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CO-SENSITIZATION IN DYE-SENSITIZED SOLAR CELLS: A PATHWAY TO ENHANCED EFFICIENCY AND SUSTAINABLE ENERGY SOLUTIONS

Muhammad Shahid[a], Dr. Shahzad Murtaza[b], Uzman Khan[c, 1], Majid Nazir[c], Abdul Shakoor[c],
Ejaz Ahmad[c], Hafiz Muhammad Faizan Haider[c], Madiha Batool[c], Syed Ahmad Raza Bokhari[d],
Hamad Ahmad[e], Nasir Khan[f]

[a] University of Gujrat, Gujrat, Pakistan,
[b] Khwaja Fareed university of Engineering and Technology, Rahim yar khan, Pakistan,
[c] Government College University, Lahore, Pakistan,
[d] George Brown College, M5T239, Toronto, Canada
[e] University of Management and Technology, Lahore, Pakistan
[f] Lahore Garrison University, Lahore, Pakistan

[1] Corresponding Author: Dr. Uzman Khan, E-mail: uzmanuk@gmail.com
Tel: (+92)-346-7509005

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ABSTRACT:

The global pursuit of sustainable energy solutions has intensified, particularly in the face of energy crises and environmental concerns. Dyes Sensitized Solar Cells (DSSCs) have emerged as promising candidates, embodying eco-friendly technology. That review with 107 references, delves into the advancements made in enhancing the efficiency of DSSCs, focusing on the innovative approach of co-sensitization.

In the quest for improved performance, researchers have explored a plethora of metal complex sensitizers and metal-free sensitizers. While metal sensitizers exhibit superior efficiency, challenges such as cost and availability impede their widespread adoption. On the other hand, organic sensitizers, though cost-effective, grapple with efficiency limitations.

The review underscores co-sensitization as a transformative strategy, showcasing its potential to address existing shortcomings. By combining multiple sensitizers, co-sensitization facilitates efficient electron injection through precise energy alignment and molecular matching with sensitizers. The presence of co-sensitizers on the Titania surface creates a conducive environment, retarding electron recombination.

One notable advantage of co-sensitization was its ability to compensate for the absorption range deficiency inherent in individual sensitizer. The combinatorial loading of sensitizers not only extends the absorption spectrum but also ensures favorable spectral responses. That holistic approach positively impacts crucial photovoltaic properties such as current density, photovoltage, and fill factor.

The comprehensive exploration of co-sensitization in that review sheds light on its role as an innovative and emergent strategy in the field of DSSCs. The synergistic effects achieved through co-sensitization hold the key to overcoming the efficiency challenges posed by individual sensitizers. Ultimately, the enhanced efficiency achieved through co-sensitization positions DSSCs as viable and competitive contenders in the ongoing efforts to address energy crises while maintaining environmental sustainability.

KEYWORDS: Dyes Sensitized Solar Cells (DSSCs), Sensitizers and co-sensitizers, Metal sensitizers and metal-free sensitizers.

1. INTRODUCTION:

Population of the world is increasing and demand of energy also going on with the passage of time. To meet the need and requirement of energy various methods are being used. The use of fossil fuel is costly and also it is a cause of environmental pollution. Use of solar light after converting it into electric power has attracted the attention of scientist in all over the world. Global warming issues also inspire the researchers to select the alternatives of fossil fuel. Photovoltaic (PV) cells and DSSCs are keys to attain renewable energy and facing challenges of energy crises in 21st century. DSSCs are third generation of PV devices [1, 2]. DSSCs are ecofriendly, environment friendly and has impressive energy conversion efficiency. DSSCs are low in cost and are a more efficient way to convert solar energy into electrical energy. That device was providing plus points like tunability, molecular designing, flexibility, favorable weight and has light capturing ability from all angles [3, 4]. DSSCs are rapidly attracting the attention of researchers in three main fields for better performance. Firstly, chemists may use it to design sensitizers in order to overcome efficiency problems as discussed above. Secondly, physicists may use it to build new devices with innovative materials and setting photo physical parameters. Finally, these are attracting in the field of engineering to solve architectural problems with device modification. Use of sensitizers as a sensitizing martial are the most favorable implication in conversion of photo energy to electrical energy [5, 6].

Thomas Hamann suggested that efficiencies enhancement greater than 16% can be achieved by simultaneous modification of electrodes, sensitizers and electrolytes [7]. Suriati Suhaimi and coworker suggested innovation like maintaining the stability of sensitizer, improving the absorption range, semiconductor effectiveness, modifying sensitizer, electrolytic material and connection of electrode can enhance the performance of cell [8]. Renaissance of dye Sensitizer was a basic and crucial key to directly sensitize power conversion efficiency. Use of photo sensitizers with broader absorption band gives better light harvesting properties. Sensitizers were designed by modifying structure and so improving absorption range and light harvesting ability [9-12]. DSSCs are similar to Photosynthesis process, that aspect also attracted the researchers to explore natural sensitizers. Comparison of natural products like santalin and carminic acid with synthetic ones showed that natural sensitizers cannot give satisfactory performance as compared to synthetic [13, 14]. DSSCs are similar in basic light harvesting and electron separation with natural photosynthesis. Natural chlorophyll is an efficient light harvester. It has also attracted researchers to use artificial chlorophylls and similar sensitizers [15-17]. There are two main types of sensitizers first are metal incorporated compounds (metal complexes) and second are metal free organic sensitizers. Later has further two types natural and synthetic. To remove efficiency issues, metal-based sensitizers have been given priorities by scientists [8]. Dahai Peng and coworkers concluded as, to get better power conversion efficiency there are problems like poor affinity of sensitizer on the surface of semiconductor, unfavorable energy band gape and narrow absorption range. So, for attaining good affinity on semiconductor anchoring groups were added [18]. Ruthenium based sensitizers were used as they showed more light sensitizing behavior and comparatively greater efficiency. Approximately it was calculated as 11%. Ruthenium complexes show greater efficiency, broader absorption range and chemical stability than pure organics but lower molar extinction quotient. To increase molar extinction coefficient, some of the pi conjugated ligands have been reported by Z. Yu and coworkers [19]. Enlarging of pi conjugation between donor and acceptor increases the light harvesting properties in DSSCs and tend to move absorption to red shift [20]. To get maximum efficiency two factors were demonstrated one was surface engineering and second was bounding photons in visible region [21]. Better Performance of boron dipyrromethene type sensitizers were achieved by increasing the fluorescence quantum yield and fluorescence lifetime. 9-phenyl-carbazole-substituted boron dipyrromethene was reported to have better conversion ability comparatively among BODIPY type sensitizers. Interchanging triphenylamine with 9-phenyl-carbazole group gives better results because controlling the rotation and vibration of phenyl rings minimizes energy loss [22]. Simon Mathew and coworkers recorded 13% efficiency by molecular engineering of porphyrin sensitizer. Surface engineering, light entrapping strategies have been used to get superior efficiency [23].

Dye-sensitized solar cells with 13% efficiency have been achieved through the molecular engineering of porphyrin sensitizers. Thienylvinyl bipyridyl ligand, *cis*-Ru(dtbpy)(dcbpy)(NCS)2 [dtbpy = 4,4¢-di(thienylvinyl)-2,2¢-bipyridyl; dcbpy =4,4¢-dicarboxy-2,2¢-bipyridyl] codified as YX 360 was synthesized and used in DSSCs and reported better results as compared to N719. Introduction of conjugated groups increase the molar extinction coefficient and lower band absorption was improved by 10nm as the result of transfer of electron from metal to ligand [19]. Using of N, N-bis((pyridin-2-yl)methylene)-p-phenyl- lenediimine (named L1) as co sensitizer with ruthenium-complex N719 overcome the problems like absorption in visible region and recombination of electron. On the other hand, introduction of methoxy group in N, N-bis((pyridin-2-yl)methylene)-p-phenyl- lenediimine increase efficiency [24]. Kiyoshi C. D. Robson and

coworker reported that combination of organic and inorganic complex sensitizers give better efficiency [25]. Co-sensitized device with Ru-complex and metal free gives better J_{sc} and FF than individual Ru-complex [26]. By using Squaraine and Ru-complex as co-sensitizer gives power conversion efficiency 8.2% that was greater than if used individually [27].
Organic sensitizers are best for DSSCs as, they have higher absorption coefficients, they are tunable and show different structural designing and they are cheaper as compared to noble metals [28]. Two natural products i.e. carminic acid extracted from insects and santalin obtained from sandal natural plant were compared with synthetic sensitizer. Natural products give poor performance as compared to synthetic. IPCE by natural was as about 0.5% and by synthetic was 5.6% at same conditions that was almost 10% lower than designed sensitizer. Spectroscopic analysis shows that regeneration of natural sensitizers ware ten times slower as compared to synthetic sensitizers. Intramolecular electron recombination was fast and election injection was slower. These factors lower the performance of devices [14]. Light harvesting ability and short current density improvement was achieved by using sensitizers like 3,4-ethylenedioxythiophene due to their rich electron nature. Open circuit voltage can be improved by using bulky *n*-hexyl thiophene or 3, 4-ethylenedioxythiophene. Electron recombination and π-π aggregation within a sensitizer can be controlled with the bulky group usage [29].

Photovoltaic properties and performance depend upon electronic structure, photo exited properties of sensitizer and favorable energy changes in efficient electron injection. Electronic structure and photoexcitation properties of Diary amino substituents are suitable for efficient electron transfer [30]. Isomers of sensitizers also behave different from each other, n-hexyl or 2-ethyle hexyl when attached at two different positions of terthiophene. When alkyl was near to anchor group it was better than when alkyl was near to organic group because latter has greater conjugation which gives more absorption and greater light harvesting property [31].

Many appreciate able and unforgettable efforts were made to achieve better efficiency. Researchers used both the metal sensitizers and metal free sensitizers as, synthetic and natural and achieved efficiency greater than 13%. Authors have mentioned that use of metals like ruthenium and other heavy metals are expensive and less abundant. It was reported also that metals show lower molecular extinction coefficient as compared to metal free sensitizers. The use of metal free sensitizers and natural sensitizers are low cost and economically favorable but still DSSCs are facing problem of lower efficiency [32].

In that study co-sensitization was focused, it was a cunning strategy to get enhanced photovoltaic outputs. "Co-sensitization was the application of two or more sensitizers to get better outputs". It was an easy way to get panchromatic DSSCs [33-35]. Using co-sensitizers improved spectral responses about 800nm and enhanced IPCE of 80% can be achieved in future [16]. Cyanines are quite fit for co-sensitizing the device because these are tunable to give appropriate spectral responses [36]. Durr and coworkers used a method of application of more than one sensitizer by compartmenting the device. A red sensitizer was enclosed in upper compartment near to the light illumination side and black sensitizer in lower compartment. Efficiency of 10.5% was noted with current density 21.1mA/cm^2 and voltage was 545mV [37].

Generally, co-sensitization was covered in two approaches. First was Cocktail approach. In that approach solutions of two or more sensitizers are applied. Second approach was stepwise approach. In that approach, step by step application of sensitizers was performed. Ganesh Koyyada, sing and coworkers used cocktail approach to record higher efficiency of 8.19 % of Ru based sensitizer K-60 and metal free sensitizer Y1 [26]. Hyunbong Choi and coworkers reported that stepwise approach was better than loading of single sensitizer and cocktail approach [38]. Pre coating of sensitizers and simple dip techniques were used by Jeongmin Lim and coworkers. Nano particles of TiO2 were coated with sensitizer, then using dip coating of both sensitizers by applying pressure in a sequence. It was demonstrated that bilayer or multilayer can be used without thermal treatment, that was economical and stability favored [39]. Ultra-fast method was introduced to make device more efficient. Sensitizers desorption and selectively re-sensitizing method was performance oriented. In that way single device can be used for multiple sensitizers detection and desorbed material can be reused. Re-dying with N719 give efficiency 8.1%, V_{oc} 0.71 Mv, J_{sc} 17.81 mA/cm^2 and FF 0.64 [33]. Performance of DSSCs were improved from 3.02 %, to 3.80 %, by using starch calcinated ZnO photo anodes. Co-sensitization of CdS and CdSe increase power conversion efficiency up to 25.8 % compared to that which was not calcinated with starch. Power efficiency enhancement was the result of minimizing charge recombination and increasing ability of light absorption [40]. Hitoshi Kusama and coworkers used computational analysis to demonstrate the enhancement in efficiency of Ru-based (FT89) dimmers sensitized device with the Co-sensitization of organic sensitizer MK-111. It improves performance by suppressing charge recombination and sensitizer aggregation [41]. Xin Wang and coworkers used lanthanide complexes of nine coordination system as co-sensitizer with N719. They demonstrated that efficient electron injection and fast sensitizer regeneration was the result of Co-sensitization [42].

1.1 BASIC PARTS OF DSSCS:

Basically, DSSCs have five parts,

a- Transparent electrode having transparent metal coating, supporting mechanically.
b- Semiconductor coating typically Titanium oxide to promote conduction.
c- Photosensitized sensitizer for light absorption enhancement.
d- Electrolyte to reprocess electron by regenerating sensitizer.
e- A counter electrode typically platinum coated [43, 13] as illustrated in figure I (a & b).

1.2 WORKING PRINCIPLE:

Operation cycle of DSSCs complete in following steps,

a- Photoexcitation of sensitizer take place. Light passes through transparent anode to hit the sensitizer.

b- Oxidation of sensitizer as a result of transferring electron to conduction band of semiconductor.
c- Regeneration of sensitizer by taking electron from electrolyte.
d- Electrolyte comes at initial state as a result of reduction at counter electrode [44, 13] as illustrated in figure II (a & b).

1.3 CRITERIA FOR A SPECIE TO BE AN EFFECTIVE SENSITIZER:

Effective photosensitizes should cover following criteria,

a- Absorption spectra should fall in visible region and also approaching near IR region.
b- There should be presence of anchoring group on the sensitizer to effective working on semiconductor surface.
c- Higher molar extinction coefficient.
d- Stability in oxidized form so that sensitizer can reduce it easily, un-stability will affect the durability of device.
e- Chemical and thermal stability was also important for the performance of device.
e- In photo exited form, energy of sensitizer should be higher than conduction band of major electron carrier semiconductor. It should be reverse in the case of the hole carrier semiconductor to be electronic transfer more effective [Figure III (a)].

So, a best sensitizer has visible absorption range, it should stay long in exited state and should be good reducer [3, 12, 45-47]

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1.4 CRITERIA FOR A SPECIE TO BE A GOOD CO-ADSORBER:

a- It should associate the adsorption of other sensitizer, that will minimize the sensitizers aggregation.
b- It should have higher molecular extinction coefficient.
c- It Should form insulating layer so that electrolytic species may not directly approach the electrode if there was direct connection between electrode and electrolyte it will give birth to charge recombination as illustrated in figure III (b) [48, 49].

