Supplementary Material (ESI) for Journal of Materials Chemistry

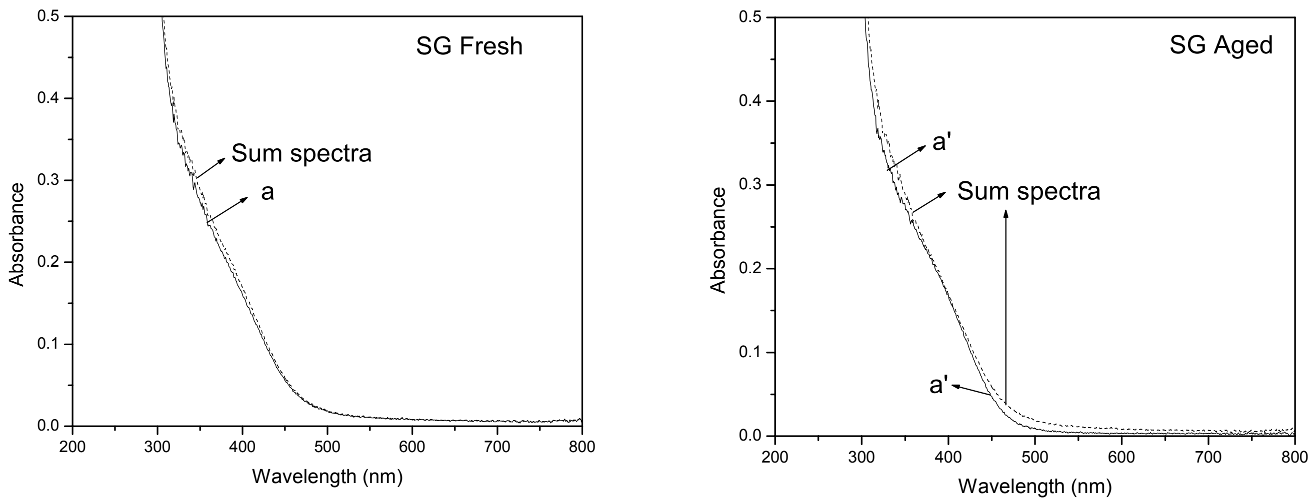
Supplementary Information

OPTICAL, PHOTOPHYSICAL AND MAGNETIC BEHAVIOR OF GMP-TEMPLATED BINARY (β-Fe_2O_3/CdS) AND TERNARY (β-Fe_2O_3/Ag/CdS) NANOHYBRIDS

Anil Kumar* and Aditi Singhal

Department of Chemistry and Centre of Nanotechnology
Indian Institute of Technology Roorkee
Roorkee – 247667, **India**

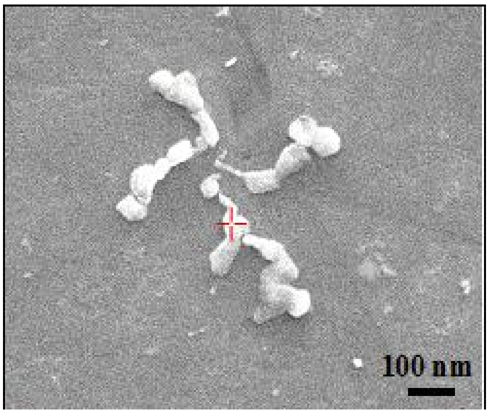
E-mail: anilkfcy@iitr.ernet.in; Fax: +91-1332-273560



X Y

Figure S1. Comparison of optical spectrum of **fresh SG (a) and aged SG (a′)** with **the respective** simple sum spectrum obtained **by the addition of absorption due to its individual components: freshly mixed – X**; **mixed after aging for the same duration as of aged SG - Y**.

SG (Aged)



c

Element	*Wt%*	*At%*
CK	06.22	10.79
NK	01.54	02.29
OK	36.22	47.21
SiK	49.99	37.12
PK	01.42	00.95
SK	01.97	00.85
AgL	00.00	00.00
CdL	01.05	00.19
FeK	01.60	00.60
Matrix	Correction	ZAF

c′

Figure S2. FESEM image and EDAX analysis of: SG- aged (c, c′).

Table S1. Comparison of observed 'd'values (Å) in XRD pattern of SG to those of standard values for hexagonal-CdS, orthorhombic- β-Fe_2O_3, and $Cd(OH)_2$

Observed Value	Hexagonal-CdS	Hexagonal-Ag	$Cd(OH)_2$ Hex. /Mono	Orthorhombic β-Fe_2O_3
6.75	-	-	6.60 (020)	-
4.53	-	-	4.52 (310)	-
3.80	-	-	3.68 (121)	-
3.57	3.56 (100)	-	-	-
3.35	3.34 (002)	-	-	3.33(130)
3.15	3.14 (101)	-	-	-
2.99	-	-	2.96(101)	-
2.93	-	-	2.93(130)	-
2.82	-	-	2.84(200)	-
2.69	-	-	-	2.62(201)
2.58	-	-	-	2.55(121)
2.48	2.43 (102)	-	-	-
2.29	-	-	-	2.28 (301)
2.23	2.23 (110)	-	-	-
2.12	-	-	2.11 (211)	-
1.96	-	-	-	1.94 (411)
1.86	1.88 (103)	-	-	-
1.82	-	-	1.83 (231)	-
1.74	1.78 (200)	-	-	-
1.62	-	-	-	1.63(450)
1.51	1.51 (104)	-	-	-
1.38	1.38 (203)	-	-	-
1.35	1.35 (210)	-	-	-
1.29	1.29 (114)	-	-	-
1.26	1.25 (105)	-	-	-
1.23	1.22 (204)	-	-	1.22(502)
1.19	1.18 (300)	-	-	-
1.141	1.15 (213)	-	-	1.142(381)

Section S3 - In a control experiment the GMP-templated β-Fe_2O_3/CdS nanohybrids were also synthesized in the absence of any excess Cd^{2+} under similar experimental conditions as used for the synthesis of SG. The morphology of this nanosystem was analyzed by AFM and FE-SEM and results of these experiments are presented in Figures S3 A and S3 B.

AFM images of the above nanosystem depicted largely the presence of spherical nanoparticles with an average surface roughness of about 15 nm (Figure S3 A-a, a′). These nanoparticles upon aging grow form spherical particles of relatively bigger size with an increase in average surface roughness to 20 nm (Figure S3 A- b, b′).

