

Supporting Information for

## Polymersome-based Ion-Selective Nano-Optodes Containing Ionophores

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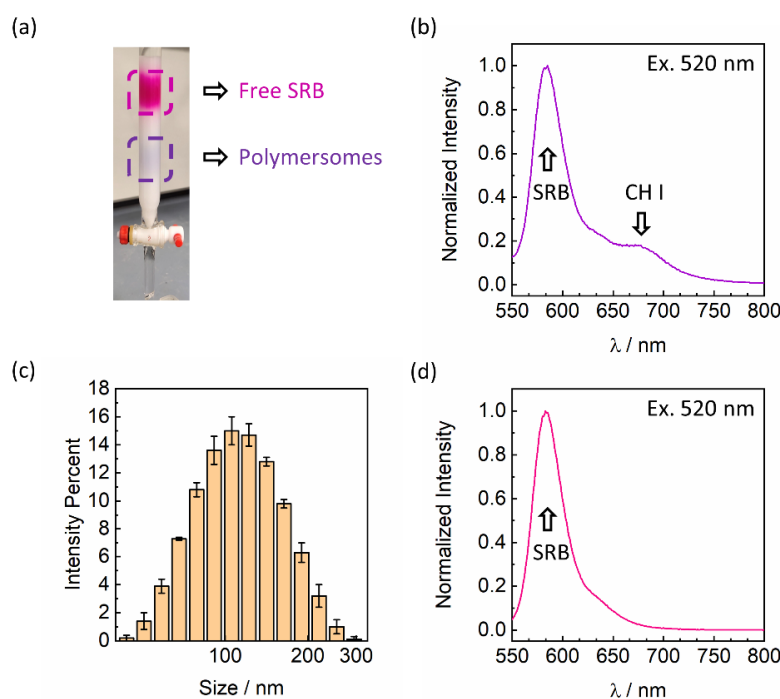
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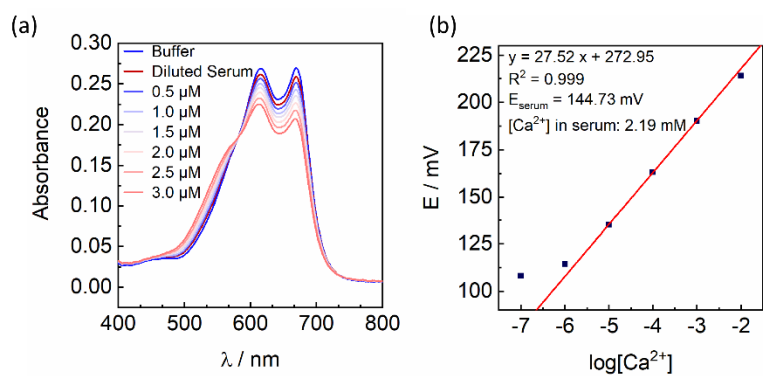
The degree of protonation  $1 - \alpha$  is calculated using the following equation:

$$1 - \alpha = \frac{A - A_{\min}}{A_{\max} - A_{\min}}$$

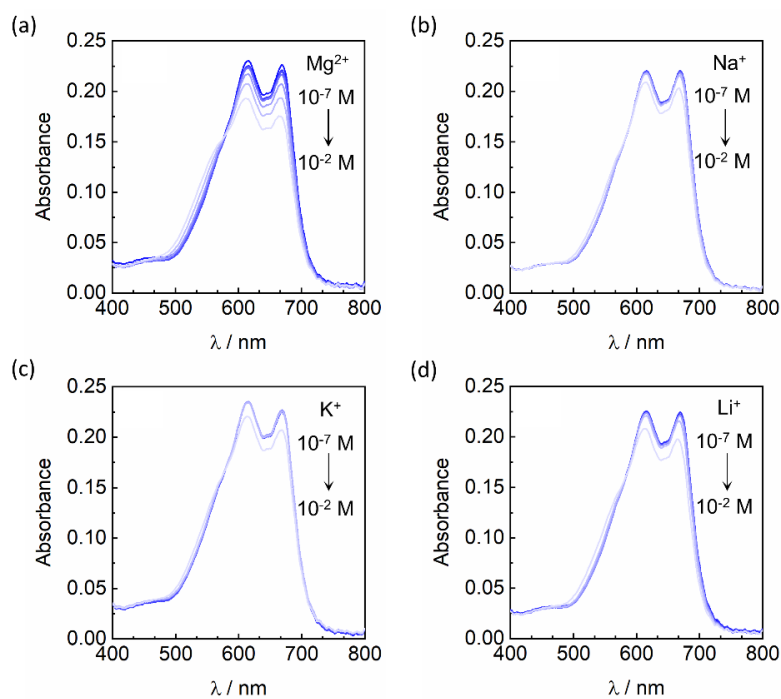
where  $A_{\min}$  is the minimum absorbance of the polymersomes at 670 nm measured in NaOH solution, and  $A_{\max}$  is the maximum absorbance measured in HCl solution.



