

## DYE-SENSITIZED SOLAR CELLS (DSSCs): THE HISTORY AND A NEW OPTICAL ACTIVITY-BASED METHOD TO PREDICT THE POWER CONVERSION EFFICIENCY

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### ABSTRACT

Improvement on the performance of dye-sensitized solar cells (DSSCs) has been a major research topic for the past thirty years. Several research efforts on increasing the efficiency of DSSC have mainly focused on the synthesis of novel sensitizers, with the continuous employment of the traditional mesoporous TiO<sub>2</sub> films as semiconductor, and the iodide/triiodide (I/I<sub>3</sub>) electrolyte as redox couple. Since not so much have been done in exploring other mesoporous semiconductors and redox electrolytes beyond these two, TiO<sub>2</sub> and I/I<sub>3</sub> couple, this paper concisely chronicles the power conversion efficiencies (PCEs) of DSSCs of different dye sensitizers, where only TiO<sub>2</sub> nanofilm and iodide/triiodide redox couple have been used as the semiconductor and electrolyte systems respectively. This list was used to obtain possible relationship between the optical properties of dyes and the PCE of the DSSC. Dye sensitizers with PCE values > 1.00% were employed. The spectral properties of each of the selected sensitizers were used to obtain their spectrum power, I( $\lambda$ ). An increase in PCE value as I( $\lambda$ ) increases was observed for 81.25% of the sixteen sensitizers considered, which suggests that a direct correlation could exist between the I( $\lambda$ ) of a sensitizer and the PCE of the DSSC of that sensitizer.

**Keywords:** Power conversion efficiency, Optical property, Spectrum power, Organic photovoltaic cells.

### INTRODUCTION

Photoelectricity is an old concept, and it is over a century old (Aronsi and Peppard, 1965). It has found applications in many modern technologies, including optoelectronics and photonics (Tributsch and Bennett, 1977; Wrighton, 1979; Tributsch, 1979; Sanusi *et al.*, 2014). Research effort towards developing this very important concept has been thorough and intense from the very beginning (Wong *et al.*, 2011; Powell, 1978; Klassen, 2011). One of the greatest breakthroughs of the concept is its application in the fabrication of solar energy converters, known otherwise as solar cells (Ichikawa *et al.*, 2001; Rath and Schropp, 1998; Morris *et al.*, 1990; Matsumura *et al.*, 1977).

K. Hauffe, R. Memming, A. Fujishima, H. Tributsch, M.S. Wrighton, H. Gerischer and K. Honda are some of the notable pioneers of the research that led to the development of dye-sensitized photovoltaic cells in the late 1960s to the mid- 1970s (Fujishima *et al.*, 1969; Tributsch and Gerischer, 1969; Hauffe *et al.*, 1970; Fujishima and Honda, 1971; Memming and Tributsch, 1971; Fujishima and Honda, 1972; Gerischer and Selzle, 1973; Hauffe and Bode, 1974; Fujishima *et al.*,

1975; Wrighton *et al.*, 1976). While some of the works at this period were focused on photolysis of water (Fujishima *et al.*, 1969; Fujishima and Honda, 1971; Fujishima and Honda, 1972; Wrighton *et al.*, 1976), a few also were aimed at converting solar energy to electricity (Hauffe *et al.*, 1970; Memming and Tributsch, 1971; Hauffe and Bode, 1974). By 1976 to late 1980s, the research on DSSCs had already been developed, with many new researchers showing interest in the field (Matsumura *et al.*, 1976; Watanabe *et al.*, 1976; Matsumura *et al.*, 1977; Bard, 1980; Nozik, 1980; Heller, 1981; Juris *et al.*, 1988; Nazeeruddin *et al.*, 1990; Amadelli *et al.*, 1990).

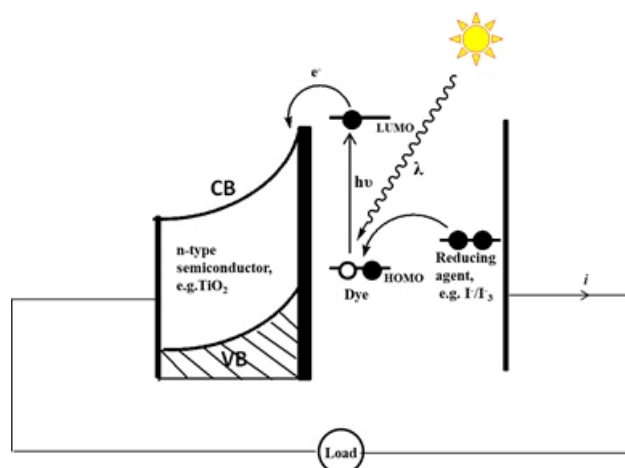
Most of the early research works on DSSCs considered the use of ZnO extensively, as the semiconductor photoanode upon which the sensitizing dyes are adsorbed for charge transfer photosensitization (Hauffe *et al.*, 1970; Hauffe and Bode, 1974; Matsumura *et al.*, 1976; Matsumura *et al.*, 1977). Other materials explored include TiO<sub>2</sub> (Matsumura *et al.*, 1976), CdS (Fujishima *et al.*, 1975), GaAs (Tributsch and Gerischer, 1969), GaP (Memming and Tributsch, 1971), AgCl (Gerischer and Selzle, 1973), AgBr (Gerischer and

Selzle, 1973) and  $\text{Cu}_2\text{O}$  (Gerischer and Selzle, 1973). Although, there was a special interest in the use of n-type  $\text{TiO}_2$  as the semiconductor photoelectrode during these early periods, it was employed only for photo-electrolytic reaction of water (Fujishima *et al.*, 1969; Fujishima and Honda, 1971; Fujishima and Honda, 1972; Wrighton *et al.*, 1976). The preference for  $\text{TiO}_2$  in this reaction stemmed from the knowledge of its property as an inert semiconductor that does not undergo decomposition upon illumination in an aqueous electrolyte (Wrighton *et al.*, 1976; Wrighton, 1979). However, such decompositions were already known to occur for several other semiconductor photoelectrodes that have been investigated (Myamlln and Pleskov, 1967; Gerischer and Mindt, 1968; Gerischer, 1970).

