Core-shell poly-methyl methacrylate nanoparticles as effective carriers of electrostatically loaded anionic porphyrin

by

Greta Varchi,* Valentina Benfenati,[‡] Assunta Pistone,[‡] Marco Ballestri, Giovanna Sotgiu, Andrea Guerrini, Paolo Dambruoso, Andrea Liscio and Barbara Ventura.*

Italian National Research Council, Institute for the Organic Synthesis and Photoreactivity, Via P. Gobetti, 101 40129 Bologna E-mail: greta.varchi@isof.cnr.it; Fax: +39 0516398349; Tel: +39 0516398283

Experimental Supplementary Information (ESI)

Contents

1. Additional data on nanoparticles

Table S1. Dynamic Light Scattering Measurements of PMMA-NPs

Run	Angle	KCps	ZAve	Polydispersity	Fit	Time
1	90.0	161.9	54.7	0.400	0.000587	12:07:18
2	90.0	162.0	55.8	0.316	0.000237	12:14:01
3	90.0	161.7	55.7	0.315	0.000255	12:20:45
4	90.0	160.9	55.5	0.310	0.000180	12:27:28
5	90.0	161.3	55.8	0.317	0.000274	12:34:11
Average	**90.0**	**161.5**	**55.5**	**0.331**		
+/-		0.5	0.5	0.038		

Table S2. ζ-potential Measurements of PMMA-NPs

Run	Pos	KCps	Mob	ζ−ptential	Width	Time
1	50.0	979.6	4.355	54.9	1.6	09:34:40
2	50.0	1054.3	4.542	57.3	1.6	09:35:36
3	50.0	1007.4	4.352	54.9	1.6	09:36:32
4	50.0	977.5	4.316	54.5	1.6	09:37:28
5	50.0	1004.2	6.072	76.6	1.6	09:38:24
Average	**50.0**	**1004.6**	**4.727**	**59.6**	1.6	
+/-		31.0	0.757	9.5	0.0	
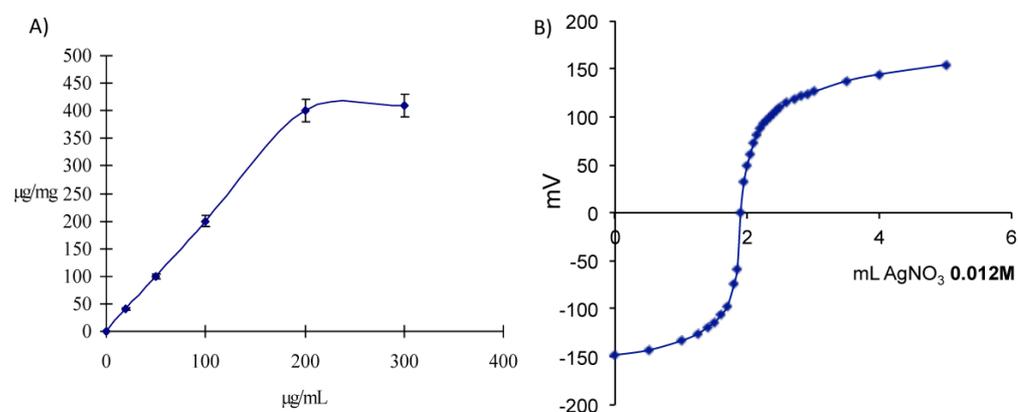
Figure S1. A) TPPS$_4$@PMMA-NPs loading calibration curve; B) PMMA-NPs titration curve.

Release experiments performed on the TPPS4@PMMA-NPs-100 sample.

