Nanomaterials-Based Light-Harvesting Systems for Potential Applications

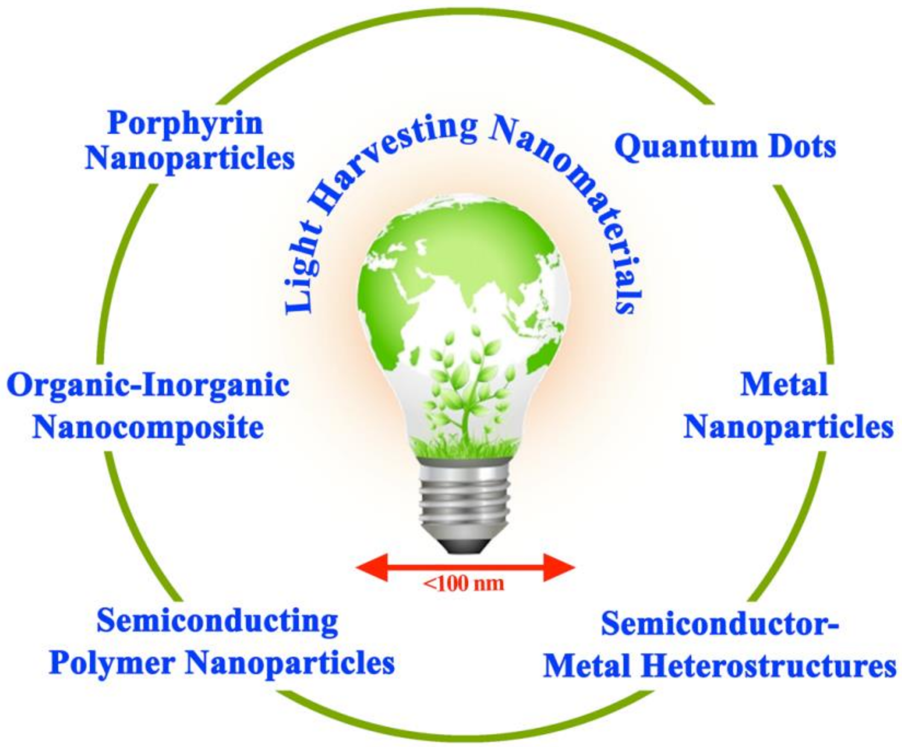
AMITAVA PATRA
Department of Materials Science
Indian Association for the Cultivation of Science
Kolkata 700 032, India

28th Mid-Year Meeting of the Indian Academy of Sciences
30th June – 1st July 2017,
Indian Institute of Science, Bengaluru

The development of the efficient artificial light harvesting system is a highly active area of research in order to mimic natural photosynthesis and convert solar energy into renewable energy.

Emphasis has been given to design and develop efficient nanomaterials based light harvesting Systems

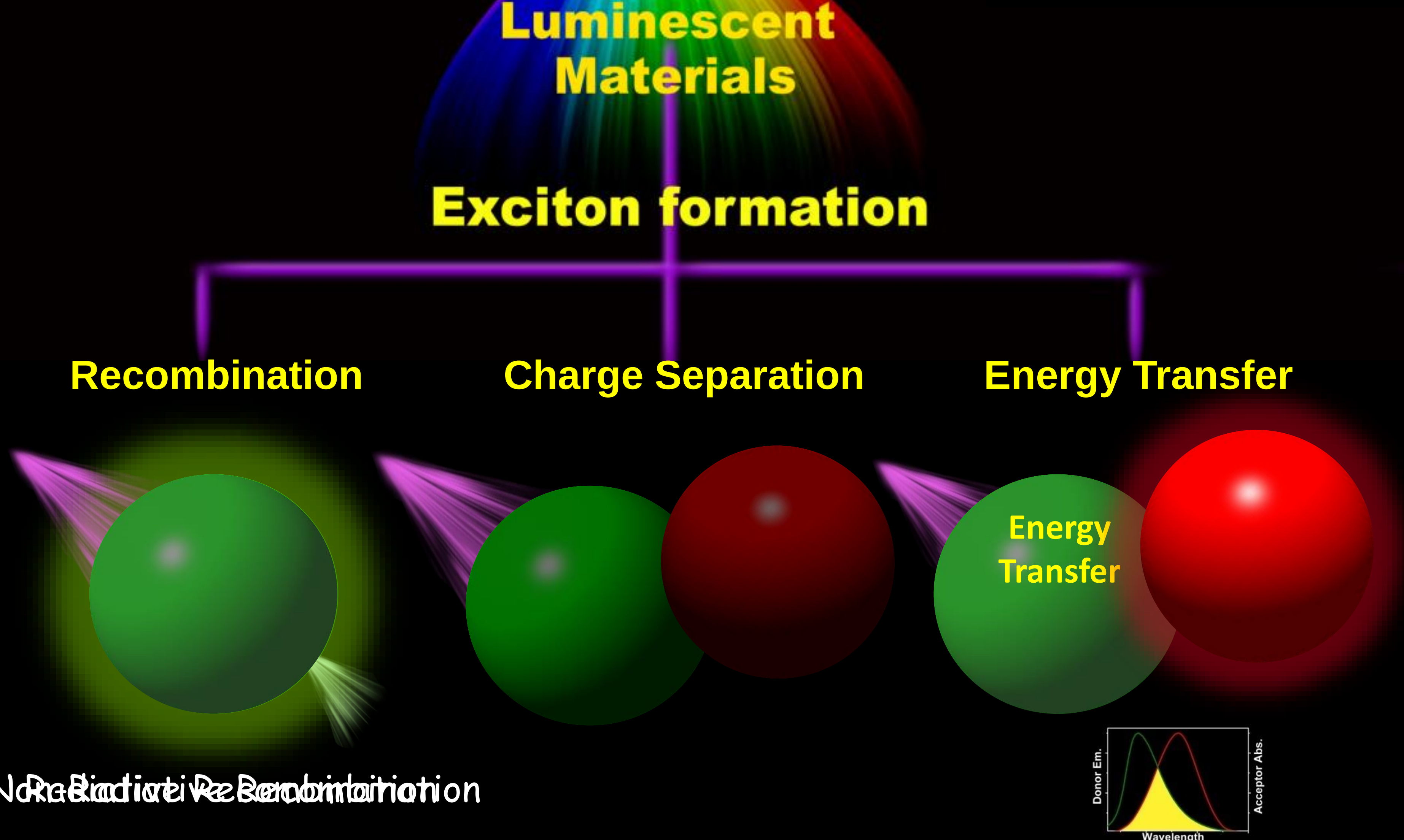
Several strategies have been undertaken…….



The efficient antenna system should have very high molar extinction co-efficient, excellent photostability and ability to transfer its energy.

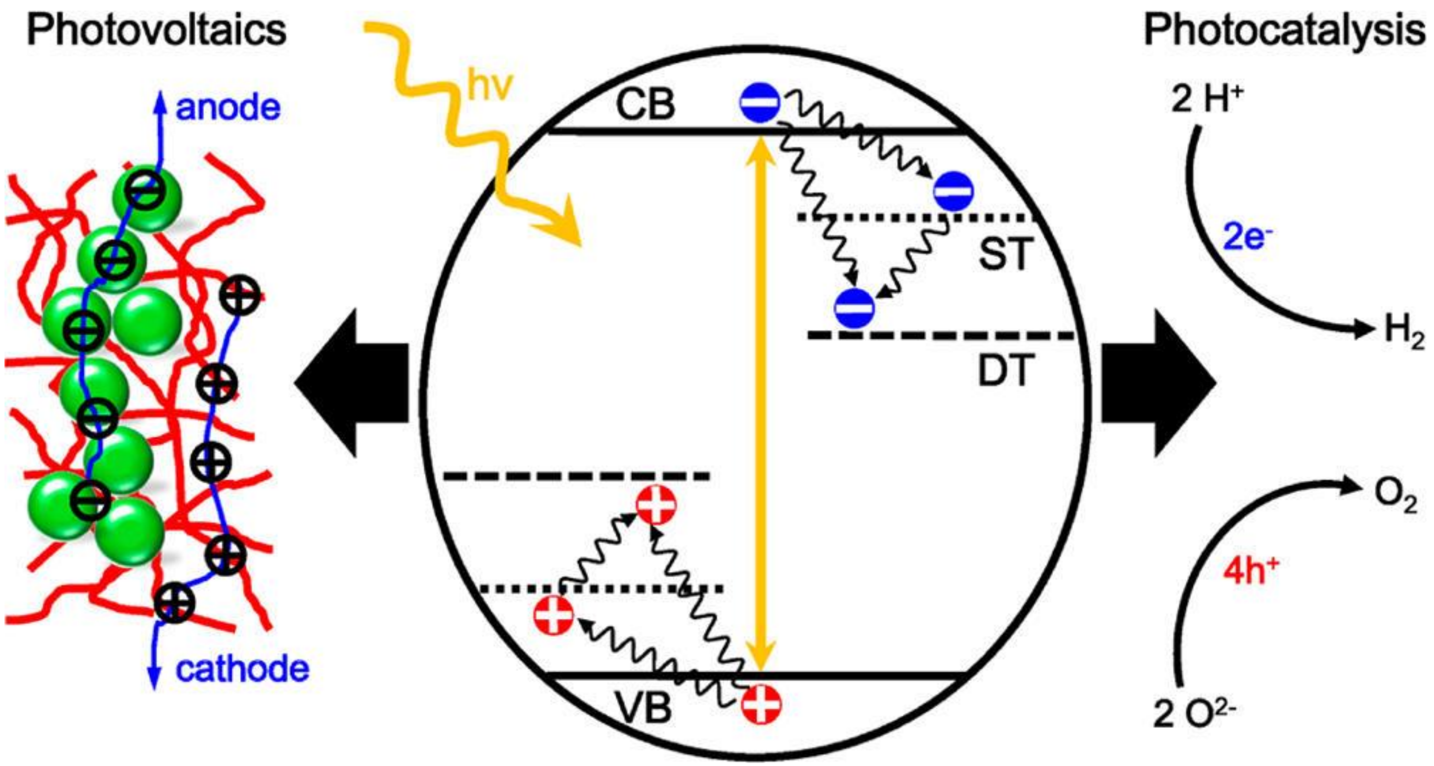
Most fundamental
processes in
Light harvesting systems:

- Exciton dynamics
- Charge transfer
- Energy Transfer



In the case of photovoltaic applications, photocurrent generation occurs due to charge migration of photo generated electrons and holes of semiconductor nanoparticles toward opposite electrodes.

However, the photo generated electrons and holes of semiconductor NP are used for reduction and oxidation reactions to facilitate chemical conversion in the case of photocatalysis.



Outline

- ❑ Exciton dynamics
- ❑ Interfacial charge transfer in hybrid system
- ❑ Energy transfer in hybrid system
- ❑ Conclusions

CHEMICAL REVIEWS

Review

pubs.acs.org/CR

Nanoscale Strategies for Light Harvesting

Simanta Kundu and Amitava Patra*

Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

ABSTRACT: Recent advances and the current status of challenging light-harvesting nanomaterials, such as semiconducting quantum dots (QDs), metal nanoparticles, semiconductor−metal heterostructures, π-conjugated semiconductor nanoparticles, organic−inorganic heterostructures, and porphyrin-based nanostructures, have been highlighted in this review. The significance of size-, shape-, and composition-dependent exciton decay dynamics and photoinduced energy transfer of QDs is addressed. A fundamental knowledge of these photophysical processes is crucial for the development of efficient light-harvesting systems, like photocatalytic and photovoltaic ones. Again, we have pointed out the impact of the metal-nanoparticle-based surface energy transfer process for developing light-harvesting systems. On the other hand, metal−semiconductor hybrid nanostructures are found to be very promising for photonic applications due to their exciton−plasmon interactions. Potential light-harvesting systems based on dye-doped π-conjugated semiconductor polymer nanoparticles and self-assembled structures of π-conjugated polymer are highlighted. We also discuss the significance of porphyrin-based nanostructures for potential light-harvesting systems. Finally, the future perspective of this research field is given.

Exciton Dynamics

Issues:

•How the shape, size and composition of QDs influence the carrier relaxation dynamics of photo-excited QDs.

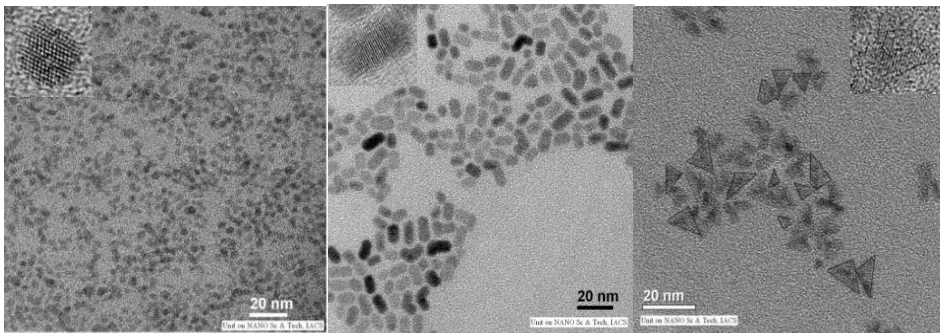
•How the surface trap state influences decay kinetics due to surface curvature and lattice strain

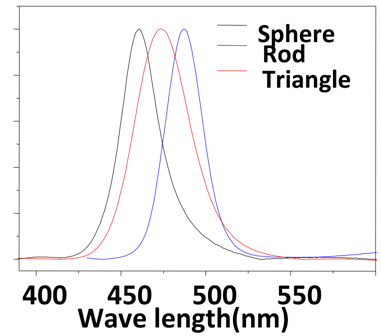
•A stochastic model of carrier relaxation dynamics of QDs has been proposed.

