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Synthesis and Characterization of Novel di-Acceptor Carbazole Derivatives for Application to Dye Sensitized Solar Cells

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Abstract

Novel three organic dyes with the general structure donor-(π-conjugated-acceptor)$_2$ (D-(π-A)$_2$) have been designed, synthesized and characterized for application to dye sensitized solar cells (DSSCs). The high soluble electron donor and acceptor groups of the dyes were carbazole and aldehyde moieties. The conjugated chain of the dyes contains a thiophene thiophene (TT) or thiophene phenyl (TP) unit. The introduction of a fluorene ring in the donor part of these dyes to increase of light harvesting, prevent dye aggregation and suppress the dark current significantly in dye-sensitized solar cells (DSSCs). The three bulky donor dyes (D1, D2 and D3), were successfully synthesized using bromination, alkylation, Ullmann coupling and Suzuki coupling reaction. The new divergent synthetic strategy was used to overcome the key bromination step. All of the novel target structures containing a bulky and high soluble carbazole group attached to a fluorene donor unit have been characterized by ^{1}H-NMR, ^{13}C-NMR, Mass spectrometry and FT-IR spectroscopy.

KEYWORDS: Carbazole; Fluorene; Thiophene; Donor-π-conjugated-acceptor

Introduction

Conjugated organic compounds have been used as potentially active components for optoelectronic devices over the past two decades [1]. Since then, the development of organic electro active and photoactive materials has been greatly progressed such as electroluminescence (EL) devices, photovoltaic devices, thin film transistors, solid state lasers and sensitizers in DSSCs [2]. The organic optoelectronic materials have been received a great deal of attention for their application over inorganic ones because of the simplicity in modification of chemical structure, optical properties and solubility [3]. Extensive studies have shown that conjugated organic molecules exhibit a variety of interesting optical, electrical, photoelectric, and magnetic properties in solid state [4]. In 1991, Grätzel and O'Regan managed to build a 7.10% photovoltaic device based on a ruthenium based chromophore dye-sensitized 10 µm thick porous TiO_2 electrode [5]. Since then, the research of DSSCs has expanded and today there is a large research community trying to understand and improve the photovoltaic efficiency of the DSSCs, because they offer the possibility of low cost conversion of photography. The performance of the DSSCs can be quantified with incident photon to current efficiency (IPCE), open circuit photovoltage (V_{oc}) and the overall efficiency of the photovoltaic cell (η). The efficiency of the DSC is related to a large number of parameters. This work has only focused on the development of efficient metal free organic sensitizers and their synthesis for application to DSSCs.

The interest in metal-free organic dye has grown in the last two decades. In 2000 Sayama and et al. published a merocyanine dye (Mb(18)-N) which gave an efficiency of 4.20% [6]. Before this milestone, the organic dyes for DSSCs performed relatively low efficiencies (η < 1.30%). Organic dyes have some advantages over conventional ruthenium based chromophores as photosensitizers, because they exhibit high molar extinction coefficients and are easily modified due to relatively short synthetic routes and especially low cost starting materials. The high extinction coefficients of the organic dyes are suitable for thin TiO_2 films required in solid-state devices where mass transport and insufficiently pore filling limit the photovoltaic performance.

In recent years, a great deal of research aimed at finding highly efficient and stable metal free organic sensitizers with push-pull like structure. A number of coumarin, indoline, and

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triphenylamine-based organic sensitizers have been intensively investigated and some of them have reached efficiencies in the range of 3 – 8% [7]. All of these sensitizers are efficient and represent one strategy in developing new chromophores reaching as high efficiency as possible and dealing with possible stability issues of the chromophore at a later stage. Although remarkable progress has been achieved in the development of organic sensitizers reaching to 9.80% of power conversion efficiency, the research on new materials with high power conversion efficiency is still required.

Organic sensitizers featuring rod-like donor-π-acceptor structure have been extensively studied. This characteristic will induce the intramolecular charge transfer (ICT) in which high molar absorptivity and broad range of light absorption [8, 9]. Compared with Ru(II) complexes in which 1 – 4 anchoring groups are present for an efficient electron transfer, one of the drawbacks of such push-pull organic dyes is that the presence of only one anchoring group might lead to inferior efficiency. In addition, these organic dyes frequently present a single, narrow absorption band in the visible region [10]. To improve the photovoltaic performance of DSSCs, considerable efforts have been devoted to optimize the structure of the organic dyes, such as increasing the amount of anchoring groups and/or extending π-conjugation to increase the molar extinction coefficient of the absorption band, which can enhance the light harvesting ability of the dyes [11]. The dye containing double/multiple anchoring groups exhibited a unique advantage of stronger bonding with theTiO_2 surface. The binding strength of dye on the TiO_2 surface is one of the major factors which affect the PCE and stability of DSSC. Strong binding of the dyes on TiO_2 not only improves adsorption but also leads to red shift in absorption, efficient charge injection and photocurrent generation [12]. Up till now the synthesis of di-anchoring dyes (2A dyes) with high solar power-to-electricity conversion efficiency is of particular interest to synthetic chemists [10]. Mostly, the dyes containing single donor and two anchors $(D(-\pi\text{-}A)_2)$ [13, 14] frequently have higher photocurrent than their congeners with only single anchor due to their longer wavelength absorption and higher absorption capability. Therefore, it is still of great necessity to further chemical structure optimization of the double anchoring dyes to achieve more efficient DSSCs.

