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Incorporation of Gallium-68 into the Crystal Structure of Prussian Blue to Form $K^{68}Ga_xFe_{1-x}[Fe(CN)_6]$ Nanoparticles: Toward a Novel Bimodal PET/MRI Imaging Agent

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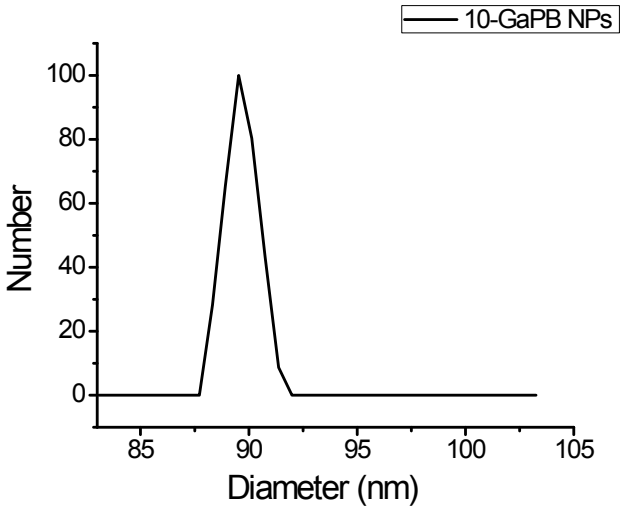

Figure S1. The DLS curve of PVP-citrate coated Ga@PBNPs.

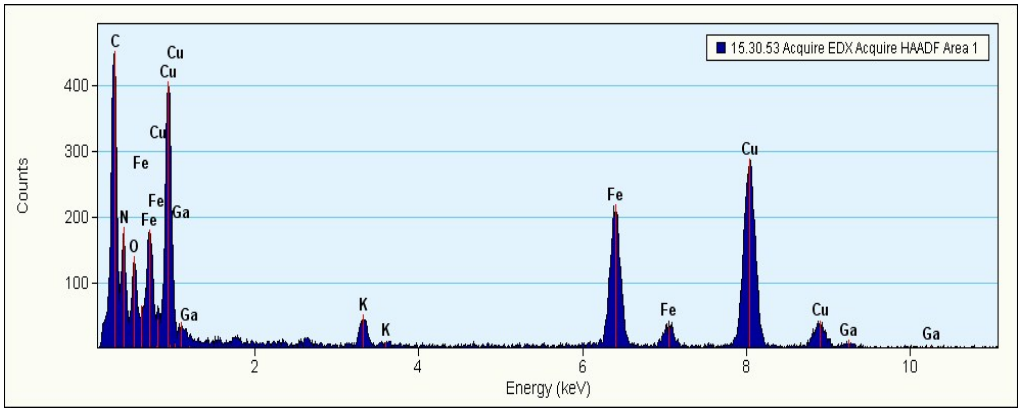

Figure S2. The EDX spectrum of PVP-citrate coated Ga@PBNPs.

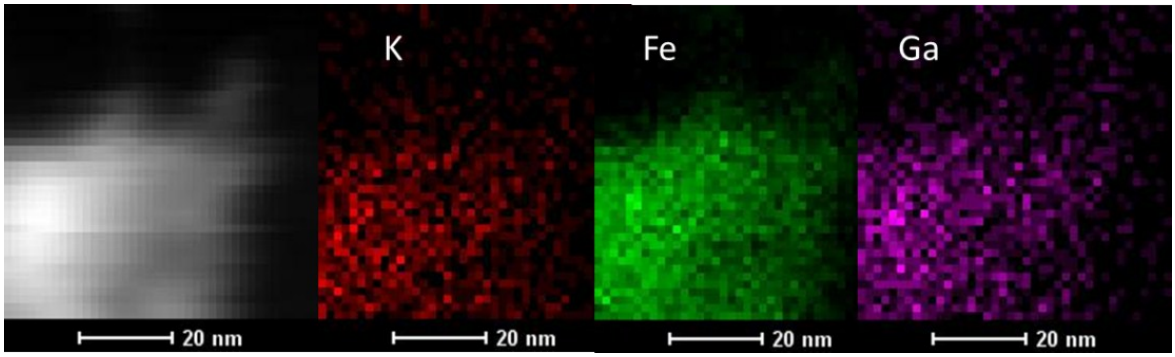

Figure S3. The EDS-STEM elemental mapping of the selected nanoparticles of PVP-citrate coated Ga@PBNPs.

