# Supplementary Information. Exploiting the Extended π-System of Perylene Bisimide for Label-free Single-Molecule Sensing

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**Figure S1.** Frontier molecular orbitals of the all perylene bisimide derivatives obtained using the DFT code SIESTA. Red corresponds to positive and blue to negative regions of the wave functions.



**Figure S2.** Optimized configurations of the single molecules (a) aPy-PBI, (b) Py-PBI, (c) P-PBI, (d) CI-PBI, and (e) S-PBI attached to two metallic leads.

#### The origin of Fano resonaces

To illustrate the origin of Fano resonances, consider the sketch showing a bound state (blue) of energy  $\varepsilon_1$ , coupled to an extended backbone state (brown) of energy  $\varepsilon_1$  by a coupling matrix element  $\alpha$ .

Side group with eigenvalue  $\epsilon$ 



It can be shown [33] that the transmission coefficient for such a combination is given by

$$T(E) = \frac{4\Gamma_{1}\Gamma_{2}}{\left(E - \varepsilon_{1} - \frac{\alpha\alpha^{*}}{E - \varepsilon}\right)^{2} + (\Gamma_{1} + \Gamma_{2})^{2}}$$
(S1)

A plot of this expression is shown in figure S5.



**Figure S3.** A plot of equation S1 for values of the level broadening due to the contacts of  $\Gamma_1 = 0.1$ ,  $\Gamma_2 = 0.1$ .



**Figure S4.** DFT calculations for the corresponding results for the room-temperature current as a function of the voltage for the five perylene bisimides in bare case.



**Figure S5.** DFT calculations of the transmission coefficients as a function of energy for Py-PBI with different configurations of the single-molecules absorbates (a) TCNE , (b) TNT, and (c) BEDT-TTF, and (the pink line) is bare case.. The fourth figure (d) shows the average of current as a function of voltage at T=300K which pass across Py-PBI with three analytes molecules (TCNE, TNT, and BEDT-TTF), where the error bars in figure S5d shows the standard deviation in the means of the currents.



**Figure S6.** DFT calculations of the transmission coefficients as a function of energy for P-PBI with different configurations of the single-molecules absorbates (a) TCNE, (b) TNT, and (c) BEDT-TTF, and (the pink line) is bare case. The fourth figure (d) shows the average of current as a function of voltage at T=300K which pass across P-PBI with three analytes molecules (TCNE, TNT, and BEDT-TTF), where the error bars in figure S6d shows the standard deviation in the means of the currents.



**Figure S7.** DFT calculations of the transmission coefficients as a function of energy for aPy-PBI with different configurations of the single-molecules absorbates (a) TCNE , (b) TNT, and (c) BEDT-TTF, and (the pink line) is bare case. The fourth figure (d) shows the average of current as a function of voltage at T=300K which pass across aPy-PBI with three analytes molecules (TCNE, TNT, and BEDT-TTF), where the error bars in figure S7d shows the standard deviation in the means of the currents.



**Figure S8.** DFT calculations of the transmission coefficients as a function of energy for Cl-PBI with different configurations of the single-molecules absorbates (a) TCNE , (b) TNT, and (c) BEDT-TTF, and (the pink line) is bare case. The fourth figure (d) shows the average of current as a function of voltage at T=300K which pass across Cl-PBI with three analytes molecules (TCNE, TNT, and BEDT-TTF), where the error bars in figure S8d shows the standard deviation in the means of the currents.



**Figure S9.** DFT calculations of the transmission coefficients as a function of energy for S-PBI with different configurations of the single-molecules absorbates (a) TCNE , (b) TNT, and (c) BEDT-TTF, and (the pink line) is bare case. The fourth figure (d) shows the average of current as a function of voltage at T=300K which pass across S-PBI with three analytes molecules (TCNE, TNT, and BEDT-TTF), where the error bars in figure S9d shows the standard deviation in the means of the currents.



**Figure S10.** The room-temperature, configurationally-averaged as a function of Fermi energy for three analyte molecules (TCNE, TNT, and BEDT-TTF) absorbed on five PBI molecules.

# Locating the optimal value of $E_F$

The optimal value of  $E_F$  was chosen by minimising the quantity

$$Y^{2}(E_{F}) = \sum_{i=1}^{5} \left( Log(G_{i}^{theo}) - Log(G_{i}^{exp}) \right)^{2}$$
(S2)

Where  $G_{i}^{theo}$  is the theoretical conductance for a given  $E_F$  and  $G_{i}^{exp}$  is the experimental conductance reported in ref [21], where *i* labels the PBIs. This mean-square deviation between theory and experiment is plotted in figure S8 and shows a minimum at  $E_F = 0.08$ eV, which is the values chosen throughout this paper.



**Figure S11.** The mean square deviation of theory from the experiment as a function of Fermi energy.

# Evaluating of error in the currents for a distribution of geometries

The error value of the 214 current curves is given by

$$\sigma_m = \sigma / \sqrt{214 - 1} \tag{S3}$$

$$\sigma = \sqrt{\frac{1}{214} \sum_{i=1}^{214} (I_i - \langle I \rangle)^2}$$
(S4)

where  $\sigma_m$  is standard deviation in the mean of current  $\langle I \rangle$ .

