

PHENOTHIAZINE-BASED DYES IN SOLAR CELL TECHNOLOGY

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Phenothiazine is a fused heterocyclic ring with strong electron-donating character which makes it an important building block for designing organic materials for solar cells applications. The present paper reviews the most recent achievements of phenothiazine-based compounds as dyes in solar cells, with special emphasis on the structure – performance relationship.

Keywords: phenothiazine, solar cells, dye, power conversion efficiency.

Obtaining of solar cells based on organic dyes has been receiving a lot of attention lately, as a promising alternative to the traditional silicone ones, with reduced production costs due to the ease of device fabrication and reasonable power conversion efficiency (PCE) [1]. Among the usual dyes, phenothiazine derivatives proved good photovoltaic performances, mainly due to the presence of sulphur and nitrogen heteroatoms, which confer to them butterfly geometry and a strong electron donating character.

Due to the increasing global energy consumption, the development of conventional energy sources has become a priority for the scientific community. Among the few energy sources of this type, solar energy is considered to be one of the most important. For this reason, since 1991, Grätzel and his collaborators started investigations on the possible obtaining of solar cells based on organic dyes (DSSC), a field which, since then has been continuously developing [2]. In general, such a device consists of four components (Fig. 1): (i) a semiconductor oxide (TiO₂) deposited on a conductive substrate, (ii) the organic dye, (iii) an electrolyte solution and (iv) the cathode [3]. When irradiation takes place, the light is absorbed by the chromophore molecules, leading to an excited state, which generates an electron flow that migrates from the dye to the conductive band (CB) of the semiconductor (TiO₂). The electron flow is further collected by the conductive substrate, entering the external circuit. At the same time, the oxidized organic compound is reduced to its fundamental state through an electronic transfer from the redox mediators in the electrolyte solution (the most common used being I^-/I_3^- and $[[Co(bpy)_3]^{2+}/^{3+}]$). This photoelectric chemical reaction cycle is complete when the oxidized species from the electrolyte solution receives electrons from the outer circuit [2]. Throughout this device construction, the organic dye plays the most

important role, influencing the power conversion efficiency (PCE), the electronic charge separation, the light absorption capability and the stability of the entire system [4].

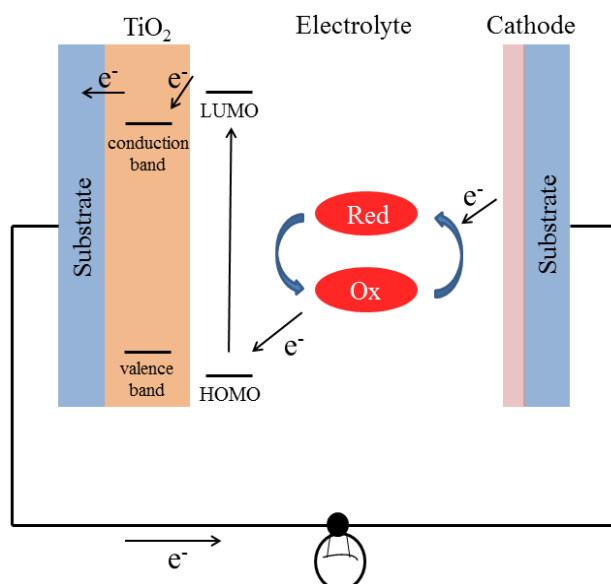
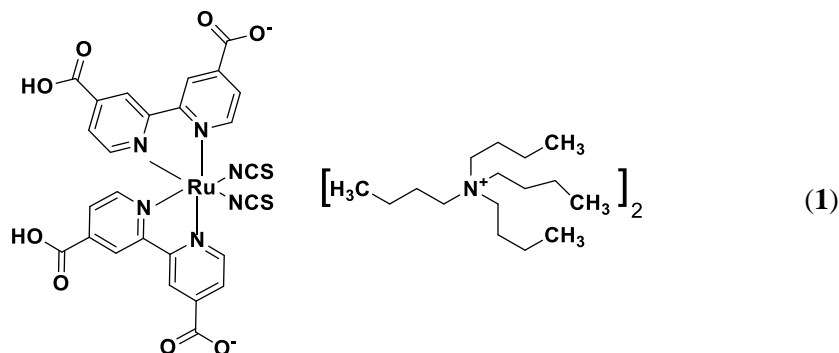


Fig. 1. Schematic representation of a solar cell

Up to now, three types of dyes have been reported in literature: organometallic complexes, pure-organic molecules, and more recently, a class of perovskites [5–7]. Among them, perovskites present the disadvantage of being toxic and relatively unstable within the device architecture. Unlike the DSSCs based on perovskites, those containing organic chromophores have many advantages, such as: low manufacturing costs, better stability, and lower toxicity [7–10]. The best photovoltaic performance achieved for DSSCs based on pure-organic chromophores and zinc or ruthenium complexes consisted of PCE values up to 12.5% [11], 11.5% [12], and 13% [13], respectively. Even though the best performance efficiency has been achieved for organometallic-based solar cells, these types of materials have limitations in their applicability at large scale because of the high production costs required [14–17]. For this reason, it is desirable to switch to the devices based on pure-organic compounds, which in some cases have proven higher performance (PCE 7.2%) [18] compared to ruthenium-based complexes (PCE 6%) [19].

