Electronic Supplementary Information

Oxidovanadium(V) complexes of aroylhydrazones incorporating heterocycles: Synthesis, characterization and study of DNA binding, photo-induced DNA cleavage and cytotoxic activities

Subhashree P. Dash,[a] Alok K. Panda,[b] Sagarika Pasayat,[a] Rupam Dinda,*[a] Ashis Biswas,[b] Edward R. T. Tiekink,[c] Subhadip Mukhopadhyay,[d] Sujit K. Bhutia,[d] Werner Kaminsky[e] and Ekkehard Sinn[f]

[a]*Department of Chemistry, National Institute of Technology, Rourkela 769008, Odisha, India.*

[b]*School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Bhubaneswar 751 013, Odisha, India.*

[c]*Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia.*

[d]*Department of Life Science, National Institute of Technology, Rourkela 769008, Odisha, India.*

[e]*Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195, USA.*

[f]*Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008, USA.*

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H4 = 164° for symmetry operation i: 1-x, 2-y, ½+z] shown as purple dashed lines, and (b) a view of the unit cell contents in projection down the *a*-axis showing the ...ABA... pattern of supramolecular layers stacked along the *b*-axis.

Fig. S7 Crystal packing in **4**: (a) a view of the two-molecule aggregate whereby centrosymmetrically related V1-containing molecules are linked by ethanol-O–H…N hydrogen bonds, (b) equivalent dimer formed by the V2-containing molecule; second orientation of the disordered ethanol molecule and all non-participating hydrogen atoms removed for clarity [O6–H6o...N1^{i} = 2.12 Å, O6...N1^{i} = 2.873(3) Å, with angle at H6o = 149° for symmetry operation i: -x, 1-y, 1-z; O6a–H6oa...N1a^{ii} = 2.31 Å, O6a...N1a^{ii} = 2.95(2) Å, with angle at H6oa = 136° for symmetry operation ii: ½-x, ½-y, -z; for the second disordered conformation: O6b–H6ob...N1a^{ii} = 2.20 Å, O6b...N1a^{ii} = 2.99(2) Å, with angle at H6ob = 164°] shown as orange dashed lines, and (c) a view of the unit cell contents in projection down the *b*-axis showing the stacking of alternating layers of V1- and V2-containing molecules along the *a*-axis. The C–H…O [C8a–H8a...O2a^{iii} = 2.57 Å, C8a...O2a^{iii} = 3.398(4) Å, with angle at H8a = 149° for symmetry operation iii: ½-x, ½+y, ½-z] and π...π [Cg(O3,C13-C16)…Cg(C1,C2,C7-C10)^{i} = 3.702(2) Å, angle of inclination = 13.45(19)°; Cg(O3a,C13a-C16a)…Cg(C1a,C2a,C7a-C10a)^{ii} = 3.641(2) Å, angle of inclination = 8.64(18)°] interactions are shown as blue and purple dashed lines, respectively.

Fig. S8 Electronic absorption spectra for **HL^{1}** (a), **HL^{2}** (b), **H$_2$L^{3}** (c) and **H$_2$L^{4}** (d) (25 μM each) upon the titration of CT-DNA (0 – 350 μM) in 10 mM Tris-HCl buffer (pH 8.0) containing 1% DMF. The inset shows the linear fit of [DNA]/(ε_a - ε_f) *vs* [DNA] from which the binding constant (K_b) was calculated using Eq. 1 (see main text).

Fig. S9. Fluorescence emission spectra of methyl green (MG) (2 μM) bound to CT-DNA (50 μM) in the presence of complex **1** (a), **2** (b), **3** (c) and **4** (d) (0–90 μM) in 10 mM Tris–HCl buffer (pH 8.0) containing 1% DMF. The arrow indicates the effect of increasing the concentration of the complex on the fluorescence emission of MG bound CT-DNA.

Fig. S10. Fluorescence emission spectra of ethidium bromide (EB) (2 μM) bound to CT-DNA (50 μM) in the presence of complex **1** (a), **2** (b), **3** (c) and **4** (d) (0–90 μM) in 10 mM Tris–HCl buffer (pH 8.0) containing 1% DMF. The arrow indicates the effect of increasing the concentration of the complex on the fluorescence emission of EB bound CT-DNA.

