

---

## Electronic Supplementary Information

### List of Figures and Tables

- <sup>5</sup> Fig. S1. CD spectra of the  $\Delta$  and  $\Lambda$  enantiomers of the complexes  $[\text{Cr}(\text{phen})_2(\text{dppz})](\text{PF}_6)_3$  (1),  $[\text{Cr}(\text{phen})_2(\text{Me}_2\text{dppz})](\text{PF}_6)_3$  (2) and  $[\text{Cr}(\text{phen})_2(\text{F}_2\text{dppz})](\text{PF}_6)_3$  (3) in acetonitrile solution.
- Fig. S2. Packing of  $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  in the unit cell.
- <sup>10</sup> Fig. S3. Packing of  $[\text{Cr}(\text{phen})_2\text{F}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  in the unit cell.
- Fig. S4. The comparison of relative absorption intensities ( $A/A_0$ ) as a function of relative DNA concentration P/D.
- <sup>15</sup> Fig. S5. UV-vis absorption spectra of  $[\text{Cr}(\text{phen})_2\text{Me}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  in the presence of increasing concentrations of CT-DNA.
- Fig. S6. UV-vis absorption spectra of  $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  in the presence of increasing concentrations of CT-DNA.
- <sup>20</sup> Fig. S7. UV-vis absorption spectra of 25mM phosphate buffer solution (pH=7) of  $\Delta$  isomer of  $[\text{Cr}(\text{phen})_2\text{dppz}]\text{Cl}_3$  with increasing concentrations of CT-DNA. Inset:  $A/A_0$  plot of  $\Delta$  and  $\Lambda$  enantiomers.
- <sup>25</sup> Fig. S8. Normalized emission spectra of  $[\text{Cr}(\text{phen})_2\text{X}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  ( $\text{X}=\text{H}, \text{Me}, \text{F}$ ).
- Fig. S9. Phosphorescence spectra of  $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  in the presence of increasing concentration of CT-DNA.
- <sup>30</sup> Fig. S10. Phosphorescence spectra of  $[\text{Cr}(\text{phen})_2\text{Me}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  in the presence of increasing concentration of CT-DNA.
- Fig. S11. The quenching of phosphorescence (at 730nm) of Cr(III) dipyridophenazine complexes in the presence of CT-DNA.
- <sup>35</sup> Fig. S12. The Scatchard plot for the association of  $[\text{Cr}(\text{phen})_2\text{F}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  with CT DNA obtained from PL quenching data.
- Fig. S13. The effect of  $[\text{NaCl}]$  on the change in  $I/I_0$  as a function of P/D for the complex  $[\text{Cr}(\text{phen})_2\text{F}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$ , with CT-DNA.  $[\text{Cr}]=16 \mu\text{M}$  in 10 mM phosphate buffer.
- Fig. S14. CD spectra of titration of *rac*- $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  ( $55 \mu\text{M}$ ) with CT-DNA ( $150 \mu\text{M}$ ) in 25 mM sodium phosphate buffer (pH=7).
- <sup>45</sup> Fig. S15. CD spectra of titration of *rac*- $[\text{Cr}(\text{phen})_2\text{F}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  ( $55 \mu\text{M}$ ) with CT-DNA ( $150 \mu\text{M}$ ) in 25 mM sodium phosphate buffer (pH=7).

---

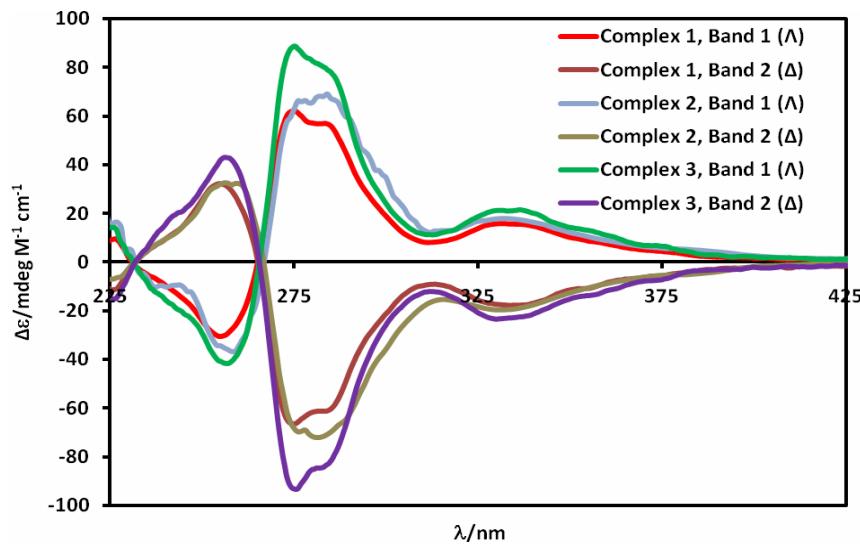
Fig. S16. ICD spectra of titration of *rac*-[Cr(phen)<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> with CT-DNA (150 μM) in 25 mM sodium phosphate buffer (pH=7).

