Published in final edited form as:

Org Electron. 2018 ; 61: . doi:10.1016/j.orgel.2018.05.035.

Electronic properties and structure of single crystal perylene

S.J. Pookpanratana^{a,*}, K.P. Goetz^{b,c}, E.G. Bittle^a, H. Haneef^b, L. You^{a,d}, C.A. Hacker^a, S.W. Robey^e, O.D. Jurchescu^b, R. Ovsyannikov^f, and E. Giangrisostomi^f

^aEngineering Physics Division, National Institute of Standards and Technology (NIST), USA

^bDepartment of Physics, Wake Forest University, USA

^cPhysical Chemistry Institute, Universität Heidelberg, Germany

^dTheiss Research, USA

^eMaterials Measurement Science Division, NIST, USA

^fInstitute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin (HZB) für Materialien und Energie, Germany

Abstract

The transport properties of electronic devices made from single crystalline molecular semiconductors typically outperform those composed of thin-films of the same material. To further understand the superiority of these extrinsic device properties, an understanding of the intrinsic electronic structure and properties of the organic semiconductor is necessary. An investigation of the electronic structure and properties of single crystal α -phase perylene (C₂₀H₁₂), a five-ringed aromatic molecule, is presented using angle-resolved ultraviolet photoemission, x-ray photoelectron spectroscopy (XPS), and field-effect transistor measurements. Key aspects of the electronic structure of single crystal α -perylenes critical to charge transport are determined, including the energetic location of the highest occupied molecular orbital (HOMO), the HOMO bandwidth, and surface work function. In addition, using high resolution XPS, we can distinguish between inequivalent carbon atoms within the perylene crystal and, from the shake-up satellite structure in XPS, gain insight into the intramolecular properties in α -perylenes. From the device measurements, the charge carrier mobility of α -perylenes is found to depend on the device structure and the choice of dielectric, with values in the range of 10⁻³ cm² V⁻¹ s⁻¹.

Keywords

Perylene; Photoemission; Single crystal; UPS; Angle-resolved photoemission

*Corresponding author. sujitra@nist.gov (S.J. Pookpanratana).

Contributions

SP planned the spectroscopic experiments, OJ planned the electrical experiments. KG and EB grew the crystals. EB and HH fabricated the devices, and HH measured the device. LY performed the AFM measurements. SP performed the XPS and UPS measurements and analyzed the results. SP, EB, CH, SR, RO, EG performed the ARTOF experiments, and the ARTOF set-up was developed and maintained by RO and EG. SP analyzed the ARTOF results with input from SR, RO, and EG. SP wrote the manuscript with input from all authors.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.orgel.2018.05.035>.

1. Introduction

With the rising use of molecular-based components in consumer electronics, the study of organic semiconductors has both fundamental and applied physical importance. Organic semiconductors present significant advantages in electronic applications compared to their inorganic counterparts: 1) they are composed of inexpensive earthabundant elements, 2) they can be synthetically modified for tailored functionality, and 3) they do not require harsh, high-temperature processing conditions. All of these features lower the cost of manufacturing and allows the incorporation of organic semiconductors in a wide range of applications, including flexible electronics. Because of these advantages in a variety of consumer electronic applications, the studies of the factors controlling fundamental carrier transport in organic semiconductors are of utmost physical importance.

Organic semiconductors can be integrated into field-effect transistors (FET), and other device structures in a variety of different physical forms: single crystal, polycrystalline thin-film, or amorphous thin-film. The highest charge carrier mobilities are routinely measured for single crystal organic semiconductors in FET devices [1–5]. This is most certainly due to the well-ordered molecular packing that facilitates coherent charge transport and the concurrent reduction of the defect density. The highly anisotropic nature of charge transport in molecular crystals usually prevents access to the high charge mobility in single crystals unless the crystals are aligned along a crystallographic direction favorable for transport [6,7], which, in the extreme case, may lead to single crystal charge carrier mobilities inferior to thin-films [8]. In addition, it was also shown that a high quality organic semiconductor is not sufficient in achieving high mobility, as the processes taking place at the semiconductor/dielectric interface can dominate the resulting device properties [9–11]. Thus, advancing our understanding of the impact of the semiconductor electronic structure on transport, such as the electronic band energies and band dispersion, requires correlated measurements of the electronic structure on single crystal materials and the resulting FET performance. Measuring and understanding the electronic structure of single crystal (SC) organic semiconductors can thus serve as a bridge between the molecular, crystalline structure and the observed electrical properties of a device, and further the development of a microscopic understanding of molecular solids.

