

## Review

## Phosphorescent molecular metal complexes in heterojunction solar cells

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## ABSTRACT

Bulk heterojunction (BHJ) solar cells have been developed intensively over the last two decades due to the cheap, flexible devices which may be obtained, although their efficiency remains below that of other emerging solar cell technologies such as dye-sensitized and perovskite solar cells. Molecular organometallic phosphors are noted for their triplet harvesting ability which has produced highly efficient organic light-emitting devices. However, triplet harvesting presents an equally appealing route to enhance the photovoltaic properties of BHJ devices. The results of studies which have used the triplet sensitizing properties of metal complexes towards increasing the efficiency of BHJ solar cells are presented here. By using small quantities of molecular phosphors as dopants, large improvements in short circuit current and power conversion efficiency may be obtained.

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## Contents

1. Introduction	84
2. Phosphors used in BHJs	86
2.1. Group 7	86
2.1.1. Rhenium	86
2.2. Group 8	88
2.2.1. Ruthenium	88
2.3. Group 9	89
2.3.1. Iridium complexes as dopants	89
2.3.2. Iridium complexes as BHJ donors	91
2.4. Group 10	92
2.4.1. Palladium and platinum	92
2.5. Group 11	95
2.5.1. Gold	95
2.6. Others	95
3. Summary and outlook	95
Acknowledgements	95
References	95

## 1. Introduction

Bulk-heterojunction (BHJ) solar cells are an emerging technology for solar energy conversion alongside dye-sensitized solar cells (DSSCs) and perovskite solar cells. Polypyridyl complexes of heavy transition metals such as ruthenium [1–11] and, more recently, of cobalt [12–22], copper [23–32], zinc [33,34] and other

earth-abundant 3d elements [35,36] are closely associated with DSSC technology while the best performing perovskite devices also rely upon heavy atoms such as tin and lead [37–42]. The development of materials suitable for BHJ devices has focused much more closely on purely organic systems.

BHJ devices utilize an electron donating material, typically an electronically delocalized oligomer [43–52] or conjugated polymer [48,50,53–61] blended with an electron accepting small molecule. While there are a large number of donor materials available, the

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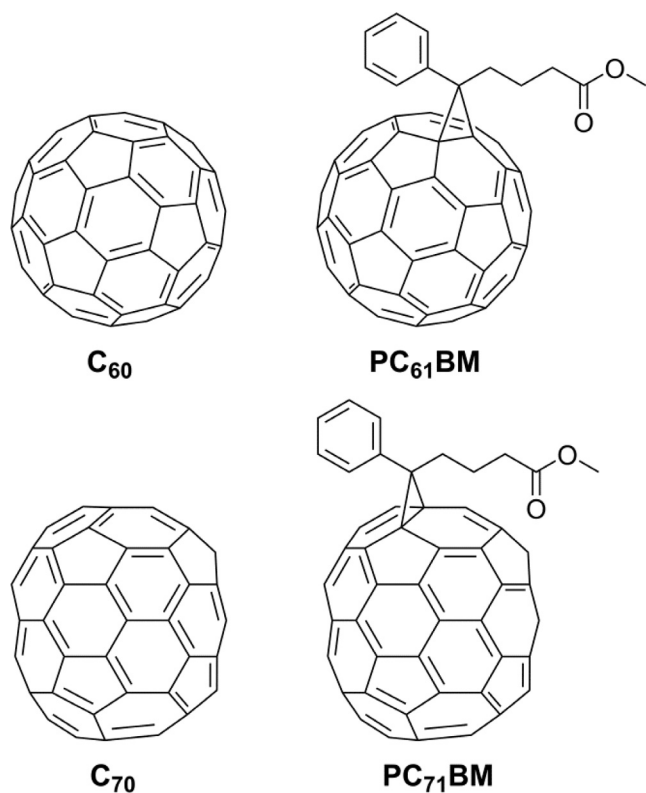
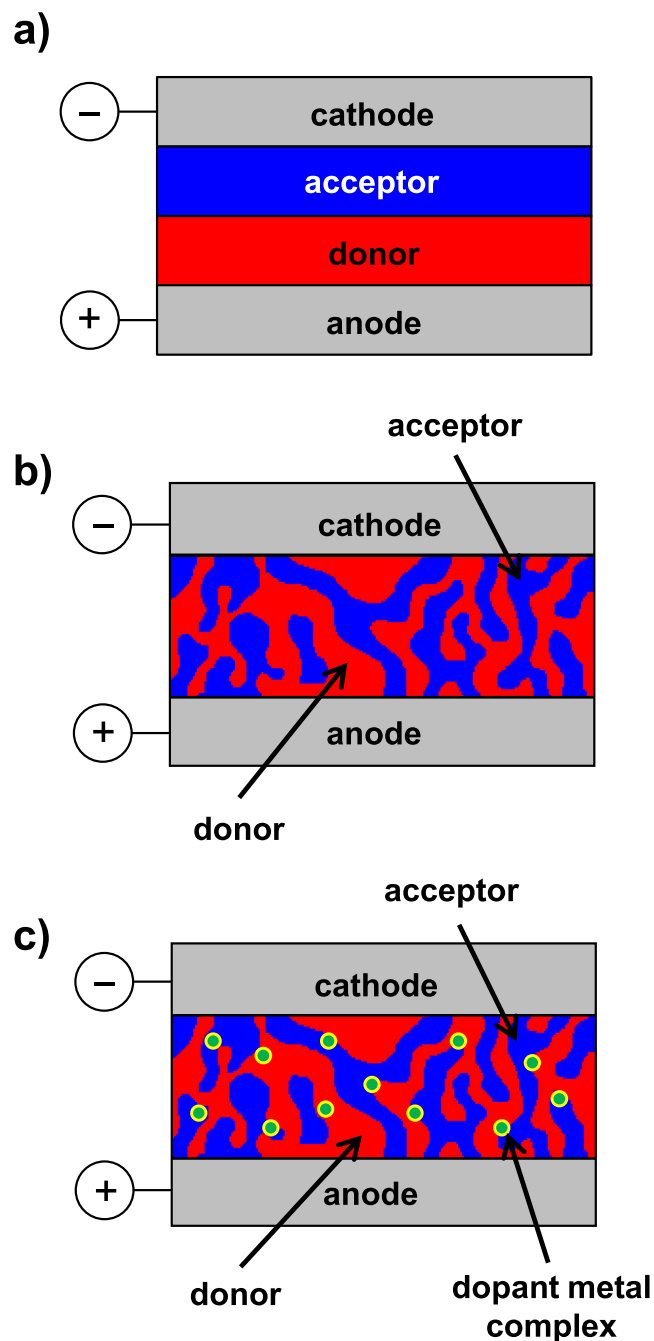


