

Review

Fused-Thiophene Based Materials for Organic Photovoltaics and Dye-Sensitized Solar Cells

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Abstract: Organic photovoltaics (OPVs) and dye-sensitized solar cells (DSSCs) have drawn great interest from both academics and industry, due to the possibility of low-cost conversion of photovoltaic energy at reasonable efficiencies. This review focuses on recent progress in molecular engineering and technological aspects of fused-thiophene-based organic dye molecules for applications in solar cells. Particular attention has been paid to the design principles and stability of these dye molecules, as well as on the effects of various electrolyte systems for DSSCs. Importantly, it has been found that incorporation of a fused-thiophene unit into the sensitizer has several advantages, such as red-shift of the intramolecular charge transfer band, tuning of the frontier molecular energy level, and improvements in both photovoltaic performance and stability. This work also examines the correlation between the physical properties and placement of fused-thiophene in the molecular structure with regard to their performance in OPVs and DSSCs.

Keywords: organic photovoltaics; dye-sensitized solar cells; solar energy; fused-thiophenes

1. Introduction

Global warming due to greenhouse gases released from the burning of fossil fuels and an ever increasing demand for energy have spurred growing interest in environmentally benign alternative energy sources, which will eventually be needed to achieve continued and sustainable economic growth. Although nuclear power plays an important role in providing the required energy, the recent disaster in Japan aroused serious doubts about environmental safety and long term reliability of this power source. Among many options with regard to new energy sources, solar energy is regarded as one of the most ideal ones because of abundant supply and inherent inexhaustibility. The photovoltaic conversion of sunlight into electric energy is the optimal way to create a modern society powered by electricity. Various technologies have thus been developed in relation to photovoltaics, such as crystalline Si, semiconductor-based cells, thin-film solar cells, organic photovoltaics (OPVs) cells and dye-sensitized solar cells (DSSCs), all competing for the future solar cell market. Among them, OPVs and DSSCs have been considered as the most promising candidates for next-generation solar cells, due to their low cost, flexibility, and roll-to-roll mass production feasibility [1,2].

As a result of significant progress in recent years, the power conversion efficiency (PCE) of OPVs and DSSCs has greatly improved, exceeding 9% and 15%, respectively, for the current state-of-the-art devices [3,4]. However, there is still a need for improvements in PCE and costs, as well as in the long-term stability of OPVs and DSSCs, if they are to be used for practical applications. Dye molecules are the most crucial elements with regard to determining the performance of a solar cell. The development of new organic or organometallic dyes with good device performance and long term stability is thus of great importance, as this will allow the more widespread practical use of this technology. Owing to a unique combination of efficient electron transfer, a moderate band gap, environmental stability, and structural versatility, thiophene-based π -conjugated systems have progressively supplanted other classes of systems [5]. In particular, with structural ring planarity, extended molecular conjugation, intermolecular S \cdots S interactions, and chemical stability, fused-thiophenes (thienoacenes) have emerged as a promising new class of π -conjugated moieties. Most notably, dithienothiophene- (DTT) [6] and benzothenobenzothiophene- (BTBT) [7] based molecules have recently been employed as building blocks in organic semiconductors (organic thin-film transistors; OTFTs), and have exhibited huge increase in hole mobility, as high as 10.2 and 43 cm²·V⁻¹·s⁻¹, respectively.

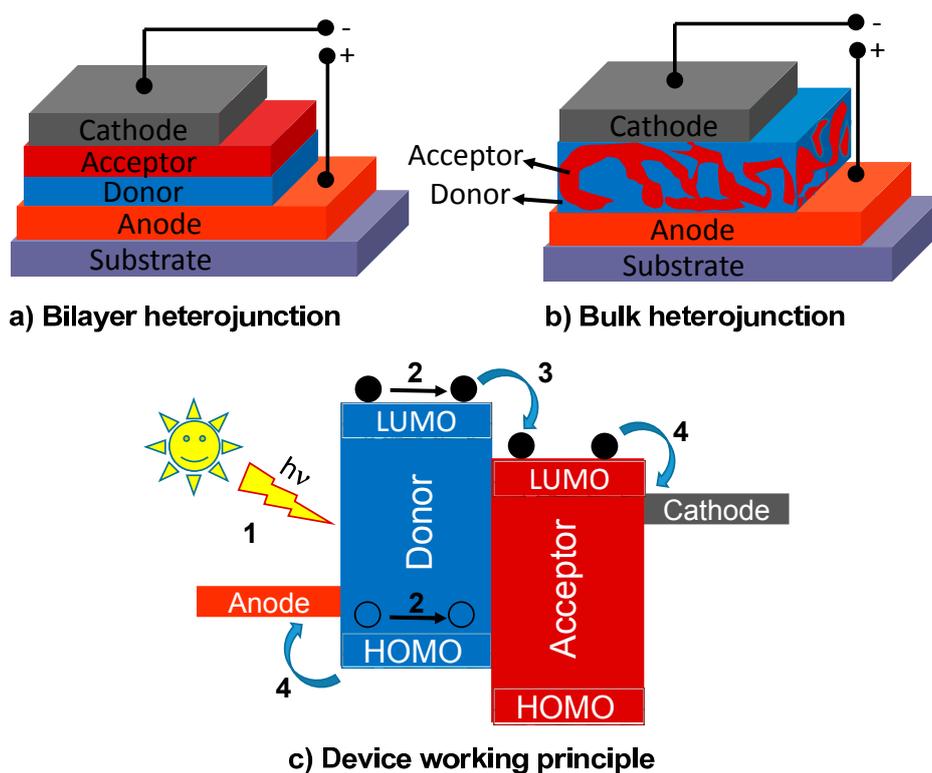
Therefore, a great deal of attention has been devoted to the performance of fused-thiophene in the particularly interesting field of OPVs and DSSCs, due to its versatility and unique properties. Herein, we review the structure-function relationships of fused-thiophene-based organic small molecules along with the most recent and significant scientific progress made in the fields of OPVs and DSSCs.

2. Organic Photovoltaics (OPV)

Organic photovoltaic (OPV) devices have attracted significant attention as a low-cost alternative to inorganic semiconductors for large area and lightweight applications [8]. Currently, polymer-based

OPVs have been shown to achieve higher power conversion efficiencies than small molecule-based OPVs. However, small molecule-based OPVs have numerous advantages, such as simple synthesis and purification methods, uniform and defined molecular structures, higher open circuit voltages (V_{oc}), and better batch-to-batch reproducibility [9,10]. Figure 1 illustrates the device structures of bilayer heterojunction (a), bulk heterojunction (b) and the fundamental steps occurring in donor-acceptor heterojunction solar cells (c).

Figure 1. Device structures of (a) bilayer heterojunction, (b) bulk heterojunction, (c) device working principle from light absorption to charge collection.



The photoenergy conversion of organic solar cells occurs in the following four steps: (i) light absorption of donor, leading to exciton formation; (ii) diffusion of the exciton within the active layer to the donor-acceptor interface; (iii) dissociation of exciton from the LUMO (lowest unoccupied molecular orbital) of the donor to LUMO of the acceptor; and (iv) collection of free charge carriers at the electrodes.

Recently, several reviews have summarized the synthesis of thiazole- and diketopyrrolopyrrole (DPP)-based small molecules and their applications in OPVs [11,12]. In this review, we particularly summarize fused-thiophene based small molecules, examining the molecular design, optical and electrochemical properties of these organic molecules, as well as their device electrical performance, as organized in Table 1.

2.1. Vacuum-Deposited Fused-Thiophene-Based Small Molecules for OPVs

Seo *et al.* prepared asymmetric electron-donor molecules based on D (donor)- π -A (acceptor) structures **1** and **2** that comprise an electron rich triphenylamine as the donor unit, thienothiophene, thiophene or thiazole as the π -spacers, and a dicyanovinylene group as the acceptor unit for

vacuum-deposited organic photovoltaic devices [13]. Chemical structures of molecules **1–8** are shown in Scheme 1. The absorption spectra of **1** and **2** in solution showed broad absorption bands over the region of 300–750 nm, and these compounds showed a broadening of the charge transfer (CT) band and a red-shift of the absorption onset by approximately 100 nm in thin films. The HOMO ((highest occupied molecular orbital) and LUMO energy levels derived from cyclic voltammetry for **1** and **2** were -5.51 eV/ -3.48 eV and -5.57 eV/ -3.58 eV, respectively. For **1**, a PCE of 5.41% was achieved with a V_{oc} of 0.87 V, a J_{sc} of 11.04 mA·cm $^{-2}$ and a fill factor (FF) of 0.57. For **2**, replacing the thiophene bridge with thiazole, the PCE was increased to 6.20% with a V_{oc} of 0.95 V, a J_{sc} of 12.01 mA·cm $^{-2}$ and an FF of 0.54. The high value of V_{oc} is attributed to its low lying HOMO level in **2**.

Hong *et al.* developed a vacuum-deposited donor material **3** based on dithieno[3,2-*b*:2',3'-*d*]thiophene (DDT) and pyrene [14]. The UV-vis spectrum of **3** showed a main absorption band at 387 nm, which originated from the DDT and pyrene units. The UV-vis spectrum of **3** in solid state showed a maximum absorption band at 412 nm. The HOMO and LUMO energy levels of **3** were -5.66 eV and -2.95 eV, respectively. The low-lying HOMO energy levels of **3** result in a large energy difference relative to the LUMO of fullerenes. The maximum V_{oc} , J_{sc} and PCE values of the BHJ device based on **3**:C $_{70}$ (1:4) were 0.98 V, 9.24 mA·cm $^{-2}$, and 3.60%, respectively.