Photoemission is the preferred technique for direct measurements of electronic properties, particularly band dispersions, that provide crucial information for implementing appropriate materials to achieve desired device functionality. While there are numerous thin-film photoemission spectroscopic measurements of organic semiconductors, there are far fewer reported attempts to measure the electronic structure for organic single crystals. The discrepancy is due both to photoemission measurement challenges that single crystals pose and to the lack of large area single crystals. The reduced conductivity of organic semiconductor crystals also presents a challenge for photoemission, compared to thinfilm counterparts, due to increased sample surface charging that often leads to distorted spectra [12]. Recently, charge compensation through a photo-induced increase in conductivity has been shown to be an effective solution, leading to high-quality measurements for a number of organic single crystals including rubrene [13,14], tetracene [14], picene [15], C₆₀ [16],

pentacene [17] and the charge-transfer complex dibenzotetrathiafulvalene- 7,7,8,8-tetracyanoquinodimethane [18].

Perylene ($C_{20}H_{12}$) is an arene compound that crystallizes in two polymorphs, an α -phase and a β -phase [19]. Derivatives of perylene are found in commercial dyes and in light emitting applications. Perylene also forms charge transfer co-crystals with tetracyanoquinodimethane [20,21,22] that exhibit tunable optical and electronic properties, as observed in FET devices [20]. Therefore, understanding the “baseline” electronic structure of perylene itself is of interest. Here, we present the first electronic structure measurements of single crystal α -phase perylene and relate these results to the perylene FET properties obtained both in bottom-gate and top-gate configurations.

We performed both laboratory- and synchrotron-based photoemission measurements to probe the electronic structure of perylene in conjunction with a continuous wave laser as illumination to increase surface conductivity and negate sample charging effects. Key electronic properties that are related to device engineering such as the work function and ionization energy are determined. Synchrotron-based measurements were performed employing a highly efficient angle-resolving, time-of-flight-based electron spectrometer [23] to provide complementary information on the HOMO position as well as the HOMO bandwidth. The HOMO bandwidth is consistent with theoretical calculations for the perylene crystal structure but within this bandwidth no clear dispersion was observed. Furthermore, core-level photoelectron measurements reveal inequivalent carbon atoms in the perylene structure and satellite features at high binding energies that provide information on intramolecular energy levels and charge dynamics. Taken together, these results constitute the first measurements of the occupied electronic energy levels for α -peryene single crystals.

2. Experimental methods

Perylene single crystals were grown by physical vapor transport (PVT) in flowing argon as reported previously [20,24]. The perylene crystals were yellow in color and routinely platelet-like in shape, with a cross-sectional area on the order of a few millimeters (as discussed in Ref. [20]) and surface topography are shown in the SI. X-ray diffraction (XRD) measurements determined that the perylene crystalline structure was the α -polymorph phase [19]. The perylene molecule skeletal structure is shown in Fig. 1a and the unit cell [19] is shown in Fig. 1b where pairs of perylene molecules are stacked in a sandwich herringbone motif. The crystal structure is monoclinic with lattice parameters $a = 1.027$ nm, $b = 1.081$ nm, $c = 1.118$ nm, $\alpha = 90^\circ$, $\beta = 100.8^\circ$, $\gamma = 90^\circ$. Due to the crystal size, identifying the relative orientation (i.e., a and b axes) of specific crystals was not possible. For spectroscopic measurements, the perylene crystals were mounted on indium foil to provide electrical contact. The crystal surface was not cleaved prior to spectroscopic measurement.

Laboratory-based photoelectron spectroscopy was performed in a commercial instrument equipped with a hemispherical electron analyzer. Ultraviolet (UV) photoelectron spectroscopy (UPS) was performed with a helium discharge lamp, using the He I resonance at 21.2 eV, a -5 V bias applied to the sample and the total energy resolution was 0.05 eV.

The energy scale was referenced to the Fermi energy of a clean Au sample. X-ray photoelectron spectroscopy (XPS) was performed in the same analysis system with a monochromatized Al K α source, and spectra with an energy resolution of 0.1 eV. As discussed previously [3], illumination by a continuous wave (cw) laser diode (404 nm) was used for all measurements to increase the conductivity of the sample and the intensity of the cw laser is not likely to alter the properties of the perylene crystal.

