

Polymer communication

Room-temperature organic ferromagnetism in the crystalline poly(3-hexylthiophene): Phenyl-C61-butyric acid methyl ester blend film

Bin Yang, Zhengguo Xiao, Yongbo Yuan, Tanjore V. Jayaraman, Jeffrey E. Shield, Ralph Skomski, Jinsong Huang*

Department of Mechanical and Materials Engineering, Nebraska Center for Materials and Nanoscience, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0656, USA

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ABSTRACT

Pronounced ferromagnetism was observed in a crystalline blend film of conjugated polymer poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) by using magnetic force microscopy measurements. A substantial room-temperature saturation magnetization of about 0.65 emu g^{-1} was measured by an alternating gradient field magnetometer. Multiple experimental evidences demonstrate the charge transfer from the P3HT to the PCBM and the formation of P3HT crystal domain are expected to be two critical factors for the originals of room-temperature organic ferromagnetism.

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1. Introduction

Conventional magnetic materials are mostly based on transition metals, including rare-earth elements. Organic ferromagnets as promising magnetic materials have caught the attention of the magnetism community due to potential applications such as organic spintronic devices, with logic, communications, and data storage. Their advantages are low cost, light weight, and large area production [1–5]. There have been tremendous efforts to search for transition metal-free ferromagnetic organic materials and developing the theory for the designing of such materials [2,4–8]. A popular strategy is to generate high-spin radicals or charge transfer complexes by doping or charge transfer. For example, an organic π -conjugated polymer, synthesized with large net spin quantum numbers through designing cross link and alternating connectivity of radical molecules with unequal spin quantum numbers, can order ferromagnetically at very low temperatures, below 10 K [9]. After that, significant efforts from multiple groups have been devoted to increasing the Curie temperature of synthetic organic ferromagnets up to room-temperature and beyond, which is important for practical applications [5,6,8,10]. Up to now, there are several reported transition metal-free RT ferromagnetic conducting or semiconducting polymers, such as perchlorate ion (ClO_4^-) doped

poly(3-methylthiophene) [5] and polyaniline:tetracyanoquinodimethane (PANiCNQ) [11]. However, the reproducibility of organic ferromagnetism is low and the intrinsic origin of ferromagnetism is still controversial.

We have discovered that a commercialized semiconducting polymer, poly(3-hexylthiophene) (P3HT), its crystalline phase exhibits RT ferromagnetism when mixed with phenyl-C61-butyric acid methyl ester (PCBM) with nanoscale phase separation (US patent application number **61/329,971**) [12]. Since P3HT is a model polymer for organic photovoltaic and transistor device applications, this discovery can not only provide new insight into organic ferromagnetism, but also lead to new applications of multifunctional organic optoelectronics by combining electronics, photonics, and magnetics. Based on our discovery [12], the multiferoic behavior of a P3HT nanowire and buckminsterfullerene (C_{60}) blend was recently observed [13]. Here, we report the room-temperature ferromagnetism in crystalline P3HT and PCBM blend films.

2. Experimental

The P3HT (Rieke, used as received), which was first pre-dissolved in 1,2-dichlorobenzene (ODCB) to form concentration of 35 mg mL^{-1} , was blended with PCBM (Nano-C, used as received) in a ratio of 1:1 by weight. The mixed solution was stirred for about 15 h at 40°C . The blend P3HT:PCBM film sample was prepared by drop casting a mixed P3HT:PCBM solution on the pre-cleaned

* Corresponding author. Tel.: +1 402 472 2640; fax: +1 402 472 1465.
E-mail address: jhuang2@unl.edu (J. Huang).

silicon substrate, and the wet film sample was slowly dried in the covered glass petri dishes in the glove box for more than 12 h. The RT magnetic hysteresis loop was measured by using an alternating gradient field magnetometer (AGFM) (Princeton Measurements Co. Model: 290002) with a sensitivity of 10 nemu, and confirmed by using a Quantum Design Magnetic Property Measurement System (MPMS-XL) magnetometer. The magnetization curves were obtained at RT in a maximum field of 1 T. For the bilayer P3HT/PCBM film samples, the P3HT solution (35 mg mL^{-1} , pre-dissolved in ODCB) was drop casted on the pre-cleaned silicon substrate, and after the P3HT film completely dried, the PCBM solution (35 mg mL^{-1} , pre-dissolved in an orthogonal solvent dichloromethane) was then drop casted on the P3HT layer. During the measurement process, we used plastic tweezers to carefully avoid the contamination of the sample and AGFM probe.

