ADVANCED SUSTAINABLE SYSTEMS

Supporting Information

The Rapid Mechanochemical Synthesis of Microporous Covalent Triazine Networks: Elucidating the Role of Chlorinated Linkers by a Solvent-Free Approach

Annika Krusenbaum, Fabien Joel Leon Kraus, Stefanie Hutsch, Sven Grätz, Mark Valentin Höfler, Torsten Gutmann, and Lars Borchardt*

WILEY-VCH

Supporting Information

The Rapid Mechanochemical Synthesis of Microporous Covalent Triazine Networks: Elucidating the Role of Chlorinated Linkers by a Solvent-free Approach

Annika Krusenbaum, Fabien Joel Leon Kraus, Stefanie Hutsch, Sven Grätz, Mark Valentin Höfler, Torsten Gutmann and Lars Borchardt*

Inhalt

1. Materials

1,3,5-triphenylbenzene (TPB) (Sigma Aldrich, 97% purity), benzene (BZ) (TCI, >99.5% purity), biphenyl (BP) (Acros Organics, 99% purity), p-terphenyl (TP) (abcr, 99% purity), triptycene (TTC) (abcr, 97% purity), 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMBP) (Sigma Aldrich, 95% purity), 2,4,6-trichloro-1,3,5-triazine (CyCl) (Sigma Aldrich, 99% purity), 4,6-dichloropyrimidine (DCY) (Sigma Aldrich, 97% purity), 3,6-dichloropyridazine (DCD) (Sigma Aldrich, 97% purity), 2,6-dichloropyrazine (DCP) (Sigma Aldrich, 98% purity), carbon tetrachloride (CCl_4) (Sigma Aldrich, >99.9% purity), and aluminium(III) chloride ($AlCl_3$) (anhydrous, Alfa Aesar, 98% purity) were purchased and used as received.

Chloroform ($CHCl_3$) and dichloromethane (DCM) were purchased in p.A. quality. Both liquids were stored over 4Å molecular sieves under inert atmosphere to remove remaining moisture.

10 mm Zirconium oxide milling balls (Type ZY-S; average weight of 3.2 g) were purchased from the Sigmund Lindner GmbH.

2. Milling parameters

Table S1. Overview over the yield, C/N ratio, specific surface area (SSA_{BET}) and the total pore volume (V_{total}) at $P/P_0 = 0.95$ for various polymers obtained during the mechanochemical reaction. If not stated otherwise, the reaction was proceeded for 60 min at 30 Hz in a MM500 mixer mill using ZrO_2 as milling material.

Polymer	Monomer	Eq	Node	Eq	Linker	Eq	Yield (%)	C/N ratio	SSA_{BET} (m^2/g)	V_{total} (cm^3/g)
CTN-1	TPB	1	CyCl	6	DCM	6	95	11.26	1136	0.72
CTN-FeCl$_3$ (a)	TPB	1	CyCl	6	DCM	6	82	-	765	0.57
CTN-SnCl$_2$ (b)	TPB	1	CyCl	6	DCM	6	21	3.42	67	0.08
CTN-AlCl$_3$ (c)	TPB	1	CyCl	6	DCM	6	99	9.04	1216	0.74
FC-DCM-1	TPB	1	-	-	DCM	6	92	-	1121	0.71
CTN-2	TPB	1	CyCl	1	DCM	6	97	13.22	658	0.37
CTN-3	TPB	1	CyCl	2	DCM	6	98	8.6	680	0.38
CTN-4	TPB	1	CyCl	3	DCM	6	>99	8.19	770	0.40
CTN-5	TPB	1	CyCl	4	DCM	6	>99	8.73	893	0.53
CTN-6	TPB	1	CyCl	5	DCM	6	>99	9.83	1004	0.63
CTN-7	TPB	1	CyCl	6	-	-	0	-	-	-
CTN-8	TPB	1	CyCl	1	MeOH	6	0	-	-	-
CTN-9	TPB	1	CyCl	1	EtOH	6	0	-	-	-
CTN-10	TPB	1	CyCl	1	^{i}PrOH	6	0	-	-	-
CTN-11	TPB	1	CyCl	1	EtOAc	6	0	-	-	-
CTN-1min (d)	TPB	1	CyCl	6	DCM	6	88	15.40	989	0.60
CTN-5min (d)	TPB	1	CyCl	6	DCM	6	81	18.64	1001	0.68
CTN-10min (d)	TPB	1	CyCl	6	DCM	6	89	15.51	862	0.51
CTN-30min (d)	TPB	1	CyCl	6	DCM	6	91	14.39	1086	0.73
CTN-BCMBP	BCMBP	1	CyCl	6	-	-	77	8.80	72	0.09
CTN-BP-1	BP	1	CyCl	6	-	-	0	-	-	-
CTN-BP-2	BP	1	CyCl	6	DCM	6	83	9.65	910	0.66
CTN-PPM-1	PP1 (e)	1	CyCl	6	DCM	6	80	24.52	1258	0.97
CTN-PPM-2	FC-DCM-1	1	CyCl	6	-	-	>99	9.40	765	0.45
CTN-PPM-3	FC-DCM-1	1	CyCl	6	DCM	6	87	11.93	1189	0.65
CTN-DCM-1	TPB	1	CyCl	6	DCM	1	>99	9.73	46	0.11
CTN-DCM-2	TPB	1	CyCl	6	DCM	2	>99	7.83	451	0.34
CTN-DCM-3	TPB	1	CyCl	6	DCM	3	>99	12.08	524	0.36
CTN-DCM-4	TPB	1	CyCl	6	DCM	4	>99	9.68	673	0.42

