Supplementary Information

Trap-states assisted electron transfer from CdSe/ZnS core shell quantum dots to Cobalt(III) complexes

Anuushka Pal[a], Sumit Srivastava[b], Rajeev Gupta[b] and Sameer Sapra[a]*

[a]Department of Chemistry, Indian Institute of Technology, Delhi-110016
[b]Department of Chemistry, University of Delhi, Delhi-110007
*Email: sapra@chemistry.iitd.ac.in

The structural representation of cobalt complexes and the distance from Co^{3+} centre to nitrogen of pyridyl ring of carbomyl ligand and end to end distance has been calculated from crystallography is shown in Figure S1.

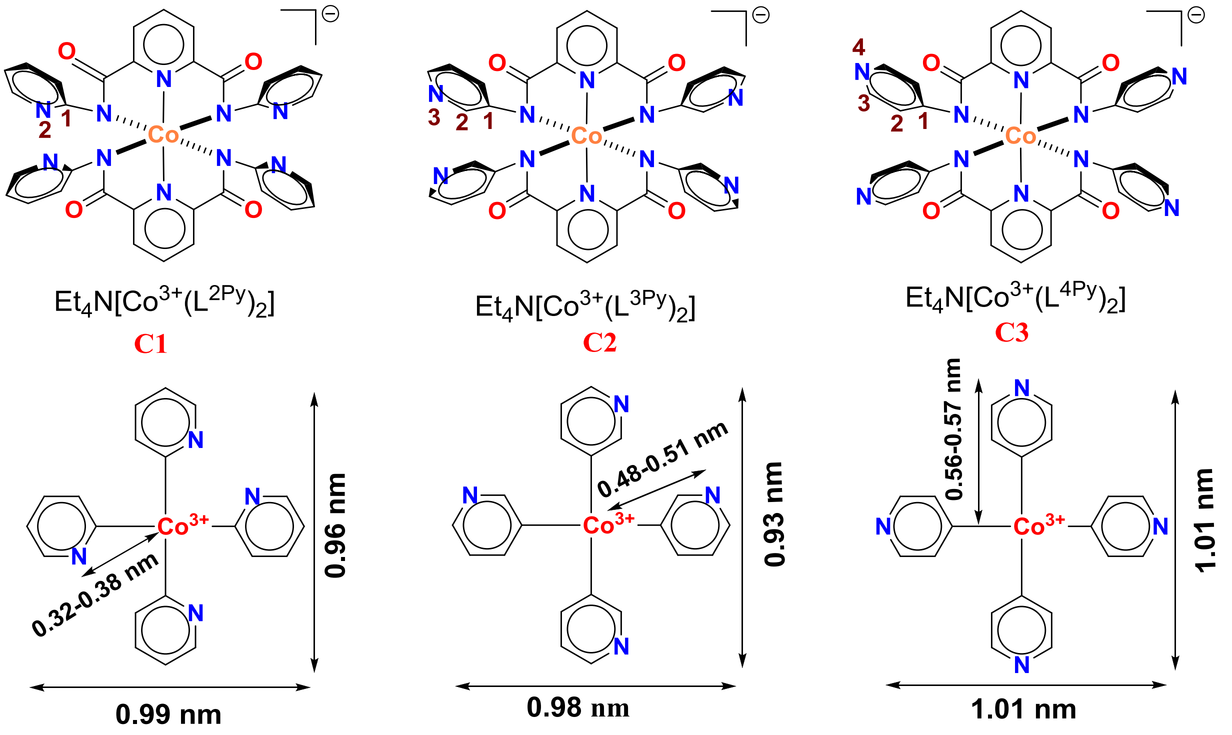

Figure S1: An enlarged view of the structures presented in Figure 1 in the manuscript

The absorption and emission spectra of synthesized QDs in chloroform is shown in Figure S2. Emission spectrum was recorded at excitation wavelength of 405 nm.