The magnetic impurity concentrations in P3HT and/or PCBM were measured by using atomic absorption spectrophotometer (Perkin–Elmer Model 3100 AAS) with nickel (Ni) and iron (Fe) lamps for the Ni and Fe concentration measurements, respectively. The AA standard solution was made by diluting iron AA standard with 1000 ppm Fe (iron metal in 3% hydrochloric acid) and nickel AA standard with 1000 ppm Ni (nickel metal in 3% nitric acid). The magnetic impurity concentrations of P3HT and PCBM were measured independently. We first weighted out some amount of

polymer and put it into a pre-cleaned crucible. The polymer was heated to $600 \text{ }^\circ\text{C}$ in an oven for 2 h, and then the residue was dissolved in 1 mL of concentrated hydrochloric acid for AAS measurement. Neither iron nor nickel should be lost upon heating unless the compound itself is volatile.

Magnetic force microscopy (MFM) images were obtained from a Digital Instrument Nanoscope IIIa Dimension 3100 Scanning Probe Microscopy with a low stray field cobalt-coated MFM tip. The MFM images were obtained through lifting mode with a tip-to-sample distance of 20 nm at RT in air. For all the MFM image measurements, prior to scanning, the charging effect was carefully excluded by purposely discharging the organic semiconductor film with an aluminum foil and using grounded conductive substrate such as indium tin oxide (ITO) glass. The external magnetic field was perpendicular to the sample surface during scanning samples by applying an external magnetic field of 200 Oe.

3. Results and discussion

The ferromagnetism of the crystalline P3HT:PCBM blend film was demonstrated by MFM imaging. Fig. 1a, c, e and g show the topography of the crystalline P3HT:PCBM blend film, the amorphous P3HT:PCBM blend film, the pristine P3HT film and the pristine PCBM film, while Fig. 1b, d, f and h show the respective