Relaxation Dynamics of Anisotropic Shaped CdS Nanoparticles

Suparna Sadhu and Amitava Patra*

Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata-700 032, India

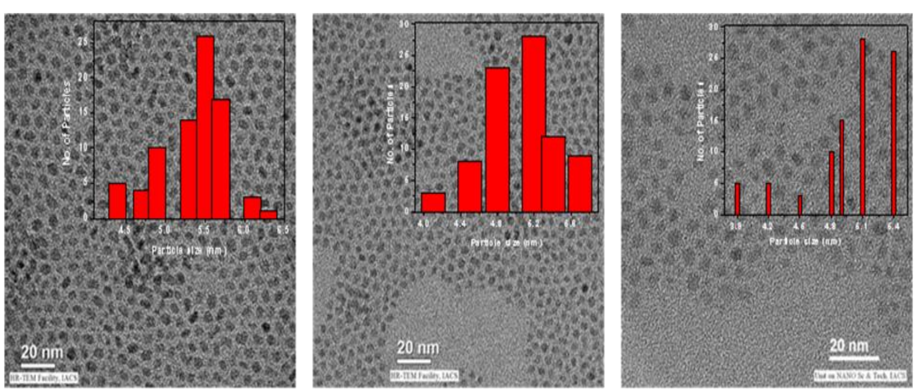




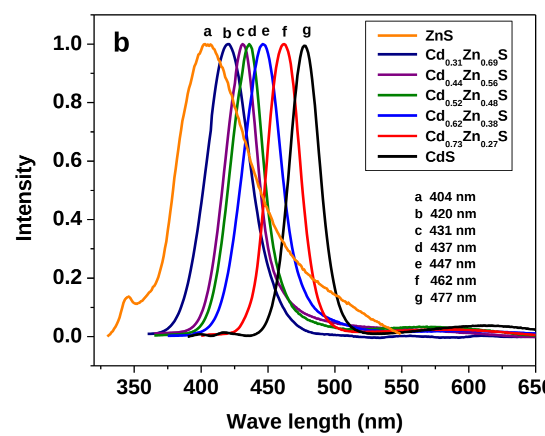
Lattice Strain Controls the Carrier Relaxation Dynamics in $Cd_xZn_{1-x}S$ Alloy Quantum Dots

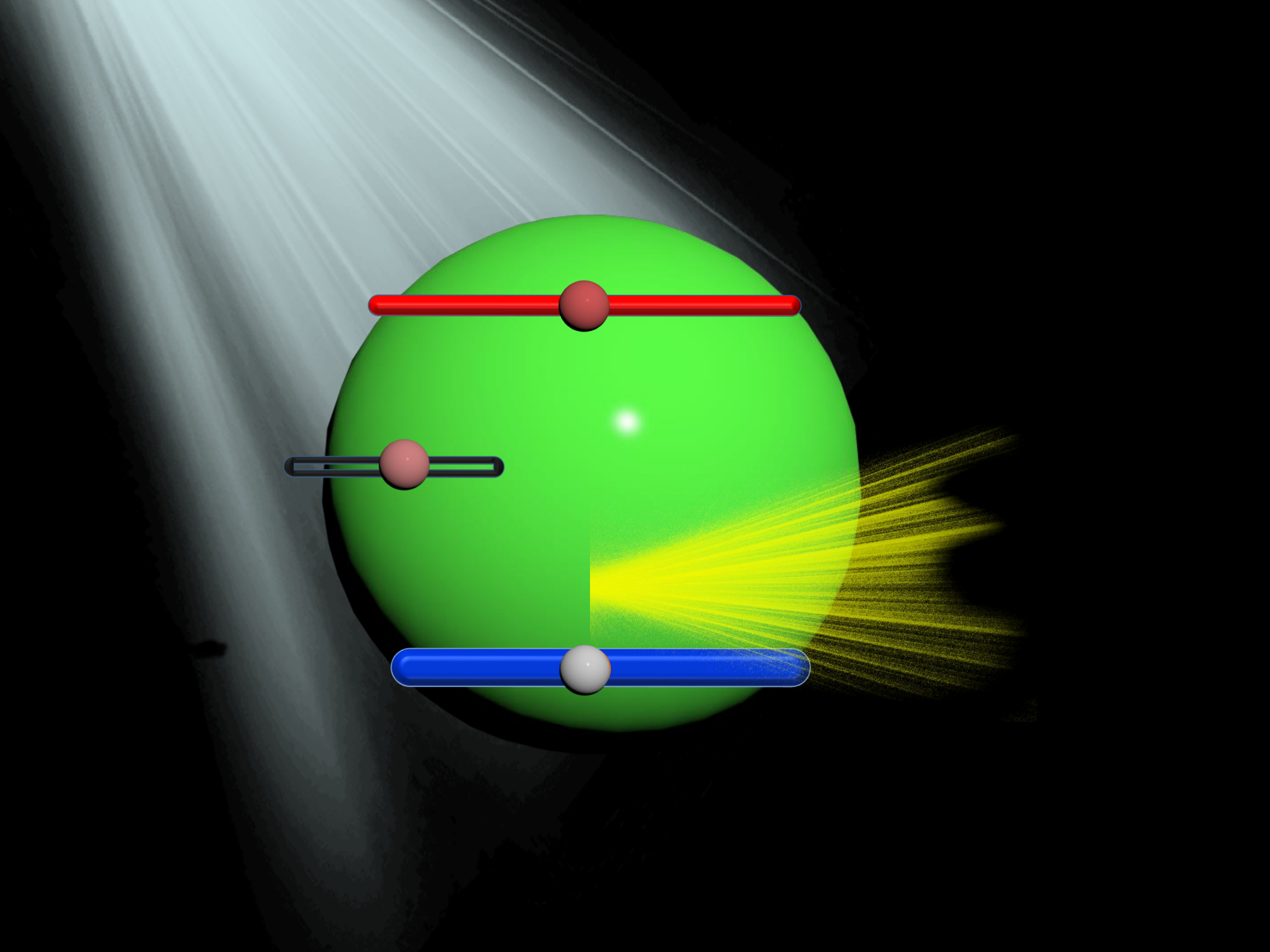
Suparna Sadhu and Amitava Patra*

Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata-700 032, India

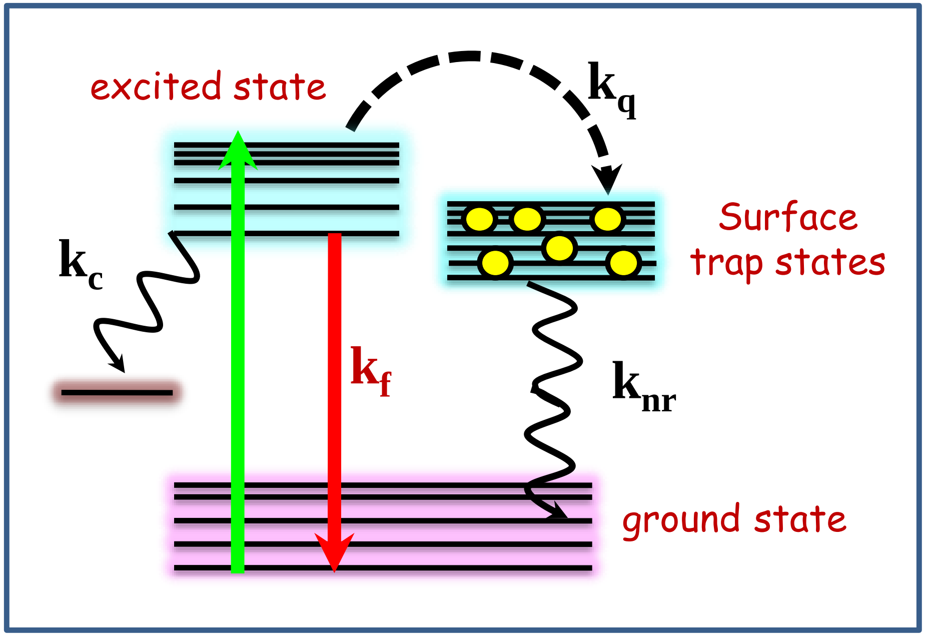


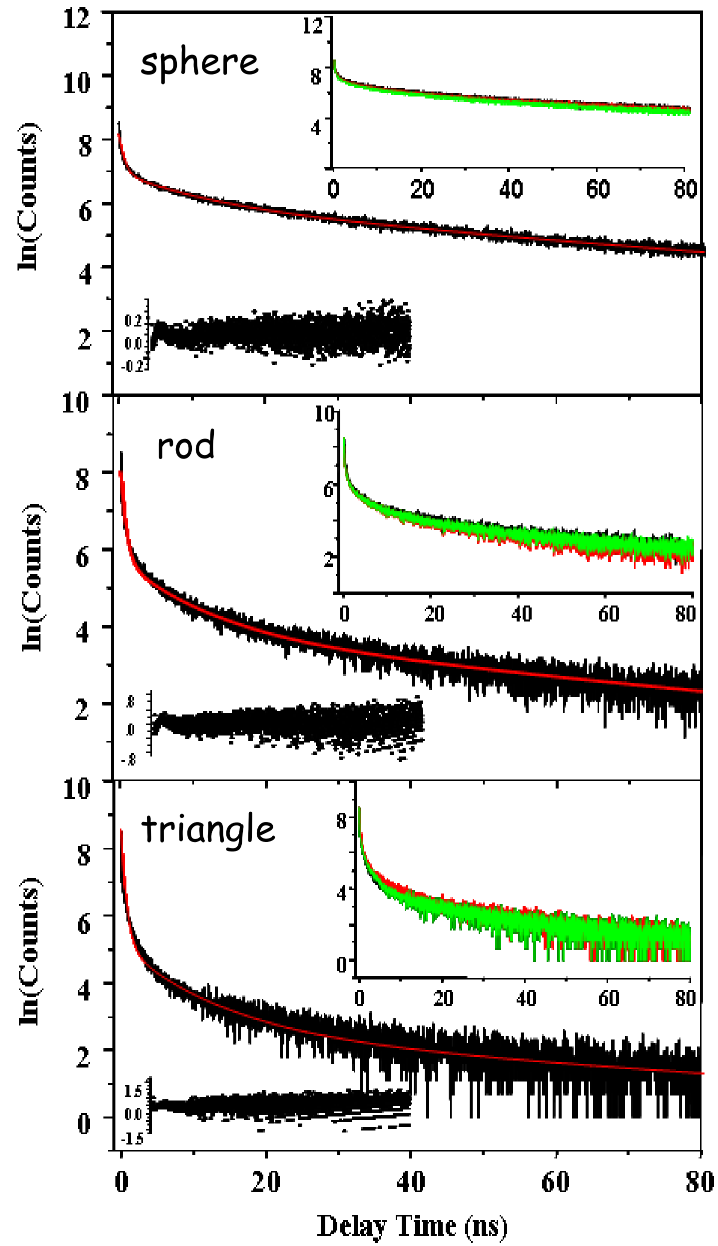
$Cd_{0.73}Zn_{0.27}S$ $Cd_{0.62}Zn_{0.38}S$ $Cd_{0.52}Zn_{0.48}S$





Stochastic model for decay dynamics:





Assumption:

- The number of surface traps present on the NCs surface follows Poisson distribution

$$\Phi(n) = (m^n / n!) \exp(-m)$$

The ensemble averaged decay curve

$$I_t = I_0 \sum_{n_t=0}^{\alpha} \sum_{n_t'=0}^{\alpha} \Phi(n_t)\Phi(n_t') \exp[-\{Ak_f + B(k_c + n_t k_q) + n'_t k_{nr}\}t]$$

n_t = the number of surface trap states participate in luminescence quenching

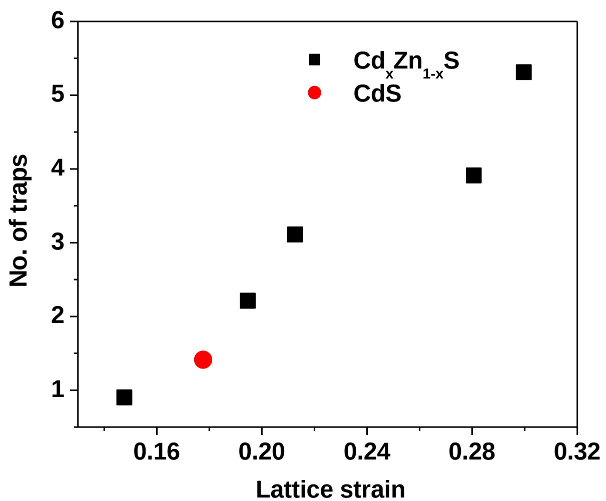
m_t average number of surface traps in quenching; $m_{t'}$ average number of surface sites for NR

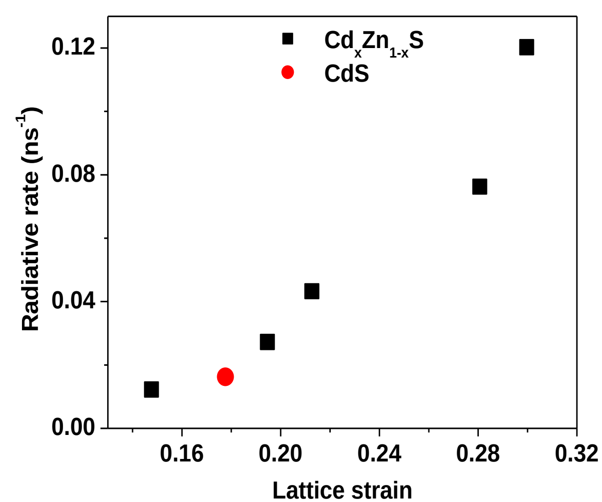
Overview of the values of carrier relaxation parameters using Stochastic Model

System	χ^2	A	k_f (ns^{-1})	B	k_c	m_t	k_q (ns^{-1})	m_t'
Sphere	0.97	0.029	0.151	0.098	0.13	11.2	1.27	1.1
Rod	0.91	0.017	0.129	0.119	0.132	21.9	1.29	1.99
Triangle	0.87	0.020	0.093	0.129	0.128	34.5	1.23	2.5

m_t average number of surface traps;
$m_{t'}$ average number of surface sites for NR relaxation

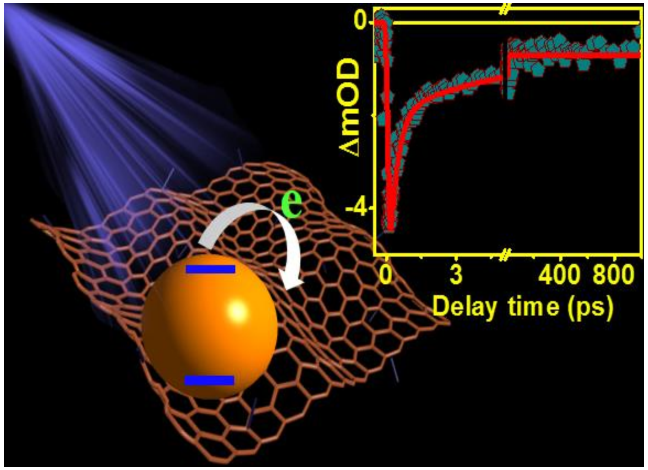
n_t = the number of surface trap states participate in luminescence quenching

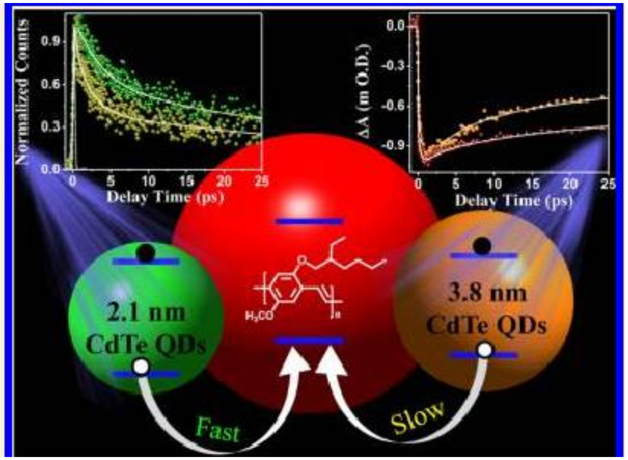


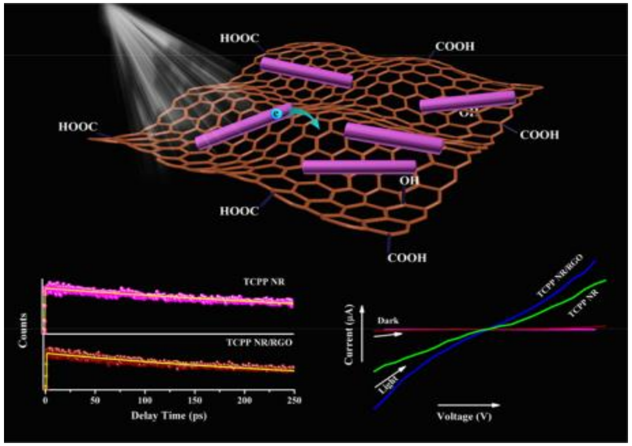


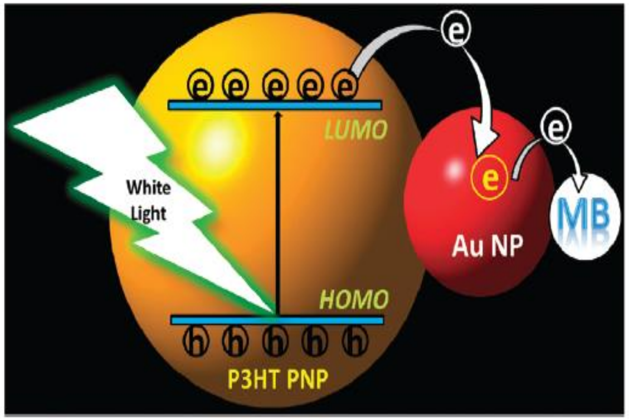
❑ Interfacial Charge Transfer in Hybrid Systems

