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Simultaneous Binding of a Cyclophane and Classical Intercalators to DNA: Observation of FRET-mediated White Light Emission

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DNA-assisted Förster Resonance Energy Transfer (FRET) between an anthracene-based cyclophane (**CP**) and mono- and bis-intercalators such as propidium iodide (**PI**) and ethidium homodimer-1 (**EHD**), respectively, have been studied using various photophysical and biophysical techniques. The cyclophane and **PI** exhibited simultaneous binding to DNA at all concentrations studied and showed DNA-assisted FRET from the excimer of cyclophane with a FRET efficiency of ca. 71%. On the other hand, the bis-intercalator **EHD**, only at lower concentrations (< 3 μM) can act as an acceptor for the energy transfer process with a lower efficiency of ca. 44%. At higher concentrations (> 15 μM), **EHD** on account of its higher binding affinity, displaces cyclophane from the DNA scaffold. Employing the ternary system comprising of the cyclophane, DNA and **PI** and fine-tuning the concentrations of the components in the molar ratio of 1:0.75:0.05 (**CP**:DNA:**PI**) we have demonstrated white light emission with CIE coordinates (0.35, 0.37).

INTRODUCTION

The development of organic white light emitting materials hold great promise for the production of highly efficient, large area light sources.[1, 2] FRET based fluorescence colour tuning, with fluorophores incorporated in various scaffolds including polymers, biomolecules, micelles, supramolecular assemblies and nanoparticles, is a widely investigated approach for white light generation.[3-18] Among these scaffolds, DNA-cationic surfactant complexes have emerged as intriguing candidates for optoelectronic applications in recent years because of their unique material properties, including solubility in organic solvents and ability to form thermally stable, transparent films.[18-24] Moreover, the predictable secondary structure, unique binding sites for small molecules and the ability to control the spatial arrangement of chromophores with nanoscale precision, makes DNA an excellent scaffold for related applications in optoelectronic devices and sensors.[5, 25-28] A key component of developing DNA based energy transfer systems is the control of distances between the bound molecules, which has important role in the DNA mediated energy transfer process.[27, 29-33] This in turn is regulated by apparent binding constants and allosteric factors when multiple chromophores are involved.[33-44] While many groups have used the interaction of chromophores with DNA in demonstrating DNA mediated white light emission,[18-23, 45] there exist need of fundamental understanding on the structure-property correlation controlling the output of the light emission.

In this context, we have started investigating the effect of simultaneous binding of ligands, which occupy orthogonal binding sites on the DNA helix, on FRET related optical properties. For example, We have recently demonstrated the simultaneous binding of an anthracene-based cyclophane (**CP**), a non-classical intercalator and a DNA intercalator, ethidium bromide (**EB**) with potential for emission colour tuning (Fig. 1).[46] The symmetric cyclophane exhibited dual emission in aqueous medium having monomer emission maximum at 430 nm and an intramolecular excimer at 550 nm.[47, 48] In presence of DNA, the excimer emission got enhanced with concomitant quenching of monomer emission. Interestingly, in presence of ethidium bromide, we could observe an efficient FRET from the cyclophane to the intercalated ethidium bromide. Finally, we used this ternary system for the demonstration of white light emission by appropriately changing the concentrations of the individual constituents.[46]

Herein, we have investigated the role of two different intercalator energy acceptors, namely ethidium homodimer-1, a

known bis-intercalator and propidium iodide, a mono-intercalator with better binding affinity than the earlier reported ethidium bromide and compared their optical properties. Our results, demonstrated that the bis-intercalator, with three order higher DNA binding affinity tend to displace the cyclophane from the DNA scaffold at comparable concentrations while propidium iodide showed a better FRET efficiency of *ca*. 71%, compared to that of ethidium bromide.

GENERAL EXPERIMENTAL TECHNIQUES

Fluorescence spectra were recorded, in 1×1 cm quartz cuvettes, on a SPEX–Fluorolog F112X spectrofluorimeter. CIE, Commission Internationale de l'Eclairage (International Commission on Illumination), chromaticity coordinates (1931) (*x*, *y*) in thin films were calculated using HORIBA Jobin Yvon Color Calculator provided with integrating sphere. Fluorescence lifetimes were measured using IBH (FluoroCube) time-correlated picoseconds single photon counting (TCSPC) system. The thin films were excited with a pulsed diode laser (<100 ps pulse duration) at a wavelength of 375 nm (NanoLED-11) with a repetition rate of 1 MHz. The detection system consisted of a microchannel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000M) and TCSPC electronics [data station Hub including Hub-NL, NanoLED controller, and preinstalled fluorescence measurement and analysis studio (FMAS) software]. The fluorescence decay profiles were deconvoluted using IBH data station software V2.1 and minimizing the χ^2 values of the fit to 1 ± 0.1. The quantum yield of fluorescence of the cyclophane **CP** in presence of DNA was calculated using equation (1).[49]

