Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Investigation of novel Mn(II) fenamato complexes with neocuproine and their effects on endometrial cell lines

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Supplementary Information

Contents

Table S1 Crystal data and structure refinement for complexes **1** and **2**.

Compound	**1**	**2**
CCDC reference number	**2219676**	**2219675**
Empirical formula	$C_{40}H_{32}N_4O_4Mn_1$	$C_{42}H_{30}N_4O_4F_6Mn_1$
Formula weight	687.7	823.7
Temperature [K]	95	95
Wavelength [Å]	1.54184	1.54184
Crystal System	orthorhombic	orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$
a [Å]	9.6882(2)	9.7662(2)
b [Å]	13.2014(2)	12.8010(1)
c [Å]	25.3636(4)	28.8216(3)
Volume [Å^3]	3243.95(10)	3603.19(9)
Z	4	4
ρ(calculated) [g.cm^{-3}]	1.408	1.518
μ [mm^{-1}]	3.715	3.696
F000	1428	1684
Crystal colour and shape	yellow needle	yellow needle
Crystal dimensions	0.20 × 0.08 × 0.03	0.19 × 0.05 × 0.04
ϑ range for data collection [°]	4.80 – 74.25	3.07 – 75.45
Reflections collected	36912	65990
Independent reflections	6565	7399
R_{int}	0.0294	0.0424
Data/restraints/parameters	6565/0/450	7399/0/522
Goodness-of-fit(1)	1.97	2.37
Final *R* indices ($I > 3\sigma/I$)	*R1* = 0.0261 *wR2* = 0.0668	*R1* = 0.0417 *wR2* = 0.0907
R indices (all data)	*R1* = 0.0279 *wR2* = 0.0697	*R1* = 0.0466 *wR2* = 0.0917
Maximum and minimum residual electron density [e. Å^{-3}]	0.47; - 0.24	0.78; - 0.53

(1) The program JANA does not refine the weighting scheme to get Goodness of fit close to 1. The displayed GOF corresponds to the experimental weighting scheme with the instability factor as an instrumental parameter.

Table S2 Selected bond lengths and angles (A, °) for **1** and **2**.

Complex	**1**	**2**
Mn1-O1	2.059(2)	2.169(2)
Mn1-O2	2.760(2)	2.331(2)
Mn1-O3	2.213(1)	2.164(2)
Mn1-O4	2.238(1)	2.328(2)
Mn1-N3	2.219(2)	2.232(2)
Mn1-N4	2.227(2)	2.256(2)
O1-Mn1-O2	51.94(6)	58.20(7)
O3-Mn1-O4	58.96(5)	57.95(7)
N3-Mn1-N4	75.79(5)	74.76(9)
O1-Mn1-O3	98.76(6)	97.84(8)
O1-Mn1-O4	109.27(6)	122.58(7)
O2-Mn1-O3	127.75(5)	119.62(7)
O2-Mn1-O4	88.28(5)	87.85(7)

Table S3 Possible hydrogen bonding interactions (A, °) for **1** and **2**.

D–H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**<(DHA)**
1				
N1-H1N1···O2	0.85(3)	2.02(3)	2.691(2)	135(2)
N2-H1N2···O4	0.92(4)	1.96(4)	2.719(2)	139(3)
C32-H1C32···O2$^{(i)}$	0.96	2.6(8)	3.399(2)	148(1)
2				
N1-H1N1···O2	0.88(4)	2.03(4)	2.723(3)	135(3)
N2-H1N2···O4	0.92(4)	1.94(4)	2.692(3)	137(3)
C13-H3C13···F2$^{(ii)}$	0.96	2.48(2)	3.231(3)	136

Symmetry code: (i) -1+x, y, z; (ii) 2-x, -½+y, ½-z

Table S4 Selected π-π interactions (A, °) for **1** and **2**.