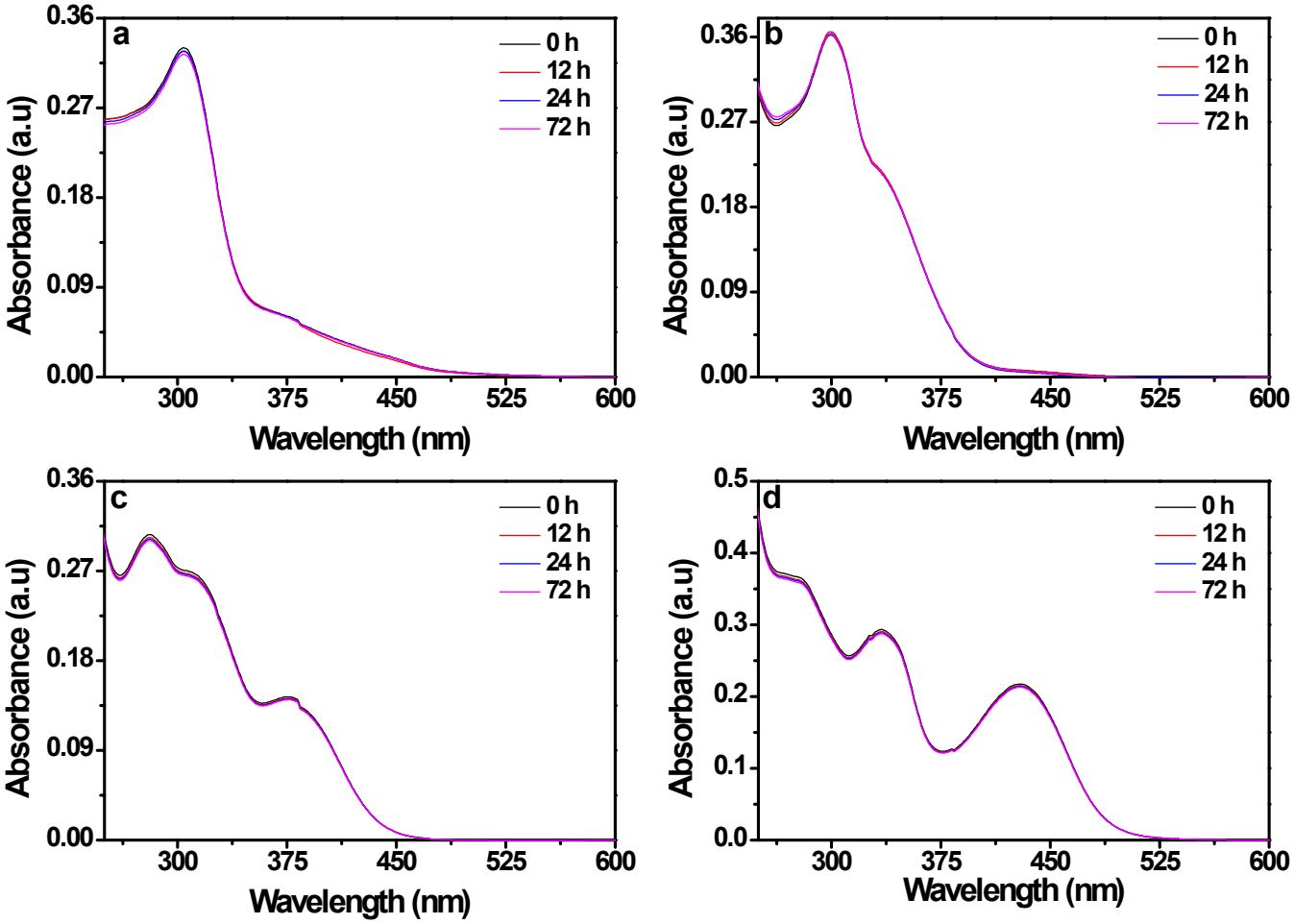
Fig. S11 Effect of DMF (1%) and ligands on the photo-induced cleavage of SC pUC19 DNA. 300 ng SC pUC19 DNA was photo-irradiated in absence and presence of 1% DMF and various ligands (100 μM) with UVA at 350 nm for 3 h. Lane 1, DNA only; Lane 2, DNA in presence of 1% DMF; Lane 3, DNA + **HL^{1}**; Lane 4, DNA + **HL^{2}**; Lane 5, DNA + **H$_2$L^{3}**; Lane 6, DNA + **H$_2$L^{4}**.

Fig. S12 Gel diagram depicting cleavage of SC pUC19 DNA by **1**–**4** in presence of various additives in 50 mM Tris-HCl buffer (pH 8.0) containing 1% DMF. SC pUC19 DNA (300 ng) in the presence of various additives was photo-irradiated at 350 nm for 3 h with **1**–**4** (100 μM). The additive concentrations were: sodium azide (0.5 mM), L-histidine (0.5 mM), KI (0.5 mM) and D-mannitol (0.5 mM). Lane 1, DNA + complex; Lane 2, DNA + complex + sodium azide; Lane 3, DNA + complex + L-histidine; Lane 4, DNA + complex + KI; Lane 5, DNA + complex + D -mannitol.

