



Cite this: *J. Mater. Chem. C*, 2015, 3, 2101

Exploiting the extended π -system of perylene bisimide for label-free single-molecule sensing†

Qusiy Al-Galiby,‡ Iain Grace,‡ Hatef Sadeghi‡ and Colin J. Lambert*

We demonstrate the potential of perylene bisimide (PBI) for label-free sensing of organic molecules by investigating the change in electronic properties of five symmetric and asymmetric PBI derivatives, which share a common backbone, but are functionalised with various bay-area substituents. Density functional theory was combined with a Greens function scattering approach to compute the electrical conductance of each molecule attached to two gold electrodes by pyridyl anchor groups. We studied the change in their conductance in response to the binding of three analytes, namely TNT, BEDT-TTF and TCNE, and found that the five different responses provided a unique fingerprint for the discriminating sensing of each analyte. This ability to sense and discriminate was a direct consequence of the extended π system of the PBI backbone, which strongly binds the analytes, combined with the different charge distribution of the five PBI derivatives, which leads to a unique electrical response to analyte binding.

Received 16th December 2014
Accepted 8th January 2015

DOI: 10.1039/c4tc02897j

www.rsc.org/MaterialsC

Introduction

Partly in response to predictions that silicon technology might soon reach the limits of its evolution,^{1,2} there is increasing interest in controlling charge transport across nanometer-scale metal–molecule–metal junctions^{3–7} and exploiting the properties of single-molecule devices. Perylene bisimide (PBIs) (also called perylene diimides)^{8–11} have emerged as one of the most investigated families of organic molecules, both for their fundamental electronic properties and their industrial applications as dyes and pigments.^{3,4} Their unique properties are primarily derived from their large extended π -systems, which in π -stacked arrays lead to a variety of intermolecular π -orbital overlaps for the different derivatives.¹² Furthermore their high electron affinities, large electron mobilities, their chemical and thermal stabilities, and variety of functional forms with different bay-area substituents has led to their widespread use in organic solar cells,^{13–16} organic field-effect transistors (OFETs)^{17,18} particularly as n-type materials,^{19,20} and organic sensors.^{21–28}

Recently, it has been experimentally demonstrated that single PBI-based molecules can be attached to gold electrodes and their electrical conductance can be measured.²⁹ In the present paper our aim is to demonstrate that the extended π systems of PBIs make them ideal candidates for the single-

molecule, label-free sensing of a variety of analytes. Chemical sensors that work as electronic noses or electronic tongues have attracted extensive attention, because they possess high sensitivity and selectivity towards target analytes, ranging from metal ions and anions to organic neutral chemicals and biological molecules.^{30–33} Label-free methods for detecting small molecules are a desirable target technology, because they avoid the need for chemical modification or separation of the analytes, potentially leading to lower costs. Examples of label-free detection include micelle-based bacterial quorum sensing²³ aptamer-based sensing platforms,²¹ label-free, sequence specific DNA sensing based on fluorescence resonant energy transfer (FRET),²² nuclear magnetic resonance,²⁴ nanoplasmonics²⁵ and surface enhanced Raman spectroscopy (SERS).²⁶ However all of these reporting strategies require expensive detectors and are not shrinkable to sub-micron-scale devices and therefore the cost-lowering advantages of label-free sensing are not yet fully realised.

In the present paper, our aim is to demonstrate room-temperature, label-free sensing at the single-molecule level by analysing the variation in electrical properties of the five PBI derivatives shown in Fig. 1, which possess the same PBI core, but with the following bay-area substituents: pyrrolidinyl (pyrrolidinyl-PBI, Py-PBI), *tert*-butyl-phenoxy (P-PBI), thiobutyl (S-PBI), and chlorine (Cl-PBI). Four molecules (Py-PBI, P-PBI, Cl-PBI, S-PBI) possess pyridyl anchor groups at opposite ends and are therefore symmetric. The fifth molecule (aPy-PBI) has a pyridyl anchor group on the top and a cyclohexyl anchor group on the bottom²⁹ and is asymmetric.

We shall demonstrate that these PBIs can sense and discriminate between the three organic analyte molecules

Department of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom.
E-mail: c.lambert@lancaster.ac.uk

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4tc02897j

‡ Authors contributed.

