Photo Electro Chemical performance evaluation of some natural dyes used in solar cells, DFT study and TD-DFT

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Abstract

Several natural dyes belonging to anthocyanin goups have been studied to evaluate their potential use in the dye sensitized solar cells (DSSCs). DFT/B3LYP 3-21G, DFT/B3LYP/ 6-31G, DFT/B3LYP/ 6-311G and TD-DFT as computational methods were used to calculate some parameters such as Egap, Voc and global electrophilicity using TiO_2 as conduction band. Comparison between the three methods were done using statistical analysis to investigate the dye which is more efficient due to their photoelectrochemical performance, especially those of the Voc and global electrophilicity properties. The obtained results showed that the delphinidin pigment been the best one between the twenty five dyes used in this study.

Key words: Photo electrochemical, solar cells, TD-DFT, global electrophilicity.

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تقدير الكفاءة الكهروكيموضوئية لبعض الصبغات الطبيعية في استخدامات الخلايا الشمسية دراسة نظرية باستخدام طريقة DFT and TD-DFT

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الخلاصة

تم دراسة مجموعة من الصبغات الطبيعية العائدة الى فصيلة anthocyanin لتقييم كفاءتهافي استخدامات خلايا الطاقة الشمسية وذلك باستخدام الطرق الحسابية التالية

DFT/B3LYP 3-21G, DFT/B3LYP/ 6-31G, DFT/B3LYP/ 6-311G and TD-DFT

تم اعتماد مجموعة من المتغيرات لتقدير فعالية هذه الصبغات وخصوصا فرق الطاقة بين الهومو واللومو (Egap) و ال Voc و global electrophilicity. تم اجراء المقارنة بين الطرق الحسابية المتاحة باستخدام المعاملات الاحصائية لتحديد معامل التكرارية نتيجة للتباين بين مخرجات ونتائج تلك الحسابات لغرض الحصول على افضل الصبغات وفق المتغيرات التي تم اعتمادها وتبين ان صبغ ال delphinidin هي الافضل بين مجموعة الصبغات التي تم دراستها

الكلمات المفتاحية : Photo electrochemical ، خلايا شمسية ، TD-DFT ، global electrophilicity .

Introduction

According to its durability characteristic, high conversion efficiency, ease of preparation and its clean environment, Dye-sensitized solar cells (DSSCs) were used as an alternative option of energy production (1-5). DSSCs were first proposed by Grätzel et al (3). It is the third generation photovoltaic device for low cost conversion of solar energy into electrical energy. In DSSCs, the dyes plays an important role in harvesting solar energy and converts it to electrical energy with aid of a semiconducting photo anode. Researcher have focused on the easily available dyes extracted from natural sources as a photosensitizer because of its large absorption coefficients, low cost and its high degree of *environmental friendliness* (6-9).

Computational calculations such as Density functional theory (DFT) and time dependent (TD-DFT) were used to study the photoelectrochemical performance of some natural dyes in their flower, leaves and roots to determine Egap (EHOMO- ELUMO), hardness, electronegativity, electrophilicity and the absorption bands of natural dyes [10,11].

Computational methods

(DFT) and TD-DFT at three levels of bases set (3-21G, 6-31G and 6-311G) combined with B3LYP correlation *functional* were used. Personal computer was used to carry out all calculations.

Materials

The following twenty five natural dyes were used: Delphinidin+glucose, Aurantinidin+glucose, Hirsutidin+glucose, Europenidin+glucose, Peonidin+glucose, Pelargonidin+glucose, Malvidin+glucose, Triacetidin+glucose, Petunidin+glucose, Apigeninidin+glucose, Capensinidin+glucose, Rosinidin+glucose, Cyanidin+glucose, Luteolinidin+glucose, α-mangostin, β –mangostin, Betalains, Peonidin, Betalains2, Betaxanthin, Bixin, Cyanidin, Delphinidin, Crocetin, Pulchellidin+glucose. The structures of these compounds were found in Ref.[12]

