

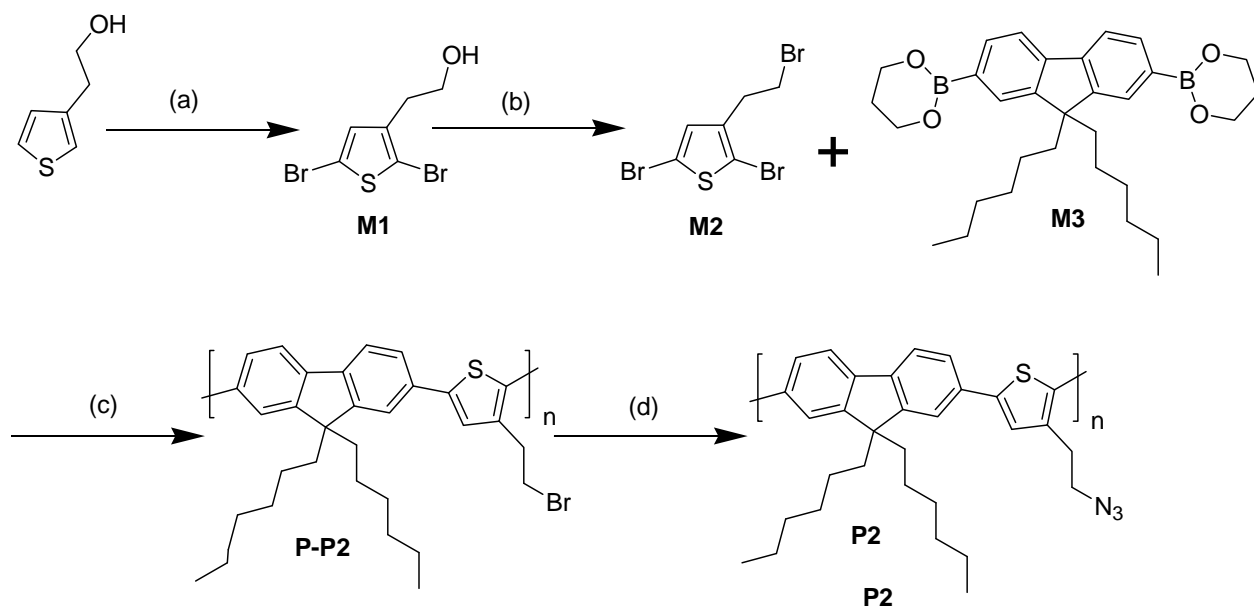
Supporting Information

Facile synthesis of cross-linked patchy fluorescent conjugated polymer nanoparticles by click reaction

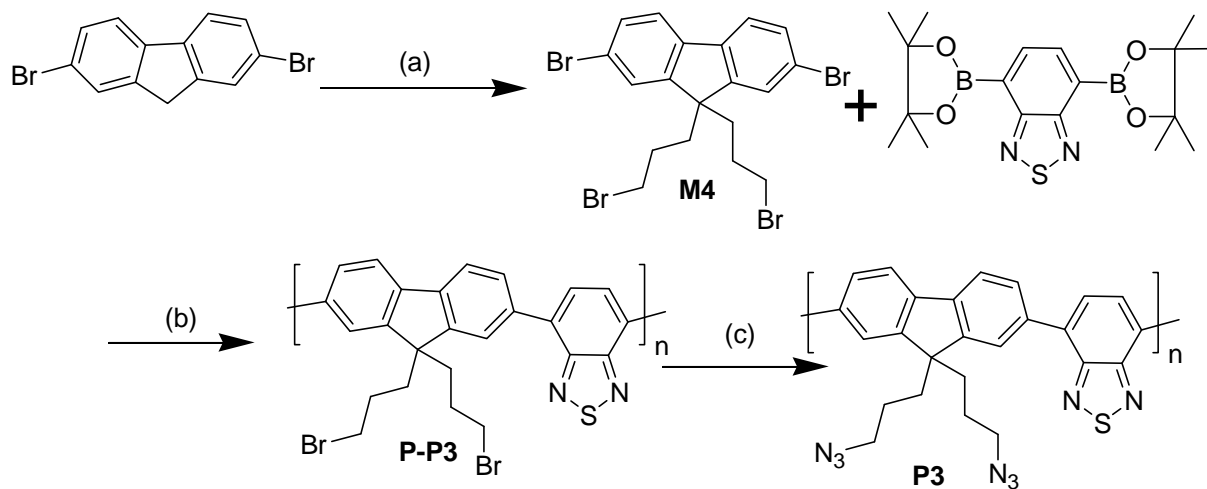
Vusala Ibrahimova, Seyma Ekiz, Özlem Gezici
Dönüs Tuncel*

Department of Chemistry and Institute of Materials Science and Nanotechnology, Bilkent
University, Ankara, 06800, Turkey
E –mail: dtuncel@fen.bilkent.edu.tr

Experimental Section



Scheme S1: Synthesis of conjugated polymer used in the preparation of nanoparticles. (a) NBS, DMF, 40 °C, 12 h, 64%, (b) PPh₃, CBr₄, THF, 12h, 35%, (c) Pd(PPh₃)₄, K₂CO₃, THF/H₂O, 80 °C, 48 h, 59%, (d) NaN₃, DMF, 90 °C 24 h, 87%.



Scheme S2: Synthesis of conjugated polymer used in the preparation of nanoparticles. (a) 1,3-dibromopropane, 50% NaOH (aq), DMSO, TBAB, 2h, RT, 67%, (b) Pd(PPh₃)₄, K₂CO₃, THF/H₂O, 80 °C, 48 h, 56%, (c) NaN₃, DMF, 90 °C 24 h, 80%.

