Electronic Supplementary Information (ESI†)

for

Photo-induced DNA cleavage activity and remarkable photocytotoxicity of lanthanide(III) complexes of a polypyridyl ligand

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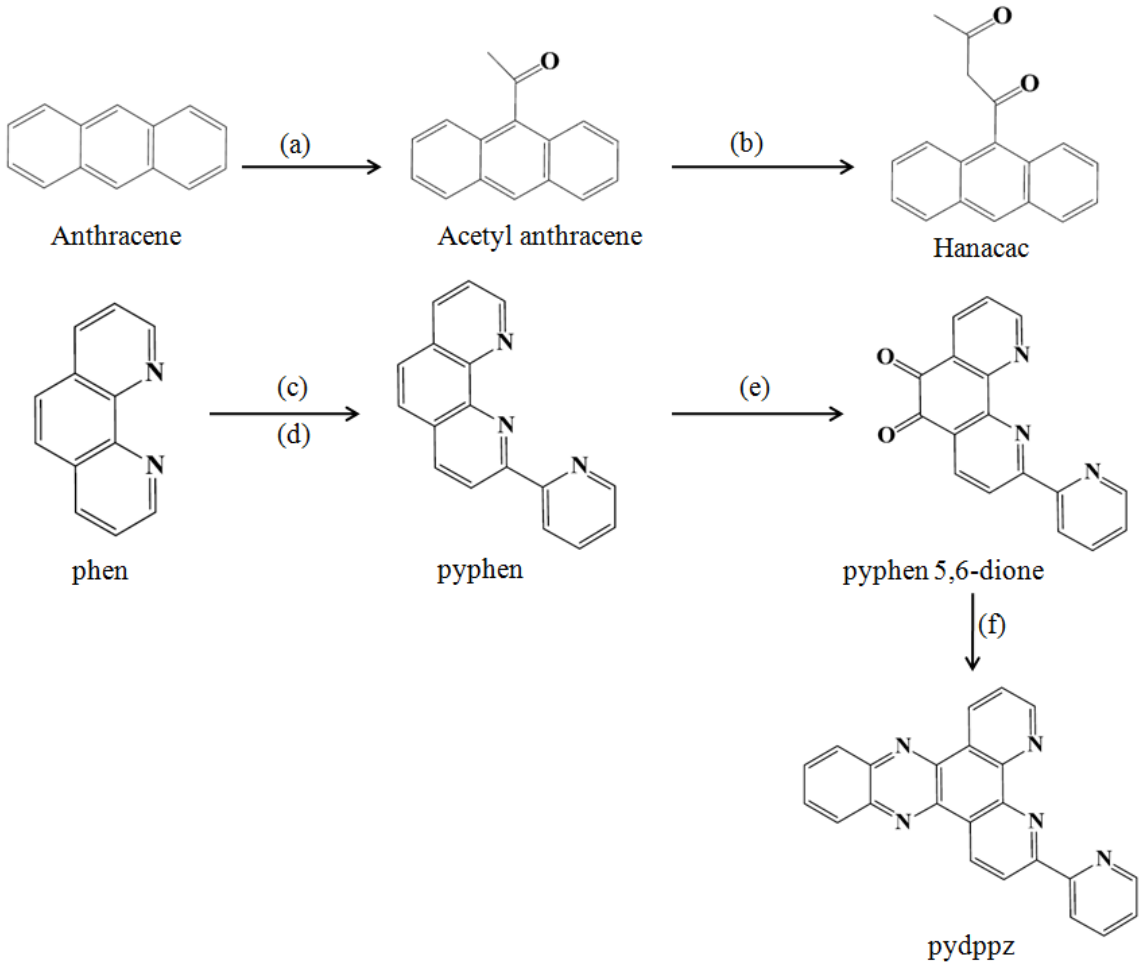
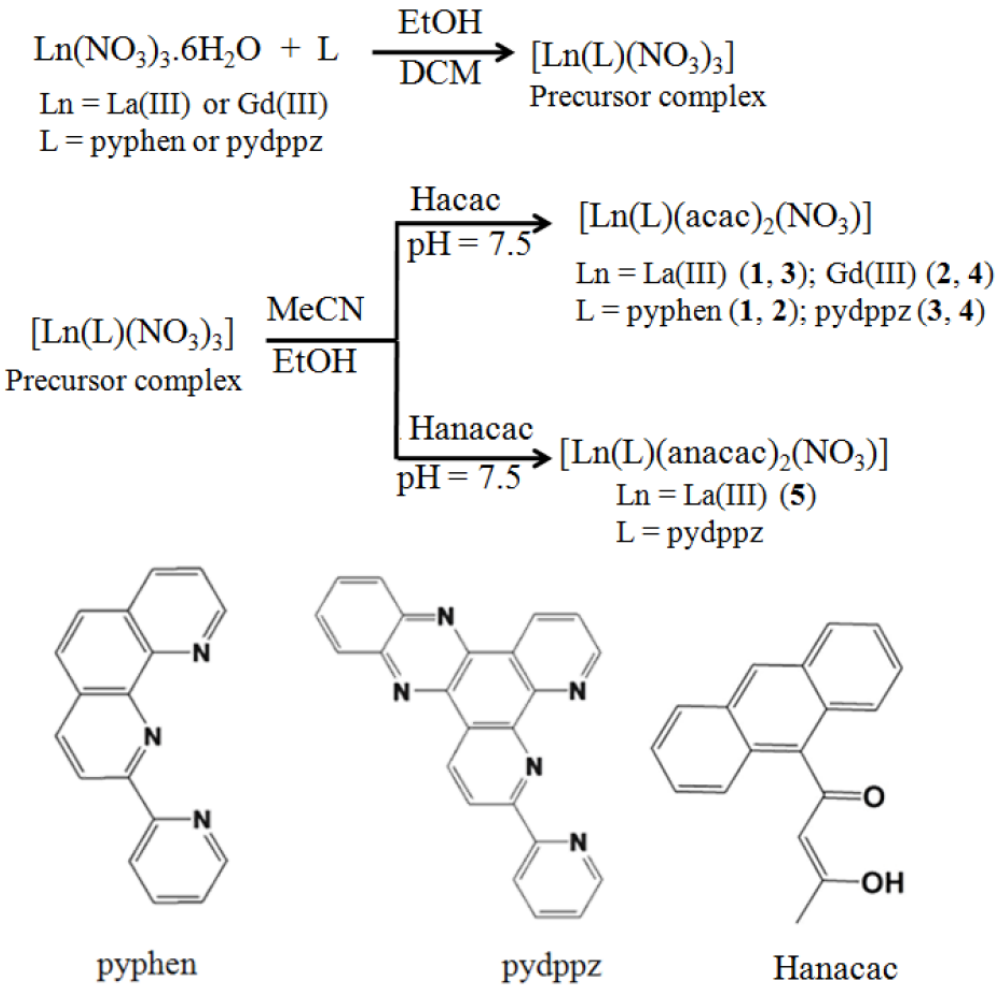


Scheme S1 Reaction conditions and the reagents used for the synthesis of the ligands: (a) Friedel-Craft reaction using acetyl chloride/aluminum chloride in dry DCM, (b) ethyl acetate and sodium sand in diethyl ether, (c) n-BuLi, 2-bromopyridine in dry THF, 6 h, –78 °C followed by basic alumina column chromatography using THF/hexane (1:5) as eluent, (d) MnO_2, overnight, (e) 2:1 H_2SO_4/HNO_3, reflux followed by neutralization with NaOH and purified by silica column chromatography (100-200 mesh) using DCM as eluent and (f) 1,2- phenylenediamine in EtOH, reflux (30 min).



Scheme S2 Generalized reaction scheme for the syntheses of the complexes **1**-**5** (DCM = dichloromethane).

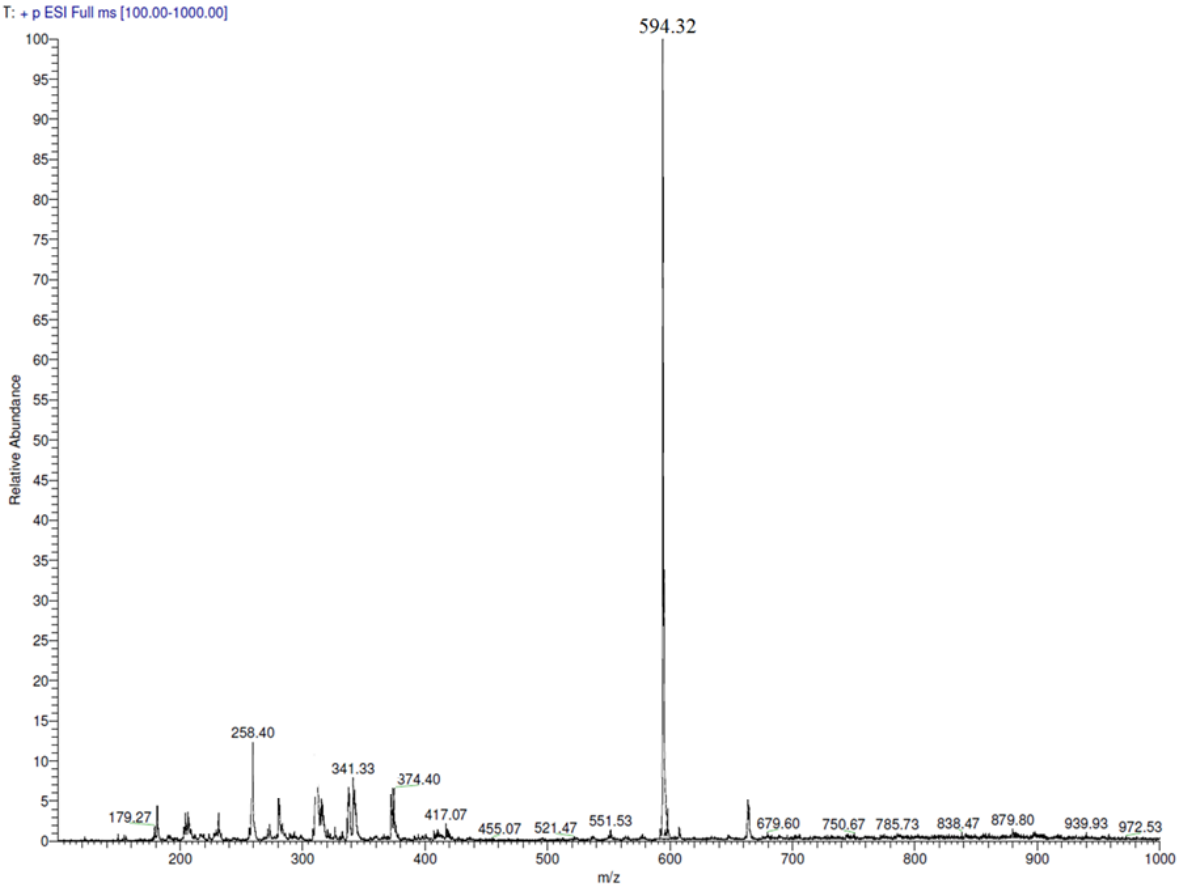


Fig. S1 ESI-MS spectrum of [La(pyphen)(acac)$_2$(NO$_3$)] (**1**) in 10% aqueous MeOH showing the prominent [M-(NO$_3^-$)]$^+$ peak. The peak at 258.40 (m/z) is due to [pyphen+H]$^+$.

