Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Reflux precipitation polymerization: a new synthetic insight in molecular imprinting at high temperature

Xiantao Shen,*[abd] Chuixiu Huang,*[bcd] Sudhir kumar Shinde,[b] Magdalena Switnicka-Plak,[e] Peter Cormack[e] and Börje Sellergren*[b]

[a.] Key Laboratory of Environment and Health, Ministry of Education & Ministry of Environmental Protection, State Key Laboratory of Environmental Health (Incubation), School of Public Health, Tongji Medical College, Huazhong University of Science and Technology, Hangkong Road #13, Wuhan, Hubei 430030, China.

[b.] Department of Biomedical Sciences, Faculty of Health and Society, Malmö University, SE20506 Malmö, Sweden.

[c.] School of Pharmacy, University of Oslo, PO Box 1068 Blindern, 0316 Oslo, Norway.

[d.] G&T Septech AS, Verkstedveien 29, 1400 Ski, Norway

[e.] Department of Pure & Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, UK

Corresponding Author

E-mail: xtshenlab@hust.edu.cn (X. Shen)
chuixiuh@student.matnat.uio.no (C. Huang)
borje.sellergren@mah.se (B. Sellergren)

1. Structures of the beta blockers

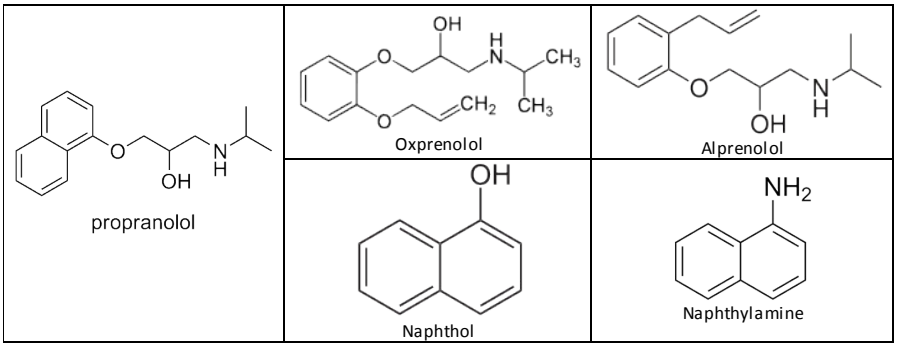


Fig. S1 Structures of propranolol, oxprenolol, alprenolol, 1-naphthol and naphthylamine.

2. Macroscopic views of the round-bottom bottle

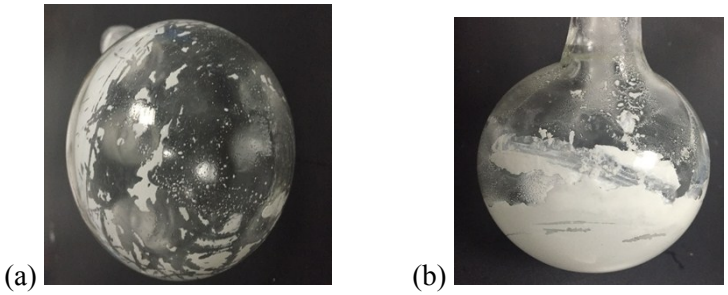


Fig. S2 Macroscopic views of the round-bottom bottle for the synethisis of the mip-RPP (a) and mip-DPP (b) MSs. Before taking the photos, both bottles were washed with 20 mL of ACN for 3 times.

3. Freundlich isotherms

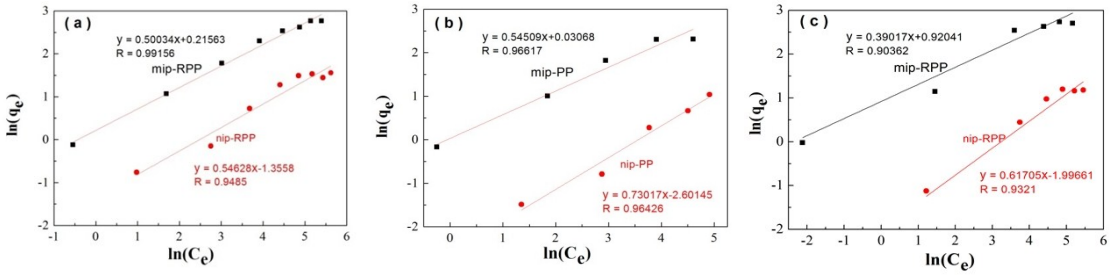


Fig. S3 Freundlich isotherms based on the adsorption of propranolol on MSs prepared by RPP (a), PP (b) and DPP (c).

4. Synthesis of Theophylline (TH) imprinted MSs

To study the effects of high temperature on molecular imprinting, TH imprinted MIP MSs were also prepared using both PP and RPP. Typically, 108 mg of TH was dissolved in 20 mL of ACN in a borosilicate glass tube with a screw cap. Afterwards, 150 µL of MAA, 600 µL of DVB and 14 mg of ABDV were added. The solution was purged with nitrogen for 5 min and sealed. Subsequently, the polymerization was initiated by placing the glass reactor into a 60 ℃ water bath, and the polymerization was kept for 24 h. After the reaction, the MSs were collected by centrifugation. To remove the template, the polymeric MSs were washed with methanol and ACN. The concentration of TH in the washing solvent was measured with a UV spectrophotometer (274 nm). When no template could be found in the washing solvent, the polymeric MSs were washed with ACN, and dried in a vacuum chamber at room temperature. In this way, the MIP MSs were synthesized and named TH-mip-PP MSs. As a control, TH-nip-PP MSs were also prepared without the addition of the template under the same condition as that for the synthesis of TH-mip-PP MSs.

