- Supplementary information -

Phosphorylated chitin and cellulose nanocrystals as colloidal bio-templates towards mesoporous aluminophosphates

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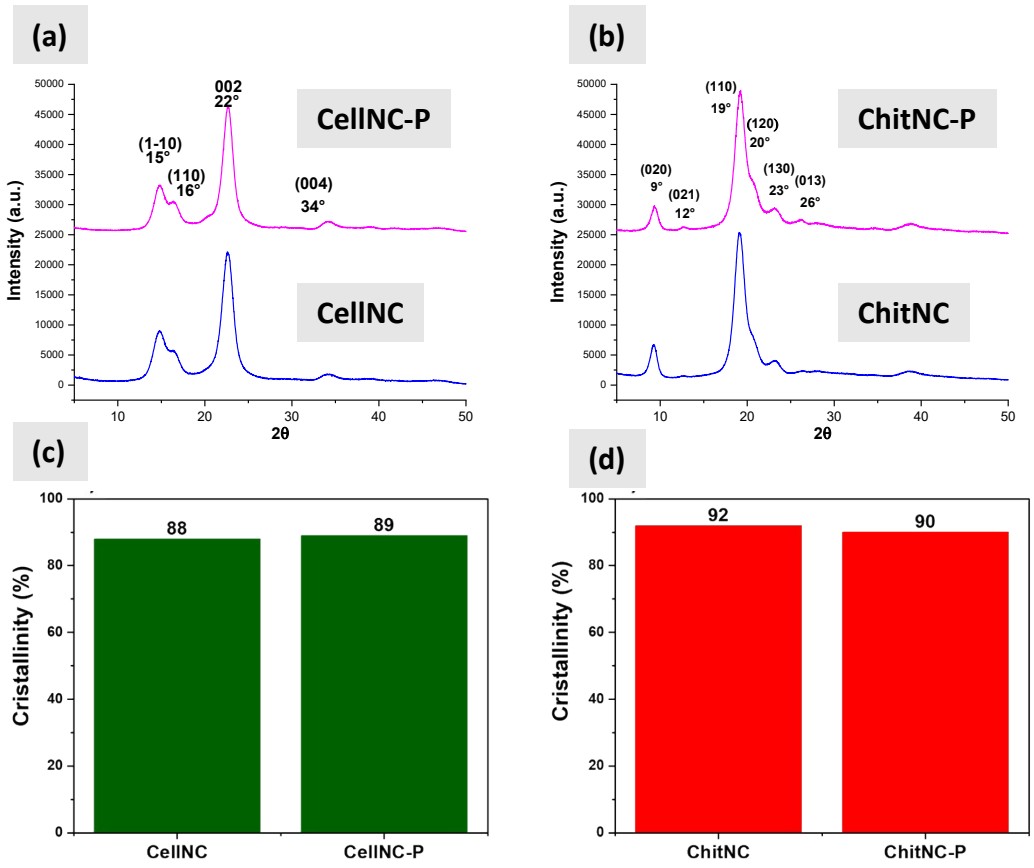

Fig. S1. X-ray diffractogram of phosphorylated polysaccharides for cellulose (a) (CellNC and CellNC-P) and chitin (b) (ChitNC and ChitNC-P). Crystallinity index values of cellulose (c) and chitin (d) before and after phosphorylation.

Crystallinity indexes were calculated using empirical formula proposed in the literature for cellulose and for chitin. They are based on the intensity ratio between specific diffraction peaks d(002) (2θ= 22°) for cellulose[1], d(110) (19.3°) for chitin[2], and amorphous diffusion at 2θ= 18° and 16°, respectively.