Synthesis of 2-(2,5-dibromothiophen-3-yl)ethanol (M1)

M1 was synthesized by the modification of literature procedure.²⁴

A mixture of 2-(3-thienyl)ethanol (2.5 g, 0.02 mol) and N-bromosuccinimide (NBS) (7.1 g, 0.04 mol) was dissolved in DMF (25mL). The reaction flask was covered in aluminum foil and the resulting mixture was stirred at 40 °C under nitrogen for 12h. After the mixture was cooled to RT, diethyl ether was added and washed with water three times. The combined organic fractions were dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. Purification was done by silica packed column chromatography using hexane as an eluent. **Yield:** 64%

¹H NMR (400 MHz, CDCl₃, δ): 6.92 (s, 1H), 3.81 (t, ³J = 6.4 2H), 2.80 (t, ³J = 6.4 2H), 1.93 (s, 1H).

Synthesis of 2,5-Dibromo-3-(2-bromoethyl)thiophene (M2)

M1 was synthesized by the modification of literature procedure.²⁴

A mixture of M1 (4.5 g, 12.8mmol) and PPh₃ (4.03 g, 15.4mmol) was dissolved in 10mL THF and cooled under ice bath. To this mixture was added CBr₄ (5.1g, 15.4mmol) in 5 mL THF dropwise. The mixture was stirred for 12h under nitrogen. Then solvent was removed and the residue was washed with dichloromethane and water. Organic layer was washed with brine, dried over Na₂SO₄. Purification was done by silica packed column chromatography using hexane as an eluent. **Yield:** 34%

¹H NMR (400 MHz, CDCl₃, δ): 6.88 (s, 1H), 3.51 (t, ³J = 7.6, 2H), 3.12 (t, ³J = 7.6 2H).

Synthesis of 2,7-Dibromo-9,9-bis-(3-bromo-propyl)-9H-fluorene (M4)

M4 was synthesized according to literature procedure.²³

2,7-dibromofluorene (3.0 g, 9.25 mmol) and tetrabutylammoniumbromide (TBAB) (0.6 g, 1.85 mmol) were dried under vacuum 30 min. Degassed DMSO (15 mL), 50% (w/w) NaOH (15 mL), 1,3-dibromopropene (13 ml, 90 mmol) were added into the mixture respectively and stirred under argon gas for two hours at room temperature. After two hours, t-butyl methyl ether (125 mL) and deionized water (50 mL) were added into the mixture and stirred 15 min. Organic layer was separated and subsequently washed with deionized water (50 ml), 2N HCl (50 ml), brine solution (50 mL) and deionized water (50 mL) respectively. After extraction, t-butyl methyl ether was evaporated by rotary evaporator and the monomer was obtained. For the purification of the product, silica-packed column chromatography was used and cyclohexane and chloroform

mixture (80:20) was used as an eluent. The solid was further purified by dissolving in CHCl_3 , precipitating into cold methanol. Colorless crystals were collected and dried under vacuum.

Yield: 67 %

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.53 (m, 6 H, Ar-H), 3.14 (t, 4H, CH_2Br , $^3J=6.4$), 2.17 (t, 4H, $-\text{CH}_2\text{CH}_2\text{Br}$, $^3J=6.4$), 1.16 (m, 4H, $-\text{CH}_2-$).

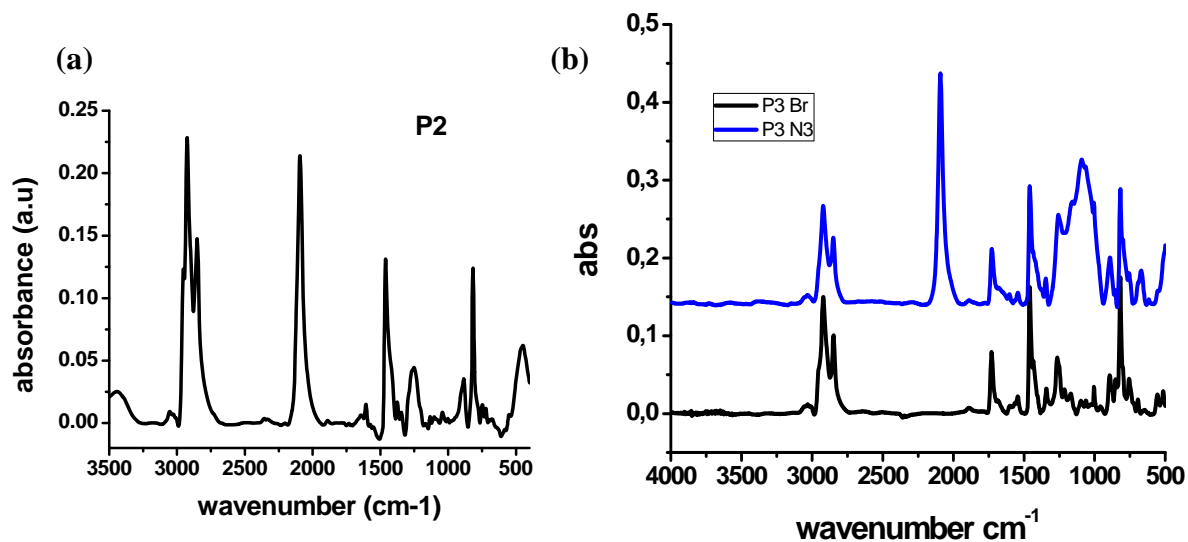
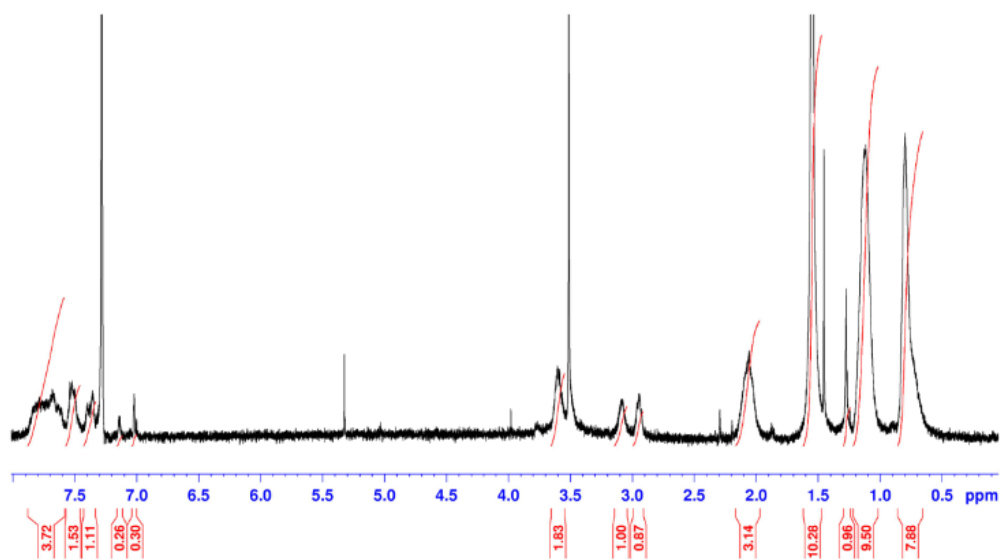