CTN-DCM-5	TPB	1	CyCl	6	DCM	5	94	12.66	1116	0.69
CTN-CHCl₃-1	TPB	1	CyCl	6	CHCl$_3$	1	65	20.62	590	0.47
CTN-CHCl₃-2	TPB	1	CyCl	6	CHCl$_3$	2	89	22.94	894	0.62
CTN-CHCl₃-3	TPB	1	CyCl	6	CHCl$_3$	3	89	36.58	1176	0.68
CTN-CHCl₃-4	TPB	1	CyCl	6	CHCl$_3$	4	83	62.04	1307	0.82
CTN-CHCl₃-5	TPB	1	CyCl	6	CHCl$_3$	5	87	65.65	1461	0.96
CTN-CHCl₃-6	TPB	1	CyCl	6	CHCl$_3$	6	81	82.01	1471	0.98
CTN-CCl₄-1	TPB	1	CyCl	6	CCl$_4$	1	90	83.03	572	0.37
CTN-CCl₄-2	TPB	1	CyCl	6	CCl$_4$	2	86	-	226	0.18
CTN-CCl₄-3	TPB	1	CyCl	6	CCl$_4$	3	92	-	92	0.09
CTN-CCl₄-4	TPB	1	CyCl	6	CCl$_4$	4	94	-	117	0.10
CTN-CCl₄-5	TPB	1	CyCl	6	CCl$_4$	5	197 (f)	16.75	0	0.00
CTN-CCl₄-6	TPB	1	CyCl	6	CCl$_4$	6	236 (f)	53.3	0	0.00
CTN-C₂H₂Cl₄	TPB	1	CyCl	6	C$_2$H$_2$Cl$_4$	6	13	12.94	72	0.12
CTN-DCD	TPB	1	DCD	6	DCM	6	78	75.23	1161	0.88
CTN-DCY	TPB	1	DCY	6	DCM	6	>99	11.60	734	0.43
CTN-DCP	TPB	1	DCP	6	DCM	6	86	40.71	1518	1.05
CTN-BZ	BZ	1	CyCl	6	DCM	6	61	8.12	457	0.23
CTN-BP	BP	1	CyCl	6	DCM	6	83	9.65	910	0.66
CTN-TP	TP	1	CyCl	6	DCM	6	81	13.49	858	0.65
CTN-TTC	TTC	1	CyCl	6	DCM	6	>99	13.62	1502	0.91

(a) Substitution of 24 eq AlCl$_3$ with 24 eq FeCl$_3$
(b) Substitution of 24 eq AlCl$_3$ with 24 eq SnCl$_2$, the low C/N ratio is due to a low amount of carbon in a highly Sn and O contaminated product
(c) Substitution of 24 eq AlCl$_3$ with 12 eq AlCl$_3$
(d) Variation of reaction time according to polymer name
(e) Porous Polymer 1 (**PP1**) synthesized by a literature protocol according to reference[42]
(f) Yield of >100% due to incorporation of node in the pores of a very rigid polymer, accompanied by >1 m^2/g SSA$_{BET}$
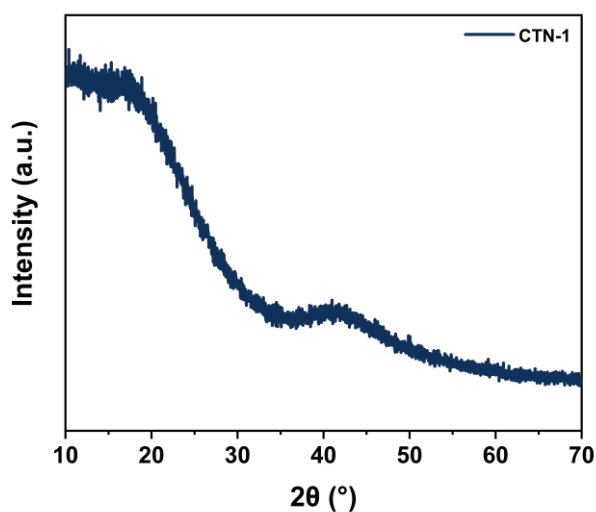
3. Characterization

Figure S1. X-ray diffraction (XRD) pattern of **CTN-1** revealing the amorphous nature of the polymer.