2.2. Solution-Processed Fused-Thiophene-Based Small Molecules for OPVs

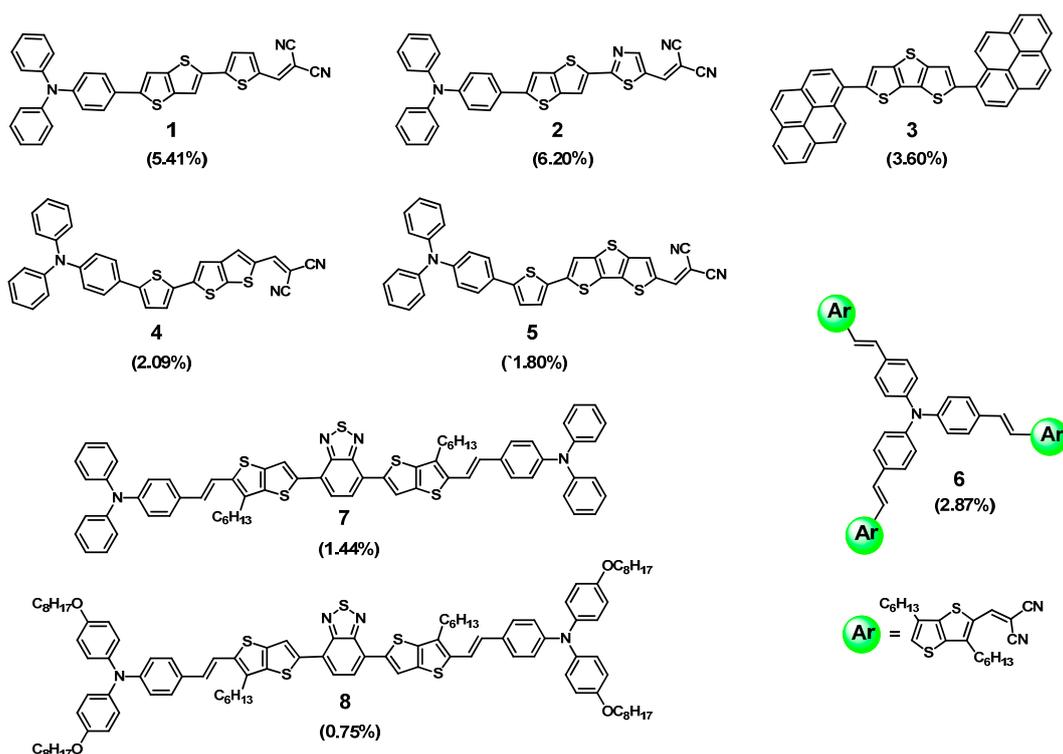
Lee *et al.* designed and synthesized a push-pull organic semiconductor (**4** and **5**) comprising a triphenylamine donor and a methylene malononitrile acceptor linked by thieno[2,3-*b*]thiophene and dithieno[3,2-*b*:2',3'-*d*]thiophene π -conjugated thiophene units [15]. The minor red-shift of the absorption band in **5** (527 nm) was due to the extended π -conjugation of the bridging units compared to **4** (523 nm). The absorption bands at longer wavelengths exhibited higher intensity for **5** than those of **4**, indicating that greater planarity and longer π -conjugation of the bridging units effectively facilitated intermolecular π - π packing interactions in the solid state. The solution-processed OPV devices based on **4**:PC $_{71}$ BM and **5**:PC $_{71}$ BM showed a PCE of 2.09% with a $J_{sc} = 7.58$ mA·cm $^{-2}$, an FF = 0.35, and a $V_{oc} = 0.80$ V for **4**; and a PCE of 1.80% with a $J_{sc} = 7.60$ mA·cm $^{-2}$, an FF = 0.31, and a $V_{oc} = 0.74$ V for **5**, respectively.

Li *et al.* synthesized a new solution-processable star-shaped D- π -A molecule **6** with triphenylamine (TPA) as the core and donor unit, dicyanovinyl (DCN) as the end group and acceptor unit, and 3,6-dihexyl-thieno[3,2-*b*]thiophene (DHT) as the π -bridge [16]. The absorption spectrum of the molecule in a chloroform solution exhibited strong absorption in a wavelength range from 300 to 650 nm, with two peaks at 429 and 542 nm, respectively. The red-shift in absorption indicated enhanced planarity in the **6** molecule. The absorption edge of **6** in the thin film was at 700 nm. The calculated HOMO and LUMO energy levels derived from cyclic voltammetry were -5.13 eV and -3.38 eV, respectively. Bulk-heterojunction OPVs were fabricated using **6** as the donor material, and either PC $_{61}$ BM or PC $_{71}$ BM as the acceptor materials. The OPV devices based on **6** as the donor and PC $_{71}$ BM as the acceptor (1:2 *w/w*) showed a V_{oc} of 0.96 V and a PCE of 2.87%. The V_{oc} of 0.96 V was among the top values for OPVs based on solution-processed TPA derivatives reported to date.

Li *et al.* also reported D-A-D type molecules (**7** and **8**) with benzothiadiazole (BT) as the acceptor unit and TPA-(4-hexyl)thieno[3,2-*b*]thiophene (TPA-HTT) or bis(octyloxy)TPA-(4-hexyl)thieno[3,2-*b*]thiophene (boTPA-HTT) as the donor units [17]. The absorption spectra of these linear molecules in

chloroform solutions exhibited strong absorption in the wavelength range from 300 to 700 nm. The absorption peaks of the thin films red-shifted a little, which indicates some aggregation of the molecules in the solid state. The absorption spectra of **7** and **8** in solutions and thin films are broader due to the larger π -conjugation of the planar thieno[3,2-*b*]thiophene unit in **7** and **8** [18]. In addition, the absorption peaks of **8** in solution and the thin film were red-shifted slightly in comparison to **6** due to the electron-donating alkoxy groups on the TPA unit in **8**. The HOMO and LUMO energy levels derived from cyclic voltammetry for **7** and **8** were -5.10 eV/ -3.42 eV and -5.01 eV/ -3.36 eV, respectively. The higher HOMO level of **8** as compared to **7** was due to the electron-donating alkoxy groups attached to TPA in **7**. The OPV devices based on **7**:PC₇₁BM and **8**:PC₇₁BM showed a PCE of 1.44% with a $J_{sc} = 5.71$ mA·cm⁻², an FF = 0.34, and a $V_{oc} = 0.74$ V for **7**; and a PCE of 0.75% with a $J_{sc} = 3.61$ mA·cm⁻², an FF = 0.31, and a $V_{oc} = 0.61$ V for **8**, respectively. Compound **8** exhibited lower PCE than that of **7**, due to the poorer morphology observed after the introduction of terminal alkoxy groups on TPA, a higher HOMO level, and poorer miscibility of the corresponding compound with PC₇₀BM.

Scheme 1. Chemical structures of OPV molecules 1–8.



Jo *et al.* synthesized an A–D–A type diketopyrrolopyrrole (DPP)-based small molecule **9** with thienothiophene as the electron donating unit [19]. Chemical structures of molecules **9**–**12** are shown in Scheme 2. The UV-vis absorption spectra showed a strong, broad absorption peak at a longer wavelength originating from the intramolecular charge transfer between the D and A units. The absorption spectra in solid state exhibited a red-shift in the maximum absorption and an onset relative to the solution state. The HOMO and LUMO energy levels of **9**, as measured by cyclic voltammetry, were -5.11 eV and -3.56 eV, respectively. The photovoltaic devices fabricated from the blends of **9** and PC₇₁BM exhibited the highest PCE of 4.0% with a J_{sc} of 9.3 mA·cm⁻², a V_{oc} of 0.81 V,

and an FF of 0.53. The morphology of the **9**/PC₇₁BM blend films with fused aromatic rings exhibited a needle-like nanoscale phase separation, which is beneficial for charge carrier transport.

Yao *et al.* reported a diketopyrrolopyrrole (DPP)-based solution-processable small molecule **10** with thieno[3,2-*b*]thiophene (TT) as the donor unit [20]. The absorption spectrum of **10** was red-shifted due to the intramolecular charge transfer (ICT) from the terminal donor (TT) to the DPP core [21]. The absorption spectra of the thin film exhibited broader bathochromic absorption for the ICT band, due to both the donor–acceptor (D–A) interactions and the extending π – π interactions caused by the strongest polarity of the amide groups in the DPP units [22]. The HOMO (–4.98 eV) and LUMO (–3.38 eV) energy levels of **10** were obtained from cyclic voltammetry. Photovoltaic devices were fabricated using **10** as the electron donor and PC₆₁BM as the electron acceptor. The best device was obtained when the donor–acceptor blend ratio was 2:1 for **10**/PC₆₁BM, with a PCE of 1.70%.

Seo, *et al.* synthesized a D–A type solution-processed small molecule **11** with dithienothiophene and diketopyrrolopyrrole chromophores [23]. The absorption spectra of **11** in both solution and thin film showed a maximum value at 670 nm. However, the absorption onset of the thin film was red-shifted by 70 nm relative to the solution due to increased aggregation and electronic delocalization in the solid state. Bulk heterojunction OPV devices were fabricated by spin-casting **11**:PC₇₁BM mixtures from chloroform solution onto substrates with various blend ratios, from 1:0.5 to 1:2. Device performance was significantly enhanced with the use of additives. The device performance was 2.19%, with a V_{oc} of 0.57 V, a J_{sc} of 9.67 mA·cm^{–2}, and an FF of 0.50.