Fig. S17. ICD spectra of titration of Δ-[Cr(phen)<sub>2</sub>dppz](Cl)<sub>3</sub> with CT- DNA (150 μM) in 25 mM sodium phosphate buffer (pH=7).

Fig. S18. ICD spectra of titration of  $\Delta$ -[Cr(phen)<sub>2</sub>dppz](Cl)<sub>3</sub> with CT- DNA (150 μM) in 25 mM sodium phosphate buffer (pH=7).

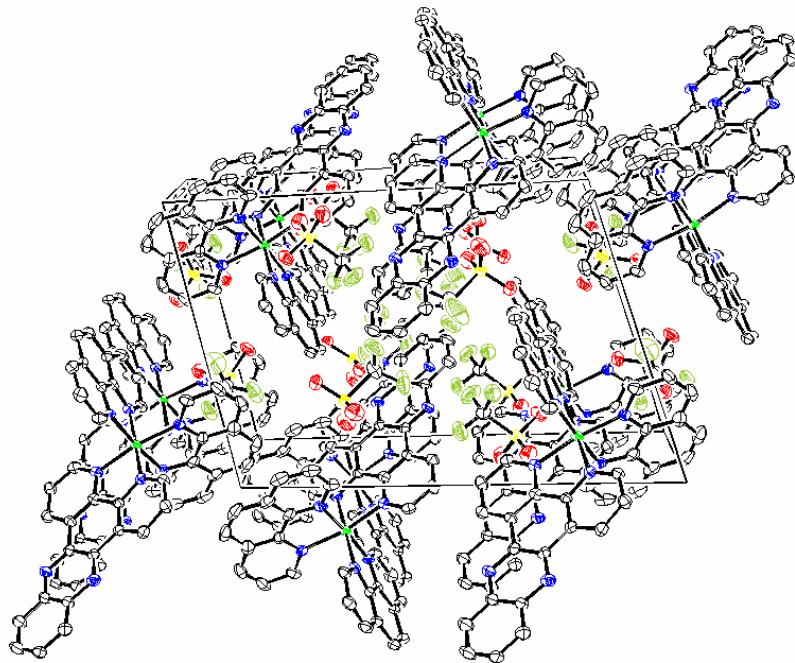
<sup>10</sup> Table S1. Crystal data and structural refinement parameters for [Cr(phen)<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> and [Cr(phen)<sub>2</sub>F<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>.

Table S2. Selected bondlengths (Å) and bondangles (°) of [Cr(phen)<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> and [Cr(phen)<sub>2</sub>F<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>.



5

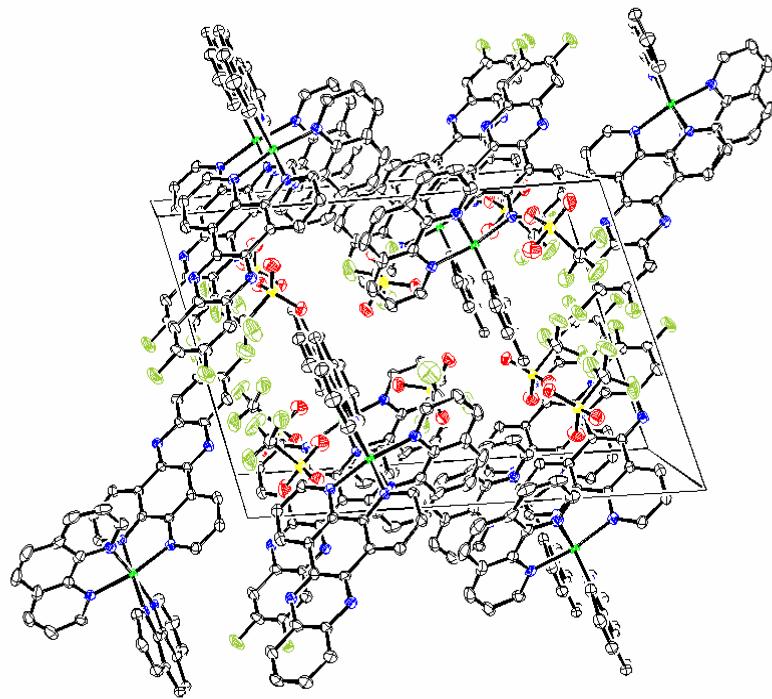
**Fig. S1.** CD spectra of the  $\Delta$  and  $\Lambda$  enantiomers of the complexes  $[\text{Cr}(\text{phen})_2(\text{dppz})](\text{PF}_6)_3$  (1),  $[\text{Cr}(\text{phen})_2(\text{Me}_2\text{dppz})](\text{PF}_6)_3$  (2) and  $[\text{Cr}(\text{phen})_2(\text{F}_2\text{dppz})](\text{PF}_6)_3$  (3) in acetonitrile solution.



