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Design and Synthesis of Fluorescent Carbon Dot Polymer and Deciphering its Electronic Structure

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ABSTRACT: Herein, we have reported one-pot synthesis of a fluorescent polymer-like material (**pCDs**) by exploiting ruthenium doped carbon dot (**CDs**) as building blocks. The unusual spectral profiles of **pCDs** with double humped periodic excitation dependent photoluminescence (EDPL) and the regular changes in their corresponding average lifetime indicate the formation of high energy donor states and low energy aggregated states due to the overlap of molecular orbitals throughout the chemically switchable π -network of **CDs** on polymerization. To probe the electronic distribution of **pCDs**, we have investigated the occurrence of photoinduced electron transfer with a model electron acceptor, menadione using transient absorption technique, corroborated with low magnetic field, followed by identification of the transient radical ions generated through electron transfer. The experimentally obtained $B_{1/2}$ value, a measure of the hyperfine interactions present in the system, indicates the presence of highly conjugated π -electron cloud in **pCDs**. The mechanism of formation of **pCDs** and the entire experimental findings have further been investigated through molecular modeling and computational model. The DFT calculations demonstrated the probable electronic transitions from surface moieties of **pCDs** to the tethered ligands.

INTRODUCTION

The polymeric form of carbon dots i.e. **pCDs**, is barely reported till date¹⁻⁶. Moreover, our understanding regarding their electronic structure and origin of excitation dependent photoluminescence (EDPL) remains vague due to their highly complex nanostructured framework⁷. The EDPL of **CDs** is apparently observed to be violating the Kasha–Vavilov rule of excitation-independent photo-luminescence (EIPL) unlike single organic fluorophore⁸⁻¹¹. It is also quite obvious that nanodomain of **CDs** is formed by polymerization pathway during pyrolysis. Here we have envisioned whether one can design a covalently linked polymer like chain by exploiting **CDs** as building blocks like amino acids in a peptide chain. This idea has motivated us to venture into the uncharted territories of designing a biomimetic polymerized carbon dots (**pCDs**) from a nonpolymeric precursor and establish their detailed PL mechanism as well as plausible electronic structures quite precisely. Our recent report indicates that the **CDs** are composed of multiple chromophoric units having sp^2 carbon network with ' $>C=C<$ ' and $\alpha\beta$ -unsaturated ketone ($>C=C-C=O$)¹². On the basis of that knowledge we have attempted to address two key intriguing questions: (i) Is it possible to make a polymer of **CDs** by coupling with a cross-linker having two mercapto ($-SH$) functional groups at two ends? (ii) What are the significant changes that could be observed regarding optical and electronic properties from **CDs** to **pCDs** after polymerization and could that explain the hitherto elusive EDPL?

To address these challenges, at first we have attempted to synthesize ruthenium (III) doped **CDs** (**Ru:CDs**) through pyrolysis of the mixture of 1g citric acid (CA) and 0.005 g $RuCl_3$ in water at 150°C (250°C in hot plate). We have preferred **Ru:CDs** over **CDs** due to their thermal stability¹². Then the purified and lyophilized **Ru:CDs** are set for polymerization by refluxing with dithiothreitol (DTT) at 120°C in DMF,

which ultimately produces light yellow hydrogel kind of materials, **Ru:CD-DTTs** abbreviated as **pCDs** (Scheme 1).

Scheme 1. Synthetic route of polymer carbon dots (**pCDs**).

