

## Electronic Supplementary Information

# Cyanosilylation of Aldehydes Catalyzed by Ag(I)- and Cu(II)-Arylhydrazone Coordination Polymers in Conventional and in Ionic Liquid Media

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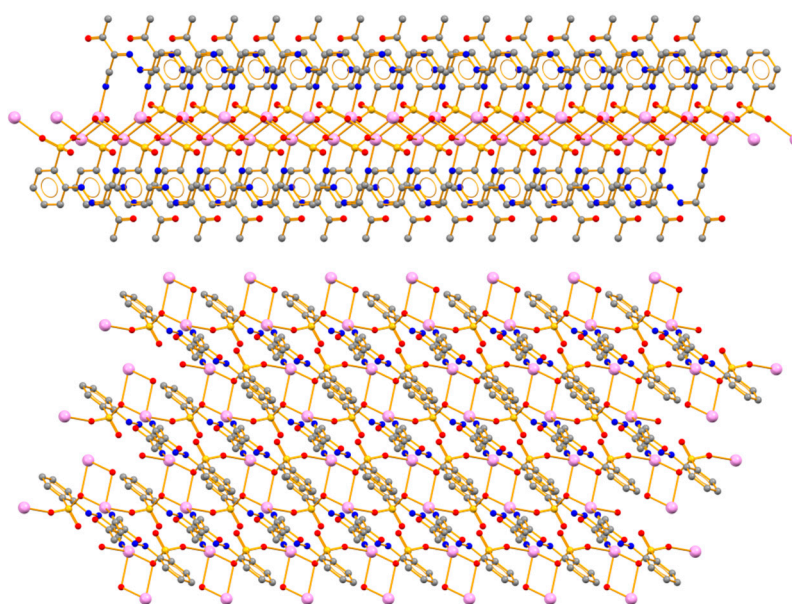
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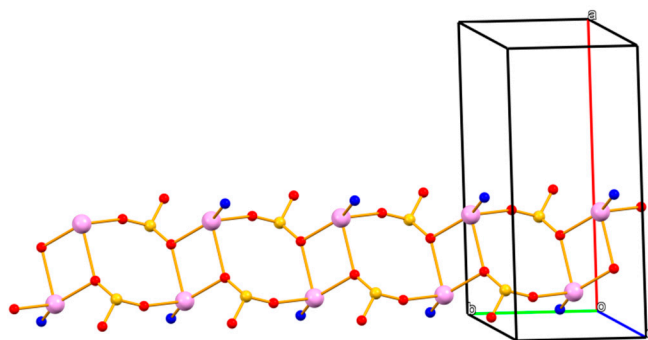
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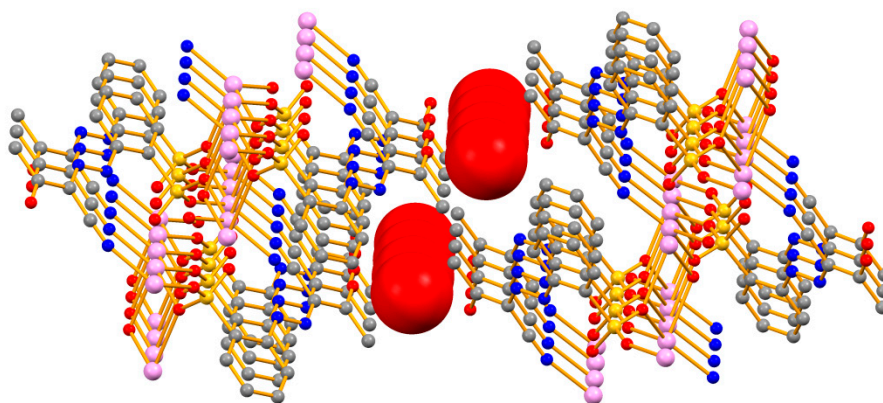
## 1. X-ray analyses



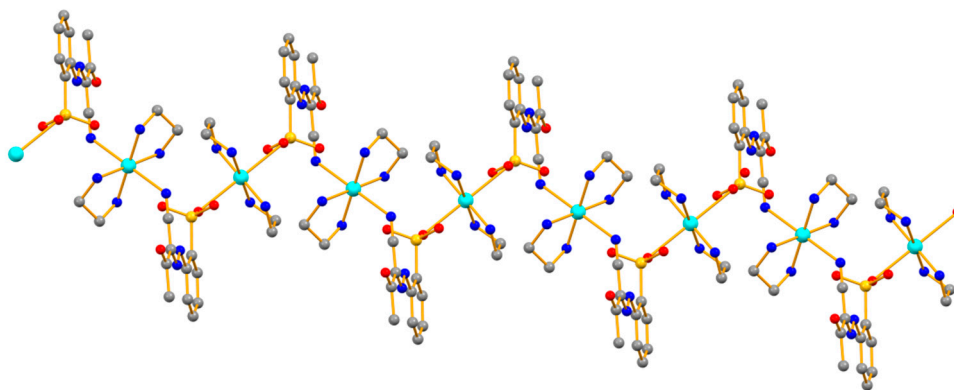
**Figure S1.** Fragments of the 2D network in compound **1** viewed (top) down the crystallographic *a* axis, and (bottom) perpendicular to the *ab* plane (90° flipped).



