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# Copper(II) complexes containing Enoxacin and heterocyclic ligands: Synthesis, crystal structures and their biological Perspectives

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## *Supplementary material file*

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## Crystallographic data

**Table S1**. Crystallographic data collection and structural refinement parameters for complexes **1** and **2**.

| | **(1)** | **(2)** |
|---|---|---|
| Formula | $C_{29}H_{35}ClCuFN_6O_{7.5}$ | $C_{24}H_{16}ClCuN_4O_4$ |
| $M_w$ | 705.62 | 398.11 |
| $T$ (K) | 298 | 293 (2) |
| Crystal system | triclinic | monoclinic |
| Space group | P -1 | C 2/c |
| a, Å | 10.6331 (5) | 23.3802 (10) |
| b, Å | 13.0935 (11) | 30.3333 (12) |
| c, Å | 14.6411 (14) | 7.5123 (3) |
| α (º) | 66.598 (9) | 90 |
| β (º) | 74.169 (7) | 97.851 (4) |
| γ (º) | 72.852 (7) | 90 |
| Volume Å$^3$ | 1759.2 (3) | 5277.8 (4) |
| Z | 2 | 11 |
| $D_{calc.}$/g cm$^{-3}$ | 1.400 | 1.378 |
| μ/mm$^{-1}$ | 0.758 | 0.970 |
| Colour | Blue | green |
| Wavelength/Å | 0.71073 | 0.71073 |
| Radiation type | MoKα | MoKα |
| $\Theta_{min}$/º | 3.4260 | 3.328 |
| $\Theta_{max}$/º | 24.1640 | 29.544 |
| Data | 7142 | 6754 |
| Parameters | 443 | 322 |
| Restraints | 412 | 0 |
| Largest Peak | 1.058 | 1.419 |
| Deepest Hole | -0.875 | -0.527 |
| GooF | 1.067 | 1.065 |
| F000 | 732 | 2224 |
| $R_1$ | 0.0985 | 0.0790 |
| $wR_2$ | 0.2741 | 0.2850 |

**Table S2. Structural parameters (chromophores and τ) for copper quinolone complexes reported.**

| Complexes | Chromophore | τ | References |
|---|---|---|---|
| [Cu(nal)(bipyam)Cl] | $CuN_2O_2Cl$ | 0.04 | 1 |
| [Cu(nal)(bpy)Cl] | $CuN_2O_2Cl$ | 0.07 | 2 |
| [Cu(*lvx*)(bipyam)Cl] | $CuN_2O_2Cl$ | 0.137 | 3 |
| Cu(*lvx*)Bphen)Cl] | | 0.0316 | |
| [Cu(erx)(phen)Cl] | $CuN_2O_2Cl$ | 0.047 | 4 |
| [Cu(pr-norf)(bpy)Cl] | $CuN_2O_2Cl$ | 0.016 | 5 |
| $[Cu(cfH)(phen)Cl]^+$ | $CuN_2O_2Cl$ | 0.027 | 6 |
| [Cu(cfH)(phen)Cl]Cl | CuN2O2Cl | 0.087 | 7 |
| [Cu(oxo)(phen)Cl] | $CuN_2O_2Cl$ | 0.075 | 8 |
| [Cu(flmq)(phen)Cl] | | 0.076 | |
| [Cu(flmq)bpy)Cl] | $CuN_2O_2Cl$ | 0.116 | 9 |
| [Cu(flmq)(bipyam)Cl] | | 0.118 | |
| [Cu(Enox)(bpy)Cl] | $CuN_2O_2Cl$ | 0.008 | **This work** |

nal = Nalidixic acid, *lvx* = Levofloxacin, erx = Enrofloxacin, pr-norf = N-propyl-norfloxacinato, cfH = Ciprofloxacin, oxo = Oxolinic acid, flmq = Flumequine, Enox = Enoxacin

