Electronic Supplementary Information

Poly(ionic liquid)s as a Distinct Receptor Material to Create Highly-Integrated Sensing Platform for Efficiently Identifying a Myriad of Saccharides

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1. Experimental Section

Materials and Characterization

Commercially available reagents and solvents for the synthesis of ionic liquids, AIE luminogens and silica particles were used as purchased from the chemical suppliers without further purification unless otherwise stated. Saccharides, sugar alcohols and glycoproteins for the sensing purpose were used without any additional processing. Deionized water, 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid buffer (HEPES, pH = 7.0) and tea solution were used for the preparation of target sugar solutions. Twelve brands of sugary beverages including Coca Cola, Pepsi Cola, Minute Maid Orange Juice, Uni-President Ice Tea, Uni-President Pear Juice, Wahaha Nutrition Express, Minute Maid Fruit Milk, Nongfu Spring Fruit Blend, Coconut Thai Mango Juice, Nongfu Spring Vitamin, Danone Lemonade, Danone Mizone were purchased from the local market. A few packs of Honey Green Tea (Lipton, Unilever) were also purchased.

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer (JEOL, ECS-400). Mass spectrometry (ESIMS) was measured on a mass spectrometer (LCMS-IT/TOF, Shimadzu). 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; excitation filter 450-480 nm, long-pass emission > 515 nm; excitation filter 510-550 nm, long-pass emission > 590 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 X-ray 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.

Experimental Details

Preparation of parent spheres

Parent AIE-doped PIL photonic spheres were prepared using an analogous method previously reported in literature.[1,2] These spheres were also fabricated by using a three-step method. First, monodisperse silica nanoparticles with a diameter of 230 nm self-assembled into ordered lattices by droplet-based microfluidics. Monodisperse silica particles with a diameter of ca. 230 nm were synthesized by the modified Stöber method.[3] Second, the solution containing 0.60 g ionic liquid monomer, 0.06 g crosslinker, 200 μL AIEgen-Blue stock methanol solution (3 mM) and 10 μL 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 with HF, the resultant parent spheres with highly ordered 3D inverse opal structure and doped AIE luminogen were fabricated. For the preparation of parent spheres with three different color AIEgens, AIEgen stock methanol solution composed of 67 μL AIEgen-Blue (3 mM), 67 μL AIEgen-Yellow (3 mM) and 67 μL AIEgen-Red (3 mM) was utilized.

Construction of various spheres with different counteranions

The bromide ions of the parent spheres were replaced by different counteranions via simple anion-exchange reactions. For example, counteranions of the parent spheres were completely converted from Br^- to dicyanamide anion (DCA) by virtue of facile anion exchange according to a reported method in literature.[2] The above parent AIE-doped PIL photonic spheres were soaked in 1 M Sodium dicyanamide aqueous solution for 12 hours to convert the counteranions from the form of Br^- to DCA. Afterwards, the converted spheres were thoroughly washed by deionized water. Thus, the sphere of DCA form for saccharides were prepared. Spheres with other 18 counteranions can be constructed by the same method.

Collection of response signals from spheres for saccharides

AIE-doped PIL photonic spheres were incubated in target saccharide solutions at room temperature for 8 hours under continuous stirring on an orbital shaker to achieve reaction equilibrium. Each sensing response to a saccharide 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 after binding (λ_1) subtracting peak position after binding (λ_0): $\Delta\lambda = \lambda_1 - \lambda_0$. Three AIEgens (AIEgen-Blue, AIEgen-Yellow and AIEgen-Red) under three different excitation modes led to three FL channels with six fluorescence responses at different wavelengths: FL-B channel (F1 for 515 nm, F2 for 554 nm), FL-Y channel (F3 for 528 nm, F4 for 560 nm), and FL-R channel (F5 for 614 nm, F6 for 642 nm). For example, the folds of fluorescence enhancement for AIEgen-Blue $\Delta F/F_0$ at 515 nm were calculated by attaining fluorescence intensity before (F_0) and after (F_1) binding with saccharides at 515 nm: $\Delta F/F_0 = F_1/F_0 - 1$.

Data analysis, classification and prediction

The database of response pattern was statistically analyzed using principal component analysis (PCA), an unsupervised method to reduce data dimensions and classify each analyte cluster. The cross-validation (leave-one-out) routine based on linear discriminant analysis (LDA) was used to evaluate predictability of the sensor array by leaving one observation out of the set and simultaneously utilizing the rest of the data as training set to generate the linear discriminant function. The detail belongings of data points could be observed from the jackknifed classification matrix. Additionally, the prediction of unknown samples was carried out by the same procedure mentioned above. The PCA and cross-validated LDA (leave-one-out) were performed using Matlab software.

Sphere-based array for real-world samples: sugary beverages

Twelve commonly accessible sugary beverages including Coca Cola, Pepsi Cola, Minute Maid Orange Juice, Uni-President Ice Tea, Uni-President Pear Juice, Wahaha Nutrition Express, Minute Maid Fruit Milk, Nongfu Spring Fruit Blend, Coconut Thai Mango Juice, Nongfu Spring Vitamin, Danone Lemonade, Danone Mizone were filtered to remove insoluble materials. Then these sugary beverages were diluted ten times with deionized water. The AIE-doped PIL photonic spheres of DCA form (AIEgen-Blue) were used for the discrimination of sugary beverages.

Sphere-based array for real-world samples: saccharide mixtures in tea solution

The tea solution was prepared by brewing 0.5 g powder of Honey Green Tea in about 200 mL of boiling distilled water and used as stock solution for saccharide mixtures. We prepared 32 analytes in tea solution including #1 (fructose, 20 mM), #2 (galactose, 20 mM), #3 (glucose, 20 mM), #4 (lactose, 20 mM), #5 (sucrose, 20 mM), #6 (fructose, galactose, all 20 mM), #7 (fructose, glucose, all 20 mM), #8 (fructose, lactose, all 20 mM), #9 (fructose, sucrose, all 20 mM), #10 (galactose, glucose, all 20 mM), #11 (galactose, lactose, all 20 mM), #12 (galactose, sucrose, all 20 mM), #13 (glucose, lactose, all 20

mM), #14 (glucose, sucrose, all 20 mM), #15 (lactose, sucrose, all 20 mM), #16 (fructose, galactose, glucose, all 20 mM), #17 (fructose, galactose, lactose, all 20 mM), #18 (fructose, galactose, sucrose, all 20 mM), #19 (fructose, glucose, lactose, all 20 mM), #20 (fructose, glucose, sucrose, all 20 mM), #21 (fructose, lactose, sucrose, all 20 mM), #22 (galactose, glucose, lactose all 20 mM), #23 (galactose, glucose, sucrose, all 20 mM), #24 (galactose, lactose, sucrose, all 20 mM), #25 (glucose, lactose, sucrose, all 20 mM), #26 (fructose, galactose, glucose, lactose, all 20 mM), #27 (fructose, galactose, glucose, sucrose, all 20 mM), #28 (fructose, galactose, lactose, sucrose, all 20 mM), #29 (fructose, glucose, lactose, sucrose, all 20 mM), #30 (galactose, glucose, lactose, sucrose, all 20 mM), #31 (fructose, galactose, glucose, lactose, sucrose, all 20 mM), #32 (tea solution without additionally adding saccharide). Sensor array composed of two three-AIE-doped poly(ionic liquid) photonic spheres (DCA and BF_4 forms) was used for the discrimination of these unprecedented complex mixtures. Based on the established training sets, blind samples from the above 32 analytes were tested for the identification.

Sphere-based arrays for other saccharide derivatives

Nine sugar alcohol solutions including adonitol, arabitol, meso-erythritol, galactitol, myo-inositol, maltitol, mannitol, sorbitol and xylitol at 50 mM were prepared using HEPES buffer (pH = 7.0). AIE-doped poly(ionic liquid) photonic spheres of DCA form (AIEgen-Blue) were incubated in target sugar alcohol solutions at room temperature for 6 hours under continuous stirring on an orbital shaker to achieve reaction equilibrium.

Seven glycoproteins including avidin, cellulase R-10, fibrinogen, glucose oxidase, hyaluronidase, horseradish peroxidase, ovalbumin at 100 nM were freshly made in HEPES buffer (pH = 7.0) and stored at 4 °C. AIE-doped poly(ionic liquid) photonic spheres of DCA form (AIEgen-Blue) were incubated in target glycoprotein solutions at 4 °C for 2 hours under continuous stirring on an orbital shaker to achieve reaction equilibrium.

Quantum chemical calculations

All of the structural optimizations were performed with Gaussian 09 package[4] at the B3LYP/6-311+g(d,p) theoretical level.[5] The obtained geometries were confirmed by frequency to ensure no imaginary frequencies. The interaction energies were calculated at the B3LYP/6-311+g(d,p) level with basis set superposition error (BSSE) correction. To further reveal the chemical origin of these interactions, the atom in molecule (AIM) and reduced density gradient (RDG) analyses were carried out by using Multiwfn software.[6,7]

2. Figures and Tables

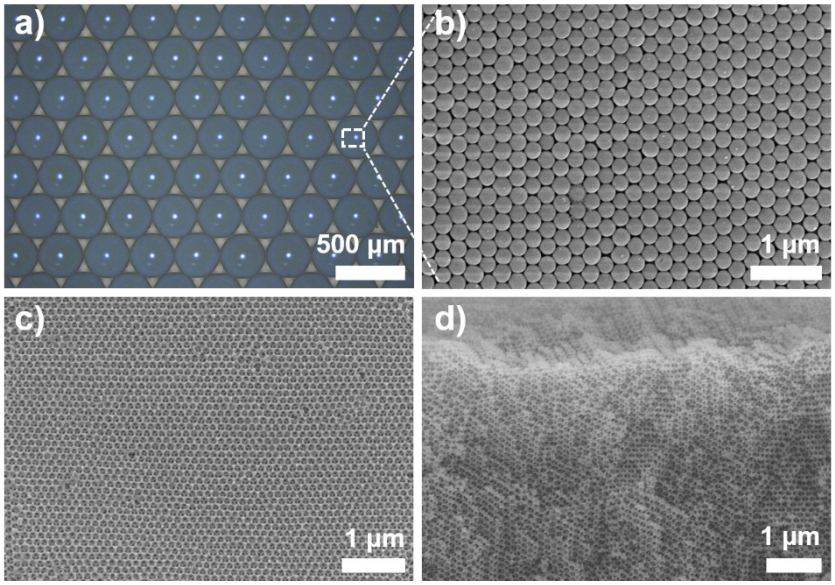

Fig. S1 (a) Reflection image; (b) SEM image of silica colloidal crystal spheres; (c) Top-view SEM image of PIL inverse opal spheres; (d) Cross-view SEM image of PIL inverse opal spheres.

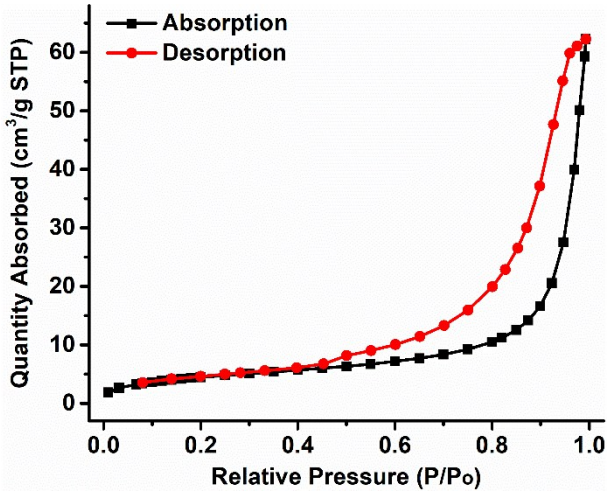

Fig. S2 Adsorption isotherm of PIL inverse opal (the specific surface area by BET: 18 m^2/g).[8]

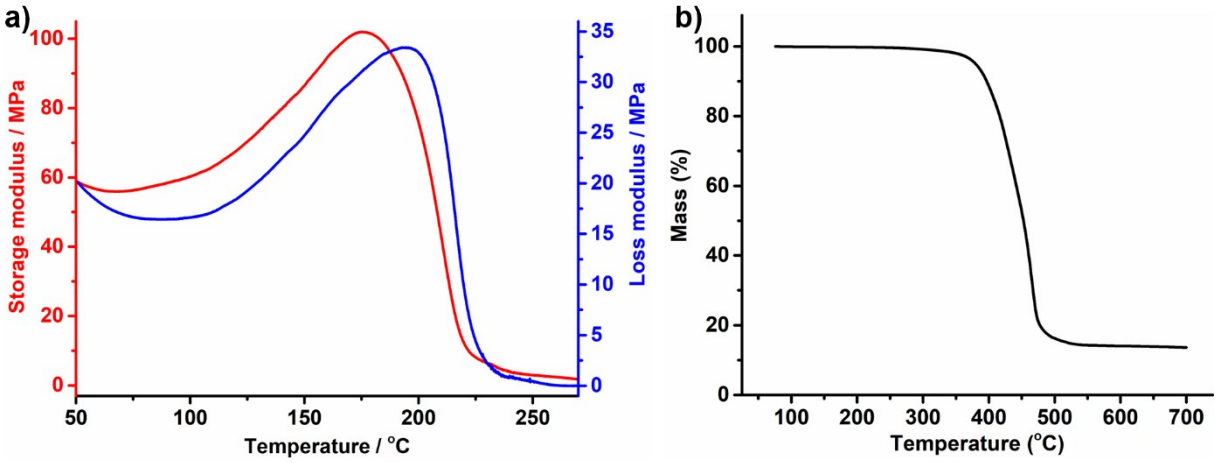

Fig. S3 (a) Dynamic mechanical analysis of PIL materials (cross-linked density described by Mc[9]: 4130 g/mol); (b)Thermal gravimetric analysis of PIL materials.

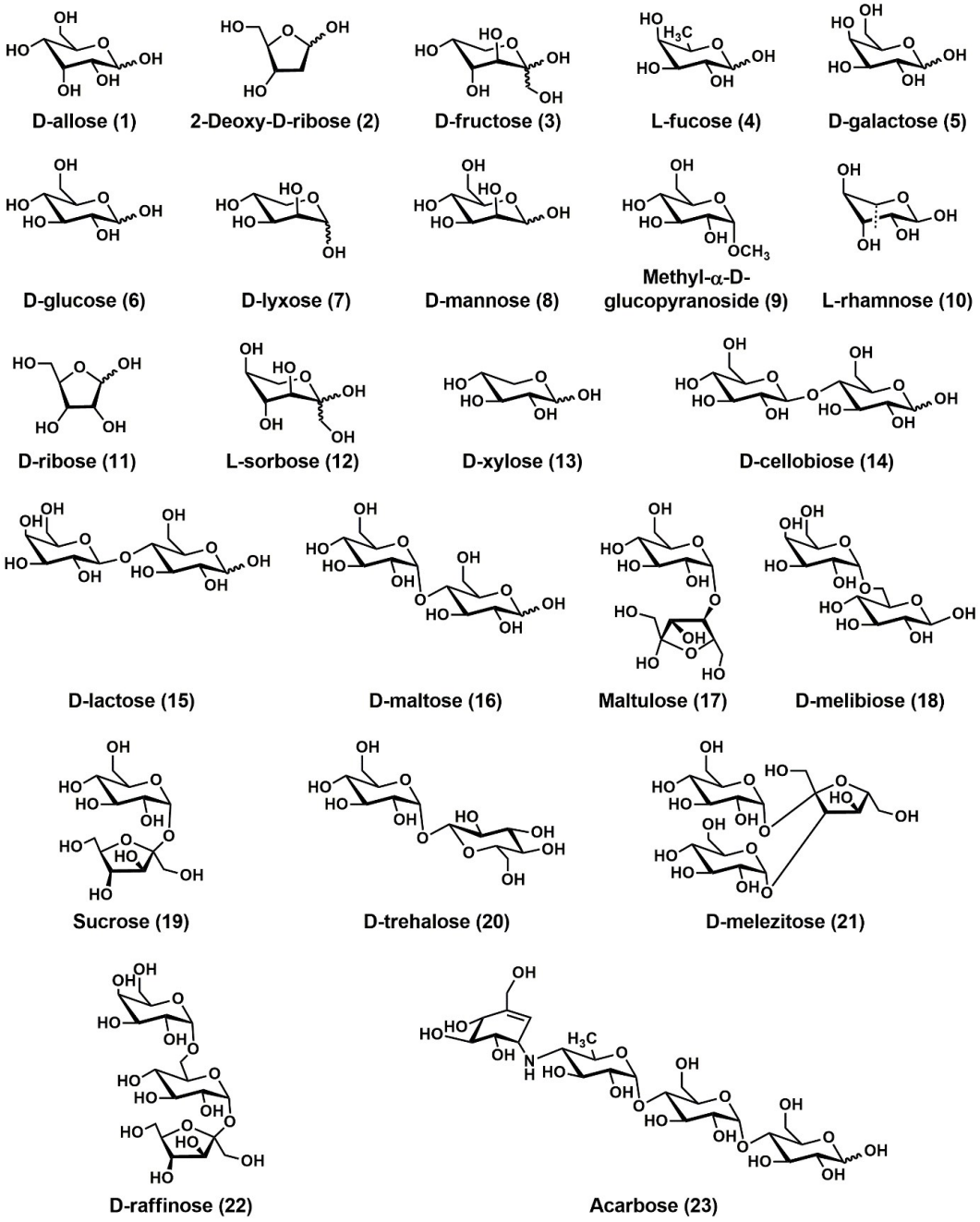

Fig. S4 Chemical structures of 23 saccharides.

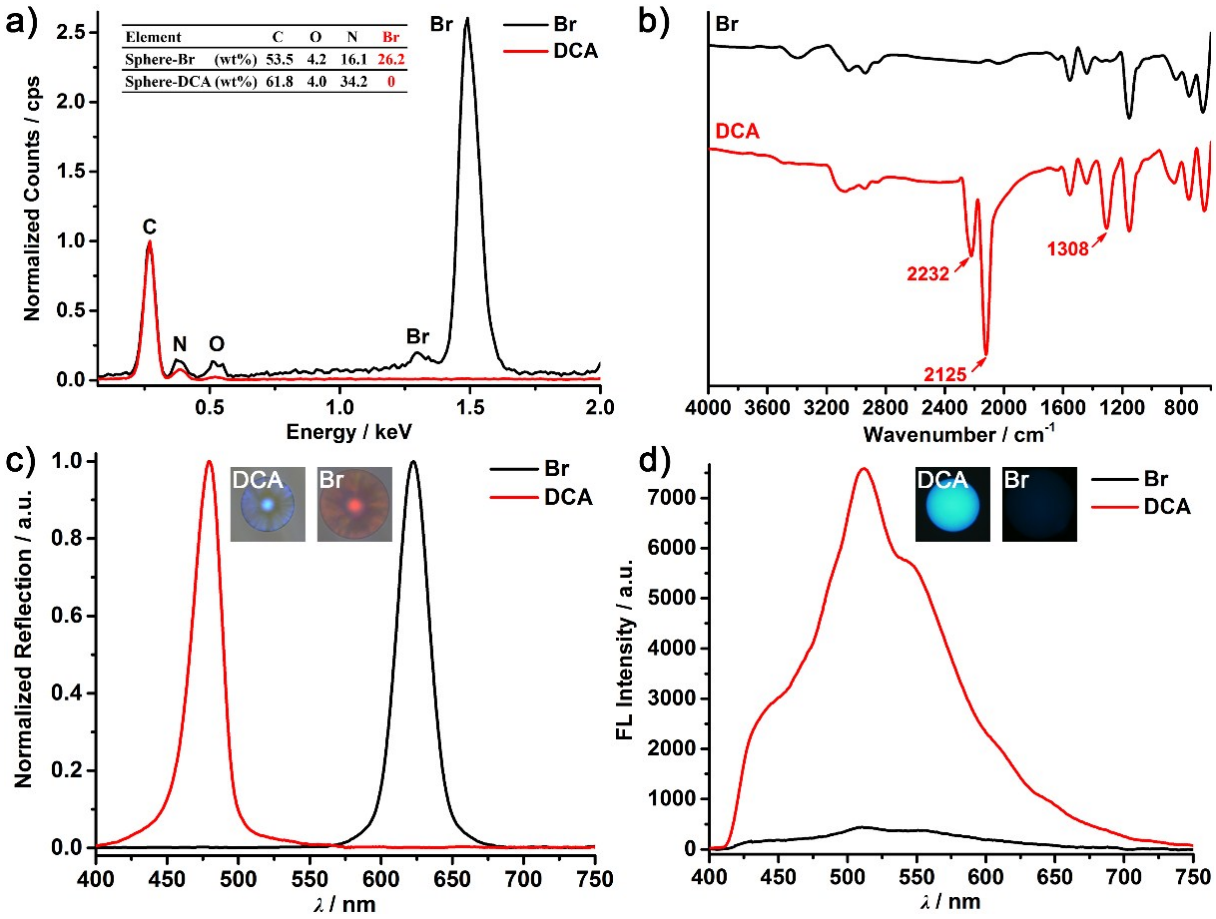

Fig. S5 The counteranions of PIL photonic spheres changing from Br^- to DCA. (a) EDX spectra; (b) FTIR spectra; (c) Reflection spectra and corresponding inserted optical images; (d) Fluorescence spectra and corresponding inserted fluorescence images.

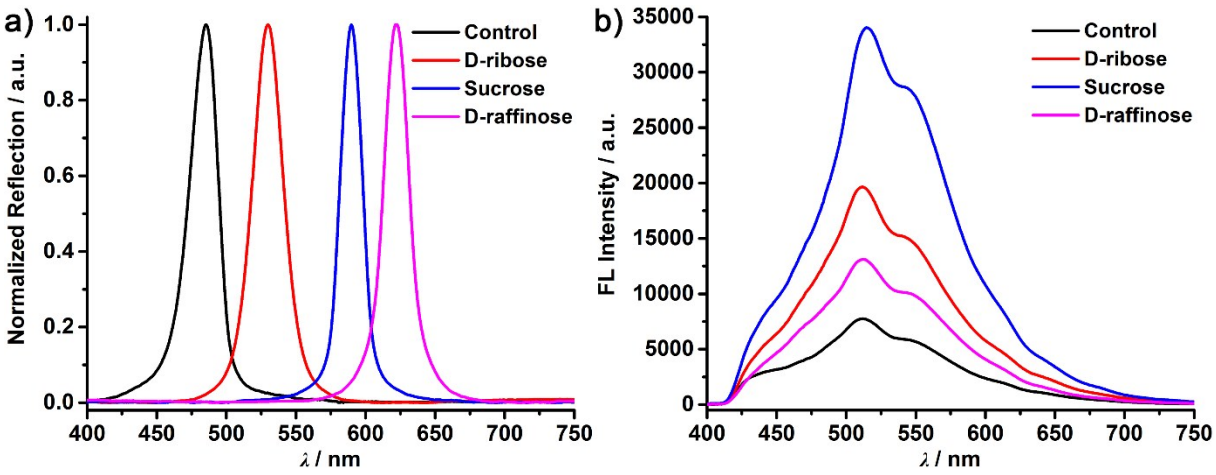

Fig. S6 Responses of dual-channel poly(ionic liquid) photonic spheres (doped with AIEgen-blue; DCA as counteranions) to saccharides at 100 mM: (a) reflection spectra; (b) emission spectra. The integration time for recording FL spectra is 200 ms.

Table S1 The jack-knifed classification procedure on one dual-channel sphere based array (DCA). Summary of 168 samples classification to 23 saccharides and 1 control with cross-validation by LDA. Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23).

Jackknifed Classification Matrix for 23 Saccharides and 1 Control Based on Single-sphere Array (DCA)																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	Control	Correct
1	7																								100%
2		7																							100%
3			7																						100%
4				7																					100%
5					7																				100%
6						7																			100%
7							7																		100%
8								7																	100%
9									7																100%
10										7															100%
11											7														100%
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21																					7				100%
22																						7			100%
23																							7		100%
Control																								7	100%
N = 168									N Correct = 168										Proportion Correct = 100%						

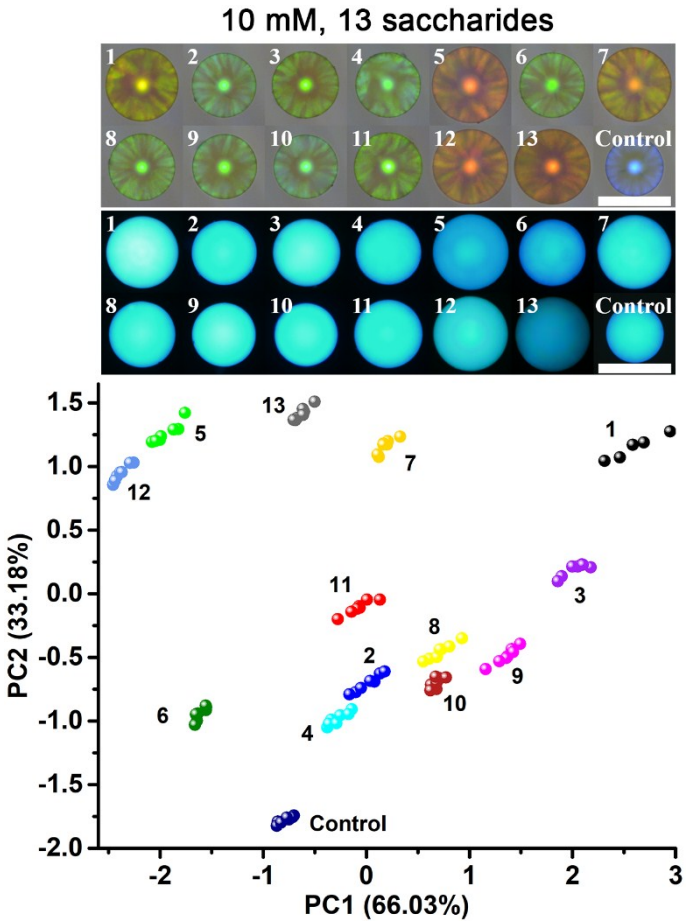

Fig. S7 Exploration of the lower detection concentration (13 saccharides at 10 mM) for the one dual-channel sphere based array (DCA). Optical and fluorescence images of spheres after response to saccharides (top; scale bars, 500 μm). 2D PCA plot for the discrimination of saccharides (bottom). Saccharides: 2-deoxy-D-ribose (1), L-fucose (2), D-lyxose (3), methyl α-D-glucopyranoside (4), L-rhamnose (5), D-cellobiose (6), D-lactose (7), D-maltose (8), D-melibiose (9), sucrose (10), D-melezitose (11), D-raffinose (12) and acarbose (13).

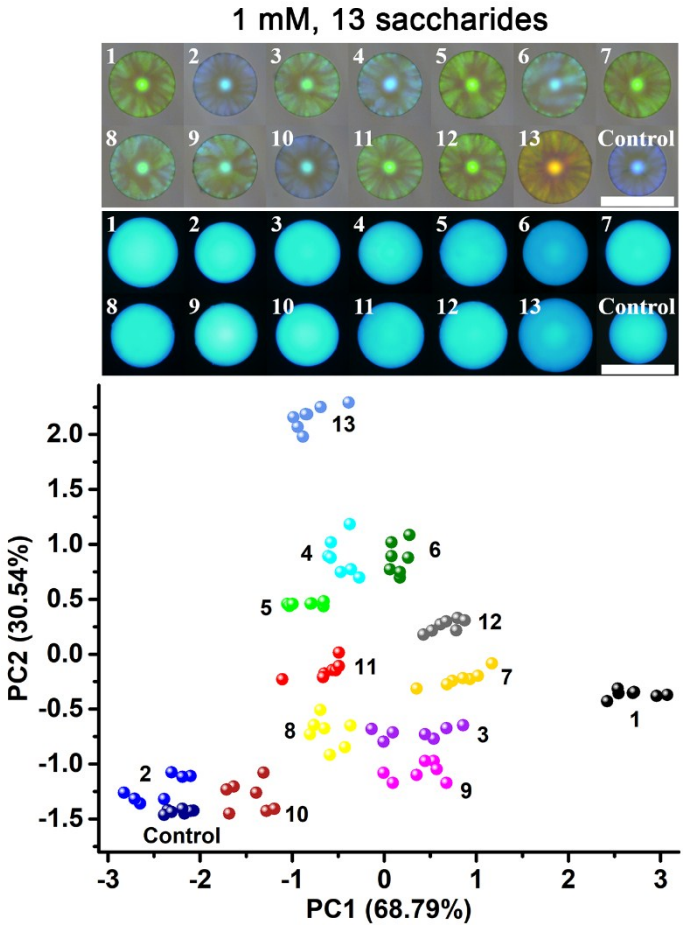

Fig. S8 Exploration of the lower detection concentration (13 saccharides at 1 mM) for the one dual-channel sphere based array (DCA). Optical and fluorescence images of AIE-doped PIL photonic spheres (DCA form) after response to saccharides (top; scale bars, 500 μm). PCA plot for the discrimination of saccharides (bottom). Saccharides: 2-deoxy-D-ribose (1), L-fucose (2), D-lyxose (3), methyl α-D-glucopyranoside (4), L-rhamnose (5), D-cellobiose (6), D-lactose (7), D-maltose (8), D-melibiose (9), sucrose (10), D-melezitose (11), D-raffinose (12) and acarbose (13).

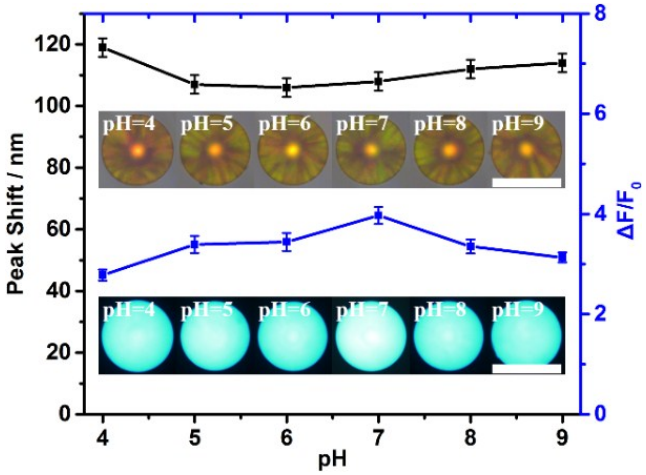

Fig. S9 The PhC and FL (at 515 nm) responses of dual-channel poly(ionic liquid) photonic spheres (doped with AIEgen-blue; DCA as counteranions) for the recognition of sucrose at 100 mM under different pH values. Insets are the corresponding optical images (top) and fluorescence images (bottom); scale bars are 500 μm.

