

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 is 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 improve the efficiency of BHJ devices. The results of studies using molecular phosphors as dopants in very small loadings can yield large increases in short circuit currents and power conversion efficiency and demonstrate that improvements in solar cell performance may be obtained by this approach.

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 studied donor materials the electron acceptor is often a fullerene such as C₆₀, C₇₀, PC₆₁BM or PC₇₁BM (figure 1)[50,62,63] although in recent years studies using non-

1 fullerene acceptors such as perylene diimide derivatives or other organic molecules capable of
2 forming stable anions have increased in profile.[64–66] The blended nature of the BHJ results in an
3 interpenetrated network of the donor and acceptor species which provides a very large interfacial
4 area between these components. As the charge transfer required for device operation occurs at
5 these interfaces, the BHJ improves charge carrier generation and transport and overcomes the
6 limitations imposed by earlier bilayer (BL) devices where the heterojunction consisted simply of
7 stacked layers of donor and acceptor.[53,67–69] Some basic differences between these device
8 architectures alongside that of a doped ternary BHJ device are shown in scheme 1.
9

14 **Figure 1**

15 **Scheme 1**

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

22 While detailed explanations of the operating principles of BHJ devices are available elsewhere,[74–
23 78] a basic representation of these processes and associated energy levels are shown in scheme 2.
24 The donor undergoes photoexcitation prior to charge transfer to an acceptor molecule. This results
25 in the formation of a transient polaron pair which consists of the electrostatically bound donor
26 radical cation and acceptor radical anion. Dissociation of this polaron pair, in competition with
27 geminate recombination back to the ground state, gives rise to free charge carriers which can
28 migrate towards the electrodes and thus an electrical current is generated.
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30 **Scheme 2**

31 The primary indicators of cell performance which will be considered here are the short circuit
32 current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and quantum efficiency (η). The first
33 three factors are related to η according to equation 1 where P_0 is the power of the incident light on
34 the device, typically the AM1.5 solar spectrum at 100 mW cm^{-2} .
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$$36 \eta = \frac{J_{sc}V_{oc}FF}{P_0} \quad (1)$$

37 A common postulation in the studies presented here is that by incorporating complexes of heavy
38 transition metals the photogenerated triplet yield will increase due to the spin-orbit coupling
39 associated with high atomic weight elements. Spin-orbit coupling converts singlet excitons to
40 formally forbidden triplet excitons by intersystem crossing (ISC).[79] This approach may be
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1 considered complementary to the use of phosphorescent complexes in organic light emitting
2 devices.[80–82]

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4 As triplet excitons in an organic material will typically have a much longer lifetime than singlet
5 excitons, an increased exciton diffusion length (L_D) accompanied with a decrease in recombination
6 will occur in phosphor sensitized OSCs primarily resulting in a greatly improved J_{sc} . Similar logic is
7 employed in the development of singlet fission based organic solar cells where one singlet exciton
8 shares energy with the singlet ground state to produce two triplet states of intermediate energy
9 which then take part in generating the photocurrent. [78,83–85] However, singlet fission relies on
10 the energy of the first excited triplet state to be approximately half that of the singlet exciton which
11 is a challenging criteria to satisfy and results in lower energy excitons which can limit the attainable
12 V_{oc} . [78,86]

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14 Although care must be taken to ensure that the frontier orbital energy levels of the dopant will not
15 have a negative impact on photovoltaic performance, such as introducing energetically favourable
16 deactivation pathways or otherwise limiting V_{oc} , phosphorescent metal complexes can be
17 implemented as dopants quite easily and alongside their ability to improve L_D and J_{sc} the metal-
18 ligand charge transfer (MLCT) and related charge transfer processes characteristic of these
19 complexes can also help to improve absorption of sunlight.

30 **Scheme 3**

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32 Energy transfer processes taking place within the triplet sensitized heterojunction including short
33 range Dexter electron transfer where an electron hops from one molecule to another and longer
34 range Förster resonance energy transfer (FRET) where the energy released upon relaxation of a first
35 molecule in an excited state transfers non-radiatively to generate an excited state in a second
36 molecule.[78,85,87–89] Both of these processes are shown in scheme 3. FRET functions very well as
37 a singlet transfer mechanism while Dexter transfer is far more efficient at transporting triplets.[90]
38 Increases in triplet yield and L_D have been definitively confirmed in phosphor doped
39 organics[87,91,92] however precise mechanisms for the energy transfer processes taking place
40 within a triplet sensitized BHJ are challenging to identify and it seems likely that both transfer
41 mechanisms are able to contribute to the improved performance.

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43 A focus on discrete molecular complexes will be maintained, readers specifically interested in the
44 use of metal containing polymers are directed to relevant literature.[93–96] Studies of complexes of
45 a range of metals will be presented and are organized according to their group in the periodic table.
46 As a further note, the reader is advised that device performance in all organic photovoltaic
47 technologies improved rapidly over the last 15 years due to improved device fabrication as much as
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to the synthesis of new materials, therefore a sense of perspective should be maintained when evaluating early studies.[78,97,98]

2. Phosphors used in BHJs

2.1 Group 7

Rhenium

Figure 2

Rhenium(I) tricarbonyl α -diimine complexes **1** (figure 2) with the general formula $fac-[Re(X)(CO)_3(\alpha\text{-diimine})]$ (where X = halide/pseudo-halide) have long-lived and ligand tunable excited states and electrochemical properties allowing them to effectively harvest solar wavelengths and convert absorbed light into useful energy.[99,100] As the structure of the α -diimine ligand is known to have a strong influence on the MLCT properties of these complexes this is a relatively straightforward property to control. These complexes are easy to synthesize and provide some of the earliest insights into the use of molecular metal complexes in OSCs.

In 2001, the group of Chan produced a series of $fac-[Re(Cl)(CO)_3(DAB)]$ (DAB = 1,4-diazabutadiene) photosensitizers **2a-e** (fig. 2) which displayed very low photoconductivity ($\sigma \approx 10^{-14} \Omega^{-1} \text{ cm}^{-1}$) when blended into a poly(carbonate) host attributed to poor charge carrier mobility.[101] However, when added as a dopant to a blend of the hole transporting material (HTM) triphenylamine in poly(carbonate) the photoconductivity increased by up to five orders of magnitude (**2d**, $\sigma = 1.3 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}$). Complex **2d** was incorporated into a BL solar cell with C_{60} as the acceptor producing a maximum open circuit voltage $V_{oc} = 0.38 \text{ V}$, FF = 0.18 and an efficiency of 2% under illumination at 460 nm and 1.9 mW cm^{-2} .[101,102]

Subsequent investigations utilized $fac-[Re(Cl)(CO)_3(DIAN)]$ (DIAN = bis(phenylimino)acenaphthene) complexes **3a-h** (fig. 2) in vacuum deposited BL and BHJ devices using C_{60} as acceptor alongside copper phthalocyanine (CuPc) and C_{60} as hole and electron transport layers respectively. [103–105] Studies of **3a** demonstrated that it is ambipolar with good electron and hole mobilities of $\mu = 2.5 \times 10^{-3}$ and $2.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively, which should enhance charge transport behavior. A BL device using **3a** demonstrated a $V_{oc} = 0.58 \text{ V}$, $J_{sc} = 0.18 \text{ mA cm}^{-2}$, and FF = 0.28 giving only $\eta = 0.03\%$. However by manufacturing the device as a BHJ through co-sublimation of **3a** and C_{60} in a 1:1 ratio the performance improved drastically with $V_{oc} = 0.45 \text{ V}$, $J_{sc} = 1.9 \text{ mA cm}^{-2}$, FF = 0.56 and $\eta = 0.48\%$.[103] Ultimately, by optimizing device construction through control of heterojunction thickness, ratio of **3a** to C_{60} and choice of HTM, devices were obtained with a $V_{oc} = 0.51 \text{ V}$, $J_{sc} = 5.07 \text{ mA cm}^{-2}$, FF = 0.51 and $\eta = 1.29\%$, an almost threefold improvement.[104,105]

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In 2008 Ma et al. reported the oligo(phenylenevinylene) cruciform **4** centered around a [Re(Cl)(CO)₃(bpy)] (bpy = 2,2'-bipyridine) moiety (fig. 2).[106] The authors postulate that the oligomer arms and rhenium α -diimine core could function as donor and acceptor respectively, so a single layer device of the complex was produced alongside a BHJ device with PC₆₁BM as the acceptor. The single layer devices performed poorly despite having a high V_{oc} = 0.72 V due to a low J_{sc} = 0.082 mA cm⁻² and FF = 0.21 giving η = 0.012%. The BHJ devices were more functional, displaying V_{oc} = 0.75 V, J_{sc} = 3.8 mA cm⁻² and FF = 0.28 giving η = 0.8%. The presence of the Re atom in **4** did show improved performance compared to the uncoordinated ligand.

While a number of other Re(I) tricarbonyl complexes have since been prepared displaying properties such as triplet-triplet annihilation and have been identified as useful triplet photosensitizers, these molecules have not been further employed in OSC devices.[107,108]

2.2 Group 8

Ruthenium

Figure 3

In 2004, dimeric ruthenium phthalocyanine [RuPc]₂ was employed in a BL device with C₆₀ displaying J_{sc} = 0.23 mA cm⁻² and V_{oc} = 0.17 V although its EQE responses showed a marked sensitivity to air.[109]

In a collaborative study in 2009, dendritic oligothiophene functionalized RuPc derivatives **5-10** (figure 3) were prepared and utilized in solution processed BHJ devices.[110] These complexes displayed strong absorbance across the UV-vis region with the magnitude of absorptivity increasing with thiophene content. However, it was complexes **5** and **8** containing **Py-3T** which produced the best devices with higher J_{sc} values making up for losses in V_{oc} when compared to the larger analogues. These complexes blended well with PC₆₁BM resulting in smooth films as measured by atomic force microscopy (AFM). **5** and **8** displayed notably improved performance when the less symmetric fullerene PC₇₁BM was used in place of PC₆₁BM (table 1). Ultimately **8**:PC₇₁BM produced the best OSCs overall with V_{oc} = 0.56 V, J_{sc} = 8.3 mA cm⁻², FF = 0.34 and η = 1.6%. All of the complexes outperformed an oligothiophene free analogue (L=L'=pyridine). An interesting trend observed for these complexes is that the V_{oc} tends to increase with increasing thiophene content which is surprising considering that the HOMO levels for the complexes are identical therefore this must indicate some further influence of the oligothiophene chains.