PBS, acetate buffer, phosphate buffer and culture media were used as the washing solutions. The spectra are recorded on the filtrates that are obtained after washing the NPs at 37°C, for differnet time intervals.
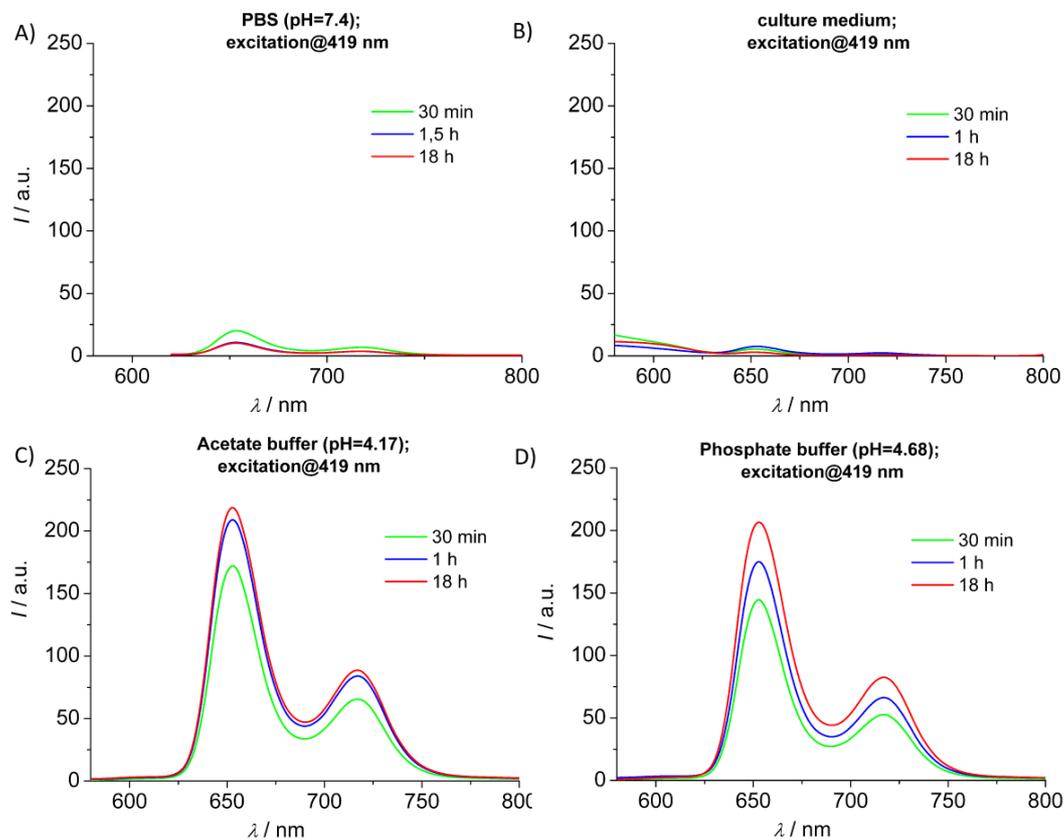
Figure S2. A-D) Emission Spectra of the filtrates under different release experimental conditions.

2. PCS data of TPPS$_4$@PMMA-NPs samples

Table S3. Dynamic Light Scattering Measurements of PMMA-NPs, TPPS$_4$ and TPPS$_4$@PMMA-NPs at different TPPS$_4$ loadings.
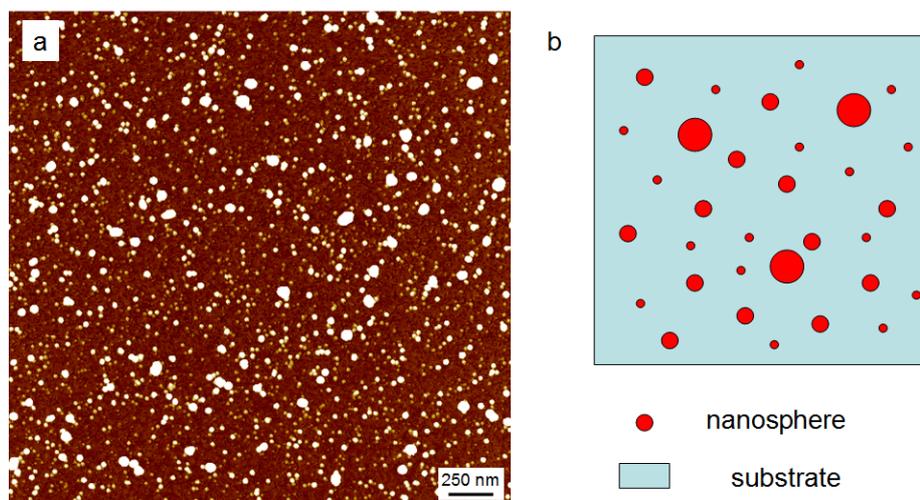
Sample	ZAve[a]	Polydispersity[b]
PMMA-NPs (0.5 mg/mL)	55,4	0,342
TPPS$_4$ (1 mg/mL)	13,1	0,132
1 (4μg $_{TPPS4}$/mg$_{particle}$)	81,6	0,461
2 (8μg $_{TPPS4}$/mg$_{particle}$)	93,5	0,526
3 (20 μg $_{TPPS4}$/mg$_{particle}$)	112,7	0,528
4 (40 μg $_{TPPS4}$/mg$_{particle}$)	143,4	0,684
5 (100 μg $_{TPPS4}$/mg$_{particle}$)	211,7	0,584