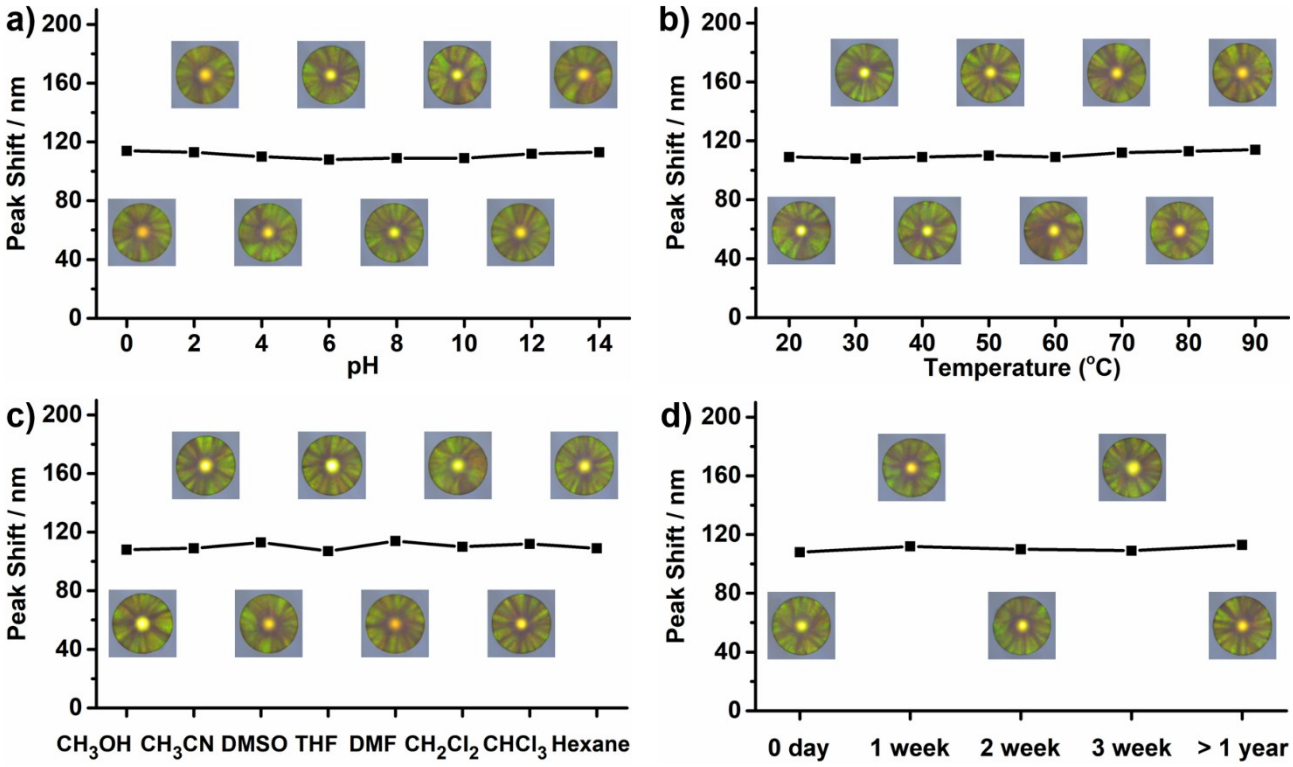

Fig. S10 Exploring the tolerance of PIL spheres to different conditions by soaking them in a wide pH range (a), heating them in a wide temperature range (b), immersing them in different organic solvents (c) and keeping them for a long period of time (d) before use.

After undergoing the above various processes, the PIL spheres can still obtain the nearly same optical response to the saccharide, implying that the sensing performance of PIL spheres are not affected by such conditions. In (a), we just soak the PIL spheres in different pH solutions, and then wash these PIL spheres with deionized water, and finally detect the saccharide in neutral aqueous solution. It doesn't mean that the detection is performed in different pH conditions. Similarly, in (b), we just heat the PIL spheres (placement in water) at different temperatures, and finally detect the saccharide at room temperature. It doesn't mean that the detection is performed at different temperatures. In (c), we just immerse the PIL spheres in different organic solvents, and then remove these organic solvents, and finally detect the saccharide in neutral aqueous solution at room temperature. It doesn't mean that the detection is performed in different organic solvents. In (d), when used for the detection of saccharides, the freshly prepared spheres (0 day) and the spheres after being kept for different periods of time can obtain the same optical response. Here, the PIL sphere with the description of "> 1 year" was previously prepared before more than one years. Notably, in (a-c), after undergoing these conditions and before performing detection, the spheres are better to be reactivated by immersing them in sodium dicyanamide aqueous solution.

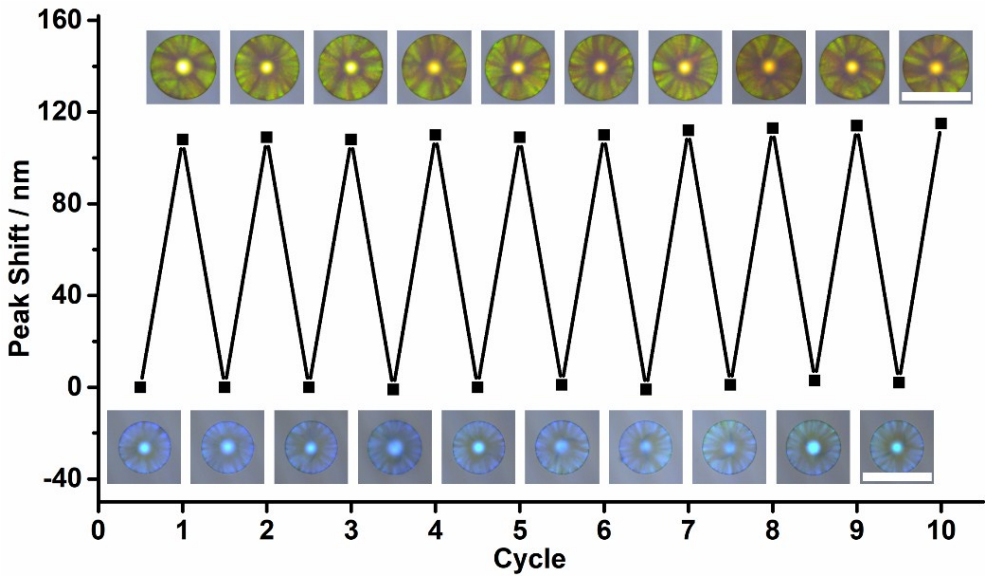

Fig. S11 Exploring the reusability of PIL spheres. The bottom is the PIL sphere before saccharide detection and the top is the PIL sphere after saccharide detection. After detection, the sphere is washed to remove the binding saccharide, and then is reactivated by immersing them in sodium dicyanamide aqueous solution.

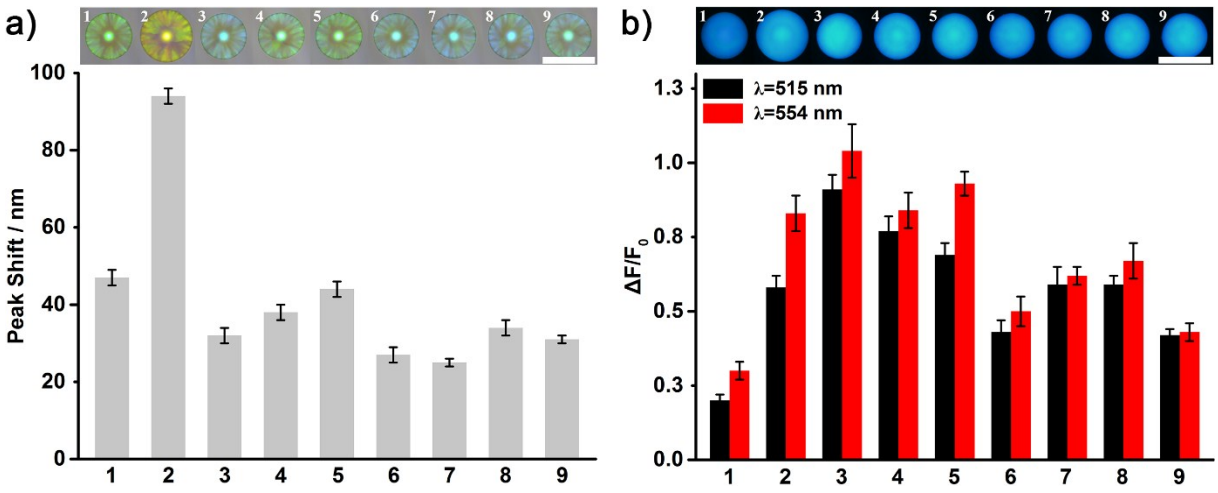

Fig. S12 Responses of dual-channel poly(ionic liquid) photonic spheres (doped with AIEgen-blue; DCA as counteranions) to nine sugar alcohols at 50 mM: (a) optical images and histogram of reflection peak shifts; (b) fluorescence images (false color, exposure time 30 ms) and histogram of the folds of fluorescence enhancement. Scale bars in (a) and (b) are 500 μm. Sugar alcohols: adonitol (1), arabitol (2), meso-erythritol (3), galactitol (4), myo-inositol (5), maltitol (6), manni-tol (7), sorbitol (8), xylitol (9).

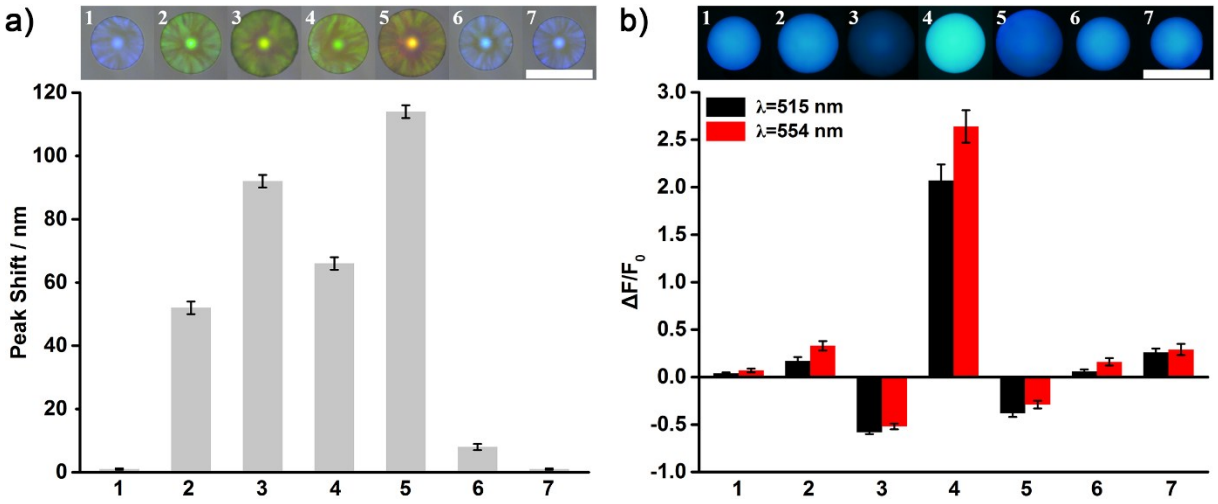

Fig. S13 Responses of dual-channel poly(ionic liquid) photonic spheres (doped with AIEgen-blue; BF_4 as counteranions) to seven glycoproteins at 100 nM: (a) optical images and histogram of reflection peak shifts; (b) fluorescence images (false color, exposure time 30 ms) and histogram of the folds of fluorescence enhancement. Scale bars in (a) and (b) are 500 μm. Glycoproteins: avidin (1), cellulase R-10 (2), fibrinogen (3), glucose oxidase (4), hyaluronidase (5), horseradish peroxidase (6), ovalbumin (7).

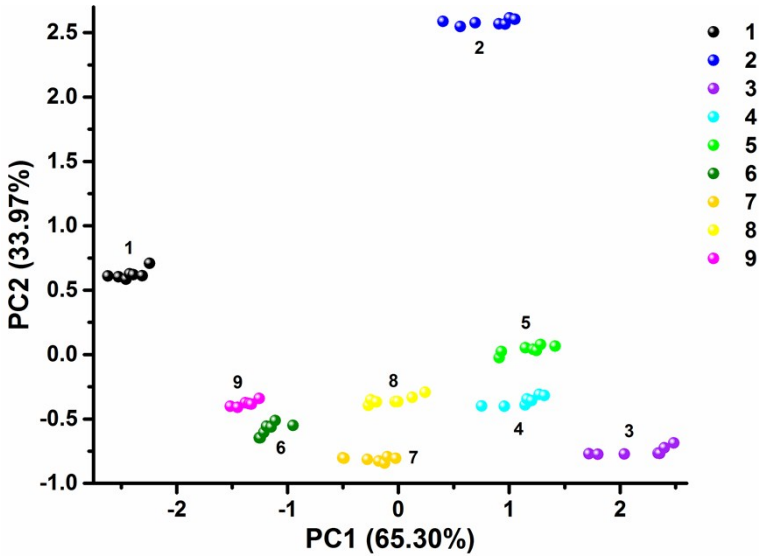

Fig. S14 PCA plot of one dual-channel photonic sphere (doped with AIEgen-blue; DCA as counteranions) for the discrimination of nine sugar alcohols at 50 mM. Sugar alcohols: adonitol (1), arabitol (2), meso-erythritol (3), galactitol (4), myo-inositol (5), maltitol (6), mannitol (7), sorbitol (8), xylitol (9).

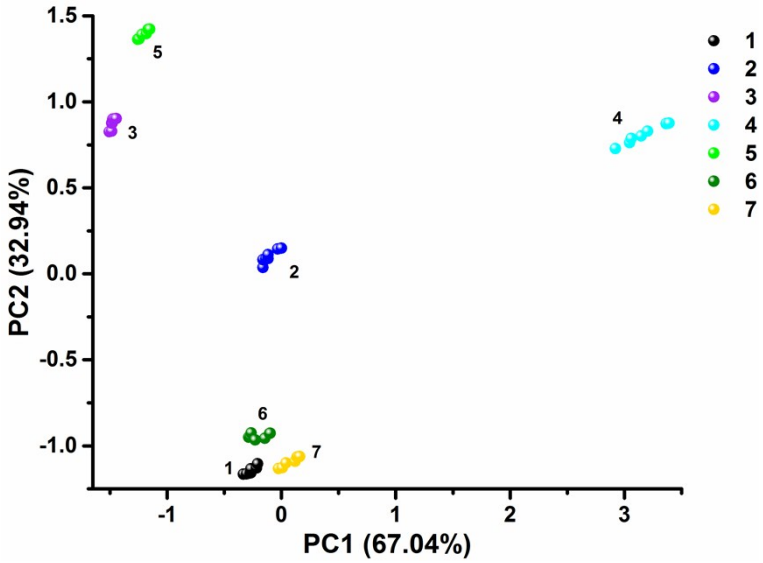

Fig. S15 PCA plot of one dual-channel photonic sphere (doped with AIEgen-blue; BF_4 as counteranions) for the discrimination of seven glycoproteins at 100 nM. Glycoproteins: avidin (1), cellulase R-10 (2), fibrinogen (3), glucose oxidase (4), hyaluronidase (5), horseradish peroxidase (6), ovalbumin (7).

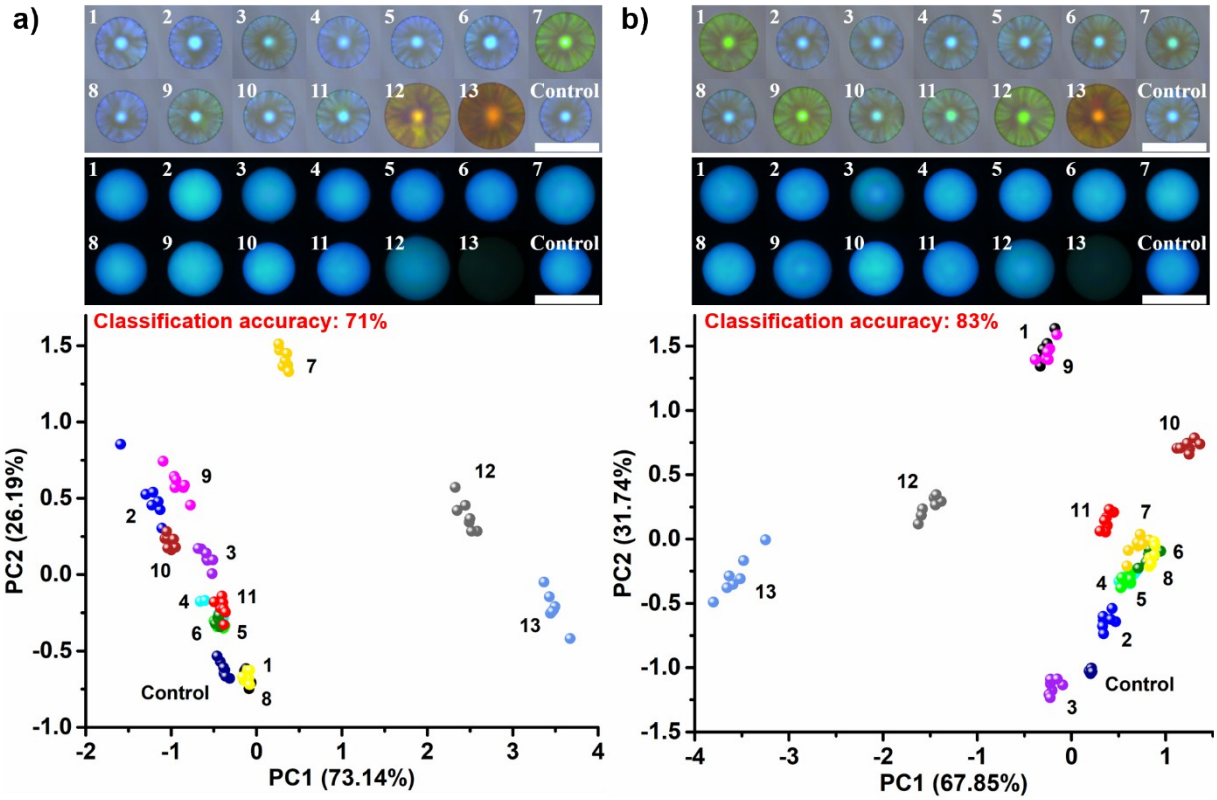

Fig. S16 Exploring the influence of cations in PIL on the saccharide identification. (a) The one dual-channel sphere based array (ammonium cation and DCA anion) for the discrimination of 13 saccharides at 10 mM. Top: optical and fluorescence images of spheres after response to saccharides (scale bars, 500 μm); Bottom: 2D PCA plot. (b) The one dual-channel sphere based array (phosphonium cation and DCA anion) for the discrimination of 13 saccharides at 10 mM. Top: optical and fluorescence images of spheres after response to saccharides (scale bars, 500 μm); Bottom: 2D PCA plot. Saccharides: 2-deoxy-D-ribose (1), L-fucose (2), D-lyxose (3), methyl α-D-glucopyranoside (4), L-rhamnose (5), D-cellobiose (6), D-lactose (7), D-maltose (8), D-melibiose (9), sucrose (10), D-melezitose (11), D-raffinose (12) and acarbose (13).

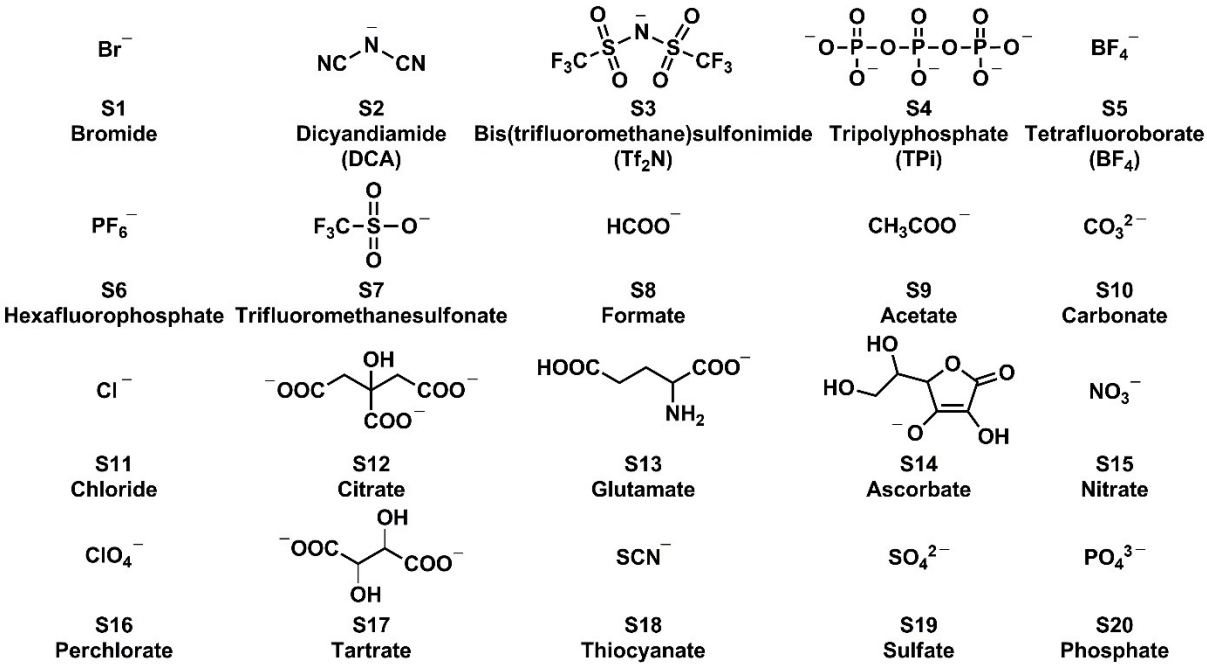

Fig. S17 Chemical structures of counteranions for sensing elements S1-S20: bromide (S1), dicyandiamide (S2), bis(trifluoromethane)sulfonimide (S3), tripolyphosphate (S4), tetrafluoroborate (S5), hexafluorophosphate (S6), trifluoromethanesulfonate (S7), formate (S8), acetate (S9), carbonate (S10), chloride (S11), citrate (S12), glutamate (S13), ascorbate (S14), nitrate (S15), perchlorate (S16), tartrate (S17), thiocyanate (S18), sulfate (S19), phosphate (S20).

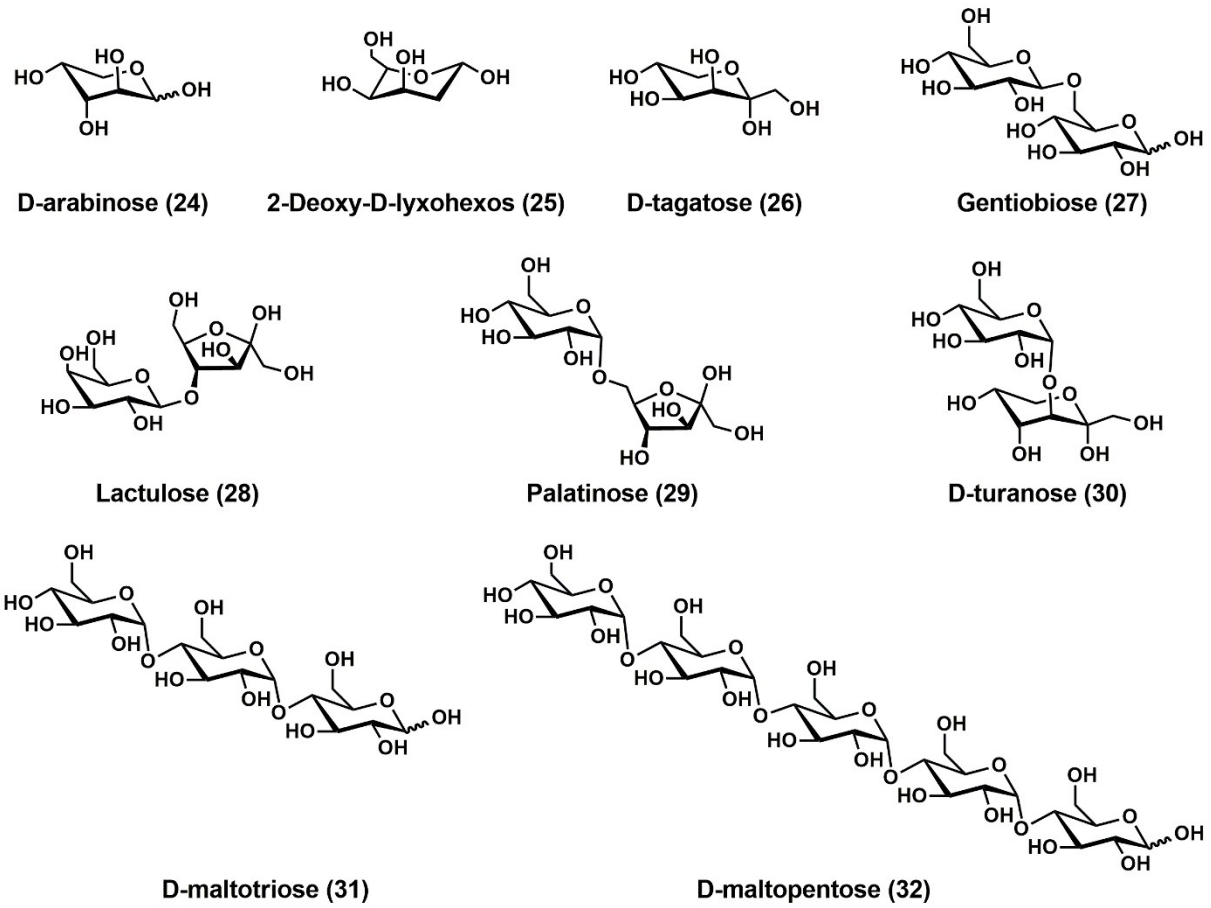

Fig. S18 Chemical structures of newly added nine saccharides.

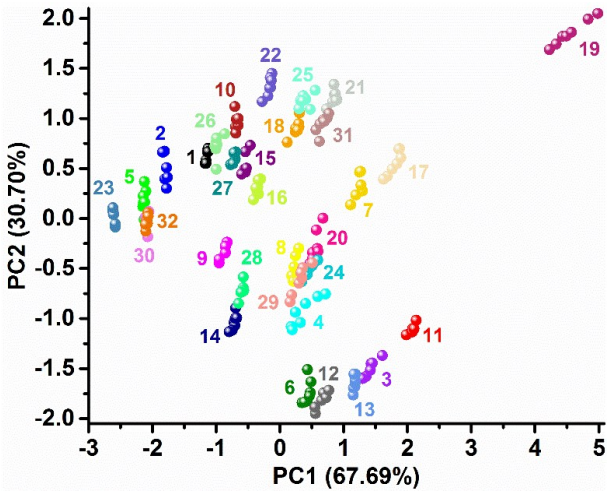

Fig. S19 PCA plot of one dual-channel photonic sphere (doped with AIEgen-blue; DCA as counteranions) for the discrimination of 32 saccharides at 100 mM. Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23), D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Table S2 The jack-knifed classification procedure on one dual-channel sphere based array (DCA, AIE-B). Summary of 224 samples classification to 32 saccharides with cross-validation by LDA. Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23) , D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Jackknifed Classification Matrix for 32 Saccharides Based on Single-sphere Array (DCA)																															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Correct
1	7																																100%
2		7																															100%
3			7																														100%
4				7																													100%
5					7																												100%
6						7																											100%
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10										7																							100%
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13													7																				100%
14														7																			100%
15															7																		100%
16																7																	100%
17																	7																100%
18																		7															100%
19																			7														100%
20																				4				3									57%
21																					7												100%
22																						7											100%
23																							7										100%
24																				1				4					2				57%
25																									7								100%
26																										7							100%
27																											7						100%
28																												7					100%
29																								2					5				71%
30																														6		1	86%
31																															7		100%
32																																7	100%
N = 224											N Correct = 215											Proportion Correct = 96%										

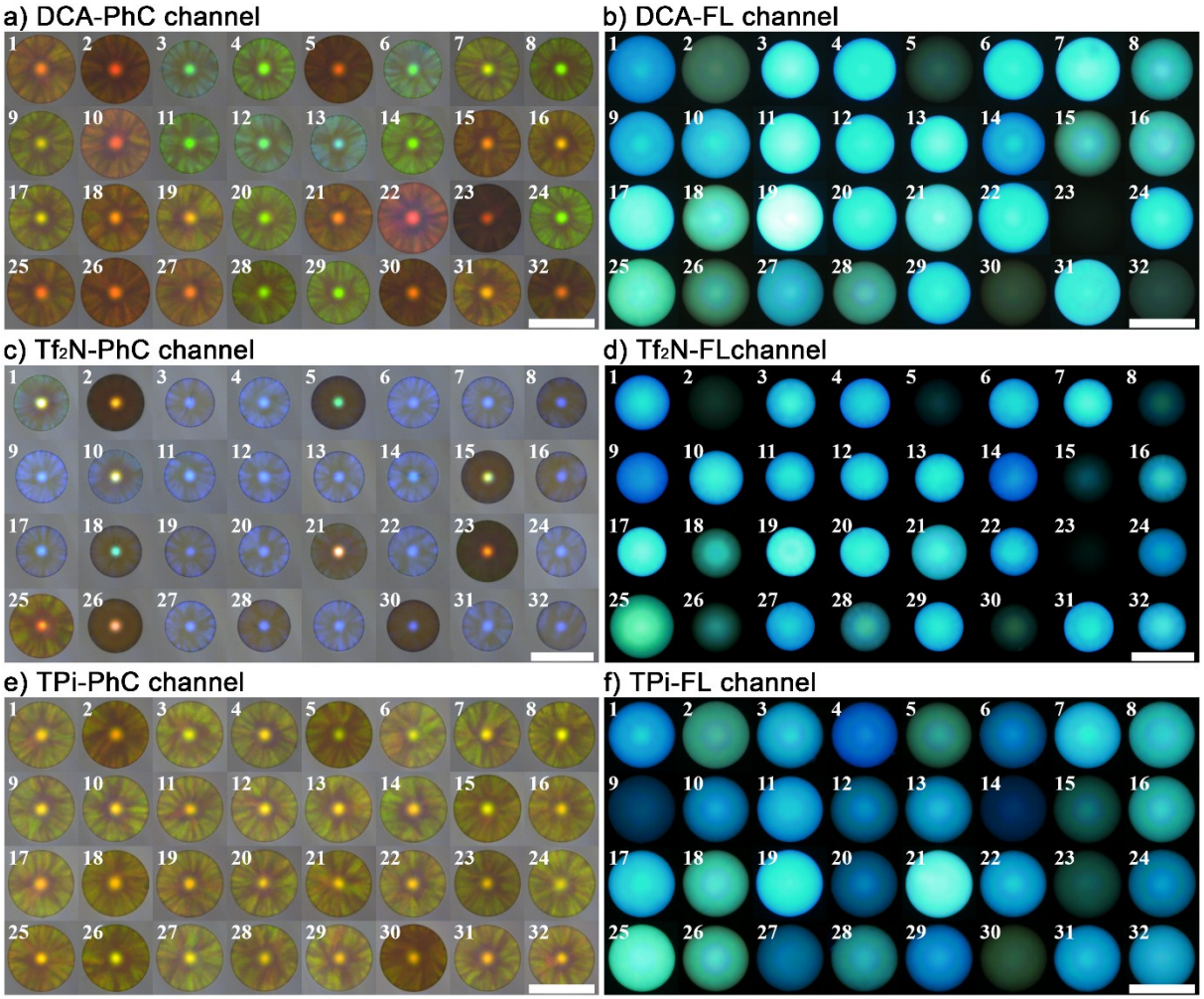

Fig. S20 Responses of three dual-channel spheres (S2, S3 and S4) based sensor array to 32 saccharides at 100 mM: (a), (c), (e) optical images; (b), (d), (f) fluorescence images (false color, exposure time 60 ms). (a) and (b) for spheres of DCA form (S2); (c) and (d) for spheres of Tf_2N form (S3); (e) and (f) for spheres of TPi form (S4). Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23) , D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