In this context, many researches focused on studies involving series of pure-organic chromophores based on phenothiazine [18], triphenylamine [19–24], tetrahydroquinoline [25, 26], carbazole [27–30], which exhibited encouraging photovoltaic performances. Among them, phenothiazine-based materials occupy an important place due to several advantages, such as: (i) the non-planar butterfly geometry of the phenothiazine molecule, which leads to the prevention of molecular aggregation

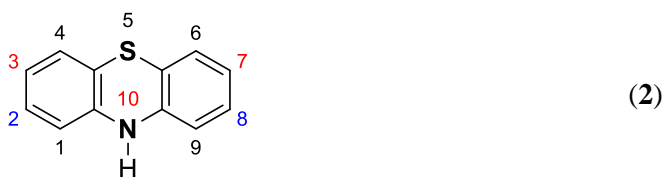
and excimer formation; (ii) the presence of sulphur and nitrogen heteroatoms, which gives a strong electron donor character, much more powerful than of other compounds, such as triphenylamine, carbazole, tetrahydroquinoline, and so on [20]. Furthermore, some studies have shown that phenothiazine-based solar cells exhibit photovoltaic performance similar to that of the commercial product N719, 10.45% vs. 11% (1) [29, 30].



Chemical structure of the commercial N719 dye

Small-molecule dyes based on phenothiazine for DSSC

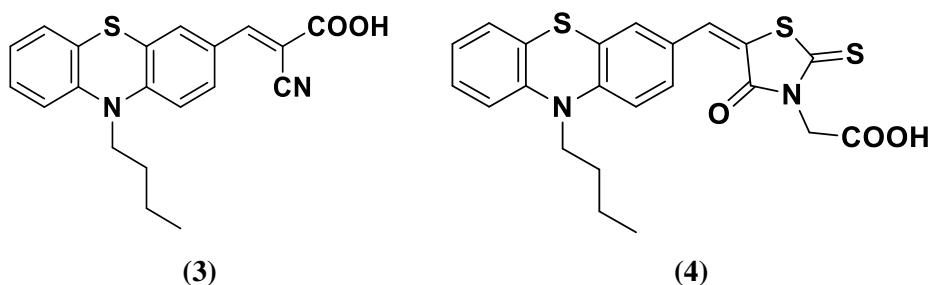
The phenothiazine molecule has attracted researchers' attention in the field of organic dyes due to its electron donating capacity, rigid structure, as well as to the advanced electronic conjugation system it promotes. In this context, many attempts have been made to improve its photovoltaic performance, especially through molecular engineering, chemical changes induced to the reactive positions 3 (C), 7 (C), and 10 (N), respectively (2). In addition to these three reactive sites, a practical interest is also manifested for grafting of electron donating units in the 2 (C) and 8 (C) positions.



Chemical structure of the phenothiazine molecule (with active site positions)

The first investigations on the applicability of phenothiazine-based chromophores to solar cells technology were carried out in 2007 by Hagfeldt and Sun [20]. They reported two relatively simple donor-acceptor (D-A) chromophores based on phenothiazine substituted with a butyl radical at the N atom and an electron

acceptor unit in the reactive position 3: a cyanoacrylic acid unit (**3**), or a rodanine-3-acetic acid unit, respectively (**4**). Tests on the photovoltaic performance of the solar cells based on these compounds led to better results for the DSSC containing dye **3**. This is why, the cyanoacrylic acid unit is the most used acceptor unit to assure an advanced electron delocalization of the organic compounds based on the phenothiazine donor.



The first dyes based on phenothiazine moiety used in the DSSC technique [20]

The π -spacer effect upon photovoltaic performance

Choosing of a suitable π -spacer in order to ensure an advanced electronic conjugation has been an important step in the obtaining of some efficient materials for organic dyes-based solar cells. Its grafting between the electron donating group and the electron accepting one leads to an advanced electronic transfer, thus leading to an extended electronic conjugation along the entire molecule (Fig. 2).

