Synthesis of new bis(acyl)phosphane oxide photoinitiators for the surface functionalization of cellulose nanocrystals

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Structure of 3b: Cambridge Crystallographic Data Centre number: 1438071, empirical formula: $C_{23}H_{26}NO_3P$, formula weight: 395.42 g/mol, crystal system: triclinic, space group: P-1, unit cell: a = 867.8(2), b = 1132.0(2), c = 1200.3(2) pm, α = 111.032(10)°, β = 94.279(10)°, γ = 105.860(10)°, volume = 1.0390(3) nm^3, Z = 2, density (calculated) = 1.264 g/cm^3, absorption coefficient = 0.156 m/mm^{-1}, F(000) = 420, crystal size 0.19 x 0.13 x 0.10 mm^3, 2Θ range for data collection 3.7 to 51.36°, index ranges $-10 \leq h \leq 9$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$, reflections collected 14714, independent reflections 3962 [R(int) = 0.0617], absorption correction none, refinement method full-matrix least-squares on F^2, data/restraints/parameters 3962/0/335, goodness-of-fit on F^2 1.047, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0402$, $wR_2 = 0.1012$, R indices (all data) $R_1 = 0.0556$, $wR_2 = 0.1082$, largest diff. peak and hole 0.39 and -0.32 $e \cdot Å^{-3}$.

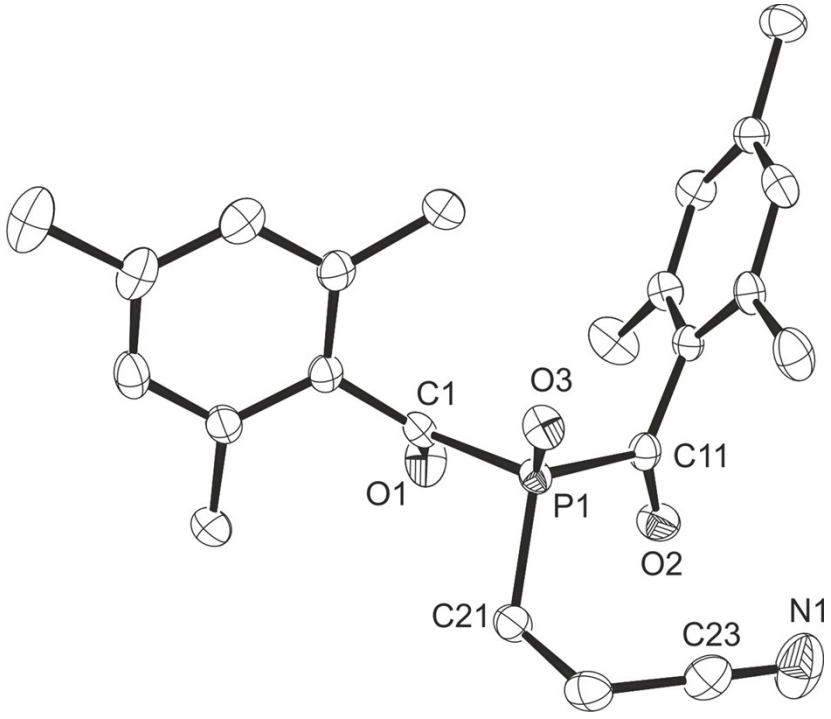

Fig. S1 ORTEP plot of **3b** (thermal ellipsoids at 50% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-C1 1.8986(19), P1-C11 1.8981(18), P1-C21 1.8115(18), P1-O3 1.4810(13), C1-O1 1.214(2), C11-O2 1.214(2), C23-N1 1.139(3), C1-P1-C21 100.85(8), C11-P1-C21 105.87(9), C1-P1-C11 97.67(8), O3-P1-C1 116.69(8), O3-P1-C11 120.05(7), O3-P1-C21 113.05(9), O3-P1-C1-O1 171.99, O3-P1-C11-O2 147.24, O1-C1-C11-O2 31.38.

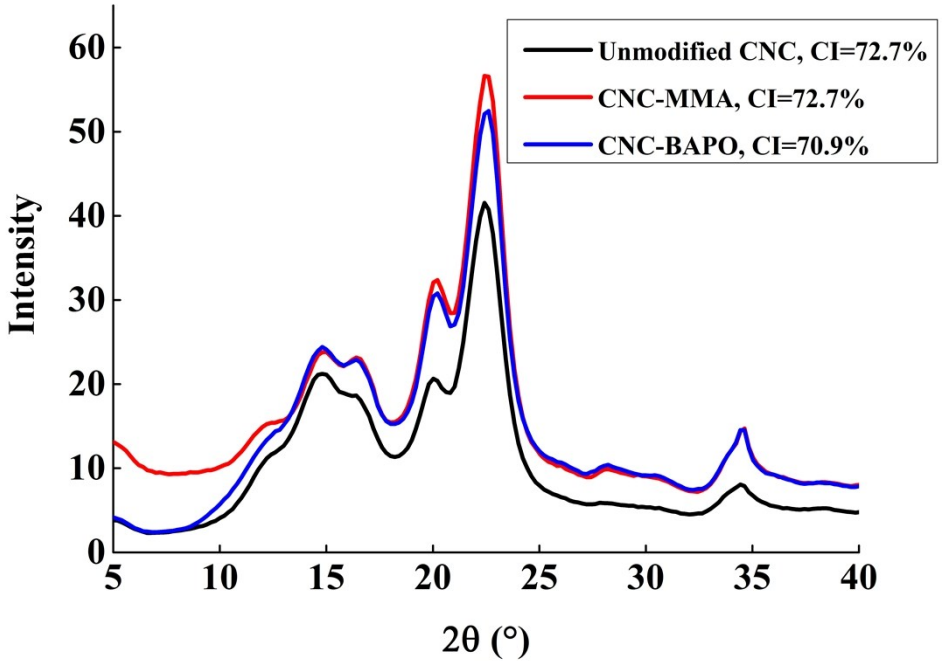

Fig. S2 X-ray diffraction patterns of the unmodified, methacrylate and BAPO functionalized nanocrystals with crystallinity indices.

Table S1 Gravimetrically determined graft yield (G), graft efficiency (G_E), molecular weight and polydispersity (PDI) of the cleaved polymers after grafting to CNC, and results from elemental analyses.