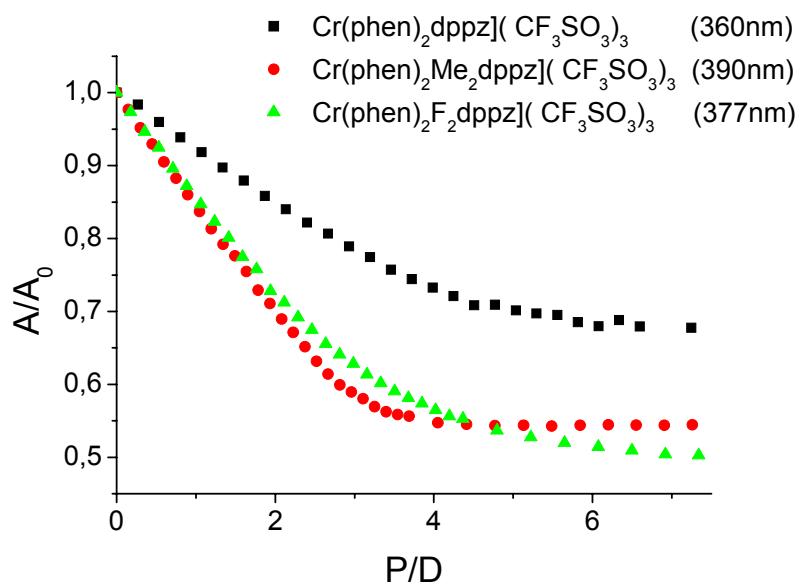
10

**Fig. S2.** Packing of  $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  in the unit cell.

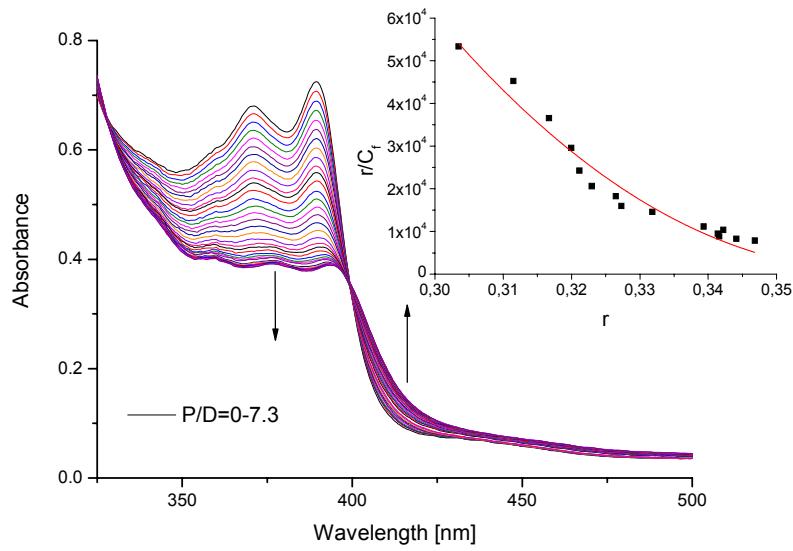
15



**Fig. S3.** Packing of  $[\text{Cr}(\text{phen})_2\text{F}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  in the unit cell.

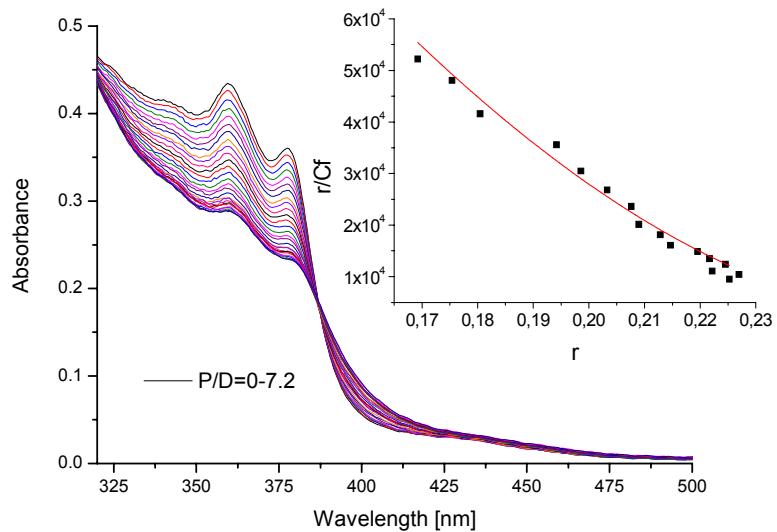


**Fig. S4.** The comparison of relative absorption intensities ( $A/A_0$ ) as a function of relative DNA concentration P/D ( $P/D = [\text{Nucleic Acid}]:[\text{Cr}]$ ) for  $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$