Table 1

Researchers in Milan incorporated the diruthenium bis(acetylide) complex **11** (fig. 3) in BHJ devices with PC₆₁BM.[111] Photoexcited charge transfer between **11** and PC₆₁BM was established however

1 short circuit currents were low $J_{sc} = 0.66 \text{ mA cm}^{-2}$ and only $\eta = 0.08\%$ was obtained. The low J_{sc} values
2 could be explained by the poor film quality of the blend. In 2017, a further series of ruthenium
3 bis(acetylide) complexes were reported by Liu et al. and showed comparable performance in BHJ
4 devices with PC₇₁BM.[112] The best performing device consisted of **12**:PC₇₁BM in a ratio of 1:4
5 displaying $V_{oc} = 0.51 \text{ V}$, $J_{sc} = 4.24 \text{ mA cm}^{-2}$, FF = 0.31 and $\eta = 0.66\%$. The other members of the series
6 had one or more triphenylamine groups bound to the terminal thiophene but did not perform well
7 in OSCs.
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12 Azadipyromethene complexes **13-15** (fig. 3) were reported by Bessette et al. and their properties
13 discussed in the context of photosensitizers for OSCs but no actually device performance was
14 reported.[113]
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16 **2.3 Group 9**

17 **Iridium Complexes as Dopants**

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20 The majority of studies of molecular Ir(III) complexes in OSCs primarily use them as dopants or
21 interlayers for existing conjugated polymer donors and significant improvements in device
22 properties can be observed when the complexes are employed in this way.
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24 **Figure 4**

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27 Yang et al. doped end-capped poly(fluorene) (PFO) with Ir(mppy)₃ **16** (figure 4) and identified a large
28 increase in triplet exciton population.[114] They then made OSCs using blends of PFO and P3HT (fig.
29 4) with CdSe nanocrystals. Doping of these OSCs with **16** at a loading of 10 wt% caused a 200%
30 increase in J_{sc} for PFO and 100% increase for P3HT indicating that the presence of the
31 phosphorescent dopant yielded more, long-lived charge carriers. For PFO a 50% increase in V_{oc} was
32 also observed.
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36 In a detailed study in 2008 the groups of Howe and Hu noted an 80% increase in η by doping 5 wt%
37 Ir(ppy)₃ **17** (fig. 4) into an MEH-PPV/PC₆₁BM. The dopant improved the J_{sc} from 0.6 to 1.1 mA cm^{-2}
38 under illumination of 8 mW cm^{-2} at 500 nm leading to the improved efficiency.[115] A similar J_{sc}
39 response was observed at wavelengths from 370 to 700 nm. The V_{oc} and FF were essentially
40 unaffected at 0.82 V and 0.29 respectively. By substituting **17** with aluminium tris(hydroxyquinoline)
41 (Alq₃) which has comparable HOMO and LUMO levels, no such increase was observed. The presence
42 of the Ir complex was shown to increase L_D from 3.5 to 6.0 nm. The authors conclude that these
43 changes are due to spin-orbit coupling populating the triplet manifold and minimizing
44 recombination.
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Devices utilizing the small molecule donor NPD (fig. 4) doped with 5 wt% **17** also demonstrated an 80% increase in η alongside an improved FF and a near doubling of the L_D in the donor layer from 6.5 nm to 11.8 nm, again attributed to an increased triplet population.[116]

In 2011, Winroth et al. optimized the loading of **17** into a BHJ of the archetypical donor and acceptor pairing P3HT and PC₆₁BM. [117] At 5 wt% **17** improved all device parameters including the V_{oc} from 0.26 to 0.41 V, the short circuit current from -4.64 to -14.4 μ A, FF from 0.34 to 0.47 and η at 340 nm jumped from 0.825 to 9.48% however η dropped slightly from 1.14 to 0.92% when measured at 600 nm. This study identified that the dopant can perform a number of roles simultaneously including harvesting high energy photons and introducing extra heterojunctions for exciton dissociation. This work also identified that the deterioration of performance at higher dopant levels is due to morphological changes induced by the metal complex inhibiting the packing of P3HT chains therefore doping levels must be carefully controlled.

Figure 5

Yu et al. reported on the effect of inserting a layer of the complex bis(2-(4-tert-butylphenyl)benzothiazolato-*N,C*²) iridium (acetylacetonate) **18** (figure 5) between the donor and acceptor layers of a BL device of pentacene and C₆₀. [118] This extra layer was labelled a multicharge separation (MCS) layer and increasing the thickness of this layer from 0 to 8 nm resulted in the V_{oc} increasing from 0.325 to 0.488 V alongside a decrease in J_{sc} from 10.72 to 5.88 mA cm⁻². At an MCS film thickness of 1 nm the FF = 0.48 which ultimately provided the highest η = 1.85%. Similar dependencies were observed when the non-phosphorescent complex CuPc was employed as the MCS although in this case an optimized MCS film thickness of 4 nm yielded η = 1.98%. Yu performed a second study of devices consisting of CuPc as donor and C₆₀ as acceptor with varying amounts of **18** doped into the CuPc layer. [119] The extent of doping was optimized to 25 wt% with larger concentrations of **18** leading to deteriorated charge transport. Overall device performance improved marginally from η = 1.23% in the non-doped device to η = 1.42% in the **18** doped device due primarily to an increase in J_{sc} from 6.48 to 8.23 mA cm⁻² and the L_D from 10 to 17.4 nm, indicating improved triplet sensitization. When these studies are considered together it appears that the presence of the MCS layer seems merely to increase series resistance and recombination rates while diminishing any influence from the triplet sensitizer. Upon considering that charge transfer to form polaron pairs prior to charge separation occurs at the interface of donor and acceptor interface it is perhaps unsurprising that the MCS layer can be a hindrance therefore the strategy of distributing the complex as a dopant throughout the BHJ seems much more promising.

Wang and Zhang utilized iridium tris(2-(benzo[*b*]thiophen-2-yl)pyridine) **19** (fig. 5) to dope BHJ solar cells of P3HT:PC₆₁BM and primarily examined the sensitivity of device performance to annealing

1 temperature.[120] They concluded that an optimum annealing temperature exists for each dopant
2 concentration above which performance decreases attributed to aggregation of the metal complex
3 dopants disrupting film morphology.
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5 The groups of Kim, Kwon and Hong utilized a somewhat complex device using the ionic iridium
6 complex **20** (fig. 5) as a triplet–singlet energy donor in the presence of polyethylene oxide (PEO) in
7 conjunction with the BHJ pairing of P3HT:PC₆₁BM.[121] They postulated that improved
8 morphological properties will arise from the hydrophobic quinolone based ligand while the mobile
9 Na⁺ ions in PEO will minimize electrode energy barriers. While efficient energy transfer between **20**
10 and P3HT was identified, in practice the gains in device efficiency were modest with the best
11 consisting of a blend of P3HT:PC₆₁BM:**20**:PEO in the weight ratio of 1:0.8:0.01:0.01 and annealed at
12 150 °C. High J_{sc} of over 10 mA cm⁻² were observed however the FF of the devices deteriorated in the
13 presence of **20**. A noteworthy result from this study is that simply incorporating PEO itself in the
14 absence of **20** actually gave rise to markedly increased V_{oc} , J_{sc} , and FF in the non-doped, non-
15 annealed P3HT:PC₆₁BM BHJ.[121]
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25 Yao et al. presented a study focused upon the influence of varying levels of
26 tris(phenylpyrazole)iridium **21** as a dopant in BHJ devices consisting of P3HT and the indene-C₆₀-
27 bisadduct ICBA, the structure of which is shown in figure 5.[122] In the presence of 0.1 wt% **21** V_{oc}
28 and FF values showed almost no variation going from 0.827 V and 0.65 when non-doped and 0.821 V
29 and 0.63 after doping. However the presence of **21** did yield an increase in J_{sc} from 10.09 to 11.76
30 mA cm⁻² thereby a moderate improvement in η from 5.41 to 6.08%. Upon annealing at 150 °C the J_{sc}
31 of the doped device increased further to 12.40 mA cm⁻² which ultimately provided $\eta = 7.08\%$.
32 Femtosecond time-resolved photoluminescence spectra revealed that energy transfer with **21**
33 increased the L_D of the P3HT:ICBA blend from 1.35 to 1.53 nm. The presence of **21** in the BHJ also
34 resulted in smoother films while thermal studies in conjunction with AFM and secondary ion mass
35 spectroscopy identified that the annealing temperature can be used to control the vertical
36 distribution of the complexes in the heterojunction. Prior to annealing the complexes have settled
37 towards the bottom of the active layer. As the annealing temperature increases the complexes
38 migrate vertically through the BHJ eventually reaching an optimum distribution in which to assist
39 charge generation and transport. Increasing the annealing temperature further has a detrimental
40 effect on device performance as had been observed in other studies.[120]
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54 Figure 6

55 An elegant example of how heavy metal complexes can be employed as dopants was presented by
56 Qian et al. whereby trace amounts of the iridium complex **22** (figure 6) were “doped” into the high
57 performance polymer PTB7 in very small quantities by Stille type copolymerization to produce the
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1 new metallopolymer **23**. [123] By synthesizing batches of **23** with controlled levels of doping
2 between 0 and 5% then incorporating these polymers into BHJ devices with PC₇₁BM as acceptor they
3 obtained cells with $V_{oc} = 0.75$ V, $J_{sc} = 18.14$ mA cm⁻², FF = 0.64 and $\eta = 8.71\%$. Improvements in η of
4 up to 45% were observed compared to PTB7 at a dopant loading of 1%. These improvements were
5 primarily attributed to large increases in J_{sc} and moderate increases in FF. Similarly to previous
6 studies, further increasing the dopant concentration proved detrimental to performance and AFM
7 imaging identified the smoothest morphology at 1% loading. This is further evidence that the
8 presence of the octahedral Ir complex can assist in minimizing phase separation, cavity formation
9 and other morphological defects if implemented correctly.

