

Supporting information for:

A Plasticizer-Free Miniaturized Optical Ion Sensing Platform with Ionophores and Silicon-based Particles

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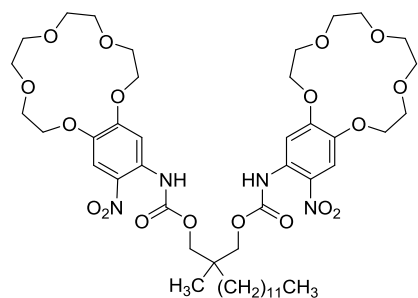
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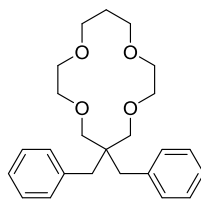
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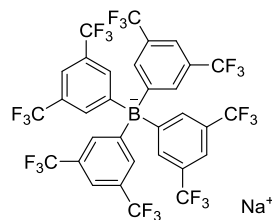
Chemical Structures and names of the compounds used in this work.



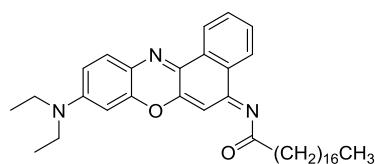
Potassium ionophore III
BME 44



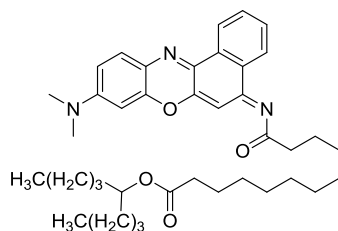
Lithium ionophore VI



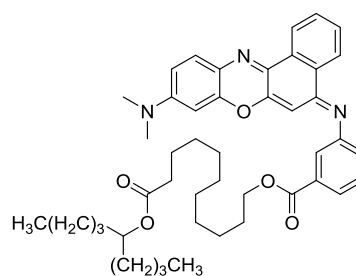
Na TFPB



ETH 5294
Chromoionophore I



ETH 2439
Chromoionophore II



ETH 5418
Chromoionophore VII

Major Chemical compositions of the Sylgard® 184 from Dow Corning.

Sylgard® 184 base part A contains:

- 1) Poly(dimethylsiloxane), vinyl terminated, CAS No: 68083-19-2
- 2) Tetra(trimethylsiloxy)silane, CAS No: 3555-47-3
- 3) Dimethylvinylated and trimethylated silica, CAS No: 68988-89-6

Curing agent contains:

- 1) Poly (dimethyl,methylhydrogensiloxane), CAS No: 68037-59-2
- 2) Poly(dimethylsiloxane), vinyl terminated, CAS No: 68083-19-2
- 3) Tetramethyl tetra vinyl cyclotetrasiloxane, CAS No: 2554-06-5
- 4) Dimethylvinylated and trimethylated silica, CAS No: 68988-89-6

Calculations of degree of protonation 1- α .

1- α was calculated according to the following equation, where A_{max} was the maximum absorbance of the protonation band determined in buffer solutions without addition of primary ions (K^+ or Li^+), A_{min} was the minimum absorbance of the protonation band determined in 1 mM NaOH solutions.

$$1 - \alpha = \frac{A - A_{min}}{A_{max} - A_{min}} \quad (S1)$$

Selectivity coefficients

According to the literature¹, the theoretical response function for a classical ionophore-based optodes containing an ionophore, a cation-exchanger, and a neutral chromoionophore can be expressed in Eqn. S2,

$$a_M = \frac{1}{nK_1} \left(\frac{aH^+\alpha}{1-\alpha} \right)^z \frac{R_T - (1-\alpha)Ind_T}{\{L_T - n^{-1}p[R_T - (1-\alpha)Ind_T]\}^p} \quad (S2)$$

where a_M is the activity of the target ion with a charge n ; p is the complex stoichiometry; K_I is the overall exchange constant; α is the fraction of deprotonated chromoionophore; aH^+ is the proton activity in the aqueous phase; R_T , Ind_T and L_T are the total concentrations of ion-exchanger, chromoionophore and ionophore, respectively. By fitting the experimental data with equation S2, the selectivity can be obtained where α equals 0.5 using previously described methods.¹