EXPERIMENTAL SECTION

Materials and methods: All the chemicals and solvents required for syntheses of **Ru:CD**, **Ru:CD-DTTs**, **Ru:CD β ME** are of analytical grade. Citric acid (CA) [$\geq 99.5\%$], ruthenium(III) chloride hydrate, dithiothreitol (DTT) are purchased from Sigma Aldrich. Triple distilled water is used for the preparation of all the aqueous solutions. Solvents required for syntheses and spectroscopic studies have been purchased from SRL. Steady-state absorption and fluorescence spectra are recorded by using JASCO V-650 absorption spectrophotometer and Spex Fluoromax-3 Spectro-fluorimeter. Time-resolved emission spectra are traced using a picosecond pulsed diode laser based TCSPC fluorescence spectrometer and MCP-PMT as

Figure 1: AFM image of **Ru:CD-DTTs** (a) 2-D image (b) 3-D image (c) Phase contrast image; (d) TEM image with low magnification, (e) TEM image with high magnification of **Ru:CD-DTTs**; (f) STEM-HADF image of area chosen for EDX mapping (index: EDX map) (g) STEM-HAADF image with high magnification of area chosen for chemical mapping in (f) and (g); (h) chemical map of C (red), (i) chemical map of O (yellow), (j) chemical map of S (cyan).

a detector. Respective transient intermediates are produced with third harmonic (355 nm) output of nanosecond flash photolysis set-up (Applied Photophysics) containing Nd:YAG (Lab series, Model Lab 150, Spectra Physics)¹³. TEM imaging is carried out using an FEI, TECNAI G2 F30, S-TWIN microscope operating at 300 kV equipped with a GATAN Orius SC1000B CCD camera. High-angle annular dark-field scanning/transmission electron microscopy (STEM-HAADF) is employed here using the same microscope. Cyclic voltammetry (CV) measurement is recorded with AUTOLAB-30 potentiostat/galvanostat. A platinum electrode and a saturated Ag/AgCl electrode are used as counter and the reference electrodes respectively. The glass carbon electrode is used as the working electrode. The cyclic voltammograms are recorded between -1 and 1V w.r.t. reference electrode at a different scan rate (2–20mV/s).

Synthesis of Ru:CDs : **Ru:CDs** are synthesized in accordance with our previous report¹.

Synthesis of Ru:CD-DTTs: A mixture of 500 mg of lyophilized **Ru:CDs** and 100 mg of 1, 4-Dithiothreitol (DTT) is refluxed in 3 ml of dimethyl formamide (DMF) at 120°C in stirring condition for 24 hours. After removal of DMF, excess DTT is removed by multiple washing with dichloromethane (DCM). A pure solution of **Ru:CQD-DTTs** is collected and then lyophilized and stored at 4°C.

Synthesis of Ru:CDβMEs: A mixture of 500 mg of lyophilized **Ru:CDs** and 50 μl of β-Mercaptoethanol (βME) is refluxed in 3 ml of dimethyl formamide (DMF) at 120°C in stirring condition for 24 hours. After removal of DMF, excess βME is removed by multiple washing with DCM. A pure solution of **Ru:CDβMEs** is collected and then lyophilized and stored at 4°C.

RESULTS AND DISCUSSION

Characterization of Ru:CD-DTTs (pCDs): The surface morphology of the **Ru: CD-DTTs** is observed by atomic force microscopy (AFM), which shows a signature of network formation on the mica-surface (Figure 1a, b, c). The peak and the valley regions are elevated by ~2-2.5 nm and ~ 0.5 nm from the surface as obtained from the 3D image (Figure 1b). The bright-field transmission electron microscopic (BF-TEM) images (Figure 1d & 1e) show a large (10-80 μm by length) polymeric structure which is formed by the attachment of multiple small **CDs** (diameter ~10 nm, Figure S1). The average atomic percentage of C:S:O is ~59:31:10 as shown in the inset of Figure 1f. Figures 1g–j represents STEM-HAADF images and corresponding EDX map for C, O and S, respectively.