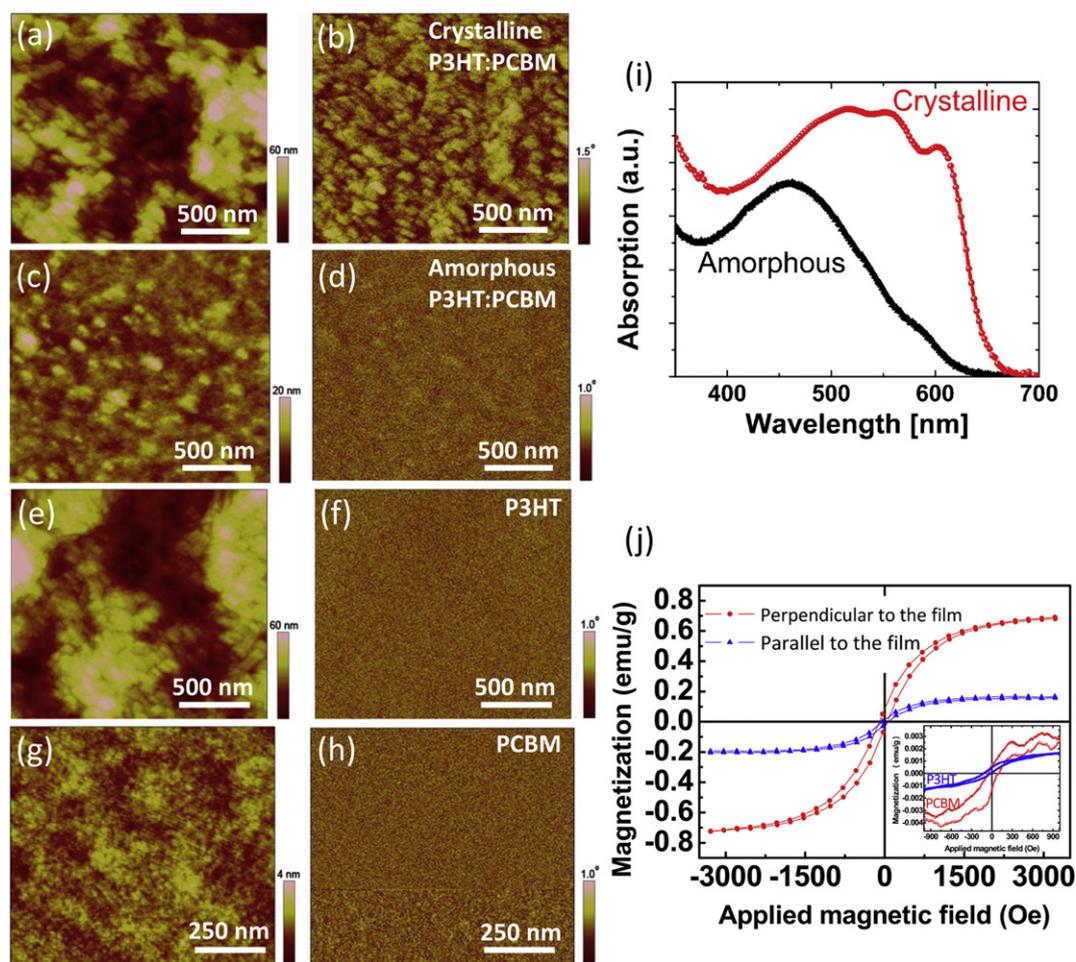


Fig. 1. MFM images of the crystalline P3HT:PCBM blend film: (a) topography; (b) phase. MFM images of the amorphous P3HT:PCBM blend film: (c) topography; (d) phase. MFM images of the pristine P3HT film: (e) topography; (f) phase. MFM images of the pristine PCBM film: (g) topography; (h) phase. (i) Absorption spectra of the slow drying film which shows a crystalline phase and fast drying film which shows an amorphous phase. (j) Magnetic hysteresis loops of the crystalline P3HT:PCBM blend film in the direction of perpendicular and parallel to the sample surface, and the inset shows the hysteresis loops of the pristine P3HT and PCBM films. All the hysteresis loops were measured under illumination of visible light.

phase contrasts of each sample. Magnetic domains with sizes ranging from tens to hundreds of nanometers were clearly observed in the crystalline P3HT:PCBM film, as shown in Fig. 1b. However, magnetic domains do not appear in the amorphous P3HT:PCBM blend film, as shown in Fig. 1d. This shows that the nanoscale magnetic domains are correlated with the crystallization of the P3HT. Here the crystallization of P3HT was realized by slowing down the drying rate of the wet P3HT:PCBM film, which was used to increase the power conversion efficiency of the polymer solar cells in our previous study [14]. The crystallization of P3HT was characterized by the absorption spectra of these films. As shown in Fig. 1i, an evident vibronic absorption peak is observed in slow drying P3HT:PCBM film which is caused by the crystallization of P3HT, whereas there is no similar absorption feature observed in the fast drying film, which indicates the amorphous of P3HT. On the other hand, neither pristine P3HT film (Fig. 1f) nor pristine PCBM film (Fig. 1h), fabricated by the slow-drying technique as well to ensure good crystallinity, shows evident magnetic domains. Therefore, the blending of P3HT and PCBM is critical for ferromagnetic ordering. In summary, there are two criteria for organic RT ferromagnetism: 1) crystallization of P3HT; 2) blending of the P3HT and PCBM. To confirm the organic ferromagnetism, a typical magnetic hysteresis loop with AGFM measurement was obtained at room-temperature in air. The out-of-plane saturation magnetization was found to be approximately 0.65 emu g^{-1} and the coercive magnetic field was about 100 Oe (Fig. 1j). The magnetic hysteresis was confirmed by the superconducting quantum interface device (SQUID) measurement. Fig. 1j shows that the magnetization is

anisotropic: the red line (in web version) (circles) represents the out-of-plane ferromagnetism, whereas the blue line (triangles) refers to in-plane ferromagnetism. In addition, the inset figure in Fig. 1j shows magnetization for pristine P3HT film and PCBM film, which are over 100 times smaller than their blend film. These observations suggest ferromagnetism in the crystalline P3HT:PCBM blend film.

