Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Selective Capturing and Fluorescence "Turn On" Detection of Dibutyl Phthalate Using Molecular Imprinted Nanocomposite

Jayanta Dolai, Haydar Ali and Nikhil R. Jana*

School of Materials Science, Indian Association for the Cultivation of Science, Kolkata-700032, India

*Corresponding authors E-mail: camnrj@iacs.res.in

Supporting Note 1. In order to analyse very low concentration of DBP in environmental samples, chloroform extraction has been coupled to pre-concentrate DBP. First, 1000 mL DBP solution (2.5 nM or 0.7 µg/L) is prepared separately in different environmental water matrices (tap water, lake water, river water and waste water). Next, 10 mL of the above solutions is taken in 15 mL vial and stirred with 1.0 mL chloroform. Then entire chloroform extract of DBP is collected, chloroform is evaporated and entire DBP is dissolved in one mL fresh water. Thus DBP is concentrated by 10 times. Then these samples were then used for fluorescence 'turn on' based assay with MIP and the recoveries were calculated using the calibration curve. Result shows very good recoveries in all water matrices. (Table S3) Using this pre-concentration approach our method can be applied for analysis of environmental samples with the DBP concentration as low as 2.5 nM (or 0.7 µg/L).

Table S1. Summary of reported molecular imprinted composite-based detection of DBP.

Monomer, crosslinker, nanoparticle	*Sensing technique*	*Linear range (μM)*	*Limit of detection (μM)*	*Imprinting factor*	*Portable sensor*	*Reference*
methacrylic acid, ethylene glycol dimethacrylate	chemilumine scence	0.3 - 20	0.2	2	no	47
Mn doped ZnS, acrylamide, ethylene glycol dimethacrylate	fluorescence	5.0 - 50	0.08	2.2	no	48
methacrylic acid, ethylene glycol dimethacrylate	HPLC	5 -30	0.08	2	no	49
Mn doped ZnS, acrylamide, ethylene glycol dimethacrylate	fluorescence	5–50	0.4	2.1	no	50
α-cyclodextrin, tetrafluoreterep hthalonitrile, GO	fluorescence	0.025 - 1	0.024	4	TLC plate-based kit	this work

Table S2. Varied synthetic conditions used to prepare different MIP.

Set	*α-CD:TFN*	*GO (mg/mL)*	*DBP detection limit (μM)*	*Imprinting Factor*
MIP-1	2	3.5	0.15	4
MIP-2	3	3.5	0.024	4.5
MIP-3	4	3.5	0.25	2.6
MIP-4	3	2.5	0.5	3
MIP-5	3	4.5	0.45	2.7

Table S3. MIP-based detection of DBP in real water via pre-concentration approach.

Samples	Spiked (µg/L)	Found (µg/L)	Recoveries (%)
Tap water	0.7	0.67	95 ± 2
Lake water	0.7	0.59	84 ± 5
River Water	0.7	0.61	87 ± 3
Waste water	0.7	0.64	91 ± 3

Table S4. MIP-based detection of DBP in various real water samples.

Sample	***Added (µM)***	***Detected (µM)***	***Recovery (%)***
Tap Water	0.1	0.096	96
	0.05	0.046	92
Lake Water	0.1	0.089	89
	0.05	0.049	98
River water	0.1	0.088	88
	0.05	0.048	96
Waste water	0.1	0.095	95
	0.05	0.044	88

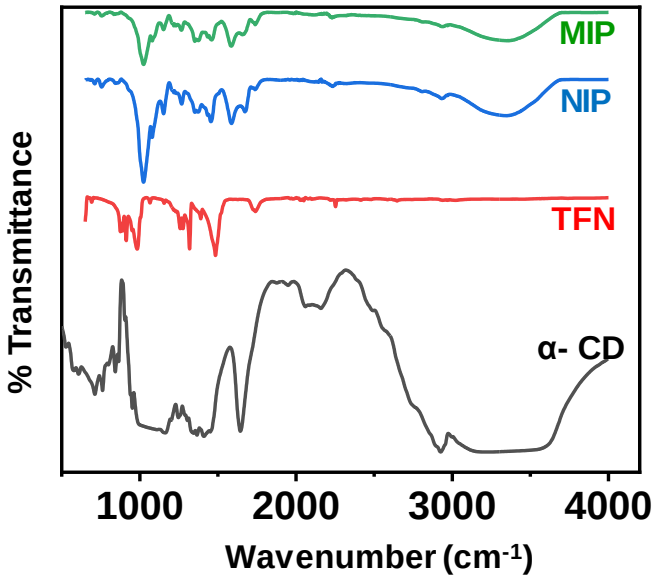

Figure S1. FTIR spectra of MIP, NIP, TFN, and α-CD showing the formation of the polymer nanocomposite. C–F stretching band around 1455 cm^{-1} appears for MIP and NIP.