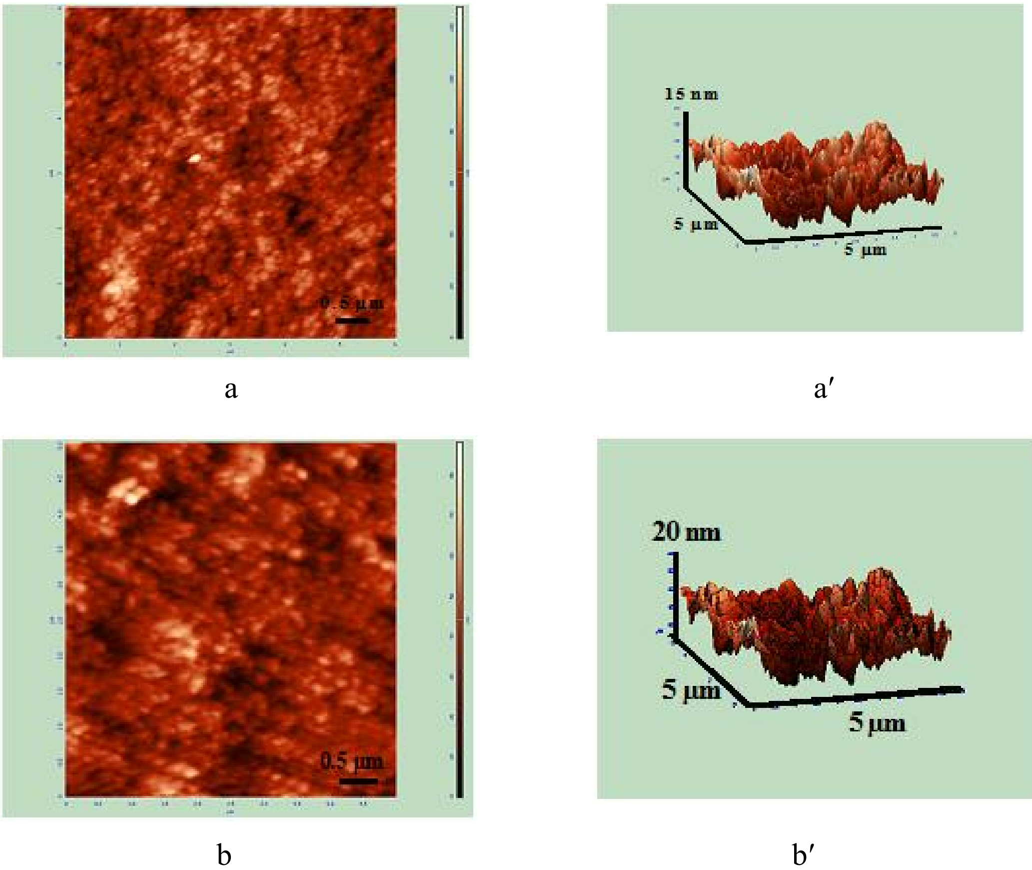
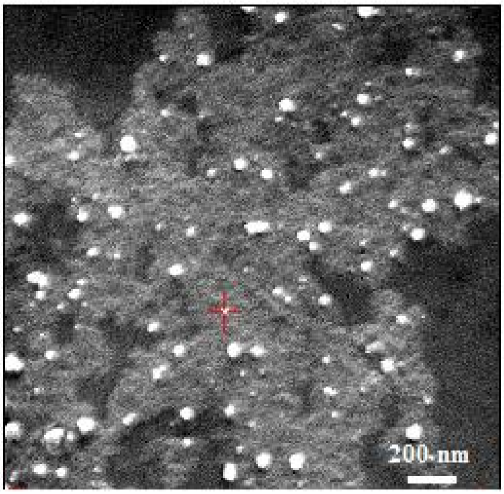


Figure S3 A. AFM images of GMP-templated β-Fe_2O_3/CdS nanohybrids having CdS, which contained stoichiometric amount of Cd^{2+} and SH^-. Fresh particles (a, a′) and aged particles (b, b′), without any excess of Cd^{2+}

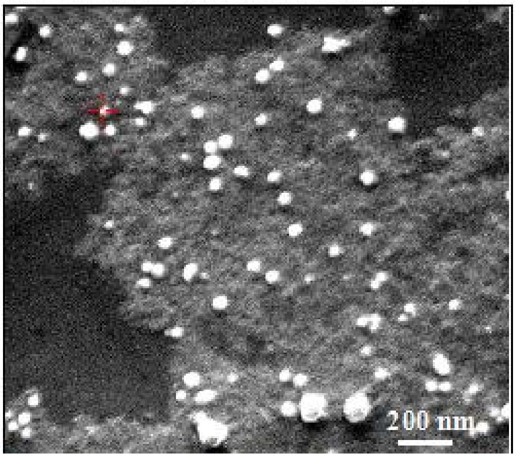
FE-SEM images of the fresh and aged GMP-templated β-Fe_2O_3/CdS nanohybrid in the absence of excess Cd^{2+} are given in (Figure S3 B). FESEM image of the fresh nanohybrid depicts the formation of spherical nanoparticles (Figure S3 B-a, a′) and upon aging forms slightly bigger size spherical particles without exhibiting formation of any organized structure. (Figure S3 B- b, b′).



a

Element	Wt%	At%
CK	04.58	14.28
NK	01.42	01.93
OK	38.40	34.85
SiK	44.42	37.92
PK	00.52	00.30
SK	00.19	00.11
AgL	00.00	00.00
CdL	00.24	00.12
FeK	00.27	00.11
AuL	11.96	10.48
Matrix	Correction	ZAF

a′



b

Element	Wt%	At%
CK	07.47	16.72
NK	03.53	02.36
OK	36.45	45.80
SiK	39.58	32.91
PK	00.53	00.38
SK	00.21	00.15
AgL	00.00	00.00
CdL	00.85	00.16
FeK	01.00	00.40
AuL	10.39	01.12
Matrix	Correction	ZAF

b′

Figure S3 B. FESEM images and EDAX analysis of GMP-templated β-Fe_2O_3/CdS nanohybrids having CdS, which contained stoichiometric amount of Cd^{2+} and SH^-. Fresh particles (a, a′) and aged particles (b, b′), without any excess of Cd^{2+}

Table S2 A. Fluorescence intensity of GMP- templated CdS obtained after the addition of different amounts of [β-Fe_2O_3] internally at pH = 9.2. (λ_{ex} = 340 nm; λ_{em} = 570 nm).