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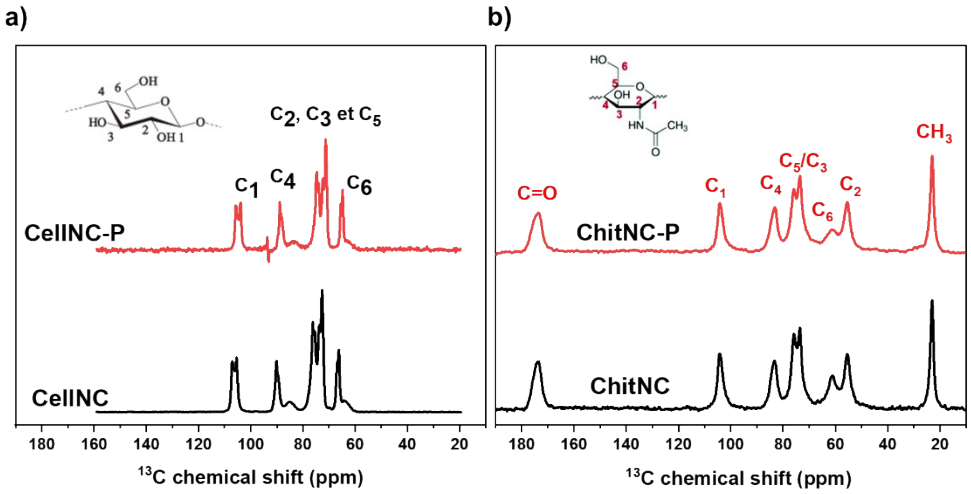

Fig. S2. ^{13}C solid state NMR spectra of polysaccharide nanocrystals before and after phosphorylation.

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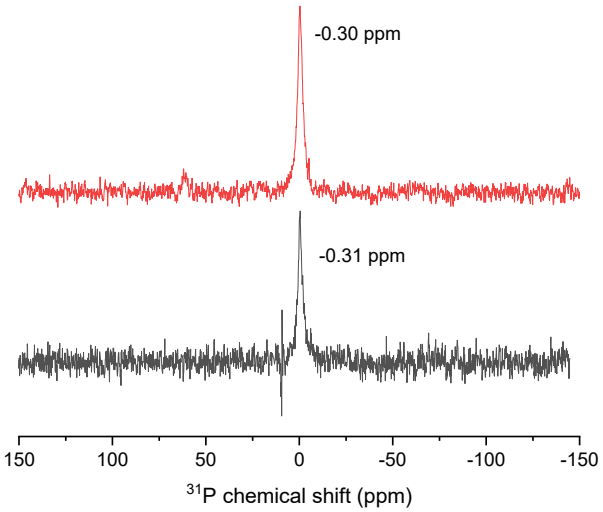

Fig. S3. ^{31}P solid-state NMR spectra for CellNC-P (black, bottom) and ChitNC-P (red, top)

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Table S1. EDX and XPS analysis of chitin and cellulose nanocrystals before and after phosphorylation

	ChitNC				**ChitNC-P**			
Element atom. % / ratio	**Exp[al] EDX**		**Exp[al] XPS**	Calculated	**Exp[al] EDX**		**Exp[al] XPS**	Calculated
	Mean ± SD (n=5)	SD		DA 80%	Mean ± SD (n=5)	SD		DA80% +0.35P
C	**64.7**	**1.3**	**60.2**	56.7	**61.6**	**4.3**	**54.9**	51.4
N	**10.4**	**0.6**	**6.5**	7.5	**8.1**	**1.8**	**6.2**	6.8
O	**24.9**	**1.1**	**33.0**	35.8	**28.1**	**2.9**	**35.1**	39.5
Cl							**1.3**	
C/O	**2.6**	**0.2**	**1.8**	1.6	**2.2**	**0.4**	**1.6**	1.3
C/N	**6.2**	**0.4**	**9.2**	7.6	**8.1**	**2.4**	**8.8**	7.6
O/N	**2.4**	**0.2**	**5.0**	4.8	**3.6**	**1.0**	**5.6**	5.9
P					**2.2**	**1.4**	**2.5**	2.4
P/C					**0,04**	**0,02**	**0.04**	0.05
P/O					**0.08**	**0.05**	**0.07**	0.06
P/N					**0.40**	**0.13**	**0.39**	0.35