Figure S1: FTIR spectra of (KBr pellets) (a) poly[(9,9-dihexylfluorene)-co-alt-(2,5-(3-azidoethylthiophene), (b) poly[(9,9-dibromopropane-9H-fluorene)-co-alt-(benzothiadiazole)] and poly[(9,9-diazidopropane-9H-fluorene)-co-alt-(benzothiadiazole)].

(a)



(b)

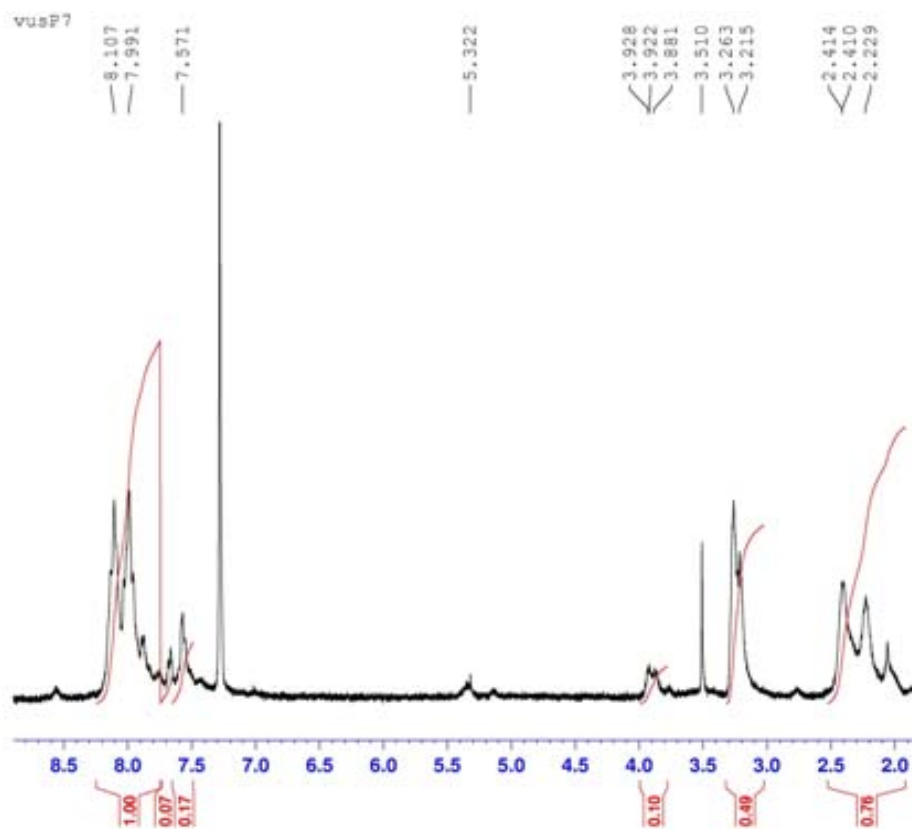
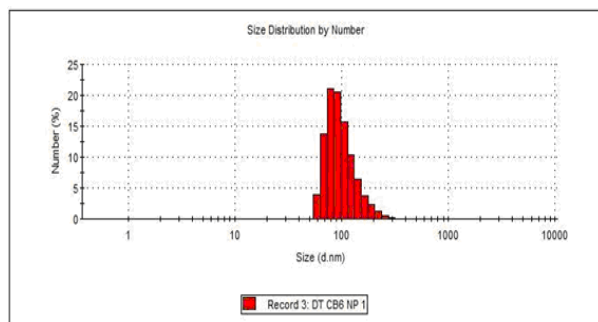
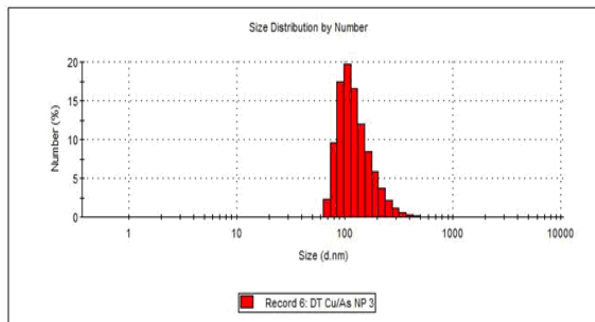


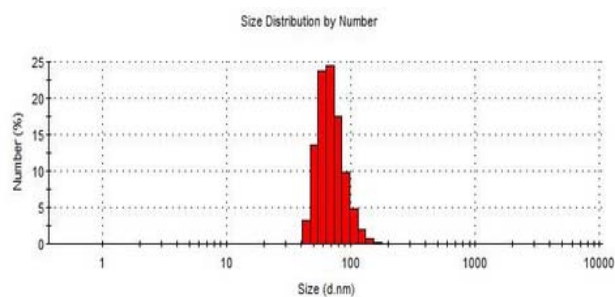
Figure S2: $^1\text{H-NMR}$ spectra of the polymers **(a)** poly[(9,9-dihexylfluorene)-co-alt-(2,5-(3-azidoethylthiophene **(b)** poly[(9,9-diazidopropane-9H-fluorene)-co-(benzothiadiazole)]