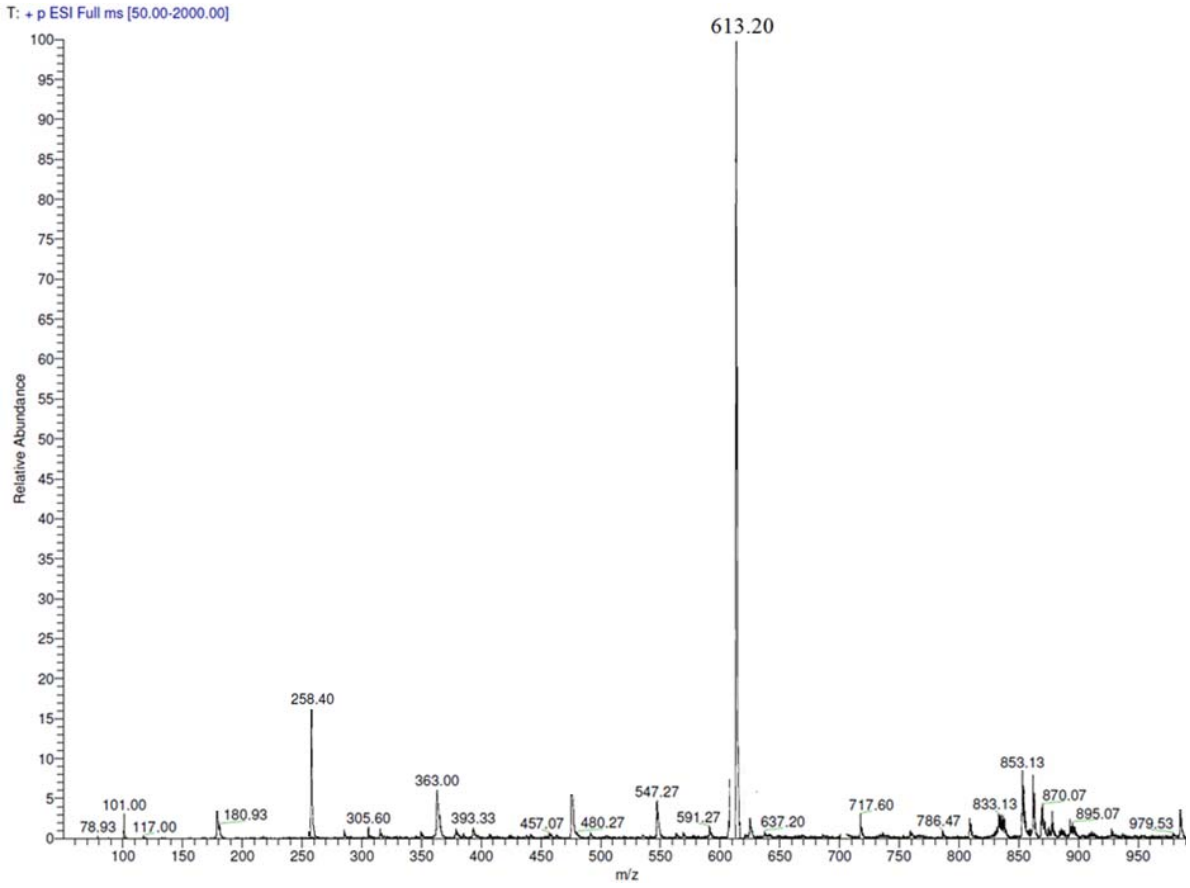


Fig. S2 ESI-MS spectrum of [Gd(pyphen)(acac)$_2$(NO$_3$)] (**2**) in 10% aqueous MeOH showing the prominent [M-(NO$_3^-$)]$^+$ peak. The peak at 258.40 (m/z) is due to [pyphen+H]$^+$.

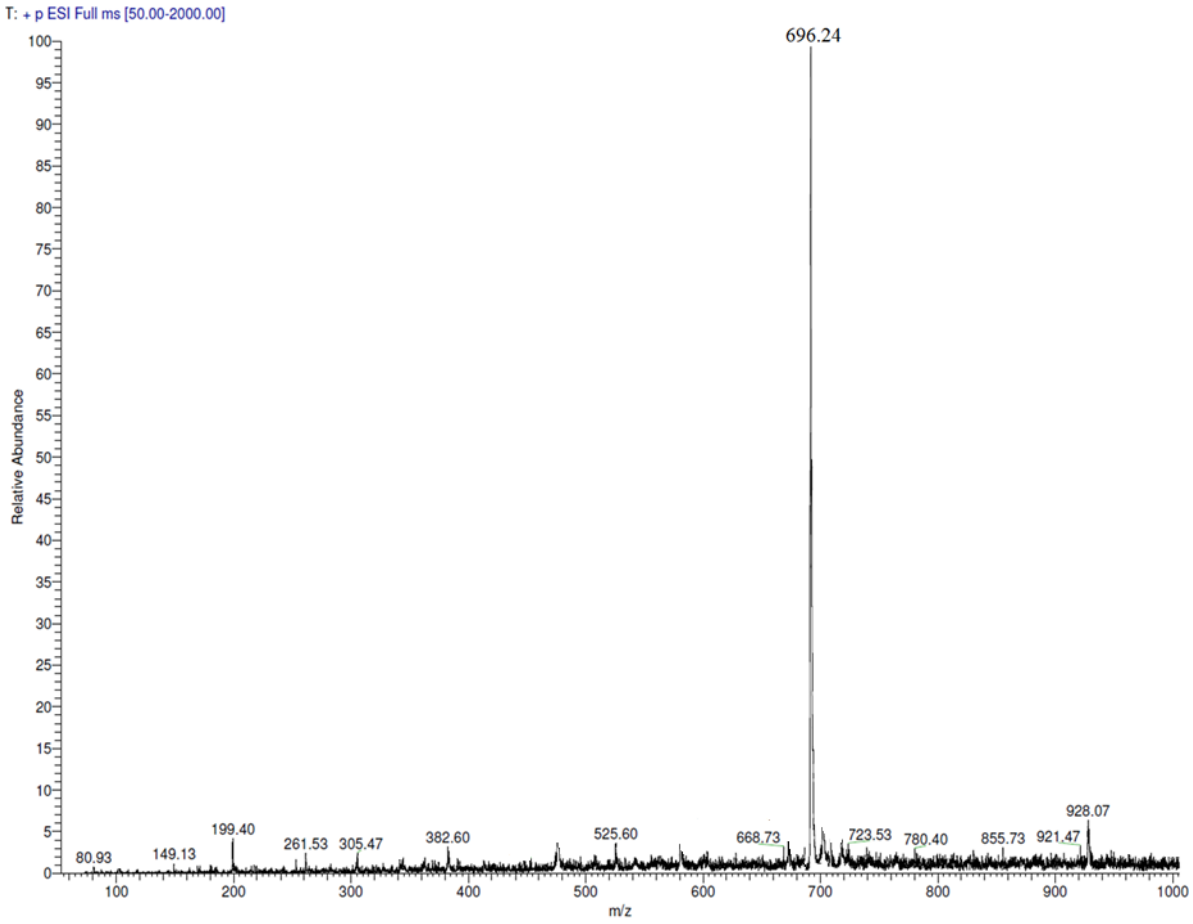


Fig. S3 ESI-MS spectrum of [La(pydppz)(acac)$_2$(NO$_3$)] (**3**) in 10% aqueous MeCN showing the prominent [M-(NO$_3^-$)]$^+$ peak.

