

Electrochemically Fabricated Phthalocyanine-based Molecular Conductor Films and Their Potential Use in Organic Electronic Devices

Masaki Matsuda^{1*}, Nobuaki Kinoshita¹, Mika Fujishima¹, Shukichi Tanaka², Hiroyuki Tajima³, and Hiroyuki Hasegawa⁴

¹*Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan*

²*KARC, National Institute of Information and Communications Technology, Kobe 651-2492, Japan*

³*Institute for Solid State Physics, the University of Tokyo, Kashiwa 277-8581, Japan*

⁴*Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan*

*E-mail address: masaki@sci.kumamoto-u.ac.jp

Nanocrystalline films of phthalocyanine-based molecular conductors were fabricated using a short-time electrocrystallization method with two indium tin oxide (ITO) electrodes. The size and morphology of the nanocrystals could be controlled by adjusting the electrocrystallization conditions, and the ITO substrate was successfully covered with nanocrystals of the molecular conductor. The J - V characteristics of devices with the configuration ITO/nanocrystals:C₆₀/Al showed a reverse rectifying effect accompanied by a photovoltaic effect under 660 nm wavelength irradiation, which is close to the gap between the HOMO and the LUMO of phthalocyanine.

By tuning the molecular arrangement and degree of charge transfer, many highly conducting materials of varying electronic structures have been reported in the field of molecular conductors. Such materials display fascinating phenomena such as superconductivity, metal-insulator transition, magnetic-field-induced superconductivity, and giant negative magnetoresistance.¹⁻³⁾ We expect that the high carrier mobility of molecular conductors could lead to their application as components of organic devices. To achieve practical applications, however, methods to fabricate thin film molecular conductors are desired.

So far, several fabrication methods have been reported, such as vapor deposition of the molecular conductor or the co-evaporation of component molecules.^{4,5)} Unfortunately, these techniques are costly and both time and energy consuming, and can only be applied to molecules that are resistant to heat decomposition. On the other hand, thin film fabrication by conventional wetting processes such as spin-coating is exceedingly difficult, as virtually all molecular conductors are insoluble in common organic solvents. Furthermore, molecular conductor films obtained by the spin-coating method, would display reduced carrier mobility owing to the random arrangement of the molecules. Thus, to obtain molecular conductor films, novel, simple techniques are required for covering substrates with nanocrystals.

Recently, nanocrystals formed from a CuTCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) charge-transfer complex have been fabricated by metathesis and electrochemical techniques.^{6,7)} Hasegawa reported a “nanoscale-electrocrystallization” method, and suggested that short-time electrocrystallization can scale down the size of the molecular conductors.⁸⁾ Since electrocrystallization is a conventional technique that can be adopted for constructing molecular conductors of varying electronic structures under ambient conditions, its use for the fabrication of molecular conductor films could well lead to time and energy savings.

Moreover, the technique is applicable to multiple systems that lead to the development of organic devices.

In this study, by employing two indium tin oxide (ITO) electrodes, we applied short-time electrocrystallization to the fabrication of nanocrystals and crystalline films of phthalocyanine-based molecular conductors having different electronic structures. Because of their high resistance to light and heat, phthalocyanines (Pcs) are not only widely used as dyes but also as components of p-type semiconductors in organic electronics devices such as organic light-emitting diodes (OLED), organic field-effect transistors (OFET), and organic photovoltaic cells (OPVC).⁹⁻¹¹⁾ This implies that our suggested approach has potential for practical applications. For OPVC, in particular, the high mobility of Pc-based molecular conductors could contribute toward improvement of the quantum efficiency. We thus fabricated $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ and $\text{Co}(\text{Pc})(\text{CN})_2 \cdot 2\text{CHCl}_3$ (where TPP = tetraphenylphosphonium and $\text{Co}(\text{Pc})(\text{CN})_2$ = dicyano(phthalocyaninato)cobalt), being a 3/4-filled one-dimensional conductor and a two-dimensional Mott insulator, respectively.^{12,13)} The morphology and the structural and electrical properties of the obtained nanocrystals covering the ITO electrode were characterized by electron microscopy, conducting AFM, and electron diffraction methods. We furthermore fabricated a device of the configuration $\text{ITO}/\text{Co}(\text{Pc})(\text{CN})_2 \cdot 2\text{CHCl}_3:\text{C}_{60}/\text{Al}$ and investigated its properties.

