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9-(p-Tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazole – a new donor building-block in the design of sensitizers for dye-sensitized solar cells

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Abstract

The novel donor building-block - 9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazole was designed and employed in the synthesis of dye-sensitized solar cell (DSSCs). An effective, high-yielding synthesis of 4,6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(p-tolyl)-1,2,3,4,4a,9a-hexahydrocarbazole from 1,2,3,4,4a,9a-hexahydrocarbazole was realized. Three new metal-free organic sensitizers, containing the new donor building block were prepared by a stepwise approach from 4,7-dibromobenzo[c][1,2,5]chacogenadiazoles. A 2,1,3-Benzothiadiazole dye containing hexahydrocarbazole donor, thiophene as π-spacer and cyanoacrylate as anchoring electron acceptor showed photovoltaic properties higher than the well-known WS-2 sensitizer with PCE = 5.86%. Although benzoa- and –selenadiazole dyes have a bathochromic shift (24-30 nm) in the UV-vis spectra, and smaller energy gap E\(_g\) (about 0.1 eV), they have lower photovoltaic parameters, including PCE of 1.5-2.3%. Introducing a new donor 9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazole into the construction of the DSSCs has broadened possibilities for the optimization of their photovoltaic properties.

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1. Introduction

In the last couple of decades, dye-sensitized solar cells (DSSCs) have attracted worldwide research attention due to their potential for low cost production, easy fabrication and relatively high power conversion efficiency [1-3]. A dye sensitizer, a photoanode, a redox electrolyte and a counter electrode are the essential components for a typical DSSC. Among other components of DSSCs, the dye sensitizer is responsible for harvesting sunlight, initiating charge transfer, and injecting electrons into the photoanode. Efficient sensitizers have been developed based on ruthenium polypyridine complexes, zinc porphyrins [4-6] and metal-free organic dyes, among which the latter have been most intensively investigated [7-11]. Most typical organic dyes are designed with a donor-π-bridge-acceptor (D-π-A) configuration due to easy synthesis and efficient intramolecular charge transfer (ICT) properties [12-15]. The electronic interaction between donor (D) and acceptor (A) results in strong charge-transfer absorption bands that harvest sunlight for photon-to-electron conversion. Recently, Zhu and Tian proposed a new concept of the D–A–π–A motif for designing a generation of stable and efficient organic dyes [16-18]. Compared to D–π–A dyes, the properties of D–A–π–A dyes can be readily adjusted by incorporation of an auxiliary acceptor between the donor and π-bridge, which broadens the absorption and enhances efficient ICT for high performance DSSCs [19]. Some electron-withdrawing heterocyclic systems, such as diketopyrrolopyrrole, benzotriazole, benzothiadiazole, quinoxaline, benzoselenadiazole, pyridazinothiadiazole and many others have been used to design a D-A-π-A framework [20-25]. It was reported that the auxiliary acceptor is beneficial for extending absorption wavelength and enhancing the electron coupling, thus greatly improving photovoltaic properties and the stability of organic sensitizers [18]. Furthermore, the evolution of the π-bridge unit is essential in the molecular engineering of sensitizers, due to enhanced light absorption and photoinduced charge separation, as well as delayed charge recombination [26]. The most common electron withdrawing group widely employed as terminal acceptor is cyanoacrylic acid due to its strong binding on the surface of mesoporous TiO₂ through carboxylic acid anchoring groups [27]. Various other molecular engineering methods to improve the light harvesting efficiency of organic dyes involve an increase in the electronic richness of the donor moieties [28]. Introduction of electron-rich moieties on the donor segment helps to broaden the absorption spectra, and attachment of energy delocalizing chromophores causes prolongation of excited state lifetime and facilitates the electron injection into the conduction band of TiO₂ [29]. In general, triarylamine, indoline, tetrahydroquinoline, phenothiazine, phenoxazine are routinely used as donors [30]. 4-(p-
Tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole donor has been shown to be one of the most effective donors [20,22]. A few attempts to modify this moiety with a change of p-tolyl to other aryl groups have been made [31-39], but they have not achieved significant success.

In this work we aimed to design a new donor building block - 9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazole, which is varied from 4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole by one extra CH₂ group, and to investigate the influence of this group on the photovoltaic properties of the organic sensitizers. Three novel dyes with various chalcogen atoms (oxygen, sulfur and selenium) in 2,1,3-benzochalcogenadiazole internal acceptor were synthesized and studied. The optical, electrochemical and photophysical properties of these dyes were investigated to disclose important design criteria for the discovery of further new organic dyes.

2. Experimental details

2.1. Materials

The reagents were purchased from commercial sources and used as received. Solvents were purified by distillation from the appropriate drying agents.

2.2. Synthesis and characterization of compounds:

2.2.1. Synthesis of 4,6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(p-tolyl)-1,2,3,4,4a,9a-hexahydrocarbazole 4.

2,9-(p-Tolyl)-1,2,3,4,4a,9a-hexahydrocarbazole 2.

