Light-Assisted Charge Propagation in Networks of Organic Semiconductor Crystallites on Hexagonal Boron Nitride

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Introducing organic semiconductors as additional building blocks into heterostructures of 2D materials widens the horizon of their applications. Organic molecules can form self-assembled and self-aligned crystalline nanostructures on 2D materials, resulting in well-defined interfaces that preserve the intrinsic properties of both constituents. Thus, organic molecules add unique capabilities to van der Waals heterostructures that have no analogues in inorganic matter. This study explores light-assisted charge propagation in organic semiconductor networks of quasi-1D needle-like crystallites, epitaxially grown on insulating hexagonal boron nitride. Electrostatic force microscopy is employed to demonstrate that upon external illumination it is possible to change the conductivity of organic crystallites by more than two orders of magnitude. Furthermore, by exploiting the highly anisotropic optical properties of the organic nanoneedles, a selective charge propagation along the crystallites is triggered that matches the orientation of the molecular backbones with the incident light’s polarization direction. These results demonstrate the possibility to use a “light-gate” to switch on the conductivity of organic nanostructures and even to guide the charge propagation along desired directions in self-assembled crystallite networks.

1. Introduction

Van der Waals (vdW) heterostructures—where the different 2D material layers are placed or epitaxially grown on top of each other—have great potential for the fabrication of functional materials and interfaces with novel properties, different from those of the individual building blocks.\[^{11-10}\] However, using only 2D “building blocks” limits the variety of potential structures that could be realized. Introducing organic semiconductors as an additional ingredient widens the horizon of applications for vdW heterostructures.\[^{11-15}\] These small building blocks can form self-assembled and self-aligned nanostructures and layers governed mainly by vdW interactions with 2D substrates.\[^{11,14-18}\] Due to the weak coupling and the vdW nature of the interface between organic semiconductors and 2D materials,\[^{19}\] intrinsic properties of both building blocks are commonly preserved down to the monolayer.\[^{15,20,21}\] even giving rise to peculiar nanomechanics of the interface.\[^{22}\] Still, coupling through vdW interactions is very interesting for many applications, especially in high performance opto-electronics and sensing.\[^{14}\] Many different proof-of-concept structures have been realized, starting from the usage of graphene as an electrode material in organic-based field-effect devices (FETs),\[^{23-25}\] through gate tunable vdW heterojunctions with MoS\(_2\) and organic semiconductors,\[^{26-28}\] and employing hexagonal boron nitride (hBN) as a vdW gate dielectric.\[^{25,29-32}\]

With a breakdown field of \(\approx 1\) \(\text{GVm}^{-1}\),\[^{33}\] hBN is especially suitable as ultrathin, atomically smooth, and essentially trap-free vdW gate dielectric material. As such, hBN has been extensively employed in vdW heterostructures with other 2D materials\[^{23,7,9,10}\] and will remain the vdW dielectric material of choice, especially when considering recent advances in the synthesis of large area hBN films.\[^{14,35}\] In the case of organic semiconductors, hBN has been successfully used as gate dielectric for organic-FETs with epitaxially grown rubrene, pentacene, C\(_60\), and C\(_8\)-BTBT channel materials.\[^{25,29-32}\] Furthermore, vertical and lateral heterostructures of pentacene and C\(_8\)-BTBT have been realized on hBN.\[^{36}\] While the applications above mentioned rely on extended organic semiconductor layers on hBN, an interesting alternative approach is to use self-assembled and self-aligned quasi-1D nanostructures.\[^{11,14}\] On hBN, formation of quasi-1D needle-like crystallites has been...
demonstrated for spin-coated oleamides and vapor deposited phenylenes.[16,37]

