Supplementary Information

Interpolyelectrolyte complexes of a biguanide cationic polyelectrolyte: formation of core/corona nanoparticles with double-hydrophilic diblock polyanion

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1. Molar mass distribution of MFC from size exclusion chromatography
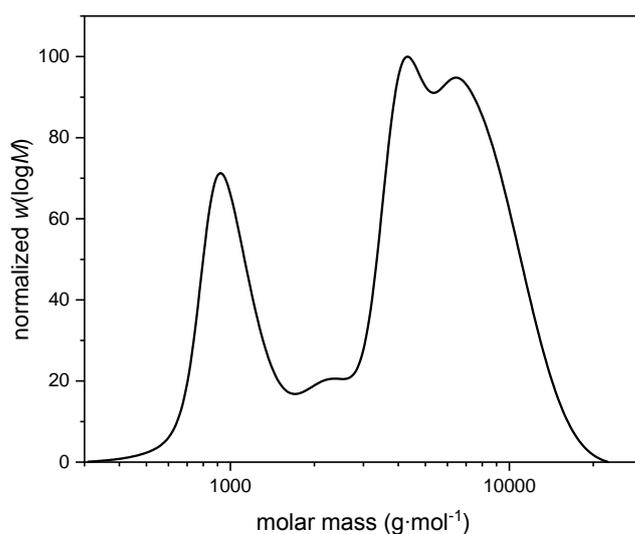
Figure S1. Molar mass distribution of MFC obtained by SEC with a relative calibration to pullulan standards.

2. ^{1}H, ^{13}C, ^{1}H-^{13}C HSBC and ^{1}H-^{13}C HSQC NMR spectra of metformin hydrochloride
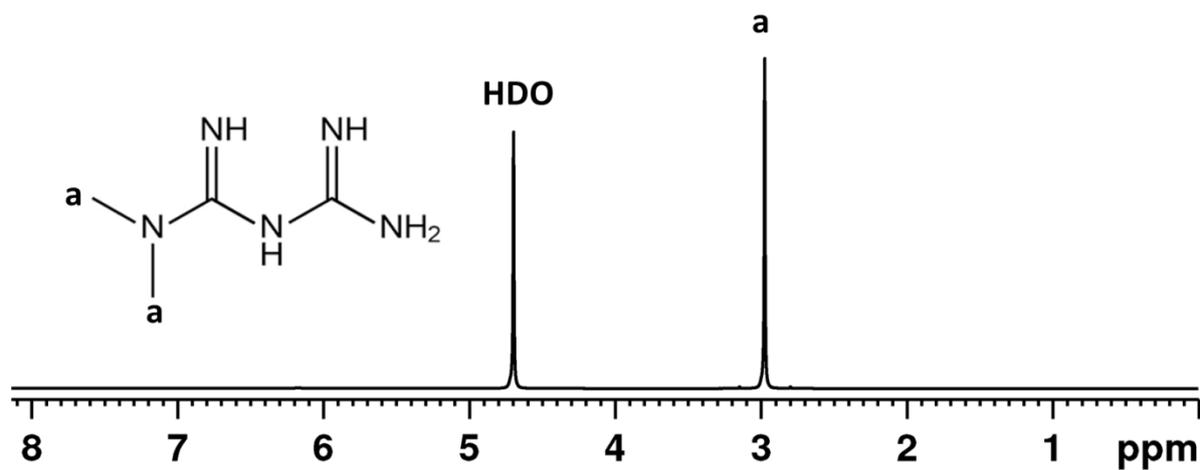
Figure S2. ^{1}H NMR spectrum of metformin hydrochloride measured in D_2O at 298K.