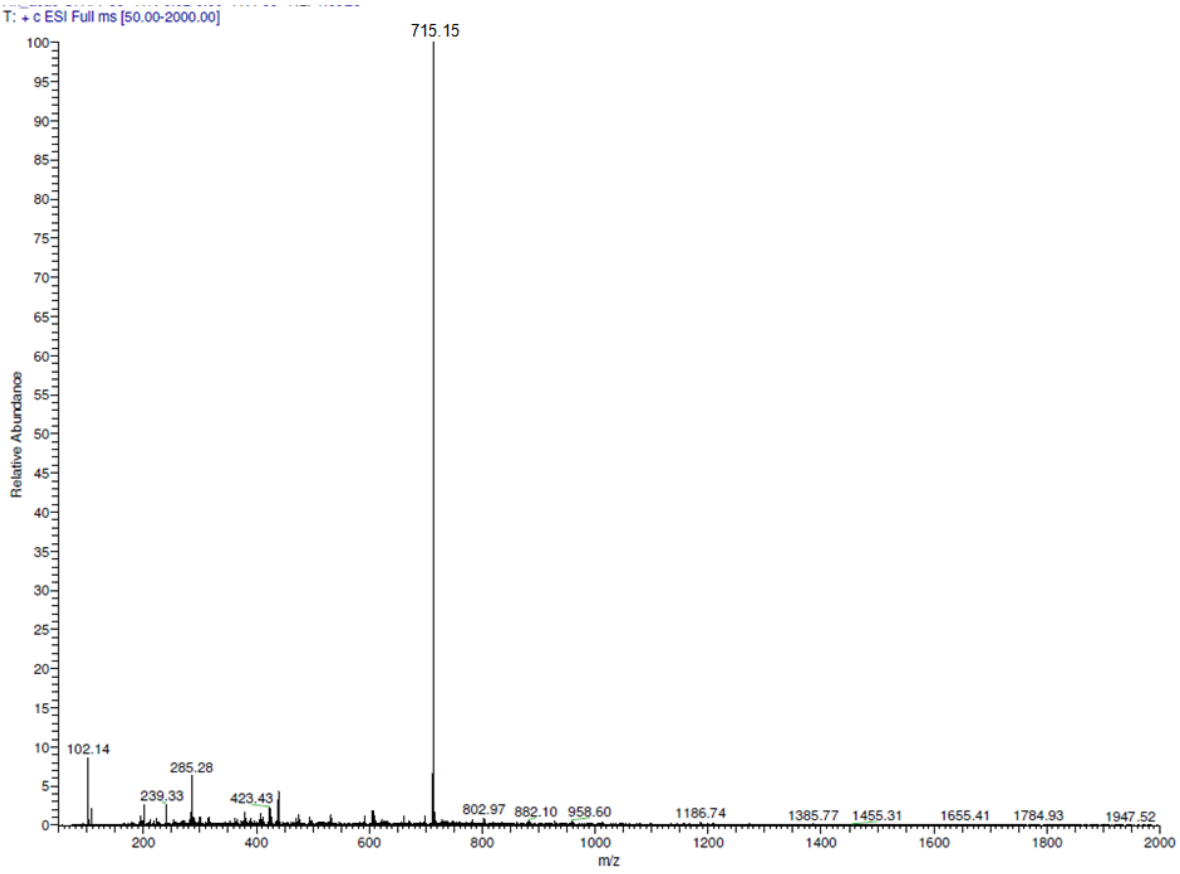


Fig. S4 ESI-MS spectrum of [Gd(pydppz)(acac)$_2$(NO$_3$)] (**4**) in 10% aqueous MeCN showing the prominent [M-(NO$_3^-$)]$^+$ peak.

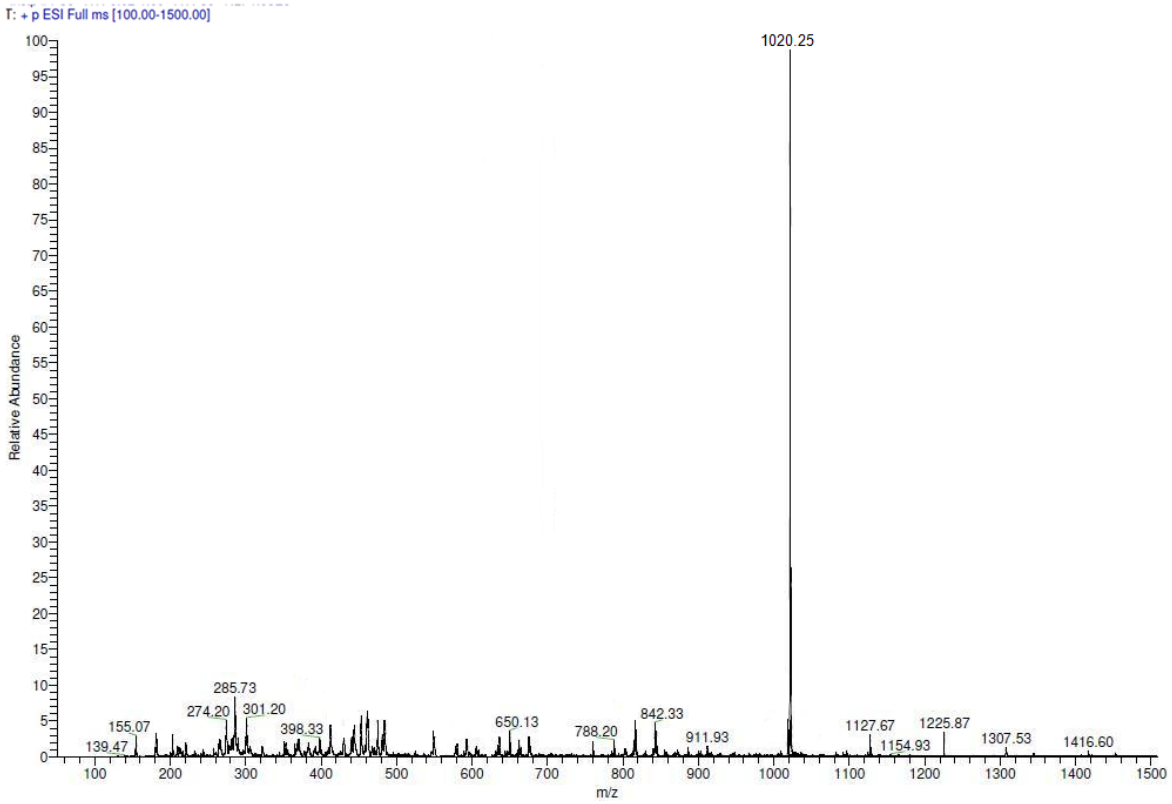


Fig. S5 ESI-MS spectrum of [La(pydppz)(anacac)$_2$(NO$_3$)] (**5**) in 10% aqueous MeOH showing the prominent [M-(NO$_3^-$)]$^+$ peak. The minor peak at 285.73 (m/z) is due to [Hanacac + Na]$^+$.

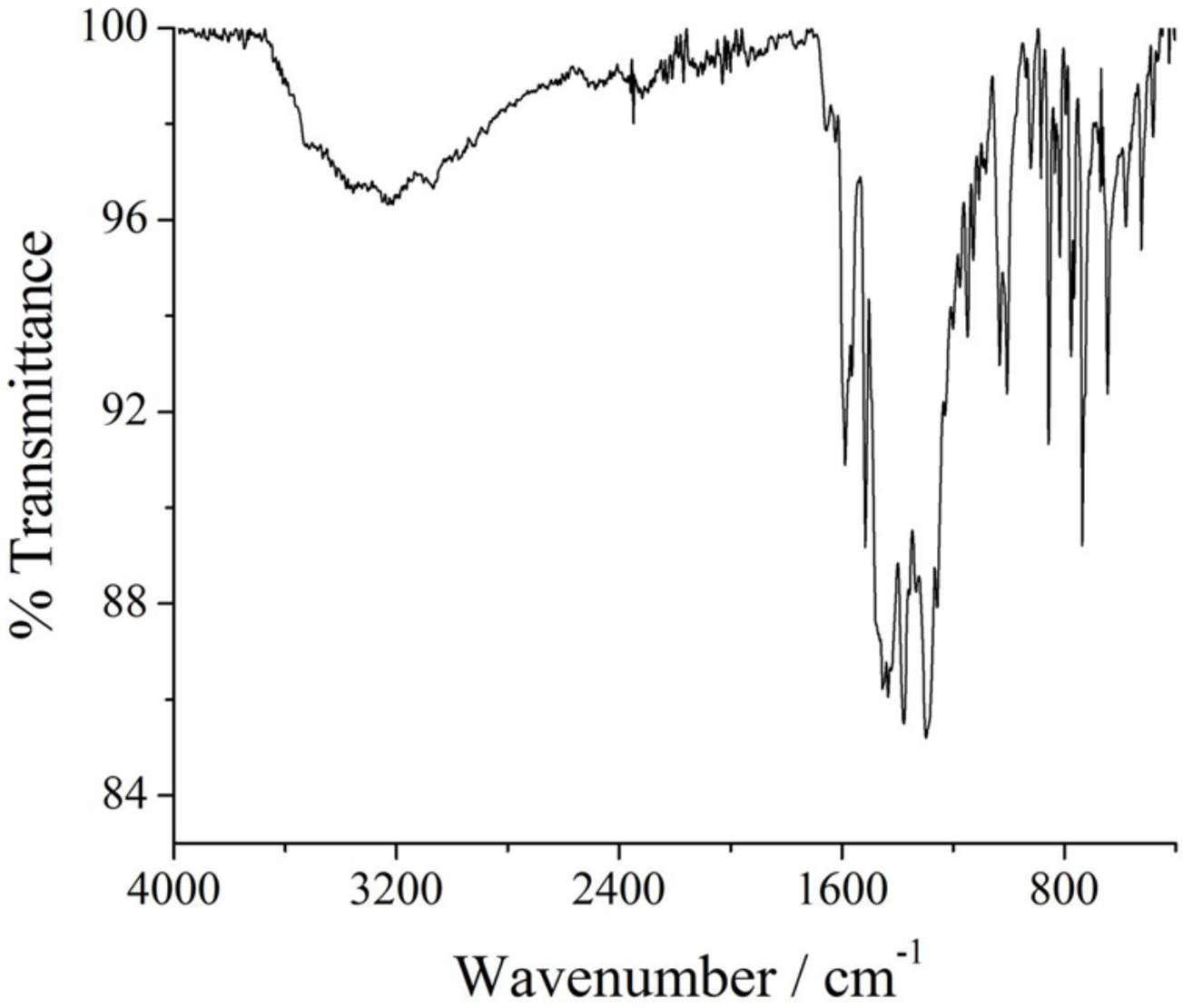


Fig. S6 IR spectrum of [La(pyphen)(acac)$_2$(NO$_3$)] (**1**).

