Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of γ-cyclodextrin substituted bis(acyl)phosphane oxide derivative (BAPO-γ-CyD) serving as multiple photoinitiator and crosslinking agent

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Materials

γ-Cyclodextrin (Mn = 1297.14 g/mol) was purchased from ABCR. Acryloyl chloride, n-methyl pyrrolidone (NMP), Tetramethylguanidine (TMG), HCl in DEE, hydrogen peroxide (H_2O_2 35%), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, 1,6 hexanediol diacrylate (HDDA, Mn = 226.27 g/mol) and poly(ethylene glycol) methyl ether methacrylate (PEGMEM, Mn = 500 g/mol) were obtained from Sigma Aldrich and used as received without further purification. Dimethoxyethane (DME) and toluene were degassed and purified using an Innovative Technologies PureSolv system.

Synthesis of acrylated-γCyclodextrin (Ac-γ-CyD, 3)

After being dried at 90 °C under high vacuum for 24 h, γ-CyD (20 g, 15.42 mmol, 1 eq.) was charged in a 500 mL round-bottom flask containing 160 mL of anhydrous n-methyl-pyrrolidone (NMP). The reaction mixture was stirred under protective atmosphere of Argon, till γ-CyD was totally dissolved. Then acryloyl chloride (36.07 mL, 0,44 mol, 28.8 eq.) was added dropwise at 0 °C. After stirring for 72 h at r.t. and 300 rpm, the reaction mixture was slowly dropped into 2 L of DI-H_2O to precipitate the product as a white powder. After decanting the mixture for 30 min. at r.t., Ac-γCyD (36.6 g, 67%) was filtered and washed four times using DI-H_2O. Finally, the product was dried for two days under high vacuum before being characterized by means of ^{1}H NMR, ^{13}C{^{1}H} NMR, ATR-FTIR and MALDI-MS.

Synthesis of BAPO-γCyclodextrin (BAPO-γ-CyD, 5)

A solution of Ac-γ-CyD (2 g, 0.81 mmol, 1 eq.), bis(2,4,6-trimethylbenzoyl)hydrogenphosphane (BAP-H) (2.93 g, 8.9 mmol, 11 eq.) and TMG (0.11 mL, 0.89 mmol, 1.1 eq.) in 90 mL of DME was prepared in a 250 ml Schlenk flask. After stirring for 1 h at 300 rpm and 50 °C, the solvent was removed under reduced pressure. The yellow olily residue was dissolved in 90 mL of Toluene. After the addition of HCl (HCl in DEE, 0.45 mL, 0.89 mmol, 1.1 eq.) at r. t., the mixture was left to stir for 1 h and then filtered over celite. Then, aq. H_2O_2 (0.84 mL, 9.8 mmol, 12 eq., 35%) was added dropwise in the dark at 0 °C. After stirring vigorously at r.t. for 1 h, the solvent was removed under reduced pressure to yield BAPO-γ-CyD as a light-yellow powder (4.7 g, 95%). The product was dried for two days under high vacuum before being characterized by means of ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, ATR-FTIR and MALDI-MS; and then stored in the dark at 4 °C.

Solution NMR spectroscopy

^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR spectra were recorded on Bruker 500 spectrometer operating at 500.26 MHz, 125.80 MHz and 202.50 MHz, respectively. Chemical shifts δ were measured according to IUPAC and are given in parts per million (ppm) relative to TMS and H_3PO_4 for ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{31}P{^{1}H} NMR.

ATR-FTIR spectroscopy

ATR spectra were recorded between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans per sample using a Tensor 27 FT-IR spectrometer (Bruker, Switzerland).

MALDI-MS

Mass spectrometry measurements were carried out by the MS Service (Laboratory of Organic Chemistry) at ETH Zürich.

UV-Vis spectroscopy

UV/vis spectra were recorded on a UV/vis/NIR lambda-19-spectrometer (range 200 - 600 nm) in 10 mm Quartz cells. The molar extinction coefficients (ε) were calculated using the following equation (**S1.1**):

$$\varepsilon = -\log\left(\frac{I}{I_0}\right)\frac{1}{cl} = \frac{A}{cl} \qquad S1.1$$

where c is the concentration, l the extinction pathway (1 or 10 mm cuvette) and A is the absorption at 365 nm.

