Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

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Experimental section

General

All chemicals were obtained from commercial sources and used without further purification. NMR spectra were taken by using a Bruker DPX 300 spectrometer (300 MHz ^{1}H NMR) or a Bruker AMX 500-MHz with a TXI gradient probe. All spectra are referenced to residual solvent signal or TMS. NMR assignments were based on proton, dosy, roesy, cosy, hmbc and hmqc spectra. HPLC was performed on a Waters system by using a 1525EF pump and a 2489 UV detector. For preparative HPLC a Dr. Maisch, GmbH, Reprosil-Pur 120 C18-AQ 10 µm (250×20 mm) column was used and a gradient of 0.1 % TFA in H_2O/CH_3CN (95:5) to 0.1 % TFA in H_2O/CH_3CN (5:95) in 40 min was employed. For analytical HPLC a Dr. Maisch, GmbH, Reprosil-Pur C18-AQ 5 µm (250×4.6 mm) column was used and a gradient of 0.1 % TFA in H_2O/CH_3CN (95:5) to 0.1 % TFA in H_2O/CH_3CN (5:95) in 40 min was employed. MALDI-ToF measurements were performed on a Bruker Microflex.

***fac*-Ir(ppy)$_2$(ppy-β-Ala-en) (2)**

fac-Ir(ppy)$_2$(ppy-β-Ala-OH) (**1**) (7.7 mg, 10 µmol), synthesized as previously described[1], and PyBOP (5.7 mg, 11 µmol) were dissolved in 1 ml dry MeCN and added dropwise to a stirred solution of ethylenediamine (17 µl, 250 µmol) in 2 ml MeCN. The solution was stirred overnight in the dark at room temperature and followed by TLC (1% HOAc in EtOAc). The product was purified using preparative HPLC. The product fraction was lyophilized to give 3.4 mg (42% yield) of an orange powder.

MS (MALDI-ToF): $[C_{39}H_{35}IrN_6O_2]^+$ calcd 812.25, found 812.07. ^{1}H NMR (500 MHz, CD_3OD): δ= 8.12 (d, 2H, Py3), 8.06 (d, 1H, Py4), 8.03-8.00 (m, 3H, Py3', Py6), 7.78 (d, 1H, Ph3), 7.73-7.69 (m, 4H, Py4', Ph3'), 7.62-7.60 (m, 2H, Py6'), 6.98 (q, 2H, Py5'), 6.89-6.84 (m, 3H, Ph4, Ph4'), 6.77-6.68 (m, 6H, Ph5, Ph5', Ph6, Ph6'), 3.55 (m, 2H, B), 3.42 (t, 2H, A), 3.02 (t, 2H, A'), 2.46 (t, 2H, C).

***fac*-Ir(ppy)$_2$(ppy-β-Ala-cystamine) (3)**

fac-Ir(ppy)$_2$(ppy-β-Ala-OH) (**1**) (7.7 mg, 10 µmol), synthesized as previously described[1], PyBOP (5.7 mg, 11 µmol) and DIPEA (135 µl, 800 µmol) were dissolved in 2 ml dry MeCN and added dropwise to a stirred solution of cystamine dihydrochloride (56.3 mg, 250 µmol) in 2 ml dry DMSO. The solution was stirred for an additional 2 hours in the dark at room temperature. After evaporation of the solvents *in vacuo*, the product was purified by preparative HPLC chromatography. The product fraction was lyophilized to give 5.1 mg (56% yield) of an orange powder.

MS (MALDI-ToF): $[C_{41}H_{39}IrN_6O_2S_2]^+$ calcd 904.22, found 904.14. ^{1}H NMR (500 MHz, CD_3OD): 8.13 (d, 2H, Py3), 8.07 (d, 1H, Py4), 8.04-8.01 (m, 3H, Py3', Py6), 7.78 (d, 1H, Ph3), 7.74-7.70 (m, 4H, Py4', Ph3'), 7.61 (m, 2H, Py6'), 6.99 (q, 2H, Py5'), 6.89-6.84 (m, 3H, Ph4, Ph4'), 6.77-6.69 (m, 6H, Ph5, Ph5', Ph6, Ph6'), 3.55 (t, 2H, B), 3.49 (t, 2H, A), 3.24 (t, 2H, A'), 2.94, 2.81 (2t, 4H, D, D'), 2.44 (t, 2H, C).

***fac*-Ir(ppy)$_2$(ppy-β-Ala-en-Cy5) (5)**

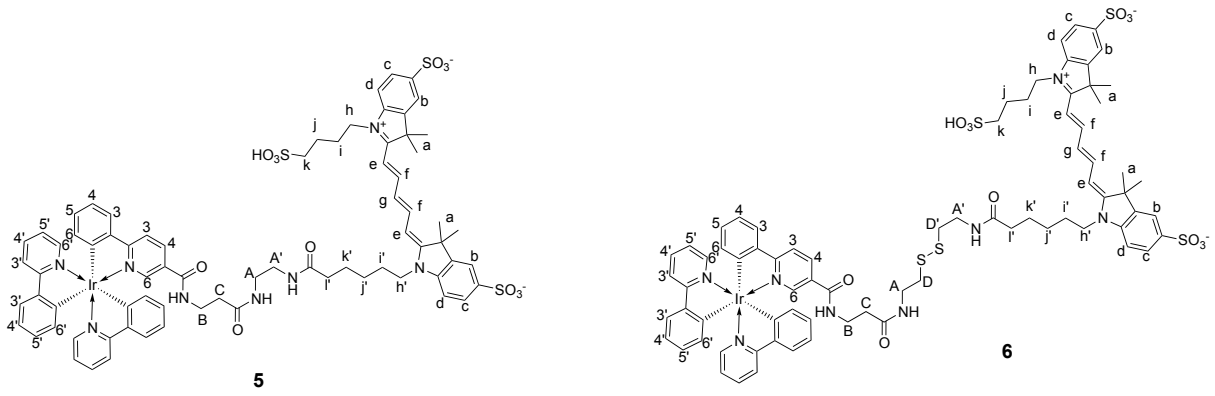
Cy5-COOH (4) (2.5 mg, 3.0 µmol), synthesized as described before[2], PyBOP (1.6 mg, 3.1 µmol) and DIPEA (2 µl, 10 µmol) were dissolved in 1 ml dry DMSO and stirred for 5 minutes at room temperature. A solution of *fac*-Ir(ppy)$_2$(ppy-β-Ala-en) (**2**) (2.0 mg, 2.5 µmol) in 0.5 ml dry DMSO was added and the reaction was stirred in the dark at room temperature for an additional 3 days. The solution was acidified with TFA and H_2O was added. The solution was purified using preparative HPLC. The product fraction was collected and lyophilized to give 2.0 mg (64 % yield) of a bluish green powder.

MS (MALDI-ToF): $[C_{74}H_{78}IrN_8O_{12}S_3]^+$ calcd 1559.45, found 1559.44. ^{1}H NMR (500 MHz, CD_3OD): δ= 8.27 (m, 2H, f), 8.15-7.97 (m, 4H, Py3, Py3', Py4), 7.91-7.86 (m, 5H, b, c, Py6), 7.78 (m, 2H, Ph3'), 7.71-7.66 (m, 3H, Py4', Ph3), 7.58 (m, 2H, Py6'), 7.30 (dd, 2H, d), 6.97 (m, 2H, Py5'), 6.87-6.65 (m, 12H, Ph4, Ph4', e, g, Ph5, Ph5', Ph6, Ph6'), 4.02 (m, 4H, h, h'), 3.56 (t, 2H, B), 3.20 (m, 4H, A, A'), 2.91 (m, 2H, k), 2.41 (t, 2H, C), 2.08 (t, 2H, l'), 1.92 (m, 4H, i, j), 1.77-1.70 (m, 14H, i', a), 1.58 (t, 2H, k), 1.34 (m, 2H, j').

