Supporting Information

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Synthesis and chemical characterizations. 1,12-dibromododecane ($Br(CH_2)_{12}Br$ (3.4 g, 1.0 10^{-2} mol) and sodium azide (NaN_3, 4 eq., 2.6 g) were dissolved in DMF (20 mL) and heated at 80 °C overnight. After cooling to r.t., water was added (100 mL) and 1,12-diazidododecane was extracted with Et_2O (3x20 mL). Organic fractions were combined and dried over anhydrous sulfate magnesium and solvent was evaporated to dryness. Yield was quantitative.

1,12-diazidododecane (1g, 4.0 10^{-3} mol) and 2-ethynylpyridine (206 mg, 2.0 10^{-3} mol) were then dissolved in a mixture of CH_2Cl_2 (5 mL) and water (3 mL) at r.t. Sulfate copper (II) pentahydrate (50 mg, 2.0 10^{-4} mol) and sodium ascorbate (80 mg, 4.0 10^{-4} mol) were then added. After 12 h stirring at r.t., water (10 mL) and CH_2Cl_2 (10 mL) were poured onto the mixture. The product was extracted with CH_2Cl_2 (2x30 mL), the organic fractions combined and dried over anhydrous sulfate magnesium. Solvent was removed under vacuum. Flash Chromatography (EVF column, 5g, D24 silicium) with CH_2Cl_2:AcOEt (from 1:0 to 4:1) gave pyta-$C_{12}N_3$ (500 mg, 1.1 10^{-3} mol, 35 % yield).

Rhenium pentacarbonyl chloride (72 mg, 2.0 10^{-4} mol) and pyta-$C_{12}N_3$ (71 mg, 2.0 10^{-4} mol) were dissolved in toluene (2 mL) and heated 3 h at 70 °C. A precipitate was formed when cooling to r.t. Filtration led to a yellow solid of $Re(CO)_3Cl$-pyta-$C_{12}N_3$ (**1**) (80 mg, 1.2 10^{-3} mol, 60 % yield).

Characterizations of **1,12-diazidododecane**:

^{1}H NMR *($CDCl_3$, 300 MHz) δ (ppm):* 3.23 (4H, t, *J* = 6.9 Hz), 1.56 (4H, m), 1.30 (16H, m).

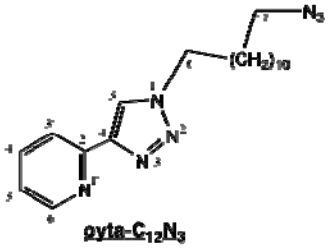
^{13}C NMR *($CDCl_3$, 75 MHz) δ (ppm):* 51.47 (2 (CH_2)-N_3), 29.47-26.72 (10 (CH_2)).

Characterizations of **pyta-$C_{12}N_3$**:

^{1}H NMR *($CDCl_3$, 300 MHz) δ (ppm):* 8.54 (1H, dd, *J* = 4.9, 1.8 Hz, 6'-py*H*), 8.14 (1H, dd, *J* = 8.0, 0.9 Hz, 3'-py*H*), 8.10 (1H, s, 5-triaz*H*), 7.73 (1H, ddd, *J* = 8.0, 7.8, 1.8 Hz, 4'-py*H*), 7.18 (1H, ddd, *J* = 7.8, 4.9, 0.9 Hz, 5'-py*H*), 4.40 (2H, m, 6-(CH_2)-triaz), 3.22 (2H, m, 17-(CH_2)-N_3), 1.93 (2H, m, 7-(CH_2)), 1.54 (2H, m, 16-(CH_2)), 1.30 (16H, m, 8 (CH_2)).

^{13}C NMR *($CDCl_3$, 75 MHz) δ (ppm):* 150.40 (2'-py*C*), 149.34 (6'-py*C*), 148.30 (4-triaz*C*), 136.85 (4'-py*C*), 122.75 (5'-py*C*), 121.76 (5-triaz*C*), 120.14 (3'-py*C*), 51.43 (17-CH_2), 50.46 (6-CH_2), 30.20-26.40 (10 (CH_2)).

HRMS$^+$ (ESI)*:* calcd for $C_{19}H_{29}N_7Na$ ([M + Na]$^+$): m/z 378.2377. Found: m/z 378.2381.