## Classification of the amount of charge-transfer complex

In particular we used the customised basis set definitions to investigate the effects on the Mulliken population count in SIESTA when using the generalized gradient approximation (GGA-PBE) for the exchange and correlation (GGA) [1], but we also made these calculations with the local density approximation (LDA-CA) [2] and van der waals interactions. The Hamiltonian and overlap matrices are calculated on a real-space grid defined by a plane-wave cutoff of 150 Ry. Each PBI molecule with three analytes which are (TCNE, BEDT-TTF, and TNT) are relaxed into the optimum geometry until the forces on the atoms are smaller than 0.02 eV/Å. Tolerance of Density Matrix is 10<sup>-4</sup>, and in case of the isolated molecules a sufficiently-large unit cell was used. For steric and electrostatic reasons.

**Table S1.** shows DFT calculation of charge- transfer complex and binding energy of TCNE which is analyzed around the backbone of five PBI molecules where all configurations were found in optimum position among 214 configurations for each PBI molecule.

	Py+	TCNE	aPy-	+TCNE	S+	TCNE	P+T	CNE	Cl+	TCNE
GGA									X X X	
	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)
	0.311	-0.301	0.317	-0.293	0.279	-0.294	0.292	-0.245	0.289	-0.027
LDA	A weight a second		-X-		An grant		Strain States		the second	
	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)
	0.32	-0.955	0.331	-1.021	0.295	-1.075	0.298	-0.783	0.293	-0.477
Vdw					A		X		***********************	
	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)
	0.307	-0.7166	0.342	-1.0281	0.279	-0.8636	0.294	-0.8643	0.08	-0.4054

**Table S2.** shows DFT calculation of charge- transfer complex and binding energy of BEDT-TTF which is analyzed around the backbone of five PBI molecules where all configurations were found in optimum position among 214 configurations for each PBI molecule.

	Py+BE	DT-TTF	аРу+ В	EDT-TTF	S+ BE	DT-TTF	P+ BEI	OT-TTF	CI+ BE	DT-TTF
GGA	GA GA									
	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	∆E(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)
	-0.043	-0.284	-0.053	-0.199	-0.007	-0.225	-0.179	-0.151	-0.239	-0.1820
LDA	Harris and the second		Area and a constraint of the second s		A Contractor		-		and and a second	
	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)
	-0.222	-1.236	-0.148	-0.991	-0.104	-1.2	-0.214	-1.2	-0.299	-1.0837
VdW	At the state of th		Xarray Xarray		A and a second		X X			and ye
	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)
	-0.166	-1.184	-0.079	-1.0064	-0.064	-1.1611	-0.133	-1.1837	-0.224	-1.0432

**Table S3.** shows DFT calculation of charge- transfer complex and binding energy of TNT which is analyzed around the backbone of five PBI molecules where all configurations were found in optimum position among 214 configurations for each PBI molecule.

	Py+	TNT	aP	y+TNT	S-	+TNT	P+1	ΓNT	Cl+	-TNT
GGA										
	ΔQ	ΔE(eV)	ΔQ	∆E(eV)	ΔQ	∆E(eV)	ΔQ	∆E(eV)	ΔQ	ΔE(eV)
	0.023	-0.141	0.11	-0.097	0.132	-0.102	0.049	-0.0921	0.011	-0.015
LDA	£5 <b>**</b> **		-\$ <b>\$</b>		<b>}</b> } }	n de la companya de l	Þ.		**** \$2***	( 8 <sup>300</sup> 2))
	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)
	0.028	-0.813	0.12	-0.833	0.331	-0.8754	0.054	-0.85	0.011	-0.5032
Vdw	<b>∑*≈</b>		4.		¥~**	enter Anter a de la companya de la companya Anter a companya de la	X		**** \$_***	( 
	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)	ΔQ	ΔE(eV)
	0.023	-0.933	0.114	-0.723	0.048	-0.966	0.051	-1.082	0.024	-0.614



**Figure S12.** Optimized configurations of a single TCNE adsorbed on (a) Py-PBI, (b) aPy-PBI, (c) S-PBI, (d) P-PBI, and (e) Cl-PBI attached to two metallic leads.



**Figure S13.** Optimized configurations of a single TNT adsorbed on (a) Py-PBI, (b) aPy-PBI, (c) S-PBI, (d) P-PBI, and (e) Cl-PBI attached to two metallic leads.



**Figure S14.** Optimized configurations of a single BEDT-TTF adsorbed on (a) Py-PBI, (b) aPy-PBI, (c) S-PBI, (d) P-PBI, and (e) Cl-PBI attached to two metallic leads.



