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Novel Distyryl BODIPY-Fullerene Dyads: Preparation, Characterization and photosensitized singlet oxygen generation efficiency

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Abstract

A novel type mono- and bis- distyryl- BODIPY- fullerene dyads **6** and **7** were prepared by Bingel cyclopropanation. Distyryl- BODIPY derivative (**3**) was reacted with methyl malonyl chloride and malonyl dichloride respectively for the synthesis of compounds **4** and **5** as light-harvesting antennas that contain one and two BODIPY units. Via the Bingel cyclopropanation of these BODIPYs (**4** and **5**) with fullerene- C_{60} in the presence of CBr_4 and DBU, distyryl-BODIPY- fullerene dyads **6** and **7** were obtained. All newly synthesized compounds were characterized by MALDI- MS, ^{1}H ^{13}C NMR and elemental analysis. Moreover, the photophysical and photochemical properties of these heavy atom free dyads were investigated for determination of their photosensitizer and fluorescence abilities in near IR region to generate singlet oxygen.

Keywords: Borondipyrromethenes, fullerenes, Singlet Oxygen, photochemistry, sensitizers, UV/Vis spectroscopy

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1. Introduction

The covalent functionalization of the fullerenes to construct versatile adducts has developed rapidly in the last few years and fullerene- C_{60} is by far the most studied fullerene, can be considered a versatile building block in organic chemistry.[1,2] Many fullerene- C_{60}- based, donor–acceptor systems, in which fullerene- C_{60} is covalently linked to active groups, were synthesized, to investigate their photophyisical properties based on electron and energy transfer.[3-8] The diverse addition patterns of fullerene based conjugates make them attractive to generate widespread application.[9] For this purpose, several methodologies were developed to covalent linkage of fullerene- C_{60} with other molecules.[6] An important application is the designing fullerene adducts for material sciences.[10] Some of these materials could be used in artificial light harvesting systems owing to the high capacity of the fullerene- C_{60} as an electron acceptor.[11-13] Furthermore, these incorporations are important headway to understand and mimic the photosynthetic materials. Amongst the organic dyes, derivatives of BF_2- chelated dipyrromethene (BODIPY), “porphyrin’s little sister”, are extensively used in constituting these artificial photosynthetic models thanks to their unique properties.[14] BODIPYs generally act as excellent antennae with favorable photophyisical properties like large molar absorptivities, high fluorescence quantum yields, and relatively long singlet excited state lifetimes, that can be tuned easily via chemical modification of the BODIPY core.[15, 16] One of the drawbacks of these chromophores is their relatively short absorption and emission wavelength, which can be extended by introducing two styryl groups at the 3- and 5- positions of the BODIPY core. With more extended π- conjugated system, distyryl BODIPYs, can absorb and emit at longer wavelengths (ca. 650 nm).[17] BODIPY dyes as photosensitizer are relatively new members of the photosensitizer community.[18] Alteration of the excited state dynamics via deliberate modifications that promote ISC and collateral singlet oxygen generation is possible. One general method to enhance ISC involves substitution of heavy atoms (eg., bromine and iodine) onto the BODIPY core owing to their heavy atom effect.[19,20] However, BODIPY- based photosensitizers that undergo efficient ISC without requiring the spin- orbital coupling of heavy atom substituents on the core structure remained very rare.[21] Thus it is still difficult to attract the triplet state of BODIPYs without heavy atoms also it is not always convenient to prepare brominated/ iodated organic chromophore, since the ISC property of the chromophore cannot be guaranteed.[22] One common strategy to design

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new organic triplet photosensitizers is the functionalization of a known fluorophore, however it is not applicable to design new organic chromophores as photosensitizer since there is no constituted relationship between the ISC and molecular structures.[23-27]

The idea of preparing BODIPY- fullerene- C_{60} dyads originated from the fact that BODIPYs are attractive molecules due to their aforementioned unique properties. Moreover, BODIPY derivatives are frequently encountered in sophisticated photophysical systems.[28, 29] Recently, we have reported the synthesis, characterization, photophyisical/ photochemical properties of new BODIPY- fullerene and monostyryl BODIPY- fullerene dyads, that showed efficient singlet oxygen generation capacities.[23]

To investigate the singlet oxygen capacities of dyads that have chromophore with extended conjugation herein, we devised visible light- harvesting distyryl- BODIPY- fullerene (**6**, **7**) systems as Near- IR heavy atom free organic triplet photosensitizers (Scheme 1). Distyryl- BODIPYs were used as the light harvesting antennae, where fullerene- C_{60} units act as the spin convertor. The dyads (**6** and **7**) showed strong absorption of visible light with very small fluorescence quantum yields. The synthesized dyads (**6**, **7**) were used as oxidizer of 1,3-diphenylisobenzofuran (DPBF) which was driven by photosensitization of singlet oxygen ($^1O_2$).

First, we synthesized light harvesting antennae distyryl- BODIPY (**3**) that obtained in high yield. Distyryl- BODIPY (**3**) was reacted with methyl malonyl chloride to give BODIPYs **4** and malonyl dichloride to obtain BODIPYs **5**. Bingel cyclopropanation between BODIPYs (**4** and **5**), fullerene- C_{60}, and carbon tetrabromide gave novel BODIPY- fullerene dyads (**6**- **7**). The identity of newly synthesized BODIPYs (**4** and **5**) and BODIPY- fullerene dyads (**6**- **7**) were confirmed by ^{1}H NMR, ^{13}C NMR, matrix-assisted laser desorption/ ionization time- of- flight mass spectrometry and elemental analysis techniques. The new dyads contain one or two different light- harvesting antennae associated with long absorption wavelength, resulting in 642 nm absorption bands.