**Fig. S1** Purification of  $\text{Ca}^{2+}$ -selective polymersomes encapsulating the hydrophilic dye (SRB) through Gel Chromatography (Sephadex G-25 Superfine). (a) Picture of the column during the separation process (the magenta section: free SRB; the purple section: polymersomes). (b) The fluorescence emission spectrum of the purple polymersome section. (c) The hydrodynamic size distribution of the purple polymersome section. (d) The fluorescence emission spectrum of the free SRB section.



**Fig. S2** (a) Absorption spectra of the  $\text{Ca}^{2+}$ -selective polymersome solution with serum and known additional  $\text{CaCl}_2$ . (b) Calibration and determination of the  $\text{Ca}^{2+}$  concentration in diluted human serum by the  $\text{Ca}^{2+}$ -selective electrodes.

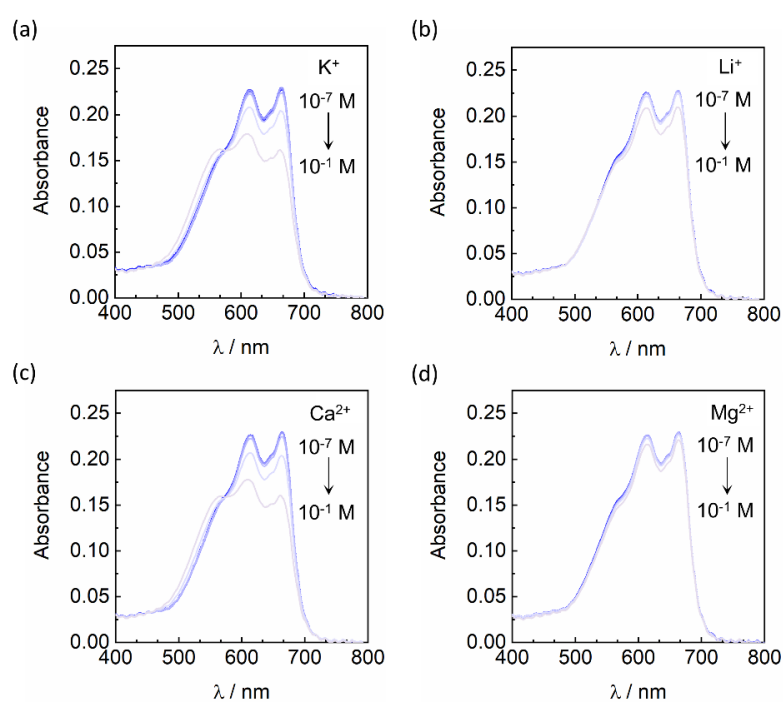


**Fig. S3** Absorption spectra of the  $\text{Ca}^{2+}$ -selective polymersomes with different interfering ion concentrations (from  $10^{-7}$  M to  $10^{-2}$  M). (a)  $\text{MgCl}_2$ , (b)  $\text{NaCl}$ , (c)  $\text{KCl}$ , and (d)  $\text{LiCl}$ .

**Table S1** Comparison of selectivity coefficients between the  $\text{Ca}^{2+}$ -selective polymersomes in this work and various previous Nano-Optodes

Matrix	$\log K_{\text{Ca,Mg}}$	$\log K_{\text{Ca,Na}}$	$\log K_{\text{Ca,K}}$	$\log K_{\text{Ca,Li}}$
Polymersome*	-4.17	-5.08	-4.64	-4.63
PEG-lipid, DOS <sup>1</sup>	-4.00	-	-	-
PVC, DOS <sup>2</sup>	-3.30	-4.90	-4.30	-
Lipid, wax, oil <sup>3</sup>	-3.91	-3.86	-3.87	-4.26

\* The transition points of response curves were used to calculate the selectivity coefficients where the  $1-\alpha$  value was 0.61.