Table S2. Calculated and found elemental compositions in at.% and the respective C/N ratios for **CTN-1** and **FC-DCM-1**. The values were measured by X-ray photoelectron spectroscopy (XPS), therefore no hydrogen is present.

Polymer	Calculated (at.%)					Found (at.%)				
	C	N	O	Cl	C/N ratio	C	N	O	Cl	C/N ratio
CTN-1	91.7	8.3	-	-	11.05	85.6	7.6	3.4	3.4	11.26
FC-DCM-1	100.0	-	-	-	-	96.4	-	3.2	0.4	-

5
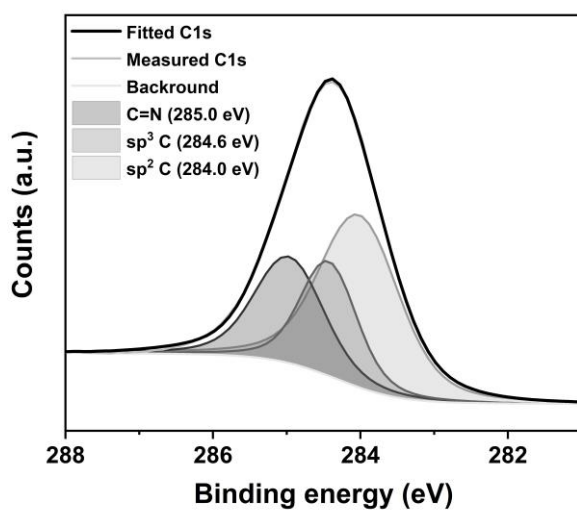
Figure S2. C1s XPS spectrum of **CTN-1** revealing three different carbon species inside the polymer, which can be attributed to the carbon atoms of the triazine node (dark grey, at 285.0 