# **Electronic Supplementary Information**

## AIE-Doped Poly(ionic liquid) Photonic Sphere: A Single-Sphere Based Customizable Sensing Platform for Discrimination of Multianalytes

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## Contents

General	S2
Part 1 preparation of parent AIE-doped poly(ionic liquid) photonic spheres	S3
Synthesis of ionic liquid monomer, crosslinker and AIE luminogen	S3
Preparation of parent spheres	S5
Part 2 spheres of OH <sup>-</sup> form for the discrimination of amino acids and	d their
mixtures	
Preparation of spheres of OH <sup>-</sup> form	S9
Spheres of OH <sup>-</sup> form for the discrimination of 20 natural amino acids	S9
Spheres of OH <sup>-</sup> form for the discrimination of mixtures of amino acids	S13
Part 3 spheres of OH <sup>-</sup> form for the discrimination of phosphate derivatives	S15
Part 4 customizable spheres of CSBA form for the discrimination of chiral dicarboxylic ac	idsS16
Part 5 customizable spheres of citrate form for the discrimination of metal ions	S17
References	S17

## General

Commercially available reagents and solvents were used as purchased from the chemical suppliers. Deionized water, 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid buffer (HEPES, pH = 7.2)and human urine from volunteers were used for the preparation of target analyte solutions. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400 MHz NMR spectrometer (JEOL, ECS-400). Electrospray ionization mass spectrometry (ESIMS) was measured on a mass spectrometer (Bruker, Esquire-LC). The fluorescence measurements of AIE activity were carried out using a fluorescence spectrometer (Perkin-Elmer, LS55). The optical images of spheres were recorded by an optical microscope (OLYMPUS, 51M) equipped with a CCD camera (OLYMPUS, UTV0.5XC-3). The fluorescence images of spheres were taken using an inverted fluorescence microscope (OLYMPUS, IX71; excitation filter 330-385 nm; long-pass emission > 420 nm) equipped with a CCD camera (OLYMPUS, DP73). The reflection spectra and emission spectra of spheres were measured by a microscope equipped with a fiber optic spectrometer (Ocean Optics, USB2000+). The size and structure of nanoparticles and spheres were characterized using scanning electron microscope (SEM) (Hitachi, SU8010). Energy-dispersive Xray spectroscopy (EDX) measurements were performed with the spectrometer attached on SEM system. The FTIR spectra of spheres were obtained with an attenuated total reflection IR spectroscopy (Bruker, VERTEX70). The PCA and cross-validated LDA (leave-one-out) were performed using Matlab software.

## Part 1 preparation of parent AIE-doped poly(ionic liquid) photonic spheres

#### Synthesis of ionic liquid monomer, crosslinker and AIE luminogen

Imidazolium-based ionic liquid monomer (IL monomer, i.e., 1-propyl-3-vinylimidazolium bromide), crosslinker (IL crosslinker, i.e., 1,6-di(3-vinylimidazolium) hexane bromide) and AIE luminogen were synthesized.



Fig. S1 Synthetic routes to imidazolium-based ionic liquid monomer, crosslinker and AIE luminogen.

**Synthesis of IL monomer.** IL monomer was prepared according to reported procedures in literature.<sup>[1]</sup> <sup>1</sup>H NMR (400 MHz, DMSO): δ 9.52 (1H, s), 8.21 (1H, s), 7.94 (1H, s), 7.30 (1H, dd, *J* = 8.8 Hz, *J* = 15.6 Hz), 5.96 (1H, dd, *J* = 2.3 Hz, *J* = 15.7 Hz), 5.43 (1H, dd, *J* = 2.3 Hz, *J* = 8.7 Hz), 4.17 (2H, t, *J* = 7.1 Hz), 1.91-1.79 (2H, m), 0.88 (3H, t, *J* = 7.4 Hz).

Synthesis of IL crosslinker. IL crosslinker was prepared according to reported procedures in literature.<sup>[2]</sup> <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  9.72 (2H, s), 8.26 (2H, s), 8.01 (2H, s), 7.34 (2H, dd, J = 8.8 Hz, J = 15.7 Hz), 6.00 (2H, dd, J = 2.3 Hz, J = 15.6 Hz), 5.42 (2H, dd, J = 2.3 Hz, J = 8.8 Hz), 4.23 (4H, t, J = 7.2 Hz), 1.82-1.87 (4H, m), 1.31 (4H, t, J = 6.8 Hz).

