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Tunable and switchable magnetoresistance of P3HT:PCBM organic framework

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ABSTRACT

This letter demonstrates a multifunctional electronic device based on an organic multiferroic fabricated with newly synthesized polythiophenes and fullerene derivative polymers with crystal sizes in the millimeter and micrometer scales, respectively. The novelty of the presented framework is the insensitivity to the fabrication process and physical demonstration of organic multiferroics. Devices with drastically different functionalities were fabricated using the same processing steps. We demonstrate a non-contact magnetic field sensor based on magneto-resistivity. Remarkably, the same device exemplifies a magnetic data storage characteristics.

1. Introduction

Heterojunctions of polythiophenes polymers, *e.g.*, poly 3-hexylthiophene-2,5-diyl (P3HT) blended with fullerene derivative molecules, *e.g.*, phenyl-C_{61}-butyric acid methyl ester (PCBM), are at the forefront of the organic photovoltaics and emerging organic ferromagnetism and magnetoresistance transistor technologies [1]. However, field-dependent and voltage-dependent magneto-resistant behavior remains debatable based on multiple particle-spin interaction mechanisms. This research investigates the potential underlying interactions responsible for the response of organic magnetoresistance within the P3HT:PCBM framework under electric and magnetic fields, pointing to organic multifunctional devices. Magnetoresistance is an imperative mechanism for spintronics for developing flexible magnetic field sensors and computer memory [2].

The individual constituents of an organic magneto-resistive framework, *i.e.*, fullerene-derivative molecules and polythiophenes, and their heterojunctions usually have positive magnetoresistances (negative is also fundamentally plausible) and can be responsive to even small magnetic fields. Majumdar *et al.* reported a 13% positive magnetoresistance for P3HT:PCBM when submitted to a 300 mT magnetic field, attributed to enhanced Coulombic attractions of the electron-hole pairs [3]. Ern and Merrifield [4] demonstrated triplet-polaron interactions to explicate the fluorescence of organic crystals, later discussed in terms of magnetoresistance by Desai *et al.* [5]. The model suggests that triplet excitons and polarons scatter, resulting in a charge carrier mobility reduction. Applying a magnetic field could quench the triplets (*e.g.*, triplet–triplet annihilation), leading to fewer scattering events and decreasing the electric resistance. Bobbert *et al.* proposed alterative mechanism based on bipolaron and polaron spin-blocking interactions, locking the charge carriers [6]. The density of bipolarons depends on the magnetic field, while their polarity hinges on the distance of their Coulombic repulsion. Majumdar *et al.* later reported a strong correlation between the magnetoresistance and magnetization of P3HT:PCBM blends, suggesting a similar mechanism to those observed in inorganic ferromagnetic materials [7].

The magnetic behavior within the P3HT:C60 framework exhibited Villari magnetostriction and converse magnetoelectricity [8], which depended on the illumination and P3HT crystallinity [8]. Ferromagnetism was also reported in P3HT:PCBM blends, affirming dependence on charge transfer efficiency, orientation, illumination, and P3HT crystallinity [9]. Millimeter-scale PCBM crystals were recently synthesized using P3HT:PCBM blends [10], where the PCBM crystals exhibited the largest magnetic domains (*ca.* 10s μm) of any organic magnetic material (~10 nm). However, the mechanisms for the magnetic field effects on these organic semiconductors with 'colossal' crystallites remains ambiguous. This study measures the magnetoresistance and the ferromagnetic response of P3HT:PCBM blends with large PCBM crystals, while explicating the mechanisms.

2. Materials and methods

Regioregular poly (3-hexylthiophene) (Rieke Metals) was completely dissolved in *ortho*-dichlorobenzene (ODCB) with a concentration of 35

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mg/mL. Phenyl-61-butyric acid methyl ester (Nano-C) was then added to the solution in a 1:1 weight ratio and stirred at 40 °C for 15 h. The solution was drop cast onto a 50 × 50 mm glass substrate. Samples were left in a controlled environment to cure for enhanced crystallinity. All fabrication steps were performed in an N_2 environment, while all characterization steps were done under ambient conditions.

