Electronic Supplementary Material (ESI) for Materials Advances.

Understanding tyrosine self assembly: From dimer assembly to magnetized fluorescent nanotubes embedded into PVA films

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Material and Methods

Materials

Tyrosine (L-Tyr-OH) was purchased from Sigma-Aldrich and was used as such. Milli-Q water (resistivity ~18.2 MΩ) was used for all experiments.

UV-Visible spectroscopy

Optical spectroscopy was done using Agilent Cary Bundle UV-Visible spectroscope at different concentration of phenylalanine aqueous solutions.

Photoluminescence spectroscopy

Photoluminescence emission spectra of the phenylalanine aqueous solutions at different concentrations was recorded using Agilent made Cary Bundle fluorescence spectrophotometer. The PL spectra were recorded for different excitation wavelengths using same slit parameters.

FE-SEM and EDS analysis

The FE-SEM micrographs were recorded to investigate the morphology of tyrosine self-assembled structure. In a general procedure, 10 µl of freshly prepared phenylalanine solution at concentration 1 mg/mL was air dried on the surface of Ag film pasted on FE-SEM step. Pt coating was applied on the samples to make it conductive and followed by FE-SEM analysis on a Hitachi, SU8010 electron microscope, operating at 10–15 kV.

SAXS analysis of phenylalanine self-assembly in both solution and deposited phase

The small angle X-ray scattering data was recorded using SAXSpace Anton Paar with generator model no. ID3003 and Eiger R1M vertical detector. The line collimation analysis was done to obtain SAXS data for suspended tyrosine micro rod crystals. The tyrosine solution was placed in 1mm quartz capillary for the SAXS analysis. The scattering background for capillary tube, deionized water for solution phase was subtracted prior to the SAXS analysis of tyrosine assembly. The beam stop length of 0 and 0.1 mm was used for liquid sample. The scattering data points were selected from 50 to 900 q values for the GIFT analysis. The lower and higher marginal q values were ignored for obtaining the noise free PDDFs. The Lagrange multiplier for the stability of PDDFs was selected at 0.00.

X-ray diffraction analysis

XRD studies were performed to investigate the d-spacing as well as the crystallinity of tyrosine self-assembled structures. For this, purpose, 5mg of dried self-assembled sample was characterized by Shimadzu XRD 6000 diffractometer with Cu K_a radiation (k = 1.54 Å)

Density function theory (DFT) analysis

The density function theory optimization of the Tyr-DA was performed using Gaussian software with model 3 and 3-21G as basis set. The solvent free calculations were carried out to obtain optimized Phe-DA structure.

Confocal Laser scanning microscopy

The CLSM images were captured by depositing 10 µl of air dried hydrogel fibrils on microscopic glass slide and images were captured using Zeiss, LSM 510 confocal laser scanning microscope.

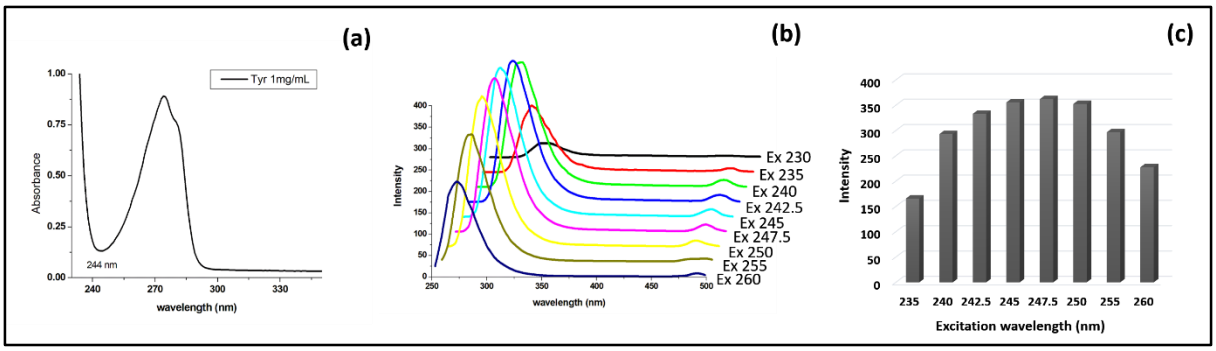


Figure S1 Absorbance spectrum of tyrosine at 1 mg/mL depicting breaking of exciton at 244 nm (a); PL spectra of Tyrosine (concentration 1 mg/mL) at different excitation wavelength depicting phononless band at 247.5 nm (b-c).