Recently, Chen *et al.* synthesized a solution-processable A–D–A type organic small molecule (**12**) with diketopyrrolopyrrole (DPP) as the terminal acceptor units and pentathiophene as the central donor unit [24]. The absorption spectra of **12** in solution showed only one main absorption band at 600 nm, indicating an intermolecular charge transfer (ICT) between the donor and acceptor units. The absorption bands of **12** in the thin films were significantly broadened, extending the absorption onset to 782 nm. The HOMO and LUMO energy levels of **12**, as measured by cyclic voltammetry, were –5.10 eV and –3.58 eV, respectively. The optimized solar cells based on **12**/PC₇₁BM (1:1, w/w) resulted in a PCE up to 2.39% with a J_{sc} of 6.82 mA·cm^{–2}, a V_{oc} of 0.77 V, and an FF of 0.46.

3. Dye-sensitized Solar Cells (DSSCs)

Dye-sensitized solar cells (DSSCs) are efficient photovoltaics designed to convert solar energy to electricity, and since the report by O'Regan and Grätzel they have been considered to be one of the most promising next-generation renewable energy sources presently available, due to their ease of fabrication, high efficiency, and low material cost [25]. Consequently, various research groups have extensively studied the detailed operating scheme of DSSCs to identify the processes that actually limit their performance [26]. The general structure of a DSSC is composed of a transparent conducting oxide substrate, a mesoporous semiconductor film adsorbed with photosensitizer dyes, an electrolyte layer containing redox couples, and a counter electrode, as shown in Figure 2. The main processes in DSSC involve absorption of sunlight by a photosensitizer dye anchored on the mesoporous TiO₂ surface, and subsequent electron injection from the photo-excited dye molecules into the TiO₂ conduction band. The electrons are then percolated through a thin mesoscopic semiconductor film towards the conduction substrate and flow into the external circuit. Simultaneously, the oxidized dyes

are regenerated to their neutral state by the reducing species in the electrolyte solution and complete the whole circuit. DSSC devices thus repeat the cycle continuously without consuming any material to generate electric power from sunlight. Unfortunately, besides the desired pathway of the electron transfer processes, some loss reactions also occur during device operation. The injected electrons in the TiO₂ can recombine with either oxidized dyes (recombination) or the redox mediator molecules (back reaction). A unique feature of DSSCs compared to other photovoltaic technologies is to separate the function of light absorption from the charge carrier transport, which allows the optimization of the device by careful screening of the light absorber and charge transport materials.

Scheme 2. Chemical structures of OPV molecules 9–12.

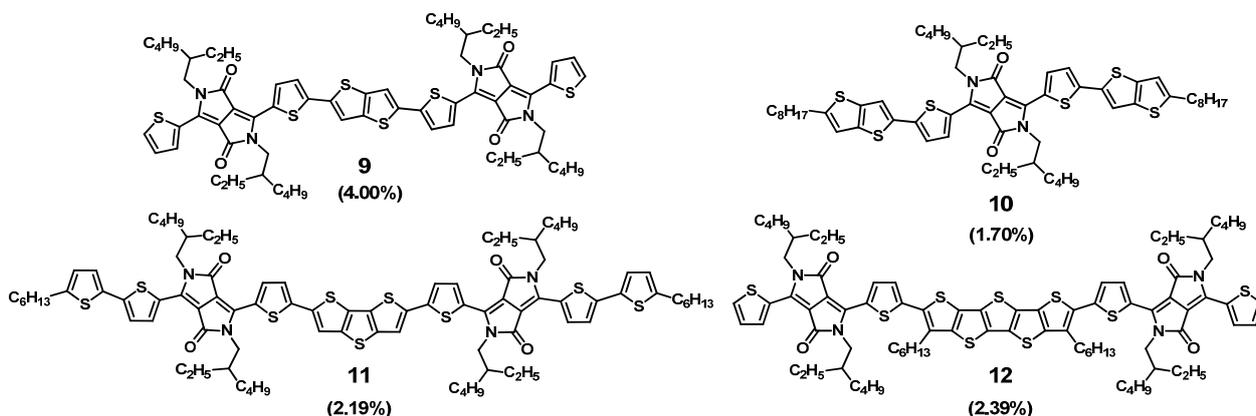
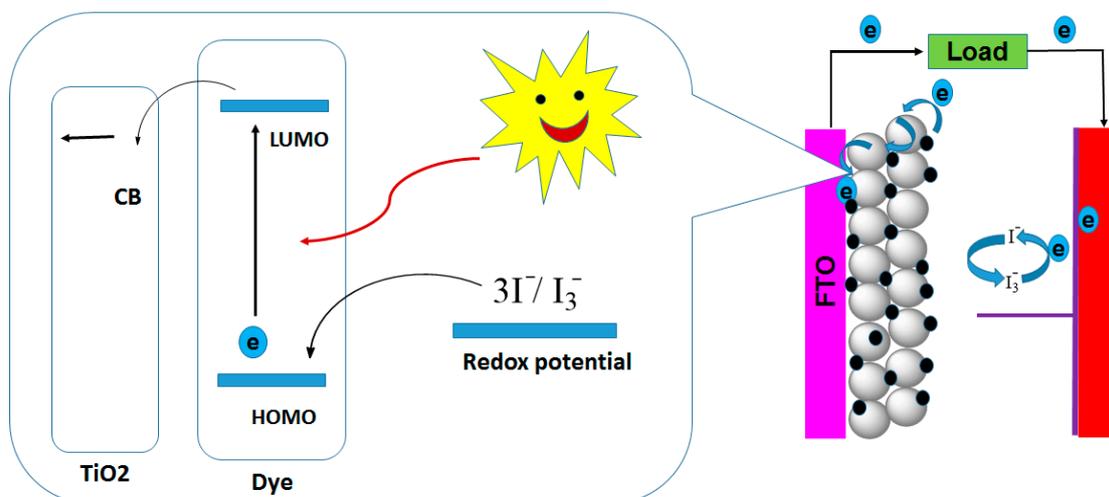


Table 1. Photophysical and photovoltaic performance of organic photovoltaics (OPVs) based on fused-thiophene containing organic semiconductors.

Cpd.	λ_{\max} (nm)	HOMO (eV)	LUMO (eV)	Band gap (eV)	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF	PCE (%)	Ref.
1 ^a	528	-5.51	-3.48	2.03	11.04	0.87	0.57	5.41	[13]
2 ^a	537	-5.57	-3.58	1.99	12.01	0.95	0.54	6.20	[13]
3 ^a	387	-5.66	-2.95	2.71	9.24	0.98	0.40	3.60	[14]
4 ^b	523	-5.15	-3.51	1.65	7.58	0.80	0.35	2.09	[15]
5 ^b	527	-5.13	-3.46	1.66	7.60	0.74	0.31	1.80	[15]
6 ^b	542	-5.13	-3.38	1.75	6.80	0.96	0.43	2.87	[16]
7 ^b	568	-5.10	-3.42	1.68	5.71	0.74	0.34	1.44	[17]
8 ^b	585	-5.01	-3.36	1.65	3.61	0.61	0.34	0.75	[17]
9 ^b	618	-5.11	-3.56	1.54	9.3	0.81	0.53	4.00	[19]
10 ^b	617	-4.98	-3.38	1.60	5.74	0.78	0.38	1.70	[20]
11 ^b	670	-5.00	-3.50	1.50	7.67	0.57	0.5	2.19	[23]
12 ^b	600	-5.10	-3.58	1.52	6.82	0.77	0.46	2.39	[24]

^a via vacuum deposition; ^b via solution process.

Figure 2. Representation of the construction and operational principle of dye sensitized solar cell.



The dye sensitizer plays a key role in the sunlight absorption and electron generation/transfer processes in a typical DSSC [1]. To improve the photovoltaic performance of DSSCs, the ideal sensitizers should meet the following requirements: (i) the absorption spectrum of the photosensitizer adsorbed TiO₂ film should cover the entire visible region with a high molar extinction coefficient to enable efficient light harvesting; (ii) molecular frontier orbital energy levels of the photosensitizers should be favorable for electron injection into the conduction band of TiO₂ and dye regeneration from the redox electrolyte; (iii) the dye molecules should possess a molecular structure capable of suppressing the dye aggregation on the semiconductor surface and charge recombination at the TiO₂/electrolyte interface; (iv) the dye should have suitable anchoring groups, such as carboxylates or phosphonates, in order to obtain high charge injection efficiencies; and (v) the photosensitizer should have photo and thermal stability to ensure that the DSSCs have a long life.