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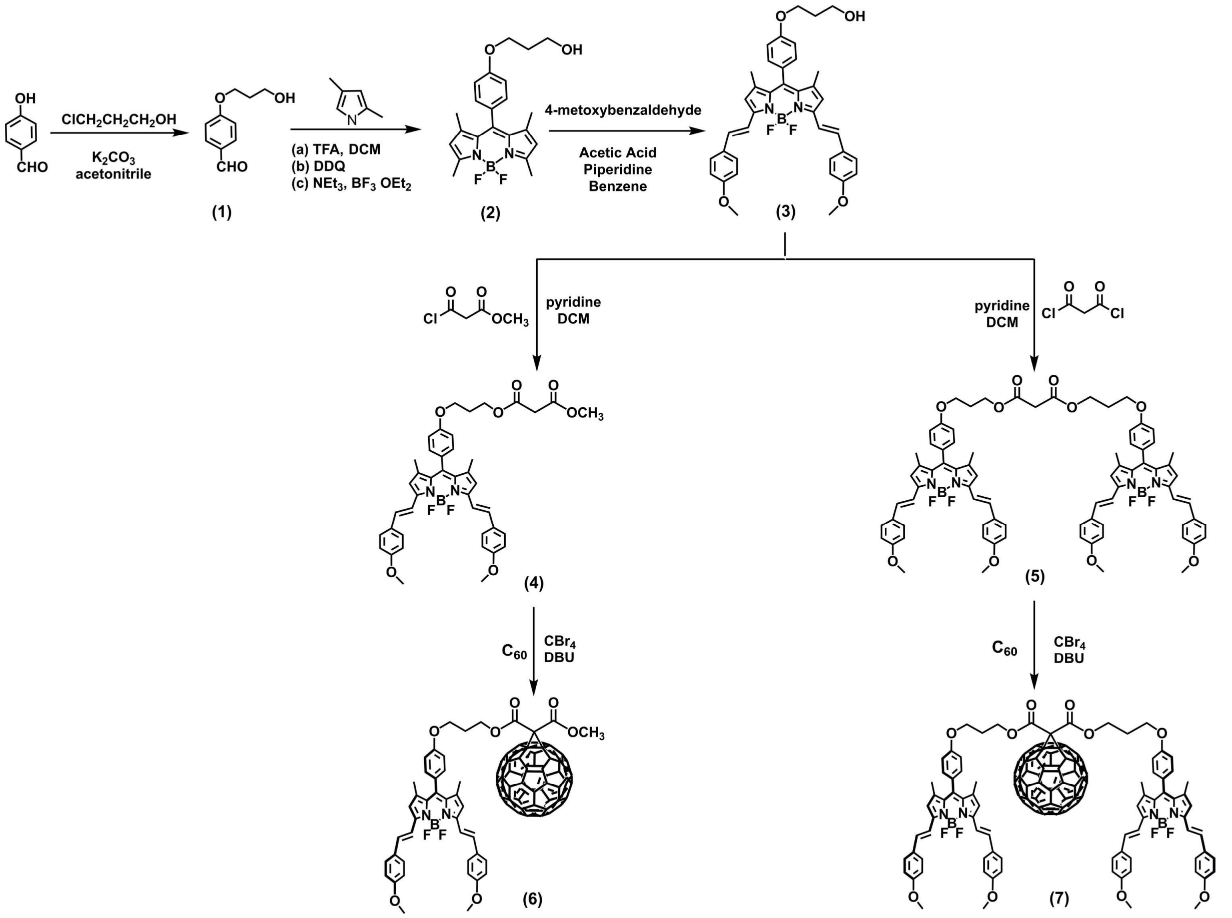

Scheme 1. Synthesis of the Distyryl- BODIPY- C_{60} Dyads

2. Experimental

2.1. General

Materials

The deuterated solvent ($CDCl_3$) for NMR spectroscopy, silica gel, dichloromethane, piperidine, trifluoroacetic acid, p-chloranil, triethylamine, Boron trifluoride diethyl etherate, pyridine and 4-metoxybenzaldehyde were provided from Merck. Following chemicals were obtained from Sigma Aldrich; fullerene, toluene, tetrahydrofuran, glacial acetic acid was purchased from Sigma Aldrich. 4-metoxybenzaldehyde, potassium carbonate, 2,4-dimethylpyrrole, methyl malonyl chloride, malonyl chloride, carbon tetrabromide were purchased from Acros Organics. 3-chloro-

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1-propanol was provided from Alfa Aeasar. Benzene, acetonitrile were purchased from VWR. DBU was provided from ABCR. All other chemicals used for the synthesis were reagent grade unless otherwise specified.

Equipment

Electronic absorption spectra were recorded with a Shimadzu 2101 UV spectrophotometer in the UV-visible region. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. The fluorescence lifetimes were obtained using Horiba- Jobin- Yvon- SPEX Fluorolog 3-2iHR instrument with Fluoro Hub-B Single Photon Counting Controller at an excitation wavelength of 620 nm and 630 nm. Signal acquisition was performed using a TCSPC module. Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. Mass spectra were acquired in linear modes with average of 50 shots on a Bruker Daltonics Microflex mass spectrometer (Bremen, Germany) equipped with a nitrogen UV- Laser operating at 337 nm.^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on a Varian 500 MHz spectrometer. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60 Å, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60 Å, 230-400 mesh). Suction column chromatography was performed on silica gel (Merck, Kieselgel 60 Å, 70-230 mesh).

2. 2. Synthesis

Compounds **1** and **2** were prepared according to procedure described previously (Scheme 1).[23]

2.2.1. Synthesis of compound 3

Compound **2** (100 mg, 0.251 mmol) and 4-(metoxy) benzaldehyde (73 mg, 0.54 mmol) dissolved in benzene (40 mL). Piperidine (0.3 mL) and glacial acetic acid (0.3 mL) were added. The solution was refluxed using Dean- Stark apparatus. When the solution was concentrated, reaction was followed by TLC until dark blue-colored product became the major product. Compound **3**

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was purified by silica gel column chromatography using Ethylacetate – Hexane (1:1) (230-400 mesh) (yield: 36%).