Carbazole derivatives represent the second strategy, starting from highly photo-stable sensitizers, dealing with the efficiency issue by introducing different substituents on the carbazole framework. The carbazole moiety serving as donor part in sensitizers has been widely studied in recent years because of the electron rich property and planarity. However, the planarity of the carbazole caused π-π aggregation leading to decrease the performance of the DSSCs. This class of carbazole dye has high absorption coefficients in the visible region. Electron injection from singlet states of the dye into the conduction band of a semiconductor is generally faster than that from triplet and it conserves more potential from the light capture. Some carbazole derivatives have been used as sensitizer in DSSCs, but their efficiency was low. Recently, the carbazole compounds-based dye-sensitized solar cells have reached efficiencies around 5.15 – 8.30% [15 – 17]. Organic dyes containing difluorenylamine donor have been extensively studied. Ko and co-workers for the first time introduced difluorenylamine donor in organic dyes and achieved high power conversion efficiency above 8.00% [18]. Thomas and co-workers synthesized fluorene-based dyes which showed longer wavelength absorption when compared to dyes containing phenylene linker [19]. The superior efficiency of the fluorene-based dyes is attributed to the fluorenylamine unit which offers strong donating strength, bulky structure which suppresses the aggregation and keeps away the electrolyte from TiO_2 film. The beneficial properties of fluorenylamine unit are due to the following reasons: (1) bulky trigonal structure with rigidity and extended conjugation and (2) the presence of alkyl chains at C9-position. Also, it has been found that light harvesting potential of the dyes containing fluorenylamine donor is largely dependent on the nature of linker which crucially alters the donor-acceptor interactions. To the best of knowledge, no previous report has described the Y shape dyes containing single donor with two π- acceptor groups $(D(-\pi\text{-}A)_2)$.

In this paper, three novel carbazole derivative dyes $(D(-\pi\text{-}A)_2)$ were designed and synthesized, named D1, D2 and D3 which differ in their structure by the nature of the π-conjugated bridge and the donor groups as shown in Fig. 1. The 9-position of the carbazole donor moiety of D1 and D2 were substituted with 9,9-didodecylfluorene containing *tert*-butylcarbazole unit at 2-position of the donor unit to enhance the light collection. Two thiophene thiophene (TT) or thiophene phenyl (TP) unit were introduced between the carbazole donor and aldehyde acceptor of D1 and D2 respectively on the principle of extension of the π-bridge which can make electron delocalize to a plurality of atoms, reduce the π-π* energy, increase the molar extinction coefficient value and promote the maximum absorption wavelength to red shift. The structure of D3 is similar to D1 but the *tert*-butylcarbazole terminal group is replace by the second generation of *tert*-butylcarbazole located at the edge of the donor molecular part on the opposite side of the acceptor group. To the best of our knowledge, this is the first time when metal-free organic dyes of such structure have been developed. To give rise to a donor-π-acceptor type compound due to its potential role in the modulation of the HOMO-LUMO gap with the HOMO lower than the redox potential of the I^-/I_3^- electrolyte (– 4.30 eV) and the LUMO less negative than the conduction bane of the TiO_2 electrode (– 4.00 eV) [20], the aldehyde acceptor moieties were decorated at the end of these molecules.

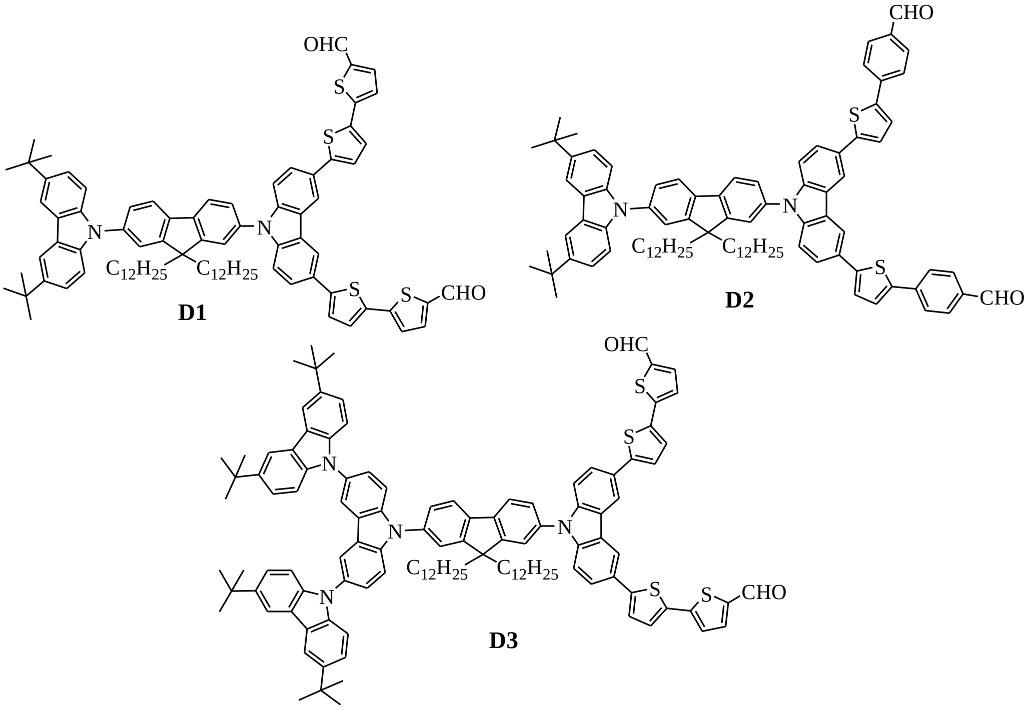

Fig. 1 Molecular structure of the target molecules (D1, D2 and D3)

Materials and Methods

^{1}H-NMR and ^{13}C NMR spectra were recorded on Brüker AVANCE (300 MHz)/ (500 MHz) spectrometer and were fully decoupled. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Multiplicities are quoted as singlet (s), broad (br), doublet (d), triplet (t), and multiplet (m). The IR spectra were performed on a Perkin-Elmer FT-IR spectroscopy as KBr disks or neat liquid between two sodiumchloride plates. The absorption peaks are quoted in wavenumber (cm^{-1}). High resolution mass spectrometry (HRMS) analysis was measured on Autoflex II Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrometer.

