

Organic Solar Cells with Semitransparent Metal Back Contacts for Power Window Applications

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To provide truly transparent solar cells for power window applications, both semiconductor and electrode materials have to have a very low absorption over as much of the visible spectrum as possible. We present some promising visible transparent semiconductor combinations, namely zinc-phthalocyanine or zinc-naphthalocyanine together with soluble fullerenes in

conjunction with a method for obtaining highly transparent thin metal films by tuning the interference patterns in the multilayer organic solar cells structure. In an optimal combination, solar cells with an efficiency of about 0.5% and a peak transparency of more than 60% in the visible part of the spectrum were fabricated.

Introduction

Organic solar cells have reached power conversion efficiencies of around 5%^[1–3] and show the promise of cost-efficient conversion of solar radiation into electrical energy. The technological advantages of organic solar cells over their inorganic counterparts include their low weight, flexibility, ease of production, and low material consumption.^[4,5] One special property of organic semiconductor materials is that owing to the electron transitions between energetically well-separated π orbitals, the transmission spectrum usually shows discrete absorption bands in limited spectral regions. This behavior is in contrast to the three-dimensional band absorption in inorganic semiconductors and hinders full absorption coverage of the solar irradiation spectrum.^[6]

However, at the same time, such distinct absorption bands can leave transmission windows in the visible part of the spectrum, giving the possibility to design solar cells which transmit visible light but convert ultraviolet and near-infrared light into electricity. This property is especially appealing in the design of solar power windows, where the visible light transmission should be maximized while UV and NIR radiation can be absorbed to reduce glare and heating in direct sunlight as well as generate electrical power. Inorganic solar cells can hardly fulfill this function, as they will always absorb and convert the whole spectrum above the band gap.

Besides finding the right photoactive materials with a broad transmission window in the visible spectrum and optimizing the efficiency of a solar cell built from these materials, all other components of the solar cell, especially the electrodes, have to be equally transparent in the desired wavelength region. Several methods to achieve bifacial organic solar cells have been described already, using transparent metal oxide and/or conducting polymer electrodes on both sides of the active layer.^[7,8] A method that allows the use of the standard ITO/PEDOT:PSS/active layer/metal electrode structure (ITO: indium tin oxide; PEDOT: poly(3,4-ethylenedioxythiophene); PSS: poly(styrenesulfonic acid)) but selectively suppresses the reflection

of the metal layer would be more appealing. An effort in this direction was made with the design of top-emitting organic light-emitting devices (OLEDs) by utilizing the interference effects in thin transparent films^[9] and with the construction of organic solar cells and photodetectors with high transmission through a metal contact into the device.^[10] The coupling of light out of the OLED or into the photodiode is enhanced by coating a transparent organic layer on top of the thin silver electrode. If the coupled microcavities of the device^[11,12] and top layers are tuned appropriately, a high transmission of the silver layer can be reached by suppressing the reflection of the metal over a certain wavelength range.

Herein, we present a similar method for using this aforementioned effect to enhance the visible transmission through a solar cell with strong absorption in the UV and NIR regions. Using zinc phthalocyanine and a fullerene derivative, devices with a transmission of over 50% in the blue and green part of the solar spectrum could be achieved which still give above 0.5% solar power conversion efficiency. Using zinc naphthalocyanine as donor chromophore, solar cells which are highly transparent over nearly the whole visible spectrum were prepared.

Results and Discussion

The materials used to fabricate the solar cells reported here are shown in Figure 1 a–c. The active layer transmission of de-

