Electronic Supplementary Information

Characterization of the Interactions between Substrate, Cu^{II} complex and DNA and their Role in Rate Accelerations in DNA-based Asymmetric Catalysis

Apparao Draksharapu, Arnold J. Boersma, Wesley R. Browne and Gerard Roelfes

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1. Characterization of $(Aza)_2$-Cu^{II} complex

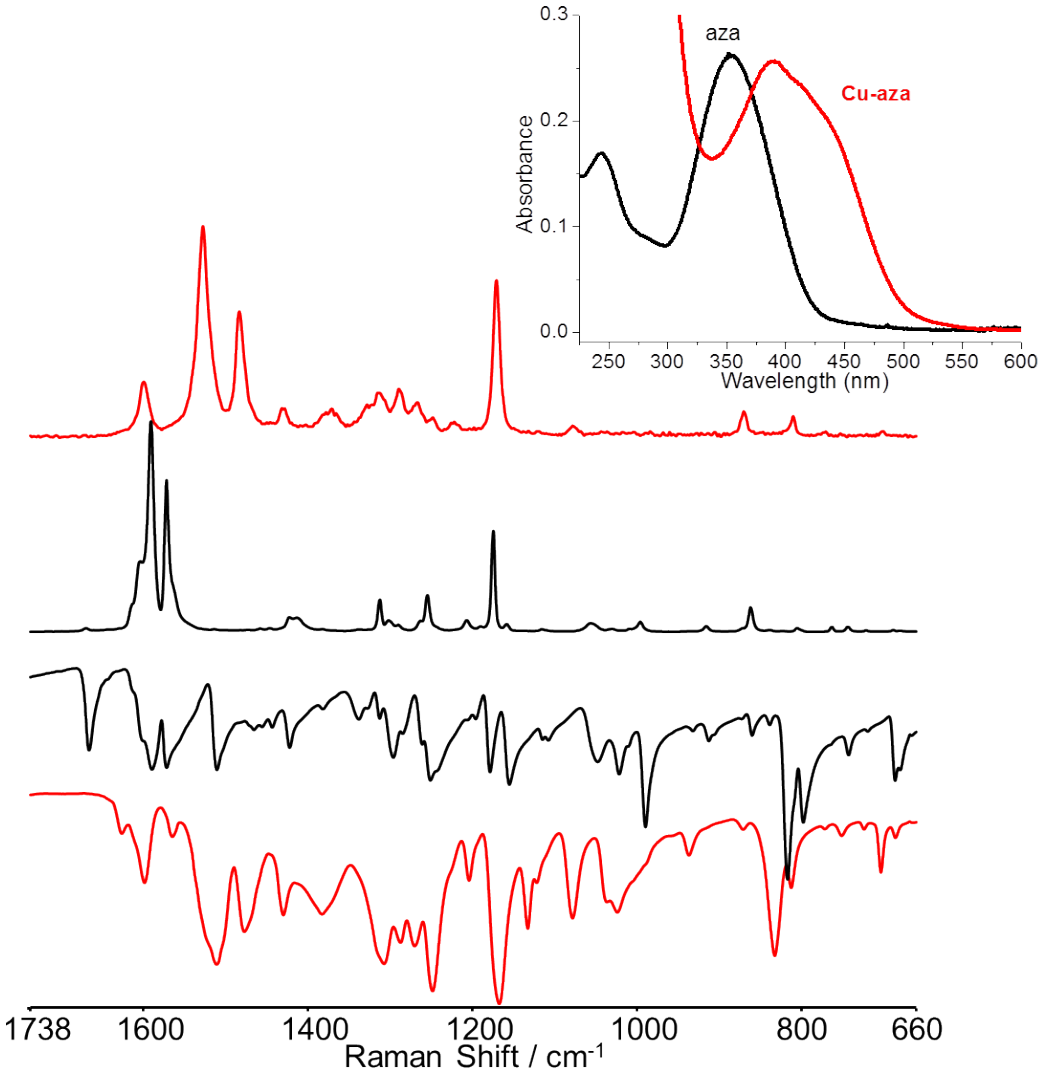

Fig. S 1 Solid state FTIR and Raman (at λ_{exc} 785 nm) (inset: UV/Vis absorption in water with 1 vol% of CH_3CN at 15 µM) spectra of **Aza** (black) and **$(Aza)_2$-Cu^{II}** (red).