Ground State Spectroscopic Properties of (pCDs). The **Ru:CD-DTTs** show a strong absorption in the UV region,

with a tail extending upto 600nm (Inset: Figure 2A). The Raman corrected EDPL spectrum of **Ru:CD-DTTs** mostly shows double humped nature at each switchable excitation wavelength (Figure 2A); whereas the EDPL spectra of the native carbon dots i.e. **Ru:CDs** are sharp with a single peak similar to small fluorogenic organic molecules (Figure 2B). The nature of excitation dependent PL spectra of **Ru:CD-DTTs** (Figure 2A) is significantly different from those of **Ru:CDs** (Figure 2B). We hypothesize that the unusual periodic double humped nature of the PL profile of **Ru:CD-DTTs** is due to the polymerization of individual dot (i.e. **Ru:CD**). To disentangle the individual emission maximum from **pCDs** at each excitation wavelength, the fluorescence spectra are deconvoluted using 'Fityk software'¹⁴. The deconvoluted spectra typically show two or more than two maxima at each excitation wavelength, for $\lambda_{\text{ex}} = 280 \text{ nm} \rightarrow \lambda_{\text{em}} = 360 \text{ and } 420 \text{ nm}$; $\lambda_{\text{ex}} = 300 \text{ nm} \rightarrow \lambda_{\text{em}} = 370 \text{ and } 445 \text{ nm}$; $\lambda_{\text{ex}} = 320 \text{ nm} \rightarrow \lambda_{\text{em}}^{\text{max}} = 435 \text{ and } 510 \text{ nm}$; $\lambda_{\text{ex}} = 350 \text{ nm} \rightarrow \lambda_{\text{em}} = 440 \text{ and } 505 \text{ nm}$; $\lambda_{\text{ex}} = 370 \text{ nm} \rightarrow \lambda_{\text{em}} = 450, 505 \text{ and } 545 \text{ nm}$; $\lambda_{\text{ex}} = 400 \text{ nm} \rightarrow \lambda_{\text{em}} = 510 \text{ and } 554 \text{ nm}$; and $\lambda_{\text{ex}} = 420 \text{ nm} \rightarrow \lambda_{\text{em}} = 520 \text{ and } 560 \text{ nm}$, respectively (Figure 2C). A significant reduction in PL intensity is also observed when the excitation wavelength is successively red-shifted by 20 nm as shown in the Figure 2 (A, C). Moreover, we have observed some crossovers among the deconvoluted PL spectra (Inset: Figure 2C). Now a query may arise that why do the PL spectra of **pCDs** differ from monomeric unit **CDs**? Recently, It has been reported the existence of chemically switchable multiple conjugated moieties within nanodomain of **CDs**^{12,15,16}. Though it is extremely difficult to identify those

chromophores within **CDs** separately due to their highly complex structure, recently *Reckmeier et. al.* have identified the high energy and low energy aggregated (π - π -stacked, H-Type) states as well as an energy transfer state within **CDs**. The UV spectrum of **pCDs** shows a tail towards longer wavelengths extending up to 600 nm with a clear shoulder at 410 nm. Consequently, we have observed one of the features of **pCDs** that depicts the presence of a large number of low energy states, originating from the aggregated fluorophores due to polymerization. If **pCDs** would behave like a single fluorophore then the high energy absorption peak around 260 nm could be assigned to π - π^* transitions, emerging from conjugated π electrons of the aromatic units of the blue ended fluorophores, while the peak around 410 and 550 nm could be assigned to the corresponding n - π^* transitions. However, such distinct assignments may not hold up when aggregated aromatic structures are involved. In case of **pCDs**, aggregation induced overlap of molecular orbitals results in the formation of additional low energy states.

The unusual double humped PL spectra of **pCDs** reveal several contributing emission units from the **CDs**, especially in the lower energy region¹⁵. Therefore, between two humps, the emission peak at blue end could be attributed to the high energy aggregated fluorophores. Since both the bands arise after polymerization, an energy transfer pathway may exist from high energy (410 nm in UV) to low energy aggregates which fluoresce around 510 nm as shown in Figure 2A and 2A inset.

