Supplementary Material (ESI) for New Journal of Chemistry
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Electronic Supplementary Information for

Supramolecular self-organization in constitutional hybrid materials

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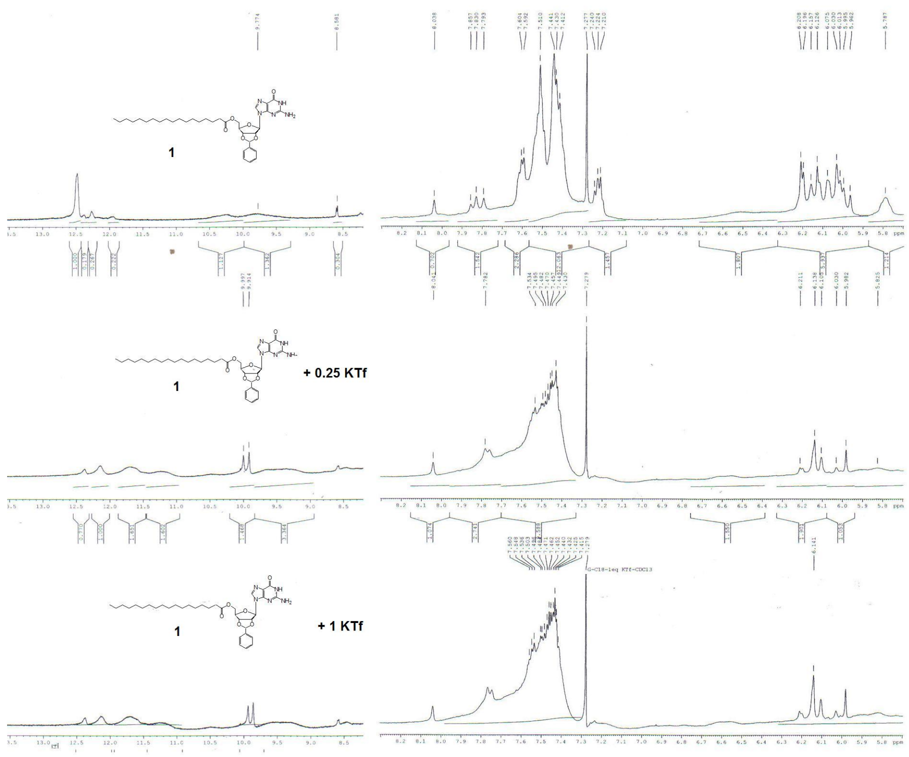


Figure 1S. Portion of ^{1}H NMR spectra in *$CDCl_3$* at 25°C of **1**, **1**+0.25 KTf and **1**+1 KTf