One of the earliest reports, if not the first, on the use of  $\text{TiO}_2$  as a photoelectrode for the conversion of solar energy to electricity in a solid/liquid junction dye-sensitized solar cell was published by Matsumura *et al.* in 1976. In this report, alizarin dyes were employed as photosensitizers, and their photoelectrochemical behaviors on  $\text{TiO}_2$  and  $\text{ZnO}$  surfaces were described. One interesting finding from this investigation was the regeneration of the default state of the  $\text{TiO}_2$ -dye system when soaked in a dark electrolyte solution, after it had been initially photo-bleached due to continuous illumination (Matsumura *et al.*, 1976). This finding gave credence to the reports from the previous authors regarding  $\text{TiO}_2$  photostability in an electrolyte solution (Myamlln and Pleskov, 1967; Gerischer and Mindt, 1968; Fujishima *et al.*, 1969; Gerischer, 1970; Wrighton *et al.*, 1976). However, this property was not found in  $\text{ZnO}$  when it was investigated by the same group a year after, using Rose Bengal and Rhodamine B as photosensitizers (Matsumura *et al.*, 1977). By this second report, the results previously reported for both semiconductors ( $\text{TiO}_2$  and  $\text{ZnO}$ ) (Matsumura *et al.*, 1976) were confirmed.

Later in 1977, Matsumura *et al.* further provided the first empirical description of the mechanism of photocurrent generation in a dye-sensitized solar cell (Matsumura *et al.*, 1977). The previous explanation of the mechanism (Memming, 1972), even though is very similar to that of Matsumura and coworkers, did not seem to be adequately supported by strong empirical evidence. It was clear in Matsumura's report that the photosensitization is due to the dye adsorbed on the semiconductor surface (Matsumura *et al.*, 1977), and not from the bulk dye solution (Memming, 1972). This confirmed that the operational principle of DSSCs, and the preference for  $\text{TiO}_2$  as the semiconductor photoanode of choice, had already been established before 1980 (Hauffe *et al.*, 1970; Memming and Tributsch, 1971; Hauffe and Bode, 1974; Gerischer and Willig, 1976; Matsumura *et al.*, 1976; Wrighton *et al.*, 1976; Matsumura *et al.*, 1977; Wrighton, 1979).

For an n-type semiconductor with adsorbed dye molecules, the operational principle of DSSCs as given by Matsumura *et al.* (1977), can simply be described by the illustrative diagram in Figure 1. When light is absorbed by the sensitizer, a charge separation at the interface occurs between the photoexcited dye molecules and the semiconductor via a photo-induced electron transfer. This transfer takes place from the highest occupied molecular orbital (HOMO) of the dye through the lowest unoccupied molecular orbital (LUMO), to the conduction band (CB) edge of the  $\text{TiO}_2$  semiconductor. The electron-hole pair generated is then transported to the external circuit. The original state of the dye is regenerated by a redox couple system (e.g.,  $\text{I}^-/\text{I}_3^-$ ), while it is itself regenerated at the counter electrode by the electrons passing through the load (Matsumura *et al.*, 1977). It was clear from the Matsumura's report that electron injection from an excited LUMO state of the dye, into a CB edge would be possible only if the dye's excited states are adequately higher than the semiconductor's CB edge as shown in Figure 1 (Matsumura *et al.*, 1977).



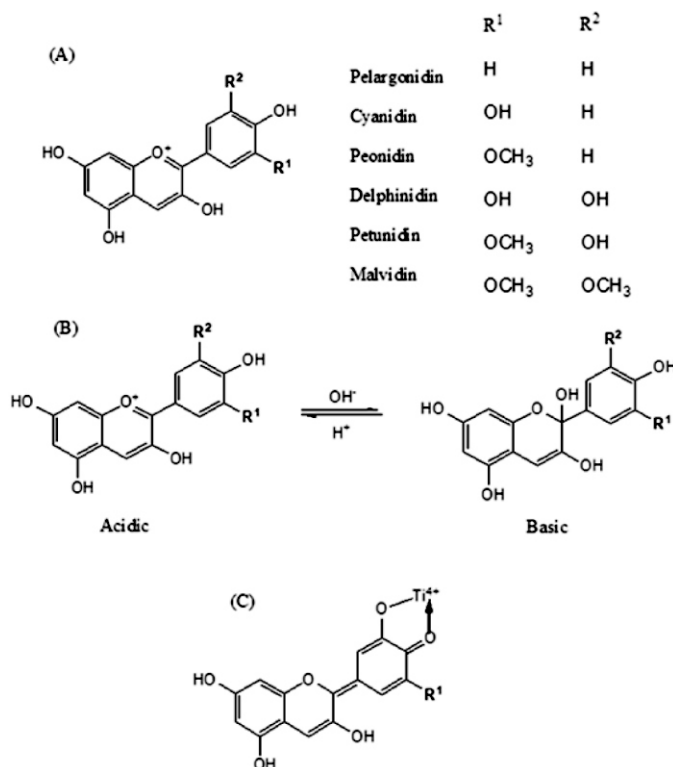
**Figure 1:** Mechanism of electron injection into the conduction band (CB) edge of the semiconductor photoanode from the lowest unoccupied molecular orbital (LUMO) of the sensitizing dye in a dye-sensitized solar device. Adapted from Matsumura *et al.*, 1977.