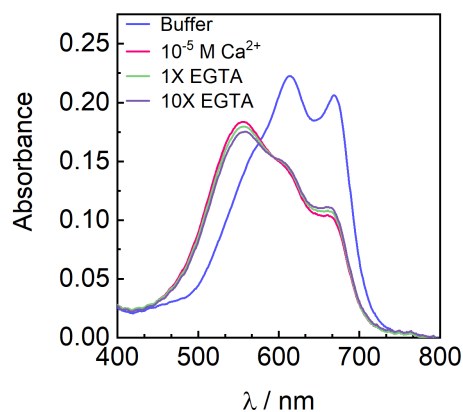


**Fig. S4** Absorption spectra of the  $\text{Na}^+$ -selective polymersomes with different interfering ion concentrations (from  $10^{-7}$  M to  $10^{-1}$  M). (a) KCl, (b) LiCl, (c)  $\text{CaCl}_2$ , and (d)  $\text{MgCl}_2$ .

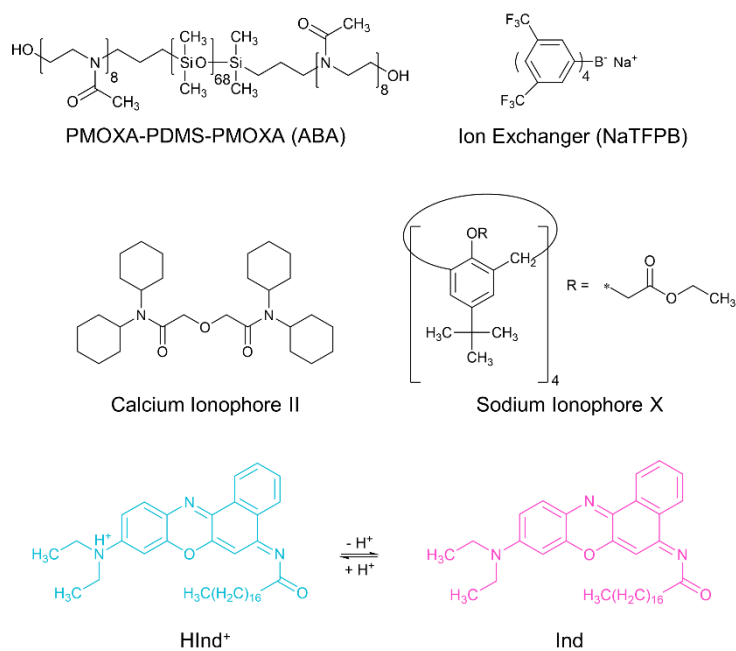
**Table S2** Comparison of selectivity coefficients between the  $\text{Na}^+$ -selective polymersomes in this work and the previous PS-PEO Nano-Optodes

Matrix	$\log K_{\text{Na,K}}$	$\log K_{\text{Na,Li}}$	$\log K_{\text{Na,Ca}}$	$\log K_{\text{Na,Mg}}$
Polymersome*	-2.36	-3.56	-2.42	-4.30
PS-PEO <sup>4</sup>	-2.3	-3.2	-2.8	-3.8

\* The transition points of response curves were used to calculate the selectivity coefficients where the  $1-\alpha$  value was 0.67.



**Fig. S5** Irreversible response of the  $\text{Ca}^{2+}$ -selective polymersomes to  $\text{Ca}^{2+}$  upon the addition of the well-known chelator ethylene glycol tetraacetic acid, EGTA, (1X mean the addition of  $10^{-5}$  M EGTA while 10X mean the addition of  $10^{-4}$  M EGTA).



**Fig. S6** Chemical structures of the copolymer matrix (PMOXA-PDMS-PMOXA, ABA), ion exchanger (NaTFPB), ionophores (Calcium Ionophore II and Sodium Ionophore X), and chromoionophore I (protonated  $\text{HInd}^+$  and deprotonated Ind forms).

#### References:

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