$$R = \pi r_B^0 \sqrt{\frac{\frac{m_0}{M}}{\frac{\mu}{m_0 \varepsilon_\infty^2} - \frac{E_{ex}^{QD}}{R_y}}}$$

Equation S1 Radius of zero dimensional confined structure

For m_e and $m_h = 0.5\, m_0$

$$M = m_e + m_h$$

$$M = 0.5\, m_0 + 0.5\, m_0$$

$$M = m_0$$

and

$$\mu = m_e\, m_h / m_e + m_h$$

$$= 0.5\, m_0 * 0.5\, m_0 / 0.5\, m_0 + 0.5\, m_0$$

$$= 0.25 m_0^2 / m_0$$

$$= 0.25\, m_0$$

Calculation S1 Scheme depicting methodology used for calculating translational mass and reduced mass

Zero dimensional Quantum well model For Emission peak at 303 nm at excitation 247.5 nm

$$Radius\ of\ QD = \pi * r_B^0 \sqrt{\frac{\frac{m_0}{M}}{\frac{\mu}{m_0 \varepsilon_\infty^2} - \frac{E_{ex}^{QD}}{Ry}}}$$

where $r_B^0 = Bohr\ radius$
$m_0 = free\ electron\ mass$
$\mu = reduced\ mass$
$N = Refractive\ index\ (1.33)$
and $\varepsilon_\infty = n^2 = 3.13$

$$R = 3.14 * 0.052 \sqrt{\frac{1}{\frac{0.25 m_0}{m_0 \varepsilon_\infty^2} - \frac{E_{ex}^{QD}}{13.56}}} \quad \text{nm}$$

$$R = 3.14 * 0.052 \sqrt{\frac{1}{\frac{0.25}{3.13} - \frac{E_{ex}^{QD}}{13.56}}} \quad \text{nm}$$

Exciton binding energy
$E_{ex}^{QD} = 0.0715\ eV$

$$R = 3.14 * 0.052 \sqrt{\frac{1}{\frac{0.25}{3.13} - \frac{0.0715}{13.56}}} \quad \text{nm}$$

$$R = 0.60\ nm$$

Calculation S2 Size calculation of tyrosine coupled dimer state using zero dimensional quantum well model