	CellNC				**CellNC-P**			
Element atom. % / ratio	**Exp[al] EDX**		**Exp[al] XPS**	Calculated	**Exp[al] EDX**		**Exp[al] XPS**	Calculated [#]
	Mean ± SD	SD			Mean ± SD	SD		+0.35P
C	**70.1**	**1.5**	**57.9**	53.7	**64.8**	**4.7**	**55.0**	47.6
O	**29.4**	**1.6**	**41.8**	45.9	**34.0**	**4.4**	**40.9**	49.2
S	**0.45**	**0.05**	**0.35**	0.40	**0.19**	**0.04**	**0.40**	0.40
Cl							**0.9**	
C/O	**2.4**	**0.2**	**1.4**	1.2	**1.94**	**0.37**	**1.34**	0.97
S/C	**0.0065**	**0.0006**	**0.0060**	0.0075	**0.0029**	**0.0007**	**0.0073**	0.0084
S/O	**0.0155**	**0.0023**	**0.0084**	0.0087	**0.0056**	**0.0016**	**0.0097**	0.0081
P					**0.95**	**0.53**	**2.8**	2. 8
P/C					**0.02**	**0.01**	**0.05**	0.06
P/O					**0.03**	**0.01**	**0.07**	0.06

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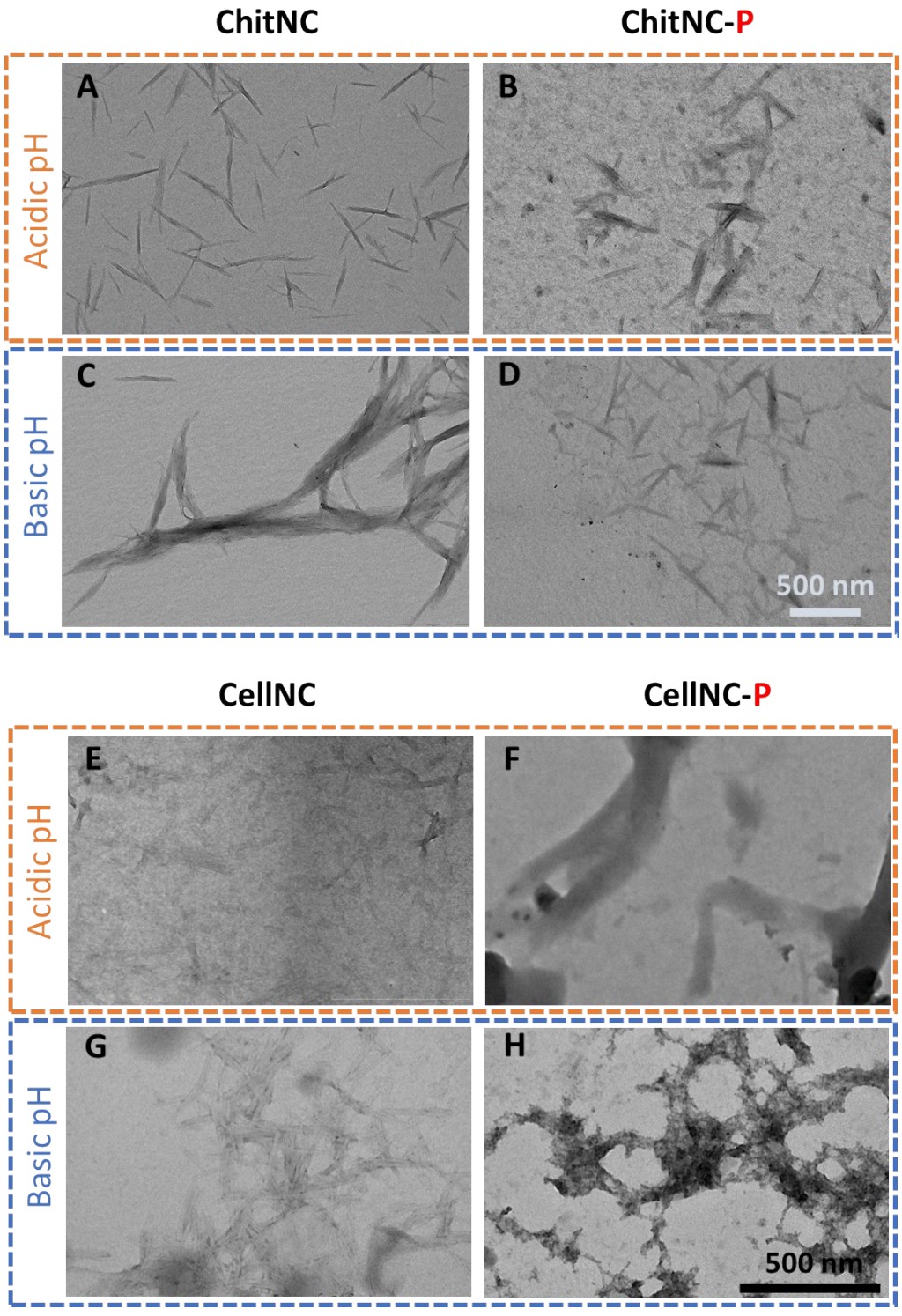