**Table S3. DNA-binding constant ($K_b$) values for copper complexes reported.**

| Complexes | $K_b$, ($M^{-1}$) | References |
|---|---|---|
| [Cu(HEnox)(bpy)Cl] | $1.5\times10^5$ | **This work** |
| $[Cu(phen)_2Cl]$ | $2.87\times10^5$ | |
| HEnox = Enoxacin | | |
| $[Cu(flmq)(H_2O)_2]$ | $8.39(\pm0.45)\times10^3$ | |
| [Cu(flmq)(bipyam)Cl] | $1.07(\pm0.12)\times10^5$ | 9 |
| [Cu(flmq)(bpy)Cl] | $1.79(\pm0.30)\times10^5$ | |
| flmq = Flumequine, bipyam = 2,2'-dipyridylamine, bpy = 2,2'-bipyridine | | |
| $[Cu(\mathbf{L}')(H_2O)_2](ClO_4)_2$ | $0.0013\times10^5$ | |
| $[Cu(\mathbf{L}')(bpy)]ClO_4$ | $0.036\times10^5$ | |
| $[Cu(\mathbf{L}')(phen)]ClO_4$ | $0.10\times10^5$ | 10 |
| $[Cu(\mathbf{L}')(dpq)]ClO_4$ | $0.21\times10^5$ | |
| $[Cu(\mathbf{L}')(dppz)]ClO_4$ | $1.02\times10^5$ | |
| $[Cu(\mathbf{L}')(dmdppz)]ClO_4$ | $0.074\times10^5$ | |
| $\mathbf{L}'$ = 2-[2-dimethylaminoethylimino)methyl]phenol) | | |
| $[Cu(nal)(diimine)H_2O]$ | $079-1.84\times10^5$ | 11 |
| nal = Nalidixic acid, diimine = 2,2'-bipyridine, 1,10-phenanthroline, 5,6-dimethyl-1,10-phenenthroline | | |
| $[Cu(nfH)_2]Cl_2.6H_2O$ | $4.08(\pm0.37)\times10^4$ | 12 |
| $[Cu(nfH)_2Cl_2].2H_2O$ | $1.97(\pm0.10)\times10^4$ | |
| nfH = Norfloxacin | | |
| $[Cu(phen)_3]^{2+}$ | $0.98(\pm0.12)\times10^4$ | |
| $[Cu(5,6\text{-}dmp)_3]^{2+}$ | $3.80(\pm0.05)\times10^4$ | 13 |
| $[Cu(dpq)_3]^{2+}$ | $7.50(\pm0.19)\times10^4$ | |

| | | |
|---|---|---|
| phen = 1,10-phenanthroline, 5,6-dmp = 5,6-dimethyl-1,10-phenanthroline, dpq = dipyrido[3,2-*d*:2',3'-flquinoxaline] | | |
| [Cu(***L1***)$_2$] | 1.41(±0.04)×10$^5$ | |
| [Cu(***L2***)$_2$] | 0.78(±0.05)×10$^5$ | 14 |
| [Cu(***L3***)$_2$] | 1.42(±0.03)×10$^5$ | |
| ***L1*** = 2-((3,4-dimethylisoxazol-5-ylimino)methyl-6-tert-butylphenol, ***L2*** = 2-((3,4-dimethylisoxazol-5-ylimino)methyl-4,6-ditertbutylphenol, ***L3*** = 2-((3,4-dimethylisoxazol-5-ylimino)methyl-4,6-dibromophenol | | |
| [Cu(cfH)(**A1**)Cl] | 2.66×10$^4$ | |
| [Cu(cfH)(**A2**)Cl] | 2.62×10$^4$ | |
| [Cu(cfH)(**A3**)Cl] | 1.67×10$^4$ | 15 |
| [Cu(cfH)(**A4**)Cl] | 1.27×10$^4$ | |
| [Cu(cfH)(**A5**)Cl] | 4.72×10$^4$ | |
| **A1** = 4'-(4-chloro phenyl)-2,2':6'2''-terpyridine, **A2** = 4'-(3-chloro phenyl)-2,2':6',2"-terpyridine, **A3** = 4'-(4-bromo phenyl)-2,2':6'2"-terptridine, **A4** = 4'-(3-bromo phenyl)-2,2':6',2"-terpyridine, **A5** = 4'-(3-bromo phenyl)-2,2':6',2"-terpyridine, cfH = Ciprofloxacin | | |
| [Cu(phen)(*L-Ser*)H$_2$O] | 1.42×10$^5$ | 16 |
| [Cu(bpy)$_2$NO$_3$] | 1.18×10$^4$ | |
| *L-Ser* = L-Serine | | |
| [Cu(***L1***)ClMeOH] | 4.1×10$^4$ | 17 |
| [Cu(***L2***)ClMeOH] | 3.78×10$^4$ | |
| ***L1*** = 2-acetylpyridinebenzoylhydrazone, ***L2*** = 2-acetylpyridine thiophene-2-carboxylic acid hydrozone | | |
| [Cu(ph-tpy)HQ] | 6.3−7.4×10$^4$ | |
| [Cu(ph-tpy)CQ] | | |
| [Cu(ph-tpy)NQ] | | 18 |
| [Cu(Fc-Tpy)HQ] | | |
| [Cu(Fc-tpy)CQ] | | |
| [Cu(Fc-tpy)NQ] | | |
| [Cu(Fc-tpy)$_2$] | | |
| Ph-tpy = 4'-phenyl-2,2':6',2"-terpyridine, Fc-tpy = 4'-ferrocenyl-2,2':6',2"-terpyridine, HQ = 8-hydroxyquinoline, CQ = 5-chloro-7-iodo-8-hydroxyquinolone, NQ = 5-nitro-8-hydroxyquinolone | | |