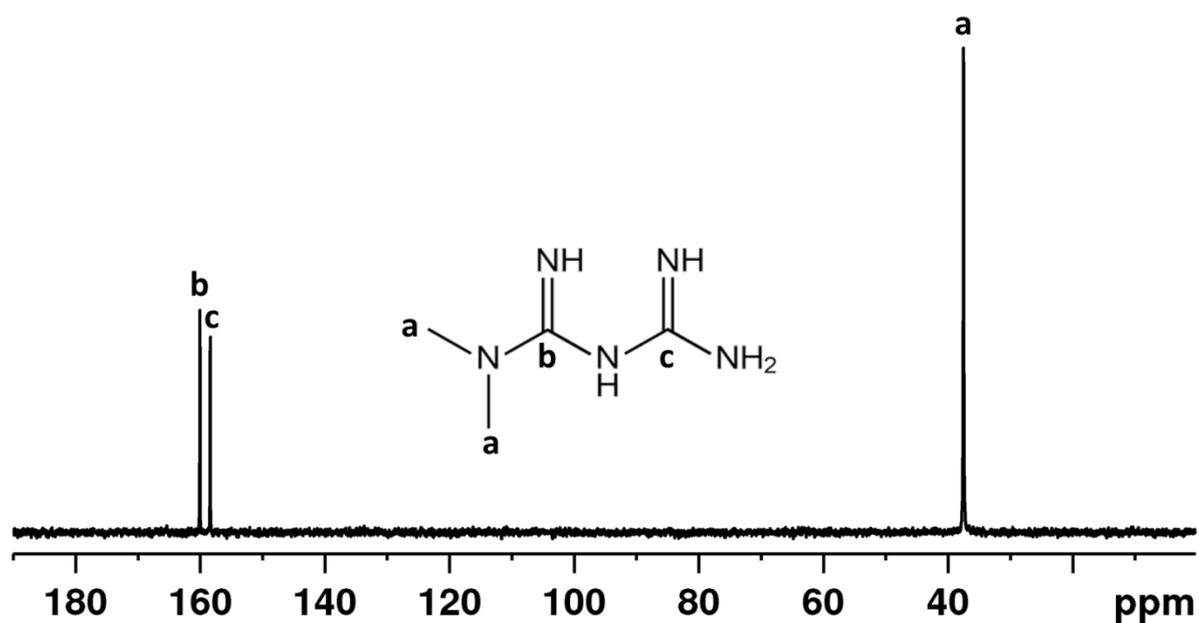
Figure S3. ^{13}C NMR spectrum of metformin hydrochloride measured in D_2O at 298K.
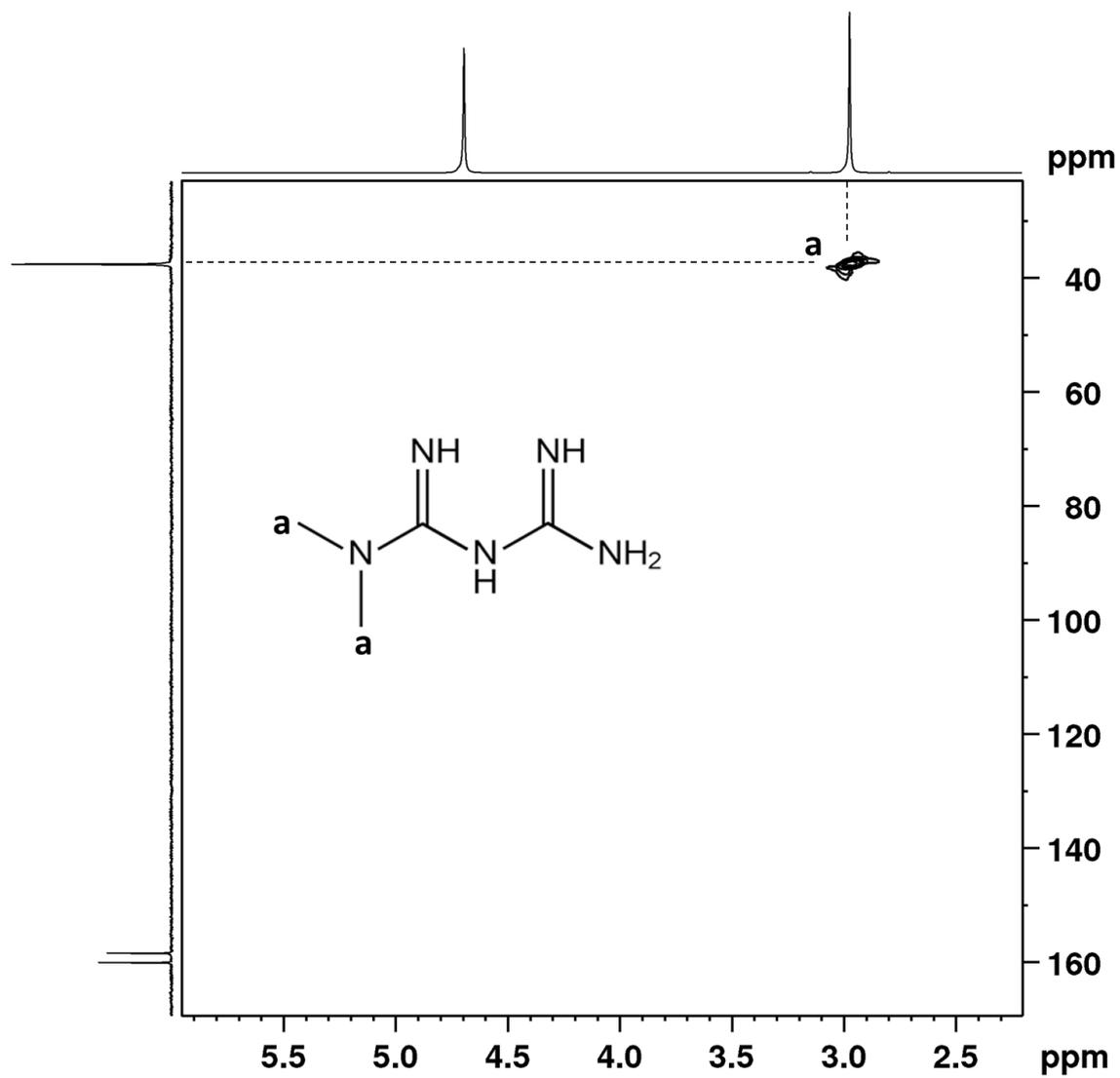
Figure S4. ^{1}H-^{13}C me-HSQC NMR spectrum of metformin hydrochloride measured in D_2O at 298K.