[β-Fe_2O_3] x10^{-4} (mol dm^{-3})	Fluorescence intensity of GMP- templated CdS after addition of different conc of [β-Fe_2O_3] internally (I) (a.u.)	Fluorescence intensity ratio* (I_o/I)
0.0	160	1.00
0.56	148	1.08
1.13	137	1.18
1.69	128	1.25
2.25	119	1.34
2.8	110	1.45

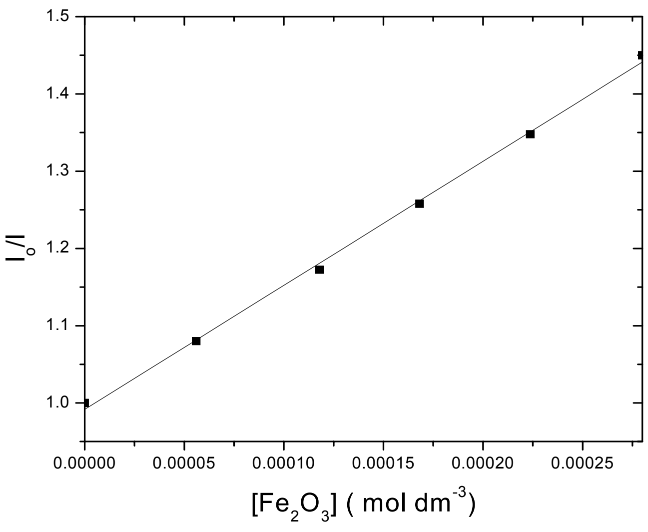


Figure S4 A. Stern-Volmer plot of fluorescence intensity ratio (I_o/I) *vs*. [β-Fe_2O_3] (mol dm^{-3}), where β-Fe_2O_3 is added internally to GMP-templated CdS.

Table S2 B. Emission lifetime ratios of GMP- templated CdS obtained after the addition of different amounts of [β-Fe_2O_3] internally at pH = 9.2. (λ_{ex} = 340 nm; λ_{em} = 570 nm).

[β-Fe_2O_3] x10^{-4} (mol dm^{-3})	Emission lifetime of GMP-templated CdS after addition of different [β-Fe_2O_3] internally <τ> (ns)	Emission lifetime ratio* (<τ_o>/ <τ>)
0.0	42	1.00
0.56	36	1.16
1.13	31	1.35
1.69	28	1.50
2.25	25	1.68
2.8	22	1.90

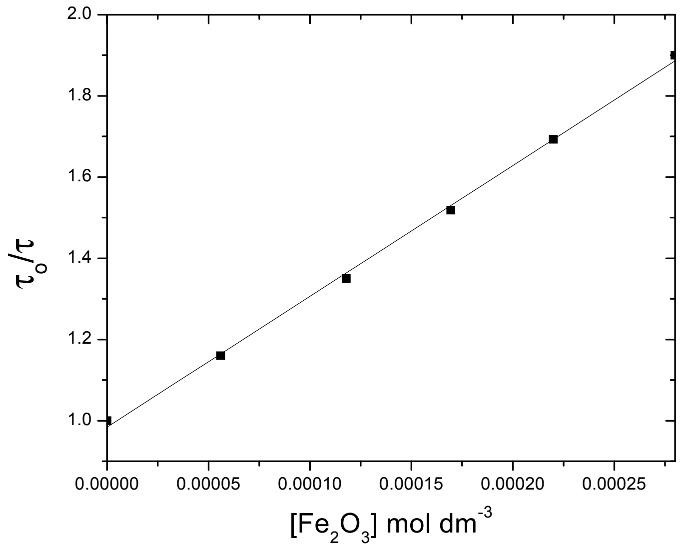
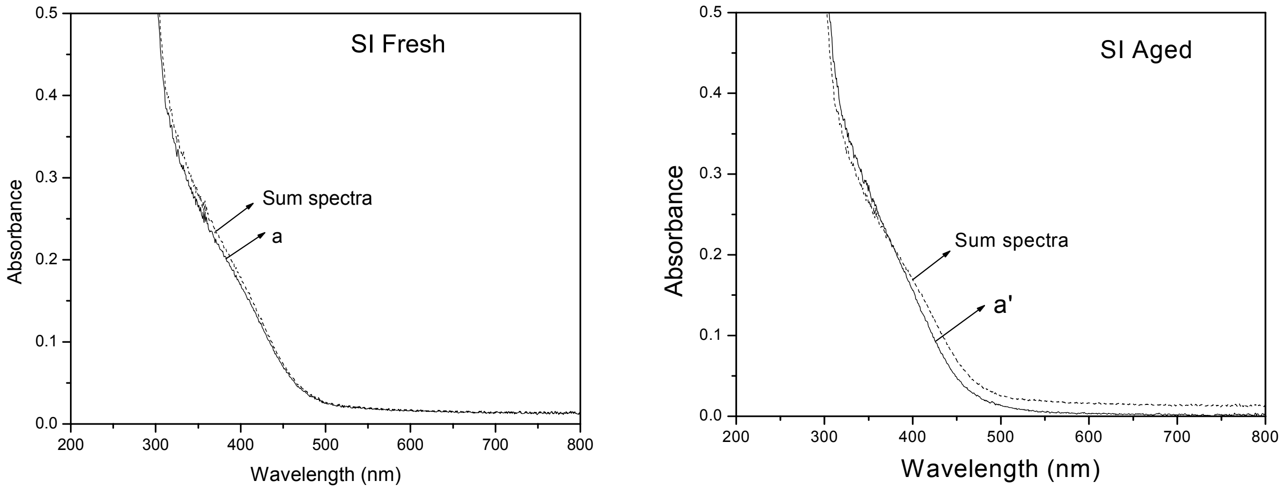


Figure S4 B. Stern-Volmer plot of emission lifetime ratio (<τ_o>/<τ>) *vs*. [β-Fe_2O_3] (mol dm^{-3}), where β-Fe_2O_3 is added internally to GMP templated CdS.



X Y

Figure S5. Comparison of optical spectrum of **fresh SI (a) and aged SI (a′)** with **the respective** simple sum spectrum obtained **by the addition of absorption due to its individual components: freshly mixed – X**; **mixed after aging for the same duration as of aged SI - Y**.

.

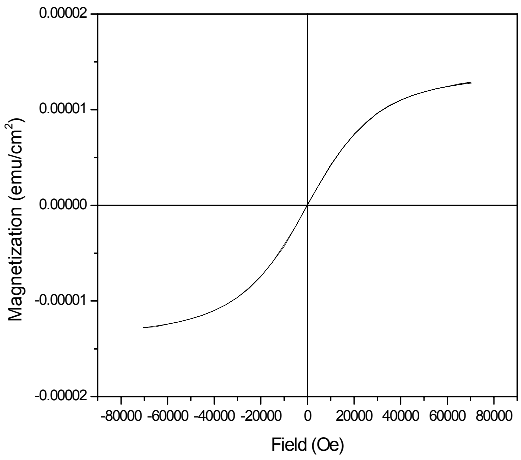


Figure S6. M-H curves of colloidal Ag at ±7 T and 5 K

Table S3. Comparison of observed 'd'values (Å) in XRD pattern of SI to those of standard values for hexagonal-CdS, orthorhombic-β-Fe_2O_3, hexagonal-Ag, and $Cd(OH)_2$