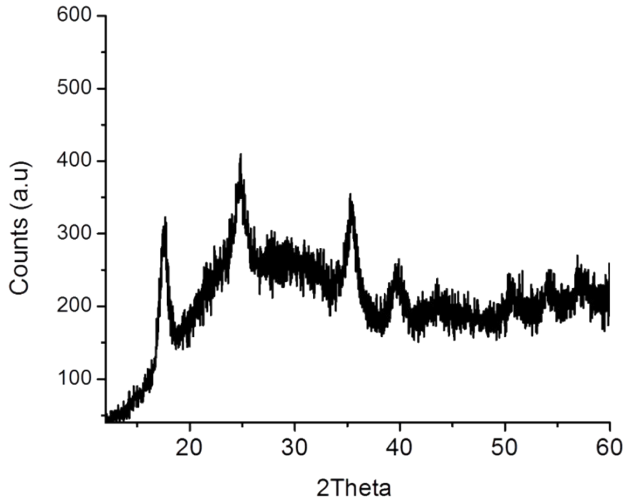

Figure S4. The X-ray powder diffraction patterns of PVP-citrate coated Ga@PBNPs.

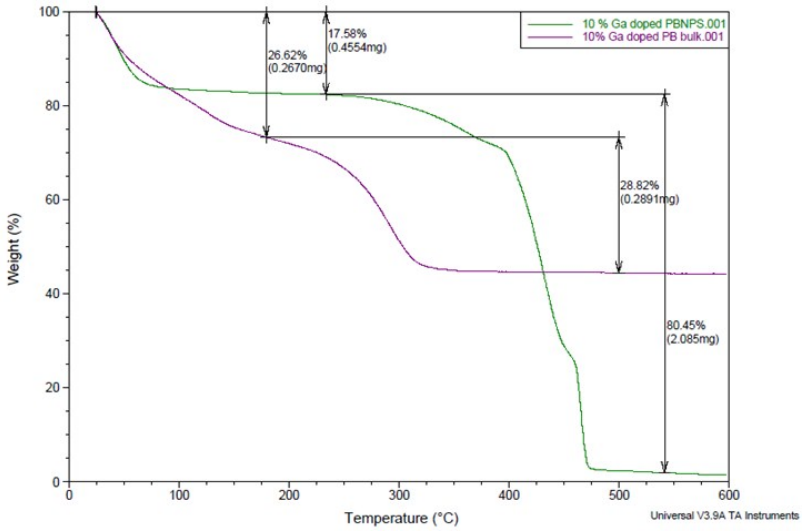

Figure S5. The TGA curve of PVP-citrate coated Ga@PBNPs (green) and the bulk $KGa_{0.05}Fe_{0.95}[Fe(CN)_6]$ (purple).