The use of organic semiconductors in vdW heterostructures offers many advantages; since the organic layers or nanostructures form through self-assembly, there is no need for elaborate transfer procedures,[38] and the resulting heterostructures are self-aligned with respect to the high-symmetry directions of their 2D material support.[14–16,37] Furthermore, organic chemistry offers almost an infinite variety of molecular “building blocks.” Especially, adding functional groups to the backbone of the molecules has been a well-established molecular design pathway to engineer desired structural, transport, and opto-electronic properties.[39–45] Incorporation of functional groups commonly leads to H-bonding between neighboring molecules, which then governs intermolecular interactions and packing, thus stabilizing the thin film structures.[39,43,45–48] Such behavior has also been observed in many natural systems, as dyes and pigments (e.g., indigo) which form π-stacked structures through H-bonding.[49–51] The relevance of H-bonding on performance and stability of organic-based FETs has been demonstrated, e.g., in the case of epindolidione—an analogue to tetracene—achieving higher field-effect mobility, better on–off ratio, and much better long-term air stability.[41]

Studies that investigate opto-electrical properties of 2D material/organic semiconductor hybrid structures are mainly based on extended organic layers, while involvement of self-assembled organic nanostructures on 2D materials is lacking. This is especially interesting, since frequently these nanostructures have in-plane anisotropy of both optical and electrical properties. Thus, we present an effort to enable and control the direction of charge propagation within quasi-1D organic semiconductor crystallite networks epitaxially grown on hBN. Using electrostatic force microscopy (EFM), we are able to image the distribution of the charges within the crystallite networks. We demonstrate that the propagation of excess charges within the self-assembled organic crystallite networks on hBN can be externally controlled by a light source. Furthermore, by using linearly polarized light, charge propagation along a preselected direction in the crystallite network is stimulated.

2. Results and Discussion

The results section is separated into five subsections. The first two subsections introduce the molecular species, the structure of the crystallites, their epitaxial relation to hBN, and the anisotropy of their optical properties. The third subsection presents both light-assisted EFM setups applied here. The fourth subsection demonstrates single point charging experiments, enabling the concept of charge trapping and light assisted charge propagation along the crystallites. The final subsection covers time-resolved charging and discharging of individual crystallites where the charges are injected via a macroscopic side-contact and the back-gate electrode (independent from the EFM probe). For both experimental setups, complementary measurements were conducted under nonpolarized and linearly polarized illumination.

2.1. DHTA7 Crystallite Networks on hBN

Epitaxially grown networks of quasi-1D needle-like crystallites of dihydrodrotetraazaheptacene (DHTA7) are considered (Figure 1a). Molecules were synthesized following the routes described in our previous work.[48,52] Compared to the parenting linear oligoacene heptacene, the dihydropyrazine unit provides two additional electrons that are delocalized over the entire molecule.[52] It was demonstrated on a similar system[48] that H-donor (N–H) and H-acceptor (N=C) sites tend to form H-bonds between the neighboring molecules. The selected molecular species offers several crucial advantages for this study. Intralayer H-bonding stabilizes DHTA7 nanostructures, allowing for prolonged air exposure. Optical properties of DHTA7 allow the use of visible light lasers for charge manipulation experiments, and in particular high in-plane optical anisotropy enables the demonstration of polarization-dependent charge propagation.