- ➢ Photoinduced Electron Transfer
- ➢ Photoinduced Hole Transfer

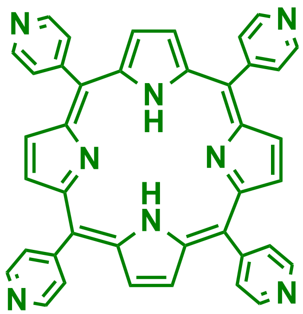




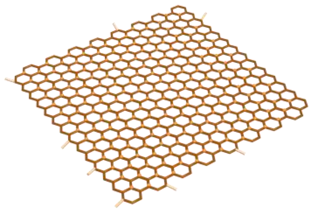




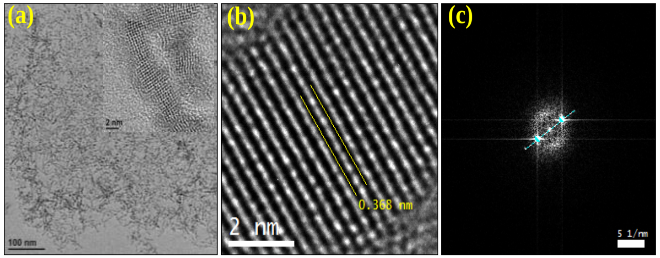
Electron Transfer Process in QD-Porphyrin-GO Hybrid System



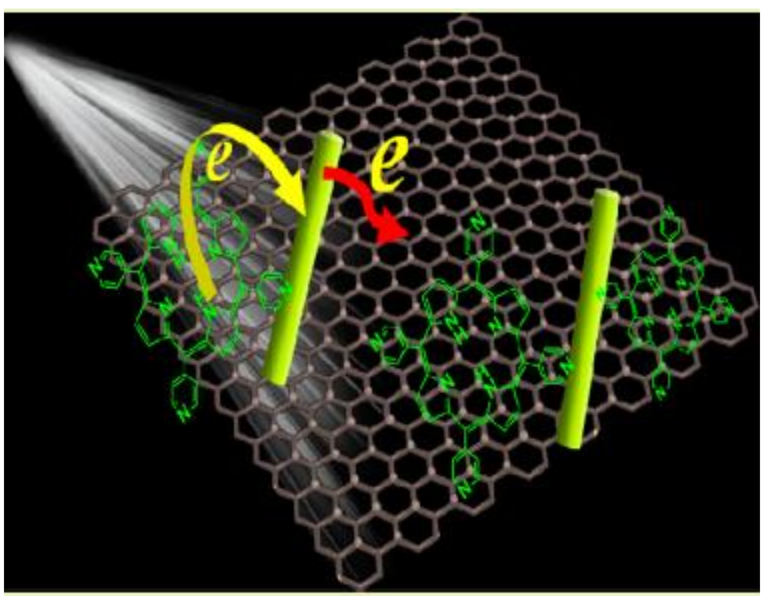
Porphyrin

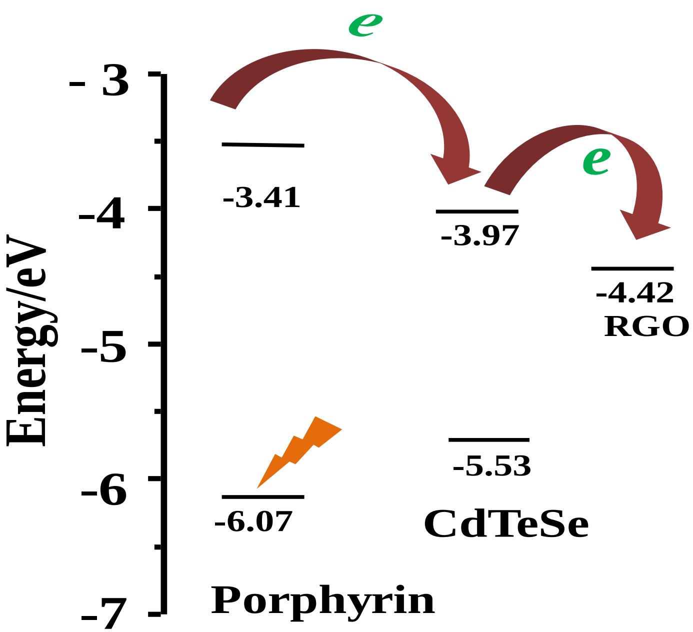


Reduced Graphene Oxide(RGO)



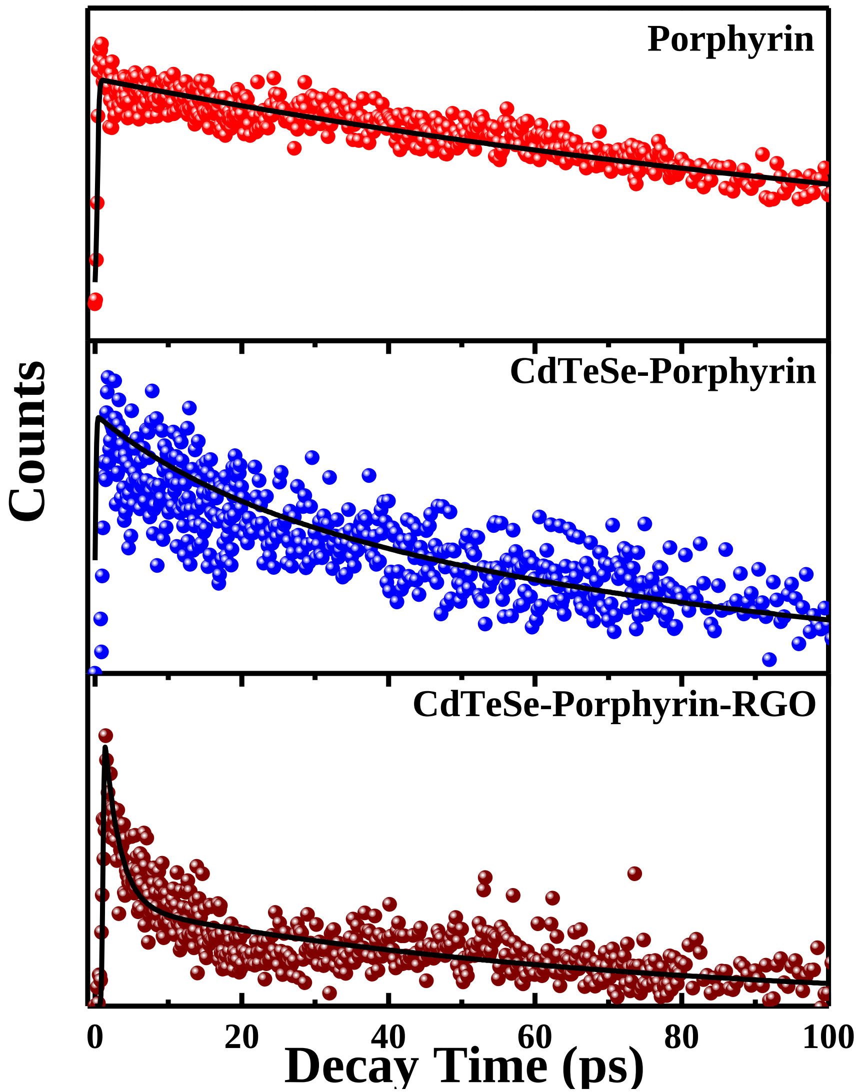
TEM images of CdTeSe



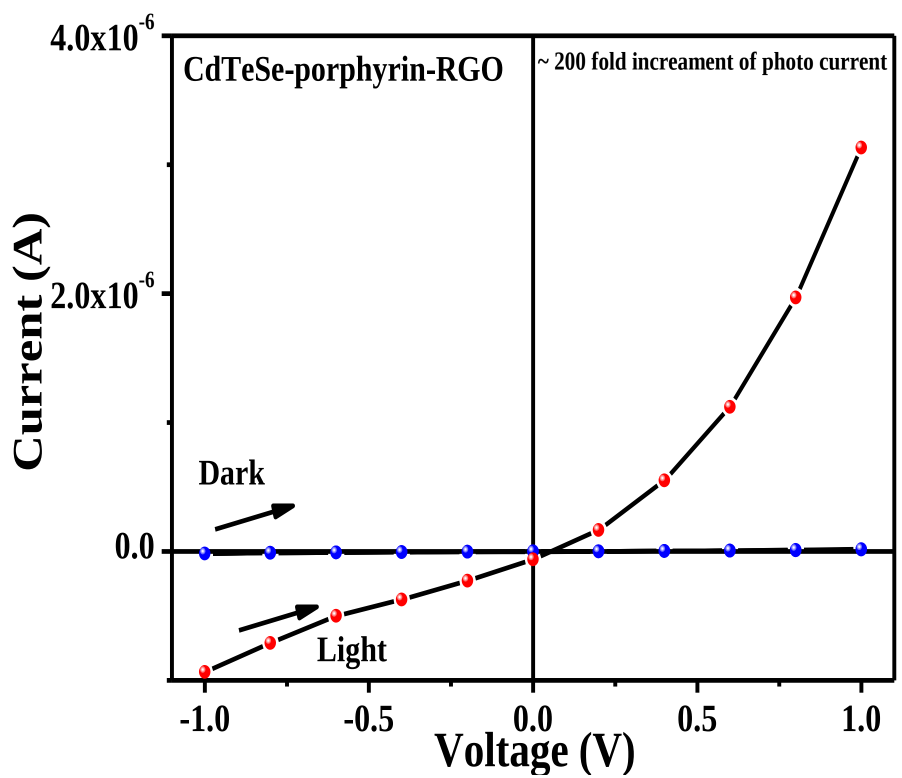


ACS Sustainable Chem. Eng. 2017, 5, 3002−3010

Ultrafast electron transfer process

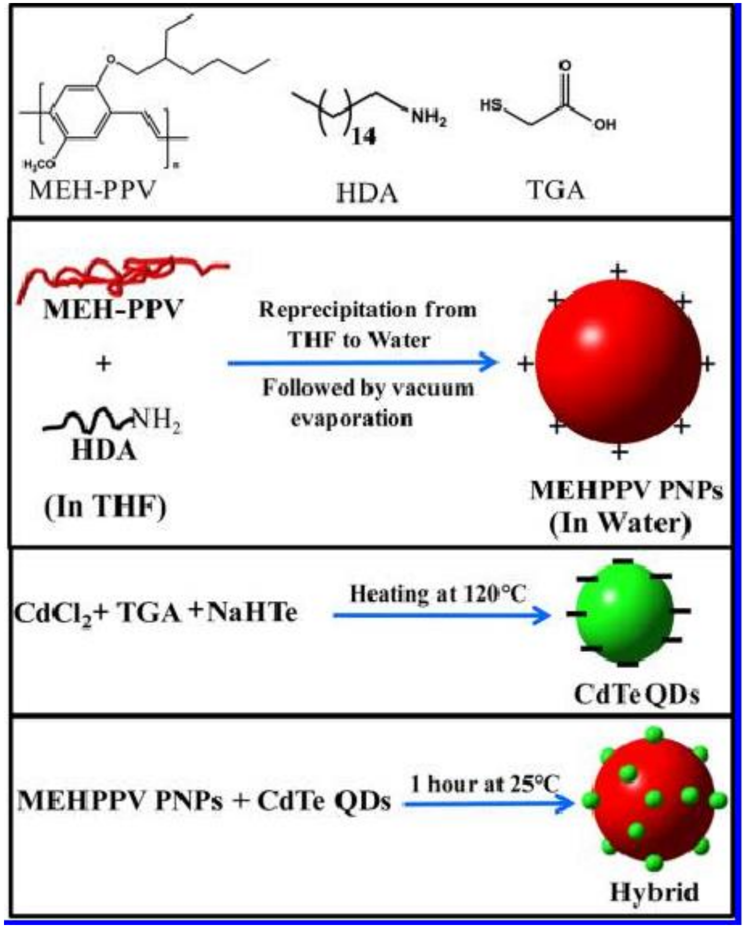


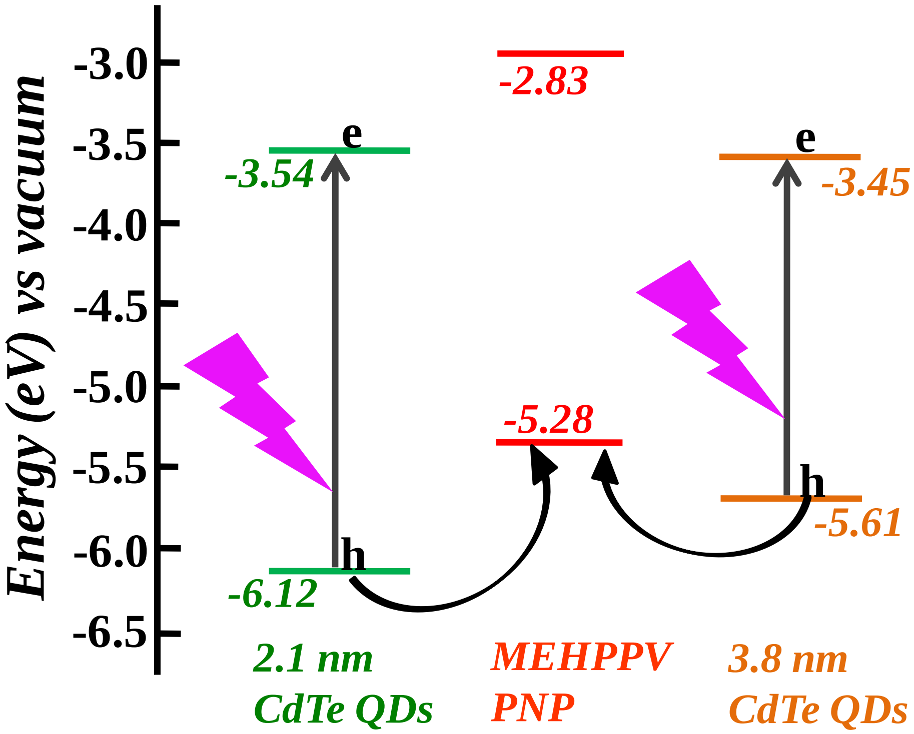
System	τ_1 (a_1) (ps)	τ_2 (a_2) (ps)
Porphyrin	-	195
Porphyrin/CdTeSe	25.22 (0.45)	174 (0.55)
Porphyrin/CdTeSe/RGO (0.2 ml)	5.58 (0.44)	206 (0.56)