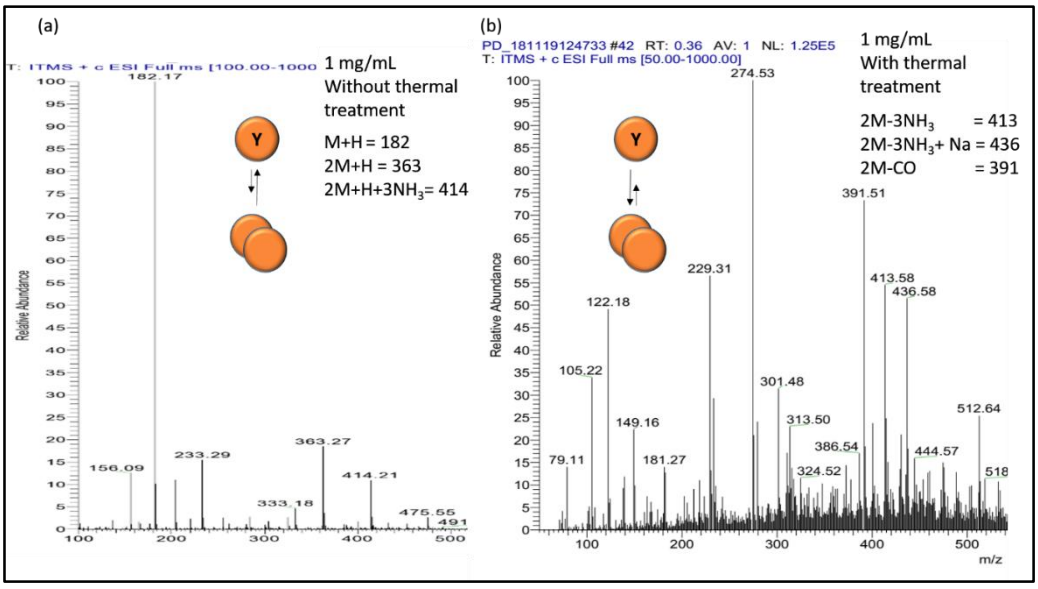


Figure S2 ITMS of tyrosine 1 mg/mL solution before thermal treatment (a) and after thermal treatment (b).

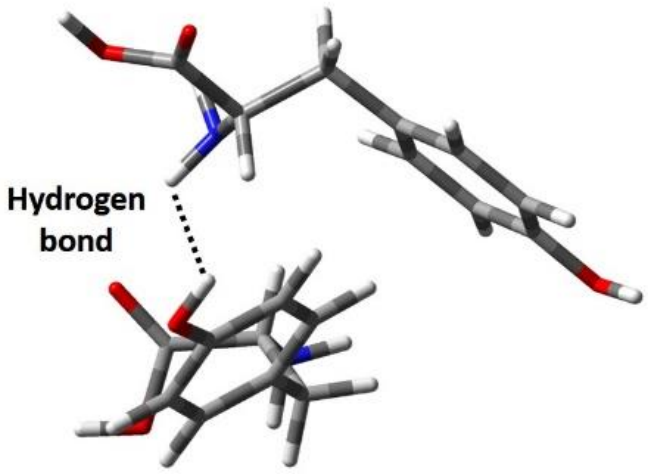


Figure S3 Tyrosine dimer assembly structure containing a hydrogen bond interaction as optimized by DFT

