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Microwave Synthesized Functional Dyes

Sheetal Marganakop, Pramod Kattimani,
Sudha Belgur Satyanarayana and Ravindra Kamble

Abstract

Microwave chemistry involves the application of microwave radiation to chemical reactions and has played an important role in organic synthesis. Functional dyes are those with hi-tech applications and this chapter attempts to provide an overview of the recent developments in microwave-assisted synthesis of functional dyes. Emphasis has been paid to the microwave-assisted synthesis of dye molecules which are useful in hi-tech applications such as optoelectronics (dye-sensitized solar cells), photochromic materials, liquid crystal displays, newer emissive displays (organic-light emitting devices), electronic materials (organic semiconductors), imaging technologies (electrophotography viz., photocopying and laser printing), biomedical applications (fluorescent sensors and anticancer treatment such as photodynamic therapy). In this chapter, the advantages of microwaves as a source of energy for heating synthesis reactions have been demonstrated. The use of microwaves to functional dyes is a paradigm shift in dye chemistry. Until recently most academic laboratories did not practice this technique in the synthesis of such functional dyes but many reports are being appeared in the journals of high repute.

Keywords: microwave-assisted organic synthesis, functional dyes, solar cells, fluorescent sensors, organic-light emitting diodes, photochromic materials

1. Introduction

Microwaves are the portion of the electromagnetic spectrum with the wavelengths from 1 mm to 1 m with corresponding frequencies between 300 MHz and 300 GHz. The frequencies used for cellular phones, radar, and television satellite communications are within this portion of the electromagnetic spectrum [1]. Microwaves have been employed in a non-classical heating technique which is popularly known as "Bunsen Burner of the 21st century" and has attained enormous importance since many materials (solids or liquids) can transform electromagnetic energy into heat. The microwave-assisted organic synthesis (MAOS) has made revolutionary changes in the methodology since there is a dramatic enhancement in the yield of the reaction, modifications of selectivity, increased purity of products, simplified work-up procedure, and above all reduction in the reaction time. These are the primary benefits over conventional methods. The microwave technique has been applied efficiently in the organic synthesis, polymer chemistry, material sciences,

nanotechnology, biochemical processes, thermal food processing, hydrothermal and solvothermal processing, etc. [2]. The energy efficiency is higher in the case of microwave heating in comparison with the conventional heating as evidenced by one such Suzuki reaction in which there is an 85 fold reduction in energy demand when compared to a reaction on an oil bath and a microwave reactor [3].

During a chemical reaction under the conventional heating, the energy is introduced by convection, conduction, and radiation of heat from the surfaces of the reactants in the solution, and the energy transfer occurs due to thermal gradients. But in the case of the microwave irradiation, the energy is introduced through the electromagnetic field interaction into the molecules and the transfer of electromagnetic energy to thermal energy is energy conversion instead of heat transfer. This variation in the mode of introduction of energy leads to the advantages of using microwaves during chemical reactions. The microwaves penetrate easily into the bulk and, hence, heat evolves throughout the volume of the reaction mixture. As a result, fast and uniform heating of the reaction mixture can be advanced. In conventional heating, it is necessary to slow rates of heating to minimize the steep thermal gradients and obviate the process-induced stresses. As microwaves can transfer energy into all volumes of the reaction mixture, the potential exists to reduce the processing time and enhance the overall quality [4].

Although the use of microwaves for organic synthesis is widespread, the documentation of this technology to the synthesis of the functional dyes is a relatively new development. The use of microwave energy for their synthesis has the potential to offer similar advantages in reduced reaction times and energy savings for obtaining useful materials such as dyes possessing hi-tech applications.

2. Functional dyes

Color plays an important role in the world in which we are living. Color can sway thinking, change actions, and cause reactions. If properly used, color can even save on energy consumption. The colors are characterized by their ability to absorb light in the visible spectrum (from 380 to 750 nm). The dyeing industry is in existence since 2000 years BCE wherein dyes were obtained from natural sources *viz*., plants, insects/animals, and mineral [5, 6]. A drastic development occurred after the discovery of the dye Mauveine by W.H. Perkin in 1856 while trying to synthesize quinine [7]. Dyes are the organic compounds with three essential groups in their molecules *viz*., the chromophore, the auxochrome, and the matrix. The chromophore is an active site of the dye which may be an atom or group whose presence is responsible for the color of a dye. The auxochrome is responsible for the intensity of the color of the dye with lone pairs of electrons.

It was Yoshida and Kato who used the term "functional dye" for the first time in 1981 due to the advancements and growth of dye chemistry related to high-technology (hi-tech) applications that are divergent from the well known traditional applications [8]. Hi-tech applications of dyes include the fields *viz*., optoelectronics (i.e. Dye-sensitized solar cells), photochemical materials, liquid crystal displays (LCD), and the newer emissive displays i.e. organic light-emitting diodes (O-LED), electronic materials (organic semiconductors), imaging technologies (electrophotography which includes photocopying and laser printing), thermal printing, and especially ink-jet printing, biotechnology (in dye-affinity chromatography for the purification of proteins and enzymes), biomedical applications (fluorescent sensors and anticancer treatments such as photodynamic therapy). All these fields were responsible for the design and synthesis of newer dyes to meet new and demanding criteria. Dyes, and related ultraviolet and particularly infrared active molecules,

which have been specifically designed for these hi-tech applications, are called functional dyes.

Common dyes have been synthesized by applying mainly the conventional methods and also by microwave assistance. In the following sections the functional dyes used in solar cells, fluorescent sensors, fluorescent dyes to print on fibres, photochromic materials, O-LEDs, and dyes with advanced applications which were synthesized only under microwave irradiation are discussed.

2.1 Dyes (sensitizers) used in solar cells

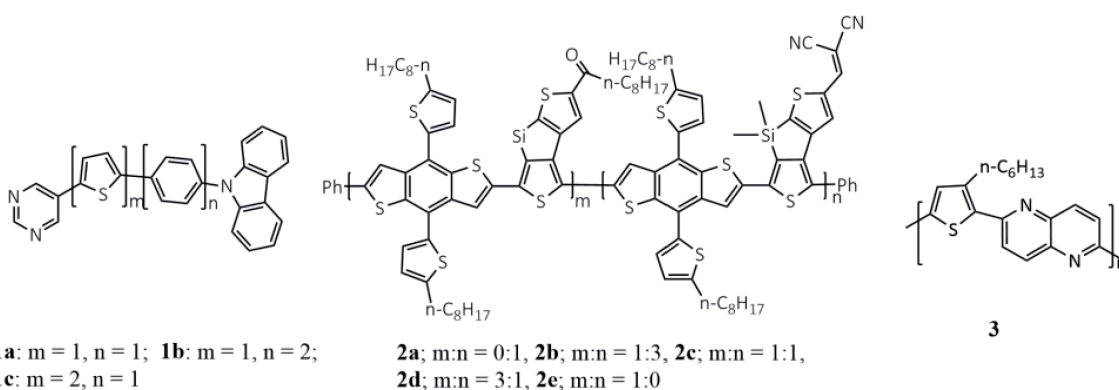### 2.1.1 Dye-sensitized solar cells (DSSCs)

To prevent harmful impact on the environment by conventional energy sources it is necessary to use the alternative energy sources, specially, the solar cells. The conversion of sunlight into electricity is a clean, abundant, and renewable energy source. The amount of energy available from the sun to the earth is of the order of 3×10^{24} joules/year thus making it the best among sustainable energies. Photovoltaic devices have been fabricated using inorganic materials of high purity and energy-intensive processing techniques. The fabrication using these inorganic materials is not economical and often used scarce toxic materials. Therefore, such solid-state junction devices have been challenged by the 3rd generation dye-sensitized solar cells (DSSCs) which are based on interpenetrating network structures containing metal-free organic dyes as sensitizers [9].

In the conventional systems, the semiconductor does the task of light absorption as well as charge carrier transport. However, these two functions are separated in DSSCs by the metal-free organic dye and TiO_2 in presence of an electrolyte. Hence, new ways of manufacturing the solar cells that can be scaled economically up to large volumes are essential. In this regard, a new generation of DSSCs also known as "Grätzel cells" has been fabricated by O'Regan and Grätzel [10]. A Grätzel cell consists of nanoporous titanium dioxide applied on transparent conducting oxide which is further made to absorb the dye from its solution. This film loaded with dye/sensitizer is immersed in an electrolyte containing a redox couple and placed on a platinum counter electrode. After irradiation, the excited electron from the dye (sensitizer) is transferred to the conduction band of TiO_2 and diffuses through its porous network to the contact. Thus oxidized dye is further reduced to the original state by the supply of electrons through a liquid electrolyte redox couple within the pores [11].

