Trap healing and ultralow-noise Hall effect at the surface of organic semiconductors

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Fundamental studies of intrinsic charge transport properties of organic semiconductors are often hindered by charge traps associated with static disorder present even in optimized single-crystal devices. Here, we report a method of surface functionalization using an inert non-conjugated polymer, perfluoropolyether (PFPE), deposited at the surface of organic molecular crystals, which results in accumulation of mobile holes and a 'trap healing' effect at the crystal/PFPE interface. As a consequence, a remarkable ultralow-noise, trp-free conduction regime characterized by intrinsic mobility and transport anisotropy emerges in organic single crystals, and Hall effect measurements with an unprecedented signal-to-noise ratio are demonstrated. This general method to convert trap-dominated organic semiconductors to intrinsic systems may enable the determination of intrinsic transport parameters with high accuracy and make Hall effect measurements in molecular crystals ubiquitous.

Organic semiconductors attract substantial interest owing to their potential in development of flexible electronics, solar cells and displays[1]. To better understand the fundamental processes governing the operation and limitations of organic devices, the intrinsic physical properties of these materials must be systematically investigated in disorder-free molecular crystals[2,3]. Such an effort, however, is often hindered by disorder that can be strong enough to mask the intrinsic physical properties even in seemingly perfect molecular crystals[4,5]. Indeed, electrical and spectroscopic measurements reveal that many organic crystals are, in fact, trap dominated, despite the absence of grain boundaries[4,6]. Obviously, charge and exciton transport in such systems will not faithfully reflect the impact of molecular packing. Thus, availability of even cleaner systems, where traps are suppressed, is much desired for the fundamental research.

Trapping usually results from imperfections associated with chemical impurities and structural defects[7]. Among the various ways of reducing trap density, growing pristine single crystals[2], minimization of exposure to ambient environment[8], and the use of low-k gate dielectrics in organic field-effect transistors[9] (OFETs) are common. As these methods all target controlling the generation of traps, so far there has not much been done to minimize the effect of existing traps.

Here, we report a method of surface functionalization of organic molecular crystals using an inert non-conjugated polymer, PFPE, deposited on the crystals' surface. PFPE, also known as Fomblin oil, induces a surface charge accumulation and trap healing at the crystal/PFPE interface: shallow traps at the surface of the semiconductor are converted into (filled) deep traps through an attractive interaction between the localized holes in the semiconductor and the dipole moments inherent to the structure of PFPE. As a consequence of this effect, anisotropic surface conductivity originating from specific molecular packing of organic crystals emerges even in trap-dominated systems, where such anisotropy was masked by disorder before the PFPE functionalization. In addition, recovery of intrinsic mobility in trap-dominated systems functionalized with PFPE is observed. The trap-healing effect also

results in a remarkably low-noise charge transport at the interface that has led us to the observation of an extremely low-noise Hall effect with an unprecedented signal-to-noise ratio, permitting Hall effect measurements in low magnetic fields ($B < 1\,T$) and at extremely small excitation currents (as low as $I \sim 1\,nA$).

In our experiment, PFPE is applied directly to the surface of a crystal with pre-fabricated electrical contacts (Methods), while the conductivity of the sample is monitored (Fig. 1). Given an extreme chemical inertness of PFPE, its very high electrical resistivity ($\rho > 10^{14}\,\Omega\,cm$) and the absence of mobile ions (Supplementary Section 6), one would not anticipate any marked changes in the sample's surface conductivity per square, σ. The only foreseeable change might be a moderate reduction of σ due to the formation of interfacial Fröhlich polarons (the dielectric constant of PFPE is ~2; ref. 10). Very surprisingly, however, we have consistently observed that σ in a variety of p-type organic semiconductors, including single crystals and thin films, markedly increases when an interface with PFPE is formed. As an example, typical behaviour of rubrene single crystals is shown in Fig. 1. The conductivity increases instantaneously, usually by a factor of 10–30, on the application of PFPE oil, followed by a quick transient decrease and then a prolonged gradual increase that may span days. The saturated PFPE-induced σ can exceed that of untreated pristine rubrene crystals by a factor of 10^2–10^3, reaching an absolute value of 10^{-7}–$10^{-6}\,S$.

