Electronic Supplementary Information

To the paper entitled

Effect of potential supramolecular-bond promoters on the DNA-interacting abilities of copper-terpyridine compounds

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Table S1. Crystal data and structure refinement for ligand **Naphtpy**

Empirical formula	$C_{26}H_{19}N_3O$
Formula weight (g mol^{-1})	389.44
Temperature (K)	100(2)
Crystal system	monoclinic
Space group	$P2_1$
Crystal size (mm^3)	0.288 × 0.084 × 0.024
a (Å)	5.908(2)
b (Å)	8.824(2)
c (Å)	18.775(5)
β (°)	96.643(18)
V (Å^3)	972.3(4)
Z	2
ρ_{calcd} (g cm^{-3})	1.330
μ (mm^{-1})	0.083
F(000)	408
ϑ for data collection (°)	2.55–21.86
Reflections collected / unique	6241 / 3001
Completeness to theta	98.8
Data / restraints / parameters	3001 / 1 / 271
Goodness-of-fit on F^2	1.125
Final R indices [$I>2\sigma(I)$]	R1 = 0.0963, wR2 = 0.2477
R indices (all data)	R1 = 0.1215, wR2 = 0.2762
largest diff. peak and hole (e Å^3)	0.477 and –0.508

Figure S1. Representation of the molecular structure of **naphtpy** with the atom-numbering scheme.

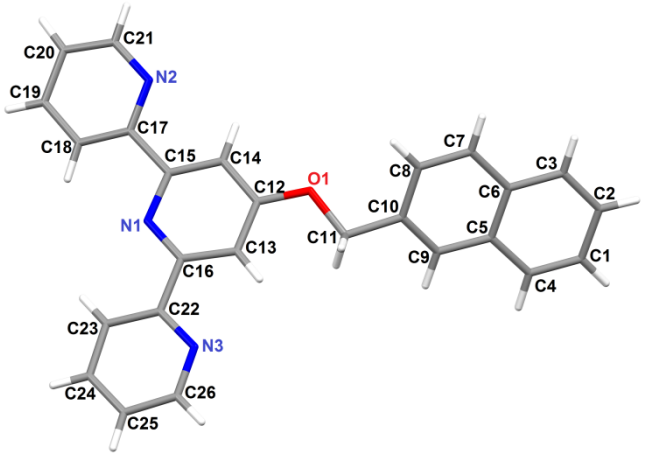

Table S2. Crystal data and structure refinement for complexes **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{15}H_{12}ClCuN_5O_7$	$C_{26}H_{21}CuN_4O_5$, NO_3, CH_4O
Formula weight (g mol^{-1})	473.29	627.07
Temperature (K)	100(2)	150(2)
Crystal system	monoclinic	monoclinic
Space group	*C*2/c	$P2_1/n$
Crystal size (mm^3)	0.04 × 0.08 × 0.45	0.40 × 0.04 × 0.02
a (Å)	8.684(2)	7.2118(9)
b (Å)	19.023(5)	19.471(2)
c (Å)	10.487(3)	37.885(5)
α (°)	90	90
β (°)	96.817(3)	91.302(2)
γ (°)	90	90
V ($Å^3$)	1720.2(8)	5318.5(11)
Z	4	8
ρ_{calcd} (g cm^{-3})	1.827	1.566
μ (mm^{-1})	1.869	1.118
F(000)	956	2584
ϑ for data collection (°)	4.35–33.59	3.12–33.52
Reflections collected / unique	5165 / 2054	56092 / 15461
Completeness to theta	96.2	99.4
Data / restraints / parameters	2054 / 0 / 137	15461 / 40 / 773
Goodness-of-fit on F^2	1.104	1.014
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0354, wR2 = 0.0947	R1 = 0.0572, wR2 = 0.1648
R indices (all data)	R1 = 0.0388, wR2 = 0.0972	R1 = 0.0684, wR2 = 0.1734
largest diff. peak and hole (*e* $Å^3$)	0.510 and –0.667	1.478 and –0.707

Table S3. Selected coordination bond lengths (Å) and angles (°), and intermolecular contacts for complexes **1** and **2**