One difficulty in the fabrication and characterization of organic ferromagnets is the possibility of contamination by ferromagnetic impurities (e.g., Fe and Ni). For the origin of ferromagnetic property of P3HT:PCBM blend film, the contamination by large ferromagnetic particles can be ruled out in our sample because the domains are uniformly distributed in the whole area, as shown by the MFM images. Since Ni and Fe are used as catalysts in the synthesis of P3HT and PCBM [15,16], there is a concern that these ferromagnetic impurities in P3HT and PCBM materials might cause the room-temperature ferromagnetism. In order to determine the maximum possible contribution of ferromagnetism from these impurities, the Ni and Fe concentrations in P3HT and PCBM were analyzed by AAS. The total concentrations of Ni and Fe were 876 ppm and 200 ppm, respectively. This result can partially explain the very low magnetizations of the pure P3HT film and PCBM film from the AGFM measurement, as shown in the inset of Fig. 1j. The total maximum magnetization caused by Ni and Fe impurities in P3HT:PCBM blend film at room-temperature is equivalent to approximately 0.09 emu g^{-1} , assuming all these impurities contributed to the ferromagnetism, which is seven times smaller than the saturation magnetization (0.65 emu g^{-1}) of

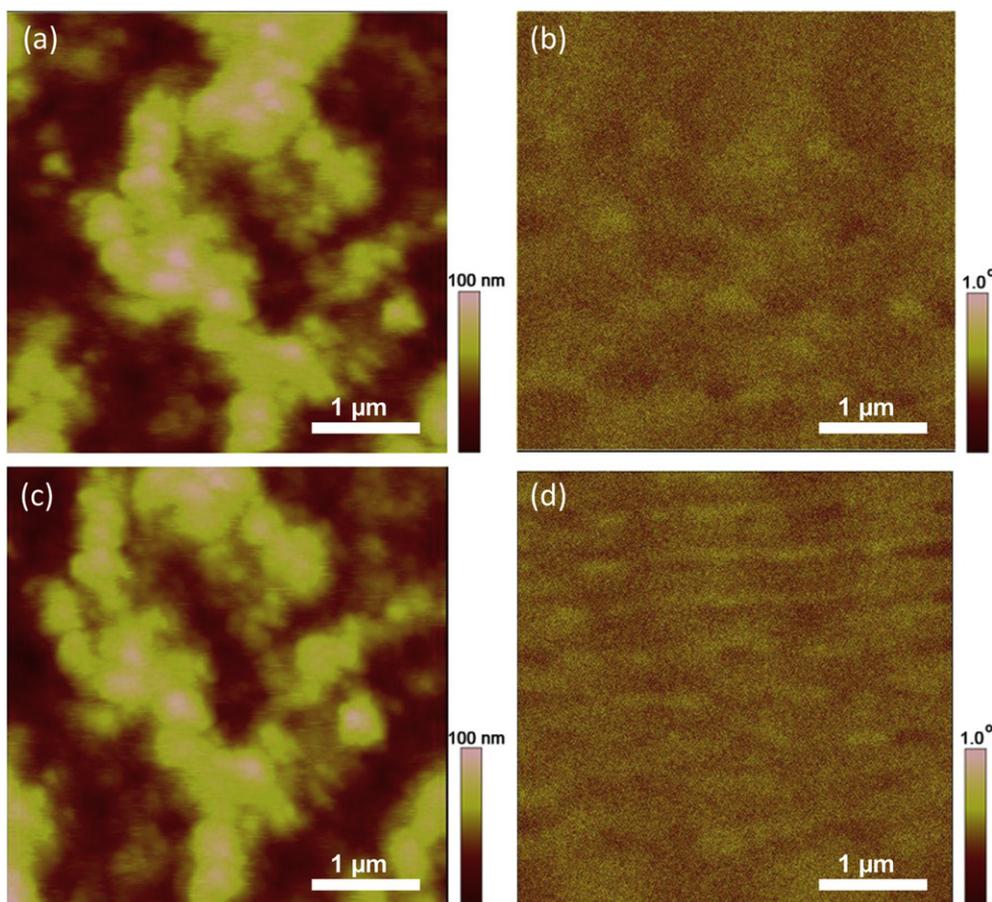


Fig. 2. Domain changes in an applied magnetic field without changing the film surface morphology. The crystalline P3HT:PCBM blend film in zero external magnetic field: (a) topography image; (b) phase image. The crystalline P3HT:PCBM blend film in a magnetic field of 200 Oe perpendicular to the film plane: (c) topography image; (d) phase image.

P3HT:PCBM blend film. Therefore, even though the magnetic impurities contributed some measured magnetization, the majority of magnetization originates from the intrinsic properties of the P3HT:PCBM blend film, in agreement with the absence of ferromagnetic domains in pure P3HT and PCBM films (Fig. 1).

To further confirm the organic ferromagnetism of P3HT:PCBM blend film, the MFM images were collected at an applied magnetic field of 200 Oe which is above the coercive field of this blend material. The topography and phase contrast before applying external magnetic field are shown in Fig. 2a and b, respectively. Despite of the weak magnetic response, which is most likely due to too fast drying speed of the wet P3HT:PCBM blend film, it