Synthesis and characterization of 2,3-diaminomaleonitrile derivatives by one pot Schiff base reaction and their application in dye synthesized solar cells.

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ABSTRACT

In one pot reaction, three new 2,3-diaminomaleonitrile (DAMN) derivative dyes were prepared by simple Schiff base reaction. The compounds were designed as a sensitizer in dye synthesizes solar cells (DSSCs). Many conditions have been used to provide the methodology to get a best yield. The prepared dyes were characterized by melting point, elemental microanalysis, mass spectroscopy, FT-IR, ^{1}H NMR, and UV-Vis spectroscopy. Computational study was carried out to support our results. The DSSC data was shown the best performance for SA3 dye with 0.38% efficiency at AM 1.5 then SA2 with 0.22% and the last dye is SA1 with 0.09%, compared to control cell (N719) 5.4%.

Keywords: One pot reaction, 2,3-diaminomaleonitrile, Schiff base, DSSCs.

INTRODUCTION

Photovoltaic technology is one of the most important techniques which involved generating a clean energy from free sun light [1-3]. During the last two decades, Dye-sensitized solar cells arguably offer a promising photovoltaic technology due to their fabrication process and methods which is cheap and simple [4-8]. DSSCs have other specific advantages represented by the possible flexibility, chemical versatility, colorful appearances and a vast synthetic way to different organic and organometallic molecular structures [9-13]. In 1991, M. Grätzel and co-workers was developed the first effective DSSCs, with a power conversion efficiency (PCE) of 7% under the illumination of AM 1.5 [14]. Ten years later, Nazeeruddin M. and coworkers was used nano-poweder (TiO_2) as a semiconductor electrodes and the efficiency of DSSCs was reported to be 11.4 % [15]. A wide range of organic dyes with the donor and acceptor system has been designed for DSSCs [16-18].

The free metal organic dyes have many advantages over organometallic dyes such as cost efficiency, high extinction coefficient, and environmentally friendly [19-21]. The best organic dyes in DSSC are based on the chromophore as a donor part such as dimethylaniline [22-24] and coumarins derivatives [25-27]. Also, π bridge are played a significant rules in dyes design, for instance, Michele C. and co-worker reported the synthesis of two porphyrin dyes with two different π bridge spacer. The two dyes (PorF and PorT) were used furan and thiophen respectively as a π conjugation linker between same donor and acceptor parts. A significant differences in efficiencies (η) has been noticed, which based furan dye (η=4.5%) being more efficient than thiophen dye (η=3.6%) [28]. Peng G. and co-worker published their work used four different dyes with the elongation of π-conjugated bridge by using 3,4-ethylenedioxythiophene (EDOT) as a π bridge spacer. Unexpectedly, the longest π-bridge dye showed the lowest efficiency [29].

2,3-diaminomaleonitrile (DAMN) has used to prepare a wide range of organic compounds due to the significant applications of DAMN derivatives to synthesis symmetrical and unsymmetrical dyes with different physical and chemical properties [30-34]. There are few studies available about the DAMN derivative as a dye in DSSCs. This paper describes the synthesis of three unsymmetrical push-pull systems by using Schiff base reaction in one pot process. The three dyes are based in DAMN as a π conjugation linker, benzene derivative as a donor part and benzoic acid as a acceptor part and these dyes are used as dyes in DSSCs. Different types of conditions were used in these reactions to get a best yield for final compound. Finally, the advantages of one pot reaction protocol was represented by a significant reduce in synthesis time and purification cost [35-37].

EXPERIMENTAL SECTION

Materials

All starting materials and solvents were purchased from Alfa Aesar, TCI and Sigma-Aldrich and used as received without any purification. All reactions were run under a nitrogen atmosphere. Silica gel of column chromatography was used from Merck (40-63 µm 60 Å).

Instruments

^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance-DPX-250/400 spectrometer operating 400/100 MHz respectively, using tetramethylsilane (TMS) as an internal standard and DMSO-d^{6} or $CDCl_3$ as the solvent. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrometer. Mass spectra were obtained on a Bruker MicroTOF QII. Element Analyses (C, H and N) were tested on a Perkin Elmer 240 C analyzer. Computational studies

were performed using Gaussian 09 software. The molecular structure were initially optimized by semi-empirical (AM1) and then reoptimized by Density- functional theory (DFT).