16 **Figure 7**

17 In a 2016 report a variety of Ir phosphors **24-27** (figure 7) were studied as triplet-singlet energy
18 transfer dopants in a PTB7:PC₇₁BM BHJ. [124] Photoluminescence spectroscopy confirmed energy
19 transfer between the complexes and PTB7 and the best performing complex **25** showed little change
20 in V_{oc} and FF but a significant improvement in J_{sc} from 13.3 to 16.1 mA cm⁻² increasing η from 7.23 to
21 8.62%. These improvements were correlated to both the efficient energy transfer between dopant
22 and host and the large FRET radius of **25** at 8.2 nm. Similar behavior was identified between **27** and
23 P3HT. This study also identified explicitly that the complex must be blended into the active layer
24 itself to have any effect, simply using the complex as a further layer in its own right did not enhance
25 performance.

26 A report from earlier this year also used an Ir(III) phosphor as a FRET pairing with P3HT and and
27 efficiencies of up to 4.44% were obtained with 1 wt% dopant and solvent annealing. This is an
28 improvement of almost 50% over a non-doped, non-annealed device. [125] Unfortunately however,
29 the complex is written as bis(1-phenylisoquinoline) acetylacetonate iridium(III) Ir(piq)₂(acac) **28** but
30 the structure in the supporting information is that of **29** (both shown in figure 6) therefore these
31 results must be interpreted with some caution.

34 **Iridium Complexes as BHJ Donors**

35 Despite the promising results obtained using Ir complexes as dopants, a number of studies have
36 employed Ir complexes as donor materials in their own right although the results of these studies
37 have been less encouraging.

39 **Figure 8**

40 Lee et al. synthesized the short series of complexes **30-32** (figure 8) with 2-picolinic acid as the
41 ancillary ligand which were then employed as donors alongside PC₆₁BM in solution processed BHJs
42 and C₆₀ in thermally evaporated BHJ devices. [126] Photoinduced charge transfer between donor
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1 and acceptor was identified although photovoltaic performance was low with the best device
2 consisting of an evaporated BHJ of **31**:C₆₀ having $V_{oc} = 0.49$ V, $J_{sc} = 2.32$ mA cm⁻², FF = 0.53 and $\eta =$
3 0.60%.
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5 In 2012, Wang et al. utilized bis(1,2-diphenyl-1*H*-benzoimidazole) iridium (acetylacetonate) **33** (fig. 8)
6 in conjunction with C₆₀ to produce vacuum deposited BL devices.[127] The *J-V* curves of these
7 devices displayed an S-shaped kink attributes to the low hole mobility of **33** ($\mu = 6.49 \times 10^{-6}$ cm² V⁻¹ s⁻¹)
8 ¹). This kink could be resolved by carefully controlling the donor layer thickness and by using a thin
9 layer of a hole transporting material such as NPD (fig. 4) at the donor/anode interface, ultimately
10 producing cells with $V_{oc} = 0.78$ V, $J_{sc} = 4.82$ mA cm⁻², FF = 0.60 and $\eta = 2.23\%$. An improvement in
11 efficiency of 35% compared to devices without the NPD layer.
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18 Fleetham and co-workers produced a BL device using the azaperylene complex **34** (fig. 8) as donor
19 and C₆₀ as acceptor.[128] The azaperylene ligand conferred a very broad absorption profile to the
20 complex, with triplet absorption stretching into the near-IR and giving the complex favorable solar
21 energy harvesting properties. The performance of this complex in solar cells was compared to
22 control devices fabricated with platinum(II) octaethylporphine (PtOEP, fig. 8) and zinc(II)
23 phthalocyanine (ZnPc). L_D for each complex was measured and, as expected, both of the 5d metal
24 complexes **34** (10.1 nm) and PtOEP (12.0 nm) had a longer exciton diffusion length than ZnPc (<5
25 nm). Despite having a slightly shorter L_D than PtOEP, **34** actually produced the most efficient devices
26 at $\eta = 2.8\%$ (rather high for a simple bilayer device) thanks to its improved V_{oc} of 0.99 V versus 0.62 V
27 for PtOEP ($\eta = 1.8\%$), the ZnPc device performed the most poorly ($\eta = 1.4\%$). The V_{oc} of **34** proved
28 very sensitive to film thickness, but demonstrated robust stability towards temperature over the
29 range of 100-300 K. The differences in L_D between **34** and PtOEP and the variations in V_{oc} with
30 respect to film thickness and temperature were attributed by the authors to the influence of the
31 octahedral geometry of **34** compared to the planar PtOEP molecules of which will tend to stack
32 leading to favorable charge transport pathways.
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45 Figure 9

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47 At time of writing, the most recent report of a device relying upon an Ir complex as the sole donor in
48 an OSC utilized complexes of 2-(2'-pyridyl)benzothiophene ligands functionalized with 4-
49 methoxyphenyl **35** and 4-triphenylamine **36** moieties (figure 9) alongside the acac analogue 2,2,6,6-
50 tetramethyl-3,5-heptanedione as the ancillary ligand.[129] These complexes were employed in BHJ
51 devices with PC₇₁BM at very high acceptor loadings. Devices were poor with the best performing
52 devices consisting of **35**:PC₇₁BM (1:2.5) with $V_{oc} = 0.77$ V, $J_{sc} = 4.30$ mA cm⁻², FF = 0.35, $\eta = 1.2\%$ and
53 **36**:PC₇₁BM (1:2) having $V_{oc} = 0.74$ V, $J_{sc} = 6.52$ mA cm⁻², FF = 0.42, $\eta = 2.0\%$. The triphenylamine
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1 substituted **36** showed better performance in all respects. The authors identified the very short
2 excited state lifetimes of **35** (108 ns) and **36** (122 ns) in the solid state as a limiting factor.
3

4 **2.4 Group 10**

5 **Palladium and Platinum**

6 PtOEP (fig. 8) was used in a bilayer device reported by Shao and Yang with C₆₀ as acceptor.[130]
7

8 Despite the low mobility of PtOEP at $\mu = 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ a $V_{oc} = 0.66 \text{ V}$, $J_{sc} = 5.6 \text{ mA cm}^{-2}$, FF = 0.57 and
9 $\eta = 2.1\%$ were obtained. L_D of the heterojunction was estimated to be 30 nm by measuring the
10 dependence of η on the thickness of the PtOEP layer. The magnitude of L_D is ascribed solely to a long
11 exciton lifetime of PtOEP itself which the authors note has a triplet lifetime of approximately 90
12 μs . [131]
13

14 Subsequently, Rand et al. doped PtOEP into the poly(p-phenylene vinylene) derivative Super Yellow
15 at a loading of 5 wt% in a BL device alongside C₆₀ to obtain a device with a 10% improvement in
16 photocurrent compared to the non-doped device.[132] They identified that the presence of the
17 heavy Pt atom was essential to producing improved photovoltaic performance by comparing it to a
18 device that used the metal free ligand octaethylporphine as a dopant which lead to a decrease in all
19 device parameters. L_D were estimated at 9 and 4 nm for the sensitized and non-sensitized devices
20 respectively with the difference attributed to the presence of triplet excitons in the PtOEP device.
21

22 **Figure 10**

23 In 2007 a single layer solar cell was prepared using the fullerene functionalized thiophene-2,5-
24 di(platinum bis(acetylide)) complex **37** (figure 10).[133] It was envisioned that the Pt centers will
25 undergo photoinduced electron transfer to the pendant fullerenes while also encouraging ISC to
26 form triplet charge separated states as the authors had observed for a related polymer in a BHJ with
27 PC₆₁BM.[134] While photophysical evidence supported aspects of this postulation, device
28 performance was ultimately poor with $\eta < 0.06\%$ which the authors attributed to the heavy Pt atom
29 assisting in both ISC upon excitation and rapid reverse ISC from the triplet state back to the short
30 lived singlet state.
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32 The groups of Thompson and Forrest conducted comparative studies of Pt and Pd
33 tetraphenylbenzoporphyrin (PtTPBP and PdTPBP, fig. 10) derivatives in layered heterojunction
34 devices with C₆₀ alongside other donors including CuPc, PtOEP, tetracene, rubrene and others. While
35 the overall efficiencies of the TPBP complexes outperformed most other donors (PdTPBP $\eta = 1.8\%$,
36 PtTPBP $\eta = 1.9\%$) they did not display the high J_{sc} observed in other triplet sensitized devices due to
37 their poor absorbance with respect to the solar spectrum.[135,136] This was followed by a report on
38 PtTPBP focused on studying the ISC processes occurring in a phosphor doped organic
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1 semiconductor, specifically diphenyltetracene **38**. [137] By controlling the thickness of a film of **38**
2 doped with 5 wt% PtTBPB this triplet sensitized layer was used as the donor in a BL with C₆₀. The
3 formation of triplet excitons due to the presence of the Pt phosphor in **38** was identified as occurring
4 in the picosecond timescale and was observed to increase J_{sc} from 30 $\mu\text{A cm}^{-2}$ in a film of pristine **38**
5 to 66 $\mu\text{A cm}^{-2}$ in the doped film.
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9 In 2009, Li et al. utilized the carbazole functionalized Pt porphine complex **39** (fig. 10) as a dopant in
10 a P3HT:C₆₀ BL device. Though the extent of doping is not clear the presence of **39** improved all device
11 properties. V_{oc} and J_{sc} almost doubled going from 0.214 to 0.412 V and 2.546 to 4.152 mA cm^{-2} which
12 increased η from 0.17 to 0.70%. Devices doped with **39** were compared to those doped with CdTe
13 nanoparticles and the molecular dopant was shown to be superior. In a device consisting of just
14 **39**:C₆₀ values of J_{sc} and η are both very low due to the poor charge carrier mobility of the Pt
15 complex. [138]
16