1.5 OVERALL EFFICIENCY OF DSSCS WAS DEFINED AS:

$$\boldsymbol{\eta = Voc \times jsc \times FF \,/\, Pin}$$

V_{oc} was open circuit voltage and was the difference of Fermi energy level of semiconductor and Redox potential of electrolyte.

J_{sc} was directly proportional to efficiency of light harvesting, electron generation efficiency and charge collection efficiency from device to external circuit

$$\boldsymbol{Jsc = \emptyset LH \times \emptyset G \times \emptyset C}$$

J_{sc} was short current density and FF was the fill factor and P_{in} was the light intensity which irradiates the device. FF was the ratio of power and product of V_{oc} and J_{sc}. So, to achieve superior efficiency J_{sc} and V_{oc} are two factors which effect profoundly [8, 50-54]**.**

2. Co-sensitization of metal sensitizers:

Zinc porphyrin LD14 (No.1, Figure 1) was co-sensitized with Porphyrin sensitizer LDD1 (No.2, Figure 1) by noting improved efficiency of 10.4 %. Enhanced IPCE was attributed to broadened absorption range from 400-900nm, to suppression in sensitizer aggregation and enhancement in current density [55]. Michael D. Brown and coworker demonstrated that Co-sensitization of two sensitizers as TT1 (No.3, Figure 1) and D102 (No.4, Figure 1) enhanced the power conversion efficiency 3.9% to 4.7% and absorption spectra dramatically enhanced from visible to IR region. Co-sensitization made charge transfer and regeneration quick. Experimental and spectroscopic analysis showed that combination of sensitizers enhanced the current density. These parameters respond better power conversion efficiency. About unexpected increase in efficiency researchers showed possibility of that charge aggregation within molecule was broken by using reported technique. That unique route provides second chance for sensitizers to generate charge and also resonant energy transfer was efficient [56]. Co-sensitization of zinc porpharene, LD12 (No.5, Figure 1) and CD5 (No.6, Figure 1) was investigated and efficiency of 9% was achieved. Remarkable enhanced efficiency was resulted as compared to single LD12 and CD5 7.5% and 5.7% respectively [57]. Triple Co-sensitization of an organic sensitizer CD4 (No.7, Figure 1), YD2-oC8 (No.8, Figure 1), and YDD6 additionally double Co-sensitization of YD2-Oc8 by varying CD4 and YDD6 was investigated. All the sensitizers individually, doubly and triply were checked. Using cocktail approach triple co-sensitized device highest efficiency of 10.4% was noted [58]. In that way cocktailing of porphyrin sensitizers enhances efficiency [59]. Recent progress with respect to Co-sensitization of porphyrin showed efficiency 13% [60].

Molang Cai and co-worker stated that tributyl phosphate (TBP, Table 1) and Ruthenium (II) (N719, Table 1) were collectively used and it was noted that TBP fragmentation occur. These fragments and Ru-sensitizer show photoelectric conversion efficiency-oriented adsorption at the surface of Titania by stopping aggregation of sensitizer and electron recombination. TBP adjusted itself in a favorable way that it created stearic hindrance on Ruthenium (II) (N719). And it minimizes hydrogen bonding among sensitizer molecules. Experimental analysis showed that TBP divided in four types. There are two carboxylic acids on N719 (No.9, Figure 2) which may show strong aggregation by hydrogen bonding between sensitizer molecules. By effective attachment on Titania surface there are no free carboxylic acids to make hydrogen bonding in that way sensitizer aggregation was controlled and J_{sc} was improved. Spectral comparison showed hydrogen bonding was formed between carboxylic groups as donor moiety of Ruthenium (II) (N719) and accepter moiety phosphonyl group of TBP. Fragments of TBP create stearic hindrance on sensitizer molecule so, sensitizer molecule gain stability and hydrogen bonding. As the electron density will increase, the performance of the cell will be improved. V_{oc} was improved by suppression of charge recombination additionally TBP has also performance-oriented effect on Titania band shift. So, by adding a pair of Ruthenium (II) (N719) and TBP. It will increase the efficiency up to 9.50%, almost 40% improvement [61]. To encourage efficient electron injection metal complex co-sensitizer with N719 play important role. Absorption spectrum can also be increased by adding additives [62-63].

Adsorption of phenothiazine structure holding sensitizers and porphyrin sensitizers improve outputs in two ways by retarding back electron transfer and improving spectral responses. These two factors enhance the efficiency more than 10%. Co-sensitized sensitizers give better efficiency than individual Porphyrin and phenothiazine showing 7.4% and 8.2% respectively. Analysis shows that phenothiazine adjusts itself in the spaces of porphyrin sensitizer and makes insulation layer on Titania that stops direct electrolyte approach on electrode also. If electrolyte approaches directly, it decreases efficiency by electron recombination. Co-sensitization also gives a better spectral response which showed co adsorbents reoriented themselves to the surface of semiconductor [64]. Porphyrin based sensitizers are co-sensitized with non-porphyrin sensitizers that phenomena improved the absorption spectra. Chen and coworker reported that enhanced efficiency about 5.75% was achieved by enhancing J_{sc} and V_{oc} values. Besides molecular engineering, co-sensitization was appreciable way to solve the lower efficiency problem [65]. Co-sensitization of reported D-D-π-A type sensitizers give improved efficiency 7.78% i.e. almost 95% as compared to N719 (No.9, Figure 2) sensitizers when chenodeoxycholic acid (CDCA, Table 1 & 2) was used as co-adsorbent. CPhT2PA: CDCA (1:10, Table 1) that pair and mole ratio was very efficient or co-sensitizing. All experimental and theoretical observation showed that collectively behaving of primary donor (phenothiazine) and auxiliary donor (carbazole) enhanced the electron donating character of sensitizer that shows favorable absorption range. So improved absorption range enhanced J_{sc} [66].

Metal free sensitizer D131 (No.17, Figure 3) and Ru sensitizer C106 (No.18, Figure 3) having indole-based conjugated group were used by stepwise approach to increase absorption spectra range and light harvesting ability. Both sensitizers have LUMO energy level above the semiconductor so electron injection was remarkably fast. Efficient electron injection increases the value of J_{sc} and improvement in the power conversion efficiency was about 94%. Co-sensitization stops the chances of direct connection of electrolyte and electrode. That aspect reduces the electron recombination, so V_{oc} was enhanced. Enhancement in J_{sc} and V_{oc} collectively improve the efficiency [21]. Ru based sensitizers and metal free sensitizers were co-sensitized and efficiency enhancement of 9.26% was recorded. DFT and other spectroscopic analysis shows that molecular matching and energy alignment increases the V_{oc} [50]. Amino naphthalene, with one pyridinecarboxaldimine substituent and same with two pyridine carboxaldimine groups were used as co adsorbent with N719(No.9, Figure 2). Co-adsorber with double anchoring substituent gives better result than single one. Overall efficiency was increased from 5.28% to 6.51% as compared to N719 single sensitizer. Suppressing charge recombination and favoring absorption range will modify and enhance the electron life time. So, device efficiency will also be improved [67]. Using N, N'-bis((pyridin-2-yl)(methyl)methylene)-o-phenylenediamine (named BPPI)(No.24, Figure 4) as a co adsorbent will compensate the deficiency of absorption region of N719. Presence of anchoring pyridine substituent on BPPI and Co-sensitization increase efficiency from 5.29% (single N719) to 6.22% (co-sensitized) under same conditions. Optical properties were improved by adjusting longer absorption and higher molecular extinction coefficient. Photon loss was controlled and light harvesting ability was enhanced. Electrochemical properties were improved by molecular matching and energy alignment. Photo voltage properties like J_{sc} and V_{oc} was improved and also aggregation was suppressed [68].

Co-sensitization of three indole-based co-sensitizers DBA-3(No.25, Figure 4), DBA-4(No.26, Figure 4), DBA-5(No.27, Figure 4) with auxiliary electron donors and ruthenium sensitizer NCSU-10(No.28, Figure 4) showed that among all DBA-4 gives better results. Different spectroscopic analysis showed better photophysical properties. Absorption spectrum showed two bands one was due to π-π* excitation and second was due to charge transfer between donor to acceptor. Spectral results as absorption, emission and fluorescence show that co-sensitization gives higher molar extinction coefficient and favorable spectra region. Electrochemical studies showed charge was efficiently injected. Cyclic voltammetry was used to verify the potential to efficient transfer of electron. Energy alignment and Redox potential showed that both electron transfer and sensitizer regeneration was profoundly affected to give improved result. Molecular matching was so favorable by making compact layer on photoanode that no backward electron loss. All these factors associate each other and overall efficiency was noted 10.12% [69]. An organic WS-5(No.29, Figure 4) and porphyrin sensitizer XW4 (No.30, Figure 4) were co-sensitized. Profound effect of co-sensitizers showed that improved absorption spectra range which was deficient in single porphyrin case. Favorable panchromatic light harvesting properties and charge injection was observed in case of co-sensitizing. Finally, enhanced power conversion efficiency was observed up to 10.41%. Comparison of spectra shows that cocktail approach of co-sensitization was achieving dramatic improvement in absorption spectra. Single porphyrin sensitizers were deficient in absorption point of view [35]. Similarly, WS-5(No.29, Figure 4) and porphyrin sensitizer XW11 (No.124, Figure 16) combinedly result the efficiency of 11.5% [70]. ZnP-triazine-$(gly)_2$ (No.31, Figure 5) was co-sensitized with a tertiary aryl amine moiety showed as D(No.32, Figure 5) with two ethynyl-pyridine groups and a terminal cyano-acetic acid group. Power conversion efficiency was enhanced 7.34% as compared to un-co-sensitized zinc porphyrin 4.72%. These spectrums and experimental results show that by co-sensitizing, the performance, the favorable parameters like broader absorption spectra, higher molecular extinction coefficient, better light harvesting properties, improved J_{sc}, profoundly affected V_{oc}, fast electron transfer, suppressed electron recombination and enhanced electron life time are achieved by co-sensitization of the sensitizers [71].

Loading of sensitizers can be precisely controlled by ultra-fast method reported by Peter J. Holliman and coworkers. Complications due to difference in partition coefficient and molar extinction coefficient were solved by dyeing desorption re-dying because both coefficients directly affect the spectral out comings. Ru-based sensitizers (N719, Table 1 & 2) and metal free sensitizers

(SQ1 and D149, Table 1 & 2) were used and 8.1% efficiency was noted. Ultra-selective, ultra-fast method was used for co-sensitizing of sensitizers. Alkalis are used for desorption because matching of pKb values. Bu4NOH was a good desorber because, it shows good performance at room temperature. Ultra-fast total, partial and selective desorption and re-dying all were used individually and spectral responses were analyzed. It was concluded that base of efficiency was related to appropriate spectral responses. Combining more sensitizers improve spectral responses by precise loading of sensitizers. Use of ultra-selective and fast method was a cheaper and low-cost way. Fantastic advantage was that single device can be used for multiple purpose [33]. A series of three (FNE57- FNE59, Table 1) donors - π-acceptor zinc porphyrin sensitizers were synthesized to determine the effect of co-sensitization. Electron donor group and accepter group cyano-acrylic acid and carbazole respectively were not changed. Place of auxiliary acceptor was changed and performance was examined. Metal free sensitizers showed as FNE46 (Table 1) was co-sensitized with zinc porphyrin sensitizers. Stepwise approach was preferred over cocktail approach. Optical properties and Photovoltaic properties were elevated by using that approach. Ultimately co-sensitization enhance spectal response, improve J_{sc}, V_{oc} and prolonged electron lifetime. So, these factors profoundly affect efficiency, which may increase to 8.14% [72].

Co-sensitization was not limited to synthetic metal compounds but also fruitful for natural species. Co-sensitization of natural chlorophyll-based cell was performed to characterize the cell. Multiple application of Chl-a-type with -b-Chl, or Chl-c-type (Table 1, Figure 6) showed enhanced performance. Special enhancement was in the case of co-sensitization of Phe-a- and Chl-c- and power conversion efficiency was 5.4%. Photocurrent and photo voltage were improved so, efficiency was enhanced [15]. 3, 30-(5,50-(9-hexyl-9H-carbazole-3,6-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) showed as D(No.32) was co-sensitized with N719, 7.5% efficiency was achieved by stepwise approach. That was reasonable enhancement as compared to individual efficiencies of Ru-based and metal free Sensitizers (5.78 %) and (3.95 %) respectively. By co-sensitization absorption range, light harvesting properties, photocurrent and photovoltage was improved so reasonable efficiency was enhanced [73]. 2,6-bis(1-phenyliminoethyl)-pyridine denoted as MO (No.44, Figure 7), was structurally modified. A methyl group was introduced in its phenyl moiety. On the bases of position of attaching methyl substituent like ortho and para, the coming derivatives was denoted as M1o (No.45, Figure 7), M1p (No.47, Figure 7) and M2 (No.46, Figure 7). These derivatives were used as co-sensitizers with N719 and outputs regarding DSSCs were investigated. It was demonstrated that co-sensitization suppresses the sensitizers aggregation by making compact layer on semiconductor. In that way it discourages the electron backward falling by prolonging life time of electron. Energy alignment makes efficient electron injection and sensitizer regeneration. Increasing number of electrons in phenyl ring improves performance by improving J_{sc}. Position of methyl was crucial in co-sensitizers selection. Para position also dramatically improve fall factor. M1p (No.47, Figure 7) and N719 (No.9, Figure 2) pair give highest efficiency value (7.32%), that value was about 35% improved than device which was single sensitized by Ru-based N719 sensitizers and showing efficiency 5.43% [74].

Polyphenylenes were co-sensitized with Ru-based N719 sensitizers. Electron recombination was suppressed, electron injection was improved, J_{sc} and V_{oc} was enhanced and efficiency was reached up to 9.68% compared with single N719 8.34% (75). Co-sensitization of N719 and metal free coumarin gives enhanced PCE of 9.9% which was higher than the single sensitizer. N719 give 8.2 % and Coumarin shows 6.9 % PCE [76]. Co-sensitization of Ru-based sensitizers shown as JK-142 (No.51, Figure 7) and metal free sensitizer bipyridyl ligand substituted by a 3-carbazole-2-thiopheny shown as JK-62 (No.52, Figure 7). Conjugation of organic sensitizers with metal sensitizers improves absorption spectral responses by giving red shift. Molecular alignment at surface of semiconductor take place as JK-142 has large size. So, by adding co-sensitizers that deficiency was covered and proper layer was formed by combined sensitizers. Higher efficiency 10.2% was achieved which was better than the efficiency of N719 8.68% under same conditions [77].