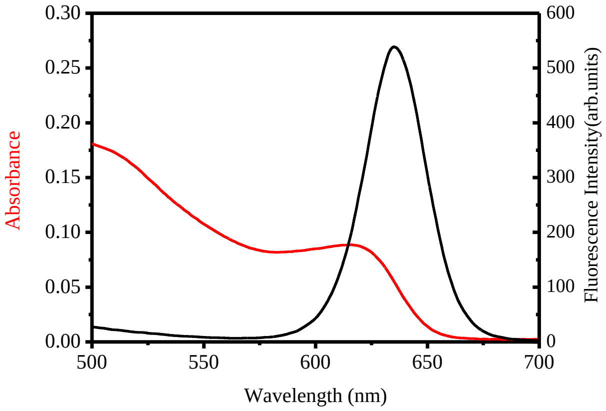

Figure S2: The absorption and emission spectrum of QD.

The absorption spectra of QDs with different concentrations of complex are shown in Figure S3 (a). The concentration of complexes was varied from 0 to 27.30 μM. The experimental absorption spectra of QDs with the maximum concentration of complexes (27.30 μM) and calculated absorption spectra of QDs with complexes by the summation of absorption spectra of pure QDs and complexes at the maximum concentration is shown in Figure S3 (b). These two curves overlap indicating that there is no shift in the absorption spectra of QDs on addition of complexes.

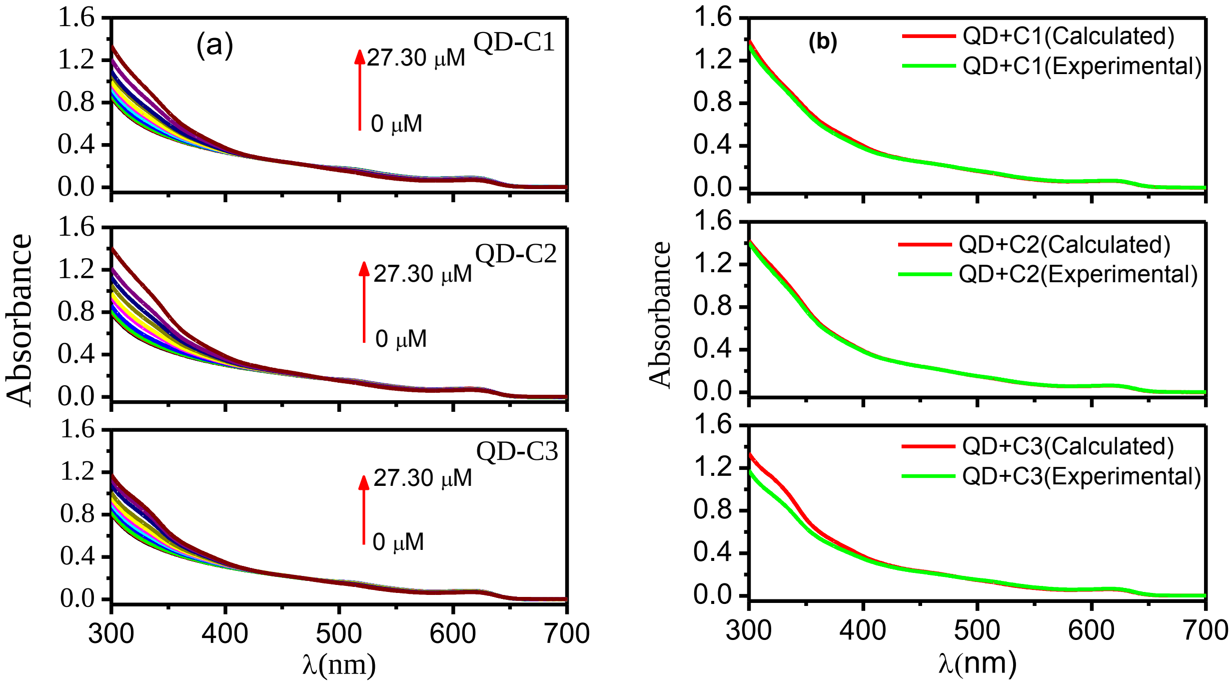

Figure S3: Absorption spectra of QDs with different concentrations of complexes (a). Experimental and calculated absorption spectra of QDs with the maximum concentration of complexes (27.30μM) (b).

The TEM image of QDs is shown in Figure S4 (a) The reported size calculated from TEM images by taking the average size of 300 particles was 6-7 nm (b) TEM image of QDs after addition of 27.3μM of complex (C3). The histogram of the size distribution of QDs is shown below the respective images.

