Supporting Information

for

Direct Light-induced (Co-)Grafting of Photoactive Polymers to Graphitic Nanodiamonds

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Instruments

Size Exclusion Chromatography (SEC)

The SEC measurements in THF were performed on a Polymer Laboratories PL - GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead - size guard column (50 × 7.5 mm) followed by three PLgel 5 µm Mixed - C and one PLgel 3 µm Mixed - E columns (300 × 7.5 mm) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 mL·min^{-1}. The SEC system was calibrated using linear poly(styrene) (PS) standards S3 ranging from 474 to $2.5 \cdot 10^6$ g·mol^{-1}. Calculation of the molecular weight proceeded via the Mark-Houwink parameters for polystyrene, i.e. $K = 14.1 \cdot 10^{-5}$ dL·g^{-1}, $\alpha = 0.70$.[1] The samples were filtered through polytetrafluorethylene (PTFE) membranes with a pore size of 0.2 µm prior to injection.

The SEC measurements of the PNIPAM samples were performed with *N*, *N* -dimethylacetamide (DMAC) as eluent containing 0.03 wt% LiBr on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column (50 × 7.5 mm) followed by three PLgel 5 × Mixed C columns (300 × 7.5 mm), and a differential refractive index detector at 50 °C with a flow rate of 1.0 mL · min^{-1}. The SEC system was calibrated against linear poly(methyl methacrylate) standards with molecular weights ranging from 700 to $2 \cdot 10^6$ Da. The samples were filtered through polytetrafluorethylene (PTFE) membranes with a pore size of 0.2 µm prior to injection.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The synthesized compounds were analyzed *via* ^{1}H and ^{13}C NMR spectroscopy using a Bruker Avance 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz) or Bruker Avance III 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) spectrometer. Samples were dissolved in $CDCl_3$. The δ-scale was referenced with tetramethylsilane ($\delta = 0.00$) as internal standard. Abbreviations used in the description of the materials' synthesis include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), broad multiplet (bm), and unresolved multiplet (m).

Thermogravimetric analysis (TGA)

TGA was performed on a TGA Q5000 from TA Instruments. Pre-dried samples were measured in air atmosphere with the following heating sequence:

1.) Ambient temperature → 100 °C, 10 °C / min

2.) Isothermal at 100 °C for 10 min (taking solvent impurities in some samples into consideration, TGA curves are normalized to weights at 120 °C)

3.) 100 °C → 800 °C, 10 °C / min

X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed using a K-Alpha+ XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Avantage software is described elsewhere.[2] All samples were analyzed using a microfocused, monochromated Al K_α X-ray source (400 µm spot size). The K-Alpha+ charge compensation system was employed during analysis, using electrons of 8 eV energy, and low-energy argon ions to prevent any localized charge build-up. The spectra were fitted with one or more Voigt profiles (BE uncertainty: ±0.2eV) and Scofield sensitivity factors were applied for quantification.[3] All spectra were referenced to the C 1s peak attributed to C-C, C-H at 285.0 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au, respectively.

ATR FTIR spectroscopy

IR spectra from polymer/ND powders were recorded on a Bruker Alpha ATR FTIR spectrometer.

Sonifier

NDs were dispersed using a Branson Sonifier W450 (400 Watt) with a micro tip. The polymer grafted NDs were dispersed using a Bandelin Sonorex Digitec ultrasound bath.

Photoreactor

The samples were irradiated with an Arimed B6 lamp at a distance of 15 cm (1.57 mW cm^{-2}). The samples were stirred during the grafting experiments. An emission spectrum of the UV lamp and a UV-Vis absorbance spectrum of 4-((2-formyl-3-methylphenoxy)methyl)benzoic acid can be found in the literature.[4]

Materials

4-((2-formyl-3-methylphenoxy)methyl)benzoic acid was prepared according to a literature procedure.[5] Detonation nanodiamonds (purified / grade G01) were purchased from PlasmaChem GmbH (Berlin) and used as received. 2-(Dodecylthiocarbonothioylthio)propionic acid (DoPAT) was provided from Lanxess Deutschland GmbH. Polyethylene glycol (PEG, M_n = 2000 g mol^{-1}, Sigma-Aldrich), triethylene glycol (TEG, Sigma-Aldrich), *N*,*N′*-dicyclohexylcarbodiimide (DCC, 99%, Acros), 4-(dimethylamino)pyridine (DMAP, 99%, abcr), *N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDC·HCl, 99+%, Roth), 2,2′-azobis(isobutylonitrile) (AIBN, VWR), chloroform-d_1 ($CDCl_3$, 99.8%, EURISO-TOP), dimethyl-d6 sulfoxide (DMSO-d_6, 99.8%, EURISO-TOP) were used as received. *N*-isopropylacrylamide (NIPAM, TCI, 98%) was recrystallized from hexane before usage. Styrene and pentafluorostyrene were passed through a column of basic alumina prior to polymerization. *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile, diethyl ether, ethyl acetate, and cyclohexane were purchased as analytical grade (Sigma-Aldrich) and used as received.

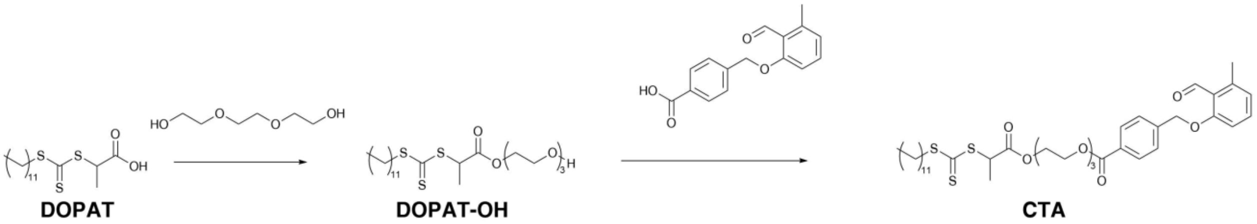
Thermal annealing of NDs (grND). Pristine NDs (PlasmaChem, purified grade 01) were annealed in a quartz tube at 900 °C using a tube furnace, under reduced pressure (approx. 2×10^{-2} mbar, dynamic vacuum), for two hours (see table below for the detailed annealing protocol).

Temperature program	Time / h	Comments
rt → 900 °C	2	Slow heating rate prevents NDs to be swirled up
isothermal at 900 °C	2	After the 2 h the oven was turned off
900 °C → 500 °C	2	Quartz tube was left in tube furnace
500 °C → rt	1	Quartz tube was removed from the oven to cool to rt

Synthesis of o-methyl benzaldehyde functional linear PEG. PEG (2000 Da, 700 mg, 0.35 mmol, 1.00 equiv), *N*,*N′*-dicyclohexylcarbodiimide (144 mg, 0.70 mmol, 2.00 equiv), 4-dimethylaminopyridine (32.1 mg, 0.26 mmol, 0.750 equiv) and methyl 4-((2-formyl-3-methylphenoxy)methyl)benzoic acid (378 mg, 1.40 mmol, 4.00 equiv) were dissolved in a mixture of 10 mL of anhydrous DMF and 1 mL anhydrous DCM and stirred for 20 h. After removal of the precipitate by filtration, the solvent was removed under reduced pressure and the residue was precipitated three times in 35 mL of cold diethyl ether.

^{1}H NMR (400 MHz, chloroform-*d*) *δ*/ppm = 10.75 (s, 1H, C*H*O), 8.08 (d, *J* = 8.3 Hz, 2H, Ph), 7.50 (d, *J* = 8.4 Hz, 2H, Ph), 7.36 (dd, *J* = 8.4, 7.6 Hz, 1H, Ph), 6.94 – 6.80 (m, 2H, Ph), 5.23 (s, 2H, $PhCH_2O$), 4.60 – 4.40 (m, 2H, $COOCH_2$), 3.92 – 3.79 (m, 2H, $COOCH_2CH_2$), 3.64 (s, $(C_2H_4O)_n$, 194 H), 2.59 (s, 3H, $PhCH_3$).

Synthesis of 11-methyl-10-oxo-13-thioxo-3,6,9-trioxa-12,14-dithiapentacosyl 4-((2-formyl-3-methyl-phenoxy)methyl)benzoate (CTA).



2-(Dodecylthiocarbonothioylthio)propionic acid (5.00 g, 14.3 mmol, 1.00 equiv), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (4.10 g, 21.4 mmol, 1.50 equiv), 4-(dimethylamino)-pyridin (174 mg, 1.43 mmol, 0.100 equiv), triethylene glycol (42.8 g, 285 mmol, 20.0 equiv) were dissolved in 30 mL of anhydrous dichloromethane and stirred for 15 h. 150 mL saturated $NaHCO_3$ solution was added and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with 1 N HCl, water and brine. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield 2-(2-(2-hydroxyethoxy)ethoxy)ethyl 2-(((dodecylthio)carbonothioyl)thio)propanoate (DoPAT-OH, 6.70 g, 13.9 mmol, 97 %).

^{1}H NMR (400 MHz, chloroform-*d*) *δ*/ppm = 4.84 (q, *J* = 7.4 Hz, 1H, SC*H*), 4.39 – 4.26 (m, 2H, $COOCH_2$), 3.82 – 3.55 (m, 10H, triethylene glycol spacer), 3.45 – 3.26 (m, 2H, SCH_2), 1.68 (m, 2H, CH_2CH_3), 1.61 (d, *J* = 7.4 Hz, 3H, CH_3CH), 1.48 – 1.15 (m, 18H, $(CH_2)_9$), 0.88 (t, *J* = 7.0 Hz, 3H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) *δ*/ppm = 222.2, 171.3, 72.6, 70.8, 70.6, 69.0, 64.9, 62.0, 48.1, 37.4, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.2, 29.1, 28.0, 22.8, 17.0, 14.3.

ESI-MS: $[M + Na]^+$, $[C_{22}H_{42}O_5S_3Na]^+$, theoretical: 505.209; experimental: 505.211.