Based on these requirements, various photosensitizers, including metal-polypyridyl complexes, porphyrins, phthalocyanines, and metal-free organic dyes, have been developed and applied to DSSCs over the past two decades [27]. Among them, ruthenium and porphyrin dyes have exhibited high efficiency, although their large-scale application is limited due to many practical issues. On the other hand, metal-free organic sensitizers with good availability, ease of structural tuning, and high extinction coefficients, have recently received great attention [28,29]. However, only a few metal-free organic sensitizers have achieved >9% photovoltaic efficiency in DSSCs in combination with the classical iodide electrolyte. Moreover, achieving long-term device stability is still a great challenge. Compared to ruthenium complexes, organic dyes have many advantages, such as low material cost, ease of tuning in the spectral response and band gap, and flexibility with regard to systematic structural modification. Furthermore, the performance of the DSSCs can be effectively improved by molecular engineering, most often of sensitizers. The most commonly reported organic sensitizers for DSSCs have the structure of an electron donor- π -bridge-electron acceptor (D- π -A) chemical architecture [29]. In addition, star-burst multi-donors [30], D-A- π -A [31] and a reconfigured cross shape of double D- π -A branched dyes [32] have also been developed to modulate the spectral responses and energy levels of sensitizers. Upon light harvesting, these push-pull structures induce an intramolecular charge transfer (ICT) from donor to acceptor through the π -bridge. Moreover, hundreds of metal-free organic

dyes have been molecularly engineered in the donor, π -bridge, and acceptor moieties to tune their absorption spectra, as well as their HOMO and LUMO levels. Among the metal-free organic dyes, fused-thiophene-incorporated sensitizers, holding a validated efficiency of 9.8% without any co-adsorbent and exhibiting long-term stability, are promising candidates for highly efficient DSSCs.

Fused-thiophenes are well-known electron-rich compounds, which makes them good electron donors and important building blocks for a wide variety of materials with electronic and optical applications [33]. The performance of fused-thiophene is associated with the role of sulfur d -orbitals, which mix well with aromatic π -orbitals, such that electron-transfer across the π -center to the acceptor unit is facilitated, thereby enabling prolonged injection efficiency [34]. Furthermore, fused thiophene derivatives exhibit excellent photo and thermal stability, affording improved performance as photosensitizers. In the following section, fused-thiophene-based organic sensitizers are reviewed, with a specific focus on the relationship between the molecular structures, optical absorption, and energy levels, as well as the photovoltaic performance, as summarized in Table 2.

Fused-Thiophene-Based Sensitizers in Dye-Sensitized Solar Cells

As discussed above, to obtain organic dyes with both red-shifted absorption and high stability, introduction of new π -conjugation segment into the dye molecule is important. Yang *et al.* first introduced the thienothiophene moiety as the π -conjugation segment in compound **13**, along with rhodamine-3-acetic acid as an anchoring moiety and diethylaniline as a donor to form the D- π -A dye system [35]. Chemical structures of dyes **13–28** are shown in Scheme 3. DSSC based on **13** exhibited a higher photocurrent of $J_{sc} = 15.23 \text{ mA}\cdot\text{cm}^{-2}$ with a PCE efficiency of 6.2% as compared to a di(thiophen-2-yl)ethane-based analogue molecule.

Later, Jiang *et al.* replaced the donor and acceptor moieties with methyl-triphenylamine and cyanoacetic acid, respectively [36]. As a result, a **14**-sensitized solar cell increased the photo-current density ($J_{sc} = 15.4 \text{ mA}\cdot\text{cm}^{-2}$) and open-circuit voltage ($V_{oc} = 693 \text{ mV}$), thus enhancing the cell performance ($\eta = 6.57\%$).

Wang *et al.* reported a series of organic dyes (**15–18**) that contain a triphenylamine unit as the donor and cyanoacetic acid as the acceptor [37]. These sensitizers were prepared with different alkyl chains on the triphenylamine unit to tune their HOMO energy levels. The incident photon-to-electron conversion efficiencies (IPCE) of these sensitizers exhibited a high plateau of over 85%. The short-circuit photocurrents and light-harvesting efficiencies for DSSCs based on **15**, **16**, and **17** increased gradually along with the red-shifted photocurrent response. The DSSC based on methoxy substituted molecule **16** showed an improved power-conversion efficiency ($J_{sc} = 13.38 \text{ mA}\cdot\text{cm}^{-2}$; $\eta = 6.54\%$) as compared to that of molecule **15** ($J_{sc} = 11.74 \text{ mA}\cdot\text{cm}^{-2}$; $\eta = 5.93\%$). Further introduction of a methoxy group in the TPA part of molecule **17** switched the up-shift of the HOMO level and increased the device efficiency ($J_{sc} = 13.56 \text{ mA}\cdot\text{cm}^{-2}$; $\eta = 6.80\%$). Under the same conditions, a longer alkoxy chain containing dye molecule **18** displayed improved photovoltaic parameters ($J_{sc} = 14.49 \text{ mA}\cdot\text{cm}^{-2}$; $V_{oc} = 693 \text{ mV}$; $\eta = 7.05\%$) with a solvent-free ionic liquid electrolyte; this could be attributed to a slower charge recombination rate and longer electron lifetime due to two hexyl chains with a TPA moiety. In view of the structure-property relationship of these dye molecules, the dihexyloxy-substitution on the

TPA was undoubtedly successful. In combination with a solvent-free ionic liquid electrolyte, these dyes exhibited excellent stability under thermal and light-soaking dual stress.

Recently, Seo, *et al.* [38] reported the push-pull structured organic dye molecule **19** composed of 3-hexyl thiophenes and a planar fused-thiophene (TT) ring as a π -conjugated linker, which increased the conjugation length to broaden the absorption spectrum and the molar extinction coefficient. Various photoelectrode films were utilized to improve the light-harvesting capability as well as the photon conversion efficiency. The high and broad IPCE value (93% at 460 nm) of the **19**-sensitized DSSC within the visible region was attributed to the π -conjugated linker composed of thiophenes and a thienothiophene ring. Dye molecule **19**-based DSSC with a hierarchically structured TiO₂ (HS-TiO₂) electrode showed a surprisingly high J_{sc} value of 20.9 mA·cm⁻² among the reported meta-free sensitized DSSCs. A solar-cell device based on sensitizer **19** yielded high overall conversion efficiencies of up to 9.18% and 7.44% after 800 h of irradiation with a light intensity of 100 mW·cm⁻², using an HS-TiO₂ electrode without an antireflection layer.

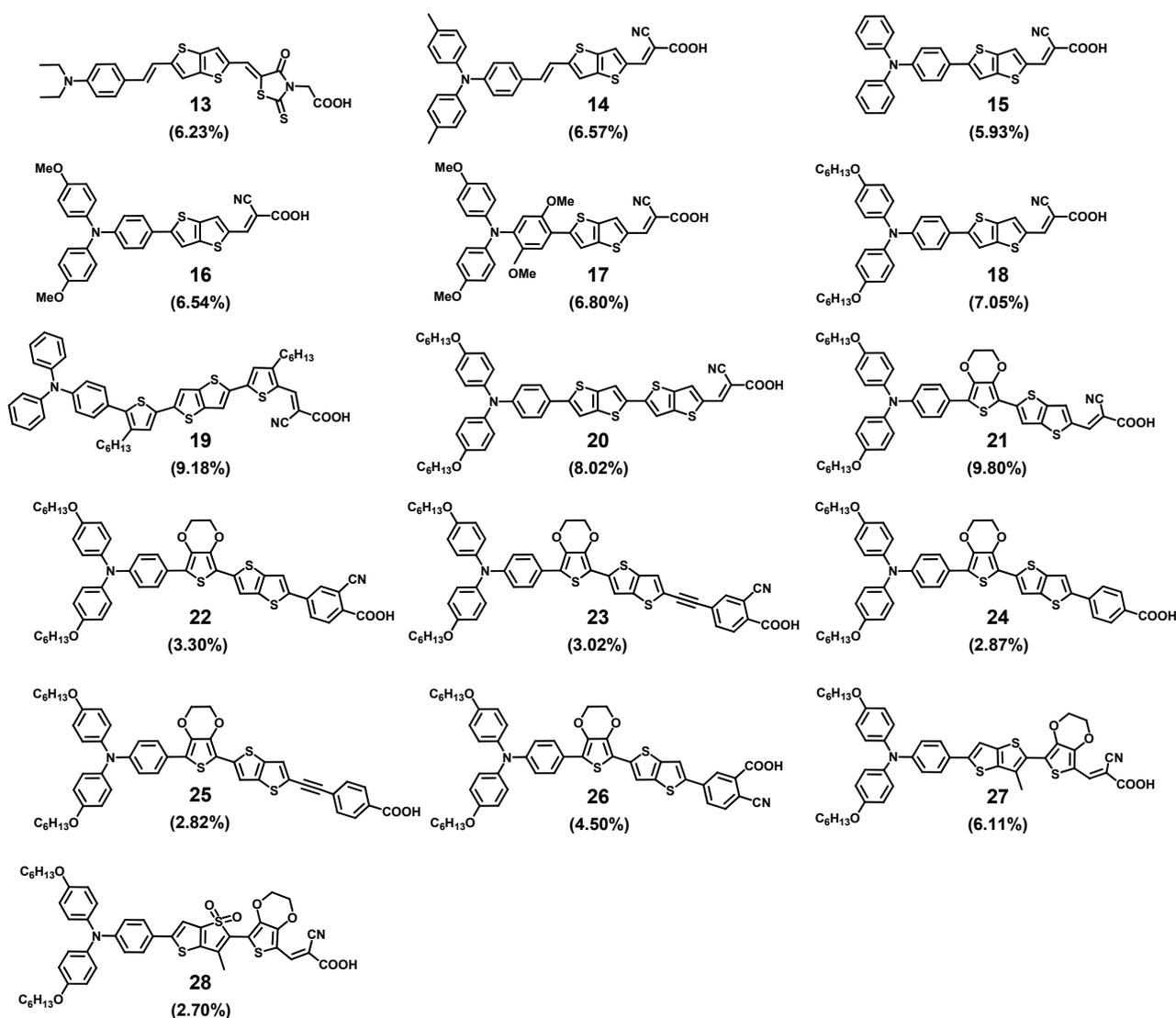
To further enhance the light-harvesting capacity and to gain insights into the related optoelectronic properties, Wang *et al.* investigated the cell performance of sensitizers **20** and **21**, using an extension of the thienothiophene π -spacer with thienothiophene and 3,4-ethylenedioxythiophene (EDOT) units, respectively [39,40]. The IPCE of dye **20** exceeded 80% in the range of 400–610 nm, yielding a high J_{sc} (15.2 mA·cm⁻²) value and an overall conversion efficiency of 8.02%. Using solvent-free ionic-liquid electrolytes, the sensitizer yielded a reasonable conversion efficiency of 6.5%. In particular, this cell showed good stability during 1000 h operation under full sunlight-soaking conditions at 60 °C. Nevertheless, bithienothiophene dye **20** exhibited only an 8 nm bathochromically-shifted absorption peak (λ_{max} = 524 nm) compared to its counterpart dye **18** (λ_{max} = 516 nm). In contrast, when the spacer was incorporated with EDOT and thienothiophene, the absorption peak of **21** (λ_{max} = 552 nm) was red-shifted by 36 nm compared to that of **18**. DSSC based on dye **21** with a double layer TiO₂ film had an IPCE of greater than 90% in the range of 440–590 nm, along with an impressive efficiency of 9.8% in an iodine electrolyte consisting of 1.0 M 1,3-dimethyl-imidazolium iodide, 50 mM LiI, 30 mM I₂, 0.5 M *t*-butylpyridine, and 0.1 M guanidium thiocyanate in acetonitrile-veleronitrile (85:15, *v/v*). It should be noted that along with a high J_{sc} (16.1 mA·cm⁻²) related to good light-harvesting, dye **21** also exhibited a high V_{oc} (803 mV) and an FF (0.759). Interestingly, the researchers claimed that the device with a solvent-free ionic liquid electrolyte showed cell performance of 8.1%. Moreover, they demonstrated the high stability and efficiency of a DSSC based on **21** in a solvent-free electrolyte.