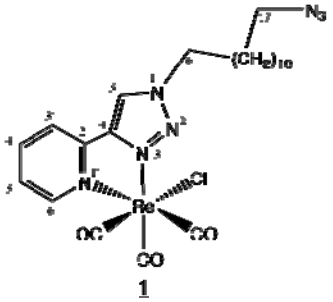
Characterizations of **1**:

^{1}H NMR *($CDCl_3$, 300 MHz) δ (ppm):* 8.90 (1H, m, 6'-py*H*), 8.48 (1H, s, 5-triaz*H*), 7.88 (2H, m, 4' and 3'-py*H*), 7.36 (1H, m, 5'-py*H*), 4.36 (2H, m, 6-(CH_2)-triaz), 3.20 (2H, m, 17-(CH_2)-N_3), 1.93 (2H, m, 7-(CH_2)), 1.54 (2H, m, 16-(CH_2)), 1.30 (16H, m, 8 (CH_2)).

^{13}C NMR *($CDCl_3$, 75 MHz) δ (ppm):* 197.35 (C≡O), 195.80 (C≡O), 188.96 (C≡O), 153.00 (6'-py*C*), 149.29 (2'-py*C*), 148.60 (4-triaz*C*), 139.49 (4'-py*C*), 125.78 (5'-py*C*), 123.84 (5-triaz*C*), 122.29 (3'-py*C*), 52.40 (17-CH_2), 51.47 (6-CH_2), 30.94-25.61 (10 (CH_2)).

HRMS$^+$ (ESI)*:* calcd for $ReC_{22}H_{29}O_3N_7ClNa$ ([M + Na]$^+$): m/z 684.1462. Found: m/z 684.1449.

HPLC *purity* was checked with a Dionex C18 analytical column. Using a CH_3CN:H_2O (0.1 % TFA) mixture from 1:4 to 1:0 in 30 minutes, retention time of **1** was 21 minutes (7:3) and its purity was > 96 %.



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NMR, UV and IR signals (see Figure 1A-b and Figure S1) are in agreement with a *fac* stereochemistry of the $Re(CO)_3$ moiety.[1]

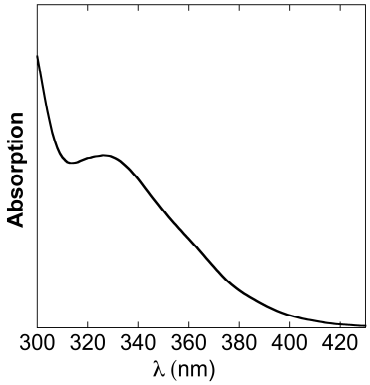

Figure S1. Absorption spectrum of **1** ($6.0\ 10^{-5}$ M in water:ethanol 1:1).

Multimodal imaging. IR spectra were recorded, either for a cell-collection using a classical FTIR spectrometer or at the single cell level with synchrotron radiation FTIR spectromicroscopy (SR-FTIR-SM at SMIS beamline, SOLEIL synchrotron, France). Luminescence studies were performed using several techniques: synchrotron radiation UV spectromicroscopy (SR-UV-SM at DISCO beamline, SOLEIL synchrotron, France) to record spectra inside cells, wide field and confocal microscopies to elucidate the cellular distribution of **1**.

Cell culture. MDA-MB-231 hormone independent breast cancer cells obtained from the Human Tumour Cell Bank were used for the experiments. Both control and treated cells were processed in a similar way. They were seeded on slides (deposited in 35x10 mm Petri dishes) in order to reach confluency after 48 h of incubation at 37 °C under an atmosphere of 95% air/ 5% CO_2. The nature of the slides depended on the spectroscopic technique carried out (see below). Medium was removed and fresh growth medium (2 mL DMEM charcoal desteroided) was added to each flask of control cells. In the case of treated cells, 2 mL of a solution of **1** in fresh growth medium (10 or 25 µM prepared from a $5\ 10^{-3}$ M stock solution in DMSO) were added. The cells were incubated at 37 °C under an atmosphere of 95% air/ 5% CO_2 for a period of 1 h. The media was then removed and the cells were washed 3 times with phosphate buffered saline (D-PBS, 1X, 2 mL). Cells were fixed by 4 % paraformaldehyde (PFA) for 20 minutes at room temperature and washed 3 times with D-PBS (0.1X, 2 mL). Slides were air-dried.