The morphology of the fabricated samples was examined under a scanning electron microscope (SEM, FEI Quanta 200), while the magnetic phase was detected using a magnetic force microscope (MFM, AFMWorkshop-TT1). The surface conductivity of the synthesized P3HT:PCBM organic framework was probed using conductive atomic force microscope (C-AFM). The newly synthesized P3HT:PCBM crystallinity was characterized using an X-ray diffractometer (XRD, Philips XPert) with $\lambda = 1.5404$ Å at 45 kV. Magnetic characterization was performed using a Quantum Design MPMS in DC mode at room temperature and dark conditions. Magnetoresistivity was measured under different levels of magnetic field while applying a voltage between two brass needle probes and reporting the current (Keithley-6514) under halogen light source (3250 K) illumination.

3. Results and discussion

The first remarkable outcome of the synthesized organic polymer framework is the colossal crystal size (*ca.* 10s µm here vs. 10s nm previously [8,9]), attributed to enhancing the volume-to-surface area ratio [10]. We previously reported the synthesis of these relatively large-scale crystals [10], whereas the emphasis herein is on probing their multifunctional properties. The optical micrograph (Fig. 1a) exemplifies the ubiquity and size of the PCBM crystals. The P3HT and the PCBM remain in separate phases such that the P3HT solidification displaces the PCBM molecules and gives rise to colossal crystals. Fig. 1b is SEM micrograph illustrating the morphology of the rhombohedral PCBM crystals repeatably synthesized (several batches). Fig. 1c shows MFM micrographs of the P3HT:PCBM crystal, elucidating large magnetic domains. The MFM micrographs have are recalled from [10] to contextualize the multifunctional performance. Fig. 1d shows the conductivity map of P3HT:PCBM using C-AFM, illustrating a network of high conductivity domains clustered attributed to the dispersion of PCBM through the P3HT matrix. Fig. 1e shows XRD spectra, demonstrating the P3HT:PCBM crystallinity.

The volumetric magnetization of the P3HT:PCBM crystal blend (Fig. 2a.) [10] portrays soft magnetic behavior with a negligible remanent magnetization of 6.4memu/cm^3 and a low coercive magnetic field of 9.4 Oe. P3HT:PCBM has a trace quantity of pinning sites that stimulate the soft magnetic response and improve reversible magnetization (switchable magnetics). P3HT:PCBM have magnetic saturation surpassing many room-temperature organic ferromagnetic materials, *e.g.*, PANiCNQ (0.1 emu/g), 1,3,5-Trizaine (0.04 emu/g), single layer graphene (0.02 emu/g), and previous P3HT:PCBM films [11,12,13,14,15]. The enhanced response is attributed to the PCBM crystallinity acceptor, strengthening the unpaired electron exchange while weakening the electron–phonon interactions.

The conjugated π-bonds of P3HT allow for an electrically conductive behavior, while the donor–acceptor paradigm of P3HT:PCBM results in a semiconductor-type behavior. Spring-loaded brass needle probes were placed 5 mm apart to measure the transport along the surface of the fabricated films, intentionally encompassing multiple crystals. Since the latter is considered a defining attribute of the fabricated films, intrinsic to the film morphology, and contributed to the reported magnetoresistance. Future research can emphasize the transport phenomena of the individual crystals by miniaturizing the presented experimental setup shown in the inset of Fig. 2b. Fig. 2b plots the I-V curve in an aligned DC magnetic field, reporting an asymmetric response. The I-V curve becomes quasi-symmetric, exemplifying a quasilinear response in the first quadrant while being highly nonlinear in the third quadrant in the absence of a magnetic field. On the other hand, the I-V curves are unevenly linear at moderate biasing magnetic fields, *i.e.*, polarity-dependent slopes, attributed to the potential alignment of the magnetic spins with the bias field. The nonohmic-to-ohmic transition is due to the enhanced electron transport phenomena. The voltage polarity-dependence might be associated with spin–orbit mechanisms that prohibit spin scattering.

