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Electronic Supplementary Information

for

Bio-imaging with neutral luminescent Pt(II) complexes showing metal···metal interactions†

by

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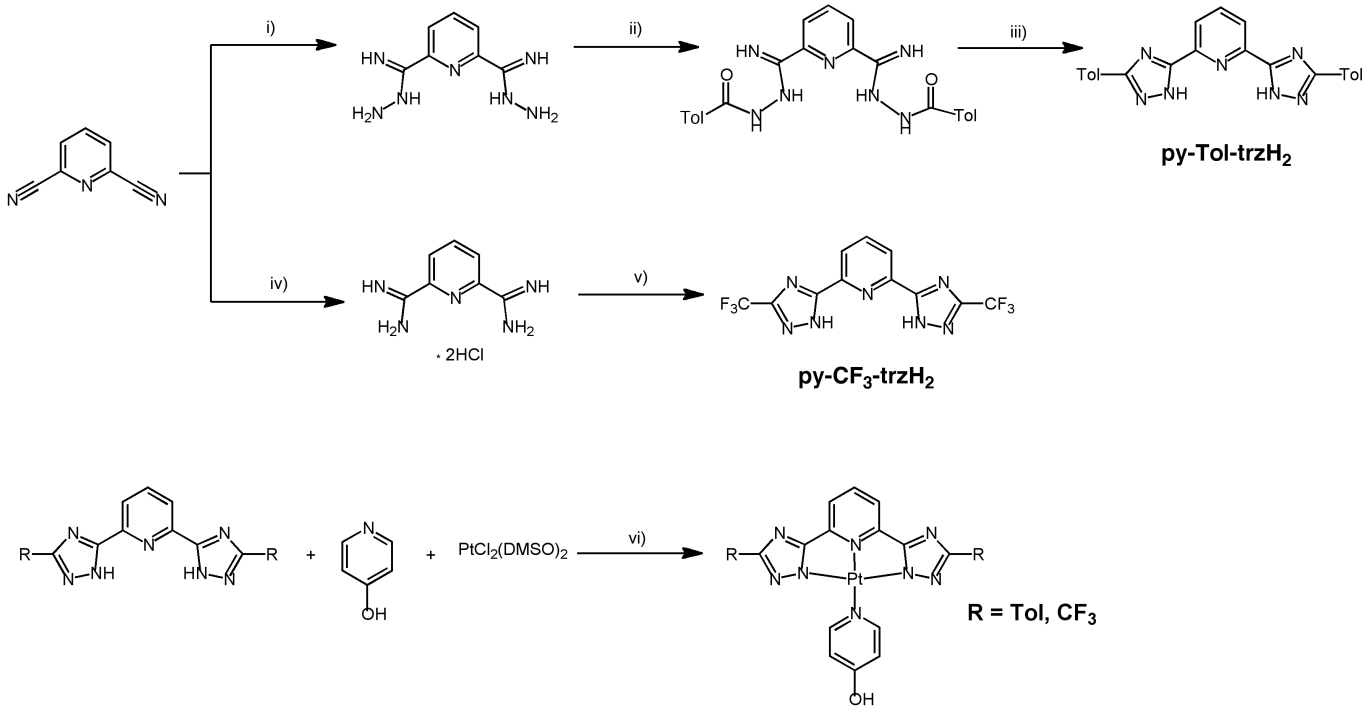

Scheme S1. Schematic synthetic pathway employed for the preparation of the ligands **py-Tol-trzH$_2$** and **py-CF$_3$-trzH$_2$** as well as the corresponding complexes **Tol-Pt-4OHpy** and **CF$_3$-Pt-4OHpy**. *i*) EtOH, NH_2NH_2, room temperature, overnight; *ii*) DMF, RCOCl, K_2CO_3, 0^{o}C → room temperature, overnight; *iii*) ethylenglycole, 180^{o}C, 4 hours; *iv*) MeOH, MeONa, NH_4Cl; *v*) THF, $CF_3CONHNH_2$ in situ, NaOH, reflux; *vi*) 2-methoxyethanol:H_2O, Et_3N (2.2 eq.), 83^{o}C, overnight.