A unique structural feature of PFPE is the C^+F–$(CF_3)^-$ polar group protruding out of its backbone (Fig. 1). Density functional theory computations suggest that this group has the largest local dipole moment in the PFPE structure, pointing from the CF_3 group towards the backbone (Supplementary Section 1). In addition, the calculations also show that C^+F–$(CF_3)^-$ groups help to partially linearize the PFPE chain by keeping it from folding on itself. The combination of these properties has an interesting consequence: C^+F–$(CF_3)^-$ groups carrying dipole moments might produce a local electric field normal to the semiconductor/PFPE interface, with the orientation favouring hole accumulation in the semiconductor. Indeed, some other perfluorinated polymers with a similar composition, but without such polar groups, show little or no effect

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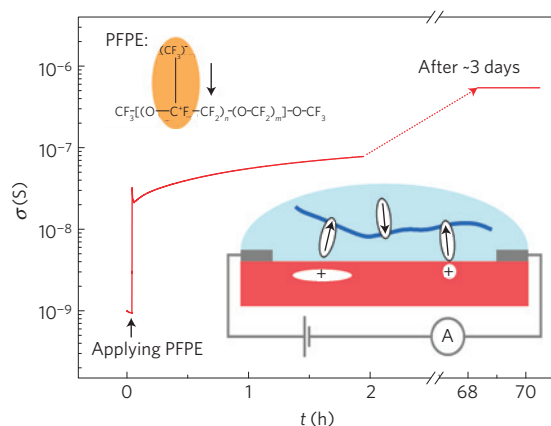*e-mail: podzorov@physics.rutgers.edu

Figure 1 | Surface charge accumulation in rubrene single crystals with PFPE polymer. Surface conductivity per square, $\sigma(t)$, monitored while a drop of PFPE is deposited at the crystal's surface. The sharp increase of σ at $t \approx 0$ corresponds to the moment of applying PFPE, after which σ monotonically increases until reaching a saturation. PFPE molecular structure and device geometry are shown. The shaded area in the PFPE structure indicates one of the local dipoles inherent to PFPE discussed in the text. The schematic illustrates the proposed mechanism of charge induction and the trap-healing effect: local PFPE dipoles induce mobile holes in the semiconductor near the interface, where the attractive dipole–charge interaction is stronger for the charges with wavefunctions localized by traps.

on the surface conductivity of rubrene (Supplementary Section 2). This model is also strongly supported by the thermal annealing experiment, showing that PFPE functionalization occurs much faster at elevated temperatures and results in an irreversible increase of the surface conductivity of crystal/PFPE samples (Supplementary Section 3). In the following, we describe the remarkable transport properties of the conducting interface formed between two insulating materials—an organic semiconductor and PFPE polymer. One particularly interesting result is that owing to the Coulombic interaction between the induced charge and the permanent dipoles in PFPE, such surface functionalization 'heals' shallow hole traps in the organic semiconductor, effectively converting a trap-dominated system to an intrinsic one and leading to an ultraquiet intrinsic charge transport regime and an extremely low-noise Hall effect.

As a consequence of low-symmetry molecular packing, charge transport in molecular crystals is usually anisotropic[11–15]. However, such anisotropy can be observed only in highly ordered single crystals. In fact, even in single crystals, electronic trap states resulting from a small amount of disorder may dominate charge transport and make anisotropy vanish[16,17]. Therefore, observation of an anisotropic conductivity is a clear sign of intrinsic charge transport, not dominated by randomly distributed traps and scattering centres. Our study of PFPE-induced surface conductivity in the two exemplary organic single crystals, rubrene and tetracene, reveals a highly anisotropic σ, implying that we indeed probe the intrinsic transport in these samples (Fig. 2).

