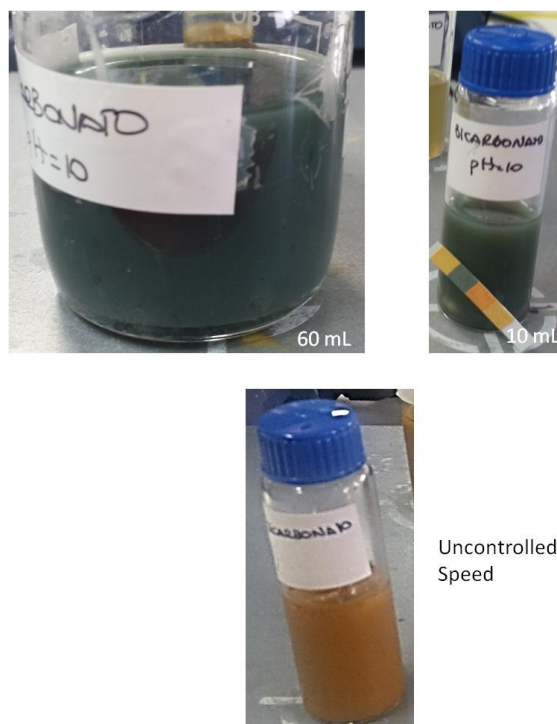


## Electronic Supplementary information (ESI)

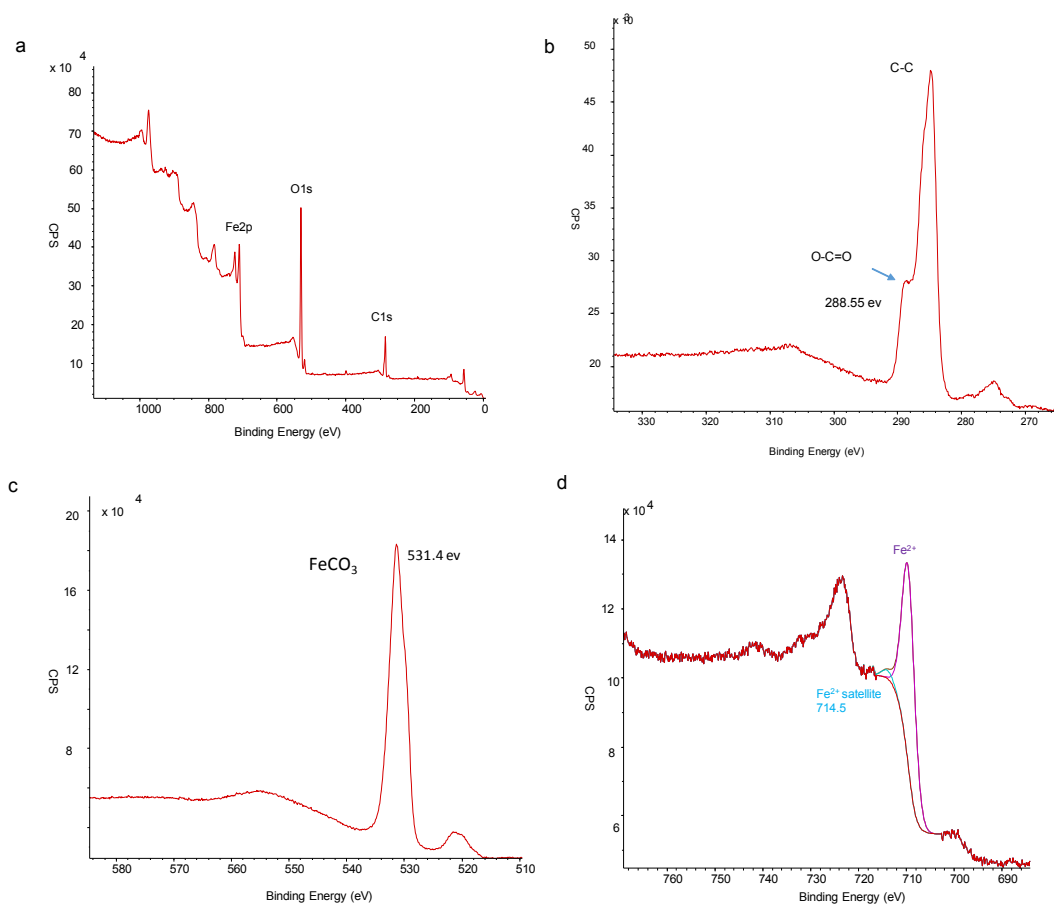
### Enzyme-induced formation of Iron hybrid nanostructures with different morphologies