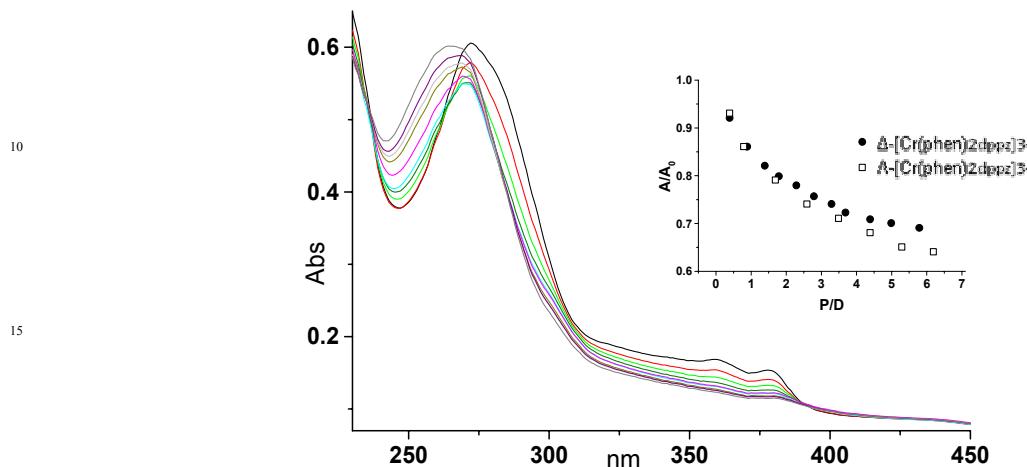


<sup>5</sup> Fig. S5. UV-vis absorption spectra of  $[\text{Cr}(\text{phen})_2\text{Me}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  (56  $\mu\text{M}$  in 100 mM phosphate buffer solution, pH=7.4) in the presence of increasing concentrations of CT-DNA. Inset: The Scatchard plot for the association of  $[\text{Cr}(\text{phen})_2\text{Me}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  with CT-DNA at 390nm. The data were fitted between 20% and 90% bound complexes using the McGhee and von Hippel model.

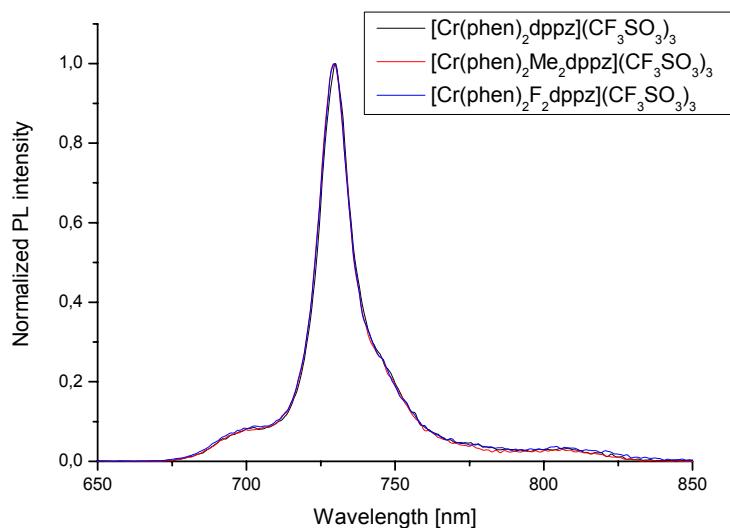
10



<sup>15</sup> Fig. S6. UV-vis absorption spectra of  $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  (31  $\mu\text{M}$  in 100 mM phosphate buffer solution, pH=7.4) in the presence of increasing concentrations of CT-DNA. Inset: The Scatchard plot for the association of  $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  with CT-DNA at 360nm. The data were fitted between 20% and 90% bound complexes using the McGhee and von Hippel model.



**Fig. S7.** UV-vis absorption spectra of 25mM phosphate buffer solution (pH=7) of  $\Delta$  isomer of [Cr(phen)<sub>2</sub>dppz](Cl)<sub>3</sub> with increasing concentrations of CT-DNA. Inset:  $A/A_0$  plot of  $\Delta$  and  $\Lambda$  enantiomers



**Fig. S8.** Normalized emission spectra of [Cr(phen)<sub>2</sub>X<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (X=H, Me, F).