In the case of rubrene, it has been previously demonstrated in OFETs that the maximum mobility occurs along **b** axis (see the inset in Fig. 2a), with $\sigma_b/\sigma_a \sim 3.5$, where σ_b and σ_a are the conductivities along the **b** and **a** axes of the crystal, respectively[11,16]. In the present experiment, we monitor σ_b/σ_a as a function of time as PFPE functionalization of the surface takes place (Fig. 2a). We use a contact geometry that defines two perpendicular channels along the desired directions and allows simultaneous measurements of σ in these directions (see Supplementary Section 4 for details). The most reliable measurement of σ_b/σ_a is obtained when PFPE-induced conductivity is quasi-saturated (at $t > 1$ h). In this regime, σ_b/σ_a
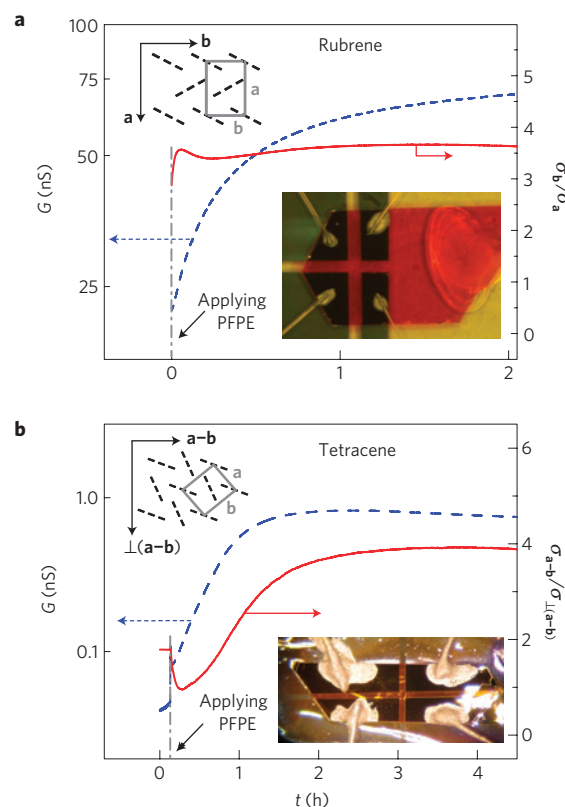

Figure 2 | Anisotropic surface conductivity induced by PFPE in molecular crystals. a,b, Surface conductivity σ is measured along two orthogonal directions *in situ*, as PFPE is applied to the (**a**, **b**) facets of rubrene (**a**) and tetracene crystals (**b**). The contacts are pre-fabricated in a cross-channel geometry (see Supplementary Section 4 for details). The dashed curve is the conductance, $G = I/V$, recorded as a function of time as the charge accumulation occurs. The solid curve in **a** is the ratio of σ along the **b** and **a** axes in rubrene; the solid curve in **b** is the ratio of σ in the **a–b** and the orthogonal $\perp$(**a–b**) direction in tetracene. As PFPE-induced conductivity saturates, these ratios reach stable values of ~ 3.6 and ~ 4 for rubrene and tetracene, respectively. The insets show the molecular packing and the unit cells in the basal plane of these crystals; the photographs show the actual devices (the horizontal edges of the crystals correspond to the **b** axis for rubrene and the **a–b** axis for tetracene—the directions along which the maximum mobility is observed in OFETs based on these crystals).

in rubrene reaches ~ 3.6, very close to the value previously reported for OFETs (ref. 11). In tetracene, quantum chemistry calculations predict that the most favourable direction for charge transport is the diagonal direction of the unit cell, **a–b** (refs 12,18). We thus measured the conductivity in tetracene crystals along the **a–b** diagonal and along the direction perpendicular to it, $\perp$(**a–b**). When PFPE-induced conductivity saturates, the conductivity anisotropy reaches $\sigma_{a-b}/\sigma_{\perp(a-b)} \sim 4$, consistent with the result previously obtained in air-gap tetracene OFETs (ref. 13).