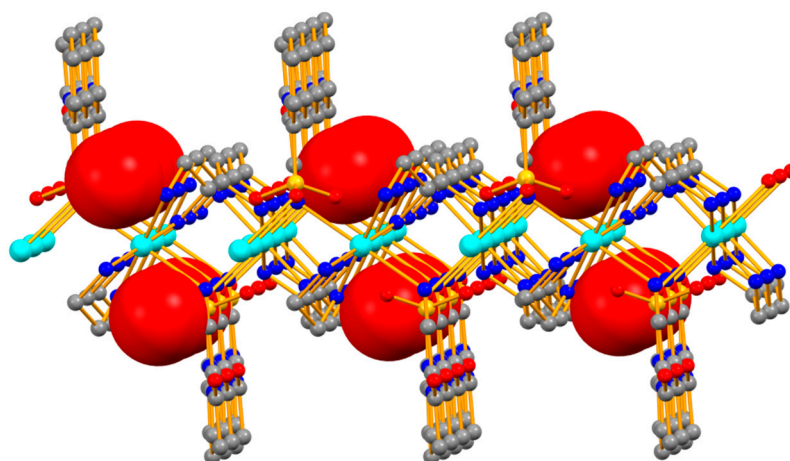
**Figure S2.** Fragment of a 1D infinite chain in compound 1 to highlight the side-sharing  $\{AgO\}_2$  and  $\{AgO_2S\}_2$  metallacycles. The non-coordinated atoms from the ligands are omitted for clarity.



**Figure S3.** Fragment of two 2D sheets of polymer 1 with intercalated water molecules (represented in space filling model).



**Figure S4.** Fragments of the 1D chain in compound 2 viewed perpendicular to the  $ab$  plane.



**Figure S5.** Fragment of chains of polymer **2** with intercalated water molecules (represented in space filling model).

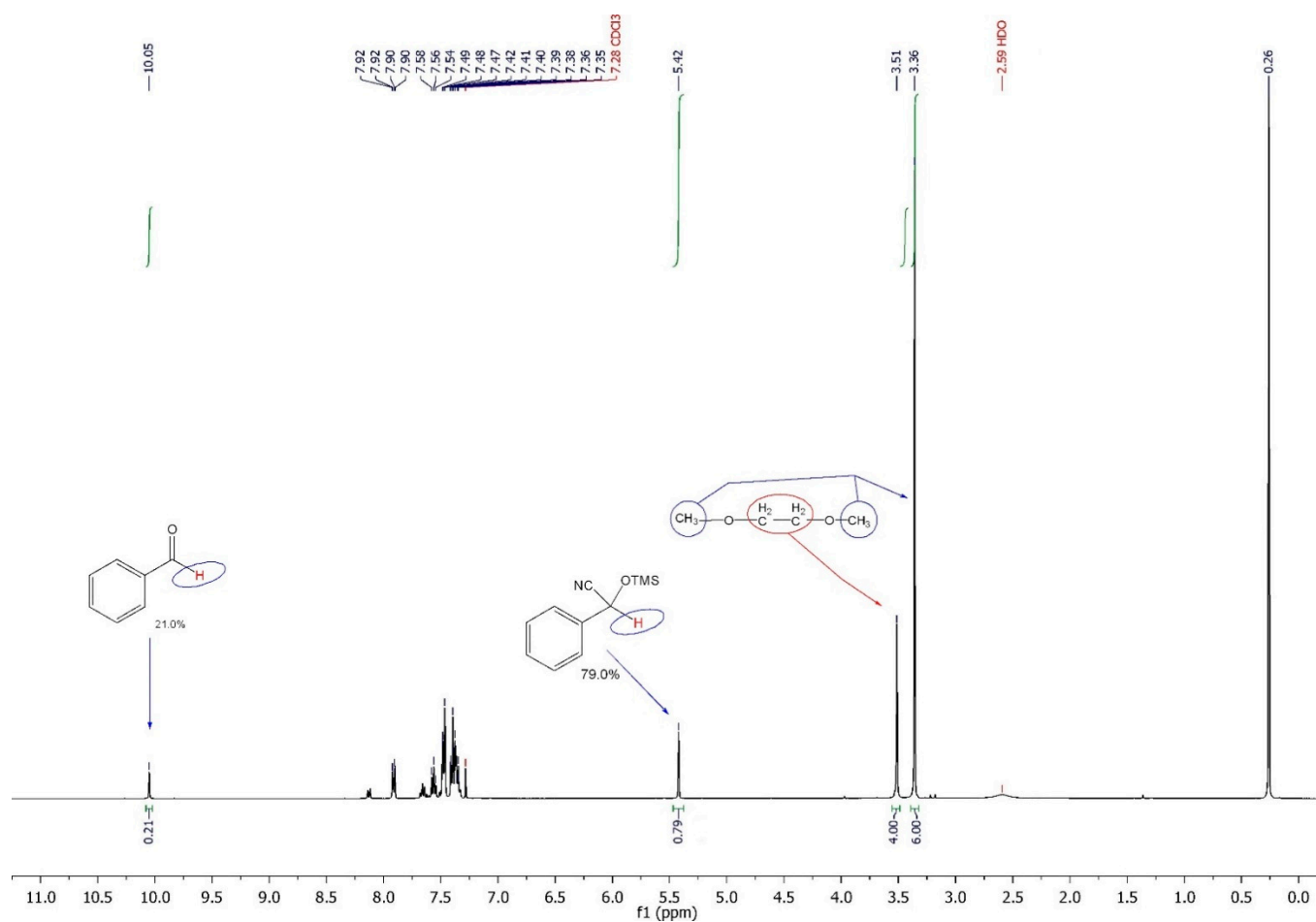
**Table S1.** Hydrogen bonding distances (Å) and angles (°) for **1** and **2**.<sup>a</sup>

