Supplemental Information

Porphyrin Dyes for Nonlinear Optical Imaging of Live Cells

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Supplemental Data Items

1. Linear optical spectra of the compounds

**Figure S1.** Linear optical spectra of the porphyrin compounds, related to Figure 2: Comparison of absorption and emission spectra (in DMF at 25 °C) of cationic charged dyes AK-1, JR-2, JF-1, AK-1.Cu and neutral dyes, JW-1, IG-1, and JF-2.

2. Cell imaging

**Figure S2.** Imaging of non-charged dyes JW-1 and IG-1 in HEK 293T cells, related to Figure 3: The fluorescence images of the dyes, JW-1 and IG-1 in the cells show no localization in the plasma membrane. No SHG was seen from the intracellular area. Scale = 20 µm (JW-1), 10 µm (IG-1).
Figure S3. Imaging of JR-2 in HEK 293T cells, related to Figure 3: The fluorescence and SHG JR-2 in HEK 293T cells. The dyes could be seen staining the intracellular organelles of the cells to give both fluorescence and SHG signals. $\lambda_{\text{ext}} = 840 \text{ nm}$, scale bar = 10 µm.

Figure S4. Co-localization of JR-2 with ER Tracker in HEK 293T cells, related to Figure 3: The SHG image is from only JR-2, while the fluorescence image is from only ER-Tracker™ Red dye detected in the red channel (570–625 nm). Fluorescence + SHG shows the co-localization of JR-2 with ER-Tracker™ Red dye. Scale bar = 20 µm.

The co-localization experiment (Figure S4) shows that SHG is generated from JR-2 dye molecules staining the intracellular organelles including endoplasmic reticulum. Although the porphyrin dye also emits fluorescence, it is not detected because the light was passed through a 570–625 nm filter (the dye does not emit in this range) before being detected through the PMT.
Figure S5. Imaging of JF-1 in LN-18 cells, related to Figure 3: Fluorescence and SHG images of JF-1 (10 µM) in LN-18 cells. $\lambda_{\text{ext}} = 840$ nm, scale bar = 20 µm.

Figure S6. Fluorescence imaging of FM4-64 in mouse brain slice, related to Figure 4: 3D image of a section of mouse brain slice stained with FM4-64 (50 µM) without Advasep. The dye could be seen absorbed all over the area staining the neural tissue and cells alike. Scale bar = 20 µm.
**Figure S7.** SHG imaging of only SHG dye, JF-1.Cu, related to Figure 6: Images of JF-1.Cu (40 µM) incubated in LN-18 cells. The LN-18 cells were cultured and maintained following the same protocol as HEK 293T cells. The dye does not emit any fluorescence but generates strong SHG signals from the plasma membrane. The overlay of fluorescence and SHG images show that no yellow color (if red and green are mixed) is generated. \( \lambda_{\text{ext}} = 850 \text{ nm} \), scale bar = 20 µm.

**Figure S8.** Imaging of FM4-64 and Di-4-ANEPPS as control experiments, related to Figure 7: Dicationic and zwitterionic dyes, FM4-64 (10 µM) and di-4-ANEPPS (10 µM) incubated in with the HEK 293T cells. The images were taken immediately after the dye incubation. FM4-64 does not get internalized in the cells just after incubation as minimal fluorescence is visible from the intracellular area. Di-4-ANEPPS is internalized by the cells apart from staining the plasma membrane. Significant fluorescence is seen from inside the cells stained with di-4-ANEPPS apart from bright SHG from the plasma membrane. \( \lambda_{\text{ext}} = 840 \text{ nm} \), scale bar = 20 µm.
Transparent Methods

1. Linear optical properties of the porphyrin-based dyes

The UV-Vis (Perkin Elmer Lambda 20) and fluorescence (Edinburgh Instruments, Spectrofluorometer FS5) measurements were performed in DMF at 25 °C.

Measurement of fluorescence quantum yields

The quantum yield of a compound is given by the equation:

$$\phi_C = \frac{I_C A_C n^2}{I_R A_R n_{\text{ref}}^2}$$

where $\phi_C$ is the quantum yield of the compound, $\phi_R$ is the quantum yield of the reference compound, $I_C$ is the fluorescence intensity of the compound, $I_R$ is the fluorescence intensity of the reference compound, $A_C$ is the absorbance of the compound (<0.1), $A_R$ is the absorbance of the reference (<0.1), $n$ is the refractive index of the solvent (DMF = 1.4305) in which the compound of interest is dissolved and $n_{\text{ref}}$ (CH$_2$Cl$_2$ = 1.4244) is the refractive index of the solvent in which the reference is dissolved. The absorbance values, $A_C$ and $A_R$ were measured at the same wavelengths at which the emission of the compounds was measured. To quantify the fluorescence intensities, $I_C$ and $I_R$, the emission spectra of the compounds were integrated over the whole region. The reference was analyzed in CH$_2$Cl$_2$ while the unknown compound was analyzed in DMF. The quantum yields of the dyes were calculated by measuring their absorbances and fluorescence intensities and then comparing them with the absorbance and fluorescence intensity of the reference compound, pyropheophorbide-a methyl ester according to the above equation. For each compound, five measurements were done at different absorbances (<0.1). The reported quantum yield of pyropheophorbide-a methyl ester ($\phi = 0.22$ in CH$_2$Cl$_2$) was used as a reference (Sasaki et al., 2010).

2. Cell Imaging

Culturing HEK 293T cells: A stock of human embryonic kidney (HEK) 293T cells was procured from ATCC (American Type Culture Collection) company. All the media and supplements were procured from Sigma Aldrich unless otherwise specified. The cells were suspended in 10 mL of phenol red free DMEM media (FluoroBrite™ from ThermoFisher Scientific) containing 4.5 g/L glucose, supplemented with 10% fetal bovine serum (FBS), 2 mM L-glutamine and 1 mM sodium pyruvate. The cell suspension was centrifuged at 200 G for 10 minutes to pellet the cells. The supernatant was discarded, and the cell pellet was suspended in 5 mL of phenol-red free supplemented DMEM media and then mixed with 10 mL of the media in a T75 flask and incubated at 37 °C in 5% CO$_2$ for 48 h. After 48 h, 1/10$^\text{th}$ of the cells were passaged to a new T75 flask with 15 mL of fresh phenol red free supplemented DMEM media to be incubated at 37 °C in a CO$_2$ incubator until they are 70% confluent. After the cells became 70% confluent, they were further passaged into six T75 flasks (1/6th of cells in each flask) until they are 70% confluent. Stock solutions were prepared from the six T75 flasks of 1 mL each at a density of 1 million cells/mL in 10% DMSO, 20% FBS supplemented DMEM media (phenol red free) and frozen at −80 °C using Mr. Frosty™ cell freezer.

The cells grown in a T25 or T75 flask were washed with Ca$^{2+}$ and Mg$^{2+}$ free Hank’s balance salt solution (HBSS) buffer after decanting the media. The cells were then re-suspended in 5 mL of supplemented media. The cell suspension (500 μL) was then mixed with 6 mL of media in a T25 flask and incubated at 37 °C in a CO$_2$ incubator until they are about 70% confluent.
**Incubation of dye:** The cells were plated in poly-D-lysine coated 50 mm glass-bottom dishes (MatTek®) at 37 °C in a CO₂ incubator to 70% confluence. When the cells were confluent, they were washed with Ca²⁺ and Mg²⁺ free HBSS buffer and incubated with the desired concentration of dye in 0.1% to 0.5% DMSO in HBSS buffer (with Ca²⁺ and Mg²⁺ ions). For co-localization and control experiments, FM4-64 was procured from Biotium under the name SynaptoRed C2. LysoTracker™ Yellow HCK-123, rhodamine 123 (RH123), di-4-ANEPPS, and ER-Tracker™ Red (BODIPY™ TR Glibenclamide) were procured from ThermoFisher Scientific.

**Cultured rat hippocampal neurons:** Cultured primary rat hippocampal neurons were a kind gift from Prof. Nigel Emptage, Department of Pharmacology at the University of Oxford. All reagents were procured from Invitrogen unless otherwise stated. Hippocampi were dissected from E18 Wistar rat embryos (Charles River Laboratory), dissociated in 0.5 mg/mL trypsin in HBSS for 15 minutes at 37 °C, washed twice in culture medium and gently triturated in culture medium using a briefly fire polished P1000 plastic pipette tip. Dissociated neurons were plated at a density of ~250/mm² on poly-D-lysine coated 50 mm glass bottom dishes from MatTek®. After attachment, neurons were incubated in Neurobasal medium supplemented with 2% fetal calf serum (FCS), 2% B27, 1% Glutamax and 1% penicillin/streptomycin. The day after plating, half the medium was changed for Neurobasal supplemented with 2% B27 and 1% Glutamax only; this medium was used for all further feeds. Cultures were maintained in an incubator at 37 °C perfused with 5% CO₂. Cultures were used for experiments at 14–21 days in vitro when synapses are mature. All animal work was carried out in accordance with the Animals (Scientific Procedures) Act, 1986 (UK).

**Mice brain slices:** Postnatal day (P) 14-21 C57BL/6 mice of both sexes were anaesthetized by isoflurane inhalation. The animals were decapitated in accordance with British Home Office regulations. The brain was removed swiftly and stored in ice-cold (0–4 °C) artificial cerebrospinal fluid (NaCl 126 mM, KCl 3 mM, NaH₂PO₄ 1.25 mM, MgSO₄ 2 mM, CaCl₂ 2 mM, NaHCO₃ 26 mM, and glucose 10 mM; pH 7.2–7.4; osmolarity 285–300 mOsm L⁻¹) for approx. 10 min (aCSF). aCSF was continuously bubbled with carbogen gas (95% O₂ and 5% CO₂) for at least 30 min before use. A thin section of dorsal surface was cut with a scalpel after separating the hemispheres. The dorsal part of the hemisphere was glued to a microtome pate for cyanoacrylate adhesive. Horizontal slices of entorhinal cortex (300–350 µm thick) were cut with a vibrotome (Leica VT 1000s) in aCSF.