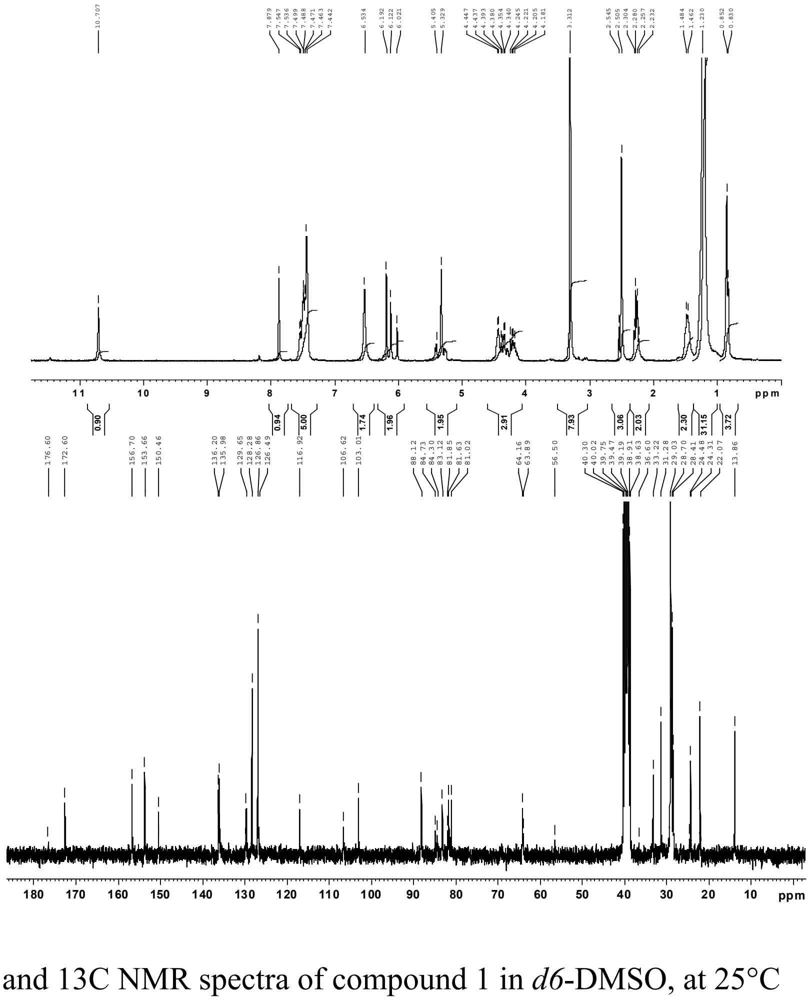


Figure 2S: 1H- and 13C NMR spectra of compound 1 in *d6*-DMSO, at 25°C

General procedure for synthesis of $\mathbf{A_{K}^{+}}$-$\mathbf{D_{K}^{+}}$, $\mathbf{A_{Ba}^{2+}}$-$\mathbf{D_{Ba}^{2+}}$ and the reference E hybrid materials

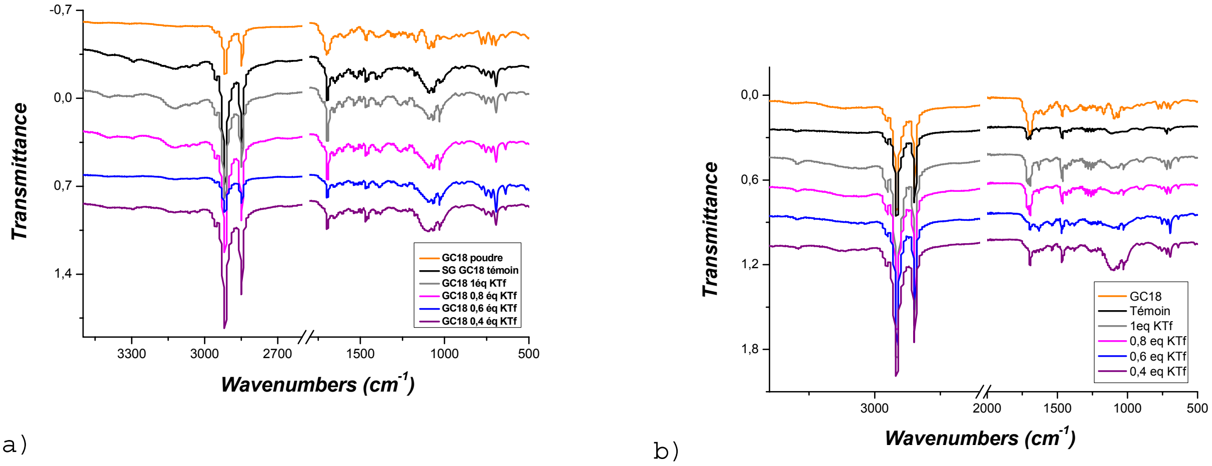
In typical run, 1 equiv of octadécyltrimethoxysilane **2** and variable amounts of compound **1** together with the templating metal salt (see Table 1S) were dissolved in chloroforme-acetone (1/0.25). 6 equiv of deionized water and 3 equiv of benzylamine (as catalyst) were added. Mixtures were stirred at 60°C during 24 hours, and then samples were slowly evaporated at room temperature to give sticky brown products which were isolated and characterized.
A second series of such hybrids $\mathbf{A_{K}^{+}}$-$\mathbf{D_{K}^{+}}$, $\mathbf{A_{Ba}^{2+}}$-$\mathbf{D_{Ba}^{2+}}$, **E** were thermically treated at 90°C during 24h

Table 1S: Experimental conditions used for the preparation of hybrid materials $\mathbf{A_{K}^{+}}$-$\mathbf{D_{K}^{+}}$, $\mathbf{A_{Ba}^{2+}}$-$\mathbf{D_{Ba}^{2+}}$ and the reference **E** material in the absence of ionic salts.