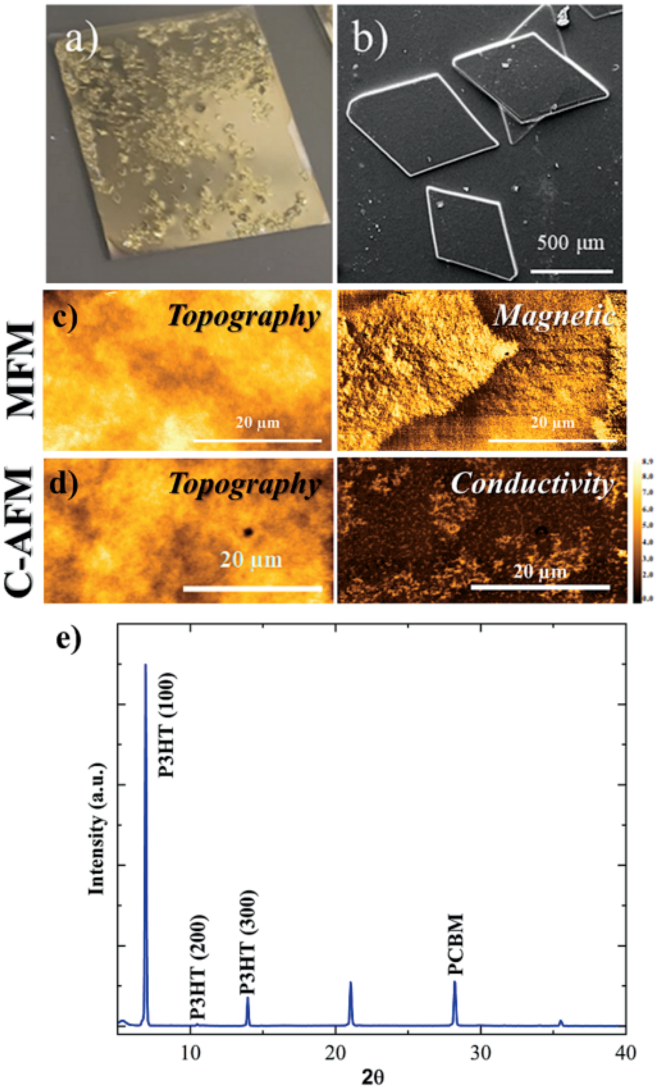

Fig. 1. (a) Synthesized P3HT:PCBM with colossal crystals (50 × 50 mm), (b) micrograph of the PCBM crystals, (c) MFM scan demonstrating the magnetic phase, (d) C-AFM mapping of surface conductivity, and (e) XRD spectra elucidating the crystallinity of the organic framework.

The magnetoresistance measurements revealed two distinctly different behaviors: field-dependent and field-switchable. Fig. 2c plots the magnetoresistance, calculated using $MR = [R(B) - R(0)]/R(0)$, where $R(0)$ and $R(B)$ are the resistances with and without an applied magnetic field, respectively, at a constant voltage (5 V). Initially, a field-switchable response occurs, where a 75% resistance drop coincides with a 200 Oe magnetic field and a negative voltage, followed by a relatively constant magnetoresistance as a function of the field. The initial run curve exhibits a negative Lorentzian magnetoresistive behavior, which can be explained with the e-h pair and bipolaron mechanisms proposed in [16] and [6], respectively. In these models, the charge carrier mobility is limited within hyperfine fields but can be released (or exacerbated, leading to a positive magnetoresistance) when an external magnetic field is applied. Further increasing the magnetic field has negligible effects on the resistance once the field is considered