can be observed that the randomly distributed domains were aligned in stripes (Fig. 2d) after applying an external magnetic field of 200 Oe without changing the morphology of the P3HT:PCBM film (Fig. 2c). This result can be explained by the rearrangement or motion of magnetic domains by the applied magnetic field so that the total energy can be minimized, which is commonly observed in ferromagnetic materials [17]. Thus, the behavior of the magnetic domains in the P3HT:PCBM blend film is a typical characteristics of ferromagnetism.

In order to demonstrate that the blending of P3HT and PCBM materials is critical for ferromagnetic ordering, a conclusive experiment was conducted by measuring the variation of ferromagnetism of a double layer P3HT/PCBM film after thermal annealing. A bilayer P3HT/PCBM was formed by drop casting PCBM

on P3HT layer supported by a clean silicon substrate. The PCBM material was dissolved in dichloromethane which is an orthogonal solvent for P3HT. The film was thermally annealed so that PCBM can diffuse into the P3HT film, which has been proved to form excellent interpenetrating bulk heterojunctions with a large contact area [18,19]. Under illumination of a 650 nm laser beam of 0.3 mW mm^{-2} , the magnetization nearly doubled after annealing the sample for 10 min, as shown in Fig. 3a. Since the material does not change during the thermal annealing process, this result directly excludes the contribution of impurities to the observed ferromagnetism. This evidence confirms that the blending of P3HT and PCBM material is crucial for the observed substantial ferromagnetism. Under thermal annealing, the PCBM preferably diffuses through the loose amorphous region of P3HT from top to the bottom of the P3HT film while it is relatively difficult to diffuse into the crystalline P3HT domains [19]. The contact area between the PCBM domains and the crystalline P3HT domains dramatically increases. With the diffusion of the PCBM into the P3HT, the individual pure P3HT domain size is reduced to within the exciton diffusion length in P3HT which facilitates efficient charge transfer from P3HT to PCBM and is expected to enhance the magnetization. As a result, the magnetization of bilayer P3HT/PCBM increased with annealing time.

The appearance of ferromagnetism by contacting between P3HT and PCBM was also directly observed in the MFM images of the double layer structure. A bilayer P3HT/PCBM was made by