It might be intuitive to think that doping can improve transport in general by filling trap states; however, we must emphasize that although this is true for disordered films[19], doping of ordered systems typically introduces additional disorder and thus has a detrimental effect on their intrinsic carrier mobility and transport anisotropy. The results reported here thus imply that PFPE functionalization induces hole accumulation without introducing additional disorder. In fact, more than that, in the rest of this Article by performing OFET and Hall effect measurements, we show that PFPE functionalization actually helps to eliminate electronic traps from the surface.

An ideal experimental approach to understand the effect of PFPE on charge transport is to compare the carrier mobilities in the same organic crystal before and after PFPE deposition. Such a comparison is possible, if one uses a recently developed method of OFET fabrication, in which free-standing gate dielectric films can be repeatedly applied to a crystal by vacuum lamination[20]. This method allows us to sequentially gate the same crystal, each time after a desired surface modification (for details, see Supplementary Section 5 and ref. 20). For example, Fig. 3a shows typical transconductance characteristics of a pristine rubrene single-crystal OFET and an OFET made on the same crystal after a very thin layer of PFPE has been deposited on it. Both devices show excellent transistor behaviour with an extended linear accumulation regime and similar mobilities. A positive shift of the field-effect onset in the PFPE-functionalized device is noticeable. This shows that in an intrinsic semiconductor, such as pristine rubrene crystals, PFPE merely induces surface hole accumulation without introducing extra traps.

However, the effect of PFPE on crystals with a significantly higher density of traps is totally unexpected. Figure 3b shows the transconductance characteristics sequentially recorded in three OFETs that use the same rubrene crystal, but in its different states: pristine, photo-oxidized and PFPE-treated. Photo-oxidation is known to introduce both shallow and deep traps in rubrene[8,21]. As a result, OFETs made on photo-oxidized rubrene are expected to have a reduced mobility, as corroborated by the data in Fig. 3b. The most surprising observation, however, is that PFPE functionalization compensates the effect of traps introduced by photo-oxidation: indeed, the transconductance characteristics of the OFET with an interfacial PFPE layer resemble those of the pristine OFETs. The linear mobility values extracted in both cases are nearly identical. Such a remarkable trap-healing effect is also observed in tetracene single crystals, as shown in Fig. 3c. In contrast to rubrene, as-grown tetracene crystals usually have a much higher density of shallow traps, in the range 10^{11}–10^{12} cm^{-2}, which is sufficient to mask the intrinsic transport properties of this system[4]. However, as Fig. 3c shows, (at least some of) these traps are eliminated from as-grown tetracene crystals by PFPE deposited at the surface, which improves the linearity and enhances the carrier mobility. We also note that trap healing occurs regardless of the exact nature of traps. For example, the same effect was observed in other trap-dominated samples, where traps were introduced by different methods (Supplementary Sections 7 and 8). Moreover, the recovery of intrinsic properties is not limited to mobility, but also includes, for example, intrinsic photoconductivity (Supplementary Section 8).

The trap-healing effect observed here is much more intriguing than it may seem at first glance. In disordered conductors, where the density of tail states is high, adding charge carriers pushes the upmost filled energy level through the tail, which may markedly facilitate charge transport. This picture, for example, holds true for OFETs operating 'in the tail' (below the mobility edge) in certain disordered systems, such as small-molecule films[19] and conjugated polymers[22]. In the case of PFPE functionalization, however, a trivial addition of charge carriers cannot explain the improved mobility. Indeed, it is well known that in most molecular crystals the charge carrier mobility is independent of carrier density, as shown in the numerous OFET studies (see, for example, refs 2,3), and this is clearly the case in our measurements (note the linearity of $\sigma(V_G)$ in Fig. 3). Therefore, not only is PFPE inducing charge carriers, but it must also be eliminating trapping.