Spectral data of **3**: Elemental analyses: Calc. (%) for $C_{38}H_{37}BF_2N_2O_4$: C, 71.93; H, 5.88; N, 4.41; found C, 71.87; H, 5.82; N, 4.32. ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K, δ ppm): 7.62 (d, *J* = 16.4 Hz, 2H, *trans*- CH), 7.58 (d, *J* = 8.68 Hz, 4H, Ar-CH), 7.21 (d, *J* = 8.71 Hz, 2H, Ar-CH), 7.20 (d, *J* = 16.28 Hz, 2H, *trans*-CH), 7.02 (d, *J* = 8.7 Hz, Ar-CH, 2H), 6.93 (d, *J* = 8.81 Hz, 4H, Ar-CH), 6.61 (s, 2H, -CH), 4.19 (t, *J* = 5.88 Hz, 2H, $-OCH_2$), 3.92 (t, *J* = 5.90 Hz, 2H, $-CH_2O$), 3.85 (s, 6H, $-CH_3$), 2.10 (m, J_1 = 5.96 Hz, J_2 = 5.94 Hz, 2H, $-CH_2-$), 1.49 (s, 6H, $-CH_3$). ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K, δ ppm): 160.36, 159.33, 152.60, 141.80, 138.17, 135.61, 133.55, 129.78, 129.61, 129.01, 127.54, 117.40, 117.32, 114.94, 114.26, 65.69, 60.32, 55.38, 32.04, 14.86. MS (MALDI-TOF) (DIT) m/z (%): Calc.: 633.28 (22.48), 634.28 (100.00), 635.28 (40.53), 636.29 (9.02), 637.29 (1.42), 638.29 (0.18); found: 635.44 $[M+H]^+$; 614.94 $[M-F]^+$.

2.2.2. Synthesis of compound 4

Compound **3** (35 mg, 0.07 mmol) were dissolved in 15 mL of DCM. Pyridine (11 mg, 0.08 mmol) was added under Ar atmosphere. The mixture cooled on an ice bath and monomethyl malonyl chloride (10 mg, 0.07 mmol) in 5 mL DCM was added dropwise. The mixture was stirred for 12 h. Reaction mixture filtered. Solvent was removed. Compound **4** has been isolated from column chromatography with silica gel (DCM) (230-400 mesh) (yield: 60%).

Spectral data of **4**: Elemental analyses: Calc. (%) for $C_{42}H_{41}BF_2N_2O_7$: C, 68.67; H, 5.63; N, 3.81; found C, 68.64; H, 5.61; N, 3.74. ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K, δ ppm): 7.62 (d, *J* = 16.65 Hz, 2H, *trans*- CH), 7.58 (d, *J* = 8.72 Hz, 4H, Ar-CH), 7.21 (d, *J* = 8.56 Hz, 4H, Ar-CH), 7.20 (d, *J* = 16.65 Hz, 2H, *trans*-CH), 7.01 (d, *J* = 8.67 Hz, 2H, Ar-H), 6.93 (d, *J* = 8.79 Hz, 2H, Ar-CH), 6.61(s, 2H, -CH), 4.41 (t, *J* = 6.3 Hz, 2H, $-OCH_2$), 4.11 (t, *J* = 6.1 Hz, 2H, $-CH_2O$), 3.86 (s, 6H, $-OCH_3$), 3.75 (s, 3H, $-OCH_3$), 3.43 (s, 2H, $-CH_2-$), 2.20 (m, J_1 = 6.22 Hz, J_2 = 6.2 Hz, 2H, $-CH_2-$), 1.49 (s, 6H, $-CH_3$). ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K, δ ppm): 166.91, 166.43, 160.35, 159.23, 152.59, 141.75, 138.11, 135.60, 133.54, 129.79, 129.59, 129.00, 127.58, 117.40, 117.30, 114.91, 114.25, 64.25, 62.39, 55.38, 52.55, 41.32, 28.53, 14.86. MS (MALDI-TOF) (No Matrix) m/z (%): Calc.: 733.30 (22.25), 734.30 (100.00), 735.30 (44.72), 736.30 (11.43), 737.31 (2.12), 738.31 (0.31); found: 734.59 $[M]^+$; 715.88 $[M-F]^+$.

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2.2.3. Synthesis of compound 5

Compound **2** (50 mg, 0.08 mmol) were dissolved in 15 mL of DCM. Pyridine (7 mg, 0.09 mmol) was added under Ar atmosphere. The mixture cooled on an ice bath and malonyl chloride (14 mg, 0.10 mmol) in 5 mL DCM was added dropwise. The mixture was stirred for 12 h. Reaction mixture filtered. Solvent was removed. Compound **5** has been isolated from column chromatography with silica gel (DCM) (230-400 mesh) (yield: 56%).

Spectral data of **5**: Elemental analyses: Calc. (%) for $C_{79}H_{74}B_2F_4N_4O_{10}$: C, 70.97; H, 5.58; N, 4.19; found C, 70.94; H, 5.54; N, 4.14. ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K, δ ppm): 7.88 (d, *J* = 16.44 Hz, 2H, *trans*-CH), 7.84 (d, *J* = 8.57 Hz, 4H, Ar- H), 7.49 (d, *J* = 8.56 Hz, 2H, Ar- CH), 7.46 (d, *J* = 16.44 Hz, 4H, *trans*- CH), 7.29 (d, *J* = 8.61 Hz, 2H, Ar- CH), 7.20 (d, *J* = 8.59 Hz, 4H, Ar- CH), 6.87(s, 2H, -CH), 4.69 (t, *J* = 6.26 Hz, 2H, $-OCH_2$), 4.40 (t, *J* = 5.92 Hz, 2H, $-CH_2O$), 4.12 (s, 6H, $-OCH_3$), 3.75 (s, 1H, $-CH_2-$), 2.49 (m, J_1 = 6.2 Hz, J_2 = 6.1 Hz, 2H, $-CH_2-$), 1.76 (s, 6H, $-CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K, δ ppm): 166.46, 160.37, 151.52, 141.70, 135.78, 135.68, 129.84, 129.58, 129.03, 128.25, 127.68, 117.48, 117.44, 117.28, 114.92, 114.26, 62.48, 55.37, 34.24, 29.71, 29.44, 21.19, 14.87. MS (MALDI-TOF) (DIT) m/z (%): Calc.: 1334.56 (4.22), 1335.56 (37.68), 1336.55 (100.00), 1337.56 (74.53), 1338.56 (32.13), 1339.56 (9.86), 1340.56 (2.37), 1341.57 (0.47); found: 1337.86 $[M]^+$; 1317.27 $[M-F]^+$.