**Synthesis of compound 2.** Compound **1** was prepared according to reported procedures in literature.<sup>[3]</sup> A mixture of compound **3** (364.1 mg, 1 mmol), 1,3-dibromopropane (807.5 mg, 4 mmol) and potassium carbonate (1.105 g, 8 mmol) in acetone (20 mL) was refluxed for 12 hours under nitrogen. After cooling to room temperature, the solution was filtered, and the filtrate was evaporated under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and subjected to column chromatography with EA (ethyl acetate)/PE (petroleum ether, 60-90 °C) (v/v, 1/50) as eluent. Compound **2** was obtained as green oil (444.6 mg, 0.73 mmol) in 73.3% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (4H, d, *J* = 8.8 Hz), 7.76 (4H, d, *J* = 7.2 Hz), 7.59-7.55 (2H, m), 7.49-7.46 (4H, m), 6.97 (4H, d, *J* = 8.8 Hz), 4.20 (4H, t, *J* = 5.8 Hz), 3.64-3.61 (4H, t, *J* = 5.8 Hz), 2.39-2.33 (4H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  156.1, 143.2, 143.1, 138.7, 135.7, 135.6, 131.5, 131.4, 130.4, 126.7, 126.5, 125.2, 112.7, 112.6, 64.2, 31.5, 29.0. MS: calcd. for C<sub>32</sub>H<sub>30</sub>Br<sub>2</sub>O<sub>2</sub>: 606.5; found: 606.3.

Synthesis of compound 3. A mixture of compound 2 (303.0 mg, 0.5 mmol) and 1-allylimidazole (216.3 mg, 2 mmol) in CH<sub>3</sub>CN (20 mL) was refluxed for 24 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and subjected to column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (v/v, 5/1) as eluent. Compound 3 was obtained as green oil (222.0 mg, 0.27 mmol) in 54.1% yield. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  9.03 (2H, s), 7.69 (2H, s), 7.60 (2H, s), 7.09 (6H, s), 6.99 (4H, d, *J* = 7.5 Hz), 6.88 (4H, d, *J* = 8.7 Hz), 6.60 (4H, d, *J* = 8.4 Hz), 6.09-5.95 (2H, m), 5.42-5.36 (4H, m), 4.81 (4H, d, *J* = 6.2 Hz), 4.43 (4H, t, *J* = 6.6 Hz), 3.98 (4H, t, *J* =

5.4 Hz), 2.35-2.29 (4H, m). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD):  $\delta$  156.9, 144.1, 139.9, 136.6, 136.1, 132.2, 131.0, 130.5, 129.3, 128.2, 127.7, 127.4, 126.0, 125.3, 122.8, 122.4, 120.8, 113.4, 64.4, 51.3, 29.2. HR-ESI: calcd. for C<sub>44</sub>H<sub>46</sub>N<sub>4</sub>O<sub>2</sub><sup>2+</sup> (m/z)<sup>+</sup>: 331.18054; found: 331.18049.

#### AIE activity of compound 3

The synthesized compound **3** here, an imidazolium-bearing tetraphenylethylene derivative, shows typical AIE activity in Figure S2 as reported for other tetraphenylethylene molecules. The solutions of compound **3** in good solvents such as  $CH_2Cl_2$  are almost non-emissive. The fluorescence of compound **5** can be turned on after aggregation induced by addition of poor solvents such as hexane into  $CH_2Cl_2$ . At 90 vol% hexane content, the fluorescence intensity is 53-fold higher than that of pure  $CH_2Cl_2$  solution, while the emission maximum is still located at 475 nm. Therefore, the synthesized compound **3** can be used as AIE luminogen.



Fig. S2 Fluorescence spectra of compound 3 (10  $\mu$ M) in the hexane/CH<sub>2</sub>Cl<sub>2</sub> mixtures with different volume fractions of hexane,  $\lambda_{ex} = 335$  nm. Insets are the fluorescence photographs of solution of compound 3 in CH<sub>2</sub>Cl<sub>2</sub> (left) and in 90% hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture (right) under illumination of a handheld UV (365 nm) lamp.

## Preparation of parent spheres

Parent AIE-doped PIL photonic spheres were prepared using an analogous method previously reported by our group.<sup>[4]</sup> These spheres were also fabricated by using a two-step method. First, monodisperse silica nanoparticles with a diameter of 170 nm self-assembled into ordered lattices by droplet-based microfluidics. Monodisperse silica particles with a diameter of ca. 170 nm were synthesized by the modified Stöber method.<sup>[5]</sup> Second, the solution containing 0.60 g ionic liquid monomer, 0.036 g crosslinker, 200  $\mu$ L AIE luminogen stock methanol solution (3 mM) and 10  $\mu$ L photoinitiator was infiltrated into the void spaces of the photonic spheres by capillary force. After polymerization under UV radiation followed by removal of silica template, the resultant parent spheres with highly ordered 3D inverse opal structure and doped AIE luminogen were fabricated.



Fig. S3 a) Optical image of silica colloidal crystal spheres; b) SEM image of silica colloidal crystal spheres inside.

### <sup>1</sup>H NMR spectra of IL monomer and crosslinker



<sup>1</sup>H NMR spectrum of IL crosslinker in DMSO.