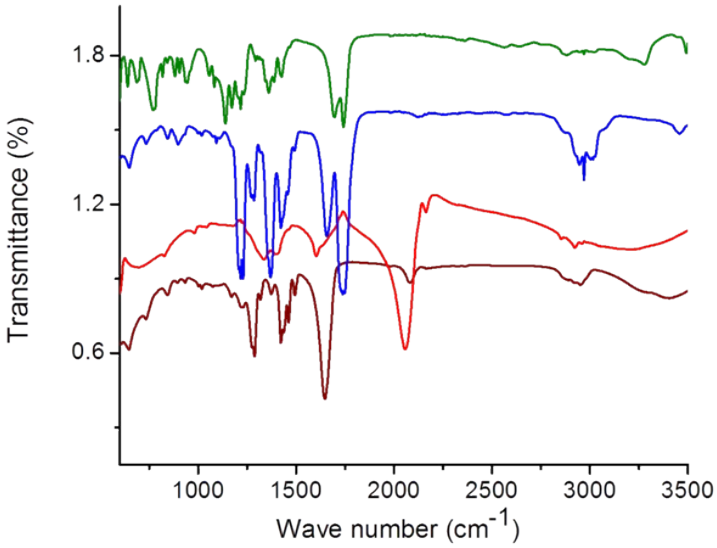

Figure S6. FT-IR spectra of citric acid (green), PVP40K (blue), PVP-citrate coated Ga@PBNPs (brown) and the bulk $KGa_{0.05}Fe_{0.95}[Fe(CN)_6]$ (red).

Structure determination from the bulk sample: Powder XRD patterns were recorded using a Bruker D8 Advance X- ray diffractometer (Kα radiation, Kβ-filter and LynxEye PSD detector) equipped with a LynxEye position detector and an incident beam Ge 111 monochromator. Powder patterns were measured from 10 to 110º 2θ with step size of 0.01446º and exposition time 800 sec per step. Given the limited number of diffraction peaks, the free positional parameters of the carbon and nitrogen atoms were fixed to values reported for the structure of $KNi[Fe(CN)_6]_{0.3}[Co(CN)_6]_{0.7}$, (Widemann, A.; Kahlert, H.; Petrovic-Prelevic, I.; Wulff, H.; Yakhmi, J. V.; Bagkar, N.; Scholz, F. Inorg. Chem. 2002, 41, 5706-5715) as noted previously. The chosen values give a reasonable C–N distance for the cyanide group. Due to correlations in the refinement the displacement parameters for all atoms were constrained to be equal. The background was modeled with a six-term polynomial and the peak shape was modeled with a TCHZ pseudo-Voigt function (Fig S6).

