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Solvent and electric field dependence of the photocurrent generation in donor:acceptor blend system*

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This paper reports that the blend films of poly (2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV) and N,N'-bis(1-ethylpropyl)-3,4: 9,10-perylene bis (tetracarboxyl diimide) (EP-PDI) with the weight ratio of 1:2.5 have been prepared by spin-coating from chloroform (CF) and chlorobenzene (CB) solutions respectively. The absorption spectra and the morphology of the blend films show that large crystal-like EP-PDI aggregates are formed in film prepared from CB solution, which corresponds to a new absorption shoulder near 590 nm, while there is no shoulder around 590 nm in the UV–Vis absorption spectra of the blend film from CF solution. The electric-field dependence spectra of the photocurrent generation quantum yield of the film from CB solution shows that at weak electric field the EP-PDI aggregates act as more efficient sensitizers, but at strong electric field the quantum yields become almost invariable over the entire spectral range no matter what the state of EP-PDI, monomer or aggregate. At strong electric field, the photocurrent generation yields of both films from CF and CB solution saturate and their yield spectra become spectrally similar, mentioning that at strong electric field the photoexcitons dissociate efficiently and the free charges are collected by the electrodes almost completely.

Keywords: solvent effect, morphology, electric field dependence, photocurrent generation
PACC: 7855K, 7280L, 8630J

1. Introduction

In recent years π-conjugated polymers were widely used for organic photovoltaic cells due to their unique features such as tuning of electronic functionality, easy structural modifications, possibility of self-assembling and mechanical flexibility.[1] But the understanding of photoinduced exciton dissociation in π-conjugated polymers remains a challenging problem. In a pure single-component sample, the photoexciton dissociation into pairs of charges needs to cost no less than 0.5 eV for a singlet excitation to overcome the strong Coulombic binding energy.[2] It is well known that photodissociation can be much more efficient in two-component donor–acceptor systems, as evidenced by the photovoltaic response of several systems.[3−6] A notable example is conducting polymer: C60 blend system.[3] Up to now, based on this system much attentions have been paid to the processing technique and device physics to obtain photovoltaic cells with high efficiency.[7,8] It was found that film processing conditions, such as thermal annealing time,[9] annealing temperature,[10] solvent effect[11] and applying electric field on the film,[9] affect the photovoltaic properties strongly in conjugated polymer: 1-(3-Methoxycarbonyl)-Propyl-1-1-Phenyl-(6,6) C61 (PCBM) blends. Especially when film-processing (poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV): PCBM) solvent was changed from toluene to chlorobenzene (CB), the energy conversion efficiency of photovoltaic cells was improved from 0.9% to 2.5%.[11]

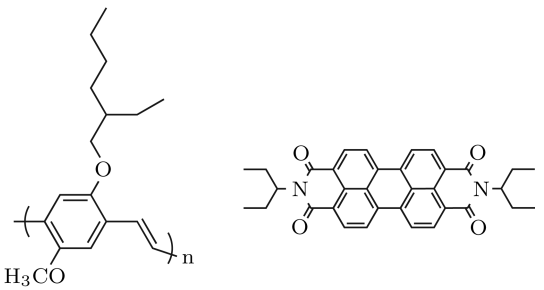
Perylene tetracarboxyldiimide (PDI) derivative is another important electron-acceptor candidate besides fullerene[6,12,13] due to its advantages such as the low-lying energy level of the lowest unoccupied orbital (about −5.8 eV), large molar absorption coefficients, good electron accepting and transporting properties, thermal stability and low cost. Recently many works of polymer: PDI bulk-heterojunction

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photovoltaic devices using PDIs as the acceptor have been finished,[14,15] which mainly involve the investigation of the material structure effect on the bulk-heterojunction photovoltaic performance. This calls for a profound investigation of the interplay among the processing, absorption behaviour, morphology and photocurrent generation in polymer: PDI blend system.