To produce MIP MSs using RPP method, 106 mg of TH, 150 µL of MAA, 600 µL of DVB and 14 mg of AIBN were dissolved in 20 mL of ACN in a round-bottom bottle. After purging with nitrogen for 5 min, the round-bottom bottle was equipped with a condenser and placed into a 90 ℃ oil bath to induce the polymerization. After the reaction, the MSs were collected by centrifugation. To remove the template, the polymeric MSs were washed with methanol containing 10% acetic acid. The concentration of TH in the washing solvent was measured with a UV spectrophotometer (274 nm). When no template could be found in the washing solvent, the polymeric MSs were washed with ACN, and dried in a vacuum chamber at room temperature. In such a way, the MIP MSs were synthesized and named TH-mip-RPP MSs. As a control, TH-nip-RPP MSs were also prepared without the addition of the template under the same condition for the synthesis of TH-mip-RPP MSs.

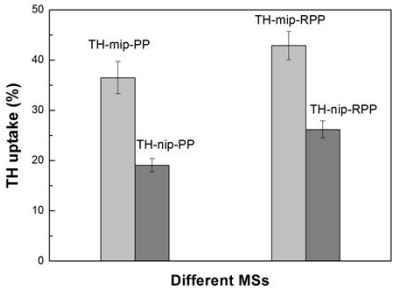
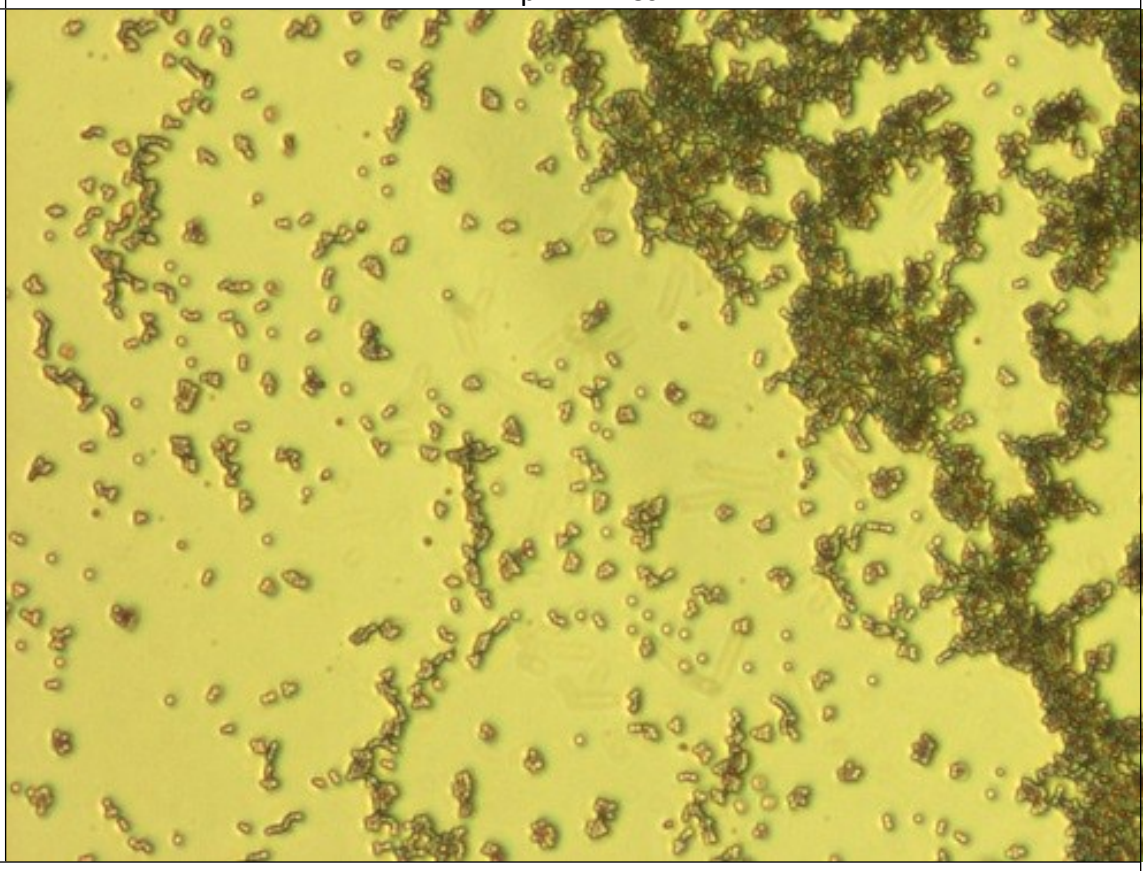
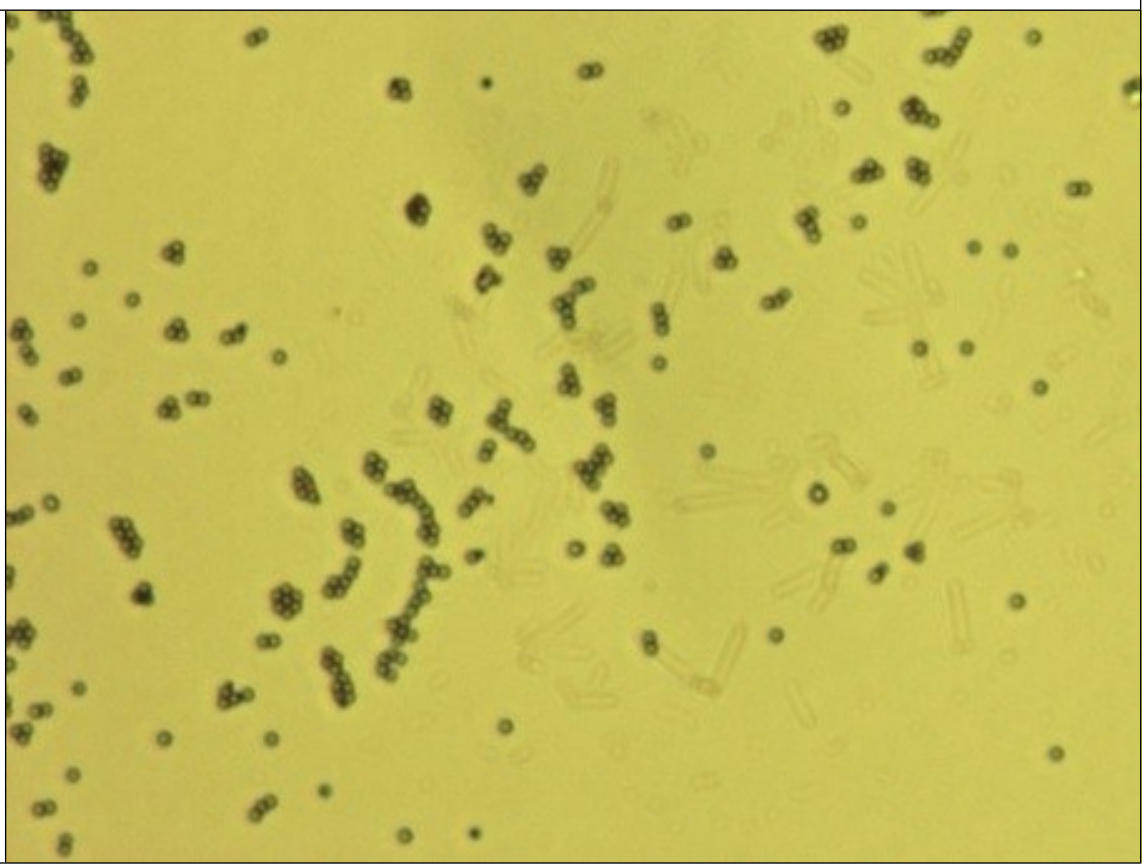
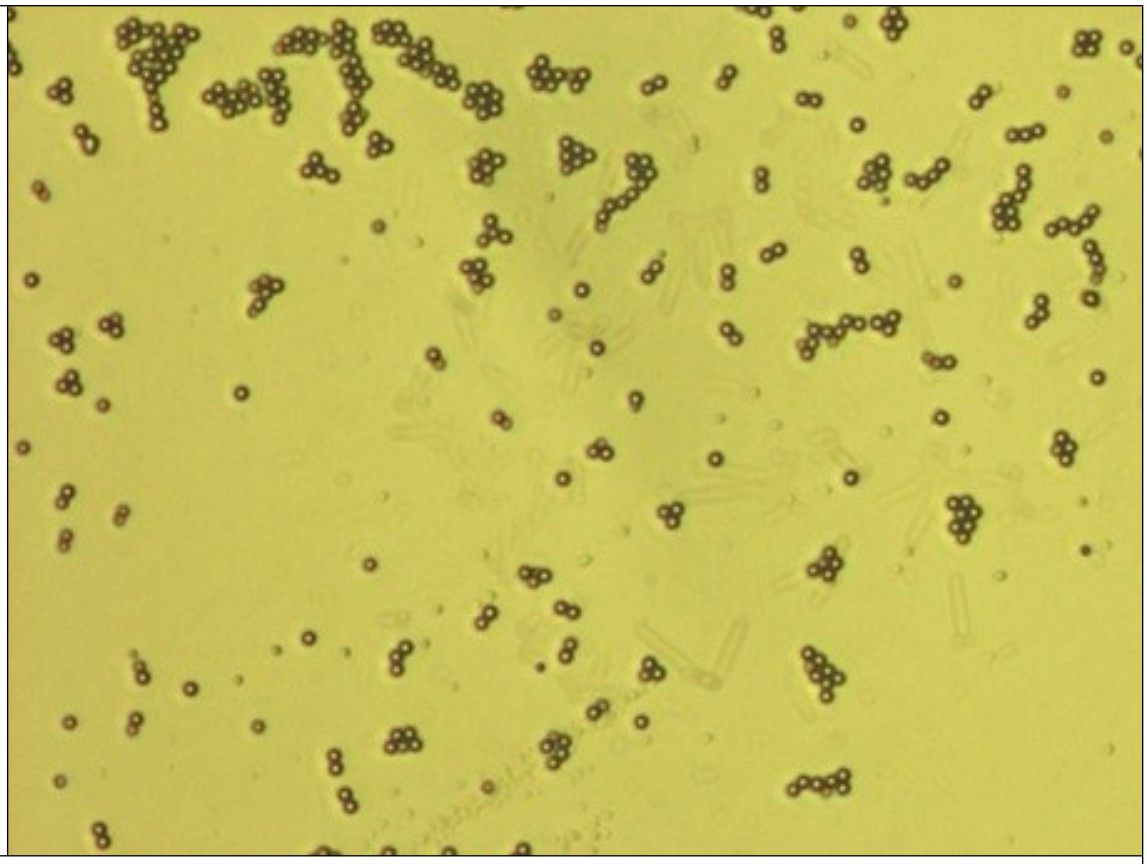
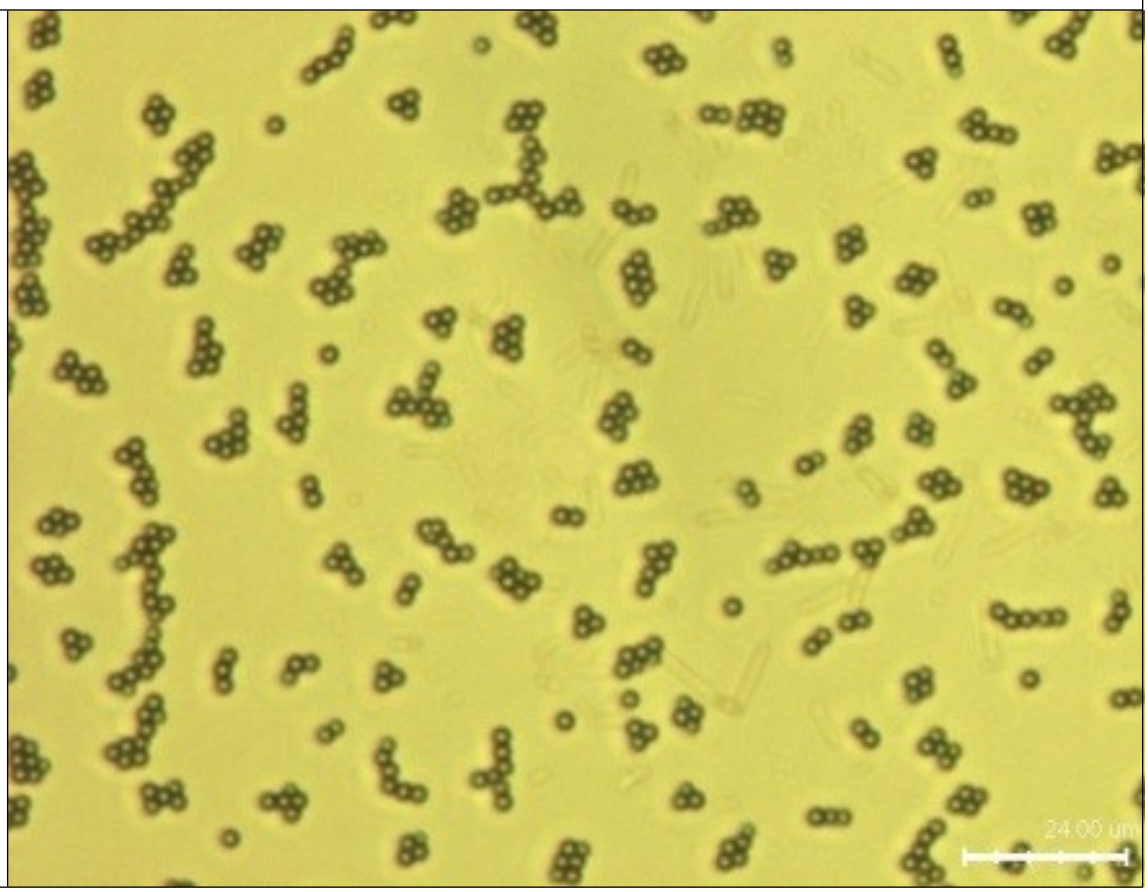