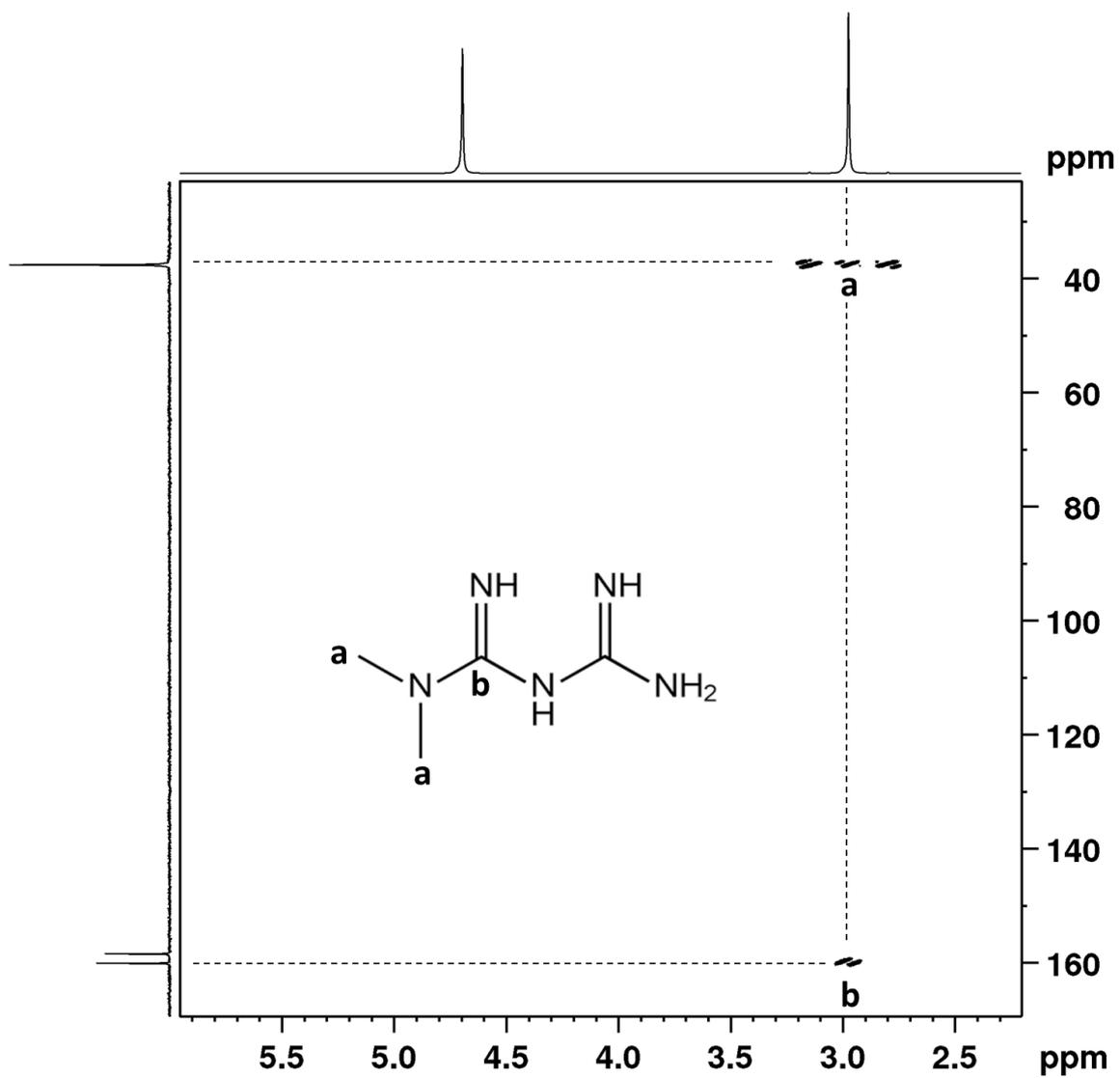
Figure S5. ^{1}H-^{13}C HMBC NMR spectrum of metformin hydrochloride measured in D$_2$O at 298K.