The organic dye sensitizers consist of three important components *viz*., electron donor (D), π-conjugated spacer (π), and electron acceptor (A). Electron acceptors are generally acid ligands which also act as anchoring groups for loading the dye on TiO_2 surface. The π-conjugated spacer (*viz*., conjugated double bonds, phenyl rings, thiophene, polythiophenes, etc) acts as a bridge to transfer electrons between the donor and the acceptor group and it is the key part which can induce a shift of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels so that the photophysical properties may be tuned. The organic dyes/sensitizers belong to different classes depending on the donors such as triphenylamine, phenothiazine, fluorene, coumarin, carbazoles, etc. which have been profusely synthesized, and their power conversion efficiency as sensitizers have been reported and reviewed exclusively [12]. The structures of the dyes/sensitizers synthesized under microwave irradiation along with the parameters such as short-circuit current (*Jsc*), open-circuit voltage (*Voc*), Fill Factor (FF), and power conversion efficiency (PCE) of the solar cells fabricated using these dyes are discussed.

2.1.2 Microwave synthesized dyes/sensitizers in DSSCs

Novel donor-π-acceptor (D-π–A) dyes bearing the pyrimidine unit as an electron acceptor appended to thiophene and carbazole unit **1a**-**c** were obtained by a combination of two processes *viz*., the microwave-assisted Suzuki cross-coupling reaction and nucleophilic aromatic substitution of hydrogen (S_NH) [13]. Among these dyes, **1b** was used as a photosensitizer in a fabricated solar cell since this dye showed a maximum extinction coefficient. The short-circuit current density (*Jsc*) was 2.04 mA cm^{-2}, and the open-circuit voltage (*Voc*) observed was 0.525 V. The calculated power conversion efficiency (PCE) of the cell (η) was 0.91 at a fill factor (FF) of 0.85. A series of dithienosilole-based terpolymers **2a**-**e** as sensitizers have been synthesized. Different dithienosilole monomers were used along with nonanoyl group and malononitrile as the electron acceptor *via* microwave-assisted Stille coupling polymerization to obtain the polymer sensitizers **2a**-**e**.


1a: m = 1, n = 1; **1b**: m = 1, n = 2; **1c**: m = 2, n = 1

2a; m:n = 0:1, **2b**; m:n = 1:3, **2c**; m:n = 1:1,
2d; m:n = 3:1, **2e**; m:n = 1:0

3

The devices obtained using these sensitizers **2a**-**e** exhibited the high open-circuit voltage (*Voc*) of 1.00–1.06 V which can be attributed to the low-lying HOMO energy levels. Sensitizer **2e** showed the best PCE of 2.32% (*Voc* = 1.06 V, *Jsc* = 5.92 mA/cm^2 and FF = 0.39) which is due to the components of the conjugated backbones and play a pivotal role in their photovoltaic performance. When the polymerisation process was optimized i.e. in polymer **2e** with higher molecular weight (Mn = 23.3 kDa) an increased PCE of 3.29% (*Voc* = 1.07 V, *Jsc* = 7.53 mA/cm^2 and FF = 0.41) was observed [14]. The above reports showed the outstanding thermal stabilities and electrical conductivity of polythiophenes. Hence, a semiconducting polymer *viz*., poly[1,5-naphthyridine-(3-hexylthiophene)] **3** was prepared by microwave-assisted *Suzuki-Miyura* cross-coupling reaction using 3-hexylthiophene-2,5-diboronic ester and 2,6-dibromo-1,5-naphthyridine [15]. This polymer **3** was used as a photosensitizer in a fabricated solar cell. The solar cell so prepared was illuminated under AM 1.5 G at 100 mW/cm^2 which showed a PCE of 0.67% with an open-circuit voltage of (Voc) 621 mV, a short-circuit current of 2.0 mA/cm^2, and a FF of 55%.

Three push-pull Donor-π-Acceptor structured dyes **4**, **5** and **6** having imidazo[1,2-*a*]pyridine heterocycles as additional π-conjugated linker was synthesized. Triphenylamine (TPA) was introduced as an electron-donor unit and cyanoacetic acid through thiophene as linker **4** and **5** or double rhodanine acetic acid **6** were employed as anchoring groups in different positions of the heterocyclic core [16]. DSSC devices with these dyes **4**–**6** were assembled and tested using different electrolytes and dye baths. The best efficiencies were obtained for dye **4** i.e. *Jsc* 2.34 (mA/cm^2), *Voc* 650 mV, FF 0.42, η (%) 0.64 and for **5** *Jsc* 2.14 (mA/cm^2), Voc 502 mV, FF 0.42, η (%) 0.45.
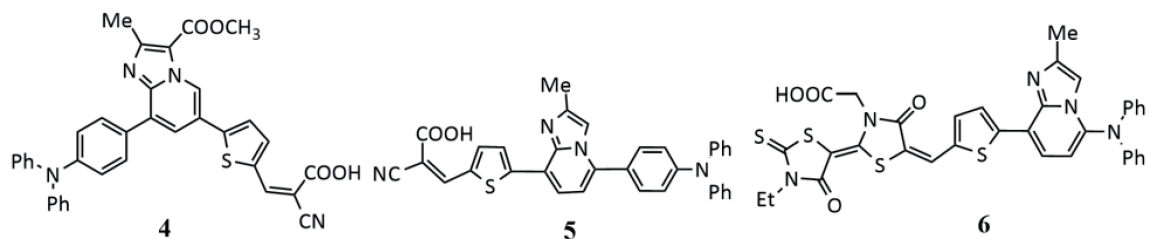
Due to inefficient electron injection from HOMO to TiO_2 conduction band or dye aggregation leading to a potential barrier the dye **6** showed the lowest efficiency irrespective of dye bath solvent and electrolytes [17].

In view of the importance of thiophene as the significant moiety in the design of polymer-based sensitizers, narrow band gap conjugated polymer **7** was obtained from 4,6-bis(4-tetradecylthien-2-yl)thieno[3,4-*c*]thiadiazole, and thieno[3,2-*b*] thiophene using Stille coupling reaction under microwave irradiation. This polymer exhibited good solution processability and absorbed the UV/Vis light from 300 nm to 1260 nm with an optical band gap of 0.98 eV in solid state. Photovoltaic devices using the blend films **8**, **9** from **7** and [6,6]-phenyl-C_{61} butyric acid methyl ester ($PC_{61}BM$) or [6,6]-phenyl-C_{71} butyric acid methyl ester ($PC_{71}BM$) having the configuration ITO/PEDOT:PSS/blend film/Ca/Al, provided power conversion efficiencies (PCEs) of 0.65%, and 1.12% respectively with light response from 300 nm to 1260 nm under AM 1.5 G with irradiation of 100 mW cm^{-2} [18].


Polymer blends
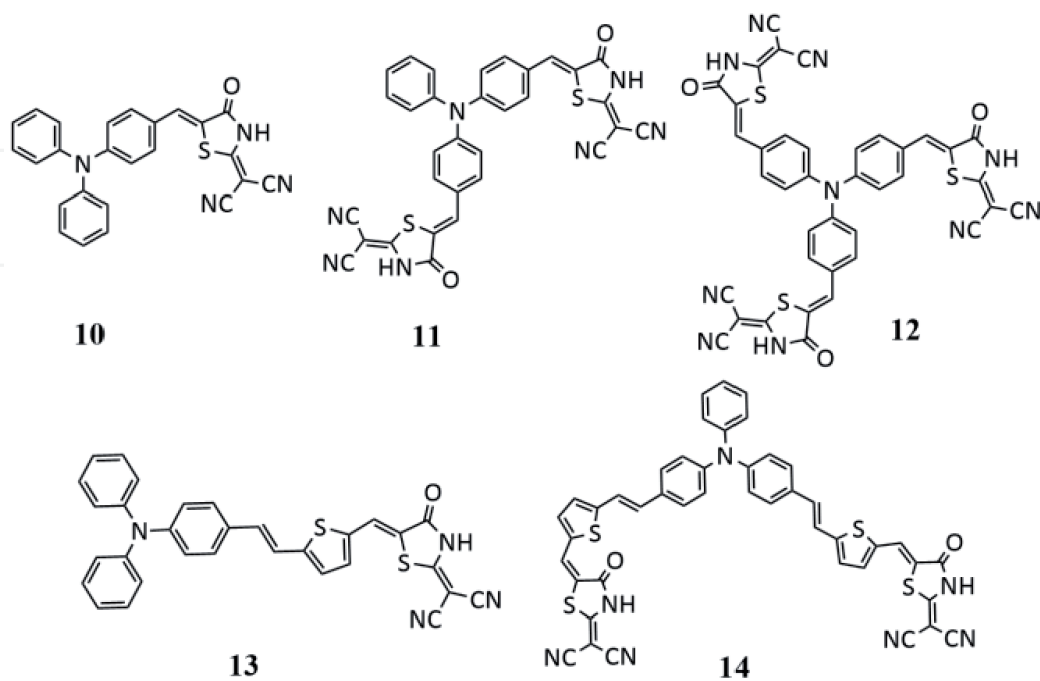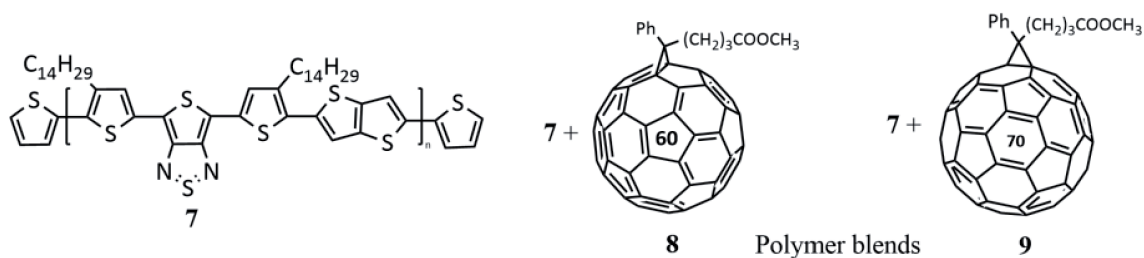
Triphenylamine based dye sensitizers **10–14** were prepared under microwave irradiation by incorporating 2-(1,1-dicyanomethylene) rhodanine which acts

