

# Possibilities of exohedral metallococomplexes of fullerenes for polymer solar cells

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Fullerenes are indispensable components of highly efficient plastic solar cells. Nevertheless, optimization of the fullerene properties has been paid much less attention than those of the polymer component. Improving the performance of polymer-fullerene solar cells needs an enhancement of solar light absorption by the active layer (to increase the photocurrent) and an increase in the energy gap between the fullerene LUMO and the polymer HUMO (to increase the open circuit voltage  $V_{oc}$ ). In this respect, exohedral metal complexes of fullerenes [1] could be new interesting acceptors for polymer-fullerene solar cells. For example,  $(\eta^2\text{-C}_{60})[\text{ML}_2]_n$  ( $\text{M}=\text{Pd}, \text{Pt}; \text{L}=\text{ligand}; n=1,4$ ) show considerably stronger absorption in the visible range as compared with  $\text{C}_{60}$  [2], and their LUMO can be significantly higher than that of  $\text{C}_{60}$  as suggested from the electrochemistry data [3]. In this work, we report on optical and electrochemistry studies of a recently synthesized fullerene metallococomplex  $(\eta^2\text{-C}_{60})\text{IrH}(\text{CO})[(+)\text{DIOP}]$  (Fig. 1) [4] as a potential acceptor for polymer-fullerene solar cells. As reference fullerenes, we use  $\text{C}_{60}$  and methanofullerene PCBM.

Fig. 2 compares absorption spectra of  $\text{IrC}_{60}$ , PCBM, and MEH-PPV in the visible spectral range where the most part of the solar energy spectrum is concentrated. It is seen that the molar extinction of  $\text{IrC}_{60}$  is considerably higher than that of PCBM. As seen in Fig. 2,  $\text{IrC}_{60}$  has strong absorption in the optical gap of MEH-PPV that could increase absorption of the red part of the solar spectrum by a polymer-metallococomplex blend.

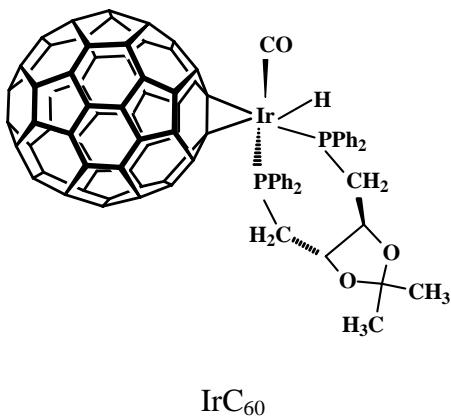


Fig. 1. Structural formula of  $(\eta^2\text{-C}_{60})\text{IrH}(\text{CO})[(+)\text{DIOP}]$ .

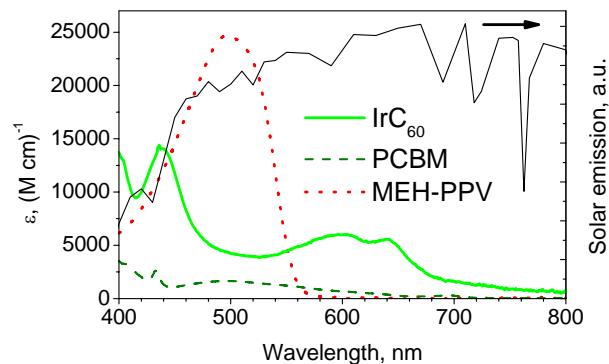


Fig. 2. Optical absorption spectra of  $\text{IrC}_{60}$ , PCBM, and MEH-PPV in toluene. Thin solid line shows the solar emission spectrum.

