Supporting Information for:

Label-Free Detection and Discrimination of Polybrominated Diphenyl-ethers Using Molecularly Imprinted Photonic Cross-Reactive Sensor Arrays

Dan Xu‡,[a] Wei Zhu‡,[a] Chen Wang,[a] Tian Tian,[a] Jian Li,[a] Yue Lan,[a] Guangxin Zhang,[b] Deqing Zhang*[b] and Guangtao Li*[a]

[a]Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, 100084 Beijing,China; [b]Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, China.

E-mail: LGT@mail.tsinghua.edu.cn

1. Experimental section

1.1 *chemicals*

Acrylic acid (AA) and tetraethoxysilane (TEOS) were purchased from Beijing Chemical Industries., Five analytes: Bisphenol A (BPA), 3,3',5,5'-Tetrabromobisphenol A (TBBPA), 4,4'-Biphenol (BIP), 2,2'-Dibromodiphenyl ether (DBDE) ,2,2',3,3'-Tetrabromodiphenyl ether (TBDE), 2,2',3,3',4,4',6,6'-Octabromodiphenyl ether (Octa-BDE), 2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether (Deca-BDE), methlenediethylene glycol dimethylacrylate (EGDMA), and 2, 2'-azobisisobutyronitrile (AIBN) were obtained from Arcos Organics. Anhydrous ethanol, ammonia, acetic acid, and other affiliated chemicals were all from local suppliers. All solvents and chemicals are of reagent quality and were used without further purification. Common glass slides were cut to be 50×20 mm^2 and immersed in a H_2SO_4/H_2O_2 mixture for 12 h, followed by rinsing with deionized water in an ultrasonic bath three times and then dried prior to use. All 7-mL vials for the formation of colloidal-crystal templates were cleaned by rinsing with the H_2SO_4/H_2O_2 mixture and deionized water. Polymethyl methacrylate (PMMA) slides (50 mm long, 20 mm wide and 1.5 mm thick) as supports for the formed MIPP film were cleaned with anhydrous ethanol. NaH_2PO_4 and Na_2HPO_4 were used as buffer solution at pH 7.6 for all molecular sensing measurements. The real lake water was obtained from a lake in Tsinghua University and filtered through a 200 μm syringe filter before use. Tap water was obtained from our lab without pretreatment before use.

1.2 *Instrumentation*

Morphology and microstructure of silica colloidal crystals and photonic hydrogel films was observed by a Hitachi S-6700 field emission scanning electron microscope. Optical Bragg diffractions were checked by an Olympus BX51M fiber optic spectrophotometer coupled to an optical microscope. The photopolymerization was performed in a UV light (FUSI Electric ST3) with 16 W. A centrifuging apparatus (Anke TDL-60B, Shanghai, China) was used for the centrifugation of colloidal particles from the reactants. The sensing properties of the fabricated MIPP films were checked by exposure to solutions of the analyte one after another from low to high concentrations in buffer solution. The shift of the Bragg diffraction wavelength of MIPP films after the exposure was measured by fiber optic spectrophotometer. Photograph of the MIPP films was obtained by using a common digital camera under a daylight lamp.

1.3 *Formation of colloidal-crystal templates*

The highly uniform silica colloidal microspheres were synthesized by using an approach based on the Stőber method. In a typical preparation, TEOS (4ml) and anhydrous ethanol (180 mL) were mixed in a 250-mL flask and stirred with a magnetic beater. Then, ammonia (17mL) was slowly added and the resulting reaction mixture was left overnight. After centrifugation and dispersion with anhydrous ethanol had been repeated four or five times to expunge residues, the monodispersed silica particles were obtained and fully dispersed in anhydrous ethanol (weight concentration ca. 1–4%), which were allotted into 7-mL clean vials for the formation of colloidal-crystal templates. A clean glass slide was

vertically placed into each vial for colloidal-crystal growth. After complete volatilization of ethanol, silica colloidal-crystal templates were formed on both sides of each glass slide.

1.4 *Synthesis of molecularly imprinted sensing element*

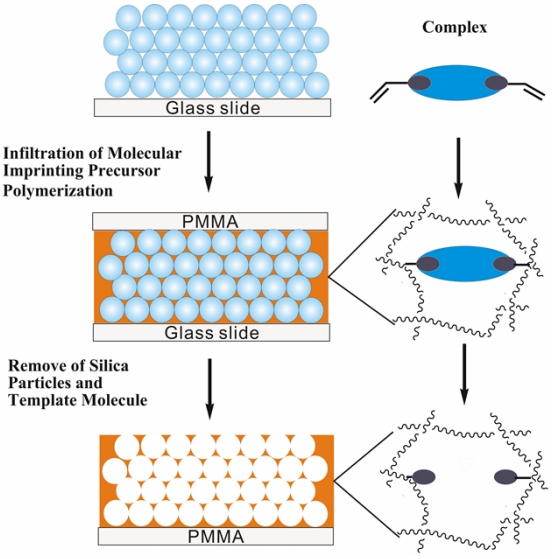


Figure S1. Illustration of the procedure used for the preparation of molecularly imprinted photonic sensing element.

1.5 *The optimization of the ratio of template molecules and monomer*

The effect of different molar ratio of template to monomer on the imprinting effect was carefully investigated in our work. As shown in Figure S2, when the template (BPA) / functional monomer molar ratio was set to 1/7, BPA imprinted sensing element exhibited an optimized optical shift to BPA for 40 nm at 10^{-6} M concentration. Whereas, for the ratio of 1/6 or 1/8, the redshift for 36 nm and 27 nm were observed, respectively. Clearly, in our system, the ratio of template to monomer cold be used to adjust the affinity (or response) of the constructed sensing elements. In our work, an optimized molar ratio of template to functional monomer was set to 1/7 for creating MIPP sensing elements.