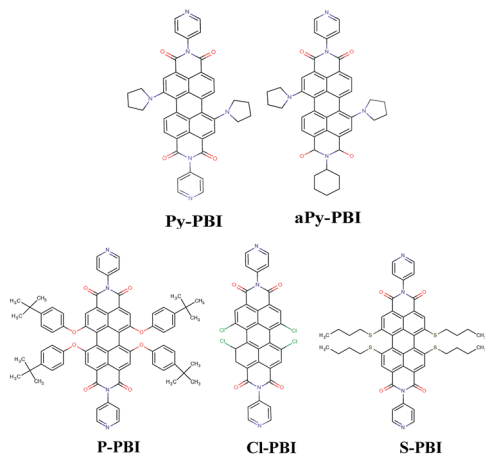


Fig. 1 PBI-based molecular structures: Py-PBI, (aPy-PBI), P-PBI, Cl-PBI and S-PBI.

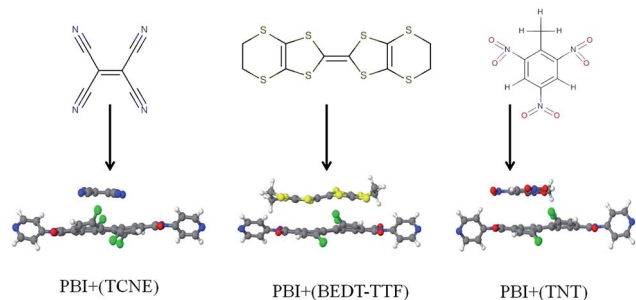


Fig. 2 The DFT calculated optimum geometries for molecular complexes of TCNE, BEDT-TTF, and TNT with the PBI molecule.

shown in Fig. 2. The chosen analytes are TNT and TCNE which are well known electron acceptors^{34,35} and the donor BEDT-TTF,^{36–38} whose π -donor capability is weaker than that of TTF.³⁹ Our aim is to demonstrate that the presence of both acceptors and donor molecules alter the conductance of a single molecule of PBI and that the combined responses of the PBIs form a unique fingerprint that can be used to discriminate between the analytes.

Computational methods

To calculate electrical properties of the molecules in Fig. 1, the relaxed geometry of each molecule was found using the density functional (DFT) code SIESTA⁴⁰ which employs Troullier–Martins pseudopotentials to represent the potentials of the atomic cores,⁴¹ and a local atomic-orbital basis set. We used a double-zeta polarized basis set for all atoms and the generalized gradient approximation (GGA-PBE) for the exchange and correlation functionals.^{42,43} The Hamiltonian and overlap matrices are calculated on a real-space grid defined by a plane-wave cutoff of 150 Ry. Each molecule was relaxed to the optimum geometry until the forces on the atoms are smaller than 0.02 eV Å^{−1} and in case of the isolated molecules, a

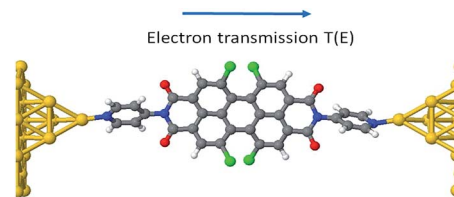


Fig. 3 An example of an optimized configuration of the system containing a single molecule (Cl-PBI) attached to two metallic leads. Further details for the rest optimized configurations of PBIs with the gold leads are in Fig. S2 of ESI.†

sufficiently-large unit cell was used, for steric and electrostatic reasons. All PBI molecules with anchor groups and bay-area substituents were found to be twisted after relaxation. Fig. S1 of ESI† shows that the frontier molecular orbitals of all five PBI derivatives are delocalized across their central backbones.

After obtaining the relaxed geometry of each isolated molecule, the molecules were then placed between gold electrodes, as shown in Fig. 3. For structures such as that shown in Fig. 3, the central region of the junction is composed of a single molecule attached to two gold (111) leads. The equilibrium distance between the N atom of each pyridyl anchor group and the centre of the apex atom of each gold pyramid was initially 1.9 Å. After geometry optimization the distance changed slightly from the initial value to a final value of 2.05 Å. Similarly, the distance between the cyclohexyl group of asymmetric molecule (aPy-PBI) and the centre of the apex atom of gold was found to be 2.89 Å.