both as electron acceptor as well as anchoring group on titanium dioxide [19]. Triphenylamine and vinyl thiophene are the donors and the π spacers. The dye containing two 2-(1,1-dicyanomethylene)rhodanine units and no thiophene units i.e. dye **11** showed the best photovoltaic performance with a short-circuit photocurrent density (Jsc) of 7.76 mA/cm^2, an open-circuit photovoltage of 0.62 V, and a fill factor of 0.68, corresponding to an overall conversion efficiency of 3.78% under AM 1.5 irradiation (100 mW/cm^2). The Jsc of the solar cells fabricated using these dyes increased in the order of **13** < **11** < **10**, **12** < **14**.

The general design of organic dye sensitizers is usually in the order D-π-A. However, molecular conjugated chromophores combining only electron donor (D) and acceptor (A) blocks have also been designed and synthesized as active materials for organic solar cells [20]. In view of this, D-A-D dyes **15**, **16** and **17** obtained by reaction of mono-formyl triarylamines with 2,3-diaminomaleonitrile. Such D-A-D dyes are expected to show absorption of two photons hence may be used in dyes and solar cells, and focused on their potentialities as a donor material in basic planar heterojunction solar cells. These compounds **15**, **16**, and **17** have been evaluated as dyes in solar cells ITO/PEDOT-PSS/dye/C60/Al. The open-circuit voltage (Voc), short-circuit current densities (Jsc), fill factor (FF), and power conversion efficiencies (PCEs) of cells of 0.28 cm^2 active area were determined under AM 1.5 simulation solar illumination. Compound **17** did not lead to devices of a quality sufficient for evaluation. Fabricated devices obtained from dyes **15** and **16** respectively gave PCEs of 0.70 and 0.53%.
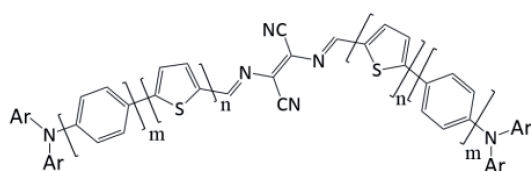
Ar = 4-CH$_3$O-C$_6$H$_4$,
15; m = 1, n = 0, **16**; m= 0, n = 1, **17**; m = 1, n = 1
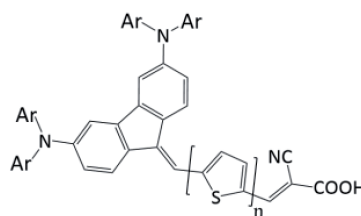
18; Ar = C$_6$H$_5$, n = 0, **19**; Ar = C$_6$H$_5$, n = 1,
20; R = C$_6$H$_5$ n = 2, **21**; R = 4-CH$_3$O-C$_6$H$_4$, n = 1,
22; R = CH$_3$O-C$_6$H$_4$, n = 2, **23**; R = C$_8$H$_{17}$O-C$_6$H$_4$, n = 2

2D-π-A dyes **18**–**20** comprising of dibenzofulvene-thiophene as π-bridge which is flanked by diarylamine donor groups and cyanoacrylic acid as anchoring as well as acceptor have been synthesized under microwave irradiation [21]. The dye **20** containing two thiophene rings as spacer shows an IPCE action spectrum with a high plateau from 390 nm to 600 nm increased open-circuit photovoltage by 40 mV and short-circuit photocurrent by 7.03 mA cm^{-2}. Using Chenodeoxycholic acid (CDCA) as the co-adsorbent material, the Jsc of **22** was increased to 14.98 mA cm^{-2} and a strong enhancement in the overall conversion efficiency (7.45%) was realized by **20** compared to **18** (1.08%) in liquid electrolyte-based DSSCs. This work was further extended by the same research group [22] in which methoxy groups were introduced on the phenyl rings i.e. dyes **21**–**22** and also long fatty alkyl chain *viz*., octyloxy was introduced in view of increasing the donor capability and to avoid the aggregation and to increase physical insulation between electrolyte system and the TiO$_2$ layer *i.e.* dye **23**. These dyes **21**–**23** exhibit rather similar photophysical properties for the lowest-lying optically active excitations and it was observed that the lowest excitation lay in all cases at 2.12–2.50 eV. Compound **21** showed a promising PCE of 5.90. The structural molecular variations evidenced positive effects on the photovoltaic performances of dyes as proved by PCEs of 7.50% and 7.80% obtained with dyes **22** and **23** respectively.

Donor-acceptor dyes **24–28** based on 3-methylquinoxaline-2(1*H*)one under microwave condition involving Knoevenagel reaction were designed with electron-donor groups such as triphenylamine (TPA) **24–26** ferrocene **25**, N,N-dimethylaminobenzene **27**, and ((*E*)-4,4′-(ethene-1,2-diyl)bis(N,N-diphenyl-aniline)) **28**. The dyes **26** and **27** showed higher power efficiency (0.31 and 0.40 respectively) as expected for their higher values of *Jsc* and *Voc*. This suggests that these structures decrease the recombination processes by preventing the approach of tri-iodide ions to the semiconductor surface, thus decreasing the electron transfer from TiO_2 conduction band to tri-iodide ions electrolyte. The higher efficiency of the dyes **26** and **27** may also be due to the enhanced conjugation of triphenyl-amine units to anchoring amide groups. This has improved the electron injection into semiconductor conduction band which helps in the photovoltaic performance. The remaining dyes did not show significant efficiencies [23].

A new series of oxindole sensitizers (**29–33**) were designed and synthesized under microwave irradiation [24]. These exhibited respectable photoelectric conversion efficiencies due to excellent electron-donating triphenylamine (TPA) donor and the thiophene in the spacer and are differentiated by various halogen-substituted oxindole acceptors. The cell performance was analyzed by fabricating solar cells. The parent dye **29** exhibited *Jsc* = 10.03 mAcm^{-2}, *Voc* = 680 mV, and FF = 0.699, corresponding to an overall η = 4.76%. The incorporation of halogen substitutions on the parent dye enhanced the PCEs. Solar cell containing fluoro substituent i.e. dye **30** achieved *Jsc* = 11.32 mA cm^{-2}, *Voc* = 690 mV, and FF = 0.695, corresponding to an overall η = 5.43%, which was approximately 14% higher than that of the non-substituted oxindole sensitizer **29**. The efficiency was increased due to increased *Jsc* which may be attributed to the electronic coupling of *fluoro* substituent in the compound **29** with the anchoring group COOH [25].
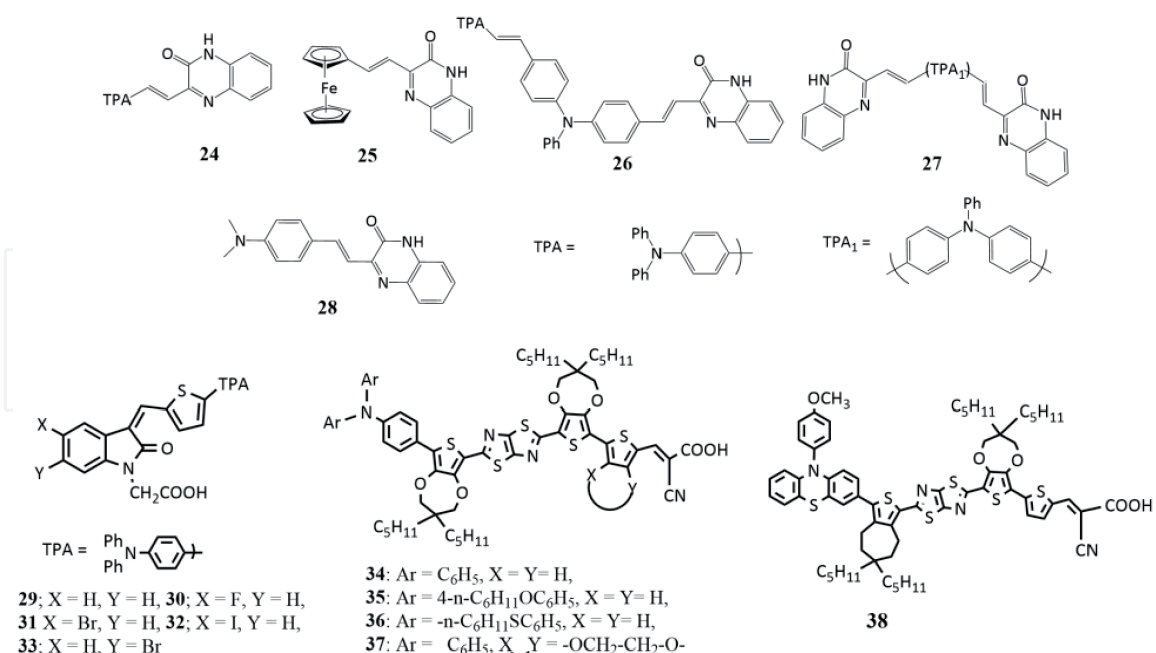