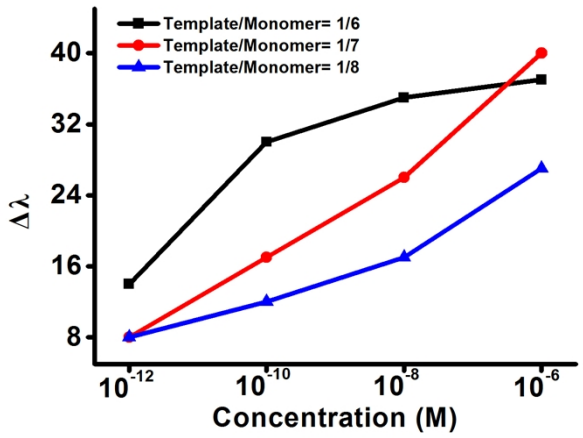
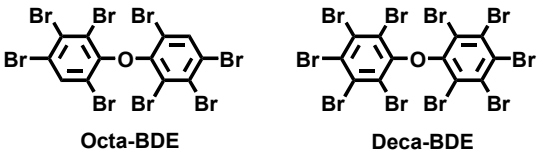


Figure S2. Plots of Bragg shifts of BPA-imprinted sensing element with different ratio of template and monomer to BPA under different concentration.

1.6 *The fabrication of MIPPs and NIPPs films*



Scheme S1. Chemical structures of Octa-BDE and Deca-BDE.

Template molecule (1 mmol), 0.5 g of AA (7 mmol) and 0.19 g of EGDMA (1 mmol) were mixed overnight in 0.2 ml of acetone and 0.3 ml anhydrous ethanol solvent for sufficient complexation. After adding 0.01 g of AIBN (6.1 mmol) and degassing with nitrogen for 10 minutes, the homogeneous mixtures were individually dropped onto colloidal templates. Once the colloidal templates became transparent, indicating successful infiltration, excess precursors were removed by covering a clean PMMA slide, and the remaining mixtures were photopolymerized in an ice bath under a UV light at 365 nm for 2 h. The sandwiches were immersed into 1% hydrofluoric acid for 2 h to separate the double slides and fully etch the silica particles. After eluting by incubating in acetic acid and water (v/v=1: 9) for 6 h, the MIPPs films on PMMA slides were rinsed with a phosphate buffer (pH 7.6, 5 mM) for removal of the target molecules from the MIPPs films. Thus, these obtained MIPPs films were kept in buffer and ready for determination. NIPPs films were also prepared for control tests with no addition of template.

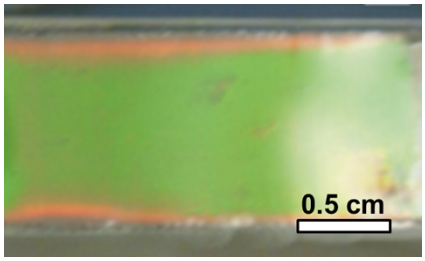


Figure S3. Photographs of molecularly imprinted inverse opal photonic film.

1.7 *Examples of Sensor Array Responses at Different Analyte Concentrations*

1) BPA imprinted sensing element against five analytes

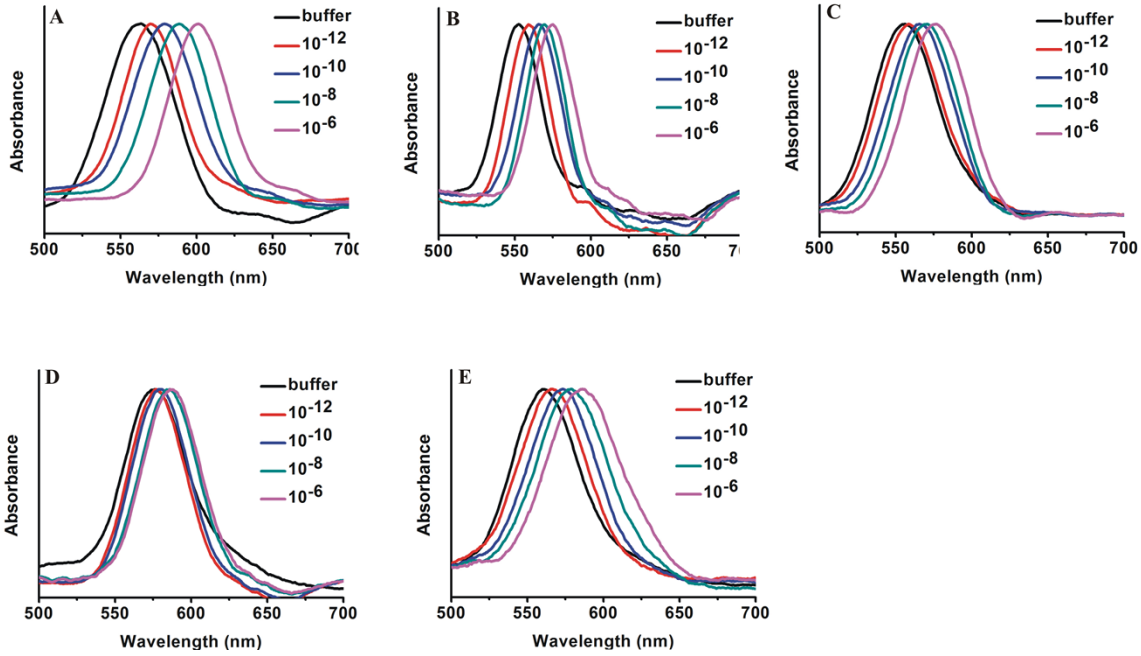


Figure S4. Optical response of BPA imprinted sensing element to different analytes with 10^{-12} M-10^{-6} M concentration range: A) BPA; B) TBBPA; C) BIP; D) DBDE; E) TBDE; All the spectra were normalized.