All reagents and solvents were purchased from Aldrich, Acros, Fluka or Thai Supplies and received unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F_{254}. Column chromatography was carried out using gravity feed chromatography with Merck silica gel mesh 60 Å. The solvent mixtures are used and the portions are given by volume.

The important intermediates of 9-(7-bromo-9,9-didodecyl-9H-fluoren-2-yl)-3,6-di-tert-butyl-9H-carbazole and 9-(7-bromo-9,9-didodecyl-9H-fluoren-2-yl)-3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazole were prepared according to the literature methods by P. Moonsin et al. [21]

Synthesis and characterization

3,6-di(thiophen-2-yl)-9H-carbazole

The intermediate, 3,6-di(thiophen-2-yl)-9H-carbazole**,** was obtained from Suzuki cross coupling between 3,6-diiodo-9H-carbazole (1.20 g, 2.38 mmol) and 2-thiophenee boronic acid (0.76 g, 5.95 mmol) in the present of $Pd(PPh_3)_4$ (0.01 g 0.04 mmol) as catalyst and 2M Na_2CO_3 (5.04 g, 47.6 mmol) in THF (15 ml) as solvent. The mixture was degassed for 2 min and protected with N_2, and then refluxed under N_2 for 12 h. After being cooled to room temperature, water (50 ml) was added. The reaction mixture was extracted with dichloromethane (30 ml × 3). The organic phase was washed with water (100 ml), and brine solution (50 ml), dried over sodium sulfate anhydrous, filtered and the solvent was removed to dryness. The residue was purified by column chromatography over silica gel eluting with 40% dichloromethane: hexane to give 3,6-di(thiophen-2-yl)-9H-carbazol as green wish solid (0.72 g , 96%).

FT-IR (KBr) : ν_{max} = 3424.34, 3098.03, 3064.42, 3014.00, 2924.36, 2845.93, 2336.13, 1700.69, 1625.17, 1605.59, 1574.82, 1530.06, 1485.23, 1465.73, 1429.20, 1393.00, 1348.25, 1325.87, 1291.41, 1255.94, 1240.87, 1216.78, 1174.82, 1135.66,1082.51, 1046.15, 1023.77, 956.64, 897.90, 872.72, 847.55, 807.64, 746.85, 697.63, 643.35, 605.42, 567.83, 497.90 and 427.97 cm^{-1}

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.33 (2H, *s*), 8.13 (1H, NH, *s*), 7.71 (2H, *d*, J = 8.10), 7.43 (2H, *d*, J = 8.10 Hz), 7.36 (2H, *d*, J = 3.00 Hz), 7.27 (2H, *d*, J = 7.20 Hz) and 7.12 (2H, *t*, J = 8.10 Hz) ppm

^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.53, 139.45, 128.54, 128.00, 126.67, 124.92, 123.86, 122.28, 117.99, and 111.06 ppm.

HRMS-ESI-TOF calcd for $C_{20}H_{13}NS_2$: m/z 331.05 found 331.12 [M$^+$]

9-(7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-3,6-di(thiophen-2-yl)-9H-carbazole

To a 100 ml flask 9-(7-bromo-9,9-didodecyl-9H-fluoren-2-yl)-3,6-di-tert-butyl-9H-carbazole (0.99 g, 1.15 mmol), 3,6-di(thiophen-2-yl)-9H-carbazole (0.38 g, 1.15 mmol), copper iodide (0.11 g, 0.57 mmol), potassium phosphate (0.61 g, 2.89 mmol) and toluene (30 ml) was added. The mixture was degassed and protected under nitrogen gas, and then *trans*-1,2-diaminocyclohexane (0.08 g, 0.57 mmol) was injected. The reaction mixture was refluxed for 24 h under N_2 atmosphere. After cooling to room temperature, the reaction mixture was filtered with silica gel and wash by dichloromethane (50 ml × 3). The combined organic solution was washed with water (100 ml), brine solution (100 ml), dried over sodium sulfate anhydrous, filtered and the solvent was stripped off under vacuum. The crude product was purified by column chromatography eluting with 30% dichloromethane: hexane to afford 9 -(7 -(3 ,6 -di-tert-butyl-9 H-carbazol-9 -yl)-9 ,9 -didodecyl-9 H-fluoren-2 -yl)-3 ,6 -di(thiophen-2 -yl)-9 H-carbazole as light green viscous (0.53 g, 70%).

FT-IR (KBr) : ν_{max} = 3904.76, 3574.22, 3546.21, 3182.07, 2917.70, 2724.20, 2666.66, 2459.38, 2028.01, 1885.31, 1801.39, 1613.98, 1455.87, 1376.84, 1303.49, 1261.53, 1169.23, 1154.85, 1074.12, 970.62, 937.06, 914.68, 889.51, 841.95, 724.47, 559.44, 514.68, 486.71, 441.95 and 400.00 cm^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.43 (2H, *s*), 8.18 (2H, *s*), 7.98 (2H, *t*, J = 5.70 Hz), 7.73 (2H, *d*, J = 8.10 Hz), 7.60 (4H, *d*, J = 7.50 Hz), 7.52 – 7.39 (8H, *m*), 7.30 (2H, *d*, J = 9.60 Hz) ppm, 7.14 (2H, *t*, J = 3.90 Hz), 2.11 (4H, *t*, J = 18.70 Hz), 1.49 (18H, *s*), 1.25 – 1.19 (40H, *m*) and 0.83 (6H, *t*, J = 6.00 Hz) ppm

^{13}C-NMR (125 MHz, $CDCl_3$) δ 153.05, 152.81, 145.42, 142.97, 141.04, 140.05, 139.36, 136.21, 128.06, 125.00, 123.98, 123.66, 122.41, 116.39, 110.35, 109.24, 40.28, 34.80, 32.08, 31.97, 30.20, 30.06, 29.73, 29.72, 29.70, 29.49, 29.40, 29.36, 24.20, 22.73, 22.69, 14.14 and 14.03 ppm