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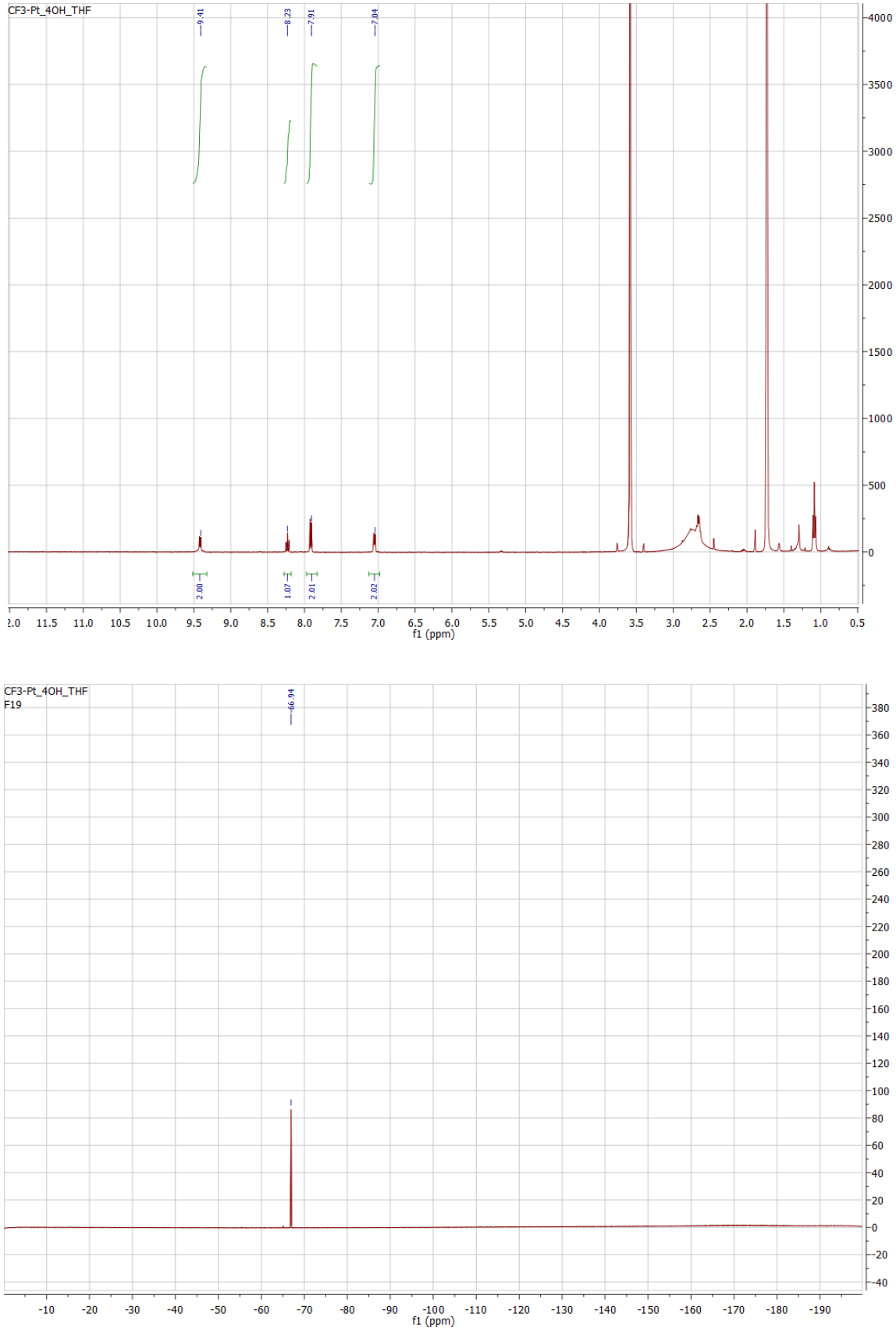

Fig. S1 ^{1}H (*top*) and ^{19}F (*bottom*) NMR for the complex **CF_3-Pt-4OHpy** recorded in THF-d_8 at 298K.