Fig. S4. TEM observations of chitin and cellulose nanocrystals before and after phosphorylation. The acidic and basic pH of the suspensions are as follows: ChitNC: 4.1 (A) and 9.1 (C); ChitNC-P: 4.5 (B) and 9.4 (D), CellNC: 3 (E) and 12 (G); CellNC-P: 3 (F) and 12 (H). Dilute suspensions (0.01 wt%) were deposited on TEM grids (Carbon / Formvar coated) and allowed to dry before imaging. Observations were performed on a JEOL 1200 EX2 microscope operating at 100 kV.

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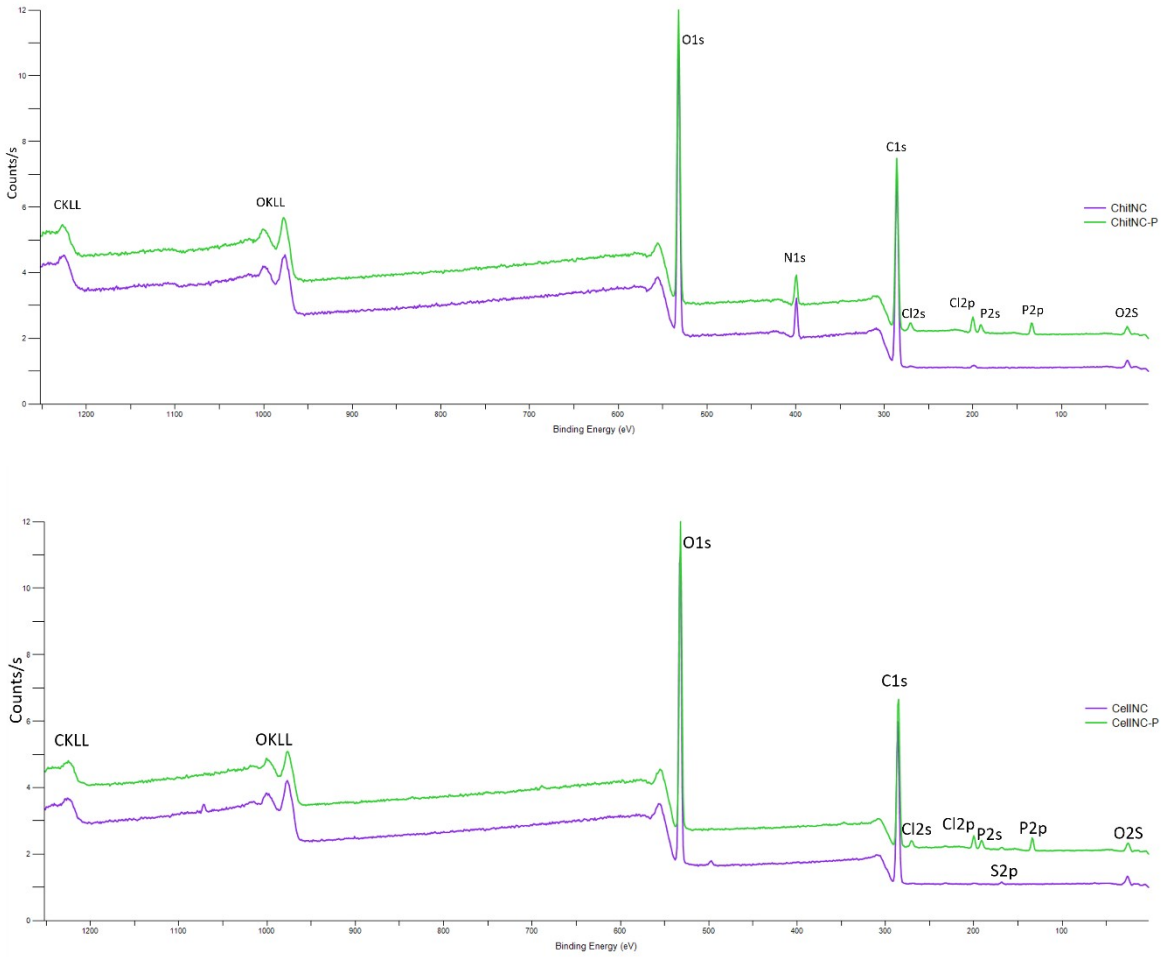