Fig. S4 Uptake of TH by TH-mip-PP, TH-nip-PP, TH-mip-RPP and TH-nip-RPP MSs. The MS concentration was 5 mg mL^{-1}. The TH concentration (in pure ACN) was 67 µM.

5. Optical microscope measurement

Time	mip-RPP MSs
15 min	
30 min	

1 h	
2 h	

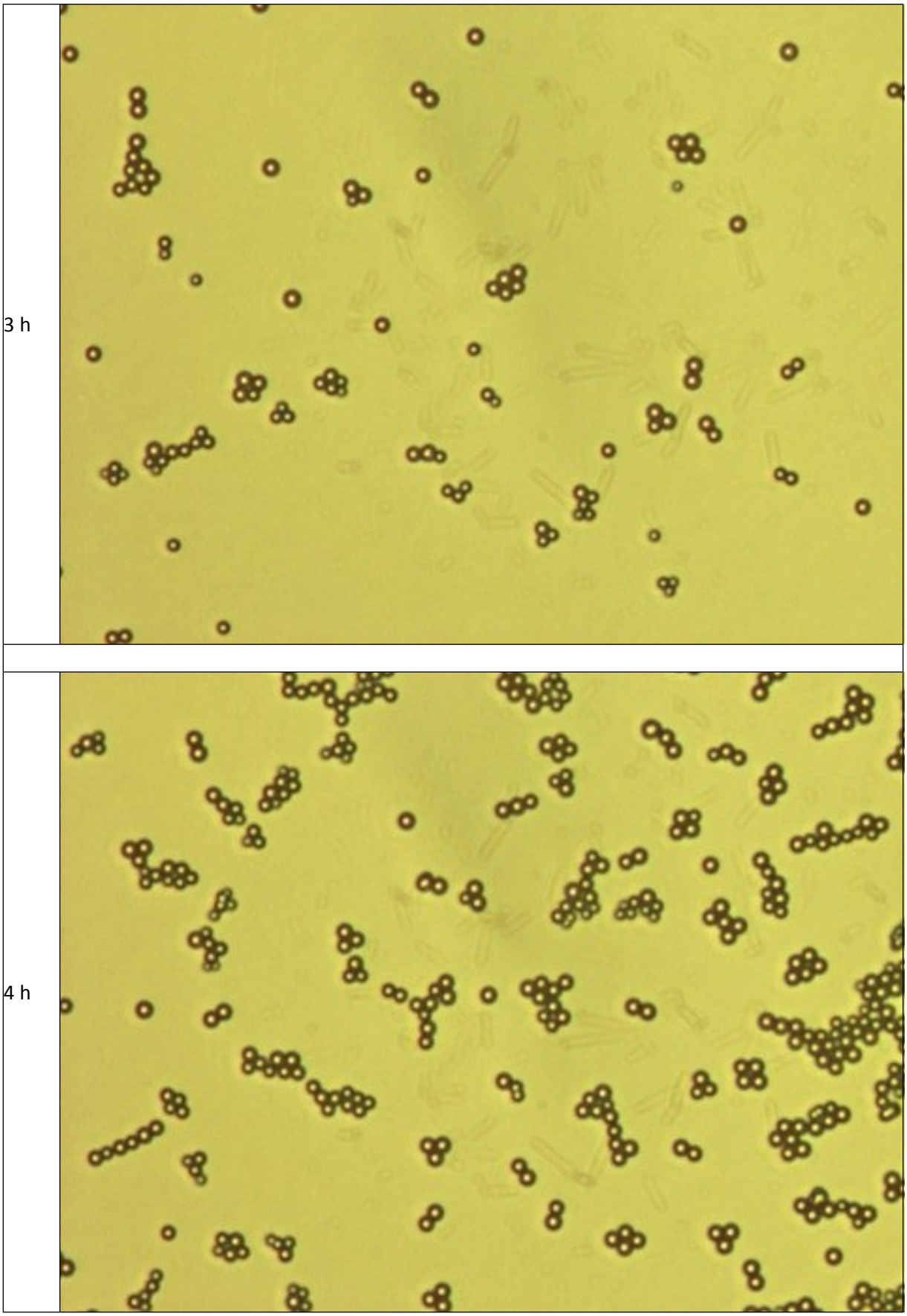


Fig. S5 Optical microscope images of the mip-RPP MSs synthesized with different polymerization time. The scale bar for all images is the same, as presenting in mip-RPP MSs (2 h) (with a diameter of 1.8±0.1 μm, confirmed by SEM in Fig. 1).