Figure 1b presents a ball-and-stick model of the preferred position of a pair of DHTA7 molecules confined in a plane, as obtained by density functional theory (DFT) calculations. An interplay of dipolar interaction, steric repulsion, and (N–H–N) intralayer hydrogen bonding, results in the preferred relative position of the two DHTA7 molecules fixed in a plane. Thus, one molecule is shifted by 79° along the long axis direction with respect to the other (Figure 1b,c, also relaxed in x direction). Since the fastest growing direction of the crystallites is in the direction of the hydrogen bond formation, this slight shift between the neighboring molecules will define the angle between the long axis of the crystallite (long needle axis-LNA) and the long axis of the molecules (LMA) within the crystallite.[53] In the case of the molecules confined in a plane, this angle is ≈80.8°, according to the calculations. The presence of intralayer H-bonds strengthens the molecular interactions, orients neighboring molecules into a head-to-tail arrangement, and enables π–π packing of the subsequent layers, as observed in a similar system.[46] Thus, the unit cell of DHTA7 consists of four molecules, forming a tetramer. A side view of the unit cell—as obtained by DFT calculations—is shown in Figure 1d, also indicating a slight tilt (~8.5°) of the plane of the molecules with respect to the (001) plane. It is worth mentioning that if the calculated bulk structure of DHTA7 is considered together with (001) as its contact plane to hBN, then the angle between the LMA and the LNA should be ~79°. This discrepancy is addressed in the next subsection. In the case of vdW epitaxy, rotational commensuration is maintained in spite of the lattice mismatch.[20] Preferred adsorption sites of individual molecules, combined with the LMA-LNA relation, and point-group symmetry of the substrate will result in the specific growth directions of the crystallite network.[37,53] Since DHTA7 has an acene backbone, its preferred adsorption on hBN is with its LMA in a zigzag direction, as obtained by DFT calculations. The particular preferred adsorption site of DHTA7 on hBN shown in Figure 1e is favored by ~200 meV over the other high symmetry adsorption sites with DHTA7’s LMA in either zigzag or armchair directions of hBN. As a consequence of the flat-lying adsorption of individual molecules, elongated needle-like DHTA7 crystallites grow. It is worth mentioning that self-assembly and self-alignment of elongated nanostructures of small rod-like molecules is possible only on certain crystalline substrates, most of which are conductive. Exceptions are van der Waals dielectric surfaces, where many acene- and phenylene-based molecules tend to nucleate in
a flat lying orientation. On conventional dielectric surfaces (see Figure S1, Supporting Information), DHTA7 exhibits quasi layer-by-layer growth with the molecular backbone being almost perpendicular to the substrate plane, and therefore self-assembly and self-alignment of the elongated nanostructures is not possible. An example of the epitaxially grown DHTA7 crystallite network on multilayer hBN is shown in the atomic force microscopy (AFM) image presented in Figure 1f. Straight crystallites with rather constant width and height (in the order of 50–100 nm, and 5–10 nm, respectively) and with six preferential growth directions were observed on all of the hBN samples. The growth directions were found to follow a very specific pattern, as revealed by the 2D Fast Fourier Transform (2D FFT) of a binary mask generated from the topography image (Figure 1f) and presented in Figure 1g. The crystallites tend to grow in six preferred directions, as three chiral pairs separated by $60^\circ$, and split by $(17.6 \pm 0.8)^\circ$ within each pair. Such pattern is substrate-mediated, and follows the tri-fold rotation and mirror symmetry of the hBN lattice. Thus, in between the chiral-paired growth directions lies a high symmetry direction of the underlying substrate. Considering the preferred adsorption site of individual molecules on hBN (Figure 1e), it is expected that the long molecular axis is aligned with the zigzag direction of hBN. Then, considering the H-bonding and the relative position of the neighboring molecules fixed on a plane (as shown in Figure 1b), the growth directions of the crystallites match very well the theoretically predicted split of $(\pm 9.2)^\circ$. This indicates that the observed chiral-pairs in the preferred growth directions of the crystallites are split from an armchair direction of the hBN substrate. Thus, it is possible to determine the crystallographic orientation of the underlying 2D materials in this manner, as is also indicated in the insets of Figure 1f,g. In order to highlight the ambient stability of these nanostructures, Figure S2 in the Supporting Information compares the morphologies of the as-grown sample with those obtained after one year of exposure to ambient air.

### 2.2. Anisotropic Optical Properties of DHTA7

Owing to the anisotropic building blocks (rod-like molecules), many macroscopic properties of organic semiconductor single-crystals are also highly anisotropic. As such, strong anisotropy of the in-plane optical absorption of DHTA7 was observed through contrast changes with respect to the relative angle...
between the direction of light polarization and the LNA of individual crystallites.

Figure 2a–d shows optical microscopy images (120 × 120 µm²) used to analyze the contrast of three individual crystallites, labeled with (1–3). The particular thickness of the hBN support (≈90 nm) was selected to enhance the contrast of the crystallites due to multiple reflections from the substrate. The contrast \( C(\phi) \) of individual DHTA7 crystallites as a function of the linear polarizers' angle \( \phi \) was expressed as:

\[
C(\phi) = \frac{I_{\text{hBN}}(\phi) - I_{\text{DHTA7}}(\phi)}{I_{\text{hBN}}(\phi)},
\]

where \( I_{\text{hBN}} \) and \( I_{\text{DHTA7}} \) stand for the reflected light intensities. \( \phi \) is set in such way that \( \phi = 0° \) when the angle of the polarizer and \( y \) axis of the optical image coincide. The polarization angle dependence of the contrast for three crystallites of the same chirality (LNAs differ by 60°) is shown in Figure 2e. By knowing the angle between the LNA of each crystallite and the polarization direction it is possible to deduce the angle between LMA and LNA. The angle between the LMA and LNA was found to be 79° ± 3° for all of the examined DHTA7 crystallites on hBN. This discrepancy indicates that—at the interface with hBN—are flat lying and dictate the growth direction of the crystallites, as found by AFM. As the further layers within the crystallite grow, the molecules rearrange to better