Electron transfer rate is 17.4 x 10-2 ps-1

Hole Transfer Process between CdTe QD-MEHPPV Polymer NP



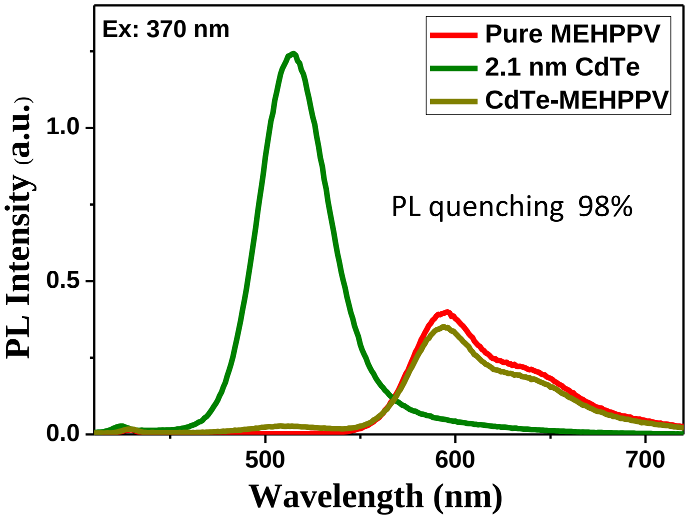


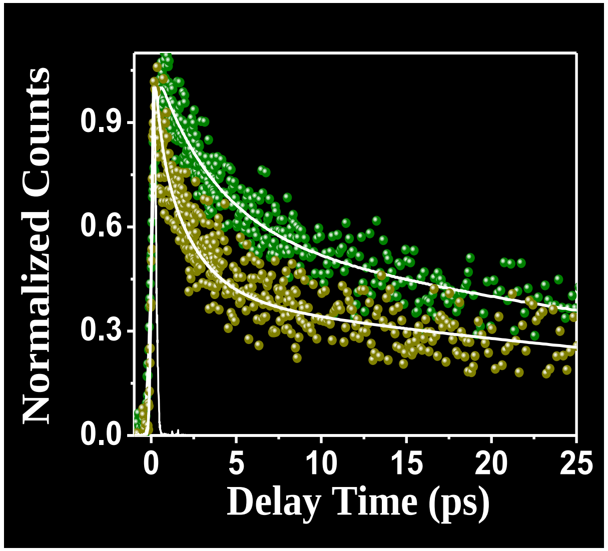
MEH-PPV: poly[2-methoxy-5-(2-ethylhexyloxy)-1,4phenylenevinylene
HDA: Hexadecylamine
TGA : Thioglycolic acid

J. Phys. Chem. C 2016, 120, 25142–25150.

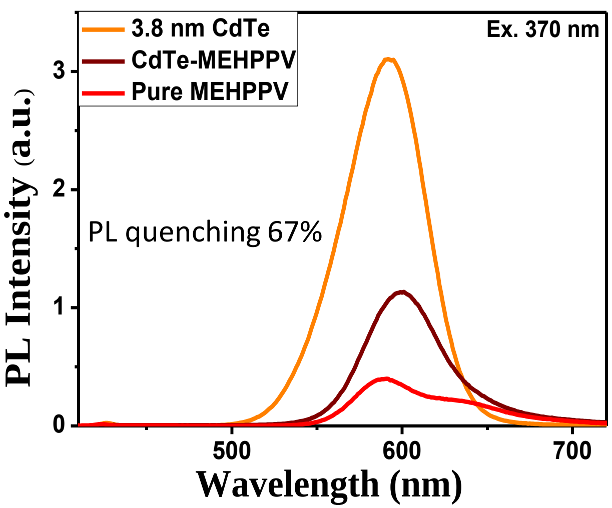
Spectroscopic study of Hybrid Nano-composite

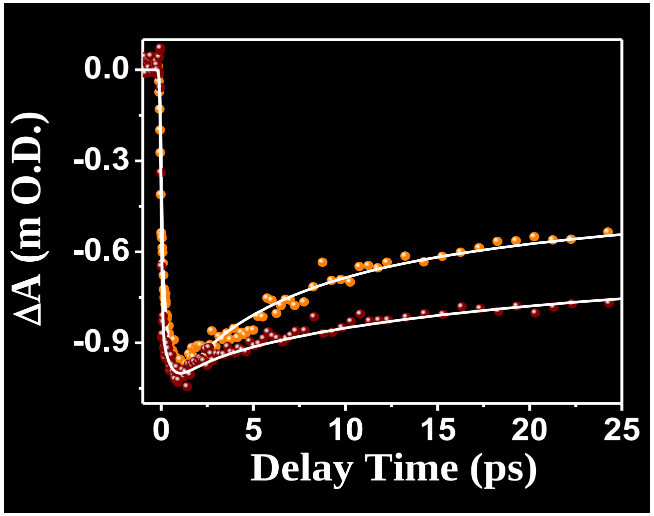
Composite with 2.1 nm QDs:





Composite with 3.8 nm QDs

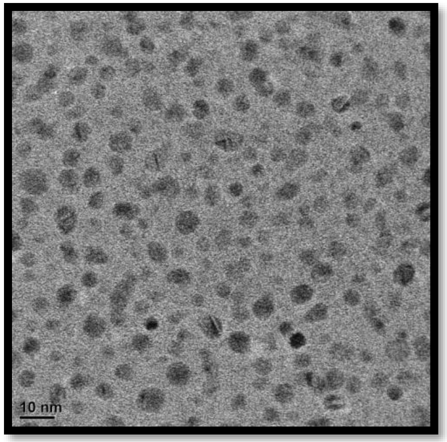




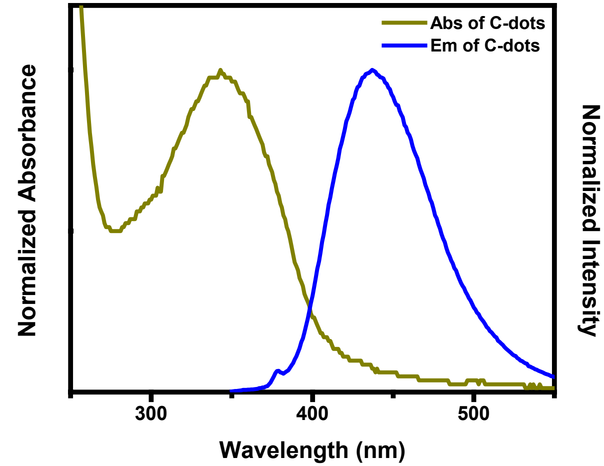
Hole Transfer from 2.1 QDs to PNP is 390 fs
Hole transfer from 3.8 nm QD to PNP is 120 ps

Electron and Hole Transfer Processes in C-dots-ZnO Nanocrystals

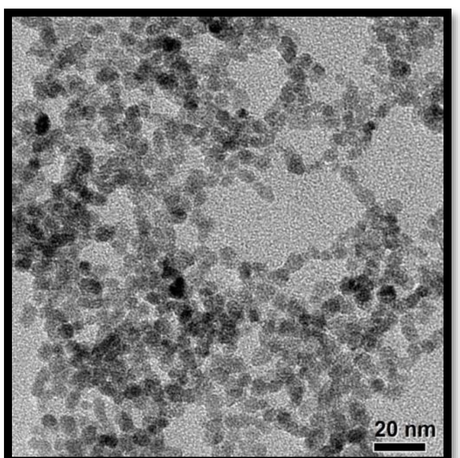
Carbon dots



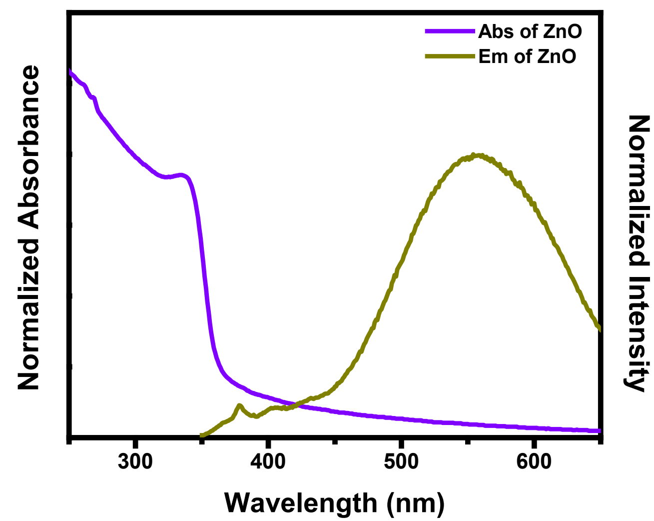
particles are nearly mono-dispersed and ~5 nm in size with blue emission at 440 nm



Zinc Oxide Nanoparticles



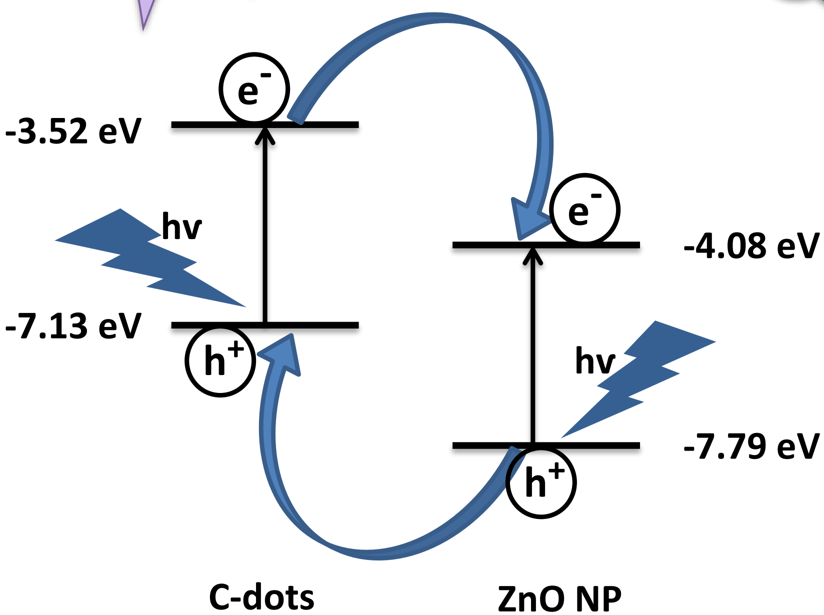
Mono-dispersed nearly 5-6 nm ZnO NPs show a yellow emission at ~550 nm

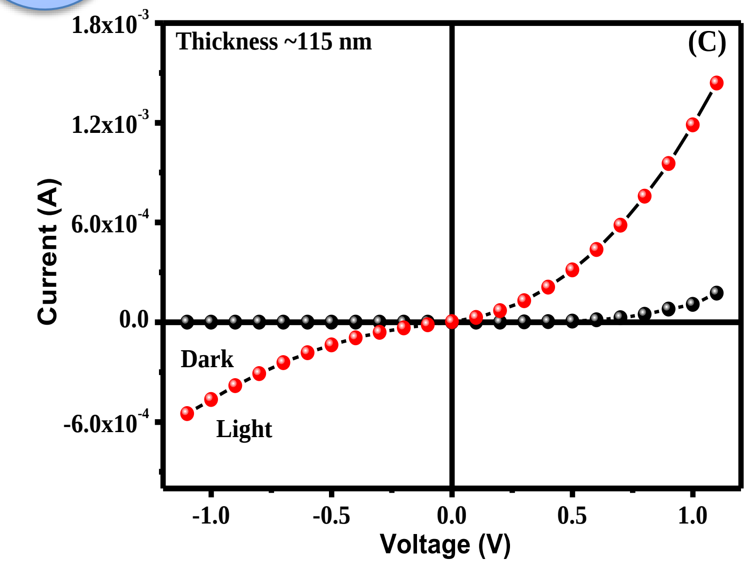


Nanoscale, 2017, 9, 6791–6799

Photoinduced Charge Separation

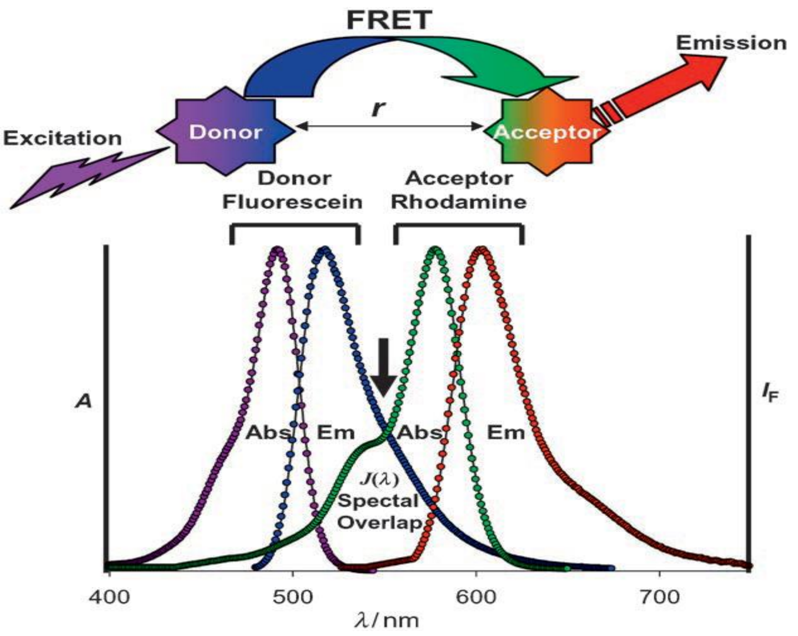
Thickness dependent study reveals that ~115 nm thickness produces the highest 11 fold photocurrent





- The excited electron transfers from LUMO of C-dot to the conduction band of ZnO NP with a rate of $3.7 \times 10^9\ s^{-1}$
- Hole transfers from valence band of ZnO to HOMO of C-dot with a rate of $3.6 \times 10^7\ s^{-1}$.

Nanoparticles-Based Energy Transfer



$$k_T(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

$$R_0 = 0.211\left[\kappa^2 n^{-4} \phi_{dye} J(\lambda)\right]^{1/6}$$

$$E = \frac{nR_0^6}{nR_0^6 + r_n^6}$$

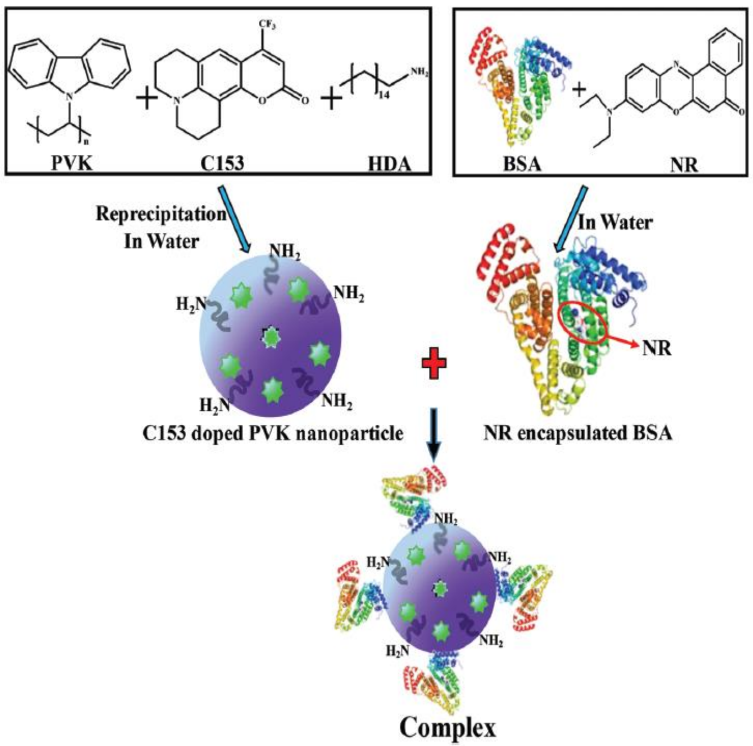
✓The <u>large size of QD's</u> compared to organic dyes provided design of such configuration where <u>multiple acceptors</u> could interact with a single donor, which <u>enhances FRET efficiency</u> and thus measurement sensitivity.