Preparation of dyes

The three Schiff base dyes were synthesized by same procedure, figure (1). 1.0 mmol of one of aldehyde derivatives (benzaldehyde (1a), 4-(dimethylamino) benzaldehyde (2a), 3,5-dimethoxybenzaldehyde (3a)) and 1.5 mmol of DAMN were introduced to 2-neck round-bottom flask under a nitrogen atmosphere. Absolute ethanol (50 mL) was added to the mixture with two drops of glacial acetic acid as a catalyst. The mixture was allowed to stir for 5 hours at 80℃. After this time 2.0 mmole of 4-carboxybenzaldehyde was dissolved in 10 mL of absolute ethanol and added *via* a syringe to the mixture and left to stir at 80 ˚C for 15 hours. The mixture was allowed to cool at room temperature and the crude product was left to precipitate overnight in the mother solution. Then, the precipitate was filtered and washed with cold methanol. The crude product was purified by column chromatography (SiO_2, DCM:acetion; 9:1) to give a compound as a powder.

Dye characterization

4-((E)-(((E)-2-((E)-benzylideneamino)-1,2-dicyanovinyl)imino)methyl) benzoic acid (SA1).

Yield 36%; mp. 211-213 ˚C; FT-IR, cm^{-1} (rel.intensity), 3411(w), 2245 (s), 1788 (s), 1682(s), 1575 (m), 1433, 1082 (m), 863 (w), 776 (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (s, 1H, CH), 8.63 (s, 1H. CH), 8.09 (d, *J* = 9.1 Hz, 2H, Ar-H), 7.70 (d, *J* = 9.1 Hz, 2H, Ar-H), 7.60-7.39 (m, 5H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.95, 147.11, 136.73, 136.40, 135.66, 135.49, 133.06, 129.61, 129.60, 129.50, 129.05, 127.12, 115.28. Anal. Calcd. For $C_{19}H_{12}N_4O_2$: C, 69.51; H, 3.68; N, 17.06. Found: C, 69.53; H, 3.64; N, 17.10. EI-MS: *m/z* 328.

4-((E)-(((E)-1,2-dicyano-2-((E)-(4-(dimethylamino)benzylidene)amino)vinyl)imino)methyl) benzoic acid (SA2).

Yield 45%; mp. 231-233 ˚C; FT-IR, cm^{-1} (rel.intensity), 3432 (w), 2854 (m), 2259 (s), 1716 (s), 1641 (m), 1544 (m), 1419 (s), 1290 (m), 1091 (m), 860 (w), 769 (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.68 (s, 1H, CH), 8.44 (s, 1H. CH), 8.06 (d, *J* = 9.1 Hz, 2H, Ar-H), 7.64 (d, *J* = 9.1 Hz, 2H, Ar-H), 7.39 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.96 (d, *J* = 8.4 Hz, 2H, Ar-H), 2.93 (s, 6H, CH). ^{13}C NMR (CDCl3, 100 MHz): δ 168.95, 154.62, 147.11, 136.73, 136.40, 135.66, 131.23, 129.61, 127.12, 122.95, 115.28, 111.56, 41.91. Anal. Calcd. For $C_{23}H_{23}N_5O_2$: C, 68.81; H, 5.77; N, 17.44. Found: C, 68.86; H, 5.75; N, 17.42. EI-MS: m/z 401**.**

2.3.3. 4-((E)-(((E)-1,2-dicyano-2-((E)-(3,5-dimethoxybenzylidene) amino)vinyl)imino)methyl) benzoic acid (SA3).