D-H...A	D-H	H...A	D...A	D-H...A	Symmetry operation
<b>1</b>					
N1-H1N...O1	0.82(10)	1.89(10)	2.673(8)	158(11)	<i>intra</i>
N5-H5O...O4	0.94(10)	1.90(10)	2.829(9)	166(10)	<i>x,-1+y,z</i>
<b>2</b>					
O1-H1W...O4	0.89(2)	1.86(2)	2.748(9)	177(9)	<i>x,y,1+z</i>
O1-H2W...O3	0.90(2)	1.95(3)	2.825(9)	164(9)	<i>-x,-y,-z</i>
N4-H4A...O2	0.89(2)	2.41(5)	3.229(9)	152(8)	<i>-1+x,y,z</i>
N4-H4B...O1	0.90(2)	2.19(6)	2.952(9)	142(8)	<i>intra</i>
N5-H5A...O1W	0.90(2)	2.15(4)	3.000(10)	158(9)	<i>x,y,-1+z</i>
N5-H5B...O1	0.92(2)	2.33(7)	3.029(9)	133(8)	<i>-x,-y,-z</i>
N6-H6A...O1	0.90(2)	2.23(7)	2.980(10)	141(8)	<i>1+x,y,z</i>
N6-H6B...O2	0.89(2)	2.30(5)	3.136(9)	155(9)	<i>intra</i>
N7-H7A...O1W	0.89(2)	2.27(3)	3.158(10)	172(9)	<i>-x,-y,-z</i>
N7-H7B...O2	0.89(2)	2.13(4)	2.973(10)	157(9)	<i>intra</i>

## 2. Calculation of aldehyde cyanosilylation conversion values by <sup>1</sup>H NMR analysis of crude products

a) Table 5, entry 4

The <sup>1</sup>H NMR spectrum of crude products from benzaldehyde cyanosilylation (with addition of internal standard - 1,2-dimethoxyethane) under the conditions described at Table 5, entry 4 (in MeOH), is displayed in Figure S6.



**Figure S6.**  $^1\text{H}$  NMR spectrum of crude products from benzaldehyde cyanosilylation with TMSCN using 5 mol% of catalyst **2** (Table 5, Entry 4).

b) Table 5, entry 4

Conversion is calculated by dividing characteristic peak area of the corresponding product by sum of characteristic peak areas of substrate and corresponding product.

$$\text{Conversion (\%)} = [a/(a + b)] \times 100\%$$

a: characteristic peak area of the corresponding product.