Photo-differential scanning calorimetry (Photo-DSC)

The tests were performed at 25 °C under N_2 atmosphere (30 mL/min), using a Mettler Toledo DSC. The light source was provided by a Hamamatsu LC8 lamp (cutoff filter under 400 nm, 0.6 mW/cm^2) equipped with an 8 mm light guide.
At the beginning of the measurements, an isothermal period of 120 s was scheduled before the irradiation was activated for 300 s. Subsequently, another isothermal period of 120 s was observed before the second irradiation period of

another 300 s was started. The DSC curve from the second irradiation period was subtracted from the first in order to provide a DSC curve, which excludes all thermal effects due to light dissipation.
From the resulting DSC curves, the heat flux; t_{onset}, the time to start the polymerization, t_{max}, the time to reach the maximum of heat flux, the double bond (C=C) conversion (DBC, **S1.2**) and the rate of conversion (Rp, **S1.3**) were obtained.

$$DBC\ \% = \frac{\left(\int_0^t \frac{dH}{dt}\right) x\ M_w}{\Delta H_T} x\ 100 \qquad S1.2$$

$$Rp = \frac{d(DBC)}{dt} = \frac{\left(\frac{dH}{dt}\right)}{\Delta H_T} \qquad S1.3$$

where M_w and ΔH_T are the molecular weight and the theoretical heat of polymerization of the monomer ($M_{w,HDDA}$= 226.27 g/mol and $\Delta H_{T,HDDA}$= 172 kJ/mol[1,2]).

Photo-rheology

Real-time photo-rheology measurements were performed using an Anton PAAR Modular Compact Rheometer (Physica MCR 302) in parallel-plate mode (25 mm diameter) and the visible-light source was provided by positioning the light guide of the Hamamatsu LC8 lamp (6 mW/cm^2) under the bottom plate. During the measurements, the gap between the two glass plates was set to 0.2 mm and the sample was kept under a constant shear frequency of 1 Hz and strain amplitude of 1%. The irradiating light was switched on after 60 s to let the system stabilizing before the onset of polymerization. The kinetic of photopolymerization was studied as a function of the changes in the shear modulus (G') of the sample versus the exposure time. From the resulting curves, the delay (or induction) time (i.e. the irradiation time required to induce chemical crosslinking) and the slope of the curves ($\Delta G'/\Delta t$, indication of the curing rate, measured in the first 30 s after t_d) can be obtained.

Preparation of the samples

Cylindrical samples were prepared by casting **I**, **II**, **III** and **IV** in a PDMS mold (0.75 cm diameter, 0.5 cm thick) and irradiating 4 min with visible light (Hamamatsu LC8, 8 mW/cm^2). All the samples were then postcured under UV light for 2 min and finally removed from the mold.

Swelling ratio

The samples were placed in deionized water for 24 h at r.t.. Then, the samples were removed from the water at different time interval and weighed after having wiped off the surface droplets with wet paper to gently remove excess water.[3] The swelling degree (SW %) was measured gravimetrically using the following equation (**S1.4**):

$$SW\ (\%) = \frac{W_t - W_0}{W_0} x\ 100 \qquad S1.4$$

where W_t is the weight of the soaked sample at a certain time and W_0 is the initial weight of the dried sample.
The water content of the samples at equilibrium (EWC) was also evaluated as follows (**S1.5**):

$$EWC\ (\%) = \frac{W_t - W_0}{W_t} x\ 100 \qquad S1.5$$

Gel content measurements

The gel content (insoluble fraction) of the products was determined following this procedure: the samples were first weighted and immersed in water for 24 hours at r.t. to dissolve the soluble fraction (non-cross-linked polymer) and

then dried for 24 h in a vacuum furnace (500 mbar, 70 °C). The gel content (GC) was calculated as weight difference before and after solvent extraction.[3]

Characterization of acrylated-γ-Cyclodextrin (Ac-γ-CyD, 3)