Observed Value	Hexagonal-CdS	Hexagonal-Ag	$Cd(OH)_2$ Hex. /Mono	Orthorhombic β-Fe_2O_3
6.80	-	-	6.60 (020)	-
4.43	-	-	4.52 (310)	-
3.69	-	-	3.68 (121)	-
3.33	3.34 (002)	-	-	3.33(130)
2.95		-	2.96(101)	-
2.67	-	-	-	2.62 (201)
2.52	-	2.50 (004)	-	-
2.40	2.43 (102)	-	-	-
2.28	-	-	-	2.28(301)
2.22	2.23 (110)	-	-	-
2.10	-	2.20 (112)	-	-
1.99	-	2.00 (103)	-	-
1.85	1.88 (103)	-	-	-
1.83	-	-	1.83 (231)	-
1.76	1.78 (200)	-	-	-
1.66	1.67 (004)	-	-	-
1.63	-	-	-	1.63(450)
1.51	1.51 (104)	-	-	-
1.44	-	1.44 (110)	-	-
1.38	1.38 (203)	-	-	-
1.35	1.35 (210)	-	-	-
1.29	1.29 (114)	-	-	-
1.26	-	1.25 (008)	-	-
1.23	-	1.24 (201)	-	1.22(502)
1.19	1.18 (300)	-	-	-
1.17	-	1.17 (203)	-	-
1.14	-	-	-	1.142(381)

Section S7 - In a control experiment the GMP-templated β-Fe_2O_3/Ag/CdS nanohybrids were also synthesized in the absence of any excess Cd^{2+} under similar experimental condition as used for the synthesis of SI. The morphology of this nanosystem was analyzed by AFM and FE-SEM and results of these experiments are presented in Figures S7 A and S7 B.

AFM images of the above nanosystem depicted largely the presence of spherical nanoparticles with an average surface roughness of about 20 nm (Figure S7A-a, a′). These nanoparticles upon aging grow to form aggregates forming nanorods like structure with an increase in average surface roughness to 25 nm (Figure S7A- b, b′).

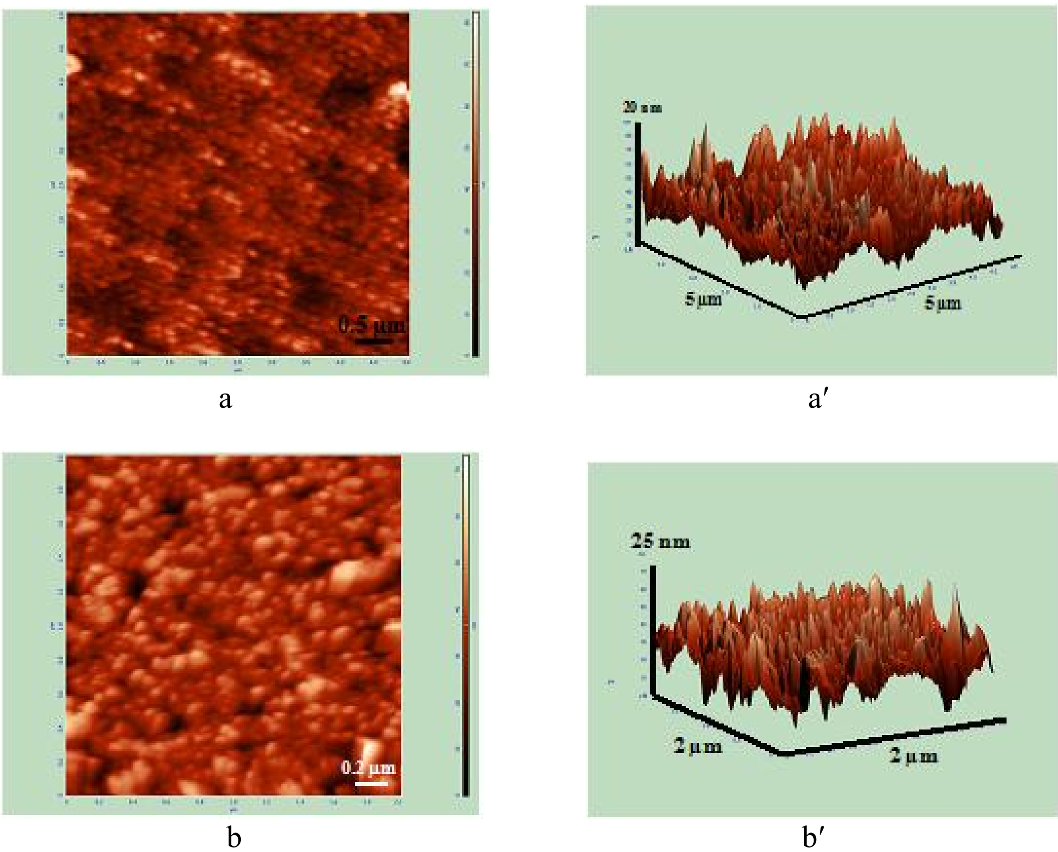
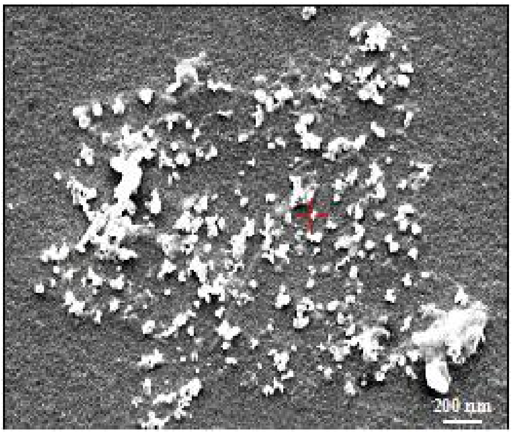


Figure S7 A. AFM images of GMP-templated β-Fe_2O_3/Ag/CdS nanohybrids having CdS, which contained stoichiometric amount of Cd^{2+} and SH^-. Fresh particles (a, a′) and aged particles (b, b′), without any excess of Cd^{2+}

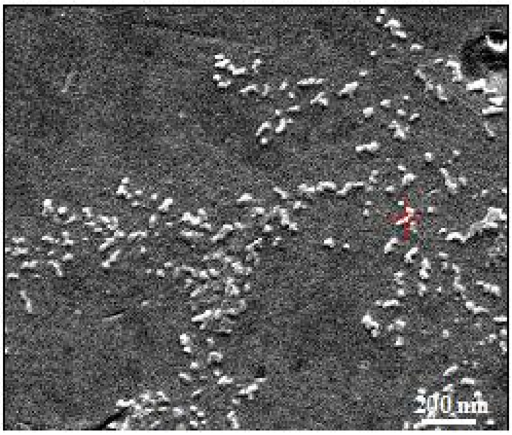
FE-SEM images of the fresh and aged GMP-templated β-Fe_2O_3/Ag/CdS nanohybrid in the absence of excess Cd^{2+} are given in (Figure S7 B). FESEM image of the fresh nanohybrid depicts the formation of spherical nanoparticles (Figure S7 B-a, a′) and these particles start to form rods with chain like structure upon aging without exhibiting formation of any organized structure (Figure S7 B- b, b′).