In 50 ml round-bottom flask, 1,2,3,4,4a,9a-hexahydrocarbazole 1 (520 mg, 3 mmol), p-bromotoluene (513 mg, 3 mmol), cesium carbonate (1.36 g, 4.2 mmol), palladium acetate (3.5 mg, 15μmol), tris-tert-butylphosphine (72 μl, 0.3 mmol) and 10 ml dry xylene were added. After boiling for 20 h under argon, the mixture was diluted with petroleum ether and purified on a silica gel column to obtain colorless oil, 2 (715 mg, 80%). 1H NMR (300 MHz, δ, ppm): 7.24 (m, 4H), 7.20 (d, J=2.8 Hz, 1H), 7.10 (t, J=7.6 Hz, 1H), 6.82 (t, J=7.6 Hz, 1H), 6.80 (d, J=7.6 Hz, 1H), 4.10 (m, 1H), 3.28 (m, 1H), 2.43 (s, 3H), 1.91-1.72 (m, 4H), 1.63-1.57 (m, 2H), 1.50-1.42 (m, 2H). 13C NMR (75 MHz, δ, ppm): 149.36, 141.05, 134.91, 133.04, 129.87, 126.98, 123.18, 123.02, 118.62, 109.02, 64.66, 40.64, 28.25, 25.89, 22.92, 21.30, 20.95. HRMS-ESI (m/z): [M]+ calcd for (C₁₉H₂₁N) 263.1667, found 263.1670, [M+H]+ calcd for (C₁₉H₂₂N) 264.1747, found 264.1744. IR, ν, cm⁻¹: 3404, 2939, 2905, 2846, 1579, 1470, 1435, 1311, 1273, 1233, 1047, 971, 862, 798, 586, 485. Rf=0.41 (petroleum ether/ ethylacetate = 25:1).
3,6-Bromo-9-(p-tolyl)-1,2,3,4,4a,9a-hexahydrocarbazole 3.

To a solution of 2 (450 mg, 1.7 mmol) and DMSO (133μl, 1.9 mmol) in 15 ml ethylacetate was added dropwise hydrobromic acid (48%, 0.45 ml, 3.76 mmol) at 60 ºC. After 5 minutes K₂CO₃ was added (300 mg) and the mixture was stirred another 1 h. After cooling down to room temperature the mixture was diluted with ethyl acetate, washed with water, and evaporated under reduced pressure. The organic layer was evaporated, the residue was purified on a silica gel column with petroleum ether to obtain colorless oil, 3 (494 mg, 85%). The sample was used in the next step as it is.

4,6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(p-tolyl)-1,2,3,4,4a,9a-hexahydrocarbazole 4.

In 25 ml round-bottom flask compound 3 (480 mg, 1.4 mmol), B₂Pin₂ (540 mg, 2.14 mmol), and potassium acetate (480 mg) were dissolved in 10 ml of dioxane. The solution was degassed for 20 minutes with a stream of argon, Pd₂dba₃ (9.5 mg, 10 μmol) and X-Phos (20 mg, 40 μmol) were added simultaneously. The reaction was then brought to 80 ºC for 8 h, and then diluted with ethylacetate and filtered through a thin pad of celite. The mixture was evaporated and the compound purified on a silica gel column with a ethylacetate/petroleum ether mixture 1/50 as eluent to obtain a pale yellow oil, 4 (450 mg, 82%). ¹H NMR (300 MHz, δ, ppm): 7.66 (s, 1H), 7.63 (d, J=8 Hz, 1H), 7.23 (q, J=8.5 Hz, 4H), 6.77 (d, J=7.9 Hz, 1H), 4.12 (m, 1H), 3.28 (m, 1H), 2.42 (s, 3H), 1.91-1.72 (m, 4H), 1.63-1.57 (m, 2H), 1.41 (m, 14H). ¹³C NMR (75 MHz, δ, ppm): 152.15, 140.28, 135.04, 134.01, 133.54, 129.93, 129.49, 123.37, 108.14, 83.23, 64.77, 40.31, 27.97, 25.89, 25.00, 24.83, 22.75, 21.22, 20.98. HRMS-ESI (m/z): [M+H]⁺ calcld for (C₁₂H₁₂NBO₂) 390.2603, found 390.2603. IR, ν, cm⁻¹: 3237, 2929, 2858, 1603, 1515, 1460, 1382, 1233, 1198, 815, 739, 642. Rf = 0.34 (petroleum ether/ ethylacetate = 10:1).

2.2.2. General procedure for the cross-coupling of 4,7-dibromobenzo[c][1,2,5]chalcogenadiazoles 5 and boronic ester 4.

In 50 ml round-bottom flask, 4 (450 mg, 1.2 mmol) and 4,7-dibromobenzo-1,2,5-chalcogenadiazole 5 (1.2 mmol) were dissolved in 15 ml of dioxane, and 2 M K₂CO₃ (10 ml) was added. The mixture was degassed for 20 minutes with a stream of argon, after which time Pd(PPh₃)₄ (67 mg, 60 μmol, 5%) was added. After refluxing for 10 h, the mixture was extracted with ethylacetate; organic solvent was then removed under reduced pressure. The residue was purified on a silica gel column with eluent ethylacetate/petroleum ether = 1:25.

4-Bromo-7-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)benzo[c][1,2,5]thiadiazole (6a)
Orange solid with mp 127-129 °C (330 mg, 58%). $^1$H NMR (300 MHz, δ, ppm): 7.88 (d, J=7.6 Hz, 1H), 7.73 (s, 1H), 7.65 (d, J=8.3 Hz, 1H), 7.52 (d, J=7.7 Hz, 1H), 7.22 (m, 4H), 6.86 (d, J=8.3 Hz, 1H), 4.17 (m, 1H), 3.35 (m, 1H), 2.39 (s, 3H), 1.97-1.87 (m, 1H), 1.84-1.72 (m, 3H), 1.62-1.41 (m, 4H). $^{13}$C NMR (75 MHz, δ, ppm): 154.1, 153.5, 150.1, 140.3, 135.5, 134.8, 133.7, 132.5 130.0, 128.7, 126.9, 126.7, 124.2, 123.2, 111.1, 108.8, 64.8, 40.6, 28.3, 25.9, 22.8, 21.2, 21.0. HRMS-ESI (m/z): [M+H]$^+$ calcd for (C$_2$H$_2$Br$_3$S) 476.0791, found 476.0792. UV-Vis (CH$_2$Cl$_2$, λ$_{max}$, nm/logε): 276/4.38, 415/3.83. IR, ν, cm$^{-1}$: 2923, 2852, 1605, 1513, 1466, 1377, 1328, 1256, 883, 807, 506. R$_f$ = 0.37 (15 petroleum ether/1 ethylacetate).

