

## Optical control of the exciton diffusion length in organic solar cells

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One of the bottlenecks to high efficiency in organic solar cells (OSC) is constituted by the short diffusion length of excitons. Typically this diffusion length is on the order of 10nm which is many times shorter than the absorption length of many of the materials employed in organic photovoltaics. One way around this problem came with the bulk hetero-junction OSCs. However, this device architecture limits the ability of the separated charges to reach the electrodes, and an optimization of the efficiency of the device would require a controlled 3-D nano-structuring to provide the proper channels to increase the mobility of these charges.

An alternative route was recently proposed and consists in using an optical cavity to increase the diffusion length [1]. It was shown that it is possible to increase the exciton lifetime by changing the electromagnetic environment of the exciton when placing a high quantum yield fluorescence photovoltaic materials within a non-symmetric optical cavity. As in the Purcell effect [2], the spontaneous emission of the radiative system in the excited state (exciton) is inhibited. Numerical calculations in Ref. [1] indicated that by using a device architectural design where the electrodes are a high reflecting mirror and a thin metal forming a non symmetric optical cavity, one would be able to enhance the efficiency of an OSC by 3 times. Additional numerical results also from Ref. [1] showed that this factor could be further increased to about 5 or 6 times if additional nano-structuring were introduced. If we consider that bi-layer OSC can have efficiencies of up to 3%, by implementing such photonic control one would be able to achieve OSC with 15% efficiency or higher.

To achieve such efficiencies, however, there are many hurdles that must be overcome. Although highly fluorescent polymers such as PPV or MEH-PPV have shown good photovoltaic properties when combined with the appropriate electron acceptor [3], the best organic electron acceptors, such as fullerenes, do not show much fluorescence at all. Laser dyes such as rhodamines which are highly fluorescent in solution and have shown good electron acceptor behavior [4], when packed in a solid film, their fluorescence is quenched down to a value below 1%. Another major issue is that the most common OSC device architecture uses an ITO layer as a transparent electrode. To form an open optical cavity one would require two metallic electrodes which could act as good conductors as well as mirrors to control the fluorescence.

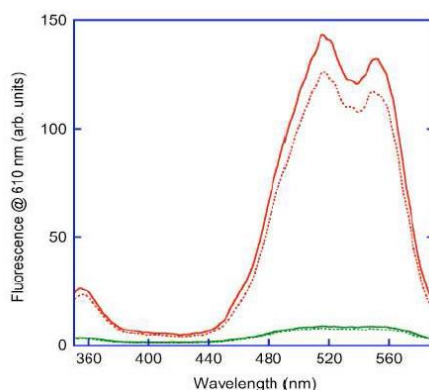


Fig. 1 Fluorescence measured at 610 nm when the pumping wavelength changes from 350 to 590 nm. The fluorescence of a thin solid sample of bare Rh6G is shown in green when deposited on an exciton blocking (solid line) or quenching (dashed line). The fluorescence of Rh6G linked to a PMMA backbone is shown in red when deposited on an exciton blocking (solid line) or quenching (dashed line). In the Rh6G-PMMA sample, PAA was added as a spacer between the Rh6G-PMMA chains.

Here we show, on the one hand, that by chemically binding highly fluorescent chromophores in a non-conjugated polymer chain, the fluorescent quantum yield in a solid film can be enhanced by more than 16 times. On the other hand, the route to provide an optical cavity control of the fluorescence is achieved by replacing the ITO electrode in a bi-layer cell with an ultrathin metal electrode. The organic bi-layer is sandwiched in between such electrode which is partially reflecting in the region where the organic active layer fluoresces, and another which is a good conductor and acts as a highly reflecting mirror.

The comparison between the fluorescence of spin-coated Rhodamine 6G (Rh6G) and the Rh6G chemically bound to the PMMA backbone is shown in Fig. 1. When comparing the red and green curves from Fig. 1, we observe that the fluorescence efficiency increases by more than 16 times. In the same figure we show the comparison of the fluorescence when the solid layer is deposited on an exciton blocking or quenching substrate. These preliminary results seem to indicate that the polymer backbone does not affect negatively the exciton diffusion length.

Table 1 Comparison of the working parameters of an OSC when the bottom electrode is an ITO substrate or a thin metal electrode which is partially reflecting at the fluorescent band of the photovoltaic material used.

Semi-transparent contact	Reflectivity (%)	Current (mA/cm <sup>2</sup> )	V <sub>oc</sub> (mV)	Fill factor (%)
ITO	9.8	-0.33±0.07	1026±18	34±2
5 nm metal	11,77±0,90	-0.086±0.011	946±45	25±2
10 nm metal	24,37±1,46	-0.074±0.017	934±53	25±2
15 nm metal	37,01±2,13	-0.025±0.006	782±77	17±3

We have also studied the performance of an OSC when the ITO transparent electrode is replaced by a thin metal electrode that could be used to form the fluorescence control optical cavity. Preliminary results which are summarized in Table 1 indicate that when a 10 nm thick metal electrode is used the reflectivity is close to 25% while the parameters that characterize the solar cell are similar to those of the cell fabricated with a 5 nm electrode which exhibits a reflectivity of only 12%. Open circuit voltage is considerably high for all the fabricated cells, however, there is a significant reduction of the short circuit current for the cells with the metal electrodes relative to the one that uses ITO. It is expected that an optimization of the metal composition of such electrode will significantly reduce such difference.

In summary, we have been able to establish the route to fabricate OSC where the exciton diffusion length can be controlled using an optical cavity. We have shown that it is possible to partially prevent the fluorescence quenching of molecular dyes in solid by fixing the position of the chromophore to a polymer backbone. Preliminary results indicate that it is possible to fabricate OSC using only metals as electrodes. The reflectivity provided by the semitransparent electrode of the solar cells we fabricated is sufficient to form the optical cavity necessary to control the exciton diffusion length in cells fabricated with high quantum yield fluorescent materials. The results presented open the route to fabricate highly efficient bi-layer organic cells.

## References

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