2) TBBPA imprinted sensing element against five analytes

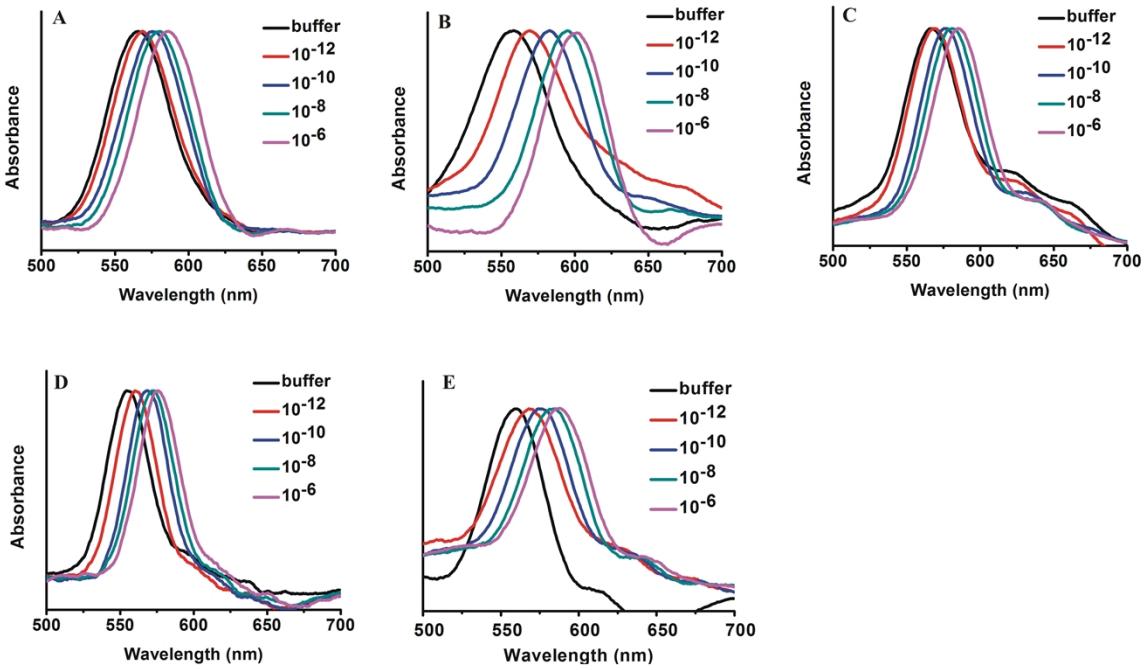


Figure S5. Optical response of TBBPA imprinted sensing element to different analytes with 10^{-12} M-10^{-6} M concentration range: A) BPA; B) TBBPA; C) BIP; D) DBDE; E) TBDE; All the spectra were normalized.

3) BIP imprinted sensing element against five analytes

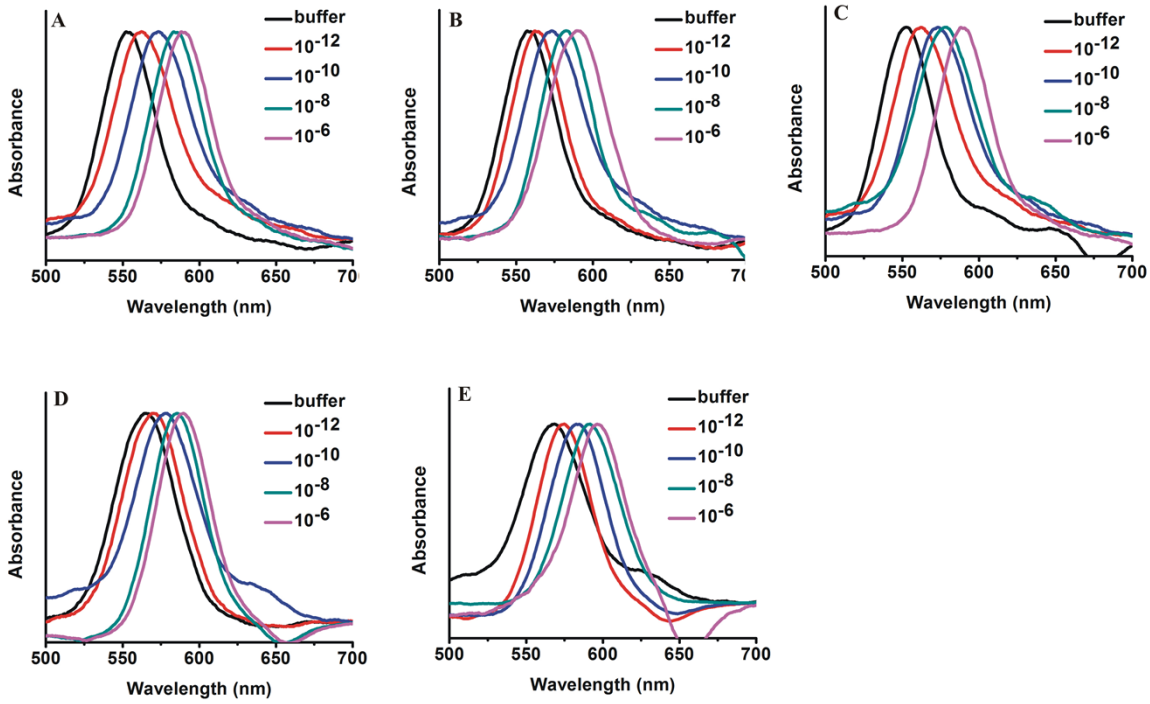


Figure S6. Optical response of BIP imprinted sensing element to different analytes with 10^{-12} M-10^{-6} M concentration range: A) BPA; B) TBBPA; C) BIP; D) DBDE; E) TBDE; All the spectra were normalized.