***fac*-Ir(ppy)$_2$(ppy-β-Ala-cystamine-Cy5) (6)**

Cy5-COOH (**4**) (2.0 mg, 2.4 μmol), synthesized as described before[2], PyBOP (1.3 mg, 2.5 μmol) and DIPEA (2 μl, 10 μmol) were dissolved in 1 ml dry DMSO and stirred for 5 minutes at room temperature. A solution of *fac*-Ir(ppy)$_2$(ppy-β-Ala-cystamine) (**3**) (2.0 mg, 2.0 μmol) in 0.5 ml dry DMSO was added and the reaction was stirred in the dark at room temperature overnight and the product was purified using preparative HPLC. The product fraction was collected and lyophilized to give 1.1 mg (33% yield) as a bluish green powder.

MS (MALDI-ToF): $[C_{76}H_{82}IrN_8O_{12}S_5]^+$ calcd 1651.4, found 1650.6. ^{1}H NMR (500 MHz, CD_3OD): δ= 8.28 (m, 2H, f), 8.13-7.98 (m, 4H, Py3, Py3', Py4), 7.91-7.86 (m, 5H, b, c, Py6), 7.78-7.67 (m, 5H, Py4', Ph3', Ph3,), 7.59 (m, 2H, Py6'), 7.35-7.26 (dd, 2H, d), 6.98 (m, 2H, Py5'), 6.86-6.67 (m, 12H, Ph4, Ph4', e, g, Ph5, Ph5', Ph6, Ph6'), 4.05 (m, 4H, h, h'), 3.55-3.36 (m, 6H, B, A, A'), 2.91 (m, 2H, k), 2.81-2.75 (m, 4H, D, D'), 2.46 (t, 2H, C), 2.17 (t, 2H, l'), 1.94 (m, 4H, i, j), 1.77-1.61 (m, 16H, i', a, k'), 1.34 (m, 2H, j').



Scheme S1. Proton numbering for NMR assignments

Spectroscopic measurements

UV-VIS spectra were measured on a Perkin Elmer Lambda Bio 20 spectrometer. Room temperature fluorescence and phosphorescence emission spectra were measured with a Horiba Jobin Yvon VS140 Linear Array Spectrometer. For excitation a Luxeon III blue 457 nm LED and a Luxeon III red 627 nm LED were used. For luminescence measurements, the absorbance was kept below 0.1 to prevent inner filter effects. In the experiments were SDS micelles were formed, luminescence intensity measurements were performed using a Perkin Elmer S55.

Low temperature luminescence spectra were measured in a closed glass vial containing **5** in H_2O or H_2O:EtOH 1:1. An optical fiber was attached to the vial and it was emerged in a bath of liquid N_2. After reaching equilibrium in temperature (77 K), the sample was excited using a laser of 405 nm or 633 nm. Emission spectra were measured with a Horiba Jobin Yvon VS140 Linear Array Spectrometer. Long integration times (50s) were needed due to ice formation and low emission intensities.

Luminescence lifetime measurements were carried out using time-correlated single photon counting. Iridium complexes (**1-3, 5, 6**) were dissolved in MeOH:PBS 4:1 and excited using a picosecond pulsed

diode laser (PicoQuant LDH-P-C-375, 372 nm) operated at 2.5 MHz. Luminescence emission was detected at 600 nm on a microchannel plate detector. Reduction of the disulfide bond in the cuvette was performed by addition of 10 mg cysteamine hydrochloride to a solution of **6**. Lifetimes of compounds **1-3** were fit to a monoexponential decay model, and for compounds **5** and **6** a biexponential fit was used. Luminescence lifetime of Cy5 (**4**) was determined in MeOH:PBS 4:1. The solution was excited using a picosecond pulsed diode laser (PicoQuant LDH-P-C-375, 372 nm) operated at 10 MHz. Luminescence emission was detected at 680 nm on a microchannel plate detector.
In all cases, GraphPad Prism 6 was used for fitting of curves.

Disulfide cleavage in solution
To monitor activation of Cy5 fluorescence, Ir-S-S-Cy5 (**6**) was dissolved in 1 ml MeOH:phosphate buffer (10 mM pH 7.0) 4:1 to a concentration of 0.6 mM. Cysteamine hydrochloride (10 mg, 88 mmol) was added and fluorescence spectra were measured every 5 minutes by excitation with 627 nm light. To monitor $Ir(ppy)_3$ phosphorescence activation, Ir-S-S-Cy5 (**6**) was dissolved in 1 ml MeOH:phosphate buffer (10 mM pH 7.0) 4:1 to a concentration of 5 mM. The experiment was performed at higher concentration due to the lower brightness of $Ir(ppy)_3$ compared to Cy5. Cysteamine hydrochloride (10 mg, 88 mmol) was added and fluorescence spectra were measured every 5 minutes by excitation with 457 nm light. Both reactions were performed in a closed cuvette at room temperature and shielded from light.

Cell culture
The murine breast cancer cell line 4T1 (kindly provided by Dr. Olaf van Tellingen, NKI/AvL, Amsterdam, The Netherlands) was maintained in Dulbecco's minimum essential medium (DMEM) enriched with 10% fetal bovine serum and 5 mL Penicillin/Streptomycin (10000 units/mL Penicillin; 10000 µg/mL Streptomycin) (all Life Technologies Inc., Breda, The Netherlands). Cells were kept under standard culture conditions.

Confocal imaging
Live cell images were taken on a Leica SP5 confocal microscope under 63x magnification. $Ir(ppy)_3$ luminescence was measured using a 458 nm excitation Ar laser line and emission was collected at 560-620 nm. Cy5 fluorescence was measured using a 633 nm HeNe excitation laser and emission was collected at 650-700 nm.

Micelle formation
To a solution of **5** (0.4 µM) in saline (0.9% NaCl in H_2O) was added sodium dodecyl sulfate (SDS) (60 mM in saline) in portions of 10 µl. In total 11 additions were used to achieve a final concentration of 2.2 mM SDS. After approximately 20 seconds equilibrating, luminescence intensity was measured after each addition using excitation of 630 nm and emission of 670 nm.

Partial activation by interaction with cell membrane
4T1 murine breast cancer cells were grown on a glass-bottom well, after which they were incubated at 0-4 °C in a 1 µM solution of Ir-S-S-Cy5 (**6**) or Ir-Cy5 (**5**) in DMEM for 1 hour. The cells were washed with PBS and kept on ice to prevent internalization.

Disulfide cleavage in living cells
4T1 murine breast cancer cells were grown on a glass-bottom well, after which they were incubated at 37 °C in a 1 µM solution of Ir-S-S-Cy5 (**6**) in DMEM for 24 hours. Shorter incubation time showed no

clear visualization of the $Ir(ppy)_3$ phosphorescence, only a weak Cy5 fluorescence signal could be seen. Cells were thoroughly washed with PBS. In one experiment, Ir-S-S-Cy5 was added shortly before imaging to a concentration of 5 µM (Figure S11). LysoTracker Green® was added in a concentration of 50 nM (Figure S10). As a negative control, cells were incubated with **5** under similar conditions. No negative effects of the compounds on cell growth were observed.