[a] Average of three measurements PCS hydrodynamic diameter
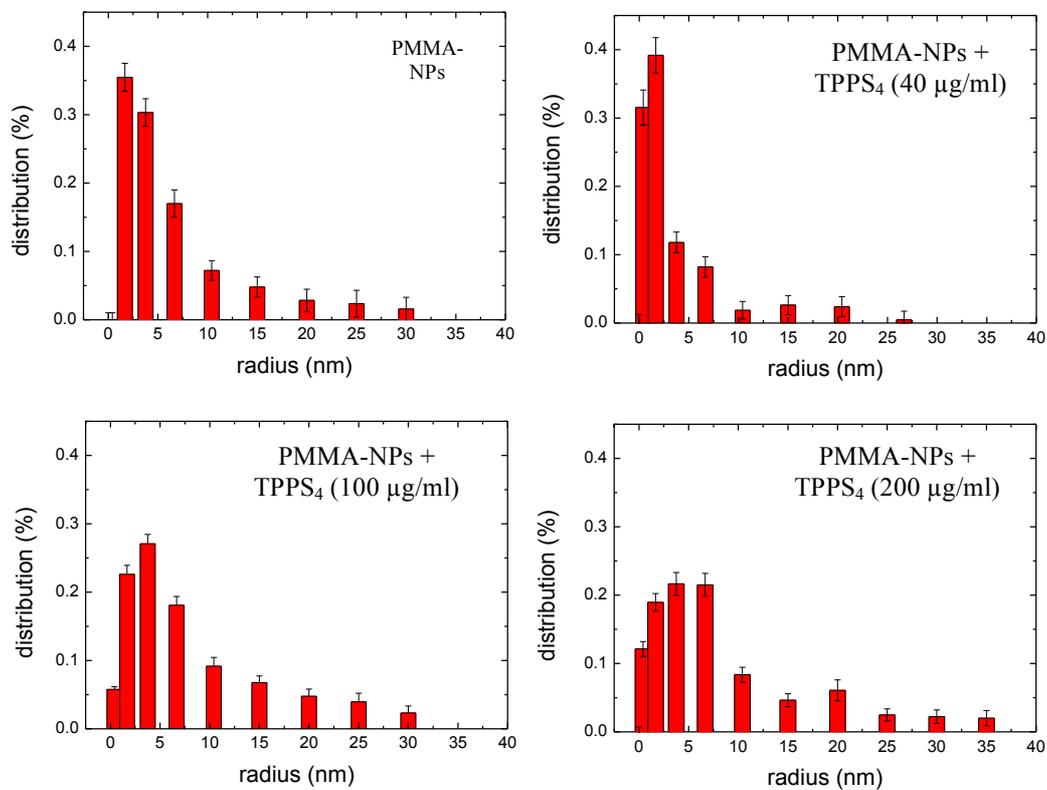
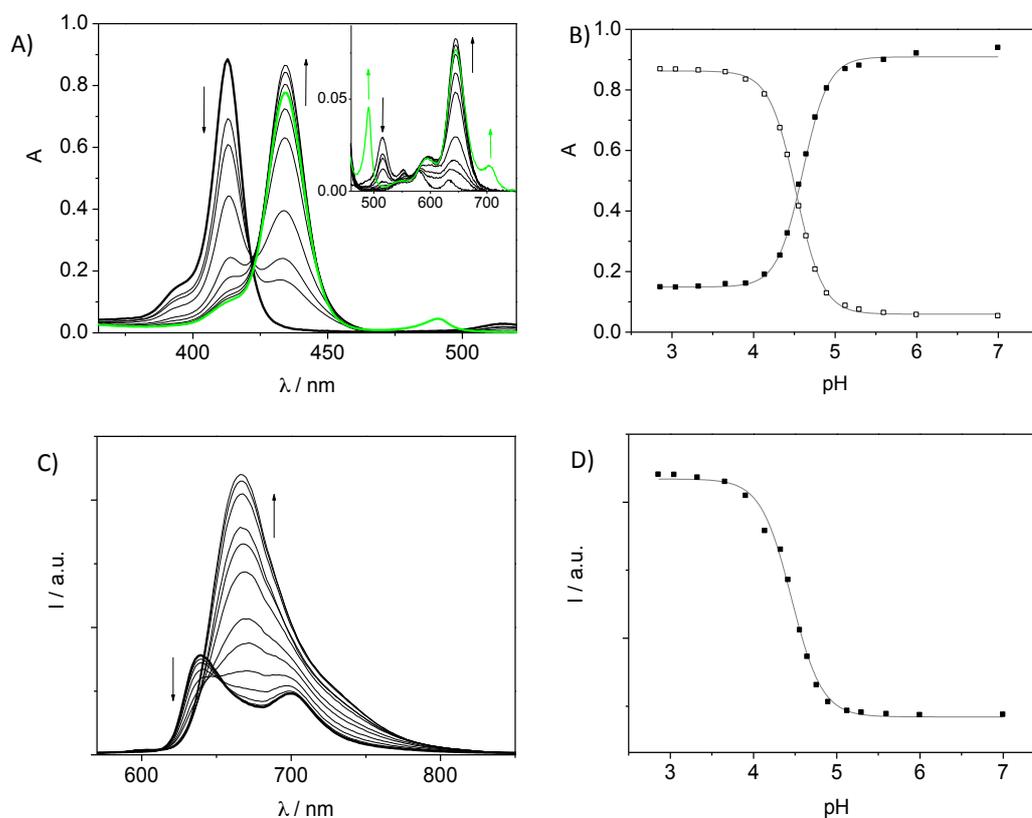[b] Average of three measurements