Mathematical equations:

I (ionization potential) =- HOMO

A (electron affinity) =- LUMO

X (electronegativity) = (I+A)/2

Global hardness $\eta = (I-A)/2$

$\mu = -X$

Global electrophilicity $\omega=\mu^2/2\eta$

Voc/TiO_2 = ELUMO (Donor) - 4.0

Theoretical calculations

HOMO, LUMO and open circuit voltage (Voc) were calculated using DFT with different basis set (table-1), while Global electrophilicity were calculated numerically using the above equation (table-2)

Results and discussion

Both Voc and global electrophilicity were adopted as a measure of photosensitizer efficiency in this study using TiO_2 as *band* gap semiconductor. The lower the global electrophilicity, the more efficient the solar cell [(12)]. The higher the Voc, *the* better light absorption and the higher electron mobility [(13)]. The results observed due to the different methods used, show that there are some differences in the efficiency sequence of the calculated compounds between these methods. To overcome this problem, statistical analysis were inserted in this study to determine the possible approximation. *The sequence of values given by the iterative* method was selected to be the suitable one for this purpose. Considering both factors (Voc and global electrophilicity), Table 3 and 4 with fig. 1 and 2 show that the delphinidin pigment represents the most efficient between the all dyes studied, owing to *its highly iterative* nature with the three method.

Table- 1: Voc/TiO_2 calculated by different methods

Type of Dyes		DFT/B3LYP 3-21G			DFT/B3LYP/ 6-31G			DFT/B3LYP/ 6-311G		
		HOMO	LUMO	Voc	HOMO	LUMO	Voc	HOMO	LUMO	Voc
1	Del+ g	-5.992	-1.043	2.957	-5.852	-0.955	3.045	-5.774	-0.875	3.125
2	Aur+g	-5.738	-0.901	3.099	-5.615	0.953	3.047	-5.615	-0.953	3.047
3	Hir+g.	-5.948	-0.965	3.035	-6.053	-1.098	2.902	----	----	----
4	Eur+g	-5.898	-0.891	3.109	-5.778	-0.909	3.091	----	----	----
5	Peo.+g	-5.955	-1.019	2.981	-5.936	-1.117	2.883	-5.847	-1.005	2.995
6	Pel+g	-5.575	-0.894	3.106	-5.831	-1.033	2.967	-5.640	-0.951	3.049
7	Mal+g	-5.912	-0.979	3.021	-5.922	-0.864	3.136	----	----	----
8	Tri+g	-5.272	-0.883	3.117	-5.910	-1.039	2.961	-5.815	-0.935	3.065
9	Pet+g	-5.125	-1.897	2.103	-6.023	-0.992	3.008	-5.941	-0.997	3.003
10	Pul+g	-5.826	-0.904	3.096	-5.873	-0.982	3.018	-5.795	-0.905	3.095
11	Api+g	-5.695	-0.916	3.084	**5.696-**	**0.948-**	3.052	-5.696	-0.948	3.052
12	Cap+g	-5.807	-0.821	3.179	-5.910	-1.005	2.995	----	----	----
13	Ros+g	-5.76	-0.859	3.141	-6.071	-1.111	2.889	-6.062	-1.093	2.907
14	Cya+g	-5.785	-0.933	3.067	**5.983-**	**1.078-**	2.922	-5.759	-0.888	3.112
15	Lut+g	-5.269	-0.379	3.621	-5.081	-2.005	1.995	-5.069	-1.982	2.018
16	Cya	-5.789	-0.846	3.154	-5.802	-0.87	-3.67	-5.802	0.87	-3.13
17	Peo	-5.755	-0.808	3.192	-5.807	-0.874	-3.13	-5.807	-0.874	-3.126
18	Del	-5.76	-0.777	3.223	-5.8	-0.822	3.18	-5.8	-0.822	3.178
19	Bet	-9.27	-3.46	0.54	-9.291	-3.558	0.442	-9.291	-3.558	0.442
20	Bet2	-9.377	-2.453	1.547	-9.61	-2.421	1.579	-9.61	-2.421	1.579
21	Cro	-11.34	-7.519	-3.519	-11.33	-7.677	-3.68	-11.33	-7.677	-3.677
22	Bix	-11.05	-7.833	-3.833	-11.02	-7.949	-3.95	-11.02	-7.949	-3.949
23	α-mag	-10.86	-4.512	-0.512	-10.78	-4.551	-0.55	-10.78	-4.551	-0.551
24	Betax	-10.08	-9.458	-5.458	-10.02	-9.546	5.546	-10.02	-9.546	-5.546
25	β –ma	-10.77	-4.484	-0.484	-10.90	-4.555	-0.55	-10.90	-4.555	-0.555