eV), to sp^3 hybridized carbon of the C1 bridge (medium grey, at 284.6 eV) and to sp^2 hybridized carbon of the aromatic rings (light grey, at 284.0 eV).
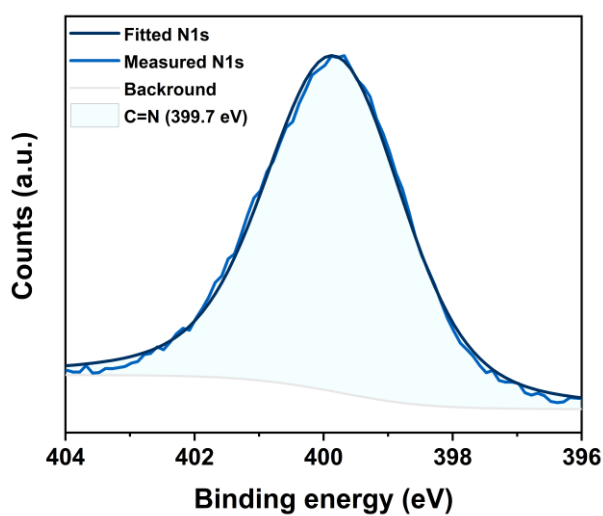
Figure S3. N1s XPS spectrum of **CTN-1** revealing one nitrogen species inside the polymer, which is attributed to the nitrogen atoms of the triazine node (light blue, at 399.7 eV).
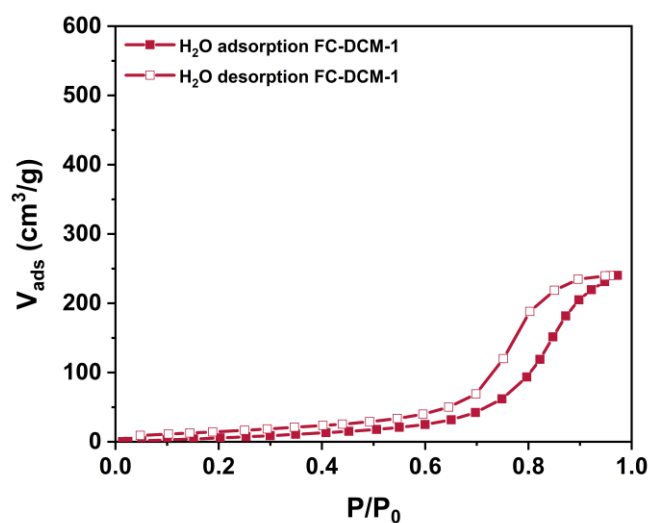
Figure S4. Water adsorption (full squares) and desorption (empty squares) of the reference polymer **FC-DCM-1** containing no nitrogen.
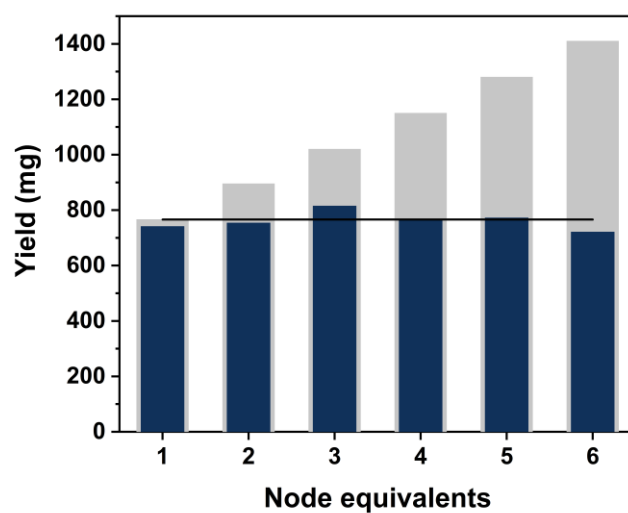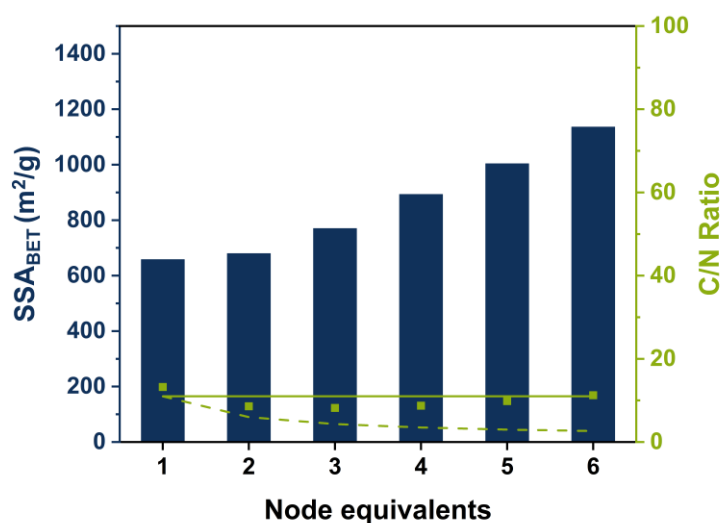