S4
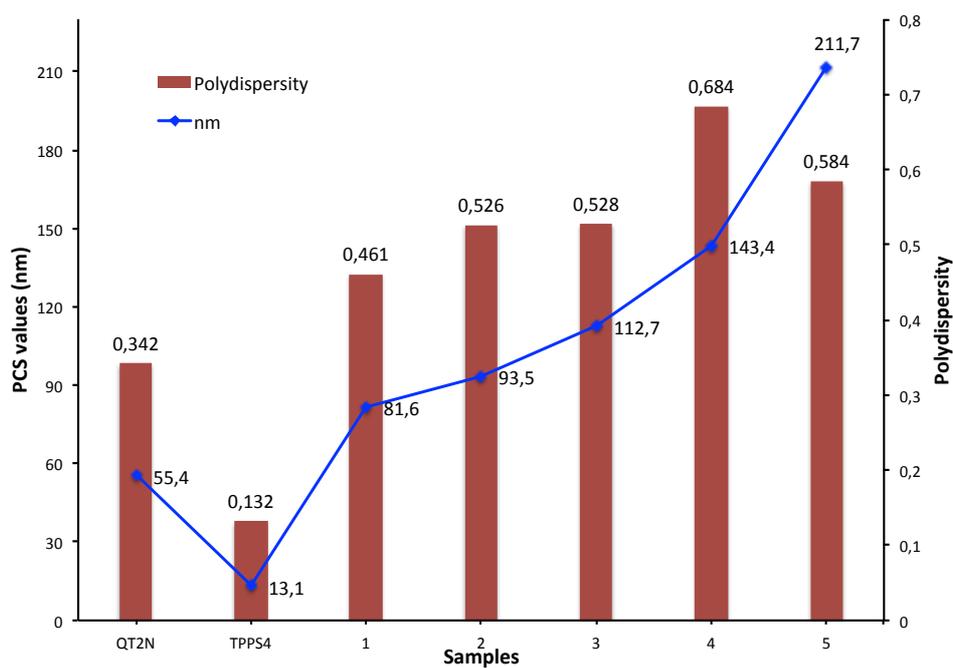
3. AFM characterization

Figure S3. a) AFM image of PMMA nanospheres on native silicon oxide. b) simple scheme of the AFM image. Z-range = 6 nm

Size distribution

Figure S4. Distribution of nanoparticle radius for different TPPS$_4$ concentration.