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18 The limitations on L_D that are imposed by poor charge mobility were clearly identified in two papers
19 by Jabbour et al. [139,140] which were published concomitantly with a similar investigation by Lane
20 et al. [141] These studies focus on group 10 phthalocyanine complexes and serve well to validate
21 each other. Jabbour's initial study utilized ZnPc, PdPc and PtPc alongside CuPc for comparison. [139]
22 The complexes were incorporated into BL devices with the acceptor perylene tetracarboxylic
23 bisbenzimidazole (PTCBI). Both the donor and acceptor layers were 20 nm in thickness and the films
24 of all materials displayed similar morphology. Of the four complexes tested PdPc was the most
25 efficient. While CuPc, ZnPc and PtPc all displayed $J_{sc} \approx 3.0 \text{ mA cm}^{-2}$, PdPc had $J_{sc} = 4.0 \text{ mA cm}^{-2}$
26 thereby providing the most efficient solar cells. Surprisingly PtPc produced the poorest device due to
27 a very combination of low J_{sc} and the influence of its high HOMO energy limiting the V_{oc} . The low J_{sc}
28 of PtPc is perhaps the most surprising result, however estimated L_D values increased in the order
29 PtPc(5.6 nm) < CuPc(5.8 nm) < ZnPc(6.2nm) << PdPc(10.1nm). PtPc was then shown to have a hole
30 mobility almost two orders of magnitude lower than the other members of the series which explains
31 its low J_{sc} . The 3d metal complexes CuPc and ZnPc actually displayed the largest charge mobility but
32 only intermediate J_{sc} therefore a combination of high mobility (compared to Pt) and enhanced
33 exciton lifetime thanks to ISC explains the improved performance of PdPc. The authors confirmed
34 this by making further devices of CuPc and PdPc with C₆₀ as acceptor and increased J_{sc} was again
35 observed for PdPc. A subsequent comparison of ZnPc and PdPc in HJ architectures with a p-i-n
36 configuration yielded similar results. [140] The study by Lane et al. was being conducted at the same
37 time and compared NiPc, PdPc, and PtPc as donors in vacuum deposited BL devices alongside C₆₀.
38 While PtPc outperformed NiPc in this instance due to the higher HOMO of NiPc limiting its V_{oc} ,
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1 trends comparable to those observed in the preceding studies were made with PdPc clearly superior
2 to NiPc and PtPc.[141]

3 4 **Figure 11**

5 The group of Fréchet synthesized multichromophoric Pt-acetylide oligomers **40-42** (figure 11) with
6 varying chain lengths and employed them in BHJ devices with PC₆₁BM and PC₇₁BM.[142] As the
7 frontier orbitals are located over the Pt acetylide and 2,1,3-benzothiadiazole moieties the optical
8 and electrochemical properties of all three molecules are almost identical, therefore increasing the
9 oligothiophene chain length should only affect charge transport and morphological properties.
10 Ultimately the two shorter oligomers **40** and **41** displayed higher charge mobility possibly due to
11 their better film forming properties while the best devices were obtained with the intermediate
12 length terthiophene terminated **41** displaying $V_{oc} = 0.82$ V, $J_{sc} = 8.45$ mA cm⁻², FF = 0.43 and $\eta = 3.0\%$
13 in conjunction with PC₇₁BM.
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16 In a study of platinum acetylide polymers in BHJ solar cells Li et al. synthesized the 9,10-
17 anthraquinone oligomers **43** and **44** (fig. 11) however they only produced devices with the related
18 polymers in conjunction with PC₆₁BM which performed poorly.[143]

19
20 Pd and Pt 8-hydroxyquinoline (Pd_q₂ and Pt_q₂, fig. 11) and 5,7-dimethyl-8-hydroxyquinoline
21 complexes (PdMe₂q₂ and PtMe₂q₂, fig. 11) were reported by Che et al. in 2011 and were
22 incorporated by vacuum deposition into organic field effect transistor (OFET) and BL solar cell
23 devices with C₆₀ as acceptor. While the Pd and Pt complexes displayed similar morphologies the Pt
24 complexes in this instance had marginally higher charge mobility than their Pd analogues as
25 measured in the OFETs and also produced more efficient solar cells. The J_{sc} of Pt(Me₂q)₂ based OSCs
26 was particularly high at 14.8 mA cm⁻² and it had a $V_{oc} = 0.42$ V, FF = 0.38 and $\eta = 2.4\%$.[144]

27 28 **Figure 12**

29 A further series of Pt acetylide oligomers **45-48** (figure 12) published in 2012 were studied in OFET
30 and BHJ devices at a range of film thicknesses.[145] PC₇₁BM was used as the acceptor in a ratio of
31 **45-48**:PC₇₁BM = 1:4. **45** and **46** ultimately produced devices with high $J_{sc} > 7.0$ mA cm⁻² and $\eta = 2.37$
32 and 2.34% respectively. Again, the BHJ performance correlated well with the OFET measured
33 mobility.
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36 In 2015 multichromophoric Pt bis(acetylide) complexes **49** and **50** (fig. 12) were produced with the
37 best performing BHJ device consisting of **49**:PC₇₁BM (1:1) displaying $V_{oc} = 0.75$ V, $J_{sc} = 4.14$ mA cm⁻²,
38 FF = 0.45 and $\eta = 1.40\%$ in the presence of the additive 1,8-diiodooctane.[146]

39 40 **Figure 13**

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Ma et al. used a triphenylamine substituted porphyrin to produce a range of metal complexes including those of Ni, Pd, and Pt **51-53** (figure 13) for BHJ devices with PC₆₁BM.[147] Similar to the studies on Pc complexes[139–141] Pt was outperformed again by the Pd complex **52**. The triplet exciton lifetime of the Pd complex **52** is 890 μs compared to just 80 μs for **53**[148] and **52** also proved to have the best charge transport properties with a hole mobility of $1.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ compared to $6.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The OSC of **52** displayed the highest performance by a significant margin having $V_{oc} = 0.90 \text{ V}$, $J_{sc} = 2.70 \text{ mA cm}^{-2}$, FF = 0.25 and $\eta = 0.84\%$.

Finally, in 2016 Qin and collaborators presented cruciform Pt-bis(acetylide) complexes **54** and **55** (figure 13) which they employed in BHJ devices with PC₆₁BM and PC₇₁BM.[149] The devices of **54** displayed high FF compared to other Pt bis(acetylide) complexes and in optimized BHJ displayed J_{sc} values as high as 11.9 mA cm^{-2} for **54**:PC₇₁BM (1:0.8) and 10.7 mA cm^{-2} for **54**:PC₆₁BM (1:0.8) leading to $\eta = 5.6\%$ and 5.1% respectively. These are very high values compared to other devices consisting of a sole Pt donor.

2.5 Group 11

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Figure 14

In 2014 Lai et al. reported the synthesis of three Au(III) corrole complexes **56-58** (figure 14) and used them as donor materials in vacuum deposited OSCs with C₇₀ and as triplet sensitizers for the polymer PTB7 in solution processed BHJ devices with PC₇₁BM.[150] Monolayer devices of C₇₀ alone displayed $V_{oc} = 1.23 \text{ V}$, $J_{sc} = 1.19 \text{ mA cm}^{-2}$, FF = 0.32 and $\eta = 0.5\%$. Upon addition of just 5% of the standout material **57** to the C₇₀ the post-annealing J_{sc} increased almost tenfold to 10.34 mA cm^{-2} and the FF improved to 0.46, these improvements offset a drop in V_{oc} from 1.23 to 0.85 V and resulted in a device with $\eta = 4.0\%$ overall. All of the complexes **56-58** led to improved performance at loading of only 3-7% therefore it is not unreasonable to consider them as having “doped” C₇₀ as much as having acted as a formal donor. A similar improvement in the performance of a solution processed PTB7:PC₇₁BM BHJ was observed upon addition of 5% **57** which led to a $V_{oc} = 0.74 \text{ V}$, $J_{sc} = 14.18 \text{ mA cm}^{-2}$, FF = 0.57 and $\eta = 6.0\%$. Compared to the fullerene-only devices the presence of the donor polymer PTB7 had a very beneficial effect on the FF.

2.6 Others

Mixed porphyrin/phthalocyanine sandwich complexes of a number of lanthanides have been employed in devices which seem like a hybrid of a BHJ and a DSSC using PC₆₁BM or *N,N'*-bis(1-ethylhexyl)-3,4,9,10-perylenebis(dicarboximide) (PDI) as acceptor and a “buffer layer” of TiO₂. Device

1 performance is modest with the best $\eta = 0.82\%$ for Eu(III) but many of the devices did not function at
2 all without TiO₂ being present.[151,152]
3

4 **3. Summary and Outlook**

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6 The studies presented here clearly show that the presence of a metal based triplet sensitizer can
7 provide notable improvements in one or all of the key performance indicators in OSCs with J_{sc} values
8 showing particularly pronounced improvements due to energy transfer processes leading to
9 increased triplet population and extended L_D .
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12 Comparing the results obtained using metal complexes as dopants to those using the same or similar
13 complexes as the sole donor material, it is quite clear that the former approach presents the
14 greatest promise. The majority of these complexes have low charge mobility themselves and the
15 sheer cost of precious metal complexes would appear to preclude their use as a major component of
16 any device. Metal complex dopants also show a strong influence on heterojunction morphology
17 which presents another opportunity to use these materials to influence charge transport properties.
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19
20 The results obtained using Au(III) corroles as donors are particularly compelling as some of these
21 devices are essentially sensitized fullerene monolayers and the presence of a small amount of these
22 complexes resulted in a tenfold increase in the short circuit current of the fullerene. The tendency
23 for planar Pd complexes to outperform those of Pt complexes is also noteworthy as studies of Pd
24 complexes as active components in organic optoelectronics are much less frequently encountered.
25

26
27 Though challenges remain including truly unravelling the underlying mechanisms of operation,
28 identifying structure-property relationships that influence charge carrier transport, and controlling
29 the location and distribution of the metal phosphors in the ternary blend,[153] the fact that addition
30 of very small amounts of metal complexes to the active layer has already been observed to improve
31 BHJ efficiencies by up to four times identifies that this is a truly promising approach to the
32 continued development of BHJ technologies. The knowledge being gained from studies on other
33 ternary systems should be extremely helpful in advancing this premise.
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36 Producing molecules with bespoke optical and electronic behavior is an ideal area for inorganic and
37 particularly coordination chemists to thrive therefore the application of metal complexes to BHJ
38 solar cells can provide fertile ground for the development of useful new materials and technologies.
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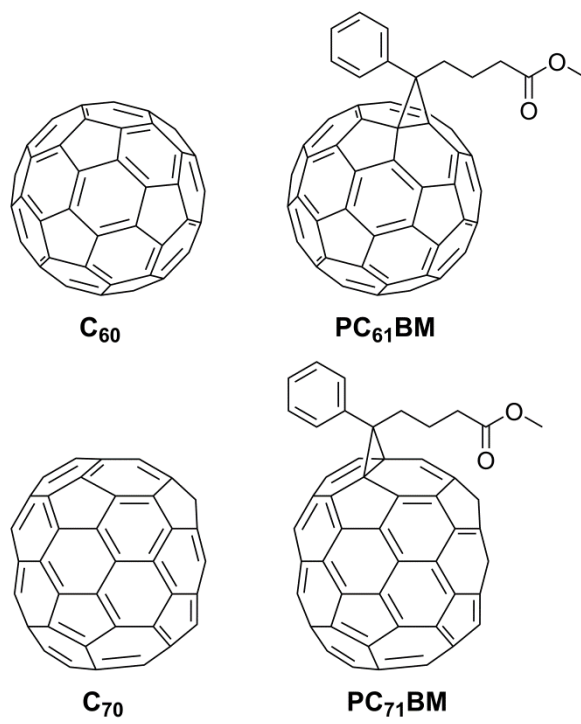