In the early 1990s, Grätzel and O'Regan (O'Regan and Grätzel, 1991) made a stunning contribution to the field by employing only a dye-adsorbed-TiO<sub>2</sub> film (no bulk dye solution as being done before) that was well deposited on a conducting substrate, e.g., fluorine-doped tin oxide (FTO) glass slide, as the photoanode. One of the remarkable feats achieved by the Grätzel cell is the miniaturization of the device components.

### PROGRESS MADE IN ENHANCING THE POWER CONVERSION EFFICIENCIES (PCEs) OF SENSITIZERS IN OVER FOUR DECADES

Over the last four decades, there has been continued interest in the development of new dye sensitizers for DSSC applications (Myamlln and Pleskov, 1967; Gerischer and Mindt, 1968; Gerischer, 1970; Memming, 1972; Gerischer and Willig, 1976; Memming, (1978/79); Nozik, 1980; Desilvestro *et al.*, 1985; Furlong *et al.*, 1986; Vlachopoulos *et al.*, 1988; Amadelli *et al.*, 1990; Gerischer, 1990; Nazeeruddin *et al.*, 1990; Willig *et al.*, 1990; O'Regan and Grätzel, 1991; Gao *et al.*, 2000; Nazeeruddin *et al.*, 2001; Wang *et al.*, 2004; Wang *et al.*, 2004; Nazeeruddin *et al.*, 2005; Wang *et al.*, 2005; Wang *et al.*, 2005; Kuang *et al.*, 2006; Kuang *et al.*, 2006; Kuang *et al.*, 2007; Chen *et al.*, 2007; Karthikeyan *et al.*, 2007; Kawano *et al.*, 2007; Gao *et al.*, 2008; Ito *et al.*, 2008; Kuang *et al.*, 2008; Kuang *et al.*, 2008; Funaki *et al.*, 2009; Song *et al.*, 2009; Dai *et al.*, 2011; Islam *et al.*, 2011; Kisserwan and Ghaddar, 2011; Paek, 2011; Yella *et al.*, 2011;

Yen, 2011; Mathew *et al.*, 2014; Zhu *et al.*, 2017). Several dye molecules ranging from natural (Figure 2) to synthetic have been deployed as sensitizers in DSSCs since the early 1990s, when the first report of Grätzel and O'Regan was published (O'Regan and Grätzel, 1991; Gao *et al.*, 2000; Fernando and Senadeera, 2008). *Hibiscus surattensis* (HST) plant had been shown to give a high yield of anthrocyanidin (Figure 2) and had produced a PCE value of 1.14% from its DSSC (Fernando and Senadeera, 2008), Table 1. A good sensitizer must meet demanding specifications, such as the presence of viable anchoring groups, or strong points of attachment to the semiconductor surface (Memming, 1978/79; Desilvestro *et al.*, 1985; Furlong *et al.*, 1986; Vlachopoulos *et al.*, 1988; Gerischer, 1990; Willig *et al.*, 1990; O'Regan and Grätzel, 1991), a wide and intense absorption spectral range (Kuang *et al.*, 2006; Karthikeyan *et al.*, 2007; Kuang *et al.*, 2007; Kuang *et al.*, 2008; Funaki *et al.*, 2009; Dai *et al.*, 2011; Kisserwan and Ghaddar, 2011), good solubility property in polar organic solvents (Wang *et al.*, 2005; Kuang *et al.*, 2006; Song *et al.*, 2009; Paek *et al.*, 2010; Yen *et al.*, 2011), and high photochemical and photothermal stability (Nazeeruddin *et al.*, 2004; Kuang *et al.*, 2006; Kuang *et al.*, 2007; Gao *et al.*, 2008; Kuang *et al.*, 2008). A list of known sensitizers with significant power conversion efficiencies (PCEs), i.e. PCE > 1, since the discovery of DSSC to date has been compiled, and the respective PCE values have been placed side-by-side with the corresponding dyes (Table 1).



**Figure 2:** (A) Fundamental structures of the most abundant anthocyanidins. (B) Anthocyanidins in acidic and basic media (C) Chelation mechanism of anthocyanidins with TiO<sub>2</sub> (curled from Fernando and Senadeera, 2008).

**Table 1:** List of some of the dyes reported in the literature and their power conversion efficiencies (PCEs) arranged in increasing order. PCE values are generally for 100 mW/cm<sup>2</sup> (1.0 sun) light intensity except where indicated.