Figure S5. Determination of the amount of the node cyanuric chloride incorporated into the final **CTN** for different amounts of node utilized during synthesis, while other reaction parameters are kept constant. Gray bars: Theoretical yield of the respective polymer if all node equivalents are incorporated; Black solid line: Theoretical yield of the respective polymer if one node equivalent is incorporated; Blue bars: Measured yield of **CTN**s. The measured yields are in accordance with the theoretical yield for only one equivalent of node build into the polymer (independent on the amount of node utilized during synthesis).

Figure S6. Determination of the amount of the node cyanuric chloride incorporated into the final **CTN** for different amounts of node utilized during synthesis, while other reaction parameters are kept constant. Green dashed line: Theoretical C/N ratio of the respective polymer if all node equivalents are incorporated; Green solid line: Theoretical C/N ratio of the respective polymer if one node equivalent is incorporated; Green squares: Measured C/N ratios; Blue bars: Specific surface areas (SSA$_{BET}$) of **CTN**s. Since the measured C/N ratios are in accordance with the theoretical C/N ratio for only one equivalent of node build into the polymer (independent on the amount of node utilized during synthesis), but a higher amount of node results in a higher SSA$_{BET}$ of the polymer, the excess cyanuric chloride was found to serve as a porogen during the polymerization, which is removed during the workup.
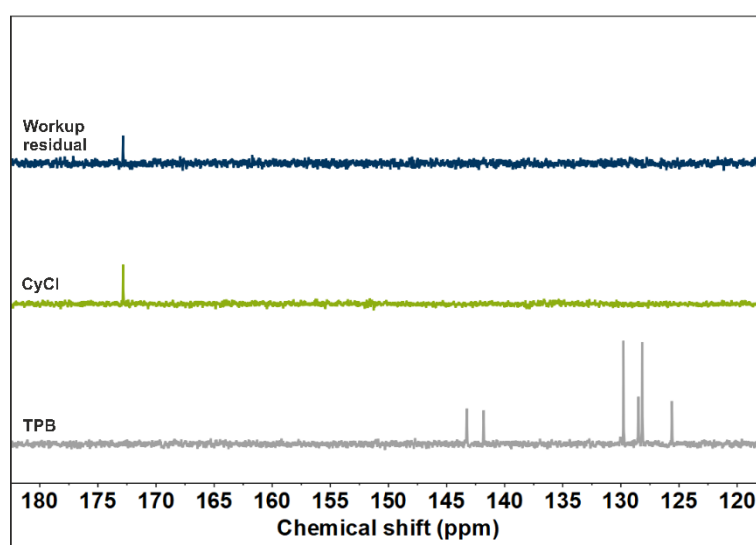
Figure S7. ^{13}C-NMR (200 MHz, Acetone-d$_6$) of the workup residual of **CTN-1** found after removing the volatiles of the organic phase under reduced pressure (blue) in comparison to the node cyanuric chloride (green) and the monomer 1,3,5-triphenylbenzene (grey). After the workup, the unreacted equivalents CyCl are washed out by the acetone rinse, while the TPB is completely incorporated in the polymer. The ^{13}C-NMR of the water phase neither contained CyCl nor TPB.
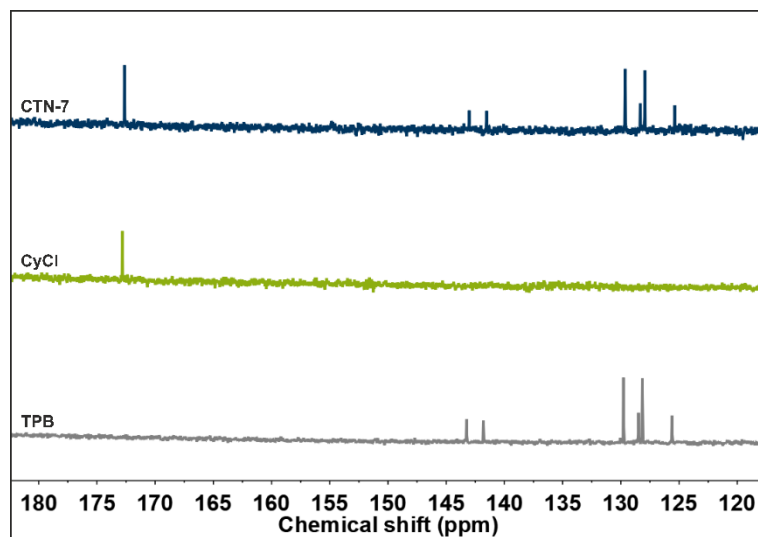
Figure S8. ^{13}C-NMR (200 MHz, Acetone-d$_6$) of **CTN-7** (blue) before workup in comparison to the node cyanuric chloride (green) and the monomer 1,3,5-triphenylbenzene (grey), showing no formation of a soluble polymer.
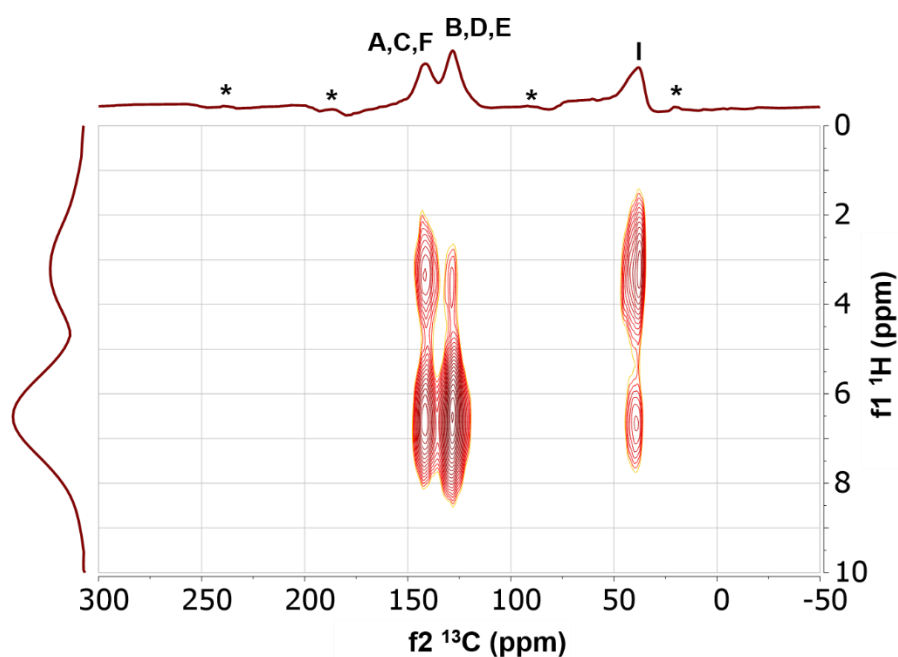