Nanocrystals were fabricated using a custom-built electrolysis set-up, employing two ITO substrates as the working electrodes. Before electrocrystallization, the ITO substrates were soaked in acetone and cleaned using ultrasonic agitation for 15 min, followed by their positioning in the electrolysis set-up at 5 mm distance from each other. The distance between the ITO electrodes affected both size and morphology of the obtained nanocrystals, and at a close distance, these parameters could be controlled through adjustment of the applied current.

Here, the distance of 5 mm is the technical limit of the custom-built set-up at the present stage. The starting materials of the molecular conductors, $\text{K}[\text{Co}(\text{Pc})(\text{CN})_2]$ and $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$, were synthesized by procedures described in literature.¹²⁾ To fabricate nanocrystals, short-time electrocrystallization under a constant current of 50 μA or 1 mA was performing using a saturated acetonitrile solution of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$, and a 1:1 acetonitrile/chloroform solution of $\text{K}[\text{Co}(\text{Pc})(\text{CN})_2]$. The nanocrystals obtained on the anode were observed using a JEOL JSM-6390LV scanning electron microscope (SEM) at an acceleration voltage of 15 kV, and selected-area electron diffraction (SAED) measurements were performed for $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ using a JEOL JEM-2000EX transmission electron microscope (TEM). The electrical properties of the obtained single crystals were measured using a JEOL JSPM-5200 scanning probe microscope (SPM), operated with a Nanoworld NCHPt cantilever. An OPVC of the structure $\text{ITO}/\text{Co}(\text{Pc})(\text{CN})_2 \cdot 2\text{CHCl}_3:\text{C}_{60}/\text{Al}$ was fabricated by vacuum deposition of commercially available C_{60} (Aldrich) on the obtained nanocrystalline films, followed by Al electrode deposition. The thicknesses of the ITO, C_{60} , and Al layers were 190, 50, and 30 nm, respectively.

Figure 1 (a) shows a SEM image of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ crystals deposited on the ITO electrode, using constant current of 50 μA for 90 s. Uniform needle-like crystals, generally ranging from 150 nm to 250 nm in width and 500 nm to 1 μm in length, suggest a similar one-dimensional molecular arrangement as observed in the bulk state. To further confirm the crystallinity and molecular arrangement of the obtained crystal, a SAED measurement was performed using a TEM (Fig. 1(b)). By using the lattice parameters of the bulk crystal of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$,¹²⁾ the diffraction pattern could be solved with an error of less than 5%. The results thus indicate that the nanocrystals grown on the ITO substrate have the same one-dimensional molecular arrangement as the bulk crystal. It should be noted that the dimensions of the obtained crystals are too large to induce a quantum effect, and the

electronic structure of the nanocrystals is the same as that for the bulk crystal. It is, therefore, suggested that the nanocrystals have an equally high hole mobility of ca. $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹²⁾

Figure 1(c) shows a SEM image of crystals of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$. In contrast to crystals obtained at $50 \mu\text{A}$ for 90 s ., a SEM image of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ crystals deposited on the ITO electrode at a constant current of 1 mA for 200 ms , shows the substrate surface to be nearly fully covered with the nanocrystals (Fig. 1(c)), allowing the fabrication of molecular conductor films whose crystal morphology can be controlled by adjusting the conditions used for short-time electrocrystallization. These results can be rationalized by the fact that the amount of product in an electrochemical reaction is both proportional to the electrolysis time and the current.

