Supporting Information

Interaction of meso-tetrakis(N-methylpyridinyl)porphyrin with single strand DNAs - poly(dA), poly(dT), poly(dG) and poly(dC): A Photophysical Study

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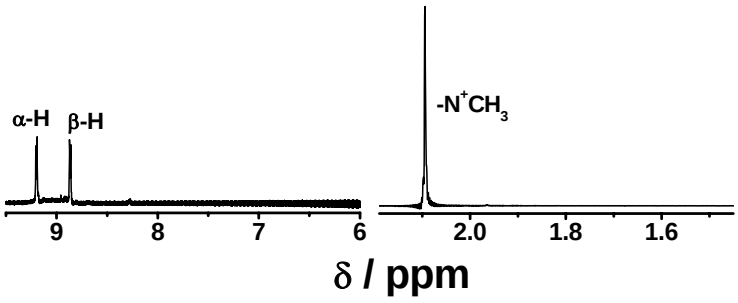

Figure S1. ^{1}H NMR spectrum of TMPyP(Cl) in D_2O[1]

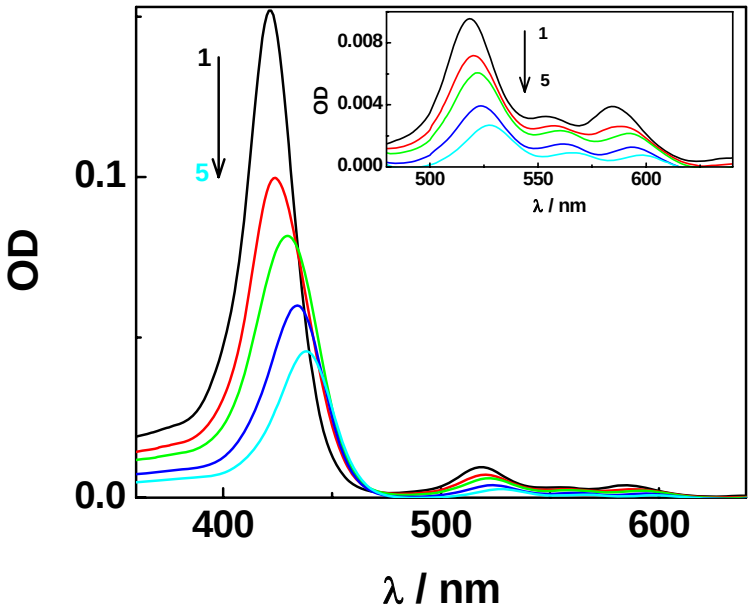

Figure S2. Absorption spectra of TMPyP (0.7 μM) in Tris buffer at different $(dA)_{40}$ concentrations. $[(dA)_{40}]$/nM: (1) 0, (2) 4, (3) 6, (4) 8 and (5) 30. Inset shows an enlarged view of the Q-band absorptions under the same conditions.

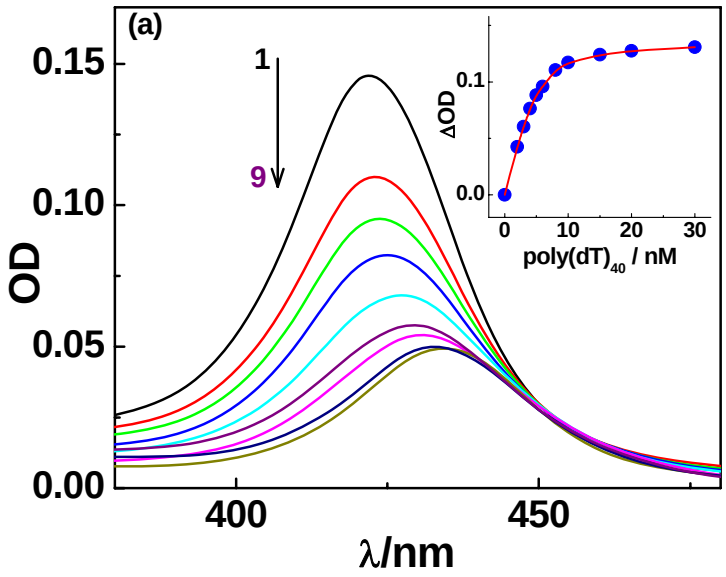

Figure S3. Absorption spectra of TMPyP (0.7 μM) in Tris buffer at different $(dT)_{40}$ concentrations. $[(dT)_{40}]$/nM: (1) 0, (2) 2, (3) 3, (4) 4, (5) 6 (6) 8, (7) 10, (8) 20 and (9) 30. Inset shows the absorbance changes at 420 nm with different $(dT)_{40}$ concentrations.