Element	***Wt%***	***At%***
CK	08.58	16.22
NK	01.20	01.93
OK	32.40	34.85
SiK	44.42	35.98
PK	00.52	00.31
SK	00.15	00.10
AgL	00.26	00.16
CdL	00.22	00.11
FeK	00.29	00.12
AuL	11.96	10.32
Matrix	Correction	ZAF

a

a′



Element	***Wt%***	***At%***
CK	09.45	16.72
NK	03.00	05.00
OK	34.47	45.80
SiK	39.53	29.91
PK	00.55	00.38
SK	00.21	00.14
AgL	00.53	00.36
CdL	00.88	00.17
FeK	01.09	00.41
AuL	10.30	01.11
Matrix	Correction	ZAF

b

b′

Figure S7 B. FESEM images and EDAX analysis of GMP-templated β-Fe_2O_3/Ag/CdS nanohybrids having CdS, which contained stoichiometric amount of Cd^{2+} and SH^-. Fresh particles (a, a′) and aged particles (b, b′), without any excess of Cd^{2+}

Table S4. IR spectral data of Na_2-GMP, Cd^{2+}-GMP, GMP-templated CdS, GMP-templated β-Fe_2O_3/CdS nanohybrid (SG), GMP-templated β-Fe_2O_3/Ag/CdS nanohybrid (SI).

Group/ Moeity	Na_2-GMP (cm^{-1})	Cd^{2+} - GMP (cm^{-1})	GMP-CdS (cm^{-1})	GMP- β-Fe_2O_3/CdS (SG) nanohybrid (cm^{-1})	GMP- β-Fe_2O_3/Ag/CdS (SI) nanohybrid (cm^{-1})
-NH-	3439(br)	3414(br)	3417(br)	3456(br)	3436(br)
>C=O	1694 (br)	1691(m)	1694(s)	1695(s)	1693(s)
-NH_2	1640(m)	1638(m)	1638(s)	1652(s)	1646(s)
Pyrimidine/ Imidazole	1531(s)	-	-	1531(s)	1538 (s)
N-7-C-8 + C-8-H	1490(s)	1471(s)	1479(m)	1471(m)	1472 (m)
Imidazole	1363(s)	-	1361(br)	1376(br)	1380(br)
Pyrimidine	1236(s)	-	1231(sh)	1266(m)	1245(m)
PO_3^{2-}	1080(m)	1087(m)	1089(br)	1087(m)	1089(m)
PO_3^{2-}	979(s)	976(s)	978(s)	975 (s)	976 (s)
Sugar ring	865(sh)	863(sh)	865(sh)	875(sh)	862(sh)
P-O-5'-sugar	822(s)	806(sh)	800(br)	797(m)	797 (m)
P-O	784(s)	771(s)	779(s)	776(m)	778(m)
Ring mode	628(m)	626(br)	626(br)	624(m)	629(m)
Fe-O	-	-	-	472(br)	472(m)
NO_3^-	-	-	-	-	450 (m) 530 (m) 2340 (m) 2363 (s)

Table S5 . Lifetimes of samples SG ad SI at pH=9.2 (λ_{ex}= 340 nm; λ_{em}= 650 nm).

Sample	**Component 1**		**Component 2**		**Component 3**		**<τ>**	**χ^2**
	τ_1 (ns)	**Emission %**	**τ_2 (ns)**	**Emission %**	**τ_3 (ns)**	**Emission %**	**(ns)**	
(a) Fresh samples								
SG	0.095 (0.23)	11.72	8.45 (0.039)	16.65	59.45 (0.026)	71.63	44	1.0
SI	1.65 (0.47)	6.74	13.83 (0.078)	9.39	89.95 (0.15)	83.87	91	1.1
(b) Aged samples								
SG	0.868 (0.135)	11.53	6.92 (0.024)	17.82	54.68 (0.014)	70.65	40	1.1
SI	0.878 (0.145)	9.47	7.81 (0.023)	16.32	67.09 (0.016)	74.21	72	1.0

(Value in bracket is pre-exponential factor corresponding to respective τ)

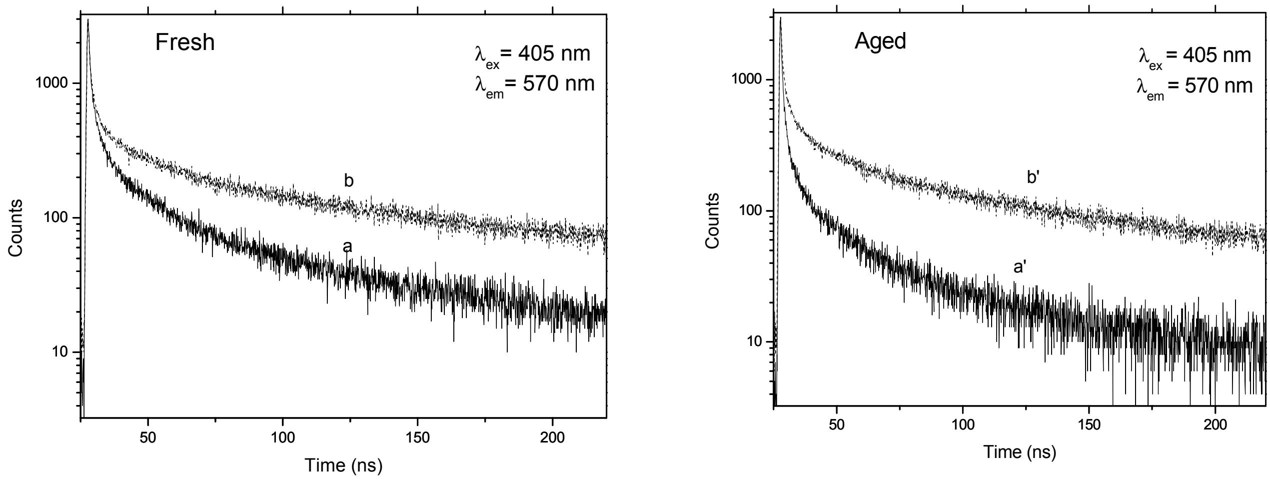
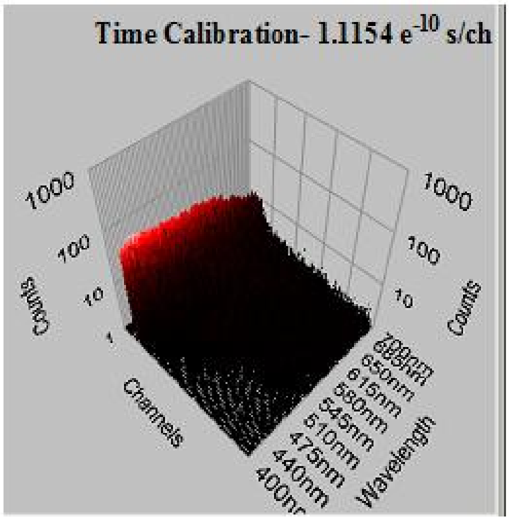