The molecular conductors exhibits various electronic states, and $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ forms a $3/4$ -filled one-dimensional metallic band.¹²⁾ Considering practical applications, it is important that the proposed film fabrication method can be applied to the fabrication of different electronic states. Figure 1(d) shows a SEM image of nanocrystals of $\text{Co}(\text{Pc})(\text{CN})_2 \cdot 2\text{CHCl}_3$ obtained by applying a constant current of 1 mA for 200 ms . Here, the HOMO, derived from Pc, contains a single electron and forms a half-filled band, thus making it a Mott insulator owing to on-site Coulomb repulsion.¹³⁾ The crystals fully cover the surface of the ITO electrode, and the observed plate-like morphology is similar to that observed for bulk crystals having a two-dimensional molecular arrangement.

To confirm the electrical conductivity of the obtained nanocrystals, the PtIr-coated SPM cantilever was brought into direct contact with a single nanocrystal, forming an ITO/nanocrystal/cantilever sandwich structure. The results obtained from measurement of the current versus voltage (I - V) characteristics for crystals of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ (Fig. 2(a)) and $\text{Co}(\text{Pc})(\text{CN})_2 \cdot 2\text{CHCl}_3$ (Fig. 2(b)) clearly revealed that both crystals are conductive and thus, short-time electrocrystallization is a reliable method for fabricating molecular conductor

films.

Because Pc-based semiconductors behave as p-type materials, the junction between the $\text{Co(Pc)(CN)}_2 \cdot 2\text{CHCl}_3$ Mott insulator and an n-type C_{60} semiconductor may be employed for constructing organic electronic devices such as photovoltaic cells. Using the nanocrystals fabricated on the ITO electrode, a bulk heterojunction (BHJ) type solar cell was readily obtained by depositing C_{60} , followed by Al electrode deposition. The current density versus voltage (J - V) characteristics, measured in the dark and under light irradiation ($\lambda_{\text{max}} = 660 \text{ nm}$), of the BHJ device with the ITO/ $\text{Co(Pc)(CN)}_2 \cdot 2\text{CHCl}_3$: C_{60} /Al configuration, as well as that of an ITO/ C_{60} /Al structured Schottky-type reference cell, are shown in Fig. 3(a) and (b), respectively. In dark conditions, the BHJ device showed reverse rectifying characteristics, while the reference device showed clear rectification behavior. Although similar reverse rectifying behavior has been reported for organic heterojunction systems that exhibit charge transfer between donor and acceptor molecules,¹⁴⁾ there are no reports on reverse rectification behavior for heterojunction systems involving ordinary closed-shell Pcs and C_{60} . Therefore, the uncommon reverse rectifying characteristics of the present BHJ system must be derived from the unique features of the $\text{Co(Pc)(CN)}_2 \cdot 2\text{CHCl}_3$ Mott insulator, whose half-filled HOMO band is split into upper and lower bands owing to electronic correlation. Following the cyclic voltammetry measurements reported in reference 15, the HOMO level of the Co(Pc)(CN)_2 unit was determined to be ca. 5.2 eV, which is below the typical work function of ITO of 4.5–4.7 eV.^{16–18)} Thus, in the case of our phthalocyanine-based Mott insulator, electronic injection from ITO into the upper HOMO band might be more favorable than hole injection from ITO into the lower HOMO band, leading to reverse rectifying characteristics when electron transport dominates the J - V characteristics.

Under illumination, the reference device did not show a photovoltaic effect, which is fully consistent with a previous report on this same Schottky-type device, showing that a

photovoltaic effect was absent under AM 1.5 illumination.¹⁹⁾ On the other hand, the BHJ device did show a photovoltaic effect by irradiation with light at a wavelength of 660 nm, corresponding to the Q-band (i.e., HOMO-LUMO excitation band) of Pc.²⁰⁾ Although there is room for improvement of the performance of this prototype device, the observed photovoltaic effect nevertheless indicates that excitons generated by light absorption in this Pc-based Mott insulator (composed of open-shell Pcs) are effectively separated into charge carriers by the heterojunction with C₆₀, suggesting the potential use of these molecular conductor films in organic electronic devices.