HRMS-ESI-TOF calcd for $C_{77}H_{92}N_2S_2$: m/z 1108.67 found 1108.86 [M$^+$]

3,6-bis(5-bromothiophen-2-yl)-9-(7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-9H-carbazole

A stirred solution of 9 -(7 -(3 ,6 -di-tert-butyl-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2 -yl)-3 ,6 -di(thiophen-2 -yl)-9 H-carbazole (0.51 g, 0.46 mmol) in THF (10 ml) was added NBS (0.16 g, 0.94 mmol) in small portions in a flask covered with aluminum foil. The mixture was stirred at room temperature for 12 h, and then poured into ice-cold water 20 ml. The mixture was extracted with dichloromethane (20 ml × 3). The combined organic layer was washed with water 50 ml, brine solution 30 ml and dried over anhydrous Na_2SO_4. The solvent was removed to dryness. The product was obtained by column chromatography eluting with 30% dichloromethane: hexane to give a light green viscous of 3,6-bis(5-bromothiophen-2-yl)-9-(7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-9H-carbazole (0.49 g, 86%).

FT-IR (KBr): ν_{max} = 3019.52, 2957.98, 2927.22, 2851.54, 2392.15, 1734.26, 1608.39, 1521.67, 1481.79, 1420.97, 1367.83, 1325.87, 1292.30, 1215.55, 1046.15, 976.22, 925.87, 875.52, 756.28 and 668.69 cm^{-1}

^{1}H-NMR (300 MHz, CDCl$_3$) δ 8.32 (2H, *s*), 8.21 (2H, *s*), 7.98 (2H, *d*, *J* = 8.40 Hz), 7.63 (2H, *d*, *J* = 6.00 Hz), 7.57 (2H, *d*, *J* = 3.00 Hz), 7.57 – 7.43 (10H, *m*), 7.13 (2H, *d*, *J* = 3.60 Hz), 7.09 (2H, *d*, *J* = 3.30 Hz), 2.10 (4H, *s*), 1.52 (18H, *s*), 1.34 – 1.22 (40H, *m*) and 0.86 (6H, *t*, *J* = 6.00 Hz) ppm

^{13}C-NMR (75 MHz, CDCl$_3$) δ 153.11, 152.80, 146.82, 143.00, 141.23, 139.33, 130.90, 126.48, 124.70, 123.76, 123.67, 123.52, 122.52, 116.41, 110.55, 110.37, 109.23, 55.79, 40.25, 34.80, 32.07, 31.93, 30.03, 29.73, 29.72, 29.69, 29.47, 29.36, 24.19, 22.68 and 14.12 ppm

HRMS-ESI-TOF calcd for $C_{77}H_{90}N_2S_2Br_2$: *m/z* 1266.49 found 1266.77 [M$^+$]

The D1 was obtained from Suzuki cross coupling between 3,6-bis(5-bromothiophen-2-yl)-9-(7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-9H-carbazole(0.19 g, 0.13 mmol) and 2-formylthiophene boronic acid (0.06 g, 0.41 mmol) in the present of Pd(PPh$_3$)$_4$ (0.003 g 0.002 mmol) as catalyst and 2M Na_2CO_3 (0.29 g, 2.78 mmol) in THF (15 ml) as solvent. The mixture was degassed for 2 min and protected with N_2, and then refluxed under N_2 for 12 h. After being cooled to room temperature, water (30 ml) was added. The reaction mixture was extracted with dichloromethane (20 ml × 3). The organic phase was washed with water (50 ml), and brine solution (20 ml), dried over sodium sulfate anhydrous, filtered and the solvent was removed to dryness. The residue was purified by column chromatography over silica gel eluting with 60% dichloromethane: hexane to give D1 as orange wish solid (0.72 g, 96%).

FT-IR (KBr) : ν_{max} = 3056.88, 2952.39, 2919.26, 2853.21, 1871.17, 1662.87, 1629.98, 1610.79, 1516.82, 1547.75, 1481.97, 1443.60, 1394.26, 1377.82, 1364.11, 1323.00, 1292.85, 1202.70, 1164.03, 1122.92, 1006.47, 1076.32, 1048.92, 1018.77, 972.17, 947.50, 917.35, 876.24, 840.61, 804.98, 791.27, 757.90,717.27, 665.19, 613.12 and 541.86 cm^{-1}

^{1}H-NMR (300 MHz, CDCl$_3$) δ 9.87 (2H, *s*), 8.44 (2H, *s*), 8.17 (2H, *s*), 8.00 – 7.96 (2H, *m*), 7.73 – 7.68 (6H, *s*), 7.60 – 7.27 (14H, *m*), 2.04 (4H, *t*, *J* = 12.0 Hz), 1.53, (18H, *s*), 1.23 – 1.17 (40H, *m*) and 0.87 (6H, *t*, *J* = 12.0 Hz) ppm

^{13}C-NMR (75 MHz, CDCl$_3$) δ 182.59, 153.13, 152.76, 147.47, 147.19, 144.84, 143.86, 142.99, 141.41, 141.30, 139.24, 137.56, 136.97, 134.26, 127.35, 126.50, 126.25, 124.80, 123.76, 123.66, 123.47, 121.13, 117.94, 116.41, 110.67, 109.19, 55.78, 40.23, 34.79, 32.06, 31.92, 30.02, 29.72, 29.48, 29.37, 24.18, 22.68 and 14.13 ppm

HRMS-ESI-TOF calcd for $C_{87}H_{96}N_2O_2S_4$: *m/z* 1328.64 found 1328.99 [M$^+$]

The D2 was obtained from Suzuki cross coupling between 3,6-bis(5-bromothiophen-2-yl)-9-(7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-9H-carbazole (0.23 g, 0.17 mmol) and 4-formylphenyl boronic acid (0.10 g, 0.70 mmol) in the present of Pd(PPh$_3$)$_4$ (0.004 g 0.003 mmol) as catalyst and 2M Na_2CO_3 (0.37 g, 3.52 mmol) in THF (15 ml) as solvent. The mixture was degassed for 2 min and protected with N_2, and then refluxed under N_2 for 12 h. After being cooled to room temperature, water (30 ml) was added. The reaction mixture was extracted with dichloromethane (20 ml × 3). The organic phase was washed with water (50 ml), and brine solution (20 ml), dried over sodium sulfate anhydrous, filtered and the solvent was removed to dryness. The residue was purified by column chromatography over silica gel eluting with 60% dichloromethane: hexane to give D2 as orange wish solid (0.11 g, 46%).