DoPAT-OH (1.00 g, 2.13 mmol, 1.00 equiv), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (613 mg, 3.20 mmol, 1.50 equiv), 4-(dimethylamino)-pyridin (122 mg, 26.1 mmol, 0.100 equiv), 4-((2-formyl-3-methylphenoxy)methyl)benzoic acid (577 mg, 2.13 mmol, 1.00 equiv) were dissolved in 10 mL of anhydrous dichloromethane and 3 mL of anhydrous DMF and stirred for 15 h. 150 mL saturated $NaHCO_3$ solution was added and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with 1 N HCl, water and brine. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, ethyl acetate/cyclohexane, 1/1) to obtain 1.12 g (1.55 mmol, 73%) of 11-methyl-10-oxo-13-thioxo-3,6,9-trioxa-12,14-dithiapentacosyl 4-((2-formyl-3-methylphenoxy)methyl)benzoate.

^{1}H NMR (400 MHz, chloroform-*d*) δ/ppm = 10.75 (s, 1H, C*H*O), 8.09 (d, *J* = 8.3 Hz, 2H, Ph), 7.50 (d, *J* = 8.0 Hz, 2H, Ph), 7.36 (t, *J* = 8.0 Hz, 1H, Ph), 6.85 (m, 2H, Ph), 5.23 (s, 2H), 4.82 (q, *J* = 7.4 Hz, 1H, SC*H*), 4.56 – 4.44 (m, 2H, SCH_2), 4.33 – 4.22 (m, 2H, $PhCO_2CH_2$), 3.90 – 3.81 (m, 2H, TEG), 3.78 – 3.62 (m, 6H, TEG), 3.39 – 3.28 (m, 2H, TEG), 2.59 (s, 3H, $PhCH_3$), 1.67 (m, 2H, CH_2CH_3), 1.59 (d, *J* = 7.4 Hz, 3H, CH_3CH), 1.25 (m, 18H, $(CH_2)_9$), 0.87 (t, *J* = 6.8 Hz, 3H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ/ppm = 222.1, 192.1, 171.3, 166.3, 162.0, 142.4, 141.6, 134.5, 130.3, 130.1, 127.0, 124.8, 123.8, 110.5, 77.5, 77.4, 77.2, 76.8, 70.9, 70.9, 70.1, 69.4, 69.1, 65.0, 64.4, 48.1, 37.4, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.2, 29.1, 28.0, 22.8, 21.6, 17.0, 14.3, 1.2.

ESI-MS: $[M + Na]^+$, $[C_{38}H_{54}O_8S_3Na]^+$, theoretical: 757.287; experimental: 757.292.

Polymerizations

RAFT polymerization of styrene. Azobisisobutyronitrile (AIBN) and CTA were dissolved in styrene (1.50 g, [AIBN]:[CTA]:[S], 1:10:3000) and degassed by four consecutive freeze-pump-thaw cycles. The polymerization mixture was stirred at 60 °C for 21 h. The polymer was purified by threefold precipitation in cold methanol.

RAFT polymerization of *N*-isopropylacrylamide. Azobisisobutyronitrile (AIBN), CTA and *N*-isopropylacrylamide were dissolved in DMF ([M] = 3.50 mol L^{-1}, [AIBN]:[CTA]:[NIPAM], I: 1:7.5:525, II: 1:7.5:1050, III: 1:7.5:2100) and degassed by four consecutive freeze-pump-thaw cycles. The polymerization mixture was stirred at 60 °C for 1 h 45 min, 4 h and 6 h, respectively. The polymer was purified by threefold precipitation in cold diethyl ether.

RAFT polymerization of pentafluorostyrene. Azobisisobutyronitrile (AIBN) and CTA were dissolved in pentafluorostyrene (750 mg, [AIBN]:[CTA]:[PFS], 1:7.5:1050) and degassed by four consecutive freeze-pump-thaw cycles. The polymerization mixture was stirred at 60 °C for 17 h. The polymer was purified by threefold precipitation in cold methanol.

Photo-grafting. In a typical grafting procedure, grNDs were dispersed in acetonitrile at a concentration of 1 mg mL^{-1} by ultra-sonication for one hour. Subsequently, the polymer was added to obtain a 1 mg mL^{-1} solution and the reaction mixture was degassed by purging with nitrogen for 15 min. The reaction mixture was placed in the custom-built photoreactor, stirred and irradiated with UV light overnight. The obtained reaction mixture was washed four times with acetonitrile by consecutive centrifugation, ultrasound assisted (ultrasound bath) redispersion cycles and dried under reduced pressure. The grafting experiments with PPFS and PS were performed in THF.

Photo-co-grafting. The co-grafting experiments were performed in THF with a PNIPAM I and PPFS and a molar ratio of 25, 50 and 75 %, respectively. The procedure for the grafting reaction and subsequent workup is as described above.

XRD

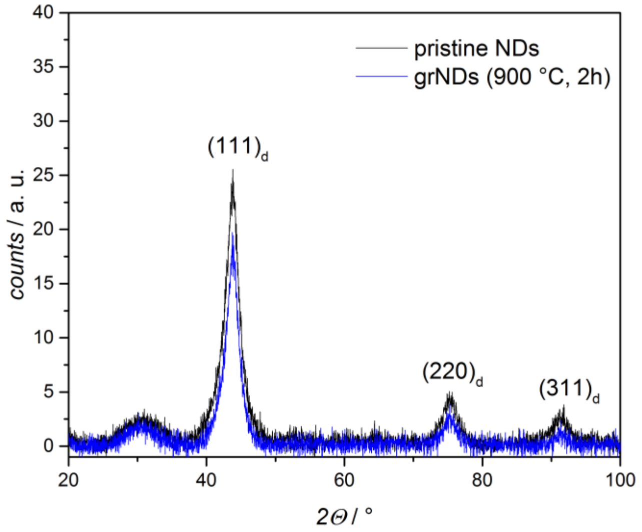


Figure S1: XRD patterns for pristine NDs and graphitized NDs (grNDs).

HRTEM

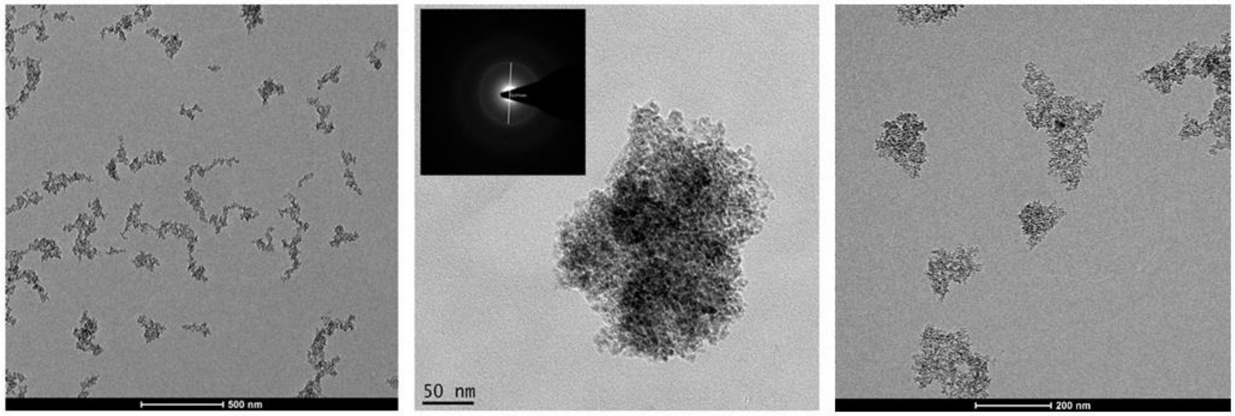


Figure S2: Left: Overview HRTEM image of grNDs. Center: Representative HRTEM image grND cluster. The inlet shows the selected area electron diffraction (SAD) pattern. Right: HRTEM image of ND@PNIPAM/PPFS I.

NMR spectroscopy

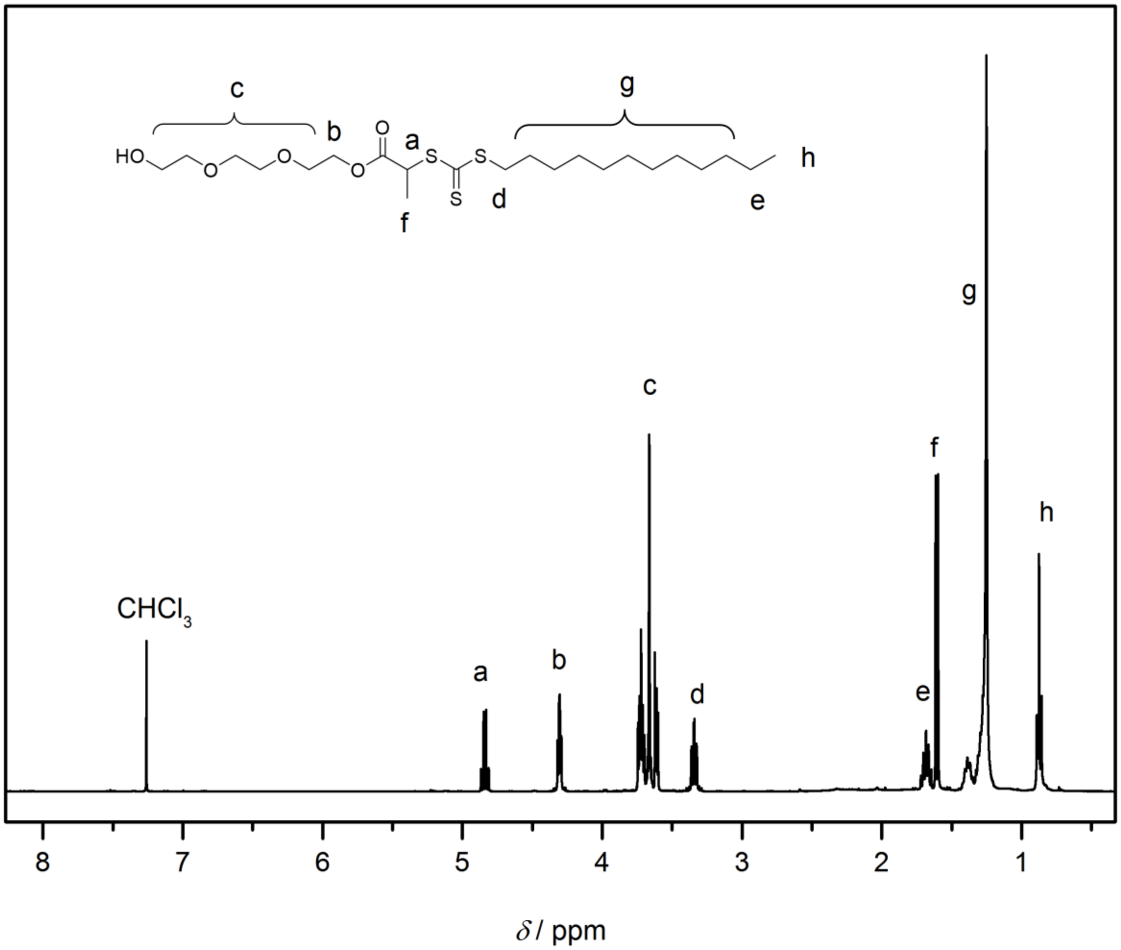


Figure S3: ${}^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of DoPAT-OH.