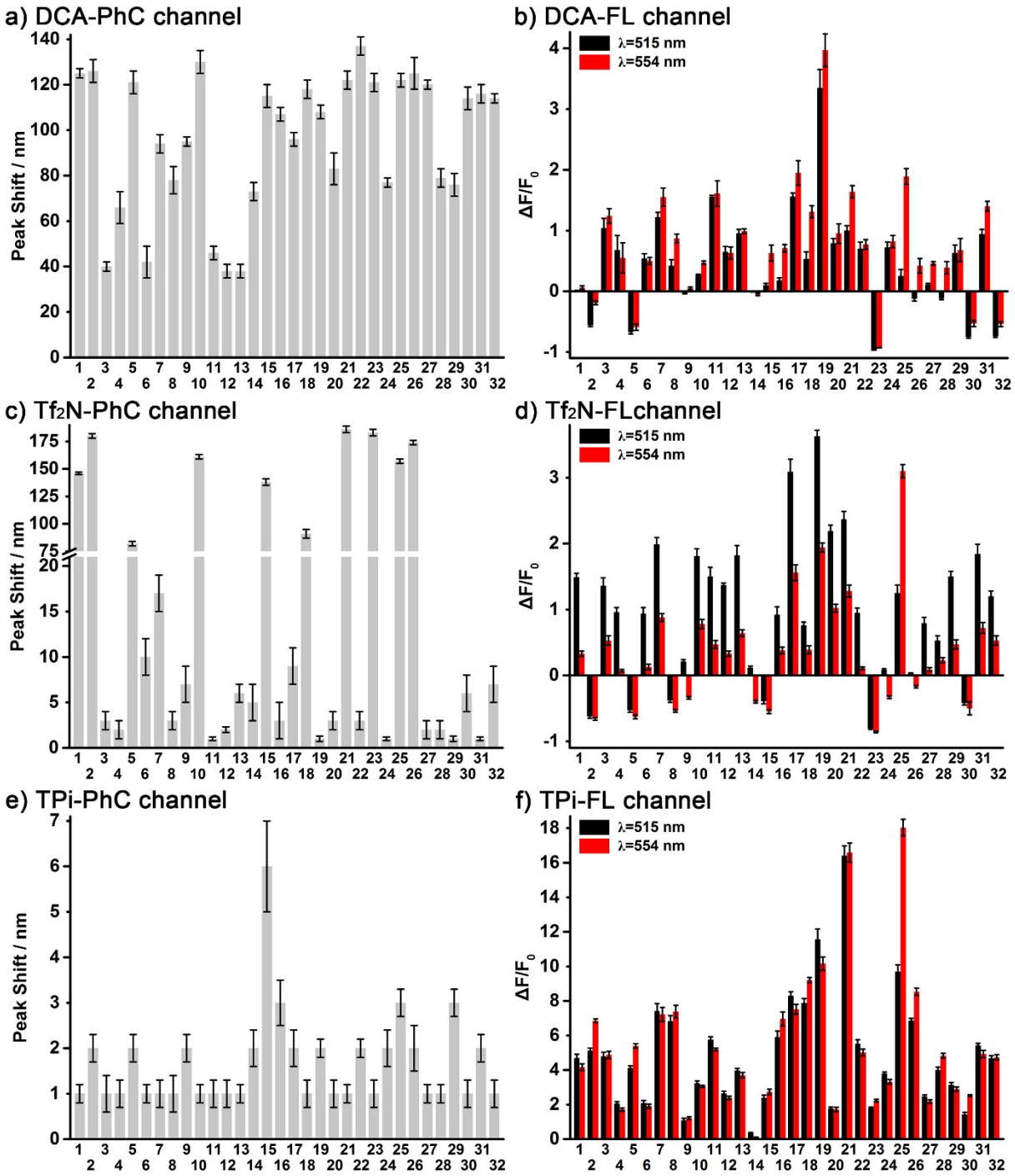

Fig. S21 Responses of three dual-channel spheres (S2, S3 and S4) based sensor array to 32 saccharides at 100 mM: (a), (c), (e) histogram of reflection peak shifts; (b), (d), (f) histogram of the folds of fluorescence enhancement. (a) and (b) for spheres of DCA form (S2); (c) and (d) for spheres of Tf_2N form (S3); (e) and (f) for spheres of TPi form (S4). Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23) , D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

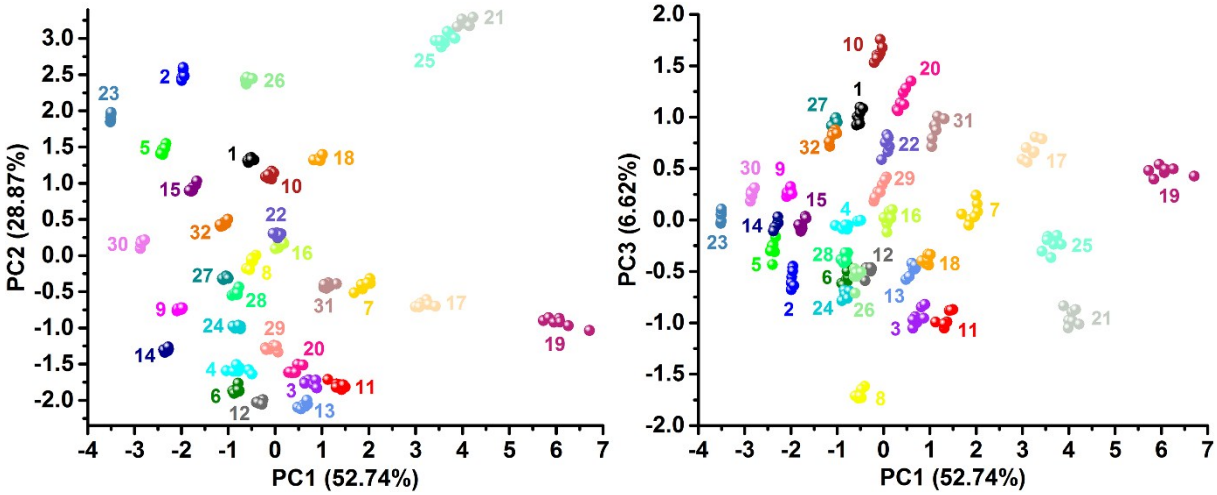

Fig. S22 PCA plot of three dual-channel spheres (S2, S3 and S4) based sensor array for the discrimination of 32 saccharides at 100 mM (left: PC2 versus PC1; right: PC3 versus PC1). Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), mal-tulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23), D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Table S3 The jack-knifed classification procedure on three dual-channel spheres based array (S2, S3 and S4). Summary of 224 samples classification to 32 saccharides with cross-validation by LDA. Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23) , D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Jackknifed Classification Matrix for 32 Saccharides Based on Three-sphere Array (DCA, Tf_2N, TPi)																															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Correct
1	7																																100%
2		7																															100%
3			7																														100%
4				7																													100%
5					7																												100%
6						7																											100%
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28																												7					100%
29																													7				100%
30																														7			100%
31																															7		100%
32																																7	100%
N = 224											N Correct = 224																						Proportion Correct = 100%

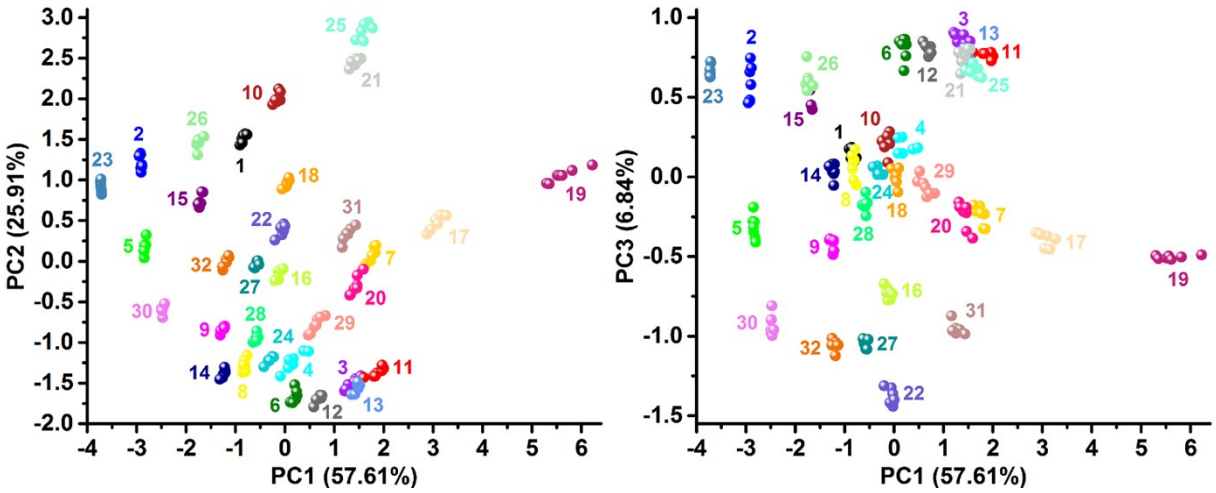

Fig. S23 PCA plot of two dual-channel spheres (S2 and S3) based sensor array for the discrimination of 32 saccharides at 100 mM (left: PC2 versus PC1; right: PC3 versus PC1). Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23), D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Table S4 The jack-knifed classification procedure on two dual-channel spheres based array (S2 and S3). Summary of 224 samples classification to 32 saccharides with cross-validation by LDA. Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23) , D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Jackknifed Classification Matrix for 32 Saccharides Based on Two-sphere Array (DCA, Tf_2N)																																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Correct
1	7																																100%
2		7																															100%
3			7																														100%
4				7																													100%
5					7																												100%
6						7																											100%
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29																													7				100%
30																														7			100%
31																															7		100%
32																																7	100%
N = 224											N Correct = 224																						Proportion Correct = 100%

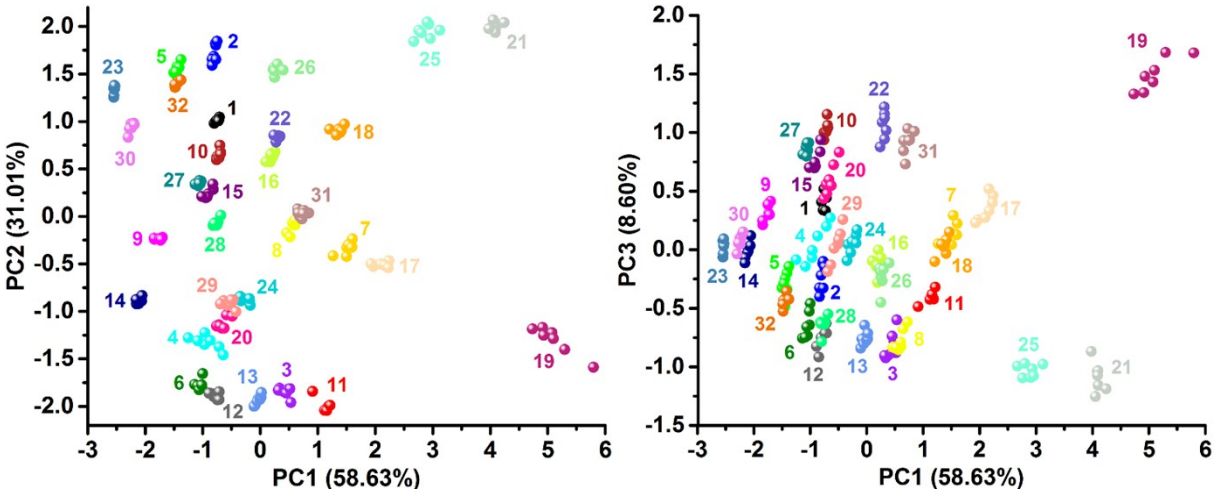

Fig. S24 PCA plot of two dual-channel spheres (S2 and S4) based sensor array for the discrimination of 32 saccharides at 100 mM (left: PC2 versus PC1; right: PC3 versus PC1). Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23), D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Table S5 The jack-knifed classification procedure on two dual-channel spheres based array (S2 and S4). Summary of 224 samples classification to 32 saccharides with cross-validation by LDA. Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23) , D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Jackknifed Classification Matrix for 32 Saccharides Based on Two-sphere Array (DCA, TPi)																																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Correct
1	7																																100%
2		7																															100%
3			7																														100%
4				7																													100%
5					7																												100%
6						7																											100%
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29																													7				100%
30																														7			100%
31																															7		100%
32																																7	100%
N = 224											N Correct = 224																						Proportion Correct = 100%

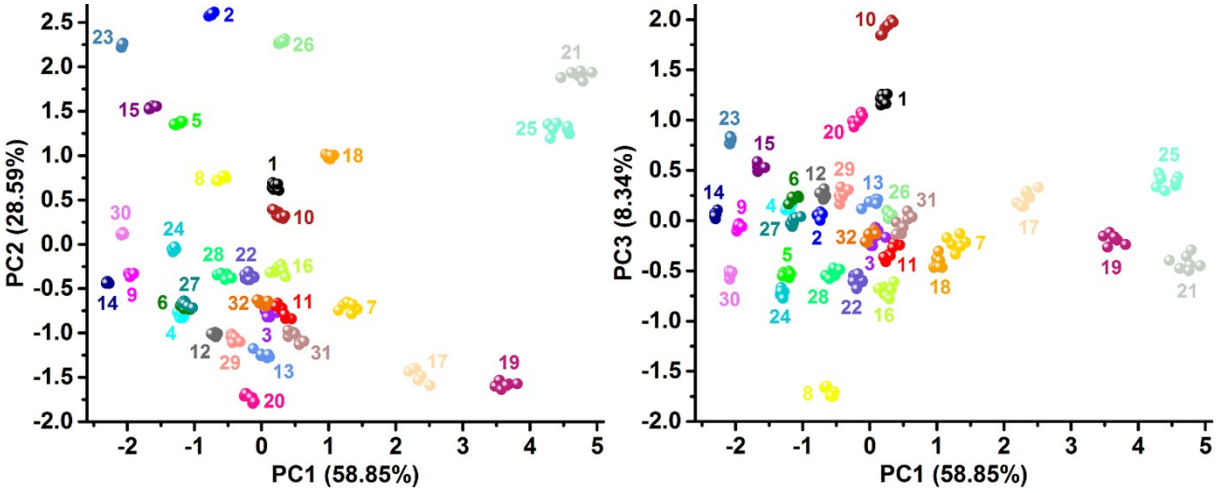

Fig. S25 PCA plot of two dual-channel spheres (S3 and S4) based sensor array for the discrimination of 32 saccharides at 100 mM (left: PC2 versus PC1; right: PC3 versus PC1). Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23), D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Table S6 The jack-knifed classification procedure on two dual-channel spheres based array (S3 and S4). Summary of 224 samples classification to 32 saccharides with cross-validation by LDA. Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23) , D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Jackknifed Classification Matrix for 32 Saccharides Based on Two-sphere Array (Tf_2N, TPi)																																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Correct
1	7																																100%
2		7																															100%
3			7																														100%
4				7																													100%
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29																													7				100%
30																														7			100%
31																															7		100%
32																																7	100%
N = 224											N Correct = 224											Proportion Correct = 100%										

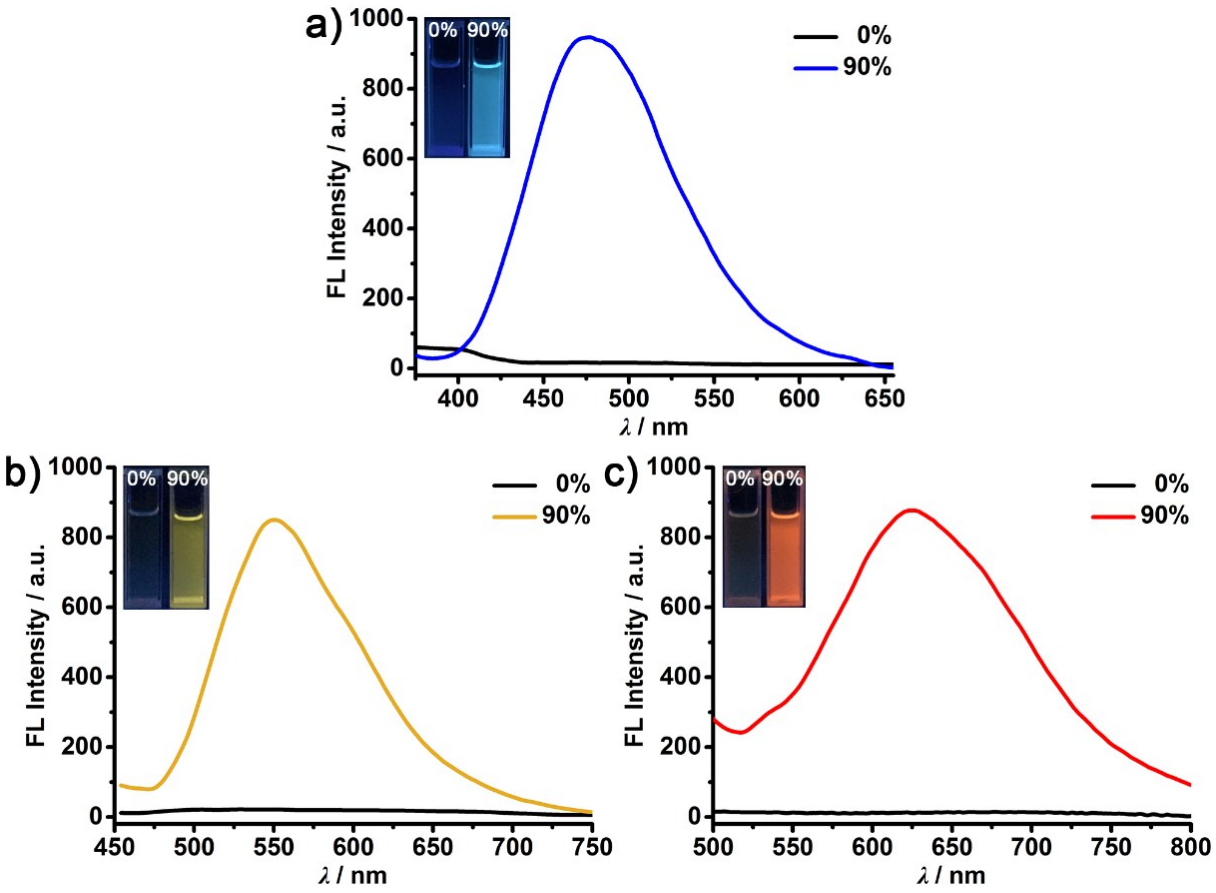

Fig. S26 Fluorescence spectra of AIEgen-blue (a), AIEgen-yellow (b) and AIEgen-red (c) at 10 μM in the hexane/CH_2Cl_2 mixtures with different volume fractions of hexane. Insets are the fluorescence photographs of solution of AIEgen in CH_2Cl_2 (left) and in 90% hexane/CH_2Cl_2 mixture (right) under illumination of a handheld UV (365 nm) lamp.

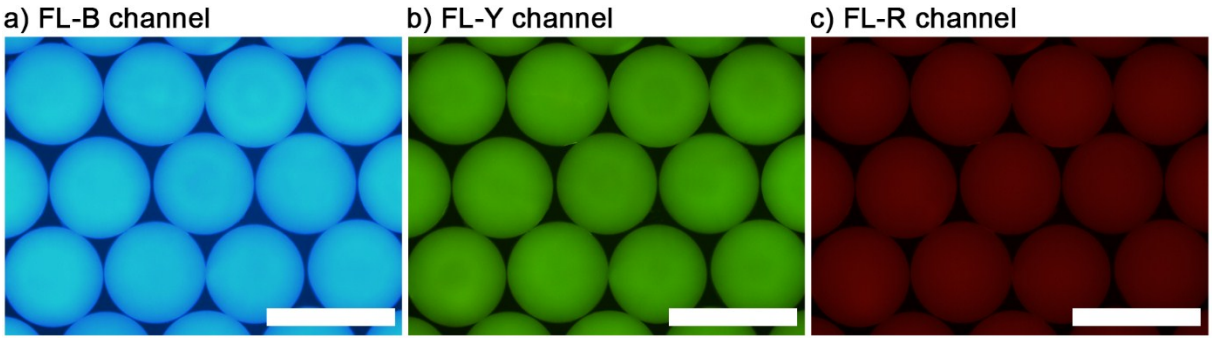

Fig. S27 Fluorescence image of quadruple-channel poly(ionic liquid) photonic spheres (doped with AIEgen-blue, AIEgen-yellow, and AIEgen-red; DCA as counteranions) under three different excitation modes. (a) FL-B channel images (false color, exposure time 30 ms); (b) FL-Y channel images (false color, exposure time 60 ms); (c) FL-R channel images (false color, exposure time 60 ms). Scale bars in (a), (b) and (c) are 500 μm.

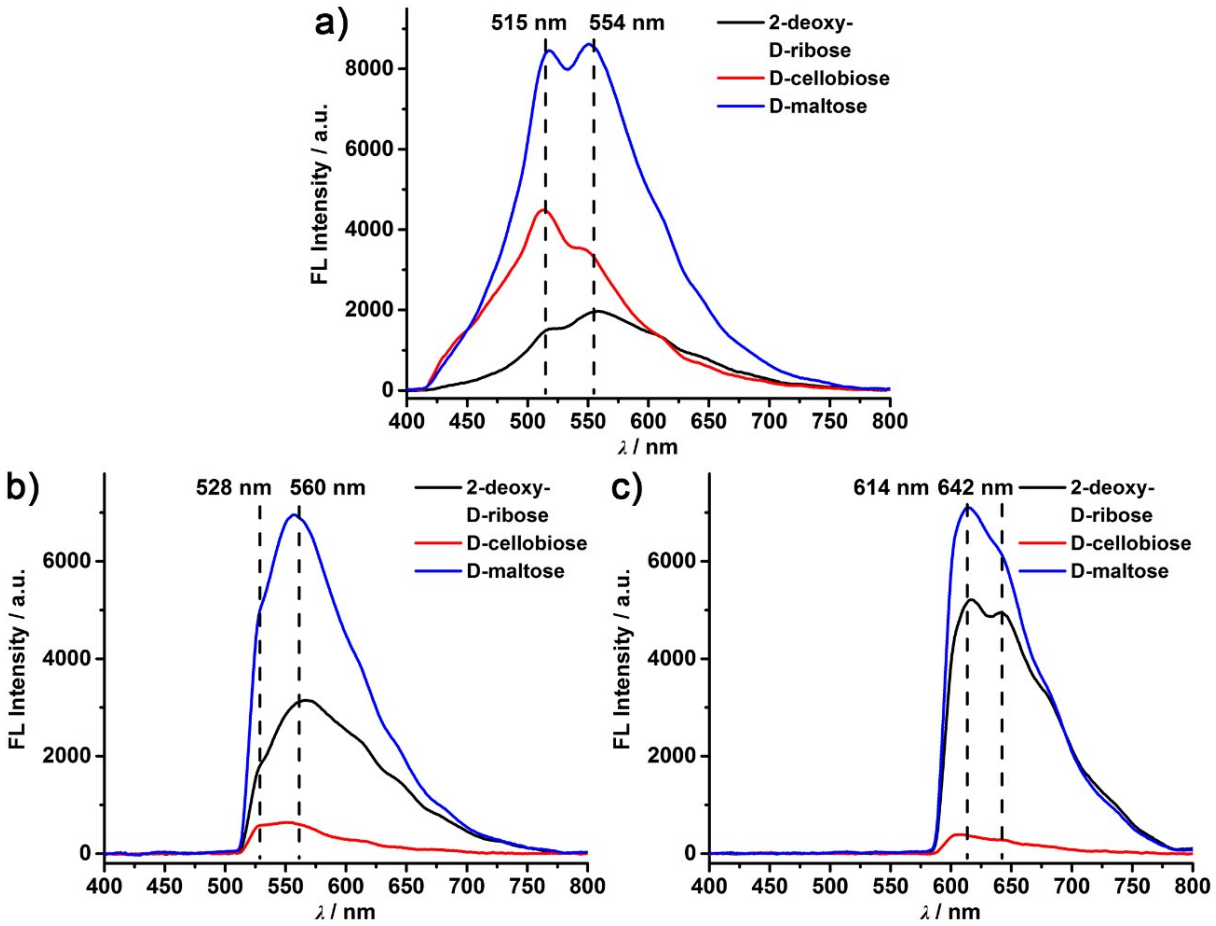

Fig. S28 Fluorescence spectra of one quadruple-channel photonic sphere (doped with AIEgen-blue, AIEgen-yellow, and AIEgen-red; DCA as counteranions) under three different excitation modes after binding with saccharides. (a) FL-B channel spectra; (b) FL-Y channel spectra; (c) FL-R channel spectra. The integration time for recording FL spectra is 200 ms.

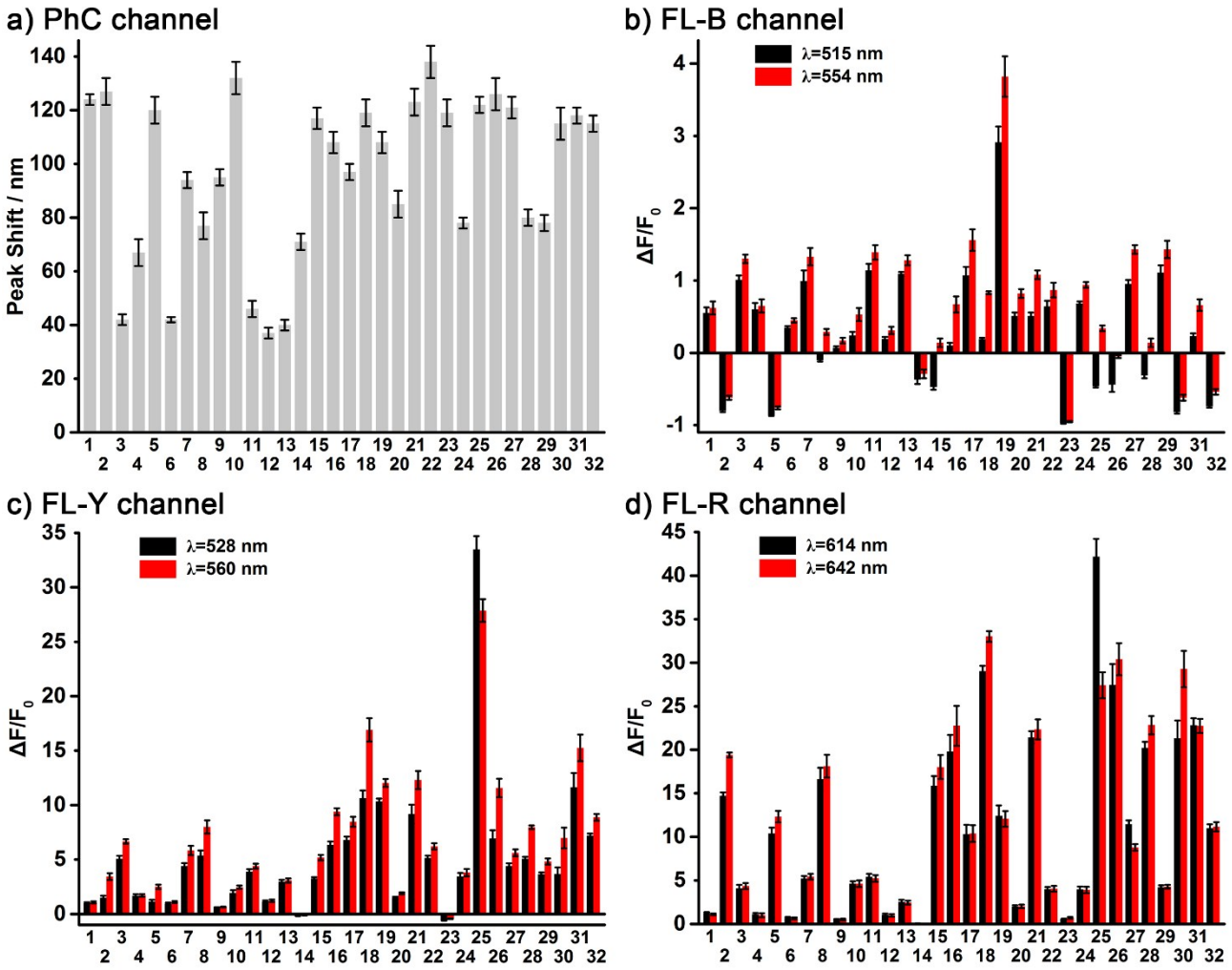

Fig. S29 Responses of one quadruple-channel photonic sphere (doped with AIEgen-blue, AIEgen-yellow, and AIEgen-red; DCA as counteranions) to 32 saccharides at 100 mM: (a) histogram of reflection peak shifts; (b), (c) and (d) histogram of the folds of fluorescence enhancement in B, Y and R channels, respectively. Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23) , D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

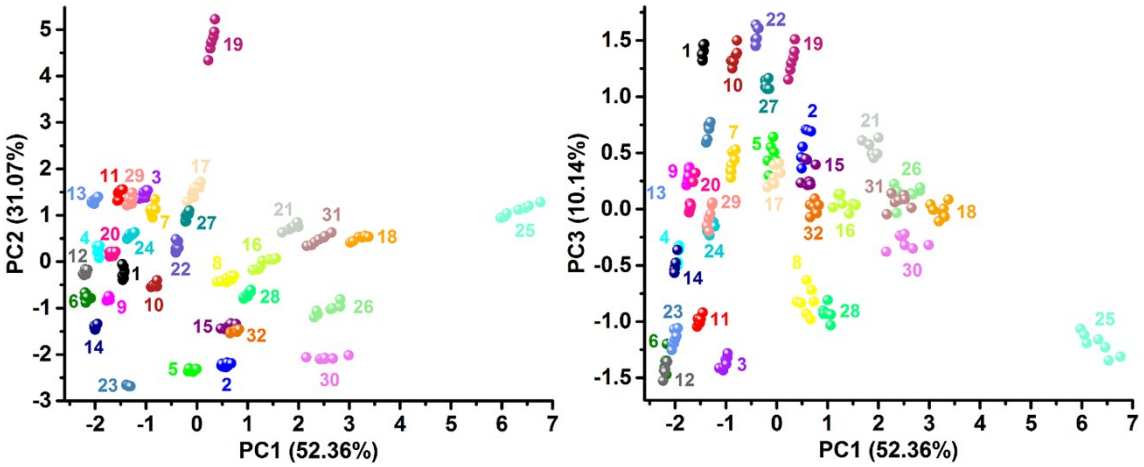

Fig. S30 PCA plot of one quadruple-channel photonic sphere (doped with AIEgen-blue, AIEgen-yellow, and AIEgen-red; DCA as counteranions) for the discrimination of 32 saccharides at 100 mM (top: PC2 versus PC1; bottom: PC3 versus PC1). Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23), D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Table S7 The jack-knifed classification procedure on one quadruple-channel sphere based array (DCA, AIE-B, Y, R). Summary of 224 samples classification to 32 saccharides with cross-validation by LDA. Saccharides: D-allose (1), 2-deoxy-D-ribose (2), D-fructose (3), L-fucose (4), D-galactose (5), D-glucose (6), D-lyxose (7), D-mannose (8), methyl α-D-glucopyranoside (9), L-rhamnose (10), D-ribose (11), L-sorbose (12), D-xylose (13), D-cellobiose (14), D-lactose (15), D-maltose (16), maltulose (17), D-melibiose (18), sucrose (19), D-trehalose (20), D-melezitose (21), D-raffinose (22), acarbose (23) , D-arabinose (24), 2-deoxy-D-lyxohexos (25), D-tagatose (26), gentiobiose (27), lactulose (28), palatinose (29), D-turanose (30), D-maltotriose (31), D-maltopentose (32).

