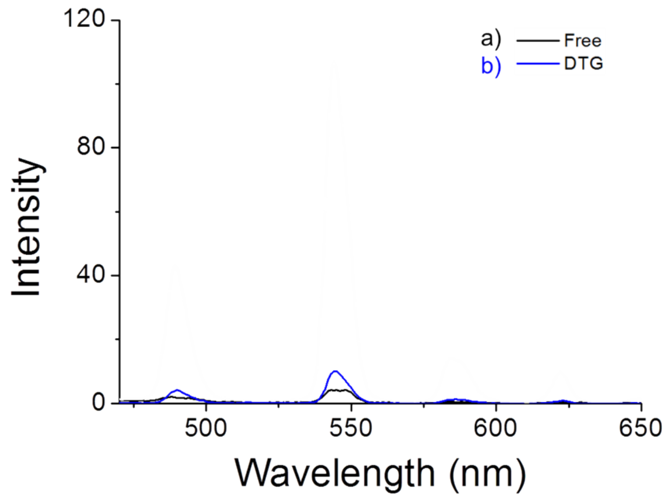


Fig. S10 Photoluminescence spectra of supramolecular gel **1**+Tb^{3+} (a) in the absence and (b) the presence of DTG (1.0×10^{-4} M).

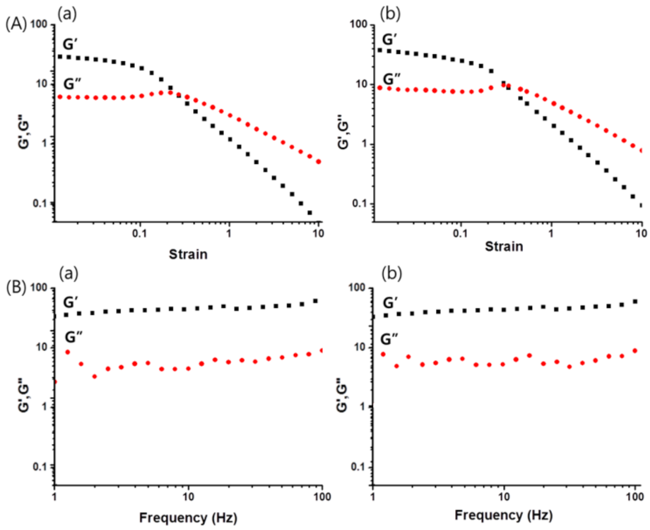


Fig. S11 (A) Strain sweep at a frequency of 0.01 rad s^{-1} of supramolecular gel **1**+Tb^{3+} in (a) the absence and (b) the presence of alanine (1.0 equiv). (B) Frequency sweep at a strain of 0.01% of supramolecular gel **1**+Tb^{3+} (a) the absence and (b) the presence of alanine (1.0 equiv).

Table. S1 Proteins sequences used in this study.