Angle-resolved electronic structure measurements were carried out at the BESSY II synchrotron facility (Helmholtz-Zentrum Berlin) on beamline PM4 [25]. This beamline is equipped with a high-detection efficiency, angle-resolved time-of-flight (ARTOF) [23] spectrometer that allows simultaneous collection of angle-resolved photoemission data over a large solid angle ($\pm 15^\circ$ or ± 0.26 rad) while maintaining a low total soft x-ray dose on the organic single crystal. Measurements were performed with a photon energy of 60 eV at room temperature, and the energy scale was referenced to Fermi energy of a Au sample. As in the laboratory-based measurements, a cw laser (473 nm) was employed to increase the conductivity in the sample. The geometries of the excitation source and electron energy analyzer used for measurement at the PM4 beamline and at NIST are shown in Fig. 1c, at both locations the sample normal is oriented along the electron analyzer. The bipolar coordinate system used for the presentation of the ARTOF data are also shown in Fig. 1c.

FETs were fabricated in two device configurations: bottom contact-bottom gate and bottom contact-top gate. The bottom contact-top gate devices were obtained using a heavily doped n-type Si wafer as the bottom gate and a 200 nm thermally grown silicon oxide (SiO₂) as the gate dielectric. Source and drain electrodes, composed of a thin Ti adhesion layer (3 nm) and Au (40 nm), were patterned using photolithography or a shadow mask and deposited by physically vapor methods. The substrates were first cleaned by immersing them in a hot acetone bath for 10 min and hot isopropanol bath for 10 min, followed by a UV ozone exposure for another 10 min and finally rinsing with deionized water. The perylene crystals were then laminated by hand onto the prefabricated substrates. For devices in the bottom contact-top gate configuration, parylene dielectric was then deposited over the laminated crystals (additional details are in the SI). Parylene is a polymer with good mechanical and dielectric properties and forms thin conformal coatings [26]. Finally, Au was thermally evaporated over the parylene film to form the top gate electrode. The FETs were characterized in air, at room temperature, using an Agilent 4155C Semiconductor Parameter Analyzer [27]. At least ten devices of each structure were evaluated.

3. Results and discussion

The electrical properties of α -peryene single crystals were evaluated by integrating them into field effect transistors. Fig. 2 shows typical current-voltage characteristics of a device made in the bottom contact-top gate configuration, with an optical image of the device as an inset. The FET shown in Fig. 2 yielded a hole saturation mobility (μ) of $5.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, an on/off ratio of 3×10^4 , a subthreshold slope (S) of 3.19 V per decade, and a threshold voltage (V_{th}) of -17.5 V . The average mobility obtained on devices with a top-gate dielectric was $\mu_{\text{avg, TG}} = (4.8 \pm 2.3) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while devices with the bottom gate configuration and SiO₂ as the gate dielectric yielded $\mu_{\text{avg, BG}} = (1.32 \pm 0.24) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

s^{-1} . The μ values measured are comparable to an earlier report of perylene SC laminated onto a bottom contact-bottom gate structure ($2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [28]. The devices with a top gate structure consistently outperformed those with the bottom gate geometry. In the top gate configuration, a larger mobility is to be expected due to the overall lower contact resistance [29] and lower trap density at the perylene-parylene dielectric interface when compared to the perylene-SiO₂ dielectric interface [11,30]. The mobility of carriers estimated from device measurements will be revisited in conjunction with the results derived from angle-resolved photoemission measurements.

To complement the device measurements of α -perylenes, photoemission-based measurements of single crystal α -perylenes are presented to further understand the intrinsic properties of the material. In the absence of irradiation with the laser diode, lab-based UPS measurements of the perylene crystal result in a featureless spectrum (Fig. 3b, black dash line) with no significant evidence of the electronic features typically observed in spectra obtained from thin-films [31]. The photoemission spectra are broadened and distorted due to charging associated with the low electrical conductivity in the crystal samples. With the cw laser incident simultaneously on the sample, the count rate increased by a factor of ≈ 150 (at 1.3 eV below the Fermi energy) and multiple HOMO peaks in the photoemission spectra of α -perylenes were easily identified in the low binding energy region of the UPS spectrum in Fig. 3b (blue solid line). The spectrum of single crystal α -perylenes in Fig. 3b resembles that observed for polycrystalline thin-films [31,32]. The center energy of the HOMO structure, associated with the highest occupied a_u molecular orbital, is $1.30 \text{ eV} \pm 0.05 \text{ eV}$ below the Fermi energy and the low binding energy onset is $0.90 \text{ eV} \pm 0.05 \text{ eV}$. Features arising from a series of lower lying occupied levels are also clearly resolved.