Figure S8. Fluorescence decay curves of SG (a, a′) and SI (b, b′). Fresh samples (X) and aged samples (Y) at pH = 9.2. (λ_{ex} = 405 nm; λ_{em} = 570 nm)

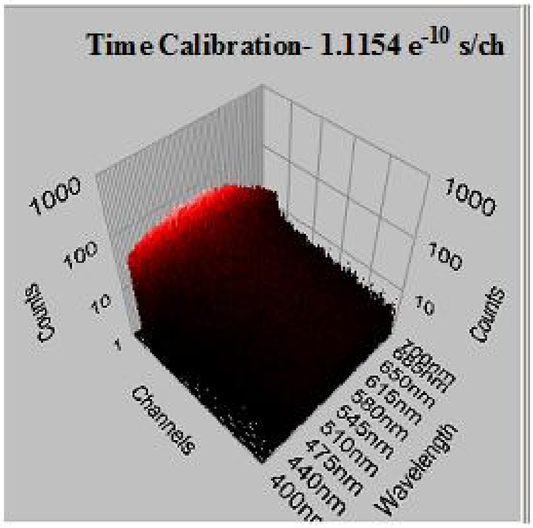
Table S6. Lifetimes of samples SG and SI at pH=9.2 (λ_{ex}= 405 nm; λ_{em}= 570 nm)

Sample	Component 1		Component 2		Component 3		<τ>	χ^2
	τ_1 (ns)	Emission %	τ_2 (ns)	Emission %	τ_3 (ns)	Emission %	(ns)	
(a) Fresh samples								
SG	0.74 (0.277)	22.57	5.83 (0.035)	22.53	43.37 (0.011)	54.90	25	1.10
SI	0.67 (0.280)	12.41	5.91 (0.034)	13.32	59.56 (0.018)	74.27	45	1.16
(b) Aged samples								
SG	0.31 (0.455)	34.55	3.82 (0.023)	21.27	35.39 (0.005)	44.18	17	1.28
SI	0.44 (0.319)	12.86	5.17 (0.032)	15.15	55.51 (0.014)	71.99	41	1.08

(Value in bracket is pre-exponential factor corresponding to respective τ)



a



b

Figure S9. Three-dimensional time resolved emission spectra (TRES) of SG (a) and SI (b).

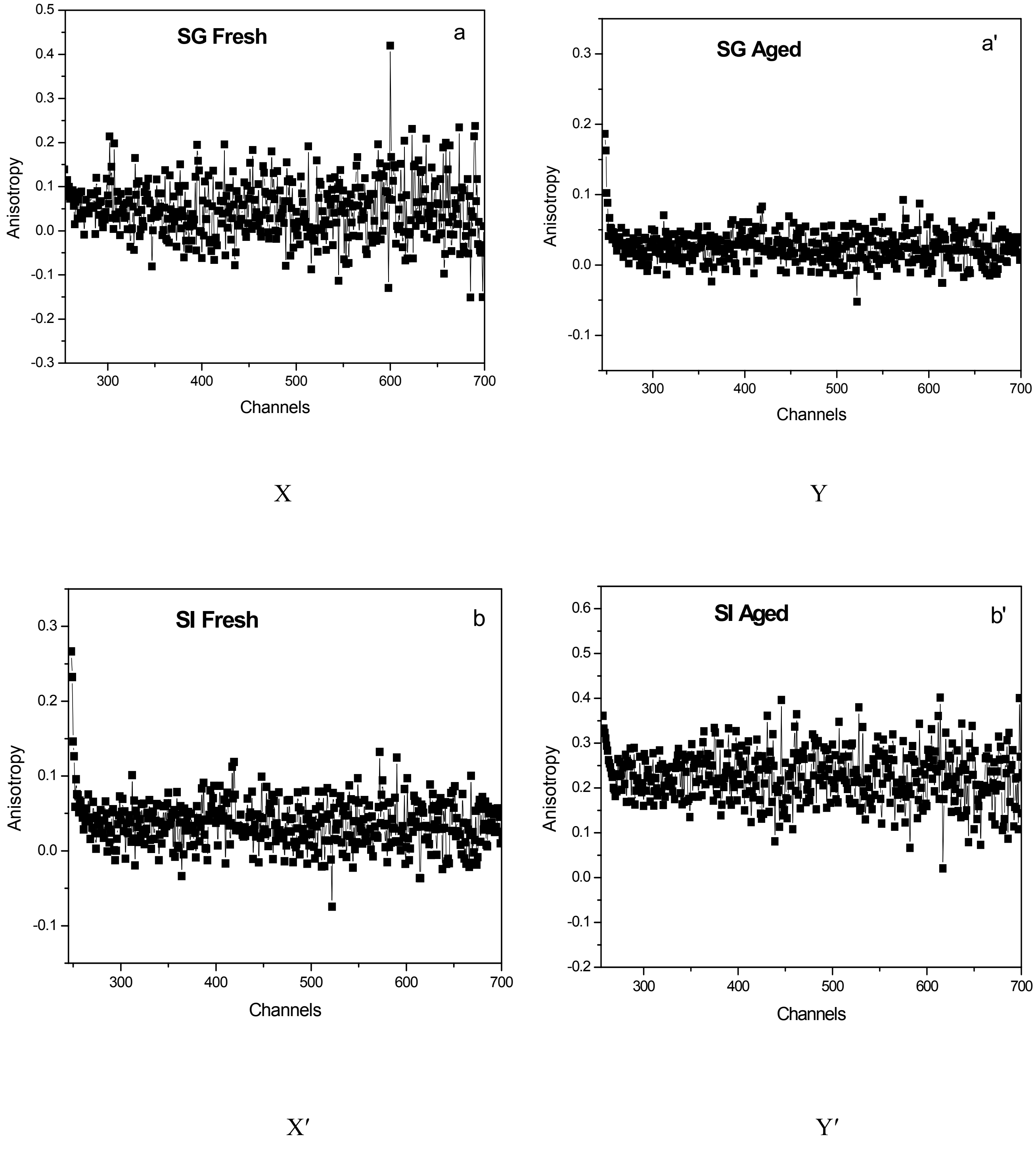


Figure S10. Anisotropy curves of SG (a, a′), SI (b, b′). Fresh particles (X, X′); Aged particles (Y, Y′).