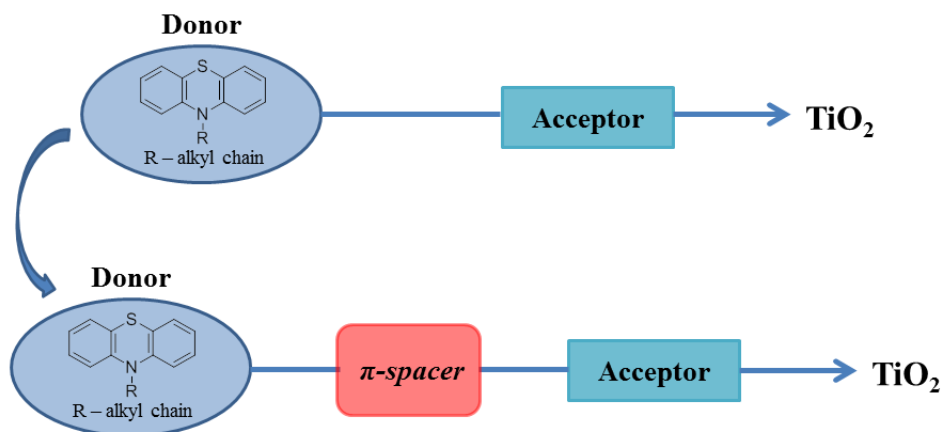
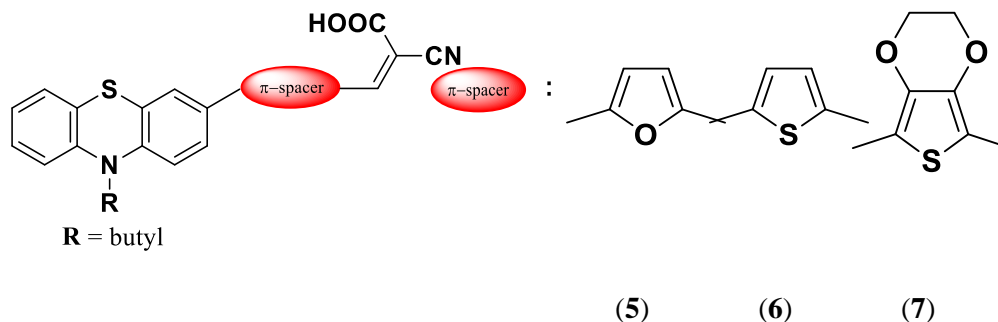


Fig. 2. Representation of the transformation of D-A type dyes into D- π -A ones

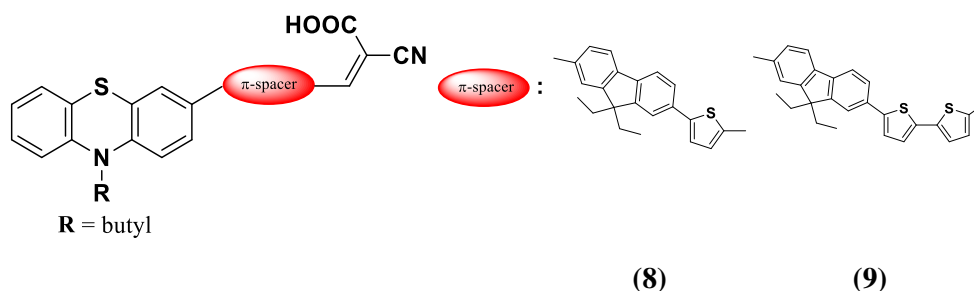
To study the effects of π -spacers on solar cell performance, Kim and his collaborators synthesized new phenothiazine derivatives by modifying compound (**3**),

or by introducing three different π -spacers - such as furan (**5**), thiophene (**6**) or 3, 4-ethylenedioxythiophene (**7**) [31]. Out of these three compounds, the highest PCE value (6.58%) was recorded for dye (**5**).



Chemical structure of D- π -A type dyes [31]