S/N	Cpd	PCE (%)	Ref.	S/N	Cpd	PCE (%)	Ref.	S/N	Cpd	PCE (%)	Ref.
1.	HST	1.14	Fernando, and Senadeera, (2008)	18.	17	6.60	Yen <i>et al.</i> , 2011	35.	32	8.20	Wang <i>et al.</i> , 2004
2.	1	1.50	Karthikeyan <i>et al.</i> , 2007	19.	18	6.60	Nazeeruddin <i>et al.</i> , 2004	36.	33*	8.40	Yella <i>et al.</i> , 2011
3.	2	2.00	Dai <i>et al.</i> , 2011	20.	19	6.63	Yen <i>et al.</i> , 2011	37.	34	8.42	Chen <i>et al.</i> , 2007
4.	3	2.03	Dai <i>et al.</i> , 2011	21.	20	6.75	Paek <i>et al.</i> , 2010	38.	35	8.43	Ito <i>et al.</i> , 2008
5.	4	2.20	Funaki <i>et al.</i> , 2009	22.	21	6.91	Yen <i>et al.</i> , 2011	39.	36	8.70	Nazeeruddin <i>et al.</i> , 2004
6.	5	2.51	Dai <i>et al.</i> , 2011	23.	15*	6.92	Nazeeruddin <i>et al.</i> , 2004; Ni <i>et al.</i> , 2012	40.	37	9.00	Kuang <i>et al.</i> , 2007
7.	6	3.00	Dai <i>et al.</i> , 2011	24.	22	7.00	Wang <i>et al.</i> , 2005; Kuang <i>et al.</i> , 2006	41.	38	9.02	Chen <i>et al.</i> , 2007
8.	7	3.40	Karthikeyan <i>et al.</i> , 2007	25.	23	7.04	Etgar <i>et al.</i> , 2013	42.	39	10.2	Wang <i>et al.</i> , 2004
9.	8	3.70	Funaki <i>et al.</i> , 2009	26.	24*	7.13	Yen <i>et al.</i> , 2011	43.	24*	10.3	Nazeeruddin <i>et al.</i> , 2005
10.	9	4.50	Kisserwan, and Ghaddar, 2011	27.	25 <sup>a</sup>	7.21	Kuang <i>et al.</i> , 2008	44.	40	10.4	Nazeeruddin <i>et al.</i> , 2001
11.	10	5.36	Song <i>et al.</i> , 2009	28.	26	7.39	Chen <i>et al.</i> , 2007	45.	41	11.0	Gao <i>et al.</i> , 2008
12.	11	5.94	Yen <i>et al.</i> , 2011	29.	15*	7.40	Wang <i>et al.</i> , 2005	46.	33*	11.0	Bessho <i>et al.</i> , 2010
13.	12	6.10	Zhu <i>et al.</i> , 2017	30.	27	7.50	Nazeeruddin <i>et al.</i> , 2004	47.	24*	11.2	Nazeeruddin <i>et al.</i> , 2005
14.	13	6.10	Zhu <i>et al.</i> , 2017	31.	28	~ 7.60	Islam <i>et al.</i> , 2011	48.	42	11.3	Nazeeruddin <i>et al.</i> , 1990
15.	14	6.22	Paek <i>et al.</i> , 2010	32.	29	7.89	Kuang <i>et al.</i> , 2008	49.	43	11.9	Yella <i>et al.</i> , 2011
16.	15*	6.36	Yen <i>et al.</i> , 2011	33.	30	8.02	Kuang <i>et al.</i> , 2007	50.	44	12.0	Mathew <i>et al.</i> , 2014
17.	16	6.44	Yen <i>et al.</i> , 2011	34.	31	8.10	Kuang <i>et al.</i> , 2006	51.	45	13.0	Mathew <i>et al.</i> , 2014

a: low intensity/diffused light/0.3 × full sunlight (i.e., 0.3 × 100 mW/cm<sup>2</sup> intensity). \*Same sensitizers with different values of PCE under standard AM 1.5 sunlight and 100 mW/cm<sup>2</sup> (1 full sun) intensity.

In this paper, effort has been made to address the vacuum created by the insufficient information on the reaction-structure relationship of dyes with respect to their role as sensitizers in solar cells. Such information is needed because it would provide the requisite knowledge to researchers working to design new and efficient sensitizers with high PCE values (> 20%). Furthermore, the

paper could serve as a compendium of sensitizers with PCE values above 1.00%. Literature dyes with PCE > 1.00% were selected (Table 1 and Figure 3) and have been arranged in the order of increasing magnitude to illustrate the enhancement achieved in PCE values over a period of four decades.