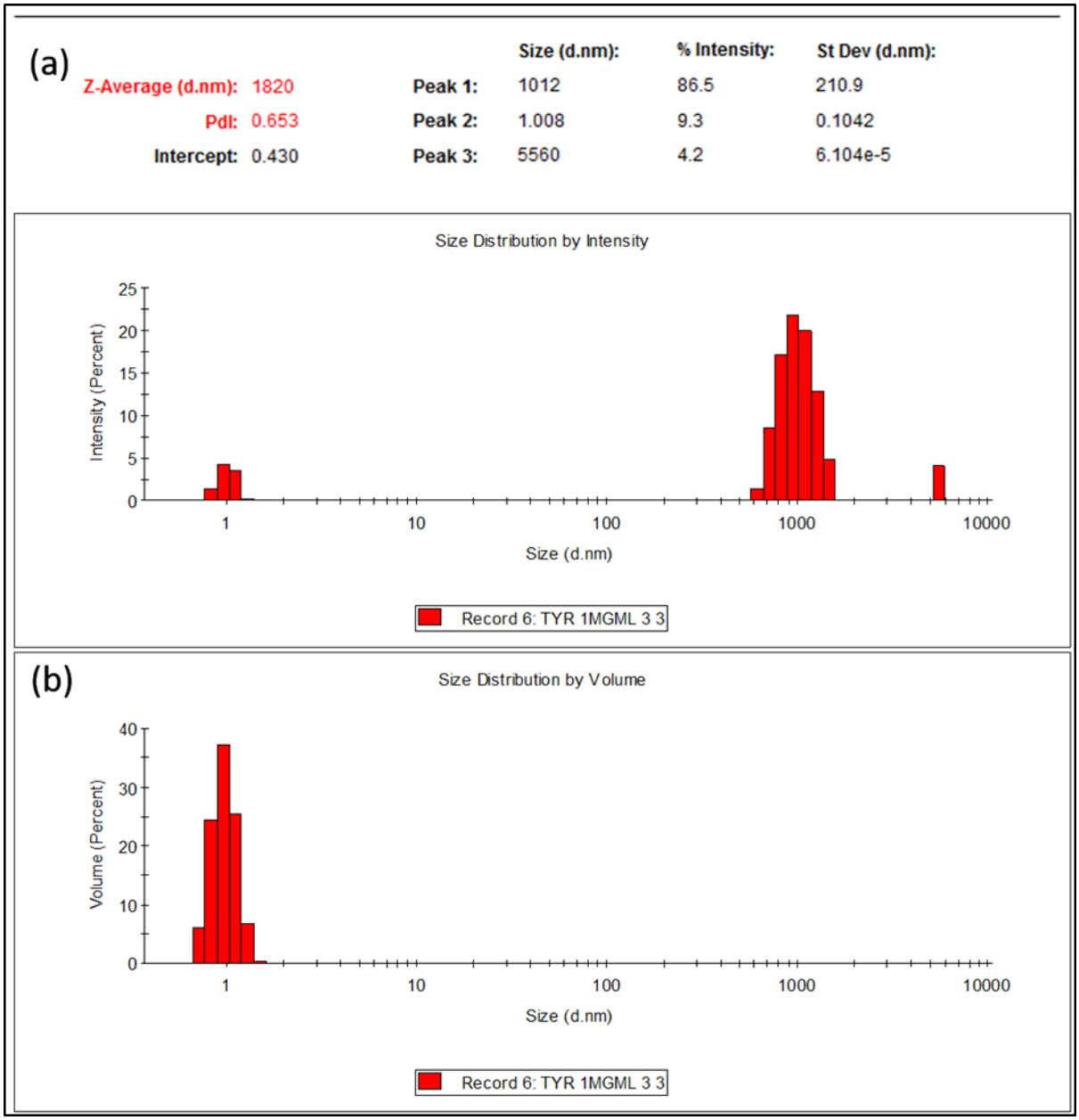


Figure S4 DLS of tyrosine at 1 mg/mL displaying intensity distribution (a); and volume distribution (b).