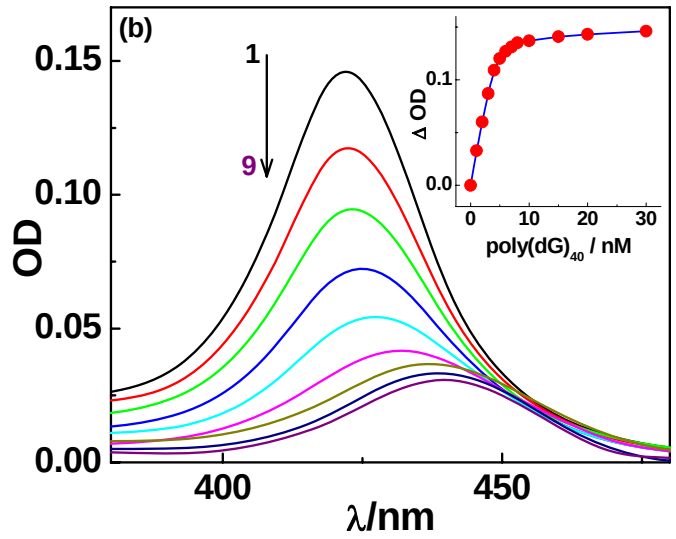

Figure S4. Absorption spectra of TMPyP (0.7 μM) in Tris buffer at different $(dG)_{40}$ concentrations. $[(dG)_{40}]$/nM: (1) 0, (2) 1, (3) 2, (4) 3, (5) 4 (6) 6, (7) 10, (8) 20 and (9) 30. Inset shows the absorbance changes at 420 nm with different poly$(dG)_{40}$ concentrations.

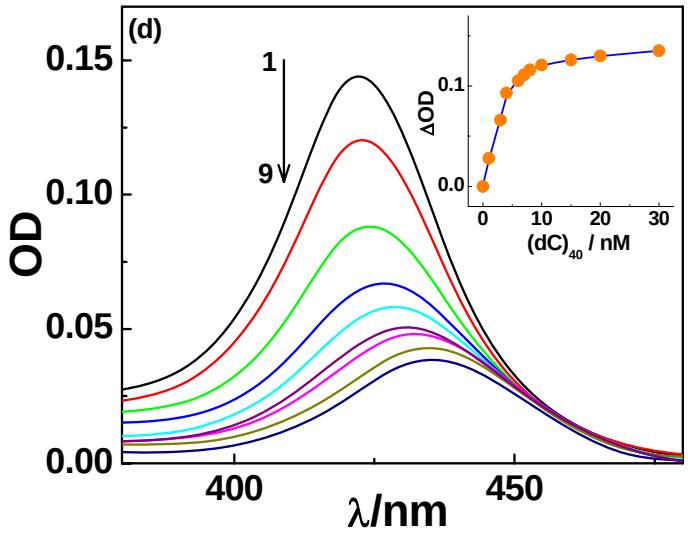

Figure S5. Absorption spectra of TMPyP (0.7 μM) in Tris buffer at different $(dC)_{40}$ concentrations. $[(dC)_{40}]$/nM: (1) 0, (2) 1, (3) 3, (4) 4, (5) 6 (6) 8 (7) 10, (8) 20 and (9) 30. Inset shows the absorbance changes at 420 nm with different poly$(dC)_{40}$ concentrations.

Note S1

Considering the multiple binding modes of TMPyP with the ss-DNA homopolymers (absorption and fluorescence spectra and lifetime measurements indicate the presence of both monomeric and aggregated forms of TMPyP bound to the poly(dN)) and also because of the fact that saturation in the binding isotherm is obtained at very low poly(dN) concentrations (nano molar) with respect to the porphyrin dye concentration (~0.7 μM), (*cf.* Inset, Fig. 1 and Fig. S3-5, SI), it was difficult to determine the binding constants quantitatively, in the present systems. However, assuming that at the saturation point of the binding isotherm, all the binding sites in the poly(dN) are occupied by the dye molecules and all binding sites are equivalent, an approximate value for the overall binding constant was estimated as follows.[2,3]

Analyzing the binding process as reaction (1),

$$\text{poly(dN)}_{40} + \text{nTMPyP} \underset{}{\overset{K}{\rightleftharpoons}} \text{poly(dN)}_{40}\bullet(\text{TMPyP})_n \qquad (1)$$

the overall binding constant (K) can be expressed as,

$$K = \frac{\left[\text{poly(dN)}_{40}\bullet(\text{TMPyP})_n\right]}{\left[\text{poly(dN)}_{40}\right]\times\left[\text{TMPyP}\right]^n} \qquad (2)$$