The substitution of fluoro substituent with other halo substituents showed further enhancement in the DSSC performance. Among all the halogen sub-stituted sensitizers, the bromo substituted sensitizer **31** exhibited the highest photovoltaic parameters (*Jsc* = 12.46 mA cm^{-2}, Voc = 720 mV, and FF = 0.708) with an overall conversion efficiency (η) of 6.35%. The improved photocurrent of the

sensitizer **31** suggested that compared to fluoro substitution, the bromo substituted dye exhibited better cell performance. Interestingly, the altered position of the substituent with respect to the anchoring group exhibited a negative effect on the solar cell performance. The dye **33** anchored DSSC showed lower current density (Jsc = 9.66 mA cm^{-2}, Voc = 630 mV, and FF = 0.690), that is corresponding to an overall η = 4.21% which is due to the absence of electronic coupling of substitution with the anchoring group.

Computationally designed thiazolo [5,4-*d*]thiazole-based D-π-A organic dyes **34–38** have been synthesized [26]. These have been further derivatized with bispentylpropylenedioxythiophene (ProDOT) moieties in the π-spacer and triaryl-amine and phenothiazine **34–37** and **38** respectively as donors. Bulky and electron-rich ProDOT groups enhanced the physical–chemical properties, including visible light absorption instead of the presence of the electron-poor thiazolothiazole. Small-scale (0.25 cm^2) devices using these dyes **34–38** showed the PCEs up to 7.71%, surpassing those obtained with two different reference dyes. Transparent larger area cells (3.6 cm^2) also showed good η values up to 6.35%, not requiring the use of a co-adsorbent, and retained their initial efficiency over a period of 1000 h storage at 85°C. Following the promising results obtained with small-scale DSSCs (0.25 cm^2), the authors fabricated larger area (3.60 cm^2) strip cells to analyze the effect of increased active surface area on the efficiency and stability. Small-scale solar cells built with **34–38**, both transparent and opaque, gave good power conversion efficiencies (η up to 7.71%), which in the case of dyes **36** and **38** were clearly superior to those obtained with standard Ru-dye Z907. Larger-scale strip cells featuring thin films of transparent TiO$_2$ (3–5 mm) and a high stability electrolyte, gave efficiencies in line with those obtained with the smaller devices, with dye **36** being once again the best sensitizer (η up to 6.35%).

Two isoindigo-based conjugated polymers **39–40** composed of isoindigo with 2-decyltetradecane (DT) and bithiophene with/without fluorination were prepared under microwave irradiation [27].
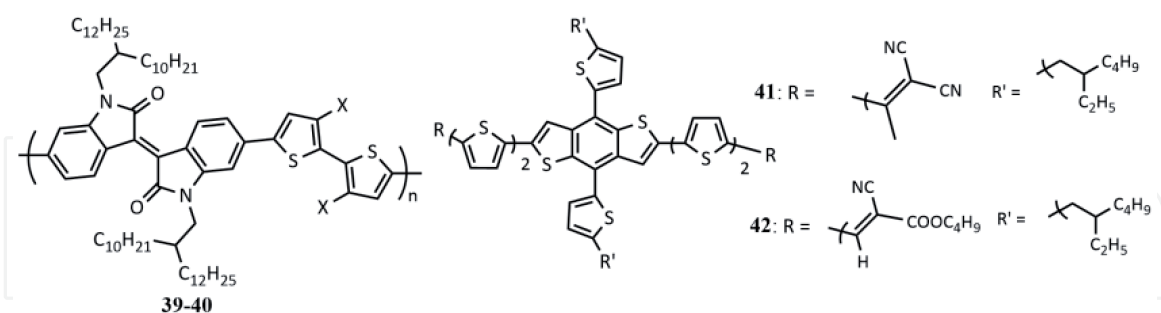
Fabrication of the solar cells was produced using *o*-xylene and diphenyl ether (DPE) as solvent and additive. To measure the photovoltaic performance of polymers the solar cells were fabricated using polymer sensitizers **39** and **40** with an inverted configuration (ITO/ZnO/polymer: PC71BM/MoO$_3$/Ag). The optimum blend ratio of polymer to PC71BM was 1:1.5 (w/w) for the two polymers. The polymer sensitizer **39** based cell showed a lower PCE of 4.92% with a V_{OC} of 0.89 V, a J_{SC} of 9.21 mA/cm^2, and a FF of 0.60. Whereas the sensitizer **40** exhibited a PCE of 8.80% with a V_{OC} of 1.06 V, a short-circuit current density (J_{SC}) of 12.58 mA/cm^2, and a FF of 0.66.

Novel dye sensitizers **41** and **42** with the sequence A-π-D-π-A which contains benzo[1,2-*b*:4,5-*b'*]bisthiophene as a core moiety with different terminal acceptor

were designed and synthesized. The effects of either methyl dicyanovinyl end group **41** or *n*-butyl cyanoester end group **42** on solubility, thermal properties, optical properties, charge transport, morphology, and photovoltaic performance were investigated [28]. Devices for these dye sensitizers **41** and **42** were fabricated at the optimal donor/acceptor weight ratio of 1:1 as-cast without annealing. Sensitizer **41** exhibited a short-circuit current (*J*sc) of 5.09 mA/cm^2, a V_{OC} of 1.09 V, a fill factor (FF) of 28.08%, and a PCE of 1.56% whereas, sensitizer **42** showed a *Voc* of 1.03 V and achieved a much better PCE performance of 6.17%, due to much higher FF of 59.08% and much higher short-circuit current (*J*sc) of 10.11 mA/cm^2. The external quantum efficiency (EQE) of these dyes have a similar broad photo response wavelength range of 300–700 nm while in the whole range, the EQE values of dye **42** are much higher than dye **41**. The EQE peak of **42** is about 48% at around 676 nm, while the EQE value of **41** is below 15% at all wavelength, which leads to the poor performance of the device. *J*sc values calculated from the EQE spectra are 3.36 mA/cm^2 for dye **41** and 9.89 mA/cm^2 for **42** respectively.
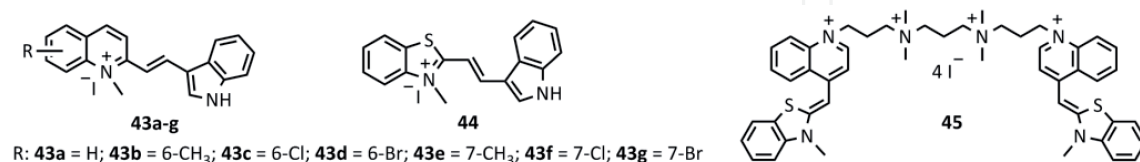
2.2 Fluorescent dyes

Fluorescence is a photophysical process which involves the emission of light by the substance as a consequence of the absorption of electromagnetic radiation. In most of the cases, the emitted light radiation has a longer wavelength (λ_{em}) than the absorbed light radiation (λ_{abs}). Likewise, fluorescent dyes, also known as *'fluorophores'* or *'reactive dyes'* remit light radiation upon absorption. Earlier, fluorescent dyes were extensively used in the textile industries to color fibers, cotton, yarns, and silk. Eventually, the use of fluorescent dyes has become a key technique for the detection and elucidation of biological structures by fluorescence emission technology. Because of their high photostability, and intense brightness, fluorescent dyes have been significantly used in fluorescent labeling (staining) of biomolecules. Fluorescent quenching studies have helped to detect DNA and proteins in biological systems. Techniques such as immunofluorescence, fluorescence microscopy, and flow cytometry rely upon fluorescent dyes. Currently, the requirement of fluorescent dyes insisted greatly because of their ample applications which could be substantiated through microwave-assisted synthesis. The advantages of microwave applications for the synthesis of fluorescent dyes have been intensively discussed [29].