## <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compound 2



<sup>1</sup>H NMR spectrum of compound **2** in CDCl<sub>3</sub>.



<sup>13</sup>C NMR spectrum of compound **2** in CDCl<sub>3</sub>.



<sup>1</sup>H NMR spectrum of compound **3** in CD<sub>3</sub>OD.



<sup>13</sup>C NMR spectrum of compound **3** in CD<sub>3</sub>OD.

## Part 3 Spheres of OH<sup>-</sup> form for the discrimination of amino acids and their

#### mixtures

#### Preparation of spheres of OH<sup>-</sup> form

Counteranions of the parent spheres were completely converted from Br to OH<sup>-</sup> by virtue of facile anion exchange according to a reported method in literature.<sup>[6]</sup> The above parent AIE-doped PIL photonic spheres were soaked in N<sub>2</sub>-saturated 1 M KOH aqueous solution for 24 h to convert the counteranions from the form of Br<sup>-</sup> to OH<sup>-</sup>. This procedure was repeated three times to ensure thorough conversion of counteranions. Afterwards, the converted spheres were washed by N<sub>2</sub>-saturated deionized water until the pH of residual water was neutral. Thus, spheres of OH<sup>-</sup> form for target multianalytes (amino acids and phosphate derivatives) were prepared. Remarkably, a very significant Bragg diffraction wavelength red-shift up to 157 nm was observed after the anion replacement, accompanying with a distinct color change of spheres from cyan to red by naked eye (Figure S5a). Energy-dispersive X-ray spectra further confirmed the complete conversion of Br<sup>-</sup> to OH<sup>-</sup> since no Br could be detected after the anion conversion (Figure S5b).

#### Spheres of OH<sup>-</sup> form for the discrimination of 20 natural amino acids

AIE-doped PIL photonic spheres of OH<sup>-</sup> form were incubated in 1 mL amino acid solutions for three days at room temperature under continuous stirring on an orbital shaker to achieve reaction equilibrium. Each sensing response to an analyte was measured with seven individual spheres to test reproducibility. Then the optical images, fluorescence images, reflection spectra and fluorescence spectra of spheres after binding with analytes were recorded. It should be noted that reflection spectra and emission spectra could be easily achieved on a microscope equipped with a fiber optic spectrometer in different detection modes. Bragg diffraction peak shifts ( $\Delta\lambda$ ) were obtained by peak position before binding ( $\lambda_0$ ) subtracting peak position after binding ( $\lambda_1$ ):  $\Delta\lambda = \lambda_0 - \lambda_1$ . The folds of fluorescence enhancement  $\Delta F/F_0$  at 515 nm (or at 554 nm) were calculated by attaining fluorescence intensity before (F<sub>0</sub>) and after (F<sub>1</sub>) binding with amino acids at 515 nm (or at 554 nm):  $\Delta F/F_0 = F_1/F_0 - 1$ . Then, the data was processed using PCA and LDA by Matlab.



Fig. S4 Chemical structures and name abbreviations of 20 amino acids.



**Fig. S5** a) Reflection spectra and corresponding inserted optical images of PIL-Br and PIL-OH; b) EDX spectra of PIL-Br and PIL-OH. PIL-Br and PIL-OH represent PIL photonic spheres of Br<sup>-</sup> and OH<sup>-</sup> form.



**Fig. S6** Responses of AIE-doped PIL photonic spheres (OH<sup>-</sup> form) to 20 natural amino acids at 10 mM: a) reflection spectra; b) emission spectra. The integration time for recording FL spectra is 200 ms.



**Fig. S7** PhC channel responses of AIE-doped PIL photonic spheres (OH<sup>-</sup> form) to 20 natural amino acids at 1 mM: a) optical images, c) reflection spectra, e) histogram of reflection peak shifts; FL channel responses of AIE-doped PIL photonic spheres (OH<sup>-</sup> form) to 20 natural amino acids at 1 mM: b) fluorescence images, d) emission spectra, f) histogram of the folds of fluorescence enhancement. The exposure time for capturing FL images is 30 ms while the integration time for recording FL spectra is 200 ms.



**Fig. S8** AIE-doped PIL photonic spheres of OH<sup>-</sup> form for the discrimination of 20 natural amino acids at 1 mM: a) 3D PCA plot; b) corresponding magnified plot of the red circle region in a).

#### Spheres of OH<sup>-</sup> form for the discrimination of mixtures of amino acids

AIE-doped PIL photonic spheres of OH<sup>-</sup> form were incubated in 1 mL mixtures of amino acids for three days at room temperature under continuous stirring on an orbital shaker to achieve reaction equilibrium. The concentration of individual amino acid in an arbitrary mixture was 10 mM.