As discussed earlier, permanent dipoles inherent to the PFPE structure can induce mobile holes at the surface of an organic semiconductor interfaced with PFPE. Now we further propose that attractive Coulombic interaction between such dipoles and the induced charges helps to eliminate shallow traps. Owing to their
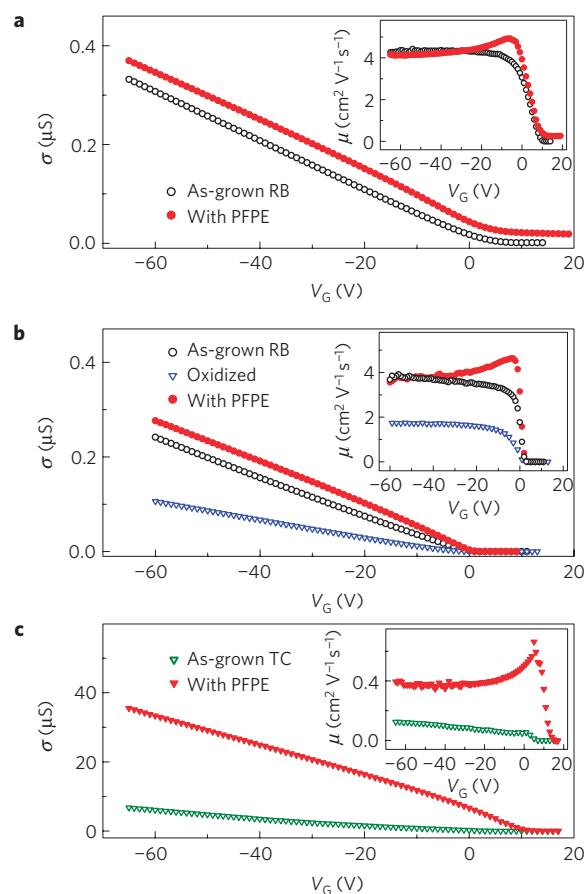

Figure 3 | Trap-healing effect of PFPE revealed in FET measurements.
a–c, OFET transfer characteristics measured in single crystals of rubrene (RB; **a,b**) and tetracene (TC; **c**) using a vacuum lamination approach (detachable Mylar gate dielectric). **a**, Pristine single-crystal rubrene OFETs before and after an interfacial PFPE layer is deposited on the crystal. **b**, OFETs prepared (sequentially) on a pristine rubrene crystal (black open circles), then on the same crystal after it was photo-oxidized (blue open triangles), and finally on the same oxidized crystal treated with PFPE (red filled circles). **c**, Single-crystal tetracene OFETs made using an as-grown crystal (green open triangles) and the same crystal treated with PFPE (red filled triangles). A few-hour waiting period was required after PFPE deposition and before Mylar lamination to achieve full recovery of photo-oxidized crystals. In all of these structures, the PFPE layer was much thinner than the 2.5-μm-thick Mylar gate insulator (for more details, see Supplementary Sections 5–7). The insets show the linear regime field-effect mobilities extracted from the corresponding transfer curves.

delocalized nature, mobile charge carriers are much less affected by such a charge–dipole interaction. On the other hand, charges (temporarily) localized on shallow traps must experience a stronger Coulombic attraction to the nearby dipoles located on the other side of the interface. In addition, the polymer can locally rearrange at the surface of the crystal in response to the presence of a localized charge below the interface to minimize the Coulomb energy (for instance, PFPE dipoles can rotate). Such a mechanism of self-trapping can make localization by shallow traps even stronger. At a distance of 1 nm, for example, the Coulomb energy of a hole interacting with a dipole of 1 D is around 30 meV, already greater than the thermal energy at room temperature. This potential, superimposed on the potential of a shallow trap, further localizes the carrier and thus converts a shallow trap into a (filled) deep trap. As more shallow traps become converted to (filled) deep traps, trap and release events become less frequent, and the remaining

charge carriers move as intrinsic (mobile) carriers, with mobility approaching the intrinsic value.