For imaging experiments, the slices were stored in aCSF and bubbled continuously with carbogen using a perfusion setup. For pressure injection delivery, the dye was dissolved in HBSS buffer solution using 0.1% DMSO and delivered using a pulled patch-clamp–based pipette from Harvard Instruments.

**Microscope:** The imaging experiments were performed using an Olympus FV1200MPE-BX61WI microscope equipped with Mai Tai® eHP DeepSee™ Ti:Sapphire laser (70 fs pulse width, 80 MHz repetition rate, continuously tunable between 690–1040 nm) from Spectra-Physics. The light was focused using a 2 mm working distance 25X multiphoton objective (XLPLN25XWMP2). For TPEF, the reflected light was passed through a 750 nm short pass filter before being passed through a 540 nm long pass (LP) filter or a dichroic mirror separating the light to pass through green (495–540 nm) and red (570–625 nm) band pass filters and then was detected by PMT detectors (Hamamatsu R3896 for green
and Hamamatsu IR sensitive PMT-R10699 for red). For SHG, the light in the transmitted direction was collected through a 0.9 NA air-based condenser and then passed through a band-pass filter (405–435 nm) before being detected through a PMT detector (Hamamatsu R3896). All the images were acquired in analog-integration mode unless otherwise specified. The images were processed using Olympus Fluoview software and Imaris x64 7.7 software. The images presented here are scanned with a pixel dwell time of 2–12.5 µs/pixel at 512 × 512 pixels.

All the images are taken at 870 nm at ≤5 mW laser power unless otherwise specified. The concentration of the dyes are, \( \text{AK-1} = 20 \, \mu\text{M} \) (HEK 293T cells), 40 \( \mu\text{M} \) (cultured neurons), 25 \( \mu\text{M} \) (rat brain slices), \( \text{JF-1} = 10 \, \mu\text{M} \), \( \text{AK1.Cu} = 20 \, \mu\text{M} \), \( \text{JF-2} = 10 \, \mu\text{M} \) (840 nm), \( \text{JR-2} = 5 \, \mu\text{M} \) (840 nm), \( \text{JR-3} = 10 \, \mu\text{M} \) (840 nm), \( \text{JW-1} = 20 \, \mu\text{M} \), \( \text{IG-1} = 20 \, \mu\text{M} \), \( \text{FM4-64} = 20 \, \mu\text{M} \) (multimodal imaging), \( \text{FM4-64} = 10 \, \mu\text{M} \) (for comparison with di-4-ANEPPS, 840 nm), \( \text{di-4-ANEPPS} = 10 \, \mu\text{M} \) (840 nm), \( \text{RH123} = 20 \, \mu\text{M} \), LysoTracker™ Yellow HCK-123 = 3 \( \mu\text{M} \), and the ER-Tracker™ Red = 5 \( \mu\text{M} \).

3. Supplemental synthetic procedures

**General synthetic procedure:** All commercial reagents and solvents were procured from Sigma Aldrich unless specified. The chloroform, dimethylformamide, pyridine, tetrahydrofuran, and dimethylsulfoxide were procured from Fisher Scientific, and dichloromethane was procured from Honeywell Riedel-de-Haën. Deuterated solvents were procured from Aldrich. The SX-1 resins for size-exclusion chromatography was procured from Bio-Beads® and the Dowex® chloride anion exchange resin were procured from Sigma Aldrich. The Geduran® Si 60 silica gel was used for flash column chromatography. Benchtop centrifuge from Eppendorf was used to wash the final compound \( \text{AK-1} \) with solvents during its purification. Compounds 1, 2, \( \text{JR-2} \) and \( \text{JR-3} \) were synthesized as per our previously reported literature procedure (Lopez-Duarte et al., 2013; Reeve et al., 2009).

Chemical reactions were performed under inert atmosphere (Ar gas) unless otherwise stated. NMR spectra were acquired on 400 MHz (Bruker AVIIIHD 400) and 500 MHz (Bruker AVII 500, Bruker AVIIIHD 500) spectrometers. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as internal standard. MALDI-ToF (Waters MALDI micro) spectrometer was used for mass analysis.
3.1 Synthesis of JF-2 and JF-3

Scheme S1. Synthetic procedure for JF-1 and JF-2, related to Figure 1. In the last step, 1-iodo-5-triethylammonium-pentane was used as the alkylating agent to synthesize JF-1, while 1,4-butane sultone was used to synthesize JF-2.

Compound 12 was synthesized according to the literature procedure (Tykwinski et al., 1996).
Compound 5: Dipyrrromethane was synthesized as per literature procedure (Littler et al., 1999). Briefly, formaldehyde (33% w/w solution in water, 10.8 mL, 120 mmol) was added to pyrrole (200 mL, 2.88 mol) and the solution degassed by repeated evacuation and stirring under Ar at RT. Trifluoroacetic acid (1.08 mL, 14.1 mmol) was added by syringe under vigorous stirring and in the Ar atmosphere. The reaction proceeded for 5 min before CH₂Cl₂ (200 mL) was added, followed immediately by Na₂CO₃ (aq., sat., 200 mL). The organic layer was washed with Na₂CO₃ (aq.) (sat., 2 × 200 mL) and water (2 × 200 mL), then dried over Na₂SO₄. The solvent and then excess pyrrole were evaporated under reduced pressure. Distillation of the oily residue in a Kugelrohr apparatus (180 °C, 0.6 mbar) yielded the product 5 as a white solid. The product solidifies in the collecting vial into a robust stone difficult to remove. The convenient way to collect it is by washing with CH₂Cl₂. Yield: 6.9 g, 40%. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 7.76 (br s, 2 H, NH), 6.64 (m, 2 H, pyrrole α-H), 6.16 (m, 2 H, pyrrole β-H), 6.04 (m, 2 H, pyrrole β-H), 3.96 (s, 2 H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 121.2, 117.4, 108.4, 106.5, 26.4.

Porphyрин 7: This compound was prepared by adapting a literature procedure (Balaz et al., 2009). Dipyrrromethane 5 (2.34 g, 16.0 mmol) and 3-(2-[2-(methoxy-ethoxy)-ethoxy]-ethoxy)-benzaldehyde 6 (4.30 g, 16.0 mmol) were dissolved in DCM (2.4 L). The solution was stirred vigorously and degassed by bubbling with N₂ for 0.5 h and trifluoroacetic acid (1.2 mL) was added via syringe under gentle bubbling of N₂. The flask was shielded from light with tinfoil. Benzaldehyde (2.4 L) was added to NBS (2.1 eq., 480 mg, 2.7 mmol) in chloroform (50 mL) and pyridine (0.4 mL) was added dropwise over 60 min. The mixture was stirred for 1 h and the progress was monitored by TLC (SiO₂; DCM:EtOAc 3:1 or DCM:acetone 20:1). After quenching with acetone (5 mL), the solvents were removed under reduced pressure; the crude material was dissolved in toluene and extracted three to four times with water to remove the N-hydroxysuccinimide. After the product 8 was eluted from a silica column with (SiO₂; DCM: EtOAc 3:1) and evaporation of
the solvent, porphyrin 8 was obtained in form of a purple viscous oil. **Yield**: 1.21 g, 95–99 %. **1H NMR** (500 MHz, CDCl$_3$/ 1% pyridine-d$_5$) δ/ppm: –2.76 (br. s, 2H), 3.32 (s, 6H), 3.47–3.51 (m, 4H), 3.60–3.64 (m, 4H), 3.67–3.71 (m, 4H), 3.76–3.80 (m, 4H), 3.93–3.98 (m, 4H), 4.30–4.39 (m, 4H), 7.35–7.41 (m, 2H), 7.61–7.69 (m, 2H), 7.72–7.78 (m, 4H), 8.82–8.95 (m, 4H, J = 4.4 Hz), 9.59 (d, 4H, J = 4.8 Hz). **13C NMR** (125 MHz, CDCl$_3$/ 1% pyridine-d$_5$) δ/ppm: 59.0 (OCH$_3$), 77.9, 101.1, 101.4, 107.9, 114.4, 121.0, 121.2, 127.6, 127.7, 132.4, 142.5, 157.2 (CH$_3$, CH$_2$). m/z (MALDI-TOF): 944.95 (C$_{46}$H$_{42}$Br$_2$N$_2$O$_8$ Si, [M]+, requires 944.18, 100%); m/z (HRMS, MICRO-TOF): 965.1728 (C$_{46}$H$_{42}$Br$_2$N$_2$NaO$_8$ Si, [M+Na]$^+$, requires 965.1731).

**Compound 9**: Chlorotrihexylsilane (15.2 mL, 41.6 mmol) was added dropwise under Ar to a stirred solution of ethynylmagnesium bromide (0.50 M in THF, 100 mL, 50.0 mmol). The reaction mixture was heated at reflux for 1 h before HCl (aq.) (10%, 80 mL) was added. The organic layer was washed with water (80 mL) and dried over Na$_2$SO$_4$. The product was dried at a reduced pressure of 0.4 mbar for 30 min to yield a yellow oil. **Yield**: 10.0 g, 77.9%. **1H NMR** (400 MHz, CDCl$_3$) δ/ppm: 2.35 (s, 1 H, =CH), 1.41–1.22 (m, 24 H, CH$_2$), 0.89–0.83 (m, 9 H, CH$_3$), 0.63–0.56 (m, 6 H, CH). **13C NMR** (100 MHz, CDCl$_3$) δ/ppm: 94.1, 88.5, 33.3, 31.6, 23.9, 22.7, 14.3, 13.2. m/z (ESI$^+$) 307.3 (C$_6$H$_{13}$Si, M requires 308.3).