For each relaxed structure, such as Fig. 3, we use the GOLLUM method⁴⁴ to compute the transmission coefficient $T(E)$ for electrons of energy E passing from the left gold electrode to the right electrode. GOLLUM is a next-generation code, born out of the non-equilibrium transport code SMEAGOL code⁴⁵ and is optimised for computing scattering properties of a range of quantum systems such as molecular junctions. Once $T(E)$ is computed, we calculate the zero-bias electrical conductance G using the Landauer formula:

$$G = I/V = G_0 \int_{-\infty}^{\infty} dE T(E) \left(-\frac{df(E)}{dE} \right) \quad (1)$$

where $G_0 = \left(\frac{2e^2}{h} \right)$ is the quantum of conductance, and $f(E)$ is Fermi distribution function defined as $f(E) = [e^{(E-E_F)/k_B T} + 1]^{-1}$ where k_B is Boltzmann constant $k_B = 8.62 \times 10^{-5}$ eV K^{−1} and T is the temperature. Since $f(E)$ is a function of the Fermi energy E_F , the conductance G is a function of the energetic locations of the molecular orbitals of the PBI-analyte complexes relative to E_F . Since the quantity $(-df(E)/dE)$ is a normalised probability distribution of width approximately equal to $k_B T$, the above integral represents a thermal average of the transmission function $T(E)$ over an energy window of the width $k_B T$ ($=25$ meV at room temperature). In what follows, we shall demonstrate that either the zero-bias conductances or the current–voltage (I – V) relations of each complex can be used to discriminate between the different analytes. To compute the electrical current I at finite voltage V we use the expression^{33,46}

$$I = \left(\frac{2e}{h}\right) \int_{-\infty}^{\infty} dE T(E) [f_{\text{left}}(E) - f_{\text{right}}(E)] \quad (2)$$

where $f_{\text{left}}(E) = [e^{(1/k_B T)(E - E_F^{\text{left}})} + 1]^{-1}$ and $f_{\text{right}}(E) = [e^{(1/k_B T)(E - E_F^{\text{right}})} + 1]^{-1}$, with $E_F^{\text{left}} = E_F + \frac{eV}{2}$ and $E_F^{\text{right}} = E_F - \frac{eV}{2}$.

Results and discussion

To benchmark our calculations, we first compared our theoretical predictions with experimental measurements of ref. 29, where it was found that the electrical conductances of the bare PBIs are ordered as follows: Cl-PBI < PBI < S-PBI < aPy-PBI < Py-PBI. For each of these molecules, Fig. 4a shows the transmission coefficients $T(E)$ as a function of energy E , relative to the DFT-predicted Fermi energy E_F^{DFT} . Fig. 4a shows that the effect of the bay substituent atoms is to shift the position of the HOMO resonances of the bare PBIs, while the LUMOs remain pinned close to the Fermi energy. The corresponding room-temperature conductances as a function of E_F are shown in Fig. 4b.

It is well-known that DFT can give an incorrect value for the Fermi energy and therefore we use eqn (1) to evaluate the room-temperature conductance for a range of values of E_F in the vicinity of E_F^{DFT} and then choose the value of E_F which yields the closest agreement with experiment. For a given value of E_F , the five theoretical conductances obtained from Fig. 4b were

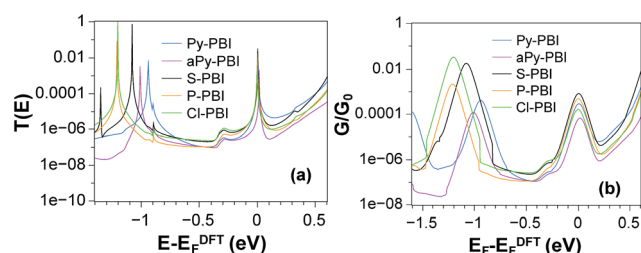


Fig. 4 (a) Transmission coefficients as a function of energy for the five perylene bisimides. (b) Room-temperature conductance as a function of the Fermi energy.