Panchromatic engineering was easy way to enhance efficiency of N719. Co-sensitization of N719 and at P3OT (poly (3-octylthiophene)) at N–Zn/TiO2 anode showed better result than individual ones [78]. Cadmium complexes are also good co-sensitizers. Cd (II) was co-sensitized with N719 by using sequential approach. Ru based N719 has weaker absorption range so, that deficiency can be compensated by Cd co-sensitizers. Co-sensitization shows broader absorption and injects electron quickly. In that way photo voltage, current and PCE were improved [79, 80]. Metal free sensitizers and N719 were co-sensitized to get enhanced efficiency of 4.67%. That efficiency was greater than individual N719 and J1 with efficiencies of 3.27% and 3.26% respectively. Improvement in efficiency was attributed to improvement in spectral responses [81].

An organic sensitizer Y3 and Ru-base sensitizers (No.121-123, Figure 16) was investigated in single and double loading. Co-sensitization gave enhanced efficiency. That enhanced efficiency was attributed to minimize the sensitizer aggregation and suppression of charge back flow. Performance of single loaded device was badly affected by inefficient charge transfer [82]. Co-sensitization of three sensitizers (D131, D149, and N3, Table 1 & 2) was optimized to get better performance. Combination of these sensitizers enhance the efficiency by energy alignment and quick electron transfer [83].

3. CO-SENSITIZATION OF METAL FREE SENSITIZERS:

Metallic complexes show better results but problems of synthetic rout and economy created research space for metal free sensitizers [84]. Co-sensitization of organic sensitizers were also an easy way to enhance efficiency. A merocyanine sensitizer Y (No.54, Figure 8), hemicyanine sensitizer R (No.55, Figure 8), and squarylium cyanine sensitizer B (No.56, Figure 8) were Co-sensitized for investigation. Triple Co-sensitization shows better result than single one. Reported efficiency of 6.5%, was appreciable. Prompted J_{sc} and suppressed aggregation was also reported [85]. Metal free sensitizer 3-{59-[N, N-bis(9,9-dimethylfluorene-2-yl)phenyl]- 2,29-bisthiophene-5-yl}-2-cyanoacrylic acid denoted as JK-2 (No.57, Figure 8) was co-sensitized with Squalene sensitizer SQ1 (No.33, Figure 5). In that sensitization an enhanced IPCE of 7.43% was noted [86]. Coi and coworker arranged multiple layered schemes as TiO2/JK-2/Al2O3/SQ1 to get better efficiency of 8.65% than traditional JK-2/ SQ-1 approach with efficiency of 8.01% [38]. A new compound Diketopyrrolopyrrole DPP07 (No.58, Figure 8) was investigated as sensitizer in DSSCs and it showed efficiency of 7.7%. Co-sensitizers like NT35 (No.59, Figure 8) and D35 (No.35, Figure 5) enhanced efficiency of 8.31% and 8.60% was noted [87, 88]. Organic sensitizer having 9,10-dihydrophenanthrene central unit of structure and aryl amine as substituent (BP-1 to BP-3, Table 2) were co-sensitized with squaraine sensitizer denoted as SQ2(No.62, Figure 9). Highest efficiency was noted when 8 volumes of BP2 (No.61, Figure 9) and 2 volumes of SQ2 were used. Efficiency was recorded 8.14%, that was higher than metal free single sensitizer [89]. Multiple loading of black sensitizer with Y1 and Y2 additives showed improvement in device performance. With multiple loading IPCE showed dramatic increase in efficiency and well absorption rang. Improved efficiency 11.4% was noted with suppression of sensitizer aggregation, electron injection enhancement and both J_{sc} and V_{oc} improvements [48]. 2,6-conjugated 9,10-bis(hexyloxy)anthracene shown as (Ant1 to Ant4) were co-sensitized. Single Ant3 give efficiency of 7.52%. Co-sensitization with SQ2 gives 8.08% and co-sensitization with chenodeoxycholic acid (CDCA) give 9.11% efficiency [90]. Metal free sensitizers D149 (No.71, Figure 10), D205 (No.72, Figure 10) were co-sensitized with D131 in cocktail co-sensitization approach. It was reported equimolar loading of in-doline based sensitizers give good efficiency and by adding co adsorbents efficiency was the best. Enhancement in IPCE was attributed to improvement in absorption range, charge injection efficiency, molar extinction coefficient and suppression of sensitizer aggregation and charge recombination [91].

New method of co-sensitization was introduced by using Donor–pi–Acceptor sensitizers having a pyridyl moiety which has dual advantage to arrange itself at the surface of Titania. One way was to attach at Bronsted acid sites showing hydrogen bonding and second approach was to covering Lewi’s acid sites by forming coordinate covalent bond. That method was most effective and efficiency oriented by suppressing the competitive adsorption. That was cunning approach to cover surface of anode to minimize the chances of charge recombination [92]. A New compound 4-(bis(9,9-dimethyl-9H-flouren-2-yl)amino)benzoic acid (HC-Acid) was used as co-adsorbent at the surface of titania with NKX2677(No.79, Figure 11) and HC-Acid (No.77, Figure 11). That was a compete traditional co-adsorbent approach with deoxycholic acid (DCA). It acts as anti-stacking agent and secondly gives better harvesting properties at shorter wavelength region. Improved efficiency of 9.09% was noted and attributed to basic efficiency enhancing factors [93].

Pyrenoimidazole based metal free sensitizers denoted as 5c (No.80, Figure 11) was co-sensitized with unsymmetrical squaraine sensitizer denoted as SQ2 (No.62, Figure 9) by using cocktail approach. Loading of co-sensitization increase the efficiency up to 6.24%. Co-sensitization improve the absorption responses, light harvesting abilities, device stability, charge transfer efficiency and photochemical properties [94]. Three devices were fabricated with natural sensitizers. One fabrication was done by xanthene’s and second was loaded by Anthocyanin and third was applied by mixture of xanthene's and Anthocyanin. All were processed to check performance. Co-sensitized loading gives higher efficiency of 1.41% greater than average of individual ones. Anthocyanin was collected from pomegranate juice and Xanthene was also known as Rose Bengal. Improvement in efficiency was attributed to improvement in ideality factor [28]. Co-sensitization of M-Red (No.81, Figure 11) or D-Red (No.82, Figure 11) with S-Blue (No.83, Figure 11) increased the spectral responses positively. All factors like stopping of sensitizer aggregation, photovoltaic properties and efficiency was favorably improved. PCE was increased almost 31.7% [95]. Eosin and Jambolana were co-sensitized to discourage the charge recombination. Overall efficiency was improved 0.1377 % which was greater than single ones [96]. Benzoxadiazole based Donor–Acceptor–pi–Acceptor metal free sensitizers denoted as WS62 (No.84, Figure 12) and WS64 (No.85, Figure 12) were prepared and co-sensitized with S0 (No.86, Figure 12), S1 (No.87, Figure 12) and S2 (No.88, Figure 12). S0 (No.86, Figure 12), S1 (No.87, Figure 12) have shorter conjugation length so lower performance. S2 (No.88, Figure 12) has higher pi conjugation so greater efficiency oriented. When WS64 (No.85, Figure 12) and S2 (No.88, Figure 12) are investigated the efficiency of 7.9% was achieved. J_{sc} improvement was profoundly affected by molecular designing and size of co-sensitizer. Molecular matching of sensitizer and co-sensitizer make impact layer on Titania surface so, charge recombination was suppressed [97]. R. Agosta and coworkers reported that co-sensitization of sensitizers give better results. Single G2 (No.89, Figure 12) sensitizer was compared with co-sensitized sensitizer as DTB-B (No.91, Figure 12) and DTB-T (No.90, Figure 12). It was noted that improved absorption spectra and better room for co-adsorbers to attach on the surface of semiconductor and minimum charge aggregation was due to Co-sensitization. Electron transfer process was made effective by removal of bulky group from bigger sensitizer and designing the simple co-sensitizers to adsorb properly on the surface of semiconductor. Combined application of sensitizers improves performance as well light harvesting ability [98]. Yong Hua and coworker prepared metal free phenothiazine-cored organic TP1 (No.92, Figure 12), TP2 (No.93, Figure 13) –TP4 (No.95, Figure 13) sensitizers. They reported among four compounds TP3 (No.94, Figure 13) give better responses of co-sensitization with squaraine sensitizer YR6 (No.96, Figure 13). Molecular matching and proper alignment stop the sensitizer aggregation and good spectral responses. The suitability on surface of semiconductor suppresses the charge recombination and appreciate the electron injection. So, enhanced efficiency of 9.84% was noted [99].

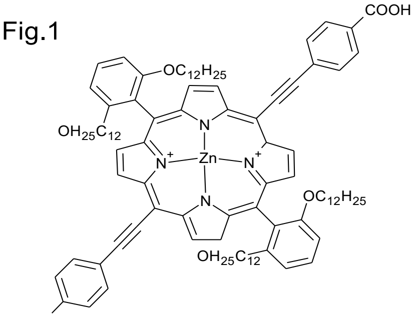
Quinoxaline metal free sensitizer Q21 (No.98, Figure 13) after introducing CPDT replacer of thiophene was co-sensitized with metal free sensitizer, enhanced efficiency of 10.41% was noted. That efficiency was better than single sensitizer Q21 of 9.03%. Researchers demonstrated that appropriate molecular alignment minimizes charge recombination. All other factors on which efficiency was dependent like absorption range, VOC, JSC and FF were improved. Cocktail approach was preferred [100]. 4′,6-Diamidino-2-phenylindole (DAPI) and 2-(4 ethoxy phenyl-5-(4 methyle-1-piperzenyle)-2,5bi-1H-benziimedazole trihydrochloride was co-adsorbed by improving short-circuit current density (J_{sc}). These energy delay species were added in N719

(No.9, Figure 2) sensitizer and the power conversion efficiency enhancement was observed that was dramatically improved. DAPI (No.99, Figure 13) co-sensitization provides 10.49% and H33342 (No.100, Figure 13) provides 10.47% efficiency [101].

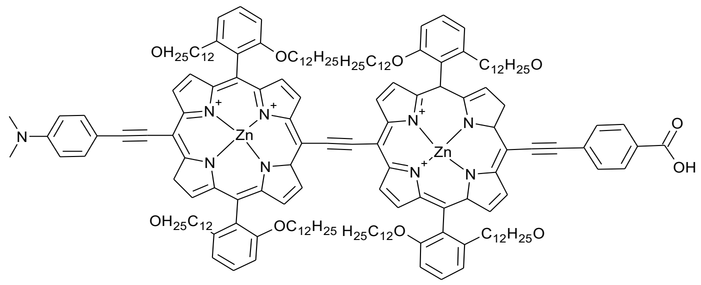
"π stacking effect" was deactivation of conjugation effect of sensitizer by inter molecular interaction while "shielding effect" was stopping electrolyte material to photo anode. Both metal free co-sensitization bis(3-methylphenyl)phosphinic acids showed as BMPP (No.101, Figure 13) and chenodeoxycholic acid showed as CDCA was reported to have maximum efficiency. CDCA has greater anti-π-stacking effect and BMPP showed shielding effect significantly. By co-adsorption two types of effects as anti-π-stacking effect and shielding effect was made fit for improved PCE. When co-adsorbent and sensitizer was applied in same concentration PCE improvement was about 60%. Both species collectively show improvement in J_{sc} and V_{oc} in that way efficiency was enhanced [102]. Three metal free sensitizers with design of donor-pi-accepter groups were co-sensitized with squaraine SQ2 (No.62, Figure 13) sensitizer. These H-shaped sensitizers enhance the performance about 70% as compared to SQ2 sensitizer single one. Pyrrole substituent at these sensitizers play favorable role in intermolecular charge transfer because it has electron donating nature and active sites. Among all conformations co-sensitizing of Meta position with SQ2 was more performance oriented. 7.44% efficiency with Meta positioned and SQ2 was noted. Optical properties and molar extinction coefficients were increased to double as shown by single one. That fantastic increase was the result of presence of two D-π-A groups per H-type sensitizer. Also, another plus point was that they make shielding and insulating layer on Titania surface to enhance light harvesting abilities [103]. Sensitizers as 3,3′-diethyloxacarbocyanine iodide (1), 3,3′-diethylthiacarbocyanine iodide (2), 3,3′-diethylthiadicarbocyanine iodide (3) and 3,3′-diethylthiatricarbocyanine iodide (4) were investigated computationally (No.105-108, Figure 14). Chemical analysis and engineering approaches were used to optimize the Co-sensitization outputs. Co-sensitization of 1p* and 4p give maximum spectral responses. Anchoring at para position shows anti π_π stacking effect. 1p* and 4p have suitable energy alignment, appropriate molecular matching and suitable geometry to use as co-sensitizers [36].

Panchromatic engineering leads to better performance. Benzothiadiazole T4BTD-A (No.109, Figure 15) sensitizers and squaraine sensitizers HSQ3 (No.110, Figure 15) and HSQ4 (No.111, Figure 15) metal free sensitizers show panchromatic absorption spectral responses. Both isomers of squaraine were also compared. T4BTD-A+HSQ3 also give better conversion efficiency of 7.0% but T4BTD-A+HSQ4 showed the best as 7.7%. J_{sc} was improved by improving light harvesting by associating factors of Benzothiadiazole sensitizers and *cis*-squaraine. V_{oc} was improved by controlling the electrons backward recombination [104]. Three sensitizers of class triphenylamine denoted as TPA3T1A, (No.112, Figure 15) TPA3T2A (No.113, Figure 15) and TPA3T3A (No.114, Figure 15). TPA3T1A and TPA3T2A were analyzed for co-sensitization with TPA3T3A. Improvement in efficiency from 5.27% to 5.83% was recorded. The main sensitizer covers 73% space on Tio2 and co-sensitizer cover remaining 27% space. These co-sensitizers suppress the charge recombination and enhance photovoltaic performance [105]. Two metal free sensitizers WS-39 (No.115, Figure 15) and WS-2 (No.116, Figure 15) were co-sensitized to compensate the photovoltaic properties and reinforcement advantageous factors combinedly to enhance efficiency of 9.48%. That efficiency was better than single WS-39 (8.67%) and WS-2 (8.48%). Both sensitizers fight against charge recombination affectively [34]. Phloxine B and Bromophenol blue was co-sensitized to investigate device efficiency. Enhanced efficiency of 1.35% was noticed that was due to improvement in absorption region of singly loaded device [106]. Squaraine-based sensitizer (SQ2) and a diarylaminofluorene-based metal free sensitizer JD1 (No.119, Figure 16) were combinedly loaded to check the performance of DSSCs. Enhanced efficiency of 6.36% was attributed to broadening absorption range. Single sensitized device with JD1 and SQ-2 shows efficiency of 5.44% and 4.11% respectively [107].

