

Supporting Information

DNA-Assisted White Light Emission through FRET

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General experimental details, calculation of FRET parameters and Figures S1–S8 showing absorption, emission and decay profiles of **CP-1** and **CP-2** in the presence and absence of DNA and **EB**.

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Experimental Section

General Techniques: All experiments were carried out at room temperature (25 ± 1 °C), unless otherwise mentioned. An Elico pH meter was used for pH measurements. UV–Vis and fluorescence spectra were recorded in 1×1 cm quartz cuvettes. The electronic absorption spectra were recorded on a Shimadzu UV–VIS–NIR spectrophotometer. Fluorescence spectra were recorded on a SPEX–Fluorolog F112X spectrofluorimeter. Quinine sulfate ($\Phi_F = 0.546$) was used as the standard for determination of fluorescence quantum yields. Fluorescence lifetimes were measured using IBH picosecond time correlated single photon counting system. 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 . Time resolved emission spectra (TRES) were obtained using the Data Station software of an IBH picosecond time correlated single photon counting system. To measure TRES, the time resolved fluorescence decay curves were measured for a range of wavelengths from 400 to 700 nm (at 10 nm intervals) to construct a 3D data set of counts versus time versus wavelength. The 3D dataset was then sliced orthogonally to the time axis to produce 2D spectra of counts versus wavelength in order to visualize how the emission spectrum evolved during the fluorescence lifetime. Solvents and reagents were purified and dried by usual methods prior to use. Doubly distilled water was used in all the studies.

Materials. Calf thymus (CT) DNA, ethidium bromide and cetyl trimethyl ammonium chloride used in the present study 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 ($M_w=3\times 10^5$ g mol⁻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.¹ Synthesis of the cyclophane derivatives **CP-1** and **CP-2** were accomplished as reported earlier.² DNA–CTMA complex was prepared as per the literature procedure and its methanolic solution was used in all the studies.³

Calculation of FRET efficiency and donor–acceptor distance: To calculate the efficiency of FRET and the distance between the donor and acceptor moieties equation (1) was used.

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

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 1.2, 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 $J(\lambda)$ is the overlap integral, which expresses the degree of spectral overlap between the donor emission and the acceptor absorption given by equation 2,

$$J(\lambda) = \frac{\int_0^\alpha F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda}{\int_0^\alpha F_D(\lambda) d\lambda} \quad (2)$$

where, $F_D(\lambda)$ is the fluorescence intensity of the donor in the wavelength range of λ to $\lambda + d\lambda$ and is dimensionless and $\varepsilon(\lambda)$ is the extinction coefficient (in $M^{-1}cm^{-1}$) of the acceptor at λ . From the value of R_0 obtained from equation 1, the donor–acceptor distance (r) can be calculated using equation 3,

$$r^6 = [R_0^6 (1 - E)]/E \quad (3)$$

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 4.

$$E = 1 - (\tau_{DA}/\tau_D) \quad (4)$$

References

1. M. Hariharan, J. Joseph and D. Ramaiah, *D. J. Phys. Chem. B* 2006, **110**, 24678–24686.
2. P. P. Neelakandan and D. Ramaiah, *Angew. Chem. Int. Ed.* 2008, **47**, 8407–8411.
3. L. Wang, J. Yoshida and N. Ogata, *Chem. Mater.* 2001, **13**, 1273–1281; Y. Ner, J. G. Grote, J. A. Stuart and G. A. Sotzing, *Angew. Chem. Int. Ed.* 2009, **48**, 5134–5138.