2.2.4. Synthesis of compound 6

Compound **4** (20 mg, 0.027 mmol) were dissolved in 15 mL of toluene. C_{60} (27 mg, 0.038 mmol) and CBr_4 (9 mg, 0.027 mmol) was added to the solution. The mixture stirred for 30 min. 1,8 diazabicyclo [5.4.0]undec-7-ene (DBU, 8.2 mg, 0.054 mmol) in toluene (10 ml) was added dropwise. The mixture was stirred over night at room temperature. Compound **6** has been isolated by flash column chromatography with DCM (230-400 mesh) (yield: 25%).

Spectral data of **6**: Elemental analyses: Calc. (%) for $C_{102}H_{39}BF_2N_2O_7$: C, 84.30; H, 2.71; N, 1.93; found C, 84.16; H, 2.69; N, 1.83. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ ppm): 7.61 (d, *J* =18.04 Hz, 2H, *trans*-CH), 7.58 (d, *J*=8.79 Hz, 4H, Ar-CH), 7.23 (d, *J* =7.86 Hz, 2H, Ar-CH), 7.20 (d, *J*=15.77 Hz, 2H, *trans*-CH), 7.04 (d, *J* =8.44 Hz, 2H, Ar-CH), 6.93 (d, *J* =8.34 Hz, 4H, Ar-CH), 6.61 (s, 2H, -CH), 4.77 (t, *J*=5.74 Hz, 2H, $-OCH_2$), 4.21 (t, *J* = 5.34 Hz, 2H, $-CH_2O$),

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4.08 (s, 3H, -OCH$_3$), 3.86 (s, 6H, -OCH$_3$), 2.41 (m, J_1 = 6.01 Hz, J_2 =6.0 Hz, 4H, -CH$_2$-), 1.49 (s, 6H, -CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$, 298 K, δ ppm): 171.10, 160.34, 145.28, 145.22, 145.20, 144.91, 144.65, 143.89, 143.85, 143.05, 143.03, 142.93, 142.18, 141.91, 141.85, 141.54, 140.99, 138.78, 137.84, 136.57, 129.00, 128.19, 125.26, 60.36, 53.41, 41.34, 36.07, 21.02, 14.17, 11.40. MS (MALDI-TOF) (DHB) (m/z (%): Calc.: 1451.28 (19.44), 1452.28 (100.00), 1453.28 (99.79), 1454.29 (54.26), 1455.29 (20.32), 1456.29 (5.83), 1457.0 (1.36); 1458.30 (0.27) found: 1453.35 [M]$^+$.

2.2.5. Synthesis of compound 7

Compound **5** (25 mg, 0.02 mmol) were dissolved in 15 mL of toluene. C$_{60}$ (18.7 mg, 0.026 mmol) and CBr$_4$ (6.2 mg, 0.02 mmol) was added to the solution. The mixture stirred for 30 min. 1,8 diazabicyclo [5.4.0]undec-7-ene (DBU, 5.7 mg, 0.04 mmol) in toluene (10 mL) was added dropwise. The mixture was stirred over night at room temperature. Compound 7 has been isolated by flash column chromatography with DCM (230-400 mesh) (yield: 21%).

Spectral data of **7**: Elemental analyses: Calc. (%) for $C_{139}H_{72}B_2F_4N_4O_{10}$: C, 81.21; H, 3.53; N, 2.73; found C, 81.15; H, 3.50; N, 2.66. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K, δ ppm): 7.59 (d, J =16.95 Hz, 4H, *trans*-CH), 7.55 (d, J = 8.40 Hz, 8H, Ar-CH), 7.22 (d, J =8.45 Hz, 4H, Ar-CH), 7.17 (d, J =16.95 Hz, 4H, *trans*-CH), 7.04 (d, J =8.27 Hz, 4H, Ar-CH), 6.91 (d, J =8.41 Hz, 8H, Ar-CH), 6.58 (s, 4H, -CH), 4.76 (t, J = 6.17 Hz, 2H, -OCH$_2$), 4.22 (t, J = 5.85 Hz, 2H, -CH$_2$O), 3.84 (s, 12H, -OCH$_3$), 2.40 (m, J_1 = 6.35 Hz, J_2 = 5.86 Hz, 2H, -CH$_2$-), 1.47 (s, 12H, -CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$, 298 K, δ ppm): 192.49, 192.46, 192.45, 180.30, 160.36, 144.74, 143.88, 143.86, 143.64, 143.19, 143.14, 143.13, 143.09, 143.05, 143.01, 142.80, 142.19, 141.86, 129.92, 129.57, 129.55, 129.50, 129.03, 129.03, 129.01, 128.96, 128.51, 114.25, 114.23, 114.22, 114.20, 53.42, 29.71, 22.66, 22.62, 14.12. MS (MALDI-TOF) (DIT) m/z (%): Calc.: 2052.54 (2.86), 2053.54 (27.42), 2054.54 (85.03), 2055.54 (100.00), 2056.54 (69.77) 2057.55 (34.40), 2058.55 (13.12), 2059.55 (4.08), 2060.56 (1.08), 2061.56 (0.25); found: 2055.19 [M]$^+$.