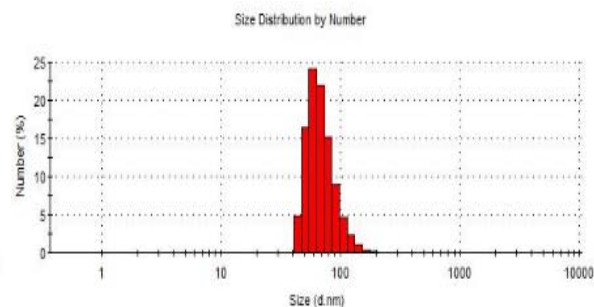
a)



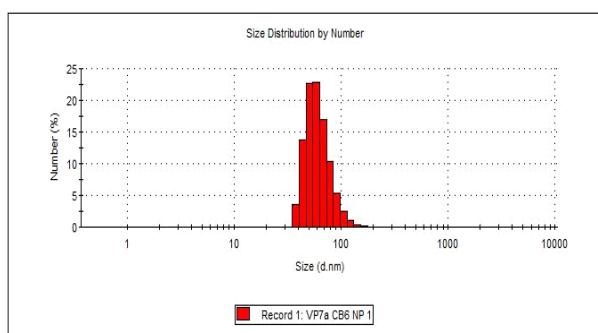
b)



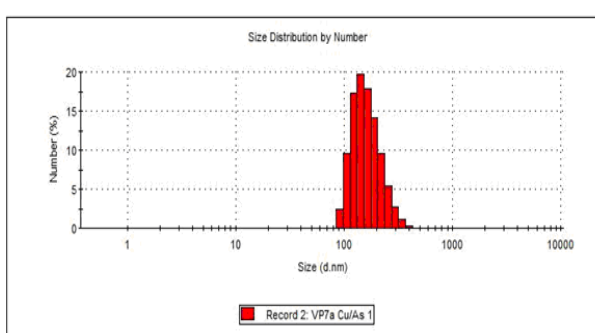
c)



d)



e)



f)

Figure S3: Dynamic light scattering results **a)** P1 CPN-**b)** P1 CPN-a **c)** P2 CPN-**d)** P2 CPN-a
e) P3 CPN-**f)** P3 CPN-a

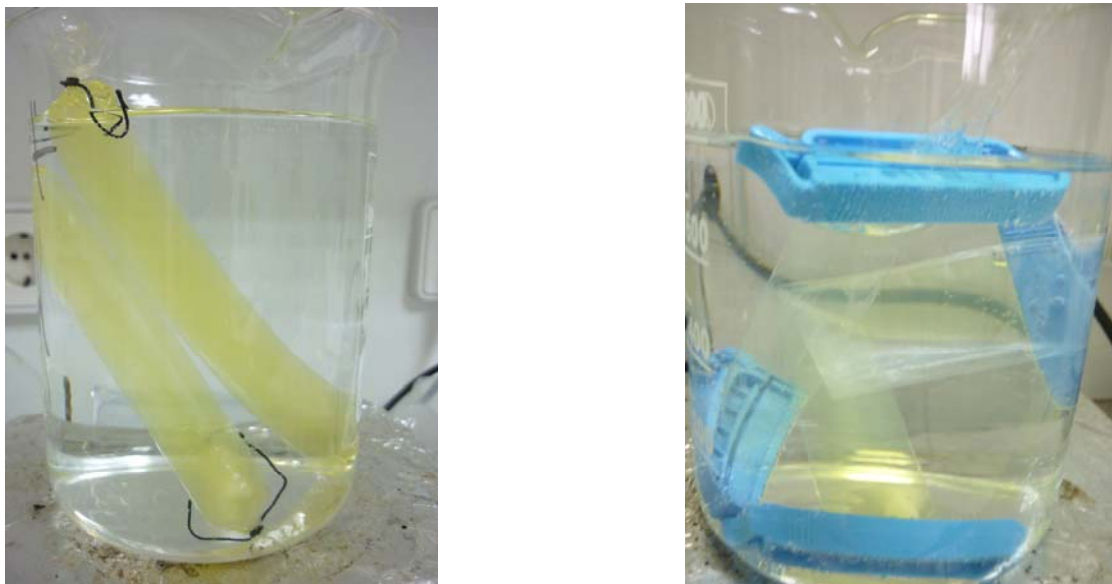


Figure S4: The aqueous dispersion of nanoparticles in the dialysis tubes in a beaker filled with water.