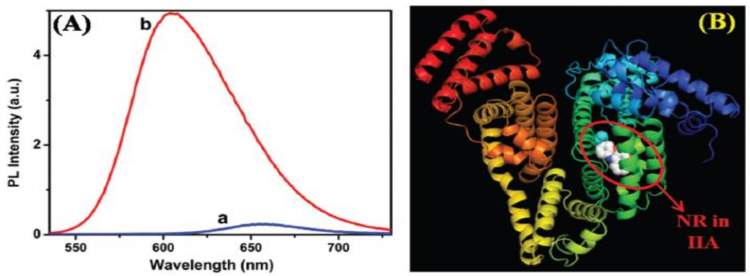
Issues:
<u>Size,</u> Shape & Composition Dependent Energy Transfer
FRET or Non-Forster?
Quenching dynamics
Kinetic model

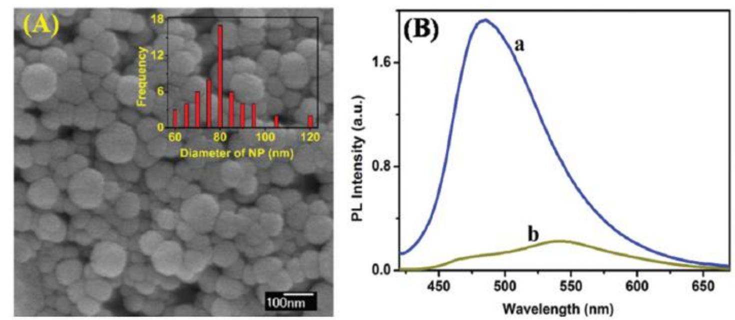
Cite this: *Nanoscale*, 2016, **8**, 16034

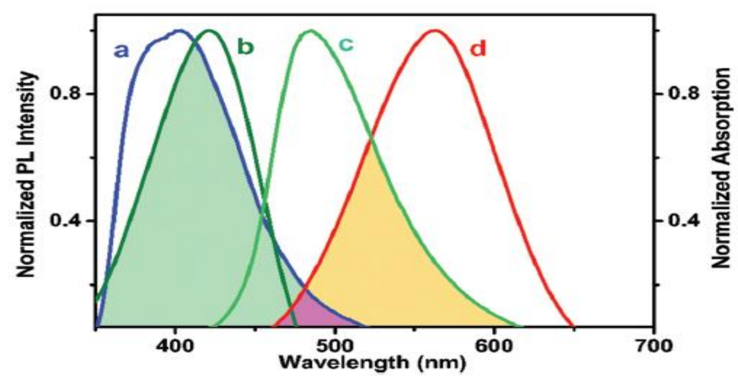
Functionalized dye encapsulated polymer nanoparticles attached with a BSA scaffold as efficient antenna materials for artificial light harvesting†

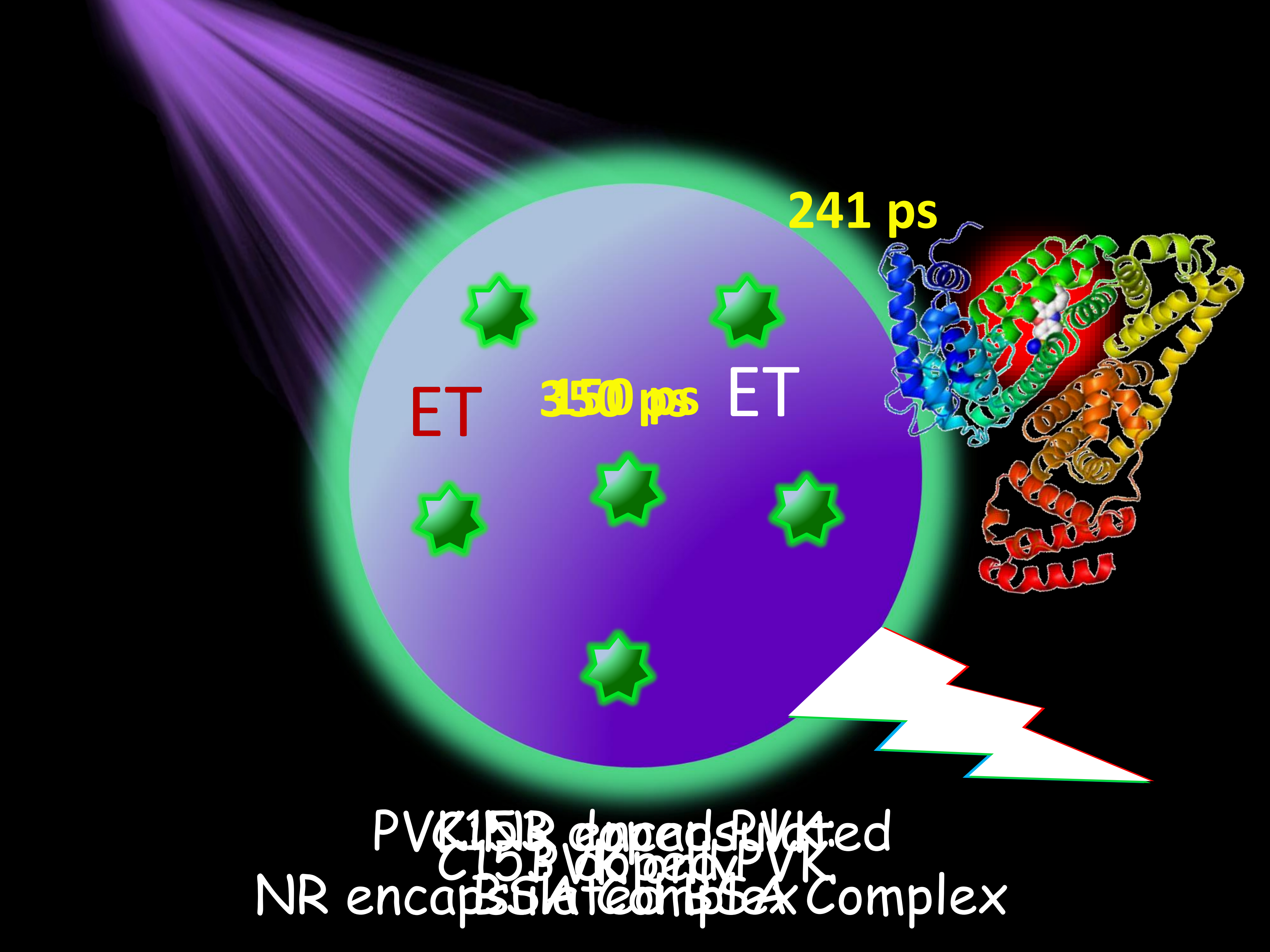
Bikash Jana, Santanu Bhattacharyya and Amitava Patra*










241 ps
ET
ET

Estimation of Antenna Effect and effective absorption coefficient

Antenna Effect, $$AE = (I_{DA340} \cdot f - I_{A340})/I_{A525}$$

$$\varepsilon_{eff} = AE \times \varepsilon_A$$

I_{DA340} and I_{A340}, I_{A525} are emission intensity of NR encapsulated BSA in presence and absence of PVK (λ_{ex}340 nm, λ_{ex}525 nm). ‘f’ represents the fraction of the total fluorescence coming from the encapsulated NR dye molecules due to energy transfer process. ε_A is the maximum absorption coefficient of the acceptor.

Table 2 Light harvesting properties of NR (0.64 μM) in two complexes

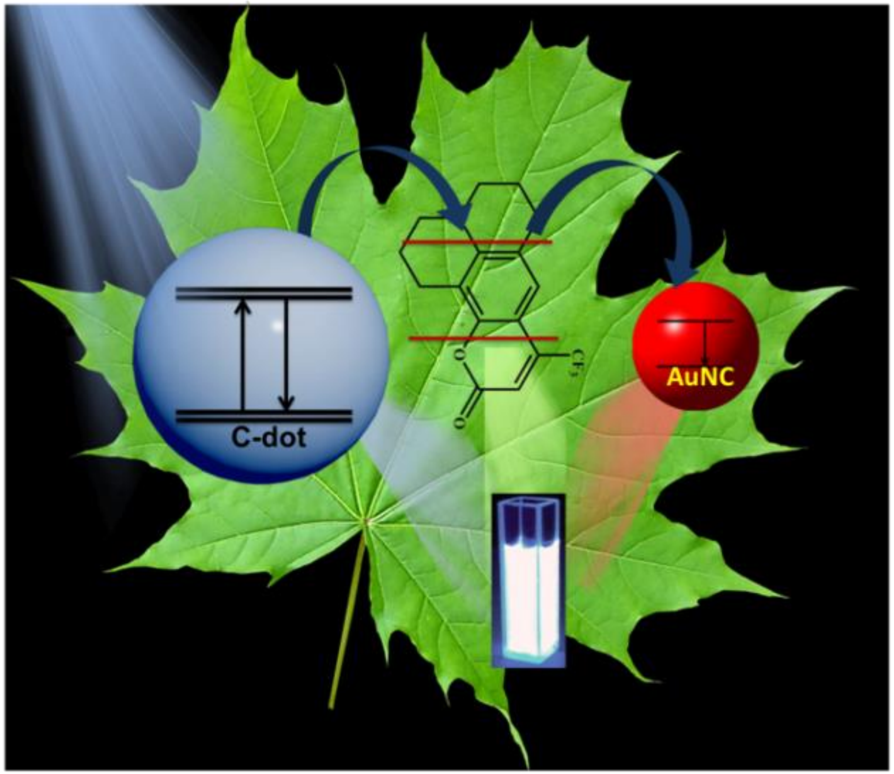
System	Antenna effect	Effective extinction coefficient ($10^4 \times M^{-1}\ cm^{-1}$)
PVK NP–NR dye encapsulated BSA	28	73.10
C153 doped PVK NP–NR dye encapsulated BSA	31	80.93

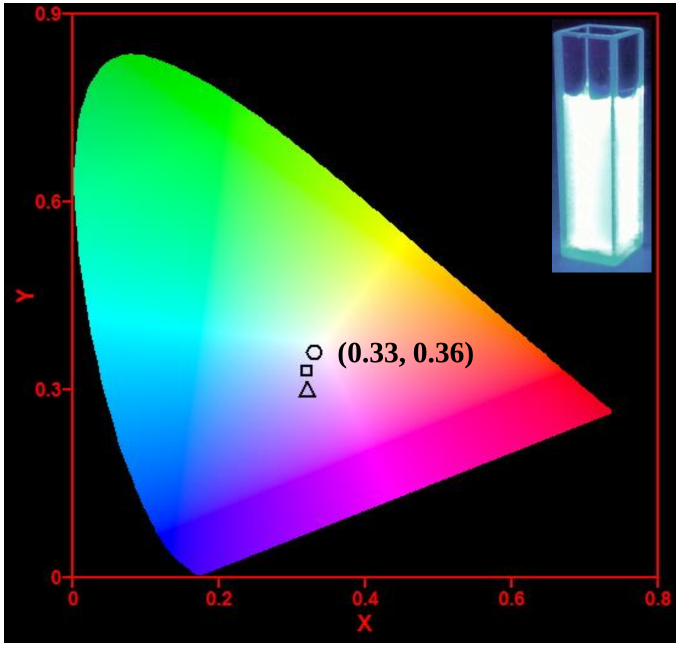
ChemPubSoc Europe
DOI: 10.1002/chem.201601849
CHEMISTRY A European Journal
Full Paper

Light Harvesting and Generation |*Hot Paper*|

Light Harvesting and White-Light Generation in a Composite of Carbon Dots and Dye-Encapsulated BSA-Protein-Capped Gold Nanoclusters

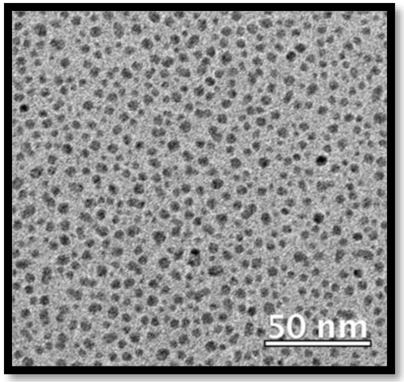
Monoj Kumar Barman, Bipattaran Paramanik, Dipankar Bain, and Amitava Patra*[a]

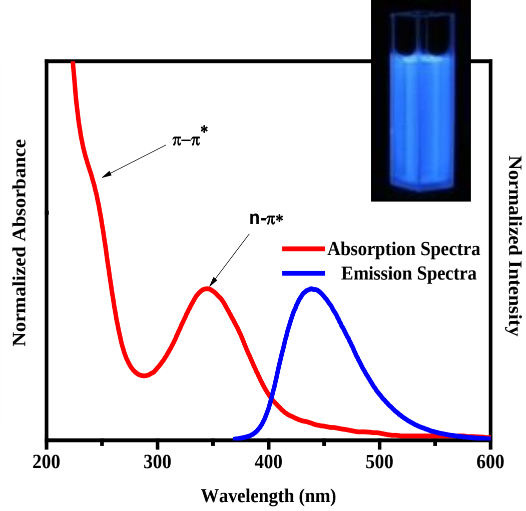




Carbon dots:

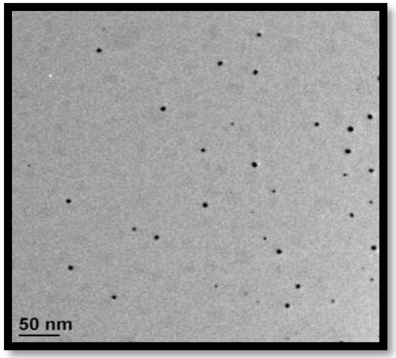
❖ Carbon dots were synthesized hydrothermally using citric acid and Polyethylenimine, branched (BPEI).

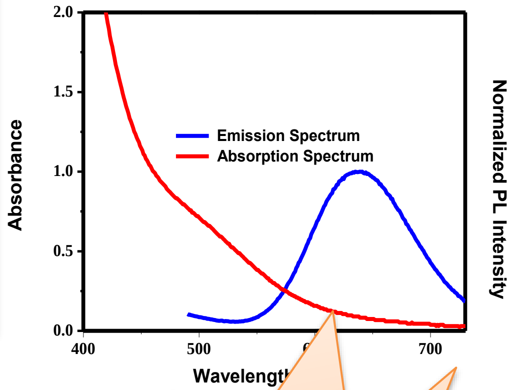


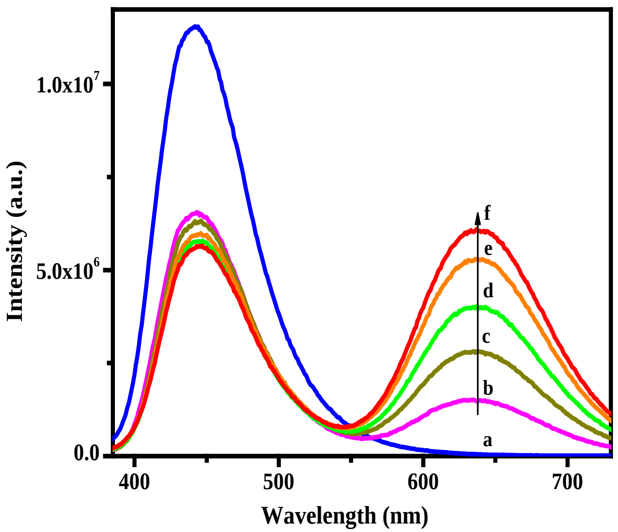


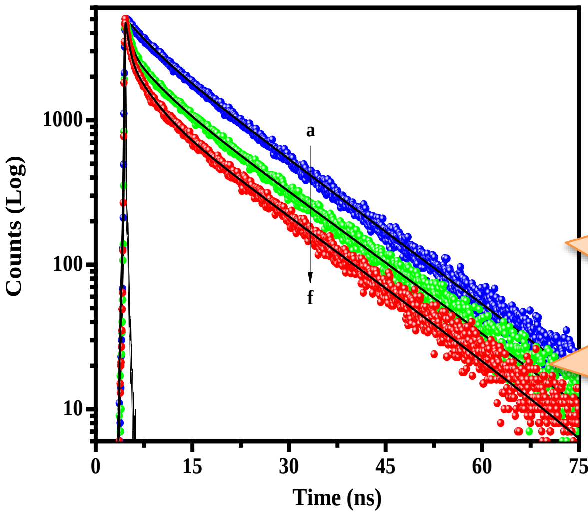
Protein capped Gold nanocluster:

Gold nanocluster (Au NC) capped by BSA protein, were synthesized using BSA and $HAuCl_4$ under basic condition (pH ≈ 11).