Sample	G (%)	G_E (%)	M_n (kg/mol)	M_w (kg/mol)	PDI	C (%)	H (%)	P (%)	S (%)
Unmodified CNC						41.88	6.40		1.00
CNC-MMA						43.43	6.27		0.95
CNC-BAPO						46.10	6.32	1.02	0.60
CNC-*g*-PMMA	477.2	79.7	76.7	250.6	3.27	57. 07	7.99	0.16	0.11
CNC-*g*-PBuA	311.2	75.4	9.5	17.4	1.82	61.02	9.06	0.21	0.13
CNC-*g*-PNIPAAm	292.4	73.5	25.2	69.5	2.76	58.41	9.37	0.21	0.12
CNC-*g*-PHEA	197.8	66.3				48.85	6.96	0.30	0.16

The sulfur content decreased after adding BAPO, which is likely caused by nucleophilic displacement of the sulfate group, which acts as leaving group.

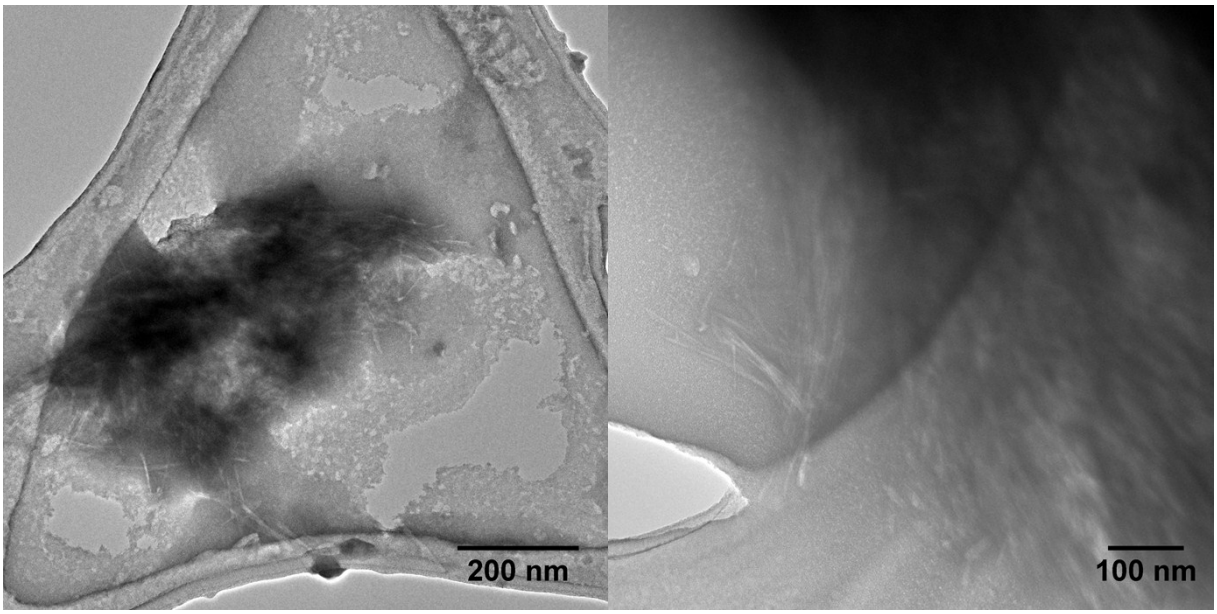

Fig S3a Transmission electron micrographs of CNC-BAPO after UV irradiation in the absence of monomer. Cellulose nanocrystals were crosslinked, but the dimensions were preserved.

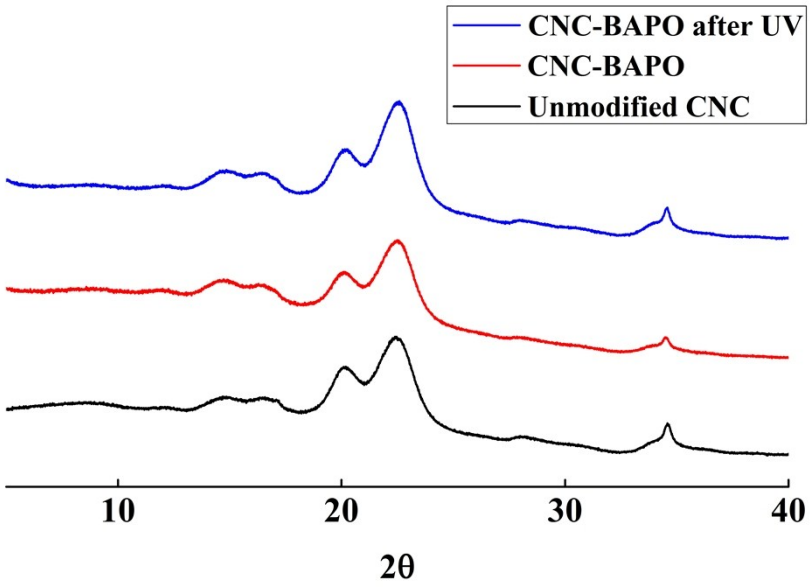

Fig S3b X-ray diffraction patterns of unmodified, BAPO functionalized nanocrystals before and after UV irradiation. The three samples show similar patterns.

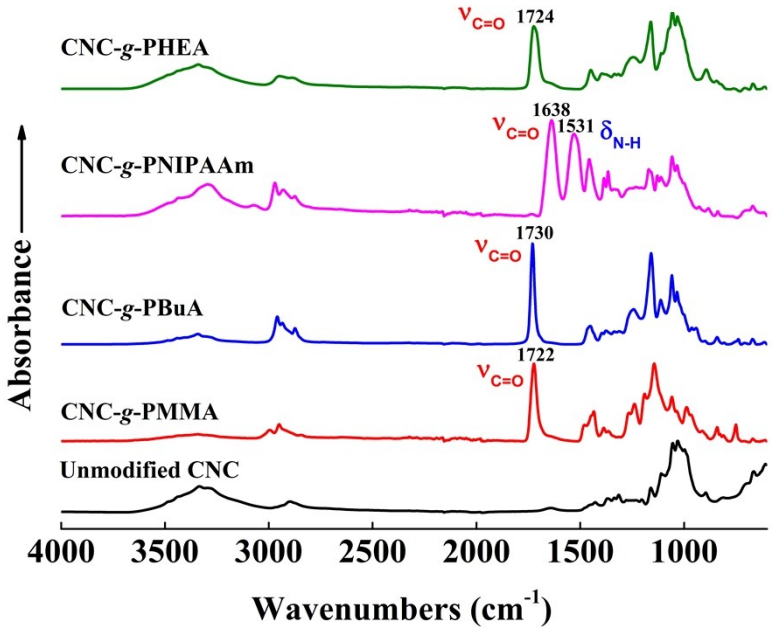

Fig. S4 FT-IR spectra of the polymer grafted samples.