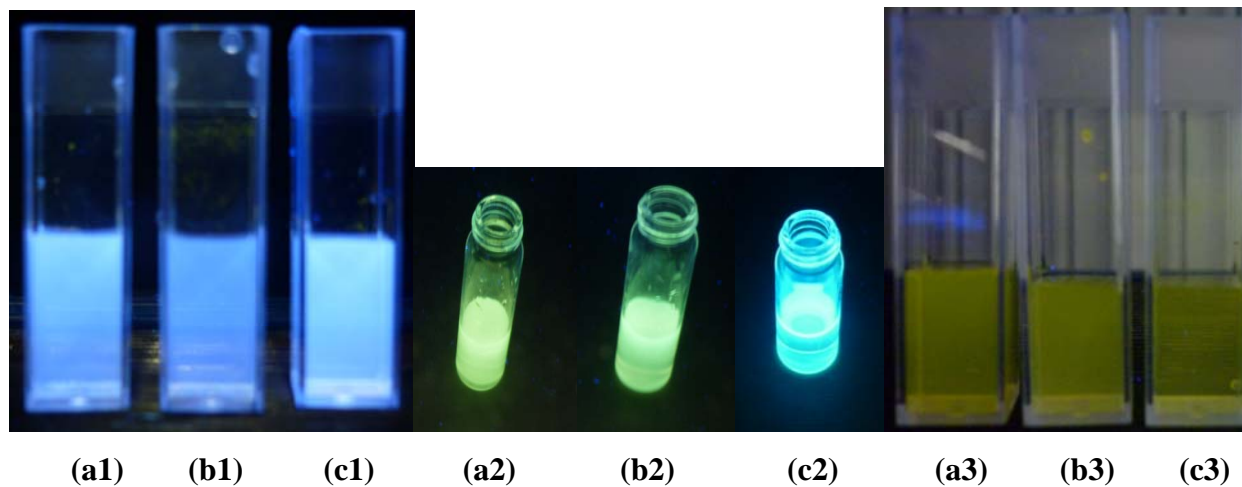


Figure S5: Images of nanoparticle dispersions under 366nm light (a1) P1-CPN-b (b1) P1-CPN-a (c1) P1 (a2) P2-CPN-b (b2) P2-CPN-a (c2) P2 (a3) P3-CPN-b (b3) P2-CPN-a (c3) P3