3. 1H, 13C, 1H-1H COSY, 1H-13C HSQC and 1H-13C HMBC NMR spectra of MFC with peak assignements
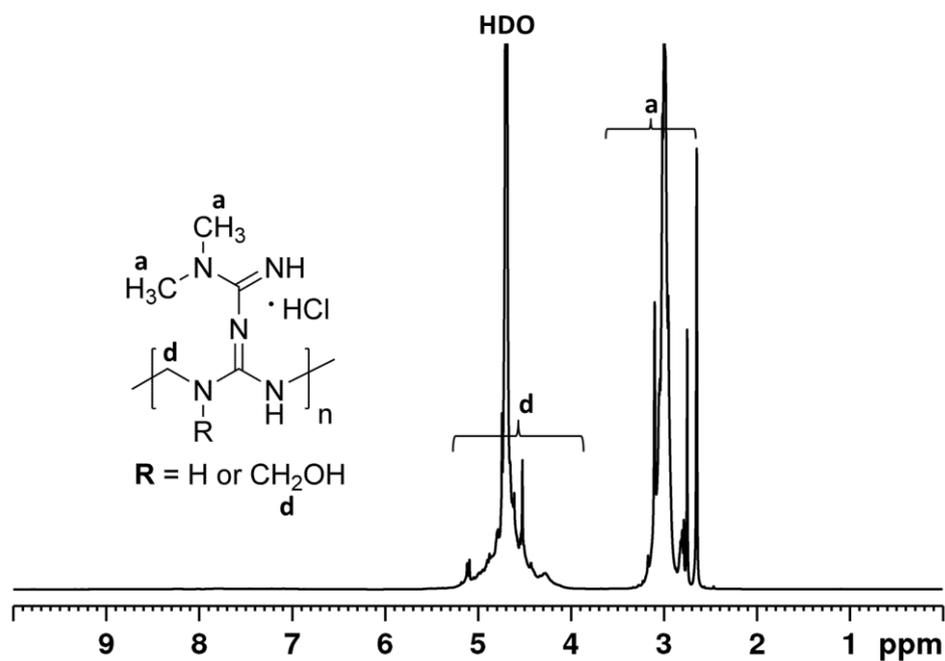
Figure S6. ^{1}H NMR spectrum of MFC measured in D$_2$O at 298K.
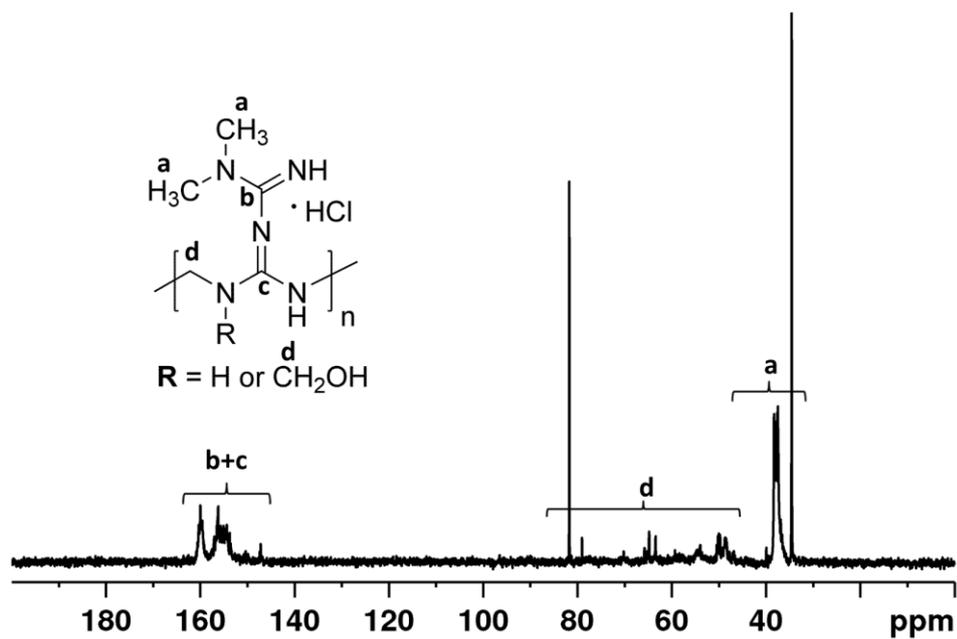
Figure S7. ^{13}C NMR spectrum of MFC measured in D$_2$O at 298K.