Figure 2: (A) Raman corrected PL of **Ru:CD-DTTs** obtained at different excitation wavelengths, progressively increasing from 300 nm to 450 nm [Inset: absorption spectra of **Ru:CD-DTTs**]. (B) Photoluminescence spectra of **Ru:CDs** (control) with varied excitation wavelengths (C) Deconvoluted presentation of respective PL-profile where broad spectra represent individual peak for each hump. Inset: possibility of energy transfer from blue to red end as obtained from deconvoluted PL-spectra [D→G]. Fluorescence decay profiles of **Ru:CD-DTTs** at different excitation wavelengths. [$\lambda_{\text{ex}} = 280, 295, 340 \text{ and } 375 \text{ nm}$].

Table 1: Fluorescence life times (τ) with corresponding % contributions (α) of **Ru:CD-DTTs** with the gradual addition of MQ (10 μ M -100 μ M)

$\lambda_{\text{excitation}}$ (nm)	$\lambda_{\text{emission}}$ (nm)	τ_1 ns	α_1	τ_2 ns	α_2	τ_3 ns	α_3	$\langle\tau\rangle$ ns
280	360	2.3	47.78	0.82	31.05	8.5	21.17	5.71
	420	3.9	14.23	35.6	73.31	0.74	12.45	34.82
295	370	1.4	67.2	5.4	27.35	15.5	5.46	6.86
	445	4.5	19.63	35.7	48.94	1.0	31.43	33.63
340	440	3.9	25.88	1.23	54.32	9.33	19.80	6.23
	505	2.12	35.51	15.6	53.22	7.2	11.28	14.15
375	450	1.13	51.10	10.96	20.50	5.4	28.40	7.6
	554	2.05	49.22	6.63	32.59	0.38	18.19	5.07

On the contrary, **Ru:CDs** are unable to show prominent double humped PL spectra like **Ru:CD-DTTs**. This may be due to the higher rigidity and lack of orientation of the appropriate chromophoric units, which would facilitate energy transfer. The rigidity of the chromophores are too high to allow overlap of molecular orbitals inside **Ru:CDs**' compact nanodomain, hence reduces the probability of generation of energy transfer states¹⁷. The linker (DTT) is responsible to maintain the optimum condition for overlap between adjacent dots in **Ru:CD-DTTs** which favours the generation of aggregated states as well as energy transfer state. Formation of similar type of aggregated states has been reported when CDs are assembled and that looks like pCDs¹¹. Now, there may be an ambiguity that is whether the above mentioned states are observed due to polymerization or doping of sulphur (S). To get rid of this, we have synthesized **Ru:CD- β MEs** by modifying the surface of **Ru:CDs** with β -mercaptoethanol (β ME) [Scheme S1]. The idea is that the β ME may create an environment similar to DTT by S doping but be unable to form polymer chain due to presence of single -SH moiety. The TEM images of **Ru:CD- β MEs** (Figure S2A-C) show the signature of individual and random aggregated dots. Moreover, the **Ru:CD- β MEs** show excitation dependent PL spectra like **Ru:CDs** but not like pCDs. The excitation spectra at different emission wavelengths for pCDs, **Ru:CDs** and control explain the heterogeneity of fluorophores present within their nanodomain (Figure S2 D, E, F).

Time Resolved Electronic Properties of (pCDs): The formation of aggregated states due to polymerization of CDs affects the excited singlet state as observed in the PL spectra. It is also obvious that the PL lifetime of the CDs will be affected due to polymerization which leads to formation of high and low energy aggregated states. Therefore, we have attempted to measure the fluorescence lifetimes (τ) of the pCDs. We have recorded the PL decay kinetics of **Ru:CDs** (control, Figure S 3e-h, Table S1a), **Ru:CD- β MEs** (control, Figure S 3a-d, Table S1b) and **Ru:CD-DTTs** (Figure 2D-G, Table 1) using a TCSPC kinetic spectrometer (λ_{ex} = 280 nm, 295 nm, 340 nm and 375 nm). Each decay profile is best fitted with tri-exponential function giving rise to three components of lifetime with different percentages of contribution (Table