Jackknifed Classification Matrix for 32 Saccharides Based on Single-sphere Array (DCA, AIE-B, Y, R)																															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Correct
1	7																																100%
2		7																															100%
3			7																														100%
4				7																													100%
5					7																												100%
6						7																											100%
7							7																										100%
8								7																									100%
9									7																								100%
10										7																							100%
11											7																						100%
12												7																					100%
13													7																				100%
14														7																			100%
15															7																		100%
16																7																	100%
17																	7																100%
18																		7															100%
19																			7														100%
20																				7													100%
21																					7												100%
22																						7											100%
23																							7										100%
24																								7									100%
25																									7								100%
26																										7							100%
27																											7						100%
28																												7					100%
29																													7				100%
30																														7			100%
31																															7		100%
32																																7	100%
N = 224											N Correct = 224											Proportion Correct = 100%										

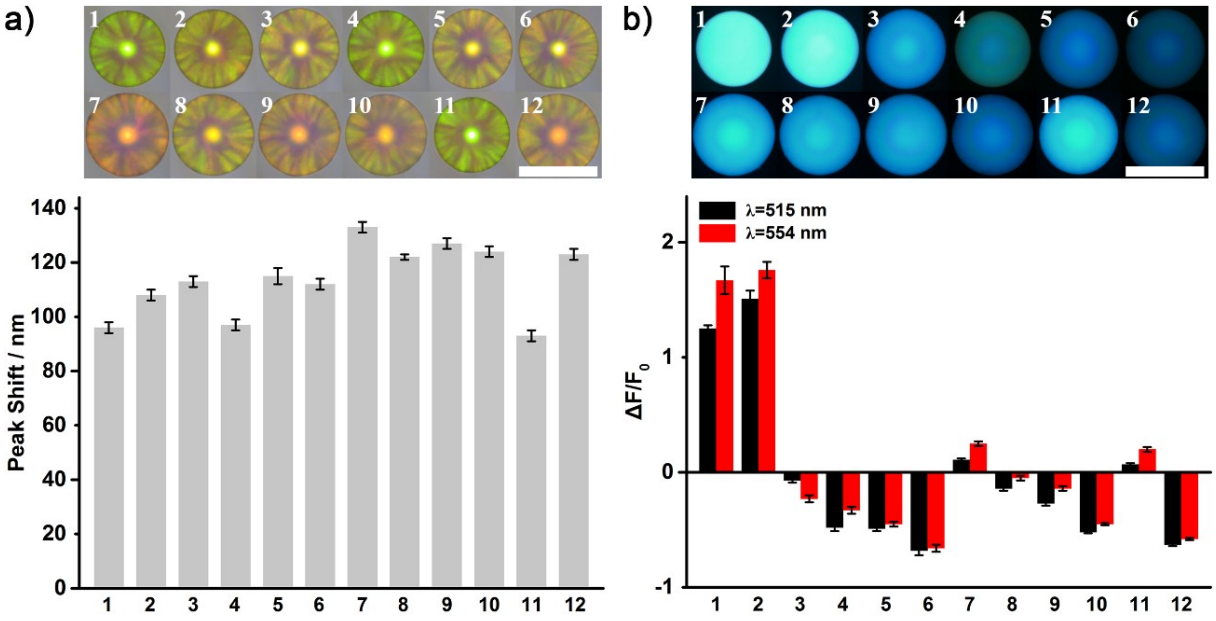

Fig. S31 Responses of one dual-channel photonic sphere (doped with AIEgen-blue; DCA as counteranions) to 12 sugary beverages whose pH values are not adjusted before analysis: (a) optical images and histogram of reflection peak shifts; (b) fluorescence images (false color, exposure time 30 ms) and histogram of the folds of fluorescence enhancement. Scale bars in (a) and (b) are 500 μm. Sugary beverages: Coca Cola (1), Pepsi Cola (2), Minute Maid Orange Juice (3), Uni-President Ice Tea (4), Uni-President Pear Juice (5), Wahaha Nutrition Express (6), Minute Maid Fruit Milk (7), Nongfu Spring Fruit Blend (8), Coconut Thai Mango Juice (9), Nongfu Spring Vitamin (10), Danone Lemonade (11), Danone Mizone (12).

Table S8 Ingredient list of 12 sugary beverages.

Entry	Name	Ingredient	Carbohydrate Content (g / 100 mL)
1	Coca Cola	water, fructose-glucose syrup, white sugar, carbon dioxide, caramel, phosphoric acid, caffeine, food flavor	11.2
2	Pepsi Cola	water, fructose-glucose syrup, white sugar, carbon dioxide, caramel, phosphoric acid, caffeine, food flavor	10.6
3	Minute Maid Orange Juice	water, fructose-glucose syrup, white sugar, orange pulp, concentrate orange juice, citric acid, sodium citrate, carotene, vitamin C, food flavor	9.7
4	Uni-President Ice Tea	water, fructose-glucose syrup, white sugar, instant black tea, malic acid, citric acid, concentrate lemon juice, sodium citrate, vitamin C, sodium hexametaphosphate, stevioside, sodium bicarbonate, food flavor	9.2
5	Uni-President Pear Juice	water, fructose-glucose syrup, white sugar, concentrate pear juice, citric acid, sodium citrate, isoascorbic acid, vitamin C, sodium chloride, sodium carboxymethyl cellulose, food flavor	9.2
6	Wahaha Nutrition Express	water, white sugar, whole milk powder, lactic acid, sodium citrate, sodium pyrophosphate, guar gum, aspartame, acesulfame, xanthan gum, concentrate apple juice, skim milk powder, taurine, vitamin E, zinc citrate, nicotinamide, sodium carboxymethyl cellulose, food flavor	6.0
7	Minute Maid Fruit Milk	water, fructose-glucose syrup, white sugar, whole milk powder, concentrate whey protein, phosphoric acid, sodium citrate, acesulfame, pectin, xanthan gum, aspartame, citric acid, coconut milk, food starch, food flavor, zinc gluconate, vitamin E, nicotinamide, sodium carboxymethyl cellulose	7.8
8	Nongfu Spring Fruit Blend	water, white sugar, concentrate juice, mango puree, guava puree, citric acid, sodium citrate, isoascorbic acid, vitamin C, pectin, malic acid, carotene, xanthan gum, sodium carboxymethyl cellulose, food flavor	8.0
9	Coconut Thai Mango Juice	water, fructose-glucose syrup, white sugar, Alfonso mango puree, coconut fruit, citric acid, sodium citrate, isoascorbic acid, potassium sorbate, scesulfame, sodium carboxymethyl cellulose, food flavor	5.5
10	Nongfu Spring Vitamin	water, fructose-glucose syrup, white sugar, concentrate grape juice, isoascorbic acid, citric acid, malic acid, lutein, carotene, taurine, magnesium sulfate, nicotinamide, vitamin B_6, vitamin B_{12}, food flavor	5.5
11	Danone Lemonade	water, white sugar, lemon juice, apple juice, citric acid, sodium citrate, malic acid, pectin, sucralose, food flavor	5.0
12	Danone Mizone	water, fructose-glucose syrup, white sugar, apple juice, citric acid, acetic acid, vitamin C, vitamin B_6, nicotinamide, sucralose, disodium ethylenediaminetetraacetate, food flavor	4.8

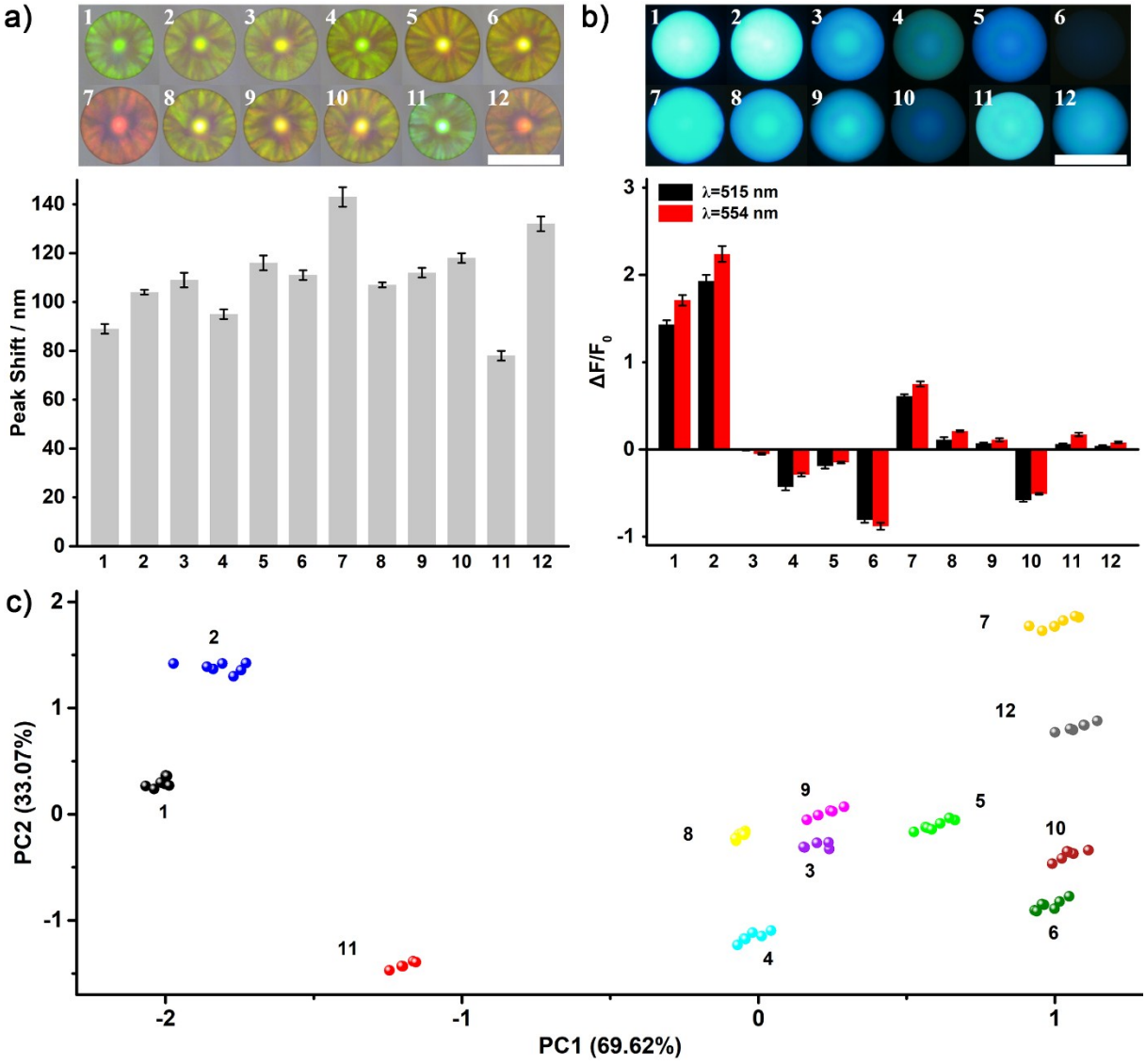

Fig. S32 One dual-channel photonic sphere (doped with AIEgen-blue; DCA as counteranions) for identifying 12 sugary beverages whose pH values are adjusted to the same level (pH = 7) before analysis. (a) Responses of optical images and histogram of reflection peak shifts; (b) Responses of fluorescence images (false color, exposure time 30 ms) and histogram of the folds of fluorescence enhancement; (c) PCA plot. Scale bars in (a) and (b) are 500 μm. Sugary beverages: Coca Cola (1), Pepsi Cola (2), Minute Maid Orange Juice (3), Uni-President Ice Tea (4), Uni-President Pear Juice (5), Wahaha Nutrition Express (6), Minute Maid Fruit Milk (7), Nongfu Spring Fruit Blend (8), Coconut Thai Mango Juice (9), Nongfu Spring Vitamin (10), Danone Lemonade (11), Danone Mizone (12).

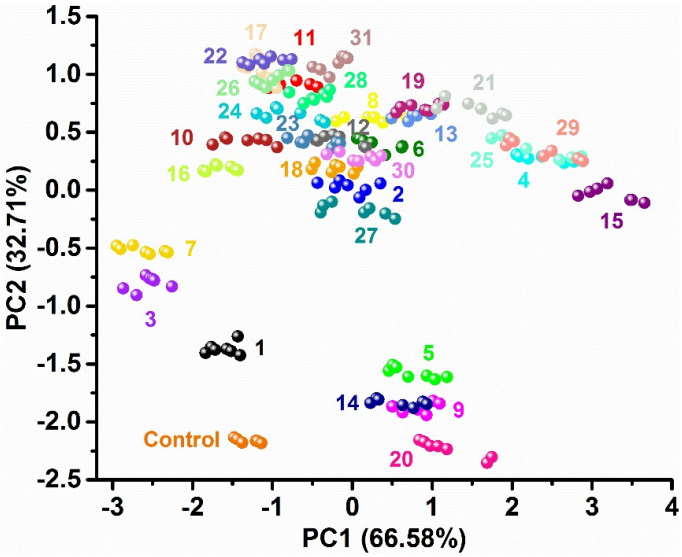

Fig. S33 PCA plot of one dual-channel photonic sphere (doped with AIEgen-blue; DCA as counteranions) for the discrimination of 1 control analytes, 5 unitary analytes and 26 mixture analytes at 20 mM for all saccharides in tea. The 5 unitary analytes: A (1), B (2), C (3), D (4), E (5); 26 mixture analytes: AB (6), AC (7), AD (8), AE (9), BC (10), BD (11), BE (12), CD (13), CE (14), DE (15), ABC (16), ABD (17), ABE (18), ACD (19), ACE (20), ADE (21), BCD (22), BCE (23), BDE (24), CDE (25), ABCD (26), ABCE (27), ABDE (28), ACDE (29), BCDE (30), ABCDE (31). A-E represent fructose, galactose, glucose, lactose and sucrose, respectively.

Table S9 The jack-knifed classification procedure on one dual-channel sphere based array (DCA, AIE-B). Summary of 224 samples classification to 31 saccharide mixtures and 1control in tea with cross-validation by LDA. The 5 unitary analytes: A (1), B (2), C (3), D (4), E (5); 26 mixture analytes: AB (6), AC (7), AD (8), AE (9), BC (10), BD (11), BE (12), CD (13), CE (14), DE (15), ABC (16), ABD (17), ABE (18), ACD (19), ACE (20), ADE (21), BCD (22), BCE (23), BDE (24), CDE (25), ABCD (26), ABCE (27), ABDE (28), ACDE (29), BCDE (30), ABCDE (31). A-E represent fructose, galactose, glucose, lactose and sucrose, respectively.

Jackknifed Classification Matrix for 31 Saccharide Mixtures and 1 Control Based on Single-sphere Array (DCA, AIE-B)																															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	Control	Correct
1	7																																100%
2		7																															100%
3			7																														100%
4				7																													100%
5					7																												100%
6						6						1																					86%
7							7																										100%
8								6					1																				86%
9									7																								100%
10										7																							100%
11											5															2							71%
12												5											2										71%
13								1					5						1														71%
14														7																			100%
15															7																		100%
16																7																	100%
17																	3					2				1		1					43%
18																		7															100%
19													2						5														71%
20																				7													100%
21																			1		6												86%
22																						7											100%
23												2											5										71%
24																								7									100%
25				3																					4								57%
26											2						2									3							43%
27																											7						100%
28																												7					100%
29																													7				100%
30																														7			100%
31																															7		100%
Control																																7	100%
N = 224											N Correct = 200											Proportion Correct = 89%										

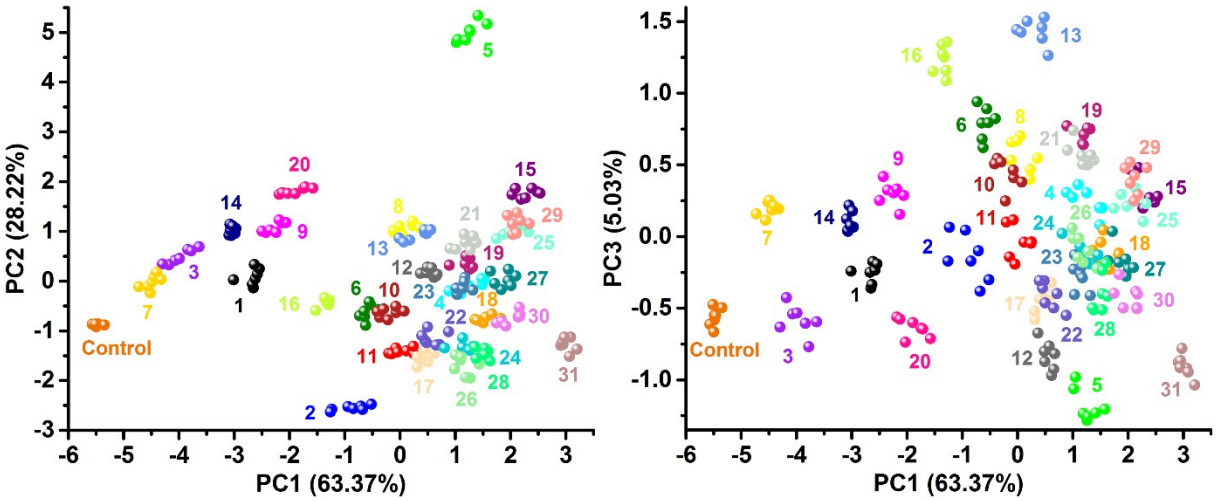

Fig. S34 PCA plot of one quadruple-channel photonic sphere (doped with AIEgen-blue, AIEgen-yellow, and AIEgen-red; DCA as counteranions) for the discrimination of 1 control analytes, 5 unitary analytes and 26 mixture analytes at 20 mM for all saccharides in tea (left: PC2 versus PC1; right: PC3 versus PC1). The 5 unitary analytes: A (1), B (2), C (3), D (4), E (5); 26 mixture analytes: AB (6), AC (7), AD (8), AE (9), BC (10), BD (11), BE (12), CD (13), CE (14), DE (15), ABC (16), ABD (17), ABE (18), ACD (19), ACE (20), ADE (21), BCD (22), BCE (23), BDE (24), CDE (25), ABCD (26), ABCE (27), ABDE (28), ACDE (29), BCDE (30), ABCDE (31). A-E represent fructose, galactose, glucose, lactose and sucrose, respectively.

Table S10 The jack-knifed classification procedure on one quadruple-channel sphere based array (DCA, AIE-B, Y, R). Summary of 224 samples classification to 31 saccharide mixtures and 1control in tea with cross-validation by LDA. The 5 unitary analytes: A (1), B (2), C (3), D (4), E (5); 26 mixture analytes: AB (6), AC (7), AD (8), AE (9), BC (10), BD (11), BE (12), CD (13), CE (14), DE (15), ABC (16), ABD (17), ABE (18), ACD (19), ACE (20), ADE (21), BCD (22), BCE (23), BDE (24), CDE (25), ABCD (26), ABCE (27), ABDE (28), ACDE (29), BCDE (30), ABCDE (31). A-E represent fructose, galactose, glucose, lactose and sucrose, respectively.

Jackknifed Classification Matrix for 31 Saccharide Mixtures and 1 Control Based on Single-sphere Array (DCA, AIE-B, Y, R)																															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	Control	Correct
1	7																																100%
2		7																															100%
3			7																														100%
4				7																													100%
5					7																												100%
6						7																											100%
7							7																										100%
8								7																									100%
9									7																								100%
10										7																							100%
11											7																						100%
12												7																					100%
13													7																				100%
14														7																			100%
15															7																		100%
16																7																	100%
17																	6					1											86%
18																		7															100%
19																			7														100%
20																				7													100%
21																					7												100%
22																	1					6											86%
23																							7										100%
24																								6				1					86%
25																									7								100%
26																								1		5		1					71%
27																											7						100%
28																								1				6					86%
29																													7				100%
30																														7			100%
31																															7		100%
Control																																7	100%
N = 224											N Correct = 218											Proportion Correct = 97%										

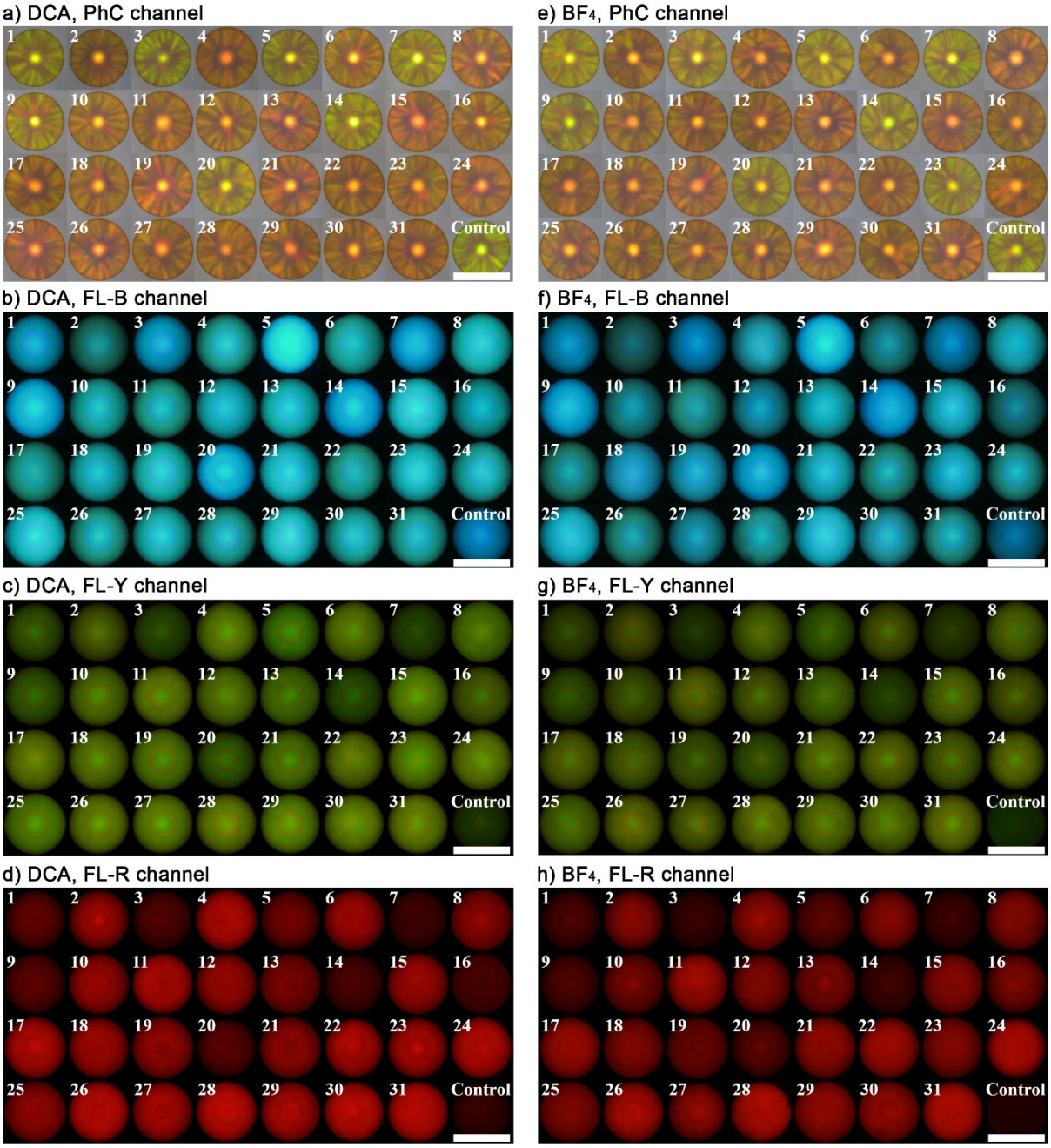

Fig. S35 Responses of sensor array composed of two quadruple-channel poly(ionic liquid) photonic spheres (DCA and BF_4^- as counteranions, respectively) to 1 control analytes, 5 unitary analytes and 26 mixture analytes at 20 mM for all saccharides in tea: (a), (e) optical images; (b), (f) fluorescence-B channel images; (c), (g) fluorescence-Y channel images; (d), (h) fluorescence-R channel images (false color, exposure time 30 ms). The 5 unitary analytes: A (1), B (2), C (3), D (4), E (5); 26 mixture analytes: AB (6), AC (7), AD (8), AE (9), BC (10), BD (11), BE (12), CD (13), CE (14), DE (15), ABC (16), ABD (17), ABE (18), ACD (19), ACE (20), ADE (21), BCD (22), BCE (23), BDE (24), CDE (25), ABCD (26), ABCE (27), ABDE (28), ACDE (29), BCDE (30), ABCDE (31). A-E represent fructose, galactose, glucose, lactose and sucrose, respectively.

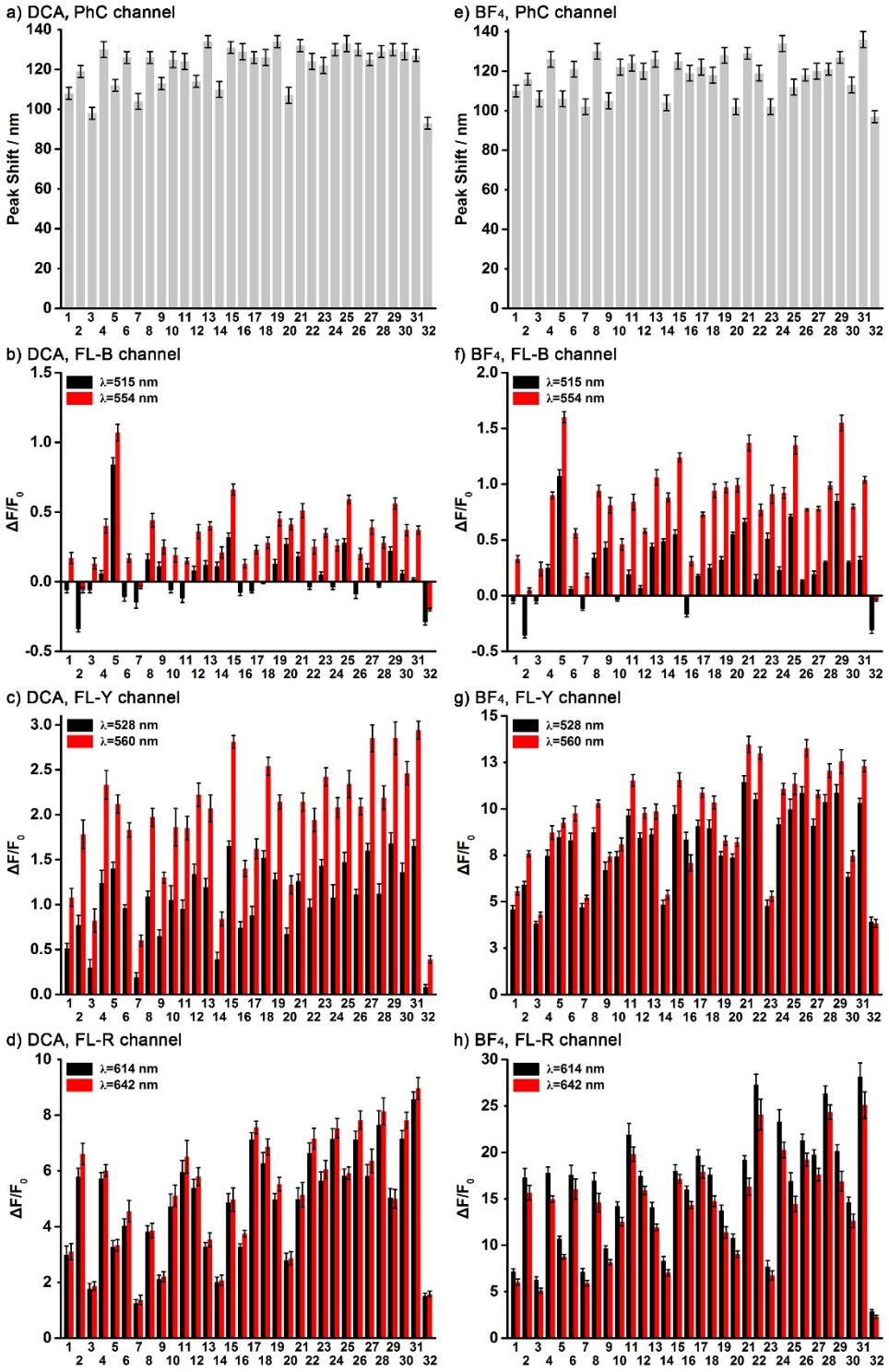

Fig. S36 Responses of sensor array composed of two quadruple-channel poly(ionic liquid) photonic spheres (DCA and BF_4^- as counteranions, respectively) to 1 control analytes, 5 unitary analytes and 26 mixture analytes at 20 mM for all saccharides in tea: (a), (e) histogram of reflection peak shifts; (b), (f) histogram of the folds of fluorescence enhancement in B channel; (c), (g) histogram of the folds of fluorescence enhancement in Y channel; (d), (h) histogram of the folds of fluorescence enhancement in R channel. The 5 unitary analytes: A (1), B (2), C (3), D (4), E (5); 26 mixture analytes: AB (6), AC (7), AD (8), AE (9), BC (10), BD (11), BE (12), CD (13), CE (14), DE (15), ABC (16), ABD (17), ABE (18), ACD (19), ACE (20), ADE (21), BCD (22), BCE (23), BDE (24), CDE (25), ABCD (26), ABCE (27), ABDE (28), ACDE (29), BCDE (30), ABCDE (31). A-E represent fructose, galactose, glucose, lactose and sucrose, respectively.

