Optimize the power conversion efficiency of organic photovoltaic solar cells

Introduction

Organic photovoltaic (OPV) are 'plastic' solar cells that can be made cheaply and easily as you can use techniques like roll to roll printing, inject printing and spray coating. Current generation solar cells take several years of use before they payback the energy required in their manufacture, OPVs are so efficient that their energy payback is only 24hours. Power conversion efficiencies (PCEs) of OPVs are now around 14%. To commercialise them, we need to figure out how best to manufacture them.

Organic photovoltaic devices have a sandwich architecture. The bottom layers Al/Mg and LiF are the bottom electrode. The important part is the bulk heterojunction, shown in red in the figure below, which comprises of a low band gap polymer which is the electron donor and fullerene which is the electron acceptor. Addition of an additive helps with forming and bridging separate nanodomains of donor and acceptor. Solar cells work by using light to form an exciton which then separates into an electron-hole pair and you want these to be separated from each other, which is why you want separate nanodomain of donor and acceptor. The top of the solar cell is PEDOT:PSS (a conducting polymer) and ITO (indium tin oxide), a see-through electrode, which together act as the top electrode.

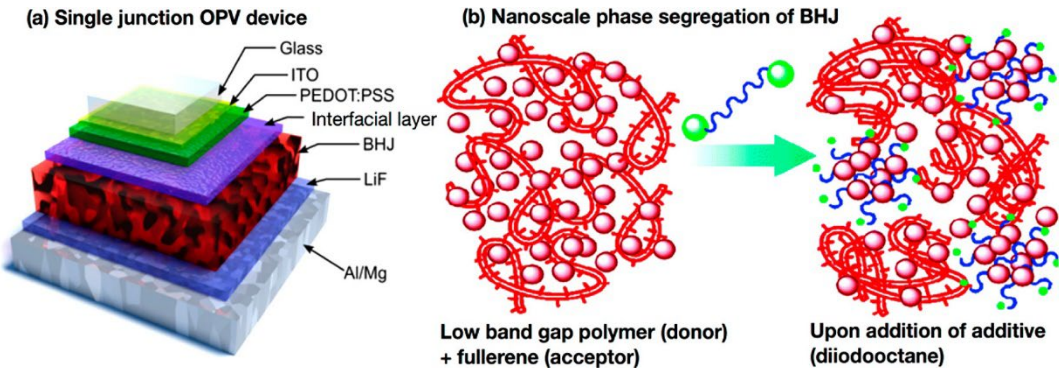

Figure 1. (a) Schematic of single junction organic photovoltaic (OPV) devices, showing the bulk heterojunction (BHJ; in red), and the multiple interfacial layers in the device. (b) Schematic of BHJ morphology: in this case, a low band gap polymer donor and a fullerene acceptor undergoing nanoscale phase segregation into discrete nanoscale domains of donor and acceptor. The use of an additive is often purported to assist in nanodomain formation, as shown here. Taken from [ACS Nano 2018, 12, 7434−7444]

The task

The task is to optimise the construction of this type of solar cell. Donor weight percentage is a measure of the ratio of donor to acceptor in the heterojunction. Total solution concentration is the concentration of the spin-coating solution. Bulk heterojunction spin-case speed is a measure of how fast you spin the device when coating it with the bulk heterojunction mixture. Processing additive is the amount of additive (diiodooctane) added to the mixture.

The thickness of a spun film is determined by the spin speed, solvent vapour pressure and solution viscosity, as both the donor weight percentage and total solution concentration can affect viscosity, the first three factors can all affect the thickness of the final BHJ layer. The additive (diiodooctane) increases the drying time for the film, helping to separate the hetereojunction out into nanodomains of donor and acceptor rich areas.

Factors selected:

Name	Factors	Factor range	No. of levels
Donor	Donor weight percentage	10-55 (wt %)	4
Conc.	Total solution concentration	10-25 (mg/mL)	4
Spin	Bulk heterojunction spin-case speed	600 - 3000 (rpm)	4
Add.	Processing additive	0-12 (vol %)	4

We shall use the shortened names from the table above.

Files:

1. \`solar_cells_1.csv\` results from the first experiment, fractional factorial, 4 factors and 4 levels, here we have 16 experiments, one failed to solidify.
2. \`'solar_cells_2.csv'\` has results from the second experiment, a fractional factorial, 3 factors and 3 levels. This covers a smaller range..