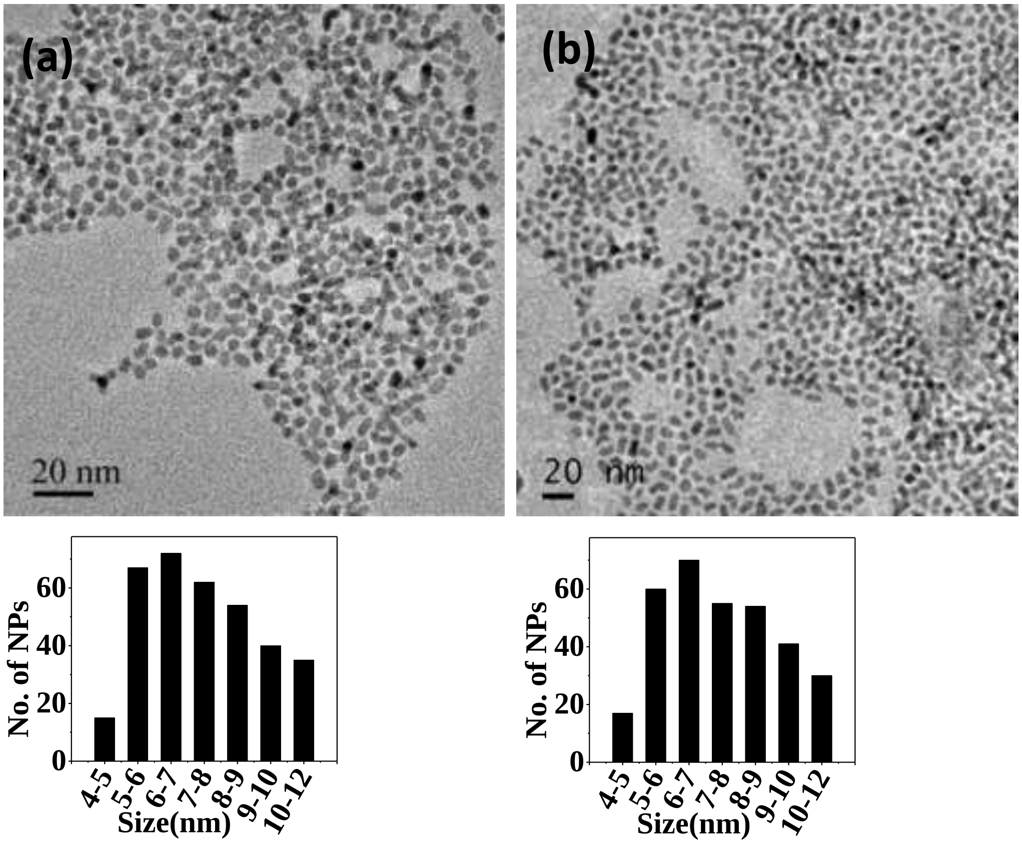

Figure S4: TEM images of QDs (a) without and (b) with C3 complex. Shown below the TEM images are the histograms for particle size distributions.

Fluorescence decay parameters of QD-C1 and QD-C2 system are listed in Table S1 and S2 respectively.

Table S1: Fluorescence decay parameters of QD-C1

Conc of C1(μM)	τ_1(ns)	α_1	τ_2(ns)	α_2	<τ>(ns)
0	3.39	0.84	20.51	0.16	12.55
0.49	3.11	0.83	18.73	0.17	11.73
0.97	2.80	0.82	17.52	0.18	11.31
3.50	2.58	0.81	16.85	0.19	11.21
5.53	2.51	0.81	15.41	0.19	10.12
7.63	2.43	0.81	14.84	0.19	9.74
9.67	2.24	0.81	14.11	0.19	9.32
13.2	2.17	0.81	13.01	0.19	8.51
17.00	1.88	0.80	11.77	0.20	7.91
20.33	1.80	0.80	11.41	0.20	7.69
27.30	1.78	0.80	10.64	0.20	7.08