Rocio Benavente,<sup>a</sup> David Lopez-Tejedor,<sup>a</sup> Maria del Puerto Morales,<sup>b</sup>

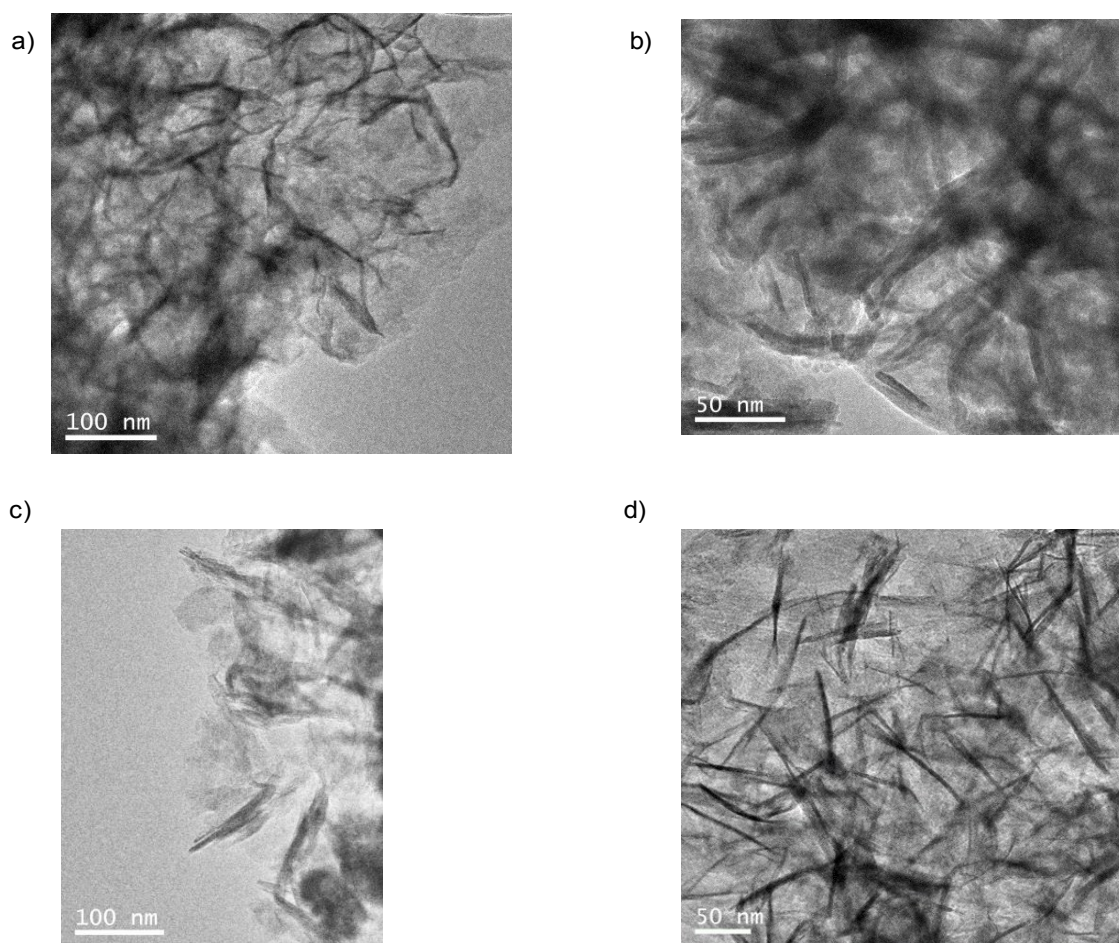
Carlos Perez-Rizquez<sup>a</sup> and Jose M. Palomo<sup>\*a</sup>



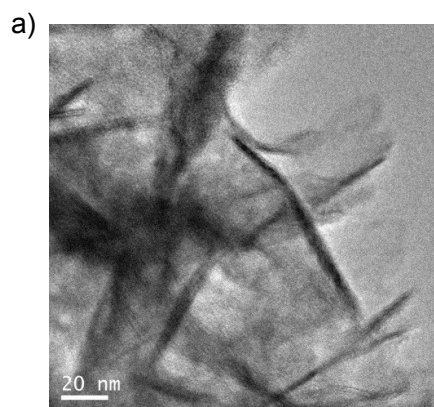
**Figure S1.** Images of bionanohybrid reaction at different conditions.