2.3. The parameters for fluorescence quantum yields

The fluorescence quantum yields (Φ_F) of compounds **4**- **7** were determined by the comparative method (Eq. (1)).[30]

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$$\emptyset F = \emptyset F_{Std} \frac{F.A_{Std}.n^2}{F_{Std}.A.n^2_{Std}} \qquad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the compounds (**4**- **7**) and the standard, respectively. A and A_{Std} are the respective absorbances of compounds (**4**- **11**) and the standard at the excitation wavelengths, respectively. The refractive indices (n) of the solvents were employed in calculating the fluorescence quantum yields in different solvents. Zinc (II) phthalocyanine (Φ_F= 0.2/ DMSO) was employed as the standard.[31]

2.4. The parameters for singlet oxygen quantum yields

Singlet oxygen generating capability of compounds **6** and **7** were done using singlet oxygen trap molecule 1,3- diphenylisobenzofuran (DPBF) and methylene blue (MB) as reference. Singlet oxygen can be monitored using photobleaching and subsequent decrease in absorbance of DPBF. 630 nm (4.0 mW/cm^2) led bulb was used as light source. 630 nm light was exposed from 5 cm cell distance and absorbances were taken intervals for each solution (Eq. (2)).

$$\Phi_\Delta(dyad) = \Phi_\Delta(ref)\left[\frac{k(dyad)}{k(ref)}\right]\left[\frac{F(ref)}{F(dyad)}\right]\left[\frac{PF(ref)}{PF(dyad)}\right] \qquad (2)$$

where dyad and ref designate the “BODIPY- fullerene photosensitizer” and “MB” respectively. k is the slope of difference in change in absorbance of DPBF (414 nm) with the irradiation time. F is the absorption correction factor, which is given by F= $1-10^{-OD}$ (OD at the irradiation wavelength), and PF is light intensity (energy flux, mW/ cm^2).

3. Results and discussion

3.1. Synthesis and structural characterization

The 4-(3-hydroxypropoxy) benzaldehyde (**1**) and related BODIPY (**2**) were readily available[23] and it was quite obvious that this derivative can be converted to distyryl- BODIPY (**3**) via double Knoevenagel condensation. Compound **3** was transformed to malonyl moiety functionalized

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BODIPYs (**4** and **5**) by substitution reaction with methyl malonyl chloride and malonyl dichloride in DCM in the presence of pyridine at 0 °C to obtain the compounds **4** and **5** respectively. Compounds **4** and **5** were capable of forming methanofullerenes with C_{60}. After reacting in toluene with fullerene- C_{60} in the presence of carbontetrabromide and DBU as described by the literature procedure, removal of side products and unreacted fullerene- C_{60} by column chromatograpy resulted in the isolation of a blue solids (**6** and **7**).[23, 32] The isolated solids were vacuum dried and identified as the desired products by ^{1}H, ^{13}C NMR, MALDI- MS and elemental analysis and the results were consistent with the assigned formulations (See ESI).

The mass spectra of all compounds (**1**- **7**) were obtained by MALDI-TOF MS and the spectra revealed the peak groups representing the protonated molecular ions (Fig. 1). Well- resolved ^{1}H NMR spectra of distyryl BODIPY- fullerene dyads (**6** and **7**) showed sets of signals of meso-aromatic and distyryl benzene protons for ~7- 8 ppm region. The observed 16 Hz proton- proton coupling constants at ~7.61 and ~7.20 ppm for compound **6** and ~7.59 and ~7.17 ppm for compound **7** proved an E conformation of the double bonds as expected. The pyrrole rings -CH protons for compounds **6** and **7** appeared as sharp singlets ~6.6 ppm. The -CH_2 were appeared ~4.2- 4.8 ppm as triplet and ~2.4 ppm as multiplet. The –OCH_3 protons of malonyl moieties in compound **6** showed ~4.1 ppm and styryl –OCH_3 emerged for compounds (**6**, **7**) ~3.8 ppm. The -CH_3 protons on the BODIPY cores were observed at ~1.4 ppm as sharp singlets (Fig. 2).