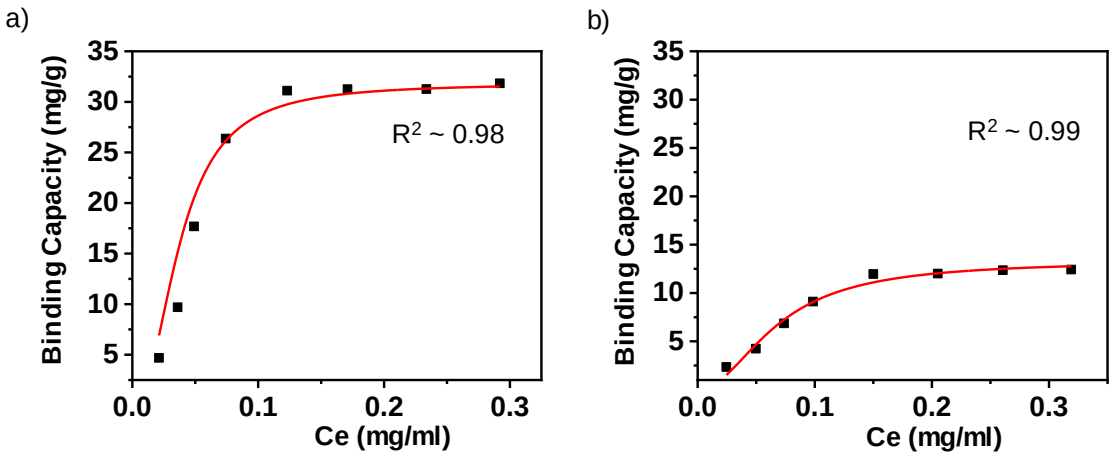

Figure S2. Langmuir adsorption isotherm for DBP by MIP (a), NIP (b). The experimental data fitted into Langmuir isotherm as given below: q_e = qmax.K.C_f/(1+K.C_f), where C_f is the equilibrium concentration, q_{max} is the maximum amount of adsorbate that is adsorbed onto the adsorbent, q_e is the equilibrium binding capacity, and K is the Langmuir constant. The maximum binding capacity that is obtained with Langmuir adsorption model is 33 mg/g for MIP and 11 mg/g for NIP.

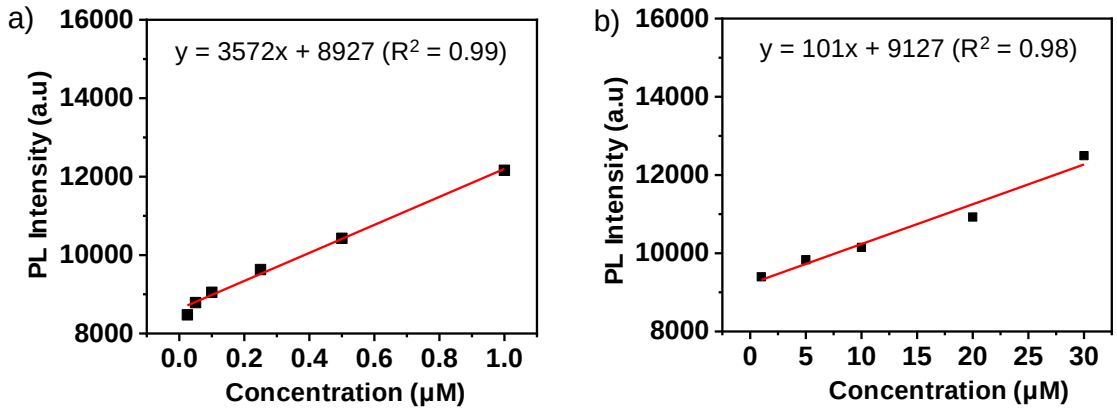

Figure S3. Linear calibration curves of fluorescence intensity with the variation of DBP concentration for MIP (a) and NIP (b). Limit of detection (LOD) = 3б/K, where б is the standard deviation of blank measurement, K is the slope of the linear curve. LOD calculated for MIP and NIP appears as 24 nM and 3.5 μM, respectively.