Yield 44%; mp. 254-256 ˚C; FT-IR, cm^{-1} (rel.intensity), 3008(s), 2241 (s), 1691 (s), 1665(s), 1583 (m), 1411 (s), 1186 (s), 1051 (m), 872 (w), 782 (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (s, 1H, CH), 8.65 (s, 1H. CH), 8.09 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.70 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.78-6.67 (m, 3H, H-Ar), 3.82 (s, 6H, CH). ^{13}C NMR (CDCl3, 100 MHz): δ 168.95, 162.18, 147.11, 146.77, 139.90, 136.73, 136.40, 135.66, 129.61, 127.12, 115.28, 106.57, 102.25, 56.04. Anal. Calcd. For $C_{21}H_{16}N_4O_4$: C, 64.94; H, 4.15; N, 14.43. Found: C, 65.02; H, 4.12; N, 14.39. EI-MS: m/z 388.

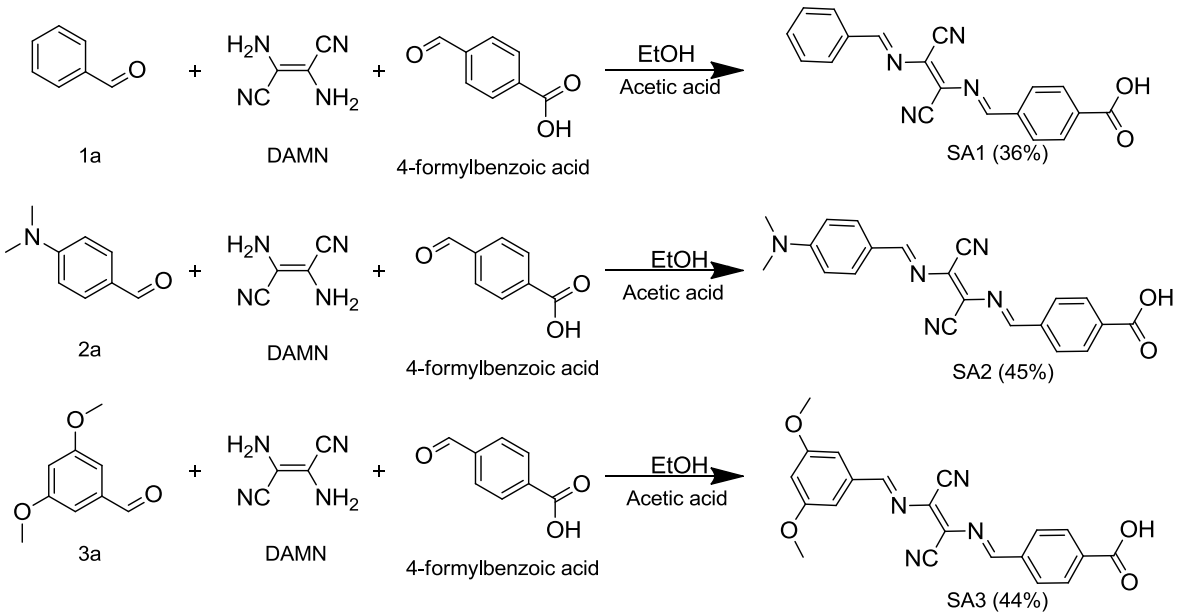

Fig. 1. The synthesis scheme of SA1, SA2 and SA3 dyes.

Preparation of DSSCs

ITO conductive glass sheets were cleaned by using detergent solution in an ultrasonic bath for 10 minutes, then rinsed with distilled water and ethanol. TiO_2 was prepared by adding 15 ml of ethanol to the 3.0 gm of TiO_2 nano powder (10-25 nm, US Research Nanomaterial, Inc, USA) and then added 2.5 ml of Triton X-100. The mixture was stirred using small magnetic bar for 45 minutes to form TiO_2 paste. The TiO_2 paste was dropped to the top of ITO glass sheet by using an eye pipette and then deposited by doctor blade technique to form a TiO_2 thin layer (0.5 cm^2 area). The glass sheet with then TiO_2 layer was heated at 70 ˚C for 30 minutes then sintered at 400 ˚C for 45 minutes. After cooling, the deposit TiO_2 was immersed in the dye solution (10^{-3} M) for 5 hours. The counter electrode was made by sketching pencil (graphite pencil) on the surface of another conductive glass (ITO). The TiO_2 thin layer with dye and counter electrode were assembled to form a DSSC by sandwiching with a redox electrolyte solution (I^-/I_3^-).