S1 a, b, c). In some of the cases there are two components with very close lifetimes and amplitudes. However, to consider the contributions from each set of electronic states of individual fluorophore to the average lifetime, a multi exponential function is required for fitting. This observation infers the presence of multiple types of fluorophore with different emissive state. The $\langle\tau\rangle$ obtained at each λ_{ex} for pCDs is unusually higher than the **Ru:CDs**, specially in the blue ended region [for λ_{ex} = 280 nm, 5.71 ns $\rightarrow$ 34.8 ns; λ_{ex} = 295 nm, 6.86 ns $\rightarrow$ 33.6 ns; λ_{ex} = 340 nm, 6.23 ns $\rightarrow$ 14.1 ns; λ_{ex} = 375 nm, 5.07 ns $\rightarrow$ 7.6 ns] (Table 1). We propose that the photo excited pCDs molecules are quite stable due to their overlapping molecular orbitals, which gives rise to an increase in $\langle\tau\rangle$ of CDs after polymerization. Furthermore, the generation of energy transfer states can alter the PL lifetime^{18,19} as observed in case of **Ru:CD-DTTs**.

Although, we have no direct way to prove the existence of the above mentioned energy states for such highly complex structure, however the above mentioned individual experiment and previous reports helps us to hypothesize about the existence of aggregated states and energy transfer state in pCDs. In contrast, the steady change in donor-accepter lifetime by ~ 2 ns (Figure S 3a-d, Table S1b) of **Ru:CD- β MEs** at similar excitation wavelengths indicates the remote possibility of formation of high and low energy aggregated states only due to S-modification. Polymerization of the **Ru:CDs** is the prime factor for formation of aggregated and energy transfer states in **Ru:CD-DTTs**. The extent of change in $\langle\tau\rangle$ for pCDs is not uniform throughout the entire excitation wavelength studied and gets reduced in the red region. This may be answered by investigating the distribution patterns of those probable fluorophoric units inside CDs nanodomain. As **Ru:CDs** are derived from CA, therefore they possess $\alpha\beta$ -unsaturated ketone, which may undergo Michael Addition type of reactions with thiols¹². Here as a result of DTT induced polymerization, the moieties associated with the higher wavelength of excitation may be blue shifted or their PL is quenched^{20,21} hence show a reduced intensity in the region of low energy aggregated states. However, the blue ended moieties, are not affected as they reside inside the compact nanodomain¹².

Figure 3: Construction of 3D model of polymer carbon dots (**pCDs**) by MD simulation. (a) Layer by layer assembly of I, II, III, IV, V and VI. (b) MD simulation of DTT decorated single carbon dots. (c) MD simulation of DTT functionalized single polymer carbon dots (**pCDs**).

Computational Model of **pCDs**.

To acquire more precise physical views of the polymer formation mechanism and unique spectroscopic properties of **pCDs**, we have attempted to simulate a plausible computational model on the basis of our spectroscopic findings and previously published literature on the thermal decomposition of CA^{12,22,23}. Acid catalyzed condensation reactions, which may create building blocks - 1, 2, 3, 4, 5, 6, etc (Figure S6)¹². To construct a 3D model we have taken two assumptions: either (a) those moieties (in our case: 1-6) evolved during the metamorphosis of **CDs** and packed up according to their increasing conjugation, which is partially supported by photobleaching experiment of **CDs**, indicating layer by layer structure (Figure 3, S7, S9)¹² or (b) all the building blocks (1-6) may be organized randomly in a closed cell of 10 nm (Figure S8, S10) and (ii) mostly the chromophores on the surface of the dots undergo Michel addition reaction with DTT and polymerize accordingly (Figure 3). For the sake of simplicity we have ignored the contribution of Ru(III). However, MD simulation reveals that the **pCDs** are very stable in aqueous medium and with the progress of time they convert into a more compact sphere (Video S1) due to π -stacking and inter-molecular hydrogen bonding interactions among the different building blocks (Figure S13).

Excited State Behavior and Electron Transfer Phenomenon in **pCDs**.