Table S2: Fluorescence decay parameters of QD-C2

Concentration of C2(μM)	τ_1(ns)	α_1	τ_2(ns)	α_2	<τ>(ns)
0	3.39	0.84	20.51	0.16	12.55
0.49	2.95	0.81	17.34	0.19	11.29
0.97	2.31	0.79	14.62	0.21	10.03
3.50	2.08	0.79	13.52	0.21	9.86
5.53	1.98	0.78	12.36	0.22	8.60
7.63	1.93	0.79	11.86	0.21	8.08
9.67	1.93	0.78	11.78	0.22	8.16
13.2	1.94	0.79	11.58	0.20	7.85
17.00	1.85	0.78	10.8	0.22	7.41
20.33	1.73	0.79	10.49	0.21	7.14
27.30	1.74	0.79	10.07	0.21	6.95

Analysis of quenching rate

The quenching rate k'_q for complexes is listed in Table S3. For calculation of k'_q an assumption was made that radiative rate k_r is due to QDs only. When quencher is added it opens an additional non-radiative pathway k'_q without affecting the radiative decay rate.

$$\tau_{QD} = \frac{1}{k_r}$$

$$\tau_{Complex} = \frac{1}{k_r + k'_q}$$

where τ_{QD} is the average lifetime of ~~of~~ QDs and $\tau_{Complex}$ is the average lifetime of Complex-QDs. Therefore quenching rate can be estimated by

$$k'_q = \frac{1}{\tau_{Complex}} - \frac{1}{\tau_{QD}}$$

$$k'_q = nk_q$$

k_q is the quenching rate constant and n is the number of free quenchers causing dynamic quenching.

Table S3: Quenching analysis data for different quencher concentrations

Conc(μM)	Quencher (moles)	k'_q (C1) (ns^{-1})	nC1 Number of C1	k'_q (C2) (ns^{-1})	nC2 Number of C2	k'_q (C3) (ns^{-1})	nC3 Number of C3
0.49	$1*10^{-9}$	0.0055	3.0	0.0089	3.0	0.0157	1.9
0.97	$2*10^{-9}$	0.0087	4.7	0.0210	6.7	0.0301	3.6
3.50	$7*10^{-9}$	0.0095	5.1	0.0217	7.2	0.0682	8.2
5.53	$12*10^{-9}$	0.0191	10.3	0.0366	12.2	0.0829	10.1
7.63	$17*10^{-9}$	0.0229	12.4	0.0441	14.7	0.0901	10.9
9.67	$22*10^{-9}$	0.0276	14.9	0.0429	14.3	0.1024	12.4
13.23	$32*10^{-9}$	0.0377	20.4	0.0471	15.7	0.1148	13.9
17.00	$47*10^{-9}$	0.0467	25.2	0.0553	17.8	0.1219	14.8
20.33	$57*10^{-9}$	0.0503	27.2	0.0603	20.1	0.1244	15.0
27.30	$77*10^{-9}$	0.0615	33.2	0.0641	21.4	0.1528	18.5

Quantum Yield

Photoluminescence quantum yield (QY) were obtained by comparison with standard dye (Rhodamine 6G) by exciting the sample at 505 nm in ethanol using equation given below.

$$QY_{QD} = QY_{R6G} \times \frac{F_{QD}}{F_{R6G}} \frac{Abs_{R6G}}{Abs_{QD}} \times \frac{n_{QD}^2}{n_{R6G}^2}$$

where F_{QD} and F_{R6G} are the integrated fluorescence emission of the QDs and the Rhodamine 6 G, respectively. Abs_{QD} , $Abs_{R6G}$are the absorbance at the excitation wavelength of the QDs and the R6G, respectively, $QY_{QD}$and QY_{R6G} are the quantum yields of the QDs and the reference (QY =94%) The refractive indices of the solvents in which the QDs and dye are prepared are given by n_{QD} (1.446) and n_{R6} (1.368) respectively. The values of F_{QD} and F_{R6G} are determined from the photoluminescence spectra by integrating the emission intensity over the desired spectral range.

The calculated quantum yield of QDs was found out to be 0.82%

FRET Calculations has been done by using PHOTOCHEMCAD software.