4-Bromo-7-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)benzo[c][1,2,5]oxadiazole (6b)

Orange solid with mp 142-144 °C (328 mg, 65%). $^1$H NMR (300 MHz, δ, ppm): 7.80 (s, 1H), 7.73 (d, J=8.4 Hz, 1H), 7.64 (d, J=7.5 Hz, 1H), 7.35 (d, J=7.5 Hz, 1H), 7.22 (q, J=8.5 Hz, 4H), 6.82 (d, J=8.3 Hz, 1H), 4.18 (m, 1H), 3.34 (m, 1H), 2.40 (s, 3H), 1.98-1.88 (m, 1H), 1.84-1.72 (m, 3H), 1.62-1.41 (m, 4H). $^{13}$C NMR (75 MHz, δ, ppm): 150.9, 150.2, 149.0, 139.9, 135.8, 134.7, 134.0, 130.1, 128.2, 125.8, 124.8, 123.4, 112.1, 108.9, 104.8, 64.9, 40.5, 28.2, 25.9, 22.7, 21.2, 21.1. HRMS-ESI (m/z): [M+H]$^+$ calcd for (C$_2$H$_2$Br$_3$O) 462.1000, found 462.0989. UV-Vis (CH$_2$Cl$_2$, λ$_{max}$, nm/logε): 310/4.21, 480/4. IR, ν, cm$^{-1}$: 2925, 2853, 1606, 1514, 1482, 1380, 1269, 806. R$_f$=0.46 (10 petroleum ether/1 ethylacetate).

4-Bromo-7-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)benzo[c][1,2,5]selenadiazole (6c)

Orange solid with mp 178-180 °C (410 mg, 65%) $^1$H NMR (300 MHz, δ, ppm): 7.80 (d, J=7.5 Hz, 1H), 7.64 (s, 1H), 7.57 (d, J=8.2 Hz, 1H), 7.35 (d, J=7.5 Hz, 1H), 7.22 (m, 4H), 6.85 (d, J=8.2 Hz, 1H), 4.17 (m, 1H), 3.34 (m, 1H), 2.39 (s, 3H), 1.93-1.71 (m, 4H), 1.63-1.53 (m, 2H), 1.47-1.39 (m, 2H). $^{13}$C NMR (75 MHz, δ, ppm): 158.8, 158.7, 149.9, 140.3, 136.4, 135.2, 133.5, 132.5, 129.9, 128.9, 127.5, 126.7, 124.4, 123.1, 113.8, 108.6, 64.7, 40.5, 28.2, 25.8, 22.8, 21.1, 20.9. HRMS-ESI (m/z): [M+H]$^+$ calcd for (C$_2$H$_2$Br$_3$Se) 524.0224, found 524.0224. UV-Vis (CH$_2$Cl$_2$, λ$_{max}$, nm/logε): 323/4.56, 495/3.99. IR, ν, cm$^{-1}$: 2927, 2853, 1605, 1513, 1481, 1380, 1268, 806. R$_f$=0.58 (5 petroleum ether/1 ethylacetate).

2.2.3. General procedure for the cross-coupling reaction of mono-adducts 6a-c and tert-butyl 2-cyano-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)acrylate 7.

In 50 ml round-bottom flask, mono-adduct 6a-c (0.45 mmol) and ester 7 (220 mg, 0.61 mmol) were dissolved in 10 ml of dioxane, and then 2M K$_2$CO$_3$ (10 ml) was added. The mixture was
degassed for 20 minutes with a stream of argon, Pd(PPh₃)₄ (30 mg, 26 μmol, 5%) was added. After refluxing for 12 h, the mixture was extracted with ethylacetate and solvent was removed under reduced pressure. The residue was purified on a silica gel column with eluent ethylacetate/petroleum ether = 1:20.

tert-Butyl 2-cyano-3-(5-(7-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylate 8a.

Dark red solid with mp 194-196°C (135 mg, 41%). ¹H NMR (300 MHz, δ, ppm): 8.28 (s, 1H), 8.26 (d, J=4.2 Hz, 1H), 8.06 (d, J=7.6 Hz, 1H), 7.89 (d, J=4.1 Hz, 1H), 7.82 (s, 1H), 7.76 (d, J=8.6 Hz, 1H) 7.71 (d, J=7.6 Hz, 1H), 7.23 (s, 4H), 6.87 (d, J=8.3 Hz, 1H), 4.19 (m, 1H), 3.36 (m, 1H), 2.39 (s, 3H), 1.97-1.90 (s, 1H) 1.85-1.75 (m, 3H), 1.62 (s, 9H), 1.58-1.40 (m, 4H). ¹³C NMR (75 MHz, δ, ppm): 161.8, 154.0, 152.7, 150.2, 149.1, 145.4, 140.1, 137.8, 135.8, 135.4, 133.6, 129.9, 129.0, 128.0, 127.9, 127.0, 125.9, 124.2, 123.2, 123.0, 116.3, 108.7, 100.1, 83.4, 64.8, 40.5, 28.2, 28.0, 25.8, 22.7, 21.1, 20.9. HRMS-ESI (m/z): [M]+ calecd for (C₃₇H₃₄NaO₂S₂) 630.2118 , found 630.2112. UV-Vis (CH₂Cl₂, λmax, nm/logε): 318/4.41, 414/4.31, 523/4.44. IR, ν, cm⁻¹: 2931, 2855, 2180, 1709, 1605, 1585, 1510, 1458, 1363, 1248, 1152, 808. Rf = 0.44 (petroleum ether/ ethylacetate = 5:1).

tert-Butyl 2-cyano-3-(5-(7-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)benzo[c][1,2,5]oxadiazol-4-yl)thiophen-2-yl)acrylate 8b.