Consider the growth directions of DHTA7 needle-like crystallites on hBN, an LMA-LNA angle of ≈81° is obtained (Figure 1f,g). Considering the growth directions of DHTA7 needle-like crystallites on hBN, an LMA-LNA angle of ≈81° is obtained (Figure 1f,g). This matches rather well the value predicted by the calculation of the molecular arrangement when individual molecules are fixed in a plane (Figure 1b). On the other hand, the value obtained for the LMA-LNA angle from polarization dependent optical contrast measurements (Figure 2f) is ≈79°, which matches well the expected angle considering the calculations for the bulk DHTA7 structure. This discrepancy indicates that—in the most likely case—the molecules at the interface with hBN are flat lying and dictate the growth direction of the crystallites, as found by AFM. As the further layers within the crystallite grow, the molecules rearrange to better
accommodate the bulk structure, consequently leading to a slight tilt (by ~2°) of the LMA, with respect to the substrate plane and the molecules at the interface. Because the polarized light probes the entire crystallite, main contribution comes from the bulk and the rearrangement at the interface is not observed in the C(φ) curves. However, the molecular layers at the very interface to hBN govern the growth directions of the whole crystallites.

Figure 2h shows the visible-light absorption of DHTA7 molecules dissolved in dimethyl sulfoxide (DMSO) and of a single crystallite grown on hBN. Here, intersecting lines indicate the wavelengths of the lasers used for EFM based light-assisted manipulation of the charges within the crystallites. In the crystallites a down-shift in energy of the absorption bands’ edge occurs due to intermolecular interactions. Redshifted absorption edges in the crystalline solid were also reported for other organic semiconductors.[43,54] Details on the absorption measurements for the individual DHTA7 crystallites on hBN are provided in the Experimental Section.

2.3. Light-Assisted EFM Setups

In this study, two different methods have been established to introduce excess charges into DHTA7 crystallite networks (see Figure 3). In both cases, complementary experiments were carried out, in the dark (minimizing external light sources) as well as with an external laser beam focused at the AFM tip apex. EFM was employed to image the excess charge distribution along the crystallite networks. In the case of the EFM experiments without an external light source, the unavoidable near-infrared feedback laser of the scanning probe microscope was still partly illuminating the sample. No effects from the feedback laser were observed. More technical details on sample preparation and light-assisted EFM setups are presented in the Experimental Section.

In the first charging approach, DHTA7 crystallite networks supported by hBN flakes are considered. The excess charges are inserted into a single point in the network using an EFM probe in contact mode, and by applying a bias voltage to the tip (Vtip). This is referred to as a single point charging experiment, and a scheme of such a setup is shown in Figure 3a.

In the second charging approach, a more elaborate sample is considered where graphite (or few-layer graphene) side contacts are placed on a side of a hBN flake,[38] and the DHTA7 crystallites are grown subsequently. Graphite flakes were used to inject charges—in a back-gate configuration (VSG)—into individual crystallites that have either nucleated at the edge or have terminated the growth at the graphite flake, which forms a side contact to the crystallites. A scheme of the sample and the setup is shown in Figure 3b.

2.4. Single-Point Charging Experiments

In order to probe opto-electrical properties of quasi-1D organic crystallites, single-point charging experiments were carried out with and without an external laser light source that illuminated a sample region in a radius of ~15 µm around the charging point. An example of a single-point charging experiment and light-assisted charge propagation is presented in Figure 4. The chosen sample area exhibits crystalline needles which grew in several different directions, branching from a single point in the middle of the scanning area; the same sample area as already shown in Figure 1f. In the charging experiments presented in Figure 4, the middle of the branching crystallites was used every time as a point in which the charges were injected into the network. That particular point was chosen in order to highlight the capability of controlling the direction of charge propagation by a linearly polarized light source.