FRET depends on separation between the donor and acceptor and the distance between donor acceptor couple is usually of order 10-100 Å. Using the Förster theory of dipole–dipole interaction, the energy transfer efficiency E for a single donor with multiple identical acceptors can be expressed as,

$$E = \frac{1}{1+(r/R_0)^6}$$

Where $R_0$is the Förster radius of the FRET pair for a single donor–single acceptor situation, at which $E = 50\%$ and r is the apparent donor–acceptor distance or at which the half of the donor molecules decay via FRET and other half by the other usual radiative and non radiative paths. The Förster radius R_0given by

$$R_0 = \left(\frac{\left[9000 \times \ln 10\, k_p^2 Q_Y J\right]}{128\pi n_D^4 N_A}\right)^{\frac{1}{6}}$$

where Q_Y is the quantum yield of the donor, n_D is the refractive index of the medium and its value is estimated to be1.4,N_A isAvogadro's number,$k_p^2$is the orientation factor and its value varies between 0 (for orthogonal alignment) and 4 (for parallel dipoles), and for randomly orientated fluorophores $k_p^2 = 2/3$.The Förster distance depends on the overlap integral, $J$of the donor emission spectrum with the acceptor absorption spectrum and their mutual molecular orientation as expressed by the following equation

$$J = \int f_D(\lambda)\varepsilon_A\, \lambda^4 d\lambda$$

Wheref_D is the fluorescence intensity of the donor in the range λ to $\lambda + \Delta\lambda$, where the total area under the curve is unity,ε_A is the acceptor extinction coefficient

Cyclic Voltammetry

The Cyclic voltammograms of complexes (Figure S5) were recorded on electrochemical workstation under three electrode configurations at scan rate of - 0.1 V/s. The glassy carbon was used as working electrode, platinum wire as auxiliary electrode while saturated calomel as reference electrode. The concentration of complex was ~ 1mM and (TBAP: tetrabutyl ammonium perchlorate) ~ 0. 1 mM as supporting electrolyte.

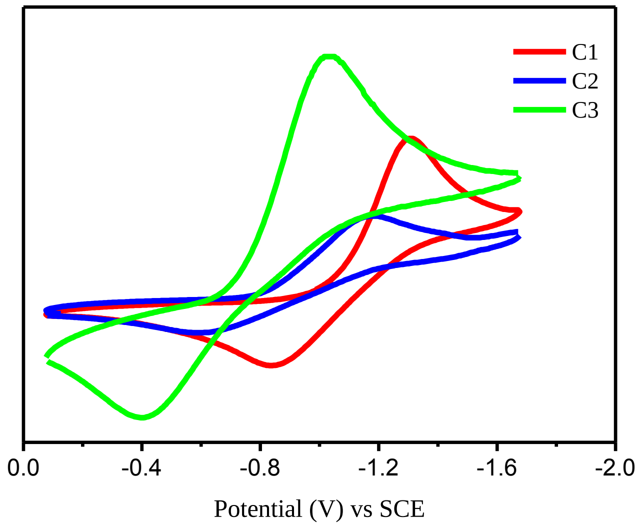

Figure S5. Cyclic voltammogram of complexes C(**1 – 3)** in CH_3CN.

Table S4: Electrochemical data for $Et_4N[Co^{3+}(L^{nPy})_2]$ complexes in acetonitrile solvent

Complex	**$E_{1/2}$(V vs SCE)**
$Et_4N[Co^{3+}(L^{2Py})_2]$ (**1**)	-1.10
$Et_4N[Co^{3+}(L^{3Py})_2]$ (**2**)	-0.87
$Et_4N[Co^{3+}(L^{4Py})_2]$ (**3**)	-0.72

To convert the potential value referenced to saturated calomel electrode(SCE) into vacuum is given by the equation given below:

$$E_{LUMO} = -(E_{Red}(SCE) + 4.681)$$

where $E_{Red}(SCE)$ is the reduction potential with respect to saturated calomel electrode and 4.681 is the value according to vacuum level (4.44 ev for NHE (normal hydrogen electrode) and 0.241V difference between SCE and NHE reference electrode). Similarly HOMO level can be calculated by

$$E_{HOMO=} - (E_{Oxi}(SCE) + 4.681)$$

The calculated HOMO-LUMO of complexes and QDs is listed in Table S5

	LUMO(eV)	HOMO(eV)
QDs	-3.63	-5.57
C1	-3.73	-5.50
C2	-3.88	-5.64
C3	-4.03	-5.77

The optical band gap of QDs and complexes as shown in Figure S6 calculated by using Tauc relation.