2.2.1 Cyanine dyes

Cyanine dyes are found to be important functional dyes due to their typical optical properties, and act as sensitizers in solar cells, photography, and laser discs [30]. A significant property of cyanine dyes is the affinity for biological structures, specifically for DNA, and possesses wide color change, high photostability and increased fluorescent intensity when bound to biological structures [31]. Due to high fluorescence quantum yields and high molar extinction coefficients, they have been extensively used in cell imaging and gel staining techniques. Typically, cyanine dyes are obtained by heating a mixture of substituted quaternary salts with bisaldehyde or bis-imine. Accordingly, a series of cyanine dyes **43a-g** were synthesized by the condensation of quaternary salts of quinoline derivatives with 1*H*-indole-3-carbaldehydes in the presence of piperidine under solvent-free microwave irradiation at 126–329 W in 89–98% yields in only 2–5 min. The fluorescence spectra of the dyes showed absorption maxima (λ_{abs}) at 453–471 nm. However, in the presence of DNA, a

bathochromic shift (red shift) at 483–499 nm was observed. Further, the living cell imaging experiments of the dyes **43b**, **43e**, and **44** have shown preferable staining of the head of the human sperm containing the nuclear DNA. Also, the motility of the sperm didn't slow down which indicated low cell cytotoxicity. Hence, these dyes could be used as potential fluorescent probes for labeling DNA to measure human sperm viability [31]. Likewise, the condensation of benzothiazole with quarternary salts of quinoline which upon coupling with the tertiary diamine linkers gave tetracationic analogous (bis-intercalators) of monomethine cyanine dyes **45**. The steady-state fluorescence spectral studies of **45** revealed greater labeling affinity toward DNA and proved for singlet oxygen sensitization property, and found to be a potential candidate for photodynamic therapy [32].

R: **43a** = H; **43b** = 6-CH_3; **43c** = 6-Cl; **43d** = 6-Br; **43e** = 7-CH_3; **43f** = 7-Cl; **43g** = 7-Br
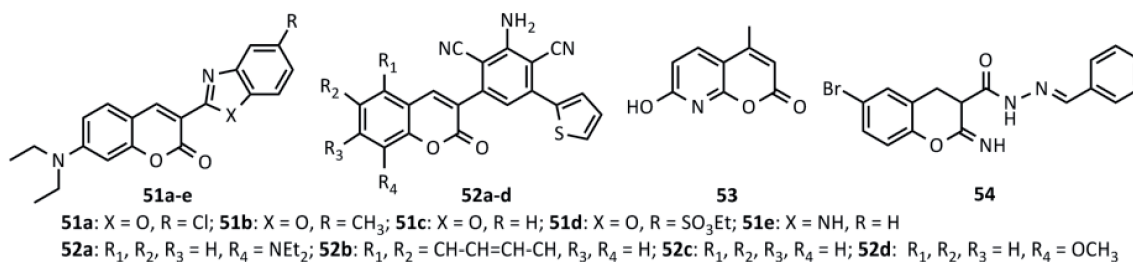
2.2.2 Naphthalimide dyes

1,8-Naphthalimide dyes are proved to be important fluorescent compounds due to their greater photostability and high fluorescent quantum yield. The basic spectral properties of these dyes depend on the polarization of naphthalimide molecule as a result of electron donor-acceptor interaction occurring between the substituents at the C-4 position and the carbonyl groups of the imide ring. Generally, 1,8-naphthalimide dyes are prepared *via* the substitution reaction of naphthalimides with various nucleophiles. The aromatic nucleophilic substitution reaction of 4-bromo-*N*-alkylnaphthalimides with amines, alkoxides, and thiols in the presence of KF/Al_2O_3 under solvent-free microwave irradiation yielded corresponding fluorescent dyes **46–48** which exhibited increased fluorescent intensity in the polar solvents [33]. Similarly, the derivatives **49** and **50** were obtained by the substitution reaction of 1,8-naphthalimides with primary amines. These dyes were further evaluated for the free radical scavenging properties against 2,2-diphenyl-1-picrylhydrazyl (DPPH). The results showed IC_{50} values at lower concentrations than the common synthetic antioxidant 2,6-ditertiarybutyl-4-methylphenol (BHT) [34].
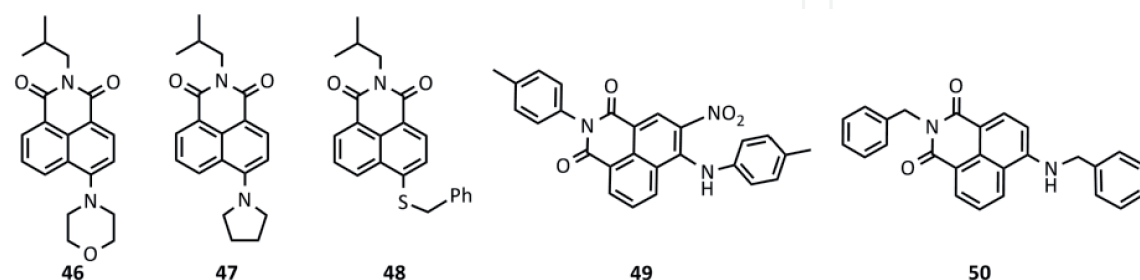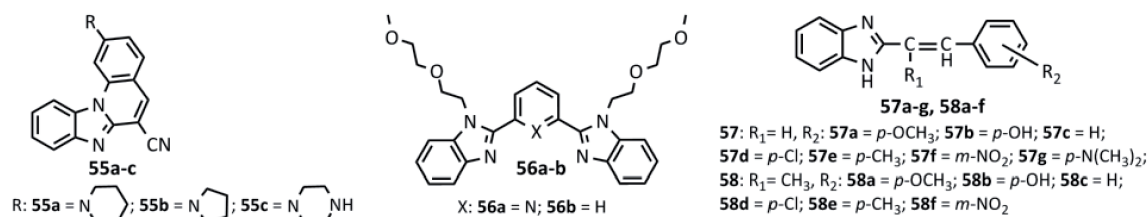

2.2.3 Coumarin dyes

Coumarin dyes have been found commercial significance due to their intense fluorescence and are widely employed as fluorescent brighteners [35]. A one-pot

microwave promoted synthesis of benzimidazol/benzoxazol functionalized coumarin dyes (**51a-e**) was developed which involved the reaction of 4-diethylamino-2-hydroxybenzaldehyde, diethylmalonate, and *o*-phenylenediamine/*o*-hydroxyaniline in *n*-pentanol within 3 min. The synthesized dyes showed higher fluorescence emission intensity and the dyes **51a-c** were further investigated for the effects of ink media on the fluorescence properties. Dye **51b** has exhibited an intense green fluorescence at 531 nm for mixed very long alkyl resin and maleic varnish in 60:40 ratios at 1% (w/w) concentration, and the fluorescence emission intensity of the dye reduced by 11% after 30 h of exposure to light. As a result, the dye **51b** could potentially be used in security offset ink [36]. Similarly, one-pot three-component microwave-assisted reaction of 7-diethyl-amino-coumarin ethylidene malononitrile, aromatic aldehydes and malononitrile to get highly fluorescent 3,5-disubstituted-2,6-dicyanoaniline coumarin dyes **52a-d** at 80°C in good yields in 2 min are prepared. The optical and thermal screening studies of **52a-d** exhibited excellent photophysical and thermal stability properties [37]. A group of 8-aza-7-hydroxy-4-methylcoumarin dye **53** was synthesized by reacting 2,6-dihydroxypyridine hydrochloride with ethylacetoacetate in the presence of magnesium bromide as a Lewis acid catalyst. This fluorophore is adequately soluble in water and has a high fluorescent quantum yield and showed increased fluorescence in protic solvents at neutral pH, which could be useful in biosensors that are required for finding biologically active compounds [38]. Furthermore, a microwave-assisted Knoevenagel condensation of salicylaldehyde and cyano-N'-methyleneacetohydrazide in the presence of piperidine catalyst gave 3-carbohydrazide coumarin fluorescent dye (**54**) which could be used to print polyester and polyamide fabrics [35].
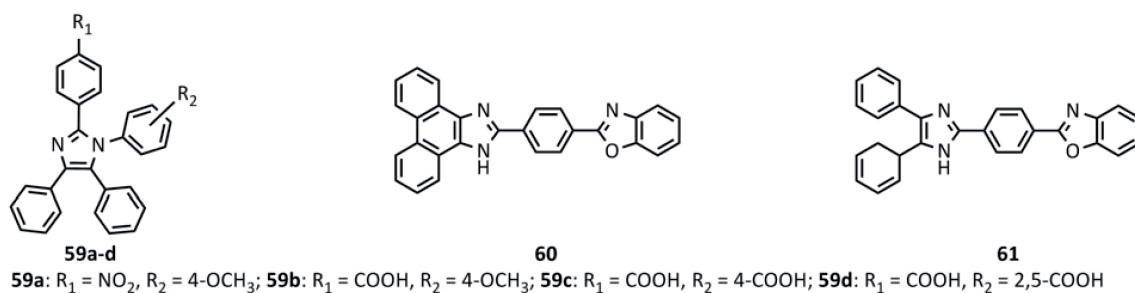