Next, to probe the intrinsic free electronic distribution of **pCDs**, we have attempted to illustrate photoinduced electron transfer (PET) between multicolored π -moieties of **Ru:CD-DTTs** and a model electron acceptor, menadione (MQ)^{16,24,25}. The PL of **Ru:CD-DTTs** at λ_{ex} = 350 nm in PBS buffer (pH = 7.4) is quenched with increasing [MQ] (10-100 μ M). The observed PL is also associated with a blue shift by 8 nm that may occur due to the change in the local environment of the emissive states of excited **Ru:CD-DTTs** (Figure 4a) which has been induced by hydrophobic nature of reduced MQ. This has also been reflected in the MD simulation where MQ motions are prominent on the surface of **pCDs** (Video S2). **Ru:CD-DTTs** linked MQ are found to make and break the stacking interactions intermittently with the surface chromophores of **pCDs** that is probably responsible for the change in the polarity of the local environment as well as enhancement of the average diameter of the dots present in polymer by $\sim$ 4 nm and the diffused cloudy nature of the **Ru:CD-DTTs-MQ** as observed from TEM images (Figure 4b). Now, the occurrence of dynamic quenching with increasing [MQ] is confirmed from the decrease in the longest lifetime (τ_2) [8.3 $\rightarrow$ 6.8 ns], which has almost 50% contribution to $\langle\tau\rangle$,

Figure 4: (a) Steady-state fluorescence spectra of **Ru:CD-DTTs** with increasing **[MQ]** (10-100 μM) upon excitation at 330 nm in PBS buffer, pH = 7.4. Inset: corresponding Stern-Volmer plots; (b) Bright field TEM images of **Ru:CD-DTTs-MQ** adducts. (c) Time-resolved fluorescence decay spectra of **Ru:CD-DTTs** with increasing **[MQ]** (10-100 μM). (λ_{ex} = 340 nm). (d) Transient triplet-triplet absorption spectra of: **Ru:CD-DTTs**, **MQ**, and mixture of both in PBS buffer, pH = 7.5 at 1 μs after laser flash (λ_{ex} = 355 nm) in absence (red line) and presence (blue line) of MF (e) The difference of absorbance ($\Delta\text{O.D.}$) with variation of MF for **Ru:CD-DTTs-MQ** (0.1 mM) monitored at 410 nm for $B_{1/2}$ measurement. (f) Cyclic voltammogram (6 scans average) for **Ru:CD-DTTs**, **MQ** (1.5 mM) and **Ru:CD-DTTs-MQ** complex in PBS buffer (10 mM; pH=7.2 $\pm$ 0.2) [inset: schematics of redox couples] (g, h) Different conformations of **pCDs-MQ** adduct. (i) HOMO (H) and LUMO (L) energy levels for receptor (MQ) and acceptor **pCDs** moieties and probable PET pathway as calculated computationally using the B3LYP/6-31g+ (d) level of theory in water as a model solvent.

while τ_1 and τ_3 remain unaltered (Figure 4c and Table S2). Here, probably the diffusion-controlled electron transfer phenomenon occurs which needs time from microseconds

to submicroseconds²⁶. Therefore dynamic quenching due to electron transfer is unable to perturb other two faster components (of the order of pico second) of lifetime.

Laser flash photolysis.

To get direct evidence of such electron transfer from the excited **pCDs** to **MQ** we have performed laser flash photolysis experiments corroborated with magnetic field which can identify the transient radical ions with respect to their optical density (O. D.). Figure 4d depicts the transient absorption spectra ($\lambda_{\text{ex}} = 355 \text{ nm}$) of individual **Ru:CD-DTTs** and **MQ** (0.1 mM) and their mixtures in PBS buffer. The spectrum of **Ru:CD-DTTs** shows a significant peak around 370 nm with a broad shoulders from 450 nm to 550 nm, whereas that of **MQ** has absorption maximum at 360 nm. Increase in **[MQ]** to **Ru:CD-DTTs** in PBS increases the O.D. value of **pCDs** at 370 nm by 62% along with the generation of a new peak around 410 nm. From the earlier report it is found that the absorption maximum of transient **[MQ $^{\cdot-}$]** radical anion is around 400 nm²⁷. Therefore, it can be inferred that the electron transfer occurs from **Ru:CD-DTTs** to **MQ**, generating **[MQ $^{\cdot-}$]** radical anions and corresponding **[Ru:CD-DTT $^{+}$]** radical cations with absorption maximum around 410 nm and 550-580 nm respectively. The decay profiles of the transient species at 410 nm are shown in the Figure S4 and the corresponding lifetime of **[MQ $^{\cdot-}$]** is found to be 3.9 μs .