2. Comparison between Aza-Cu^{II}dmbpy and (Aza)$_2$-Cu^{II} complexes

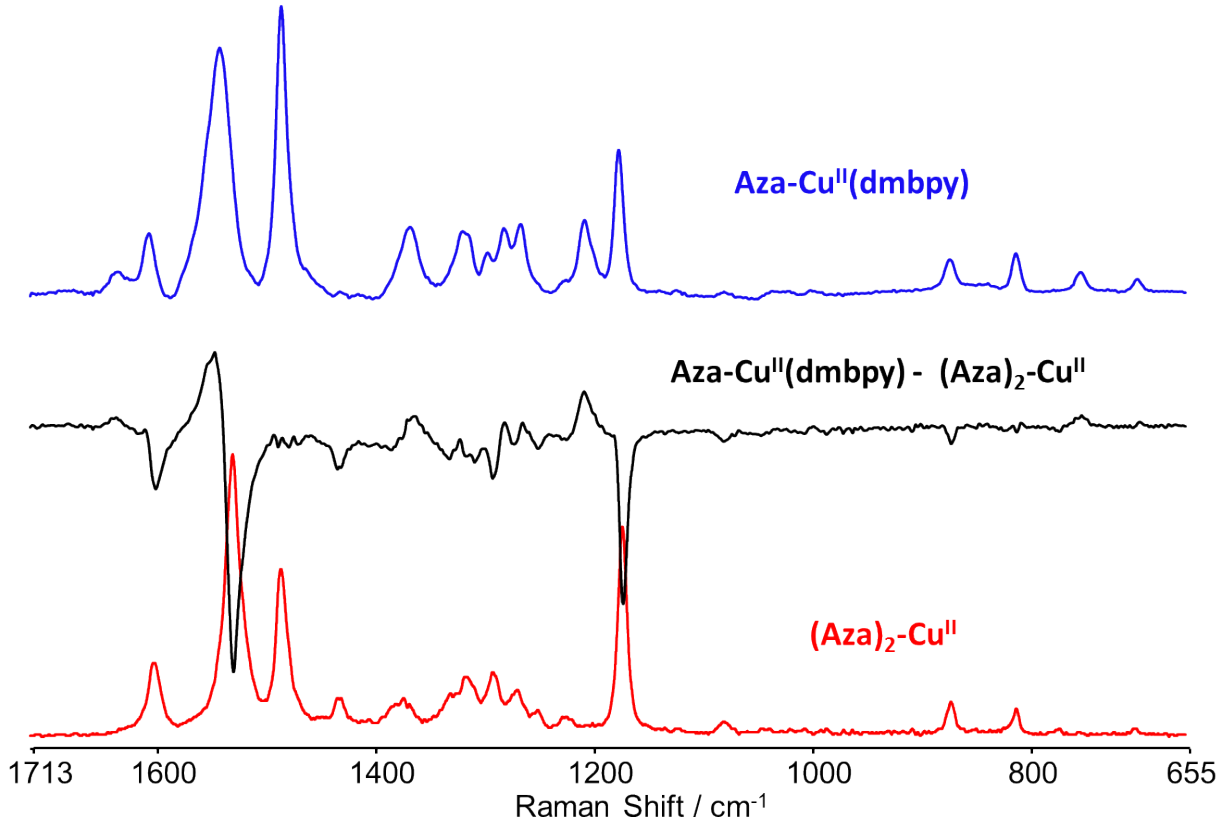

Fig. S 2 Solid state Raman spectra of **(Aza)$_2$-Cu^{II}** at λ_{exc} 785 nm (bottom), **Aza-Cu^{II}dmbpy** dispersed in KCl at λ_{exc} 473 nm (top). Centre: A scaled subtraction of the spectrum of lower spectrum from the upper spectrum.

3. Comparison between solid and solution state structure of $(Aza)_2$-Cu^{II}

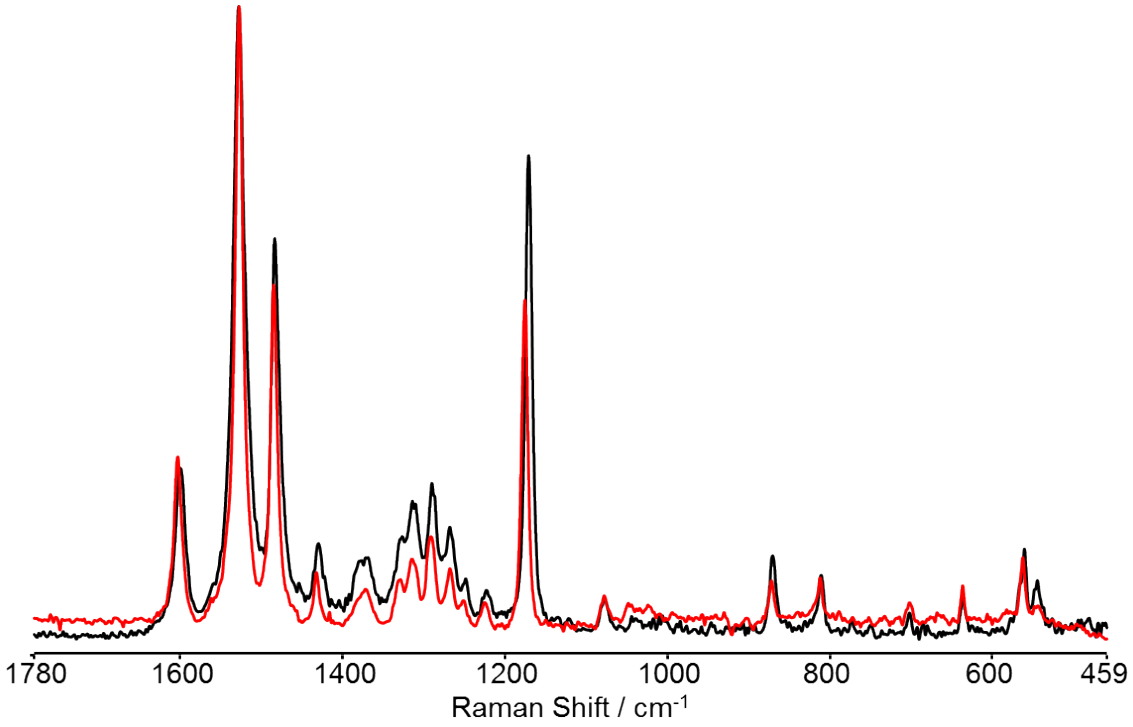

Fig. S 3 Raman spectra of **$(Aza)_2$-Cu^{II}** in solid state (black) and in acetonitrile/water (1:1 v/v, red) at λ_{exc} 785 nm.

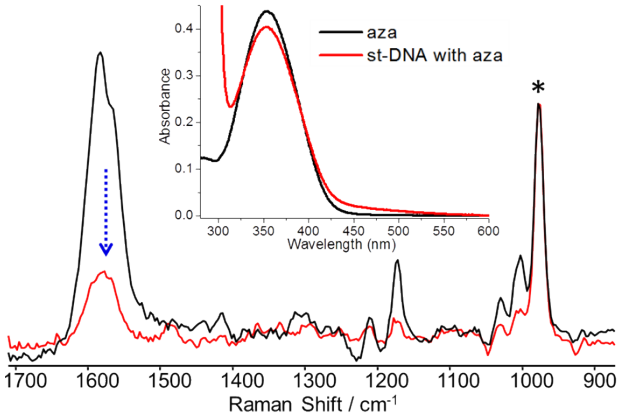

Fig. S 4 Resonance Raman spectra at λ_{exc} 355 nm of **Aza** in the absence (black) and presence (red) of st-DNA. Conditions: st-DNA (1.3 mg/mL) and **Aza** (20 μM) in 20 mM MOPS buffer (pH 6.5). Raman Spectra were solvent subtracted followed by a multipoint baseline correction. *SO_4^{2-} internal standard (50 mM). Inset: UV/Vis absorption spectra of solutions used to record Raman spectra.

4. Cu^{II}dmbpy/$Cu^{II}d_{12}$-dmbpy and Aza in the presence and absence of st-DNA

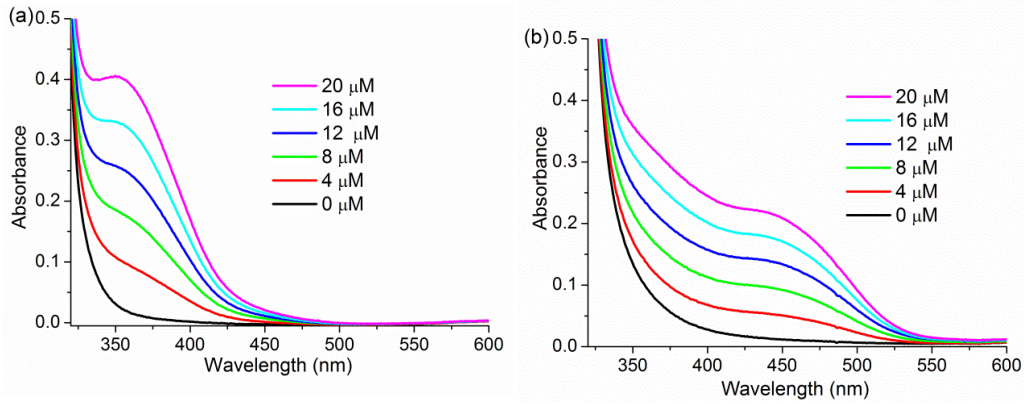

Fig. S 5 Titration of **Aza** to **Cu^{II}dmbpy** (0.3 mM) (a) without and (b) with st-DNA (1.33 mg/mL) in 20 mM MOPS buffer monitored by UV/Vis absorption spectroscopy. Legend: final concentration of **Aza**.