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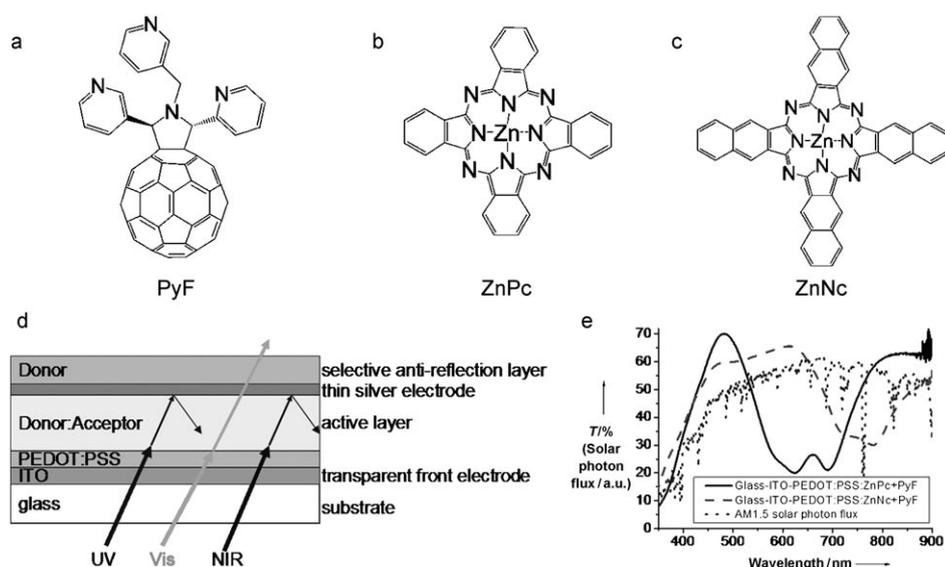


Figure 1. The semiconductor materials used in this study. a) Pyrrolidinofullerene with three pendant pyridyl rings (PyF), b) zinc-phthalocyanine (ZnPc), and c) zinc-naphthalocyanine (ZnNc). d) Structure of the solar cell devices, with a scheme indicating the working mechanism of the selective antireflection layer. e) Optical transmission spectra of the solar cell active layers together with the AM1.5G solar photon flux spectrum.

vices based on zinc phthalocyanine (ZnPc) or zinc naphthalocyanine (ZnNc) and a pyrrolidinofullerene with three pendant pyridyl rings (PyF)^[13,14] is depicted in Figure 1e. Devices of this kind using ZnPc as a donor have been presented previously.^[15,16] They have the advantage that the very pronounced transmission window of the ZnPc or ZnNc is preserved in them as there is only a very small amount of fullerene present in the device. Further optimization of the devices might include additional transport layers as often used in small-molecule organic solar cells as well as co-evaporation of the donor and acceptor phases to increase the power conversion efficiencies of the devices.^[1,3]

The dotted line indicates the AM1.5G standard solar photon flux, which shows that the maximum number of photons per wavelength can be harvested in the NIR region. Integration of the AM1.5G spectrum shows that the sun emits approximately 26% of the photons in the visible part of the spectrum, 2.5% of the photons in the UV region, and 34.5% of the photons in the NIR region up to 1100 nm. The rest of the photons have too low energies to be efficiently converted in a single-layer solar cell.

Figure 1d shows a sketch of the device structure, indicating the interference effect that gives rise to the transparency of the solar cells. The requirements for the antireflection layer are that it has to be transparent in the same range as the solar cell active layer, that it shows a high index of refraction to yield a strong interference effect, and that it is easy to process. We used the donor material from the solar cell itself that will obviously be transparent in the same range. Phtalocyanines show a high index of refraction in the desired visible wavelength range and are already part of the production process. A further advantage is that the silver electrode layer can serve as a back mirror to enhance the absorption in the spectral range where

the active layer absorbs, because there the antireflection layer is also not transparent and thus suppresses any possible undesired interference effects.

A critical factor in designing the solar cells is to choose the right thickness of the silver electrodes to yield good enough conductivities while being very thin to reduce losses due to absorption inside the metal which cannot be suppressed by the interference. The evolution of sheet resistance versus transmission of thin silver layers on glass with a 3.5-nm thick layer of chromium is listed in Table 1. Thinner silver layers did not form a continuous film and showed no reproducible sheet resistance. Note that in the thinnest possi-

Table 1. Transparency and sheet resistances of silver layers on glass and 3.5-nm thick layer of chromium compared with the ITO/PEDOT:PSS bottom electrode on glass.