Complex **1**[a]			
Distances			
Cu1–O1	2.430(2)	Cu1–O4	1.915(2)
Cu1–N2	2.022(2)	Cu1–N3	1.932(2)
Angles			
N2–Cu1–N3	80.06(5)	N3–Cu1–N2a	80.06(5)
N2a–Cu1–O4	99.94(5)	O4–Cu1–N2	99.94(5)
O1–Cu1–O1a	175.70(5)		
Hydrogen bonds			
O4–H4a···O2a	2.765(2)	O4–H4a–O2a	171(3)
O4–H4···O2d	2.765(2)	O4–H4–O2d	171(3)
π–π interactions			
Cg3···Cg4	3.953(2)	C2···C7g	3.375(3)
Complex **2**[b]			
Distances			
Cu1–O2	2.184(2)	Cu1–O5	1.969(2)
Cu1–N1	2.024(2)	Cu1–N2	1.931(2)
Cu1–N3	2.029(2)		
Cu2–O7	2.245(2)	Cu2–O10	1.952(2)
Cu2–N5	2.021(2)	Cu2–N6	1.928(2)
Cu2–N7	2.022(2)		
Angles			
N1–Cu1–N2	80.50(9)	N2–Cu1–N3	79.61(9)
N3–Cu1–O5	97.47(9)	O5–Cu1–N1	99.80(9)
N5–Cu2–N6	80.13(8)	N6–Cu2–N7	80.36(8)
N7–Cu2–O10	95.87(9)	O10–Cu2–N5	101.61(9)
Hydrogen bonds			
O5–H5A···O14	2.646(3)	O5–H5A–O14	169(4)
O5–H5B···O7	2.737(3)	O5–H5B–O7	171(3)
O10–H10A···O2	2.701(3)	O10–H10A–O2	169(3)
O10–H10B···O14d’	2.630(3)	O10–H10B–O14d’	169(3)
O1S–H1S···O12	2.895(7)	O1S–H1S–O12	148
O2Si’–H2Si’···O11	2.897(7)	O2Si’–H2Si’–O11	155
π–π interactions			
Cg4···Cg14’	3.872(1)	Cg6···Cg12	3.582(1)
C6···C54e’	3.390(3)	C6···C55e’	3.394(3)
C11···C51e’	3.400(4)	C18···C38e’	3.320(3)
C20···C40e’	3.329(4)	C24···C36e’	3.327(3)

[a] Symmetry operations: a = 1–x, y, 1/2–z; d = 1/2–x, 1/2–y, 1–z; g = 3/2–x, 1/2–y, 1–z. [b] Symmetry operations: d’ = 1+x, y, z; e’ = –1/2+x, 1/2–y, 1/2+z; i’ = 1–x, 1–y, 1–z.

Figure S2. Representation of the molecular structure of **1** with the partial atom-numbering scheme. The hydrogen atoms (except the two hydrogens of the coordinated water molecule) are not shown for clarity. Symmetry operation: a = 1–x, y, 1/2–z.

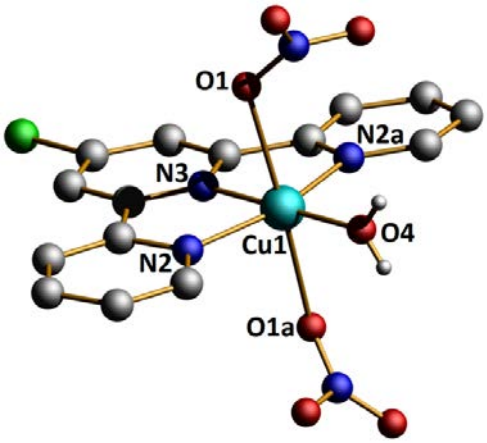

Figure S3. Views of the crystal packing of **2** showing the a) π–π interactions (Cg3···Cg4 = 3.953(2) Å; C2···C7g = 3.375(3) Å); b) H-bonding network between the water molecule and nitrate ions (O4–H4a···O2a = 2.765(2) Å; O4–H4···O2d = 2.765(2) Å). Symmetry operations: a = 1–x, y, 1/2–z; d = 1/2–x, 1/2–y, 1–z; g = 3/2–x, 1/2–y, 1–z.