FT-IR (KBr) : ν_{max} = 3056.88, 2952.39, 2919.26, 2853.21, 1871.17, 1662.87, 1629.98, 1601.79, 1516.82, 1547.75, 1481.97, 1443.60, 1394.26, 1377.82, 1364.11, 1323.00, 1292.85, 1202.70, 1164.03, 1122.92, 1006.47, 1076.32, 1048.92, 1018.77, 972.17, 876.24, 840.61, 804.98, 791.27, 757.90, 717.27, 665.19, 613.12 and 541.86 cm^{-1}

^{1}H-NMR (300 MHz, CDCl$_3$) δ 10.03 (2H, *m*), 8.49 (2H, s), 8.21 (2H, s), 8.01 (2H, *t*, *J* = 6.00 Hz), 7.94 (4H, *d*, *J* = 7.80 Hz), 7.84 (4H, *d*, *J* = 8.10 Hz), 7.79 (2H, *d*, *J* = 8.10 Hz), 7.62 (4H, *d*, *J* = 7.20 Hz), 7.58 – 7.44 (10H, m), 2.09 (4H, *s*), 1.52, (18H, *s*), 1.28 – 1.22 (40H, *m*) and 0.85 (6H, *t*, *J* = 6.90 Hz) ppm

^{13}C-NMR (75 MHz, CDCl$_3$) δ 191.70, 191.39, 174.09, 153.13, 152.78, 143.00, 140.21, 139.28, 134.93, 130.56, 128.04, 126.25, 125.54, 123.65, 123.49, 116.40, 110.62, 109.19, 66.69, 62.12, 55.79, 53.42, 40.25, 34.78, 32.05, 31.94, 31.91, 30.45, 30.02, 29.73, 29.69, 29.68, 29.37, 29.35, 29.12, 28.94, 24.18, 22.70, 22.66, 14.12, 14.09 and 14.04 ppm

HRMS-ESI-TOF calcd for $C_{91}H_{100}N_2O_2S_2$: *m/z* 1316.72 found 1317.36 [M$^+$]

3,6-di-tert-butyl-9-(9-(7-(3,6-di(thiophen-2-yl)-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-9H-carbazole9-(2-bromo-9,9-didodecyl-9H-fluoren-7-yl)-9H-carbazole

To a 100 ml flask 9-(9-(7-bromo-9,9-didodecyl-9H-fluoren-2-yl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-3,6-di-tert-butyl-9H-carbazole (2.08 g, 1.60 mmol), 3,6-di(thiophen-

2-yl)-9H-carbazole (0.53 g, 1.60mmol), copper iodide (0.30 g, 1.60 mmol), potassium phosphate (1.02 g, 4.80 mmol) and toluene (50 ml) was added. The mixture was degassed and protected under nitrogen gas, and then *trans*-1,2-diaminocyclohexane (0.18 g, 1.60 mmol) was injected. The reaction mixture was refluxed for 24 h under N_2 atmosphere. After cooling to room temperature, the reaction mixture was filtered with silica gel and wash by dichloromethane (50 ml × 3). The combined organic solution was washed with water (50 ml), brine solution (50 ml), dried over sodium sulfate anhydrous, filtered and the solvent was stripped off under vacuum. The crude product was purified by column chromatography eluting with 10% dichloromethane: hexane to afford 3,6-di-tert-butyl-9-(9-(7-(3,6-di(thiophen-2-yl)-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-9H-carbazole9-(2-bromo-9,9-didodecyl-9H-fluoren-7-yl)-9H-carbazole as light green solid (1.36 g, 57%).

FT-IR (KBr) : ν_{max} = 3416.53, 3053.60, 2928.18, 2854.98, 2305.06, 1611.43, 1481.45, 1422.40, 1364.55, 1324.50, 1265.19, 1234.83, 895.87, 812.72, 739.35 and 705.24 cm^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.51 (2H, *s*), 8.36 (2H, *s*), 8.25 (4H, *s*), 8.15 (1H, *d*, *J* = 6.00 Hz), 8.10 (1H, *d*, *J* = 6.00 Hz), 7.85 – 7.69 (10H, *m*), 7.55 (6H, *d*, *J* = 6.00 Hz), 7.47 – 7.44 (6H, *m*), 7.35 (2H, *s*), 7.20 (2H, *s*), 2.14 (4H, *t*, *J* = 6.00 Hz), 1.55 (36H, *s*), 1.17 – 1.15 (40H, *m*) and 0.81 (6H, *t*, *J* = 6.00 Hz) ppm

^{13}C-NMR (125 MHz, $CDCl_3$) δ 153.24, 153.13, 146.71, 142.58, 141.12, 140.44, 140.14, 139.83, 136.40, 130.88, 126.50, 126.02, 124.70, 123.76, 123.57, 122.53, 121.69, 121.37, 119.41, 117.77, 116.24, 111.07, 110.51, 110.38, 109.07, 40.22, 34.73, 32.04, 31.85, 30.01, 29.64, 29.45, 29.29, 24.23, 22.63 and 14.09 ppm

HRMS-ESI-TOF calcd for $C_{109}H_{122}N_4S_2$: *m/z* 1550.11 found 1551.77 [M^+]