In summary, a short-time electrocrystallization method enabled us to fabricate nanocrystalline films of phthalocyanine-based molecular conductors on ITO electrodes. SEM imaging revealed that the size and morphology of nanocrystals could be controlled by adjusting the electrocrystallization conditions, and that the ITO substrate could be fully covered with nanocrystals of the molecular conductor. We, therefore, investigated the application of the fabricated films in organic electronic devices. The *J-V* characteristics of a device of the configuration ITO/Co(Pc)(CN)₂·2CHCl₃:C₆₀/Al, where Co(Pc)(CN)₂·2CHCl₃ is a phthalocyanine-based Mott insulator, showed a reverse rectifying effect accompanied by a photovoltaic effect. Our results demonstrate the utility of the short-time electrocrystallization method for the fabrication of molecular conductor films, and strongly indicate that their application in organic electronic devices is feasible. Further studies on these molecular conductor films having various electronic states will focus on their broader application in organic electronic devices such as OLEDs and OFETs.

Acknowledgements

This study was supported in part by Mazda foundation, Adaptable and Seamless Technology Transfer Program through Target-driven R&D (AS232Z01592D) from Japan

Science and Technology Agency, Grant-in-Aid for Scientific Research on Innovation Area of Molecular Degrees of Freedom (No. 23110720) from the Ministry of Education, Culture, Sports and Technology of Japan, and Grant-in-Aid for Scientific Research (c) (No. 24550204) from Japan Society for the Promotion of Science.

References

- 1) *Organic conductors, superconductors and magnets*, ed. L. Ouahab and E. Yagubskii (Kluwer Academic Publishers, 2004).
- 2) S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, T. Tokumoto, A. Kobayashi, and H. Kobayashi: *Nature* **410** (2001) 908.
- 3) N. Hanasaki, M. Matsuda, H. Tajima, E. Ohmichi, T. Osada, T. Naito, and T. Inabe: *J. Phys. Soc. Jpn.* **75** (2006) 033703.
- 4) Y. Takahashi, T. Hasegawa, Y. Abe, Y. Tokura, and G. Saito: *Appl. Phys. Lett.* **88** (2006) 073504.
- 5) N. A. Kato, M. Fujimura, S. Kuniyoshi, K. Kudo, M. Hara, and K. Tanaka: *Appl. Sur. Sci.* **130-132** (1998) 658.
- 6) A. R. Harris, A. K. Neufeld, A. P. O'Mullane, and A. M. Bond: *J. Mater. Chem.* **16** (2006) 4397.
- 7) K. Hiraishi, A. Masuhara, T. Yokoyama, H. Kasai, H. Nakanishi, and H. Oikawa: *J. Crystal Growth* **311** (2009) 948.
- 8) H. Hasegawa, T. Kubota, and S. Mashiko: *Thin Solid Films* **438** (2003) 352.
- 9) C. W. Tang and S. A. van Slyke: *Appl. Phys. Lett.* **51** (1987) 913.
- 10) Z. Bao, A. J. Lovinger, and A. Dodabalapur: *Appl. Phys. Lett.* **69** (1996) 3066.
- 11) C. W. Tang: *Appl. Phys. Lett.* **48** (1986) 183.
- 12) H. Hasegawa, T. Naito, T. Inabe, T. Akutagawa, and T. Nakamura: *J. Mater. Chem.* **8** (1998) 1567.
- 13) K. Morimoto and T. Inabe: *J. Mater. Chem.* **5** (1995) 1749.
- 14) H. Wang, J. Wang, H. Huang, X. Yan, and D. Yan: *Org. Electron.* **7** (2006) 369.
- 15) J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch, and J. Daub: *Adv. Mater.* **7** (1995) 551.