Cg(I)···Cg(J)	**d(Cg···Cg)**	**α**	**β**	**γ**
1				
Cg2···Cg1$^{(iii)}$	3.5858(11)	6.02(9)	20.4	26.3
Cg3···Cg1$^{(iii)}$	3.8892(11)	2.58(9)	30.3	28.1
2				
Cg2···Cg1$^{(iii)}$	3.7894(15)	5.17(13)	25.2	30.3
Cg3···Cg1$^{(iii)}$	3.6820(16)	4.47(13)	22.7	26.7

Symmetry code: (iii) 1+x, y, z

Aromatic rings centres of gravity: Cg1 (C33-C34-C35-C36-N4-C36 in **1**, C35-C36-C37-C38-N4-C39 in **2**); Cg2 (C8-C9-C10-C11-C12-C13); Cg3 (C21-C22-C23-C24-C25-C26 in **1**, C22-C23-C24-C25-C26-C27 in **2**),

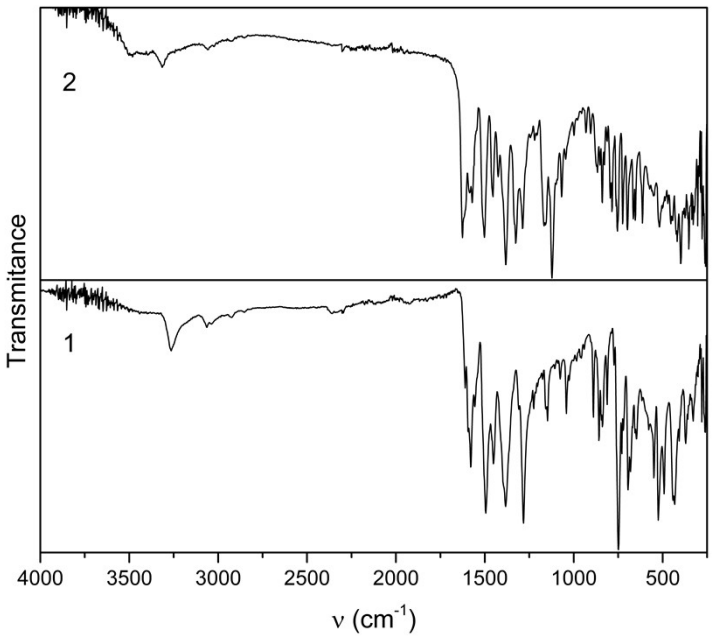

Fig. S1 Comparison of solid-state FT-IR ATR spectra of complexes **1** and **2**.

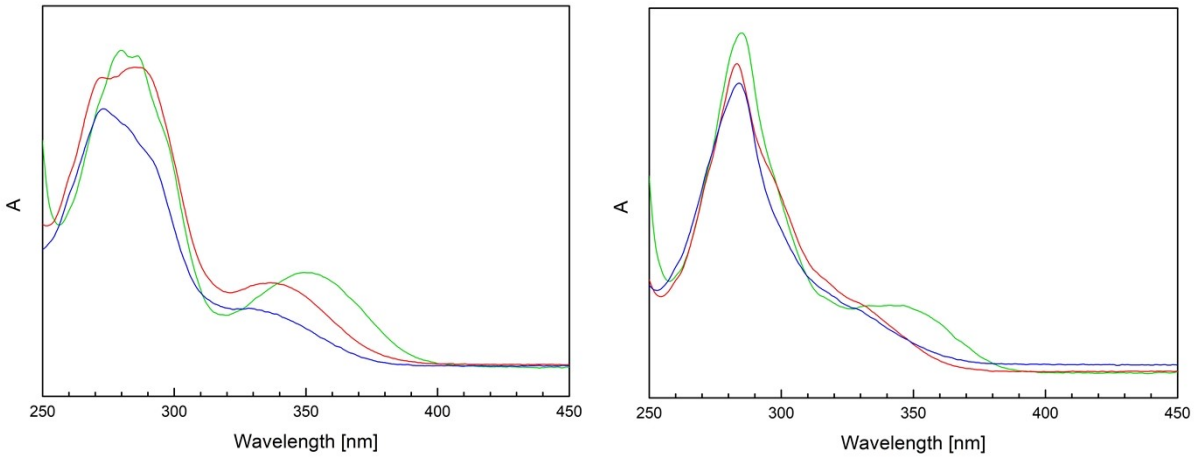

Fig. S2 Absorption spectra of 10 μM solutions of **1** (left) and **2** (right) in water (blue), methanol (red) and dichloromethane (green).