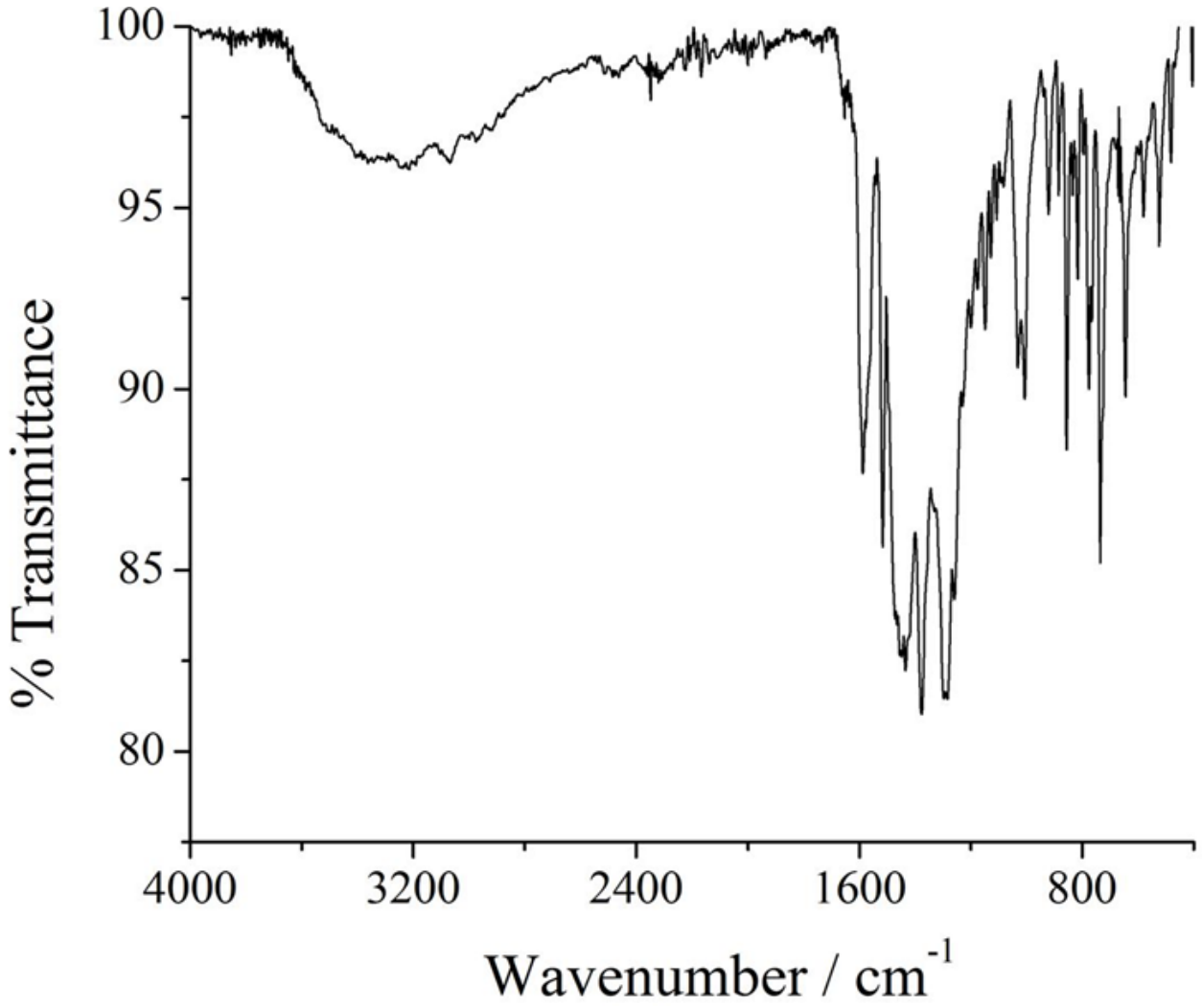


Fig. S7 IR spectrum of [Gd(pyphen)(acac)$_2$(NO$_3$)] (**2**).

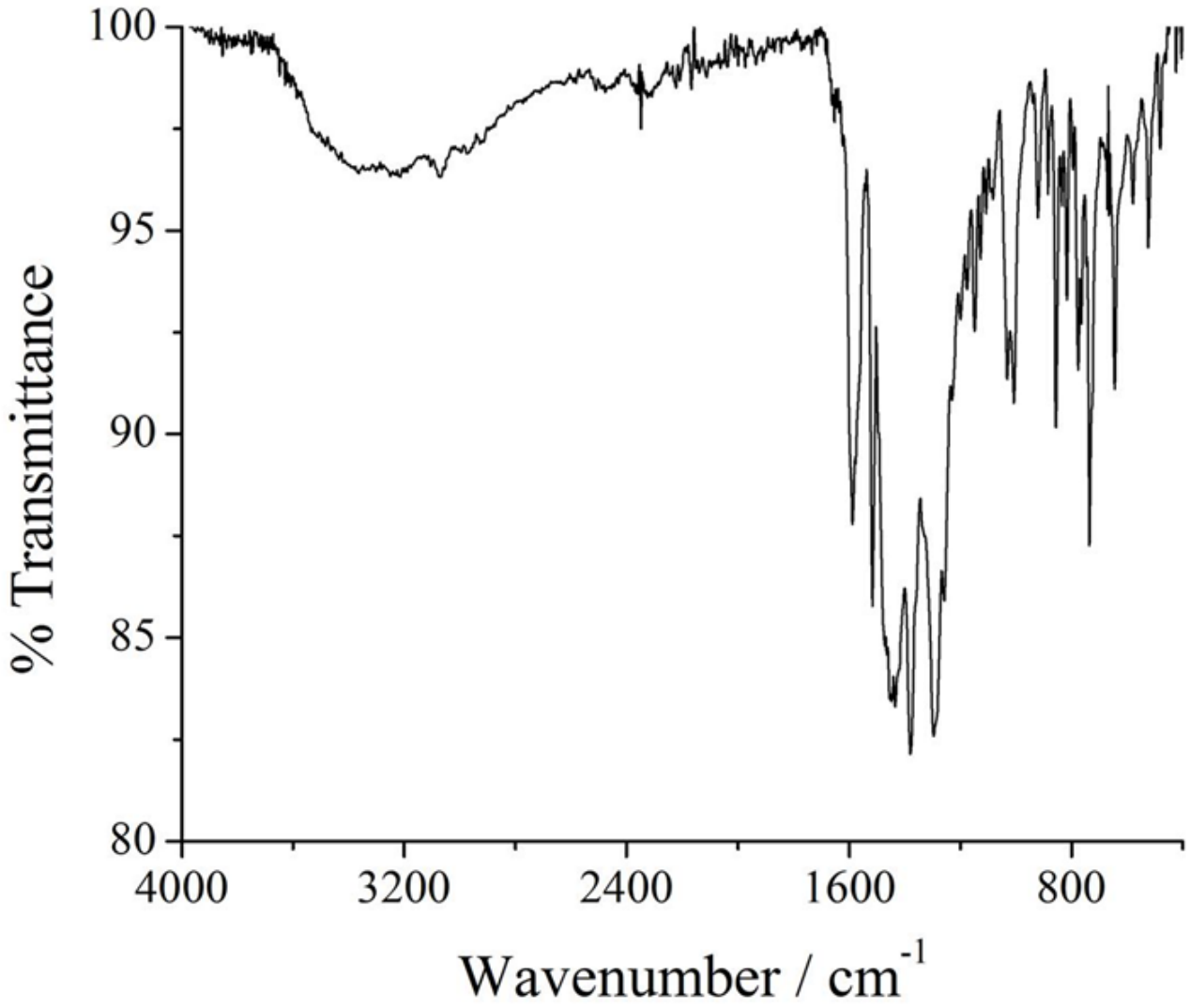


Fig. S8 IR spectrum of [La(pydppz)(acac)$_2$(NO$_3$)] (**3**).