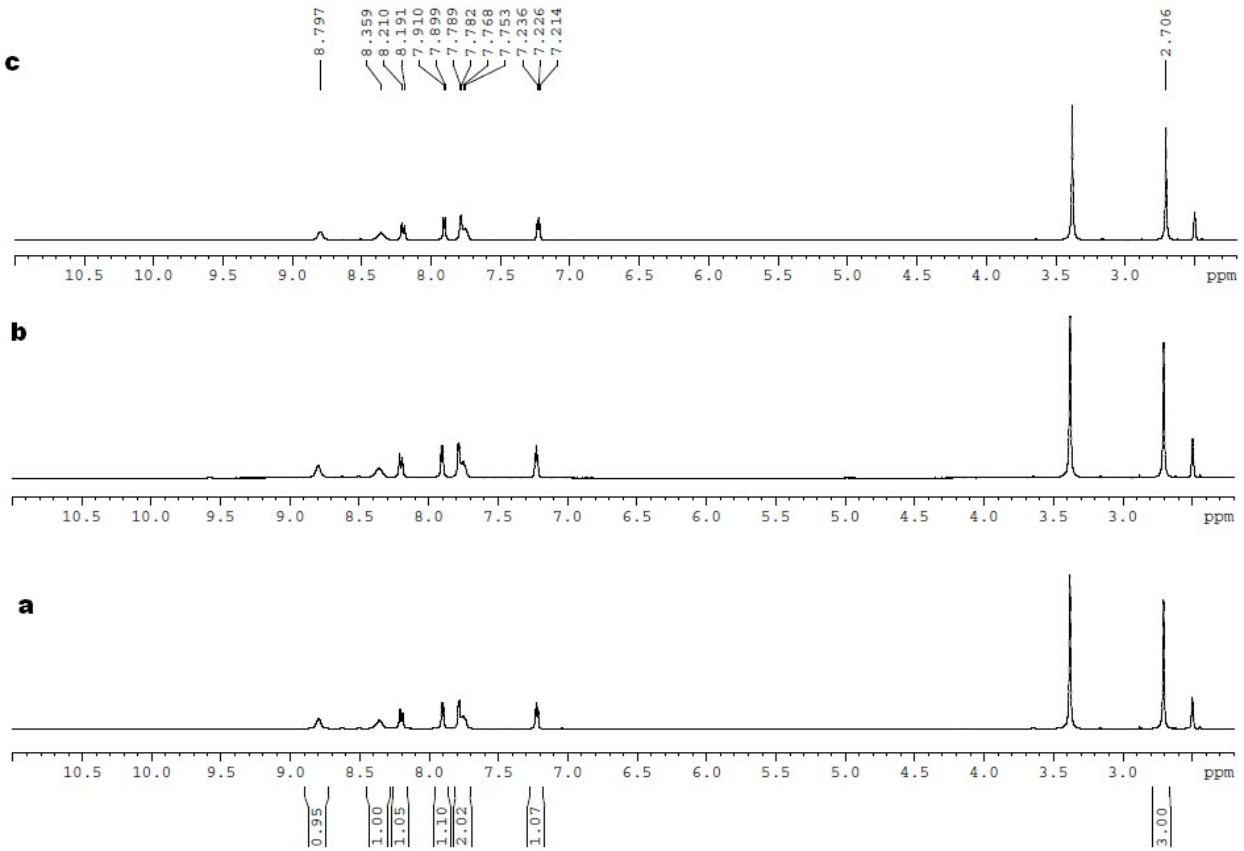
Table S1 Binding constant (K_b) values for the "CT-DNA-ligand" interactions.[a]

Ligand	Binding constant (K_b) (M^{-1})
HL[1]	7.42×10^3
HL[2]	3.88×10^3
H_2L[3]	2.91×10^4
H_2L[4]	2.48×10^3

[a] The DNA binding constant was determined by the UV-vis spectral method.

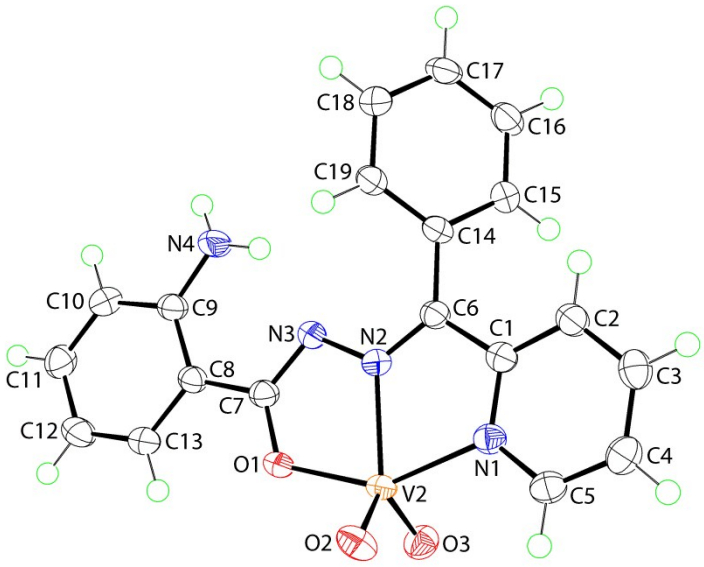

a
b
c
d
0 h
12 h
24 h
72 h
Absorbance (a.u)
Wavelength (nm)
0.00
0.09
0.18
0.27
0.36
0.1
0.2
0.3
0.4
0.5
300
375
450
525
600

(A)


c
8.797
8.359
8.210
8.191
7.910
7.899
7.789
7.782
7.768
7.753
7.236
7.226
7.214
2.706
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm
b
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm
a
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm
0.95
1.00
1.05
1.10
2.02
1.07
3.00

(B)