5. Cu^{II}dmbpy/$Cu^{II}d_{12}$-dmbpy and Aza in the presence and absence of st-DNA

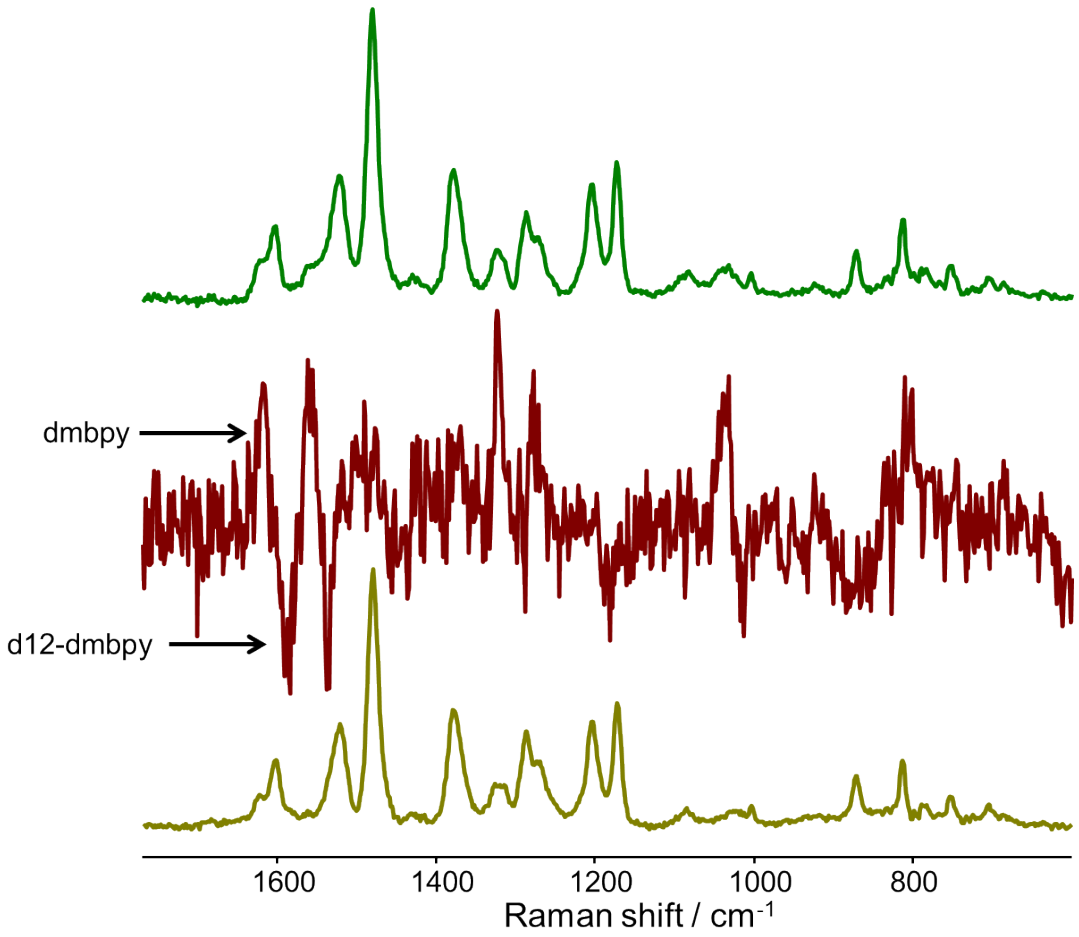

Fig. S 6 Resonance Raman spectra at λ_{exc} 473 nm of (top) **Cu^{II}dmbpy** or (bottom) **$Cu^{II}d_{12}$-dmbpy** (0.3 mM) and **Aza** (4 μM) with st-DNA 1.33 mg/mL st-DNA in 20 mM MOPS. Centre: A scaled subtraction of the spectrum of lower spectrum from the upper spectrum showing dmbpy modes as positive signals and d_{12}-dmbpy modes as negative signals.