- 16) K. Sugiyama, H. Ishii, Y. Ouchi, and K. Seki: *J. Appl. Phys.* **87** (2000) 295.
- 17) J. S. Kim, J. H. Park, and J. H. Lee: *Appl. Phys. Lett.* **91** (2007) 112111.
- 18) A. Sharma, B. Kippelen, P. J. Hotchkiss, and S. R. Marder: *Appl. Phys. Lett.* **93** (2008) 163308.
- 19) T. Taima, M. Chikamatsu, R. N. Bera, Y. Yoshida, K. Saito, and K. Yase: *J. Chem. Phys. B* **108** (2004) 1.
- 20) M. Matsuda, T. Naito, T. Inabe, N. Hanasaki, H. Tajima, T. Otsuka, K. Awaga, B. Narymbtov, and H. Kobayashi: *J. Mater. Chem.* **10** (2000) 631.

Figure captions

Fig. 1. (a) SEM image of TPP[Co(Pc)(CN)₂]₂ crystals deposited on ITO electrodes during the electrocrystallization process, at a constant current of 50 μ A for 90 s. (b) SAED patterns of a nanocrystal of TPP[Co(Pc)(CN)₂]₂. (c) SEM image of TPP[Co(Pc)(CN)₂]₂ crystals deposited on ITO with a constant current of 1 mA for 200 ms. (d) SEM image of Co(Pc)(CN)₂ crystals on ITO obtained via the same process.

Fig. 2. I - V characteristics of crystals of (a) TPP[Co(Pc)(CN)₂]₂ and (b) Co(Pc)(CN)₂ · 2CHCl₃, as measured by a PtIr SPM cantilever in an ITO/nanocrystal/cantilever sandwich configuration.

Fig. 3. J - V characteristics measurements in the dark (black dashed line) and under light irradiation ($\lambda_{\text{max}} = 660$ nm; red solid line) for (a) the BHJ device of configuration ITO/Co(Pc)(CN)₂:C₆₀/Al and (b) the Schottky-type reference device of configuration ITO/C₆₀/Al. The cross-section of the device is also depicted.