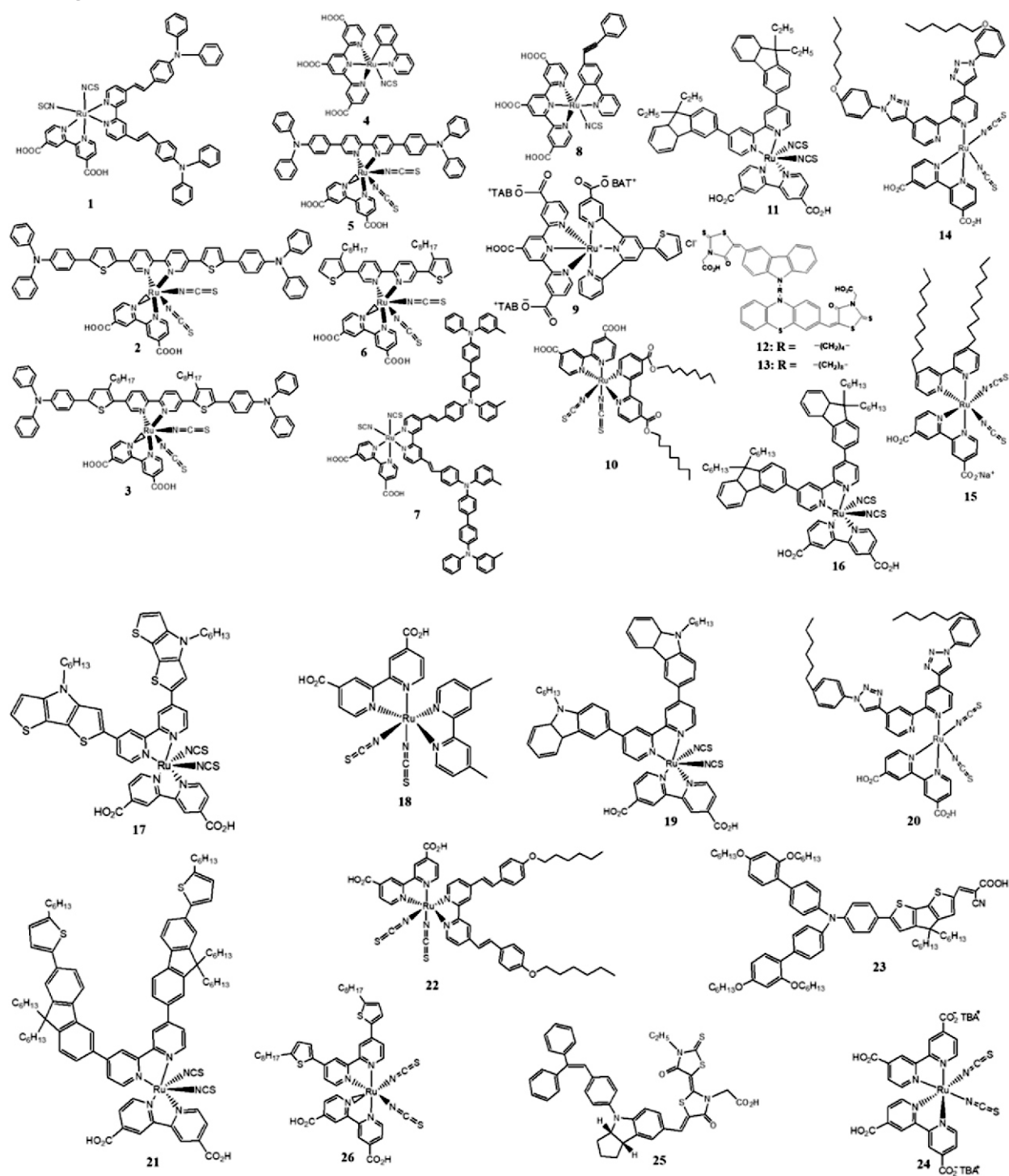


Figure 3: Chemical structures of the selected dye sensitizers.

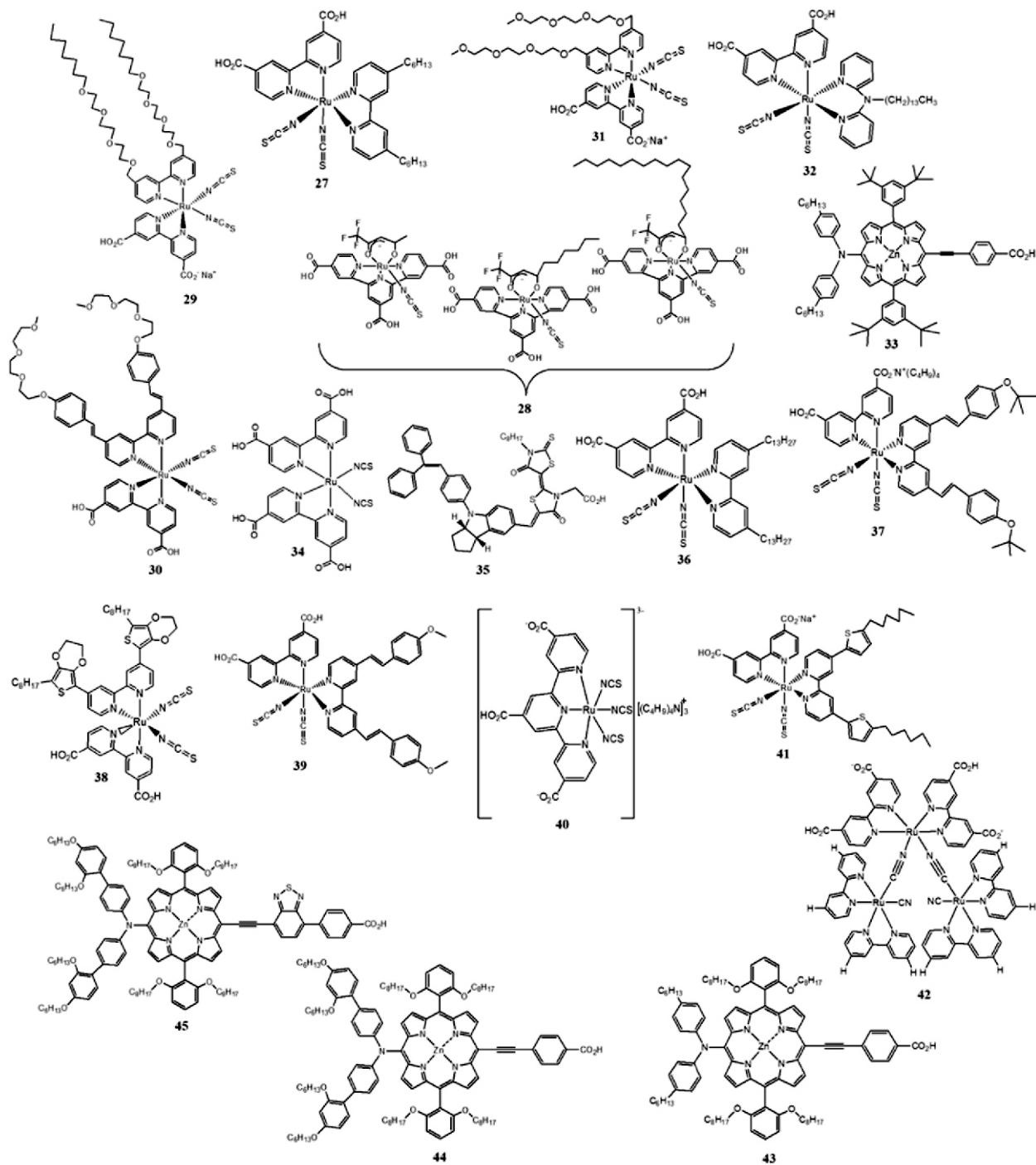


Figure 3 (contd.): Chemical structures of the selected dye sensitizers.

### HOW CAN THE STRUCTURE OF A POTENTIALLY IDEAL SENSITIZER BE BETTER PREDICTED?

Predicting the structural features of an ideal sensitizer for DSSC application has become very important in the development of efficient solar cells. By ideal, we mean a sensitizer that can produce a PCE value greater than 20%. One question that keeps coming to mind is, which

method is most suitable to predict the structure of an ideal sensitizer? Despite several attempts to answer this question (Nazeeruddin *et al.*, 2005; Gao *et al.*, 2008; Dai *et al.*, 2011), no satisfactory answer is yet to be provided to date. What is missing in most of the previous attempts was taking a very vital property of a sensitizer, such as the optical property, and linking the features in that property to the PCE value. This is what has

been carefully done in this paper using the available literature data. It is therefore envisaged that this would provide the needed information for predicting the efficiency of a sensitizer. The dye samples employed in the method development were selected from the list in Table 1, subject to the availability of their electronic absorption spectra.