The charging experiments were carried out in the following manner. First, the chosen sample area was imaged by EFM to confirm that there are no excess charges present prior to the charging experiments. Then, the EFM probe was brought into contact with a chosen point on the crystallite network (using contact mode, with low contact force). As soon as the probe touched the sample, a bias voltage was applied between the probe and the samples’ back gate. In the particular case presented in Figure 4, charging was done for 15 s with Vtip = −10 V. During the charging, three different illumination conditions were tested: i) without any external light source; ii) with externally coupled unpolarized 635 nm laser beam focused at the apex of the tip; and iii) with linearly polarized laser beam. Immediately after charging, the laser light was switched off and the sample area (15 × 15 µm²) around the charging point was imaged by EFM, as respectively shown in Figure 4b–d. In between two subsequent single point charging experiments the sample was exposed to white light for several minutes (in order to dissipate excess charges) and rechecked by EFM.

Figure 4b presents the results of a single point charging experiment carried out in the dark. As can be seen from the EFM phase image, the injected charges remain exclusively in

![Figure 3. Light-assisted EFM setups: schematic representations of light-assisted EFM setups used for single-point charging experiments a), and for the experiments where the excess charges are injected from an external side contact b).](image-url)
a \approx 1 \mu m wide region around the charging point. This indicates that the charges are unable to propagate along the organic crystallites and most likely stay in defect sites of the crystallites in the area near the charging point. The image presented in Figure 4b is obtained \approx 2 min after the charging, and the charged region is visible in the EFM phase shift even after \approx 30 min if the sample is not illuminated. If the same charging experiment is repeated with an external unpolarized 635 nm laser beam focused at the tip apex (with \approx 30 \mu m spot diameter), a strikingly different charging landscape is observed. As can be seen from Figure 4c, the charges, injected at the branching point of the crystallites spread along all directions, traveling several micrometers away from the charging point, and even crossing the boundaries between crystallites.

Most likely, during the charging (with or without an external light source) injected charges relax to trap states in the gap of the organic semiconductor, thus remaining spatially localized. However, absorption of a photon lifts a trapped charge to the transport levels, wherefrom the charge can propagate along the crystallite. Since excess charges are constantly inserted by the EFM probe, the excited charges will propagate through drift-diffusion, spreading from the injection point as long as the external light source is turned on. Interestingly, since immediately after the charging the external light source is switched off, the propagating charges are “frozen” back to the trap states and subsequent imaging of a static charge distribution is possible with EFM.

As demonstrated in Figure 2, light absorption in the crystallites strongly depends on the light polarization. Since the light absorption is required to enable charge propagation, electrical response of the crystallites is expected to strongly depend on the polarization of the incident light. Figure 4d demonstrates the effect of conductivity enhancement by linearly polarized light, when the same single-point charging experiment is repeated as in Figure 4b,c. As can be seen in Figure 4d, excess charges can propagate further along the crystallites that better match their LMA with the polarization direction. Using this mechanism, it is possible to “guide” the charge propagation along a certain direction within the crystallite network, controlled externally simply by changing the polarization direction.

The single-point charging experiments clearly demonstrate the effects of light-assisted charge propagation within DHTA7 crystallite networks. However, in these experiments the same probe is used first to inject the charges and subsequently to image the charge distribution. Thus, such experiments inherently do not allow to directly probe the charge propagation through a crystallite as a function of time. Only indications of the time-dependent charge propagation were observed in the single-point charging experiments by varying the scan speed and illumination conditions after the charging. For this reason, the experiments presented in the following subsections use an external contact to inject the charges and EFM measurements to temporally resolve charge propagation within the crystallites.

2.5. Time-Resolved Charge Propagation of Externally Injected Charges

Using the samples and the setup as shown in Figure 3b allows for charge injection into the crystallites without the EFM probe. The same principles of light-assisted charge manipulation in DHTA7 crystallites—as shown in Figure 4—were also tested with the charges injected from an “external” contact.