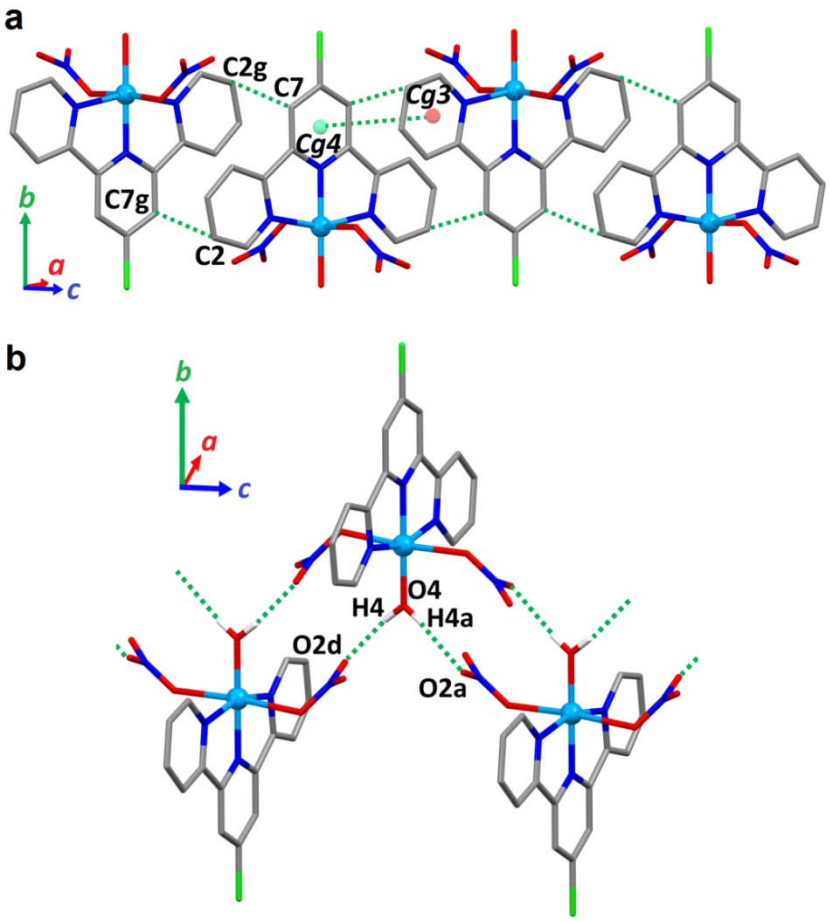

Figure S4. View of the crystal packing of **2** showing the formation of a supramolecular chain along the crystallographic *a* axis, which is generated through hydrogen bonds between lattice nitrate ions and coordinated water molecules. O5···O14 = 2.646(3) and O10j···O14 = 2.630(3) Å. Symmetry operation: *j* = 1–x, 1–y, 1–z.

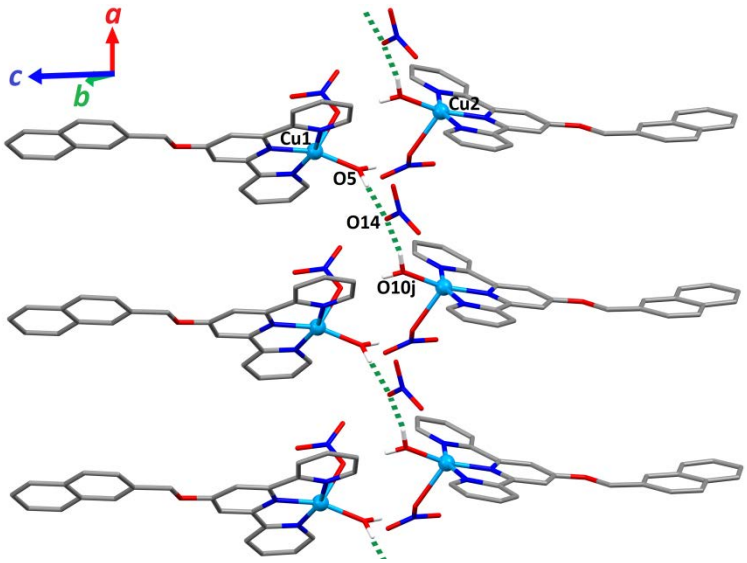

Figure S5. Absorption spectra of a) **2** and b) **3** in Tris-HCl buffer (pH = 7.2) upon addition of ct-DNA. Complex concentration: 25 µM; [ct-DNA]: 0–100 µM. The concentration of ct-DNA was determined from its absorption intensity at 260 nm with a molar extinction coefficient of 6600 M^{-1} cm^{-1}.

