

Supporting Information

**Functionalization of Manganite Nanoparticles and their
interaction with biologically relevant small ligands:
Picosecond Time-Resolved FRET Studies**

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S1: Synthesis of LSMO

The manganite nanoparticles we have used for functionalization are basically a hole doped LSMO ($\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$). The parent compound of LSMO is, LaMnO_3 which is an antiferromagnetic insulator with ABO_3 type structure. The system becomes ferromagnetic metallic via double exchange mechanism, by doping with divalent ion (like Ca, Sr etc). The bulk LSMO is ferromagnetic at room temperature and the crystal structure is found to be rhombohedral. For functionalization of this manganite system we need to reduce the size of the particles. Hence we need low temperature synthesis route. We have prepared LSMO using Chemical Solution Deposition (CSD) technique (the acetate/nitrate route). This is a modified sol gel technique designed specially for the preparation of complex oxide nanoparticles. The reaction mechanism was first given by Shankar¹ et. al.

We have taken high purity (> 99%) metal acetates (procured from Sigma Aldrich) and then dissolved in the desired stoichiometric proportions in acetic acid and water. To this solution, an appropriate amount of ethylene glycol (molecular weight = 62.07 gm/mol) was added and heated until the sol was formed. The gel was dried overnight at 150⁰C. Pyrolysis was done at 350⁰C and 450⁰C followed by a sintering at higher temperature to obtain the desired chemical phase. For the manganites, phase pure samples can be obtained at temperatures as low as 650⁰C. Using this CSD method precise control of the stoichiometry can be achieved. The final product is more homogeneous chemically. Particle size can be controlled by regulating the annealing time and temperature. A major challenge encountered in the synthesis of nanocrystalline

multicomponent oxides is the poor control of stoichiometry and homogeneity at the nano level. The CSD technique overcomes this problem successfully. This is related to the use of ethylene glycol which has an extremely important role in the reaction mechanism. It helps in forming a close network of cations from the precursor solution thereby assisting the reaction and also phase formation at low temperatures. Phase formation and phase purity was characterized by X-ray diffraction using Cu K α radiation ($\lambda = 0.15$ nm). The average particle sizes of the NPs were estimated from XRD and TEM data was ~ 14.1 nm. Figure S1 (a) shows the TEM image of as-prepared NPs and their size distribution is shown in the inset. The magnetic measurements of the as prepared crude NPs were performed with a SQUID Magnetometer model MPMS XL 7 of Quantum Design, USA made. Figure S1 (b) shows the temperature dependence of the magnetic moment (M versus T) and indicates that T_C (Curie Temperature) is above the room temperature. Inset of the figure S1 (b) shows the hysteresis curve, characteristic of the ferromagnetism.

S2: Time resolved measurements

The observed fluorescence transients were fitted by using a nonlinear least square fitting procedure to a function ($X(t) = \int_0^t E(t')R(t-t')dt'$) comprising of convolution of the IRF ($E(t)$) with a sum of exponential ($R(t) = A + \sum_{i=1}^N B_i e^{-t/\tau_i}$) with pre-exponential factors (B_i), characteristic lifetimes (τ_i) and a back ground (A). Relative concentration in a multi exponential decay was finally expressed as:

$$c_n = \frac{B_n}{\sum_{i=1}^N B_i} \times 100$$

The quality of the curve fitting was evaluated by reduced chi-square and residual data.

S3: Donor-Acceptor distance measurement from FRET

To estimate the FRET efficiency of the donor (NPA, 2AP) and hence to determine the distance of the donor-acceptor pair, we followed the methodology described in chapter 13 of the book². The Förster distance (R_0) is given by

$$R_0 = 0.211 [\kappa^2 n^{-4} Q_D J(\lambda)]^{1/6} \quad (\text{in } \text{Å}) \quad (1)$$

Where κ^2 is a factor describing the relative orientation in space of the transition dipoles of the donor and acceptor. For donor and acceptor that randomize by rotational diffusion prior to energy transfer, the magnitude of κ^2 is assumed to be 2/3. In the present study the same assumption has been made. The refractive index (n) of the medium was assumed to be 1.4. Q_D , is the quantum yield of the donor in absence of the acceptor. $J(\lambda)$, the overlap integral, which express the degree of spectral overlap between the donor emission and the acceptor absorption, is given by,

$$J(\lambda) = \frac{\int_0^{\infty} F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda}{\int_0^{\infty} F_D(\lambda) d\lambda} \quad (2)$$

where $F_D(\lambda)$ is the fluorescence intensity of the donor in the wavelength range of λ to $\lambda+d\lambda$ and is dimensionless. $\varepsilon_A(\lambda)$ is the extinction coefficient (in $\text{M}^{-1} \text{cm}^{-1}$) of the acceptor at λ . If λ is in nm, then $J(\lambda)$ is in units of $\text{M}^{-1} \text{cm}^{-1} \text{nm}^4$. Once the value of R_0 is known, the donor-acceptor distance (r) can easily be calculated using the formula,

$$r^6 = [R_0^6 (1 - E)] / E \quad (3)$$

Here E is FRET efficiency, measured by using the lifetimes of the donor in the absence τ_D and presence τ_{DA} of acceptor.