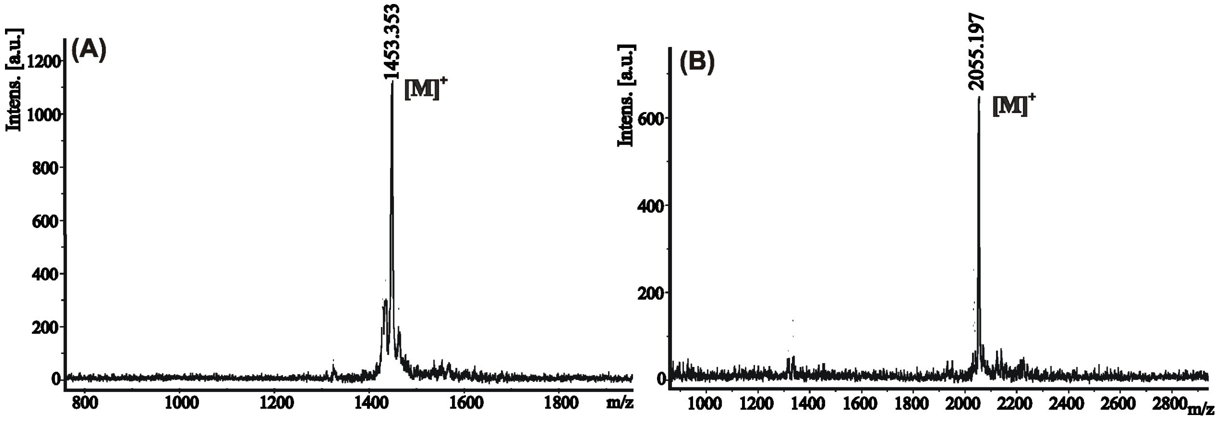

Fig. 1. MALDI- MS spectra of (A) compound **6**, (B) compound **7**

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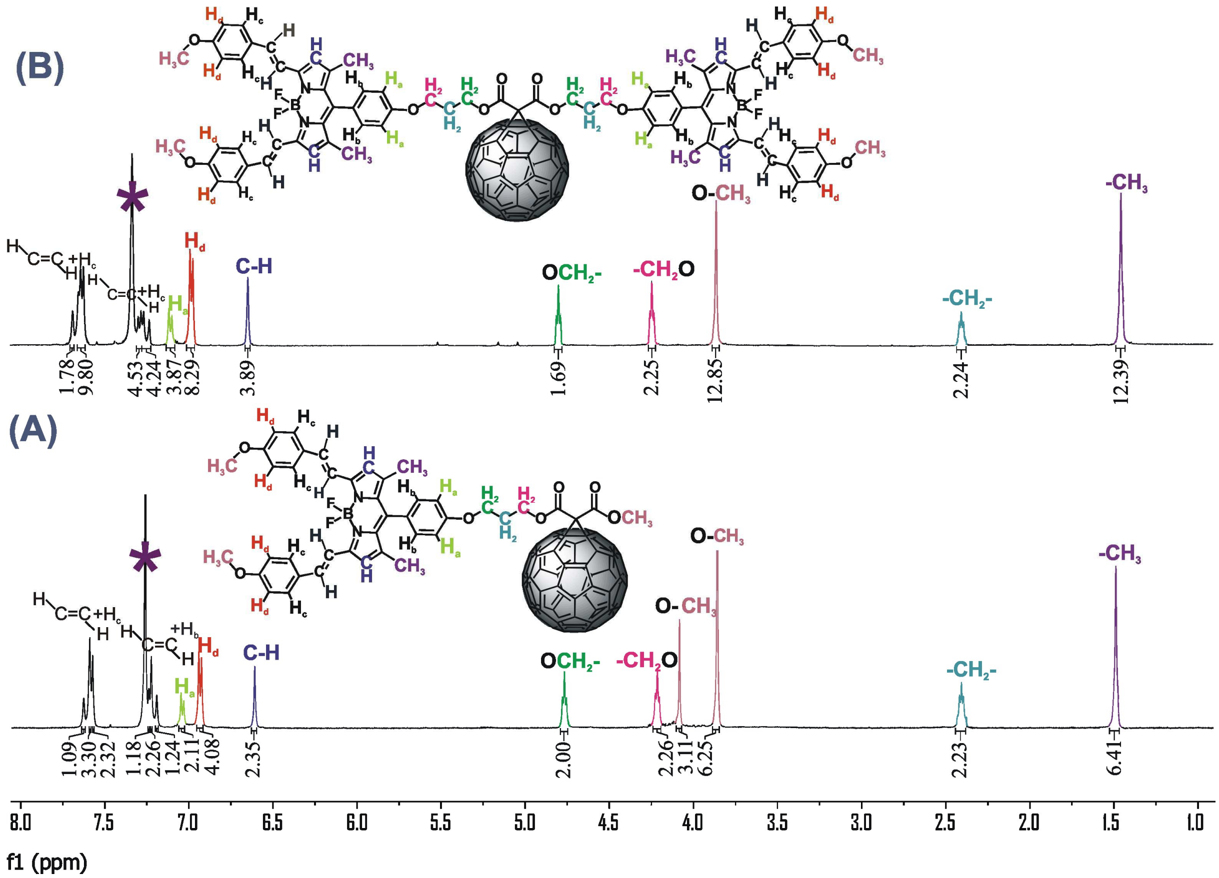

Fig. 2. ^{1}H- NMR spectra of (A) compound **6**, (B) compound **7** in $CDCl_3$

3.2. Photo-physical properties

3.2.1. Electronic absorption spectra

The UV/ Vis absorption spectra of the BODIPYs (**4**, **5**) and dyads **6** and **7** were recorded in dichloromethane and are shown in Fig. 3A. BODIPYs **4** and **5** showed major characteristic absorption band at 642 nm that exhibited similar features of distyryl BODIPY compounds, corresponding to the π- π* transition of the BODIPY antennae.[15] The molar extinction coefficients (ε) of BODIPY dyes (**4** and **5**) at 642 nm were 8.9 x 10^{4} and 18.3 x 10^{4} M^{-1} cm^{-1} respectively. Similarly, the maximum absorption bands of mono- and bis- distyryl- BODIPY- C_{60} antenna dyads **6** and **7** were observed at 643 nm as broader bands and the molar extinction

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coefficients were 8.1 x 10^4 and 1.6 x 10^4 M^{-1} cm^{-1} (Table 1). To collect the excitation energy more efficiently, a photosensitizer should show strong absorption of visible or UV light where the molar absorption coefficient of dyad **6** was higher than dyad **7**.[20]

The photostability is preferred for many fluorescent photosensitizers. The photostabilities of BODIPYs (**4** and **5**) and dyads (**6** and **7**) were investigated for 60 min in dichloromethane solutions (Fig. S10). The fluorescence intensities of BODIPYs **4** and **5** and dyads **6** and **7** were remained the same as initial value. Consequently, it was found that all synthesized compounds **4-7** showed excellent photostabilities.

Table 1. Photophyisical and Photochemical features of compounds 4-7

Compound	$^{*}\Phi_F$	$^{**}\Phi_\Delta$	$^{***}\tau_F$ **(ns)**	ε^{****}, 10^4 (M^{-1} cm^{-1})	**Absorption Wavelength** λ_{ab} **(nm)**	**Emission Wavelength** λ_{em} **(nm)**
4	0.58	0.03	3.97	8.9	642	653
5	0.31	0.04	2.49	18.3	642	655
6	0.015	0.89	-	1.6	643	655
7	0.005	0.42	-	8.1	644	656

* Fluorescence quantum yield ** Singlet oxygen quantum yield
*** Fluorescence lifetime **** Molar extinction coefficients
† below nanosecond level

3.2.2. Fluorescence spectra

The fluorescence emission spectra of compounds were investigated 6.7 μM dichloromethane solution at room temperature. Upon excitation at the BODIPY units at 620 nm for BODIPYs **4** and **5** and 630 nm for dyads **6** and **7**, BODIPYs **4** and **5** gave strong fluorescence bands at 653 nm where emissions of dyads **6** and **7** effectively quenched (Fig. 3B). Fluorescence emission peaks of BODIPY (**4** and **5**) exhibit characteristic emissions of distyryl BODIPYs such as narrow bandwidth, with high quantum yield. When comparing to these two BODIPYs (**4**, **5**) with the mono- and bis- distyryl- BODIPY- C_{60} dyads (**6** and **7**) showed lover fluorescence. The presence

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of the C_{60} moiety in BODIPY- fullerene dyads (**6** and **7**) effectively, leading to virtually invisible fluorescence emission (Figure 3B).