Figure 1

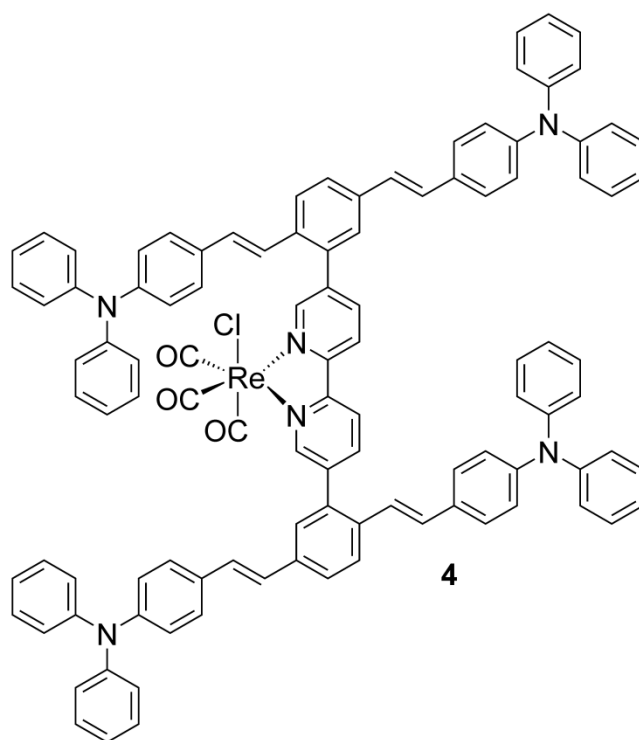
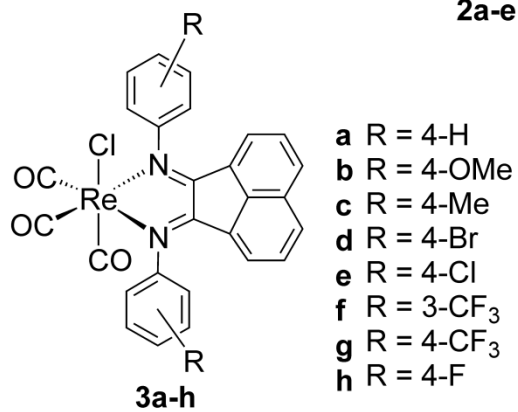
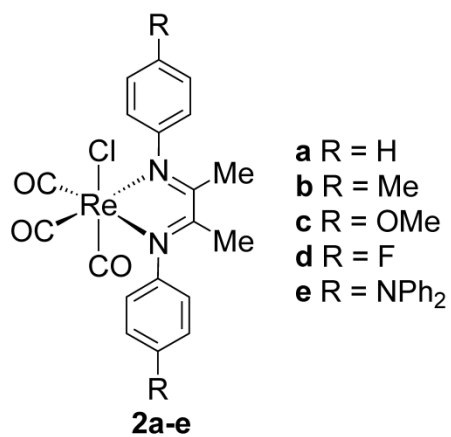
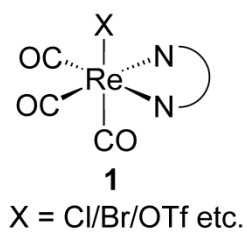


Figure 2

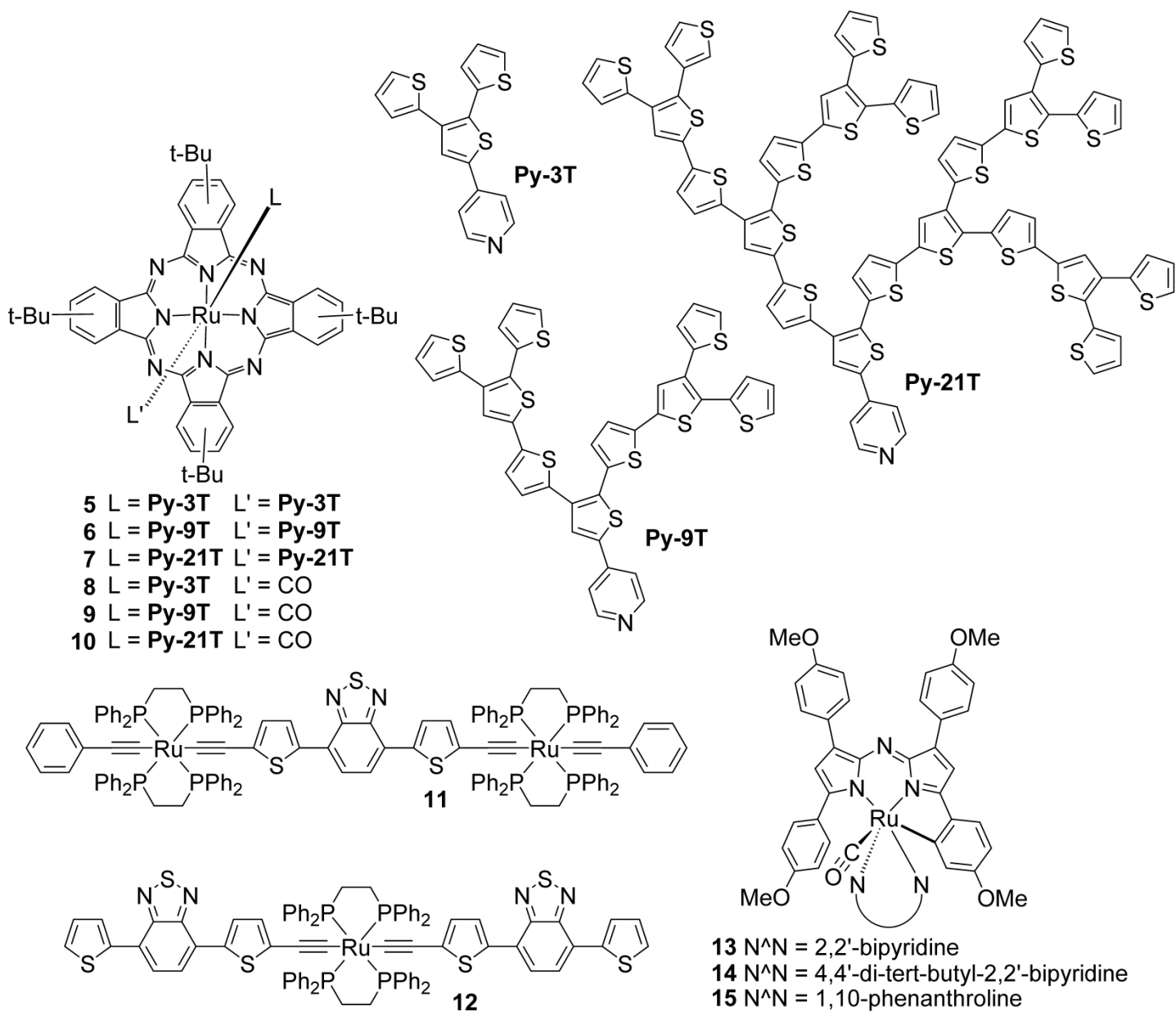


Figure 3

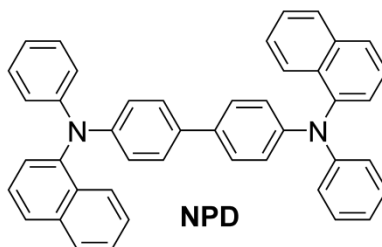
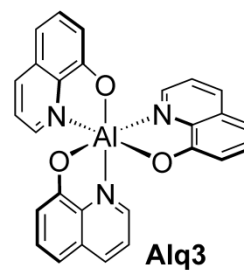
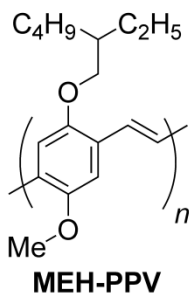
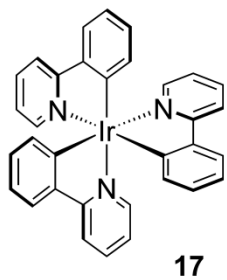
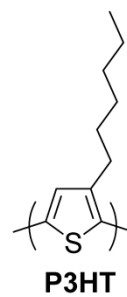
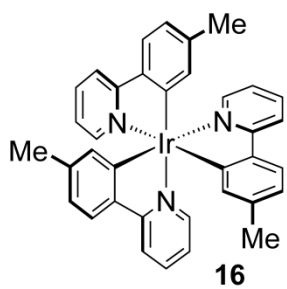