6. Cu^{II}bpy and Aza in the presence and absence of st-DNA

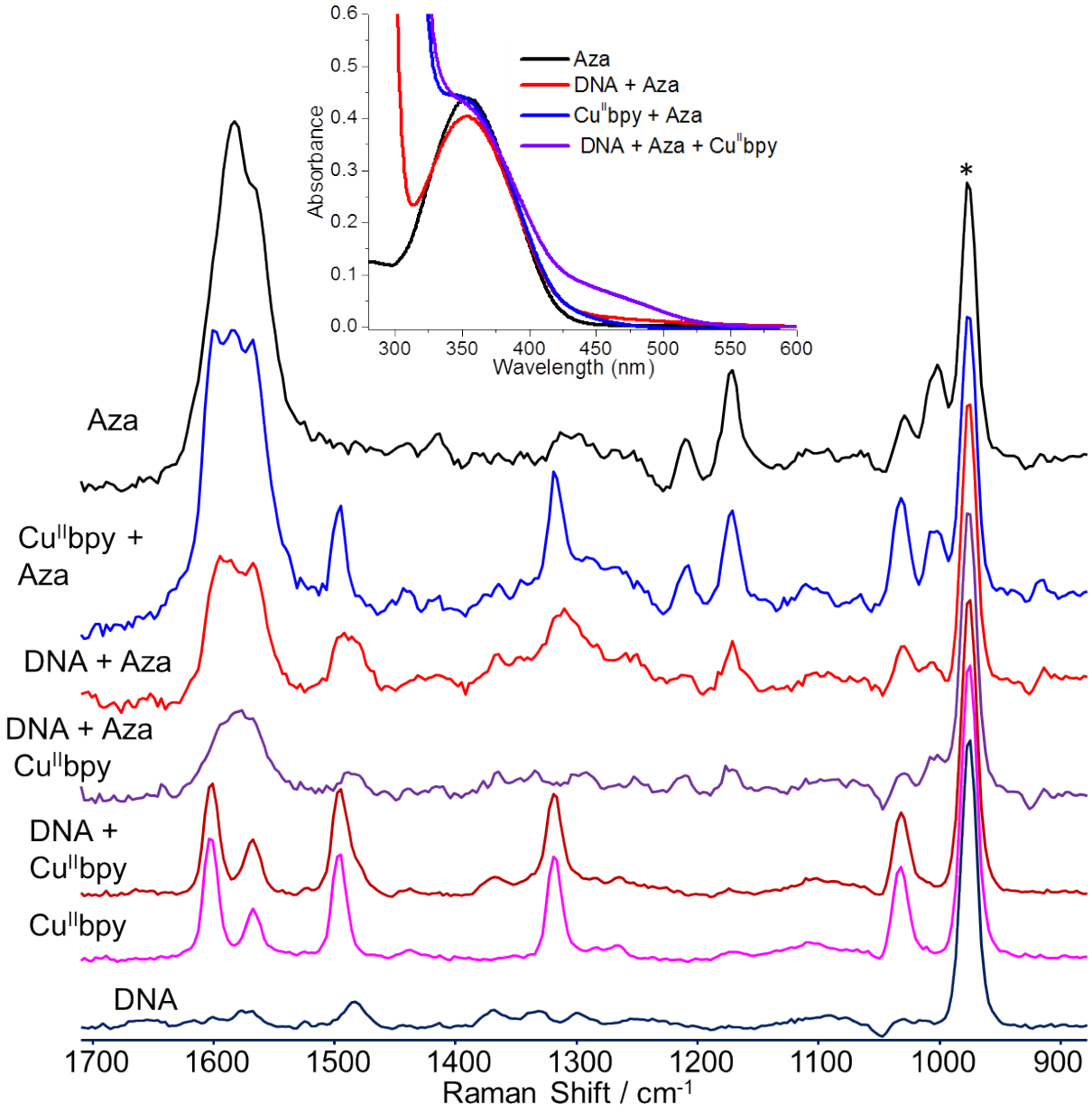

Fig. S 7 Resonance Raman spectra of **Aza** and **Cu^{II}bpy** in the absence and presence of st-DNA at λ_{exc} 355 nm. 20 μM **Aza**, 0.3 mM **Cu^{II}bpy**, 1.33 mg/mL st-DNA in 20 mM MOPS. * SO_4^{2-} as an internal standard (50 mM). Inset: UV/Vis absorption spectra of solutions used to record Raman spectra.

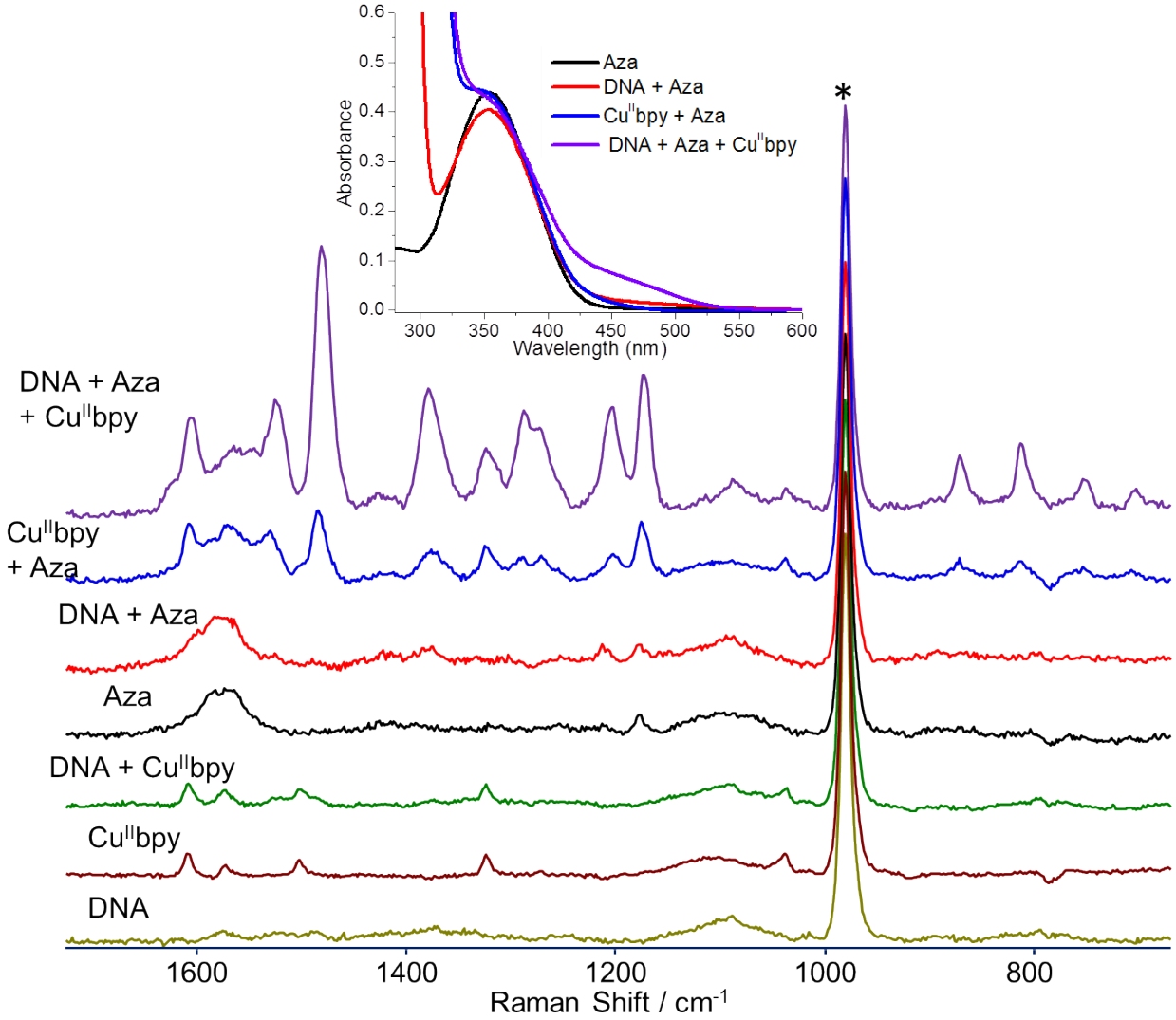

Fig. S 8 Resonance Raman spectra of **Aza** and **Cu^{II}bpy** in the absence and presence of st-DNA at λ_{exc} 473 nm. 20 µM **Aza**, 0.3 mM **Cu^{II}bpy**, 1.33 mg/mL st-DNA in 20 mM MOPS. * SO_4^{2-} as an internal standard (50 mM). Inset: UV/Vis absorption spectra of solutions used to record Raman spectra.