The data is taken from:

"How To Optimize Materials and Devices via Design of Experiments and Machine Learning: Demonstration Using Organic Photovoltaics", Bing Cao, Lawrence A. Adutwum, Anton O. Oliynyk, Erik J. Luber, Brian C. Olsen, Arthur Mar, and Jillian M. Buriak, ACS Nano 2018, 12, 7434−7444

Task 1. Create a linear (main factors only) model (4 marks)

Create a linear model, i.e. a model that has just the main effects (also known as a first order model or main effects model) Fit your linear model to the first experiment's data and calculate R2 and Q2 for your fitted model. Then answer the questions.

Question 1.1 For the first screening experiment, (solar_cells_1), If the experimentalists had chosen to do a full factorial experiment, rather than a fractional factorial experiment, excluding repeats and centrepoints, how many experiments would they have had to do? (1 mark)

A. Two levels, four factors, $2^4 = 16$
B. Four levels, four factors, $4^4 = 256$
C. Four levels, two factors, $4^2 = 16$
D. Two levels, three factors, $2^3 = 8$
E. Three levels, three factors, $3^3 = 27$

Answer: B. The number of experiments is given by L^k where L is the number of levels of each of factors and k is the number of factors.

Question 1.2 What terms are in the linear (main terms only) model? (1 mark)

A. Donor, Conc, Spin, Donor**2, Donor*Spin, Conc.*Spin
B. Donor, Conc., Spin, Add, Donor*Spin, Donor*Add
C. Donor, Conc., Spin and Add
D. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2
E. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add
F. Donor, Conc., Spin, Donor**2, Conc.**2, Spin**2
G. Donor, Conc., Spin, Add, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add

Answer: C. The main terms are those that describe the input factors. The model is linear as it has no higher order terms, therefore there are no square or cross terms, therefore the model can only contain Donor, Conc, Spin and Add.

Question 1.3 What is the Q^2 of the main effects model (1 mark)

A. -1.9
B. +0.014
C. 0.17
D. 0.604
E. 0.871

Answer: C. 0.17. It's not a great model

Question 1.4: What is the biggest main **effect** in the main effect model? (1 mark)

A. Donor
B. Conc.
C. Spin.
D. Add

Answer B. Conc. The coefficient plot gives the normalised coefficients so we can directly compare the effect of each factor on the system by comparing the size of the normalised coefficients. The largest coefficient is Conc. Indicating that the concentration is the largest effect. (Also, the effect size is 2* normalised coefficients).

Task 2. Create a parsimonious quadratic model (6 marks)

Create a **quadratic**, **parsimonious** and **hierarchical** model. Starting with a **quadratic model**, and making sure that all models are **hierarchical**, optimise the model by removing **only** the **statistically insignificant terms**. Keep a note of the terms removed and the Q^2 and R^2 values.

Question 2.1 What terms are in a **quadratic** model (**before** you optimise the model)? (1 mark)

A. Donor, Conc, Spin, Donor**2, Donor*Spin, Conc.*Spin
B. Donor, Conc., Spin, Add, Donor*Spin, Donor*Add
C. Donor, Conc., Spin and Add
D. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2
E. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add
F. Donor, Conc., Spin, Donor**2, Conc.**2, Spin**2
G. Donor, Conc., Spin, Add, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add

Answer: D. A quadratic model adds in square terms for each of the factors, so we have the four main terms and the four square terms.

Question 2.2. What is a parsimonious model? (1 mark)

A. A model with only at statistically significant terms
B. A model where a lower order term (e.g. a linear term or main term) must be present in the model if a higher order term (e.g. square or interaction term) is present.
C. A model with only square and linear terms
D. A model with only interaction and linear terms
E. A model which tries to fit the data well using a few factors as possible
F. A model with a high Q^2

Answer: E. A parsimonious model tries to fit the data using as few variables as possible. This may be done by removing the statistically insignificant terms, but its does not have to be, you can remove statistically significant ones if you want. It is usually done to give a higher Q^2 but that is not part of the definition of a parsimonious model. It may contain any type of terms.

Question 2.3. What is a **hierarchical** model? (1 mark)

A. A model with only at statistically significant terms
B. A model where a lower order term (e.g. a linear term or main term) must be present in the model if a higher order term (e.g. square or interaction term) is present.
C. A model with only square and linear terms
D. A model with only interaction and linear terms
E. A model which tries to fit the data well using a few factors as possible
F. A model with a high Q^2

Answer: B. The model is built up such that the higher order terms are derived from the lower orders ones.

