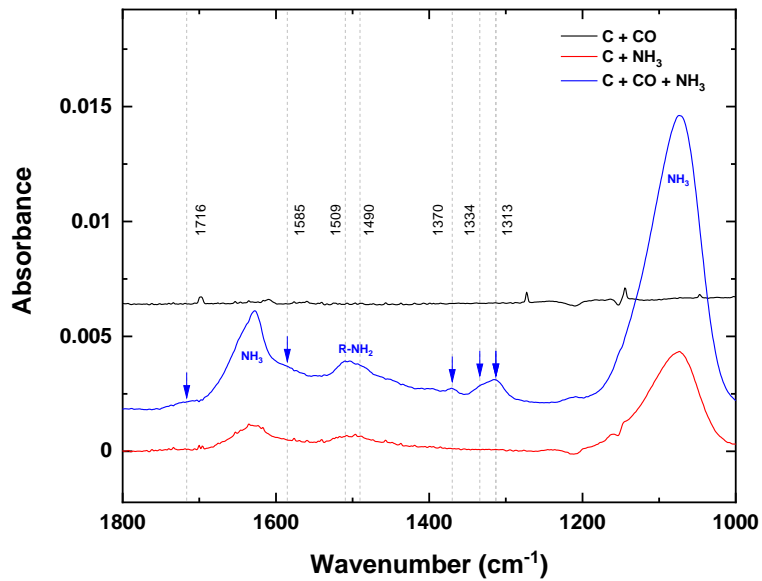
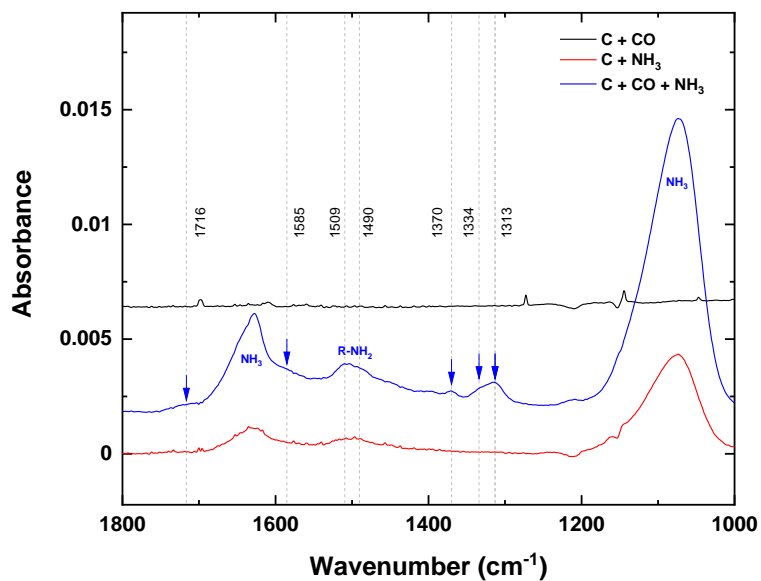


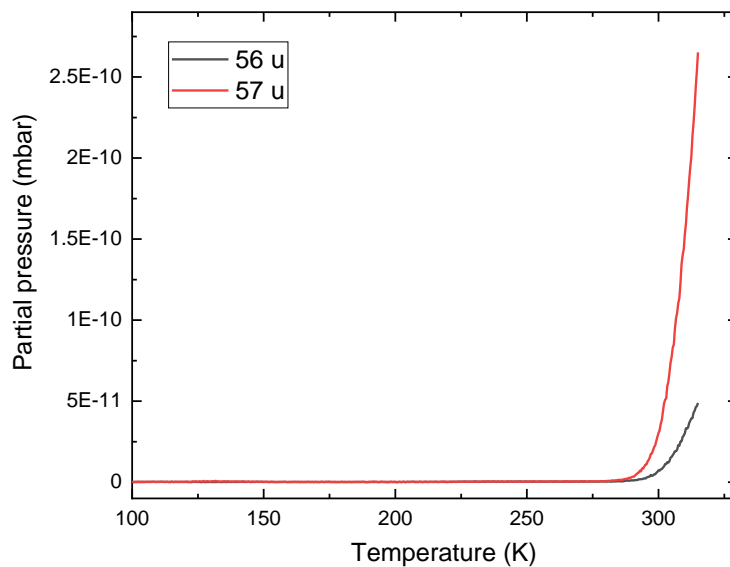
Supplementary Figure 1. The IR absorption spectra of 300 K residues from a - C + CO + NH₃, b - C + NH₃, and c - C + CO control experiments. a.