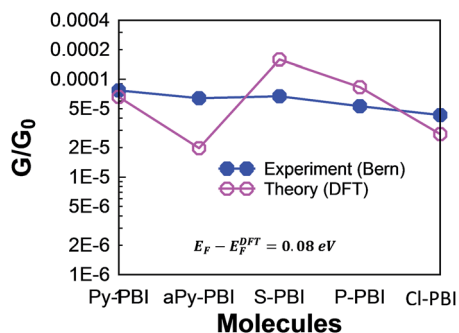


Fig. 5 Comparison between the experimental²⁹ and theoretical conductances of the bare PBIs, obtained with E_F shifted by 0.08 eV relative to the bare DFT value.

compared with the experimentally-measured conductances²⁹ and a value of $E_F = E_F^{\text{DFT}} + 0.08$ eV was chosen to yield the closest fit to experiment (see ESI† for more details). Fig. 5 shows the resulting comparison between experiment and theory.

Molecular complexes

For the five PBI molecules in Fig. 1, the formation of molecular complexes with each of the three different analytes TCNE, BEDT-TTF and TNT was investigated using DFT. In each case, after geometry relaxation, the charge transferred between the two molecules and the binding energy was computed (this data is shown in Tables S1–S3 of the ESI†) the calculations show that TCNE and TNT gain electrons from the backbone of PBI, but the BEDT-TTF donates electrons to the backbone. As an example, Fig. 6 shows the optimised TCNE-(Py-PBI) complex, in which TCNE pi-stacks a distance $Y = 0.37$ nm above the perylene. The details of all optimised PBI-adsorbate complexes attached to gold electrodes are shown in Fig. S12–S14 of the ESI.†

Fig. 7a–c show the transmission coefficients $T(E)$ due to the binding of each of the three analyte molecules on Py-PBI. For the two acceptor molecules TCNE and TNT, there is a shifting of the HOMO resonance and extra resonances appear close to the LUMO. For the donor BEDT-TTF a resonance also appears in the HOMO–LUMO gap, accompanied by additional resonances below the HOMO. Fig. 7d shows the corresponding I - V characteristics of each of the complexes, demonstrating that for optimally-bound complexes, the distinct I - V curves can be used to discriminate between BEDT-TTF and the other analytes, although the difference between TCNE and TNT is smaller.

The results of Fig. 7 correspond only to optimally-bound analytes. At room temperature, the adsorbates are subject to thermal fluctuations and will sample many positions across the PBI backbones. To investigate the role of fluctuations, for each

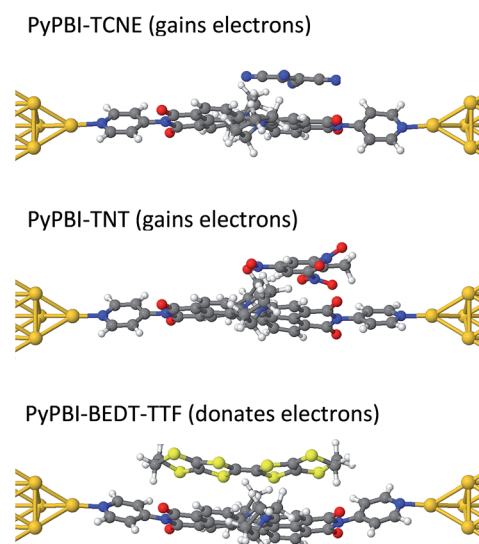


Fig. 6 Optimized configuration Py-PBI with (TCNE, TNT, and BEDT-TTF) which obtained from optimum configuration attached to two metallic leads.