Dark purple solid with mp 120-122 °C (127 mg, 46%). ¹H NMR (300 MHz, δ, ppm): 8.27 (s, 1H), 8.24 (d, J=4.1 Hz, 1H), 7.90 (s, 1H), 7.83 (m, 3H), 7.57 (d, J=7.5 Hz, 1H), 7.23 (q, J=8.5 Hz, 4H), 6.85 (d, J=8.3 Hz, 1H), 4.19 (m, 1H), 3.37 (m, 1H), 2.40 (s, 3H), 1.97-1.90 (s, 1H) 1.85-1.75 (m, 3H), 1.62 (s, 9H), 1.58-1.40 (m, 4H). ¹³C NMR (75 MHz, δ, ppm): 161.5, 151.0, 149.0, 148.0, 147.2, 145.2, 139.7, 138.7, 135.7, 135.7, 134.0, 131.3, 130.0, 129.4, 128.9, 128.5, 125.1, 124.9, 123.3, 118.6, 116.1, 108.8, 100.8, 83.6, 64.9, 40.3, 28.1, 28.0, 25.8, 22.6, 21.0, 21.0. HRMS-ESI (m/z): [M+H]+ calecd for (C₃₇H₃₄NaO₂S) 615.2424, found 615.2411; [M+Na]+ calecd for (C₃₇H₃₄Na₃O₅SNa) 637.2244, found 637.2245. UV-Vis (CH₂Cl₂, λmax, nm/logε): 310/4.30, 405/4.18, 550/4.41. IR, ν, cm⁻¹: 2927, 2854, 2216, 1702, 1605, 1578, 1513, 1482, 1370, 1268, 807, 654. Rf = 0.52 (petroleum ether/ ethylacetate = 5:1).

tert-Butyl 2-cyano-3-(5-(7-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)benzo[c][1,2,5]selenadiazol-4-yl)thiophen-2-yl)acrylate 8c.

Dark purple solid with mp 98-100 °C (192 mg, 49%). ¹H NMR (300 MHz, δ, ppm): 8.28 (s, 1H), 8.15 (d, J=4.1 Hz, 1H), 8.00 (d, J=7.5 Hz, 1H), 7.91 (d, J=4.1 Hz, 1H), 7.74 (s, 1H), 7.67 (d, J=8.3 Hz, 1H), 7.58 (d, J=7.5 Hz, 1H), 7.22 (s, 4H), 6.86 (d, J=8.3 Hz, 1H), 4.18 (m, 1H),...
3.36 (m, 1H), 2.40 (s, 3H), 1.97-1.88 (s, 1H) 1.84-1.72 (m, 3H), 1.61 (s, 9H), 1.58-1.40 (m, 4H). 13C NMR (75 MHz, δ, ppm): 162.0, 159.7, 158.3, 150.2, 149.6, 145.7, 140.3, 137.5, 137.4, 136.7, 135.3, 133.7, 130.0, 129.3, 128.4, 127.9, 126.3, 124.8, 124.6, 123.2, 116.5, 108.7, 99.9, 83.5, 64.8, 40.6, 28.3, 28.1, 25.9, 22.7, 21.2, 21.0. HRMS-ESI (m/z): [M+H]+ calcld for (C37H34Na2O2Se) 679.1643, found 679.1628. UV-Vis (CH2Cl2, λmax, nm/logε): 326/4.57, 405/4.33, 550/4.55. IR, ν, cm⁻¹: 2929, 2853, 2215, 1719, 1601, 1511, 1470, 1370, 1278, 1160, 840, 733. Rf = 0.38 (petroleum ether/ethylacetate = 5:1).

2.2.4. General procedure for hydrolyses of ethers 8a-c.

In a 25 ml round-bottom flask, 8a-c (0.15 mmol, 96 mg, 92 mg and 104 mg respectively) was dissolved in a 5 ml solution of 1/3 CF3COOH/CHCl3. After stirring for 4 h under argon, the mixture was diluted with dichloromethane, washed with water, and removed under reduced pressure. The residue was purified on a silica gel column with eluent methanol/dichloromethane/acetic acid = 10:50:1.

2-Cyano-3-(5-(7-((p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid (MAXI14)

Dark red solid with mp >300 °C (79 mg, 91%). 1H NMR (300 MHz, DMSO-d6, δ, ppm): 8.19 (m, 2H), 8.10 (s, 1H), 7.88 (s, 1H), 7.85 (d, J=7.7 Hz, 1H), 7.79 (m, 2H), 7.23 (m, 4H), 6.80 (d, J=8.3 Hz, 1H), 4.21 (m, 1H), 2.32 (s, 3H), 1.90-1.82 (m, 1H) 1.74-1.59 (m, 3H), 1.47-1.33 (m, 4H). 13C NMR (75 MHz, DMSO-d6, δ, ppm): 162.9, 153.6, 152.5, 149.5, 143.5, 140.2, 139.9, 138.7, 135.4, 135.1, 133.9, 133.2, 130.4, 129.2, 127.7, 127.6, 127.3, 126.7, 124.5, 123.5, 122.8, 120.0, 111.5, 108.6, 64.2, 27.9, 25.7, 22.5, 21.1, 21.0. MS-MALDI (m/z): [M]+ calcld for (C33H26Na2O2S2) 574.1497, found 574.2726. UV-Vis (CH2Cl2/MeOH (2%), λmax, nm/logε): 365/4.10, 482/4.19. IR, ν, cm⁻¹: 2924, 2853, 2211, 1720, 1610, 1578, 1515, 1474, 1377, 1268, 806. Rf = 0.47 (ethylacetate/methanol = 2:1).