Fig. 1. Fullerene acceptors commonly employed in organic solar cells.

electron acceptor is often a fullerene such as  $C_{60}$ ,  $C_{70}$ ,  $PC_{61}BM$  or  $PC_{71}BM$  (Fig. 1) [50,62,63] although in recent years studies using non-fullerene acceptors such as perylene diimide derivatives or other organic molecules capable of forming stable anions have increased in profile [64–66]. The blended nature of the BHJ results in an interpenetrated network of the donor and acceptor species which provides a very large interfacial area between these components. As the charge transfer required for device operation occurs at these interfaces, the BHJ improves charge carrier generation and transport and overcomes the limitations imposed by earlier bilayer (BL) devices where the heterojunction consisted simply of stacked layers of donor and acceptor [53,67–69]. Some basic differences between these device architectures alongside that of a doped ternary BHJ device are shown in Scheme 1.

Here, the use of molecular metal complexes in BHJ and related BL devices will be presented in order to demonstrate the large extent to which the use of high triplet yield organometallics can improve organic solar cell (OSC) performance, particularly when used as dopants. The doped devices are an example of ternary BHJ devices whereby a third component helps to improve one or more device parameters. Ternary cells are among the most promising technologies under development and have led to BHJ efficiencies exceeding 10% [70–73].

While detailed explanations of the operating principles of BHJ devices are available elsewhere [74–78], a basic representation of these processes and associated energy levels are shown in Scheme 2. The donor undergoes photoexcitation prior to charge transfer to an acceptor molecule. This results in the formation of a transient polaron pair which consists of the electrostatically bound donor radical cation and acceptor radical anion. Dissociation of this polaron pair, in competition with geminate recombination back to the ground state, gives rise to free charge carriers which can migrate towards the electrodes and thus an electrical current is generated.



Scheme 1. Simplified architecture of BL, BHJ and phosphor doped ternary devices.

The primary indicators of cell performance which will be considered here are the short circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor (FF) and quantum efficiency ( $\eta$ ). The first three factors are related to  $\eta$  according to equation 1 where  $P_0$  is the power of the incident light on the device, typically the AM1.5 solar spectrum at  $100 \text{ mW cm}^{-2}$ .

$$\eta = \frac{J_{sc} V_{oc} FF}{P_0} \quad (1)$$

A common postulation in the studies presented here is that by incorporating complexes of heavy transition metals the photogenerated triplet yield will increase due to the spin–orbit coupling associated with high atomic weight elements. Spin–orbit coupling converts singlet excitons to formally forbidden triplet excitons by

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