The current work is to study the relation between the film structure and the photocurrent generation of the blend films composed of MEH-PPV as a donor and EP-PDI as an acceptor (chemical structure shown in Fig.1) by changing film-processing solvents from chloroform (CF) to CB. The effects of solvent on absorptions, morphologies and photocurrent generations of the blend films were investigated by UV–visible absorption, atomic force microscopy (AFM) and the photocurrent measurement. A shoulder appearing near 590 nm in the absorption spectrum and the AFM image gives an indication of the formation of EP-PDI aggregates in the blend film from CB solution. The aggregates of EP-PDI act as more efficient sensitizers for photocurrent generation at weak electric field. But at high voltage the strong electric field makes the absorption photoexcitation dissociate and the free charge carriers collect effectively by the electrodes no matter what the state of EP-PDI.



(a) (b)

Fig.1. Chemical structure of materials, (a) MEH-PPV and (b) EP-PDI.

2. Experimental

MEH-PPV and EP-PDI were synthesized according to Refs.[16,17]. The molecular weight M_w of MEH-PPV was 7.15×10^5 g/mol and a polydispersity of 5.6 determined by gel permeation chromatography. Analytical grade CF and CB were dried over CaH_2 and distilled.

MEH-PPV: EP-PDI blend films (w/w, 1:2.5) were spin-coated from CF and CB solutions respectively. The active films for absorption, AFM and photovoltaic cells were prepared in the same experimental condition. The thicknesses of films were measured on AMBIOS XP-2 profilmeter. The film prepared from CF is about 100 nm while prepared from CB is about 80 nm. The absorption measurement was finished by using a Shimadzu UV-3100 Spectrometer. AFM measurement was carried out on a Nanoscope IIIa Dimension 3100.

Single-layer bulk-heterojunction photovoltaic devices were fabricated by using indium tin oxide (ITO, sheet resistance of $20\,\Omega/\square$)-coated glass substrates as the transparent anodes which were cleaned by using CF, acetone and iso-propanol sequently. The poly (ethylene dioxythiophene): poly(tyrenesulfonic acid) (PEDOT/PSS, Bayer PVP Al 4083) was spin-coated on the ITO glass, and then the film was dried in a vacuum oven at 120 °C for 10 min. The active layers were built by spin-coating. The photovoltaic devices were completed by vapour depositing an Al layer as the cathode through a mask at a pressure of 4×10^{-4}Pa. The effective area of the device was $2 \times 2\,mm^2$. The photocurrent spectra response was measured under illumination of monochromatic light from the xenon lamp by using a monochromator (Jobin Yvon, TRIAX 320) and detected by computer-controlled Stanford SR830 lock-in amplifier with Stanford SR540 chopper. Different voltage was applied by the computer-controlled Keithley 2400 SourceMeter for the electric field dependence of the photocurrent yield. A calibrated silicon photodiode (UDT Instruments) was used as a standard for the determination of the photocurrent generation quantum yield. The photocurrent measurement was performed in the vacuum at room temperature.

3. Result and discussion

3.1. Absorption

Figure 2 shows the absorption spectra of MEH-PPV: EP-PDI (w/w, 1:2.5) blend films from CB and CF solution, MEH-PPV in the spin-coated film and EP-PDI in three different states (in dilute solution, dispersed in polystyrene (PS) (w/w, 1:2.5) film prepared from CF solution and in cast film). Here the optoelectric-inactive PS is used as a polymer matrix

to observe the EP-PDI absorption in blend prepared from CF.

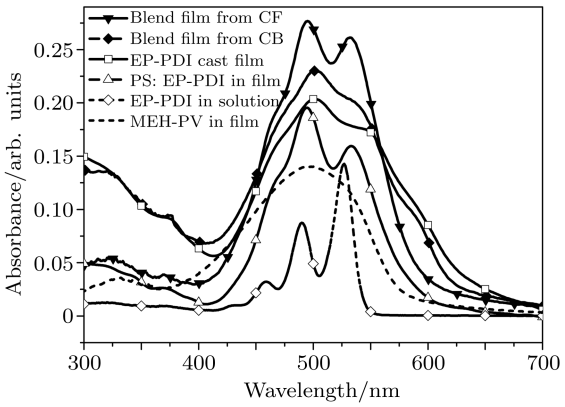


Fig.2. Absorption spectra of blend films MEH-PPV: EP-PDI (w/w, 1:2.5) from CF and CB solutions, MEH-PPV in spin-coated film, EP-PDI in three states (in dilute solution, dispersed in PS: EP-PDI (w/w, 1:2.5) and in cast film).