Table S7. Fluorescence anisotropy data of SG and SI

Sample	**Fluorescence Anisotropy (r)**
(a)Fresh samples	
SG	0.12
SI	0.27
(b) Aged samples	
SG	0.19
SI	0.37

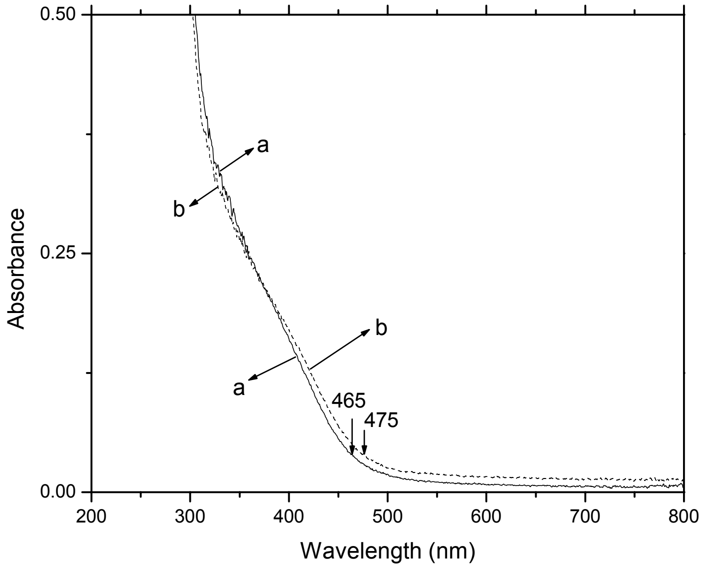


Figure S11. Optical absorption spectra of the fresh samples of SG (a); SI (b).

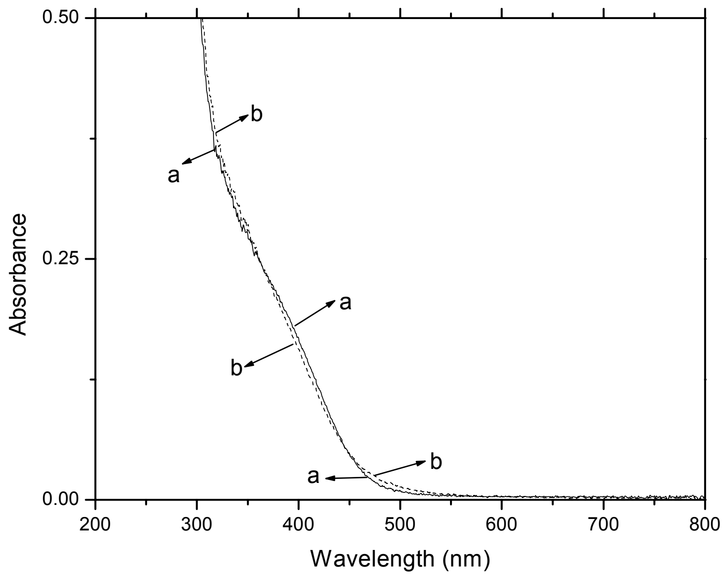


Figure S12. Optical absorption spectra of the aged samples of SG (a); SI (b).

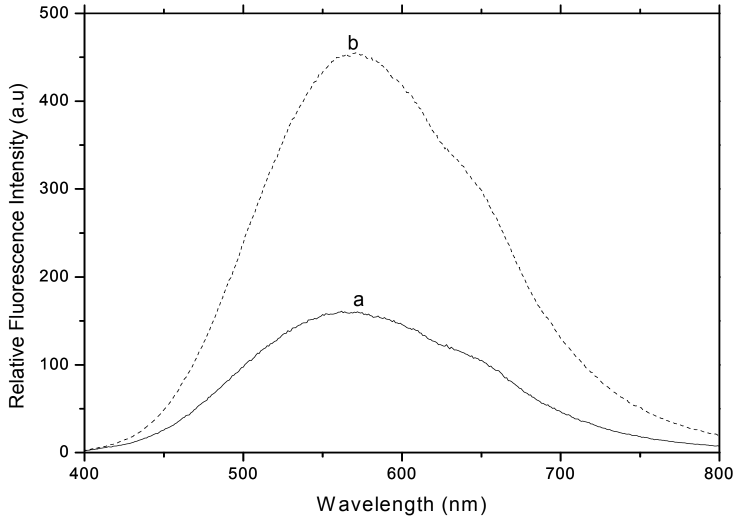


Figure S13. Emission spectra of the fresh samples of SG (a); SI (b).

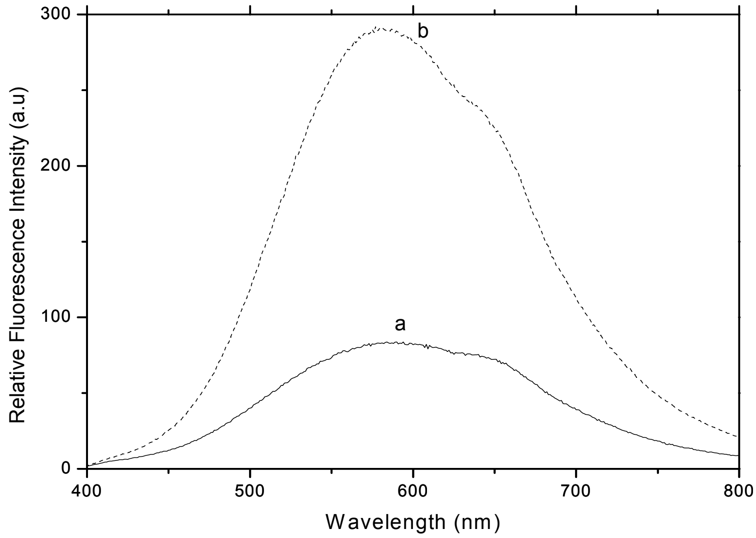


Figure S14. Emission spectra of the aged samples of SG (a); SI (b).