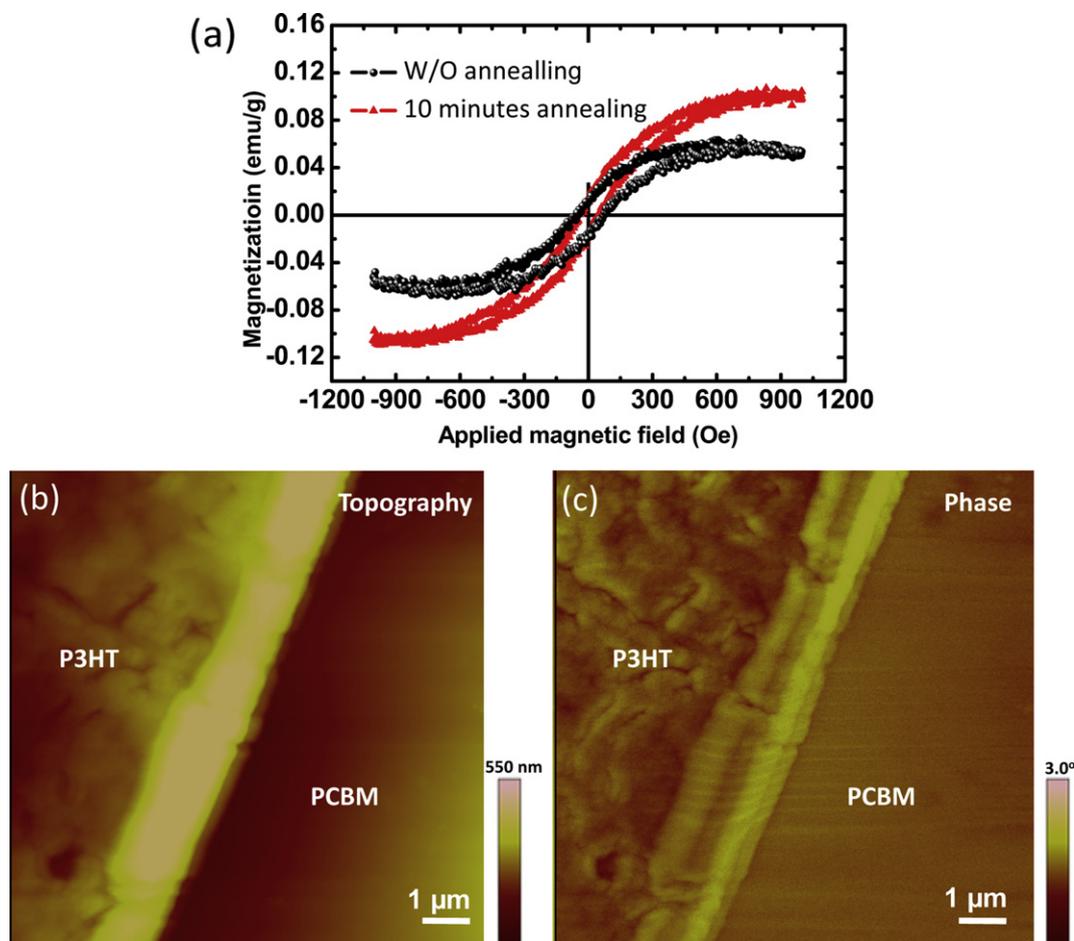


Fig. 3. (a) Magnetic hysteresis loops measured by AGFM of the bilayer P3HT/PCBM film before and after the thermal annealing at $150 \text{ }^\circ\text{C}$ for 10 min in air, both measurements conducted under illumination of a 650 nm laser beam of 0.3 mW mm^{-2} (b–c) the MFM images of the interface between P3HT layer and PCBM layer: (b) topography; (c) the corresponding phase contrast.

laminating a thin layer of P3HT onto pre-fabricated PCBM film which was spin-coated onto a clean silicon substrate. The MFM was used to scan the cross section region of the bilayer P3HT/PCBM film. Fig. 3b and c show the topography and phase contrast, respectively. No evident magnetic domains were observed in the non-contact region of P3HT and PCBM, whereas pronounced ferromagnetic domains can be found in the contact region of P3HT and PCBM.