Lifetime imaging cells

FD-FLIM images were obtained with LI-FLIM hardware (Lambert Instruments, Roden, Netherlands) and software (v.1.2.23.59) with a modulated GaAs intensifier fiber-optically coupled to a digital CCD-camera (LI^2CAM, Lambert Instruments) attached to the microscope (Leica DMIRE2; Leica Microsystems, Heidelberg, Germany) with a 63× objective (numerical aperture 1.3, glycerine-immersion). A 1-W, 442-nm LED was modulated at 1 MHz, and light passed a CFP/YFP filtercube (excitation 436/12 & 500/20, dichroic 445 & 515, emission 467/37 & 545/45). Emitted light (emission peak at ~570 nm) was collected from iridium-compound loaded cells, plated on 24-mm coverslips. Rhodamine 6G in H_2O was used as reference (τ_{phase}: 3.83 ns at 37°C) (Sigma-Aldrich, St. Louis, MO, USA). The cells were placed in preheated (37°C) 4-(2-hydroxyethyl)-1-piperazineethane-sulfonic acid (HEPES)–buffered saline (140 mM NaCl, 5 mM KCl, 1 mM $MgCl_2$, 1 mM $CaCl_2$, 10 mM glucose, and 10 mM HEPES, pH 7.4) after washing with PBS. All the experiments were performed at 37°C. Average lifetime was determined by averaging a minimum of four cells.

Calculation of Förster distance

R_0 was estimated based on the standard formulas, assuming a $Ir(ppy)_3$ quantum yield of 0.05 in H_2O (rough estimation) and an extinction coefficient of Cy5 of 250,000.
Importing the emission spectrum of $Ir(ppy)_3$ and the absorption spectrum of Cy5 in an excel sheet developed by H. Gabor and J. Szollosi[3] resulted in a calculated R_0 of 4.8 nm

Supporting results

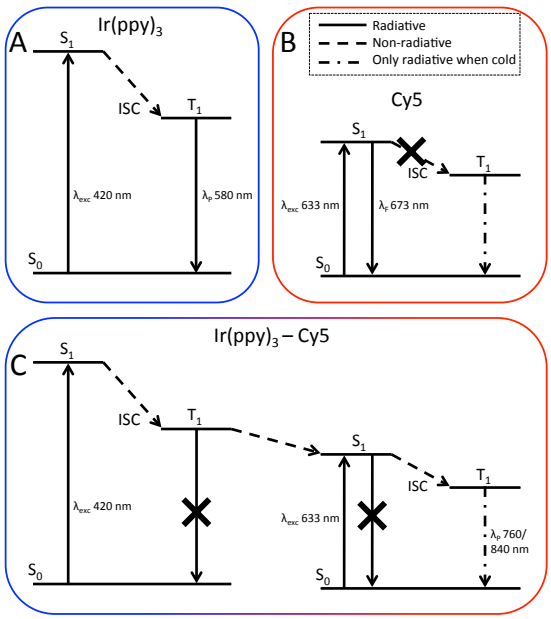


Figure S1. Simplified Jablonski diagram of A) $Ir(ppy)_3$, B) Cy5 and C) $Ir(ppy)_3$-Cy5 covalently linked. ISC = Inter System Crossing

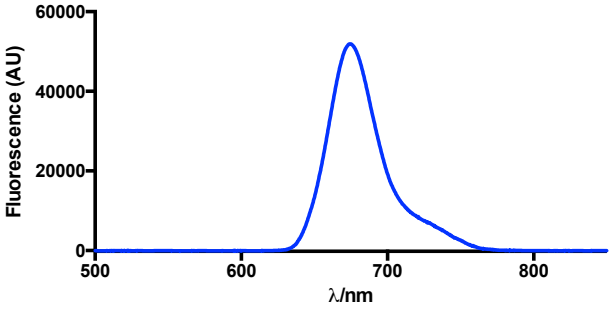


Figure S2. Luminescence emission of 5 by excitation at 457 nm in MeOH:PBS 4:1. There is no phosphorescence of $Ir(ppy)_3$ (FRET donor) visible, only emission from Cy5 (FRET acceptor) can be detected.

Mechanisms partial activation

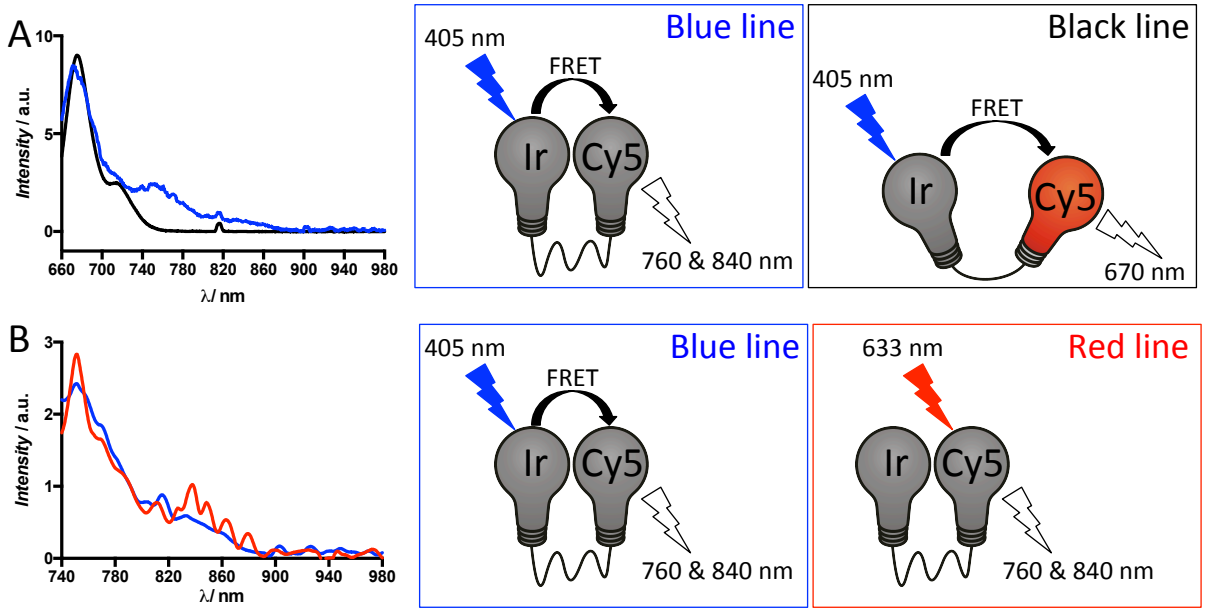


Figure S3. A) Normalized luminescence spectra of **5** at 77 K by excitation at 405 nm, using different solvents: MilliQ (blue line) and 50% EtOH in MilliQ (black line) and a corresponding schematic drawing of the difference between the compound in different solvents. B) Smoothed zoom of the spectra of **5** at 77 K in H_2O, showing the two distinct triplet emissions of Cy5 and a corresponding schematic drawing of the difference between different excitation sources. Two different lasers were used; 405 nm for $Ir(ppy)_3$ excitation leading by FRET to Cy5 excitation (blue line) and 633 nm for Cy5 excitation (red line).