**Table S4. Stern-Volmer quenching constant ($K_{SV}$) values for copper complexes reported.**

| **Complexes** | $K_{SV}$, **(M$^{-1}$)** | **References** |
|---|---|---|
| [Cu(HEnox)(bpy)Cl] | 2.56×10$^5$ | **This work** |
| [Cu(phen)$_2$Cl] | 1.75×10$^5$ | |
| HEnox = Enoxacin | | |
| [Cu(phen)(*L-Ser*)H$_2$O] | 2.42×10$^4$ | 16 |
| [Cu(bpy)2NO$_3$] | 2.03×10$^4$ | |
| *L-Ser* = L-Serine | | |
| [Cu(***L1***)ClMeOH] | 2.91×10$^3$ | 17 |
| [Cu(***L2***)ClMeOH] | 3.11×10$^4$ | |

| | | |
|---|---|---|
| ***L1*** = 2-acetylpyridine benzoyl hydrazine, ***L2*** = 2-acetylpyridine thiophene-2-carboxylic acid | | |
| [Cu(*lvx*)(bpy)($H_2O$)] | $6.12\times10^4$ | 19 |
| *lvx* = Levofloxacin, bpy = 2,2'-bipyridine | | |
| [Cu(*pzta*)(*L-ArgH*)($H_2O$)] | $2.906\times10^4$ | 20 |
| [Cu(*pzta*)(*L-Met*)($H_2O$)] | $4.28\times10^4$ | |
| *Pzta* = 6-(pyrazine-2-yl)-1,3,5-triazine-2,4-diamine, *L-ArgH* = protonated L-Argininate, *L-Met* = L-Methioninate | | |
| [Cu(***L***)$Cl_2$] | $1.73\times10^5$ | 21 |
| ***L*** = piperidin-2-yl-N-(pyridine-2-yl)ethylidene | | |
| [Cu(***L***)(diimine)($ClO_4$)] | $0.71-141\times10^5$ | 22 |
| ***L*** = 2-((1H-imidazol-2-yl)methylene)-N-phenylhydrazinecarbothiamide and diimine = 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridyl, 2,2'-dipyridylamine | | |
| [Cu(*5-nsal*)(bipy)$ClO_4$] | $3.05\times10^3$ | |
| [Cu(*2-hnap*)(bipy)($ClO_4$)] | $3.59\times10^3$ | 23 |
| [Cu(5-nsal)(biim)($ClO_4$)] | $2.14\times10^3$ | |
| [Cu(*2-hnap*)(biim)($ClO_4$)] | $2.33\times10^3$ | |
| biim = 2,2'-bi-1H-imidazole, *5-nsal* = 5-nitrosalicylaldehyde and *2-hnap* = 2-hydroxynapthaldehyde | | |
| [Cu(*Bzimpy*)(***L***)$H_2O$] | 0.203−0.215 | 24 |
| *Bzimpy* = 2,6-bis(benzimidazole-2yl)pyridine, ***L***= 2,2'-bipyridine and ethylene | | |
| [Cu(indo)$_2$(bipyam)] | $1.37\times10^5$ | 25 |
| indo = indomethacin | | |
| [Cu(***L1***)$_2$] | $0.67\times10^4$ | 26 |
| [Cu(***L2***)$_2$] | $0.26\times10^4$ | |
| [Cu(***L3***)$_2$] | $0.26\times10^4$ | |
| ***L1*** = 2-((3,4-dimethylisoxazol-5-ylimino)methyl)-6-tert-butylphenol, ***L2*** = 2-((3,4-dimethylisoxazol-5-ylimino)methyl)-4,6-tert-butylphenol, ***L3*** = 2-((3,4-dimethylisoxazol-5-ylimino)methyl)-4,6-dibromophenol | | |