2-Cyano-3-(5-(7-((p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)benzo[c][1,2,5]selenadiazol-4-yl)thiophen-2-yl)acrylic acid (MAXI15)

Dark purple solid with mp >300 °C (83 mg, 88%). 1H NMR (300 MHz, DMSO-d6, δ, ppm): 8.13 (d, J=4.1 Hz, 1H), 8.08 (m, 2H), 7.81 (s, 1H), 7.77 (d, J=4.1 Hz, 1H), 7.68 (m, 2H), 7.23 (m, 4H), 6.78 (d, J=8.4 Hz, 1H), 4.20 (m, 1H), 2.32 (s, 3H), 1.90-1.82 (m, 1H) 1.74-1.59 (m, 3H), 1.47-1.33 (m, 4H). 13C NMR (75 MHz, DMSO-d6, δ, ppm): 163.3, 158.5, 157.32, 148.7, 144.0, 140.0, 139.8, 138.1, 135.2, 134.5, 134.2, 132.5, 129.9, 129.0, 127.8, 127.2, 127.0, 126.0, 124.7, 124.4, 122.2, 119.4, 109.9, 107.9, 63.7, 27.4, 25.2, 22.0, 20.6, 20.4. MS-MALDI (m/z): [M]+ calcld for (C33H26Na2O2Se) 622.0944, found 622.2408. UV-Vis (CH2Cl2/MeOH (2%),
\( \lambda_{\text{max}}, \text{nm/log } \varepsilon \): 375/4.14, 512/4.12. IR, \( \nu, \text{cm}^{-1} \): 2924, 2853, 2214, 1718, 1604, 1582, 1511, 1466, 1378, 1271, 1151, 809. \( R_f = 0.49 \) (ethylacetate/ methanol = 2:1).

2-Cyano-3-(5-(7-(9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)benzo[c][1,2,5]oxadiazol-4-yl)thiophen-2-yl)acrylic acid (MAX123)

Dark purple solid with mp >300 ºC (77 mg, 92%). \( ^1 \text{H NMR} \) (300 MHz, DMSO-d6, \( \delta \), ppm): 8.17 (s, 1H), 8.06 (d, \( J=3.9 \) Hz, 1H), 7.94 (d, \( J=7.5 \) Hz, 1H), 7.88 (s, 1H), 7.81 (m, 2H), 7.75 (d, \( J=7.6 \) Hz, 1H), 7.21 (q, \( J=8.4 \) Hz, 4H), 6.77 (d, \( J=8.4 \) Hz, 1H), 4.21 (m, 1H), 2.32 (s, 3H), 1.91-1.82 (m, 1H) 1.74-1.64 (m, 2H), 1.62-1.53 (m, 1H), 1.47-1.33 (m, 4H). \( ^{13} \text{C NMR} \) (75 MHz, DMSO-d6, \( \delta \), ppm): 164.5, 150.1, 148.9, 148.0, 142.8, 141.3, 140.0, 138.1, 136.5, 135.7, 133.4, 130.4, 129.6, 129.2, 128.6, 128.2, 126.6, 124.9, 123.3, 119.2, 118.4, 109.4, 108.6, 64.2, 27.8, 25.6, 22.4, 21.0. MS-MSMALDI (m/z): [M]\(^+\) calcd for (C\(_{33}\)H\(_{28}\)N\(_4\)O\(_3\)S) 558.1725, found 558.2721. UV-Vis (CH\(_2\)Cl\(_2\)/MeOH (2%), \( \lambda_{\text{max}}, \text{nm/log } \varepsilon \): 367/3.66, 506/3.85. IR, \( \nu, \text{cm}^{-1} \): 2930, 2855, 2214, 1715, 1586, 1512, 1482, 1370, 1266, 1153, 808. \( R_f = 0.51 \) (ethylacetate/ methanol = 2:1).

![Scheme 1. Chemical structures of MAX114, MAX123 and MAX115.](image-url)
Scheme 2. Synthesis of new donor building block 1. The reaction conditions: (i) Pd(OAc)$_2$, PtBu$_3$, Cs$_2$CO$_3$, xylene; (ii) HBr, DMSO, ethylacetate (iii) B$_2$Pin$_2$, KOAc, Pd$_2$dba$_3$, X-Phos, dioxane.

Scheme 3. Synthesis of sensitizers. The reaction conditions: (i) Pd(PPh)$_3$)$_4$, K$_2$CO$_3$, dioxane; (ii) CF$_3$COOH, CHCl$_3$.

3. Results and Discussion

3.1 Synthesis and characterization

The molecular structures of the dyes, containing the novel donor building-block - 9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazole, are shown in Scheme 1. 4,6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(p-tolyl)-1,2,3,4,4a,9a-hexahydrocarbazole 4 was prepared in four steps from 1,2,3,4,4a,9a-hexahydrocarbazole 1 Scheme 2. Buchwald-Hartwig arylation of hexahydrocarbazole with p-iodotoluene in the presence of Pd(OAc)$_2$, P$^t$Bu$_3$ and Cs$_2$CO$_3$ in xylene afforded the p-tolyl derivative in good yield (80%). Bromination of the aromatic ring with a mixture of HBr and DMSO followed by Miyaura borylation with 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) in the presence of palladium catalyst Pd$_2$dba$_3$, ligand X-Phos and KOAc in 1,4-dioxane gave key the donor component in good yield.
The general strategy for the synthesis of dyes with D-A1-π-A2 motif follows a stepwise approach shown in Scheme 3. Internal acceptors A1 - 4,7-dibromobenzo[c][1,2,5]thiadiazole 5a [41], 4,7-dibromobenzo[c][1,2,5]oxadiazole 5b [42] 4,7-dibromobenzo[c][1,2,5]selenadiazole 5b [43] and π-spacer-acceptor moiety - tert-butyl (2-cyano-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)acrylate [44] were prepared by known procedures. The cross-coupling reactions of 4,7-dibromobenzo[c][1,2,5]chalcogenadiazoles (5) with donor boronic ester 4 in the presence of Pd(PPh3)4 as a catalyst and aqueous solution K2CO3 in THF successfully gave mono-adducts 6a-c in moderate yields. The second cross-coupling of 7-bromobenzo[c][1,2,5]chalcogenadiazoles 6a-c with acceptor tert-butyl ester gave bis-adducts 8a-c in high yields. Final hydrolysis of compounds 8a-c with CF3CO2H resulted in the formation of the target MAX dyes in high yields. All dyes were purified by column chromatography before measurement of the physical and electrochemical properties as well as solar cell device fabrication.