$$E = 1 - (\tau_{DA} / \tau_D) \quad (4a)$$

The energy transfer efficiency (E) is also measured using the relative fluorescence intensity of the donor in absence (F_D) and presence (F_{DA}) of the acceptor.

$$E = 1 - (F_{DA} / F_D) \quad (4b)$$

It has to be noted that Eq (3) holds rigorously only for a homogeneous system (i.e., identical donor acceptor complexes) in which the donor and the donor-acceptor complex have single-exponential decays. However, for donor-acceptor systems decaying with multi exponential lifetimes², Energy transfer efficiency (E) is calculated from the amplitude weighted lifetimes $\langle \tau \rangle = \sum_i \alpha_i \tau_i$ where α_i is the relative amplitude contribution to the lifetime τ_i . We have used the amplitude weighted time constants for τ_D and τ_{DA} to evaluate E in the Eq. (4a).

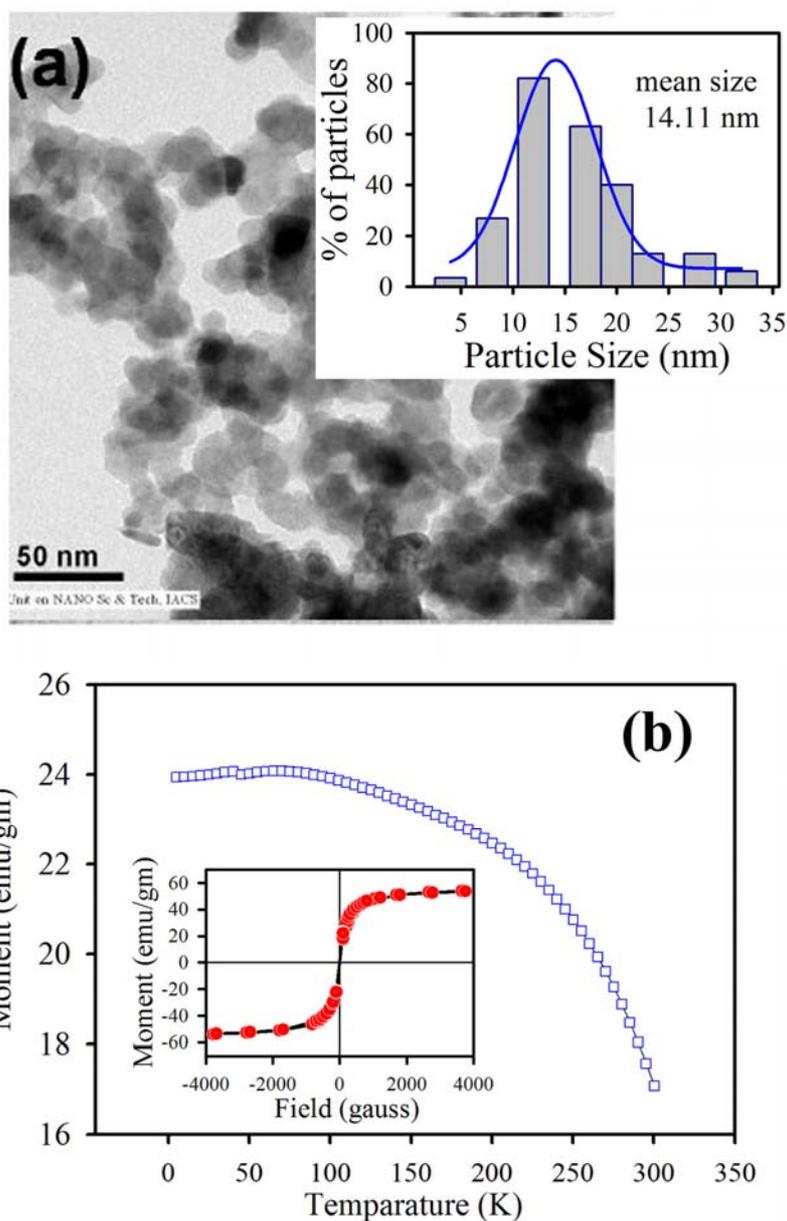


Figure S1. (a) presents the TEM image of the as prepared LSMO NPs and the inset showing the particle size distribution. (b) shows M versus T plot of as-prepared bulk NPs and the inset shows the hysteresis in the M versus H plot at 300 K. Room temperature ferromagnetic behavior is clearly evident from the hysteresis in the M versus H plot.

References:

- (1) Shankar, K. S.; Raychaudhuri, A. K. *J Mater. Res.* **2006**, *21*, 27
- (2) Lakowicz, J. R. *Principles of fluorescence spectroscopy*; 3rd ed.; Kluwer Academic/Plenum: New York, 1999.