The constraint to  $\text{TiO}_2$  as the semiconductor and iodide/triiodide as the redox couple was deliberate. It was done to limit the effect of varying semiconductor materials and redox couples on the PCE values, knowing that PCEs are not independent of the nature of the semiconductors and the redox couples employed in DSSCs. We narrowed down to these two materials to eliminate factors from the use of other semiconductors and redox couples, that could introduce variations into the PCE measurements. In addition, since not so much has been done in exploring other mesoporous semiconductors and redox electrolytes beyond these two,  $\text{TiO}_2$  and  $\text{I}^-/\text{I}_3^-$  couple, there would be fewer number of dyes to be selected from for the purpose of this study.

Four properties were considered critical to determining the efficiency of dye sensitizers - they include: (1) intense absorption over the whole spectral range of the sensitizer, (2) high solubility, (3) viable anchor groups, and (4) high photothermal and photochemical stabilities (Memming, (1978/79); Desilvestro *et al.*, 1985; Furlong *et al.*, 1986; Vlachopoulos *et al.*, 1988; Gerischer, 1990; Willig *et al.*, 1990; O'Regan and Grätzel, 1991; Gao *et al.*, 2000; Nazeeruddin *et al.*, 2001; Nazeeruddin *et al.*, 2004; Wang *et al.*, 2004; Wang *et al.*, 2004; Nazeeruddin *et al.*, 2005; Wang *et al.*, 2005; Wang *et al.*, 2005; Kuang *et al.*, 2006; Kuang *et al.*, 2006; Kuang *et al.*, 2007; Chen *et al.*, 2007; Karthikeyan *et al.*, 2007; Kawano *et al.*, 2007;

Fernando and Senadeera, 2008; Gao *et al.*, 2008; Ito *et al.*, 2008; Kuang *et al.*, 2008; Kuang *et al.*, 2008; Funaki *et al.*, 2009; Song *et al.*, 2009; Dai *et al.*, 2011; Islam *et al.*, 2011; Kisserwan and Ghaddar, 2011; Paek, 2011; Yella *et al.*, 2011; Yen, 2011; Mathew *et al.*, 2014; Zhu *et al.*, 2017). An efficient solar cell should produce electricity under both diffuse and full sunlight conditions. The PCEs of DSSCs obtained with diffuse (low intensity incident) sunlight have been repeatedly shown to be higher than those obtained using  $100 \text{ mW/cm}^2$  (1 full sun) light intensity, showing that the output power produced by a DSSC is not directly proportional to the intensity of the incident sunlight (Kuang *et al.*, 2006; Kuang *et al.*, 2006; Kuang *et al.*, 2007, Gao *et al.*, 2008; Kuang *et al.*, 2008). The report herein therefore contained PCE data obtained under AM 1.5 at 1 full sun intensity except where otherwise stated, to set a uniform standard of comparison between multiple sensitizers.

## OPTICAL AND SOLUBILITY PROPERTIES

The optical and solubility properties of sensitizers can be directly or indirectly evaluated from their electronic spectral data. The PCE values of the sensitizers have been compared to the spectrum power,  $I(\lambda)$ , evaluated from the dyes' spectral data (Table 2). The effects of other components of DSSCs, like the mesoporous semiconductor layer and the liquid electrolyte system have been exempted in this consideration. This is because the selected dyes were mostly for DSSCs in which only titanium (IV) oxide and iodide-triiodide electrolyte couple were used as the n-type semiconductor photoanode and the p-type counter electrode respectively. The net effects of the semiconductor and the electrolyte systems on the efficiency of the DSSCs for each of the selected dyes have therefore been assumed to be negligible.

**Table 2:** Selected dye samples whose electronic absorption spectra are available in literature.

Sensitizer	%PCE	$\Delta\lambda_1$ /nm	$\Delta\epsilon_1$ /eV	$\Delta\lambda_2$ /nm	$\Delta\epsilon_2$ /eV	$\Delta\lambda_3$ /nm	$\Delta\epsilon_3$ /eV	$\Delta\lambda_4$ /nm	$\Delta\epsilon_4$ /eV	$\Delta\lambda_5$ /nm	$\Delta\epsilon_5$ /eV	$\Delta\lambda_6$ /nm	$\Delta\epsilon_6$ /eV	I( $\lambda$ )	Ref. for Absorption Spectra
<b>1</b>	1.50	70	17.71	135	9.184	60	20.66	-	-	-	-	-	-	47.56	Karthikeyan <i>et al.</i> , 2007
<b>3</b>	2.03	65	19.07	40	31.00	130	9.537	-	-	-	-	-	-	59.61	Dai <i>et al.</i> , 2011
<b>5</b>	2.51	60	20.66	140	8.856	35	35.42	-	-	-	-	-	-	64.94	Dai <i>et al.</i> , 2011
<b>6</b>	3.00	30	41.33	80	15.50	100	12.40	-	-	-	-	-	-	69.22	Dai <i>et al.</i> , 2011
<b>7</b>	3.40	55	22.54	55	22.54	120	10.33	75	16.53	-	-	-	-	71.95	Karthikeyan <i>et al.</i> , 2007
<b>8</b>	3.70	60	20.66	50	24.80	120	10.33	200	6.199	120	10.33	-	-	72.32	Funaki <i>et al.</i> , 2009
<b>10</b>	5.36	35	35.42	65	19.07	110	11.27	110	11.27	-	-	-	-	77.04	Song <i>et al.</i> , 2009
<b>11</b>	5.94	25	49.59	50	24.80	75	16.53	150	8.266	-	-	-	-	99.19	Yen <i>et al.</i> , 2011
<b>16</b>	6.44	23	53.91	52	23.84	75	16.53	150	8.266	-	-	-	-	102.5	Yen <i>et al.</i> , 2011
<b>17</b>	6.60	25	49.59	40	31.00	85	14.59	150	8.266	-	-	-	-	103.4	Yen <i>et al.</i> , 2011
<b>19</b>	6.63	30	41.33	30	41.33	140	8.856	100	12.40	-	-	-	-	103.9	Yen <i>et al.</i> , 2011
<b>21</b>	6.91	25	49.59	100	12.40	70	17.71	-	-	-	-	-	-	79.70	Yen <i>et al.</i> , 2011
<b>26</b>	7.39	25	49.59	45	27.55	80	15.50	100	12.40	-	-	-	-	105.0	Chen <i>et al.</i> , 2007
<b>29</b>	7.89	50	24.80	80	15.50	130	9.537	-	-	-	-	-	-	49.83	Kuang <i>et al.</i> , 2008
<b>30</b>	8.02	50	24.80	70	17.71	70	17.71	90	13.78	-	-	-	-	74.00	Kuang <i>et al.</i> , 2007
<b>32</b>	8.20	60	20.66	30	41.33	45	27.55	30	41.33	95	13.05	110	11.27	155.2	Wang <i>et al.</i> , 2004