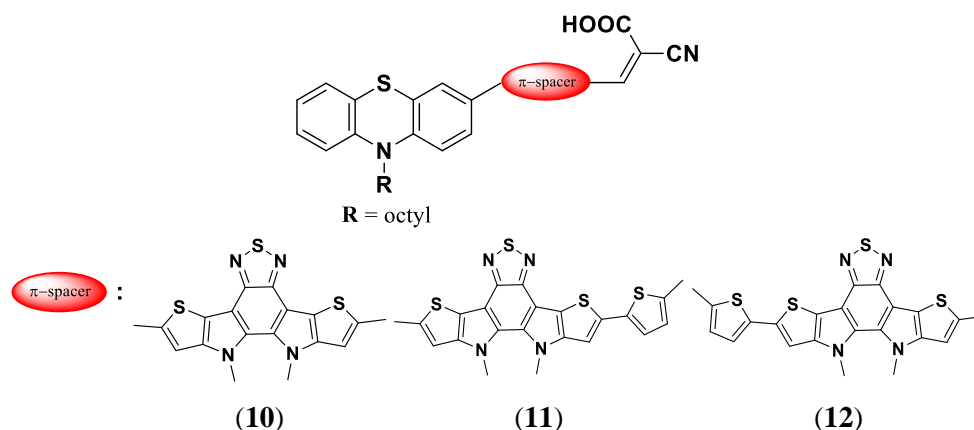
In a similar manner, Baheti and co-workers synthesized two dyes using the fluorene-thiophene unit (**8**) and the fluorene-bithiophene one (**9**) as π -spacers, obtaining a power conversion efficiency of 2.96% and 3.30%, respectively [32].



Chemical structure of D- π -A type dyes [32]

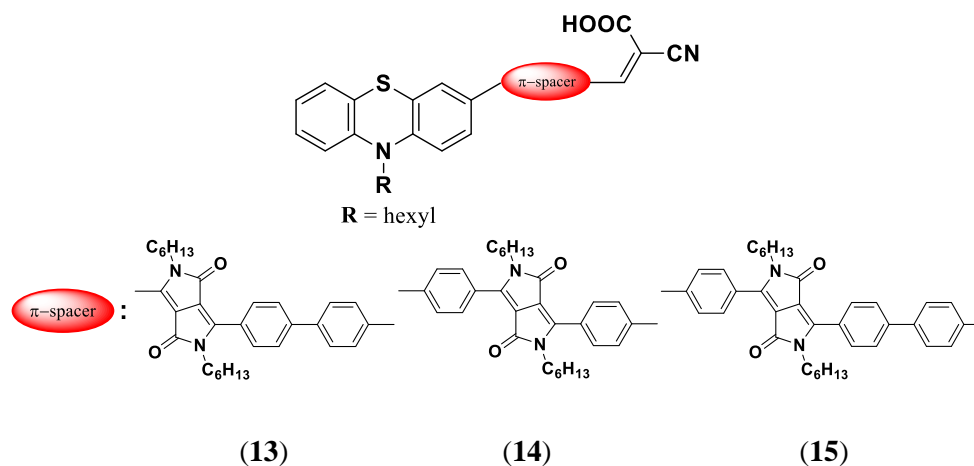
In the field of the D- π -A chromophores based on phenothiazine, a significant contribution is also brought by the Derong Cao group of researchers, who synthesized a new class of compounds by combining the electron donating phenothiazine molecule with an electron accepting one, based on cyanoacrylic acid, using different π -spacers, such as dithienopyrrolobenzothiadiazole (DTPBT) (**10**), DTPBT-thiophene (**11**), and thiophene-DTPBT (**12**) [33]. These compounds exhibited a broad band in the visible absorption region, with a very intense peak attributed to the intramolecular charge transfer ($\epsilon > 45\,000\text{ M}^{-1}\text{ cm}^{-1}$). DTPBT is a compound with a planar geometry composed of several fused rings, containing both electron-rich and electron-deficient entities creating strong intermolecular interactions, which further leads to π - π stacking phenomena, known as responsible for quenching the fluorescence. For this reason, and for a better performance of the device, a co-adsorbent,

such as chenodeoxycholic acid (CDCA), should be added. Upon addition of co-adsorbent (1 mM), the performance of the device based on compound **(10)** presented a PCE value of 5.42%.



Chemical structure of D- π -A type dyes [33]

In order to further improve the efficiency and also to explore the relationship between the π -spacer and the photovoltaic performance, Cao and co-workers have synthesized three compounds which contain a diketopyrrolopyrrol unit (DPP) **(13)** and some phenyl units **(14)** **(15)**. Among these three compounds, dye **(13)** showed better electronic transfer between the donor and acceptor. The solar cell based on this compound showed a power conversion efficiency of 5.16%. These results suggest that both the position and number of phenyl units significantly influence the photovoltaic performance.