Table S11 The jack-knifed classification procedure on two quadruple-channel spheres based array (DCA, AIE-B, Y, R; BF_4^-, AIE-B, Y, R). Summary of 224 samples classification to 31 saccharide mixtures and 1control in tea with cross-validation by LDA. The 5 unitary analytes: A (1), B (2), C (3), D (4), E (5); 26 mixture analytes: AB (6), AC (7), AD (8), AE (9), BC (10), BD (11), BE (12), CD (13), CE (14), DE (15), ABC (16), ABD (17), ABE (18), ACD (19), ACE (20), ADE (21), BCD (22), BCE (23), BDE (24), CDE (25), ABCD (26), ABCE (27), ABDE (28), ACDE (29), BCDE (30), ABCDE (31). A-E represent fructose, galactose, glucose, lactose and sucrose, respectively.

Jackknifed Classification Matrix for 31 Saccharide Mixtures and 1 Control Based on Two-sphere Array (DCA, AIE-B, Y, R; BF4, AIE-B, Y, R)																														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	Control	Correct
1	7																																100%
2		7																															100%
3			7																														100%
4				7																													100%
5					7																												100%
6						7																											100%
7							7																										100%
8								7																									100%
9									7																								100%
10										7																							100%
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26																										7							100%
27																											7						100%
28																												7					100%
29																													7				100%
30																														7			100%
31																															7		100%
Control																																7	100%
N = 224											N Correct = 224											Proportion Correct = 100%										

Table S12 The identification of 32 blind samples which have been tested as training data sets[10] where two quadruple-channel spheres based array (DCA, AIE-B, Y, R; BF_4^-, AIE-B, Y, R) is used for 31 saccharide mixtures and 1control in tea. A-E represent fructose, galactose, glucose, lactose and sucrose, respectively.

sample#	Identification	Verification	sample#	Identification	Verification
1	ABD	ABD	17	E	E
2	CE	CE	18	ABCE	ABCE
3	AB	AB	19	ADE	ADE
4	BCDE	BCDE	20	A	A
5	BDE	BDE	21	AE	AE
6	CDE	CDE	22	ABDE	ABDE
7	B	B	23	AD	AD
8	BE	BE	24	ACE	ACE
9	ACD	ACD	25	BCE	BCE
10	Control	Control	26	ACDE	ACDE
11	ABCD	ABCD	27	AC	AC
12	BD	BD	28	BC	BC
13	ABC	ABC	29	C	C
14	CD	CD	30	ABE	ABE
15	ABCDE	ABCDE	31	BCD	BCD
16	D	D	32	DE	DE
100% identified					

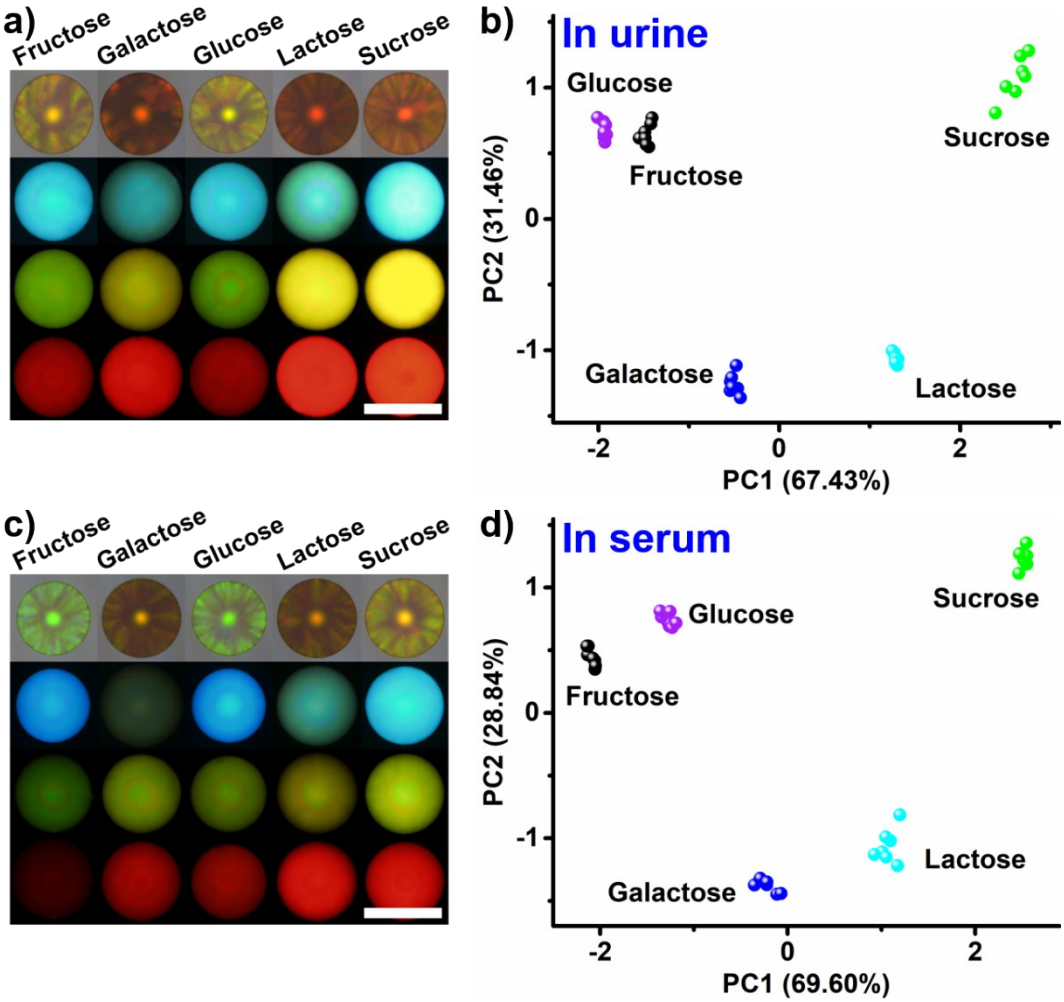


Fig. S37 Using one quadruple-channel poly(ionic liquid) sphere (doped with AIEgen-blue, AIEgen-yellow and AIEgen-red) to discriminate five saccharides (fructose, galactose, glucose, lactose and sucrose) in different background solutions: (a-b) in urine; (c-d) in serum. (a, c) Optical response profiles after binding saccharides; (b, d) Corresponding PCA plots.

3. Synthetic experiments

Synthesis of Ionic Liquids

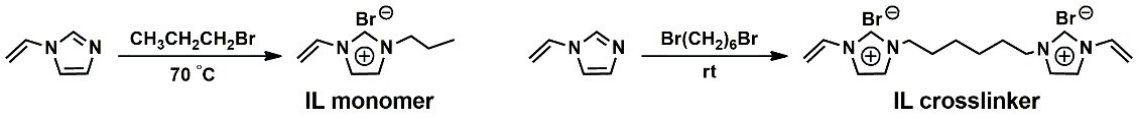


Fig. S38 Synthetic routes to ionic liquid monomer and crosslinker.

Synthesis of IL monomer

IL monomer was prepared according to reported procedures in literature.[11] ^{1}H NMR (400 MHz, DMSO-d_6): 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.[12] ^{1}H NMR (400 MHz, DMSO-d_6): δ 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 AIEgen-Blue

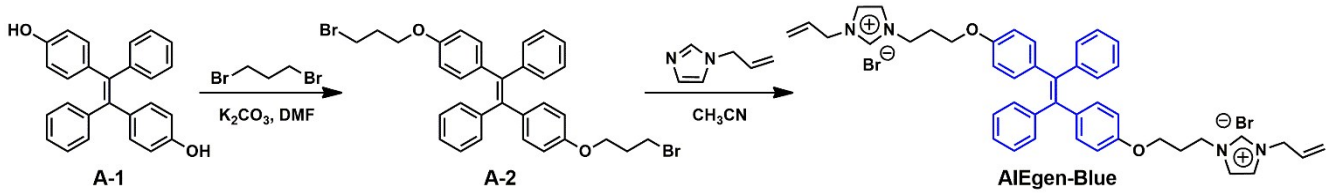


Fig. S39 Synthetic routes to AIEgen-Blue.

Synthesis of compound A-2

Compound **A-1** was prepared according to reported procedures in literature.[13] A mixture of compound **1** (364.1 mg, 1.0 mmol), 1,3-dibromopropane (807.5 mg, 4.0 mmol) and potassium carbonate (1.105 g, 8.0 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_2Cl_2 and subjected to column chromatography with EA (ethyl acetate)/PE (petroleum ether, 60-90 °C) (v/v, 1/50) as eluent. Compound **A-2** was obtained as green solid (444.6 mg, 0.73 mmol) in 73.3% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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). ^{13}C NMR (100 MHz, $CDCl_3$): δ 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 m/z: calcd. for $C_{32}H_{30}Br_2O_2Na^+$ ([M+Na]$^+$): 629.0; found: 629.0.

Synthesis of AIEgen-Blue

A mixture of compound **A-2** (303.0 mg, 0.5 mmol) and 1-allylimidazole (216.3 mg, 2.0 mmol) in CH_3CN (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_2Cl_2 and subjected to column chromatography with CH_2Cl_2/CH_3OH (v/v, 5/1) as eluent. **AIEgen-Blue** was obtained as green solid (222.0 mg, 0.27 mmol) in 54.1% yield. ^{1}H NMR (400 MHz, CD_3OD): δ 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). ^{13}C NMR (100 MHz, CD_3OD): δ 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 m/z: calcd. for $C_{44}H_{46}N_4O_2^{2+}$ ([M-2Br]$^{2+}$): 331.1805; found: 331.1805.

Synthesis of AIEgen-Yellow

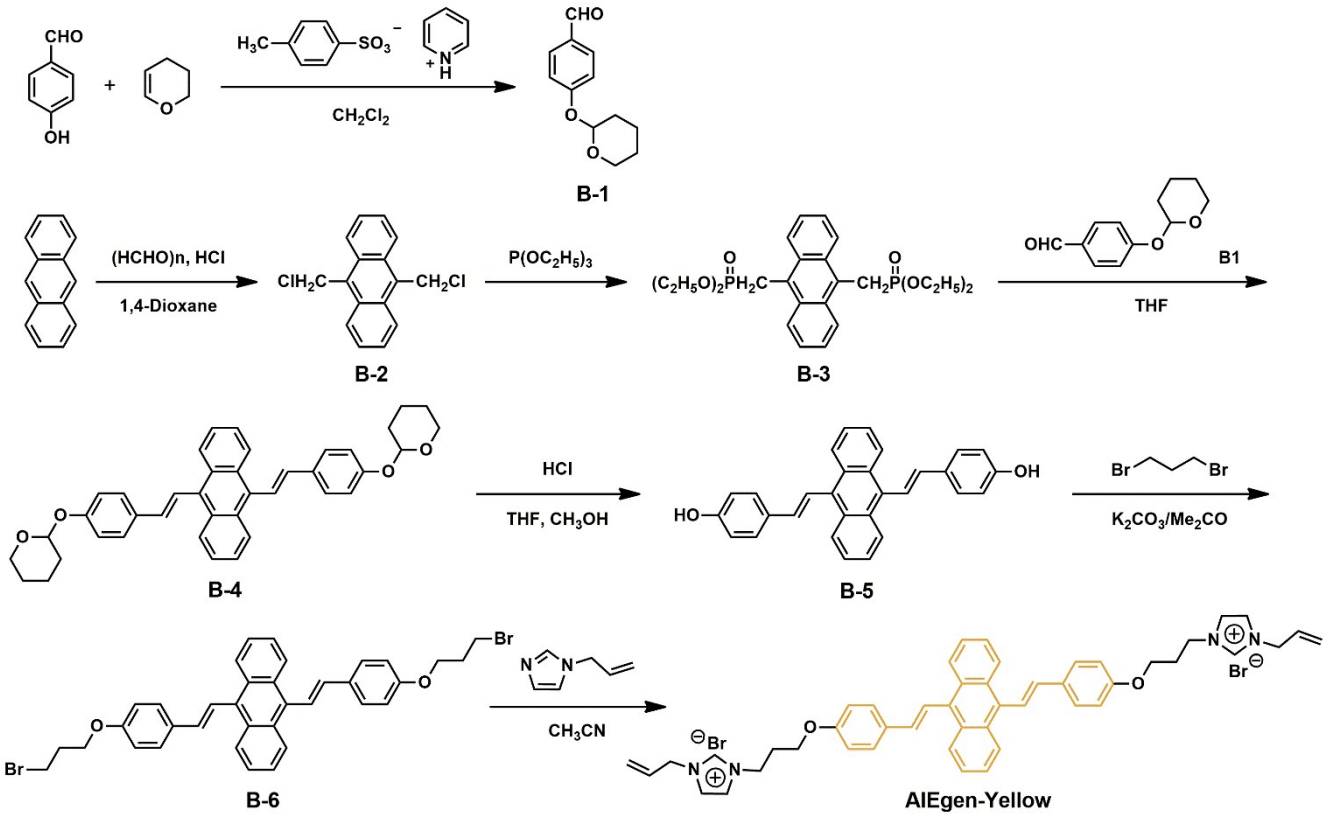


Fig. S40 Synthetic routes to AIEgen-Yellow.

Compound **B-1 to B-6** were synthesized according to reported procedures in literature.[14]

Synthesis of compound B-1

Pyridinium p-toluenesulphonate (0.63 g, 2.5 mmol) was added to a suspension of 4-hydroxybenzaldehyde (5.81 g, 47.5 mmol) and 3,4-dihydro-2H-pyran (6.4 g, 76.1 mmol) in anhydrous CH_2Cl_2 (100 mL). The reaction mixture was stirred at room temperature overnight under nitrogen. The crude reaction mixture was washed with saturated aqueous $NaHCO_3$ and brine, dried with anhydrous Na_2SO_4, and evaporated in vacuo. The resultant crude product was purified by column chromatography on silica gel with EA (ethyl acetate)/PE (petroleum ether, 60-90 °C) (v/v, 1/6) as eluent. Compound **B-1** was obtained as yellow oil (8.37 mg, 40.6 mmol) in 85.4% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.89 (s, 1H), 7.83 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 5.55 (t, J = 3.1 Hz, 1H), 3.88-3.82 (m, 1H), 3.66-3.61 (m, 1H), 2.06-1.97 (m, 1H), 1.91-1.88 (m, 2H) 1.74-1.66 (m, 2H), 1.64-1.60 (m, 1H).

Synthesis of compound B-2

A mixture of anthracene (17.82 g, 100.0 mmol), paraformaldehyde (15.20 g) and concentrated hydrochloric acid (37%, 24 mL) in 1,4-dioxane (144 mL) was refluxed for 2 hours under HCl atmosphere. Then removing the HCl atmosphere, the reaction mixture was further refluxed for 3 hours. After cooling to room temperature, the suspension was filtered, and the filter residue was washed with 1,4-dioxane and water. Compound **B-2** was obtained as yellow solid (19.23 g, 77.8 mmol) in 77.8% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42-8.36 (m, 4H), 7.69-7.63 (m, 4H), 5.61 (s, 4H).

Synthesis of compound B-3

A mixture of compound **B-2** (5.00 g, 20.2 mmol) and triethyl phosphite (18 mL) was refluxed for 12 hours under nitrogen. After cooling to room temperature, the suspension was filtered, and the filter

residue was washed with petroleum ether. Compound **B-3** was obtained as yellow-green solid (9.12 g, 19.1 mmol) in 94.4% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41-8.35 (m, 4H), 7.61-7.54 (m, 4H), 4.24 (d, J = 20.3 Hz, 4H), 4.04-3.66 (m, 8H), 1.07 (t, J = 7.1 Hz, 12H).

Synthesis of compound B-4

Compound **B-3** (2.39 g, 5.0 mmol) and potassium *tert*-butoxide (1.68 g, 15.0 mmol) were dissolved in anhydrous THF (100 mL). A solution of 2.47 g of compound **B-1** (12.0 mmol) in 20 mL of anhydrous THF was added dropwisely at 0 ^{o}C. Then the reaction mixture was allowed to warm to room temperature and stirred overnight. After solvent evaporation, the residue was redissolved into 5 mL of CH_2Cl_2 and reprecipitated into 200 mL of methanol. Compound **B-4** was obtained as yellow solid (2.78 g, 4.8 mmol) in 95.4% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44-8.36 (m, 4H), 7.80 (d, J = 16.4 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.49-7.43 (m, 4H), 7.15 (d, J = 8.7 Hz, 4H), 6.88 (d, J = 16.5 Hz, 2H), 5.52 (t, J = 3.1 Hz, 2H), 4.01-3.91 (m, 2H), 3.69-3.61 (m, 2H), 2.13-1.83 (m, 4H) 1.82-1.45 (m, 8H).

Synthesis of compound B-5

Compound **B-4** (1.75 g, 3.0 mmol) was dissolved in 100 mL of THF and 5 mL of methanol, and then 10 mL of 2 M HCl aqueous solution was added into the above solution. The reaction solution was stirred at room temperature overnight. After solvent evaporation, the residue was washed with methanol. Then the residue was redissolved into 5 mL of CH_2Cl_2 and reprecipitated into 200 mL of methanol. Compound **B-5** was obtained as yellow solid (1.12 g, 2.7 mmol) in 90.0% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): 9.65 (s, 2H), 8.40-8.35 (m, 4H), 7.88 (d, J =16.5 Hz, 2H), 7.64 (d, J = 8.6 Hz, 4H), 7.57-7.50 (m, 4H), 6.86 (d, J = 8.6 Hz, 4H), 6.81 (d, J = 16.5 Hz, 2H).

Synthesis of compound B-6

A mixture of compound **B-5** (491.2 mg, 1.2 mmol), 1,3-dibromopropane (969.1 mg, 4.8 mmol) and potassium carbonate (1.327 g, 9.6 mmol) in acetone (20 mL) was refluxed for 24 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_2Cl_2 and subjected to column chromatography on silica gel with CH_2Cl_2/PE (petroleum ether, 60-90 ^{o}C) (v/v, 1/2) as eluent. Compound **B-6** was obtained as yellow solid (615.2 mg, 0.94 mmol) in 78.1% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.47-8.40 (m, 4H), 7.82 (d, J = 16.4 Hz, 2H), 7.66 (d, J = 8.7 Hz, 4H), 7.52-7.46 (m, 4H), 7.03 (d, J = 8.7 Hz, 4H), 6.91 (d, J = 16.5 Hz, 2H), 4.22 (t, J = 5.8 Hz, 4H), 3.68 (t, J = 6.4 Hz, 4H), 2.46-2.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 136. 8, 132.8, 130.5, 129.6, 127.8, 126.5, 125.1, 123.1, 114.9, 68.5, 32.4, 30.0. MALDI-MS m/z: calcd. for $C_{36}H_{33}Br_2O_2^+$ ([M+H]$^+$) : 657.1; found: 657.3.

Synthesis of AIEgen-Yellow

A mixture of compound **B-6** (328.2 mg, 0.5 mmol) and 1-allylimidazole (216.3 mg, 2.0 mmol) in CH_3CN (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_2Cl_2 and subjected to column chromatography on neutral alumina with CH_3OH/CH_2Cl_2 (v/v, 1/20) as eluent. **AIEgen-Yellow** was obtained as yellow solid (253.1 mg, 0.29 mmol) in 58.1% yield. ^{1}H NMR (CD_3OD, 400 MHz): 8.35-8.28 (m, 4H), 7.76 (d, J = 16.4 Hz, 2H), 7.72 (d, J = 2.0 Hz, 2H), 7.63 (d, J = 2.0 Hz, 2H), 7.61 (d, J = 8.8 Hz, 4H), 7.47-7.40 (m, 4H), 6.95 (d, J = 8.8 Hz, 4H), 6.78 (d, J = 16.5 Hz, 2H), 6.11-5.95 (m, 2H), 5.49-5.37 (m, 4H), 4.86 (t, J = 1.3 Hz, 4H), 4.49 (t, J = 6.9 Hz, 4H), 4.11 (t, J = 5.6 Hz, 4H), 2.46-2.34 (m, 4H). ^{13}C NMR (100 MHz, CD_3OD): δ 159.6, 137.9, 133.7, 131.7, 130.6, 128.8, 127.2, 126.0, 124.0, 123.9, 123.6, 121.9, 115.6, 65.9, 52.7, 30.4. HR-ESI m/z: calcd. for $C_{48}H_{48}N_4O_2^{2+}$ ([M-2Br]$^{2+}$): 356.1883; found: 356.1888.

Synthesis of AIEgen-Red

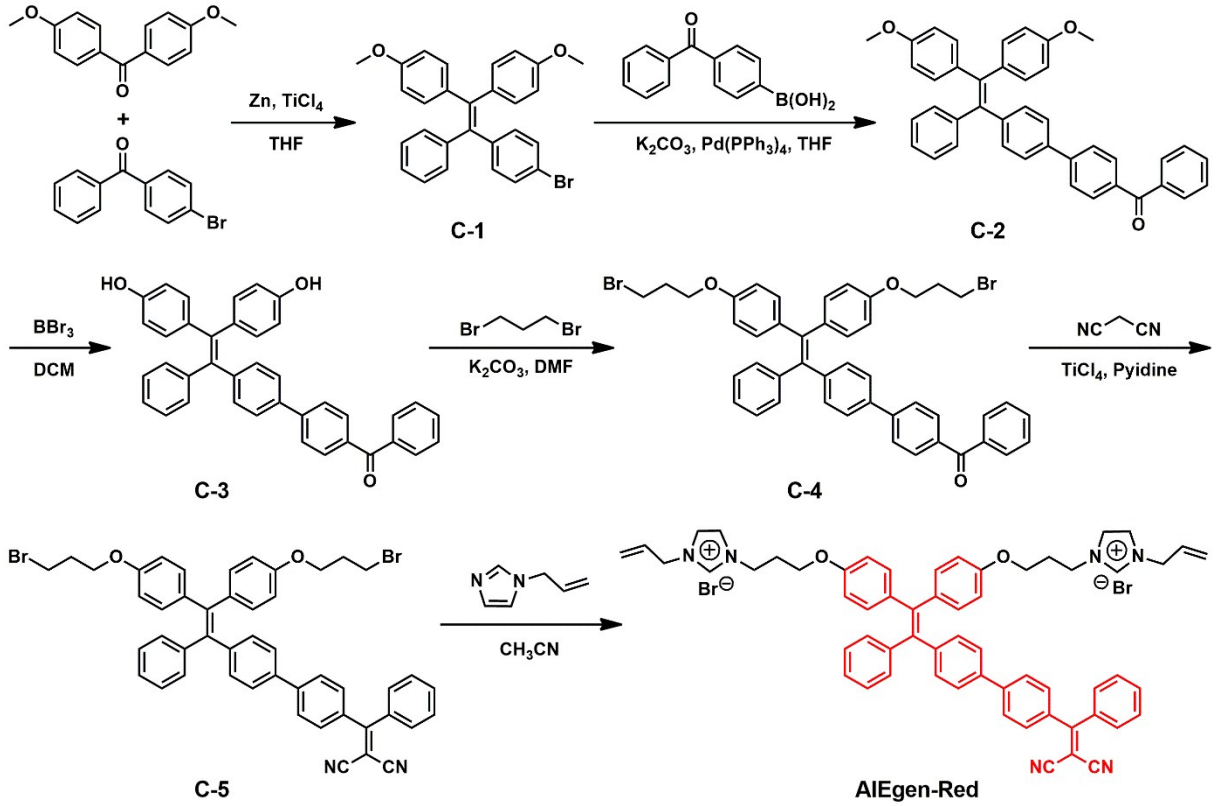


Fig. S41 Synthetic routes to AIEgen-Red.

Synthesis of compound C-1

Compound **C-1** was synthesized according to reported procedures in literature.[15] A mixture of bis(4-methoxyphenyl)methanone (4.86 g, 20.0 mmol), 4-bromo-benzophenone (6.27 g, 24.0 mmol), and Zn powder (6.50 g, 100.0 mmol) in anhydrous THF (250 mL) was stirred at 0 °C under nitrogen. To the above reaction mixture was slowly added $TiCl_4$ (80 mL, 80.0 mmol) in CH_2Cl_2 and then the mixture was refluxed overnight. The reaction solution was cooled down in ice-water bath and saturated K_2CO_3 aqueous (10 wt%, 125 mL) was added slowly. The mixture was extracted with ethyl acetate. The organic layer was separated, washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The resultant crude product was purified by column chromatography on silica gel with EA (ethyl acetate)/PE (petroleum ether, 60-90 °C) (v/v, 1/50) as eluent. Compound **C-1** was obtained as light yellow solid (4.31 g, 9.1 mmol) in 45.7% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (d, 2H, J = 8.6 Hz), 7.15-7.07 (m, 3H), 7.02-6.97 (m, 2H), 6.95-6.86 (m, 6H), 6.68-6.60 (m, 4H), 3.75 (d, 6H, J = 11.0 Hz).

Synthesis of compound C-2

Compound **C-2** was synthesized according to an analogous procedure in literature.[16] 4-benzoylphenylboronic acid (678.1 mg, 3.0 mmol) and compound **C-1** (942.8 mg, 2.0 mmol) were dissolved in THF (30.0 mL). To the above mixture K_2CO_3 aqueous solution (2 M, 8.0 mL) and Aliquat 336 (404.2 mg, 1.0 mmol) were added. The mixture was stirred for 40 minutes under nitrogen at room temperature. Then the catalyst $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol) was added and the reaction mixture was refluxed for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate and the combined organic phase was concentrated under reduced pressure. The resultant crude product was

purified by column chromatography on silica gel with EA (ethyl acetate)/PE (petroleum ether, 60-90 °C) (v/v, 1/20) as eluent. Compound **C-2** was obtained as green solid (975.8 mg, 1.7 mmol) in 85.3% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.81 (m, 4H), 7.70-7.64 (m, 2H), 7.62-7.57 (m, 1H), 7.53-7.48 (m, 2H), 7.44-7.39 (m, 2H), 7.17-7.09 (m, 5H), 7.09-7.04 (m, 2H), 7.02-6.93 (m, 4H), 6.69-6.62 (m, 4H), 3.75 (d, 6H, J = 1.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 158.2, 158.1, 144.8, 144.5, 144.1, 140.7, 138.5, 137.8, 137.1, 136.2, 136.0, 132.6, 132.3, 132.0, 131.4, 130.7, 130.0, 128.3, 127.8, 126.6, 126.4, 126.2, 113.1, 113.0, 55.1. MS m/z: calcd. for $C_{41}H_{33}O_3^+$ ([M+H]$^+$) : 573.2; found: 573.2.

Synthesis of compound C-3

To an anhydrous CH_2Cl_2 solution (20 mL) of Compound **C-2** (572.7 mg, 1.0 mmol) at 0 °C was added boron tribromide (3.0 mL, 3.0 mmol) in CH_2Cl_2 solution. The reaction mixture was allowed to warm to room temperature and stirred for 4 hours. The reaction was quenched by ice water and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The resultant crude product was purified by column chromatography on silica gel with acetone/CH_2Cl_2 (v/v, 1/20) as eluent. Compound **C-3** was obtained as green solid (502.7 mg, 0.9 mmol) in 92.3% yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.36 (d, 2H, J = 10.3 Hz), 7.86-7.77 (m, 4H), 7.76-7.73 (m, 2H), 7.71-7.66 (m, 1H), 7.61-7.55 (m, 4H), 7.20-7.03 (m, 5H), 7.01-6.94 (m, 2H), 6.84-6.72 (m, 4H), 6.56-6.47 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.8, 156.6, 156.5, 145.0, 144.6, 144.1, 141.8, 137.7, 137.6, 136.5, 136.0, 134.6, 133.1, 132.6, 132.1, 131.4, 131.0, 130.0, 129.1, 128.4, 126.9, 126.7, 126.6, 115.2, 115.1. MS m/z: calcd. for $C_{39}H_{29}O_3^+$ ([M+H]$^+$) : 545.2; found: 545.2.

Synthesis of compound C-4

A mixture of compound **C-3** (272.3 mg, 0.5 mmol), 1,3-dibromopropane (403.8 mg, 2 mmol) and potassium carbonate (552.8 mg, 4 mmol) in acetone (20 mL) was refluxed for 24 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_2Cl_2 and subjected to column chromatography on silica gel with EA (ethyl acetate)/PE (petroleum ether, 60-90 °C) (v/v, 1/5) as eluent. Compound **C-4** was obtained as yellow solid (252.1 mg, 0.3 mmol) in 64.1% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.88-7.80 (m, 4H), 7.70-7.66 (m, 2H), 7.62-7.57 (m, 1H), 7.53-7.47 (m, 2H), 7.44-7.40 (m, 2H), 7.18-7.10 (m, 5H), 7.09-7.05 (m, 2H), 6.83-6.73 (m, 4H), 6.69-6.62 (m, 4H), 4.03 (t, 4H, J = 6.7 Hz), 3.58 (t, 4H, J = 6.4 Hz), 2.32-2.24 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 157.4, 157.3, 144.8, 144.4, 144.1, 140.6, 138.7, 137.8, 137.2, 136.5, 136.0, 132.7, 132.6, 132.3, 132.0, 131.4, 130.7, 130.0, 128.3, 127.8, 126.6, 126.5, 126.3, 113.7, 113.6, 65.1, 32.4, 30.1. MS m/z: calcd. for $C_{45}H_{39}Br_2O_3^+$ ([M+H]$^+$) : 787.1; found: 787.1.