**Porphyrin 10**: The dibrominated porphyrin 8 (0.99 g, 1.05 mmol), trihexylsilylacetylene 9 (1.0 g, 3.14 mmol), Pd$_2$(dba)$_3$ (30 mg, 0.03 mmol), triphenylphosphine (60 mg, 0.21 mmol) and copper(I) iodide (20 mg, 0.1 mmol) were dried under vacuum in a Schlenk tube and flushed with argon. Toluene (20 mL) and triethylamine (10 mL) were added by syringe and solution was degassed by three freeze-thaw cycles. Once it had returned to room temperature, the mixture was stirred for 0.5 h and then heated to 40 °C until no further change was observed (ca. 3 h; TLC: DCM:EtOAc; 15:1). After the reaction mixture was cooled to room temperature, it was diluted with toluene (100 mL) and added into a separating funnel that was filled with 150 mL saturated ammonium chloride solution. The mixture was washed several times with water and the solvent was evaporated. A silica column with 15:1 DCM:EtOAc as the eluent gave the porphyrin 10 as a purple viscous oil. **Yield**: 1.32 g, 89%. **1H NMR** (500 MHz, CDCl$_3$ / 1% pyridine-d$_5$) δ/ppm: –2.12 (br. s, 2H, NH), 0.90–0.98 (m, 18 H, CH$_3$), 1.03–1.09 (m, 12 H, CH$_2$), 1.35–1.49 (m, 24 H, CH$_3$), 1.55–1.63 (m, 12 H, CH$_2$), 1.76–1.85 (m, 12 H, CH$_3$), 3.34 (s, 6 H, OCH$_3$), 3.49–3.53 (m, 4 H, OCH$_2$), 3.62–3.67 (m, 4 H, OCH$_2$), 3.69–3.75 (m, 4 H, OCH$_2$), 3.79–3.84 (m, 4 H, OCH$_2$), 3.96–4.02 (m, 4 H, OCH$_2$), 4.34–4.40 (m, 4 H, OCH$_2$), 7.37–7.43 (m, 2 H, CH), 7.69 (t, 4 H, J = 7.6 Hz, CH), 7.79–7.83 (m, 4 H, CH), 8.90 (d, 4 H, J = 4.6 Hz, CH), 9.56 (d, 4 H, J = 4.7 Hz, CH). **13C NMR** (125 MHz, CDCl$_3$/ 1% pyridine-d$_5$) δ/ppm: 13.8, 14.2, 22.7, 24.4, 31.7, 33.3 (CH$_3$, CH$_2$), 59.0 (OCH$_3$), 67.8, 69.9, 70.5, 70.7, 70.9, 71.9 (OCH$_3$), 101.1, 101.4, 107.9, 114.4, 121.1, 121.4, 127.6, 127.69, 130.7 br., 131.6 br., 142.6, 157.4 (C=C, CH$_3$, CH$_2$). m/z (MALDI-TOF) 1401.54 (C$_{66}$H$_{12}$NaO$_8$Si$_2$, [M+H]$^+$, requires 1400.92, 100%); m/z (HRMS, MICRO-TOF): 1421.8981 (C$_{66}$H$_{12}$Na$_4$O$_8$Si$_2$, [M+Na]$^+$, requires 1421.9006).

**Mono desilylated porphyrin 11**: Porphyrin 7 (0.44 g, 0.314 mmol), was dissolved in chloroform (100 mL) and a solution of 0.6 eq. of TBAF (0.2 mL; 1.0 M in THF) was added slowly. The progress was monitored by TLC (SiO$_2$: DCM:EtOAc; 10:1; 3:1). Once the mixture showed first indications of
the double deprotected derivative the mixture was quenched with acetic acid (12 μL, 0.2 mmol). After 5 min, MeOH (10 mL) was added and the mixture was then passed through a short column of SiO₂. The solvent was evaporated under reduced pressure and the remaining crude mixture was purified by flash chromatography on silica, eluting with DCM:EtOAc of increasing polarity (15:1 → 10:1). Hereby the unreacted starting material (7, 241 mg, 55% yield) eluted as first, followed from the mono (11, 100 mg, 28% yield) and double deprotected porphyrin. The alkyne 11 has limited stability under normal laboratory conditions, so it is normally prepared and used immediately (without further purification and characterization) in the following coupling step, for this reason the product is dried in a Schlenk tube, ready for use in the next step. It can be stored overnight as a dry solid at -20 °C.

Donor substituted porphyrin 13: The mono-deprotected porphyrin 11 (200 mg, 0.18 mmol), 1-iodo-4-N,N-dioctylamino-benzene 12 (160 mg, 0.36 mmol), Pd₃(dbb)₂ (4.1 mg, 9 μmol), triphenylphosphine (10 mg, 36 μmol) and copper(I) iodide (4 mg, 18 μmol) were dried under vacuum and degassed by three freeze-thaw cycles. After the reaction mixture was cooled to room temperature, it was diluted with toluene (7 mL) and added into a separating funnel that was filled with 150 mL saturated ammonium chloride solution. Toluene (7 mL) and triethylamine (4 mL) were added by syringe and solution was degassed by three freeze-thaw cycles. Once it had returned to room temperature, the mixture was stirred at for 0.5 h and then heated to 40 °C until no further change was observed (2–3 h; TLC: DCM:EtOAc; 20:1). After the reaction mixture was cooled to room temperature, it was diluted with toluene (100 mL) and added into a separating funnel that was filled with 150 mL saturated ammonium chloride solution. The mixture was washed several times with water and the solvent was evaporated. A silica column with 20:1 DCM: EtOAc as the eluent gave the porphyrin 13 as a green glass. Yield: 208 mg, 81%. ¹H NMR (400 MHz, CDCl₃ / 1% pyridine-d₅) δ/ppm: –1.89 (br. s, 2H, NH); 0.87–0.94 (m, 15H; CH₃); 0.99–1.05 (m, 6H; CH₂); 1.25–1.44 (m, 32H; CH₂); 1.51–1.59 (m, 6H; CH₂); 1.64–1.72 (m, 4H; CH₂); 1.72–1.80 (m, 6H; CH₂); 3.31 (s, 6H; OCH₃), 3.35–3.41 (m, 4H; NCH₂); 3.47–3.51 (m, 4H; OCH₂); 3.61–3.65 (m, 4H; OCH₂); 3.68–3.72 (m, 4H, OCH₂); 3.77–3.81 (m, 4H, OCH₂); 3.95–3.99 (m, 4H, OCH₂); 4.32–4.37 (m, 4H, OCH₂); 6.79 (d, 2H, J = 8.5 Hz, CH₂), 7.35–7.39 (m, 2H, CH), 7.63–7.67 (m, 2H, CH), 7.75–7.79 (m, 4H, CH), 7.86 (d, 2H, J = 8.5 Hz, CH), 8.82 (d, 4H, J = 4.6 Hz, CH), 9.56 (d, 2H, J = 4.7 Hz, CH), 9.66 (d, 2H, J = 4.6 Hz, CH). ¹³C NMR (125 MHz, CDCl₃ / 1% pyridine-d₅) δ/ppm: 13.8, 14.1, 14.2, 22.7, 24.3, 27.2, 27.3, 29.3, 29.5, 31.6, 31.8, 33.3 (CH₃), 51.1 (NCH₂), 59.0 (OCH₃), 67.7, 69.9, 70.5, 70.6, 70.9, 71.9 (OCH₂), 90.2, 100.0, 100.8, 103.7, 108.0, 109.1, 111.5, 114.4, 121.0, 121.2, 127.61, 127.63, 133.1, 142.7, 148.4, 157.3 (C≡C, CH₃), C₆H₅). m/z (MALDI-TOF): 1432.70 (C₉₀H₁₂₂N₄O₅Si₂; [M+]+, requires 1432.93, 100%); m/z (HRMS, MICRO-TOF): 1454.9175 (C₉₀H₁₂₂N₄O₅Si₂; [M]+Na+, requires 1454.9190).

Desilylated porphyrin 14: The porphyrin 13 (160 mg, 0.11 mmol), was dissolved in chloroform (50 mL) and degassed by gentle bubbling with nitrogen for 10 min. To this solution 2 eq. of a solution of TBAF (0.22 mL, 1.0 M in THF) was added slowly and the progress was monitored by TLC (SiO₂: DCM: EtOAc; 20:1; 10:1). Once the mixture was completely desilylated it was quenched by equimolar amounts of glacial acid and stirred for 5 min MeOH (5 mL) was added and the mixture was then plugged over SiO₂. Compound 14 has similar to 11 limited stability under normal laboratory conditions, so it is normally prepared and used immediately (without further purification and characterization) in the following
coupling step, for this reason the product is dried in a Schlenk tube, ready for use in the next step. Due to a TLC clean cleavage reaction, the theoretical yield was assumed to be 100% (127 mg). It can be stored overnight as a dry solid at -20 °C.