Fig. S5. XPS survey spectra for ChitNC, ChitNC-P, CellNC and CellNC-P.

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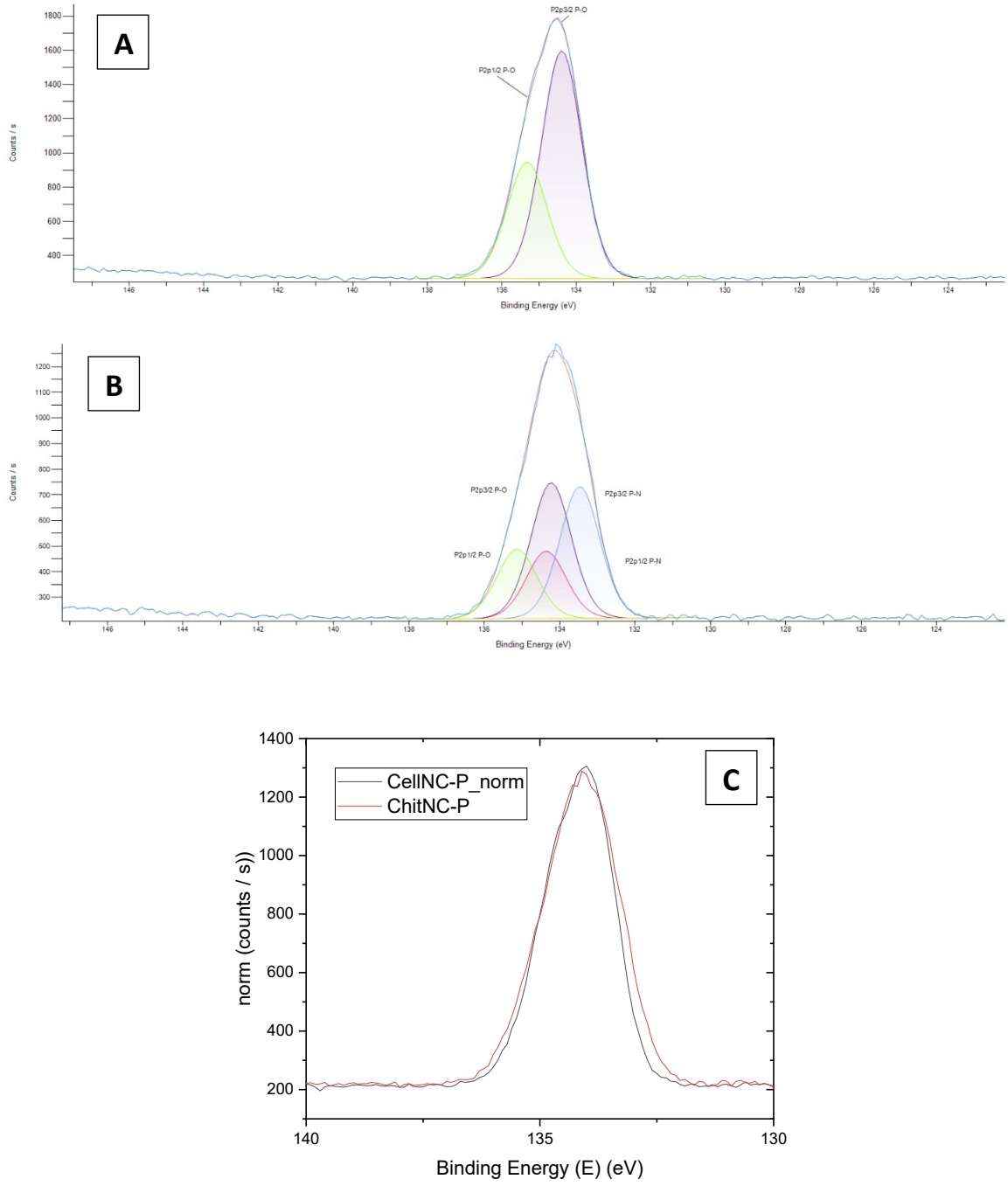

