

Electronic Supplementary Information (ESI)

A simple method for preparation of molecularly imprinted nanofiber materials with signal transduction ability

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1. Preparation of molecularly imprinted nanoparticles and control nanoparticles

Molecularly imprinted nanoparticles were synthesized using a precipitation polymerization method.¹ Briefly, (*R,S*)-propranolol in its free base form (137 mg, 0.53 mmol) was dissolved in 40 ml of acetonitrile in a 150 mm × 25 mm borosilicate glass tube equipped with a screw cap. Methacrylic acid (113 mg, 1.31 mmol), trimethylolpropane trimethacrylate (684 mg, 2.02 mmol) and azobisisobutyronitrile (28 mg, 3 wt% of monomer) were then added. The solution was purged with a gentle flow of argon for 5 min and sealed under argon. Polymerization was carried out by inserting the borosilicate glass tube in a water bath pre-set to 60 °C for 24 h. After polymerization, particles were collected by centrifugation. The template was removed by batch-mode solvent extraction with methanol containing 10% acetic acid (v/v), until no template could be detected from the washing solvent by spectrometric measurement. Polymer particles were finally washed with acetone and dried in a vacuum chamber. A non-imprinted control polymer (control nanoparticles) was synthesized under identical condition except for omission of the template.

2. Electrospinning

Electrospinning of composite nanofiber was carried out at room temperature at a high voltage of 20 kV (HV Power Supply, Gamma High Voltage Research, Ormond, FL). The spinneret used in the experiments had an inner diameter of 0.8-0.9 mm. A grounded aluminum foil was used as the counter electrode and mounted at a distance of 15-25 cm from the spinneret. Continuous composite fibers were collected on the aluminium foil in the form of a fibrous mat. In preliminary tests, methyl ethyl ketone (MEK) was found to be a suitable solvent for electrospinning PS nanofibers. Moreover, to improve the uniformity of the PS and DPA-doped PS nanofibers, a non-ionic surfactant, Triton X-100 was added in the initial electrospinning solution. Polystyrene (M_w: 230,000 g mol⁻¹), DPA, Triton X-100 were dissolved in methyl ethyl ketone, followed by addition of nanoparticles. The suspension obtained contained 12.5 wt% polystyrene. The DPA content was 8% and the nanoparticle

content was 50%, both based on the weight of polystyrene. Triton X-100 content was 0.6% of the total weight. The suspension was stirred for 10 min, sonicated for 20 min and once again vigorously stirred for 10 min before electrospinning. The nanofiber mats obtained were dried in a vacuum chamber for at least 24 h. **Figure S1** shows an SEM image of DPA-doped PS nanofibers without nanoparticles.

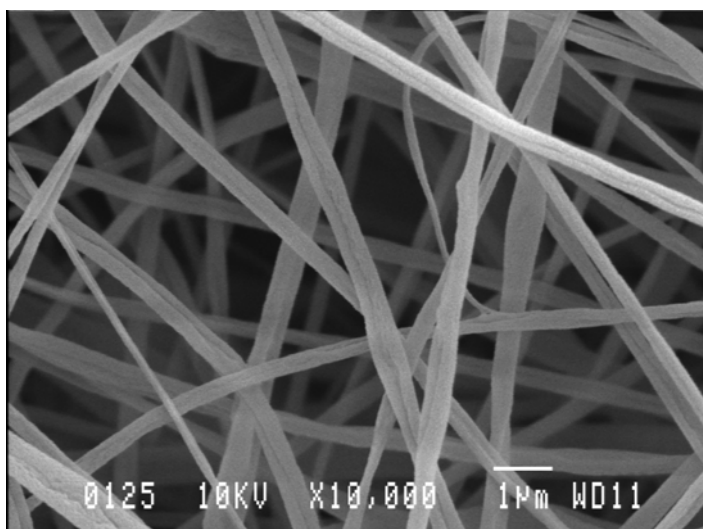


Figure S1. SEM image of electrospun PS nanofibers doped with DPA.

3. Proximity scintillation measurement

The proximity scintillation counting was measured using β -radiation counter Rackbeta 1219 (LKB Wallac, Sollentuna, Sweden). In a series of polypropylene microcentrifuge tubes, nanofiber mat was immersed in a mixture of 25 mM citrate buffer (pH 6.0):acetonitrile (50:50, v/v). ^3H -labeled (*S*)-propranolol (0.246 pmol, specific activity: 555 GBq mmol⁻¹, NEN Life Science Products, Inc. Boston, MA, USA) was added and the volume topped with the same solvent to 1 mL. The microcentrifuge tubes were incubated at room temperature overnight. A rocking table ensured gentle mixing. After incubation, the tubes were transferred into 6-mL insert counting vials and placed in 20-mL standard counting vials and counted for 1 min. Each sample was measured three times and the error bar is standard deviation of triplicate measurements.

4. Liquid scintillation measurement

From each of the microcentrifuge tubes used in proximity scintillation counting, 500 μl of supernatant was taken and mixed with 10 ml of liquid scintillation cocktail, Ecoscint A (National Diagnostics, Atlanta, GA, USA) in 20-mL standard counting vials. Liquid scintillation counting was performed using the same equipment as described above. The

amount of bound ^3H -labeled (*S*)-propranolol was calculated by subtracting the free amount from the total amount added. The results obtained are shown in **Figure S2**.

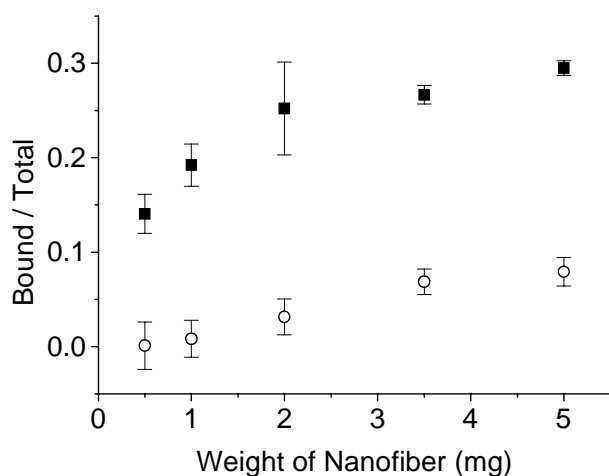


Figure S2. The ratio of Bound ^3H -labelled (*S*)-propranolol vs. the amount of nanofiber used as determined by liquid scintillation counting. The initial concentration of the ^3H -labelled (*S*)-propranolol was 0.246 nM.

5. Scintillation proximity assay in dilute urine sample

Human urine sample (100 μl) was spiked with (*R*)- and (*S*)-propranolol hydrochloride. This was diluted with 400 μl of 25 mM citrate buffer (pH 6.0) containing ^3H -labelled (*S*)-propranolol (0.246 pmol), and then mixed with 500 μl of acetonitrile. The pH of the final solution was around 6.2. Proximity scintillation counting for the samples were carried out as described in **Section 3**.

1. K. Yoshimatsu, K. Reimhult, A. Krozer, K. Mosbach, K. Sode, L. Ye, *Anal. Chim. Acta*, 2007, **584**, 112.