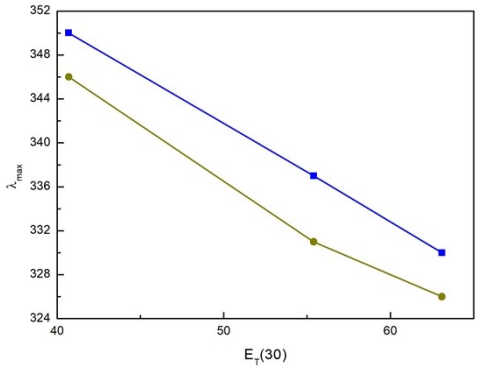

Fig. S3 Dependence of position of second absorption band (π→π* transition of *fen* and *flu* ligands) in the absorption spectra of **1** (blue) and **2** (green) on the solvent polarity represented by $E_T(30)$ scale.

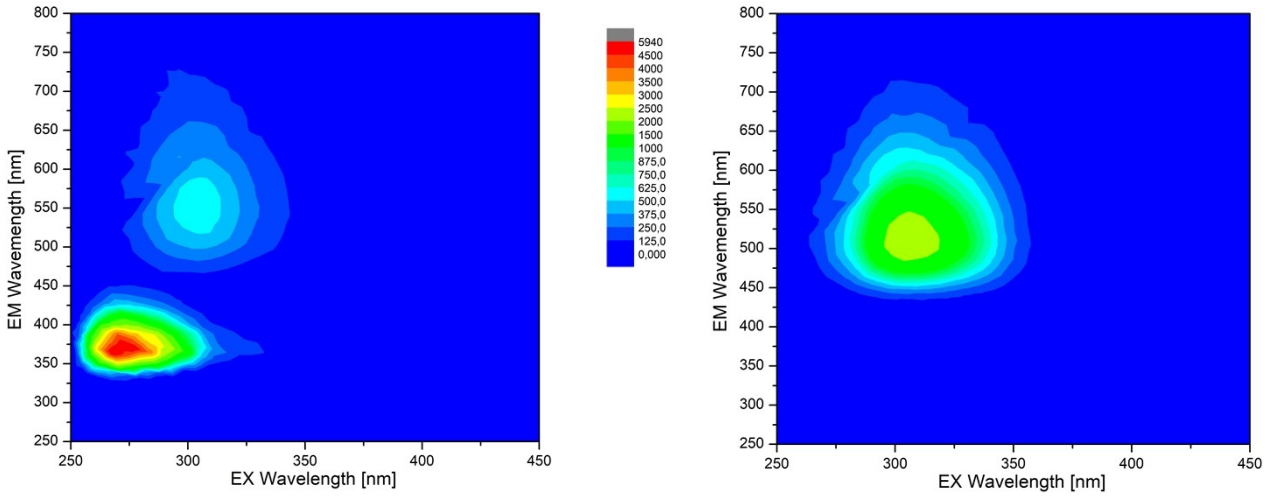

Fig. S4 Excitation-emission matrices (EEMs) of complex **1** (left) and **2** (right) in 10 μM DMSO solutions adjusted to the same intensity colour scale for better comparison (Rayleigh and Raman scattering is masked).