Question 2.4 What terms are in the **quadratic parsimonious hierarchica**l model (i.e. **after** you optimise the model)? (2 marks)

A. Donor, Conc, Spin, Donor**2, Donor*Spin, Conc.*Spin
B. Donor, Conc., Spin, Add, Donor*Spin, Donor*Add
C. Donor, Conc., Spin and Add
D. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2
E. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add
F. Donor, Conc., Spin, Donor**2, Conc.**2, Spin**2
G. Donor, Conc., Spin, Add, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add

Answer: F. We start from the saturated quadratic model which has the terms: Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2, this model has a R2 of 0.815 and Q2 of -0.176. The smallest statistically insignificantly different from zero term is Add**2, so we remove it, this improves the model, as we now have a R2 of 0.813 and Q2 of 0.086. At this point, there is only one term that is statistically insignificantly different from 0, and that is Add. This is a main effect, but we can remove as there are no higher order terms that rely in it (as we've just removed the Add**2 term which did). We remove this term and we now have a R2 of 0.813 and a Q2 of 0.332. At this point, all the terms are statistically significant, so we stop here, leaving a model with the terms Donor, Conc., Spin, Donor**2, Conc.**2, Spin**2

Question 2.5: What is the Q2 of the final quadratic parsimonious hierarchical model you've built? (1 mark)

A. 0.56
B. 0.815
C. 0.332
D. 0.086
E. 0.813

Answer: C.

Task 3. Create a parsimonious interaction model (5 marks)

Create **hierarchical parsimonious interaction** model. Starting with a **interaction model**, and making sure that all models are **hierarchical**, optimise the model by removing **only** the **statistically insignificant terms**. Keep a note of the terms removed and the Q^2 and R^2 values.

Question 3.1 What terms are in the parsimonious hierarchical interaction model (i.e. **after** you optimise the model)? (2 marks)

A. Donor, Conc, Spin, Donor**2, Donor*Spin, Conc.*Spin
B. Donor, Conc., Spin, Add, Donor*Spin, Donor*Add
C. Donor, Conc., Spin and Add
D. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2
E. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add
F. Donor, Conc., Spin, Donor**2, Conc.**2, Spin**2
G. Donor, Conc., Spin, Add, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add

Answer: B. Donor, Conc., Spin, Add, Donor*Spin, Donor*Add. We start from a full interaction model and remove Conc*Add to geta Q^2 of 0.086. Then we removed Spin*Add to get a Q^2 of -0.555. Then we remove Conc.*Spin (it's just slightly smaller than the next term) to get a Q^2 of 0.0133, then we remove Donor*Conc. To get a Q^2 of 0.315. There are now no more statistically insignificant terms to remove, so we stop here. This leaves us with the following terms: Donor, Conc., Spin, Add, Donor*Spin, Donor*Add.

Question 3.2: What is the Q^2 of the parsimonious, hierarchical interaction model? (1 mark)

A. 1
B. -1.79
C. 0.777
D. 0.315
E. 0.761
F. -0.555

Answer: D. 0.315

Question 3.3. Which of the models you have trained so far is the best, and why? (1 mark)

A. The linear model as it is nice and simple (has the smallest number of terms)
B. The saturated quadratic model as it has the best R^2
C. The parsimonious quadratic model as it has the best Q^2
D. The saturated interaction model as it has interaction terms in it, which we need as there are interactions between the factors that control the width of the hetereojunction material.

Answer: C. The parsimonious quadratic model has the best Q^2 so we expect it to do the best job of predicting the PCE for new devices, and this is what we want to do. The saturated quadractic model has the best R^2, which makes it the best at fitting the data we have, but as the Q^2 is so small it is overtrained and thus not likely to be useful for predicting the PCE of new devices. The linear model is simple, but it is too simple as it is missing the higher order effects, which we expect will be important as the higher order models have a higher Q^2 than the linear model.

Task 4. Build and optimize a full saturated model (5 marks)

The scientists decided to do a second experiment to optimise the system. They choose to keep only 3 of the main effects, and then decide to investigate these factors at 3 different levels, running a further 12 experiments. Import this new data, combine it with the data from the first experiment and then train a parsimonious, hierarchical model.

You will have to drop a column from the first input dataframe so both sets of input data have only 3 factors and then concatenate the dataframes. There is code on how to do this in the answers to last week's workshop.

You will then need to remake the saturated input dataframe as well.

You will want to start with a full saturated model and then remove the statistically insignificant terms.

Question 4.1 From looking at your models from task 2 and task 3, which factor would you chose to drop and why? (1 marks)

A. Donor: Because it is the cross terms in the interaction model
B. Conc. Because there are no interaction terms containing Conc.
C. Spin. Because Spin**2 was the largest quadratic term
D. Add. Because it's the smallest main effect in the interaction model
E. Donor: because it is the smallest main effect in the interaction model
F. Conc. Because it's the largest main effect in the interaction model
G. Spin. Because it is the smallest main effect in the quadratic model
H. Add. Because it was removed from the best model

Answer: H. The additive term (Add) should have been removed from the quadratic model as both the Add**2 and Add terms are statistically insignificant, and as this is the better of the two models, it suggests that Add can be ignored in further investigations of the system.