Later, Grätzel *et al.* group modified the anchoring group into cyano-substituted benzoic acid to make efficient sensitizers (**22–26**) [41,42]. They found that the cyano-substituent improved the ICT and allowed for a better adsorption on TiO₂, thus leading to improved DSSC performance. Moreover, DSSC based on **26**, with the cyano-substituent in a *para*-position, showed better photovoltaic performance, with a maximum IPCE of 80% and an efficiency of 4.50% in contrast with dye **22**, which had a cyano-group in the *meta*-position (η = 3.30%). The insertion of an acetylene bond between the TT spacer and the benzoic acid (**23** and **25**) had no significant influence on cell performance.

Further, Xue *et al.* studied the structure-function relationship of dye molecules incorporating electron-rich and electron-deficient thienothiophene units. Two push-pull organic dyes (**27** and **28**) incorporating a binary spacer in orderly TT (3-methylthieno[3,2-*b*]thiophene (MTT) and 3-methylthieno[3,2-*b*]thiophene-4,4-dioxide (MTTO), respectively) and EDOT units showed similar absorption peaks

at 494 and 492 nm, respectively. Importantly, the MTT bridged dye **27** enhanced not only the J_{sc} ($14.47 \text{ mA}\cdot\text{cm}^{-2}$), but concomitantly the V_{oc} (670 mV), yielding a high conversion efficiency (6.11%). The higher efficiency of **27** was attributed to an effective semiconductor surface blocking capability that occurred as a result of injecting the photogenerated electrons inside the TiO_2 network with prolonged electron lifetime [43].

Scheme 3. Chemical structures of dyes **13–28**.



Wang *et al.* further optimized the thienothiophene dye by introducing a fluorine-based triarylamine moiety to suppress the aggregation and molecular stacking, based on dye **15** [44]. Such a variation in the donor moiety brought a 21 nm red-shift in the absorption spectra. The IPCE (incident photon conversion efficiency) exceeded 80% from 450 to 580 nm, reaching a maximum of 91%. DSSC based on **29** with an acetonitrile-based electrolyte under an irradiance of AM 1.5G full sunlight showed an efficiency of 7.8% through enhancement of the J_{sc} ($13.35 \text{ mA}\cdot\text{cm}^{-2}$) and V_{oc} (777 mV). In addition, the devices based on a solvent-free ionic liquid electrolyte and an all-solid-state hole-transporting material exhibited impressive cell performances of 7.0% and 4.8%, respectively, and also showed excellent light soaking stability at 60 °C for 1000 h. Chemical structures of dyes **29–40** are shown in Scheme 4.

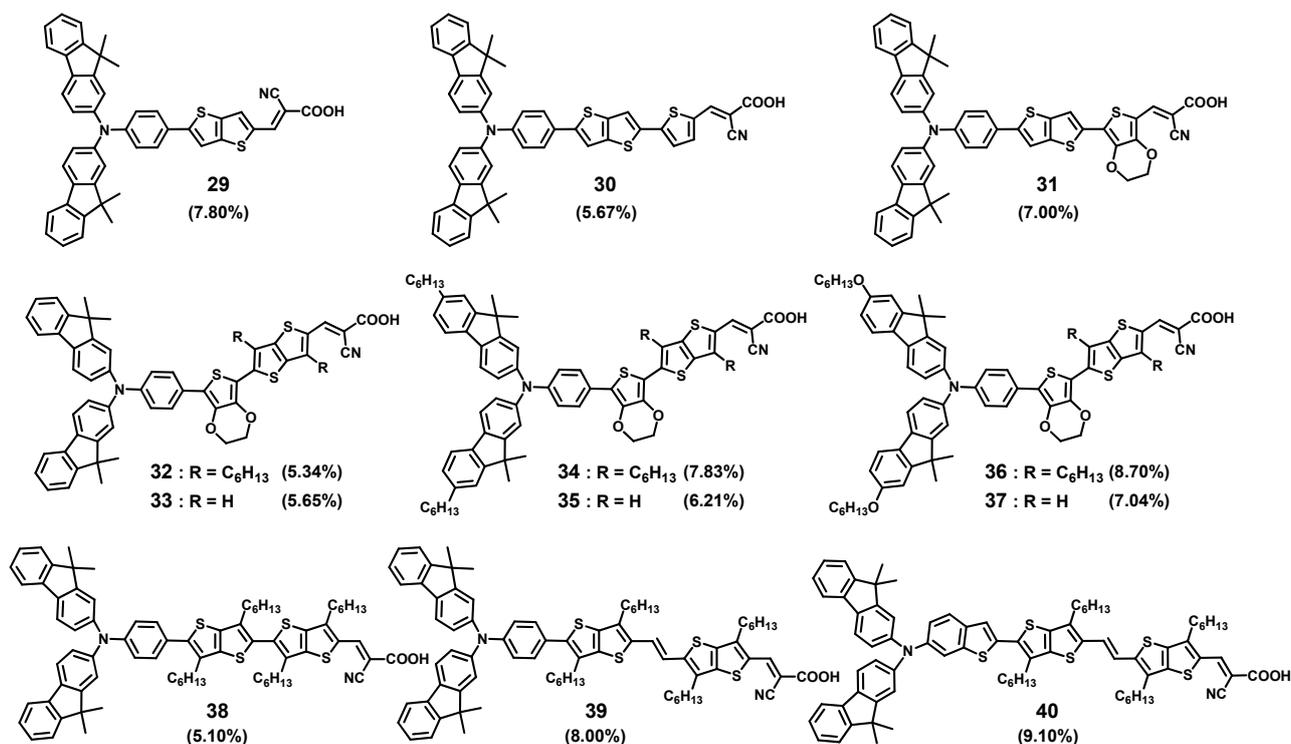
More recently, Ko *et al.* developed two organic dyes by incorporating thienothiophene-thiophene **30** and thienothiophene-EDOT **31** as the π -bridges [45]. However, such a small variation in the π -conjugation of the two dyes resulted in a 33 nm difference in their absorption spectra. In a CHCl_3 solution, **31** bearing EDOT as an electron linker, showed a significant red shift in the long-wavelength band (469 nm) compared with that of dye **30** (436 nm). When adsorbed onto the TiO_2 , the absorption peak maximum was blue-shifted by 28 nm for **30** and red-shifted by 4 nm for **31**. These blue- and red-shifts of the absorption peaks on the TiO_2 film were attributed to *H*- and *J*-aggregation, respectively. Retardation of the charge recombination caused by the existence of the EDOT group linked to the thienothiophene segment effectively suppressed the approach of I_3^- ions in the electrolyte to the TiO_2 surface, resulting in an increase in the electron lifetime. As a consequence, an improvement in the V_{oc} (731 mV) and hence a high PCE (7.00%) was achieved for the DSSC based on **31**.

