# Bi-layer GaOHPc:PCBM/P3HT:PCBM organic solar cell

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**Abstract:**. For production organic bulk heterojunction polymer solar cell one of the best materials is regioregular poly-3-hexylthiophene (P3HT), which is widely used as a donor molecule and a hole transporter, with soluble fullerene derivative (PCBM) as acceptor and electron transporter. The main drawback of this highly efficient blend is its limited spectral range, covering only 350-650 nm spectral interval. So main aim of present work was to extend the spectral range of the cell up to 850 nm by adding second bulk heterojunction layer of complementary absorption spectrum to P3HT:PCBM layer. For this purpose hydroxygallium phthalocyanine (GaOHPc) and PCBM blend was used as additional layer because GaOHPc has strong and wide intermolecular charge transfer (CT) absorption band around 830-850 nm. Thus novel organic bi-layer bulk heterojunction system (GaOHPc:PCBM/P3HT:PCBM) has been built by spin coating technique having high charge carrier photogeneration efficiency in 350 – 850 nm spectral range. It was found that thermal annealing in vacuum at 100C increases short circuit photocurrent external quantum efficiency (EQE) values more than 2 – 3 times, and these values reach more than 45%  at P3HT absorption band (525 nm) and 25% at GaOHPc band (845 nm) for low light intensities ($10^{12}$ photon/(cm$^2$*s)).

*Keywords: Full polymer film, heterojunction, organic solar cell.*

## 1. Introduction

At present, crystalline Si solar cells are by far most dominant PVs used, occupying more than 95% of the market [1]. But the main obstacle for the market implementation of these cells is the large production cost of Si-based technologies [2]. A promising approach towards low-cost photovoltaic devices is fabrication of solar cells based on organic materials [3-6]. The bulk heterojunction approach appears to be one of the most promising concepts of creating efficient, low-cost and easily producible solar cells [7,8]. For this purpose one of the best materials is regioregular poly-3-hexylthiophene (P3HT) [8-11], which is widely used as a donor molecule and a hole transporter, with soluble fullerene derivatives as acceptors and electron transporters. Blends of these molecules in PV cells exhibit the efficiency of light power conversion up to 5% [9-11]. Still, it is not sufficient to meet realistic requirements for commercialization. The main drawback of this highly efficient blend is its limited spectral range [7-9], which covers 350–650 nm interval, allowing only ~ 35% of the full solar spectrum energy to be used. In the present work, we tried to extend the spectral range of the cell by additional bulk heterojunction layer of hydroxygallium phthalocyanine (GaOHPc), which has a strong and wide intermolecular charge transfer (CT) band around 830 nm [12,13] and soluble fullerene PCBM. The choice of GaOHPc was dictated by the following reasons: 1) high thermal and chemical stability of phthalocyanines as compared with the most of molecular materials; 2) the NIR absorption providing the possibility to extend the photosensitivity spectral range (up to the NIR region) of the blend; 3) the CT character of the IR absorption band, which promises high efficiency of charge carrier photogeneration [13,14]; 4) the solubility in chloroform, which allows its processing by spin coating [12]. In this work we show, that by adding second bulk heterojunction layer of GaOHPc:PCBM to P3HT:PCBM cell we obtain bi-layer system GaOHPc:PCBM/ P3HT:PCBM which photosensitivity spectrum covers vide spectral range from 350 to 850 nm. It was found that

thermal annealing of cells in vacuum $10^{-5}$ - $10^{-6}$ mbar at 100C increases short circuit photocurrent external quantum efficiency (EQE) more than 2-3 times.