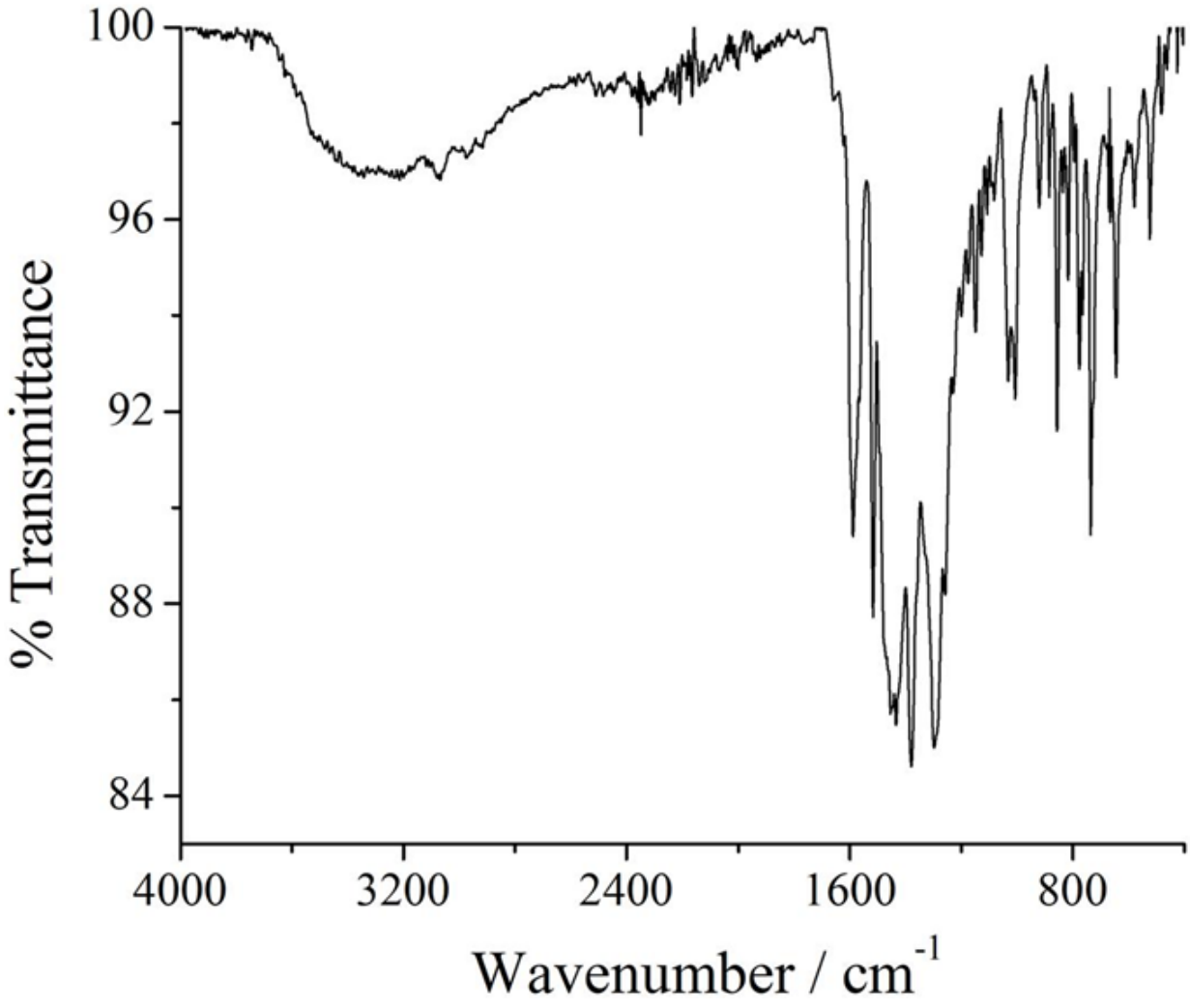


Fig. S9 IR spectrum of [Gd(pydppz)(acac)$_2$(NO$_3$)] (**4**).

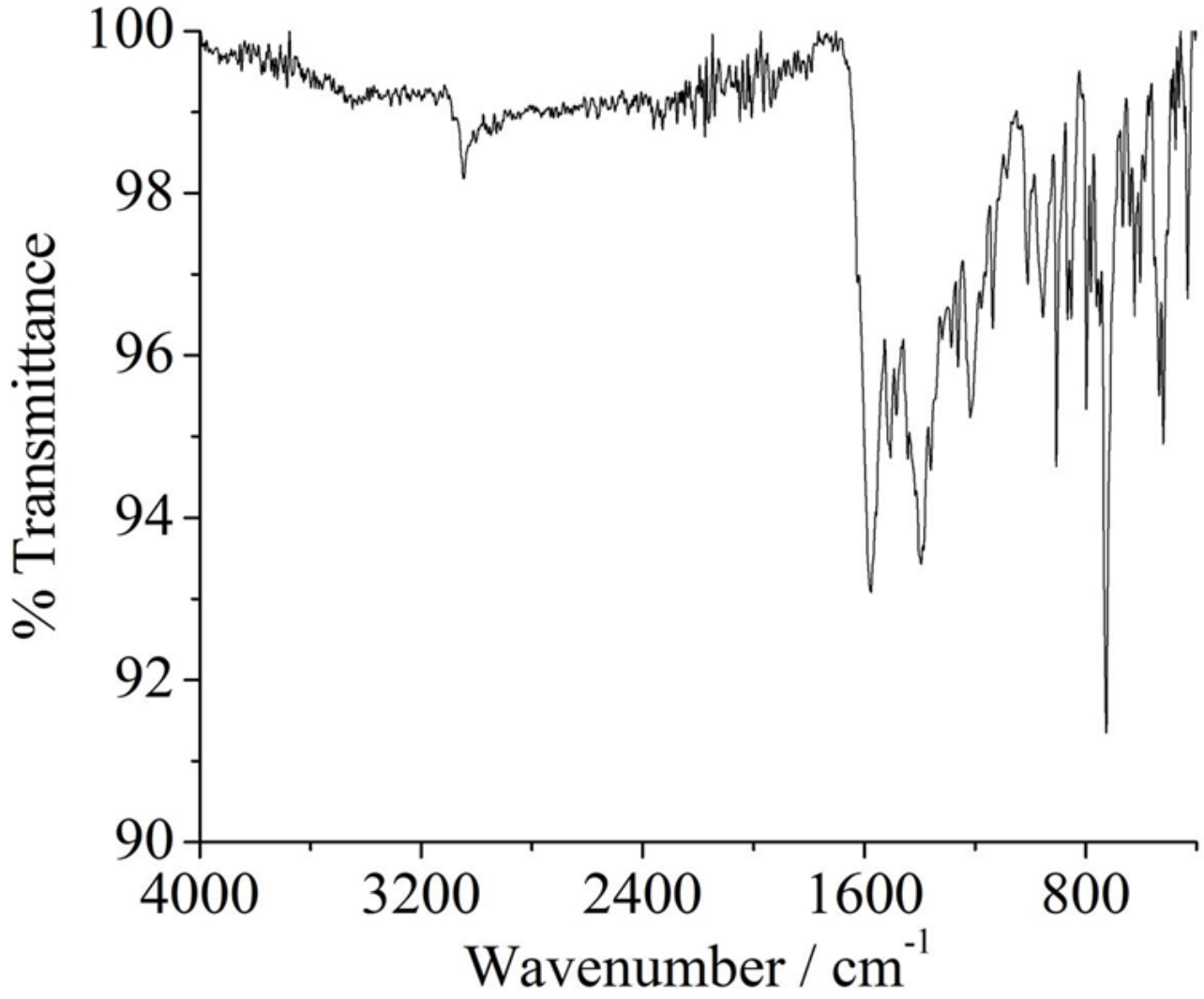


Fig. S10 IR spectrum of [La(pyphen)(anacac)$_2$(NO$_3$)].

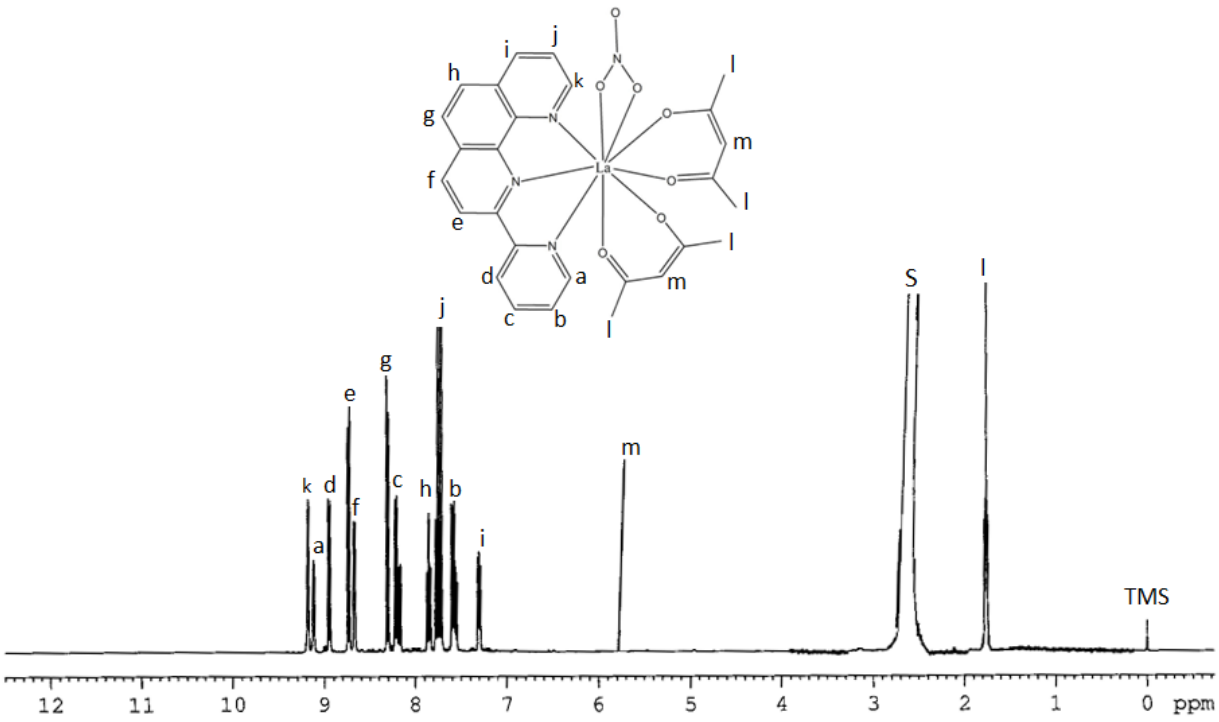


Fig. S11 ^{1}H NMR spectrum of [La(pyphen)(acac)$_2$(NO$_3$)] (**1**) in DMSO-d_6. The peak marked S between 2-3 ppm is due to solvent.