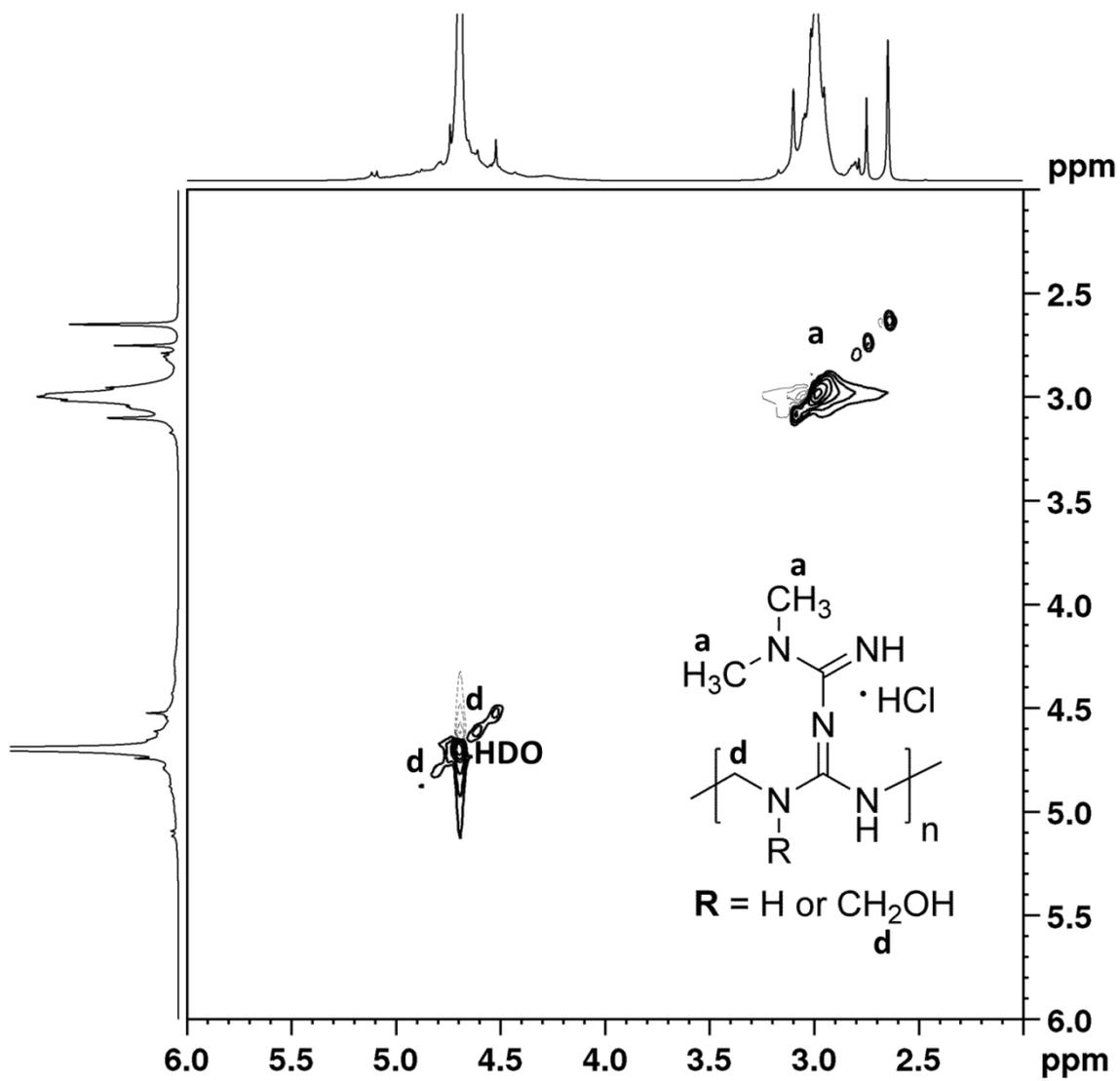
Figure S8. ^1H-^1H COSY NMR spectrum of MFC measured in D_2O at 298K.