## 2. Methodology

For the electron donor and hole transporter in main bulk heterojunction layer we chose regioregular poly 3-hexylthiophene (P3HT) with an average molecular weight of 87000 (Sigma Aldrich) and for acceptor and electron transporter – [6,6]-Phenyl-C61 – butyric acid methyl ester (PCBM) with purity better than 99,5 % (from American Dye Source). The additional bulk heterojunction layer was composed from hydroxygallium phthalocyanine (GaOHPc) as electron donor and PCBM as electron acceptor. The molecules used and cell arrangement is shown in Figure 1.
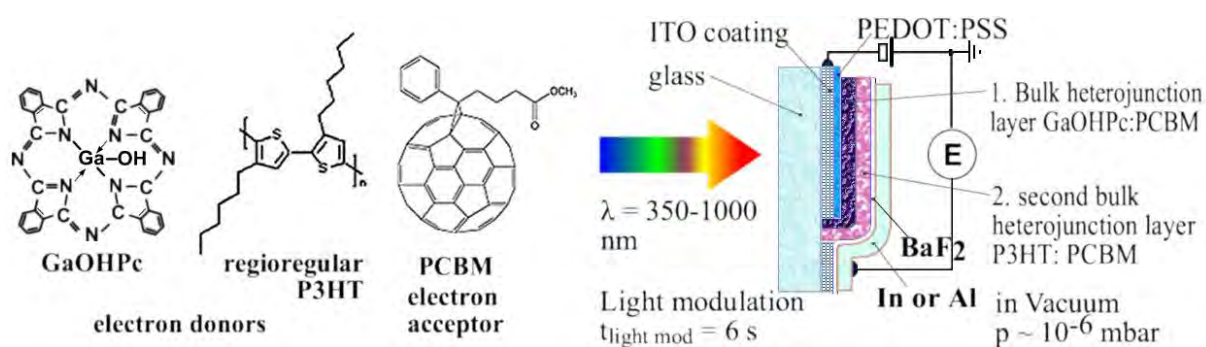


*Fig. 1. Molecules used and cell arrangement.*

As the sample substrate ITO – covered glass with Rsu = 4~10 Ohm/Sq was used. The ITO electrode after cleaning and etching anode configuration was covered with a 30 nm thick PEDOT:PSS (Clevios 1000) plus 5% DMSo +5% isopropanol to increase its conductivity [15] by spin coating at 9000 rpm, and dried for 30 min. at 140C in vacuum $10^{-5}$ mbar. This electrode was covered by GaOHPc:PCBM blend from the solution in chloroform and chlobenzene mixture by spin coating. This procedure was repeated till optical density of GaOHPc:PCBM layer reaches 0.5 – 0.6 at 840 nm. After drying in vacuum $10^{-5}$ mbar at 85C this layer was covered by second bulk heterojunction layer of P3HT:PCBM (1:1 by weight) by spin coating from the solution in chlorbenzene. As top electrode the In or Al was evaporated in vacuum of $10^{-5}$ – $10^{-6}$ mbar with surface resistance Rsu ~ 10 Ohm/Sq. In the case of In electrode, the 0.5 – 0.7 nm thick BaF$_2$ layer was incorporated under In by evaporation in vacuum. The thickness of BaF$_2$ layer during evaporation process in vacuum was controlled by 20 Mhz crystal oscillator and frequency meter. The photocurrent measurements were carried out at RT and 100C in vacuum of $10^{-6}$ – $10^{-5}$ mbar. The samples were illuminated using grating monochromator by chopper modulated monochromatic light through the ITO electrode in the 350 – 1000 nm spectral region with intensity $10^9$ – $10^{16}$ photon/(cm$^2$*s) (see Fig.1). Light modulation period was chosen as 6 s long and intensity was controlled by calibrated Si photodiode. The synchro-detection technique with the use of PC controlled data storage equipment [16] was employed for measuring the spectral dependences of photocurrent quantum efficiency: EQE = $I_{photo}/\Phi$ (where $I_{photo}$ is the photocurrent (electrons/s) and $\Phi$ is photon flux (photons/s) incident upon the active area of sample)

## 3. Results and discussion

The spectral dependences of the external quantum efficiency (EQE) of short circuit photocurrent for low incident light intensities $10^{11}$ – $10^{12}$ photon/ (cm$^2$*s) and the optical