**Table S5. Quenching rate constant ($k_q$) values for copper complexes reported.**

| **Complexes** | $k_q$ | | **References** |
|---|---|---|---|
| | **BSA** | **HSA** | |
| [Cu(HEnox)(bpy)Cl] | $1.29\times10^{13}$ | $2.06\times10^{13}$ | **This work** |
| [Cu(phen)$_2$Cl] | $2.34\times10^{13}$ | $2.67\times10^{13}$ | |
| HEnox = Enoxacin | | | |
| [Cu(flmq)$_2$($H_2O$)$_2$] | $5.28(\pm0.18)\times10^{12}$ | $1.35(\pm0.08)\times10^{13}$ | |
| [Cu(flmq)(bipyam)Cl] | $5.28(\pm0.28)\times10^{12}$ | $8.04(\pm0.30)\times10^{12}$ | |
| [Cu(flmq)(bpy)Cl] | $2.68(\pm0.18)\times10^{12}$ | $7.84(\pm0.24)\times10^{12}$ | 9 |
| [Cu(flmq)(phen)Cl] | $2.51(\pm0.22)\times10^{12}$ | $2.25(\pm0.05)\times10^{13}$ | |
| [Cu(flmq)$_2$(py)$_2$] | $2.04(\pm0.19)\times10^{12}$ | $7.85(\pm0.24)\times10^{12}$ | |
| flmq = Flumequine | | | |
| [Cu(nfH)(phen)Cl] | $1.92(\pm0.13)\times10^{13}$ | $5.45(\pm0.12)\times10^{12}$ | |
| [Cu(nfH)$_2$]$Cl_2$ | $5.35(\pm0.32)\times10^{12}$ | $5.19(\pm0.18)\times10^{12}$ | 12 |
| [Cu(nfH)$_2$$Cl_2$] | $1.39(\pm0.08)\times10^{12}$ | $6.48(\pm0.28)\times10^{12}$ | |
| [Cu(ofloH)$_2$][($CuCl_2$)$_2$] | $1.92(\pm0.10)\times10^{12}$ | $5.91(\pm0.32)\times10^{12}$ | |

| | | | |
|---|---|---|---|
| nfH = Norfloxacin, ofloH = Ofloxacin | | | |
| [Cu(*pzta*)(L-ArgH)($H_2O$)] | | $2.526\times10^{12}$ | 20 |
| [Cu(*pzta*)(L-Met)($H_2O$)] | | $2.559\times10^{12}$ | |
| *pzta* = 6-(pyrazine-2-yl)-1,3,5-triazine-2,4-diamine, L-ArgH = protonated L-Argininate and L-Met = L-Methioninate | | | |
| [Cu(***L1***)] | $9.47(\pm0.31)\times10^{12}$ | | |
| [Cu(***L2***)] | $6.21(\pm0.17)\times10^{12}$ | | 27 |
| [Cu(***L3***)] | $7.18(\pm0.33)\times10^{12}$ | | |
| ***L1*** = Bis*[Z]*-N-(5-methoxy-2-oxoindolin-3-ylidene)pyrrolidine-1-carbothiohydrazide, ***L2*** = Bis*[Z]*-N-(5-methoxy-2-oxoindolin-3-ylidene)morpholine-4-carbothiohydrazide, ***L3*** = Bis*[Z]*-N-cyclohexyl-2-(5-methoxy-2-oxoindolin 3ylidene)hydrazinecarbothioamide | | | |
| [Cu(*dicl*)$_2$($H_2O$)$_2$] | $1.06(\pm0.08)\times10^{13}$ | | |
| [Cu(*en*)$_2$($H_2O$)$_2$] | $1.25(\pm0.07)\times10^{13}$ | | 28 |
| [Cu(*pn*)$_2$($H_2O$)$_2$] | $1.29(\pm0.06)\times10^{13}$ | | |
| [Cu(*temed*)(*dicl*)$_2$] | $1.22(\pm0.08)\times10^{13}$ | | |
| *dicl* = deprotonated diclofenac, *en* = ethylenediamine, *pn* = propan-1,3-diamine and *temed* = N,N,N',N'-tetramethylethylene-diamine | | | |
| [Cu(**L**)(OAC)] | | $7.3\times10^{12}$ | |
| [Cu(**HL**)($C_2O_4$)(EtOH)] | | $5.3\times10^{12}$ | 29 |
| [Cu(**L**)(Bza)] | | $6.6\times10^{12}$ | |
| [Cu(**L**)(Sal)] | | $6.8\times10^{12}$ | |
| **HL** = 1-(((2-hydroxypropyl)ethyl)imino)methyl)naphthalene-2-ol, Bza = Benzoic acid, Sal = Salicylic acid | | | |

