Supporting Information for:

Catalytically Active Single-Chain Polymeric Nanoparticles: Exploring Their Functions in Complex Biological Media

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1. Materials and Methods

Chemicals

All commercial reagents and solvents were obtained from Acros, Biosolve, or Sigma-Aldrich, except for deuterated chloroform and deuterated 2-propanol, which were purchased from Cambridge Isotopes Laboratories. AIBN was recrystallized from methanol. All other commercial reagents and solvents were used without additional purification. 4-Cyano-4-methyl-5-(phenylthio)-5-thioxopentanoic acid was kindly provided by SyMO-Chem (Eindhoven, The Netherlands). Texas red cadaverine was obtained from Eurogentec. Naph-OH,[1] Bipyamine,[2] BTAamine[2] and **P3**[2] were prepared according to previously described literature procedures. The synthesis of **pPFPA**, **P2** and the substrates **S1-S4** are reported elsewhere.[3]

Instruments

NMR spectra were measured on a Varian Mercury Vx 400 MHz and/or a Varian 400MR 400 MHz. Deuterated solvents used are indicated in each case. ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Circular dichroism measurements were performed on a Jasco J-815 spectropolarimeter where the sensitivity, time constant and scan rate were chosen appropriately. Cells with an optical path length of 0.5 cm were used. Dialysis was performed in Spectra/Por Dialysis membranes (Spectrum Laboratories), with a molecular weight cutoff of 6-8 kDa. DMF-SEC measurements were carried out in PL-GPC-50 plus from Polymer Laboratories (Varian Inc. Company) equipped with a refractive index detector and working in DMF containing 10 mM LiBr at 50 °C (flow rate: 1 mL min^{-1}) on a Shodex GPC-KD-804 column (exclusion limit = 400 kDa.; 0.8 cm i.d. × 300 mm) or on a Shodex GPC-KD-805 column (exclusion limit = 5000 kDa.; 0.8 cm i.d. × 300 mm) which were calibrated with poly(ethylene oxide) (PEO) samples (Polymer Laboratories). THF-SEC measurements were performed on a Shimadzu-system with two Agilent Technology columns in series (PLgel 5 mm mixed C [200–2 000 000Da] and PLgel 5 mm mixed D [200–40 000 Da]) and equipped with a RI detector (Shimadzu RID-10A) and a PDA detector (Shimadzu SPD-M10A), with THF as eluent at a constant flowrate of 1.0 mL min^{-1}. Dynamic light scattering measurements were performed on a Malvern mV Zetasizer equipped with an 830 nm laser. LC-MS was measured on ThermoScientific LCQ Fleet, using H_2O/CH_3CN (0.1% formic acid) as eluent. Fluorescence measurements (*in vitro*) was performed on a Jasco FP-6500 spectrofluorometer.

Delivery methods

Three different procedures were employed for the cellular delivery of SCPNs. The described procedures were used to visualize cell internalization by confocal microscopy, measure cell toxicity and test performances for catalysis and PDT in living cells.

For the endocytosis-based delivery HeLa cells were seeded at approximately 70% confluency and cultured overnight in DMEM with 10% FBS at 37C with 5% CO_2. Subsequently the medium was discarded, cells were washed twice with PBS and fresh medium containing 2.5 mg/mL of SCPNs was added. Cells were incubated for 24 h to allow SCPNs internalization and subsequently washed twice with PBS and supplemented with fresh medium. For 2-color imaging

and colocalization cell nuclei was stained with Hoechst and lysosomes with 50 mM Lysotracker for 10 min.

Electroporation was performed using a cellaxes device according to manufacturer instructions for HeLa cells. Cells were seeded to full confluency and cultured overnight before electroporation. A 10 mg/mL solution of SCPNs in PBS was loaded into the tubing of the instrument and the electrode put in contact with the cell dish. 20 μL of SCPN solution was dispensed followed by 30 seconds of electroporation using pulses at 100 V. Cell were let resting for 2 h after which the medium was refreshed in order to remove the free SCPNs not internalized and the dead cells harmed by electroporation.

For extracellular measurements a concentrated solution of SCPNs in PBS was added to the cell medium to reach a final concentration of 1 mg/mL. Cells were therefore kept up to 3 h at 37 °C 5% CO_2, in this time span no significant internalization was observed.

Confocal imaging

Fluorescent cell images were acquired with a Leica TCS SP5 AOBS equipped with a 40x water immersion objective and a temperature-controlled incubation chamber maintained at 37 °C. Fluorescence was excited with the inbuilt white laser that allows for accurate selection of the excitation wavelength. Texas red-labeled SCPNs (**P1**) were excited at 560 nm and emission was detected from 575 nm to 650 nm using the high-sensitivity PMT detector of the setup. Porphyrin-labeled polymer P3 was excited using an additional 403 nm solid state laser and fluorescence measured between 600 nm and 700 nm. Depropargylated rhodamine substrate was excited at 488 nm and fluorescence measured between 500 nm and 530 nm.

Toxicity

To assess toxicity of SCPNs live dead assay was performed according to provider protocol. Briefly, HeLa cells were seeded at approximatively 70% confluency and cultured overnight in DMEM with 10% FBS at 37 °C with 5% CO_2. Subsequently the medium was discarded, cells were washed twice with PBS and fresh medium was added. SCPNs were subsequently delivered at different concentrations and incubation time according to the different procedures reported above. At this point the SCPN-containing medium was discarded and the reagents for the live dead assay added. After 10 minutes cells in the green channel (corresponding to the live cells stained by Calcein-AM) and in the red channel (corresponding to the dead cells stained by ethidium bromide homodimer) were counted. Cell viability was therefore calculated and compared with the control where the same volume of PBS was added.

Porphyrin PDT

For the singlet oxygen generation measurements HeLa cells were incubated with different concentrations of **P3** for 24 h. The emission spectra of the porphyrin inside cells were measured exciting the fluorescence with the 403 nm laser while varying the detection between 430nm and 800nm (spectral window of 5 nm). To test the ability to generate singlet oxygen and induce cell death cells were irradiated with the 403 nm laser, (average power of 160 mW per pulse (each

pulse is 55 ps) at a repetition rate of 42 MHz) and the cell viability compared with adjacent not irradiated area. Cell viability was measured with live dead assay (administrated 30 min after irradiation) according to the protocol described above.

Catalysis in a cell

Rhodamine depropargylation was chosen to test the ability of SCPNs to catalyze a reaction in the cellular media. The synthesis of the substrate as well as the in vitro ability of SCPNs to catalyze this reaction are reported elsewhere.[5] SCPNs were delivered either in the cytosol or in the extracellular space as reported above. Subsequently propargylated rhodamine was added in the medium to reach a final concentration of 10 mM. Confocal images were performed after 3 h of incubation in order to test the conversion of the substrate into the fluorescent product. For the time lapse measurement of substrate conversion HeLa cells were seeded into a 96 well, treated with SCPNs and subsequently with the substrate as described above. All samples and controls were performed in triplo and the plotted result is the average of three measurements. Fluorescence was measured using a Tecan plate reader exciting the samples at 488 nm and measuring from 500 to 550 nm.

SCPNs preparation for catalysis.

P1@Pd(II) was prepared by mixing **P1** solution in PBS with Na_2PdCl_4 in water, at a final concentration of **P1** 1mg/mL, [Bipy] = 60 μM and Na_2PdCl_4= 50 μM. Mixing was performed at room temperature 1 h before usage.

P2@Cu(I) was prepared by mixing **P2** solution in PBS with $CuSO_4$ in water, at a final concentration of **P2** 1 mg/mL, [Phen] = 83.3 μM; $CuSO_4$ 41.6 μM, (phen:Cu=2:1). NaAsc at a final concentration of 1 mM was added to reduce Cu(II) to Cu(I) *in situ*. Mixing was performed at room temperature 1 h before usage.