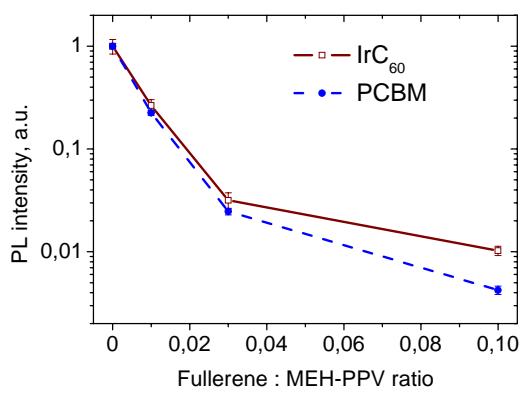


Fig. 3. MEH-PPV PL intensity in MEH-PPV/IrC<sub>60</sub> and MEH-PPV/PCBM blended films drop-cast from chlorobenzene.

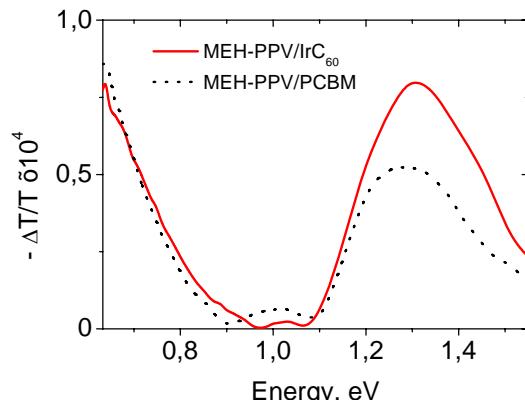


Fig. 4. PIA spectra of MEH-PPV/IrC<sub>60</sub> (1:0.1 mol/mol) and MEH-PPV/PCBM (1:0.1 mol/mol). The PIA spectra were recorded at room temperature for pump at 532 nm and chopping frequency 75 Hz.

To evaluate the LUMO energy of IrC<sub>60</sub>, we performed the cyclic voltammetry (CV) studies in tetrahydrofuran with Bu<sub>4</sub>NPF<sub>6</sub> (0.2 M) as a supporting electrolyte. Similar to the pristine C<sub>60</sub>, the CV data for IrC<sub>60</sub> show several reversible reduction peaks; however, they have considerably more negative potentials as compared with those of pristine C<sub>60</sub>. The first reduction potential of IrC<sub>60</sub> is higher by 0.43 V than that of C<sub>60</sub>. Polymer-fullerene solar cells demonstrate the linear dependence of the V<sub>oc</sub> on the first reduction potential of the fullerene derivative with the slope close to unity [5,6]. Taking into account that the first reduction potential of PCBM is about 0.1 V lower than that of C<sub>60</sub>, one can expect that using the metallofullerenes instead of PCBM in polymer-fullerene solar cells results in increasing the V<sub>oc</sub> by ~0.3 V.

Photoinduced charged transfer in polymer-fullerene blends is known to occur with extremely high efficiency that provides high performance of polymer-fullerene solar cells. To characterize the photoinduced charge transfer reaction in MEH-PPV/IrC<sub>60</sub> blends, we applied photoluminescence (PL) and photoinduced absorption (PIA) spectroscopies with excitation at 532 nm. We also used a well-studied MEH-PPV/PCBM system as a reference. Fig. 3 shows MEH-PPV PL intensity in MEH-PPV/fullerene blended films as a function of fullerene molar concentration. It is seen that the PL quenching efficiency of IrC<sub>60</sub> is about that of PCBM indicating fast decay of the MEH-PPV exciton due to energy or charge transfer. The difference in PL quenching for the acceptor concentration 0.1 could result from different fullerene aggregation in the blends. Fig. 4 compares PIA spectra in MEH-PPV/IrC<sub>60</sub> and MEH-PPV/PCBM blends. It is seen that the spectra in both blends are very similar and include two characteristic MEH-PPV polaron bands at 1.3 eV and below 0.6 eV. The close shape and intensity of PIA spectra observed in the MEH-PPV/IrC<sub>60</sub> and MEH-PPV/PCBM blends imply that long-lived photoinduced charges are generated in them with close efficiencies and lifetimes.

In conclusion, our data suggest that exohedral metallofullerenes deserve further studies as promising acceptors for organic solar cells.

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