**Figure S2. XPS analysis of 15min-reduced FeCO<sub>3</sub>NRs-CALB.** a) XPS full spectrum. b) XPS spectrum of C1s. c) XPS spectrum of O1s. d) XPS spectrum of Fe2p.

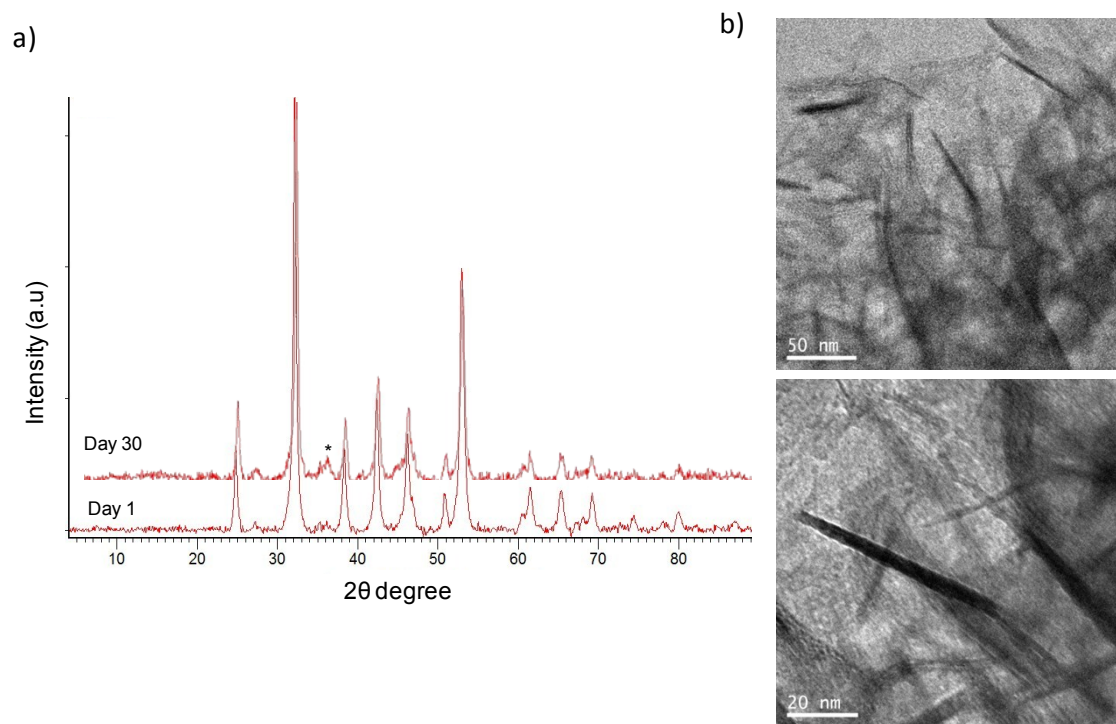


**Figure S3. TEM images of different reduced-FeNRs-CALB hybrids.** a) non-reduced FeCO<sub>3</sub>NRs-CALB, b) 15min-reduced FeCO<sub>3</sub>NRs-CALB, c) 30min-reduced FeCO<sub>3</sub>NRs-CALB, d) 45min-reduced FeCO<sub>3</sub>NRs-CALB or 60min-reduced FeCO<sub>3</sub>NRs-CALB.