4) Nonimprinted sensing element against five analytes

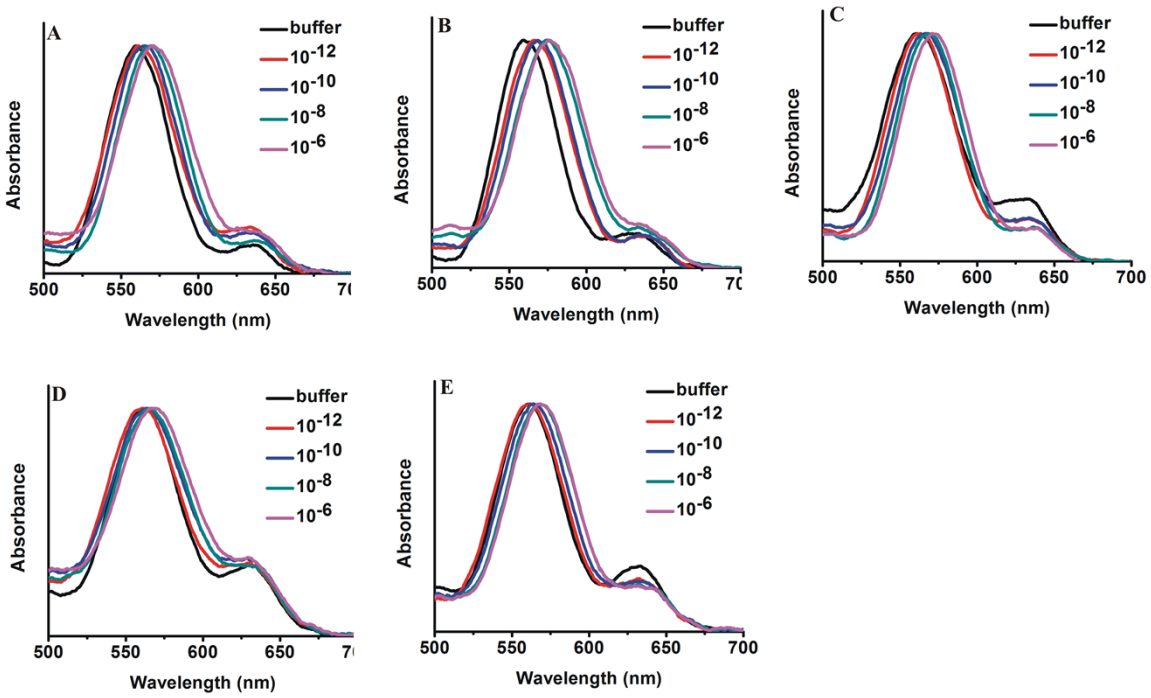


Figure S7. Optical response of nonimprinted sensing element to different analytes with 10^{-12} M-10^{-6} M concentration range: A) BPA; B) TBBPA; C) BIP; D) DBDE; E) TBDE; All the spectra were normalized.

2. Data analysis

To evaluate whether the recognition patterns can be applied for discrimination and identification, principal component analysis (PCA) and Leave-One-Out (or jack-knife) cross-validation procedure were used to perform multivariate analyses. For PCA, factor scores were used to draw 2D and 3D score plots. Jack-knifed classification matrices were taken to evaluate discrimination results. Each response was measured in five replicates.

Table S1. Bragg shifts (nm) of sensor array versus five analytes at concentration of 10^{-8} M

sensing elements	BPA imprinted polymer	TBBPA imprinted polymer	BIP imprinted polymer	Non imprinted polymer
BPA (1)	27	15	31	9
BPA (2)	29	14	29	8
BPA (3)	28	16	30	7
BPA (4)	30	17	32	8
BPA (5)	27	14	29	7

TBBPA (1)	17	37	29	15
TBBPA (2)	18	38	28	14
TBBPA (3)	16	36	27	13
TBBPA (4)	19	39	26	14
TBBPA (5)	16	38	27	15
BIP (1)	14	15	25	7
BIP (2)	16	13	27	6
BIP (3)	15	14	26	8
BIP (4)	14	12	28	9
BIP (5)	16	14	27	8
DBDE (1)	10	17	17	4
DBDE (2)	9	18	19	5
DBDE (3)	8	16	20	3
DBDE (4)	10	19	18	5
DBDE (5)	9	17	17	4
TBDE (1)	17	19	26	8
TBDE (2)	19	20	27	7
TBDE (3)	20	18	25	6
TBDE (4)	18	17	26	7
TBDE (5)	18	18	27	6

Table S2. Variables contribution in the PCs (Concentration: 10^{-8} M)

	PC1	**PC2**	**PC3**
BPA (1)	-20.1332	38.2809	-7.811
BPA (2)	-18.6908	38.9017	-5.1753
BPA (3)	-20.3376	38.2271	-5.4485
BPA (4)	-21.8044	40.9683	-6.0083
BPA (5)	-18.3544	37.0825	-5.7434
TBBPA (1)	-42.5352	27.3763	-9.4827
TBBPA (2)	-43.0638	27.4607	-7.5902
TBBPA (3)	-40.7503	25.3375	-7.9341
TBBPA (4)	-43.822	27.17	-5.4904
TBBPA (5)	-43.2811	25.4045	-8.4209
BIP (1)	-18.8379	23.9979	-9.555
BIP (2)	-16.8326	26.7766	-9.8545
BIP (3)	-18.3215	25.5945	-10.4096
BIP (4)	-16.9462	26.128	-13.2058
BIP (5)	-18.4222	26.9483	-10.5677

DBDE (1)	-18.9668	15.9056	-4.3509
DBDE (2)	-20.4152	16.1252	-6.4676
DBDE (3)	-17.9729	15.7309	-7.177
DBDE (4)	-21.268	16.3478	-5.045
DBDE (5)	-18.9607	15.065	-4.8699
TBDE (1)	-23.0399	26.7524	-8.2391
TBDE (2)	-23.7638	28.704	-7.1819
TBDE (3)	-21.3741	28.589	-5.2917
TBDE (4)	-20.8394	27.664	-7.7032
TBDE (5)	-21.5511	27.9346	-7.684