**Donor acceptor substituted porphyrin 16:** The desilylated porphyrin 14 (127 mg, 0.11 mmol), 1-iodo-pyidine 15 (120 mg, 0.58 mmol), Pd$_2$(dba)$_3$ (2.7 mg, 3 μmol), bis-diphosphino-ferrocene (DPPF) (3.5 mg, 1.5 μmol) and copper(I) iodide (2.2 mg, 6 μmol) were dried under vacuum in a Schlenk tube and flushed with argon. Toluene (7 mL) and diisopropylamine (4 mL) were added by syringe and solution was degassed by three freeze-thaw cycles. Once it had returned to room temperature, the mixture was stirred at for 0.5 h and then heated to 40 °C until no further change was observed (1–2 h; TLC: DCM:MeOH; 20:1). After the reaction mixture was cooled to room temperature, it was diluted with toluene (100 mL) and added into a separating funnel that was filled with 150 mL saturated ammonium chloride solution. The mixture was washed several times with water and the solvent was evaporated. A subsequent chromatography on silica (20:1 chloroform:MeOH); BIO-Beads® S-X1 (size-exclusion; 200–400 mesh, toluene:pyridine; 100:1) and silica (30:1 chloroform:MeOH) gave 16 as a green glass. **Yield:** 115 mg, 85%. **1H NMR (500 MHz, CDCl$_3$/ 1% pyridine-d$_5$) δ/ppm: -1.81 (br. s, 2H, NH); 0.87–0.94 (m, 6H; CH$_3$), 1.21–1.42 (m, 20H; CH$_2$), 1.62–1.72 (m, 4H; CH$_2$), 3.30 (s, 6H; OCH$_3$), 3.34–3.40 (m, 4H; NCH$_2$), 3.45–3.50 (m, 4H, OCH$_2$), 3.59–3.64 (m, 4H, OCH$_2$), 3.67–3.71 (m, 4H, OCH$_2$), 3.76–3.80 (m, 4H, OCH$_3$), 3.93–3.98 (m, 4H, OCH$_2$), 4.32–4.37 (m, 4H, OCH$_3$), 6.77 (d, 2H, J = 8.6 Hz, CH), 7.34–7.39 (m, 2H, CH), 7.62–7.76 (m, 2H, CH), 7.74–7.80 (m, 4H, CH), 7.80–7.86 (m, 4H, CH), 8.76–8.82 (m, 4H, CH), 8.85 (d, 2H, J = 4.5 Hz, CH), 9.55 (d, 2H, J = 4.5 Hz, CH), 9.64 (d, 2H, J = 4.5 Hz, CH). **13C NMR (125 MHz, CDCl$_3$/ 1% pyridine-d$_5$) δ/ppm: 14.1(CH$_3$), 22.6, 27.1, 27.3, 29.3, 29.5, 31.8 (CH$_2$), 51.0 (NCH$_2$), 58.9 (OCH$_3$), 67.7, 69.8, 70.5, 70.6, 70.9, 71.8 (OCH$_2$), 90.3, 93.8, 96.8, 97.7, 100.7, 104.7, 108.8, 111.5, 114.4, 121.0, 121.7, 125.3, 127.6, 132.0, 133.2, 142.5, 148.5, 150.0, 157.3 (C=≡C, CH$_2$, C$_6$H$_4$). **m/z (MALDI-TOF)** 1288.27 (C$_{77}$H$_{98}$N$_8$O$_8$, [M+H]$^+$), requires 1228.7, 100%); **m/z (HRMS, MICRO-TOF):** 1249.6880 (C$_{77}$H$_{98}$N$_8$O$_8$, [M+Na]$^+$, requires 1249.6712); **General procedure for the alkylation with 1-iodo-5-triethylammonium-pentane:** The doubly charged compounds JF-1 and JF-1.Cu were prepared by mixing precursors 16, 16.Cu (approx. 50 mg) with and an excess of 1-iodo-5-triethylammonium-pentane (approx. 500 mg) in 2-pentanone (4 mL). The mixture was heated under argon to 80–90 °C. The reaction progress was monitored by TLC (SiO$_2$: chloroform:MeOH; 20:1) and after the most of the starting material was consumed (approx. 4 h), the solvent was removed under reduced pressure. Washing the crude mixture of JF-1.Cu on a filter paper with water allowed removing the excess of 1-iodo-5-triethylammonium-pentane, whereas the porphyrin free base JF-1 was dissolved. The remaining metallic green (JF-1, JF-1.Cu) crude mixture was dissolved in NH$_4$Cl saturated water-methanol mixture (90:1) and extracted using chloroform/ethanol mixtures until the aqueous layer was mostly decolored. The solvents were removed under reduced pressure and the crude mixture was redissolved in NH$_4$Cl saturated water-methanol mixture (90:1) and extracted with chloroform/ethanol. After evaporation of the solvent, the reaction mixture was dissolved in toluene and filtered from the ammonium chloride. A further purification by DOWEX 50 ion exchange resin (MeOH) and BIO-Beads® SX-1 size-exclusion (200–400 mesh) using toluene as solvent, microfiltration and precipitation from toluene using n-hexane as antisolvent yielded the doubly charged compounds. The analytical purity was determined by NMR.
5-Iodo-Triethylammonium-pentane-iodide: The compound was prepared adapting a literature procedure for similar compounds (Sebastiano et al., 2001). A solution of acetone (100 mL), 1,5-diiodopentane (16.2 g, 0.05 mol, 7.44 mL) and triethylamine (5.06 g, 0.05 mol, 7.0 mL) was vigorously stirred at 20 °C for 24 h. The amount of the solvent was reduced to 25 mL and the solution was filtered from the precipitate. Addition of diethyl ether to the mother liquor precipitated the reaction product. Yield: 3.2 g, 15%. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 1.39 (t, 9H, J = 6.2 Hz, NCH₃), 1.55 (quint, 2H, J = 7.2 Hz, CH₂), 1.75–1.87 (m, 2H, CH₂), 1.93 (quint, 2H, J = 7.1 Hz, CH₂), 3.22–3.28 (m, 2H, ICH₂), 3.30–3.37 (m, 2H, NCH₂), 3.50 (quint, 6H, J = 6.2 Hz, CH₂). ¹³C NMR (120 MHz, DMSO-d₆) δ/ppm: 6.9 (IH₃), 8.4 (CH₃), 21.2, 27.1, 32.3 (CH₂), 53.8, 57.6 (NCH₂); m/z (HRMS, MICRO-TOF): 298.1018 (C₁₁H₂₈ IN, [M]+, requires 298.1026).

Double charged porphyrin free base JF-1: The reaction of porphyrin 16 (57 mg, 0.046 mmol) with 1-iodo-5-triethylammonium-pentane (500 mg, 1.2 mmol) in 2-pentanone (4 mL) yielded JF-1. Yield: 48 mg, 75%. ¹H NMR (500 MHz, DMSO-d₆) δ/ppm: −1.60 (br. s, 2H, NH); 0.86–0.93 (m, 6H; CH₂), 1.17–1.23 (m, 9H; CH₂), 1.25–1.43 (m, 22H; CH₂), 1.56–1.66 (m, 4H; CH₂), 1.66–1.75 (m, 2H; CH₂), 2.05–2.14 (m, 2H, CH₂), 3.12–3.21 (m, 8H; NCH₂), OCH₃), 3.26 (q, 6H, J = 7.2 Hz, NCH₂), 3.35–3.44 (m, 8H; NCH₂, OCH₃), 3.48–3.52 (m, 4H, OCH₂), 3.55–3.58 (m, 4H, OCH₂), 3.63–3.67 (m, 4H, OCH₂), 3.83–3.90 (m, 4H, OCH₂), 4.32–4.41 (m, 4H, OCH₂), 4.72 (t, 2H, J = 6.8 Hz, NCH₂), 6.87 (d, 2H, J = 8.7 Hz, CH), 7.48–7.53 (m, 2H, CH), 7.76–7.84 (m, 6H, CH), 7.92 (d, 2H, J = 8.7 Hz, CH), 8.82 (d, 2H, J = 4.5 Hz, CH), 8.88–8.93 (m, 4H, CH), 9.30 (d, 2H, J = 6.3 Hz, CH), 9.71 (d, 2H, J = 4.5 Hz, CH), 9.83 (d, 2H, J = 4.5 Hz, CH). ¹³C NMR (125 MHz, DMSO-d₆) δ/ppm: 7.2, 14.0 (CH₃), 20.5, 22.2, 22.3, 26.4, 26.8, 28.7, 28.9, 30.1, 31.2 (CH₂), 50.1, 52.0, 55.7 (NCH₂), 58.0 (OCH₃), 60.1 (NCH₂), 67.6, 69.1, 69.6, 69.8, 70.0, 71.2 (OCH₂), 90.2, 93.4, 94.6, 102.9, 105.5, 106.1, 107.0, 111.6, 114.9, 120.7, 122.8, 127.2, 128.3, 129.1, 133.5, 139.1, 141.4, 144.6, 148.8, 157.2 (C=C, CH₂, C₆). m/z (MALDI-TOF): 1431.53 (C₈₈H₁₁₂ClN₈O₈ [M-HCl]+, requires 1432.84, 100%). m/z (HRMS, MICRO-TOF): 698.9380 (C₈₈H₁₁₂N₆O₈, [M]+, requires 698.9398). UV-Vis (DMF, 25 °C) λmax (log ε): 448 (5.03); 642 (4.54); 727 (4.67).
Figure S9. $^1$H-NMR spectrum of JF-1 (d$_6$-DMSO, 500 MHz), related to Figure 1.

Double charged copper porphyrin JF-1.Cu:
The reaction on octyl version of 16.Cu (66 mg, 0.051 mmol) (synthesized by inserting copper in 16) with 1-iodo-5-triethylammonium-pentane (514 mg, 1.2 mmol) in 2-pentanone (4 mL) gave JF-1.Cu. Yield: 61 mg, 78%. m/z (MALDI-TOF): 1494.37 (C$_{88}$H$_{112}$ClCuN$_7$O$_8$, [M-HCl]$^+$, requires 1494.76, 100%); m/z (HRMS, MICRO-TOF): 729.3995 (C$_{44}$H$_{113}$CuN$_7$O$_8$, [M]$^{2+}$, requires 729.3968). UV-Vis (DMF, 25 °C) $\lambda_{max}$ (log $\varepsilon$): 449 nm (4.97); 686 nm (4.65).