3.2 Photophysical and electrochemical properties

The response region in sunlight for DSSCs is determined primarily by the UV-Vis absorption of the sensitizer. Therefore, we initially characterized the spectral response of the MAX series in DCM/MeOH (V/V = 98/2) at 4×10⁻⁵ mol L⁻¹ (Fig. 1). The absorption peaks (λmax) and their corresponding molar absorption coefficients (ε) are listed in Table 1. As shown in Fig. 1, all these dyes exhibit two absorption regions. The absorption peaks between 350-400 nm mainly correspond to the π-π* electron transition. The broad absorption bands in the 450-550 nm region are assigned to an intramolecular charge transfer (ICT) process between the donor and anchor/acceptor group, which produces the efficient charge-separated excited state. Despite the fact that the extinction coefficient of the sulfur-containing derivative MAX114 is as close as possible to the same value of the previously-described WS-2 dye (15.5 × 10³ M⁻¹·cm⁻¹ and 16.7 × 10³ M⁻¹·cm⁻¹, correspondingly) [16], the second absorption band suffers strong hypsochromic shift from λmax = 533 nm for WS-2 to 482 nm for MAX114. Thus, a small change in the donor fragment (addition of one CH₂ group in the indoline ring) has a significant effect on the second absorption maximum, which indicates a high sensitivity of intramolecular electron transfer to even small variations in the structure of the donor part of the molecules.

We found that the nature of the chalcogen in the internal acceptor affects the long-wave absorption maximum. MAX dyes show a significant bathochromic shift during the replacement
of the sulfur atom in the 1,2,5-chalcogenadiazole ring on the more electronegative oxygen atom (24 nm), and the more electropositive atom of selenium (30 nm). At the same time, the short-wave absorption maximum (about 370 nm) is practically independent of the chalcogen atom in the heterocycle: the deviation is no more than 10 nm. Probably, such a nonlinear dependence can be explained, on the one hand, by a decrease in the electronegativity of sulfur in comparison with oxygen, which reduces the efficiency of intramolecular charge transfer by reducing the electron acceptor effect of the chalcogenadiazole fragment. On the other hand, an increase in the radius of the atom in the transition from sulfur to selenium seems to contribute to the ICT process due to the presence of d-orbitals in the selenium atom that can participate in the conjugation. The extinction coefficient was also dependent on the nature of the chalcogen: the smallest extinction was observed for the oxygen-containing compound MAX123 (6.8 × 10^3 M^-1·cm^-1). However, in this case, the dye based on thiadiazole showed values that do not correspond to the linear change in the sequential change of chalcogen atoms: the extinction coefficient for the sulfur-containing dye (MAX114) was 15.5 × 10^3 M^-1·cm^-1, while the selenium analogue (MAX115) showed a value of 13.0 × 10^3 M^-1·cm^-1. Thus, the maximum conjugation has dyes based on sulfur and selenium, and the introduction of an electronegative oxygen atom with a minimum radius probably alters the geometry of the molecule, reducing the conjugation. The calculated E_g opt for known dye WS-2 is much less compared to the dyes of the MAX series. It is surprising that the oxygen and selenium dyes (MAX115 and MAX123) showed better results, compared with the sulfur-containing compound MAX114, which is the closest analog of WS-2 (Table 1).
Fig. 1 UV-Visible absorption (a) in DCM/MeOH (V/V = 98/2) at 4×10⁻⁵ mol L⁻¹ of MAX dyes.

Table 1. UV-Visible absorption properties of the MAX series in DCM/MeOH (V/V = 98/2) solutions.

| Dye   | \( \lambda_{\text{max}1} \), [nm][a] | \( \varepsilon_{\text{max}1} \times 10^3 \), [M⁻¹·cm⁻¹][a] | \( \lambda_{\text{max}2} \), [nm][a] | \( \varepsilon_{\text{max}2} \times 10^3 \), [M⁻¹·cm⁻¹][a] | \( \lambda_{\text{onset}} \), [nm][a] | \( E_{\text{g, opt}} \), eV[b] |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| MAX114 | 365              | 12.5             | 482              | 15.5            | 595             | 2.087           |
| MAX115 | 375              | 13.8             | 512              | 13.0            | 629             | 1.975           |
| MAX123 | 367              | 4.4              | 506              | 6.8             | 633             | 1.962           |
| WS-2   |                  |                  | 533              | 16.7            | 675             | 1.840           |

[a] Absorption peaks (\( \lambda_{\text{max}}, \lambda_{\text{onset}} \)) and molar extinction coefficients (\( \varepsilon \)) in DCM/MeOH (V/V = 98/2)  
[b] Calculated by 1242/\( \lambda_{\text{onset}} \)[c] [16]

To estimate the energy value of the frontier orbitals, the potential values of the first oxidation and reduction peaks on the cyclic voltammetry curves of the investigated compounds in DMF were obtained. Figure 2 shows a cyclic voltammogram of the new sensitizers obtained
versus ferrocene/ferrocenium (Fc/Fc+) at a scan rate of 100 mVs\(^{-1}\). Electroreduction peaks, as seen in Fig.1, are reversible at low potential sweep rates. Electrooxidation of all compounds is irreversible even at a sweep rate of 10 Vs\(^{-1}\). Relevant electrochemical data for the compounds are presented in Table 2. Assuming a value of -5.1 eV [45,46] for the absolute potential of the Fc/Fc+ couple in non-aqueous electrolytes, \(E_{\text{HOMO}}\) and \(E_{\text{LUMO}}\) were calculated using equations (1) and (2):

\[
E_{\text{HOMO}} \text{ (eV)} = -|e|(E_{\text{ox Fc/Fc+}} + 5.1) \quad (1)
\]

\[
E_{\text{LUMO}} \text{ (eV)} = -|e|(E_{\text{red Fc/Fc+}} + 5.1) \quad (2)
\]