Silver thickness [nm]	T [%] at 500 nm	Sheet resistance [Ω/\square]
8	41	5.6
10	33	4.7
13	22.5	4
15.5	14	2.6
19	10	2.4
200 nm ITO/60 nm PEDOT	78	22

ble silver films, the sheet resistance is lower by nearly a factor of four than in the 200 nm ITO electrode on glass used for the bottom contact. Calculations using literature values for the optical constants of silver^[17] show that the absorption in a silver layer of 10 nm thickness is below 3% with 63% reflection. Therefore, the transmission of a silver layer can be significantly enhanced by the right interference pattern.

Figure 2 shows measurements on solar cells that contain ZnPc and PyF in the active layer. The transmission through the solar cell with different thicknesses of the silver layer in the back electrode is depicted in Figure 2a. The absorption gap in the solar cell active layer between 450 nm and 550 nm is clearly visible as a maximum in the transmission spectrum. At a thickness of 19 nm of the silver layer, the transmission is far below 10% all over the visible spectrum. This result indicates that most of the light that is not absorbed in the active layer of the solar cell is reflected by the silver layer. The transmission in the window of low absorption increases by a factor of about six to 48% when the electrode thickness is reduced to 10 nm. Surprisingly, the devices with an 8-nm thick electrode do not show a higher transmission. However, the transmission

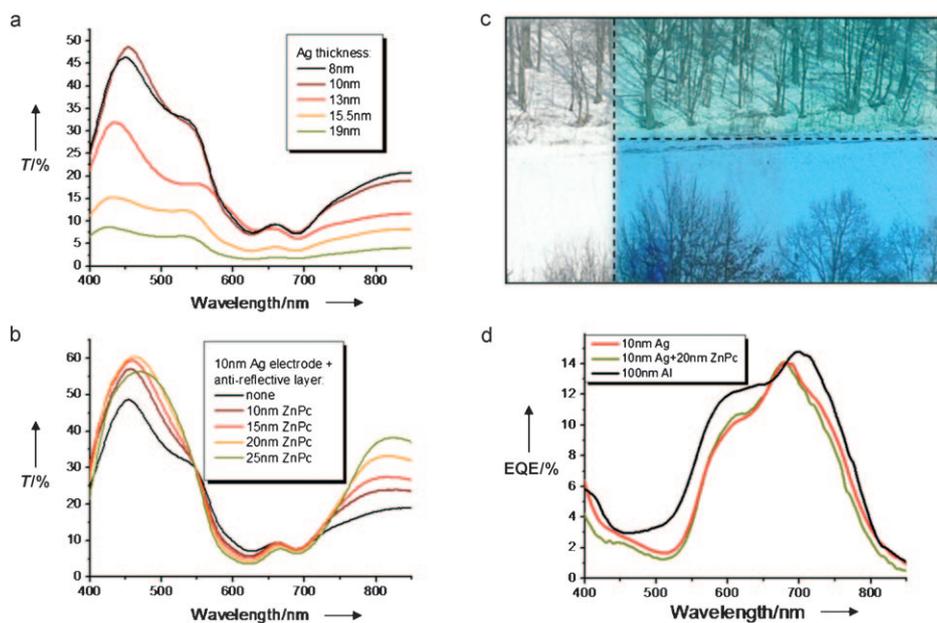


Figure 2. Solar cells based on ZnPc and PyF. a) Optical transmission spectra of cells with different thicknesses of silver back electrode. b) Optical transmission spectra of a cell with a 10-nm thick silver back electrode and added ZnPc anti-reflection layer of various thicknesses. c) Looking at a winter landscape through a glass window (left side), the solar cell active layer (upper right side), and the completed solar cell with a 10-nm thick silver electrode and 20-nm thick ZnPc anti-reflection layer. d) External quantum efficiency spectrum of cells with different back electrodes with and without anti-reflection layer.

will also change as a result of the interference effects that will become more pronounced as the silver layer becomes more transparent.