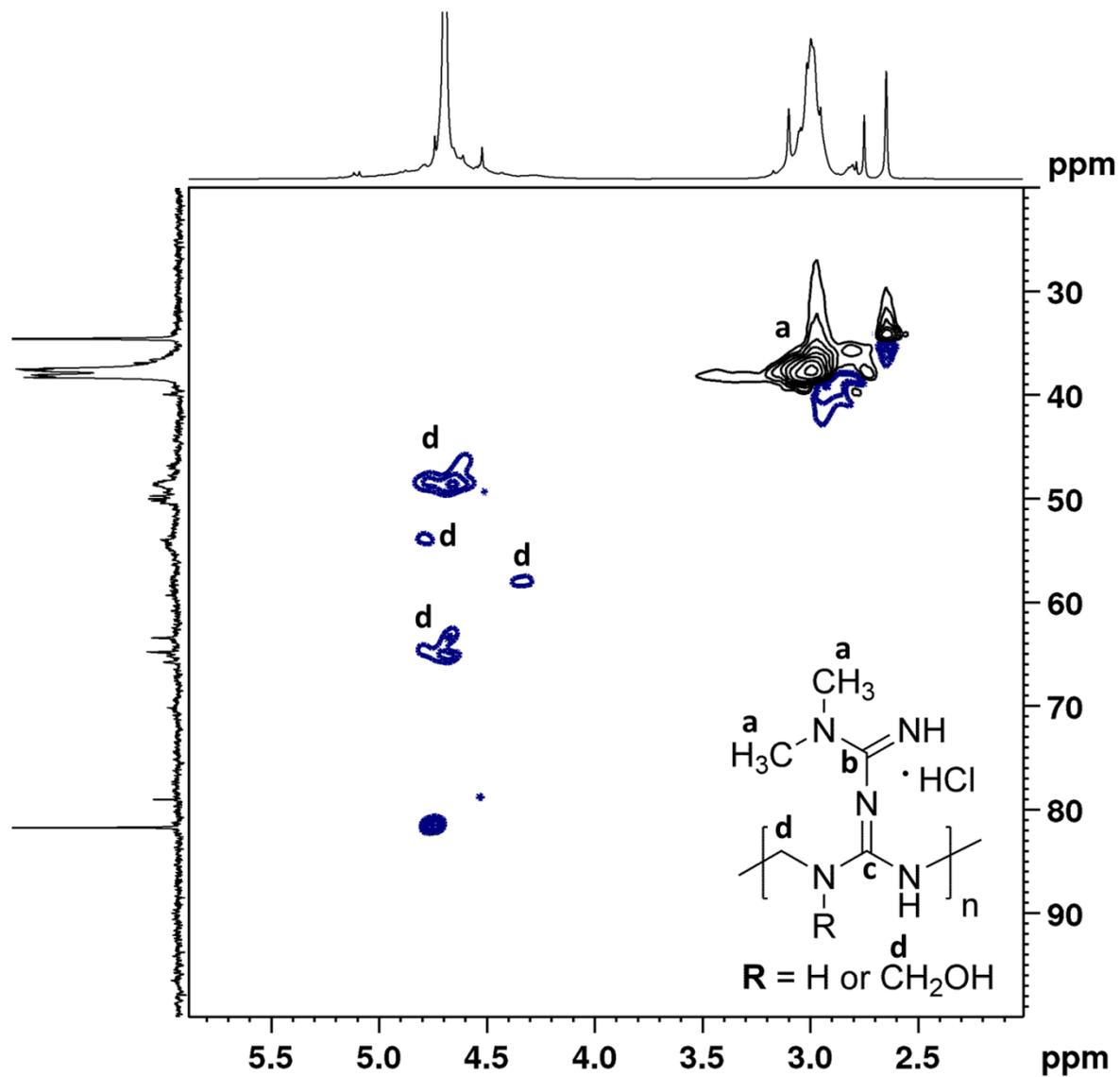
Figure S9. ^{1}H-^{13}C me-HSQC NMR spectrum of MFC measured in D$_2$O at 298K.