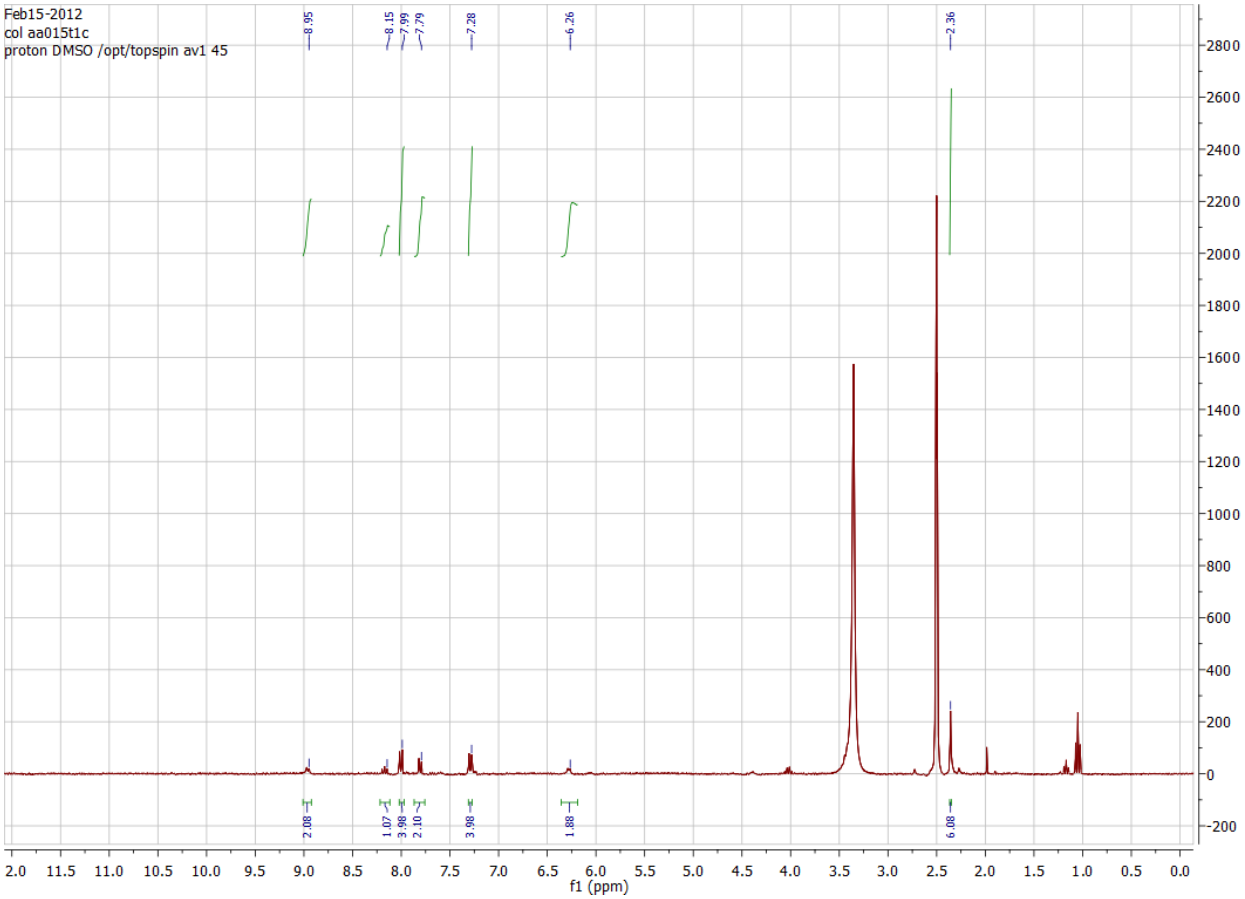

Fig. S2 ^{1}H NMR for the complex **Tol-Pt-4OHpy** recorded in DMSO-d_6 at 298K.