RESULTS AND DISCUSSION

Synthesis of Dyes

The general one pot dyes reaction scheme is given in figure (1). Schiff base reaction process was used to prepare three dyes for DSSC devices by using different aromatic compounds. The aldehyde derivatives (1a, 2a and 3a in figure 1) were used as a donor part, DAMN as a π-bridge and benzoic acid as an acceptor part. Different conditions were used to obtain maximum yields for these reactions, and table (1) shows the summary of these reactions with different conditions. In these conditions were used a different equivalents addition of starting materials with different types of solvent to get a best yield. The best yields in these conditions were given around 36%, 45%, and 44% as a product for compounds SA1, SA2 and SA3 respectively. The best yield was achieved by reacting 1 mole of donor with 1.5 mole of DAMN for 6 hours then added 2 mole of acceptor to continuous reaction to get the final product.

Table 1. The conditions of one pot reaction in different equivalent (eq), solvent and time.

Conditions	Donor	DAMN	Acceptor	solvent	Time	Yield
1	1.0 eq(1a)	1.0 eq	1.0 eq	EtOH	20 hr.	18%
2	1.5 eq(1a)	1.0 eq	1.0 eq	EtOH	20 hr.	15%
3	1.5 eq(1a)	1.0 eq	1.5 eq	EtOH	20 hr.	15%
4	1.0 eq(1a)	1.5 eq	1.5 eq	EtOH	20 hr.	30%
5	1.0 eq(1a)	1.5 eq	2.0 eq	EtOH	20 hr.	36%
6	1.0 eq(1a)	1.5 eq	2.0 eq	DMF	20 hr.	28%
7	1.0 eq(1a)	1.5 eq	2.0 eq	THF	20 hr.	18%
8	1.0 eq(2a)	1.5 eq	2.0 eq	EtOH	20 hr.	45%
9	1.0 eq(3a)	1.5 eq	2.0 eq	EtOH	2- hr.	44%

FT-IR Spectroscopy

The FTIR spectra of three dyes indicates a strong broad band for carboxylic acid at ~3400 cm^{-1} for OH stretching and strong sharp band at ~1700 cm^{-1} for C=O stretching. One strong band was observed in the three dyes within ~2250 cm^{-1} due to nitrile group of DAMN. A medium two bands were absorbs in ~1630 and ~1410 cm^{-1} for C=N stretching and C-N stretching respectively for Schiff bass reaction. A many weak to medium bands were observed between 990 and 650 cm^{-1} due to in plane and out of plane of C-H vibration for benzene ring. A medium intensity band was observed at 1291 cm^{-1} due to C-N stretching (N-CH_3) for SA2 compound and strong band was observed at 1186 cm^{-1} due to stretching of O-ether bond for SA3 compound.

Proton NMR spectroscopy

The proton NMR ($CDCl_3$) of the first dye (SA1) shows two singlet peaks at δ 8.65 and 8.63 for two protons of two C-H groups, which resulted from Schiff base reaction. Two doublets peak were investigated at δ 8.02 and 7.70, also multiples peak from δ 7.60 to 7.39 for C-H proton of two benzene rings. The second dye (SA2) indicates singlet peaks at δ 8.68 and 8.44 for two C-H groups. Four doublet peaks as δ 8.06, 7.64, 7.39 and 6.96 due to 8 protons in two benzene rings. Singlet peak shows at δ 2.93 for 6 protons of dimethyl amine group. The last dye (SA3) shows two singlet peaks at δ 8.66 and 8.65 for two C-H groups and two doublet peaks for four protons appears at δ 8.09 and 7.70 with multiples peak between 6.78 and 6.67 for two benzene rings. One singlet peak was investigated at δ 3.82 for 6 protons of two ether group (See supplementary information data).

UV-Vis spectroscopy

The UV-Vis spectroscopy of three dyes (fig. 2) carried out in acetonitrile as a solvent. The three dyes SA1, SA2 and SA3 show a strong absorption band in the visible region with λ_{max} at 398, 440 and 442 nm respectively as well as good molar absorptivity ranging from 1.61×10^4 to 1.76×10^4 M^{-1}. cm^{-1} and this is may be due to π-π* transition within conjugated between benzene rings in a day. The absorption band showed the red shift direction on going from SA1 to SA2 and SA3. Finally, the optical band gab (E_{opt}) of the dyes SA1, SA2 and SA3 were 2.88, 2.53 and 2.50 eV respectively.