4. Additional photophysical data

Figure S5. Panel A) Absorption spectra obtained upon titration with HCl of a water solution of TPPS$_4$ 2.3 ×10^{-6} M: solid lines refer to pH variation from 7.0 to 3.0, the green line refers to pH 1.5. The Q-band region is displayed in the inset. Panel B) Absorbance at 413 nm (filled squares) and at 434 nm (open squares) plotted as a function of pH, the fittings are reported as grey curves. Panel C) Emission spectra obtained upon titration with HCl of a water solution of TPPS$_4$ 2.3 ×10^{-6} M: pH variation from 7.0 to 3.0, excitation at 422 nm. Panel D) Emission intensities at 668 nm plotted as a function of pH, the fitting is reported as a grey curve.
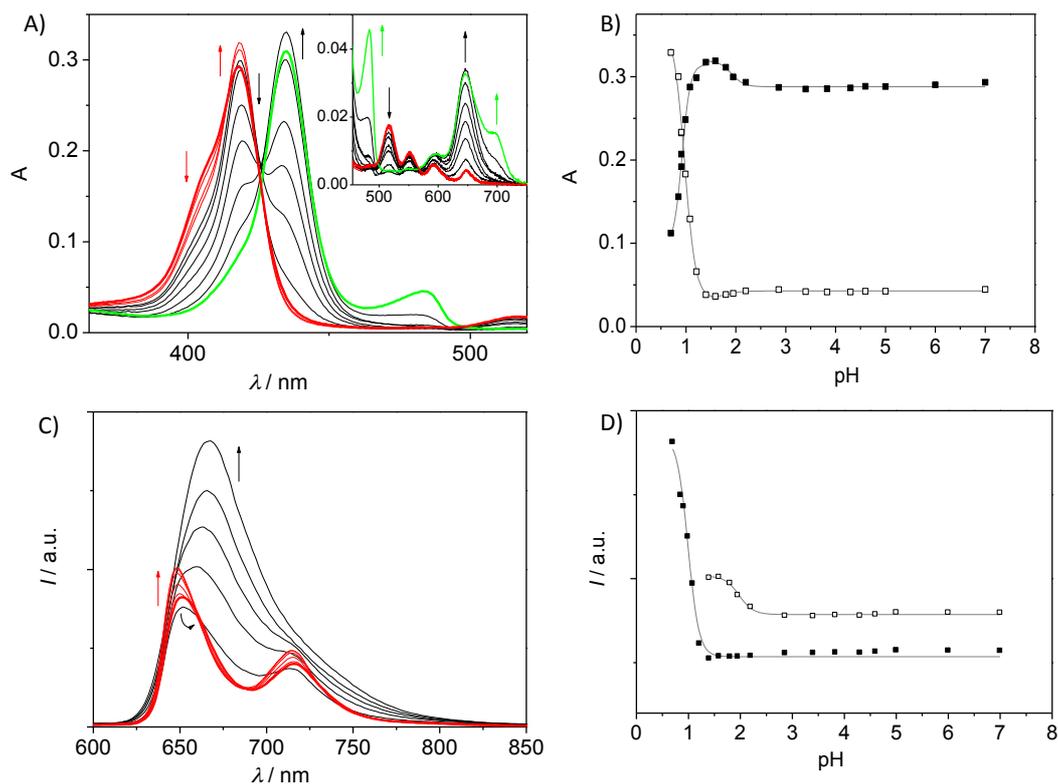
Figure S6. Panel A) Absorption spectra obtained upon titration with HCl of a water solution of TPPS$_4$@PMMA-NPs-**100**. The Q-band region is displayed in the inset. Red curves: pH variation from 3.0 to 1.5 (identical curves from pH 7.0 to pH 3.0 are not displayed); black curves: pH variation