Fig. S6. P-O bonds (or components) (134.2 ±0.2 eV) and P-N bonds (133.5 ±0.2 eV) of P 2p XPS spectra deconvolution for phosphorylated nanoparticles CellNC-P (A) and ChitNC-P (B), and blow-up of superimposed spectra (C).

8.

Table S2. EDX analysis of spray dried hybrid materials obtained with chitin and cellulose nanocrystals phosphorylated or not, and associated with Al_{13} clusters.

	ChitNC-Al13		ChitNC-P-Al13			CellNC-Al13		CellNC-P-Al13	
	atom. %	**±SD**	**atom. %**	**±SD**		**atom. %**	**±SD**	**atom. %**	**±SD**
C	43.5	4.8	48.2	3.3	C	43.50	4.93	49.00	10.42
O	42.1	4.5	37.5	3.6	O	44.42	3.68	41.49	6.80
N	4.7	0.9	2.9	0.4	S	0.55	0.24	0.23	0.12
P			2.3	1.5	P			0.53	0.16
Al	9.6	1.6	9.1	2.6	Al	11.53	3.17	8.76	3.79
	mol ratio	**±SD**	**mol ratio**	**±SD**		**mol ratio**	**±SD**	**mol ratio**	**±SD**
C/O	1.1	0.2	1.30	0.18	C/O	1.0	0.2	1.2	0.5
C/N	9.3	1.0	16.6	2.1	S/C	0.013	0.006	0.005	0.003
O/N	9.2	2.2	12.9	1.8	S/O	0.014	0.005	0.005	0.003
P/C			0.05	0.03	P/C			0.012	0.005
P/O			0.06	0.04	P/O			0.013	0.003
P/N			0.83	0.62	P/S			2.8	1.2
Al/C	0.22	0.05	0.19	0.06	Al/C	0.27	0.09	0.20	0.11
Al/P			5.1	2.1	Al/P			16.5	5.7
Al/N	2.1	0.6	3.3	1.4	Al/S	22.5	5.3	41.3	11.4
Al/O	0.23	0.04	0.25	0.08	Al/O	0.26	0.08	0.20	0.07