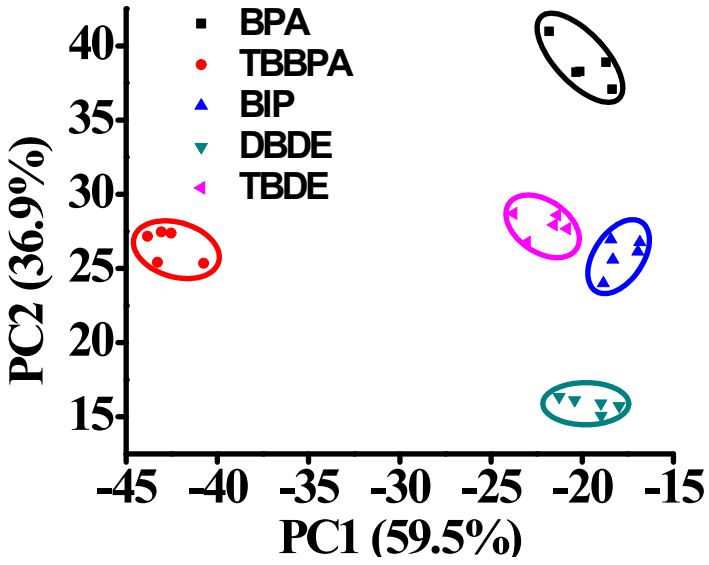


Figure S8. Two-dimensional PCA plot for the identification of five analytes (10^{-8} M) by MIPPs sensor array.

Table S3. Leave-One-Out cross-validation matrix (Concentration: 10^{-8} M)

	BPA	TBBPA	BIP	DBDE	TBDE
BPA	5	0	0	0	0
TBBPA	0	5	0	0	0
BIP	0	0	5	0	0
DBDE	0	0	0	5	0
TBDE	0	0	0	0	5
Total N	5	5	5	5	5
N correct	5	5	5	5	5
Proportion	1	1	1	1	1

N=25 N Correct=25 Proportion Correct=1.00

Table S4. Bragg shifts (nm) of sensor array versus five analytes at concentration of 10^{-10} M

sensing elements	BPA imprinted polymer	TBBPA imprinted polymer	BIP imprinted polymer	Non imprinted polymer
BPA (1)	18	11	19	6
BPA (2)	16	10	18	5
BPA (3)	19	12	17	6
BPA (4)	20	10	17	4
BPA (5)	18	11	19	5
TBBPA (1)	14	25	20	9
TBBPA (2)	13	25	21	9
TBBPA (3)	13	26	19	7
TBBPA (4)	12	24	18	7
TBBPA (5)	12	26	20	7
BIP (1)	12	8	23	2
BIP (2)	10	9	20	4
BIP (3)	13	10	22	3
BIP (4)	12	9	21	4
BIP (5)	13	10	20	2
DBDE (1)	5	13	13	1
DBDE (2)	4	12	13	0
DBDE (3)	6	11	11	1
DBDE (4)	5	13	12	1
DBDE (5)	4	11	14	0
TBDE (1)	9	14	18	3
TBDE (2)	10	13	16	4
TBDE (3)	11	12	17	4
TBDE (4)	8	12	18	5
TBDE (5)	11	13	16	3

Table S5. Variables contribution in the PCs (Concentration: 10^{-10} M)

	PC1	**PC2**	**PC3**
BPA (1)	-20.9529	17.9318	-7.745
BPA (2)	-18.9376	16.2215	-7.861
BPA (3)	-21.6676	17.5189	-5.4529

BPA (4)	-19.5175	18.8619	-5.1524
BPA (5)	-20.5935	17.7715	-7.7642
TBBPA (1)	-33.1351	9.5482	-9.5636
TBBPA (2)	-33.0633	9.1395	-10.9095
TBBPA (3)	-32.7701	7.6086	-9.1165
TBBPA (4)	-30.5432	7.289	-8.8135
TBBPA (5)	-32.6983	7.1998	-10.4624
BIP (1)	-16.0692	15.3604	-14.3093
BIP (2)	-16.4179	12.4875	-12.4754
BIP (3)	-18.2208	15.0632	-12.8225
BIP (4)	-17.2135	14.4707	-12.4394
BIP (5)	-17.4268	14.1257	-11.0711
DBDE (1)	-15.8136	3.5675	-8.3957
DBDE (2)	-14.3049	3.043	-8.9364
DBDE (3)	-13.9476	4.454	-6.2862
DBDE (4)	-15.5963	3.179	-7.5104
DBDE (5)	-13.662	3.8647	-9.8825
TBDE (1)	-19.6359	8.5871	-10.8805
TBDE (2)	-18.9895	9.2007	-8.6909
TBDE (3)	-18.6357	10.8198	-9.1764
TBDE (4)	-18.345	8.9767	-11.4244
TBDE (5)	-18.9192	9.8377	-8.2495

Table S6. Leave-One-Out cross-validation matrix (Concentration: 10^{-10} M)

	BPA	TBBPA	BIP	DBDE	TBDE
BPA	5	0	0	0	0
TBBPA	0	5	0	0	0
BIP	0	0	5	0	0
DBDE	0	0	0	5	0
TBDE	0	0	0	0	5
Total N	5	5	5	5	5
N correct	5	5	5	5	5
Proportion	1	1	1	1	1