Attempts at structural optimization of thienothiophene-based dyes **32–37** have also been made by incorporating long alkyl groups into the spacer group and triphenylamine derivatives [46]. Compared with hexyl-substituted thienothiophene **32**, an unsubstituted TT group on the spacer unit of **33** extended the photoresponse to a panchromatic spectrum. It is notable that increasing the donating capability of the triphenylamine unit with hexyl or hexyloxy groups enhanced their absorption spectrum, while showing a blue-shift compared to the corresponding dyes with an unsubstituted TT spacer group. DSSC based on **36** and a redox electrolyte consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.05 M I_2 , 0.1 M LiI, and 0.5 M TBP (4-*tert*-butylpyridine) in acetonitrile exhibited an IPCE of greater than 85% in the range of 440–620 nm, with the absorption onset at 800 nm. The **36**-sensitized device had the highest conversion efficiency among the six sensitizers, because of its broad and intense photocurrent action spectrum. Under standard global AM 1.5 solar conditions, the **36**-sensitized cell resulted in a J_{sc} of $17.49 \text{ mA}\cdot\text{cm}^{-2}$, a V_{oc} of 0.70 V and an FF of 0.70, corresponding to an overall conversion efficiency of 8.70%. Under the same conditions, the dye **37**-sensitized cell exhibited an efficiency of 7.04%. Moreover, the open circuit voltage and short circuit photocurrent for the device based on **36** were significantly higher than those of the other dye molecules. Importantly, the V_{oc} of the **36**-based cell increased by 40 mV relative to that of the **37**-based cell. This improved V_{oc} value was attributed to the suppression of a dark current through the blocking effect of the hexyl group substituted at the thienothiophene unit. This study revealed that either the end or middle alkyl chains of the dye molecules played a significant role in the attenuation of the interfacial charge recombination, which is a key determinant of the photovoltage. Also, the **36**-based ionic liquid electrolyte DSSC showed good photo- and thermal-stability, and maintained almost constant performance during 1000 h of light soaking at 60 °C.

Efficient organic sensitizers **39** and **40**, consisting of a dimethylfluorenylamino-appended thienothiophene-vinylene-thienothiophene unit with aliphatic chains to maintain the planar geometry of the conjugated linker, along with dye **38** comprising a thienothiophene-thienothiophene unit, were synthesized for comparison [47]. This type of structural modification with thienothiophene increased the extinction coefficient of the sensitizer (**38**, λ_{max} = 372 nm; **39**, λ_{max} = 480 nm; **40**, λ_{max} = 490 nm) by extending the π -conjugation of the bridging linker as well as augmenting its hydrophobicity, and also increased the stability under long-term light soaking and thermal stress. A molecular-orbital calculation revealed smooth movement of the electron from the phenyl- or benzo[*b*]thiophene to the cyanoacetic acid moiety. Under AM 1.5 irradiation, dye **40**, consisting of benzothiophene and a TT-vinylene-TT

unit in a volatile electrolyte, resulted in a J_{sc} of $17.61 \text{ mA}\cdot\text{cm}^{-2}$, a V_{oc} of 0.71 V , and an FF of 0.72 , corresponding to an efficiency of 9.1% . Under the same conditions in a solvent-free ionic liquid electrolyte, it displayed a high conversion efficiency of 7.9% , and showed long-term stability under light soaking at 60°C .

Scheme 4. Chemical structures of dyes 29–40.



Recently, Ko *et al.* introduced a planar 4,4-dimethyl-4H-indeno[1,2-*b*]thienothiophene bridging unit into the sensitizer (**41**), in which a 2-phenylthienothiophene was bridged by a dimethyl-methylene at the 2',3'-position, and showed enlargement of the π -conjugation of the indenothienothiophene unit, because the methylene bridge rendered the indenothienothiophene coplanar [48]. Chemical structures of dyes **41**–**54** are shown in Scheme 5. The IPCE of **41** exceeded 75% in the spectral range from 426 to 590 nm, and the photovoltaic performance in a volatile electrolyte afforded a PCE of 8.40% ($J_{sc} = 15.50 \text{ mA}\cdot\text{cm}^{-2}$; $V_{oc} = 0.73 \text{ V}$; FF = 0.75). Using a polymer gel electrolyte, dye **41** resulted in a J_{sc} of $16.61 \text{ mA}\cdot\text{cm}^{-2}$, a V_{oc} of 0.60 V and an FF of 0.72 , corresponding to an overall conversion efficiency of 8.31% . In addition, they claimed that the long-term stability of **41** in a quasi-solid electrolyte could be attributed to the rigid planar bridging unit.

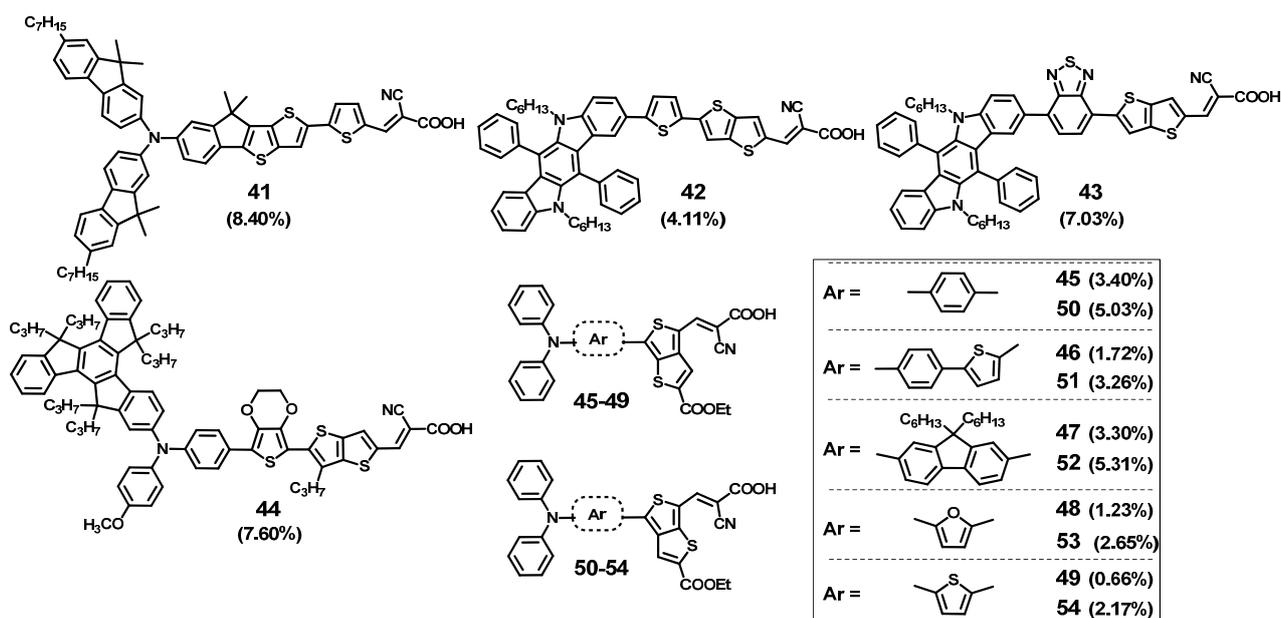
Tian *et al.* developed two organic sensitizers, **42** and **43**, containing thiophene-thienothiophene and bezothiadiazole-thienothiophene as the π -spacer, respectively, in order to enhance the photovoltaic performance and stability [49]. Furthermore, they introduced an indolocarbazole moiety and two phenyl rings connected to the central core of the donor to suppress dye aggregation when the dyes were loaded onto TiO₂ film. In the case of the CT bands of these dyes, the introduction of a bezothiadiazole unit with TT ($\lambda_{max} = 522 \text{ nm}$) resulted in a red-shifted band compared to the thiophene-TT unit ($\lambda_{max} = 464 \text{ nm}$). The larger J_{sc} ($13.96 \text{ mA}\cdot\text{cm}^{-2}$) of dye **43** demonstrated the beneficial influence of the higher and broader IPCE values. As a consequence, the overall conversion

efficiency of **43** was 6.40%. It should be noted that the DSSC based on **43** in a CHCl_3 -EtOH solvent mixture exhibited very good performance, with η up to 7.03%, a J_{sc} of $14.81 \text{ mA}\cdot\text{cm}^{-2}$, a V_{oc} of 0.69 V and an FF of 0.69.

Liang *et al.* developed a truxene-based organic sensitizer **44** bearing the binary π -conjugated linkers EDOT and an MTT unit [50]. Dye **44** showed a broad absorption spectrum covering a wide range of the visible region with superior light-harvesting efficiency, due to the strong electron-donating nature of MTT and relatively small torsional angles between the plane of the donor and that of the acceptor. The DSSC based on dye **44** with a cobalt electrolyte composed of 0.25 M $[\text{Co(II)(phen)}_3](\text{PF}_6)_2$, 0.05 M $[\text{Co(III)(Phen)}_3](\text{PF}_6)_3$, 0.5 M TBP and 0.1 M lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI) in acetonitrile afforded a J_{sc} of $11.9 \text{ mA}\cdot\text{cm}^{-2}$, a V_{oc} of 0.830 V, an FF of 0.70, and a PCE of 6.9%. In comparison, the dye **44**-sensitized cell with an iodine electrolyte exhibited a slightly increased J_{sc} of $12.2 \text{ mA}\cdot\text{cm}^{-2}$ but a remarkably decreased V_{oc} of 675 mV, leading to a relatively lower efficiency of 5.6%. It is noteworthy that varying the TBP concentration from 0.5 to 0.8 M in the cobalt electrolyte significantly enhanced the V_{oc} by as much as 70 mV, as well improving efficiency by up to 7.6%.