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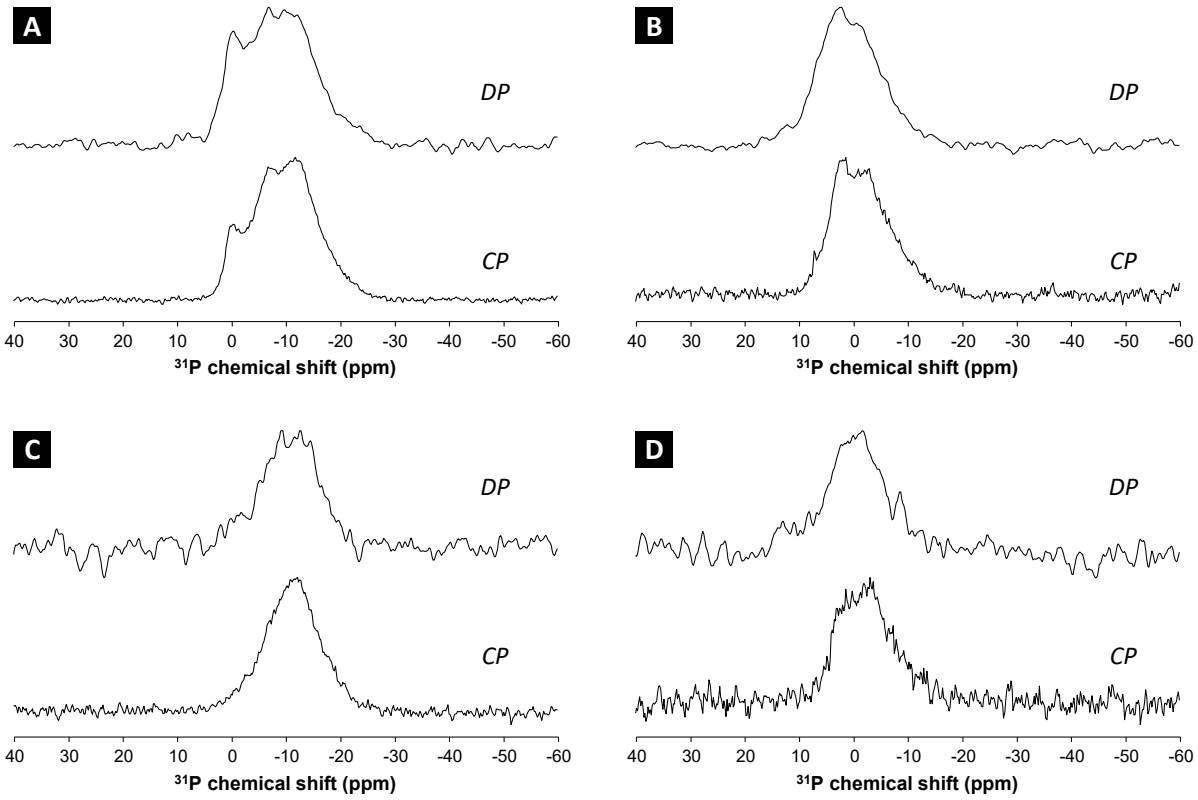

Fig. S7. ^{31}P direct polarization (DP) or $^{31}P\{^{1}H\}$ cross-polarization (CP) MAS NMR spectra of hybrid (A,C) and calcined (B,D) spray-dried samples from phosphorylated chitin (A,B) and cellulose (C,D) nanocrystals. The $^{31}P\{^{1}H\}$ CP-MAS spectra were obtained using a contact time of 2 ms and acquiring 256 scans. The ^{31}P DP-MAS spectra were obtained using a recycling delay of 30 s and acquiring 32 scans.