51a-e; **52a-d**; **53**; **54**

51a: X = O, R = Cl; **51b:** X = O, R = CH₃; **51c:** X = O, R = H; **51d:** X = O, R = SO₃Et; **51e:** X = NH, R = H

52a: R₁, R₂, R₃ = H, R₄ = NEt₂; **52b:** R₁, R₂ = CH-CH=CH-CH, R₃, R₄ = H; **52c:** R₁, R₂, R₃, R₄ = H; **52d:** R₁, R₂, R₃ = H, R₄ = OCH₃

2.2.4 Benzimidazole dyes

Benzimidazole dyes are known to exhibit photophysical, photovoltaic, and optical properties [39]. An approach has been made to synthesize benzimidazoquinolines **55a-c**, substituted with piperidine, pyrrolidine, and piperazine moieties by uncatalyzed amination protocol under microwave heating in relatively high yields (56–90%), which by conventional heating after several days gave **55a-c** only in low yields (<10%). The emission spectra of **55a-c** showed an increase in the fluorescence intensity when interacted with the calf thymus DNA (*ct*-DNA) [40]. The microwave promoted synthesis of bis-benzimidazolyl derivatives upon *N*-alkylation gave water-soluble fluorescent dyes **56a-b**. These dyes proved to be highly selective fluorescent probe toward Zn²⁺ in aqueous solution and the mixture of dye-Zn²⁺ could detect picric acid by fluorescence quenching [41]. Under solvent-free microwave irradiation, a series of 2-substituted styryl benzimidazole dyes **57a-g** and **58a-f** were prepared by the condensation of 2-alkyl benzimidazoles with aromatic aldehydes in the presence of acetic anhydride [42].

55a-c

R: **55a** = N⟨ ⟩; **55b** = N⟨ ⟩; **55c** = N⟨ ⟩NH

56a-b

X: **56a** = N; **56b** = H

57a-g, 58a-f

57: R₁ = H, R₂: **57a** = *p*-OCH₃; **57b** = *p*-OH; **57c** = H; **57d** = *p*-Cl; **57e** = *p*-CH₃; **57f** = *m*-NO₂; **57g** = *p*-N(CH₃)₂; **58**: R₁= CH₃, R₂: **58a** = *p*-OCH₃; **58b** = *p*-OH; **58c** = H; **58d** = *p*-Cl; **58e** = *p*-CH₃; **58f** = *m*-NO₂
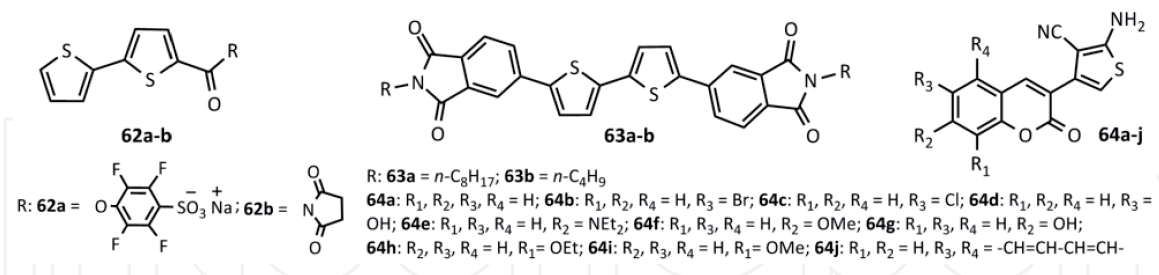
2.2.5 Imidazole dyes

The imidazole moiety is immensely employed in DSSC's [43]. Interestingly these dyes **59a**-**d**, **60**, and **61** are prepared by one-pot condensation of α-diketone (benzil), aryl aldehydes, and ammonium acetate in the presence of glacial acetic acid under microwave irradiation. Furthermore, the dyes **59a**-**d** have been proved to be potential antimicrobial agents against *E. coli*, *B. subtilis*, *S. aureus,* and *L. monocytogenes* [44]. The dye **60** exhibited a strong two-photon upconverted blue fluorescent emission peak around 443–476 nm [45].

59a-d

59a: R₁ = NO₂, R₂ = 4-OCH₃; **59b**: R₁ = COOH, R₂ = 4-OCH₃; **59c**: R₁ = COOH, R₂ = 4-COOH; **59d**: R₁ = COOH, R₂ = 2,5-COOH
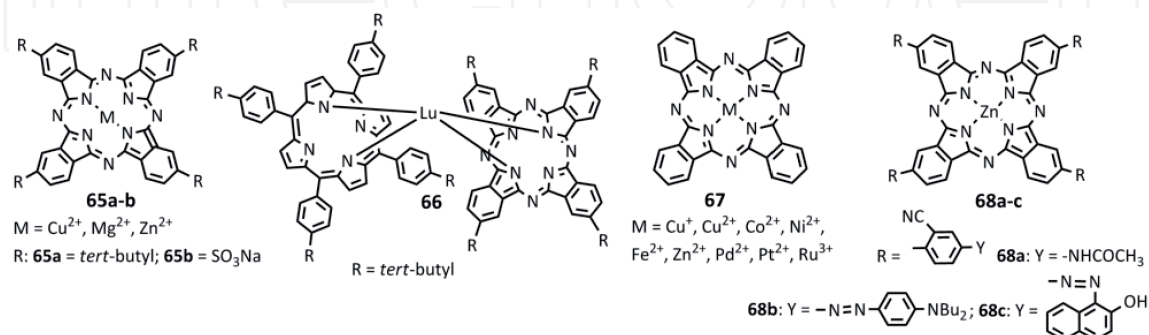
60

61

2.2.6 Thiophene dyes

Thiophene oligomers and polymers have put forward extensive applications in organic electronics, owing to their remarkable performance as organic semiconductors [46]. A series of thiophene oligomer based fluorophores appended with 4-sulfo-2,3,5,6-tetraflurophenyl ester **62a**, *N*-hydroxysuccinimidyl ester **62b**, and phthalimide **63a-b** are prepared efficiently in shorter reaction times by sequential Pd(II) catalyzed Suzuki cross coupling reaction by taking advantage of microwave irradiation. The dyes **62a-b** were evaluated for their labeling toward monoclonal antibodies Anti-CD38. The dye **62a** showed a larger bathochromic shift compared to **62b** and exhibited greater affinity toward the monoclonal antibody [47]. The cyclic voltammetry, UV–visible spectroscopy, and X-ray crystallographic studies of the dyes **63a** and **63b** revealed π-π stacking packing mode which led to increased charge carrier mobility envisaging as an ambipolar semiconductor with applications in both Organic Thin-Film transistors (OTFT) and Organic-light Emitting Transistors (OLET) [46, 48]. A one-pot three-component synthetic route was used to prepare thiophene-coumarin based dyes **64a-j** in 92–96% yields from hours to min by the use of microwave irradiation technique from 3-acetyl coumarin, malononitrile, and elemental sulphur (S₈). The spectroscopic data of the dyes **64a-j** showed a bathochromic shift in various solvents. The dye **64g** was further investigated for its pH sensitivity *via* deprotonation and reverse protonation in two solvent systems (DMSO and DMSO/H₂O binary mixture) using absorption and fluorescence techniques. The -OH group of **64g** is susceptible to deprotonation under alkaline medium (TBAOH, tetrabutylammonium hydroxide)

and reverse protonation by the addition of trifluoroacetic acid (TFA). A distinct fluorescence color change from light blue to green was observed with the incremental addition of TBAOH to the solution of **64g** and reverse phenomena was observed with the incremental addition of TFA [49].