Fig. S1


C17
C18
C16
C19
C15
C14
N4
C10
C9
C6
C1
C2
N3
N2
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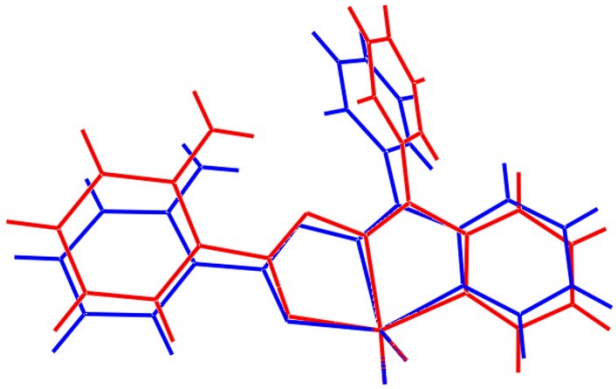
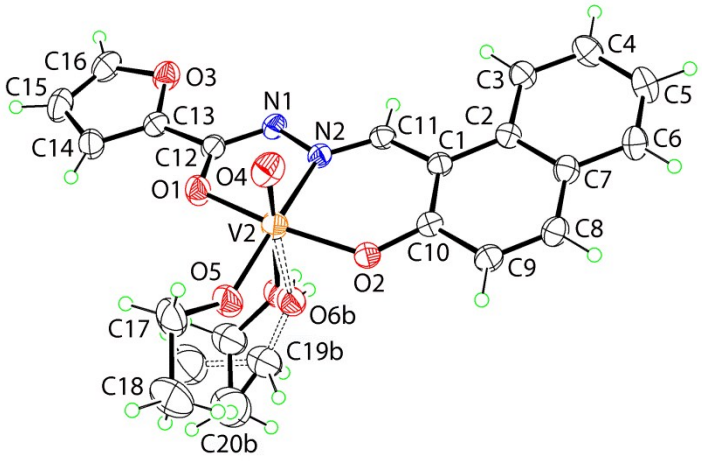
C3
C7
C12
C13
O1
N1
C4
V2
C5
O2
O3

(a)

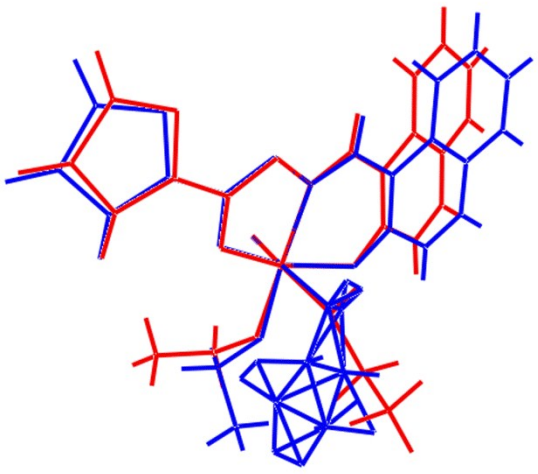


(b)

Fig. S2


C16
O3
C15
C13
N1
N2
C11
C2
C4
C3
C5
C14
C12
C1
C6
O1
O4
C7
V2
C8
O5
C10
C9
O2
O6b
C17
C19b
C18
C20b

(a)



(b)

Fig. S3

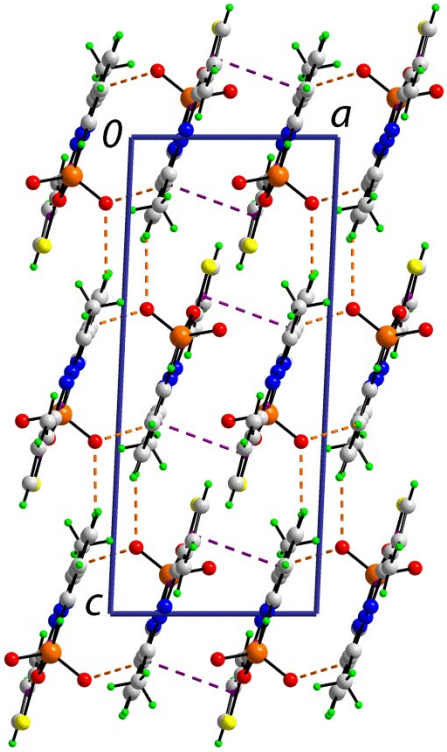
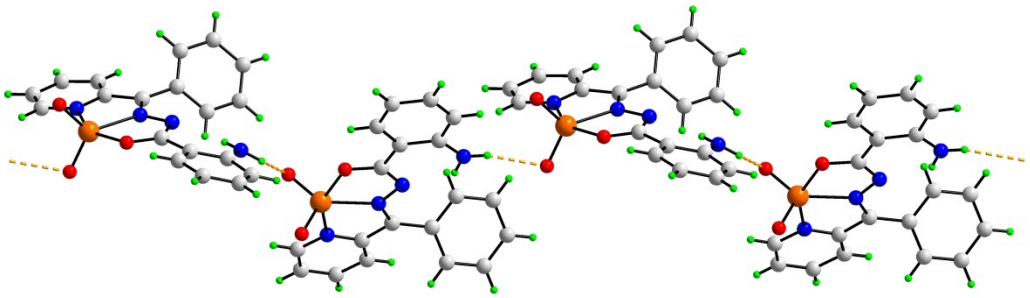
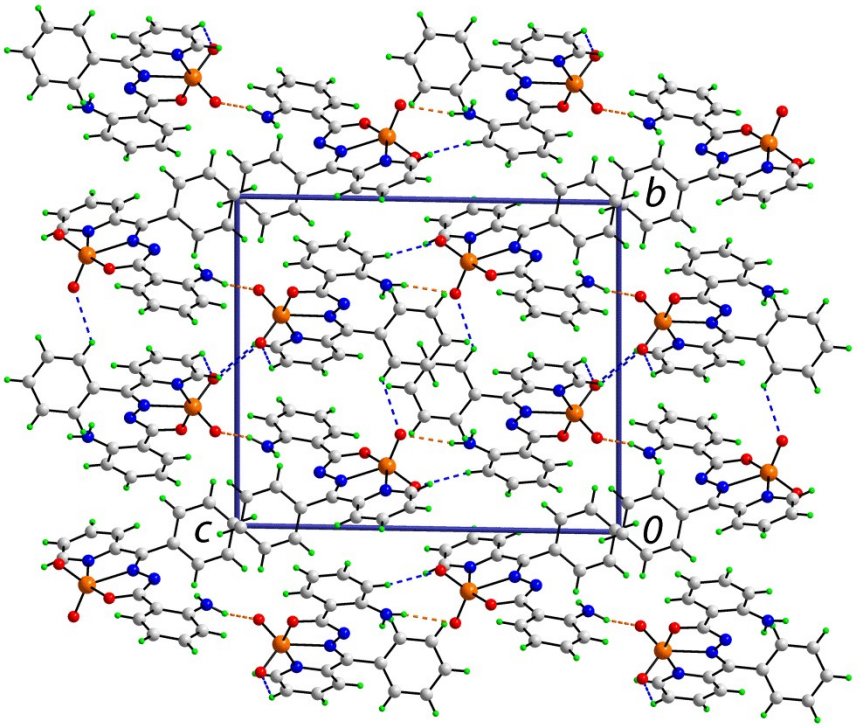