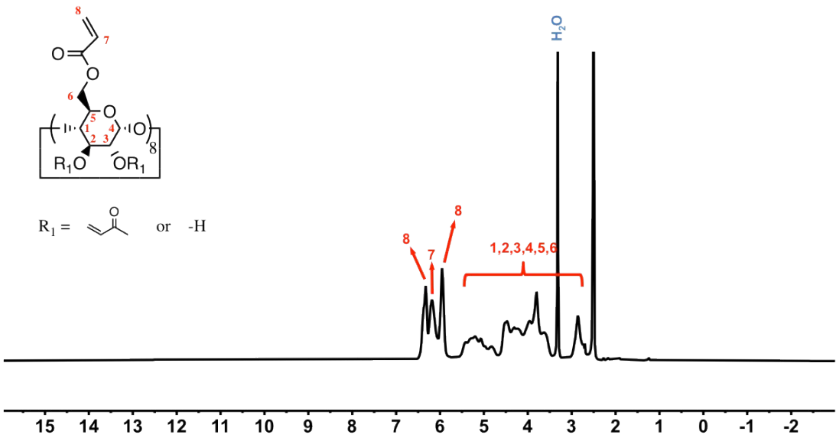

Figure S1: ^{1}H NMR of acrylated-γ-cyclodextrin (Ac-γ-CyD, **3**) in DMSO.

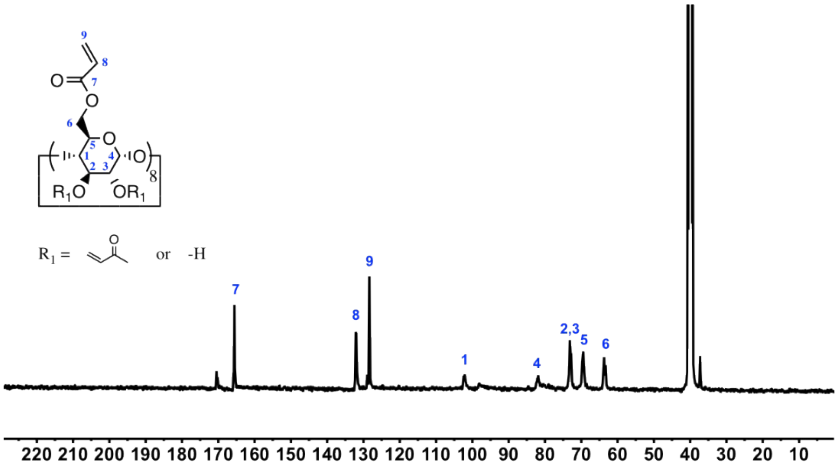

Figure S2: ^{13}C{^{1}H} NMR of acrylated-γ-cyclodextrin (Ac-γ-CyD, **3**) in DMSO.