$$\Phi_u = \frac{A_s F_u n_u^2}{A_u F_s n_s^2} \Phi_s \qquad (1)$$

where, A_s and A_u are the absorbance of standard and unknown, respectively. F_s and F_u are the areas of fluorescence peaks of the standard and unknown and n_s and n_u are the refractive indices of the solvents used for the standard and unknown, respectively. Quinine sulfate (Φ_s = 0.546) was used as the standard for determination of fluorescence quantum yields.[50, 51] Solvents and reagents were purified and dried by usual methods prior to use. Dried methanol was used for all the studies. All experiments were carried out at room temperature (25 ± 1 °C), unless otherwise mentioned.

Materials

Calf thymus (CT) DNA, Propidium iodide and ethidium homodimer-1 were purchased from Sigma–Aldrich and used as received. A solution of CT DNA was sonicated for 1 h to minimize the complexities arising from DNA flexibility and filtered through a 0.45 μm Millipore filter ($M_w = 3\times10^5$ gmol^{-1}). The concentrations of DNA solutions were determined by using the average extinction coefficient value of 6600 M^{-1}cm^{-1} of a single nucleotide at 260 nm. **CP** was prepared according to the literature procedure.[47, 48]

Calculation of FRET efficiency and donor-acceptor distance

To calculate the efficiency of FRET and the distance between the donor and acceptor moieties equation (2)[49, 52] was used.

$$R_0 = 0.211[\kappa^2 n^{-4} Q_D J(\lambda)]^{1/6} \text{ (in Å)} \qquad (2)$$

where R_0 is the Förster distance, κ^2 is a factor describing the relative orientation in space of the transition dipoles of the donor and acceptor and assumed to be equal to 1.25,[53-55] n is the refractive index of the medium and assumed to be 1.3, Q_D is the quantum yield of the donor in the absence of acceptor and J(λ) is the overlap integral, which expresses the degree of spectral overlap between the donor emission and the acceptor absorption given by equation (3),[49, 52]

$$J(\lambda) = \frac{\int_0^{\alpha} F_D(\lambda)\, \varepsilon_A(\lambda)\, \lambda^4\, d\lambda}{\int_0^{\alpha} F_D(\lambda)\, d\lambda} \qquad (3)$$

where, $F_D(\lambda)$ is the fluorescence intensity of the donor in the wavelength range of λ to λ+ dλ and is dimensionless and ε(λ) is the extinction coefficient (in M^{-1}cm^{-1}) of the acceptor at λ. The orientation factor (κ^2), we assumed a value of 1.25 instead of 0.67,[53-55] since the DNA-bound molecules are not in random orientation. From the value of R_0 obtained from equation 2, the donor–acceptor distance (r) can be calculated using equation (4),[49, 52]

$$r^6 = [R_0^6\,(1 - E)]/E \qquad (4)$$

where, E is the efficiency of energy transfer, which is calculated from the lifetimes of the donor in the absence and presence of acceptor (τ_D and τ_{DA}) as per the equation (5).[49, 52]

$$E = 1 - (\tau_{DA}/\tau_D) \qquad (5)$$

RESULTS AND DISCUSSION

FRET between CP and DNA intercalators

Ethidium bromide (**EB**), propidium iodide (**PI**) and ethidium homodimer-1 (**EHD**) (Fig. 1) are phenanthridinium derivatives, which exhibit weak fluorescence in aqueous medium and their fluorescence intensities were known to be enhanced in the presence of DNA.[56] The DNA mono-intercalators **EB** and **PI** bind to DNA with association constants of 1.4 x 10^5 M^{-1} and 8.6 x 10^5 M^{-1}, respectively.[44] On the other hand, **EHD**, which contains two phenanthridinium moieties was found to undergo bis-intercalation with an association constant of 2 x 10^8 M^{-1}.[30, 41, 43] The anthracene-based cyclophane (**CP**) interacts with DNA through non-classical partial intercalation and exhibit a bathochromically shifted excimer emission, which can be utilized for energy transfer to suitable acceptor molecules.[46, 48] The excimer emission at 570

nm has been confirmed by recording the excitation spectra of the cyclophane with and without DNA and they are found to be similar to the corresponding absorption spectra (Fig. S1†). First we investigated the utility of the dicationic molecule **PI** as the excited state energy acceptor in the FRET process. The absorption and emission changes observed with **PI** are similar to that of **EB** (Fig. S2-S3†), though the binding affinity of **PI** towards DNA is slightly higher. The calculated spectral overlap between the cyclophane excimer emission and **PI** absorption are found to be higher than that with **EB**. The energy transfer efficiency between **CP** and **PI** was calculated to be *ca.* 71% as against 62% with **EB**. Hence the FRET between **CP** and **PI** was found to be higher and the calculated donor-acceptor distance is 1.7 nm.