**Table S6. The binding constant ($k_{SAs}$) values for copper complexes reported.**

| **Complexes** | $K_{SAs}$ | | **References** |
|---|---|---|---|
| | **BSA** | **HSA** | |
| [Cu(HEnox)(bpy)Cl] | $5.98\times10^{5}$ | $5.66\times10^{5}$ | This work |
| [Cu(phen)$_2$Cl] | $8.57\times10^{5}$ | $6.60\times10^{13}$ | |
| HEnox = Enoxacin | | | |
| [Cu(nal)$_2$$H_2O$] | $1.68(\pm0.15)\times10^{5}$ | $1.46(\pm0.01)\times10^{5}$ | 1 |
| [Cu(nal)(bipyam)Cl] | $6.05(\pm0.41)\times10^{5}$ | $1.91(\pm0.1)\times10^{5}$ | |
| nal = Nalidixic acid | | | |
| [Cu(*lvx*)(bipyam)Cl] | $3.75(\pm0.01)\times10^{5}$ | $1.47(\pm0.01)\times10^{12}$ | |
| [Cu(*lvx*)(Bphen)Cl] | $7.77(\pm0.02)\times10^{5}$ | $1.55(\pm0.01)\times10^{12}$ | 3 |
| Bipyam = 2,2'-dipyridylamine, Bphen = Bathophenanthroline | | | |
| [Cu(flmq)$_2$($H_2O$)$_2$] | $4.29(\pm0.35)\times10^{4}$ | $7.55(\pm0.35)\times10^{4}$ | 9 |
| [Cu(flmq)(bipyam)Cl] | $2.62(\pm0.16)\times10^{5}$ | $1.58(\pm0.10)\times10^{5}$ | |
| [Cu(flmq)(bpy)Cl] | $1.14(\pm0.03)\times10^{5}$ | $1.26(\pm0.08)\times10^{5}$ | |
| [Cu(flmq)(phen)Cl] | $3.24(\pm0.26)\times10^{5}$ | $1.28(\pm0.14)\times10^{5}$ | |
| [Cu(flmq)$_2$(py)$_2$] | $1.20(\pm0.08)\times10^{5}$ | $1.27(\pm0.09)\times10^{5}$ | |
| flmq = Flumequine | | | |
| [Cu(nfH)(phen)Cl] | $7.09\times10^{4}$ | $4.22\times10^{4}$ | |
| [Cu(nfH)$_2$]$Cl_2$ | $6.16\times10^{4}$ | $8.84\times10^{4}$ | 12 |
| [Cu(nfH)$_2$$Cl_2$] | $4.51\times10^{4}$ | $4.51\times10^{4}$ | |
| [Cu(ofloH)$_2$][($CuCl_2$)$_2$] | $5.56\times10^{4}$ | $4.27\times10^{4}$ | |

nfH = Norfloxacin, ofloH = Ofloxacin

| | | | |
|---|---|---|---|
| [Cu(fluf)(bipyam)Cl] | $9.55(\pm0.11)\times10^4$ | $5.45(\pm0.39)\times10^4$ | 30 |
| [Cu(fluf)(phen)Cl] | $3.14(\pm0.12)\times10^4$ | $1.09(\pm0.42)\times10^5$ | |
| [Cu(fluf)(bpy)Cl] | $8.74(\pm0.08)\times10^4$ | $7.65(\pm0.10)\times10^4$ | |
| $[Cu(fluf)_2(py)_2]$ | $1.75(\pm0.07)\times10^4$ | $1.11(\pm0.05)\times10^5$ | |

fluf = flufenamic acid

## 1. DNA binding study

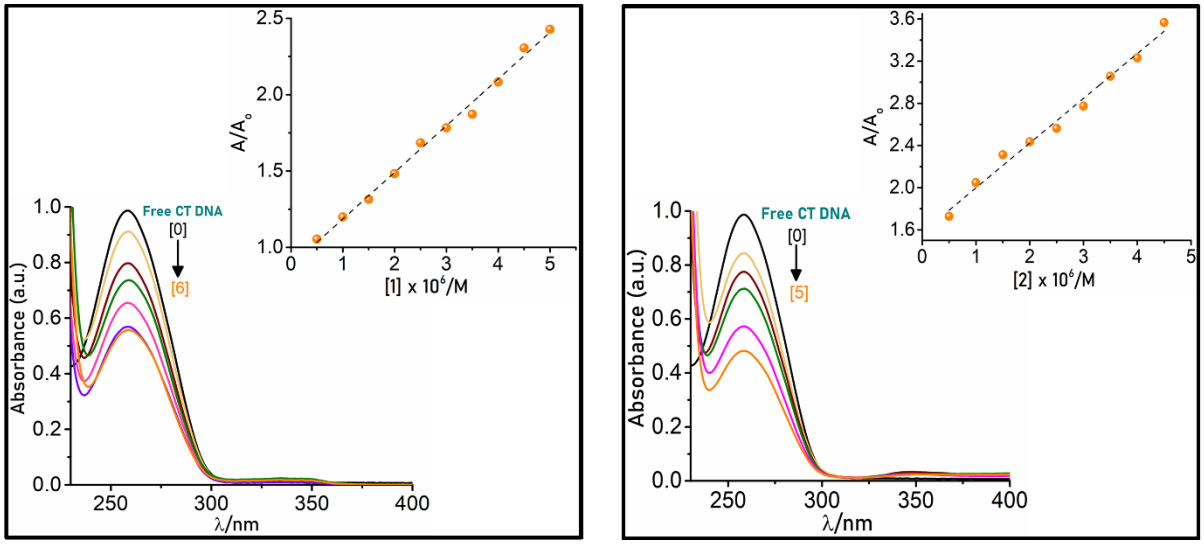


**Figure S1**. UV absorbance spectra of CT DNA in a buffer solution containing 150 mM NaCl and 15 mM trisodium citrate at pH 7.4 in the absence as well as the presence of the diverse concentration of complexes **(a) 1** and **(b) 2**. The arrows (↓) illustrations the changes occur upon the addition of increasing amounts of complexes. Inset plots of $A/A_0$ versus [complex] at $\lambda_{max}$ = 340 nm.