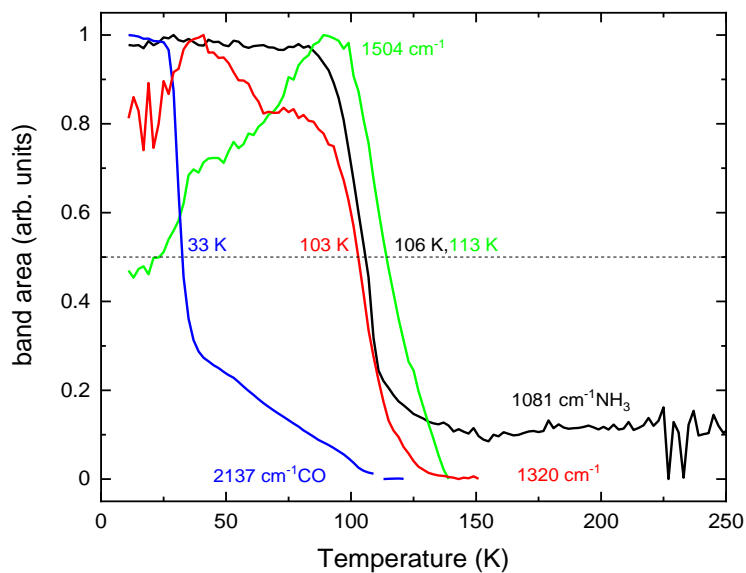
Supplementary Figure 2. The comparison of IR absorption spectra in the range of vibrations of CO and NH_n groups of the materials produced by codeposition of the reactants on the substrate at 10K. The bands that are observed only when three reactants are deposited are marked by arrows.



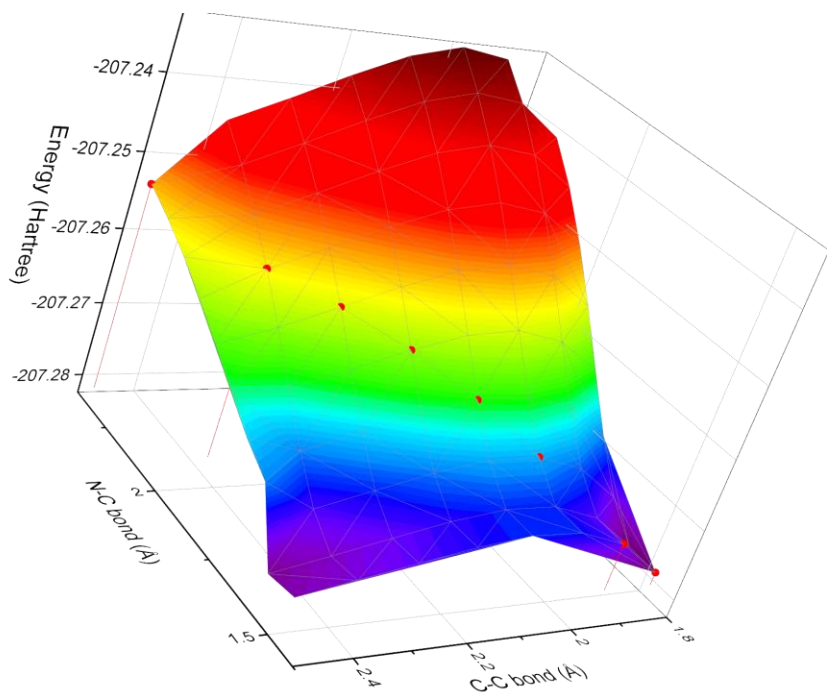
Supplementary Figure 3. The comparison of IR absorption spectra in the range of vibrations of C=O group of the materials produced by codeposition of different reactants on the substrate at 10K. The type of reactants are given in the figure. The band that is observed only when three reactants are deposited are marked by arrow.



Supplementary Figure 4. The TPD curves measured by quadrupole mass spectrometer monitoring the mass 57 u, corresponding to the $\text{NH}_2\text{CH}=\text{CO}$ molecule, and its expected fragment the mass 56 u. The partial pressure is given around QMS considering the same ionization cross section as for nitrogen.



Supplementary Figure 5. The TPD curves obtained from the IR spectra. The curves show the intensity of the IR absorption bands associated with the different molecules. The peak maximum of the studied bands and the assignment (if available) are given in the figure. The horizontal dashed line shows the 50% intensity. The temperatures of its crossing with the TPD curves are given.



Supplementary Figure 6. Potential energy surface for the formation of the first energy well structure in Fig. 2. Red data points show the barrierless pathway for the formation of the H₃NCCO molecule.