7. Cu^{II}phen and Aza in the presence and absence of st-DNA

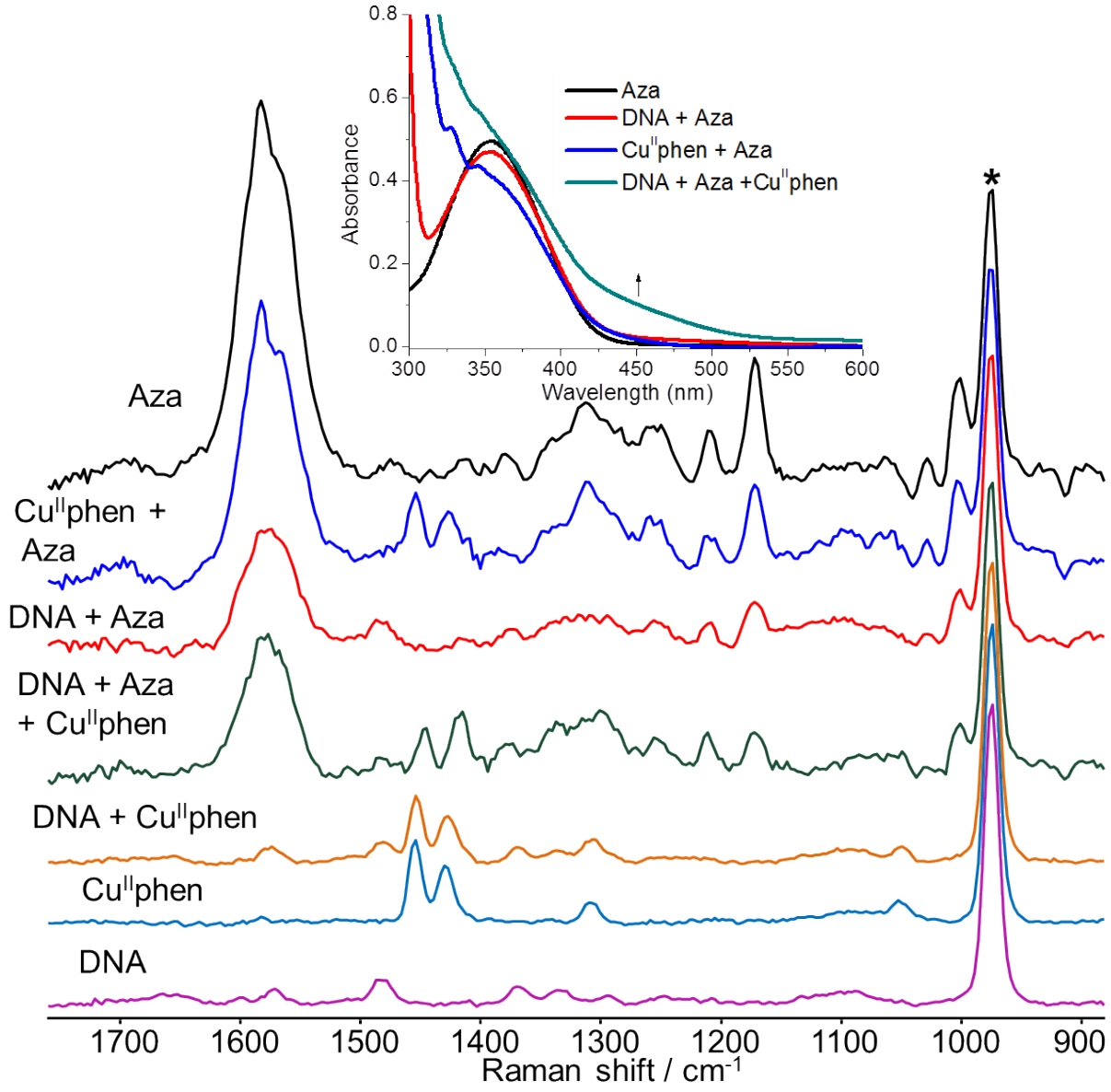

Fig. S 9 Resonance Raman spectra of **Aza** and **Cu^{II}phen** in the absence and presence of st-DNA at λ_{exc} 355 nm. 20 µM **Aza**, 0.3 mM **Cu^{II}phen**, 1.33 mg/mL st-DNA in 20 mM MOPS. * SO_4^{2-} as an internal standard (50 mM), # acetonitrile. Inset: UV/Vis absorption spectra of solutions used to record Raman spectra.