**Fig. S9** PhC channel responses of AIE-doped PIL photonic spheres (OH<sup>-</sup> form) to 1 control analyte, 5 unitary analytes and 26 mixture analytes: a) optical images, c) reflection spectra, e) histogram of reflection peak shifts; FL channel responses of AIE-doped PIL photonic spheres (OH<sup>-</sup> form) to 1 control analyte, 5 unitary analytes and 26 mixture analytes: b) fluorescence images, d) emission spectra, f) histogram of the folds of fluorescence enhancement. A-E represent Lys, Cys, Trp, Ile and Glu, respectively. The exposure time for capturing FL images is 30 ms while the integration time for recording FL spectra is 200 ms.

Sample#	Identification	Verification	
1	AE	AE	
2	BDE	BDE	
3	С	С	
4	ABCD	ABCD	
5	Control	Control	
6	BD	BD	
7	ADE	ADE	
8	AC	AC	
9	Е	Е	
10	ACD	ACD	
11	BC	BC	
12	ABE	ABE	
13	DE	DE	
14	ABDE	ABDE	
15	D	D	
100% identified			

**Table S1** The identification of 15 blind samples which have been tested as training data sets before.

## Part 3 Spheres of OH<sup>-</sup> form for the discrimination of phosphate derivatives

AIE-doped PIL photonic spheres of  $OH^2$  form were incubated in 1 mL phosphate derivative solutions for 6 hours at room temperature under continuous stirring on an orbital shaker to achieve reaction equilibrium. The concentration of phosphate derivatives was 10  $\mu$ M.



Fig. S10 Chemical structures and name abbreviations of nine phosphate derivatives.



**Fig. S11** PhC channel responses of AIE-doped PIL photonic spheres (OH<sup>-</sup> form) to nine phosphate derivatives at 10  $\mu$ M: a) optical images, c) reflection spectra, e) histogram of reflection peak shifts; FL channel responses of AIE-doped PIL photonic spheres (OH<sup>-</sup> form) to nine phosphate derivatives at 10  $\mu$ M: b) fluorescence images, d) emission spectra, f) histogram of the folds of fluorescence enhancement. The exposure time for capturing FL images is 30 ms while the integration time for recording FL spectra is 200 ms.

## Part 4 customizable spheres of CSBA form for the discrimination of chiral

#### dicarboxylic acids

The chiral spiral borate lithium was synthesized according to a reported method.<sup>[7]</sup> The parent AIEdoped PIL photonic spheres of Br<sup>-</sup> form were soaked in 0.5 M chiral spiral borate lithium aqueous solution for 24 h to convert the counteranions from the form of Br<sup>-</sup> to chiral spiral borate anion (CSBA). After this counteranion conversion, disappearance of Br peaks (11.6 wt%) at 1.340 and 1.480 keV, detection of B (8.0 wt%) at 0.183 keV, as well as typical adsorption bands of CSBA at 1720, 1494 and 694 cm<sup>-1</sup> were observed, indicating the complete conversion of Br<sup>-</sup> to CSBA.



**Fig. S12** a) EDX spectra of PIL-Br and PIL-CSBA; b) FTIR spectra of PIL-Br and PIL-CSBA. PIL-Br and PIL-CSBA represent PIL photonic spheres of Br and CSBA form.

AIE-doped PIL photonic spheres of CSBA form were incubated in 1 mL chiral dicarboxylic acid solutions for 12 hours at room temperature under continuous stirring on an orbital shaker to achieve reaction equilibrium. The concentration of chiral dicarboxylic acids was 10 mM.

#### Part 5 customizable spheres of citrate form for the discrimination of metal ions

The parent AIE-doped PIL photonic spheres of Br form were soaked in 1 M sodium citrate (CA) aqueous solution for 24 h to convert the counteranions from the form of Br to CA. After this counteranion conversion, 47 nm Bragg peak shift, disappearance of Br peaks (16.4 wt%) at 1.340 and 1.480 keV, typical adsorption band of CA at 1367 cm<sup>-1</sup> were observed, indicating the complete conversion of Br to CA.



**Fig. S13** a) Reflection spectra and corresponding inserted optical images of PIL-Br and PIL-CA; b) EDX spectra of PIL-Br and PIL-CA; c) FTIR spectra of PIL-Br and PIL-CA. PIL-Br and PIL-CA represent PIL photonic spheres of Br and CA form.

AIE-doped PIL photonic spheres of citrate form were incubated in 1 mL metal ion solutions (pH = 5, 10 mM PBS buffer) for 1 hour at room temperature under continuous stirring on an orbital shaker to achieve reaction equilibrium. The concentration of metal ions was 100  $\mu$ M. All ten metal ions (Al<sup>3+</sup>, Ba<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Sn<sup>2+</sup>, Zn<sup>2+</sup>) were used in the form of chloride.

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