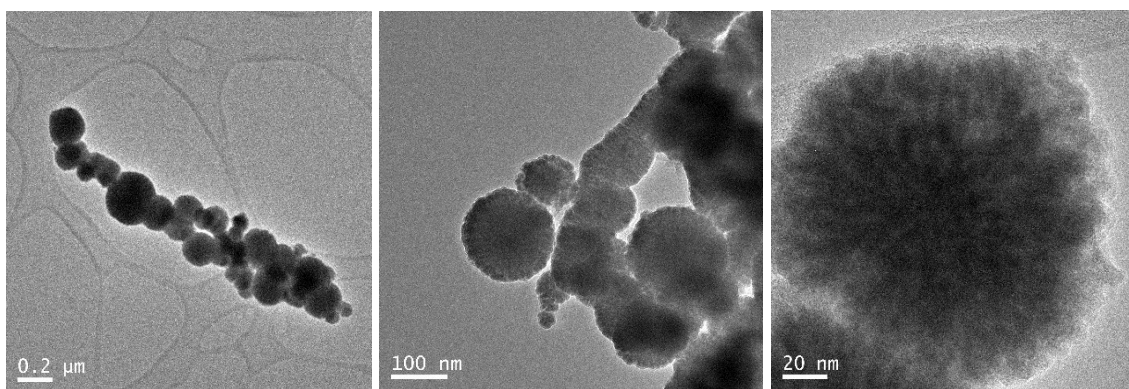


b) \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

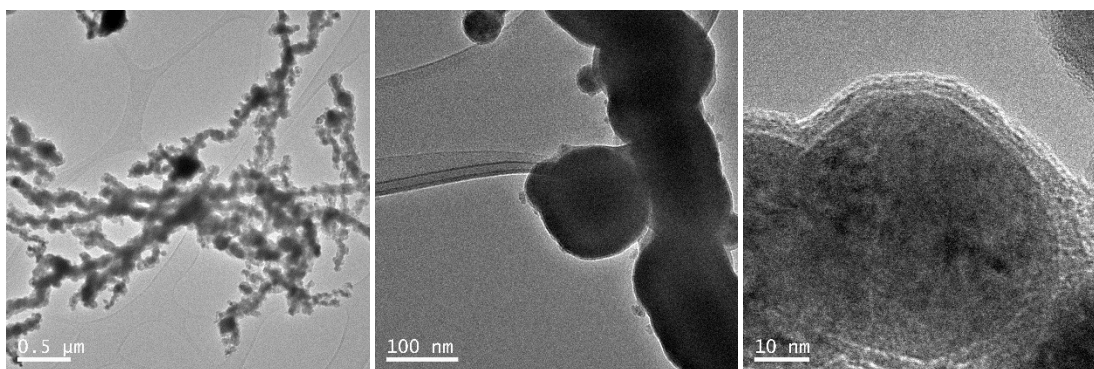
**Figure S4.** A. TEM image of 360 min-reduced  $\text{FeCO}_3\text{NRs-CALB}$  hybrid. B.  $\text{FeCO}_3$  nanorods size at different reducing times in the presence of sodium borohydride.



**Figure S5. Characterization of 15 min-reduced Fe-CALB hybrid.** A) XRD spectrum from the preparation (day 1) to 30 days. B) TEM images at different magnification of the hybrid after 30 days.



**Figure S6.** TEM analysis of CALB-Fe(0)nanoflowers.



**Figure S7.** TEM analysis of Fe(0)nanoparticles without protein.

```

      10          20          30          40          50
MALPSGS DPA FSQPKSVL DA GLTCQGASPS SVSKPILLVP GTGTTGPQSF
      60          70          80          90         100
D SNWIPLSTQ LGYTPCWISP PPFMLND TQV NTEYMVNAIT ALYAGSGNNK
      110         120         130         140         150
LPVLTWSQGG LVAQWGLTFF PSIRSKV DRL MAFAP DYKGT VLAGPL DALA
      160         170         180         190         200
VSAPSVWQQT TGSALTTALR NAGGLTQIVP TTNLYSAT DE IVQPQVSNP
      210         220         230         240         250
L DSSYLFNGK NVQAQAVCGP LFVID DHAGSL TSQFSYVVGR SALRSTTGQA
      260         270         280         290         300
RSAD YGIT DC NPLPAND LTP EQKVAAAALL APAAAAIVAG PKQNC E P DLM
      310
PYARPFVAVGK RTXSGIVTPS L

```

**Length:**321

**Mass (Da):**33,433

**Figure S8.** Amino acids sequence of CALB. Asp and Glu marked in yellow. Sequence obtained from <https://www.uniprot.org/uniprot/B6DAC2>..