9-(9-(7-(3,6-bis(5-bromothiophen-2-yl)-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-3,6-di-tert-butyl-9H-carbazole

A stirred solution of 3,6-di-tert-butyl-9-(9-(7-(3,6-di(thiophen-2-yl)-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-9H-carbazole9 - (2 -bromo-9 ,9 -didodecyl-9 H-fluoren-7 -yl)-9 H-carbazole (1.02 g, 0.66 mmol) in THF (10 ml) was added NBS (0.26 g, 1.45 mmol) in small portions in a flask covered with aluminum foil. The mixture was stirred at room temperature for 12 h, and then poured into ice-cold water 20 ml. The mixture was extracted with dichloromethane (20 ml × 3). The combined organic layer was washed with water 50 ml, brine solution 30 ml and dried over anhydrous Na_2SO_4. The solvent was removed to dryness. The product was obtained by column chromatography eluting with 20% dichloromethane : hexane to give a light green solid of 9-(9-(7-(3,6-bis(5-bromothiophen-2-yl)-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-3,6-di-tert-butyl-9H-carbazole (0.94 g, 85%).

FT-IR (KBr) : ν_{max} = 3459.99, 3052.32, 2927.30, 2854.68, 2304.67, 1610.03, 1583.83, 1481.42, 1393.80, 1364.23, 1324.78, 1295.42, 1264.55, 1168.89, 1034.22, 979.43, 921.60, 895.53, 813.68, 794.49, 737.38, 655.91 and 613.48, cm^{-1}

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.36 (2H, *s*), 8.32 (2H, *s*), 8.21 (4H, *s*), 8.13 (1H, *d*, *J* = 12.00 Hz), 8.09 (1H, *d*, *J* = 6.00 Hz), 7.81 (2H, *d*, *J* = 6.00 Hz), 7.73 (2H, *d*, *J* = 12.00 Hz), 7.69 – 7.65 (10H, *m*), 7.40 (6H, *d*, *J* = 18.00 Hz), 7.17 (2H, *d*, *J* = 6.00 Hz), 7.12 (2H, *d*, *J* = 6.00 Hz), 2.17 (4H, *t*, *J* = 6.00 Hz), 1.50 (36H, *s*), 1.29 – 1.20 (40H, *m*) and 0.84 (6H, *t*, *J* = 6.00 Hz) ppm

^{13}C-NMR (75 MHz, $CDCl_3$) δ 153.29, 153.17, 146.76, 142.62, 141.18, 140.49, 140.19, 136.45, 131.03, 130.91, 126.56, 126.05, 124.75, 123.80, 123.59, 123.19, 122.57, 121.90, 119.45, 117.81, 116.26, 111.09, 110.42, 109.10, 55.97, 53.42, 40.25, 34.75, 32.07, 31.86, 30.03, 29.66, 29.63, 29.61, 29.47, 29.30, 24.27, 22.64, 14.31 and 14.09 ppm

HRMS-ESI-TOF calcd for $C_{109}H_{120}N_4S_2Br_2$: *m/z* 1706.73 found 1707.78 [M^+]

The D3 was obtained from Suzuki cross coupling between 9-(9-(7-(3,6-bis(5-bromothiophen-2-yl)-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-3,6-di-tert-butyl-9H-carbazole (0.54 g, 0.32 mmol) and 2-formylthiophene boronic acid (0.15 g, 0.96 mmol) in the present of $Pd(PPh_3)_4$ (0.007 g 0.006 mmol) as catalyst and 2M Na_2CO_3 (0.67 g, 6.40 mmol) in THF (15 ml) as solvent. The mixture was degassed for 2 min and protected with N_2, and then refluxed under N_2 for 12 h. After being cooled to room temperature, water (30 ml) was added. The reaction mixture was extracted with dichloromethane (20 ml × 3). The organic phase was washed with water (30 ml), and brine solution (20 ml), dried over sodium sulfate anhydrous, filtered and the solvent was removed to dryness. The residue was purified by column chromatography over silica gel eluting with 50% dichloromethane: hexane to give D3 as orange wish solid (0.34 g, 60%).

FT-IR (KBr) : ν_{max} = 3053.79, 2927.16, 2854.80, 1711.88, 1656.13, 1480.96, 1441.29, 1364.55, 1265.15, 1226.47, 1053.92, 889.51, 800.00 and 739.17 cm^{-1}

^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.91 (2H,s), 8.48 (2H, *s*), 8.21 (2H, *s*), 8.16 (4H, *s*), 8.13 – 8.09 (2H, *m*) 7.83 – 7.73) (12H, *m*), 7.69 – 7.29 (16H, *m*), 2.18 (4H, *s*), 1.51 (36H, *s*), 1.21 – 1.18 (40H, *m*) and 0.83 (6H, *t*, *J* = 6.00 Hz) ppm

^{13}C-NMR (75 MHz, $CDCl_3$) δ 182.53, 182.42, 166.77, 144.84, 143.89, 142.64, 141.38, 140.18, 137.49, 136.90, 132.49, 130.89, 128.82, 127.34, 126.48, 123.77, 123.60, 123.53, 123.20, 116.27, 109.10, 68.19, 56.00, 38.77, 34.75, 32.07, 30.40, 29.72, 29.63, 29.67, 29.64, 29.62, 28.95, 23.79, 22.64, 14.19, 14.08, 14.06 and 10.98 ppm

HRMS-ESI-TOF calcd for $C_{119}H_{126}N_4S_2O_4$: *m/z* 1770.88 found 1771.94 [M^+]

Results and Discussion

The new photosensitizers based on donor-π-diacceptor structure (D1, D2 and D3) were developed, with carbazole and fluorene donor, thiophen thiophene (TT) or thiophene phenyl (TP) linkers and diacceptor of aldehyde. The choice of carbazole donor was supported by its strong absorption and good donor properties. Fluorene was then added as donor to extend the π-conjugated system and to enhance thermal stability.