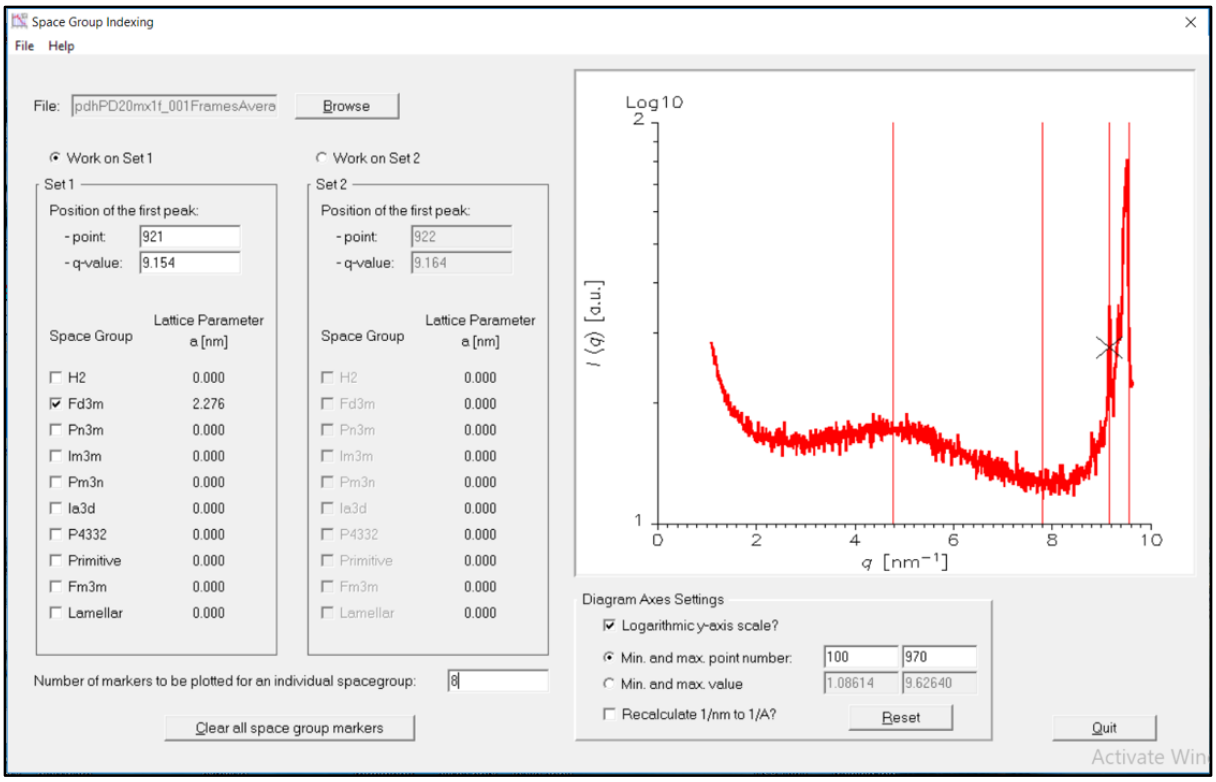


Figure S5 Space group indexing of SAXS pattern depicting Fd3m space group with unit cell parameter 2.276 nm.

For FCC lattice (Fd3m),

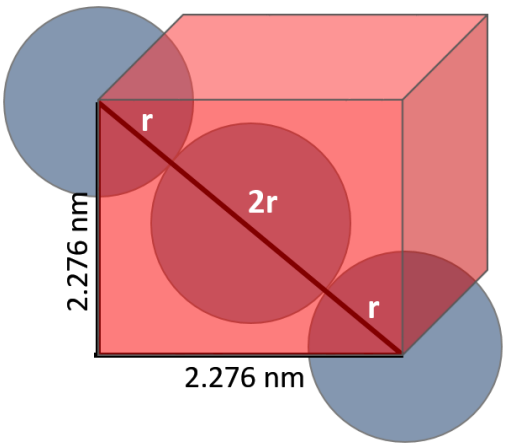
If unit cell parameter $= 2.276\ nm$
and radius of lattice point (r)

$$4r = \sqrt{(2.276)^2 + (2.276)^2}$$

$$4r = \sqrt{10.36}$$

$$4r = 3.218$$

$$r = 0.80\ nm$$



Calculation S3 Space group indexing calculation depicting radius of lattice point to be 0.80 nm.

Debye Scherrer equation

(*Average nano crystallite size*) *D*
using highest intensity peak at* $2\theta = 18.07$ *in XRD

$$D(Average\ nanoparticle\ size) = \frac{k * \lambda}{d\ cos\theta}$$

$$where \quad k = 0.94$$
$$\lambda = 0.154\ nm$$

$d = FwHm$ (*Full width half maxima*) *of most intense peak at 18.07*

$$d\ (2\theta) = 0.63\ degree$$

$$d = \frac{22 * 0.63}{7 * 180} radian$$

$$\Rightarrow \quad D = \frac{0.94 * 0.154\ nm}{0.158 * \text{Cos } 9.035}$$

$$D = \frac{0.94 * 0.154\ nm}{0.0111 * 0.9875}$$

$$D = 13.33\ nm$$

Calculation S4 Calculation of nano crystallite size using Debye Scherrer equation.