Fig.1



LD14(No.1)



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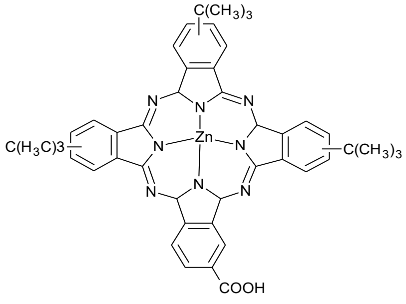
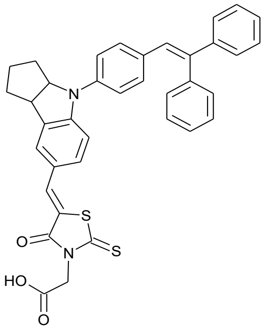
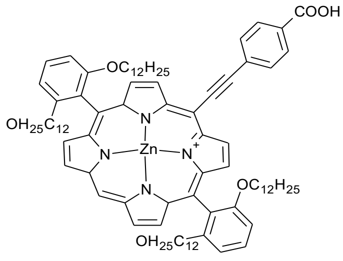


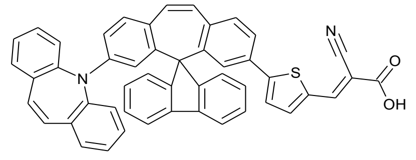
TT1(No.3)



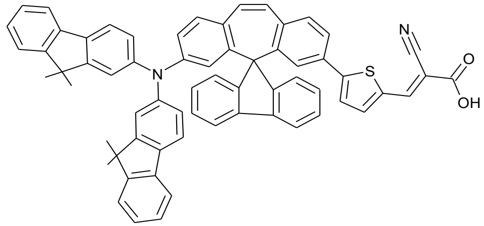
D102(No.4)



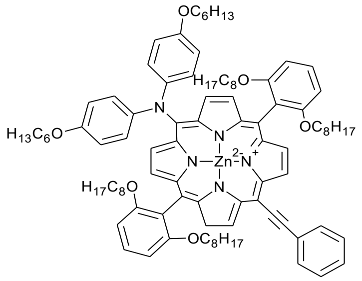
LD12(No.5)



CD5(No.6)



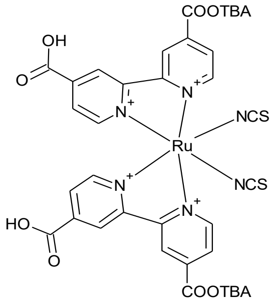
CD4(No.7)



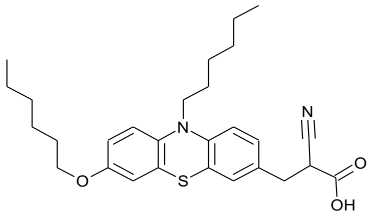
YD2-OC8(No.8)

Figure 1: Chemical structures of 1 to 8 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

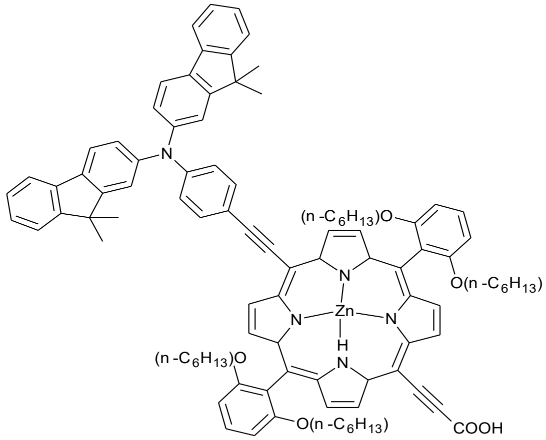
Fig.2



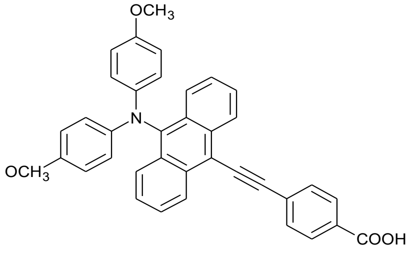
N719(No.9)



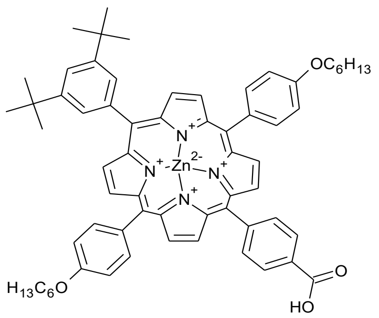
PT-C6(No.10)



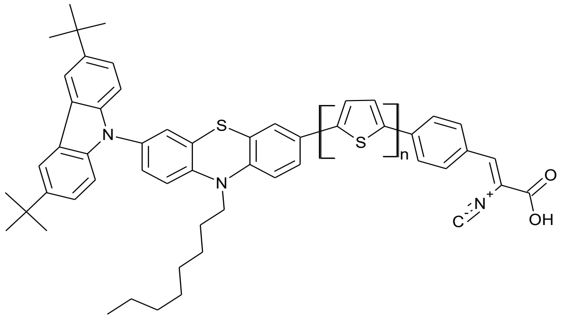
ZnP(N0.11)



C1(NO.12)



XC1(No.13)



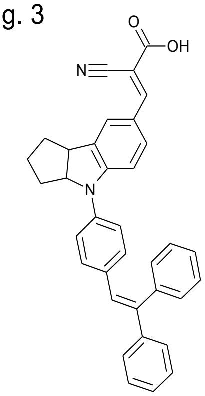
n=o CPhPA

n=1 CPhTPA

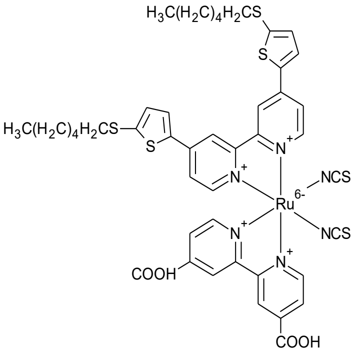
n=2 CPhT2PA(No.14-16)

Figure 2: Chemical structures of 9 to 16 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

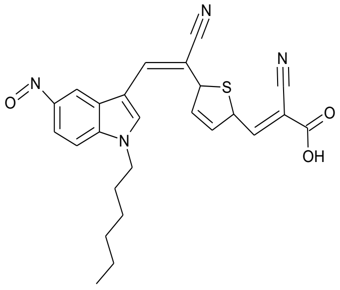
Fig. 3



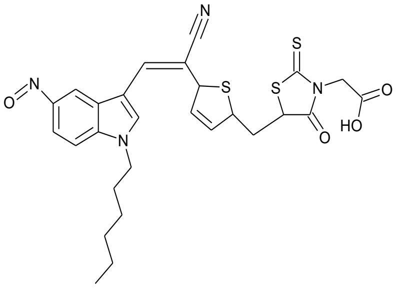
D131(No.17)



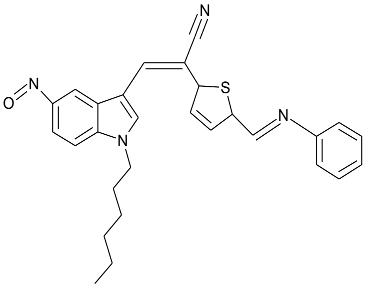
C106(No.18)



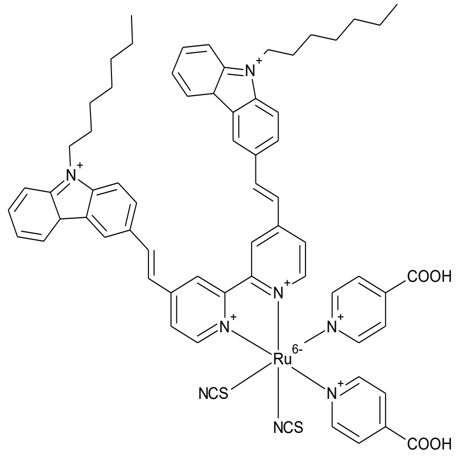
N1(No.19)



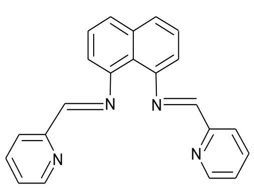
N2 (No.20)



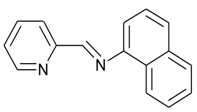
N3(No.21)



HD-14(No.22)



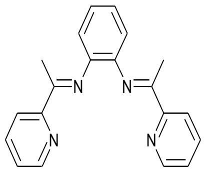
SDP(No.23)



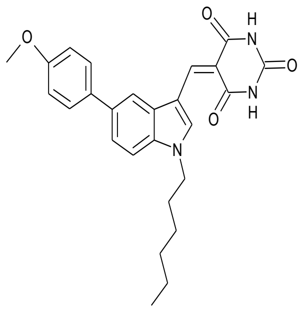
USP(No.23-a)

Figure 3: Chemical structures of 17 to 23a sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

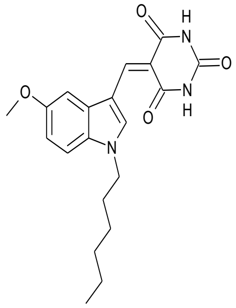
Fig. 4



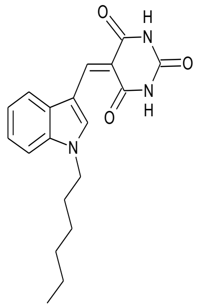
BPPI(No.24)



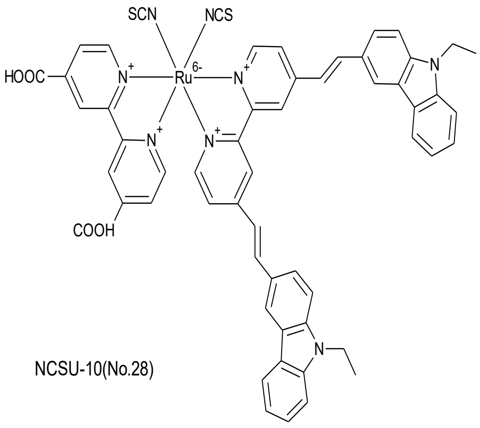
DBA-3(No.25)



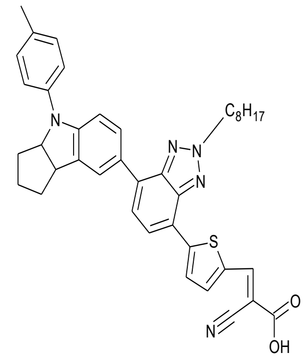
DBA-4(No.26)



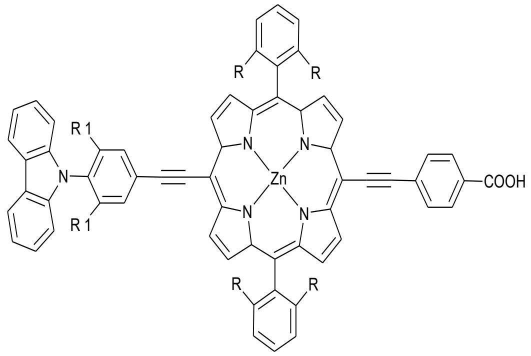
DBA-5(No.27)



NCSU-10(No.28)



WS-5(No.29)

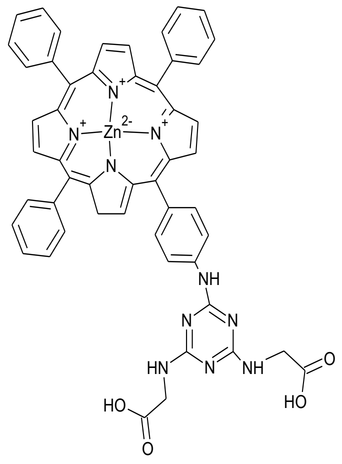


xw4(No.30)

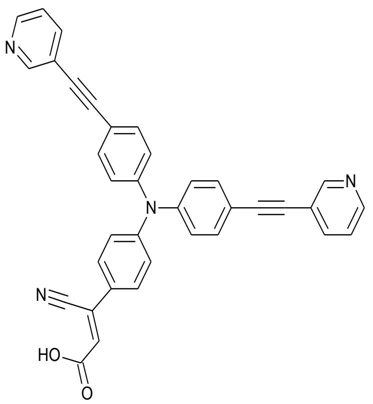
R=OC12H25 R1=OC6H13

Figure 4: Chemical structures of 24 to 30 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

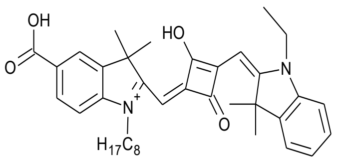
Fig.5



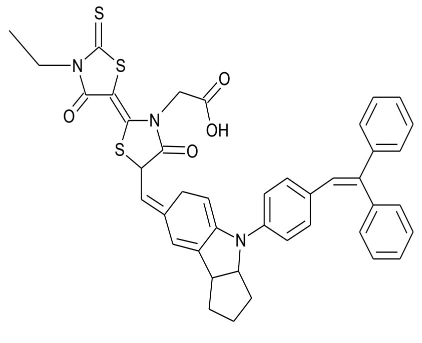
ZnP triazin (gly)2(N0.31)



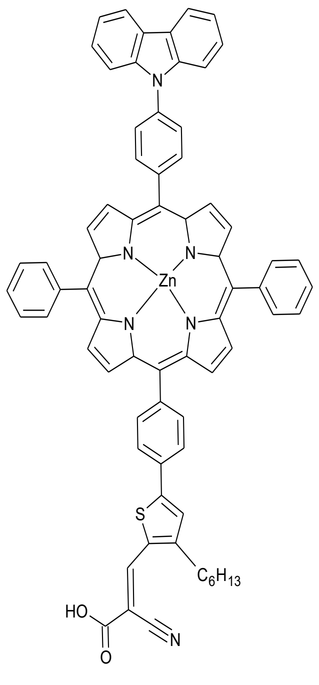
D(No.32)



SQ1(No.33)



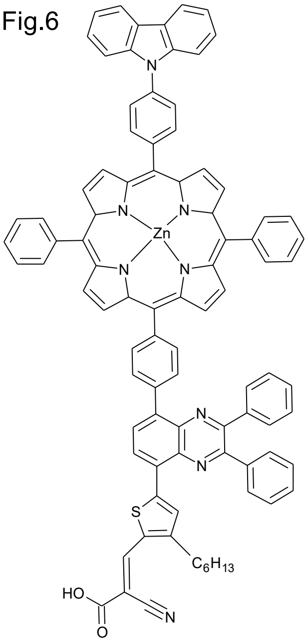
D149(No.34)