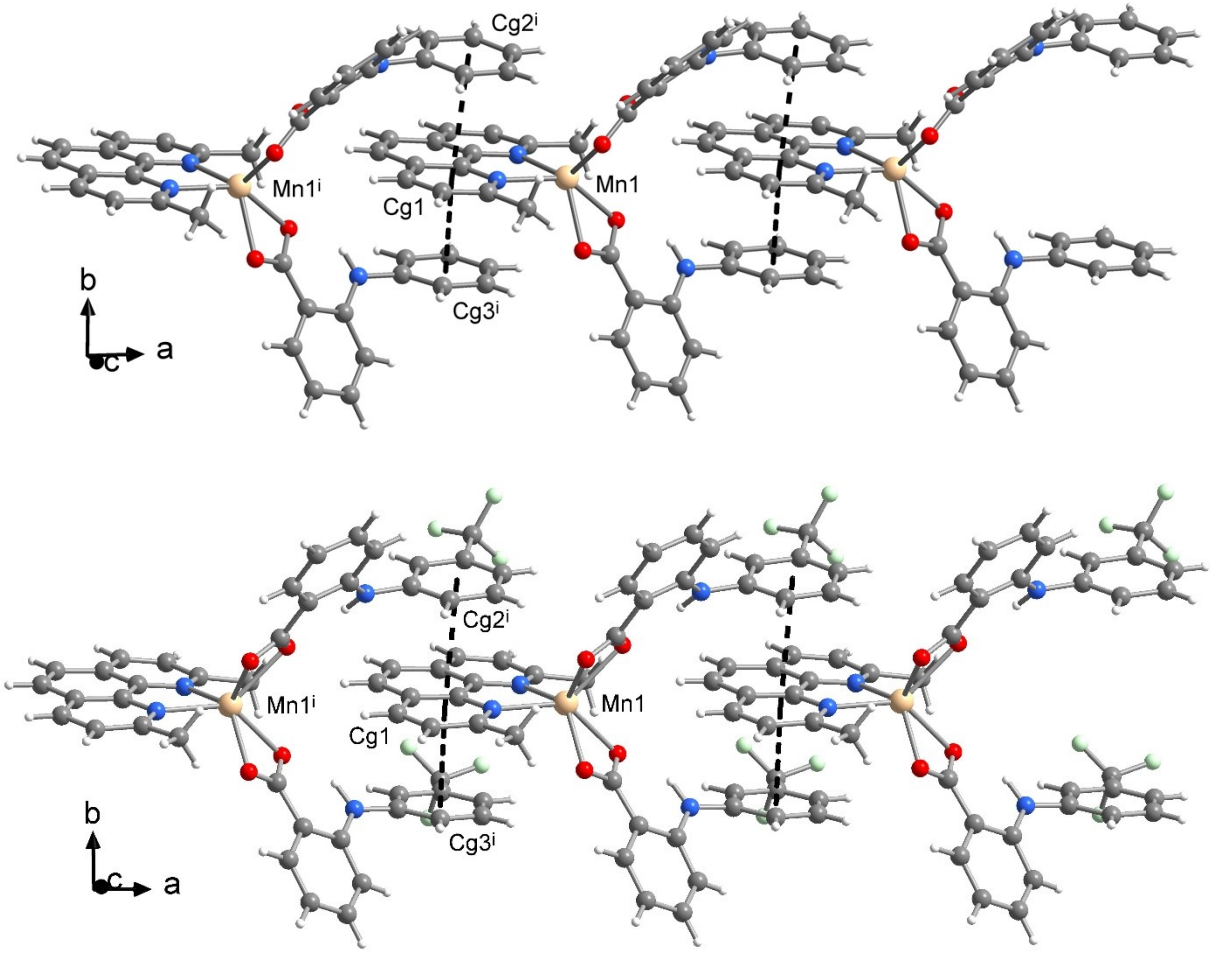

Fig. S5 Crystal packing of **1** (top) and **2** (bottom) showing intermolecular π-π stacking interactions (black dashed lines) linking complex molecules into supramolecular chains along *a*-axis. Symmetry codes: (i) -1+x, y, z