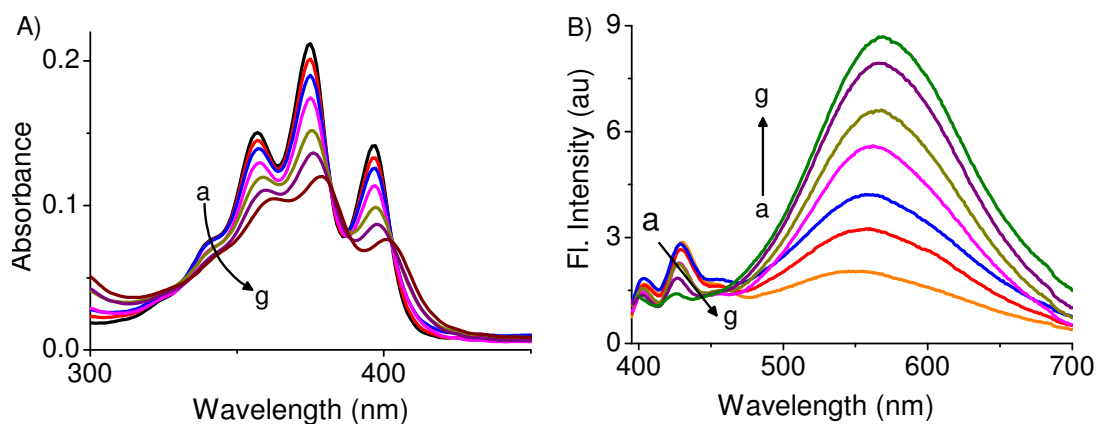


Figure S1. Changes in absorption (A) and emission (B) spectra of **CP-1** (14 μM) with the addition of DNA in phosphate buffer (pH 7.4). [DNA], (a) 0; (g) 40 μM. Excitation wavelength, 380 nm.

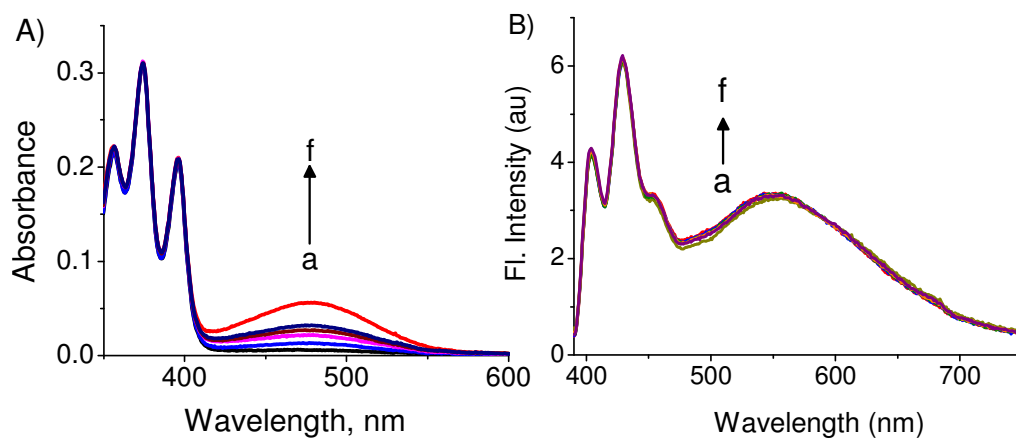


Figure S2. Changes in (A) the absorption and (B) the emission spectra of **CP-1** (23 μM) with the sequential addition of **EB** in phosphate buffer (pH 7.4). [**EB**], (a) 0; (f) 8.8 μM. Excitation wavelength, 380 nm.

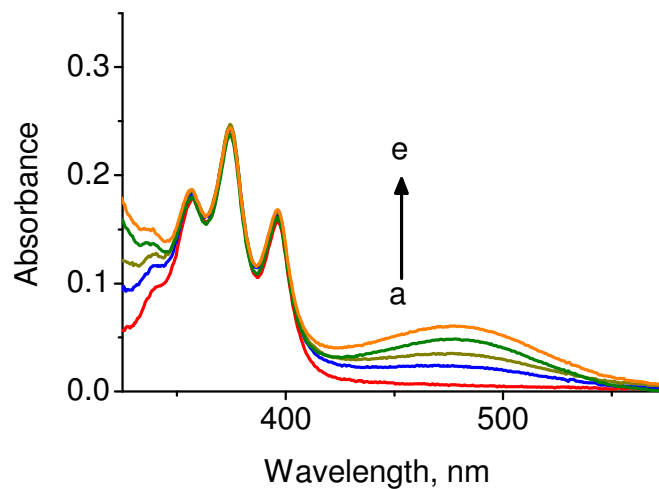


Figure S3. Changes in the absorption spectrum of **CP-1** (14 μM) in presence of DNA (40 μM) with the addition of **EB** in buffer (pH, 7.4) [**EB**], (a) 0; (e) 8.6 μM .