The quenching of Cy5 is proposed to take place by spin-orbit coupling that is induced by the nearby Ir atom. This effect allows the normally forbidden transition from the singlet excited state to a triplet excited state of Cy5, which emits at 77 K at 760 nm (*trans*-T_1) and 840 nm (*cis*-T_1).[4]

The main peak in Figure S3A at 670 nm corresponds to emission from the S_1 state of Cy5. This peak is always visible, although much more intense in a more apolar solvent (spectra are normalized for comparison). The triplet peaks at 760 nm and 840 nm are only visible in pure H_2O at 77 K. The small peaks at 810-815 nm in the blue and black lines are the result of reflection of the 405 nm laser.

The triplet emissions of Cy5, that were only visible at low temperatures due to spin-orbit coupling, are not present when a more apolar solvent was added (Figure S3A, black line). This indicates that the solvent induces a conformational change that makes spin-orbit coupling less efficient. This effect is observed with direct Cy5 excitation (633 nm) and with $Ir(ppy)_3$ excitation (405 nm) leading to a Cy5 excited state by FRET (Figure S3B).

2D ROESY NMR was used to investigate interactions between Cy5 and $Ir(ppy)_3$ (see Appendix). In CD_3OD there are no cross-peaks observed, for **5** nor **6**, between Cy5 (a-g) and $Ir(ppy)_3$ (Py3-Py6, Ph3-Ph6); all ROESY peaks in the aromatic region correspond to internal Cy5 interaction or internal $Ir(ppy)_3$ interactions. We can conclude that in CD_3OD there is no close proximity of the two subunits, corroborating conclusions based on he optical data. Unfortunately, the solubility of 5 and 6 is not high enough in D_2O to record ROESY spectra that could confirm the close proximity of the subunits in H_2O/PBS.

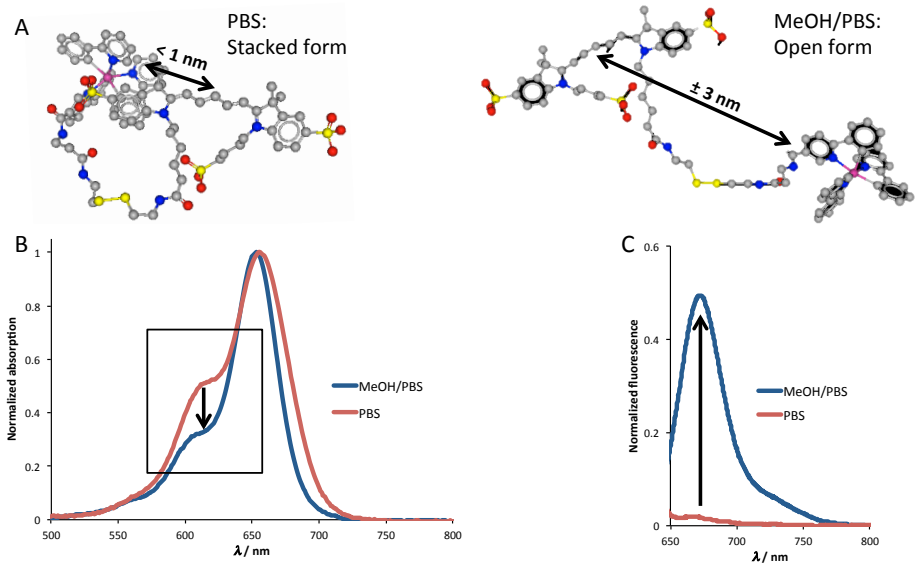


Figure S4. A) Schematic image of **6** with short or longer distance between the luminophores. B) The shoulder at 610 nm is indicative for stacking interactions (in the black square). This shoulder is decreased by addition of MeOH (black arrow), indicating a decrease of stacking interactions. C) Fluorescence intensity is higher in MeOH:PBS 4:1 than in PBS (effect by MeOH is indicated by the black arrow). Emission spectra were collected by excitation with 627 nm light and spectra are normalized to Cy5 (**4**).

By changing the solvent from H_2O to a more apolar medium, there is a clear change in the absorption spectra of Cy5 (Figure S4B). A decrease is observed in the peak that indicates stacking interactions.[5] This conformational change corresponds to a decrease in spin-orbit coupling efficiency (see above), leading to a 30-fold Cy5 signal increase (Figure S4C).

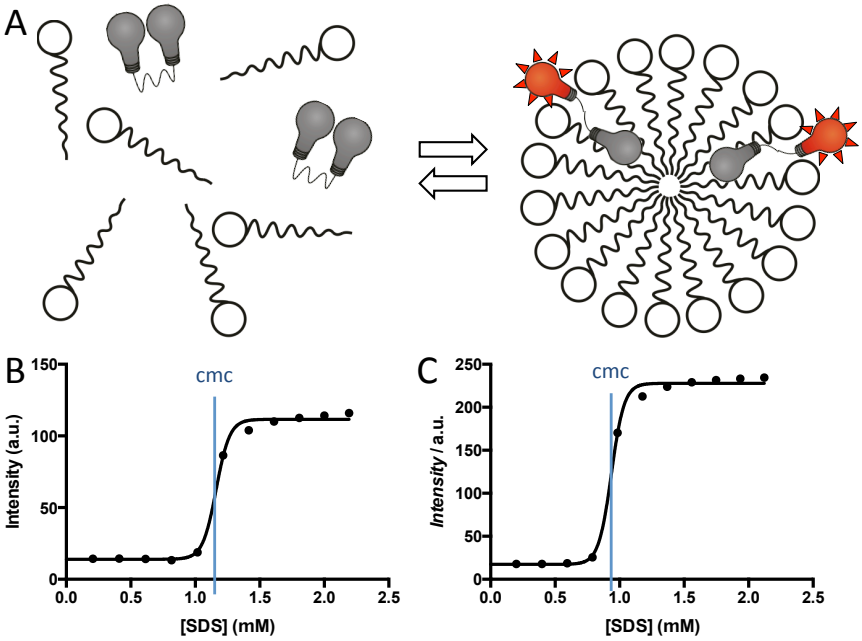


Figure S5. A) Artist impression of the interaction of our $Ir(ppy)_3$-Cy5 compounds with SDS below (single molecules, left side of the arrow) and above (micelles, right side of the arrow) the critical micelle concentration. B) Luminescence intensity of Cy5 in **5** in increasing amounts of SDS in 0.9% NaCl in H_2O. A sigmoidal fit shows a critical micelle concentration (cmc) of 1.16 mM, which is in line with Below the cmc, low intensity is observed. C) The same curve for **6**.

The critical micelle concentration found with this experiment is in line with literature value of SDS.[6] Above this concentration, micelles are formed. Micelle formation gives a steep increase in luminescence intensity of both **5** and **6** (Figure S5). We propose that again a change in polarity results in a decrease in spin-orbit coupling, resulting in an increase in Cy5 luminescence intensity. The increase in **6** –the compound with the largest spacer length of the two– is larger, which indicates a greater efficiency in conformational change compared to **5**.

The SDS micelles were used as a model for the cell membrane. Interaction of the compounds with the cell membrane also leads to local activation of Cy5 emission. Incubation of the cells with **5** (Figure 2) or **6** (Figure S6) for 1h showed similar results.