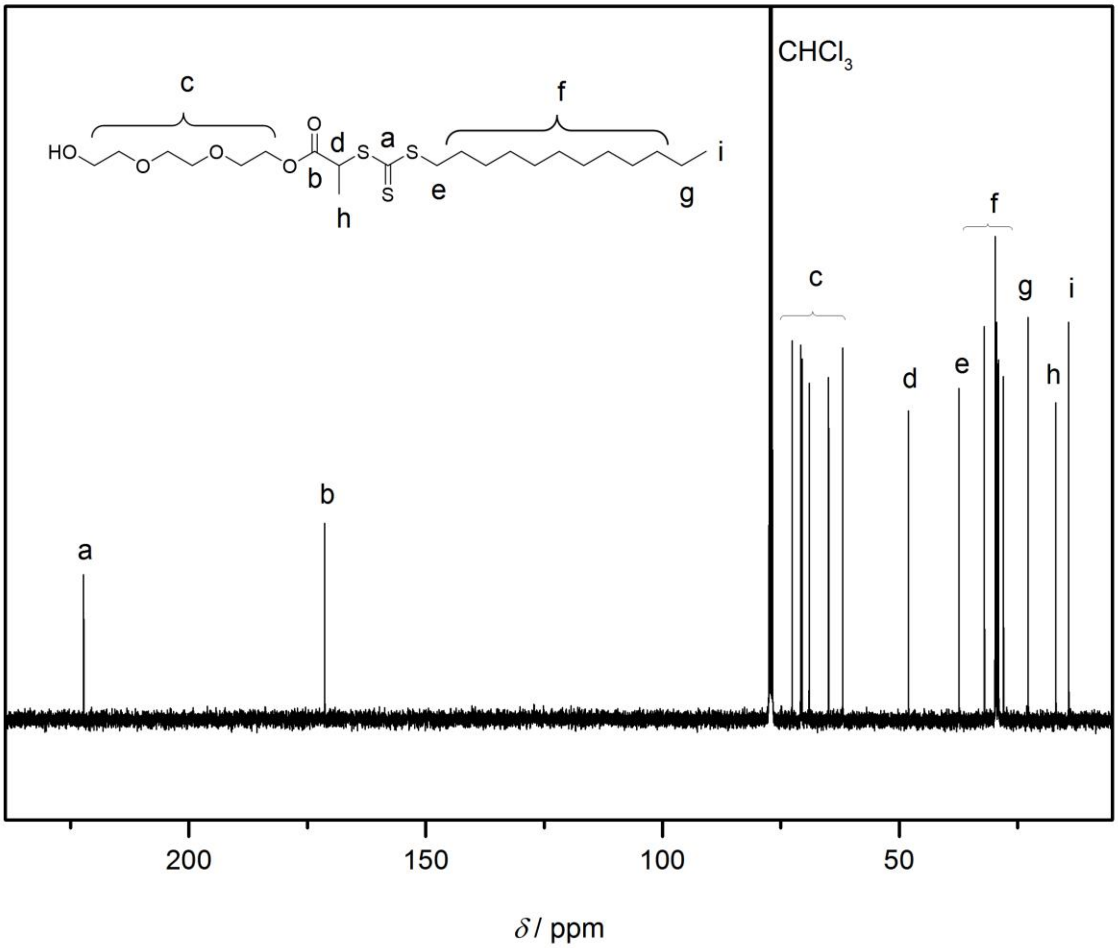


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of DoPAT-OH.

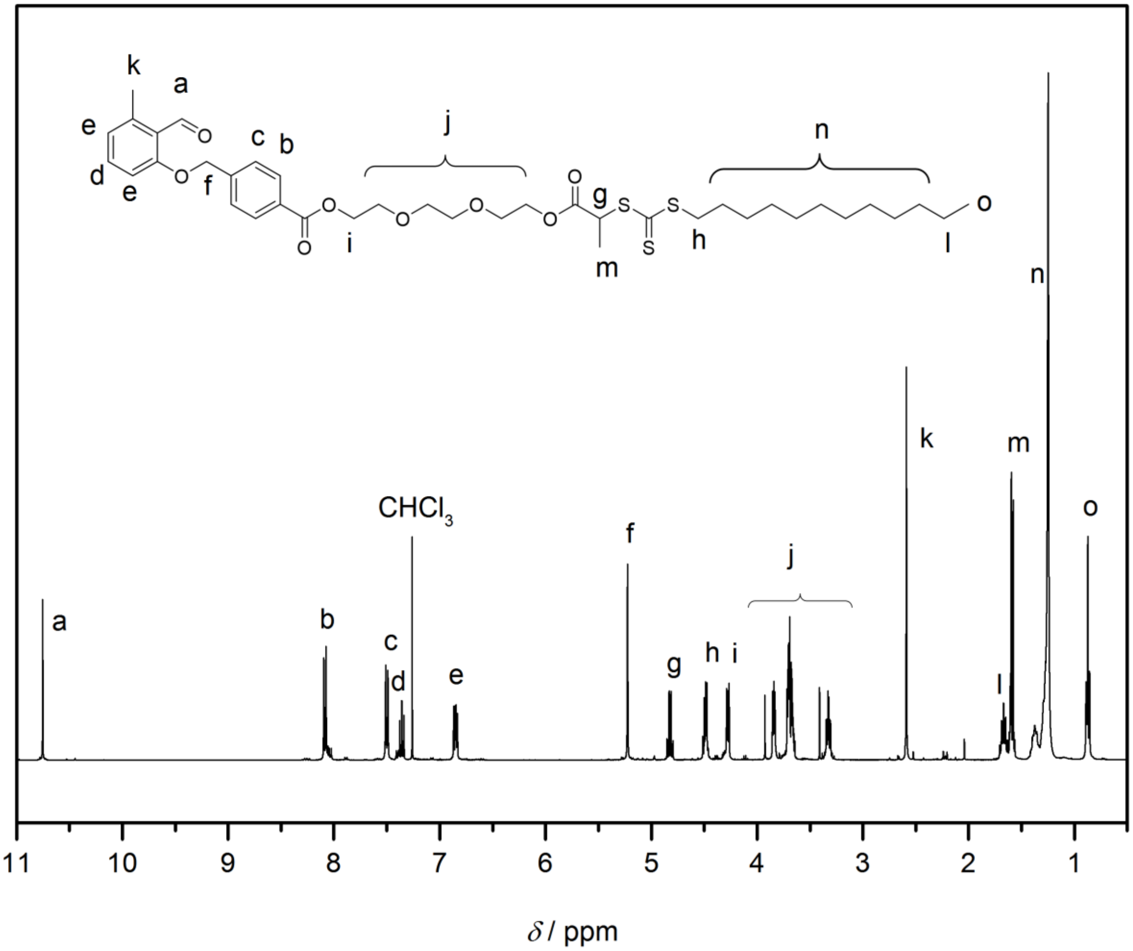


Figure S5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of CTA.

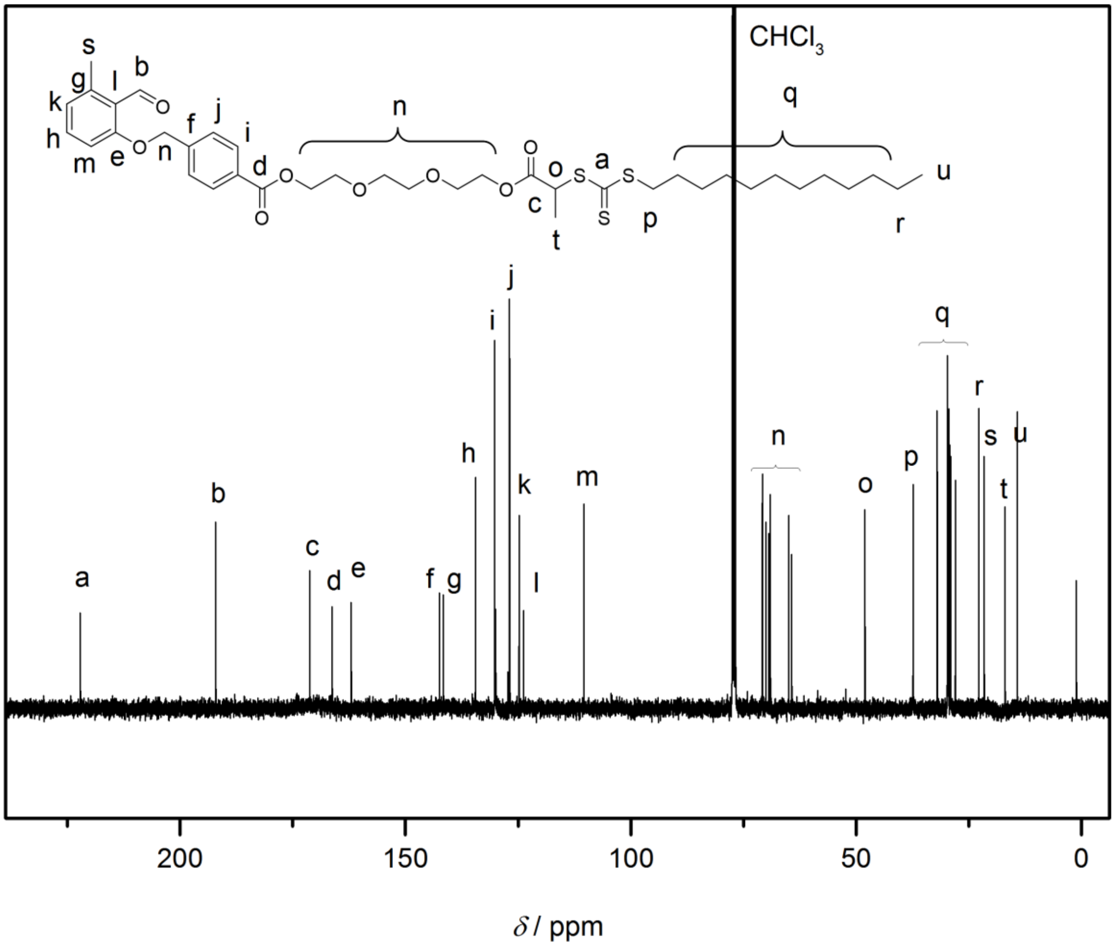


Figure S6: $^{13}C\{^1H\}$ NMR spectrum (101 MHz, $CDCl_3$) of CTA.