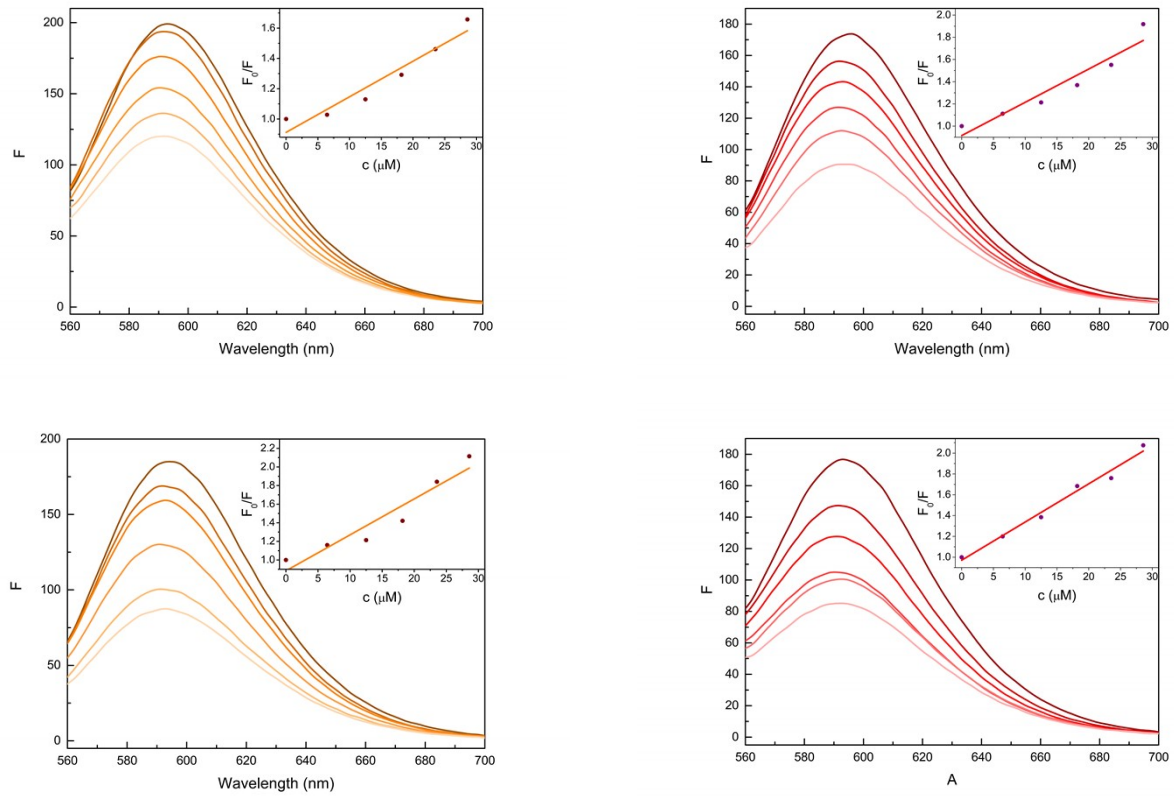

Fig. S6 Fluorescence emission spectra of DNA-EB complex (λ_{ex} = 520 nm) prepared by using isolated genomic DNA samples from studied cell lines 12Z (orange) and SK-UT-1 (red) upon gradual addition of **1** (above) and **2** (bellow) in the concentration range 0 – 28.5 μM.

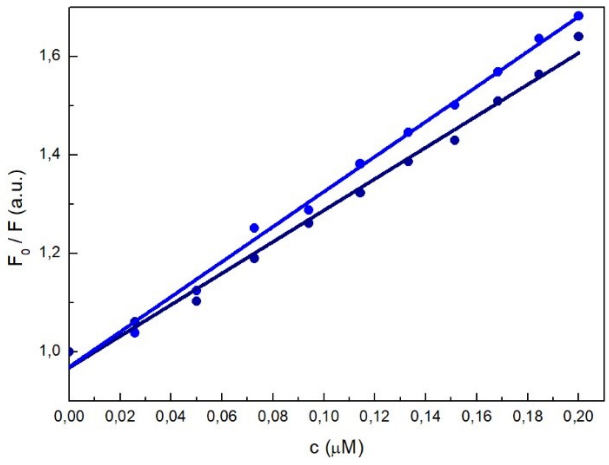

Fig. S7 Linear-fitted Stern-Volmer plots showing the quenching of HSA fluorescence emission maximum upon addition of complexes **1** (blue) and **2** (dark blue).