N=25 N Correct=25 Proportion Correct=1.00

Table S7. Bragg shifts (nm) of sensor array versus five analytes at concentration of 10^{-12} M

sensing elements	BPA imprinted polymer	TBBPA imprinted polymer	BIP imprinted polymer	Non imprinted polymer
BPA (1)	9	4	9	2
BPA (2)	7	5	10	3
BPA (3)	8	6	10	2
BPA (4)	10	4	9	1
BPA (5)	9	4	8	3
TBBPA (1)	7	11	10	7
TBBPA (2)	6	10	9	6
TBBPA (3)	5	9	9	5
TBBPA (4)	7	9	8	5
TBBPA (5)	7	8	8	5
BIP (1)	3	2	8	2
BIP (2)	4	3	8	2
BIP (3)	5	4	9	3
BIP (4)	4	5	7	1
BIP (5)	3	3	9	1
DBDE (1)	2	5	7	-2
DBDE (2)	3	6	6	0
DBDE (3)	4	7	5	0
DBDE (4)	2	5	6	-1
DBDE (5)	3	4	5	0
TBDE (1)	5	7	8	0
TBDE (2)	5	6	7	1
TBDE (3)	4	5	6	1
TBDE (4)	4	7	6	2
TBDE (5)	6	7	7	0

Table S8. Variables contribution in the PCs (Concentration: 10^{-12} M)

	PC1	**PC2**	**PC3**
BPA (1)	-10.6693	5.33	-2.3143
BPA (2)	-11.0887	3.6273	-0.5798
BPA (3)	-11.4596	3.6105	-2.1652
BPA (4)	-10.5485	6.0318	-3.4964
BPA (5)	-10.9832	4.9107	-2.0877
TBBPA (1)	-16.5616	-1.0615	-0.6037

TBBPA (2)	-14.6124	-1.1811	-0.5883
TBBPA (3)	-12.9801	-0.9757	-0.2007
TBBPA (4)	-13.6831	-0.0859	-1.7395
TBBPA (5)	-13.1914	0.6327	-1.3363
BIP (1)	-6.3095	2.7974	1.6195
BIP (2)	-7.3111	2.6862	0.633
BIP (3)	-9.2603	2.8059	0.6177
BIP (4)	-7.3468	1.0182	-1.1445
BIP (5)	-6.4873	2.4982	0.9897
DBDE (1)	-4.4347	0.0861	-1.7745
DBDE (2)	-6.3809	-0.5387	-1.9355
DBDE (3)	-7.0657	-0.975	-3.2943
DBDE (4)	-4.7486	-0.3333	-1.5479
DBDE (5)	-5.0808	0.5734	-1.5014
TBDE (1)	-8.5262	0.6078	-2.7608
TBDE (2)	-8.3484	0.907	-2.131
TBDE (3)	-7.03	0.6931	-1.5168
TBDE (4)	-8.644	-0.8384	-1.7243
TBDE (5)	-8.7193	0.8902	-3.7163

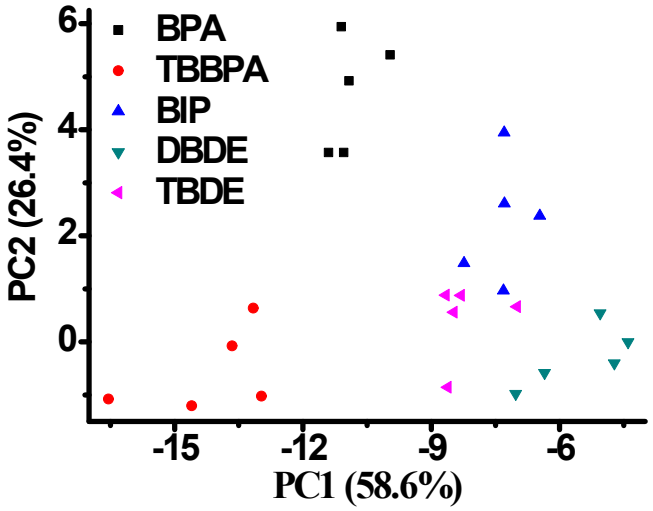


Figure S9. Two-dimensional PCA plot for the identification of five analytes (10^{-12} M) by MIPPs sensor array.

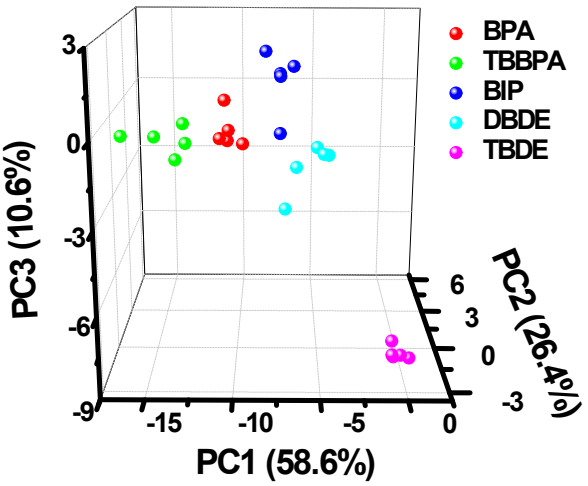


Figure S10. Three-dimensional PCA plot for the identification of five analytes (10^{-12} M) by MIPPs sensor array.

Table S9. Leave-One-Out cross-validation matrix (Concentration: 10^{-12} M)

	BPA	TBBPA	BIP	DBDE	TBDE
BPA	5	0	0	0	0
TBBPA	0	5	0	0	0
BIP	0	0	5	0	0
DBDE	0	0	0	5	0
TBDE	0	0	0	0	5
Total N	5	5	5	5	5
N correct	5	5	5	5	5
Proportion	1	1	1	1	1

N=25 **N** Correct=25 Proportion Correct=1.00

Table S10. Bragg shifts (nm) of sensor array versus mixture at concentration of 10^{-10} M of each analyte; 1: TBDE solution; mixture 2: (TBDE and BPA); mixture 3: (TBDE, BPA, and TBBPA); mixture 4: (TBDE, BPA, TBBPA and BIP)

sensing elements	BPA imprinted polymer	TBBPA imprinted polymer	BIP imprinted polymer
1-1	10	11	20
1-2	13	12	20