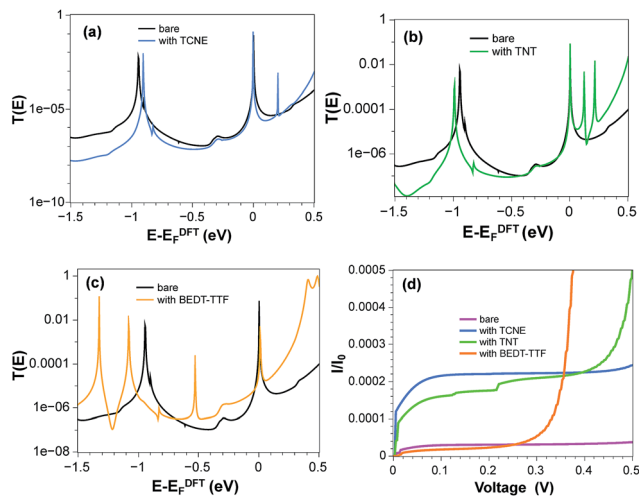


Fig. 7 Transmission coefficients as a function of energy at $T = 0$ K for optimum configuration of Py-PBI with (a) TCNE, (b) TNT, and (c) BEDT-TTF. (d) shows the current as a function of voltage at $T = 300$ K for the bare Py-PBI and in the presence of the three analytes (TCNE, TNT, and BEDT-TTF).

PBI molecule we repeated the above calculations for 214 configurations of each adsorbate. The results for the Py-PBI molecule are shown in Fig. 8a–c. For illustrative purposes, we only show 35 configurations (the results for all 214 transmission curves are shown in Fig S5–S9 of ESI†). In each case we see that fluctuations in the position of the analyte cause the transmission resonances to shift over a range of energies. In many cases, these possess a characteristic Fano line shape, associated with the interaction between localized states on the analytes

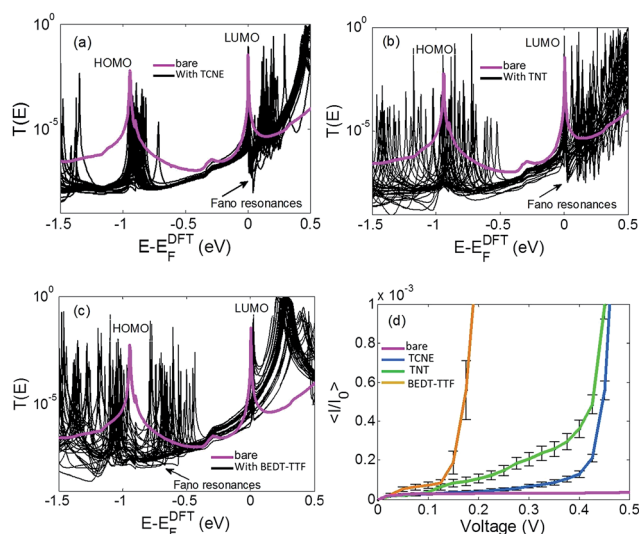


Fig. 8 Illustrates the transmission curves of 35 fluctuation position in case Py-PBI to explain the effect of adsorption of analytes molecules (a) TCNE, (b) TNT, (c) BEDT-TTF, and (d) shows the ensemble-averaged of current as a function of voltage at $T = 300$ K for bare Py-PBI and in the presence of the three analyte molecules (TCNE, TNT, and BEDT-TTF), where the error bars in Fig. 8d shows the standard deviation in the means of the currents.

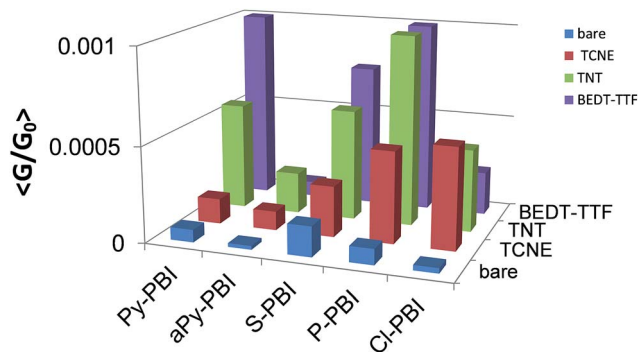


Fig. 9 The room-temperature, ensemble-averaged conductance across the PBI family due to charge transfer complex formation (obtained from the average of the 214 configurations of the TCNE, BEDT-TTF and TNT) around the backbone of five PBIs.

and extended states on the PBI backbones.^{47,48} After computing the ensemble average of these curves, the resulting the ensemble-averaged, room-temperature current as a function of voltage is shown in Fig. 8d, along with the standard deviation in their means (see ESI† for more details).