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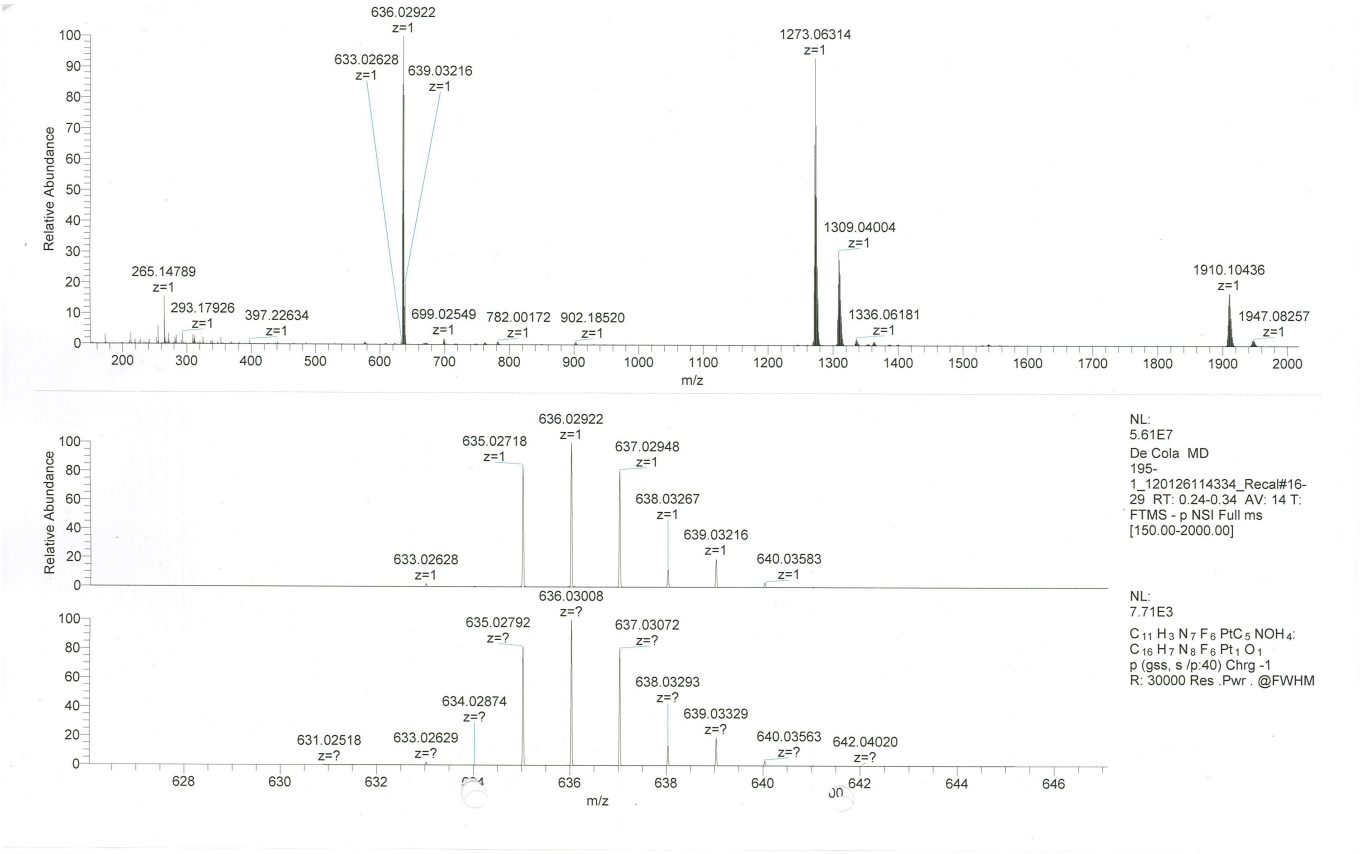

Fig. S3 HR-MS spectrum of the complex **CF_3-Pt-4OHpy**.