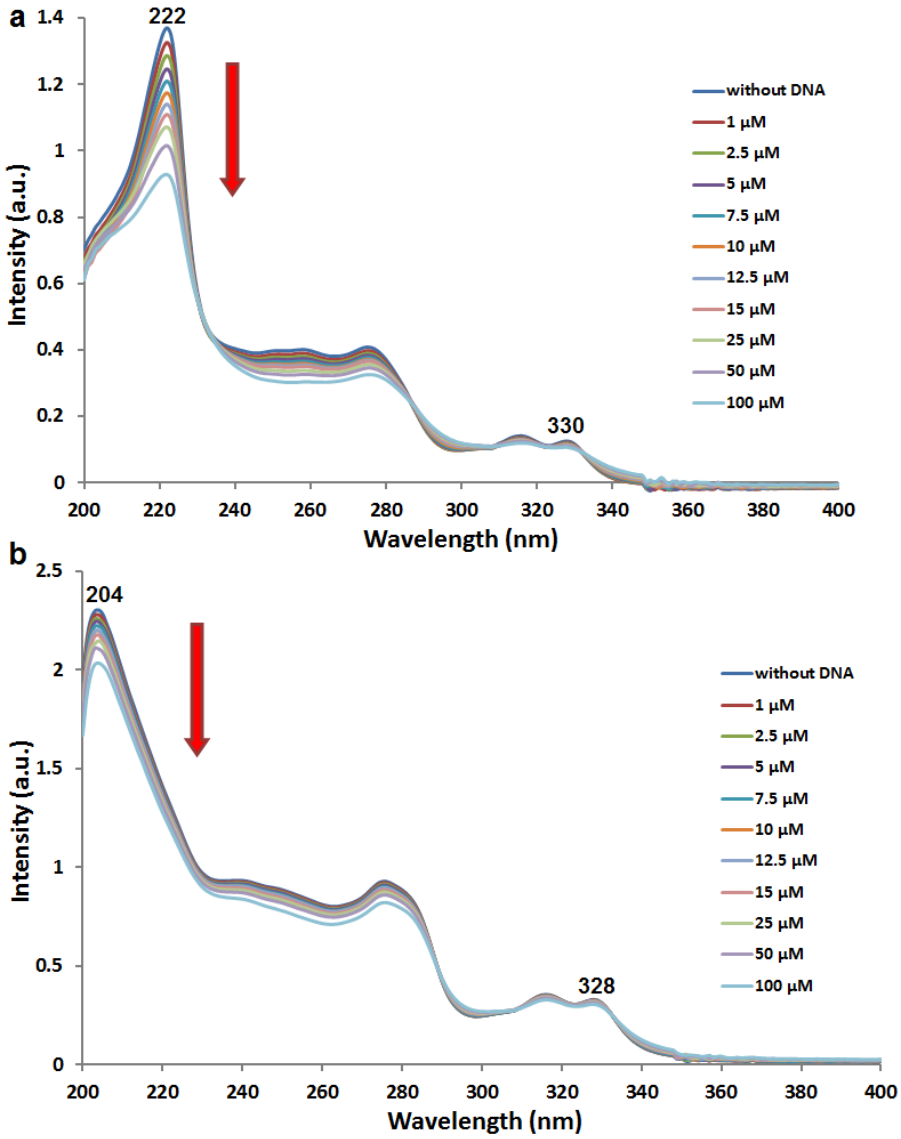

Figure S6. Emission spectra of the DNA–EB complex (concentration = 25 µM), λ_{exc} = 514 nm and λ_{em} = 610 nm, upon addition of increasing amounts of a) **2** and b) **3** (concentration range: 5–200 µM). The red arrow illustrates the decrease in fluorescence intensity with the increase of [complex].