This demonstrates that even in the presence of fluctuations, BEDT-TTF produces a distinctly different I - V curve from the other two analytes.

The corresponding room-temperature, ensemble-averaged zero-bias conductances for all analytes and backbone molecules are shown in Fig. 9. This demonstrates that not only I - V curves, but also the conductance of each PBI backbone changes due to the adsorption of a single analyte molecule. For any one PBI derivative (e.g. P-PBI TNT compared with BEDT-TTF), the change in conductance upon binding may not discriminate between all analytes. However, the spectrum of five conductance changes forms a unique fingerprint, which can be used to discriminate between all three analytes.

Conclusion

We have presented a study of the electron transport properties of five PBI derivatives with various bay-area substituents: pyrrolidinyl (aPy-PBI, Py-PBI), *tert*-butyl-phenoxy (P-PBI), thiobutyl (S-PBI), and chlorine (Cl-PBI). Recent experimental papers measuring the electrical conductance of backbone molecules in different solvent have shown that the conductance can be changed by the solvent, even when the solvent does not form a complex with the backbone.⁴⁹ In our case, the analytes bind to the backbones with up to 1 eV of binding energy and the conductance changes are much larger. Our results compare well with recent experimental values for the electrical conductance of these molecules in the absence of adsorbates. We analyzed the change in conductance of these molecules when single molecules of three analytes (TCNE, TNT, and BEDT-TTF) were adsorbed onto the PBI backbones and found that the resulting changes in the ensemble-averaged room-temperature conductances produced a unique fingerprint for each analyte, which allows their discriminating sensing at the single molecule level.

These conductance changes arose from a combination of charge redistribution associated with charge-transfer-complex formation, and the formation of a Fano resonances associated with the interaction of a bound state on the adsorbate and extended orbitals of the PBI backbones.

Acknowledgements

This work is supported by UK EPSRC grants EP/K001507/1, EP/J014753/1, EP/H035818/1, the European Union Marie-Curie Network MOLESCO 606728 and the Iraqi Education Ministry, Al Qadissiya University.