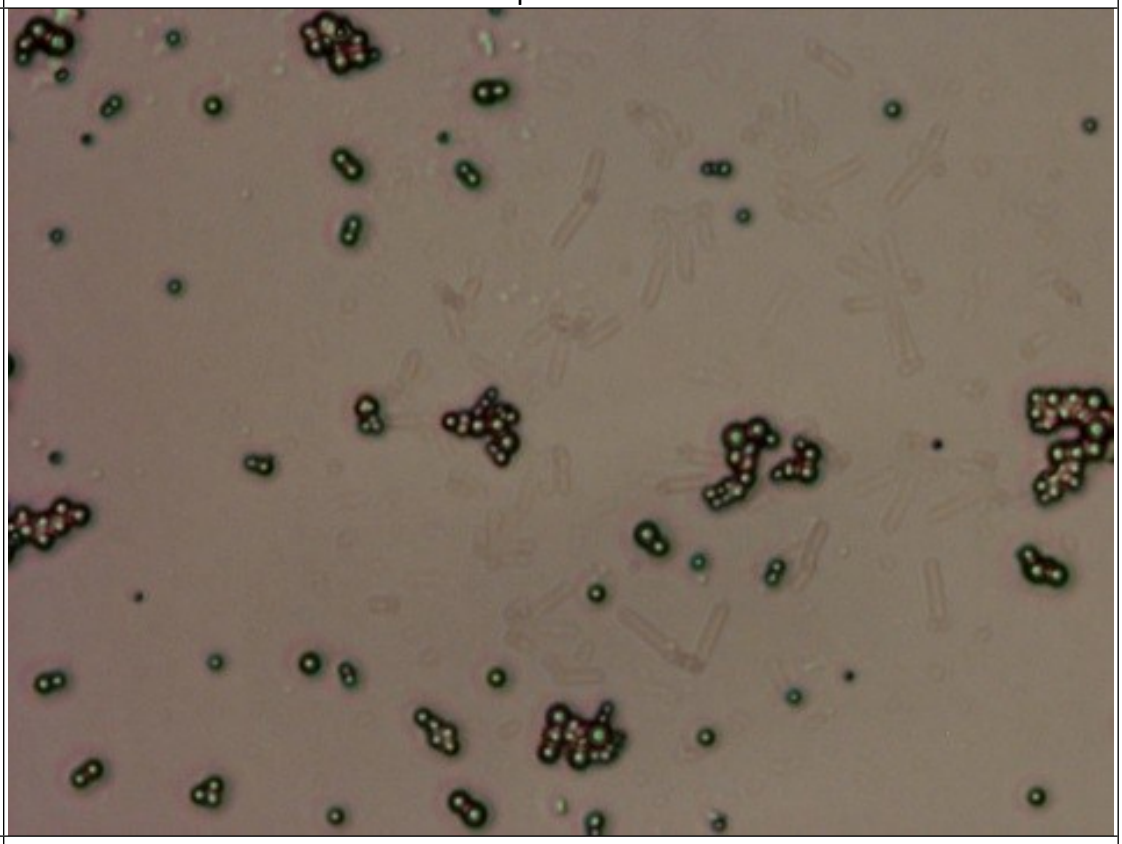
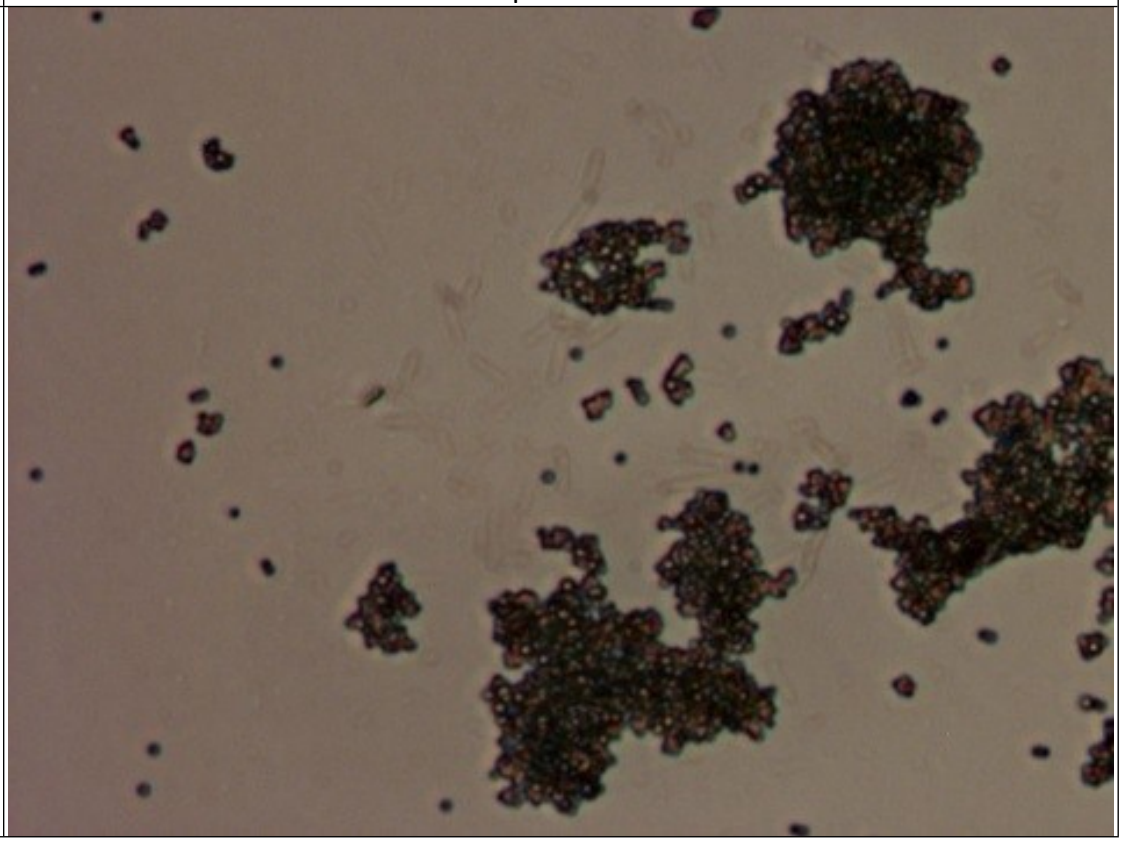
Time	mip-PP MSs
24 h	
Time	nip-PP MSs
24 h	

Fig. S6 Optical microscope images of mip-PP and nip-PP MSs MSs. The scale bar is the same as that for mip-RPP MSs (2 h).