Figure S9. ^{1}H→^{13}C FSLG HETCOR TOSS spectrum of **CTN-1** recorded at 8 kHz spinning at 14 T. Signals marked with * are residues of the spinning sidebands suppressed by the TOSS sequence. The ^{1}H→^{13}C FSLG HETCOR TOSS spectrum of **CTN-1** was recorded to look on proximities between protons and carbons in the polymer. Next to the cross-peaks of the aromatic carbons (signals A-E in the ^{13}C dimension) with aromatic protons (at 6.5 ppm in the ^{1}H dimension) and the cross-peaks of the aliphatic carbons (signal I) with aliphatic protons (at 3-3.5 ppm) there are additional cross-peaks visible with lower intensity. These cross-peaks of the aromatic carbons (signals A-E in the ^{13}C dimension) with aliphatic protons (at 3-3.5 ppm) and cross-peaks of the aliphatic carbons (signal I) with aromatic protons (at 6.5 ppm in the ^{1}H dimension), which are obtained at a relatively short contact time of 0.5 ms, clearly show the close proximity between aliphatic and aromatic moieties in the polymer. This confirms the incorporation of DCM in the polymer.
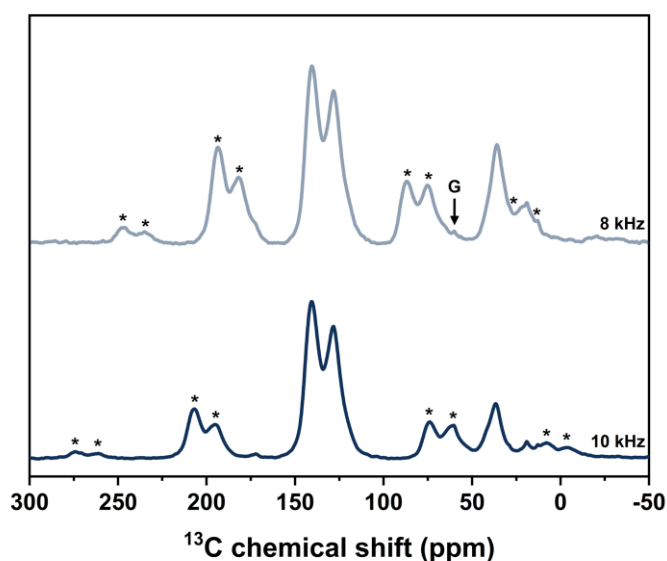
Figure S10. $^1H \rightarrow {}^{13}C$ CP MAS spectra of **CTN-1** recorded at 8 kHz (top; light blue) and at 10 kHz (bottom, dark blue) spinning. The lower spinning frequency at 8 kHz results in a shift of the spinning sidebands (marked with asterisks), allowing to observe signal G, which is masked at a spinning of 10 kHz.

Equation S1. Calculation of the E-factor of the solvent-based CTN synthesis[37] and of the mechanochemical CTN synthesis. While the solution-based reaction required a workup in DCM, methanol and water, the mechanochemical product was only shortly rinsed with water and acetone, minimizing the ecological impact further. However, as usually the solvents are reused and don't count as waste, the calculation is accomplished without the work up.

$$E - factor = \frac{total\ waste\ mass}{product\ mass}$$

- Solvent-based CTN synthesis[37]:
  - DCM: m = 133 g (100 ml)
  - TPB: m = 2.45 g
  - CyCl: m = 1.48 g
  - AlCl$_3$:   m = 3.00 g
  - Polymer: m = 2.71 g (88% yield)

$$E - factor = \frac{m(DCM) + m(AlCl_3)}{m(Polymer)} = \frac{133\ g + 3.00\ g}{2.71\ g} = \mathbf{50.18}$$