Synthesis of compound C-5

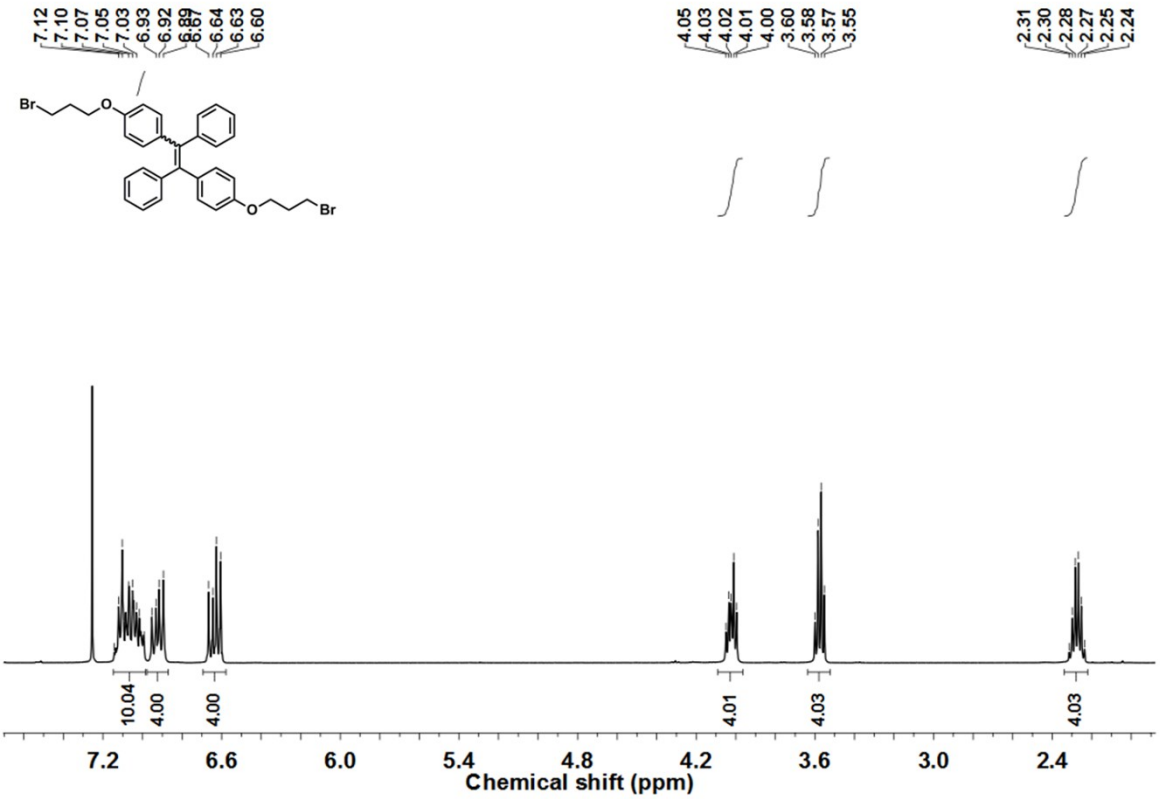
Compound **C-5** was synthesized according to an analogous procedure in literature.[17] A mixture of Compound **C-4** (157.3 mg, 0.2 mmol) and malononitrile (19.8 mg, 0.3 mmol) in anhydrous CH_2Cl_2 (10 mL) was stirred at 0 °C. Then $TiCl_4$ (0.6 mL, 0.6 mmol) in CH_2Cl_2 was added slowly and the reaction solution was stirred for 30 minutes. Pyridine (47.5 mg, 0.6 mmol) was injected and the solution was stirred for another 30 minutes. The mixture was allowed to reflux for 4 h. After cooling to room temperature, the reaction solution was poured into water and the resulting mixture was extracted with CH_2Cl_2. The organic layer was separated, washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel with EA (ethyl acetate)/PE (petroleum ether, 60-90 °C) (v/v, 1/6) as eluent. Compound **C-5** was obtained as red solid (151.5 mg, 0.18 mmol) in 90.8% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69-7.63 (m, 2H), 7.62-7.57 (m, 1H), 7.52-7.44 (m, 6H), 7.42-7.37 (m, 2H), 7.17-7.09 (m, 5H), 7.08-7.02 (m,

2H), 6.99-6.91 (m, 4H), 6.70-6.61 (m, 4H), 4.03 (t, 4H, J = 5.6 Hz), 3.58 (t, 4H, J = 6.4 Hz), 2.32-2.23 (m, 4H). ^{13}C NMR (100 MHz, CD_3OD): δ 174.6, 157.5, 157.4, 145.3, 145.0, 144.1, 140.9, 138.6, 136.6, 136.5, 136.2, 134.6, 132.8, 132.7, 132.2, 131.5, 131.2, 130.6, 129.0, 127.9, 127.1, 126.5, 126.4, 114.2, 114.1, 113.8, 113.7, 80.9, 65.2, 32.5, 30.2. MS m/z: calcd. for $C_{48}H_{38}Br_2N_2O_2Na^+$ ([M+Na]$^+$): 857.1; found: 857.1.

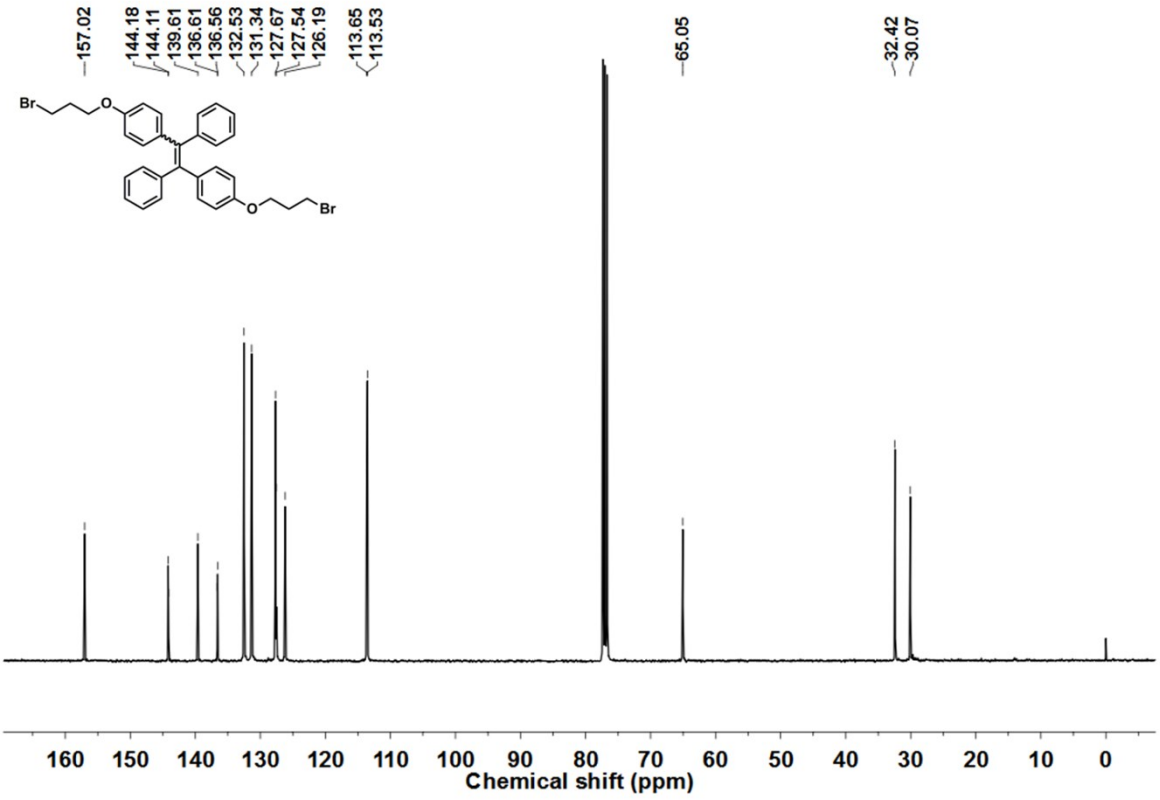
Synthesis of AIEgen-Red

A mixture of compound **C-5** (125.2 mg, 0.15 mmol) and 1-allylimidazole (64.9 mg, 0.60 mmol) in CH_3CN (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_2Cl_2 and subjected to column chromatography on neutral alumina with CH_3OH/CH_2Cl_2 (v/v, 1/20) as eluent. **AIEgen-Red** was obtained as red solid (84.2 mg, 0.08 mmol) in 53.4% yield. ^{1}H NMR (CD_3OD, 400 MHz): δ 7.78-7.72 (m, 2H), 7.71-7.67 (m, 2H), 7.65-7.59 (m, 2H), 7.58-7.43 (m, 9H), 7.16-7.07 (m, 5H), 7.05-7.00 (m, 2H), 6.98-6.87 (m, 4H), 6.71-6.58 (m, 4H), 6.10-5.92 (m, 2H), 5.45-5.31 (m, 4H), 4.84-4.74 (m, 4H), 4.43 (t, 4H, J = 10.0 Hz), 3.99 (t, 4H, J = 6.7 Hz), 2.39-2.28 (m, 4H). ^{13}C NMR (100 MHz, CD_3OD): δ 175.8, 158.7, 158.6, 146.2, 146.1, 145.4, 142.1, 140.5, 138.3, 138.0, 137.8, 136.3, 133.9, 133.8, 133.7, 133.2, 132.5, 132.4, 132.0, 131.9, 131.6, 130.0, 129.0, 128.0, 127.5, 124.1, 123.8, 122.1, 122.0, 114.8, 114.7, 82.5, 65.7, 52.9, 30.7. HR-ESI m/z: calcd. for $C_{60}H_{54}N_6O_2^{2+}$ ([M-2Br]$^{2+}$): 445.2149; found: 445.2148.

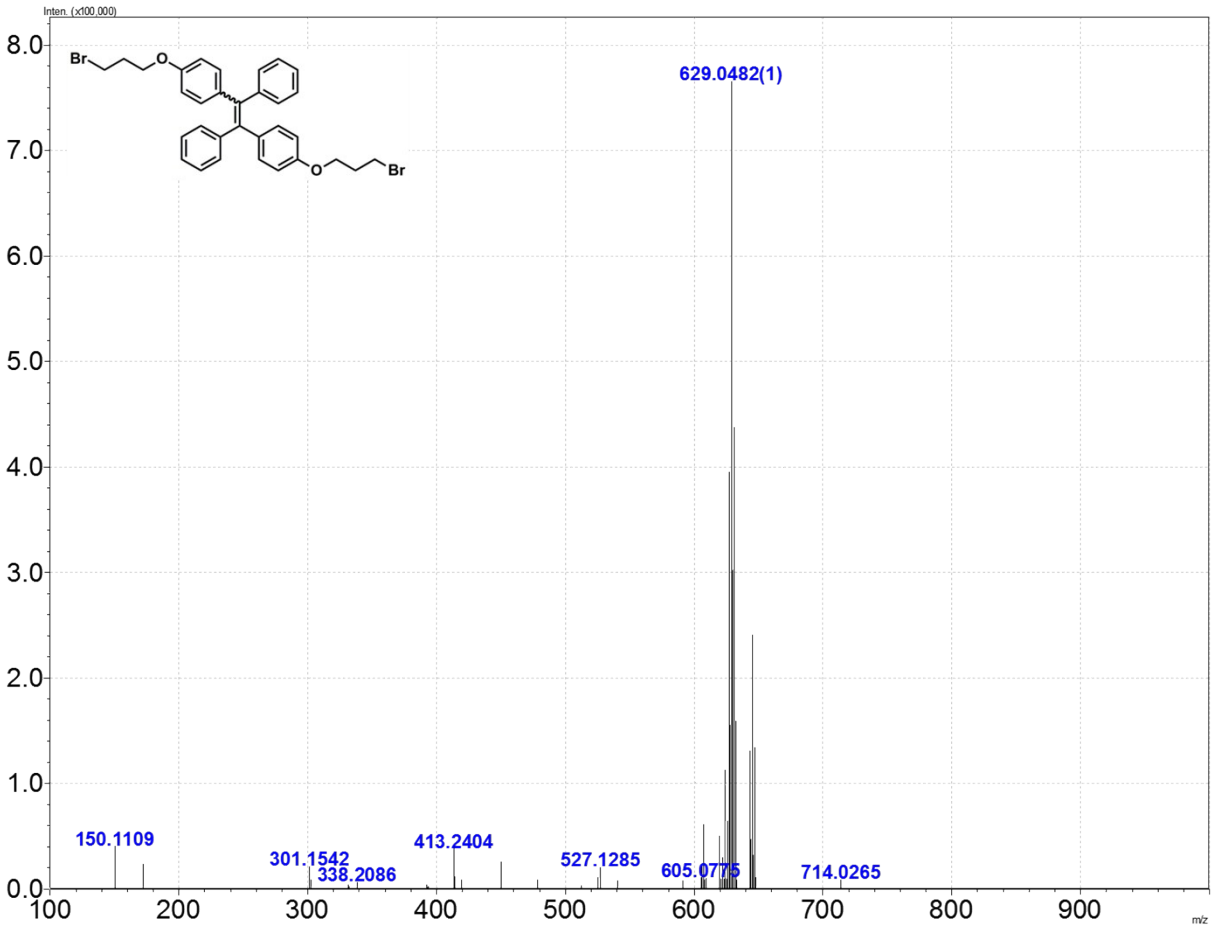
Appendixes



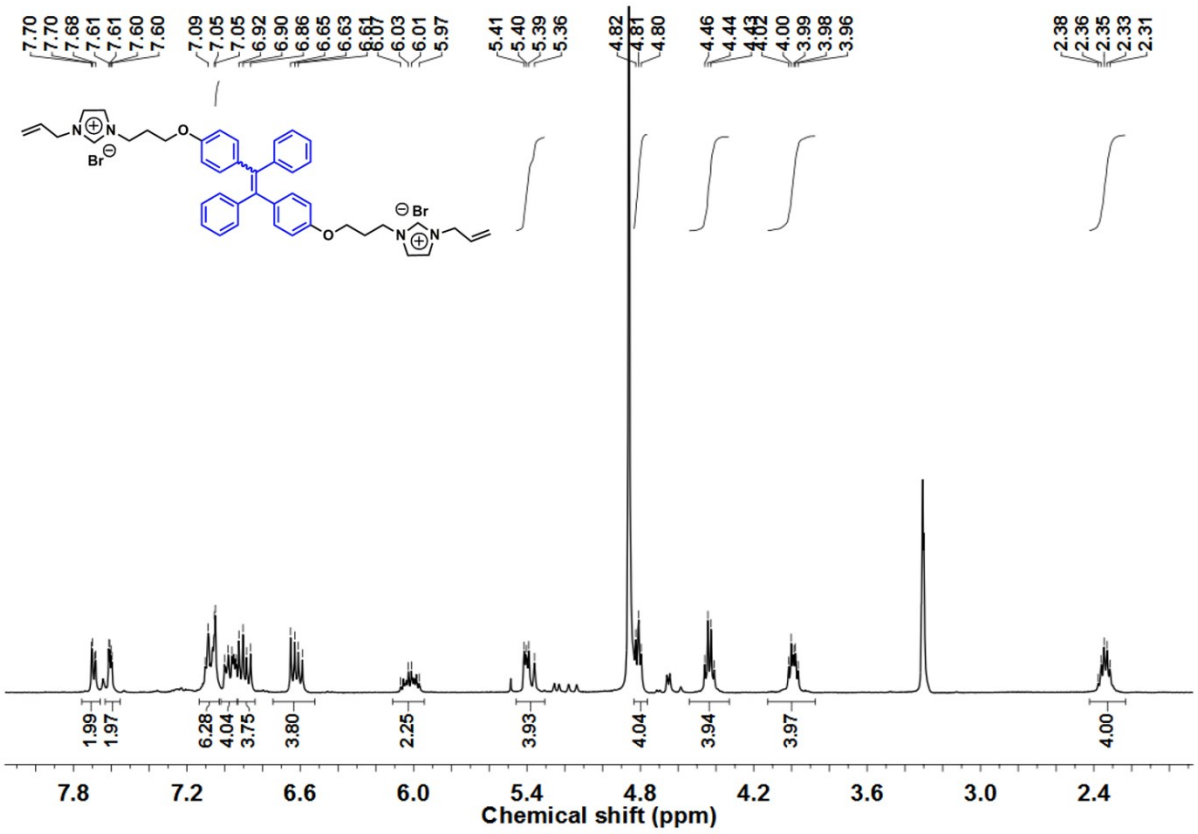
^{1}H NMR spectrum of **A-2** in $CDCl_3$.



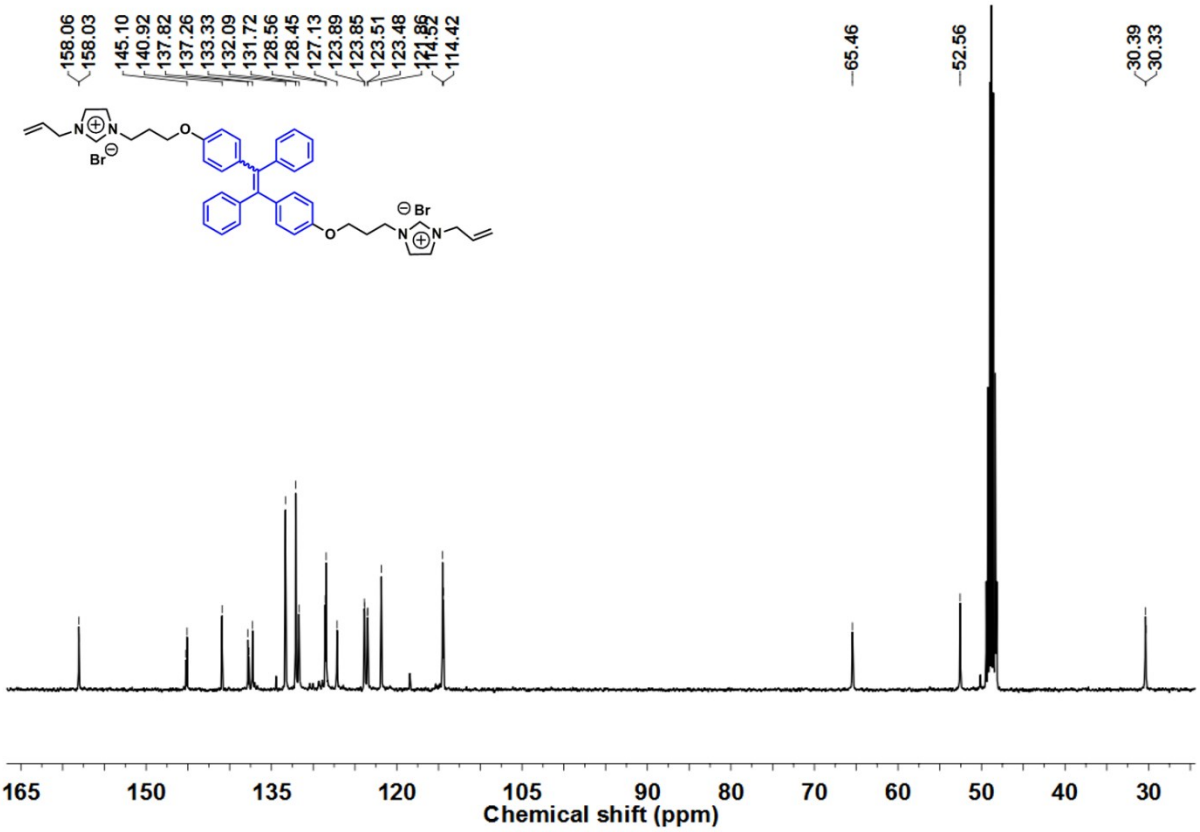
^{13}C NMR spectrum of **A-2** in $CDCl_3$.



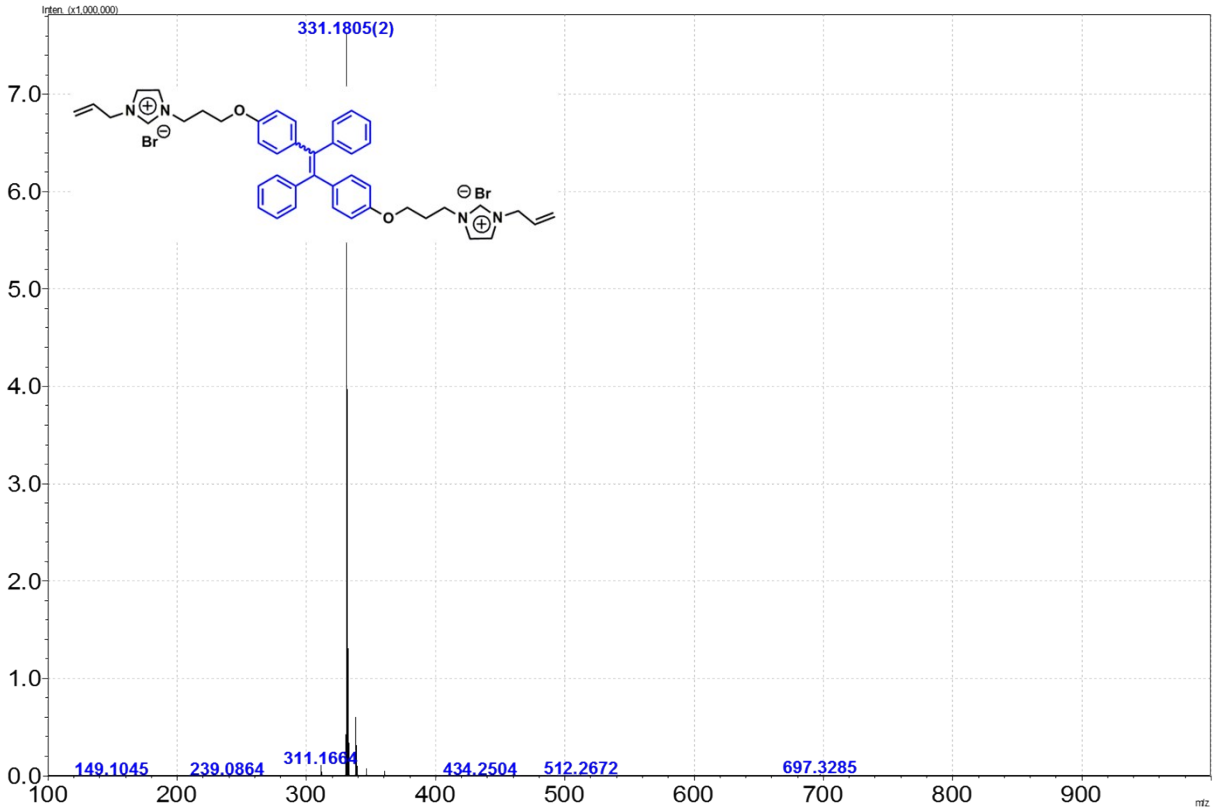
MS spectrum of **A-2**



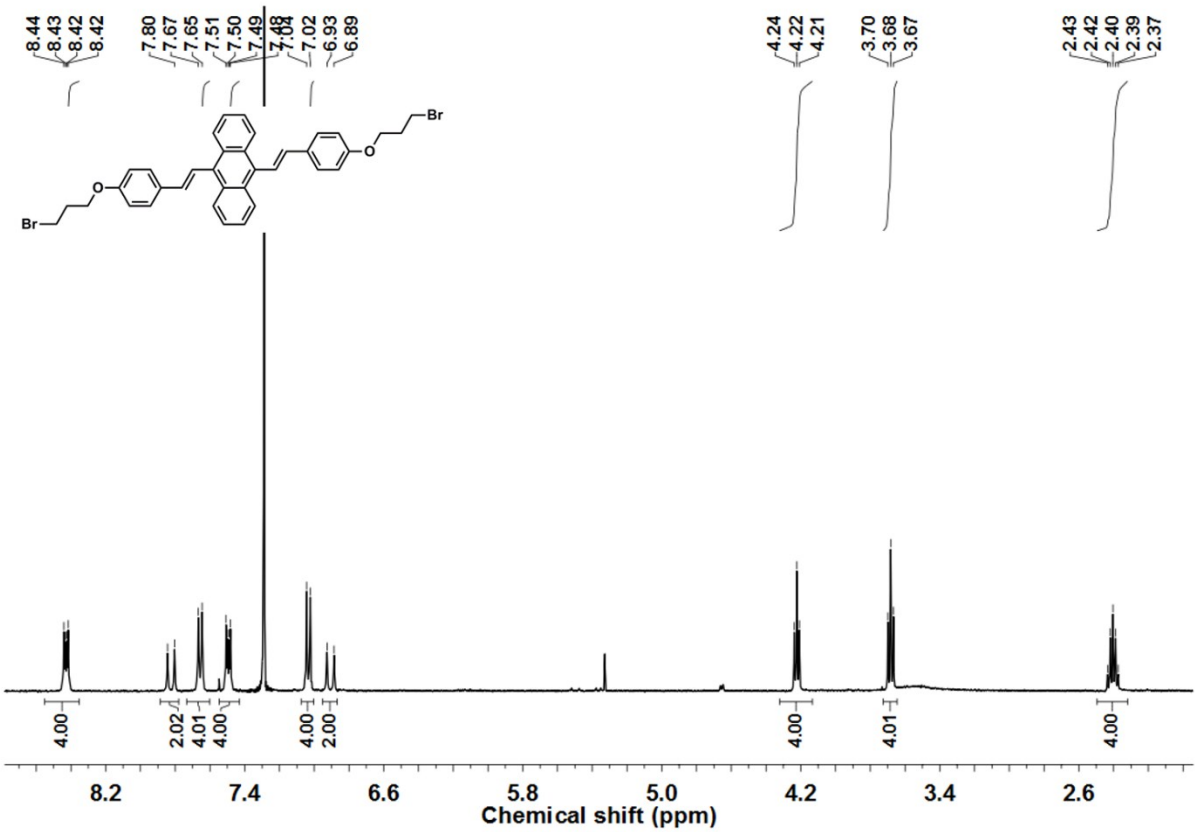
^{1}H NMR spectrum of **AIEgen-Blue** in CD_3OD.



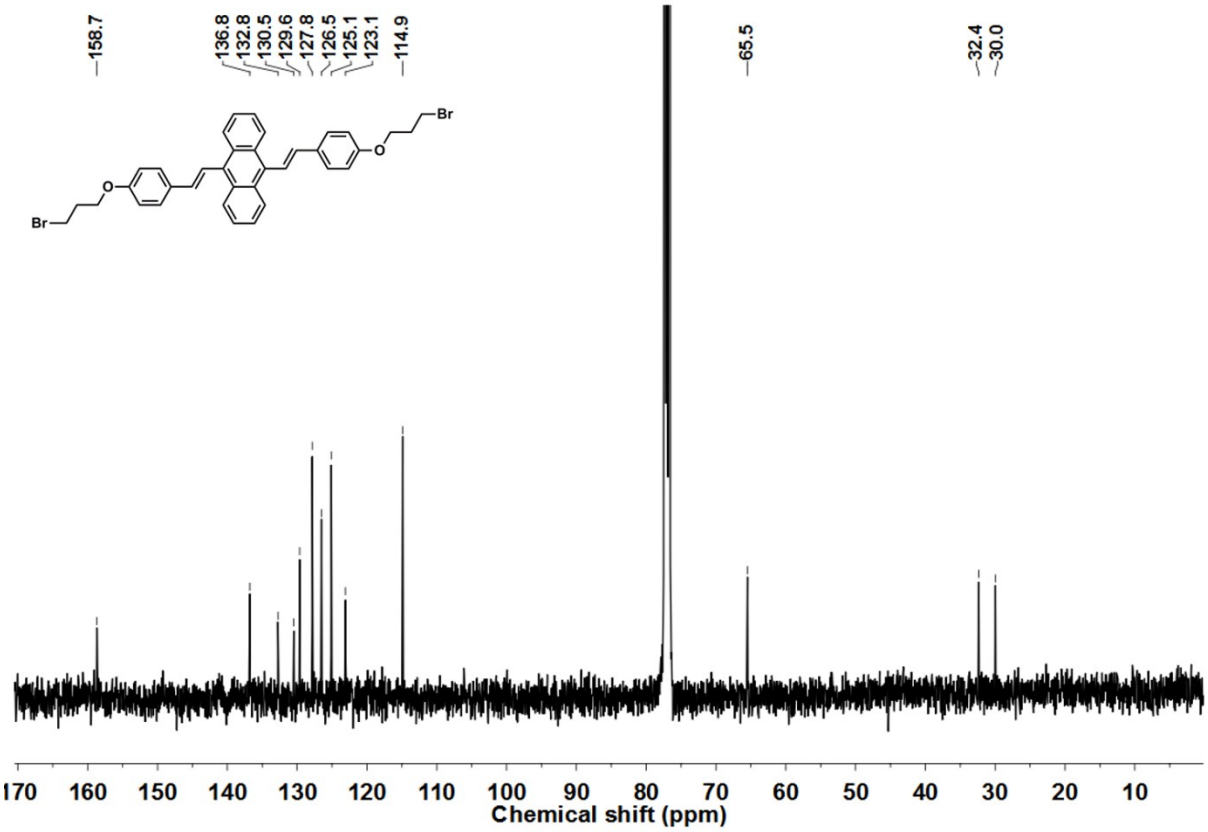
^{13}C NMR spectrum of **AIEgen-Blue** in CD_3OD.