R: **63a** = *n*-C$_8$H$_{17}$; **63b** = *n*-C$_4$H$_9$
64a: R$_1$, R$_2$, R$_3$, R$_4$ = H; **64b**: R$_1$, R$_2$, R$_4$ = H, R$_3$ = Br; **64c**: R$_1$, R$_2$, R$_4$ = H, R$_3$ = Cl; **64d**: R$_1$, R$_2$, R$_4$ = H, R$_3$ = OH; **64e**: R$_1$, R$_3$, R$_4$ = H, R$_2$ = NEt$_2$; **64f**: R$_1$, R$_3$, R$_4$ = H, R$_2$ = OMe; **64g**: R$_1$, R$_3$, R$_4$ = H, R$_2$ = OH; **64h**: R$_2$, R$_3$, R$_4$ = H, R$_1$ = OEt; **64i**: R$_2$, R$_3$, R$_4$ = H, R$_1$= OMe; **64j**: R$_1$, R$_2$ = H, R$_3$, R$_4$ = -CH=CH-CH=CH-

2.2.7 Inorganic dyes

Inorganic dyes are procured when the organic dyes are combined with appropriate metals. Typically monoazodyes containing additional groups such as amino, hydroxyl, and carboxyl groups which are capable of forming coordination complexes with metal ions are used. This organo-metallic combination could lead to enhanced optical properties. The synthesis of organo soluble 4-*t*-butylphthalocyanine (TBPc) and organo soluble sodium salt of sulfonated phthalocyanine (Pc-SO$_3$Na) metal complexes of Cu^{2+}, Mg^{2+}, and Zn^{2+} (**65a-b**) has been reported. Further, lutetium complex [Lu(TBPor)(TBPc)] **66** ligated with 4-*t*-butylporphyrin (TBpor) and 4-*t*-butylphthalocyanine (TBPc) rings were obtained *via* the reaction of lutetium acetate (LuOAc) with corresponding ligands under microwave irradiation. The prepared complexes were blended with *N,N'*-bis-(1,5-dimethylhexyl)-3,4:9,10-perylene-bis-(dicarboximide) [PDHEP] and SnO$_2$ glass to fabricate photoelectric cells. The SnO$_2$ glass/Mg-Pc(SO$_3$Na)$_4$/PDHEP/Al photoelectric cell exhibited a short-circuit photocurrent of 116 μA/cm^2, whereas SnO$_2$ glass/Lu(TBpor)(TBpc)/PDHEP/TiO$_2$/Al photoelectric cell showed increased short-circuit photocurrent of 691.3 l μA/cm^2 under the illumination of white light at 1.201 mW/cm^2 [50]. The metal-free phthalocyanine and metallophthalocyanine complexes (**67** and **68a-c**) of Cu$^+$, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Pd^{2+}, Pt^{4+}, and Ru^{3+} was prepared by the reaction of corresponding azo dyes with metal salts using microwave heating, which were obtained in poor yields by conventional heating [51].

65a-b
M = Cu^{2+}, Mg^{2+}, Zn^{2+}
R: **65a** = *tert*-butyl; **65b** = SO$_3$Na

66
R = *tert*-butyl

67
M = Cu$^+$, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Pd^{2+}, Pt^{2+}, Ru^{3+}

68a-c
68a: Y = -NHCOCH$_3$
68b: Y = −N=N−⟨⟩−NBu$_2$; **68c**: Y =
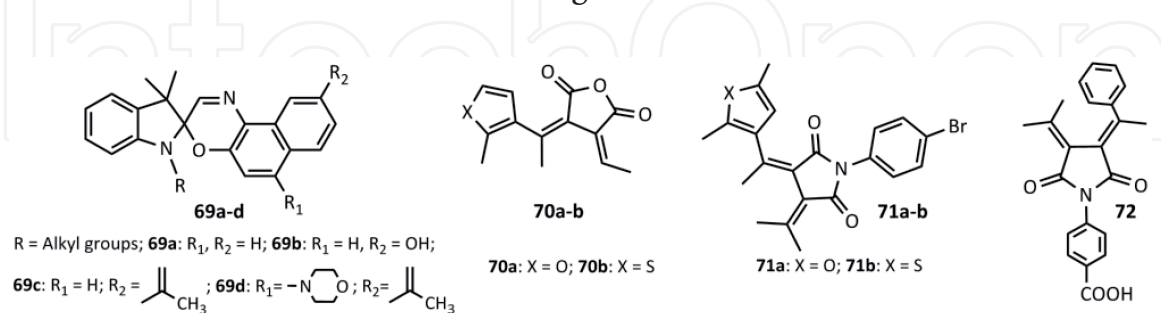
2.3 Photochromatic dyes

Some materials at their molecular level exhibit a property of changing their absorption spectra on exposure to light radiation. This is usually a reversible change and is accompanied with alteration in the physical or chemical property. This kind

of photo transformation is referred to as photochromism. The reverse change may be induced thermally (photochromism type T) or photochemically (phtochromism type P). The discovery of photochromic materials can be retraced to the middle of 19th century when Hirshberg and his team (1950) have contributed significantly towards the synthesis and mechanistic studies of photochromic materials. Hirshberg coined the term "Photochromism" from Greek words 'photos' meaning light and 'chroma' means color. Varieties of materials like minerals, nanoparticles, inorganic–organic compounds, organic dyes, polymers, and biomolecules have been explored to exhibit photochromic property. They have been in use in modern applications like erasable optical memory media, photo-optical switch components, sunscreen applications, contact lenses, security glasses, and thin films. Some of the organic photochomic compounds undergo reversible light-driven reaction hence these compounds are often incorporated into polymers, liquid crystals, and other such matrices. Although the decade 1950–1960 has remarked synthesis of photochromic materials with the advancement in newer supportive technologies such as spectroscopy the field has not gained acceleration. This is due to the sensibility of organic materials towards the light which makes them undergo degradation (they were not fatigue resistant). After the report of the synthesis of fatigue resistant spironapthoxazines many-fold increase in the applications of photochromic materials has been reported. Spiropyrans, spriooxazines, chromenes, fulgides, fulgimides, diarylethenes, spirodihydro indazolines, azocompounds, polyarenes, quinones, anils are the photochromic dyes in the industrial and general application field [52]. In the recent past attempts have been made to apply microwave-assisted synthetic methods to the total synthesis or in one or two intermediate steps.
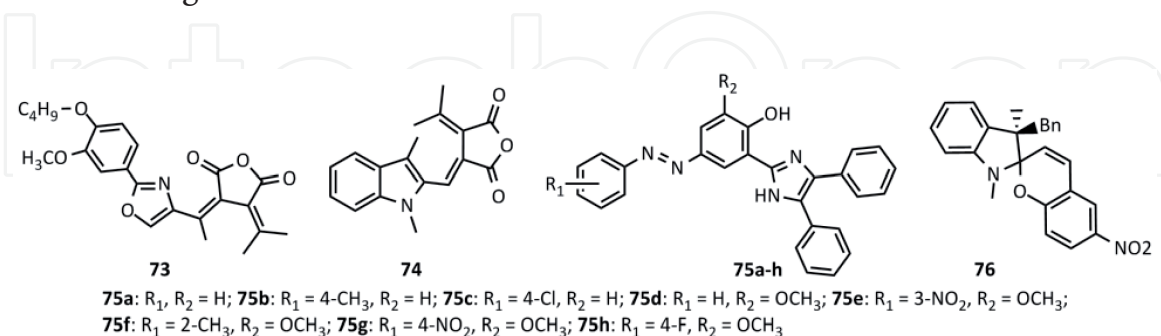
Spirooxazines are the important photochromic dyes being popularly seen in very common to high tech applications. Due to their brilliant light fatigue resistance nature, they are the dyes of bright prospects. The reports of the synthesis of spiro-oxazines by conventional methods are many. Successful efforts have also been made to obtain them by environment-friendly microwave-assisted synthetic methods. Spirooxazine **69a** has been prepared under microwave conditions, starting from 1-nitroso-2-naphthol in presence of triethylamine as a catalyst in a CEM focused microwave reactor provided with temperature control [53]. Electric power 25–35 W, temperature 80–180°C were found to be the optimized conditions to get yields comparable to the traditional thermal method. Indolinespironaphthooxazine **69b-d** have been prepared from 1-nitroso-2,7 dihydroxy naphthalene by a microwave irradiation technique [54]. The reaction was carried out in microwave synthesizer (MAS-I). Microwave irradiation was done at 600 W. The products were obtained in very good yield within a few minutes of reaction time.

Fulgides **70a-b** and their derivatives fulgimides **71a-b** are an important class of photochromatic materials used mainly in optical memory devices and optical switches. Fulgides are intense colored compounds which are good in resisting the photodegredation in comparison to fulgimides. However, fulgimides have better resistance to acid or base hydrolysis further that their N-substituent can be used as a link to prepare photochromic films. Both these classes of compounds have been thoroughly researched. A successful attempt to synthesize fulgimides using domestic microwave ovens has been made [55]. As compared to classical thermal method microwave-assisted esynthesis has led to 3 fold times reduction in duration of synthesis, an increase in the yield up to 2 times, and minimization of the use of organic solvents. The efficient synthesis of N-functionalized fulgimides **72** was achieved under microwave irradiation [56]. Fulgides were converted to fulgimides in two steps in the presence of DMAP and DCC by microwave irradiation in presence of pyridine and xylene as the solvent. They have attained from 50 to 84% increase in

yield by benign microwave method in very short reaction time. Oxazole and indole based heterocyclic fulgides **73, 74** were synthesized by microwave method using clay as a catalyst from fulgenic acids [57]. Their synthesis involved stirring of the blended mixture of fulgenic acid and montmorillonite KSF along with isopropyl acetate in a flask. The yield was improved to 72–84% by MWAS as compared to the conventional Stobbe condensation method. One-pot three-component microwave-assisted synthesis of novel azo-imidazoles **75a-h** is reported which exhibited photochromatic property with UV–Visible light [58]. Azo dye, ammoniumacetate, and benzil were reacted under microwave irradiation using acetic acid as solvent.