**Figure S15.** DFT calculations using LDA approximation of the transmission coefficients as a function of energy at T=0K for optimum configuration of Py-PBI with (a) TCNE, (b) TNT, and (c) BEDT-TTF. The fourth figure (d) shows the current as a function of voltage at T=300K for the bare Py-PBI and in the presence of the three analyte molecules (TCNE, TNT, and BEDT-TTF).



**Figure S16.** DFT calculations using LDA approximation of the transmission coefficients as a function of energy at T=0K for optimum configuration of S-PBI with (a) TCNE, (b) TNT, and (c) BEDT-TTF. The fourth figure (d) shows the current as a function of voltage at T=300K for the bare S-PBI and in the presence of the three analyte molecules (TCNE, TNT, and BEDT-TTF).



**Figure S17.** DFT calculations using LDA approximation of the transmission coefficients as a function of energy at T=0K for optimum configuration of P-PBI with (a) TCNE, (b) TNT, and (c) BEDT-TTF. The fourth figure (d) shows the current as a function of voltage at T=300K for the bare P-PBI and in the presence of the three analyte molecules (TCNE, TNT, and BEDT-TTF).



**Figure S18.** DFT calculations using LDA approximation of the transmission coefficients as a function of energy at T=0K for optimum configuration of Cl-PBI with (a) TCNE, (b) TNT, and (c) BEDT-TTF. The fourth figure (d) shows the current as a function of voltage at T=300K for the bare Cl-PBI and in the presence of the three analyte molecules (TCNE, TNT, and BEDT-TTF).



**Figure S19.** DFT calculations using LDA approximation of the transmission coefficients as a function of energy at T=0K for optimum configuration of aPy-PBI with (a) TCNE, (b) TNT, and (c) BEDT-TTF. The fourth figure (d) shows the current as a function of voltage at T=300K for the bare aPy-PBI and in the presence of the three analyte molecules (TCNE, TNT, and BEDT-TTF).

It is interesting to note that the behaviour of the ensemble average is qualitatively differenet from the ensemble average. Figure S19 shows the transmission coefficient for the molecule aPy-PBI, in the absence and presence of the analytes. It is clear that the conductance in the presence of the analytes in their optimal binding configurations is lower than in the case of bare molecule. In contrast, figure S7 shows that the ensemble-averaged conductance, is higher in the presence of the analytes.

#### Quantifying the sensitivity of the PBIs for discriminating sensing.

To quantify the potential of the five PBI derivatives (labeled j=1,..., 5) for the discriminating sensing of the three analytes TCNE, TNT and BEDT-TTF, (labeled n=1,2,3) we calculated the ensemble-averaged, room-temperature currents  $I_{jn}$  as a function of voltage V and computed the following correlators of the currents

$$A_{j}^{nm} = \int_{-V/2}^{V/2} dV (I_{jn}(V) - I_{jm}(V))^{2}$$
(S5)

These were then normalized by the squared currents of the bare backbones to yield the quantities:

$$X_{j}^{nm} = \frac{A_{j}^{nm}}{\int_{-V/2}^{V/2} dV (I_{j}(V_{bare}))^{2}}$$
(S6)

For  $n \neq m$ , table 1 shows the values of  $X_{j}^{nm}$  obtained for V=1volt. Clearly, as defined,  $X_{j}^{nm} = 0$  when n = m. In practice, a sensing event would involve measurement of a new set of curves ( $I_{jm}(V)$  in equation 2) and combining these with a 'calibration set of curves ( $I_{jn}(V)$ in equation 2), in which case  $X_{j}^{nm}$  would be small but not zero when n = m.

**Table 1.** The values of  $X_{j}^{nm}$ 

J	PBIs	X <sup>12</sup> <sub>j</sub>	X <sup>13</sup> <sub>j</sub>	$X_{j}^{23}$
1	aPy-PBI	0.3043	0.2776	0.0044
2	Cl-PBI	0.0031	0.2457	0.2508
3	P-PBI	0.0021	0.4101	0.4011
4	Py-PBI	0.3641	0.4365	0.9161
5	S-PBI	0.0309	0.1344	0.1748
SUM		0.7045	1.5043	1.7472

Table 1 and figure 14 shows the value of  $X_{j}^{nm}$  when  $n \neq m$ . Ideally, to avoid false positives, these numbers should be as large as possible and since they are largest for Py-PBI, we conclude that Py-PBI is the best individual sensor. Nevertheless, for the most accurate discriminating sensing, the fingerprint of an analyte across all five backbones should be used.



**Figure 14.** Comparison between the normalized correlators  $X_{j}^{nm}$  where *n* labels the three analytes (TNT, TCNE, and BEDT-TTF) and *j* labels the five PBIs. V=1.0 volts.

#### Movies

The following movies show the different configurations of the analytes on the PBI backbones, used to compute the transmission curves of figure 8 a-c and the I-V curves of figure 8d.



### References

1. Perdew, J.P., K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple. Physical review letters, 1996. 77(18): p. 3865.

2. Perdew, J.P. and Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy. Physical Review B, 1992. 45(23): p. 13244.