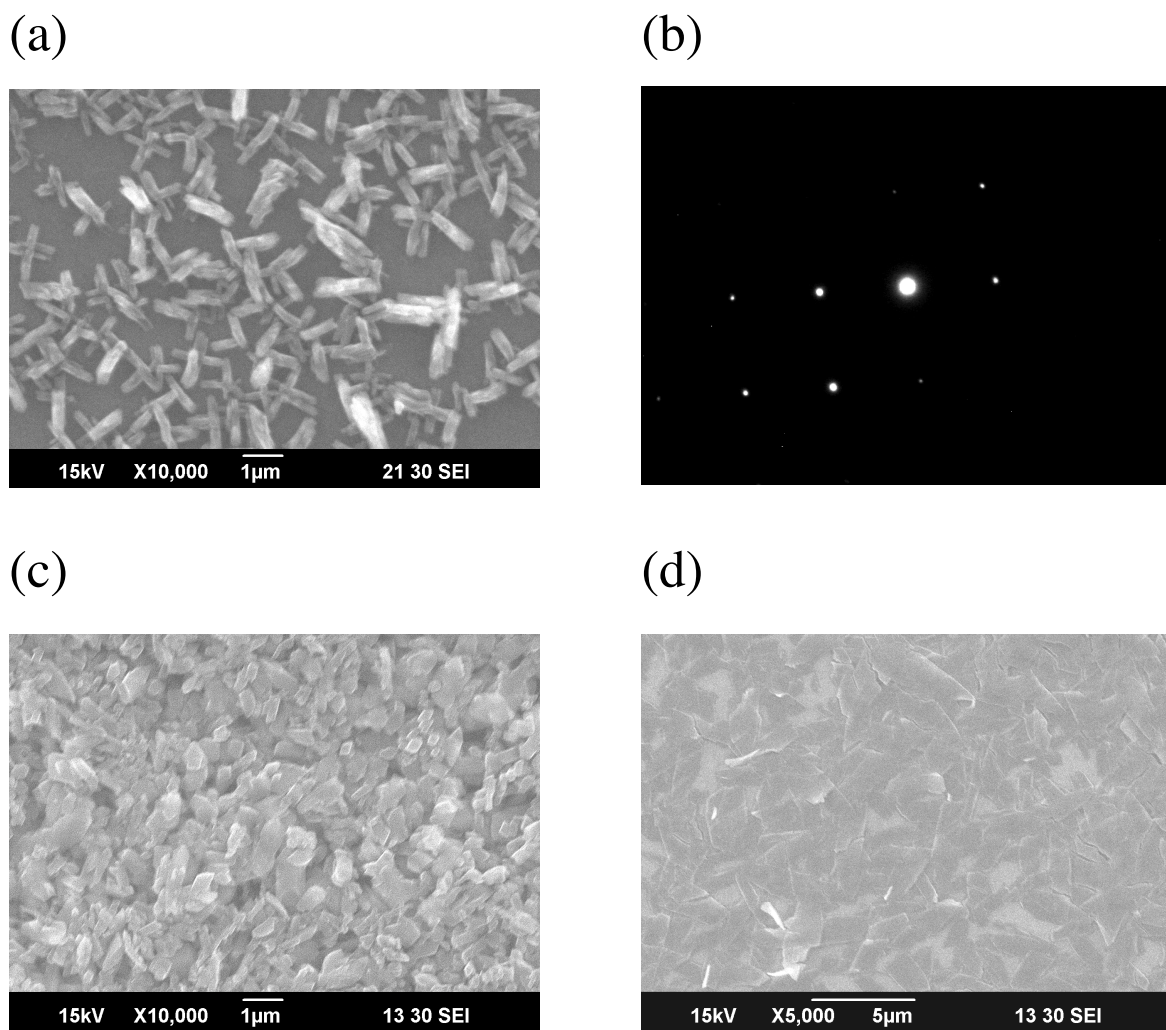


Fig. 1. (a) SEM image of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ crystals deposited on ITO electrodes during the electrocrystallization process, at a constant current of $50 \mu\text{A}$ for 90 s. (b) SAED patterns of a nanocrystal of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$. (c) SEM image of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ crystals deposited on ITO with a constant current of 1 mA for 200 ms. (d) SEM image of $\text{Co}(\text{Pc})(\text{CN})_2$ crystals on ITO obtained via the same process.