Porphyrin JF-2: To a solution of the corresponding porphyrin 16 (52 mg, 42.4 µmol) in acetophenone (2 mL) was added an excess of 1,4-butane sulfone (1.2 mL, 11.7 mmol) and the resulting solution was vigorously stirred at 110–130 °C for approx. 5 h under Ar atmosphere with regular TLC monitoring (SiO$_2$: chloroform:MeOH; 20:1). After the starting material was almost consumed, the reaction was quenched by
evaporating the solvents. The slurry crude reaction mixture of JF-2 was directly purified by BIO-Beads® S-X1 size-exclusion (200–400 mesh) using toluene as solvent. Microfiltration and precipitation of the evaporated prod from toluene using n-hexane as bad solvent yielded the charged compounds. **Yield:** 48 mg (83%).

**1H NMR** (500 MHz, DMSO-d₆) δ/ppm: −1.85 (br. s, 2H, NH); 0.85–0.93 (m, 6H; CH₃), 1.21–1.37 (m, 20H; CH₂), 1.51–1.60 (m, 4H; CH₂), 1.68 (quint, 2H, J = 7.6 Hz, CH₂), 2.11 (quint, 2H, J = 7.6 Hz, CH₂), 2.55 (t, 2H, J = 7.6 Hz, SO₃CH₂), 3.16 (s, 6H; OCH₃), 3.30–3.39 (m, 8H; NCH₂, OCH₂), 3.48–3.52 (m, 4H, OCH₂), 3.55–3.59 (m, 4H, OCH₂), 3.63–3.67 (m, 4H, OCH₂), 3.85–3.89 (m, 4H, OCH₂), 4.32–4.40 (m, 4H, OCH₂), 4.64 (t, 2H, J = 6.8 Hz, NCH₂), 6.75 (d, 2H, J = 8.4 Hz, CH), 7.48–7.53 (m, 2H, CH), 7.69–7.84 (m, 8H, CH), 8.59 (d, 2H, J = 5.4 Hz, CH), 8.71–8.80 (m, 4H, CH), 9.19 (d, 2H, J = 6.4 Hz, CH), 9.49 (br s, 4H, CH).

**13C NMR** (125 MHz, DMSO-d₆) δ/ppm: 14.0 (CH₃), 21.7, 22.1, 26.4, 26.8, 28.7, 28.9, 30.0, 31.3 (CH₂), 50.1, 50.4 (SO₃CH₂, NCH₂), 58.0 (OCH₃), 60.2 (NCH₂), 67.6, 69.1, 69.6, 69.8, 70.0, 71.2 (OCH₂), 90.0, 93.1, 94.4, 102.4, 105.1, 105.7, 107.0, 111.4, 114.8, 120.7, 122.6, 127.3, 128.2, 128.7, 133.3, 138.6, 141.4, 144.4, 148.6, 157.2 (C≡C, CHAr, C₆).

**m/z** (MALDI-TOF): 1362.90 (C₈₁H₉₈N₆O₁₁S, [M]+, requires 1362.70, 100%); **m/z** (HRMS, MICRO-TOF): 1385.6862 (C₈₁H₉₈N₆NaO₁₁S, [M+Na]+, requires 1385.6906). **UV-Vis** (DMF, 25 °C) λₑₒₓ (log ε): 446 (5.05); 640 (4.58); 726 (4.72).

**Figure S10.** ¹H NMR spectrum of JF-2 (d₆-DMSO, 500 MHz, DOSY experiment), related to Figure 1.
3.2 Synthesis of AK-1 and AK-1.Cu

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\begin{align*}
\text{Compound 18:} & \quad \text{Compound 18 was synthesized according to the literature procedure (Yi et al., 2016). Briefly, } N,N,N',N'-\text{tetramethyl-1,3-propanediamine 17 (5.0 g) was dissolved in diethyl ether} (100 \text{ mL}) \text{ and stirred. Methyl iodide (2.38 mL, 1 eq.) was added dropwise and the reaction mixture was stirred for 20 min until white precipitate formed. The white precipitate was washed with water} (100 \text{ mL}) \text{ three times and dried under high vacuum to yield 18 as a white amorphous powder. Yield: 1.45 g, 14%.} \\
\text{1H NMR} & \quad (400 \text{ MHz, } D_2O) \quad \delta/\text{ppm}: 3.31 (m, 2H), 3.12 (s, 9H), 2.41 (m, 2H), 2.21 (s, 6H), 1.96 (m, 2H). \\
\text{13C NMR} & \quad (100 \text{ MHz, } D_2O) \quad \delta/\text{ppm}: 64.7, 54.6, 52.8, 43.6, 20.1. \\
\text{m/z (ESI+)} & \quad 145.2, 146.2 (C_6H_{21}N_2^+ \text{ M}^+ \text{ requires 145.2, } C_8H_{22}N_2^+ [M+H]^+ \text{ requires 146.2).}
\end{align*}
\]

\[
\begin{align*}
\text{Compound 19:} & \quad \text{3-(Dimethylamino)-N,N,N-trimethylpropan-1-aminium iodide 18 (600 mg, 2.2 mmol) was dissolved in acetonitrile (5 mL) and stirred followed by addition of 1,3-diiodopropane (2.7 mL, 22.0 mmol, 10 eq.). The reaction mixture was refluxed for 24 h. The solvent was evaporated under reduced pressure to form a yellow solid powder, which was washed with acetone to give 19 as a white powder. Yield: 1.2 g, 93%.} \\
\text{1H NMR} & \quad (400 \text{ MHz, } D_2O) \quad \delta/\text{ppm}: 3.52 (m, 2H), 3.45 (m, 4H), 3.29 (t, 2H, } J = 6.4 \text{ Hz), 3.21 (s, 9H), 3.18 (s, 6H), 2.36 (m, 4H). \\
\text{13C NMR} & \quad (100 \text{ MHz, } D_2O) \quad \delta/\text{ppm}: 62.3, 64.9, 60.0, 53.2, 51.0, 25.5, 17.0, -0.3. \\
\text{m/z (ESI+)} & \quad 441.0 (C_{11}H_{22}N_2^+, \text{ M}^+ \text{ requires 441.0).}
\end{align*}
\]

\[
\begin{align*}
\text{Compound 3:} & \quad \text{N'-(3-Iodopropyl)-N',N',N,N,N'-pentamethylpropane-1,3-bis(aminium)-diiodide 19 (1.0 g, 1.7 mmol) was dissolved in water just below saturation concentration. Ammonium hexafluorophosphate (900 mg, 5.1 mmol, 3 eq.) solution in water was added dropwise and stirred at RT for 15 min to form}
\end{align*}
\]

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\text{Scheme S2. Synthetic procedure for AK-1, Related to Figure 1.}
\]
precipitates. The precipitate was washed with water (100 mL) and dried under high vacuum to give product 3 as white solid. $^1$H NMR (400 MHz, d$_6$-DMSO) $\delta$/ppm: 3.38 (m, 2H), 3.31 (m, 4H), 3.24 (t, 2H, $^3$J = 6.8 Hz), 3.11 (s, 9H), 3.09 (s, 6H), 2.22 (m, 4H). $^{13}$C NMR (100 MHz, d$_6$-DMSO) $\delta$/ppm: 63.9, 61.8, 59.6, 52.6, 50.6, 25.8, 16.8, 1.5. m/z (ESI+) 459.0, 460.0.0 (C$_{11}$H$_{27}$F$_2$IPN$_2$+ M$^+$ requires 459.0, C$_{11}$H$_{26}$F$_2$IPN$_2$+ [M+H]$^+$ requires 460.0).

**Compound 20:** Compound 20 was synthesized as per literature procedure (Reeve et al., 2009). n-Butyl lithium (11.2 mL, 2.5 M solution in hexane) was added dropwise to a stirred solution of trihexylsilyl acetylene 9 (6.6 g, 21.3 mmol), in dry THF (18 mL) at 0 °C. The mixture was stirred for 15 min at 0 °C and then another 15 min at RT. The reaction mixture was quenched with HCl (10% v/v, 50 mL), washed with H$_2$O and extracted with Et$_2$O. The solution was dried over Na$_2$SO$_4$ and concentrated to give 20 as yellow oil. **Yield:** 6.71 g, 93.5%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 9.17 (s, 1 H, CHO), 1.45–1.20 (m, 24 H, 2 hexyl-H), 0.89 (t, 9 H, $^3$J = 6.7 Hz, 6 hexyl-H), 0.68 (m, 6 H, 1-hexyl-H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$/ppm: 175.9, 103.6, 102.5, 33.1, 31.5, 23.8, 22.7, 14.2, 12.6.