Comparing the absorption spectra of the dilute solution and cast film of EP-PDI, we find that the latter is much broader and features a broad red shifted tail while the absorption spectra of MEH-PPV in dilute solution (not shown) and spin-coated film are almost the same. The absorption spectrum of EP-PDI in dilute solution contains absorption peaks, which was assigned to the $\pi-\pi^*$ electronic transition of PDIs. The 0–0 transition band appears at 526 nm with vibronic progression at 488 nm and 457 nm. In the absorption spectra of EP-PDI dispersed in PS film there is an increase in absorbance both above and below the $\pi-\pi^*$ 0–0 transition relative to that of EP-PDI in dilute solution, which is a signature of aggregates with variable conformation. Their character ranges between H-type (i.e. parallel arrangement) and J-type (head to tail arrangement of the dipoles).[18] In the absorption spectra of EP-PDI cast film, a shoulder at 590 nm develops which could be attributed to the further aggregates.

In the absorption spectra of the blend films, the absorption band of the blend film from CF would be superposed of the two absorption bands of MEH-PPV film and EP-PDI dispersed in PS film while the absorption of the blend film from CB is superposition of MEH-PPV film and EP-PDI cast film. This means the strong aggregates of EP-PDI form when the blend film is prepared from CB solution, which is confirmed by the AFM measurement further.

3.2. Morphology

The AFM images (in Fig.3) show the morphological changes in the blend films from CF to CB solutions. The length scale is 5 μm. The change of colour covers a difference in height of 100 nm. The film from CF whose root mean square (RMS) of height is 4.94 nm is smoother than that from CB with RMS 7.05 nm. It can be seen that in the film from CB many large EP-PDI crystal-like domains grow, the largest one up to dimensions of 1.3 μm $\times$ 0.1 μm. The reason could be that CB has higher boiling point than that of CF. During the film-forming process from CB solution the planar EP-PDI molecules have more time to form crystal-like aggregates due to the strong π–π interaction between the molecules. The large crystal-like aggregates contribute to the absorption near 590 nm.

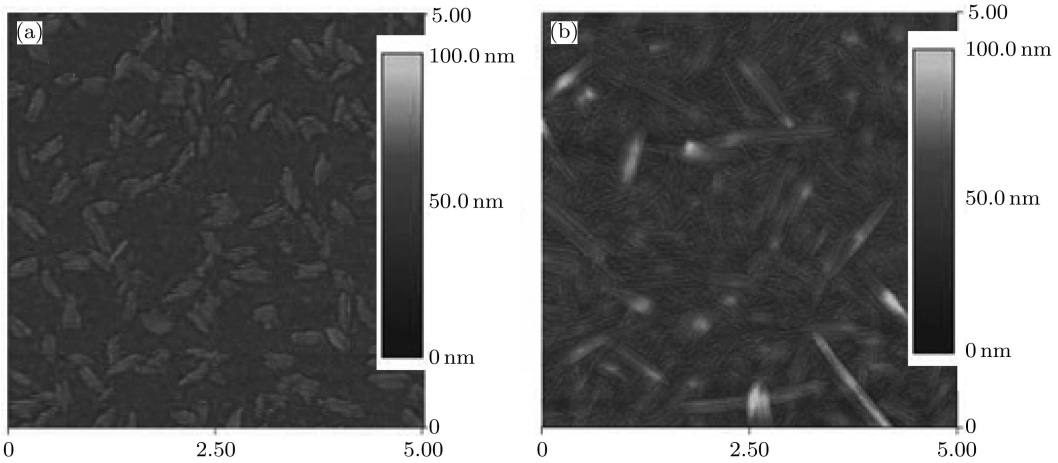


Fig.3. 5 μm $\times$ 5 μm AFM images recorded in tapping mode of films of MEH-PPV: EP-PDI (w/w, 1:2.5) from different film-forming solvents: (a) CF; (b) CB.