	Hybrid material	Compound, **1**	KTf	Ba$_2$Tf
Octadecyltrimethoxysilane, **2** m= 0.1g (1 equiv)	**A** 100%, **1**	m= 0.170g (1 equiv)	m= 0.013g (0.25 equiv/**1**)	m= 0.029g (0.25 equiv/**2**)
	B 80%, **1**	m= 0.136g (0.8 equiv)	m= 0. 010g (0.25 equiv/**2**)	m= 0.023g (0.25 equiv/**2**)
	C 60%, **1**	m= 0.102g (0.6 equiv)	m= 0.008g (0.25 equiv/**2**)	m= 0.017g (0.25 equiv/**2**)
	D 40%, **1**	m= 0.068g (0.4 equiv)	m= 0.005g (0.25 equiv/**2**)	m= 0.012g (0.25 equiv/**2**)
	E 100%, **1**	m= 0.170g (1 equiv)	m= 0g	m= 0g

A reference sol-gel sample E, was prepared in the absence of salt triflates, under the same reaction conditions.

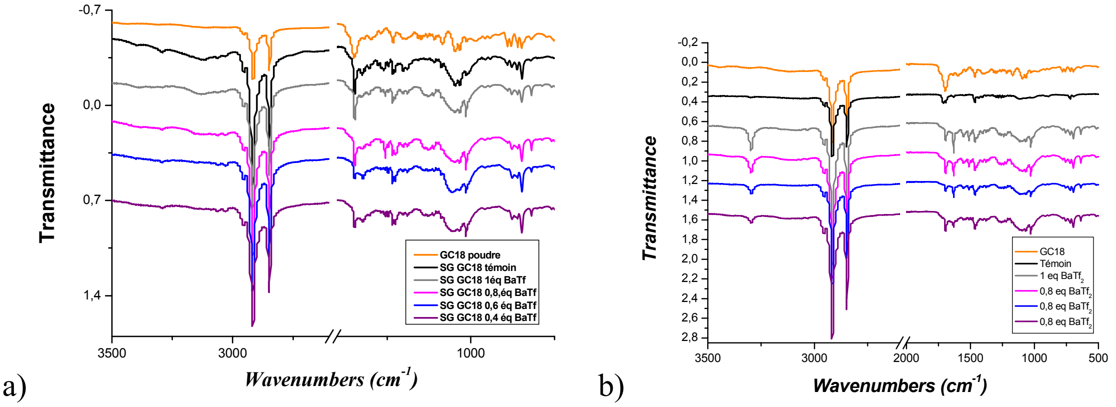
FTIR and NMR spectroscopic analyses



a)

b)

Figure 3S. Infrared spectra of hybrid materials **A-E** in the presence of KTf: (a) before and after (b) thermal treatment at 90°C



a)

b)

Figure 4S. Infrared spectra of hybrid materials **A-E** templated by in the presence of $BaTf_2$: (a) before and after (b) the thermal treatment at 90°C

X-ray powder diffraction (XPRD) studies: Fig 4S shows X-ray diffraction (XRD) pattern of three samples which contain compound **1** and equilibrated with different salt as potassium, sodium and barium triflate. The presence of the Bragg diffraction peak at 2θ = 26.8 corresponding to a spacing of 3.41 Å in presence of potassium triflate and 3.36 Å in presence of sodium or barium triflate is representative for the π-π stacking distance between two planar G-quartets [9]