Fig. S4



(a)



(b)

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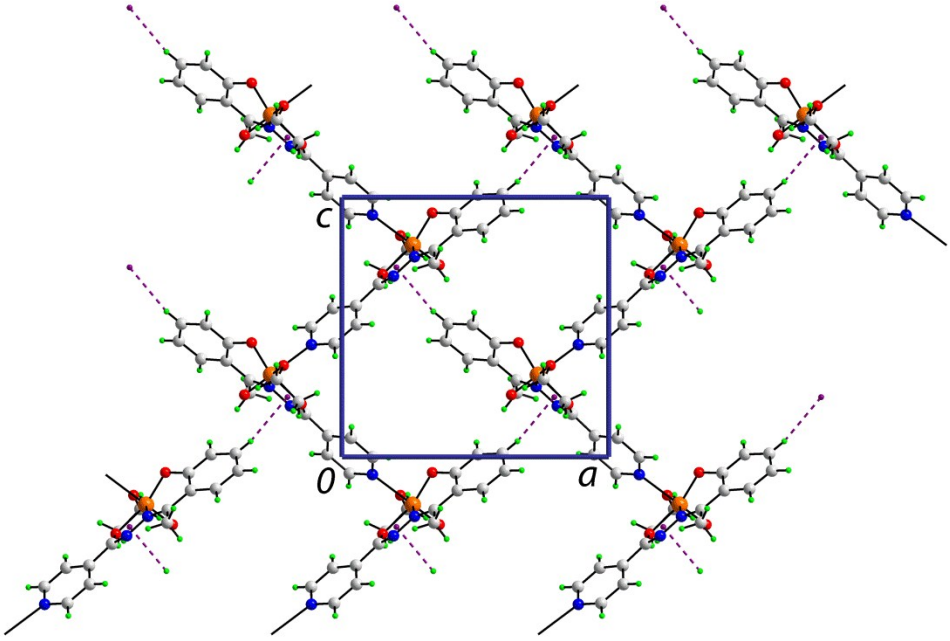