If the initial concentration of TMPyP is a and the concentration of poly(dN)_{40} at 50% of the total change of the monitoring parameter, i.e. absorbance, is b (as determined from the binding isotherms shown in the Inset, Fig. 1 and Figs. S3-5, SI), then K can be expressed as

$$K = \frac{a/2n}{b\times(a/2)^n} \qquad (3)$$

Here n is the binding stoichiometry, which can be approximately considered to be 20, since at saturation one TMPyP molecule is available for two nucleobases. Substituting the known values for a and b and considering n = 20 for the $\text{poly(dN)}_{40}\bullet(\text{TMPyP})_n$ system, the overall binding constant for all the polynucleotides studied, is estimated to be about $4\text{-}8\times10^{129}$. Thus, the average binding constants of the dye with the individual nucleotides in the ss-DNA homopolymers can be estimated to lie in the range of ~$2\text{-}3\times10^6$ M^{-1}.

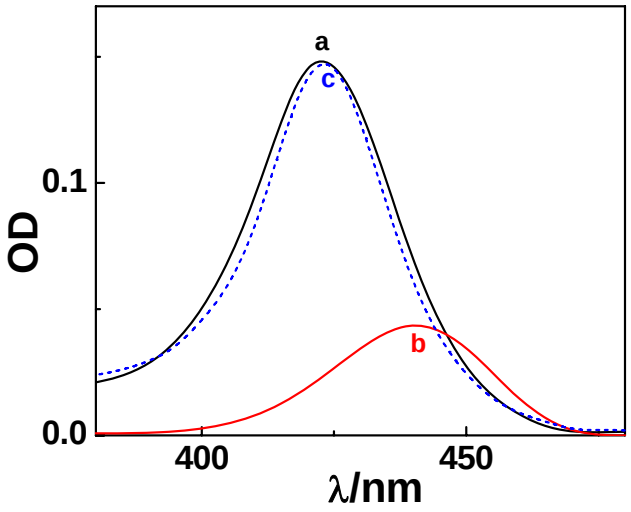

Figure S6. Absorption spectra of TMPyP (0.7 μM) in Tris buffer at different poly(dA)$_{40}$ concentrations. [poly(dA)$_{40}$]/nM: (a) 0, (b) 30. Dotted line (c) shows the reversal in the absorption spectra on addition of 1M NaCl to the solution corresponding to (b).

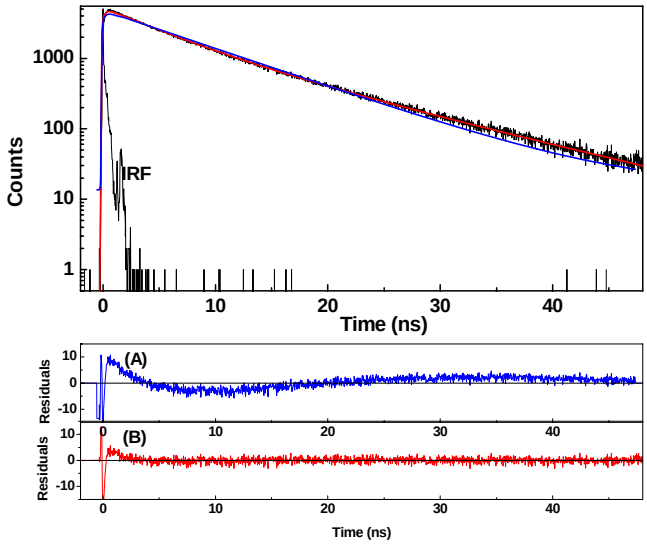

Figure S7. Fluorescence decay traces at 660 nm for TMPyP (0.7 μM) in the presence of 10 nM (dT)$_{40}$, and the corresponding fitted curves considering mono-exponential (blue line) and bi-exponential (red line) functions. The residual traces for the fitting with (A) mono-exponential (blue line) and (B) bi-exponential (red line) functions are also shown, which clearly indicates the bi-exponential nature of the fluorescence decay.