The work function of α -perylenes was determined based on the low kinetic energy region of the UPS measurement. A significant increase in the count rate (≈ 18 times) was also observed in this portion of the spectrum with the addition of the cw laser excitation. Extrapolating the leading edge of the secondary electron cut-off region, shown in Fig. 3a, to the baseline produced a value of $4.8 \text{ eV} \pm 0.1 \text{ eV}$ for the work function of the α -perylenes SC. With this value of work function, the ionization energy for α -perylenes is $6.1 \text{ eV} \pm 0.1 \text{ eV}$. The ionization energy of thin-film perylenes had previously been reported to be about 5.2 eV where the structural phase was not confidently identified [31].

High-resolution core level spectra (laser-assisted) of the α -perylenes crystal were also obtained and a typical result is provided in Fig. 4. The C 1s spectrum of α -perylenes exhibits a main spectral feature centered at about 284.6 eV. As with UPS, the C 1s XPS spectrum is distorted and shifted without cw laser excitation (not shown). But under laser illumination, the main XPS C 1s emission spectrum is consistent with previous studies of perylenes thin-films [33].

The main C 1s peak was fit using a linear least squares routine and Voigt lineshapes. As observed for other aromatic hydrocarbon organic compounds, the least squares routine required two Voigt peaks to properly fit the main C 1s emission feature due to the existence of two inequivalent carbon atoms [17,34,35]. The Gaussian widths for the two peaks were coupled and an underlying linear background was included.

The resulting two C 1s components are shown as the blue and green solid lines in Fig. 4. The peak centered at $284.8 \text{ eV} \pm 0.1 \text{ eV}$ (blue solid line, Fig. 4) of the main C 1s feature, and is attributed to carbon atoms with unsaturated bonds [34] in the perylene molecule (i.e., bonded to two carbon atoms and one hydrogen atom). The other spectral feature centered at $284.3 \text{ eV} \pm 0.1 \text{ eV}$ (green solid line, Fig. 4) arises from the carbon atoms with saturated carbon bonds [34] (i.e., bonded to three carbon atoms). This assignment is consistent with the spectral areas for the two peaks derived from the fitting routine, where the area of the unsaturated carbons (284.8 eV component, in blue Fig. 4) is 60% of the total area of the main C 1s line.

There are additional weak XPS spectral features observed within 10 eV at higher binding energies of the main C 1s peak. These spectral features are typical of molecular compounds and identified as satellites arising from shake-up processes associated with the main C 1s line excitation that lead to simultaneous excitation of electrons from the HOMO level to higher unoccupied levels. The satellite spectral features are magnified ($\times 7$) and shown as an inset in Fig. 4. At least three different satellites peaks can be identified. They were also fit using Voigt lineshapes to extract the center peak positions for each satellite (labelled as A, B, and C) which are listed in Fig. 4. The satellite at $286.6 \text{ eV} \pm 0.1 \text{ eV}$ (feature A in Fig. 4) is closest to the main C 1s XPS feature, and is about $2.0 \text{ eV} \pm 0.1 \text{ eV}$ from the center of the main C 1s line. In linear polyacenes, this satellite was attributed to an excitation of a HOMO electron to the lowest unoccupied molecular orbital (LUMO) [35]. Photoluminescence spectra of the α -polymorph of perylene crystals display a maximum at about 2.0 eV [36], consistent with the assignment of this satellite to a HOMO-to-LUMO transition. Although detailed assignments for the other satellites have not been determined, the C 1s core level spectra provide interesting additional information on the perylene intramolecular electronic structure and electronic dynamics upon photoexcitation.

Angle-resolved photoemission measurements were carried out at the BESSY II synchrotron to search for evidence of electronic dispersion in the frontier orbitals of α -peryene, and thus provide insight to the contribution of band-like energy levels in this material. The state-of-the-art ARTOF spectrometer allows measurement of photoemission spectra in the complete conical acceptance of $\pm 150^\circ$ ($\pm 0.26 \text{ rad}$). This provides a dataset with information on band dispersion for a very large segment of the Brillouin zone without the need to rotate the sample or the spectrometer. Although direct comparison of the data acquired with a single-photon energy to calculated band structure is not straightforward, due to potential effects additional dispersion in the direction of the surface normal, this is sufficient to test for the existence of significant dispersion that could signal band-like behavior.