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      10          20          30          40          50
MRSSLVLFV SAWTALASPI RREVSQDLFN QFNLFAQYSA AAYCGKNNDA
      60          70          80          90         100
PAGTNITCTG NACPVEEKAD ATFLYSFEDS GVGDTVGF LA LDNTNKLIVL
      110         120         130         140         150
SFRGSRSEIN WIGNLNFDLK EINDICSGCR GHDGFTSSWR SVADTLRQKV
      160         170         180         190         200
EDAVREHPDY RVVFTGHSLG GALATVAGAD LRGNGYDIDV FSYGAPRVGN
      210         220         230         240         250
RAFAEFLTVQ TGGTLYRITH TNDIVPRLPP REFGYSHSSP EYWIKSGTLV

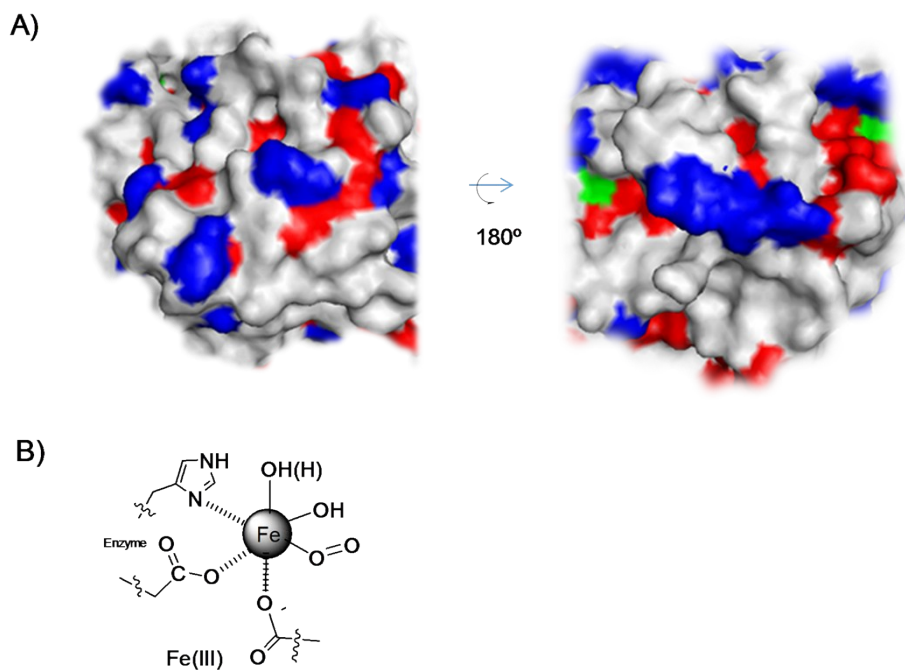
PVTRNDIVKI EGI DATGGNN QPNIPDIPAH LWYFGLIGTC L

```

**Length:**291

**Mass (Da):**31,807

**Figure S9.** Amino acids sequence of TLL. Asp and Glu marked in yellow.His in green. Sequence was obtained from <https://www.uniprot.org/uniprot/O59952>



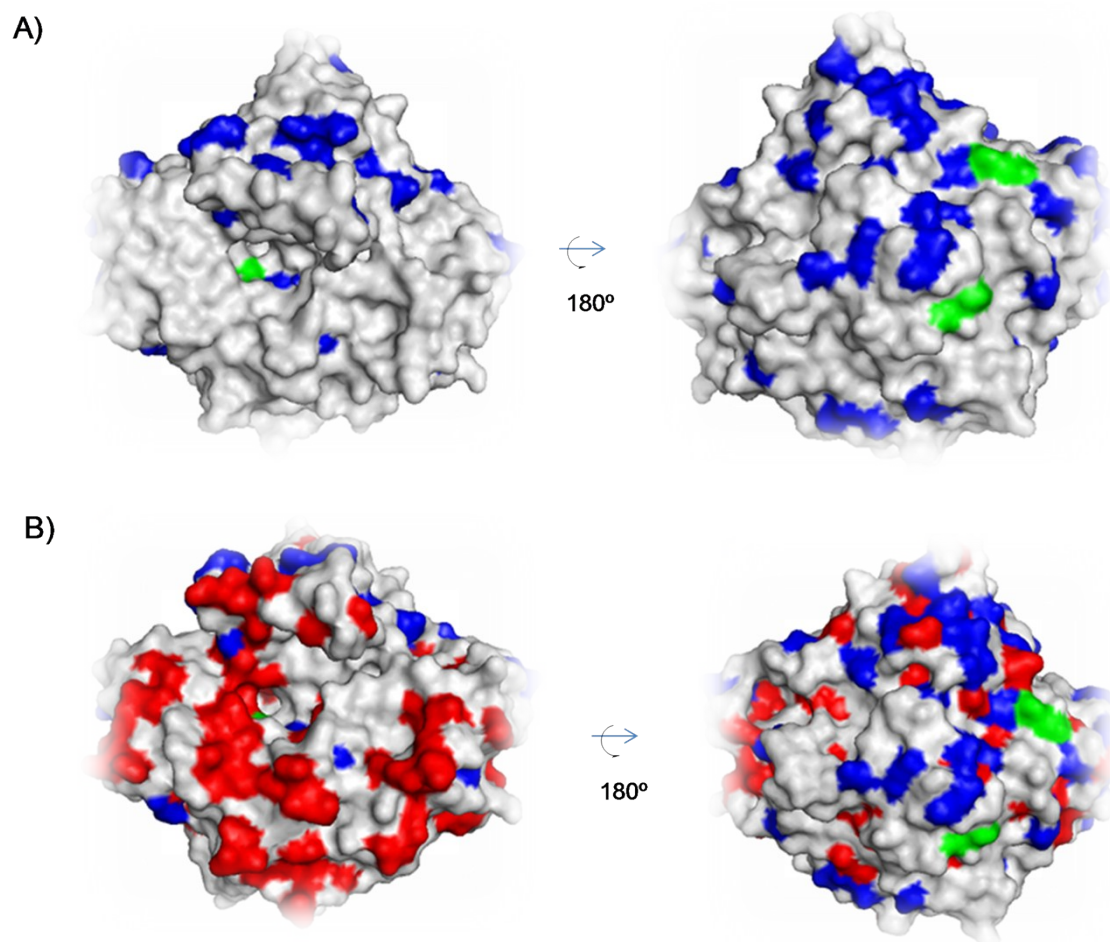
**Figure S10.** A) 3D-surface of TLL with several aminoacid residues marked. Asp and Glu residues (blue), His (green), hydrophobic residues (Phe, Leu, Ile, Ala) (red). Pymol program using pdb file 1DT3 was used to prepare figures. B) Proposed iron coordination species induced by the protein in the presence of Triton X-100.

10	20	30	40	50
ME <b>L</b> LALALSLI	ASVAAAPTAT	LANG <b>D</b> TITGL	NAIINE <b>E</b> AFLG	IPFA <b>E</b> PPVGN
60	70	80	90	100
LRFK <b>D</b> PVPYS	GSL <b>D</b> GGQFTS	YGPSCMQQNP	<b>E</b> GT <b>E</b> ENLPK	AAL <b>D</b> LVMSK
110	120	130	140	150
V <b>F</b> EAVSPS <b>E</b>	<b>D</b> CLTINVVRP	PGTKAGANLP	VMLWIFGGGF	<b>E</b> VGGTSTFPP