If we assume that one PCBM molecule produces one uncompensated spin when contacting P3HT polymer, corresponding to a spin of $1 \mu_B$ per molecule, then a magnetic moment about 1.1×10^{18} spins (μ_B) magnetic moments can be generated in the P3HT:PCBM blend film. This is because there are about 1.1×10^{18} PCBM molecules in a P3HT:PCBM blend film obtained by drop casting 50 μL P3HT:PCBM mixture solution with concentration of 3.5% onto the silicon substrate. Therefore, the total measurable magnetization should be 5.3 emu g^{-1} , which is about one order of magnitude larger than the experimentally measured value of 0.65 emu g^{-1} . This result is reasonable because PCBM nanodomains are formed during the slow drying process of the P3HT:PCBM wet film. A part of PCBM molecules inside the nanodomains might not contribute the magnetization because of their non-contact with the P3HT polymer. This interface mechanism is also likely to provide a pathway for the interatomic exchange necessary to create room-temperature ferromagnetism, as opposed to low temperature magnetic order. However, if the charge transfer is the only reason for the observed ferromagnetism, the amorphous blend film should have higher ferromagnetism than the crystalline P3HT:PCBM blend film because the former has much larger donor/acceptor contact surface area due to the absence of phase separation. Conversely, the crystalline P3HT:PCBM blend film has larger ferromagnetism than the amorphous blend film as observed in Fig. 1a–d. Therefore, as mentioned previously, the pronounced ferromagnetism is observable due to not only the charge transfer from the P3HT to the PCBM in the blend film with large contact surface area, but also the crystallization of P3HT film. The intrinsic connection between the origin of ferromagnetism and crystallization of P3HT film is still under investigation.

4. Conclusions

In conclusion, we discovered room-temperature ferromagnetism in the polymer P3HT mixed with PCBM, and the observed

saturation magnetization was approximately 0.65 emu g^{-1} . The origin of organic ferromagnetism was associated with the crystallization of P3HT and charge transfer between the P3HT and the PCBM. The detailed origin of the ferromagnetism is still under investigation. This discovery can provide a guide for future ferromagnetic materials design and serve as a platform to explore the multiferoic electric-optical-magnetic applications.

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References

- [1] Korshak YV, Medvedeva TV, Ovchinnikov AA, Spector VN. *Nature* 1987;326:370–2.
- [2] Miller JS, Epstein AJ, Reiff WM. *Chem Rev* 1988;88(1):201–20.
- [3] Xiong ZH, Wu D, Vardeny ZV, Shi J. *Nature* 2004;427(6977):821–4.
- [4] Cinchetti M, Heimer K, Wüstenberg JP, Andreyev O, Bauer M, Lach S, et al. *Nat Mater* 2008;8(2):115–9.
- [5] Nascimento OR, de Oliveira AJA, Pereira EC, Correa AA, Walmsley L. *J Phys Condens Matter* 2008;20:035214.
- [6] Epstein AJ, Miller JS. *Synt Met* 1996;80(2):231–7.
- [7] Gotschy B, Gompper R, Klos H, Schilder A, Schütz W, Völkel G. *Synt Met* 1996;77(1–3):287–90.
- [8] Miller JS. *Adv Mater* 2002;14(16):1105–10.
- [9] Rajca A, Wongsriratanakul J, Rajca S. *Science* 2001;294(5546):1503.
- [10] Pejaković DA, Kitamura C, Miller JS, Epstein AJ. *Phys Rev Lett* 2002;88(5):57202.
- [11] Zaidi NA, Giblin SR, Terry I, Monkman AP. *Polymer* 2004;45(16):5683–9.
- [12] Huang J, Yang B, Shield J. *APS March Meet* 2011;56(1).
- [13] Ren S, Wuttig M. *Adv Mater* 2012;24:724–7.
- [14] Li G, Shrotriya V, Huang J, Yao Y, Moriarty T, Emery K, et al. *Nat Mater* 2005;4(11):864–8.
- [15] Chen TA, Wu X, Rieke RD. *J Am Chem Soc* 1995;117(1):233–44.
- [16] Humbles JC, Knight BW, LePeq F, Wudl F, Yao J, Wilkins CL. *J Org Chem* 1995;60(3):532–8.
- [17] Mohanty J, Engel-Herbert R, Hesjedal T. *Appl Phys A: Mater Sci Process* 2005;81(7):1359–62.
- [18] Lee KH, Schwenn PE, Smith ARG, Cavaye H, Shaw PE, James M, et al. *Adv Mater* 2010;23(6):766.
- [19] Treat ND, Brady MA, Smith G, Toney MF, Kramer EJ, Hawker CJ, et al. *Adv Energy Mater* 2011;1(1):82–9.