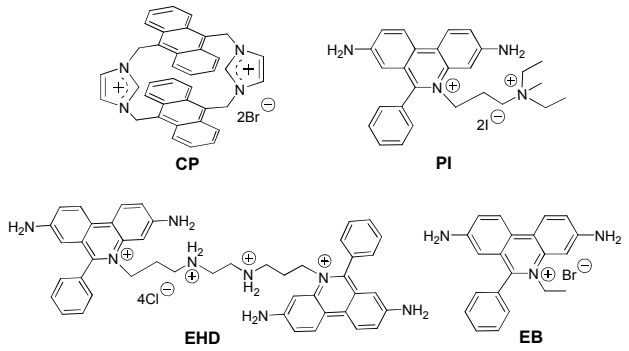

Fig. 1 Structures of molecules used for the study.

In order to understand how the bis-intercalator behaves in the energy transfer process, we monitored the absorption and emission parameters of the cyclophane in presence of **EHD**. At lower concentrations of the intercalator, we observed the excitation energy transfer to the acceptor molecule (Fig. 2 & Fig. S4†). Interestingly, when we further increase the concentration to 15 μM it was observed that there is a gradual quenching of the acceptor fluorescence. The absorption changes also complement this observation. At 15 μM

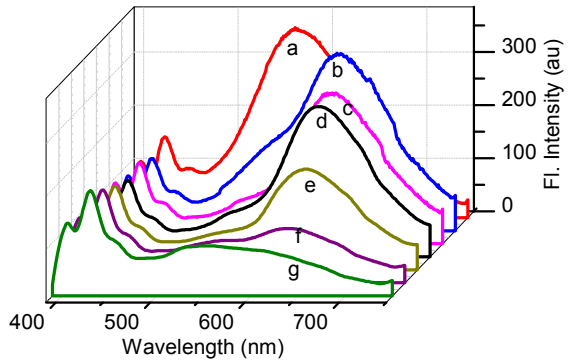

Fig. 2 Changes in the emission spectra of DNA–bound **CP** by the addition of **EHD** in phosphate buffer. [**CP**], 16 μM; [DNA], 27 μM; [**EHD**], (a) 0 and (g) 15 μM. Excitation wavelength, 380 nm.

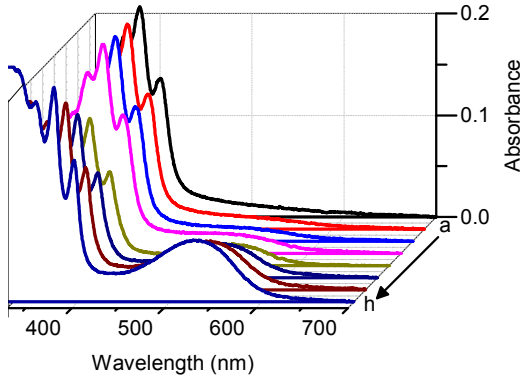

Fig. 3 Changes in the absorption spectra of DNA-bound **CP** by the addition of **EHD** in phosphate buffer (10 mM, 7.4) containing 2 mM NaCl. [**CP**], 16 μM; [DNA], 27 μM; [**EHD**], (a) 0 and (h) 15 μM.

concentration of **EHD**, we observed *ca.* 38% hyperchromicity in the anthracene absorption region, indicating thereby the less significant interactions between **CP** and DNA (Fig. 3). Moreover, at 15 μM concentrations of **EHD**, the system exhibited an emission spectrum, which is similar to that of the free cyclophane in buffer medium. An explanation for these observations is based on the fact that at these higher concentrations, the bis-intercalator, **EHD** found to displace **CP** from the DNA template on account of its higher binding affinity.