FNE57(No.35)

Figure 5: Chemical structures of 31 to 35 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

Fig.6



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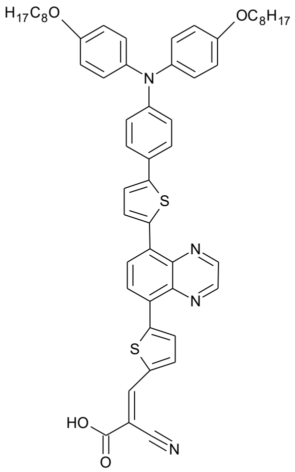

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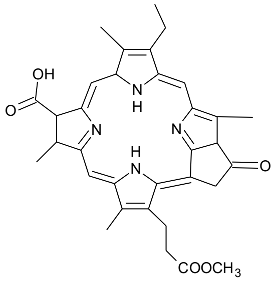
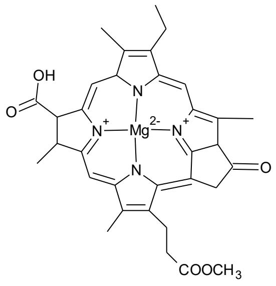
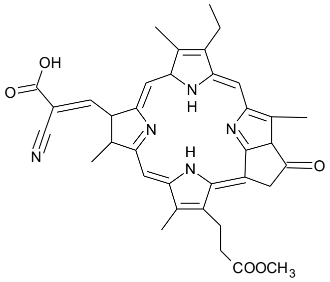


Phe a(No.38)

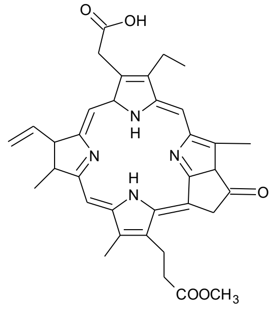


Mg-Phe a(No.39)

a-type

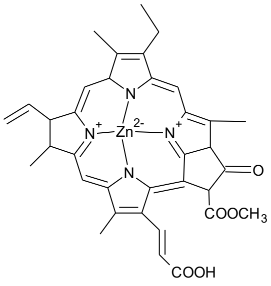


Phe Y(No.40)



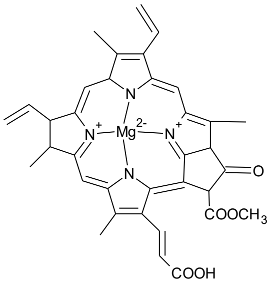
Phe b(No.41)

b-type



Zn-Phe c1(No.42)

c-type

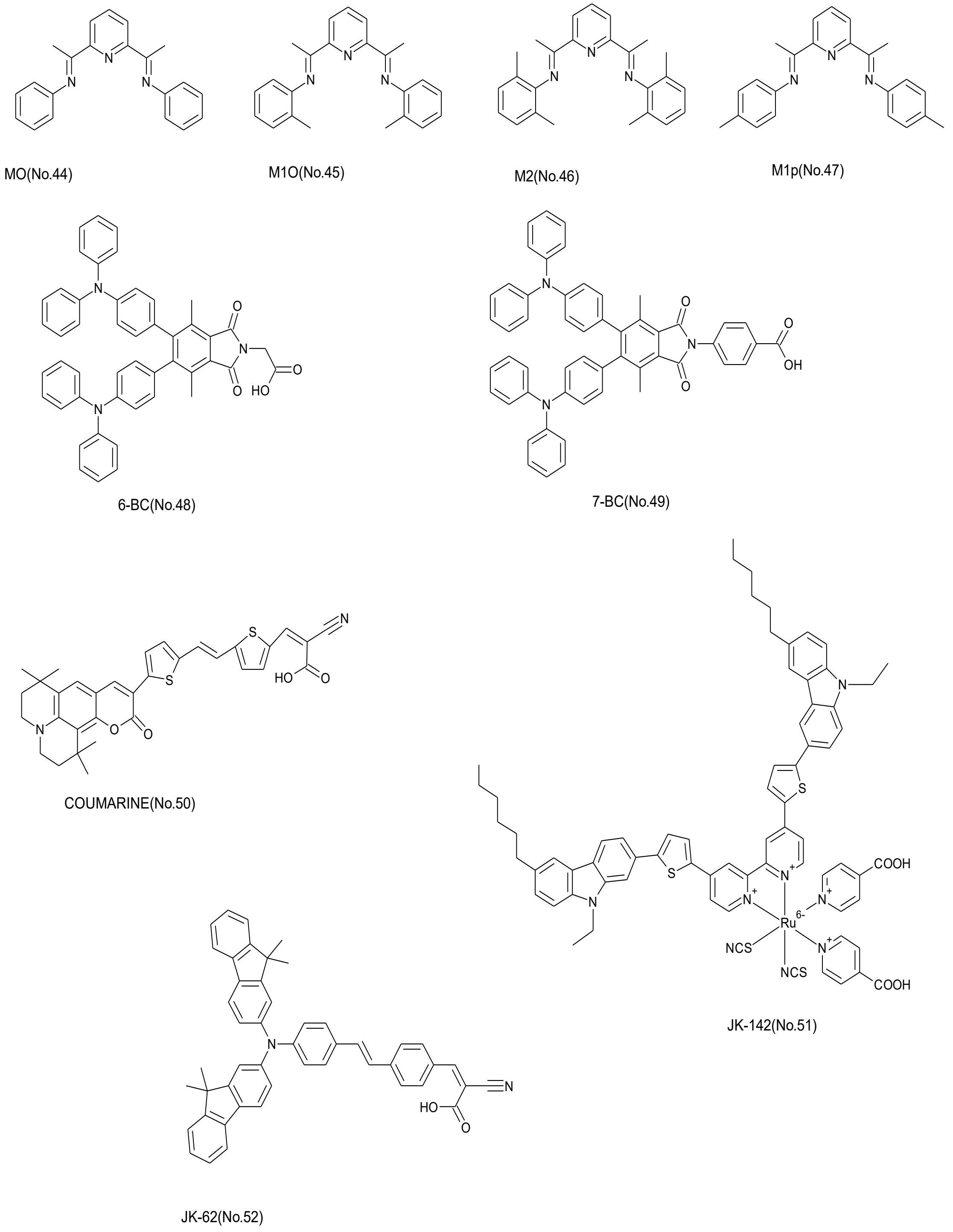


Mg-Phe c2(No.43)

(Chl C2)

Figure 6: Chemical structures of 36 to 43 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

Fig.7



MO(No.44)

M1O(No.45)

M2(No.46)

M1p(No.47)

6-BC(No.48)

7-BC(No.49)

COUMARINE(No.50)

JK-142(No.51)

JK-62(No.52)

Figure 7: Chemical structures of 44 to 52 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

Fig.8

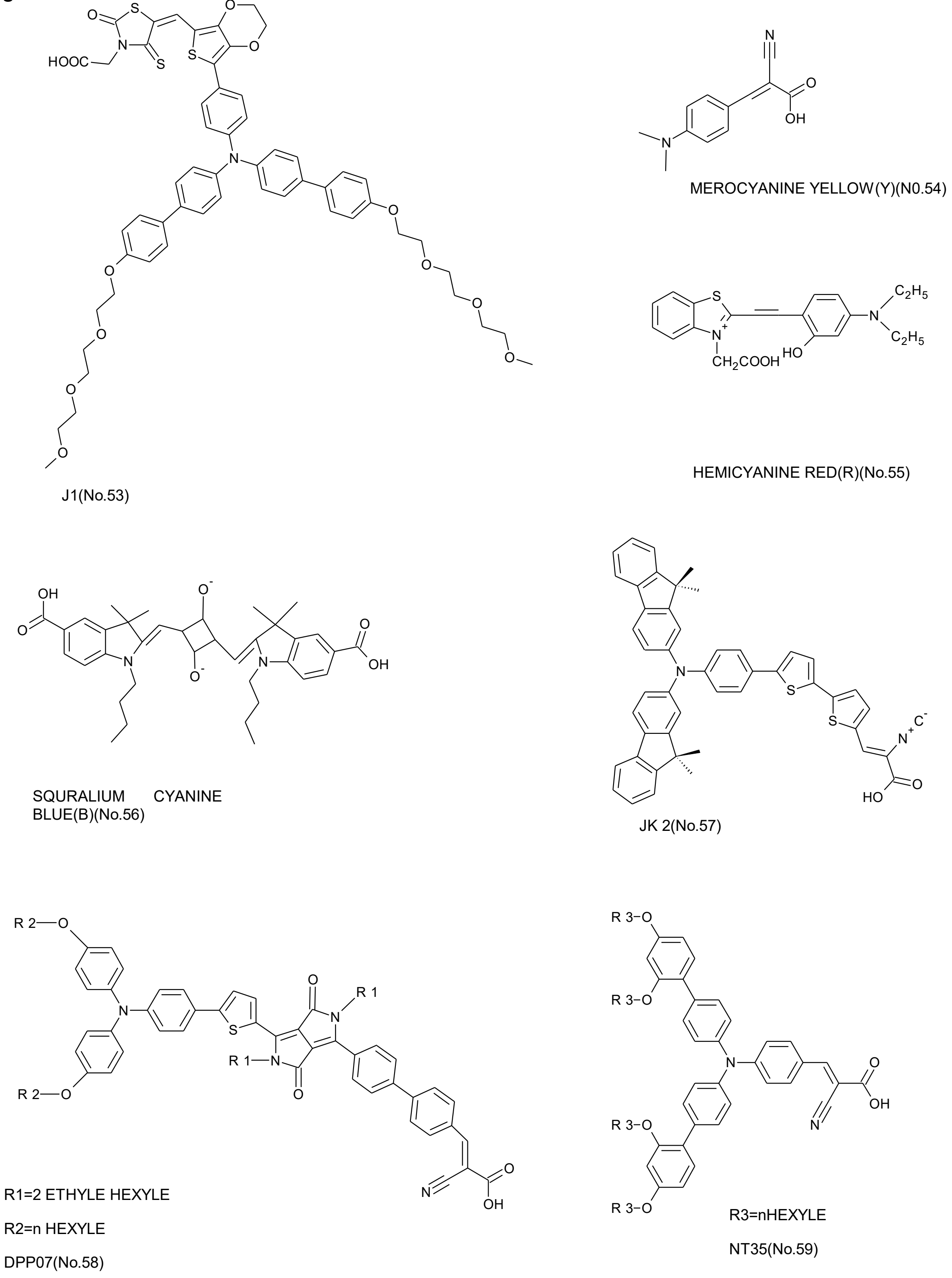
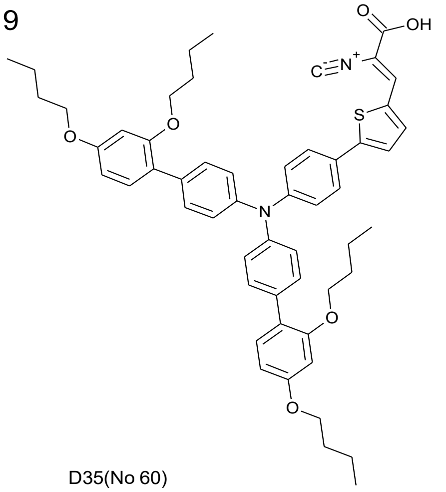
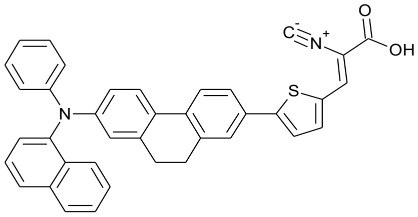


Figure 8: Chemical structures of 53 to 59 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

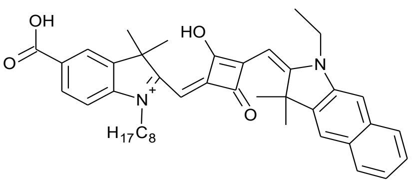
Fig.9



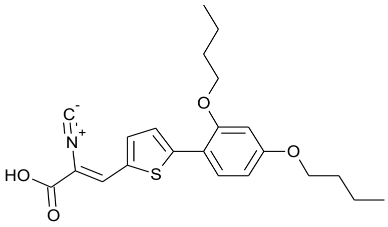
D35(No 60)



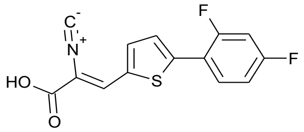
BP2(No.61)



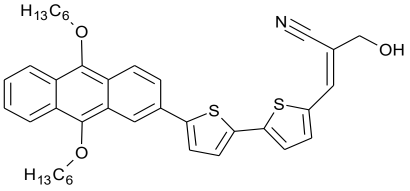
SQ2(No.62)



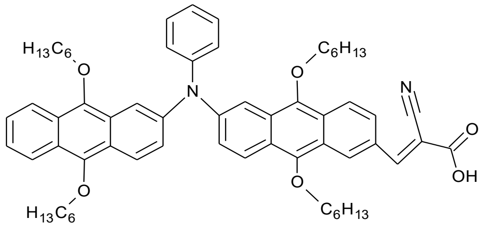
YY1(No.63)



YY2(No.64)



Ant1(No.65)