Supplementary Table 1. The mass peaks observed in the ex situ analysis of the 300 K residue. Masses correspond to protonated species [analyte+H]⁺ as detected in experiment, while assignment is given for the analyte.

MASS	COUNTS	ASSIGNMENT
201.0983	219568	Gl ₄ (NH ₂ CH ₂ ends) C ₇ H ₁₃ N ₄ O ₃
258.1195	165487	Gl ₅
315.1412	105818	Gl ₆
372.1627	56078	Gl ₇
429.1842	21739	Gl ₈
486.2057	15781	Gl ₉
189.098	1388446	Gl ₄ (NH ₂ NH ₂ ends) C ₆ H ₁₃ N ₄ O ₃
246.1194	509908	Gl ₅
303.141	121422	Gl ₆
360.1627	50370	Gl ₇
417.1842	18616	Gl ₈
474.2057	11917	Gl ₉
172.0714	362672	Gl ₃ (exact polymer) C ₆ H ₁₀ N ₃ O ₃
229.093	175596	Gl ₄
286.114	93262	Gl ₅
343.136	55089	Gl ₆
400.157	35490	Gl ₇
457.178	16591	Gl ₈
174.0871	367120	Gl ₃ (exact polymer + H ₂) C ₆ H ₁₂ N ₃ O ₃
231.108	262322	Gl ₄
288.13	119467	Gl ₅
345.151	65474	Gl ₆
402.173	28327	Gl ₇
459.194	14628	Gl ₈
184.0715	457345	Gl ₃ (exact polymer + CH) C ₇ H ₁₀ N ₃ O ₃
241.0929	250906	Gl ₄
298.114	87861	Gl ₅
355.136	49995	Gl ₆
412.157	25223	Gl ₇
469.179	13877	Gl ₈
198.0871	238076	Gl ₃ (exact polymer + C ₂ H ₃) C ₈ H ₁₂ N ₃ O ₃
255.108	97056	Gl ₄
312.13	77725	Gl ₅
369.151	44642	Gl ₆
426.173	17160	Gl ₇
156.0766	383597	Gl ₃ (NH ₂ NH ₂ ends + C ₂) C ₆ H ₁₀ N ₃ O ₂
213.098	295559	Gl ₄
270.119	128775	Gl ₅
327.141	80091	Gl ₆
384.162	30402	Gl ₇
168.0766	239784	Gl ₃ (NH ₂ NH ₂ ends + C ₃ H) C ₇ H ₁₀ N ₃ O ₂
225.0981	259786	Gl ₄
282.119	112662	Gl ₅

339.141	60541	GI ₆	
396.162	37179	GI ₇	
453.183	15029	GI ₈	
191.114	13708	GI ₃	(NH ₂ NH ₂ ends + H ₂) C ₆ H ₁₅ N ₄ O ₃
248.135	82003	GI ₄	
305.1567	339660	GI ₅	
362.178	44675	GI ₆	
419.199	13724	GI ₇	
185.1031	657156	GI ₄	(NH ₂ NH ₂ ends, -O +C) C ₇ H ₁₃ N ₄ O ₂
242.1245	337857	GI ₅	
299.146	123962	GI ₆	
356.167	60163	GI ₇	
413.188	34643	GI ₈	
470.211	15248	GI ₉	
173.1031	378772	GI ₄	(NH ₂ NH ₂ ends, -O) C ₆ H ₁₃ N ₄ O ₂
230.125	138257	GI ₅	
287.146	115564	GI ₆	
344.167	33097	GI ₇	
401.189	18335	GI ₈	
183.0874	379942	GI ₄	(NH ₂ NH ₂ ends, -O +CH ₂) C ₇ H ₁₁ N ₄ O ₂
240.109	148396	GI ₅	
297.13	83123	GI ₆	
354.152	31393	GI ₇	
411.173	13063	GI ₈	
157.0606	339455		C ₆ H ₉ N ₂ O ₃
214.082	117609		
271.151	54266		
328.125	34221		
385.147	27692		
253.0904	327530		C ₇ H ₁₅ N ₃ O ₇
310.112	45682		
367.133	7652		
204.109	20844		C ₆ H ₁₄ N ₅ O ₃
261.1305	277321		
318.152	18823		
375.173	15283		
196.069	733000		C ₅ H ₁₂ N ₂ O ₆
253.0904	327530		
310.112	45681		
154.0585	426849		C ₃ H ₁₀ N ₂ O ₅
211.08	285845		
268.101	100122		
325.123	22401		