Green-sensitive organic photodetector with high spectral sensitivity for image sensor application

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CMOS image sensor based on silicon photodetectors has been the conventional route for the fabrication of high performance mobile phone cameras, but this technology now suffers from resolution limitation due to the broad absorption spectrum of Si in the visible region and its low coefficient of absorption. The hybrid CMOS imager using an organic semi-conducting layer with a higher coefficient and lower mobility has been successfully tested as an alternative to Si.[1] The use of organic materials led to a reduction of optical and electrical crosstalks for better performances, and also to the possible reduction of spectral crosstalk by modifying the molecular structure for better absorption at specific wavelengths. Additional development of organic molecules is however needed, to improve device efficiency, in particular the external quantum efficiency (EQE).

Among small molecules, boron-subphthalocyanine chloride (SubPc), characterized by narrow absorption band with high absorption coefficient in the 500-600 nm range,[2] is a promising material candidate for application to organic photodetector (OPD). In this study, we tested SubPc and a modified SubPc, F5-SubPc, as new donor or acceptor materials. These materials were combined with other small molecules, N,-N dimethyl quinacridone (DMQA) as a donor and dibutyl-substituted dicyanovinyl-terthiophene (DCV3T) as an acceptor, that were previously tested as excellent materials for green-sensitive OPD.[3] On the basis of the energy level diagram of these four materials, we selected three material combinations for device fabrication: device A (SubPc / F5-SubPc), device B (SubPc / DCV3T) and device C (DMQA / SubPc). The devices were fabricated with a simple photodiode architecture comprising a MoOx layer as a hole transporting layer and by using thermal evaporation with a bulk hetero-junction (BHJ) structure for the active layer.

The molecular structures and absorption spectra of the four materials taken separately are shown in Figure 1. The absorption spectra of Figure 1b confirm the interesting optical properties of the two SubPc derivatives with coefficient absorption over $1.4x10^5$ cm^{-1} and narrow full-width-at-half-maxima (FWHM) under 80 nm. The EQE spectra of the three fabricated devices at an applied reverse bias of 5V are shown in Figure 2. EQE values were the highest for devices B and C with 62.5% at 520 nm and 60.5% at 550 nm, respectively, and the lowest for devices A with 51% at 530 nm. The differences in maximum EQE values were further investigated by analyzing J-V characteristics in relation with carrier mobilities evaluated with the space-charge-limited current (SCLC) model and surface morphology measured by Atomic Force Microscopy (AFM). We found that the EQE values are notably dependent on the active layer morphologies, and that all devices showed a different behavior to the applied bias voltage, depending on their materials combination. The selected materials combinations showed FWHM values below 200 nm, except for the device including DCV3T, due to the broader absorption of this material. The use of SubPc derivatives led thus to a reduction of spectral crosstalk, in particular to the suppression of blue or red absorption. Considering all data, the device combining DMQA with SubPc showed the best characteristics for OPD application, and confirmed the high potential of SubPc-based molecules for OPD.

References

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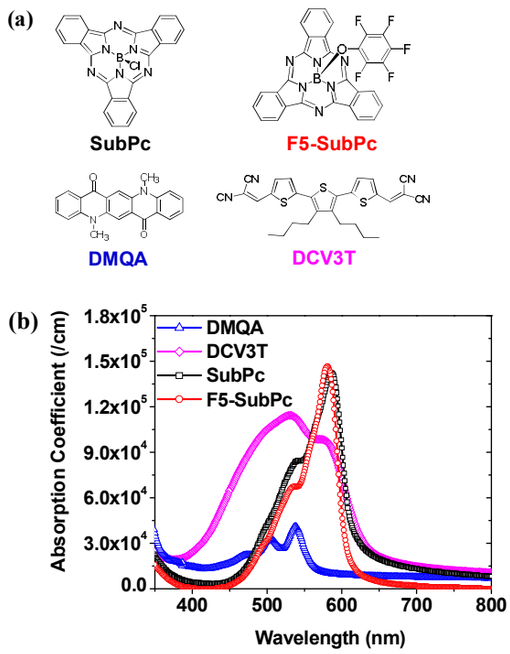

Figure 1. (a) Molecular structures of the active materials for high spectral sensitivity. (b) The absorption spectra of the materials.

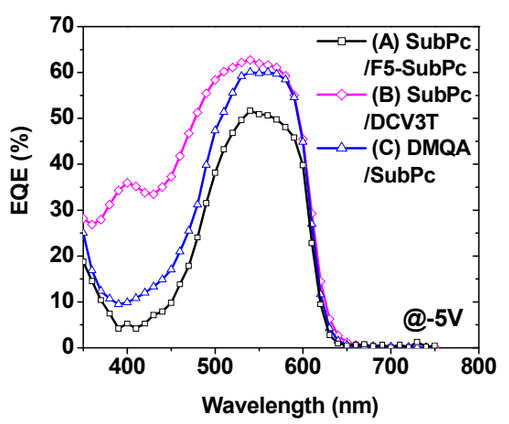

Figure 2. The external quantum efficiency (EQE) spectra of bulk hetero-junction (BHJ) organic photodiodes at an applied reverse voltage of 5V.