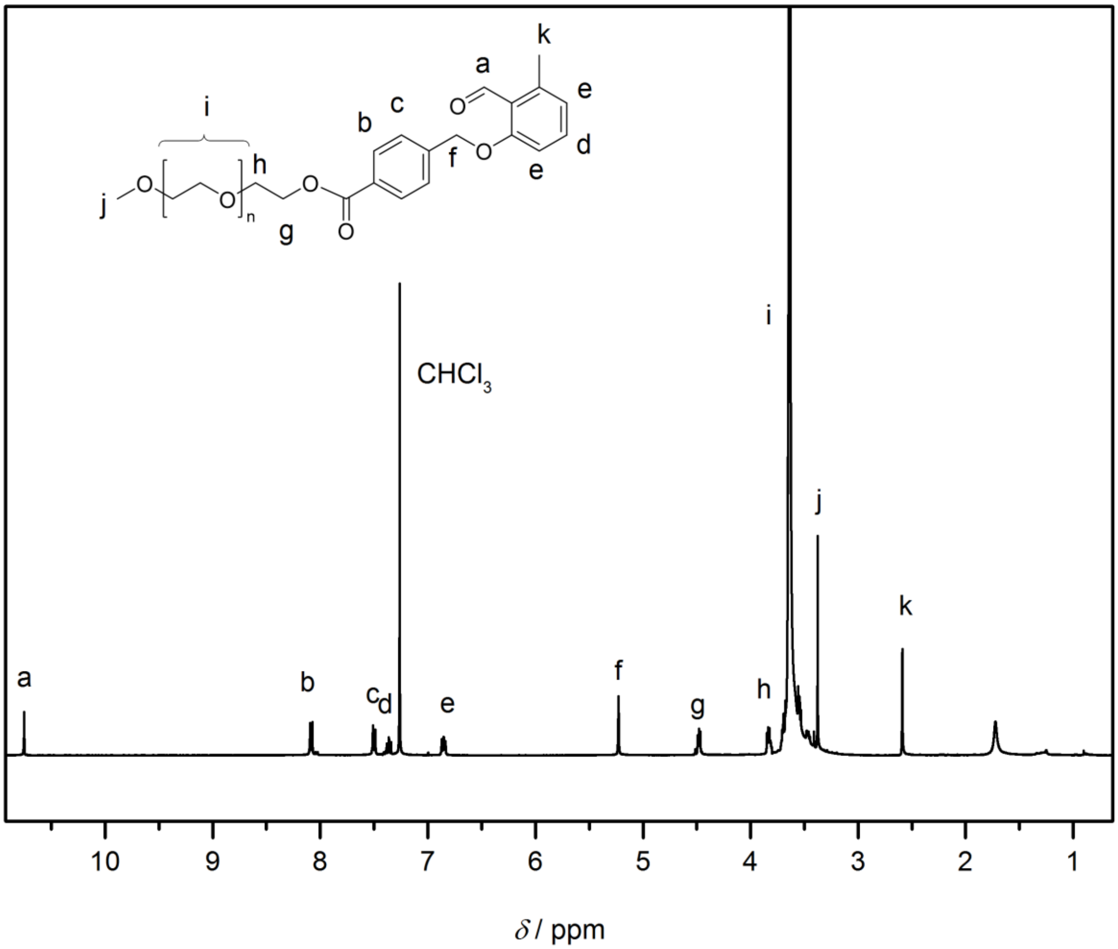


Figure S7: ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of *o*-methyl benzaldehyde functional PEG.

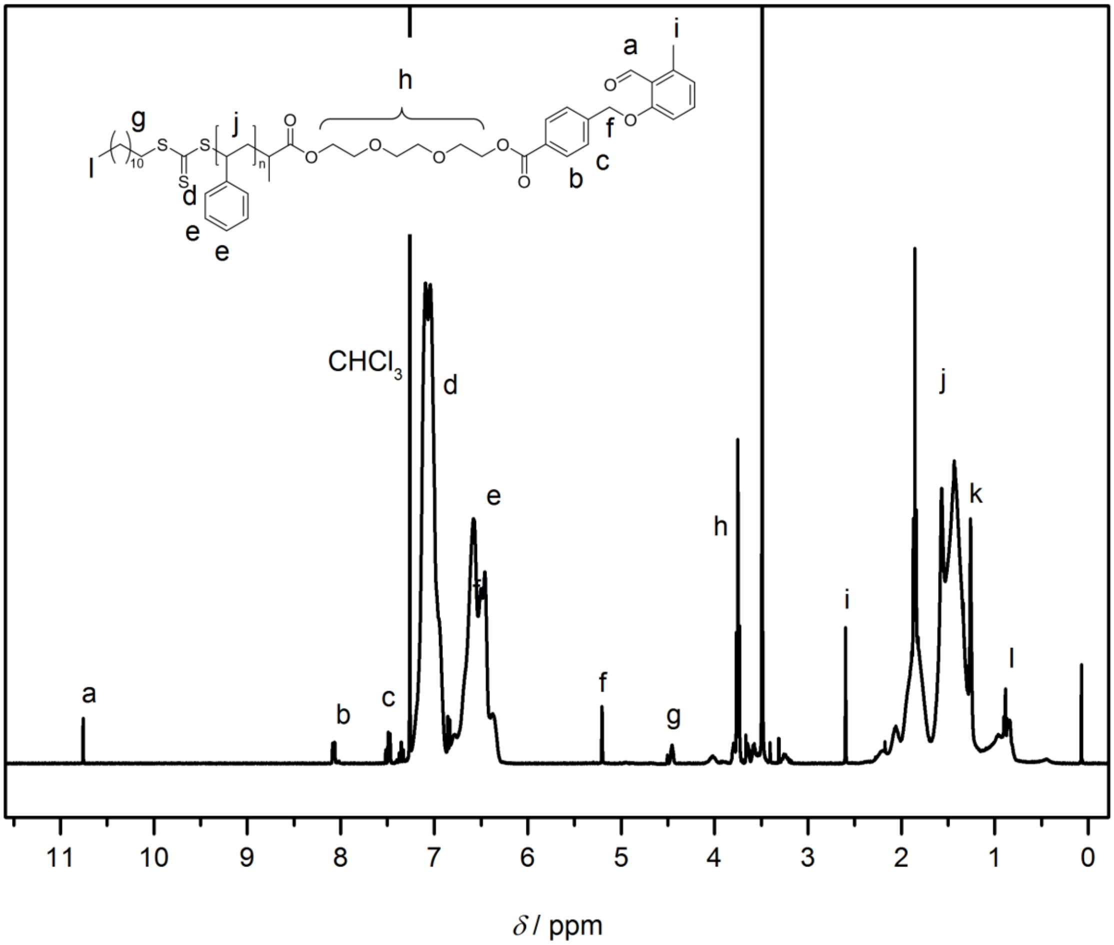


Figure S8: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *o*-methyl benzaldehyde functional PS.

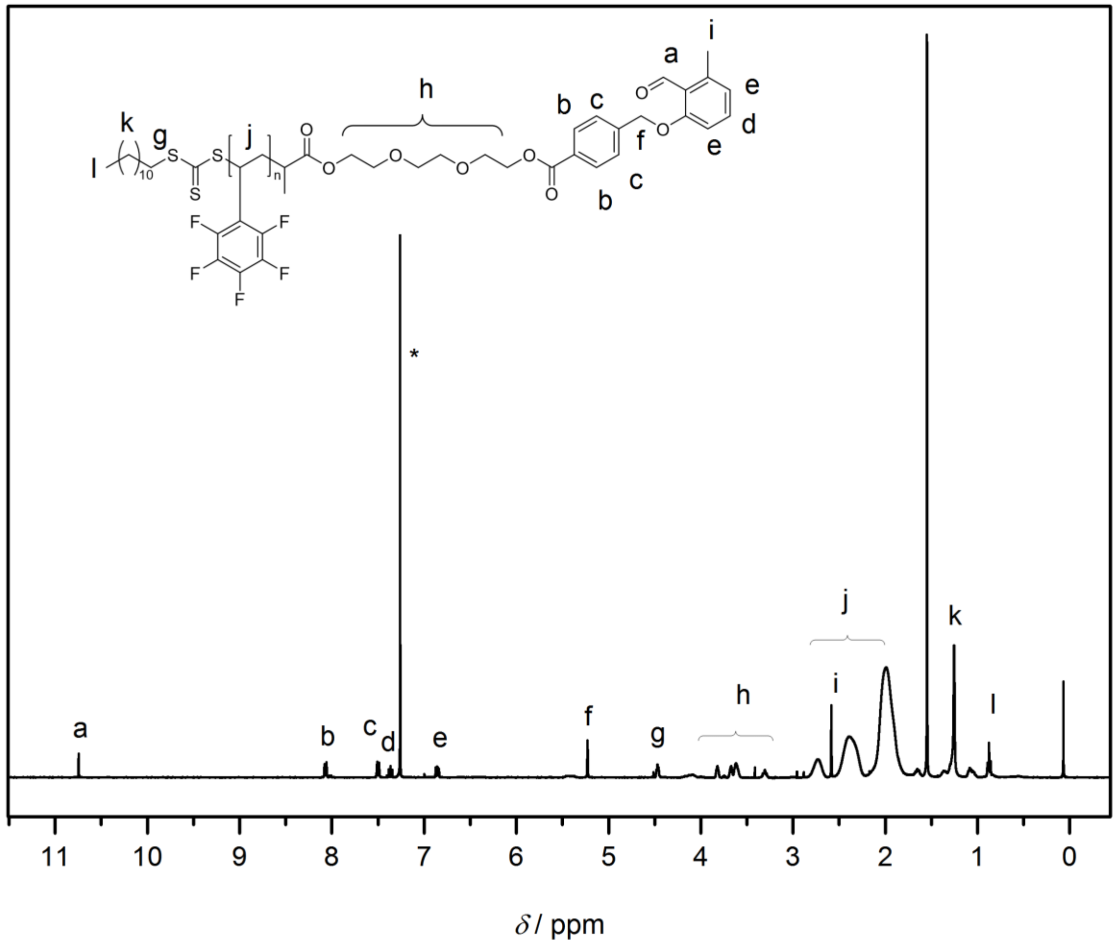


Figure S9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *o*-methyl benzaldehyde functional PPFS.