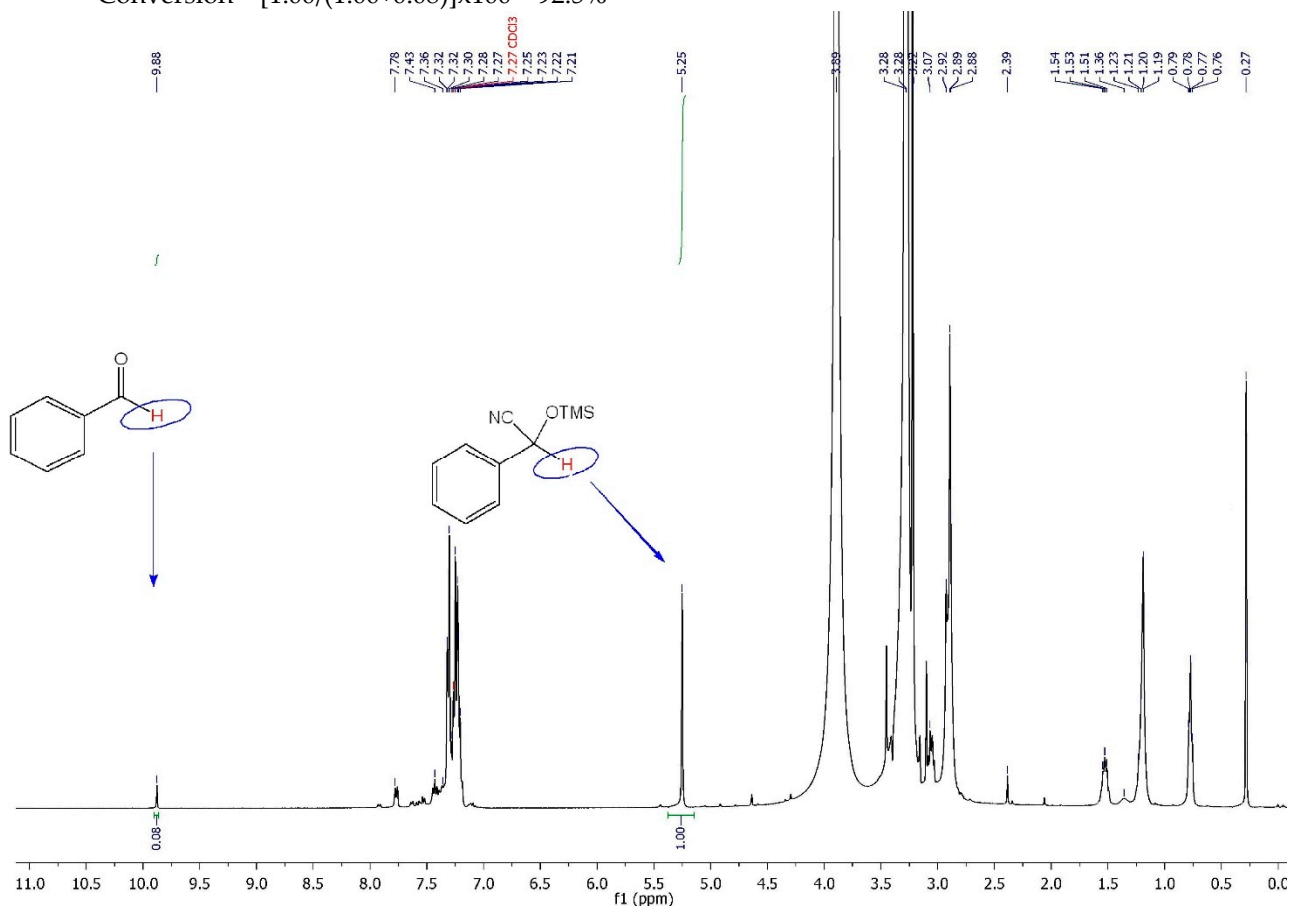
b: characteristic peak area of substrate.

The  $^1\text{H}$  NMR spectrum of crude products from benzaldehyde cyanosilylation in a mixture of [DHTMG][L-Lactate] : MeOH (1:10, v/v) (2 mL) under the conditions described at Table 2, is displayed in Figure S7.

Characteristic peak area of 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile = 1.00

Characteristic peak area of benzaldehyde = 0.08

$$\text{Conversion} = [1.00/(1.00+0.08)] \times 100 = 92.5\%$$



**Figure S7.**  $^1\text{H}$  NMR spectrum of crude products from benzaldehyde cyanosilylation with TMS-CN using 5 mol% of catalyst **2** in a mixture of [DHTMG][L-Lactate] : MeOH (1:10, v/v) (2 mL) (Table 5, Entry 4).