Figure 5a presents a topography overview (left) and the corresponding EFM phase prior to charge injection (right) of crystallites grown on hBN and connected to a graphite flake (bottom-right) that acts as a grounded contact. In order to probe charge propagation within the crystallite as a function of time, a single line that intersects the crystallite is repeatedly scanned by EFM at a certain distance from the graphite contact. Thus, the y axis in Figure 5b represents a time scale and the scanning frequency (0.6 Hz) defines the time delay between the two points of vertical intersection lines.

Figure 5b demonstrates charging and discharging of a crystallite when \( V_{SG} \) is switched between 0 and \( -10 \) V or vice versa (considering the sign of \( V_{SG} \) as shown in Figure 3b). The right two panels show charging of the crystallite—seen as EFM phase shifts—with and without an external light source respectively. The particular measuring point in Figure 5b was 4.10 \mu m away from the graphite contact. An unpolarized 520 nm laser beam was focused to a \approx 35 \mu m diameter spot near the tip apex. The entire crystallite in between the graphite contact and the EFM probe was illuminated. Figure 5c shows EFM phase cross-sections taken along the middle of the crystallite, comparing the response with and without laser illumination. As observed in single-point charging experiments, much stronger response is
detected when an external light source illuminates the crystallite. More details on the $V_{\text{SG}}$-dependence of the crystallite response are provided in Section S3, and within Figure S3 in the Supporting Information. Additional experiments with point-charging of the crystallite (shown in Figure 5) with the graphite side contact (Figure S4, Supporting Information), faster bias alteration (Figure S5, Supporting Information), and with changing illumination conditions (Figure S6, Supporting Information) are presented in Section S4 in the Supporting Information.

Since EFM detects long range electrostatic interaction as a phase shift, for any semi-quantitative evaluation of the data it is required to connect the measured EFM phase shift ($\Delta \phi$) to the actual potential values at the sample surface ($V_{\text{needle}}$). If the capacitive interaction between the tip and the sample is approximated as an ideal capacitance, the measured phase shift will be proportional to the square of the potential difference between the tip and the surface,$^{[55]}$ as: $\Delta \phi = \alpha (V_{\text{needle}} - V_{\text{tip}})^2$, where $\alpha = (Q/2k)(\partial^2 C/\partial z^2)$, here $Q$ and $k$ stand for the quality factor and the spring constant of the cantilever, and $\partial^2 C/\partial z^2$ represents a second partial derivative of the local tip-sample capacitance with respect to the tip-sample distance.$^{[55]}$

Figure 5d shows an example of the dependence of $\Delta \phi$ when ($V_{\text{needle}} - V_{\text{tip}}$) is swept forward and backward between $-8$ and $+8$ V. The curve presented in Figure 5d is shifted such that the minimal value matches zero on the $x$-axis. This shift of $\Delta \phi$ from zero in ($V_{\text{needle}} - V_{\text{tip}}$) comes from the work-function difference between the tip and the crystallite (also see Figure S3, Supporting Information). A quadratic fit to the data—presented in Figure 5d—yields $\alpha = (3.5 \pm 0.8) \times 10^{-3}$ radV$^{-2}$. Thus, it is possible to convert EFM phase shifts into potential changes at the sample surface. Figure 5e presents the recalculated surface potential from the EFM phase shifts presented in Figure 5c. The fitting to the potential evolution was done by assuming a semi-infinite RC delay line model (inset of Figure 5e) response to a step voltage excitation.$^{[56]}$ Knowing the gate capacitance and the geometry factors (including the distance from the contact), the only fitting parameter is the resistivity of the RC line, i.e., the resistivity of the DHTA7 crystallite. The resistivity values obtained for the crystallite shown in Figure 5e are $\rho_{\text{on}} = 3.47 \times 10^7 \Omega$m and $\rho_{\text{off}} = 1.12 \times 10^9 \Omega$m, with and without 520 nm laser illumination, respectively. Further, the same model was tested with respect to the lateral distance from the
graphite contact to the points where the measurements were carried out, and an example is presented in Figure 5f. More details on a semi-infinite RC delay line model are provided in Section S5 in the Supporting Information including a scheme of the assumed model geometries (Figure S7, Supporting Information).