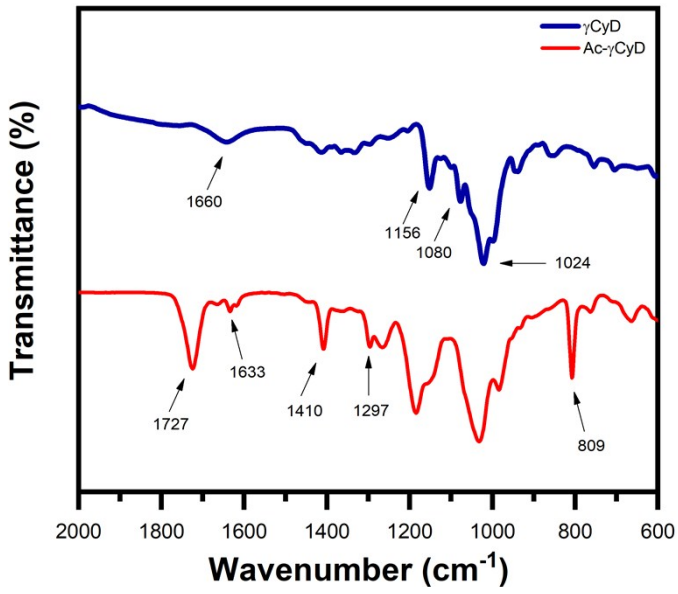

Figure S3: Comparison between the ATR-FTIR spectra of γ-cyclodextrin (γ-CyD, **1**) and acrylated-γ-cyclodextrin (Ac-γ-CyD, **3**).
^{1}H-NMR (500.26 MHz, d6-DMSO, 298 K): d [ppm] = 2.8 - 5.2 (H1, H2, H3, H4, H5, H6), 5.95 (-CH=$\underline{CH_2}$), 6.18 ($\underline{CH}$=CH_2) and 6.32 (-CH=$\underline{CH_2}$).
^{13}C{^{1}H}-NMR (125.80 MHz, d6-DMSO, 298 K): d [ppm] = 63.46 (C6), 69.39 (C5), 72.83 (C3), 73.18 (C2), 81.86 (C4), 102.13 (C1), 128.36 (-CH=$\underline{CH_2}$), 132.06 ($\underline{CH}$=CH_2) and 165.58 (-C=O).
IR (ATR [cm^{-1}]): 1727 (νC=O), 1633 (νC=C), 1410 (νH-C=CH_2), 1297 cm^{-1} (νC-O)$_{unsat.\ \alpha\text{-}\beta}$, 1156 cm^{-1} (νC-O-C)$_{glucopyran.}$, 1080 cm^{-1} (νC-O)$_{6,glucopyran}$, 1024 cm^{-1} ((νC-C) + (νC-O))$_{glucopyran}$ and 809 (νC-H).

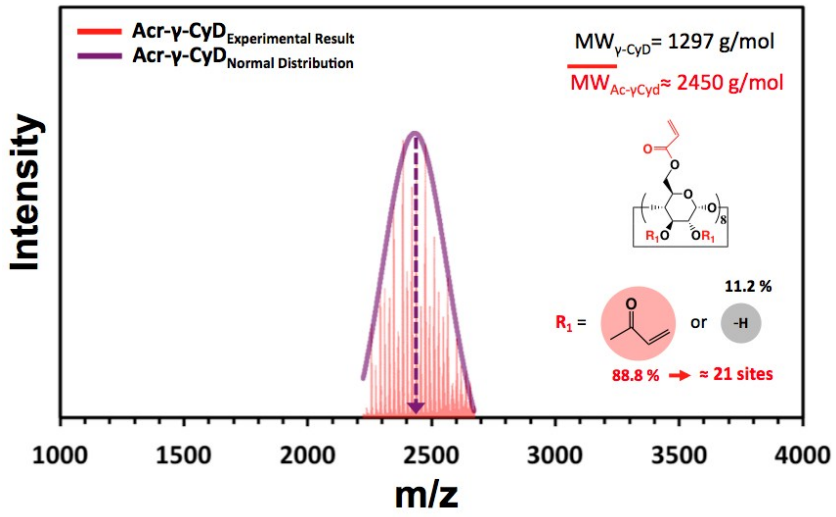

Figure S4: MALDI MS spectrum of acrylated-γ-cyclodextrin (Ac-γ-CyD, **3**). The degree of substitution was calculated considering the average molecular weight of **3** (M_w = 2450 g/mol), estimated from the normal distribution of the m/z peaks appearing in the MALDI spectrum. According to these data, 21 hydroxyl groups were acrylated on average.

Characterization of BAPO-γCyclodextrin (BAPO-γ-CyD, 5)

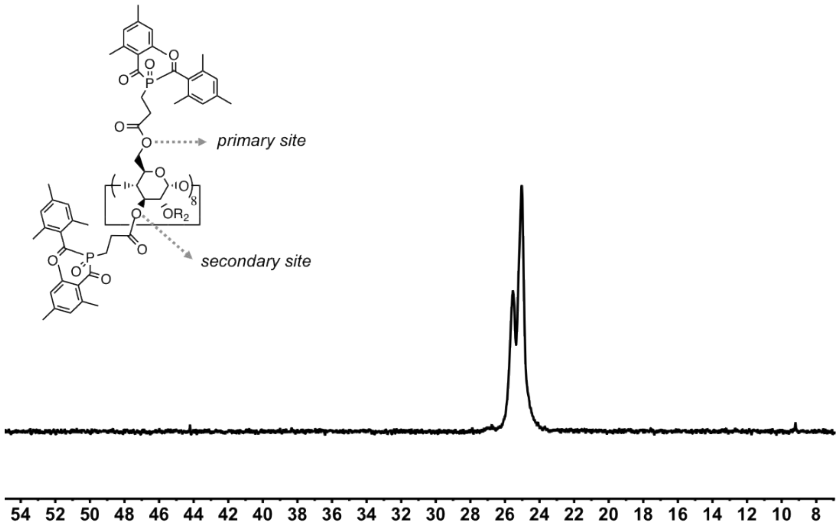

Figure S5: ^{31}P{^{1}H} NMR of BAPO-γ-cyclodextrin (BAPO-γ-CyD, **5**) in DMSO.