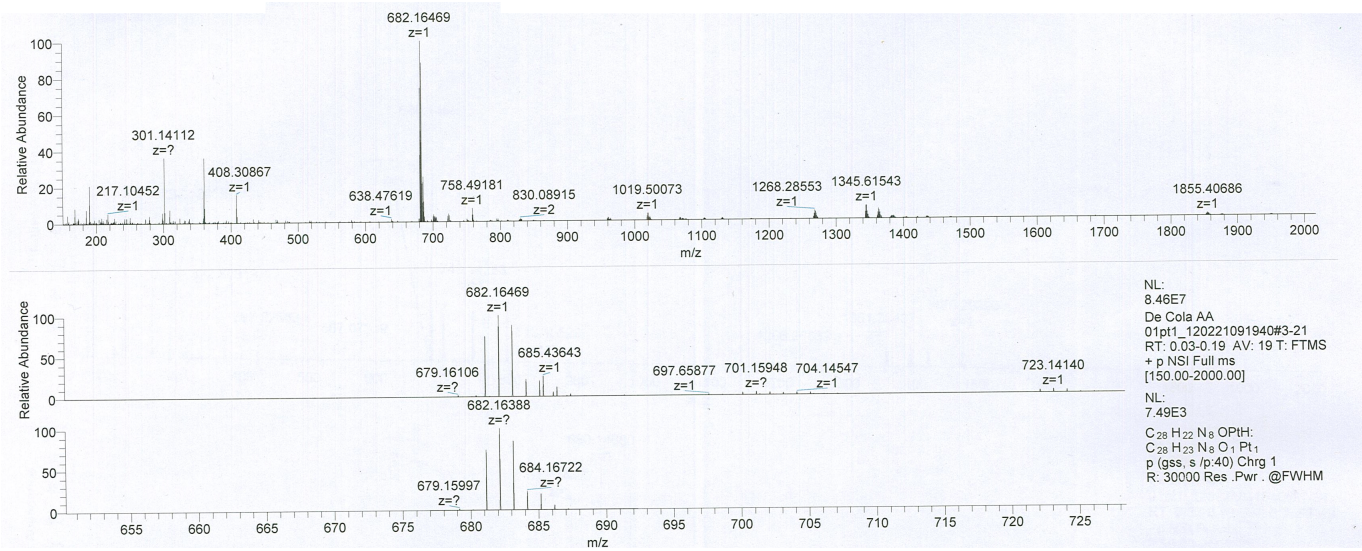

Fig. S4 HR-MS spectrum of the complex **Tol-Pt-4OHpy**.

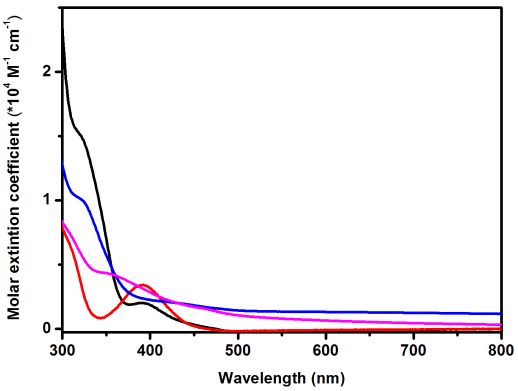

Fig. S5. Electronic absorption spectra for complex **Tol-Pt-4OHpy** in DMSO (black trace) and DMSO:H_2O 1:99 $^{v}/_{v}$ (blue trace) and for complex **CF_3-Pt-4OHpy** in DMSO (red trace) and DMSO:H_2O 1:99 $^{v}/_{v}$ (magenta trace). For both the platinum complexes, the high scattering at longer wavelengths confirms the formation of aggregates upon addition of H_2O.

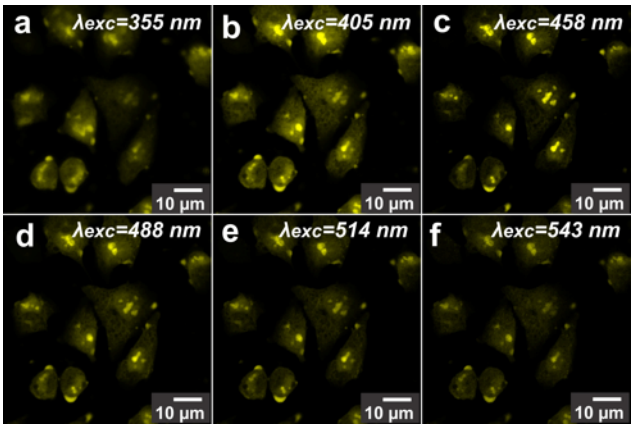

Fig. S6. Fluorescence confocal microscopy images of **CF_3-Pt-4OHpy** internalized in HeLa cells after 4 hours incubation in PBS. The samples were excited at 355 nm (a), 405 nm (b), 458 nm (c), 488 nm (d), 514 nm (e), and 543 nm (f).