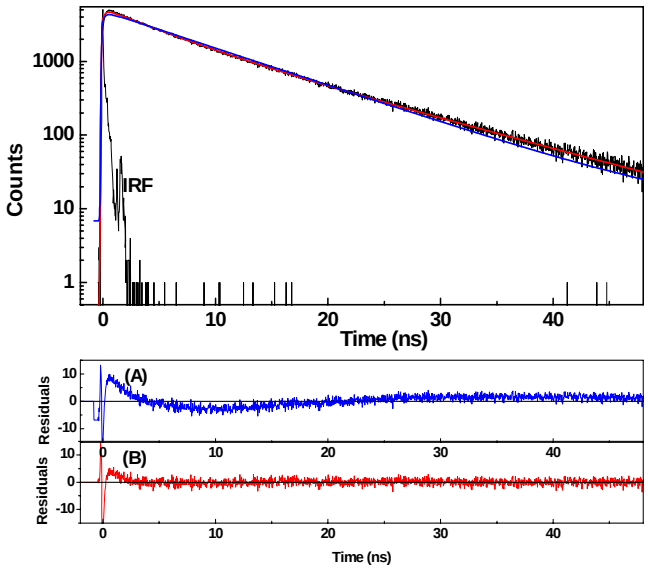

Figure S8. Fluorescence decay traces at 660 nm for TMPyP (0.7 μM) in the presence of 10 nM $(dC)_{40}$, and the corresponding fitted curves considering mono-exponential (blue line) and bi-exponential (red line) functions. The residual traces for the fitting with (A) mono-exponential (blue line) and (B) bi-exponential (red line) functions are also shown, which clearly indicates the bi-exponential nature of the fluorescence decay.

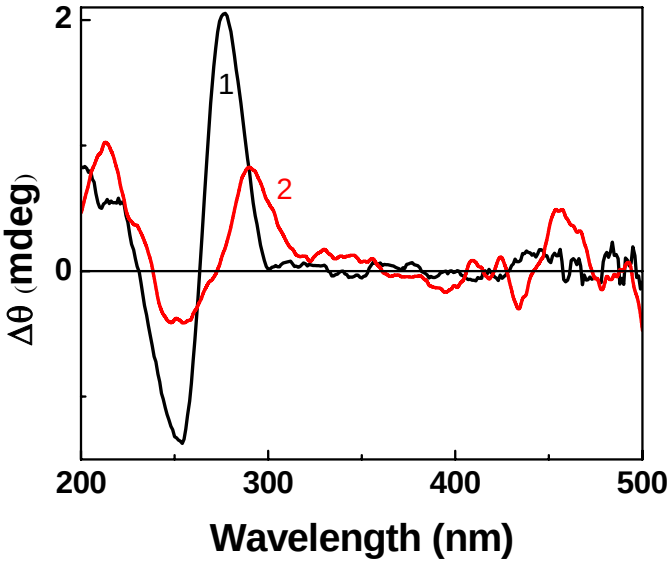

Figure S9. CD spectra of $(dT)_{40}$ alone (2μM) (1) and in the presence of TMPyP (40 μM) (2).

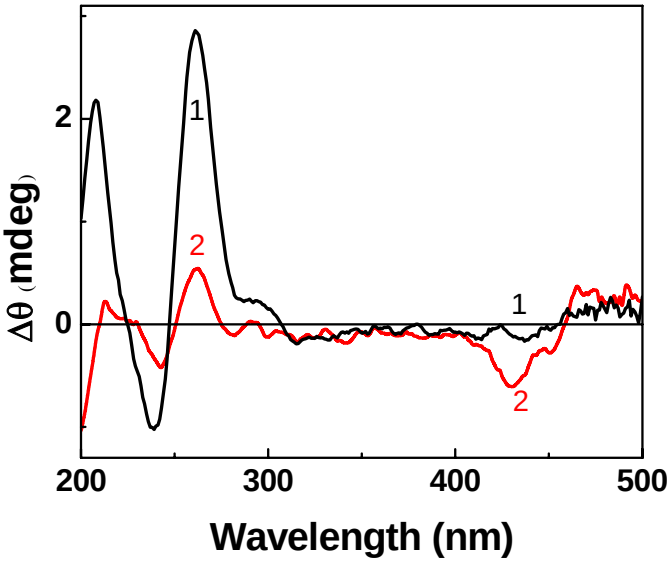

Figure S10. CD spectra of $(dG)_{40}$ alone (2μM) (1) and in the presence of TMPyP (40 μM) (2).

References

1. Mohanty J, Bhasikuttan A C, Dutta Choudhury S and Pal H 2008 *J. Phys. Chem. B* **112** 10782
2. Aich P and Dasgupta D 1990 *Biochem. Biophys. Res. Commun.* **173** 689
3. Shaikh M, Dutta Choudhury S, Mohanty J, Bhasikuttan A C and Pal H 2010 *Phys. Chem. Chem. Phys.* **12** 7050