- Mechanochemical CTN synthesis:
  - DCM: m = 0.83 g (0.63 ml)
  - TPB: m = 0.50 g
  - CyCl: m = 1.81 g (1.50 g (5eq) waste, as 1 eq is incorporated)
  - AlCl$_3$:   m = 5.22 g
  - Polymer: m = 0.72 g (95% yield)

$$E - factor = \frac{m(CyCl) + m(AlCl_3)}{m(Polymer)} = \frac{1.50\ g + 5.22\ g}{0.72\ g} = \mathbf{9.33}$$
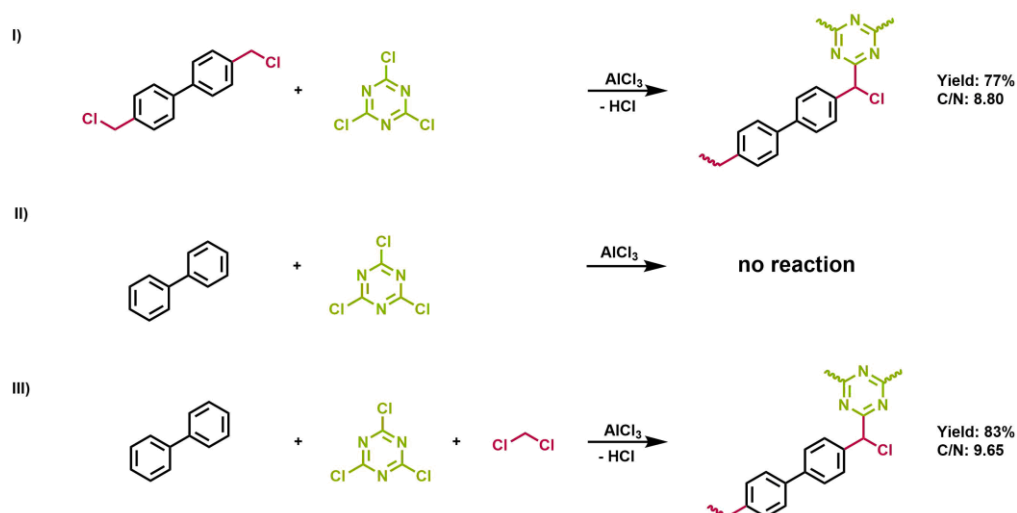
Figure S11. Model reactions proving linkage over C1 moiety. I) The reaction of cyanuric chloride and the monomer 4,4'bis(chloromethyl)1,1'biphenyl (BCMBP), already exhibiting the C1 linker, leads to the formation of nitrogen-containing polymers without the addition of DCM (**CTN-BCMBP**). II) The same reaction utilizing biphenyl (BP) as the monomer, not exhibiting C1 linker, results in no reaction (**CTN-BP-1**). III) The addition of DCM to II) again leads to the formation of a nitrogen-containing polymer (**CTN-BP-2**).
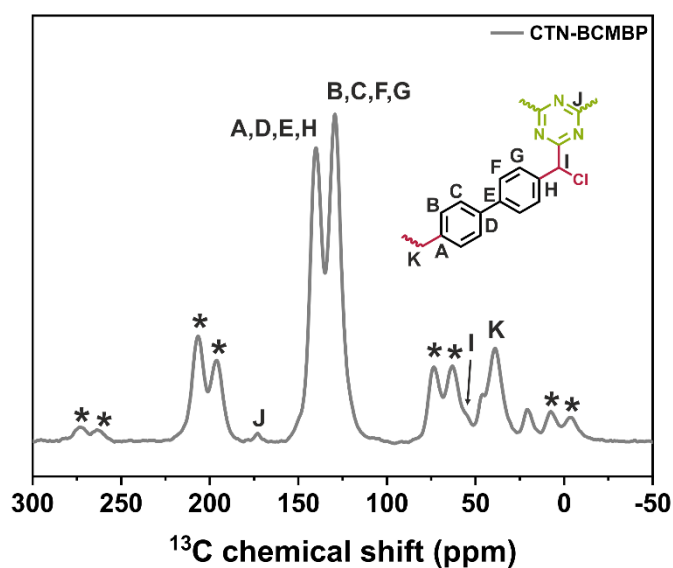
Figure S12. $^1H \rightarrow ^{13}C$ CP MAS spectrum of the model compound **CTN-BCMBP** recorded at 10 kHz spinning. The peaks are labelled as A-K and are assigned to the model structure. Signal I is masked by a spinning sideband, which are marked with asterisks. Observing the signals I and K underlines the formation of CHCl (I) and CH_2 (K) moieties by C1 bridge formation even for a synthesis carried out with a monomer already exhibiting the C1 linker and without the further addition of DCM.
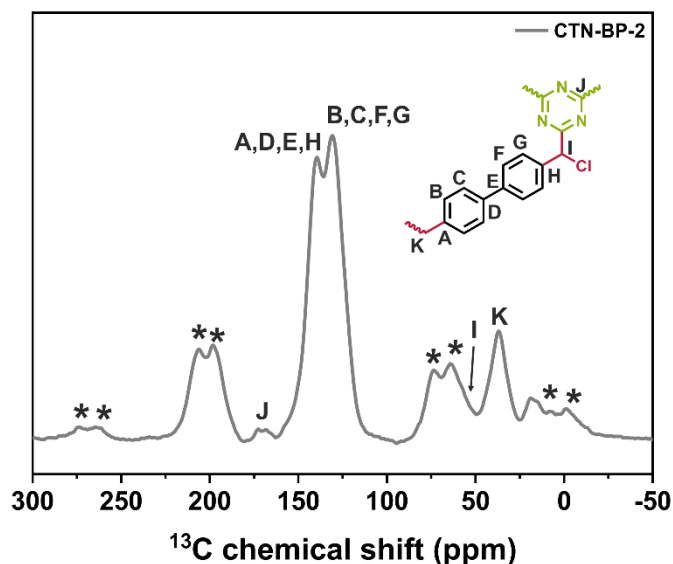