Earlier, the dye A1 was designed and attempted to synthesize following the expected approach as depicted in Fig. 2. The Ullmann coupling product, 9-(7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-9H-carbazole (2), was obtained in high yield by treating of 9-(7-bromo-9,9-didodecyl-9H-fluoren-2-yl)-3,6-di-tert-butyl-9H-carbazole (1) with carbazole. However, the next key step of the bromination reaction failed to give the desired intermediate (3) that cased from nonselective bromination reaction of carbazole and 3,6-di-tert-butyl-9H-carbazol moieties. To overcome of the bromination step, divergent synthetic strategy was presented by introduction of the thiophene unit connecting to the carbazole unit to generate a key divergent intermediate.

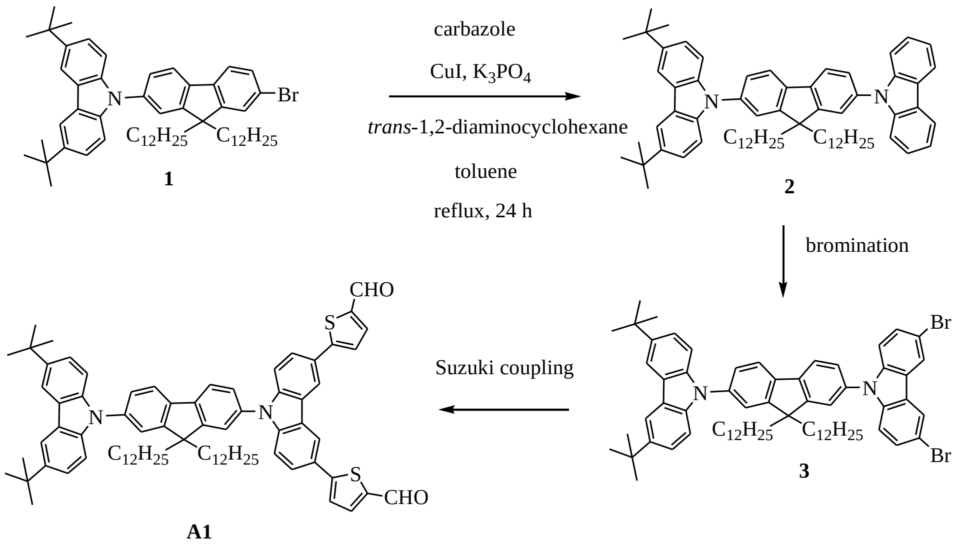

Fig. 2 The first attempt for synthesis of the dye A1.

D1 and D2 were successfully synthesized via the new synthetic route presented in Figure 3, where the didodecyl groups are substituted at the C-9 position of fluorene ring. The introduction of long chain hydrocarbon moieties and bulky of *tert*-butyl group is expected to not only protecting of interaction between the backbones of these molecules, but also increasing the thermal stability and solubility. The starting material, 9-(7-bromo-9,9-didodecyl-9H-fluoren-2-yl)-3,6-di-tert-butyl-9H-carbazole (1), was synthesized according to the previous literature procedure [20].

In this work, a new synthetic strategy was used to prepare the key intermediates, 6 as described in Fig. 3. Firstly, the two thiophene moieties were introduced to carbazole by Suzuki coupling reaction of 3,6-diiodo-9H-carbazole and 2-thiopheneboronic acid to give 3,6-di(thiophen-2-yl)-9H-carbazole (4) in moderate yield. Next, Ullmann coupling reaction of 9-(7-bromo-9,9-didodecyl-9H-fluoren-2-yl)-3,6-di-tert-butyl-9H-carbazole (1) and 3,6-di(thiophen-2-yl)-9H-carbazole could afford 9-(7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-3,6-di(thiophen-2-yl)-9H-carbazole (5) in moderate yield. Subsequently, bromination reaction of the resulting product (5) with NBS can get the first key intermediate, 3,6-bis(5-bromothiophen-2-yl)-9-(7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-9H-carbazole (6) in high yield. Because the more reactive of thiophene with bromination reaction than that of carbazole unit, this key step was successes. Finally, the D1 and D2 were successfully obtained in acceptable yield by Suzuki coupling reaction of the bromination product (6) with 2-formylthiophene boronic acid and 4-formyltphenyl boronic acid respectively.

The D3 with bulky donor moiety was synthesized via the same synthetic strategy of D1 and D2 as depicted in Figure 3, starting from Ullmann coupling reaction of 9-(9-(7-bromo-9,9-didodecyl-9H-fluoren-2-yl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-3,6-di-tert-butyl-9H-carbazole [20] and 3,6-di(thiophen-2-yl)-9H-carbazole to give 3,6-di-tert-butyl-9-(9-(7-(3,6-di(thiophen-2-yl)-9H-carbazol-9-yl)-9,9-didodecyl-9H-fluoren-2-yl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-3-yl)-9H-carbazole9-(2-bromo-9,9-didodecyl-9H-fluoren-7-yl)-9H-carbazole (8). Subsequently, bromination reaction of the Ullmann coupling product with NBS to afford the key intermediate (9) in high yield. Finally, Suzuki coupling reaction of the bromination product with 2-formylthiophene boronic acid can obtain D3 with acceptable yield.