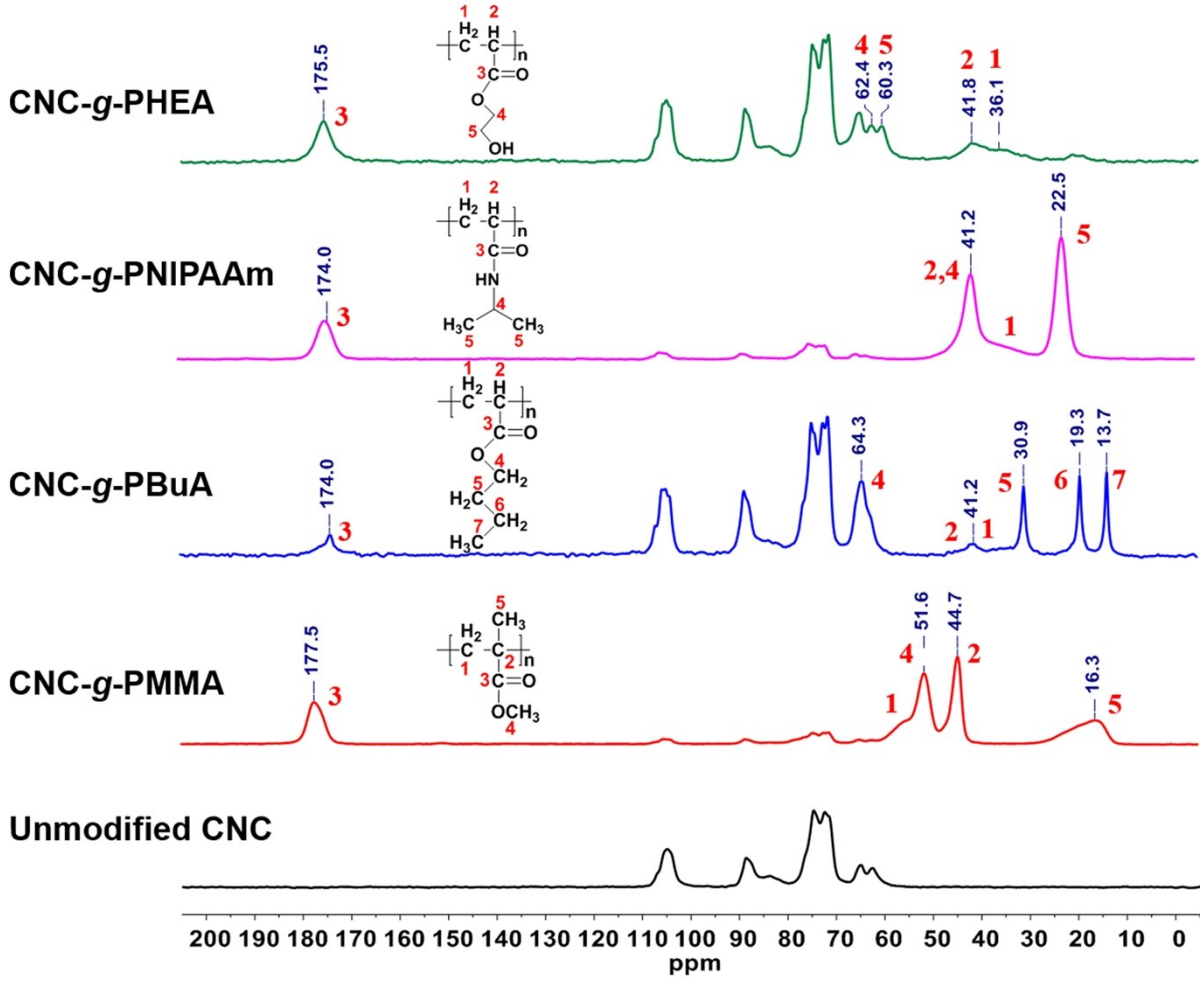

Fig. S5 ^{13}C CP-MAS NMR spectra of the polymer grafted samples with assignments of resonances.