Figure S13. $^1H \rightarrow ^{13}C$ CP MAS spectrum of the model compound **CTN-BP-2** recorded at 10 kHz spinning. The peaks are labelled as A-K and are assigned to the model structure. Signal I is masked by a spinning sideband, which are marked with asterisks. Observing the signals I and K underlines the formation of CHCl (I) and CH_2 (K) moieties by C1 bridge formation for a synthesis carried without a monomer exhibiting the C1 linker, solely by the addition of DCM. Please note the high resemblance between the $^1H \rightarrow ^{13}C$ CP MAS spectra of **CTN-BCMBP** and of **CTN-BP-2**, showing the formation of two similar polymers by two different synthesis routes.
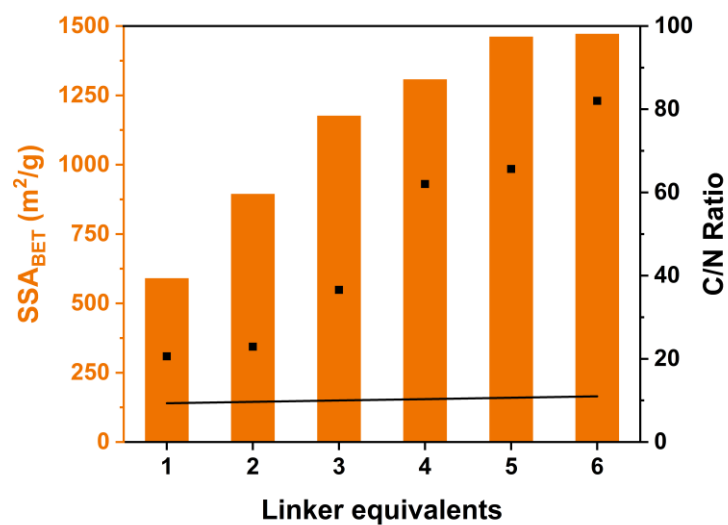
Figure S14. Dependency of SSA$_{BET}$ (orange bars) and C/N ratio (black squares) on the addition of different equivalents of CHCl$_3$ to the reaction mixture (1 eq TPB, 6 eq CyCl and 24 eq AlCl$_3$). The black solid line indicates the theoretical C/N ratio for each sample.
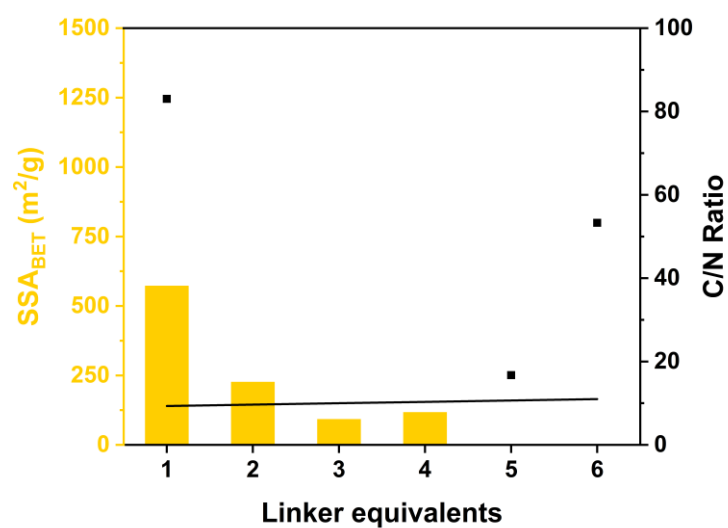

Figure S15. Dependency of SSA$_{BET}$ (yellow bars) and C/N ratio (black squares) on the addition of different equivalents of CCl$_4$ to the reaction mixture (1 eq TPB, 6 eq CyCl and 24 eq AlCl$_3$). For the addition of 2-4 eq of CCl$_4$, no nitrogen was detected in the sample. The black solid line indicates the theoretical C/N ratio for each sample.