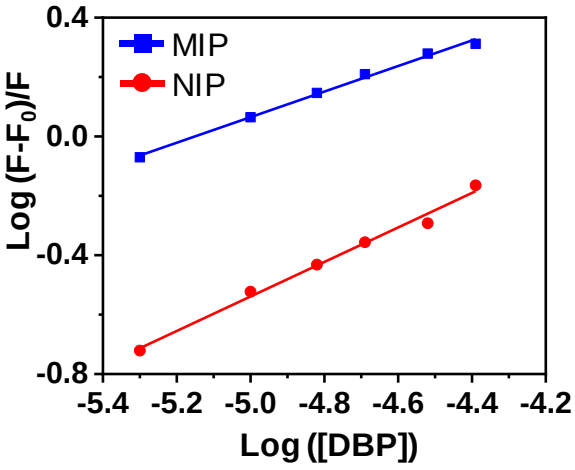

Figure S4. Calculation of binding constant between MIP/NIP and DBP by plotting log {(F – F_0)/F} vs log ([DBP]) following the equation: log {(F–F_0)/F} = n log ([DBP]/K_D), where F_0 and F are the fluorescence intensity before and after addition of DBP. The binding constant (K_B) = 1/K_D (M^{-1}) and values appears as 8.2×10^4 and 3.5×10^3 for MIP and NIP, respectively.

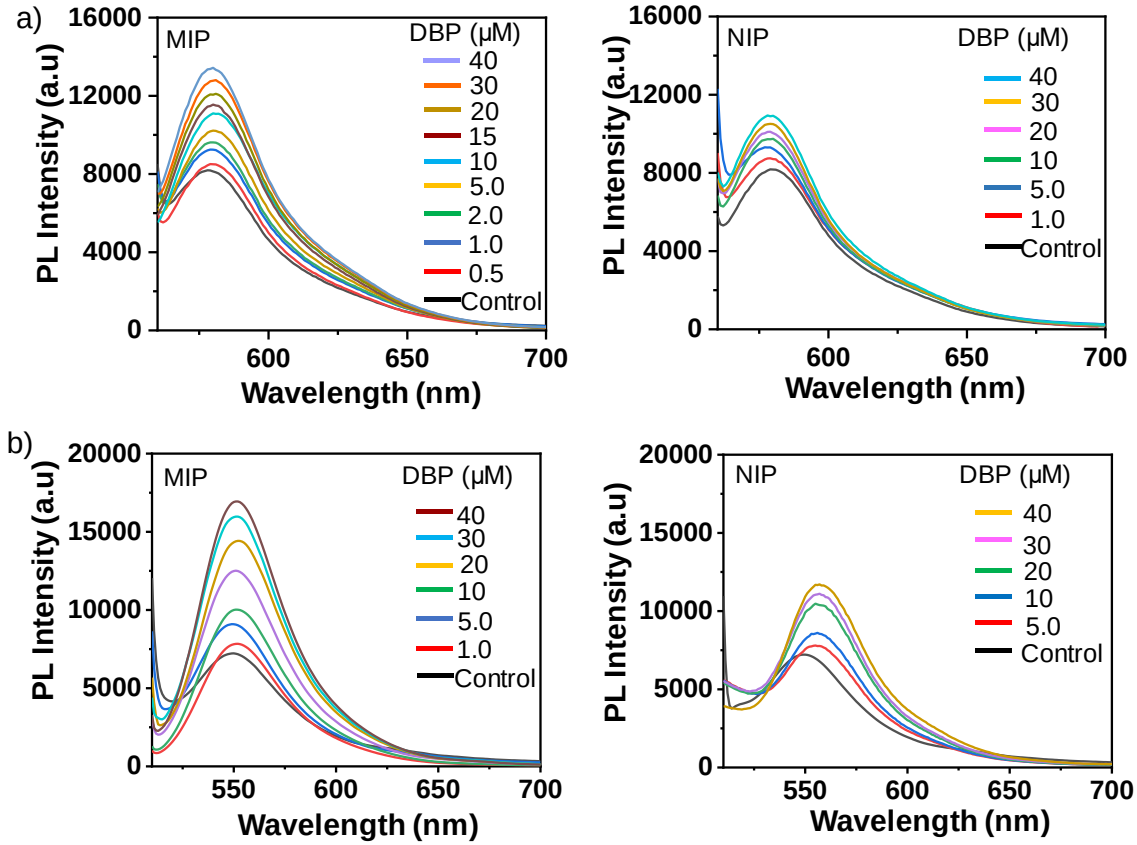

Figure S5. Fluorescence 'turn on' response using rhodamine B (emission maxima = 580 nm) (a) and rhodamine 6G (emission maxima = 550 nm) (b). The selectivity as well as sensitivity is not up to the mark with these dyes.