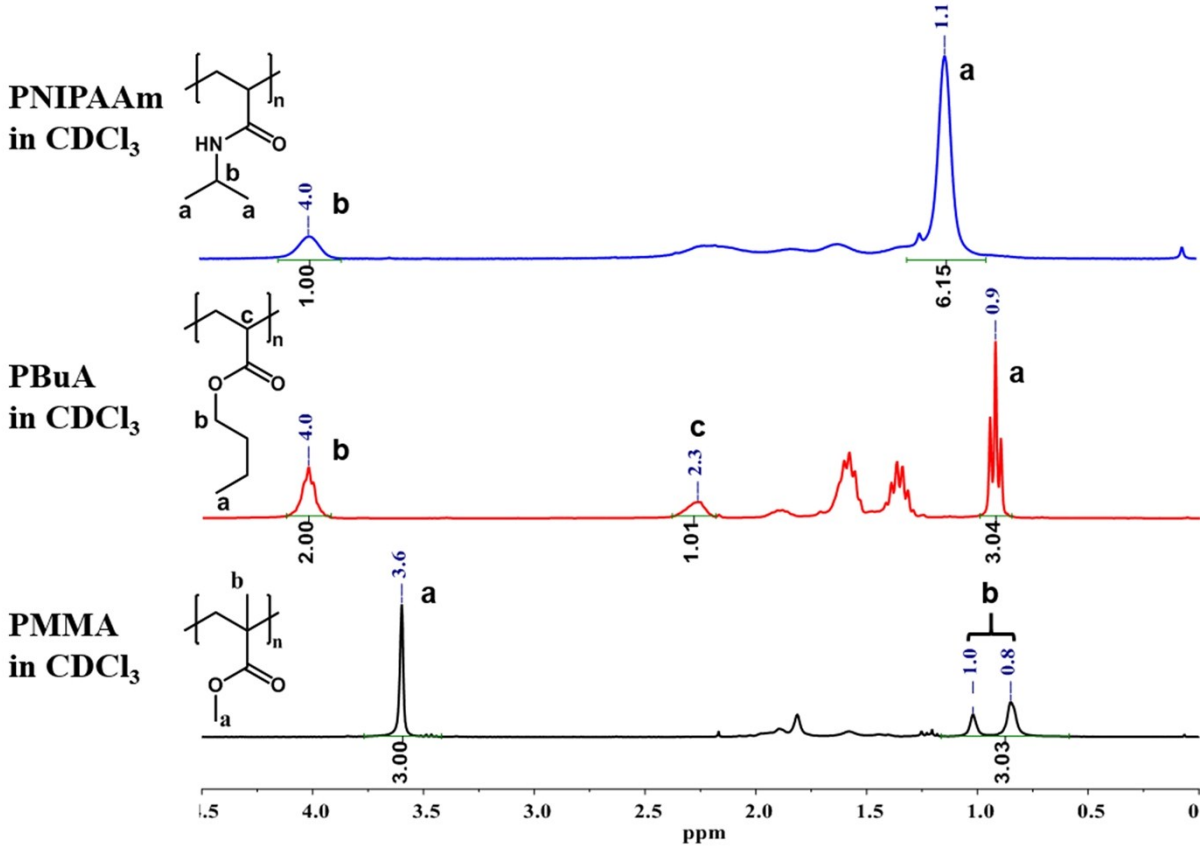

Fig. S6 ^{1}H NMR spectra of the cleaved polymers with assignments of resonances.

Table S2. TGA and DSC data of samples

Sample	TGA			DSC		T_g [°C]
	$T_{5\%}$[a] [°C]	T_m[b] [°C]	Y_c[c] [%]	T_H[d] [°C]	T_C[e] [°C]	
Unmodified CNC	251	306	0.8			
CNC-BAPO	247	294	18.3			
CNC-*g*-PMMA	241	397	1.3	123	114	105[f]
CNC-*g*-PBuA	275	420	5.6	-46	-51	-54[f]
CNC-*g*-PNIPAAm	273	417	3.7	143	136	130[f]
CNC-*g*-PHEA	277	447	1.3	-4	-13	-15[g]

[a] Temperature at which 5 % weight loss occurred. [b] Temperature at which the maximum rate of degradation is observed.
[c] Char yield at 800°C. [d] Glass transition temperature during heating. [e] Glass transition temperature during cooling.
[f] Reference values of homopolymers from Polymer handbook (4th ed.), John Wiley & Sons, 1999, pp. 199-204.
[g] Reference value from CRC Handbook of Enthalpy Data of Polymer-Solvent Systems, CRC Press, 2006, page 423.

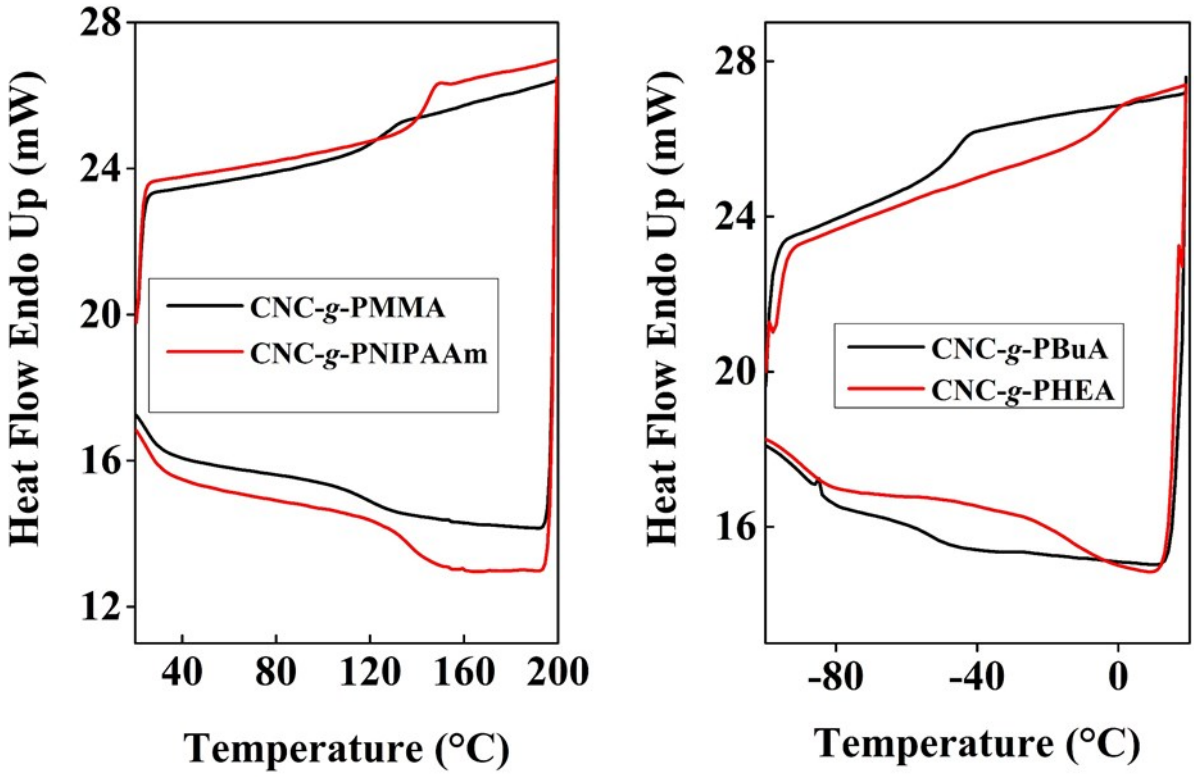

Fig. S7 DSC thermograms of grafted samples, the data of cooling and reheating were recorded.