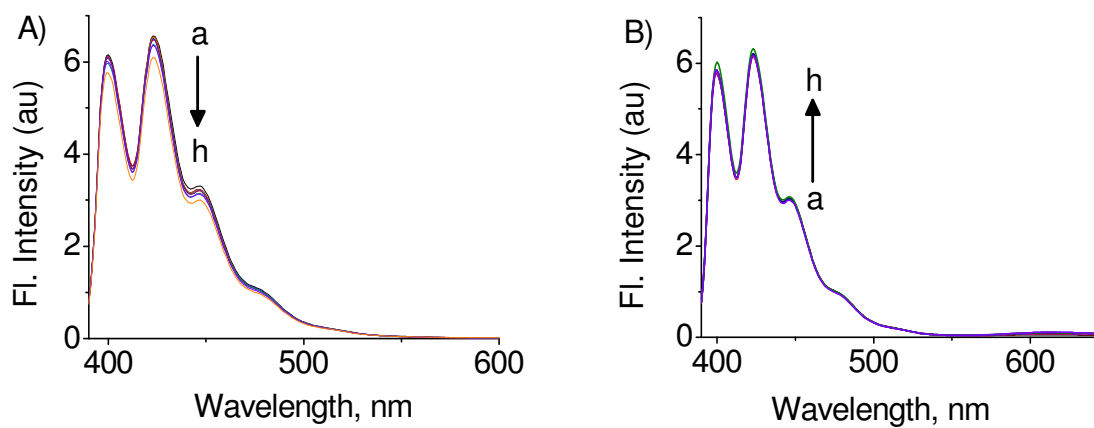


Figure S4. Changes in the emission spectrum of **CP-2** (17 μM) (A) with the addition of DNA followed by (B) the addition of **EB** in buffer (pH 7.4). [DNA], (a) 0; (h) 45 μM and [**EB**], (a) 0; (h) 9.2 μM . Excitation wavelength, 380 nm.

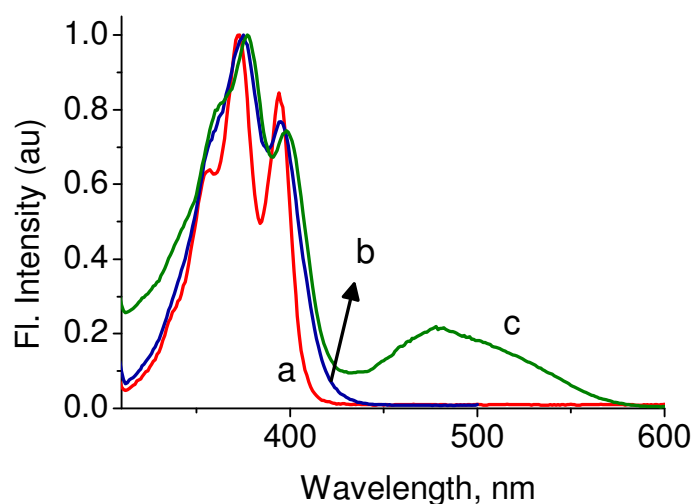


Figure S5. Excitation spectra of **CP-1** (14 μM) (a) **CP-1** alone, (b) in the presence of DNA (40 μM) and (c) in the presence of DNA (40 μM) and **EB** (8.6 μM) collected at 612 nm in buffer.

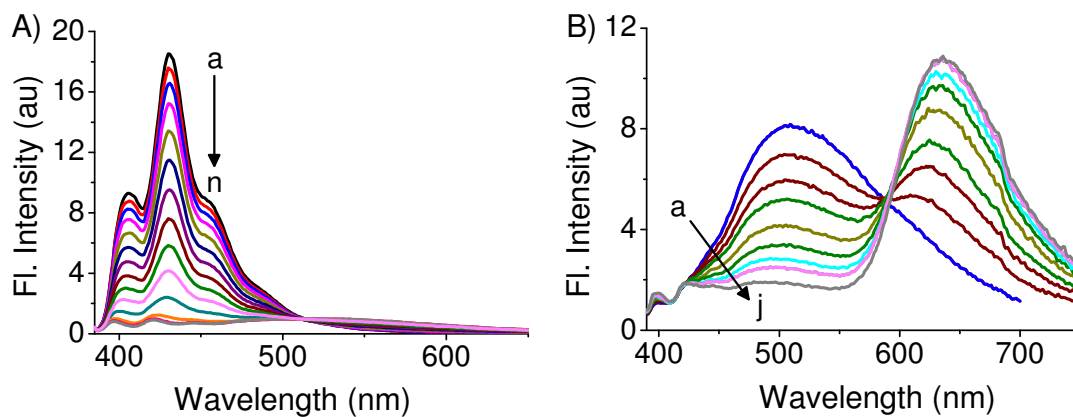


Figure S6. Changes in the emission spectrum of **CP-1** (9.2 μM) by the addition of (A) DNA-CTMA (B) followed by **EB**. [DNA-CTMA] (a) 0; (n) 40 μM , [**EB**] (a) 0; (j) 5.4 μM . Excitation wavelength 380 nm.