The solubility and spectral properties of each of the dyes in Table 2 were estimated from the absorbance and the electronic absorption spectral data presented in the original articles (see references in Table 1). The Lambert-Beer equation (Equation 1) that relates absorbance and concentration of color solution was used to estimate the solubility of the sensitizers since  $c \propto A$ . However, A can only be used as c if it satisfies the condition,  $A \leq 1.00$ .

$$A = \epsilon cl \quad (1)$$

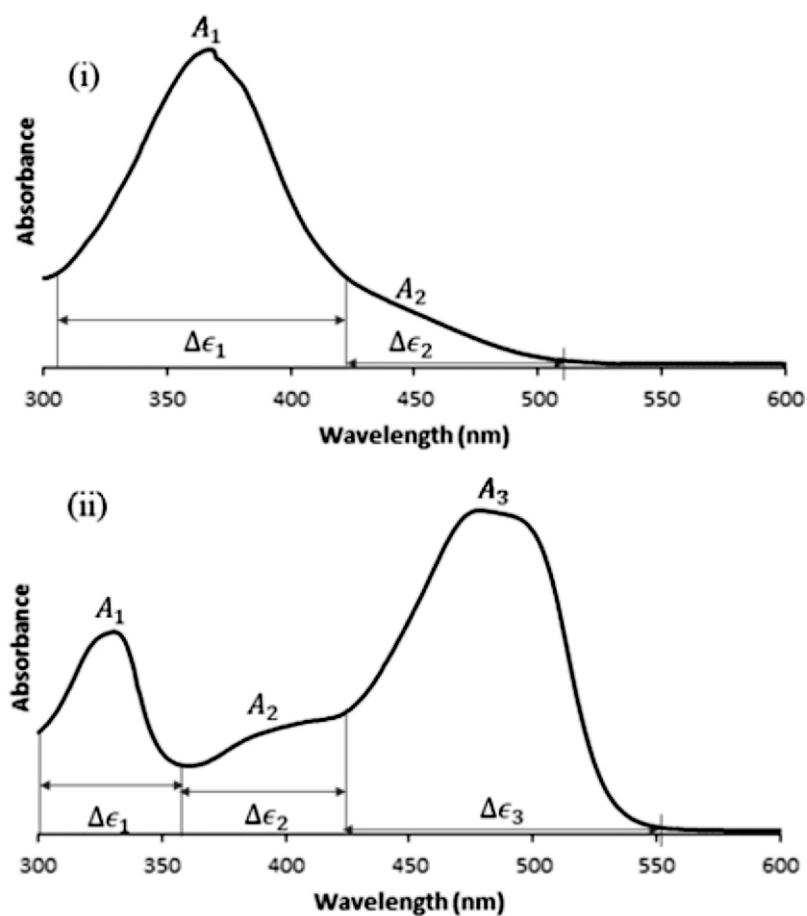
Practically, the electronic absorption spectra of sensitizers can be taken only in a suitable solvent. As a result, the effect of solvents on dyes' solubility is negligible. Solvent effect would only become significant when electronic property is the target. Also, it is worthy of note that the concentration of the sensitizers that gave the respective absorption spectra in the selected articles are not in most cases uniform, therefore, it would be misleading to directly compare the absorbances (solubility property) of dyes prepared at different concentrations. What was done instead was to normalize the respective absorbances to 1.00.

The spectrum power,  $I(\lambda)$ , has been defined as a function of the absorption bands and the intensity of the bands over the whole spectral range, according to Equation 2:

$$I(\lambda) = A \sum \Delta\epsilon_n \quad (2)$$

where A = absorbance at the  $\lambda_{max}$  (which has been taken to be 1.00 here),  $\Delta\epsilon_n$  = the energy that corresponds to the bandwidth of each of the absorption bands in eV, and n = number of absorption bands within the spectral range of the sensitizer.  $I(\lambda)$  was estimated by integrating the area under the absorption spectral curve of the sensitizer. In practice, to compare PCE values of two different sensitizers using Equation 2, equal concentration of the sensitizers must be prepared to obtain their electronic absorption spectra, from where the A expressed in the equation would be obtained. Figure 4 represents hypothetical spectral data that describes how the  $\Delta\epsilon_n$  were obtained.