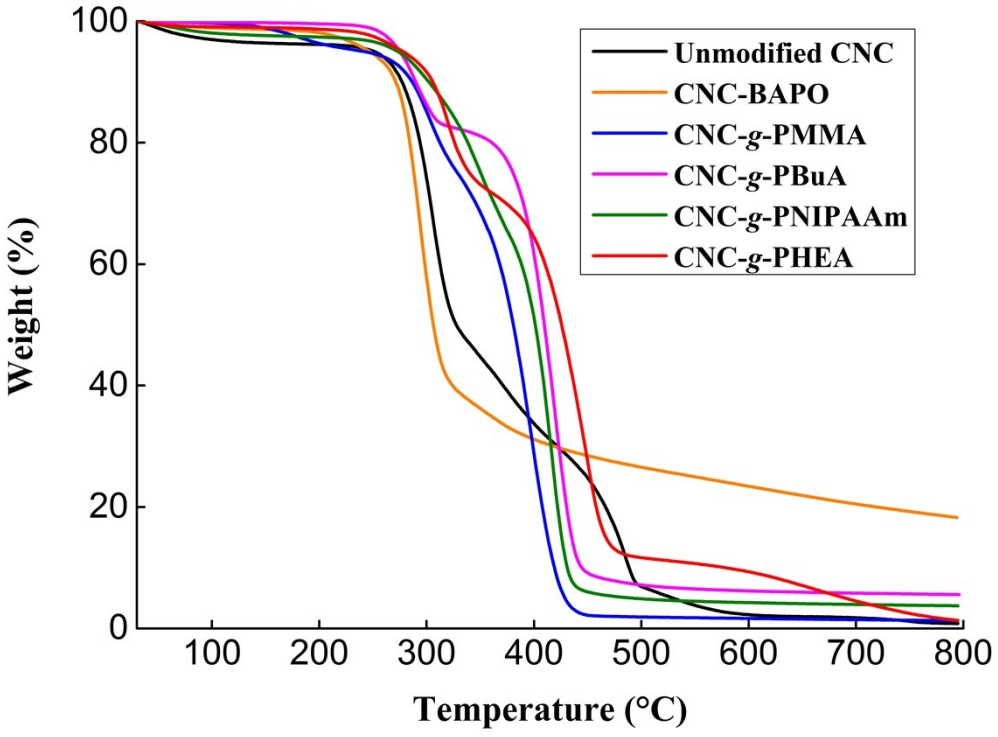

Fig. S8 TGA thermograms of samples

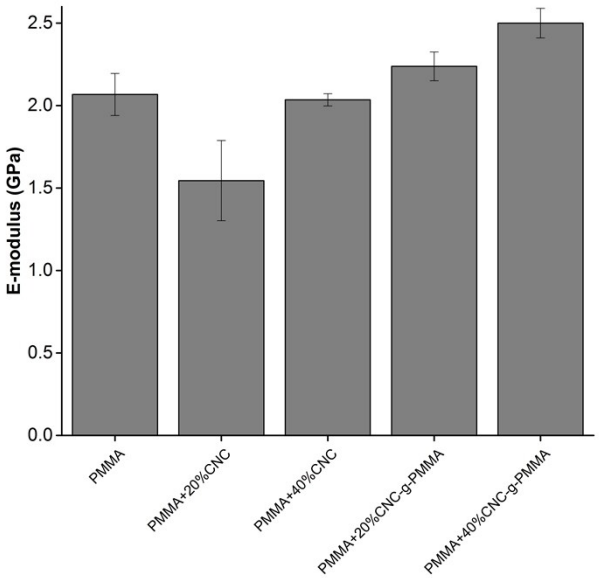

Fig. S9a Elastic modulus (*E*) of PMMA composites.

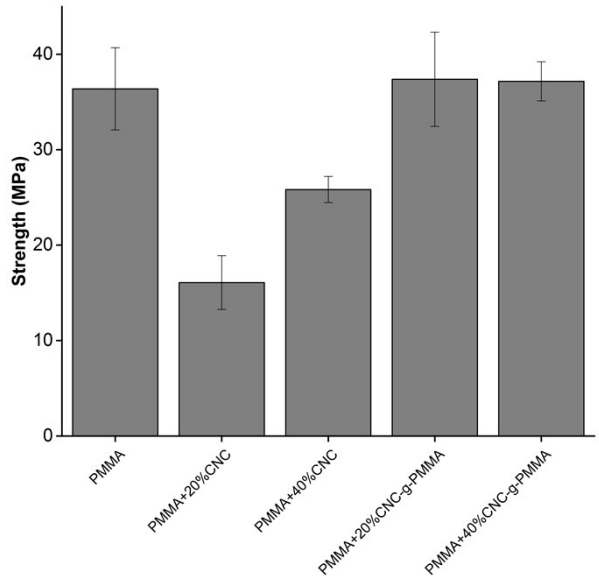

Fig. S9b Tensile strength of PMMA composites.

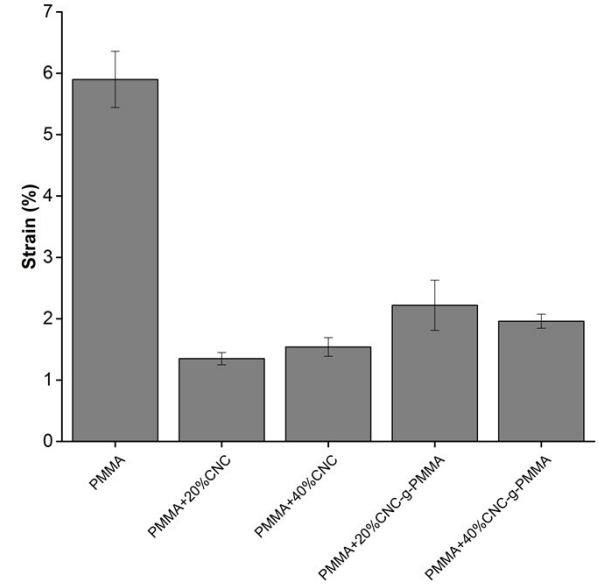

Fig. S9c Elongation at break of PMMA composites.

