Supporting Information

Selective discrimination of toxic polycyclic aromatic hydrocarbons (PAHs) in water by targeting π -stacking interactions

Jose Muñoz,[‡] Ángel Campos-Lendinez,[‡] Núria Crivillers, Marta Mas-Torrent^{*}

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) and CIBER-BBN, Campus UAB, 08193 Bellaterra, Spain

*e-mail: mmas@icmab.es

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Figure S1: CV characterization of: bare ITO (black, ES1), ITO–silane (red, ES2) and the four different ITO–silane–PAH (blue, ES3-Nap; orange, ES3-Ant; green, ES3-Flt and purple, ES3-Pyr) electrodes. Experimental conditions: Redox marker: 0.01 M $[Fe(CN)_6]^{3-/4-}$; scan rate: 50 mV·s⁻¹.



Figure S2: EIS characterization of: bare ITO (black, ES1), ITO–silane (red, ES2) and the four different ITO–silane–PAH (blue, ES3-Nap; orange, ES3-Ant; green, ES3-Flt and purple, ES3-Pyr) electrodes. Experimental conditions: Redox marker: 0.01 M $[Fe(CN)_6]^{3./4-}$; freq.: 100 kHz – 0.1 Hz, bias: +150 mV, AC amplitude: 5 mV.



Figure S3: Water contact angle measurements of a) bare ITO (ES1), b) ITO-silane (ES2) and ITO-silane-PAH made of c) pyrene (ES3-Pyr), d) naphthalene (ES3-Nap), e) anthracene (ES3-Ant) and f) fluoranthene (ES3-Flt). Water drops of 3 μ L were employed. See Table S1 for the corresponding values.



Figure S4: EIS experiments at the bare **S1** electrode in the presence of increasing concentrations of pyrene as a model PAH target. [Pyr] employed: a) 0, b) 1.75, c) 3.50 and d) 7.00 ppb. Note that no significant electrochemical changes or no lineal trend were observed even using concentrations 10^3 times higher than the ones used for the **S3**–based recognition platforms (at ppt levels). Accordingly, this fact verifies the key role of the PAH-based recognition agent in the SAM-based platform for the sensitive supramolecular recognition of the PAH targets.



Figure S5. Additional non-interfering experiment using **ES3-Pyr** electrode to detect PAH molecules with the same number of aromatic rings (n=4), such as pyrene (Pyr), 1-aminopyrene (Pyr-NH₂) and fluoranthene (Flt). While the **ES3-Pyr** recognition platform is capable to discriminate between PAH molecules of different nature (*i.e.*, Pyr and Flt, note the lower % signal response (< 10%) for Flt) since the structure of fluoranthene differs significantly from the original PAH-based recognition platform, this platform cannot discriminate between PAH molecules exhibiting the same molecular skeleton (*i.e.*, Pyr and Pyr-NH₂, which only differ by a single functionality and therefore, the % signal is \approx 95%). EIS experiments were run utilizing a fix concentration of PAHs ([PAH] = 7 ppt).



Figure S6: EIS validation experiment at the different **ES3**-based recognition platforms employing a standard EPA 525 PAH complex mixture, which contains 13 different PAHs at 2 ppt each, including Ant and Pyr and excluding Nap and Flt (as the blanks). The non-interfering method shows the EIS signal before (black line) and after incubating the corresponding **ES3** surfaces in the presence of the standard PAH solution (red line).

Supporting Information Tables

Electrodes	^a ΔE (V)	${}^{a}I_{p}\left(\mu A\right)$	${}^{\mathrm{b}}\mathrm{R}_{\mathrm{CT}}(\Omega)$	¢θ (°)
ES1	0.24	1.73	22	82.9 ± 0.1
ES2	0.25	1.05	105	62 ± 4
ES3-Nap	0.27	0.64	208	81 ± 1
ES3-Ant	0.27	0.93	112	76.2 ± 0.2
ES3-Flt	0.32	0.83	156	65.5 ± 0.4
ES3-Pyr	0.59	0.68	175	74 ± 4

Table S1: Summary of the characterization data acquired by ^aCV, ^bEIS and ^ccontact angle at each functionalization stage.

Table S2: Data derived from the electronic tongue approximation study (Figure 3) at each EIS

 step employing the four different ES3 recognition platforms.

Electrode	PAH target	[PAH] _x (ppt)	Step i)		Step ii)			
			[PAH] _T (ppt)	$\Delta \mathbf{R'}_{CT}$ ($\mathbf{\Omega}$)	[PAH] _T (ppt)	Δ R' _{CT} (Ω)	∆R' _{CT} _{increase} (%)	
ES3-Nap	Nap	2	2	0.165	8	0.172	4.3	
ES3-Ant	Ant	2	2	0.279	8	0.291	4.4	
ES3-Pyr	Pyr	2	2	0.367	8	0.395	7.7	
ES3-Flt	Flt	2	2	0.166	8	0.177	7.1	
Sensing discrimination study for a [PAH] _{target} = 4 ppt in a complex mixture								
Electrode	PAH target	[PAH] _x spiked	[PAH] _{target} (ppt)	[PAH] _T (ppt)	∆R' _{CT} expected	∆ R' _{CT} obtained	% Recovery	
		(ppc)			(Ω)	(Ω)		
ES3-Nap	Nap	2	4	10	(Ω) 0.232	(Ω) 0.222	95.7	
ES3-Nap ES3-Ant	Nap Ant	2 2 2	4	10 10	(Ω)0.2320.364	(Ω) 0.222 0.430	95.7 118	
ES3-Nap ES3-Ant ES3-Pyr	Nap Ant Pyr	2 2 2 2	4 4 4	10 10 10	 (Ω) 0.232 0.364 0.540 	(Q) 0.222 0.430 0.481	95.7 118 89.0	

Table S3: Validation method for the determination of PAHs in water using a standard PAH complex mixture employing the different **ES3**-based recognition platforms. (*) Signal derived from the y-intercept.

Recognition platform	PAH target	[PAH] _x (ppt)	$ \Delta \mathbf{R}_{CT} $ expected (Ω)	$ \Delta \mathbf{R}_{\mathrm{CT}} $ obtained (Ω)	% Recovery
ES3-Nap	Nap	0	0.083*	0.072	87
ES3-Ant	Ant	2	0.336	0.292	87
ES3-Flt	Flt	0	0.045*	0.046	102
ES3-Pyr	Pyr	2	0.414	0.420	101