**Porphyryn 21:** Porphyryn 21 was prepared according to an adapted literature procedure (Anderson, 1992). Dipyrromethane (1.55 g, 10.60 mmol) was dried in vacuo for 1 h before addition of dry CH$_2$Cl$_2$ (600 mL) and trihexylsilyl propynal (3.7 g, 11.00 mmol). The solution was freeze-pump-thaw degassed and BF$_3$.OEt$_2$ (450 μL, 3.64 mmol) was added and the mixture was stirred at room temperature for 45 min in the dark. After this time, DDQ (3.43 g, 15.11 mmol) was added and the mixture was stirred under air for 10 min. The crude mixture was passed through a large silica plug (CH$_2$Cl$_2$) and further purified by flash chromatography on silica (4:1 40–60 °C petrol ether: CH$_2$Cl$_2$). Fractions were evaporated to give 21 as a purple oil. **Yield:** 1.65 g, 16.8%. $^1$H NMR (400 MHz, CDCl$_3$) with 1% C$_6$D$_5$N $\delta$/ppm: 10.09 (s, 2 H, meso-H), 9.67 (d, 4 H, $^3$J = 4.5 Hz, β-H), 9.28 (d, 4 H, $^3$J = 4.5 Hz, β-H), 1.86–1.74 (m, 12 H, hexyl-H), 1.64–1.54 (m, 12 H, hexyl-H), 1.50–1.35 (m, 24 H, hexyl-H), 1.10–1.02 (m, 12 H, hexyl-H), 0.93 (t, 18 H, $^3$J = 7.06 Hz, hexyl-H).

**Porphyryn 22:** Porphyryn 22 was prepared according to literature procedure (Reeve et al., 2009). Amylene stabilized CHCl$_3$ was passed through alumina and then mixed with 1% of dry EtOH. Porphyryn 21 (500 mg, 0.54 mmol) was dissolved in the CHCl$_3$ (25 mL). The solution was put under Ar before n-Bu$_4$NF (0.54 mL, 1 M in THF) was added. The reaction was carefully monitored by TLC (PET ether 40–70 °C : EtOAc 10 : 1) - spotted every 10 min. When starting material and monodeprotected product appeared roughly equal in intensity, the reaction was quenched by pouring directly onto a silica plug in CH$_2$Cl$_2$. Crude reaction mixture was purified by flash chromatography on SiO$_2$ (PET ether 40–60 °C : EtOAc 20 : 1 : 1). Fractions containing monodeprotected porphyryn 22 were evaporated to dryness to give a purple glass. **Yield:** 145 mg, 42%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 9.83 (s, 2H, meso-H), 9.57 (d, 2H, $^3$J = 4.3 Hz, β-H), 9.52 (m, 2H, β-H), 9.13 (m, 4H, β-H), 4.21 (s, 1H, acetylene-H), 1.92–1.82 (m, 6H, hexyl-H), 1.70–1.60 (m, 6H, hexyl-H), 1.56–1.40 (m, 12H, hexyl-H), 1.16–1.06 (m, 6H, hexyl-H), 0.98 (t, 9H, $^3$J = 7.0 Hz, hexyl-H), −3.65 (br s, 2H, -NH).
Compound 23: Compound 23 was prepared as per literature procedure (Mohr et al., 1997). 4-Iodoaniline (5.00 g, 22.8 mmol) was mixed with butyl iodide (10 mL, 88.0 mmol) with Na₂CO₃ (8.00 g) in DMF (13 mL). The mixture was degassed and then stirred under Ar for 18 h at 100 °C. The crude mixture was diluted with toluene, washed with water. The crude reaction was again mixed with chloroform and washed with water (3 × 200 mL) and dried over Na₂SO₄. The solvent was evaporated, and the crude material was purified by column chromatography on silica (9:1 40–60 °C petrol ether:CH₂Cl₂). Yield: 7.6 g, 100%. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 7.41 (d, 2 H, ³J = 9.09 Hz, Ar-H), 6.41 (d, 2 H, ³J = 9.17 Hz, Ar-H), 3.22 (t, 4 H, ³J = 7.53 Hz), 1.53 (m, 4 H), 1.33 (m, 4 H), 0.94 (t, 6 H, ³J = 7.34 Hz). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 147.7, 137.7, 114.1, 100.1, 50.8, 29.3, 20.4, 14.1. m/z (ESI+) 332.0, 333.0 (C₁₉H₂₂I₂N, M+H requires 332.0, M+2H requires 333.0).

Porphyrin 24: 5-Ethynyl-15-[(triethysilyl)ethynyl]porphyrin 22, (140 mg, 0.218 mmol), Pd₂dba₃ (22 mg, 0.021 mmol), PPh₃ (25 mg, 0.095 mmol), and CuI (5 mg, 0.026 mmol) were transferred and dried in a Schlenk tube in vacuo for 1 h. DIPA (8 mL) and toluene (8 mL) were added and the reaction mixture thoroughly freeze-pump-thaw degassed (3 cycles). 4-Iodo-N,Ν-dibutylaniline 23 (721 mg, 2.18 mmol) was added to the reaction mixture and the mixture was stirred at 50 °C for 1 h under Ar. Progress of the reaction was monitored by TLC (PET ether 40–60 °C : EtOAc 10 : 1). Upon completion, the mixture was passed through a silica plug (CH₂Cl₂) and evaporated to dryness to give 24. Yield: 172 mg, 93%. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 9.91 (s, 2H, meso-H), 9.65 (m, 2H, β-H), 9.58 (d, 2H, ³J = 4.3 Hz, β-H), 9.18 (m, 4H, β-H), 7.92 (d, 2H, ³J = 8.6 Hz, aniline-H), 6.84 (d, 2H, ³J = 8.6 Hz, aniline-H), 3.42 (t, 4H, ³J = 7.8 Hz, butyl-H), 1.90–1.80 (m, 6H, hexyl-H), 1.77–1.38 (m, 26H, butyl-H, hexyl-H), 1.13–1.03 (m, 12H, butyl-H, hexyl-H), 0.97 (t, 9H, ³J = 6.8 Hz, hexyl-H), −2.83 (br s, 2H, -NH). m/z (MALDI-TOF): 843.57, 844.56, 845.56 (C₃₆H₂₄N₂Si, M requires 843.56, M+H requires 844.56, M+2H requires 845.56).

Porphyrin 25: Intermediate porphyrin 25 was prepared as follows: TBAF (1.0 M in THF, 0.402 mL, 0.402 mmol) was added to a solution of 24 (170 mg, 0.201 mmol) in CH₂Cl₂ (30 mL) and stirred for 20 min at RT. The reaction mixture was passed through a silica plug (CH₂Cl₂) and evaporated to dryness to give 25. Yield: 112 mg, 100%. The crude product mixture contained trihexylsilane as byproduct. The crude product mixture was taken forward for Sonogashira coupling without any further purification because of high reactivity of the product. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 10.01 (s, 2H, meso-H), 9.72 (d, 2H, ³J = 4.5 Hz, β-H), 9.63 (d, 2H, ³J = 4.5 Hz, β-H), 9.25 (m, 4H, β-H), 7.91 (d, 2H, ³J = 8.8 Hz, aniline-H), 6.83 (d, 2H, ³J = 8.8 Hz, aniline-H), 4.20 (s, 1H, acetylene-H), 3.43 (m, 4H, butyl-H), 1.75–1.65 (m, 4H, butyl-H), 1.52–1.42 (m, 4H, butyl-H), 1.05 (t, 6H, ³J = 7.4 Hz, butyl-H), −2.61 (br s, 2H,-NH).
Porphyрин 1: N,N-Dibutyl-4-[15-этиллен]погарин-5-yl)этиланилин 25 (112 мг, 0.201 ммоль) was mixed with Pd₂dba₃ (18 мг, 20.1 мкмоль), PPh₃ (21 мг, 80.0 мкмоль), Cul (4 мг, 21.0 мкмоль) и 4-iodopyridine (400 мг, 2.014 ммоль) were dried in vacuo for 1 h before DIPA (9 мл) и toluene (9 мл) were added and the mixture freeze-pump-thaw degassed. The mixture stirred at 40°C for 3 h under Ar. Upon completion, the mixture was passed through a silica plug (CH₂Cl₂ with 5% MeOH) then purified by flash chromatography (CH₂Cl₂:THF 5:1 to 3:1) and the fractions were evaporated to dryness. The product was recrystallized (MeOH layered over CHCl₃) to give 1 as a green solid. Yield: 115 мг, 90%. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 9.89 (s, 2H, meso-H), 9.66 (m, 2H, β-H), 9.52 (m, 2H, β-H), 9.16 (m, 4H, β-H), 8.84 (m, 2H, pyridine-H), 7.91 (d, 2H, 3J = 8.8 Hz, aniline-H), 7.88 (m, 2H, pyridine-H), 6.84 (d, 2H, 3J = 8.8 Hz, aniline-H), 3.44 (m, 4H, butyl-H), 1.77–1.67 (m, 4H, butyl-H), 1.53–1.43 (m, 4H, butyl-H), 1.05 (t, 6H, 3J = 7.4 Hz, butyl-H), −2.61 (br s, 2H, -NH). m/z (MALDI-ToF): 638.89, 639.84, 630.79 (C₄₅H₆₅N₆, M requires 638.31, M+H requires 639.31, M+2H requires 640.31). UV-Vis (DMF, 25 °C) λ_max (log ε): 692 нм (4.36), 614 нм (4.41), 422 нм (4.89).