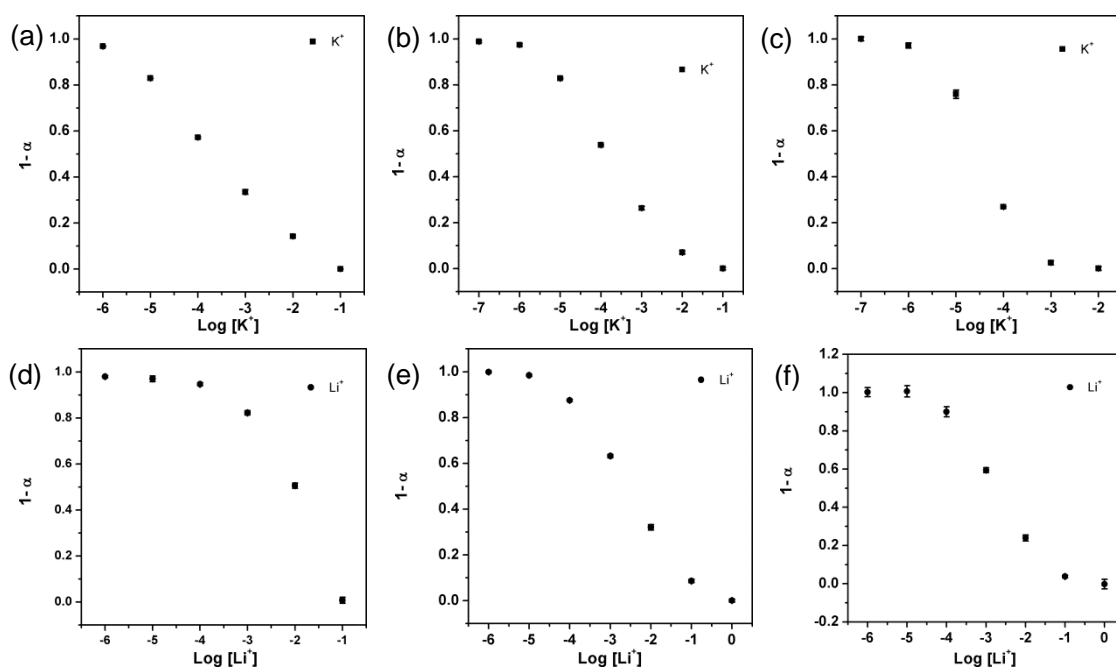


Figure S1. Averaged response of the K^+ -selective PDMS nano-ISOs (a) and PEGylated nano-ISOs (b) and SiO_2 micro-ISOs (c) to various concentrations of K^+ ions. Response of the PDMS nano-ISOs for Li^+ (d), Li^+ -selective PEGylated nano-ISOs (e) and SiO_2 micro-ISOs (f) to various concentrations of Li^+ ions. Error bars (standard deviations) were taken from 3 individual measurements.

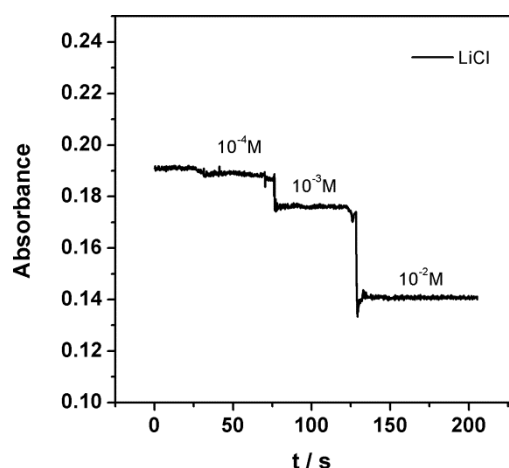


Figure S2. Response time of the PDMS nanospheres containing lithium ionophore VI in 10mM pH 7 Tris-HCl. After each addition the suspension was mixed by pipetting the suspension up and down.