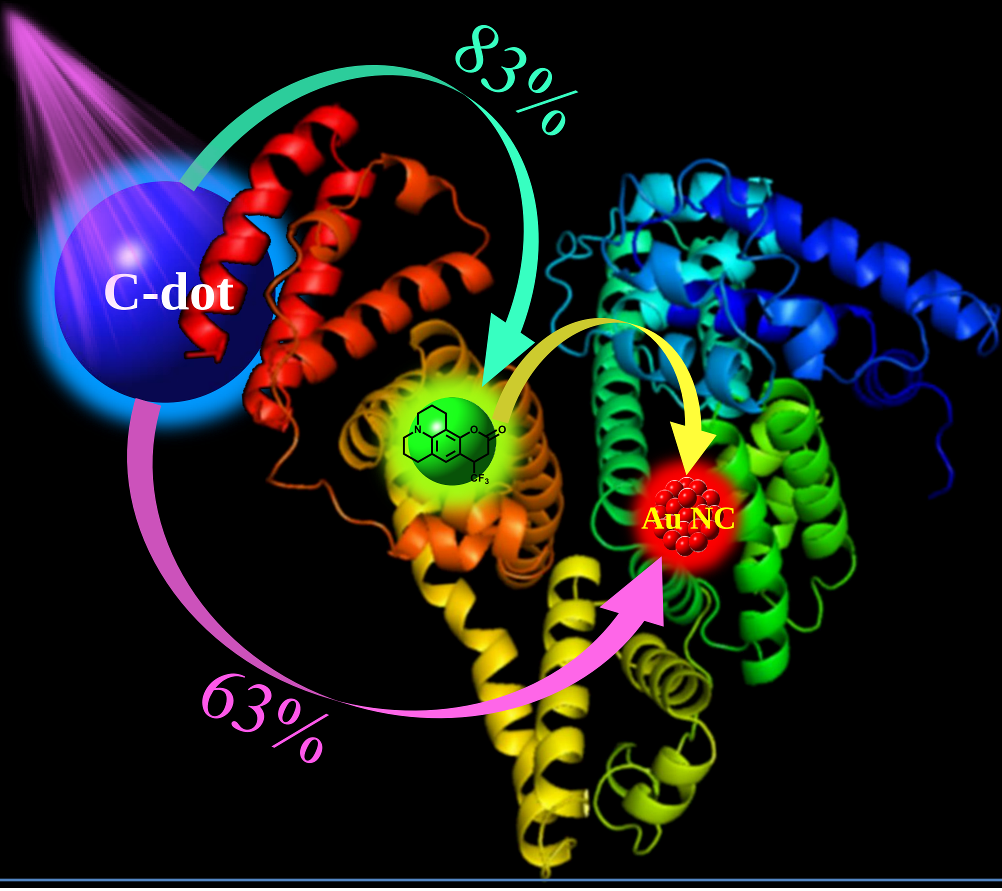


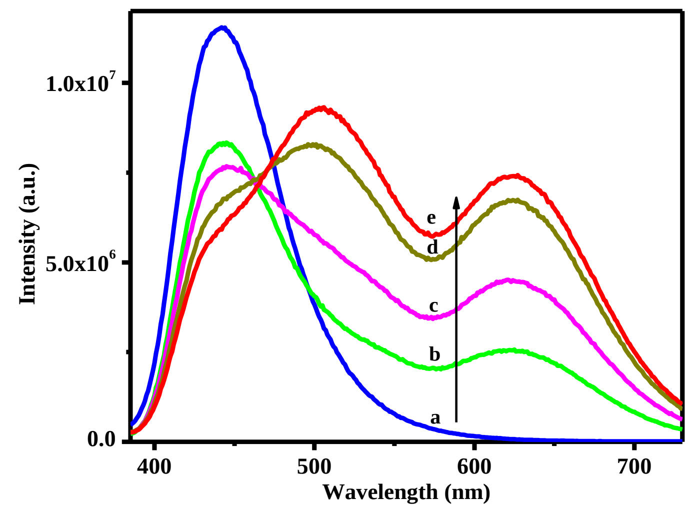






63% energy transfer
NEED MODIFICATION





Systems	τ_1 (α_1) ns	τ_2 (α_2) ns	τ_3 (α_3) ns	<τ> ns	Energy Transfer Efficiency (%)	Rate of Energy Transfer (s^{-1})
C-dots		4.03 (0.28)	13.07 (0.72)	10.54		
C-dot-Au NC	0.47 (0.56)	3.05 (0.22)	13.14 (0.22)	3.83	**63.00**	1.66×10^8
C-dot-C153-Au NC	0.31 (0.77)	2.39 (0.13)	12.78 (0.10)	1.82	**83.00**	4.50×10^8

CONCLUSIONS

❑ The fundamental understanding of luminescent nanomaterials remains a frontier area of research because of potential applications in light harvesting systems.

❑Interesting findings reveal that the charge transfer between QD's- polymer NP and C dots-ZnO composites may open up new possibilities in designing of artificial light harvesting system for future applications.

❑Interesting findings reveal that the efficient energy transfer in polymer nanoparticle- dye assemblies may open up new possibilities in designing of artificial light harvesting system for future applications.

❑C-dots and Au cluster based materials for light harvesting

Acknowledgements

DAE-SRC Outstanding Investigator Award
Unilever Industries private limited, Bangalore

Present Students:

1. B. Paramanik, SRF
2. M. Barman, SRF
3. Rajesh Bera, SRF
4. Bikash Jana, SRF
5. Bodhisatwa Mondal, JRF
6. Dipankar Bain, JRF
7. Arnab Ghosh, JRF
8. Miss Subarna Maity , JRF
9. Avisek Dutta, JRF
10. Goutam Ghosh, JRF

1. Dr. Piyali Mitra, National Post Doctoral Fellowship, DST.
2. Dr. Soma Das, National Post Doctoral Fellowship, DST.


"And miles to go before I sleep.."

ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Design of CdTeSe–Porphyrin–Graphene Composite for Photoinduced Electron Transfer and Photocurrent Generation

Rajesh Bera, Bikash Jana, Bodhisatwa Mondal, and Amitava Patra*

Department of Materials Science, Indian Association for the Cultivation of Science, 2A & B Raja S.C. Mullick Road, Jadavpur, Kolkata 700 032, India

Decay dynamics in anisotropic shaped CdS nanocrystals

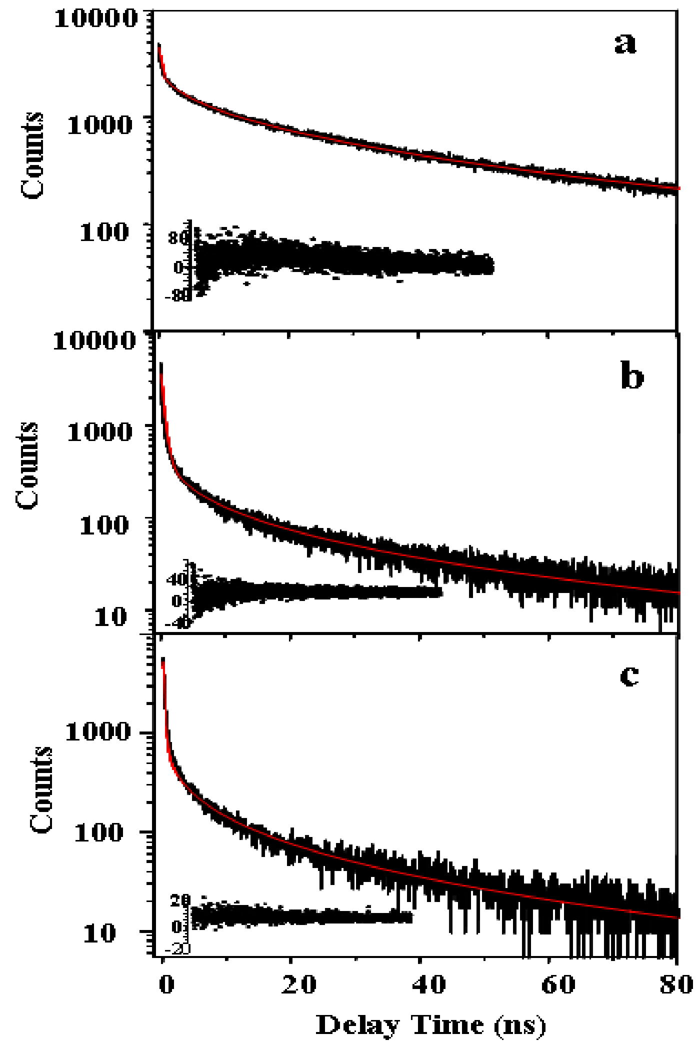
The decay curves of different shaped CdS QDs are analyzed by stretched exponential function.

$$I(t) = a\exp(-[t/\tau_0]^{\beta})$$

β = *stretching exponent*

Average life time = $\langle\tau\rangle = \left(\frac{\tau_0}{\beta}\right)\Gamma\left(\frac{1}{\beta}\right)$

$$I(t) = b\exp(-t/\tau_0) + a\exp(-[t/\tau_0]^{\beta})$$



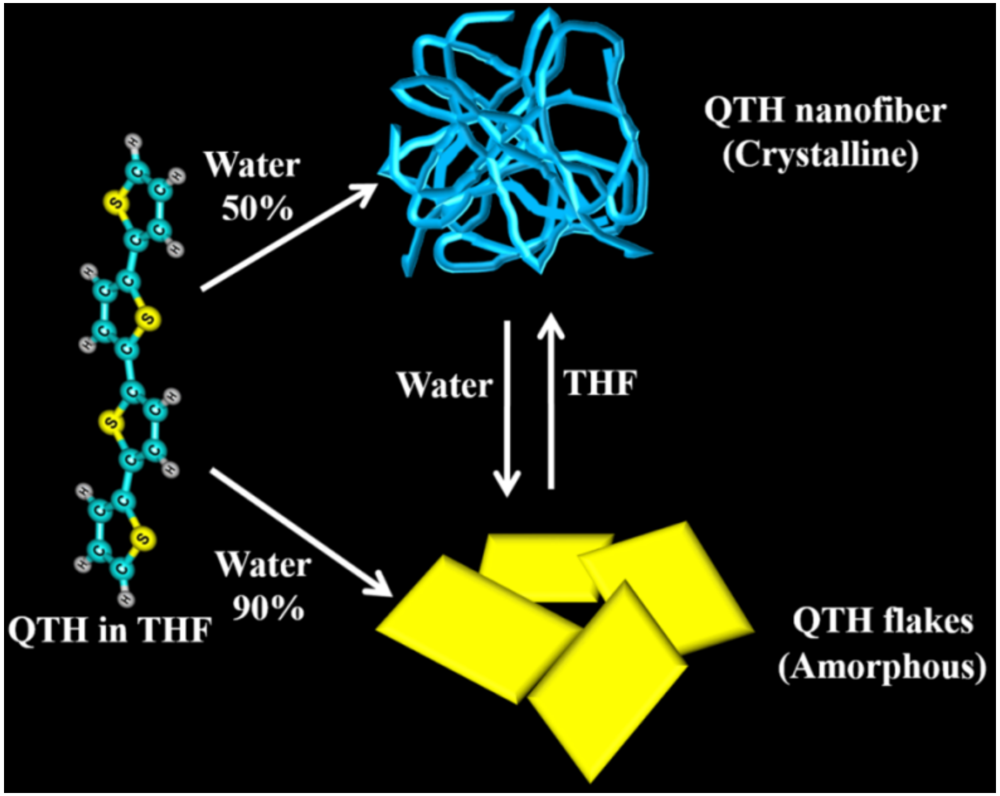
Decay parameters for different shape CdS NCs

System	Reduced χ^2	a	τ_0	β	b	% fast component	$\langle\tau\rangle$ (ns)
Sphere(a)	0.89	2500	4.1	0.4	110	4%	13.63
Rod(b)	0.9	1320	0.49	0.31	3876	74.6%	3.95
Triangle(c)	0.85	1400	0.19	0.27	4208	75.1	2.96

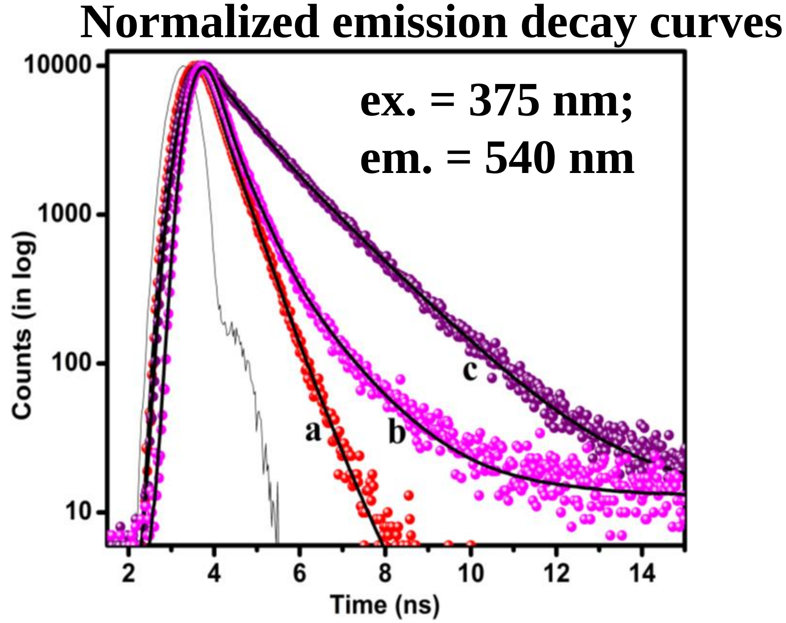
% fast component = $100\times b/(a+b)$

Photoswitching and Thermoresponsive Properties of Conjugated Multi-chromophore Nanostructured Materials

*Santanu Bhattacharyya, Bikash Jana, Sumanta Sain, Monoj Kumar Barman, Swapan Kumar Pradhan, and Amitava Patra**



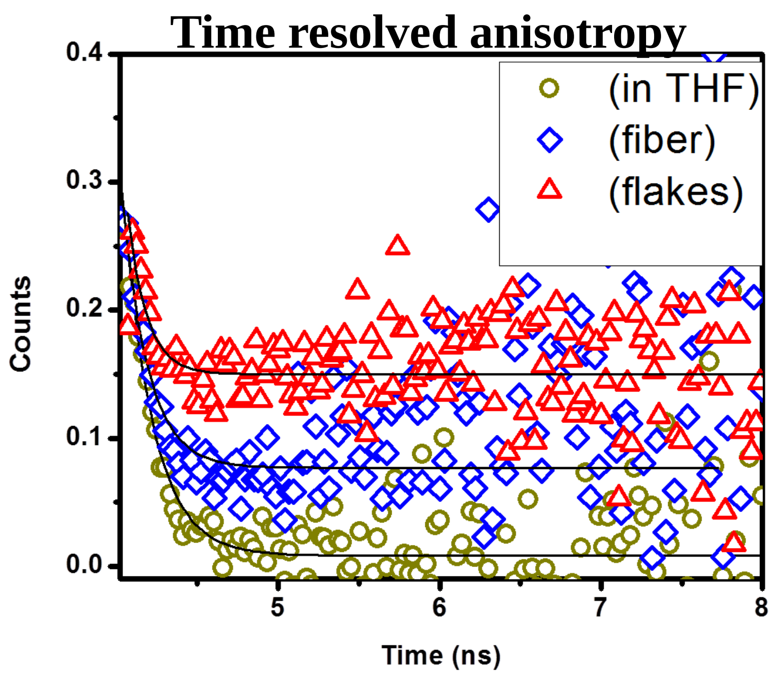
Small, 2015 *11,* 6317–6324.