Notes and references

- 1 J. R. Heath and M. A. Ratner, *Mol. Electron.*, 2003, 43–44.
- 2 G. Cuniberti, G. Fagas and K. Richter, *Introducing Molecular Electronics*, Springer, 2010.
- 3 A. Aviram and M. A. Ratner, Molecular rectifiers, *Chem. Phys. Lett.*, 1974, **29**(2), 277–283.
- 4 C. Li and H. Wonneberger, Perylene imides for organic photovoltaics: yesterday, today, and tomorrow, *Adv. Mater.*, 2012, **24**(5), 613–636.
- 5 Z. Chen, *et al.*, Tetrachloro-substituted Perylene Bisimide Dyes as Promising n-Type Organic Semiconductors: Studies on Structural, Electrochemical and Charge Transport Properties, *ChemPhysChem*, 2004, **5**(1), 137–140.
- 6 Y. Wen, *et al.*, Improvements in Stability and Performance of *N,N'*-Dialkyl Perylene Diimide-Based n-Type Thin-Film Transistors, *Adv. Mater.*, 2009, **21**(16), 1631–1635.
- 7 Z. Donhauser, *et al.*, Conductance switching in single molecules through conformational changes, *Science*, 2001, **292**(5525), 2303–2307.
- 8 B. Xu, *et al.*, Large gate modulation in the current of a room temperature single molecule transistor, *J. Am. Chem. Soc.*, 2005, **127**(8), 2386–2387.
- 9 I. Díez-Pérez, *et al.*, Ambipolar transport in an electrochemically gated single-molecule field-effect transistor, *ACS Nano*, 2012, **6**(8), 7044–7052.
- 10 X. Li, *et al.*, Thermally activated electron transport in single redox molecules, *J. Am. Chem. Soc.*, 2007, **129**(37), 11535–11542.
- 11 C. Li, *et al.*, Electrochemical gate-controlled electron transport of redox-active single perylene bisimide molecular junctions, *J. Phys.: Condens. Matter*, 2008, **20**(37), 374122.
- 12 M. C. R. Delgado, *et al.*, Tuning the charge-transport parameters of perylene diimide single crystals *via* end and/or core functionalization: a density functional theory investigation, *J. Am. Chem. Soc.*, 2010, **132**(10), 3375–3387.
- 13 C. W. Tang, Two-layer organic photovoltaic cell, *Appl. Phys. Lett.*, 1986, **48**(2), 183–185.
- 14 X. Zhan, *et al.*, A high-mobility electron-transport polymer with broad absorption and its use in field-effect transistors and all-polymer solar cells, *J. Am. Chem. Soc.*, 2007, **129**(23), 7246–7247.
- 15 S. K. Lee, *et al.*, Electrochemistry, spectroscopy and electrogenerated chemiluminescence of perylene, terrylene, and quaterylene diimides in aprotic solution, *J. Am. Chem. Soc.*, 1999, **121**(14), 3513–3520.
- 16 G. Seybold and G. Wagenblast, New perylene and violanthrone dyestuffs for fluorescent collectors, *Dyes Pigm.*, 1989, **11**(4), 303–317.
- 17 M. Thelakkat, P. Pösch and H.-W. Schmidt, Synthesis and characterization of highly fluorescent main-chain copolyimides containing perylene and quinoxaline units, *Macromolecules*, 2001, **34**(21), 7441–7447.
- 18 H. Tian, *et al.*, Wide spectral photosensitization for SnO₂ nanoporous electrode with soluble perylene derivatives and cyanine dyes, *Synth. Met.*, 2001, **121**(1–3), 1557–1558.
- 19 P. Ranke, *et al.*, Electroluminescence and electron transport in a perylene dye, *Appl. Phys. Lett.*, 1997, **71**(10), 1332–1334.
- 20 J. J. Dittmer, E. A. Marseglia and R. H. Friend, Electron trapping in dye/polymer blend photovoltaic cells, *Adv. Mater.*, 2000, **12**(17), 1270–1274.
- 21 B. R. Baker, *et al.*, An electronic, aptamer-based small-molecule sensor for the rapid, label-free detection of cocaine in adulterated samples and biological fluids, *J. Am. Chem. Soc.*, 2006, **128**(10), 3138–3139.
- 22 Z. Liu, H.-L. Wang and M. Cotlet, Energy Transfer from a Cationic Conjugated Polyelectrolyte to a DNA Photonic Wire: Toward Label-Free, Sequence-Specific DNA Sensing, *Chem. Mater.*, 2014, **26**(9), 2900–2906.
- 23 B. Davis, J. Richens and P. O'Shea, Label-Free Critical Micelle Concentration Determination of Bacterial Quorum Sensing Molecules, *Biophys. J.*, 2011, **101**(1), 245–254.
- 24 P. D. Garimella, *et al.*, Hyperpolarized xenon-based molecular sensors for label-free detection of analytes, *J. Am. Chem. Soc.*, 2013, **136**(1), 164–168.
- 25 H. Im, *et al.*, Label-free detection and molecular profiling of exosomes with a nano-plasmonic sensor, *Nat. Biotechnol.*, 2014, **32**(5), 490.
- 26 M. Li, *et al.*, Stamping surface-enhanced Raman spectroscopy for label-free, multiplexed, molecular sensing and imaging, *J. Biomed. Opt.*, 2014, **19**(5), 50501.
- 27 J. Ren, *et al.*, New fluoride fluorescent chemosensors based on perylene derivatives linked by urea, *Dyes Pigm.*, 2005, **64**(3), 193–200.
- 28 T. H. Rehm, *et al.*, Interaction of spermine-alanine functionalized perylene bisimide dye aggregates with ds-DNA/RNA secondary structure, *Chem. Sci.*, 2012, **3**(12), 3393–3397.
- 29 C. Li, *et al.*, Charge transport through perylene bisimide molecular junctions: an electrochemical approach, *Phys. Status Solidi B*, 2013, **250**(11), 2458–2467.
- 30 I. Ghosh, Creative Chemical Sensor Systems, Topics in Current Chemistry, 277, ed. Thomas Schrader (University of Duisburg-Essen, Germany), Springer, Berlin, Heidelberg, New York, 2007, xiv+ 304 pp., \$269.00, ISBN 978-3-540-71546-7, *J. Am. Chem. Soc.*, 2008, **130**(13), 4570–4571.
- 31 P. D. Beer and P. A. Gale, Erkennung und Nachweis von Anionen: gegenwärtiger Stand und Perspektiven, *Angew. Chem.*, 2001, **113**(3), 502–532.