Table - 2 Global electrophilicity calculated by different methods

Type of Dyes		Global electrophilicity		
		DFT/B3LYP 3-21G	DFT/B3LYP/6-31G	DFT/B3LYP/ 6-311G
1	Del+g	2.499	2.364	**2.255**
2	Aur+g	2.276	2.313	2.313
3	Hir+g.	2.396	2.579	----
4	Eur+g	2.299	2.295	----
5	Peo.+g	2.463	2.579	2.423
6	Pel+g	2.234	2.445	2.315
7	Mal+g	2.406	**2.276**	----
8	Tri+g	**2.157**	2.477	2.334
9	Pet+g	3.818	2.444	2.434
10	Pul+g	2.300	2.401	2.294
11	Api+g	2.286	2.324	2.324
12	Cap+g	**2.202**	2.436	----
13	Ros+g	2.234	2.599	2.575
14	Cya+g	2.325	**1.27**	**2.267**
15	Lut+g	**1.630**	4.08	4.025
16	Cya	2.225	**2.256**	**2.256**
17	Peo	2.176	**1.130**	**2.261**
18	Del	**2.143**	**2.202**	**2.202**
19	Bet	6.972	7.199	7.198
20	Bet2	5.053	5.033	5.032
21	Cro	23.266	24.711	24.711
22	Bix	27.703	29.25	29.25
23	α-mang	9.304	9.432	9.432
24	Beta	151.365	199.09	199.097
25	β –mang	9.252	9.408	9.408

Table-3 The best five values of Voc/TiO_2 in each method

DFT/B3LYP/3-21G		DFT/B3LYP/ 6-31G		DFT/B3LYP /6-311G	
Lut+g	3.62	Bet	0.442	Bet	0.442
Del	3.22	Bet2	1.579	Bet2	1.579
Peon	3.19	Mal+g	3.13	Del	3.178
Cap+g	3.17	Del	3.178	Del+g	3.12
Rosi+g	3.14	Eur+g	3.09	Cya+g	3.11