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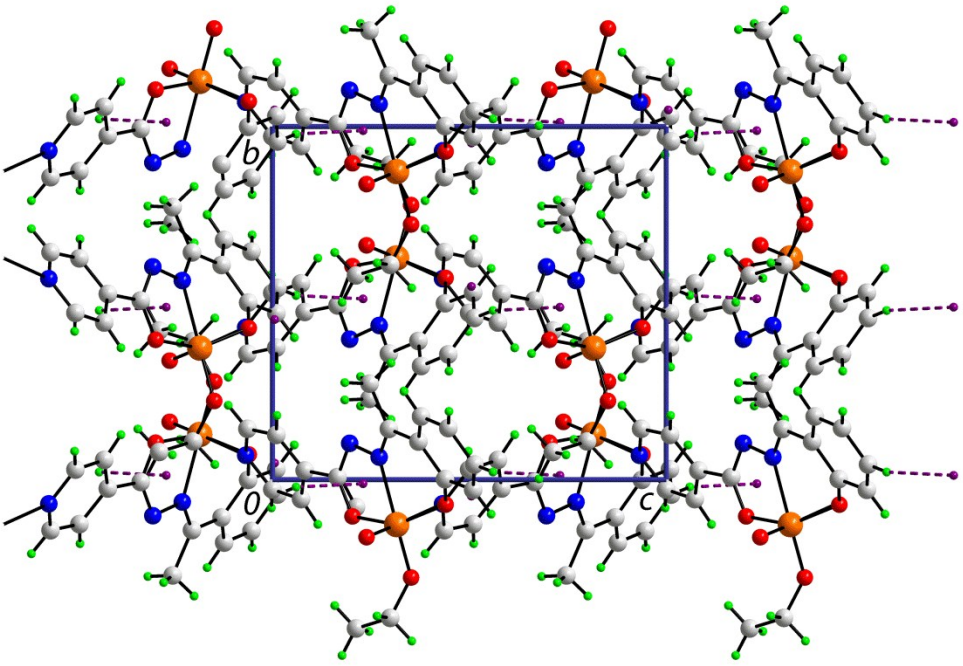
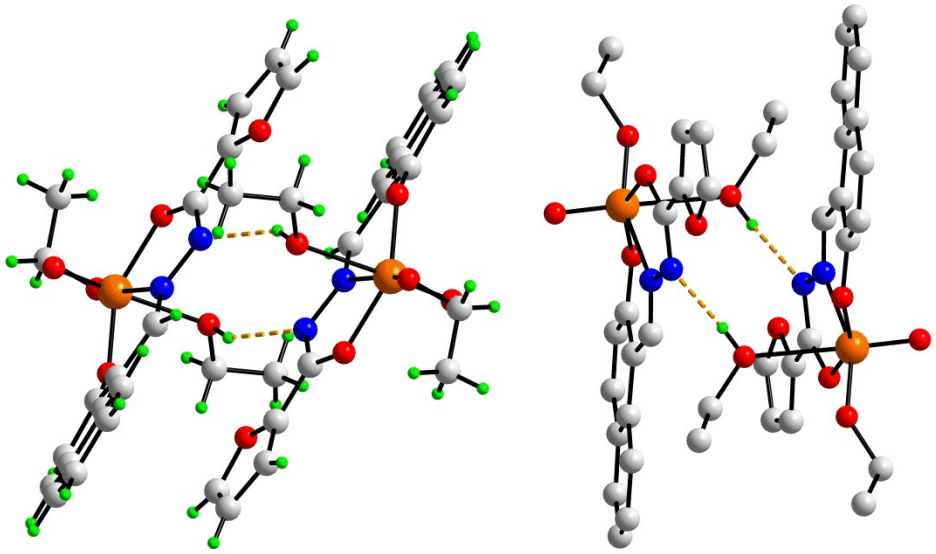
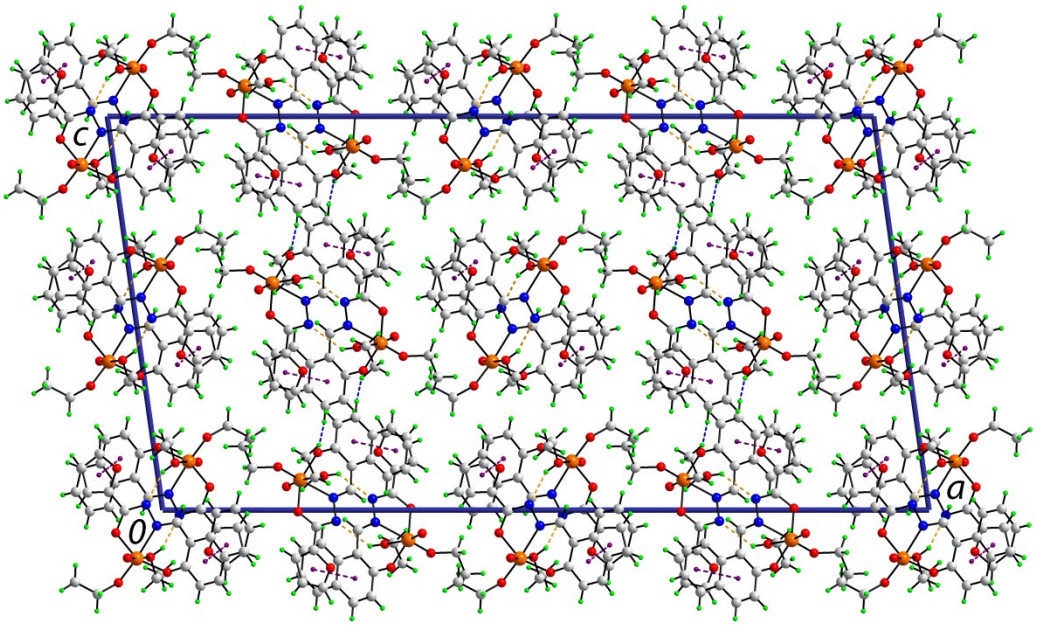


(b)

Fig. S6



(a) (b)



(c)