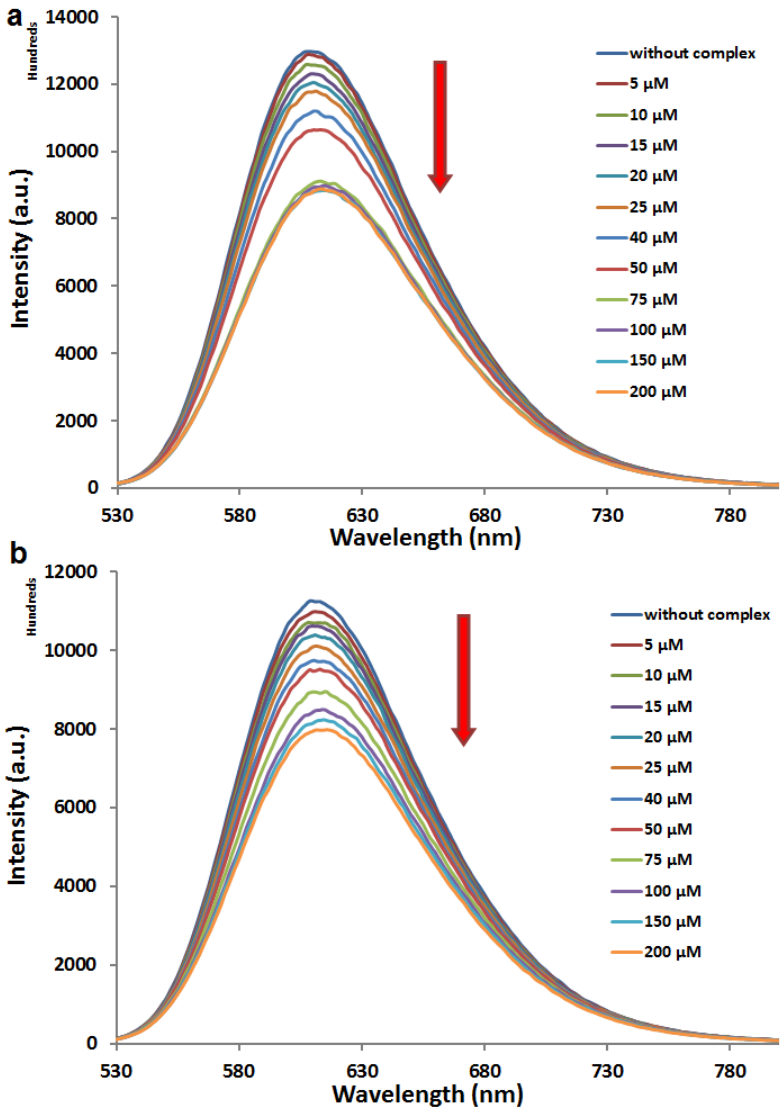

Figure S7. Cell-viability assays (single-point screening, % of cell viability) of the free ligands (**Cltpy**, **Naphtpy** and **Bimztpy**) and complexes **1–3** in different cancer cell lines, namely A549 (lung adenocarcinoma), A375 (melanoma), MCF-7 (breast adenocarcinoma), PC3 (prostate adenocarcinoma), SKOV3 (ovary adenocarcinoma) and SW620 (colorectal adenocarcinoma), using [compound] = 10 µM and an incubation time of 24 h. The results are mean ± SD of three separate experiments.

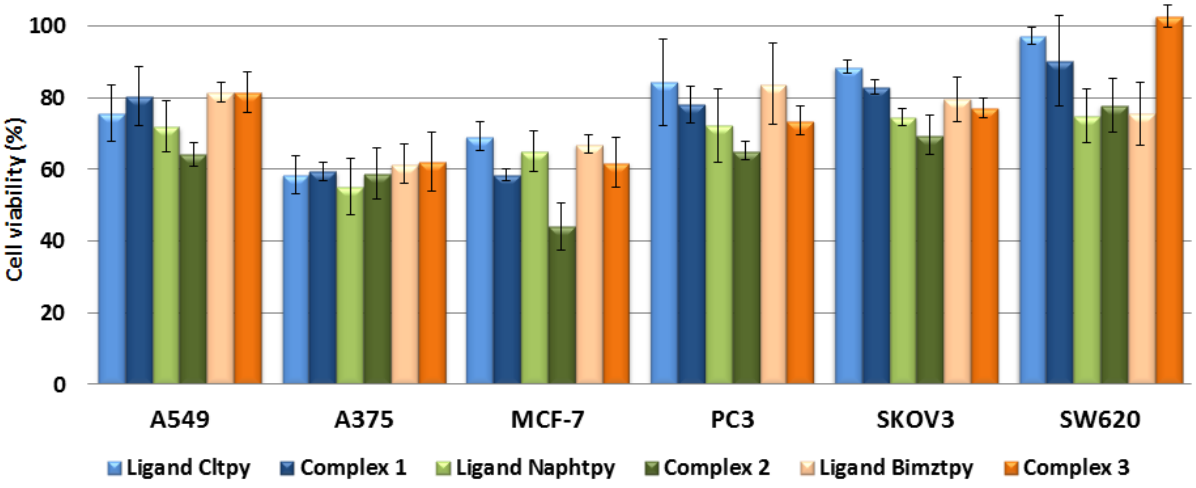

Table S4 Cell-viability assays (single-point screening, % of cell viability) of the free ligands (**Cltpy**, **Naphtpy** and **Bimztpy**) and the copper complexes **1–3** in different cancer-cell lines, *i.e.* A549 (lung adenocarcinoma), A375 (melanoma), MCF-7 (breast adenocarcinoma), PC3 (prostate adenocarcinoma), SKOV3 (ovary adenocarcinoma) and SW620 (colorectal adenocarcinoma), using a pre-set [compound] of 10 µM (single-point assay) and an incubation time of 24 h. The data shown are means ± SD of three independent experiments.