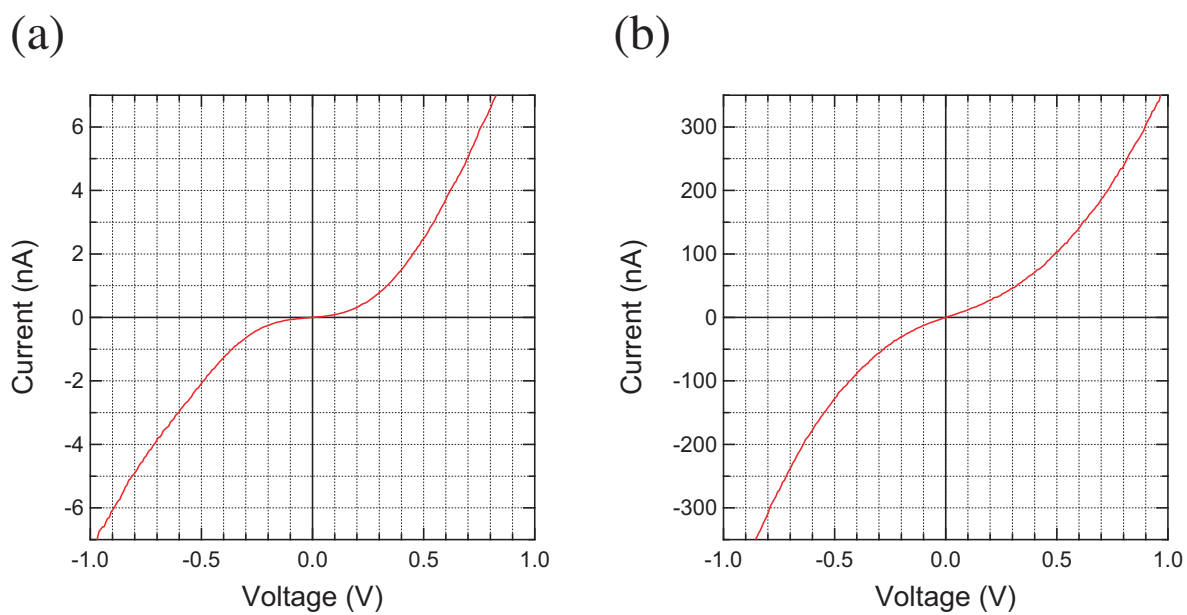


Fig. 2. $I-V$ characteristics of crystals of (a) $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ and (b) $\text{Co}(\text{Pc})(\text{CN})_2 \cdot 2\text{CHCl}_3$, as measured by a PtIr SPM cantilever in an ITO/nanocrystal/cantilever sandwich configuration.

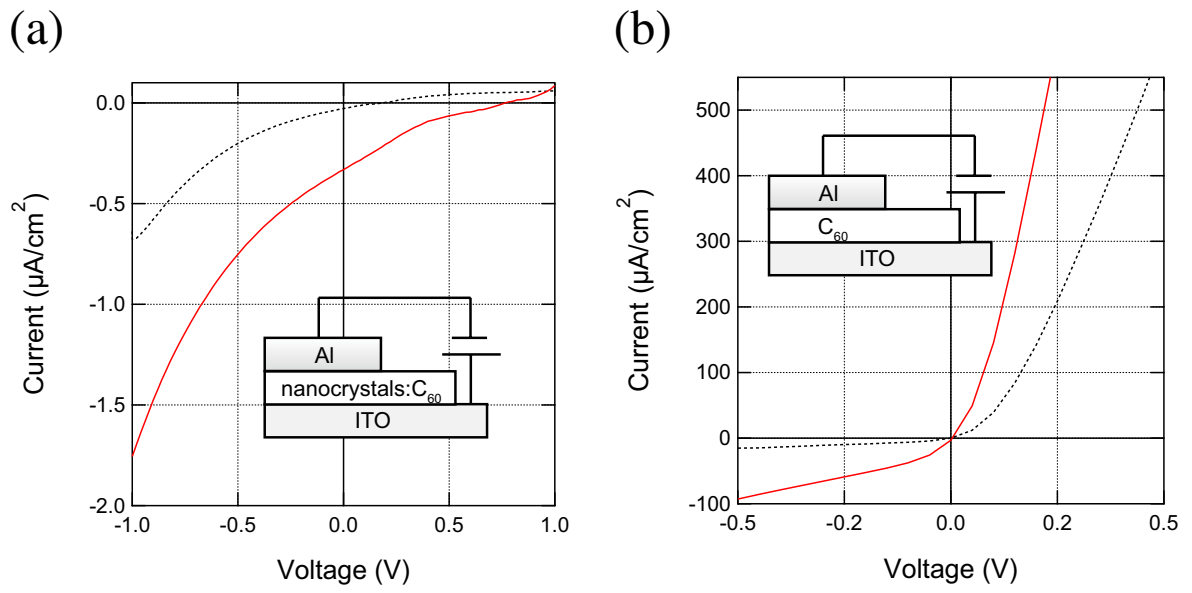


Fig. 3. J - V characteristics measurements in the dark (black dashed line) and under light irradiation ($\lambda_{\text{max}} = 660 \text{ nm}$; red solid line) for (a) the BHJ device of configuration ITO/ $\text{Co}(\text{Pc})(\text{CN})_2$: C_{60} /Al and (b) the Schottky-type reference device of configuration ITO/ C_{60} /Al. The cross-section of the device is also depicted.