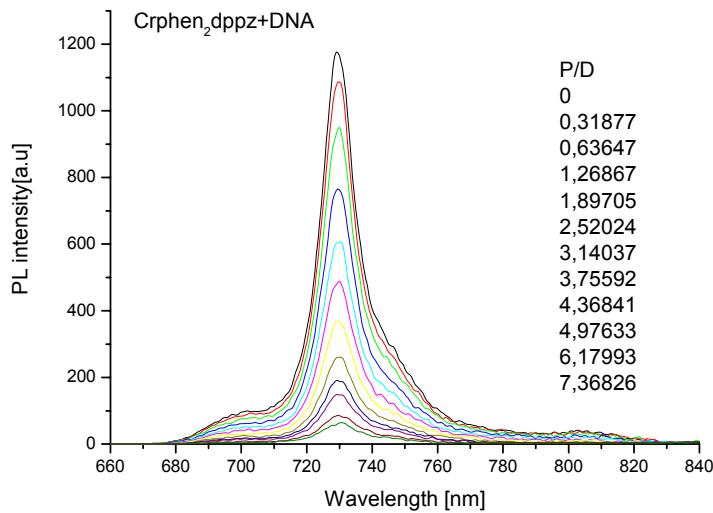


Fig. S9. Phosphorescence spectra of  $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  ( $65\mu\text{M}$  in  $100\text{mM}$  phosphate buffer solution) in the presence of increasing concentration of CT-DNA.

10

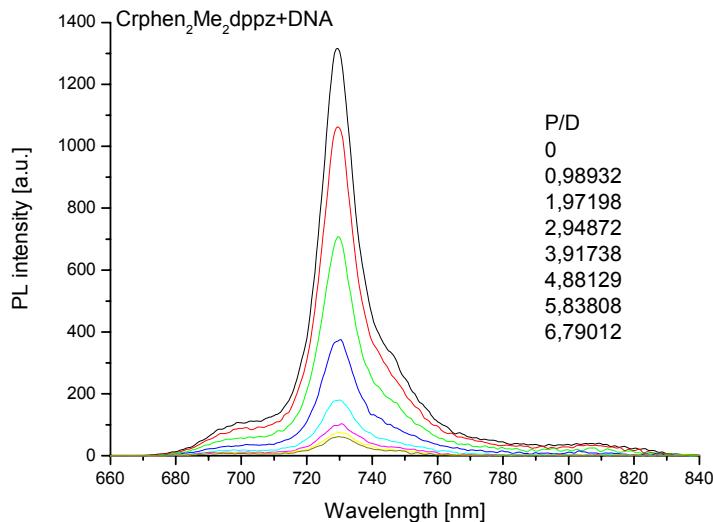


Fig. S10. Phosphorescence spectra of  $[\text{Cr}(\text{phen})_2\text{Me}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  ( $42\mu\text{M}$  in  $100\text{mM}$  phosphate buffer solution) in the presence of increasing concentration of CT-DNA.

15

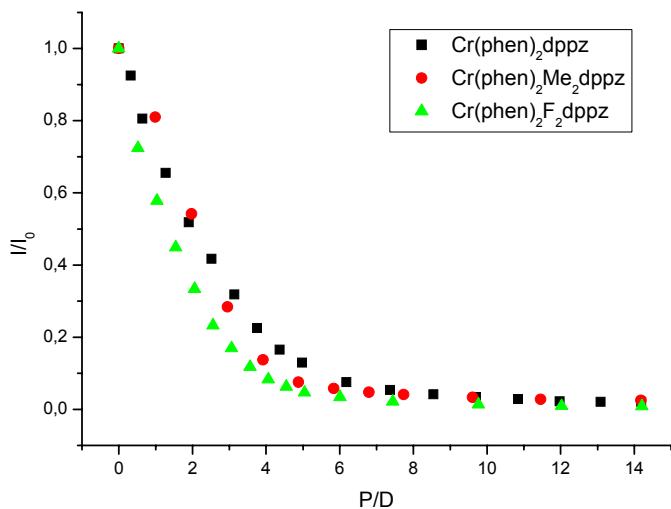


Fig. S11. The quenching of phosphorescence (at 730nm) of Cr(III) dipyridophenazine complexes in the presence of <sub>5</sub> CT-DNA.