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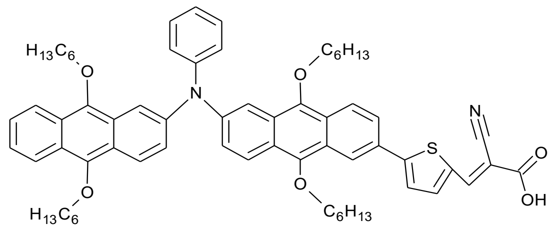
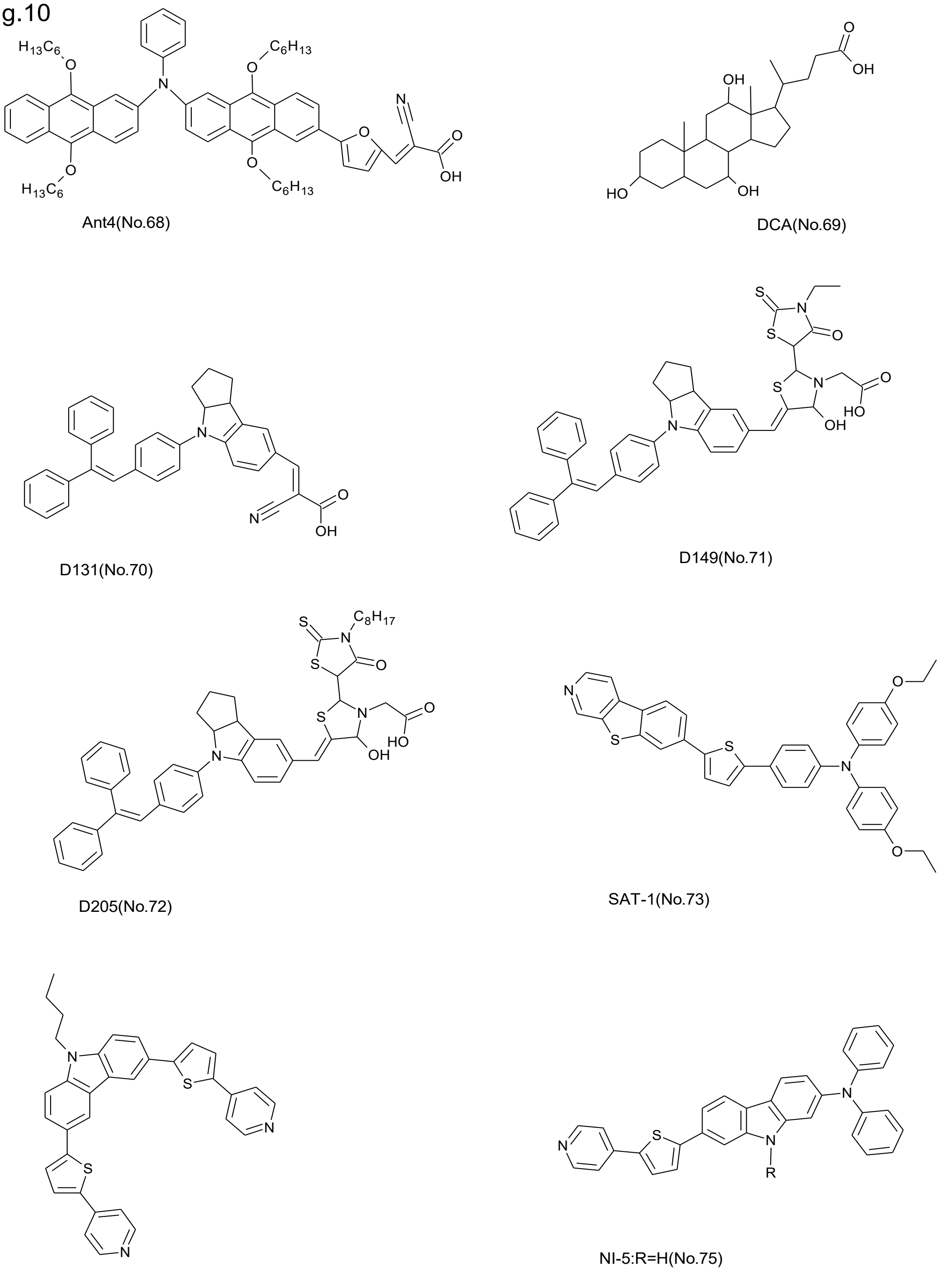


Ant3(No.67)

Figure 9: Chemical structures of 60 to 67 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

Fig.10



Ant4(No.68)

DCA(No.69)

D131(No.70)

D149(No.71)

D205(No.72)

SAT-1(No.73)

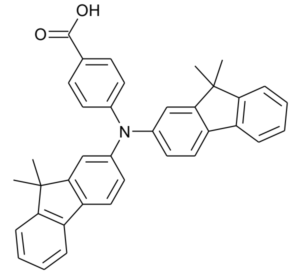
YNI-2(No.74)

NI-5:R=H(No.75)

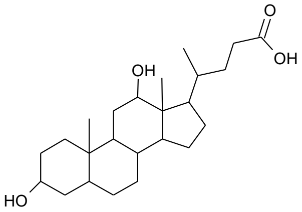
NI-6:R=n-Bu(No.76)

Figure 10: Chemical structures of 68 to 76 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

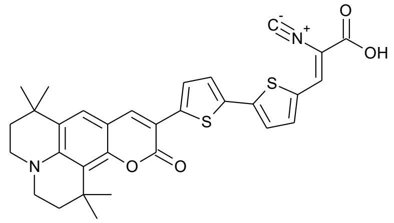
Fig.11



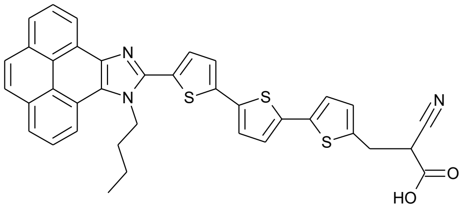
HC-acid(No.77)



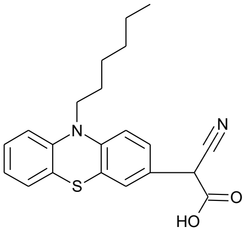
DCA(No.78)



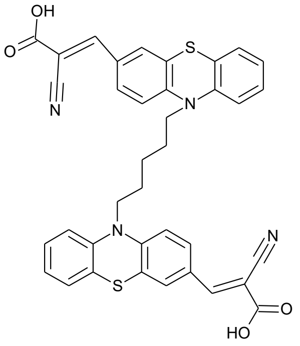
NKX2677(No.79)



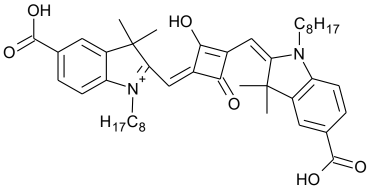
5c(No.80)



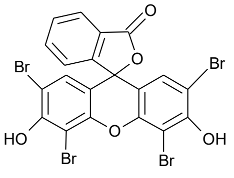
M-RED(No.81)



D-RED(No.82)



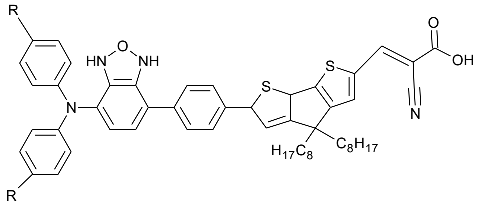
S-BLUE(No.83)



EOSINE(No.84)

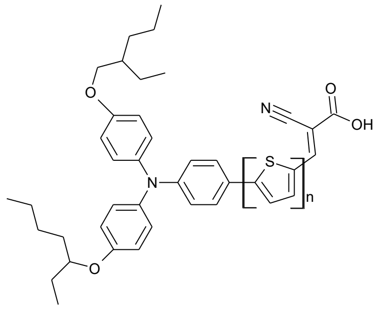
Figure 11: Chemical structures of 77 to 84 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

Fig.12



WS62 R=H(No.84)

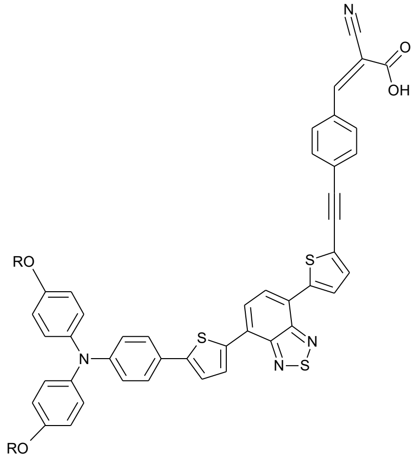
WS64 R=OC6H13(No.85)



S0 n=0(No.86)

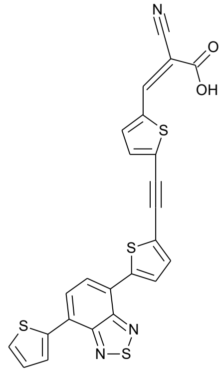
S1 n=1(No.87)

S2 n=2(No.88)

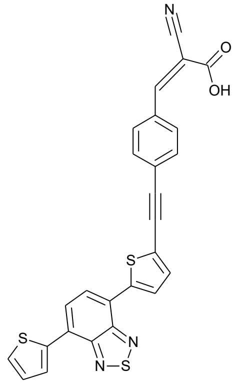


R=2-ETHYLE-METHYLE

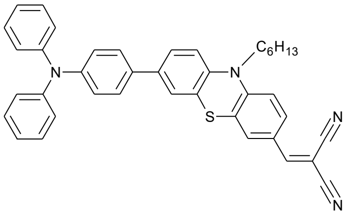
G2(No.89)



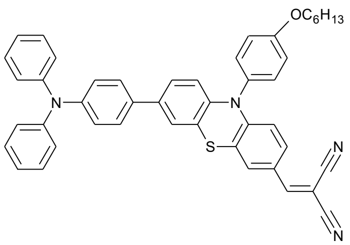
DTB-T(No.90)



DTB-B(No.91)



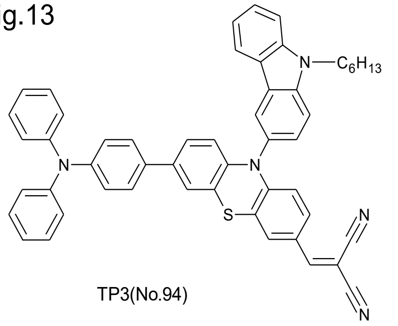
TP1(No.92)



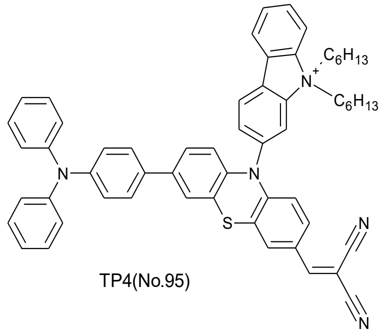
TP2(No.93)

Figure 12: Chemical structures of 84 to 93 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

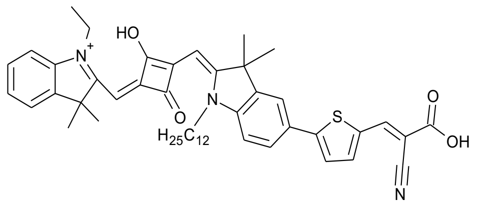
Fig.13



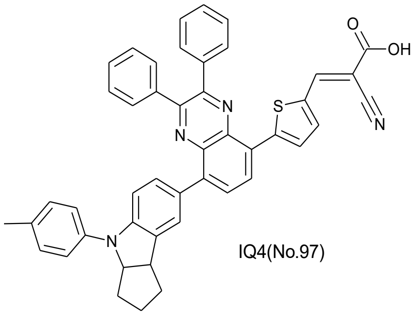
TP3(No.94)



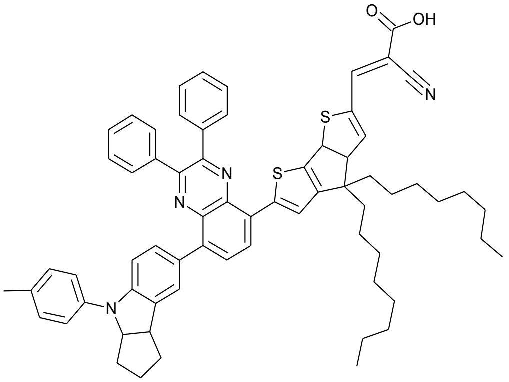
TP4(No.95)



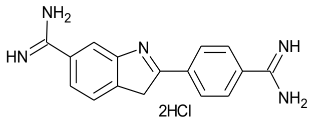
YR6(No.96)



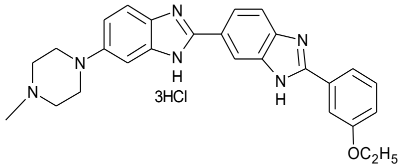
IQ4(No.97)



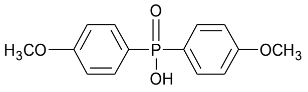
IQ21(No.98)



DAPI(No.99)



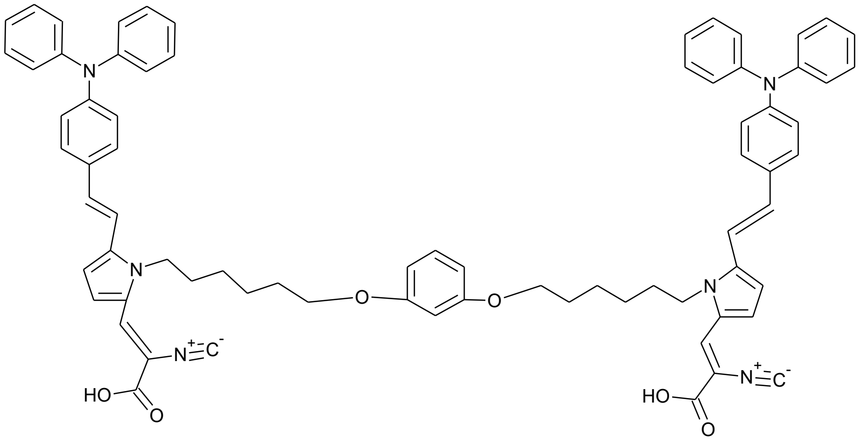
H33342(No.100)



BMPP(No.101)

Figure 13: Chemical structures of 93 to 101 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

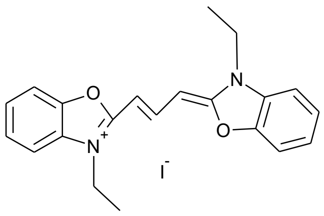
Fig.14



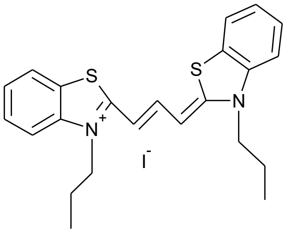
L1-101 FOR ORTHO(No.102)

L1-102 FOR META(No.103)

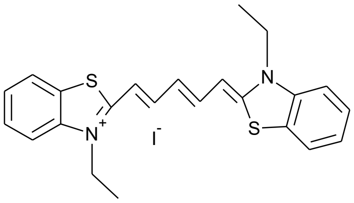
L1-103 FOR PARA(No.104)



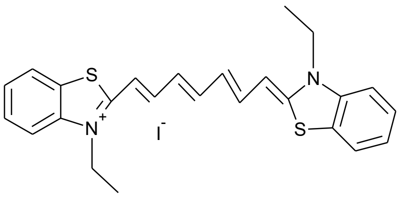
CYANINE-1(No.105)



CAYANINE-2(No.106)