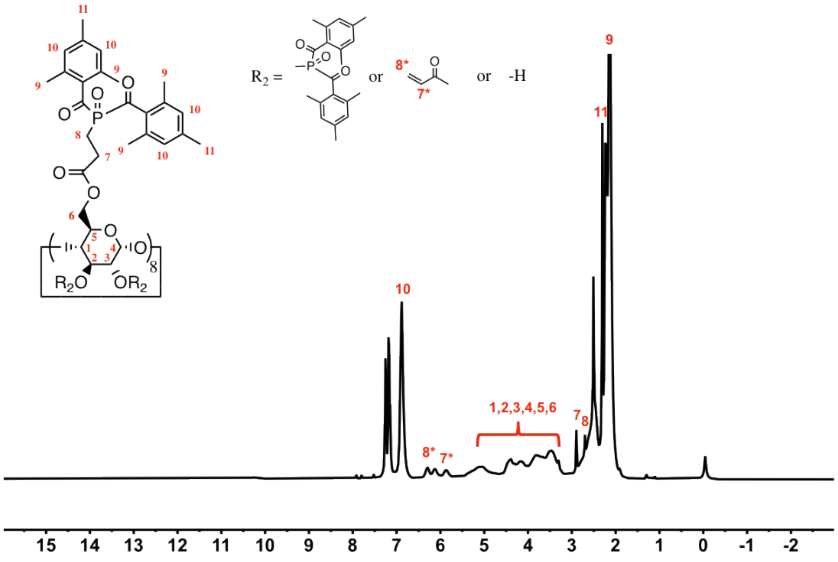

Figure S6: ^{1}H NMR of BAPO-γ-cyclodextrin (BAPO-γ-CyD, **5**) in DMSO.

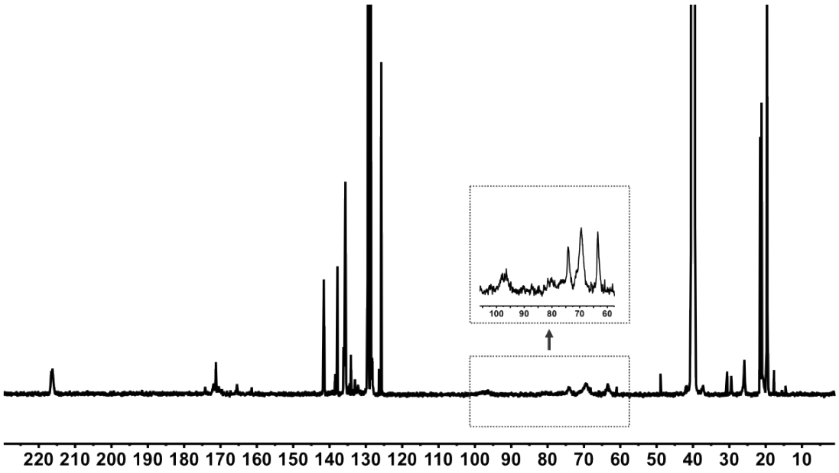

Figure S7: ^{13}C{^{1}H} NMR of BAPO-γ-cyclodextrin (BAPO-γ-CyD, **5**) in DMSO.