As a result, \(E_{\text{LUMO}}\) of MAX114 (-3.48 eV), MAX115 (-3.57 eV) and MAX123 (-3.63 eV) are higher in energy than the conduction band edge of nanocrystalline TiO\(_2\) (-4.2 eV) [47], indicating that the electron injection process from the excited dye molecules to the TiO\(_2\) conduction band is energetically permitted. However, in the series of three dyes, there is no linear dependence of these values in the transition from an oxygen-containing analogue MAX115 to a selenium-containing one MAX123. The minimum value of \(E_{\text{LUMO}}\), is seen for the dye based on thiadiazole MAX114. Since the energy of the LUMO depends on the degree of conjugation of the molecule [48,49], it can be assumed that an increase in the electronegativity of the central chalcogen atom by transition from thiadiazole to oxadiazole leads to too strong charge separation, while the transition to a more voluminous selenium atom leads to a reduction in conjugation due to an increase in the radius of the central atom and changes in the geometry of the molecule.

The \(E_{\text{HOMO}}\) level of MAX114 (-5.39 eV), MAX115 (-5.34 eV) and MAX123 (-5.44 eV) show more negative values than the energy level of I/I\(^3\)\(^{-}\) redox (-5.2 eV) [50], therefore, dye regeneration should be thermodynamically favorable. Since the HOMO energy is dependent mostly on the nature of the donor fragment of the molecules, it is not surprising that the values of \(E_{\text{HOMO}}\) for all three dyes differ by no more than 0.1 eV.

Comparison of the \(E_{\text{LUMO}}\) level of MAX114 with the corresponding values of the known analogue WS-2 (Table 2, [52]), differing in the size of the alicycle in the donor part of the molecule, leads to the conclusion that the replacement of the cyclopentane fragment in the donor in WS-2 to cyclohexane in MAX114, apparently leads to a decrease in the degree of conjugation of the molecule. The decrease in the \(E_{\text{HOMO}}\) level of MAX114 compared to WS-2 by 0.38 eV indicates an increase in the degree of delocalization of the donor fragment containing the cyclohexane ring.
The electrochemical gap energy \( E_{g}^{CV} \) for each dye is calculated from the difference between their \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \). All \( E_{g} \) values (Table 2) satisfy the design expectation that this value for dye-sensitized solar cells should be less than 2.5 eV [51]. As a result, all dyes have enough energetic driving force for efficient DSSCs using a nanocrystalline titania photocatalyst and the \( \Gamma^{-}/I_{3}^{-} \) redox couple.

![Cyclic voltammogram](image)

**Fig. 2.** Cyclic voltammogram showing reduction (a) and oxidation (b) of \( \text{MAX 114} \) (1), \( \text{MAX 115} \) (2), \( \text{MAX 123} \) (3). Scan rate 100 mVs\(^{-1}\), electrolyte 0.1 M Bu\(_4\)NClO\(_4\) in DMF. (c) Schematic diagram of energy levels of TiO\(_2\) conduction band, dyes and \( \Gamma^{-}/I_{3}^{-} \) redox couple.

**Table 2.** Electrochemical properties of the dyes in DMF solutions.

| Compound | \( E_{\text{red}} \) (vs Fc/Fc\(^{+}\))[\( \text{a} \)] | \( E_{\text{LUMO}} \)[\( \text{b} \)] | \( E_{\text{ox}} \) (vs Fc/Fc\(^{+}\))[\( \text{a} \)] | \( E_{\text{HOMO}} \)[\( \text{b} \)] | \( E_{g} \)[\( \text{c} \)] |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| MAX 114  | -1.62 eV        | -3.48 eV        | 0.29 eV         | -5.39 eV        | 1.91 eV         |
| MAX 115  | -1.53 eV        | -3.57 eV        | 0.24 eV         | -5.34 eV        | 1.77 eV         |
| MAX 123  | -1.47 eV        | -3.63 eV        | 0.34 eV         | -5.44 eV        | 1.80 eV         |
Here $E^{\text{onset}}_{\text{ox}}$ and $E^{\text{onset}}_{\text{red}}$ are oxidation and reduction peak potential relative to Fc/Fc$^+$ respectively.

b Energies of frontier orbitals were calculated according to equations (1) and (2)

c $E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$

Unsurprisingly, the $E_g$ data of the MAX dyes obtained from the CV data agree well with the absorption onset. Thiadiazole dye (MAX114) has a bit higher $E_g$ than its selenium and oxygen counterparts. This enhancement can lead apparently to a longer lifetime of the first excited state of MAX114, which should have a positive impact on the photovoltaic efficiency of solar cells made on its basis. These data once again prove the better photovoltaic properties of fused thiadiazoles compared to oxa- and selenadiazole analogs, which leads to nonlinear changes in the properties of a number of chalcogen atoms. The $E_g$ value for the known dye WS-2 is close to its structural analogue MAX114, which should lead to close parameters of solar cells based on these compounds.