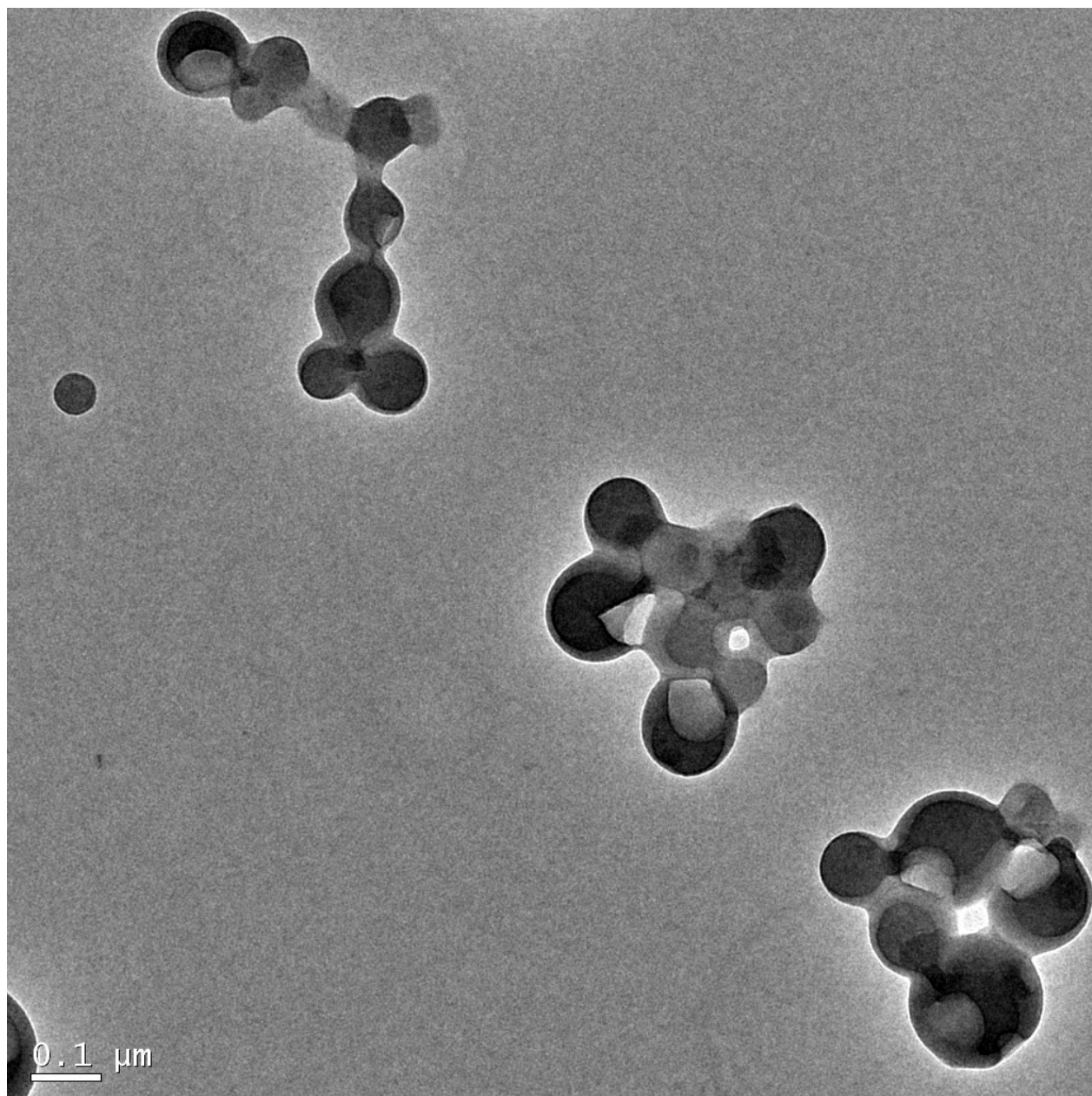


Figure S6: TEM image of P1-CPNa

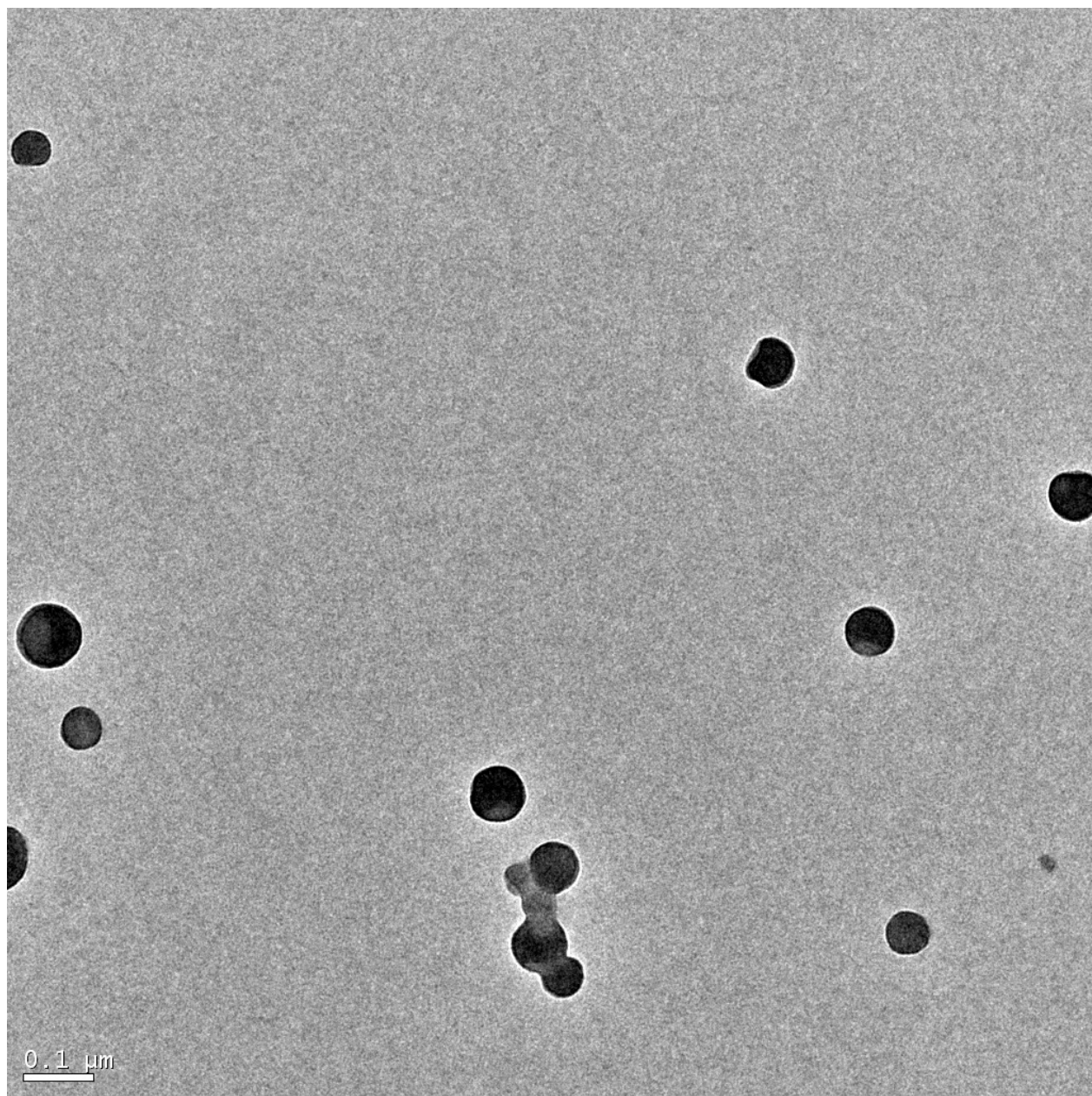


Figure S7: TEM image of P1-CPNb

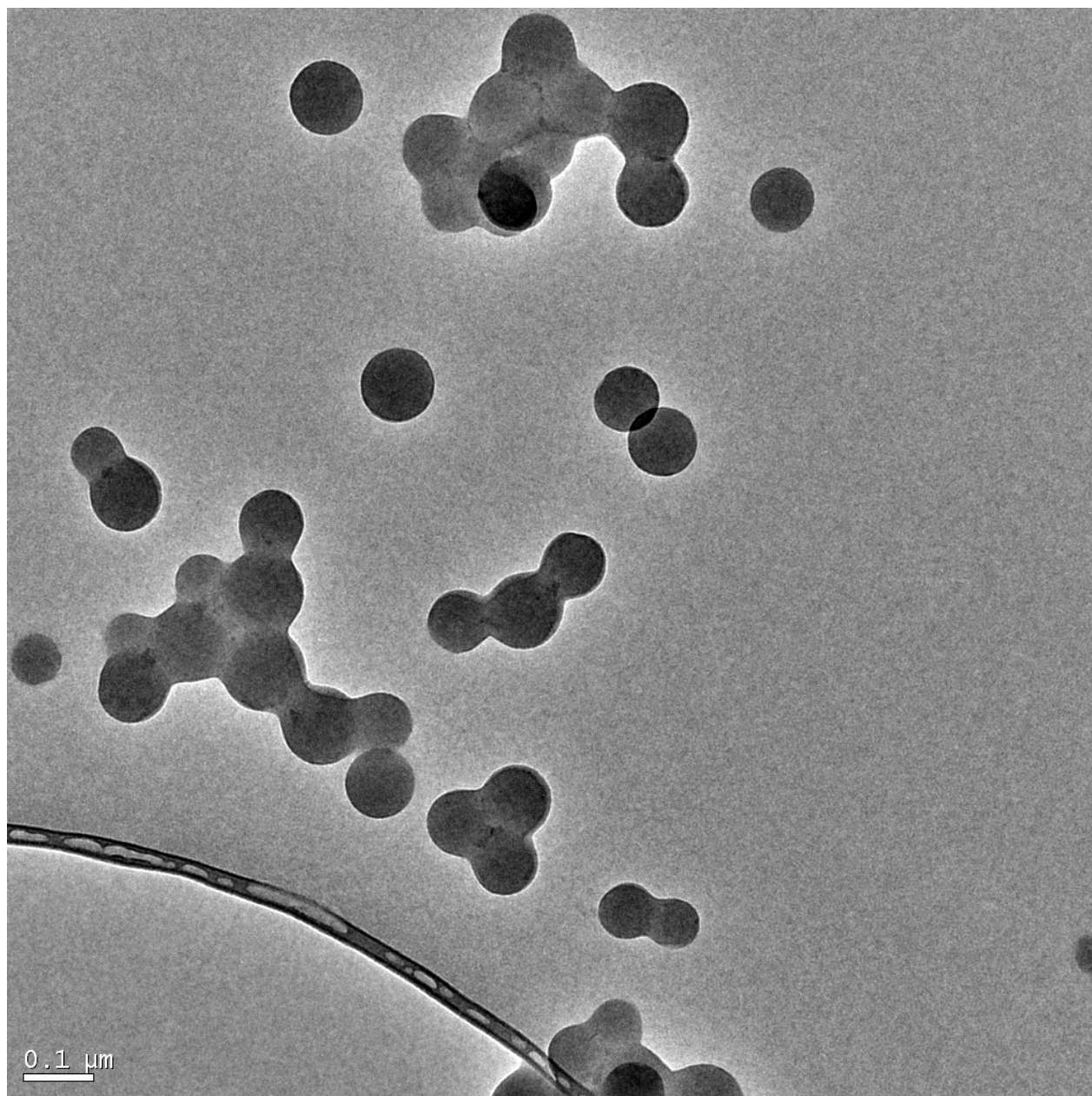


Figure S8: TEM image of P2-CPNa

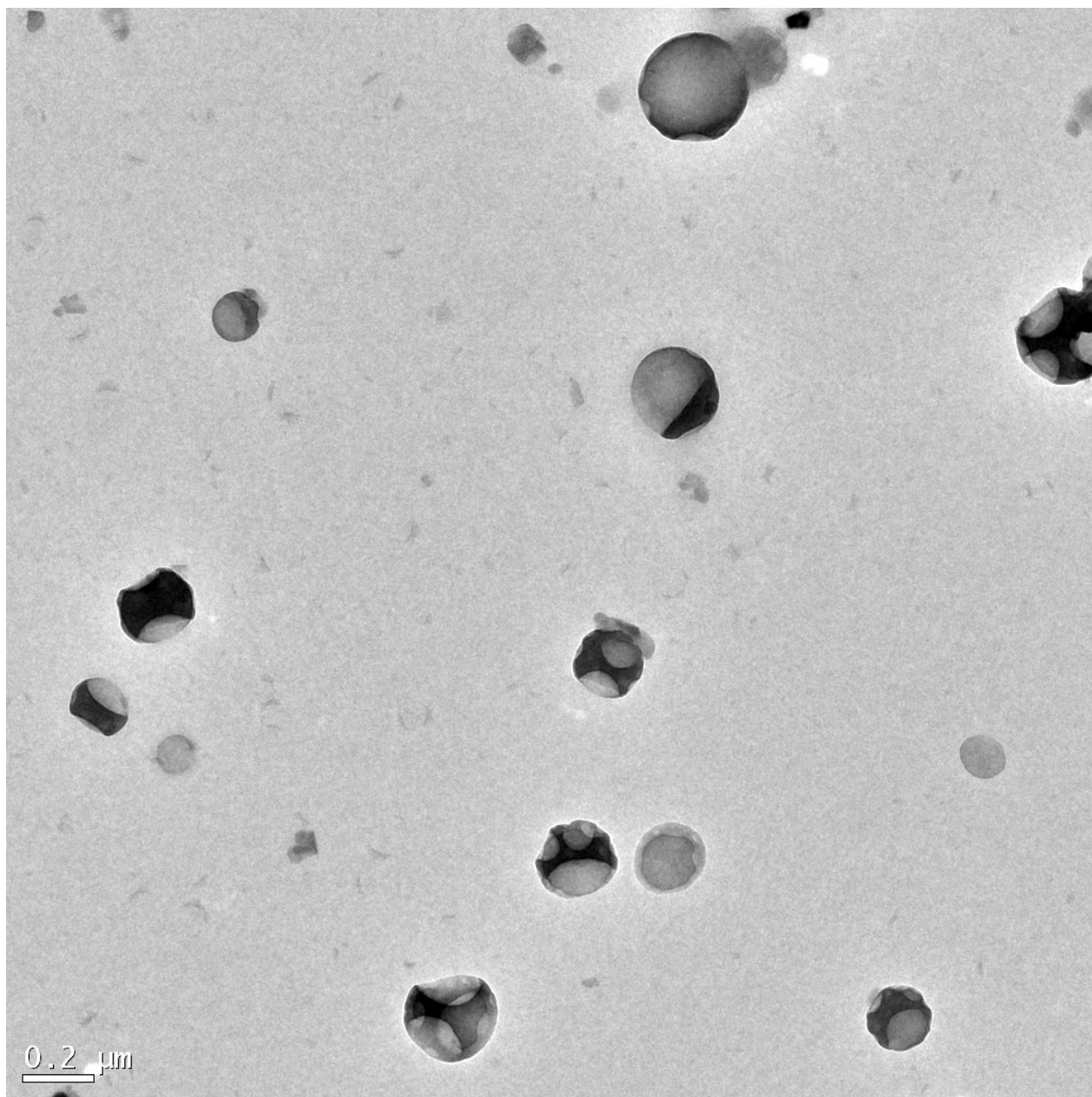