Porphyрин AK-1: Porphyrin 1 (15 мг, 22.5 ммоль) was mixed with N'- (3-iodopropyl)-N',N',N',N'-pentamethylpropane-1,3-diaminium-di(hexafluorophosphate) 3 (600 мг, 1 ммоль, 45 экв.) и dried under high vacuum at 50 °C for 4 h. Dry dimethylacetamide (1.5 мл) was added to the mixture and the reaction mixture was stirred at 115 °C for 6 h in inert atmosphere. TLC (20% THF in DCM) confirmed the consumption of starting material. Solvent was evaporated from crude mixture which was then purified by size-exclusion column chromatography (SX-1 beads in DMF). The second band (product) was passed through a Dowex 1X8 chloride form ion-exchange chromatography column. The reaction mixture was then sequentially washed with water (3 x 30 мл), MeOH (3 x 30 мл) и diethyl ether (1 x 30 мл). The process of ion-exchange and washing was repeated. In the end, the reaction mixture was again passed through the size-exclusion column chromatography (SX-1 beads in DMF). The solvent was evaporated under reduced pressure to yield the product AK-1 as green solid. Yield: 11 мг, 50%. ¹H NMR (500 MHz, d₆-DMSO at 50 °C) δ/ppm: 10.46 (s, 2H, meso-H), 9.90 (d, 2H, 3J = 4.5 Hz, β-H), 9.78 (d, 2H, 3J = 4.5 Hz, β-H), 9.65 (d, 2H, 3J = 4.5 Hz, β-H), 9.56 (d, 2H, 3J = 4.5 Hz, β-H), 9.28 (d, 2H, 3J = 6.1 Hz, pyridine-H), 9.00 (d, 2H, 3J = 6.1 Hz, pyridine-H), 7.99 (d, 2H, 3J = 8.4 Hz, aniline -H), 6.92 (d, 2H, 3J = 8.4 Hz, aniline-H), 4.77 (t, 2H, 3J = 4.4 Hz, CH₃) 3.52 (m, 2H, CH₃), 3.35 (t, 4H, 3J = 7.6 Hz, butyl-H), 3.36 (m, 4H, 2CH₃), 3.15 (m, 15 H, methyl-H), 2.64–2.54 (m, 2H, CH₂), 2.28–2.18 (m, 2H, CH₂), 1.68–1.58 (m, 4H, butyl-H), 1.49–1.39 (m, 4H, butyl-H), 1.01 (t, 6H, 3J = 7.4 Hz, butyl-H). m/z (MALDI-ToF): 1114.96 (C₅₄H₇₃N₆P₂, M requires 1115.46). UV-Vis (DMF, 25 °C) λ_max (log ε): 709 нм (4.37), 631 нм (4.24), 440 нм (4.67). Quantum yield ϕ, (DMF, 25 °C): 0.0033.
Porphyrin AK-1.Cu: Porphyrin AK-1 (7 mg, 7.5 µmol) was dissolved in DMF (1 mL). Excess of copper(II) acetate monohydrate (30 mg) was dissolved in MeOH (1 mL) and mixed with the DMF containing porphyrin. The mixture was heated for 8 h at 50 °C after which the solvent was evaporated under reduced pressure. The formation of the product was confirmed by UV-Vis spectroscopy. The crude mixture was re-dissolved in DMF (0.5 mL) and passed through a small plug of SX-1 beads. The solvent was evaporated, and the porphyrin was washed with methanol and distilled water two times each. The purified product was dried under high vacuum overnight. **Yield**: 5.0 mg, 67%. **m/z (MALDI-ToF)**: 1176.27 (C₅₄H₆₃N₆F₁₂P₂Cu, M requires 1176.37). **UV-Vis (DMF, 25 °C)** $\lambda_{\text{max}}$ (log $\varepsilon$): 668 nm (4.51), 441 nm (4.74).
3.3 Synthesis of IG-1

Scheme S3. Synthetic procedure for IG-1, related to Figure 1.

Compounds 26, 27, 28, 29, and 30 were synthesized according to the literature procedures (Dominguez et al., 1961; Newkome et al., 1991; Selve et al., 1991; Snow and Foos, 2003).

Compound 32: Iodoisophthalic acid 31 (500 mg, 1.7 mmol) was refluxed in SOCl₂ (15 mL, 200 mmol) for 16 h. Excess of thionyl chloride was removed by distillation and the resulting acid chloride was dissolved under high vacuum. The 3-iodoisophthalic acid chloride (563 mg, 1 eq.) was not characterized and instead it was dissolved in dry THF (3 mL) and used immediately in the following peptide coupling step. The solution of Behera’s amine 30 (1.56 g, 2.2 eq.) with Et₃N (277 μL) was also prepared in dry THF (3 mL) and added dropwise to the solution of bis-acid chloride. Reaction mixture was left to stir overnight at room temperature. The reaction mixture was concentrated to form a viscous yellow crude oil. Purification was carried out by flash chromatography on SiO₂ (PET ether 40–60 °C:EtOAc 10:1 to 5:1 to neat EtOAc). The fraction containing the product was concentrated and dried under high vacuum overnight to afford 32 as a white
crystalline powder. **Yield:** 702 mg, 37.5%. **^1^H NMR** (400 MHz, CDCl$_3$) δ/ppm: 8.30 (d, 2H, J = 1.6 Hz, Ar-H), 8.28 (t, 1H, J = 1.4 Hz, Ar-H), 7.31 (s, 2H, Amide-H), 2.30 (t, 12H, J = 7.4 Hz, CH$_2$) 2.12 (t, 12H, J = 7.4 Hz, CH$_2$), 1.44 (t, 54H, t-Bu).

**Compound 33:** Compound 32 (200 mg, 184 µmol, 1 eq.) was dissolved in formic acid (8.1 mL) and left stirring at room temperature for 24 h. On the next day, the solution was concentrated and toluene (8 mL) was added to help azeotropically remove the residual formic acid. On evaporation, the product 33 was obtained as a white powder. **Yield:** 138 mg. **^1^H NMR** (400 MHz, DMSO-d$_6$) δ/ppm: 12.24 (br. s, 6H, Acid-H), 8.26 (m, 2H, Ar-H), 8.15 (m, 1H, Ar-H), 7.75 (br. s, 2H, Amide-H), 2.17 (t, 12H, J = 7.6 Hz, CH$_2$), 1.98 (t, 12H, J = 8.8 Hz, CH$_2$).

**Compound 4:** 3-iodoisophthalic acid 33 (50 mg, 67 µmol, 1 eq.) was dissolved in dry DMF (0.2 mL) and cooled in an ice bath to 0 °C. In parallel compound 28 (247 mg, 800 µmol, 12 eq.) was dissolved in dry DMF (0.2 mL) and also cooled to 0 °C. To each cooled solution DIPEA (0.070 mL, 800 µmol, 12 eq.) was added. Next, to the solution of compound 33, COMU (El-Faham and Albericio, 2010) coupling reagent (218 mg, 800 µmol, 12 eq.) was added and stirred for 1 min before the solution of amine was added dropwise. Combined solutions were stirred for 1 h at 0 °C and an additional 2 h at room temperature. Crude reaction mixture was worked up by diluting with EtOAc (20 mL) and a following washing with HCl (1.0 M, 2 × 5 mL), NaHCO$_3$ (1.0 M, 2 × 5 mL) and saturated NaCl (2 × 5 mL). The aqueous phase was additionally washed with DCM (4 × 200 mL) (until no more UV active compound partitioned into DCM) which was then combined with the organic phase. The product was purified by size-exclusion chromatography (CHCl$_3$) to obtain 4 as an oil. **Yield:** 131 mg, 78%. **^1^H NMR** (400 MHz, CDCl$_3$) δ/ppm: 8.76 (br s, 2H, amide-NH), 8.40 (s, 1H, Ar-H), 8.30 (s, 2H, Ar-H), 3.63–3.47 (br m, 74H, TEG-CH$_2$), 3.35 (s, 9H, TEG-OCH$_3$), 3.33 (s, 9H, TEG-OCH$_3$), 2.46 (t, 6H, J = 6.2 Hz, CH$_3$), 2.15 (t, 6H, J = 6.2 Hz, CH$_3$).

**Porphyrin 1.Zn:** Trihexylsilylacetylene,15-ethynyl porphyrin 2 (21 mg, 20.6 µmol, 1.5 eq.) and Pd(PPh$_3$)$_4$ (4.16 mg, 3.6 µmol, 0.2 eq.), Cul (0.7 mg, 3.6 µmol, 0.2 eq.) and compound 4 (30 mg, 12 µmol, 1 eq.) were transferred and dried in a Schlenk tube in vacuo for 1 h. THF (0.5 mL) and DIPA (0.5 mL) was added and the reaction mixture thoroughly freeze-pump-thaw degassed (4 cycles). Bu$_4$NF (0.18 mL, 180 µmol, 1 M in THF, 15 eq.) was added to the reaction mixture and the mixture was freeze-pump-thaw degassed again (another 2 cycles) then brought to 50 °C and stirred for 3 h under N$_2$. Progress of the reaction was monitored by TLC (PET ether 40–60 °C:EtOAc:Py 10:1:1). On completion the mixture was passed through a silica plug (PET ether 40–60 °C:EtOAc 3:1), concentrated and purified by flash chromatography on SiO$_2$ (PET ether 40–60 °C: CH$_2$Cl$_2$:Py 20:1 to 10:1:1 to pure CH$_2$Cl$_2$). **Product 1.Zn** was obtained as a green solid. **Yield:** 30 mg, 80%. **^1^H NMR** (400 MHz, CDCl$_3$) δ/ppm: 9.97 (s, 2H, meso-CH), 9.78 (m, 4H, β-CH), 9.24 (m, 4H, β-CH), 8.80 (br s, 2H, amide-NH), 8.58 (s, 2H, Ar-H), 8.53 (s, 1H, Ar-H), 7.84 (d, 2H, J = 8.8 Hz, Ar$_{aniline}^-$-H), 6.75 (d, 2H, J = 8.9 Hz, Ar$_{aniline}^-$-H), 3.61–3.23 (s, 148H, TEG(CH$_2$)$_2$-H), 3.20 (s, 18H, TEG(CH$_2$)$_2$-H), 3.18 (s, 18H, TEG(CH$_2$)$_2$-H), 2.50 (t, 12H, J = 6.8 Hz, CH$_3$), 2.22 (t, 12H, J = 6.4 Hz, CH$_3$), 1.63 (m, 6H, octyl-CH$_2$), 1.38–1.21 (m, 22H, octyl-CH$_2$), 0.85 (t, 6H, octyl-CH$_3$).