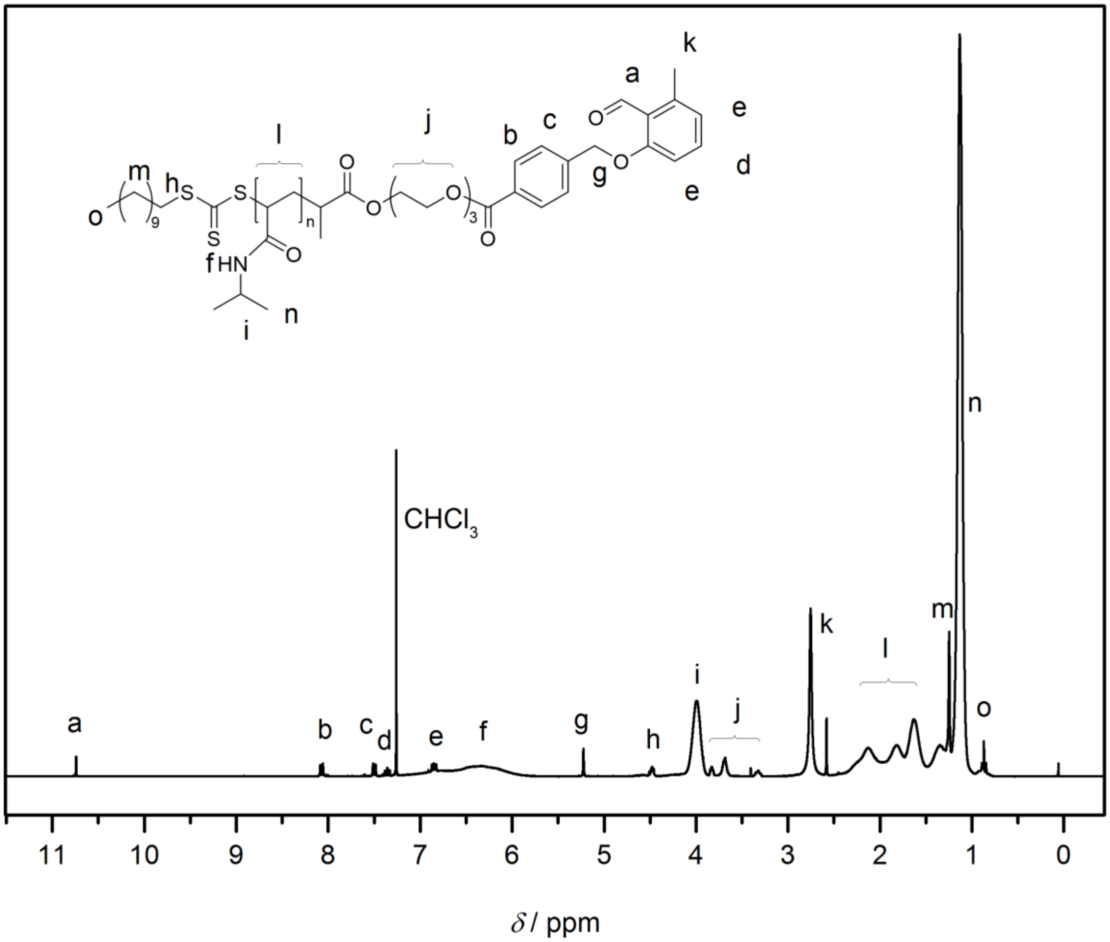


Figure S10: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *o*-methyl benzaldehyde functional PNIPAM I.

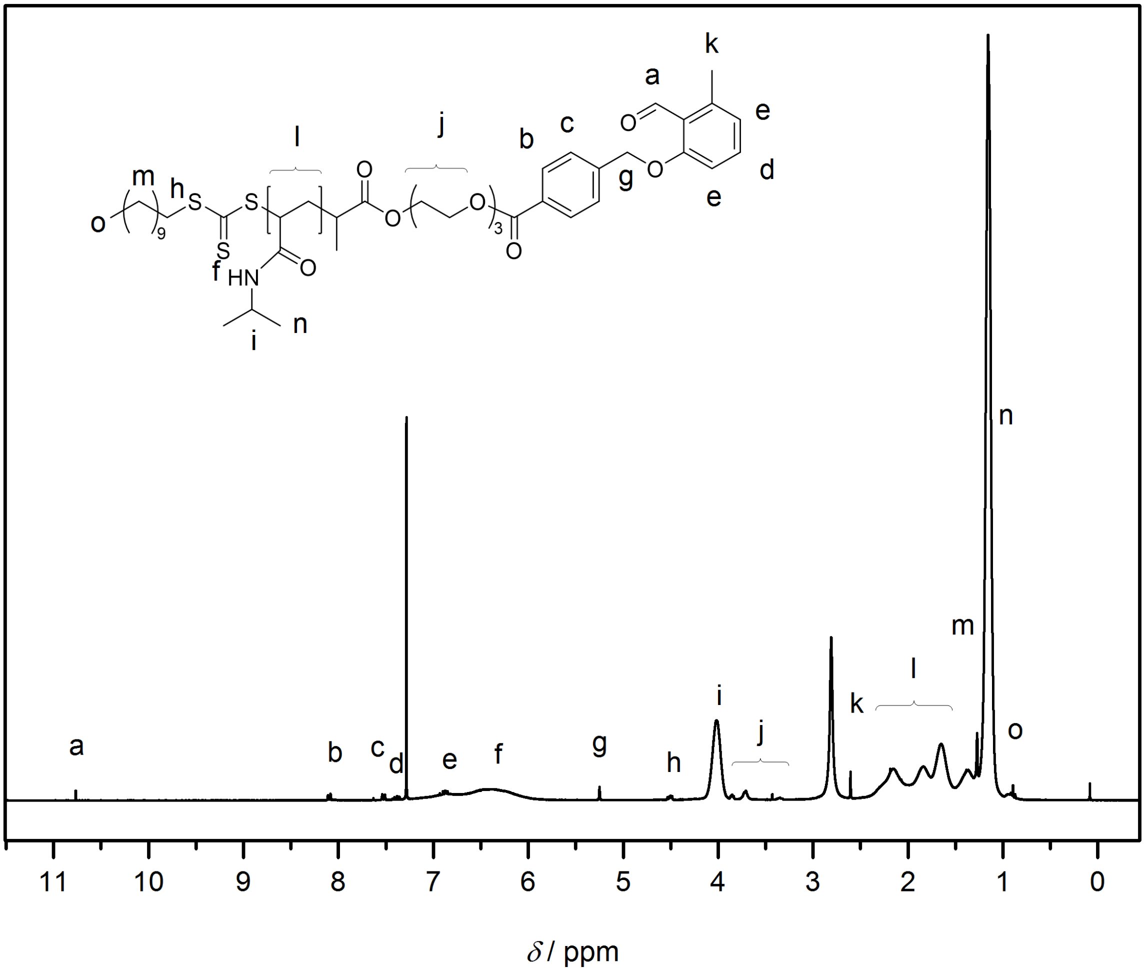


Figure S11: ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of *o*-methyl benzaldehyde functional PNIPAM II.