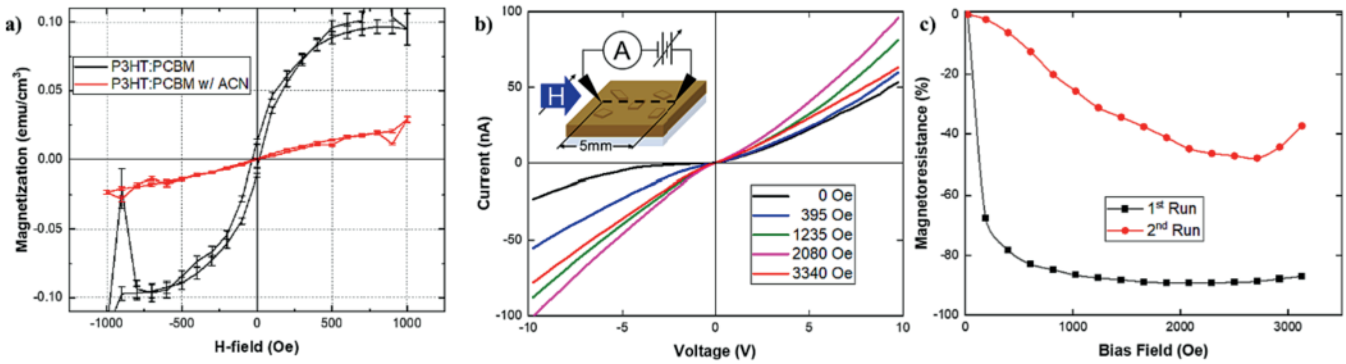

Fig. 2. (a) Magnetic hysteresis of large P3HT:PCBM crystals, (b) Current-Voltage curves at different magnetic field strengths ranging from 0 to 3400 Oe, and (c) the corresponding magnetoresistance response.

insignificant and the charge carrier mobility has been unleashed. Thereafter, *i.e.*, every run afterward, the magnetoresistance exhibits a quasi-linear response with increasing magnetic field at a slope of 22 %/kOe. The negative pseudolinear magnetoresistive behavior is explained by the bipolaron mechanism based on a different rate of polaron hopping [6] and by the excitonic pair mechanism [17]. Upon exceeding 2 kOe, a reversion response manifested, which could be due to classical magnetoresistance that typically requires large magnetic fields to have a meaningful effect. Overall, the field-dependent and field-switchable behaviors of P3HT:PCBM enable their use in organic magnetic field sensors due to the linearity of the magnetoresistance response and organic magnetic memory since the magnetic field switches conductivity ON/OFF. Finally, the Schottky barrier will be assessed in the future.

Ren *et al.* postulated the application of organic multiferroics in spintronics, which is demonstrated herein in terms of the switchable magnetoresistive response of P3HT:PCBM using a magnetic field to manipulate spin–orbit interactions. Fig. 3 exemplifies a uniform magnetic field (600 Oe) switches the current, leading to a magnetoresistance of 11 ± 3% for H > 200 Oe, substantiating their multifunctionality. The reduction in the current as a function of the number of cycles is attributed to the repeated switching of bias field and its effect of the magnetic spins. However, the long-term repeatability of the field-switchable response is a matter of for future research.

4. Conclusion

The colossal size of the newly fabricated P3HT:PCBM organic framework revealed electromagnetically manipulated functionalities. The magnetic field-dependent and switchable behaviors of P3HT:PCBM indicate suitability for sensing applications based on the magnetoresistance linearity and organic memory systems since moderate field results in switchable electrical conductivity, respectively. The approach can be extended to study the long-term switchable response of this organic multiferroics framework to transform wearable and flexible electronics.

CRediT authorship contribution statement

Scott Newacheck: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nha Uyen Huynh:** Visualization, Methodology, Investigation, Formal analysis, Data curation. **George Youssef:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

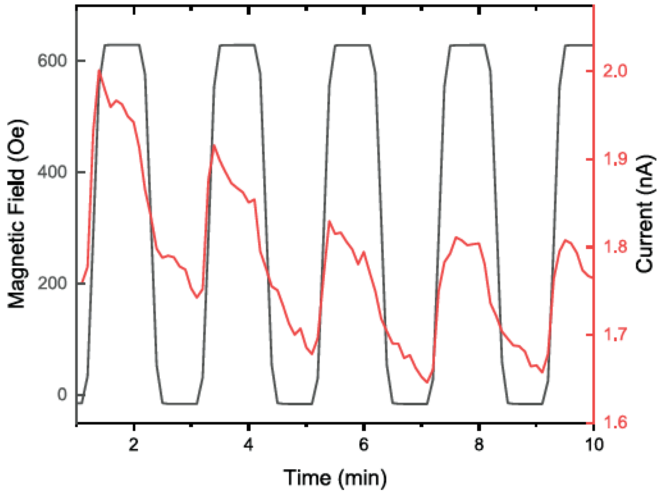

Fig. 3. Magnetic field switchable magnetoresistance in P3HT:PCBM under continuous illumination of white light at room temperature.

Data availability

Data will be made available on request.

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