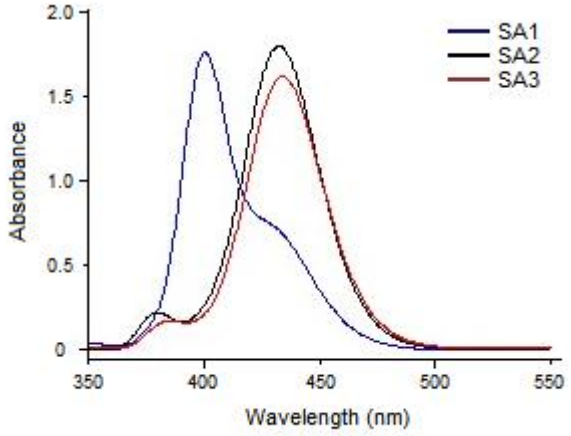

Fig. 2. Absorption spectra of the three dyes SA1, SA2 and SA3 (1×10^{-4} M).

Theoretical calculation

The geometry and electronic properties of the three dyes were investigated theoretically by using density functional theory (DFT), which performed by using in Gaussian 09 software. All dyes

calculations were tested under vacuum by using Lee–Yang–Parr's gradient corrected correlation (B3LYP) functional and 6-311G (d, p) basis set [38, 39]. The molecular orbital and geometry for three dyes showed in figure (3). For compound SA1 and SA2, The HOMO orbital is delocalized throughout the benzene ring and dimethylaniline respectively as well as on the DAMN part. The LUMO for the same dyes is delocalized over the DAMN and benzoic acid (acceptor part). These mixing in electron distribution between donor and acceptor part are negatively affect to the charge separation in the dye and that led to effect of dye efficiency in solar cell. On the other hand, the HOMO orbital in dye SA3 is delocalized over dimethoxybenzene and the LUMO is delocalized throughout the DAMN and benzoic acid which made charge separation in the dye.

The optimization geometry of the three dyes were shown a planer shape with the substitution in dimethyl amine for compound SA2 and dimethoxy in compound SA3 laying out of plane to a void dye aggregation which improved the solubility.

The computed energy gab for the SA1, SA2 and SA3 were 2.56, 2.50 and 2.51 eV respectively and these results are similar to the E_{opt} results.

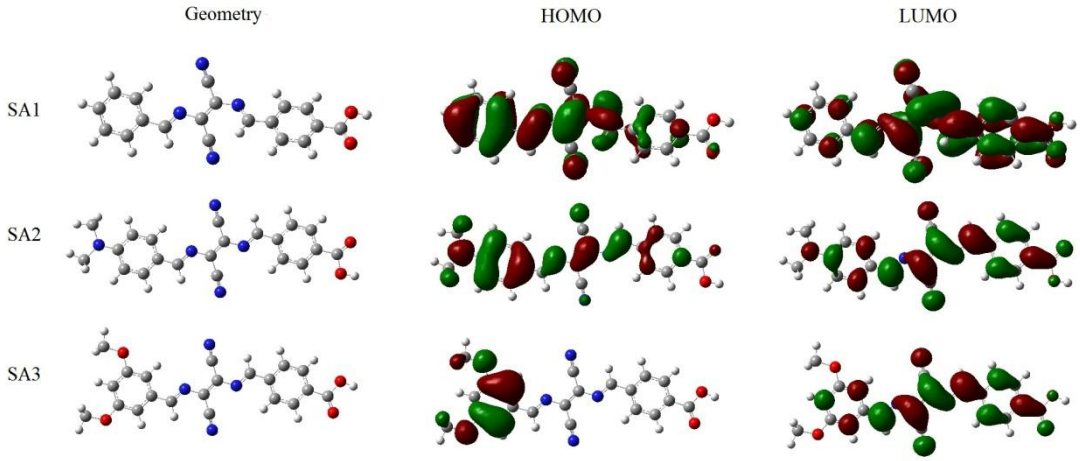

Fig. 3. The geometry and frontier molecular orbital of a three dyes (SA1, SA2 and SA3) calculated by DFT.