## 2. Viscosity experiment

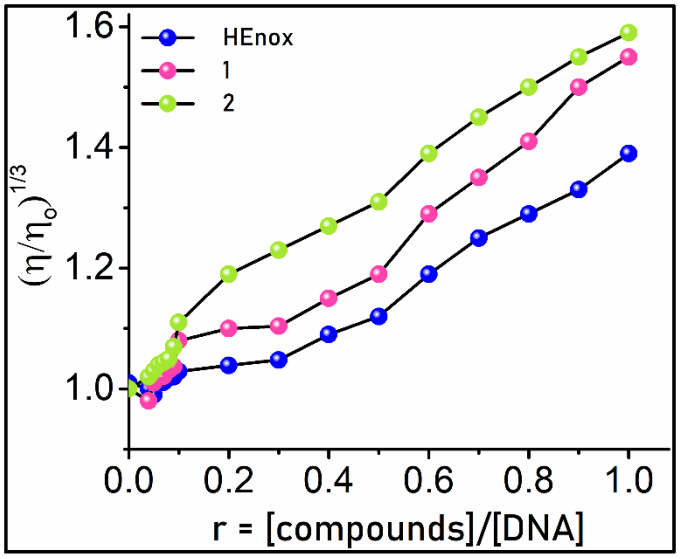


**Figure S2**. The relative viscosity $(\eta/\eta_o)^{1/3}$ of CT DNA solution in buffer solution upon the addition of the compounds at increasing amounts (r = 0−1) (r = [compouds]/[DNA].