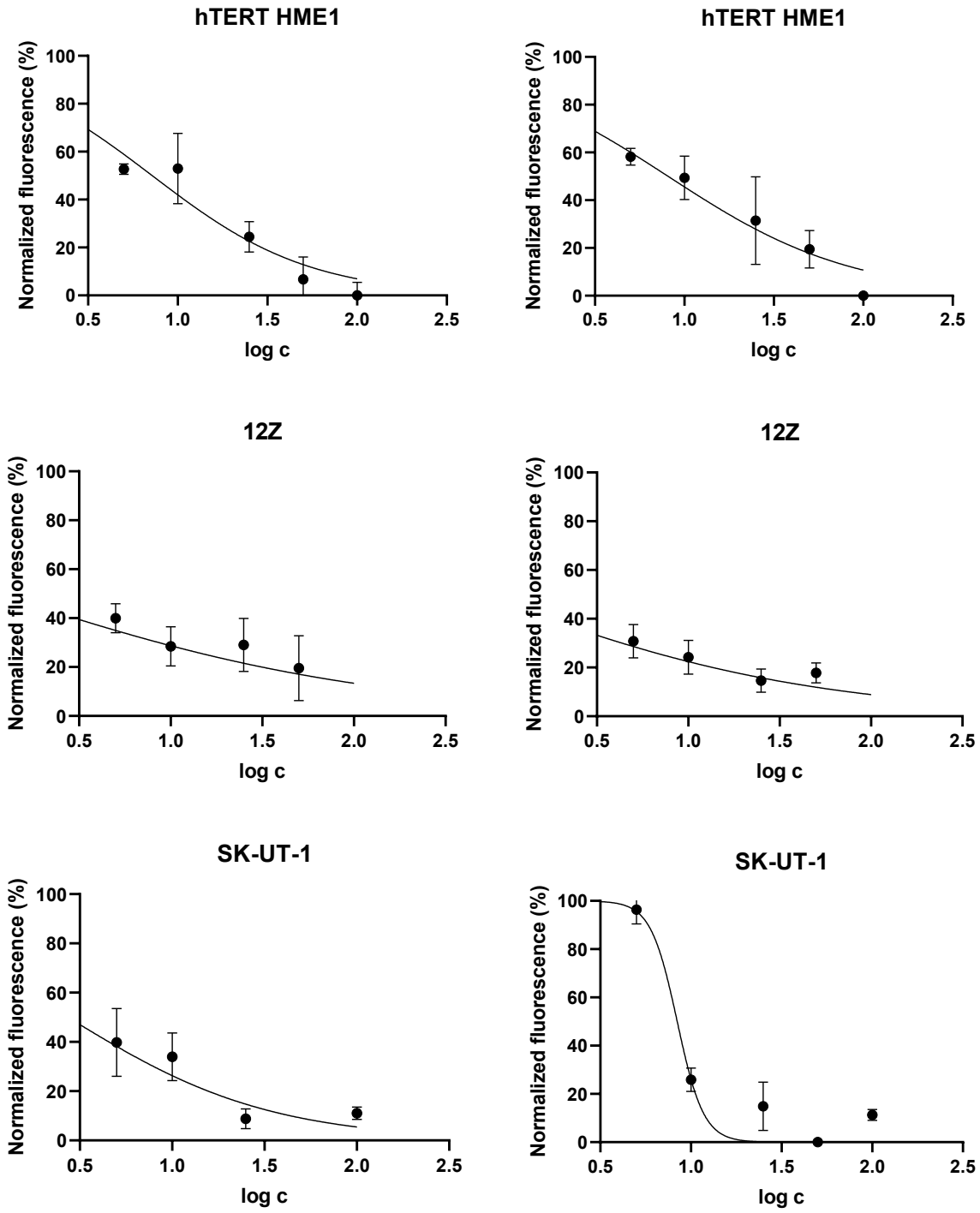

Fig. S8 Cell viability of tested cell lines upon treatment by complexes **1** (left) and **2** (right) after 24 h with concentration displayed on a logarithmic scale.