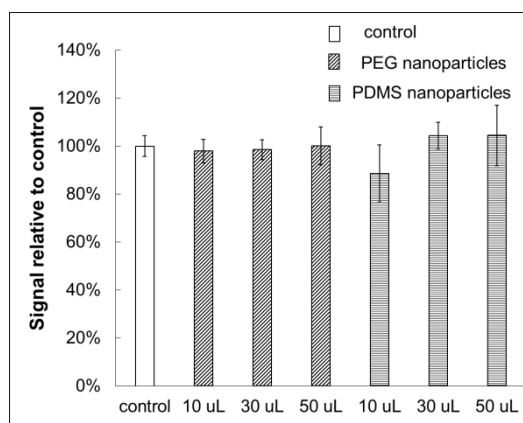


Figure S3. The cytocompatibility of the PEGylated organosilica nanoparticles (▨) and PDMS nanoparticles (▩) determined using a Cell Counting Kit-8 (CCK-8) assay. HeLa cells were incubated in 100 μ L medium containing 10 μ L, 30 μ L, and 50 μ L nanoparticles. The assay was evaluated after 24 hours of incubation. Error bars (standard deviations) were taken from 5 individual measurements.

Table S1. A comparison of several ionophore-based ion-selective nanosensors and microsensors.

Ion-selective particals	Materials	Methods	Particle size (diameter)	Target ions
Quantum dots based ²	Quantum dots, PVC, PEG, DOS	Self-assemble	~100 nm	Na ⁺
Polymeric nanoparticles ³	PMAO, PVA, BHMTA	Self-assemble	250 nm or 130 nm	K ⁺
K ⁺ -NS nanoparticles ⁴	Pluronic F68, Pluronic P123, DOS	Self-assemble	~60 nm	K ⁺
Pluronic F127 nanospheres ⁵	Pluronic F-127, DOS	Self-assemble	~40 nm	K ⁺ , Na ⁺
PEBBLEs ⁶	Decyl methacrylate, Hexanediol	Free-radical polymerization	500 nm - 600 nm	K ⁺

	dimethacrylate, PEG, DOS			
Polystyrene microspheres ⁷	polystyrene	Surface adsorption	0.8 μm	K^+
PVC Microspheres ⁸	PVC, DOS, PEG	Sonication	10 μm	Na^+
Conjugated polymers nanoparticles ⁹	PVA, POT, DOS	Precipitation in mixed solvent	~250 nm	K^+
PCL-based nanosensors ¹⁰	PCL, acetyl-tri-n-hexyl citrate, PEG	Precipitation in mixed solvent	~260 nm	Na^+
nBA-HDDA nanospheres ¹¹	nBA, HDDA AIBN, PVA	Free-radical polymerization	~200 nm	K^+
PDMS nanoparticles in this work	Pluronic F127, Sylgard 184 base, 184 curing agent	Precipitation and crosslinking	~100 nm	K^+ , Li^+
PEGylated organosilica nanoparticles in this work	Trimethoxy(propyl)silane, methoxy-PEG-silane	Stöber process	~100 nm	K^+ , Li^+
Silica microspheres in this work	SiO_2 microspheres, methoxy-PEG-silane	Stöber process	5 μm	K^+ , Li^+ , H^+

Abbreviations:

PVC: poly(vinyl chloride),

PEG: poly(ethylene glycol),

nBA: n-butyl acrylate,

PMAO : poly(maleic anhydride-alt-1-octadecene),

PVA :poly(vinyl alcohol),

BHMTA : bis(hexamethylene)triamine,

DOS: bis(2-ethylhexyl) sebacate,

AIBN: 2,2'-azobisisobutyronitrile,

HDDA: hexanedioldiacrylate,

POT: poly(3-octylthiophene-2,5-diyl),

PVA: poly(vinyl alcohol),

PCL: polycaprolactone,

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