The measured photoemission intensities of several of the highest occupied levels of α -peryene are shown in Fig. 5a and b, as a function of photoelectron emission angles in θ_x and θ_y as illustrated in Fig. 1c and in reference [23]. The spectra acquired in θ_x and θ_y emission angles (in Fig. 5a and b) are integrated and shown in Fig. 5c, where the spectral shape is virtually identical with that measured by UPS as shown in Fig. 3b. In Fig. 5c, the center of the HOMO “band” is found to be $1.75 \text{ eV} \pm 0.05 \text{ eV}$ below the Fermi energy in all emission angles available (in Fig. 5a and b). When compared to the UPS measurements, the HOMO center derived from the ARTOF measurement is shifted by about 0.4 eV away from

the Fermi energy. This discrepancy could have contributions from several sources, including differences in residual surface photovoltage effects from different excitation energies or fluences, differences in the defects of different α -perylene crystals, and/or different energy scale calibrations between the two different electron spectrometers.

This difference does not impact the primary focus of the ARTOF-derived measurements which was to ascertain information on the HOMO “bandwidth” and on searching for band-like behavior in α -perylene. The complete data set collected over the $\pm 15^\circ$ (± 0.26 rad) conical solid angle with the ARTOF analyzer was searched for evidence of angular dependence in the frontier electronic levels of α -perylene. The representative 2D plots in Fig. 5a and b reveal that although there are small variations in the intensity and width of the HOMO and HOMO-1 levels with emission angle in the ARTOF measurements, identification of the presence or absence of band dispersion in the α -perylene over the accessible angular range (corresponding to $\pm 0.8 \text{ \AA}^{-1}$) inconclusive. We can, however, estimate the average maximal “bandwidths” of the HOMO and HOMO-1 levels to be about $0.4 \text{ eV} \pm 0.1 \text{ eV}$ and $0.7 \text{ eV} \pm 0.1 \text{ eV}$, respectively, as estimated from the fullwidth at half maximum at multiple emission angles in the range of -0.1 radians to 0.1 radians. This places an upper limit on any band-like dispersion in the α -perylene electronic structure.

Calculations of the electronic structure of α -perylene revealed that the HOMO region has contributions from three bands with a_u molecular orbital character [37]. Based on those results [37], we can estimate that the maximum width of the frontier α -perylene HOMO varies from 0.25 eV to 0.08 eV across the Brillouin zone, and is somewhat weakly dispersive compared to other organics such as pentacene or rubrene. The HOMO-1 “bandwidth” is calculated to be about 0.8 eV [37] and this is consistent with the measured results shown in Fig. 5.

Unfortunately for our goal of determining if α -perylene displays band-like character, several factors, including the theoretically suggested small dispersion in α -perylene, could complicate the ability to follow band movement across the Brillouin zone. Increased surface relaxation, adsorption, and/or disorder may mask the ability to measure the electronic structure with surface-sensitive photoemission. Evidence supporting this conjecture is found in recent work revealing the band dispersion for single crystal pentacene using an excitation source in the far UV (10 eV) which resulted in a more “bulk-like” measurement. It was not previously possible to observe HOMO “band” dispersion in pentacene single crystals when using conventional, more surface-sensitive UV excitation sources. It has been proposed that rubrene does not undergo significant surface relaxation [38], and correspondingly, its HOMO “band” dispersion has been observed using a range of vacuum UV excitation energies [13,14], lending further support for the importance of surface effects. Finally, we note that the relatively high vapor pressure [39] for perylene suggests that increased thermal disordering effects, as proposed in “dynamic disorder” model of transport [40] in organic systems, may be important and lead to decreased band-like character. It is thus not surprising that clear dispersion in the α -perylene HOMO band is not experimentally observable in the photoemission results supplied in Fig. 5, and this can be a result of many possibilities.