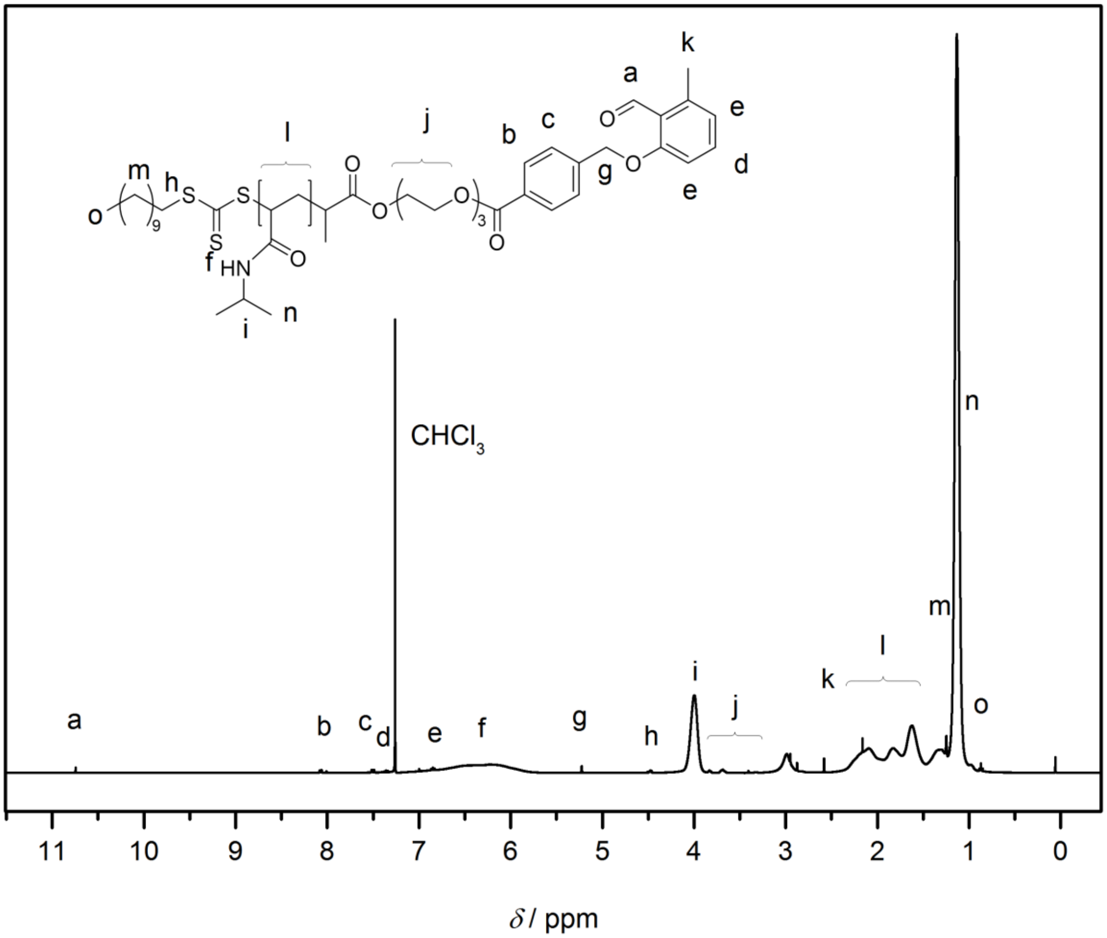


Figure S12: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *o*-methyl benzaldehyde functional PNIPAM III.

ESI MS of PEG

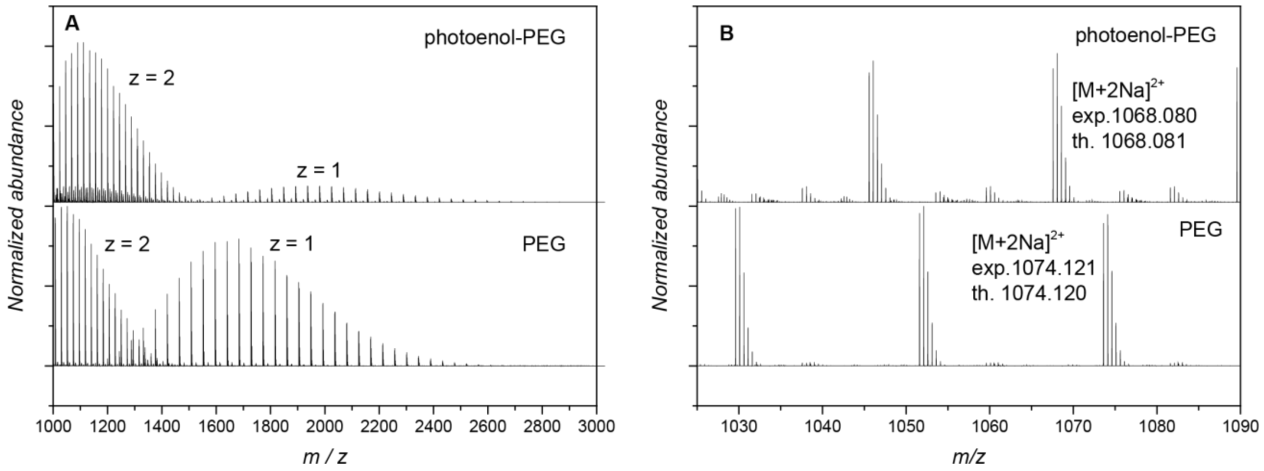


Figure S13: ESI MS spectra of PEG and photoenol functionalized PEG (A: overview; B: magnified area of the spectrum).

IR spectroscopy

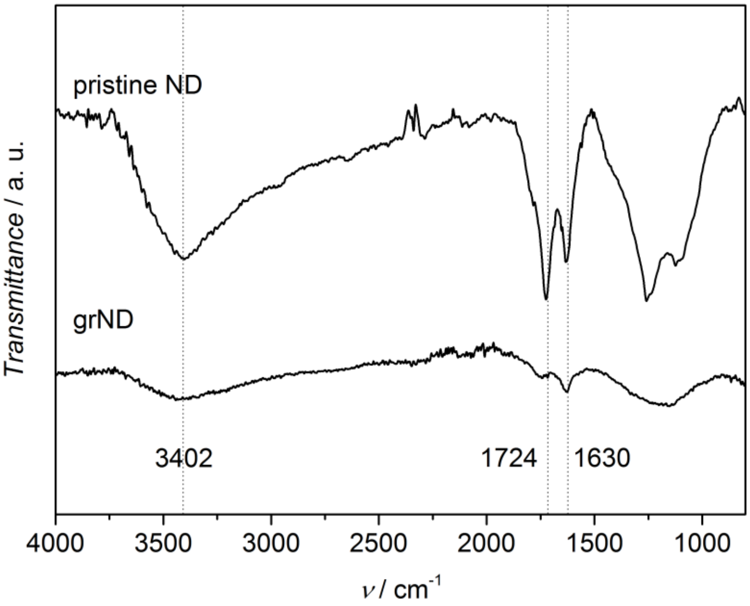


Figure S14: FT-IR spectra of pristine nanodiamonds and graphitized NDs (grND).

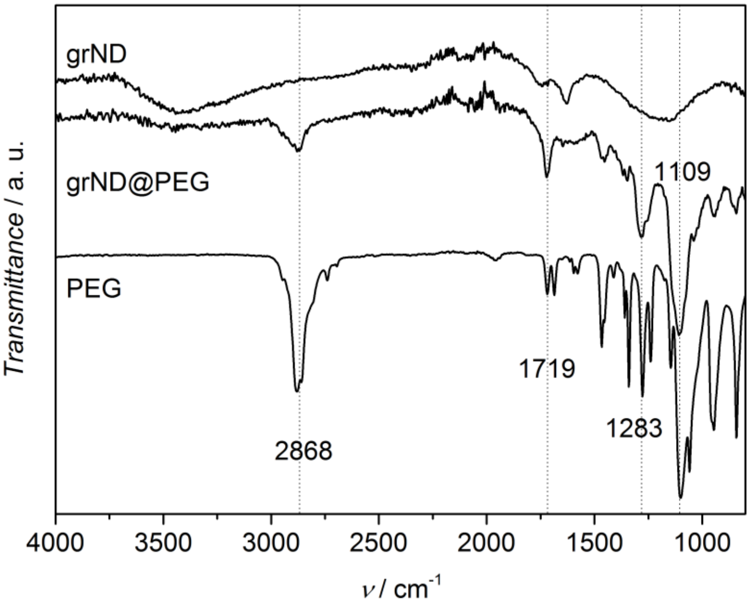


Figure S15: FTIR spectra of grND, grND@PEG and PEG.

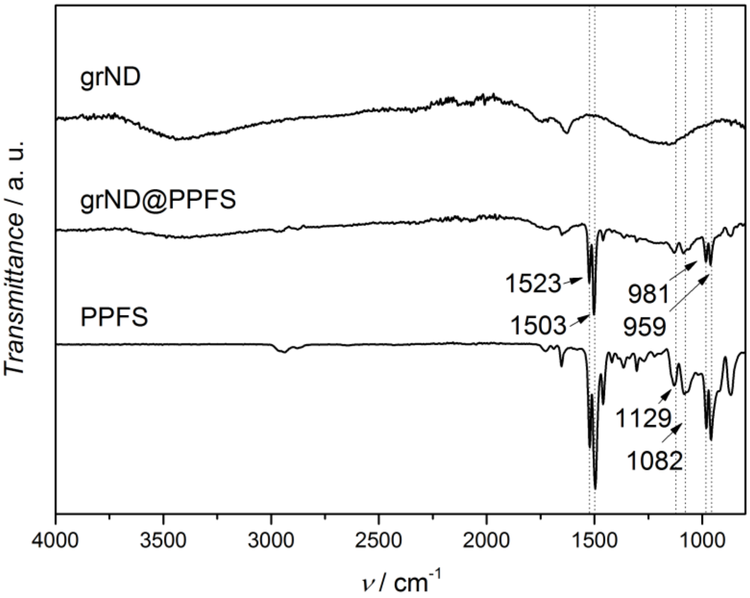


Figure S16: FTIR spectra of grND, grND@PPFS and PPFS.

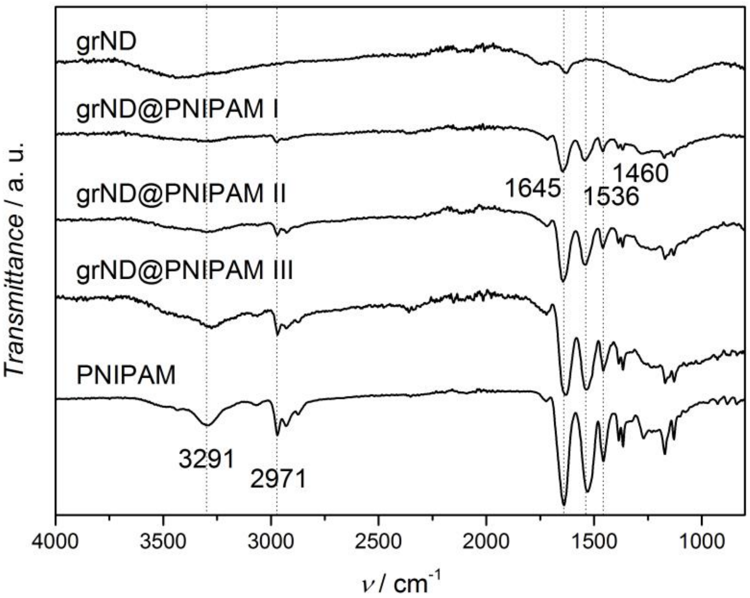


Figure S17: FTIR spectra of grND, grND@PNIPAM I-III and PNIPAM II.