## 3. Stern-Volmer quenching plots of EtBr

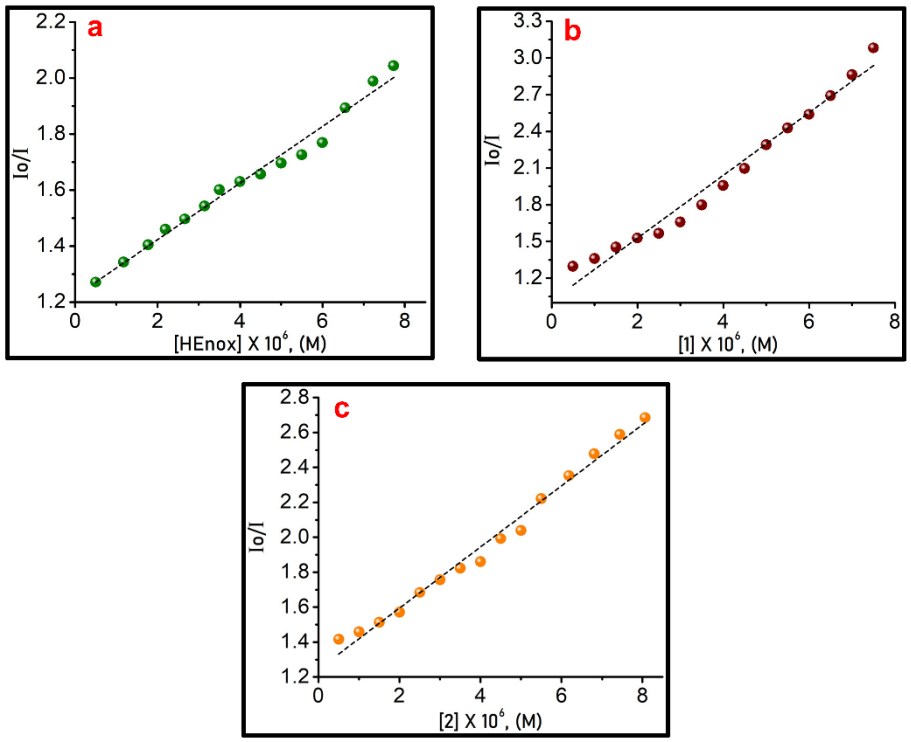


**Figure S3.** Stern-Volmer quenching plots of EtBr bound to CT DNA HEnox and complexes **1** and **2**.

## 4. Stern–Volmer quenching plots of BSA

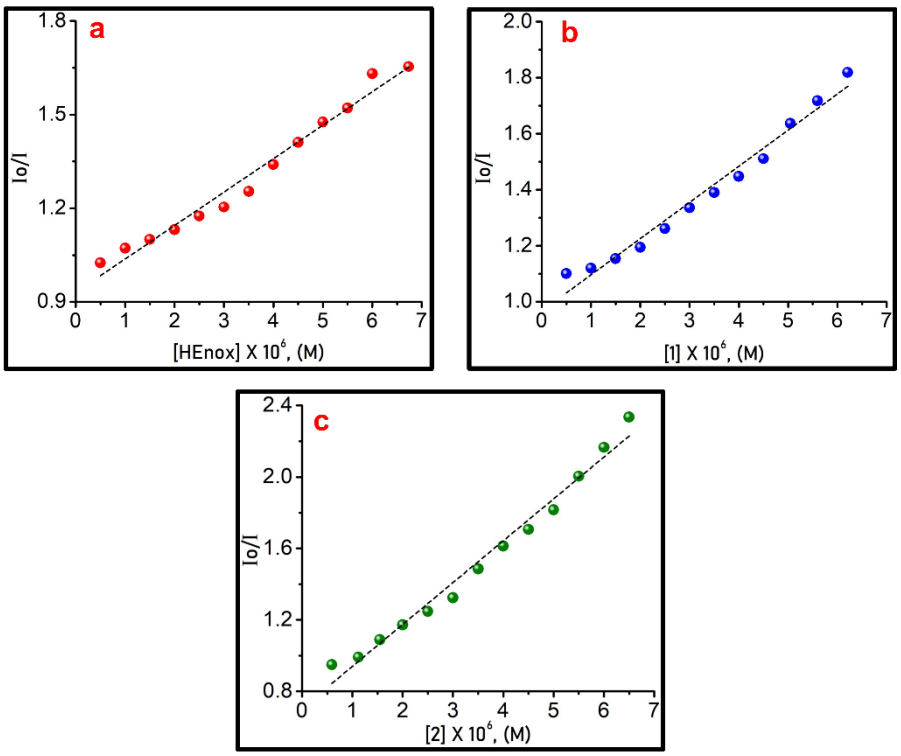


**Figure S4**. **(A)–(C)** Stern–Volmer quenching plots of BSA for HEnox and complexes **1** and **2**.

## 5. Stern–Volmer quenching plots of HSA

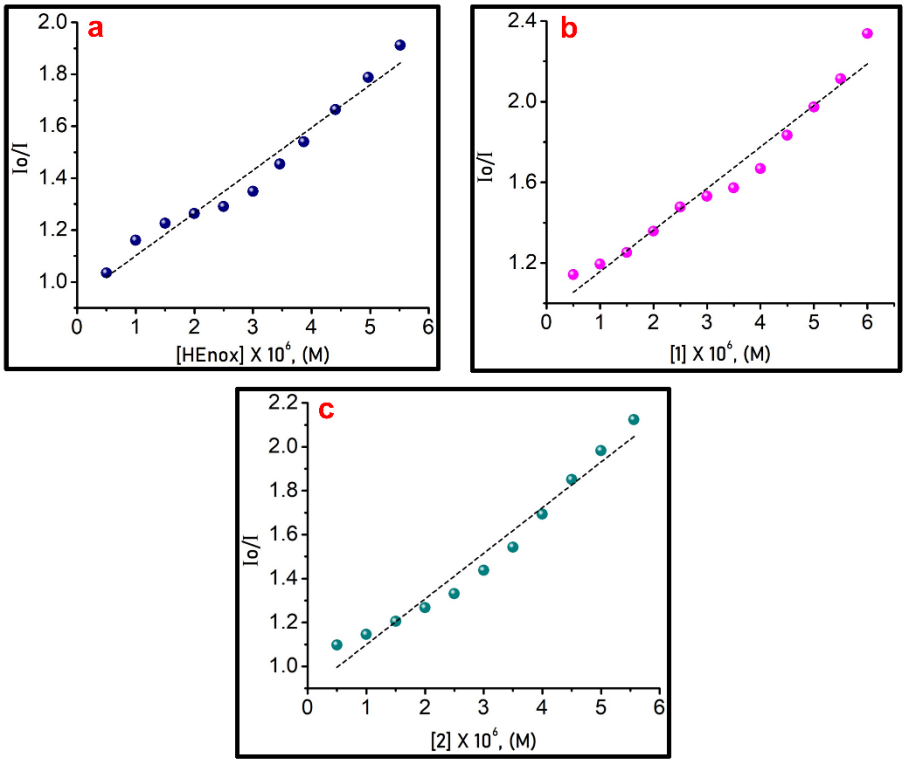