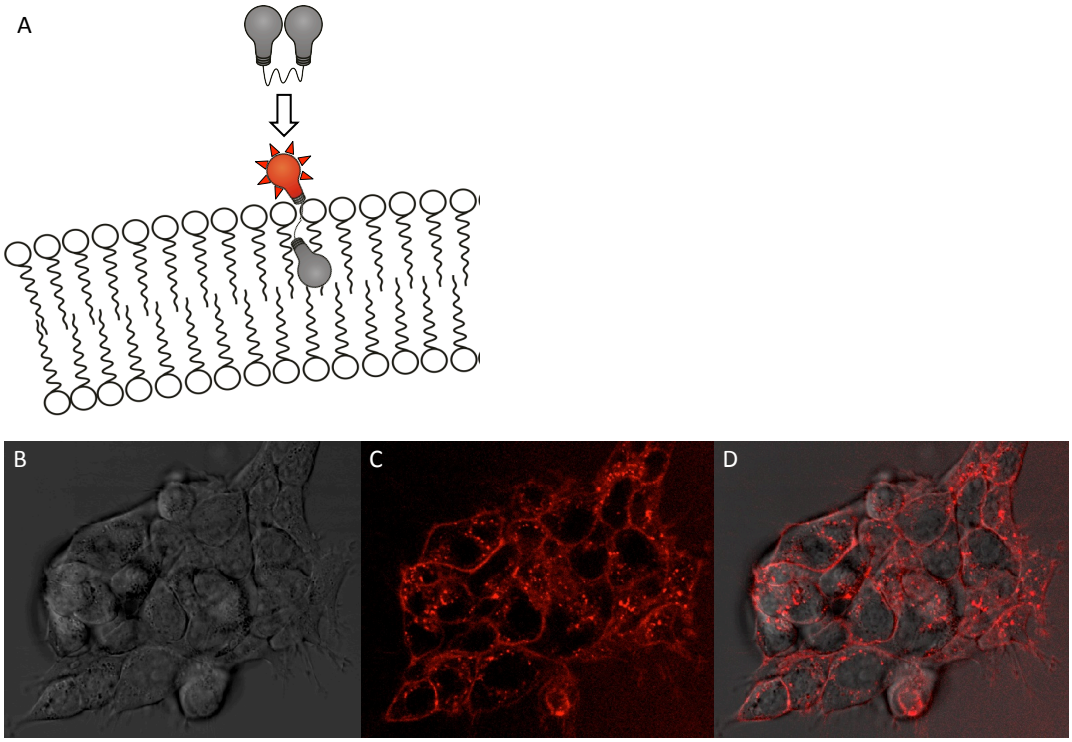
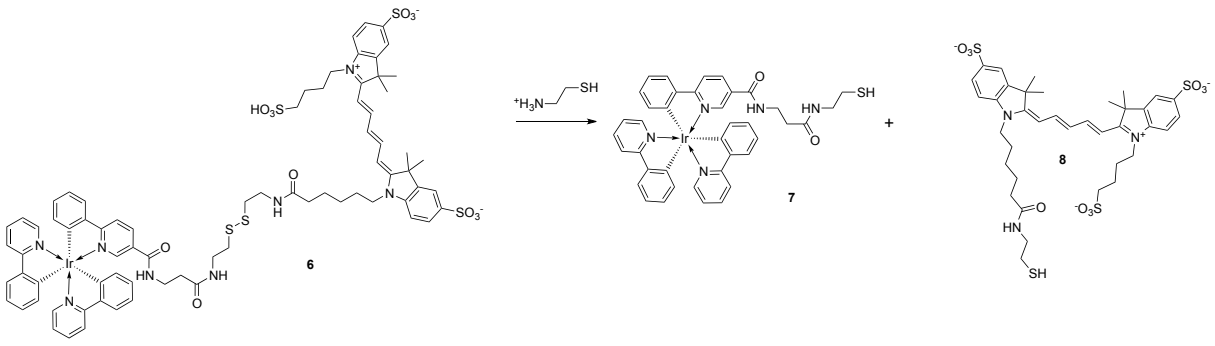


Figure S6. A) An impression of the proposed interaction of our compounds with a cell membrane B-D) Confocal microscope image showing partial activation of **6** in the membranes of 4T1 cells when the cells were incubated with **6** for 1h at 4 °C. B) Differential interference contrast, C) Cy5 emission in red, D) overlay.

Cleavage of the disulfide linker

Cleavage of **6** by cysteamine was first followed in PBS, since this solvent mimics the in vitro environment, and a solution of **6** in PBS showed efficient quenching of both luminophores. This showed a great increase in the intensity of Cy5 emission (Figure S7). However, no $Ir(ppy)_3$ phosphorescence was recovered after cleavage. To study this effect further, **7** was synthesized by reduction of the disulfide bond of **3** with Zn powder in acidic solution[7]. Compound **7** was very poorly soluble in PBS, explaining the lack of phosphorescence activation. For further research, MeOH:PBS 4:1 was used as a suitable solvent.



Scheme S2. Cleavage of the disulfide bond of **6** by cysteamine

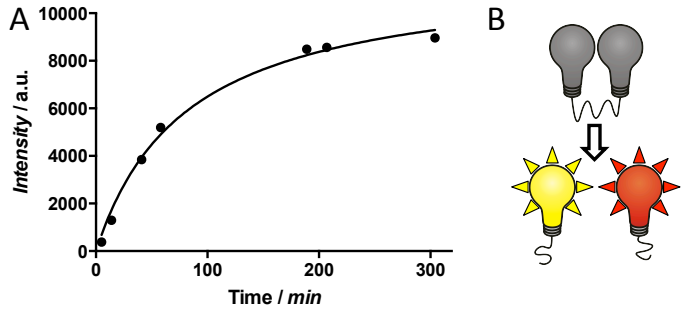


Figure S7. A) Activation of Cy5 luminescence after addition of cysteamine to a solution of **6** in PBS, fitted with a curve for a catalytic reaction. In PBS, no activation of $Ir(ppy)_3$ phosphorescence was seen due to poor solubility of product $Ir(ppy)_3$-SH (**7**) in PBS. B) Schematic representation of the cleavage reaction.

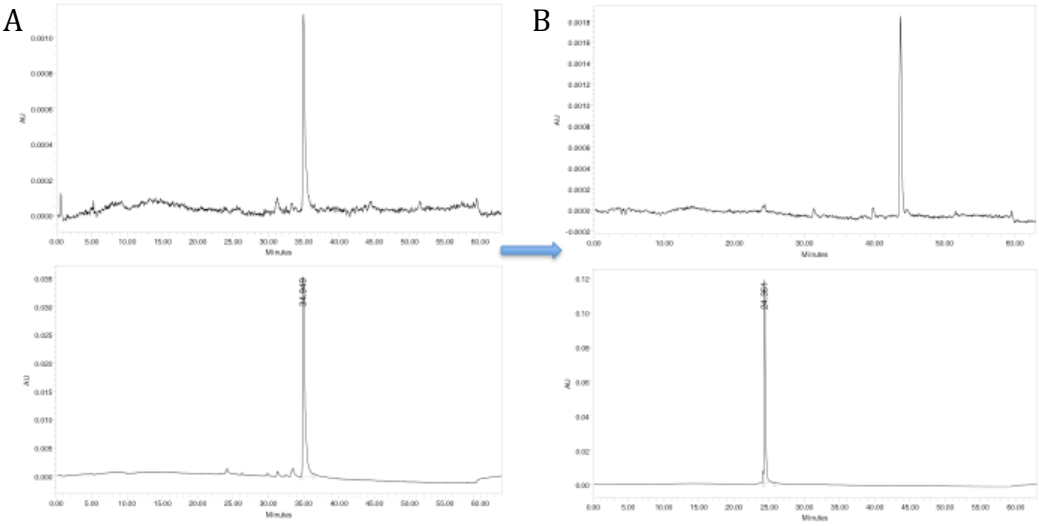


Figure S8. HPLC traces of A) **6** as synthesized and B) after reaction with cysteamine, followed at 420 nm (top) and 650 nm (bottom)