**Figure 4:** Hypothetical electronic spectra showing how  $\Delta\epsilon_n$  was obtained for the sampled dyes.

Table 2 shows  $I(\lambda)$  estimated using Equation 2 for the selected sensitizers among those listed in Table 1 (they are those whose spectra were available and were clearly printed in the literature). The PCE are seen to be increasing as  $I(\lambda)$  increases, except for dyes **21**, **29**, and **30**, where  $I(\lambda)$  have shown no regular trend with the PCE. It was observed that 81.25% (13 out of 16) of the sensitizers showed increasing  $I(\lambda)$  as the PCE increases, while the remaining 18.75% (3 out of 16) showed no regular trend of the  $I(\lambda)$  with increase in PCE. This approximate method is good enough for consideration, because it shows more than 80% tolerance level to some randomly selected PCE values from the literature. One to three outliers in a total of 16 values show high tolerability of the approximate method. Therefore, it would be

accurate to deduce that an increase in  $I(\lambda)$  would be expected to lead to an increase in PCE.

### ANCHOR GROUP EFFECTS AND PHOTOTHERMAL/PHOTOCHEMICAL STABILITIES

Empirical data to reveal the influence of anchor groups and photothermal/photochemical stabilities of sensitizers on the efficiency of DSSCs are scarce. As a result, it is difficult to convincingly deduce the role of anchor groups and photothermal/photochemical properties of sensitizers on DSSC efficiency. The few reports available are very subjective because they were not arrived at by any standard parameter that is based on systematic experimental findings (Table 3).

**Table 3:** Anchor group and the qualitative report on photochemical and photothermal stabilities of the selected dye samples

cpd	Anchor grp/chain length	Position to the bipyridyl axis	Spacer btw the bipyridyl and anchor grp	Light soaking	Thermal stability
1	triphenylamine* and -CO <sub>2</sub> H**	3*, 3**	vinyl	-	-
3	octylthiophenyl-phenylbenzidine* and -CO <sub>2</sub> H**	4*, 3**	-	-	-
5	triphenylamine* and -CO <sub>2</sub> H**	4*, 3**	-	-	-
6	triphenylamine-octylthiophenyl* and -CO <sub>2</sub> H**	4*, 3**	-	-	-
7	tetraphenylbenzidine* and CO <sub>2</sub> H**	3*, 3**	vinyl	-	-
8	carboxypyridyl*, -CO <sub>2</sub> H** and ethynylbenzene***	5*, 3**, 4***	-	-	-
10	octyl acetate* and CO <sub>2</sub> H**	3*, 3**	-	-	-
11	fluorene (2 HC extension)* and -CO <sub>2</sub> H**	3*, 3**	-	-	-
16	fluorene (6 HC extension)* and -CO <sub>2</sub> H**	3*, 3**	-	-	-
17	dithieno[3,2-b;2',3'-d]pyrrole* and -CO <sub>2</sub> H**	3*, 3**	-	-	-
19	carbazole* and -CO <sub>2</sub> H**	3*, 3**	-	-	-
21	carbazole (hexylthiophene)* and -CO <sub>2</sub> H**	3*, 3**	-	-	-
26	octylthiophenyl* and -CO <sub>2</sub> H**	3*, 3**	-	-	-
29	1-(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)heptyl* and -CO <sub>2</sub> H**	3*, 3**	-	-	good
30	1-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl* and -CO <sub>2</sub> H**	3*, 3**	Vinyl	93% of initial performance	93% of initial performance
32	CO <sub>2</sub> H*	3*	-	-	-

Note that HC = Hydrocarbon

For example, Table 3 shows a summary of the anchor groups and the qualitative remarks on the photothermal/photochemical properties of the sensitizers as they affect the efficiency of DSSCs. A remark indicates that one of the sensitizers has good photothermal stability, a statement that is difficult to appreciate scientifically because it does not quantitatively reveal the depth of the “good”. Again, the 93% of the initial performance recorded for another sensitizer, even though were obtained by comparing the values of the PCE before and after thermal heating and light soaking, does not evidently show that the 7% reduction in performance was due to thermal or chemical degradation of the sensitizer.

All the selected sensitizers have -CO<sub>2</sub>H around their periphery (Figure 3) to act as the anchor point to the TiO<sub>2</sub> surface. They also have other

different substituent groups to improve their electron donor efficiency. The positions of both the -CO<sub>2</sub>H and the substituent groups to the bipyridyl axis of the complexes were indicated accordingly with symbols (◊), (◊\*) or (◊\*\*), Table 3. In all, none of these substituent groups and their positions have been specifically and scientifically shown to affect the performance of the dyes in a particular way. These facts make it difficult to rely on the effects of the nature and position of anchor groups, and the roles of photochemical and photothermal stabilities as presently given in the literature on the efficiency of DSSCs. It further justifies why only the optical and solubility properties could be the only two viable parameters that could be suggested for now as the appropriate parameter to predict the trend of PCEs of a set of selected sensitizers.

**PERSPECTIVE AND CONCLUSION**

Several research techniques have been employed to increase the efficiency of DSSCs, and these have led to the development of different classes of potential sensitizers, redox-active electrolytes, advanced mesoporous TiO<sub>2</sub> surface, and advanced solid-state polymeric semiconducting thin films for DSSCs. However, all these efforts have yielded very little results, compared to what is desired, which is having the overall efficiency of DSSC in the 20 – 30% range. Despite this reality, it may not be correct to opine that there was no dye among those considered here that possessed the requisite molecular electronic properties to produce high efficiency DSSC. The optimization of the various components of the DSSC could be what is missing to obtain high performance. Also, the availability of a correct modeling method that can mimic a real DSSC for accurate prediction of relevant photovoltaic properties would help in attaining the desired efficiency range. In this paper, the spectral properties of sixteen different sensitizers have been employed to obtain a new modeling parameter called the spectrum power of sensitizer  $I(\lambda)$ , which could be a useful index for predicting the PCE of a DSSC.

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