Figure S9: TEM image of P3-CPNa

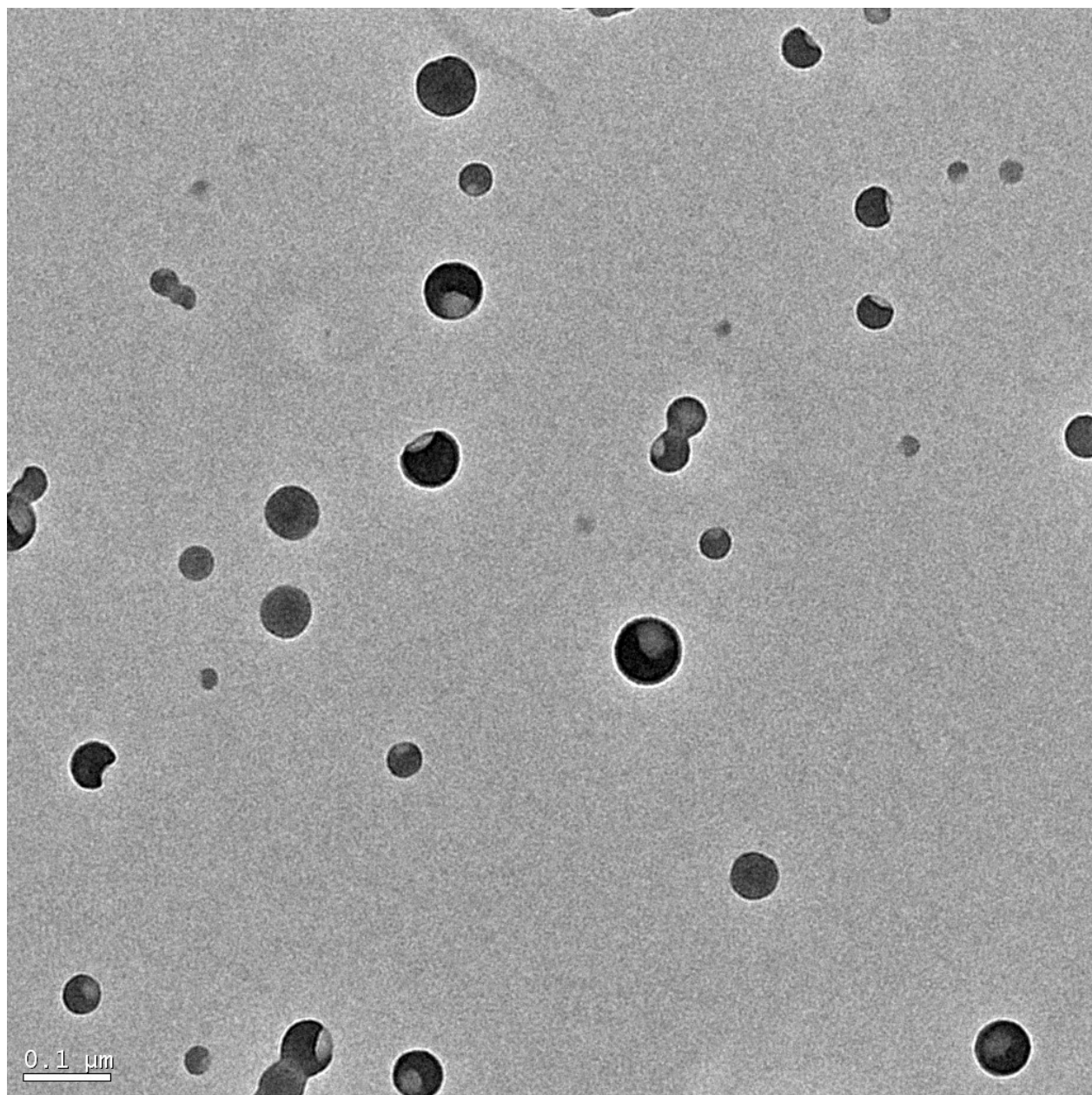


Figure S10: TEM image of P3-CPNb

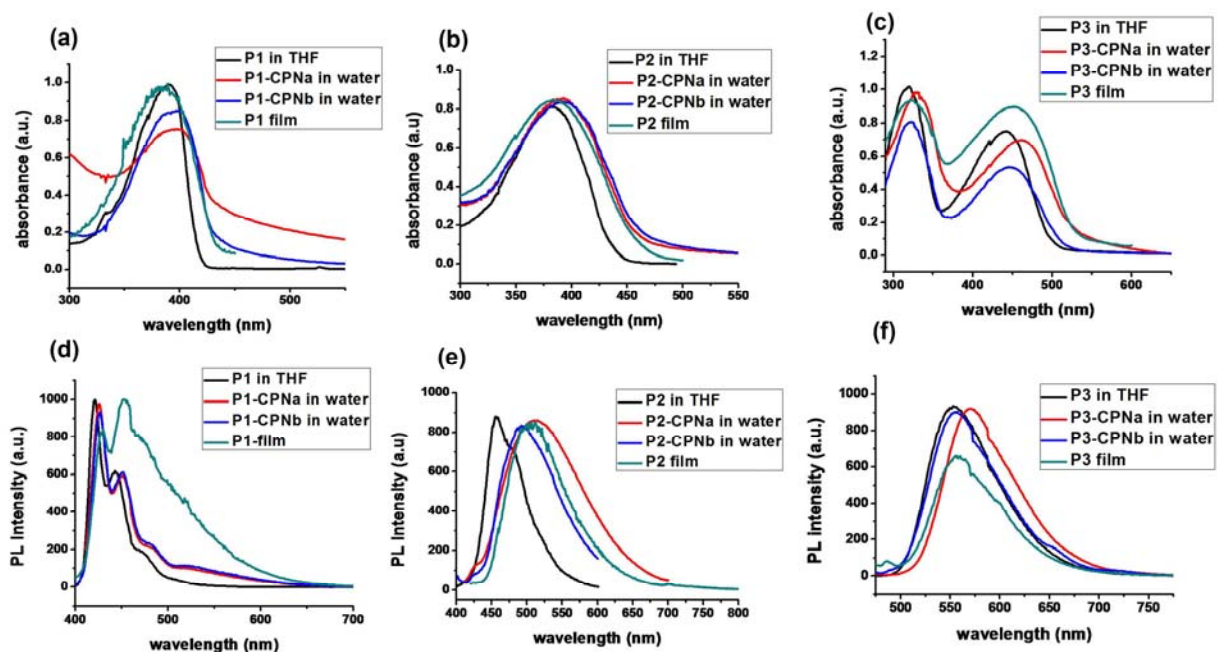


Figure S11: UV-Vis absorption spectra of **P1-P3** in THF, in film, dispersions of nanoparticles in water (**P1-CPNa**, **P2-CPNa**, **P3-CPNa**, **P1-CPNb**, **P2-CPNb**, **P3-CPNb**) (a, b, c) and emission spectra of **P1-P3** in THF, in film, dispersions of nanoparticles in water (**P1-CPNa**, **P2-CPNa**, **P3-CPNa**, **P1-CPNb**, **P2-CPNb**, **P3-CPNb**) (d, e, f).