**Figure S5**. **(A)–(C)** Stern–Volmer quenching plots of HSA for HEnox and complexes **1** and **2**.

## 6. Scatchard plots of BSA

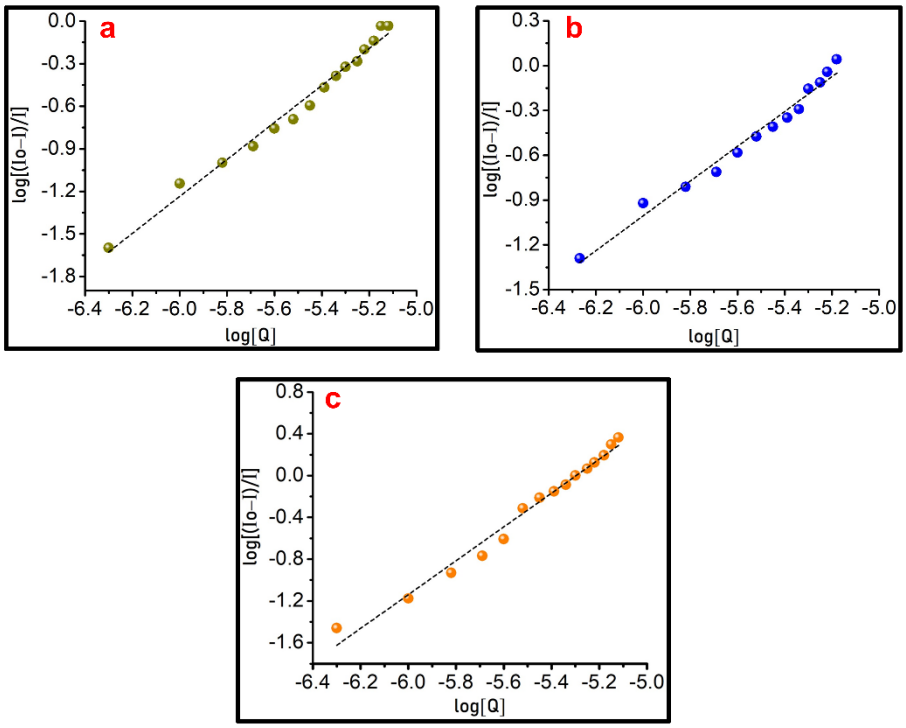


**Figure S6**. **(A)–(C)** Scatchard plots of BSA for HEnox and complexes **1** and **2**.

## 7. Scatchard plots of HSA

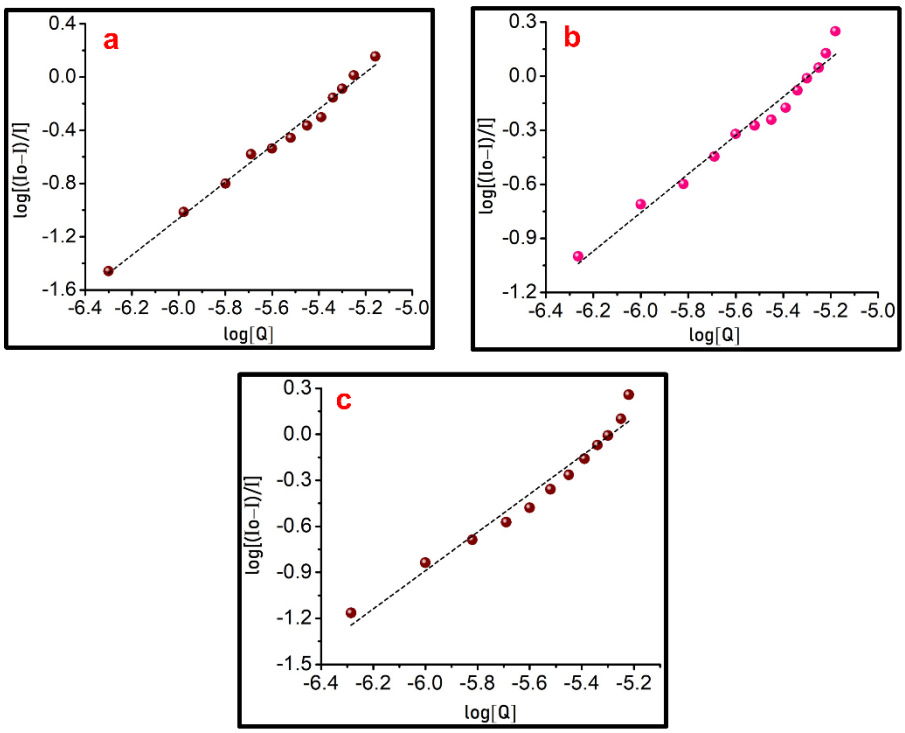


**Figure S7**. **(A)–(C)** Scatchard plots of HSA for HEnox and complexes **1** and **2**.

## References


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