1-3	12	13	22
1-4	11	13	22
1-5	11	12	23
2-1	18	16	27
2-2	19	17	26
2-3	20	15	26
2-4	19	17	25
2-5	18	16	26
3-1	25	22	35
3-2	24	22	33
3-3	22	24	31
3-4	23	26	33
3-5	22	24	32
4-1	31	19	45
4-2	30	21	40
4-3	27	23	41
4-4	29	20	42
4-5	30	22	43

Table S11. Leave-One-Out cross-validation matrix (mixture at concentration of 10^{-10} M)

	1	2	3	4
1	5	0	0	0
2	0	5	0	0
3	0	0	5	0
4	0	0	0	5
Total N	5	5	5	5
N correct	5	5	5	5
Proportion	1	1	1	1

N=20 N Correct=20 Proportion Correct=1.00

Table S12. Bragg shifts (nm) of sensor array versus mixture at concentration of 10^{-10} M of each analyte dissolved in tap water; 1: TBDE solution; mixture 2: (TBDE and BPA); mixture 3: (TBDE, BPA, and TBBPA); mixture 4: (TBDE, BPA, TBBPA, BIP and Octa-BDE) and mixture 5 (TBDE, BPA, TBBPA, BIP, Octa-BDE and Deca-BDE); For Octa-BDE and Deca-BDE, saturated solution were used.

sensing elements	BPA imprinted polymer	TBBPA imprinted polymer	BIP imprinted polymer
1-1	7	7	8
1-2	8	9	10
1-3	10	8	11
1-4	8	10	9
1-5	7	8	8
2-1	14	13	20
2-2	12	10	19
2-3	13	11	22
2-4	12	12	20
2-5	14	10	20
3-1	22	24	26
3-2	20	21	24
3-3	23	22	24
3-4	22	21	25
3-5	20	24	27
4-1	27	34	34
4-2	25	31	31
4-3	27	32	34
4-4	25	32	32
4-5	25	31	31
5-1	32	40	42
5-2	30	37	39
5-3	29	38	40
5-4	30	40	41
5-5	29	40	43
6-1	34	46	50
6-2	32	45	49
6-3	31	47	48
6-4	31	48	48
6-5	34	45	51

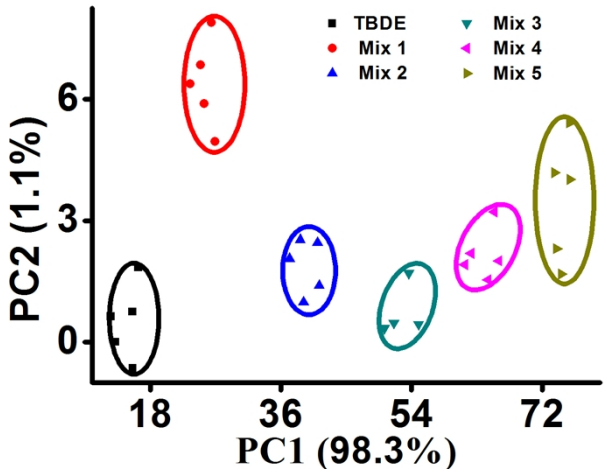


Figure S11. 2D PCA plot for the identification of TBDE and five different mixtures dissolved in tap water at concentration of 10^{-10} M by MIPPs sensor array: mixture 1 (TBDE and BPA); mixture 2 (TBDE, BPA, and TBBPA); mixture 3 (TBDE, BPA, TBBPA and BIP); mixture 4 (TBDE, BPA, TBBPA, BIP and Octa-BDE) and mixture 5 (TBDE, BPA, TBBPA, BIP, Octa-BDE and Deca-BDE); For Octa-BDE and Deca-BDE, saturated solution were used.

Table S13 Leave-One-Out cross-validation matrix (mixture at concentration of 10^{-10} M)

	1	2	3	4	5	6
1	5	0	0	0	0	0
2	0	5	0	0	0	0
3	0	0	5	0	0	0
4	0	0	0	5	0	0
5	0	0	0	0	5	0
6	0	0	0	0	0	5
Total N	5	5	5	5	5	5
N correct	5	5	5	5	5	5
Proportion	1	1	1	1	1	1

N=30 N Correct=30 Proportion Correct=1.00

Table S14. Bragg shifts (nm) of sensor array versus mixture at concentration of 10^{-10} M of each analyte dissolved in lake water; 1: TBDE solution; mixture 2: (TBDE and BPA); mixture 3: (TBDE, BPA, and TBBPA); mixture 4: (TBDE, BPA, TBBPA, BIP and Octa-BDE) and mixture 5 (TBDE, BPA, TBBPA, BIP, Octa-BDE and Deca-BDE); For Octa-BDE and Deca-BDE, saturated solution were used.

sensing elements	BPA imprinted polymer	TBBPA imprinted polymer	BIP imprinted polymer
1-1	10	15	12
1-2	11	13	9
1-3	8	12	11
1-4	8	12	9
1-5	9	13	10
2-1	15	19	20
2-2	15	16	17
2-3	14	18	18
2-4	13	17	17
2-5	13	16	20
3-1	17	23	30
3-2	14	22	28
3-3	15	22	27
3-4	16	21	28
3-5	17	21	30
4-1	28	22	38
4-2	27	20	36
4-3	27	21	37
4-4	29	20	34
4-5	30	23	38
5-1	32	26	40
5-2	31	24	40
5-3	30	24	42
5-4	30	25	39
5-5	31	25	42
6-1	42	37	51
6-2	39	36	50
6-3	41	34	52
6-4	39	34	52
6-5	40	35	50