3.3. Photocurrent generation

Figure 4 shows the normalized photocurrent action spectra of device ITO/PEDOT/MEH-PPV: EP-PDI (from CF)/Al (defined as device 1) and ITO/PEDOT/MEH-PPV: EP-PDI (from CB)/Al (defined as device 2) under short-circuit condition and at high electric field. Comparing the photocurrent spectra of devices 1 and 2 under short-circuit condition, we find that the spectra of device 2 are much broader and a shoulder near 590 nm can be observed obviously. The shoulder of the photocurrent spectra near 590 nm are attributed to the aggregates which was mentioned in the absorption and morphology measurement. But at high electric field (about 2×10^6 V/cm), the shoulder vanishes and the normalized photocurrent spectra of two devices look similar.

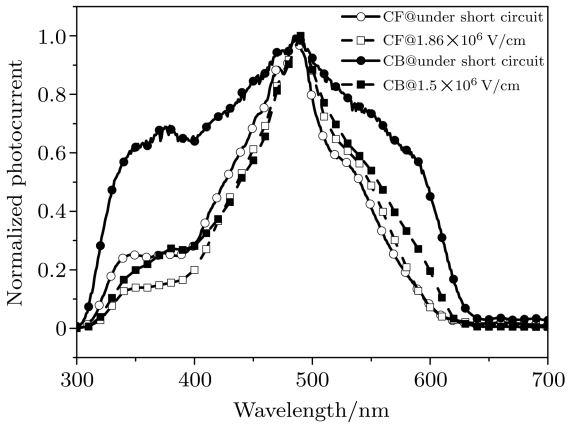


Fig.4. Normalized photocurrent spectra of device 1 under short circuit condition (open circle) and 1.86×10^6 V/cm (open rectangle) and those of device 2 under short circuit condition (filled circle) and 1.5×10^6 V/cm (filled rectangle).

In order to investigate the photocurrent generation process, sequent voltages from low (positive) to high (negative) were applied on the devices. The quantum yield of photocurrent generation ($\varphi_{\rm ph}$) (absorbance was considered) was calculated according to the following equation:

$$\varphi_{\rm ph} = \frac{1240 \times I_{\rm ph}(\mu {\rm A} \cdot {\rm cm}^{-2})}{\lambda({\rm nm}) \times P_{\rm in}(\mu {\rm W} \cdot {\rm cm}^{-2}) \times (1 - {\rm e}^{-2.3A})} \quad (1)$$

Where $I_{\rm ph}$ is the photocurrent ($\mu {\rm A} \cdot {\rm cm}^{-2}$), $P_{\rm in}$ is the incident light intensity ($\mu {\rm W} \cdot {\rm cm}^{-2}$), λ is the wavelength (nm) and A is absorbance of the active film.

The quantum yields of the devices at different voltages are shown in Fig.5. The results demonstrate that the photocurrent generation is strongly dependent on the applied voltage, i.e., the applied electric field $(V_{\rm oc} - V)/d$ where d is the sample thickness and $V_{\rm oc}$ is the voltage of the open circuit. For the device 1, at low electric field the yield is low (slightly above 10^{-3}) and almost independent of wavelength within the experimental accuracy. For the yield spectra of device 2, a maximum develops at about 590 nm where aggregates absorb at low electric field but at high electric field the maximum vanishes.

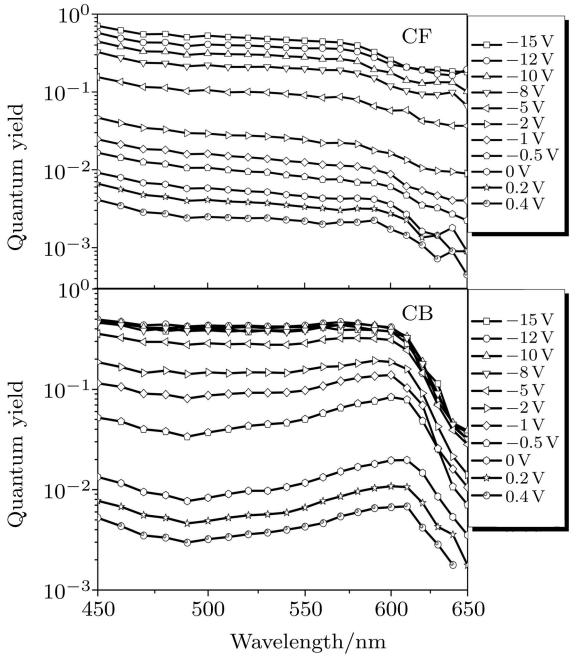


Fig.5. The quantum yield spectra of device 1 (up) and 2 (down) at different applied voltage.