The electronic properties of α -perylene determined from photoemission are summarized in Fig. 6 as an energy diagram. Key energy levels and electronic properties directly involved with charge transport in a device, such as the ionization energy and HOMO width, are directly determined for single crystal α -perylene. The ionization energy of α -perylene was determined as $6.1 \text{ eV} \pm 0.1 \text{ eV}$ and suggests that a high work function material would be optimal for hole carrier injection when α -perylene is integrated into a device. The HOMO “bandwidth” is relatively narrow at $0.4 \text{ eV} \pm 0.1 \text{ eV}$ and flat, and the latter characteristic has implication for the possible electronic applications of perylene. The intramolecular information derived from the C 1s spectrum are also indicated in the energy diagram where the two types of carbon atoms, with saturated and unsaturated bonds, have an energy difference of $0.5 \text{ eV} \pm 0.1 \text{ eV}$. The intramolecular dynamics within the α -perylene also provide an estimate of the HOMO-LUMO transition as $2.0 \text{ eV} \pm 0.1 \text{ eV}$.

Finally, we connect the results from FET-based transport measurements mentioned earlier with conclusions from the photoemission measurements. If band theory is applied, then the flat HOMO “band” seen in Fig. 5 predicts that the charge mobility in α -perylene is very small (i.e., $\mu_{\text{a}} \propto (E/k^2)^{5/2}$). This is consistent with the mobility estimated from α -perylene FET devices which yielded a mobility on the order of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. There is qualitative consistency (in terms of a band transport model) in comparison with pentacene for which larger dispersion in the HOMO has been observed by photoemission [41] and the charge mobility has been reported between $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [7,42,43]. Not all electronic applications require materials with high charge mobility, and the information in Fig. 6 provides key electronic information that may be beneficial for integrating α -perylene in other applications.

4. Conclusion

The electronic structure and properties of single crystal α -phase perylene have been investigated by photoemission and presented here. With the assistance of a cw laser to facilitate conductivity at the crystal surface, key electronic properties, such as the ionization energy and HOMO width, are reliably measured and determined. The HOMO “band” does not display significant dispersive characteristics and is relatively narrow, in agreement with the low charge carrier mobility evaluated from FET measurements. Core level PES measurements can differentiate between saturated and unsaturated carbons in perylene and the shake-up satellites provided insight on the dynamics of photoexcitation. Our measurements of the intrinsic electronic properties of single crystal organic semiconductors are central to linking the observed extrinsic transport properties of single crystals and to enhance physical understanding of organic semiconductors.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

We thank Dr. John Suehle for providing the cw laser used for the NIST-based measurements, and Dr. Nam Nguyen and Dr. Sebastian Engmann for x-ray diffraction measurements. We thank the HZB for the allocation of synchrotron

radiation beamtime. The device work at Wake Forest University was supported by the National Science Foundation, under grant DMR-1627925.