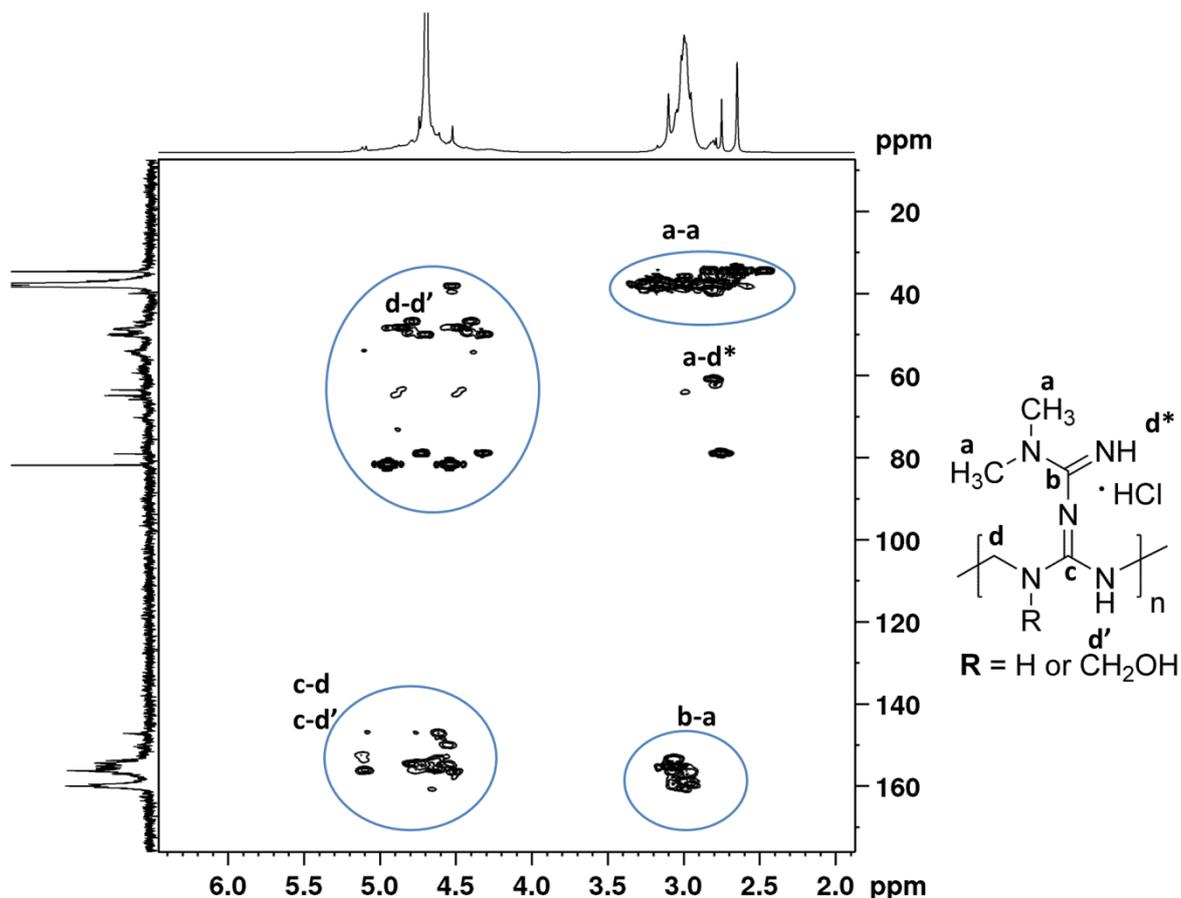
Figure S10. ^1H-^{13}C HMBC NMR spectrum of MFC measured in D_2O at 298K.

4. Discussion of NMR spectra

1D and 2D NMR spectra were used for structural characterization of the starting metformin and the metformin-based condensate MFC. In case of neat metformin hydrochloride, the ^1H, ^{13}C, ^1H-^{13}C me-HSQC and ^1H-^{13}C HMBC spectra were recorded. In **Fig. S2**, the ^1H NMR spectrum of metformin hydrochloride measured in water, together with signal assignment, is presented. Only one signal at δ= 2.97 ppm related to methyl groups "a" is observed. The ^{13}C NMR spectrum of metformin hydrochloride with assignment of all observed resonances is shown in **Fig. S3**. The signal of carbons of methyl groups "a" is observed at δ= 37.48 ppm, while two signals of quaternary carbons "b" and "c" are at δ= 160.03 and 158.38 ppm, respectively. In the HSQC spectrum (**Fig. S4**), only one correlation signal (from methyl groups) is observed as expected. The HMBC spectrum (**Fig. S5**) was useful for the correct assignment of quaternary carbons, using the cross-peak "b" that appears between protons of methyl groups and the carbon "b" closest to the methyl group.