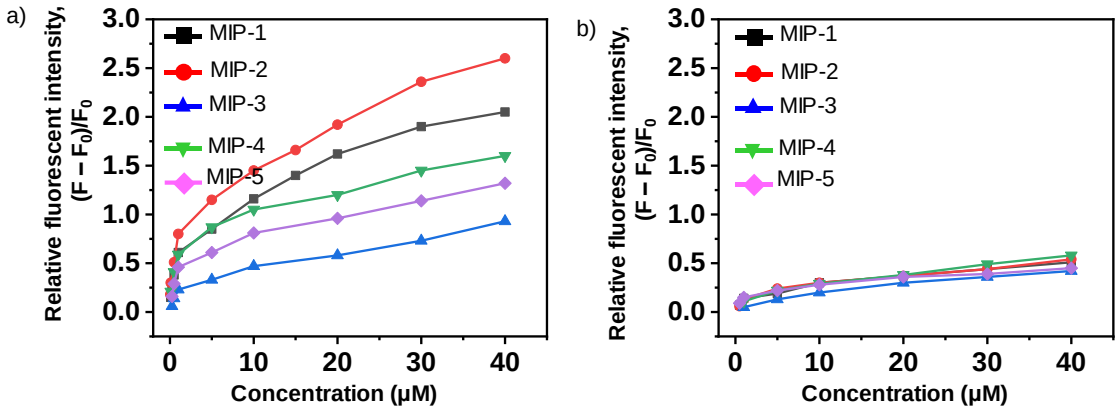

Figure S6. Effect of variation of monomer to crosslinker ratio (α-CD to TFN) on "turn on" fluorescence response in DBP detection for MIP (a), NIP (b). The fluorescence response is very much dependent on the extent of cross-linking and MIP-2 provides best fluorescence response in term of selectivity and sensitivity.

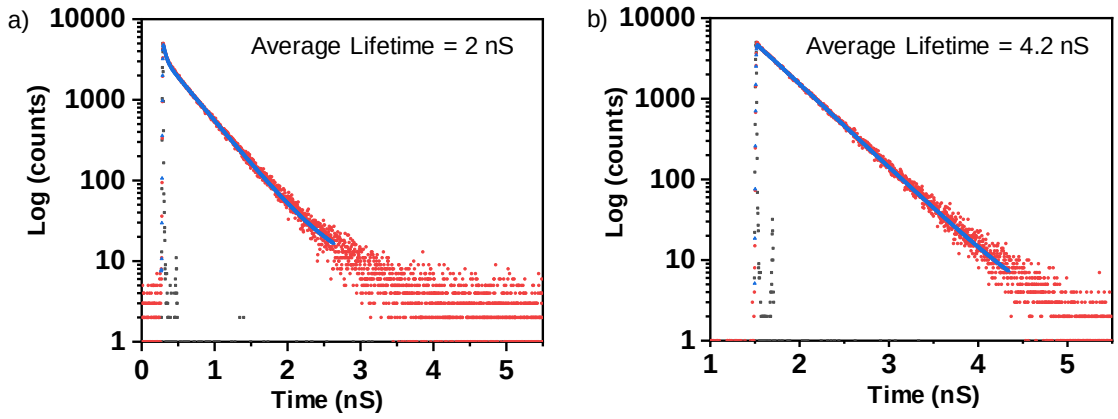

Figure S7. Fluorescence lifetime decay curve of fluorescein after binding with MIP (a) and after release via DBP addition (b). The fluorescence lifetime increases in presence of DBP due to inhibition of non-radiative energy transfer.