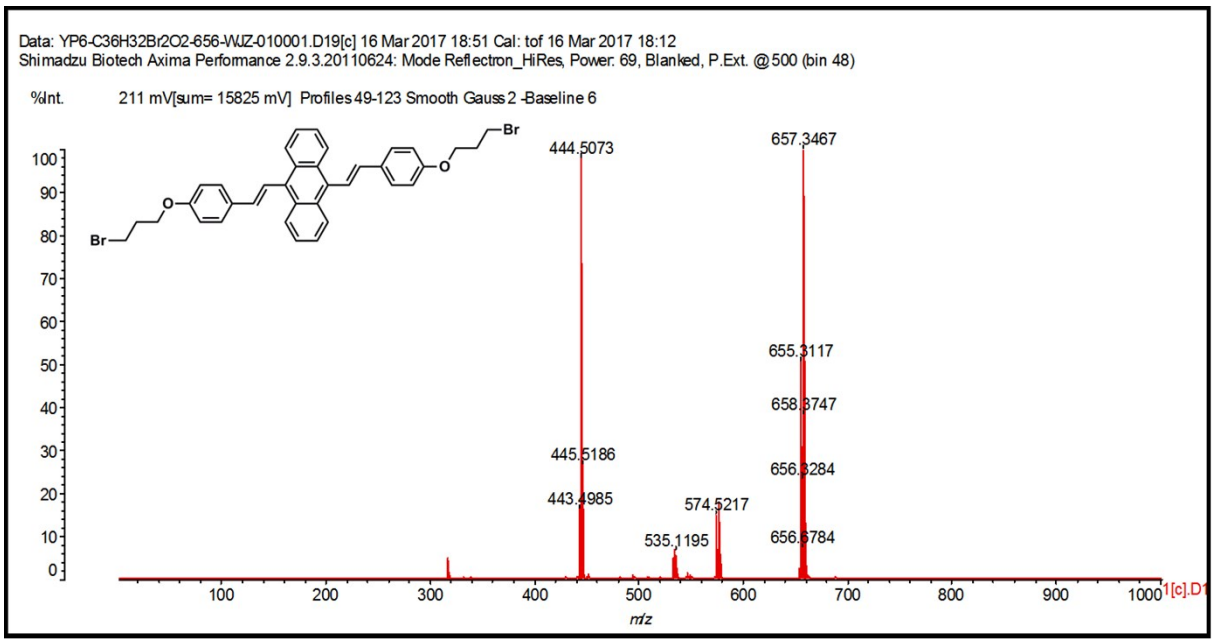
MS spectrum of **AIEgen-Blue**



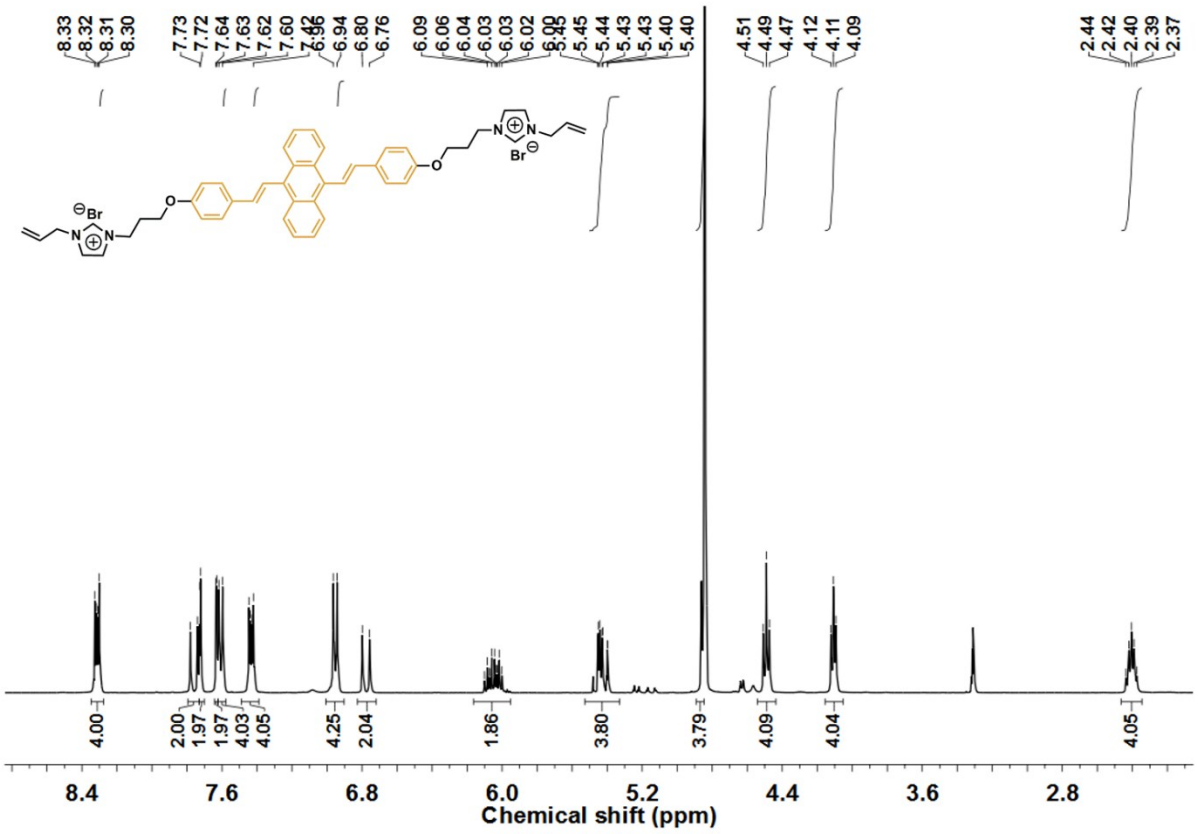
^{1}H NMR spectrum of **B-6** in $CDCl_3$.



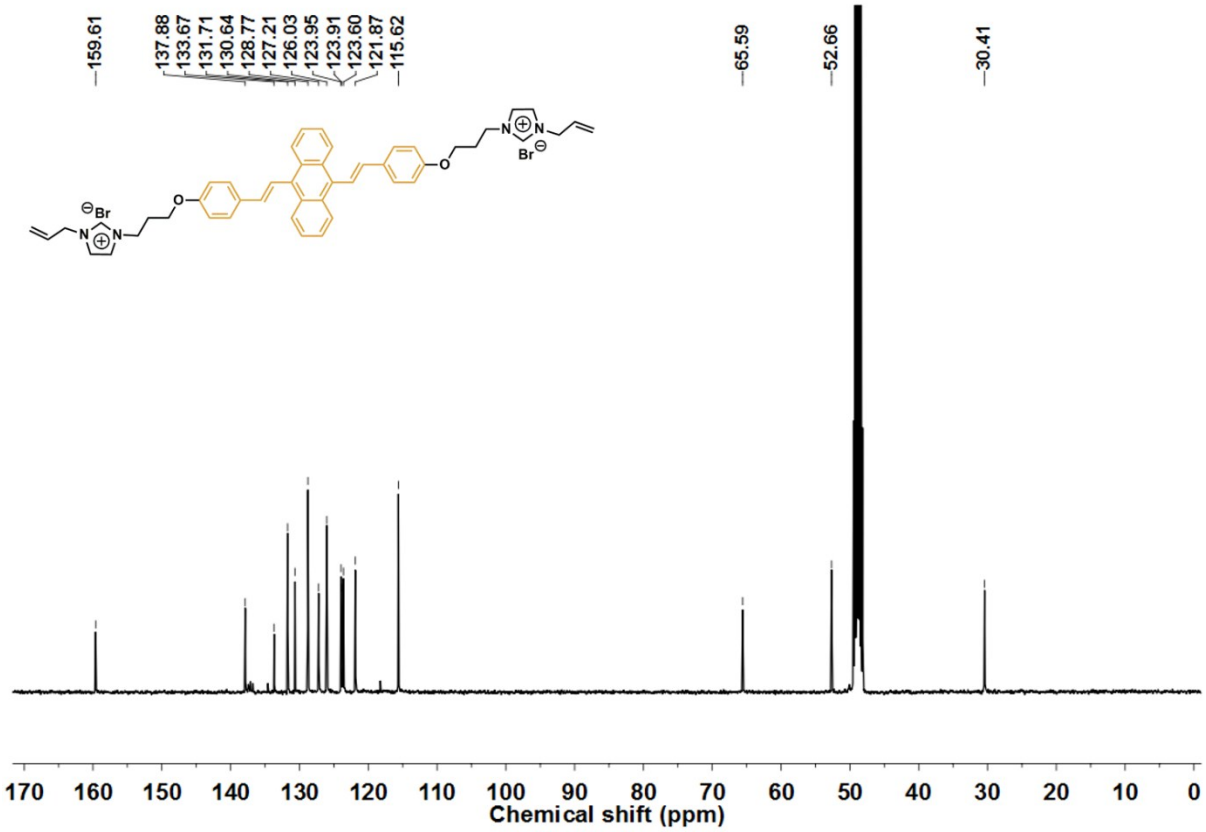
^{13}C NMR spectrum of **B-6** in $CDCl_3$.



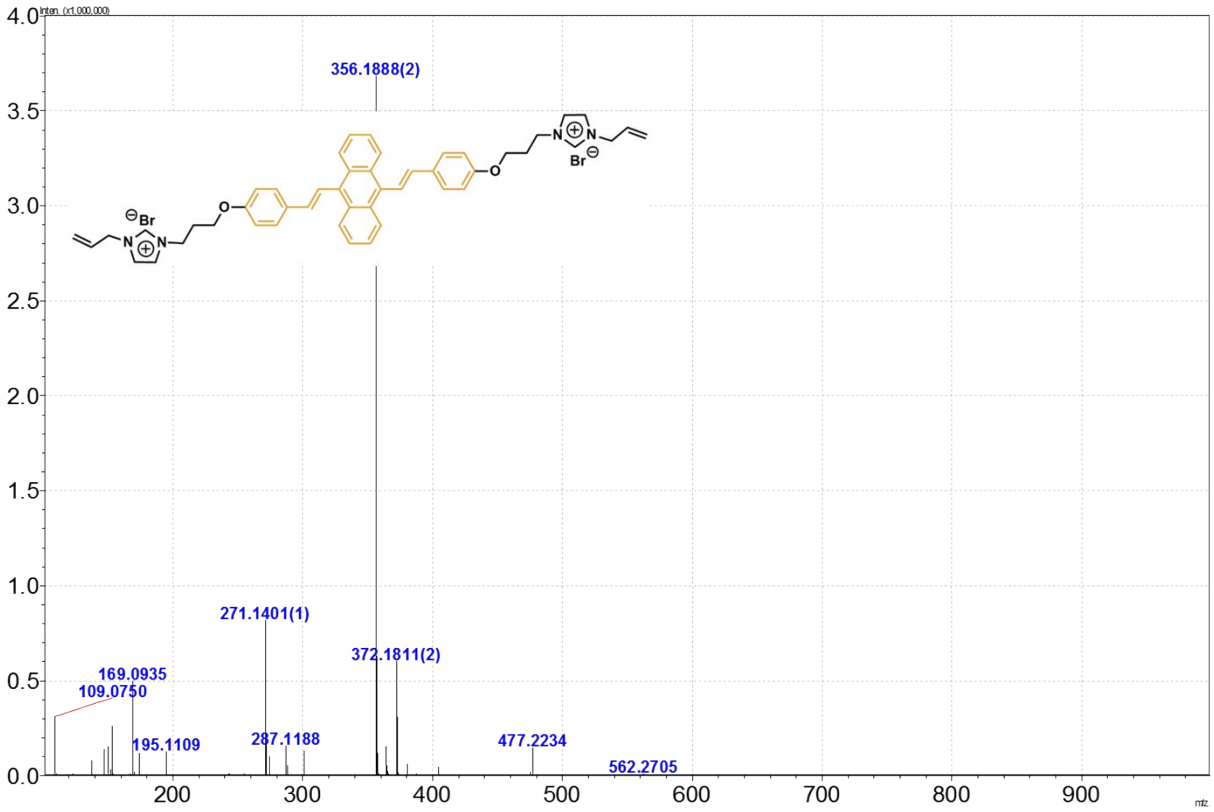
MS spectrum of **B-6**



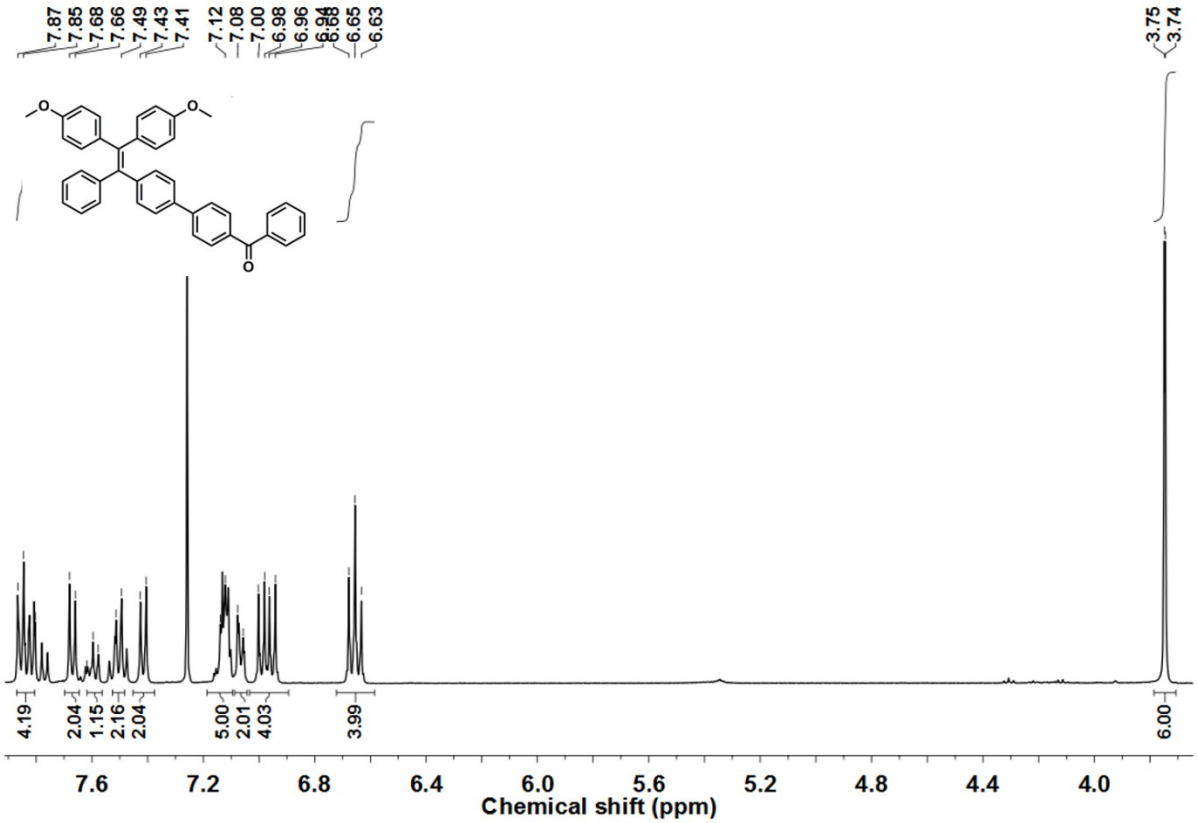
^{1}H NMR spectrum of **AIEgen-Yellow** in CD_3OD.



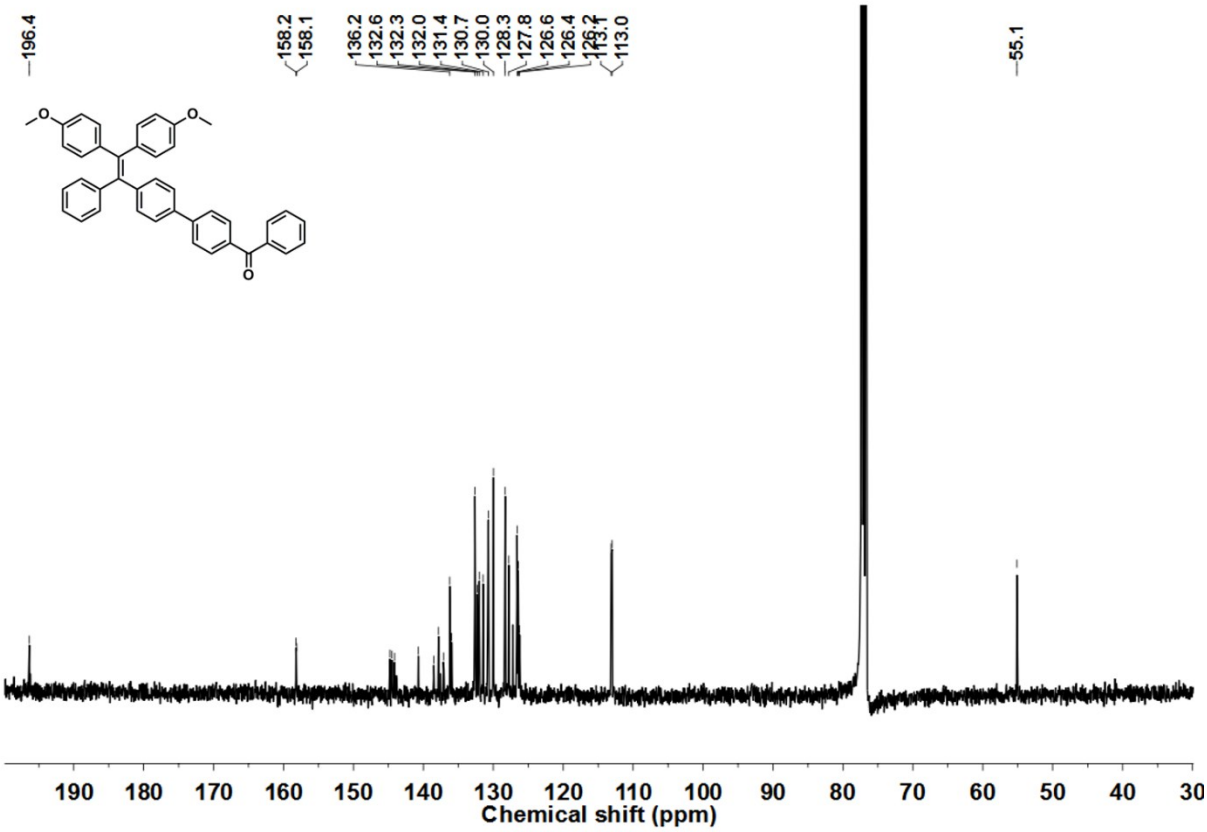
^{13}C NMR spectrum of **AIEgen-Yellow** in CD_3OD.



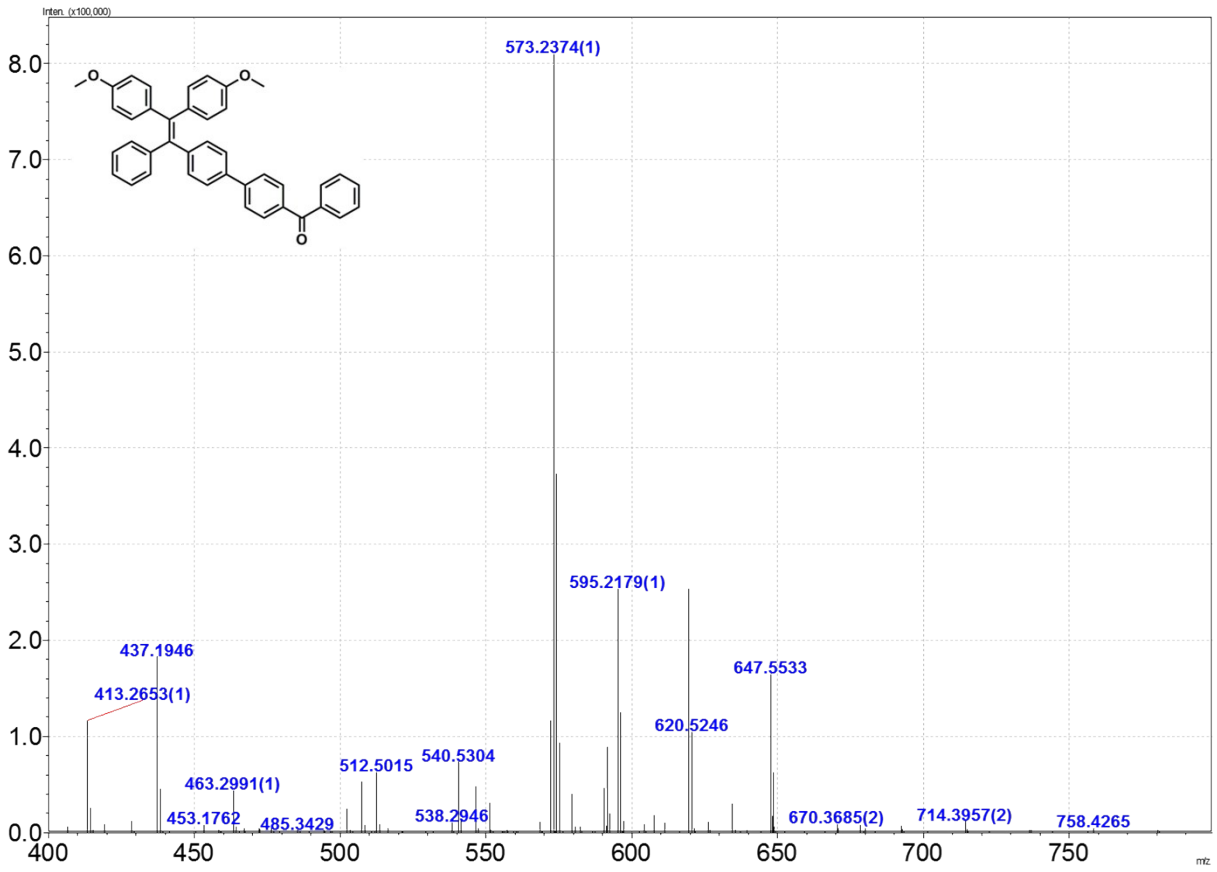
MS spectrum of **AIEgen-Yellow**.



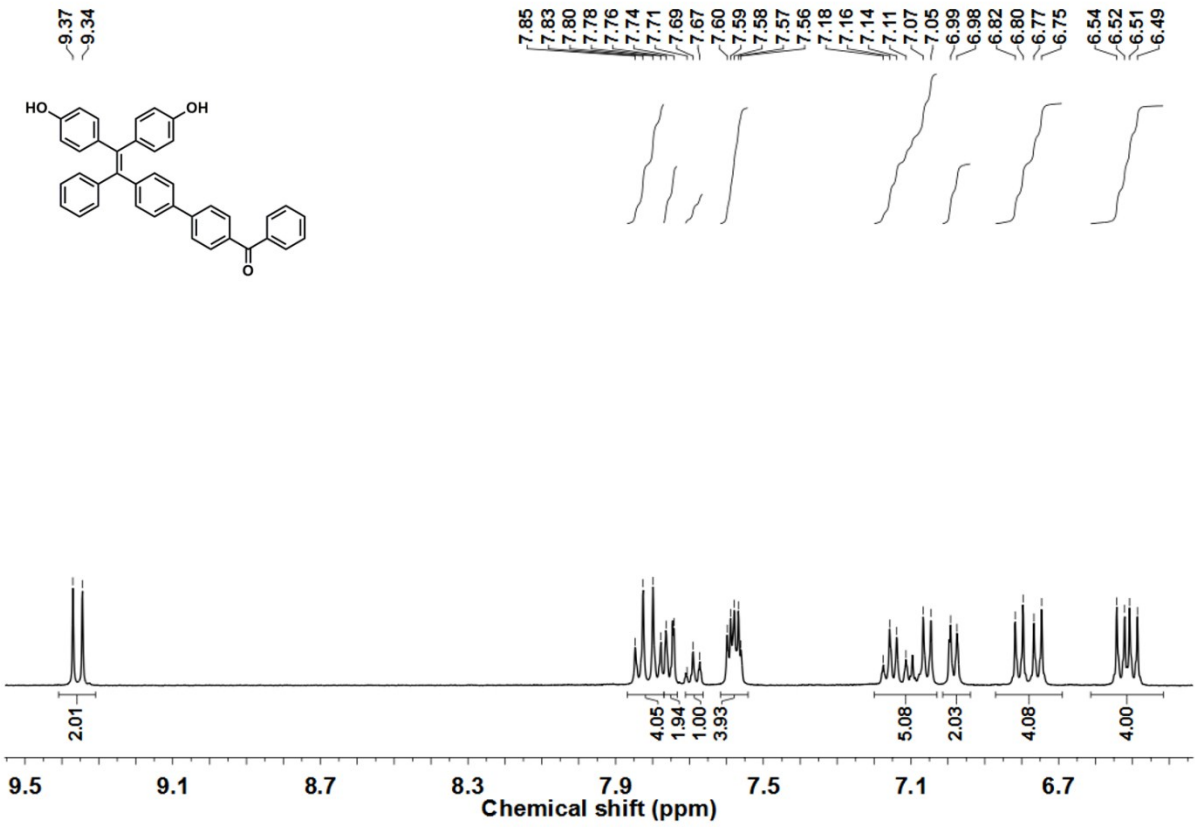
^{1}H NMR spectrum of C-**2** in $CDCl_3$.



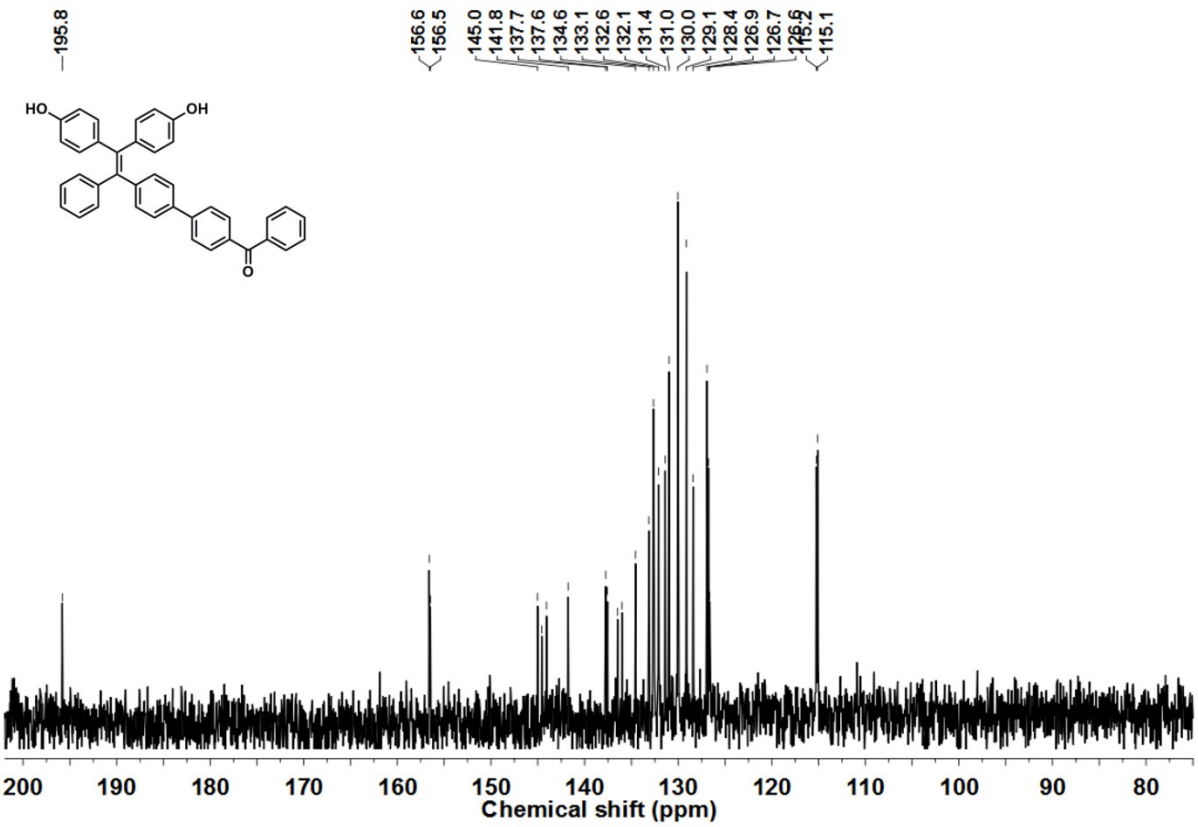
^{13}C NMR spectrum of **C-2** in $CDCl_3$.