properties of novel bi-layer bulk heterojunction system G aOHPc:PCBM/P3HT:PCBM are shown in Fig.2 for top Al electrode and Fig.3 for top BaF$_2$/In electrode.
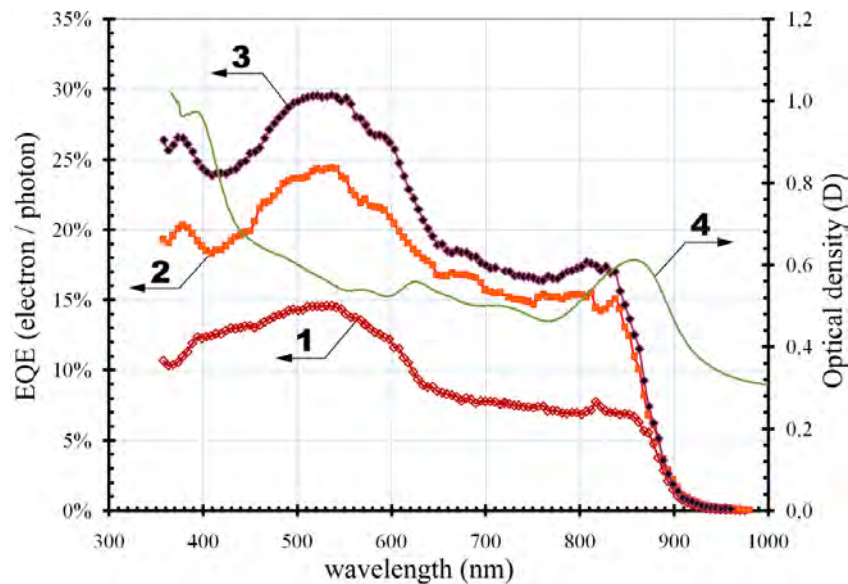


*Fig. 2. Spectral dependences of external quantum efficiency (EQE) of short circuit photocurrent at light intensity $10^{11}$ photon/(cm$^2$*s) and optical density for ITO/PEDOT:PSS/ GaOHPc: PCBM/P3HT:PCBM/Al cell:*
*1 - EQE at room temperature (RT) for unheated sample;*
*2 - EQE at T = 100C;*
*3 - EQE at RT after sample therm. annealing in vacuum at T = 100C;*
*4 - Optical density of bi-layer system GaOHPc:PCBM/P3HT: PCBM.*
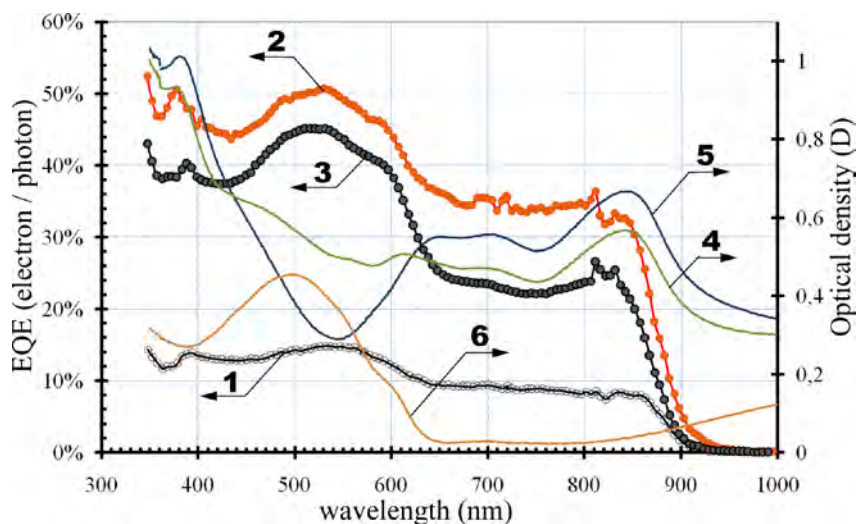


*Fig. 3. Spectral dependences of external quantum efficiency (EQE) of short circuit photocurrent at light intensity $10^{12}$ photon/(cm$^2$*s) and optical density for ITO/PEDOT:PSS/GaOHPc:PCBM/P3HT:PCBM /BaF$_2$/In cell:*
*1 - EQE at room temperature (RT) for unheated sample;*
*2 - EQE at T=100C;*
*3 - EQE at RT after sample annealing in vacuum at T=100C;*
*4 - Optical density of bi-layer system GaOHPc:PCBM/P3HT:PCBM;*
*5 - Optical density of GaOHPc:PCBM layer;*
*6 – Optical density of P3HT:PCBM layer.*