Device testing

The three sensitizers were tested as a dye in DSSCs by using iodide/triiodide as electrolyte solution between two electrodes and the devices were tested at AM 1.5 (100 mW cm^{-2}). Power conversion efficiency (PCE) of dyes was measured by open circuit voltage (V_{oc}), short circuit current (J_{sc}) and fill factor (FF) and all the results are shown in table (2). There is a big difference in *I-V* curve data between SA3 and other dyes (see supplementary information). The J_{sc} value of compound SA3 is 1.21 mA/cm^2 and for SA1 and SA2 are 0.15, 0.77 respectively, indicating that the charge mobility of SA3 dye is more efficient than other dyes [40]. The *I-V* curve data inform that the best efficiency was recorded with SA3 dye (0.38%) then with SA2 (0.22%) and finally with SA1 (0.09%). The low efficiency of the three dyes were may be due to the mixing of electron

distribution donor and accepter in DAMN part and that effected to the charge separation between two parts.

Table 2. *I-V* data for SA1, SA2 and SA3 dyes with N719 as a control.

Dyes	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)	PCE avg. (%)
SA1	0.15	0.82	35.6	0.09	0.07
SA2	0.77	0.82	36.1	0.22	0.19
SA3	1.21	0.91	37.9	0.38	0.34
N719	10.2	0.76	64.2	5.40	5.38

CONCLUSION

In conclusion, three novel dyes containing a DAMN as π-bridge spacer was synthesized in one pot reaction. The design of the dyes has given us to investigate the ability of DAMN compound as a π-conjugated spacer on DSSCs performance. The reactions conditions were optimized to get the highest yield. All dyes were characterized by different techniques such as FT-IR, ^{1}H NMR, elemental microanalysis, mass spectroscopy and UV-Vis. The computational studies of these dyes were shown a mixing in electron distribution between donor and acceptor in π-bridge part (DAMN) which affected to the efficiency of dyes in DSSC devises and the three dyes were indicated a poor efficiency in DSSC.

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REFERENCES

[1] Singh GK. 2013,Solar power generation by PV (photovoltaic) technology: A review. *Energy*.53:1-13.

[2] Gong J, Sumathy K, Qiao Q, Zhou Z. 2017,Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends. *Renewable and Sustainable Energy Reviews*.68:234-46.

[3] Malinowski M, Leon JI, Abu-Rub H. 2017,Solar Photovoltaic and Thermal Energy Systems: Current Technology and Future Trends. *Proceedings of the IEEE*.105:2132-46.