Using a semi-infinite RC delay line model,[56] the resistivity of several DHTA7 crystallites was estimated, for 520 and 635 nm unpolarized laser excitations with beam power of 0.8 ± 0.2 mW and without illumination. The obtained values were rather consistent and varied less than 60%. The following average resistivity values considering five different DHTA7 crystallites were obtained: $(4.1 \pm 2.4) \times 10^6 \, \Omega \, m$ for 635 nm excitation, $(6.3 \pm 3.5) \times 10^7 \, \Omega \, m$ for 520 nm excitation, and $(2.5 \pm 1.1) \times 10^8 \, \Omega \, m$ for the cases without external illumination. As such, light-assisted enhancement of the conductivity of DHTA7 crystallites by a factor of $10^4$ and $10^5$ was obtained for 635 and 520 nm excitations, respectively. The observed difference in conductivity enhancement between red and green lasers is in agreement with the absorption spectra of DHTA7 crystallites (Figure 2h). Using higher laser power would enhance conductivity even further; however, heating of the sample by the laser source was found to make EFM measurements unstable for reliable parameter extraction.

As demonstrated for the single-point charging experiments (Figure 4d), the effect of light polarization on the changes in the crystallite conductivity was also tested for charges injected from a graphite side contact. In the case presented in Figure 6, the slow scan axis was not disabled in order to obtain the angle between the crystallite and the fast scan direction and to better align the incident light polarization with the particular LMA direction. During the scan, $V_{SG}$ was altered between 0 and $-5 \, V$, and also the polarization of a 635 nm laser is quickly rotated (within 2–3 scan lines) between parallel and perpendicular to the LMA direction (with ±2° tolerance). The simultaneously obtained EFM phase image is presented in Figure 6b. The effect of the laser light polarization on the charging of the crystallites is striking. Only in the case when the incident light has the polarization parallel to the LMA of the crystallite a strong response in EFM to a change of $V_{SG}$ was observed. A slow rise of the potential after switching on the gate voltage was observed in the case of a light polarization perpendicular to the LMA direction, and was found to be about 50% higher than in the dark case. This was attributed to the fact that the optical path of the AFM system slightly depolarizes the beam, and the angle between the crystallite and the polarization direction cannot be perfectly tuned to match the absorption minimum. Nonetheless, the experiments presented in Figure 6 clearly demonstrate the possibility to control the conductivity of the organic crystallites only by changing polarization direction of the incident light beam. For additional measurements, please see Section S6 and Figure S8 in the Supporting Information.

3. Conclusion

In summary, we have demonstrated the possibility to control charge propagation in organic quasi-1D crystallite networks, epitaxially grown on hBN, using a light source. With light absorption acting as a mediator to free the charges from spatially localized traps, it is possible to “switch” the conductivity of the organic nanostructures on demand. Furthermore, by exploiting the anisotropic optical properties of organic crystallites, we demonstrate that it is possible to “guide” the charge propagation along a desired direction of the crystallite network merely by applying linearly polarized light.

Interfaces between organic semiconductors and 2D materials show great promise for future applications in electronics, optoelectronics, and sensing.[14,31,36,57] Going beyond extended organic layers and vertical heterostructures by employing inherent self-assembly and self-alignment of organic nanostructures on 2D materials,[13,14] can enable many novel functionalities. As an example, we have demonstrated control over charge propagation in organic nanostructures by changing of the light polarization direction. Further concepts could involve forming multilayer or core–shell based networks of organic nanostructures,[53] in order to enhance conductivity of the crystallites and to enable further functionalities through, e.g., formation of lateral p–n junctions of organic nanostructures.