HPLC analysis with dual-channel absorption detection at 420 nm and 650 nm (to follow $Ir(ppy)_3$ and Cy5, respectively) showed that **6** (35 minutes) was completely removed and that two new peaks emerged, one with absorption at 420 nm (42 minutes) and another with absorption at 650 nm (25 minutes). This indicated that Cy5 (**8**) and $Ir(ppy)_3$ (**7**) were formed. The peak with absorption at 420 nm had the same retention time as the synthesized desired product **7**, confirming the selective cleavage of the disulfide bond.

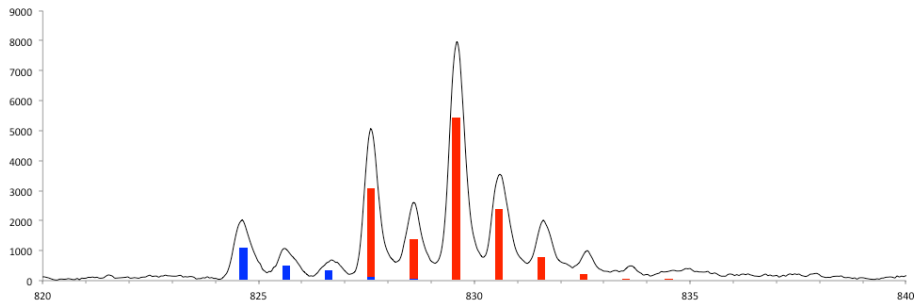


Figure S9. MALDI mass spectrum of 6 after reaction with cysteamine. Overlay with calculated mass spectra of 7 (in red) and 8 (in blue)

Mass spectrometry also confirmed successful cleavage of the disulfide bond. The products were also analyzed by MALDI mass spectrometry (figure S9). This showed two peaks with m/z of 829 and 824, corresponding to *fac*-$Ir(ppy)_2$(ppy-β-Ala-CH_2CH_2SH) (**7**) and Cy5-CH_2CH_2SH (**8**).

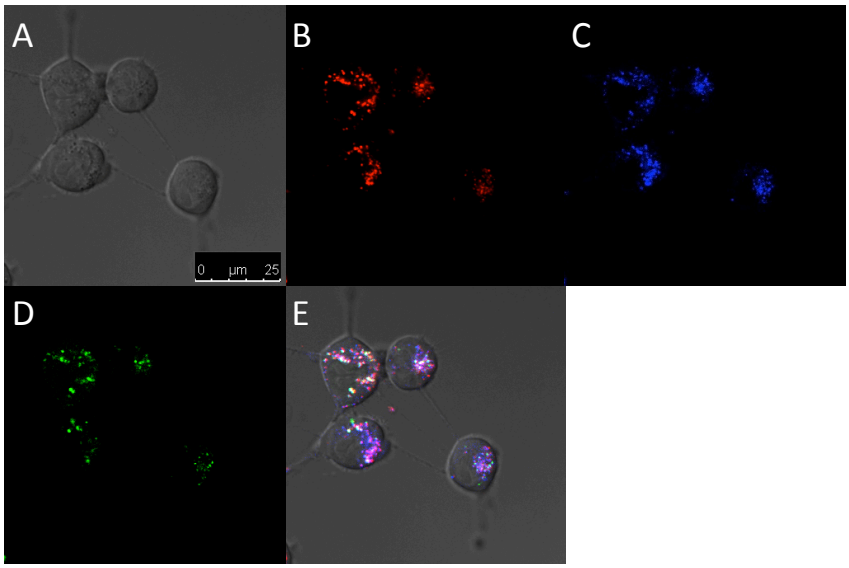


Figure S10. Confocal microscopy images of viable 4T1 cells incubated for 24h at 37°C with 6. A) differential interference contrast, B) Cy5, C) $Ir(ppy)_3$, D) LysoTracker® Green, and E) overlay of channels

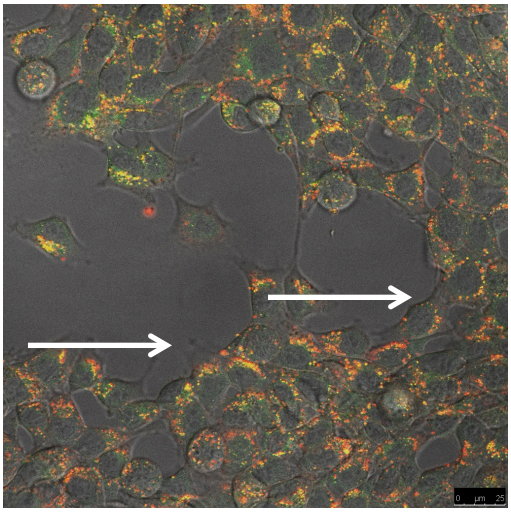


Figure S11. Confocal microscopy images of viable 4T1 cells incubated for 24h at 37°C with **6** (1 µM); a high concentration of **6** (5 µM) was added minutes before imaging (seen as an optical blue solution). Overlay of differential interference contrast, $Ir(ppy)_3$ (green) and Cy5 (red). The area between the cells (white arrows) shows no signal, underlining the difference in intensity before and after cleavage.

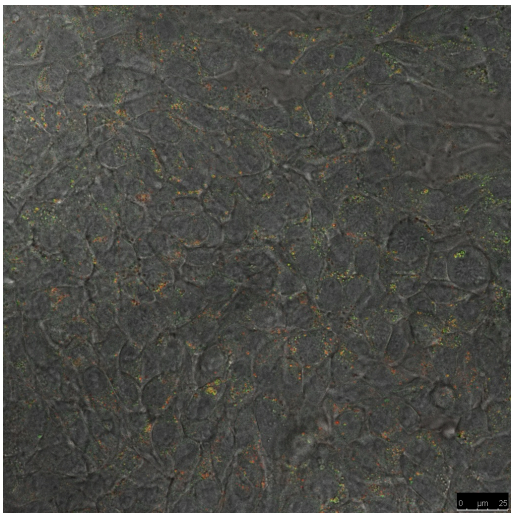


Figure S12. Confocal microscopy images of viable 4T1 cells incubated for 24h at 37°C with **5**. Overlay of differential interference contrast, $Ir(ppy)_3$ (Green) and Cy5 (red). These results show that the 'uncleavable' probe shows only very little signal.