QTH in THF (a), QTH fiber (b), and QTH flakes (c)

System	$\langle \tau_1 \rangle$ (ps)	$\langle \tau_1 \rangle$ (ps)	$\langle \tau \rangle$ (ps)
QTH in THF	430 (100%)		430
QTH Fiber	470 (74%)	1040 (26%)	618
QTH Flakes	490 (28%)	1750 (72%)	1400

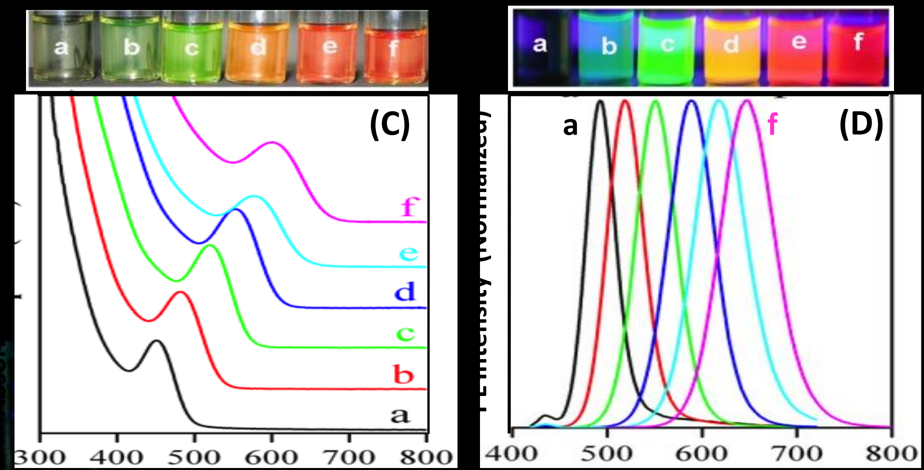
Increases indicating H-aggregation in Flakes

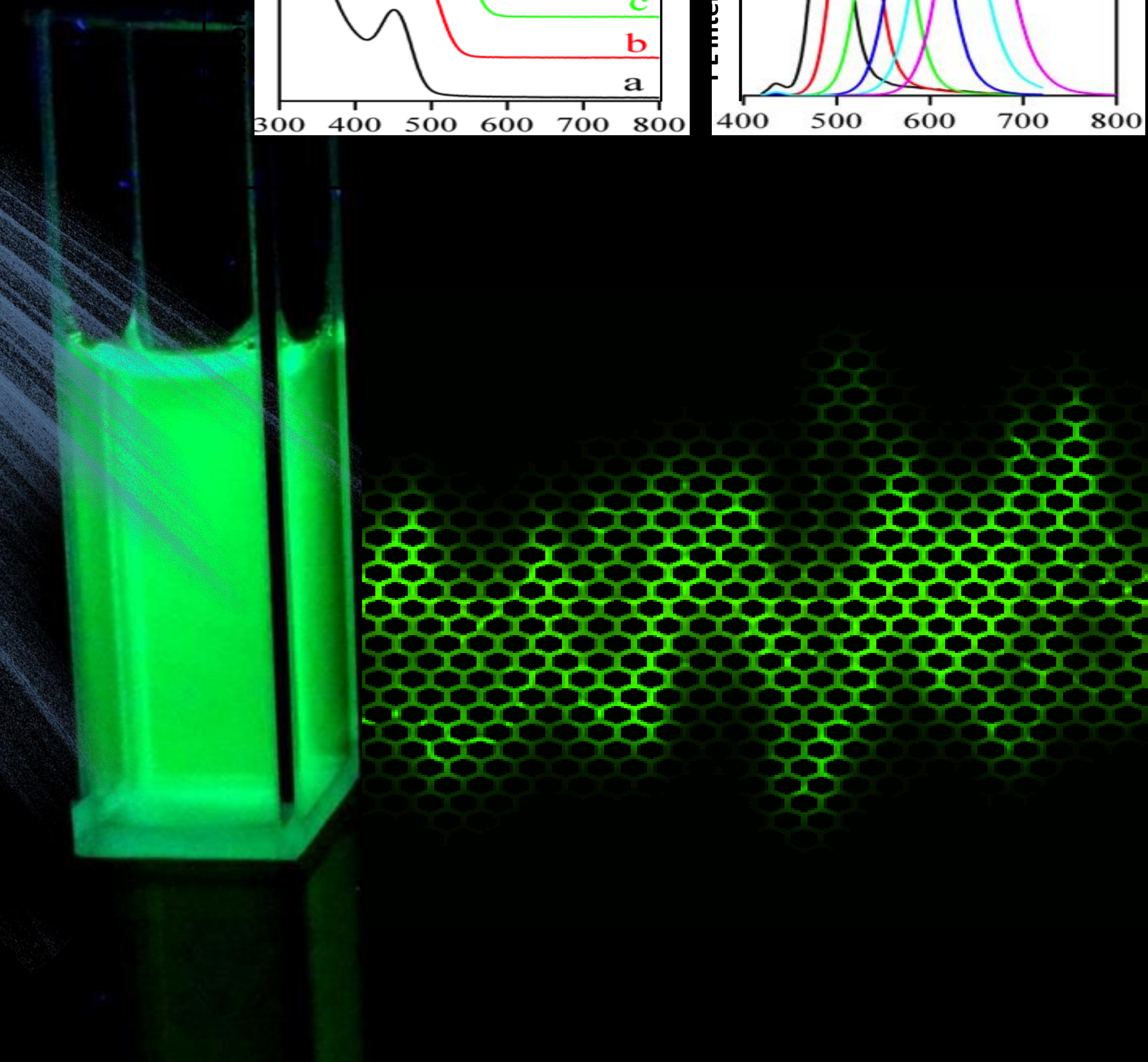


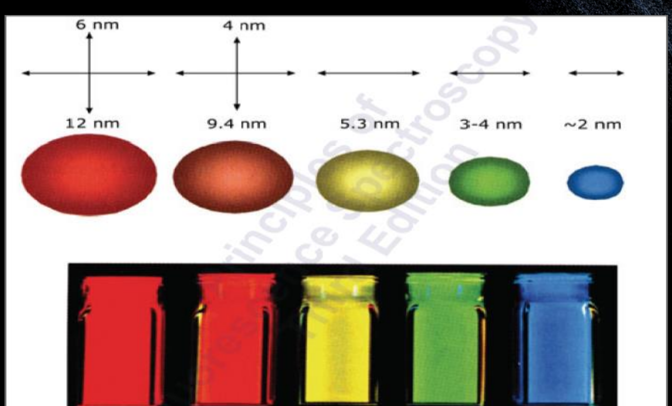
System	Residual anisotropy, r(α)	Initial anisotropy, r(0)	Re-orientation time (ps)
QTH in THF	0	0.26	184
QTH Fiber	0.08	0.26	158
QTH Flakes	0.15	0.21	117

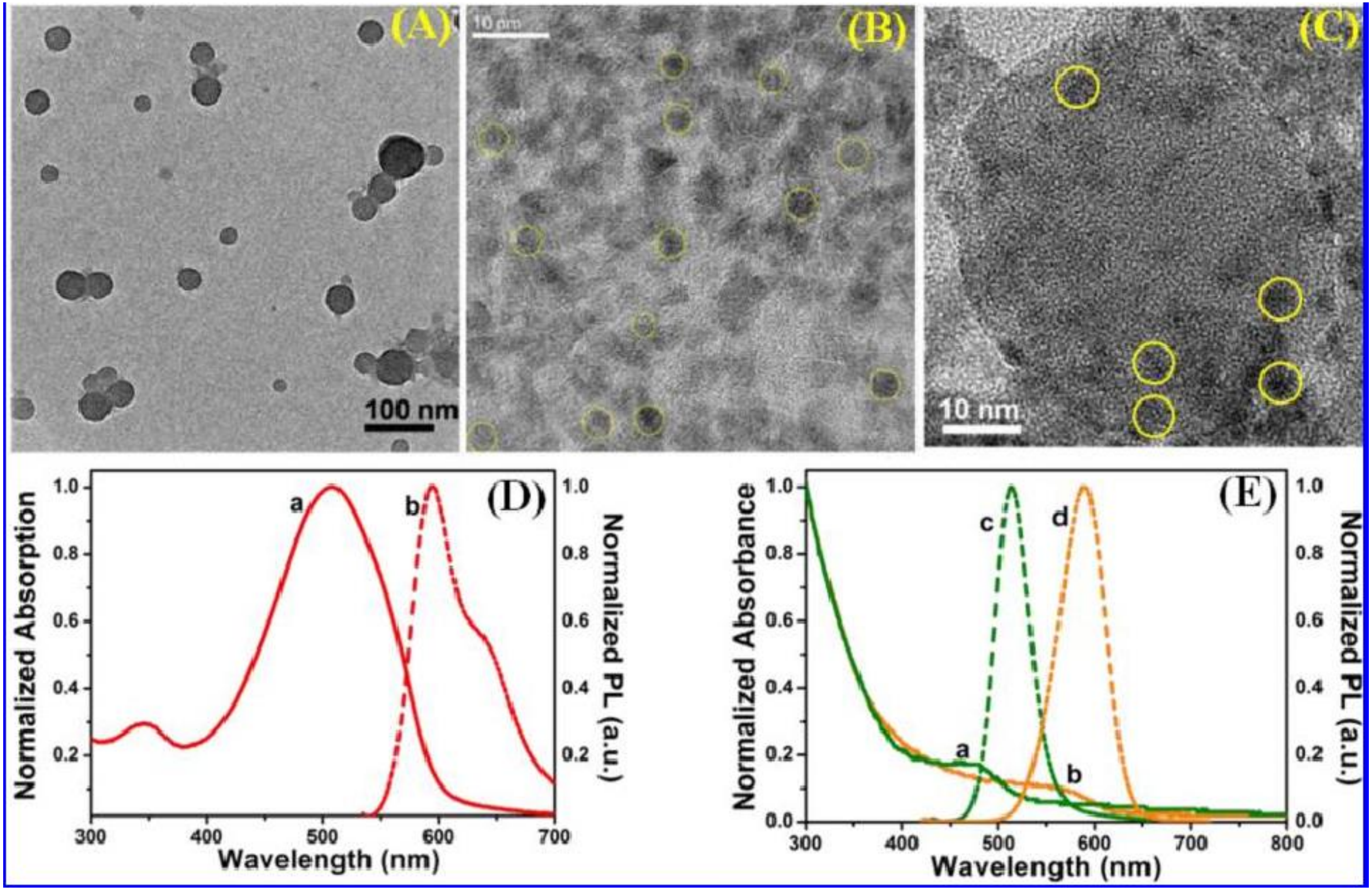
Increases hindered rotation of chromophoric units from Fiber to Flakes

Semiconductor QD







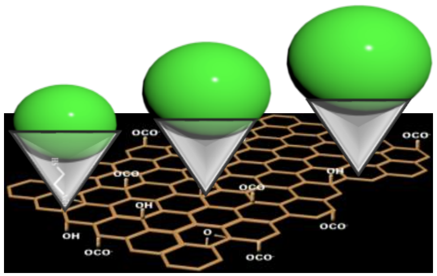


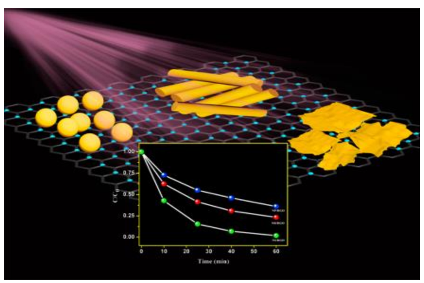
(A)
(B)
(C)
100 nm
10 nm
10 nm
(D)
a
b
Normalized Absorption
Normalized PL (a.u.)
Wavelength (nm)
(E)
a
b
c
d
Normalized Absorbance
Normalized PL (a.u.)
Wavelength (nm)

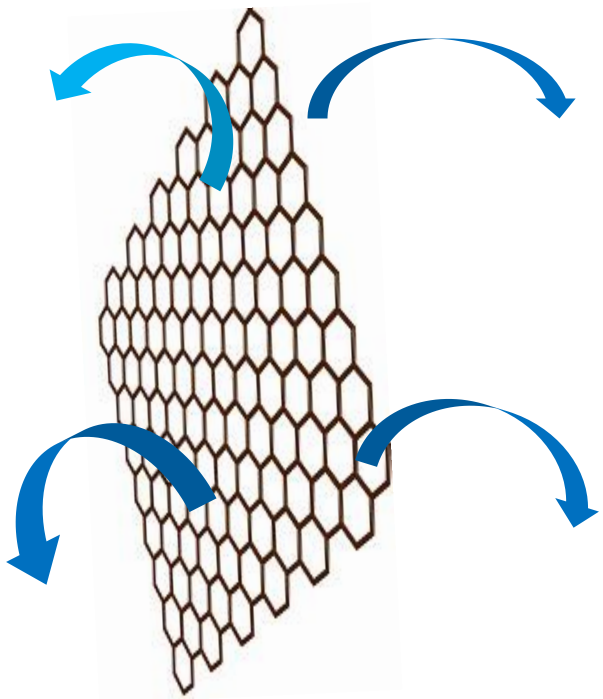
Graphene based hybrid materials

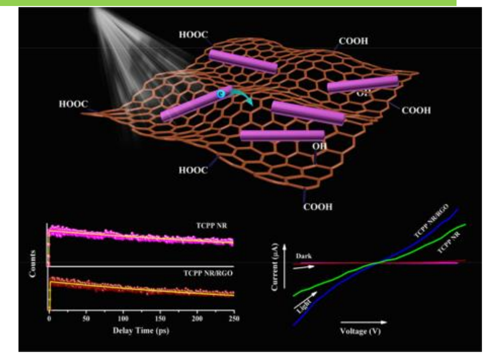
Graphene-inorganic hybrid materials

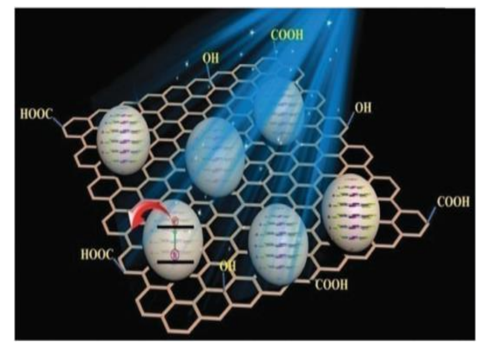
Graphene-organic hybrid materials

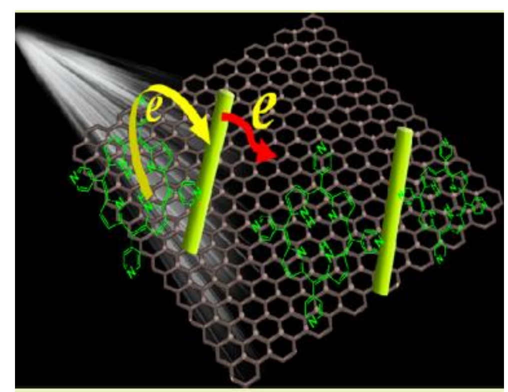




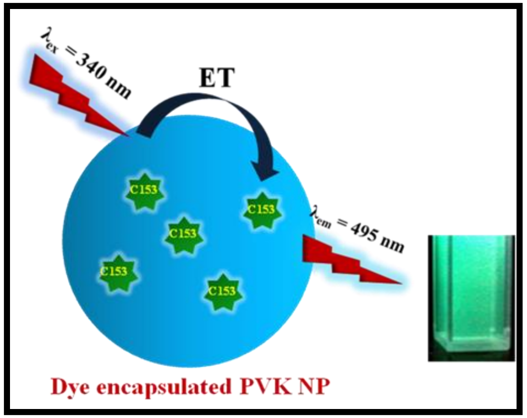


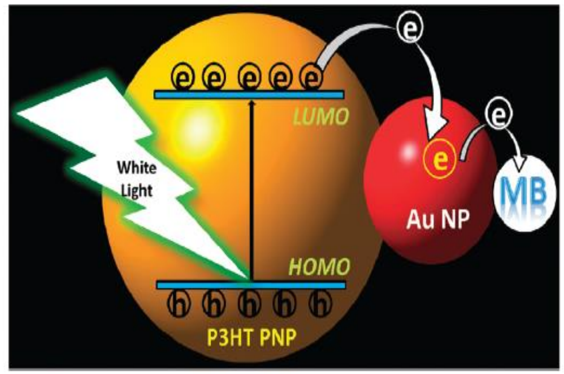


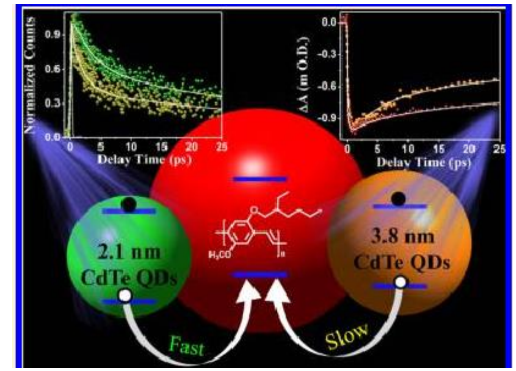




ACS Sustainable Chem. Eng., 2016, 4, 1562–1568.
J. Mater. Chem. C, 2016, 4, 6027-6036.
J. Phys. Chem. C, 2013, *117* (45), 23987–23995.
ACS Appl. Mater. Interfaces, 2015, 7, 13251–13259.
ACS Sustainable Chem. Eng., 2017, 5, 3002−3010