It is seen that absorption spectrum of GaOHPc:PCBM layer (curve 5 in Fig. 3) supplements well the P3HT:PCBM spectrum (curve 6 in Fig.3) enabling practically uniform absorption in 350 – 900 nm region of bi-layer bulk heterojunction system GaOHPc:PCBM/P3HT:PCBM (curves 4 in Fig.2 and Fig.3). Introducing GaOHPc:PCBM layer in the cell extends its photosensitivity spectrum beyond 850 nm (see curves 1 – 3 in Fig.2 and 3), but short circuit photocurrent EQE value for illumination in GaOHPc CT absorption band is 1.7 – 2 times less than for that in the P3HT absorption band possibly due to lower hole polaron mobility in GaOHPc fractal structure than in P3HT. The cell thermal annealing at 100C in vacuum for 48 hours after top electrode deposition significantly increases EQE values for all cells (compare curves 3 and 1 in Fig.2 and 3) due to change of morphology of used organic layers leading to increase of hole, and electron polaron mobilities and also probably by better contact with top electrode [10].
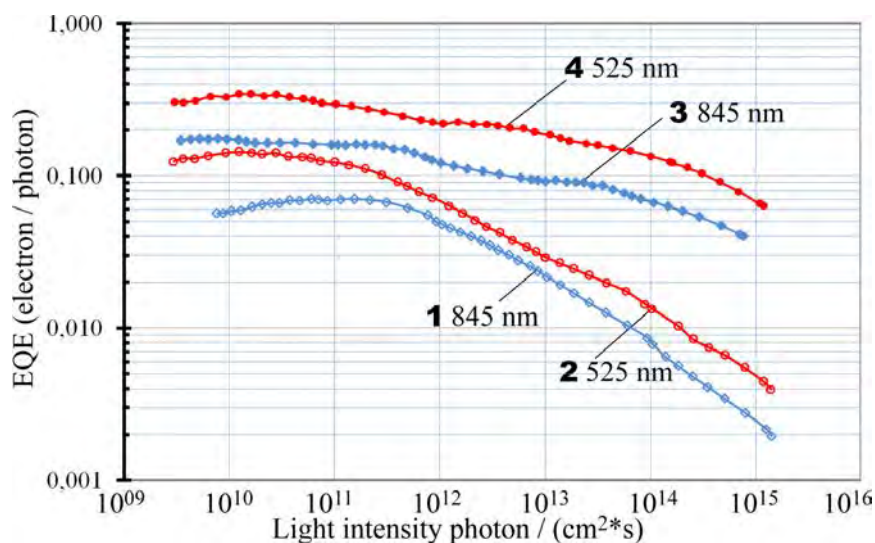


*Fig. 4. Short circuit photocurrent external quantum efficiency (EQE) dependence on incident light intensity at room temperature for Al top electrode before annealing (curves 1,2) and after thermal annealing at 100C in vacuum (curves 3,4).*
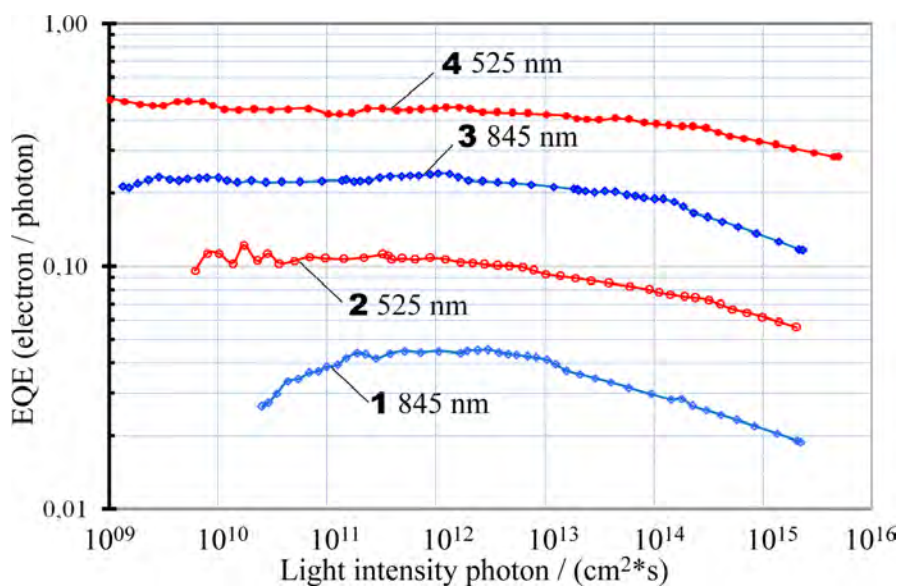