160	170	180	190	200
AQMITKSIAM	GKPI <b>H</b> VSVN	YRVSSWGFLA	G <b>D</b> EIKAE <b>G</b> SA	NAGL <b>K</b> DQRLG
210	220	230	240	250
MQWVA <b>D</b> NIAA	FG <b>D</b> DPTKVTI	F <b>G</b> E <b>S</b> AGSMSV	M <b>C</b> HILW <b>N</b> D <b>G</b> D	NTYK <b>G</b> KPLFR
260	270	280	290	300
AGIMQSGAMV	PS <b>D</b> AV <b>D</b> GIY <b>G</b>	<b>N</b> E <b>I</b> F <b>D</b> LLASN	AGCGSAS <b>D</b> KL	ACLRGVSS <b>D</b> T
310	320	330	340	350
L <b>E</b> DATN <b>N</b> TPG	FLAYSSLRLS	YLPR <b>D</b> GVNI	T <b>D</b> D <b>M</b> YALV <b>R</b> E	GKYANIPV <b>I</b> I
360	370	380	390	400
G <b>D</b> Q <b>N</b> D <b>E</b> GTFF	GTSSLNVTTD	AQAR <b>E</b> YFKQS	FV <b>H</b> AS <b>D</b> A <b>E</b> I <b>D</b>	TLMTAYPG <b>D</b> I
410	420	430	440	450
TQGS <b>P</b> D <b>T</b> GI	LNALTPQFKR	ISAVL <b>G</b> DLGF	TLARRYFL <b>N</b> H	YTG <b>G</b> TKYSFL
460	470	480	490	500
SKQLSGLPVL	G <b>T</b> F <b>H</b> S <b>N</b> D <b>I</b> V <b>F</b>	QDYLLGSGSL	IYNNAFIAFA	T <b>D</b> L <b>D</b> PNTAGL
510	520	530	540	
LVKW <b>P</b> E <b>Y</b> TSS	SQSGNNLMMI	NALGLY <b>T</b> G <b>K</b> D	N <b>F</b> R <b>T</b> A <b>G</b> Y <b>D</b> A <b>L</b>	FSNPPSFFV

**Length:**549

**Mass (Da):**58,550

**Figure S11.** Aminoacid sequence of CRL. Asp and Glu marked in yellow.His in green. Sequence was obtained from <https://www.uniprot.org/uniprot/P20261>



**Figure S12.** 3D-surface of CRL with several aminoacid residues marked. A) Asp and Glu residues (blue), His (green). B) Asp and Glu residues (blue), His (green), hydrophobic residues (Phe, Leu, Ile, Ala) (red). Pymol program using pdb file 1CRL was used to preparing figures.