Magnetic Field Effect on radical ions.

The formation of radical ions **[MQ $^{\cdot-}$, Ru:CD-DTT $^{+}$]** and the spin state of the primary geminate solvent separated ion pairs (SSIPs) are confirmed by applying magnetic field (MF) of the order of 0.08 tesla, which can perturb the effects produced by hyperfine interactions present in the system²⁸. During diffusion, when the inter-radical distance between the components of the spin-correlated geminate SSIP becomes $\sim 10 \text{ \AA}$, the exchange interaction between free electrons becomes negligible and their singlet (S) and triplet (T_0 & $T_{\pm}$) states become degenerate leading to maximum intersystem crossing through hyperfine interactions present in the system²⁹. Application of an external MF of the order of hyperfine interactions will reduce intersystem crossing through Zeeman splitting of the $T_{\pm}$ states and increase the geminate radical ion pairs with initial spin correlation^{30,31}. Here, we observe a substantial magnetic field effect (MFE) in the transient absorption of **Ru:CD-DTTs** with **MQ** as shown in Figure 4d. In presence of MF of 0.08 T, we observe that the absorbance increases at around 410 nm and 510 nm, which are already assigned for **[MQ $^{\cdot-}$]** and **[Ru:CD-DTT $^{+}$]** respectively. The rate constants obtained from representative decay profile of the **[MQ $^{\cdot-}$]** at 410 nm in absence and presence of MF is 3.9 μs and 4.06 μs respectively (Inset: Figure 4d). Figure 4e shows the change in "difference in absorbance" ($\Delta\text{O.D.}$) with the varied magnitude of externally applied MF at 410 nm. It is found that $\Delta\text{O.D.}$ increases with increase in MF and eventually reaches a saturation value. The particular MF required to attain half of the saturation value for a particular system is known as $B_{1/2}$, a measure of the hyperfine interaction present in the system, which is found to be 0.011 T for the present case. According to Weller *et al*³²

$$B_{1/2} = \frac{2(B_1^2 + B_2^2)}{B_1 + B_2} = 0.011 \text{ T} \quad \dots\dots\text{(III)},$$

where,

$$B_i = \left[\sum a_{iN}^2 I_N(I_N + 1) \right]^{1/2} \quad \dots\dots\text{(IV)},$$

where a_{iN} is the hyperfine coupling constant of i^{th} electron with the N^{th} nucleus and I_N is the ground state nuclear spin quantum number of the respective nucleus. The calculated B_1 value for

MQ $^{\cdot-}$ radical anion³³ is $5.27 \times 10^{-4} \text{ T}$. Hence from equation (III and IV), the guess value of B_2 for **[Ru:CD-DTT $^{+}$]** is calculated as $69 \times 10^{-4} \text{ T}$, assuming the calculated and experimental values of $B_{1/2}$ to be comparable. The calculated B_2 value is quite high, possibly due to the presence of highly conjugated π -electron clouds³⁴ in **[Ru:CD-DTT $^{+}$]**. The hopping of electrons on the surface of **[Ru:CD-DTT $^{+}$]**, which contains a large number of conjugations, may broaden the energy levels of spin states. Hence, the excess MF is required to decouple the energetically broadened degenerate triplet states, T_0 and $T_{\pm}$. In **Ru:CD-DTTs-MQ** system both the intermolecular and intramolecular electron transfer processes may be possible.

Electrochemistry of pCDs.