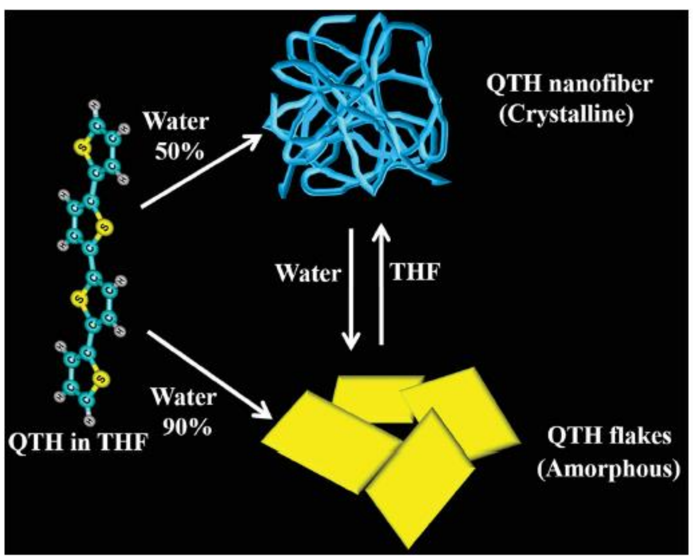


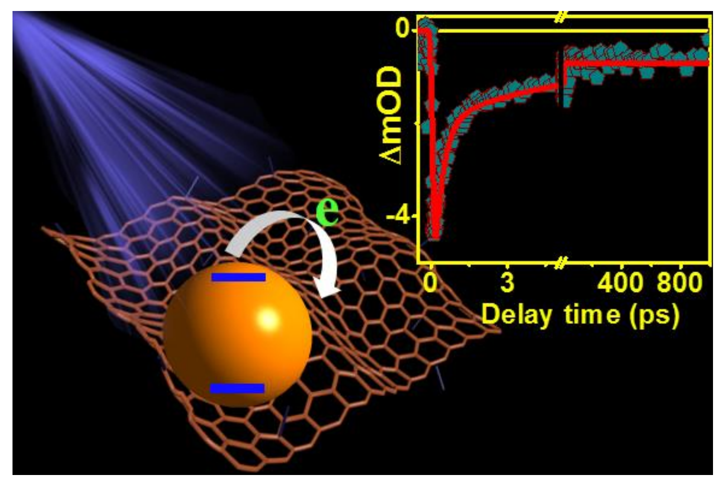


Dye doped PNP, JPCC

PNP- Au NP, PCCP

JPCC, 2016



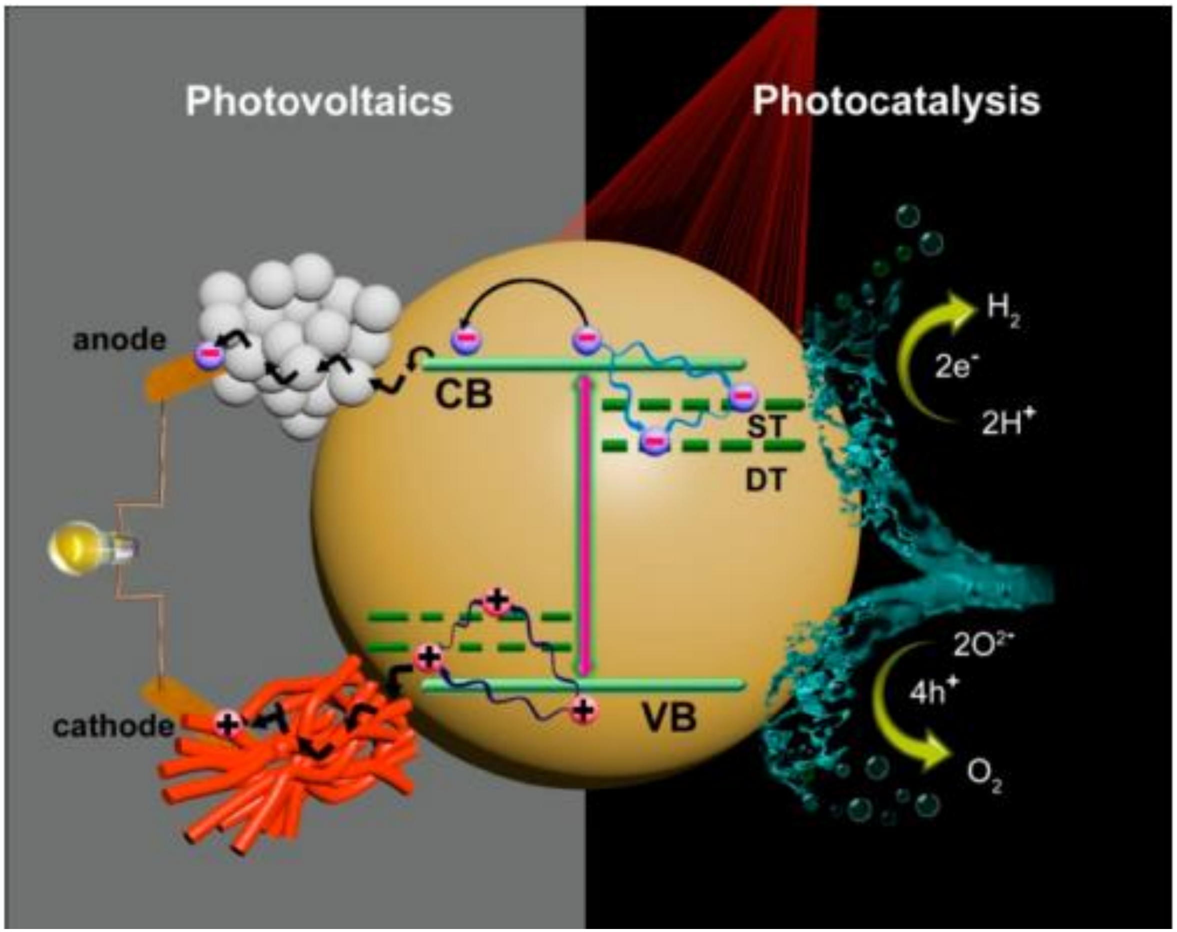


Self assembled nanostructures, Small

PNP -GO, ChemPhyChem, 2017

In the case of photovoltaic applications, photocurrent generation occurs due to charge migration of photogenerated electrons and holes of semiconductor nanoparticles toward opposite electrodes.

However, the photogenerated electrons and holes of semiconductor NP are used for reduction and oxidation reactions to facilitate chemical conversion in the case of photocatalysis.

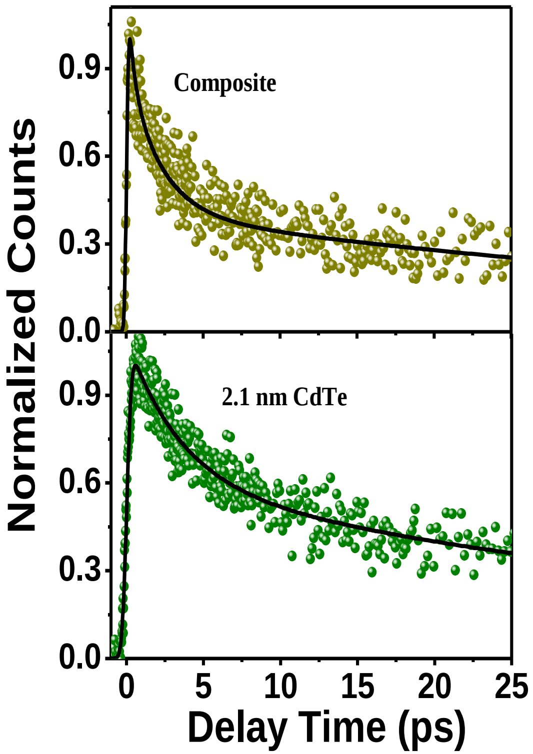


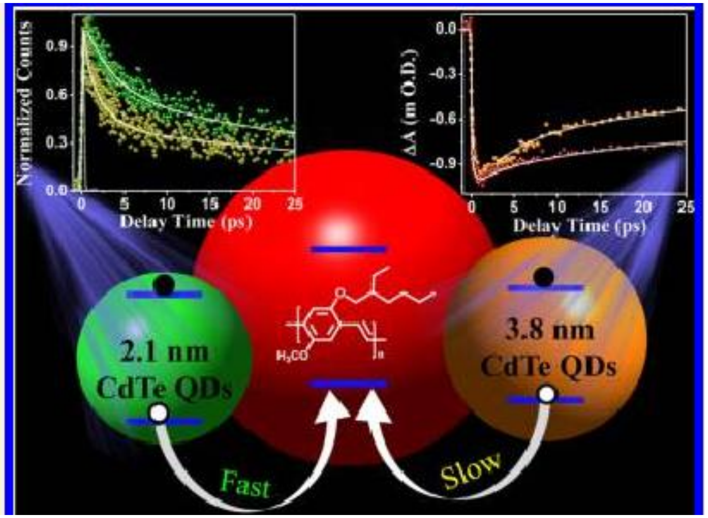
π-conjugated polymer nanoparticle

Our focus on understanding……

- Rotational dynamics of dye encapsulated polymer nanoparticle
- Exciton dynamics and exciton diffusion
- Charge transfer dynamics between polymer nanoparticle-QD hybrids
- Energy transfer between Polymer nanoparticle-porphyrin hybrids
- Electronic process in self assembled multichromophoric system

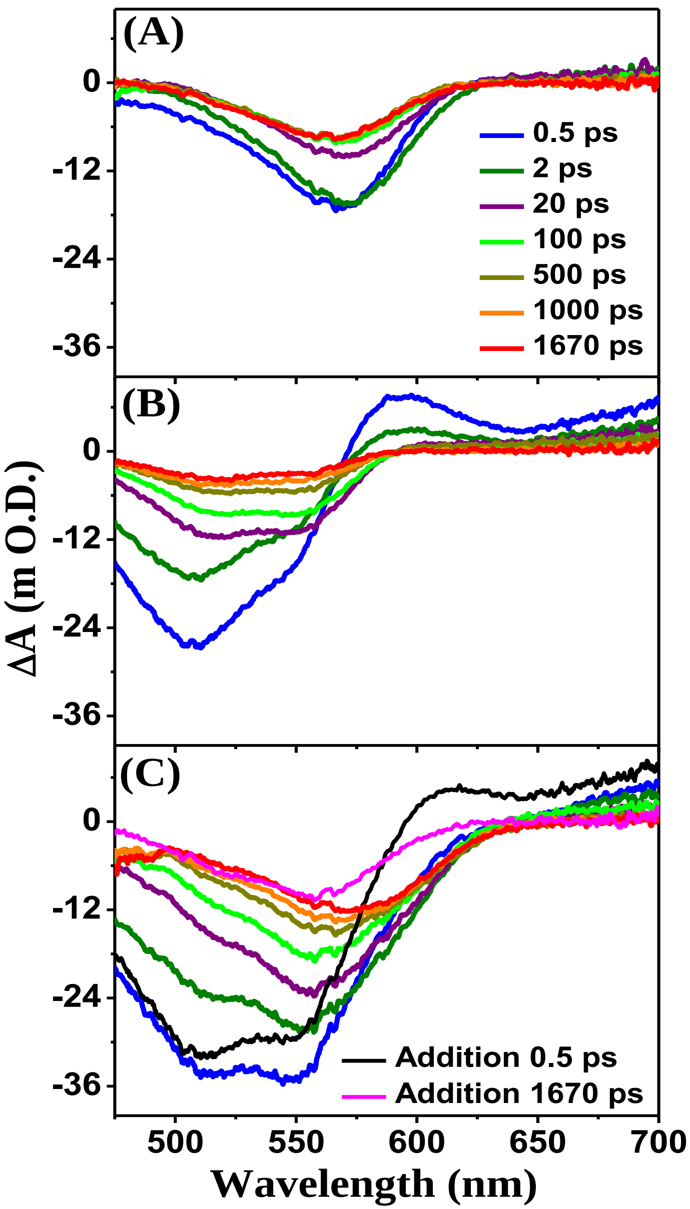
Ultrafast spectroscopic study





In composite, the appearance of the faster component (390 fs) is attributed to the hole Transfer from QDs to PNP.

Transient Absorption in 3.8 nm QDs and Composite:



Kinetic fitting parameters for bleach recovery at 570 nm for CdTe (3.8 nm), MEHPPV PNPs and composite:

Sample	τ_1^g	τ_2^g(ps)	τ_1^r(ps)	τ_2^r(ps)	τ_3^r(ps)
CdTe (3.8 nm)	>100fs (60%)	0.4 (40%)	4 (35%)	20 (21%)	>400 (44%)
MEHPPV PNPs	>100fs (45%)	5 (55%)	-	95 (63%)	>400 (37%)
Composite	>100fs (70%)	0.6 (30%)	12 (30%)	120 (23%)	>400 (47%)

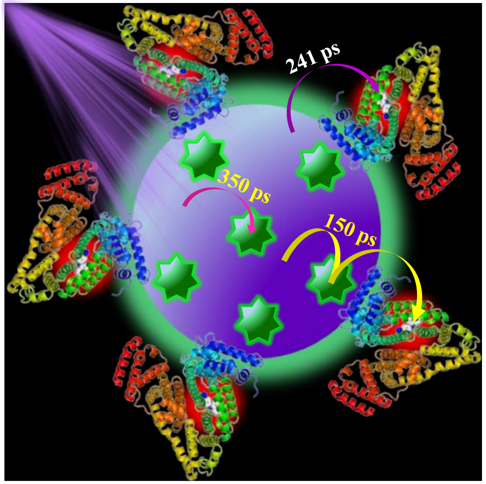


Fig. 3 Spectral overlap between the emission spectrum of PVK PNPs (a) and absorption spectrum of C153 (b), emission spectrum of C153 (c) and absorption spectrum of NR (d).