Cell culture

HeLa cells were cultured in DMEM supplemented with serum (10% fetal bovine serum) and penicillin/streptomycin (at a final concentration of 50 to 100 I.U./mL penicillin and 50 to 100 μg/mL streptomycin). For kinetics catalysis experiments, cells were seeded at 100% confluency (87500/cm^2) 24h before performing the experiment.

For fluorescence microscopy cells were seeded in a 8-well Labtek chamber (0.8 cm^2/well, coverglass, Nunc-Thermo Scientific). For kinetics experiments, cells were seeded in a 96 well plate and during the experiment, medium was supplemented with Hepes buffer.

Fluorescence spectroscopy

Tecan infinite 200 Pro microplate reader with Tecan i-control software was used for the kinetics experiments. Excitation was set at 480 nm (bandwith 10 nm) and emission was measured from 520 to 530 nm (bandwith 20 nm) with an emission wavelength step size of 2 nm and gain set to 83. During the measurements temperature was set to 37 ºC.

For short time kinetics, 13 cycles of 10 min interval time were used, while for long time kinetics, 400 cycles of 10 min interval time were used.

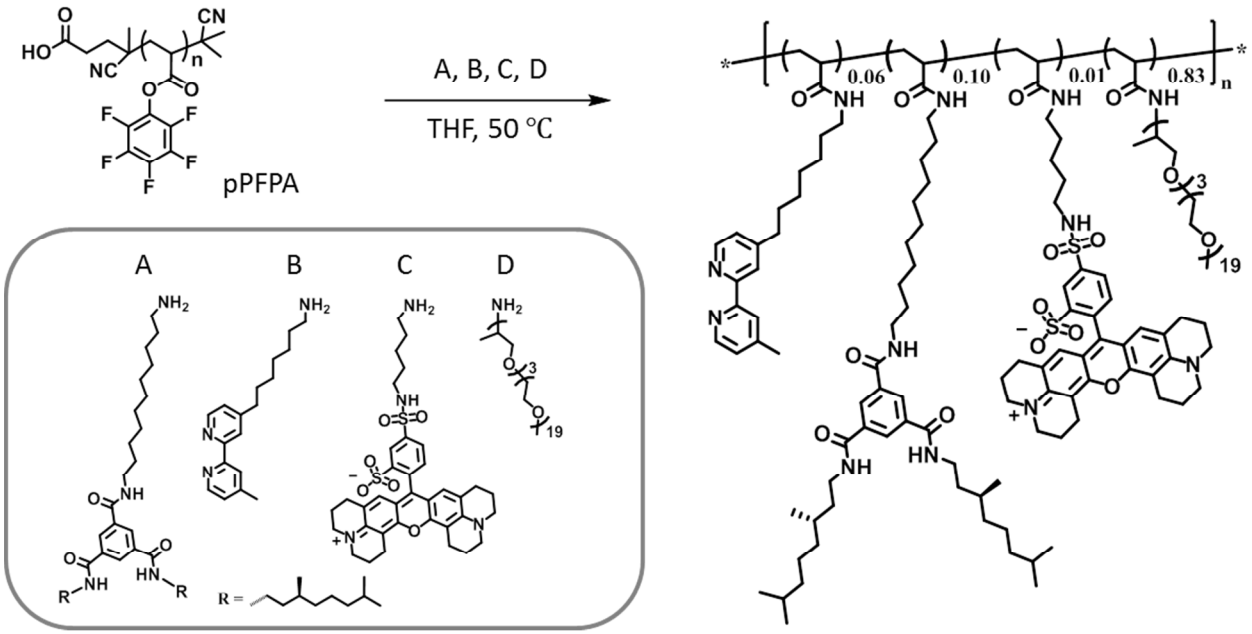
Epifluorescence microscopy

Epifluorescence images were acquired using a Nikon N-STORM system in Epi mode equipped with a Nikon 20x objective (air, 0.5 NA) and an epifluorescence lamp (Intensilight C-HGFIE). FITC filter was used to acquire images with a Hamamatsu ORCA- Flash 4.0 camera at 200 ms exposure time, 256 x 256 pixel region (pixel size 0.16 μm). Oko lab chamber was used to keep the cells at 37 ºC and 5% CO_2.

Cytotoxicity Cytotoxicity was evaluated with Presto Blue assay. HeLa cells were seeded in a 96 well plate at 100 % confluency and incubated with SCPNs complexed or not with the metals and with the respective substrate for 4 h and 24 h at 37 ºC, 5% CO_2. Concentrations used were the same as for the catalysis experiments. Presto Blue solution was added 1 h before the end of the incubation time at a 1x final concentration. The fluorescence was read in a Tecan infinite 200 Pro microplate reader in which excitation was set at 560 nm (bandwith 10 nm) and emission was measured at 590 nm.

2. Synthetic procedures

Synthesis of P1: pPFPA (M_n = 18.0 kDa, $Đ$ = 1.28, n = 120, 40 mg, 1.0 eq.) and BTA-amine (11 mg, 10 eq.) were placed in a flask with a stirrer, dissolved in 5 mL of dry THF and the mixture was heated to 50 °C for 2 h. Next, Bipy-amine (2.85 mg, 6 eq.) dissolved in THF was added and reacted for 2 h. Then a stock solution of Texas-red Cadaverine (116 μL, 10 mg/ml, 1 eq.) in DMF and a drop of triethylamine was added into the reaction mixture and reacted for 4 h. Finally, Jeffamine M1000 stock solution in THF (350 μL, 1 g/mL, 250 eq.) was added into the mixture and stirred at 50°C overnight. The reaction solution was then dialyzed against THF for 2 days, then methanol for 2 days. The final polymer was obtained by precipitate in pentane and dried by high vacuum. ^{1}H-NMR ($CDCl_3$): δ = 8.6~8.1 (broad Ar-*H*, BTA, Ar-*H*, Bipy and Ar-*H*, dye), 7.15 (s, broad, Ar-*H*, Bipy), 6.0~7.0 (broad, -CO-NH-), 3.0~4.2 (broad, NH-C*H*$_2$, CO_2-CH_2-C*H*$_2$-O, O-C*H*$_3$), 2.2-0.6 (m, C*H*, C*H*$_2$, C*H*$_3$). SEC/DMF: M_n = 30.8 kD, $Đ$ = 1.25 (GPC-DMF).



Scheme S1: *Synthesis of polymer* ***P1****, A) BTA-amine; B) Bipy-amine; C) Texas-red-amine; D) Jeffamine@M1000.*