Taking the 10-nm thick silver film as a reference, the anti-reflection layer was evaporated onto the top of the device. A further increase in transmission up to above 60% was observed when a ZnPc film of 20 nm thickness was deposited on top of the Ag electrode (Figure 2b). This behavior has to be compared with the 78% transmission through the glass substrate with ITO and PEDOT:PSS. The devices have a distinct blue-green color with the electrode visible as a deeper blue area as can be seen in Figure 2c.

The external quantum efficiency (EQE) spectra of three devices are plotted in Figure 2d to show the influence of the transparency of the electrodes on the performance of the photovoltaic power conversion. The device with the 100-nm Al full back mirror shows a higher conversion efficiency in the range of low absorption around 500 nm wavelength, indicating that the higher transmission naturally lowers the amount of converted photons as the reflected photons are not again absorbed by the active layer in the multiple passes. Differences in the shapes of the spectra between the devices with Ag and Al electrodes are probably due to the difference in the optical constants of the metals, leading to different reflection and therefore interference characteristics. These differences are visible in the absorption profile of the solar cell active layer and therefore also in the quantum efficiency spectrum.

The data extracted from the I - V characteristics are listed in Table 2 (see also Figure 4b,c). The performances of the devices are similar to previously published data,^[15,16] and the solar sim-

ulator power conversion efficiency of the transparent device is about two-thirds of the efficiency of the non-transparent device. Some of this difference originates in the lower fill factor of the devices with the silver top contacts which is most likely due to an interface barrier between the fullerene and the Cr/Ag electrodes.

To obtain a broader transparency window, solar cells employing zinc naphthalocyanine (ZnNc) as a donor material were investigated (Figure 3). The transmission of the active layer of ZnNc as displayed in Figure 1e is very high between 420 nm and 650 nm, which gives the films a faint greenish-yellow color and allows for high visible transparency. By using a 10 nm thin silver back electrode and a ZnNc layer of 25 nm thickness as

Table 2. Photovoltaic performance of solar cells based on ZnPc and PyF with different metal back electrodes.

Top electrode	I_{sc} [mA cm ⁻²]	V_{oc} [mV]	Fill factor [%]	PCE [%]
100 nm Al	3.3	550	50	0.9
3.5 nm Cr+10 nm Ag	2.5	580	42	0.6
3.5 nm Cr+10 nm Ag+20 nm ZnPc	2.45	580	42	0.6

antireflection layer on top of it, it is possible to achieve quite transparent solar cells (Figure 3b).

Figure 3a shows the transmission spectra for various thicknesses of the ZnNc anti-reflection layer. The maximum transmission stays significantly below the values reached for the ZnPc system, but the transmission window is much broader. At a thickness of the anti-reflection layer of about 25 nm, a good compromise between the spectral width of the transmission window and absolute transmission maximum value is reached.

The photovoltaic performance of solar cells with ZnNc as an electron-donor material is still rather poor. In studies on devices with a 100 nm Al mirror electrode, the typical parameters were a short-circuit current (I_{sc}) of 2.1 mA cm⁻², an open-circuit voltage (V_{oc}) of 320 mV, a fill factor of 0.36, and a power conversion efficiency (PCE) of about 0.2%. The output parameters of the corresponding transparent devices were lower by at least a factor of two. Full I - V characteristics can be found in Figure 4a,c. The synthesis and purification of ZnNc as well as the vacuum deposition are not fully refined and optimized yet. The advantage of broad-band transparency will certainly trigger growing interest in solar cells based on ZnNc and PyF or