Experimental Section

General considerations

All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in a M Braun dry-box containing an atmosphere of purified argon. UV irradiation was carried out with a mercury vapour pressure lamp (Heraeus TQ 150, 150 W) inside a quartz dip tube, which was immersed into a temperature controlled solvent bath. Elemental analyses were performed at the Mikrolabor of ETH Zürich. UV/vis spectra were recorded on an UV/vis/NIR lambda-19-spectrometer (range 200 - 1000 nm) in 10 mm quartz cell. The melting points were determined with a Büchi M-560 device.

Materials

Cellulose nanocrystals were purchased from the University of Maine, with a sulfur content of 0.99%, and were purified by Soxhlet extraction with ethanol for 24 h before further modification.[1] DME, DMF, n-hexane, and toluene were degassed and purified using an Innovative Technologies PureSolv system. Methacrylate, methyl methacrylate and *N*-isopropylacrylamide were obtained from Acros. Butyl acrylate and 2-hydroxyethyl acrylate were purchased from Fluka. Acrylates were passed through basic alumina columns to remove inhibitors immediately before the polymerization experiment, except *N*-isopropylacrylamide, which was recrystallized from hexane three times. Acrylonitrile, ethanol, acetone and diethyl ether were purchased from Sigma-Aldrich and were used as received without further purification. Sulfuric acid (95%) and sodium hydroxide were supplied by Merck. Poly(methyl methacrylate) was obtained from Alfa Aesar with M_w = 550 kDa. Deionized water was used in all experiments.

Synthesis of Methyl 3-(bis(2,4,6-trimethylbenzoyl)phosphoryl)propanoate (3a)

A solution of $HP(COMes)_2$ (514 mg, 1.57 mmol, 1 eq.) and trimethylamine (22 µL, 0.16 mmol, 0.1 eq.) in dme (5 mL) was prepared in a 20 mL Schlenk flask. Methyl acrylate (0.142 mL, 1.57 mmol, 1 eq.) was added. After stirring for 12 h at 40 °C, the solution was allowed to cool down to r.t.. A solution of HCl in Et_2O (0.1 mL, 0.16 mmol, 0.1 eq., 2M) was added. The reaction mixture was stirred for 1 h at r.t., before the solvent was removed under reduced pressure. The solid residue was dissolved in toluene (6 mL) and the precipitate of triethylamine hydrochloride was separated by filtration. The solution volume was reduced *in vacuo* to 2 mL and layered with hexane (1 mL). The obtained yellow solid was collected by filtration and dried under high vacuum for 12 h to yield 0.62 g of methyl 3-(bis(2,4,6-trimethylbenzoyl)phosphino)propanoate (**2a**).

A 20 mL Schlenk flask was charged with **2a** (0.33 g, 0.79 mmol, 1 eq.), which was dissolved in toluene (5 mL). To this solution, tert.-butyl hydroperoxide (0.16 mL, 0.87 mmol, 1.1 eq., 5.5 M in decane) was added dropwise at 0 °C. After stirring vigorously at r.t. for 12 h, the solvent was removed under reduced pressure. The obtained yellow oil was washed with hexane (3 x 5 mL) and dried under high vacuum for 6 h to yield 0.301 g of product (0.70 mmol, 89%).

^{1}H-NMR (C_6D_6, 298 K): δ [ppm] = 2.06, 2.14 (s, 6 H, *p*-C*H*$_3$ Mes), 2.44, 2.47 (s, 12 H, *o*-C*H*$_3$ Mes), 2.45 (m, 2 H, C*H*$_2$CO), 2.76 (m, 2 H, C*H*$_2$P), 3.33 (s, 3 H, OC*H*$_3$), 6.64, 6.73 (s, 4 H, *H*$_{ar}$ Mes); **^{13}C{^{1}H}-NMR** (C_6D_6, 298 K): δ [ppm] = 20.2 (d, *o*- *C*H$_3$ Mes), 21.2 (s, *p*- *C*H$_3$ Mes), 22.1 (d, $^1J_{PC}$ = 55.34 Hz, *C*H$_2$P), 26.3 (d, $^2J_{PC}$ = 3.77 Hz, *C*H$_2$CO), 51.8 (s, O*C*H$_3$), 129.1, 129.7 (s, *C*^{3,5} Mes), 136.1, 136.5 (s, *C*^{2,6} Mes), 136.8 (d, $^2J_{PC}$ = 41.51 Hz, *C*^{1} Mes), 141.4 (s, *C*^{4} Mes), 172.1 (d, $^3J_{PC}$ = 11.32 Hz, *C*OOMe), 216.1 (d, $^1J_{PC}$ = 55.35 Hz, *C*OMes); **^{31}P{^{1}H}-NMR** (**(**C_6D_6, 298 K): δ [ppm] = 26.5.

UV/Vis λ[nm] = 242 (sh.), 292, 362, 394; **IR (**ATR [cm^{-1}]): 2920 (m, C-H st), 1741 (m, C=O st), 1670, 1640 (m, C=O st Mes); 1190 (s, P=O st), 1037 (m); **ESI MS** $[M + H]^+$ m/z = 429.1825, meas. 429.1820.

Synthesis of 3-(Bis(2,4,6-trimethylbenzoyl)phosphoryl)propanenitrile (3b)

A solution of $HP(COMes)_2$ (500 mg, 1.53 mmol, 1 eq.) and trimethylamine (21 µL, 0.15 mmol, 0.1 eq.) in dme (5 mL) was prepared in a 20 mL Schlenk flask. Acrylonitrile (0.1 mL, 1.53 mmol, 1 eq.) was added. After stirring for 12 h at 60 °C, the solution was allowed to cool down to r.t.. A solution of HCl in Et_2O (0.1 mL, 0.15 mmol, 0.1 eq., 2M) was added. The reaction mixture was stirred for 1 h at r.t., before the solvent was removed under reduced pressure. The solid residue was dissolved in toluene (7 mL) and the precipitate of triethylamine hydrochloride was separated by filtration. The solution volume was reduced *in vacuo* to 2 mL and layered with hexane (1 mL). The obtained yellow crystalline solid was collected by filtration and dried under high vacuum for 12 h to yield 0.55 g of 3-(bis(2,4,6-trimethylbenzoyl)phosphino)propanenitrile (**2b**).