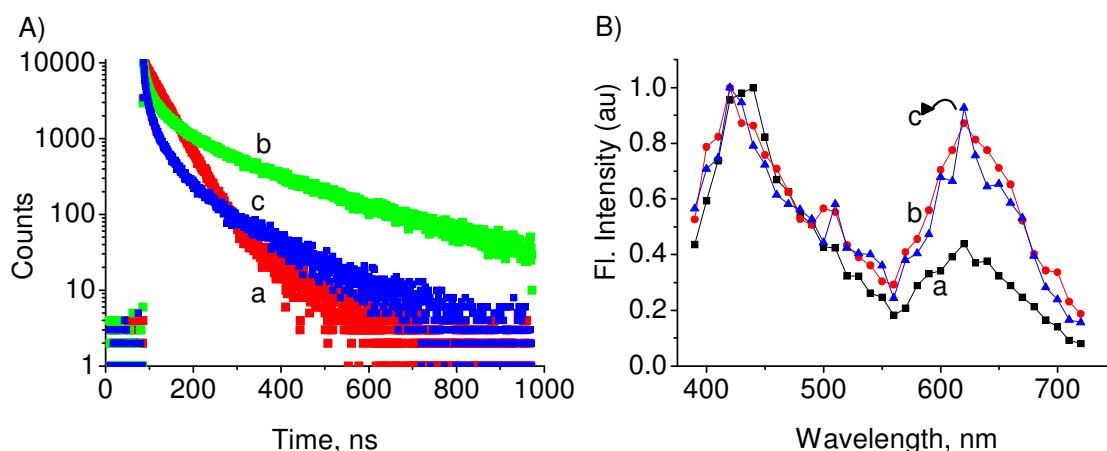


Figure S7. (A) Fluorescence decay profiles of **CP-1** (9.2 μM) (a) alone, (b) in the presence of DNA-CTMA (40 μM) and (c) in the presence of DNA-CTMA and **EB** (5.4 μM) monitored at 612 nm. (B) Time-resolved emission spectrum (TRES) of **CP-1** (9.2 μM) in the presence of DNA (40 μM) and **EB** (5.4 μM) in methanol monitored at (a) 0.98, (b) 9.8 and (c) 42 ns after excitation. Excitation wavelength, 375 nm.

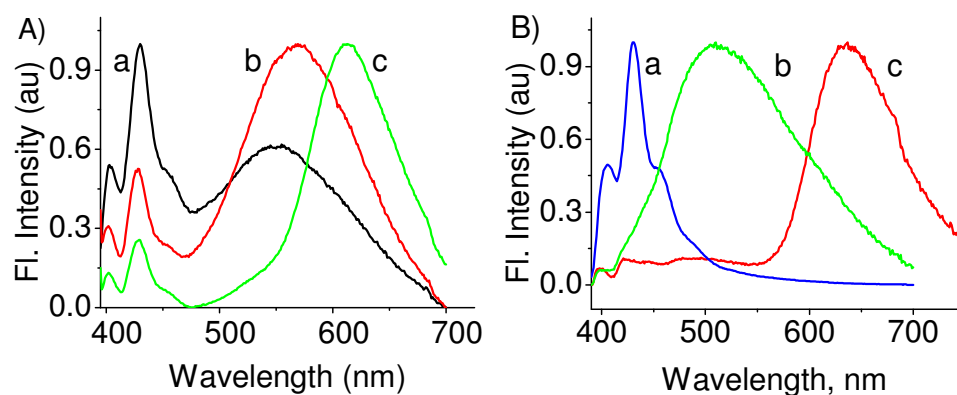


Figure S8. Normalized emission spectra of (a) **CP-1** alone, (b) **CP-1** bound to DNA or **CP-1** bound to DNA-CTMA and (c) in presence of **EB** in solutions of (b) in (A) buffer and (B) methanol.