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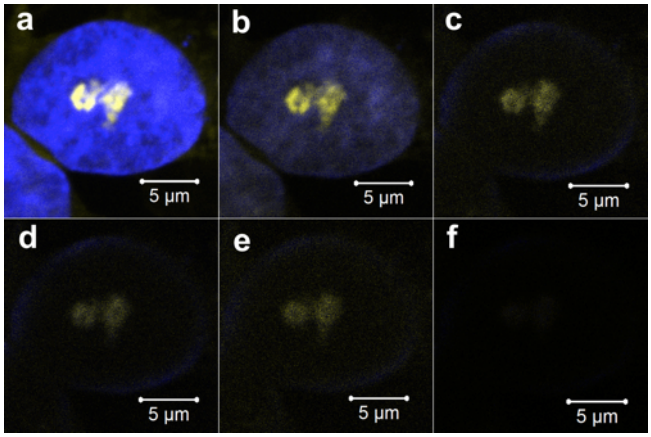

Fig. S7. Fluorescence confocal microscopy images showing the photostability of **CF_3-Pt-4OHpy** towards photobleaching relative to DAPI. Panels (c-e) show that DAPI (blue) has been already photobleached meanwhile **CF_3-Pt-4OHpy** (yellow) still maintains its emission even after 20 minutes of continuous UV irradiation at 405 nm. The sample was continuously excited with high power laser (32 mW) for 5 minutes and subsequently imaged at low power acquisition (1.2 mW) every 5 minutes for a total time of 25 minutes

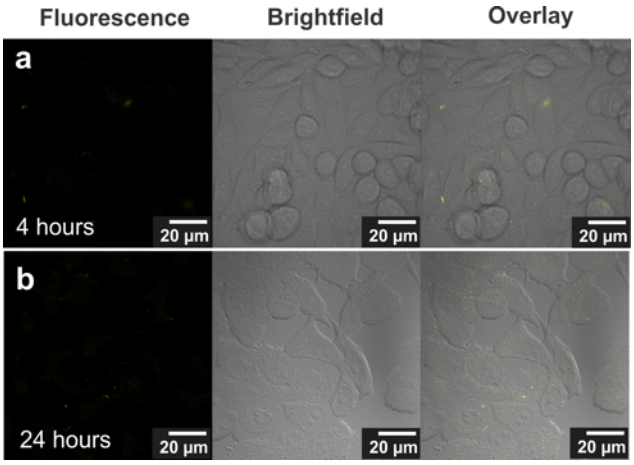

Fig. S8 Fluorescence confocal microscopy images showing no uptake of **CF_3-Pt-4OHpy** in HeLa cells even after (a) 4 and (b) 24 hours incubation time in culture media. Cells were excited at 405 nm.

Table S1. Single-crystal X-ray crystallographic data and structure refinement for CCDC-988918.

Identification code		CCDC-988918
Empirical formula		C20 H20 F6 N8 O3 Pt S2
Formula weight		793.65
Temperature		193(2) K
Wavelength		0.71073 Å
Crystal system, space group		Triclinic, P1
Unit cell dimensions:		
	a = 4.8448(4) Å	α = 78.203(4)º
	b = 9.8850(7) Å	β = 83.713(4)º
	c = 14.1315(13) Å	γ = 88.665(5)º
Volume		658.49(9) $Å^3$
Z, Calculated density		1, 2.001 Mg m^{-3}
Absorption coefficient		5.569 mm^{-1}
F(000)		384
Crystal size		0.25 × 0.18 × 0.12 mm
Theta range for data collection		1.48 to 30.03 deg
Limiting indices		–6<=h<=6, –13<=k<=13, –19<=l<=18
Reflections collected / unique		6995 / 5305 [R(int) = 0.0313]
Completeness to θ = 30.03°		98.6%
Absorption correction		Semi-empirical from equivalents
Max. and min. transmission		0.42889 and 0.35078
Refinement method		Full-matrix least-squares on F^2
Data / restraints / parameters		5305 / 4 / 352
Goodness-of-fit on F^2		1.189
Final R indices [I > 2θ(I)]		R_1 = 0.0437, wR^2 = 0.1178
R indices (all data)		R_1 = 0.0471, wR^2 = 0.1317
Absolute structure parameter		0.268(15)
Largest diff. peak and hole		2.027 and –2.847 e $Å^{-3}$

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Movie S1. Fluorescence confocal microscopy movie showing the externalization of complex **CF_3-Pt-4OHpy** over 40 minutes time-lapse of continuous irradiation at 405 nm. The images were acquired every 2 minutes.

Movie S2. Fluorescence confocal microscopy movie showing the light-induced internalization of **CF_3-Pt-4OHpy** in culture media after continuous irradiation at 405 nm. The images were acquired every minute over 75 minutes time-lapse.