R = Alkyl groups; **69a**: R_1, R_2 = H; **69b**: R_1 = H, R_2 = OH;

69c: R_1 = H; R_2 = [structure] ; **69d**: R_1= –N O ; R_2= [structure]

70a: X = O; **70b**: X = S

71a: X = O; **71b**: X = S

At optimal power 230 W microwave irradiation for 2 min duration 87% yield of the dye **75a**-**h** was obtained. It did not involve any thermal degradation by-products and economical use of organic solvents makes this protocol a green synthetic method. The microwave synthetic method was applied to successfully prepare photochromic spiropyran **76** [59]. Spiropyrans are spiro-fused indolochromenes. Due to their photochromic isomerization property, they are used in optical switches and sensors. The synthesis involves one-pot two-step reaction. Initially, water-mediated reaction was carried out between 1, 2, 3-trimethylindole, and benzyl bromide under microwave environment. Microwave irradiation was done at De Rosa and Soriente's conditions (i.e. 200 MW power and 150°C temperature for 8 minutes). Then, the resulting reaction mixture after a simple workup procedure was treated with 5-nitrosalicylaldehyde under microwave irradiation using ethanol as the solvent. They have obtained product **76** in excellent yield after the flash chromatographic workup procedure. It is an environmentally benign synthetic method using a minimum amount of solvent.


75a: R_1, R_2 = H; **75b**: R_1 = 4-CH$_3$, R_2 = H; **75c**: R_1 = 4-Cl, R_2 = H; **75d**: R_1 = H, R_2 = OCH$_3$; **75e**: R_1 = 3-NO$_2$, R_2 = OCH$_3$; **75f**: R_1 = 2-CH$_3$, R_2 = OCH$_3$; **75g**: R_1 = 4-NO$_2$, R_2 = OCH$_3$; **75h**: R_1 = 4-F, R_2 = OCH$_3$

2.4 Organic-light emitting diodes (*O*-LEDs)

The light-emitting diode (LED) is a light-emitting semiconducting material when current flows through it. The current flow induced light emission was first observed by Captain Henry Joseph Round in 1907. Light emission takes place when electrons undergo a transition from the conduction band to the empty valence band. The band gap in semiconducting material decides the color of emitted light. *O*-LED are

the LEDs in which the light-emissive electroluminescent film is made up of organic molecules. In the case of *O*-LEDs the highest occupied molecular orbital (HOMO) is the conduction band, and the lowest unoccupied molecular orbital (LUMO) is the empty valence band of organic substance. *O*-LEDs are preferred over LEDs due to the facts that an *O*-LED is thinner and have a better display property; it has brighter, fast responsive, and long-range contrast display. Moreover, *O*-LEDs have wider viewing angles with low driving voltage property. *O*-LEDs can be conveniently fabricated on a glass surface at low temperatures. Organic semiconducting materials are in the crystalline or polymeric phase. Organometallic compounds, polymers, and even simple organic molecules like aryl amines are used in *O*-LEDs. The research in the field of *O*-LEDs is in rapid progress as these displays are already in use in modern electronic and optoelectronic appliances like heads-up displays, billboard-type displays, automotive dashboards, home and office lighting, and flexible displays. The synthetic invention of these organic moieties is a progressive field, and the microwave-assisted synthetic methods of *O*-LEDs have also started sprouting in recent years [60, 61].

The amalgamation of organic moieties and inorganic matrices results in the synergetic effects by augmenting of the properties like flexibility and shape ability with stability [62]. Poly (2-hydroxyethyl methacrylate) (PHEMA) silica-hybrids have been prepared by microwave irradiation [63]. Organoboron dye diketonate BF$_2$ complex **77**, borondipyrromethene (BODIPY) **78**, and (1,3-boron di(iso)indomethene dye **79** can be integrated into these PHEMA silica hybrids.
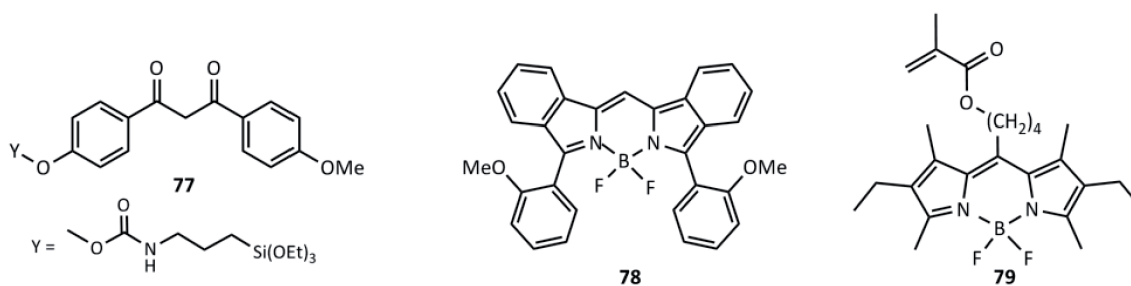
N,N-Diphenylamine (DPA) were transformed to form precursors for *O*-LEDs using solid state microwave-assisted organic synthetic method [64]. This reaction was carried out in the MAS II SINEO microwave reactor in presence of Iodine and alumina. The temperature range of 125–133°C was optimized and the reaction was completed in 15 minutes at 500–600 W power of the reactor. After typical work up procedure they ended up with two fractional mixtures of compounds **80** to **85** with fluorescence property were obtained.
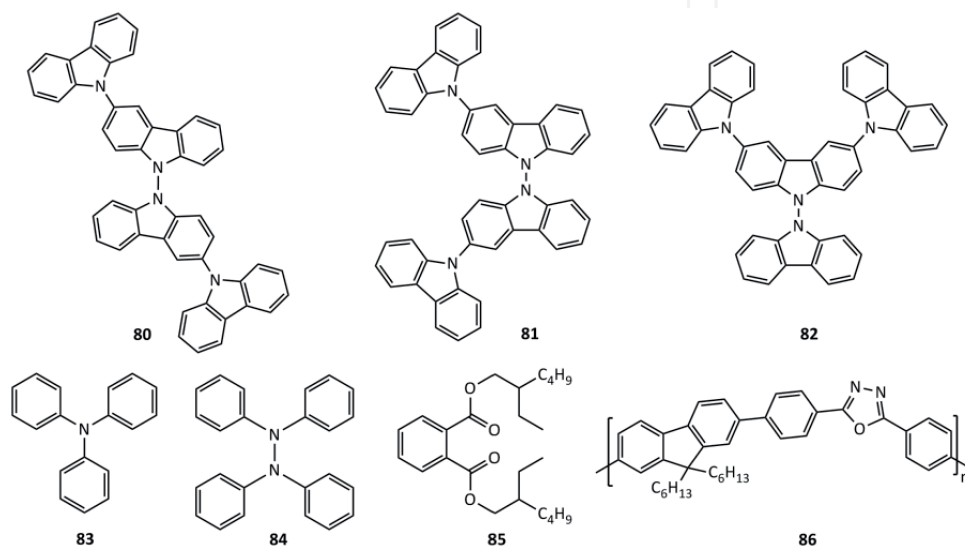
Polyfluorene is regarded as an important source for the development of *O*-LEDs. It emits blue light and the color of the light can be tuned by means of doping, structural engineering, preparing materials with tuned properties [65]. Microwave-assisted synthesis of π conjugated polymers were reported and this method was proved to be an advantageous method over multi-step expensive conventional method. They have effectively used microwave conditions in oxidative polymerization of 2,5-diphenyl-1,3,4-oxadiazole and 9,9-dihexyl-fluorene monomers to get poly (dihexyl fluorene-co diphenyl oxadiazole) (POF) **86** in the presence of FeCl$_3$ catalyst.

3. Conclusions

Since from the centuries, dyes have played a very important role in human life. The functional dyes have changed the technologies drastically and have gained immense importance now a day. A specific property of the dye depends on the various factors such as the donor, electron acceptor/π-conjugation, linker, etc. present at appropriate positions. More effort has been established into searching for better dyes with expected properties. Microwave-assisted synthesis has changed the methodology of organic synthesis and hence is also efficiently applied in the synthesis of functional dyes. Therefore, a number of dyes synthesized under microwaves along with their applications were discussed. There is a possibility for further development in organic synthetic methodology under microwaves to obtain dyes having wider applications in organic photovoltaics, fluorescence sensors, photochromic materials, OLEDs, etc.

Acknowledgements

Author details

Sheetal Marganakop[1], Pramod Kattimani[2], Sudha Belgur Satyanarayana[3] and Ravindra Kamble[4]*

1 Government First Grade College, Paschapur, Karnataka, India

2 J.S.S. Arts, Science and Commerce College, Falls Road, Gokak, India

3 Department of Chemistry, Yuvaraja's College, University of Mysore, Mysore, India

4 Department of Chemistry, Karnatak University, Dharwad, India

*Address all correspondence to: ravichem@kud.ac.in

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