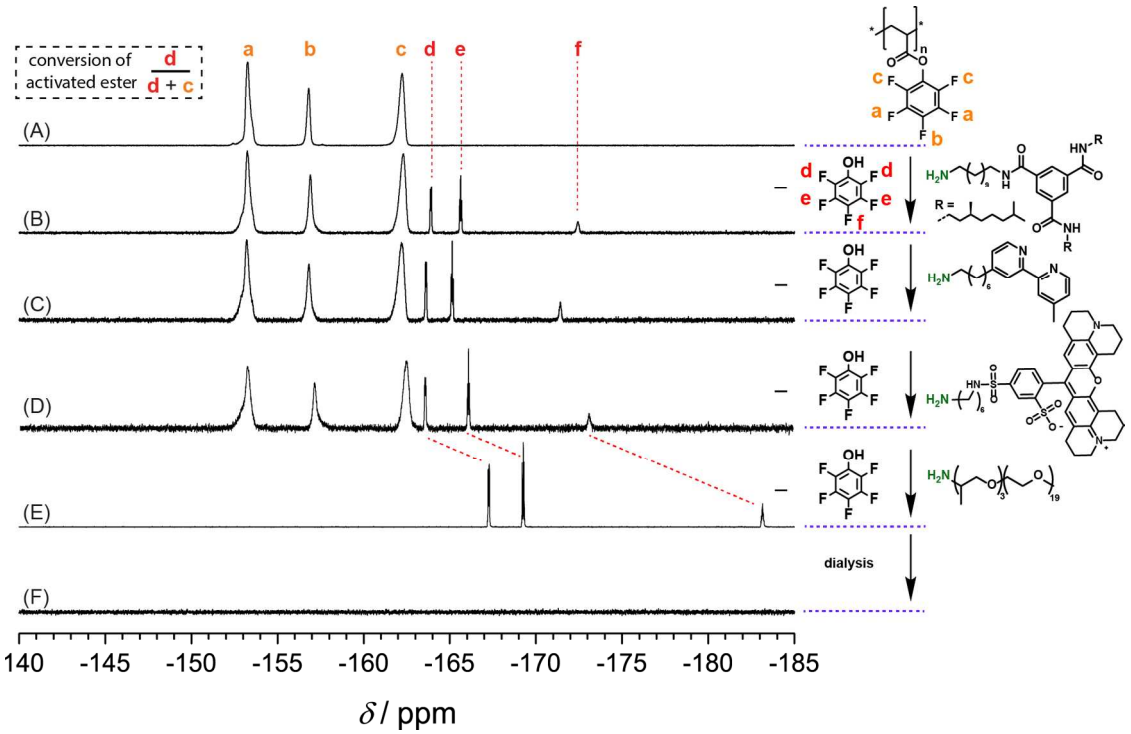
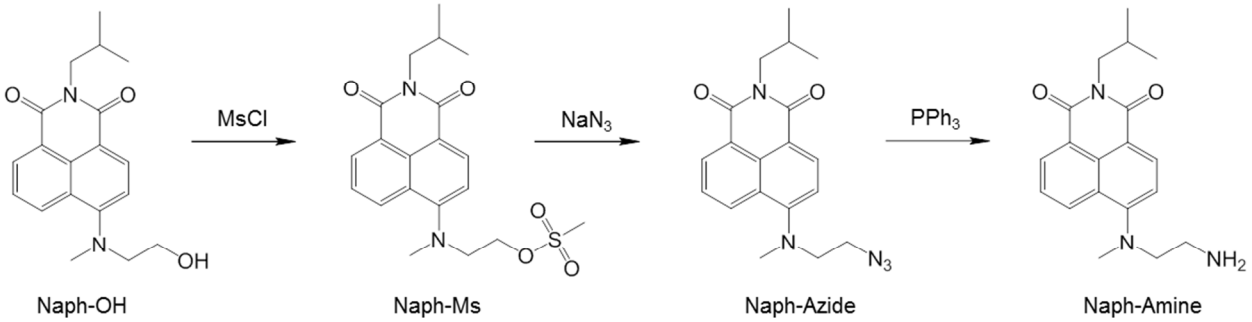


Figure S1: *^{19}F NMR spectra in $CDCl_3$ of pPFPA and its sequential modification with BTA-amine, Bipy-amine, Texas-red-amine and Jeffamine*

Synthesis of 6-((2-aminoethyl)(methyl)amino)-2-isobutyl-1H-benzo[de]isoquinoline-1,3(2H)-dione:



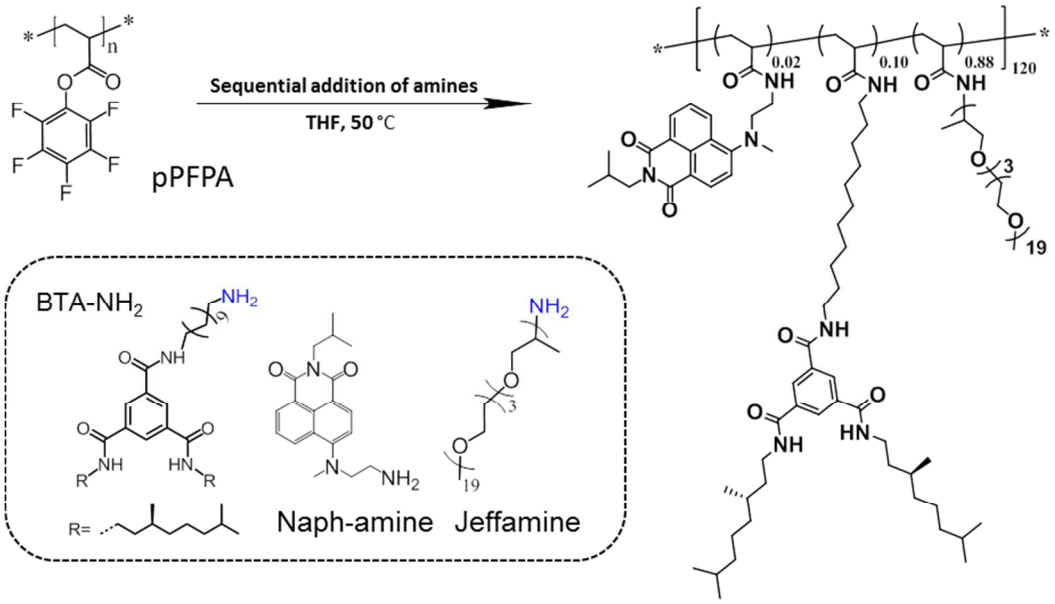
Naph-OH was synthesized according to reference 1a.

Naph-Ms: 1.3 gram Naph-OH was weighted into a 100 mL flask, was then dissolved in 50 mL Chloroform. The flask was put in an ice bath and cooled. After addition of 2.5 mL di-isopropylethylamine, 1 mL methansulfonylchloride was added dropwisely. The ice bath was removed after 30 mins. The reaction mixture was stirred at room temperature for another 1.5 hours, LC-MS confirmed the completion of the reaction and the desired product was formed. The reaction mixture was washed with HCl (1N), sodium carbonate (aq. 5%) and brine. The organic phase was dried with sodium sulfate. After filtration and removal of the solvent, pure product was obtained. Yield 1.45 gram, 89.8%. ^{1}H-NMR ($CDCl_3$): δ = 8.60 (dd, 1H); 8.50 (m,

2H); 7.72 (dd, 1H); 7.29 (d, 1H); 4.48 (t, 2H); 4.04 (d, 2H); 3.70 (t, 2H); 3.13 (s, 3H); 2.96 (s, 3H); 2,23 (m, 1H); 0.98 (d, 6H). ^{1}C-NMR ($CDCl_3$): δ = 164.72, 164.22, 155.43, 132.20, 131.35, 130.30, 130.06, 126.32, 125.86, 123.30, 117.04, 115.98, 65.93, 55.26, 47.07, 42.18, 37.75, 27.41, 20.32. LC-MS: calcd. $[M+H]^+$ = 405.14, obs. 405.17

Naph-Azide: 1.45 gram Naph-Ms and 800 mg sodium azide were weighted into a 100 mL flask, and were dissolved in 50 mL DMF. The mixture was stirred under argon atmosphere at 80 ℃ for 5 hours. After cooling to room temperature, the mixture was pour into 300 mL water and was extracted with 100 mL ethyl acetate. The organic phase was washed with water and brine, then was dried by sodium sulfate. After filtration and removal of the solvent under vacuum, pure product was obtained, yield 1.05 gram, 83.3 %. ^{1}H-NMR ($CDCl_3$): δ = 8.60 (dd, 1H); 8.53 (m, 2H); 7.72 (dd, 1H); 7.27 (d, 1H); 4.04 (d, 2H); 3.56 (m, 2H); 3.10 (s, 3H); 2.96 (s, 3H); 2.25 (m, 1H); 0.98 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.77, 164.27, 155.61, 132.22, 131.30, 130.54, 130.11, 126.41, 125.77, 123.24, 116.87, 115.70, 55.54, 48.64, 47.05, 42.38, 27.42, 20.33. LC-MS: calcd. $[M+H]^+$ = 352.17, obs. 352.17