Identification of their structures was accomplished using a combination of analysis of the ^{1}H-NMR, ^{13}C-NMR, Mass spectrometry and FT-IR spectroscopy spectra pattern. The ^{1}H-NMR in $CDCl_3$ of di-acceptor D1, D2 and D3 showed a characteristic singlet signal at chemical shift around 10.03 – 9.87 ppm of two protons of aldehyde(CHO) group, singlet signal at chemical shift around 8.49 – 8.44 ppm of two protons of 4H and 5H in carbazole moiety, singlet signal at chemical shift around 8.21 – 8.17 ppm of two protons of 4H and 5H of the other carbazole unit, doublet signal at 7.94 ppm and 7.84 ppm are assigned to H of phenyl ring, respectively. The rest of aromatic protons are overlap with each other which is difficult to identify. Moreover, four of methylene protons ($-CH_2-$) of dodecyl side chains were observed at chemical shift 2.18-2.04 indicate that this alkyl group connected to 9-position of fluorene moiety. The IR spectrum of these compound reveals C=O stretching of carbonyl group around 1734 – 1656 cm^{-1}, C=C stretching of aromatic ring at 1610 – 1481 cm^{-1}, C-H stretching of aromatic compound at 3053 – 3019 cm^{-1} and C-H stretching of aliphatic side chain at 2952 – 2851 cm^{-1}. The ^{13}C-NMR in $CDCl_3$ of the dyes showed a characteristic singlet at chemical shift around 182.59 – 182.42 ppm of carbon of aldehyde (CHO) group.

The chemical structures of these dyes were strongly supported by HRMS-ESI-TOF mass spectroscopy. All of the target dyes are good soluble in a wide variety of organic solvents including most chlorinated solvents because of the presence of *tert*-butyl and dodecyl groups in the donor moities.

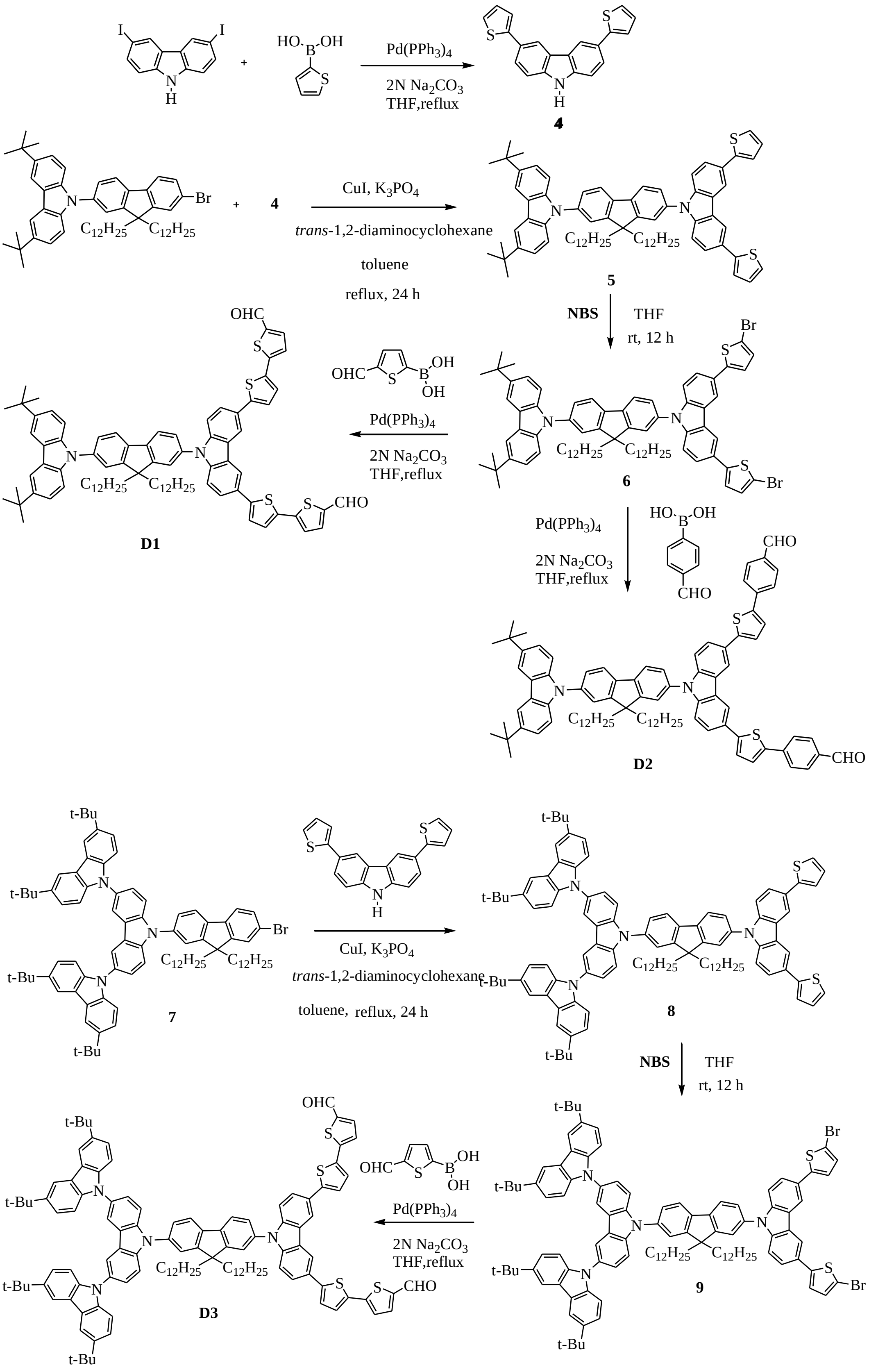

Fig. 3 The synthetic route of D1, D2 and D3.

Conclusion

This work demonstrated the design, synthesis and characterization of organic materials (D1, D2 and D3) with the structure of donor-π-conjugated-donor-π-conjugated-diacceptor (D-(π-A)$_2$). The new divergent synthetic strategy was used to overcome the bromination step in the synthesis of the key intermediate. Common flash column chromatography was used to isolate the product of each reaction. The three high soluble dyes were identified by ^{1}H-NMR, ^{13}C-NMR, Mass spectrometry and FT-IR spectroscopy. This work provides a simple method for synthesis and characterization of di-acceptors material. Work is underway in the laboratory to utilize these building blocks of the dyes for creating both cyanoacrylic acid and carboxylic acceptor materials. The physical and optical properties including performance of the DSSCs of these materials is under investigation and will reported in the future.

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