## Electronic Supporting Information (ESI)



Figure S1. ${ }^{1} \mathrm{H}$ NMR spectra of complex $1 \mathrm{CD}_{3} \mathrm{CN}$. The chemical shifts are expressed in ppm. The chemical structures represented belong to the coordinating ligands 2,2'-bipyridine (bipy) and bathocuproine ( BC ). The hydrogens are labeled by numbers and are assigned to the peaks on the spectra. * represents the hydrogens on the phenyl groups which are detected as a multiplets on the spectrum and $\dagger$ represents the solvent residual peaks. The peak at 0 corresponds to TMS.


Figure $\mathrm{S} 2 .{ }^{13} \mathrm{C}$ NMR spectra of complex $\mathbf{1}$ in $\mathrm{CD}_{3} \mathrm{CN}$. The chemical shifts are expressed in ppm and the characteristic peaks for the complex are at $\delta=167.36,158.62,158.34,153.86,152.76$, $150.40,150.23,138.77,138.60,136.73,130.66,130.55,130.03,128.78,128.42,128.32,128.24$, 125.78, 125.46, 125.37, 26.39.


Figure S3. HRMS of complex 1. The $\mathrm{m} / \mathrm{z}$ value is assigned to the peaks and the y axis represents the percent abundance of the signals (\%). The exact mass of the counter-ion free complex [M$\left.2\left(\mathrm{PF}_{6}\right)\right]^{2+}$ was found to 387.1034 as compared to 387.1029 which is the theoretical mass.

TOF/TOF ${ }^{\text {TM }}$ Reflector Spec \#1 MC[BP = 773.1, 29350]


Figure S4. MALDI spectrum of complex $\mathbf{1}$. The $\mathrm{m} / \mathrm{z}$ value is assigned to the peaks and the y axis represents the percent intensity of the signals (\%). The complex was detected as $\left[\mathrm{Ru}(\text { bipy })_{2}(\mathrm{BC})\right.$ $\left.-\mathrm{H}^{+}\right]^{+}$at $\mathrm{m} / \mathrm{z}=773.1$.


Figure S5. LC-MS/MS calibration curve of $\left[\mathrm{Ru}(\text { bipy })_{2} \mathrm{BC}^{2}\right] \mathrm{Cl}_{2}$.


Figure S6. LC-MS/MS calibration curve of $\left[\mathrm{Ru}(\text { bipy })_{2} \mathrm{phen}\right] \mathrm{Cl}_{2} . \mathrm{y}=5.16 \mathrm{E}-08 \mathrm{x}+6.55 \mathrm{E}-04 ; \mathrm{R}^{2}=$ 0.998 .


Figure S7. LC-MS/MS calibration curve of BC. $\mathrm{y}=7.07 \mathrm{E}-07 \mathrm{x}-8.12 \mathrm{E}-03 ; \mathrm{R}^{2}=0.988$.


Figure S8. ESI-MS full scan spectrum of 1:1 bipy:BC mixture. bipy: $\mathrm{m} / \mathrm{z}\left[\mathrm{M}+\mathrm{H}^{+}\right]^{+}=157.11$, $B C: m / z\left[M+H^{+}\right]^{+}=361.22$.


Figure S9. LC-MS/MS analysis for the uptake of complex 1 (a), BC (a, inset), and complex 2 (b) by A549 cells. Results are averages of four different experiments ( $\pm$ SEM) and are expressed in $\mathrm{nmol} / 10^{6}$ cells, as estimated from the calibration curves (Figures S5, S6, and S7).


Log Concentration ( $\mu \mathrm{M}$ )

Figure S10. Effect of complex 1 on the survival of MSCs. Treatment was performed with 3-fold dilutions of the complex starting at $120 \mu \mathrm{M}$. Cytotoxicity was evaluated in both dark and light conditions (blue LED at a power of $100 \mathrm{~mW} / \mathrm{cm}^{2}$ ) and the experiment was repeated three times, with measurements performed in triplicates. $\mathrm{IC}_{50}$ (Dark) $=52 \pm 13 \mu \mathrm{M}, \mathrm{IC}_{50}$ (Light) $=0.024 \pm$ $0.002 \mu \mathrm{M}, \mathrm{p}<0.05$. The graph shown here corresponds to a single representative trial.