The critical difference between the charge accumulation in OFETs and at the crystal/PFPE interface is that a uniform gate electric field in OFETs does not energetically discriminate between localized and delocalized charges in the channel. This qualitatively explains the data in Fig. 3. These data are also consistent with our understanding of as-grown rubrene crystals as an intrinsic (not dominated by traps) system, as has been shown by numerous OFET studies[23,24]. Indeed, pristine rubrene crystals have a very small shallow trap density, and hence the improvement in the linear mobility due to the trap healing is negligible (Fig. 3a).

Figure 4a shows raw data of Hall effect measurements performed in (ungated) rubrene crystals functionalized with PFPE (see Supplementary Section 9 for more details). A very clear Hall signal, V_{Hall}, is observed with its magnitude and polarity in perfect correlation with the magnetic field, B. The extracted Hall mobility is around $\mu = 6.5\,cm^2\,V^{-1}\,s^{-1}$, which is consistent with the values obtained in OFETs made using low-k gate dielectrics[10]. The mobile charge carriers are holes with a density $n = 10^{11}$–$10^{12}\,cm^{-2}$, depending on the stage of functionalization at which the Hall measurements are performed.

We want to emphasize two important features of the Hall measurement reported here. First, our device structure is much more simple than the sophisticated OFET architecture previously used in Hall effect measurements[23–26]. The fabrication of these ungated devices is straightforward: it takes only a drop of PFPE oil deposited in air at room temperature at the crystal surface with pre-fabricated contacts. Second, the sensitivity of our method is unprecedented by any existing Hall measurement in organic semiconductors. The noise in the raw data for V_{Hall} at $I_{SD} = 200\,nA$ is essentially non-existent (Fig. 4a). The lower inset in Fig. 4a compares typical raw V_{Hall} traces obtained from three types of rubrene device in the same measurement set-up: OFETs with a parylene gate dielectric, air-gap OFETs and the rubrene/PFPE interface, clearly showing the superior signal-to-noise ratio of the new method. Even at an extremely small excitation current of 1 nA, the signal is still well above the noise floor (Fig. 4b). Figure 4c shows an example where the Hall effect is clearly demonstrated in a PFPE-functionalized rubrene crystal at small magnetic fields (<0.3 T). Such magnetic fields are well within the reach of typical small-size laboratory electromagnets that do not require any cryogenic liquids for operation (for details on Hall measurements in low magnetic fields, see Supplementary Section 10). In the following, we explain how such a remarkable sensitivity can result from the fundamentally improved charge transport due to the trap-healing effect.