Figure 6 shows the quantum yield as a function of electric field (data are extracted from Fig.5). Two different wavelengths (500 nm and 590 nm) were chosen to observe the field dependence of the quantum yield. The two wavelengths correspond to two different states of acceptor. 500 nm corresponds to the absorption of the bulk of EP-PDI and 590 nm corresponds to the absorption of the aggregates of EP-PDI in the film from CB solvent. For the device 1, the yield $\varphi_{\rm ph}(F)$ increases equivalently at 500nm and 590 nm and level off at 0.53 and 0.4 at the electric field of 1.86×10^6 V/cm. For the device 2, the yield $\varphi_{\rm ph}$(F) at 590 nm increases less strongly than that at 500 nm and saturates to a similar value of 0.43 at the electric field of 1.0×10^6 V/cm. In addition, comparing the $\varphi_{\rm ph}$(F) curve of devices 2 and 1 upon excitation both at 500 nm and 590 nm, the yield of device 2 saturates more easily at weak electric field.

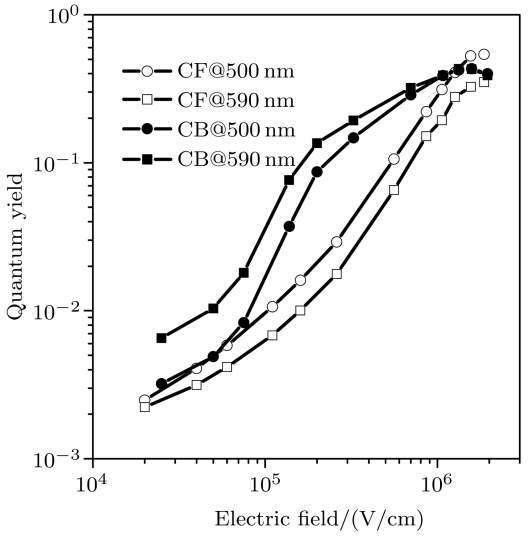


Fig.6. The quantum yield spectra of photocurrent generation of device 1 at 500 nm (open circle) and 590 nm (open rectangle) and device 2 at 500 nm (filled circle) and 500 nm (filled rectangle).

Combined with Fig.5 and Fig.6, the results demonstrate that (i) photogeneration in a 1:2.5 MEH-PPV: EP-PDI blend (both from CF and CB) is a strongly field dependent process, (ii) within the spectral range of S1←S0 transition of non-aggregate EP-PDI the action spectrum for photogeneration is flat for the device 1, (iii) for the device 2 at weak electric field the EP-PDI aggregates which absorb near 590 nm act as more efficient sensitizers of charge generation than in other spectral region, but at strong electric field the photocurrent generation spectra become flat, (iv) from moderate electric field (10^5 V/cm), the yield of device 2 (sublinear) increases less strongly than that of device 1 (superlinear).

The photocurrent generation in organic donor: acceptor photovoltaic system includes several processes. First, excitons generate after absorption of light, either by the donor or by the acceptor. The excitons diffuse in either of the domains towards the donor: acceptor interface where charge transfer will occur. After dissociation, a geminate of electron–hole pair which respectively comes from the donor and the acceptor is formed. Due to the low dielectric constants (ε_r) of the molecular materials and polymers (ε_r ranges typically from 2 to 4), these electron–hole (e–h) or polaron pairs are strongly bound by Coulombic interaction, with binding energies of typically several tenths of an electron volt. In order to generate a photocurrent, the bound e–h pairs must dissociate into free charge carriers and subsequently move to the electrodes before recombination processes take place.[19] The dissociation of e–h geminate pair is a crucial factor for photocurrent generation.