Fluorescent organelle staining. For Golgi staining, growth medium (DMEM charcoal desteroided) was removed and cells were incubated at 4°C with a 5 µM solution of BODIPY TR C_5-ceramide complexed to BSA (B-34400 from Invitrogen) in growth medium for 30 minutes. The medium was then removed and the cells were washed twice with cold phosphate buffered saline (D-PBS, 1X, 2 mL). For colocalization experiments with **1**, 2 mL of a 25 µM solution of **1** in fresh growth medium (prepared from a $5\ 10^{-3}$ M stock solution in DMSO) were added. The cells were incubated at 37 °C under an atmosphere of 95% air/ 5% CO_2 for a period of 1 h. The media was then removed and the cells were washed 3 times with phosphate buffered saline (D-PBS, 1X, 2 mL). Cells were fixed by 4 % paraformaldehyde (PFA) for 20 minutes at room temperature and washed 3 times with D-PBS (0.1X, 2 mL). Slides were air-dried.
The nuclei were stained with DAPI (15 nM in water) directly on fixed cells, when slides where on the microscope motorized stage.

Nature of the slides. Fluorescence and confocal imaging were performed on glass slides, synchrotron UV spectromicroscopy on quartz slides and synchrotron radiation FTIR spectromicroscopy on fluorine (CaF_2) disks.

Cells incubation for FTIR spectroscopy on a cell population.[2] MDA-MB-231 hormone independent breast cancer cells obtained from the Human Tumour Cell Bank were used for the experiments. Both control cells and treated were processed in a similar way. They were seeded in order to reach confluency after 24 h and incubated at 37 °C under an atmosphere of 95% air/ 5% CO_2. Cells were washed with phosphate buffered saline (D-PBS, 1x) and fresh growth medium (10 mL DMEM charcoal desteroided) was added to each flask followed in the case of treated cells by the appropriate solution of **1** (prepared from a 10^{-2} M stock solution in DMSO). Cells were incubated at 37 °C under an atmosphere of 95% air/ 5% CO_2 for a period of 1 h. The media was then removed and cells were washed with D-PBS (5 mL). Trypsin (trypsin-EDTA 1x, 0.05 % trypsine, 0.53 mM EDTA) was added and cells were harvested after 5 min at 37 °C under an atmosphere of 95% air/ 5% CO_2. 5 mL of D-PBS was added and the resulting suspension was centrifuged (5 min, 1500 g) and the supernatant discarded. After addition of 5 mL of D-PBS and resuspension, the number of cells per pellet was estimated by counting in a Mallassez chamber. The remaining 4 mL suspension was centrifuged (5 min 1500g), the supernatant discarded and a sufficient volume of D-PBS was added to obtain *ca.* 50000 cells per 10 µL. Cells were resuspended and 10 µL of the suspension was deposited onto a nitrocellulose disk. The disks were air-dried (*ca.* 2 h). FTIR spectra were recorded using a Bruker Tensor 27 with subtraction of the spectrum of control cells.

Fluorescence imaging. Epifluorescence imaging of **1** was performed using an IX71 (Olympus) microscope equipped with a CCD (Orca-ER, Hamamatsu, Corporation, Sewickley, PA) and X60 (Plan Apo, NA 1.42) objective. **1** was monitored using a in house filter set (excitation D350/50x; beam splitter 400DCLP; emission HQ560/80m—Chroma Technology) and excited using a Hg lamp (100 W) attenuated by a neutral density filter (ND-1). Nucleus was monitored using a DAPI filter set (excitation D350/50x; beam splitter 400DCLP; emission D460/50m—Chroma Technology) and BODIPY using a Texas Red filter set (excitation ET560/40x; beam splitter T585LPXR; emission ET630/75m—Chroma Technology). Microscope settings and functions were controlled using Simple PCI software (Hamamatsu). Image analysis was performed using ImageJ Software and Simple PCI software. Colocalization coefficients[3,4] were calculated using ImageJ plugin *Colocalization Indices*. Confocal fluorescence images were taken on a Zeiss LSM 710 confocal microscope using an X63 (NA 1.40) objective and 405 nm laser excitation. 3D reconstruction of the z-stacks was made with ImageJ software.