Lin *et al.* designed and synthesized a series of new organic sensitizers, **45–54**, containing a non-linear TT moiety of ethyl thieno[3,4-*b*]thiophene-2-carboxylate (ETTC) in the conjugated spacer [51]. This ETTC moiety and its isomeric forms were used in the sensitizers of *n*-type DSSCs. They replaced the phenyl group of the TPA attached with ETTC with phenyl thienyl, fluorene, furan, and a thienyl entity to enhance the light absorption properties. Replacement of a phenyl unit by a thienyl unit resulted in considerable red shift of the λ_{max} values, which was attributed to low delocalization energy of thiophene. However, in terms of the photovoltaic performance, the sulphur atom near to the acceptor isomeric form of TT (**50–54**) exhibited much better cell performance than its isomer with a sulphur atom away from the acceptor. DSSCs based on **50** and **52** showed the best performance among the prepared sensitizers, with efficiencies of 5.03% and 5.31%, respectively.

Scheme 5. Chemical structures of dyes **41–54**.



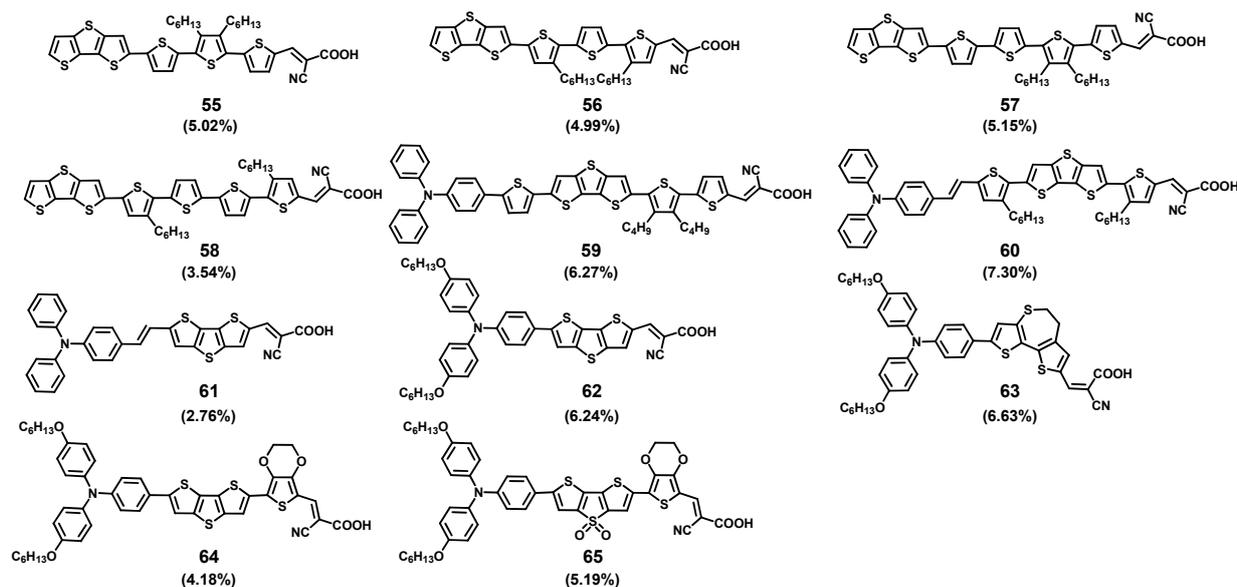
Lin *et al.* reported a series of nonarylamine type organic sensitizers, **55–58**, incorporating a dithienothiophene (DTT) unit as electron donor, an oligothiophene moiety as the conjugated spacer, and 2-cyanoacrylic acid as the electron acceptor [52]. Chemical structures of dyes **55–65** are shown in Scheme 6. These compounds had an intense adsorption band at 426–440 nm, and the conversion efficiencies of the DSSCs ranged from 3.54% to 5.15%. Density functional calculations proved that the HOMOs of these dyes largely populated on the DTT moiety as well as on the thienyl conjugation chains, indicating the efficient donating ability of the DTT entity. The higher cell efficiency of **57** as compared to other dye molecules was attributed to the higher J -aggregation value, with significantly improved light-harvesting efficiency.

Kozma *et al.* demonstrated that a sterically hindered 3,4-dialkyl thiophene ring could be advantageously incorporated with a DTT π -spacer into the dye molecule to prevent dye aggregation on the TiO₂ surface, and to enhance the tolerance of the cell towards water in the electrolyte. The cell based on **59** exhibited high conversion efficiency of 6.27% without the use of coabsorbant agents [53]. Noticeably, 100 mM DCA increased the V_{oc} , but significantly depressed the current density, resulting in very poor PCE.

In addition, Bach *et al.* developed sensitizer **60** based on a 2,6-bis[2-(3-hexylthienyl)]dithieno [3,2-*b*;2,3-*d*]thiophene core as the π -spacer [54]. Structural modification through an additional double bond and 3-hexylthiophene in the spacer caused it to exhibit a broad absorption spectrum and inhibited the electron recombination from the TiO₂ nanoparticle to the radical cation of the dye, due to the presence of the hexyl substituents. In a 12 + 6 μm double layer TiO₂ film, this dye exhibited a broad IPCE spectrum range starting from 800 nm with a high plateau at 67%. Through the optimization of the **60**-sensitized solar cell via an increase of the coabsorbant concentration up to 20 mM, the performance of the cell increased to 7.3% with a V_{oc} of 679 mV, a J_{sc} of 14.4 mA cm⁻², and an FF of 0.73. Removal of the 3-hexyl thiophene in the π -conjugation linker resulted in a hypsochromic shift in the absorption spectrum that was reflected in the performance of the device based on sensitizer **61** [55].

To develop and evaluate the potential of fused-thiophene based sensitizers, Lee *et al.* reported two organic dyes with dithienothiophene (DTT) and dithienothiepine (DPE) as bridging motifs [56]. Both of the dye molecules **62** and **63** showed similar maximum absorption wavelengths ($\lambda_{max} = 453$ and 455 nm, respectively), and **63** exhibited a band edge red-shift by ~50 nm in its absorption spectrum, with significantly reduced molar absorptivity as compared to **62**. The red-shifted absorption spectrum and low absorptivity could possibly be attributed to the reduced angular tension and the disrupted planarity of the π -conjugated conformation of the DPE motif, respectively. The devices fabricated with **62** and **63** exhibited a PCE of 3.57%, with a J_{sc} of 7.52 mA·cm⁻², a V_{oc} of 0.67 V and an FF of 0.71 for **62**, and a PCE of 4.03% with a J_{sc} of 8.24 mA·cm⁻², a V_{oc} of 0.67 V and an FF of 0.73 for **63**, respectively. The higher J_{sc} in the case of **63** might have been caused by the increased absorption range. Further, the addition of CDCA coabsorbant (30 mM) resulted in a significant increase in the photovoltaic performance of the devices based on **62** and **63** (6.24% and 6.63%, respectively), but relatively smaller increases in the V_{oc} . Importantly, the device based on DTT incorporating dye **62** exhibited long-term stability after 250 h of light soaking at 60 °C, but the DPF-based device showed a decrease in all parameters.

Scheme 6. Chemical structures of dyes 55–65.



Apart from the MTT and MTTO, other electron-rich/deficient fused thiophenes, such as dithienothiophene (DTT) and dithienothiophene-4,4-dioxide (DTTO), have also been incorporated into a D- π -A configuration by Liang *et al.* [43] Compared to the DTT counterpart, the introduction of DTTO into the binary spacer is advantageous with regard to light harvesting in terms of both the maximum absorption and the molar absorptivity. Alteration of the π -spacer into electron deficient segment **65** enhanced J_{sc} as well as V_{oc} , leading to high photon-to-current conversion efficiency of 5.19%. This result revealed that the electron-deficient DTT moiety is a promising candidate for efficient organic dyes.

Further, Lin *et al.* engineered the molecular structure of DTT-based organic sensitizer **66** featuring 3,4,5-tris (dodecyloxy)phenyl and cyanoacrylic acid moieties as the electron-donor and electron-acceptor units, respectively [57]. Chemical structures of dyes **66–74** are shown in Scheme 7. To extend the length of conjugation, bithiophene (**67**) or bithiazole (**68**) moiety was appended to the DTT unit to enhance the capacity for charge transfer and increase the range of absorption. As expected, the elongation of the π -conjugation in **67** and **68** resulted in red-shifted and broader absorptions than those of **66**. The highest PCE was obtained for the DSSC incorporating **67**, mainly because it had the highest short current density ($J_{sc} = 9.98 \text{ mA} \cdot \text{cm}^{-2}$). The remaining parameters (V_{oc} and FF) were similar for the DSSCs based on **66–68**. The IPCE spectrum of **67** featured the broadest response in the range 300–750 nm, with a maximum value of 64%, which led to the highest conversion efficiency ($\eta = 3.72\%$; $V_{oc} = 0.58 \text{ V}$; $J_{sc} = 9.98 \text{ mA} \cdot \text{cm}^{-2}$; and FF = 0.65). This result was attributed to the greater packing nature of **67**, which enhanced electron injection into the TiO_2 .