A 20 mL Schlenk flask was charged with **2b** (0.42 g, 1.1 mmol, 1 eq.), which was dissolved in toluene (5 mL). To this solution, aqueous hydrogen peroxide (0.26 mL, 2.42 mmol, 2.2 eq., 30%) was added dropwise at 0 °C. After stirring vigorously at r.t. for 12 h, the solvent was removed under reduced pressure. The obtained yellow solid was recrystallized from toluene layered with hexane and stored at -10 °C (48 h). The crystalline solid was dried under high vacuum for 12 h to yield 0.37 g of product (0.94 mmol, 85%).

^{1}H-NMR (C_6D_6, 298 K): δ [ppm] = 2.06, 2.14 (s, 6 H, *p*-CH_3 Mes), 2.23, 2.47 (s, 12 H, *o*-CH_3 Mes), 2.30 (m, 4 H, PCH_2CH_2), 6.62, 6.73 (s, 4 H, H_{ar} Mes); **^{13}C{^{1}H}-NMR** (C_6D_6, 298 K): δ [ppm] = 20.1 (s, *o*- *C*H_3 Mes), 20.9 (d, $^1J_{PC}$ = 80.74 Hz, *C*H_2P), 21.2 (s, *p*- *C*H_3 Mes), 22.6 (d, $^2J_{PC}$ = 50.71 Hz, *C*H_2CN), 118.2 (d, $^3J_{PC}$ = 14.25 Hz, *C*N), 128.5, 129.1 (s, $C^{3,5}$ Mes), 136.2, 136.5 (s, $C^{2,6}$ Mes), 136.2 (d, $^2J_{PC}$ = 41.24 Hz, C^1 Mes),139.6, 141.9 (s, C^4 Mes), 214.7 (d, $^1J_{PC}$ = 53.06 Hz, *C*OMes); **^{31}P{^{1}H}-NMR (**C_6D_6, 298 K): δ [ppm] = 23.3.

UV/Vis λ[nm] = 242 (sh.), 296, 361, 394; **IR (**ATR [cm^{-1}]): 2922 (w, C-H st), 2347 (w), 1675 (m, C=O st Mes); 1607 (m, ar C=C), 1163, 1146 (s, P=O st); **ESI MS** $[M + NH_4]^+$ m/z = 413.1989, meas. 413.1985; **m.p.** 126 °C.

Synthesis of CNC-MMA

CNC-MMA were prepared according to a modified literature procedure.[2] In a 500 mL Schlenk flask, 5.06 g dry CNC (about 94 mmol total hydroxyl groups) were dispersed in 200 mL DMF using an ultrasonication treatment at 0 °C for 0.5 h. Then, 15.1 mL dry pyridine and 29.7 mL degassed methacrylic anhydride (6 eq. to CNC) were added. The suspension was heated to 60 °C and stirred for further 18 h under argon. After the reaction has completed, the suspension was centrifuged and the modified CNC were subsequently washed three times with a toluene/ethanol/acetone mixture (4/1/1 by vol.). Further purification was achieved with a Soxhlet extraction with acetone for 24 h.

Synthesis of CNC-BAPO

First remaining acetone in the purified **CNC-MMA** was exchanged for ethanol by three centrifugations and redispersion operations. After the last centrifugation step, the CNC suspension in ethanol was introduced in a 500 mL Schlenk flask and 250 mL of ethanol was added. The suspension was degassed with argon for 30 min, then 10.2 g $HP(COMes)_2$ (1 eq. to the glucose chain units of CNC) and 0.43 mL triethylamine (0.1 eq) were added. The mixture was allowed to stir for 2 days at 60 °C under argon. The flask was covered with aluminum foil in order to prevent decomposition of the product. Subsequently, 4.7 mL of aqueous H_2O_2 (1.5 eq., 35%) was added dropwise to the suspension at 0 °C. The mixture was allowed to slowly

warm to r.t. and stirred vigorously for 12 h. Then, the suspension was centrifuged and the modified nanocrystals were purified by Soxhlet extraction for 1 day. After drying in a vacuum oven at 45°C for 2 days, a yellow powder was obtained and stored in a desiccator over P_2O_5.

Polymerization of acrylic monomers

Typically, 0.25 g **CNC-BAPO** were introduced into a quartz tube with a stirring bar and the reaction vessel degassed. In a separate flask, a solution of 25 mmol acrylate monomer in 10 mL DMF was prepared and degassed by three freeze-pump-thaw cycles. This solution was injected into the quartz tube. A yellow suspension was obtained after stirring for 30 min at 0 °C. Subsequently, the sample was irradiated with UV light for 1 hour under vigorous stirring at room temperature.

The yellow suspension turned white after the irradiation and was precipitated into 100 mL cold ethanol. The solid substance was collected by filtration and washed with cold ethanol to remove residual monomer. For 2-hydroxyethyl acrylate and *N*-Isopropylacrylamide, diethyl ether was used instead of ethanol. This precipitate was then purified by Soxhlet extraction with acetone for 1 day to separate the homopolymer from the grafted copolymer, except for **CNC-*g*-PHEA**, which was treated with methanol instead. The homopolymer was obtained by removing the solvent and dried together with the grafted CNC in a vacuum oven at 65 °C until constant masses were obtained.

Gravimetric calculations

The weights of grafted CNC and retrieved homopolymers were used to calculate graft yield(G), and graft efficiency(G_E) in each product with the following formulae (1)-(2):

$$Graft\ yield = G = \frac{m_G}{m_{Cell}} \times 100\% \qquad (1)$$

$$Graft\ efficiency = G_E = \frac{m_G}{m_G + m_P} \times 100\% \qquad (2)$$

where m_G is the mass of the grafted polymer; $m_P is\ the\ mass\ of\ the\ homopolymer$; m_{Cell} is the mass of the cellulose nanocrystals.

Isolation of grafted polymer

Cellulose backbone was hydrolyzed by methods adapted from the literature.[3,4]

For **CNC-*g*-PMMA** and **CNC-*g*-PBuA**, 200 mg of grafted CNC were mixed in a flask with 10 mL of acetone and 15 mL of THF. After addition of 1 mL of concentrated sulfuric acid (98%), the mixture was refluxed for 12 hours. The resulting brown slurry was poured into cold ethanol and the precipitated polymer was washed with ethanol, dissolved in acetone, filtered, and precipitated again in cold ethanol.