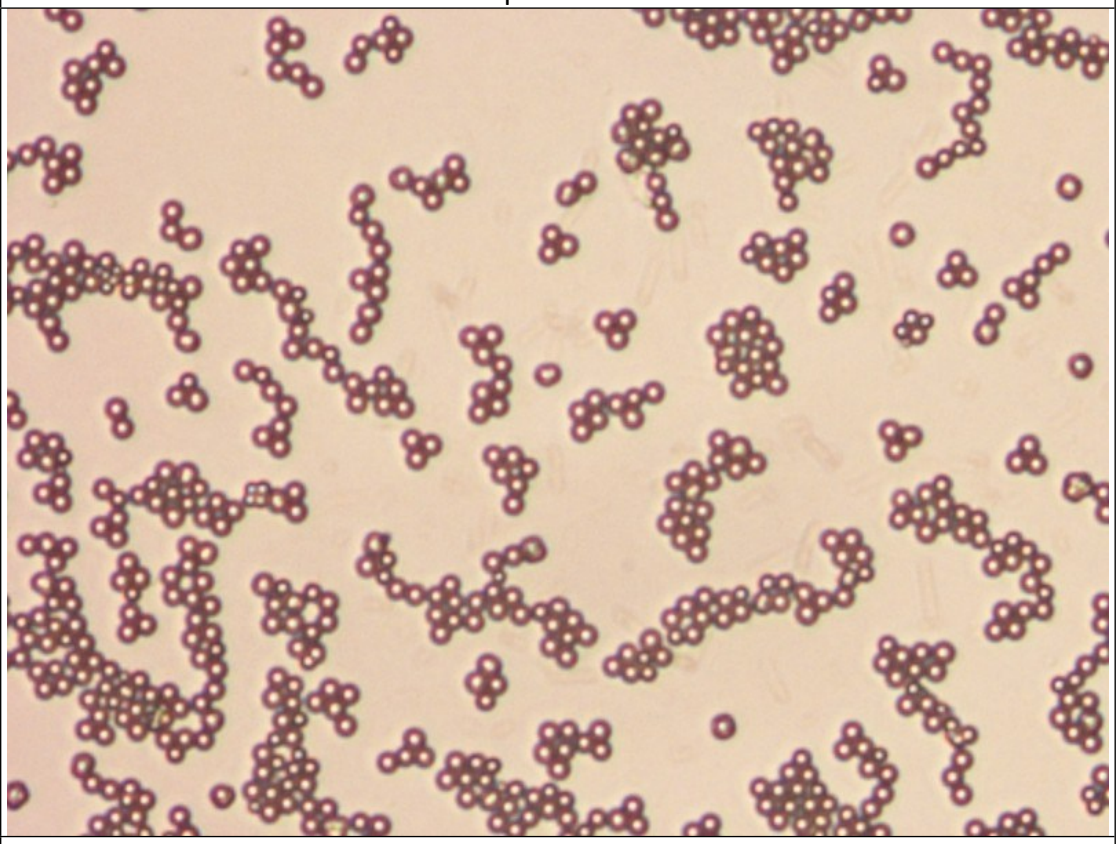
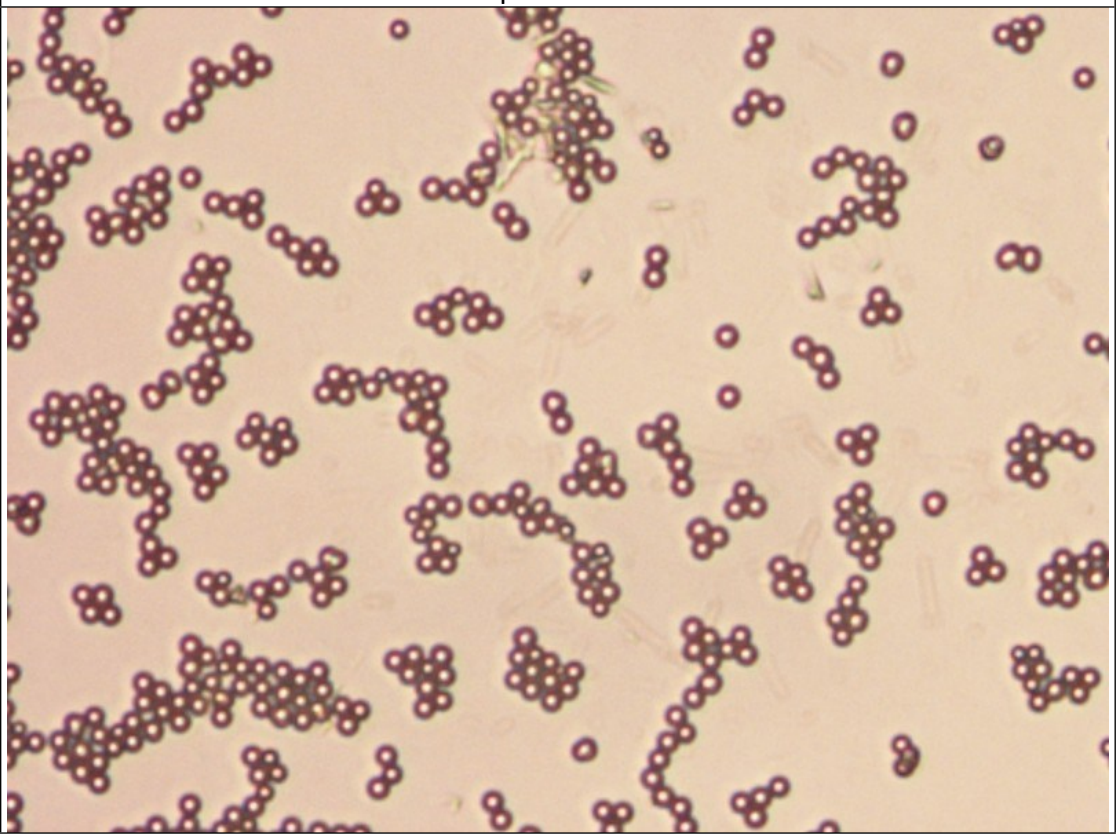
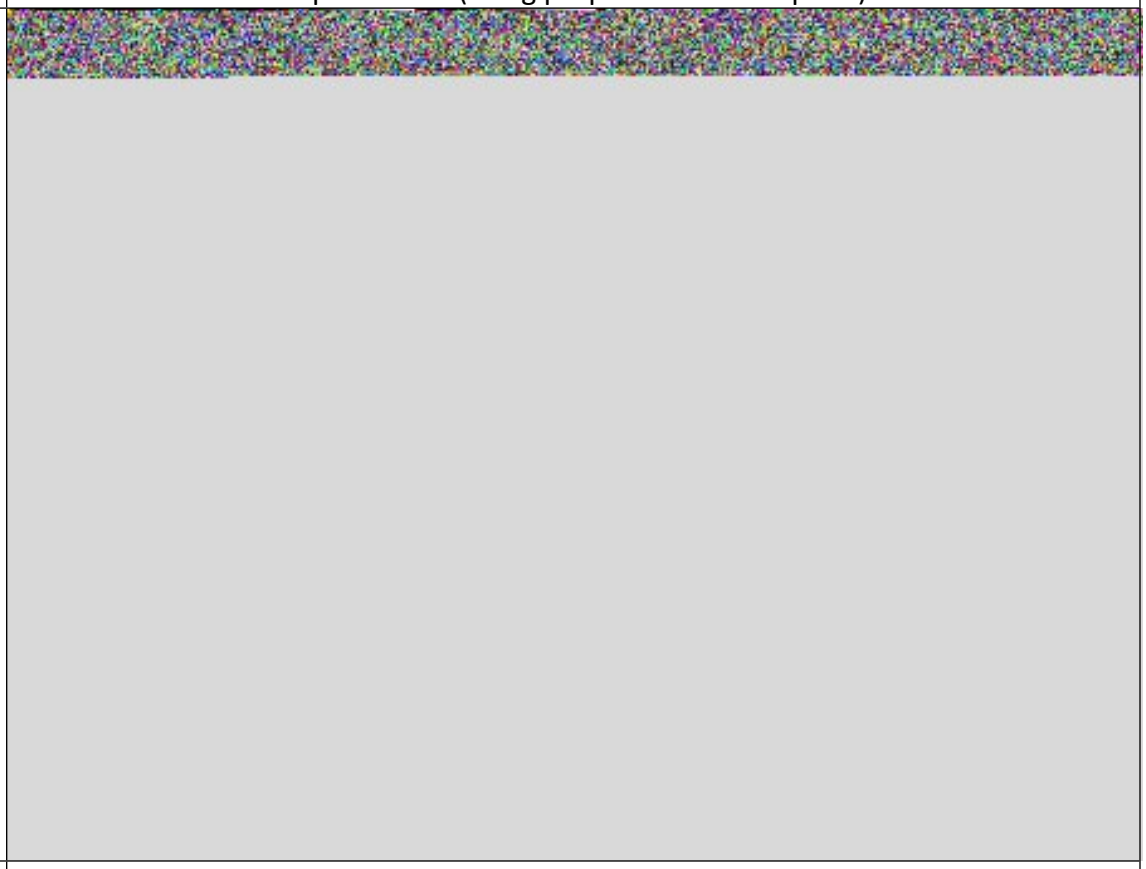