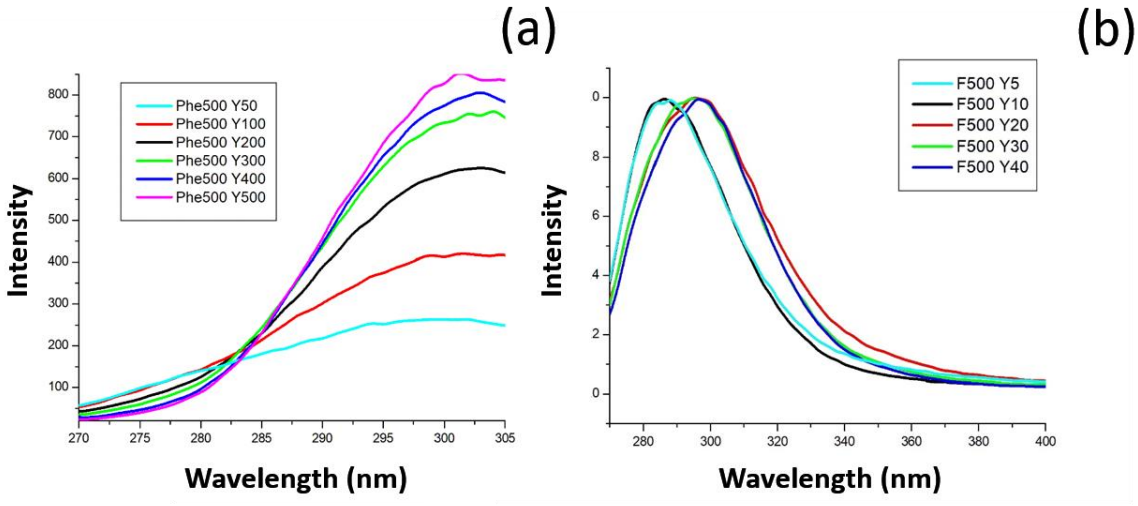


Figure S6. PL spectra displaying the FRET between TyrMR and Phenylalanine coassembly (a); Red shift in the PL emission with increase in the concentration of TyrMR concentration (b).

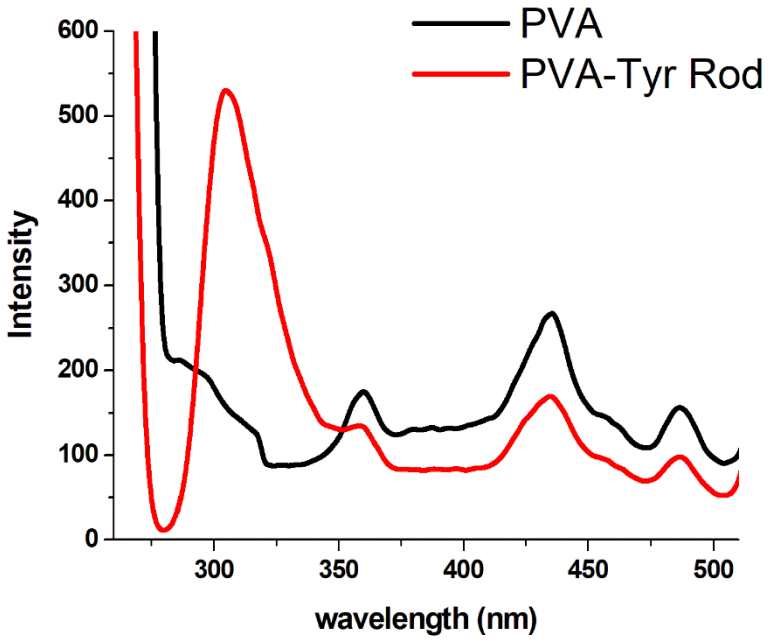


Figure S7 PL spectra of TyrMR:PVA binary composite and only PVA at excitation wavelength of 247 nm