Classic Onsager theory mentioned that the dissociation of e–h germinate pair is strongly dependent on the electric field.[20] Furthermore, in terms of Onsager-type geminate pair dissociation, the improved ordering can increase the thermalization length of an e–h pair and these geminate e–h pairs are more loosely bound. Concomitantly, the dissociation yield of the e–h pair increases. Im *et al*[12] have found that in the blend film (phenyl substituted copolymeric polyphenylenevinylene (Ph-PPV): EP-PDI) with higher concentration of EP-PDI the e–h geminate pairs are more loosely bound than those in low concentration and the dissociation efficiency of e–h geminate pair increases rapidly. For the device 2, at low electric field the aggregates of EP-PDI induce the e–h dissociation more efficiently than the bulk of EP-PDI. In addition, the crystal-like domains supply an ordered channel for electron transport which reduces the probability of recombination or trapping. So at weak electric field the aggregates of acceptor act as more efficient sensitizers of photocurrent generation. But at strong electric field where photocurrent generation saturates regardless of the bulk state and aggregates of EP-PDI, they saturate to a similar value though they increase at a different speed. In the same principle, Fig.6 shows that the photocurrent generation of device 2 whose active film from CB consists of many small and large crystal-like clusters saturates at weaker electric field than that of device 1.

4. Conclusions

The current study substantiates the notion that the film-forming solvent and the morphology structure have a profound influence on the photocurrent generation of a MEH-PPV:EP-PDI donor:acceptor blend. Supported by absorption measurement and AFM technique it is observed that EP-PDI aggregates when the MEH-PPV: EP-PDI (w/w, 1:2.5) blend film is processed from CB solvent. The electric field dependence of photocurrent generation shows that the e–h geminate pairs in EP-PDI aggregates are loosely bound and at weak electric field the aggregates act as a more efficient sensitizer but at strong electric field the spectrum of photocurrent generation becomes flat regardless of the states of EP-PDI.

References

[1] Hoppe H and Sariciftci N S 2004 *J. Mater. Res.* **19** 1924

[2] Rissler J, Bässler H, Gebhard F and Schwerdtfeger P 2001 *Phys. Rev.* B **64** 045122

[3] Sariciftci N S, Smilowitz L, Heeger A J and Wudl F 1992 *Science* **258** 1474

[4] Tian R Y, Yang R Q, Peng J B and Cao Y 2005 *Chin. Phys.* **14** 1032

[5] Feng W, Cao M, Wei W, Wu H C, Wan M X and Yoshino K 2001 *Acta Phys. Sin.* **50** 1157 (in Chinese)

[6] Schmidt-Mende L, Fechtenkotter A, Mullen K, Moons E, Friend R H and MacKenzie J D 2001 *Science* **293** 1119

[7] Ma W L, Yang C, Gong X, Lee K and Heeger A J 2005 *Adv. Funct. Mater.* **15** 1617

[8] Li G, Shrotriya V, Huang J, Yao Y, Moriarty T, Emery K and Yang Y 2005 *Nat. Mater.* **4** 864

[9] Padinger F, Rittberger R S and Sariciftci N S 2003 *Adv. Funct. Mater.* **13** 85

[10] Mihailetchi V D, Xie H X, de Boer B, Koster L J A and Blom P W M 2006 *Adv. Funct. Mater.* **16** 699

[11] Shaheen S E, Brabec C J, Sariciftci N S, Padinger F, Fromherz T and Hummelen J C 2001 *Appl. Phys. Lett.* **78** 841

[12] Im C, Tian W J, Bässler H, Fechtenkotter A, Watson M D and Müllen K 2003 *J. Chem. Phys.* **119** 3952

[13] Feng W, Xu Y L, Yi W H, Zhou F, Wang X G and Katsumi Y 2003 *Chin. Phys.* **12** 426

[14] Li J L, Derschke F, Wu J S, Grimsdale A C and Müllen K 2006 *J. Mater. Chem.* **16** 96

[15] Shin W S, Jeong H H, Kim M K, Jin S H, Kim M R, Lee J K, Lee J W and Gald Y S 2006 *J. Mater. Chem.* **16** 384

[16] Neef C J and Ferraris J P 2000 *Macromolecules* **33** 2311

[17] Langhals H 1985 *Chem. Ber.* **118** 4641

[18] Delcano T, Duff J and Aroca R 2002 *Appl. Spectrosc.* **56** 744

[19] Brabec C J, Zerza G, Cerullo G, De Silvestri S, Luzzati S, Hummelen J C and Sariciftci N S 2001 *Chem. Phys. Lett.* **340** 232

[20] Onsager L 1938 *Phys. Rev.* **54** 554