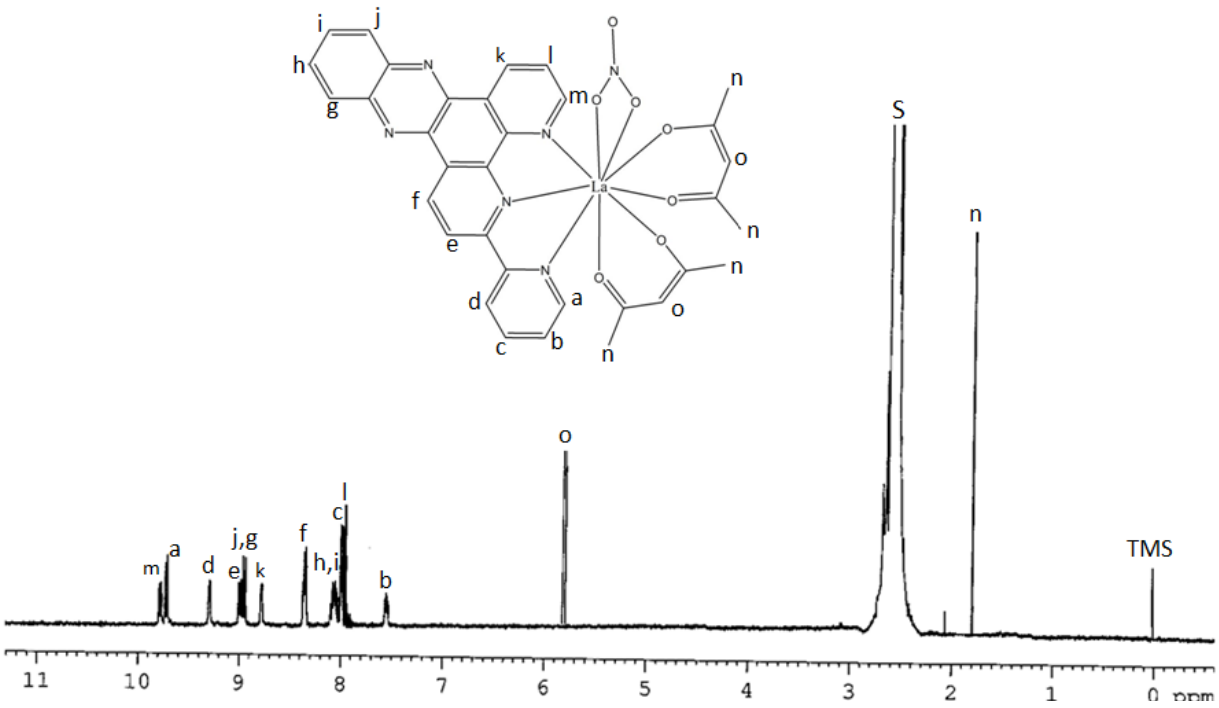


Fig. S12 ^{1}H NMR spectrum of [La(pydppz)(acac)$_2$(NO$_3$)] (**3**) in DMSO-d_6. The peak marked S between 2-3 ppm is due to solvent.

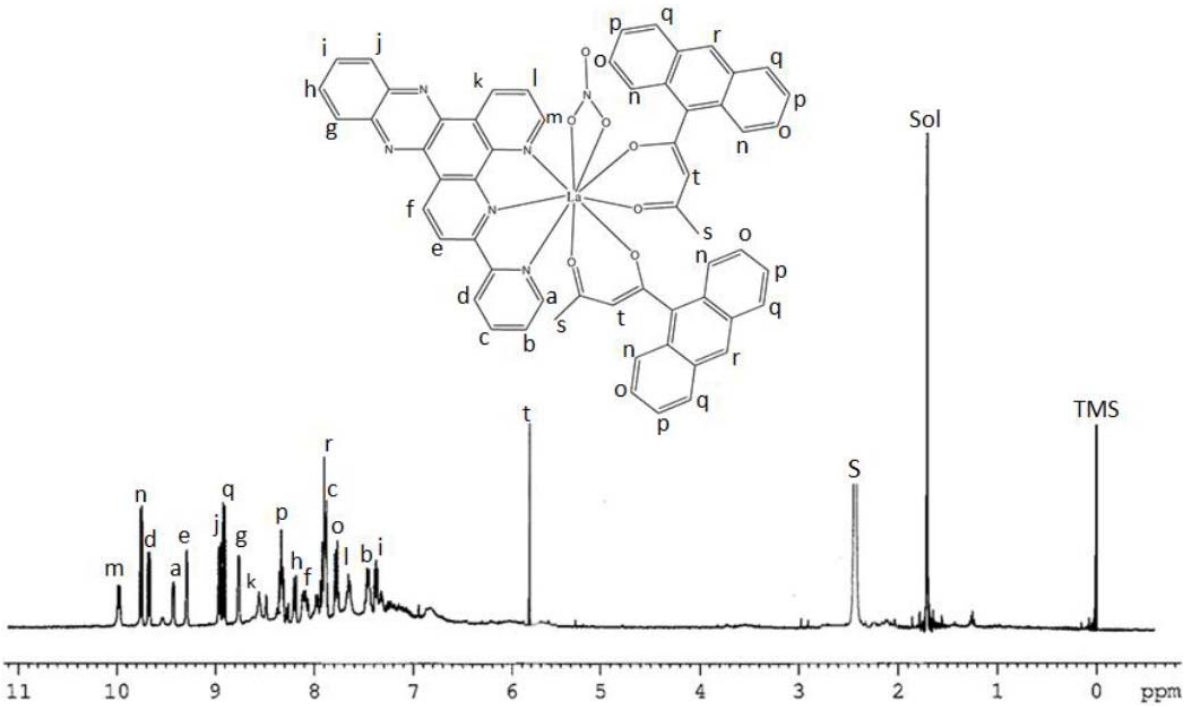


Fig. S13 1H NMR spectrum of [La(pydppz)(anacac)$_2$(NO$_3$)] (**5**) in DMSO-d_6. The peak marked Sol between 2-3 ppm is due to solvent.

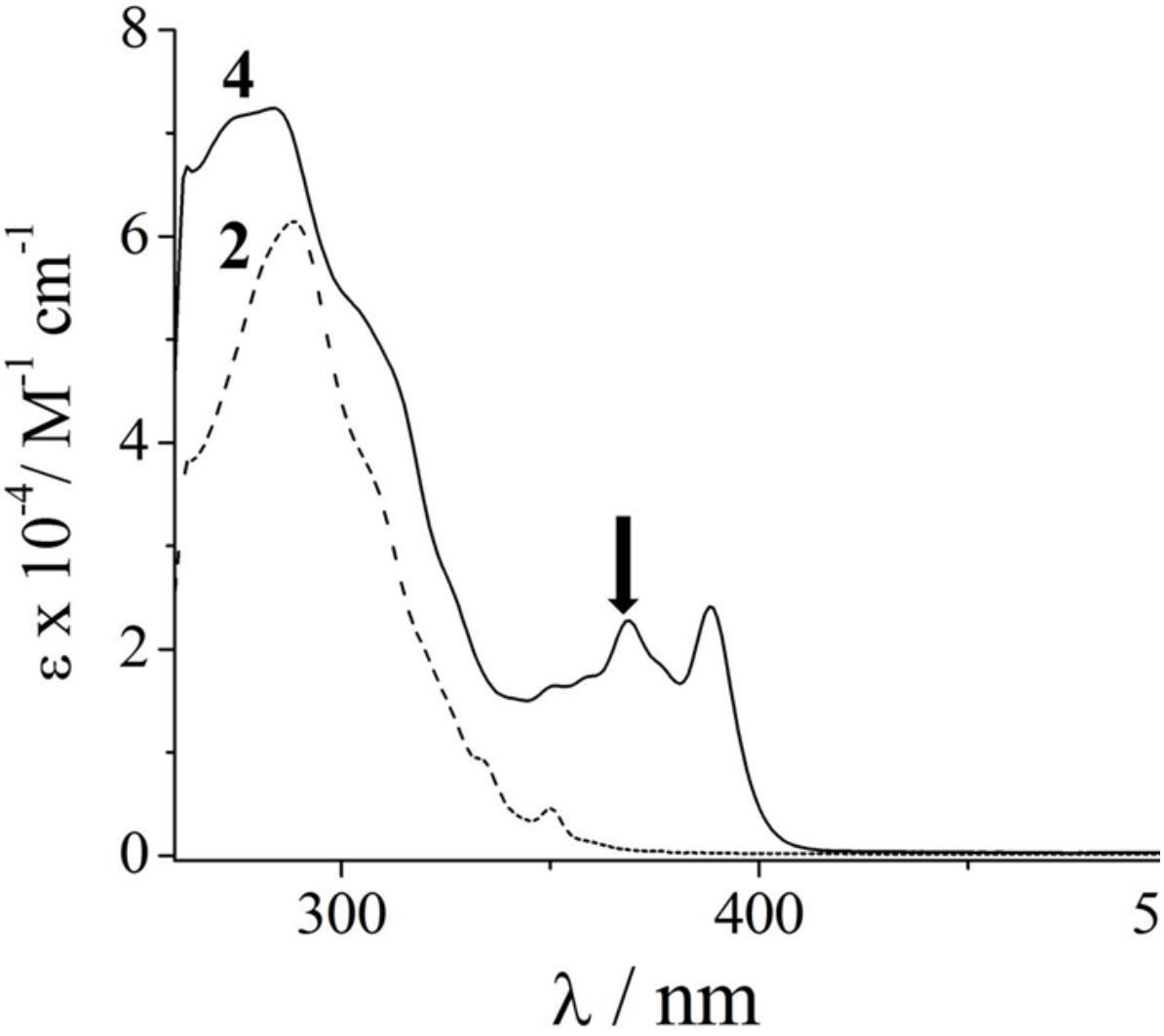


Fig. S14 The electronic absorption spectra of complexes **2** (- - -) and **4** (—) in DMF. The wavelength 365 nm used for the DNA photocleavage experiments is indicated by a downward arrow.