Naph-Amine: 1.0 gram Naph-Azide was weighted into a 250 mL flask, and was dissolved in 100 mL THF:water (95:5 v:v) mixture. 800 mg triphenyl phosphine was then added. The mixture was stirred at room temperature overnight. After evaporating all the solvent under vacuum, the residue was extracted with DCM/water. The organic phase was further washed with brine and was dried over sodium sulfate. After filtration, the solvent was removed through evaporation under vacuum. The product was obtained after column chromatography (eluent DCM:methanol 92:8 v:v), obtain product, yield 750 mg, 81%. ^{1}H-NMR ($CDCl_3$): δ = 8.57 (m, 1H); 8.49 (d, 2H); 7.69 (dd, 1H); 7.23 (d, 1H); 4.04 (d, 2H); 3.41 (t, 2H); 3.06 (m, 5H); 2.23 (m, 1H); 0.98 (d, 6H). ^{1}C-NMR ($CDCl_3$): δ = 164.84, 164.33, 156.51, 132.40, 131.18, 130.67, 130.16, 126.26, 125.43, 123.22, 116.18, 115.23, 58.96, 47.02, 42.23, 39.42, 27.42, 20.33. LC-MS: calcd. $[M+H]^+$ = 326.18, obs. 326.17



Scheme S2: *Synthesis of polymer* ***P4****.*

Synthesis of P4: The synthesis of **P4** follows the similar procedure as **P1**. 25 mg pPFPA (M_n = 18.0 kDa, $Đ$ = 1.28, n = 120, 1.0 eq.) was dissolved in 2 mL THF. BTA-amine (6.9 mg, 10 eq.) and Naph-Amine (0.68 mg, 2 eq.) were dissolved in 2 mL of THF and added into the pPFPA solution. The mixture was heated to 50 °C for 2 h. Next, Jeffamine M1000 stock solution in THF (350 μL, 1 g/mL) was added into the mixture and stirred at 50°C overnight. The reaction solution was then dialyzed against THF for 3 days, then methanol for 1 day. The final polymer was obtained by precipitate in pentane and dried by high vacuum. ^{1}H-NMR ($CDCl_3$): δ = 8.6~8.0 (broad Ar-*H*, BTA, Ar-*H*, Ar-*H*, dye), 7.9-7.0 (m, Ar-*H*, dye), 6.0~7.0 (broad, -CO-NH-), 2.9~4.3 (broad, NH-C*H*$_2$, CO_2-CH_2-C*H*$_2$-O, O-C*H*$_3$), 2.2-0.6 (m, C*H*, C*H*$_2$, C*H*$_3$). SEC/DMF: M_n = 28.5 kD, $Đ$ = 1.23 (GPC-DMF).

3. Spectroscopic and light-scattering characterization of the SCPNs

Metal-complexation of P1 and P2 studied by UV-vis spectroscopy

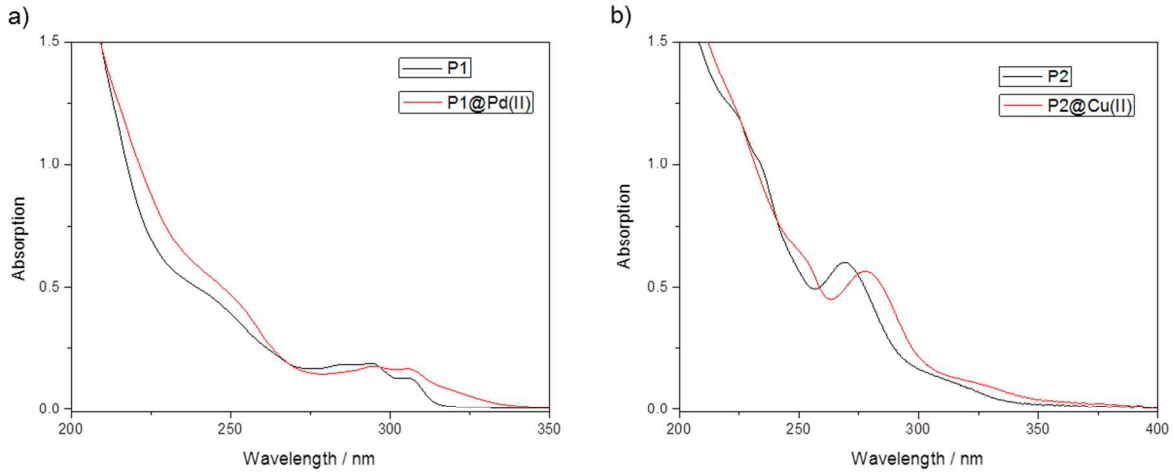


Figure S2: *a) UV-vis spectra of* ***P1*** *(black, 0.5 mg/mL) and* ***P1@Pd(II)****(red, 0.5 mg/mL, [Bipy]:[Na_2PdCl_4]=1:1); b) UV-vis spectra of* ***P2*** *(black, 0.5 mg/mL) and* ***P2@Cu(II)*** *(red,0.5 mg/mL, [Phen]:[$CuSO_4$]=2:1).*

Spectroscopic characterization of P1 and P4

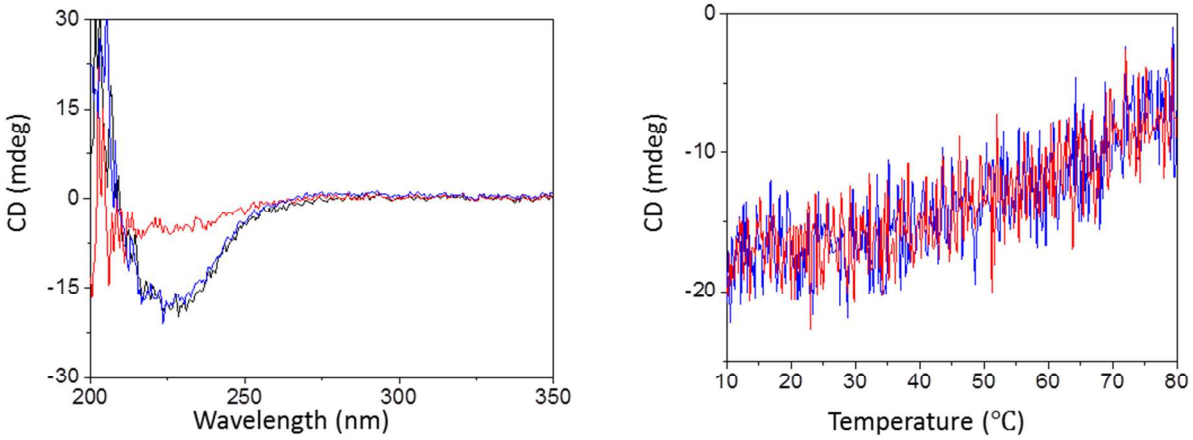


Figure S3: *(Left) CD spectra of* ***P1*** *at 10 °C (black), 90 °C (red) and* ***P1@Pd(II)*** *at 10 °C (blue); (right) temperature-wavelength scan measured at a cooling rate of 60 K h^{-1} at λ = 223 nm for solutions of* ***P1*** *in PBS buffer (0.5 mg/mL, l = 0.5 cm).*

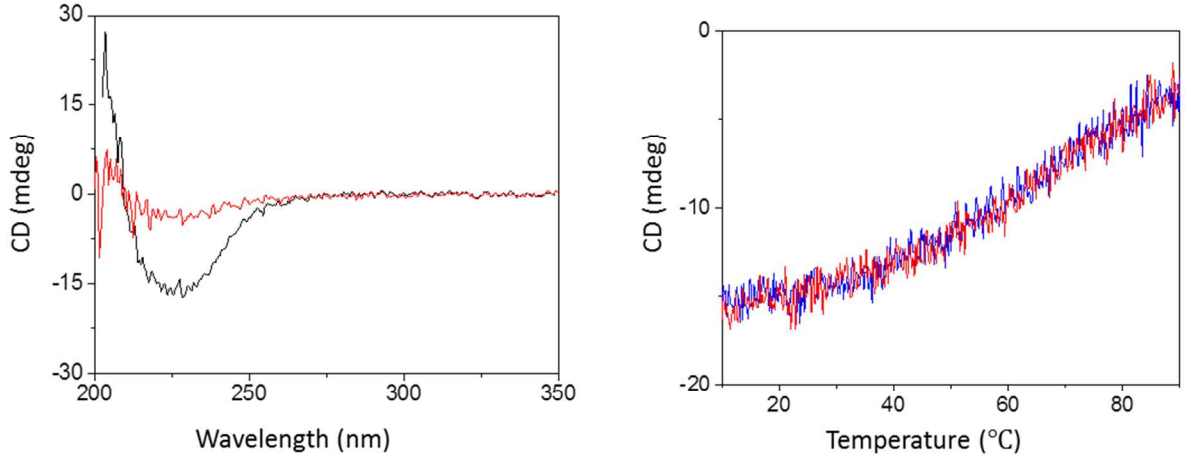


Figure S4: *(Left) CD spectra of* ***P4*** *at 10 °C (black) and 90 °C (red); (right) temperature-wavelength scan measured at a cooling rate of 60 K* h^{-1} *at* λ *= 223 nm for solutions of* ***P4*** *in water (0.5 mg/mL, l = 0.5 cm).*