from 1.5 to 0.7; green curve: pH 0.6. Panel B) Absorbance at 418 nm (filled squares) and at 434 nm (open squares) plotted as a function of pH. Panel C) Emission spectra of the solutions of Panel A); excitation at 414 nm in the pH range 7.0-1.5 and at 426 nm in the pH range 1.5-0.7. Panel D) Emission intensities at 646 nm (filled squares) and at 668 nm (open squares) plotted as a function of pH. The fittings are reported as grey curves.
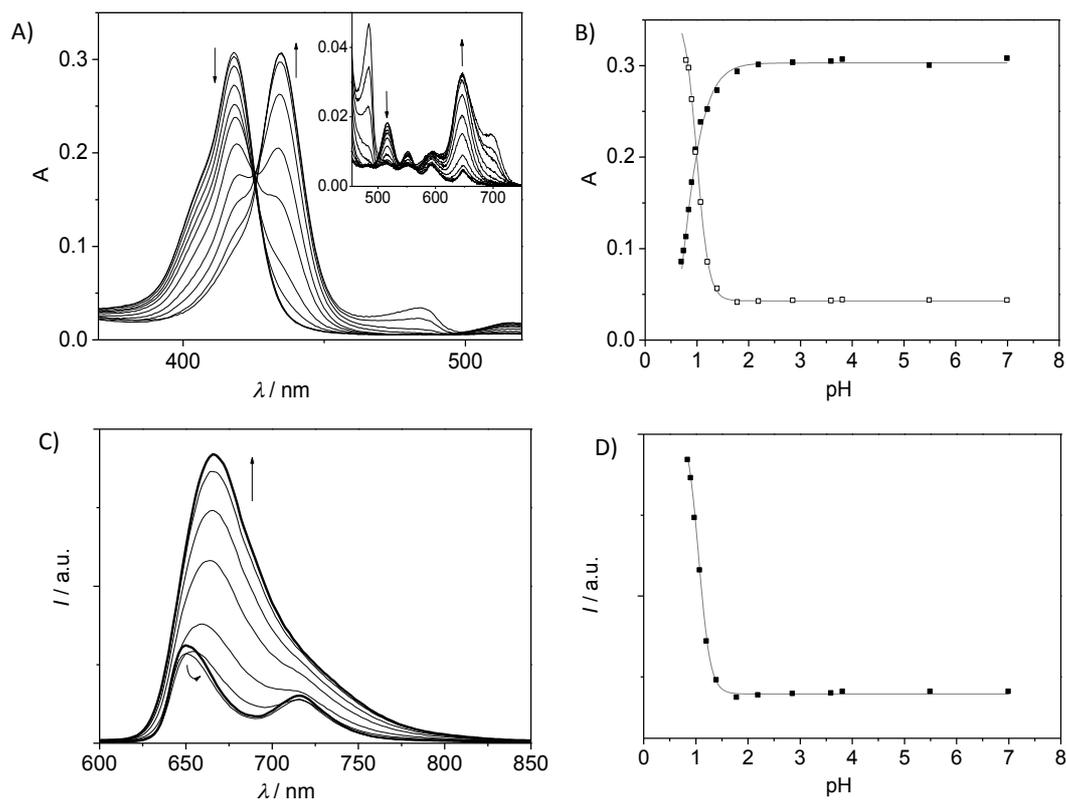
Figure S7. A) Absorption spectra obtained upon titration with HCl of a water solution of TPPS$_4$@PMMA-NPs -**200** µg$_{TPPS4}$/mg$_{particle}$. The Q-band region is displayed in the inset. pH variation from 3.0 to 0.7 (identical curves from pH 7.0 to pH 3.0 are not displayed). B) Absorbance at 418 nm (filled squares) and at 434 nm (open squares) plotted as a function of pH. (C) Emission spectra of the solutions of Panel A); excitation at 427 nm. D) Emission intensities at 668 nm plotted as a function of pH. The fittings are reported as grey curves.