Fig. S7

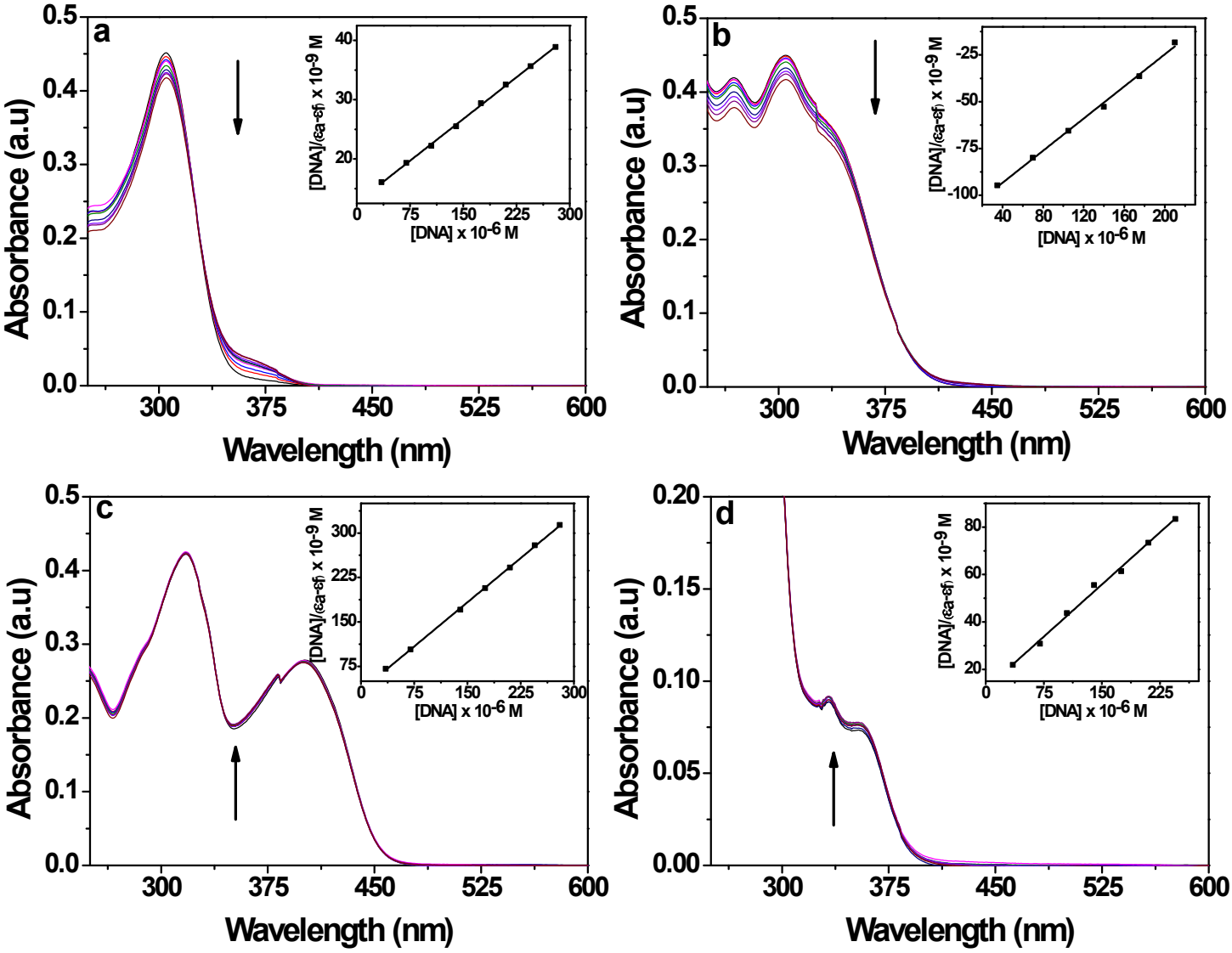

a
Absorbance (a.u)
Wavelength (nm)
[DNA]/(εa-εf) x 10-9 M
[DNA] x 10-6 M
b
Absorbance (a.u)
Wavelength (nm)
[DNA]/(εa-εf) x 10-9 M
[DNA] x 10-6 M
c
Absorbance (a.u)
Wavelength (nm)
[DNA]/(εa-εf) x 10-9 M
[DNA] x 10-6 M
d
Absorbance (a.u)
Wavelength (nm)
[DNA]/(εa-εf) x 10-9 M
[DNA] x 10-6 M