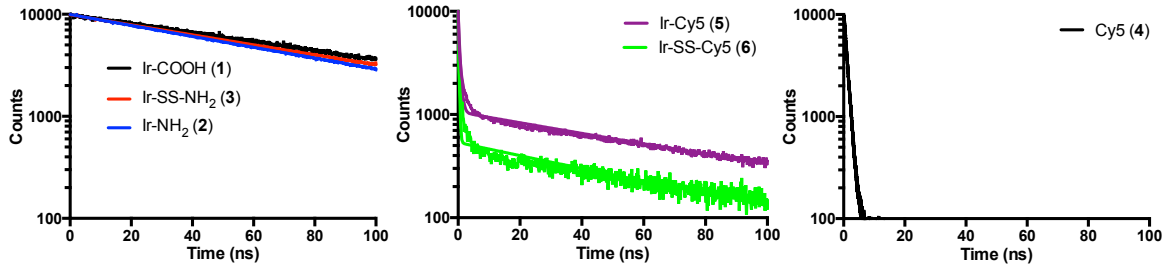


Figure S13. Luminescence decay traces at 600 nm (680 nm for **4**) of selected compounds. All compounds were dissolved in MeOH:PBS 4:1, excited with 372 nm at 2.5 MHz (10 MHz for **4**). All graphs are set to 10000 counts at t = 0.

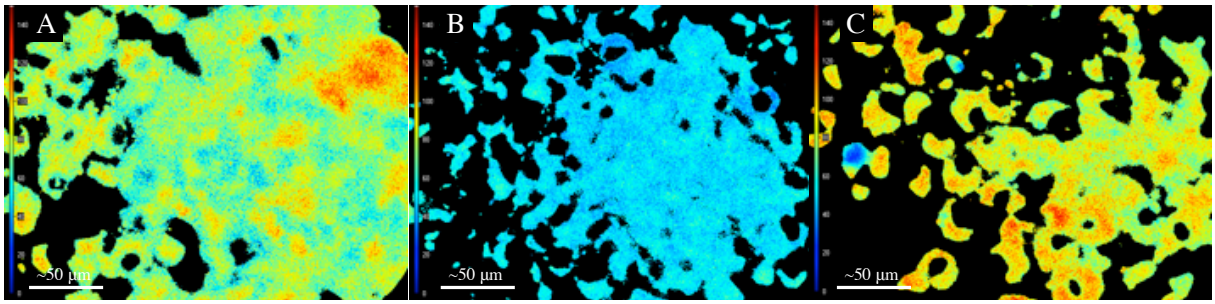


Figure S14. FLIM images of 4T1 cells, showing the difference in lifetime between A) **3** (Ir-S-S-NH_2), **B) 5** ($Ir(ppy)_3$-Cy5, quenched) and **6** ($Ir(ppy)_3$-S-S-Cy5 activatable).

There is a clear difference between the uncleavable compound **5** (Figure S14B) and the cleaved compound (Figure S14C). The lifetime observed after cleavage of the disulfide bond in **6** is similar (90 ns) to the lifetime of free $Ir(ppy)_3$ (Figure S14A), and both correspond to the lifetimes measured in solution (see Table 1, main text).

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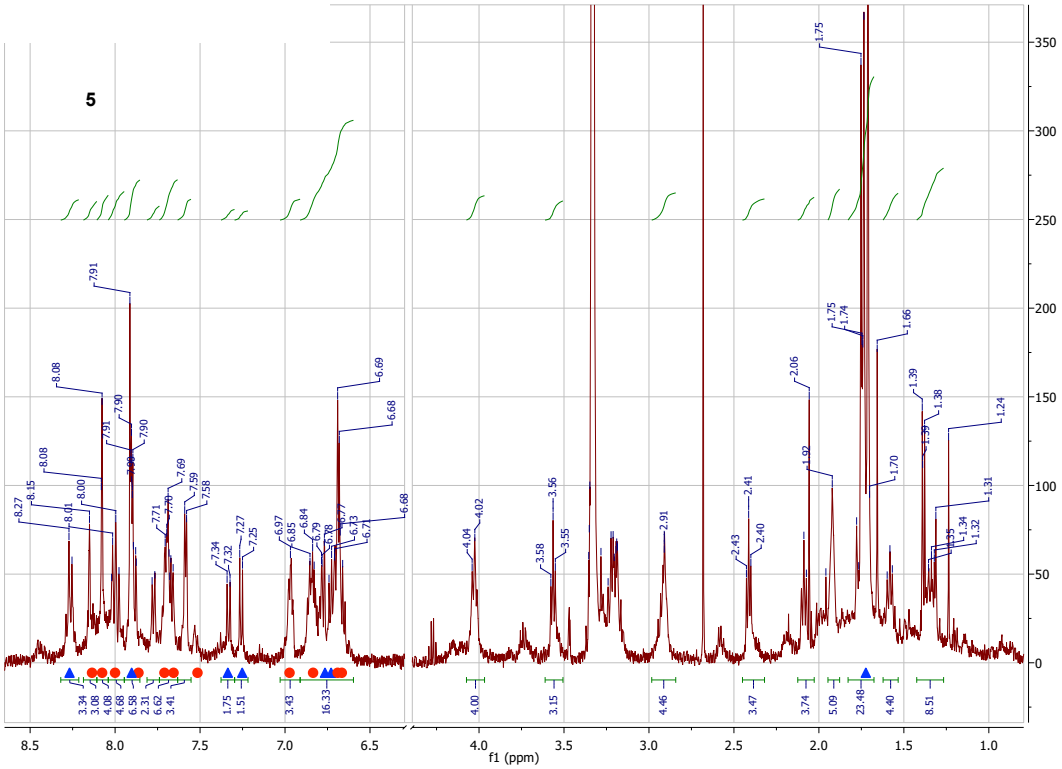
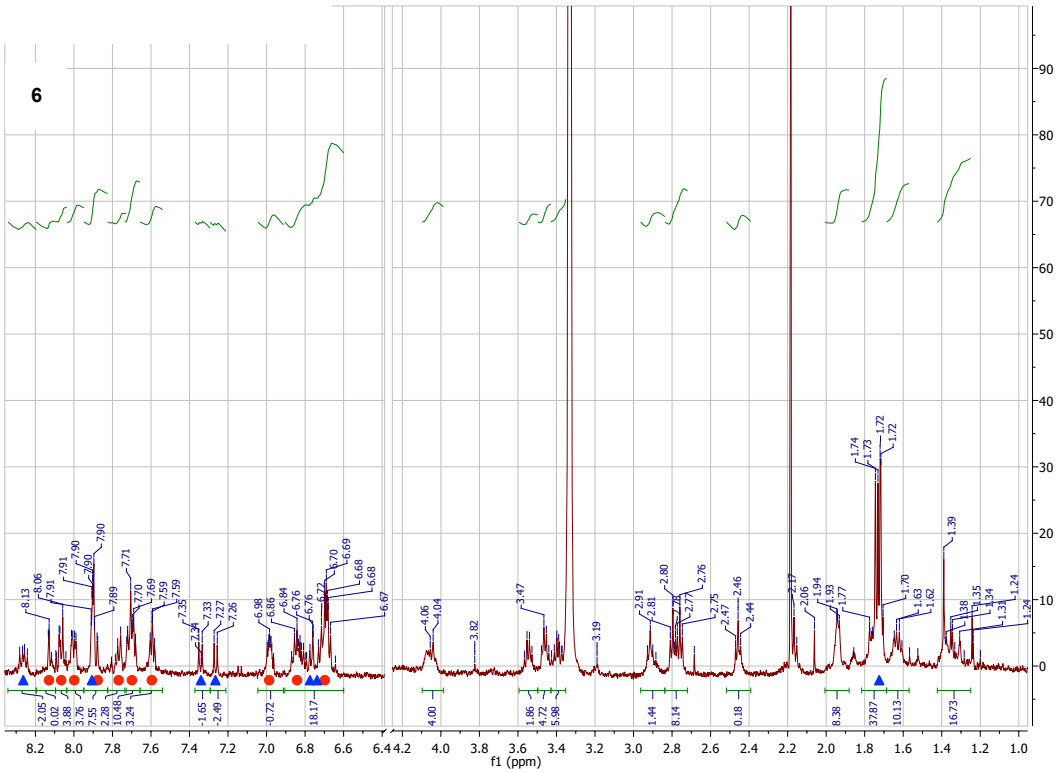
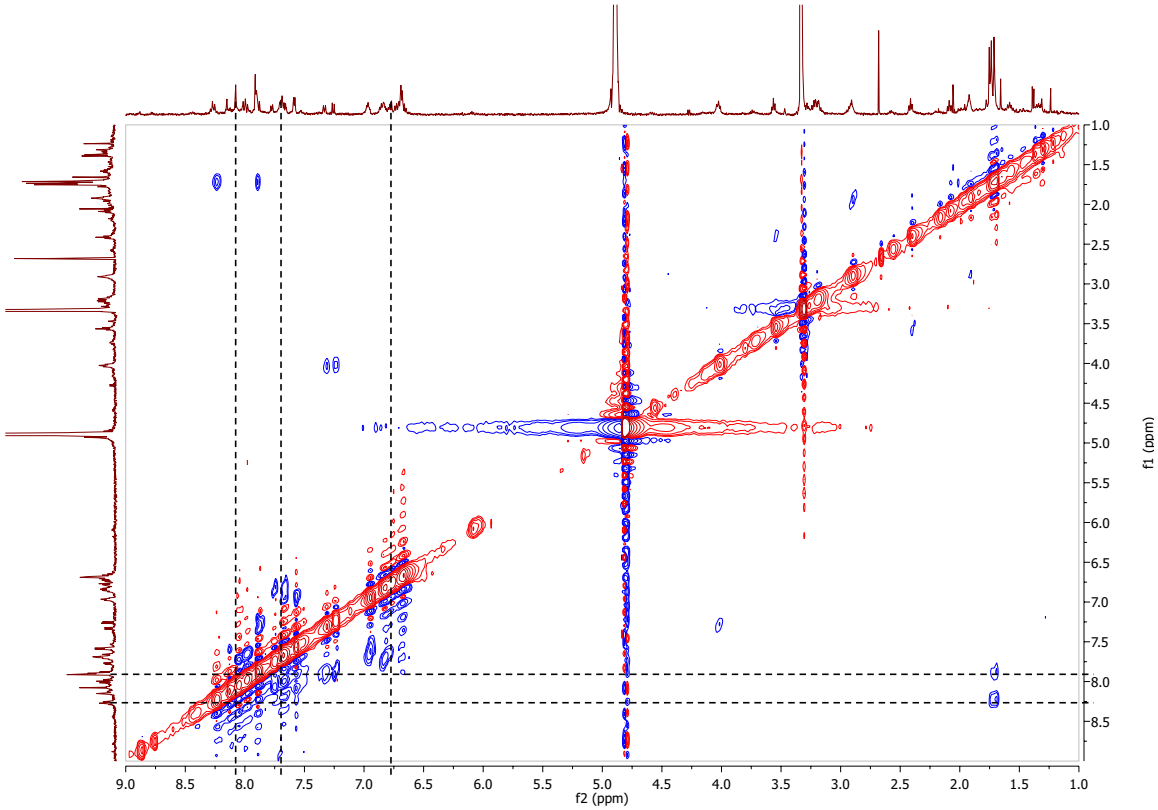
Appendix: NMR spectra