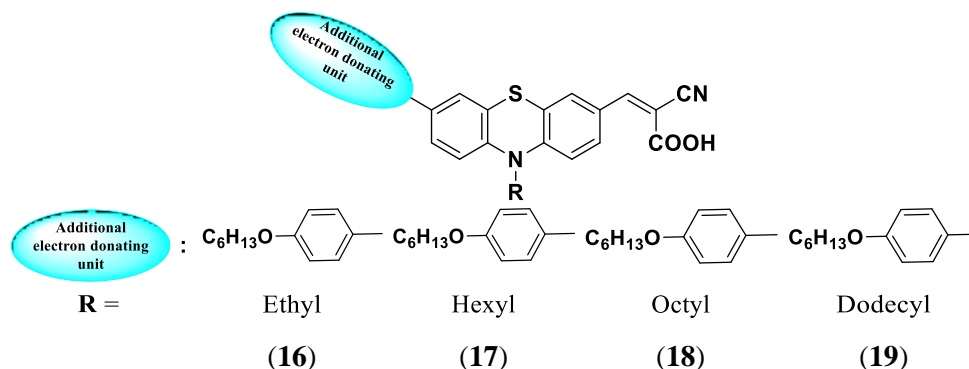


Chemical structure of D- π -A type dyes [33]

A comparative analysis between the structure-photovoltaic efficiency relationships revealed that the introduction of π -spacers between the electron donating units (phenothiazine) and the electron accepting ones represents the most important strategy in the improvement of the photovoltaic performance of DSSCs. However, if the π -spacers exhibiting an advanced electronic conjugation are too large, aggregation by π - π stacking may occur, when the electron transfer appears between the dye molecules, thus leading to a decrease in the efficiency of electron injection. Moreover, the bulky π -systems can lead to the photodegradation of dye molecules, reducing the stability of the solar cell device.

Donor – Donor – Acceptor type dyes based on phenothiazine (D – D – A)

The development of the DSSCs domain has applied numerous strategies for the improvement of phenothiazine-based dyes by molecular modification, that may lead to an increase in the absorption spectrum area and, implicitly, of the performance of the devices. One of these strategies is the introduction of an additional electron donating entity into position 7 (C) of the phenothiazine unit, generating the formation of D – D – A structures.



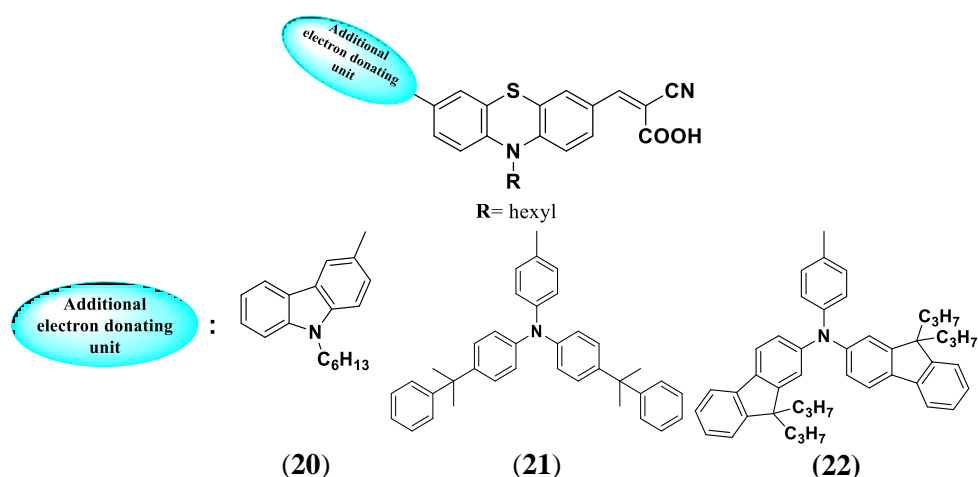
Chemical structure of D-D-A type dyes [30]

In this respect, a very good candidate is represented by the alkoxy-phenyl groups, known for their very pronounced electron donating character. Hua *et al.* reported a series of phenothiazine-based compounds, in which the cyanoacrylic acid acts as an electron acceptor unit, and the (4-hexyloxy) –phenyl group plays the role of an additional electron donating unit (**16–19**) [30].

Out of the four compounds, compound **(17)** showed the highest value of power conversion efficiency: 8.18%.

Another class of compounds with a strong electron donating character is represented by arylamine derivatives, such as carbazole, triphenylamine or indoline. Wang and collaborators have obtained three high-performance chromophores,

using as additional electron donor units: 9-hexyl-9H-carbazole (**20**), bis(4-(2-phenylpropan-2-yl)phenyl)amine (**21**) and N-phenyl-9,9-dipropyl-N-(9,9-dipropyl-9H-fluoren-2-yl)9H-fluoren-2-amine (**22**), with PCE values of 7.13%, 6.14%, and 6.46% respectively [34].