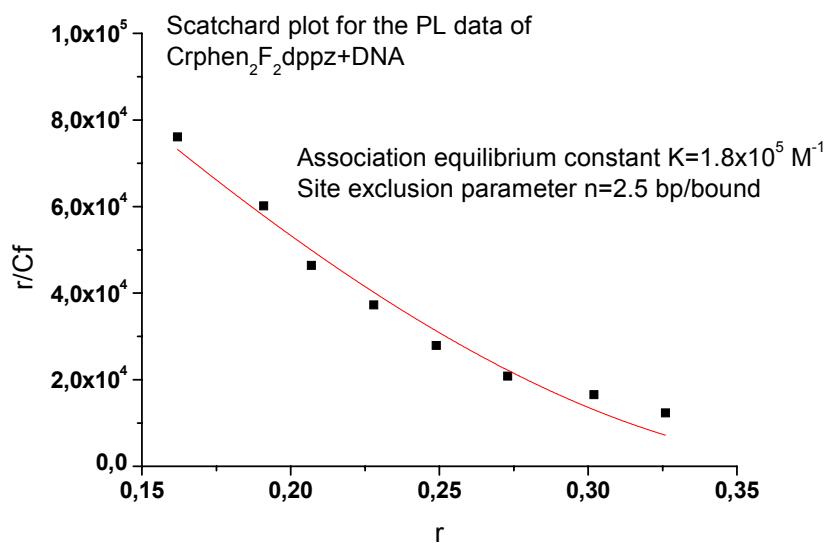
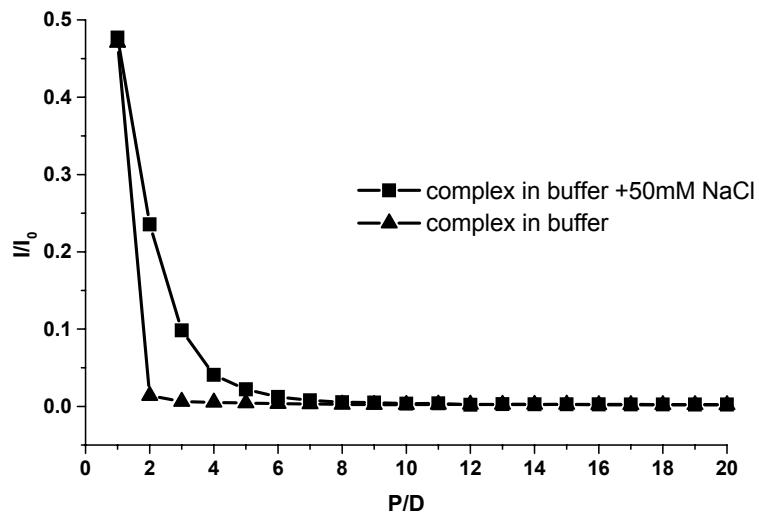
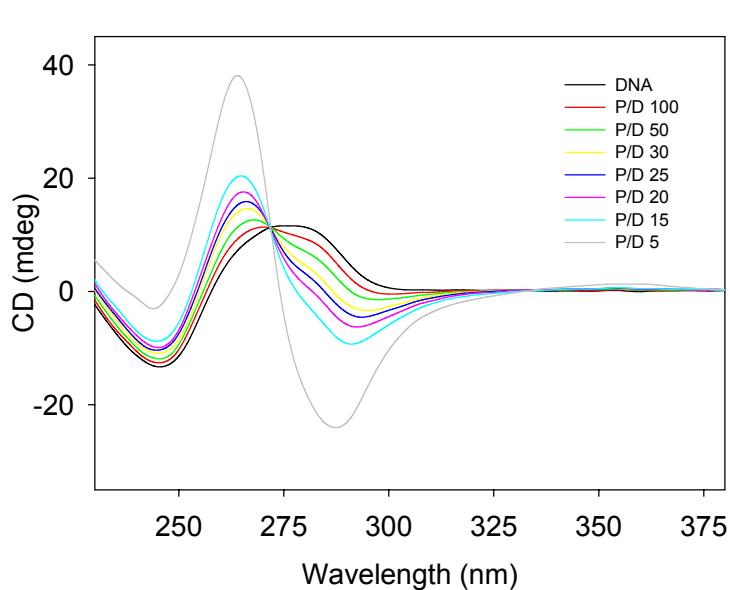


Fig. S12. The Scatchard plot for the association of [Cr(phen)<sub>2</sub>F<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> with CT-DNA obtained from PL quenching data. The resulting fitting parameters are in very good agreement with those obtained from absorption measurements.



**Fig. S13.** The effect of [NaCl] on the change in  $I/I_0$  as a function of P/D for the complex  $[\text{Cr}(\text{phen})_2\text{F}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$ , with CT-DNA.  $[\text{Cr}] = 16 \mu\text{M}$  in 10 mM sodium phosphate buffer

5



10

**Fig. S14.** CD spectra of titration of *rac*- $[\text{Cr}(\text{phen})_2\text{F}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  ( $55 \mu\text{M}$ ) with CT-DNA ( $150 \mu\text{M}$ ) in sodium phosphate buffer (pH=7).