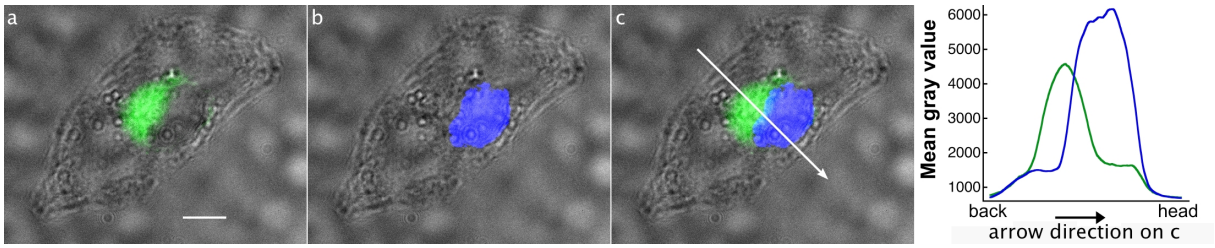

Figure S2. ***Left***: MDA-MB-231 cell incubated with **1** (25 µM, 1 h). Bright field image (scale bar 10 µm) superimposed to epifluorescence images: (*a*) and (*b*) respectively localization of **1** (green) and nucleus staining with DAPI (blue); (*c*) merge of **1** (green) and DAPI (blue). ***Right***: intensity profiles along the arrow on *(c)* image: **1** (green trace), DAPI (blue trace).

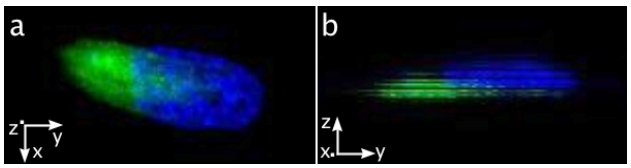

Figure S3. MDA-MB-231 cell incubated with **1** (25 µM, 1 h). Confocal merges of **1** (green) and DAPI (blue): (*a*) under Z-axis and (*b*) under x-axis (clockwise rotation of 90° along y-axis from *(a)* to *(b)*).

Synchrotron radiation FTIR spectromicroscopy (SR-FTIR-SM). Spectra were recorded at the SMIS beamline (Synchrotron SOLEIL) which exploits the edge and bending radiations of a bending magnet.[5] Spectra were recorded in transmission on a Nicolet Continuum XL microscope (Thermo Fischer) equipped with a 50x50 µm² liquid nitrogen cooled MCT/A detector, a 32X/NA 0.65 Schwarzschild objective, a Prior XYZ motorised stage, and coupled to a Nicolet 5700 spectrometer (Thermo Fischer) equipped with a Michelson interferometer, and a KBr beam splitter. The confocal aperture was set at 6x6 µm² and the microscope was operated in semi-confocal mode. Spectra were recorded with 250 scans at 4 cm^{-1} resolution in the 1040-3700 cm^{-1} range. Maps were recorded by raster scanning the cells with steps of 3 µm in X and in Y with 250 scans at 4 cm^{-1} resolution in each square. Average time lapse for the scanning of an entire cell was 6 hours. Chemical maps were created with the Omnic software (Thermo Fischer) by measuring and plotting the integral of specific bands (in Figure 3, the following integration limits were used, E: 1936 – 1881 cm^{-1}, A_1: 2036 – 2009 cm^{-1}, phosphate asymmetric stretching: 1272 – 1197 cm^{-1}). An Olympus Fluorescence Illuminator accessory was attached on the right port of the microscope and equipped with an Ushio USH102D mercury lamp and a U-MWU filter cube (excitation 330-385 nm, dichroic mirror with 400 nm cut-off).

Additional chemical maps recorded at the SMIS beamline are shown in Figure S4 (integration limits used: E: 1939 – 1885 cm^{-1}, A_1: 2034 – 2009 cm^{-1}, phosphate asymmetric stretching: 1273 – 1199 cm^{-1}, amide I: 1716 – 1591 cm^{-1}). These maps were recorded by raster scanning the cells with steps of 2 µm in X and in Y with 128 scans at 4 cm^{-1} resolution in each square. The confocal aperture was set at 6x6 µm² and the microscope was operated in semi-confocal mode. The luminescence imaging was performed using an IX71 (Olympus) microscope equipped with a CCD (Orca-ER, Hamamatsu, Corporation, Sewickley, PA) and X20 (Plan FLN, NA 0.5) objective.