Similarly to the neat metformin, the structure of the MFC condensate was studied by the combination of 1D and 2D NMR methods. In **Fig. S6**, the ^{1}H NMR spectrum with the structure of the expected repeat unit is presented. As the structure of the products of the polycondensation reaction can be quite complex (e.g., it may include branched structures), only the main structural features can be estimated. In this case, two main types of protons are observed as broad signals: first – assigned to methyl groups "a" at $\delta \approx$ 3.30-2.60 ppm, second methylene groups "d" at $\delta \approx$ 5.60-3.86 ppm, with the neighboring heteroatom (N or O) and partially overlapped with the signal of water. Sharper resonances at δ= 2.65 and 2.75 ppm suggest the presence of low molar mass compounds or mobile end-groups. In the same way the ^{13}C NMR spectrum can be solved, as shown in **Fig. S7**. Here, three types of carbons are observed: "a" – methyl groups at $\delta \approx$ 39.00-34.00 ppm, "b+c" – quaternary carbons at $\delta \approx$ 162.00-146.00 ppm and "d"- methylene groups attached to a heteroatom at $\delta \approx$ 82.00-42.00 ppm. Similarly as in the ^{1}H NMR spectrum, some sharp signals related to low molar mass products are observed. To further confirm the proposed structure, 2D ^{1}H-^{1}H COSY NMR spectrum was recorded (**Fig. S8**). No cross-signals were detected, suggesting that methyl and methylene groups are not in the close neighborhood (at least a 6-bond distance). Multiplicity edited HSQC experiment (**Fig. S9**) confirmed the shift ranges of the methyl "a" and methylene groups "d". Generally, in this experiment, the cross-peaks of CH_3 and CH groups appear as positive (black) and of CH_2 groups as negative (blue). In the HMBC spectrum, groups of correlation signals confirming the suggested structure were observed (**Fig. S10**). Note that there is one additional cross-peak observed (marked as a-d*), which suggests that in some repeat units, the methylene group is be attached to the nitrogen connected to carbon "b" by a double bond, i.e., $=N-CH_2-OH$ group is present instead of $=NH$. This agrees with the conjugated character of the biguanide group where a number of resonance structures are plausible, different nitrogens can be protonated, and some degree of polymer branching cannot be ruled out.
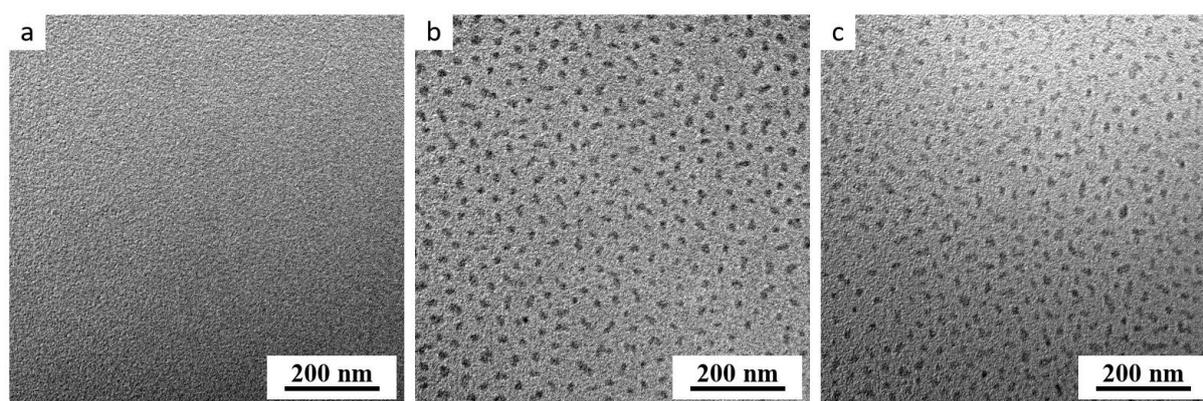
Figure S11. Cryo-TEM images of (a) 10 mg mL^{-1} MFC aqueous solution and MFC/PMAA-PEO aqueous solutions, PMAA-PEO concentration 2 mg mL^{-1}, MFC to PMAA mass ratios (b) w = 1 and (c) w = 2.