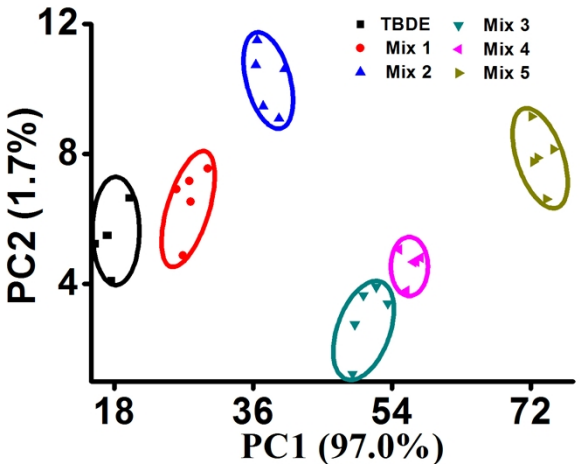


Figure S12. 2D PCA plot for the identification of TBDE and five different mixtures dissolved in lake water at concentration of 10^{-10} M by MIPPs sensor array: mixture 1 (TBDE and BPA); mixture 2 (TBDE, BPA, and TBBPA); mixture 3 (TBDE, BPA, TBBPA and BIP); mixture 4 (TBDE, BPA, TBBPA, BIP and Octa-BDE) and mixture 5 (TBDE, BPA, TBBPA, BIP, Octa-BDE and Deca-BDE); For Octa-BDE and Deca-BDE, saturated solution were used.

Table S15. Leave-One-Out cross-validation matrix (mixture at concentration of 10^{-10} M)

	1	2	3	4	5	6
1	5	0	0	0	0	0
2	0	5	0	0	0	0
3	0	0	5	0	0	0
4	0	0	0	5	0	0
5	0	0	0	0	5	0
6	0	0	0	0	0	5
Total N	5	5	5	5	5	5
N correct	5	5	5	5	5	5
Proportion	1	1	1	1	1	1

N=30 N Correct=30 Proportion Correct=1.00

Table S16. Bragg shifts (nm) of sensor array versus mixture dissolved in tap water; mixture 1: (10^{-12} M TBDE, 10^{-10} M BPA, and 10^{-10} M TBBPA); mixture 2: (10^{-10} M TBDE, 10^{-10} M BPA, and 10^{-10} M TBBPA); mixture 3: (10^{-8} M TBDE, 10^{-10} M BPA, and 10^{-10} M TBBPA); mixture 4: (10^{-12} TBDE, 10^{-10} M BPA, 10^{-10} M TBBPA and 10^{-10} M BIP), mixture 5: (10^{-10} TBDE, 10^{-10} M BPA, 10^{-10} M TBBPA and 10^{-10} M BIP) and mixture 6: (10^{-8} TBDE, 10^{-10} M BPA, 10^{-10} M TBBPA and 10^{-10} M BIP).

sensing elements	BPA imprinted polymer	TBBPA imprinted polymer	BIP imprinted polymer
1-1	10	11	7
1-2	9	13	9
1-3	7	12	10
1-4	7	11	9
1-5	9	13	10
2-1	17	20	36
2-2	14	19	33
2-3	15	19	34
2-4	16	21	38
2-5	17	21	38
3-1	24	29	40
3-2	27	30	42
3-3	26	31	40
3-4	25	30	40
3-5	24	31	42
4-1	14	16	20
4-2	15	17	22
4-3	16	18	23
4-4	15	18	22
4-5	16	17	20
5-1	28	20	34
5-2	27	19	31
5-3	26	20	34
5-4	27	20	32
5-5	29	22	36
6-1	36	26	43
6-2	35	29	45
6-3	36	28	42
6-4	36	26	43
6-5	33	29	45

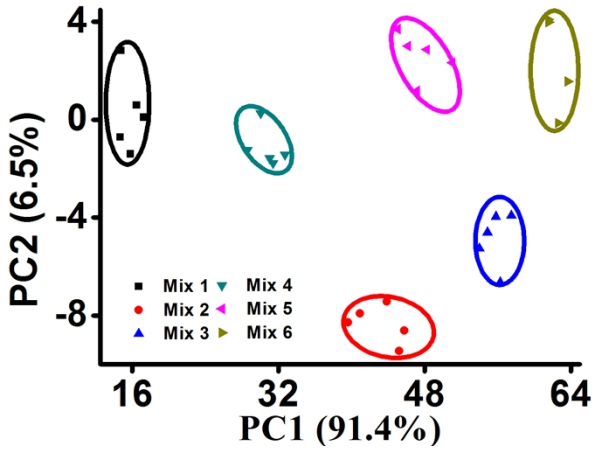


Figure S13. 2D PCA plot for the identification of six different mixtures dissolved in tap water by MIPPs sensor array: mixture 1: (10^{-12} M TBDE, 10^{-10} M BPA, and 10^{-10} M TBBPA); mixture 2: (10^{-10} M TBDE, 10^{-10} M BPA, and 10^{-10} M TBBPA); mixture 3: (10^{-8} M TBDE, 10^{-10} M BPA, and 10^{-10} M TBBPA); mixture 4: (10^{-12} TBDE, 10^{-10} M BPA, 10^{-10} M TBBPA and 10^{-10} M BIP), mixture 5: (10^{-10} TBDE, 10^{-10} M BPA, 10^{-10} M TBBPA and 10^{-10} M BIP) and mixture 6: (10^{-8} TBDE, 10^{-10} M BPA, 10^{-10} M TBBPA and 10^{-10} M BIP).

Table S17. Leave-One-Out cross-validation matrix six different mixtures

	1	2	3	4	5	6
1	5	0	0	0	0	0
2	0	5	0	0	0	0
3	0	0	5	0	0	0
4	0	0	0	5	0	0
5	0	0	0	0	5	0
6	0	0	0	0	0	5
Total N	5	5	5	5	5	5
N correct	5	5	5	5	5	5
Proportion	1	1	1	1	1	1

N=30 N Correct=30 Proportion Correct=1.00