Fluorescence lifetime studies and time resolved spectroscopy

To further understand the FRET between **CP** and phenanthridinium derivatives in the presence of DNA, we investigated the fluorescence lifetimes of **CP** under different conditions. **CP** in the aqueous medium exhibited a bi-exponential decay with lifetimes of 13.4 and 52.6 ns, which can be assigned to monomer and excimer, respectively.[47] Interestingly, in the presence of DNA we observed significant enhancement in the excimer lifetime with a concomitant decrease in the monomer lifetime. For example, the excimer lifetime of **CP** in the buffer medium (52.6 ns) has been enhanced to 143.1 ns, in the presence of 38 μM DNA. Then we investigated the role of FRET acceptors such as **PI** and **EHD** in the fluorescence lifetime of cyclophane excimer. For example, at 8 μM concentration of **PI**, a bi-exponential decay with lifetimes of 55.7 and 20.2 ns was observed, wherein the long-lived species correspond to the cyclophane excimer. This reduction in excimer lifetime from 143.1 to 55.7 ns can be attributed to the effective excitation energy transfer from **CP** to **PI** (Fig. 4A).

The time-resolved emission spectroscopic (TRES) technique was utilized further to understand FRET process. When a system containing **CP**, DNA and **PI** was excited at 380 nm and analyzed immediately after excitation (2 ns), we observed an emission spectrum with maximum at 430 nm and a small shoulder at 625 nm (Fig. S5†). However, gradually with time, the intensity of the peak at 625 nm was found to increase with the complete disappearance of monomer peak at 430 nm.

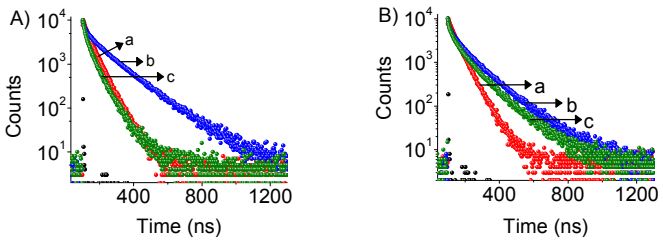

Fig. 4 (A) Fluorescence decay profiles of **CP** (a) alone, (b) in the presence of DNA and (c) in the presence of DNA and **PI** when monitored at (a) 430 nm, (b) 570 nm and (c) 620 nm, respectively in phosphate buffer (10 mM, 7.4) containing 2 mM NaCl. [**CP**], 16 μM; [DNA], 38 μM; [**PI**] 8 μM. (B) Fluorescence decay profiles of CP (a) alone, (b) in the presence of DNA and (c) in the presence of DNA and **EHD** when monitored at (a) 430 nm, (b) 570 nm and (c) 620 nm in phosphate buffer (10 mM, 7.4) containing 2 mM NaCl buffer. [**CP**], 16 μM; [DNA], 27 μM; [**EHD**], 3.8 μM. Excitation wavelength, 375 nm.

Importantly, the absence of the emission band at 570 nm corresponding to the excimer of **CP** in the presence of **PI** at various time scales points to the fact that its formation is quenched due to the existence of an efficient FRET from **CP** excimer to **PI**. After 60 ns, the system exhibited a broad peak at 625 nm, corresponding to **PI** through FRET from **CP**. Thus, at longer time scale, we could observe emission from the acceptor only, which is a clear confirmation for the existence of excited-state energy transfer from the excimer of **CP** to **PI** (Fig. S5†).

With the bis-intercalator **EHD** at 3 μM concentrations, the system showed a bi-exponential decay with lifetimes of 93.2 and 22.2 ns. The reduction of excimer lifetime from 143.1 ns to 93.2 ns in presence of **EHD** is an indication of FRET from CP to the intercalated **EHD** (Fig. 4B). Further evidence was provided through the TRES studies with 3 μM concentrations of the bis-intercalator **EHD**, wherein we observed the cyclophane monomer emission at 430 nm immediately after excitation (Fig. S6†). But at longer time scale (60 ns), we observed an emission band around 620 nm, which corresponds to **EHD**. However, at 15 μM concentrations of **EHD**, the system exhibited bi-exponential decay with lifetimes of 16 ns and 52.8 ns, when monitored at 550 nm. These lifetime values correspond to the monomer and excimer emissions of free **CP** in the aqueous medium (Fig. S7A†). These experiments once again confirmed that at higher concentrations (*ca.* 15 μM), **EHD** displaces **CP** from the DNA scaffold thereby ruling out

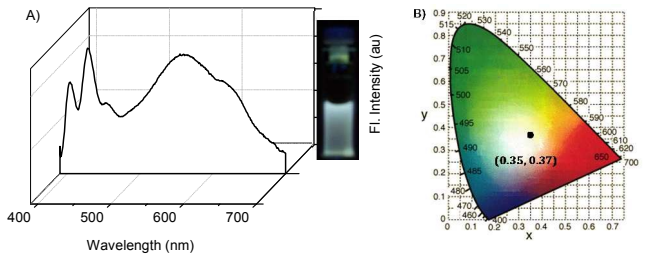

Fig. 5 A) Emission spectrum of a solution containing **CP**, DNA and **PI** in the ratio 1:0.75:0.05 in aqueous medium. Excitation wavelength, 380 nm. Insets show the fluorescence of the same solution under UV lamp (365 nm). B) CIE Coordinates of the white light emission.