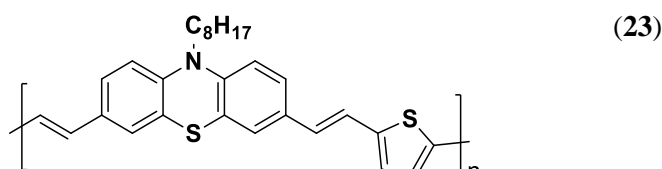


Chemical structure of D-D-A type dyes [34]

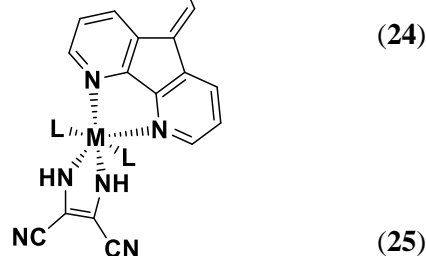
Phenothiazine-based polymers for DSSCs

Another class of dyes used in DSSCs is represented by the macromolecular compounds with advanced electronic conjugation. However, they attracted a relatively low interest due to the lack of solubility, the complicated manufacturing process and the limitation of photovoltaic performance. In this field, Zhong *et al.* have developed a series of chromophores (**23–25**) based on polymeric metallic complexes, recording a power conversion efficiency of 1.57% [35].

M = Zn; L = CH₃COO⁻



M = Li; L = Cl⁻

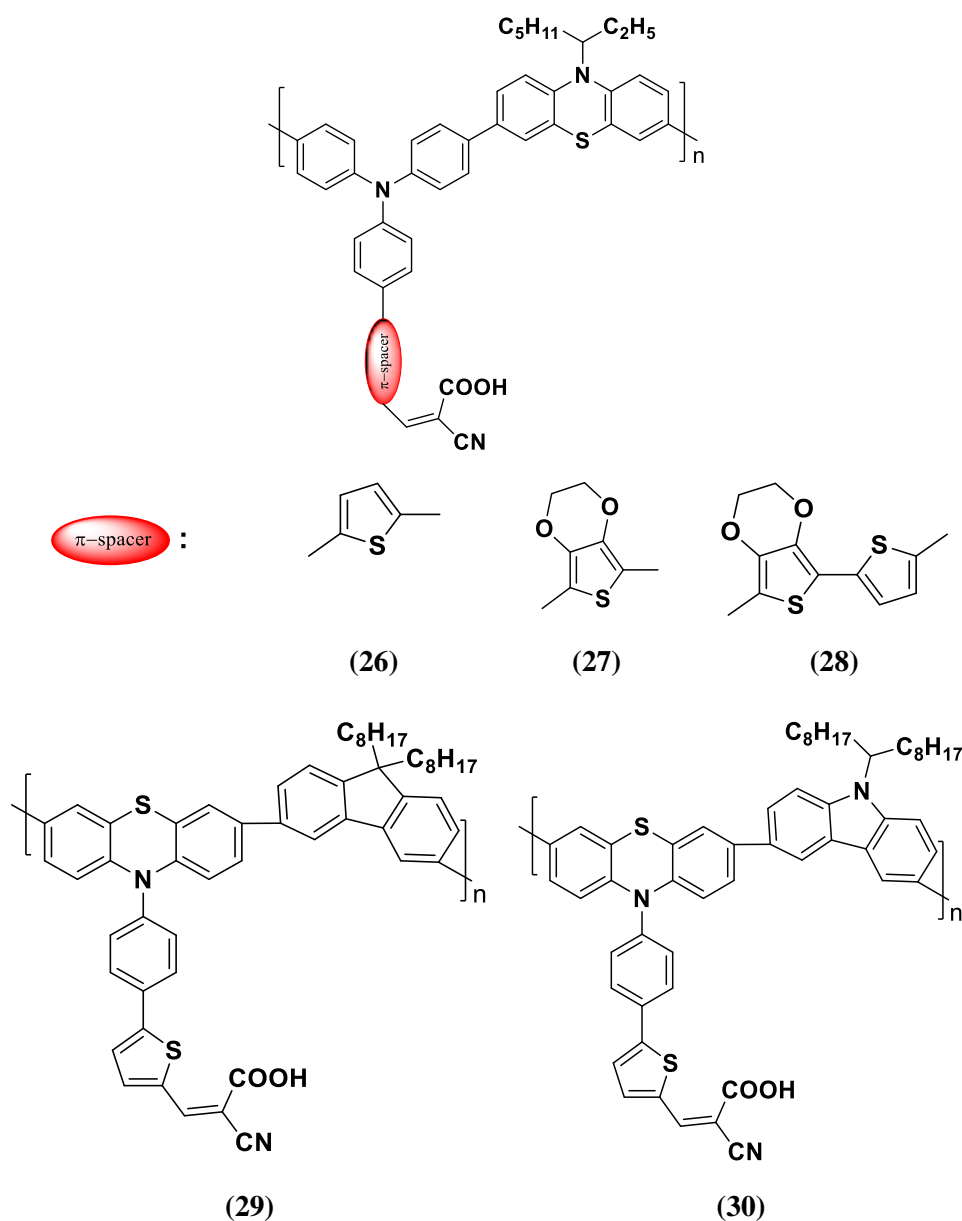


M = Co; L = Cl⁻



Chemical structure of phenothiazine-based polymeric metallic complexes dyes [35]

An increase in the photovoltaic performance was recorded when purely phenothiazine-based polymeric compounds were used, with various π -spacers (26–30), attaining PCE values up to 4.7% [36].