Capture and release of charge carriers by traps is one of the major sources of electric noise in semiconductors[27]. A careful examination of $1/f$ noise in single-crystal rubrene OFETs, for example, reveals that trapping on slow traps ($\tau \sim 0.1$–$100\,s$) in the channel (rather than fluctuations of contact resistance) is the dominant source for such noise (Supplementary Sections 11 and 12). These slow traps are different from the ultrashallow traps previously studied by electron spin resonance, whose characteristic time is much smaller ($\sim$1 nS; ref. 28). In organic semiconductors, Hall voltages are much smaller than those in their inorganic counterparts, because μ in van der Waals crystals is typically much smaller. Thus, even a small noise can make reliable detection of the Hall signal virtually impossible. This is the main reason why it is so difficult to obtain high-quality Hall effect data in organic semiconductors even in a band-like transport regime. In PFPE-functionalized samples, an attractive Coulombic interaction between temporarily trapped holes and dipoles in the nearby PFPE molecules increases an effective activation energy of the whole ensemble of traps and thus results in a suppression of fluctuations, which is convincingly demonstrated in our $1/f$-noise
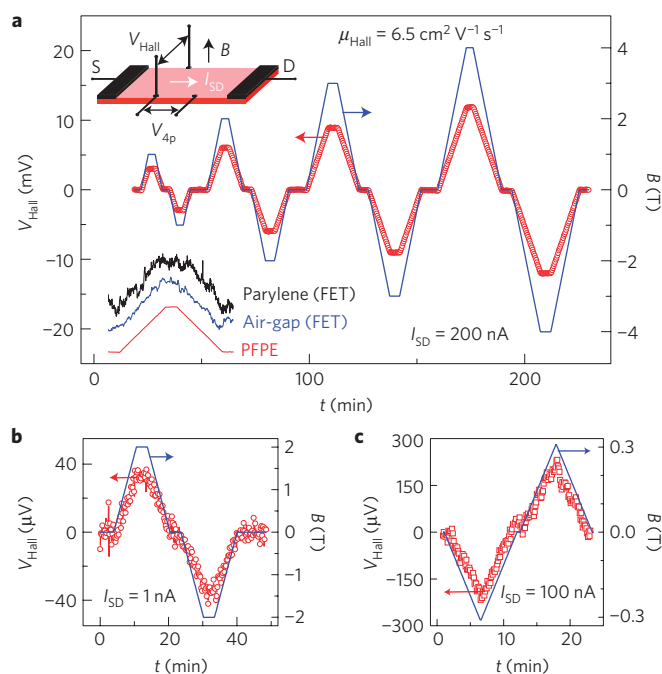
Figure 4 | Hall effect at the surface of rubrene functionalized with PFPE.
a, Raw Hall voltage V_{Hall} signal (symbols) recorded while the magnetic field B (solid line) is swept up and down with alternating polarities. The sample is biased at a constant source–drain current, $I_{SD} = 200\,nA$. The upper inset shows sample geometry. The lower inset compares typical traces of Hall voltage recorded in different rubrene single-crystal devices as B is swept from 0 to 2 T and back to 0: FETs with parylene gate insulator (black; ref. 23), air-gap FETs (blue; ref. 23) and ungated rubrene/PFPE devices (red). **b,c**, Hall effect measurement performed in rubrene/PFPE at a very small excitation current, $I_{SD} = 1\,nA$, and small magnetic fields, $|B| < 0.3\,T$, respectively. The outstanding signal-to-noise ratio and a superior sensitivity of the new method based on PFPE functionalization are evident.

measurements (Supplementary Section 11), and hence the extreme sensitivity of Hall measurements reported here.

Two interesting counter examples of conducting interfaces, in terms of the absence of a Hall signal, are given by tetracene single crystals functionalized with PFPE and rubrene functionalized with self-assembly monolayers. The latter is discussed in Supplementary Section 14, and here we focus on the tetracene/PFPE case. Charge transport at the tetracene/PFPE interface is highly anisotropic in accord with its molecular packing (Fig. 2b), thus indicating that it is intrinsic. Nevertheless, we were not able to detect a Hall signal in this system, even though the strongly suppressed noise in our Hall measurements should have allowed us to do that if the system were band-like (see Supplementary Section 13 for detailed estimates). The systematic absence of a Hall effect suggests that the intrinsic charge transport in tetracene is not band-like, in contrast to rubrene, but rather an (anisotropic) incoherent hopping. Here we would like to emphasize the indispensable role of PFPE functionalization in reaching this conclusion. An organic semiconductor may not show a Hall effect for two reasons: either its intrinsic charge transport is incoherent hopping, or the band-like conduction is trap-dominated to such an extent that noise masks the Hall signal. One can claim that transport in a crystal is (intrinsically) hopping only if both anisotropy and an absence of a Hall effect are confirmed, with noise in Hall measurements being smaller than the Hall voltage expected for a band conductor with similar longitudinal (FET) mobility. Thus, our experiment reveals that the intrinsic charge transport mechanism in tetracene is an anisotropic hopping.