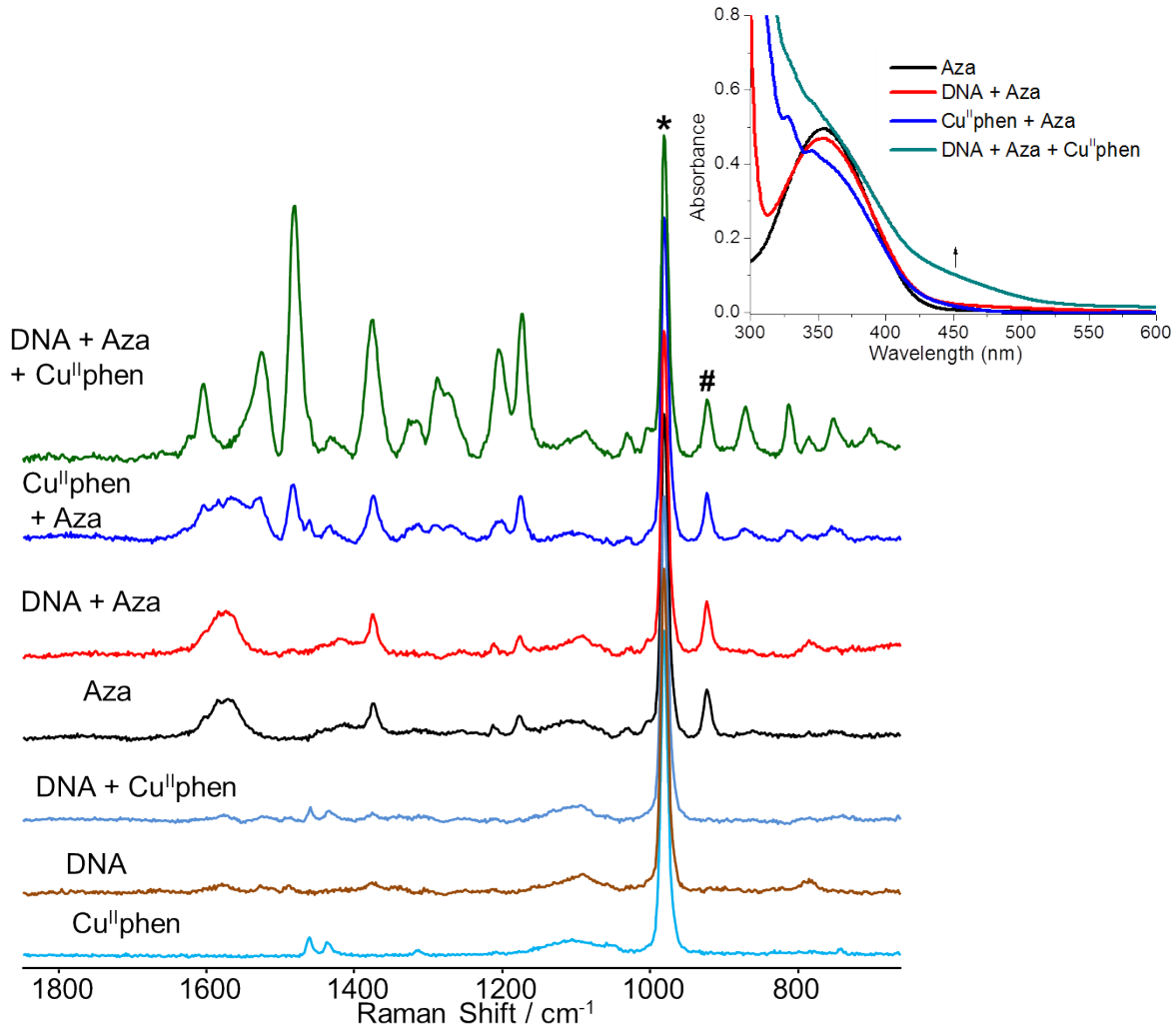

Fig. S 10 Resonance Raman spectra of **Aza** and **Cu^{II}phen** in the absence and presence of st-DNA at λ_{exc} 473 nm. 20 µM **Aza**, 0.3 mM **Cu^{II}phen**, 1.33 mg/mL st-DNA in 20 mM MOPS. * SO_4^{2-} as an internal standard (50 mM), # acetonitrile. Inset: UV/Vis absorption spectra of solutions used to record Raman spectra.

8. Cu^{II}terpy and Aza in the presence and absence of st-DNA

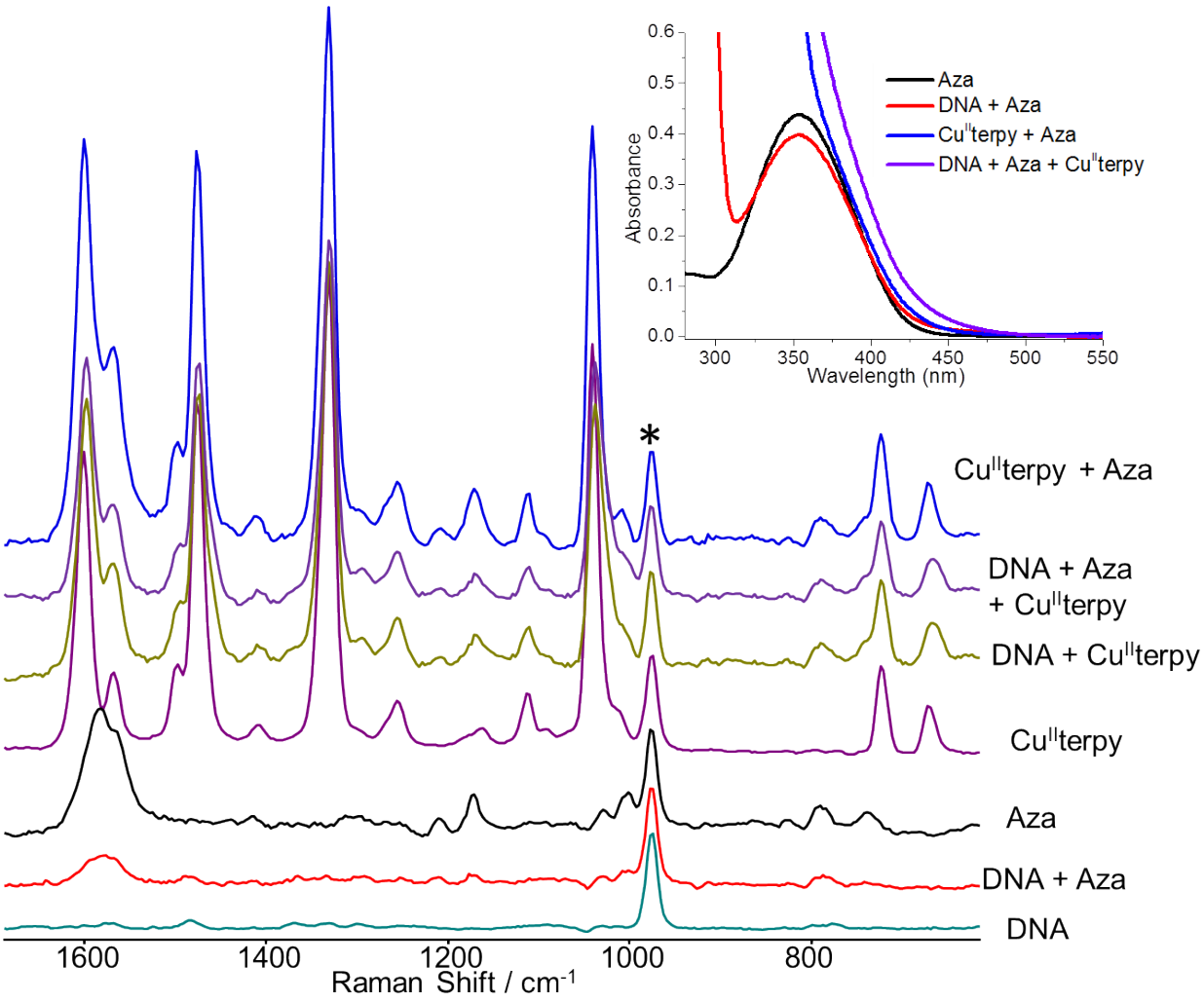

Fig. S 11 Resonance Raman spectra of **Aza** and **Cu^{II}terpy** in the absence and presence of st-DNA at λ_{exc} 355 nm. 20 µM **Aza**, 0.3 mM **Cu^{II}terpy**, 1.33 mg/mL st-DNA in 20 mM MOPS. * SO_4^{2-} as an internal standard (50 mM). Inset: UV/Vis absorption spectra of solutions used to record Raman spectra.