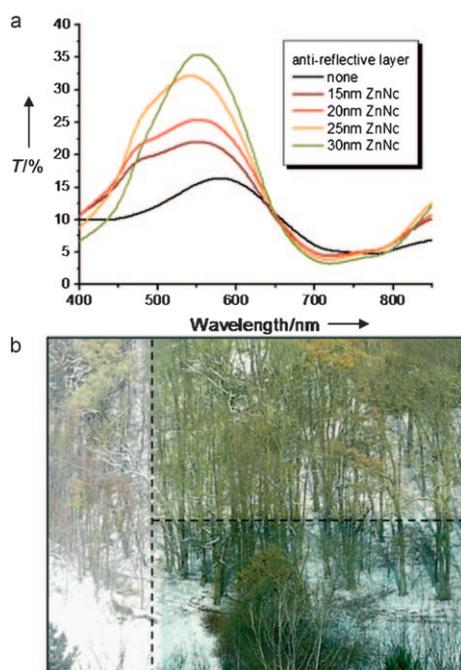


Figure 3. Solar cells based on ZnNc and PyF. a) Optical transmission spectra of cells with a 10-nm thick silver electrode and ZnNc antireflection layers of various thicknesses. b) Looking at a winter landscape through a glass window (left side), the solar cell active layer (upper right side), and the completed solar cell with a 10-nm thick silver electrode and 25-nm thick ZnNc antireflection layer

similar combinations of materials that lead to a broad transmission window in the visible spectrum for yielding high-efficiency transparent solar cells.^[18,19]

Conclusions

We combined organic semiconductor materials that display a high transmission in the visible part of the spectrum with a novel way of realizing metal electrodes with spectrally selective high transmittance. This combination enabled us to fabricate highly transparent power windows using organic solar cells that could be coated on the inner surfaces of double-glazed windows, where a good encapsulation would be automatically provided. Additionally, the solar cells would functionalize the windows with UV- and NIR-blocking layers, which are necessary in modern building facades to reduce heating and cooling losses. The energy of this radiation can thus be not only absorbed or back-reflected but also converted into valuable electrical energy. As the fabrication relies mainly on low-temperature vacuum evaporation, these power window type solar cells would not add greatly to the production cost of the double-glazed window systems.

Experimental Section

Materials Synthesis

Pyrrolidinofullerene (PyF) was synthesized according to previously reported procedures.^[13,14] To achieve a higher purity of this materi-