the possibility of FRET under these conditions. In the TRES analysis, at higher concentrations of **EHD**, the spectrum immediately after excitation (2 ns) exhibited two peaks at 430 and 625 nm, correspond to cyclophane monomer emission and energy transferred emission from **EHD**. However, with time, we could observe reduction in the intensity of **EHD** emission and the observation of the formation of a new peak around 540 nm, which corresponds to the excimer emission of the cyclophane in the buffer medium (Fig. S7B†).

Based on the fluorescence and lifetime data, we calculated the efficiency of energy transfer between various donor-acceptor pairs and the corresponding donor-acceptor distances. The energy transfer efficiency between **CP** and **PI** was found to be *ca.* 71% whereas, the FRET efficiency between **CP** and 3 μM **EHD** was found to be *ca.* 44%. The donor-acceptor distances between **CP-PI** and **CP-EHD** systems were found to be *ca.* 17 and 24 Å, respectively (Table 1). The rate of FRET in various donor-acceptor systems were also calculated and tabulated (Table 1).

Table 1. Different parameters of FRET between cyclophane (CP) and various acceptors[a]

Acceptor	Rate of energy transfer (10^7 s^{-1})	Forster distance (Å)	D-A distance (Å)	FRET efficiency (%)
EHD[a]	0.15	18.7 ± 0.5	24 ± 0.5	44 ± 2
PI[a]	1.67	19.7 ± 0.2	17 ± 0.2	71 ± 1
EB[b]	1.14	34.2 ± 0.1	31.5 ± 0.1	62 ± 1

[a] Average of three independent measurements. [b] Data taken from ref. 46

Demonstration of white light emission

To demonstrate white light emission in aqueous medium, we utilized the FRET between **CP** and **PI** in presence of DNA since the energy transfer efficiency between **CP** and **PI** was found to *ca.*71%. This can be achieved by taking the individual components in proper ratio so that the emission spectrum can cover the entire visible region (400-700 nm). In this context, we have taken **CP**, DNA and **PI** in the molar ratio of 1:0.75:0.05 in 3 mL of the aqueous medium, and recorded the emission spectrum upon 380 nm excitation. The observed emission spectrum covered the entire visible region, wherein, the blue region was contributed by the emission from the cyclophane monomer (at 430 nm), green region by the cyclophane excimer (at 560 nm) and the red region by the DNA intercalated **PI** molecule (at 620 nm) (Fig. 5). We have calculated the CIE coordinates of the emission spectrum and which are found to be (0.35, 0.37). These values are very close to the CIE coordinates of pure white light emission (0.33, 0.33). It is interesting to note that the amount of the acceptor molecule required in this case was quite low (*ca.* 2 mol%) because of the existence of an efficient FRET process.

CONCLUSIONS

In conclusion, we have investigated the interactions between the cyclophane **CP** and DNA intercalators such as **PI** and **EHD** using various photophysical techniques. In presence of DNA, we observed that these energy acceptors significantly quenched the excimer emission intensity of the cyclophane with the concomitant formation of new peak in the red region through FRET mechanism. The steady-state and time-resolved fluorescence emission studies have revealed that, these phenanthridinium derivatives were efficient excited-state energy acceptors. Based on the energy transfer efficiency studies, the system containing **CP** and **PI** was found to be the best donor–acceptor pair, in comparison with the bis-intercalator **EHD** and the mono-intercalator **EB** and the system exhibited an energy transfer efficiency of *ca.* 71%. Using the **CP**–DNA–**PI** system in the molar ratio of 1:0.75:0.05 in 3 mL of aqueous medium, we obtained an emission spectrum with the CIE coordinates (0.35, 0.37), which correspond to pure white light emission. These studies further confirmed that both efficiency and nature of DNA binding, and the spectral overlap between donor and acceptor systems play significant role in the generation of DNA–assisted white light emission.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Absorption and emission changes of DNA-bound **CP** in presence of **PI**, Fluorescence decay profile of DNA-bound **CP** in presence of higher EHD concentrations, TRES analysis of DNA-bound **CP** and **PI** and TRES analysis of DNA-bound **CP** and **EHD**. See DOI: 10.1039/b000000x/

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