Fig. S8

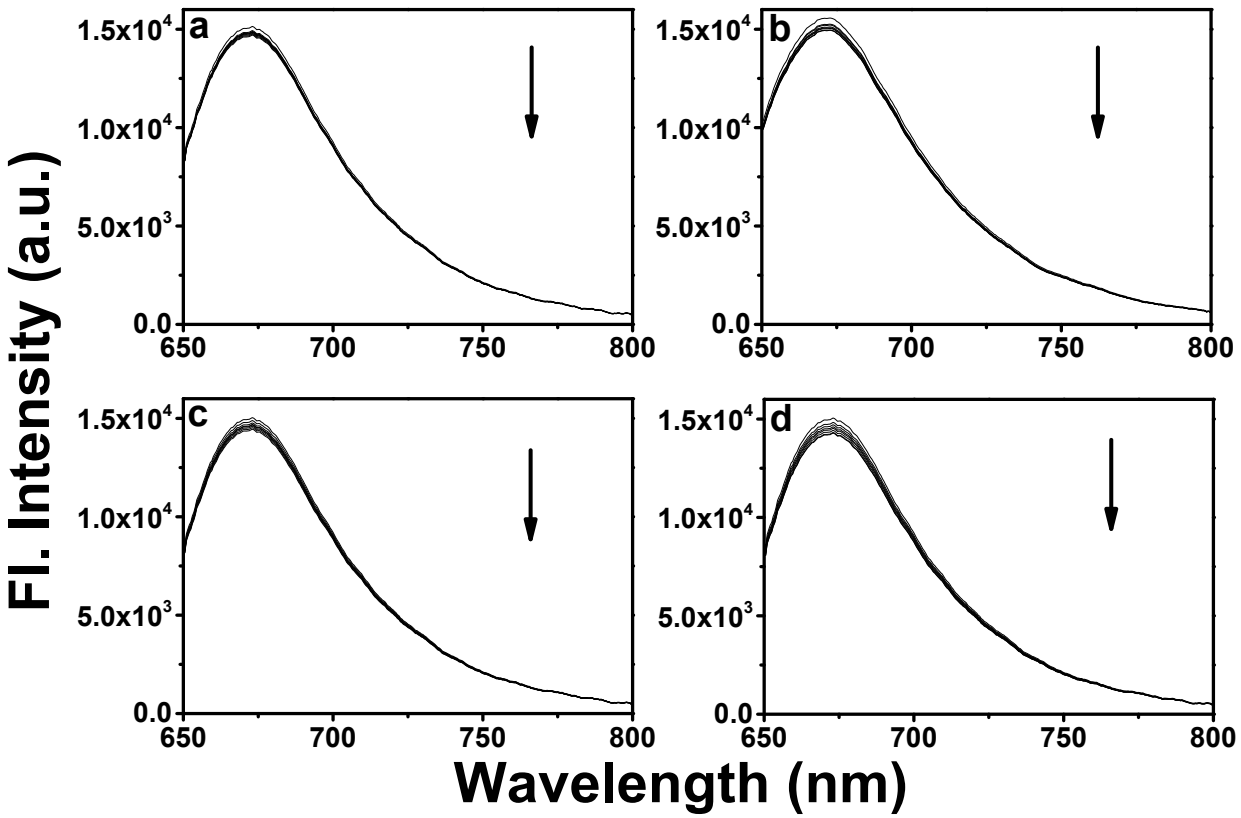
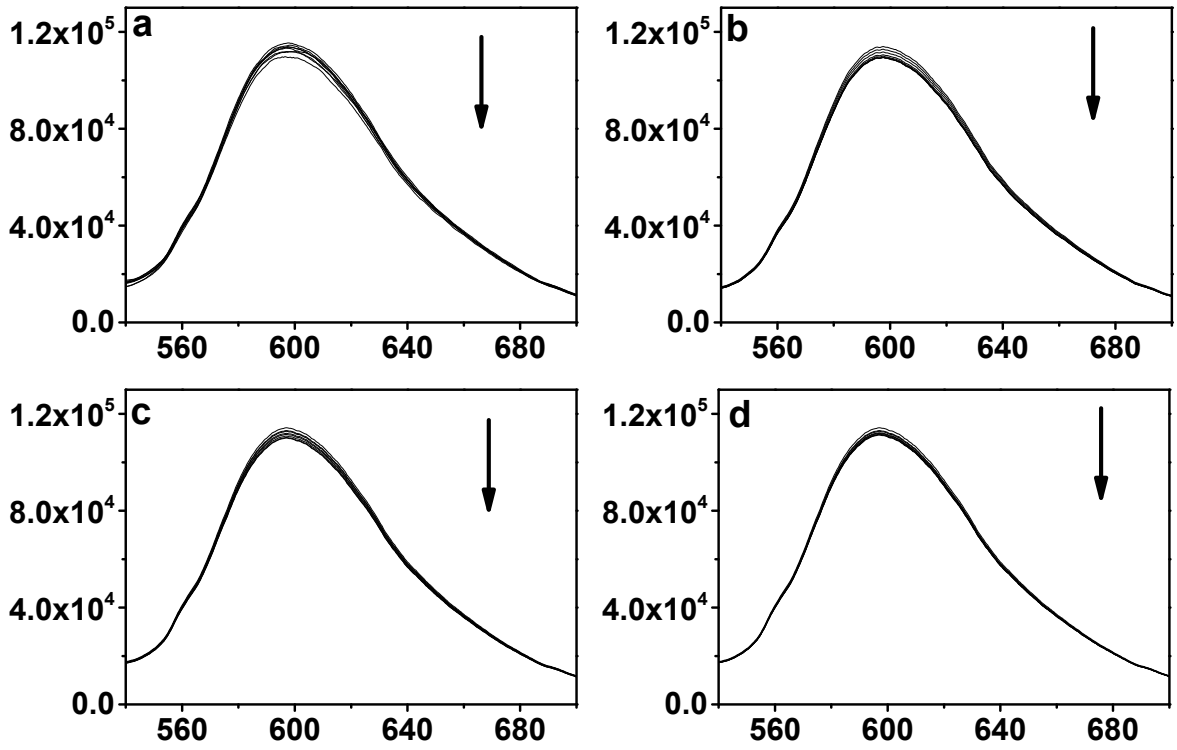

a
b
c
d
1.5x10^4
1.0x10^4
5.0x10^3
0.0
650
700
750
800
Fl. Intensity (a.u.)
Wavelength (nm)

Fig. S9



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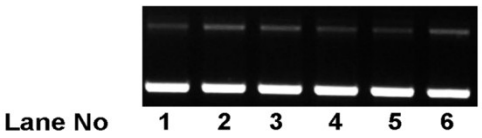

Fig. S11

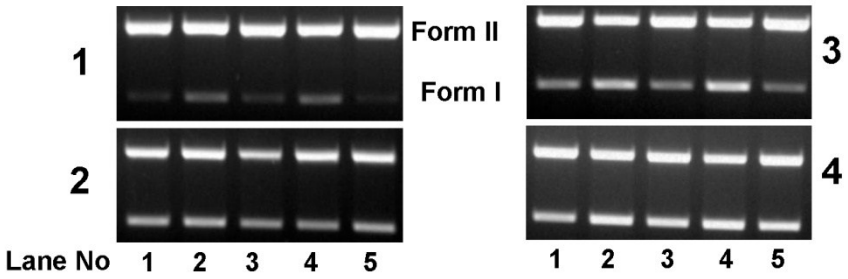

Fig. S12