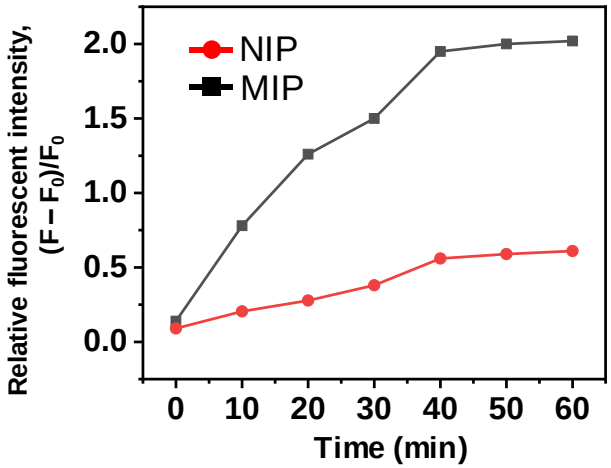

Figure S8. Fluorescence 'turn on' kinetic by addition of DBP to MIP/NIP-fluorescein. This result shows that the dye displacement maximises around 60 min of contact time with DBP.

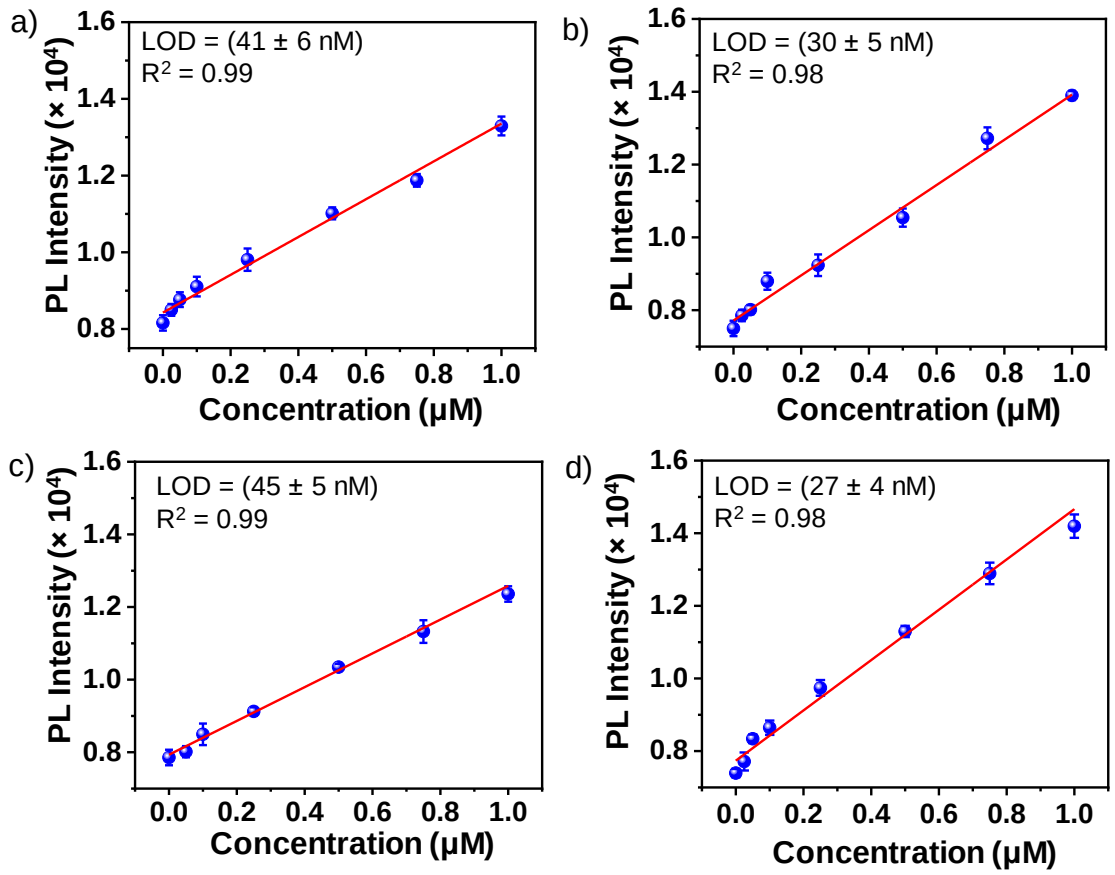

Figure S9. Linear fluorescence increment calibration curve and LOD values for DBP detection with MIP in different real water matrices. a) tap water, b) lake water, c) river water and d) waste water. All experiments were performed at 25 °C and error bar represents three independent experiment.