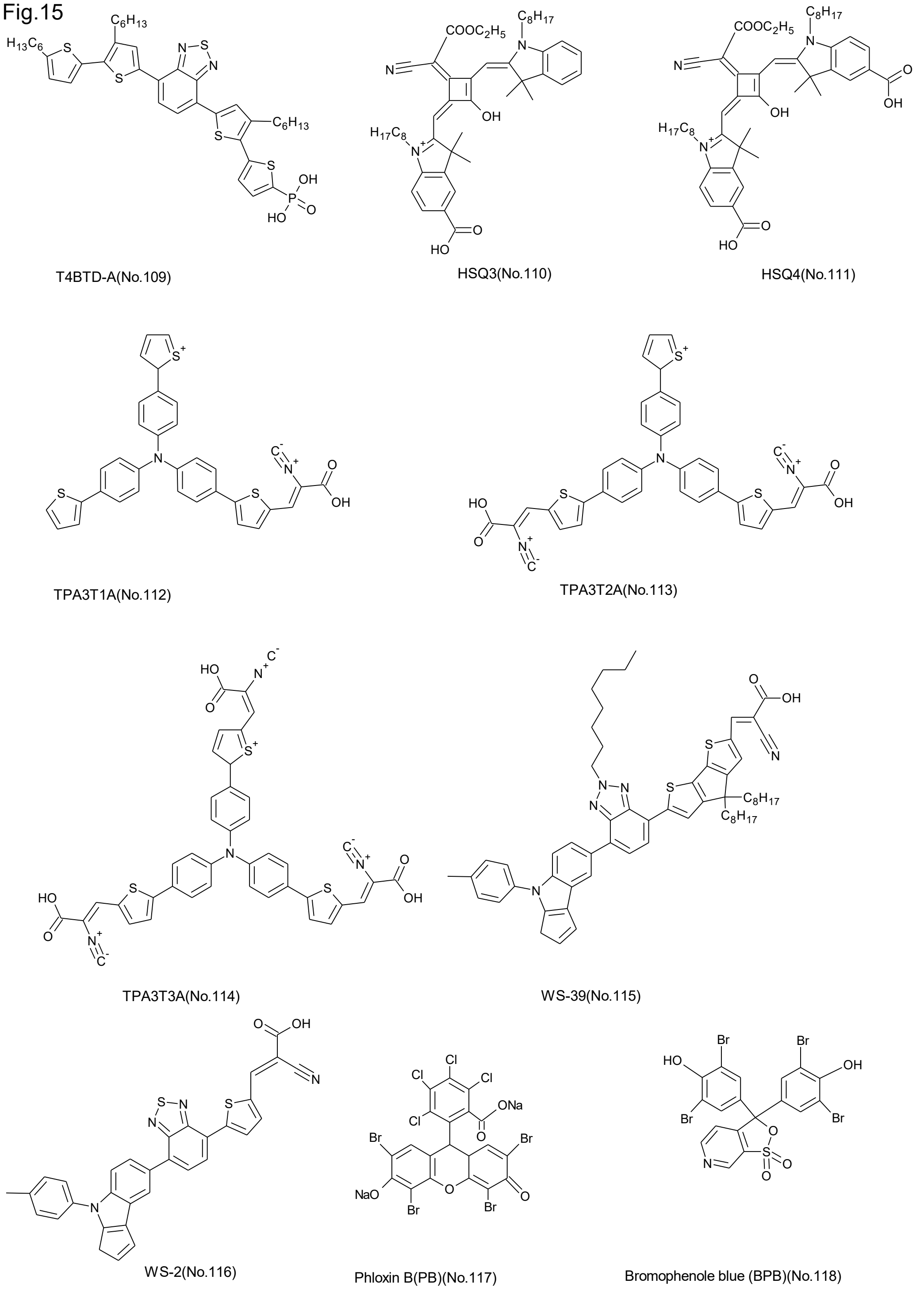
CYANINE-3(No.107)



CYANINE-4(No.108)

Figure 14: Chemical structures of 102 to 108 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

Fig.15



T4BTD-A(No.109) HSQ3(No.110) HSQ4(No.111)

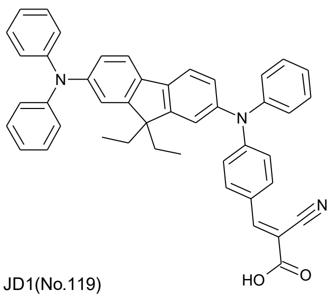
TPA3T1A(No.112) TPA3T2A(No.113)

TPA3T3A(No.114) WS-39(No.115)

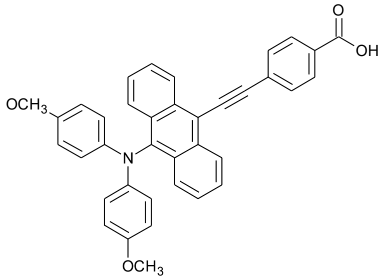
WS-2(No.116) Phloxin B(PB)(No.117) Bromophenole blue (BPB)(No.118)

Figure 15: Chemical structures of 109 to 118 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

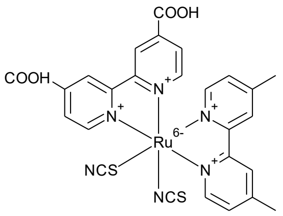
Fig.16



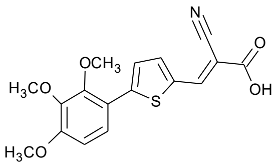
JD1(No.119)



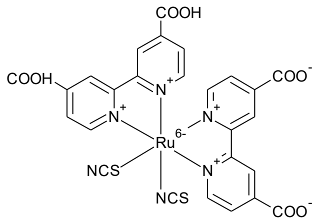
C1(No.120)



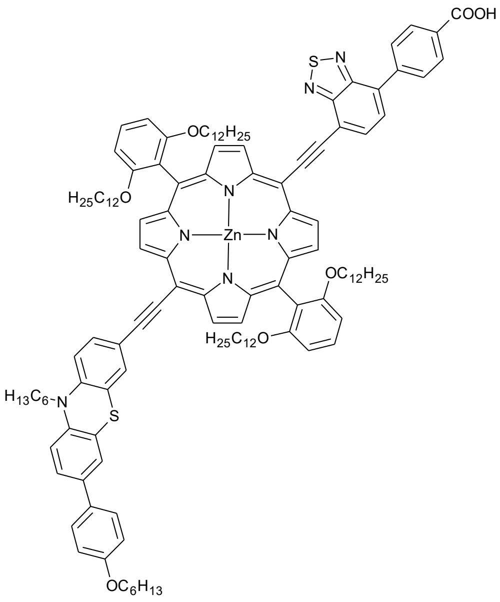
Ru dye(No.121)



Y3(No.122)



N3(No.123)



XW11(No.124)

Figure 16: Chemical structures of 119 to 124 sensitizers and Co-sensitizers used in DSSCs. Figures were created using chem-Draw software.