- 32 A. D. McFarland and R. P. Van Duyne, Single silver nanoparticles as real-time optical sensors with zeptomole sensitivity, *Nano Lett.*, 2003, **3**(8), 1057–1062.
- 33 H. Sadeghi, S. Bailey and C. J. Lambert, Silicene-based DNA nucleobase sensing, *Appl. Phys. Lett.*, 2014, **104**(10), 103104.
- 34 S. Chowdhury and P. Kebarle, Electron affinities of di- and tetracyanoethylene and cyanobenzenes based on measurements of gas-phase electron-transfer equilibria, *J. Am. Chem. Soc.*, 1986, **108**(18), 5453–5459.
- 35 E. M. Kosower, *Organic Charge-Transfer Complexes*, ed. R. Foster, Academic Press, New York, 1969, xii, 472 pp., illus. \$22.50. *Organic Chemistry*, vol. 15, American Association for the Advancement of Science, 1970.
- 36 V. Khodorkovsky, J. Becker and J. Farges, *Organic Conductors: Fundamentals and Applications*, Matcel Dekker, New York, 1994, pp. 75–88.
- 37 W. K. Maser, Organic superconductors (including fullerenes): Synthesis, structure, properties, and theory, ed. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo, Prentice Hall, Englewood Cliffs, NJ 1992, 400 pp., hardcover, \$91.00, ISBN 0-13-640566-5, *Adv. Mater.*, 1994, **6**(1), 87.
- 38 J. M. Williams, *et al.*, Rational design of synthetic metal superconductors, *Prog. Inorg. Chem.*, 1987, **35**, 51–218.
- 39 Y.-I. Kim, Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) Charge Transfer Compounds with Copper(II) Halides: (BEDT-TTF) $\sim$ 1 $\sim$ 5CuX $\sim$ 2 (X = Cl, Br), *Bull. Korean Chem. Soc.*, 2003, **24**(9), 1389–1392.
- 40 J. M. Soler, *et al.*, The SIESTA method for *ab initio* order-N materials simulation, *J. Phys.: Condens. Matter*, 2002, **14**(11), 2745.
- 41 N. Troullier and J. L. Martins, Efficient pseudopotentials for plane-wave calculations, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1991, **43**(3), 1993.
- 42 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.*, 1996, **77**(18), 3865.
- 43 B. Hammer, L. B. Hansen and J. K. Nørskov, Improved adsorption energetics within density-functional theory using revised Perdew–Burke–Ernzerhof functionals, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**(11), 7413.
- 44 J. Ferrer, C. J. Lambert, V. M. García-Suárez, D. Z. Manrique, D. Visontai, L. Oroszlany, R. Rodríguez-Ferradás, I. Grace, S. W. D. Bailey, K. Gillemot, H. Sadeghi and L. A. Algharagholy, GOLLUM: a next-generation simulation tool for electron, thermal and spin transport, *New J. Phys.*, 2014, **16**(9), 093029.
- 45 A. R. Rocha, *et al.*, Towards molecular spintronics, *Nat. Mater.*, 2005, **4**(4), 335–339.
- 46 H. Sadeghi, *et al.*, Graphene Sculpture Nanopores for DNA Nucleobase Sensing, *J. Phys. Chem. B*, 2014, **118**(24), 6908–6914.
- 47 T. A. Papadopoulos, I. M. Grace and C. J. Lambert, Control of electron transport through Fano resonances in molecular wires, *Phys. Rev. B*, 2006, **74**, 193306.
- 48 C. M. Finch, V. M. García-Suárez and C. J. Lambert, Giant thermopower and figure of merit in single-molecule devices, *Phys. Rev. B*, 2009, **79**, 033405.
- 49 V. Fatemi, M. Kamenetska, J. B. Neaton and L. Venkataraman, Environmental Control of Single-Molecule Junction Transport, *Nano Lett.*, 2011, **11**(5), 1988–1992.