Protein	Sequence
Aldolase **(158 kDa)**	Fructose-1,6-Bisphosphate Aldolase From Rabbit Muscle In Complex With A C-Terminal Peptide Of Wiskott-Aldrich Syndrome Protein. PHSHPALTPEQKKELSDIAHRIVAPGKGILAADESTGSIAKRLQSIGTENTEENRR FYRQLLLTADDRVNPCIGGVILFHETLYQKADDGRPFPQVIKSKGGVVGIKVDK GVVPLAGTNGETTTQGLDGLSERCAQYKKDGADFAKWRCVLKIGEHTPSALAI MENANVLARYASICQQNGIVPIVEPEILPDGDHDLKRCQYVTEKVLAAVYKAL SDHHIYLEGTLLKPNMVTPGHACTQKYSHEEIAMATVTALRRTVPPAVTGVTF LSGGQSEEEASINLNAINKCPLLKPWALTFSYGRALQASALKAWGGKKENLKA AQEEYVKRALANSLACQGKYTPSGQAGAAASESLFISNHAY
Thyroglobulin **(669 kDa)**	thyroglobulin precursor [Bos taurus] MALALWVFGLLDLICLASANIFEYQVDAQPLRPCELQRERAFLKREDYVPQCA EDGSFQTVQCGKDGASCWCVDADGREVPGSRQPGRPAACLSFCQLQKQQILLS SYINSTATSYLPQCQDSGDYSPVQCDLRRRQCWCVDAEGMEVYGTRQQGRPA RCPRSCEIRNRRLLHGVGDRSPPQCSPDGAFRPVQCKLVNTTDMMIFDLVHSYS RFPDAFVTFSSFRSRFPEVSGYCYCADSQGRELAETGLELLLDEIYDTIFAGLDL ASTFAETTLYRILQRRFLAVQLVISGRFRCPTKCEVERFAATSFRHPYVPSCHPD GEYQAAQCQQGGPCWCVDSRGQEIPGTRQRGEPPSCAEDQSCPSERRRAFSRL RFGPSGYFSRRSLLLAPEEGPVSQRFARFTASCPPSIKELFLDSGIFQPMLQGRDT RFVAPESLKEAIRGLFPSRELARLALQFTTNAKRLQQNLFGGRFLVKVGQFNLS GALGTRGTFNFSHFFQQLGLPGFQDGRALADLAKPLSVGLNSNPASEAPKASKI DVALRKPVVGSFGFEVNLQENQNALQFLSSFLELPEFLLFLQHAISVPEDIARDL GDVMEMVFSSQGCGQAPGSLFVPACTAEGSYEEVQCFAGDCWCVDAQGRELA GSRVRGGRPRCPTECEKQRARMQSLLGSQPAGSSLFVPACTSKGNFLPVQCFNS ECYCVDTEGQPIPGTRSALGEPKKCPSPCQLQAERAFLGTVRTLVSNPSTLPALS SIYIPQCSASGQWSPVQCDGPPEQAFEWYERWEAQNSAGQALTPAELLMKIMS YREAASRNFRLFIQNLYEAGQQGIFPGLARYSSFQDVPVSVLEGNQTQPGGNVF LEPYLFWQILNGQLDRYPGPYSDFSAPLAHFDLRSCWCVDEAGQKLEGTRNEP NKVPACPGSCEEVKLRVLQFIREAEEIVTYSNSSRFPLGESFLAAKGIRLTDEELA FPPLSPSRETFLEKFLSGSDYAIRLAAQSTFDFYQRRLVTLAESPRAPSPVWSSAY LPQCDAFGGWEPVQCHAATGHCWCVDGKGEYVPTSLTARSRQIPQCPTSCERL RASGLLSSWKQAGVQAEPSPKDLFIPTCLETGEFARLQASEAGTWCVDPASGEG VPPGTNSSAQCPSLCEVLQSGVPSRRTSPGYSPACRAEDGGFSPVQCDPAQGSC WCVLGSGEEVPGTRVAGSQPACESPQCPLPFSVADVAGGAILCERASGLGAAA GQRCQLRCSQGYRSAFPPEPLLCSVQRRRWESRPPQPRACQRPQFWQTLQTQA QFQLLLPLGKVCSADYSGLLLAFQVFLLDELTARGFCQIQVKTAGTPVSIPVCD DSSVKVECLSRERLGVNITWKLQLVDAPPASLPDLQDVEEALAGKYLAGRFAD LIQSGTFQLHLDSKTFSADTSIRFLQGDRFGTSPRTQFGCLEGFGRVVAASDASQ DALGCVKCPEGSYFQDEQCIPCPAGFYQEQAGSLACVPCPEGRTTVYAGAFSQT HCVTDCQKNEVGLQCDQDSQYRASQRDRTSGKAFCVDGEGRRLPWTEAEAPL VDAQCLVMRKFEKLPESKVIFSADVAVMVRSEVPGSESSLMQCLADCALDEAC GFLTVSTAGSEVSCDFYAWASDSIACTTSGRSEDALGTSQATSFGSLQCQVKVR SREGDPLAVYLKKGQEFTITGQKRFEQTGFQSALSGMYSPVTFSASGASLAEVH LFCLLACDHDSCCDGFILVQVQGGPLLCGLLSSPDVLLCHVRDWRDPAEAQAN ASCPGVTYDQDSRQVTLRLGGQEIRGLTPLEGTQDTLTSFQQVYLWKDSDMGS