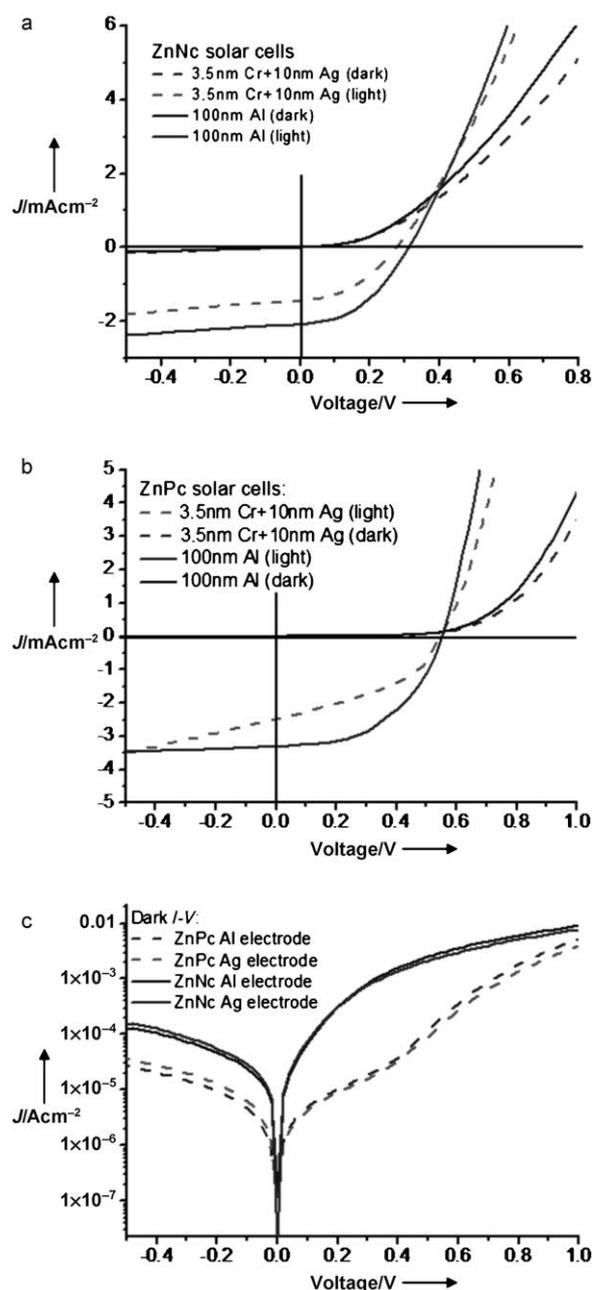


Figure 4. I - V characteristics of the solar cells. a) Linear I - V characteristics of solar cells based on ZnNc. b) Linear I - V characteristics of solar cells based on ZnPc. c) Logarithmic I - V characteristics in the dark.

al, we performed column chromatography three times using toluene/methanol mixtures as eluent. The solution of pure PyF obtained after the final chromatography step was concentrated on a rotary evaporator to a volume of 2–4 mL, and then the product was precipitated with hexane (50 mL), separated by centrifugation, washed with hexane (5–6 times), and dried in air.

Zinc naphthalocyanine (ZnNc) was synthesized according to a known method^[20] from zinc acetate and naphthalene-2,3-dicarbonitrile using 1,8-diazabicyclo[5.4.0]undec-7-ene as a base and 1-butanol as a solvent. The obtained crude ZnNc material was initially sonicated several times with methanol to wash out impurities. Afterwards, it was heated at 450 °C under vacuum ($\approx 10^{-3}$ mbar) for

about 24 h to remove the more volatile impurities of unconsumed organic precursors. The chemical purity of the ZnNc sample estimated from chemical analysis data was 98–99%.

Solar Cell Preparation

The solar cells were fabricated on an etched and cleaned substrate of indium tin oxide (ITO)-coated glass. A layer of PEDOT:PSS (Baytron PH) of about 60 nm was spin-coated onto the ITO, and the substrate was transferred to a vacuum chamber, where 40 nm ZnPc or ZnNc was deposited by thermal evaporation from a quartz crucible at a pressure of about 10^{-6} mbar. The fullerene acceptor PyF was deposited from a 10 mg mL^{-1} solution of PyF in CHCl_3 by placing one drop of solution on the sample while it was rotating at 8000 rpm (2000 rpm when coating on the ZnNc films) on a spin-coater.

Optical calculations compared to the transmission spectra of the active layers indicated a thickness of the fullerene layer of 25–30 nm in the case of spin-coating on ZnPc and 30–35 nm after spin-coating on ZnNc. During the spin-coating, a small amount of ZnPc was washed away, as it becomes slightly soluble in CHCl_3 by complexation with PyF.^[15] Transmission measurements indicated that the thickness decreases by less than 5 nm. The ZnNc layer was not significantly influenced by the spin-coating, as ZnNc is completely insoluble even when complexed to PyF.

To finish the device, a 3.5-nm thick Cr contact layer was deposited again in the vacuum chamber, followed by the silver electrodes and the antireflection layer. The contact layer of Cr is mainly needed to avoid short-circuiting between the silver of the back electrode and the PEDOT:PSS film. After confirming the photovoltaic behavior of the cells, another layer of ZnPc was evaporated stepwise onto the silver electrode to serve as an antireflection layer.

Measurements

The transmission spectra were measured using a Varian Cary3 UV/Vis spectrophotometer against air as a 100% baseline reference. A KHS Steuernagel solar simulator adjusted to give 100 mW cm^{-2} of AM1.5G irradiation by using a calibrated Si photodiode was used to illuminate the solar cells to determine the photovoltaic performance. I - V curves were measured with a Keithley 236 sourcemeter. The external quantum efficiency spectra were determined by shining light from a 75 W Xe lamp through an Acton monochromator and a chopper and measuring the resulting short-circuit current with an EG&G lock-in amplifier. All electrical measurements were made in a N_2 glovebox to minimize degradation. The solar cells showed no significant degradation after repeated transport through ambient conditions to reach the evaporation chamber, spin-coater, and transmission measurements.

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