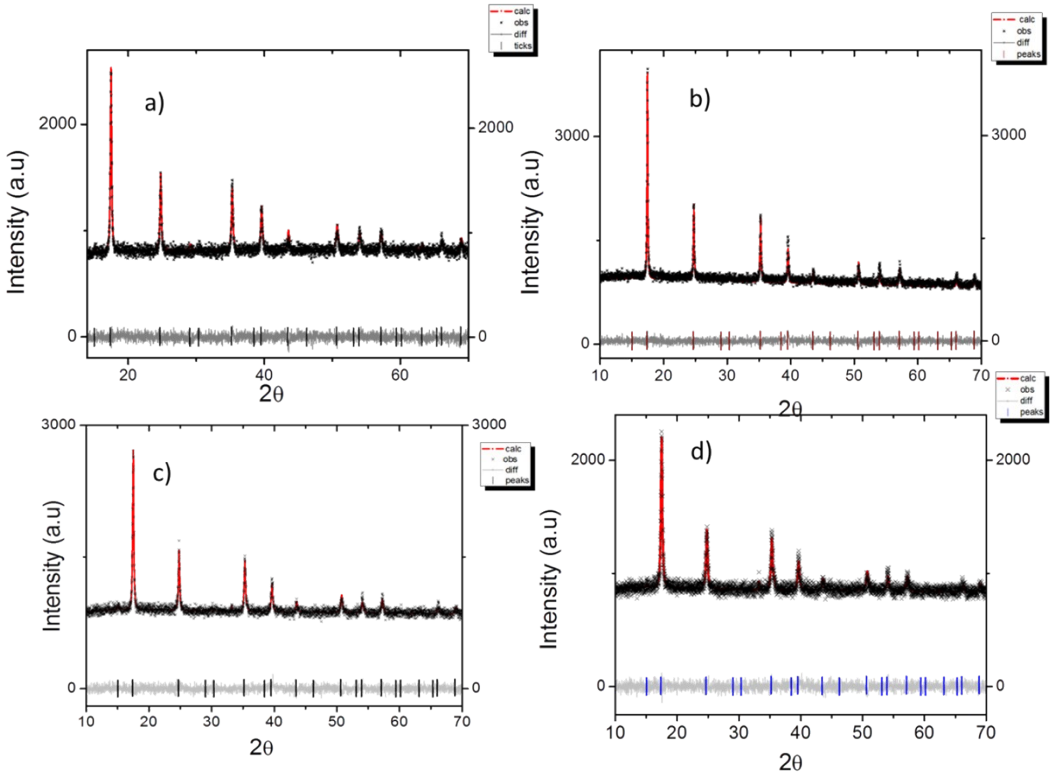

Figure S7. Observed XRD data for the bulk $KGa_xFe_{1-x}[Fe(CN)_6]\cdot nH_2O$ given in black with calculated pattern given in red. The difference between observed and calculated is given in grey.

The tick marks denotes the peak location for the known structure. a) $KGa_{0.02}Fe_{0.98}[Fe(CN)_6]\cdot nH_2O$; b) $KGa_{0.05}Fe_{0.95}[Fe(CN)_6]\cdot nH_2O$; c) $KGa_{0.07}Fe_{0.93}[Fe(CN)_6]\cdot nH_2O$; d) $KGa_{0.10}Fe_{0.90}[Fe(CN)_6]\cdot nH_2O$.

Table S1. Structural information obtained from XRD data of $KGa_xFe_{1-x}[Fe(CN)_6]$ in space group *Fm-3m* (No. 225)

Compositions	**a (Å)**	**V(Å^3)**	**R_{wp}**	**R_{exp}**
$KGa_{0.02}Fe_{0.98}[Fe(CN)_6]$	10.1958 (1)	1059.90 (4)	3.602	3.445
$KGa_{0.05}Fe_{0.95}[Fe(CN)_6]$	10.1925(7)	1058.87(2)	3.539	3.294
$KGa_{0.07}Fe_{0.93}[Fe(CN)_6]$	10.1847(1)	1056.44(3)	3.358	3.321
$KGa_{0.10}Fe_{0.90}[Fe(CN)_6]$	10.1856 (1)	1056.72 (5)	3.406	3.359

Table S2. Results of elemental analysis for four different Ga-doped PB samples and their lattice parameters.

Compound	**Empirical formula**	**Chemical formula suggested by ICP-OES elemental analysis**	**a (A^o)**
100% Ga PB	$KGa[Fe(CN)_6]$	$KGa_{0.92}Fe_{0.08}[Fe(CN)_6]$	10.1274
5% Ga doped PB	$KGa_{0.05}Fe_{0.95}[Fe(CN)_6]$	$KGa_{0.02}Fe_{0.98}[Fe(CN)_6]$	10.1958
10% Ga doped PB	$KGa_{0.10}Fe_{0.90}[Fe(CN)_6]$	$KGa_{0.05}Fe_{0.95}[Fe(CN)_6]$	10.1925
15% Ga doped PB	$KGa_{0.15}Fe_{0.95}[Fe(CN)_6]$	$KGa_{0.07}Fe_{0.93}[Fe(CN)_6]$	10.1847
20% Ga doped PB	$KGa_{0.20}Fe_{0.95}[Fe(CN)_6]$	$KGa_{0.10}Fe_{0.90}[Fe(CN)_6]$	10.1856