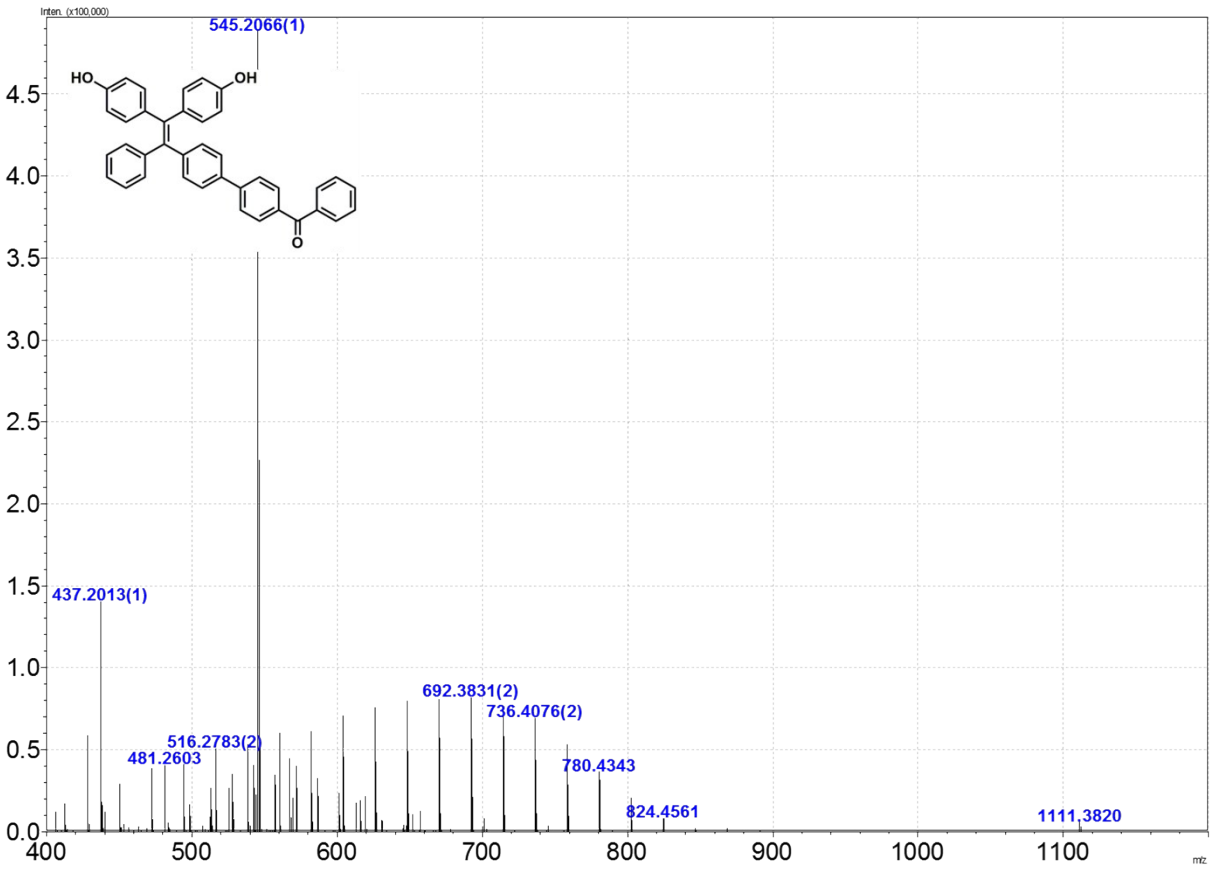
MS spectrum of **C-2.**



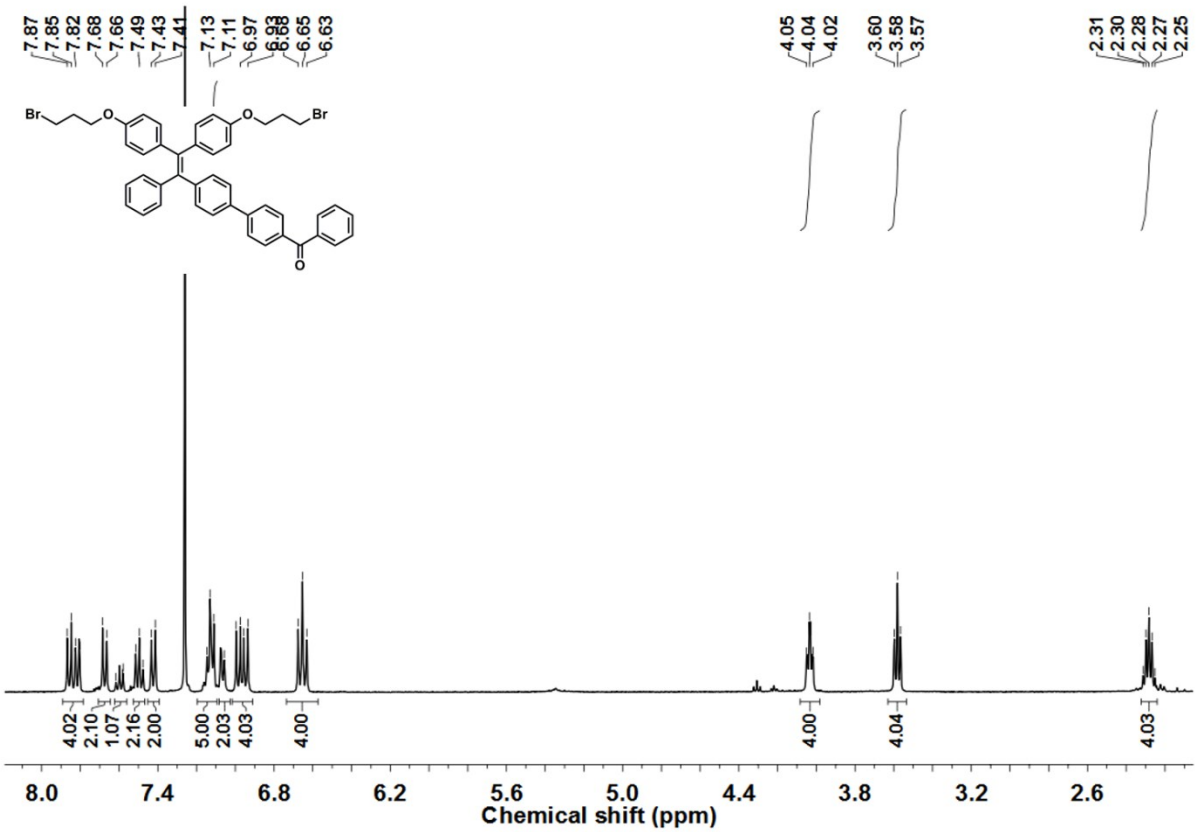
^{1}H NMR spectrum of C-**3** in DMSO.



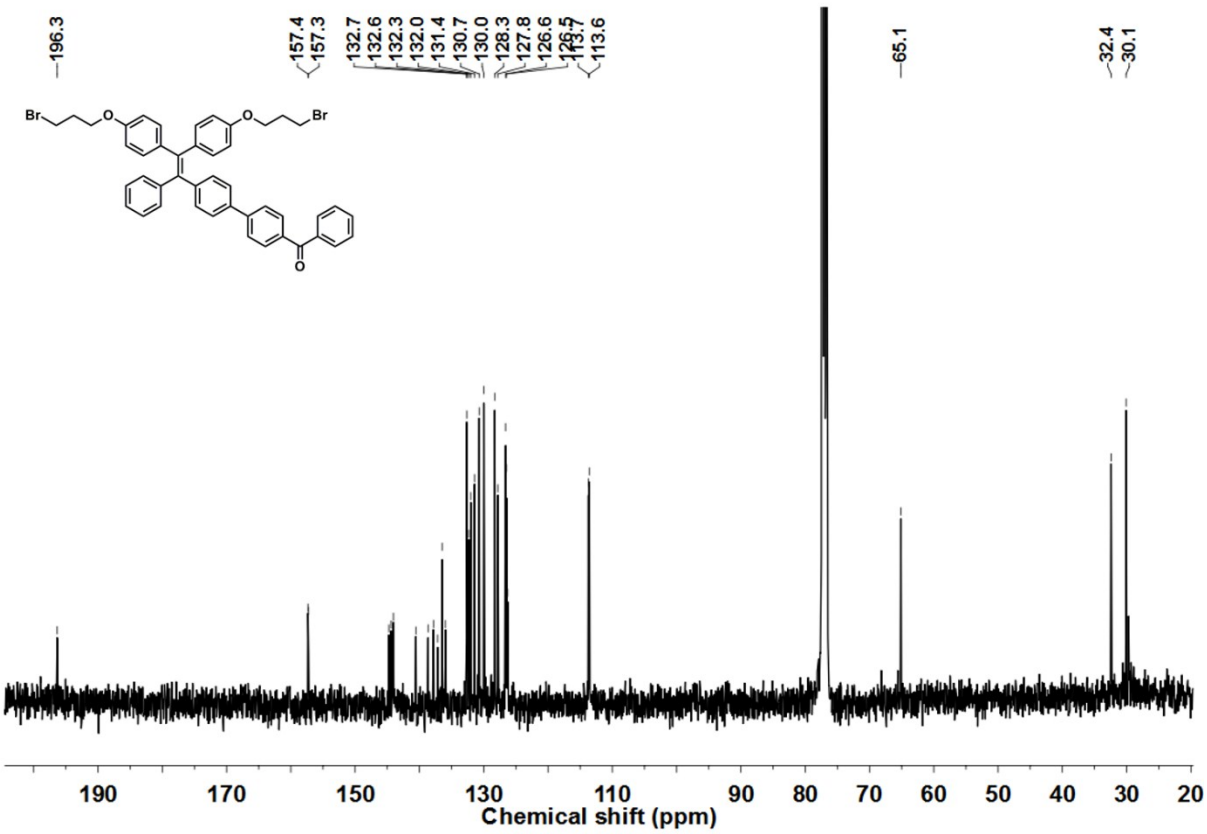
^{13}C NMR spectrum of C-**3** in DMSO.



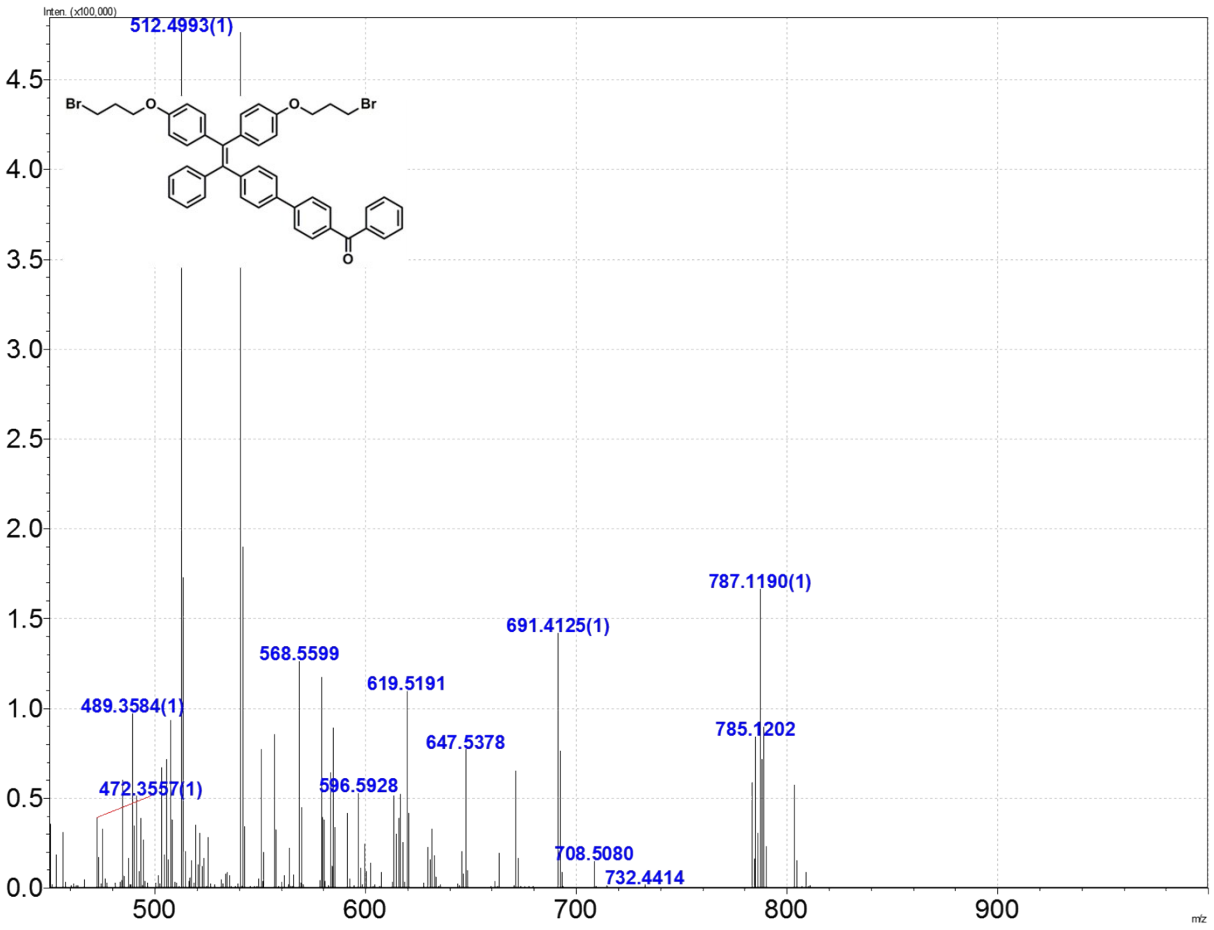
MS spectrum of C-**3**.



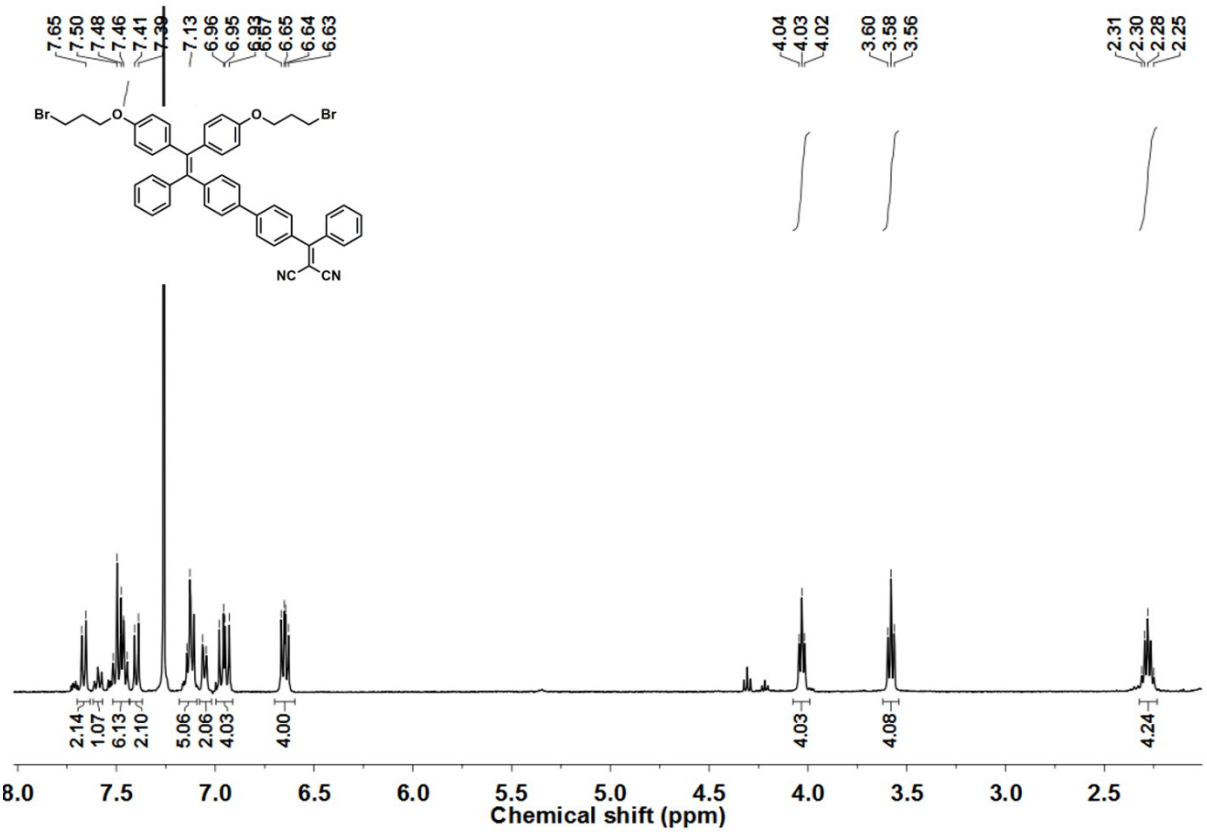
^{1}H NMR spectrum of C-**4** in $CDCl_3$.



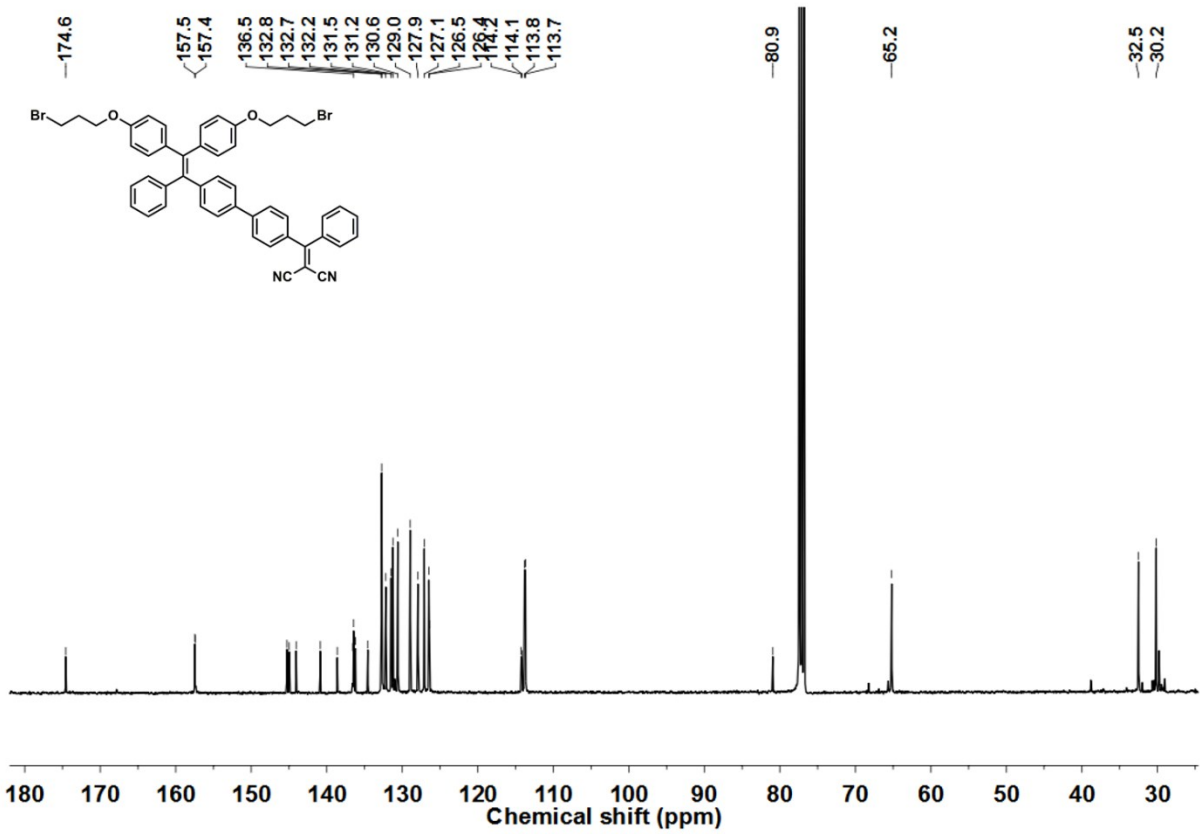
^{13}C NMR spectrum of C-**4** in $CDCl_3$.



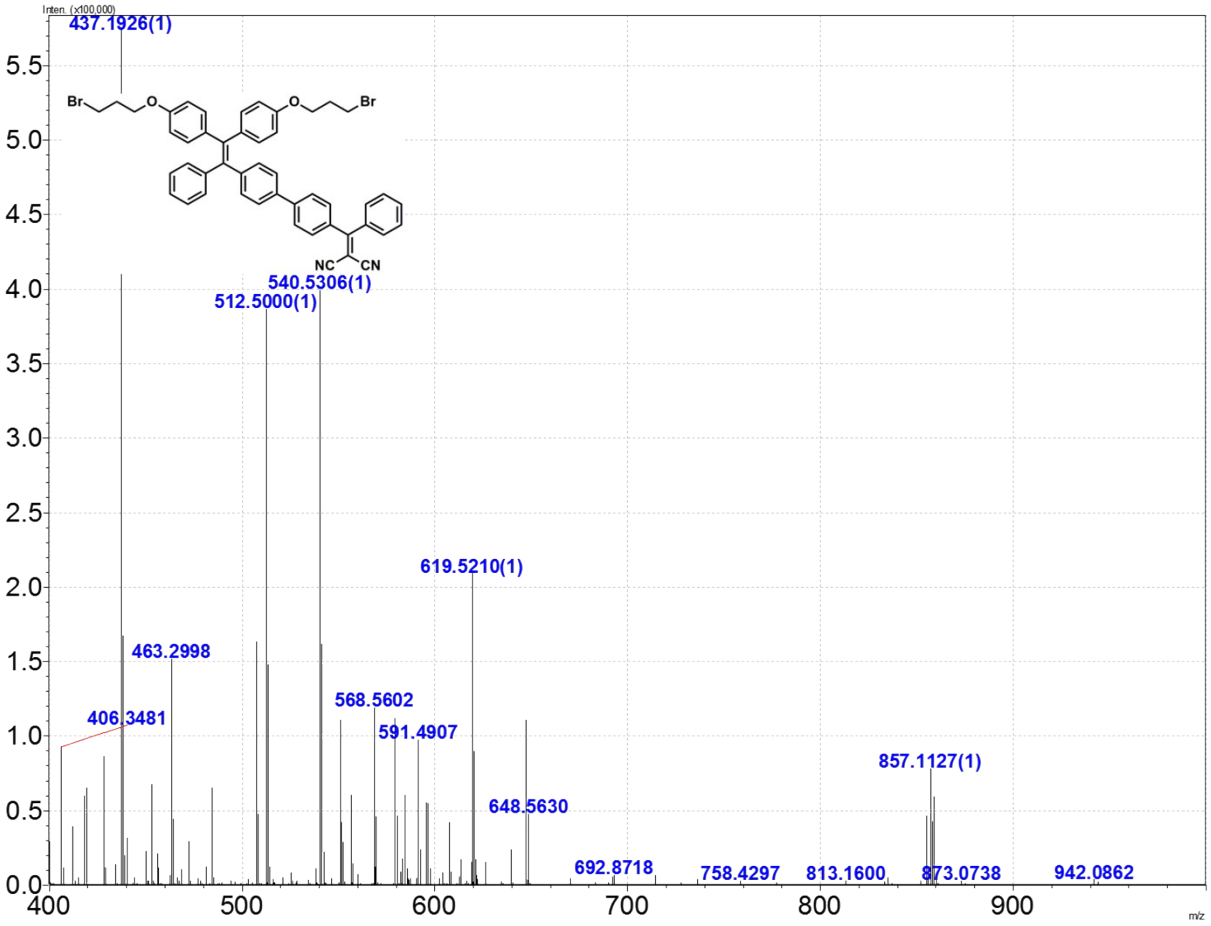
MS spectrum of C-**4**.



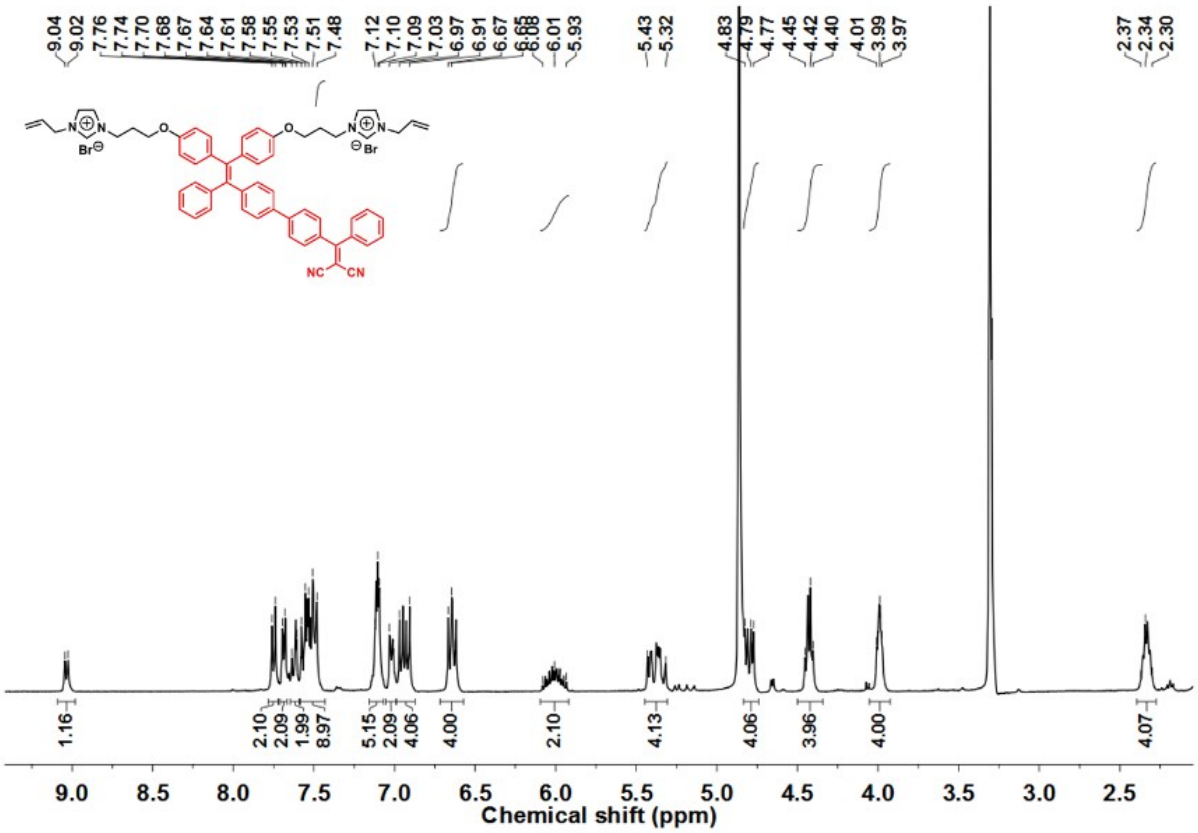
^{1}H NMR spectrum of C-**5** in $CDCl_3$.



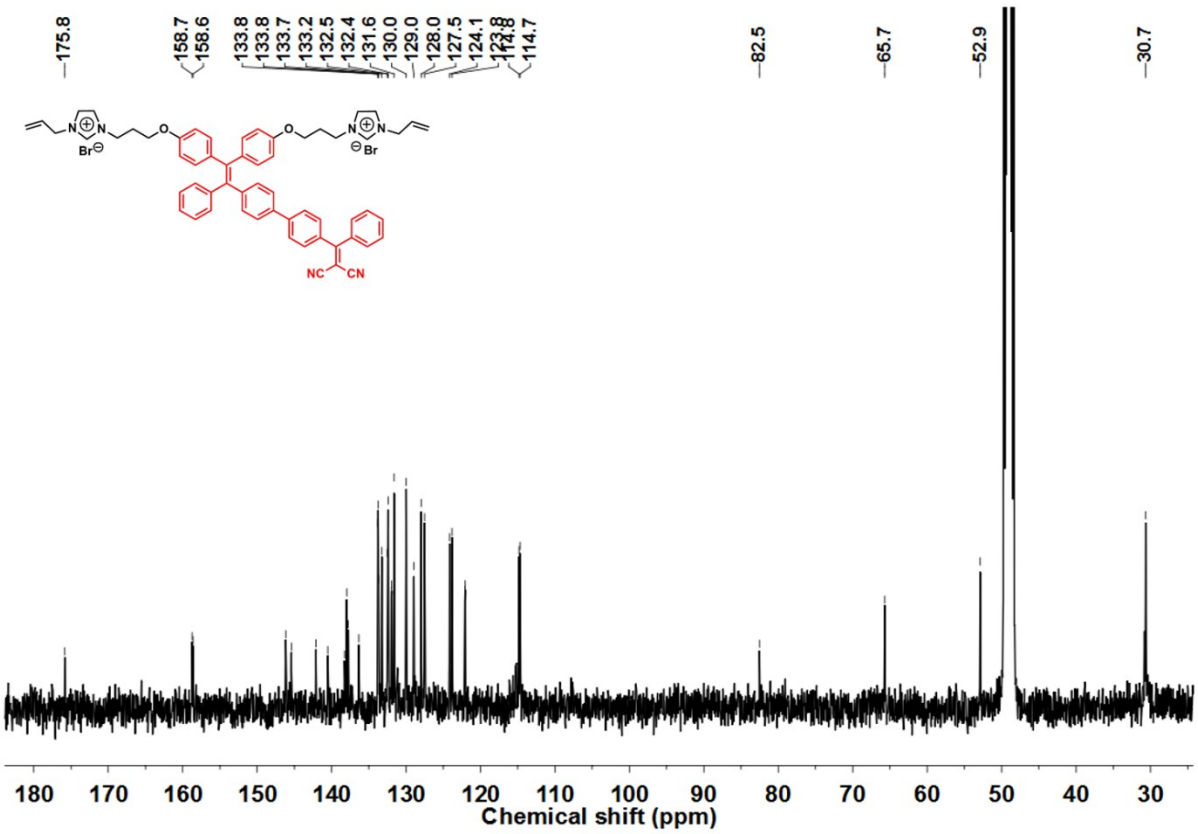
^{13}C NMR spectrum of C-**5** in $CDCl_3$.



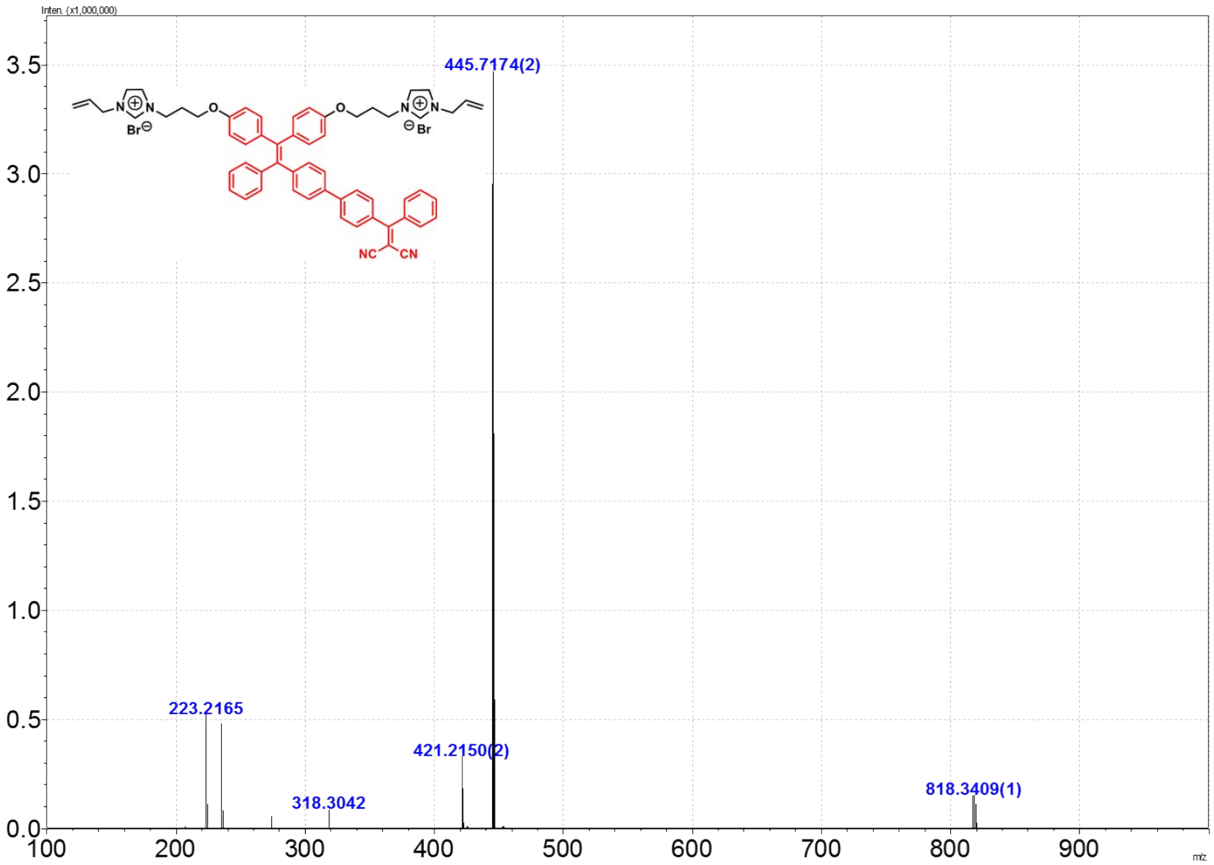
MS spectrum of C-**5**.



^{1}H NMR spectrum of **AIEgen-Red** in CD_3OD.



^{13}C NMR spectrum of **AIEgen-Red** in CD_3OD.



MS spectrum of **AIEgen-Red**.

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