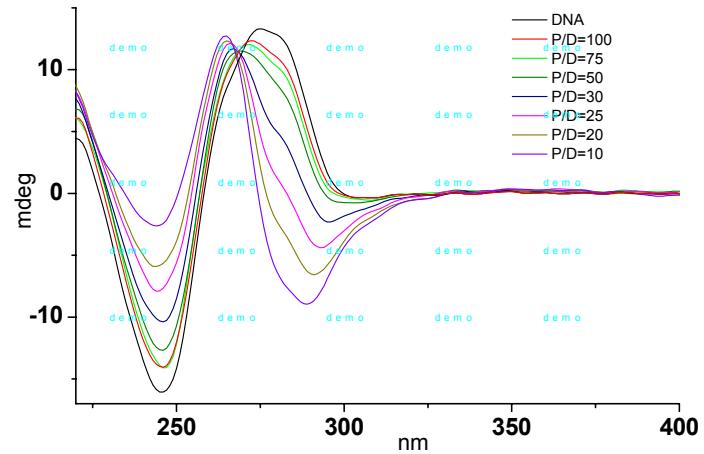
15

20

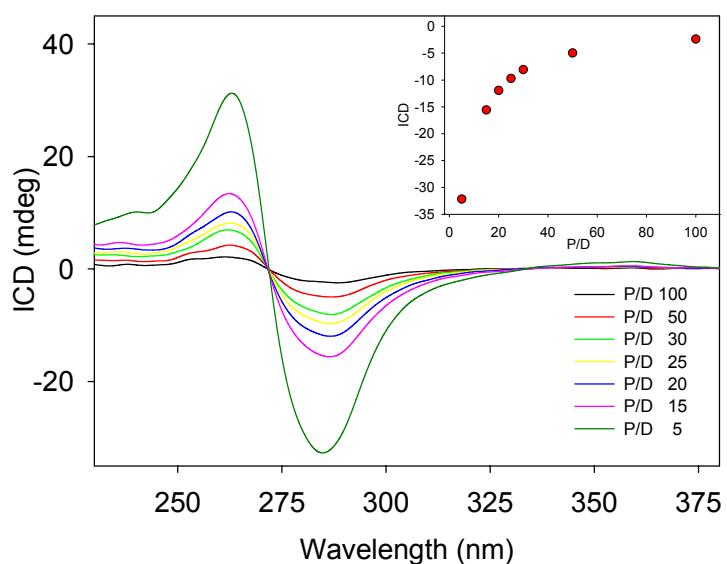
25

30

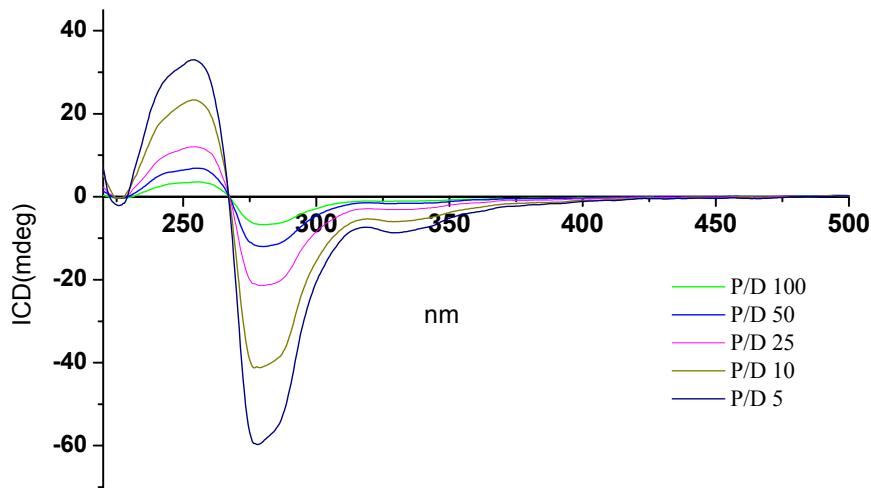
35



**Fig. S15. CD spectra of titration of *rac*-[Cr(phen)<sub>2</sub>F<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (55 μM) with CT-DNA (150 μM) in 25 mM sodium phosphate buffer (pH=7).**

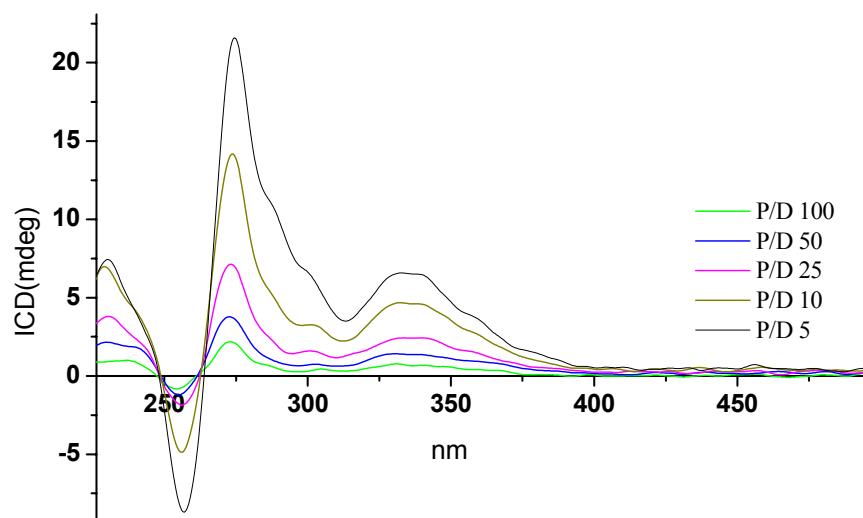


**Fig. S16. ICD spectra of titration of *rac*-[Cr(phen)<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> with CT-DNA (150 μM) in phosphate buffer (pH=7).**



5

**Fig. S17.** ICD spectra of titration of  $\Delta$ -[Cr(phen)<sub>2</sub>dppz](Cl)<sub>3</sub> with CT-DNA (150  $\mu$ M) in 25 mM sodium phosphate buffer (pH=7).