Question 4.2 For the second experiment, (solar_cells_2), where the scientists decided to use three factors at three levels, if the experimentalists had chosen to do a full factorial experiment, rather than a fractional factorial experiment, **excluding** repeats and centrepoints, how many experiments would they have had to do? (1 mark)

A. 16
B. 27
C. 9
D. 128
E. 15

Answer: B. 27, three levels and three factors is 3^3 or 27 experiments.

Question 4.3 What terms are in the saturated model (i.e. **before** you optimise the model)? (1 mark)

A. Donor, Conc, Spin, Donor**2, Donor*Spin, Conc.*Spin
B. Donor, Conc., Spin, Add, Donor*Spin, Donor*Add
C. Donor, Conc., Spin and Add
D. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2
E. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add
F. Donor, Conc., Spin, Donor**2, Conc.**2, Spin**2

G. Donor, Conc., Spin, Add, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add

Answer: E. The saturated model contains all possible terms of order up to 2, i.e. all the main terms, all the interaction terms and all the square terms.

Question 4.4 What terms are in the parsimonious hierarchical model (i.e. **after** you optimise the model)? (2 marks)

A. Donor, Conc, Spin, Donor**2, Donor*Spin, Conc.*Spin
B. Donor, Conc., Spin, Add, Donor*Spin, Donor*Add
C. Donor, Conc., Spin and Add
D. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2
E. Donor, Conc., Spin, Add, Donor**2, Conc.**2, Spin**2, Add*2, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add
F. Donor, Conc., Spin, Donor**2, Conc.**2, Spin**2
G. Donor, Conc., Spin, Add, Donor*Conc., Donor*Spin, Donor*Add, Conc*Spin, Conc.*Add, Spin*Add

Answer: F. All the cross-terms are removed in the following order: Conc*Spin, Donor*Spin, Donor*Conc, this gives us an R^2 of 0.871 and 0.695

Task 5: Optimising the devices. Using the best model that you have trained (as measured by Q^2), find some conditions to optimise the devices. (5 marks)

One way to do this is to plot a 4D contour plot with Donor on the x axis, Conc. On the y axis and Spin as the constant slices (i.e. x_key is the donor %, y_key is the concentration and c_key is the spin). To do this, I suggest that you look at the model answer option C from the worksheet last week to see how you can input your model into the four_D_contour_plot function (you will have to rewrite the my_function to do this). Use spin constants of 1000, 1500, 2000 for the slices (e.g.
x_limits=[inputs[x_key].min(),inputs[x_key].max()],
y_limits=[inputs[y_key].min(),inputs[y_key].max()],
constants=[500,1500,2500]).

The other way is to feed the data into the best model directly, I would suggest looking at doenut.predict_from_model.

Question 5.1: Which model is the best? Which model have you chosen to use? (1 mark)

A. The linear (main effects) model from task 1

B. The full quadratic model from task 2 (pre-optimisation)
C. The parsimonious quadratic model from task 2 (post-optimisation)
D. The full interaction model from task 3 (pre-optimisation)
E. The parsimonious interaction model from task 3 (post-optimisation)
F. The saturated model from task 4 (pre-optimisation)
G. The parsimonious model from task 4 (post-optimisation)

Answer: G. The model with the best Q2 is the parsimonious model from task 4. The parsimonious quadratic model from task 2 has the same factors, but it is a not as good a model as it has not been trained on as much data.

Question 5.2: What conditions will give a device with a power conversion efficiency (PCE) of above 7%? (4 marks)

A. Donor %: 20, Conc.: 12, Spin: 500,
B. Donor %: 40, Conc.: 16, Spin: 1500,
C. Donor %: 35, Conc.: 22, Spin: 1500,
D. Donor %: 45, Conc.: 18, Spin: 2500,
E. Donor %: 20, Conc.: 17, Spin: 2500

Answer: C. If you managed to plot the 4D contour plot with this data as described, then you can read these value off the graph. Alternatively, you could have made a dataframe of these options and put them into your model to directly calculate the predictions and see which one is over 7%.

0 `Donor %'

1 `Conc.',

2 `Spin',

3 `Add.'

Square terms

4 `Donor %**2`

5 `Conc.**2`

6 `Spin**2`

7 `Add.**2`

Adding interaction terms:

8 `Donor %*Conc.`

9 `Donor %*Spin`

10 `Donor %*Add.`

11 `Conc.*Spin`

12 `Conc.*Add.` x

13 `Spin*Add.`