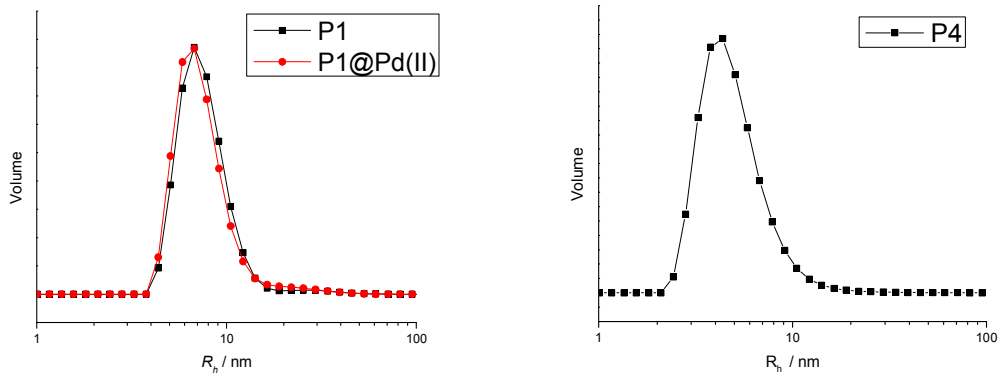


Figure S5. *DLS results of* ***P1*** *(1 mg/mL in water,* R_h *= 7.60 nm);* ***P1@Pd(II)*** *(1 mg/mL,* $[Na_2PdCl_4]$ *= 50* μM *,* R_h *= 7.87 nm) and* ***P4*** *(1 mg/mL,* R_h *= 5.17 nm)*

4. Cellular internalization of SCPNs

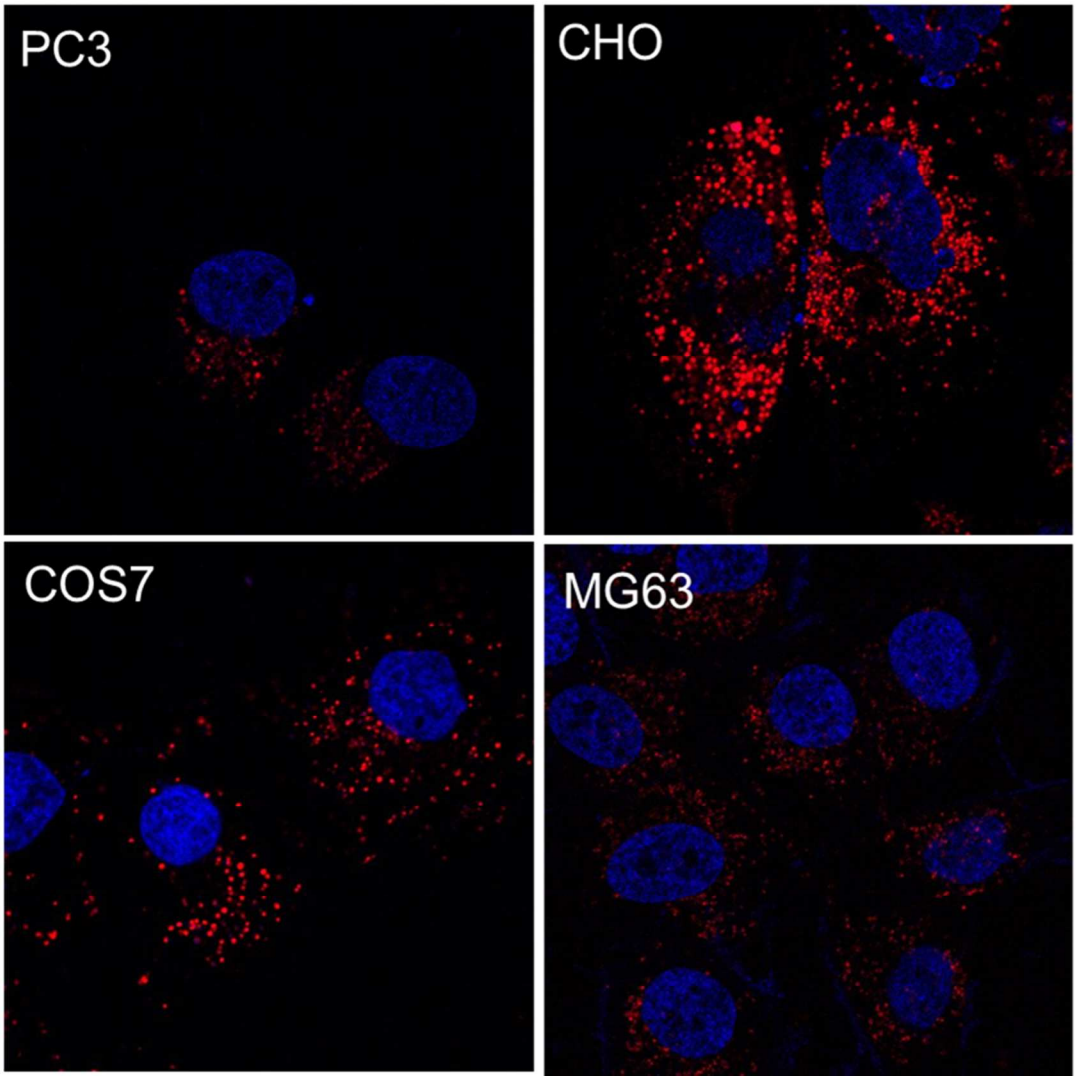


Figure S6. *Confocal microscopy of live cells (PC3, CHO, COS7, MG63) incubated with* ***P1*** *SCPNs for 24 h at 2.5 mg/mL.*

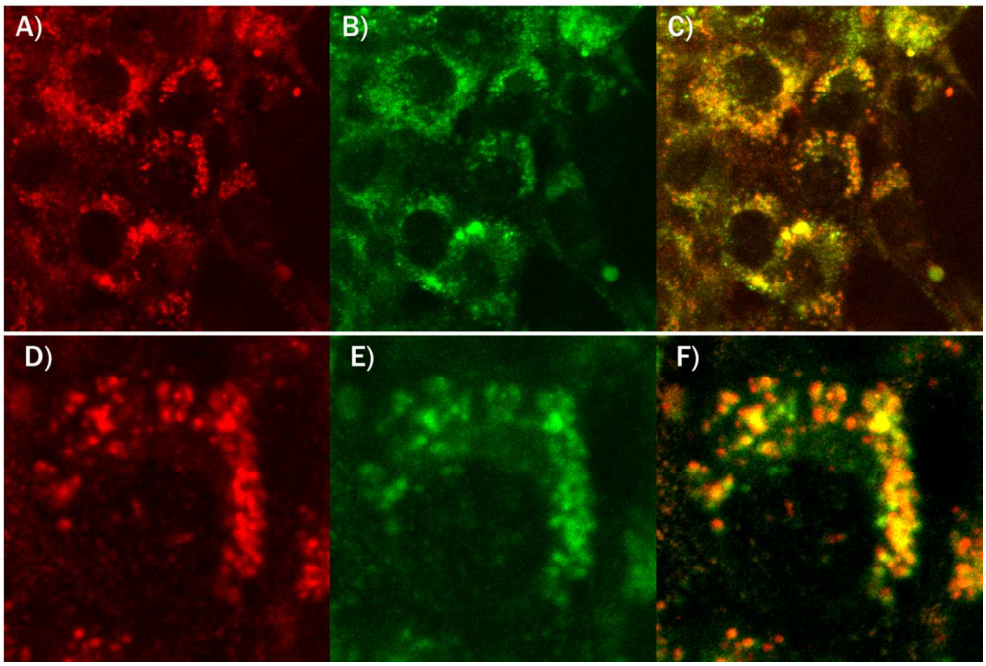


Figure S7*. Confocal microscopy images of HeLa cells incubated with SCPNs based on* ***P1****, at 2.5 mg/mL for 24 h. A and D)* ***P1*** *SCPNs, Texas Red fluorescence; B and E) Lysosensor green; C and F) colocalization. Lower panels are a zoom in from upper panels.*