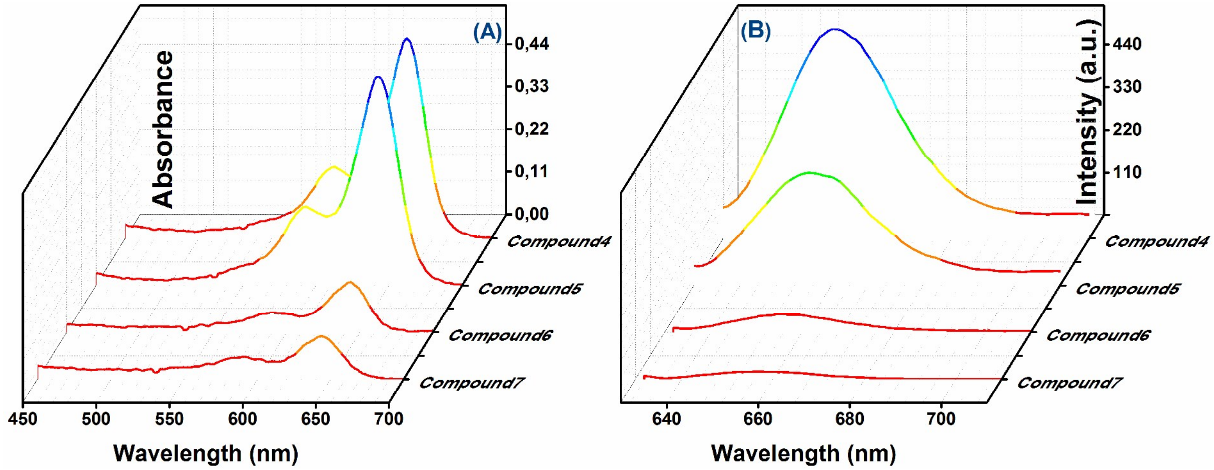

Fig. 3. Electronic (A) absorption (B) emission spectra of compounds **4- 7** in dichloromethane.

3.2.3. Singlet oxygen measurements

Singlet oxygen can be generated via energy transfer from a triplet state of the photosensitizer to ground state molecular oxygen. Since triplet photosensitizers are not only used for triplet energy transfer, they find application area in the field of photocatalytic organic reactions, photodynamic therapy (PDT), and photooxidation via sensitizing $^1O_2$.[33] A good photosensitizer should absorb the excitation light strongly preferably in the visible light region and has high yield of ISC to efficiently outcome the triplet state. In general, most transition metal complexes based photosensitizers, exhibit effective ISC, but weak absorption of visible. Since there is no established relationship between ISC yield and molecular structure, the complexity of valuation of the ISC quantum yield of an organic chromophore without heavy atoms generally hobble the developing a new triplet photosensitizer.[24, 25]

Herein near- IR light- harvesting fullerene- C_{60} dyads were used as an $^1O_2$ sensitizer for photooxidation of DPBF (Fig. 4). The ease of tuning photophyisical properties of BODIPYs dyes

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empowered us to build up dyad systems that allowed working on the near- IR range. BODIPY dyes without heavy atom essentially comes with their bright fluorescence and low intersystem crossing yield that cause low singlet oxygen quantum yields.[34] Therefore, first we studied fluorescence quantum yields of compounds **4**- **7**. The fluorescence quantum yields (Φ_F) of compounds **4**- **7** were measured in dichloromethane and unsubstituted ZnPc in DMSO solution (λ_{em} = 677 nm) was employed as the standard. The fluorescence quantum yields of BODIPYs **4** and **5** and dyads **6** and **7** were found to be 0.58, 0.31, 0.015 and 0.005 respectively (Table 1). As expected, the fluorescence quantum yields of BODIPYs **4** and **5** were sorely diminished after the espousing with the fullerene- C_{60}.[20] Also, the fluorescence lifetimes (τ_F) of the BODIPYs **4** and **5** were determined using the time correlated single photon counting (TCSPC) technique in dichloromethane. The related lifetime spectra obtained using this technique were supplied in Fig. S5 and were found to be 3.97 ns for BODIPY **4** and 2.49 ns for BODIPY **5**. The lifetimes of prepared dyads **6** and **7** were too low to be able to acquire required data in a nanosecond instrument. Because emission in these dyads were much lower caused the lower emission intensity, the lifetimes of dyads **6** and **7** are probably in picosecond level.

Thus, herein dyads **6** and **7** were used as heavy atom free organic triplet photosensitizers for the formation of endoperoxide from DPBF to produce 1,2- dibenzoylbenzene. The singlet oxygen generation capacities of the conjugates were determined by monitoring the dye-sensitized photooxidation of 1,3-diphenylisobenzofuran (DPBF).[35] For this, a solution of the dyad **6** and **7** (6.7 μM) and DPBF (absorbance around 1.1) was irradiated using red LED (4.0 mW/cm^2) and the decrease in the absorption band of DPBF at 414 nm was monitored. In order to facilitate correlation to previously reported sensitizers, the activity was studied in dichloromethane. Initially, to annihilate any contributions to the absorbance signals of DPBF from obscure reactions without light, all solutions were kept for 20 min in dark. As expected, absorbance peaks of DPBF for all solutions did not lead any chance. Upon irradiation of BODIPY- fullerene dyads (**6** and **7**) (6.7 μM) in aerated dichloromethane solutions, $^3O_2$ was sensitized to $^1O_2$ by the dyads, DPBF was then decomposed by the reactive $^1O_2$, thus the characteristic absorption of DPBF at 414 nm decreased drastically almost 70% and 55% in 60 second (Fig. 4). The presence of singlet oxygen was monitored by consistent decrease of the selective singlet oxygen trap molecule. Singlet oxygen caused remarkable degradation of DPBF after each irradiation for 10 s of dyads **6**