Cell line → Compound ↓	A549	A375	MCF-7	PC3	SKOV3	SW620
Cltpy	76 ± 7.8	58 ± 5.3	69 ± 4.0	84 ± 12.0	89 ± 1.8	97 ± 2.4
1	80 ± 8.2	59 ± 2.6	58 ± 1.7	78 ± 5.1	83 ± 1.9	90 ± 12.7
Naphtpy	72 ± 7.1	55 ± 7.9	65 ± 5.6	72 ± 10.4	75 ± 2.5	75 ± 7.5
2	64 ± 3.3	59 ± 7.1	**44 ± 6.7**[a]	65 ± 2.6	70 ± 5.6	78 ± 7.5
Bimztpy	82 ± 2.7	61 ± 5.5	67 ± 2.5	84 ± 11.3	80 ± 6.2	76 ± 8.8
3	81 ± 5.7	62 ± 8.3	62 ± 7.0	74 ± 4.0	77 ± 2.9	103 ± 3.3

[a] Sole cell viability below 50%.

Figure S8. Cell-viability assays (single-point screening, % of cell viability) of the free ligands (**Cltpy**, **Naphtpy** and **Bimztpy**) and complexes **1**–**3** in different cancer cell lines, namely A549 (lung adenocarcinoma), A375 (melanoma), MCF-7 (breast adenocarcinoma), PC3 (prostate adenocarcinoma), SKOV3 (ovary adenocarcinoma) and SW620 (colorectal adenocarcinoma), with an incubation time of 48 h and using **A**) [compound] = 10 µM and **B**) [compound] = 50 µM. The results are mean ± SD of three separate experiments.