Figure 4

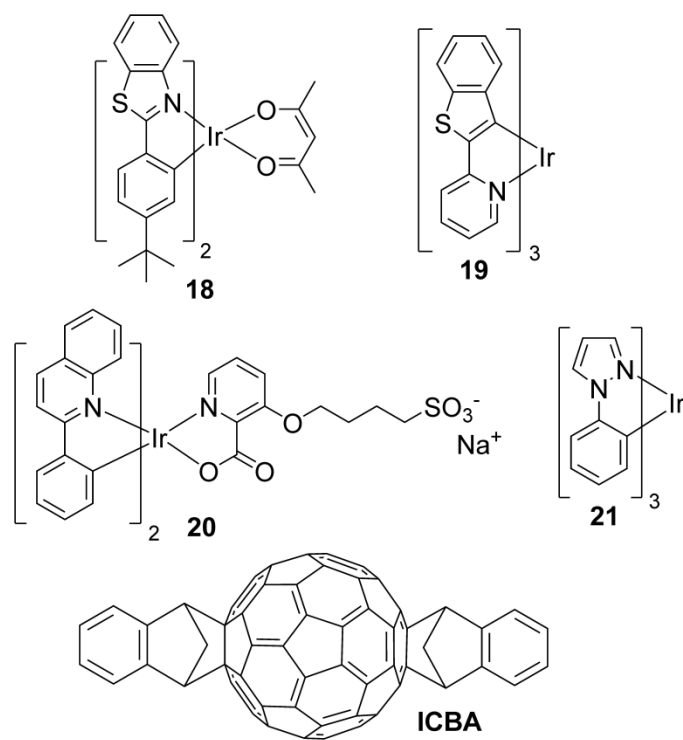


Figure 5

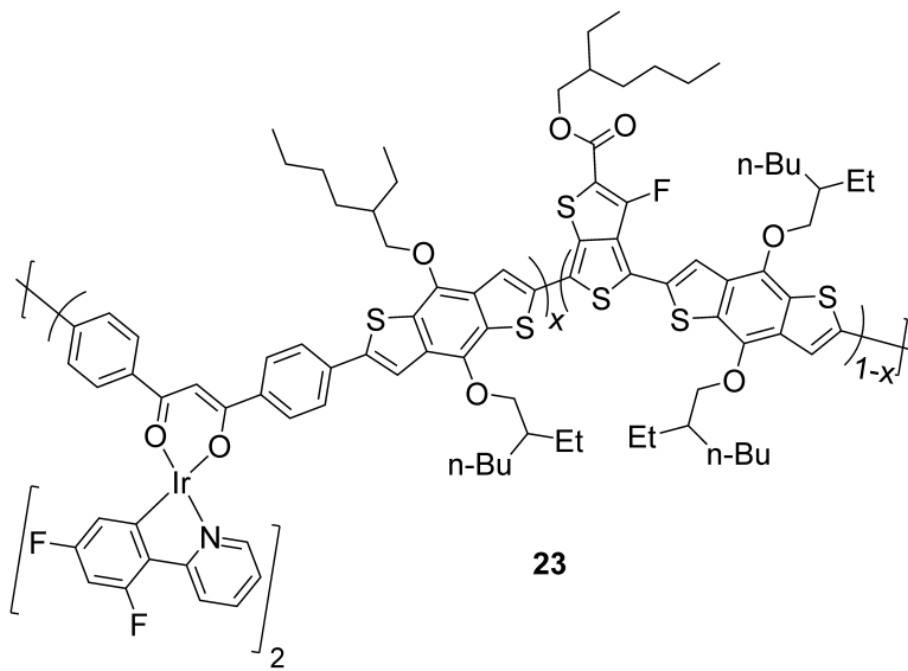
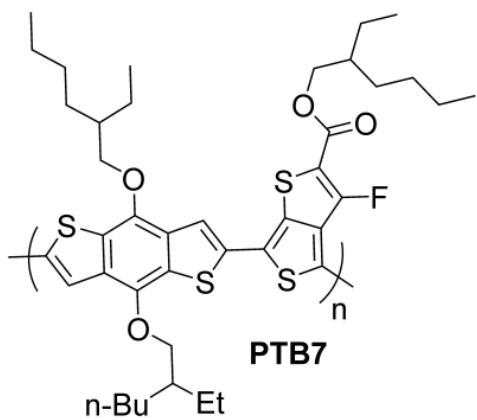
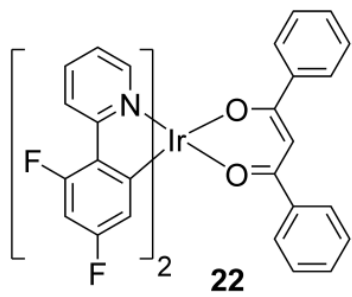