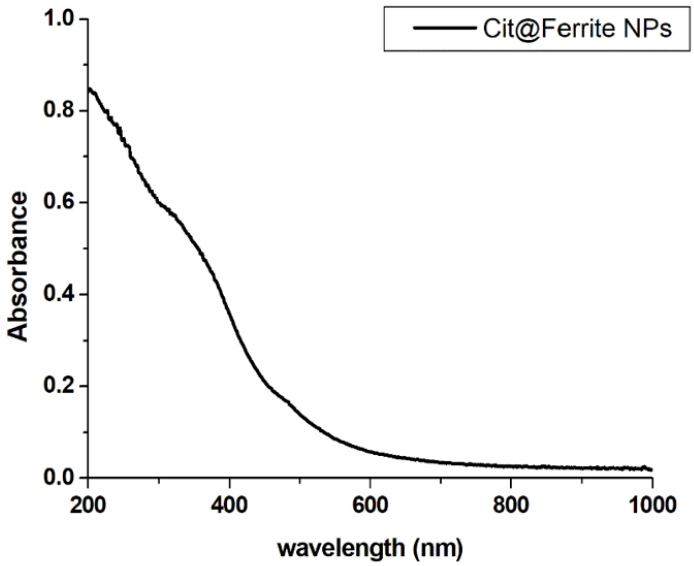


Figure S8 UV-Vis spectra of synthesized ferrite nanoparticles (FeNPs)