Thyroglobulin **(669 kDa)**	RSESMGCRRDTEPRPASPSETDLTTGLFSPVDLIQVIVDGNVSLPSQQHWLFKHL FSLQQANLWCLSRCAGEPSFCQLAEVTDSEPLYFTCTLYPEAQVCDDILESSPKG CRLILPRRPSALYRKKVVLQDRVKNFYNRLPFQKLTGISIRNKVPMSDKSISSGF FECERLCDMDPCCTGFGFLNVSQLKGGEVTCLTLNSLGLQTCSEEYGGVWRIL DCGSPDTEVRTYPFGWYQKPVSPSDAPSFCPSVALPALTENVALDSWQSLALSS VIVDPSIRNFDVAHISTAAVGNFSAARDRCLWECSRHQDCLVTTLQTQPGAVRC MFYADTQSCTHSLQAQNCRLLLHEEATYIYRKPNIPLPGFGTSSPSVPIATHGQL LGRSQAIQVGTSWKPVDQFLGVPYAAPPLGEKRFRAPEHLNWTGSWEATKPRA RCWQPGIRTPTPPGVSEDCLYLNVFVPQNMAPNASVLVFFHNAAEGKGSGDRP AVDGSFLAAVGNLIVVTASYRTGIFGFLSSGSSELSGNWGLLDQVVALTWVQT HIQAFGGDPRRVTLAADRGGADIASIHLVTTRAANSRLFRRAVLMGGSALSPAA VIRPERARQQAAALAKEVGCPSSSVQEMVSCLRQEPARILNDAQTKLLAVSGPF HYWGPVVDGQYLRETPARVLQRAPRVKVDLLIGSSQDDGLINRAKAVKQFEES QGRTSSKTAFYQALQNSLGGEAADAGVQAAATWYYSLEHDSDDYASFSRALE QATRDYFIICPVIDMASHWARTVRGNVFMYHAPESYSHSSLELLTDVLYAFGLP FYPAYEGQFTLEEKSLSLKIMQYFSNFIRSGNPNYPHEFSRRAPEFAAPWPDFVP RDGAESYKELSVLLPNRQGLKKADCSFWSKYIQSLKASADETKDGPSADSEEE DQPAGSGLTEDLLGLPELASKTYSK
Catalase **(232 kDa)**	The Crystal Structure Of Bovine Liver Catalase Without Nadph. ADNRDPASDQMKHWKEQRAAQKPDVLTTGGGNPVGDKLNSLTVGPRGPLLV QDVVFTDEMAHFDRERIPERVVHAKGAGAFGYFEVTHDITRYSKAKVFEHIGK RTPIAVRFSTVAGESGSADTVRDPRGFAVKFYTEDGNWDLVGNNTPIFFIRDAL LFPSFIHSQKRNPQTHLKDPDMVWDFWSLRPESLHQVSFLFSDRGIPDGHRHMD GYGSHTFKLVNADGEAVYCKFHYKTDQGIKNLSVEDAARLAHEDPDYGLRDL FNAIATGNYPSWTLYIQVMTFSEAEIFPFNPFDLTKVWPHGDYPLIPVGKLVLNR NPVNYFAEVEQLAFDPSNMPPGIEPSPDKMLQGRLFAYPDTHRHRLGPNYLQIP VNCPYRARVANYQRDGPMCMMDNQGGAPNYYPNSFSAPEHQPSALEHRTHFS GDVQRFNSANDDNVTQVRTFYLKVLNEEQRKRLCENIAGHLKDAQLFIQKKA VKNFSDVHPEYGSRIQALLDKYNEEKPKN
Ferritin **(440 kDa)**	Tetragonal Crystal Structure Of Native Horse Spleen Ferritin. SSQIRQNYSTEVEAAVNRLVNLYLRASYTYLSLGFYFDRDDVALEGVCHFFREL AEEKREGAERLLKMQNQRGGRALFQDLQKPSQDEWGTTLDAMKAAIVLEKSL NQALLDLHALGSAQADPHLCDFLESHFLDEEVKLIKKMGDHLTNIQRLVGSQA GLGEYLFERLTLKHD
Ribonuclease A **(13.7 kDa)**	ribonuclease A, partial [Bos taurus] PSLGKETAAAKFERQHMDSSTSAASSSNYCNQMMKSRNLTKDRCKPVNTFVH ESLADVQAVCSQKNVACKNGQTNCYQSYSTMSITDCRETGSSKYPNCAYKTTQ ANKHIIVACEGNPYVPVHFDASV
Chymotrypsino-gen A	Crystal Structure Of Bovine Procarboxypeptidase A-S6 Subunit Iii, A Highly Structured Truncated Zymogen ENGEDAVPYSWSWQVSLQYEKDGAFHHTCGGSLIAPDWVVTAGHCISTSRTY QVVLGEYDRSVLEGSEQVIPINAGDLFVHPLWNSNCVACGNDIALVKLSRSAQL GDKVQLANLPPAGDILPNEAPCYISGWGRLYTGGPLPDKLQQALLPTVDYEHC

(25 kDa)	SQWDWWGITVKKTMVCAGGDTRSGCNGDSGGPLNCPAADGSWQVHGVTSFV SAFGCNTIKKPTVFTRVSAFIDWIDETIASN
Albumin **(67 kDa)**	Crystal Structure Of Bovine Serum Albumin DTHKSEIAHRFKDLGEEHFKGLVLIAFSQYLQQCPFDEHVKLVNELTEFAKTCV ADESHAGCEKSLHTLFGDELCKVASLRETYGDMADCCEKQEPERNECFLSHKD DSPDLPKLKPDPNTLCDEFKADEKKFWGKYLYEIARRHPYFYAPELLYYANKY NGVFQECCQAEDKGACLLPKIETMREKVLTSSARQRLRCASIQKFGERALKAW SVARLSQKFPKAEFVEVTKLVTDLTKVHKECCHGDLLECADDRADLAKYICDN QDTISSKLKECCDKPLLEKSHCIAEVEKDAIPENLPPLTADFAEDKDVCKNYQE AKDAFLGSFLYEYSRRHPEYAVSVLLRLAKEYEATLEECCAKDDPHACYSTVF DKLKHLVDEPQNLIKQNCDQFEKLGEYGFQNALIVRYTRKVPQVSTPTLVEVSR SLGKVGTRCCTKPESERMPCTEDYLSLILNRLCVLHEKTPVSEKVTKCCTESLV NRRPCFSALTPDETYVPKAFDEKLFTFHADICTLPDTEKQIKKQTALVELLKHKP KATEEQLKTVMENFVAFVDKCCAADDKEACFAVEGPKLVVSTQTALA
DTG	DTGSDGGGGGLTGGNLKGGGELTGGNGGGGGGGTGR

Reference

1. N. Iki, N. Morohashi, F. Narumi, T. Fujimoto, T. Suzuki, S. Miyano, *Tetrahedron Lett.*, 1999, **40**, 7337.