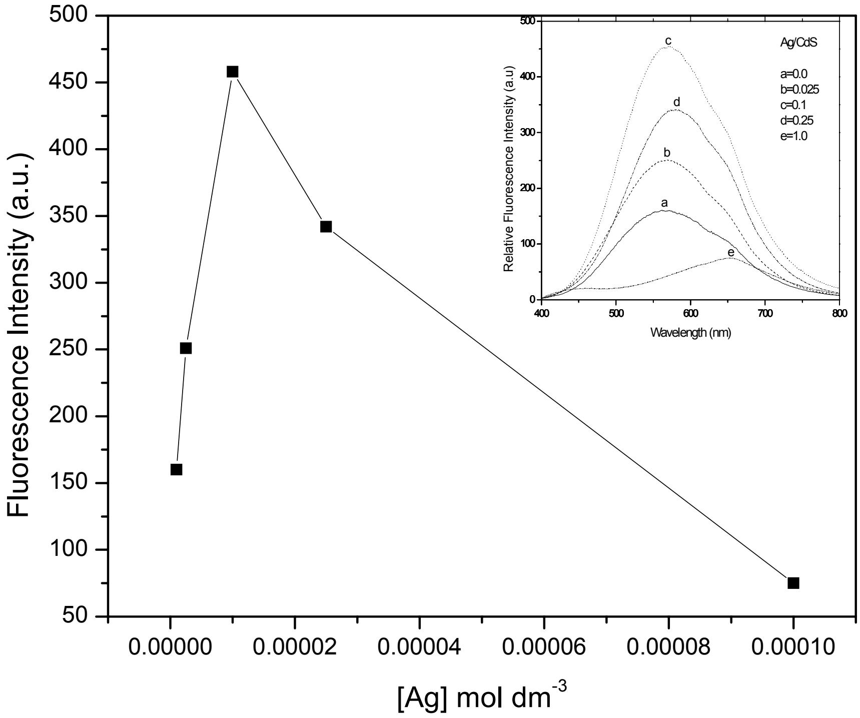


Figure S15. Plot of variation of fluorescence intensity of GMP-templatated β-Fe_2O_3/Ag/CdS nanohybrids as a function of [Ag] (mol dm^{-3}) (λ_{ex}= 340 nm).
Inset shows the emission spectra of GMP-templated β-Fe_2O_3/Ag/CdS nanohybrid containing varied [Ag] (mol dm^{-3}): $1x10^{-6}$ (a); $2.5x10^{-6}$ (b); $1x10^{-5}$ (c); $2.5x10^{-5}$ (d); $1x10^{-4}$ (e). (λ_{ex}= 340 nm).

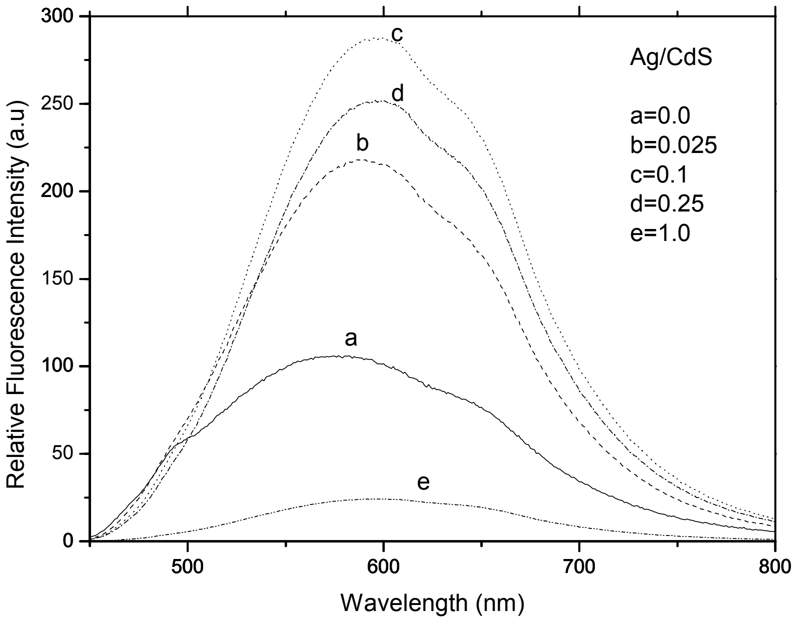


Figure S16. Emission spectra of GMP-templated β-Fe_2O_3/Ag/CdS nanohybrids containing varied [Ag] (mol dm^{-3}): $1x10^{-6}$ (a); $2.5x10^{-6}$ (b); $1x10^{-5}$ (c); $2.5x10^{-5}$ (d); $1x10^{-4}$ (e). pH=9.2 (λ_{ex}= 420 nm).

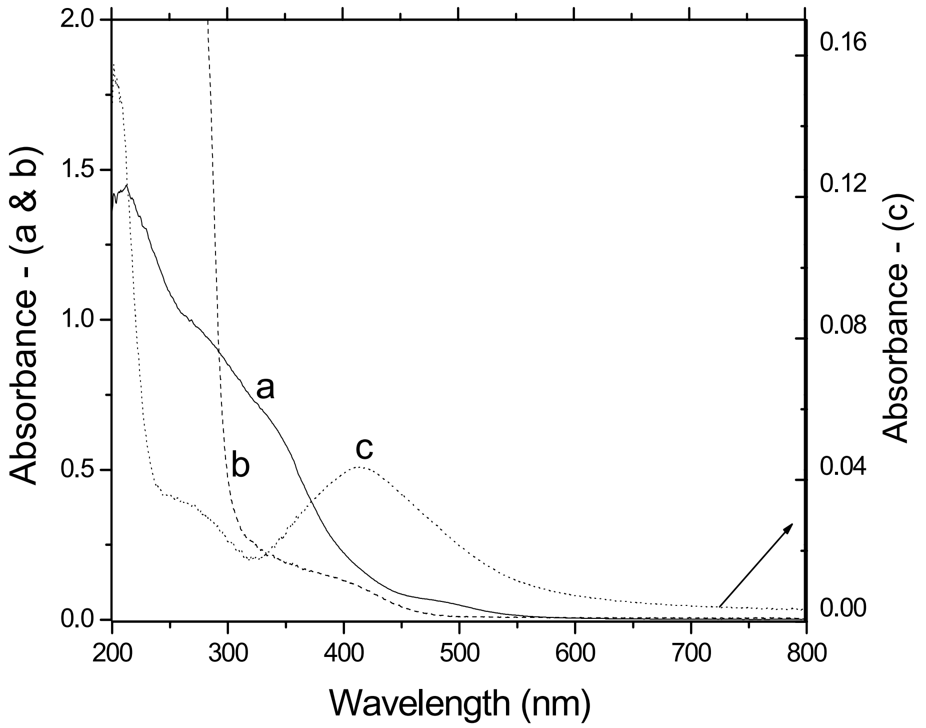


Figure S17. Optical absorption spectra of β-Fe_2O_3 (a), GMP-templated CdS (b), Ag nanoparticles (c), containing the amount as used for the synthesis of GMP-templated β-Fe_2O_3/Ag/CdS.