References

- [1]. Ward JW, Lamport ZA, Jurchescu OD, ChemPhysChem 16 (6) (2015) 1118–1132. [PubMed: 25757210]
- [2]. Menard E, Podzorov V, Hur SH, Gaur A, Gershenson ME, Rogers JA, Adv. Mater 16 (23–24) (2004) 2097–2101.
- [3]. Nakayama K, Hirose Y, Soeda J, Yoshizumi M, Uemura T, Uno M, Li W, Kang MJ, Yamagishi M, Okada Y, Miyazaki E, Nakazawa Y, Nakao A, Takimiya K, Takeya J, Adv. Mater 23 (14) (2011) 1626–1629. [PubMed: 21472790]
- [4]. Xie W, McGarry KA, Liu F, Wu Y, Ruden PP, Douglas CJ, Frisbie CD, J. Phys. Chem. C 117 (22) (2013) 11522–11529.
- [5]. Mas-Torrent M, Durkut M, Hadley P, Ribas X, Rovira C, J. Am. Chem. Soc 126 (4) (2004) 984–985. [PubMed: 14746442]
- [6]. Podzorov V, Menard E, Borissov A, Kiryukhin V, Rogers JA, Gershenson ME, Phys. Rev. Lett 93 (8) (2004) 086602. [PubMed: 15447211]
- [7]. Lee JY, Roth S, Park YW, Appl. Phys. Lett 88 (25) (2006) 252106.
- [8]. Lamport ZA, Li R, Wang C, Mitchell W, Sparrowe D, Smilgies D-M, Day C, Coropceanu V, Jurchescu OD, J. Mater. Chem. C 5 (39) (2017) 10313–10319.
- [9]. Mei Y, Diemer PJ, Niazi MR, Hallani RK, Jarolimek K, Day CS, Risko C, Anthony JE, Amassian A, Jurchescu OD, Proceedings of the National Academy of Sciences, vol. 114, 2017, pp. E6739–E6748 (33).
- [10]. Stassen AF, d Boer RWI, Iosad NN, Morpurgo AF, Appl. Phys. Lett 85 (17) (2004) 3899–3901.
- [11]. Hulea IN, Fratini S, Xie H, Mulder CL, Iossad NN, Rastelli G, Ciuchi S, Morpurgo AF, Nat. Mater 5 (2006) 982. [PubMed: 17086169]
- [12]. Zimmermann GSU, Wüstenhagen V, Karl N, Dudde R, Koch EE, Umbach E, Mol. Cryst. Liq. Cryst 339 (2000) 231–259.
- [13]. i Machida S, Nakayama Y, Duhm S, Xin Q, Funakoshi A, Ogawa N, Kera S, Ueno N, Ishii H, Phys. Rev. Lett 104 (15) (2010) 156401. [PubMed: 20482000]
- [14]. Vollmer A, Ovsyannikov R, Gorgoi M, Krause S, Oehzelt M, Lindblad A, Mårtensson N, Svensson S, Karlsson P, Lundqvist M, Schmeiler T, Pflaum J, Koch N, J. Electron. Spectrosc. Relat. Phenom 185 (3–4) (2012) 55–60.
- [15]. Xin Q, Duhm S, Bussolotti F, Akaike K, Kubozono Y, Aoki H, Kosugi T, Kera S, Ueno N, Phys. Rev. Lett 108 (22) (2012) 226401. [PubMed: 23003630]
- [16]. Bussolotti F, Yang J, Hiramoto M, Kaji T, Kera S, Ueno N, Phys. Rev. B 92 (11) (2015) 115102.
- [17]. Yasuo N, Yuki U, Masayuki Y, Keiichirou Y, Kazuhiko M, Satoshi K, Hisao I, Nobuo U, J. Phys. Condens. Matter 28 (9) (2016) 094001. [PubMed: 26871646]
- [18]. Goetz KP, y Tsutsumi J, Pookpanratana S, Chen J, Corbin NS, Behera RK, Coropceanu V, Richter CA, Hacker CA, Hasegawa T, Jurchescu OD, Advanced Electronic Materials 2 (10) (2016) n/a–n/a.
- [19]. Botoshansky M, Herbstein FH, Kapon M, Helv. Chim. Acta 86 (4) (2003) 1113–1128.
- [20]. Vermeulen D, Zhu LY, Goetz KP, Hu P, Jiang H, Day CS, Jurchescu OD, Coropceanu V, Kloc C, McNeil LE, J. Phys. Chem. C 118 (42) (2014) 24688–24696.
- [21]. Salzillo T, Masino M, Kociok-Köhn G, Di Nuzzo D, Venuti E, Della Valle RG, Vanossi D, Fontanesi C, Girlando A, Brillante A, Da Como E, Cryst. Growth Des 16 (5) (2016) 3028–3036.
- [22]. Hu P, Du K, Wei F, Jiang H, Kloc C, Cryst. Growth Des 16 (5) (2016) 3019–3027.
- [23]. Ovsyannikov R, Karlsson P, Lundqvist M, Lupulescu C, Eberhardt W, Föhlisch A, Svensson S, Mårtensson N, J. Electron. Spectrosc. Relat. Phenom 191 (0) (2013) 92–103.
- [24]. Laudise RA, Kloc C, Simpkins PG, Siegrist T, Cryst J Growth 187 (3) (1998) 449–454.