4. Experimental Section

Preparation of hBN and hBN/Graphite Stacks: Flakes of hBN were prepared by mechanical exfoliation from single crystals (obtained from hq graphene), using a “scotch-tape” method, as described in ref. [58]. Thicker hBN flakes—≈200 µm wide—with height between 80 and
160 nm were chosen due to enhancement in optical contrast of DHTA7 crystallite networks, allowing fast inspection of the crystallites simply by means of optical microscopy. Graphite and few-layer graphene flakes were also prepared using a "scotch-tape" method from bulk Kish graphite. Flakes, 10–50 nm high and =400 µm long, were transferred on top of preselected hBN flakes in a way to cover only one side of the flake. The transfer was done using polydimethylsiloxane (Gel-Pak-DLG-X4) following the procedure described in ref. [38]. This way, a large area of the hBN flakes was left uncovered and allowed for uninterrupted subsequent self-assembly of the crystallite networks. Crystallites that were in contact with graphite were found quite frequently.

vdW Epitaxy of DHTA7 Fiber Networks: DHTA7 crystallite networks were grown on hBN by hot wall epitaxy (HWE),[58] at ~8 x 10⁻⁷ mbar base pressure of the growth chamber. The source and wall temperatures of the HWE system were set to 580 and 600 K, resulting in a growth rate of (0.35 ± 0.05) mono-layers (ML) per hour, where 1 ML is defined as a fully closed layer of up-right standing molecules that forms on the SiO₂ substrate surrounding hBN flakes. Similar growth behavior of up-right standing DHTA7 islands was reported on Al₂O₃ substrates.[60] Formation of long DHTA7 crystallites was observed for substrate temperatures ranging from 355 to 395 K. Individual crystallites longer than 300 µm were observed at higher substrate temperatures (380–395 K). In most cases, the surface coverage was ~0.60 ML.

Optical Absorption of Individual DHTA7 Crystallites: The absorption of several individual DHTA7 crystallites was measured in the visible range from 380 to 700 nm, using a Zeiss Axio Lab1 confocal microscope and a 100x magnification lens. hBN flakes were deposited onto PDMS/glass substrates, and significantly larger (than for the EFM experiments) DHTA7 crystallites were grown by increasing the deposition temperature and the growth time. DHTA7 crystallites used for these experiments were ~15 µm long, 4–6 µm wide, and 100–200 nm thick. Since all the layers in the support were transparent in the visible range, the absorption of individual DHTA7 crystallites in a transmission setup was measured. A monochromatic light source (illuminating from the bottom) was coupled to the optical microscope equipped with a camera with full manual control over the image acquisition properties (ensuring the same acquisition conditions for each wavelength). The light intensity was measured in integer steps of 5 nm within three selected regions of interest (ROI) (about 2 x 10 µm²). ROIs were selected on the organic crystallite (avoiding the edges) and on the hBN/PDMS/glass substrate on both sides ~5 µm away from the crystallite (to ensure uniform illumination intensity). From this, the optical absorption of the crystallites was obtained.

Linearly Polarized Optical Microscopy: The optical microscopy images with linearly polarized white light source (halogen lamp) were taken using a Zeiss Axio Lab1 confocal microscope, and a 20x magnification lens with ~10 mm working distance. A linear polarizer, mounted on a 360° manual rotation stage, was placed between the sample and the lens, and aligned with respect to the CCD camera of the microscope using a linearly polarized light source as a sample.

Light-Assisted EFM Setup: The morphology and EFM measurements were carried out on an Asylum Research MFP-3D AFM system operating under ambient conditions. Top-view AppNano Access EFM (Pt-Ir coated) probes were used, with a typical spring constant of ~2.7 Nm⁻¹ and tip radius of ~30 nm. EFM measurements were performed in a two-pass mode, with a lift height of 50 nm and V₀ = ±3 V. Semiconductor laser diodes (635 and 520 nm wavelengths) were used for light-assisted EFM measurements. Beam power was measured at the sample surface and was in all cases below 1 mW for the unpolarized, and below 0.5 mW for linearly polarized beams. The focusing optics (10x lens) of the AFM system was used to couple the laser beams and for positioning of the laser spot onto the sample surface. The spot diameter was estimated by an optical camera and determined to be 30–40 µm, yielding a light intensity at the sample surface below 2 µW µm⁻². Positioning of the laser spot was controlled independently from the tip and sample, with an accuracy of ±2 µm. Due to the complex optical path of the AFM, on the sample surface light polarization above 85% was retained for either parallel or perpendicular directions with respect to the x axis of the AFM scanner (with tolerance of ±2°).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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