*Fig. 5. Short circuit photocurrent external quantum efficiency (EQE) dependence on incident light intensity at room temperature for samples with In/BaF$_2$ electrode before annealing (curves 1,2) and after thermal annealing at 100C in vacuum (curves 3,4).*

Highest EQE values were achieved for cells with top $BaF_2$/In electrode which after annealing reached values more than 45% (electron/photon) at P3HT absorption band (525 nm) and 25% (electron/photon) at GaOHPc charge transfer absorption band (845 nm) (curve 3 Fig.3), at room temperature and light intensity $10^{12}$ photon/(cm$^2$*s). By increasing light intensities, EQE values decrease as shown in Fig.4 and Fig.5 probably due to low charge carrier mobilities. This photocurrent sublinear dependence on light intensity diminishes after thermal annealing (compare curves 3,4 with 1,2 in Figs 4 and 5) supporting idea, that improvements by thermal annealing at least partly can be explained by increase of charge carriers mobilities. Comparing curves in Fig.4 and Fig.5, we see that cells with top $BaF_2$/In electrodes has more linear photocurrent dependence on light intensity than cell with top Al electrode. Also fill factors (FF) are higher for cells with top $BaF_2$/In electrode than Al electrode (compare photocurrent efficiency dependences on applied external voltage in Fig.7 and Fig.6). It possibly can be explained by too thick $Al_2O_3$ formation under Al electrode, as spin coating procedure was performed in air and not in glove box with $N_2$ or argon atmosphere. So prepared organic layers would contain some $O_2$ in their volume which was not removed in vacuum camera before Al thermal deposition. This $O_2$ could slowly diffused out towards Al electrode during sample measuring procedure and form isolating $Al_2O_3$ layer, as it was discovered by Fan and Faulkner in 1978 [17] even for samples prepared in vacuum by thermal deposition.
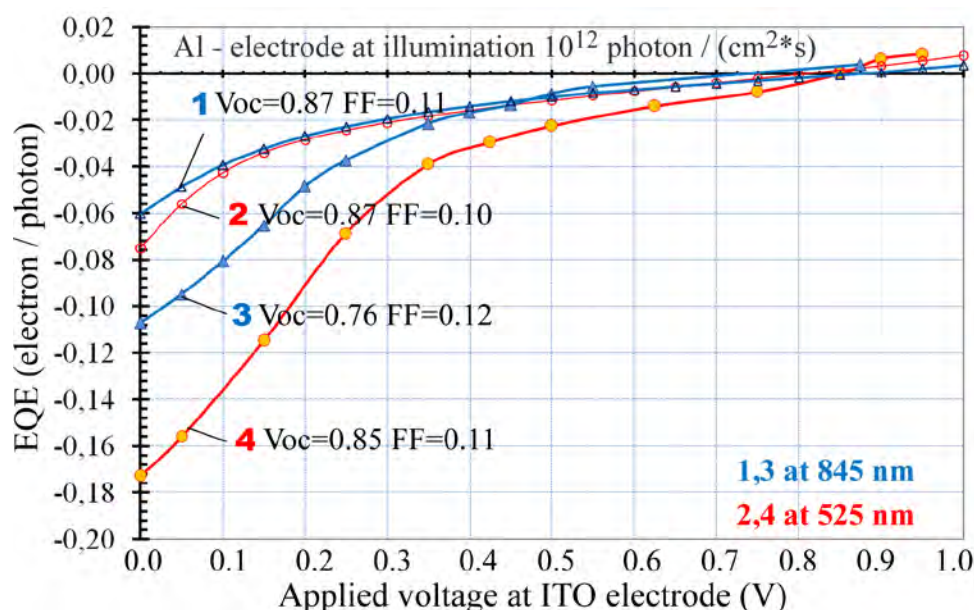


*Fig. 6. Photocurrent EQE dependences on applied external voltage for cells with Al electrode at room temperature before annealing (curves 1,2) and after annealing at 100C (curves 3,4), at light intensity $10^{12}$ photon/(cm2*s). Also open circuit voltages (Voc) and fill factors (FF) are shown.*