It is quite expected that **Ru:CD-DTTs** is a reservoir of excess electron and proton due to the presence of highly π -conjugated nanodomain as well as numerous numbers of $-\text{COOH}$ and $-\text{OH}$ moieties that is supported by experimental findings¹². Therefore, cyclic voltamogramme has been explored with an aim to study whether **Ru:CD-DTTs** can donate electron or proton to **MQ** without any photo activation. Two reversible two-electron wave separated by 670 mV, are observed in case of **MQ** (Figure 4f; Peak-1, 2)^{35,36}. On addition of **Ru:CD-DTTs** in **MQ** [0.5 $\rightarrow$ 1.5 mM] (Figure S5), the intensity of the cathodic current at -558 mV increases by ~ 3 times along with a red shift of -258 mV (Peak-2 $\rightarrow$ 4). This is due to the reduction of **MQ** by protonation or electron transfer from **Ru:CD-DTTs** via the formation of **Ru:CD-DTT:MQH $_2$** complex by Michel addition reaction³⁷. The corresponding positive Peak-3 of the complex at 0.19 V can be explained by the reverse oxidation reaction of the **Ru:CD-DTT:MQH $_2$** to **Ru:CD-DTT:MQ**.

DFT Calculation on Electron Transfer Reaction.

Electronic nanostructures are difficult to be controlled at the atom by atom level, which is generally true for very large molecules. Here we have demonstrated that it is possible to visualise electronic transition density differences in **pCDs** as a diagnostic tool to monitor the changes in the shape of the orbitals involved in the transition. Figure 4g-h shows the two possible ways for orientation of **MQ** which show $\sim 5 \text{ \AA} \rightarrow 12 \text{ \AA}$ separation distance from polymer surface as obtained from MD simulation. The arrow from the thin film of the aromatic moieties signifies the electron transfer pathway. The respective transition in figure 4i illustrates the HOMO and LUMO of the surface of **pCDs** as well as **MQ** with respective orbital energy. The probable electron transfer occurs from HOMO to LUMO of donor surface on laser irradiation, then the single electron is transferred to LUMO of **MQ** resulting the formation of radical ions of their respective spin state. The other possible electron transfer pathways from different surface tethered moieties (1-6) to **MQ** (keto and enol forms) are shown in Figure S14 a $\rightarrow$ f where the **pCDs** are found to be acting as an electron donor as well as an electron acceptor.

CONCLUSION

In conclusion, this article reports a one-pot two-step synthetic protocol of a photoluminescent water soluble polymer composed of CDs. The unusual double humped periodic excitation dependent photoluminescence (EDPL) profiles along with the changes in average PL lifetime of **pCDs**

indicate the formation of high energy donor state and low energy aggregate state due to overlap of molecular orbitals between the chemically switchable π -network of CDs after polymerization. Next, we are able to highlight the free electron distribution on the surface of pCDs, by identifying pCD+• radical ions produced through PET to a model electron acceptor. The electron transfer process is further modulated through perturbation of hyperfine interaction by an external magnetic field. The optimization of MFE is controlled by exchange interaction between the Π -electron clouds of polymer dots and the electron acceptor. Moreover, the anomalous $B_{1/2}$ value of polymer dot radical obtained from the MFE indicates the presence of highly conjugated Π -electron clouds in pCDs. Electrochemistry also supports the electron transfer event. Ultimately DFT calculations reveal the best possible mechanism of PET, which explains why CDs can act as an electron donor as well as acceptor. The overall observations also suggest that the major source of PL in pCDs is ensembles of chromophores with variable excitation and emission features within there nanodomains and the EDPL of CDs is an inhomogeneous effect, in which different subtypes of dots emit at different wavelengths, however the individuals merely follow the Kasha-Vavilov rule.

ASSOCIATED CONTENT

Supporting Information

Detailed synthetic protocol, additional spectroscopic data, TEM, details of MD-simulations and theoretical calculations are available in supporting information.

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Notes

The authors declare no competing financial interest

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