For **CNC-*g*-PNIPAAm**, 200 mg were placed in 30 mL of 2% NaOH solution for 48 h under stirring. Following the saponification, the dispersion was brought to neutral pH with 6 N HCl and then centrifuged (12'000 rpm at 10 °C for 20 min) to separate the CNC from the cleaved polymer in the supernatant. The supernatant was then dialyzed against DI water until a minimum in conductivity was reached.

Cleaved and purified polymers were dried for further analysis.

Preparation of PMMA composites

Cellulose nanocrystals were first dispersed in toluene by stirring at room temperature for 14 h. The desired amount of PMMA (4% in toluene) was added and the resulting suspension was homogenized by using a Ultra-Turrax at 15'000 rpm for 3 min.. Solid films were obtained by casting the suspension on Teflon plates and evaporation of toluene at room temperature. To

remove any traces of solvent, the films were heated at 50°C for 24 h and subsequently stored in a desiccator that contained silica gel until they were analyzed. The thickness of composite films was around 0.1 mm.

Solution NMR spectroscopy

^{1}H, ^{13}C, ^{31}P NMR spectra were recorded on Bruker 500 spectrometer operating at 500.23 MHz, 125.78 MHz and 202.51 MHz, respectively. All ^{1}H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the ^{1}H (residual) and ^{13}C chemical shifts of the solvent as a secondary standard.

Single crystal X-ray analysis

X-ray crystallographic measurement was performed on an Oxford Xcalibur diffractometer equipped with CCD $Mo_{K\alpha}$ radiation (0.71073 Å). Refinement against full matrix (versus F^2) was obtained with SHELXT-97. Non-hydrogen atoms were anisotropically refined.

Solid-state ^{13}C and ^{31}P CP-MAS NMR spectroscopy

Solid-state ^{13}C and ^{31}P CP-MAS NMR spectra were recorded at RT on a Bruker Avance 400 NMR spectrometer (Bruker BioSpin AG, Fällanden, Switzerland) using a 4 mm CP-MAS probe. Approximately 30 - 40 mg of dried material was packed in a 4 mm zirconia rotor. The ^{13}C and ^{31}P CP-MAS NMR spectra were recorded at 100.6 and 162.0 MHz, respectively, using the following parameters: 3.5 µs 90° excitation pulse on ^{1}H channel, 3 ms contact time with a ramp from 100 to 50% of power level on the proton channel, 10'000 (^{13}C) and 13'000 Hz (^{31}P) MAS rates, 4 s relaxation delays, 71 kHz SPINAL 64 proton decoupling was applied during acquisition, and appropriate numbers of scans were recorded to yield reasonable signal-to-noise ratios.

TEM Characterization

TEM samples were measured by using a JEOL 2200FS instrument (JEOL, USA) at an accelerating voltage of 200 kV. 5 µL of untreated nanocrystal suspension in water (0.01 wt%) or of the BAPOs modified nanocrystal in ethanol, were deposited on holey carbon-coated copper grid (200 mesh), negatively stained with uranyl acetate and allowed to dry before measurement.

X-ray Diffraction Analysis.

X-ray diffraction (XRD) measurements of all samples were performed using a Bruker D8 Advanced diffractometer (Cu Kα radiation: l = 1.54184 Å; tube parameters: V = 40 kV, I = 40 mA) with a parallel incident beam prepared by a Göbel Xray mirror. The patterns were recorded with a 1D position sensitive detector (VÅNTEC). The powder samples were measured using a flat sample holder in reflection mode. The scans were recorded in the 2θ range 5–40 °.

Crystallinity Index (CI)

The crystallinity index (CI) was evaluated using the Buschle-Diller and Zeronian equation[5]:

$$CI = 1 - \frac{I_{am}}{I_{200}}$$

where I_{200} is the intensity of the 200 lattice plane at 2θ = 22.4 ° and I_{am} represents the peak intensity at 18 °, which corresponds to the amorphous material in cellulose.

Infrared Spectroscopy (FTIR-ATR).

FT-IR spectra of the dried samples were recorded using a Tensor 27 FT-IR spectrometer (Bruker, Switzerland). For each sample, the diamond crystal of an Attenuated Total Reflectance (ATR) accessory was brought into contact with the area to be analyzed. The contact area was a circle of about 1.5 mm in diameter. All spectra were recorded between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans per sample.

Thermogravimetric Analysis (TGA).

TGA analyses were conducted by using a TGA7 apparatus (PerkinElmer, USA). The dried samples (~5 mg) were heated from 30 to 800 °C at a constant rate of 20 °C/min under a He atmosphere.

Differential Scanning Calorimetry (DSC).

DSC analyses were conducted by using a DSC7 apparatus (PerkinElmer, USA). The dried samples (~5 mg) were measured by a heat-cool-reheated method at a constant rate of 20 °C/min under a He atmosphere.

Gel permeation chromatography (GPC)

Measurements were performed on a Viscotek GPC unit. Detection: Triple Detector Array TDA 302 (refractive index, small and wide angle light diffraction and viscosity) and UV detector Viscotek 2500 (λ = 254 nm). The solution of a polymer sample is passed through two columns (Polymer Laboratories, PLgel 5 µm Mixed-C and PLgel 5 µm Mixed-D) to achieve a separation of polymers by size. The temperature was maintained at 35 °C during the measurement. The sample concentration was 1 mg/mL in DMF, the injection volume 100 µL and the flow-rate 1 mL/min. Data analysis: universal calibration with 13 monodisperse PS standards.

Tensile tests

PMMA composite films were cut into dog-bone-shaped specimens with a length of 50 mm, a width of 8.5 mm at the clamping zone, and a width of 4 mm at the stretching zone. The modulus of elasticity (*E*), nominal tensile strength (σ), and elongation at break of the composites were analyzed by using a Universal Testing System Z010 (Zwick, Germany) with a loading cell of 200 N and a deformation rate of 2 mm/min. Measurements were performed in a conditioned room (50% RH and 23°C), and the results were the average of five measurements.

References

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