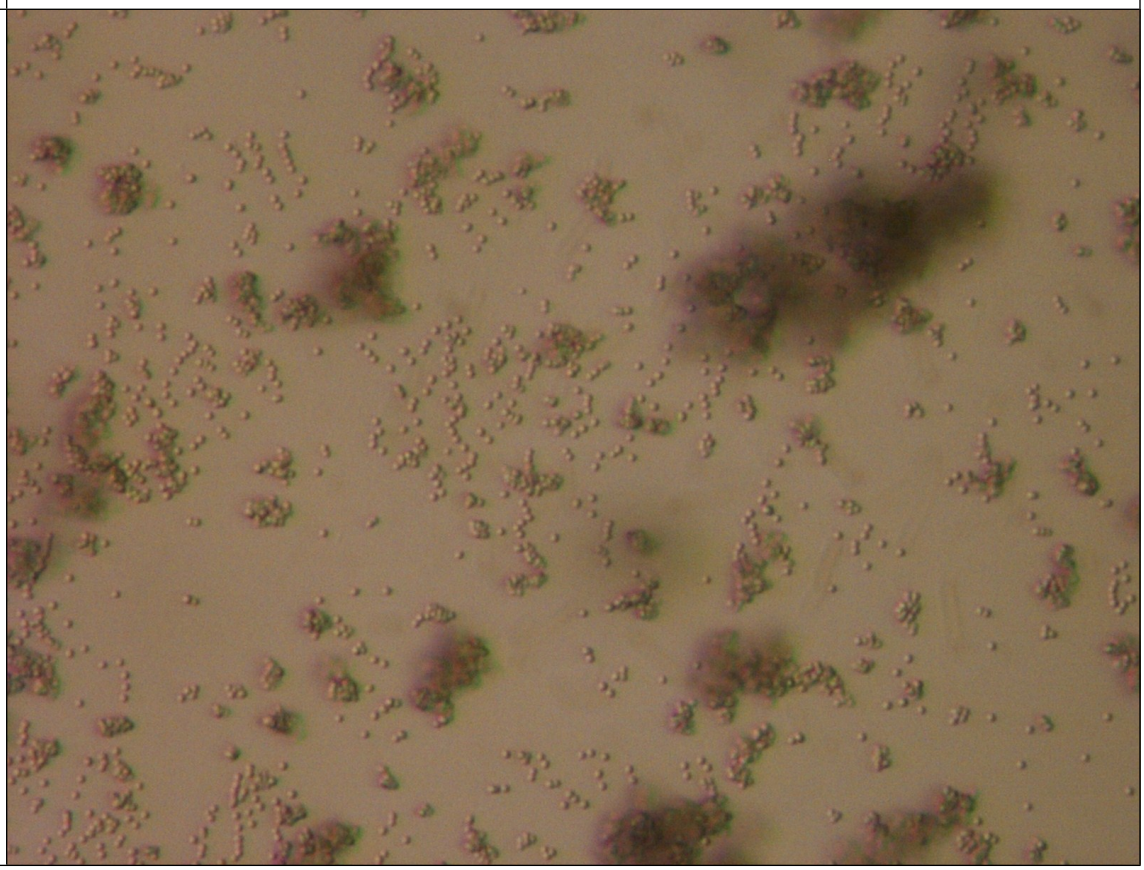
Time	mip-DPP MSs
3 h	
Time	nip-DPP MSs
3 h	