Figure 6

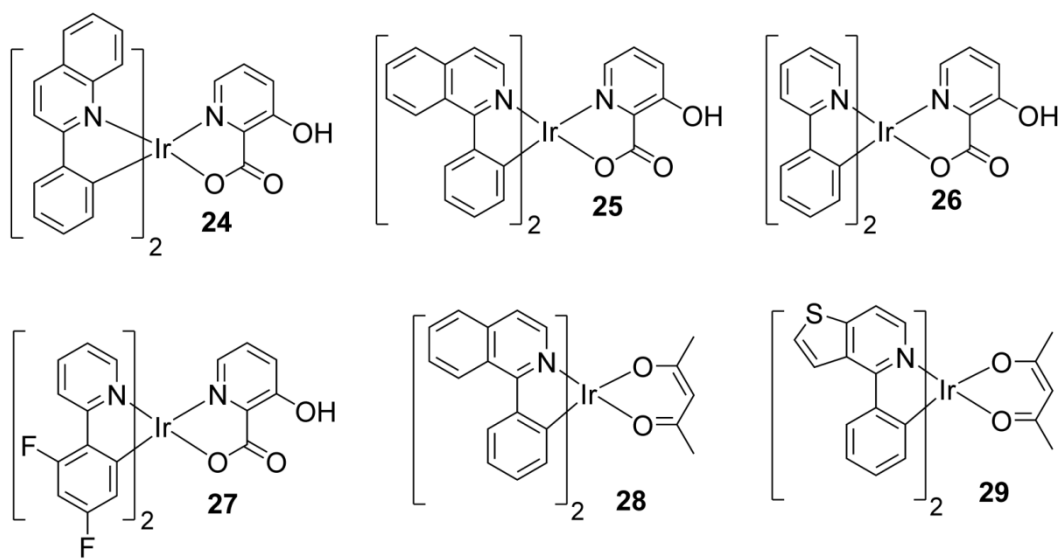


Figure 7

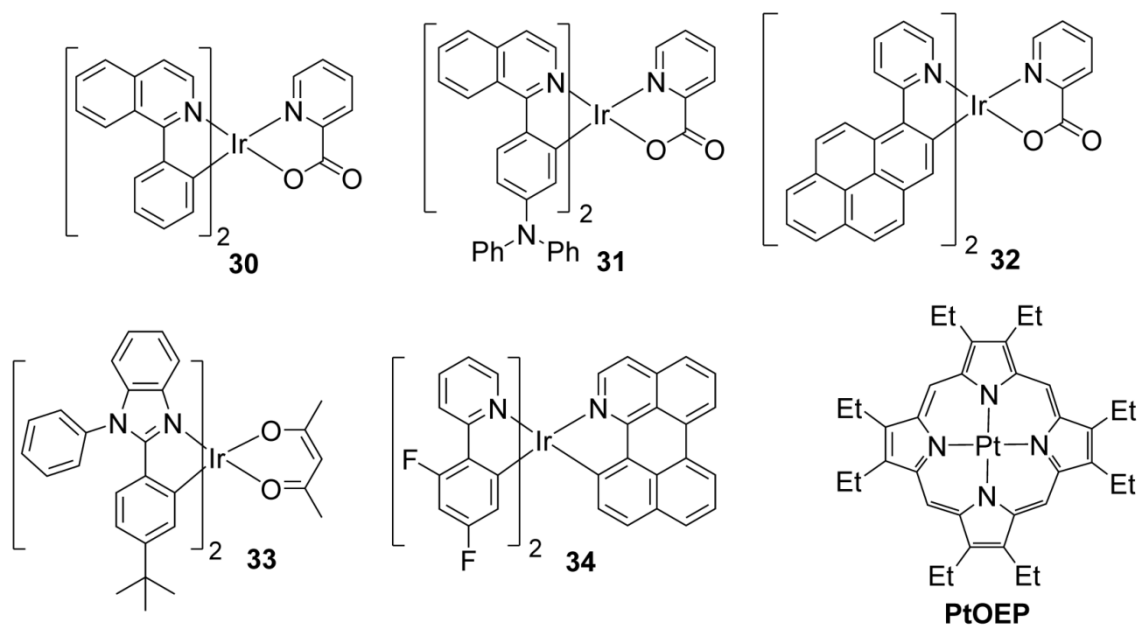


Figure 8

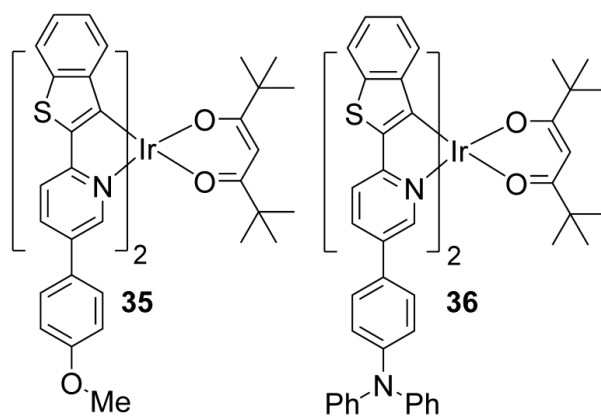


Figure 9

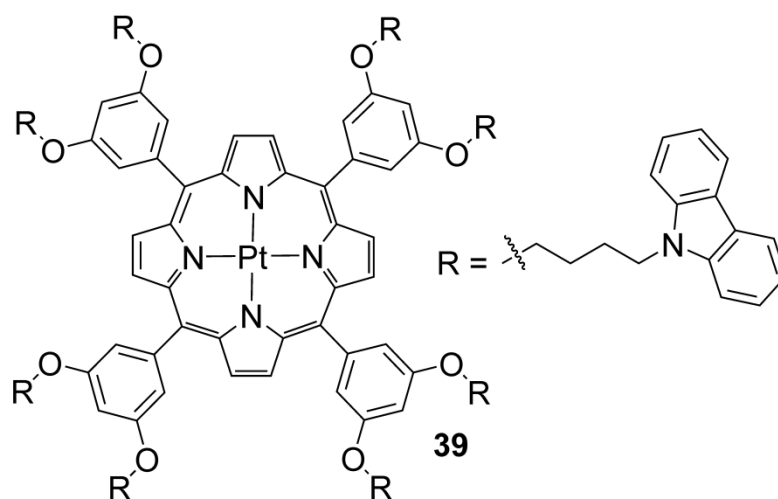
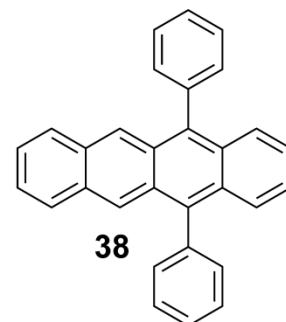
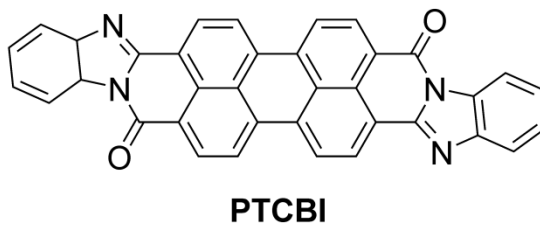
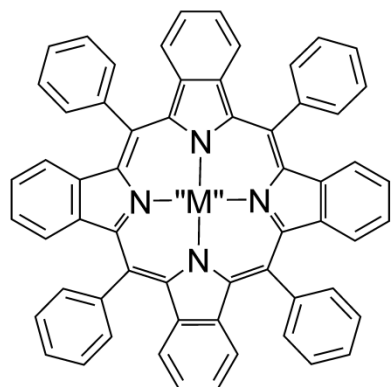
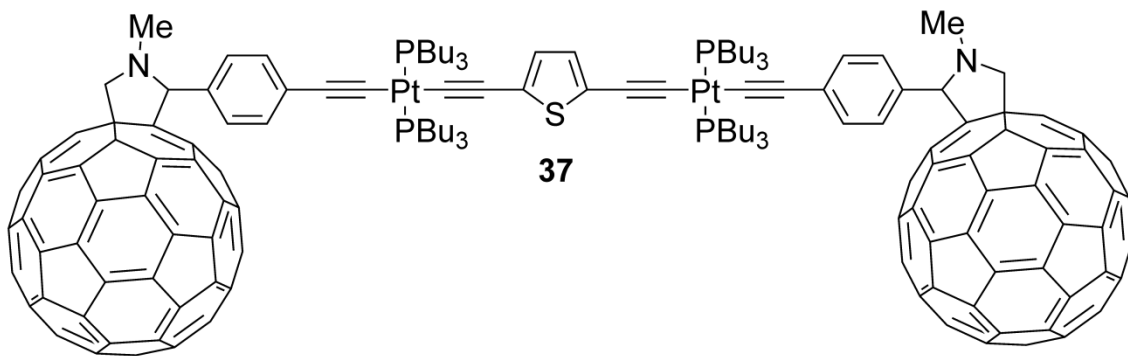
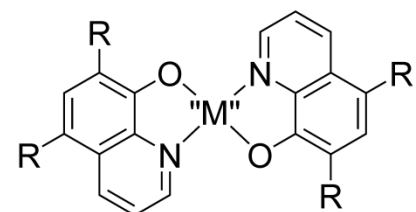
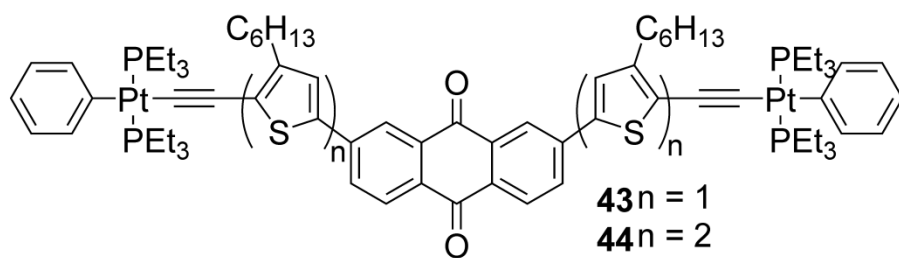
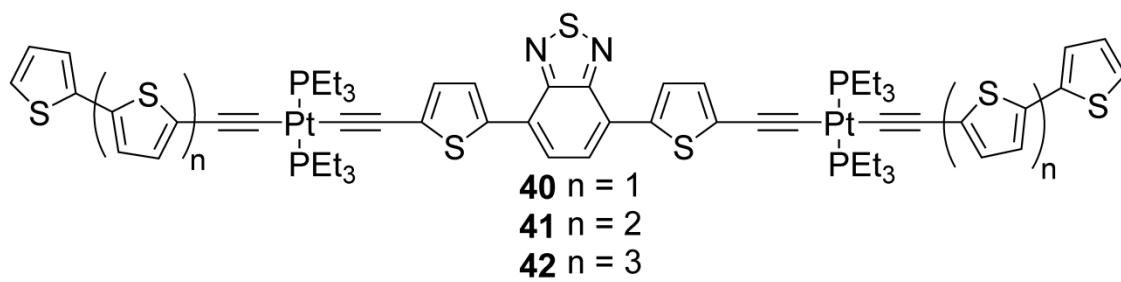


Figure 10



Mq₂: R = H, M = Pd, Pt
M(Me₂q₂): R = Me, M = Pd, Pt

Figure 11

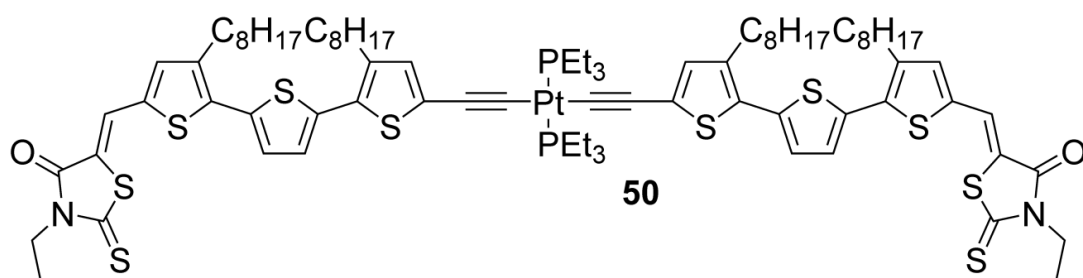
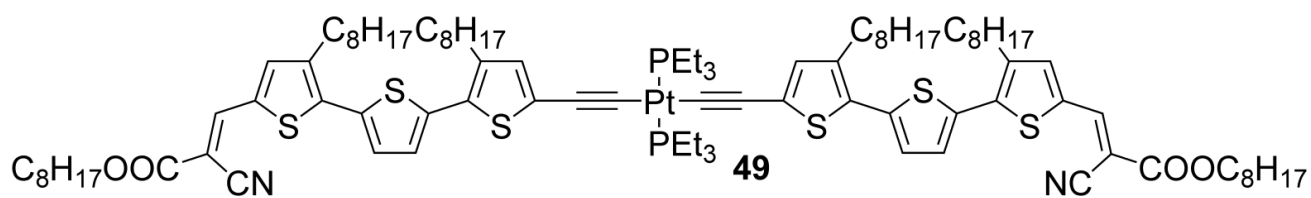
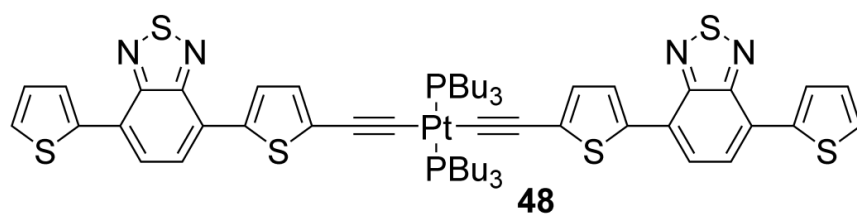
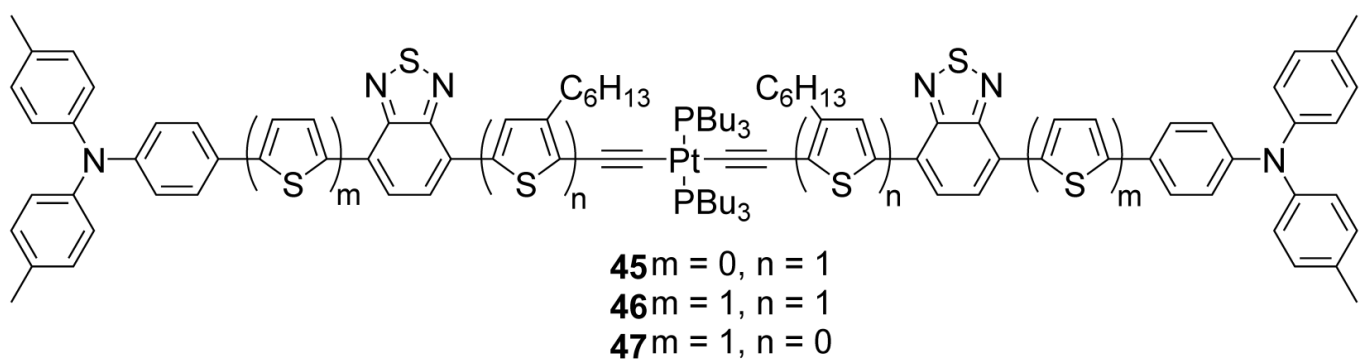