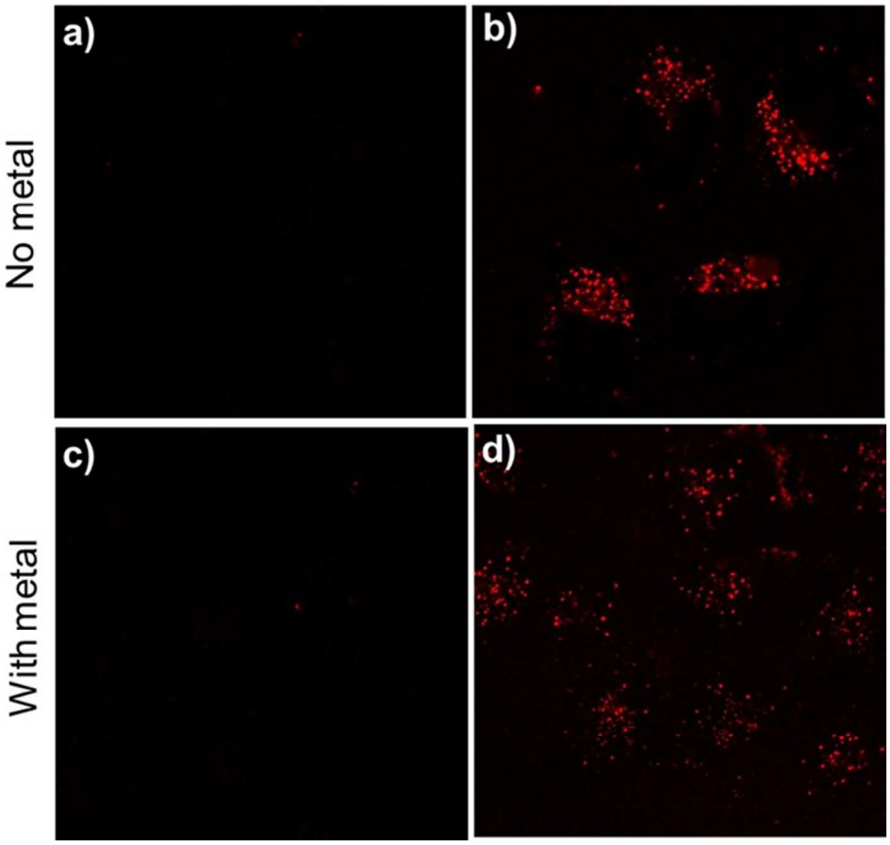


Figure S8. *Confocal microscopy of live HeLa cells incubated with* ***P1*** *SCPNs (a, b) or with* ***P1@Pd(II)*** *(c, d) for 3 h at mg/mL (a, c) or 24 h at 2.5 mg/mL (b,d).*

5. Fluorescence characterization of P4

In polymer **P4** both a hydrophobic collapse induced by the hydrophobic side chains and intramolecular H-bond formation between the BTA units into helical arrays are operative and "fold" a single polymer chain into a compartmentalised single chain polymeric nanoparticle in aqueous media. The terminology "folding" is applied when both hydrophobic collapse and helical hydrogen bond formation is operative, the formed is assessed by the use of a solvatochromic dye whereas the latter is sensitively probed by CD spectroscopy (Figure S4). The hydrophobic collapse results in hydrophobic interior whereas the hydrogen bond formation induces the formation of a structured inner compartment.

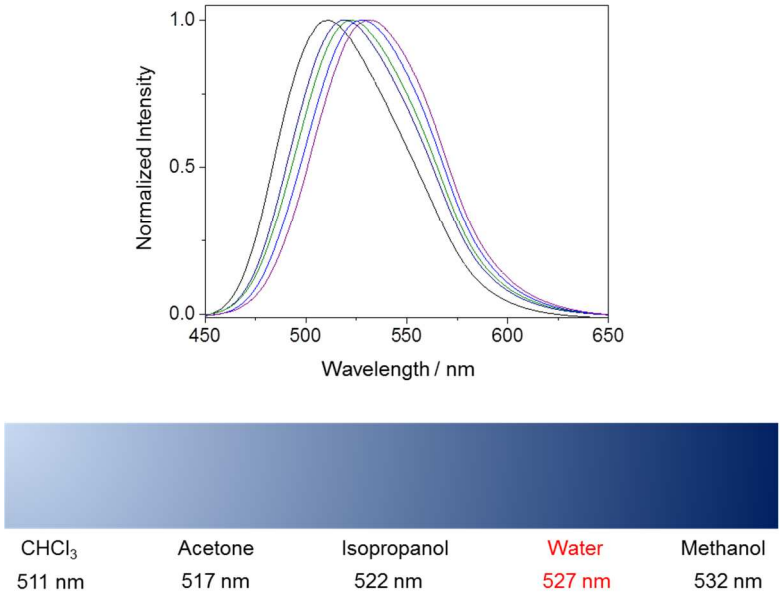


Figure S9: *The emission wavelength of* ***P4*** *(0.5 mg/mL, ex: 440 nm) shifts in solvents with varying polarity.*

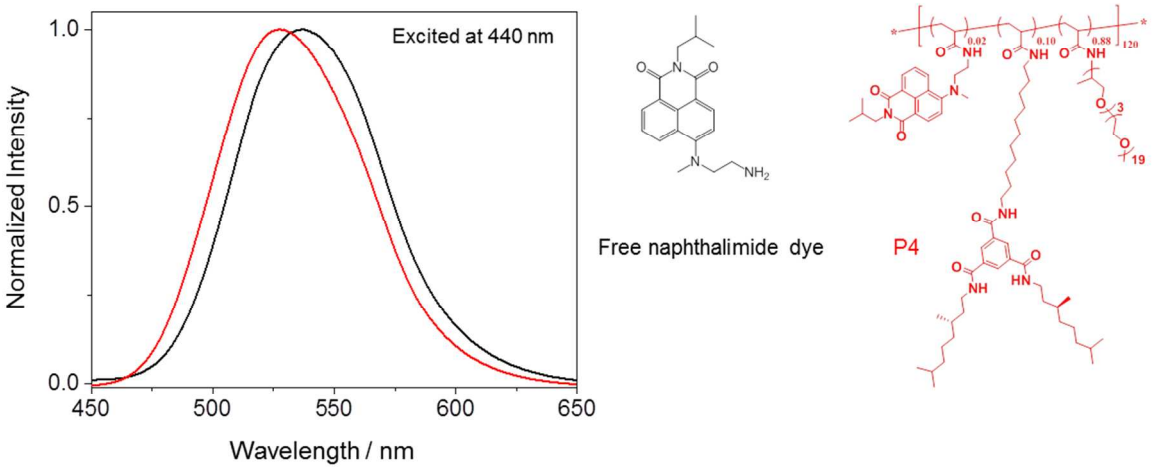


Figure S10: *Comparing* ***P4*** *with the free naphthalimide dye Naph-Amine (red:* ***P4*** *0.5 mg/mL in water; black: Naph-Amine 10 μM in water with 0.1% DMSO)*