**m/z (MALDI-TOF):** 3129.85 ([M+Na]$^+$ 100%, C$_{158}$H$_{257}$N$_{13}$O$_{42}$ZnNa$^+$ requires 3129.75).
Porphyrid IG-1: Compound IG-1.Zn (5.0 mg, 1.6 µmol, 1 eq.) was dissolved in CHCl₃ (0.5 mg) in a dry round bottom flask. TFA (12.5 µL, 100 eq.) was added at once to the solution of the porphyrin. Reaction was allowed to proceed for 15 min. On completion, the reaction was stopped by pouring the reaction mixture into a flask with large volume of CHCl₃ (50 mL) and washing the resultant diluted solution with saturated solution of NaHCO₃ until basic pH is reached. Organic phase was separated and dried with MgSO₄, then filtered and concentrated. Product was obtained as a dark green solid. **Yield:** 3.5 mg, 70 %. **1H NMR** (400 MHz, CDCl₃) δ/ppm: 10.05 (s, 2H, meso-CH), 9.71 (m, 4H, β-CH), 9.27 (d, 2H, J = 4.6 Hz, β-CH), 9.24 (d, 2H, J = 4.5 Hz, β-CH), 8.86 (br s, 2H, amide-NH), 8.61 (s, 2H, Ar-H), 8.58 (s, 1H, Ar-H), 7.84 (d, 2H, J = 8.4 Hz, Ar-aniline-H), 6.75 (d, 2H, J = 8.9 Hz, Ar-aniline-H), 3.6–3.23 (m, 160 H, TEG(CH₂-CH₃)), 2.22 (t, 12H, J = 6.5 Hz, CH₂), 1.64 (m, 6H, octyl-CH₂), 1.38–1.21 (m, 22H, octyl-CH₂), 0.86 (t, 6H, octyl-CH₃), ~2.28 (s, 4H, NH-ring). **m/z (MALDI-TOF):** 3066.78 ([C₁₅₈H₂₅₉N₁₃O₄₄Na⁺ [M+Na]⁺ requires 3066.84). **UV-Vis** (DMF, 25 °C) 𝜆ₘₐₓ (log ε): 430 nm (4.83); 614 nm (4.34); 692 nm (4.30).

**Figure S12:** 1H-NMR spectrum of IG-1 (CDCl₃, 400 MHz), related to Figure 1.
3.4 Synthesis of JW-1

![Reaction Scheme](image)

**Scheme 4.** Synthetic procedure for JW-1, related to Figure 1.

Compounds 35, 36, and 37 were synthesized as per the protocol followed during synthesizing intermediates for IG-1.

**Compound 38:** Iodoisophthalic acid 31 (0.50 g, 1.7 mmol) was refluxed in SOCl₂ (15.0 mL, 207 mmol) for 16 h to form 34. SOCl₂ was removed under reduced pressure and the brown/red oily residue was dried under high vacuum for several hours. The oil was stored under N₂ and used within 24 h. The oil (81 mg, 0.25 mmol) was dissolved in THF (1.7 mL) and added dropwise to a solution of 37 (340 mg, 0.59 mmol) in THF (1.7 mL) and Et₃N (83 µL, 0.59 mmol) at 0 °C. The reaction was stirred at 20 °C for 3 h and then the precipitate was filtered, and the solvent was evaporated under reduced pressure. The crude residue was dissolved in CH₂Cl₂, washed with 1.0 M aq. HCl and extracted with CH₂Cl₂. The organic layers were dried over MgSO₄ and filtered. Size-exclusion chromatography used to purify the product to yield 38. **Yield:** 0.26 g, 73 %. **¹H NMR** (400 MHz, d₆-DMSO) δ/ppm: 7.74 (d, J = 1.2 Hz, 2 H), 7.31 (t, J = 1.2 Hz, 1 H), 3.36–3.72 (m, 96 H), 3.31 (s, 12 H). **¹³C NMR** (100 MHz, d₆-DMSO) δ/ppm: 169.7, 138.8, 136.5, 124.7, 93.6, 71.9, 70.6, 70.5, 70.4, 69.1, 68.6, 59.0, 49.8, 45.0. **m/z (ESI⁺)** 724.3110 (C₆₀H₁₁₂N₂O₂₆ (M + 2Na)²⁺: 724.3127 requires 724.3110).
Porphyрин JW-1.Zn: To a pre-dried Schlenk tube were added porphyрин 2 (25 mg, 25 μmol), 38 (35 mg, 25 μmol), Pd(PPh₃)₄ (2.9 mg, 2.5 μmol) and CuI (0.5 mg, 3 μmol). These were dried under vacuum for 30 mins, then the flask purged with N₂ to allow addition of THF (1 mL) and DIPA (1 mL). The mixture was freeze pump-thaw degassed 3 times, then Bu₄NF (1.0 M solution in THF, 0.25 mL, 0.25 mmol) was added and the reaction heated to 50 °C under N₂. After 2 h, the reaction was passed through a column of silica, eluting with THF : 1% pyridine then CHCl₃ : 10% MeOH : 1% pyridine. The crude mixture was concentrated and purified by size-exclusion chromatography (CHCl₃) to isolate the desired product as a green solid after drying. **Yield:** 25 mg, 50%. **¹H NMR** (400 MHz, CDCl₃) δ/ppm: 10.05 (s, 2 H, meso-H), 9.85 (d, J = 4.3 Hz, 2 H, β-H), 9.78 (d, J = 4.5 Hz, 2 H, β-H), 9.33 (d, J = 4.5 Hz, 2 H, β-H), 9.31 (d, J = 4.3 Hz, 2 H, β-H), 8.14 (d, J = 1.5 Hz, 2 H, Ar-ortho-H), 7.91 (d, J = 8.8 Hz, 2 H, aniline-H), 7.52 (t, J = 1.5 Hz, 1 H, Ar-para-H), 6.82 (d, J = 9.1 Hz, 2 H, aniline), 3.10–3.93 (m, 112 H, HEG, N-CH₂-C₅H₁₅, O-CH₃), 1.29–1.44 (m, 20 H), 0.93 (t, J = 6.3 Hz, 6 H). **¹³C NMR** (125 MHz, CDCl₃ with 1% d₅-pyridine) δ/ppm: 170.9, 152.1, 151.8, 149.2, 148.2, 137.7, 133.0, 132.4, 131.8, 131.4, 130.8, 130.5, 125.0, 124.7, 111.5, 109.6, 107.7, 102.8, 98.4, 97.6, 94.9, 94.2, 91.0, 71.8, 71.8, 70.6, 70.5, 70.3, 70.2, 69.2, 69.0, 59.0, 58.9, 51.1, 49.9, 45.3, 31.8, 29.5, 29.3, 27.3, 27.2, 22.7, 14.1. MS Calcd for. m/z (MALDI-TOF): 2034.94 (C₁₀₆H₁₅₅N₆O₂₆Zn [M + Na] requires 2035.05).

Porphyрин JW-1: Porphyрин JW-1.Zn (10 mg, 4.9 μmol) was dissolved in CHCl₃ (4.4 mL) and the solution was stirred. TFA (88 mL, 1.2 mmol) was added and the reaction stirred for further 1 h, after which aq. sat. NaHCO₃ was added (2 mL). The product was washed with water (2 × 5 mL), extracted with CHCl₃ (2 × 5 mL), dried over MgSO₄ and concentrated. The product was precipitated as a film by addition of 60–80 petrol ether to a CH₂Cl₂ solution, followed by careful evaporation of the CH₂Cl₂ and addition of pentane, yielding the clean product JW-1. **Yield:** 8.7 mg, 90%. **¹H NMR** (400 MHz, CDCl₃) δ/ppm: 10.09 (s, 2 H, meso-H), 9.75 (d, J = 4.4 Hz, 2 H, β-H), 9.69 (d, J = 4.7 Hz, 2 H, β-H), 9.32 (d, J = 4.6 Hz, 2 H, β-H), 9.29 (d, J = 4.3 Hz, 2 H, β-H), 8.14 (br s, 2 H, Ar-ortho-H), 7.91 (d, J = 8.5 Hz, 2 H, aniline-H), 7.56 (s, 1 H, Ar-para-H), 6.82 (d, J = 8.9 Hz, 2 H, aniline-H), 3.26–3.93 (m, 112 H, HEG, N-CH₂-C₅H₁₅, O-CH₃), 1.68–1.78 (m, 9 H), 1.23–1.42 (m, 33 H), 0.93 (t, J = 6.8 Hz, 6 H), −2.27 (br. s., 2 H, N-H). **¹³C NMR** (125 MHz, CDCl₃) δ/ppm: 169.8, 147.5, 144.1, 136.7, 132.3, 131.3, 130.6, 129.8, 129.4, 128.8, 124.2, 123.4, 110.5, 107.9, 106.0, 102.1, 99.4, 96.9, 94.4, 91.7, 88.5, 70.9, 70.8, 70.8, 69.6, 69.5, 69.5, 69.3, 69.2, 68.2, 67.9, 58.0, 57.9, 52.4, 50.1, 48.9, 44.3, 30.8, 28.5, 28.3, 26.3, 26.2, 21.7, 13.1. m/z (MALDI-TOF): 1971.77 (C₁₀₅H₁₅₄N₆O₂₆Na₂ (M + Na) requires 1972.14). **UV-Vis** (DMF, 25 °C) λₘₐₓ (log ε): 425 nm (5.01); 615 nm (4.57); 693 nm (4.53).
Figure S13. $^1$H-NMR spectrum of JW-1 (CDCl$_3$, 400 MHz), related to Figure 1.
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