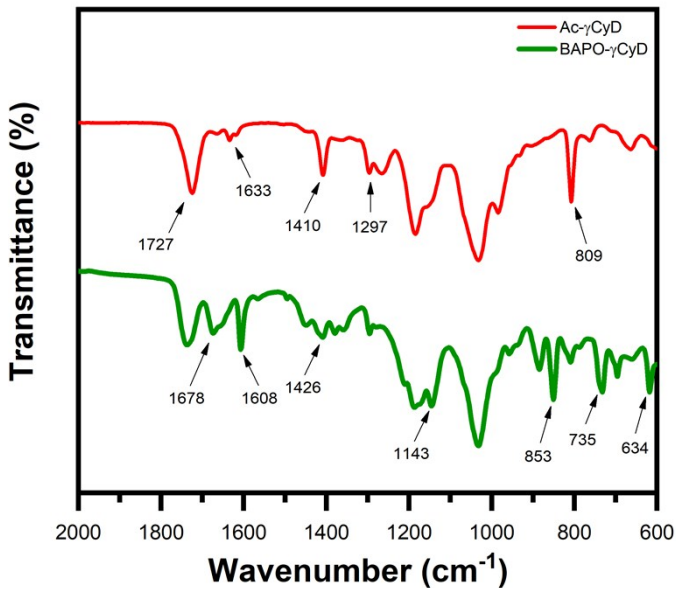

Figure S8: Comparison between the ATR-FTIR spectra of acrylated-γ-cyclodextrin (Ac-γ-CyD, **2**) and BAPO-γ-cyclodextrin (BAPO-γ-CyD, **5**).

$^{31}P\{^{1}H\}$ NMR (202.50 MHz, d6-DMSO, 298 K): d [ppm] = 25.04 and 25.51

^{1}H-NMR (500.26 MHz, d6-DMSO, 298 K): d [ppm] = 2.13 - 2.23 (s, 18 H, o-CH_3Mes and p-CH_3Mes), 2.65 (m, 4H, P-CH_2 CH_2), 2.8 - 5.2 (H1, H2, H3, H4, H5, H6), 5.95 (-CH=$\underline{CH_2}$), 6.18 ($\underline{CH}$=CH_2), 6.32 (-CH=$\underline{CH_2}$) and 6.77 (s, 4 H, H_{ar}Mes).

$^{13}C\{^{1}H\}$-NMR (125.80 MHz, d6-DMSO, 298 K): d [ppm] = 19.62 (s, o-CH_3Mes), 20.70 (s, p-CH_3Mes), 20.94 (s, -PCH_2CH_2), 25.58 (s, -PCH_2CH_2CO), 63.46 (C6), 69.39 (C5), 72.83 (C3), 73.18 (C2), 81.86 (C4), 100.13 (C1), 127.6 (s, $C_{3,5}$Mes), 128.36 (-CH=$\underline{CH_2}$), 132.06 ($\underline{CH}$=CH_2), 134.8 (s, $C_{2,6}$Mes), 137.0 (s, C_4Mes), 142.5 (d, C_1Mes), 165.58 and 170.45(-C=O) and 216.54 (s, 1, COMes).

IR (ATR [cm^{-1}]): 1727 (νC=O), 1678 (νC=O), 1608 (νC_{ar}=C_{ar}); 1426 (νP-CH_2), 1297 cm^{-1} $(\nu C\text{-}O)_{unsat.\ \alpha\text{-}\beta}$, 1156 cm^{-1} $(\nu C\text{-}O\text{-}C)_{glucopyran}$, 1143 (νP=O), 1080 cm^{-1} $(\nu C\text{-}O)_{6,glucopyran}$, 1024 cm^{-1} $((\nu C\text{-}C) + (\nu C\text{-}O))_{glucopyran}$, 853 and 796 ($oop_{bending}$), 735 ($\nu C\text{-}H_{bending}$) and 634 (νP-C). Rest peaks are attributed to residual acrylate groups.

UV/Vis λ[nm] = 300, 365, 400 (sh.).

MALDI MS of BAPO-γ-CyD (**5**): the degree of substitution was calculated considering the average molecular weight of **5** (M_w = 5900 g/mol), estimated from the normal distribution of the m/z peaks appearing in the MALDI spectrum. According to these data, about 10 bis(acyl)phosphane oxide units could be successfully grafted to **3**.

References

1. M. Mitterbauer, P. Knaack, S. Naumov, M. Markovic, A. Ovsianikov, N. Moszner, and R. Liska, *Angew. Chem. Int. Ed.* **2018**, 57, 12146–12150·
2. C. Gorsche, T. Koch, N. Moszner, R. Liska, *Polym. Chem.* **2015**, 6, 2038-2047.
3. J. Wang, A. Chiappone, I. Roppolo, F. Shao, E. Fantino, M. Lorusso, D. Rentsch, K. Dietliker, C. F. Pirri, and H. Grützmacher, *Angew. Chem. Int. Ed.* **2018**, 57, 2353 –2356.