Calibration curve for co-grafting experiments

Mixtures of different ratios of PNIPAM and PPFS (15 – 90 % PNIPAM) were prepared by mixing two stock solutions in THF (2 mg·mL^{-1}) in the desired ratio and evaporating the solvent under reduced pressure. Subsequently, IR absorption spectra were recorded (Figure S18) and the ratio of the integrals of the area from 1690.2 – 1585.4 cm^{-1} and from 998.2 – 971.6 cm^{-1} were used to plot a calibration curve (Figure S19).

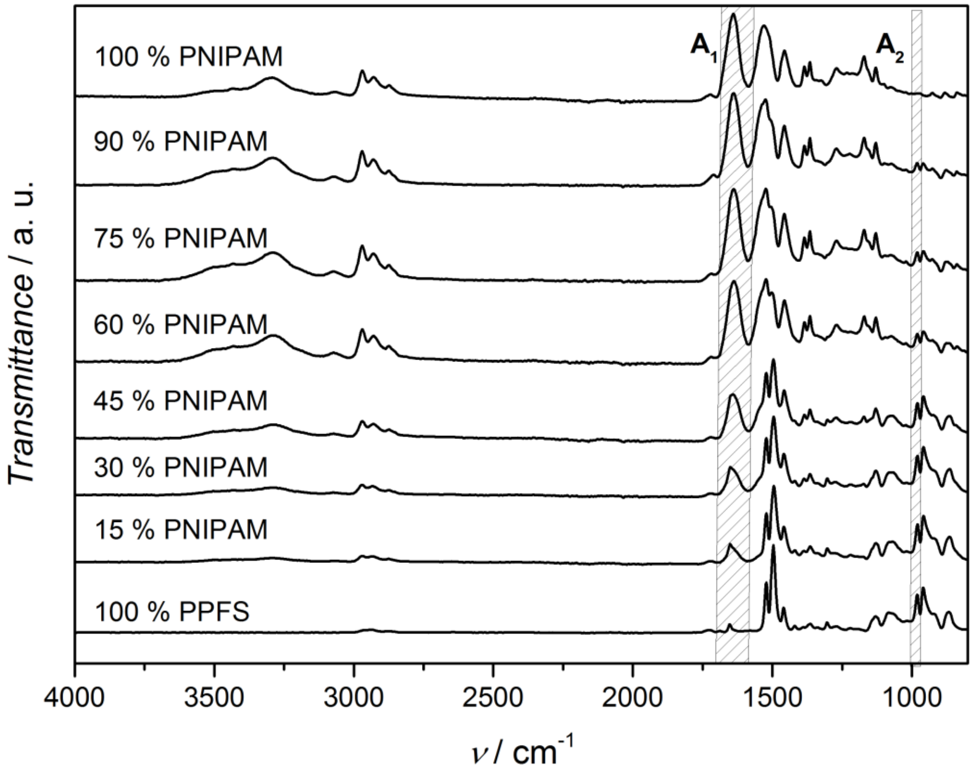


Figure S18: ATR FTIR absorption spectra of different PNIPAM PPFS mixtures.

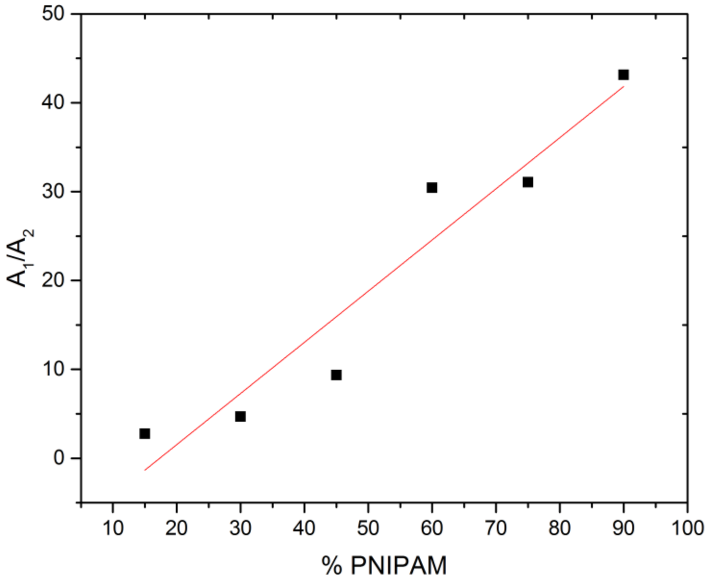


Figure S19: Calibration curve for the co-grafting of PNIPAM and PPFS (A$_1$: area of absorbance band at 1690.2 – 1585.4 cm^{-1}, A$_2$: area of absorbance band at 998.2 – 971.6 cm^{-1}).

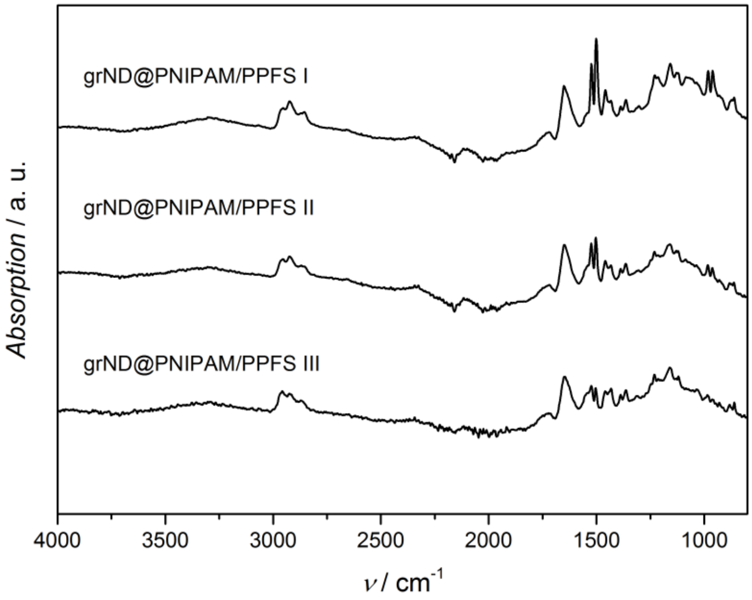


Figure S20: FTIR absorption spectra of co-grafted NDs.

Thermogravimetric analysis

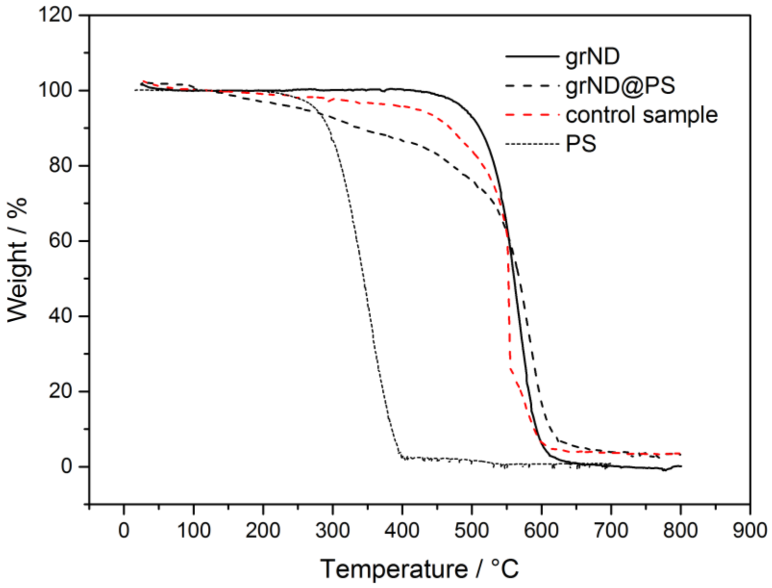


Figure S21: TGA curves for graphitized NDs before (grNDs) and after the photo-grafting of PS (grND@PS) and of the control sample (not irradiated sample).

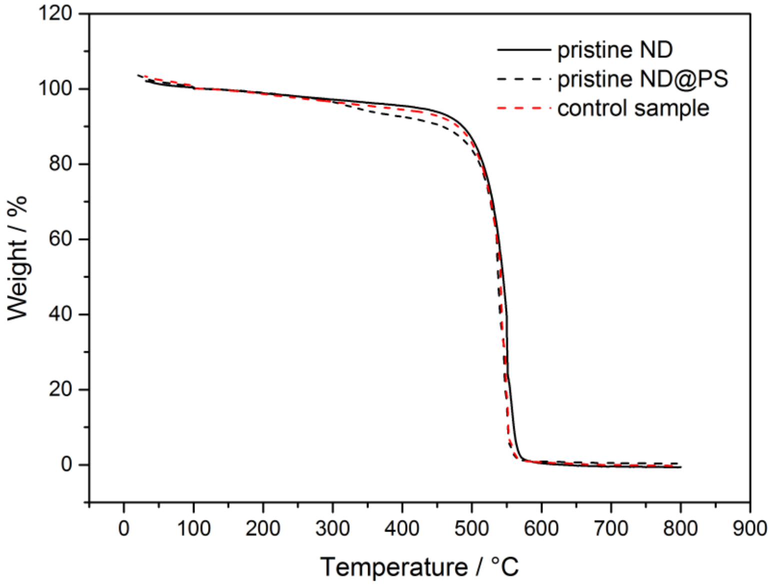


Figure S22: TGA curves of pristine NDs before and after the photo-grafting of PS (pristine ND@PS) and of the control sample (not irradiated sample).