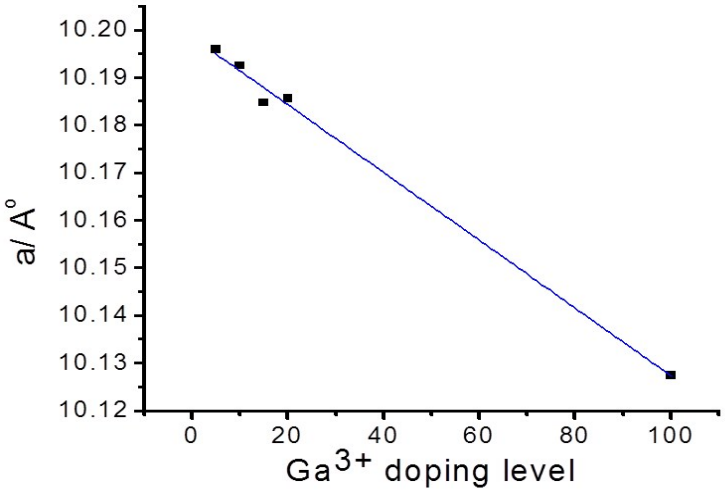

Figure S8. The Vegard's plot of lattice parameters in the $KGa_xFe_{1-x}[Fe(CN)_6]$ series.

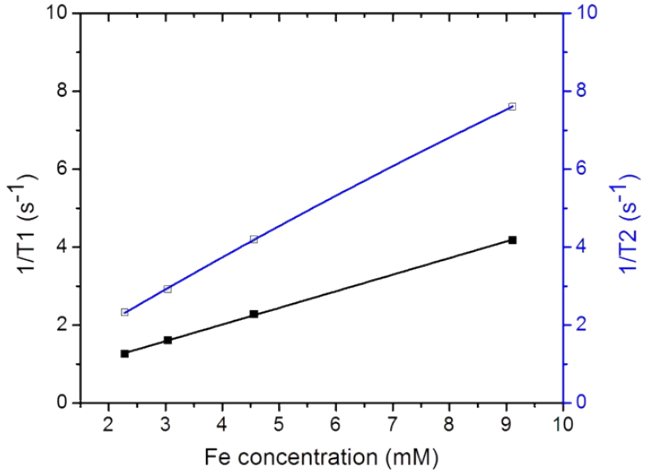

Figure S9. Plots of $1/T_i$ (i = 1, 2) *vs* the Fe^{3+} concentration at magnetic field strength of 1.4 T for PVP-citrate coated Ga@PBNPs.

Surface functionalization of $KGa_{0.05}Fe_{0.95}[Fe(CN)_6]$ NPs by fluorescence dye molecules and cell uptake studies. For the preparation of $KGa_{0.05}Fe_{0.95}[Fe(CN)_6]$, an aqueous Ga^{3+} (0.1 mM), Fe^{3+} (0.9 mM) (total M^{3+} concentration-1 mM, 40 mL) solution containing PVP and citrate (average MW=40,000, ~ 400 mg, citric acid-200 mg) and 1.0 mL of 1 mM of ethylenediamine were slowly mixed and reacted with $K_4[Fe(CN)_6]$ (1.0 mM, 40 mL) under vigorous stirring. Primary amine functionalities available on nanoparticle surface allow the conjugation of carboxyflourescene dye on Ga@PB NPs (*ca* 4 mM). Dialysis was performed using the MWCO-12000 membrane to remove the unreacted carboxyflourescene dye. Fluorescence emission spectrum was acquired to confirm the surface functionalization (See S9).

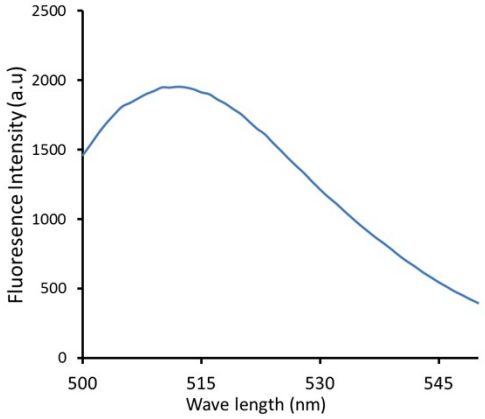

Figure S10. Fluorescence spectrum of carboxyfluorescein dye-labeled Ga@PBNPs.