[4] Abdalhadi SM, Connell A, Zhang X, Wiles AA, Davies ML, Holliman PJ, et al. 2016,Convenient synthesis of EDOT-based dyes by CH-activation and their application as dyes in dye-sensitized solar cells. *Journal of Materials Chemistry A*.4:15655-61.
[5] Shalini S, Balasundaraprabhu R, Kumar TS, Prabavathy N, Senthilarasu S, Prasanna S. 2016,Status and outlook of sensitizers/dyes used in dye sensitized solar cells (DSSC): a review. *International Journal of Energy Research*.40:1303-20.
[6] Prabavathy N, Shalini S, Balasundaraprabhu R, Velauthapillai D, Prasanna S, Muthukumarasamy N. 2017,Enhancement in the photostability of natural dyes for dye-sensitized solar cell (DSSC) applications: a review. *International Journal of Energy Research*.41:1372-96.
[7] Sugathan V, John E, Sudhakar K. 2015,Recent improvements in dye sensitized solar cells: A review. *Renewable and Sustainable Energy Reviews*.52:54-64.
[8] Shakeel Ahmad M, Pandey AK, Abd Rahim N. 2017,Advancements in the development of TiO2 photoanodes and its fabrication methods for dye sensitized solar cell (DSSC) applications. A review. *Renewable and Sustainable Energy Reviews*.77:89-108.
[9] Mozaffari S, Nateghi MR, Zarandi MB. 2017,An overview of the Challenges in the commercialization of dye sensitized solar cells. *Renewable and Sustainable Energy Reviews*.71:675-86.
[10] Urbani M, Grätzel M, Nazeeruddin MK, Torres T. 2014,Meso-Substituted Porphyrins for Dye-Sensitized Solar Cells. *Chemical Reviews*.114:12330-96.
[11] Obotowo IN, Obot IB, Ekpe UJ. 2016,Organic sensitizers for dye-sensitized solar cell (DSSC): Properties from computation, progress and future perspectives. *Journal of Molecular Structure*.1122:80-7.
[12] Carella A, Borbone F, Centore R. 2018,Research Progress on Photosensitizers for DSSC. *Frontiers in Chemistry*.6.113-127
[13] Ludin NA, Al-Alwani Mahmoud AM, Bakar Mohamad A, Kadhum AAH, Sopian K, Abdul Karim NS. 2014,Review on the development of natural dye photosensitizer for dye-sensitized solar cells. *Renewable and Sustainable Energy Reviews*.31:386-96.
[14] O'Regan B, Grätzel M. 1991,A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. *Nature*.353:737-40.
[15] Nazeeruddin MK, Péchy P, Renouard T, Zakeeruddin SM, Humphry-Baker R, Comte P, et al. 2001,Engineering of Efficient Panchromatic Sensitizers for Nanocrystalline TiO2-Based Solar Cells. *Journal of the American Chemical Society*.123:1613-24.
[16] Kim B-G, Zhen C-G, Jeong EJ, Kieffer J, Kim J. 2012,Organic Dye Design Tools for Efficient Photocurrent Generation in Dye-Sensitized Solar Cells: Exciton Binding Energy and Electron Acceptors. *Advanced Functional Materials*.22:1606-12.

[17] Choi H, Baik C, Kang SO, Ko J, Kang M-S, Nazeeruddin MK, et al. 2008,Highly Efficient and Thermally Stable Organic Sensitizers for Solvent-Free Dye-Sensitized Solar Cells. *Angewandte Chemie International Edition*.47:327-30.
[18] Lin RY-Y, Wu F-L, Li C-T, Chen P-Y, Ho K-C, Lin JT. 2015,High-Performance Aqueous/Organic Dye-Sensitized Solar Cells Based on Sensitizers Containing Triethylene Oxide Methyl Ether. *ChemSusChem*.8:2503-13.
[19] Hara K, Sato T, Katoh R, Furube A, Ohga Y, Shinpo A, et al. 2003,Molecular Design of Coumarin Dyes for Efficient Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry B*.107:597-606.
[20] Jiao Y, Zhang F, Grätzel M, Meng S. 2013,Structure–Property Relations in All-Organic Dye-Sensitized Solar Cells. *Advanced Functional Materials*.23:424-9.
[21] Mishra A, Fischer MKR, Bäuerle P. 2009,Metal-Free Organic Dyes for Dye-Sensitized Solar Cells: From Structure: Property Relationships to Design Rules. *Angewandte Chemie International Edition*.48:2474-99.
[22] El-Meligy AB, Koga N, Iuchi S, Yoshida K, Hirao K, Mangood AH, et al. 2018,DFT/TD-DFT calculations of the electronic and optical properties of bis-N,N-dimethylaniline-based dyes for use in dye-sensitized solar cells. *Journal of Photochemistry and Photobiology A: Chemistry*.367:332-46.
[23] Naik P, Su R, Babu DD, El-Shafei A, Adhikari AV. 2017,Structurally simple D–A-type organic sensitizers for dye-sensitized solar cells: effect of anchoring moieties on the cell performance. *Journal of the Iranian Chemical Society*.14:2457-66.
[24] Hara K, Sato T, Katoh R, Furube A, Yoshihara T, Murai M, et al. 2005,Novel Conjugated Organic Dyes for Efficient Dye-Sensitized Solar Cells. *Advanced Functional Materials*.15:246-52.
[25] Sánchez-de-Armas R, San Miguel MÁ, Oviedo J, Sanz JF. 2012,Coumarin derivatives for dye sensitized solar cells: a TD-DFT study. *Physical Chemistry Chemical Physics*.14:225-33.
[26] Wang Z-S, Cui Y, Hara K, Dan-oh Y, Kasada C, Shinpo A. 2007,A High-Light-Harvesting-Efficiency Coumarin Dye for Stable Dye-Sensitized Solar Cells. *Advanced Materials*.19:1138-41.
[27] Wang Z-S, Cui Y, Dan-oh Y, Kasada C, Shinpo A, Hara K. 2007,Thiophene-Functionalized Coumarin Dye for Efficient Dye-Sensitized Solar Cells: Electron Lifetime Improved by Coadsorption of Deoxycholic Acid. *The Journal of Physical Chemistry C*.111:7224-30.
[28] Cariello M, Abdalhadi SM, Yadav P, Decoppet J-D, Zakeeruddin SM, Grätzel M, et al. 2018,An investigation of the roles furan versus thiophene π-bridges play in donor–π-acceptor porphyrin based DSSCs. *Dalton Transactions*.47:6549-56.
[29] Gao P, Tsao HN, Yi C, Grätzel M, Nazeeruddin MK. 2014,Extended π-Bridge in Organic Dye-Sensitized Solar Cells: the Longer, the Better? *Advanced Energy Materials*.4:1301485.
[30] Tsuzuki K, Tada M. 1986,The syntheses of pteridin-2-one derivatives from diaminomaleonitrile (DAMN). *Journal of Heterocyclic Chemistry*.23:1299-301.