	λ_{max}/nm
Naphtalimide dye in PBS	540
Naphtalimide dye in chloroform	507
Naphtalimide dye in DMEM	530
Naphtalimide dye in DMEM + serum	518
P4 in PBS	530
P4 in chloroform	511
P4 in DMEM	521
P4 in DMEM + serum	524

Table S1. *Emission maxima of naphthalimide dye (Naph-Amine) and* ***P4*** *in different medium.*

6. P1 and P2-catalyzed deprotections *in vitro*

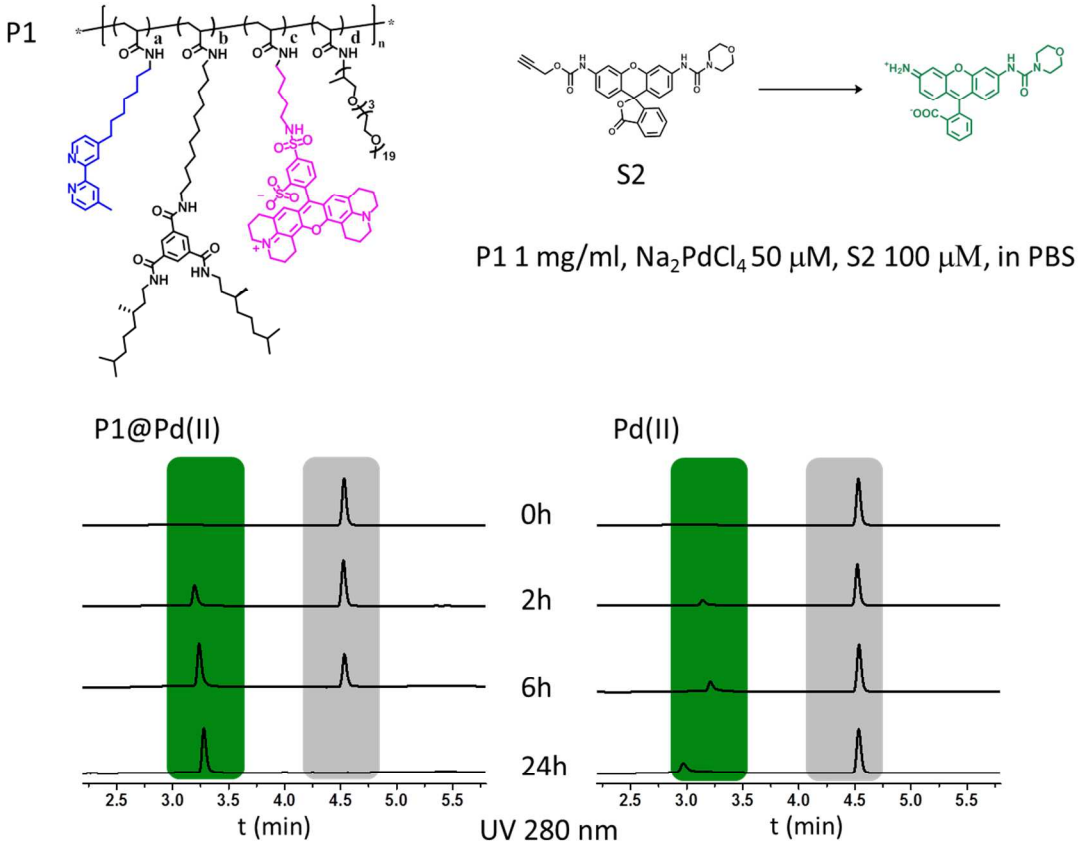


Figure S11: P1@Pd(II) *catalyzed depropargylation reaction of* ***S2*** *([Bipy] = 60 μM; Na_2PdCl_4= 50 μM, [**S2**] = 100 μM). LC−MS traces of reaction mixture at different reaction times, monitored with UV detection. The results of the control experiment that only use Pd(II) is also shown (grey area: substrate; green area: MC-Rh 110).*

General procedure: 1 mL **P1** solution (1 mg/mL in PBS) was put into a 1.5 mL vial. 5 μL Na_2PdCl_4 solution (10 mM in water) was added through a liquid-transferring pipette. The mixture was gently shaken and stood for 10 mins to ensure fully complexation. 10 μL substrate stock solution (10 mM in DMSO) was added to start the reaction. The mixture was checked by LC-MS at different reaction time to monitor the conversion.

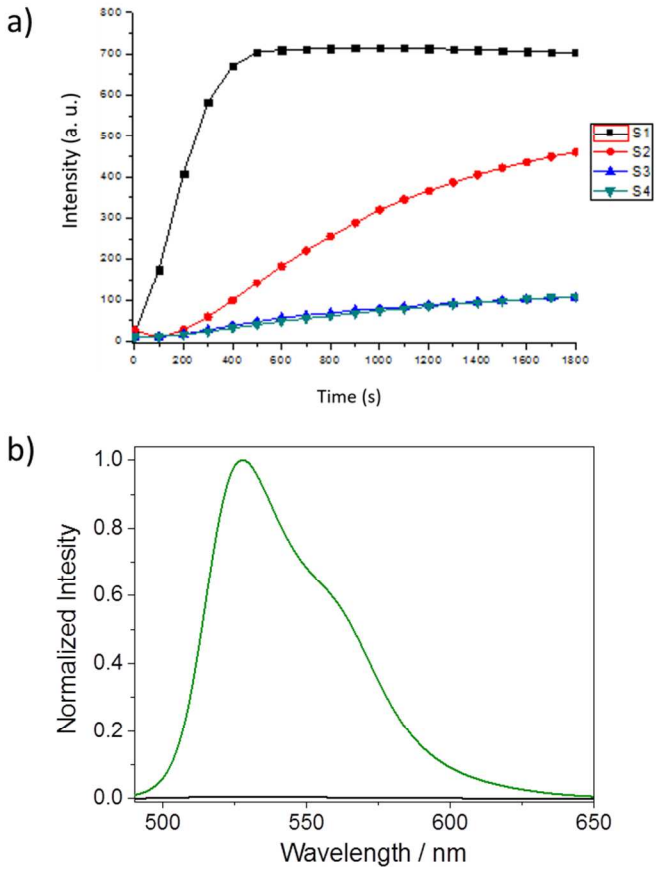


Figure S12: *a)* ***P2@Cu(I)*** *catalyzed depropargylation reaction of* ***S1-S4*** *(in water, [Phen] = 20 μM; [$CuSO_4$] = 10 μM,* ***[S1-S4]*** *= 30 μM, [NaAsc] = 1 mM, ex. 485 nm, em. 520 nm). b) Emission spectrum of* ***S1*** *before (black) and after (green) the depropargylation reaction.*

General procedure: 2 mL **P2** solution (0.2 mg/mL in water) was put into a quartz cuvette, 10 μL $CuSO_4$ was added for complexation. After 10 mins, 20 μL substrate stock solution (3 mM, DMSO) was added, the mixture was gently shaken to obtain a homogeneous solution. Then 10 μL NaAsc solution (200 mM in water) was added into the cuvette to initiate the reaction. The cuvette was immediately put into the fluorometer for time-dependent recording.