This could be the main reason for extremely low fill factor values (0.10 – 0.12) and high open circuit voltages Voc= 0.76 – 0.85 V for cells with top Al electrode (Fig.6). The cells with top $BaF_2$/In electrode exhibit higher fill factor values: 0.21 - before annealing and 0.22 – 0.29 after annealing, but low open circuit voltages: 0.42 V - before annealing and 0.43 – 0.48 V after annealing (see Fig.7). These low FF values could be explained by high electric resistance of GaOHPc:PCBM layer which could be diminished in future by appropriate doping.
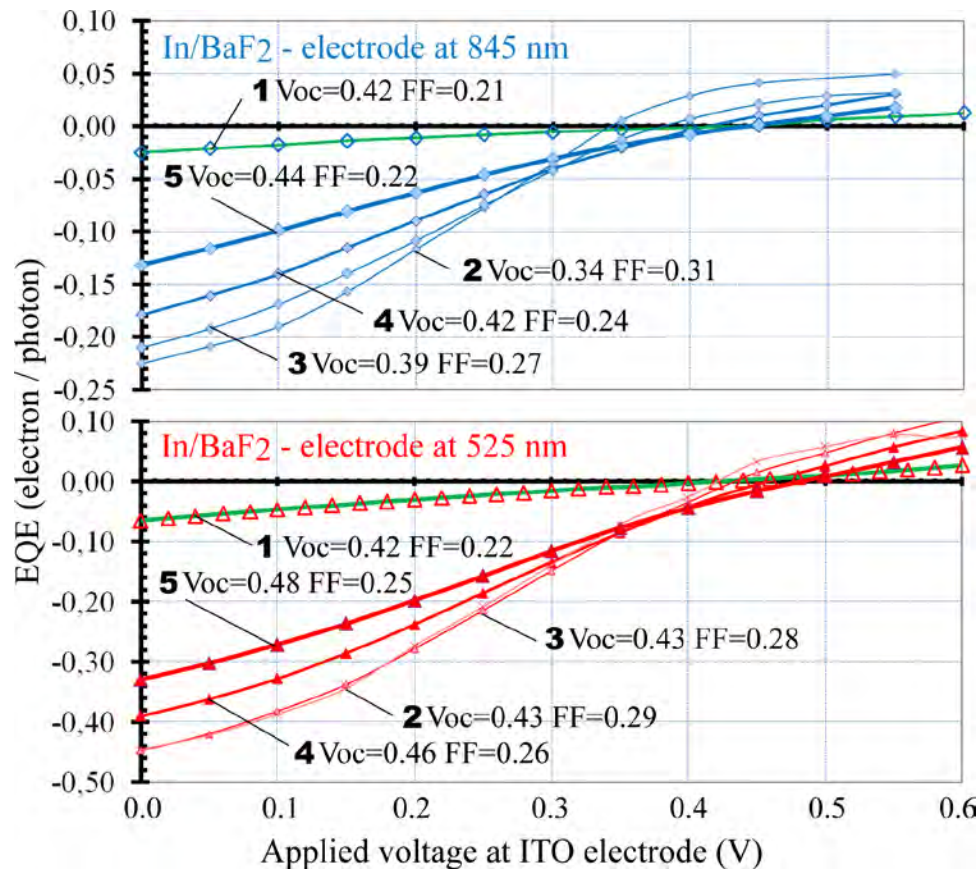
*Fig. 7. Photocurrent EQE dependences on applied external voltage for cells with In/BaF$_2$ electrode at room temperature before annealing at light intensity $10^{15}$ photon/(cm$^2$*s). (curves 1) and after annealing at 100C (curves 2-5), at following light intensities:*
*2 - $10^{12}$ photon/(cm$^2$*s); 3 - $10^{13}$ photon/(cm$^2$*s); 4 - $10^{14}$ photon/(cm$^2$*s); 5 - $10^{15}$ photon/(cm$^2$*s).*
*Also open circuit voltages (Voc) and fill factors (FF) are shown.*

## 4. Conclusions

1) The novel organic bi-layer bulk heterojunction system is built having high charge carrier photogeneration efficiency in 350-850 nm spectral range at low light intensities.
2) Thermal annealing significantly increases EQE values for all cells.
3) Thermal annealing significantly increases linearity of photocurrent dependences from light intensity.
4) Cells with In/BaF$_2$ electrode have higher EQE values and fill factors, than cells with top Al electrode.

## 5. Acknowledgments

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