[31] Zhou H, Wang J, Chen Y, Xi W, Zheng Z, Xu D, et al. 2013,New diaminomaleonitrile derivatives containing aza-crown ether: Selective, sensitive and colorimetric chemosensors for Cu(II). *Dyes and Pigments*.98:1-10.
[32] Anitha C, Sheela CD, Tharmaraj P, Shanmugakala R. 2013,Studies on Synthesis and Spectral Characterization of Some Transition Metal Complexes of Azo-Azomethine Derivative of Diaminomaleonitrile. *International Journal of Inorganic Chemistry*.2013:436275.
[33] Aruna, Rani B, Swami S, Agarwala A, Behera D, Shrivastava R. 2019,Recent progress in development of 2,3-diaminomaleonitrile (DAMN) based chemosensors for sensing of ionic and reactive oxygen species. *RSC Advances*.9:30599-614.
[34] Li Z, Liu C, Wang J, Wang S, Xiao L, Jing X. 2019,A selective diaminomaleonitrile-based dual channel emissive probe for Al3+ and its application in living cell imaging. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*.212:349-55.
[35] Fuse S, Sugiyama S, Maitani MM, Wada Y, Ogomi Y, Hayase S, et al. 2014,Elucidating the Structure–Property Relationships of Donor–π-Acceptor Dyes for Dye-Sensitized Solar Cells (DSSCs) through Rapid Library Synthesis by a One-Pot Procedure. *Chemistry – A European Journal*.20:10685-94.
[36] Matsumura K, Yoshizaki S, Maitani MM, Wada Y, Ogomi Y, Hayase S, et al. 2015,Rapid Synthesis of Thiophene-Based, Organic Dyes for Dye-Sensitized Solar Cells (DSSCs) by a One-Pot, Four-Component Coupling Approach. *Chemistry – A European Journal*.21:9742-7.
[37] Irie S, Fuse S, Maitani MM, Wada Y, Ogomi Y, Hayase S, et al. 2016,Rapid Synthesis of D-A'-π-A Dyes through a One-Pot Three-Component Suzuki–Miyaura Coupling and an Evaluation of their Photovoltaic Properties for Use in Dye-Sensitized Solar Cells. *Chemistry – A European Journal*.22:2507-14.
[38] Lee C, Yang W, Parr RG. 1988,Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*.37:785-9.
[39] Becke AD. 1993,Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics*.98:5648-52.
[40] Qu S, Wang B, Guo F, Li J, Wu W, Kong C, et al. 2012,New diketo-pyrrolo-pyrrole (DPP) sensitizer containing a furan moiety for efficient and stable dye-sensitized solar cells. *Dyes and Pigments*.92:1384-93.