Figure 12

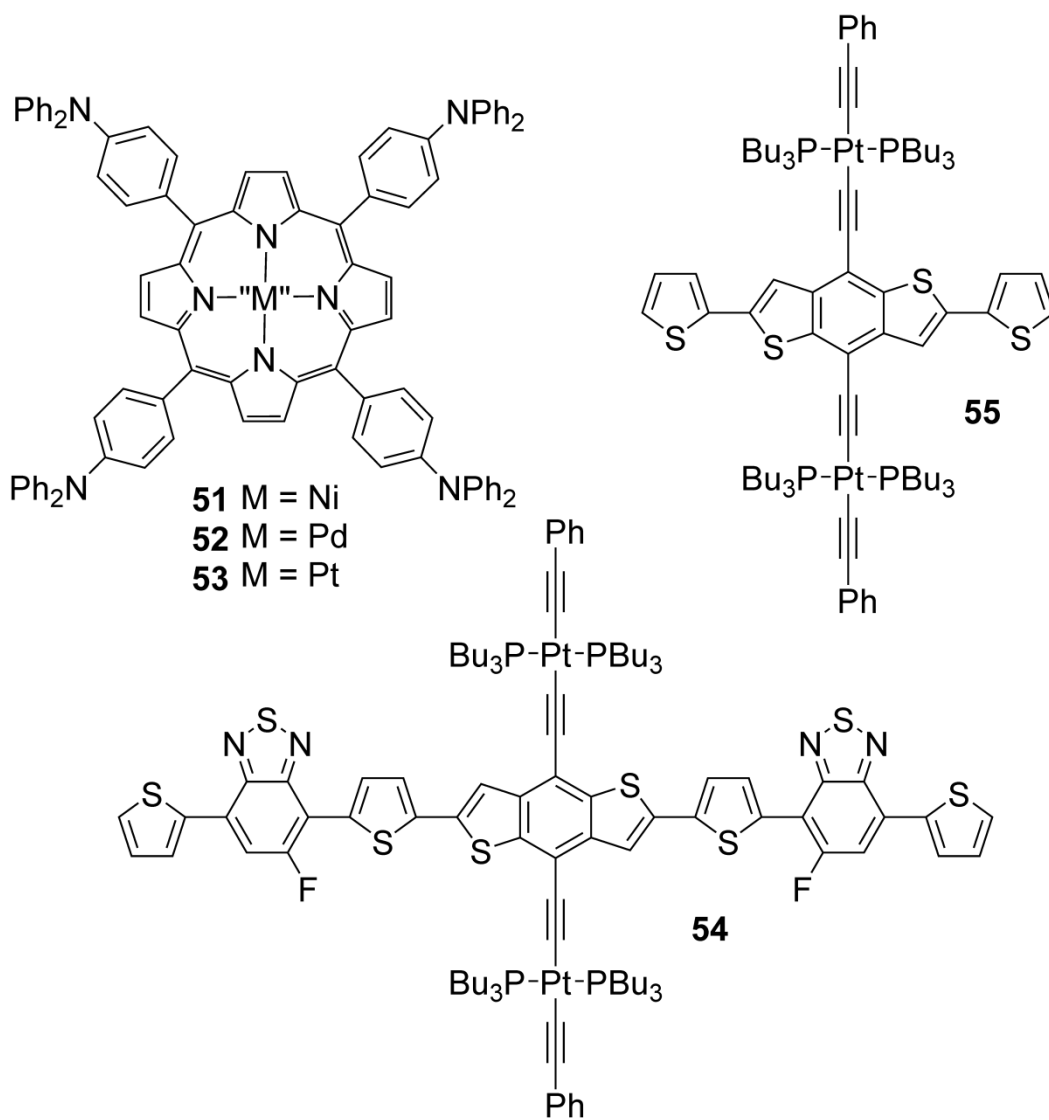


Figure 13

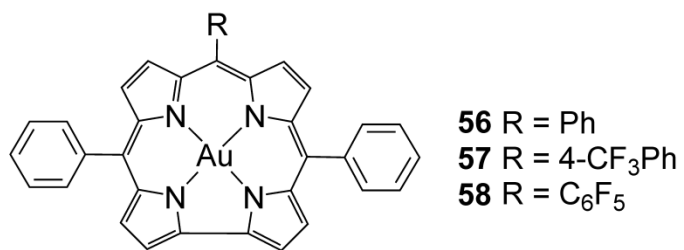


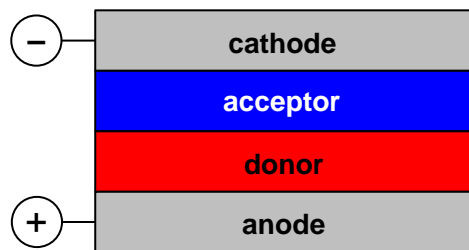
Figure 14

Donor:Acceptor	V_{oc} (V)	J_{sc} (mA cm⁻²)	FF	η (%)
5:PC₆₁BM	0.55	5.1	0.37	1.0
8:PC₆₁BM	0.48	4.5	0.37	1.0
5:PC₇₁BM	0.55	7.1	0.38	1.5
8:PC₇₁BM	0.56	8.3	0.34	1.6

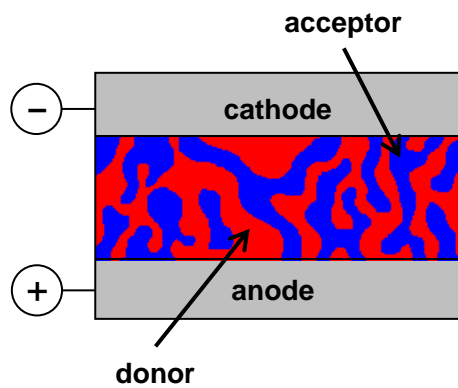
Table 1

Scheme 1

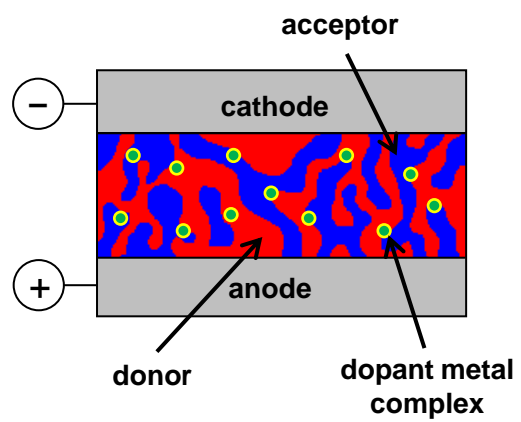
a)



b)

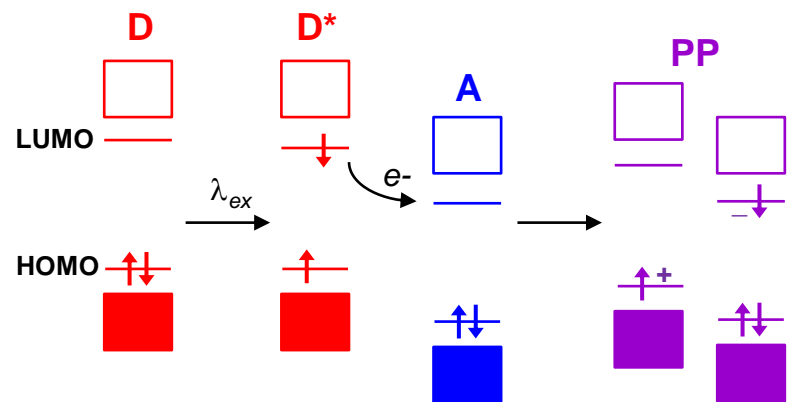


c)

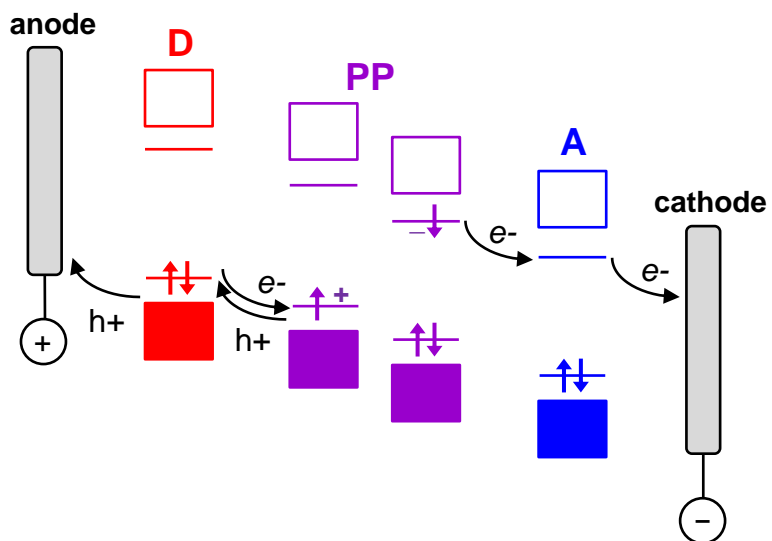


Scheme 2

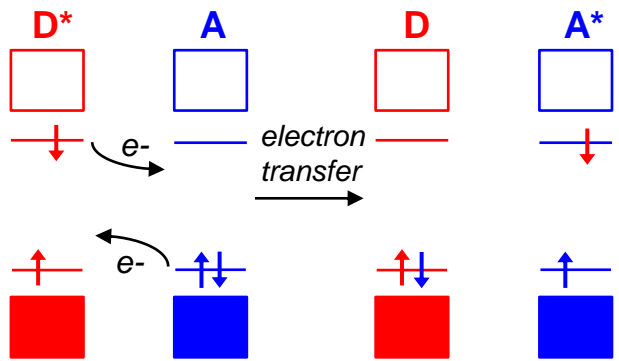
Step 1:



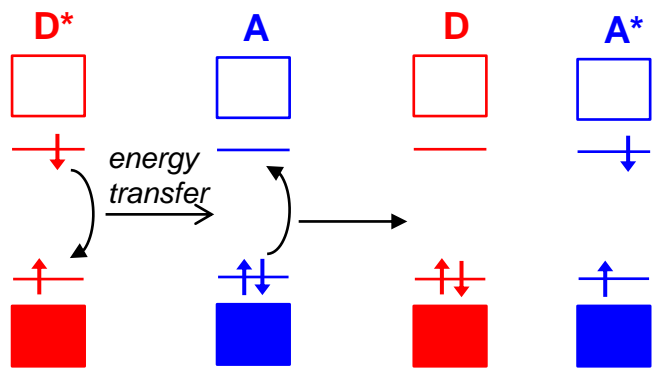
Step 2:

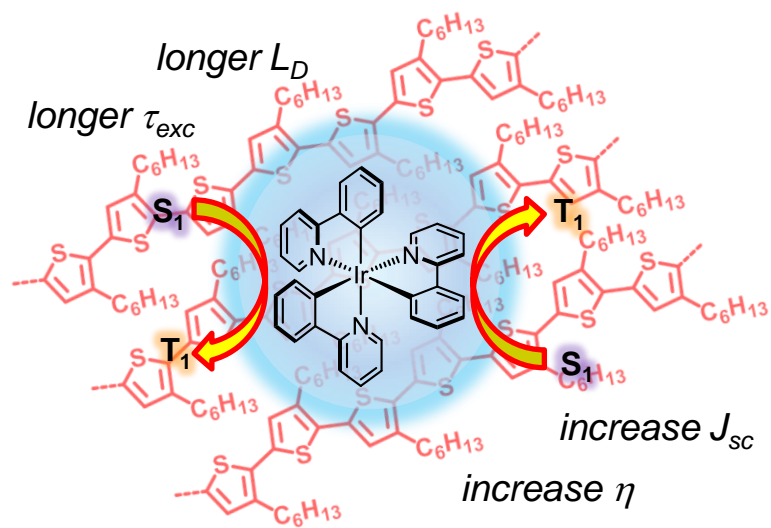


Dexter Electron Transfer



Förster Resonance Energy Transfer





Graphical abstract – synopsis

Phosphorescent metal complexes can act as triplet sensitizers in organic heterojunction solar cells. Energy transfer and spin-orbit coupling processes between the phosphor and the organic matrix greatly increases the number of triplet excitons formed upon photoexcitation which can contribute to significant improvements in device efficiency.