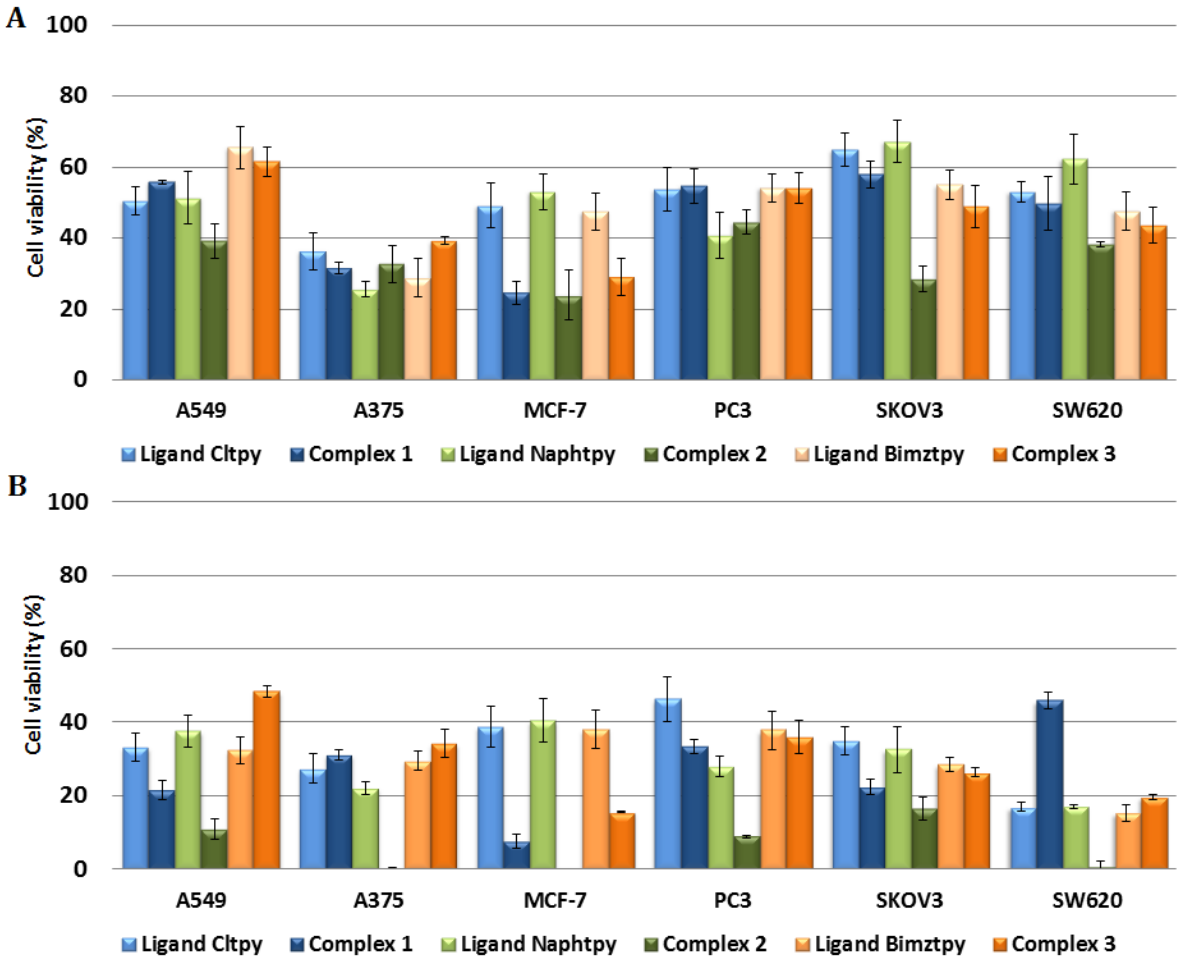

Table S5 Cell-viability assays (single point screening, % of cell viability) of the free ligands (**Cltpy**, **Naphtpy** and **Bimztpy**) and the copper complexes **1**–**3** in different cancer-cell lines, *i.e.* A549 (lung adenocarcinoma), A375 (melanoma), MCF-7 (breast adenocarcinoma), PC3 (prostate adenocarcinoma), SKOV3 (ovary adenocarcinoma) and SW620 (colorectal adenocarcinoma), using pre-set compound concentrations of 10 µM and 50 µM (single-point assays) and an incubation time of 48 h. The data shown are means ± SD of three independent experiments.[a]

Cell line → Compound ↓	A549	A375	MCF-7	PC3	SKOV3	SW620
[Compound] = 10 µM						
Cltpy	50 ± 4.1	36 ± 5.3	49 ± 6.3	54 ± 6.1	65 ± 4.7	53 ± 2.8
1	56 ± 0.4	32 ± 1.6	**25 ± 3.3**	55 ± 4.9	58 ± 3.7	50 ± 7.5
Naphtpy	51 ± 7.4	26 ± 2.1	53 ± 4.9	41 ± 6.4	67 ± 6.0	62 ± 6.9
2	39 ± 4.8	33 ± 5.2	**24 ± 7.0**	44 ± 3.4	28 ± 3.7	38 ± 0.8
Bimztpy	66 ± 5.9	29 ± 5.4	47 ± 5.2	54 ± 3.9	55 ± 4.2	48 ± 5.4
3	62 ± 4.1	39 ± 1.1	29 ± 5.1	54 ± 4.3	49 ± 5.9	44 ± 5.0
[Compound] = 50 µM						
Cltpy	33 ± 3.9	27 ± 4.0	39 ± 5.6	46 ± 6.1	35 ± 3.9	**17 ± 1.2**
1	**21 ± 2.5**	31 ± 1.4	**8 ± 2.0**	33 ± 2.1	**22 ± 2.0**	46 ± 2.2
Naphtpy	37 ± 4.3	**22 ± 1.6**	40 ± 5.9	28 ± 2.7	33 ± 6.3	**17 ± 0.4**
2	**11 ± 2.8**	**0 ± 0.2**	**0 ± 0.0**	**9 ± 0.4**	**16 ± 3.0**	**1 ± 1.6**
Bimztpy	32 ± 3.5	29 ± 2.6	38 ± 5.1	38 ± 5.2	29 ± 1.9	**15 ± 2.3**
3	48 ± 1.7	34 ± 3.8	**15 ± 0.2**	36 ± 4.5	26 ± 1.2	**20 ± 0.7**

[a] The greatest cytotoxicities (% cell viability ≤ 25%) are shown in bold.