10. ^{27}Al NMR spectrum fitting procedure for the calcined sample

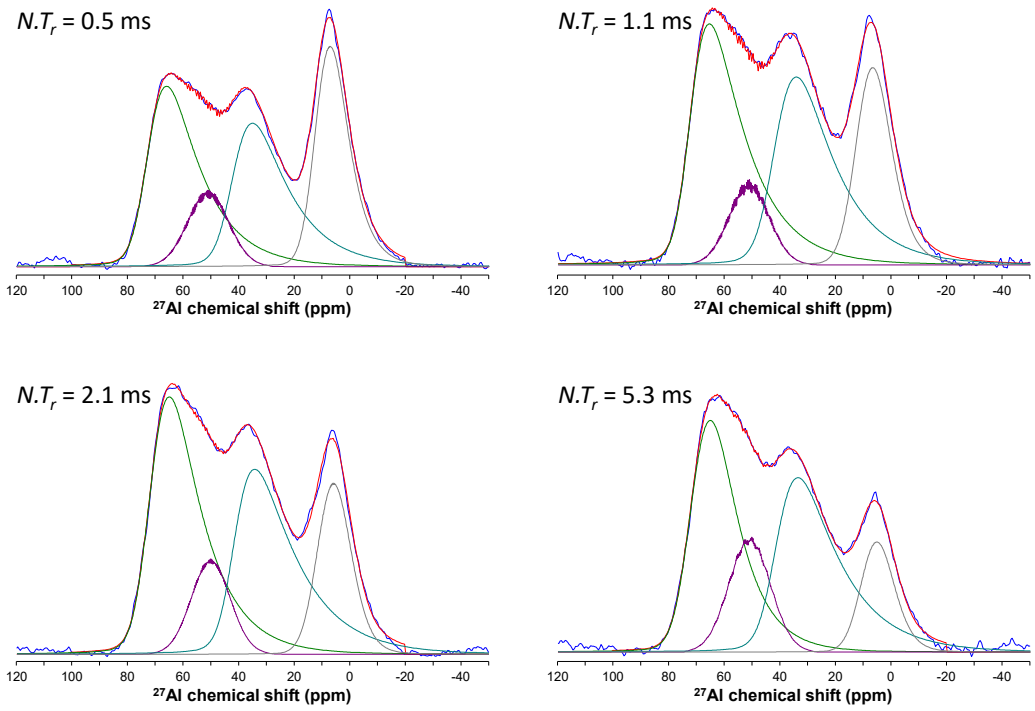

Fig. S8. The ^{27}Al solid-state MAS NMR spectra of the calcined ChitNC-P@Al_{13} have been fitted using a mathematical function that describes the distribution in the quadrupolar coupling parameters and the related electric field gradient through the Czjzeck model.[3,4] This function is incorporated in the *Dmfit* software.[5,6] We used the model "CzSimple" that implements a rapid version of the Czjzek distribution of quadrupolar interaction for the distribution of the isotropic chemical shift (Gaussian Isotropic Model) with an uncoupled distribution of isotropic chemical shift.[7,8] In this model, C_Q is the quadrupolar coupling constant of the Czjzek/GIM distribution, and FWHM CS is the full width at half maximum of the isotropic chemical shift gaussian distribution. A minimum of four Czjzeck functions are necessary to fit correctly the ^{27}Al spectra. For all the spectra obtained in the ^{27}Al{^{31}P} REDOR experiment without ^{31}P irradiation, the NMR parameters of four Czjzeck functions were optimized by a free evolution during the least-square fits. The figure shows the results obtained for ^{27}Al spectra obtained at different dephasing times *N.T*$_r$. The main values of the NMR parameters with their standard deviations (STD) are presented in the table below. These values were considered for the final fits of all ^{27}Al spectra in the REDOR analysis without further optimization of parameters excepting the amplitude.

Function n°	δ_{iso} (ppm)	STD (ppm)	FWHM CS (ppm)	STD (ppm)	C_Q (kHz)	STD (kHz)
1	73.0	0.8	11	0.7	7000	590
2	51.7	0.2	16	3.4	1700	510
3	42.0	0.5	12	2.3	6500	1500
4	10.3	1.1	11	1.8	4300	540

References

1 L. Segal, J. J. Creely, A. E. Martin and C. M. Conrad, *Textile Res. J.*, 1959, **29**, 786–794.

2 M. Wang, H. Xue, Z. Feng, B. Cheng and H. Yang, *PLOS ONE*, 2017, **12**, e0177673.

3 J.-B. d'Espinose de Lacaillerie, C. Fretigny and D. Massiot, *J. Magn. Reson.*, 2008, **192**, 244–251.

4 G. Le Caër and R. A. Brand, *J. Phys.: Condens. Matter*, 1998, **10**, 10715.

5 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calve, B. Alonso, J. O. Durand, B. Bujoli, Z. H. Gan and G. Hoatson, *Magn. Reson. Chem.*, 2002, **40**, 70–76.

6 *Dmfit* software: https://nmr.cemhti.cnrs-orleans.fr/Dmfit/help/Models/Default.aspx.

7 D. R. Neuville, L. Cormier and D. Massiot, *Geochim. Cosmochim. Acta*, 2004, **68**, 5071–5079.