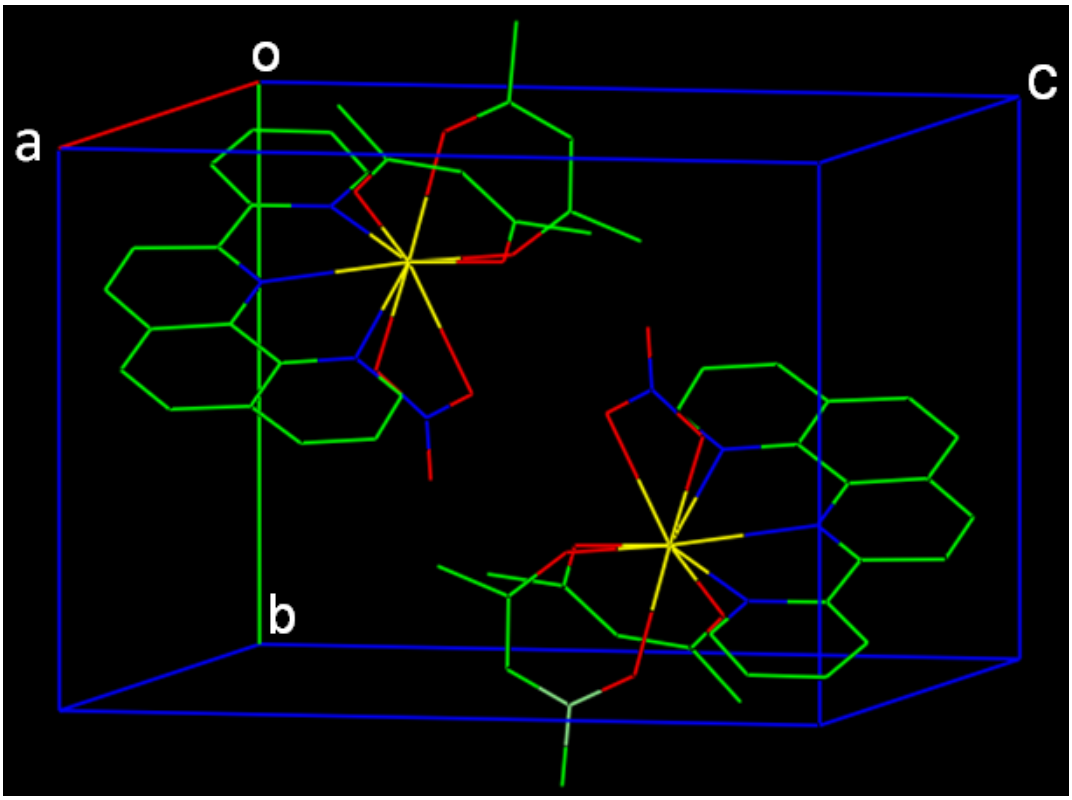


Fig. S15 Unit cell packing diagram of the complex [Gd(pyphen)(acac)$_2$(NO$_3$)] (**2**). The complex crystallized in the triclinic *P*-1 space group with *Z* = 2.

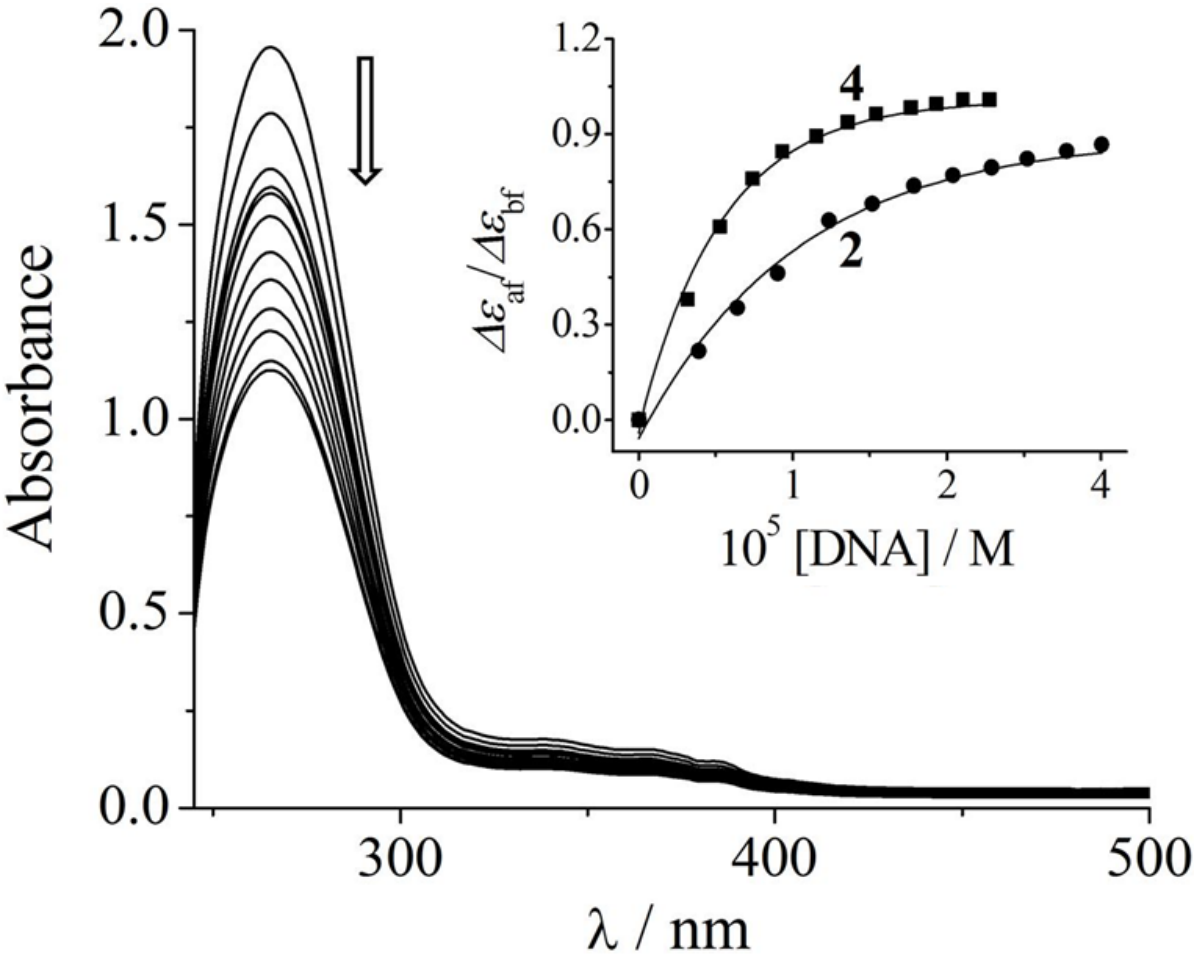


Fig. S16 Absorption spectral traces of complex **4** in 5 mM Tris-HCl buffer (pH 7.2) on increasing the quantity of calf thymus DNA. The inset shows the plots of $\Delta\varepsilon_{af}/\Delta\varepsilon_{bf}$ vs. [DNA] for [Gd(pyphen)(acac)$_2$(NO$_3$)] (**2**, ●) and [Gd(pydppz)(acac)$_2$(NO$_3$)] (**4**, ■).

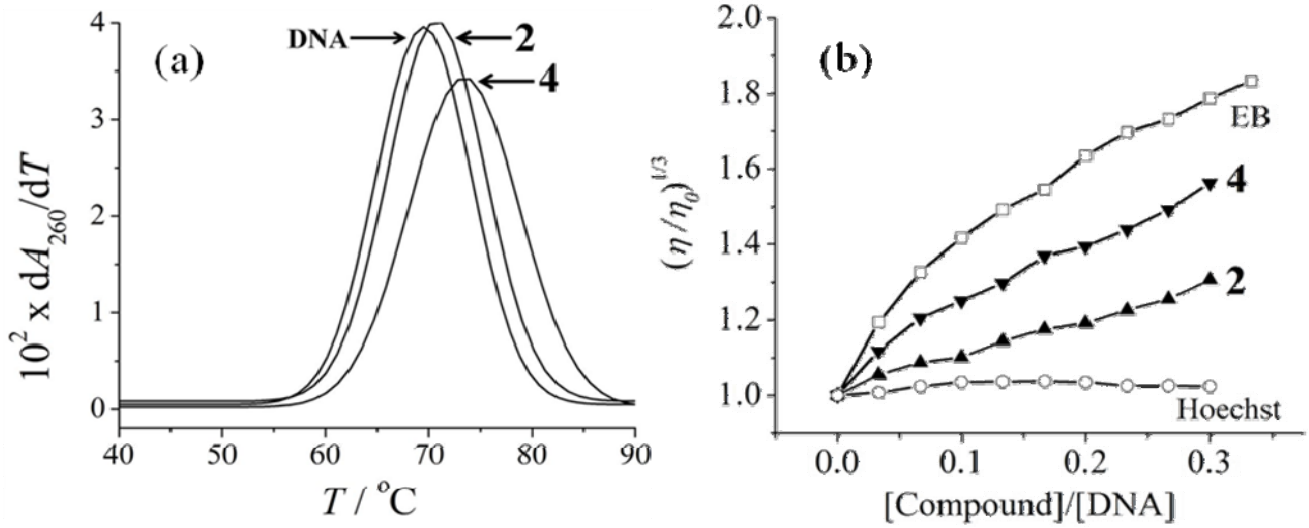


Fig. S17 Derivative plots of dA_{260}/dT vs. T for the thermal denaturation of 180 μM calf thymus DNA alone and on addition of complexes **2** and **4**. (b) Plots of $(\eta/\eta_0)^{1/3}$ vs. [compound]/[DNA] showing the effect of increasing concentration of the complexes [Gd(pyphen)(acac)$_2$(NO$_3$)] (**2**,▲), [Gd(pypdppz)(acac)$_2$(NO$_3$)] (**4**,▼), ethidium bromide (EB, □) and Hoechst 33258 (○) on the relative viscosities of CT-DNA at 37.0(± 0.1) °C in 5 mM Tris-HCl buffer (pH 7.2) containing 2.5 – 20% DMF and 180 μM calf thymus DNA.

