Supplementary Information

DNA targeting polyaza macrobicyclic dizinc(II) complexes promoting high \textit{in vitro} caspase dependent anti-proliferative activity against human carcinoma cancer cells†

Sellamuthu Anbu,\textsuperscript{a} Rajendran Ravishankaran,\textsuperscript{b} Anjali A. Karande,\textsuperscript{b} and Muthusamy Kandaswamy\textsuperscript{a}*

\textsuperscript{a}Department of Inorganic Chemistry, School of Chemical Sciences, University of Madras, Guindy Maraimalai Campus, Chennai 600 025, India.
\textsuperscript{b}Department of Biochemistry, Indian Institute of Science, Bangalore - 560 012, India.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{esimsc.png}
\caption{ESI-MS spectrum of complex \([\text{Zn}_2\text{L}^1\text{ClO}_4]_2(\text{H}_2\text{O})_2\) (1) showing the parent ion peak in MeCN. The peak corresponds to \([\text{M–2ClO}_4]^{2+}\) species.}
\end{figure}
Figure S2. ESI-MS spectrum of complex $[\text{Zn}_2L^\text{a}(\text{bpy})_2(\text{H}_2\text{O})_2]((\text{ClO}_4)_4$ (2) showing the parent ion peak in MeCN. The peak corresponds to $[\text{M}–2\text{ClO}_4]^{2+}$ species.
Figure S3. ESI-MS spectrum of complex \([\text{Zn}_2L^{1b}(\text{phen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4\) (3) showing the parent ion peak in MeCN. The peak corresponds to \([\text{M–2ClO}_4]^{2+}\) species.
Figure S4. ESI-MS spectrum of complex $[\text{Zn}_2\text{L}^2(\text{ClO}_4)_2(\text{H}_2\text{O})_2]\text{(ClO}_4\text{)}_2$ (4) showing the parent ion peak in MeCN. The peak corresponds to $[\text{M}–2\text{ClO}_4]^{2+}$ species.
Figure S5. ESI-MS spectrum of complex \([\text{Zn}_2 \text{L}^{2b}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4\) (5) showing the parent ion peak in MeCN. The peak corresponds to \([\text{M–2ClO}_4]^{2+}\) species.
**Figure S6.** ESI-MS spectrum of complex $[\text{Zn}_2\text{L}^{2\text{b}}\text{phen}](\text{H}_2\text{O})_2]\text{(ClO}_4)\text{_4} \ (6)$ showing the parent ion peak in MeCN. The peak corresponds to $[\text{M–2ClO}_4]^{3+}$ species.
**Figure S7.** Energy minimized structure of 2,2′-bipyridine coordinated macrobicyclic dizinc(II) complex 2. Color code; Zn = green, O = red, N = blue, C = grey.

**Figure S8.** Energy minimized structure of 2,2′-bipyridine coordinated macrobicyclic dizinc(II) complex 5. Color code; Zn = green, O = red, N = blue, C = grey.
**Fig. S9.** CD spectra recorded over the wavelength range 230–320 nm for solutions containing 2:1 ratio of CT–DNA (200 μM) and dinuclear Zn\(^{II}\) complexes 3, 4 and 6 (100 μM) in 50 mM Tris–HCl / NaCl buffer (pH = 7.5). (a = CT DNA, b = 4 + DNA, c = 3 + DNA, d = 6 + DNA).

**Fig. S10.** SDS-PAGE analysis showing cleavage of bovine serum albumin (BSA, 5 μM) by dizinc(II) complexes 1–6 in 50 mMTris-HCl buffer having 5% DMF (pH=7.2) for an exposure time of 2 h. lane 1, molecular marker; lane 2, BSA control; lanes 3-8, dizinc(II) complexes 1-6 (50 μM), respectively.
Fig. S11. Cytotoxic effect of dizinc(II) complexes 2, 3, 4 and 6 in HeLa cells assessed by lactate dehydrogenase activity in medium and cell lysate for 24h.