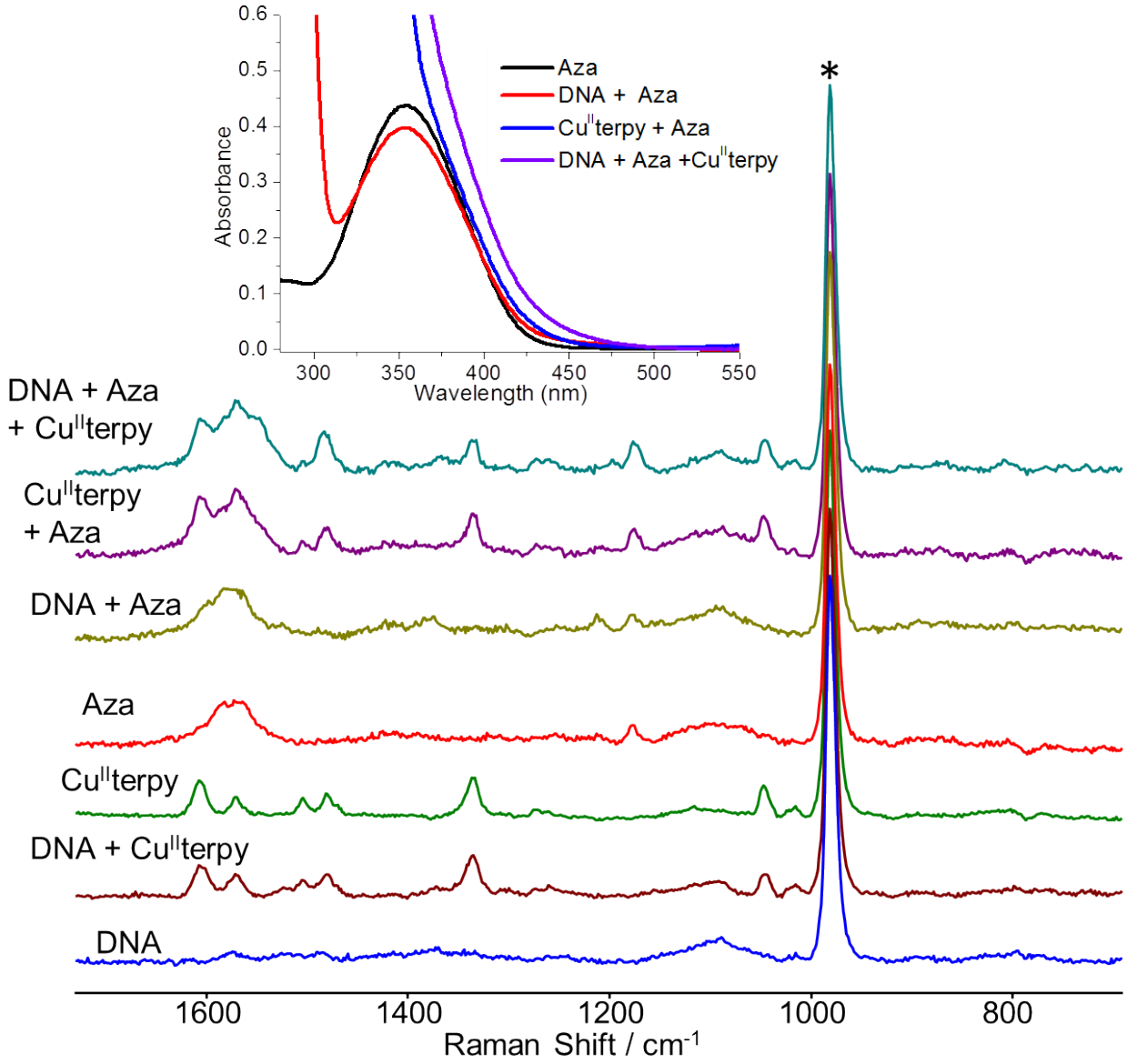

Fig. S 12 Resonance Raman spectra of **Aza** and **Cu^{II}terpy** in the absence and presence of st-DNA at λ_{exc} 473 nm. 20 µM **Aza**, 0.3 mM **Cu^{II}terpy**, 1.33 mg/mL st-DNA in 20 mM MOPS. * SO_4^{2-} as an internal standard (50 mM). Inset: UV/Vis absorption spectra of solutions used to record Raman spectra.

9. RR spectra (λ_{exc} 473 nm)Copper(II) complexes with Aza in the presence and absence of st-DNA

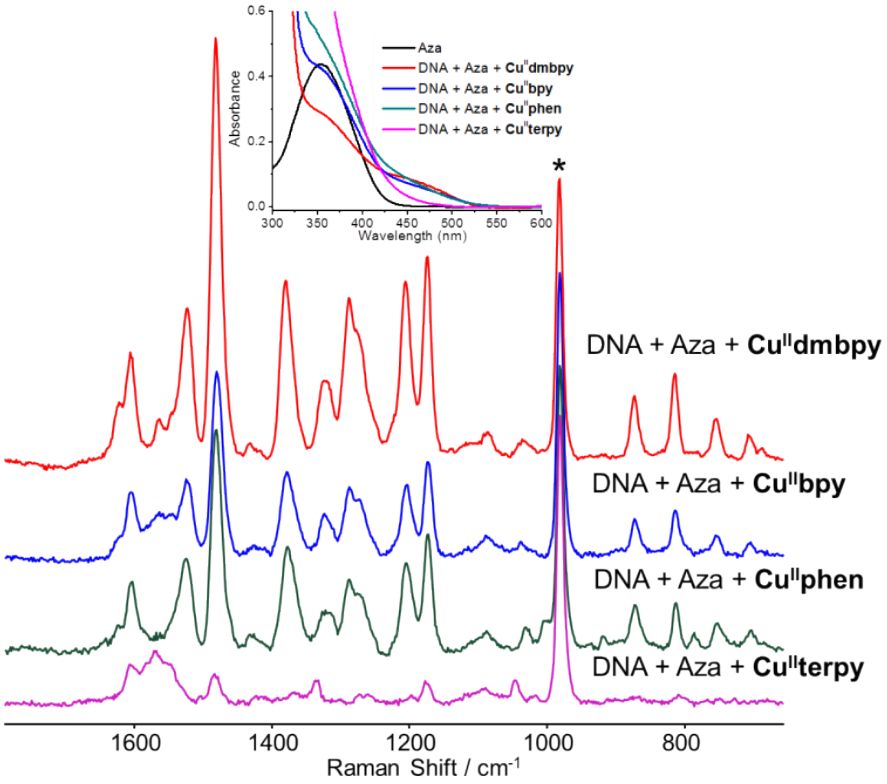

Fig. S 13 Resonance Raman spectra of st-DNA/Cu complex/**Aza** at λ_{exc} 473 nm. **Cu^{II}dmbpy**, **Cu^{II}bpy, Cu^{II}phen** and **Cu^{II}terpy** (0.3 mM), **Aza** (20 μM) and st-DNA (1.33 mg/mL) in 20 mM MOPS buffer. * internal standard SO_4^{2-} (50 mM). Inset: UV/Vis absorption spectra of solutions used to record Raman spectra.

10. EPR spectral data

Table S1 EPR parameters **Cu^{II}dmbpy** obtained from fitting to spectral data

Complex	$g_{\|}$	$g_{\perp}$	$A_{\|}$	$A_{\perp}$	$g_{\|}/A_{\|}$
		In buffer			
Cu^{II}dmbpy	2.31	2.07	158	15	146
st-DNA/**Cu^{II}dmbpy**	2.30	2.07	160	-	144
st-DNA/**Cu^{II}dmbpy /aza**	2.27	2.07	174	-	130
		In buffer : ethanol 1:2			
Cu^{II}dmbpy	2.32	2.07	154	14	151
Cu^{II}dmbpy/aza [a]	2.29	2.07	161	14	142
Cu^{II}dmbpy/aza[b]	2.27	2.07	170	14	134

[a] Fig. S14 spectra b – e, [b] Fig S14.spectrum f.