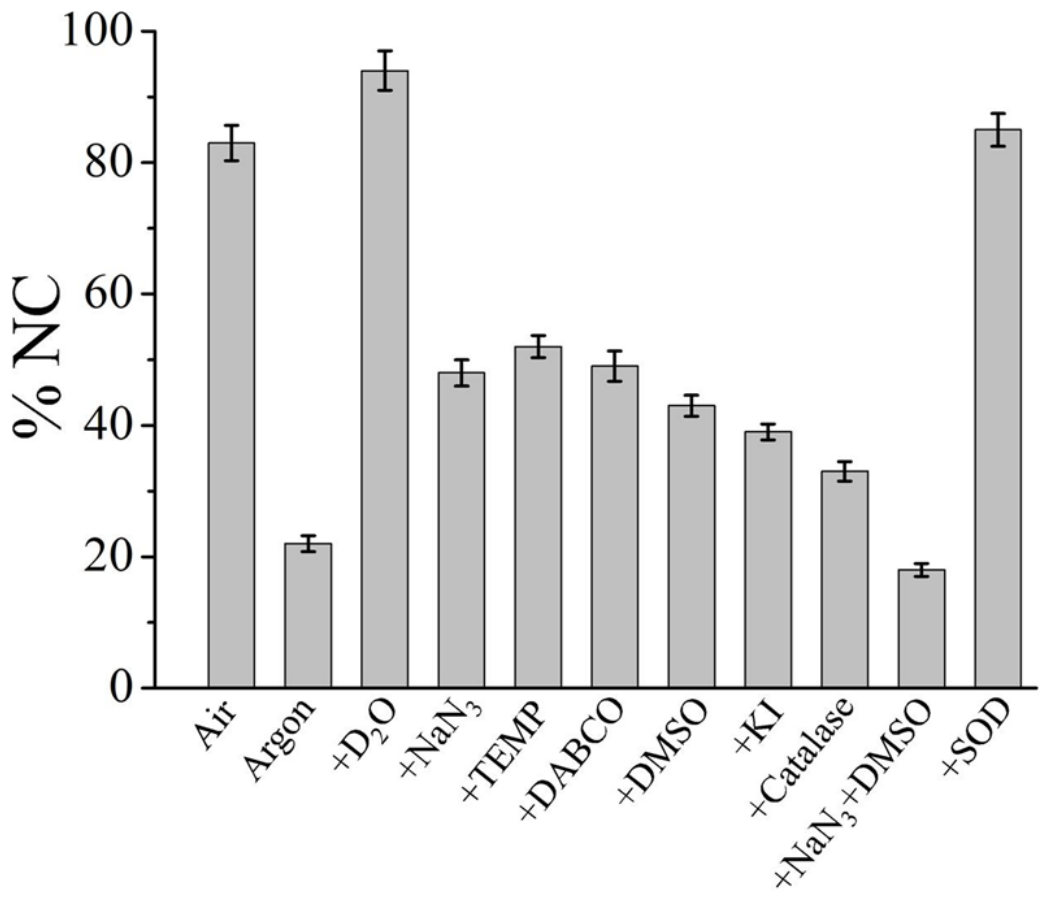


Fig. S18 Bar diagram showing the extent of photocleavage of SC pUC19 DNA (0.2 μg, 30 μM) by [Gd(pydppz)(acac)$_2$(NO$_3$)] (**4**) in the presence of various additives in Tris-HCl buffer containing 10% DMF. The complex concentration and exposure time are 1.0 μM and 2 h, respectively. The additive concentrations/quantities are: sodium azide, 500 μM; KI, 500 μM; TEMP, 500 μM; DABCO, 500 μM; D_2O, 16 μL; DMSO, 4 μL; catalase, 4 units; SOD, 4 units.

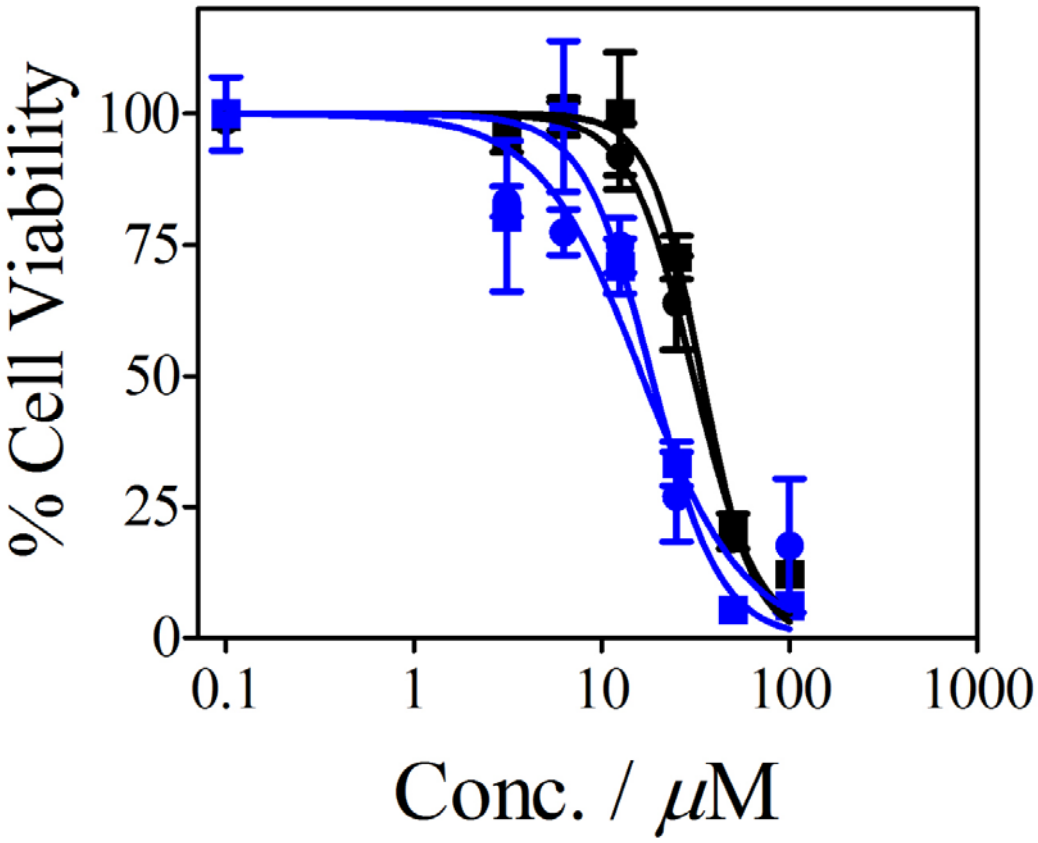


Fig. S19 Cell viability plots showing the photocytotoxicity of the pydppz complexes **1** and **2** in HeLa cells on 4 h incubation in dark followed by exposure to UV-A light of 365 nm (0.55 J cm^{-2}) for 15 min as determined from the MTT assay. The non-linear fitted curves for dark-treated and photo-exposed cells for complex **1** are shown by black circles (●) and blue circles (●), respectively. For complex **2**, they are shown by black squares (■) and blue squares (■), respectively.

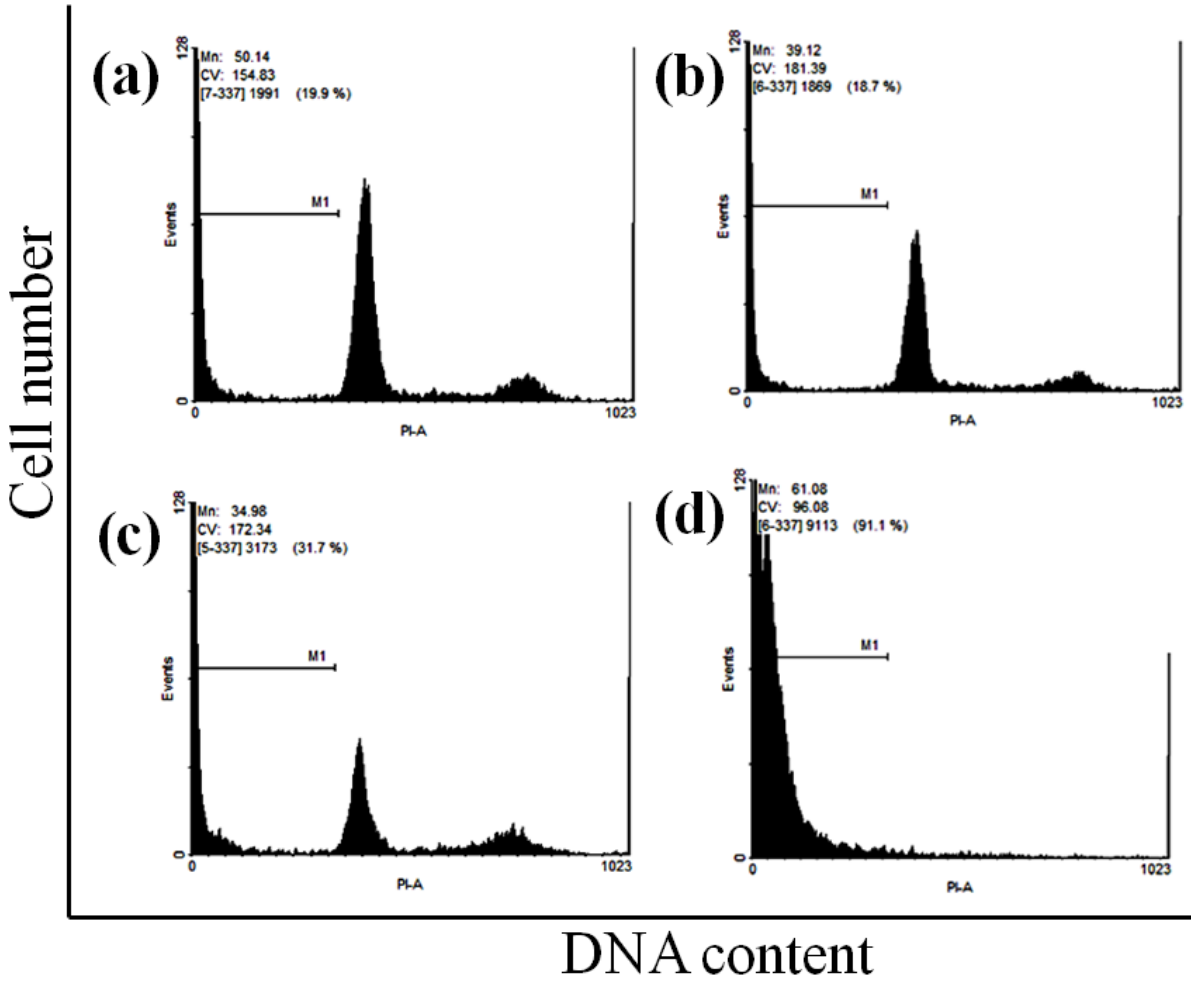


Fig. S20 Complex **4** induced apoptotic cell death by flow cytometric analysis: (a) control cells in the dark, (b) control cells in UV-A light, (c) cells treated with complex **4** in the dark and (d) cells treated with complex **4** (0.6 μM) in UV-A light (photoexposure time = 15 min, incubation time = 24 h).