7. Viability of catalytic SCPNs

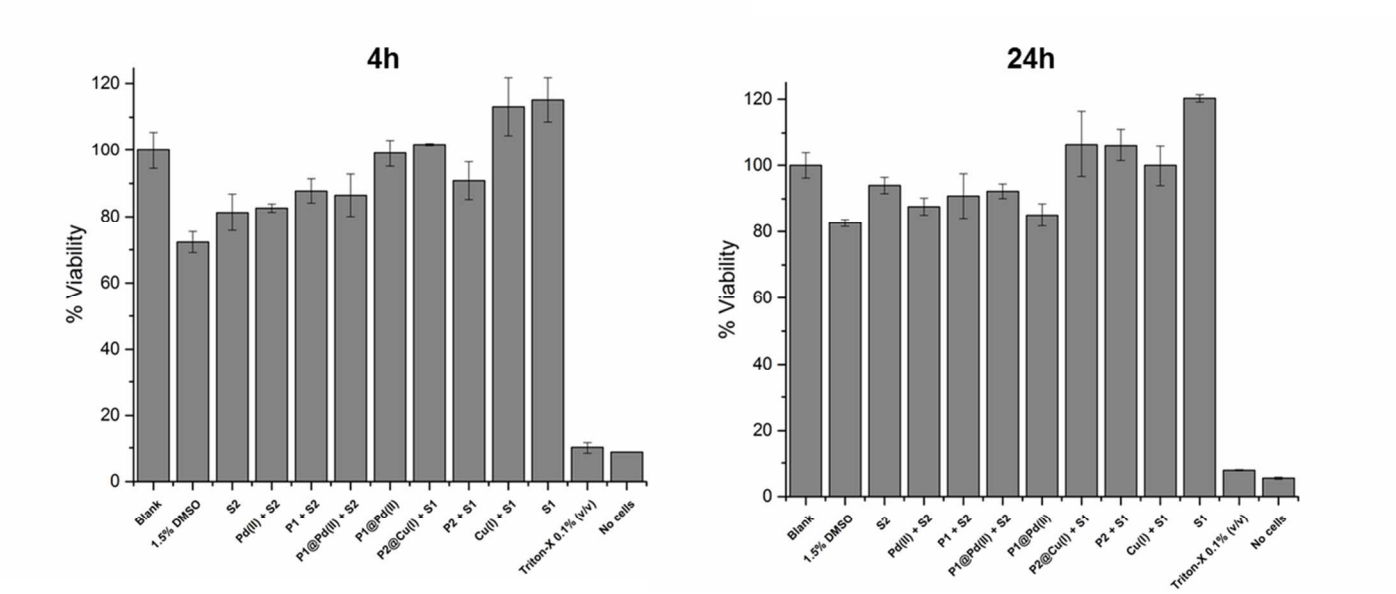


Figure S13*: Results obtained from the Presto Blue assay on the viability of HeLa cells after 4 h or 24 h incubation in catalysis conditions with Cu(I) and Pd(II) with and without substrates, and in the presence and absence of the polymer.*

8. Fluorescence results of P1 and P2-catalyzed deprotections in biological media

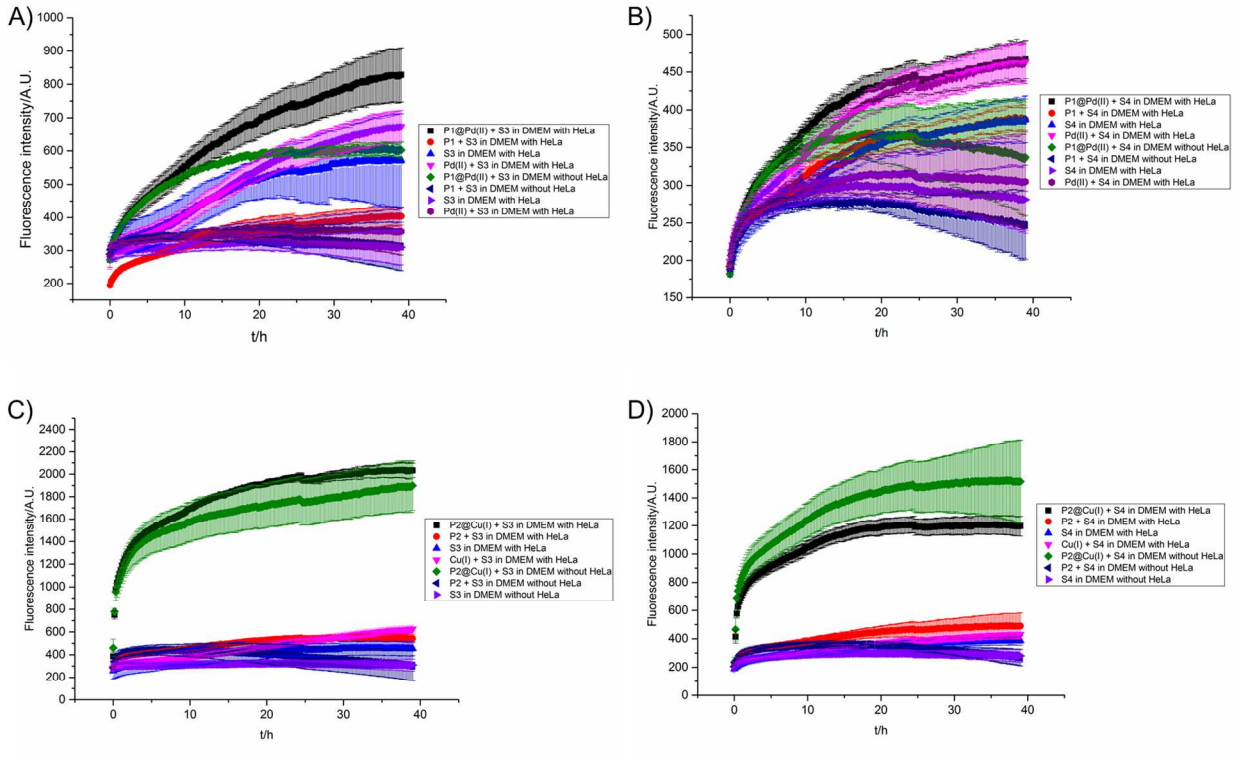
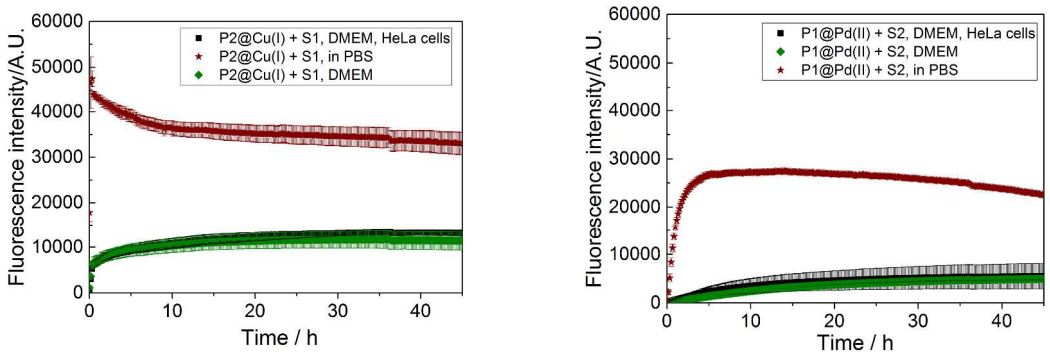


Figure S14: ***P1@Pd(II)*** *and* ***P2@Cu(I)*** *catalyzed depropargylation reaction of* ***S3*** *(A, C) and* ***S4*** *(B, D) with Hela cells in full medium. DMEM is supplemented with 10% serum. Concentration of the substrates = 30 μM;* ***P1@Pd(II):*** *[Bipy] = 60 μM; [Na_2PdCl_4] = 50 μM;* ***P2@Cu(I):*** *[Phen] = 66.7 μM; [$CuSO_4$] = 33.3 μM, [NaAsc] = 1 mM.. Catalysis monitored by fluorescence detection at different times.*



(A) (B)

Figure S15: *(A)* ***P2@Cu(I)*** *catalyzed depropargylation reaction of* ***S1*** *incubated in DMEM+10 % serum with and without HeLa cells or PBS; ([Phen] = 66.7 μM; [$CuSO_4$] = 33.3 μM, [**S1**] = 30 μM, NaAsc 1 mM). (B)* ***P1@Pd(II)*** *catalyzed depropargylation reaction of* ***S2*** *incubated in DMEM+10 % serum with and without HeLa cells or PBS; ([Bipy] = 60 μM; [Na_2PdCl_4] = 50 μM, [**S2**] = 30 μM. Catalysis was monitored by fluorescence detection of MC-Rh 110.*

9. References.

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