Chemical structure of phenothiazine-based polymeric dyes [36]

To conclude, it can be ascertained that the phenothiazine entity plays a very important role in the field of DSSCs based on organic compounds, being the most promising electron donating unit in such devices.

REFERENCES

1. URBANI M., GRÄTZEL M., NAZEERUDDIN M., TORRES T.S., *Meso-Substituted Porphyrins for Dye-Sensitized Solar Cells*, Chem. Rev., 2014, **114**, 12330–12396.
2. O'REGAN B., GRÄTZEL M., *A low cost, high efficiency solar cell based on dye-sensitized colloidal TiO₂ films*, Nature, 1991, **353**, 737–740.
3. GRÄTZEL M., *Recent advances in sensitized mesoscopic solar cells*, Acc. Chem. Res., 2009, **42**, 1788–1798.
4. HAGFELDT A., BOOSCHLOO G., SUN L.C., KLOO L., PETTERSSON H., *Dye-sensitized solar cells*, Chem. Rev., 2010, **110**, 6595–6663.
5. A. KOJIMA, K. TESHIMA, Y. SHIRAI, *et al.*, *Organometal halide perovskites as visible-light sensitizers for photovoltaic cells*, J. Am. Chem. Soc., 2009, **131**, 6050–6051.
6. KIM H.S., LEE C.R., IM J.H. *et al.*, *Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%*, Sci. Rep., 2012, **2**, 591.
7. ZHOU H.P., CHEN Q., G. LI *et al.*, *Interface engineering of highly efficient perovskite solar cells*, Science, 2014, **345**, 542–546.
8. MISHRA A., FISCHER M.K.R., BAUERLE P., *Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules*, Angew. Chem. Int. Ed., 2009, **48**, 2474–2499.
9. HAGFELDT A., GRÄTZEL M., *Light-induced redox reactions in nanocrystalline systems*, Chem. Rev., 1995, **95**, 49–68.
10. ZHANG S.F., YANG X.D., NUMATA Y. *et al.*, *Highly efficient dye-sensitized solar cells: progress and future challenges*, Energy Environ. Sci., 2013, **6**, 1443–1464.
11. YAO Z.Y., ZHANG M., WU H. *et al.*, *Donor/acceptor indenoperylene dye for highly efficient organic dye-sensitized solar cells*, J. Am. Chem. Soc., 2015, **137**, 3799–3802.
12. MATHEWS S., YELLA A., GAO P. *et al.*, *Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers*, Nat. Chem., 2014, **6**, 242–247.
13. CHEN C.Y., WANG M., LI J.Y. *et al.*, *Highly efficient light-harvesting ruthenium sensitizer for thin-film dye-sensitized solar cells*, ACS Nano, 2009, **3**, 3103–3109.
14. STENGEL I., POOTRAKULCHOTE N., DYKEMAN R.R. *et al.*, *Click-functionalized Ru(II) complexes for dye-sensitized solar cells*, Adv. Energy Mater., 2012, **2**, 1004–1012.
15. CHEN C.Y., POOTRAKULCHOTE N., HUNG T.H., *Ruthenium sensitizer with thienothiophene linked carbazole antennas in conjunction with liquid electrolytes for dye-sensitized solar cells*, J. Phys. Chem. C, 2011, **115**, 20043–20050.
16. FELDT S.M., GIBSON E.A., GABRIELSSON E. *et al.*, *Design of organic dyes and cobalt polypyridine redox mediators for high-efficiency dye-sensitized solar cells*, J. Am. Chem. Soc., 2010, **132**, 16714–16724.
17. CHEN C.Y., CHEN J.G., WU S.J. *et al.*, *Multifunctionalized ruthenium-based supersensitizers for highly efficient dye-sensitized solar cells*, Angew. Chem. Int. Ed., 2008, **47**, 7342–7345.
18. XU B., SHEIBANI E., LIU P. *et al.*, *Carbazole-based hole-transport materials for efficient solid-state dye-sensitized solar cells and perovskite solar cells*, Adv. Mater., 2014, **26**, 6629–6634.
19. WANG P., ZAKEERUDDIN S. M., MOSER J. E., NAZEERUDDIN M. K., SEKIGUCHU T., GRÄTZEL M., *A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte*, Nat. Mater., 2003, **2**, 402.