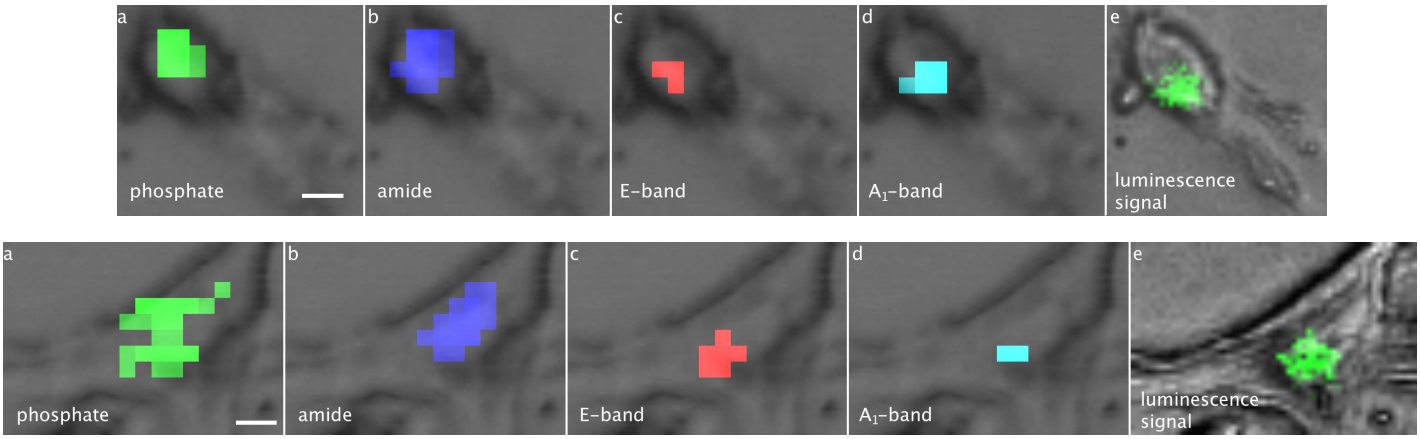

Figure S4. Two MDA-MB-231 cells incubated with **1** (10 µM, 1 h). SR-FTIR mappings, hot spots (see above for integration limits) (pixel size: 2x2 µm^2): *(a)* phosphate asymmetric stretching (green), (*b)* amide I stretching (blue)*, (c)* E-band (red), *(d)* A_1-band (cyan). *(e)* Epifluorescence image indicating the localization of **1** (green).

Synchrotron radiation UV spectromicroscopy (SR-UV-SM). Spectra were recorded at the Disco beamline (Synchrotron SOLEIL). Quartz coverslips with confluent fixed cells were deposited onto an inverted glycerin immersion objective (100x Ultrafluar, CARL ZEISS). Excitation was provided by the fully tuneable excitation from a bending magnet at Synchrotron SOLEIL[6] (350 nm excitation with a 0.2 nm bandpass). The fluorescence emission spectrum of the selected pixels was recorded through a spectrograph.[7]

FTIR spectra acquisition (for solid compound). Spectra were recorded on a Perkin Elmer Spectrum 100 equipped with an ATR sampling accessory and analysed using Perkin Elmer Spectrum software.

UV spectra acquisition. Solutions of **1** in different organic solvents were studied in quartz cuvettes with Varian Cary 300 Bio UV-Visible Spectrophotometer. Spectra analysis was performed using Cary Win UV software.

Fluorescence emission studies. Photon Technology International LPS 220 Spectrofluorimeter (with Felix software) and Jasco FP-8300 Spectrofluorimeter (with Spectra Manager software) were used to monitor emission properties of **1** in different solvents. Absolute emission quantum yields were measured by the method of Demas and Crosby[8] using quinine sulfate in 1 N sulfuric acid as the standard with a known emission quantum yield of 0.546 (λ_{ex} = 330-350 nm). The emission quantum yields of the samples were determined according to:

$$\phi_s = \phi_r \left(\frac{A_r}{A_s}\right)\left(\frac{D_s}{D_r}\right)\left(\frac{n_s^2}{n_r^2}\right)$$

where the subscripts s and r refer to the sample and the standard reference solution respectively; *n* is the refractive index of the solvents; *D* is the integrated emission intensity; A is the absorbance at the excitation wavelength (A < 0.1) and Φ is the luminescence quantum yield.
Quantum yields of **1** were nearly constant over 330 to 350 nm excitation and were typical of rhenium-pyta MLCT emitters[9].

Solvent	$\lambda^{abs}_{\max\ MLCT}$ (nm)	ε(L · mol^{-1} · cm^{-1})	$\lambda^{em}_{\max\ MLCT}$ (nm)	ϕ_s
H_2O/EtOH (1:1)	324	4.5 10^3	510	0.0019
CH_3CN	332	3.7 10^3	527	0.0018
CH_2Cl_2	346	4.0 10^3	525	0.0049

Table S1. Maximum wavelengths of emission and quantum yields of **1** in different solvents

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