Tetrahydroquinoline was used as a donor due to its prominent electron-donating ability in the DTT-based sensitizers (**69** and **70**) by Yan *et al.* [58]. Different lengths of π -spacers were adopted for expansion of the π -conjugation backbone, adjusting the absorption spectra and HOMO/LUMO energy level of the dyes. A bathochromic shift in the absorption spectrum was achieved by the introduction of the C=C bond. A small structural change in the dyes, with/without C=C bond, resulted in significant changes in redox energy and in the adsorption characteristic of the dyes on the TiO_2 surface,

significantly affecting the DSSC performance based on these dyes. The elimination of the C=C bond in the spacer of the dye structure **70** was useful for obtaining high PCE values of 2.92% under simulated AM 1.5 irradiation ($100 \text{ mW} \cdot \text{cm}^{-2}$).

Structural modification of fused DTT-based dye **70** was performed through introducing different donating moieties of carbazole and indoline, yielding dyes **71–73** [59]. Sensitizers **72** and **73** incorporating the substituted indolines donor exhibited a red-shifted absorption relative to that of **71**, which contained a carbazole moiety. Consequently, DSSCs based on dye **72** and **73** showed an impressive total solar-to-electric conversion efficiency of 6.11% and 6.38%, respectively.

To eliminate the dye desorption during long-term device operation, Wang *et al.* reported a DTT-based sensitizer **74** by employing a fluorene-based triarylamine moiety as the donating group and volatile acetonitrile based electrolytes, showing efficiency of 8.0% with double layer titania film ($7 + 4 \mu\text{m}$) [60]. In combination with a solvent-free ionic liquid electrolyte, this dye exhibited excellent stability during a long-term accelerated test under light-soaking and thermal dual stress.

Scheme 7. Chemical structures of dyes **66–74**.

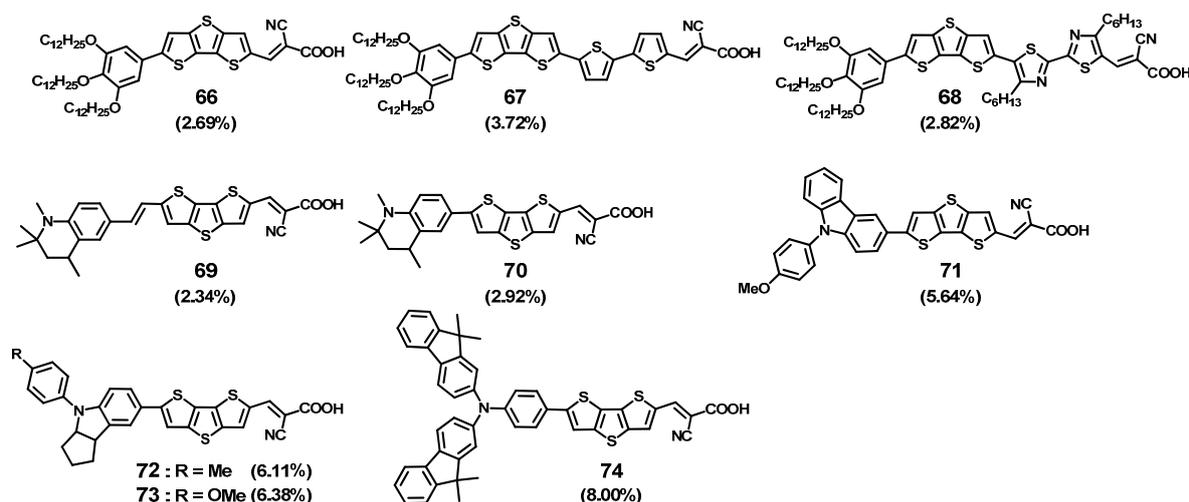


Table 2. Photophysical and photovoltaic performances of dye-sensitized solar cells (DSSCs) based on fused-thiophene containing organic sensitizers.

Dye	λ_{max} (nm)	J_{sc} ($\text{mA} \cdot \text{cm}^{-2}$)	V_{oc} (mV)	FF	η (%)	Ref.
13	488	15.23	560	0.730	6.23	[35]
14	443	15.4	610	0.700	6.57	[36]
15	493	11.74	661	0.764	5.93	[37]
16	512	13.38	664	0.736	6.54	[37]
17	517	13.56	673	0.745	6.80	[37]
18	516	14.49	693	0.702	7.05	[37]
19	450	20.9	687	0.639	9.18	[38]
20	524	15.2	720	0.733	8.02	[39]
21	552	16.1	803	0.759	9.80	[40]
22	437	7.8	600	0.705	3.30	[41]
23	445	6.56	629	0.737	3.02	[42]
24	432	5.78	688	0.718	2.87	[42]
25	439	5.70	685	0.717	2.82	[42]

Table 2. Cont.

Dye	λ_{max} (nm)	J_{sc} (mA·cm ⁻²)	V_{oc} (mV)	FF	η (%)	Ref.
26	443	8.05	756	0.733	4.50	[42]
27	494	14.47	670	0.630	6.11	[43]
28	492	7.56	567	0.630	2.70	[43]
29	514	13.35	777	0.749	7.80	[44]
30	436	11.51	670	0.731	5.67	[45]
31	469	13.26	732	0.723	7.00	[45]
32	450	13.02	570	0.720	5.34	[46]
33	481	13.81	590	0.680	5.65	[46]
34	455	16.34	640	0.740	7.83	[46]
35	476	15.22	580	0.700	6.21	[46]
36	466	17.49	700	0.700	8.70	[46]
37	484	15.94	660	0.670	7.04	[46]
38	372	9.4	710	0.750	5.10	[47]
39	480	15.7	690	0.740	8.00	[47]
40	490	17.6	710	0.720	9.10	[47]
41	485	15.50	727	0.746	8.40	[48]
42	449	9.40	644	0.680	4.11	[49]
43	486	14.81	688	0.690	7.03	[49]
44	500	11.9	900	0.710	7.60	[50]
45	524	8.80	560	0.690	3.40	[51]
46	546	4.86	520	0.690	1.72	[51]
47	496	8.14	580	0.700	3.30	[51]
48	553	3.64	500	0.680	1.23	[51]
49	570	2.92	440	0.520	0.66	[51]
50	509	12.6	610	0.660	5.03	[51]
51	536	9.21	540	0.660	3.26	[51]
52	477	12.2	640	0.680	5.31	[51]
53	523	7.52	530	0.660	2.65	[51]
54	548	6.64	510	0.650	2.17	[51]
55	429	12.09	620	0.670	5.02	[52]
56	426	12.72	610	0.640	4.99	[52]
57	440	13.31	620	0.620	5.15	[52]
58	440	9.48	570	0.660	3.54	[52]
59	465	13.5	715	0.650	6.27	[53]
60	489	14.4	697	0.730	7.30	[54]
61	472	7.3	570	0.650	2.76	[55]
62	453	12.08	680	0.760	6.24	[56]
63	455	12.66	690	0.760	6.63	[56]
64	497	11.42	600	0.610	4.18	[43]
65	514	13.52	620	0.620	5.19	[43]
66	443	6.85	570	0.700	2.69	[57]
67	476	9.98	580	0.650	3.72	[57]
68	473	6.77	600	0.700	2.82	[57]
69	467	6.87	514	0.660	2.34	[58]

Table 2. Cont.

Dye	λ_{max} (nm)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	V_{oc} (mV)	FF	η (%)	Ref.
70	444	8.84	522	0.630	2.92	[58]
71	428	13.45	618	0.679	5.64	[59]
72	481	15.85	589	0.671	6.11	[59]
73	485	16.17	595	0.663	6.38	[59]
74	525	14.33	734	0.760	8.00	[60]

4. Conclusions

This review article discussed recent developments with regard to using fused-thiophene based organic molecules for various photovoltaic applications, such as OPVs and DSSCs. Due to their unique characteristic properties, fused-thiophenes have been incorporated in the donor and π -spacer of the molecules. The photophysical properties and device performance of the organic small molecules are summarized in Tables 1 and 2 for comprehensive comparison, as well as to provide an overview of the field. Promising results with overall power conversion efficiencies of 6.20% and 9.80% are obtained from the fused-thiophene incorporated organic structure for OPVs and DSSCs, respectively. The major advantage is that such devices are easy to design and have a very high light-absorbing capacity, so that thinner films can be used to generate optimal photovoltaic performance. Importantly, fused-thiophene sensitizers with solvent-free ionic liquid electrolyte exhibited impressive efficiencies and long-term stability under light-soaking and thermal dual stress.

Despite the excellent performance of fused-thiophenes in OTFTs [61–66], fused-thiophene-based OPV and DSSC studies are still in their infancy. It is well known that there are a number of factors determining the efficiency of the photovoltaic cells, and that the multiparameter problem remains to be solved. It is important to design sophisticated and appropriate organic molecules that satisfy the needs of OPV and DSSC technologies [67–75]. Undoubtedly, there are still vast opportunities to improve performance in this area, and thus to secure an exciting future for OPV and DSSC technologies. Therefore, it is believed that continued efforts should be made with regard to the engineering of fused-thiophene based molecules and device fabrication techniques, in order to realize the potential of fused-thiophene materials in OPVs and DSSCs.

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Author Contributions

Prabakaran Kumaresan reviewed the OSC dyes papers and drafted the OSC part. Sureshraj Vegiraju reviewed the OPV papers and drafted the OPV part. Yamuna Ezhumalai worked on figures and schemes revision, Shueh Lin Yau, Choongik Kim, Wen-Hsi Lee and Ming-Chou Chen are advisors of Prabakaran Kumaresan, Sureshraj Vegiraju, Yamuna Ezhumalai, and all worked on the manuscript revision.

Conflicts of Interest

The authors declare no conflict of interest.

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