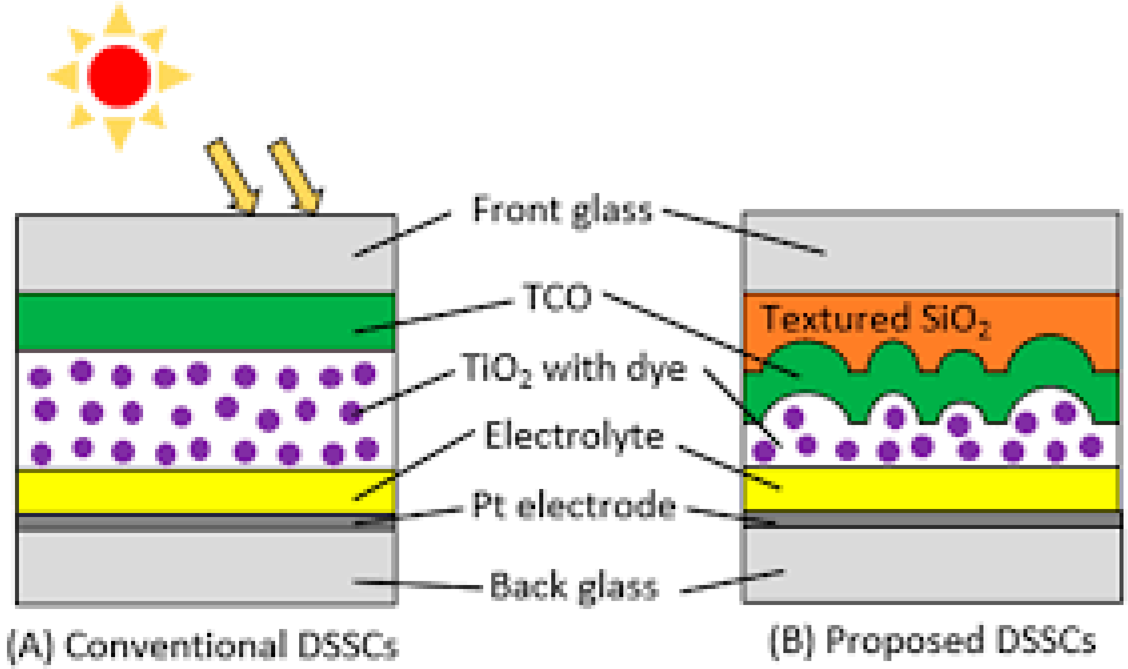


Figure I (a & b): Basic Parts of DSSCs

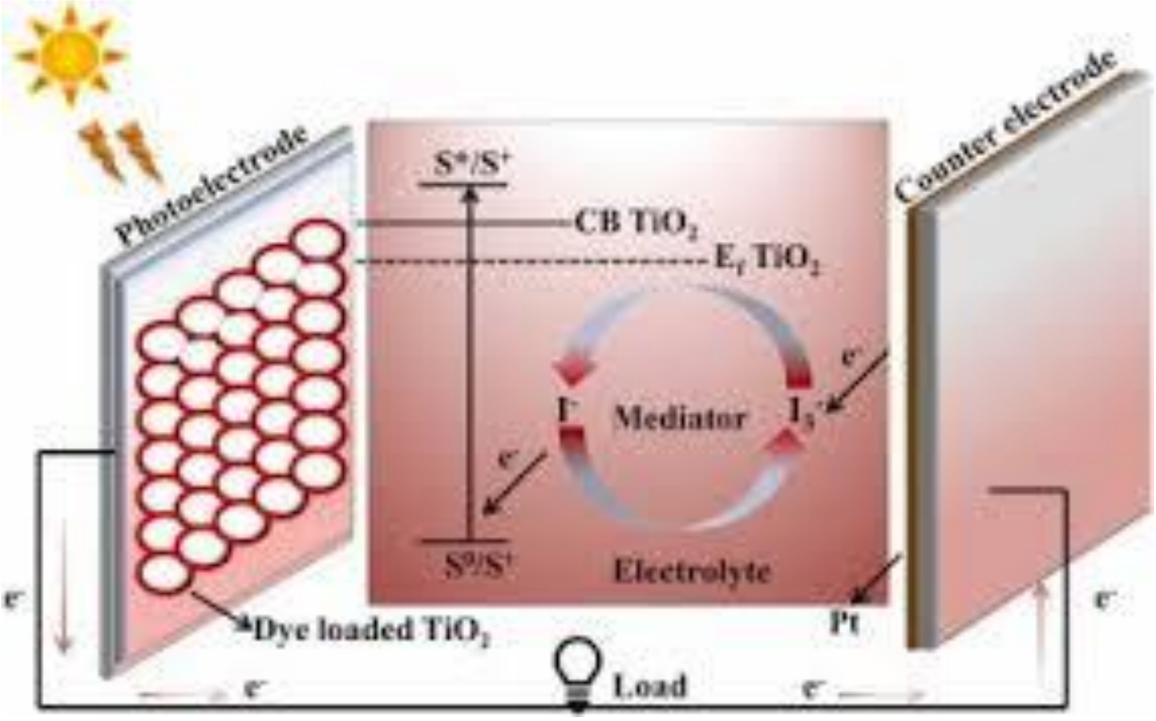


Figure II (a): Working principle of DSSCs

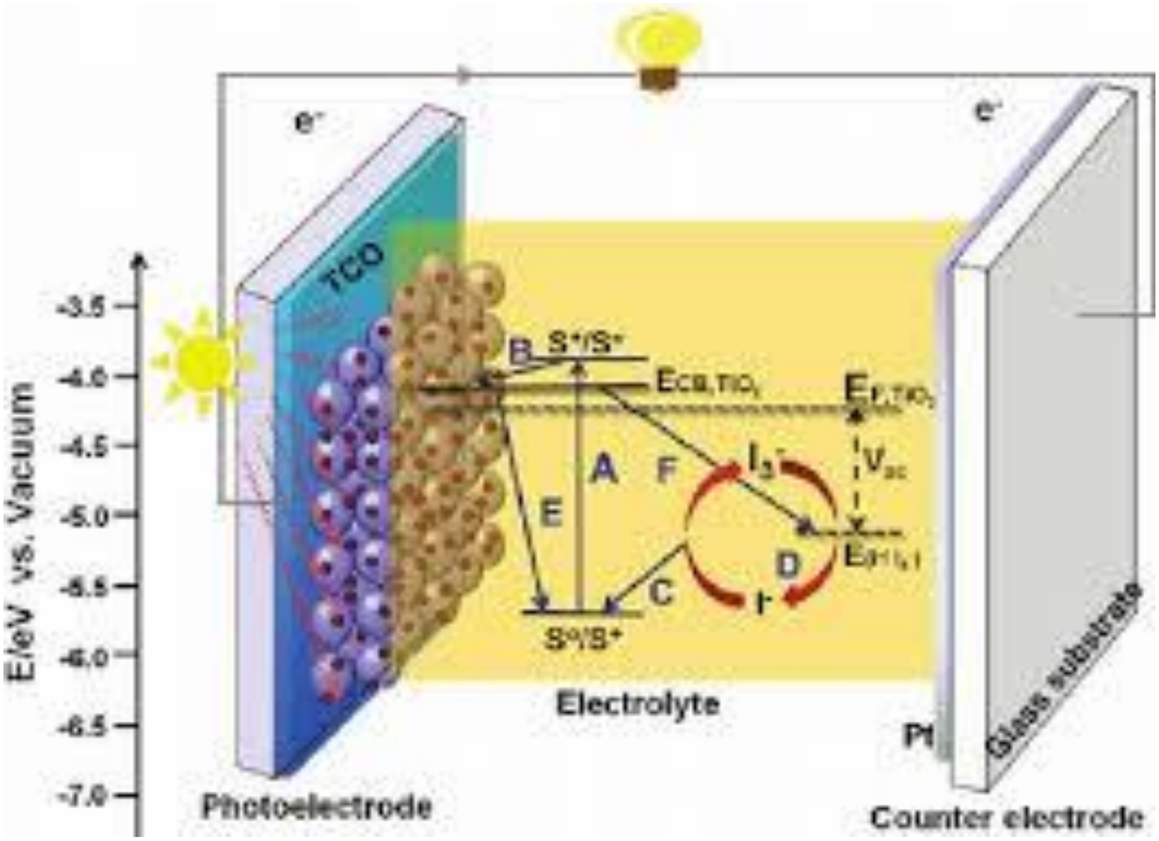


Figure II (b): Working principle of DSSCs

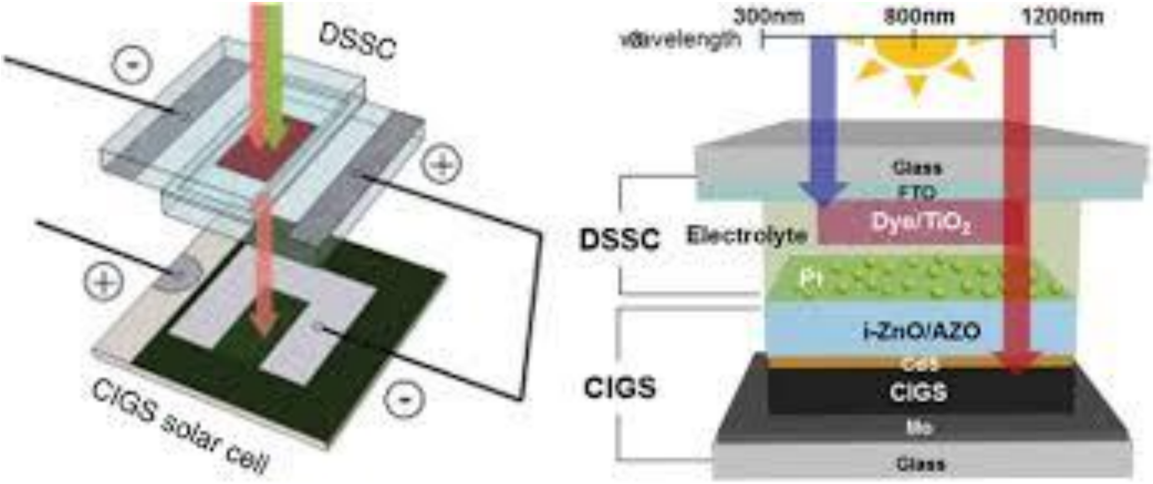


Figure III (a): Criteria for a specie to be an effective sensitizer

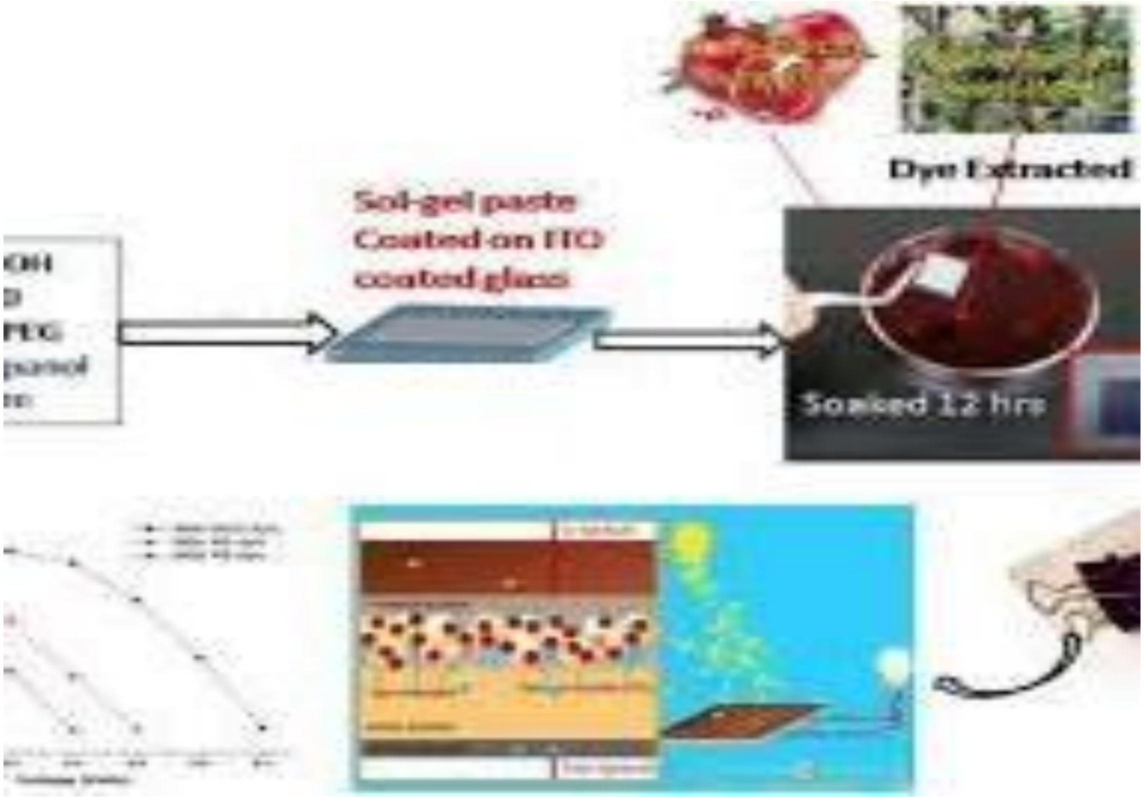


Figure III (b): Criteria for a specie to be a good co-adsorber

Table 1. Photovoltaic Parameters for Co-sensitization of Metal Sensitizers:

Sensitizer code x/y/z (Sensitizer Number)	**J_{sc} (mA cm^{-2})**	**V_{oc} (mV)**	***FF* *(%)***	**η (%) for co-sensitized DSSCs**	**Single sensitizers η (%) x/y/z**	**Reference**
LD14/LDD1 ½	21.5	705	62	10.4	9.2/8.8	55
D102/TT1 4/3	9.4	800	60	4.7	3.9/1.1	56
LD12 /CD5 5/6	16.74	736	73	9.0	7.5/5.7	57
YD2 oC8/CD4/ YDD6 8/7	19.28	753	71	10.4	8.8/5.8/4.7	58
N719/TBP 9/-	19.11	710	70	9.50	6.74/-	59
ZnP/PT-C6 11/10	19.61	739	69	10.1	7.4/8.2	60
XC1/C1 13/12	13.44	>707	≅61	5.75	4.81	61
CPhT2PA/CDCA 16/78	15.22	740	69	7.78	5.86/-	62
C106/D131 18/17	20.6	766	70	11.1	9.5/ 5.6	21
HD-14/N3 22/21	21.29	670	65	9.26	9.20/ 1.44	50
SDP/N719 23/9	13.19	750	66	6.51	5.28/-	63

USP/N719 23-a/9	12.73	750	67	6.40	5.28/-	63
BPPI/N719 24/9	12.98	703	66	6.22	5.29/-	64
NCSU-10/DBA-4 28/26	22.69	715	62	10.12	8.84/-	65
WS-5/XW4 29/30	18.79	774	72	10.41	<10.41	35
ZnP-triazine-(gly)2/D 31/32	14.78	700	71	7.34	4.72	66
SQ1/D149 33/34	17.81	710	64	8.1	6.5/3.1	33
FNE57/FNE46 35/37	16.59	676	70	7.88	4.9/6.8	67
FNE59/FNE46 36/37	17.03	683	70	8.14	6.2/6.8	67
Phe-a /Chl-c	14.0	600	64	5.4	3.4 /3.8	15
N719/D 9/32	14.63	660	75	7.24	5.78/3.95	68
M1p/N719 47/9	16.48	720	62	7.32	5.43/-	69
7-BC /N719 49/9	18.18	750	71	9.68	-/8.34%	70
N719/Coumarin 9/50	*21*	*710*	*67*	9.9	8.2/6.9	71

Table1. Continued

Sensitizer code x/y/z (Sensitizer Number)	**J_{sc} (mA cm^{-2})**	**V_{oc} (mV)**	**FF (%)**	**η (%) for co-sensitized DSSCs**	**Single sensitizers η (%) x/y/z**	**Reference**
JK-142/JK-62 51/52	18.61	740	74	10.20	7.28/5.36	72
P3OT/N719 -/9	7.91	659	50	2.64	0.06/2.28	73
TMCB-1/N719 -/9	17.99	700	61	7.68	5.47	74
TCMB-4/n719 -/9	16.69	710	58	6.85	5.47	74
Cd-1/N719 -/9	17.48	750	63	8.27	2.19/6.50	75
Cd-2/N719 -/9	17.39	740	60	7.73	2.02/6.50	75

J1/N719 53/9	10.92	630	68	4.67	3.26/3.27	76
Ru sensitizer/Y3 116/117	14.32	602	73	6.29	5.21/3.30	99
D149/N3 34/118	14.45	857	76	9.52	7.01/8.77	100
XW11/WS-5	20.33	770	---	11.5	<11.5	104

Table 2. Photovoltaic Parameters for Co-sensitization of Metal Free Sensitizers:

Sensitizer code x/y/z (Sensitizer Number)	**J_{sc} (mA cm^{-2})**	**V_{oc} (mV)**	***FF (%)***	**η (%) for co-sensitized DSSCs**	**Single sensitizers η (%) x/y/z**	**Reference**
Y/R/B 54/55/56	15.8	525	63	6.5	2.8/4.6/3.9	77
JK2/SQ1 57/33	16.1	655	70	7.38	7.00/ 4.23	78
JK-2/SQ1 57/33	16.9	662	71	8.01	7.48/4.02	38
JK-2/Al2O3/SQ1 57/-/33	17.6	696	70	8.65	7.48/-/4.02	38
DPP07/NT35 58/59	16.9	690	71	8.31	7.67/5.05	79
DPP07/D35 58/60	17.0	720	70	8.60	7.67/6.56	79
BP-2/SQ2 61/62	21.33	660	58	8.41	5.95/3.78	80
Black sensitizer/Y1/63	20.88	743	72	11.28	10.70/-	48
Ant3/CDCA 67/78	18.44	740	66	9.11	7.52	81
Ant3/SQ2 67/62	18.01	690	65	8.08	7.52/3.81	81
D149/D131 71/70	11.9	570	69	4.53	3.46/ 1.77	82
D205/D131 72/70	10.8	550	69	4.16	3.98/1.77	82
SAT-1/NI-6 73/76	4.52	505	61	1.39	0.79/1.47	83
SAT-1/YNI-2 73/74	5.56	561	64	1.99	0.79/2.02	83
NKX2677/HC-Acid 79/77	18.01	663	76	9.09	6.59/1.21	84
SQ2/5c 62/80	17.86	610	57	6.24	3.98/5.33	85
Pomegranate/ Rose Bengal	1.57	650	54	1.41	1.01/ 1.56	28

M-Red/S-Blue 81/83	7.69	620	66	3.17	2.85/1.29	86
D-Red/S-Blue 82/83	9.74	670	65	4.23	3.21/1.29	86
Jambolana/ Eosin -/84	0.1	215	25	0.1377	_	87
WS62/S1 84/87	10.9	621	74	5	4.4/4.9	88
WS62/S2 84/88	14.5	641	70	6.5	4.4/6.3	88
WS62/S0 84/86	9.0	623	73	4.1	4.4/4.4	88
WS64/S1 85/87	12.8	647	72	6.2	5.6/4.9	88
WS64/S2 85/88	14.9	738	72	7.9	5.6/4.9	88
WS64/S0 85/86	9.8	672	73	4.8	5.6/4.9	88

Table 2. Continued

Sensitizer code x/y/z (Sensitizer Number)	**J_{sc} (mA cm^{-2})**	**V_{oc} (mV)**	***FF* *(%)***	**η (%) for co-sensitized DSSCs**	**Single sensitizers η (%) x/y/z**	**Reference**
G2/DTB-B 89/91	13.86	670	67	6.22	5.58/1.10	89
G2/DTB-T 89/90	15.33	710	72	7.84	5.58/1.80	89
TP3/YR6 94/96	19.18	721	71	9.84	8.00/2.16	90
IQ21/S2 98/88	19.8	731	72	10.04	9.2/ -	91
DAPI/N719 99/9	19.74	743	71	10.49	0.08/9.49	92
H33342/N719 100/9	19.87	727	72	10.47	0.04/9.49	92
LI-101/SQ2 102/62	16.47	685	63	7.10	5.58/4.28	94
LI-102/SQ2 103/62	16.62	714	63	7.44	5.98/4.28	94
LI-103/SQ2 104/62	15.98	718	63	7.19	5.75/4.28	94
LI-54/SQ2/62	12.68	686	71	5.62	5.39/4.28	94
T4BTD-A/HSQ3 109/110	17.21	611	67	7.05	6.38/4.81	95
T4BTD-A/HSQ4 109/111	18.09	588	73	7.77	6.38/5.78	95
TPA3T1A/TPA3T2A /TPA3T3A 112/113/114	15.11	618	62	5.83	4.01/4.60/5.27	96
WS-39/WS-2	18.25	731	71	9.48	8.67/8.48	34

115/116						
Phloxine B/ Bromophenol blue 117/118	5.6	606	53	1.35	0.81/0.51	97
JD1/SQ2 -/62	15.13	640	66	6.36	5.44/4.11	98

CONCLUSION:

In summary, dye-sensitized solar cells (DSSCs) emerge as a promising alternative due to their tunability, cost-effectiveness, and environmental friendliness. That technology addresses the dual challenges of energy production and environmental protection, particularly in mitigating global warming gases. Scientists have dedicated considerable efforts to enhance DSSC efficiency, exploring a myriad of sensitizers, both synthetic and natural, including metal complexes and metal-free sensitizers.

The pivotal aspects of panchromatic engineering and surface design play a crucial role in augmenting cell performance. Ongoing research endeavors focus on achieving heightened efficiency, with co-sensitization emerging as a clever strategy. That review delves into co-sensitization, examining combinations such as metal complexes with metal-free sensitizers, metal-free with metal-free, and synthetic with natural sensitizers. Both cocktail and stepwise approaches are explored, with co-sensitizers preventing direct electrolyte and electrode contact, thereby inhibiting charge reverse flow, improving electron injection efficiency, and suppressing electron recombination.

Efficiency improvements are observed in key parameters like current density, photovoltage, and fill factor. Nevertheless, the review underscores that there was ample research space to further exploit co-sensitization as an efficiency-enhancing strategy. Molecular matching of central sensitizers and co-sensitizers remains an avenue for exploration, either by investigating existing sensitizers or synthesizing novel sensitizers. As we venture into that research frontier, the potential for refining DSSCs technology and contributing to sustainable energy solutions becomes increasingly evident.

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No potential conflict of interest.

ORCID:

Uzman Khan http://orcid.org/0000-0002-5199-8232
Muhammad Jahangir http://orcid.org/0000-0001-7751-3531

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