<sup>10</sup> **Fig. S18.** ICD spectra of titration of  $\Delta$ -Cr(phen)<sub>2</sub>dppz](Cl)<sub>3</sub> with CT-DNA (150  $\mu$ M) in 25 mM sodium phosphate buffer (pH=7).

**Table S1. Crystal data and structural refinement parameters for  $[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$  and  $[\text{Cr}(\text{phen})_2\text{F}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$ .**

	$[\text{Cr}(\text{phen})_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$	$[\text{Cr}(\text{phen})_2\text{F}_2\text{dppz}](\text{CF}_3\text{SO}_3)_3$
Empirical Formula	$\text{C}_{45}\text{H}_{26}\text{CrF}_9\text{N}_8\text{O}_9\text{S}_3$	$\text{C}_{45}\text{H}_{24}\text{CrF}_{11}\text{N}_8\text{O}_9\text{S}_3$
Formula weight (M)	1141.92	1177.90
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Lattice constants		
a (Å)	10.331(3)	10.2634(14)
b (Å)	13.214(3)	13.262(2)
c (Å)	19.073(5)	19.284(3)
$\alpha$ (°)	72.494(18)	73.745(7)
$\beta$ (°)	74.473(19)	74.983(8)
$\gamma$ (°)	68.319(15)	67.915(8)
Volume V(Å <sup>3</sup> )	2271.0(10)	2299.8(6)
Z	2	2
Calculated density ( $\rho$ ) (Mg m <sup>-3</sup> )	1.670	1.701
Absorption coefficient ( $\mu$ ) (mm <sup>-1</sup> )	0.495	0.498
F(000)	1154	1186
$\theta$ Range for data collection	2.84 – 25.00	1.12 – 25.00
Limiting Indices	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -22 ≤ l ≤ 22	-12 ≤ h ≤ 11, -15 ≤ k ≤ 15, -22 ≤ l ≤ 22
Reflections collected	35508	18396
Unique Reflections	6722 [R <sub>int</sub> =0.0726]	6379 [R <sub>int</sub> =0.0339]
Completeness to $\theta$	25 (99.8%)	25 (90.1%)
Data / restraints / parameters	7991/0/677	7288/0/695
Goodness-of-fit on F <sup>2</sup>	1.211	1.024
Final R indices [I > 2σ (I)]	$R_I = 0.0873, wR_2 = 0.1451$	$R_I = 0.0475, wR_2 = 0.1508$
R indices (all data)	$R_I = 0.1069, wR_2 = 0.1531$	$R_I = 0.0549, wR_2 = 0.1769$

Format

Format

**Table S2. Selected bondlengths (Å) and bondangles (°) of [Cr(phen)<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> and [Cr(phen)<sub>2</sub>F<sub>2</sub>dppz](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>.**

[Cr(phen) <sub>2</sub> dppz](CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub>		[Cr(phen) <sub>2</sub> F <sub>2</sub> dppz](CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub>	
Cr1 – N1	2.052(4)	Cr1 – N3	2.051(3)
Cr1 – N2	2.058(4)	Cr1 – N4	2.059(3)
Cr1 – N3	2.062(4)	Cr1 – N5	2.051(3)
Cr1 – N4	2.053(4)	Cr1 – N6	2.056(3)
Cr1 – N5	2.049(4)	Cr1 – N7	2.064(3)
Cr1 – N6	2.059(4)	Cr1 – N8	2.062(3)
N1 – Cr1 – N3	96.19(16)	N6 – Cr1 – N8	80.63(11)
N1 – Cr1 – N4	172.86(16)	N5 – Cr1 – N8	172.55(10)
N1 – Cr1 – N6	94.13(16)	N4 – Cr1 – N8	92.38(10)
N2 – Cr1 – N3	86.95(16)	N6 – Cr1 – N7	86.64(10)
N5 – Cr1 – N6	80.26(16)	N3 – Cr1 – N4	79.77(10)
F1 – C40 – C39	120.1(3)	F1 – C40 – C41	117.4(3)
F2 – C41 – C42	120.1(4)	F2 – C41 – C40	118.1(3)