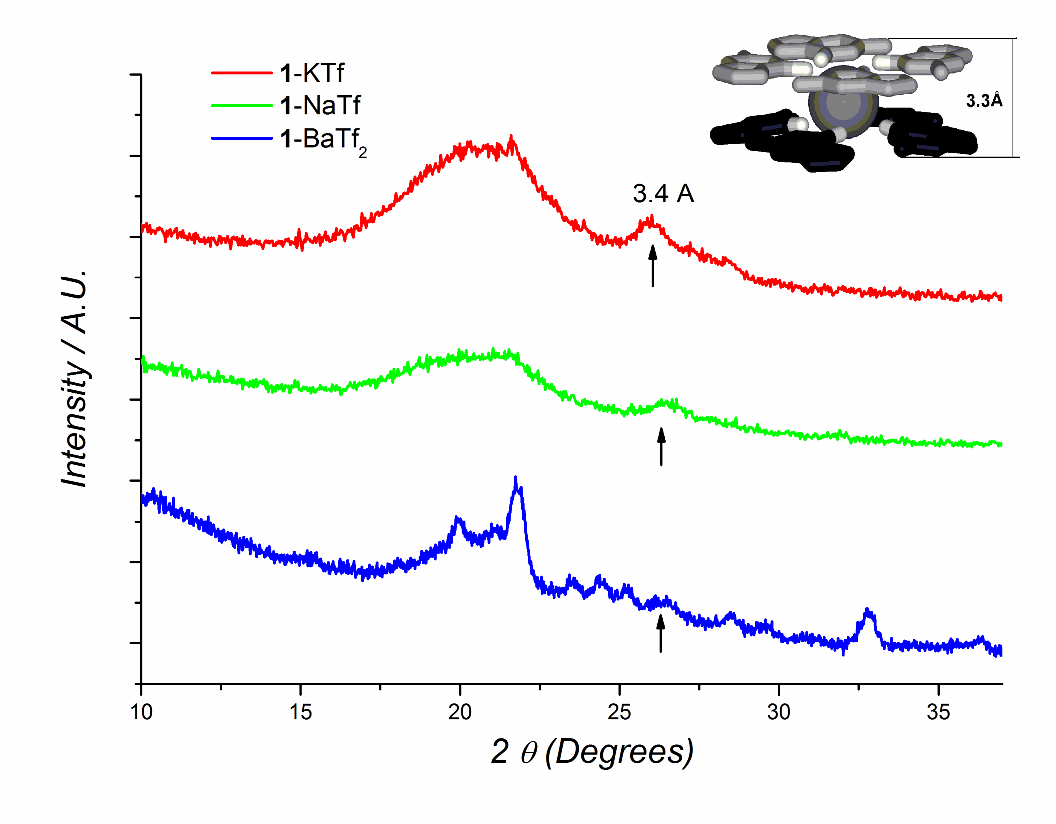
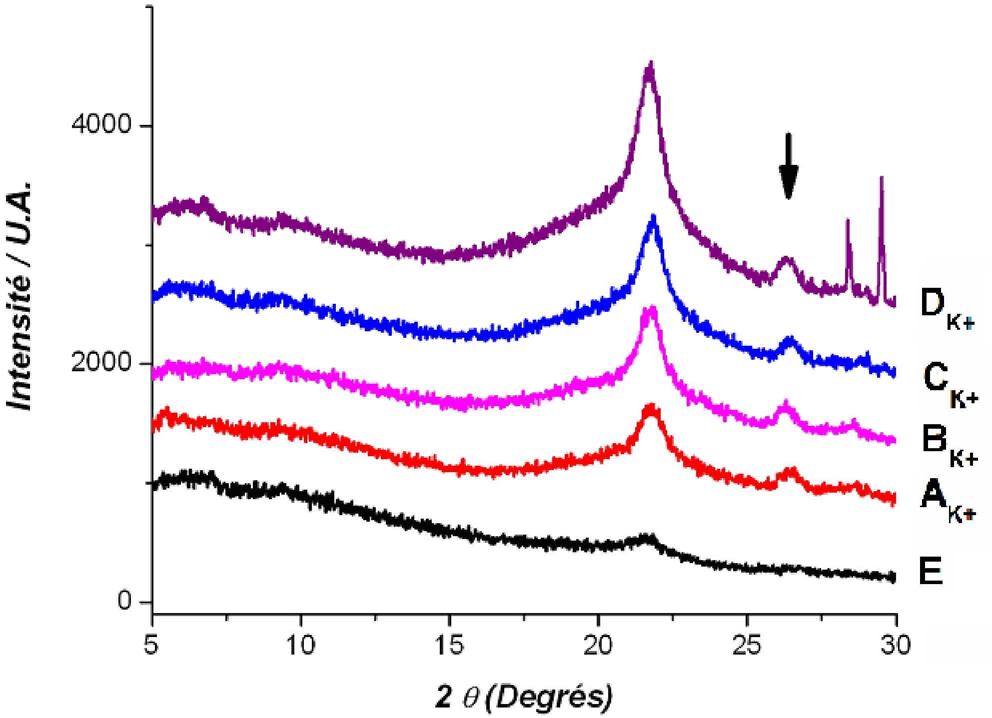


Figure 5S: XPRD patterns of non-templated lipophilic guanosine **1** equilibrated with Na^+, K^+ and Ba^{2+} templating cations. The π-π stacking between planar G-quartets in stick representation from crystallographic data (the K^+ ion is shown as a sphere).