- [25]. Giangrisostomi E, Ovsyannikov R, Sorgenfrei F, Zhang T, Lindblad A, Sassa Y, Cappel UB, Leitner T, Mitzner R, Svensson S, Mårtensson N, Föhlisch A, J., *Electron. Spectrosc. Relat. Phenom* 224 (4 2018) 68–78.
- [26]. Brutting WA, Chihaya, Wiley-VCH, 2012.
- [27]. i. Certain commercial equipment, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.
- [28]. Kotani M, Kakinuma K, Yoshimura M, Ishii K, Yamazaki S, Kobori T, Okuyama H, Kobayashi H, Tada H, *Chem. Phys* 325 (1) (2006) 160–169.
- [29]. Kim CH, Bonnassieux Y, Horowitz G, *IEEE Electron. Device Lett* 32 (9) (2011) 1302–1304.
- [30]. Diemer PJ, Lamport ZA, Mei Y, Ward JW, Goetz KP, Li W, Payne MM, Guthold M, Anthony JE, Jurchescu OD, *Appl. Phys. Lett* 107 (10) (2015) 103303.
- [31]. Friedlein R, Crispin X, Pickholz M, Keil M, Stafström S, Salaneck WR, *Chem., Phys. Lett* 354 (5–6) (2002) 389–394.
- [32]. Kang SJ, Yi Y, Cho K, Jeong K, Yoo KH, Whang CN, *Synth. Met* 151 (2) (2005) 120–123.
- [33]. Casu MB, Yu X, Schmitt S, Heske C, Umbach E, *J. Chem. Phys* 129 (24) (2008) 244708. [PubMed: 19123527]
- [34]. Schöll A, Zou Y, Jung M, Schmidt T, Fink R, Umbach E, *J. Chem. Phys* 121 (20) (2004) 10260–10267. [PubMed: 15549902]
- [35]. Rocco MLM, Haeming M, Batchelor DR, Fink R, Schöll A, Umbach E, *J. Chem. Phys* 129 (7) (2008) 074702. [PubMed: 19044787]
- [36]. Pick A, Klues M, Rinn A, Harms K, Chatterjee S, Witte G, *Cryst. Growth Des* 15 (11) (2015) 5495–5504.
- [37]. Fedorov IA, Zhuravlev YN, Berveno VP, *J. Chem. Phys* 138 (9) (2013) 094509. [PubMed: 23485315]
- [38]. Morisaki H, Koretsune T, Hotta C, Takeya J, Kimura T, Wakabayashi Y, *Nat., Commun* 5 (2014) 5400. [PubMed: 25377483]
- [39]. Karen N, Dieter L, Antonius K, *Angew Chem. Int. Ed. Engl* 34 (16) (1995) 1735–1736.
- [40]. Aragón J, Troisi A, *Phys. Rev. Lett* 114 (2) (2015) 026402. [PubMed: 25635554]
- [41]. Nakayama Y, Mizuno Y, Hikasa M, Yamamoto M, Matsunami M, Ideta S, Tanaka K, Ishii H, Ueno N, *J. Phys. Chem. Lett* 8 (6) (2017) 1259–1264. [PubMed: 28240895]
- [42]. Jurchescu OD, Baas J, Palstra TTM, *Appl. Phys. Lett* 84 (16) (2004) 3061–3063.
- [43]. Jurchescu OD, Popinciuc M, van Wees BJ, Palstra TTM, *Adv. Mater* 19 (5) (2007) 688–692.

Fig. 1.

(a) Chemical structure of perylene and (b) crystal structure of the α -perylene (hydrogen atoms have been omitted). In (c), schematic of laser-assisted photoemission measurements with crystal axes, excitation source (β) angle with respect to the sample surface normal and photoelectron emission angles θ_x and θ_y are identified for a bipolar coordinate system. Different β are identified for the measurements performed at NIST and at beamline PM4 in BESSYII.

Fig. 2.

(a) Drain current (I_D) versus gate-source voltage (V_{GS}) plot in the saturation regime (source-drain voltage $V_{DS} = -40$ V) in a bottom contact-top gate perylene single crystal FET. (b)

Output characteristics for the same FET in (a). The channel length and width of this device were 100 μm and 317 μm , respectively. In (a), the top right inset shows an image of the crystal prior to perylene deposition, and the bottom left inset shows the chemical structure of perylene.

Fig. 3. UPS measurements performed with (in solid blue) and without (in dash black) laser assistance, with the (a) secondary electron cut off and (b) highest molecular orbitals of the α -perylene single crystal regions shown. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4.

XPS C 1s region of single crystal α -perylene also measured with assistance of a cw laser. Data are shown as open symbols, while the fits are shown as a solid line. The blue solid line represents carbon atoms with unsaturated carbon bonds, while the green solid line represents atoms with saturated carbon bonds. The inset (magnified by a factor of ~ 7) highlights the satellite region of the spectrum and are labeled A, B, and C. The uncertainty in the energetic fit positions is ± 0.1 eV. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5.

Angle-resolved HOMO using the ARTOF spectrometer as a function of photoelectron emission angle in (a) θ_x and (b) θ_y . In (c), spectra integrated in θ_x and θ_y from (a) and (b) show the HOMO. Measurements were performed with a photon energy of 60 eV and cw laser at 473nm.

Fig. 6. Summarized results from spectroscopic measurements as an energy diagram where the Fermi energy (E_F) and vacuum level (E_{vac}) are indicated. For the energy levels and HOMO width indicated here, the uncertainty is $\pm 0.1 \text{ eV}$.