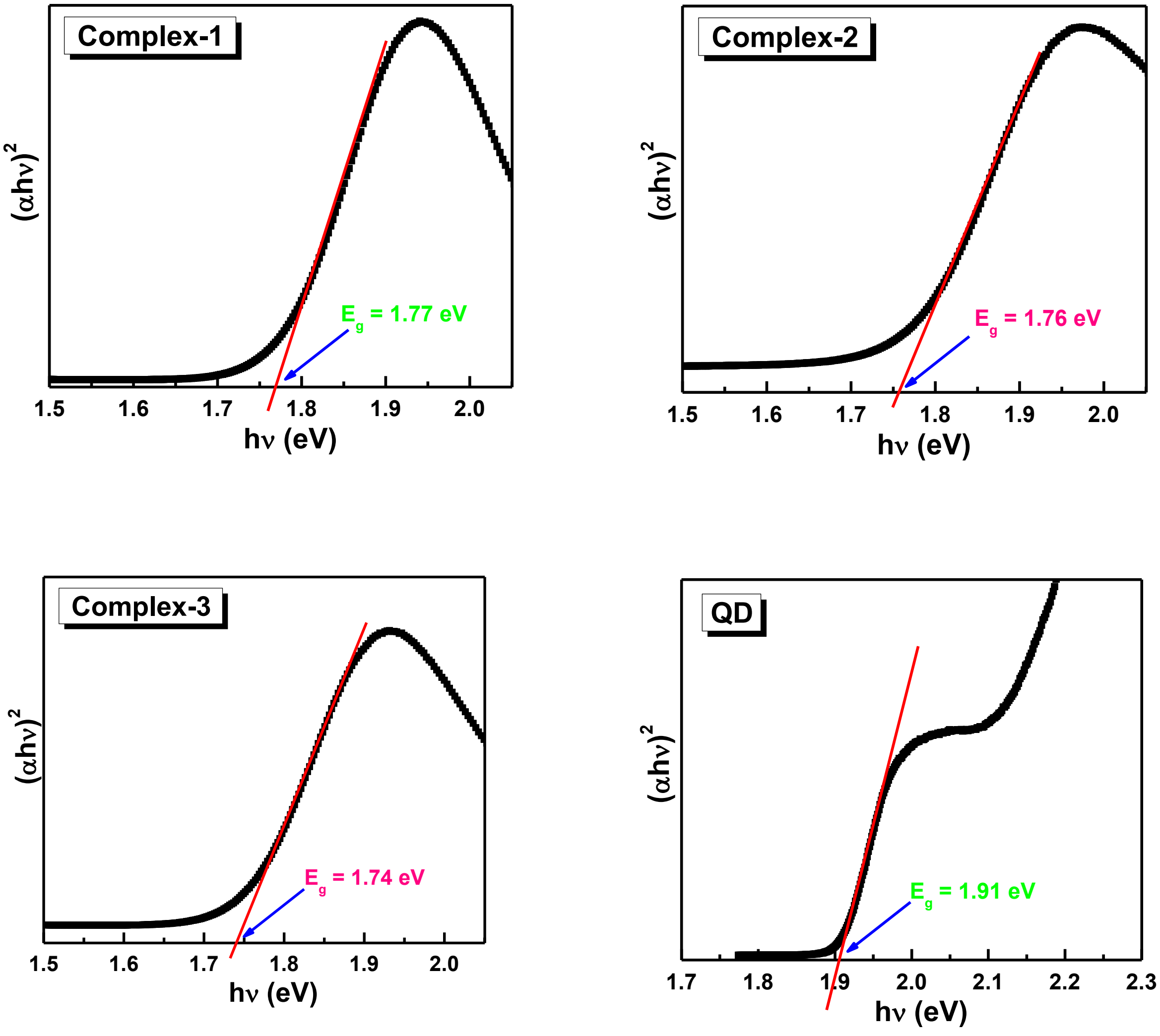

Figure S6. Absorption spectra of C1, C2, C3 and QD.