```

      10          20          30          40          50
MSDKKSLMPL VGIPGEIKNR LNILDFVKND KFFTLYVRAL QVLQARDQSD
      60          70          80          90         100
YSSFFQLGGI HGLPYTEWAK AQPQLHLYKA NYCTHGTVLF PTWHRAYEST
      110         120         130         140         150
WEQTLWEAAG TVAQRFTTSD QAEWIQAAKD LRQPFWDWGY WPNDPDPFIGL
      160         170         180         190         200
PDQVIRDKQV EITDYNGTKI EVENPILHYK FHPIEPTFEG DFAQWQTTMR
      210         220         230         240         250
YPDVQKQENI EGMIAGIKAA APGFREWTFN MLTKNYTWEL FSNHGAVVGA
      260         270         280         290         300
HANSLEMVHN TVHFLIGRDP TLDPLVPGHM GSVPHAAFDP IFWMHHCNVD
      310         320         330         340         350
RLALWQTMN YDVYVSEGMN REATMGLIPG QVLTEDSPLE PFYTKNQDPW
      360         370         380         390         400
QSDDLEDWET LGFSYPDFDP VKGKSKEEKS VYINDWVHKH YGFVTTQTEN
      410         420         430         440         450
PALRLLSSFQ RAKSDHETQY ALYDWVIHAT FRYYELNNSF SIIFYFDEGE
      460         470         480         490         500
GCTLESIIGT VDAFRGTTSE NCANCARSQD LIAEGFVHLN YYIGCDIGQH
      510         520         530         540         550
ADHEDDAVPL YEPTRVKEYL KKRKIGCKVV SAEGELTSLV VEIKGAPYYL
      560
PVGEARPKLD HEKPIVILDD IIRNVN