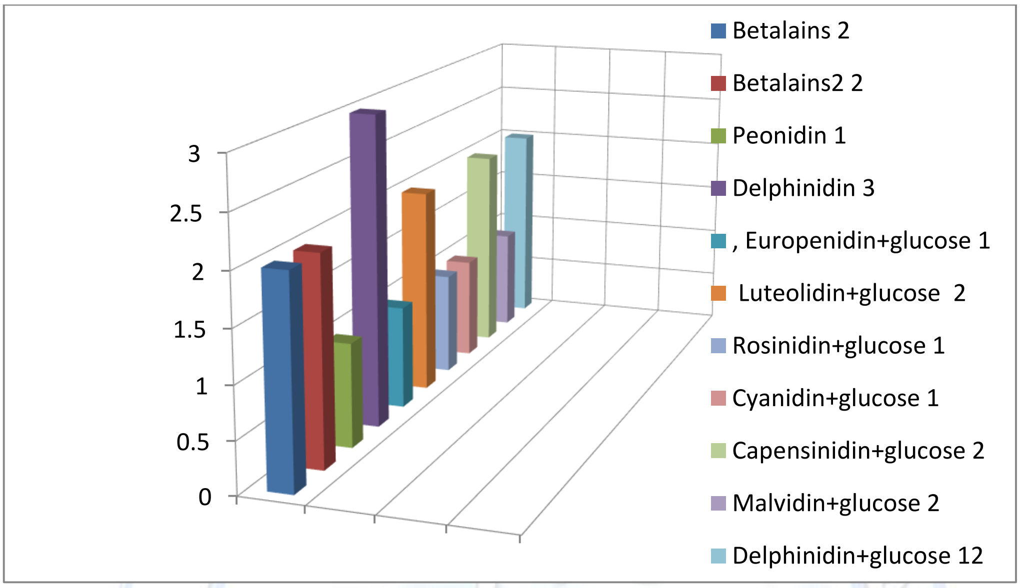

Fig-1 *Iterative* analysis of Voc by different calculation methods

Table-4 The best five values of Global electrophilicity in each method

DFT/3-21G		DFT/B3LYP 6-31G		DFT/B3LYP 6-311G	
Lu+g	1.630	**Pen**	1.13	**Del**	2.202
Del	2.143	Cya+g	1.27	Del+g	2.255
Tri+g	2.157	**Del**	2.20	Cya	2.256
Pen	2.176	Cya	2.26	**Pen**	2.261
Cap+g	2.202	Mal+g	2.27	Pul+g	2.294

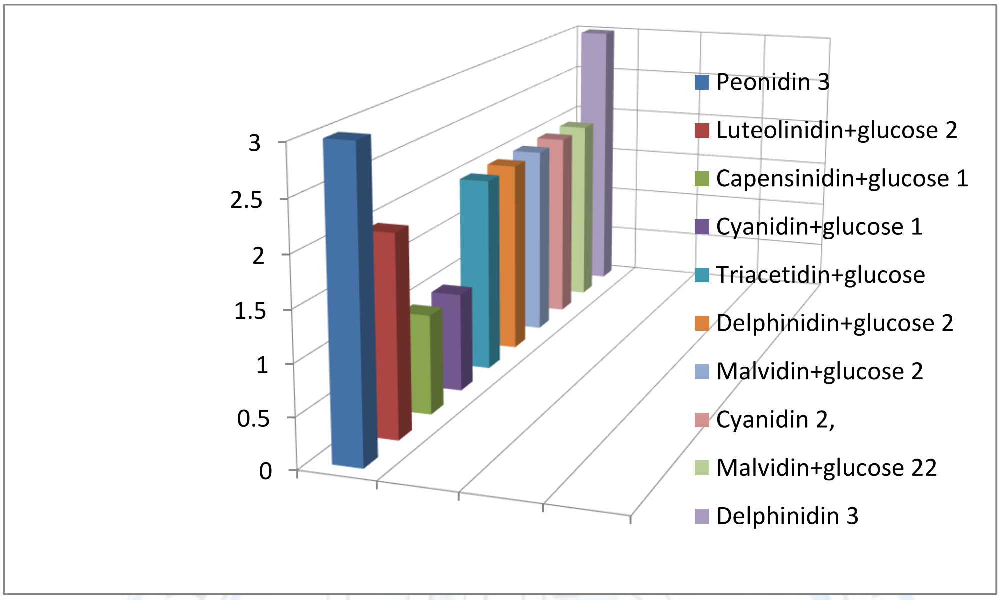

Fig-2* Iterative *analysis of Global electrophilicity by different calculation methods

Conclusion

Between 25 natural dyes studied theoretically by DFT method using different basis sets, it has been found that the delphinidin pigment being the most potent option for using as efficient dye using in DSSCs owing to *its highly iterative* nature with the three method.

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