The same premise was observed in XPRD patterns of hybrid materials **A-E** templated in the presence of (a) KTf and b) $BaTf_2$ (Fig 5S), after the thermal treatment at 90°C, 24h. The presence of the Bragg diffraction peak at $2\theta = 26.8$ corresponding to a spacing of 3.41 Å is representative for the π-π stacking distance between two planar G-quartets [9]



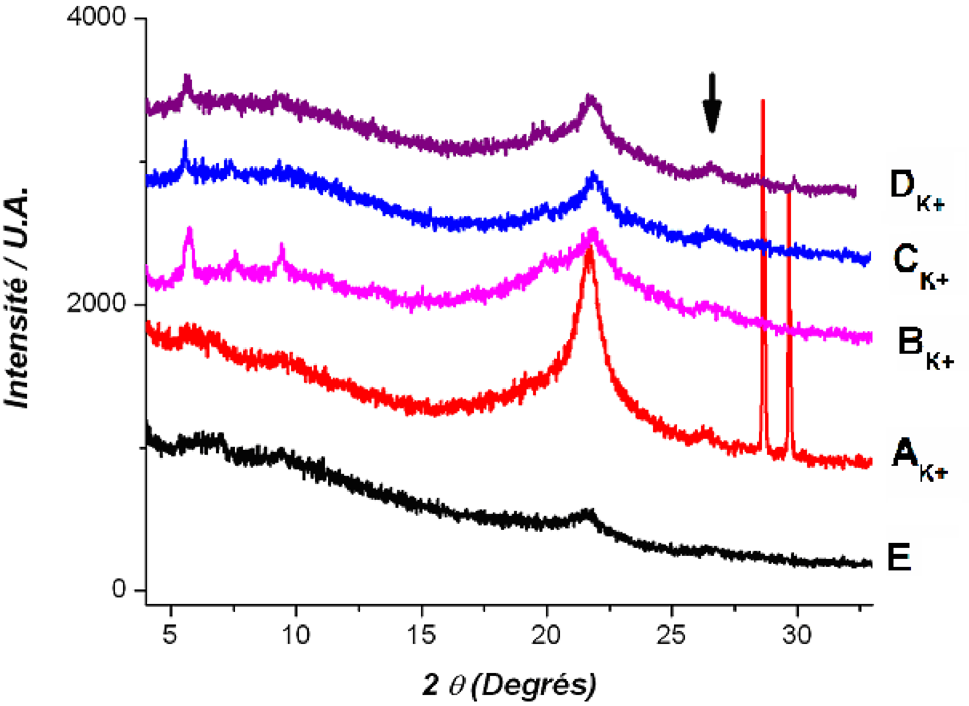


Figure 6S: XPRD patterns of hybrid materials **A**-**E** templated in the presence of (a) KTf and b) $BaTf_2$ after the thermal treatment at 90°C, 24h.

General procedure for synthesis of A_i-B_i ureidocrown-ethers hybrid materials In typical run, 1 equiv of **3** and variable amounts of compound **4** together (see Table 2S) were dissolved in acetone. 6 equiv of deionized water and 3 equiv of benzylamine (as basic catalyst) or different amounts of HCl 4N (as acidic catalyst) were added. The sols were briefly stirred and allowed to react at room temperature under static conditions for 1 week and then samples were slowly evaporated at room temperature to give white powders which were isolated and characterized.

Table 2S: Experimental conditions used for the preparation of hybrid materials **A_i-B_i**, h= hydrolysis ratio $n_{H2O}/n_{(EtO)3Si}$

4 (%wt)	**3** (%wt)	Benzylamine (µl)	HCl 4N h=0.1 (µl)	HCl 4N h=0.5 (µl)
A_0, B_0 (100%)	-	11.32	0.56	2.81
A_{10}, B_{10} (90%)	10	10.19	0.50	2.50
A_{20}, B_{20} (80%)	20	9.05	0.44	2.22
A_{40}, B_{40} (60%)	40	6.79	0.33	1.65
A_{50}, B_{50} (50%)	50	5.66	0.28	1.42
A_{60}, B_{60} (40%)	60	4.52	0.21	1.08
A_{80}, B_{80} (10%)	80	2.26	0.10	0.51