20. CAI N., WANG Y.L., XU M.F. *et al.*, *Engineering of push-pull thiophene dyes to enhance light absorption and modulate charge recombination in mesoscopic solar cells*, *Adv. Funct. Mater.*, 2013, **23**, 1846–1854.
21. CHAI Z.F., WU M., FANG M.M. *et al.*, *Similar or totally different: the adjustment of the twist conformation through minor structural modification, and dramatically improved performance for dye-sensitized solar cell*, *Adv. Energy Mater.*, 2015, **5**, 1500846.
22. SCRASCIA A., DE MARCO L., LARICCHIA S. *et al.*, *Fluorine–thiophene-substituted organic dyes for dye sensitized solar cells*, *J. Mater. Chem. A*, 2013, **1**, 11909–11921.
23. LI H.Y., YANG Y.Z., HOU Y.Q. *et al.*, *Organic sensitizers featuring 9,10-diaryl substituted anthracene unit*, *ACS Sustain. Chem. Eng.*, 2014, **2**, 1776–1784.
24. LI Q.Q., SHI J., LI H.Y. *et al.*, *Novel pyrrole-based dyes for dye-sensitized solar cells: from rod-shape to “H” type*, *J. Mater. Chem.*, 2012, **22**, 6689–6696.
25. CHEN R.K., YANG X.C., TIAN H.N. *et al.*, *Effect of tetrahydroquinoline dyes structure on the performance of organic dye-sensitized solar cells*, *Chem. Mater.*, 2007, **19**, 4007–4015.
26. HAO Y., YANG X.C., CONG J.Y. *et al.*, *Engineering of highly efficient tetrahydroquinoline sensitizers for dye-sensitized solar cells*, *Tetrahedron*, 2012, **68**, 552–558.
27. KOUMURA N., WANG Z.S., MORI S. *et al.*, *Alkyl-functionalized organic dyes for efficient molecular photovoltaics*, *J. Am. Chem. Soc.*, 2006, **128**, 14256–14257.
28. WANG Y.Q., CHEN B., WU W.J. *et al.*, *Efficient solar cells sensitized by porphyrins with an extended conjugation framework and a carbazole donor: from molecular design to cosensitization*, *Angew. Chem. Int. Ed.*, 2014, **53**, 10779–10783.
29. VENKATESWARARAO A., THOMAS K.R.J., LI C.T. *et al.*, *Functional tuning of organic dyes containing 2,7-carbazole and other electron-rich segments in the conjugation pathway*, *RSC Adv.*, 2015, **5**, 17953–17966.
30. VENKATESWARARAO A., THOMAS K.R.J., LEE C.P. *et al.*, *Organic dyes containing carbazole as donor and π -linker: optical, electrochemical, and photovoltaic properties*, *ACS Appl. Mater. Interfaces*, 2014, **6**, 2528–2539.
31. KIM S.H., KIM H.W., SAKONG C. *et al.*, *Effect of five-membered heteroaromatic linkers to the performance of phenothiazine-based dye-sensitized solar cells*, *Org. Lett.*, 2011, **13**, 5784–5787.
32. BAHETI A., THOMAS K.R.J., LI C.T. *et al.*, *Fluorene-based sensitizers with a phenothiazine donor: effect of mode of donor tethering on the performance of dye-sensitized solar cells*, *ACS Appl. Mater. Interfaces*, 2015, **7**, 2249–2262.
33. HUANG Z.S., FENG H.L., ZANG X.F. *et al.*, *Dithienopyrrolobenzothiadiazole-based organic dyes for efficient dye-sensitized solar cells*, *J. Mater. Chem. A*, 2014, **2**, 15365–15376.
34. WANG S.B., WANG H.R., GUO J.C. *et al.*, *Influence of the terminal electron donor in D-D- π -A phenothiazine dyes for dye-sensitized solar cells*, *Dyes Pigm.*, 2014, **109**, 96–104.
35. XIE Q.F., ZHOU J., HU J.M. *et al.*, *Synthesis and Photovoltaic properties of branched chain polymeric metal complexes containing Phenothiazine and Thiophene derivative for dye-sensitized solar cells*, *J. Chem. Sci.*, 2015, **127**, 395–403.
36. TAN H.J., PAN C.Y., WANG G. *et al.*, *Synthesis and characterization of conjugated polymers with main-chain donors and pendent acceptors for dye-sensitized solar cells*, *RSC Adv.*, 2013, **3**, 16612–16618.