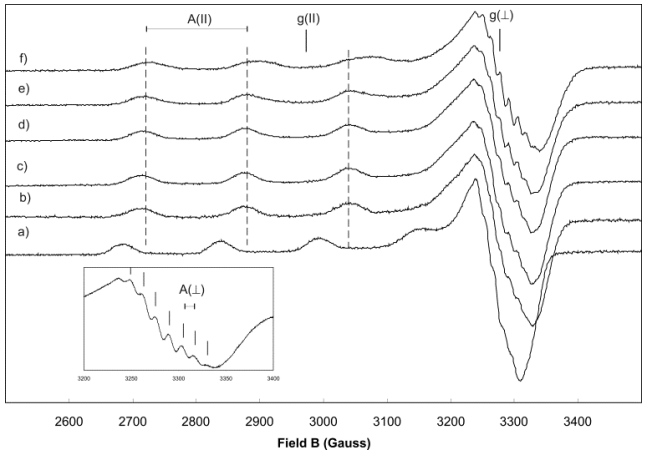

Fig. S 14 EPR (9.46 GHz) spectra at 77 K of **Cu^{II}dmbpy** (0.3 mM) in EtOH:MOPS buffer (20 mM) 2:1 v/v, pH 6.5) with **Aza** a) 0.0 mM b) 0.3 mM, c) 0.6 mM, d) 1 mM, e) 2 mM and f) 6 mM. Inset expansion of spectrum f. Conditions: microwave power 20 mW; field modulation amplitude 10 G; time constant 81.92 ms; average of 3 scans.

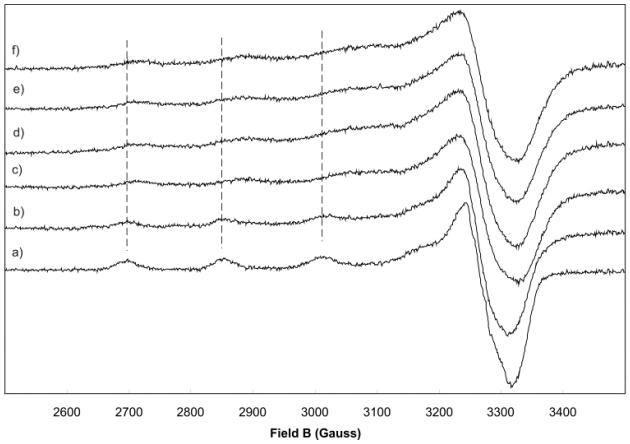

Fig. S 15 EPR (9.46 GHz) spectra at 77 K of (a) **Cu^{II}dmbpy** (0.3 mM in MOPS (20 mM) pH 6.5, 1.8 vol% DMSO) and (b) with st-DNA (1.4 mg/mL) and 0.0 mM, (c) 0.3 mM, (d) 0.6 mM, (e) 1 mM and (f) 2 mM of **Aza**. Conditions: microwave power 20 mW; field modulation amplitude 10 G; time constant 81.92 ms; average of 3 scans.

Table S 2 EPR parameters **Cu^{II}terpy** obtained from fitting to spectral data.

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$g_{\parallel}/A_{\parallel}$
	In buffer			
Cu^{II}terpy	2.27	2.07	166	137
st-DNA/ **Cu^{II}terpy**	2.27	2.07	166	137
st-DNA/ **Cu^{II}terpy/aza**	2.26	2.07	167	135
	In buffer : ethanol 1:2			
Cu^{II}terpy	2.27	2.07	160	142
Cu^{II}terpy/aza[a]	2.25	2.07	160	141
Cu^{II}terpy/aza[b]	2.25	2.07	161	140

[a] Fig. S16 spectrum b, [b] spectrum Fig. S16 c – f.

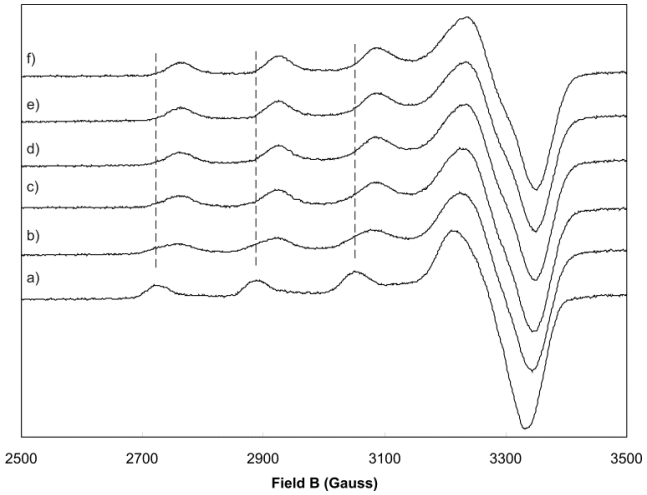

Fig. S 16 EPR (9.46 GHz) spectra at 77 K of **Cu^{II}terpy** (0.3 mM in EtOH:MOPS (20 mM) 2:1 v/v, pH 6.5) with **Aza** a) 0.0 mM b) 0.3 mM, c) 0.6 mM, d) 1 mM, e) 2 mM and f) 6 mM. Conditions: microwave power 20 mW; field modulation amplitude 10 G; time constant 81.92 ms; average of 3 scans.

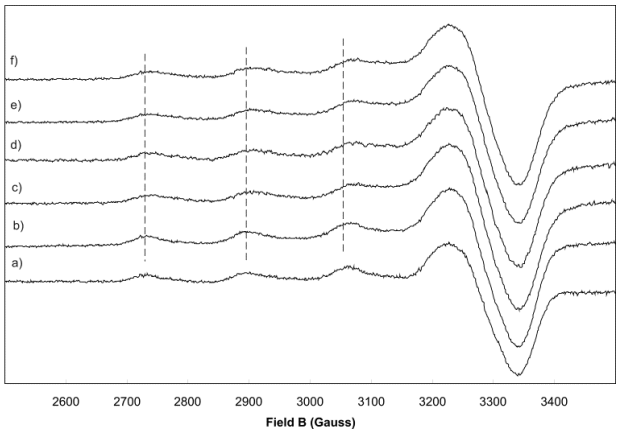

Fig. S 17 EPR (9.46 GHz) spectra at 77 K of (a) **Cu^{II}terpy** (0.3 mM in MOPS (20 mM) pH 6.5, 1.8 vol% DMSO) and (b) with st-DNA (2.0 mg/mL) and (c) 0.3 mM, (d) 0.6 mM, (e) 1 mM and (f) 2 mM of **Aza**. Conditions: microwave power 20 mW; field modulation amplitude 10 G; time constant 81.92 ms; average of 3 scans.