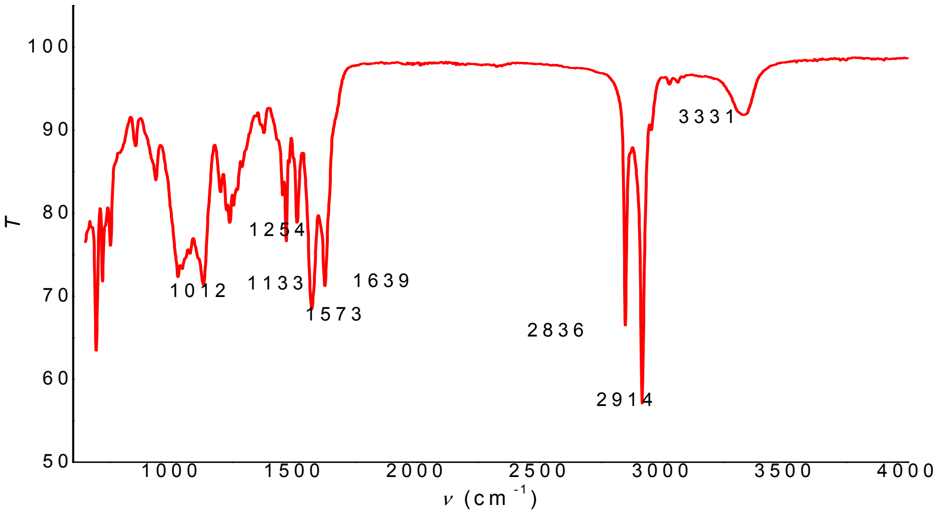
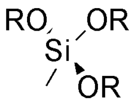
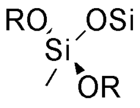


Figure 7S FTIR spectra of hybrid material **B_{50}**

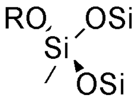
Table 3S. ^{29}Si MAS-NMR spectroscopic results of **B$_i$** hybrids, n=condensation number: $n = (T^1 + 2T^2 + 3T^3)/(T^1 + T^2 + T^3)$; Condensation degree $\% = (n/3)\cdot 100$



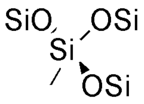
T^0



T^1



T^2



T^3

Sample	n	Condensation degree (%)	T^1 (%)	T^2 (%)	T^3 (%)
B$_0$	2.74	91.63	0	23.16	76.18
B$_{40}$	2.39	79.97	8.07	43.91	48.01
B$_{60}$	2.37	79.04	6.19	50.55	43.27
B$_{80}$	2.09	69.86	5.84	78.68	15.48

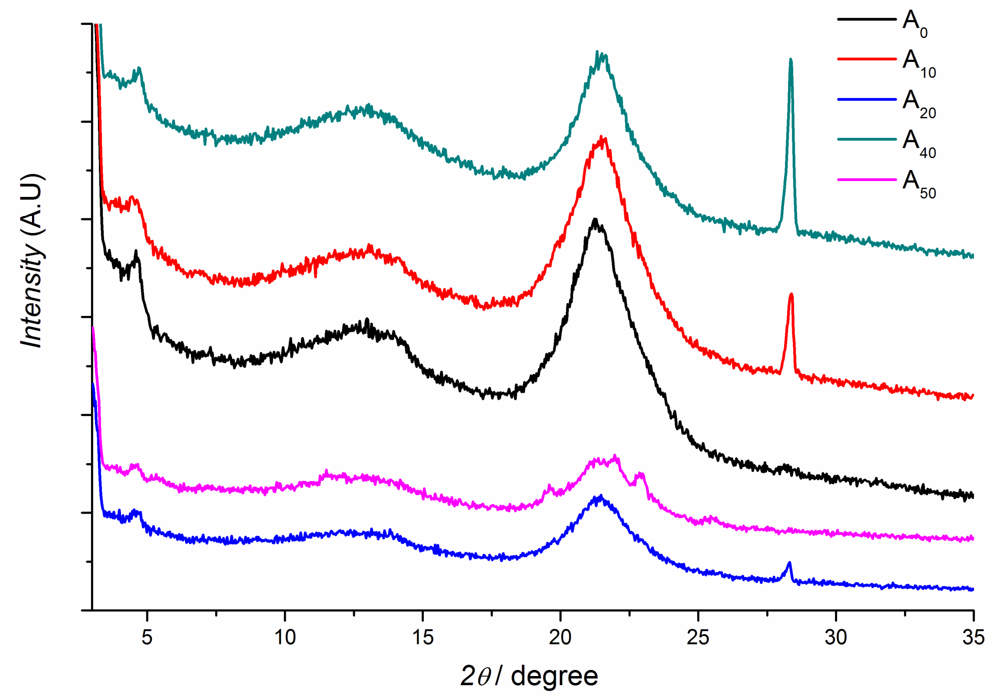


Figure 8S: XPRD patterns of hybrid materials **Ai** prepared under acidic catalysis HCl 4N