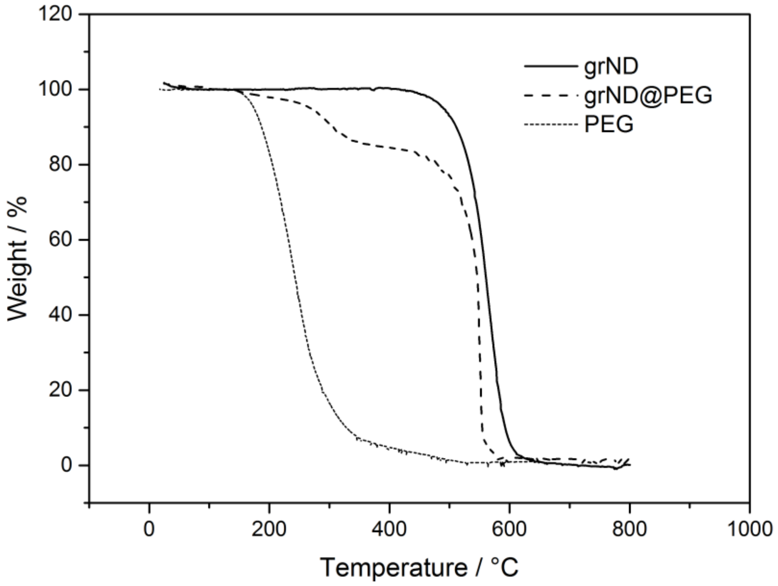


Figure S23: TGA curves of grNDs and grND@PEG and PEG.

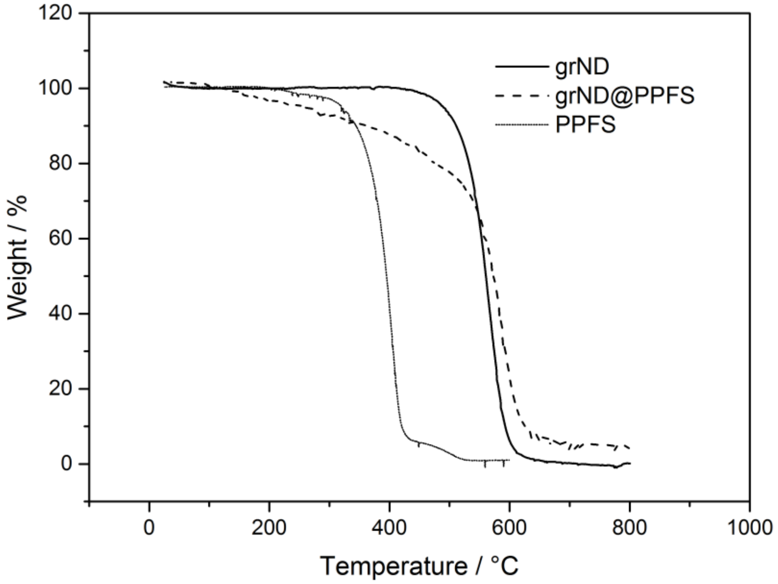


Figure S24: TGA curves of grNDs and grND@PPFS and PPFS.

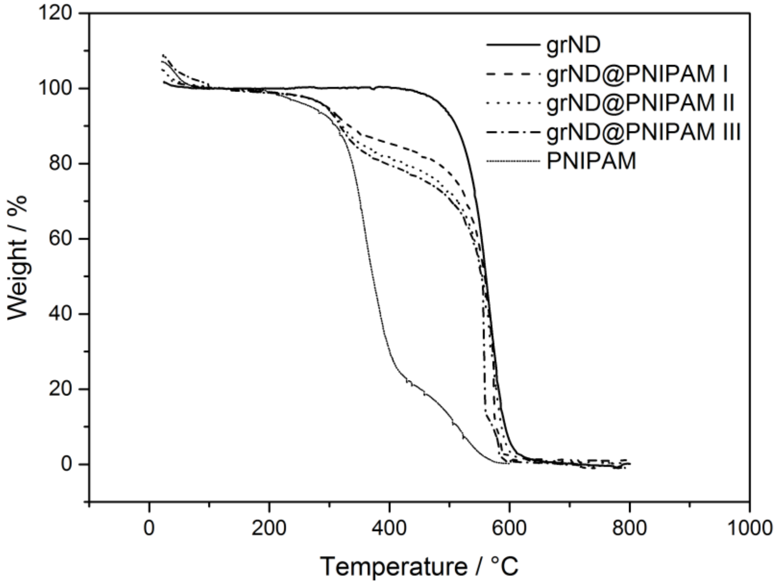


Figure S25: TGA curves of grNDs, grND@PNIPAM I-III and PNIPAM.

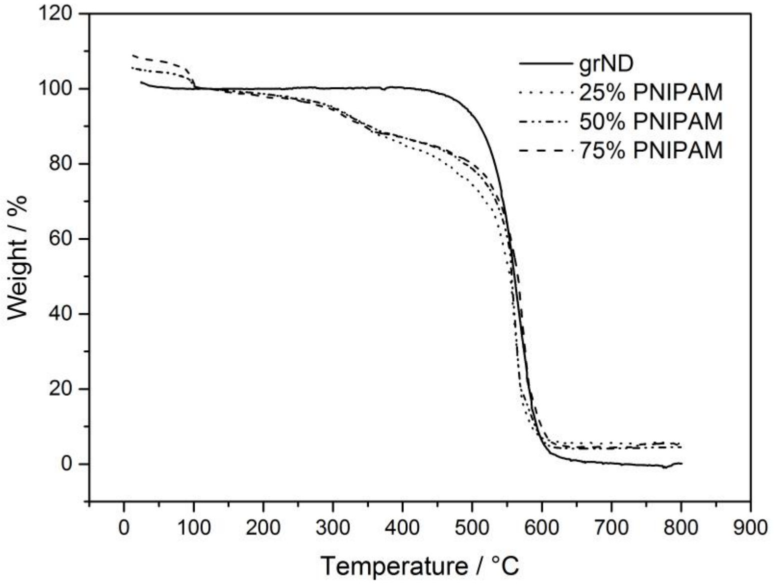


Figure S26: TGA curves of grNDs, grND@PNIPAM/PPFS I-III.

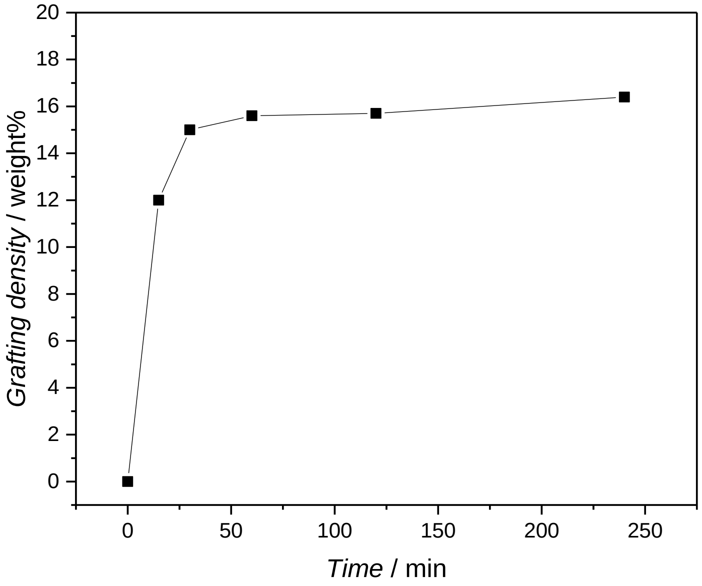


Figure S27: Kinetics for the grafting of photoenol functional PEG to grNDs. The grafting densities were determined by TGA.

XPS

Table S1: Summary of the XPS data for pristine NDs and grNDs.

Peak assignment	**pristine NDs**		**grNDs**	
	Binding energy / eV	**Atomic %**	**Binding energy / eV**	**Atomic %**
sp^2, graphitic	*284.2*	*9.8*	*284.6*	*21.8*
C-C, C-H, sp^3	285.0	46.3	285.0	51.13
C-O, C-N[a]	286.2	30.1	286.3	14.8
C=O	288.1	4.2	287.8	3.93
N 1s	399,8	1.6	399.2	1.09
N 1s	403,2	0.4	402.5	0.3
O 1s	531.3	2.6	531.1	3.44
O 1s	532.6	5.0	532.2	3.51

The graphitic component is given as measured without energy correction (see discussion in the main paper). All other peaks are referenced to C-C, C-H (sp^3) at 285,0 eV.

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[a] An additional contribution to this signal is assumed and further discussed in the main text of the publication.

DLS

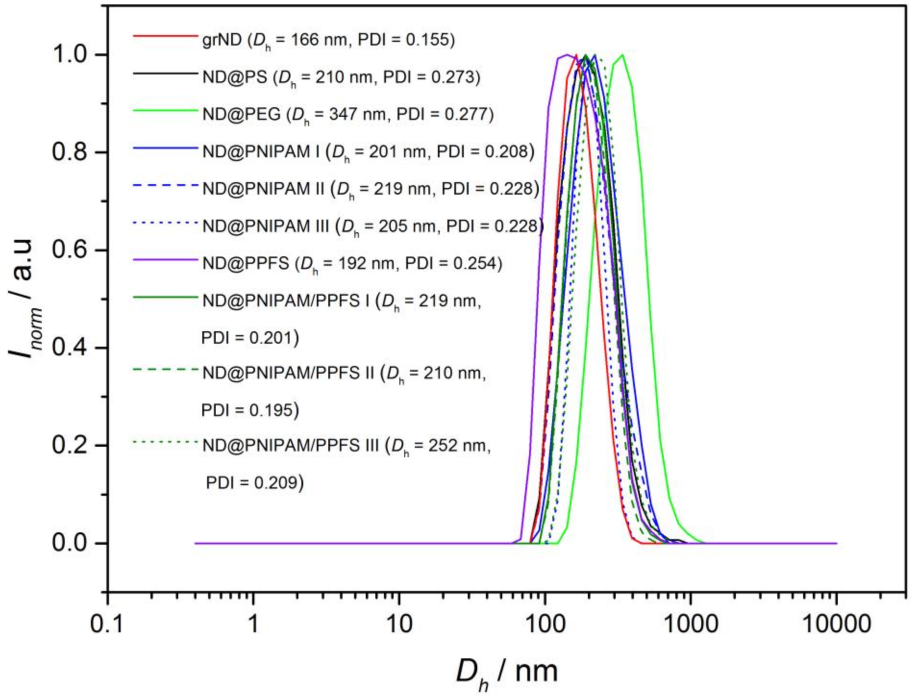

Figure S28: Number weighted hydrodynamic diameter distributions of the prepared functional NDs determined by DLS.

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