Fig. S7 Optical microscope images of mip-DPP and nip-DPP MSs MSs. The scale bar is the same as that for mip-RPP MSs (2 h).

Time	mip-RPP MSs (using propranolol as template)
2 h	
Time	E2-mip-RPP MSs (using 17 β-estradiol as template)
2 h	

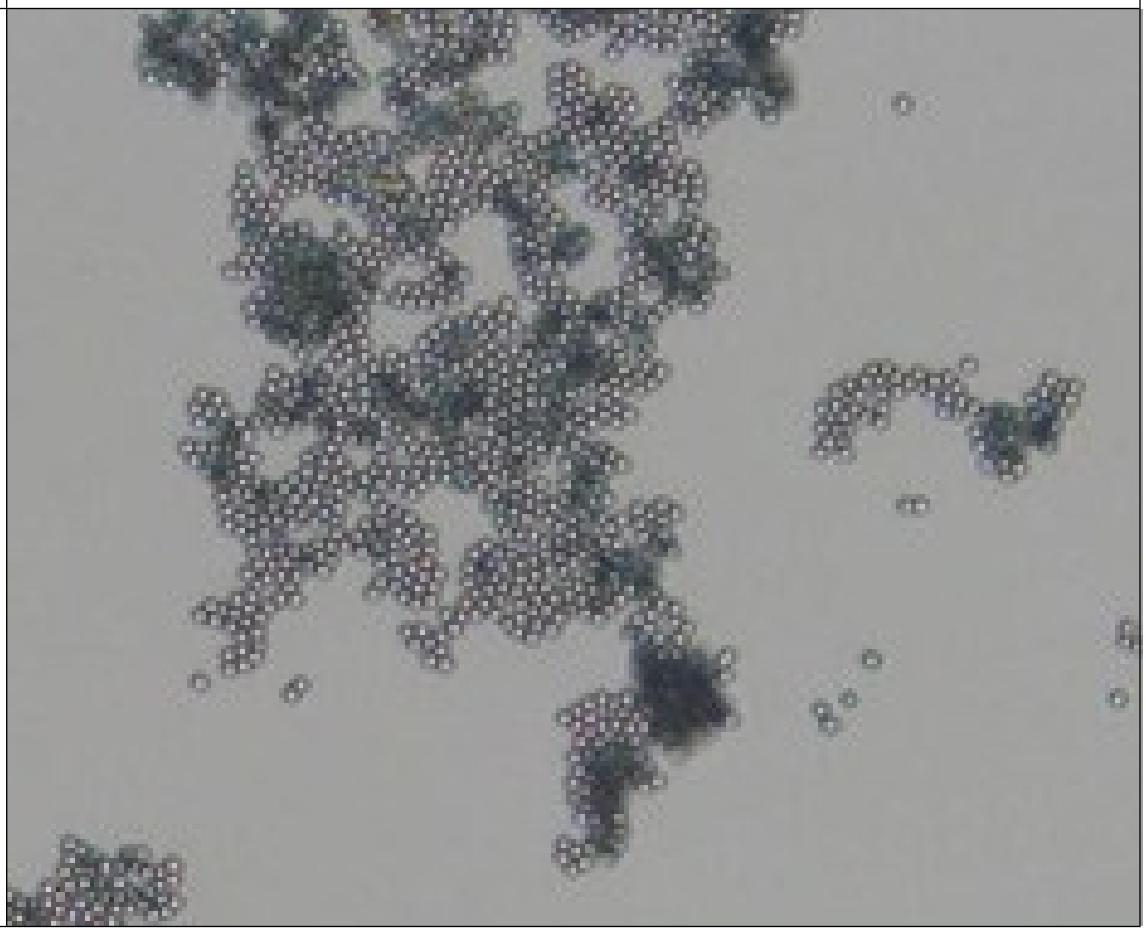
Time	nip-RPP MSs
2 h	

Fig. S8 Optical microscope images of mip-RPP, E2-mip-RPP and nip-PP MSs MSs. The scale bar is the same as that for mip-RPP MSs (2 h).

6. SEM measurement

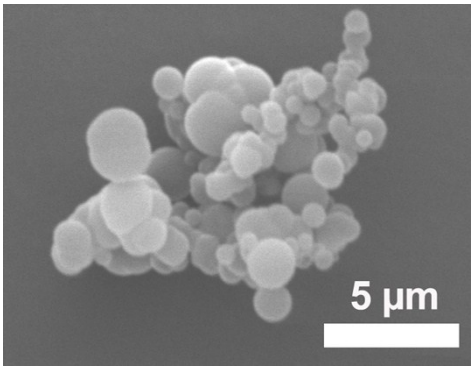


Fig. S9 SEM image of nip-RPP MSs. The image was taken from the dark part of nip-RPP MSs in Fig. S8.

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