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and **7** under the light from 630 nm red led light.[21] Under the same experimental conditions, singlet oxygen measurements of the dyad molecules (**6** and **7**) and methylene blue as the reference molecule were performed. Each solutions of dyads (**6**- **7**) without DPBF were also triggered with light for 15 min and no changes were observed in the absorbance intensities that confirmed these compounds were not degraded under the conditions of singlet oxygen measurement. Singlet oxygen quantum yields (Φ_Δ) of compounds (**6** and **7**) were calculated according to the literature.[23] Methylene blue used as the reference compound had a singlet oxygen quantum yield of 0.57 under the conditions of the study in dichloromethane (Fig. S13). Singlet oxygen quantum yields (Φ_Δ) of dyads (**6** and **7**) were found 0.89, and 0.42 in dichloromethane, respectively. Singlet oxygen generation capacities of heavy atom free BODIPYs **4** and **5** were also checked to assure the fullerenes ISC effect and be able to comprehend with the capacities of dyads (Fig. S14 and Fig. S15). As expected the singlet oxygen capacities of heavy atom free BODIPYs were too low and singlet oxygen quantum yields were calculated as 3% and 4% respectively. After the cyclopropanation of fullerene to the BODIPYs **4** and **5** the Φ_F values were drastically decreased ~98% indicating enhanced ISC in dyads **6** and **7** ($\Phi_F + \Phi_{ISC} = 1$; non-radiative channel is neglected).[25] Φ_Δ of dyad **6** was calculated to be 1.5- fold that of the methlyne blue ($\Phi_\Delta = 0.57$) and 2.0- fold that of rose Bengal ($\Phi_\Delta = 0.43$).[36] The ISC yield was found to be much less efficient in dyad **7,** which was substituted with bis BODIPY antennae's but showed lower molar extinction coefficient. Φ_Δ value of dyad **7** was calculated as 0.42 that is close to the rose Bengal. Since, light harvesting antennae of the dyads (**6** and **7**) were designed to contain one and two BODIPY moiety, one may expect to see regularity in the singlet oxygen generation abilities. However, the outcome was quite contrary to the expectation. This is because there is no established relationship between the ISC and molecular structures.[23-27] Even a slight derivatization, may diminish the ISC. The work reported in this and our previous paper reminded us to use caution when designing other potential systems as photosensitizer.

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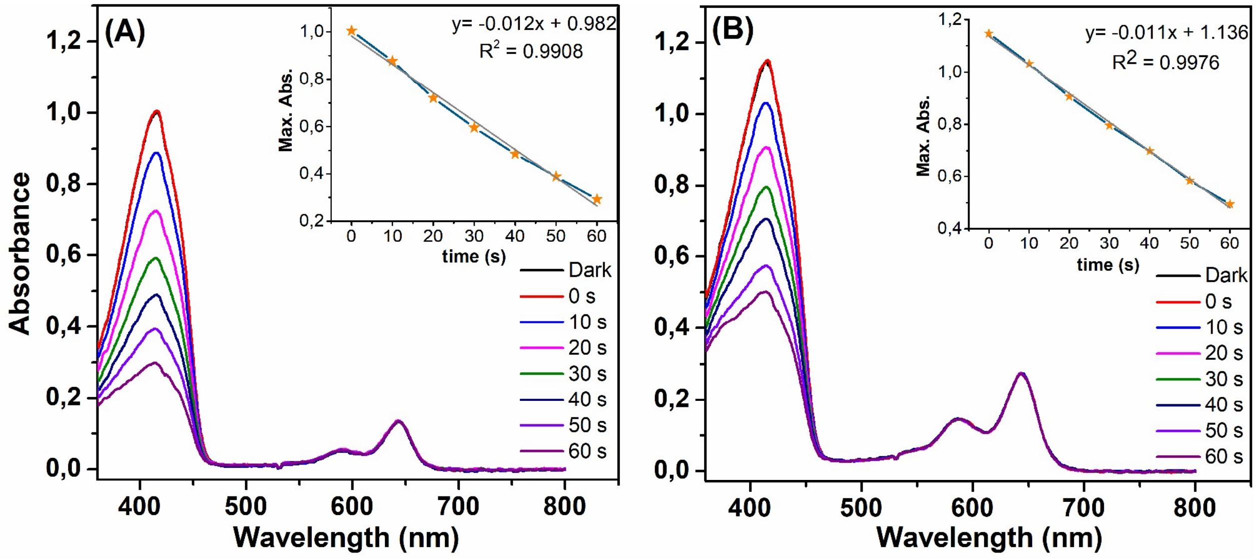

Fig. 4. Decrease in absorbance spectrum of DPBF in the presence of (A) compound **6** (6.7 μM), (B) compound **7** (6.7 μM) in dichloromethane.

Conclusion

In conclusion, novel mono- and bis- distryl BODIPY- fullerene dyads were prepared and characterized via elemental analysis, MALDI- MS, ^{1}H and ^{13}C NMR spectra. The dyads showed strong absorption of red light. Upon photoexcitation, the dyads were used as singlet oxygen ($^1O_2$) photosensitizers and the photosensitizing efficiency of the dyads compared to the known methylene blue and rose Bengal triplet photosensitizers. We propose the BODIPY- fullerene dyads can be used as a structure motif for heavy-atom-free organic triplet photosensitizers, for which the absorption can be readily tuned by using different antennas to be able to work on convenient range of visible light.

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Novel Distyryl BODIPY-Fullerene Dyads: Preparation, Characterization and photosensitized singlet oxygen generation efficiency

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