In intrinsic crystals, such as pristine rubrene, the density of traps is rather low, so that both field-effect and Hall measurements yield nearly identical mobilities. The results reported here nevertheless clearly demonstrate that although residual traps in an intrinsic crystal may not have much effect on mobility, they can still significantly affect charge transport by acting as noise sources. The trap-healing by PFPE not only improves the longitudinal mobility (in trap-dominated samples), but also very efficiently suppresses the electric noise generated by traps. As a result, truly intrinsic charge transport becomes experimentally accessible, as we have demonstrated in an intrinsic band-like semiconductor (rubrene) and in an intrinsically hopping system (tetracene). This shows the power and potential of this method of surface functionalization for the studies of intrinsic transport properties of organic semiconductors.

Methods

Single crystals of rubrene and tetracene were grown by physical vapour transport (optimized procedures can be found at http://www.physics.rutgers.edu/~podzorov/index.php). Raw materials were purchased from Sigma-Aldrich (rubrene: catalogue no. 551112; tetracene: no. 698415). Typical growth conditions were: the carrier gas was ultrahigh-purity He at a flow rate of 100 cm^3 min^{-1}; the temperature at the sublimation zone 310 °C for rubrene and 290 °C for tetracene; the typical growth duration was ~24 h.

PFPE polymer (under the brand name Fomblin oil) was purchased from Kurt J. Lesker (catalogue no. MFY25/6BB).

Electrical contacts were hand painted on the (**a**, **b**) facets of the crystals with a graphite paint (Aquadag E, aqueous suspension of colloidal graphite from Ted Pella, thoroughly mixed with deionized water). Gold wires (25 μm thick) were attached to the graphite contacts for wiring the sample to instrumentation. The typical channel length, L, and width, W, were 2–5 mm. More details on device fabrication can be found in the Supplementary Information.

Photo-oxidation of rubrene crystals was performed in a hermetic chamber (with glass optical windows), filled with an atmosphere of ultrahigh-purity O$_2$ gas, under illumination with a broadband white light from a xenon lamp with an integral power density at the sample position of about 85 mW cm^{-2}. An ultraviolet filter was placed between the lamp and the sample to avoid ultraviolet damage of the organic semiconductor. For the procedure used in recovery of photo-oxidized samples with PFPE, see Supplementary Section 7.

For the transport anisotropy measurements, silver contacts were thermally evaporated through a shadow mask that defined two perpendicular channels. A Keithley 2400 source meter was used to apply the bias voltage, and a Keithley 6514 electrometer was used to measure the current. In OFET measurements, two 2400 source meters were used to apply the source–drain bias and gate voltage, and a 6514 electrometer was used to measure the source–drain current. In the Hall effect measurements, a Keithley 2400 source meter was used to apply a constant excitation current, and two Keithley 6514 electrometers were used to measure the longitudinal and Hall voltages. All measurements in this work were performed in the dark at temperatures close to room temperature. Hall measurements were carried out in an Oxford ^{4}He cryostat equipped with a superconducting magnet, or using an electromagnet (in B fields <1 T).

To achieve the ultralow-noise conduction regime, such as the one shown in Fig. 4, a minimum amount of PFPE should be applied to the surface of an organic semiconductor, just enough to cover the entire area of the channel with as thin a PFPE layer as possible. An overflow of PFPE or immersion of samples in a PFPE reservoir may result in instabilities and excessive fluctuations. In addition, the crystal/PFPE interface must be kept in a horizontal orientation to prevent slow flow of PFPE oil, which seems to be disruptive for the functionalization process. It typically takes a few hours before the trap healing fully sets in and the very low-noise transport regime can be observed.

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Author contributions

B.L., Y.C., D.F., H.T.Y., K.C. and H.N. performed crystal growth, device fabrication and measurements. B.L., Y.C. and V.P. designed the experiments and analysed data. V.P. guided the work. Y.C. and V.P. wrote the manuscript with input from all authors.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to V.P.

Competing financial interests

The authors declare no competing financial interests.