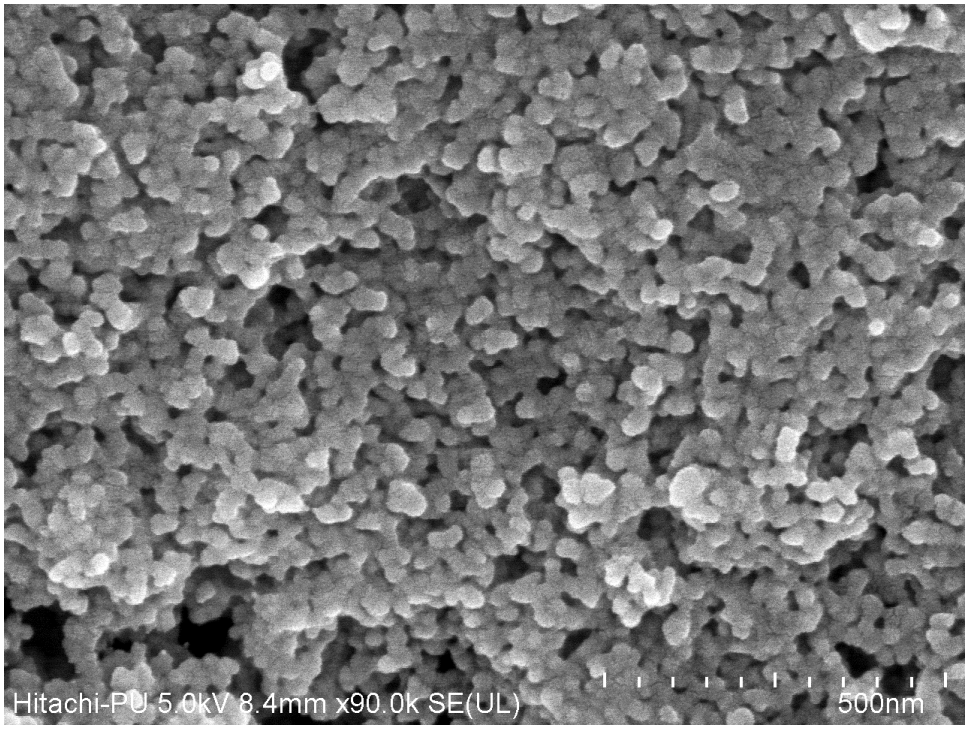


Figure S9 FESEM image of synthesized FeNPs with average size of ~30 nm

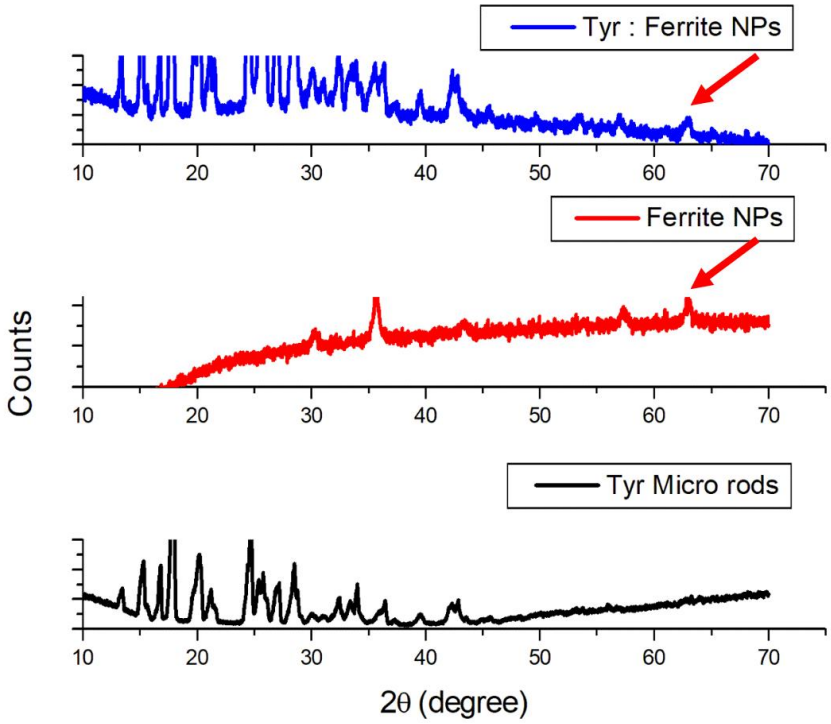
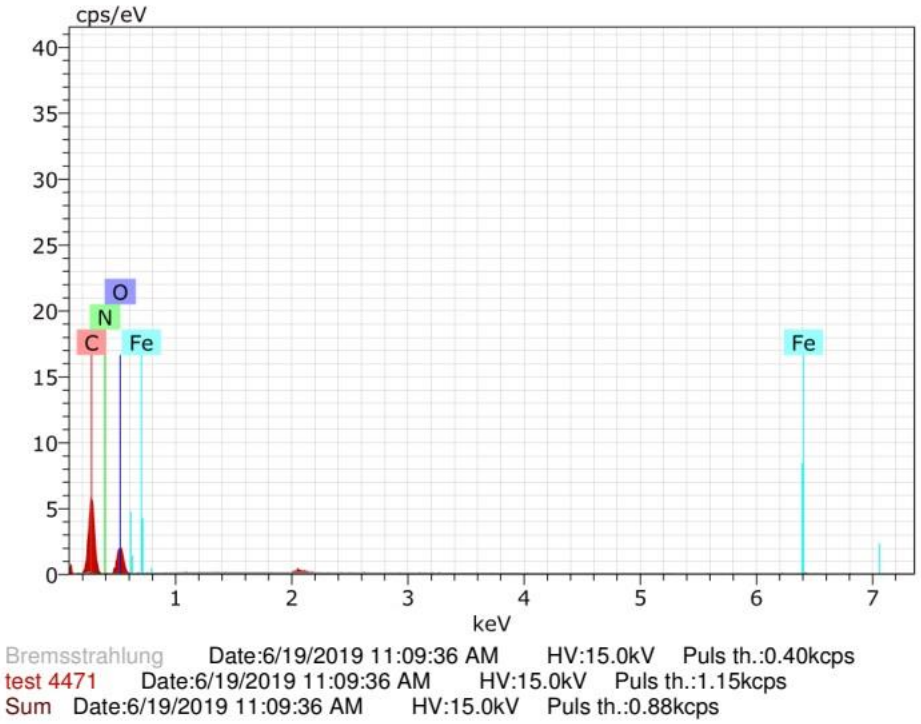


Figure S10 XRD diffraction pattern of only TyrMR; FeNPs and TyrMR:FeNP nanocomposite



Spectrum: test 4471

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	55.48	55.48	62.71	28.22
Nitrogen	K-series	3.68	3.68	3.57	7.97
Oxygen	K-series	39.28	39.28	33.34	24.91
Iron	K-series	1.55	1.55	0.38	0.72
	Total:	100.00	100.00	100.00	

Figure S11 EDS mapping of TyrMR:FeNPs:PVA ternary nanocomposite