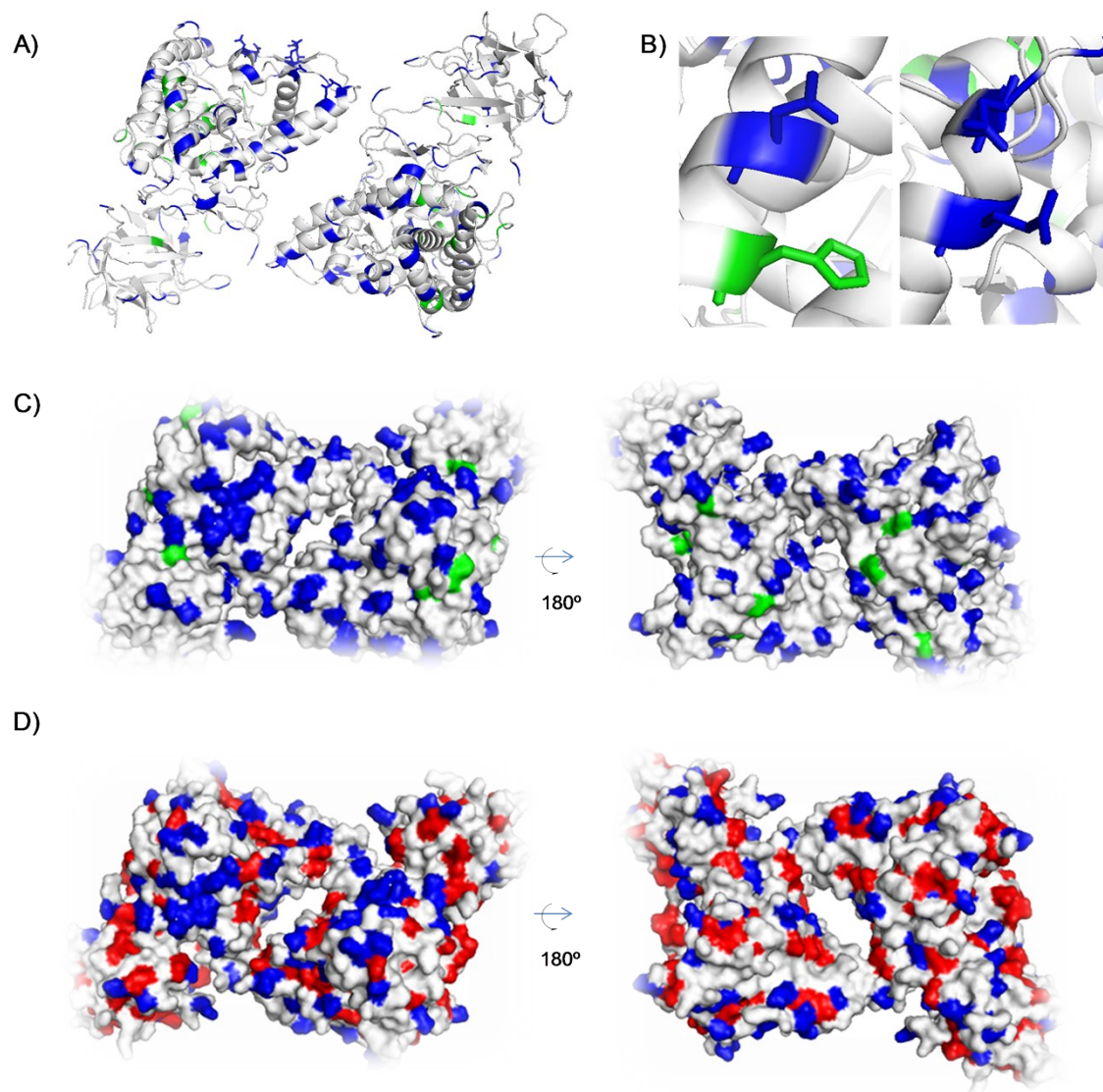
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**Length:**576

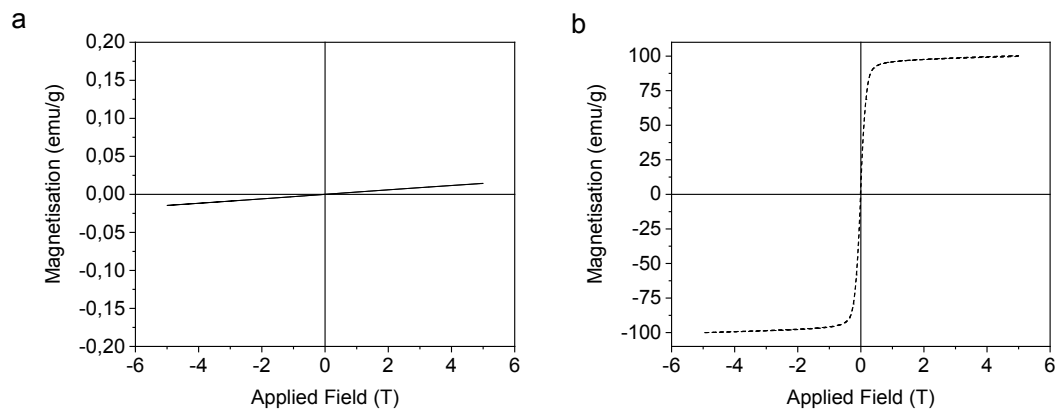
**Mass (Da):**66,267

### Homodimer HL units

**Figure S13.** Aminoacid sequence of tyrosinase from *A. bisporus*. Asp and Glu marked in yellow. His marked in green. Sequence was obtained from <https://www.uniprot.org/uniprot/C7FF04>



**Figure S14.** A. 3D-structure of Tyrosinase from *A. bisporus* (TYR). B. Typical part of amino acids residues involved on the iron coordination. C) 3D-surface of TYR with several amino acid residues marked. Asp and Glu residues (blue), His (green). D) 3D-surface of TYR with several amino acid residues marked. Asp and Glu residues (blue), His (green), hydrophobic residues (Phe, Leu, Ile, Ala) (red). Pymol program using pdb file 2y9w was used to preparing figures.



**Figure S15. Magnetization hysteresis loops of Fe-protein hybrids. A) using ovoalbumin. B) using catalase.**