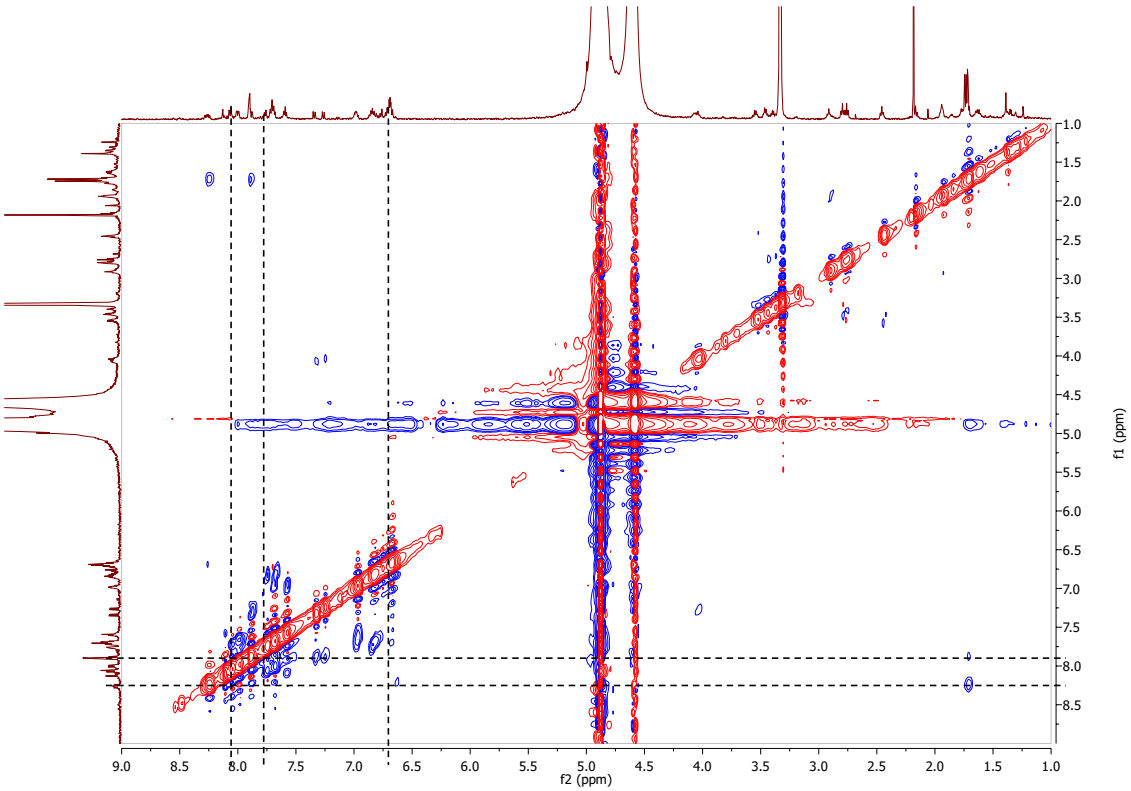
^{1}H-NMR of **5** in CD_3OD. Red circles indicate peaks from $Ir(ppy)_3$; blue triangles indicate peaks from Cy5



^{1}H-NMR of **6** in CD_3OD. Red circles indicate peaks from $Ir(ppy)_3$; blue triangles indicate peaks from Cy5



ROESY spectrum of **5** in CD_3OD



ROESY spectrum of **6** in CD_3OD

In both ROESY spectra, the vertical lines represent some selected peaks of $Ir(ppy)_3$; the horizontal lines are drawn on selected peaks of Cy5. On the intersections of these lines (and all other $Ir(ppy)_3$ and Cy5 peaks), no ROESY signals were observed.