3.3 DSC performance

To study the influence of the chalcogen atom in chalcogenadiazole ring of the central acceptor unit of the dye on the photovoltaic efficiency, we constructed DSSCs based on the dye series MAX. Commercially available ruthenium dye N719 was chosen as a reference dye. The J-V curves are shown on Fig. 3 and the results are summarized in Table 3. Fill factors (FF) have similar values for all dyes in the MAX series, from 0.61 to 0.64, therefore PCE values will depend mainly on open-circuit voltage ($V_{oc}$) and short-circuit current density ($J_{sc}$). $V_{oc}$ values for all three dyes of the MAX series are approximately equal to each other. There are two main factors that result in the variation of $V_{oc}$. The first is the quasi-Fermi level shift and the second is recombination of injected electrons with oxidized sensitizer or electrolyte. The three dyes possess similar structures such that suppression of electronic recombination is likely to be similar in each case. To confirm this, the electron lifetime of the conduction band electrons in the TiO$_2$ (= electron lifetime) was analyzed by electrochemical impedance spectroscopy. Fig. S4 shows the electron lifetime plot against $V_{oc}$ with the MAX DSSCs. The values were derived from the peak frequency in the Bode plots. In comparison with the reference N719, the electron lifetime trends are similar among the series, ranging around 2-5 ms at 0.8-1.0 sun. The results are coherent with the similar $V_{oc}$ values achieved by the three dyes. Accordingly, the primary factor for the voltage is more likely to be the quasi-Fermi level shift due to the different amount of injected electrons from the excited dyes into the conduction band of TiO$_2$ with various LUMO levels.
The $J_{sc}$ of the benzothiadiazole dye MAX114 is significantly higher than the oxygen analogue MAX123. The selenadiazole MAX115 sits between MAX114 and MAX123. This is consistent with the fact that the dye MAX114 has the highest extinction coefficient but is contrary to the values of long-wavelength absorption maxima. Since all three dyes have similar HOMO values (the difference does not exceed 0.1 eV), it is likely that the oxidized state, formed after electron injection, in all three dyes is easily regenerated to the neutral state. The interesting fact is that the values of LUMO energy level of synthesized dyes change nonlinearly when moving from oxygen-containing MAX123 through sulfur- (MAX114) to selenium-analogues (MAX115). Thiadiazole derivative MAX114 has the higher LUMO level whilst the values of LUMO energy level of MAX115 and MAX123 are, respectively, 0.09 and 0.15 eV lower. The energy gap values of MAX115 and MAX123 dyes obtained by cyclic voltammetry are 0.14 and 0.11 eV, respectively, less than the $E_g$ of the MAX114 dye. The energy gap values obtained from the optical data are consistent with the $E_g^{CV}$ values: the difference between the values exceeded 0.1 eV. The combination of these factors leads to relatively low values of the photovoltaic efficiency of oxygen-containing dye in comparison with the sulfur and shows that the performance of sulfur-based dyes should be superior than oxygen and selenium-based dyes.

The dark current in DSSCs based on N719 dye is less than that for the MAX series dyes, which means less effective suppression of charge recombination from TiO$_2$ to the electrolyte for the latter.

It is interesting to note that the current-voltage characteristics for DSSCs based on the dye WS-2, performed under similar conditions [52], are lower than the similar dye MAX114, differing by one CH$_2$ group in the donor alicyclic fragment. The most important difference for WS-2 and MAX114 was found for $J_{sc}$ and consequently for PCE; 5.07 and 5.86%, respectively. The incident photon-to-current efficiency curves (Fig. S25) also support the superior $J_{sc}$ of MAX114 to WS-2. Unlike the UV-Visible absorption in solution (Fig. 1), the optical absorption of MAX114 is efficient throughout the visible spectrum. The poorer results for MAX115 and MAX123 are consistent with our predictions above.

Table 3. $J$-$V$ characteristics for DSSCs based on the dyes MAX series and N719$^{[a]}$. 


| Dye     | V_{oc} (mV) | J_{sc} (mA cm^{-2}) | FF | η (%) |
|---------|-------------|---------------------|----|-------|
| MAX114  | 0.64        | 14.75               | 0.62 | 5.86  |
| MAX115  | 0.65        | 13.75               | 0.64 | 5.78  |
| MAX123  | 0.64        | 11.90               | 0.61 | 4.66  |
| N719    | 0.78        | 15.32               | 0.63 | 7.54  |
| WS-2    | 0.59        | 11.8                | 0.63 | 5.07  |

[a] The data given for MAX dyes and N719 were obtained with 8 µm (4 µm transparent + 4 µm scattering) TiO₂ films and CDCA additive. The data for WS2 was taken from the paper [52] and were obtained with 12 µm (8 µm transparent + 4 µm scattering) TiO₂ films and no CDCA additive.

![J-V characteristic for DSSCs based on the dyes MAX series and N719](image)

**Fig. 3.** J-V characteristic for DSSCs based on the dyes MAX series and N719

### 4 Conclusions

In summary, we have synthesized 4,6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(p-tolyl)-1,2,3,4,4a,9a-hexahydrocarbazole - a new donor building-block for DSSCs. Three novel D-A-π-A metal-free organic sensitizers were obtained using this donor. 2,1,3-Benzothiadiazole sensitizer MAX114 based on 9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazole showed higher PCE by comparison to the well-known 4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indolyl building block, which is varied from extensively investigated 4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole by one excessive CH₂ group in indoline cycle (see, for example, dye WS-2 and other similar dyes). Interestingly these higher PCE values for MAX114 were achieved despite significant hypsochromic shift in the UV-vis spectrum and a slightly higher E_{g} than the WS-2 dye. This can be explained by the changes of the E_{LUMO} and E_{HOMO} levels, which depend on the donor strength of the condensed alicyclic
fragment, affecting the degree of conjugation of the molecules and also on molecular geometry, changing in the transition from cyclopentene to cyclohexene derivative, which affects the delocalization of the charge. Surprisingly, replacement of the chalcogen atom in the central acceptor 2,1,3-benzochalcogenadiazole block from the sulfur atom to a more electronegative oxygen atom or a more voluminous selenium atom leads to nonlinear dependence with bathochromic shift (24-30 nm) in the UV-vis spectra, and bigger energy gap $E_g$ of about 0.1 eV. Nevertheless, the exchange of oxygen- and selenium atoms in benzochalcogenadiazole to sulfur atom leads to a sharp increase in photovoltaic parameters, including PCE. In summary, the 9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazole donor building block opens new possibilities to improve the photovoltaic efficiency of organic sensitizers in DSSCs and demonstrates the importance of tuning also the non-conjugated aliphatic part of the donor group.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at …

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